
Laboratory Prototypes of Thermo-Chemical and Sorption Storage Units

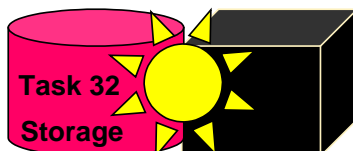
A Report of IEA Solar Heating and Cooling programme - Task 32

**Advanced storage concepts
for solar and low energy buildings
Report B3 of Subtask B**

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Laboratory Prototypes of Thermo-Chemical Storage Units

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A technical report of Subtask B



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Executive Summary

Four laboratory prototypes of thermochemical and sorption storage are described in this report. Measured results and projected heat storage densities for units of 70 and 1000 kWh storage for single family houses are reported. All four prototypes are closed sorption units and act as thermally driven heat pumps. Two work with absorption: three phase absorption process, Thermo Chemical Accumulator (TCA) with Lithium Chloride/water, and two phase absorption with Sodium Hydroxide/water. Two work with adsorption, one with zeolite and the other with silica gel. The different technologies are at very different stages of development. The TCA technology is in the process of commercialisation by the Swedish company ClimateWell AB, and over 20 storage systems have been installed, mostly in Spain. A further 100-200 are planned for 2007. The other technologies are in the prototype stage with no companies intending to develop and market them. The Modestore store (silica gel /water) was developed in a European project, and the main company within the project (Sortech) is commercialising the technology as a heat pump with essentially no heat storage.

The storage density for cold (based on total system volume), when compared to water, is more favourable than for heat. For the ClimateWell 10 commercial prototype the storage density for cold is 4.7 that of water whereas for heat it is only 1.2 times greater. This is due to the fact that the temperature range available for water storage for cold is much smaller ($\sim 10^{\circ}\text{C}$) than for heat ($\sim 60^{\circ}\text{C}$).

For short term heat storage, none of the technologies have a significant advantage compared to water in terms of storage density. The energy density can only be slightly greater than that for water, mainly due to the space required for heat exchangers and other components. In addition all of the storage systems irreversibilities in the processes themselves during charge and discharge. Most of this is due to the different temperature levels of charge/discharge and the related sensible energy between these.

For longer term storage (1000 kWh) the energy density for the TCA technology and NaOH storage systems is nearly three times that of water. In addition, once the sensible heat from the solution has been lost, the energy can be stored indefinitely, a significant advantage compared to water.

In terms of material cost, all materials are expensive compared to water, with NaOH being by far the least expensive. The cost for the whole storage system has not been estimated here. For the ClimateWell 10, the projected cost is $\sim 8000\text{€}$ for a heat pump system consisting of two units in parallel, with a total heat storage capacity of 70 kWh.



IEA Solar Heating and Cooling Programme

The International Energy Agency (IEA) is the energy forum for 26 of the Economic Cooperation and Development's (OECD) 30 member countries. Established in 1974 after the first "oil shock," the IEA is committed to carrying out a comprehensive program of energy cooperation among its member countries and the Commission of the European Communities. The IEA is the source of authoritative energy statistics as well as research and analysis on all aspects of world energy.

Since 1974, the IEA has provided a legal framework, through IEA Implementing Agreements such as the *Solar Heating and Cooling Agreement*, for international collaboration in energy technology research and development (R&D) and deployment. This IEA experience has proved that such collaboration contributes significantly to faster technological progress, while reducing costs; eliminates technological risks and duplication of efforts; and brings multiple other benefits, such as swifter expansion of the knowledge based and easier harmonization of standards.

The *Solar Heating and Cooling Programme* was one of the first IEA Implementing Agreements to be established. Since 1977, its 20 members have been collaborating to advance active solar, passive solar and photovoltaic technologies and their application in buildings and other areas, such as agriculture and industry.

Australia	Finland	Portugal
Austria	France	Spain
Belgium	Italy	Sweden
Canada	Mexico	Switzerland
Denmark	Netherlands	United Kingdom
European Commission	New Zealand	United States
Germany	Norway	

A total of 35 Tasks have been initiated, 25 of which have been completed. Each Task is managed by an Operating Agent from one of the participating countries. Overall control of the program rests with an Executive Committee comprised of one representative from each contracting party to the Implementing Agreement. In addition to the Task work, a number of special activities—Memorandum of Understanding with solar thermal trade organizations, statistics collection and analysis, conferences and workshops—have been undertaken.

What is IEA SHC Task 32

“Advanced Storage Concepts for solar and low energy buildings” ?

The main goal of this Task is to investigate new or advanced solutions for storing heat in systems providing heating or cooling for low energy buildings.

- The first objective is to contribute to the development of advanced storage solutions in thermal solar systems for buildings that lead to high solar fraction up to 100% in a typical 45N latitude climate.
- The second objective is to propose advanced storage solutions for other heating or cooling technologies than solar, for example systems based on current compression and absorption heat pumps or new heat pumps based on the storage material itself.

Applications that are included in the scope of this task include:

- new buildings designed for low energy consumption
- buildings retrofitted for low energy consumption.

The ambition of the Task is not to develop new storage systems independent of a system application. The focus is on the integration of advanced storage concepts in a thermal system for low energy housing. This provides both a framework and a goal to develop new technologies.

The Subtasks are:

- Subtask A: Evaluation and Dissemination
- Subtask B: Chemical and Sorption
- Subtask C: Phase Change Materials
- Subtask D: Water tank solutions

Duration

July 2003 - December 2007.

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IEA SHC Task 32 Subtask B

“Chemical and Sorption”

This report is part of Subtask B of the Task 32 of the Solar Heating and Cooling Programme of the International Energy Agency dealing with solutions of storage based on adsorption or absorption processes and on thermochemical reactions.

The density of storage for these techniques compared to that of water is theoretically 2 to 10 depending on the temperature range of comparison.

The topic of storing energy in an absorption process is not new. For cooling purposes at least it has been exploited since decades. A new technology from Sweden, a three phase system both for cooling and heating purposes is however recent and was studied within Task 32.

Adsorption promising techniques on silicagel or zeolite materials, long time forgotten for solar energy, have been investigated in Task 32. Results are presented in this document.

Thermochemical reactions deserve much more effort than the one Task 32 could raise. Unfortunately despite its huge potential very few research money has been invested in this topic for decades. We hope Task 32 has helped to re-open this way of storing solar energy in a dense manner.

The report does not cover all aspects of the targeted topic of a Subtask since the rules of an IEA SHC Task is that participating countries share information on projects they decide to bring in the Task.

Projects presented in this report reflects the knowledge of the participating body presenting the project.

The Operating Agent would like to thank the authors of this document for their implication in the search of future storage solutions for solar thermal energy, the key to a solar future for the heating and cooling of our buildings.

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on behalf of the Swiss Federal Office of Energy

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1 INTRODUCTION

Four different prototype storage units have been tested within Subtask B. A summary of these is given in Table 1, and the detailed results are given in the following chapter. For each of them the main characteristics are described and the test results from the lab prototype are given. The resulting key figures for the prototypes (listed below) are presented together with projected sizes and heat storage densities for hypothetical stores with 70 and 1000 kWh storage for single family homes. The former represents a short term store whereas the latter represents a longer term store. In the final section the prototypes are compared in terms of energy density and material cost.

Table 1 Summary of prototype storage units studied in Subtask B.

Type of Technology	Material	Stage of Development	Investigating Institute
Closed three phase absorption	Lithium Chloride / water	Multiple field installations	Solar Energy Research Center SERC, Sweden
Closed two phase absorption	Sodium hydroxide / water	Lab prototype	EMPA, Switzerland
Closed adsorption	Zeolite /water	Lab prototype	SPF, Switzerland
Closed adsorption	Silicagel / water	Single field installation	AEE-Intec, Austria

1.1 Definitions

The following terms used in this report are defined here.

Energy density of the material is often dependent on the operating conditions of the unit in which the material is used. This is defined together with storage density for each of the units. The relevant key figure as defined in the report A1 of IEA-SHC Task 32 is given in parentheses.

Energy density of the material (NRJ4.1)

This is the ratio of the storage capacity to the volume of the active substance when fully loaded with water in the case of sorption, or combined with the other substance in the case of other chemical reactions. In this context fully loaded means in terms of the design operating conditions of the prototype store and not the theoretical maximum of the material. During operation the store will not always operate over the full range of loading under all conditions. This value indicates the maximum value expected during normal operation and not an average value.

Energy density of prototype store (NRJ4.2)

This is the ratio of the storage capacity to the volume of all storage vessels required in the prototype unit including pipes for transfer between the various vessels and including any separate vessels for heat exchange. This represents the practical heat storage density in the prototype storage and is again related to the maximum storage during normal operation, and not an average.

Floor space required

This is the “footprint” of the storage unit including all vessels, valves and pumps necessary for its operation.

Relative density compared to water

This is the ratio of the storage capacity of the prototype store to that of an equivalent water store used in the temperature range 25-85°C (69.2 kWh/m³), unless otherwise stated.

Estimated size for 70 / 1000 kWh store

This an estimate of the size that the storage unit would have, including all parts necessary for the same design charging rate and load as the prototype, if it were to have a storage capacity of 70 or 1000 kWh – for the same conditions and performance as the prototype.

Charge / Discharge Rate

These are the design charge / discharge rates for the prototype and are a measure of the heat exchange transfer rather than the storage capability. They should be the maximum values, but if this maximum value is only valid for part of the time, then a range is given.

Boundary Conditions

The boundary conditions are given for all relevant parameters such as temperature, degree of loading and heating rates.

2 PROTOTYPE STORAGE UNITS

2.1 TCA Heat Pump and Storage Unit ClimateWell 10

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2.1.1 Background

The thermo-chemical accumulator (TCA) is an absorption process that uses a working pair, not only in the liquid, vapour and solution phases but also with solid sorbent [1], and was patented in 2000. This makes it significantly different from the traditional absorption processes in that it is a three phase process (solid, solution and vapour). All other absorption processes are two phase processes with either solution + vapour or solid + vapour.

The TCA technology has been developed principally for cooling applications but it will also be used for space heating during winter in certain applications. The first prototypes had serious problems with reliability, which seem to have been solved in the generation of prototypes that have been working for over 6 months without need for maintenance or vacuum pumping. The third generation prototypes have been tested only by the developing company (ClimateWell AB) at there in house test rig under the supervision of SERC. The flow rates in the external circuits was lower than those that the unit is designed for, resulting in abnormally high temperature differences between inlet and outlet, especially on the condensor/evaporator. The presented results are based on measurements made in November 2005 on an industrial prototype that was soon after installed in a system in Spain. Analysis of the results showed errors in one of the four circuits (charging circuit) so the energy quantities had to be estimated based on the electrical heating rate in the circuit and estimated losses. The tests were performed in order to calculate the COP of the unit for use in a cooling application.

2.1.2 Design and Operating Principles

The basic process is a batch process, with separate charge (desorption) and discharge (absorption) phases. Figure 1 shows the schematic of a TCA unit, where the solution is pumped over a heat exchanger in the reactor via a spreader to increase the wetted area and improve heat transfer. Water is desorbed from the solution during charging and the solution comes closer and closer to saturation. When it reaches saturation point further desorption at the heat exchanger results in the formation of solid crystals that fall under gravity into the vessel. Here they are prevented from following the solution into the pump by a sieve, thus forming a form of slurry in the bottom of the vessel.

For discharging, where the process is reversed, saturated solution is pumped over the heat exchanger where it absorbs the vapour evaporated in the evaporator. The heat of evaporation is provided either by the building (cooling mode) or from the environment (heating mode). The solution becomes unsaturated on the heat exchanger, but when it falls into the vessel it has to pass through the slurry of crystals, where some of the crystals are dissolved to make the solution fully saturated again. In this way the solution is always saturated and the net result is a dissolving of the crystals into saturated solution. The heat of condensation and binding energy release is transferred to the environment (cooling mode) or to the building (heating mode).

More details can be found in [2] and [3].

The TCA the following characteristics:

- High energy density storage in the solid crystals.
- Good heat and mass transfer, as this occurs with solution.

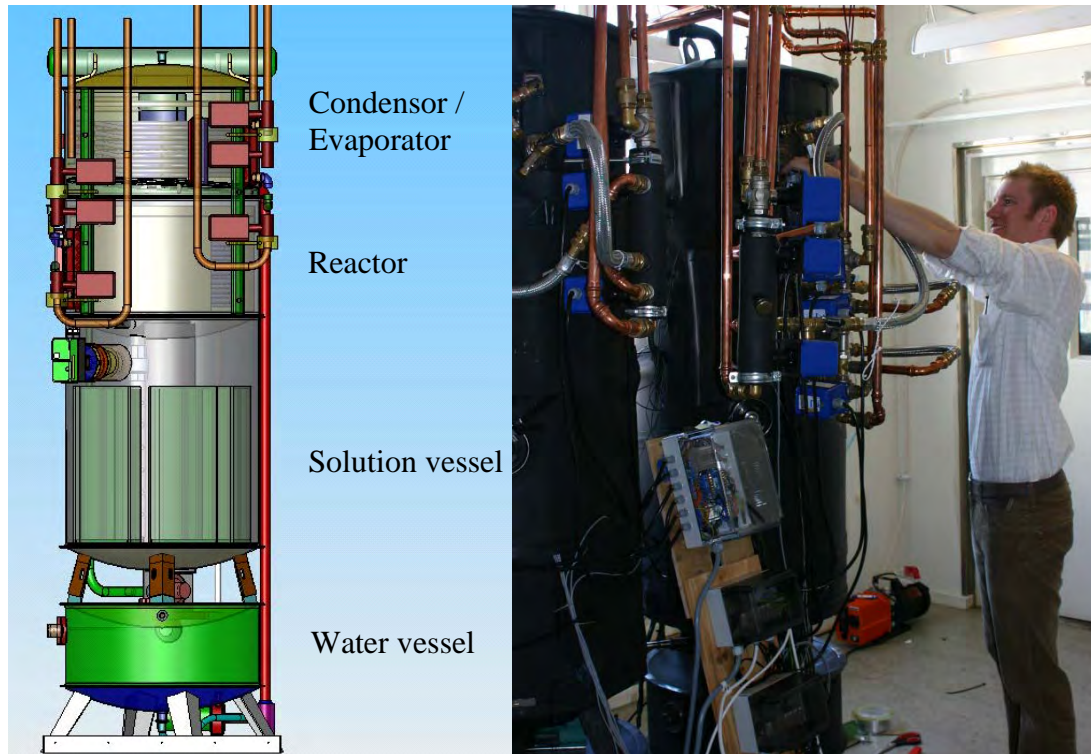


Figure 1. TCA store, third generation (CW10), with schematic (left) and during installation in the test rig (right).

2.1.3 Laboratory Test Results

The test results from the lab measurements and calculations based on these are summarised in Table 2. These show that the energy storage for one prototype unit of the TCA, when operated as for a cooling application is approximately 35 kWh heat, and 22 kWh cooling energy. This is the equivalent of an energy density for the material, LiCl salt, of 253 kWh/m³ or 3.6 times that of water (25 - 85°C). This could be increased if the solution was used over a larger concentration range, but this has been restricted by the control algorithm for the cooling applications that the unit is designed for. Due to the physical design of the unit, with the necessary heat exchangers, pipes and stores for solution and water, it is only 1.2 times that of water when these are included. This improves to a factor 1.6 if a store of 70 kWh is used and to 2.7 for a store for 1000 kWh.

Table 2. Test results a single unit of a third generation TCA prototype. All figures based on test results for two full cycle measurements carried out at ClimateWell AB, November 2005. Conditions relevant for cooling application.

Parameter	Measured Performance	Boundary Conditions
Storage materials weight: LiCl salt Water Steel	54 kg 117 kg 47 kg	
Storage capacity for heat	35 kWh	At charging / discharge rates (below)
Floor space required for prototype	0.46 m ²	
Energy density of material (NRJ4.1) (ratio to water 25/85°C)	253 kWh/m ³ (3.6)	
Energy density of prototype - heat (NRJ4.2) (ratio to water 25/85°C)	85 kWh/m ³ (1.2)	Based on short term storage
Energy density of prototype - cold (ratio to water 7/17°C)	54 kWh/m ³ (4.7)	Based on cooling energy that can be extracted and comparison to cold water storage
Charge rate	15 kW	13/25°C to/from condensor 46 – 87°C to reactor during charge
Discharge rate	8 kW	21/12°C to/from evaporator 25°C constant inlet temperature to reactor, ~30°C outlet
Estimated size for 70 kWh (ratio to water 25/85°C)	0.64 m ³ (1.6)	A pure scaling up of prototype with same size for reactor and condensor, but increased store sizes
Estimated size for 1000 kWh (ratio to water 25/85°C)	5.29 m ³ (2.7)	Assumes same size for reactor and condensor, scaled up solution and water stores.
Cost of solution (same volume as energy density)	3600 €/m ³	

Figures 2 and 3 show the charging and discharging profiles from the lab measurements respectively. The charging temperature range is from 40 - 85°C for the charging rate of 15 kW (estimated). The inlet temperature to the condensor, which controls quite directly the required charging temperature, was held constant at approximately 13°C. The flow rate through the condensor/evaporator was very low resulting in high temperature rises over the heat exchanger that adversely affects performance and temperature lift. This can be seen in Figure 3.

During discharge the inlet to the reactor was kept constant at 25°C, the outlet (heating supply) temperature being thus dependent on this and the heating rate, being roughly 30°C for most of the measurement. The high discharge rate at the start of the discharge is mainly from sensible cooling of the solution and water, the heat pumping only starting after some 10 minutes.

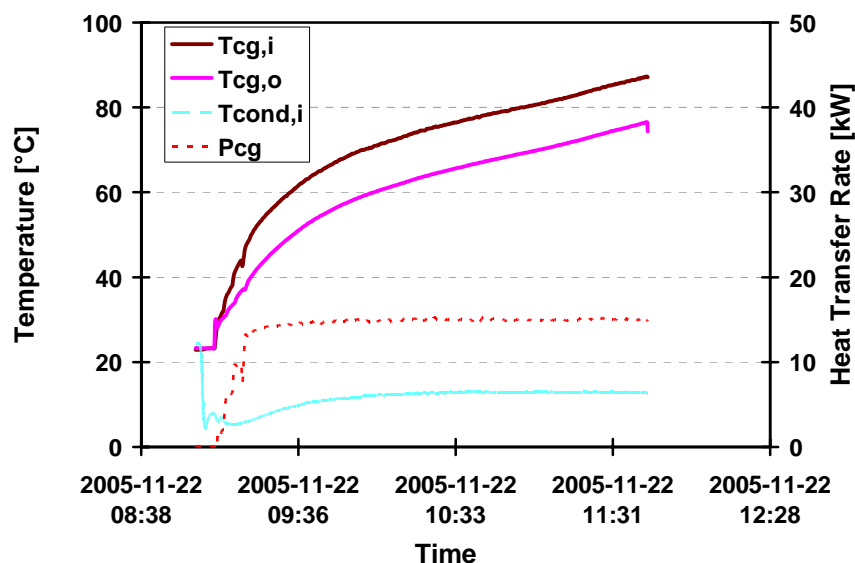


Figure 2. Charge profile for the laboratory tests used to compile data for Table 2.

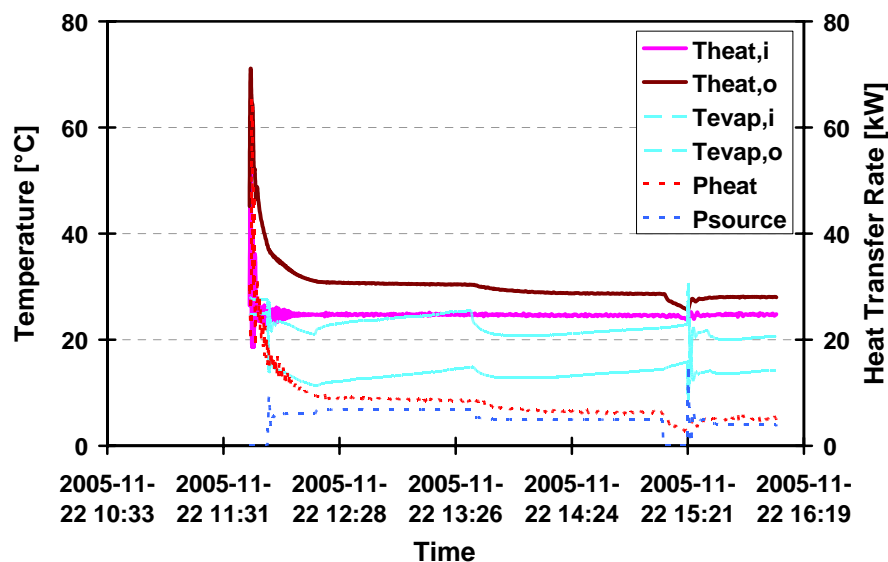


Figure 3. Charge profile for the laboratory tests used to compile data for Table 2.

2.1.4 Development Status

The TCA technology is still under development and should be considered as a relative recent invention. The company developing it is focussing on the solar cooling market, with some winter cooling, as well as to a certain extent on tri-generation systems. There are no plans for developing the technology as a purely heat storage device, although the integral heat/cold storage is used in the solar cooling applications where no external cold or hot store is required as long as the load is not too large during the night.

Commercialisation of the technology for cooling applications is in progress, with some 11 M€ of risk capital being invested. Most effort is going towards rational serial production, but significant effort is being used for system and control development, improved performance and also to investigations of alternative salts.

2.1.5 Acknowledgements

The work reported here has been financed by the Swedish National Energy Agency through the projects P21241-1 and P21543-1.

2.1.6 References

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2.2 Sorption storage unit with Zeolite (Silicagel) / water

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2.2.1 Background

In the adsorption process the heat of adsorption $\Delta h_A = \Delta h_v + \Delta h_B$ (heat of evaporation Δh_v ; binding energy Δh_B) is released and the combined solid sorbent plus the adsorbed sorbate are heated up [1-3]. Because the theoretical energy density of water vapour adsorbed on Zeolite is in the range of 180 kWh/m^3 , the size of a water storage tank could be significantly reduced. While the measurements of the heat of adsorption Δh_A of water vapour on Zeolite and Silicagel are nearly confirming these values [2], in the sorption storage system design, all the losses have to be considered and the temperature levels in the discharge cycle as well as in the charging cycle are of significant importance. But a much more important point is that in case of discharging the storage tank the heat of evaporation Δh_v has to be delivered to the system. So in principle, the storage system is a thermally driven heat pump. The environment or a solar thermal system can be used as the supplying energy source for the heat of evaporation Δh_v . In case of charging the sorption tank i.e. drying the sorbent material, thermal energy sources at temperatures of up to $200 \text{ }^\circ\text{C}$ for Zeolite and $120 \text{ }^\circ\text{C}$ for Silicagel are needed. Applying these materials, lower charging temperatures are leading to lower energy outputs of the storage system. As in case of delivering the required heat of evaporation to the system solar thermal vacuum tube collectors can be used to dry the sorbent material.

2.2.2 Operating Principles and Design

The operating principles of an open and a closed sorption storage system can be read for example in the papers of HAUER 2000 and MITTELBACH et al 2000, respectively. So, the following explanations focus on the planning and experimental work done at SPF.

The power P of a sorption storage system is directly correlated with the uptake of water vapour $c(T, p)$ by the sorption material as a function of time t multiplied by the heat of adsorption $\Delta h_A(c)$: $P \sim dm/dt(c, T) * \Delta h_A(c, T)$. And the total energy is the integration with respect to the time t . Because all the power P determining variables are functions of the temperature T and the pressure p [4] the temperature level at which the process will run is very important. With the aim to design an efficient storage system, an experimental set-up to measure the speed of adsorption dm/dt of water vapour on Zeolite and Silicagel and the temperature development in the fixed bed of solid sorbent material was built. The findings will help to understand how the process behaves and assist with the design of an efficient sorption module heat exchanger, which is one of the key components of the system. Measurements in a Laboratory sorption unit with a new rib heat exchanger immersed in the solid, spherical shaped sorption material were made.

In Figure 4 the experimental set-ups are shown schematically. On the left the unit for measuring the adsorption speed dm/dt of water vapour on Zeolite and on Silicagel in function of time t is shown, [5]. And on the right of Figure 4 a schematic of the sorption system with the new rib heat exchanger for measuring the power output is shown.

Spherical Zeolite 13 X particles with an average diameter of 1 mm and granular Silicagel 490 with a particle size distribution of 3 – 5 mm were used as sorbent materials. The bulk densities are 650 kg/m^3 for Zeolite 13 X and 470 kg/m^3 for Silicagel 490. The BET surface of

Zeolite 13 X is in the range of $500 \text{ m}^2/\text{g}$ and $800 \text{ m}^2/\text{g}$ and for Silicagel 490 it is $400 \text{ m}^2/\text{g}$ [6, 7]. Zeolite 13 X and Silicagel 490 have an average pore size of 1 nm and 9 nm, respectively. In humid air the water uptake $c(p, T)$ of the two different sorbent materials is approximately 25 wt. % and 80 wt. % for Zeolite 13 X and Silicagel 490, respectively. The sorbent material fixed bed was dried at a temperature of $T = 100 \text{ }^\circ\text{C}$ by the electrical heating and simultaneous pumping with the turbo-molecular and the mechanical vacuum pumps. The temperature $T(t, z)$ and weight $m(t)$ increase was measured in fixed beds of Zeolite 13 X and Silicagel 490 adsorbing water vapour of different vapour pressures $p(T)$ and temperatures T , respectively. Power output measurements with the new rib heat exchanger immersed in the solid sorption material were only made with spherical shaped Zeolite 13 X particles of 1 mm average diameter, Figure 4 right.

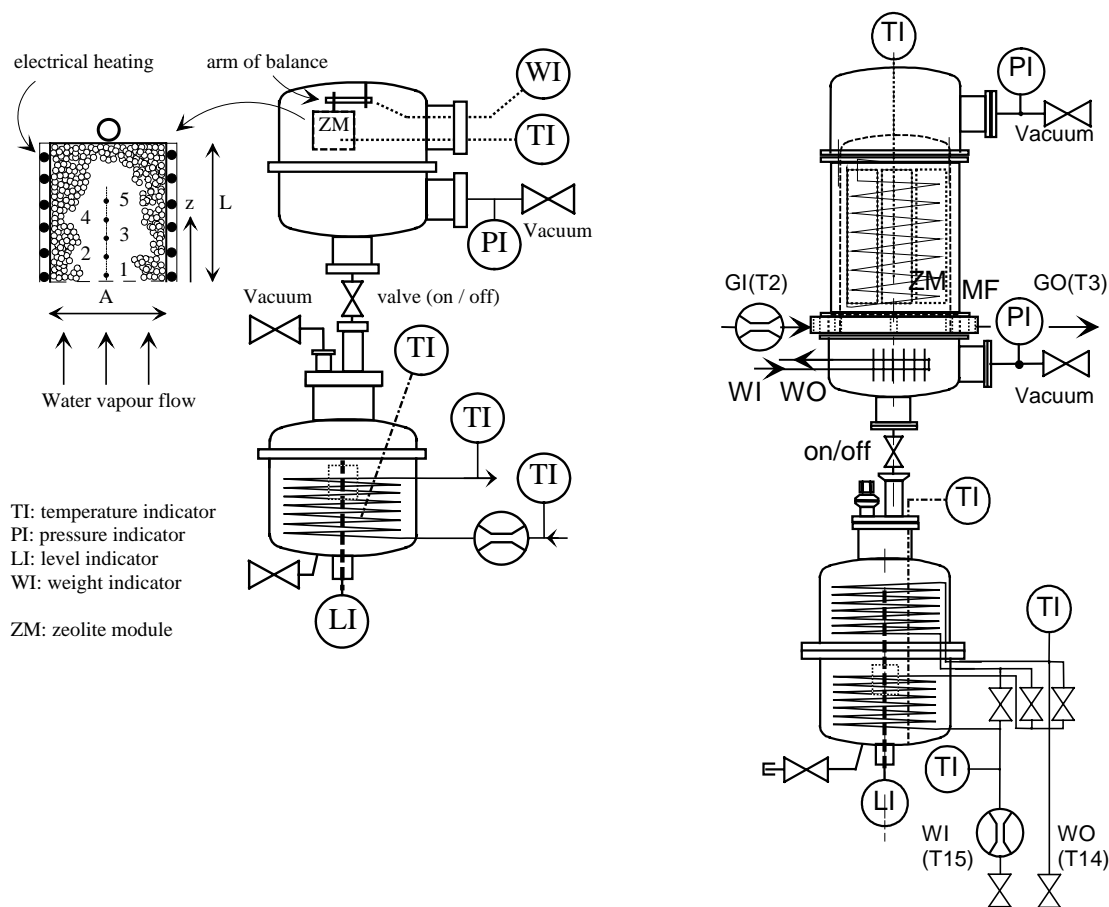


Figure 4. Left: Schematic of the experimental set-up with two vacuum chambers to measure time dependent mass adsorption on granular Zeolite and Silicagel and the temperature development as a function of time and position z (1 cm to 5 cm) in the fixed bed (ZM) of solid sorbent material (left). On the right, a schematic of the laboratory sorption unit (with new rib heat exchanger) to measure temperature profiles and power out put is shown. In both schematics the lower chamber contains the sorbate water and the upper chamber the fixed sorbent bed container. Right schematic: PI Pressure Indicator, TI Temperature Indicator, LI Level Indicator, GI Glycol In, GO Glycol Out, WI Water In, WO Water out.

2.2.3 Laboratory Test Results

For Silicagel the $m(t)$ data points in Figure 5 show two different ranges separated at the measurement time t i.e. adsorption time t of about $t = 300 \text{ s}$ at a temperature $T = 22 \text{ }^\circ\text{C}$ in the

water tank. In both time ranges, from 0 s to $t = 300$ s and from $t = 300$ s to $t = 3200$ s the measured data are fitted with two linear functions. The slope of the first linear curve is $dm/dt = 2 \times 10^{-2}$ g/s while the derivation of the second linear curve of $dm/dt = 1.7 \times 10^{-3}$ g/s is more than an order of magnitude smaller. Zeolite 13 X shows similar behaviour but the two time ranges are separated at a time t of $t = 400$ s and in the first range the adsorbed water vapour per time t is with $dm/dt = 3 \times 10^{-2}$ g/s 1.5 times higher than for Silicagel 490. In the second time range the mass adsorption speed is $dm/dt = 5 \times 10^{-3}$ g/s. In Figure 6 the mass $m(t)$ data points as a function of time t are shown for Zeolite 13 X at a temperature $T = 22$ °C in the water tank.

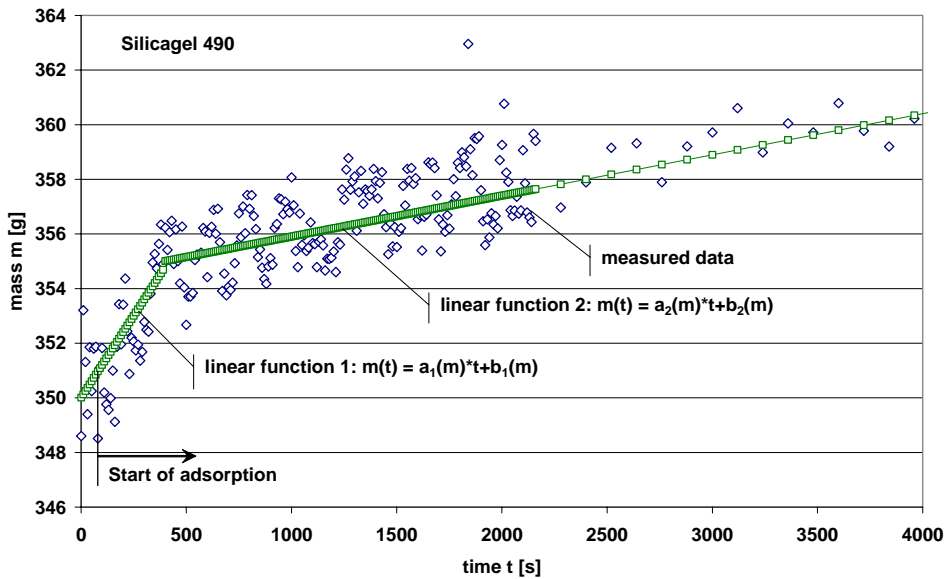


Figure 5: Increase of mass as a function of time in the fixed bed of Silicagel 490 by adsorption of water vapour at a pressure of $p(\text{H}_2\text{O}, T=22 \text{ °C}) = 24.8$ mbar. In the first $t = 300$ s the data points can be fitted by a liner function (1) with a slope of $dm/dt = 2 \times 10^{-2}$ g/s, while the measured data at a time $t > 300$ s can be approximated by a liner function (2) with a slope of $dm/dt = 1.7 \times 10^{-3}$ g/s.

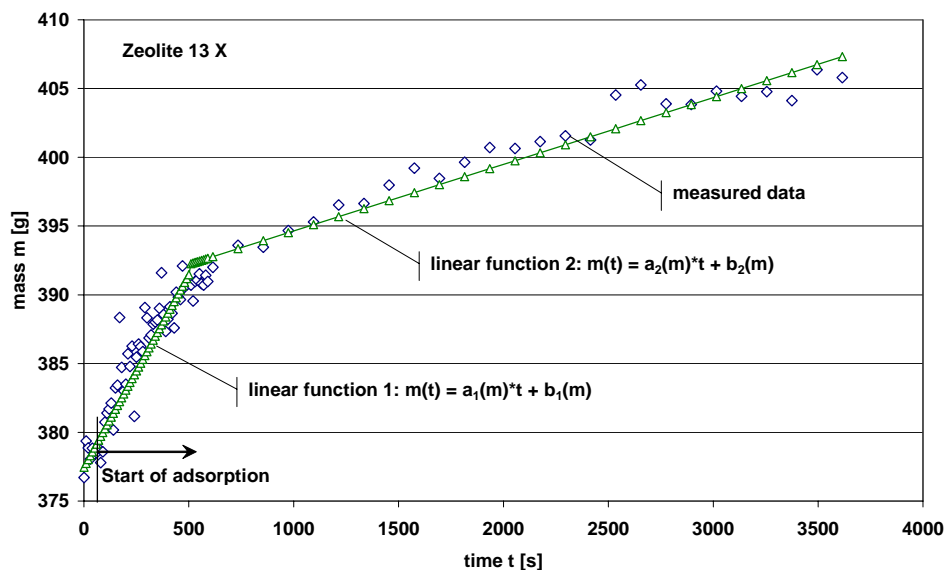


Figure 6: Increase of mass as a function of time in the fixed bed of Zeolite 13 X by adsorption of water vapour at a pressure of $p(\text{H}_2\text{O}, T=22 \text{ °C}) = 24.8$ mbar. In the first $t = 400$ s the data points can be fitted by a liner function (1) with a slope of $dm/dt = 3 \times 10^{-2}$ g/s, while the measured data at a time $t > 400$ s can be approximated by a linear function (2) with a slope of $dm/dt = 5 \times 10^{-3}$ g/s.

The dynamic behaviour of Zeolite 13 X and Silicagel 490 under adsorption of water vapour is different. Zeolite 13 X shows a higher water vapour uptake rate than Silicagel 490. Two adsorption speed ranges were identified for Silicagel 490 and Zeolite 13 X. At the beginning of the adsorption process the measured curves $m(t)$ can be approximated by linear functions. The transition from the higher gradient to the lower gradient takes place at an adsorption process time of approximately $t = 300$ s for Silicagel 490 and $t = 400$ s for Zeolite 13 X. SAHA 1995, BOELMAN 1995 and BOELMAN 1997 are reporting about operational conditions and coefficient of performance COP of an adsorption refrigeration machine working with Silicagel. The optimum cooling power output is in a cycle time of $t = 250$ s to $t = 300$ s while the COP of the machine increases up to $\text{COP} = 0.5$ at a cycle time of $t = 1800$ s. For a measurement time $t > 1$ h the weight $m(t)$ increases as a function of time t for the two sorbent materials Silicagel and Zeolite is again reduced compared to the previous two time ranges. The data for the temperature $T(z, t)$ in function of the position and time t are shown in GANTENBEIN 2006.

A solution of the mass balance equation in the bulk of the fixed bed and in a particle is shown in Figure 7 right. The qualitative curves are calculated with a parabolic concentration profile $c(r/R_p) \sim (r/R_p)^2$, which is according to YANG, 1998 and DO, 1997 a reasonable assumption. Judging Figure 5, 6 and 7, right and considering the total mass in the experimental fixed bed it can be seen that the maximum concentration $c(p, T)$ of water adsorbed on Zeolite and Silicagel are far from the theoretical in the measured time range. So the 6 g of water on Silicagel 490 and the 12 g of water on Zeolite 13 X in the first 300 s and 400 s are mainly adsorbed on the surface of the sorption materials. Because of the vapour pressure curve $p(T, c)$ of Silicagel and Zeolite, the higher system temperature limits the water uptake $c(p, T)$ at a given pressure [4, 8]. Dunne [9] and Tatlier [10] are therefore reporting and arguing to apply solid sorption material layers for adsorption cooling.

These results have been considered in the design of the heat exchangers immersed in the granular water vapour adsorbing materials. The heat exchangers are the key components of a thermo-chemical energy storage system. Because of the low heat conductivity of Zeolite and Silicagel and the low heat transfer rates in the fixed-bed configuration, a distance of the adsorbing material to the heat conduction surfaces should not be exceeded. This led VAILLANT, 2002 to the construction of a fin tube heat exchanger with a fin distance of one particle diameter. But the high mass relation of the heat exchanger to the sorption material is still resulting in massive thermodynamic penalties.

For these reasons, a rib heat exchanger with nine heat conduction fluid carrying pipes in parallel was built, considering the pressure p and temperature T depending heat transfer coefficients in the bulk of the fixed bed [11, 12]. The distance from one rib to a other was set to $d(1) = 7$ mm in the x direction and the distance of the pipes was either $L = 45$ mm in the z direction and $L = 60$ mm in the y direction. In Figure 7 a schematic of a part of the rib heat exchanger is shown.

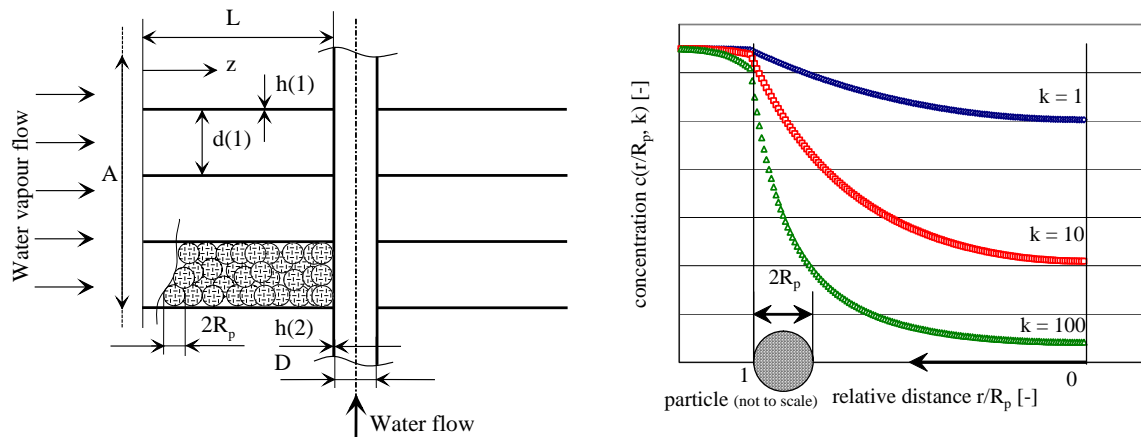


Figure 7. Schematic of a heat exchanger section with marked parameters (left). The heat exchanger can be either cylindrical or rectangular. On the right hand, a qualitative concentration profile $c(r/R_p)$ in a spherical solid sorption particle depending on the diffusion resistance k during adsorption is shown (right). The particle with a diameter $2R_p$ as shown is not to scale compared to the concentration profile $c(r/R_p)$.

KATO et al 2006 showed an optimum power per volume at a fixed bed height of 4 mm for the CaCl₂/CH₃NH₂ materials combination and a fixed bed height of 7 mm for the system MgO/Water in a chemical heat pump unit.

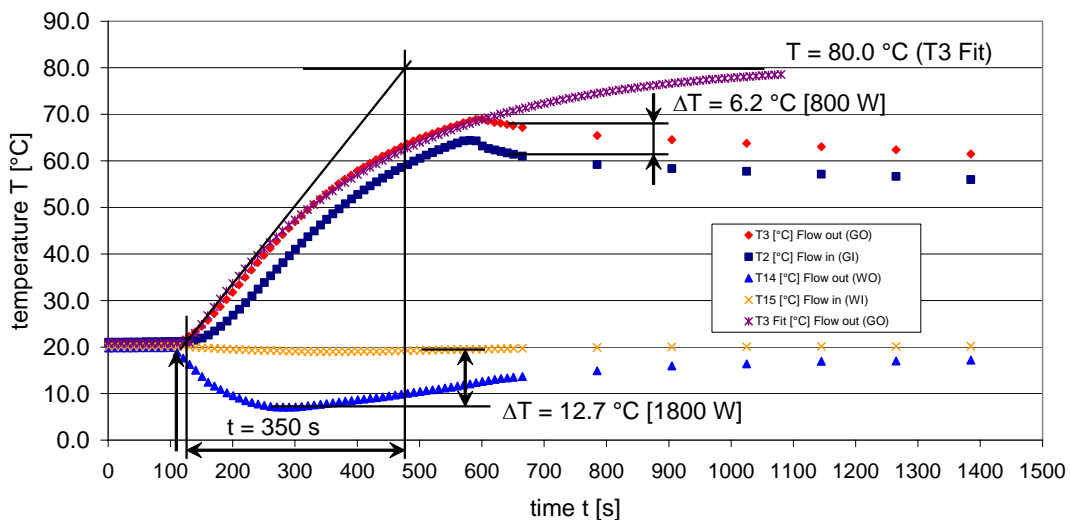


Figure 8. Typical discharge temperature profile for the sorption unit with the materials combination Zeolite – Water. The temperature curves T_2 and T_3 are showing the sorption module heat exchanger inlet and outlet temperature of the heat transfer fluid, respectively. The inlet (T_{15}) and outlet temperatures (T_{14}) of the water tank heat exchanger are showing the cooling effect during the sorption process. For comparison the outlet temperature T_3 of the sorption module heat exchanger is fitted with an exponential curve (T_3 Fit), with the assumption of the temperature increase in the sorption module is similar to the voltage charging curve of a storage capacitance.

First measurements showing the temperature profiles in the sorption unit (Figure 4 right) can be seen in Figure 8. A temperature increase of up to $T = 70$ °C in the external fluid carrying circuit is reached in the laboratory sorption storage system at a water vapour pressure of $p(\text{H}_2\text{O}, T=20$ °C) = 23.4 mbar in the water tank. The maximum heating power in sorption

module reached 800 W at a temperature level $T > 55$ °C. In the Water tank a maximum cooling power of 1800 W could be measured.

With the prerequisite of the basic physical similarity of thermal and electrical systems a fit to the temperature curve T3 (T3 Fit) was made by applying the exponential behaviour of the capacitance charging to the sorption unit. The current sorption module has a time constant of approximately 350 s, which again shows the low heat transfer rates from the Water vapour adsorbing Zeolite to the rib heat exchanger [11, 12].

The energy density of the Zeolite – Water module was determined in function of the Zeolite drying temperature. In table 3 the results are summarized:

Table 3: Energy density E in function the heating temperature T.

Heating Temperature T [°C]	Energy Density E [kW/m ³]
110	33.0
150	54.4
180	57.8

In Table 4 an over view about the results under the experimental conditions is given.

Table 4: Summary of the test results.

Parameter	Measured Performance	Boundary Conditions
Storage material weight	7 kg	Zeolite 13 X
Storage capacity for heat	1 kWh	$T > 55$ °C / Laboratory
Floor space required for prototype ¹	0.3 x 0.3 m ²	No flanges – welded
Energy density of material (NRJ4.1) (ratio to water 25/85)	180 kWh/m ³ (~ 3)	No temperature level specified
Energy density of prototype (NRJ4.2) (ratio to water 25/85)	57.8 kWh/m ³ (~ 1)	Related to the sorption module (180 °C / 20 °C)
Charge rate	-	-
Discharge rate heating / cooling [kW]	0.8 kW / 1.8 kW	180 °C / 20 °C
Estimated size for 70 kWh (ratio to water 25/85) ²	1.2 m ³ (~ 1)	Heat and mass transfer are the same
Estimated size for 1000 kWh (ratio to water 25/85) ²	17 m ³ (~ 1)	Scale up possible
Cost for material	2-3000 €/m ³	Dependent on quantity

¹ Related to the sorption module in the upper tank shown in Figure 4 right and that all flanges are replaced by a welding seam.

² These values are estimated and provided that the scaling up to a sorption system of the assumed size is possible.

The drying temperature of $T = 180$ °C for Zeolite is reached under laboratory conditions with an electrical heater and will not be easily reached by solar collectors at a reasonable power.

But on the other hand if the temperature level in the Water tank is increased the power output and the energy density will be increased [5].

2.2.4 Development Status

To measure the adsorption speed of water vapour on the sorbent materials the experiments were done without cooling the fixed bed and so the sorption materials reached a steady state at an equilibrium temperature T_{equ} that is higher than in case of cooling the sorbent material. By cooling the fixed bed to a temperature level lower than the equilibrium temperature $T_1 < T_{\text{equ}}$ in the adsorption process, the load $c(T, p)$ with water vapour will be higher, $c(T_1, p) > c(T_{\text{equ}}, p)$ for $T_{\text{equ}} > T_1$, and so the power will be increased. While this was the case in the experiments of which data are shown in Figure 8 the measurement of the speed of adsorption could not be performed in parallel and so the relation between the temperature T of the sorption material and the power of the laboratory sorption unit is unknown.

Nevertheless, various questions remain to be answered. For instance: Is the mass transfer zone travelling with a constant speed through the fixed bed independent of the depth z ? Or, is there a limit in the length L because of the water vapour pressure drop while it is flowing through the granular material and the maximum pressure available is the water vapour pressure $p(T)$? What is the optimum particle size distribution to a constant flow i.e. a constant power density? But the key question is raised by the observed transition from a high to a low speed of adsorption at a time of 6 to 7 minutes. Is the adsorption process of water vapour on Zeolite or Silicagel diffusion limited and such systems working on the basis of the heat pump principle are more suitable for either cooling application and/or – as the working principle suggests – for heat pump application with short cycle time and not for long cycle time heat storage?

The future work will be dealing with analysing the speed of adsorption at a time scale of up to several hours and identifying system designs to achieve optimum power density and energy density. In addition further work will be needed to scale up the laboratory system to a prototype sorption heat pump / storage system.

2.2.5 Acknowledgements

Financial support of the Swiss Federal Office of Energy is gratefully acknowledged. The author also would like to acknowledge F. Flueckiger who designed the data acquisition concept and W. Camenisch who did the welding of the laboratory equipment. Special acknowledgment goes to the members of the IEA Task 32 group for very fruit full discussions.

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2.3 Solid Sorption Storage System (MODESTORE)

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2.3.1 Background

Solid sorption storage technology with the working pair silica gel / water for long-term storage of solar heat for space heating applications has been under development by AEE INTEC for several years. In a first EU-Project called HYDES, the general functioning of the technology could be shown [1]. As a next step, an improved prototype system (2nd generation) was developed in the framework of another EU-Project called MODESTORE [2, 4]. A lab-scale unit of this improved prototype was tested in the laboratory and the results are presented in this report. Then, an again slightly changed and scaled up version of this prototype was installed in a pilot plant installation in a single-family house in Austria [3].

2.3.2 Design and Operating Principles

The operating principle of the system is described below.

- 1. Charging process (desorption, drying of silica gel):** Heat from a high temperature source is fed into the device, heats the silica gel and vapour is desorbed from the silica gel. The desorbed vapour is led to the condenser and is condensed at a lower temperature level. The heat of condensation has to be withdrawn to the environment.
- 2. Storage period:** The dry silica gel is separated from the water (the connecting valve is closed). As long as these components stay separate, heat storage without losses is possible if the sensible heat involved is neglected.
- 3. Discharging process (adsorption, loading of silica gel with water vapour):** The valve between the evaporator and the adsorber is opened. The water evaporates in the evaporator taking up heat at a low temperature level. The vapour is adsorbed and releases the adsorption heat at a higher temperature level. This is the useful heat.

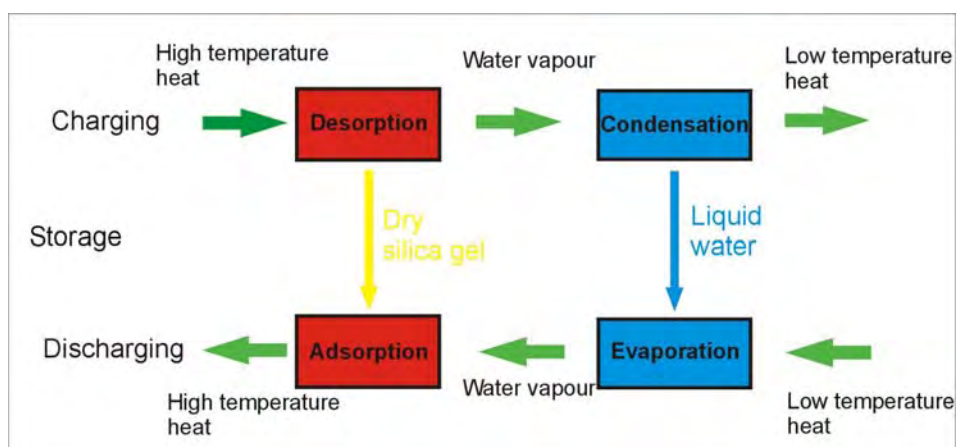


Figure 9. Working principle of an adsorption heat store

Within the framework of the EU-project MODESTORE, a prototype storage module has been developed (Figure 10). The upper part contains the adsorber and a spiral heat exchanger. In the center, there is a vertical channel for vapour diffusion. The spiral heat exchanger consists

of perforated sheet copper with copper pipes soldered to it. The lower part contains the heat exchanger that serves as evaporator and condenser. At the bottom, the container is connected to a second container that holds the water that is not adsorbed. For desorption, the water is pumped from the storage module as it accumulates at the bottom. For adsorption, water is led into the bottom of the storage container and heated. The total size of the container is approximately 350 litres.

The advantage of the new design is that it is very compact. All major components (adsorber and evaporator/condenser heat exchanger) are included in a single container. The distances between adsorber and evaporator/condenser are very short. The vapour does not have to pass through narrow pipes which reduces the pressure losses.

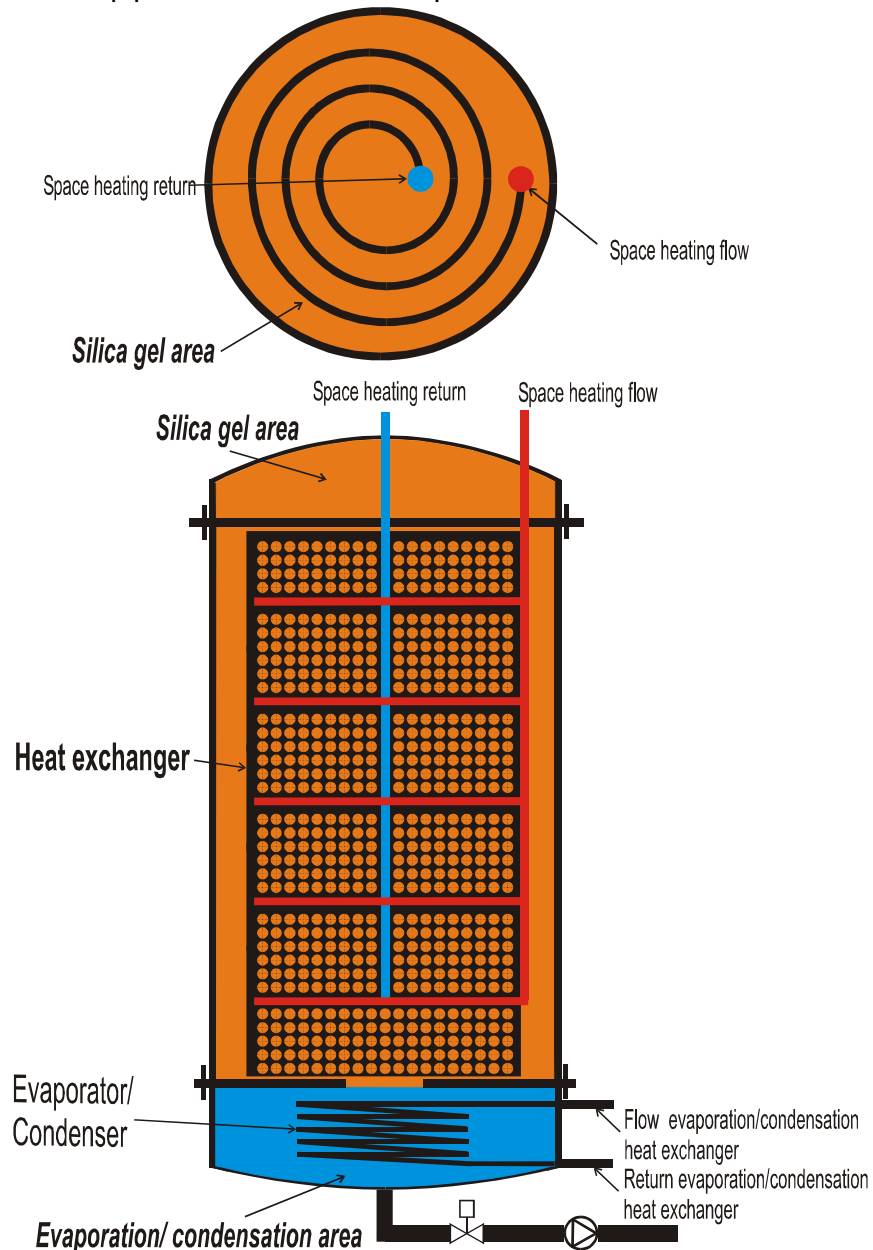


Figure 10. Scheme of the 2nd generation prototype

This design improves the heat and mass transfer compared to earlier designs where the adsorber and evaporator/condenser were situated in separate containers and were connected by a pipe. The cross section area which is available for the transport of water vapour from the evaporation/condensation area to the silica gel packing and vice versa, is

increased and ensures low pressure drops and good mass transfer between the components.

In addition, in previous prototype systems [1] the evaporator was submerged at the bottom of a large tank containing the entire water for adsorption. This led to poor heat transfer from the evaporator to the water surface where evaporation takes place. In the new design only a small amount of water for evaporation is pumped into the evaporator area at the bottom of the tank module. This improved the heat transfer significantly.

2.3.3 Laboratory Test Results

Test results showed that the temperature lift for the material combination silica gel and water is only sufficient up to a water content of the silica gel of about 13%. On the other hand, water contents of less than 3% are not realistic to reach given the temperature available from flat plate solar collectors and the temperature of an available heat sink.

Therefore, the material has to operate between these limits of water content (3-13%). That means that the storage density of the material is significantly lower than initially expected. The parameters shown in Table 5 are based on this given range of water contents which leads to a storage capacity of this lab-scale unit of only 13 kWh. The corresponding energy density of the material is 50 kWh/m³ which is less than water that has an energy density of 70 kWh/m³ for a temperature difference of 25 – 85°C. Due to the physical design of the unit, with the necessary heat exchanger, space for water vapour diffusion and an additional tank for the stored water, the energy density of the system goes down to 33 kWh/m³ or about half of that of water.

The figures for larger store sizes are estimated on the basis that the additional space necessary for vapour diffusion increases slightly slower than the sorption material volume. However, the comparison of energy density to water improves only slightly.

Table 5: Test results a laboratory-scale unit of a second generation sorption storage system (MODESTORE).

Parameter	Measured Performance	Boundary Conditions
Storage materials weight: Silica gel (dry) Water Steel Copper	200 kg 30 kg 100 kg 50 kg	Laboratory-scale unit was equipped with two large flanges so that the system could be taken apart, for a real application this would not be necessary and reduce the amount of steel needed
Storage capacity for heat	13 kWh	At charging / discharge rates (below)
Floor space required for prototype	0.4 m ²	
Energy density of material (NRJ4.1) (ratio to water 25/85°C)	50 kWh/m ³ (0.71)	
Energy density of prototype - heat (NRJ4.2) (ratio to water 25/85°C)	33.3 kWh/m ³ (0.48)	
Charge rate	1-1.5 kW	
Discharge rate	0.5 - 1 kW	
Estimated size for 70 kWh (ratio to water 25/85°C)	1.7 m ³ (0.59)	Assumes a slightly lower ratio of sorption material volume to additional system volume.
Estimated size for 1000 kWh (ratio to water 25/85°C)	23 m ³ (0.62)	Assumes a slightly lower ratio of sorption material volume to additional system volume.
Cost of material	4300 €/m ³	For relatively small quantities

Figures 11 and 12 show two charging processes with different condensation temperatures. The heat source temperature is 88°C and the final water content (X_{iso}) reached in the silica gel is about 4.3 % at 38°C condensation temperature and 2.3% at 16°C condensation temperature.

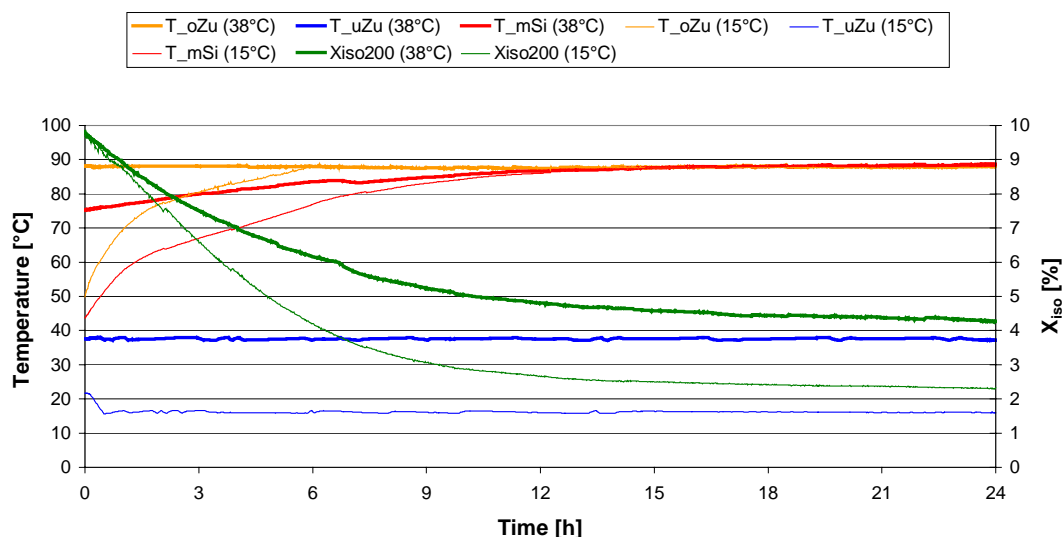


Figure 11. Desorption with two different condensation temperatures, water content and temperatures

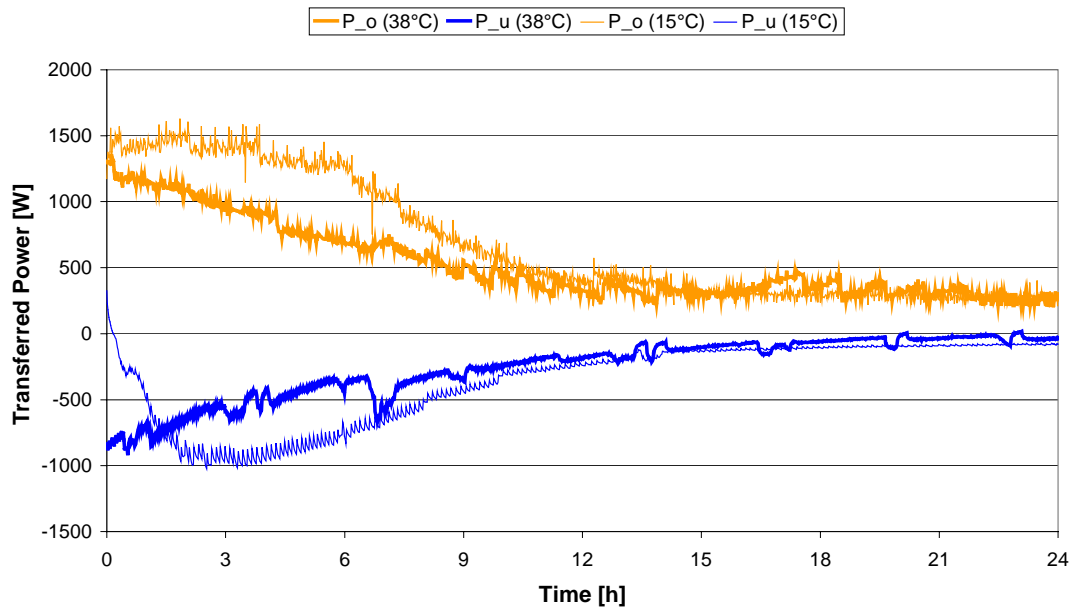


Figure 12. Desorption with two different condensation temperatures, transferred power

It could also be shown that it is possible to operate the system if the heating process and the condensation process are not simultaneous. This case could be relevant if the store is heated during the day using the solar collectors and no heat sink is available at the same time. In that case, the collectors can function as a heat sink at night.

A discharging cycle is shown in the following figures. The adsorption started at an adsorber temperature of 55°C. Water was led into the evaporator area and evaporation started right away although the evaporator was not heated. The temperatures measured in the water surrounding the heat exchanger and in the evaporator loop decreased below 10°C. On the other hand, the adsorber temperature increased rapidly to almost 70°C. Then, it decreased again because the store was discharged into the space-heating loop.

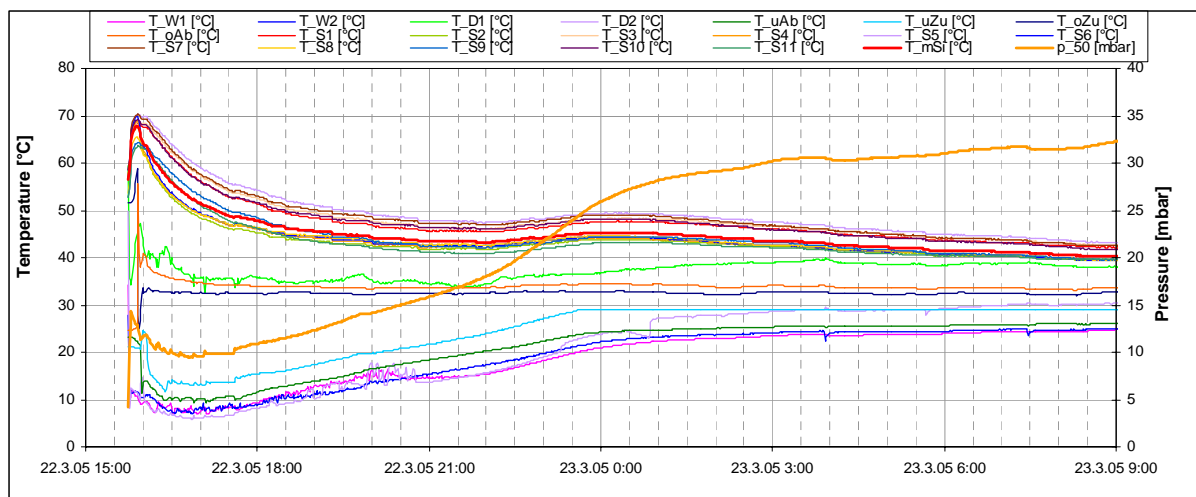


Figure 13. Temperatures and pressure, adsorption test

The results show that high temperatures can easily be reached in the adsorber if it is still very dry.

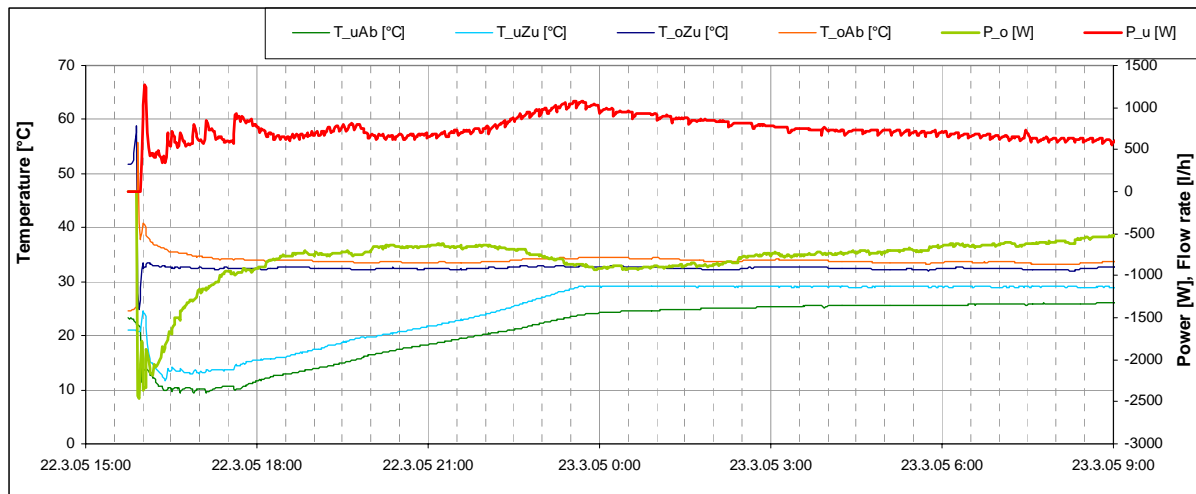


Figure 14. Power and temperatures, adsorption test

The power withdrawn to the space-heating loop was not very constant but depended on the current store temperature because inlet temperature and flow rate were kept constant. In the beginning of the test with store temperatures of almost 70°C, the power withdrawn reached almost 2500 W. Then, it decreased to between 500 and 1000 W. Of course, this is not a realistic situation for a space-heating loop. If the temperatures available in the store are higher than needed, the mixing valve in the space-heating loop will decrease the flow rate and the power discharged from the store will stay the same.

2.3.4 Development Status

The laboratory tests show that the sorption storage system works in principle. Some constructive measures to improve the system operation could be identified and were incorporated into a pilot plant system for a single-family house.

However, the main problem remains the low storage density due to the adsorption characteristics of the material combination. The materials used here are not suitable for an application for heat storage for solar space heating.

For reaching the goal of seasonal storage, very large storage volumes would be necessary. While this might be technically feasible, it does not make a lot of sense because the system would be very expensive and the main problem remains, that almost all of the energy (for evaporation) has to be delivered in winter by the solar thermal system even if at a lower temperature.

More materials research is needed to identify a different sorption material and working fluid combination where the fraction of the binding energy is higher compared to the evaporation enthalpy. Another possibility would be a materials combination with lower evaporation temperatures.

2.3.5 Acknowledgements

The work reported here has been financed by the European Commission, the Austrian Ministry for Transport, Innovation and Technology and the Austrian Federal State of Styria.

2.3.6 References

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2.4 NaOH Storage

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2.4.1 Background

A laboratory prototype has been built. With that, the performance of the built in heat exchanger shall be shown. The concentration ratios of the lye at different temperatures and the corresponding vapour pressure are crucial for the heat power and the heat capacity. With that prototype, those parameters shall be optimised.

2.4.2 Design and Operating Principles

The storage is working like a two stage heat pump. The driving force is the differences of the lye concentrations. To charge the storage, NaOH is concentrated with the help of solar heat. To discharge the storage, vapour is absorbed by the concentrated NaOH. For marginal conditions where the required temperature lift during discharge is greater than is possible with the weak solution, it is proposed to operate the system in two stages with two units. The first unit lifts the temperature from the ground heat exchanger with weak solution and the second unit lifts from this intermediate temperature to the final required temperature. Two sets of discharge are required for this operation, but a the solution can be used over a greater concentration range.

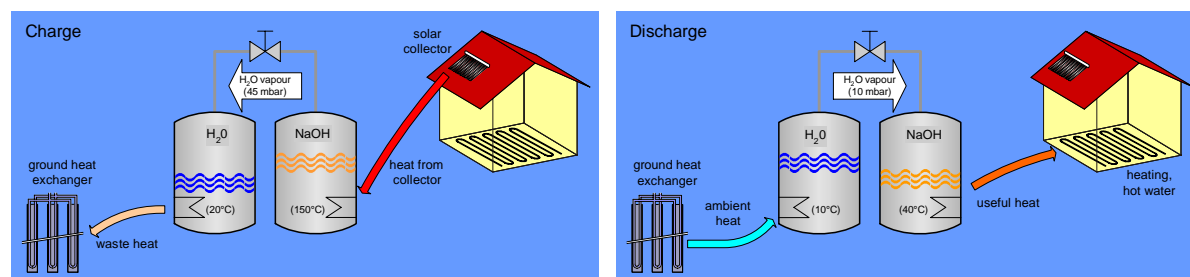


Figure 15. Schematic of the NaOH store.

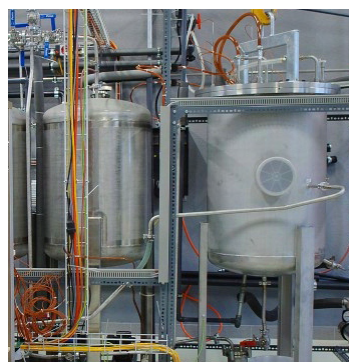


Figure 16. Picture of the NaOH store.

2.4.3 Laboratory Test Results

No test results until now.

Table 6 Design specification for NaOH storage (Calculated Values)

Parameter	Calculated Performance	Boundary Conditions
Storage materials weight: NaOH H ₂ O	160 kg 160 kg	Laboratory Prototype
Storage capacity for heat	8.9 kWh	Laboratory Prototype
Floor space required for prototype	2 m ²	Laboratory Prototype
Energy density of material (NRJ4.1) (ratio to water 25/85°C)	250 kWh/m ³ (3.6)	Two stage prototype
Energy density of prototype (NRJ4.2) (ratio to water 25/85°C)	5 kWh/m ³ (0.07)	No effort has been made to optimize the volume of the Laboratory Prototype
Charge rate	1 kW	Laboratory Prototype
Discharge rate	1 kW	Laboratory Prototype
Estimated size for 70 kWh (ratio to water 25/85°C)	1.3 m ³ (0.75)	Two stage storage
Estimated size for 1000 kWh (ratio to water 25/85°C) ¹	5 m ³ (2.9)	Two stage storage
Cost of material	250 €/m ³	

¹ Assumptions: About 1m³ is needed for heat exchangers, pumps, valves and empty vessels.

Temperature boundary conditions:

Laboratory prototype	Hot side	Cold side
Charging (Desorption of vapor)	95°C	20°C
Discharging (Adsorption of vapor)	70°C	10°C
Two stage prototype		
Charging (Desorption of vapor)	150°C	20°C
Discharging (Adsorption of vapor)	70°C	10°C

The actually laboratory prototype is build to show the principle, to measure temperatures and pressures and to show the handling. It isn't build for optimizing the volume and the heat capacity!

2.4.4 Development Status

Make all the foreseen measurements with the now built prototype. Expand the prototype with the second stage.

3 COMPARISON OF PROTOTYPES

The different technologies are at very different stages of development. All are closed systems and act as thermally driven heat pumps. The TCA technology is in the process of commercialisation by the Swedish company ClimateWell AB, and over 20 storage systems have been installed, mostly in Spain. A further 100-200 are planned for 2007. However, the storage system is sold as a chemical heat pump with the main emphasis on cooling, the storage for cold being more important than for heat. The complete systems usually have solar collectors with gas backup, and are designed for both heating and cooling. The storage density for cold, when compared to water, is also more favourable, with a factor 4.7 for the commercial prototypes as opposed to only 1.2 for heat storage. This is due to the fact that the temperature range available for water storage for cold is much smaller ($\sim 10^{\circ}\text{C}$) than for heat ($\sim 60^{\circ}\text{C}$). The other technologies are in the prototype stage with no companies intending to develop and market them. The Modestore store was developed in a European project, and the main company within the project (Sortech) is commercialising the technology as a heat pump with essentially no heat storage. The other two technologies are at the lab prototype stage.

For short term heat storage, none of the technologies have a significant advantage compared to water in terms of storage density. The energy density can only be slightly greater than that for water, mainly due to the space required for heat exchangers and other components. In addition all of the storage systems lose heat during the charge and discharge process due to irreversibilities in the processes themselves. Most of this is due to the different temperature levels of charge/discharge and the related sensible energy between these. However, for longer term storage the energy density for the TCA and NaOH storage systems is nearly three times that of water. In addition, once the sensible heat from the solution has been lost, the energy can be stored indefinitely, a significant advantage compared to water.

In terms of material cost, all materials are expensive compared to water, with NaOH being by far the least expensive. The cost for the whole storage system has not been estimated here. For the ClimateWell 10, the projected cost is $\sim 8000\text{€}$ for a heat pump system consisting of two units in parallel, with a total heat storage capacity of 70 kWh.

Parameter	TCA 80-100°C	NaOH 95°C test 150°C calculated	Modestore 88°C	SPF 180°C
Type of technology	Closed three phase absorption	Closed two phase absorption	Closed adsorption	Closed adsorption
Cost of material	3600 €/m ³	250 €/m ³	4300 €/m ³	2-3000 €/m ³
Storage materials weight:	LiCl salt 54 kg Water 117 kg Steel 47 kg	NaOH 160 kg Water 160 kg	Silica gel 200 kg Water 30 kg Steel 100 kg Copper 50 kg	Zeolite 13X 7 kg
Storage capacity for heat	35 kWh	8.9 kWh	13 kWh	1 kWh
Floor space required for prototype	0.46 m ²	2 m ²	0.4 m ²	0.3 x 0.3 m ²
Energy density of material (NRJ4.1) (ratio to water 25/85°C)	253 kWh/m ³ (3.6)	250 kWh/m ³ (3.6)	50 kWh/m ³ (0.71)	180 kWh/m ³ (~ 3)
Energy density of prototype - heat (NRJ4.2) (ratio to water 25/85°C)	85 kWh/m ³ (1.2)	5 kWh/m ³ (0.07)	33.3 kWh/m ³ (0.48)	57.8 kWh/m ³ (~ 1)
Energy density of prototype - cold (ratio to water 7/17°C)	54 kWh/m ³ (4.7)	-	-	-
Charge rate	15 kW	1 kW	1-1.5 kW	-
Discharge rate	8 kW	1 kW	0.5 - 1 kW	0.8 kW / 1.8 kW
Estimated size for 70 kWh (ratio to water 25/85°C)	0.64 m ³ (1.6)	1.3 m ³ (0.75)	1.7 m ³ (0.59)	1.2 m ³ (~ 1)
Estimated size for 1000 kWh (ratio to water 25/85°C)	5.3 m ³ (2.7)	5 m ³ (2.9)	23 m ³ (0.62)	17 m ³ (~ 1)

4 Conclusions

For short term heat storage, none of the prototypes that have been reported here have a significant advantage compared to water in terms of storage density. The energy density can only be slightly greater than that for water, mainly due to the space required for heat exchangers and other components. In addition all of the storage systems lose heat during the charge and discharge process due to irreversibilities in the processes themselves. Most of this is due to the different temperature levels of charge/discharge and the related sensible energy between these. The tested prototypes can be used as thermally driven heat pumps, although only one is designed (and tested in the field) for this application. The energy density for cold storage for this prototype is significantly higher than for water (over 5 times) mainly due to the fact that only a small temperature range can be used for the water store.

For longer term storage the energy density for the TCA and NaOH storage systems is nearly three times that of water. In addition, once the sensible heat from the solution has been lost, the energy can be stored indefinitely, a significant advantage compared to water. However, the cost of the material is very important for long term storage, and Lithium Chloride is too expensive for this. Further research into materials is required to gain higher energy densities that using a material that is inexpensive. It is not possible at this stage to determine definitely which type of process is best suited for long term storage, but the current materials for closed adsorption are long way from being of interest for this application.