
Thermal Properties of Materials for Thermo-chemical Storage of Solar Heat

**A Report of IEA Solar Heating and Cooling programme - Task 32
“Advanced storage concepts for solar and low energy buildings”**

Report B2 of Subtask B

May 2005

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A technical report of Subtask B



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IEA Solar Heating and Cooling Programme

The *International Energy Agency* (IEA) is an autonomous body within the framework of the Organization for Economic Co-operation and Development (OECD) based in Paris. Established in 1974 after the first “oil shock,” the IEA is committed to carrying out a comprehensive program of energy cooperation among its members and the Commission of the European Communities.

The IEA provides 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; to eliminating technological risks and duplication of efforts; and to creating numerous other benefits, such as swifter expansion of the knowledge base 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 members have been collaborating to advance active solar and passive solar and their application in buildings and other areas, such as agriculture and industry. Current members are:

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

A total of 39 Tasks have been initiated, 30 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 32 *Advanced Storage Concepts for Solar and Low Energy Buildings*
- Task 33 *Solar Heat for Industrial Processes*
- Task 34 *Testing and Validation of Building Energy Simulation Tools*
- Task 35 *PV/Thermal Solar Systems*
- Task 36 *Solar Resource Knowledge Management*
- Task 37 *Advanced Housing Renovation with Solar & Conservation*
- Task 38 *Solar Assisted Cooling Systems*
- Task 39 *Polymeric Materials for Solar Thermal Applications*

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*
- Task 28 *Solar Sustainable Housing*
- Task 27 *Performance of Solar Facade Components*
- Task 29 *Solar Crop Drying*
- Task 31 *Daylighting Buildings in the 21st Century*

Completed Working Groups:

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

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

September 2007

What is IEA SHC Task 32

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

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

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

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

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

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

The Subtasks are:

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

Duration

July 2003 - December 2007.

www.iea-shc.org look for Task32

IEA SHC Task 32 Subtask B

“Chemical and sorption storage”

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

Adsorption promising techniques based on silicagel or zeolite materials, long time forgotten for solar energy, have been investigated in Task 32.

Chemical reactions adapted to storage of solar heat for the purpose of heating a building have also been looked at.

The report presents work done by participants in Task 32, as a first step, to choose, and gather information on thermal properties of some material suitable for storing heat in the range 0 – 100 C.

Knowledge on materials is a prerequisite to be able to design storage units, exchangers and finally thermal solar installations including a dense storage.

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

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NOTICE:

The Solar Heating and Cooling Programme, also known as the Programme to Develop and Test Solar Heating and Cooling Systems, functions within a framework created by the International Energy Agency (IEA). Views, findings and publications of the Solar Heating and Cooling Programme do not necessarily represent the views or policies of the IEA Secretariat or of all its individual member countries.

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1 INTRODUCTION

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. For chemical storage, heat is required in an endothermic process to split compounds into several products. For a cyclic process, the products of the reaction or sorption process have to be reconverted to the original compound in an exothermic reaction, where heat can be utilized for the load. The exothermic reaction is generally at a lower temperature than that of the endothermic reaction. Many compounds result in products that can be stored over long periods without significant energy losses, making long term heat storage possible.

The main **advantages** of chemical storage including sorption:

- High energy density resulting in small volume of material.
- Many systems act as heat pumps making cooling as well as heating possible.

The main **disadvantages**:

- Greater complexity in the system (closed systems).
- Many compounds are relatively expensive.
- Relatively high temperatures required.
- Limited experience with long-term operation (after many thousand cycles).

2 Classification of Thermo-Chemical Storage Principles

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.

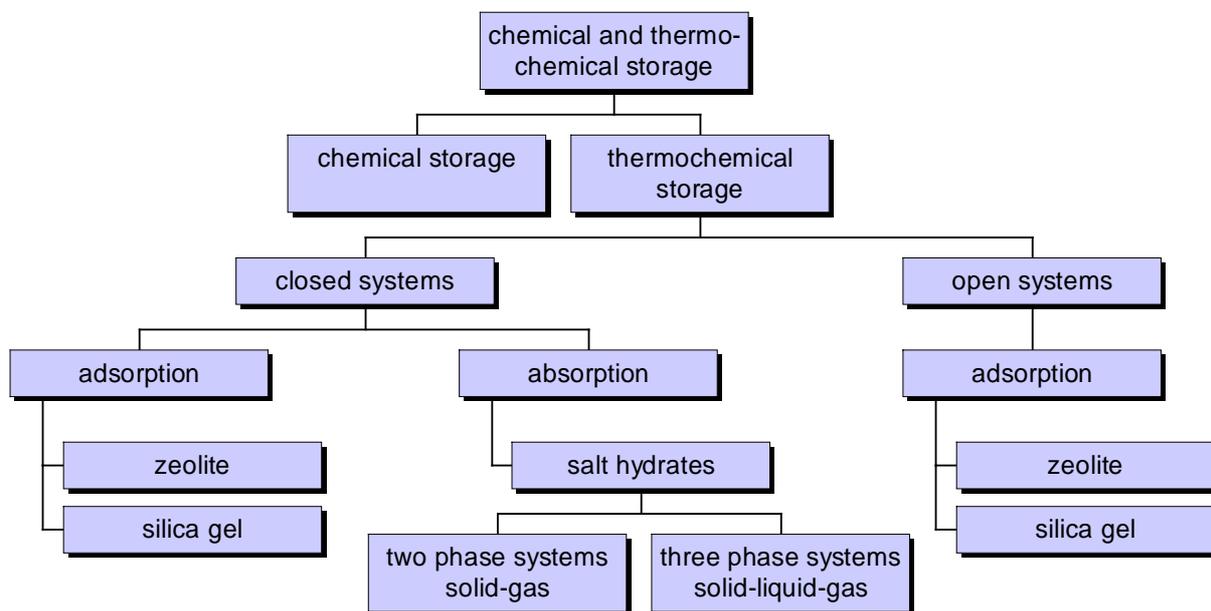


Figure 1. Classification of chemical and thermo-chemical processes for heat storage applications.

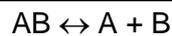
For closed systems, two main lines can be defined: adsorption and absorption. Adsorption is the bonding of a gas on the surface of a solid, in the absorption process a new compound out of the absorbent and the working fluid is formed. This is mainly the case in salt hydrates or salt ammoniates. Two and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

3 THERMODYNAMICS AND MATERIAL PROPERTIES

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



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.

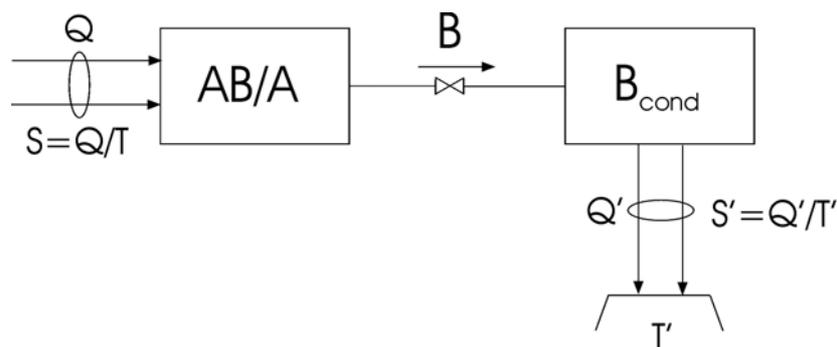


Figure 2. Indirect heat storage by way of a reversible thermo-chemical reaction. Closed system with condensation of the gaseous working fluid. [1]

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 ($\text{kg}_{\text{H}_2\text{O}}/\text{kg}_{\text{sorbent}}$) for solid adsorbents.

$\Delta H_a = \Delta H_v + \Delta H_b$	Equ. 1
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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 $c(T, p)$ [$\text{kg}(\text{sorbate})/\text{kg}(\text{sorbent})$] 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 1 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.

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 **Na₂S (353 Wh/kg)**, **CaCl₂ (271 Wh/kg)**, **MgCl₂ (233 Wh/kg)**, and **LiCl (197 Wh/kg)**.

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

Absorption	Solid – Gas Reaction	Adsorption
NH ₃ – H ₂ O: 110 Wh/kg	H ₂ O – Na ₂ S: 353 Wh/kg	H ₂ O – zeolite 4A: 23 Wh/kg
H ₂ O - NaOH: 277 Wh/kg	H ₂ O – MgCl ₂ : 233 Wh/kg	H ₂ O – silica gel: 40 Wh/kg
	H ₂ O – CaCl ₂ : 271 Wh/kg	
	H ₂ O – 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 Na₂S 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.

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 Figures 3-6 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.

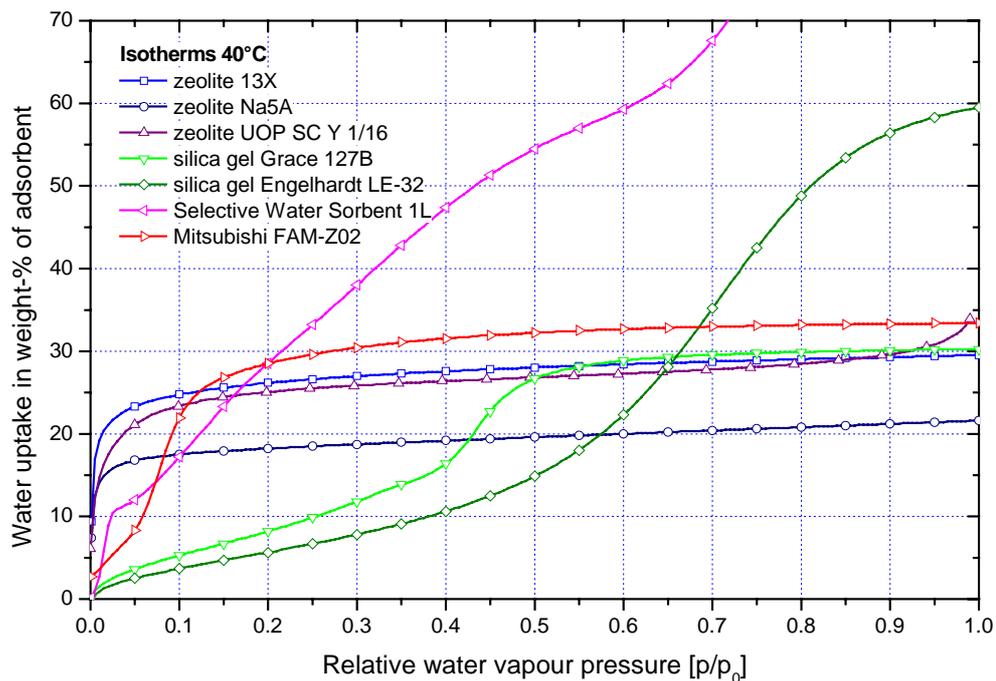


Figure 3. Water adsorption isotherms (40°C) for a selection of adsorption materials. Source: Fraunhofer ISE

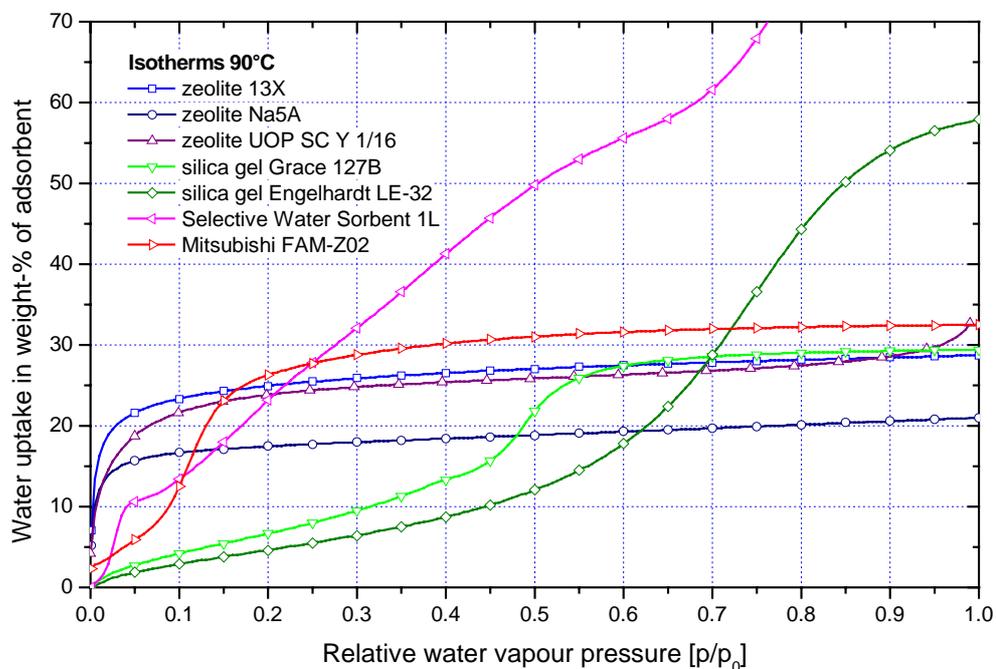


Figure 4. Water adsorption isotherms (90°C) for a selection of adsorption materials. Source: Fraunhofer ISE

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 adsorption 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.

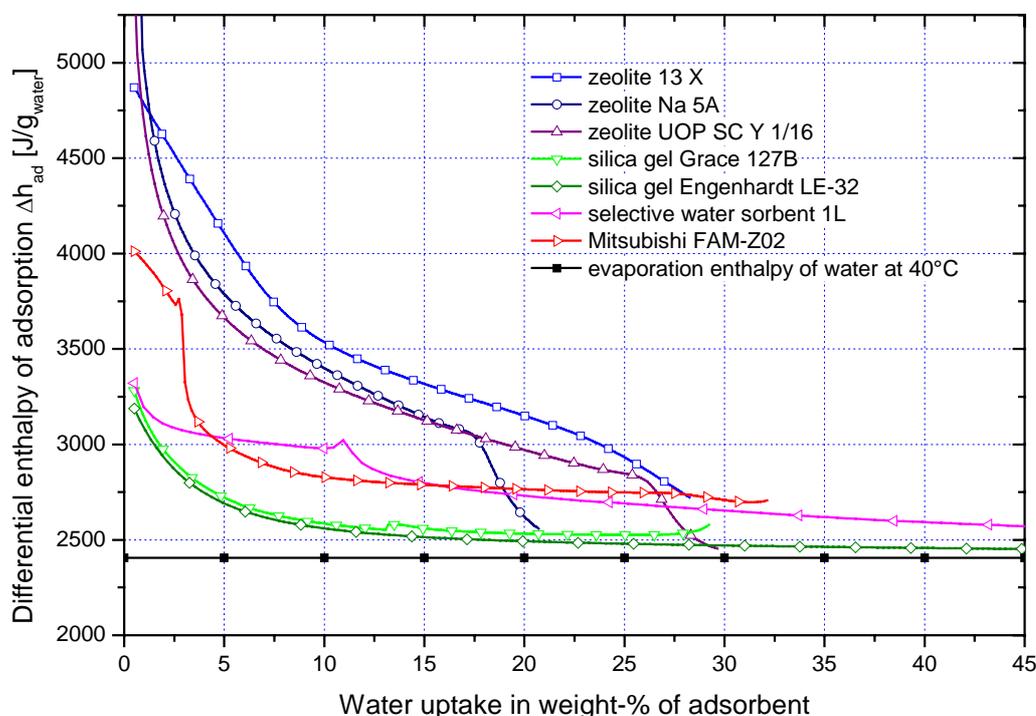


Figure 5. Differential heat of adsorption over water uptake at 40°C

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 of Equ. 1 and the binding enthalpy H_b .

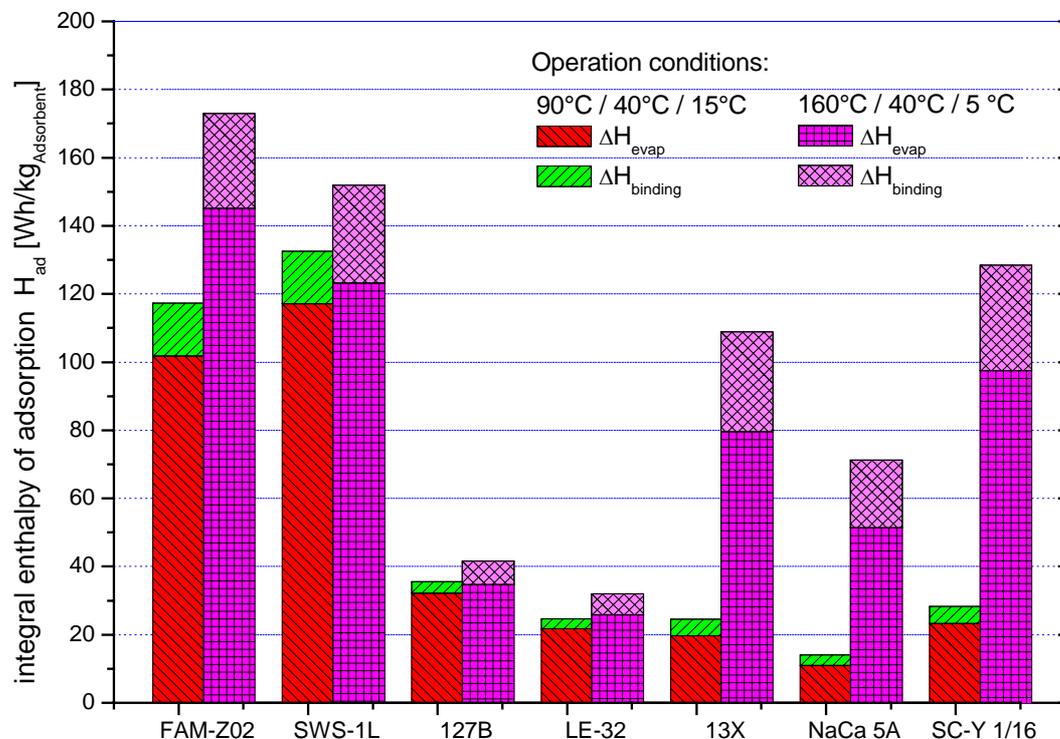


Figure 6. Integral heat of adsorption (in Wh/kg_{Adsorbent}) for two operation conditions for seven different adsorption materials.

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 m³ 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/m³ and 820 kg/m³.

4 MATERIALS FOR SEASONAL STORAGE IN HOMES

In an extensive recognisance 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 3 which shows the five most attractive candidate materials [14].

Table 3 Promising chemical solar storage candidate materials, identified by ECN/UU, The Netherlands [14].

Material name	Dissociation reaction			energy storage density of C GJ/m ³	turnover temperature °C	realisation potential %
	C <=>	B +	A			
Magnesium sulphate	MgSO ₄ ·7H ₂ O	MgSO ₄	H ₂ O	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 ₂ O	2,2	150	4,8%
Calcium sulphate	CaSO ₄ ·2H ₂ O	CaSO ₄	H ₂ O	1,4	89	4,3%

An indicator was defined in the study, called the realisation potential. This was calculated based on a set of criteria 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 MgSO₄·7H₂O and CaSO₄·2H₂O are hydrates that fall under sorption processes. The iron complexes FeCO₃ (carbonate) and Fe(OH)₂ (hydroxide) can be viewed upon as attractive chemical storage materials with reasonable storage densities 1.2 - 2.6 GJ/m³ at acceptable temperature levels 150-180 °C. The Silicon based system as described by Auner et al., 2003 [15] 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 H₂O.

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.

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