International Energy Agency

Solar Heating & Cooling Programme

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Thermal energy storage for solar and low energy buildings

State of the art
by the IEA Solar Heating and Cooling Task 32

June 2005

Editor
Jean-Christophe Hadorn

This book was published in 2006 as part of IEA SHC Task 32: Advanced Storage Concepts for Solar Thermal Systems in Low Energy Buildings.

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The paper version, which sold for 35 €, is out of print so to ensure that its important contribution to solar heat storage is not lost a digital version is now available. The digital copy is identical to the book in its technical content and chapters. To download the digital version go to https://task32.iea-shc.org/publications

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JC Hadorn – Sept. 7th, 2020

INTERNATIONAL ENERGY AGENCY
Solar Heating & Cooling Programme

Jean-Christophe Hadorn (Ed.)

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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 authorative energy statistics as well as researcy 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.

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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.

The Tasks of the IEA Solar Heating and Cooling Programme, both underway and completed are as follows:

Current Tasks:

Task 27	*Performance of Solar Facade Components*
Task 28/ ECBCS Annex 38	*Solar Sustainable Housing*
Task 29	*Solar Crop Drying*
Task 31	*Daylighting Buildings in the 21st Century*
Task 32	*Advanced Storage Concepts for Solar and Low Energy Buildings*
Task 33	*Solar Heat for Industrial Processes*
Task 34/ ECBCS Annex 43	*Testing and Validation of Building Energy Simulation Tools*
Task 35	*PV/Thermal Systems*

Task Defintion Phase:

Solar Resource Knowledge Management

Completed Tasks:

Task 1	*Investigation of the Performance of Solar Heating and Cooling Systems*
Task 2	*Coordination of Solar Heating and Cooling R&D*
Task 3	*Performance Testing of Solar Collectors*
Task 4	*Development of an Insolation Handbook and Instrument Package*
Task 5	*Use of Existing Meteorological Information for Solar Energy Application*
Task 6	*Performance of Solar Systems Using Evacuated Collectors*
Task 7	*Central Solar Heating Plants with Seasonal Storage*
Task 8	*Passive and Hybrid Solar Low Energy Buildings*
Task 9	*Solar Radiation and Pyranometry Studies*
Task 10	*Solar Materials R&D*
Task 11	*Passive and Hybrid Solar Commercial Buildings*
Task 12	*Building Energy Analysis and Design Tools for Solar Applications*
Task 13	*Advance Solar Low Energy Buildings*
Task 14	*Advance Active Solar Energy Systems*
Task 16	*Photovoltaics in Buildings*
Task 17	*Measuring and Modeling Spectral Radiation*
Task 18	*Advanced Glazing and Associated Materials for Solar and Building Applications*
Task 19	*Solar Air Systems*
Task 20	*Solar Energy in Building Renovation*
Task 21	*Daylight in Buildings*
Task 23	*Optimization of Solar Energy Use in Large Buildings*
Task 22	*Building Energy Analysis Tools*
Task 24	*Solar Procurement*
Task 25	*Solar Assisted Air Conditioning of Buildings*
Task 26	*Solar Combisystems*

Completed Working Groups:

CSHPSS, ISOLDE, Materials in Solar Thermal Collectors, and the Evaluation of Task 13 Houses

To find more IEA Solar Heating and Cooling Programme publications or learn about the Programme visit our Internet site at **www.iea-shc.org** or contact the SHC Executive Secretary, Pamela Murphy, e-mail: pmurphy@MorseAssociatesInc.com.

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
The Task duration is July 2003 - December 2006.
www.iea-shc.org look for Task32

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Sweden
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Switzerland
The Swiss Federal Office of Energy – Bern www.suisse-energie.ch

The Netherlands
SenterNOVEM, the Netherlands organisation for energy and the environment www.senternovem.nl

ECN, Energy research Centre of the Netherlands www.ecn.nl

The Swiss Federal Office of Energy for partial support of a dutch expert www.suisse-energie.ch

Glossary

Adsorption is the physical bonding of the sorbate to the sorbent. No chemical change occurs.

Absorption is the chemical bonding of the sorbate to the sorbent, and the sorbent undergoes a chemical change.

Chemical Storage – A storage unit or system that uses a chemical reaction to store energy (heat)

Combisystem – A solar thermal installation that can deliver heat for the domestic hot water and for the space heating system

Congruent melting - Melting process where the chemical or material melts homogenously.

Free-cooling - cold is collected and stored from ambient air during night, and is relieved to the indoor ambient during the hottest hours of the day.

Graphite-compound-PCM – PCM embedded inside a graphite matrix to improve heat transfer.

Ice storage – A storage unit or system that uses ice to store the solidification latent heat of water

Incongruent melting - Melting process where the chemical or material melts non homogenously.

Inorganic– includes all chemical compounds except the many which are based upon chains or rings of carbon atoms.

Inorganic PCM – Inorganic materials, such as salt hydrates or other salts, used as PCM.

Latent Heat - The quantity of heat (energy) absorbed or released by a substance undergoing a change of state, such as ice changing to water or water to steam, at constant temperature and pressure

Low energy building – A building with a low heat and cold demand. Typically 30 to 50 kWh/m2 year as a maximum value, where as common building stock in year 2000 in most countries is close to 120 to 150 kWh/m2 y. It is most effective to first save energy and then to produce the remaining demand by active means such as a solar installation. Designing a building for low energy is becoming state-of-the-art.

Microencapsulation – Technique to encapsulate chemicals providing a material with a shell size minor or around 1 mm.

Nucleator – Substance that can be added in very small quantities to another to avoid the subcooling of the second one. For this to happen, the melting temperature of the nucleator must be higher to the one of the main substance.

Organic– Organic compounds are composed of carbon and hydrogen, and can possibly contain any of the other elements such as nitrogen, oxygen, phosphorus, and sulfur.

Organic PCM – Organic material, such as paraffin or fatty acids, used as PCM.
PCM Storage – A storage unit or system that uses a Phase Change Material partly (in a mixture) or totally (bulk)

Phase Change Material (PCM) – Material used in heat or cold storage in its liquid-solid transformation. The energy used is the latent heat or enthalpy.

Seasonal Storage – A unit or system that can store heat for long period of time, such as from summer time to winter time to overcome the winter months with less solar input than the summer months.

Segregation - Effect that appears when a chemical or material, usually a salt hydrates melts incongruently. After the melting process, due to the different density of the water and salt, they separate, therefore, when the solidification process occurs, the properties of the material have changed.

Sensible Heat – The quantity of heat (energy) that is stored in a material without change of phase of the material, heat is stored thanks to a temperature difference or swing

Solar building – A building (one family house, commercial building, administrative, etc..) that uses solar energy to meet some or all of its heating needs (space heating or domestic hot water) and/or its cooling needs (solar cooling). Solar energy can be used in a passive way (without auxiliary energy, olike through the windows or a greenhouse) or in an active way (with some auxiliary pump or fan). In this report, the passive solar is supposed to be already part of the house, and only the remaining heating load is to be met by some other active solar devices.

Solar collector – A device that can collect solar radiation at 10 to 200 C for building applications

Solar nomenclature: www.iso.org

Slurry - Water or a liquid containing a high concentration of suspended solids (can be ice particles or microcapsules of PCM material)

Sorption is the bonding of a gas to a solid or into a solution. In a sorption process the gas is usually referred to as the sorbate and the solution or solid is known as the sorbent.

Subcooling – When a product is still liquid below its melting temperature.

Tank storage – A tank shape device that can store heat (energy)

Thermal storage - A unit or material that can store energy for some time in an efficient way that is with few heat losses.

Water tank storage – A storage tank that uses primarily water to store heat (sensible heat).

Working fluid is in an absorption or adsorption system the fluid that is evaporated in the evaporator, ab- or adsorbed in the ab- or adsorbent and condensed in the condenser
during the process. For a cooling machine it is also called the refrigerant.

For more terms see: Energy Dictionary, Distionnaire de l´energie, Energiewörterbuch,
Diccionario de la energia, World Energy Council, 1992, ISBN 2-909832-00-7

1. Scope of this document:

Heat and cold storage for solar and low energy buildings

by Jean-Christophe Hadorn

Heat storage : diurnal and seasonal needs

Heat storage is an age-old topic of engineering and technology development. Many “hot tanks and vessels” have been invented and used throughout history as heat storage is a neccessity for intermittent energy sources such as solar energy.

A **diurnal storage** provides at night, heat that was collected during the day, for example for solar domestic hot water systems. It is approximately a 24 hours storage capacity.
How to store heat collected during the summer to use in the winter remains a technical challenge after more than 30 years of research and development. A storage system able to store heat from summer to winter months is called a **seasonal storage**. The goal is to increase the solar fraction that is the fraction of our heating needs that we can meet with solar. Solutions have been found using big water tanks, water pits, deep aquifers, or sub-surface soil using pipes or duct to create a heat exchanger. About 100 pilot plants have been built since the 1970s that have been instrumented, monitored and the results presented to a broad audience. The outcome is that seasonal heat storage of solar energy is feasible for group of houses with an annual heat load exceeding 500 MWh/year. The storage vessel must be big in order to have few heat losses related to its capacity. The size of such stores is in the order of 1 to 5 m3 of water or equivalent for 1 m2 of solar collectors.
Solutions for single family house have also been found: in a ultra-low energy building, a water tank from 3 to 30 m3, depending on the size of the house and the climate, can help to reach 100% solar fractional savings in good conditions. However the challenge remains of how to reach high solar fractional savings with a compact storage that would not need to occupy a large portion of a cellar !

What is a high solar fractional saving ? There is no definition ! The IEA Solar Heating and Cooling Task 32 “Advanced storage concepts for solar and low energy buildings” (SHC Task 32) has considered that reaching more than 50% of the needs with solar energy is a good start. Why 50% ? because at this point, the auxilary heating system, such as gas, oil or wood, that covers the periods when solar energy is not available, would really become an auxiliary and not the main contributor to the heating (or cooling) needs of the building.

Cold storage

Cold storage is developing for summer cooling purposes for large commercial or administrative buildings. Best current solutions are aquifer storage technologies, inherited from the R&D for heat storage, but with no temperature problem since the store operates lower than 25°C. Market penetration of aquifer cold storage for large buildings is noteworthy in the north of Europe.

At present there is not on the market any simple solar devices for cooling a single family house, although some cold storage units could be already available, in the form of water in plastic balls.

Low energy buildings

Single family houses are the pioneer segment for low energy buildings. Low energy houses (40-45 kWh/m2 per year for space heating) combined with solar heat production are becoming more attractive to energy concerned persons, communities or authorities seeking to give a strong name to "sustainable development". Examples flourish in Germany with the Passiv Haus concept and in Switzerland with Minergie, which captures already 10% of the segment of the new houses market. France is introducing the concept of building with positive energy, that is producing more than it needs, in terms of heat and electricity.

High insulation standards, high quality glass and windows, heat recovery systems, and passive solar devices such as shading devices, help to decrease the need for heating and cooling to a low standard, 4 times less than what was the standard 20 years ago.
However, an efficient and cost effective means for storing solar energy for heating during the winter months is still needed in low energy houses.

Scope of the document

This document is about the art of storing heat or cold for a solar or a low energy house, in compact devices that could reach a mass market in the future, if humanity decides that solar energy is to play a central role in the sustainable developement of mankind.

Experts of IEA SHC Task 32 prepared this overview of past experiences and current storage solutions for single family houses as a building block for the next generation of systems and technologies for storing solar heat at a 100% solar fraction.

This document does not explicitely address the available seasonal heat storage technologies for high thermal loads that is for group of houses or large buildings.
The document reflects the knowledge of IEA SHC Task 32 experts at the beginning of the Task.
It adresses all forms of storage that could be considered for a single family house:

- storage in the structure of the building itself, as passive houses have shown the need and interest ,
- storage in water in all types of containers,
- storage in materials that are able to change phase at adequate temperature, called PCM or Phase Change Materials,
- storage by sorption in different highly porous material such as silicagel or zeolithe,
- storage in chemicals, where there is a great lack of R&D work due to lack of programs funded in this thema.

In order to store heat or cold, the heat or the cold has to be produced ! In this document, thermal energy can be produced either by solar collectors by a heat pump or by any type of boiler.

Read also:

http://www.iea-eces.org/techniques/techniques.html

Who could benefit from this report ?

- Energy engineers
- Architects
- Builders
- Managers of national or private thermal energy research programmes
- Thermal Solar energy companies
- Energy systems designers and consultants
- Researchers in thermal energy components and systems
- Energy planners
- Energy systems simulation engineers

2. The need for storage of heat and cold in a low energy buildings

by Jean-Christophe Hadorn

There are 3 fundamentals objectives for which energy needs to be stored: Economics, strategy or environment !

A store is based on **economics** when it allows:

- To reduce the financial losses
- To induce new revenues.

A store is decided based on a **strategical** decision when it allows

- To meet a demand that otherwise would not be met
- To meet a demand at a reduced cost, but this brgins back to an economical reason.

But a store can also reduce the impacts on **environment** when it allows:

- To smooth or reduce the emissions during transient operations or cycling of boilers.

Based on these principles, there are 6 reasons that would make a storage necessary as shown in figure 1.

Class	**STRATEGY**	**STRATEGY**	**STRATEGY**	**ECONOMICS**	**ENVIRONMENT**	**STRATEGY**
Reason	Time	Space	Capacity	Economics	Emmissions	Transmission
Storage is needed because	Supply & Dermand are not in phase	Supply & Demand do not occur at the same location	Supply < Demand Mostly at peak times	Variable prices or fees or tariffs	Cycling (on/off) must be reduced	There is no technology available to send a flux (like electricity through induction)
Goal	reduce intermittence	increase availability by transportation	increase supply at a given time	increase revenues by buying at low tariff and selling at high tariff	reduce the emissions	Fill the gap
Examples	- Warehouses for seasonal agricultural products - Fridge for food - Water tanks for solar energy	- Tanks and tankers for oil distribution	- Buffer stores of all kinds - Batteries in a stand alone PV application	- Peak load Dams - Ice storage for cooling loads at day time	- Water tanks for Heat pumps - New PCM storage vessel for boilers	- Batteries in electrical cars rather than electricity taken from the road or from a line

Table 1: the need for storing energy can be derived from 6 basic reasons

In this document, we will focus on heat storage for solar buildings.

The main reasons for storing are therefore:

- Time: there is no solar energy available at night or in winter months although a strong demand of heat can be observed
- Smoothing : A heat pump could operate with intermittence following the load, but this is not to recommend since it is better to let the heat pump operate at rather constant conditions on the warm side, with a storage to smooth the load
- Reduce cycling: a gas boiler can have more thant 60'000 cycles par year ! A store can reduce this number and help to reduce the emmissions.

Note that heating with solar energy is a time storage problem, while solar cooling does not imply a necessity for storing since supply is often in perfect conjunction with demand: when there is much sun the cooling loads increase but the sun is strong to meet it through absorption machines for example.
However cooling loads also occur when no sun is present, mainly for commercial buildings with high internal loads.

One of the main difficulty of solar energy for heating is the seasonal variation of the availability of the solar resource. In wintertime when heating load is high, the sun provides less energy than in summertime.

Seasonal storage

To overcome this, a long term storage from sommer to winter should be designed ! So-called seasonal storages have desserved much attention since the years 1973 in the solar community.
At present they are some good solutions for community projects or big buildings with heat loads over500 MWh/year. For single family houses, there is not yet a solution to this problem.

This book will show the existing and promising long term storage solutions for solar buildings.

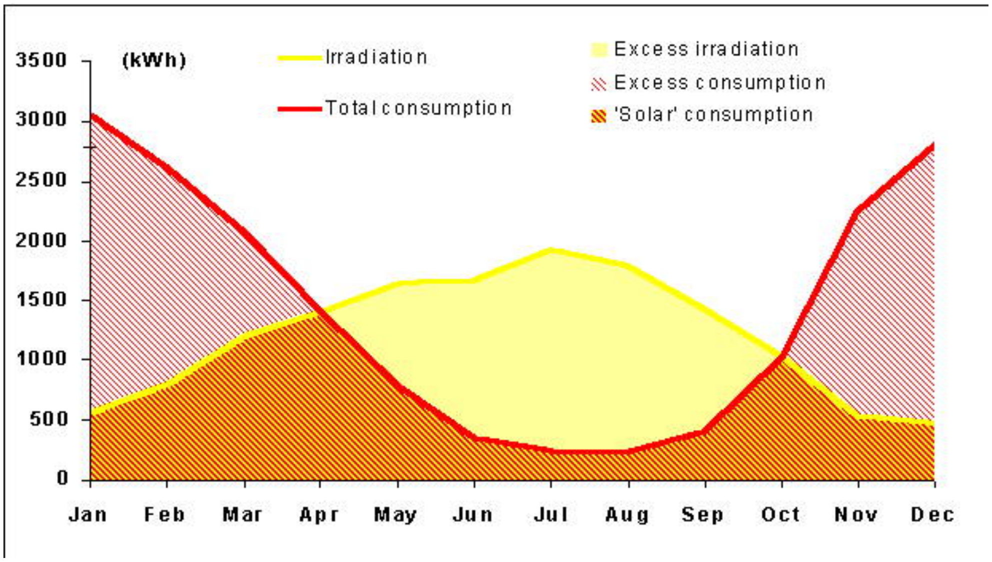


Figure 2: the need for seasonal storage , excess of solar heat in summer months, deficit in winter months (figure from T. Letz)

How large is a seasonal store for a solar house ?

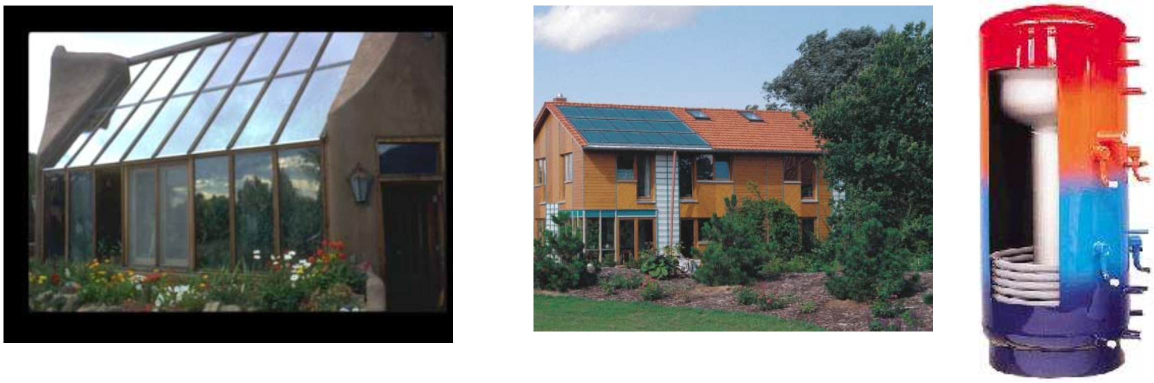
Consider a standard low energy house of 200 m2 as heated area in the climate of Zurich Switzerland occupied by four persons. The annual heat demand will be approximately:

2'500 kWh for heating + 3'600 kWh for domestic hot water preparation = 6'100 kWh/year.

Note that this could be covered in a boiler with 80% efficiency by an oil volume of 800 liters ! This is very low compared to the standard current average consumption of swiss houses which is closer to 3'000 to 3'500 liters per year, that is 4 times more !

Passive solar
Storage in the
building structure

Active solar
Storage in a water tank



100 m2 of concrete 20 cm thick
from 18C to 25C = 100 kWh of storage
No heat losses , dissipation into the house !

1 m3 = 1000 l of water in a tank
from 10C to 90C = 100 kWh of storage
Heat losses over one day < 20%

Figure 3: low energy houses, passive and active storage (Source: Hadorn, IEA Task 26 and supplier documents)

The energy for hot water preparation has not been reduced but the heat demand for space heating has been reduced by **a factor 4** due to all well known measures taken in low energy houses:

- enhanced insulation of the building envelope (walls, roof)
- advanced window frames and glazing
- no thermal bridges (balcony, basement perimeter, head of slabs,..)
- heat recovery from exhausted ventilation air
- passive design (thermal mass) and features (greenhouse or veranda)
- general design respecting solar passive architecture principles (buffer zones, orientation, protection,..)
- low temperature heat distribution system.

Many build examples around the world show that this low level of heat demand can be reached with a little financial effort in the order of 5% of the total cost of a house provided the owner is aware of the possibility and that architects and engineers have the necessary skills to design such a low energy house. Passivhaus in Germany and Minergie® houses in Switzerland are such examples gaining market share in the segment of new housing since 2000.

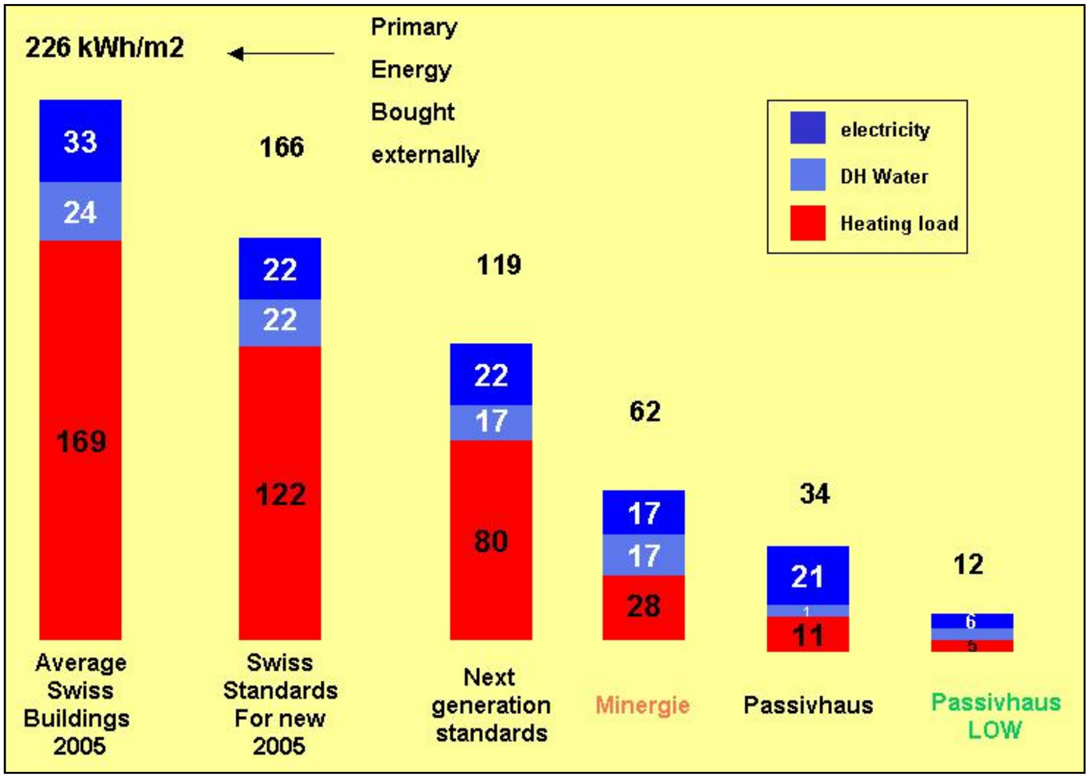


Figure 4: Reducing the load by a factor 4 is feasible as shown by PassivHaus in Germany or Minergie® houses in Switzerland (Source: Suisseenergie, Minergie@, PassivHaus, Hadorn)

Now the question raised by every owner of such a future low energy house is “how do I cover the remaining load ?”
Let us examine what solar energy can do, without considering the potential cooling need in summer as this point.

In Zurich meteorological conditions, good solar collectors can deliver at 30 to 40 C 400 kWh/year per m2. To cover 100% of the annual load of our reference house, only 15 m2 of solar collector would then be needed ! A pretty small area ! But of course there is a time gap between solar availability and heating demand, between summer and winter.

How large should be the smallest store to reach 100% solar ?

Experience and simulations have shown that we have to consider that there will be approximately 2 months without available solar energy for domestic hot water preparation and that half of the total heat demand occurs during these two months. It is for example from mid December to mid February as a first approximation.

Thus the heat that have to be stored to overcome the less sunny periods is :
2500 / 2 + 3’600 / 12 * 2 = 1’850 kWh
which is significantly less than 100% of the annual load due to the good design of our low energy building that can take advantage of the passive effect of the sun during autumn and spring to reduce the need of an auxiliary active heat source.

How can we produce this amount of energy before winter ?

Our good collectors can produce from say June to November about 200 kWh/m2 on excess from the hot water need during this period. Thus less than 10 m2 of solar collectors would be needed if the storage device had no loss ! A great challenge ! With a water tank for storage, even well insulated (say 50 cm of insulation), experience and simulation show that 20 to 30 m2 of solar collectors are necessary. Which is still not very much !

How can we store this amount of energy ?

Several materials can be considered as candidate. Table 2 shows the main potential solutions for storing heat.

Material	Heat capacity J/kg K	Density kg/m3	Energy kWh/m3 K	Volume of material for a 1850 kWh store, 30 to 100C m3
Water tank	4190	1000	1.163	23
Concrete	1130	2400	0.753	35
Earth (dry)	800	1300	0.289	91
Earth (wet)	2000	1700	0.944	28
Cast iron up to 200C	452	7900	0.992	27
Phase change material at 80C	latent 230000	at 60C 1127	105 kWh/m3 latent sensible 0.482	18
Chemical reaction at 200C			1000 kWh/m3 chemical	2

Table 2 : Different solutions to store 1'850 kWh from 30 to 100C, without heat losses, at atmospheric pressure (see also other chapters)
Note that the container volume and the volume of the insulation material is not included in the volume requirment given in the las t column of the table !

A water tank should be at least 23 m3 to store our needs, but subject to heat losses it will be probably closer to 30 m3 even well insulated by at least 60 cm of insulating material all around.
Storing in earth is an interesting alternative since big volumes can be obtained easily beneath a house or in a garden. A storage of 50 m3 would mean an excavation of 1 m only over a square of 7,5 m by 7,5 m. Not much. But experience and many simulations have shown that without insulation heat at almost 100 C would not stay more than a few days in such a storage ! A heavy insulation all around the storage volume is necessary, making the necessary excavated volume double.

Phase change material is an alternative to water in a tank, but as it can be seen the volume cannot be drastically reduced and the container (ie the tank) has still to be built. However, losses might be reduced and better stratification effects due to PCM in an appropriate level might also give further advantage.
A combination of water and PCM seems promising in this respect.

The smallest storage volume would be 2 m3 if we could supply heat at 200C for a chemical reaction to occur, splitting for example one compound into 2 parts that would recombine in wintertime delivering under control almost all the initial energy back.
Such a chemical reaction is possible with several candidates, but has not been deeply tested for two reasons:

- the cost of the material or its containment,
- the limitation in temperature reached by current flat plate non concentrating collectors that are usually chosen due to ease of handling on the roof of a house.

This limitation is now being removed since advanced flat plate collector or evacuated tube collectors can reach 200C in summer days and still have an acceptable efficiency.

What about storage heat losses ?

There is no deep mystery !
The longer the storage period, the more efficient has to be the insulation material around the store !

For a one day storage, optimum size of insulating material such as mineral wool is around 8 to 12 cm.
For storage aiming at a few days, 20 to 25 cm are necessary.
For seasonal storage, at least 50 cm are a necessity up to 80 or even 100 cm, and thermal bridges have to be totally avoided.

How then can the solar fraction be increased ?

There are four ways to increase the solar fraction in a solar building:

1. decrease the heat demand by any passive or energy savings measures
2. increase the efficiency of the collectors and the storage, that is reduce losses.
3. increase the collector area to produce more energy but mainly in summertime resulting in more need for seasonal storage !
4. increase the heat capacity of the store.

Recent standard combisystems combines 15 m2 of flat plate solar collector and a 1 m3 of storage, and can cover up to 50% of the heating demand of a well insulated house in mid Europe climate. The specific storage capacity is in that case 67 l/m2 of solar collector.

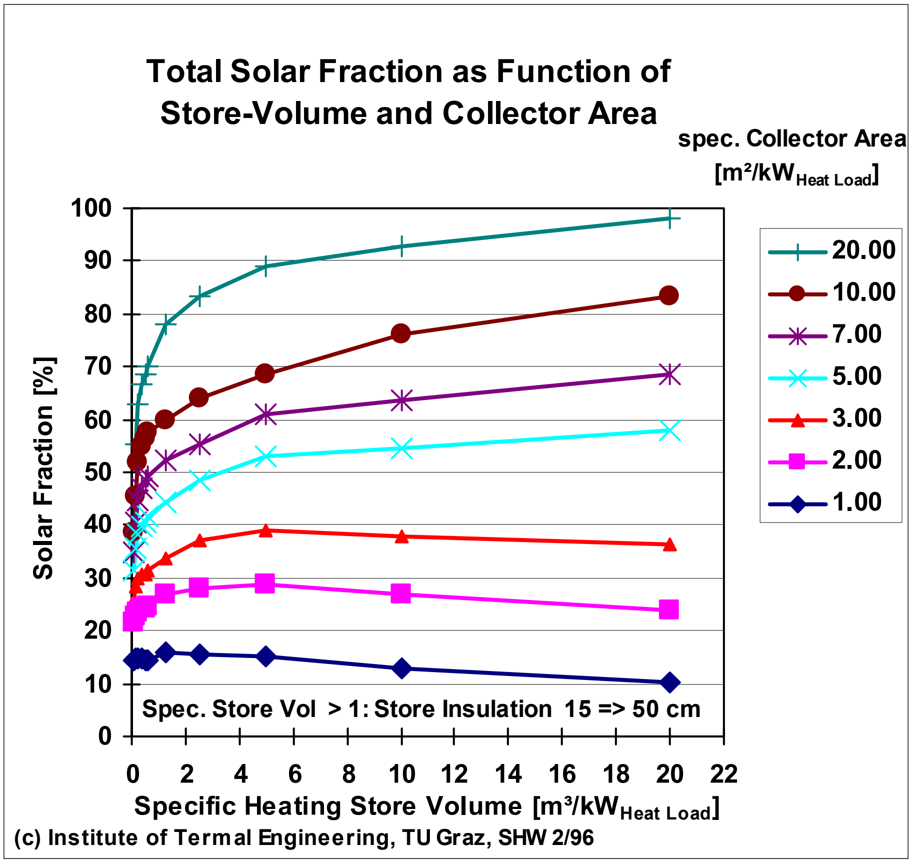


Figure 5: Solar fraction (= 1- Conventional heat delivered/Total heat demand) depending on specific collector area Acoll_p [m²/kWheat-load] and specific store volume Vstore_p [m³/kWheat-load] for small stores (top) and big stores (bottom) in Austrian conditions (Streicher, 2000).

To reach more than 90% solar fraction, depending of course on the climate and the availability of sun shine during cold periods in winter, about 1000 l/m2 are needed, that would be in our example a 15 m3 storage.
Figure 5 shows for mid european conditions the relationship between the storage volume and the solar fraction for several solar collector areas. Increasing the store volume beyond 4 m3/kW heat load does not increase drastically the solar fraction in the climat of Graz. Still for a 6kW house, this is 24 m3 of storage for 120 m2 of collectors to reach 90% solar fraction.

Reducing this volume of storage to reach high solar fraction is a next challenge for the solar thermal engineers. This book explores several options.

Several options to store thermal energy for solar and low energy buildings exist. Storage solutions can be assessed through a number of criteria given in the following table:

Quality Criteria for a thermal storage

The important criteria for the storage itself are:

1. Capacity and density (kWh/m3 = kWh/kg * kg/m3)
2. Loading and unloading rate (kW)
3. Efficiency of storage (Eout/Ein, Eout = Ein - Losses)
4. Stability (mechanical, chemical)
5. Chemical compatibility with the container and exchange loop
6. Reversibility during a number of cycles
7. Cost (cts€/kWh): material, container, room needed, access, maintenance, number of cycles achieved
8. Toxicity
9. Recyclability, assessed through a Life Cycle Analysis

The storage material is not the only component of a storage. The heat exchanger plays a crucial role since heat has to be injected into the store when it is available (say noon during a solar day) and withdrawn from the store at any time even in peak load conditions. The heat exchanger should therefore also satisfy some basic criteria:

1. Rating (max power in and out)
2. Hydraulic head losses (should be in accordance with the pump capabilities)
3. Cost (it is always an optimisation parameter).

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3. Thermal storage in building structures: thermally activated building systems (tabs)

by Beat Lehmann, Robert Weber, Jean-Christophe Hadorn

Introduction

A growing recognition of the need for energy efficiency and the benefits of passive heating and cooling systems on indoor comfort have prompted the search for new heating and cooling concepts for buildings. Thermally active building systems (*tabs*) [1] have been shown to meet these new requirements in terms of both performance and cost. As the name suggests, *tabs* are technical solutions specifically designed to integrate the building's structural fabric in the overall energy strategy. Particular building elements, typically structural floors and slabs, serve as a heat sink whose dynamic thermal behaviour is exploited to provide either cooling by the absorption of energy from the internal environment or space heating through the release of stored energy. Such use of the building's thermal mass serves to flatten out peaks in energy demand. The large surface area of these elements permits substantial heat flows between space and structure, even for relatively small temperature differences. This, in turn, allows the use of natural cooling or low-grade heat sources, such as the ground, outside air or recovered process heat.

Up to now *tabs* are mainly used for the heating and especially cooling of commercial buildings. Therefore the following description of the system is based on the specific circumstances of this application case. Nevertheless the main observations are also valid for *tabs* applied in residential buildings.

Comfort in buildings

Human performance is significantly impaired by indoor temperatures that rise above or fall below certain thresholds. Consequently, comfortable temperatures are not a luxury but play a vital part in creating a pleasant working and living environment. Investigations on comfort conducted by Professor O. Fanger in the 1970s revealed that room temperature does not have to be constant, but can vary within certain bounds. Depending on the type of clothing indoor temperatures between 21-26°C are felt as comfortable. Heating, ventilation and cooling systems must now be dimensioned to allow optimum use of this admissible comfort range and economical use of the required heating and cooling energy.

Heat balance of a room

The highly insulated building envelopes common today have lowered energy requirements quite considerably, thus creating novel possibilities for heating and cooling of rooms. Attention can therefore be paid to systems based on low-temperature heating and natural cooling. At the same time, the fully glazed facades favoured by contemporary architects entail higher loads that frequently cancel out the enhanced performance of modern glazing systems. Solar loads thus continue to play a pivotal role, particularly in summer and the mid-season months. Room heat is also generated by people, devices and lighting, so that modern office buildings need cooling throughout most of the year. As high room temperatures tend to coincide with high outside air temperatures, the direct use of external air as a cooling source may normally be ruled out. A suitable storage system is therefore needed to bridge the gap between the day-time cooling demand and the availability of coolness at night. Additionally the maximum heat and cooling output of natural energy sources tends to be limited. In the case of cooling, for example, the required duty frequently exceeds the potential output from a particular source. Here, as in the previous case, an appropriate storage system is needed to meet the loads imposed by internal spaces, even at times with lower source outputs. Storage systems such as cold-water tanks, however, occupy a lot of space. Engineers have therefore turned their attention to using the building structure, particularly the ceilings and floors, as a central storage system. Given concrete's high density and specific heat capacity, buildings made of it have a considerable thermal storage capacity. With appropriate management of the building, its mass can be used efficiently, in any such unit, to transform the structure into a thermally active building system.

How tabs work

Figure 1 shows the principles and temperature cycle underlying the use of a *tabs*. A minimum room temperature of 21°C is assumed for the morning (Point ①). The heat gains in the room arising from the building occupants, technical equipment and solar influx through the windows push up the air and room temperatures to around 26°C (① - ③) in the course of the day. Convective emissions from the heat sources account for the greater part of the air temperature rise (① - ②'). The difference between the air and room surface temperatures increases until the convective heat generated by the heat sources has been transferred via the air to these surfaces. This convective component disappears as soon as the heat loads are removed (③ - ④). As the thermally active surfaces constantly absorb energy from the heat sources, they undergo a gradual temperature rise (① - ④), thereby "charging" the heat store. Consequently, the air and room temperatures in a space enclosed by thermally active elements do not remain constant, but fluctuate within the temperature range established by Fanger (① - ③). To re-establish the initial temperature the following day, the "building accumulator" has to be discharged (④ - ⑤), otherwise the initial room temperature will be even higher than it was at the start of the previous day. Heat is rejected from the building structure by means of water pipes embedded in the concrete slabs. Depending on type and magnitude of the heat sources, "discharge" may be limited to the night-time hours or spread throughout the day. *tabs* may be used for space cooling as well as for heating.

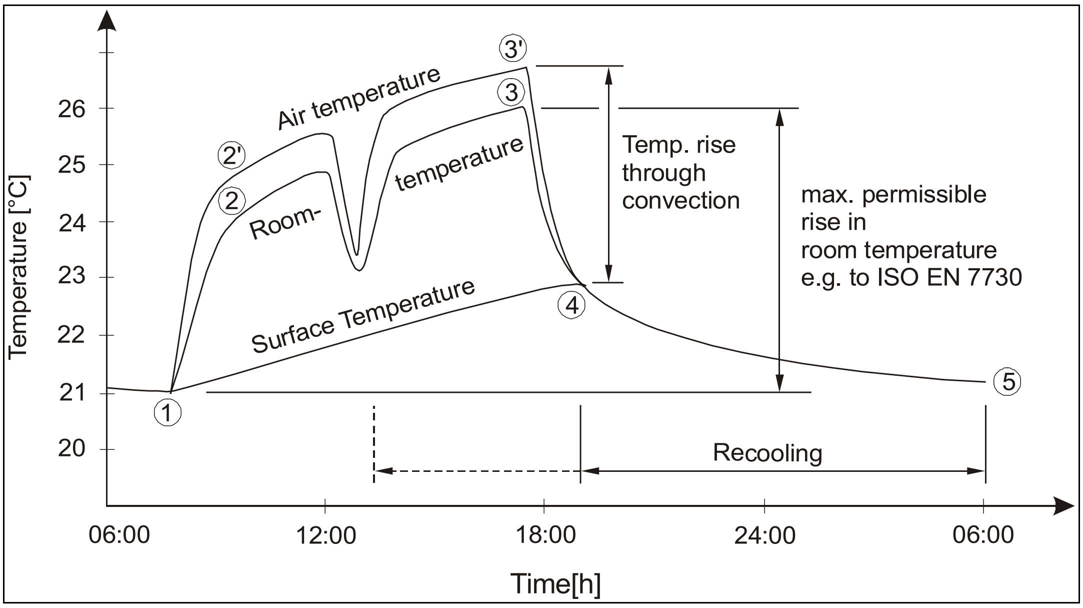

Fig. 1: Typical temperature cycle for tabs application (Source: EMPA, CH)

Energy supply

The energy required to operate the *tabs* may, in principle, be supplied by any conceivable source. Often used systems for cooling comprise refrigeration plants, adiabatic cooling with cooling towers, ground-source vertical-borehole heat exchangers or even groundwater. Conceivable solutions for heating purposes are heat pumps, condensing boilers as well as solar direct heating. These systems essentially vary in terms of capacity and achievable flow temperatures. The relationship between these two parameters must therefore be fine-tuned to meet the conditions of the current application.

Modelling of *tabs*

Because the building structure is acting as a storage medium, steady state calculation methods e.g. for floor heating systems are not applicable. Based on the time dependant two-dimensional heat transfer equation and by using the analogy between thermo and electric resistances a simple physical model has been developed (Fig. 2).

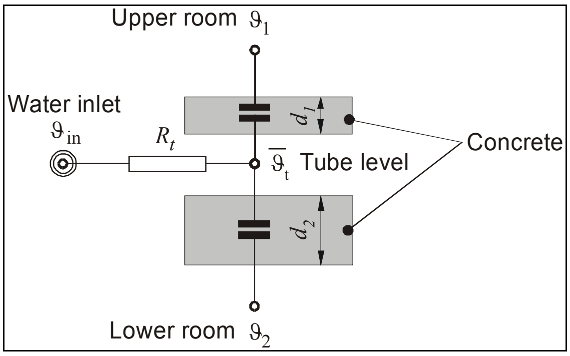

Fig. 2: One-dimensional model for the calculation of the heat transfer through the concrete slab (Source: EMPA)

The tube system in the building structure can be described by the following equation:

$R_t = R_w + R_r + R_x + R_z$

The total thermal resistance R_t between the water inlet and the average slab temperature on the tube level is the sum of four different resistances. The first term of the equation, R_w, is the reciprocal heat transfer coefficient for laminar or turbulent flow in the tube. R_r is the thermal resistance of the tube material. The coefficient R_x depends on the distance between the tubes and R_z takes the temperature variation along the tube (third dimension) into account. All coefficients can be calculated by analytical equations. The heat flux from the tube level to both sides of the slab is expressed by a time dependent one-dimensional heat transfer equation. By using the resistance model, the two-dimensional heat transfer problem can be reduced to a one-dimensional equation. This is an advantage for its integration into building and system simulation programs like TRNSYS [2] as those normally base on one-dimensional wall descriptions. With the aid of that model it is possible to design and optimize slab cooling and heating systems in a very early stage of the planning process.

The theoretical background of the physical model as well as practical recommendations for engineers have been summarized in a design guideline [1].

Limits

Using tabs as a low temperature thermal storage, the question arises if it would be possible to store solar heat for 100% of the heating needs of a building in the building structure itself without having to implement another type of storage ? Storing in the structure (walls, floors, …) is limited by the available thermal mass which was not designed for energy purposes but for structural reasons. It has been shown that a daily storage of passive solar heat is possible in walls and that the daily heat wave penetration is limited to 14 cm of concrete. This means that there is no need to have thicker walls for energy reasons. It has also been shown on the example of a villa in mid European climate, that the annual solar fraction cannot exceed 40 to 50% due to the limited available storage in the building structure even if solar collectors area is not the limitation [3]. If a higher solar fraction is a goal, it is necessary to implement a dedicated storage, such as those which will be discussed in this book.

These results are however very much climate dependant, a short term storage like the building structure being more efficient in a cold but every day sunny climate than in a mild but foggy winter.

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4. Storage in the building : Direct Solar Floor

by Thomas Letz

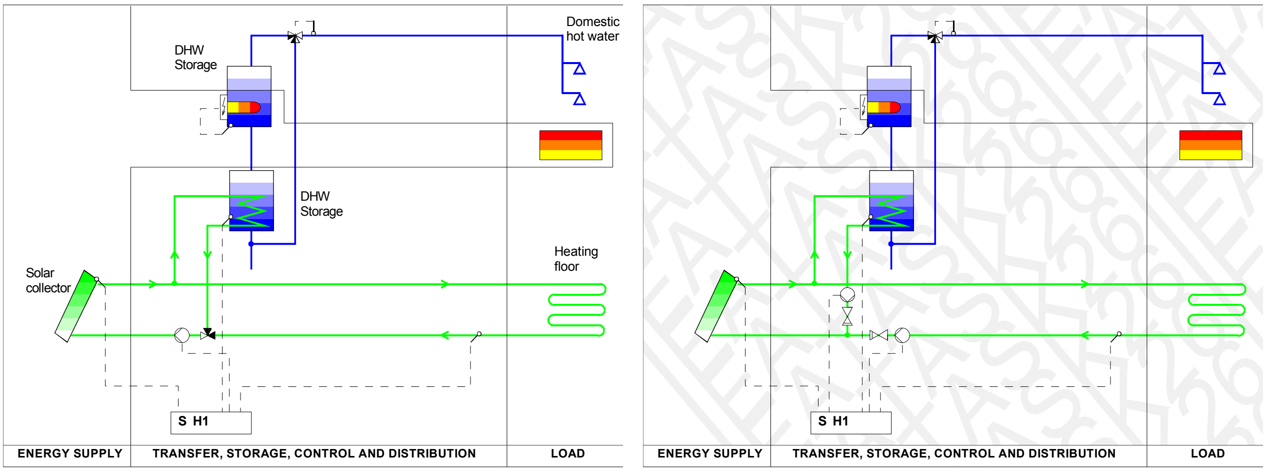
After the oil shock in 1973, solar energy seemed to be an easy possible answer to the lack of energy. Many active solar combisystems have been installed in France, with rather complicated hydraulic diagrams and big storage tanks, required by the low insulation of the houses and the high space heating demand. Most of them did not work properly, so that many users progressively lost confidence in these active systems. In order to radically simplify diagrams, a new concept named Direct Solar Floor (DSF) was elaborated at the beginning of the 80's [1] and improved during the last twenty years. The main idea was to remove the space heating tank, and to directly store solar energy in concrete slabs.

4.1 First diagrams

The very first developed systems only used the heating floors as a heat storage and as a heat emitter for solar heat. The floors are fed directly with the antifreeze heat carrying fluid. Auxiliary energy for space heating is provided by a separated heating system, like a wood stove or electric heaters. Auxiliary energy for Domestic Hot Water is provided either by a separated electrical DHW tank, or by an electric heater integrated in the top part of the solar DHW tank. Figure 1 shows the very first hydraulic diagrams proposed.

In the first one, a three way-valve is moved by the user twice a year, in order to connect the solar collector to the heating floor in wintertime or to a DHW tank in summertime. Only one pump and a simple differential controller are used. Difficult to imagine a simpler system !

In the second one, performances are improved by a double differential controller, which runs the pump of the colder loop (space heating or DHW). This diagrams allows to pre-heat DHW at the beginning of a sunny day in wintertime, when the DHW tank is full of cold water, until this tank reaches the temperature of the concrete slab. When the temperature measured on the return pipe of the heating floor exceeds a fixed set-point temperature (what means that the concrete slab is "full"), the pump of this space heating loop is turned off. Temperature then increases in the solar collector, allowing to further heat DHW.

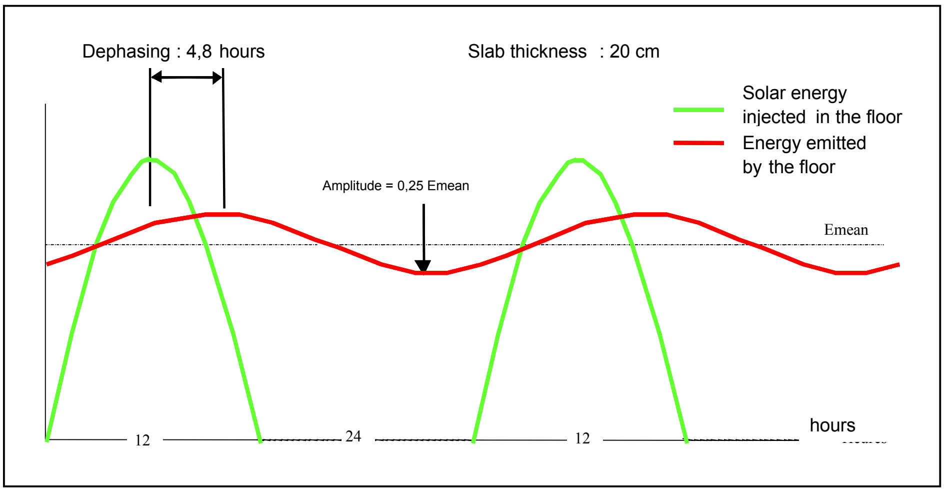


(source : ASDER, France) (source : IEA task 26)

Fig 1. First hydraulic diagrams

Utilizability of solar irradiation is therefore improved compared to usual combisystems with water heat storages, because the solar collector can work with a very low temperature due to the lack of heat exchanger between it and the heat emitters. The thickness of the slab has to be increased, in order to have a higher storage capacity. A 10 cm thick floor with an 100 m² area and a delta T of 10 K can store as much thermal energy as a 1 m³ water storage with a delta T of 45 K. In very first DSF, this thickness has been empirically increased until 20 to 30 cm. Pipes are placed at the bottom of the slab, so that it takes a few hour before the solar heat injected in the floor is released in the room through the floor surface. Moreover, the heat released by the floor is smoothed compared to the solar energy injected in the pipes. The thicker the slab is, the more accentuated this effect is (figure 2).

Several tens of such systems have been installed between 1985 and 1990 in France. This principle can still be used with good comfort in rather small houses, with an open inside architecture, where a single central auxiliary wood stove can be easily installed with a good repartition of heat in all rooms.



(source : ASDER, France)

Fig 2. How a thick concrete slab works (simplified presentation)

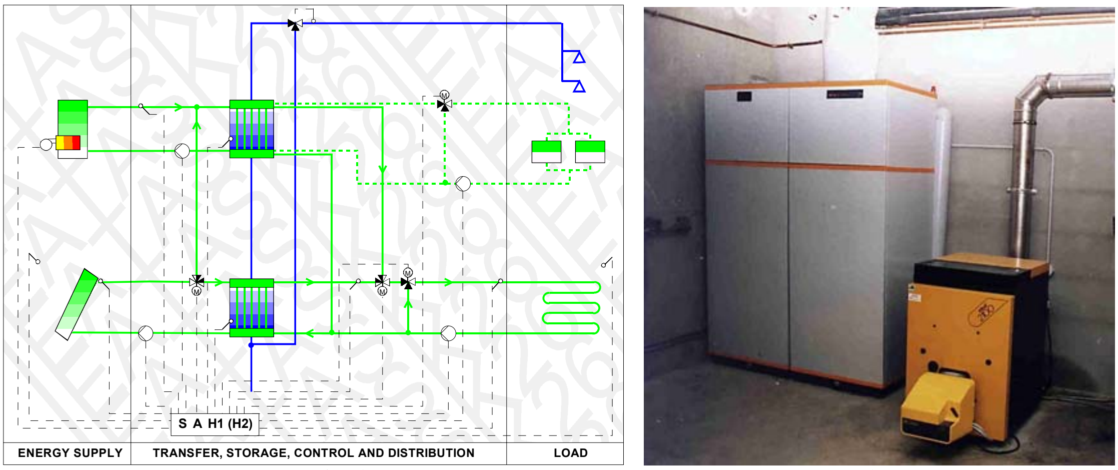
However, a disadvantage of these simple diagrams is the fact that, in wintertime, the main part of space heating energy is not delivered by the floor, but by the auxiliary system. Consequently, the comfort advantage of a low temperature heat emitter is not used at the time where it would be needed at most.

4.2 **Improvements**

That is why a research and development program for a new hydraulic diagram and a controller fulfilling following criteria has been undertaken by a French manufacturer (CLIPSOL) with the technical help of ASDER [2] :

- coupling of auxiliary and solar energy for space heating, with automatic switching from a mode to an other
- the controller manages the solar and the auxiliary energy for space heating and the preparation of domestic hot water
- the DHW auxiliary energy is provided by the same boiler as for the auxiliary space heating
- possibility to monitor the system easily

Figure 3 shows the result of this development. As previously, there is no storage tank for space heating energy. Domestic Hot Water is produced by two smaller tanks (2 * 250 litres) respectively connected with the solar collector and with the auxiliary boiler. The thickness of the heating floor has to be decreased in order to have a good control of the heat released in the rooms. A thickness between 12 and 15 cm has been determined by simulations as an optimum between a good storage capacity and a good control capability. Additionally, the solar heat storage capacity for space heating has been improved, by allowing the inside air temperature to exceed the set-point air temperature with some degrees, so that more solar heat can be stored in the floor and in the house structure.



(source : IEA task 26) (source : CLIPSOL, France)

Fig 3. Direct Solar Floor with Integrated Auxiliary energy (2 DHW tanks)

Beside the initial requirements described before, additional advantages of this diagram are :

- the auxiliary boiler is connected to the auxiliary DHW tank, which acts as a buffer and decreases the number of starts and stops of the burner. Lifetime of the boiler is then increased and polluant emissions decreased.
- hydraulic partition between the different loops (solar loop, boiler loop, space heating floor loop)
- in summertime, a three-way valve allows connection between the solar collector and the auxiliary DHW tank, then increasing the size of storage volume for DHW.
- a space heating loop with radiators can be optionnaly connected.
- possibility to cool down both DHW tanks in summertime, for overheating protection.
- a monitoring equipment (flow-meters and additional temperature sensors) can be connected to the controller, which integrates monitoring capabilities and remote overview of the system.

Between 1994 and 1998, a dissemination program of this system has been managed in several regions in France with financial support from Europe, the Ademe (French Agency for Environment and Energy Management) and the Region Rhône – Alps. 75 houses have been realized and monitored, in order to obtain data in very different configurations. Realized houses characteristics present a great diversity :

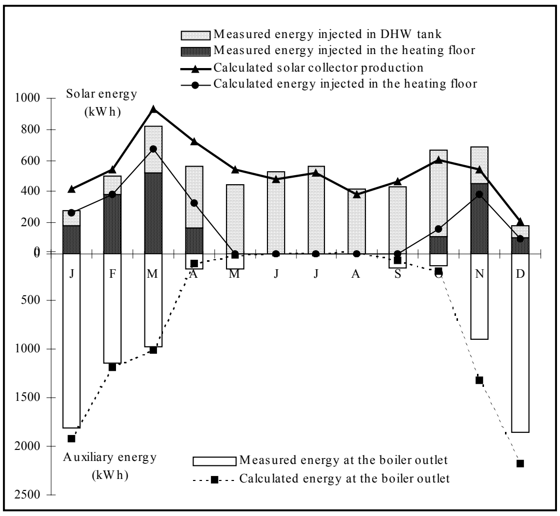
- floor area between 90 and 340 m²
- solar collector area between 12 and 36 m²
- varied geographical locations and climates : altitude between 10 and 1300 m
- between 2 and 16 inhabitants.
- in some cases, a swimming pool is heated in summer
- average cost of an installation (excl. VAT) : approximately 17 000 €, including 3 200 € for installation and pipes. Approximately half of that cost is for solar part, that is 8 500 €. When users install their system themselves, the global cost is reduced about 1 900 to 2 500 €.

Main results are [3] :

- solar fraction at the load level (space heating and Domestic Hot Water) : between 22 and 62 %
- average annual efficiency of solar collectors : between 27 and 47 %
- fractional energy savings : between 25 and 55 %

- yearly energy savings : between 7 000 and 16 000 kWh, that is between 440 and 800 kWh/m² solar collector. This last figure is obtained in some particular cases, with high energy load in summer (swimming pool, high occupancy leading to a high DHW demand).

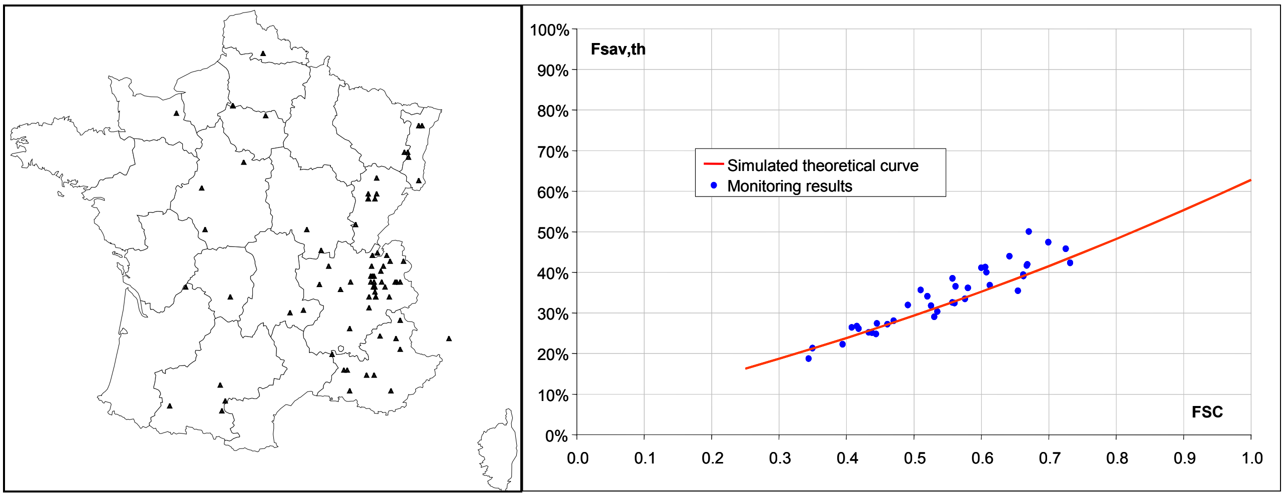
Monitoring results have been used to validate a new dimensioning method [4] specially developed for DSF (figure 4).



(source : ASDER, France)

Fig 4. Comparison between measured and computed values

Results are widespread, due to the wide range of parameters. In order to evaluate the behaviour of the system without taking into account the climate, the load and the size of the system, the FSC method has to be used [5]. Figure 5 shows results expressed as fractional energy savings (Fsav,th) vs Fractional Solar Consumption (FSC), and compares them with the theoretical curve obtained with Trnsys simulations for this system. Monitored results are close to theoretical ones, and seem even higher in some cases.



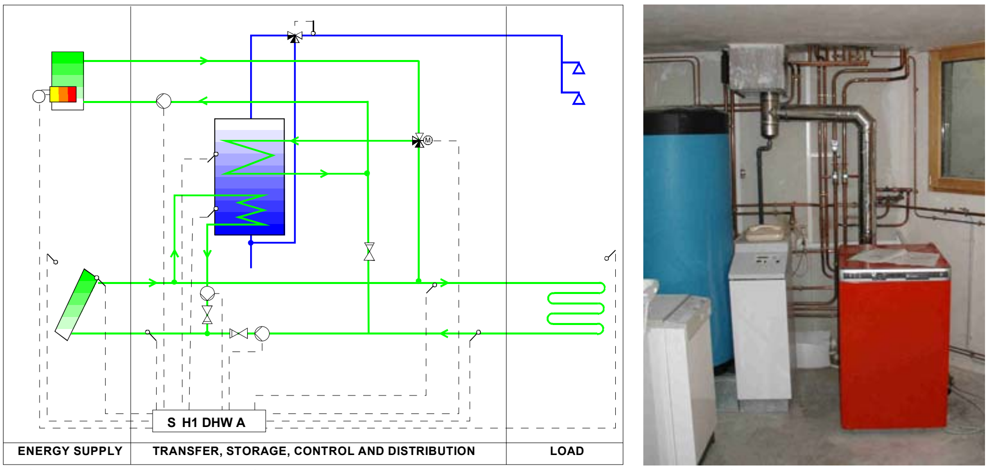
(source : ASDER, France) (source : ASDER, France)

Fig. 5 : Location of the houses and monitoring results

4.3 **Further improvements**

After the developments mentioned above, which proved the effectiveness of connecting the solar loop and the auxiliary loop to the same floor heating loop (this solution was not obvious, because there is no stratification in the floor, and it was feared that the storage capacity for solar heat could be dramatically decreased by the auxiliary heat injected in the floor), CLIPSOL designed a new simpler hydraulic diagram, with a single DHW tank (figure 6). The technical unit is now placed beside a 330 litres DHW storage tank.

This device has the same control and monitoring features as the previous system.



(source : ASDER, France) (source : ASDER, France)

Fig 6. Direct Solar Floor with Integrated Auxiliary energy (1 DHW tank)

Some measurements have been done in the framework of an Altener project [6], which allowed to compare different European solar combisystems, and proved once again the relevance of the DSF concept (figure 7). Relatively high fractional energy savings (> 50 %) could be obtained in two cases : first, for a house located in the South of France with a sunny and mild climate, and second for a low energy house located in a sunny mountain climate.

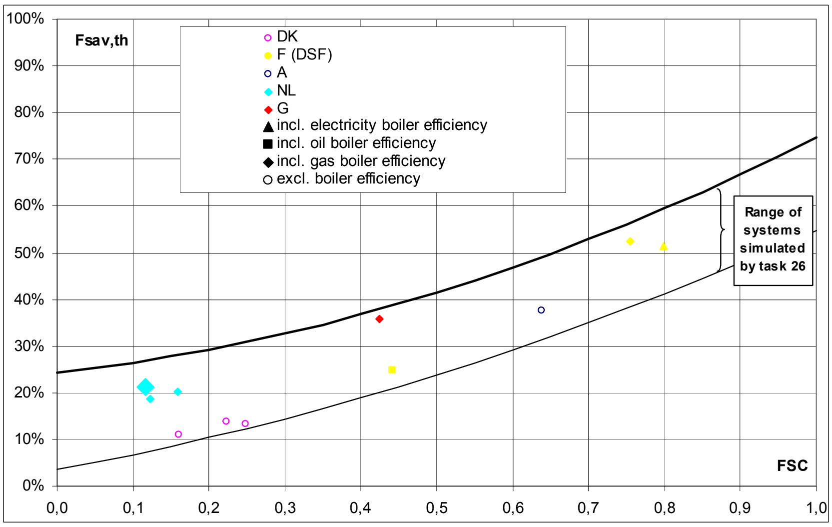


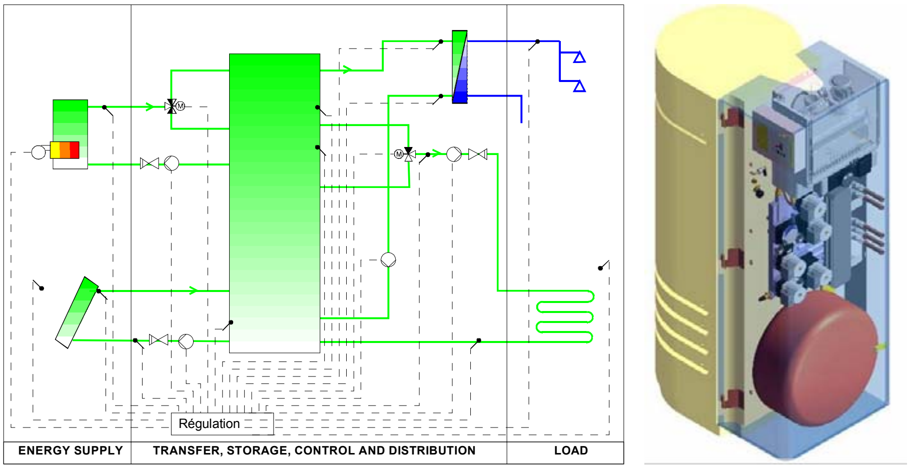
Fig 7. Monitoring results (Altener combisystems project)

(source : ASDER, France)

4.4 Last developments

In order to improve compactness, decrease the space requirements and make the work of installers easier, a new compact system has been designed (figure 8), with an optional integrated boiler (condensing gas or electrical). The floor area needed is very low (less than 1 m²).

400 litres of antifreeze are stored in the tank, and DHW is produced by an external flat plate heat exchanger. All pumps and three-way valves are gathered on a plastic component in which different pipes are moulded. Heat stratification in the storage tank is improved by three-way valves included in the auxiliary boiler loop and in the space heating loop. All pumps are speed controlled, so that the flow can be adjusted to what is needed, and electrical consumption is lowered as far as possible.



(source : CLIPSOL, France)

(source : CLIPSOL, France)

Fig 8. Direct Solar Floor with Integrated Auxiliary energy (flat plate heat exchanger for DHW preparation)

4.5 **Conclusion**

DSF is a combisystem well adapted for new buildings or heavy retrofits, where the particular thicker heating floor can be easily installed. Successive hydraulic concepts have been developed, allowing to reach a high degree of components integration, good thermal performances and reduced parasitic electricity consumption.

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5. Combistores

by Wolfgang Streicher, Chris Bales

5.1 General

One of the key elements of a solar heating system is the hot water store. The store has to fulfil several tasks:

- Deliver sufficient energy to the heat sink (with appropriate mass flow and temperature).
- Decoupling of mass flows of heat sources and heat sinks.
- Store heat from unsteady heat sources (solar) from times where excess heat is available to times when too little or no heat is available (either short term storage from day to night or over one to a few days, or seasonal storage).
- Extend the running times for auxiliary heating devices in order to increase their efficiency and lower its startup/shutdown emissions.
- Allow a reduction in heating capacity of auxiliary heating devices.
- Store the heat at the appropriate temperature levels without mixing (stratification) in order to avoid exergy losses.

In general, the most cost-effective and common type of store is a short term store, with capacity for one to a few days of the thermal load [1]. However, long term stores, where heat from the summer is stored for use in the winter, have also been developed and used, both for small and large scale applications [2].

At present, the largest market for solar thermal applications is the domestic market [3]. These domestic systems can be split into three types:

- solar domestic hot water (SDHW) systems that use solar heat only for the hot water load;
- solar combisystems, also known as solar domestic hot water and heating (SDHW&H) systems, that use solar heat for both hot water and space heating loads; and
- swimming pool systems where solar heat is used for heating a swimming pool.

Of the three systems, solar combisystems are the most complex due to the fact that there are two different loads to supply using two separate heat sources, solar collectors and an auxiliary heat supplier. In these systems the thermal store is normally the central part of the system, and heat is usually stored from both the solar collectors and the auxiliary heater. The two loads are often supplied from the store. In order to accomplish this, the store generally requires heat exchangers for the solar collector loop and for preparation of hot water, although immersed tanks or separate tanks can also be used for the latter. Due to the many options available, many different solutions have been developed and even marketed [4].

Several studies [5-9] have showed that the design of the stores in solar combisystems greatly affects the overall system performance, making it necessary to have a good design. This is also true for stores in solar hot water systems. Thus specific testing methods have been developed to judge properties of water stores in solar heating systems, in addition to methods for testing the whole system such as the DST method for solar hot water systems [10] and the DC [11] and CCT [12] methods for solar combisystems. The most commonly used method for testing solar hot water stores is the European prestandard ENV 12977-3 [13], where the store is subjected to a number of simple and specific test sequences, and then parameters are identified for a simulation model. The method is part of a system test method, ENV 12977-2 [14], where components are tested separately to give verified simulation models, and the whole system is then simulated to calculate annual system performance. This method can be applied to both solar hot water and solar combisystems.

In the following sections some guidelines are given for achieving good function in hot water stores is solar heating systems.

5.2 Heat Storage material

Table 1 shows the properties of different heat storage media for sensible heat storage. Significant is the volumetric heat capacity for the size of the store. But all other properties have to be taken also into account.

Table 1 : Heat storages, characteristics of storage media

	Water (1 bar)	Concrete	Rock compact	Earth	
Property				With gravel	Clay
Spec. heat cap. c_{pSt} (50°C) [J/kgK]	4171	1130	800	1840	880
Density ρ_{St} (50°C) [kg/m^3]	988	2400	2600	2000	1500
Volumetric heat capacity $c_{pStv} = c_{pSt} \cdot \rho_{St}$ [10^6 J/m^{3}K]	4.12	2.71	2.08	3.68	1.32
volum. heat capacity [kWh/m^{3}K]	1.16	0.75	0.58	1.02	0.36
Heat conductivity λ_{St} (50°C) [W/mK]	0.64	2,3	2.5	0.52	1.28
Possible temperature range	0 - 100	0-130	unlimited	unlimited	unlimit.
Poisones	no	no	no	no	no
Long term temperature stable	yes	yes	yes	yes	yes
Inflammable	no	no	no	no	no
Corrosion problems	low	low	low	low	low
Price	cheap	cheap	cheap	cheap	cheap
Environmental benign	yes	yes	yes	yes	yes

5.3 Geometries and Volumes of a combisystem water store

Fig.1 shows the principle of a water store with two energy inputs (solar and auxiliary) with water as storage medium. In the following some lay-out aspects of the tube-connections to the different heat sources and heat sinks are described in order to show the complexity of such a system.

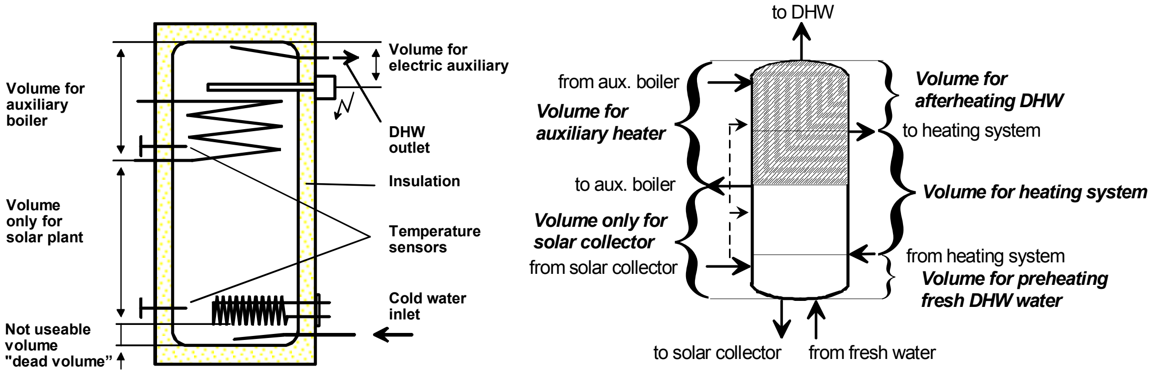

Fig.1 Zones for a hot water store of a DHW-system (left) and a solar combisystem (right)

5.4 Stratification – the key to good system performance

The hotter the water, the lower the density of the water becomes. Hot water thus naturally and stably finds its way above layers of cold water. This phenomenon makes it possible to have **stratification**, with **zones** of different temperatures in one physical store. The zones indicated in Fig.1 can therefore be at different temperatures, and more specifically at the temperatures required of the loads for domestic hot water and space heating. To keep stratification means, that no temperature losses due to mixing of different temperatures in the store occur. Stratification allows an optimal use of the store with limited heat losses and in addition can be used to ensure that the collector inlet temperature is as low as possible. However, it is not obvious or easy to maintain good stratification in the store. In fact, the terms stratified and stratifying are used for slightly different phenomenon and approaches. The following diagrams and descriptions show important differences in how the store can be charged. The same distinctions can be applied to discharging the store. To maintain stratification, all charging and discharging must be done in a way to improve or maintain the stratification. If only one heat source or sink causes significant mixing, it can destroy the benefit of the stratification created by other sources/sinks.

Two criteria need to be met if stratification is to be relevant:

- the daily volume "turnover" in the store should not be significantly more than the volume of the store itself,
- the heat source(s) should be able to generate a significant temperature difference, in essence be capable of generating stratification in the store.

However, stratification is less important for certain systems and for certain store designs. For example if the whole store is used for a small (<20°C) temperature interval, then stratification leads to no significant benefits.

5.5 Heat Input and Output

Fig.2 shows schematically what happens within the store when charging with an internal heat exchanger and with direct connections. The water heated by the internal heat exchanger starts to rise and mixes with the surrounding water. In this way the heat is transferred to a large volume of water, which is heated slowly. The net result is usually a zone of uniform temperature above the heat exchanger. This zone extends as far as another zone with higher temperature, if one exists. Once the temperature of this higher zone is reached, both zones will be heated uniformly at the same temperature. Below the heat exchanger, the store is unaffected. The temperature sensor for the internal heat exchanger has to be placed in the region of the heat exchanger. Below it would not measure the temperature increase during charging and above it would give the signal for the heat source to start charging too late.

There is a small temperature gradient in the store at the same height as the heat exchanger. An electric element in the store acts in a similar way, but due to the relatively high power and small heat transfer area, the heated water does not mix fully with the surrounding store water resulting in a small temperature gradient above the heater.

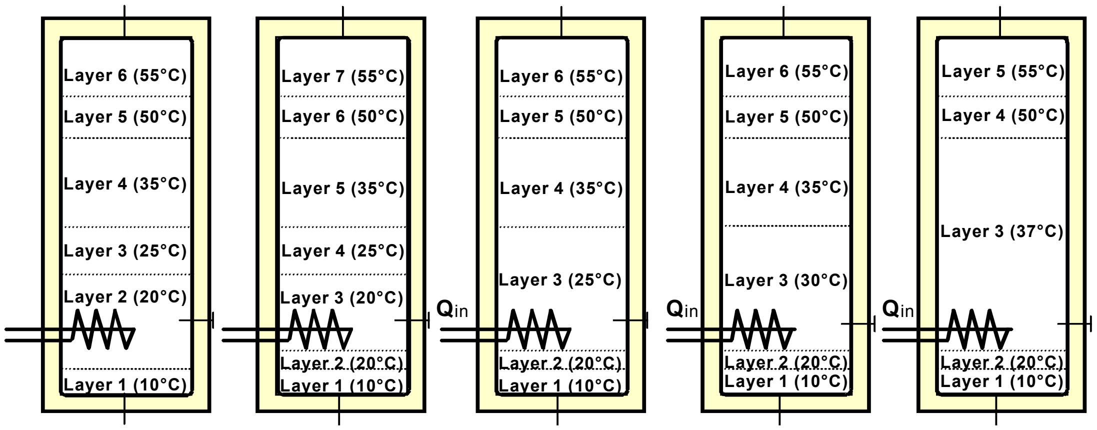

Fig.2: Charging using an internal heat exchanger.

With a direct connection there is some mixing in the store at the inlet. The degree of mixing is dependent on the inlet velocity and the difference in temperature of the incoming water and that of the store at the inlet. The zone above the inlet will be unaffected by the incoming water if the latter is colder (Fig. 3 right). Beneath the inlet the store water is pushed down and out through the outlet. However, if the incoming water is hotter than the upper zone, then heat will be transferred into that zone, causing mixing there, as well as into the volume below the inlet (Fig. 3 left). A large volume is thus affected, and the temperature below the inlet will be significantly lower than that entering the store. The temperature of the inlet water from both the collector and the space heating circuits vary in time, and there will be times when the incoming water is hotter than the water in the store at the inlet, and other times it will be colder.

Charging with direct connections thus tends to enhance stratification, with the volume of the zone increasing during charging. In contrast, charging with an internal heat exchanger tends to destroy stratification. In the store of a solar combisystem, there are several heat sources as well as sinks, and so the flows and stratification are complex.

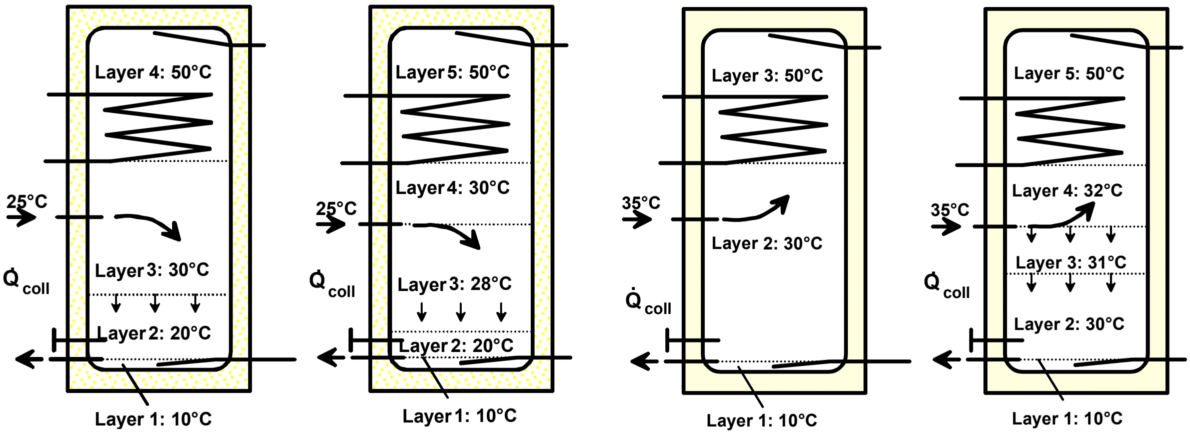

Fig. 3: Charging using direct connections i.e. from a heat exchanger (left: inlet temperature higher than store, right: inlet temperature lower than store). The zone at the top of the tank with direct connections will be affected if the inlet temperature is higher than the temperature at the top of the tank (Streicher, 2003).

Both the internal heat exchanger and the direct inlet are not perfect for creating stratification, so different methods have been applied to improve stratification. The first, and simplest, is to increase the number of internal heat exchangers, as illustrated in the store on the left of Fig.4. This arrangement creates more zones between the heat exchangers and thus a greater degree of stratification. However, the whole of each zone gets heated/cooled by the heat exchangers, and the temperature in the zones does not change rapidly. In order to create a variable volume zone that can be heated/cooled quickly, several manufacturers have added a **stratifying tube** to the internal heat exchanger, as illustrated in the left middle store of Fig.4. It uses an internal heat exchanger located in the stratifying tube. This tube then acts in a similar way to a direct inlet. However, the flow in the tube and thus the temperature at the outlet of the tube is dependent on the temperatures in the store as well as of the heat source, as the flow is the result of natural convection. This flow can vary considerably depending on the conditions within the store. Thus with this method, the water entering the store from the tube can be either hotter or colder than the surrounding water.

Another method is to use a **stratifying unit** with several outlets, as illustrated in the right hand stores of Fig.4. This arrangement allows water to exit the unit at the height with approximately the same temperature in the store, thus maximising stratification. This can be of benefit when the temperature inlet to the store varies with time, as it does with the solar input and the return from the heating circuit. Stratifier units are better than the other two, but require careful attention. The flow in the tube should be within a limited range; otherwise the water comes out at an incorrect height because the momentum in flow direction is higher than the force from density difference to make the flow bend towards an outlet. In addition it is important to minimise drawing in of water through outlets into the passing flow in the tube, otherwise there is mixing on the way up, resulting in lower outlet temperatures. This is being performed by one way flaps for the middle-right store and with a relatively large diameter of the stratifying tube for the store on the very right, which reduces the difference of the dynamic pressure in the tube compared to the static pressure outside and therefore the forces for the drawing in of water. Of course, also the stratifying tube on the middle-left can be constructed with several outlets like the one in the middle-right.

The store on the very right uses the same tube for the inlet of the secondary side of the collector (from the top inner tube to the stratifying tube) and the inlet of the return pipe from the space heating system from the bottom.

Such stratifying units have been successfully used with both internal and external heat exchangers in the solar circuit and for the return from the space-heating loop.

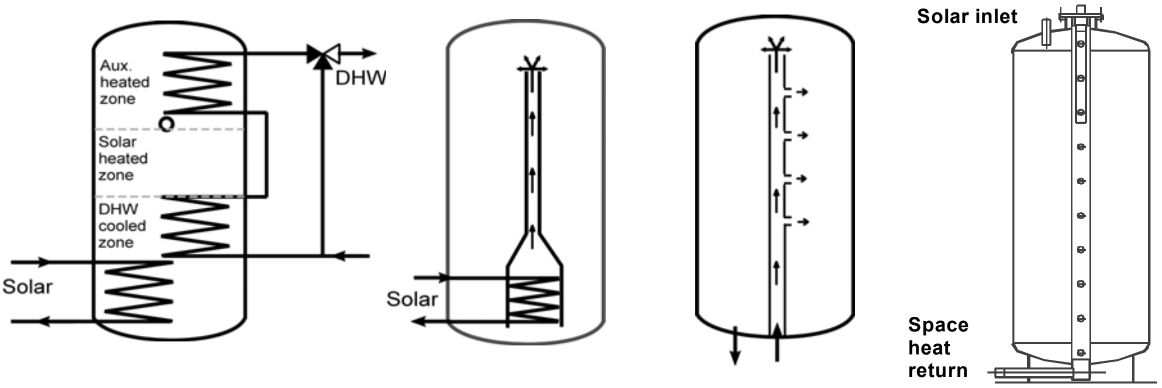

Fig.4: ***Four different methods of causing: several internal heat exchangers (left), stratifying tube with single outlet (middle-left) and stratifying units with multiple outlets (middle-right and right). The stratifying unit can be used with an internal heat exchanger or for other inlets that vary in temperature.***

Stratifying tubes and units with internal heat exchangers work with natural convection as mentioned above. It is important that the pressure drop through the tube/unit, the heat exchanger effectiveness and the expected heat transfer rate are matched so that the flow in the tube is similar to that in the collector circuit, thus ensuring low temperatures to the collector and high outlet temperatures. Both stratifying tubes and units can be used advantageously in low-flow systems.

Fig.5 shows how a good stratification unit works when the temperature in the tube is between that at the top and at the bottom of the store, in fact between that at the second and third outlets.

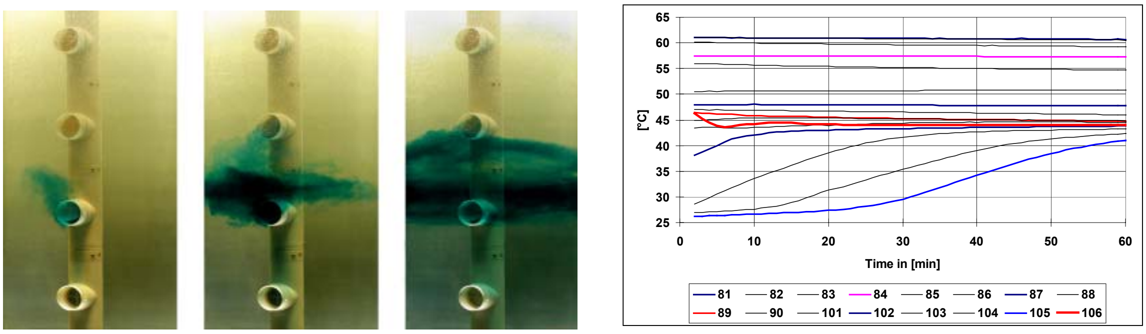

Fig.5: ***Stratifying unit for hot water stores showing outlet into the middle of the store visualization with ink (Source: Solvis, Germany), measurement of tank temperatures in different heights (Essert, 1995).***

Connection of Collector to storage

The collector circuit usually has an antifreeze/water mixture as the heat transfer fluid. A heat exchanger is therefore required for heat transfer to the store. Exceptions are systems that use the drainback principle. For small collector areas (< 15 m²) an internal heat exchanger located at the bottom of the store and a high flow strategy in the collector (maximum temperature rise in the collector about 10°C) is recommended. If collector areas are bigger, external heat exchangers are preferred, because they can exchange higher thermal capacities with small temperature loss. The input to the collector should always be as cold as possible, in order to keep its efficiency high. Therefore the internal heat exchanger is mounted at the bottom of the store. If more than one internal heat exchangers are used to deliver solar heat to the store, one of them has to be placed at this position.

For external heat exchangers the connecting tube to the collector is mounted at the bottom of the store, where the coldest water is. The height of the input from the collector into the store varies with different applications.

For so-called **high-flow** systems with flow in the collector circuit of approximately 50 l/h.m2 collector area, the temperature rise in the collector is of the order of 10°C. The input into the store for these high-flow systems should be near the bottom of the store, and the store is heated slowly from the bottom to the top. An exception to this rule is for stores with more than one heat exchanger in the collector loop.

For so-called **low-flow** systems with a specific collector flow of 10-15 l/h.m^{2}collector area, the temperature rise in the collector is of the order of 40-50°C for an irradiance of 1000 W/m^2. The input to the store for low-flow systems should be higher up than for the high-flow systems, the best height depending on the flow and system design. It can be advantageous to use a stratifying unit to make sure that the heat from the collector goes to the right level in the store. Low flow should not in general be used with internal heat exchangers, as these cannot fully use the high temperature built up in the collector, and the resulting temperature in the store is much lower as the water in the store gets mixed rapidly. Moderate flows can be used, but in this case the internal heat exchanger should have a greater vertical extent than when using high flows.

Connection of Auxiliary heater to storage

The inlet tube from the auxiliary heater should be on the top of the tank. Several aspects determine the outlet position to the auxiliary heater:

- There shall be always enough hot water in the store to fulfil the heat sink demands. The volume for the auxiliary heater can be calculated from the power of the auxiliary heater and the maximum heat sink demand over a specific time period.
- The auxiliary heater often needs a minimum running time (especially solid wood burners). The volume between auxiliary heater in- and outlet must allow this minimum running time.
- The outlet to the auxiliary heater should be as high as possible (taking into account the above aspects) in order to leave as big volume as possible to the solar collector.
- If the auxiliary heater has enough power and can be power controlled it can be also positioned after the store in the forward pipe to the heat sink. This construction provides maximum storage capacity for the solar collector.

Connection of DHW heater to storage

The DHW-outlet needs most often the highest temperature of the combisystem (50-60°C). Therefore it is located at the top of the tank. The fresh water (or the water from a heat exchanger for DHW-production) is always the coldest part and therefore located at the bottom. The volume heated by the auxiliary must be big enough to guarantee that all demand of DHW can be met (i.e. 140 l at 45°C for a hot bath).

Connection of Heating system to storage

The space heating system temperatures range between the mains water temperature and that necessary for DHW. Consequently, the zone for the heating system is positioned in the middle of the tank. During the heating season space heating is the dominant heat sink. Therefore the volume for this is kept relatively large.

5.6 Heat losses from the tank

Well insulated stores of less than 1 m^3 in solar combisystems have losses of 500 to 1000 kWh/year. If the store is poorly insulated, this can be significantly more, greatly reducing the system performance. The real heat losses from a store are generally much greater than the theoretical one, mainly due to convection of the air inside the insulation, air leakages and thermal bridges. Pipe connections at the sides and especially the top cause significant extra heat losses (Vajen, 1996).

Another cause, and unnecessary losses, is unplanned natural convection (thermosyphon) in external circuits. This can easily be avoided by non-return valves. However, it is also possible to have natural convection within a single pipe [15] (see fig 7), without flow through the whole circuit.

Some general rules to achieve low heat losses are:

- Use close-fitting insulation to avoid natural convection under the insulation.

- Reduce the number of thermal bridges and connections to the side and top of the store. This can be achieved by having all connections at the bottom.
- Avoid natural convection in external circuits and connections to the store.

5.7 General hydraulic rules

Two general rules to avoid mixing or increased heat loss by pipes connected to the store are shown in Fig. 6 and **Fig.7**.

- Vertical flow-inlet pipes to the tank should be equipped with a plate acting as a horizontal diffuser. Otherwise the momentum of the incoming fluid destroys stratification over a significant height of the store. On the right side a CFD simulation of Jivan Shaw (2004) of an inlet pipe with and without a plate is shown. Another solution for this problem is shown in Fig.7 on the right. The inlet tube is directed horizontally into the store. So no or only little vertical momentum occurs.

- Horizontal pipes and vertical pipes to the top of the tank should be equipped with a thermosyphon break in order to prevent natural convection within the tube as shown in **Fig.7**. Such natural convection heats up tubes without volume flow and therefore results in unnecessary heat losses.

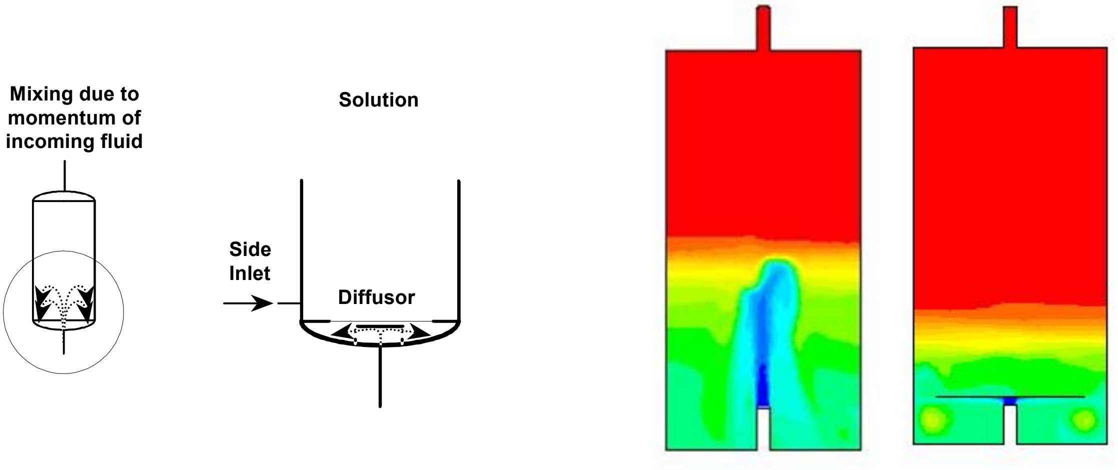

Fig. 6: Flow inlet geometries to avoid mixing and pipes connected to the side of the store (Streicher, 2003, Jivan Shaw, 2004)

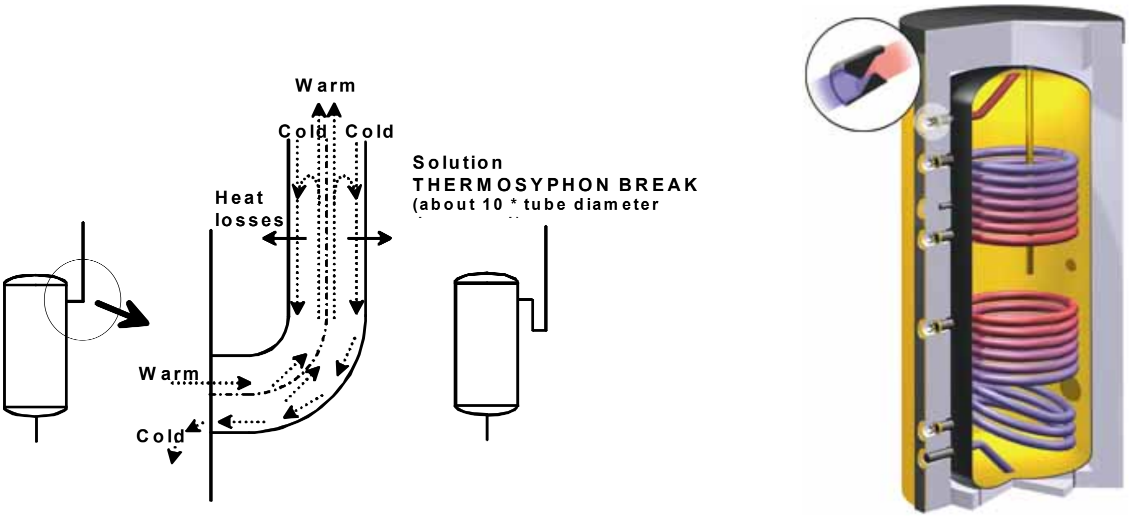

Fig.7: Thermosyphon break to avoid storage heat loss in connecting tubes (Streicher, 2003, Wagner, 2001)

5.8 Built examples

Fig.7 right and
Fig.8 show examples for modern water stores. The not useable volume is kept very small, either by bending the solar heat exchanger very close to the bottom of the tank or by using a stratification unit that takes the water from the bottom of the tank to the solar heat exchanger. Flow inlets have either a diffuser or kept horizontally. Solar heating volume and auxiliary heating volume are clearly defined.

Whereas the store in Fig.7 is designed only for one heat sink (domestic hot water), the stores in figure 8 are stores for solar combisystems.

Fig. 8 left shows a combistore including an auxiliary gas condensing boiler developed by Solvis, Germany. Condensation of the flue gas is assured, because the condensation heat exchanger is located below the combustion chamber, where the surrounding water is colder than around the combustion chamber. Additionally long running times of the gas burner are assured, because of the volume that has to be heated in the tank. The heat from the solar collector is delivered to the tank by an internal heat exchanger that induces a natural convection in a stratifying tube and the store. Domestic hot water is produced via an external heat exchanger with variable mass flow on the store side. No thermosyphon problem occurs, because all connecting tubes are attached to the bottom of the store. This compact systems needs only to be attached to the gas grid, the chimney, the solar collector loop, the fresh water and domestic hot water line and the space heating loop. All necessary pumps and controls are in the system. With such compact designs the possibility of failures during installation are fairly small.

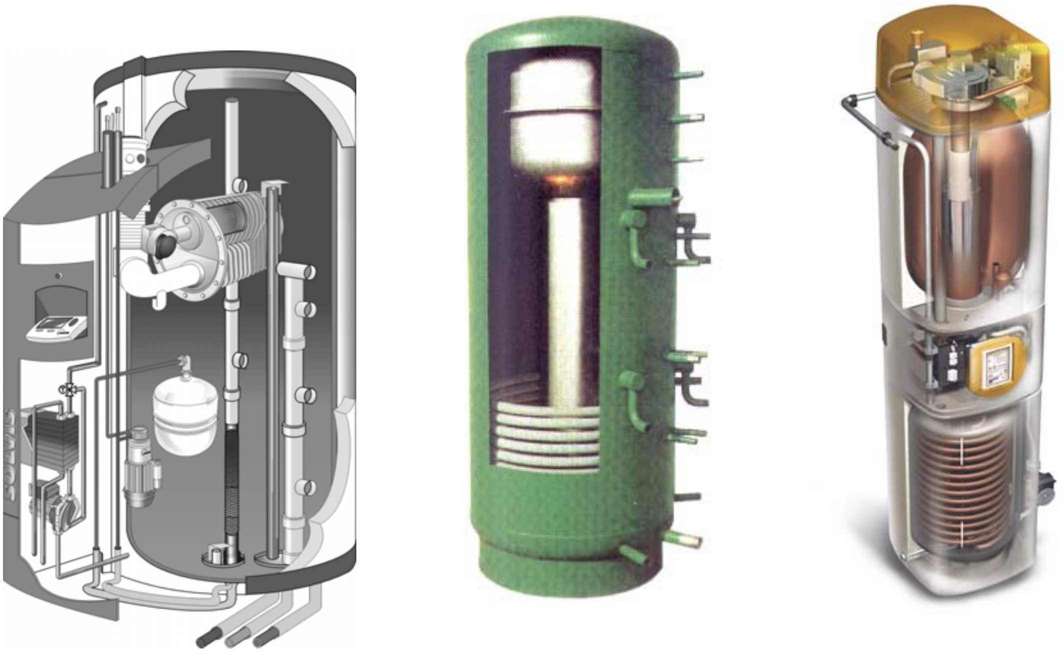

Fig.8: Examples of advanced water stores (Solvis, 2004, left, Jenni, middle, Daalderop, 2004 right)

In figure 8 middle a combistore with included DHW store is shown. It was developed in the early 1990th by Jenni in Switzerland. The DHW store has a reservoir in the upper part to deliver enough water for a hot bath tub and a preheating zone down the whole store to the bottom. Solar heat is delivered via an internal heat exchanger at the bottom of the store. All inlet/outlet connections are already equipped with a thermosyphon break.

Figure 8 right shows a solar combistore system from the Netherlands (Daalderop). The lower store has domestic water in the heat exchanger and the collector fluid around in an 100 l volume, that acts also as drain back vessel for the collector loop. In the upper store a gas burner is integrated. Space heat can be taken out by an internal heat exchanger in the upper store (which is not shown in this picture).

A more detailed description of different water stores of solar combisystems can be found in Streicher, 2003 and Weiss, 2003)

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6. Combisystem performance investigation

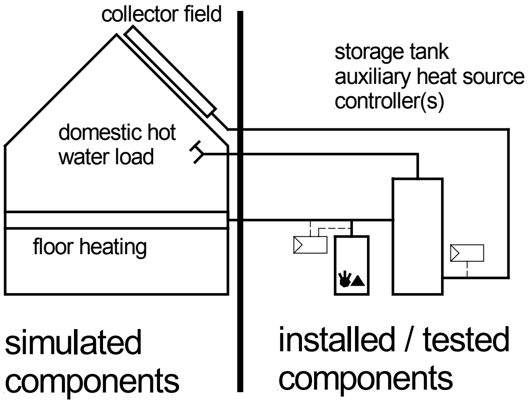
by Michel Haller, Peter Vogelsanger

At the Institute for Solar Technology SPF in Switzerland, a test facility has been established to determine the performance of small solar combisystems. With the so called Concise Cycle Test (CCT) 18 systems from different manufacturers have been tested until 2005. The results show that several of the tested products have a very good performance with solar savings of up to 30% even if the collector area is restricted to 15 m² and if the total annual heat load for domestic hot water preparation and space heating is a considerable 18.5 MWh. Details of the test procedure and the results of the test can be downloaded (in German only) from the SPF website [1].

6.1 Concise Cycle Test (CCT) method

The CCT procedure is performed in three steps:

1. The system, including the storage tank, the auxiliary heat source and the controller(s), is installed in the test facility and is hydraulically connected to the installation of the laboratory. The laboratory installation is simulating the collector array, the floor-heating system and the DHW-load for a twelve days period (TRNSYS-simulation) and measuring at the same time the response of the system in terms of energy consumption and delivery. The conditions of weather and load applied during the test cycle resemble the conditions used for annual performance simulations (step 3).
2. After the twelve-days measurement, parameter identification is performed with a TRNSYS simulation of the storage tank, auxiliary heater and controllers to match the measured system behaviour of the twelve-days test.
3. The identified parameters are used for the simulation of a whole year under conditions as encountered in the region of Zurich, Switzerland.



Pic.1: Schematic drawing of the tested and simulated components

Pic.2: system of a Swiss manufacturer in the test facility

6.2 Performance of the tested systems

The consumption of conventional energy (oil, gas, electricity) of the solar system was compared with the consumption of a typical state of the art reference system without solar collectors. The difference is the net energy savings and may be used as a performance indicator.

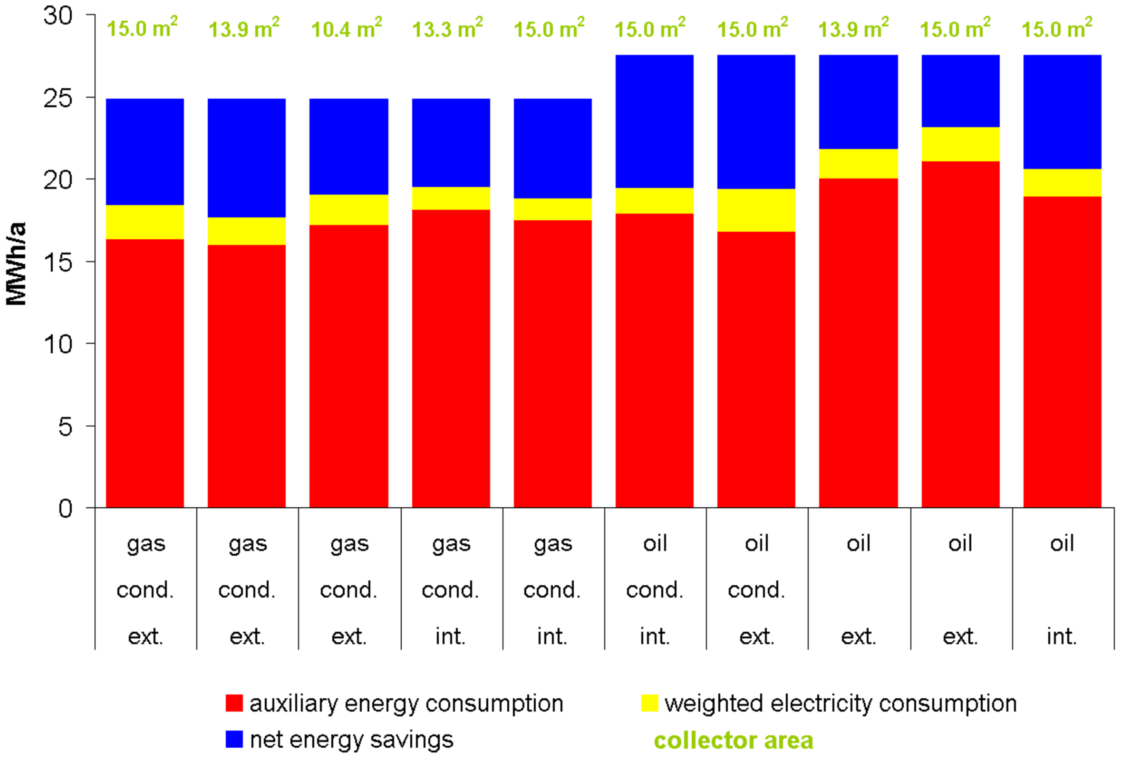


Fig. 1: Performance of successfully tested combisystems as determined by the CCT method. "gas" and "oil" refer to the type of auxiliary energy used. Systems which use condensing boiler technology are marked with "cond.". The abbreviation "int" stands for systems with the burner built directly into the storage tank, whereas systems with external boilers are marked with "ext". Calculations of energy consumption are based on the upper heating values for oil and natural gas. The difference in the total column heights are due to the fact that different reference systems are used for oil and gas systems [3]. The collector area was free to be chosen by the manufacturer of the system. An upper limit had been set to 15 m² by the test institute. Many manufacturers chose to use this maximum collector area for the test[1].

Considering the assumed reference conditions with a rather high consumption of oil or gas the energy savings of the systems tested successfully are remarkably high: 23-39%. Subtracting the additional electricity demand of the solar system, weighted by a factor of 3, still leaves net energy savings of 16-30%. Detailed values and additional information about these tests are available from the SPF internet site (German only) [5].

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[1] The maximum collector area of 15 m² lead in some cases to uneven numbers of collector modules. This was accepted in order not to disadvantage a manufacturer just because of his module size. This procedure was possible because the collector modules where tested in advance, and the performance indicators from these collector-tests were used in the system's test to simulate the collector array.

6.3 Interpretation of CCT test results

The resulting energy savings are strongly influenced by a number of factors that vary between different installations of a system. Similarity of conditions for the test sequence and the annual calculations is a fundamental assumption of the CCT method. The test sequence is not optimized for modelling and parameter identification. Consequently the model gained from the test sequence and subsequently used for annual simulations is not very precise: It reflects the system's performance under the assumed conditions but might not be suitable for the prediction of annual system performance under other conditions (e.g. climate, load). Values calculated by the CCT method are therefore only valid for the one set of reference conditions used [3].

Also the system performance varies with the system settings (such as pump speed selection) and controller settings. The system settings have to be determined prior to starting the test sequence. It is impossible to adjust the settings perfectly beforehand to equalize the comfort level (e.g. the amount of domestic hot water available, which strongly influences any system's energy performance) between every system.

The systems using different fuels as auxiliary energy source may not be compared on the basis of energy savings because different reference systems were defined.

6.4 Lessons learnt

Several systems submitted to the test did not perform as expected by the manufacturer. Either the systems did not operate as intended or their performance was insufficient. The results of the systems with poor performance are not included in figure 1. One severe problem can have a great adverse impact on the performance of an otherwise well designed and built solar system. A non-exhaustive list of such problems is presented here:

- Unreliable functioning of hydraulic elements (mixing valves e.g.) or hydraulic elements that have been connected to the controller in a wrong way. This can lead to total malfunctioning.
- Faulty positioning of temperature sensors. Some storage tanks allow the sensors to be positioned freely on the outer surface of the tank, leaving it up to the mechanic fitter to make the system work or not. A badly positioned temperature sensor can lead to overheating of the tank by the auxiliary (see figure 3) or other unwanted behaviour of the system.
- Connecting tubes to the tank without siphoning or insufficient insulation on tubes and other parts of the tank (figure 4). This can lead to considerable heat loss.
- Energy loss through the chimney. There will always be an air mass flow in the chimney during operation of the burner, but mass flow has to be avoided during stand by. Systems that fail to prevent mass flow through the chimney during stand by are subject to substantial extra heat losses particularly if the burner is integrated into the tank.

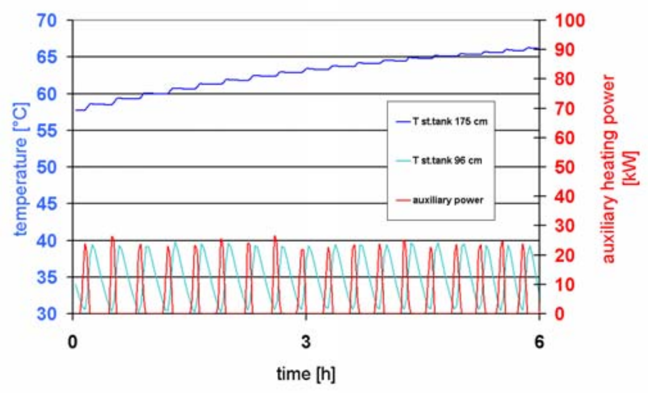

Fig. 3: Effect of a badly positioned temperature sensor. T st.tank 175 cm = temperature of the storage tank at 175 cm above ground. The integrated auxiliary burner shuts off too late when providing heat for space heating. Thus, with each on/off-cycle the temperature in the uppermost part of the storage tank increases. Higher temperatures lead to higher heat loss of the tank.

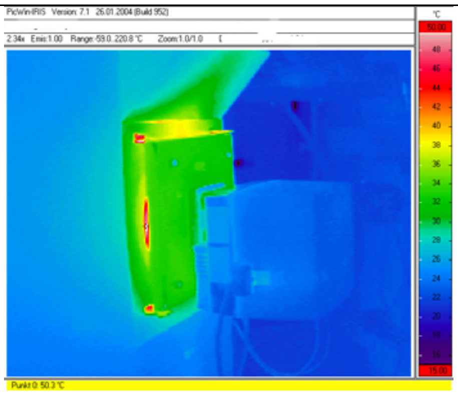

Fig. 4: Energy loss of an integrated burner. Temperature of the tank is 60 °C, heated up by solar (burner was not running). The temperature of the burner cover plate is 34 (green) to 46 °C (red).

6.5 Conclusions

Conclusions drawn from the testing of state of the art solar systems are:

- The energy performance of the best tested systems is very high. Also the comfort of domestic hot water (availability) is high.
- Different technological solutions for energy input and withdrawal have lead to similarly good performance, provided that the solutions are dimensioned and designed properly. Figure 8 illustrates different technological solutions applied in conjunction with well performing solar combisystems. In comparison to pure domestic hot water systems the variety is far greater.
- The possibility of errors in system design and assembly are innumerable. The system's performance is not a function of the best part of the system, but it is determined by the most poorly performing part of the system. An excellent collector for example will not lead to high energy savings if the controller and the storage tank are not designed and assembled with equal care and experience. It is therefore important to test systems as a whole, including storage tank, controller(s) and the auxiliary heater, since problems often occur in the interaction of these different parts.

General results of the performance tests are presented in a summary [1]. Results of a number of combisystem tests are available from the website of the Institute for Solar Technology SPF in Switzerland [5].

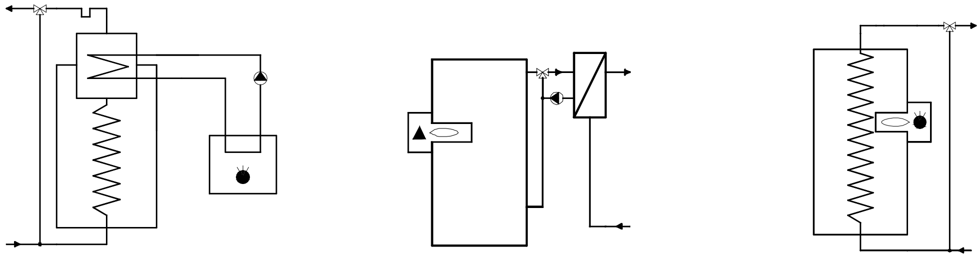

Fig. 6: three successful concepts of domestic hot water preparation with a solar storage tank

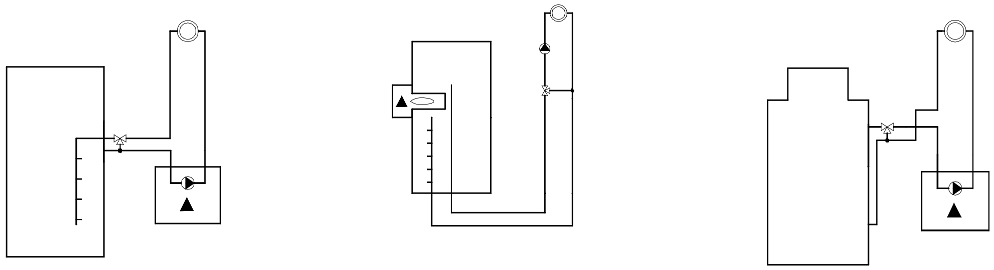

Fig. 7: three successful concepts of space heating with a solar storage tank

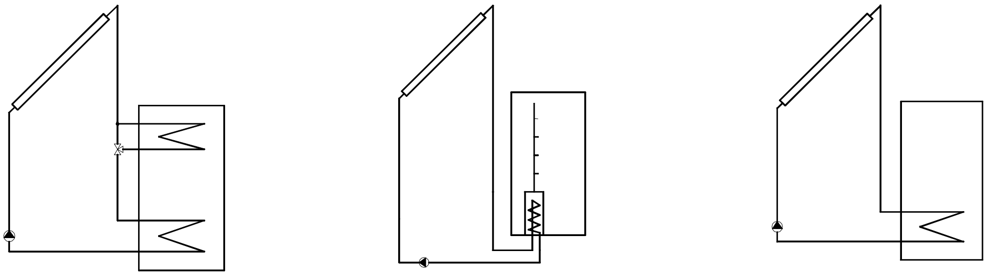

Fig. 8: three successful concepts for the connection of the solar collectors to the storage tank

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7. Insulation materials for advanced water storages

by Jørgen M. Schultz

7.1 Introduction

This chapter gives an overview of different insulation materials that may be of interest for insulation of solar storage tanks. In order to understand the special characteristics of the different insulation materials the heat transfer mechanisms involved are shortly described. In the following sections different insulation materials are described with respect to material characteristics and some comments on the easiness of application for tank insulation.

The material properties listed in this paper are typical values, which gives an idea of the possibilities but in case of a specific design a more detailed survey of the market is required.

7.2 Heat transfer in insulation products

In general insulation products are made up of a skeleton of solid material with a lot of cavities in between the solid parts (Fig. 1). The heat transfer takes place as thermal conduction in the solid material in parallel with thermal radiation and conduction in the cavities.

7.2.1 Conduction in the solid

The conduction through the solid part of the material depends mainly on the thermal conductivity of the solid material, the effective contact areas in the skeleton and the overall solid distance between the two surfaces of the material.

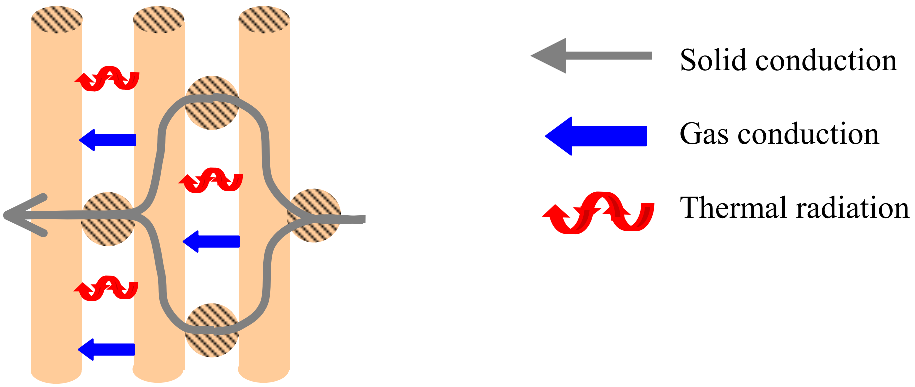


Fig 1. Illustration of heat transport in a fibrous insulation material e.g. mineral wool. Heat flow perpendicular to the fibres.

7.2.2 Thermal radiation in the cavities

The thermal radiation in the cavities depends on the emissivity and absorptance of the solid surfaces surrounding the cavity. Most materials have an absorptance close to 100% for thermal radiation leaving the emissivity as the governing parameter. The emissivity of typical building materials is in the range of 80 – 90%. This means "only" 80 – 90% of the absorbed thermal radiation is reemitted. This phenomenon is important, as the heat transfer by thermal radiation will be reduced each time the radiation has to be absorbed and reemitted. In porous materials the thermal radiation will be absorbed and reemitted many times reducing the heat transfer by thermal radiation through the material.

The radiative heat transfer can also be reduced using materials with a low-emissive surface or by coating the material with a low-emissive coating. The most well known low-emissive material is probably aluminium foil with an emissivity in the range of 4 – 20%. Fig. 2 illustrates the effect of low-emissive surfaces as well as several radiation blocking layers.

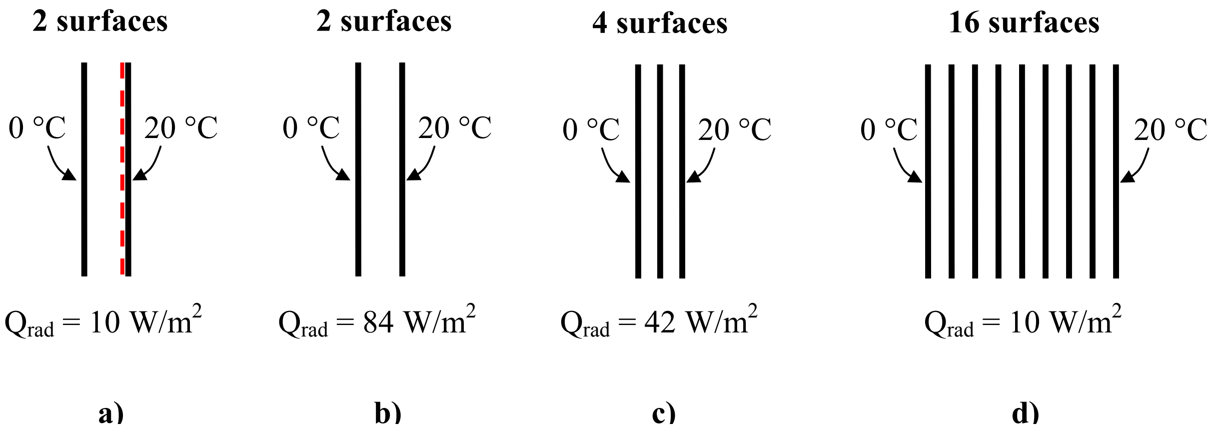


Fig 2. Calculated heat transfer by radiation.
a) One surface with an emissivity = 0.9 and one coated surface with an emissivity = 0.1.
b) Two surfaces all with an emissivity = 0.9.
c) Four surfaces, all with an emissivity = 0.9.
d) Sixteen surfaces, all with an emissivity = 0.9.

The example in figure 2 shows that subdividing one cavity into 8 cavities by means of radiation blocking layers with an emissivity of 0.9 equals the effect of having one surface in the cavity coated with an emissivity of 0.1.

7.2.3 Conduction in the cavities

The conduction in a gas-filled enclosure takes place due to internal collisions between the gas molecules. In a large volume at atmospheric pressure the distance one molecule can move before colliding with another is very limited. By the collision heat is exchanged between the molecules and through successive collisions the heat are transferred from the warm to the cold side of the enclosure. The average distance one molecule can travel before colliding with another molecule is called the *free mean path* and is calculated as:

$$\lambda = \frac{1}{\pi \times D^2 \times n} \quad [\mathrm{m}] \tag{1}$$

where λ is the free mean path [m]
D is the molecule diameter [m]
n is the number of molecules per m^3 [m^{-3}]

If average values for gaseous molecules at atmospheric pressure are used the free mean path can be calculated to approximately 10^{-7} meter. If the dimensions of the cavity holding the gas is significant larger than 10^{-7} meter the probability for a molecule to hit another molecule is much larger than hitting the walls of the cavity and an undisturbed heat transfer takes place.

The speed of the molecules governs the thermal conductivity and depends of the molecular weight, which explains the difference in thermal conductivity of different gases (table 1).

Table 1 Overview of molecular weight and thermal conductivity for different gasses.

Gas	Molecular weight	Thermal conductivity (20 °C, 1 atm)
	g/mole	W/mK
Oxygen (O_2)	32	0.026
Nitrogen (N_2)	28	0.026
Argon (Ar)	40	0.017
Dry atmospheric air	29	0.026
Krypton (Kr)	84	0.010
Xenon (Xe)	131	0.006
Cyclopentane* (C_5H_{10})	70	0.012

*Cyclopentane is a widely used blowing gas for polyurethane foam.

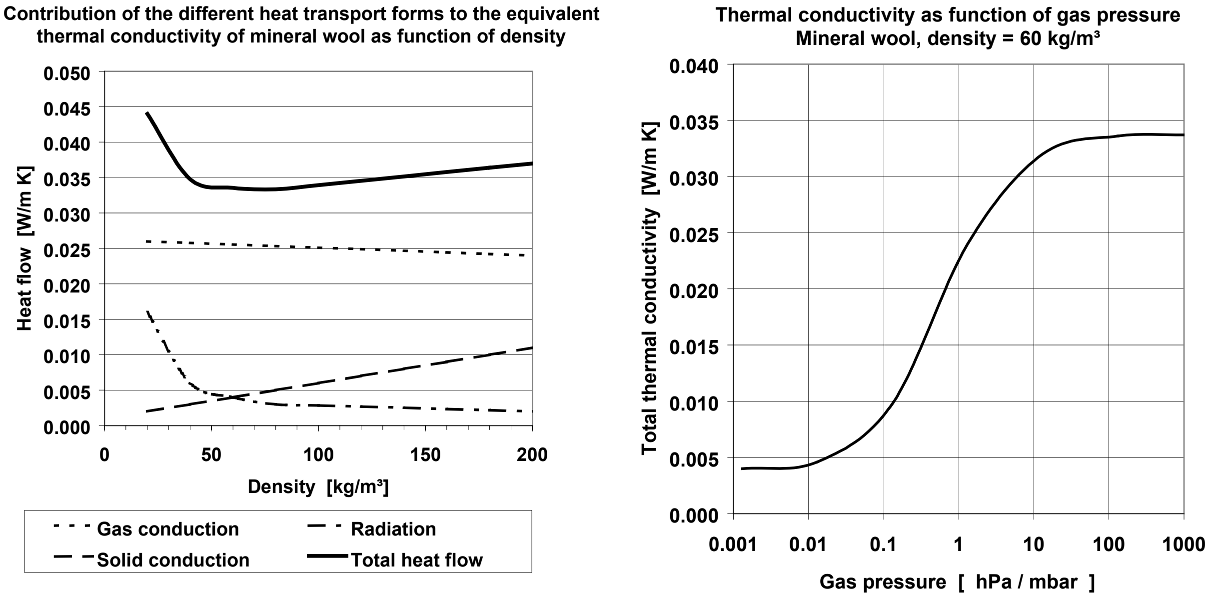
If the cavities in the insulation material is smaller than the free mean path a reduced thermal conductivity in the cavities are observed. In this case the probability for a molecule hitting another molecule is lower than that of hitting the walls of the void and the heat transfer is reduced.

Finally the thermal conduction in the cavities can be lowered or eliminated by removal of the molecules by establishing a vacuum in the pores. Reducing the number of molecules per volume increases the free mean path - see equation (1). If the free mean path becomes larger than the cavity dimension the thermal conductivity is decreased. This means that no effect of evacuation on the thermal conductivity will be seen before the gas pressure has been decreased to a level where the equivalent free mean path has a value comparable with the cavity dimension. Table 2 shows the free mean path for atmospheric air as function of the pressure in the cavity. Further decrease of the number of molecules in the cavity reduces the thermal conduction, as fewer molecules are present to transport the heat. At absolute vacuum the conduction in the gas is eliminated.

Table 2 Free mean path as function of gas pressure (atmospheric air) in the cavities

Pressure in the cavity		Free mean path
Atm	hPa (mbar)	mm
1	1000	0.0001
0.5	500	0.0002
0.1	100	0.0010
0.01	10	0.0100
0.001	1	0.1000
0.0001	0.1	1.0000
0.00001	0.01	10.0000

Fig. 3 below illustrates the different heat transport phenomena described above.



(a) (b)

Fig. 3. Example on contribution of heat transport forms to the total thermal conductivity of mineral wool as function of density (a) and the total thermal conductivity as function of gas pressure (b).

Fig. 3 (a) shows that the gas conduction at atmospheric pressure is almost independent of the density though with a slightly lower value for the high-density products due to smaller cavity dimensions. The solid conduction is proportional to the density as expected. The heat transfer by radiation for low-density products is significant due to the limited number of radiation blocking surfaces and perhaps even areas without any blocking surface. For densities higher than 50 kg/m³ the thermal radiation is almost fully blocked.

Fig. 3 (b) shows the three phases during evacuation.

1. In the range from 1000 – 10 hPa almost no effect of the evacuation is seen on the thermal conductivity, which indicates that the average cavity dimension is larger than 0.01 mm (table 2).
2. In the range from 10 – 0.01 hPa a significant decrease in thermal conductivity is seen, while the number of molecules in the cavities becomes lower.
3. Below 0.01 hPa the thermal conductivity becomes stable, i.e. the gas conduction has been eliminated. The remaining heat transport is due to radiation and conduction in the solid material.

7.3 Description of common insulation materials

The most common insulation products used in the building sector has pores or cavities filled with air. The pores or cavities can be open or closed towards the ambient. In the following the most common products are briefly described.

7.3.1 Mineral wool

Mineral wool is made from fibres of glass or stone. The fibres forms an open air-filled network kept together by means of an added bonding material. The production process can be controlled to get different density of the mineral wool for different use. High-density mineral wool products are used for situations where high compression strength is required, e.g. in slab on ground floor constructions and external insulation of foundations etc. Mineral wool is flexible, compressible and partly elastic, which makes it easy to fit to odd shapes, e.g. around pipes, heat stores etc.

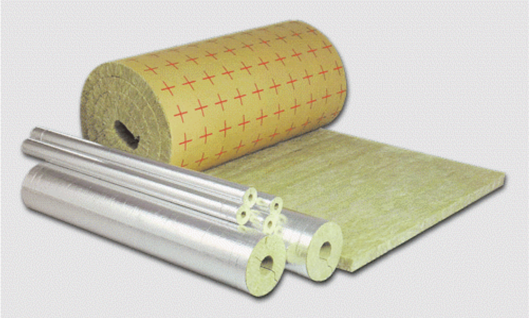


Fig. 4 Example of technical insulation products of mineral wool (Rockwool).

Thermal conductivity in praxis (T_{mean} = 10 °C):	0.036 – 0.050 W/mK (density dependant)	
Temperature dependency:	0.4 – 0.8 %/K	
Maximum temperature:	Glass wool:	250 - 400 °C
	Stone wool:	250 - 1000 °C
	(bonding material is destroyed at 250 °C)	

7.3.2 Polystyrene foam

Polystyrene is a plastic product extracted from fossil oil. Two different kind of polystyrene foam is common on the market: Expanded polystyrene (EPS) and extruded polystyrene (XPS).

Expanded polystyrene is initially formed as pellets of polystyrene foam, which further can be joined and formed into insulation boards or specific forms. The pellets can also be used directly for insulation of cavities. Special care should be given to avoid settling of the pellets, but it is possible to fill even very irregular cavities with insulation material and avoid thermal bridges due to areas without insulation. This is difficult to achieve with the boards.

Fig. 5 Expanded polystyrene (Sundolitt)

Extruded polystyrene is made from the styrene raw material by adding different chemicals and the cell structure is formed during extrusion by means of a special gas. In earlier XPS products the cells were formed by means of CFC-gasses but now these environmental harmful gasses have been substituted with non-CFC gasses. XPS-products are coloured in order to distinguish them from EPS products.

Fig. 6 Expanded polystyrene (Dow Corning)

XPS-foam has a more uniform cell structure than EPS-foam leading to higher compression strength and lower water vapour diffusion properties than EPS-products. However, both EPS- and XPS-foam can be manufactured with a wide range of compression strengths.

Thermal conductivity in praxis (T_{mean} = 10 °C):

Boards: 0.034 – 0.050 W/mK (density dependant)

Pellets: 0.050 W/mK

Temperature dependency:	0.4 – 0.5 %/K
Maximum temperature:	Approx. 80 °C

7.3.3 Polyurethane foam (PUR)

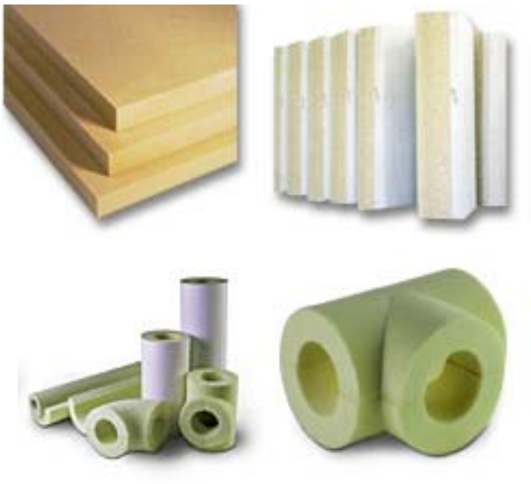


Fig. 7. Examples of PUR foam used in blocks sandwich elements and pipe insulation (Elliott®)

The combination of very good insulating properties, good gluing properties, good compressive strength and the possibility of in-situ foaming has probably made polyurethane foam the most widely used insulating foam outside the building sector. Polyurethane is foamed with a blow gas, which previously has been of the CFC kind – harmful to the environment – but now other gasses as cyclopentane is used. Polyurethane is highly porous material with closed cells holding the blowing gas. The low thermal conductivity of cyclopentane (table 1) reduces the gas conduction in the cells compared to air filled foams. The actual thermal conductivity of polyurethane depends on how well the blowing process is controlled, the density of the polyurethane foam and the age of the foam. Polyurethane foam is not completely tight against diffusion and the insulating gas will slowly diffuse out of the cells during time if the polyurethane foam is not equipped with a barrier material. However the barrier material only need excellent barrier properties against the blow gas and not for wide range of gasses.

Thermal conductivity in praxis (T_{mean} = 10 °C):	0.024 – 0.035 W/mK (density dependant)
Temperature dependency:	0.4 – 0.5 %/K (Temp. > 0 °C)
Maximum temperature:	140 °C

7.4 Description of highly porous insulation materials

7.4.1 Micro-porous insulation materials

Micro porous insulation materials make use of having pore sizes smaller than the free mean path of atmospheric air. The composition of the materials varies but in general a mixture of ceramic powder and fibres are compressed to form a rigid highly insulating block. The blocks are normally sealed with a glass fibre cloth to prevent ceramic dust to be released. The blocks can also be cast in specific forms, e.g. for pipe insulation etc. Finally, the micro porous insulation material can also be found in a flexible version in form of blankets to wrap around irregular shapes.

Fig. 8 Examples on micro porous insulation. (Microtherm)

Thermal conductivity (T_{mean} = 10 °C): 0.020 – 0.025 W/mK

Temperature dependency: 0.1%/K

Maximum temperature: 900 – 1500 °C

7.4.2 Nano-porous insulation materials

A further decrease in the average pore size leads to even lower thermal conductivities without introducing insulating gasses or the use of vacuum. Examples of such materials are the silica gels, which have pore sizes in the range of 5 – 300 nm. Fumed and precipitated silica gels are powders that primarily are used for vacuum insulation panels.

Silica aerogels that has the lowest thermal conductivity can be made in both a monolithic (tiles) and a granular form. The monolithic gels are very fragile and would only be applicable if protected against mechanical stresses. The most promising application for tank insulation will also in this case be in evacuated form. The granular form has the same advantages as the polystyrene pellets that it can fill out irregular cavities if special care is taken to avoid settling. However, the voids between the pellets increase the overall thermal conductivity.

Fig. 9. Examples of granular aerogel (Cabot – Nanogel)

Thermal conductivity (T_{mean} = 10 °C):

Fumed and precipitated silica gel	~ 0.020 W/mK
Monolithic silica aerogel	0.016 – 0.018 W/mK
Monolithic silica aerogel (IR-blocked)*	0.012 – 0.014 W/mK
Granular silica aerogel	0.020 – 0.025 W/mK

Temperature dependency:

Monolithic and fine powders:	0.1 %/K
Granular silica aerogel:	0.3 – 0.5 %/K

*IR-blocked: Carbon black added for efficient blocking of thermal radiation

Maximum temperature: Approximately 500 °C

7.5 Vacuum insulation

7.5.1 Vacuum definitions

Vacuum means in fact that no molecules at all are present, but more general vacuum refers to gas pressure lower than the atmospheric pressure. Depending on the level of depressurisation different regions of vacuum are defined, table 3 [1].

Evacuation in the rough vacuum region is almost straightforward due to the viscous flow, i.e. the pressure difference created by the vacuum pump makes the gas flow to the pump and rough vacuum can be obtained without large costs. In the high and ultra-high regions the evacuation becomes more difficult as the evacuation is based on trapping of single molecules eventually reaching the vacuum pump. The molecules travel freely and are not influenced by a pressure gradient guiding them towards the pump.

Table 3 Definition of vacuum regions [1].

Region	Pressure level	Flow
Rough vacuum	1000 – 1 hPa	*Viscous flow:* Interactions between the molecules dominates the flow which can be laminar or turbulent. The free mean path is smaller than the diameter of the conducting tube
Medium vacuum	1 – 10^{-3} hPa	*Knudsen flow:* Transition from viscous to molecular flow. The free mean path is of same size as the diameter of the conducting tube
High vacuum	10^{-3} – 10^{-7} hPa	*Molecular flow:* The molecules move freely independent of each other. The free mean path is larger than the diameter of the conducting tube
Ultra-high vacuum	< 10^{-7} hPa	

7.5.2 The "Dewar flask" principle

The ideal vacuum insulation would be an enclosure with low emissive surfaces with vacuum in between. This solution can only be realised in cylindrical geometries, which have the potential for withstanding the external atmospheric pressure acting on the outer surfaces if a reasonable material thickness should be considered. The most well known example is the Dewar flask or better known as the thermos bottle with a double-walled glass cylinder, which is silver coated on the surfaces facing the evacuated enclosure. The emissivity of silver is 0.02 – 0.03 reducing the heat transfer by radiation with 97-98 %. Further reduction of the heat loss by radiation could be achieved by adding more radiation blocking layers in the enclosure, but fixing of the layers may be difficult without creating thermal bridges that may eliminate the effect of the reduced heat transfer by radiation.

In the thermos bottle the main heat loss is due to the thermal bridge where the glass walls are joined and through the bottle lid, which both are at the top of the bottle where the temperature is highest. Looking at water storage tanks for solar heating systems, where thermal stratification is a key issue in order to keep the lower part of the tank as cold as possible the "thermos bottle" should be turned upside down in which case the thermal bridge due to the wall joining and the poor "lid insulation" will be located in the coldest part of the tank. The main drawbacks are the need for a double shell with a relatively large wall thickness to withstand the atmospheric pressure and the need for a high vacuum due to the wall distance compared to the free mean path of the air molecules.

For example if the distance between the cylindrical walls is 1 mm the pressure should be lower than 0.1 hPa before a significant decrease in gas conduction as function of gas pressure starts (see table 2) and a 99% decrease in gas conduction is achieved at a pressure of 10^{-6} hPa (the high vacuum region).

7.5.3 Vacuum insulation filler materials

To avoid the drawbacks of thermos bottle principle with respect to establishing the high vacuum and the need for a thick and strong outer cylinder wall an open-pored filler material with a sufficient compressive strength can be applied between an outer and the inner wall of the storage. In this case the external load from the atmospheric pressure is transferred through the filler material to the inner wall that initially has the sufficient strength to withstand not only the atmospheric pressure but also the much higher internal pressure from the pressurised water in the tank. The filler material should have a high porosity with small pore sizes in which case the solid conduction will be limited and reduced gas conduction can be achieved at a pressure in the rough or medium vacuum region. The filler material also eliminates the need for low emissive surface coating of the storage walls. Table 4 shows some of the most common materials used for vacuum insulation products.

Table 4 Internal pore gas pressure and corresponding thermal conductivity for different open celled materials used in vacuum insulation products

Material	Pressure	Thermal conductivity (T_{mean} = 10 °C)	Temperature dependency*
	hPa	W/mK	%/K
Polystyrene foam (open pored)	0.1	0.004	?
Polyurethane foam (open pored)	0.1	0.006	?
Precipitated silica gel	1	0.006	0.1
Fumed silica gel	10	0.004	0.1

*The thermal dependency of the thermal conductivity has not been reported, but the dependency would be lower than in the un-evacuated state due to the small amount of gas molecules in the pores.

In general vacuum insulation has a thermal conductivity of 0.005 W/mK at a mean temperature of 10 °C. The difference in pressure related to the thermal conductivity is due to differences in the average pore size for the different materials, i.e. polyurethane and polystyrene foams has pore sizes in the range of 40 – 70 μm while silica gels have pore sizes in the range of 0.01 – 1 μm.

The requirements to the level of vacuum is decreased due to the small pore sizes of the filler materials but the small pore sizes increases the diffusion coefficient, which means that evacuation through a single connection in the vacuum insulation enclosure becomes very time consuming (weeks) if a common storage size is considered.

It should be noted that no examples on direct foaming of e.g. open pored polyurethane foam in a large enclosure has been found, which might be due to technical difficulties or due to the evacuation problem for large volumes.

7.5.4 Vacuum insulation panels (VIP)

Vacuum insulation panels are commercial available products. A highly porous filler or core material is evacuated and encapsulated in a shell to keep the vacuum. Only metals with a thickness > 0.1 mm and glass is 100% gas and water vapour tight, but both materials has a relatively high thermal conductivity. This leads to a significant thermal bridge at the edges of the panel and the benefits of the vacuum insulation is more or less eliminated. Therefore all VIP's are made with a barrier film with a high but not 100% resistance against gas and water vapour diffusion.

Most barrier films consist of several different plastic layers with different orientations and one or two metallized layers to get the very high barrier properties. In some cases thin aluminium foils laminated between two layers of plastic is used, which results in excellent barrier properties but also increased edge heat losses Fig. 10, [2].

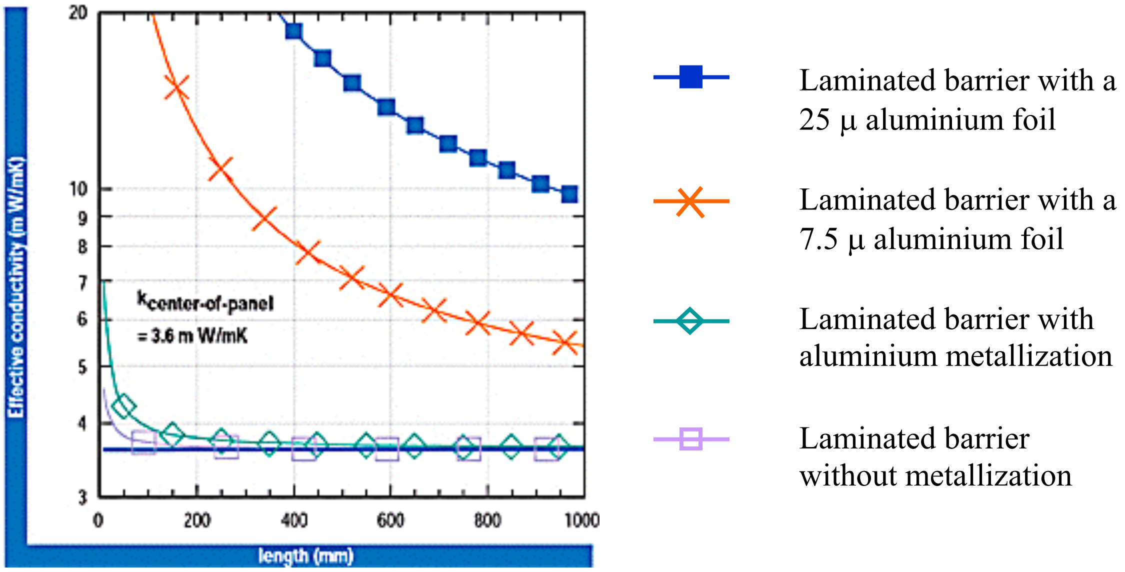


Fig. 10. Effective thermal conductivity (T_{mean} = 10 °C) of vacuum insulation panels as function of size (side length) and type of barrier for square 25 mm thick VIP's. The thermal conductivity at the centre is 0.0036 W/mK. [2].

The effect of the thermal bridges at the edges can be reduced if more layers of VIP's are applied in which case the different layers can be mounted with displaced joints.

As the laminated barrier films without foils are not 100% tight a slow pressure increase will take place in the VIP over time. Depending on the filler material even a small pressure increase could lead to significant increase in the thermal conductivity. Fig. 11 [2] shows the relation between internal gas pressure and equivalent thermal conductivity of VIP's with different filler materials.

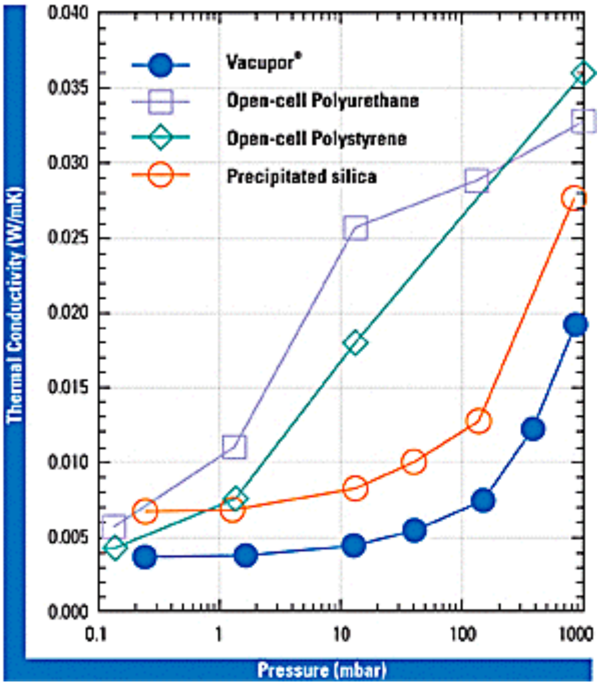


Fig. 11 Thermal conductivity (T_{mean} = 10 °C) as function of internal gas pressure in different VIP filler materials [2]. The Vacupor is based on fumed silica gel. (1 mbar ~ 1hPa).

Due to the nanostructure of silica gels a pressure increase from 1 to 100 hPa only doubles the thermal conductivity, while the same pressure increase would increase the thermal conductivity of polyurethane and polystyrene foams with a factor 5. Therefore foam based VIP's includes a so-called getter capsule that holds a material designed to adsorb gas and water vapour molecules.

The lifetime of VIP's with respect to thermal conductivity depends beside the capacity of the getter material and the effective barrier properties also on the panel volume relative to the surface area. A large volume relative to the surface area increases the panel lifetime. However a lifetime of 10 – 20 years should be expected.

Application for storage insulation

Even though vacuum insulation panels can be made in a variety of forms (Fig. 12) the most efficient way of use is to encapsulate the panels in polyurethane foam often used as insulation material for storage units. The polyurethane foam protects the vacuum barrier film against mechanical damages and furthermore reduces the gas and moisture diffusion into the VIP.

Fig. 12 Example of vacuum insulation panels [3].

The overall reduction of the storage heat loss depends of course on the total area with VIP's and their thickness, but large savings are possible:

> If 50 mm thick polyurethane insulation (thermal conductivity λ = 0.028 W/mK) is exchanged with a sandwich of 20 mm polyurethane – 10 mm VIP (λ = 0.005 W/mK) – 20 mm polyurethane, this will reduce the heat loss coefficient with approximately 50% from 0.6 W/m^{2}K to 0.3 W/m^{2}K.

Use of vacuum panels alone makes it difficult to obtain a continuous insulation layer on curved surfaces. If only vacuum insulation panels should be used the best solution would be to place the storage in a rectangular box with a plane layer of VIP panels.

7.6 Summary

Table 5 lists the thermal characteristics of the different insulation types described in this paper as well as references to some manufacturer of the materials. The list of manufacturers is not at all meant to be a complete list but only as a help to find additional information on some of the product types.

Use of polyurethane foam with the lowest possible thermal conductivity would probably be the most economic first step for improvement of the tank insulation. Table 5 shows that further significant improvement of the tank insulation can only be achieved with vacuum insulation. From a production angle of view the most applicable way is to have vacuum insulation panels embedded in polyurethane foam as already practised in freezers and refrigerators [4]. This principle protects the vacuum insulation panel against mechanical damage and the PU foam fills out all irregular shapes.

Table 5. Overview of insulation materials and their typical thermal characteristics

Material	Thermal conductivity (T_m = 10 °C) W/mK	Maximum temperature °C	References
Mineral wool			
Stone wool	0.036 – 0.050	250 – 1000	www.rockwool.com
Glass wool	0.036 – 0.050	250 – 400	www.isover.com
Polystyrene			
EPS granular	~ 0.050	80	
EPS blocks	0.034 – 0.050	80	http://plymouthfoam.com/index.html
XPS blocks	0.034 – 0.050	80	www.dow.com/styrofoam/index.htm
Polyurethane	0.024 – 0.050	140	http://www.elliottfoam.com/features.html
Micro porous insulation	0.020 – 0.025	800 – 1200	http://www.microtherm.uk.com/prod.html
Nano porous insulation			
Silica gels	~ 0.020	500	http://w1.cabot-corp.com/index.jsp
Silica aerogels monolithic	0.012 – 0.018	500	www.airglass.se
Silica aerogels granular	0.020 – 0.025	500	
Vacuum insulation			http://www.microtherm.uk.com/prod7.html
Open pored polystyrene	0.004 at 0.1 hPa	80	http://www.glacierbay.com/ultra-r.asp
Open pored polyurethane	0.005 at 0.1 hPa	140	http://www.porextherm.com/en/
Precipitated silica gel	0.006 at 1.0 hPa	500	http://www.nanopore.com/vip.html
Aerogels	0.004 at 10 hPa	500	

The thermal dependency of the tehrmal conductivity is in the range of 0.4 – 0.8 %/K for mineral wool and foams and approximately 0.1 %/K for microporous and nanoporous materials. Vacuum insulation will show less thermal dependency due to the reduction of gas molecules in the pores.

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Part II Storage in water

8. A brief history of PCMs for heat storage

by Stephane Citherlet

Since the beginning of the twentieth century, PCMs have been used for various heating applications. End 1920's, various "hot bottle" systems were developed, suitable for instance for warming babies' milk bottles. One of the patented solution consists in a sealed metallic jar in which PCM was mixed with fine sand and chunks of metal [1, 2]. Shaking the tank allowed its content to scrape the internal wall, initiating crystallisation of the supercooled salt solution, which released its latent heat.

PCM have been used also to stabilise the human body temperature when working in difficult environments. In 1950, a heat-releasing gloves made of a sponge moisten with a salt hydrate sealed between to rubber sheets was patented [3]. This heating enveloped was proposed to be used as sleeping bag or gloves in artic conditions. Nowadays, acrylic coating cloth embedding micro-encapsulated PCM has been developed for outdoor leisure [4, 5].

In 1965 a warming suit was patented for persons exposed to cold such as divers, aviators and explorers evolving in cold conditions [6]. When the lithium hydride stored in a backpack was put in contact with water, it realised heat. The latter could be transferred, via a heat exchanger, to the air contained in the suit to keep the human body warm.

On the other hand, PCM can be used to absorb excessive heat released by the human body under strenuous activities. The heat absorption by PCM plates incorporated into clothes results in a delay in the body temperature increase and hence a substantial decrease of the skin's moisture release. Both lead to an overall enhancement of the thermo-physiological wearing comfort and a reduction of dehydratation as a serious health risk, such as for fire fighters, costumed characters [7-10] .

During the 1960's the applicability of PCMs has been demonstrated in the space industry. PCM were proposed as heat sink for inertial navigation systems [11, 12]. For instance, paraffins were used to reduce temperature fluctuation, related to the spacecraft rotation, in waste containers of the Skylab orbiter. During the Apollo 15 mission, PCM was used on the Lunar Rover Vehicle. Heat generated during its use was stored in movable insulation made of paraffin. Between sorties, the insulation was brought back in the Apollo module, where the heat was released. More recently the potential of using PCMs in space suites has been investigated [8].

The electronic industry has also demonstrated an interest in PCMs early 1970s' as for transistors heat sinks. It is still nowadays a lively domain, as for instance the testing PCMs for cooling microprocessors [13, 14]. The car industry has also considered the benefits of using PCM to improve thermal comfort of the occupants [15].

8.1 Building industry

In 1970's and early 1980's, research on PCM was very active in heat storage for the building industry. Many countries have set up national projects to analyse the performances of various type of PCM. The most active countries at the time were Denmark, France, Germany, India, Japan, Sweden, USA and the east countries, that mainly covers the following topics.

8.2 Passive solar

The potential of adding PCM's to construction materials in order to increase their heat capacity, has been evaluated for solar passive energy storage since the 1970's [16-18]. Nowadays, there is a fresh outbreak as research has provided new PCMs with higher performances and manufacturing techniques allowing a better integration in construction materials. Several solutions have been analysed such as mixing PCM powder or pellets within concrete [19, 20] or within plasterboards [21-27], filling the hollow core of structure blocks [28, 29] or transparent insulation materials [30]. To reduce the solar gains trough windows, filling the gap between glazing panes has been investigated [31, 32].

8.3 Air heating

For air heating, one of the first application of PCM in a real building seems to occurs in 1948 [33]. Solar collectors made of black iron absorber plates placed behind a double glazing were used to heat the contented air, which was transported trough pipes to tanks filled with 21 tons of Glauber's salt (sodium sulfate decahydrate) located between the building partitions. This system provided a 100% solar heating during a couple of winters. Although the system seems to have well performed during this time, the PCM stability failed during the third year and as the occupants comfort could no more been achieved, the system was dismantle and replaced later by a oil furnace [34].

Nowadays latent heat storage has been tested with air-ventilation systems by hanging PCM plates in the false-ceiling gap [35], by mixing micro-encapsulated PCMs within the false ceiling board [36], by coating the false floor cavity [37] and the air ducts [37, 38], or as a central storage tank [39].

Passive solar systems with PCM bed for solar air heating installations have also been developed with the storing materials lying in a cavity placed under the ground slab [40] and under a solar roof [41]. PCM's encapsulated in a metal containers can also be used to replace ceramic bricks in an electrical stove [42].

8.4 Water heating

Although research on the use of PCMs in liquid tank began in the 1920s, their applications were not effective before 1932, when if has been proposed to immerse sealed tubes of organic PCM in a liquid tank, which could be heat with off-peak electricity [43].

In mid-1940's, a system, that can be considered as a precursor of the current solar heating storage systems, was patented [44, 45]. It intends to store natural heating and cooling in a water tank holding containers filled with different PCMs. The heat from the sun was absorbed by an absorptive panel placed on the building roof trough which the tank's water could circulate. Nowadays, this approach is still investigated either by acting on the solar collector or in the water storage tank. In the first approach the solar collectors can be placed over an immiscible layer of PCM [46] or the collectors tubes coated with PCM's [47].

On the other hand, the water tank can incorporates tubes filled with PCMs for direct solar domestic hot water production [48-52]. The water tank can also be connected to an air-ventilation with a water-to-air heat exchanger [53].

During the 1960s, several buildings were equipped with latent storage units to operate as a warm source for a heat pump, but were dismantle due to technical unreliability. Nowadays, this approach is still under development [54, 55]. The potential off-peak electricity storage with PCMs is still evaluated nowadays with new materials [23, 56, 57].

8.5 Conclusion

This section has given a brief overview of the PCMs applications trough the years. As the domain was and still is a very prolific research domain, it can not include all documents that have been published. For further reading, several reviews can be suggested which detail the PCMs' properties and applications [8, 34, 58-62] or compile a list of publications related to PCM's published during the previous century [63].

Most of the research presented above has been made easier thanks to the development of personal computers in the 1980s, which has allowed a better understanding of the PCMs' behaviour. Among all, Buddhi [64-67] and Farid [68, 69], are probably the most significant contributors in this field for more than two decades. Since the mid-1990's many other contributors have used different calculation approaches to solve the heat transfer in PCMs with analytical models [70-72] or numerical methods based, the enthalpy method [66, 73-75] and the specific heat method [76]. New simulation methods, at molecular level, are have also been investigated [77].

Finally, the identification of potential PCMs candidates for latent energy storage increase as new materials are developed in the industry every year. Currently, there are hundreds of identified PCMs. It is not the aim of this section to make the inventory of all these materials; but interested people can consults the list released by the Annex 17 of the IEA, which one goals is to identify potential materials and to overcomes technical and market barriers for the introduction of thermal energy storage using PCM [78].

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9. Ice storage

by Motoi Yamaha (guest contributor)

9.1 General

An ice storage system uses the heat of fusion of water. It is a kind of PCM storage and is wildly used in building application. Ice making was an old technology in some fields such as food industry. Its application for building HVAC system started mid 80s in USA and Japan. The background of this application was to shave the peak demand in warm summer day and to reduce size of the tank. As IT devices such as personal computers became popular, heat gain in buildings increased and resulted in large cooling loads. Electric demand for cooling became large and was concentrated in afternoon on a warm day. Electric utility companies offers discount nighttime tariff in order to reduce peak demand. Figure 1 shows the electric demand and tariff on peak day in Japan. Nighttime rate was nearly 25 % of daytime. Figure 2 shows relation between ice packing factor and size of the tank. If the ice storage tank was installed, the size of the tank was reduced to half with Ice Packing Factor of 10 to 15 %.

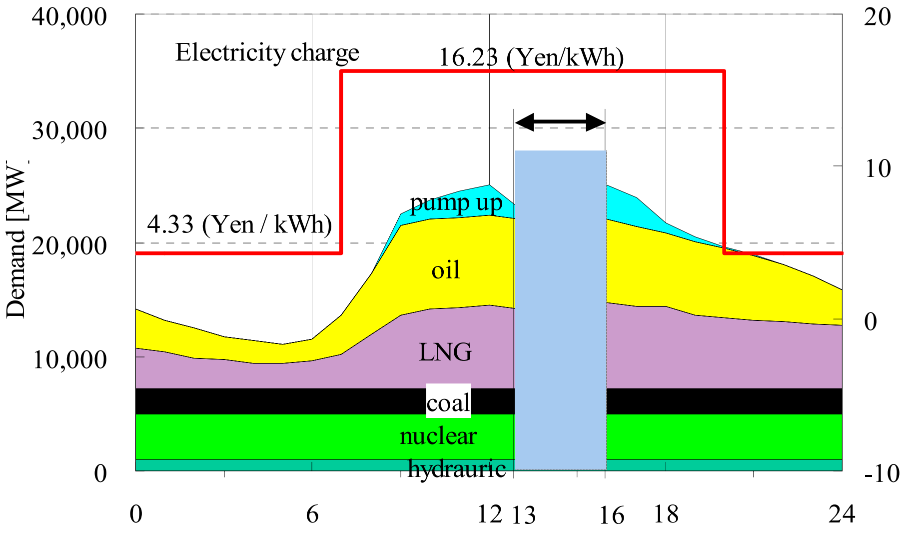


Fig. 1: Demand curve and electricity tariff in Japan

Ice storage can compensate imbalance between heat production and demand. The merits for ice storage system are summarized as follows:

- Reduction of refrigeration machine capacity which results in high efficiency for full operation
- Redundancy for HVAC system
- Utilization of nighttime discount
- On the other hand, followings are considered to be demerits:
- Lower COP due to lower evaporative temperature
- High first cost

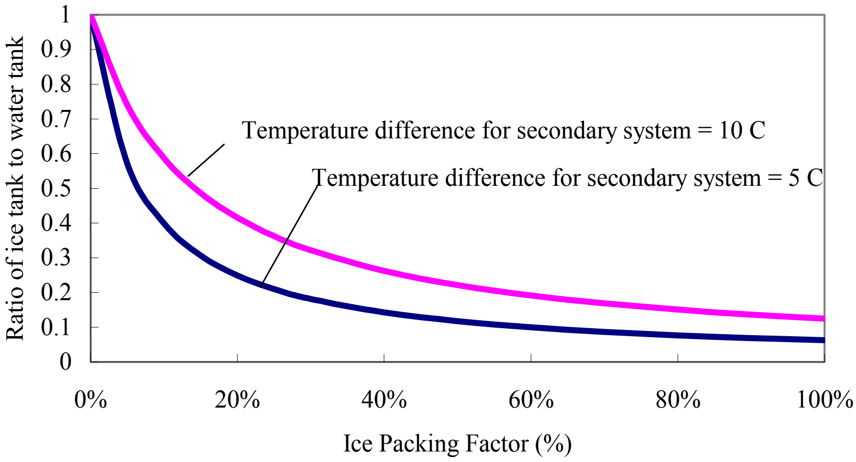


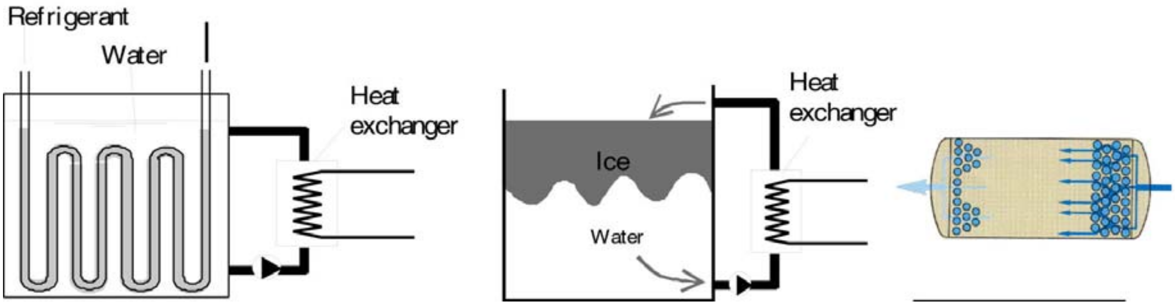
Figure 2. The relation between tank volume and Ice Packing Factor. As shown in the figure, tank volume is decreased against small IPF.

As mentioned above, since utility companies offer nighttime discount in warm countries, ice storage system can reduce operating cost and can be paid back in three to five years.

From the energy points of view; chillers in ice storage itself consume more energy than water system. However combined with cold water and air distribution system, it can reduce energy consumption because flow rate of water and air could be reduced by large temperature difference.

9.2 Types of ice storage

Figure 3 shows schematic diagram of various ice storage system. Ice storage system can be categorized into three types, which are (a) ice on coil type, (b) slurry type, and (c) encapsulated type.



(a) Ice on coil type (b) Slurry type (c) Encapsulated type

Figure 3. Types of Ice storage tanks

9.2.1 Ice on coil type

A set of curved tube or coil, in which refrigerant or glycol solution circulates, is installed in a tank and cooled inside of the coil. Ice is formed on the surface of the coil and melted from boundary between ice and water. Stored heat is usually recovered by supplying water directly to a secondary system. Some systems use a heat exchanger to reduce water heat loss. This type of ice storage is also called static type, since ice in the tank is statically fixed. In the freezing process, as thickness of the ice increases, the ice layer will be a thermal resistance so that performance of the system decreases.

In Japan, a system in which storage tank and compressor are packed as shown in Figure 4 is very popular. The ice tank is integrated in the refrigerant cycle. Ice is formed during night when outside temperature is low, and melted by hot liquid refrigerant which is sub cooled. The capacity of the machine is increased by 20 % due to sub cooling effect.

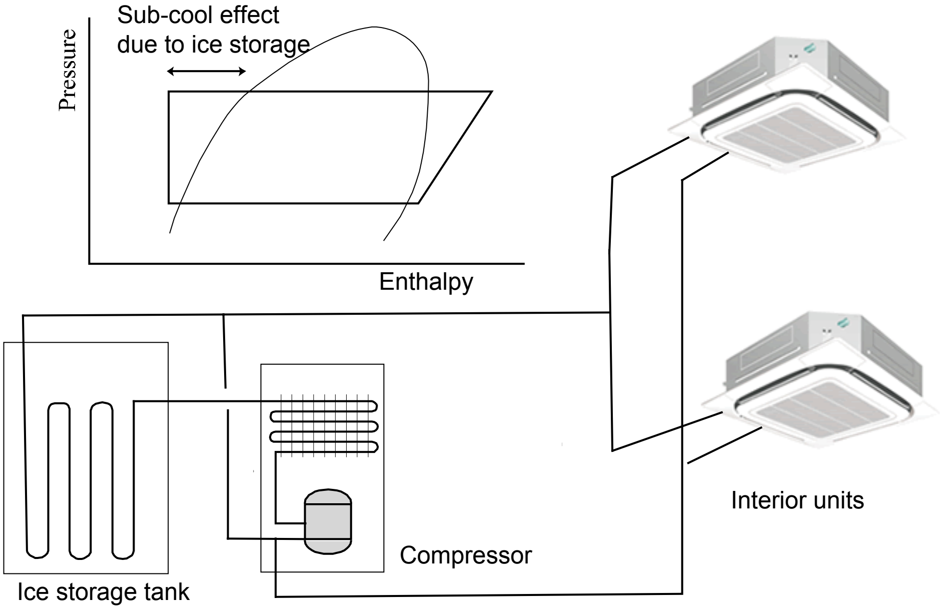


Figure 4. A diagram of package ice storage tank

9.2.2 Slurry type

Fresh water or a thin glycol solution is cooled by a heat exchanger. Fresh water becomes super cooled water, which is sub zero temperature, then a certain mechanism such as collision or vibration releases super cooled state so that some part of the water becomes ice. Figure 5 shows schematic figures of making super cooled water.

In the case of thin glycol solution, the solution becomes ice and a thicker solution by cooling. Figure 6 shows one example of such ice making system. These ice making method do not have the problem of thermal resistance of growing ice as the ice on coil type.

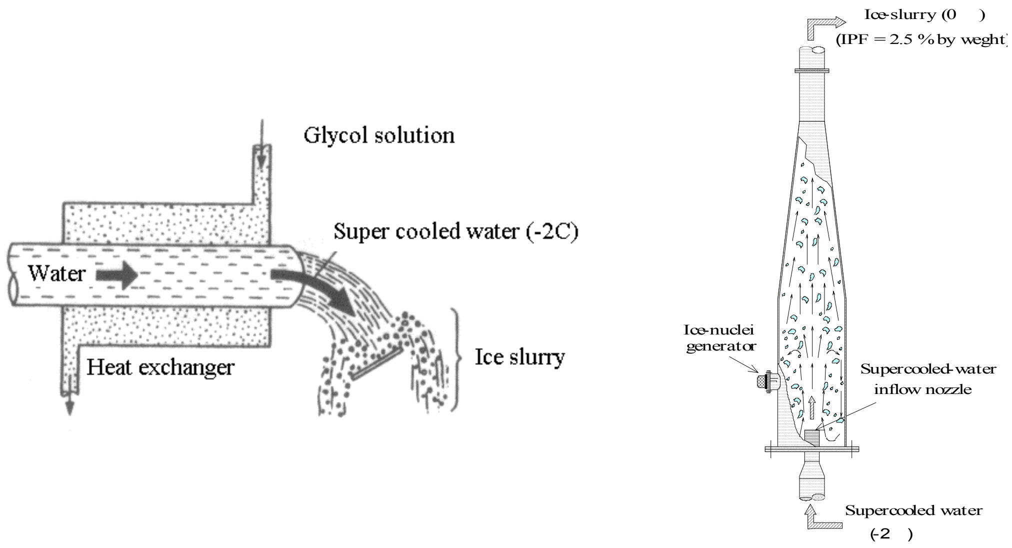


Figure 5. Slurry ice system using super cooled water

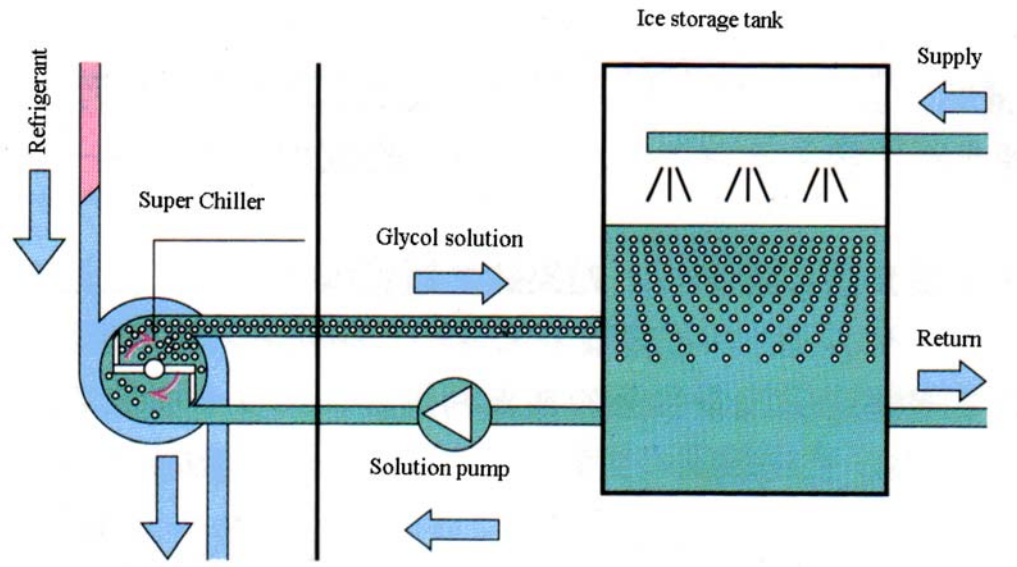


Figure 6. Slurry type using thin glycol solution

9.2.3 Encapsulated type

Small balls which contain the storage medium, water is the most popular, are packed in a vessel and are cooled and heated by an operating liquid. According to the melting temperature of the medium inside the balls, the operating temperature of the system varies.

9.3 Thermal characteristics of storage tank

9.3.1 Principal

Since water has highest density at 4°C, the thermal characteristics of the ice storage tank are complicated for the melting mode. Usually, warm water flows on top of the tank, and then water is cooled down going downward. In a way to bottom, water is mixed and reaches to the bottom when its temperature becomes 4°C. Usually, without mixing or other measures, it is difficult to get an output temperature under 4ºC for ice on coil type storage tank (Fig. 7).

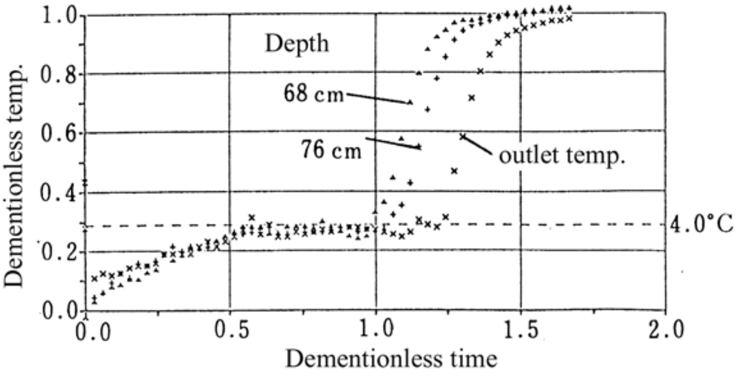


Figure 7. Temperature response of ice storage tank for melting without agitation. The outlet temperature gradually went up to 4ºC and was kept until ice was melted.

9.3.2 Ice making

For the ice on coil type ice storage tank, the water inside the tank is sometimes agitated to enhance heat transfer on the coil surface. Small water or air pumps are used for this purpose. This agitation is effective until ice is formed on the coil, because the temperature during the ice forming is uniformly the freezing point. The degree of agitation, which means the flow rate of water or air, does not have much affect on the ice making rate especially for small ice packing factor.

9.3.3 Ice melting

The mixing status in the tank has a large affection on the outlet response for the ice storage tank without agitation. If the ice packing factor is small, thermal characteristics of the tank resembles to a stratified water tank. Since the ratio of sensible heat to latent heat is relatively large, conditions should be set to maintain stratification as much as possible. Therefore, a large temperature difference in the inlet is preferable.

9.3.4 System performance

Since ice storage tanks are used in HVAC system, the performance should be evaluated from the system point of view. If the water distribution system had poor performance, the performance of tank would be worse than its design value. Furthermore, the heat load characteristics of the building also have large relation to the system performance. The system performance will be different for a building that has peaky load comparing to a building with flat load.

9.4 Heat sources

9.4.1 Artificial heat source

(a) Compression chillers

There are various artificial sources for ice storage. The most popular way to make ice is a compression chiller. Centrifugal chillers are used for large applications. Screw or reciprocal chillers are used for medium and small applications. Heat is transferred to the ice making heat exchanger by a glycol solution or a refrigerant. Since the evaporative temperature of the chiller is lower, the performance of the chiller is naturally worse than the ordinary one for comfort cooling. However, the efficiency is improved since the operation of the ice making is occurred during nighttime.

(b) Absorption chiller

Absorption chillers can not be used for ice storage system, because their refrigerant is water. However, if water is cooled down below the freezing point in the evaporator, ice slurry could be obtained. Some manufacturers are developing such absorption type ice making machines.

9.4.2 Natural heat source

In cold climates, natural heat source could be used to make ice during winter. In these cases, ice is seasonally stored, formed during winter and used in summer, so that storage period is much longer than diurnal storage. The ice could be made by circulating cold air or accumulating snow. The possibility to utilize these natural heat sources strongly depends on the weather where the system would be installed.

10. Storage techniques with Phase Change Materials

by Luisa F. Cabeza

PCMs have been a topic in research for the last 20 years. Although not many applications can be found in the market, the literature presents many interesting papers in this field. The main reviews published in the last period are those of Dincer and Rosen [1], Zalba et al. [2], Khundhair and Farid [3], and Farid et al. [4].

10.1 Building applications of PCMs

The use of PCMs for thermal storage in buildings was one of the first applications studied, together with typical storage tanks. The firsts application of PCMs described in the literature was their use for heating and cooling in buildings, by Telkes in 1975 [5], and Lane in 1986 [6]. The use of building structural components for thermal storage was pointed out already in 1975 by Barkmann and Wessling [7], and later by other authors [8-10].

An important disadvantage of lightweight buildings is their low thermal mass. They tend to have high temperature fluctuations, which result in a high heating and cooling demand. The application of PCM in such buildings is, because of their capability to smooth temperature variations, very promising [11,12].

An example of such application was developed by Mehling et al. [11]. They studied the inclusion of PCM in wood-lightweight-concrete. Wood-lightweight-concrete is a mixture of cement, wood chips or saw dust (less than 15 wt.%), water and additives. It has advantages such as good thermal insulation (between 0.15 and 0.75 W/m·K), noise insulation, good mechanical properties (density between 600 and 1700 kg/m^3), and a heat capacity between 0.39 and 0.48 kJ/kg·°C with a density of 1300 kg/m^3. Its applications are building interior, outer wall construction, storey buildings and prefabrication.

The idea of combining PCM with wood-lightweight-concrete would increase the thermal storage capacity and get lighter and thinner wall elements with improved thermal performance. The PCM chosen for such application was Rubitherm granulate GR 40, 1 – 3 mm, and GR 50, 0.2 – 0.6 mm (Fig. 1). Mixtures of 20% wood replaced by paraffin, or mixtures with additional 20% PCM were tested. They concluded that PCMs can be combined with wood-lightweight-concrete (Fig. 2), and that the mechanical properties do not seem to change significantly.

Fig. 1. Rubitherm granulate GR 40, 1 – 3 mm.

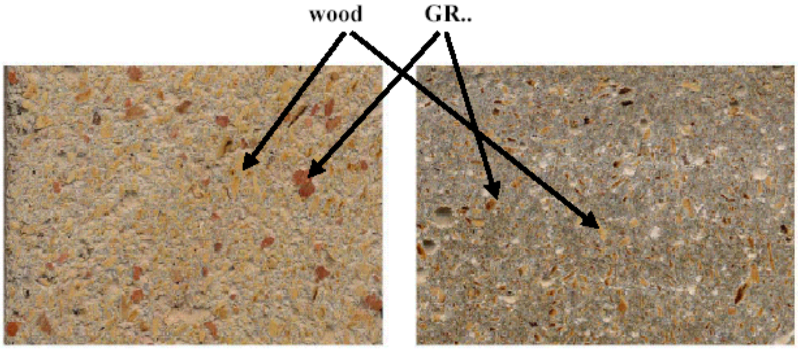


Fig. 2. PCM in wood-lightweight-concrete.

An interesting possibility in building applications is the impregnation of PCMs into porous construction materials, such as plasterboard, to increase thermal mass [13-15]. This idea has recently been widely developed by Schossig et al. [16]. They have developed a system to integrate microencapsulated organic PCMs into conventional construction materials.

The project developed by Schossig et al. [16] tried to avoid the discomfort created in summer in the lightweight buildings due to solar insulation. This aim would be reached integrating PCMs in building materials after microencapsulation (Fig. 3). They built two testrooms in a typical lightweight construction consisting of gypsum plasterboard mounted on wooden slats with insulation. One testroom was equipped with PCM-plaster and the other with conventional plaster. Their experiments showed that when night ventilation and shadings are used, the PCM efficiently decreases the temperature of the room (Fig. 4).

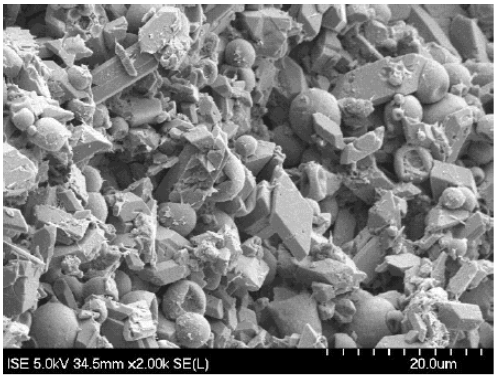


Fig. 3. SEM-picture of microencapsulated PCM in gypsum.

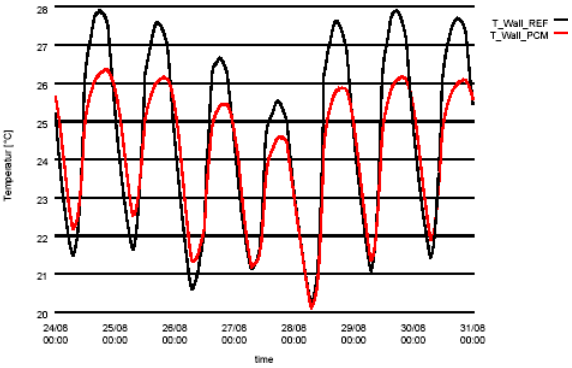


Fig. 4. Wall-temperatures with night ventilation and shading.

Another approach is to mould into concrete containers of relatively large size (compared to the thickness of the wall or ceiling), that are filled with phase change material [17]. Several researchers studied the impregnation of concrete with PCM to produce a low cost energy storage material with structural and thermostatic properties [3]. Marcos et al. [18] have recently presented the development of microencapsulated organic PCMs to be applied on concrete, avoiding problems with leakage of PCM out of the walls.

The use of PCMs to store coolness have been developed for air conditioning applications, where cold is collected and stored from ambient air during night, and its relived to the indoor ambient during the hottest hours of the day. This concept is known as free-cooling [19-25].

The concept of free-cooling (Fig. 5) was studied by Zalba et al. [19,20]. An installation which allows testing the performance of PCMs in such systems was designed and constructed. The main influence parameters were determined theoretically and experiments are performed following the Design of Experiments strategy. With the empirical model developed in this work, a real free-cooling system was designed and economically evaluated (Fig. 6).

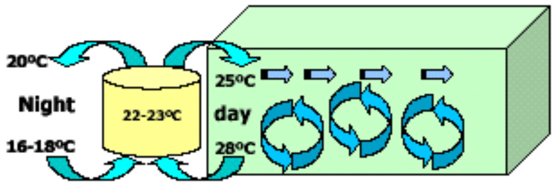


Fig. 5. Concept of free-cooling.

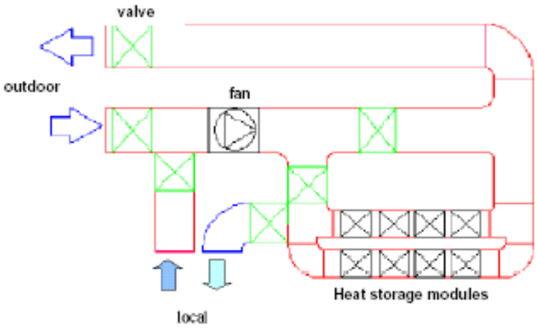


Fig. 6. General outline of the free-cooling installation.

An interesting project developed at the University of South Australia [26] is a solar air space heating system. The principle is to capture the sun's heat during the day, transfer the heat to a storage facility, and then retrieve it later when needed. The system consists of an air based roof integrated collector (Fig. 7) and a thermal storage unit containing PCM (Fig. 8).

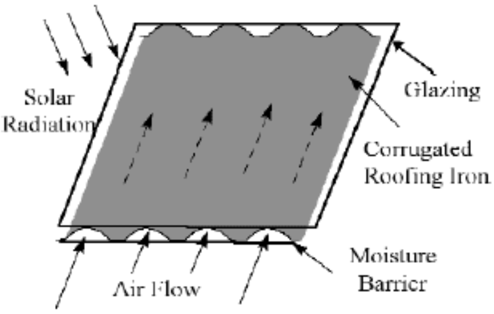


Fig. 8. Thermal storage unit with PCM.

Fig. 7. Air based roof integrated collector.

A new proposal is the use of a floor supply air conditioning system with latent heat storage. The main idea is still similar to free-cooling, but using different parts of the building [27-29].

This idea was developed by Takeda et al. [27]. Cold energy is stored in building structures and granulate PCM during night. Granulated PCM (Fig. 9), particle diameter of around 3 mm, is paved a few centimetres in thickness under the floor space (Fig. 10). The packed PCM is breathable and PCM can exchange heat with air directly.

Fig. 9. Granulated PCM used by Takeda et al. [27].

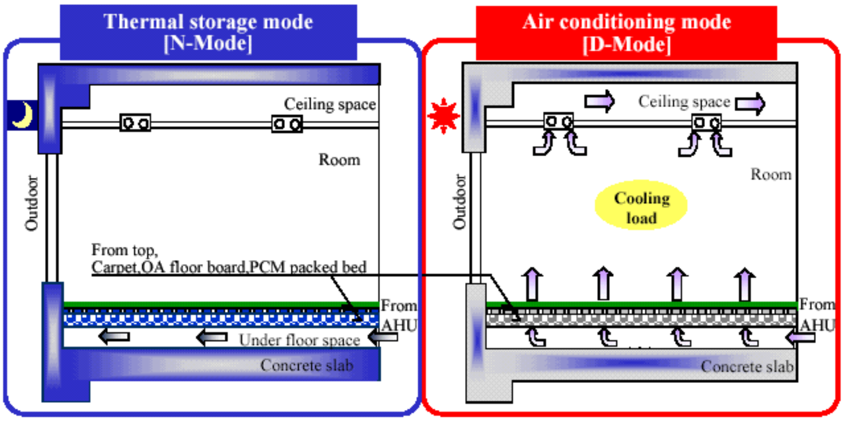


Fig. 10. PCM floor supply air conditioning system.

In order to diminish the solar gain in buildings, Ismail et al. [30,31] studied the possibility of using a window with a PCM curtain. This window is double sheeted with a gap between the sheets and an air vent at the top corner; the gap can be filled with PCM that upon freezing would prevent the temperature of the internal ambient from decreasing. Similarly, Merker et al. [32,33] have developed a new PCM-shading system to avoid overheating around the window area.

Merker et al. [32,33] investigated experimentally and numerically the charging and discharging process of a new PCM-shading system (Fig. 11) and quantified the influence of the surrounding temperatures and heat transfer coefficients. Measurements with the solar simulator (Fig. 12) and numerical simulations using the enthalpy method were found to be in good agreement. First measurements of a complete PCM-shading system using a salt hydrate were carried out with the solar simulator measuring device. The temperature rise of the shading system for a constant irradiation of 500 W/m² could be delayed for more than 7 hours.

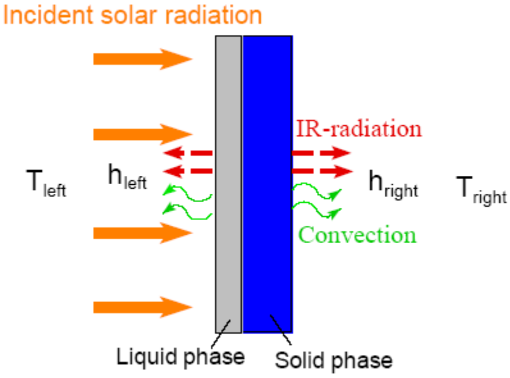


Fig. 11. Description of the PCM-shading system.

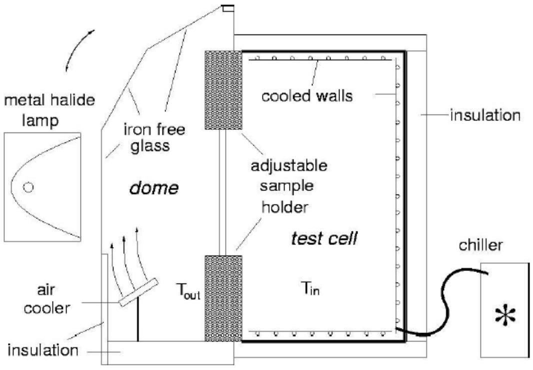


Fig. 12. Experimental set-up with a metal halide arc lampas solar simulating unit.

10.2 PCM tanks vs. water tanks

In the field of solar energy storage, Cassedy [34] claimed that today PCMs do not offer economic savings for thermal storage at low temperatures (50-100° C), since these systems (paraffin) cost about the double of the cost of hot water systems. He does, however, point out the advantages associated with materials like paraffin, such as low corrosion, and chemical stability. Similar results were reported previously by Farid [35].

Especially the high storage density at small temperature changes can be a significant advantage in solar applications and utilization of waste heat [36,37].

Mehling et al. [38,39] studied the possibility of including a PCM-module at the top of a stratified water tank. Their results stated and increase of energy storage and a better performance of the tank.

A new concept to combine hot water heat stores with stratification and latent heat storage was developed by these authors (Fig. 13). Here, the advantages of the hot water heat store with stratification remain and at the same time the storage capacity is significantly increased with the PCM. This is achieved by adding a PCM-module only at the top of the water tank, where the temperature changes are typically small. The PCM-module increases the systems heat storage density without disturbing the overall temperature stratification. It is able to compensate heat loss to the outside in the top layer and therefore ensures having some hot water even in long periods without heat input (Fig. 14).

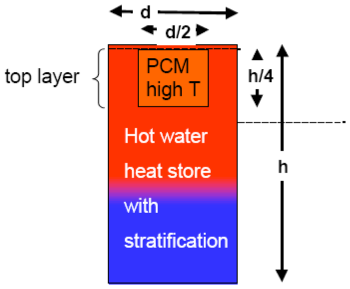


Fig. 13. Implementation of a PCM module in a stratified hot water heat store.

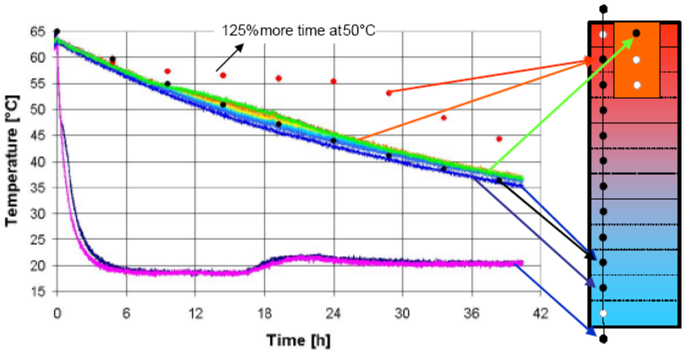


Fig. 14. Experimental and numerical results when cooling a water tank with a module of sodium acetate trihirate compared to a module of RT50.

Esen et al. [40] studied theoretically the effects of various thermal and geometric parameters on the whole PCM melting time for different PCMs and tank configurations. The configurations were those of a tank with PCM packed in cylinders and the heat transfer fluid flows parallel to it; the second is a tank where pipes containing the fluid are embedded in the PCM. Another configuration used for many years is the inclusion of the PCM in spherical containers, and those in the water tank [41,42].

The performance of a solar energy system varies significantly from day to day and from month to month making it necessary to examine its performance over a long term (Fig. 15 and 16). The main objectives of the Esen's study [43] were: (1) to use a theoretical model describing the diurnal transient behaviour of the phase change energy storage (PCES) unit, (2) to perform computer simulations and experiments in order to determine the distribution of energy, and temperature within the PCES unit, and (3) to determine the monthly space heating loads, the monthly stored energy, and monthly total solar insolation on collector surfaces, and to present comparisons of these data.

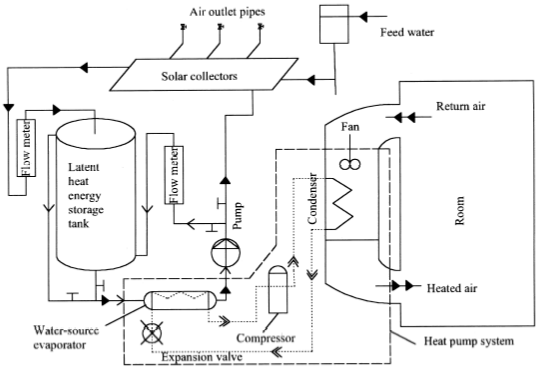


Fig. 15. Solar assisted heat pump system with latent heat storage tank.

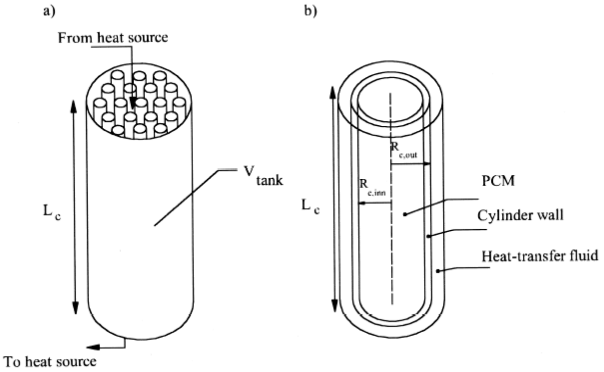


Fig. 16. Energy storage tank packed in vertical direction with cylindrical tubes (a), the model for one cylinder (b) and cylindrical control volume element.

10.3 PCM in solar collectors

Including PCM in a solar collector was first presented by Sokolov and Keizman [44], but has lately been considered by other researchers like Rabin et al. [45], Enibe [46,47], and Tey et al. [48].

Tey et al. [48] studied the potential of phase change materials to substitute water as storage substance in integrated collector storage systems. A solar water heater that combines thermal collection and storage in a single unit was designed, constructed and tested. The main characteristics of the system were the use of transparent insulation material cover, integrated copper storage cylinders and paraffin (melting point 64.1ºC) as storage substance. The integrated collector was tested with water paraffin filling the storage tank and finally filled with paraffin.

The paraffin tank (Fig. 17) acts as a thermal pad that avoids dangerous rises of temperatures and increases system efficiency. The paraffin maximum temperature is usually under 70ºC. Because lower maximum temperatures are achieved, when paraffin fills the storage cylinders as a substitute of water, smaller heat losses are found. Maximum useful efficiencies obtained for paraffin improves the ones determined for water.

Fig. 17. The storage tank and the serpentine before treated to get the selective coating.

10. 4 State of the art of phase change materials

10.4.1 Classification

In 1983 Abhat [49] gave a useful classification of the substances used for thermal energy storage, shown in Figure 18. Among the most thorough references related with phase change materials, one can cite Abhat [49], Lane [6,50], Kenisarin [36], Dincer and Rosen [1], Zalba et al. [2], and Farid [4]. These contain a complete review of the types of material which have been used, their classification, characteristics, advantages and disadvantages and the various experimental techniques used to determine the behaviour of these materials in melting and solidification.

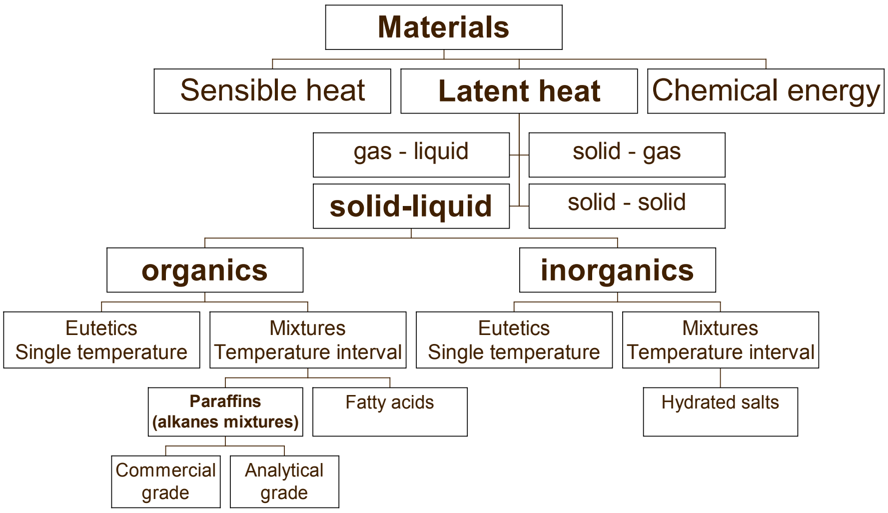


Figure 18. Classification of energy storage materials [49].

10.4.2 Non-commercial/commercial materials

Many substances have been studied as potential PCMs, but only a few of them are commercialised as so.
Tables 1 to 6 present the different substances, eutectics and mixtures (inorganic, organic and fatty acids), that have been studied by different researchers for their potential use as PCMs. Note that only melting temperatures of 16 to 30ºC have been considered for applications in buildings, and melting temperatures of 45 to 70ºC have been considered for storage tanks. Some of their thermophysical properties are included (melting point, heat of fusion, thermal conductivity and density), although some authors give further information (congruent/incongruent melting, volume change, specific heat, etc.).

Table 7 shows a list of the commercial PCMs available in the market with their thermophysical properties as given by the companies (melting point, heat of fusion and density), and the company that is producing them.

Table 1. Inorganic substances with potential use as PCM.

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m^3)
$Na_2CrO_4 \cdot 10\ H_2O$	18 [51]	n.a.	n.a.	n.a.
$KF \cdot 4\ H_2O$	18.5 [3,8,49,52,53]	231 [3,8,49,52]	n.a.	1447 (liquid, 20°C) [49] 1455 (solid, 18°C) [49] 1480 [52]
$Mn(NO_3)_2 \cdot 6\ H_2O$	25.8 [54]	125.9 [54]	n.a.	1738 (liquid, 20°C) [54] 1728 (liquid, 40°C) [54] 1795 (solid, 5°C) [54]
$CaCl_2 \cdot 6\ H_2O$	29 [1,55] 29.2 [53] 29.6 [52] 29.7 [3,8,49] 30 [51] 29-39 [5]	190.8 [1,55] 171 [3,8,49] 174,4 [5] 192 [52]	0.540 (liquid, 38.7°C) [1,55] 0.561 (liquid, 61.2°C) [55] 1.088 (solid, 23°C) [1,55]	1562 (liquid, 32°C) [1,55] 1496 (liquid) [49] 1802 (solid, 24°C) [1,55] 1710 (solid, 25°C) [49] 1634 [5] 1620 [52]
$LiNO_3 \cdot 3\ H_2O$	30 [52]	296 [52]	n.a.	n.a.
$K_3PO_4 \cdot 7\ H_2O$	45 [51]	n.a.	n.a.	n.a.
$Zn(NO_3)_2 \cdot 4\ H_2O$	45.5 [51]	n.a.	n.a.	n.a.
$Ca(NO_3)_2 \cdot 4\ H_2O$	42.7 [53] 47 [51]	n.a.	n.a.	n.a.
$Na_2HPO_4 \cdot 7\ H_2O$	48 [53]	n.a.	n.a.	n.a.
$Na_2S_2O_3 \cdot 5\ H_2O$	48 [49,51-53] 48-49 [5]	201 [49] 209,3 [5] 187 [52]	n.a.	1600 (solid) [49] 1666 [5]
$Zn(NO_3)_2 \cdot 2\ H_2O$	54 [51]	n.a.	n.a.	n.a.
$NaOH \cdot H_2O$	58.0 [53]	n.a.	n.a.	n.a.
$Na(CH_3COO) \cdot 3\ H_2O$	58 [52,56] 58.4 [53,57-63]	264 [57-63] 226 [52]	n.a.	1450 [52]
$Cd(NO_3)_2 \cdot 4\ H_2O$	59.5 [53]	n.a.	n.a.	n.a.
$Fe(NO_3)_2 \cdot 6\ H_2O$	60 [51]	n.a.	n.a.	n.a.
$NaOH$	64.3 [52]	227.6 [52]	n.a.	1690 [52]
$Na_2B_4O_7 \cdot 10\ H_2O$	68.1 [53]	n.a.	n.a.	n.a.
$Na_3PO_4 \cdot 12\ H_2O$	69 [53]	n.a.	n.a.	n.a.
$Na_2P_2O_7 \cdot 10\ H_2O$	70 [52]	184 [52]		n.a.

n.a.: not available

Table 2. Inorganic eutectics with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m^3)
51-55% $Cu(NO_3)_3 \cdot 6H_2O$ + 45-49% $LiNO_3 \cdot 3H_2O$	16.5 [36]	250 [36]	n.a.	n.a.
45-52% $LiNO_3 \cdot 3H_2O$ + 48-55% $Zn(NO_3)_2 \cdot 6H_2O$	17.2 [36]	220 [36]	n.a.	n.a.
55-65% $LiNO_3 \cdot 3H_2O$ + 35-45% $Ni(NO_3)_2 \cdot 6H_2O$	24.2 [36]	230 [36]	n.a.	n.a.
66.6% $CaCl_2 \cdot 6\ H_2O$ + 33.3% $MgCl_2 \cdot 6\ H_2O$	25 [52]	127 [52]	n.a.	1590 [52]
45% $Ca(NO_3)_2 \cdot 6H_2O$ + 55% $Zn(NO_3)_2 \cdot 6H_2O$	25 [36,49]	130 [36,49]	n.a.	1930 [36,49]
48% $CaCl_2$ + 4.3% NaCl + 0.4% KCl + 47.3% H_2O	26,8 [49,52]	188,0 [52]	n.a.	1640 [52]
67% $Ca(NO_3)_2 \cdot 4\ H_2O$ + 33% $Mg(NO_3)_2 \cdot 6\ H_2O$	30 [36,49]	136 [36,49]	n.a.	1670 [36]
60% $Na(CH_3COO) \cdot 3\ H_2O$ + 40% $CO(NH_2)_2$	31.5 [36,64] 30 [65]	226 [36,64] 200.5 [65]	n.a.	n.a.
61.5% $Mg(NO_3)_2 \cdot 6\ H_2O$ + 38.5% NH_4NO_3	52 [55]	125.5 [55]	0.494 (liquid, 65.0°C) [55] 0.515 (liquid, 88.0°C) [55] 0.552 (solid, 36.0°C) [55]	1515 (liquid, 65°C) [55] 1596 (solid, 20°C) [55]
58.7% $Mg(NO_3) \cdot 6\ H_2O$ + 41.3% $MgCl_2 \cdot 6\ H_2O$	59 [55] 58 [52] 59.1 [36,49]	132.2 [55] 132 [52] 144 [36,49]	0.510 (liquid, 65.0°C) [55] 0.565 (liquid, 85.0°C) [55] 0.678 (solid, 38.0°C) [55] 0.678 (solid, 53.0°C) [55]	1550 (liquid, 50°C) [55] 1630 (solid, 24°C) [55] 1680 (solid) [36,49]
53% $Mg(NO_3)_2 \cdot 6\ H_2O$ + 47% $Al(NO_3)_2 \cdot 9\ H_2O$	61 [36,49]	148 [36,49]	n.a.	1850 [36]

% in weight

n.a.: not available

Table 3. Non-eutectic mixtures of inorganic substances with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m^3)
$Mg(NO_3)_2 \cdot 6\ H_2O$ / $Mg(NO_3)_2 \cdot 2\ H_2O$	55.5 [51]	n.a.	n.a.	n.a.
80% $Mg(NO_3) \cdot 6\ H_2O$ + 20% $MgCl_2 \cdot 6\ H_2O$	60 [66]	150 [66]	n.a.	n.a.

% in weight

n.a.: not available

Table 4. Organic eutectics with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m³)
37.5% urea + 63.5% Acetamide	53 [49]	n.a.	n.a.	n.a.
67.1% naphthalene + 32.9% benzoic acid	67 [55]	123.4 [55]	0.136 (liquid, 78.5°C) [55] 0.130 (liquid, 100°C) [55] 0.282 (solid, 38°C) [55] 0.257 (solid, 52°C) [55]	n.a.

% in weight

n.a.: not available

Table 5. Organic substances with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m³)
Dimethyl-sulfoxide (DMS)	16,5 [67]	85.7 [67]	n.a.	1009 (solid and liquid) [67]
Paraffin C_{16}-C_{18}	20-22 [9]	152 [9]	n.a.	n.a.
Polyglycol E600	22 [1,55]	127.2 [1,55]	0.189 (liquid, 38.6°C) [1,55] 0.187 (liquid, 67.0°C) [55]	1126 (liquid, 25°C) [1,55] 1232 (solid, 4°C) [1,55]
Paraffin C_{13}-C_{24}	22-24 [49]	189 [49]	0.21 (solid) [49]	0.760 (liquid, 70°C) [49] 0.900 (solid, 20°C) [49]
1-dodecanol	26 [8] 17.5-23.3 [3]	200 [8] 188.8 [3]	n.a.	n.a.
Paraffin C_{18}	28 [49] 27.5 [68] 22.5-26.2 [3]	244 [49] 243.5 [68] 205.1 [3]	0.148 (liquid, 40°C) [68] 0.15 (solid) [49] 0.358 (solid, 25°C) [68]	0.774 (liquid, 70°C) [49] 0.814 (solid, 20°C) [49]

Paraffin C_{20}-C_{33}	48-50 [49]	189 [49]	0.21 (solid) [49]	0.769 (liquid, 70°C) [49] 0.912 (solid, 20°C) [49]
Paraffin C_{22}-C_{45}	58-60 [49]	189 [49]	0.21 (solid) [49]	0.795 (liquid, 70°C) [49] 0.920 (solid, 20°C) [49]
Paraffin wax	64 [1,55]	173.6 [1,55] 266 [52]	0.167 (liquid, 63.5°C) [1,55] 0.346 (solid, 33.6°C) [1,55] 0.339 (solid, 45.7°C) [55]	790 (liquid, 65°C) [1,55] 916 (solid, 24°C) [1,55]
Polyglycol E6000	66 [1,55]	190.0 [1,55]	n.a.	1085 (liquid, 70°C) [1,55] 1212 (solid, 25°C) [1,55]
Paraffin C_{21}-C_{50}	66-68 [49]	189 [49]	0.21 (solid) [49]	0.830 (liquid, 70°C) [49] 0.930 (solid, 20°C) [49]

n.a.: not available

Table 6. Fatty acids with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m³)
Propyl palmiate	10 [8] 16-19 [3]	186 [8]	n.a.	n.a.
Caprylic acid	16 [1,55] 16.3 [49]	148.5 [1,55] 149 [49]	0.149 (liquid, 38.6°C) [1,55] 0.145 (liquid, 67.7°C) [55] 0.148 (liquid, 20°C) [49]	901 (liquid, 30°C) [1,55] 862 (liquid, 80°C) [49] 981 (solid, 13°C) [1,55] 1033 (solid, 10°C) [49]
Capric-lauric acid (65 mol%-35 mol%)	18.0 [69] 17-21 [3]	148 [69] 143 [3]	n.a.	n.a.
Butil stearate	19 [8,36] 18-23 [3]	140 [3,8] 123-200 [70] 200 [36]	n.a.	n.a.
Capric-lauric acid (45%-55%)	21 [8]	143 [8]	n.a.	n.a.
Dimethyl sabacate	21 [36,70]	120-135 [70] 135 [36]	n.a.	n.a.
Octadecyl 3-mencaptopropylate	21 [36]	143 [36]	n.a.	n.a.
34% Mistiric acid + 66% Capric acid	24 [55]	147.7 [55]	0.164 (liquid, 39.1°C) [55] 0.154 (liquid, 61.2°C) [55]	888 (liquid, 25°C) [55] 1018 (solid, 1°C) [55]
Octadecyl thioglycate	26 [36]	90 [36]	n.a.	n.a.
Vinyl stearate	27-29 [70] 27 [36]	122 [36,70]	n.a.	n.a.
Myristic acid	49-51 [71] 54 [49] 58 [55]	204.5 [71] 187 [49] 186.6 [55]	n.a.	861 (liquid, 55°C) [55] 844 (liquid, 80°C) [49] 990 (solid, 24°C) [55]
Palmitic acid	64 [1,55] 61 [72,73] 63 [49]	185.4 [1,55] 203.4 [72,73] 187 [49]	0.162 (liquid, 68.4°C) [1,55] 0.159 (liquid, 80.1°C) [55] 0.165 (liquid, 80°C) [49]	850 (liquid, 65°C) [1,55] 847 (liquid, 80°C) [49] 989 (solid, 24°C) [1,55]
Stearic acid	69 [1,55] 60-61 [73,74] 70 [49]	202.5 [1,55] 186.5 [73,74] 203 [49]	0.172 (liquid, 70°C) [49]	848 (liquid, 70°C) [1,55] 965 (solid, 24°C) [1,55]

% in weight

n.a.: not available

Table 7. Commercial PCMs available in the market

PCM name	Type of product	Melting temperature (°C)	Heat of fusion (kJ/kg)	Density (kg/L)	Source
RT20	Paraffin	22	172	0,88	Rubitherm GmbH [75]
ClimSel C 24	n.a.	24	108	1,48	Climator [76]
RT26	Paraffin	25	131	0,88	Rubitherm GmbH [75]
STL27	Salt hydrate	27	213	1,09	Mitsubishi Chemical [77]
AC27	Salt hydrate	27	207	1,47	Cristopia [78]
RT27	Paraffin	28	179	0,87	Rubitherm GmbH [75]
TH29	Salt hydrate	29	188	n.a.	TEAP [79]
STL47	Salt hydrate	47	221	1,34	Mitsubishi Chemical [77]
ClimSel C 48	n.a.	48	227	1,36	Climator [76]
STL52	Salt hydrate	52	201	1,3	Mitsubishi Chemical [77]
RT54	Paraffin	55	179	0,90	Rubitherm GmbH [75]
STL55	Salt hydrate	55	242	1,29	Mitsubishi Chemical [77]
TH58	n.a.	58	226	n.a.	TEAP [79]
ClimSel C 58	n.a.	58	259	1,46	Climator [76]
RT65	Paraffin	64	173	0,91	Rubitherm GmbH [75]
ClimSel C 70	n.a.	70	194	1,7	Climator [76]

n.a.: not available

10.4.3 Organic/inorganic materials

A comparison of the advantages and disadvantages of organic and inorganic materials is shown in Table 8.

Table 8. Comparison of organic and inorganic materials for heat storage.

• Organics	• Inorganics
Advantages - No corrosives - Low or none undercooling - Chemical and thermal stability	Advantages - Greater phase change enthalpy
Disadvantages - Lower phase change enthalpy - Low thermal conductivity - Inflammability	Disadvantages - Undercooling - Corrosion - Phase separation - Phase segregation, lack of thermal stability

Notable among inorganic materials are hydrated salts and their multiple applications in the field of solar energy storage [1,6]. In chapter 1 of Lane [50] there is an extensive review of phase change materials and especially hydrated salts. Chapter 3 of the same work covers the different types of encapsulation and their compatibility with different materials.

A significant number of authors have based their work on organic materials such as alkanes, waxes or paraffins [35,80-85]. Within organic materials, there is a class called MCPAM (Phase change materials made up of molecular alloys), formed by alkane-based alloys which have the advantage of being thermoadjustable [86], that is, they allow alterations to the phase change temperature through their composition. There is abundant information on this subject in the literature [86-96].

As far as concerns the storage temperature or phase change, the heat transfer in accumulators can be improved choosing the PCM in such a way that its phase change temperature optimises the thermal gradient with respect to the substance with which the heat is being exchanged (Farid [35], Hassan [97], Stub [98]). For example, with paraffins and alkanes it is possible to vary the number of carbon atoms or form different molecular alloys which allows a practically continuous variation of the phase change temperature within certain ranges.

10.5 Thermophysical properties

It can be concluded from the information compiled that the main characteristics required of phase change materials are those indicated in Table 9.

Table 9. Important characteristics of energy storage materials.

Thermal properties	Physical properties	Chemical properties	Economic properties
Phase change temperature fitted to application High change of enthalpy near temperature of use High thermal conductivity in both liquid and solid phases (although not always)	Low density variation High density Small or no undercooling	Stability No phase separation Compatibility with container materials Non toxic, non flammable, non polluting	Cheap and abundant

Thermophysical properties determination

Speyer [99] gave a good overview of the thermal analysis methods in general, but also Eckert et al. [100] and should be mentioned. Naumann and Emons [53] and others [19,101] focussed their studies on thermal analysis methods for PCMs.

Analysis techniques used to study phase change are mainly conventional calorimetry, differential scanning calorimetry (DSC) (Fig. 18) and differential thermal analysis (DTA). Among studies relating to DSC, it is worth citing Flaherty [102] for characterisation of hydrocarbons and natural waxes, Giavarini [103] for characterisation of petroleum products and Salyer [80] for characterisation of paraffins.

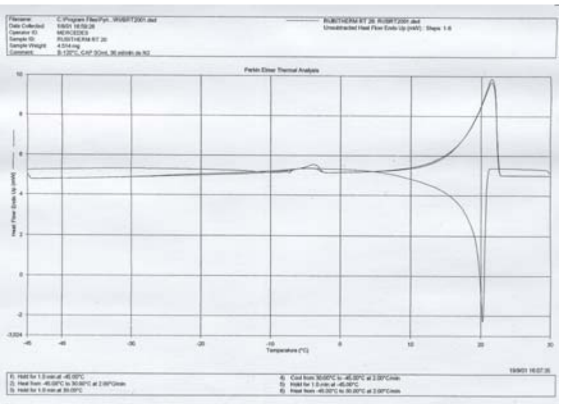


Fig. 18. DSC of paraffin RT20.

As is mentioned in Gibbs [104], there is considerable uncertainty about the property values provided by manufacturers (who give values of pure substances) and it is therefore advisable to use DSC to obtain more accurate values.

Yinping [105] reviews the above-mentioned conventional methods of PCM property analysis and points out their limitations, of which the following stand out:

Small quantities of sample are analysed (1-10 mg), although some behaviour of the PCMs depends on their quantity.

The analysis instrumentation is complex and expensive.

Phase change cannot be visually observed.

Yinping proposes a simple method for determining phase change temperature, undercooling, enthalpy, specific heat, and thermal conductivity in solid and liquid phases. Temperature – time graphs are drawn and properties evaluated for comparison with the graphs of the other known materials are used (usually pure water) as reference.

Marín et al. [106] developed a further evaluation procedure to determine specific heat and enthalpy as temperature dependent values. The results obtained are presented in the form of enthalpy-temperature curves, and an experimental improvement is proposed (Fig. 19 and 20).

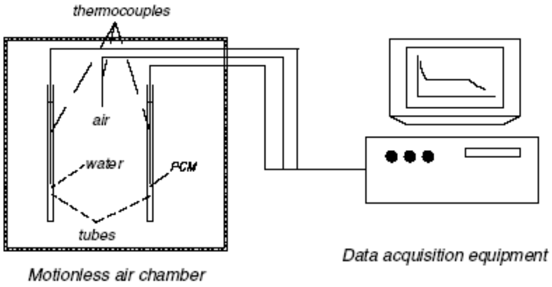


Fig. 19. Experimental set-up of the T-history method.

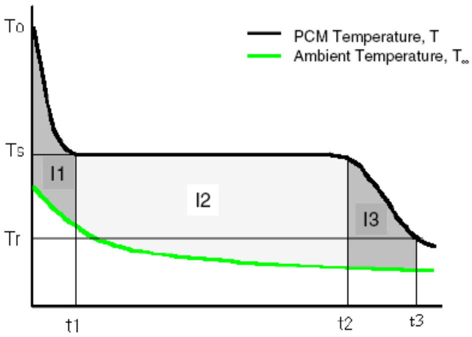


Fig. 20. Temperature–time curves for PCM and ambient air.

Another method for determining thermal conductivity in PCM at temperatures around phase change temperature is established in Delaunay [107]. This method is based on analysing one-dimensional conduction in a cylinder. Various alternatives are proposed in the literature for the enhancement of thermal conductivity such as increasing the heat transfer surface, inserting metallic fins (Sadasuke [108]) or adding metallic additives (Bugaje [109]). In Manoo [110] there are some interesting charts relating to variations in conductivity, density and enthalpy against temperature for some paraffins.

10.6 Long term stability

Insufficient long term stability of the storage materials and containers is a problem that has limited widespread use of latent heat stores. This poor stability is due to two factors: poor stability of the materials properties due to thermal cycling, and/or corrosion between the PCM and the container.

10.6.1 Stability of the PCM-container system

A relevant aspect is the useful life of these systems, and the number of cycles they can withstand without any degrading of their properties (Fig. 21 and 22). Hadjieva [81] uses three paraffin mixtures; the lack of effect of the cycles on the properties of paraffin is verified. Other authors, such as Gibbs [104], also confirm that neither the cycles nor contact with metals degrade the thermal behaviour of paraffin and that they therefore have excellent thermal stability.

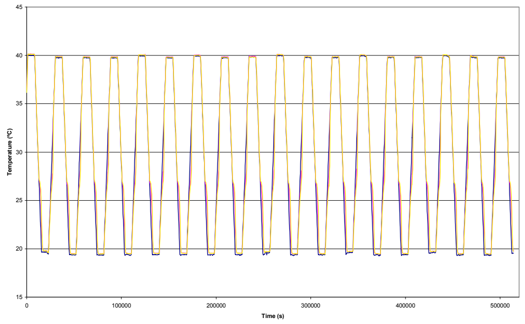


Fig. 21. Several cycles of a paraffin

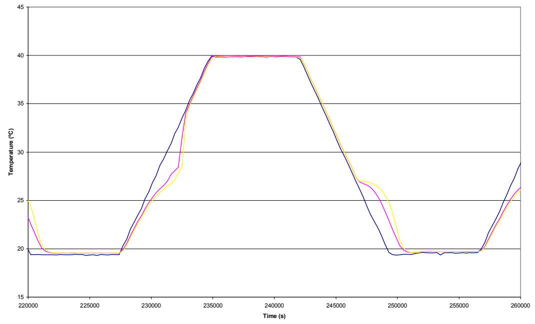


Fig. 22. One cycle of a paraffin.

10.6.2 Corrosion of the materials

Most references on corrosion tests using salt hydrates were performed with diluted salt hydrates, as typically used in the chemical industry, and only a few presented results, usually based on observation over experimental set-ups [111,112]. Porisini [113] tested the corrosion of four commercially available salt hydrates used as PCMs in 1988.

Recently, Cabeza et al. [114-117] studied corrosion resistance of five common metals (aluminium, brass, copper, steel and stainless steel) in contact with molten salt hydrates (zinc nitrate hexahydrate, sodium hydrogen phosphate dodecahydrate, calcium chloride hexahydrate, sodium carbonate, potassium hydrogen carbonate, potassium chloride, water, sodium acetate trihydrate, and sodium tiosulphate pentahydrate) in an immersion corrosion test (Fig. 23).

Fig. 23. Aluminium treated with a salt hydrate. From left to right: before treatment, after treatment, and after treatment in contact with graphite.

Some investigations have been concerned with corrosion of molten salts at high temperature. Already in 1980, Heine et al. [118] studied the corrosion performance of six molten salts melting between 235 and 857°C versus four metals used at these temperatures.

10.6.3 Phase segregation and subcooling problems

The high storage density of salt hydrate materials is difficult to maintain and usually decreases with cycling. This is because most hydrated salts melt congruently with the formation of the lower hydrated salt, making the process irreversible and leading to the continuous decline in their storage efficiency (Fig. 24).

This problem was studied first in the 70s [119-123] using the extra water principle. The extra water principle is a method that consists in adding extra water to the salt hydrate so that all the anhydrous salt can be dissolved in the water at the melting point, that is, the storage medium is a saturated salt solution at the melting point. The storage medium is stirred softly while it is cooled or heated.

Segregation can be prevented changing the properties of the salt hydrate with the addition of another material that can hinder the heavier phases to sink to the bottom [124]. This can be achieved either with gelling or with thickening materials. Gelling means adding a cross-linked material (e.g. polymer) to the salt to create a three dimensional network that holds the salt hydrate together. Thickening means the addition of a material to the salt hydrate that increases the viscosity and hereby holds the salt hydrate together [6].

Subcooling is another serious problem associated with all hydrated salts. It appears when a salt hydrate starts to solidify at a temperature below its congelating temperature (Fig. 25). Several approximations have been studied to solve this problem. One is the use of hydrated salts in direct contact heat transfer between an immiscible heat transfer fluid and the hydrated salt solution [4]. Another solution is the use of nucleators [6,125].

Fig. 24. Segregation of a salt hydrate.

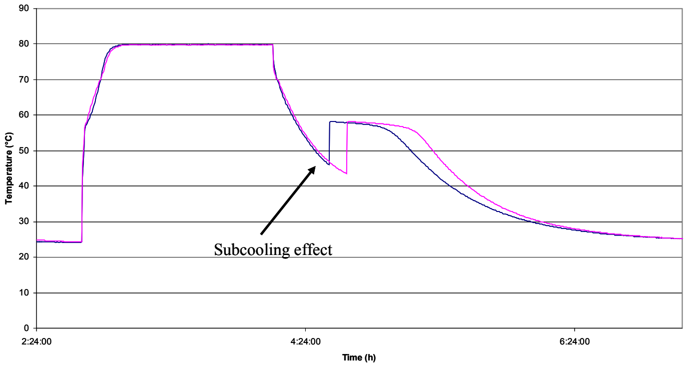


Fig. 25. Subcooling effect of a salt hydrate.

10.7 Encapsulation of the materials

The encapsulation of the PCM has developed interest in several researchers. Advantages and disadvantages of different geometries of PCM encapsulation with different materials and their compatibility was discussed by Lane [6].

For the use of PCM in buildings applications, an encapsulation of PCM (50-80%) with unsaturated polyester matrix (45-10%), and water (5-10%) was studied by Morikama et al. [8]. In the same area, Inaba [126] and Lee & Choi [10] propose using the storage substance integrated with the building materials without encapsulation ("Shape-stabilised paraffin": 74% paraffin + 26% HDPE [high-density polyethylene]). Structural stability is achieved using high-density polyethylene which retains the paraffin when in liquid phase. Hawes and Feldman [127] have considered the means of PCM incorporation: direct incorporation, immersion and encapsulation. The PCM must be encapsulated so that it does not adversely affect the function of the construction material.

For many applications, PCMs are microencapsulated, and this has been studied by several researchers [18,128,129] and developed by companies like BASF [16,130]. Nevertheless, the potential use of microencapsulated PCMs in various thermal control applications is limited to some extent by their cost. Hawlader et al. [131] have prepared and compared encapsulated paraffin waxes by complex coacervation and spray drying methods, and have shown that microcapsules have high energy storage and release capacity, which depends on core to coating ratio (Fig. 26 and 27).

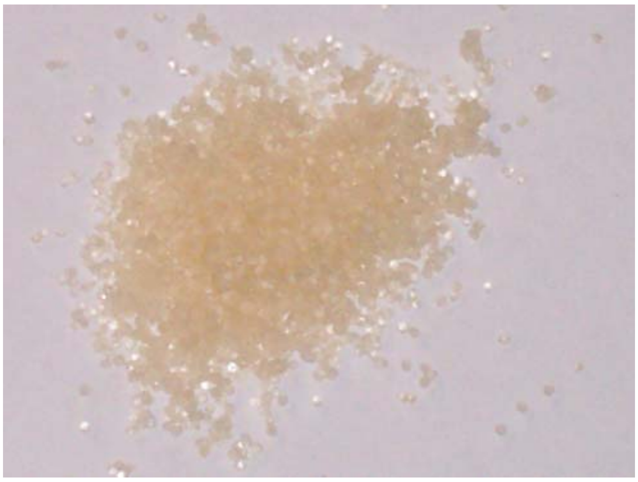


Fig. 26. Microencapsulated PCM by copolymerization.

Fig. 27. Microencapsulated PCM commercialized by BASF.

Commercial companies have found different ways of encapsulating their PCMs. For example, Cristopia [78] encapsulates the PCM in nodules (Fig. 28). The spherical nodules *(balls)* are blow moulded from a proprietary blend of polyolefins and filled with PCM. A range of PCMs allow thermal energy to be stored at temperatures between -33°C and +27°C. Rubitherm [75] developed a heat storage granulate in which approx. 35% wt. of a phase change material is bound (Fig. 29). This product offer the advantage of maintaining their macroscopic solid form during phase change.

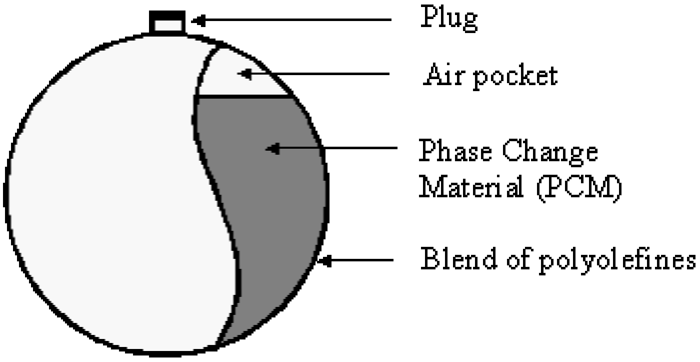


Fig. 28. Spherical nodule filled of PCM developed by Cristopia.

Fig. 29. Granulated developed by Rubitherm.

10.8 Fire retardation of PCM-treated construction materials

An article by Salyer [132] reports on reaction to fire and the possible fire-retardant additives (organic halogenous compounds) that improve the response to fire of the material. This paper covers an important number of applications in the field of heating and cooling, and sets out a review of materials, advantages, disadvantages and characteristics of a series of PCM substances applicable to thermal storage in buildings. Of the four possible PCM analysed, those with the greatest advantages were of the paraffin type (hydrocarbons; -60 to 80ºC) whose origin can be from the polymerisation of ethylene or as a by-product of petroleum.

Banu et al. [133] conducted flammability tests on energy storing wallboard. Comparison of the test results with similar data for other building materials indicates the possibility of reducing the flammability of energy storing wallboard by incorporation of a flame retardant.

10.9 Heat transfer enhancement

There are several methods to enhance the heat transfer in a latent heat thermal store. The use of finned tubes with different configurations has been proposed by various researchers such as Abhat et al. [134], Morcos et al. [135], Sadasuke [136], Costa et al. [137], Padmanabhan [138], Velraj [139,140], Ismail et al. [141] and Stritih [142] use finned tubes in thermal storage systems (Fig. 30).

Fig. 30. Heat exchanger with finned tubes.

Several other heat transfer enhancement techniques have been reported. Siegel [143] studied the improvement in solidification rate in molten salt dispersed with high conductivity particles. Another method used is to embed the PCM in a metal matrix structure [144-148]. The use of thin aluminium plates filled with PCM was developed by Bauer and Wirtz [149].

Mehling et al. [150-153] and Py et al. [154] proposed a graphite-compound-material, where the PCM is embedded inside a graphite matrix (Fig. 31). The main advantage of such a material is the increase in heat conductivity in the PCM without much reduction in energy storage, but other advantages are the decrease in subcooling of salt hydrates and the decrease of volume change in paraffins.

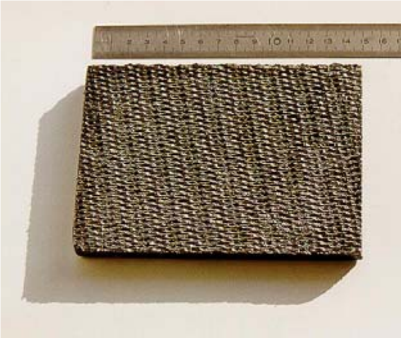


Fig. 31. Graphite-compound-material used to increase heat transfer (developed by ZAE Bayern and commercialized by SGL Technologies).

The use of graphite as heat transfer enhancement material has also been studied by other researchers, such as Fukai et al. [155-157]. They developed brushes made of carbon fibres. The feature of this method is that the volume fraction of the fibres is accurately and easily controlled and that the fibres with low volume fraction are entirely dispersed in the PCM. Xiao et al. [158] developed a composite based on paraffin, styrene-butadiene-styrene (SBS) triblock copolymer and exfoliated graphite. They claimed that in the composite paraffin undergoes solid-liquid phase change, and there is no leakage of it even in the state of melting. The composite exhibits high thermal conductivity and nearly 80% of the latent heat of fusion per unit mass of the paraffin.

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11. Microencapsulated PCM Slurries

by Andreas Heinz, Wolfgang Streicher

11.1 General Considerations about PCM slurries

One major drawback of latent thermal energy storage is the low thermal conductivity of the materials used as PCM. This circumstance makes heat transfer into / out of a thermal energy storage during charging / discharging difficult.

A lot of work has been performed in order to enhance the conductivity of the PCM by embedding structures of materials with high thermal conductivity (Velraj et al., 1999; Hamada et al., 2002) or to shorten the heat transport distances inside of the PCM by means of highly dispersed heat exchangers with low distances between fins or pipes (Domañski et al., 2000). Another strategy is to encapsulate the PCM into containers of different shapes like e.g. plates, cylinders or spheres (Arkar et al., 2003; Bruno, Saman, 2002, CRISTOPIA “nodule”). These container elements should have a high ratio of surface area to volume, or respectively a large heat transfer area per volume unit and short transport distances in the PCM itself. This results in a container that should be as small as possible.

That’s where microencapsulated PCMs become interesting. PCM containers with a diameter of 2-20 µm offer the advantage of very high surface area/volume ratios and extremely short transport distances. In addition, if these microcapsules are dispersed in a fluid (mostly water), they form a pumpable slurry that can be used as energy transport- and storage media, as a so-called PCM slurry.

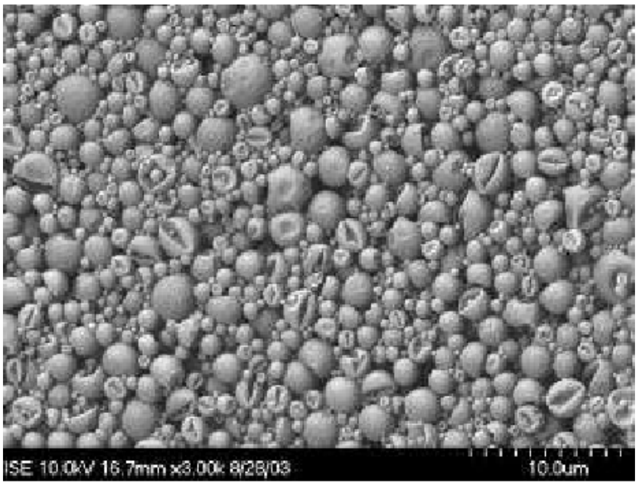

Figure 11.1.1: SEM-picture of the dried microcapsules in a PCM slurry (ISE Freiburg)

Concerning calculations, the PCM-slurry can be treated like a homogeneous material (Lumped Capacitance Method). This assumption implies that temperature gradients within the solid are negligible. This is closely approximated if the resistance to conduction within the considered body is small compared with the resistance to heat transfer between the solid and its surroundings. The fulfilment of this condition can be analysed by means of the Biot number, which should have a value of smaller than 0.1 (Incropera, DeWitt, 2002). The Biot number is given by the heat transfer coefficient h, the thermal conductivity k and the characteristic length L_c, which in this case can be assumed as the radius of a microcapsule.

$$Bi = \frac{h * L_c}{k} < 0.1$$

Equ. 11.1-1

If one calculates the Biot number for a PCM microcapsule he will get a value that is far below 0.1. This implies that within a microcapsule no conduction and therefore temperature gradients have to be considered at all. Therefore the low conductivity of PCM materials is no problem if they are microencapsulated.

11.2 Storage capacity and thermodynamic properties

The idea of latent thermal energy storage is to use the latent heat of fusion of phase change materials. The relatively large amount of latent heat of the phase transition shall provide a higher energy storage density compared to the traditional sensible heat storage systems. Unfortunately the paraffins that are used as PCM in microcapsules have a lower sensible heat capacity than water. Therefore, when a system is operated with high temperature differences, the advantage of the latent heat is reduced due to the lower sensible heat of the PCM. In such applications water storages are more favourable. Figure 11.2.1 shows the specific heat capacity of a slurry with microencapsulated paraffin with a phase transition temperature of about 60 °C as a function of temperature. The basis of the figure is a T-history measurement (Marin et al., 2002) of a wet slurry probe (50 % concentration of microcapsules in water), out of which the graphs for different concentrations were generated. The slurry used in this measurement has a melting temperature range of about 20 K, a latent heat of fusion of about 140 kJ/kg and a sensible heat capacity of about 2.7 kJ/kg.K.

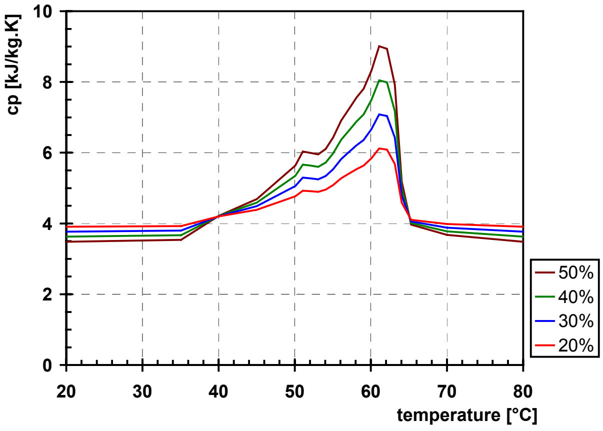

Figure 11.2.1: specific heat as a function of temperature for different concentrations of the 60°C slurry

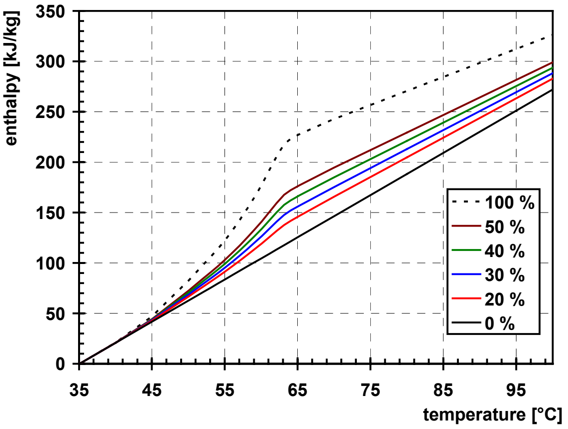

Figure 11.2.2: spec. enthalpy as a function of temperature for different conc. of the 60°C slurry

In Figure 11.2.2 the specific enthalpies for different concentrations of the slurry are shown, the zero-point of enthalpy was set to 35 °C, where the melting of the PCM sets in.

For high temperature differences of more than 20 K and especially with low concentrations of PCM the storage capacity is not much better than for water. Therefore PCM slurries should potentially be used in systems that are operated with low temperature differences. The concentration of microcapsules should be as high as possible. Figure 11.2.3 shows the theoretical improvement of the storage capacities (compared to water) of different slurry concentrations in different temperature ranges.

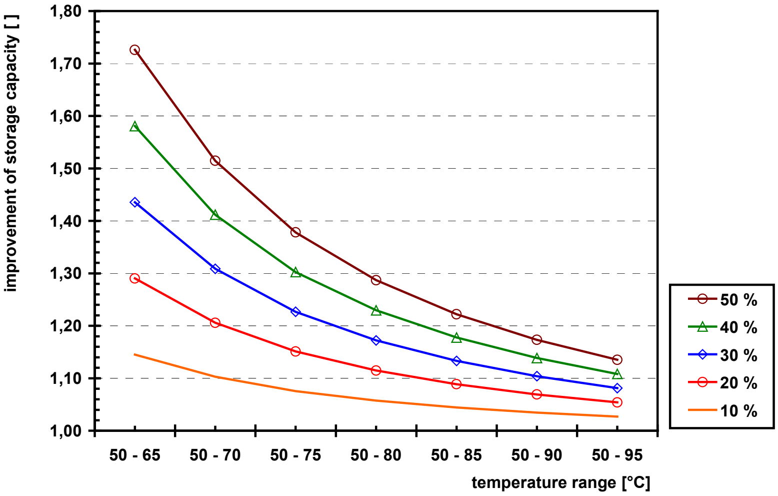

Figure 11.2.3: storage capacity enhancement (compared to water) of different concentrations of the 60 °C slurry in different temperature ranges

The viscosity of PCM slurries is strongly dependent on the concentration of microcapsules and the temperature of the slurry. Figure 11.2.4 shows the viscosity as a function of temperature for 3 different concentrations (Egolf et al., 2004). For higher concentrations the viscosity increases strongly. For instance a slurry with a concentration of 50 % and a temperature of 20 °C has a viscosity of about 300 mPa.s.

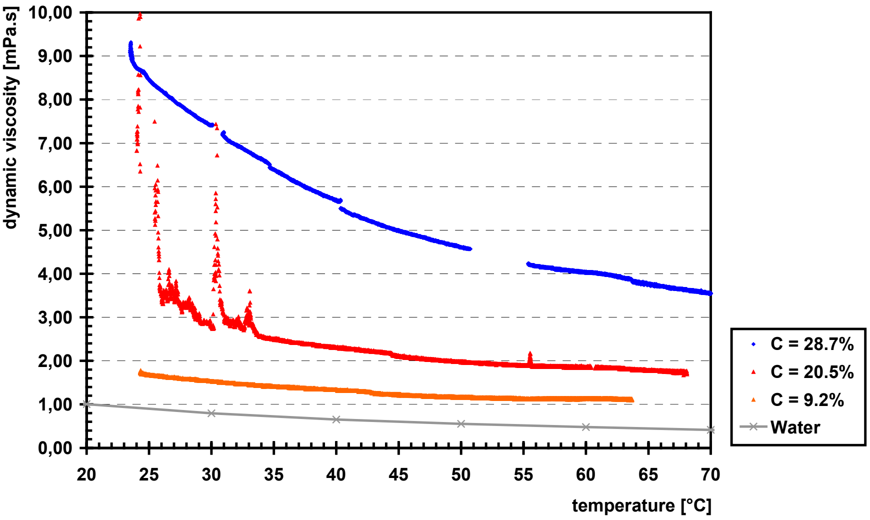

Figure 11.2.4: dynamic viscosity of a PCM-slurry as a function of concentration and temperature (Egolf et al., 2004)

11.3 Experimental work with PCM-slurries

11.3.1 Measurements in a storage tank with internal heat exchanger

An experimental storage set-up with a volume of 200 liters was built up in order to analyze the storage capacity and the heat transfer into and out of the storage tank. The tank was built out of perspex in order to be able to observe a formation of layers of different PCM-concentrations due to density differences, stratification effects etc. The slurry inside the tank was charged via a typical internal heat exchanger, movement inside of the tank was only caused by natural convection.

A PCM-slurry from BASF with a melting point of 60 °C was analyzed in the storage tank with different concentrations of microcapsules in water of about 50 %, 40 % and 30 %.

One question, that was arising, was whether there is a temperature gradient in horizontal direction in between the heat exchanger pipes. The higher the gradient, the lower the influence of convection and therefore the lower the heat transfer in horizontal direction. Thermocouples were mounted at different horizontal positions and at different vertical levels (see the arrangement in Figure 11.3.2). These sensors were calibrated to an accuracy of 0.1 K in order to be able to measure even small gradients.

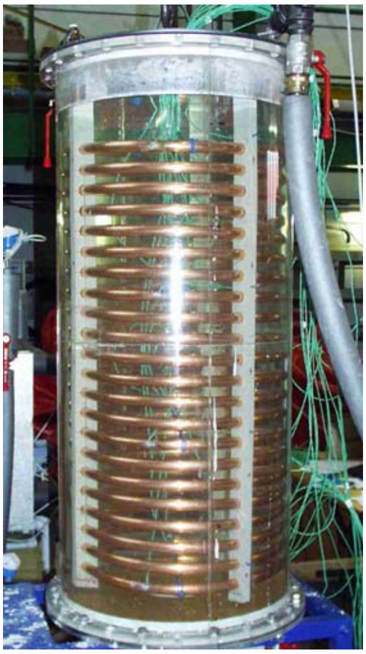

Figure 11.3.1: spiral type heat exchanger in the experimental tank

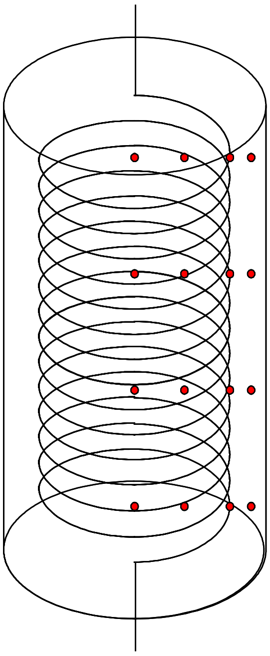

Figure 11.3.2: placement of the temperature sensors in the storage tank

In a series of measurements the tank was heated up and cooled down in a temperature range from 50 °C to 70 °C which is approximately the melting temperature range of the slurry. The flow temperature of the heat exchanger fluid was kept constantly at 70 °C for heating and 50 °C for cooling all through the experiments. The results showed that there is no (measurable) temperature gradient in horizontal direction even with a concentration of

50 %. This implies that, just as in a water tank, heat transfer is dominated by convection and that a tank filled with a PCM slurry can be operated with a standard heat exchanger.

As an example Figure 11.3.3 shows the evolution of temperatures inside the tank during an experiment with a slurry with a concentration of 50 %. 8 temperatures at 4 different vertical levels are shown, at each vertical level 2 temperatures at different horizontal positions are shown. The temperature differences are not higher than the accuracy of the used thermocouples.

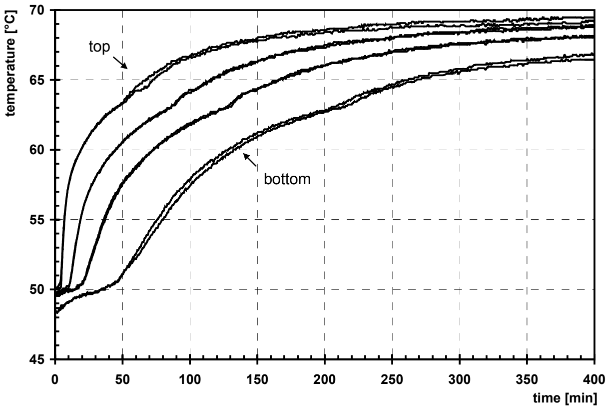

Figure 11.3.3: measured temperature curves for a 50 % concentrated slurry during charging the tank

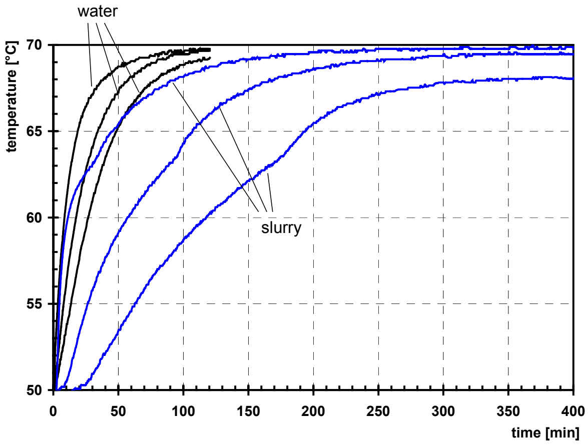

Figure 11.3.4: temperature curves in 3 different vertical positions for water and a 50 % concentrated slurry during charging the tank

Figure 11.3.4 shows a comparison of the measured temperatures in 3 different vertical positions (top, middle, bottom of the tank) during charging the tank for water and for a slurry with a concentration of 50 %. The time needed for heating up the slurry is much longer than for water, which is on one hand a result of the higher storage capacity but on the other hand mainly of the higher viscosity and therefore lower heat transfer coefficients of the slurry.

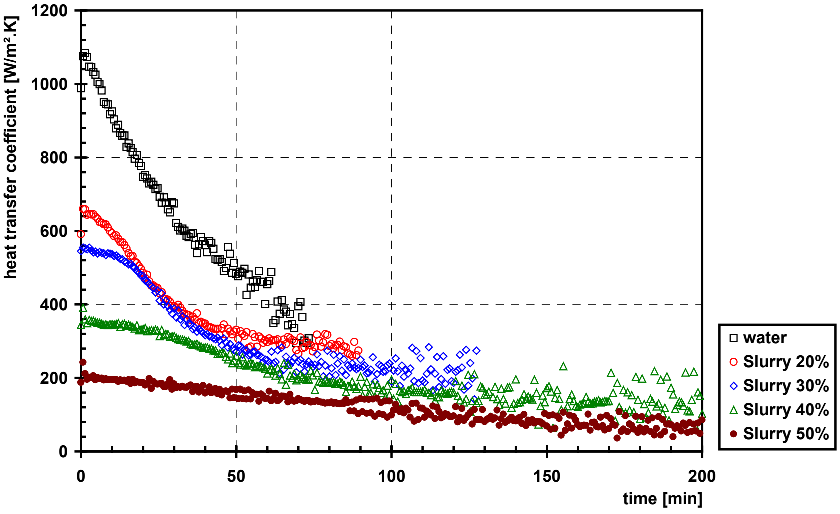

Figure 11.3.5: evolution of the heat transfer coefficients (natural convection) with time for different storage fluids during charging the storage tank

The heat transfer coefficient for natural convection was calculated out of the measured data. Figure 11.3.5 shows the evolution of the heat transfer coefficient with time during charging the tank filled with different storage fluids. The heat transfer coefficient decreases with increasing charging of the storage tank due to the decreasing temperature difference between the heat exchanger and the storage fluid. Because of the increasing viscosities the heat transfer coefficient also decreases with increasing concentration of microcapsules in the water. With the lowest used concentration of 20 % the values of the heat transfer coefficient are only around 50 % of those measured with water.

11.3.2 Analysis of the heat transfer in a flat plate heat exchanger

In a series of measurements the heat exchanger characteristics of a flat plate heat exchanger concerning the heat transfer coefficients was determined both for water and for different concentrations of PCM slurries. The heat exchanger was operated in different modes concerning the flow rates through the two fluid cycles. Side 2 was flown through by water in the first test run and by slurries with different concentrations in the second run, while side 1 was flown through by water in both test runs. The measurements were carried out for 2 different flow rates on side 1 and for 5 flow rates on side 2.

The results are shown in Figure 11.3.7. The convection heat transfer coefficient on the secondary side decreases with increasing concentrations of the slurry, due to the higher viscosity and the lower thermal conductivity. This is why the overall heat transfer coefficient is decreasing. With the lowest used concentration of 20 % the heat transfer coefficient is about 30 % lower than with water, with a concentration of 40 % it decreases to about 40 % of the values measured with water.

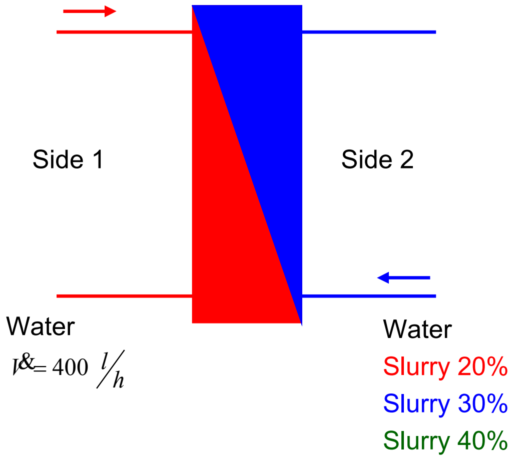

Figure 11.3.6: experimental set up for the flat plate heat exchanger

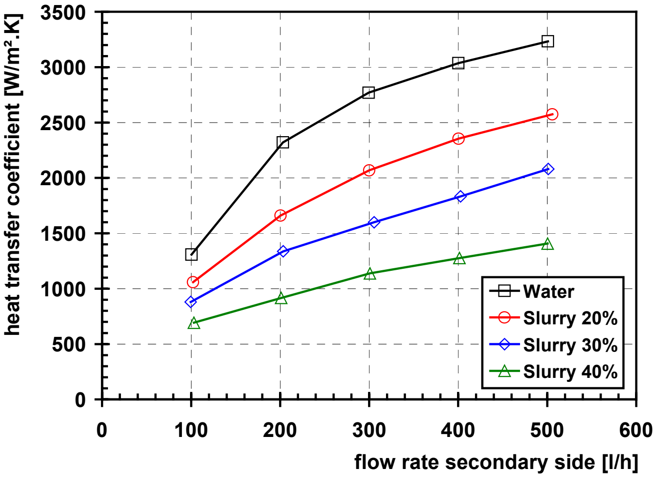

Figure 11.3.7: overall heat transfer coefficient of the heat exchanger for different fluids on the secondary side (primary side is flown through by water with 400 l/h)

side is flown through by water with 400 l/h)

In order to enable a calculation of a counterflow heat exchanger that is operated with PCM-slurries, a heat exchanger model was developed, that considers the c_p as a function of the temperature in the respective location within the heat exchanger.

As an example Figure 11.3.8 shows a comparison between an operation with water on both sides of the heat exchanger and an operation where the hot side of the heat exchanger is flown through by a slurry with a concentration of 30 %. The inlet temperatures and flow rates are the same for both calculations. The lower U-value for the slurry flow according to Figure 11.3.7 has been taken into account. Despite of the lower U-value the exchanged power of the heat exchanger is approximately the same as for a water/water flow. This is because of the higher mean temperature difference that is a result of the higher heat capacity of the slurry.

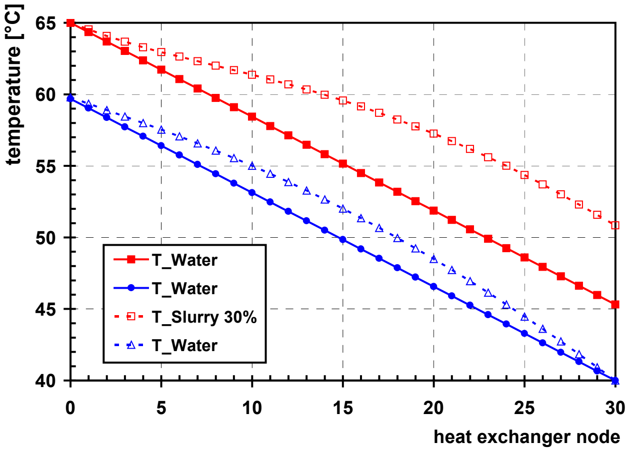

Figure 11.3.8:temperature profiles in a counterflow heat exchanger for water/water und slurry/water flow

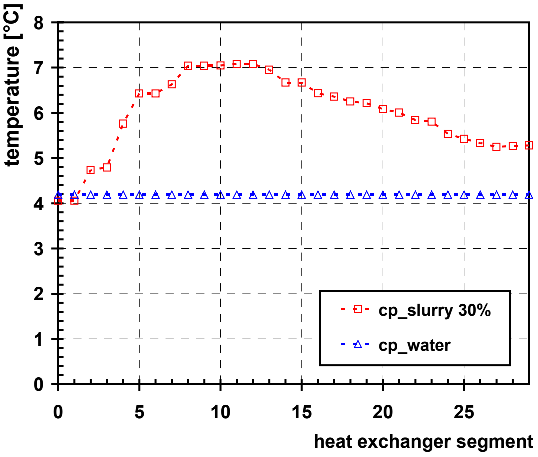

Figure 11.3.9: c_p-profiles in the heat exchanger for slurry/water

11.3.3 Pressure drop

The pressure drop over the flat plate heat exchanger was measured for different concentrations of the slurry. The results are shown in Figure 11.3.10. The pressure drop is rising with increasing concentrations of microcapsules in water due to the increasing viscosity. With increasing concentration there is also an increasing dependence of the pressure drop on the temperature (see Figure 11.3.11), which is a result of the high dependence of the viscosity on the temperature (see Figure 11.2.4).

Up to a concentration of 30 % the pressure drop is not much higher than for water, therefore this concentration should be a good compromise between storage capacity on the one hand and pressure drop on the other hand (for applications where the slurry is pumped).

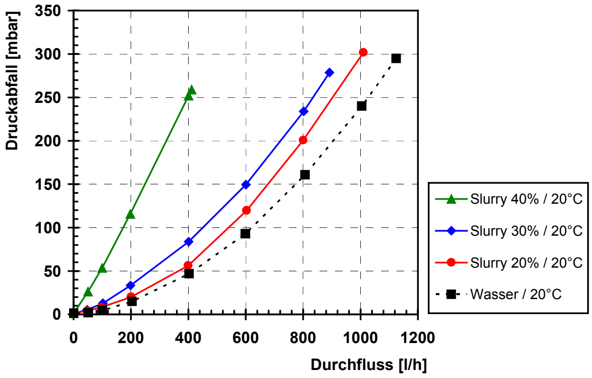

Figure 11.3.10: pressure drop in the heat exchanger for different concentrations at 20 °C

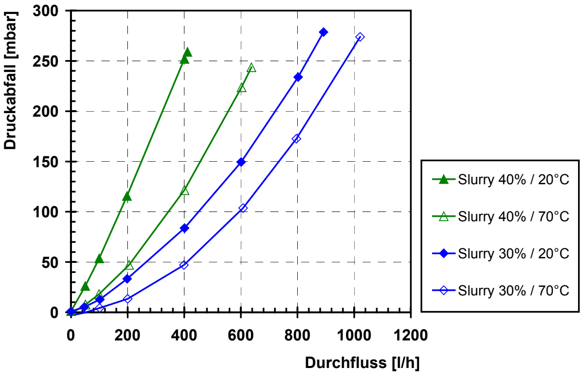

Figure 11.3.11: pressure drop in the heat exchanger for different temperatures and concentrations

Acknowlegement

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12. Sorption and Thermo-Chemical Storage

By Chris Bales, Paul Gantenbein, Andreas Hauer, Dagmar Jaehnig, Henner Kerskes, Hans-Martin Henning, Tomas Nuñez, Klaas Visscher, Eberhard Laevemann, Matthias Peltzer

Thermo-chemical storage is an indirect way to store heat. The heat is not stored directly as sensible or latent heat but by way of a physico-chemical process like adsorption or absorption that consumes heat in charging mode and releases heat in discharging mode.

12.1 Classification of Thermo-Chemical Storage Principles

By Hans-Martin Henning

Thermo-chemical storage systems can be divided into **open and closed systems**. In open systems the gaseous working fluid is directly released to the environment and thereby the entropy is released; therefore only water is a possible candidate as a working fluid. Examples of open systems are sorption processes for desiccant systems and heat storage systems based on the adsorption process.

In closed systems, not the working fluid itself but the entropy is released to the environment via a heat exchanger. Closed systems work with a closed working fluid circuit which is isolated from the atmosphere.

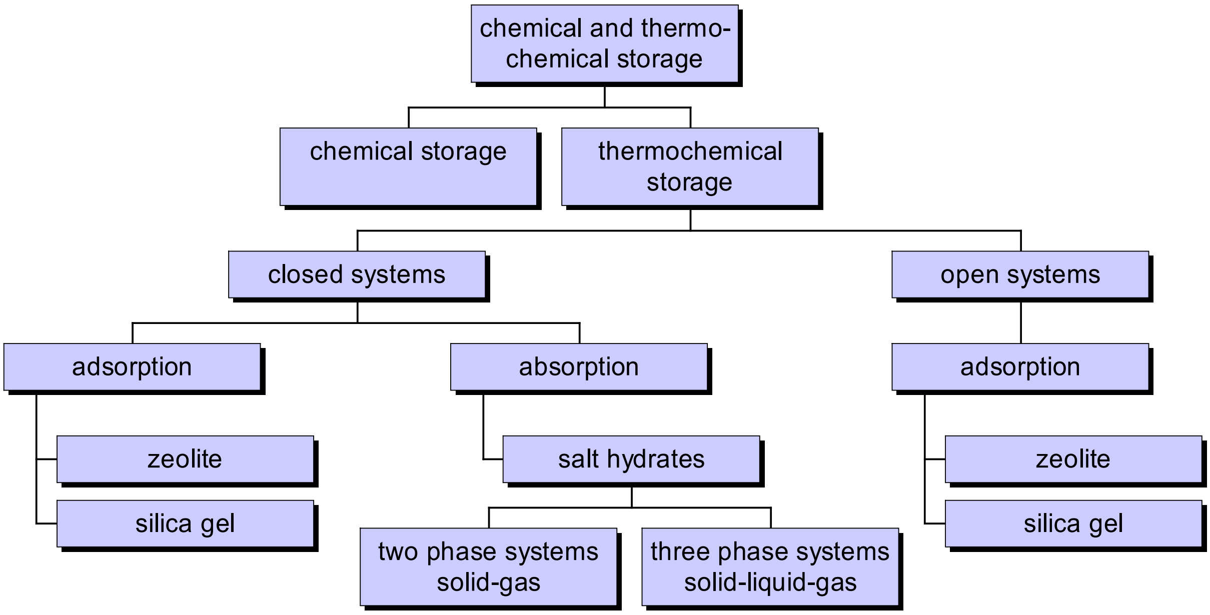

Figure 1. Classification of chemical and thermo-chemical processes for heat storage applications.

For closed systems, two main lines can be defined: adsorption and absorption. Adsorption is the bonding of a gas on the surface of a solid, in the absorption process a new compound out of the absorbent and the working fluid is formed. This is mainly the case in salt hydrates or salt ammoniates. Two and three phase systems are usual with solid-gas and solid-liquid-gas as the basic phases.

While these two concepts use the same physical principles of adsorption and/or absorption in an open system the transfer of heat and mass is supported by the fluid air which directly stems from the environment as the energy and material (water vapour) source. After fulfilling the assigned task of heat and mass transfer in the process the air is released back to the environment.

12.2 Thermodynamics and Material Properties

by Paul Gantenbein, Tomas Núñez, Dagmar Jaehnig, Henner Kerskes, Hans-Martin Henning, Chris Bales

A thermo-chemical storage system is a system consisting of a working fluid (mostly water) , also called sorbate, and a sorption material, usually referred to as the sorbent. The sorption material can be a porous solid (e.g. silica gel, zeolite) or salt-hydrate solutions with a high affinity for water.

The principle uses the fact that the sorption material releases water vapour when heated and releases heat when water vapour is adsorbed or absorbed. The process can be written as follows

$$AB \leftrightarrow A + B$$

with	A	sorption material
	B	working fluid
	AB	working fluid adsorbed or absorbed on the sorption material.

The effect of the sorption material is to provide a shift from the vapour-liquid equilibrium of the pure working fluid to another vapour-condensed phase equilibrium of the working fluid in the presence of the sorption material.

During the charging phase, heat is needed to overcome the (reversible) bonding between the working fluid molecules and the molecules of the sorption material. The gaseous working fluid is then released to the environment (open systems) or condensed i.e. the heat of evaporation and the associated entropy is released to the environment (closed systems). This means that energy and entropy flux are separated using this storage principle. In the reverse process step of storage discharge the entropy has to be taken up from the environment in order to combine again energy and entropy flux.

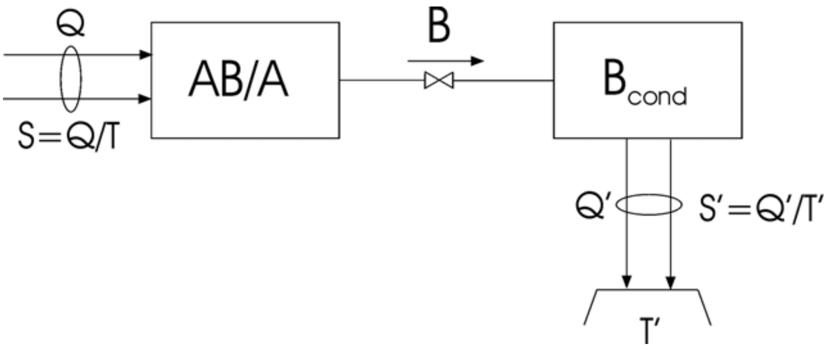

Figure 2: Indirect heat storage by way of a reversible thermo-chemical reaction. Closed system with condensation of the gaseous working fluid. [1]

This means that indirect heat storage is not independent from the environment because the entropy has to be released to the environment in charging mode and taken up from the environment in discharging mode. The advantage of an indirect heat storage is the high energy density because the entropy is not stored in the storage tank but released to the environment.

The energy of adsorption / absorption (ΔH_a) as shown in Equ. 1 is dependent on the energy for the phase change (evaporation) of the working fluid (ΔH_v) and the bonding energy of the working fluid to the sorbent (ΔH_b). The heat of evaporation is dependent on both the temperature and pressure, while the bonding energy is dependent on both these factors liquid sorbents as well as the load c ($kg_{H2O}/kg_{sorbent}$) for solid adsorbents.

$$\Delta H_a = \Delta H_v + \Delta H_b \qquad \text{Equ. 1}$$

Selection criteria / requirements for sorbate – sorbent pairs

As a prerequisite for the decision to apply an adsorption or an adsorption system together with solar collectors as heat source, a list of selection criteria for the appropriate materials has to be kept in mind. The main parameters of importance are:

- High uptake c(T, p) [kg(sorbate)/kg(sorbent)] of working fluid - if water is the sorbate, a high selectivity for water.
- High energy density - thermal energy density at the operating temperature.
- Regeneration by heat at a relatively low regeneration temperature.
- Low regeneration time.
- Mass transport of the working fluid to the sorbent.
- Heat transport to/from the sorbent.
- Easy to handle – non poisonous.
- Low costs – low investment costs.

The criteria listed above are often contradictory and an optimum has to be found.

With the focus on a high energy density, table 2 contains a list of material combinations for different types of processes. Most of the data are the theoretical storage capacity in a solar sorption cooling system is calculated for a cooling temperature of 5 °C , an ambient temperature of 35 °C and a heating temperature of 120 °C [2]. The energy density is based on the total mass (sorbent and sorbate) at the end of the sorption process. For adsorption materials this gives a very low energy density. The theoretical energy density for heat for the adsorption materials, as calculated using the data shown in figure 5, is shown in parentheses.

Absorption	Solid – Gas Reaction	Adsorption
NH_3 – H_2O: 110 Wh/kg	H_2O – Na_2S: 353 Wh/kg	H_2O – zeolite 4A: 23 Wh/kg
H_2O - NaOH: 277 Wh/kg	H_2O – $MgCl_2$: 233 Wh/kg	H_2O – silica gel: 40 Wh/kg
	H_2O – $CaCl_2$: 271 Wh/kg	
	H_2O – LiCl: 197 Wh/kg	

Table 1. Energy density of different materials combined with water from for cooling applications [2].

Mugnier and Goetz [2] studied a range of sorption materials for storage in solar cooling applications including both freezing and air conditioning cases. For air-conditioning applications their conclusion was that the greatest storage capacity could be achieved for gas-liquid systems using water with NaOH (277 Wh/kg) and for gas-solid systems with reactions using water together with Na_2S (353 Wh/kg), $CaCl_2$ (271 Wh/kg), $MgCl_2$ (233 Wh/kg), and LiCl (197 Wh/kg). These figures are for the conditions of the system studied and are for the weight of the pairs when fully loaded with water. The theoretical energy density for Na_2S is 510 Wh/kg based on data from de Boer et al [8] and recalculated to the weight when fully loaded with water.

The energy density per volume is dependent not only on the density of the materials but also how the sorbent and sorbate are stored. For a solid sorbent, mass and heat transport requirements generally lead to a significant part of the volume being used for heat exchangers and vapour channels.

12.2.1 Thermodynamics and Properties of Adsorption Materials

An infinite variety of adsorption materials exist on the market, almost all of them have been developed for other than heat transformation processes, e.g. gas drying, cleaning and separation. Several commercial and non-commercial materials have been selected. The selection was made in order to present typical representatives of each material class as well as two new developments that are interesting for heat transformation applications. The data presented here are based on measurements obtained at the Fraunhofer Institute for Solar Energy Systems ISE. Table 2 gives an overview of the selected materials and their precedence.

Table 2. Selection of typical adsorption materials

Label	Company	Type
13 X	Bayer	Zeolite 13X
NaCa 5A	Bayer	zeolite 5A
SC Y 1/16	UOP	zeolite Y
127B	Grace Davison	microporous Silica gel
LE-32	Engelhardt	macroporous Silica gel
SWS-1L	Univ. of Novosibirsk	mesoporous silica gel impregnated with $CaCl_2$
FAM-Z02	Mitsubish Chemicals Corporation	zeolite based molecular sieve

The equilibrium properties of all these materials have been measured at Fraunhofer ISE. From the measurements and through a modelling according to the adsorption theory of Dubinin [9, 13] the curves shown in Figure to Figure have been calculated. It has to be mentioned, that due to the modelling within the theory of Dubinin, the calculation of the differential enthalpy of adsorption for low percentages of water uptake (generally less than 3%) is unreliable, therefore values for Δh_{ad} below 3% uptake should be used with care.

Some comments to the selected materials:

The zeolites 13X, NaCa 5A, SC Y 1/16 and the silica gels 127B and LE-32 are commercial products available on the market. The silica gel 127B is a mesoporous silica gel, LE-32 is a silica gel with wider pores. The last one has been included in order to show the wide variety of adsorption characteristics of silica gels. The material labelled SWS-1L (‘Selective Water Sorbent’) is a mesoporous silica gel that has been impregnated with a $CaCl_2$ solution [9]. This gives the material a adsorption characteristic that is a superposition of the salts hydration and the adsorption in the silica gel pores. For an application care has to be taken with this product in order to avoid direct contact with liquid water as some of the salt may be washed out and go into solution leaving the confinement of the pores which results in a degradation of the adsorption properties. ‘Functional Adsorption Material’ (FAM-Z02) [13] is a zeolite based molecular sieve recently developed by Mitsubishi Chemicals Corporation aiming at the adsorption chiller market.

Adsorption isotherms

Two adsorption isotherms have been calculated: a 40°C and a 90°C isotherm. They are represented as a function of the **relative pressure**, which is the water vapour pressure divided by the saturation water vapour pressure at the adsorbents temperature. For the two curves this saturation pressure is 73.8 hPa and 701.1 hPa for 40°C and 90°C respectively. The relative water vapour pressure is equivalent to the relative humidity in an air-water vapour mixture.

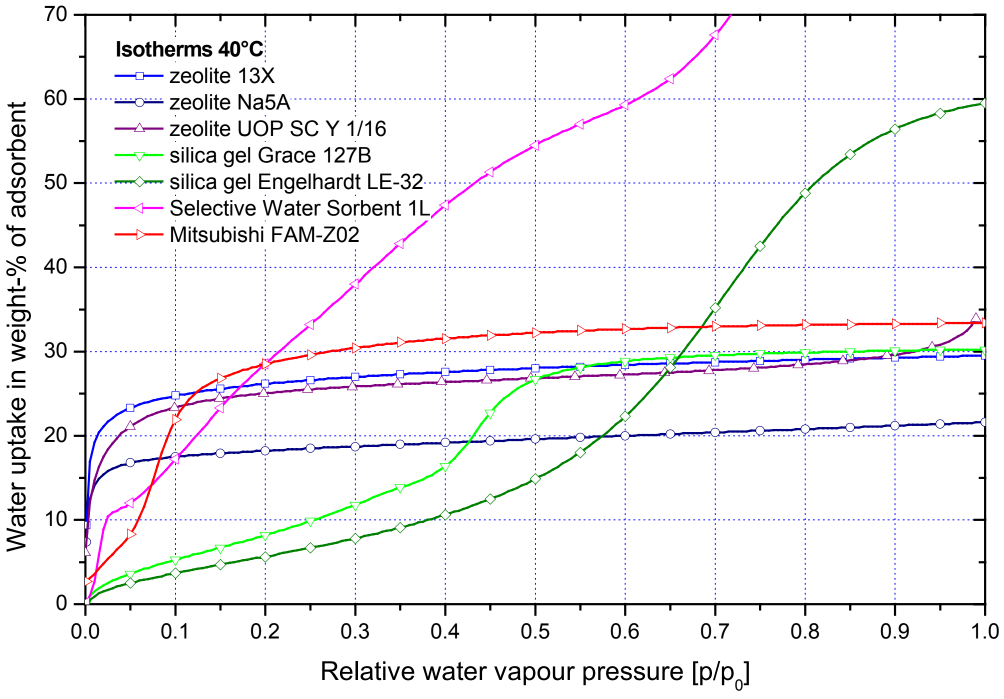

Figure 3 Water adsorption isotherms (40°C) for a selection of adsorption materials. Source: Fraunhofer ISE

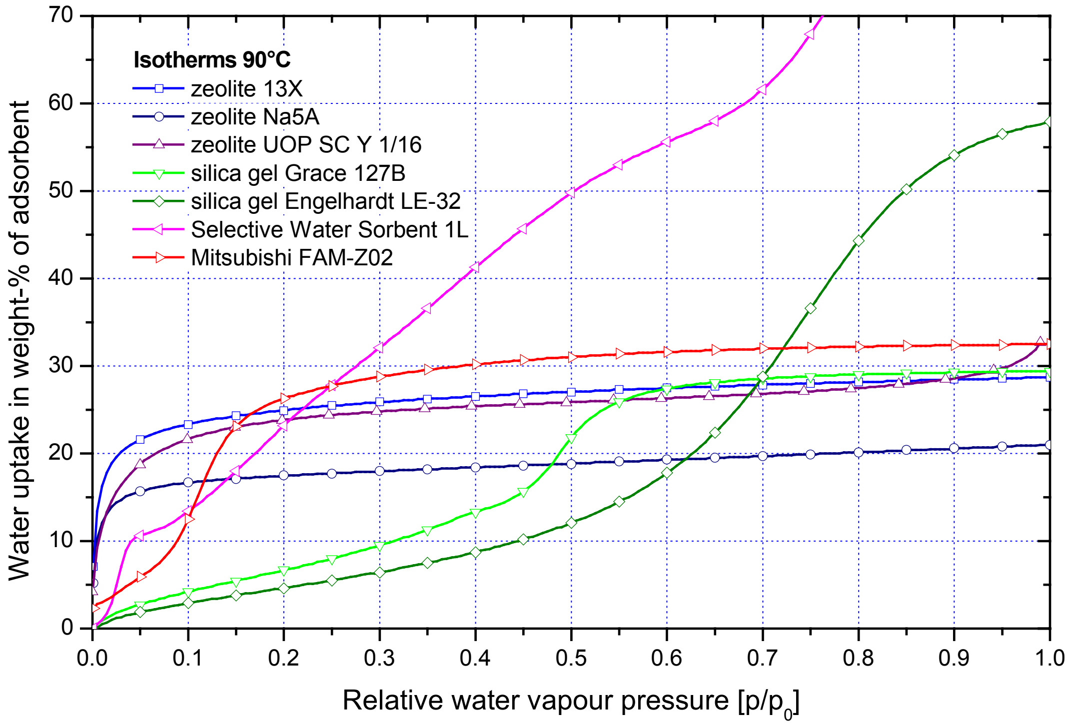

Figure 4 Water adsorption isotherms (90°C) for a selection of adsorption materials. Source: Fraunhofer ISE

These two diagrams can be used to make an estimation of the water uptake of these materials in a specific application.

The two diagrams should be used as follows:

1. Calculate the relative pressure for the operating conditions of the process. For a maximum desorption temperature of 100°C at condensation temperature of 45°C and minimum adsorption temperature of 40°C at evaporation temperature of 15°C, the relative water vapour pressure for both the desorption and adsorptiuon condition is calculated. In the example this gives $p/p_0 = 0.094$ for the desorption and $p/p_0 = 0.23$ for the adsorption process.
2. Find the final water uptake at the end of the desorption process from the relevant diagram. In this example the 90°C isotherm is used as this isotherm is the closest to the 100°C desorption condition. For silica gel Grace 127B this 4%.
3. Find the water uptake at the adsorption condition from the isotherm at 40°C. For silica gel Grace 127B this 9.2%.

Differential enthalpy of adsorption

In figure 5 the differential enthalpy of adsorption as a function of water uptake and for the temperature of 40°C is shown. Integrating this curve from the lowest loading at desorption conditions to the highest loading achieved at the end of the adsorption process gives the integral heat of adsorption involved in the ad- or desorption process. It has to be noted, that this heat does not include the sensible heat of the material during the heating up process.

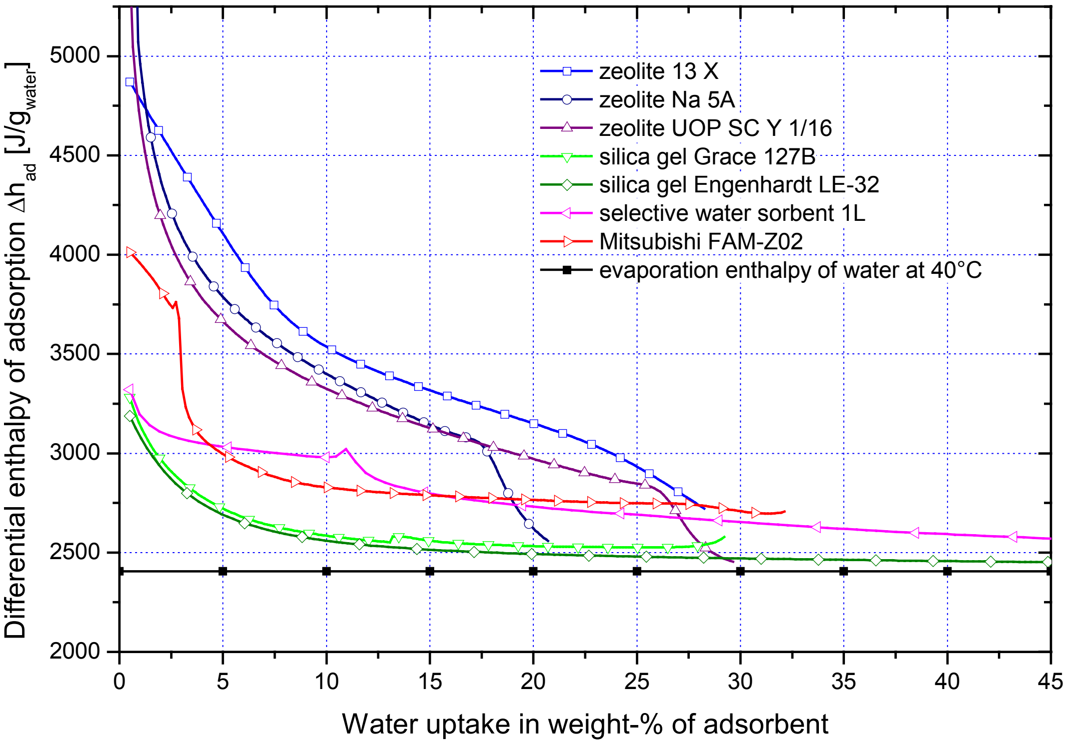

Figure 5: Differential heat of adsorption over water uptake at 40°C

As a mode of comparison of the different materials two operation scenarios were chosen for which the integral heat of adsorption as stated above were calculated. The two operation conditions are:

1. 90°C desorption temperature
   40 °C minimum adsorption temperature and condensation temperature
   15°C evaporation temperature
   label: 90°C / 40°C / 15°C
2. 160°C desorption temperature
   40 °C minimum adsorption temperature and condensation temperature
   5°C evaporation temperature
   label: 90°C / 40°C / 15°C

In the diagram of Figure 6 the columns are divided into the contribution of the evaporation enthalpy of the water H_v and the binding enthalpy H_b .

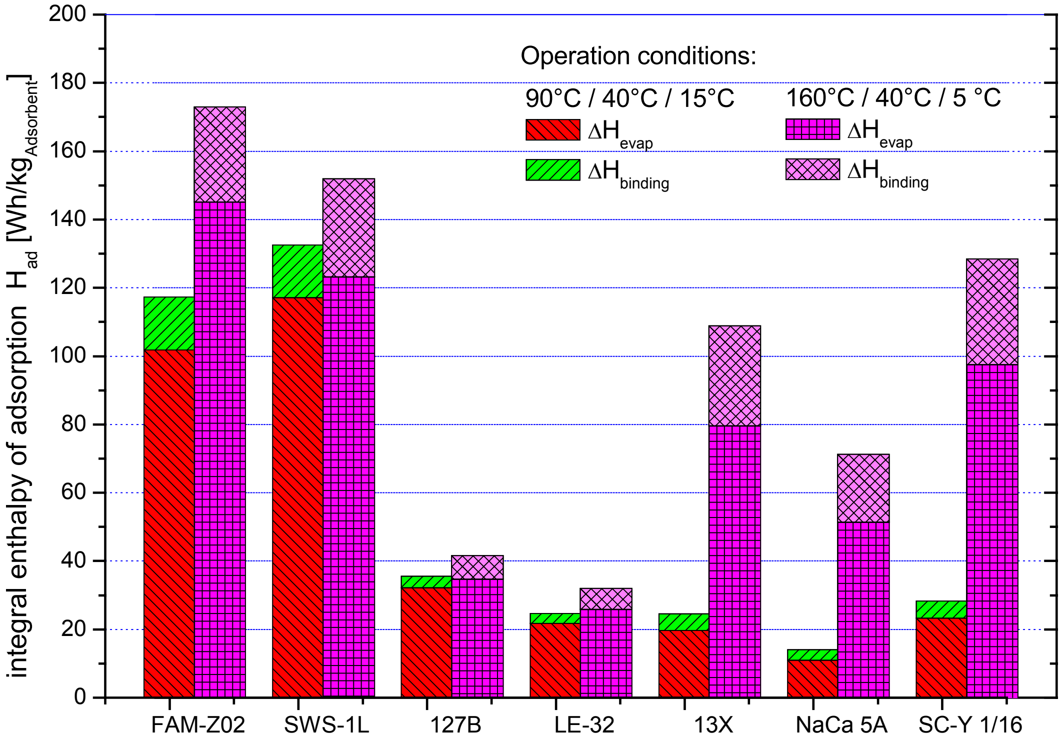

Figure 6: Integral heat of adsorption (in Wh/kg$_{\text{Adsorbent}}$) for two operation conditions for seven different adsorption materials.

The following conclusions can be drawn:

1. for low desorption temperatures the silica gels give better performance, this is even more evident, if evaporation and minimum adsorption temperatures get closer.
2. For all materials the main contribution to the integral heat of adsorption is the evaporation enthalpy. Higher contributions of the binding enthalpy come along with higher desorption temperatures as it is the case for the zeolites.
3. The adsorbents FAM-Z02 and SWS-1L show very high integral adsorption enthalpies even for low driving temperatures. This property makes these materials specially interesting for solar applications. Nevertheless, stability and corrosion problems have to be taken into account for the SWS material.
4. In order to evaluate the energy density of a storage concept based on the adsorption process the energy density given in J per m^3 is a more meaningful number. Nevertheless, this number depends not only on the bulk density of the material but also on the storage design. Therefore the heat per kg of material is given in this overview. The bulk density of the adsorbents varies between 650 kg/m^3 and 820 kg/m^3.

12.2.2 Open Sorption Systems

For the application of an open sorption system the local climate will determine the performance. So, in the system design the Mollier diagram is one of the basic tools in which the process the air will undergo can be shown. Fig. 7 shows a Mollier diagram of one possible process of an open system during discharging, see Fig. 9). The indoor air (3) is passed through the bed of the store and is dried and heated (2). It then passes through a heat recovery heat exchanger before being released to the ambient (5), heating the outside ambient air (1) to a higher temperature at the same humidity ration. This heated, fresh air (2) is then supplied to the building supplying heat in the process.

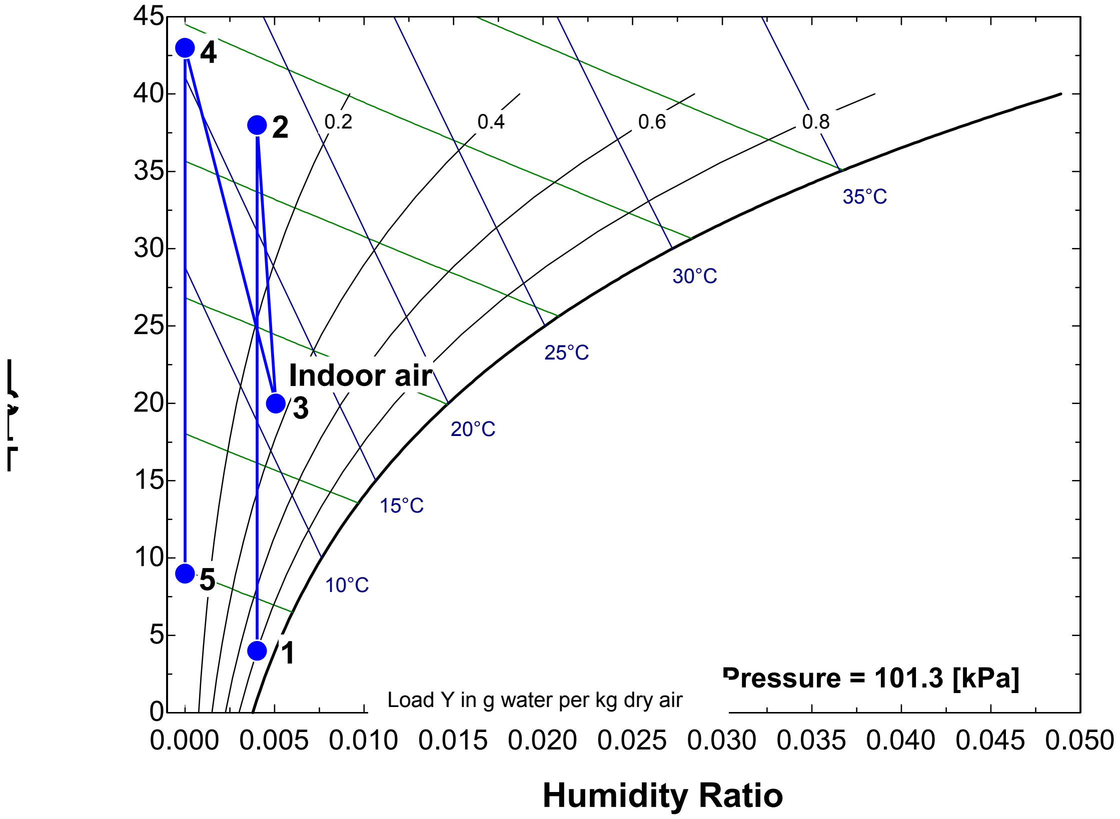

Fig. 7: Mollier-Diagram of moist air – air temperature versus humidity ratio. The circles and numbers refer to the air undergoing an open process during adsorption such as for the Monosorp system shown in Fig. 9.

The need for air conditioning has increased remarkably over the last years. Reasons for that are architectural (like the use of large glass elements, a rising internal load caused by technical equipment and last but not least higher comfort standards. Cooling load consists of two parts: the latent and the sensible load. The latent cooling load can be provided by dehumidification of the buildings supply air. Sensible cooling can be achieved by lowering the air temperature in the building.

The application of open sorption systems can provide dehumidification by the adsorption of water vapor and sensible cooling by adiabatic humidification (after a cold recovery for the dried air) at temperatures between 16 °C and 18 °C. Conventional systems have to reach temperature as low as 6 °C or lower in order to start dehumidification by condensation. For comfort reasons this cold air has to be heated up to about 18 °C before released into the building. This shows that open sorption systems can provide in general an energetically preferable solution.

12.2.3 Closed Sorption Systems

In contrary to the open system the closed sorption system uses the environment as an energy source but has no exchange of mass with it, only entropy. Closed systems require vacuum conditions in order to maximise the mass transport of sorbate to the sorbent. Three temperature levels are generally used: the highest for regeneration; the middle for exchange with the ambient or the building (heating mode); and the lowest for the building (cooling mode) or ambient (heating mode). The store acts as a chemical heat pump during discharge. This means that when used for heating, the (useful) heat released comes partly from the store and partly from the ambient or other heat source. If the working fluid is water, which is often the case, the source of heat must be high enough to evaporate water under vacuum conditions, in practice at least 5°C.

For the assigned task of the material in the closed sorption system the same selection criteria for the combination of the sorbate-sorbent material holds as for the above mentioned open system. Depending on the design, the pressure drop and the diffusion rate has to be kept in mind while the sorbate vapour flows towards or through the sorbent.

To get an idea and further on to calculate the mass and energy transfer rates, Clausius-Clapeyron curves as in Fig 8 should be known.

For the application of solar energy as the thermal energy source, the system’s performance will depend on the local climatic conditions i.e. temperature of the environment and the solar collectors. Under these conditions we can have in a circular process of the sorbate-sorbent pair as shown below in Fig. 3 with the cycle 1 to 4. The cycle assumes the same conditions as used by Mugnier and Goetz [2] with an evaporation temperature (T_v) of 5 °C, a local ambient temperature for condensation (T_c) of 35 °C and a temperature difference from the heat exchanger to the outdoor heat exchanger of 5 °C ($T_{ads,min}$(40 °C) – T_c(35 °C) = 5 °C). The solar collector temperature for desorption (T_{des}) is assumed to be 120 °C.

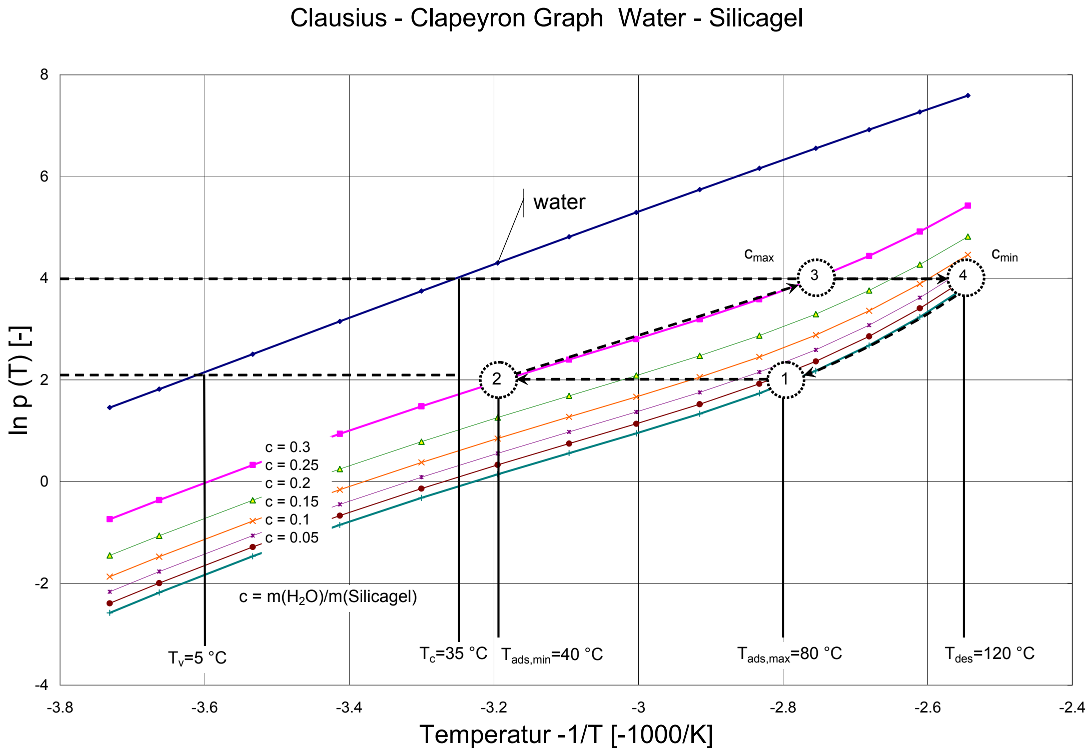

Fig. 8: Isosteres. Clausius-Clapeyron diagram of Water – Silica gel. The curves are for pure water and for silica gel with a range of loading (c) from 0.05 to 0.3 [4, 5, 6]. The circles containing the numbers 1 – 4 showing the cycle in an adsorption - desorption process as used by Mugnier and Goetz [2].

12.2.4 Comparison of Open and Closed Systems

Table 3 below summarises the main differences between open and closed sorption systems. The main differences are related to heat and mass transfer and their exchange with the ambient.

Table 3: Summary of main differences between open and closed sorption systems.

	Open Sorption System	Closed Sorption System
Operating pressure	Ambient	Vacuum (vapour pressure of sorbate)
Working pair	Water + sorbent	Sorbate + sorbent (does not have to be water)
Sorbate vapour source	Ambient	Evaporation of sorbate under vacuum
Mass transport in store	Air + water vapour	Only sorbate vapour
Heat transfer fluid to outside circuits	Air	Any suitable (via heat exchanger)

In the following sections, the different technologies are described. Most of the storage principles are still under development. The following sections give some information on the basic principles, the state of development, the ongoing work on relevant international projects and show some of the future expectations for the technology.

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12.3 Open Systems

12.3.1 MonoSorp – a seasonal adsorption storage integrated to a building ventilation system

by Henner Kerskes

About 70% of the energy demand of residential buildings is used for space heating and hot water preparation. To substitute as much as possible of fossil energy is the target for solar thermal energy. Solar combisystems as state of the art can reach up to 30 % fractional energy saving of the space heating and hot water preparation energy demand. The next step is to develop systems with energy savings higher than 50 %. For that target an efficient energy storage seems to be the key. In this context thermo-chemical storage is an interesting process. In modern well insulated low energy buildings up to 60 % of the space heating energy demand is needed to cover the air ventilation losses. Due to that fact more and more buildings are equipped with a mechanical ventilation system with heat recovery. The adsorption system described below is part of a mechanical building ventilation system and works in combination with a conventional solar combisystem /1/.

System description

The main idea is to have a simple system which provides the possibility of seasonal solar energy storage can easily be added to the existing solar and heating system. A modern low energy building with mechanical ventilation and solar combisystem, with radiator heating, is the basis of the investigation (see figure 9). When looking for a “free” heat or water vapour source for the adsorption process, the humidity of the indoor air is one choice. By blowing wet air through the adsorption bed the humidity is adsorbed by the adsorbent and the resulting heat of adsorption can be used for space heating. Using air as a carrier for water vapour leads to an open cycle process which has the advantage of being a simple system.

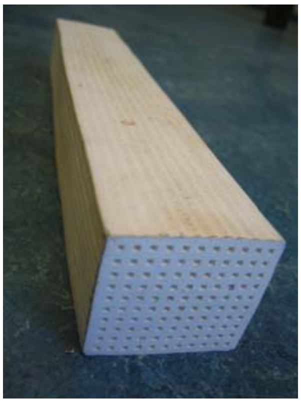


Figure 9: The zeolite honeycomb structure

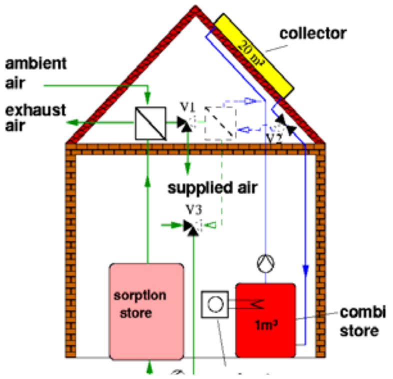
The main disadvantage of an open cycle is the great amount of air we have to move through the bed. In conventional fixed beds made of spheres, pellets or other kinds of granular adsorbent beds there is a high pressure drop and a resulting high electric power consumption of the fan. To overcome this disadvantage zeolite honeycomb structures with low void volume are used in the system, made by extrusion of zeolite A4 powder using thermoplastic polymers as plasticising aid and binder /2/. Honeycomb structures have decisive advantages compared with fixed beds of spheres or other shaped bodies. They show excellent adsorption kinetics and generate low pressure losses along the process length.

Discharging process (adsorption, loading of zeolite honeycomb with water vapour)

During space heating season the indoor air (point 3 of Fig. 7) is blown through the adsorption store. By adsorbing the humidity the heat of adsorption is warming up the air stream. The resulting temperature lift depends on the relative air humidity and is in the range of 15 – 25 °C (point 4). The warm and dry air passes through the heat recovery heat exchanger of the ventilation system (point 5). By this step the ambient air (point 1) is heated up to a temperature above the room temperature (point 2). The supplied air (ca. 40°C) becomes an active part for the space heating system of the building.

In this phase the solar combisystem is operating in its normal manner and has no effect on the adsorption store.

Figure 10: system during adsorption process



Charging process (desorption, drying of zeolite)

After a certain time the store is saturated by water vapour. The necessary heat for desorption is delivered by the solar system during summer, when the conventional solar combisystem is used just for domestic hot water preparation. With its large collector area (designed for space heating) a conventional solar combisystem has large stagnation time when it can not deliver any solar power. In the described system these time periods are used for the desorption of the adsorption store. This leads to high solar efficency.

The desorption of the zeolite requires a bed temperature of about 160°C. For this purpose only highly efficient solar collectors (vacuum tube) are suitable.

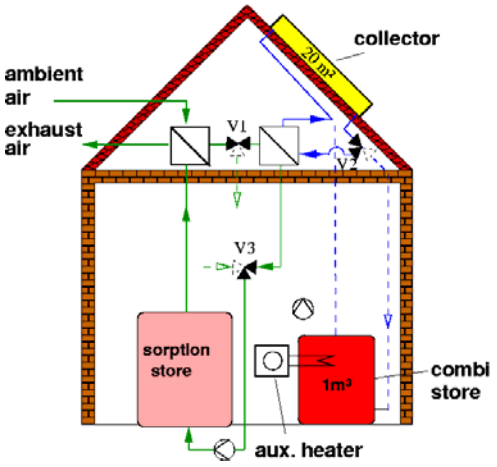


Figure 11: system during desorption process

Project Status

In preliminary tests on a zeolite honeycomb probe at laboratory scale (fig. 8) the performance of the adsorption and desorption processes were investigated. Charging and discharging cycles with a wide range of inlet conditions (temperature, humidity) were carried out. These tests were used to validate the numerical simulation of the ad- and desorption behaviour.

The simulations are based on 1-D, multiphase, dynamic models, which are solved with the simulation tool PDEX-Pack /3/.

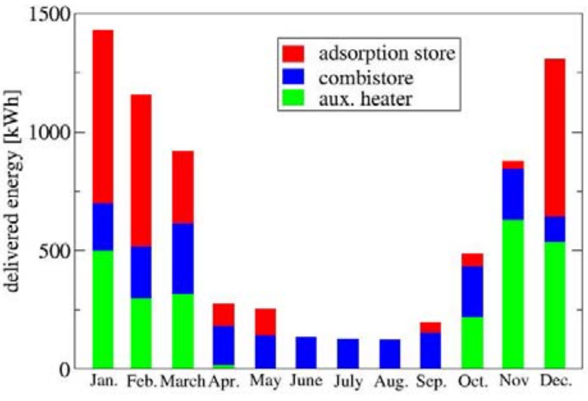
In detailed simulation studies, where the building, the heating system and the solar combisystem were modelled in TRNSYS and the sorption processes with PDEX, the overall performance of the system was analysed. Yearly energy savings for a single family house were calculated under German reference conditions.

It is planned to build up a demonstration system in laboratory scale (ca. 0.2 m^3 adsorption store) in the near future at ITW.

Results:
Yearly energy savings were calculated for the following system and boundary conditions shown in table 4.

Table 4: Key figures, boundary conditions for the simulated Monosorp system as well as monthly simulation results in diagram form.

Building	Single-family house
Climate	Würzburg
Heat load (DHW + space heating)	7256 kWh/a
Solar collector	20 m² CPC vacuum tube
Solar combistore	1 m³
Sorption store	8 m³ zeolite A4
Heat to / from	
Sorption store	2684 kWh/a
Combistore	2080 kWh/a
Aux. heater	2501 kWh/a



The calculated annual energy saving is 70 %. This is the same amount that a conventional solar combisystem can save with a 10 m³ water store and 50 m² collector area.

Advantages

The main advantage of the system is the high energy density of the adsorption store (thermo-chemical and sensible heat). Due to the complete use of solar energy delivered from the collectors for the desorption of the store, a high collector performance is achieved. There are no stagnation problems in summer. Thermal performance is enhanced by the use of the heat recovery heat exchanger in all exchanges with the ambient, minimising losses.

In addition to its thermal performance, the simplicity of the system makes it very interesting. In houses were a mechanical ventilation and a thermal solar system already exists only the adsorption store, a heat exchanger and three valves are needed. The storage itself can be built by a number of smaller honeycomb bricks. In this way even large stores can be built up inside small buildings with a wide range of geometries.

Disadvantages

The power output of the adsorption store depends on the humidity of the indoor air, and is only 1 - 1.5 kW. When using zeolite as adsorbent material high desorption temperatures of about 160°C are required. For this purpose only highly efficient solar collectors (vacuum tube) are suitable.

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12.3.2 Example of a thermal energy storage with zeolite for heating and cooling application

by Andreas Hauer

To use a thermo-chemical storage system for heating in winter and air conditioning in summer leads to an increase in operation time. This can provide substantial economic advantages. A thermo-chemical storage using Zeolite as adsorbent has been installed in Munich/Germany to heat a school building in winter and to cool a jazz club in summer time. The school building and the jazz club are connected to the district heating system of Munich.

The Zeolite system, connected to the local district heating grid, is designed to shift the peak demand for one day of the school building from day to night, allowing off-peak charging and thus increasing the total load capacity of the district heating network.

For the heating of buildings the heat of adsorption can be used in the adsorption mode. Depending on the used adsorbent and the desorption and adsorption conditions temperatures up to 160 °C can be reached. Under certain desorption conditions thermal energy can be delivered to the buildings heating system in the charging mode as well.

The cooling demand of the jazz club connected to the sorption storage system is caused by the large number of persons in the room. Therefore about ¾ of the cooling load is latent, which makes it an ideal application for an open adsorption system.

Principle of Operation

In order to reach a coefficient of performance COP_{heat} of about 1.0 or more it is important to utilize the heat of condensation during the **charging** process. The waste heat of the charging process (temperature level 35 – 40 °C and above) and the heat of condensation is supplied to the heating system of the school.

Figure 12 shows heat fluxes during charging and discharging mode. At night Zeolite is charged by air, heated up to about 130 °C - 180 °C using the steam line of the district heating system (heat of desorption Q_{Des}). Under these conditions the final water content of the Zeolite reaches 0.09 $kg_{Water}/kg_{Zeolite}$ – 0.05 $kg_{Water}/kg_{Zeolite}$.

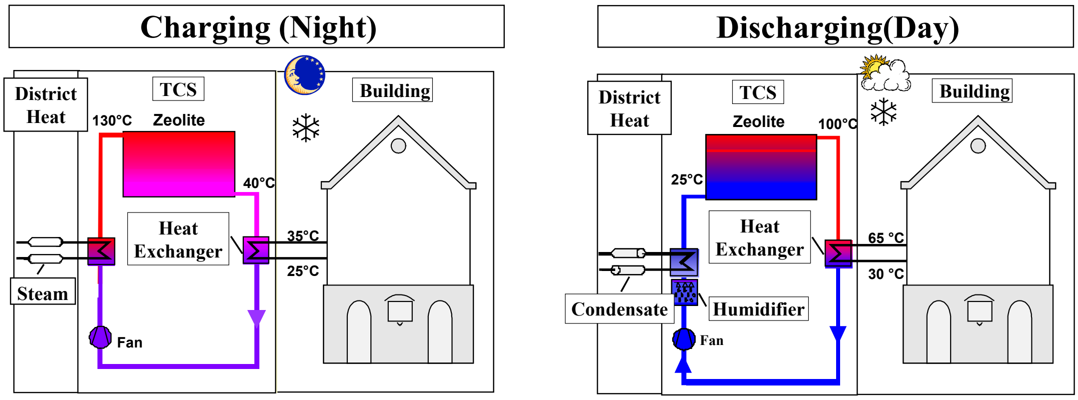


Figure 12: Charging and discharging mode for heating

The storage system is discharged in times of peak power demand. At first the air is heated up to 25 °C – 30 °C and saturated with water vapor by a humidifier. The energy for this process is provided by the low temperature return flow of the district heating system (heat of evaporation Q_{Evap},). The steam line of the district heating system is not used. The humidified air is blown into the tank containing desorbed Zeolite. The air temperature is raised to 100 °C (heat of adsorption Q_{Ads}). The thermal energy is transferred to the heating system of the school (flow temperature 65 °C) by a heat exchanger.

In order to use the Zeolite storage system as a desiccant cooling system two additional components have to be integrated. As shown in figure 13, the air stream exiting the Zeolite bed has to be cooled down (cold recovery device) before entering the supply air humidifier.

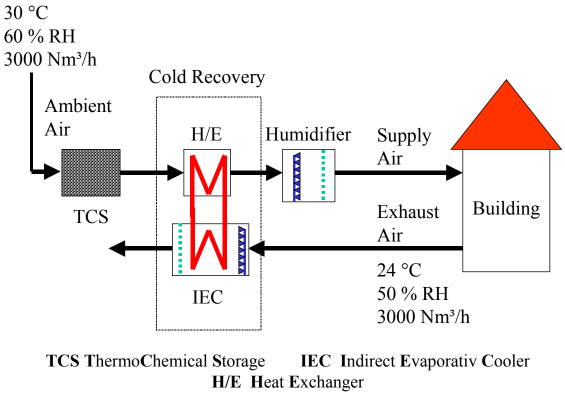


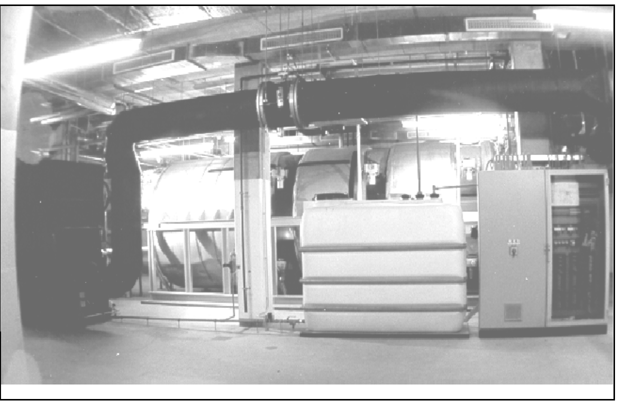
Figure 13: Additional components for air conditioning

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.

Demonstration System

The storage system is designed to cover a heat load of 95 kW over a period of 14 hours (from 7 a.m. to 9 p.m.) each day. This was achieved by using 7000 kg of Zeolite 13X for the storage tank. The tank consists of three connected cylinders arranged in a horizontal line (see background of Table 5). The storage system is connected to a combined air / radiator / floor heating system. The result is a flow temperature of 65 °C and a return temperature not higher than 35 °C. The maximum thermal power is 130 kW, the storage capacity is 1300 – 1400 kWh at 130 °C charging temperature (A. Hauer and W. Schölkopf, 2000). Table 5 shows the relevant data of the thermo-chemical storage.

Table 5: Data of the thermo-chemical storage and picture of thermo-chemical storage system (Humidifier, water tank and control unit in the front from left to right, three Zeolite modules in the back)

Mass of Zeolite	7000 kg	
Max. air flow	6000 m³/h	
Max. heating power	130 kW	
Max. cooling power	50 kW	
Energy density (heating)	up to 200 kWh/m³	
Energy density (cooling)	up to 100 kWh/m³	

A jazz club with a reasonable cooling load is located close to the storage system. The club has a floor area of 160 m² and a volume of 800 m³. The maximum capacity is about 200 persons. The room temperature should not exceed 26 °C at a relative humidity of 50 %. The maximum cooling load was calculated assuming 4.5 kW for lighting and 1 kW for other technical equipment. The result is a maximum latent cooling load of 22 kW (73 %) and sensible of 8 kW (27 %).

Results of the Demonstration Plant

Heating

In the beginning of 1997 the automatic operation of the storage system started in the heating application. Since then the required room temperatures and heating power were covered by the storage system. Problems detected in the first operation period were removed. The control strategy during discharging mode was constantly improved.

The thermal coefficient of performance COP_{heat} is defined as the ratio of thermal energy supplied to the building (heat of condensation Q_{cond} and adsorption energy Q_{ads}) and thermal energy input for charging the storage (desorption energy Q_{des}). The utilized thermal energy in the experiments is all heat actually transferred to the heating system including all losses. The experimentally achieved thermal energy density is the actually transferred thermal energy divided by the volume of the Zeolite. Table 6 ompares the experimental results to the theoretically calculated values (Hauer, A. 2000) for the given conditions.

Table 6: Comparison of experimental and theoretical results of the thermo-chemical storage system for heating

Thermal Coefficient of Performance COP_{heat}	
Theoretical COP_{heat}	1.07
Experimental COP_{heat}	0.92
Energy Density ρ_Q	
Theoretical ρ_Q	552 MJ/m³ (153 kWh/m³)
Experimental ρ_Q	446 MJ/m³ (124 kWh/m³)

Table 6 shows that 86 % of the theoretical maximum COP_{heat} and 81 % of the maximum thermal energy density were reached in the demonstration plant.

Cooling

Simulations of the storage have shown that desorption temperatures below the possible 130 °C from the district heat can lead to higher COP_{cool}. Experiments with 130 °C, 100 °C and 80 °C were carried out. Figure 8 (left) shows the 100 °C desorption as an example.

Two different coefficients of performance for dehumidification COP_{dehum} and for cooling COP_{cool} were defined:

$$\mathrm{COP}_{\mathrm{dehum}} = \frac{Q_{\mathrm{dehum}}}{Q_{\mathrm{Des}}} \quad \text{and} \quad \mathrm{COP}_{\mathrm{cool}} = \frac{Q_{\mathrm{cool}}}{Q_{\mathrm{Des}}}$$

where Q_{dehum} and Q_{cool} include the store and the store plus the heat recovery unit respectively.

The results for COP_{dehum} , COP_{cool} and energy density with respect to the volume of the packed bed of Zeolite (ρ_{cool}) for the different desorption temperatures are shown in table 7.

Table 7: Experimental results of the thermo-chemical storage for cooling.

Desorption Temperature			
	130 °C	100 °C	80 °C
COP_{dehum}	0.45	0.48	0.50
COP_{cool}	0.67	0.80	0.87
ρ_{cool}	168 kWh/m³	105 kWh/m³	100 kWh/m³

The best performance was measured using a desorption temperature of 80 °C. Below that temperature almost no dehumidification can be observed.

There is a remarkable increase from COP_{dehum} to COP_{cool}, which is caused by the heat recovery. This can be explained by the high outlet air temperatures during adsorption, which are supporting the cooling by the indirect evaporative cooler very effectively. At a desorption temperature of 80 °C a value of 0.87 could be reached. That means 87 % of the district heat were converted into cooling energy and were delivered to the jazz club.

Conclusions from the Demonstration System

The demonstration project on thermo-chemical energy storage showed results in the heating and air conditioning application with good correspondence with the theoretical calculated values. The operation control strategies have to be improved and simplified in the future.

A rough economic evaluation showed that the pay back time depends strongly on the price reduction for the off peak thermal energy, the investment costs and the number of storage cycles. Under the assumption of an 40 % reduction in winter (which is already negotiated) and a 60 % reduction in summer for the district heat energy price, investment costs of 60.000 Euro (for the described system) and 150 heating and 100 cooling cycles per year, a pay back time of 7-8 years was found. This shows that thermo-chemical energy storage systems can be competitive in the near future due to their large development potential.

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12.3.3 Storage of Solar Thermal Energy in a Liquid Desiccant Cooling System

by Eberhard Laevemann, Andreas Hauer, Matthias Peltzer

Introduction

Prochek Immobilien GmbH in Amberg, Germany, has built an office building called the “email-fabrik”, with a floorage of 5700 m². The building has been designed to have an annual energy demand for heating as low as 35 kWh/m². The high comfort standard requested and the internal heat loads require air conditioning in summer. The predicted specific annual cooling and dehumidification load is about 30 kWh/m². Thermally activated ceilings are used to heat and cool the building. In summer the ceilings are cooled by well water. Therefore humidity control is required to prevent humid air from condensing on the ceilings. The humidity is controlled by a solar driven liquid desiccant cooling and dehumidification system developed by ZAE Bayern [1].

Demonstration System Design

In summer the ventilation air has to be dehumidified to keep the required comfort and to prevent condensation on cold ceilings. The air dehumidification is done by a liquid desiccant dehumidification and cooling system, sketched in Figure 1 [2]. Warm and humid outside air is cooled and dried in a special dehumidifier by a concentrated Lithium Chloride salt solution (LiCl-H_2O) before it is blown into the atrium of the building. From there several air handling units draw the air into the offices and provide additional cooling on demand, using well water

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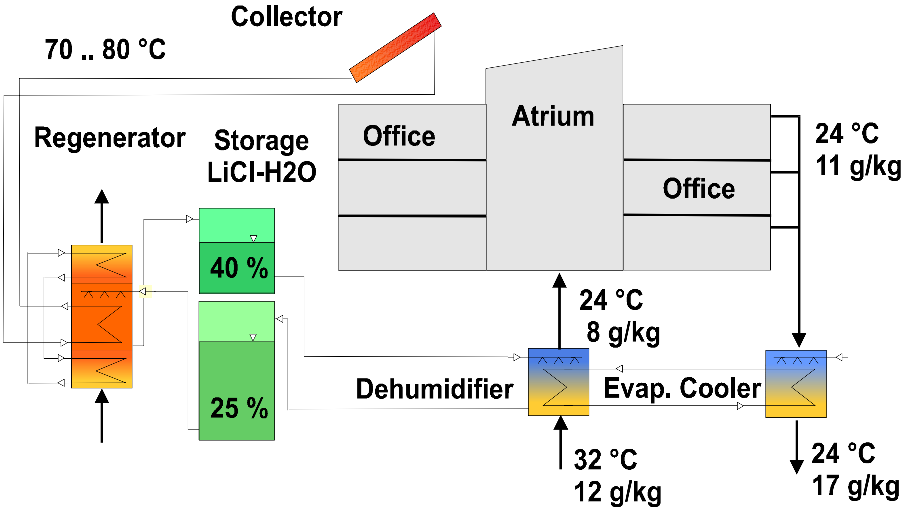

Figure 1: Sketch of the liquid desiccant cooling and dehumidification system for design conditions.

The exhaust air of the building is collected in three exhaust air handling units. Indirect evaporative coolers exploit the remaining cooling capacity of the exhaust air and cool the supply air in the dehumidifier via a water loop. This cold recovery makes the system more efficient. Depending on ambient conditions the predicted thermal coefficient of performance of the system is 1.2 to 2 [1]. The thermal coefficient of performance, COP, is defined as the enthalpy difference between outside and supply air related to the thermal energy used to drive the system.

A special low flow technique enables the dehumidifier to dilute the desiccant significantly when drying the air. The salt concentration changes from 40% to about 28 % wt. Concentrated and diluted solution are stored separately. The dehumidification process can be operated as long as concentrated solution is available. The system of concentrated and diluted solution stores energy very efficiently. The energy storage density reaches up to about 300 kWh/m³ related to the volume of the diluted solution. Since a chemical potential is stored, the storage is non degrading. No insulation of the storage tanks is required.

When solar energy is available the diluted solution is regenerated to it's original concentration in a regenerator, at temperatures of 70 to 80°C. At this temperature water evaporates from the desiccant solution and is taken to the ambient by an air flow through the regenerator. The Lithium Chloride does not evaporate. It remains in the solution and in the cycle. Heat recovery for the air flow is used to keep up the thermal coefficient of performance.

Cooling Capacity, Solar Collector and Storage Size

The desiccant cooling system is designed for a maximum air flow of 30.000 m³/h. The design point for cooling is defined as 32°C and 12 g/kg outside air state and 24.5 °C and 8.5 g/kg supply air state. Under these conditions the air cooling demand is about 80 kW and the air dehumidification demand is 70 kW. A total air conditioning capacity of 150 kW is required.

The system concept demanded that a system driven solely by solar, and no additional fossil fuel, should be used. Therefore, the required storage volume and the investment costs for collector array and storage have been calculated as a function of collector array size and solar fraction. A computer simulation of the system has been made evaluating the seasonal performance of the system under the meteorological conditions of Amberg. Figure 2 shows the results.

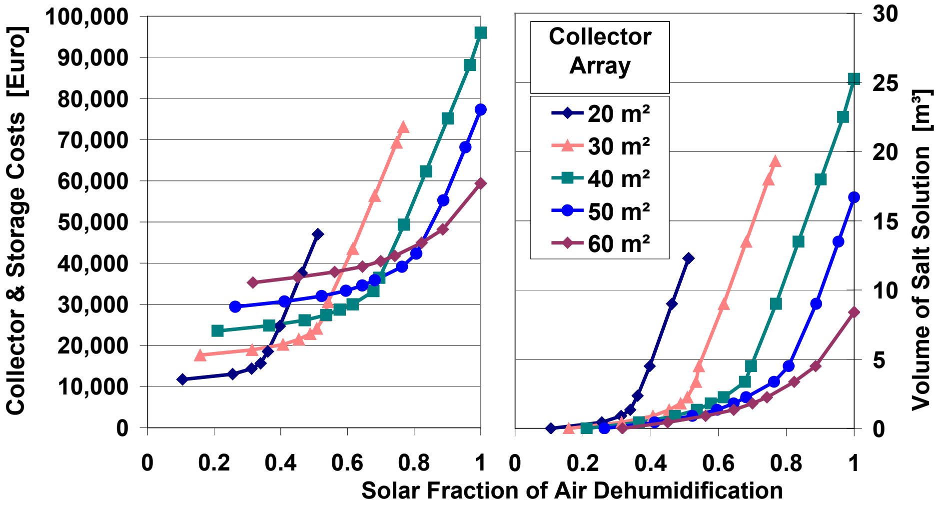

Figure 2: Investment costs of collector array and desiccant storage as a function of the solar fraction and the collector array size.

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[1] In hot and humid climates the COP will be close to 1

On the right hand side of Figure 2 lines of constant collector array size indicate the storage volume needed to achieve a certain solar fraction. The larger the collector array size, the smaller is the required volume of the stored desiccant for a given solar fraction. The left hand side of Figure 5 shows the related investment costs. A collector array size of 60 m² and a storage volume of 8.5 m³ turns out to be the most economic solution to achieve 100% solar operation.

A solar collector array of 70 m² of highly efficient flat plate collectors has been installed, providing a maximum thermal power of about 40 kW. Solar energy is collected during sunny periods in the early season and stored for several weeks until the energy is needed in short dehumidification periods in July and August. Separate tanks of 12 m³ volume are used to store diluted and concentrated solution, containing 3000 kg of Lithium Chloride salt and a varying amount of water

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Predicted Energy Balance and Investment Costs of the Desiccant Cooling System

The desiccant cooling system can provide up to 20 MWh per year of cooling and dehumidification energy. This includes the energy delivered by the cold recovery system. In addition to the regeneration of the desiccant solution the collector array has the potential to deliver about 11 MWh per year of hot water for the restaurant or the heating of the building. A connection to the heating system of the building, however, was not installed.

The necessary electrical energy for operating the desiccant system has been calculated to be about 1.5 MWh per year. Compared to a conventional system using vapor compression cooling and gas heating about 6 MWh of electrical energy and 11 MWh of thermal energy per year can be saved. The well water cooling system provides a cooling energy of 150 MWh per year and needs about 10 MWh of electrical energy. A conventional vapor compression system would need about 50 MWh of electrical energy per year.

The total investment costs of the desiccant cooling system including collector array, cold recovery, storage, and controls were planned to be about 300,000 Euro, this is 2000 Euro per kW respectively 10 Euro per (m³/h).

Operation Experience

The collector array and the components of the desiccant cooling system, such as dehumidifier, regenerator, storage and desiccant handling system, were installed in 2001. The dehumidifier and the regenerator are prototypes. Figure 3 shows the installation of the dehumidifier in October 2001. The dehumidifier is mounted into an air handling unit already installed on the roof of the building. The desiccant solution was mixed on site from salt and water and filled into the tanks in November 2001. The heat and cold recovery system was put into automatic operation in December 2001. The dehumidifier is part of this system and is used as heat exchanger in winter.

Figure 3: Installation of the dehumidifier

Summer 2002 should have been the first test period for the desiccant system. But problems occurred with leakages and unsatisfactory wetting of the surface in the dehumidifier, which is designed for very low flow rates. These problems were fixed, but unfortunately the owners of the building decided to replace the system, which has now been removed. It was possible to show that the problems with low flow of LiCl in the dehumidifier were largely fixed, but not enough time was available for reliable monitoring results.

Future Prospects

In 2005 the Jazz club supplied with dehumidification by the open zeolite system described in the previous section will also be connected to an open desiccant cooling system as described in this section. The system will be similar to that for the demonstration plant described above, but there will be an air/water heat exchanger included to provide chilled water instead of dehumidified (and chilled) air.

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12.4 Closed Systems

12.4.1 Absorption Storage: the Thermo-Chemical Accumulator (TCA) as an example of a salt-hydrate system

By Chris Bales

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. Figure shows the schematic of a TCA unit, where the solution is pumped over a heat exchanger via a spreader arm to increase the wetted area and improve heat transfer. The process has been developed by the Swedish company ClimateWell AB as a batch process under the product name ClimateWell DB220.

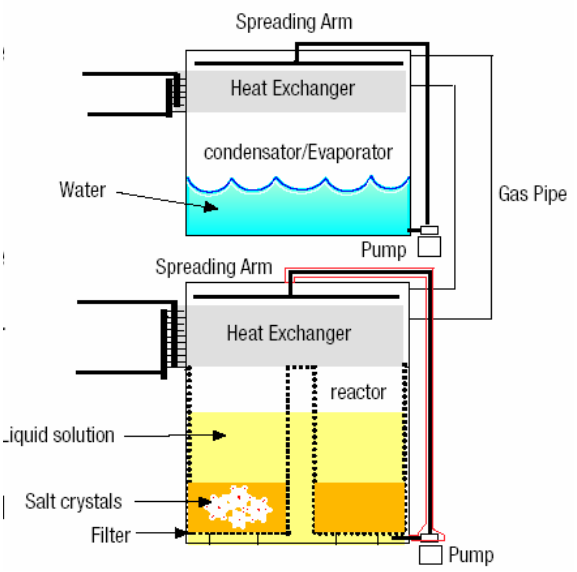


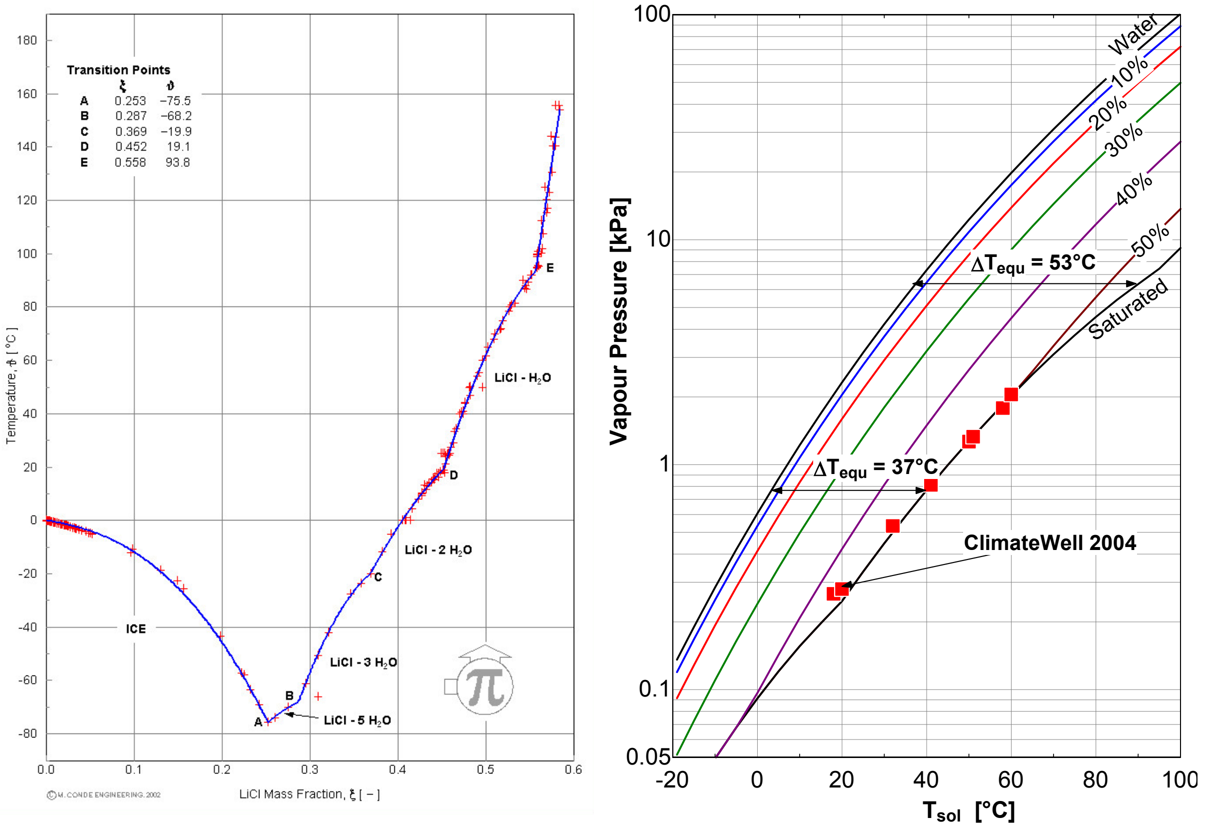
Figure 1. Schematic of a single unit thermo-chemical accumulator. (source: ClimateWell AB).

During desorption the solution comes closer and closer to saturation, and 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.

This gives the TCA the following characteristics:
High energy density storage in the solid crystals.
Good heat and mass transfer, as this occurs with solution.
Constant operating conditions, with constant temperature difference between reactor and condensor/evaporator.

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). Thus there is a flow of energy from the evaporator at low temperature to the reactor at moderate temperature.

The first TCA units have been built using water/LiCl as the active pair, and with two parallel units connected via switching valves, so that one unit can be charged while the other is being discharged. The physical properties of the working pair have been summarised [2] and empirical equations have been created for them based on data from a large number of studies over the last 100 years. The solubility line for LiCl can be seen in Figure 2a), where it is readily apparent that there are several different hydrates for LiCl. However, for the operating range of the TCA, the solution is generally operating at temperatures of 20-50°C for discharge and 65-95°C for charge, all of which are within the monohydrate range for saturated solution. The figure shows that the mass fraction for saturated solution is a function of the solution temperature. This in practice means that deltaT_{equ}, the maximum theoretical temperature lift between the reactor and condensor/evaporator, is constant for a given set of boundary conditions resulting in constant operating conditions, such as solution temperature (T_{sol}), during charging/discharging.



a)

b)

Figure 2. Data for LiCl: a) solubility line [2]; b) water vapour pressure above the solution for varying mass fractions of sorbent and solution temperature (T_{sol}). Measurements made by ClimateWell using the solution used in the TCA are shown as filled squares [3].

A Dühring chart for LiCl, Figure b), shows that the maximum value for □T_{equ} is for the saturated solution, and that for typical operating conditions of the TCA with an ambient temperature of 35°C, deltaT_{equ} is 37°C for discharging (comfort cooling or room heating), and 53°C for charging. Traditional absorption machines seek to avoid crystallisation and thus do not come close to saturation. This reduces the available temperature lift.

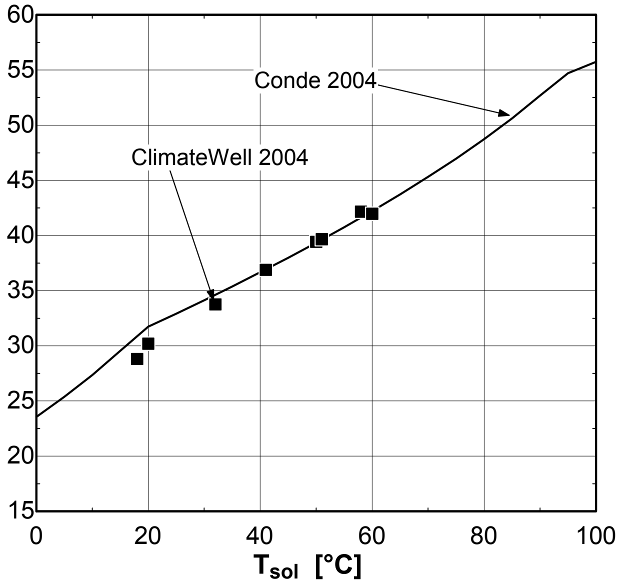


Figure 3. Relationship of deltaT_{equ} to the saturated solution temperature.

Figure 3 shows the relationship of deltaT_{equ} to the temperature of the saturated solution based on Conde’s equations (solid line) and as measured by ClimateWell AB (filled squares). Note that deltaT_{equ} is the temperature difference between the evaporator and reactor and that the temperature difference between the liquids in the external circuits is greater than deltaT_{equ} for charging and small for discharging (both cooling and heating).

This technology has been developed to the demonstration phase with extensive lab and field testing during 2004. The design storage capacity of these advanced prototypes has been 70 kW for heating (50 kWh for cooling) for two parallel units occupying a floor space of 1 m^2 with a height of 2.2 m. This gives an energy density of 32 kWh/m^3 related to the gross volume occupied in the building, but approximately 330 kWh/m^3 with respect to the volume of the solution in its most dilute state. The prototypes have been designed for cooling and heating applications and not for heat storage. The theoretical thermal COP for the prototype machines, based on short term storage with negligible heat losses from the store, is 70% for cooling and 87% for recovery of heat from the store. These figures assume no heat recovery during swapping of the units between charge and discharge as no such mechanism exists in the prototypes. Some heat recovery should be possible, which would increase the COP for both heating and cooling.

Note that there is an inbuilt conflict between the energy density for heat storage and the COP for cooling. A higher binding energy for water to the salt will result in higher energy density storage, as well as higher COP for heat recovery, but lower COP for cooling.

Other salts are being investigated, but no results are as yet available.

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12.4.2 Sodium-Sulfide/Water Storage (SWEAT system)

by Robert de Boer, Chris Bales

Background

Solar heat storage using Sodium-sulphide (Na_2S) / water has been studied previously, especially in Sweden during the 70’s and 80’s due to its high energy density in relation to its relatively low regeneration temperature (see figure 8 in Chapter 13). It uses solid sorption, but unlike the other solid sorption stores described in this handbook it uses absorption and not adsorption. The early work with Na_2S / water stores achieved working stores, but the work was stopped due to the serious problems that were encountered because of corrosion and melting of the salt. The latter resulted in areas of the store that became inactive. As with any of the closed systems described here, any gases in the store other than the vapour of the working fluid will decrease significantly the thermal performance. As corrosion leads to such gases, it is a major factor in all such systems.

The aims of the SWEAT (Salt Water Energy Accumulation and Transformation) project were to demonstrate the technical feasibility as well as the feasibility of the production procedures and process of the SWEAT modules [1]. Thus a prototype module was designed, manufactured and tested. Material choice and manufacturing procedures were studied in depth, so as to identify a construction that was reliable and that could be easily made with standard methods.

Working Principle

The properties of Na_2S / water system have previously been described in detail [2]. The most interesting equilibrium reactions of the SWEAT system are shown in Table 1 together with the equilibrium temperature difference between the water and sorbent as well as the heat of reaction. The theoretical heat storage capacity is 475 Wh/kg $Na_2S \cdot 5H_2O$ (1100 Wh/kg Na_2S), with 64% of this being available for cooling. The theoretical $COP_{cooling}$ is 0.66.

Table 1. Sorption reactions in the Na_2S / water system [1].

Reaction	deltaT equilibrium [K]	Heat of reaction [kJ/mol]
$Na_2S \cdot 5H_2O \Leftrightarrow Na_2S \cdot 2H_2O + 3H_2O$ (g)	56	189
$Na_2S \cdot 2H_2O \Leftrightarrow Na_2S \cdot ½H_2O + 1½H_2O$ (g)	61	111

The temperature-pressure diagram for the SWEAT system is shown in figure 1. It can be seen that the desorption temperature is around 80-85°C. Due to the fact that the lowest eutectic melting temperature of the salt hydrate in its operating range is 83°C, it is not desirable to exceed this temperature in normal operation. This in turn gives an upper limit for the condensation temperature of around 27°C. As melting of the salt hydrate is a realistic scenario in a real system, the construction of the store must allow this to happen reversibly.

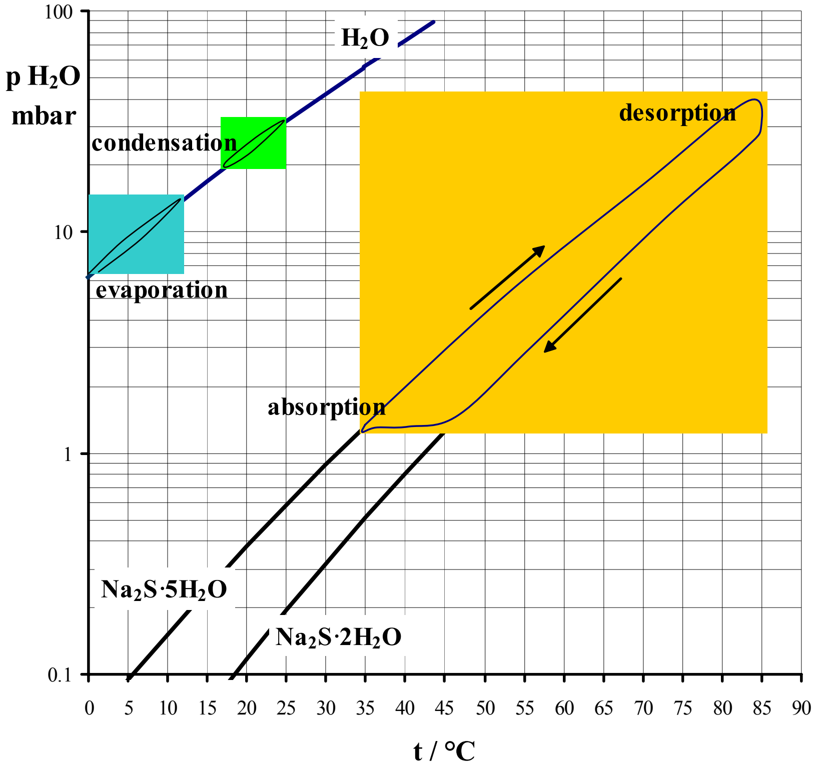

Figure 1. Temperature-pressure diagram for the SWEAT system. The absorption and desorption areas as well as those for condensation / evaporation of water are marked as shaded in the diagram [1].

SWEAT Prototype Design

The structure of the SWEAT prototype module can be seen in figure 2, showing the spiro-tube heat exchanger design. A porous support medium of cellulose fibres is used to allow partial melting of the store without significant irreversibility. A module consists of two vessels with a vapour channel connecting them: one for the evaporator / condensor; and one for the store, consisting of six Spiro-tubes in a hexagonal packing arrangement. In order to eliminate corrosion, all internal surfaces are coated with a standard industrial epoxy powder with additives to enhance degassing during the curing process at 180°C.

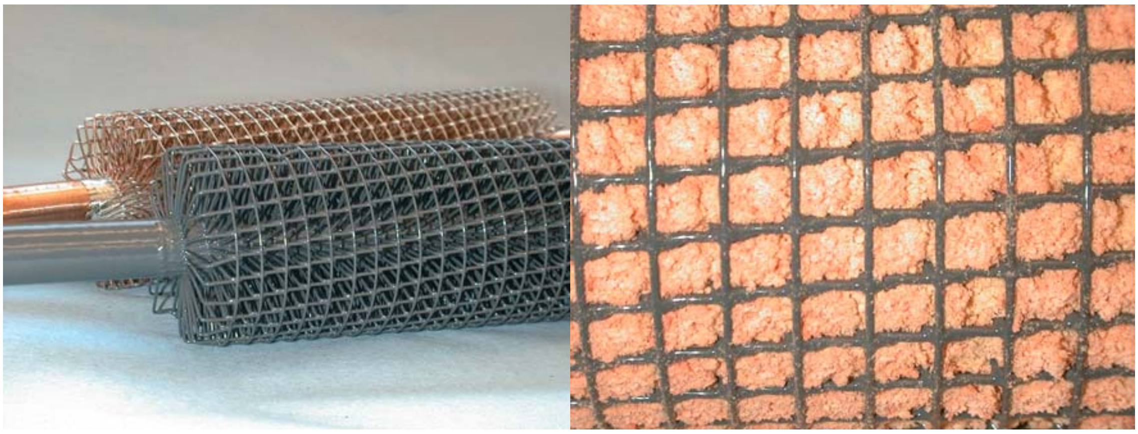

Figure 2. Picture of the Spiro-tube heat exchanger (left) and detail of the porous cellulose filling (right). The diameter of the central tube is 15 mm and that of the outside wire structure is 6 cm [1].

Prototype Results

The performance of the prototype module has been measured under a range of conditions. A simple Matlab Simulink model was also created and compared to the measured results. The model predicted the charge rate well but underestimated the discharge rate significantly. Discharge rates of 500 to 700 W were measured for evaporator temperatures of 10 to 15°C, with relatively constant rates until all the water was evaporated. The charge rate decreased during the charging process. Due to the equilibrium reactions in table 1, a minimum of 57 K temperature difference is required to start the charging process, while a minimum of 61 K is required to fully charge the store.

The measured maximum thermal storage capacities of the prototype module were 3.2 kWh for heat (2.1 kWh for cold) at a storage efficiency of 84% and $COP_{cooling}$ of 57% respectively. The latter is 85% of the theoretical maximum, and when taking heating losses etc into account, shows a relatively good agreement with the theoretical values.

The results have proven that the prototype modules work as expected and have shown that the modules can be made using standard industrial procedures. The next stage is to start industrial development and production with a company.

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12.4.3 Adsorption Storage based on Silica Gel / Water Storage: the MODESTORE project

by Dagmar Jaehnig

Principle

1. Charging process (desorption, drying of silica gel):

Heat from a high temperature source is fed into the device, heats the silica gel and vapor is desorbed from the silica gel. The desorbed vapor is condensed at a lower temperature level and then pumped out of the container into a separate reservoir. The heat of condensation has to be withdrawn to the environment.

2. Storage period:

The dry adsorbent is separated from the liquid working fluid (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 vapor):

Water is pumped into the storage tank where it evaporates in the evaporator taking up heat at a low temperature level. The vapor is adsorbed and releases the adsorption heat at a higher temperature level. This is the useful heat.

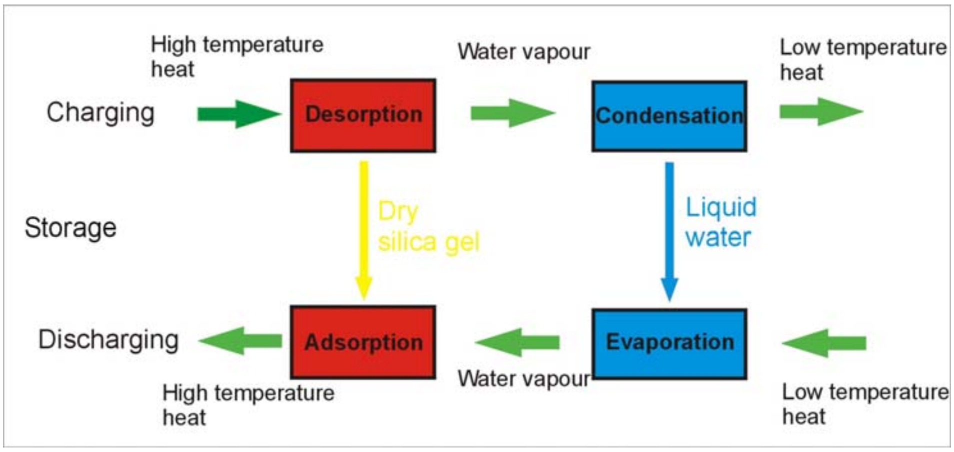

Figure 1: Working principle of an adsorption heat storage in a closed system.

Process Description

The goal in the MODESTORE project is to develop a seasonal storage for domestic hot water and space heating in a single-family house. The solar fraction should be high enough to make it possible to supply the necessary heat without a conventional fossil or biomass burner. The small auxiliary heating load can be supplied by an electric heating element.

A 2nd generation prototype system has been developed at AEE INTEC in 2004. The main idea behind the design of the 2nd generation prototype system is to enclose both the adsorber and the evaporator/condenser in a single container. A scheme of the prototype is shown in Figure 2. The total size of the laboratory-scale prototype container is approximately 350 l.

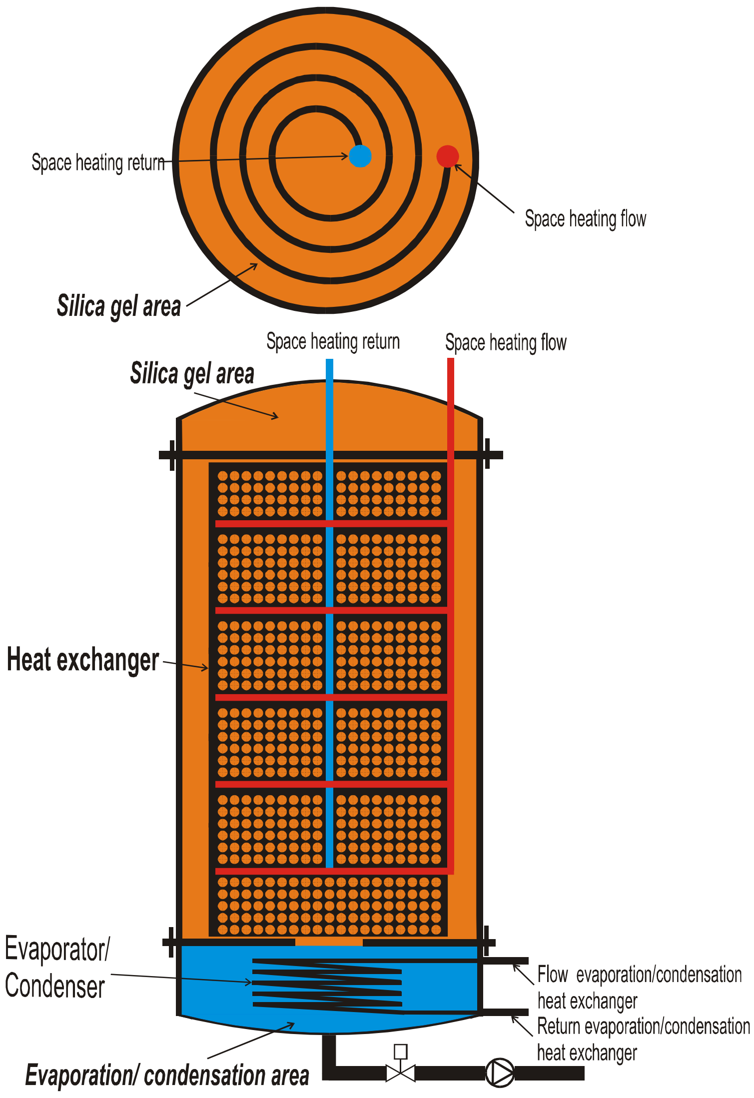

Figure 2: Scheme of the 2nd generation prototype

The two parts of the system are separated by a metal slab that bears the weight of the silica gel packing. The upper part contains the heat exchanger that transfer the heat from the heat source to the silica gel in charging mode and from the silica gel to the load in discharging mode. The upper part is entirely filled with silica gel except for a vertical slot where the water vapor can freely travel within the height of the adsorption part of the container. The silica gel packing is secured with a metal mesh to prevent it from falling in the slot.

The bottom part contains the heat exchanger that serves as evaporator in discharging mode and as condenser in charging mode. The condensed water is kept in a separate reservoir. In desorption mode, the water is withdrawn from the main storage container. In adsorption mode, only a small amount of water is pumped into the evaporator area when it is needed.

Project Status

A 2nd generation prototype system has been developed based on the experiences made with the 1st generation prototype system within the EU-HYDES project [2] where the technical feasibility of the storage concept was shown.

In the current project, a second generation prototype system was further developed and is being tested on a laboratory scale. In 2005, a larger pilot system will be installed and monitored in a low-energy single-family house in Austria.

Advantages/Disadvantages

The main advantage of a closed sorption storage system is that the energy can be stored without losses in form of dissociated sorption material and working fluid. The working pair silica gel / water has the advantage that it is non-toxic and commercially available and that heat at temperatures up to 100°C that can be reached easily with flat-plate solar thermal collectors, is sufficient for charging the store.

The disadvantages are a fairly low heat load that can be reached due to the heat transfer characteristics of the silica gel and the fact that low temperature heat has to be supplied during the heating season to evaporate the working fluid. That means that the system in its current development state is only suitable for low-energy or passive single-family houses.

Material research is still needed to find a working pair that is better suitable to the temperature and load requirements of a 100% solar space heating system.

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12.4.4 Experimental Design of a Sorption Storage Unit

by Paul Gantenbein

The vertical experimental setup at SPF (Institut für Solartechnik, Switzerland) of a closed system is shown in Fig. 1. The upper tank contains a heat exchanger immersed in a granular sorbent material like Zeolite or Silica gel. The tank underneath contains two heat exchangers which act as an evaporator (lower) and as a condenser (upper). Depending on the level of the sorbate in the lower tank, the lower heat exchanger is immersed in the sorbate. In this configuration the advantage of the system is that no moving parts are needed.

The two main steps in a real process carried out in the apparatus are called - charging and discharging. In the charging cycle, heat from a solar collector is pumped through the heat exchanger in the sorbent module (ZM). While the temperature of the sorbate-sorbent pair increases the sorbate is released as vapour and (valve between the two tanks is open) is condensed on the surface of the condenser in the lower sorbate tank. The discharging step works in the opposite direction – in the lower tank sorbate is evaporated and will be adsorbed on the sorbent material in the upper tank.

To have a correct operation in the charging and in the discharging steps, the system is kept under vacuum. This means that the non condensable gases such as air, N_2, O_2, have to be pumped out of the system. The resulting pressure in the Zeolite tank will depend on the temperature T(p, c) and the load c(p, T) of the sorbent (see Fig 8 Clausius-Clapeyron figure in section on closed systems).

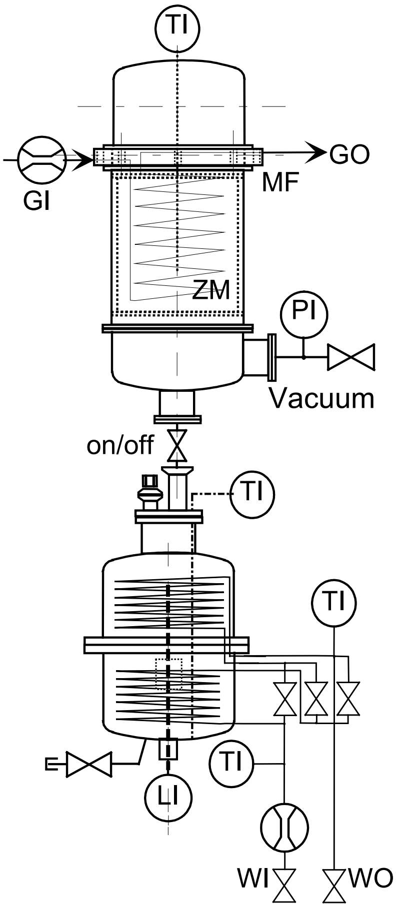

Fig. 1: Schematic of the experimental setup of a closed sorption system with no moving parts at the Institut für Solartechnik SPF - HSR University of Applied Science Rapperswil (CH). The system can be used for granular sorbent (ZM) and liquid / vapour sorbate materials. The upper tank contains a spiral heat exchanger immersed in the sorption material and the lower tank contains two heat exchangers (evaporator and condenser).

The experimental setup is built in stainless steel except the external piping.

Symbols:

FM	flow meter
GI	glycol in
GO	glycol out
LI	level indicator
MF	measurement flange
PI	pressure indicator
TI	temperature indicator
WI	water in
WO	water out
ZM	zeolite module

Project Status

The current focus of the project at the Institut für Solartechnik SPF [4] of the HSR University of Applied Science of Rapperswil is in designing more powerful heat exchangers. For the design of these main parts of the system the heat transfer process under vacuum has to be studied [1, 2].

Beside this, basic experiments were carried out to measure temperature profiles, mass transfer zones and water uptake as a function of time in the sorbent material. In these experiments other sorbate-sorbent pairs like Alcohol-activated carbon were also studied.

Further work has to be done in the range of the above mentioned basic experiments with the focus on other materials with a high inner surface [3] and on optimal system as well as component design.

Advantages

The advantage of a closed sorption storage system is that in the non operating mode the energy can be stored without losses in form of separated sorbate (Water) and sorbent (Zeolite, Silicagel) materials. The working pair Zeolite or Silicagel / Water is non poisonous, commercially available and easy to handle. Water in general is cheap. In case of silica gel the regeneration temperature T_{Reg} (100 – 120 °C) can be reached with flat plate solar thermal collectors.

Disadvantages

The disadvantages are low heat transfer rates from the granular sorbent material to the immersed heat exchanger and low diffusion rates of the sorbate in the sorbent materials. A low temperature heat source is needed, so the system works as a thermally driven heat pump.

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12.4.5 Closed system: Silica gel/water adsorption heat pump for heating and cooling

by Tomas Núñez

As stated before, an intrinsic property of all sorption systems is that they work as a heat driven heat pump, and that for closed systems this is in a batch process, with a cycle consisting of charge, storage and then discharge. If two units are used simultaneously in opposite parts of the cycle, it is possible to have a quasi-continuous cycle, with short gaps of supply when the units are swapped from/to charge/discharge. For pure heat pumping applications to produce heat or cold, rapid cycling machines are required with continuous heat sources and sinks.

For 10 years the Fraunhofer Institute for Solar Energy Systems ISE has been working with adsorption systems. First the main focus was heat storage as this process due to its expected size and slow cycling process, requires less efficient heat and mass transfer performance. On the other hand, the adsorption capacity requirements on the adsorption material is large and difficult to achieve with the adsorption materials on the market today. Thus, since about two years, together with the company SorTech AG the focus is on rapid cycling systems as the development of an economic viable system seems to be more feasible with the present adsorption materials.

The scope of this chapter is to present the development of a prototype of a small adsorption heat pump working on the adsorption pair silica gel - water. The development of this prototype has been carried out at SorTech AG and the Fraunhofer Institute. In contrast to most of the other systems shown here, the emphasis is on the heat pump effect and the storage is as small as possible to allow full cycles to be performed with the design heating and cooling rates. The “store” is thus cycled many times per day and is not able to store solar heat diurnally.

Development of the adsorption reactor

The basic unit of the developed prototype is the adsorption module. Each module has an adsorption heat exchanger (reactor) and a second heat exchanger which works as evaporator/condenser. The heat exchangers are plate fin heat exchangers made out of copper. The adsorption heat exchanger is filled with silica gel granulate while the bottom heat exchanger is partly immersed in the process water. Both heat exchangers are wrapped into a vacuum tight stainless steel container forming a sealed unit that is connected to the surroundings only by hydraulic piping. Figure 1 shows a scheme of the module construction.

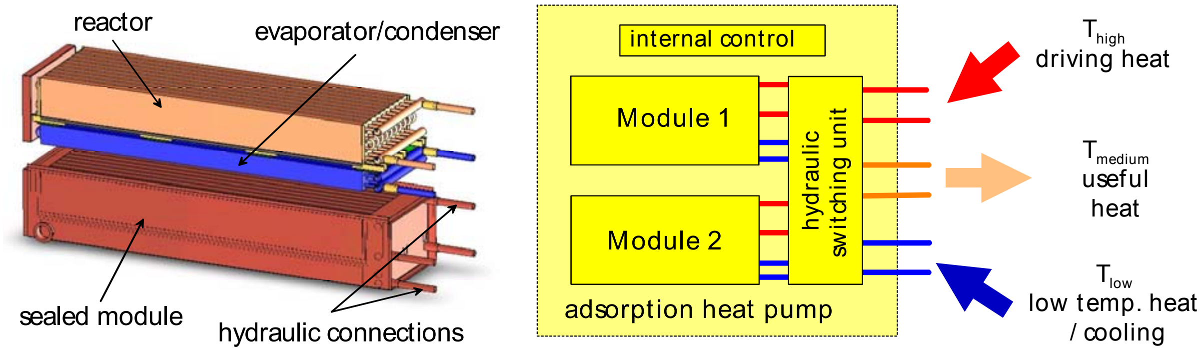


Figure 1: Construction of the adsorption modules (left) and scheme of the adsorption system consisting of two modules, a hydraulic switching unit and an internal control unit (right).

The adsorption system consists of two identical modules. The two modules are operated in an anti-cyclic mode: while one module is being regenerated with heat from the high driving temperature source the second module is operated in the adsorption phase, pumping heat from the low temperature heat source to the medium temperature level. At the same time the condensation heat from the condenser is fed into the medium temperature sink. With this operation mode a quasi-continuous heat pumping or cooling power is achieved. A hydraulic switching unit connects the two modules to the corresponding heat sources and the heat sink. For the operation of the unit an internal control unit based on a micro-controller was developed. The control unit decides on the internal switching of the system according to the external demand of power and temperature levels. The set values for the heating or cooling forward temperatures can be provided by an external control adjusting the operation of the heat pump to external conditions. Figure 1 (right) shows a schematic of the complete system.

The prototype was built at the company SorTech AG and characterised at the sorption heat pump test facility of Fraunhofer ISE. For heating operation in winter the system is driven by heat at a high temperature level e.g. a gas boiler, waste heat from a CHP unit or solar collectors. Heat from a low temperature level is pumped to the medium temperature level and released as useful heat. Floor and wall heating systems are suitable for the design temperature levels of the medium temperature heat sink. The low temperature heat source is preferably waste heat or free ambient heat at a low temperature level.

Operated as a chiller for solar cooling purposes the machine is driven by heat from solar collectors. The heat extracted from the room is rejected to the ambient by means of a dry cooler or any other kind of heat sink at the medium temperature level. For the prototype presented here driving temperatures of 75 to 95°C can be used. The low temperature source should be in the temperature range of 10°C to 20°C and the temperature level of the medium temperature sink is in the range of 25°C to 45°C.

Measurement results

Measurements in order to determine the coefficient of performance were carried out. Two coefficients of performance are defined: one for the heating and a second one for the cooling operation of the machine. The coefficient of performance for heating applications $COP_{heating}$ is calculated with the useful heat Q_{medium} at the medium temperature level and the driving heat Q_{high} at the high driving temperature level. Correspondingly, for the cooling operation the $COP_{cooling}$ is calculated as the quotient of the heat Q_{low} at the low temperature level and the driving heat Q_{high}. All heats are calculated for a whole cycle of the machine.

$$COP_{heating} = \frac{Q_{medium}}{Q_{high}} \qquad COP_{cooling} = \frac{Q_{low}}{Q_{high}} \qquad \text{Equ. 1}$$

The calculated power at the three temperature level is the mean power over a whole cycle. It is calculated as the quotient of the heat and the cycle time. This is important as the instant power is not constant during the cycle showing a sharp peak shortly after the switching process and reducing its value while the adsorption process progresses. Figure 2 shows an example of the instant power in the three hydraulic circuits. Note that the condensor from the charging unit and the sorbent bed of the discharging unit are connected in parallel to the medium temperature heat sink. In the tests, the inlet temperatures were kept constant for all three temperatures. This is not a realistic situation, especially for the medium temperature sink, as the performance of the external components depend on the heat transfer rate. This would result in less extreme peaks than those shown in Figure 2.

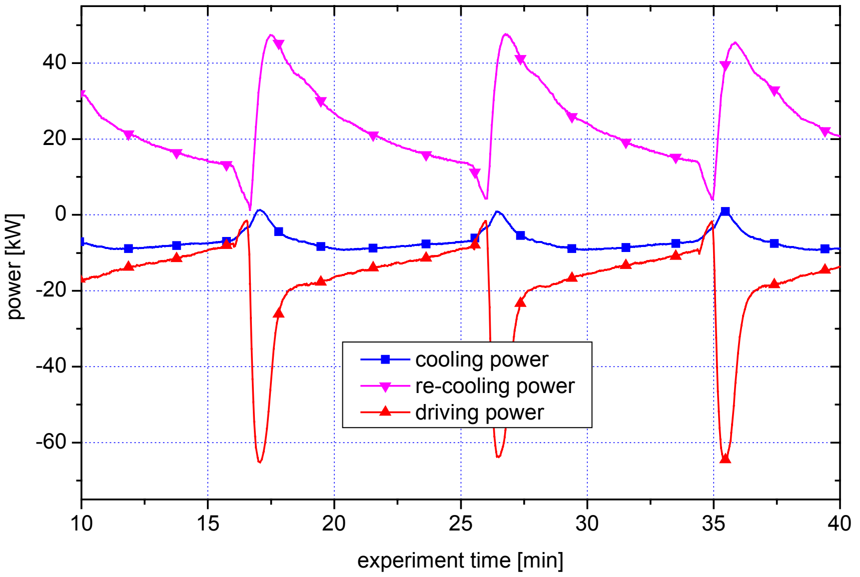


Figure 2. Diagram of the instant power in the three hydraulic circuits. Positive power means the adsorption system is delivering energy to its surrounding, negative power means it is receiving energy from its surrounding.

Other very important parameters for the evaluation of the machine are the temperature lift ΔT_{lift}, the driving temperature difference ΔT_{drive}, and the reduced temperature $T_{reduced}$. These values are calculated with the three temperature levels of the heat pumping process:

$$\Delta T_{lift} = T_{medium} - T_{low}$$ Equ. 2

$$\Delta T_{drive} = T_{high} - T_{medium}$$ Equ. 3

$$T_{reduced} = \frac{\Delta T_{lift}}{\Delta T_{drive}}$$ Equ. 4

Both parameters are calculated with different values for the heating and cooling application. For the cooling application T_{low} is the *outlet* temperature of the machine at the low temperature level while the value T_{medium} is the *inlet* temperature at the medium temperature level. For heating applications it is calculated with the *inlet* temperature of the low temperature level for T_{low} and the *outlet* temperature of the medium temperature level for T_{medium}. In this way the relevant temperature for each application is taken into account. In figure 3 the results for the coefficient of performance for heating ($COP_{heating}$) as a function of the reduced temperature $T_{reduced}$ is shown. Two curves are shown: a COP curve with optimised control and a curve representing the COP at maximum output power.

The corresponding results for the cooling applications ($COP_{cooling}$) as a function of the reduced temperature $T_{reduced}$ are shown in figure 4. Also two groups of results are plotted: the lower curve gives the COP at maximum output power, the upper dots show achieved $COP_{cooling}$ values with an optimised control.

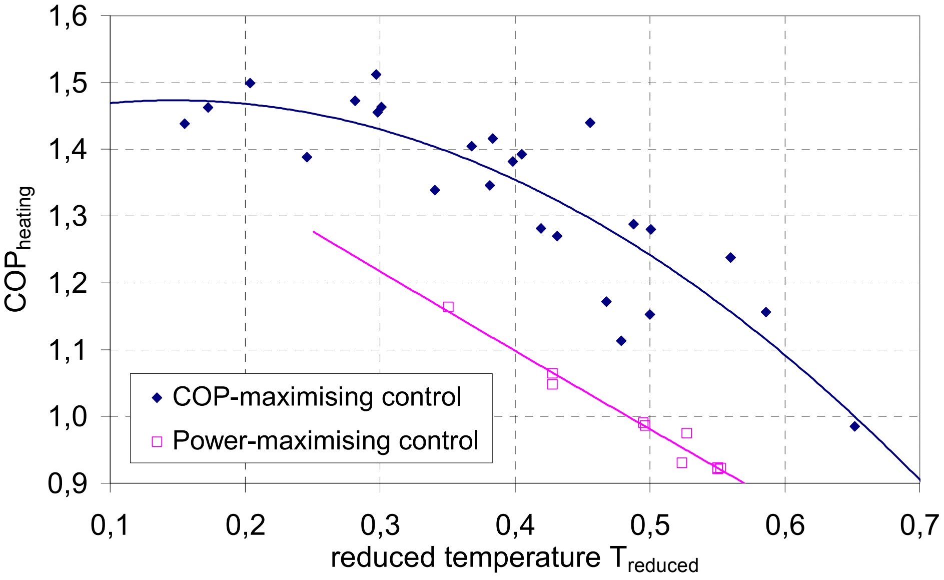


Figure 3: Coefficient of performance $COP_{heating}$ for heating operation as a function of the reduced temperature $T_{reduced}$.

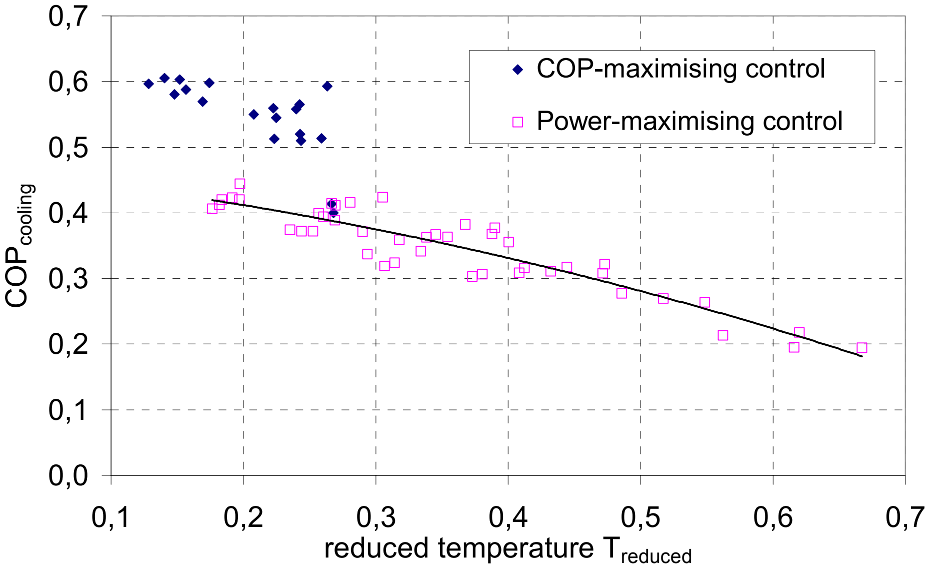


Figure 4: Coefficient of performance COP$_{cooling}$ for cooling operation as a function of the reduced temperature T$_{reduced}$.

In figure 5 the range of achieved powers as a function of the temperature lift ΔT_{lift} is presented. All these different powers are achieved only by varying the temperature levels. The driving temperatures were in the range of 80°C to 95°C, the medium temperature level between 25°C and 45°C an the low temperature level in the range of 10°C to 20°C.

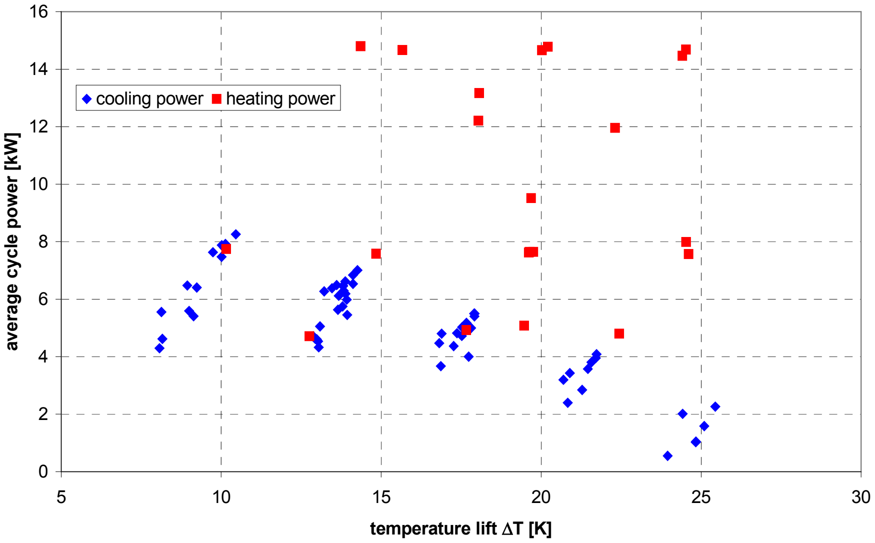


Figure 5: Mean cycle power of the system as a function of the temperature lift ΔT_{lift} for heating and cooling applications.

System integration and simulations

One system is being studied in the frame of the EU supported project MODESTORE is shown in Figure 6. The complete system consists of a solar system, a solar buffer storage, a domestic hot water storage and an adsorption heat pump. To drive the machine in the winter season a gas boiler is installed while the low temperature heat source is a ground coupled heat exchanger. In the framework of this project such a system will be installed and monitored in a field test.

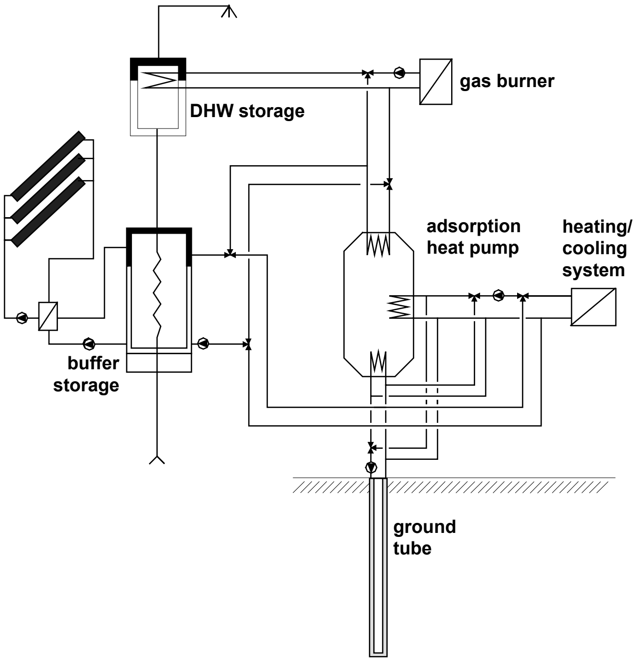


Figure 6: Complete system consisting of solar system, solar buffer storage, domestic hot water storage, adsorption heat pump and gas boiler.

The system is operated with the following concept:

Heating:

- As long as the temperature in the buffer storage is high enough to provide heat for the low temperature heating system of the building direct solar heating from the storage is provided.
- If the temperature of the buffer storage is not high enough for the heating system the adsorption heat pump is operated. It is driven by the gas boiler and the low temperature heat is extracted from the ground coupled heat exchanger. The rejected heat at the medium temperature level is provided to the heating system of the building.

Cooling:

- Cooling is provided only if the temperature of the solar buffer storage is high enough to drive the adsorption machine. In this case the evaporator is connected to the cooling surfaces of the building and the heat is rejected to the ground via the ground coupled heat exchanger. Also direct cooling via the ground coupled heat exchanger can be provided.

Further, the solar system is used year round in order to provide heat for the domestic hot water requirements.

For the estimation of energy saving potential of such a system design simulations with the load data of a residential building with 144m² of heated surface area and 30m² air-conditioned space. In the simulation model all components with the exception of the buffer storage are modelled with stationary characteristic curves. For the solar collector standard parameters for flat plate collectors with a selective coating were used. The building was separately simulated with TRNSYS obtaining a load file for the heating and cooling demand. The results for different configurations for the climate data of Freiburg/ Germany and Madrid/Spain are presented in table 1.

location	collector area	buffer storage	ADHP-type	useful solar gains	fuel savings	fuel savings	cooling	cooling covered
	m²	liter	-	KWh/m²	KWh	%	KWh	%
Freiburg	8	1000	none	382.7	3222.2	21.1	0	0
			Sortech	434.7	5178.5	33.9	220.2	19.6
	12	1250	none	309.4	3908	25.6	0	0
			Sortech	401.1	5799.1	38.0	500.8	44.5
	16	1500	none	263.9	4444.4	29.1	0	0
			Sortech	369.3	6298.7	41.3	728.9	64.8
Madrid	8	1000	none	542.2	4566.1	50.4	0	0
			Sortech	729.3	5238.9	57.8	678.3	27.3
	12	1250	none	422.7	5339.4	58.9	0	0
			Sortech	670.6	5943.2	65.6	1273	51.2
	16	1500	none	352.7	5940	65.5	0	0
			Sortech	612.2	6467.5	71.4	1740.9	70.0

Table 1: Results of the system simulations. The column ADHP-type means: none = solar combi-system without the heat pump; Sortech = results with the characteristics of the SorTech heat pump in the present development stage.

From the results it can be extracted, that the useful solar gains per m² of collector are lower for larger collector fields. This reduction is less for the systems that include the adsorption heat pump as more solar energy is used in the summer months to drive the adsorption system for cooling purposes. Further, the configurations that include the adsorption system show an increased fuel saving potential. Therefore, including the adsorption system into the heating installation of the building not only reduces the fuel needs for heating purposes by a factor of 1.3 due to the heat pumping effect but also gives a better use to the solar gains in summer as some cooling to the building is provided.

More detailed simulations with TRNSYS that are being carried out and will show the dynamic behaviour of all components and detailed temperatures specially in the ground heat exchanger.

Prospective

The present design of the adsorption system is effective and simple, but has one main disadvantage: as only one heat exchanger is used as evaporator and condenser in each module this heat exchanger is heated up and cooled down during the desorption (condensation) and adsorption (evaporation) half-cycles. Although this is a very simple and effective design from a construction point of view it reduces the achievable COP as heat or cold is lost in the process. If evaporator and condenser are separated a higher COP both for the heating as well as for the cooling case can be achieved. This design requires internal switching valves in order to direct the vapour to the corresponding heat exchanger during the different operation phases. Figure 7 shows a comparative scheme of the two designs.

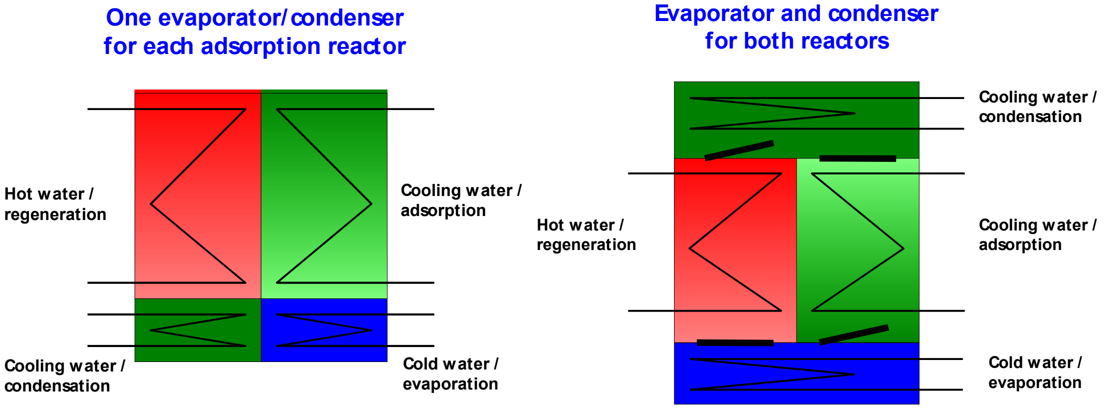


Figure 7. Scheme of two designs of the adsorption heat pump. Left: design with one evaporator/condenser for each adsorption module. Right: design with a common evaporator and condenser for both adsorbers.

In the frame of the EU-CRAFT Project SOCOLD SorTech AG and Fraunhofer are proceeding with the development of the above concept of the adsorption heat pump and chiller.

13. Storage of solar energy in chemical reactions

by Jacob Van Berkel

In principle, high storage densities can be achieved by means of chemical reactions. Many ways exist to convert solar energy (in what form so ever) into thermal energy. Quite obvious is the photo-thermal route as utilized in contemporary solar hot water and space heating systems, but also Solar Electricity Generation Systems (PV, Solar Thermal Power or the like) in combination with a compression heat pump is a way to utilize and store solar energy, in this case as electricity (exergy). Of course the photochemical route (photosynthesis) is the global solar energy conversion mechanism that has provided mankind with vast amounts of energy (stored in fossilized biomass) for heating, lighting and food.

Thermo chemical conversion & storage

The route closest to existing technology is the photo-thermo-chemical route. Solar thermal energy can be used to drive an endothermic –energy binding- reaction and thereby store solar energy. During the inverse (exothermic) reaction, the thermal energy will be released, generally at a different temperature level.
To be cyclical, the chemical compounds formed during the endothermic reaction must be reconverted into the original compounds in the exothermic reaction.

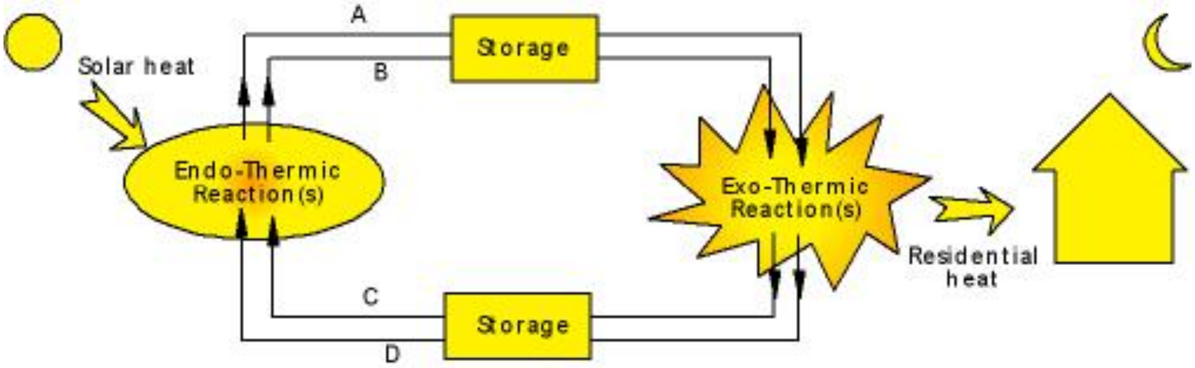


Figure 1 Schematic of Solar Energy Storage in Chemical reactions.

In the past, numerous chemical reactions have been evaluated for storage of thermal energy. "Solar chemistry" is a separate task (task II) within the Solar PACES implementing agreement of the IEA (where PACES stands for Power And Chemical Energy Systems). Solar Chemistry deals with solar-driven thermochemical and photochemical processes for:
The production of chemical energy carriers.
The processing of chemical commodities.
The detoxification and recycling of waste materials.

A separate IEA implementing agreement "Hydrogen" is directed towards production, storage of hydrogen, part is focused on photochemical conversion. Within IEA's ECES implementing agreement, Annex 10 and 17 concerned chemical energy storage and also much can be learnt from that work. In addition, the solar photochemical storage is covered by an international conference series on photochemical conversion and storage of solar energy (IPS).

Dozens of chemical reactions are known that in principle could be utilized for storage of solar energy. To name a few thermochemical reactions which have been studied for application with solar energy:

Table 1 Some Thermochemical reactions suggested for thermal energy storage. Note that energy density and reaction temperature are indicative as they depend on exact process conditions.

Compounds	Reaction	Reference	Material Energy Density	Reaction temperature [°C]
Ammonia:	$NH_3 + \Delta H \Leftrightarrow \frac{1}{2} N_2 + \frac{3}{2} H_2$	Lovegrove, 1999	67 kJ/mol	400 - 500
Methane/water	$CH_4 + H_2O \Leftrightarrow CO + 3H_2$	Hahne 1986	-	500 - 1000
Hydroxides e.g.	$Ca(OH_2) \Leftrightarrow CaO + H_2O$	Hahne 1986	3 GJ/m³	500
Calciumcarbonate	$CaCO_3 \Leftrightarrow CaO + CO_2$	Kubota, 2000; Hahne 1986	4,4 GJ/m³	800 - 900
Ironcarbonate	$FeCO_3 \Leftrightarrow FeO + CO_2$	Visscher, 2004	2,6 GJ/m³	180
Metal hydrides	$\text{metal } xH_2 \Leftrightarrow \text{metal } yH_2 + (x-y)H_2$	Hahne, 1986	4 GJ/m³	200 - 300
Metal oxides (Zn and Fe)	e.g. 2-step water splitting using Fe_3O_4/FeO redox system	Steinfield, 1999	-	2000-2500
Aluminium ore alumina		Murray, 1999	-	2100 – 2300
Methanolation-demethanolation	$CH_3OH \Leftrightarrow CO + 2H_2$	Shiizaki, 2000	-	200 - 250
Magnesium Oxide	$MgO + H_2O \Leftrightarrow Mg(OH)_2$	Kato, 2004b	3,3 GJ/m³	250 - 400

It should be noted that the energy density in 1 is based on material density. Chemical components are frequently stored in a packed bed configuration with considerably lower mass density. In addition, many reactions need storage of the compounds in separate reactors or tanks. For the MgO/H_2O compounds, for example, the practical energy density is in the range of 0,45 – 0,90 GJ/m^3 (Kato, 2004b).

Many reactions are not suitable for storage of solar energy in residential areas. In addition to common conditions for a residential thermal energy store like reasonable costs and safe and reliable operation, chemical storages need to satisfy following criteria:

1. High storage density (> 2 GJ/m^3).
2. The chemical reactions need to be:
   - Controllable and reversible at a rate sufficient to cover DHW and space heating and/or cooling loads, direct or indirect via a small intermediate buffer.
   - Take place at safe (low < say 10 bar pressure) and temperature levels within the range of domestic solar collectors (<250 °C) and DHW and space heating systems.
3. In addition, the components involved in the chemical reactions need to be:
   - Chemically stable
   - Safe and easy to handle
   - Recyclable and environmentally benign (non toxic)
   - Inflammable.

Especially the temperature level restriction and the power density (reaction kinetic) conditions pose severe limits to the chemical reactions known. In general, chemical reactions take place at acceptable power levels at elevated temperatures (say >500 °C). In the following section a few reactions will be presented that could provide solutions for moderate collector temperatures (< 250 °C).

Takashima 1999 proposed to use a solar collector as a chemical heat pump, based on the reversible reaction of 2-propanol ⇔ acetone + hydrogen. In the solar collector/distiller the 2-propanol decomposes (endothermically) at 80 °C, in a separate reactor, the two components react (exothermically) at 150 – 200 °C. In this way medium temperature solar heat can be used for higher temperature industrial processes.

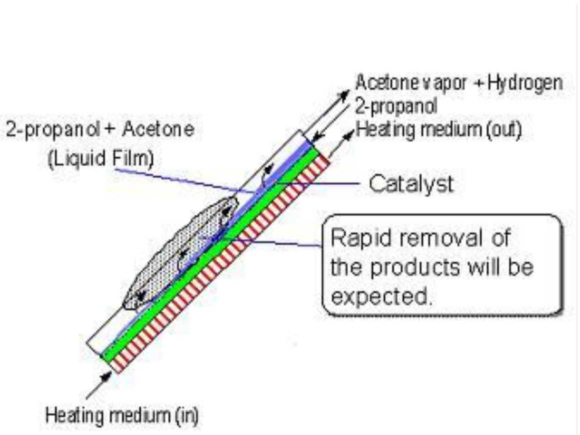


Figure 2 Falling film photochemical reactor, Takashima, 1999.

The same catalytic reaction is addressed by Anikeev, 1999 and ECN, The Netherlands, see Bach at al., 1999. Though the temperatures are quite attractive, the limitations of this system lie in the phase transformation in the dehydrogenation step and mass transfer limitations in the condenser part (Kirilov, 1999), in addition to flammability, too low selectivity (system fouling) and low storage density of the gaseous H_2. A similar medium temperature reaction is the dehydrogenation of cyclohexane/hydrogenation of benzene, see Kirilov, 1999 and the isobutene/water/tert-butnol system discussed experimentally for use heat around 50-70 °C, transforming into 120 °C (Kato, 2000).

Carbonation of CaO for storage and temperature upgrading of thermal energy is studied by Kubota, 2000. In the energy storage mode, CO_2 is desorbed from a CaO packed bed reactor and sorbed in MgO, there by avoiding the necessity of storage of large volumes of CO_2-gas. The reaction has been studied in a laboratory reactor, at 500 °C. It was demonstrated that carbonation can indeed be used for storage and temperature upgrading (from 500- to 650 °C). The reaction kinetics can be controlled by adjusting the CO2-pressure. One critical point was the integrity of the CaO packed bed particles, which showed sintering at particle sizes below 55 micrometer.

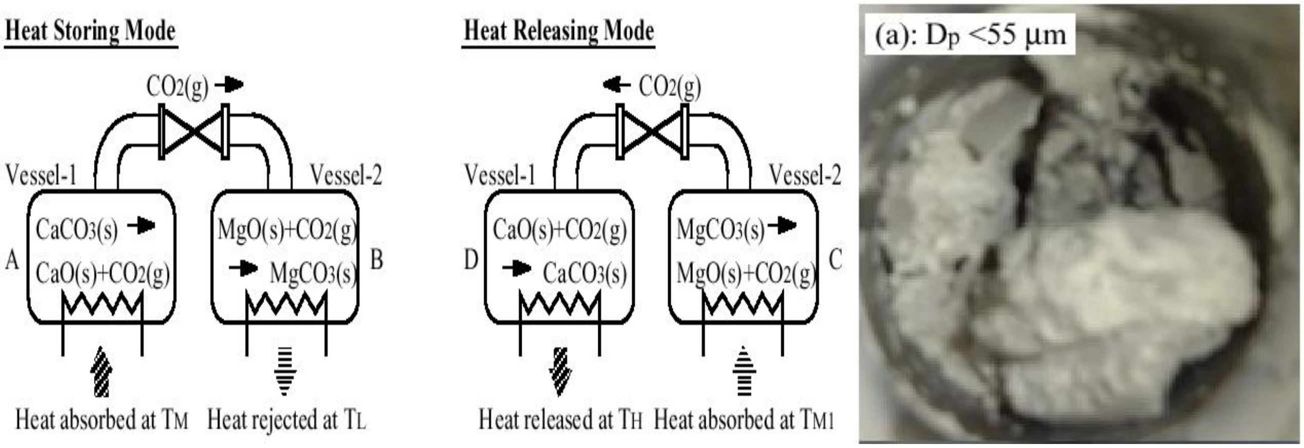


Figure 3 CaO/MgO-carbonation, Kubota, 2000.

Cabonation of CaO is also studied by Kato, 2004 and Kato, 1999. Besides storage of CO_2 in MgO, also storage in LeadOxide has been demonstrated, see Kato, 1997.

Another conversion route involves composition and decomposition of methanol (CH_3OH) in Carbon monoxide (CO) and Hydrogen (H_2), see Shiizaki, 2000. A system layout for transport of waste heat by means of a non-thermal carrier medium is given in figure 4

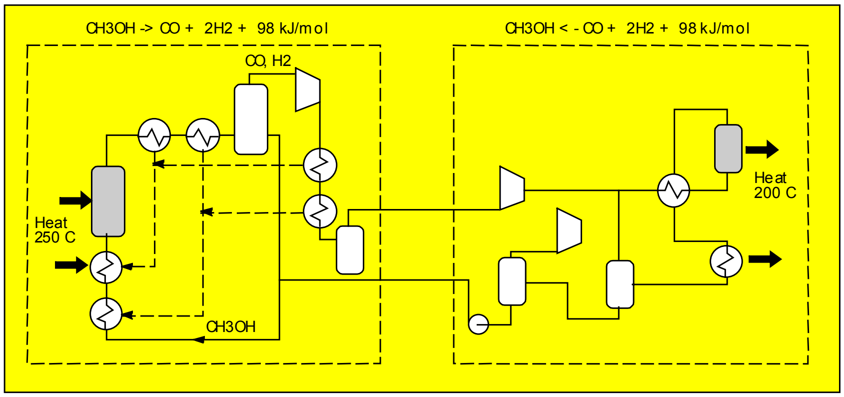


Figure 4 System schematic of a heat transport system using methanol decomposition and synthesis. The gray-filled system components are the decomposition and synthesis reactor Methanol (CH3OH) is split in CO and H_2 at a temperature of 200 - 250 °C. (Kawasaki, Shiizaki, 2000).

Research on the system shown in figure 4 has been focused on the methanol decomposition reactor, particularly with respect to the selection of the catalyst material en the heat exchange characteristics of the fixed bed type reactor. Though process simulation of the entire system shows that it may work as a heat transport system (conversion efficiency of 50 %), the function as heat storage system is less advantageous because the gaseous decomposition components CO and H_2 may require large storage volumes. One complicating factor is that thermo-chemical reactions frequently involve gaseous compounds (CO_2, H_2), which can be stored at an acceptable density only at low temperatures or/and high pressure. Both the low temperature as well as high-pressure storage options create ongoing energy losses and therefore tend to adversely affect the effective storage efficiency. One challenge in the quest for high-density storage is to find chemical compounds that do not produce gasses throughout the conversion and storage process.

A chemical heat pump process based on hydration and dehydration of magnesium oxide/hydroxide could be used for thermal energy storage (Kato, 2004a).

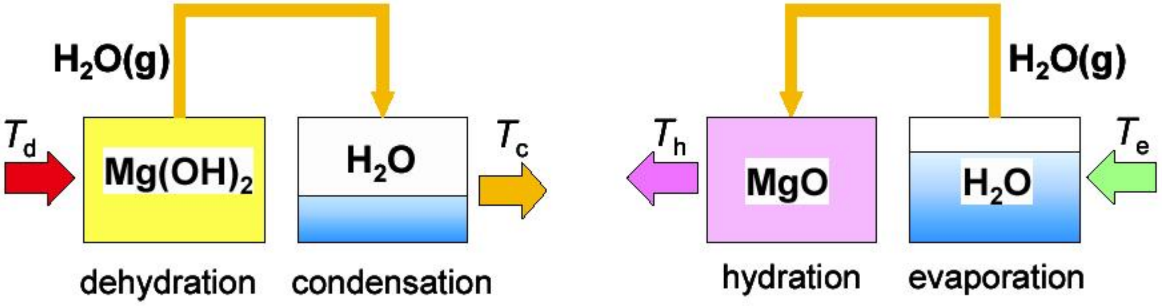


Figure 5 MgO-chemisorption process, Kato, 2004a

A laboratory scale reactor has been build. The experiments demonstrated that ultra fine particles of MgO can be used for high durability, repetitive reversible reaction for the MgO/H_2O chemical heat pump. The process operates at 250 - 400 °C and may achieve an energy storage density of 4 – 7 times that of sensible heat in water.

The quest for suitable chemical reactions for storage of solar heat in the 200 °C range also comprises (Kato, 2004b):

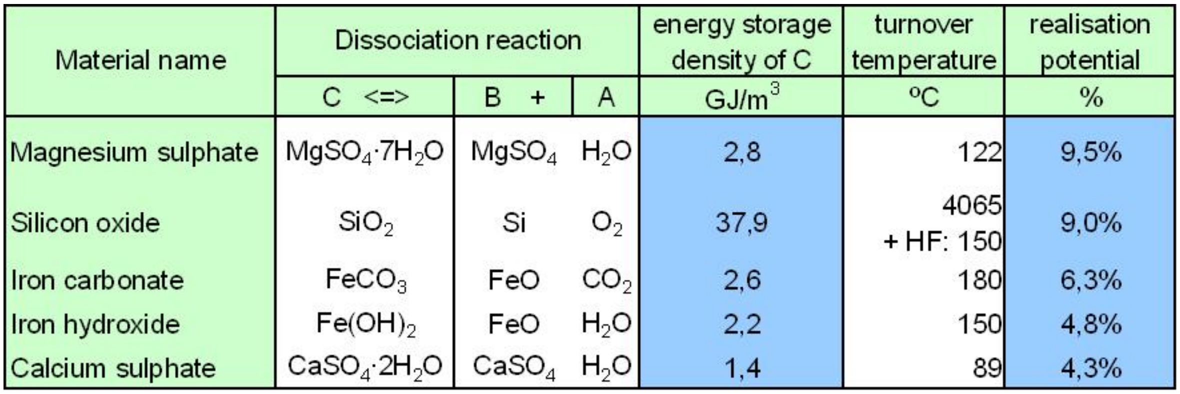
Metal oxide + water -> Metal hydroxide.

Metal oxide + NH3 -> Metal ammonium salt.

From thermodynamic data (calculating turnover temperature at which the free energy change attains the minimum), it is possible to select the most attractive candidates. In addition, Development of durable and high-reactive material is required. For the carbonation system: Metal oxide + CO_2 > Metal hydroxide, CO2 storage and work consumption for pressure change should also be taken into account.

In an extensive recognizance study for medium temperature thermo chemical storage materials, ECN and Utrecht University, The Netherlands, identified many candidate materials that were all selected with respect to criteria similar as outlined in table 1. Table 2 shows the 5 most attractive candidate materials (Visscher 2004)..

Table 2 Promising chemical solar storage candidate materials, identified by ECN/UU, The Netherlands (Visscher, 2004).



Material name	Dissociation reaction			energy storage density of C	turnover temperature	realisation potential
	C <=>	B +	A	GJ/m^3	°C	%
Magnesium sulphate	$MgSO_4·7H_2O$	$MgSO_4$	H_2O	2,8	122	9,5%
Silicon oxide	SiO_2	Si	O_2	37,9	4065 + HF: 150	9,0%
Iron carbonate	$FeCO_3$	FeO	CO_2	2,6	180	6,3%
Iron hydroxide	$Fe(OH)_2$	FeO	H_2O	2,2	150	4,8%
Calcium sulphate	$CaSO_4·2H_2O$	$CaSO_4$	H_2O	1,4	89	4,3%

An indicator was defined in the study, called the realisation potential. This was calculated based on the criteria similar to those of table 2 together with weighting factors, in order to have a single figure for comparing the suitability of the different reactions for the aims of the project.

Both $MgSO_4·7H_2O$ and $CaSO_4·2H_2O$ are hydrates that fall under sorption processes discussed in chapter 3 of this handbook. The iron complexes $FeCO_3$ (carbonate) and $Fe(OH)_2$ (hydroxide) can be viewed upon as attractive chemical storage materials with reasonable storage densities 1.2 - 2.6 GJ/m^3 at acceptable temperature levels 150-180 °C. The Silicon based system as described by Auner et al., 2003 involves is based on the reaction of silicon with oxygen and/or nitrogen. The exothermic part of the cycle is the "burning" of silicon with oxygen and/or nitrogen which is suitable for application in residential areas. The reverse (endothermic) process is the conversion of the produced silicon nitride and silicon oxide ("sand") back to silicon. This process has to be conducted in an industrial environment because it involves a complex reaction scheme with side reactions including HF and electrolysis of NaF and H_2O. The conclusion of this study is that in principle attractive materials exists, but further research is needed to determine practical aspects like reaction kinetics and mass transfer rates.

A system slightly above of the temperature limit of 250 °C, is the sodiumhydroxide storage suggested by Weber, 2003 The reversible reaction $2\ NaOH \Leftrightarrow NaO + H_2O$ can store in principle 2.6 GJ/m^3 of thermal energy at 300 °C. Quite interestingly, this reaction was used for many years around 1920 in fireless steam locomotives.

Figure 6 Fireless steam locomotive as used in around 1920 (reference unknown).

All the above systems are examples found for medium temperature applications. As mentioned before, in the field of thermo chemistry more emphasis is given to high temperature reactions (e.g. steam reforming) with temperatures that cannot be reached by solar collectors for domestic applications.

Photo-chemical conversion & storage

Sunlight can be converted into chemical energy without an intermediate thermal energy conversion step. The predominant example is photosynthesis: fixation of biomass ($C_6H_{12}O_6$) from CO_2, H_2O and solar energy. Green (bio) synthesis (naturally or artificial) is an attractive way to convert & store solar energy because of the easy distribution and storage features of the produced fuel (e.g. methanol from wood). The production efficiency of biomass by natural photosynthesis is not very high (0.25 % on average, Titchener, 1983). The low efficiency however is not the only concern (the efficiency of solar to hydro power electricity, the biggest sustainable energy source, is about a mere 1 %). The limitation here is that the raw energy carrier (biomass product; plant material) is not very convenient for storage and transport (whereas in the case of hydropower the energy carrier is water at an elevated altitude which is relatively easily stored and transported).

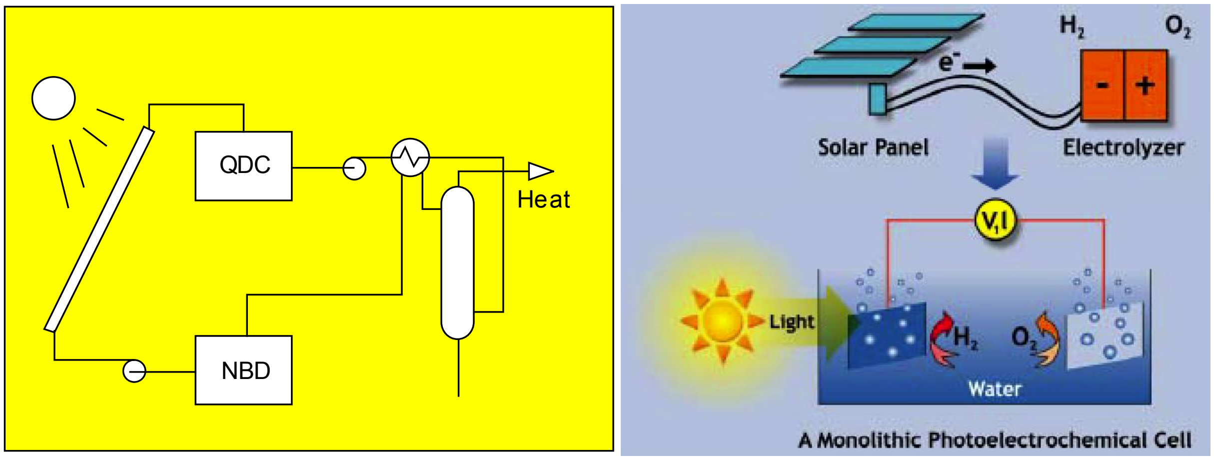
The operation of photochemical systems, basically involves two distinctive steps (Schut, 1999):

Table 3 Two steps commonly found in direct photochemical systems

Absorption of photons and excitation of molecules from their ground state to various upper vibration levels of its excited state. The absorption can occur in a direct and sensitized process (involving a additional photositiser and reactant.
Relaxation (deactivation) back to the ground state, ideally producing a useful product.

In both processes, loss-mechanisms determine the overall efficiency: i.e. not all photons can be absorbed with an energy matching the excited state, not all absorbed photons yield a useful product). In theory, the upper limit of the exergetic efficiency in photochemical conversion is 33%. In practice, the efficiency at present is much lower (~1 %).

Photochemical devices may produce electricity (like e.g. the "Gratzel cell") or a chemical substance like a hydro carbon (biomass) or hydrogen. Well known examples are biological conversion of solar energy in the atmosphere, but also in the deep-sea (Galapagos-reef?). Solar produced energy carriers (Fe^{2+}, Sulphide) serve as nutrients for bacteria (Thiobacilli) which fixate CO_2 and build biomass. Very few technical photo chemical solar storage systems have been studied till now. One example is given in figure 7.a.



a) b)

Figure 7 a) Schematic of a NBD/QDC low pressure steam/water producing photochemical system (Schut, 1999)., b) Solar hydrogen production: Replacing PV/electrolyzer (top) with a PEC system

In general, the photochemical conversion route may be characterised by a high energy density but as yet a low efficiency. The system, in which formic acid CHOOH is formed from CO_2 and H_2O, yields an energy density of 6.7 GJ/m^3, which is comparable with the energy density of hydrocarbon fuels (40 GJ/m^3). The energy efficiency is estimated at slightly less than 1%. It can be stated that considerable improvements in the conversion efficiency are necessary to make photochemical reactions competitive with other solar energy options as PV-cells and solar heat collectors. However, direct storage of electricity and heat suffers from ongoing energy losses, whereas biomass fuels can be stored for many years without significant losses.

Improvements in the conversion efficiency are expected to come from:

Increase of the exergetic efficiency of the photo collection process.

Increase of the quantum yield (reactants into products).

Within the photochemical research, water decomposition attracts most attention. Ultimate aim (i.e. within IEA framework) is to replace a combined PV-electrolyzer system with an integrated PhotoElectroChemical (PEC) cell, see figure 5.b. Most of the water decomposition cells are semi-conductor cells. A single example of direct, homogeneous water decomposition using solar energy as the sole driving force has been reported, but is unlikely to become competitive, see Bolton, 1996. Semiconductor (e.g. TiO_2) photochemical systems producing hydrogen date back to 1972, see Roloos, 2000. In this system, TiO_2 is used as the photo sensitizer that absorbs photons to excite electron. The combination of electricity producing photo-electrochemical and a water decomposition cell has lead to development of so called tandem cells. In these systems electrons produced in one part of the systems are used elsewhere in the same system for the reduction reaction. Amongst others these systems are studied e.g. in Switzerland, see BFE, 2002, and Rak, 199x. There is also research on biological water decomposition systems based on algae in water tanks. These systems directly produce hydrogen and oxygen from sunlight.

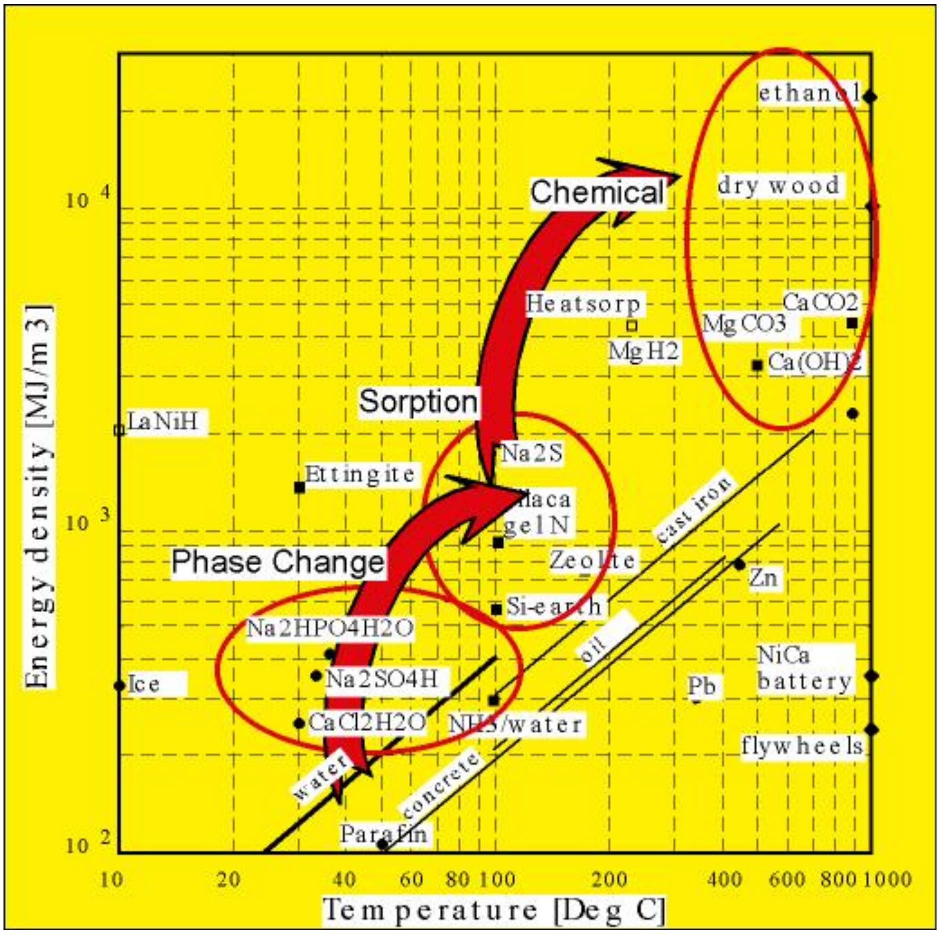
Though solar hydrogen systems potentially are attractive because of the clean and multipurpose hydrogen produced, barriers need to be overcome regarding conversion efficiency, storage density (of hydrogen) and ongoing energy losses during storage and system reliability. These factors directly are reflected in the cost of these systems, which will be the final barrier when the other problems are solved.

Resume

The state of the art of thermo-chemical and photochemical solar energy conversion systems can be characterised according to the next table:

	Thermo-chemical	Photo-chemical
Development stage	Demo	Laboratory
Storage density	Moderate	High (5-15 GJ/m^3)
Conversion and storage efficiency	Moderate 50-80 %	Low 1 %
Conversion temperature	medium (~200 °C)	Ambient temperature

Both the thermo-chemical as well as the photochemical conversion route are as yet not ready for market introduction. In the



long run however these techniques are expected to replace hot water based conversion and storage devices.

Figure 8 Temperature – density diagram of storage materials

Solar thermo chemical systems are in a laboratory demonstration phase. Work has to be done on reaction kinetics and mass transfer rates.

Given the high potential of solar produced energy carriers like liquid biofuels (long term storage efficiency, high energy density) this option is expected to take the lead sooner or later. Direct conversion of solar energy into a liquid or gaseous fuel is attractive and possible, though (as yet) efficiencies are low and (therefore) costs are high. Given the premature status of the technique, much work within photochemistry is directed towards improvements of these points.

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14. Conclusions

by Jean-Christophe Hadorn

Storing thermal energy in a cost effective way is needed to overcome solar energy interruptions and to better manage heat or cold in any thermal systems.
Several options to store thermal energy have been discussed in this book, mainly for single family house:

- Storing in the building structure
- Water tank storage
- PCM storage
- Sorption storage
- Thermo-Chemical storage

Some of these options have the potential to help to increase the market of solar energy for both heating and cooling. Some have the potential to yield to long-term or seasonal storage, even on a small scale.
The large storage solutions for seasonal storage currently available (big tanks, duct stores or aquifer storage) have not been described in this document. They are however an alternative that should be considered when designing thermal systems for loads larger than 500 MWh/year.

When dealing with smaller loads for a low energy one family house, the following questions are the basic questions that still need scientifical answers, that were adressed by Task 32:

1. Are there other solutions than water as the preferred storage medium in terms of performance and cost ?
2. Is a detached centralised storage the best solution or the storage embedded into structure can be more economical and effective ?
3. Is a single house storage a good solution compared to a large centralised storage system shared by hundreds of houses ?
4. Is there a PCM that could be both efficient and low cost ?
5. Is there a chemical reaction that could be considered to increase the solar fraction of solar installations ?
6. Are high temperature solar collectors needed then ?
7. Can we combine both heat and cold storage to meet the heating and cooling loads at a reduced specific cost ?
8. Is the goal of 100% solar with advanced storage a reasonable goal ?
9. Will hydrogen be the competitive reference for storing energy during long-term in the long run for a solar house ?
10. How can we enhance water storage tanks for solar combisystems ?

The authors of this book hope that Task 32 and others will contribute to bring some answers to these questions. The development of solar heating and cooling is indeed very dependant upon the capacity of storing solar energy when available and to later meet the load on demand.

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