



Final Report

August 2013

Task 42

Annex 24

Compact Thermal Energy Storage: Material Development for System Integration

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1 Organisational Structure of Annex 24

From past IEA SHC and ECES tasks it was concluded that a broad and basic research and development initiative is needed to find and improve thermal energy storage materials for applications, where a high storage capacity is needed. Such storage systems aim to be smaller and lighter. Therefore they are defined as “compact” thermal energy storages. This Annex 24 is an activity performed by two Implementing Agreements - Solar Heating and Cooling (SHC) and Energy Conservation through Energy Storage (ECES) - within the Technology Network of the International Energy Agency, IEA. The IEA joint Task/Annex 42/24 brings together experts from both the materials development field and the systems integration fields. In four years, the task aims at having taken the first steps towards a new generation of thermal storage technologies.

1.1 Objectives and Scope of the Annex

Objective

The overall objective of this task is to develop advanced materials and systems for the compact storage of thermal energy. This can be subdivided into seven specific objectives:

- to identify, design and develop new materials and composites for compact thermal energy storage,
- to develop measuring and testing procedures to characterise new storage materials reliably and reproducibly,
- to improve the performance, stability, and cost-effectiveness of new storage materials,
- to develop multi-scale numerical models, describing and predicting the performance of new materials in thermal storage systems,
- to develop and demonstrate novel compact thermal energy storage systems employing the advanced materials,
- to assess the impact of new materials on the performance of thermal energy storage in the different applications considered, and
- to disseminate the knowledge and experience acquired in this task.

A secondary objective of this task is to create an active and effective research network in which researchers and industry working in the field of thermal energy storage can collaborate. The fragmented R&D activities worldwide should be better coordinated.

Scope

This task deals primarily with advanced materials for latent and chemical thermal energy storage. The task deals with these materials on three different scales:

- material scale, focused on the behaviour of materials from the molecular to the ‘few particles’ scale, including e.g. material synthesis, micro-scale mass transport, and sorption reactions;

- bulk scale, focused on bulk behaviour of materials and the performance of the storage in itself, including e.g. heat, mass, and vapour transport, wall-wall and wall-material interactions, and reactor design;
- system scale, focused on the performance of a storage within a heating or cooling system, including e.g. economical feasibility studies, case studies, and system tests.

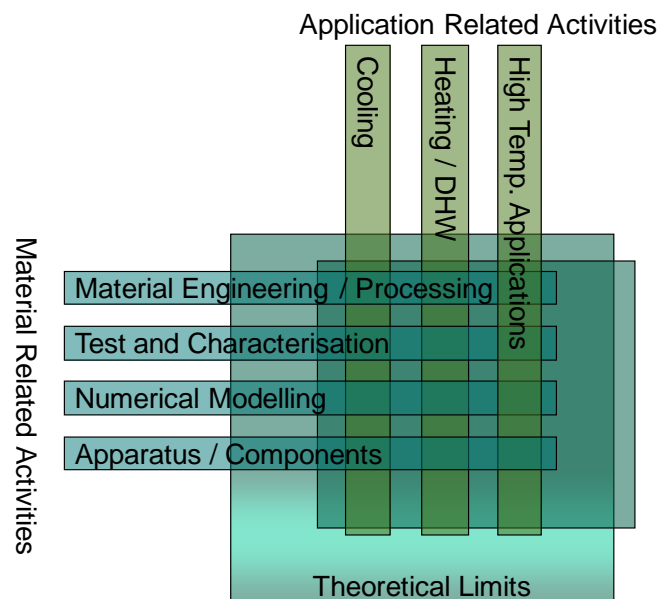
Because seasonal storage of solar heat for solar assisted heating of buildings is the main focus of the SHC IA, this will be one of the primary topics of this task. However, because there are many more relevant applications for TES, and because materials research is not and cannot be limited to one application only, this task will focus on multiple application areas.

The Applications Subtask is subdivided into three Working Groups, corresponding to three different temperature levels of thermal energy storage. These levels are:

- cooling (temperatures typically below 20°C),
- heating and domestic hot water (between 20 °C and 100 °C) and
- high temperature applications (above 100 °C).

1.2 Working Group Structure

The Task work is performed in a number of Working Groups. There are 4 materials related working groups, three applications related working groups and one “cross cutting” working group, see the schematic below. The cross cutting working group “Theoretical Limits” deals with the very basic question, what can be expected from the thermodynamic point of view.



A matrix-like structure has been chosen for the Task in order to increase the opportunities for materials experts and application experts to exchange knowledge and experience.

Each working group is lead by an expert, the working group leader. The working group leader is responsible for the coordination of the common tasks and for the achievement of the goals of the working group. The working group leaders are listed below.



Working Groups leadership

Materials:	WG Leader
Material Engineering / Processing	Elena Palomo (Univ.Bordeaux)
Test and Characterization	Stefan Gschwander (ISE)
Numerical Modelling	Camilo Rindt (TUE)
Apparatus and Components	Wim van Helden (Renewable Heat, AgentschapNL)
Applications:	
Cooling (0 °C – 20 °C)	Motoi Yamaha (Chubu Univ.)
Heating / DHW (20 °C – 100°C)	Jane Davidson (Univ.Minnesota)
High Temp.Appl. (> 100 °C)	Luisa Cabeza (Univ.Lleida)
Cross Cutting:	
Theoretical Limits	Eberhard Lävemann (ZAE)

1.3 Annex Period

The Task started 1 January, 2009 and ran until 31 December, 2012.

1.4 Annex expert meetings and Workshops

The official start of the Task is 1 January, 2009. Experts meetings and workshops were held twice a year. Below is the table giving an overview of the Annex 24 expert meetings. Eight meetings were held.

	Place	Country	Date	# part.
1	Bad Tölz	Germany	11-13 February, 2009	69
2	Lleida	Spain	21-23 September, 2009	71
3	Bordeaux	France	7+8 July, 2010	51
4	Graz	Austria	26-28 September, 2010	56
5	Belfast	United Kingdom	20+21 February, 2011	36
6	Minneapolis	United States	20-22 September, 2011	30
7	Tokyo	Japan	27-29 March, 2012	24
8	Petten	The Netherlands	18-19 October, 2012	54

1.5 Status of participation

In total, there were 55 organisations participating. It must be said, however, that there is a large number of organisations that once expressed their interest, but are not active in the Task and some of them have never or only once attended the experts meetings.

Below is the table of participants as of December 2012.



country	organisation	first name	familyname	Funding remarks	PM project	PM IEA	nat part letter
AT	AEE Intec	Alexander	Thür				
AT	IWT TU Graz	Andreas	Heinz		8	2	signed
AT	ASIC Austria Solar Innovation Center	Bernhard	Zettl	Funded	4	1,4	singed
AT	Austrian Institute of Technology AIT	Olivier	Pol	Funded	3	1,7	signed
AT	University of Innsbruck	Wolfgang	Streicher	Funded	8	2	signed
AU	University of South Australia	Frank	Bruno	Applied for funding	86	2	
BE	VITO	Johan	Van Bael	Own funding			
BE	Universite de Mons, Energy Research Centre	Marc	Frère	Funded			signed
BE	Universite de Liege	Philippe	André	Funded			signed
CA	University of Ottawa	Handan	Tezel	Funded	36		
CH	SPF	Elimar	Frank	Applied for funding			
CH	EMPA	Robert	Weber	Funded until Jan 2010	12	2	
DE	ZAE Bayern	Andreas	Hauer	ECES Funded	56	24	
DE	DLR	Antje	Woerner				
DE	ZAE Bayern	Eberhard	Lävemann	ECES Funded			
DE	Univ. Of Bayreuth	Fabian	Roesler				
DE	Vaillant	Frank	Salg	Own funding			
DE	University of Magdeburg	Franziska	Scheffler	no funding			
DE	ITW Stuttgart	Henner	Kerskes	ECES Funded	100	6	
DE	University of Erlangen	Jimi	Ofili				
DE	Fraunhofer IGB	Mike	Blicker				
DE	University of Kassel	Roland	Heinzen	Funded	48	4	
DE	Fraunhofer ISE	Stefan	Gschwander	ECES Funded	49	12	
DE	Leuphana Universität Lüneburg	Thomas	Schmidt	Funded			
DK	Technical University of Denmark	Simon	Furbo	funded until jan 2012	15,6		signed
ES	University of the Basque Country	Aitor	Urresti				signed
ES	Universidad de Zaragoza	Ana	Lazaro	Funded	19,7	1,15	signed
ES	Abengoa Solar NT	Cristina	Prieto	Applied for funding			
ES	University of Barcelona	Inés	Fernández	Own funding			signed
ES	University of Lleida	Lluisa	Cabeza	Funded	250	20	
ES	Aidico	Maria Dolores	Romero		4	1	signed
ES	Tekniker	Miren	Blanco	Funded	22	1	
ES	Tecnalia San Sebastian	Patricio	Aguirre	Funded			
ES	CIEMAT	Rocio	Bayon Cabeza	Funded	56		signed
FR	University of Bordeaux	Elena	Palomo	Funded			
FR	Thermal Science Centre of Lyon	Frédéric	Kuznik	Funded	60	10	
FR	Universite de Pau	Jean-Pierre	Bedecarrats				
FR	LTN-CNRS-Universite de Nantes	Lingai	Luo-Dong				
FR	EDF	Philippe	Stevens	Funded	48	8	
FR	INES	Philippe	Papillon	Funded			
FR	LOCIE-University of Savoie	Benoit	Stutz	Funded	40	2	
IT	University of Palermo	Valerio	Lo Brano	Funded			8 signed
JP	Chubu University	Motoi	Yamaha				
NL	Technical University Eindhoven	Camilo	Rindt	Funded	92	8	
NL	ECN	Marco	Bakker		150	24	
NL	TNO Built Environment and Geosciences Energy	Ruud	Cuypers				
SE	KTH	Viktoria	Martin	Funded	48	8	signed
SI	National Institute of Chemistry	Venceslav	Kaucic	Applied for funding	48		
TR	Gaziosmanpa University	Cemil	Alkan				
TR	Cukurova University	Halime	Paksoy	Applied for funding			
UK	University of Warwick	Changying	Zhao	Funded	100		
UK	CREST; University of Loughborough	Phil	Eames	Applied for funding	12		
UK	University of Ulster	Philip	Griffiths				
UK	University of Leeds	Yulong	Ding				
US	Fraunhofer CSE, Cambridge	Jan	Kosny	unknown			
US	University of Minnesota	Jane	Davidson	Funded	36	3	signed
US	OakRidge National Laboratory	Steve	Smith	Funded	12		

From the ECES the following countries and sponsors (and institutions) participated in the Annex:

- Germany (ZAE Bayern and Fraunhofer ISE)
- France (University of Bordeaux)
- Japan (Chubu University)
- Sweden (Royal Institute of Technology KTH)
- Turkey (Chucurova University)
- University of Lleida (and University of Barcelona)

Seventeen organisations from seven countries returned the signed SHC national participation letter to declare their official participation from this side.



1.6 Final Report Structure

Both Implementing Agreements, SHC and ECES, have different rules for the outcome of an Task or Annex. While SHC expects a number of predefined “deliverables” from the working groups at a quite detailed level, ECES expects a final report, summarizing the important findings and accepts the detailed information as appendices to the report. All citations, publications and further literature can be found in these appendices.

The final report of Annex 24 consists of an

- **Executive Summary**, focussing on the main findings,
- the **Final Report** itself, which actually summarizes the results of the work performed within the different working groups, and
- the **Deliverables** of the working groups (detailed working group reports) as appendices.

Details about the authors, the on-going R&D projects and the cited literature can be found in the appendices.

2 Executive Summary

„In a Nut-shell“

- International and inter-disciplinary collaboration in the field of material R&D for compact thermal energy storage established
- Numerous R&D activities on material development for thermal energy storage worldwide ongoing
- First steps towards a standardized test and characterization procedures for new materials taken
- White spots in the field of numerical modelling of thermal energy storage materials identified
- Operation conditions for cooling, heating/domestic hot water and high temperature applications listed
- First approaches for physical limits of energy storage density and economic limitations of energy storage applications found

Theoretical Limits

The cross cutting Working Group on „Theoretical Limits of Thermal Energy Storage” laid the basis for the following activities. In order to define the physical limits of achievable energy storage densities, it was important to make clear, that energy storage density is not a property of the storage material. It is depending on the operation conditions, the process parameters!

However thermodynamic limitations of the energy storage density can be defined. Since the energy density is coupled to the (reaction) enthalpy dH and $dH = T \cdot dS$, it can be stated that at a given temperature the energy density is depending on the change in entropy S . All storage reactions under investigation today are working by releasing a gaseous component, which leads already to very high values for dS . There is no substantial improvement of energy storage density to be expected unless the (reaction) temperature can be raised in the process. Semi-empirical rules for the dependency of the energy density on the temperature were collected and developed.

Limitation of the charging and discharging power are basically caused by technical limitations. Thermal power output can be increased by different measures, which are coupled to increasing cost. Different approaches to identify “theoretical” limits were started. It was not possible to come to a final result within this Annex, but these activities should be continued.

For the economical limits of energy storages in general a Top-Down approach was chosen. The question was answered, what is the acceptable cost (\$ per kWh storage capacity) of an energy storage under certain operation conditions and fields of application (industry/buildings). There is a strong dependency of the acceptable cost on the storage cycle number per time: A high number of cycles per year allows higher storage investment cost and by that more complex storage systems, while storage applications with only few cycles (e.g. seasonal storage) per year can only be put into prac-

tice by very inexpensive storage systems. A Bottom-Up approach, to estimate the actual cost for a certain storage system, will be discussed in the future.

Material Development

The work carried out in WGA1 opens new R&D perspectives for material development fully in line with compactness and cost effectiveness of the storage systems.

In order to lower material cost, it is a very interesting issue to evaluate alternative materials through the valorization of by-products. Materials as cheap as 0.001 €/kg with convenient performances for sensible heat storage at high temperature have been found. This research effort must be continued and extended to PCMs.

The solid-liquid transformation of materials encompasses a reversible, isothermal solid-liquid reaction and a solid-liquid phase change. As a result, exceptionally high values of energy density can be achieved when the enthalpy of reaction is significant. An anhydrous salt formed in a peritectic transition at 312°C, with energy density as high as 218 kWh/m³, has been identified. Materials formed in peritectic transitions represent a storage solution midway between latent heat and thermochemical storage solutions. For temperatures above 300°C, it is expected that they provide effective energy density comparable to that of solid-gas chemical reactions (200-400 kWh/m³) but with a simpler and much cheaper storage technology.

It is well-known that confinement in nano-pores can greatly affect the properties of a fluid. Significant changes in the melting/freezing point, as well as in the latent heat, of a PCM can be achieved in such way. It was shown that the latent heat of paraffin is increased by around 20 % when nano magnetite at 10% by weight was added to liquid paraffin. Further theoretical and experimental researches are needed to understand liquid-solid transition in nano-composites and nano-particle doped PCMs and to explore the benefits for thermal energy storage.

A novel microporous sorption material (AlPO-Tric), which is so far the most promising among the aluminophosphates for storage at low temperature, has been produced. On the other hand, the new family of MOFs (Metal-Organic-Frameworks) results in a very promising class of materials, as their modular concept allows to tune the physical properties according to the desired application operation conditions.

Some R&D activity on chemical reactions (MgCl₂·6H₂O hydration/dehydration) for seasonal storage applications has also been carried out. The research in this area is still at an early stage of development. Further research efforts are required both, at the material scale (finding suitable reactions and carrier materials) and at the reactors scale in order to enhance charging and discharging processes.

Material Characterization

Test and characterization of storage materials is crucial for the development and evaluation of novel material approaches. The comparability of measurements is a precondition of scientific work and for international R&D collaboration. To proof this, a Round-Robin-Test (RRT) was performed. Therefore a standard phase change material

sample was sent to all participating institutions for testing. The results showed a large variety of values for the melting temperature and enthalpy.

The first test results did not allow to compare measurements from different institutes. Therefore the agenda of the working group was changed and the development of a standardized measuring procedure was put into focus. A workshop on Differential Scanning Calorimeter (DSC) measurements was organized. The following RRT showed much better agreement of the result. The first steps towards an international standard for DSC measurements were taken.

The test and characterization of adsorption materials was also done by a RRT. The results were not so disappointing as in the PCM case, but only very few institutes were involved. A Standardized procedure should be discussed for the future.

Numerical Modelling

Numerous methods are available to model the physical processes in compact heat storage materials on various scales. However, it is also clear that there are quite a few white spots in both PCM- and TCM- research. Whereas the PCM-research seems to focus more on the larger scales, trying to develop models which can be used at the reactor-scale, the TCM-research so far seems to concentrate more on fundamental issues.

The importance of computer simulations of the materials applied in thermal energy storage systems is rapidly growing. This calls for validated numerical techniques on various scales, which can be used on the one hand to design new reactor concepts and on the other hand to develop new energy storage materials and/or composites. The report on State-of-the-art of numerical modeling techniques of TCM/PCM-materials shows a broad coverage of all scales (micro-, meso-, macro-, multi- and reactor-scale).

Cooling, Heating and High Temperature Applications

Goal of the application oriented working groups was the identification of relevant applications and their operating conditions. Like stated at the introduction to the activities on “Theoretical Limits”, a material can only be evaluated under actual process conditions, since e.g. the energy storage density is a process variable and not a material property. Based on ongoing R&D projects typical applications for thermal energy storage, their operation conditions and the used storage materials were assessed.

The fields of applications were classified after their temperature range: Cooling, heating/domestic hot water and high temperature applications.

For cooling applications temperatures from 50 °C for the temperature control of electric devices down to -20 °C for frozen food were taken into account. Relevant applications were also comfort cooling and dehumidification in the range from 20 °C down to 6 °C, cooling in agriculture (e.g. of greenhouses), cooling of electrical equipment (up to temperature of 70 °C) and the cooling of goods during transportation. Most of the project worked with PCM at different melting temperature.

For heating and domestic hot water mainly solar-thermal applications within a temperature range 20 – 100 °C were discussed. The storage systems were classified as



“basic solar thermal systems”, like hot water or PCM storages, as “closed-cycle solar thermal systems”, where the heat transfer is responsible for the storage performance, and as “open-cycle solar thermal systems”, where the mass transfer is governing the storage process. The latter two categories are thermochemical storages, sorption (liquid and solid) and other chemical reactions.

For applications at temperature over 100 °C four main applications were found. The continuous supply of process heat for industry by high temperature PCMs is one of them. At temperatures from 140 °C to 200 °C solar cooling is able to transform solar thermal energy into cold. High temperature PCMs can provide heat to drive e.g. an absorption chiller when cold is needed. For concentrated solar power a non-stop operation made possible by thermal energy storage could be important. For direct steam generation the constant temperature level of a PCM at discharging is an interesting property. Finally for very high temperatures up to more than 1000 °C sensible storage materials were investigated. Relevant applications in this temperature range could be adiabatic Compressed Air Energy Storages (CAES) or solar tower plants.

General Topics

An international and inter-disciplinary collaboration was established during the Annex. Now the possibilities of material development for the final performance of storage systems are better defined by the theoretical limits. Most important challenges, like standardized test procedures, and the most promising material classes were identified. In future R&D activities relevant testing under actual operation conditions will lead material development into the right direction.



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1 New or improved materials for thermal energy storage

1.1 Motivation and R&D Challenges

Main issue addressed in this working group is compactness of the storage material. Accordingly, most part of the work carried out has been focused in the development of new or improved phase change and thermochemical materials. Although compactness has been the main focus of the working group, sensible heat storage for applications at high temperature has also been considered. The activity in this area was focused on the evaluation of cheaper alternative solid materials through the valorization of by-products derived from the mining and metallurgical industry.

Main R&D challenges addressed regarding phase change materials (PCM) are:

- PCMs for storage applications where water cannot be used as storage medium: New storage materials are needed for applications where temperature is either below 0°C (cooling applications) or above 100°C (i.e. industrial applications, power generation).
- PCMs with enhanced energy density: Low thermal conductivity is one of the problems of PCMs, which leads to inefficient charging and discharging performances. Composite materials that contain highly conductive materials like graphite have been developed to enhance the heat transfer properties of PCMs. However, such efforts decrease the energy density and increase the cost. To avoid these drawbacks while increasing the PCM's thermal conductivity, a novel PCM has been prepared and characterized.
- For applications at high temperature, most commonly used PCM are pure salts and eutectic salt mixtures. The use of salts formed in peritectic reactions has been considered in the working group in order to reach higher energy densities. Besides the usual melting/crystallization process, the solid-liquid transformation of these salts involves a reversible, isothermal chemical reaction. As a result, exceptionally high values of energy density could be achieved when the enthalpy of reaction is significant.
- Solid-solid PCMs (SS-PCMs): Currently used PCMs undergo solid-liquid transitions. However, new groups of PCMs that undergo at least one solid-solid phase transition have been introduced in the last few decades. These materials change their crystalline structure from one lattice configuration to another or turn to stable amorphous at a fixed and well-defined temperature. SS-PCMs are useful because: i) they do not require nucleation to prevent supercooling, unlike solid-liquid PCMs; and ii) there is no visible change in the appearance of the PCM, and there are no problems associated with handling liquids.
- Micro-encapsulation of inorganic PCMs: Micro- or nano-encapsulated PCMs (MPCMs) has several advantages: i) increased heat transfer area, ii) reduced PCM

reactivity towards the outside environment and iii) controlled volume change of the storage material during the phase change. They can be used in building materials for thermal regulation purposes. Another application is phase-change slurries (suspension of MPCMs in a liquid carrier) to enhance the heat transport capacity of heat transfer fluids. Most parts of the research in this area have been focused on the micro-encapsulation of organic PCMs, which is now mastered, whereas the micro-encapsulation of inorganic PCMs has not gained much interest so far in spite of potential higher latent heat and lower cost. In the working group, the microencapsulation of inorganic PCM has been studied.

The development and the study of thermochemical materials has been focused on sorption materials. Main R&D challenges addressed are:

- **Novel sorption materials:** In sorption storage systems, low-cost crystalline or amorphous silica-based porous materials and their composites with hygroscopic inorganic salt hydrates have been considered as a promising water sorbents. Despite many scientific efforts, none of these materials currently meet the requirements for large-scale applications. The objective in this working group was to develop new sorption materials with improved performances. A primary aim of the research was the study of the dependency between the structure of novel microporous and mesoporous materials and their heat storage abilities. The goal was to establish and understand these dependencies in order to develop, improve, and ultimately tailor-make specific materials with particular energy storage capabilities. Different hydrophilic microporous water adsorbents and composite sorbents have been synthesized and their structural and thermo-chemical storage properties have been studied.
- **Metal-organic Frameworks (MOFs):** MOFs are a new emerging class of microporous materials possessing unique features such as huge surface areas, large pore volumes and a tunable composition. Compared to traditional adsorbents used in heat transformation applications like zeolites or aluminophosphates, MOFs exhibit a much richer variety in terms of composition, pore structure and topology. A crucial point for their use in water-based heat transformations still is the hydrothermal instability of most MOFs. However the metal-ligand network of MOFs which are synthesized in water and which contain water as a solvent template are expected to be more stable towards water. Besides, proper shaping of MOFs to solve the problem of coupled heat and mass transfer has also been investigated.

1.2 Sensible heat materials for high temperature applications.

The potential of cheap, alternative materials through the valorization of by-products derived from the mining and metallurgical industry for solid sensible storage has been evaluated. They comprise by-products of the pyrometallurgical refining process of copper (Slag P and Slag B), the powder material produced during the steelmaking process in electric arc furnace (WDF), and two by-products of the mineral industry (IB and WRutF). Two of them (IB, WDF) were prepared by compression and the others (Slag B, Slag P), for which compression or moulding was not possible, were included as aggregate in different mortar formulations using either Portland, aluminous or phosphate cements, as binder. WRutF was not shaped and it was evaluated as pow-

der. The density of the final materials ranges from 2100 kg/m³ to 4154 kg/m³, the thermal conductivity varies from 0.8 W/m/K to 3 W/m/K, and the specific heat at 300°C ranges from 340 J/kg/K to 1760 J/kg/K. The cost of the cheaper material (WDF) is 0.001 €/kg, whereas the most expensive ones are 0.15 €/kg. A performance index that balance the storage properties and the material cost has been defined and applied to compare these alternative materials with cofalite, concrete and castable ceramics (see chapter 7, Application Related Activities: High Temperature).

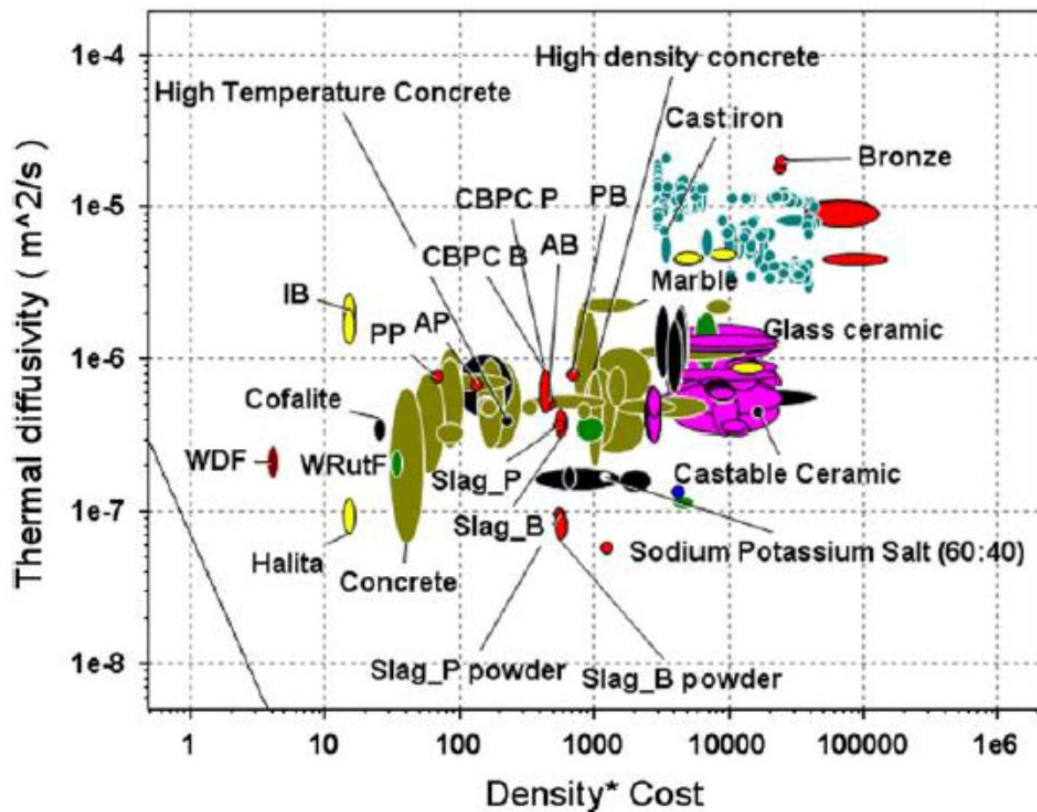


Figure 1: Thermal diffusivity vs. $\rho \cdot C_m$.

When plotting thermal diffusivity α vs. Density ρ and cost C_m in a logarithmic scale, materials that perform better with the objective of minimize cost may be compared graphically. These materials are mainly non-technical ceramics, such as concrete or even sodium chloride. Materials studied here are compared with cofalite, concrete and castable ceramics reported in literature. The new selected materials perform comparably to cofalite and concrete and quite better than castable ceramics.

1.3 Phase change materials for cooling applications.

Organic and inorganic PCMs for cooling applications have been investigated. Organic PCMs with different melting points have been prepared by mixing n-alkanes of different carbon numbers. Dodecane (C₁₂H₂₆), Tridecane (C₁₃H₂₈), Tetradecane (C₁₄H₃₀) and Pentadecane (C₁₅H₃₂) are selected and binary mixtures with different compositions for C₁₂-C₁₃, C₁₃-C₁₄, C₁₄-C₁₅ are prepared and tested. Twelve promising mixtures for cooling applications have been obtained, with melting points ranging from 10.4°C to -9.7°C and latent heats from 110 J/g to 212 J/g. Moderate subcooling was only observed for tridecane and dodecane mixtures. The potential of

14 inorganic PCMs (aqueous salt solutions) for cooling applications has also been studied. The melting points ranges from 0°C to -20°C and the latent heats vary from 160 J/g 317 J/g. The effect of the container material and the size on subcooling was investigated. It has been observed that as the sample size increases the subcooling decreases or disappears in some cases. Appropriate nucleation agents have been found for those inorganic PCMs where subcooling remains significant even in big samples.

Table 1 shows the results of using different nucleating agents for different PCMs. It can be seen that with the right nucleating agent subcooling can be avoided completely for some of the PCMs given here.

Table 1: Effect of nucleating agents on subcooling (SC) of PCMs

Phase Change Materials	Nucleating Agent	SC (°C)	Freezing Temp (°C)	Melting Temp (°C)
9.5%NH ₄ HCO ₃	1%CaO	3	-3.4	-4.1
	1%Pentaerythritol	1.7	-3.8	-4.9
16.3%NH ₄ H ₂ PO ₄	1%Pentaerythritol	2.0	-4.4	-4.4
1%Na ₂ SO ₄	0.5%Borax	2.4	-0.5	-1
1%Na ₂ SO ₄	1%Borax	2.7	-0.5	-1
	1%Borax	0	-0.2	-1.3
5%NaCl	1%Pentaerythritol	0	-3.3	-4.0
	1%silica	2.3	-3.0	-4.5
	10%silica	1.9	-3.1	-3.4
Oleic acid	-	1.5	3.5	-
Oleic acid	1%C-nanotube	0	3.9	-

1.4 Phase change materials for low temperature applications.

Three distinct activities have been carried out in this field:

New Solid-Solid Phase-Change-Materials

Poly(ethylene-co-1-tetradecylacrylate) and poly(ethylene-co-1-octadecylacrylate) copolymers were prepared as new polymeric SS-PCMs. Fatty alcohols are used in the production of SS phase changing polymers for the first time in this study. The advantage of the polymeric SS-PCMs produced is to show a secondary transition proving that the chains move freely only after a second border at higher temperatures than SS transition temperature. The majority of the polymeric SS-PCMs prepared in similar manners in the literature show only a SS transition but not melting. That is, they are amorphous above SS phase transition and their viscosities decrease with the temperature. Then they become liquid moving completely freely. Here secondary crystallites before free movements of the chains make these polymers mechanically resistive to flow and deformation. The SS transition temperature (20°C-50°C) and the corresponding enthalpy change (5 J/g - 30 J/g) of the new polymeric SSPCMs depend on the molecular weight of used fatty alcohol and its content.

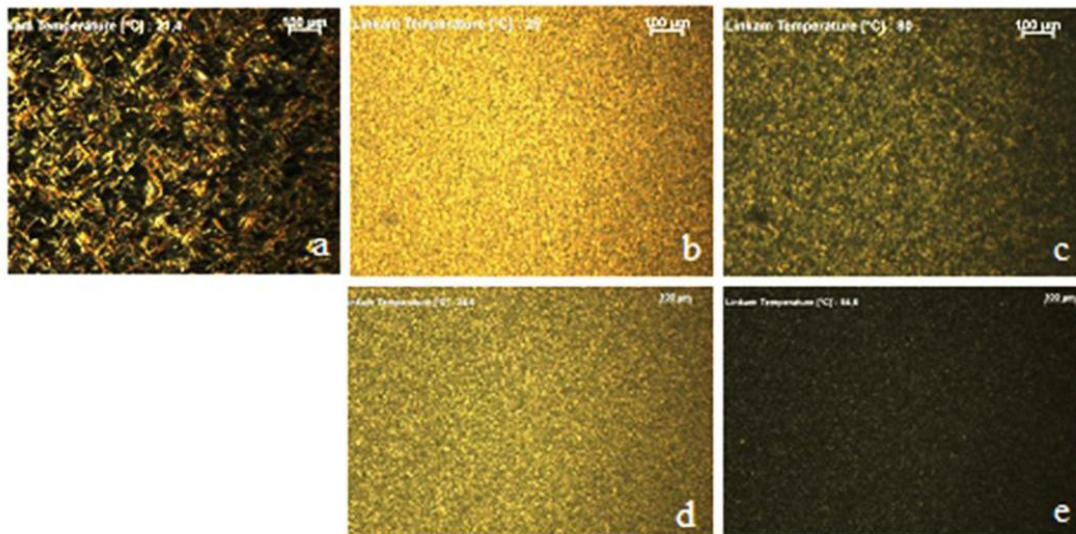


Figure 2: Polarized optical microscopy images of (a) 1-octadecanol, (b) Poly(ethylene-co- 1-octadecylacrylate) with 19 wt% octadecylacrylate below its SS-phase transition, (c) Poly(ethylene-co-1-octadecylacrylate) with 19 wt% octadecylacrylate above its SS-phase transition, (d) Poly(ethylene-co-1-octadecylacrylate) with 53 wt% octadecylacrylate below its SS-phase transition, (e) Poly(ethylene-co-1-octadecylacrylate) with 53 wt% octadecylacrylate above its SS-phase transition.

Micro-Encapsulation of Inorganic Phase Change Materials for Applications at Low Temperatures

Calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) is a classic latent heat-storage material with a melting point of 29.8°C and melting enthalpy of 170 J/g . Nanoencapsulated particles ($162\text{--}182\text{ nm}$ in diameter) of this hydrated salt have been obtained by using PU shells and interfacial polycondensation technique.

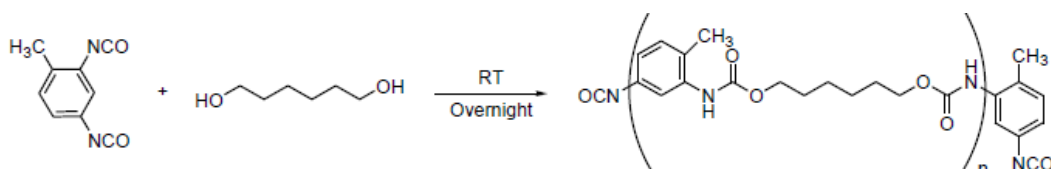


Figure 3: PU reaction for the formation of the shell for the microcapsules.

Special care has given to the negative phenomena which characterize salt hydrates: the tendency of the melt to supercooling and phase separation due to incongruent melting. Segregation has been prevented using either Methyl cellulose or Carboxymethyl cellulose as thickeners. Different nucleation agents have been investigated to reduce supercooling. Best results have been obtained with $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ incorporated in 1wt% to the hydrated salt. Supercooling has been reduced from 42°C obtained with the microencapsulated salt without nucleation agent to 22°C obtained with $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. This is a very important decrease. However, this value should be optimized by changing the ratio of nucleation agent to the hydrated salt. The melting point of the capsules ($23\text{--}24^\circ\text{C}$) is lower than that of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (29.8°C). The enthalpy change by melting is equal to 49 J/g for the microencapsulated salt without nucleation agent, and it is 68 J/g with $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.

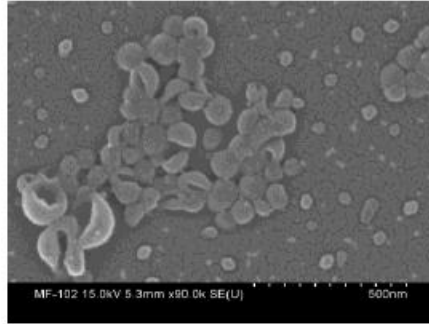


Figure 4: SEM micrographs of microencapsulated $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ with $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ as nucleation agent.

Nano Magnetite Paraffin Composite as Phase Change Material

A nano-particle (Fe_3O_4) doped paraffin with enhanced energy density has been produced. Nano magnetite (Fe_3O_4) particles were synthesized from Fe^{+2} and Fe^{+3} salt hydrates by sol-gel method, thus stabilized by oleic acid to avoid sticking of the particles to each other. Paraffin (46-48 Paraffin Merck) was melted at around 46- 48°C and nano magnetite at 10% by weight was added to liquid paraffin.

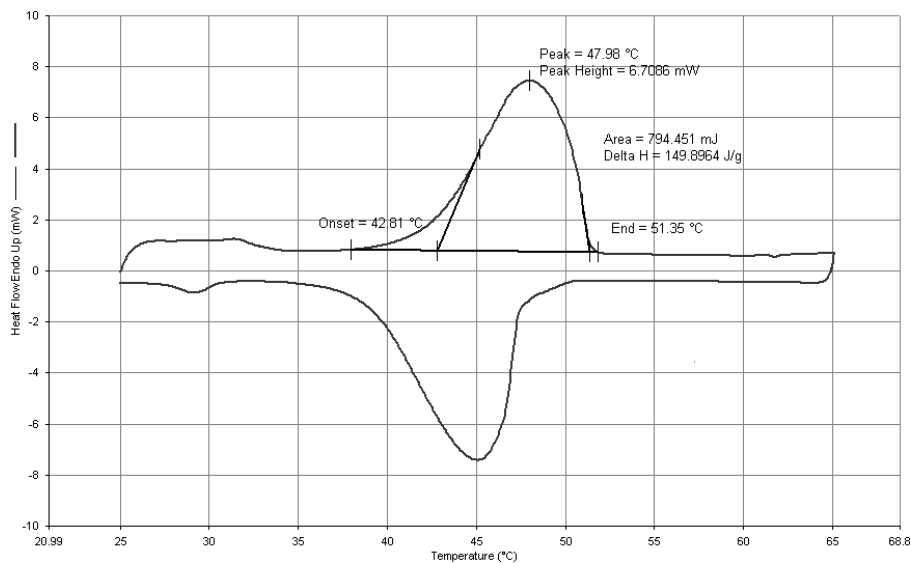


Figure 5: DSC analysis of nano magnetite paraffin composite

Table 2: DSC results for paraffin and paraffin nano composites

Samples	Melting Range (°C)	Latent Heat (J/g)
Paraffin	52.7 - 62.1	119.9
Nano magnetite-paraffin composite	54.4 - 62.1	144.2

This mixture was then stirred with ultrasonic water bath to obtain a homogeneous mixture. DSC results show that latent heat storage capacity of paraffin has been increased by around 20 % (144 J/g instead of 120 J/g) and melting range did not change

significantly. The cost of composite is only %3 higher than pure paraffin. The paraffin nano magnetite composite developed here is a promising PCM candidate. Further analysis to determine thermal stability and thermal conductivity of the composites are however required.

1.5 Phase change materials for medium temperature applications.

The potential of D-mannitol for the use in thermal energy storage applications has been investigated. Due to its polymorphism, the thermal behavior of d-mannitol is difficult to predict. The stable phase of d-mannitol is β -form which melting temperature is 167 °C and the melting enthalpy is 287.6 kJ/kg, the metastable phase is δ -form which presents a melting point of 155 °C and its enthalpy of fusion is 288.7 kJ/kg. DSC tests carried out show that both β -form and δ -form can appear when cycling D-mannitol. Indeed, transitions between β and δ phases can be observed on heating. On the contrary, the cooling process has regular behavior with solidification temperature around 120 °C.

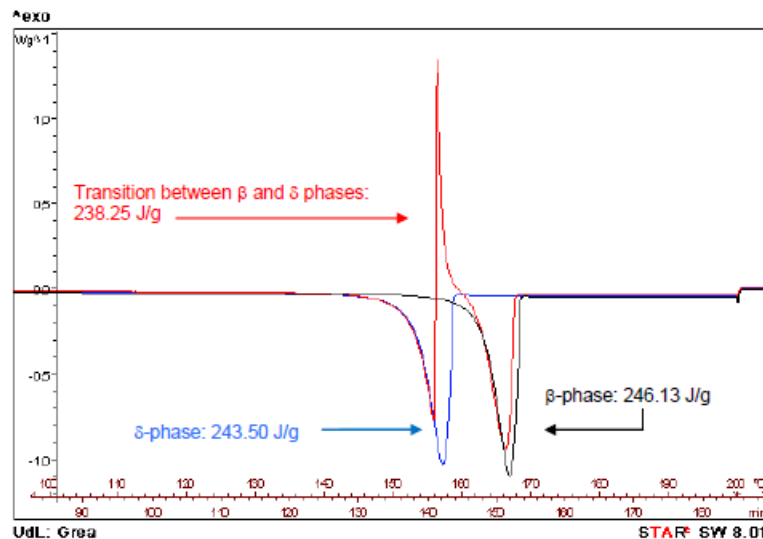


Figure 6: Three different thermal behaviours obtained through DSC analysis of d-mannitol during melting process.

Based on such results, it was possible to define a working range under which D-mannitol will be able to be used as PCM for thermal energy storage with energy density between 287.6 kJ/kg and 288.7 kJ/kg. The charging temperature required to warrant melting is 167°C (melting point of the β -form), whereas the discharging temperature has to be lower than 120°C.

1.6 Phase change materials for high temperature applications.

A new generation of carbon-salt composites with improved properties has been produced. The intended application is Concentrating Solar Power by Direct Steam Generation technology (see chapter 7.3), where saturated steam is produced at high temperature (~300°C) and pressure. The composite is made of a highly porous carbon

foam saturated with an anhydrous salt. It is obtained by infiltration of the the porous structure with molten salt. Cellular graphitic (CGC) and partially graphitized (CPGC) carbon foams have been studied.

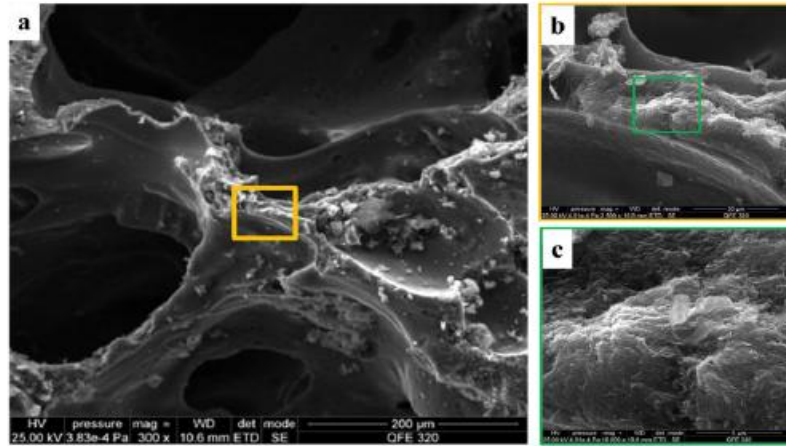


Figure 7: CPGC Foam. SEM images at various magnifications of both the surface and the bulk of the carbon skeleton a) 300x, b) 2500x, and c) 10000x.

The effective thermal conductivity at 300°C of the selected foams is high enough for the application (22-32 W/m/K). The salt used is formed in a peritectic reaction so that the enthalpy change in charge/discharge is exceptionally high (480 J/g). The peritectic transition happens at 312°C and subcooling is negligible. The volume change of the salt during solid-liquid transformations is managed by a subtle combination of geometry characteristics and thermal properties of the carbon foams, so that the composite behaves as "shape-stabilized" material at the macroscopic scale. The thermo-chemical stability of the composites have been proven by submitting them to more than 10000 cycles of charge/discharge. For composites made of CGC foams, a PyC coating of the foam has been necessary to avoid the intercalation of one of the ions of the salt into the layered structure of graphite. On the contrary, CPGP foams do not require coating because the surface of the backbone is vitreous. The working temperature of the final materials is around 312°C, and the energy density is as high as 628 MJ/m³ for CGC-salt composites and 538 MJ/m³ for CPGC-salt composites. The investment cost of the associated storage system has been estimated at 65 €/kWh for CPGC-salt composites and it is attractive enough for the intended application.

1.7 Sorption materials for low temperature applications.

Several novel sorption materials have been developed. Targeted specifications are: a charging temperature below 140 °C, energy density above 250 kWh/m³ and resistance to material degradation. The novel sorption materials, prepared hydrothermally, comprise:

- a new microporous aluminophosphate triclinic AlPO₄-34 (AlPO-Tric);
- ion-exchanged (Ca, Mg) zeolites NaP and ion-exchanged (Ca, Mg) zeolites NaX;

- a composite consisting of a disordered mesoporous network (FeKIL2) impregnated with CaCl₂ (CaCl₂-FeKIL2);
- a composite consisting of an ordered mesoporous network impregnated with CaCl₂.

Compared to the targeted specifications, the best results achieved correspond to AlPO-Tric (Figure 8).

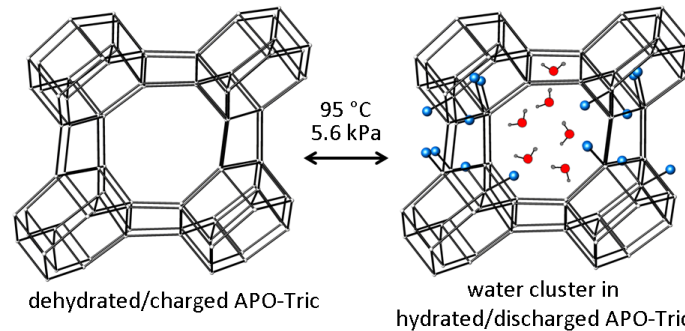


Figure 8: Water adsorption-desorption process in APO-Tric

The maximum water sorption capacity of AlPO-Tric is 318 g/kg, the heat of adsorption is 53.6 kJ/mol and the energy density in the working temperature range from 40 to 140 °C is 240 kWh/m³. Examination of the crystal structures of hydrated AlPO-Tric reveals that the driving force for the determined water sorption process is the formation of highly ordered water clusters in the pores, which is enabled by rapid and reversible changes in the Al coordination and optimal pore diameters. The ease with which changes in the Al coordination can occur in AlPO-Tric is related to the use of the fluoride route in the synthesis. This material can desorb practically all water at 95 °C, which is another important characteristic for its utilization. Besides, the hydrothermal stability of the material seems to be excellent. The AlPO-Tric performance, combining the water uptake mechanism, heat of adsorption and hydrothermal stability, is so far the most promising among the aluminophosphates for water-sorption-based heat storage applications and for heat transformation in heat pumping systems.

1.8 Sorption materials for adsorption heat pumps.

The potential of the Metal-Organic Frameworks (MOFs) for the use in adsorption heat transformation processes has been studied. Based on the available literature, several promising candidates (MIL compounds) have been identified and synthesized, comprising MIL-101(Cr), MIL-100(Cr), MIL-100(Fe) and MIL-100(Al). All of them show large water uptake but in general the adsorption occurs at high relative pressure compared to zeolites. For instance, MIL-101(Cr) has the largest water-loading spread reported so far (0.939 g/g under typical conditions). Indeed, the isotherm of the compound shows a sigmoidal shape which is advantageous for the application, as a large loading lift can be achieved within a narrow range of relative pressure. Unfortunately, the usable loading lift in the application is slightly reduced due to the hysteresis between adsorption and desorption. The hysteresis is significantly reduced in MIL-100(Cr) and MIL-100(Al) compounds, but the maximum water uptake is smaller

(0.57 g/g). First investigations on the hydrothermal stability also showed promising results with an initial stability shown for two compounds over 40 ad- and desorption cycles. Finally, with the thermal gradient approach a promising method was developed to realise highly porous and thick coatings of MOF on different supports. As a first candidate, a mechanical stable coating of HKUST-1 with a very good thermal coupling to the substrate was realized.

1.9 Conclusions

The work carried out in this working group opens new R&D perspectives fully in line with part of the objectives in the field, namely compactness and cost effectiveness.

- a) Using by-products as storage media. Due to the increasing of raw materials costs for energy storage, it is a very interesting issue to evaluate cheaper alternative materials through the valorization of by-products. Materials as cheaper as 0.001 €/kg with convenient performances for sensible heat storage at high temperature have been found. This research effort must be continued and extended to PCMs.
- b) Materials formed in peritectic transitions. The solid-liquid transformation of these materials encompasses a reversible, isothermal solid-liquid reaction and a solid-liquid phase change. As a result, exceptionally high values of energy density can be achieved when the enthalpy of reaction is significant. An anhydrous salt formed in a peritectic transition at 312°C, with energy density as higher as 218 kWh/m³, has been found in and it has been used to produce suitable carbon-salt composites for CSP applications. Materials formed in peritectic transitions represent a storage solution midway between latent heat and thermochemistry. For temperatures above 300°C, it is expected that they provide effective energy density comparable to that of solid-gas chemical reactions (200-400 kWh/m³) but with a simpler and much cheaper storage technology.
- c) Nano-composites and nano-particle doped PCMs. It is well-known that confinement in very narrow porous can greatly affect the properties of a fluid. Significant changes in the melting/freezing point, as well as in the latent heat, of a PCM can be achieved in such way. The work carried out shows that the latent heat of paraffin is increased by around 20 % when nano magnetite at 10% by weight was added to liquid paraffin. Similar results have been reported using carbon nano-tubes. The reason why nano-particles provide energy density enhancement still is unclear. It should be determined by the strength of the fluid-wall interaction relative to the fluid-fluid interaction. Further theoretical and experimental researches are needed to understand liquid-solid transition in nano-composites and nano-particle doped PCMs and to explore the benefits for thermal energy storage.
- d) Tailor-made sorption materials. The activity carried out proves that to establish and understand the dependencies between structure, composition and thermal storage performances, as well as the effects of mixing different materials, is crucial to develop, improve, and ultimately tailor-make specific materials with par-

ticular energy storage capabilities. A novel microporous sorption material (AlPO-Tric), which is so far the most promising among the aliminophosphates for storage at low temperature, has been produced in such a way. On the other hand, the new family of MOFs studied results in a very promising class of materials for the use in adsorption heat pump processes. Indeed, their modular concept allows to tune the physical properties according to the desired application boundary conditions in a wide range. Besides the development of new or improved sorption materials, the gap towards the applications has to be closed by the development of proper shaping techniques.

- e) Chemical reactions. Although not reported so far in this document, some R&D activity on chemical reactions ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ hydration/dehydration) for seasonal storage applications has also been carried out. Chemical storage can lead to even more interesting energy densities than PCMs and sorption materials, and offers so far the best potential for long-term, compact and loss-free storage. Unfortunately, the research in this area is still at an early stage of development. Further research efforts are required both, at the material scale (finding suitable reactions and carrier materials) and at the reactors scale in order to enhance charging and discharging processes.

2 Test and Characterization

The knowledge of the essential material properties of advanced storage materials is crucial for an appropriate design of the storage systems. Also for the modeling of the storage processes an accurate measurement of the relevant material characteristics is necessary.

For the test and characterization of PCM and thermochemical storage materials (TCM) their temperature dependent behavior is extremely sensitive and influences the storage performance strongly. In principle it seems to be very easy to characterize materials since there is equipment available to determine all the needed parameters, but unfortunately the accuracy of data in the ranges important for storage application is often insufficient and the procedure in which the materials will be measured influences the results.

Figure 99 gives an example of a DSC measurement using different heating rates. Every rate is leading to a different shape of the curve. The question is: Which is the correct measurement? So there are already differences caused by the measurement method itself but we get even bigger differences if we use for example DSC from different manufacturers and/or located at different laboratories.

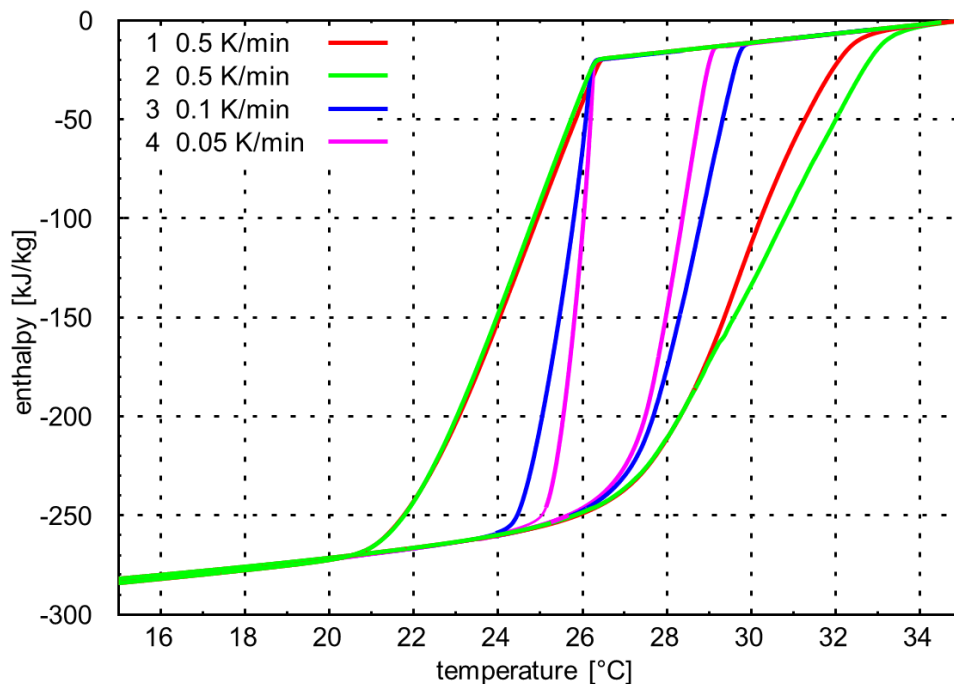


Figure 9 : Example of a DSC measurement using different heating rates.

The activities of this working group aimed to develop measurement procedures for thermal storage materials. The goal is to introduce standard procedures to make it possible to compare measurement results obtained using different measurement

equipment at different laboratories. Therefore the following targets for the working-group “Test and characterization” were defined at the beginning of the Annex:

- To determine the differences in characterization of heat storage materials for heat capacity and melting behavior, viscosity, thermal conductivity, density and cycle stability, water uptake (TCM).
- To develop measurement standards to obtain the “real” materials characteristic.
- To develop a standards that lead to the “same” results also when they are determined at different laboratories.

The work in the group started with a comparison of differential scanning calorimeter (DSC) measurement results, which is the most common equipment used to determine the melting and solidification enthalpy of PCMs as well as its melting and crystallization behavior.

The test was performed by using the same PCM sample which was sent to different laboratories and it was expected to get not the same results but to get comparable results. But the results showed really big differences and so it was realized that it will not be possible to establish a measurement procedure for all above mentioned parameters. In the case of the PCMs the working group is still focused on the DSC measurement and just started on rheometry measurements in September 2011.

2.1 Existing Standards for Material Characterization

There are a number of standards defined to measure parameters of materials that are also important when characterizing PCMs. These standards include the melting temperature and enthalpy, thermal conductivity, density, viscosity, compatibility and thermal stability. Almost all of these standards are defined for materials that primarily will not be used as heat storage material. However the characterizations of PCMs especially the determination of melting and crystallization behavior requires standards that are really applied to the phase transition of these materials.

The only standard existing so far for PCM was established in Germany. It is a standard which was defined in the frame of the RAL with the target to ensure the quality of PCM-Products. “RAL is an independent institution that is responsible for the creation of RAL Quality Marks (Gütezeichen).” [<http://www.ral-guetezeichen.de>]. A detailed description of this German testing procedure can be found in Appendix 2.

2.2 Development of a Measurement Standard for DSC measurements on PCM

A Round-Robin-Test was performed to establish a measurement standard for the thermal characterization of PCMs. It was focused on the characterization of PCMs using DSCs.

In a first step a reference PCM (synthetic octadecane synthesized by Sasol Wax), which is well known and has reliable data base, was send to a number of research institutes. No measurement procedures or calibrations were given at that point. Seven Institutes participated in these measurements. The results are shown in Figure 10 and 11.

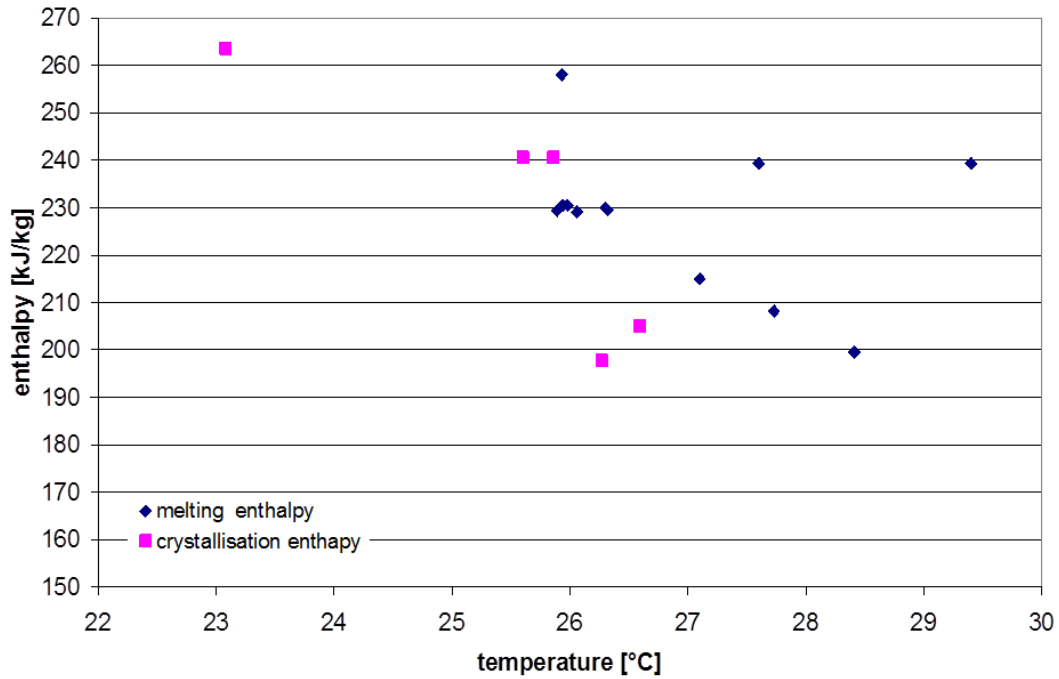


Figure 10: State of the art in DSC-measurement. Comparison of results from different laboratories.

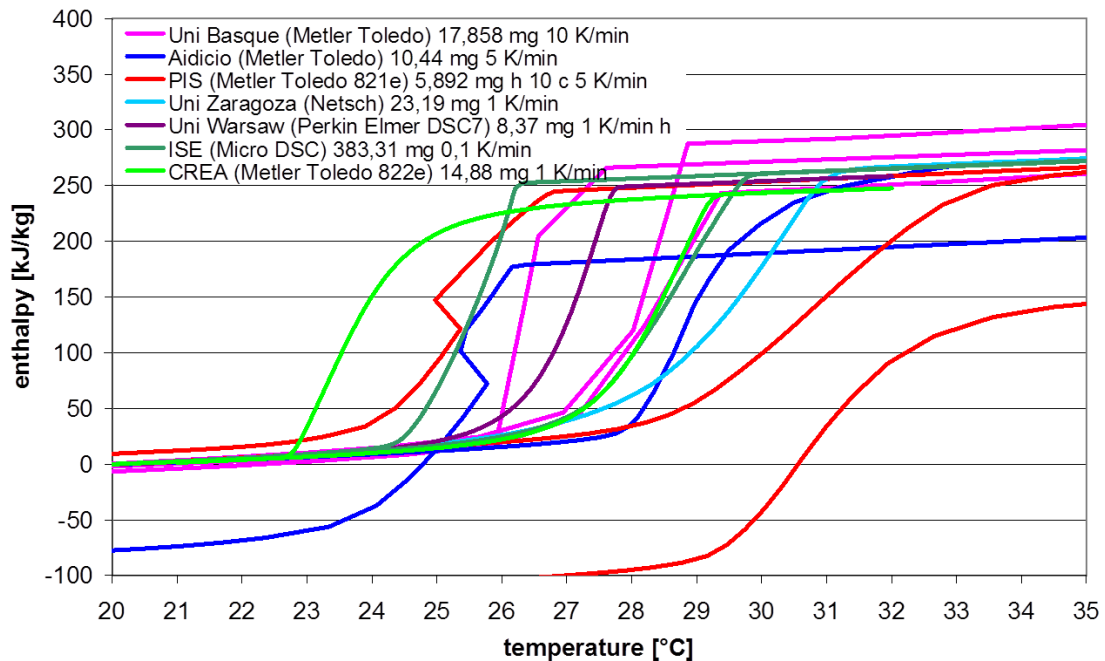


Figure 11: Results of first RRT as function of temperature (Institute and Measuring Equipment)

The results show that the measurements at different institutes are not suitable for any comparison. After this test a first definition for a measurement procedure was defined according to the definition of the German RAL standard. This definition was sent to the partner to do a second RRT.

Figure 12 shows the comparison of results of this test measured according to the defined procedure. So for the enthalpies the result is much better than the one from the first test. But the differences in temperatures are still too big to compare the results. As the resulting temperatures are much related to the DSC-equipment and the whole procedure from the calibration of the device to the preparation of samples and its measurement, it was decided to have a workshop on DSC measurement in order to learn more about the differences of DSC and to establish a common basis for the measurement procedure within the test and characterization group.

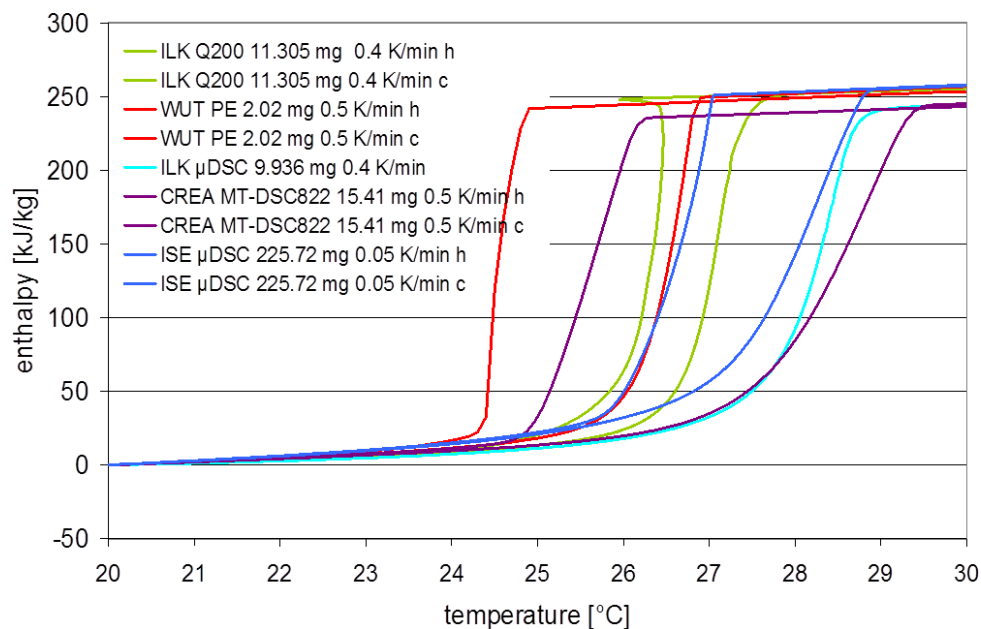


Figure 12: Comparison of DSC results measured according to the RAL pre-definition

The workshop was held in Freiburg in May 23rd until 27th 2011. For the workshop DSCs from 4 different manufacturers were used. It was possible to do the measurement on the DSCs in parallel and to compare the results right after the measurements. The influence of calibration and the crucibles of the different DSCs were discussed.

An alternative method for the evaluation of the melting enthalpy and temperature is the so called T-History method. The phase change temperature identified by this method is sharper than that obtained with DSC. No significant hysteresis is observed. Subcooling is well characterized. However, enthalpy change obtained in melting and freezing cycles reached 10% difference.

The phase change temperature for the tested 98% pure Octadecane lies between 27.2°C and 27.7°C.

2.3 Comparative Thermo-Gravimetric measurements of a TCM

Comparative measurements on the two selected reference materials (zeolite 4 ABF and 13XBF by CWK) were performed by 2 institutes. First results are promising, however there are still differences between the various measurement apparatus and methods visible.

The transformation of the data into a proper thermodynamic model, in this case according to Dubinin, shows a good correlation between thermogravimetric measurements, but a strong deviation compared to volumetric measurements (see figure 13 and 14). Further investigations are necessary.

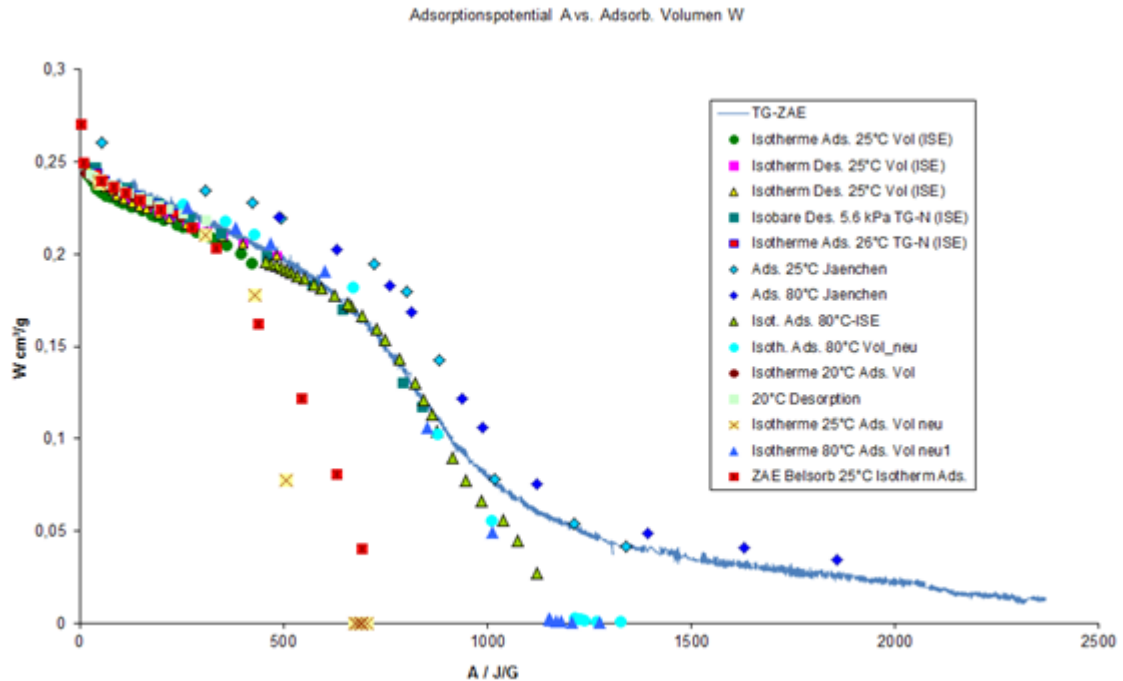


Figure 13: Overall comparison of RRT measurements performed at different labs (TH Wildau, ZAE Bayern, ISE Freiburg) with different apparatus.

However, the direct comparison between volumetric measurement at ISE and ZAE with two different apparatus (Hydrosorb vs. Belsorb) shows an excellent agreement (see figure below).

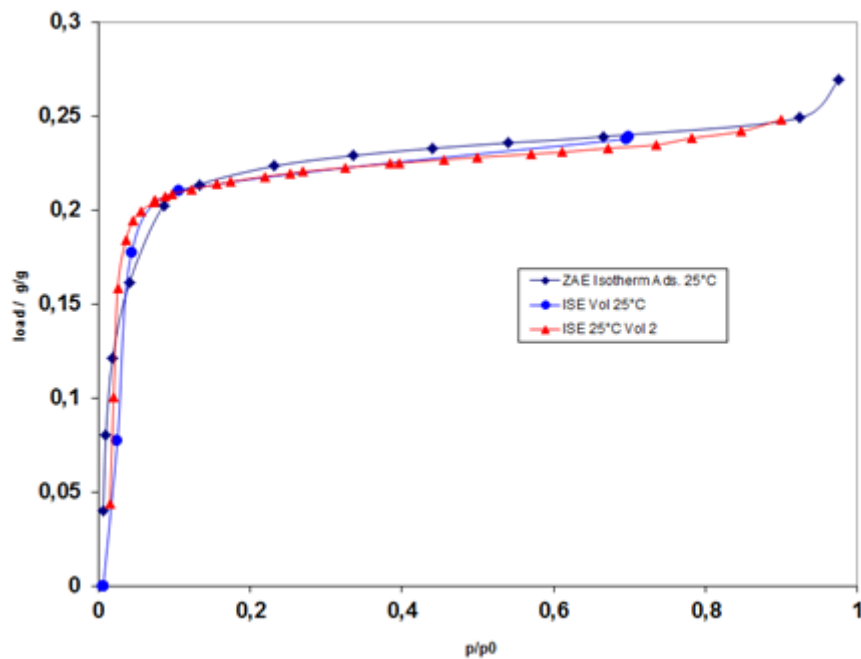


Figure 14: Direct comparison of volumetric measurements at ISE and ZAE on the reference material.

2.4 Conclusions

By performing a Round-Robin-Test it was found for the first time, that the characterization of novel storage materials did not lead to comparable results among the different research institutes worldwide. Therefore the focus of the working group has been changed and first steps toward a standardized measuring method, which finally would lead to reliable and comparable results were taken.

3 Numerical Modelling

Thermal energy can be stored in materials because of their internal energy based on the electronic structure of the basic particles like atoms, molecules, clusters or just the “unit cell”. The knowledge of the thermodynamic properties and the dynamical behaviour of all the materials and the components is the basis for the design of a storage device. In the developing process of a heat storage device experiments play a dominant role because in the prototype stadium a physical system has to be built to acquire measurement data for a fine tuning of the pilot and market product. In this development process numerical modelling plays the role of reducing the number of time consuming and cost intensive experiments. And modelling should help to understand how the limiting parameters can or should be adapted for the assigned task.

The activities in this working group are aimed at developing and testing numerical models that help to understand and optimise the material behaviour and the dynamic performance of compact thermal energy storage systems and components based on Phase Change Materials (PCM’s) and Thermo Chemical Materials (TCM’s). Ultimately, these numerical models could help to find ways to optimise the materials in combination with the system components. The activities in this working group help to lay the foundation for such models.

Scope of the activities includes the following:

- Micro-scale modelling
- Meso-scale modelling
- Macro-scale modelling
- Multi-scale approach
- Thermo-mechanical modelling
- Reactor models

Not all activities receive the same amount of attention in the Working Group and the distinction between the various scales is not always clear. Figure 15 presents an attempt to quantify the micro-, meso- and macro-scales in a time-length framework but it has to be realised that the definition of the scales is highly dependent on the actual problem, which has to be described.

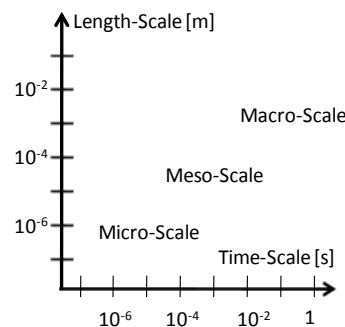


Figure 15: Definition of micro-, meso- and macro-scales in a time-length framework.

The motivation is to make a transition from rules of thumb to more precise analytic functions for the design of storage units with a low number of input parameters to transfer the dynamical behaviour through equations to a system simulation tool like TRNSYS.

3.1 Phase Change Material Models

The phase change materials used in applications can be either organic materials or inorganic materials. Organic PCMs are for example paraffins, fatty acids and the polyethylene glycol (PEG). They present a congruent phase change, they are not dangerous, and they have a good nucleation rate. The objective of numerical modeling is to predict the behavior of systems depending on the heat and/or mass transfers involved.

Meso-Scale Modelling

A new way of using PCM in building walls is to fill glass bricks with an eutectic of fatty acids. Such a wall is able to avoid overheating in summer and decrease energy consumption in winter. In this configuration, the phase change is driven by natural convection occurring during the melting and freezing processes. The interplay between the fluid flow and the moving boundary leads to a complex dynamical behaviour, as the position of the solid liquid interface becomes one of the unknowns of the problem.

The lattice Boltzmann method, developed over the last two decades, provides a powerful alternative approach at the meso-scale for studying convection involving phase changes. LBM can easily be parallelized, complex geometries can be easily implemented and melting/freezing can be mesoscopically modelled.

After testing the method for the case of natural convection in a cavity filled with air, the conduction in a PCM and melting/freezing by natural convection in a PCM was modelled. Part of this work is still on-going.

Macro-scale Modelling

One of the activities deals with two main heat transfer problems: conduction in walls and convection between wall and air. Objective is the development of a numerical model for the evaluation of PCM use in building walls. The main focus is on studying more precisely the stability of the numerical scheme and the spatial and time discretization errors.

Concerning the evaluation of the convection heat transfer between a PCM panel and the air, the value of the convection coefficient is really important for the simulation of the energy efficiency of PCM walls. But, as most of the convection coefficients used are constant or correlations developed for isothermal walls, more precise values are needed. Numerical simulations and experiments are performed in order to develop and validate CFD models that can be used to calculate time dependent convection heat transfer coefficients.

This work is still in progress. Figure 16 shows the first CFD results concerning the heat flux field near the wall.

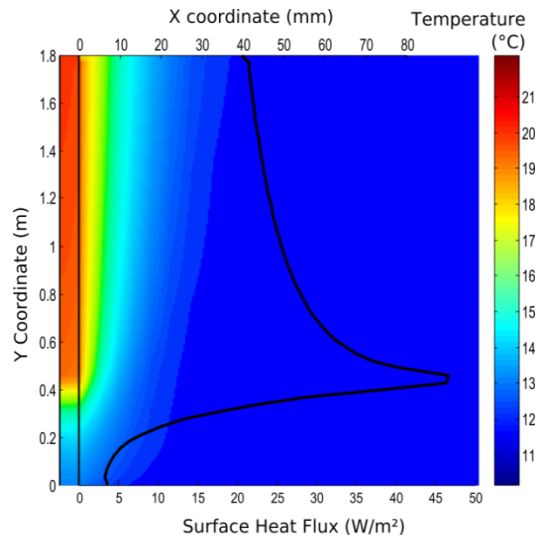


Figure 16: Convection heat transfer coefficient prediction using CFD

Another project deals with a detailed study of solid-liquid phase change modeling by the enthalpy method. In particular the effect of mushy zone constant on the melting patterns and overall melting time is investigated. Especially the effect of velocity-pressure coupling and pressure discretization schemes on the numerical results, demonstrating that different schemes, that give practically identical pictures for single-phase problems, yield considerable differences when the phase change is involved.

A macro scale simulation model for ice and PCM storage system for HVAC applications is developed in Japan. The objectives of models are to evaluate system performance of HVAC system with PCM storage. For ice storage, models for an ice tank with ice making coils and slurry ice storage are available. A PCM storage, an air distribution system with PCM in air ducts and a water tank contains PCM capsules were simulated. The effect of various design conditions, such as heat load profile, quantity of materials, or melting temperature is evaluated. The physical models in this case are based on one-dimensional heat transfer equation.

At the University of Zaragoza a model has been developed to simulate the performance of a Thermal Energy Storage unit in a real scale PCM-air heat exchanger, analyzing the heat transfer between the air and a commercially available and slab macroencapsulated PCM. The model is based on one-dimensional conduction analysis, utilizing finite differences method, and implicit formulation, using the thermo-physical data of the PCM measured in the laboratory: enthalpy and thermal conductivity as functions of temperature. The model can take into account the hysteresis of the enthalpy curve and the convection inside the PCM, using effective conductivity when necessary. Two main paths are followed to accomplish the modeling: the thermal analysis of a single plate, and the thermal behavior of the entire TES unit. Comparisons between measurements and simulations are undertaken to evaluate the models. Average errors of less than 12% on thermal power are obtained for the entire cycle.

The thermal power obtained for a full cycle experiment and its corresponding simulation are shown in figure 17.

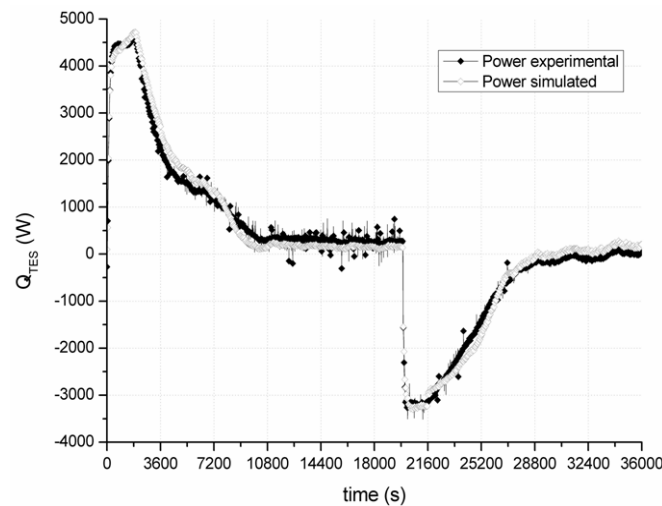


Figure 17: Full cycle comparison results between experiment and simulation

The average difference between measurements and simulations was 160 W, although differences of up to 400 W were found in specific locations of the curve.

Multi-scale approach

In order to simulate the benefits of PCM storage systems in an actual application two activities are reported. One is dealing with the implementation of PCM in the building structure. Focus of this work is on the coupling of a modeling of the phase change and the building behavior. A module of the simulation tool TRNSYS was updated (Type 260) and combined with an existing module describing the building (Type 56).

The other activity works on a photovoltaic panel coupled with a phase changing material heat storage system in hot climates. The coupling of a PCM to a PV panel allows a limitation in temperature peaks on the rear part of the panel with a consequent increase in its energy conversion efficiency. A lumped parameter model and finite difference model able to predict the thermal behavior of a PV panel coupled with phase change material was developed.

3.2 Thermo-Chemical Material Models

From first principle it is possible to store energy by means of chemical processes, making use of the reversible reactions $C + \text{heat} \Leftrightarrow A + B$. In the charging mode, solid C dissociates under the influence of solar heat into components A and B, which are stored separately. In the discharging mode, the two components (A and B) react to form solid C while releasing the stored heat. No reactions occur as long as the two components A and B are stored separately.

Micro-Scale Modelling

Atomistic simulations are used to study heat transfer and chemical reactions both on nano and micro-scale. On nanoscale, molecular dynamics models are employed. With these, the dynamics of the chemical reactions on molecular levels are calculated, ei-

ther using parameters that are determined in the models or that are derived from micro- or mesoscale experiments. Models on this level can help to understand the effect of impurities and crystal structure on the chemical parameters and thus the thermal energy storage potential of compact storage materials.

On micro scale, monte carlo models are used to describe the surface effects in micropores of salt-hydrates, a family of materials that have promising thermal energy storage capacities (see figure 18). The reaction kinetics parameters coming from molecular dynamics models are used together with the transport and diffusion mechanisms to determine the processes on micro scale. With the models, the effect of cracks in the grains of the material and the effect of nano structures on the surface can be determined. On the experimental side, new techniques have to be developed to give more direct experimental feedback to the numerical models. The experiments preferably would work on the scale of one grain of material or even on a smaller scale.

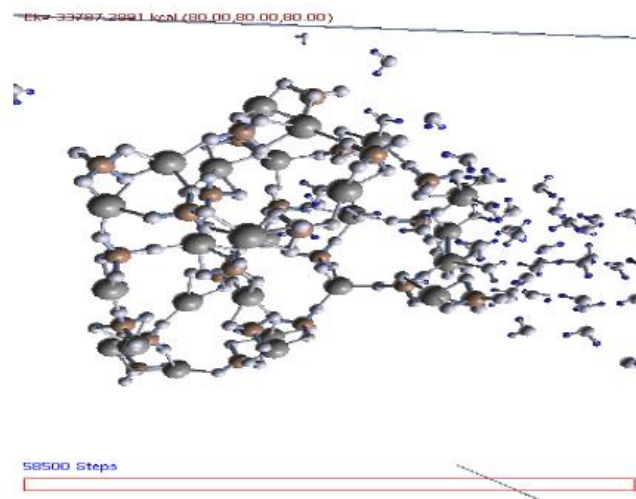


Figure 18: *The initial molecular configuration for the hydration process of MgSO₄ on molecular level consisting of 52 H₂O molecules and amorphous MgSO₄ (25 molecules) at T=300K.*

In a second activity a hybrid simulation method coupling Molecular Dynamics and Monte Carlo simulation was developed and it was primarily used to study the gas-surface interactions for a gas/liquid in contact with a solid wall. The method was applied to study the flow properties in micro/nano-channels.

Macro-scale modelling

Macro-scale modelling of adsorption processes was investigated in Germany. An open adsorption store filled with “monolithes” (zeolites extruded in honey comb structures) has been built up in lab scale. A 1-D numerical model has been used to describe heat- and mass-transfer within the store. It is assumed that the adsorption behaviour of the honey comb zeolite can be described by one representative channel. The adsorption enthalpy in this model is constant and not depending on the water load of the zeolite.

The numerical approach developed seems practical whenever sorption processes are to be modelled in one dimension. It is a computationally very efficient way of getting more detailed information about the dynamic interconnections between mass and heat

transfer – with the option to use the same model in dynamic long term system simulations.

Reactor modelling

A reactor model for Thermochemical storage using composite MgSO₄/zeolite was the topic of the following activity. The hydration-dehydration reaction occurs at a gas-solid interface. In order to optimize the rate of reaction and the thermal power released or absorbed, the active material needs to be dispersed, which increases the volume of storage. Composite materials made of magnesium sulphate are being developed with the aim of reaching an energy density of 150-400 kWh.m⁻³ at a storage temperature compatible with solar thermal panels. The hydration of MgSO₄/zeolite composites in an open system leads to higher temperature lifts and usable heat than MgSO₄/silica gel composites. The purpose of this work is to develop a reactor model that can be included for the simulation of the energy needs of an individual house.

3.3 Conclusions

It might be clear from the presented results in this chapter that numerous methods are available to model the physical processes in compact heat storage materials on various scales. However, it is also clear that there are quite a few white spots in both PCM- and TCM-research. Whereas the PCM-research seems to focus more on the larger scales, trying to develop models which can be used at the reactor-scale, the TCM-research so far seems to concentrate more on fundamental issues. The authors are aware that this conclusion might be premature because it is based on a small selection of all the work done worldwide in this area of research.

The importance of computer simulations of the materials applied in thermal energy storage systems is rapidly growing. This calls for validated numerical techniques on various scales which can be used on the one hand to design new reactor concepts and on the other hand to develop new energy storage materials and/or composites.



4 Apparatus and Components

5 Application Related Activities: Cooling

Cooling is a significant issue especially in warm climates. In Japan, one third of the electricity demand on a hot summer day or peak day is caused by the cooling demand of buildings. Thermal energy storage is used as an effective measure for peak shaving or load leveling. In some countries, discount electricity tariff in nighttime or time of day tariff are introduced to level their electricity demand. Compact thermal energy storage technologies are desirable for effective use of peak shaving.

In this working group, which is dealing with cooling applications, various applications were discussed. The applications range from frozen food to cooling parts of electric devices. Therefore the temperature range can go from $-20\text{ }^{\circ}\text{C}$ up to $70\text{ }^{\circ}\text{C}$ (for the cooling of electrical components). Figure 19 shows the applications and their temperature level.

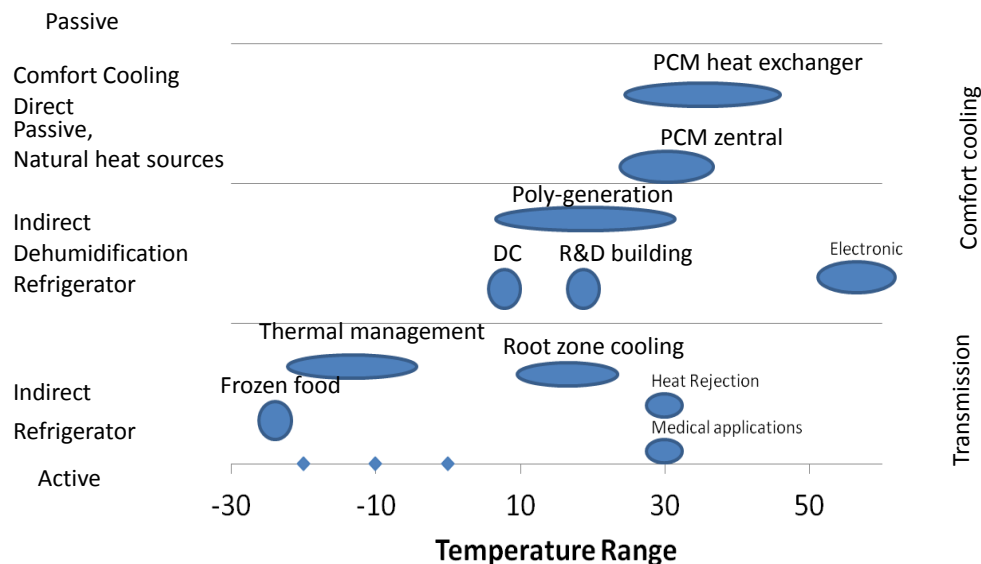


Figure 19: Temperature range of application discussed in the Working Group

The objective of this working group is to identify conditions under which the storage system is operated for each relevant application and performance criteria for material development. The main applications actually identified in the Working Group are frozen foods, HVAC and agriculture.

5.1 Relevant Cooling Applications

Comfort cooling

Comfort cooling is obviously the largest market of cooling applications. A typical HVAC (Heating, Ventilation, and Air-Conditioning) system configuration is shown in Figure 20. In warm climates, energy consumption of refrigeration machine is dominant factor of energy consumption (mostly electricity!) and cause peak demand problems. Cooling is also needed in northern regions by increasing heat gain from com-

puters raising room temperature. In countries with cooler climate, internal heat gain can be eliminated using low temperature night time air and storing it until daytime.

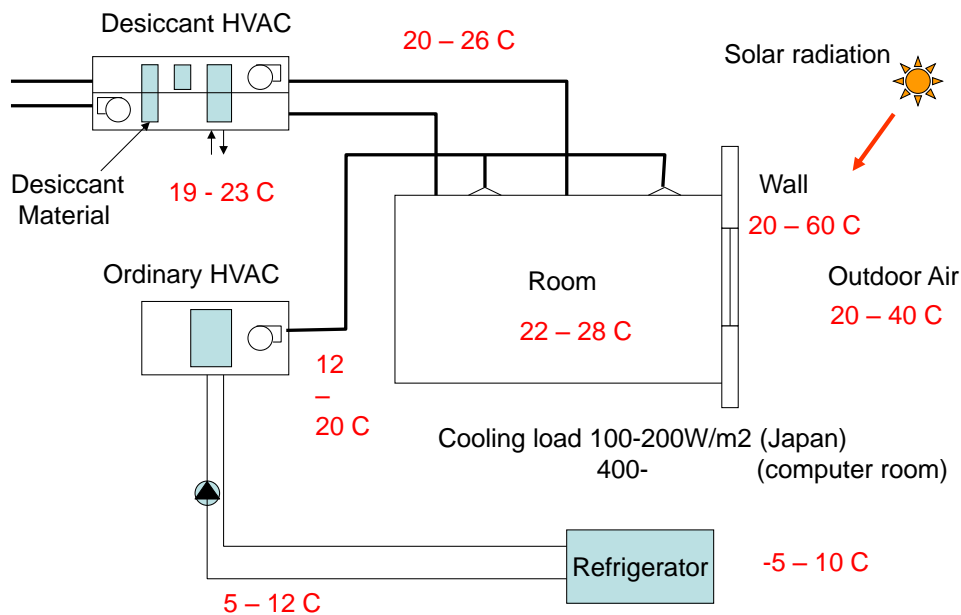


Figure 20: Schematic diagram corresponding temperature for comfort cooling

The comfort zone is constrained by temperature and humidity. Humidity control is important in humid climate. For comfort cooling in these regions, dehumidification is necessary. In this context, cooling is not just to cool the air but to take water vapor out of the air. The method of dehumidification is divided into two categories.

- Dehumidification by condensation
- Dehumidification by ab-/absorption

Dominant method today for dehumidification in HVAC is achieved by condensation.

Agriculture

Harvest of vegetables is influenced by the climatic conditions. Ornamental plant production and organic farming in greenhouses is a fast growing agricultural industry. Soilless media is preferred for growing plants in pots and containers for these products. Substrates replace soil in the soilless agriculture technic. Controlling the temperature of the root zone in substrates enhances crop growth and development. As compared to traditional systems, root zone temperature control can significantly affect root activity and the relationship between root and the aerial part of the plant. Temperature requirements of the substrate depend on the variety of plants that are grown. Phase change materials with appropriate phase change temperatures can be utilized to provide passive temperature control.

Electricity devices

As progress of information and communication technologies, we are surrounded by a lot of electric devices. Most of them have batteries which have danger of overhaeting.

Performance of lap tops can be improved by maintaining appropriate temperature. Temperature of microprocessor rise up to 70 to 80 °C and temperature becomes 40 °C to 50 °C in mainboard. Cooling temperature of electric devices is relatively high compared to other applications.

Transportation

There are products whose temperature should be kept constant while they are transported. They are medical supplies, refrigerated and frozen food.

Table 3 shows the list of actual projects within the Working Group.

Table 3 Cooling Applications in WGB1

Project	Field	Type
PCM-Zentral	Comfort cooling	PCM
Sakae DHC	Comfort cooling	PCM, Water
R & D centre	Comfort cooling	PCM
PCM air heat exchanger	Comfort cooling	PCM
Salt based cold TES	Comfort cooling	PCM
Root zone	Agriculture	PCM
Thermal energy storage using phase change materials for cold applications	Food	PCM
PCM in buildings for passive cooling	Comfort cooling	PCM

5.2 Operating Conditions

To set operating conditions of every field of applications, several indices are discussed. These are temperature range, power, density and performance indices.

Temperature range

Temperature is the condition which taken into account first of all. Phase change temperature is one of most significant characteristics of phase change materials and performance of thermo chemical materials is largely depended on their working temperature.

Storage Capacity

Both mass and volumetric storage capacity (energy storage per mass and volume) are considered. For building materials, volumetric concentration rather than mass concentration are important indices for the applications.

Power

Power is defined as output energy per unit time from a storage device depending on various factors. As for a material, thermal conductivity is key factor as well as heat transfer of apparatus which is depended on thermal conductivity of container and heat exchanger and convectional heat transfer coefficients of the working fluid. The larger the temperature difference can be achieved the more heat can be transferred per time.

Efficiency

The efficiency of a storage system can be described by the COP (Coefficient Of Performance) which is the ration of the energy input and the usable energy output of the storage.

Table 4 shows overview of boundary conditions of the applications. Since most of them are in phase of development, performance indices are still in consideration and actual values are hardly presented. As they are diurnal use, duration is within half a day long. Therefore, power can be calculated by dividing capacity by duration time.

Table 4 Overview of boundary conditions of applications in T4224

Project	Temperature	Duration	Power	Volume
PCM-Zentral	15 to 40	12 h		24 m ³
Sakae DHC	7 to 8	7 to 10	2,450W	2,000 m ³
R & D centre	16	10h	94 kW	54 m ³
PCM air heat exchanger	20 to 38	3 to 5	3.5/4.5kW	1.2m ³
Salt based cold TES	0 to 40	daily	9 – 11kW	0.3 m ³
Root zone	10 to 15	24	352kJ/ container	0.16x0.10x0.03
Thermal energy storage using phase change materials for cold applications	-18	Application dependent	Application dependent	
PCM in buildings for passive cooling	27	Application dependent	Application dependent	

6 Application Related Activities: Heating / Domestic Hot Water

Long-term, compact thermal energy storage (TES) is essential to the development of cost-effective solar and passive building-integrated space heating systems and may enhance the annual technical and economic performance of solar domestic hot water (DHW) systems. Systems should provide high energy storage density, charge and discharge temperatures that match the heat source used for charging and the intended load, adequate charge/discharge power, and employ storage materials that are stable over many cycles, non-toxic, environmentally safe. Moreover, these systems must compete effectively in the marketplace and therefore should provide an economic benefit compared to conventional heating and DHW systems, which have traditionally relied on sensible water storage.

Working Group WB2 addresses applications of compact thermal energy storage for space heating and hot water (20 to 100 °C). The activities in this working group are aimed at guiding materials development, within the limitations of these two applications, and at development of systems that use compact storage medium with the goals of improved technical and economic performance compared to traditional approaches. Because solar assisted heating of buildings is the main focus of the SHC IEA, this topic is addressed by many of the contributors to this report. However, because there are many relevant applications for TES, the working group activities encompass other applications including systems for passive building integrated climate control.

The primary activities of the working group include:

- selection of candidate materials and system configurations;
- assessment of the technical performance of systems through laboratory tests of components and systems, case studies, modeling, and/or field studies;
- assessment of the economic performance through modeling and evaluation of market potential.

This report's focus is on the development of system concepts and technical evaluation of proposed systems and the storage components of these systems through predictive modeling and laboratory testing.

6.1 Overview of Materials and Classification of Systems

Overview of Materials

Development of systems within the working group has focused on integration of phase change materials (PCMs) and thermochemical materials into active heating systems and integration of PCMs into building materials. Active systems that rely on PCMs and thermochemical storage require specialized components and operation to charge and discharge the storage vessel. Innovation at the system level is a necessary and a crucial step toward identifying desired material characteristics and successful use of newly developed storage materials.

A performance map in terms of the key constraints of material energy storage density and temperature is shown in Figure 21 for TES materials that have been used or are being investigated for solar hot water and space heating. However the values for the energy storage density (or storage capacity) are no material properties and are in most cases maximum values based on reaction enthalpy. Reported energy density ranges from 35 to 780 kWh/m³ for materials with charging temperatures between 20 and 180 °C. Thermochemical storage can have the highest energy density followed by PCM and sensible energy storage. Generally, materials with larger energy density require higher charging temperatures. Note that these energy density values are with respect to the volume of the storage material and do not include the volume of supporting equipment. In general, material energy density depends on the thermodynamic states of the storage system at charging and discharging conditions. In practice, system level energy density may be lower due to a number of factors including limitations in heat and mass transfer, and kinetics for thermochemical reactions, as well as the added volume of components required to add and extract energy from the storage vessel.

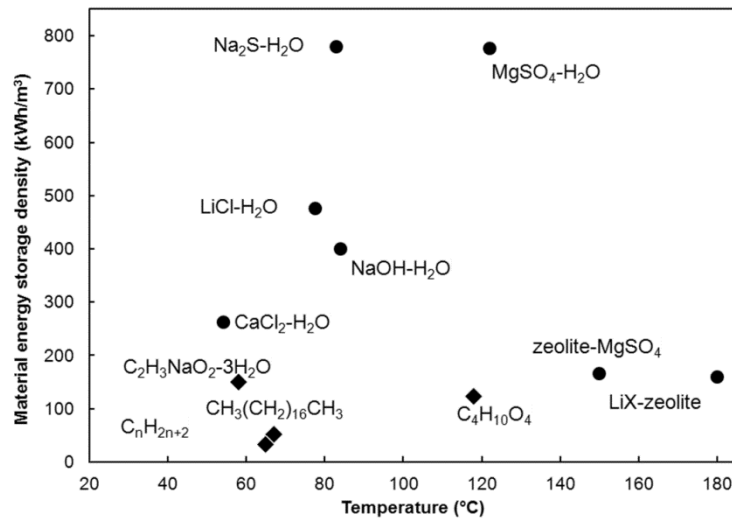


Figure 21: Material energy storage density versus charging temperatures for candidate TES materials. Latent (◆), thermochemical (●)

PCMs are well suited for applications in which the operating temperature is limited to a small range close to the phase transition temperature. The material energy storage density depends on the enthalpy of fusion, the heat capacity and the temperature limits of the system:

$$\lambda_{PCM} = \rho_{min} \int_{T_{min}}^{T_{max}} h_{fus}(T) dT + \lambda_{\Delta T, liquid} + \lambda_{\Delta T, solid} \quad (2.1)$$

where ρ_{min} is the minimum density (liquid phase), h_{fus} is the enthalpy of fusion, T_{min} and T_{max} are the temperature limits of the phase change process, and $\lambda_{\Delta T}$ is the sensible energy storage densities in the liquid and solid phases. The specific heat of most PCMs is lower than that of water. Material energy densities due to the enthalpy of fusion range from 35 kWh/m³ for paraffin to 167 kWh/m³ for sodium acetate trihydrate). A challenge for PCM storage is design of the system for adequate charging and discharging power. One constraint is the relatively low thermal conductivity of PCMs (< 1.1 W/m-K). Composite materials incorporating carbon have enhanced

thermal conductivity and have been proposed for solar thermal applications. However in some materials, increased thermal conductivity comes at the expense of energy density, which can be reduced by 35% or more due to the volume of the conductive material. Like water, PCMs have limited potential for seasonal storage but are explored here for extended periods.

A number of groups are working on the development of storage systems based on low-temperature thermochemical reactions. Thermochemical reactions store heat in chemical bonds and thermal losses are negligible compared to the enthalpy of reaction. One limitation is the charging temperature attainable with flat plate and evacuated tube collectors, $\sim 150^\circ\text{C}$ or lower.

Sorption storage, which refers to the potential energy of desiccant materials to adsorb/absorb water vapor and release heat, has been identified as a promising match to solar collectors and space heating systems. The energy storage is due to the enthalpy of sorption, h_s , which is the energy released when water vapor is sorbed onto a solid surface or into the volume of a liquid. It is the sum of the binding energy of the water and host material molecules in the condensed state, h_b , and the enthalpy of vaporization of the water, h_{fg} :

$$h_s = h_b + h_{fg} \quad (2.3)$$

The sorption energy storage capacity depends on the operating limits on mass fraction, S , (concentration) of water in the host material:

$$\lambda_{\Delta S} = \rho_{min} \int_{S_{min}}^{S_{max}} h_{fg}(S) + h_b(S) dS \quad (2.4)$$

where S is expressed as kg-H₂O/kg-total, and $S_{max} - S_{min}$ represents the total water uptake that is useful for energy storage. The mass of water that can be added and removed from the storage is function of the temperature and pressure in the system. To-date, sorption storage media have been selected primarily from commercially available materials, including physical adsorption of water vapor on porous molecular sieves, typically aluminosilicate zeolites, or silica gel, and absorption using aqueous lithium chloride (LiCl), lithium bromide (LiBr), sodium hydroxide (NaOH), or calcium chloride (CaCl₂). Reported material energy densities, based on the enthalpy of sorption, are 130 to 780 kWh/m³. The binding energy typically contributes less than 35% to the stored energy. The majority of the storage is from the enthalpy of vaporization of water. The energy capacity due to the enthalpy of vaporization increases with the amount of water absorbed. Technically, the enthalpy of vaporization is usually not stored, but transformed from a low-temperature source to a higher temperature for the load. In other words, the energy to vaporize water must come from within the system or be supplied by an external source (*e.g.* the ground or a solar thermal collector). Hence, unlike sensible and latent storage, sorption system energy density depends on the availability and the quality of the thermal energy sources and sinks. System level energy density may be substantially lower than material energy density due to the relative complexity of system integration.

6.2 Classification of Active Systems

Systems may be classified according to their interaction with the surroundings. Figure 22 illustrates the classification of solar thermal systems and describes the three system types in terms of thermodynamic terms. The basic system illustrated in Figure 22(a) does not require external sources or sinks. Water and PCM stores fall into this classification as does the liquid sorption system described in this chapter. Open- and closed-cycle sorption TES systems include energy transformation (*i.e.* heat pumping) and thus require heat or mass transfer with the surroundings independent of the solar energy, the load, and thermal loss. Closed-cycle sorption systems transform energy from the source to the load via heat transfer (Figure 22(b)). Open-cycle sorption systems transform energy via mass transfer with the surroundings (Figure 22(c)). The total enthalpy of sorption is available for both open- and closed-cycle systems. However, the enthalpy of vaporization is not stored, but transformed from a low temperature source to the temperature of the thermal load. Thus, the energy density depends on the availability and the quality of the thermal sources and sinks.

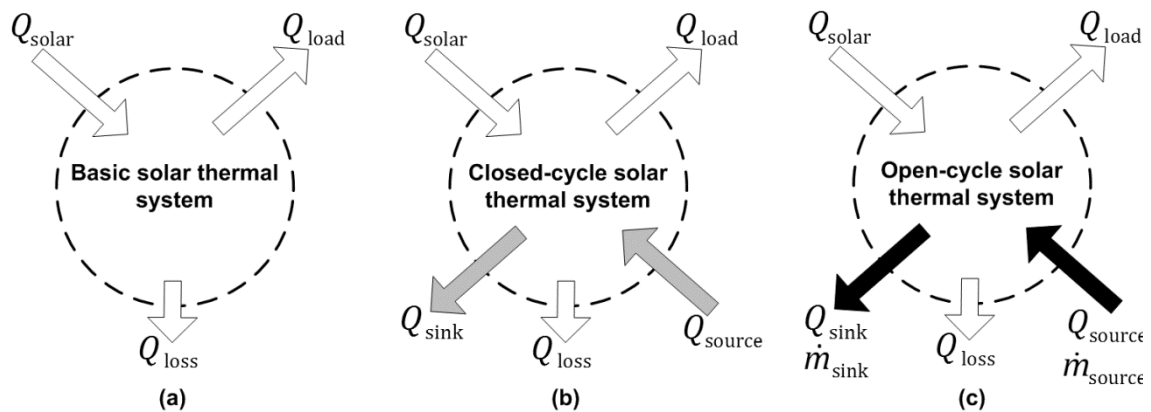


Figure 22: Thermodynamic classification of solar energy storage systems: (a) simplest system; (b) closed-cycle system that transforms energy from the source to the load via heat transfer; and (c) open-cycle system that transforms energy via mass transfer to the surroundings

The charge/discharge cycle of sorption storage systems comprises two primary steps. During charging, water is desorbed from the desiccant ideally using a sustainable heat source such as solar or waste heat. The water vapor is condensed and stored (closed-cycle) or released to the ambient (open-cycle). During discharging, the sorbent is rehydrated. For solid sorption (adsorbents), stored water may be evaporated using a low temperature source such as the ground (closed-cycle) or discharge may be accomplished using ambient air (open-cycle). Open cycle discharge requires sufficient water content in the ambient air stream. This requirement limits discharge operation to climates in which moist ambient air is available during the heating season. Rehydration releases the heat of sorption.

Solid adsorption

Beyond material selection, design and operation of a thermochemical solid adsorption storage vessel/reactor is crucial for successful implementation of long-term storage. The key challenge is ensuring adequate heat and mass transport within the medium. Material thermal conductivity of solid sorbents is low (reported values for zeolite are 0.08 - 0.16 W/m-K) and packed beds have even lower effective conductivity and less favorable kinetics. Moreover, in practice, the useful energy density is limited by thermodynamics. Because the vapor pressure of the adsorbent increases with tempera-

ture, a high rate of adsorption (high discharge power) translates to the inability to fully discharge the stored energy.

The adsorption reaction may be implemented within the storage vessel or the reactants may be transported to a separate reactor(s). In the former, the storage is referred to as an integrated storage/reactor. In the latter, the storage and reactor are referred to as separated. Figure 23 illustrates closed- and open-cycle systems, both with an integrated storage/reactor. The advantages of the integrated storage/reactor system are compactness and reduction of mechanical parts. The disadvantages are the requirement of a porous architecture to facilitate adsorption/desorption within the storage vessel and the inability to charge and discharge simultaneously. Figure 23(a) shows a closed-cycle system in which heat exchangers are embedded within the storage medium to transfer heat from the solar reactor to the load. These systems typically operate at low pressure. Charging (desorption) is indicated by dashed lines and discharging (adsorption) is indicated by solid lines. During charging, the storage/reactor is heated to drive off water vapor, which is condensed and stored in a separate vessel. The heat from the condenser is rejected to the surroundings or may be used to meet the load. To discharge the system, the stored water is transported to an evaporator where a low temperature source provides the energy for evaporation. The evaporated water passes through the storage/reactor where it is re-adsorbed releasing the chemical binding energy.

Figure 23(b) illustrates an open-cycle system in which the heat exchangers are external to the integrated storage/reactor. During charging, the heated air stream is circulated through the storage/reactor to desorb water vapor. To discharge the system, moist ambient air is passed through the storage/reactor. It exits the storage/reactor as warm dry air which is passed through a load-side heat exchanger. There is no condenser or evaporator. The advantages of the open-cycle are that there are fewer components, the system operates at atmospheric pressure, and the heat exchangers do not scale with the volume of the storage. The disadvantage is that a source of warm moist air is required during the heating season.

Figure 24 illustrates a closed-cycle absorption system. The system comprises multiple storage vessels, two reactors (for absorption/desorption), a condenser and evaporator, and heat exchangers. The concept is similar to a closed-cycle adsorption system with separated storage and reactor, but, in this case, physical transport of the sorbent and heat and mass transfer in the reactors is improved. Three storage vessels, one each for water, diluted (discharged), and concentrated (charged) solutions, are shown in this illustration to emphasize the necessity of preventing mixing prior to discharging. Mixing of the diluted and concentrated solutions releases the stored binding energy and converts the chemical potential into sensible energy,

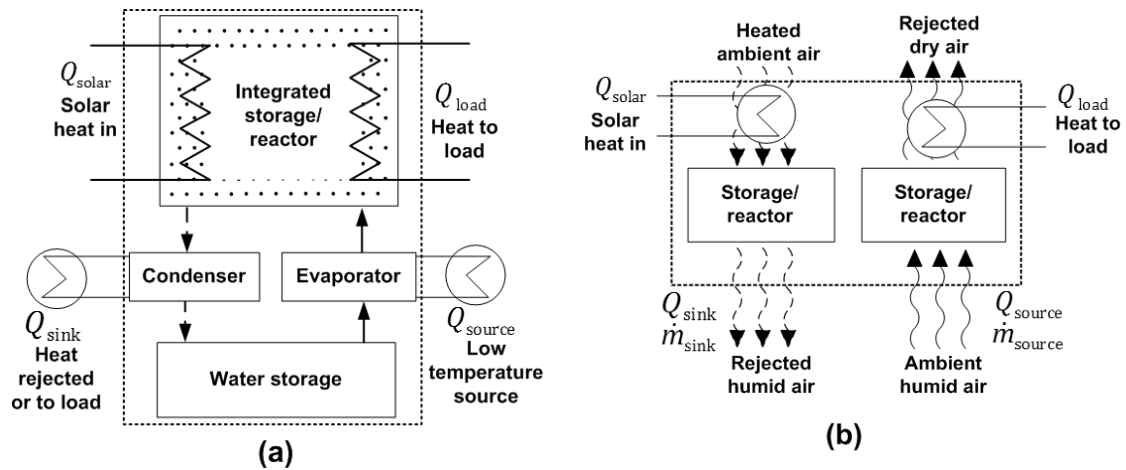


Figure 23: Schematic of closed- and open-cycle adsorption storage systems. Charging operation (desorption) is indicated by dashed lines and discharging operating (adsorption) is indicated by solid lines. (a) In the closed (low pressure) system, there is a single integrated/storage reactor with embedded heat exchangers where heat is added (charging) or removed (discharging). During charging, the energy of condensation is rejected or used to meet the load. During discharging, energy from a low temperature source evaporates water. (b) In the open system, there is a single integrated storage/reactor with external heat exchangers. During charging, incoming ambient air is heated. Water vapor evaporates into the air as it passes through the integrated storage/reactor and humid air is rejected. During discharging, humid ambient air is passed through the integrated storage reactor, water vapor is adsorbed, and heat is extracted from the dry air exiting the integrated storage reactor [Taken from Quinnell and Davidson, 2012a].

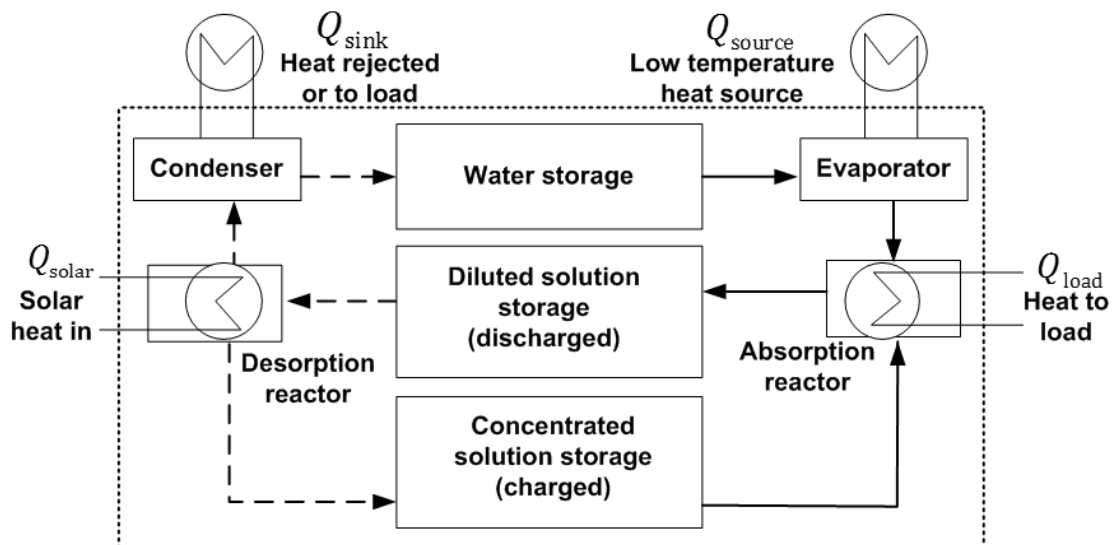


Figure 24: Schematic of a closed-cycle liquid absorption storage system. Charging operation (desorption) is indicated by dashed lines and discharging operating (absorption) is indicated by solid lines. In the closed (low pressure) system, there can be one or two separate reactors and multiple storage vessels for solution in different states (concentration). Heat is added (charging) or removed (discharging) via embedded heat exchangers in the reactors. During charging the energy of condensation is rejected or used to meet the load. During discharging energy from a low temperature source evaporates water. Solution from the storage vessels is pumped to and from the reactors [Taken from Quinnell and Davidson, 2012a].

which is subject to thermal loss to the ambient. The use of multiple storage vessels ensures long-term storage of chemical potential but decreases the system-level energy density and increases the cost.

Liquid absorption

Liquid desiccants are promising storage option because, in contrast to solid adsorption materials, they can be pumped and used as the working heat transfer fluid in solar collectors and heat exchangers. Faster heat and mass transfer rates are possible with liquid absorption. Materials recently investigated include aqueous solutions of CaCl_2 , LiCl , NaOH and KOH . Absorption materials were compared for use in low pressure (1.2 – 4.2 kPa) absorption cycles and theoretical material energy densities have been reported up to 476 kWh/m^3 , as shown in Table 5. Although energy density is an important criterion for selection, thermophysical properties, cost, and the cycle temperatures and pressures influence the choice of material. Lithium chloride (LiCl), with desorption temperature of 66°C , has the highest storage density of 476 kWh/m^3 , but also has a high absorption temperature range, 20 to 35°C . Calcium chloride (CaCl_2), with a desorption temperature of 44°C , has an energy density of 263 kWh/m^3 and a limited absorption temperature range of 20 to 23°C . Sodium hydroxide (NaOH), with a desorption temperature of 50°C , has an energy density of 233 kWh/m^3 and the highest absorption temperature of 45°C .

Table 5: Aqueous absorption materials considered for low pressure (1.2 – 4.2 kPa) absorption cycles for space heating [Hui et al., 2011].¹

Material	CaCl_2	LiCl	LiBr	NaOH	KOH
Maximum sorbent mass fraction, kg-salt/kg-soln. ²	0.40	0.44	0.59	0.35	0.51
Maximum material energy density, kWh/m^3	119	400	313	154	313
Maximum material energy density (80% solid crystals), kWh/m^3	263	476	400	233	400
Absorption temperatures, $^\circ\text{C}$	20-23	20-35	25-35	25-45	25-35
Desorption temperature, $^\circ\text{C}$	45	66	72	50	63

¹ Values assume condenser temperature and evaporator temperatures of 10 and 30°C , respectively.

² Maximum sorbent mass fractions are determined from maximum solubility at the evaporator temperature (10°C).

6.3 System Development by Task Contributors

This section includes summaries of systems under development by the working group contributors. Table 6 provides a summary of the systems presented. The following information is included in each section:

- System schematic and description of operation including any limits
- Storage material properties and attributes
- Description of novel or unique component(s)

- State of development/commercialization

Table 6: List of systems described in Section 3.1.

Report Section and Application	Storage Mechanism(s)	Storage Material	Status	Contact
3.1 Solar CombiSystem +Cooling	Sorption + Sensible	CaCl ₂ (aq)	Laboratory prototype components	USA Jane Davidson, University of Minnesota
3.2 Solar CombiSystem	Latent + Sensible	Sodium acetate tri-hydrate PCM and water	Laboratory prototype	Denmark Simon Furbo, Technical University of Denmark
3.3 Closed Solar CombiSystem (Numerical results in 4.2.1)	Sorption + Sensible	Silica gel Zeolite	Pilot demonstration	Austria Dagmar Jaehnig, AEE INTEC Germany Florian Bertsch, University of Stuttgart
3.4 Passive climate control	Latent	Encapsulated PCM	Laboratory demonstration	Spain Luisa Cabeza
3.5 Heat Pump	Latent	PCM	Small scale demonstration	Spain Luisa Cabeza
3.6 Solar CombiSystem	Sorption + Sensible	MgCl ₂ ·6H ₂ O salt hydrate	Matls. Characterization and Laboratory Prototype	The Netherlands Robert de Boer, H.A. Zondag, ECN/TUE
3.7 Solar CombiSystem +Cooling		Zeolites Salt Hydrate: CaCl ₂	Reactor prototype	The Netherlands Ruud Cuypers Christian Finck, TNO
3.8 Open Solar CombiSystem (Numerical results in 4.2.1)	Sorption + Sensible	hydrates	Laboratory demonstration	Florian Bertsch, University of Stuttgart
4.2.2 Combisystem	Latent + Sensible	PCM/Water	Numerical Simulation	Austria, Andreas Heinz,

7 Application Related Activities: High Temperature

The activities of this working group serve the underlying guidance principle of the materials development within the limitations of the application. The materials development will be directed by the desired system performance. A constant assessment of performance criteria for a given application will be used to determine the chances for a given material/system combination. These criteria can come from economic, environmental, production technology or market considerations. Activities in the Application Working Groups include, amongst others, definition of application boundary conditions, definition of required thermophysical properties for each application, selection of relevant candidate materials and system technologies and performance assessment and validation.

The working focuses its activities in High Temperature Applications, stated as applications where the working temperature is higher than 100 °C (higher than the temperature needed for heating and domestic hot water). The activities can be classified as follows:

- high temperature application in buildings from 140 °C to 200 °C (e.g. solar cooling)
- process heat for industry from 100 °C to 160 °C
- direct steam generation for solar thermal power plants from 200 °C to 450 °C
- storage for Adiabatic Compressed Air Energy Storage or gas turbines in solar tower power plants (> 400 °C)

Some of the activities within this working group were under very strict confidentiality agreements, that no results can be presented here.

7.1 Solar cooling application

Solar cooling uses solar thermally generated heat, which is used in conjunction with cooling systems to provide a renewable source of industrial and residential cooling **Fehler! Verweisquelle konnte nicht gefunden werden..**

Since solar energy is time dependent, the successful utilization of all these systems is to a very degree dependent on the TES systems used: integrating TES systems to solar cooling applications contributes to consumption peak shaving on demand peaks and hence, economic savings.

Here, an application of PCM storage in a solar cooling application is studied. In the solar cooling final plant Fresnel collectors provide solar heat to an absorption chiller which has a work temperature range from 150 °C to 200 °C. The TES tank, is placed between the solar collectors and the cooling machine (by absorption, adsorption, or desiccant cooling technology) to store the heat produced by the solar collectors at the temperature range between 140 and 200 °C, and to release it at the required time, temperature, and power, to the cooling machine.

The first stage in the materials selection was to select a temperature range adequate for the implementation on of TES systems in a real solar cooling plant. The temperature range of the storage was 140-200 °C, where 200 °C represents the maximum tem-

perature leaving the solar collectors (in this case Fresnel collectors were considered) and 140 °C the minimum inlet temperature in the absorption chiller. Another requirement was a high heat of fusion, which in this case was estimated to be higher than 150 kJ/kg. Moreover, mechanical, chemical, economic, and environmental properties of the candidates (as volumetric variation between solid and liquid, chemical stability, vapour pressure, toxicity, compatibility with the container material, price, availability, etc.) were taken into account in the selection process.

The first PCM selected was hydroquinone due to its high phase change enthalpy in both literature and DSC testing and also to the little subcooling seen at lab scale. Moreover, d-mannitol was selected as PCM for its high heat of fusion even though the material presented high subcooling at lab scale (see chapter 1.5).

Experimental set-up

A pilot plant to test accurately different TES systems working with latent or sensible heat storage materials has been constructed at University of Lleida. Figure 23 shows a scheme of the pilot plant.

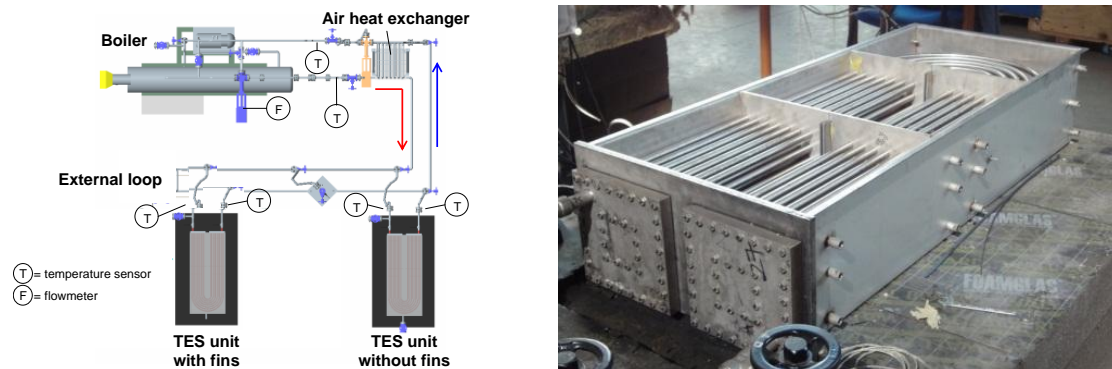


Figure 23: Scheme of the pilot plant available at University of Lleida and Overview of the TES tank

The PCM TES tank design was a shell-and-tubes heat exchanger which consists on a shell (a vessel) with a tubes bundle inside. The PCM was located in the housing of the shell part and the HTF circulates inside the bundle of tubes, which was integrated by 49 tubes distributed in square pitch. The tubes were bended in U shape and they were connected in each side to collectors which distribute the HTF (Figure 23, right).

Both high temperature TES tanks are identical with the only difference that one of them incorporates transversal squared fins in the tubes bundle in order to increase the heat exchange surface. Performance tests with both PCMs were carried out.

7.2 Process Heat for Industrial Applications

Industrial Applications

The aim a project at the University of Lleida is to demonstrate that thermal energy storage is a good tool to improve energy efficiency in the industry. To do so, it is intended to study different applications at high temperature (solar cooling –storage from the heat coming from the Sun-, industrial heat recovery from metallurgy or energy savings in the cement, pulp and other industries) and at low temperatures (food freezing, agro-alimentary and medical products conservation or solar cooling –storage of the produced cold).

It is aimed to study, experimentally and by modeling, the use of the thermal energy storage technology with PCM tanks at high and low temperatures, molten salts tanks at high temperature and tanks with solid industrial by-products to store sensible heat at high temperature, in applications such as freezing, metallurgy, solar cooling, etc. to increase energy efficiency of the Spanish industry.

Technical, economical and environmental viability study of the utilization of thermal energy storage in the described industrial applications. Once the best technology is studied and the best material for each application is selected and testes, it is intended to study the technical, economical and environmental viability of each of them, to allow it transfer to the industry.

A comparative life cycle assessment of three thermal energy storage systems for solar power plants has been carried out. The environmental impact has been analysed and compared using Life Cycle Assessment (LCA) methodology based on the Eco-Indicator 99 (EI99).

The study is focused in three systems: sensible heat storage both in solid (high temperature concrete) and liquid (molten salts) thermal storage media and latent heat storage which uses PCM.

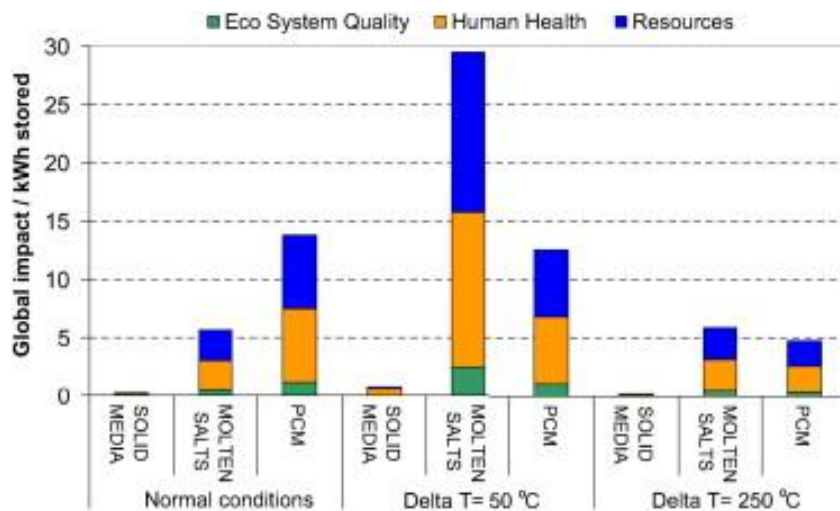


Figure 24: Global impact of each storage system for 3 different scenarios.

To compare the studied TES systems the global impact per kWh is analysed and three different scenarios are introduced: (1) normal conditions, (2) ΔT of the storage materials is set to 50 °C and (3) ΔT of the storage materials is set to 250 °C.

As seen in figure 24, the system based on solid media, due to his simplicity, shows the lowest environmental impact per kWh stored of all three systems compared. In addition, the liquid media (molten salts) shows the highest impact per kWh stored because it needs more material and complex equipment.

The project also includes the accounting of the energy and CO₂ embedded in the storage materials. This is being carried out now within the framework of Annex 25 of ECES IA.

PCM-Balls

Although more than 70% of the industrial heat demand arise at temperatures above 100°C, most thermal storage applications focus on temperatures below that level [2] and the application of Phase Change Materials (PCM) is not very common. It was the aim of our development to provide a heat storage material which:

- works in the temperature range between 100°C and 160°C,
- increases storage density by avoiding the air pockets which are applied in encapsulated PCMs to restrict internal pressure variations during phase change,
- avoids the application of metal encapsulations.

The PCM balls were designed to be used as bulk material in a packed bed with different heat transfer media.

Erythritol (melting point: 118°C), Polyethylene (HDPE, mp.: 126°C) and Adipic acid (mp.: 151°C) were chosen for the material development as a result of various tests. These tests included enthalpy measurements, cycling tests, corrosion tests and investigations concerning chemical compatibility.

It was decided use macro-encapsulated PCM and to restrict the size of the PCM capsules to 32 mm in diameter in order to achieve sufficient heat transfer properties. Because coating of solid particles has a higher potential for economic up-scaling than filling of prefabricated hollow balls shape forming of the PCM was required. Two different techniques were applied to produce PCM-blanks with 30 mm diameter: casting and pressing. Pressing turned out to be advantageous for the high melting Adipic acid (steel die, application of a parting compound) whereas casting showed the best productivity for materials with lower melting points.



Figure 25: Encapsulation of the PCM-Blanks (left) and PCM-Balls ready for Application

Different high temperature heat storage materials were encapsulated in silicone. Adipic acid in molten state turned out to be too aggressive to the silicone coating. Erythritol is a promising heat storage material due to its high volumetric storage density. Unfortunately silicone is too permeable to seal the sugar alcohol securely. Various experiments with nucleating agents to decrease supercooling brought only limited success. Silicone encapsulated HDPE balls are a promising material for thermal energy storage at elevated temperatures. The material is available with melting temperatures from about 80°C to 130°C. The long term contact of HDPE balls in molten state to air should be avoided.

Form stable PCM

For elevated temperatures of 120-130 °C, which are important for a lot of industrial processes, polyethylene (PE) was found to be one of the most promising PCM1). The manufacturing of polymer coated polyethylene balls with convenient thermophysical and technical properties was successfully demonstrated, unfortunately the technology is expensive yet1). Therefore the application of form stable melting polyethylene as a PCM without an encapsulation is of fundamental interest. In former published articles the form stability of the material during the melting process was achieved by complex and expensive chemically or radiation induced cross-linking reactions. In this paper investigations of non cross-linked but nevertheless form-stable PE are presented.

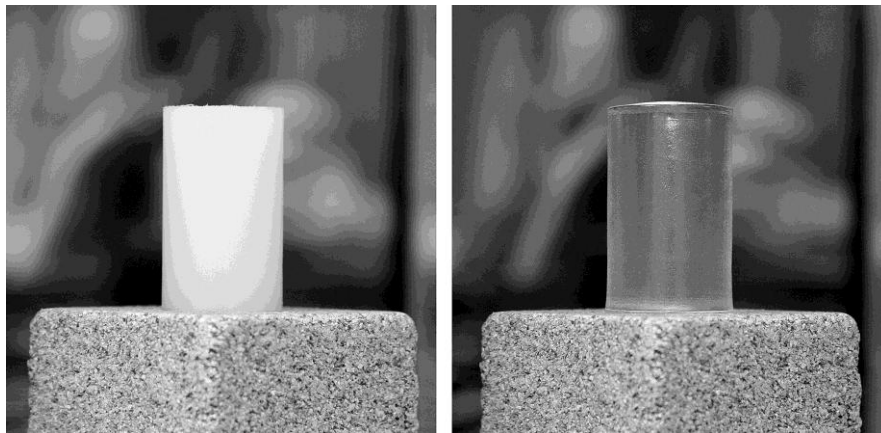


Figure 26: A freestanding PE-UHMW rod at room temperature (left) and in the molten state at 150 °C (right) in air

Form stable melting PE-UHMW was confirmed to be a promising PCM, which probably can be used as a thermal storage material without encapsulation at temperatures around 130 °C. Water (steam) is preferred as heat transfer medium.

A first attempt to test the PE-UHMW as a heat storage material was also made by Özcan10). They investigated the generation of process steam and cold production by solar collectors, a steam jet refrigerator and a latent heat storage. The application of this PCM could be confirmed in principle in a laboratory scale. However a distinct aging and degradation of the material due to the application in non-optimized environment was found. Further material and application tests are necessary.

The economic potential of the application of PE-UHMW as a PCM for heat storage can be roughly estimated as follows: Assuming a heat of fusion of 150 J/g, a prize of 4 €/kg and an expected useful life of 3650 cycles (5 years, two cycles per day), we can expect a price for thermal energy storage of 0,026 €/kWh (costs only related to the PCM).

However, all our findings described in this paper are results of first preliminary tests and need to be affirmed, specified and stated more precisely by extended and systematic investigations.

7.3 Direct Steam Generation

Concentrated solar power (CSP) is a competitive technology using renewable energy to generate electricity. The possibility to shift the production of electricity to the de-

sired periods of the day or night by means of thermal energy storage systems (TES) gives a competitive advantage over other renewable energies, such as wind or photovoltaics.

Beside the molten-salt-TES technology There are other options available, like the direct steam generation (DSG) which is commercially in use, for instance in PS10 and PS20 power tower plants, in Spain. In PS10, the TES system consists on several tanks that store the saturated steam. The DSG CSP plants present several advantages in comparison with molten salts technologies. Water/steam is used instead of oil or/and molten salts which is more environmentally friendly, less hazardous and no flammable, and there is no need of supplementary HTF heat exchangers because steam is directly sent to the turbine in the power block.

In this study, the goal was to find an appropriate metal alloy that fulfils all the requirements needed for a TES system in DSG applications. From the exergy point of view, it is desirable that the preheating of the water and superheating of the steam is given by sensible heat TES, and that the vaporization of the water is given by latent heat TES. Around 60-70% of the total energy needed to generate superheated steam is needed for the vaporization process of the water. Therefore, in this report, we focused on the study of the metal alloys that could be used as a TES system devoted to the vaporization process of the water. As the vaporization of water occurs at constant temperature at a given pressure, the melting temperature of the selected material is a key parameter to be taken into account, and should be also constant. For this reason, eutectic metal alloys could be the most appropriate materials.

The system Mg-Zn was chosen, which binary phase diagram is shown in figure 27.

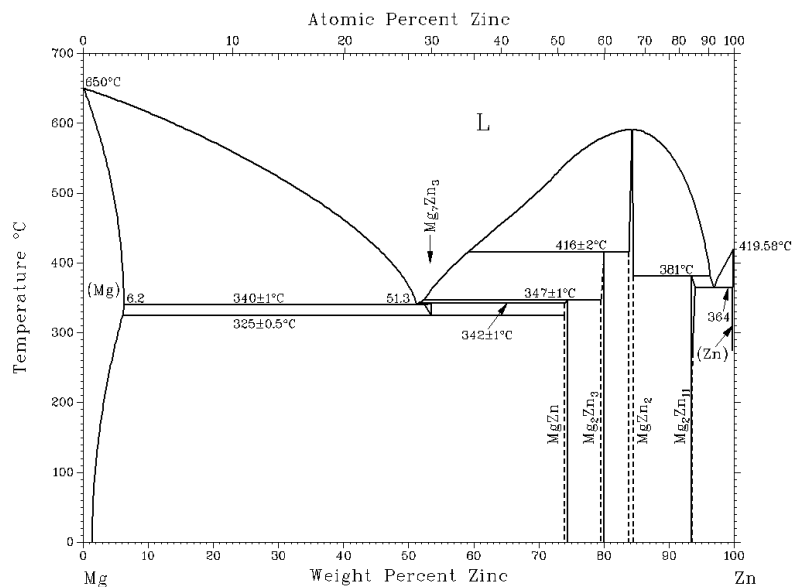


Figure 27: Binary phase diagram of Mg and Zn

The eutectic metal alloy Mg49Zn51 working as PCM for DSG would need saturated steam at approximately 160 bar to charge it (melting), and it could produce saturated steam at around 140 bar in the discharge process (solidification). Current available steam turbines are within this range of operation. For instance, the SST-700 and SST-900 turbines of Siemens can support up to 165 bar at 585 °C of superheated steam, with a power output from 20 MW to more than 250 MW. Therefore, the presented metal alloy, the eutectic Mg49Zn51, not only could be used as a TES material in DSG

applications in CSP technology, but as a TES in any other process where steam under these conditions is produced.

Concerning CSP, the technological challenge will be to construct solar collectors that will support the pressure and temperature of saturated steam at pressures around 160 bar. To the best of our knowledge, parabolic trough collectors have been tested up to 100 bar for DSG. The use of this PCM is not only devoted for parabolic trough technology, but for power tower as well as for linear Fresnel technologies.

One of the main advantages of this alloy is its high thermal diffusivity which is two orders of magnitude higher than that of molten salts. This will be significantly reflected in an easier to handle operation and lower cost of the needed heat exchanger inside the PCM storage tank, compared to molten salt PCM.

7.4 High Temperature TES for ACAES and Solar Tower Plants

A high temperature (up to 1000°C) thermal energy storage pilot (TESP) has been designed and implemented in the PROMES laboratory to test the lab-scale thermal energy storage modules made of recycled industrial wastes.

Considering the main target applications as being the ACAES and the gas turbine tower CSP processes, the selected heat transfer fluid is hot air. The TESP has been designed to allow reverse HTF flow between storage and discharge mode through the TESM.

Various shapes of the TESM are tested (granular random packing, flat plates, corrugated plates such as static mixers) for comparisons and the potential fatigues of each TESM to the repeated thermal cycles are assessed.

Pilot Installation

The TESP, illustrated by the scheme of Figure 31 and the picture of Figure 28, is composed of three major elements namely (1) the heating system, (2) the TES channel, and (3) the instrumentation.

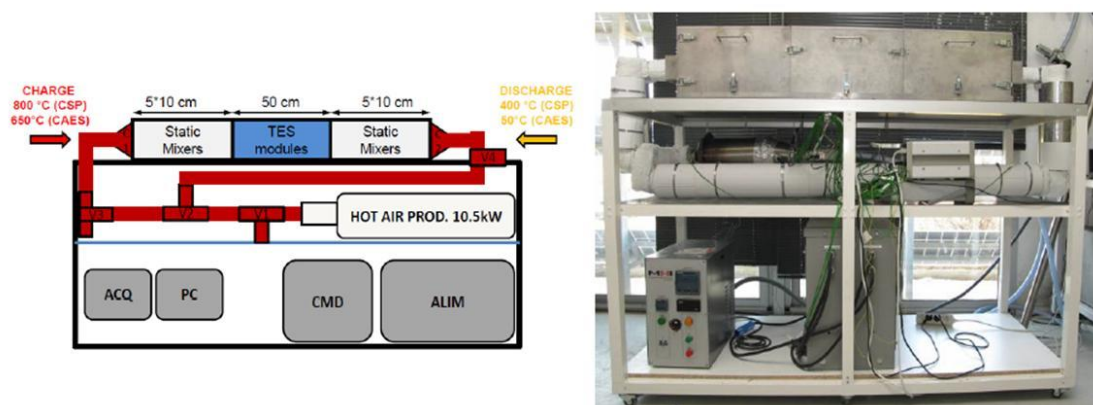


Figure 28: TESP scheme and picture

The TESP is a laboratory pilot test unit devoted to sensible heat based thermal storage materials and to applications in which the working fluid is hot air: such as ACAES and gas-turbine tower CSP. The heating system is fed by atmospheric compressed air at 3 bars which is first filtered to withdraw possible presence of oil and dust. The air is



heated by means of an electric 10.5 kW heating element. This heating system can produce hot air up to 1000°C with a flow rate of 29 Nm³/h and its temperature level is controlled by a central programmable unit.

Two conventional HTFs potentially used in CSP plants (solar salt and air) and a promising ternary nitrate salt (Hitec XL) were investigated in a large range of temperatures for molten salts (200–500 °C) and for air (500–900 °C), in direct contact with a post-industrial ceramic called Cofalit. Observation of the stability of the ceramic in the presence of molten salts and air was followed by analysis of the sample after thermal cycling by XRD and SEM. No significant corrosion of the samples was observed in the case of the nitrate salts. A small surface oxidation was observed in the case of air exposure. Direct contact between the post-industrial ceramic and the nitrate salts or air could thus be considered. This ceramic can be used as storage material in CSP plants in direct contact with molten salts and air as HTFs and also with phase change materials in the case of nitrate salts.

8 Theoretical Limits of Thermal Energy Storage

The objective of this Working Group is to determine the theoretical limits of compact thermal storage materials and systems from a physical, technical and economical viewpoint. The most general limits to thermal energy storage are imposed by the underlying physical laws. While these laws might not be directly applicable to real storage systems, they indicate an upper limit that cannot be overcome by any system. Thus, physical limits can give the context to evaluate the potential of a technical storage concept. The two main characteristics of any thermal storage system are the storage density (or capacity) and the storage power, which determine the size for each application. Storages must have operating conditions (e.g. temperature and pressure) that match both the energy source and the energy load.

- The chapter on “Physical Limits” focuses on the maximum storage density as the critical property.
- The second important property, storage power, is considered in the second chapter, “Technical Limits.” Although storage power also depends on material properties, it is generally much more dependent on system design and engineering.
- Lastly, the chapter on “Economical Limits” reviews the limitations imposed by the cost of energy storage in relation to the cost of energy, the frequency of storage use, and the user of energy storage.

8.1 Physical limits of thermal energy storage

Physics of Heat

Heat is a path-dependent variable, not a state function. Contrary to state variables (e.g. temperature, pressure, entropy) a path-dependent variable is not defined for a given system state, but rather for a given path (or process) between two states. For example, a thermal storage does not contain a quantity of heat. Rather, the thermal storage has the thermodynamic potential to transfer a quantity heat to an external system. The important consequence of this basic physical distinction in the context of thermal energy storage is that **the capacity of a thermal storage is only defined with respect to a reference state**, e.g. the state of the user and is not a material property!

According to the law of energy conservation, it is incorrect to speak of “energy consumption.” Consequently, the term “energy storage” is also troublesome because energy is always conserved. In practice energy consumption refers to an energy conversion resulting in a form of energy no longer suitable for the original task. Thus, depending on the task or user energy demand, there are forms of energy that are more and less “useful.”

The concepts of exergy and anergy are introduced to take account of this energetic quality. Energy can be divided into these two components. A quantity of thermal energy, divided into its exergy and anergy in eq. (1). The first term on the right hand side of the equation is the exergy and it can be converted into work in a reversible process. The other term is the anergy and it must be transferred to the ambient as part of the conversion of the exergy into work. Anergy itself cannot be converted to work. Exergy addresses the quality of the energy and its magnitude depends on a reference

state, in this case, the temperature of the ambient, T_a . If T_a increases, then exergy decreases and energy increases.

$$\Delta Q = \underbrace{\left(1 - \frac{T_a}{T_1}\right) \Delta Q}_{\text{Exergy}} + \underbrace{\left(\frac{T_a}{T_1}\right) \Delta Q}_{\text{Anergy}} \quad (1)$$

Figure 29 illustrates the deterioration of the heat exchanged between the processes of the representative storage system which progresses from left to right. A certain amount of Heat ΔQ can be defined as the product of temperature T_1 , indicating kind of quality since it is an intensive variable, and entropy ΔS , indicating kind of amount, since it is an extensive variable. So in figure 29 the heat is represented by blocks $\Delta Q = T * \Delta S$. In the charging process heat from the heat source is converted to heat to storage. In the discharging process heat to storage is converted to heat to user. In the end all heat is released by the user as heat to ambient.

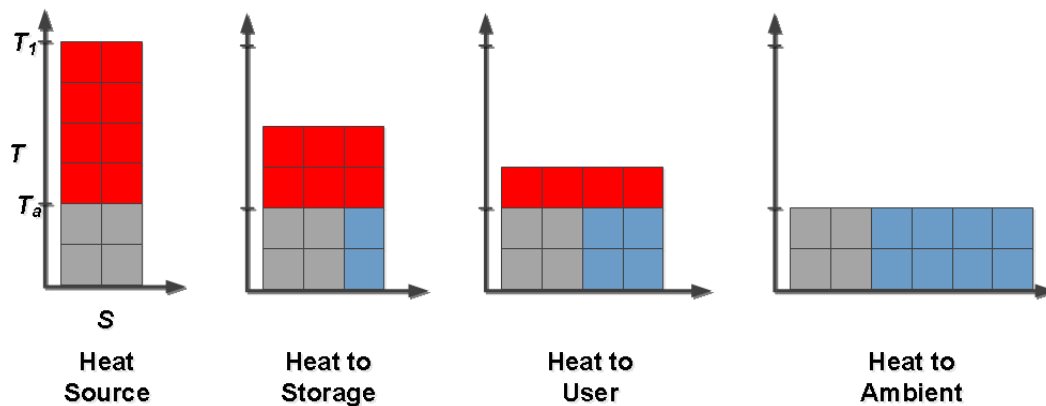


Figure 29: insert: heat from source, charging, discharging, heating
 As heat is transferred between processes, exergy (red blocks) is transformed to anergy (grey and blue blocks), while energy (total number of blocks) is conserved.

During each energy transfer between states, temperature is lowered and exergy (red) is dissipated as anergy (blue), but the total energy (the number of blocks) is conserved.

While exergy is always lowered in technical processes this is not necessarily true for temperature, pressure or any other state variable. This can be used to reduce the amount of energy which actually has to be stored to serve a certain user, as illustrated in figure 30. In the charging process heat from the heat source is converted to heat to storage in a way, that part of the heat is released to the ambient as anergy (4 blocks) and is not stored, while the rest is lifted to a higher temperature. So the same amount of exergy (6 blocks) can be stored in a smaller amount of energy (8 blocks) compared to the process shown in figure 29 (12 blocks). But now in the discharging process the anergy not stored (4 blocks) has to be regained from the ambient, using kind of a heat pump effect, to deliver the same heat to user (amount and composition) as shown in Figure 29. This effect shall be discussed more detailed in the next section.

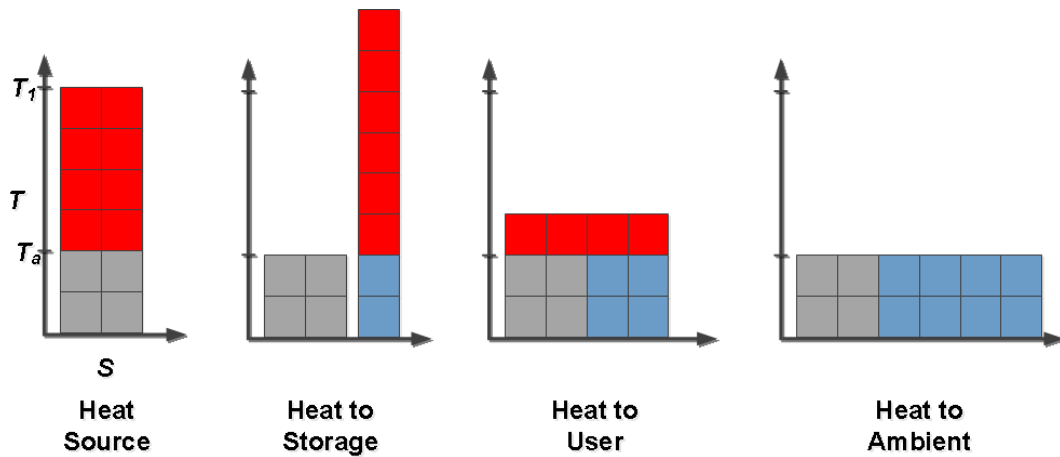


Figure 30: Using kind of a heat pump, the stored energy can have a higher temperature than the heat source in order to achieve a higher energy storage density.

More generally, the possible energy transfer between states is limited by their Gibbs-free-energy, which depends on the composition, temperature, and pressure.

Ambient-isolated and ambient-coupled heat storage

A storage is always connected to an application and to the ambient environment by heat or mass transfer. The most obvious coupling between a storage and the environment is heat loss during the storage period. Assuming an idealized, ambient-isolated thermal storage, e.g. hot water tank (sensible storage) like in figure 31, this coupling is neglected. An amount of thermal energy of 36000 kJ is delivered at 20 °C to the user, while the storage is heated up from 20 °C to 100 °C at an ambient temperature of 0 °C. The energy is supplied by the heat source and all - the exergy and anergy - must be stored in the hot water tank.

The idea of ambient-coupled storages is to lift heat to a higher exergy level during the charging process while releasing anergy to the ambient, thus concentrating energy and achieving higher storage capacities. The anergy, however, has to be recovered from the environment during the discharging cycle, otherwise energy losses occur and the storage efficiency is low.

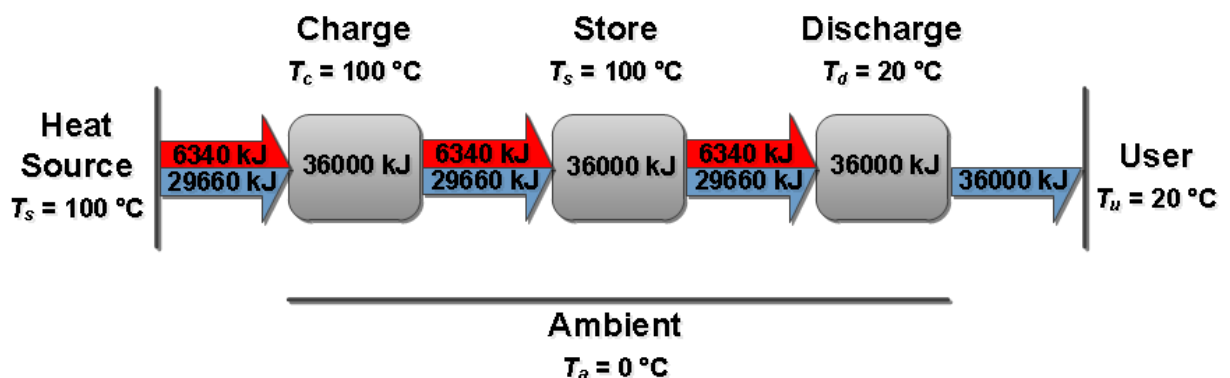


Figure 31: Input energy of 36000 kJ is required to provide space heating for 1 h at 0°C ambient temperature using an isolated sensible storage.

Such an ambient-coupled storage delivers also 36000 kJ to the user (see figure 32). The heat supplied from the heat source is 21205 kJ. In an ideal thermodynamic cycle the exergy (2456 kJ) is stripped off and transferred to the storage, while the energy (18749 kJ) is released to the ambient. Only the exergy (2463 kJ) is stored. During discharge, a heat pumping process uses the stored exergy to draw energy back from the environment and produce the same quantity and quality of discharged energy (36000 kJ at $T_d = 20\text{ C}$) as the ambient-isolated storage. There are two advantages to this ambient coupling. First, a much smaller quantity of energy (idealised just the exergy) is stored in the storage tank, in this case, increasing the effective storage density by almost 15 times. Secondly, less energy is required during the charging process because the quality of that energy is greater than required (e.g. $T_s > T_d$). However the “effective” delivered heat is the same compared to the ambient-isolated thermal storage. For this reason a higher storage capacity can be observed for ambient-coupled systems. Unlike ambient-isolated storages, ambient coupled storages depend on the ambient conditions.

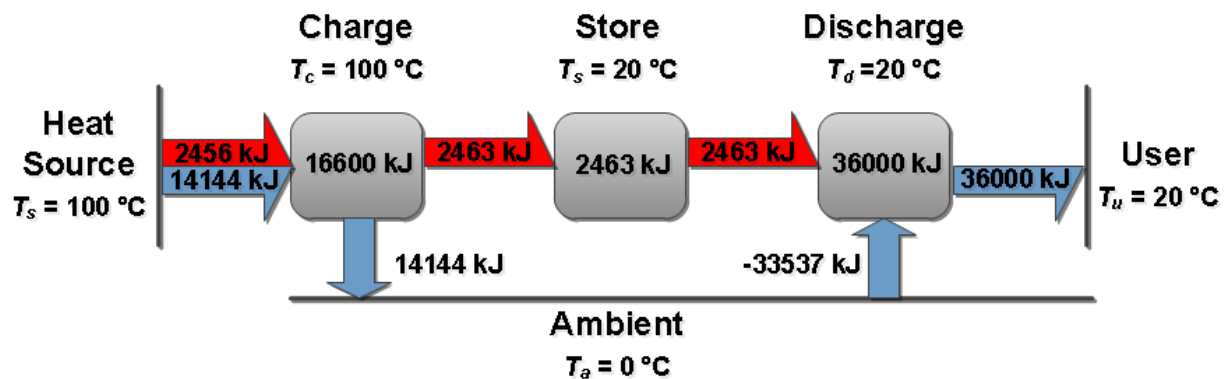


Figure 32: Using ideal thermodynamic cycles for charging and discharging, the energy which has to be supplied by the heat source and the energy to be stored can be reduced to satisfy the same user as in figure 23.

8.2 Types of Thermal Energy Storage

Thermal energy can be stored directly or indirectly. Thermal energy is directly stored as the kinetic energy of the constituent molecules and atoms of any material. A single atom or molecule holds kinetic energy through movements such as vibration, rotation, and translation. More types of movements are available at higher temperatures and thermal energy storage capacity per molecule tends to increase with increasing temperature. This type of storage corresponds to sensible TES.

In addition to the kinetic energy of the single particles, thermal energy can be stored indirectly using the intermolecular forces. These indirect methods include phase change (PCM) and thermochemical energy storage (TCS). Indirect thermal energy storage relies on the creation and destruction of molecular bonds. The types of bonds have a strong impact on the thermal energy storage potential. Bonds and typical bond strength (represented by Δh) are classified in table 7 in decreasing order of strength.

Table 7: Types of bonds and their strength

Bond	Typical Bond Strength (Δh , kJ/mol)	Examples
Ionic	700 - 15000	Na ⁺ Cl ⁻
Covalent	150 - 1000	O ₂
Hydrogen	<10 - 170	HF-HF
Metal	2 - 55	Fe
Van der Waals	- 5	-

When the bond is modified yet the material is unchanged it is termed a physical reaction. In thermal storage, this physical change is usually the phase change between solid and liquid. For example, consider the solid to liquid phase change of sodium chloride (NaCl). Ionic bonds are broken; however; in the liquid phase, the ions still interact through their electrostatic potentials and the material remains a composition of sodium and chloride ions. Chemical reactions differ from phase change in that bonds are broken to create different materials. One example is the reaction between solid calcium chloride (CaCl₂) and water. When CaCl₂ is dissolved into water, the ionic bond between calcium and chloride is destroyed and the ions form complex hydrate structures with water molecules via hydrogen bonding. The distinction between physical and chemical bonding is used to delineate between the physical limits of the two types of thermal storage addressed in this annex: 1) phase change storage and 2) thermochemical storage.

8.3 Thermodynamic Limits of Phase Change Storage

In PCM, energy storage is represented by the enthalpy of the phase change, $\Delta_{tr}h$. During phase transition, the two phases are in equilibrium and the entropy of the phase change, $\Delta_{tr}s$, is related to $\Delta_{tr}h$ and the phase transition temperature, T_{tr} , as shown in eq. (1).

$$\Delta_{tr}s = \Delta_{tr}h/T_{tr} \quad (2)$$

Empirical rules of thumb can be used to estimate melting (Richardson's rule: $\Delta_{m}s \approx 1 - 3 R$) and vaporization enthalpies (Trouton's rule: $\Delta_{v}s \approx 10.5R$) (see figure 34). However some materials show a significant deviation from these rules, thus, the rules cannot be considered a theoretic limit.

The upper limit of the phase change entropy Δs is thus expected for a material which is perfectly crystalline and of high density in the solid phase and large, asymmetric liquid phase particles with a dipole moment that do not cluster in the liquid phase.

Unfortunately, these requirements are somewhat contradictory, introducing a trade off in material selection. A material with large, asymmetric particles will typically not form perfect crystalline solids of high density. Particles with dipole moments will

typically form clusters in the liquid phase. However the concept is useful because it shows general trends and can help to understand trends within a group of materials.

The thermal energy storage density using PCMs depends on the bonds and the structure in the material for each phase. It also depends on the density of the material. With a few significant exceptions, there are empirical rules for $\Delta_{tr}s$. However the magnitude of $\Delta_{tr}s$ is apparently limited. Nonetheless, the general trends demonstrated here can serve as a guide when investigating new materials for energy storage and give a initial idea of storage density possible at the application temperature.

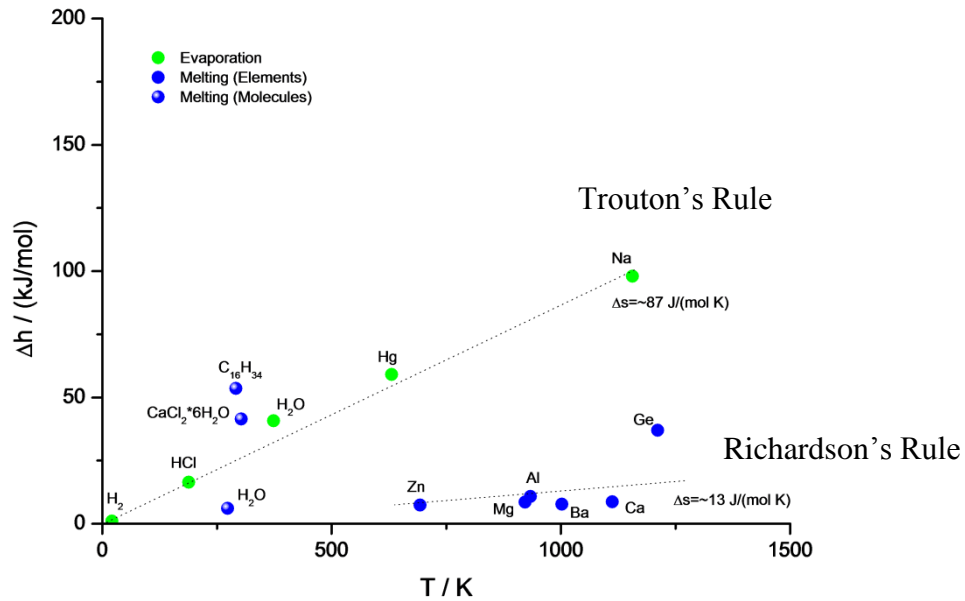


Figure 33

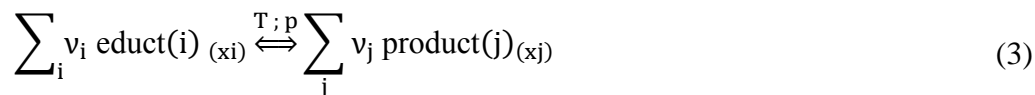
Figure 34: TES material data for melting, evaporation and chemical reactions at standard pressure 101.3 kPa. The lines denote the rules of Richardson (melting) and Trouton (evaporation).

8.4 Thermodynamic Limits of Thermochemical reactions

Thermochemical energy storage (TCS) uses bond energy of the reactants to store heat. The energy is accessible as the chemical reaction enthalpies. Unlike PCM, the destruction and creation of bonds results in different materials. Reaction enthalpies are larger than phase change enthalpies, offering an advantage for compact thermal energy storage.

Charging and discharging can occur under different operating conditions because the load does not necessarily require the same quality as the source. The energy is stored in the chemical potential for the products to react with one another. For every reaction, there is an equilibrium temperature and pressure where the formation of reactants and products is balanced.

The general formula for a reaction is





where $x_{\{i,j\}}$ indicate the phase (solid, liquid or gas) and $v_{\{i,j\}}$ are the stoichiometric coefficients of the reactants.

In TCS one must consider the temperature, pressure and concentration of reactants and products in the system. However, these requirements increase the complexity of TCS compared to sensible and PCM storage.

For charging and discharging the storage, it is necessary to favor the forward or the reverse reaction, respectively. For closed, constant pressure (isobaric) systems, the conversion ratio depends on the temperatures during the forward and reverse reactions. For non-isobaric reactions (open storage systems) the reaction depends on temperature and pressure, whereas both of them might change between charging and discharging. In general, the conversion ratio is higher for higher temperature difference between the endothermic (storage charging) and the exothermic reaction (discharging). These temperatures are specific to each reaction.

First approach to define a “rule” for thermochemical reactions

The starting equation for this is at first the definition of the Gibbs energy $\Delta G = \Delta H - T\Delta S$. With $\Delta G = 0$ in equilibrium the equation can be rewritten to.

$$\Delta H = T\Delta S$$

ΔS should be a function depending on the converted mole fractions of gas in the reaction, because the entropy increases when a condensed substance is converted to gas.

The calculation of the equilibrium entropies for different reactions from tabulated values are plotted in figure 35 over the number of converted mole fractions of gas. The function of the linear regression line at standard conditions is:

$$\Delta S / (\text{kJ/mol}) = 0.876 * n + 0.631$$

Wherein n is the number in the reaction of the converted mole fractions of gaseous components. The calculated curve is still to be validated in further runs with real measurements. The comparison of different reactions showed:

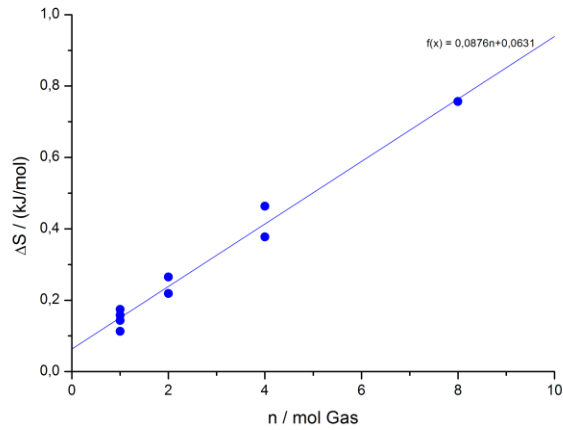


Figure 35: Reaction entropy as a function of the reacted mole fractions of gaseous components

Alternatively, the data also can be represented as in figure 36 and we receive several straight lines with different gradient depending on the converted amount of gaseous components.

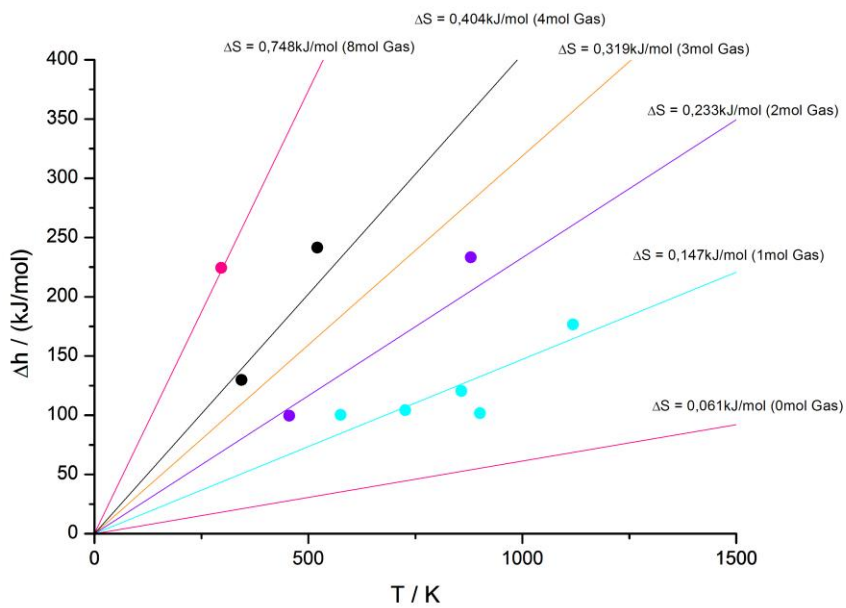
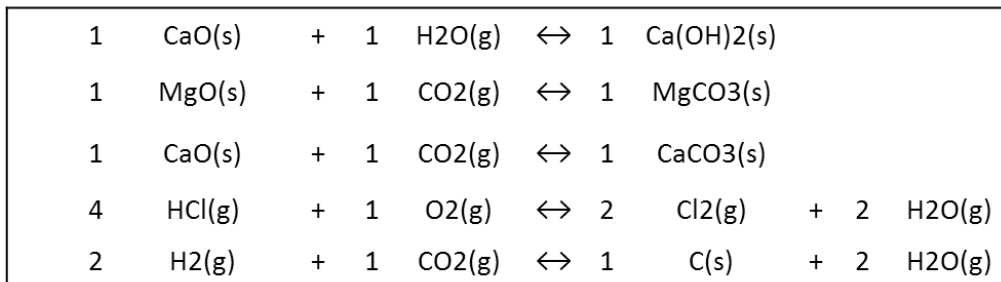


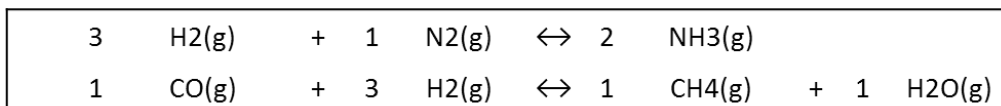
Figure 36: Enthalpy of reaction over equilibrium temperature

Table 8 lists the reactions used for the evaluation.

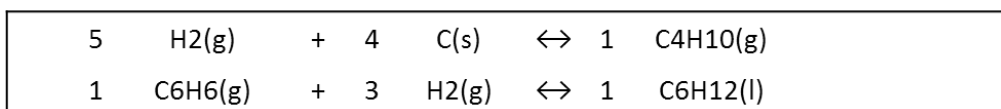
1 mol gas:



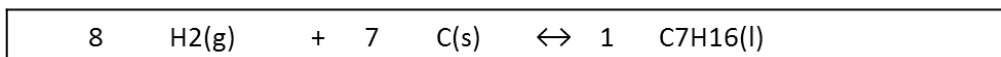
2 mole gas:



4 mole gas:



8 mole gas:



8.5 Technical limits and constraints

While physical limits determine the maximum theoretical density and the required operating conditions, technical limits generally refer to the efficiency with which these theoretical storage properties can be realized in practical systems. Technical limits are usually due to heat and mass transport limitations, slow chemical kinetics, and second law inefficiencies. Technical limits impede the power of energy storage and potentially the ability to use the full theoretical storage density.

Power is the rate at which energy is charged or discharged from the storage. Thermal storages must be capable of maintaining the required power for a given application during both charging and discharging, which may occur on different timescales and magnitudes. In addition, storages must be able to maintain power throughout the entire charging or discharging process. There also exists the common tradeoff between high power and high storage density. Often density must be sacrificed in order to increase power or vice versa.

For thermal storage, power can be ultimately reduced to rate of heat transfer. Heat transfer depends on the driving potential (e.g. temperature difference, chemical reaction, or mass transfer) transport properties, and sufficient contact area. Driving potentials are usually specified by the application or restricted by the ambient environment. For example, the driving difference for heat transfer during discharging is the temperature difference between the storage and load. The analogous driving potential for mass transfer is a difference in concentration and the driving potential to drive chemical reactions is the excess Gibbs free energy.

Transport properties of the storage materials also affect power. These depend on the physical properties of the storage materials, the arrangement of the materials in the

storage, and materials used for heat and mass exchangers and chemical reactors. For example, thermal conductivity is a physical property that characterises the diffusion rate of thermal energy through a material. Materials with low thermal conductivity will transfer heat at lower power than materials with high thermal conductivity. The analogous transport property for mass transfer is the mass diffusivity. For chemical reactions the reaction rate constant determines the speed of the reaction at each system state. These properties depend on the state of the system; thus allowing the same power to be technically limited by different mechanisms at different states of charging and discharge.

A unique difference between technical limits and physical limits is that technical limits can generally be overcome. For example, consider an application for a sensible energy storage that demands very high power. The driving temperature difference and the properties of the storage and heat exchanger materials are fixed. However, power can be increased by increasing the surface area of the heat exchanger. In this way, the technical limit is overcome. However technical solutions may require unacceptable consequences (e.g. no physical space for additional area or uneconomic solutions).

Several approaches in this topic could not lead to a common description of the technical limitations for TES within this Annex.

8.6 Economic Limits and Constraints

Besides the physical and technical limitations, economic limits exist for thermal energy storage, if they want to enter the market place. In fact these economic limits exist for all kinds of energy storages. The typical method used to discuss energy storage economics is a bottom up approach where material and manufacturing costs, operating costs, R&D costs, and site-preparation costs are lumped together for an overall estimate. This approach yields a large range of cost estimates, reflecting the uncertainty and variation in each of these components, especially for emerging technologies.

An alternative, top-down approach considers the acceptable cost of energy storage by comparing it to the marginal cost of energy production. The analysis assumes that the cost of energy storage should not exceed the cost of additional energy generation. Thus, it is a direct comparison between the cost of stored energy and that energy which is newly generated. The main advantage of this approach is that it does not require detailed information about the storage technology or implementation.

The maximum acceptable cost is calculated from the discount rate of storage capital, the payback period of the investment, the frequency at which the energy storage is charged and discharged, and the cost of energy. Using the discount rate for storage capital and the storage lifetime, the present value annuity factor (PVANF) to determine the present value of the energy storage capital can be calculated.

The analysis neglects operating costs and changes in the cost of energy production over the time period. Nevertheless, it illustrates the most important feature in energy storage economics, the relationship between acceptable storage costs, the frequency of storage cycling, and the cost of energy.

For example, in industry it is typical to seek capital improvements with rates of return greater than 25% and short pay back periods, <4 yr. This requires annuity factors on

the order of $PVANF = 0.25 - 0.3$. In the building sector, longer paybacks are acceptable, interest rates are more modest, and annuity factors are lower, $PVANF = 0.07 - 0.08$. One might also suggest a class of user that can tolerate extremely long payback periods (20+ years) because the energy investment is pursued for political or ecological reasons. In these cases annuity factors may be as low as $PVANF < 0.06$.

In figure 37, the storage costs (\$/kWh) are shown as a function of the length of the storage cycle (days) on a log-log plot for a few different combinations of discount rates and energy costs. The maximum acceptable storage costs decrease with increasing storage period. Energy storage with a storage cycle of 100 days must be 100 times less expensive than energy storage with a cycle of one day, which imposes a major restriction on the type of technologies that should be investigated for diurnal storage vs. annual storage.

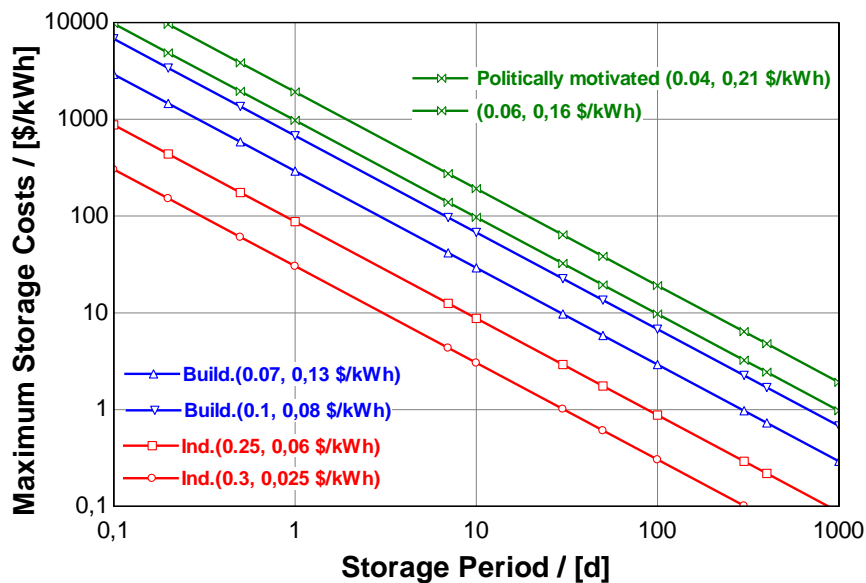


Figure 37: Maximum acceptable storage costs for three types of users for different annuity factors (PVANF) and energy costs

The large variations in maximum acceptable storage costs based on these simple factors suggest that the specific storage application (user and frequency) imposes an upper limit on storage costs for a capital investment.

Although published bottom-up-approach cost estimates vary widely, it is useful to compare these costs to the maximum acceptable storage costs. Cost ranges for thermal energy storage technologies are given in table 9.

Table 9: Estimated thermal energy storage costs.

Technology	\$/kWh	¢/kWh-delivered
Sensible storage - Water	0.1- 13	0.01
Phase change materials (PCM)	13 - 65	1.3 - 6
Thermochemical storage (TCS)	10 - 130	1 - 5

Three main findings can be formulated:



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1. All thermal storage technologies are economical, given a short enough storage period (daily storage, in figure 26). In these cases it makes sense to compare storage technologies based on technical and physical performance attributes.
 2. Seasonal storage (>100 days in figure 26) is only economical using sensible storage; other technologies require approximately an order of magnitude or more reduction in costs from their lowest estimates.
 3. For a fixed storage period, the maximum acceptable storage costs depend on the user due to variances in payback period, discount rate, and the cost of energy. As the cost to produce new energy increases, as has historically been the case, higher energy storage costs become acceptable for all users.



9 Acknowledgements

Input to this report comes from the following authors:

Ana I. Fernandez Renna, Cemil Alkan, Halime Paksoy, Maria Dolores Romero, Alenka Ristic, Stefan K. Henninger, Ana Lazaro, Eva Günther, Magali Fois, Justin Chui, Paul Gantenbein, Frédéric Kuznik, Joseph Virgone, Kevyn Johannes, H. Shmueli, G. Ziskind, Pablo Dolado, J.M. Marin, B. Zalba, Valerio Lo Brano, Giuseppina Ciulla, Silvia Nedeia, Henner Kerskes, Barbara Mette, Sebastian Asenbeck, Beyza Beyhan, Josh Quinnell, Jay Burch, H.A. Zondag, Robert de Boer, Christian Finck, Ruud Cuypers, Andreas Heinz, Dagmar Jaehnig, Simon Furbo, Florian Bertsch, Albert Castell, Eduard Oró, Antoni Gil, Camila Barreneche, Helena Navarro, Eduard Oró, Laia Miró, Roland Müller, Jörg Waschull, Siegfried Römer, Pablo Blanco-Rodríguez, Javier Rodríguez-Aseguinolaza, Nicolas Calvet, Manuel J. Tello, Stefania Doppiu, Antoine Meffre, Judith C. Gomez, Abdessamad Faik, Régis Olivès, Xavier Py, Greg C. Glatzmaier, Romuald Faure, Nicolas Tessier-Doyens, Marc Huger, A. Kere, G. Dejean, N. Sadiki, Andreas Bayer and others

The contributions were provided partly on a voluntary basis and are highly appreciated by the editor. In addition thanks go to all working group members who contributed to the fruitful discussions during the expert meetings. Without their active participation the results of this Annex would not have been possible!