Literatuurstudie reactorontwerpen 'Thermochemische Materialen' (TCM)

EOS-LT Waels

TCM Reactor design

Literature overview
Update WAELS

Author(s)

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1 Introduction

At ECN, work is done on long-term storage of (solar) heat with thermochemical materials (TCM). The first phase in this research is the characterization of suitable materials, which presently focuses on the hydration and dehydration of solid $MgSO_4$ (in powder form). In the next phase, a system should be designed in which the chosen TCM material is applied. As a start for this second phase, it was decided to make an overview of the available literature to see how others have tackled the problems in the design of such systems.

In this overview, not only seasonal thermochemical storage systems have been taken into account, but also some attention has been given to small systems such as absorption heat pumps and chillers, using a variety of absorbing materials (e.g. silicagel, zeolites, Na_2S, NaOH, LiCl). However, the designs found for such systems cannot be applied directly to our case, since for seasonal storage a very large amount of TCM is required (several cubic meters) to get a high solar fraction, which creates many additional problems related to heat- and vapor transport, as well as sensible heat loss at frequent switching on and off. Nevertheless, it was considered useful to include also small systems in this overview, since also the designs found for small systems may lead to new ideas for reactor design in large systems.

2 Background of TCM research

The work on Thermochemical heat storage has already a long history. A large amount of work has been carried out in Sweden in the late 70's and early 80's, on which Lund (1996) gives the following account:

Thermochemical heat storage as such is not on the market. One of the main industrial developments on thermochemical storage of solar heat was the so-called Tepidus system in Sweden in late 70's. It comprised a solid sodium sulphide storage based on the reaction 5 H_2O (gas) + Na_2S (solid) $\Leftrightarrow Na_2S$ x 5 H_2O (solid). The main advantage of this storage concept was a relatively high theoretical storage density ~500 kWh/m³, the low cost of the salt, and an operating temperature (55-100 °C) suitable for solar collectors. The Tepidus system had several technical problems and was disbanded in early 80's. Some renewed interest in this concept has been shown in 1990's. (Lund, 1996)

Oelert (1982) gives a sketch on the Na_2S storage system of the Swedish company Tepidus AB:

ENERGY STORING SYSTEM TEPIDUS

1 SOLAR COLLECTOR
2 ALTERNATIVE HEAT SOURCE
3 TAPWATER
4 RADIATOR
5 PUMP
6 ENERGY ACCUMULATOR
7 LOW PRESSURE DEVICE
8 CONTROL UNIT
9 SOIL HEAT EXCHANGER
10 CONDENSER / EVAPORATOR / WATERTANK
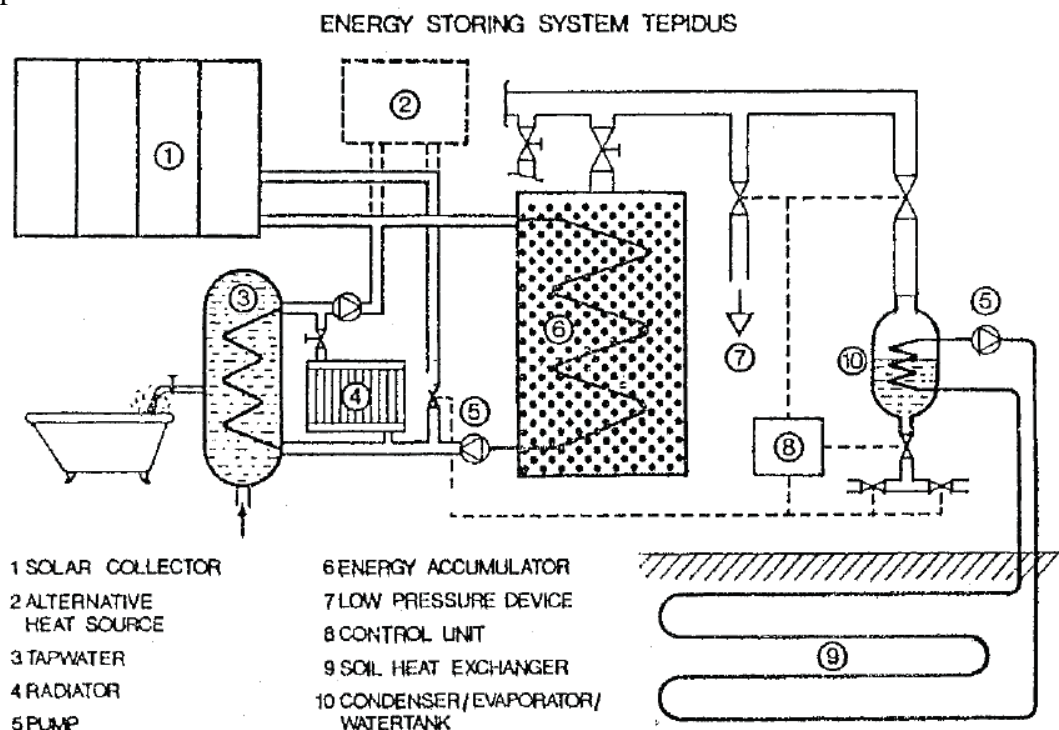
Source: Tepidus AB

Figure 1: Tepidus Na₂S system (from Oelert, 1982).

Futhermore, Brunberg (1980) indicates that two large scale demonstration projects are ongoing. Figure 2 shows one of these projects, on which he gives the following information:

The first project is a family house built in 1953 with a living area of about 80 m² where accumulators containing about 7000 kg of substance have been installed. The house will be 100% solar-heated. A sketch of the main parts of the system (Fig. ll) shows the accumulator (B) as well as the combined condenser/evaporator (C) in the basement of the house. As the house we were offered for use for the experiment is not oriented towards south and further more is screened from the sun by a nearby building we were forced to mount the solar collectors (A) on the roof of that building. In the garden a system 900 m of polyethylene pipes (D) have been dug down. The plant is already in operation but the

electronic processer of the system and facilities for recording such different parameters as heat flows, temperature and power is not yet completed. The accumulators are at present charged by heat from an electric boiler and will be discharged before the charging using solar collectors starts in March-Apr. (Brunberg, 1980)

A) SOLFANGARE   A) SOLAR COLLECTOR
B) ENERGIACKUMULATOR   B) ENERGY ACCUMULATOR
C) KONDENSOR/FORANGARE   C) CONDENSER/EVAPORATOR
D) MARKSLINGA   D) SOIL HEAT EXCHANGER
E) RADIATOR/TAPPVARMVATTEN   E) RADIATOR/TAPWATER
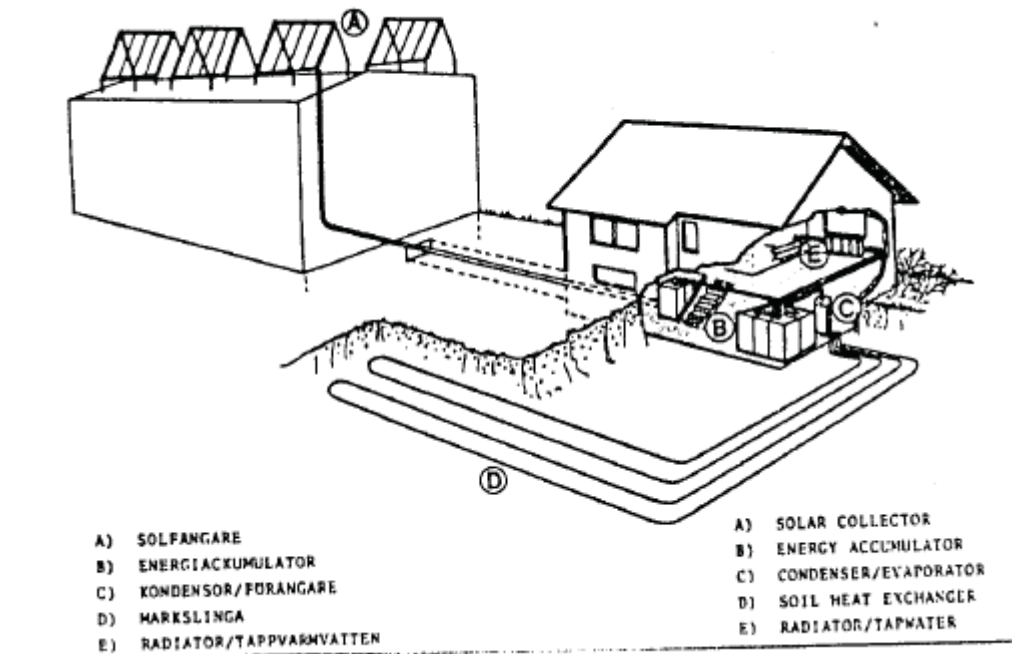
Figure 2: Demonstration project of the Tepidus system (Brunberg, 1980).

An interesting publication is the report by Oelert et al (1982), which gives an overview of the potential of a number of applications, as shown in Figure 3. As typical problem areas, he gives the heat transfer, noncondensables, parasitic energy use, the use of the heat of condensation, the interlinking of heat sources and sinks, kinetics, sensible heat losses, safety, complexity, economy, long term stability and system optimisation. In his conclusions, Oelert states that

"a solar seasonal thermochemical storage system for a single family house has a high energy conservation potential but requires ca. 5-10 times the investment of a continuous heat pump, which still has a reasonable energy conservation potential. [..] practical energy storage densities are not high enough and equipment cost is too high to qualify thermochemical heat storage economically for long term heat storage, [..] due to high complexity, thermochemical heat storage is unlikely to be able to compete against sensible (and latent) heat storage for short term purposes in most applications. [..] Thus the greatest possibilities of thermochemical storage seem to be found in medium term (=size) storage and heat transforming, but in spite of the problems described above, solar seasonal applications should also be considered since their theoretical energy conservation potential is high [..] (page 16-18)"

No.	Application		Charging source		Discharging source*		Reaction
	type	temperature °C	type	temperature °C	type	temperature °C	
1	single family house	30-60	solar	40-100	ground coil	< 15	1
2		45-60	"	70-100	"	"	2
3		45-90	industrial WH	100	"	"	3
4		45-60	"	60-90	industrial WH	< 90	4
5	multi family house	45-90	off peak el. power	550	n.a.	n.a.	5
6	omitted						
7	group central	60-100	solar	70-100	ground coil	< 15	6
8		<100	industrial WH	50-100	industrial WH	<100	7
9	district heating	100	"	150	n.a.	n.a.	8
10		130	fossil power station	190	n.a.	n.a.	"
11		<180	high temp.nucl.react	900	n.a.	n.a.	9
12a	vehicle propulsion	mechanical energy	industrial WH	>150	n.a.	n.a.	10
12b			"	160	n.a.	n.a.	11
13	utility power st.	450	fossil fired boiler	550	boiler	550	12
14	cascading	500	steel plant WH	600	steel plant WH	>100	"
15	process heat (heat pipe)	600	cement kiln WH	>800	n.a.	n.a.	13
16	process heat	<200	industrial WH	150-300	industrial WH	< 70	14
17	"	100	"	150-300	"	> 50	15
18	"	120-130	excess process steam	150	n.a.	n.a.	16
19	"	100	industrial WH	50-110	industrial WH	70	17

* If marked "n.a.", then no discharging source necessary or given by definition of case study.

1   $CaCl_2 \cdot 2CH_3OH \leftrightharpoons CaCl_2 + 2CH_3OH$
2   $Na_2S \cdot 5H_2O \leftrightharpoons Na_2S + 5H_2O$
3   $H_2SO_4 \cdot H_2O \leftrightharpoons H_2SO_4 + H_2O$
4   $Na_2S \cdot 5H_2O \leftrightharpoons Na_2S + 5H_2O$
5   $Ca(OH)_2 \leftrightharpoons CaO + H_2O$
6   $CaCl_2 \cdot H_2O \leftrightharpoons CaCl_2 + H_2O$
7   $CaCl_2 \cdot 8NH_3 \leftrightharpoons CaCl_2 \cdot 4NH_3 + 4NH_3$
8   $H_2SO_4 \cdot H_2O \leftrightharpoons H_2SO_4 + H_2O$
9   $CH_4 + H_2O \leftrightharpoons Co + 3H_2$

10   $(CaCl_2 + LiCl) \cdot H_2O \leftrightharpoons (CaCl_2 + LiCl) + H_2O$
11   $NAOH \cdot H_2O \leftrightharpoons NaOH + H_2O$
12   $Ca(OH)_2 \leftrightharpoons CaO + H_2O$
13   $SO_2 + 1/2 O_2 \leftrightharpoons SO_3$
14   $FeCl_2 \cdot 6NH_3 \leftrightharpoons FeCl_2 \cdot 2NH_3 + 4NH_3$
15   $Zeolite \cdot H_2O \leftrightharpoons Zeolite + H_2O$
16   $H_2SO_4 \cdot H_2O \leftrightharpoons H_2SO_4 + H_2O$
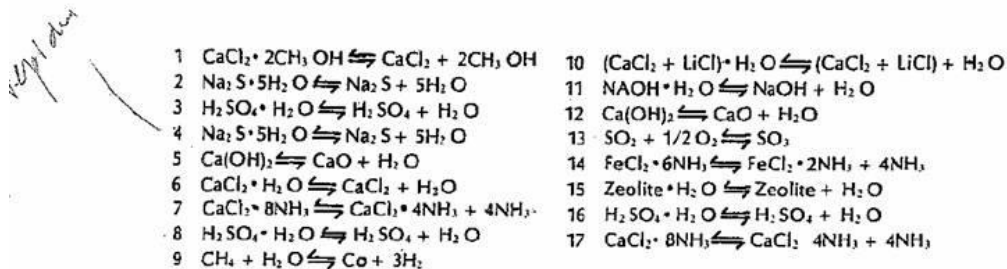17 $CaCl_2 \cdot 8NH_3 \leftrightharpoons CaCl_2 \cdot 4NH_3 + 4NH_3$

Figure 3: Systems examined by Oelert (1982)

Chart 0-2: Case study assessment

Case Study No.	Appli-cation	Heat Source	Reaction (Abbrev.)	Energy con-servation potential	Design/ Operation	Environ-mental compati-bility	Invest-ment Cost	... as com-pared to	Note
1	SFH	solar	$CaCl_2$/ CH_3OH	++	0	++	--	continuous ground coil heat pump	
2	"	"	Na_2S/H_2O	++	0	-	-	"	
3 (A)	"	inter-mittent	H_2SO_4/H_2O	+	--	--	-	source opti-misation	
4 (B)	"	"	Na_2S/H_2O	+	0	-	+	hot water storage	
5 (O)	MFH	off peak elect.	CaO/H_2O	0	--	0	+	refractory heat storage	
6									case study omitted
7	GC	solar	$CaCl_2/H_2O$	++ *)	-	0	0	seasonal hot water storage	*) in principle, but with more suitable reaction
8	"	inter-mittent ind. waste heat	$CaCl_2/NH_3$	0	0	--	-	water storage	
9	DH	fluctua-ting ind. waste heat	H_2SO_4/H_2O	0	--	---	--	conventional DH with hot water buffer	
10	"	FPP-heat Fossil power plant	"	0	-	--	-	conventional DH with hot water buffer	
11	"	Nuclear power plant	$CH_4/CO+H_2$			-			case study out-side evaluation
a 12 b	Vehicle	ind. waste heat	$CaCl_2+LiCl/$ H_2O $NaOH/H_2O$	-- / -	-- / -	0 / -	-- / --	electric vehicle	
13	utility boiler	utility boiler	CaO/H_2O	0	--	0	-	hot water buffer or steam drum	
14	PH	fluctua-ting ind. waste heat	"	+	-	0	-	sensible heat storage + WH boiler	
15	"	"	SO_2/O_2	0	--	--	---	sensible heat storage + WH boiler with cogen.	
16	"	"	$FeCl_2/NH_3$						react. thermo-dyn. unsuitable
17	"	"	zeolite	+	0	+	0	sensible heat storage with ORC	
18	"	"	H_2SO_4/H_2O	0	--	--	--	steam drum	
19 (B)	"	"	$CaCl_2/NH_3$	0	-	--	-	continuous heat transfor-mer with buffer	

++ very advantageous   0 neutral   -- very problematic
+ advantageous   - problematic

Figure 4: Oelert (1982), the assessment of the case studies presented in Figure 3.

In the USA, a large amount of work was done on chemical absorption heat pump systems, as reported e.g. the following studies
- "Thermal Energy Storage technical progress report April 1984- March 1985" by Martin (1985), reporting on the progress in the ORNL thermal energy storage program, running since 1976, which focused among other subjects on ammoniates for absorption heat pumps, with experimental work on LiCl, NaBr, $CaCl_2$, $BaCl_2$ and CaF_2
- "Evaluation of Thermally Activated Heat Pump/Desiccant Air Conditioning Systems and Components" by Parsons et al (1987)
- "Absorption fluids data survey: final report on worldwide data" by Macriss et al (1988).

In addition, some attention was given to thermochemical storage for (highly) concentrating collector systems, on which a review paper was published by Wyman et al. (1980) reviewing solar collector and thermal energy storage technologies suitable for the temperature range between approximately 100 and 500°C.

The interest in thermochemical storage seems to have largely disappeared in the beginning of the '80s, until in the last 10 years a number of research groups have taken on the subject again. The reactor concepts developed by these groups are the subject of the present memo.

3 Closed Systems with solid TCM material

3.1 Introduction

With solid TCM powders, high energy storage densities can be obtained. In the literature, only fixed bed systems could be found. However, the heat transfer and to a lesser extent the vapor transport are limiting aspects, requiring large heat exchanging volumes and thin layers. In addition, the loss of sensible heat is problematic on frequent switching on and off of reactors.

3.2 Storages

3.2.1 Introduction

Basically, two project lines can be found in this area. One line is the work on seasonal storage with silicagel-based storages that was started by the company UFE, and was continued in the EU projects HYDES and MODESTORE, and finally in the Austrian national Haus-der-Zukunft project MODESTORE. The second line is the work that is carried out by SPF in Switzerland on a small storage system of a few kWh storage capacity.

Erste Basisarbeiten für das vorliegende Projekt, die Entwicklung eines geeigneten Langzeitspeichers auf der Basis der Feststoffsorption (Silikagel), wurden 1995 von der Firma UFE SOLAR GmbH (BRD) zusammen mit dem Fraunhofer Institut für Solare Energiesysteme (ISE) begonnen.

Eine kontinuierliche Fortsetzung der Forschung in diesem Bereich erfolgte durch das von der "Europäischen Kommission" und durch das Bundesministerium für Verkehr, Innovation und Technologie geförderte Projekt HYDES, an dem auch die AEE INTEC beteiligt war (siehe Kapitel 5.1).

Im EU-Projekt MODESTORE wurde aufbauend auf den Ergebnissen aus HYDES ein Sorptionsspeicher der zweiten Generation entwickelt (siehe Kapitel 5.2).

Das vorliegende Projekt MODESTORE (Haus der Zukunft) baut auf die oben angeführten Projekte auf und hat zum Ziel, in einer ersten Pilotanlage das Funktionieren des Sorptionsspeichers in einer realen Anwendung unter Beweis zu stellen.

Project overview from Wagner (2006)

3.2.2 Silicagel & Selective Water Sorbents[1]: EU project HYDES

Project partners: AEE INTEC, Fraunhofer-ISE, UFE-Solar, AUSTRIA EMAIL AG, SOLPROS A.Y. Project time: 1998-2001, SWS storage in demonstration project Gleisdorf
- Applied sorbents
    - Grace 127B
    - Selective Water Sorbent (silicagel impregnated with CaCl2)
    - Modified silicagel from Grace
- Obtained energy density: 135 kWh/m³
- Low mean power: 1.5 kW

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[1] SWS is a combination of an adsorption material like silicagel with an absorbing material such as $CaCl_2$.

Heizungssystem

Kollektor

Winter   **Sommer**

Adsorber

Ventil

Verdampfer/
Kondensator

Sorptionsspeicher

Abwärme

collector area

electrical
flow heater

space heating

distributing bus bar 1

heat exchanger 1

heat exchanger 2

adsorber 1
tank

adsorber 2
tank

condenser/
evaporator
tank

domestic
hot water
tank

rain water
cistern

distributing bus bar 2

10
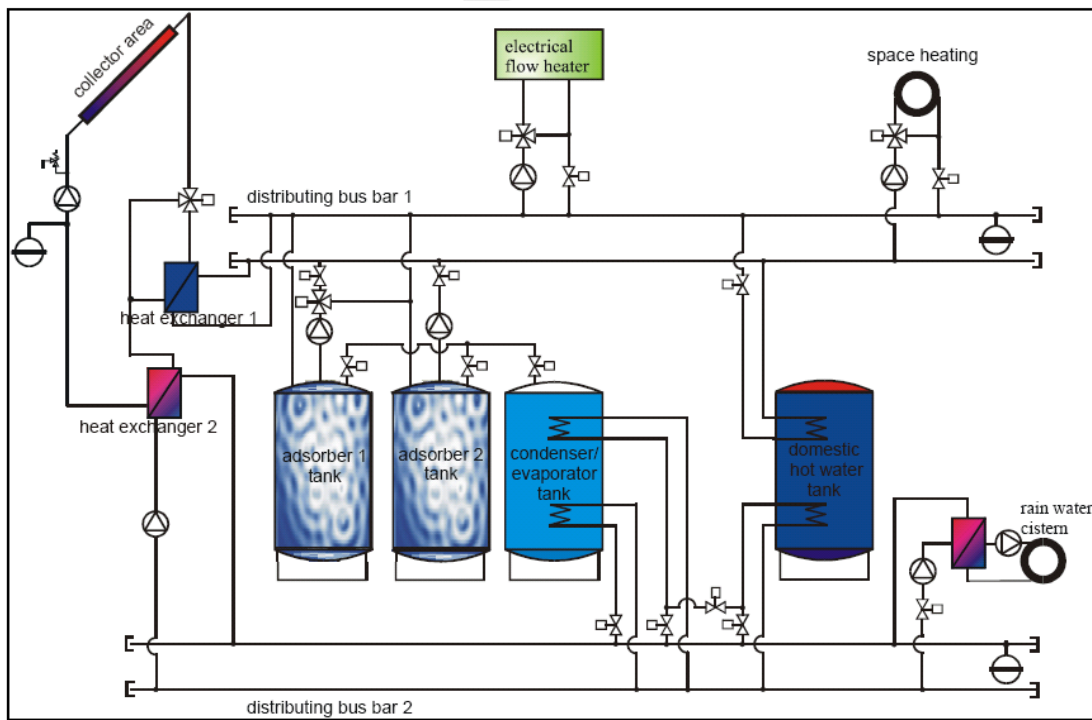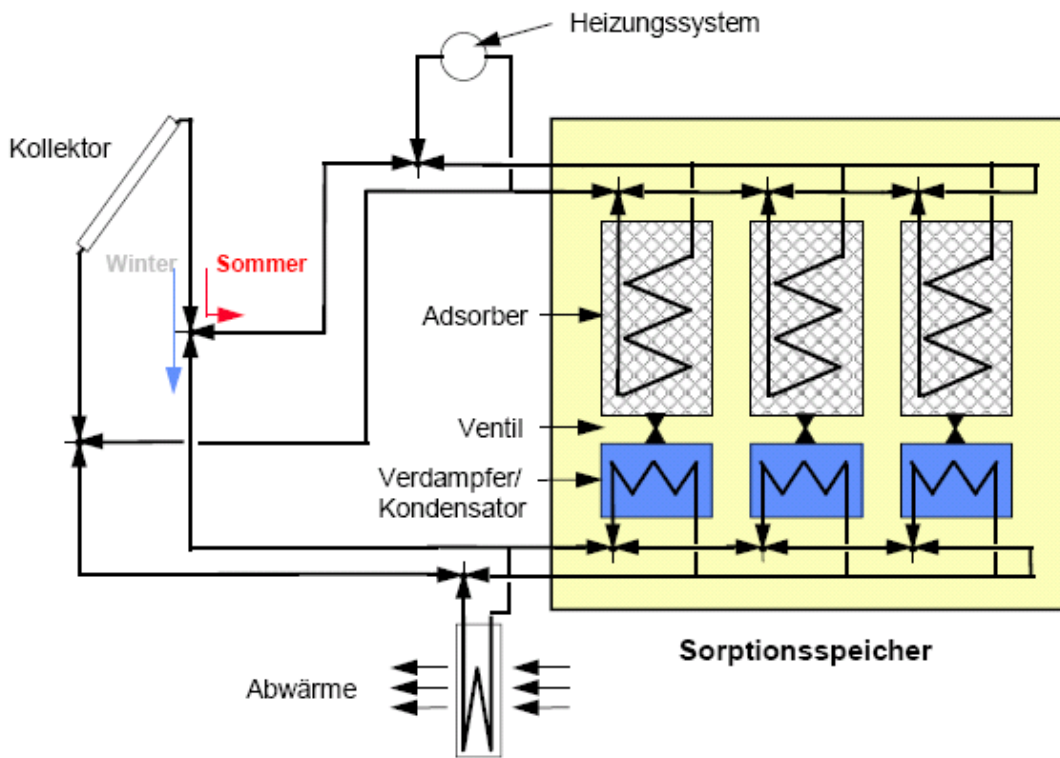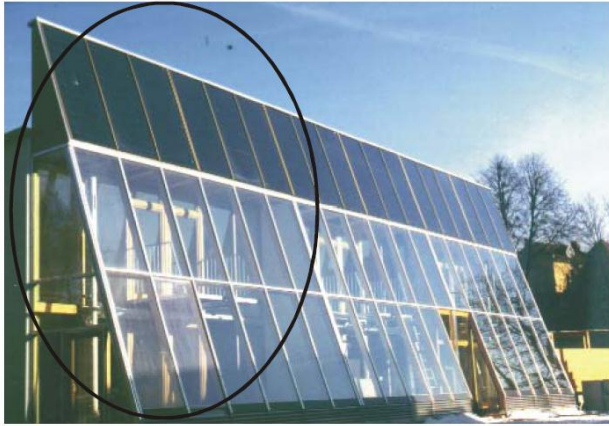
22 m2 collector.

Ergebnisse der Testmessungen
(Mai 2001):

➢ Eingesetzte Sorbens:
  Grace 127B
➢ Erreichte Energiedichte:
  133 kWh/m³
➢ Leistung
  Adsorber: 2.8 bis 10 kW
  Verdampfer: 0.7 bis 4.8 kW
➢ Betriebsart
➢ Betriebstemperaturen
  Nutztemperatur: 45°C bis
  50°C
  Maximale $T_{verd.}$ 32°C
  Desorption: 82°C

The conclusion of the project was that the system was technically feasible, but that the system control should be optimized. Storage densities of 115 kWh/m3 silicagel in one tank and 122 kWh/m3 silicagel in the other were obtained, which was roughly 1.8 times the energy density of a water storage. The theoretical maximum was given as 140-150 kWh/m3 silicagel. It was found that to obtain water fractions of below 10%, a regeneration temperatures of 80- 90 C was required and a condenser of about 30 C. For a water fraction of 2%, regeneration temperatures of over 95C were required and a condenser temperature below 20 C (which was obtained by using a rain storage as sink).

3.2.3 Silicagel – EU project Modestore[2]

The work was continued in the EU project MODESTORE. Project partners in this project were Fraunhofer ISE (project coordinator), Solpros, Ecofys, The Swedish Polytechnic in Finland, SorTech, AEE Intec, PSE GMBH.
Project partners Austrial national Modestore project: AEE Intech (Dagmar Jaehnig), together with Solution Solartechnik GmbH and Behältertechnik Pink GmbH.

In this project, a second generation system was developed, that was more integrated than the first generation system applied in the HYDES project. Also other adaptations were applied, such as a reduction in the roll distance between the copper roll heat exchanger (reduced from 5 cm to 4 cm), and it was ensured that the flow would

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[2] Modular High Energy Density Sorption Heat Storage

always be turbulent, to optimize the heat transfer. Two storage vessels were used with 500 kg silicagel each (Wagner, 2006).

Figure 2: Prototype storage module
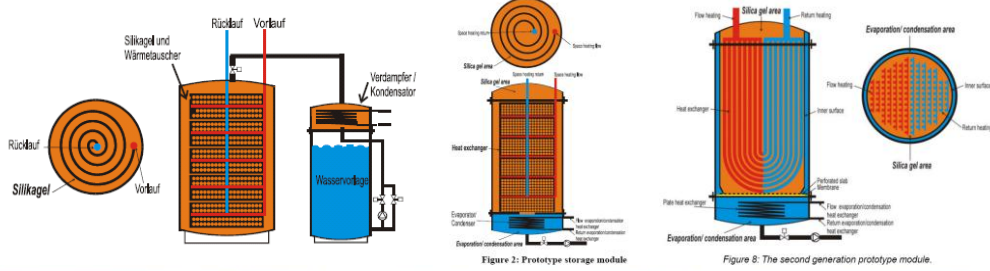
Figure 8: The second generation prototype module.

Abb. 8: Anfertigung des Sorptionswärmetauschers bei der Firma „Behältertechnik Pink GesmbH", Rohre werden ganzseitig in einem Lötofen gelötet (links) und nachher eng zusammengerollt und auf Dichtheit getestet (rechts).

AEE Intec Pilot plant

- Low energy - single family house
- Austria
- 32 m² flat plate collectors

- 900 l hot water buffer store
- 2 sorption storages 1000 kg silica gel total
- low temperature floor heatig system

The system is in operation since July 2005. The desorption works fine but the space heating lift is below expectations.

Obwohl der Betrieb des Systems zufriedenstellend verlaufen ist und das Systemkonzept in dieser Form auch in weiteren Anlagen umgesetzt werden könnte, hat sich herausgestellt, dass mit der verwendeten Materialpaarung die Sorptionsspeicherung zwar technisch umsetzbar ist, aber dass der damit zu erzeugende Temperaturhub nur in einer schmalen Bandbreite von Wasserbeladungen des Silikagels auch technisch nutzbar ist. Wenn das Silikagel sehr trocken ist, erzeugt es einen brauchbaren Temperaturhub, ab einer Beladung von etwa 13% jedoch wird der Temperaturhub so klein, dass er in einer realen Anwendung mit Wärmetauschern, Rohrleitungen und Behältern, die alle verlustbehaftet sind, nicht mehr nutzbar ist. Dies bedeutet, dass die technisch nutzbare Energiedichte dieses Materials weit von der theoretischen und auch weit von der im Labor messbaren Energiedichte entfernt ist. Somit bräuchte man sehr große Mengen des Materials, was weder technisch noch wirtschaftlich sinnvoll ist.

It was finally concluded that silicagel was not a feasible material for such seasonal storages, and that modified zeolites may be considered.

3.2.4 Silicagel & Zeolite storage (SPF)

SPF is carrying out research on a small scale absorption storage (Gantenbein, 2003).
Details of the system are shown below.

Durchgeführte Arbeiten und erreichte Ergebnisse
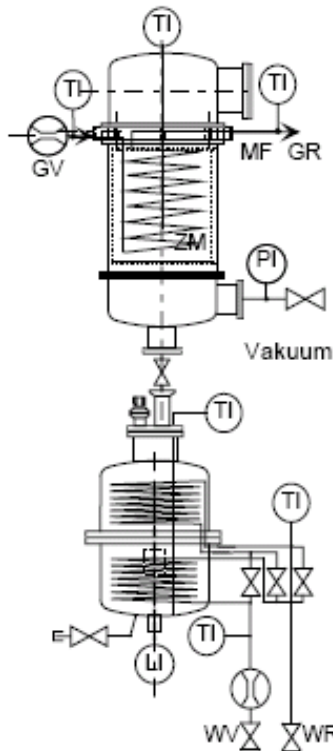
Aufbau der Anlage: Die geschlossene Sorptionsspeicheranlage wurde für eine Energie von 3 – 5 kWh dimesioniert [1, 2] und aufgebaut. Das Sorptionsmodul kann 35 l Sorbent (Sorptionsmaterial) aufnehmen und in der Wasservorlage haben 24 l Wasser Platz. Die Anlage besteht aus den folgenden Teilen: Sorptionsspeichermodul zur Aufnahme des Sorptionsmaterials (Silicagel, Zeolith); Wärmetauscher im Sorptionsmodul eingebaut; erster externer Wärmeträger (Glykol) Kreislauf zur Entnahme/Zuführung von Wärme aus/in dem/das Sorptionsmodul; Wasservorlage als Speicher für das Sorbat (Wasser); dem in der Wasservorlage eingebauten Wärmetauscher; Verbindungsrohrleitung zwischen Sorptionsmodul und Wasservorlage mit eingebautem Absperrventil (Kugelhahn); zweiter externer Kreislauf zur Entnahme/Zuführung von Wärme aus/in der/die Wasservorlage; Messfühler für Temperatur, Druck, Wasserstand und Durchfluss; Datenerfassung mit einem Logger und PC. In Fig. 1 ist eine schematische Darstellung der Anlage sowie in Fig. 2 bis 4 sind Fotos zu sehen. Als Sorptionsmaterial wurde Silicagel (UETIKON 720) mit einer Körnung von 1 – 3 mm eingesetzt.

Fig. 1: Schematischer Aufbau der Sorptions-speicheranlage. Oben ist das Sorptionsmodul (ZM) und unten ist die Wasservorlage. Im Sorptions-modul ist ein Spiralfinen Wärmetauscher und in der Wasservorlage ist ein Spiralschlauch Wärme-tauscher eingebaut. Bezeichnungen: TI, PI, LI: Temperatur-, Druck-, Niveaufühler. GV/GR: Glykolvorlauf / Glykolrücklauf; erster externer Kreislauf. WV, WR: Wasservorlauf / Wasserrücklauf; zweiter externer Kreislauf (Thermostatbad). MF: Messflansch.
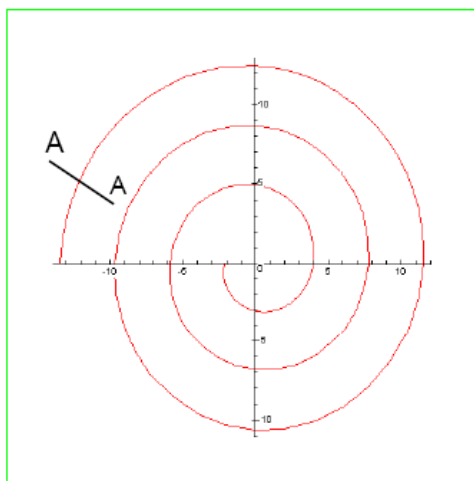
Schnitt A-A

Fig. 5: Rechts: Mittellinie des Grundrisses des „Spiralfinen Wärmetauschers" aus Kupfer. Die Mittellinie entspricht dem Wärmeträger führenden Rohr mit einem Druchmesser von 8 mm. Der Wärmetauscher hat 4 in Spiral Form gewickelte Kupferblechstreifen mit je einer Länge von 1.9 m sowie einer Breite von 0.12 m und hat damit eine Übertragungsfläche von 1.8 m^2.
Oben: Querschnitt schematisch.

Gantenbein indicates that at low pressure the radiative heat transfer is important, and therefore the heat exchanger should have a high emission.

Fig. 6: Foto des oberen Teils des Sorptionsmoduls mit Messflansch sowie den Vakuumdurchführungen für die Temperaturfühler Pt 100 und das Wärmeträgermedium.

Fig. 7: Foto des Spiralfinen Wärmetauschers von oben. Die Oberfläche ist noch nicht auf ein hohes ε behandelt. Dieser Wärmetauscher ist im Sorptionsmodul eingebaut.

Fig. 8: Foto der Wasservorlage mit den Vakuumdurchführungen an die Spiralschlauch Wärmetauscher. Der Stutzen für die Vakuumpumpe ist oben angeordnet.

Fig. 9: Foto eines Spiralschlauch Wärmetauschers von oben. Zwei solche Wärmetauscher sind in der Wasservorlage eingebaut.

Gantenbein (2006) gives a detailed study on heat transfer in the zeolite storage with the focus on heat exchanger design. He indicates that the main future work will be related to upscaling of the system and identifying optimal system designs.

3.2.5 SrBr2 – EU project SOLARSTORE (PROMES-CNRS)

In France, Goetz has been working for a long time on solid sorption materials. In Mauran, Lahmidi and Goetz (2008), a 60 kWh (0.22 GJ) TCM storage system for solar heat is described, called SOLUX, based on SrBr2x1H2O + 5H2O ⇔ SrBr2x6H2O.
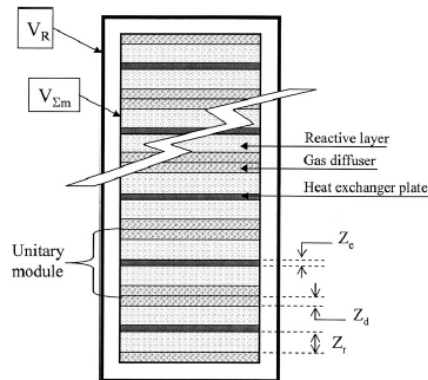
Fig. 1. Cross-section of a reactor made up of a stacking of modules. Each module consists of a plate exchanger, two layers of reagent and two diffusers of gas. The difference between the total volume of the reactor V_R and that of all the modules $V_{\Sigma m}$ constitutes the dead volume.

Table 2
Characteristics of the reactive composites with various thicknesses Z_r and number of required modules for a reactor storing 60 kWh (heating) in 1 m^3

Z_r (mm)	6	**12**	18	25	30
De_r (kWh heating/m^3 composite)	218	**154**	133	121	116
Number of modules (–)	104	**74**	57	45	39
w_{sa} (%)	93.5	**91.0**	89.7	88.9	88.4
λ_0 (W m^{-1} K^{-1})	0.996	**1.32**	1.47	1.56	1.60
λ_1 (W m^{-1} K^{-1})	0.467	**0.700**	0.817	0.896	0.934
k_0 (10^{-12} m^2)	1.93	**2.43**	2.62	2.73	2.77
k_1 (10^{-12} m^2)	0.756	**1.34**	1.59	1.75	1.82

The subscripts "0" or "1" for the conductivities λ and the permeabilities k indicate that the respective advance of the reaction is $X = 0$ ($\langle SrBr_2 \cdot 1H_2O \rangle$) or $X = 1$ ($\langle SrBr_2 \cdot 6H_2O \rangle$). The ENG apparent density in the composite is always $\rho_b = 40$ kg/m^3.

A thickness Zr of 12 mm was finally retained for the reactive layers in the prototype (named SOLUX). It is the minimal thickness which could be carried out without posing too much of a problem on the level of the hydraulic connections of the exchanger plates.

Table 3
Some characteristics of the modules, the reactor and the evaporator/condenser

Module	Reactor	Evaporator/condenser
• Number: 74	• Dimensions (m) $L \times l \times H$: $0.820 \times 0.757 \times 1.577$	• Dimensions (m) $L \times l \times H$: $0.820 \times 0.070 \times 1.577$
• Z_d: 6 mm	• Volume $V_R \approx 1\ m^3$	
• Z_e: 5 mm	• Heating storage: 60 kWh	• Volume $\approx 90\ l$
• Z_r: 12 mm	• Cooling storage: 40 kWh	• External surface area in contact with the pouring water: $3.14\ m^2$
• Surface area (2 sides) of one exchanger plate $\approx 0.44\ m^2$	• Mass of $\langle SrBr_2 \cdot 1H_2O \rangle$ at 99.3% purity: 171.3 kg	
• $\bar{\rho}_b$: 40 kg/m^3	• Mass of ENG: 15.6 kg	• Nominal flow of the pouring water for a good wetting of the tubes: 6 l/min
• De_r: 154 kWh/m^3	• Mass of exchanged (H$_2$O): 57.9 kg	
	• $V_{\Sigma m}/V_R$: 66.7%	
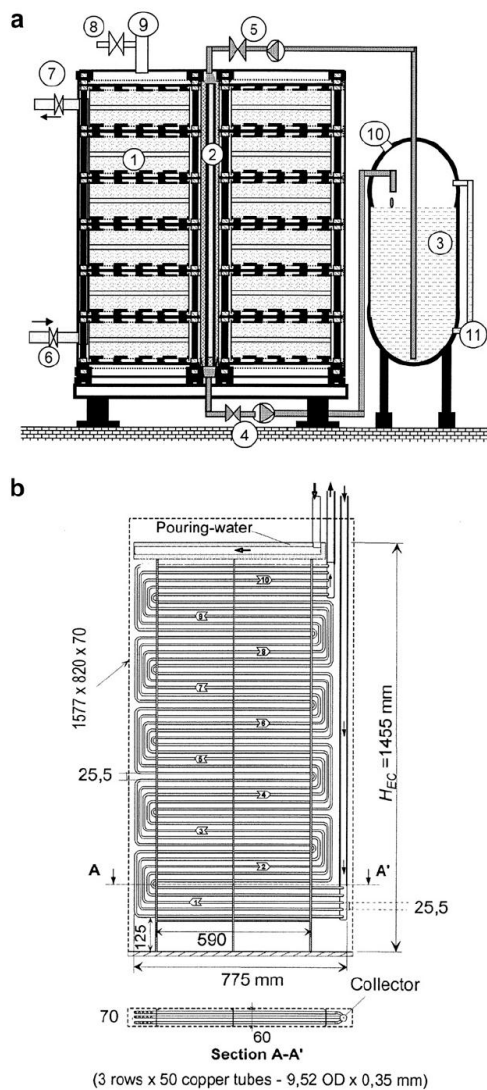
Fig. 3. Schematic drawing of the prototype SOLUX. (a) The reactor and its auxiliaries: a module (1), the evaporator/condenser (2) between the two stacks of modules, the reactive water stored in the water tank (3), the collection of the pouring-water at the EC bottom and its reintroduction at the top by means of two pumps (4, 5), the inlet and outlet collector (6, 7) of the coolant of the exchanger plates, a vacuum valve (8), the pressure (9, 10) and liquid level (11) measures. (b) Some details of the EC unit constituted by three staggered rows of five parallel tubes which are uniformly wetted with the reactive water by a shower at the top.
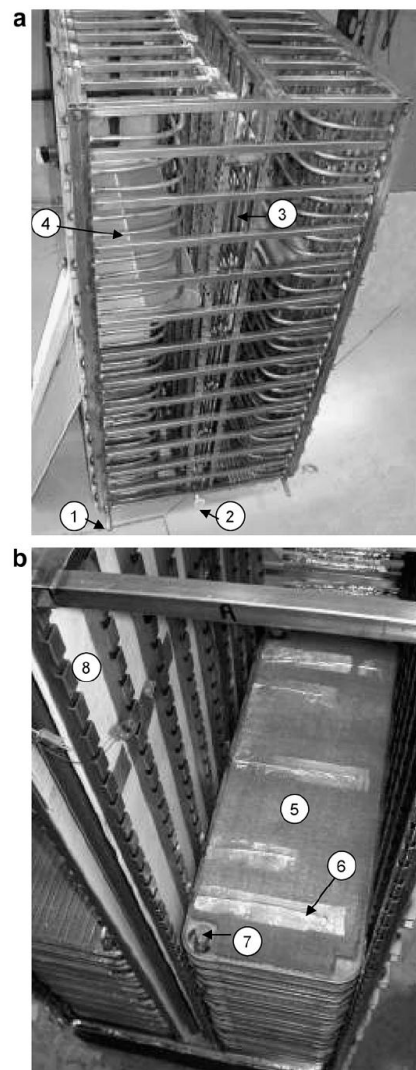
Fig. 4. Photographs of the prototype SOLUX in construction. (a) A view before introducing the modules: inlet collector of the coolant (1), outlet of the pouring-water (2) at the bottom of the evaporator/condenser (3), tube connection to a plate exchanger (4). (b) View of a module (5) with some temperature measures (6), a detail of inlet connection to a plate exchanger (7) before its welding to the tube (4), and PTFE plate (8) ensuring the containment of water streaming on the EC and its heat insulation at the same time.

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Mauran (2008) states the following: It allows storage, with a minimum of loss over indefinite duration, of 60 kWh at 70–80 °C and a later restitution of this energy to ensure, within the floor of the house, either heating in mid-season (60 kWh at 35 °C) or refreshing in summer (40 kWh with 18 °C). [..] reactive salt associated with an expanded natural graphite binder served as a consolidated composite which presents properties of transfer (conductivity and permeability) that are very satisfactory for a porous fixed bed. The relatively thin layers of reactive composite (12 mm) are laid out in alternation with plates of a heat exchanger or steam diffuser that are also thin (5–6 mm). The modular structure of the reactor facilitates a priori extrapolations in power and storage capacity. However, the heating or cooling powers of the prototype proved to be lower than those envisaged. The conductive heat transfer and especially the transfer of vapor with low pressure through the porous medium were expected to constitute the main limitations of the process; also the implementation of the composite reagent was conceived to attenuate these limitations. But in actuality, it is the transfer of heat at the interface between the consolidated composite and the wall of the exchanger, characterized by the coefficient hsw, which constituted a very strong limitation. The very low values of the coefficient hsw (between 5 and 30W/m2/ K) were not envisaged because better values (>500 W /m2 /K) had been experimentally obtained on the same or similar composites in smaller reactors. This below-average performance calls into question neither the choice of reactive salt, neither the implementation of the composite, nor the modular structure of the reactor, but exclusively the way in which the layers of reactive composite must be introduced and maintained in good thermal contact inside the reactor. These problems are currently being studied in the laboratory.

3.3 Heat pumps and chillers

3.3.1 Introduction

A different application of sorption materials is for absorption heat pumps. Such heat pumps may be based on liquid sorption materials, but also on solid sorption materials as in this chapter. The use of solid sorption has energetic and environmental benefits over conventional systems. In practice, such systems are often applied for cooling purposes; e.g solar cooling systems or industrial cooling systems based on waste heat. At present, ECN-EEI is working on a cooling system for application in cars, based on engine waste heat.

A characteristic of such systems is that cooling demand and heating supply are mostly simultaneous, which means that only very limited storage capacity is required. Often, such systems have more than one batch, so that one batch can be charged while another is discharged.

It seems that presently only companies have commercial production of adsorption chillers. Both systems are based on silicagel. The two companies are from Japan; Mayekawa and Nishiyodo. In addition, others are trying to develop such a system, such as the Chinese company Jiangsu Shuangliang Air Conditioning Equipment Co. Ltd. Information on these systems was also collected within IEA SHC task 38 on Solar Cooling (Henning, 2007). Henning summarises these products as large and heavy, with a COP of 0.6 and a driving temperature of 65-90 C. A typical layout is as given below.
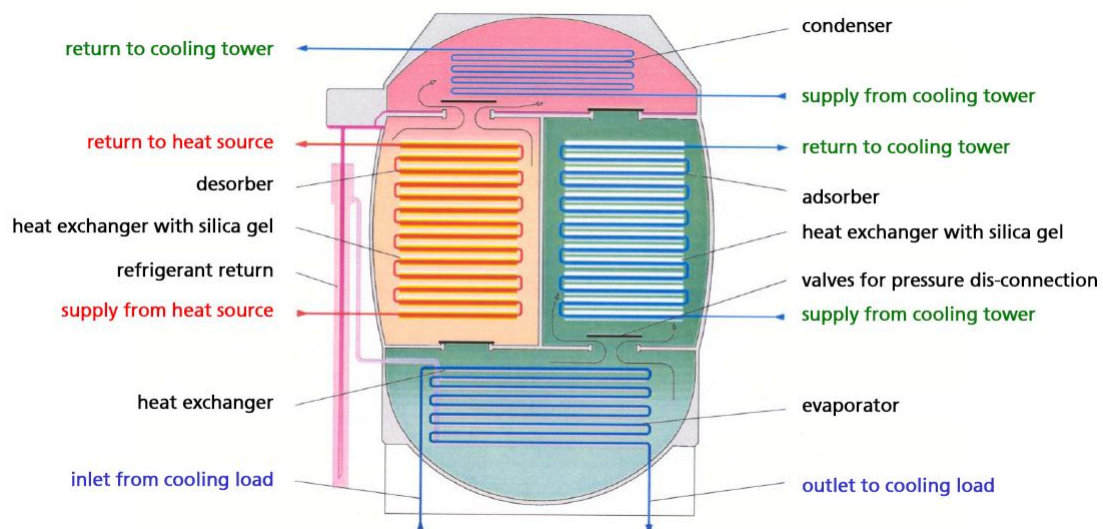
Manufacturer	Chilling power	Driving temperature (°C)	Design conditions and rated COP
Mayekawa	70 kW water / silica gel	55 – 90	T_{drive} 75°C, $T_{cooling\ water}$ 29°C, $T_{chilled\ water}$ 9°C: COP = 0.60
Nishiyodo	67 kW water / silica gel	55 – 95	T_{drive} 90°C, $T_{cooling\ water}$ 29°C, $T_{chilled\ water}$ 7°C: COP = 0.65

Table 2.2. Commercially available adsorption chillers suitable for solar-assisted air-conditioning (only smallest available size included). This list does not claim to be exhaustive.

Figure 5: Comercial silicagel chillers (from report of the Altener project Promoting solar air conditioning).

3.3.2 Silicagel chiller Mayekawa
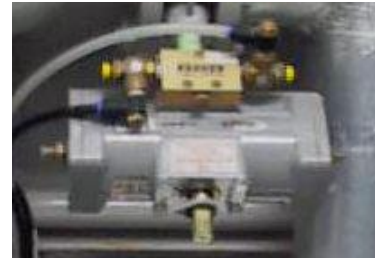
www.adsorber.de
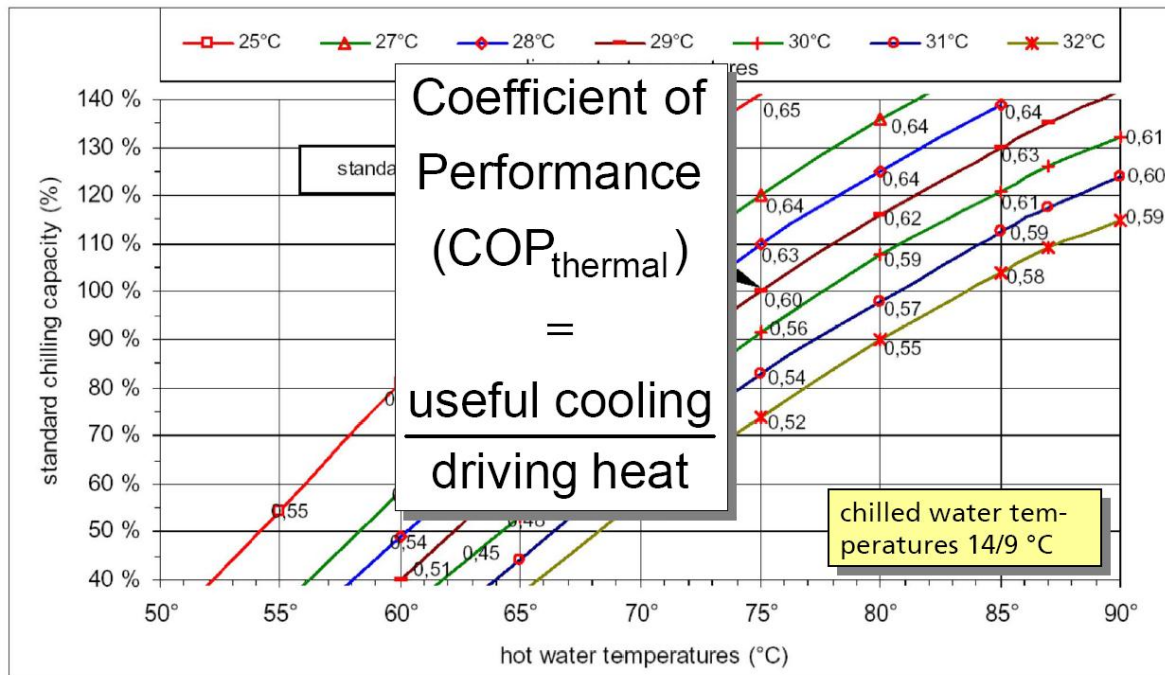
Figure 6: Mayekawa manufacturer performance data (from Henning, 2007).

A demonstration project was realized at a hospital in Kamenz, Germany. The system is a combination of fuel cell, solar system and an adsorption chiller with a chilling capacity of 105 kW (type: Mycom ADR 30 from Mayekawa). As working pair water/silicagel is used. The system is realised with a collector area of 115 m² (Sabatelli, 2005)

3.3.3 Silicagel chiller Nishiyodo
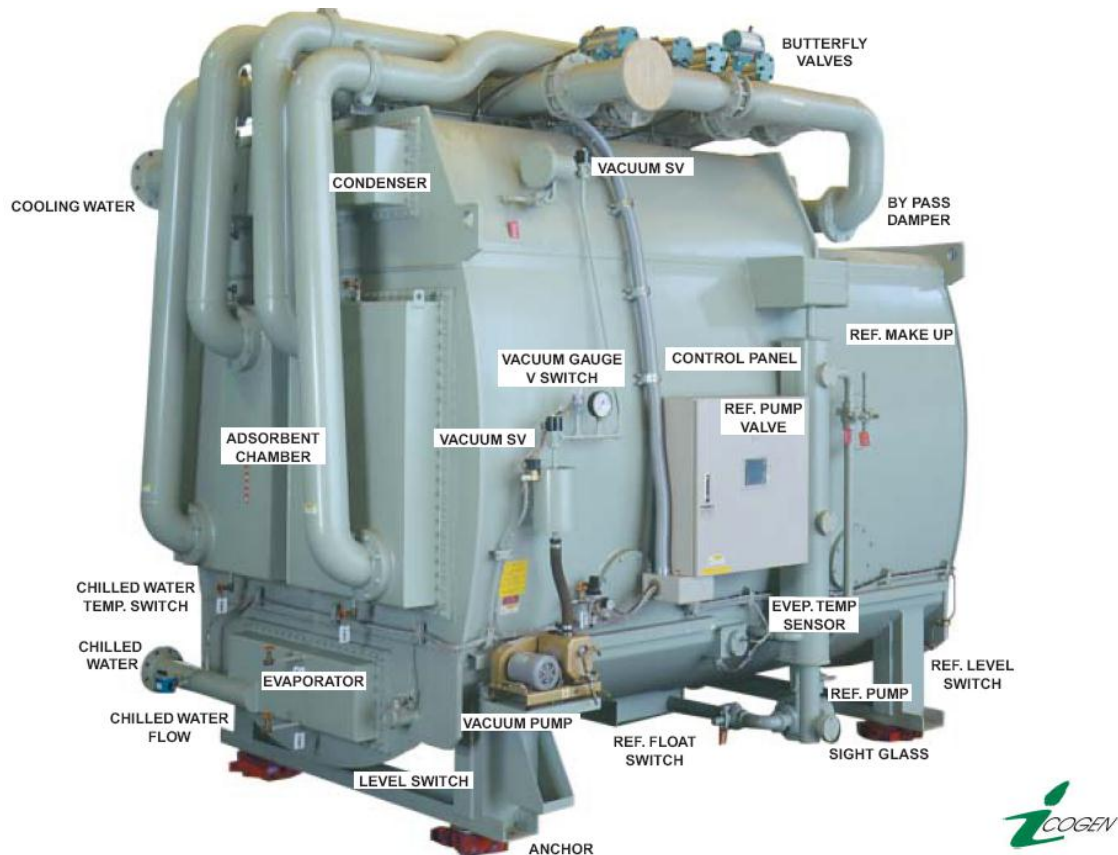
Figure 7: Silicagel chiller Nishiyodo (brochure icogen).

In a brochure of Icogen (www.icogen-sa.com), the following is stated: The Adsorption Chiller was developed and first produced by Nishiyodo Kuchou Manufacturing Company in 1986. Since being first produced the Adsorption Chiller has been used and closely evaluated in a wide area of applications in Japan and Europe [..].

STANDARD PERFORMANCE TABLE

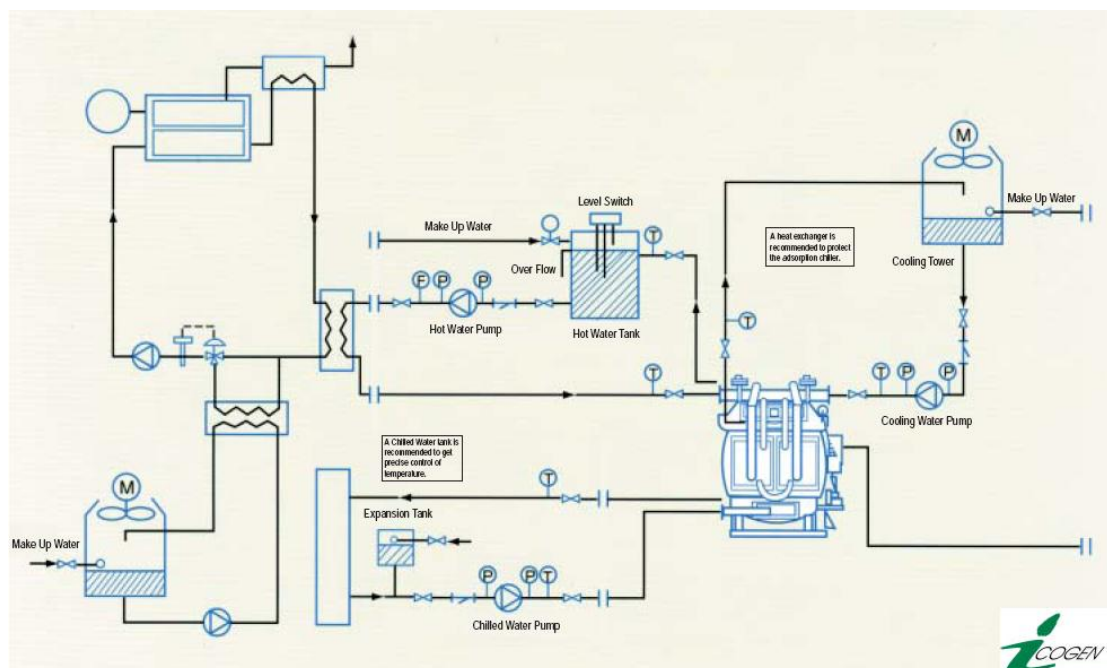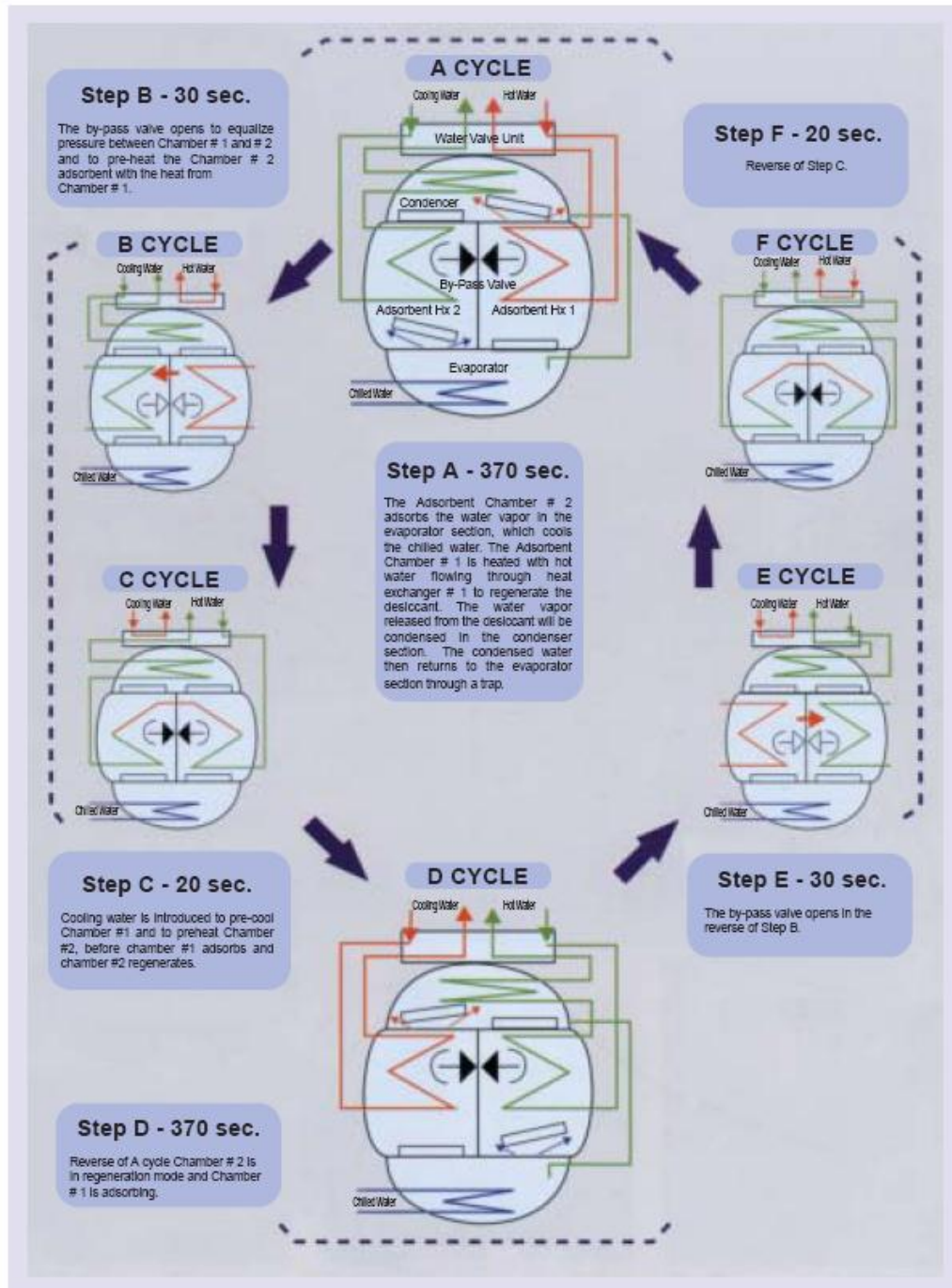|		Model	NADAC-020			NADAC-050			NADAC-075			NADAC-120			NADAC-150		
		TYPE	Economy	Standard	Standard	Economy	Standard	Standard	Economy	Standard	Standard	Economy	Standard	Standard	Economy	Standard	Standard
CAPACITY		USRT	22.47	18.87	15.27	56.96	47.78	38.96	81.38	68.25	55.65	130.20	109.20	89.04	162.75	136.50	111.30
		KW	79.02	66.36	53.69	200.30	167.99	136.98	286.14	239.99	195.68	457.82	383.98	313.09	572.27	479.97	391.36
COP			0.56	0.66	0.62	0.59	0.70	0.65	0.59	0.70	0.65	0.59	0.70	0.65	0.59	0.70	0.65
Chilled Water	IN	C	12.00	12.00	6.00	12.00	12.00	6.00	12.00	12.00	6.00	12.00	12.00	6.00	12.00	12.00	6.00
		F	53.60	53.60	42.80	53.60	53.60	42.80	53.60	53.60	42.80	53.60	53.60	42.80	53.60	53.60	42.80
	OUT	C	6.66	6.66	3.00	6.66	6.66	3.00	6.66	6.66	3.00	6.66	6.66	3.00	6.66	6.66	3.00
		F	44.00	44.00	37.40	44.00	44.00	37.40	44.00	44.00	37.40	44.00	44.00	37.40	44.00	44.00	37.40
	FLOW	m3/min	0.23	0.19	0.26	0.57	0.48	0.65	0.82	0.69	0.93	1.31	1.10	1.50	1.64	1.38	1.87
		GPM	59.80	50.22	67.73	151.58	127.14	172.77	216.55	181.62	246.82	346.48	290.59	394.91	433.10	363.24	493.64
	PRES DROP	mAq	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00
		p/in2g	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01
Cooling Water	IN	C	29.44	29.44	29.44	29.44	29.44	29.44	29.44	29.44	29.44	29.44	29.44	29.44	29.44	29.44	29.44
		F	85.00	85.00	85.00	85.00	85.00	85.00	85.00	85.00	85.00	85.00	85.00	85.00	85.00	85.00	85.00
	OUT	C	34.99	33.64	32.96	34.94	33.59	32.96	34.94	33.59	32.96	34.94	33.59	32.96	34.94	33.59	32.96
		F	94.99	92.55	91.34	94.89	92.47	91.32	94.89	92.47	91.32	94.89	92.47	91.32	94.89	92.47	91.32
	FLOW	m3/min	0.57	0.57	0.57	1.40	1.40	1.40	2.00	2.00	2.00	3.20	3.20	3.20	4.00	4.00	4.00
		GPM	149.16	149.16	149.16	369.60	369.60	369.60	528.00	528.00	528.00	844.80	844.80	844.80	1056.00	1056.00	1056.00
	Heat Rej.	Kcal/H	189620	143753	120844	465205	352153	298752	664578	503076	426789	1063325	804922	682862	1329156	1006152	853578
		MBtu/h	752.46	570.45	479.54	1846.05	1397.43	1185.52	2637.21	1996.33	1693.61	4219.54	3194.13	2709.77	5274.43	3992.67	3387.21
		KW	220.49	167.15	140.52	540.94	409.48	347.39	772.77	584.97	496.27	1236.42	935.96	794.03	1546.53	1169.94	992.53
	PRES DROP	mAq	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
		p/in2g	14.30	14.30	14.30	14.30	14.30	14.30	14.30	14.30	14.30	14.30	14.30	14.30	14.30	14.30	14.30
Hot Water	IN	C	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
		F	194.00	194.00	194.00	194.00	194.00	194.00	194.00	194.00	194.00	194.00	194.00	194.00	194.00	194.00	194.00
	OUT	C	83.76	85.55	86.17	83.66	85.50	86.08	83.66	85.50	86.08	83.66	85.50	86.08	83.66	85.50	86.08
		F	182.77	186.00	187.11	182.59	185.91	186.95	182.59	185.91	186.95	182.59	185.91	186.95	182.59	185.91	186.95
	FLOW	m3/min	0.33	0.33	0.33	0.77	0.77	0.77	1.10	1.10	1.10	1.76	1.76	1.76	2.20	2.20	2.20
		GPM	85.80	85.80	85.80	203.28	203.28	203.28	290.40	290.40	290.40	464.64	464.64	464.64	580.80	580.80	580.80
	Heat Req.	Kcal/H	121660	86684	74667	292950	207682	180952	418500	296688	258503	669600	474701	413605	837000	593376	517006
		MBtu/h	482.78	343.98	296.30	1162.50	824.13	718.06	1660.71	1177.33	1025.81	2657.14	1883.73	1641.29	3321.43	2354.67	2051.61
		KW	141.47	100.80	86.82	340.64	241.49	210.41	486.63	344.99	300.59	778.60	551.98	480.94	973.26	689.97	601.17
	PRES DROP	mAq	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
		p/in2g	11.44	11.44	11.44	11.44	11.44	11.44	11.44	11.44	11.44	11.44	11.44	11.44	11.44	11.44	11.44
Electric Power	VOLT	V	240.00	240.00	240.00	240.00	240.00	240.00	240.00	240.00	240.00	240.00	240.00	240.00	240.00	240.00	240.00
	FREQ	HZ	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00
	POWER CAP	KVA	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
	VAC. P	KW	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.40	0.40	0.40
Air Supply	Air Press.	Kg/cm2g	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
		p/in2g	71.43	71.43	71.43	71.43	71.43	71.43	71.43	71.43	71.43	71.43	71.43	71.43	71.43	71.43	71.43
	Air Consumption	L/min	9.40	9.40	9.40	9.40	9.40	9.40	9.40	9.40	9.40	9.60	9.60	9.60	9.60	9.60	9.60
		CFM	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.34	0.34	0.34	0.34	0.34	0.34
WEIGHT	EMPTY	Ton	5.00	5.00	5.00	7.50	7.50	7.50	9.20	9.20	9.20	12.10	12.10	12.10	15.00	15.00	15.00
		LB	11000	11000	11000	16500	16500	16500	20240	20240	20240	26620	26620	26620	33000	33000	33000
	RUNNING	Ton	5.50	5.50	5.50	8.50	8.50	8.50	10.40	10.40	10.40	13.70	13.70	13.70	16.40	16.40	16.40
		LB	12100	12100	12100	18700	18700	18700	22880	22880	22880	30140	30140	30140	36080	36080	36080
DIMENSION	W	mm	1500.00	1500.00	1500.00	2010.00	2010.00	2010.00	1955.00	1955.00	1955.00	2275.00	2275.00	2275.00	2305.00	2305.00	2305.00
		inch	59.06	59.06	59.06	79.13	79.13	79.13	76.97	76.97	76.97	89.57	89.57	89.57	90.75	90.75	90.75
	H	mm	2300.00	2300.00	2300.00	2620.00	2620.00	2620.00	2910.00	2910.00	2910.00	2863.00	2863.00	2863.00	2863.00	2863.00	2863.00
		inch	90.55	90.55	90.55	103.15	103.15	103.15	114.57	114.57	114.57	112.72	112.72	112.72	112.72	112.72	112.72
	L	mm	2650.00	2650.00	2650.00	3410.00	3410.00	3410.00	3440.00	3440.00	3440.00	4120.00	4120.00	4120.00	4817.00	4817.00	4817.00
		inch	104.33	104.33	104.33	134.25	134.25	134.25	135.43	135.43	135.43	162.20	162.20	162.20	189.65	189.65	189.65

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OPERATING CYCLE

The Adsorption Chiller has an evaporator section to cool the chilled water, a condenser section and two adso (silica gel) chamber/heat exchangers. The two heat exchangers alternate between cooling and heating durir chilling and regeneration process cycle (one cycle approximately 7 minutes). When one of the chamber/heat excha switches to the regeneration process it heats from the low (chilling) temperature to the regeneration temper The water vapor released from the silica gel will be condensed in the condenser section with cooling water.

Step B - 30 sec.

The by-pass valve opens to equalize pressure between Chamber # 1 and # 2 and to pre-heat the Chamber # 2 adsorbent with the heat from Chamber # 1.

Step F - 20 sec.

Reverse of Step C.

A CYCLE

B CYCLE

F CYCLE

Step A - 370 sec.

The Adsorbent Chamber # 2 adsorbs the water vapor in the evaporator section, which cools the chilled water. The Adsorbent Chamber # 1 is heated with hot water flowing through heat exchanger # 1 to regenerate the desiccant. The water vapor released from the desiccant will be condensed in the condenser section. The condensed water then returns to the evaporator section through a trap.

C CYCLE

E CYCLE

D CYCLE

Step C - 20 sec.

Cooling water is introduced to pre-cool Chamber #1 and to preheat Chamber #2, before chamber #1 adsorbs and chamber #2 regenerates.

Step E - 30 sec.

The by-pass valve opens in the reverse of Step B.

Step D - 370 sec.

Reverse of A cycle Chamber # 2 is in regeneration mode and Chamber # 1 is adsorbing.

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3.3.4 Silicagel chiller Jiangsu Shuangliang Air Conditioning Equipment

A new silicagel chiller development at the university of Shanghai, together with the company Jiangsu Shuangliang Air Conditioning Equipment Co. Ltd, is reported by Wang (2005). The simulated results show that the refrigerating capacity is more than 10 kW under a typical working condition with hot water temperature of 85C, the cooling water temperature of 31C and the chilled water inlet temperature of 15C. The COP exceeds 0.5 even under a heat source temperature of 65C.
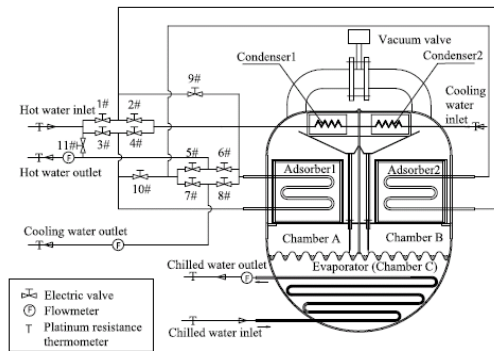
Fig. 1. Schematic diagram of the designed silica gel–water adsorption chiller.
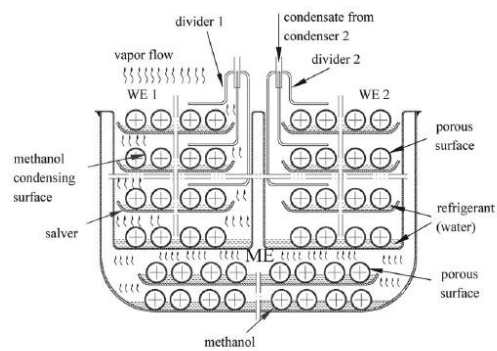
Fig. 2. Schematic diagram of the heat-pipe combined evaporator.
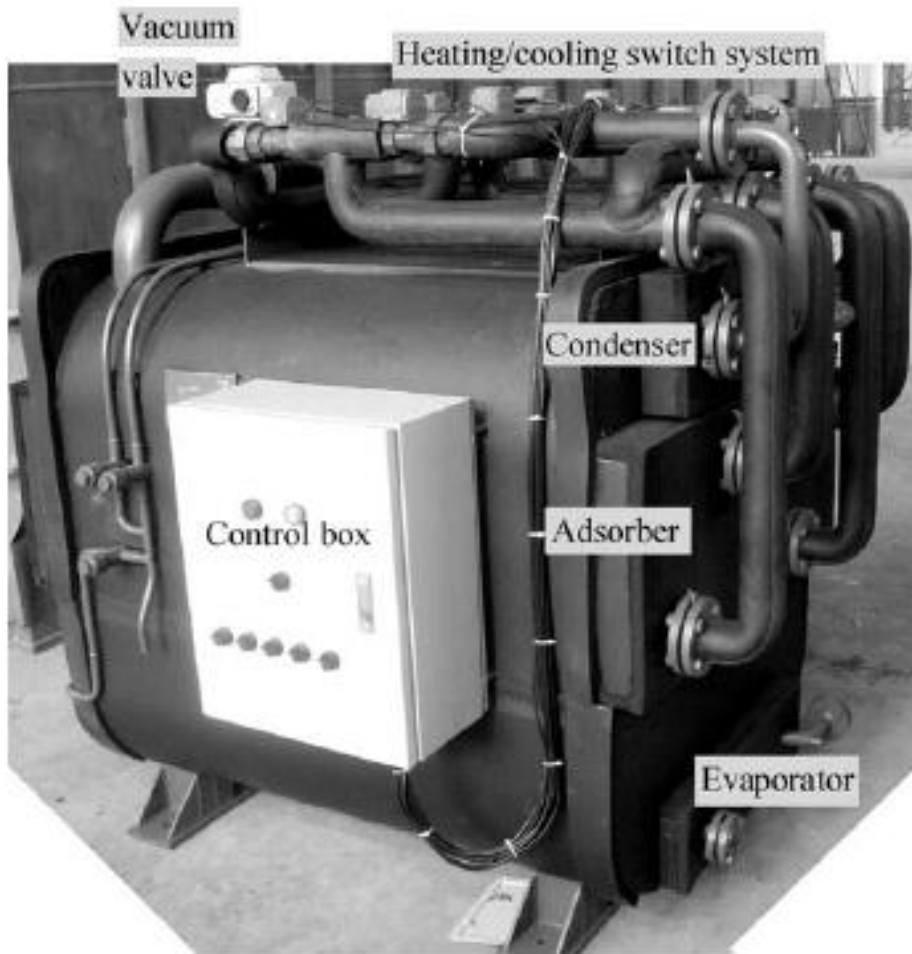
Fig. 1. Photograph of the silica gel–water adsorption chiller.

3.3.5 Na$_2$S chiller SWEAT (ECN)

This system is developed as a heat pump for cooling, using industrial waste heat.
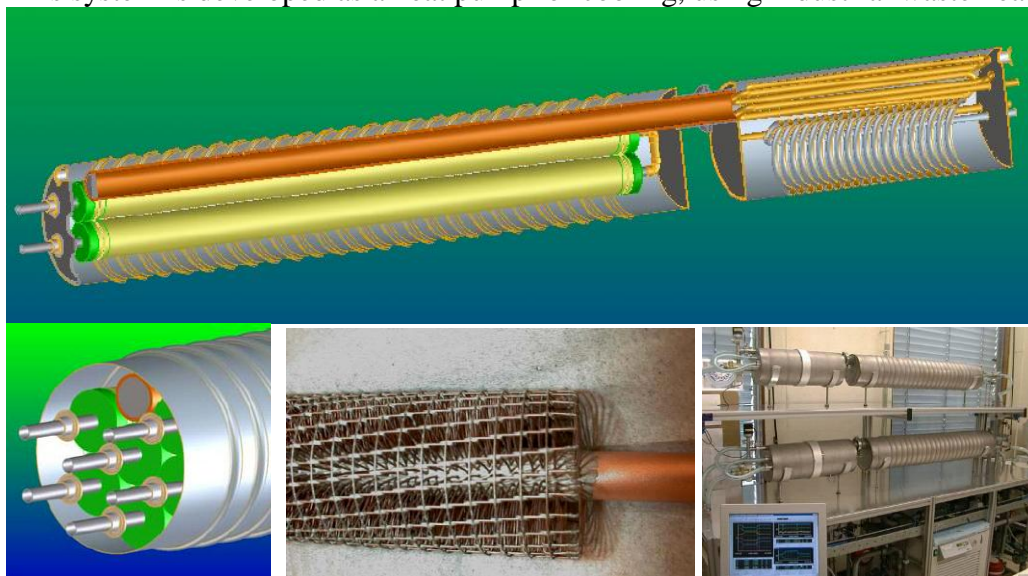
The heat transfer through the Na$_2$S is the limiting factor in the de power of the heat pump, so a very good heat exchanger is necessary. However, the Na$_2$S is strongly corrosive, which means that a very good corrosion protecting coating had to be developed.
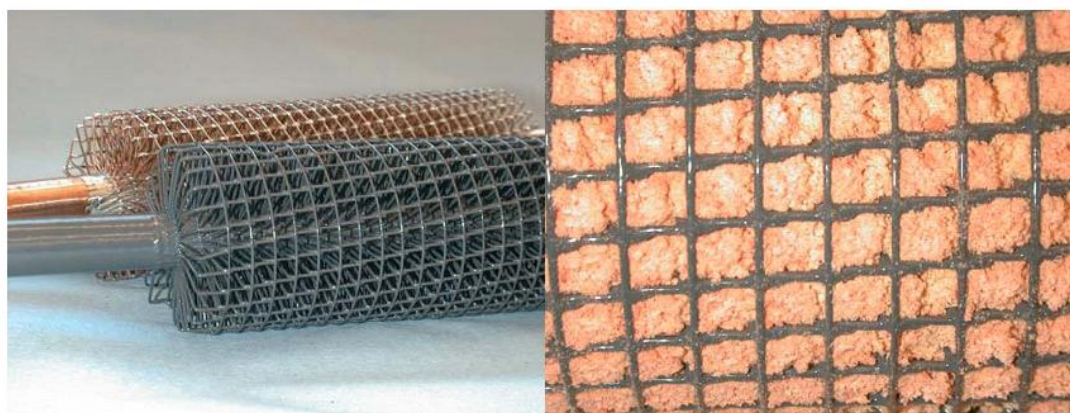
Figure 2. Picture of the Spiro-tube heat exchanger (left) and detail of the porous cellulose filling (right). The diameter of the central tube is 15 mm and that of the outside wire structure is 6 cm [1].

A support material for Na$_2$S is required, to achieve a sorbent filling of the space in between the copper wire structure that has sufficient open porosity for vapour transport, mechanical stability to hold the salt evenly divided in this space, even with occasional melting of part of the salt. A fibrous cellulose material was selected for this purpose. These fibres are chemically inert and sufficiently thermally and mechanically stable to act as support for the salt. Cellulose also has sufficient absorption capacity to maintain a molten salt at its position. The space in between the copper wires is easily filled with cellulose-Na$_2$S composite material, when applied in small grains.

Finally, however, the project was terminated, which was largely due to the large complications arising from the use of the very corrosive Na_2S. In subsequent projects for cooling applications, the focus shifted to silicagel.

3.3.6 Silicagel chiller SOCOOL (ECN)

For the Fiat research centre in Italy, a sorption cooler was developed, based on silicagel (Sorbsil A from the company Ineos Silicas) in the EU FP5 SOCOOL project. The lab tests at ECN were successful; 5 kW power was obtained. In the lab tests, poor wetting of the evaporator was a problem due to a malfunctioning pump (De Boer, 2006).
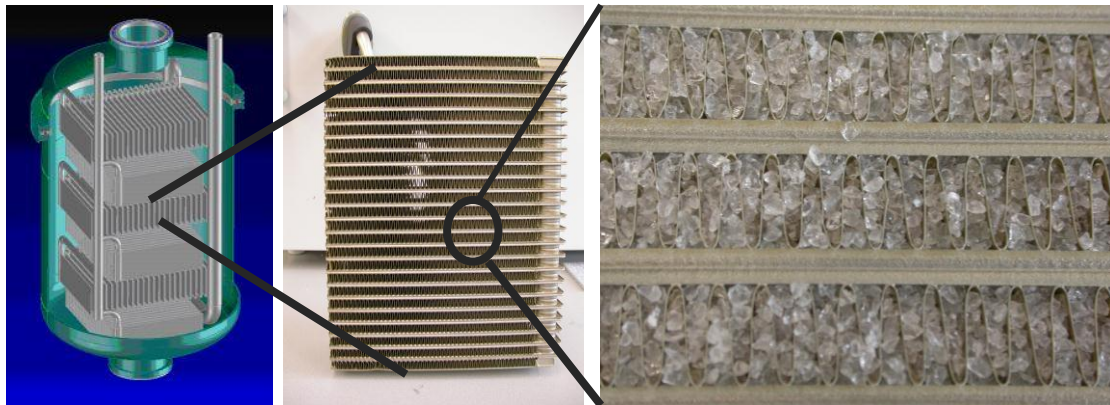
ECN EEI – SOCOOL: Silicagel impregnated heat exchanger, 1 kW, large heat exchanger area

3.3.7 Silicagel chiller TOPMACS (ECN)

At present, ECN-EEI is working together with Fiat on a sorption cooling system for cars. The ECN website gives the following information:

Prototype

In de eerste fase van het project zijn door de projectpartners vier prototypes op labschaal gebouwd. Hiervan zijn er drie uitgebreid getest. Op basis van de testresultaten is het sorptiekoelsysteem van ECN geselecteerd voor de volgende fase van het project: het bouwen en testen van een prototype in een personenauto. Omdat Fiat een belangrijke partner is in het onderzoek, zal dat een Fiat Punto zijn. Het koelsysteem van projectpartner CNR-ITAE wordt getest in een Iveco Stralis, een vrachtwagen die eveneens uit Italië afkomstig is.

"Dat is eigenlijk wel een doorbraak," vertelt ECN-onderzoeker Robert de Boer. "We hebben aangetoond dat we met onze innovatieve en energiezuinige sorptiekoeltechniek in principe voldoende koeling kunnen leveren voor een aangenaam binnenklimaat in een personenauto. Eindgebruikers als Fiat en Iveco hebben nu zoveel vertrouwen in het concept dat we een stap verder kunnen gaan. We gaan ons koelsysteem nu zo aanpassen dat we het in de kofferbak van de testauto kunnen inbouwen en dan de werking onder echte bedrijfscondities kunnen testen. Daarvoor moeten we nog wel de ontwerpen van de verdamper en de condensor aanpassen en deze componenten opnieuw bouwen." Omdat als randvoorwaarde geldt dat de nieuwe koeltechniek tenminste hetzelfde comfort moet kunnen leveren als de conventionele techniek, zal een standkachel worden gebruikt. De Boer: "Deze brander zal in principe alleen warmte leveren aan het koelsysteem wanneer nog niet genoeg restwarmte van de motor beschikbaar is, bijvoorbeeld bij een koude start. Daarnaast biedt dit de mogelijkheid om het koelsysteem te ontkoppelen van de motor, zodat de airco ook koeling kan leveren als de motor niet draait."
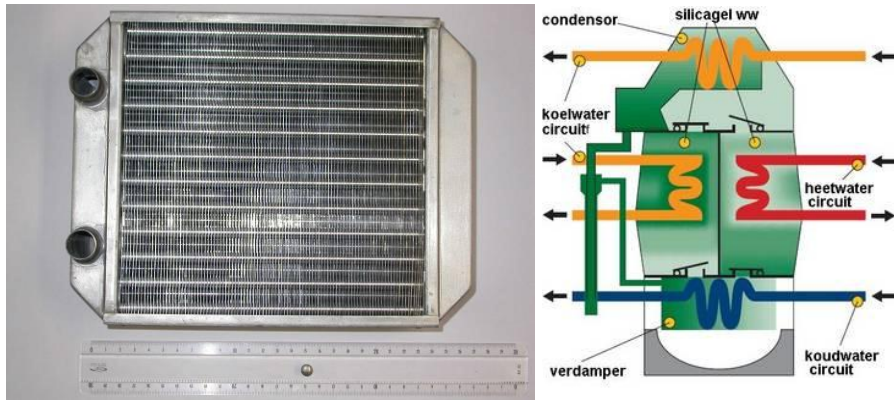
Figure 8: Car cooler to be filled with silicagel, together with TOPMACS layout scheme

3.3.8 Silicagel chiller SorTech (Sortech, Fraunhofer)

This research line started with PhD projects on characterisation of various adsorption materials at Fraunhofer ISE (Nuñez, 2001), followed by a PhD project by Smith (Smith, 2004).
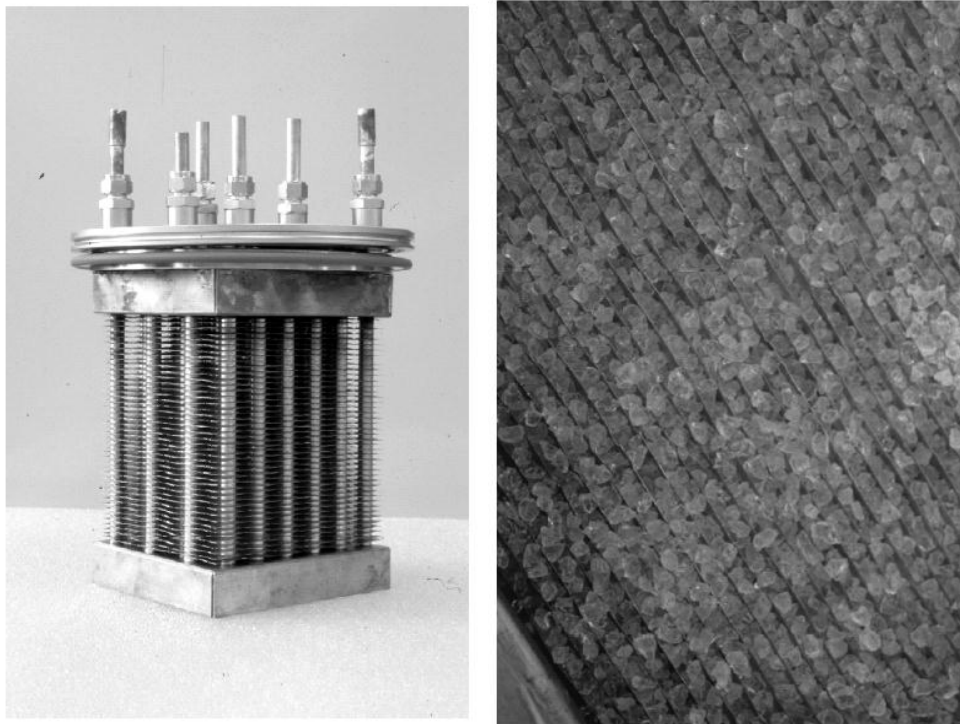
Abbildung C.3: Lamellenwärmeübertrager für die Adsorptionswärmepumpe. Der aus Kupferlamellen gefertigte Wärmeübetrager ist an den Flansch des Reaktorbehälters montiert. Durch den Flansch sind Durchführungen für den Wärmeträger (ganz links und rechts) und vier Durchführungen für Temperatursensoren.

Abbildung C.4: Silikagel im Lamellenwärmeübertrager. Die größe der Silikagelkörner entspricht in etwa dem Abstand zweier Lamellen. Lamellenabstand: ca. 5mm

The company SorTech is a spin off of Fraunhofer ISE. Together they developed an adsorption chiller (Nuñez, 2004).
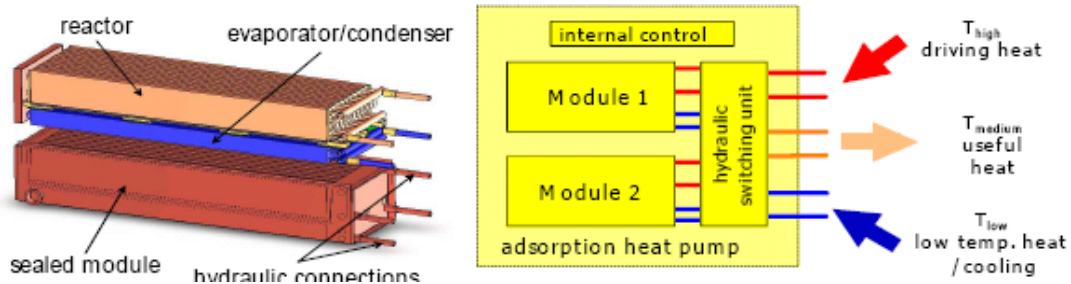
In 2006, Bales states that this is a heat pump with 20 minute storage capacity, for single family house, adsorption material not yet chosen.

In 2007, the following information was provided on the SorTech website

Die Thermo-Chiller der SorTech sind Adsorptionskältemaschinen, in denen als Adsorptionsmaterial Zeolithe oder Silikagele zum Einsatz kommen, als Kältemittel dient Wasser. Der Thermo-Chiller 01-10kW ist das Grundmodul der ersten Anlagenserie. Das System wird anschlussfertig ausgeliefert werden, beinhaltet die Steuerungseinheit sowie einen Kaltwassererzeuger mit 10 kW. Mit bis zu vier weiteren Zusatzmodulen a 10 kW wird das System auf bis zu 50 kW erweiterbar sein. Die Geräte der Serie 01 sollen einen COP von 0,6 unter folgenden Betriebsbedingungen erreichen: Kälteleistung 10 kW mit 6°C / 12°C auf der Kaltwasserseite bei einem Volumenstrom von ca. 1.500 Litern pro Stunde; Antriebstemperatur 80 °C / 75 °C bei einem Volumenstrom von ca. 3.000 Litern pro Stunde; Rückkühltemperatur von 35 °C / 30 °C bei einem Volumenstrom von ca. 4.500 Litern pro Stunde. Der Komplettpreis des Thermo-Chillers 01-10kW wird voraussichtlich im Bereich von 4.000 € - 6.000 € liegen.

Presently, at the site of SorTech (www.sortech.de), information is given on their demonstration project at Fraunhofer ISE, Location: Freiburg, Baden-Württemberg Commissioning: June 2007. The system has a 20 m2 flat-plate collector and vertical boreholes and is providing cooling for the cantine of the Fraunhofer institute.
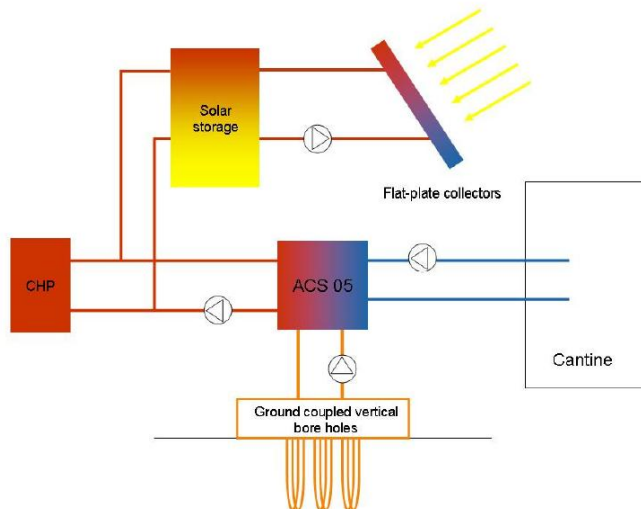
Figure 9: SorTech demonstration project at Fraunhofer ISE

The SorTech system with specification sheet is shown below.

29

Technical Data SorTech Adsorption Chiller S 05 (ACS 05)

Technology: Adsorption, single-effect
Model type: Chiller
Working pair: Silica gel/water

The system will be delivered ready for connection and includes the chilled water generator with an integrated control. The table summarises the technical data under nominal and alternative boundary conditions. The nominal cooling capacity and the COP are highly dependent on the temperatures of the three circuits. If desired, we provide you with a calculation of COP and cooling capacity under your specific conditions.

		Unit	Recommended re-cooling Wet cooling tower (nominal working point)	Radient Floor Dry cooler	Fan Coil Wet cooling tower
Cooling capacity, nominal		kW	5.5		
COP, nominal			0.60		
Cooling capacity, max.		kW		4.6	3.5
COP, max.				0.49	0.41
Chilled water circuit	Temperature in/out	°C	18/15	18/15	12/7
	Flow	m³/h	1.7		
	Loss of head	mbar	350		
	Operating pressure max.	bar	4.0		
	Supply		3/4" external thread		
Heat rejection circuit	Temperature in/out	°C	27/32	33/38	27/32
	Flow	m³/h	2.7		
	Loss of head	mbar	520		
	Operating pressure max.	bar	4.0		
	Supply		1" external thread		
Heat supply circuit	Temperature in/out	°C	75/67	85/77	90/83
	Flow	m³/h	1.0		
	Loss of head	mbar	300		
	Operating pressure max.	bar	4.0		
	Supply		3/4" external thread		
Electricity supply	Voltage	V	230 ~		
	Frequency	Hz	50		
	Power consumption	W	57		
Dimensions	Length x Width x Height	mm	795 x 1100 x 1190		
	Weight	kg	ca. 200		

We can also offer you an appropriate re-cooling unit if requested.

SorTech AG   Weinbergweg 23   Fon: +49 (0) 345 279809-0   Internet: www.sortech.de
06120 Halle (Saale)   Fax: +49 (0) 345 279809-98   E-mail: office@sortech.de

Figure 10: SorTech system

3.4 Zeolite integrated gas burner Vaillant (with RWTH Aachen)

In a cooperation between Vaillant and RTW Aachen, a gas burner with integrated zeolite heat pump was developed. BINE (2005) gives information on this system, announcing a pilot series for the end of 2005. On the present status, information is available at www.vaillant.de (Vailant, 2007).

1 Brennwert-Unit

2 Zeolith-Modul-Umschalter

3 Ausdehnungsgefäß Zeolith-Kreis

4 Zeolith-Kreispumpen

5 Wärmetauscher Zeolith-Kreis an Heizkreis

6 Wärmetauscher Regenerativkreis an Heizkreis

7 Soleumwälzpumpen

8 Solekreisumschalter
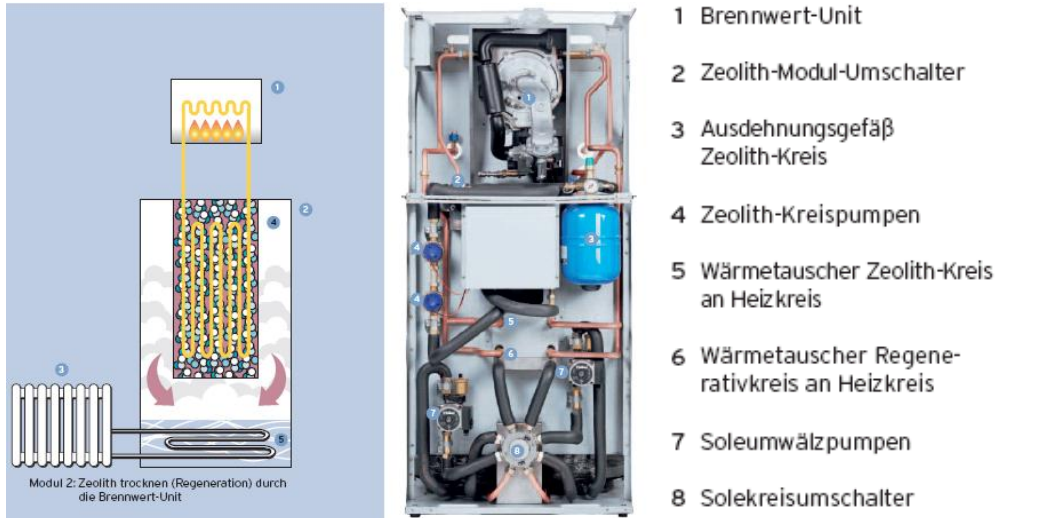
Das Zeolith-Heizgerät ist eine Wärmepumpe, die mit Erdgas betrieben wird.

Im Jahresdurchschitt wird die Energie zur Heizung und Warmwasserbereitung zu 75% aus der Verbrennung gewonnen. Weitere 25% kommen aus der Umwelt - kostenlos. Der Jahresnutzungsgrad der Zeolith-Heizgeräte liegt damit fast 30% (abs.) über dem von Brennwertgeräten. Die Steigerung im Vergleich zu Niedertemperaturkesseln liegt sogar bei rund 40% (abs.).

Der Sorptionsprozess in den Modulen läuft in zwei Schritten ab: Im ersten Teilschritt wird der Zeolith mit Hilfe eines Gasbrenners auf 200°C erwärmt. Dabei desorbiert das
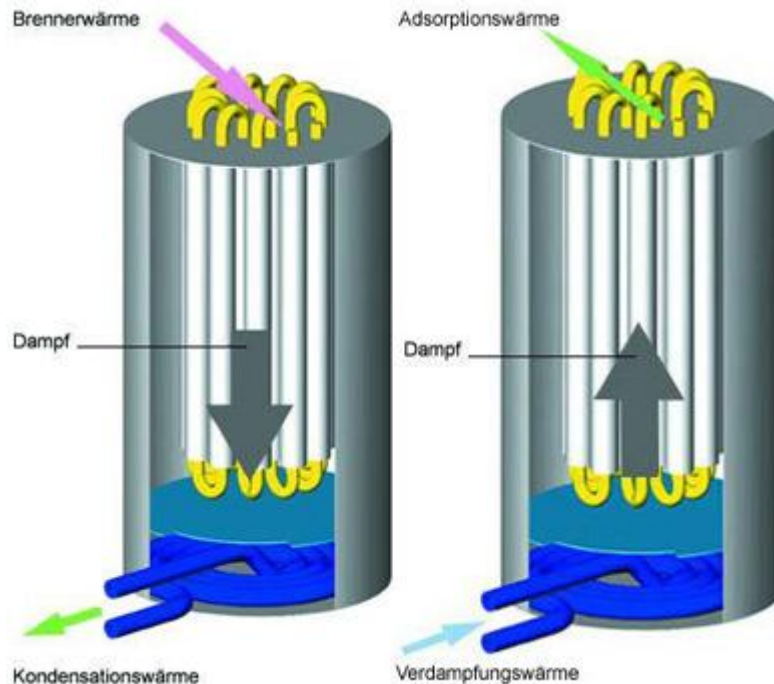
Funktionsprinzip des Zeolith Moduls

Das Herzstück des Zeolith-Heizgerätes von Vaillant sind zwei Zeolith Module. In ihrem oberen Teil befindet sich das Adsorptionsmittel Zeolith. Es ist aufgebracht auf einem Wärmetauscher (Adsorber / Desorber). Unten befindet sich ein weiterer Wärmetauscher (Kondensator / Verdampfer), als Kältemittel ist Wasser enthalten. Das Modul ist hermetisch verschlossen und arbeitet im Unterdruck bei 5 bis 200 mbar.

Wasser und strömt als Dampf in den unteren Teil des Moduls. Hier kondensiert der Dampf und gibt dabei seine Kondensationswärme ab. Dieser Schritt ist beendet, wenn der Zeolith trocken ist und sich das gesamte Wasser im unteren Teil des Moduls befindet. Nun wird der Brenner ausgeschaltet und das Modul kühlt unter Umgebungstemperatur ab. Das Wasser verdampft nun unten im Modul mit Hilfe von kostenloser Umgebungswärme. Der Dampf strömt in den oberen Teil des Moduls und wird dort vom Zeolith adsorbiert, die dabei frei werdende Adsorptionswärme wird ebenfalls genutzt. Wenn das Wasser vollständig verdampft ist, beginnt der Prozess erneut.

3.5 TCM reactor equipment for Laboratory research

Several research institutes and univerities have also publised on their research on TCM, showing figures of their experimental reactor setup. Some systems are collected below.
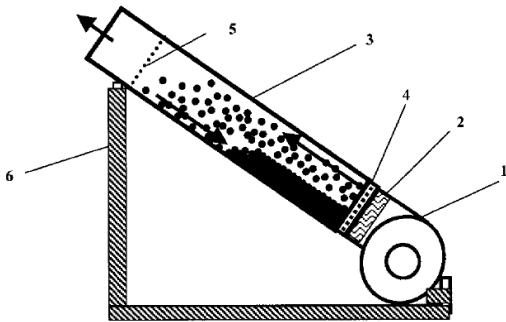
Fig. 3. Experimental set-up.
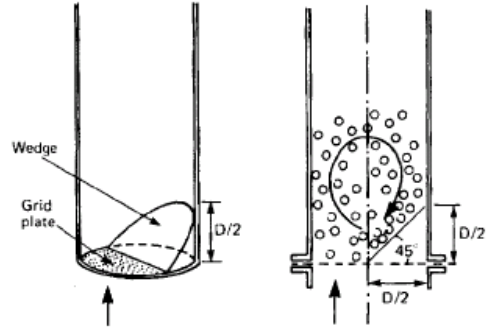
Fig. 2. Whirling bed apparatus [8].

Figure 11: 1.1.1 Fluidised bed reactor - Hamed
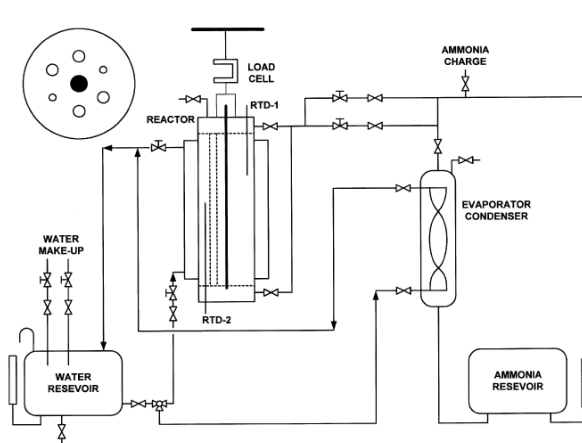
Fig. 1. Schematic diagram of the reaction equipment. The circular cross-section in the upper left hand corner of the drawing is a cross-section of the reactor indicating the radial positions of the four diffusers, the two RTD's, with the heating rod in the center.

Fig. 5. Experimental solid–gas reactor ($h = 15$ cm, $R = 2.5$ cm): (1) gas connection; (2) regulated heating resistor; (3) reactive mixture; (4) grid for gas diffusion.

Figure 12: (a) System Aidoun, (b) Goetz and Marty

4 Closed Systems with liquid TCM material

4.1 Introduction

As seen above, in the case of solid TCM material always fixed bed systems are used. In principle one would like to use a separate reactor, because this allows better heat- and vapor transport and reduces the sensible heat loss of the reactor, which is particularly important at frequent switching on and off. However, for solid TCM, the transport of the material is not straightforward. Therefore, several people have been working with liquid TCM materials.

In liquid TCM materials, two routes are available. One can either use substances such as more or less diluted solutions of NaOH, H_2SO_4, LiBr or LiCl, or one can try to suspend the solid TCM material in a liquid.

With respect to the more or less diluted solutions; typically LiBr and LiCl are interesting but expensive materials, which makes them very popular in absorption heat pumps where only very limited storage capacity and small amounts of TCM are required. NaOH and H_2SO_4 are much cheaper, but are also very corrosive, requiring costly design measures and materials for the system.

With respect to suspensions, the only group working with a suspension (TNO) has built an open system, so this concept will be found in the chapter on Open systems with liquid TCM.

4.2 Suspension system (Rocky research)

Since the late '80s, research on solid sorption is carried out by Rocky research (by Uwe Rockenfeller). Rockenfeller has over 60 patents, almost all related to solid sorption or ammonia/water heat pumps, over the period 1989-2005. In Rockenfeller (1991), the development of a solid-sorption chill storage is described, based on the absorption of ammonia in a metal inorganic salt. Several approaches were tried to optimize both thermal and mass diffusivity. Three types of system were investigated: (1) slurry system (equivalent to a suspension system like TNO), (2) carrier liquid system and (3) optimized solid bed reactor. For the slurry system, it was concluded that the pumpability of the solid required at least 35% carrier liquid. Although it was found that for the slurry system the ammonia uptake was increased by 50% compared to a fixed bed, it was concluded that issues regarding slurry distribution, agitation and vapor carryover would require too much effort to be solved within the project. As an alternative, it was tried to dissolve ammonia in a carrier liquid. A difficulty in this was the following

"liquids which are highly soluble in polar gases such as ammonia and water are also soluble in polar salts. Answers to this problem were found in long chain molecules, e.g. long chain alcohols and ammines. These media show reasonable solubility in low molecular weight polar gases, but are almost inert to most metal inorganic salts. Solubility problems are reduced by using hydroxide, carbonate or phosphate salts rather than bromides, chlorides or chlorates. However, the coordination properties of the latter group are superior to those of the first group, and this research focused on finding carrier liquids suitable for use with bromated or chlorinated metal salts."(Rockenfeller, 1991).

Since the solubility decreases with decrease in temperature, lower temperatures require higher flow rates and correspondingly higher parasitic power, which limited the cooling temperatures and severely limited the feasibility of the use of a carrier liquid.
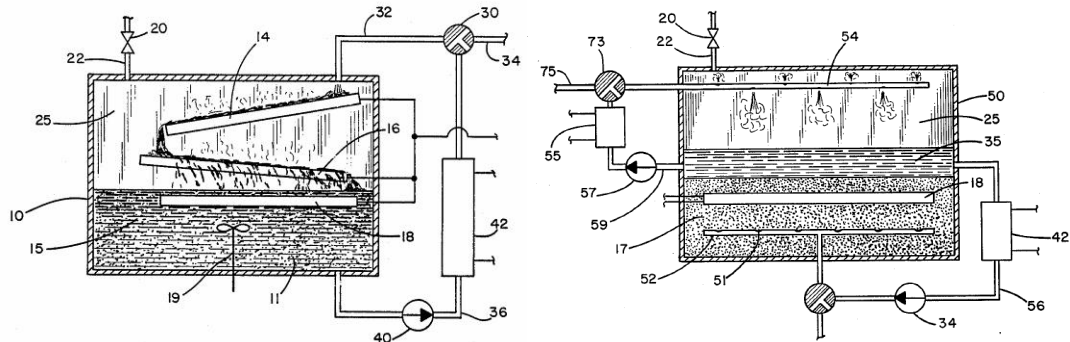
Figure 13: Different embodyments from the suspension reactor by Rockenfeller (from Rockenfeller, 1989).
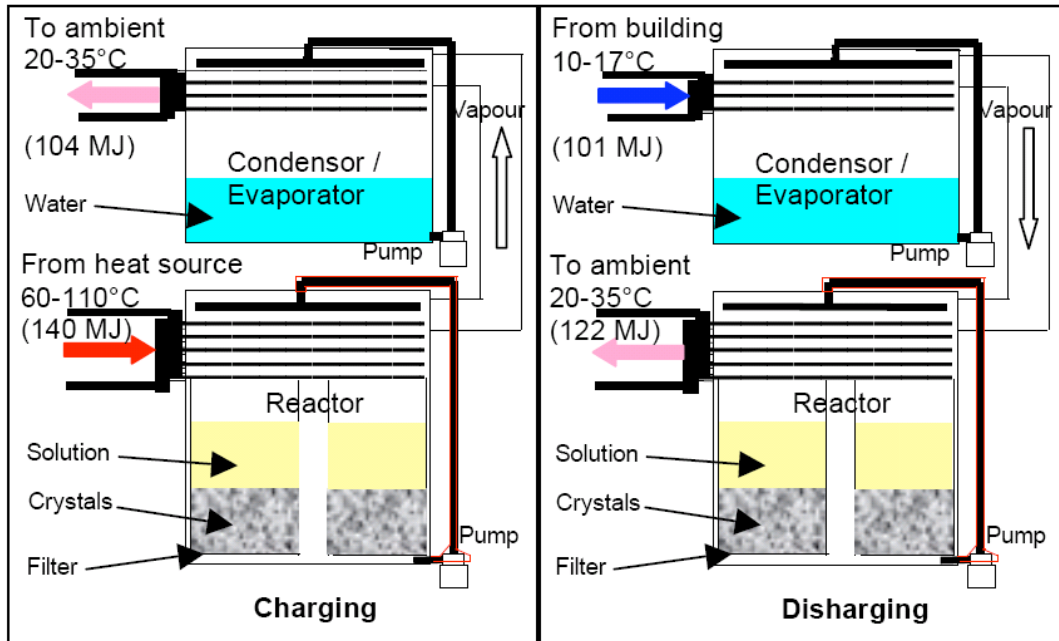
Finally, optimized bed reactors were found to be the best option, because of low cost (no slurry pumps or separation membranes required), no additional temperature drops to drive sorption into the liquid carrier, no issues with stability of carrier liquid, no contamination with carrier liquid vapour, no moving parts and most acceptable to manufacturers and users.

4.3 LiCl chiller TCA (Climatewell, DTU-SERC)
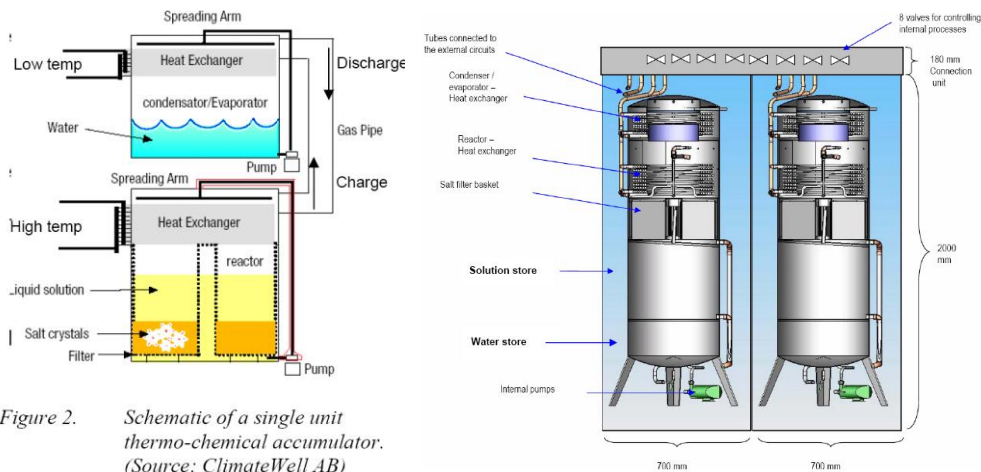
Figure 2. Schematic of a single unit thermo-chemical accumulator. (Source: ClimateWell AB)

Absorption process with three phases: solid, solution and vapour. LiCl/water are the active substances with small amounts of inhibitors. During charging (regeneration), the solution is pumped over the reactor heat exchanger and solid crystals are formed that fall under gravity and are collected in a basket. During discharge the solid crystals are dissolved using the condensed water. Charge and discharge occur at constant operating conditions during three-phase operation. A single unit can either charge or discharge. The system is marketed as ClimateWell DB220 as an advanced industrial prototype and is sold to several groups.

To ambient 20-35°C (104 MJ) — Condensor / Evaporator — Water — From heat source 60-110°C (140 MJ) — Reactor — Solution — Crystals — Filter — Pump — Vapour

To ambient 20-35°C (122 MJ) — From building 10-17°C (101 MJ) — Condensor / Evaporator — Water — Reactor — Solution — Crystals — Filter — Pump — Vapour

Charging — **Disharging**

Over time, a number of patents on the system was issued. Specific issues

4.4 NaOH seasonal storage (EMPA)

Low temperature sink — Radiation protection — High temperature source — Heating device — Water — Weak solution — Strong solution

Discharging the storage:

Water — conc. Soda lye — Processor — Vapor — diluted Soda lye — Environmental heat — Available heat — ground heat exchanger — Heating, DHW

Charging the storage:

Water — conc. Soda lye — Processor — Vapor — diluted Soda lye — Waste heat — Heat from solar collector — ground heat exchanger — Solar collector
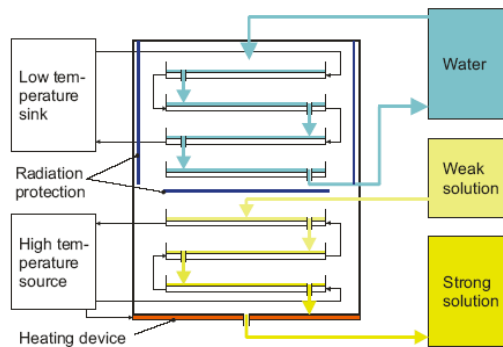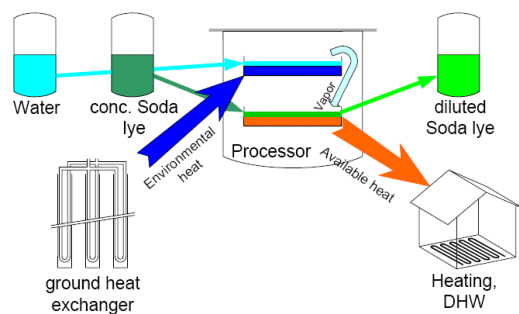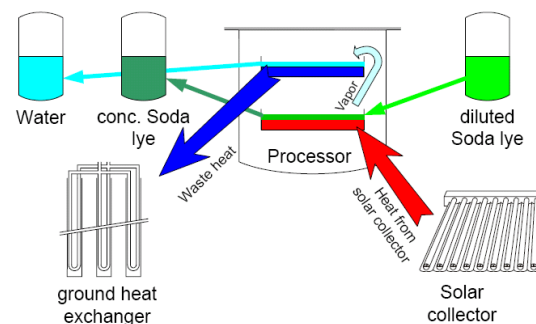
Status 2006: The storage was built and filled with soda lye in 2005, but never put into operation. The project got financing from SFOE, Fall 2006. The work on the storage has been reassumed. With the laboratory prototype, first test has been performed. At the moment, some design changes are made. First tests (without lye) showed a heavy heat loss as a result of radiation exchange between the condenser and evaporator inside the processor. (Fixed.) Loading tests has been performed. Concentration of 62 to 65% wt reached. At the moment: Replacement of silicone hoses, which has been corroded in the lye. (In progress) The viscosity of the concentrated lye is higher than expected.

The piping, especially the pumps needs a change in design. (Done.) Better efficiency and volume ratio needs a second stage (meaning: second HE pair) Crystallization at unforeseen places might be an obstacle. For low temperature application, a shift to low concentrations might be very interesting, but needs mandatory the second stage.
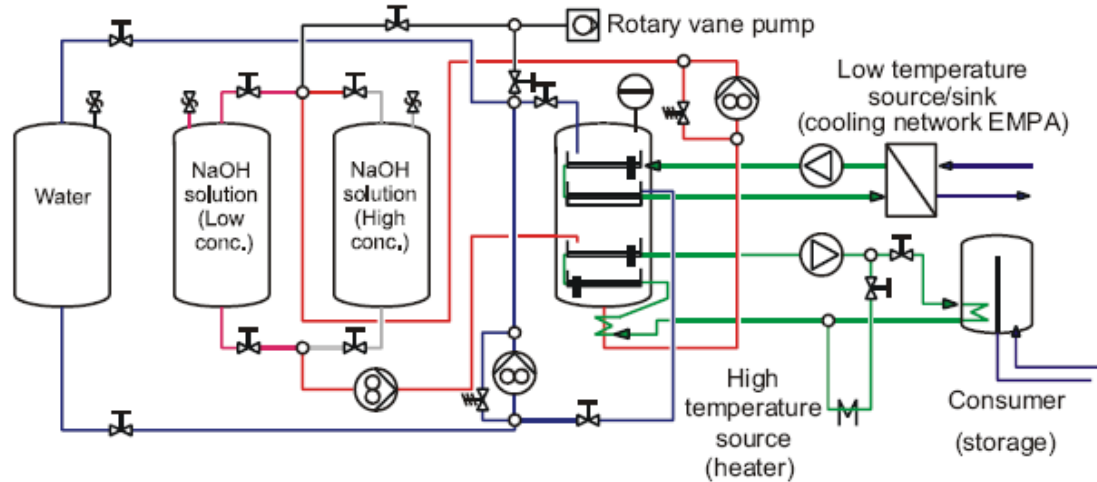
Weber (2008) gives an update on the status of the project:

An NaOH–water-based process for long-term storage of solar heat has been analyzed. The process has been demonstrated in a prototype plant with individually vacuumed storage tanks and solution/water vapor heat exchangers unit. The results show that solar heat input is required at temperature above 120C, and that, compared to conventional water storages, the system volume (tanks and heat exchangers) related heat capacity could be increased up to a factor of 6 for low-temperature space heating with 40C supply temperature. For domestic hot water supply at 65–70C, this factor is reduced to about 3. As a next step, it is planned to build a double-stage system. This will allow for lower solar heat input temperatures or higher condenser temperatures during charging, and for higher tap water temperatures or for operating with lower solutions concentrations during discharging. The system will be designed as one integral vacuum container, in which the whole storage system is placed, comprising multiple solution tanks, two process units (because of the double stage system), and the necessary piping and pumps. Thus, the vacuum container need not sustain the highly corrosive environment of the NaOH lye and may be of conventional carbon steel. As the solution tanks are fully placed in vacuum, they do not experience a high pressure difference and can be made of polypropylene. This will contribute to a cost-effective system. However, costs have also to be considered for the heat exchangers. To reach a steady and continuous heat output from the system, the partial air pressure in the system must constantly remain on a low level. Solutions, e.g. with getters or mini vacuum pumps, have to be further investigated. (Weber, 2008)

The importance of a double stage system is emphasized. The principle of this is illustrated below. The idea is that one can apply lower collector temperatures (95C) to reach high concentration, because the water vapour in the second stage is not condensed to water, but is taken up by the NaOH solution in the first stage, leading to lower vapour pressures in the second stage and correspondingly lower regeneration temperatures.
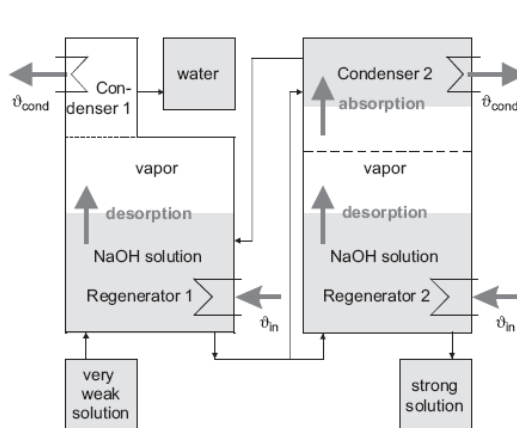
Fig. 6. The charging process with a double-stage cycle.
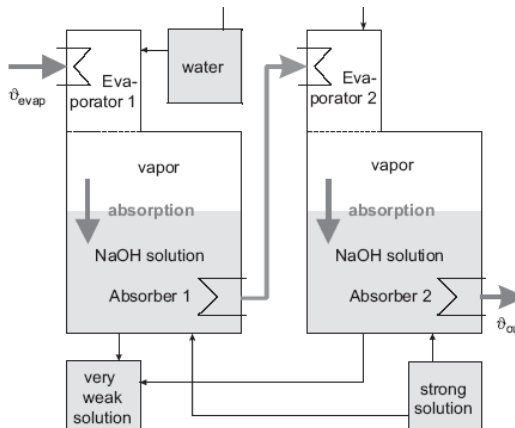
Fig. 7. The discharging process with a double-stage cycle.

4.5 LiCl chiller (ZAE)

After their initial work in open cycle zeolite systems, the focus shifted to a liquid LiCl heat pump system (Hadorn, 2005), and a demonstration project with a LiCl system was carried out at the office of Prochek Immobilien GmbH in Amberg (Laevemann, 2003).

The storage contains 3000 kg of LiCl and a varying amount of water in separate tanks with a storage volume of 12 m^3. A collector area of 70 m^2 is used. Although leakage and other problems delayed the project, Laevemann (2003) is optimistic on finishing the project successfully.
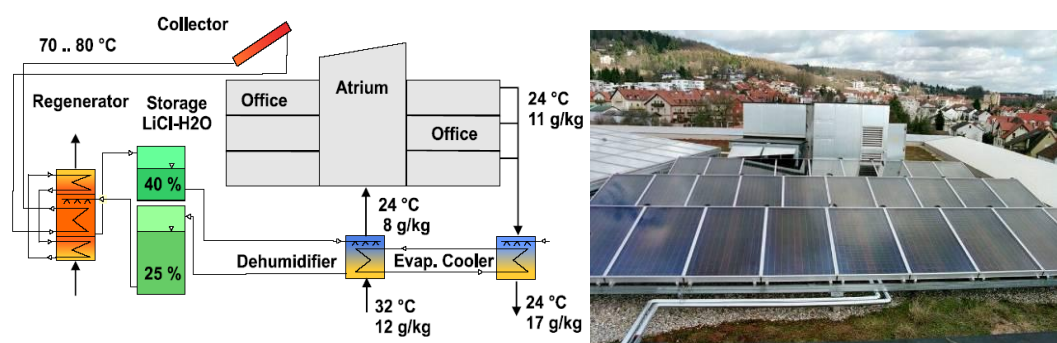
4.6 Various absorption heat pumps

Many absorption heat pumps are known functioning on liquids, mostly based on solutions of ammonia or LiBr. However, also other salts are used, such as LiCl (e.g. Laevemann 2003). Wikipedia gives the following overview:

In the early years of the twentieth century, the vapor absorption cycle using water-ammonia systems was popular and widely used but, after the development of the vapor compression cycle, it lost much of its importance because of its low coefficient of performance (about one fifth of that of the vapor compression cycle). Nowadays, the vapor absorption cycle is used only where waste heat is available or where heat is derived from solar collectors. [..]
The absorption cycle is similar to the compression cycle, except for the method of raising the pressure of the refrigerant vapor. In the absorption system, the compressor is replaced by an absorber which dissolves the refrigerant in a suitable liquid, a liquid pump which raises the pressure and a generator which, on heat addition, drives off the refrigerant vapor from the high-pressure liquid. Some work is required by the liquid pump but, for a given quantity of refrigerant, it is much smaller than needed by the compressor in the vapor compression cycle. In an absorption refrigerator, a suitable combination of

refrigerant and absorbent is used. The most common combinations are ammonia (refrigerant) and water (absorbent), and water (refrigerant) and lithium bromide (absorbent).

The classic gas absorption refrigerator cools by evaporating liquid ammonia in a hydrogen environment. The now-gaseous ammonia is then absorbed (dissolved) into water, and then later separated (boiled off from the water) by a small source of heat. This drives off the dissolved ammonia gas which is then condensed into a liquid. The liquid ammonia then enters the hydrogen-charged evaporator to repeat the cycle.

A similar system, common in large commercial plants, uses a solution of lithium bromide salt and water. Water is evaporated under low pressure from the coils that are being chilled. The water is absorbed by a lithium bromide/water solution. The water is driven off the lithium bromide solution using heat.

Another variant uses air, water, and a salt solution. Warm air is passed through a sprayed solution of salt water. The spray absorbs humidity from the air. The air is then passed through an evaporative cooler. Humidity is removed from the cooled air with another spray of salt solution. The salt solution is regenerated by heating it under low pressure, causing water to evaporate. The water evaporated from the salt solution is recondensed, and rerouted back to the evaporative cooler.

An example of a 10-ton 35 kW LiBr system is described e.g. by Pongtornkulpanich (2008). The system is charged by a 72 m^2 vacuum tube array and requires a loading temperature of 70-95 C. The nominal operating range for the hot water input is 70–95C at 2.4 l/s, resulting in chilled water at about 7C and 1.5 l/s. Cooling water is supplied by a BKC-30 RT cooling tower with a capacity of 30 tons.
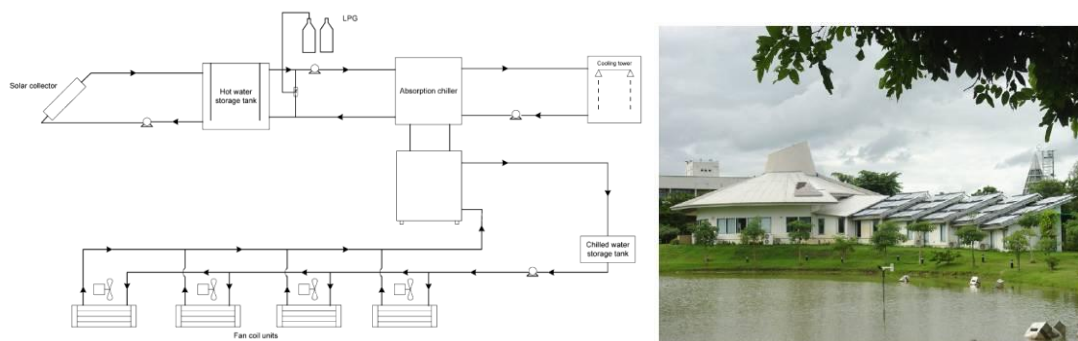
Figure 14: LiBr system (Pongtornkulpanich, 2008).

5 Open systems with solid TCM

5.1 Introduction

Open systems extract the vapor directly from the ambient. In practice, this means that open systems always use water vapor, and are often extracting the vapor from outgoing ventilation air. Since the amount of water vapor in the ambient air is not very high (roughly), this implies that the system is particularly suitable for systems with a high ventilation flow, relative to their heating demand.

5.2 Zeolite 4A seasonal storage Monosorp (ITW)

An open cycle system for integration in a ventilation system was developed at ITW (Kerskes, 2006).
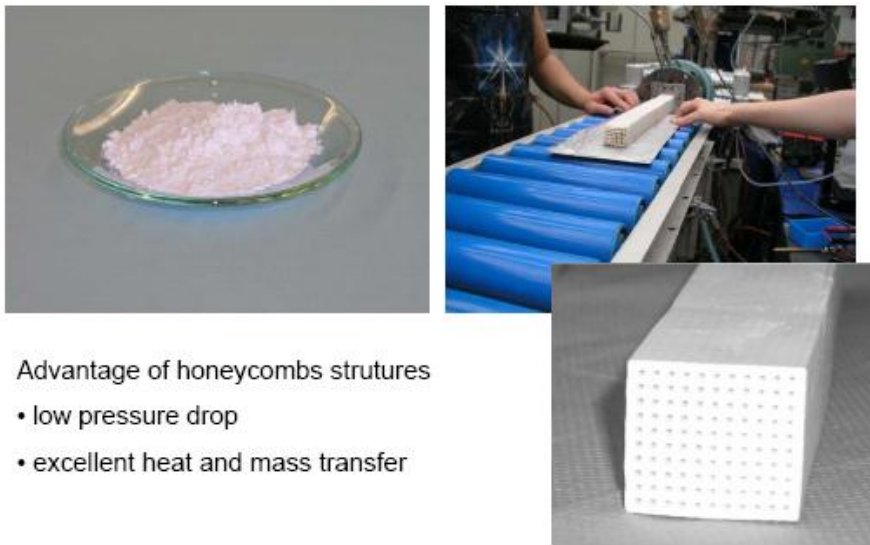
Advantage of honeycombs strutures
- low pressure drop
- excellent heat and mass transfer
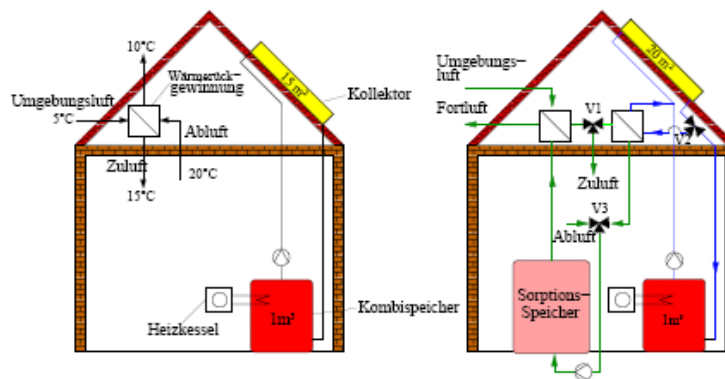
Abbildung 1: Schematische Darstellung eines Gebäudes mit und ohne Sorptionsspeicher

Water vapour is extracted by the zeolite blocks from the outgoing ventilation, resulting in very dry and hot outgoing air. Next, the heat is transferred from the outgoing ventilation air to the incoming ventilation air by means of a heat exchanger; gives 15-25 C heating. For charging, which requires 160 C, the stagnation period of a large collector vacuum tube room heating system is used. The design focuses on low pressure loss for large flow rate. Use is made of extruded zeolite 4A thermoplastic polymers as plasticising aid and binder. 4A is used because of better mechanical stability in extruded form than 13X.

5.3 zeolite 13X chiller (ZAE)

ZAE has been involved in open cycle TCM systems for a long time. Fischer (1998) refers to a first pilot project in 1990. Based on the experiences in this pilot project, in 1997 two demonstration projects started of open cycle systems with Zeolite 13X; a school and a jazz club.
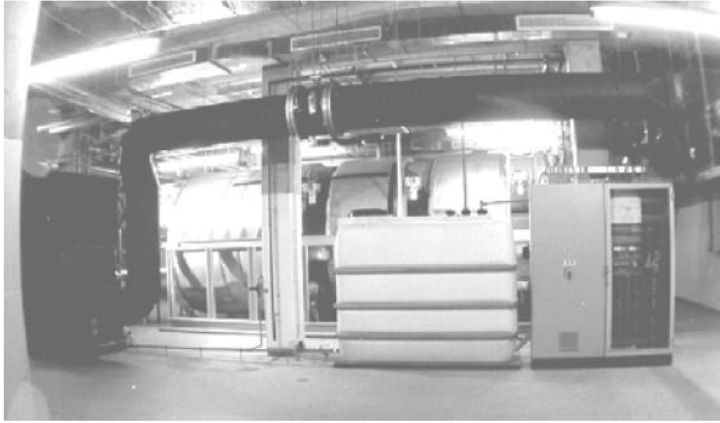
Figure 4: Thermochemical storage system (Humidifier, water tank and control unit in the front from left to right, three Zeolite modules in the back)

Figure 5: Heat exchanger and humidifier of the supply air
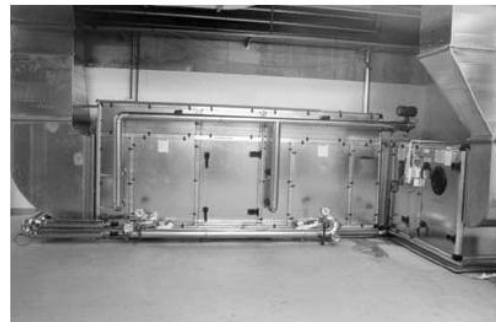
Figure 6: Indirect evaporative cooler of the exhaust air

Characterisctics of the jazz-club system are: 7000 kg of zeolite 13X, maximum heating power of 130 kW at an airflow of 6000 m3/h, 130 C regeneration temperature, in a system providing heating and cooling for a jazz club (capacity 200 persons). The tank consists of 3 connected cylinders arranged in a horizontal line.

This system has also been used in a school (max heat load 95 kW), in combination with district heating (see figure). In the description of the school project, the following information is given:

Der TCS wurde 1995 im Heizungskeller des beschriebenen Gebäudes aufgebaut [71]. Das thermochemische Speichersystem ist für 14 Stunden Vollastbetrieb (95 kW) ausgelegt. Damit kann das Schulgebäude bis zu einer Aussentemperatur von -16 ∘C einen Tag (7-21 Uhr) beheizt werden. Unter diesen Bedingungen werden 6000 m3/h durch die Schüttung geblasen. Das erfordert eine Speichermasse von ca. 7000 kg Zeolith (trocken), entsprechend einem Volumen von 10 m3. Der Gesamtspeicher ist in 3 Module aufgeteilt, die mit Luftklappen voneinander getrennt sind. Damit soll eine bessere Leistungsanpassung realisiert werden. Die Hülle des Speichers ist doppelwandig in Edelstahl ausgeführt. Zur Reduzierung der Wärmeverluste ist der Zwischenraum jeweils evakuiert. Ein Füllmaterial aus Glasfaserboard ist in der Lage, den äußeren Belastungsdruck der umgebenden

Atmosphäre und das Eigengewicht der Module aufzunehmen. Die Isolationsdicke beträgt 2 cm und die Wärmeleitfähigkeit dieser Isolation ca. 0,002 W/mK.
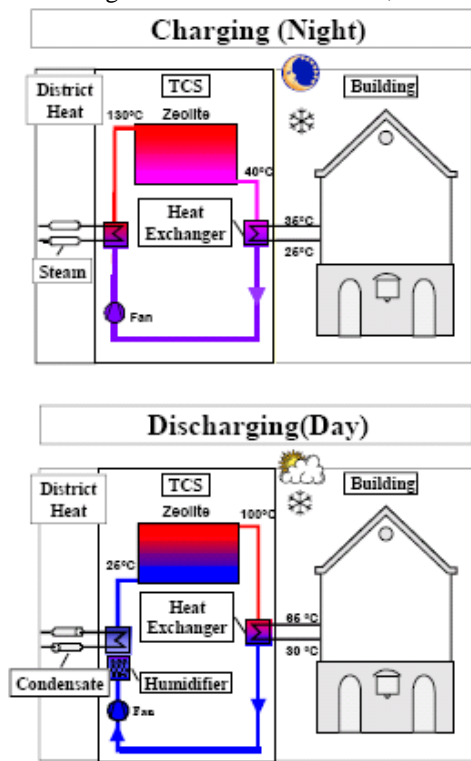

Figure 2: Charging and discharging mode for heating

In order to use the Zeolite storage system as a desiccant cooling system two additional components have to be integrated. Figure 3 shows the complete desiccant cooling system including the cold recovery device and the supply air humidifier. As shown in figure 3, the air stream exiting the Zeolite bed has to be cooled down (cold recovery device) before entering the supply air humidifier.
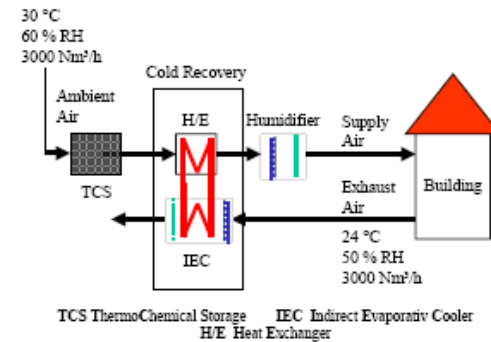
Figure 3: Additional components for air conditioning

The cold recovery device consists of an exhaust air humidifier with an integrated heat exchanger and the supply air heat exchanger, which are connected by a fluid circuit. The first can be described as an indirect evaporative cooler. The cold recovery device is able to transport 83 % of the maximum possible enthalpy difference from the exhaust air to the supply air.

In 2002, Hauer finished his PhD at the Technical University of Berlin, on the characterisation of silicagel and zeolite for open sorption systems. As part of his research, he also examined the effect of fouling by other gasses, such as CO, SO_2 and NO_2 which may negatively affect the water uptake capacity of zeolite in an open system.
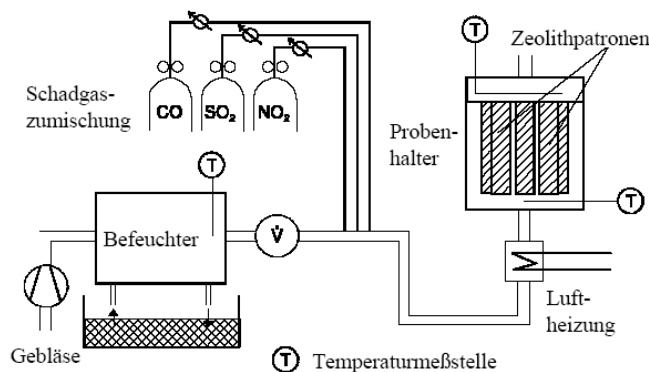
Figure 15: Experimental setup by Hauer (2002).

In later work, the focus shifted to a liquid LiCl heat pump system (Hadorn, 2005), and a demonstration project with a LiCl system was carried out at the office of Prochek Immobilien GmbH in Amberg (Laevemann, 2003).

6 Open systems with liquid TCM

6.1 Introduction

The two projects in this section are both working with a vapor-permeable membrane to separate the TCM liquid from the ambient.

With respect to the suspensions as used by TNO; a number of problems appear. First of all, a suspension fluid should be found that does not react itself with the TCM material and also allows sufficient water vapor transport to the suspended material. Secondly, the suspension should be stable for all forms (anhydrated to fully hydrated) in which the TCM material appears during the reaction, which is quite a challenge. Finally, the suspension liquid should be able to carry a very high loading fraction of TCM, in order not to reduce the energy density too much.

6.2 Na$_2$S suspension membrane seasonal storage (TNO)
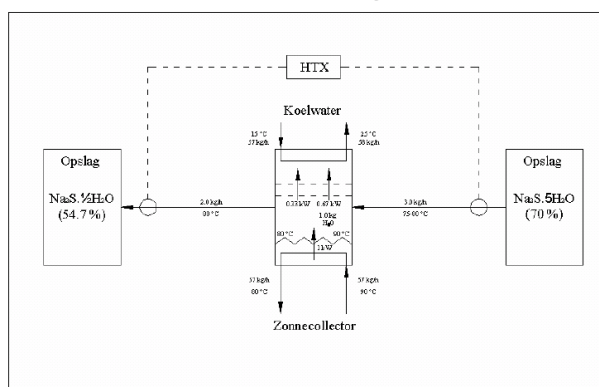
Voorbeeld van het reactorconcept t.b.v. thermochemische warmteopslag.

In de reactor vindt massa transport van waterdamp plaats tussen de verdamper/condensor (bij lage temperatuur) de adsorber/desorber (bij hoge temperatuur). Voor de prestaties van het warmteopslag systeem is het noodzakelijk dat dit massatransport vrijwel weerstandloos plaatsvindt terwijl tegelijkertijd vrijwel geen warmte-uitwisseling tussen verdamper/condensor en de adsorber/desorber plaatsvindt, zie (R2003/408).

TNO heeft hiervoor een tweetal concepten rekenkundig uitgewerkt. Eén concept gebaseerd op een membraan met een kleine warmtegeleidingscoëfficiënt en een grote massatransportcoëfficiënt en één concept gebaseerd op gescheiden compartimenten voor de adsorber/desorber en de verdamper/condensor. Uit deze analyse blijkt dat het, bij de gegeven temperatuur- en drukverschillen, niet haalbaar is om de verlangde prestaties met behulp van één membraan te realiseren. De keuze is daarmee gevallen op een reactor concept bestaande uit twee doorverbonden compartimenten.

Met een eerste labopstelling van een vergelijkbare reactor, afkomstig uit een parallelle ontwikkeling welke tot doel heeft gedestilleerd water te produceren m.b.v. restwarmte, vinden momenteel de eerste proefjes plaats.

2.5 Regenerator

2.5.1 Werking

De werking van de regenerator (Figuur 4) wordt hier beschreven voor de overgang van $Na_2S.5H_2O$ naar $Na_2S.0,5H_2O$ kristallen, daar de andere opties niet geschikt bleken voor warmtegeneratie (zie 2.7).

1. Het beladen medium ($Na_2S.5H_2O$) wordt aangevoerd vanuit de opslagtank, en deels voorverwarmd in een tegenstroom-warmtewisselaar (HTX) met het geregenereerde medium.

2. De warme slurry wordt in de regeneratormodule in contact gebracht met een in de zonnecollector verhitte waterstroom, via een dunne, dichte kunststoffilm.

3. Mits in de continue fase van het medium de waterdampspanning lager is dan de bij de bereikte temperatuur geldende evenwichtsdampspanning (zie hieronder), treden eerst 3 moleculen H_2O en vervolgens nog 1,5 moleculen H_2O uit het kristalrooster, tot $Na_2S.0,5H_2O$. Bij dit proces wordt hydratatiewarmte opgenomen door het kristal, en aangeleverd als voelbare warmte vanuit het medium. Aangenomen wordt dat dit hier energie-neutraal plaatsvindt als gevolg van het weer vrijkomen als absorptiewarmte in de continue fase.

   De hydratatiewarmte is hier gelijkgesteld aan de condensatiewarmte van water: ca. 2,4 MJ/kg water. Deze warmte dient, vermeerderd met de warmteverliezen te worden aangeleverd vanuit de zonnecollector.

4. Het bereiken van een voldoende lage waterdampspanning, in de continue fase wordt bereikt door hieruit water te verdampen. Gekozen wordt dit te laten plaatsvinden via zogenaamde Direct Contact Membrane Distillation (DCMD): het medium loopt in tegenstroom met een koelwaterstroom (met een voldoende lage dampspanning), daarvan gescheiden door een hydrofoob, poreus membraan; het verdampende water wordt in het koelwater opgenomen.

Het membraan heeft hier vier functies:
- Fysisch scheiden van medium en koelwater;
- Mogelijk maken van een – zo groot mogelijk – massatransport van waterdamp;
- Zoveel mogelijk beperken van verlies aan voelbare warmte van medium naar koelwater;
- Mogelijk maken van een goede tegenstroming tussen medium en koelwater.

Status: progress of the project was impeded due to lack of money, lack of time and change of jobs of people involved in the project.

In the first phase of the project, 50% TCM loading fraction was obtained with Na_2S. Further improvements were sought together with BIC, a company specialized in surfactants for stabilizing suspensions. As a suspension fluid an apolar fluid is required that passes the water vapor. First glycol was used but this turned out to react with the TCM. Subsequently, dibutylftalate was used, which did not react with the TCM but did impede the water vapor transport and in addition changed the surface tension of the fluid, thereby compromising the functionality of the membrane. At present, a solution is sought without membrane, such as a film of droplet evaporation reactor. Also, it was decided not to continue with the Na_2S, but to use $CaCl_2$ instead.

6.3 LiCl membrane seasonal storage (Entry Technnology)
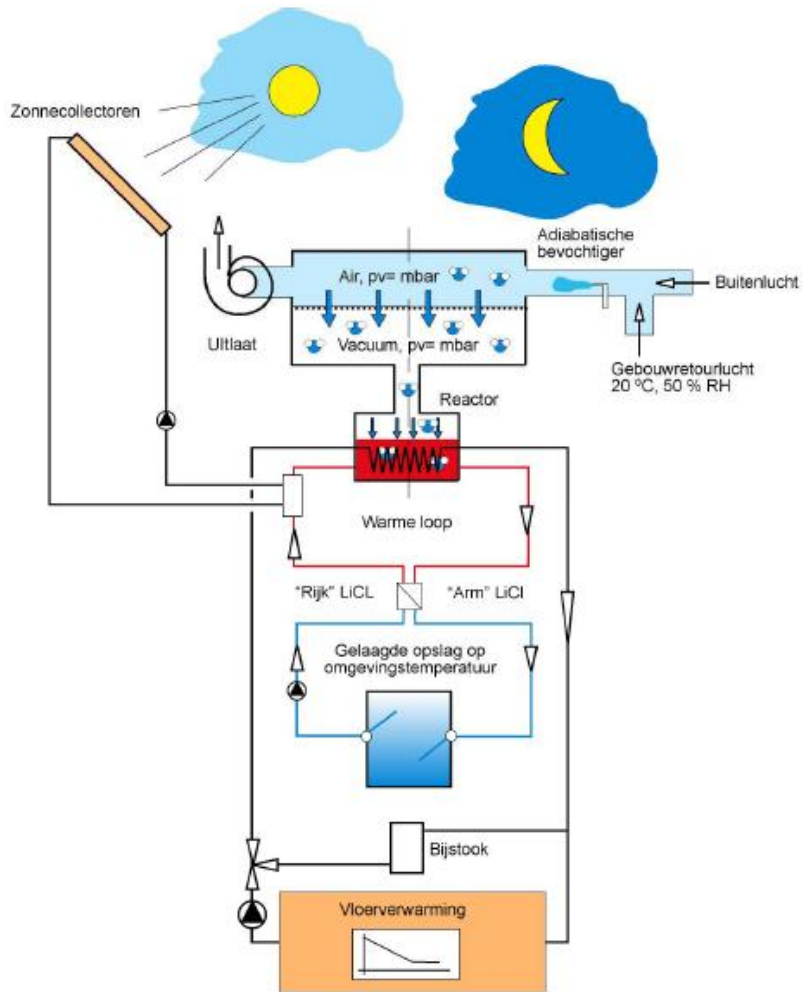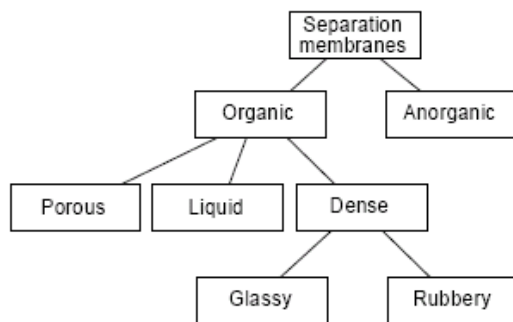

Figuur 3.9 Schematische weergagave van het membraan-sorptie systeem voor lange termijn opslag van zonne-energie
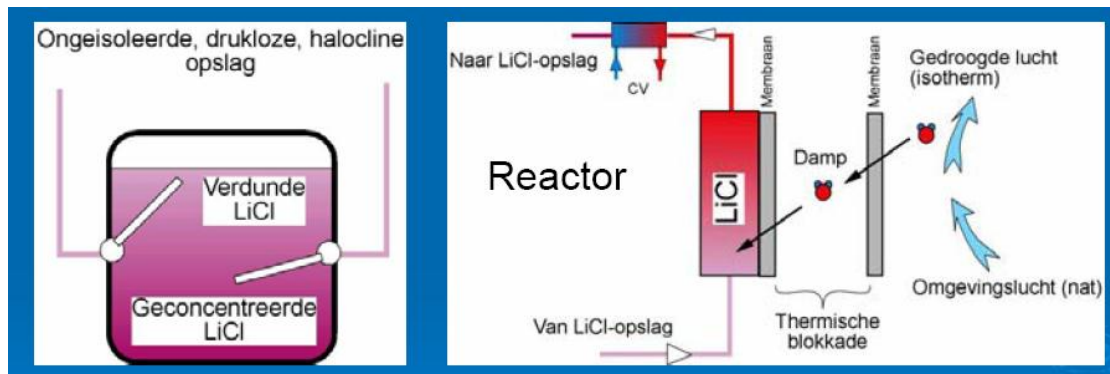
3.2   Membraan en membraanoppervlak.

Membranen zijn commercieel beschikbaar voor een veelheid van toepassingen. Te denken valt aan membranen voor waterzuivering en desalinatie, dialyse, gasscheiding e.t.c.. Figuur 3.1 geeft een classificatie van veel toegepaste membranen.

Figuur 3.1 Classificatie van veel toegepaste membraantypen.

Vanwege de beoogde toepassing als commercieel waterdamp/luchtscheidingsmembraan, in de temperatuurrange tot 35 ºC is hier een keuze voor een organisch, homogeel membraan voor de hand liggend. Wat permeabiliteit voor waterdamp betreft is daarbij geen groot verschil tussen glasachtig en rubberachtige membranen. Een voorbeeld waar waterdamp doorlatende membranen veel toegepast worden "ademende kleding" en waterdamp doorlatende folies voor gebouwisolatie. Deze membranen laten (transpiratie)vocht door, maar houden vloeibaar water en lucht (regen en wind) tegen. Het fysich-chemisch mechanisame achter semi-permeabiliteit ligt aan een verschil in oplosbaarheid (**S**) en diffusiteit (**D**) van de stoffen in de membraan matrix. Vaak is het zo dat waterdamp specifiek goed oplosbaar en diffuus is in bijvoorbeeld een amorfe fase van het copolymeer (b.v. EthyleenOxide of Amide groep).

In dit project is door middel van een desktop onderzoek ruim 13 commerciële membranen voor toepassing overwogen. Daarvan zijn drie membranen voor nader onderzoek geselecteerd. Vanwege vertrouwelijkheid naar de toeleveranciers worden de productnamen hier vertrouwelijk behandeld.

For a 6 GJ residence, it is estimated that 75% solar fraction can be achieved with a 6 m3 storage, resulting in a cost of 6000 euro/GJ and requiring 50 m2 membrane reactor (expertmeeting Platform Nieuw Gas, Utrecht, 2007).

7 Summary and conclusions

From the literature survey, it can be concluded that only a very limited number of thermochemical seasonal storages exist. The systems with a solid TCM that have been realized were on the basis of Na2S (Tepidus) and silicagel (Hydes and Modestore). In addition, a small storage based on silicagel or zeolite has been realized at SPF and an open system was based on zeolite at ITW (Monosorp). For a liquid TCM, system concepts were realized on the basis of NaOH (EMPA), a Na_2S suspension (TNO) and LiCl (Van Berkel).

None of the solid TCM systems had a separate reactor; all were fixed bed systems and the heat transfer was an important issue in all of these. In the liquid TCM systems, all had separate reactors. However, limited information was available on the exact design of these reactors. Two of them were using a membrane for the separation between TCM and liquid or air.

Although the literature inventory has given an interesting overview, it did not provide information on the design and mass transport in systems with solid TCM and a separate reactor, and the design of such a system is a very interesting challenge.

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Appendix A : TCM patents overview