



Compact Thermal Energy Storage: Material Development for System Integration

Joint task of IEA SHC Task 42 and IEA ECES Annex 29

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Collection of the Position Paper and all final deliverable papers of the joint task IEA SHC Task 42 and IEA ECES Annex 29.

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Task 42 (ECES Annex 29)

Compact Thermal Energy Storage: Material Development for System Integration

Compact Thermal Energy Storage IEA SHC Position Paper

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Compact Thermal Energy Storage – Position Paper

Aim of the Position Paper

This position paper explains the potential, the present status of development and the market status of compact thermal energy storages. Its aim is to inform policy makers, decision makers and opinion makers about the technologies and to discuss the technological and non-technological barriers and the actions needed to accelerate the development and market uptake of these very important technologies.

Executive Summary

About half of the world's final energy demand is used for heating and cooling purposes. Therefore, technologies that can efficiently and effectively store heat are of key importance. They assist to increase the share of sustainable heat sources and improve the efficiency of thermal systems. Recent research results and technical developments show that storage technologies will become even more important with increased use of Smart Grid developments.

Thermal energy storage technologies are needed to match the variable supply of sustainable heat and to optimize the performance of thermal systems. Innovative compact thermal energy storage technologies are based on the physical principles and properties of phase change materials (PCM) and on thermochemical materials (TCM). With these materials, heat can be stored in a more dense form and with fewer losses than conventional heat storage such as hot water storage tanks.

Some important application areas of compact thermal energy storage technologies are:

- seasonal storage of solar energy,
- "waste heat" recovery in industrial processes,
- improved efficiency in the operation of Smart Grids, district heating- and low-temperature distribution networks using (micro)cogeneration plants, solar thermal collector systems and heat pumps, and
- assist in the heat management of energy systems for hybrid and electric vehicles and transport systems.

The technology of compact heat storage systems is still under development. PCM products are already on the market for a number of niche applications. PCM is applied for temperature control in buildings and for transportation of vulnerable goods, such as medical items, food, etc. Although a number of TCMs exist (zeolites, salt hydrates and composite materials), their application in storage systems still needs more R&D work, especially with regard to process engineering.

The potential for thermal storage systems based on PCM and TCM technologies is huge. For example it is estimated that about 800 GWh_{th} (or 18 million cubic meters of water) is the capacity of installed solar water storages for households in the year 2012.

The potential of new compact thermal storage systems for non-solar applications is considerably higher because stored energy can replace heat and cold produced using fossil fuels. Storage technology therefore also reduces CO₂ emissions. Stored thermal energy can reduce the need for expensive peak power installations, which operate occasionally and therefore high energy costs result.

The potential of thermal energy storage technologies becomes even higher when current "Smart Grid" developments and the integration of fluctuating renewable energies into the electricity (and thermal) grids are taken into account.

The technical barriers to exploit the potential are related to the fact that the technology needs further progress on three levels 1) material level, 2) component level, 3) system level. The systems must operate in highly fluctuating environmental and meteorological conditions. Compact thermal energy storage systems in their present development stage still require complex control, which causes high investment costs in the development of prototype systems.

Further research and development is needed to overcome economic barriers. The cost of a stored kWh of thermal energy in most applications is still too high to compete with burning oil and gas, especially as negative environmental effects of the current technology – for example CO₂ emissions – are not adequately considered in common economic evaluations.

Consequently, strong support of R&D work by governmental and international research programs is needed. IEA SHC Task 42 carried out in conjunction with Annex 29 of the IEA ECES Programme is a good example of the type of activities needed to accelerate technical and economic progress.

Introduction and Relevance

About half of the worldwide final energy demand is for heating and cooling purposes. Therefore, technologies that can efficiently and effectively store heat are of key importance. They assist to increase the share of sustainable heat sources and improve the efficiency of thermal systems. Recent research results and technical developments show that storage technologies will become even more important with increased use of Smart Grid developments.

Thermal energy storage technologies are needed to match the variable supply of sustainable heat and to optimize the performance of thermal systems. Current thermal energy storage technologies, mainly based on water tanks, perform well for short-term storage. Due to heat losses, long term thermal storage with water is not efficient for small and medium sized systems. For very large water storage systems, mostly connected to district heating networks, the long-term storage efficiency is good.

Long term storage and seasonal storage of heat is especially important for the further development and application of solar energy techniques in the future energy supply systems. Conventional storage systems based on hot water tanks can also

be improved in certain details, but in order to enable a real breakthrough in thermal energy storage new materials and system technologies are needed.

Innovative compact thermal energy storage technologies are based on the physical principles and properties of phase change materials (PCM) and on thermochemical materials (TCM). With these materials, heat can be stored in a more dense form and with fewer losses than with hot water storage tanks.

PCM – Phase Change Materials

In PCM materials, the heat is stored when the material changes its state from solid to liquid or from liquid to vapor. Two main characteristics for this storage principle are the high amount of heat that can be stored and the fact that the storage takes place within a small temperature range, either the melting temperature or the evaporation temperature. The latter characteristic is also a limitation for the application of this storage method; only when heat should be stored in a limited temperature range the method has advantages over “normal” sensible heat storage. Examples of these applications, which are already on the market, are the control of room temperature by adding PCM materials into the walls of rooms. Another example is the storage of heat for operating a heat pump system by using an ice water storage tank as the low temperature heat source. During the ice formation, the heat pump is provided with a very large amount of heat at a constant (0 °C) temperature, leading to a higher performance of the heat pump.

TCM – Thermochemical Materials

With this heat storage method, the heat is stored through the separation of two different substances, in practical applications either two liquids or a solid and a vapor. The binding of the two substances can be caused by a number of physical principles or binding forces. The stronger the force, the higher the temperature needed to separate the two working materials and thus to store the heat. The range is from physical sorption caused by surface forces with storage temperatures starting at 30 °C, through chemical sorption caused by covalent attraction with temperatures above 100 °C, to chemical reactions caused by ionic forces with temperatures above 200 °C. In general, the storage density also increases with increasing temperature. There exist a large number of potential thermochemical materials, each with different properties regarding, for instance, mechanical stability, vulnerability for impurities, side reactions, vulnerability to unwanted morphological change, etc.

Application Areas

Compact thermal energy storage technologies still need further development and have a number of important application areas. Some very important ones are:

- Seasonal thermal storage of solar energy, with which the abundant energy supply in summer can be used in winter, for example for room heating purposes and heating of domestic hot water.
- Storage and transport of industrial "waste heat" from one industrial process to a place of another industrial process or to a residential area where this rejected heat can be utilized.
- Compact thermal energy storage technologies for Smart Grids to provide novel switchable supply or demand of energy in future intelligent electricity

and heating networks (Smart Grids) by coupling compact thermal storages to (micro)cogeneration or heat pumps or other sources (and sinks) of energy grids.

- Application of innovative compact thermal energy storages in hybrid or electric vehicles or other electric transportation modes to assist in the management of heat.

Compactness

The higher the amount of heat stored per cubic meter of volume, the more compact the storage technology. There is no absolute way for calculating the compactness or storage density of a certain storage technology, as this is dependent on the operational conditions of the heat storage application. The conditions that are most important are the temperatures for charging and discharging the storage and the additional space needed for the thermal insulation and the auxiliary components, such as heat exchangers, pumps, valves, vessels, and pipes. The only valid comparison of the storage densities of different technologies is for a well-defined application. On international level, first descriptions of the calculation of a key performance index on storage density are being discussed now.

Status of the Technology

PCM products are already on the market for a number of (niche) applications: for control of temperature for transportation of vulnerable goods, such as medical items, food, et cetera.

PCMs are also used in a number of building products to enable a better temperature control in buildings, especially for prevention of overheating in summer.

The demonstration of the application of PCM for transportation of heat is ongoing, while R&D is performed into novel Phase Change Materials for medium and high temperature applications, such as for industry and for Concentrating Solar Power (CSP) thermal power plants.

TCM is still in the R&D phase. A number of already existing materials (zeolites, salt hydrates and composite materials) are being applied in new system concepts for seasonal thermal storage of solar energy. First systems will be tested in the laboratory in 2015 and 2016. Field tests with these systems are expected in the years to follow. Only a few targeted programs or projects exist that work on developing improved or new TCM and the necessary engineering technology for the design storage devices. A long term target is to arrive at storage technologies that have a considerably higher storage capacity in relevant applications compared to hot water storage tanks. It is an additional and very challenging task for process-engineers to develop storage devices that operate efficiently and reliably and can be integrated easily into existing energy-management systems.

Potential

The potential for thermal storage systems based on PCM and TCM technologies is

huge. But it is very difficult to quantify or even estimate it because the possible areas of application are so broad and diversified.

With respect to solar energy alone, it is estimated that the capacity of installed solar water storages for household applications alone is about 800 GWh_{th}. (in the year 2012). This is a total water storage volume of approximately 18 million cubic meters.

The potential of new compact thermal storage systems for non-solar applications is considerably higher because stored energy can replace heat and cold produced using fossil fuels. Storage technology therefore also reduces CO₂ emissions. Stored thermal energy can reduce the need for expensive peak power installations, which operate occasionally and therefore high energy costs result.

Thermal energy storage reduces CO₂ emissions by replacing the burning of oil and gas. For an example, it has been estimated that about 1.4 million GWh per year could be saved in Europe by more extensive use of thermal energy storage. This summarizes the potential in buildings for heating and domestic hot water but also in the commercial and industrial sector for more energy efficient processes by storing heat and cold.

The potential of thermal energy storage technologies becomes even higher when current developments regarding the integration of fluctuating renewable energies into the electricity grids are taken into account. This concerns especially the integration of wind power and electricity from photovoltaics into the electricity distribution system together with an increasing number of heat pump and cogeneration systems. Research on the possibilities of thermal energy storage under these new framing conditions in the electricity sector have only recently been started and are considered to be of increasing importance for the future development of efficient energy systems. "Smart Grids" need storage technologies and they become more and more important.

Current Barriers

The development of Compact Thermal Energy Storage systems based on phase-change and thermo-chemical materials is still very much in its R&D phase. It therefore still faces strong technical, financial and non-financial challenges.

The technical barriers are related to the fact that the technology needs further progress on three levels: 1) materials, 2) components, and 3) systems. The physical phenomena, which may be phase change processes, sorption processes or thermo-chemical reactions, take place on the molecular level. Basic and applied research is still necessary to fully understand the physics and chemistry involved in order to improve and synthesize storage materials. Modeling materials and the simulation of reactions and processes on the molecular scale will also contribute to this.

While the reactions take place on the molecular scale, the energy to be stored or

released is transported on a macroscopic scale. That means that process engineers need to be able to calculate and deal with the flow of liquids, gases or vapor.

Moreover, very often components have to be designed to operate in vacuum conditions. In thermochemical reactions it is necessary to deal with heat and mass transfer, which leads to components that have to be controlled with respect to several different operational parameters in order to achieve a high energy storage performance.

This results in complex system operational conditions. They often include highly fluctuating environmental and meteorological conditions. Therefore, the systems under development still require highly complex control, which leads to high investment costs in developing prototype systems.

Consequently, if we are to realize the huge potential of compact thermal energy storage systems based on PCMs and TCMS more R&D work is needed to address these technical barriers.

Further research and development is needed to overcome economic barriers. The cost of a stored kWh of thermal energy in most applications is still too high to compete with burning oil and gas, especially for long-term storage in which only a small number of storage cycles occur during the life time of the storage. The more often a storage is loaded and unloaded (high cycle numbers) the lower becomes the cost of the stored energy. Long term storage competes against burning oil and gas, which is stored chemical energy. Negative environmental effects of burning oil and gas – for example CO₂ emissions – are not adequately considered in common economic evaluations.

The cost uncertainty of thermal energy storage technologies is a major barrier for their further development. A group of experts in the IEA-SHC Task 42 is therefore carrying out a study to evaluate storage costs in a "top-down" and in a "bottom-up approach": The top-down approach assumes that the cost of energy storage should not exceed the cost of substituted energy generation. The maximum acceptable cost is calculated from the discount rate of storage capital, the payback period of the investment, the number of storage cycles, and the cost of substituted energy. To simplify the evaluation, this analysis neglects operating costs and changes in the cost of energy production over time. On the other hand, the bottom-up approach focuses on the actual costs of real storage systems. To investigate particular storages, a questionnaire was developed which inquires among other technical parameters the costs of the storage divided into investment costs (storage material, storage tank or reactor, charging/discharging unit), operating costs, and additional costs, e.g. maintenance or installation costs. The bottom-up approach has been applied to analyze the costs of 20 thermal energy storages so far. For the most part, these innovative storages are subject of ongoing R&D work. The study is on-going. One result from the top-down approach is that the maximum acceptable storage capacity costs are in the range of 2 to 4 Euro/kWh_{cap} for the case of seasonal storage, 25 years life time and low interest rates (1%). Estimated "bottom-up" costs of compact thermal energy storage technologies under development are in the range of 2 to 15 Euro/kWh_{cap}.

Similar to the economic situation of all renewable energy technologies, initial

investment costs to implement storage technologies in energy systems are often still a very strong barrier. Adequate long-term financing innovations for initial investment costs in renewable energy system applications developed by the banks and the financial sector may assist to overcome these barriers.

Given the situation as described, it follows that an important barrier is the need for broad and well-coordinated, multinational R&D work within long-term international research programs. IEA SHC Task 42 carried out in conjunction with Annex 29 of the IEA ECES Programme is a good example and starting point for the activities needed. It is also important to establish more national and international research projects in order to achieve the necessary results in the different crosscutting scientific and engineering fields of expertise addressed by compact thermal energy storage systems based on phase-change material and thermo-chemical material technologies.

Actions Needed

What kind of actions would it take to really drive market deployment?

1. Strong support of R&D work by governmental and international research programs as described above. Compact thermal energy storage systems based on phase-change and thermo-chemical material technologies are to a large extent still in their development stage. The challenges cannot be addressed by single research groups and singularly achieved research results, but need a broad and internationally collaborative approach.
2. The companies involved in the development of compact thermal storage systems are often relatively small and highly innovative. They need strong support by governments to be able to apply their technology in the building and industrial processes sectors, in spite of the economic disadvantage they still may have.
3. Strong support of a growing number of demonstration projects is needed in order to gather operational experiences, to monitor and evaluate performance and to improve the performance of systems step-by-step. A much better basis for the further development and deployment of the huge potential of compact thermal energy storage systems will be established if these actions are taken.

Acknowledgement

The content of this paper builds upon the concepts developed in the context of the joint IEA (International Energy Agency) SHC (Solar Heating and Cooling Programme) Task 42/ECES (Energy Conservation through Energy Storage Programme) Annex 29: Compact Thermal Energy Storage: Material Development for System Integration (<http://task42.iea-shc.org/>).

IEA Solar Heating and Cooling Programme

The IEA Solar Heating and Cooling Programme members have been collaborating since 1977 to advance active solar and passive solar and their application in buildings and other areas, such as agriculture and industry. Under the management of an Executive Committee representing the members, the Programme carries out a strategy to enhance collective knowledge and application of solar heating and cooling through international collaboration.

More information can be found on the websites of the IEA Solar Heating and Cooling Programme, www.iea-shc.org and the IEA Energy Conservation through Energy Storage, www.iea-ec.es.org.

SHC 2015, International Conference on Solar Heating and Cooling for Buildings and Industry

IEA SHC Task 42 / ECES Annex 29

Compact Thermal Energy Storage

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Abstract

The IEA SHC Task 42 / ECES Annex 29 concerns thermal energy storage technologies based on Phase Change Materials (PCM) and Thermo-Chemical Materials (TCM) as well as liquid and solid sorption processes. Sensible heat storages such as hot water tanks were not investigated in the task but served as benchmarks with respect to technical and economical evaluations. This IEA task is a joint task of the IEA Solar Heating and Cooling (SHC) program and the IEA Energy Conservation through Energy Storage (ECES) program and will run up to end of December 2015. This paper gives an overview on the topics and main results of IEA SHC Task 42 / ECES Annex 29.

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Keywords: compact storage; storage engineering; storage materials; PCM; TCM; sorption technology; long term storage

1. Introduction

About half of the world's final energy demand is used for heating and cooling purposes. Therefore, technologies that can efficiently and effectively store heat are of key importance. They assist to increase the share of sustainable heat sources and improve the efficiency of thermal systems. Recent research results and technical developments show that thermal storage technologies will become even more important with increased use of Smart Grid developments.

Thermal energy storage technologies are needed to match the variable supply of sustainable heat and to optimize the performance of thermal systems. Innovative compact thermal energy storage technologies are based on the physical principles and properties of phase change materials (PCM) and on thermochemical materials (TCM). These materials

offer the technical opportunities to store heat in a more dense form and with fewer losses than conventional, sensible heat storage technologies such as hot water storage tanks.

Some important application areas of compact thermal energy storage technologies are:

- seasonal storage of solar energy,
- "waste heat" recovery in industrial processes,
- temperature control in buildings,
- improved efficiency in the operation of Smart Grids, district heating- and low-temperature distribution networks using (micro)cogeneration plants, solar thermal collector systems and heat pumps, and
- thermal storage technologies that assist in the heat management of energy systems for hybrid and electric vehicles and transport systems.

The technology of compact heat storage systems is still under development. PCM products are already on the market for a number of niche applications. PCM is applied for temperature control in buildings and for transportation of vulnerable goods, such as medical items, food, etc. Although a number of TCMs exist (zeolites, salt hydrates and composite materials), their application in storage systems still needs more R&D work, especially with regard to process engineering.

2. Task Description, Task Objectives and Scope of the Task

The objective of this joint Task was to develop advanced materials for compact storage systems, suitable not only for solar thermal systems, but also for other renewable heating and cooling applications such as solar cooling, micro-cogeneration, biomass, or heat pumps. The Task covered phase change materials (PCMs), thermochemical materials (TCMs), and composite materials and nanostructures. It included activities on material development, analysis, and engineering, numerical modeling of materials and systems, development of storage components and systems, and development of standards and test methods.

The overall goal of this task was to develop advanced materials and systems for an improved performance storing thermal energy. This goal can be subdivided into eight specific objectives:

- to identify material requirements for relevant applications, by means of numerical simulation of currently known storage technologies, using the simulation modules developed e.g. in Phase I.
- to identify, design and develop new materials and composites for compact thermal energy storage,
- to develop measuring and testing procedures to characterize 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, and to compare them to conventional 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.
- to develop an approach for the economic evaluation of compact thermal energy storage systems.

This task dealt with advanced materials for latent and chemical thermal energy storage, and excluded materials related to sensible heat storage. However, the latter category was used as reference. The task dealt with these advanced 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 subsystem, 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.

Between 35 and 50 experts participated in the experts meetings that were carried out half-yearly. They came from the following countries: Austria, Australia, Belgium, Switzerland, Germany, Denmark, Spain, France, Italy, Japan, The Netherlands, Sweden, Slovenia, Turkey, United Kingdom.

3. Structure of Task

The Task was organised in a matrix-like structure, see Figure 1. The horizontal axis represented materials-related categories. It was divided into 3 groups of similar activities in the working groups A1, A2 and A3. The vertical axis represented application and system related categories: Working group B on system development and working group C on economical evaluation of compact thermal energy storage systems.

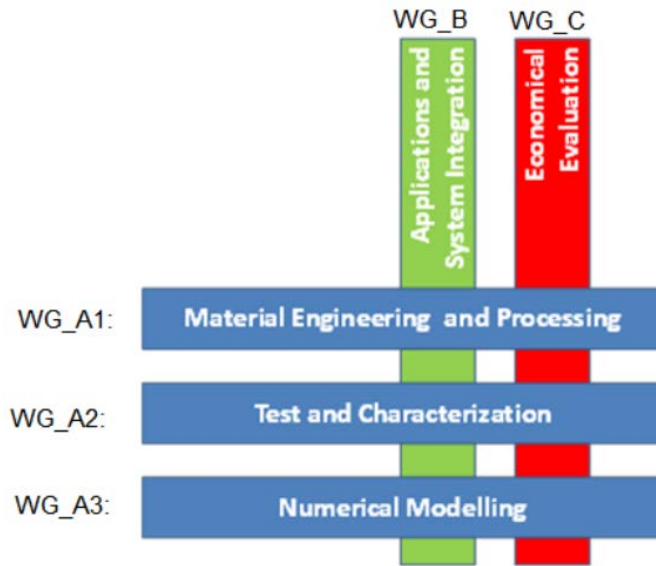


Fig. 1. Organisational structure of IEA SHC Task 42 / ECES Annex 29.

4. Results achieved

The key accomplishments of the task are summarized in the following 7 points:

1. A large number of modified and new PCM, TCM and sorption materials were investigated. New material-characterizing methods were investigated. Detailed information on the results of WG_A1 is given in the SHC2015 conference paper by Alenka Ristic et al. on “Engineering and processing of PCMs, TCMs and sorption materials” [1].
2. A new standard for an improved DSC measurement method has been developed in the task. It is described in the SHC2015 conference paper by Stefan Gschwander et al. on “Standardization of PCM characterization via

DSC” [3]. More exactly known material properties will contribute to improve the possibilities for material developments and to provide a better basis for their application in thermal energy storage systems.

3. A data base for PCM, TCM and sorption materials was developed and established. The experts of the task recommended that in the future more experts of material science and chemists from the fields of organic and inorganic chemistry should be involved in order to strengthen the development of these materials.
4. Advances have been made in the numerical modelling of materials, see SHC2015 conference paper by Silvia Gaastrat-Nedeaa al.on “Advanced numerical modelling techniques to tune the properties of heat storage materials for optimal reactor performance” [3].
5. Material application and compact thermal storage system development is the final aim of the task’s research activities. A comprehensive summary on the system developments investigated within the frame of the task is given by the SHC2015 conference paper by Wim van Helden et al. on “Applications of Compact Thermal Energy Storage” [4].
6. A new approach is under development in order to assess the possible performance of a given material for a certain application. Andreas Hauer gave a presentation on this so-called “4-temperatures approach” at the SHC 2015 conference.
7. A tool for the economic evaluation of thermal energy storages has been developed. It has been validated against conventional thermal energy storages on the market and applied to the compact thermal storage systems under development in the task, see the SHC 2015 paper by Christoph Rathgeber et al. “A simple tool for the economic evaluation of thermal energy storages” [5].

5. Conclusions

In a “Position Paper on the current status of the development of Compact Thermal Energy Storage systems” [6] the following current barriers for the development of compact thermal energy storage systems were identified:

The development of Compact Thermal Energy Storage systems based on phase-change and thermo-chemical materials is still very much in its R&D phase. It therefore still faces strong technical, financial and non-financial challenges. The technical barriers are related to the fact that the technology needs further progress on three levels: 1) materials, 2) components, and 3) systems. The physical phenomena, which may be phase change processes, sorption processes or thermochemical reactions, take place on the molecular level. Basic and applied research is still necessary to fully understand the physics and chemistry involved in order to improve and synthesize storage materials. Modelling materials and the simulation of reactions and processes on the molecular scale will also contribute to this. While the reactions take place on the molecular scale, the energy to be stored or released is transported on a macroscopic scale. That means that process engineers need to be able to calculate and deal with the flow of liquids, gases or vapour. Moreover, very often components have to be designed to operate in vacuum conditions. In thermochemical reactions it is necessary to deal with heat and mass transfer, which leads to components that have to be controlled with respect to several different operational parameters in order to achieve a high energy storage performance.

This results in complex system operational conditions. They often include highly fluctuating environmental and meteorological conditions. Therefore, the systems under development still require highly complex control, which leads to high investment costs in developing prototype systems.

It was therefore concluded that it will need the following actions to really drive market deployment:

1. Strong support of R&D work by governmental and international research programs as described above. Compact thermal energy storage systems based on phase-change and thermo-chemical material technologies are to a large extent

still in their development stage. The challenges cannot be addressed by single research groups and singularly achieved research results, but need a broad and internationally collaborative approach.

2. The companies involved in the development of compact thermal storage systems are often relatively small and highly innovative. They need strong support by governments to be able to apply their technology in the building and industrial processes sectors, in spite of the economic disadvantage they still may have.

3. Strong support of a growing number of demonstration projects is needed in order to gather operational experiences, to monitor and evaluate performance and to improve the performance of systems step-by-step. A much better basis for the further development and deployment of the huge potential of compact thermal energy storage systems will be established if these actions are taken.

I was therefore decided in December 2015 to initiate the necessary processes to establish a follow-on task within the frame of the IEA SHC and ECES programs. For further information you may contact the authors.

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The authors would like to thank all the experts in the Task42/Annex29 for their valuable and sustained contributions to the further progressing of compact thermal energy storage technologies, systems, components, materials and methods. They also wish to thank the Swiss Federal Office of Energy (SFOE), the German Federal Ministry for Economic (BMWi) and the Netherlands Enterprise Agency (RVO.nl), respectively, for the financial support of their contributions to the work of the IEA SHC Task 42 and IEA ECES Task 29.

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SHC 2015, International Conference on Solar Heating and Cooling for Buildings and Industry

IEA SHC Task 42 / ECES Annex 29

WG A1: Engineering and processing of PCMs, TCMs and sorption materials

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Abstract

An overview on the recent results on the engineering and characterization of sorption materials, PCMs and TCMs investigated in the working group WG A1 “Engineering and processing of TES materials” of IEA SHC Task 42 / ECES Annex 29 (Task 4229) entitled “Compact Thermal Energy Storage” is presented.

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1. Introduction

Thermal energy storage is an important technology for renewable energy systems and energy efficiency and is essential particularly for solar thermal systems. It is necessary to store heat efficiently for longer periods of time. Until now, no cost-effective compact storage technologies are available to do this. It is well known that materials are one of the main challenges for finding effective solutions for thermal energy storage, and that there is a need for new storage materials with a higher specific energy storage density and lower material cost.

One of the scopes of Working Group A1 “Engineering and processing of TES materials” is the engineering of thermal energy storage materials by changing the properties of existing materials and developing new materials with better performance, lower cost, and improved stability. The materials under consideration are those relevant to thermal energy storage using phase change, chemical reactions as well as sorption technologies. The activities of the working group include the synthesis of new materials, determination of material characteristics, determination of the material structure and composition, which influence the material performance, and determination of the role and importance of material containers.

The second aim of this working group is the processing of the raw materials, such as finding optimal methods for micro- and macro-encapsulation of storage materials (particularly phase change and thermochemical materials), processing of phase-change slurries and finding new combinations of materials (composites).

In the framework of the IEA SHC Task 42 / ECES Annex 29 (Task 42-29), significant R&D effort was directed toward the development of new or improved TES materials. Here, some contributions of several research groups, which are actively involved in this working group, are shown.

2. TES materials

2.1. Phase change materials

Phase change materials (PCMs) used for thermal energy storage are an important class of materials which substantially contribute to the efficient use and conservation of waste heat and solar energy. The storage of latent heat provides a greater density of energy storage with a smaller temperature difference between storing and releasing heat than the sensible heat storage method. Many different groups of materials have been investigated during the technical evolution of PCMs [1, 2].

Main issues covered PCMs during period (2013-2015) of the IEA SHC Task 42 / ECES Annex 29 (Task 42-29) are: i) PCMs for seasonal storage applications, including inorganic and new organic mixtures undergoing severe and stable undercooling; ii) low-cost PCMs coming from waste, by-products or natural resources; iii) solid-solid PCMs with enhanced stability; iv) micro/nano-encapsulated organic PCMs and microcomposites with improved performances; v) sugar-alcohol based PCMs for application at low-to-medium temperatures; vi) new PCM emulsions for cooling and industrial applications and vii) corrosion of metal and polymer containers in contact with different commonly used PCMs. Significant effort has also been done regarding the integration of PCMs into the applications, such as works related with façades and construction materials including PCMs or PCMs macro-encapsulation. New eutectic mixtures of organic or inorganic PCMs for applications at low temperature have also been produced and tested. Furthermore new imaging techniques based on infrared thermography were developed for PCMs to determine phase diagrams in record time, heterogeneous nucleation rates on flat substrates as well as temperature-dependent crystal growth rates with measurement of the temperature rise at the solid-liquid interface.

The recently finished COMTES research project (European FP7-energy program) evaluated the use of sodium acetate trihydrate (Technical University of Denmark and Graz University of Technology Austria). This salt hydrate was identified as potential PCMs for super cooling PCM heat storage, because of its large melting enthalpy (between 226 and 264 kJ/kg) and its price of 2.5-3 €/kg. Material's properties like solubility, density, thermal conductivity, heat content and dynamic viscosity were determined.

Researchers at University of Zaragoza, Spain, developed a characterization methodology for low cost PCM materials as cost is one of the most important aspects to enable their commercial expansion. This methodology has been applied to 37 samples. The complete characterization encompassed measurements of specific heat, thermal diffusivity, density, thermal conductivity, enthalpy and viscosity, as well as its resistance to thermal cycles. In this manner it can be possible to select the material and to design correctly the system for its use. The results showed: 9

high potential, 4 potential, 21 low potential and 4 null potential storage materials. The high potential storage materials included 4 paraffin materials with phase change around 50°C-70°C and latent heat of fusion (H_f) around 250 J/g, 2 natural products with phase change between -10°C and ambient temperature and H_f around 200J/g, 2 fibres by-products with phase change below zero and H_f around 200 J/g and one polymer with phase change around 60°C and H_f around 200 J/g and one with phase change between 90°C and 180°C and H_f around 300 J/g. All samples showed stable properties after thermal cycling (25 cycles) [3].

At University of Artois in France the study of the thermo-physical characterization of a composite of cement mortar integrated with 20% of micro-encapsulated PCM was carried out within an original set-up [4]. This study showed that the energy stored or released was 41% higher than the energy stored (released) by the conventional mortar in the temperature range to be observed in solar wall. The advantage of this material was that super cooling effect was not present and that the difference in thermal behaviour between fusion and cooling processes remained observable.

A new type of ventilated active façade that includes phase change materials (PCMs) in its outer layer was developed and tested at University of the Basque Country, Spain. A real-scale sample of 2.7m x 2.7m was constructed and evaluated through a PASLINK test cell [5, 6]. The façade was composed of five different layers, while the external sheet included 50 kg of RT35 from Rubitherm GmbH as PCM. This external layer was formed by an aluminium macroencapsulation system, comprised by hollow aluminium rectangular profiles placed horizontally which contained the PCM inside. Experimental results of the façade showed that the melting-solidification processes that took place in the PCM led to an increase in the heat absorption during the phase-change temperature intervals, which reduced overheating of the façade. Because of the PCM solidification, 2.5 hours after the solar radiation faded out, the air circulating through the chamber was still warmed by 2 °C. A finned flat plate latent heat thermal energy storage system for domestic hot water applications was developed by Campos-Celador et al [7]. The system could be applied to micro-cogeneration systems or solar thermal devices. It was basically formed by rectangular macroencapsulation plates arranged in series and parallel forming stacks. Water was used as a heat transfer fluid and the material employed to build the plates was aluminium. The PCM used was RT60 from Rubitherm GmbH and it was placed within the finned flat plates. An experimental prototype was constructed and tested in a suitable pilot plant. Three new binary mixtures of sugar alcohols comprising erythritol, sorbitol and xylitol for thermal storage applications in the heating and domestic hot water temperature ranges were studied [8]. Eutectic compositions underwent melting temperatures of 83.9, 86.6 and 74.9 °C, for the erythritol–xylitol; erythritol–sorbitol and xylitol–sorbitol systems, respectively. Regarding the heat storage ability, the erythritol–xylitol eutectic composition showed the largest melting enthalpy of 248.7 J/g. Experimental measurements performed by polarized thermomicroscopy showed that the mixtures presented a low crystallization rate, which limits their use in short term LHTES (Latent Heat Thermal Energy Storage) systems.

At University of Gaziosmanpaşa, Turkey, several micro/nanoencapsulated PCM materials were synthesized and characterized. Micro/nanoencapsulated capric, lauric and myristic acids (PCMs) with polystyrene (shell material) melted and frozen in the temperature range of 22-48°C and 19-49°C as they stored and released latent heat in a range of 87-98 J/g and (-84) J/g-(-96) J/g and they had good thermal durability and reasonable thermal conductivity values [9]. These advantageous properties make them potential LHTES materials for thermal regulating, solar heat pumps and solar space heating-cooling applications in buildings. Polymethylmethacrylate (PMMA)/capric-stearic eutectic mixture (C-SEM) micro/nano capsules were synthesized effectively using emulsion polymerization method. PMMA/C-SEM (1:2) micro/nano capsules showed a melting temperature of 21.37°C, which can be suitable for free cooling of buildings depending on the climatic conditions. It had a latent heat of melting of 116.25 J/g, which can be enough to integrate with conventional building materials [10]. Polystyrene (PS)/n-heptadecane micro/nano-capsules as a novel encapsulated phase change material (EPCM) were prepared. The melting temperature and latent heat of the prepared EPCM were measured as 21.48°C and 136.89 J/g, respectively. The material had good thermal durability. Thermal reliability, chemical stability, thermal conductivity and phase change reversibility of the micro/nano-EPCM were also studied. All of the results revealed that the fabricated PS/n-heptadecane micro/nano-capsules had promising LHTES potential especially for passive solar thermal regulation of textile, building, food storage container, medical and electronic materials [11]. Micro/nano encapsulated paraffin eutectic mixtures (PEMs) with polymethylmethacrylate (PMMA) shell were prepared by emulsion polymerization. The micro/nano capsules containing the highest PEM content had melting temperature range of about 20-36°C and latent heat storage capacities of about 86-169 J/g. Thermogravimetry analysis results verified that the encapsulated PEMs had good thermal reliability and chemical stability after repeated melting/freezing cycles for 5000 times.

At KTH-Royal Institute of Technology, Sweden, erythritol, xylitol and PEG 10,000 were investigated preliminarily with Temperature-History (T-history) method. This was on a study on polyols as phase change materials (PCM) for low-temperature surplus TES. For erythritol and xylitol some thermally activated change after three to five heating/cooling cycles, and for xylitol some glass transition was evidenced. For erythritol, two different melting temperatures, 118.5–120°C and 106–108°C at different cycles and an average subcooling of 18.5°C were observed. The average fusion enthalpies of the materials tested are found to be: 169 kJ/kg (PEG 10,000), 284 kJ/kg (erythritol) and 159 kJ/kg (xylitol) [12].

The influences of particle size and surface molecules on nucleation temperature/subcooling of n-octadecane/water emulsion and microencapsulated n-octadecane have been investigated at ISE Freiburg, Germany. A series of PMMA-encapsulated paraffin with various particle sizes (0.5 to 1000 µm) have been synthesized. Differential scanning calorimeter analysis showed that subcooling increases with decreasing particle sizes. Furthermore DSC analyses of emulsions with different non-ionic surfactants (e.g. Tween/Span 60/80 and PVA) have been compared. The results indicate that surfactants with paraffin-like lipophilic parts could reduce subcooling. In the German project KOLAN (03ESP357B) PCM emulsions were developed for cooling of buildings and for technical and industrial applications. The influence of non-ionic emulsifiers on the stability, viscosity and thermal behaviour of paraffin/water emulsions was examined. Therefore octadecane concentration has been kept at 30 wt. % whereas the emulsifier concentration and mixtures of emulsifiers varied. This emulsion provided storage capacity of 90 kJ/l. Stability was measured in a remoter while applying thermal and mechanical stress by shearing the emulsion at a defined heating rate. The viscosity showed always values below 20 mP as which is important to keep the pumping energy consumption low.

At ZAE Bayern, Germany, new organic PCM mixtures were developed and characterized with DSC and T-History methods. Binary mixtures of linear alkanes with saturated fatty acids (group I) and linear alkanes with monohydrated alcohols (group II) were found to form eutectic systems: hexadecane + caprylic acid (35:65), nonadecane + capric acid (40:60), pentadecane + undecanol (55:45), icosane + myristil alcohol (30:70). Measured enthalpy curves of the mixtures were comparable with the basic materials in terms of enthalpy change, phase change width and degree of subcooling. Thus, an adjustment of melting temperatures without losses in terms of melting enthalpy was obtained by mixing organic PCM of different material groups [13]. Furthermore a three-step method to determine the eutectic composition of a binary or ternary mixture was developed [14]. The method consists of creating a temperature–composition diagram, validating the predicted eutectic composition via differential scanning calorimetry and subsequent T-History measurements. The method was tested with two binary mixtures: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$. To determine the maximum storage capacity of the two eutectic mixtures, a temperature range of 15 K was chosen around the phase transition for both eutectic mixtures, i.e. a temperature range from 5 to 20°C and 5 to 10°C for $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$, respectively. An enthalpy change of about $172 \text{ J} \cdot \text{g}^{-1}$ ($302 \text{ J} \cdot \text{cm}^{-3}$) and $162 \text{ J} \cdot \text{g}^{-1}$ ($274 \text{ J} \cdot \text{cm}^{-3}$) was determined from the DSC heating curves for $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$, respectively.

The study on chitosan-gelatine (CG) microcapsules containing either caprylic (melting point; 15–17°C) or decanoic acid (melting point; 29–33°C) was performed at Nigde University, Turkey, and Cukurova University, Turkey. Microcapsules/microcomposites were prepared via complex coacervation and cross-linked by glutaraldehyde. They achieved to develop caprylic acid/CG microcapsules with a mean diameter of 0.22 µm and decanoic acid/CG microcomposites with a mean diameter of 1.06 µm via complex coacervation. FTIR (Fourier Transformed Infrared Spectroscopy) results confirmed that the both caprylic and decanoic acid retained their chemical structure after microencapsulation with CG shells. The prepared microcapsules showed microcapsules synthesized successfully with a melting temperature close to 11.5°C and a latent heat storage capacity of approximately 79 J/g. Given the non-toxic, biocompatible, and biodegradable properties of gelatine and chitosan, as well as the thermal properties of the resultant products, these capsules can be used in food package applications to ensure temperature-controlled packaging and transport [15].

Corrosion effects of metal and polymer containers for use in PCM energy and cold storage, cooling and heating applications were studied at University of Barcelona and University of Lleida in Spain. PCM are usually encapsulated in containers, hence the compatibility of the container material with the PCM has to be considered in order to design a resistant container. Four different PCMs (SP21E, PureTemp23, Ca/Pa eutectic, Ca/My eutectic) were put in containers of different metals/alloys (aluminium, copper, carbon steel, stainless steel 304 and stainless steel 316) and tested. Results showed corrosion on aluminium specimens hence caution must be taken when

selecting it as an inorganic salt container. Despite copper had a corrosion rate range of 6–10 mg/cm²yr in the two tested fatty acid formulations it could be used as the container. Stainless steel 316 and stainless steel 304 showed great corrosion resistance (0–1 mg/cm²yr) and its use would totally be recommended with any of the studied PCM [16]. Eleven salt hydrate PCMs (S10 and S46 by PCM Product, C10 and C48 by Climator, ZnCl₂·3H₂O, NaOH·1.5H₂O, K₂HPO₄·6H₂O, MgSO₄·7H₂O, Zn(NO₃)₂·4H₂O, K₃PO₄·7H₂O and Na₂S₂O₃·5H₂O) were placed in copper, aluminium, stainless steel 316 and carbon steel containers and evaluated for heating and cooling applications. Tests for cooling applications showed that commercial S10 was recommended for the use with stainless steel and aluminium, but the latter only according to the specific application. On the other hand, commercial PCM - C10 was suitable to be encapsulated with both aluminium and stainless steel. PCMs used for cooling applications (NaOH·1.5H₂O, ZnCl₂·3H₂O and K₂HPO₄·6H₂O) showed low corrosion rate when they were in contact with stainless steel. NaOH·1.5H₂O was also suitable for working with carbon steel depending on the application while ZnCl₂·3H₂O and K₂HPO₄·6H₂O could work also with copper, depending on the application. Regarding heating applications, all tested PCMs presented very low corrosion rate when working with stainless steel. Commercial S46 was also recommended for the use with aluminium according to the application. The other commercial PCM (C48) showed low corrosion rate with carbon steel and aluminium as well. Besides, MgSO₄·7H₂O was recommended to be used with aluminium, K₃PO₄·7H₂O presented low corrosion rate with carbon steel and Na₂S₂O₃·5H₂O can also be used with carbon steel and aluminium [17]. Four common metals as PCM containers: copper, aluminium, stainless steel 316, and carbon steel and four polymer materials as PCM containers were selected: polypropylene (PP), high density polyethylene (HDPE), polyethylene terephthalate (PET), and polystyrene (PS) to study the corrosion effect of different metals and polymer materials in contact with some PCM used in low temperature applications. Nine PCM formulations were analysed: three of them were based on commercial options ClimSel-18 (C-18) from the company Climator, E-21, produced by Cristopia, and E-21 with 1% of oxyethylmethyl cellulose (CMC) to thickening the solution. The rest of them were their own formulations [18]: PCM-D:19% NH₄Cl + H₂O, PCM-E: PCM-D + 1% CMC, PCM-F: PCM-D + 3% AlF₃, PCM-G: PCM-F + 1% CMC, PCM-H: PCM-D + 3% NaCl, PCM-I: PCM-H +1% CMC. Results showed that copper and carbon steel must be avoided as PCM containers, and aluminium was not recommended as well; while stainless steel 316 was recommended. Moreover, PP, PS, PET, and HDPE were not affected by a process of degradation and were also compatible with these PCMs. Thermal stability of sugar alcohols as phase change materials for medium temperature energy storage application was tested. Three promising sugar-alcohols were selected: D-mannitol, myo-inositol and dulcitol under high melting enthalpy and temperature criterion. D-mannitol and dulcitol presented poor thermal stability. Myo-inositol showed almost no decrease in thermal properties after 50 cycles for the heating process, however in the solidification part a decrease of 20% of enthalpy and 11% of temperature values was observed [19]. D-mannitol was selected for testing it in a solar cooling application due to its melting point (167°C) and a relatively high enthalpy (316.0 kJ/kg). The experiments performed by DSC have shown that the d-mannitol presents polymorphic structural changes and, therefore, its thermal properties are not always the same. Depending on the polymorphic phase obtained, d-mannitol has different melting temperature. This behaviour was corroborated in a storage tank, where it may be seen that the cooling rate of the d-mannitol is a key parameter in the formation of the different polymorphic phases [20, 21]. D-mannitol and hydroquinone were used at real solar cooling plant. For the same boundary conditions, the energy stored by d-mannitol was higher than that for hydroquinone [22].

At I2M, University of Bordeaux, France, the enhancement of latent heat by confinement of the PCM in a nanoporous structure or by addition of nano-fillers within the PCM or both was studied. Thus multi-walled carbon nanotubes (MWCNTs) were dispersed in paraffin wax RT65 obtained from Rubitherm Technologies GbmH (T_m ~ 64°C) by melt blending method. Composites with MWCNTs loadings of 0, 0.25, 0.50 and 1 wt.% have been prepared. DSC tests showed that the addition of MWCNTs did not lead to significant changes in the melting range of temperatures, although the onset temperature was slightly increased. However, the expected diminished value of the latent heat due to the replacement of the paraffin by fillers was not observed at all. On the contrary, the latent heat was significantly and progressively raised when the mass fraction of MWCNTs increased [23]. In the recent European project SAM.SSA (Sugar Alcohols based Materials for Seasonal Storage Applications, FP7 2012-2015) new sugar alcohol (SA) based materials for solar thermal seasonal storage applications have been developed and studied in-depth [24, 25]. SAM.SSA developments include new SA-based eutectic mixtures lowering the original high temperatures of the single materials, low-cost tailor-made carbon porous structures and corresponding carbon/SA composites with enhanced thermal conductivity, and SA micro-encapsulation. A new solution for efficient SA crystallization was also established. In general, SA with high heats of fusion often exhibited high

melting temperatures ($>100^{\circ}\text{C}$), which limited the choice of heat transfer fluids to be used. This was particularly discussed in solar heating and DHW applications, where cheap water-based solar collectors were required. It was established that new true eutectic mixtures using SA could be manufactured lowering the original high temperatures of the single materials. These new mixtures were proven to have relatively high latent heat (245-300 J/g), proper melting points ($77\text{--}87^{\circ}\text{C}$), and an evident subcooling effect which enabled low-cost long-term storage schemes. The studied materials were also characterized by high density values (1.3-1.4 g/cc in liquid) and moderate-to-low volume changes ($<10\%$). Achieved energy density by melting under usual working condition was comparable (even higher) to that of sorption-based storage technologies. The values ranged between 120-190 kWh/m³. Thermal conductivity values in solid state ranged from 0.8 to 1.4 W/m/K for the SAs, and from 0.2 to 0.4 W/m/K for the SA-blends. In liquid, all the studied materials showed thermal conductivity values around 0.35-0.45 W/m/K. The specific heat was 1.4 to 2 times lower than that of water. In summary, SA and SA-mixtures performed better than most of organic PCMs and showed performances similar to that of salt hydrates. However, SAs are not concerned by segregation, separation or corrosion issues which are the major drawbacks of salts hydrates. In-depth understanding of nucleation and crystal growth processes had been achieved. It was proven that the low nucleation rates which characterized sugar alcohols were due both, to the low atoms mobility imposed by highly viscous undercooled liquids and to the molecular conformational changes accompanying the liquid-to-solid transitions. Temperature dependent crystal growth rates were experimentally determined and indicated that all studied materials showed diffusion-limited crystal growth kinetics. As expected, the materials with stronger undercooling were those with lower crystal growth rates. The maximum growth rates of D-mannitol and erythritol were, respectively, 1000 $\mu\text{m/s}$ (at 127°C) and 520 $\mu\text{m/s}$ (at 57°C). They were about two orders of magnitude lower for adonitol (13 $\mu\text{m/s}$ at 77°C), L-arbitol (2.5 $\mu\text{m/s}$ at 73°C) and xylitol (3 $\mu\text{m/s}$ at 67°C). The maximum value of the growth velocity was lower than 1.5 $\mu\text{m/s}$ for all SA-blends. Overall understanding of the bubbling-crystallization process was provided and key related variables and parameters were identified. Commonly used crystallization techniques, including cooling, intentional seeding, ultrasonication and antisolvent-crystallization, were studied at first but proved to be inefficient. On the contrary, air bubbling was a simple solution which seemed to be effective and robust in triggering the SA nucleation and in accelerating total crystallization rates. The proof of the concept was achieved at the laboratory scale using small reactors (300-900 ml). It was also shown that combining solvent-antisolvent systems with bubbling can have very positive effect on SA crystallization. Furthermore new imaging techniques based on infrared thermography were developed for PCMs to determine phase diagrams in record time, heterogeneous nucleation rates on flat substrates as well as temperature-dependent crystal growth rates with measurement of the temperature rise at the solid-liquid interface at this institute. First method establishes a preliminary phase diagram in a very short time (< 3 h) that can then be refined by more detailed but more time consuming techniques. The interest has been to speed the "screening" steep which often precedes the development of a new material, in which a large number of systems and/or mixtures have to be tested [26]. The second method allows studying heterogeneous nucleation on flat substrates in a quantitative way. This method is based on the experimental observation, by using an infrared camera, of the cooling process of a large number of sub-millimetre droplets deposited on the substrate to be studied. When a droplet crystallizes, a peak is observed in the corresponding infrared signals. This peak reflects the sudden heating of the droplet due to the release of latent heat of crystallization. It allows to identify the temperature at which each droplet crystallizes and, therefore, to calculate the probability of nucleation or, alternatively, the nucleation rate as a function of the supercooling [27]. In the third method [28], the optical microscope (or CCD camera) is replaced by an infrared camera which, after calibration, allows measuring the temperature at any point of the solid-liquid interface at any time. The interest of the method has been highlighted by studying the crystal growth kinetics of sugar alcohols.

2.2. Thermochemical materials

2.2.1. Salt hydrates

Thermochemical energy storage has the potential to store heat energy ten times more than sensible and three times more than latent heat storage technologies. This technology includes chemical storage and sorption storage. Chemical storage consists of producing a reversible chemical reaction. In heat utilization processes, the dehydration (forward reaction) is used for charging, and the hydration (backward reaction) of the material for discharging the

heat from the storage unit. The performance of the system during discharging is realized by exothermic reaction and the performance during charging is realized by endothermic decomposition reaction. Salt hydrates were selected because their high energy density and low cost make them advantageous, their main disadvantages being their lower stability and relatively slow kinetics. In order to overcome these disadvantages some studies have been performed.

At Leuphana University, Germany, a study on 45 salt hydrates regarding their nontoxicity, high energy density and low cost has been conducted for low temperature thermochemical heat storage application, and only 17 of them showed reversible reaction. Further investigations showed, that only three salt hydrates were usable depending on a reactor simulation in their project “Thermal Battery” for private households and industry applications: $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ (392 kWh/m³), $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (359 kWh/m³) and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ (340 kWh/m³). The hydrates of calcium chloride (353 kWh/m³) challenged the use as storage material and it was a representative for other potential storage materials (e. g. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (351 kWh/m³)) [29]. Therefore, the economic and the physical properties were reflected as well as the use in applications of adsorption cooling and heating, absorption processes, desiccation, dehumidification and thermal storage were reviewed. Besides advantageous characteristics like storage energy density and nontoxic properties the formation of solution during hydration of the pure salt hydrates decreased the cycle stability and disabled their use as the storage material. One possibility to avoid this disadvantage was the control of temperature and water vapour pressure. If the supply of water vapour flow was limited it was possible to avoid the formation of solution ($\text{MgCl}_2 \cdot 4.5 \text{H}_2\text{O}$) [30]. However, this procedure was not manageable in macro scale because of the heterogeneous reactions occurring in the storage bulk. On the other hand mixing calcium chloride with magnesium chloride preserved cycle stability. Surprisingly the experiments showed that the cycle stability did not change despite the presence of over-hydration. Also the impregnation of salt hydrates into porous carbon materials and vermiculite prevented deliquescence and improved the diffusion of water vapor into the material, the cycle stability and heat conductivity [31, 32], but decreased the energy density. Heat exchanger modelling and lab scale experiments were done with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ [33]. It revealed that even normal solar panel can activate charging at 90 °C, though the complete charging would be finished at 120 °C.

Corrosion tests between inorganic TCM and metal vessels together with thermal cycling stability have been performed at University of Barcelona and University of Lleida in Spain. This study presented the results of an immersion corrosion test following ASTM G1 simulating an open TCM reactor, under humidity and temperature with defined conditions. Four common metals: copper, aluminium, stainless steel 316, and carbon steel, and five TCMs: CaCl_2 , Na_2S , CaO , MgSO_4 , and MgCl_2 , were studied. Copper can only be recommended with caution when combined with CaCl_2 and MgCl_2 . This metal has been mostly used as heat exchanger material because of its high thermal conductivity. Therefore, a coating is needed to protect the metal corrosion from the TCM. Carbon steel is slightly corroded with CaCl_2 and Na_2S , forming a brittle corrosion layer on the surface. Aluminium and copper showed severe corrosion when combined with Na_2S , aluminium corrosion was more significant since the specimen was totally destroyed after 3 weeks. Only stainless steel 316 can be recommended for the use as a metal container material for storing all these tested TCMs [34]. Thermo-physical characterization and thermal cycling stability of two TCMs: CaCl_2 and zeolite were examined. In this study the performance of CaCl_2 following a chemical reaction and zeolite (a sorption process) was compared for seasonal/long term storage. The main results showed that the chemical TCM was more energy-efficient than the sorption TCM. The CaCl_2 calculated energy density was 1.47 GJ/m³, being the best option to be considered to be used as TCM, even though the dehydration process of the zeolite was simpler and it happened at higher temperatures its calculated energy density was only 0.2 GJ/m³ [35].

2.2.2. Sorption materials

A specific type of TCM is sorption storage. Sorption materials attract broad interest because of their potential applicability in the field of thermal energy storage, e.g. low temperature sorption heat storage, which is based on a reversible physico-chemical process: adsorption/desorption of water on porous solid sorbents. Solid/vapor adsorptive systems are very promising for heat transformation applications as they can utilize efficiently solar energy or waste heat as driving force.

At Technical University of Applied Sciences Wildau, Germany, achievements in material development and characterization for seasonal compact thermal adsorption storage within the frame of COMTES have been performed. The proposed material for the compact thermal adsorption storage consisted of binderless beads of zeolite X with a large micropore volume. This molecular sieve with chemical composition $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{mSiO}_2$:

$n\text{H}_2\text{O}$ with $m \leq 2.35$ showed high water adsorption capacity and high thermal storage capacity. Furthermore, zeolites with a lower Si/Al-ratio but the same structure (NaYBF) have been taken into account. Both are product of the Chemiewerke Bad Köstritz (CWK) in Germany. Both zeolites had the advantage to be binder-free, meaning that they showed about 15% higher water adsorption capacities compared to adsorbents with binder. From detailed material characterization it has been found that both zeolites showed similar water adsorption capacity of slightly above 30 wt.%. However, 13XBF revealed higher adsorption heat and better kinetics compared to NaYBF (the difference between the zeolites was around 20-10 kJ/mol). For application in a seasonal heat store the high thermal energy output of the zeolite 13XBF seemed to be favorable, but higher temperature had to be provided from a solar thermal collector field for the water desorption process. From hydrothermal stability measurements it has been obtained that both types of zeolites showed no noteworthy degradation of their water adsorption capacity for the conditions expected in the seasonal sorption store (180 to 200°C, water vapor pressures in the mbar-range). They also tailored zeolite Y's adsorption properties by silicon enrichments for heat pump applications with low temperature heat as driving energy. By a partial dealumination of the parent zeolite Y by steaming the hydrophilic character of this zeolite was decreased which led to a lower desorption temperature for water. The reduction of the hydrophilic character of the conventional zeolite Y shifted the adsorption isotherms towards higher relative water vapor pressure and hence into the working area of adsorption heat pumps for low temperature utilization ($T < 100^\circ\text{C}$) [36].

Researchers at ISE Freiburg, Germany, improved sorption properties of activated carbon for specific application environments, such as the adsorption of water in an open sorption heat storage system. The optimization criteria have included all of the important parameters, such as production costs and the expense for primary energy, uptake or storage capacity, discharging power, and material stability during the typical service life of the product. The combination of a cost-effective source material and adapted modifications prepared sorption material that can compete in terms of sorption characteristics with materials that are significantly more expensive to produce. Particularly for adsorption-based thermal energy storage applications, this has been an important step towards economic and primary energy amortization of capital expenditures for thermal energy storage systems. 26 commercially available carbon materials as powder and granules were evaluated regarding the suitability of modification and water adsorption. 12 of them showed the best results. It was found out that these materials possessed pores in the range from 0.6 to 1.2 nm. Oxidation treatment was used for the modification of these AC materials. One of the first modified samples almost reaches the project-internal benchmark of water uptake of 0.3 g/g at relative pressure of 0.4.

Carbon was also used as a high thermal-conductive component in the preparation of the composite combining with microporous aluminophosphate (C-APO), which is the most promising water adsorbent in terms of equilibrium data, in order to enhance its thermal conductivity, at National Institute of Chemistry, Slovenia. Namely, this microporous aluminophosphate shows maximal water loadings of up to 32wt%, under relatively mild conditions, e.g. adsorption at 35°C (1,23kPa) and desorption at 95°C (5,67kPa). The advantages of this material are also the energy density in the working temperature range from 40 to 140°C of 240 kWh/m³, its hydrothermal and thermal stability (up to 900°C) and water desorption at 95°C. The main disadvantage of this material is its low thermal conductivity (~ 0.11 W/m/K) that reduces heat exchanges rates during sorption process. One of the strategies to improve thermal conductivity of the adsorbent is a combining aluminophosphate sorption material with material with high thermal conductivity, like porous carbon, in the form of coatings. The main condition for the preparation of carbon coatings on aluminophosphate sorption materials is thermal and structural stability of sorption materials up to 700°C, because carbon coatings are usually prepared by high-temperature treatment (500-700°C) of carbon-containing organic materials (precursors) under inert gas in the furnace. This method is mainly used for the preparation of catalysts supports and electrode materials in superconductors and fuel cells. As carbon precursors, sucrose and citric acid have been used. The aluminophosphate sorption material was coated with a thin layer of carbon by wet impregnation and dry procedure, followed by carbonization at 650°C under inert atmosphere in the furnace. The results of structure analysis showed that the preparation methods of C-APO materials had great influence on the preservation of structure and its structural properties. It was found out that wet impregnation using solutions of citric acid caused destruction of the structure, while wet impregnation with sucrose solution did not affect the structure. The amount of carbon in the samples was dependent on the type of the used carbon precursors and on the method of the preparation and it was determined to be from 1.1 to 2.4 %. Water sorption capacity was obtained at different temperatures by gravimetric method and showed that composites had similar water uptakes, while determined heats of adsorption were lower for composite materials, which could be assigned to the presence of different amounts of carbon in the

samples. The results of thermal conductivity measurements showed small increase of thermal conductivity of C-APO materials. Another strategy for the improvement of thermal conductivity was used by the preparation of aluminophosphate coating on metal plate. Water solution of aluminofosphate adsorbent and polyvinyl alcohol was deposited on cleaned stainless steel plate of 5 x 5 cm and dried overnight. The thickness of the coating was determined to be from 100 to 180 μm . The coated plate was tested of water sorption capacity and hydrothermal stability (4600 cycles). The APO coating showed similar shape of water adsorption curve as the powder material, with a steep rising of the uptake between 0.1 and 0.2 relative pressures, which is ideal for adsorption heat pumps. The mass specific uptake is lowered to some extent, due to the binder content in the coating. However there is no negative influence of the characteristics by the binder, beside the unavoidable reduction in maximum water uptake. The hydrophilic properties of water composite sorbents were improved by the preparation of the silica matrix with smaller mesopores than 10 nm, adding higher amount of hygroscopic salt and by changing the preparation procedure of the composites [37]. Water composite sorbents containing ordered mesoporous silica matrix and different contents of CaCl_2 (4 wt.%, 10 wt.%, 20 wt.%, 30wt%) were prepared by the incipient wetness impregnation. This method preserved the ordered mesoporous structure of the composites. The maximal water capacities increased with higher contents of CaCl_2 . The composite sorbents with 20 wt.% of CaCl_2 had the highest maximal water uptake of 2.33 g/g (at 0.94 p/po) and sorbed 0.62 g/g at 0.4 p/po, which is 3 times higher than maximal water uptake of the matrix. The shifts of the water isotherms to lower relative pressure for higher amounts of CaCl_2 were achieved, successfully. Tests of 20 cycles between 40°C and 140°C and a relative humidity of 76%, of all composites showed good hydrothermal stability. The lowest loss of water uptake (1.2%) after 20 cycles showed the composite containing 20 wt% of CaCl_2 . And it was 3 times lower than the loss of water uptake of similar composite containing lower amount salt [38], measured under similar conditions. No salt leaching from the matrix was detected after 20 cycles. Regeneration temperatures of the composites were in the range from 120 to 140°C depending on the amount of the salt in the composite.

3. Conclusions

This overview presents selected contributions of researchers involved in the IEA SHC Task 42 / ECES Annex 29 (Task 4229). In the scope of this task from 2013 to 2015 more than 20 institutions from more than 12 countries were taken part in working group A1: “Engineering and processing of TES materials”. During this period different new and improved PCMs and TCMs were synthesized. The physical and structural properties of these materials were determined, cycling and thermal stability was studied and the role of material containers (corrosion issues) was analyzed. New low-cost PCMs coming from waste, by-products and natural resources have been produced. Most promising ones have latent heat between 200-300 J/g and can cover TES applications at 50°C-70°C. New eutectic mixtures of linear alkanes with saturated fatty acids or monohydrated alcohols were also obtained and proved to be an efficient way for adjusting the melting point while preserving enthalpy values. New sugar alcohol based eutectic mixtures lowering the original high temperature of single materials were produced. They proved to have high latent heat (240-300 J/g), proper melting point (75-87°C) for solar heating and DHW applications, and evident subcooling effect which enable low-cost long-term storage schemes. Sugar alcohols for TES in industrial applications at higher temperatures (100-200°C) were also investigated and proved to have high compactness potential. Among TCMs new sorbent water composites containing CaCl_2 within porous silica were prepared for low temperature heat transformation applications. Binder-free zeolite X was used for a seasonal compact thermal adsorption storage and zeolite Y was dealuminated for adsorption heat pumps for low temperature utilization ($T < 100^\circ\text{C}$). Salt hydrates were impregnated into porous carbon and vermiculite in order to improve cycling stability. Different optimal methods for materials processing were also found, like microencapsulation (caprylic acid/chitosan-gelatine), micro/nanoencapsulation (capric, lauric and myristic acids with polystyrene shell), phase-change slurries (n-octadecane-water emulsion) for PCMs and new combinations of composite materials (PCMs and TCMs). TCM composites were prepared by impregnation (MgCl_2 /porous carbon or vermiculite, APO/carbon) and incipient wetness impregnation (CaCl_2 /porous silica). Improvements of TCM's properties were achieved by the oxidation treatment of activated carbon, composites of CaCl_2 /porous silica and binder-free zeolites X and Y (hydrophilicity), dealumination of zeolite Y (lower regeneration temperature), preparation of APO/carbon composite or APO coating on metal plate (thermal conductivity), mixing MgCl_2 and CaCl_2 (preservation of cycling stability), etc. The research was mainly conducted in the field of PCMs, while only few researches were performed in the field of thermochemical materials. It can be observed that mainly engineers/physicists were involved in the research of

materials and there were very few chemists. In the future, experts of material science and chemists from the fields of organic and inorganic chemistry should be more involved in order to strengthen the development of TES materials.

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Standardization of PCM characterization via DSC

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Summary

Differential Scanning Calorimetry (DSC) is a widely used method for the characterization of phase change materials (PCM). Comparative DSC measurements carried out at different laboratories within the joint IEA-SHC Task 42 and IEA-ECES Annex 29 on compact thermal storages revealed the need for a standardized methodology to reduce the deviations between these results and to determine representative and reliable PCM characteristic data.

Several comparative DSC measurements using different DSC devices have been carried out to melting and solidification develop a standardized procedure for the determination of melting and solidification enthalpy curves. Laboratory grade Octadecane (Parafol 18-97, Sasol) is used as PCM for these measurements. First comparisons showed large deviations of transition temperature and enthalpy measured at different laboratories, which led to the development of a more precisely defined standardization procedure for the characterization of PCMs.

Keywords: PCM, DSC, procedure, standardization, heating rate,

1. Introduction

An accurate material characterization of thermal energy storage materials is elementary to develop an efficient thermal storage device or application. The most important temperature related characteristics of heat storage materials is the heat capacity: Differential scanning calorimetry (DSC) measurement is the most used method for its determination.

Within the framework of IEA SHC Task 42 / ECES Annex 29 (Task 4229) seven scientific institutions work on the development of measurement standards for PCM characterization not only by DSC, but also by the T-History method. Work is also performed on methods to determine the thermal conductivity and rheological behavior. This contribution focuses on the work done for PCM characterization using DSCs.

2. Methods

Several comparative DSC measurements using different DSC devices located at different laboratories were carried out to develop a standard for the determination of the enthalpy curves for melting and solidification. Laboratory grade Octadecane (Parafol 18-97, Sasol Germany GmbH) is used as PCM for these measurements (Table 1). The first comparison without any definition for the measurement showed large deviations in terms of transition temperature and enthalpy. Thereby, the need for a standardized measurement procedure and a specification of the calibration of DSC devices became apparent.

Table 1: Chemical composition of the RRT paraffin Parafol 18-97

Component	Fraction [wt.-%]
C16	0.07
C18	98.11
iC18	0.4
Bromine	0.01

Further comparative measurements have been done according to a DSC procedure defined in the German quality label PCM-RAL [3]. This label defines how to determine the heating rate required in order to measure PCM. According to this procedure, several cycles - each consisting of a heating and cooling ramp - have to be applied to the sample. Thereby, the heating and cooling rate has to be reduced from cycle to cycle to half of the value of its precursor. A suitable heating and cooling rate is reached when the peak temperature of the heat flow signals, which is equivalent to the inflection point of the computed enthalpy curves is not lower (heating ramp) or higher (cooling ramp) than 0.2 K of the one in the cycle before (criterion 1) or if the temperature difference between peaks of the cooling and heating signal is less than 0.5 K (criterion 2). Applying this procedure reduced the deviation between the different results but deviations of total enthalpy change have been still in a range of 30 kJ/kg.

Introducing a uniform calibration of all DSCs and applying the same sample mass (approx. 10 mg) in addition to the PCM-RAL procedure result in an excellent improvement in comparability of results for the heating process. The cooling curves showed still considerable deviations [2].

Further improvement was reached by DSC baseline correction. Some DSCs show a drift of the baseline during the measurement, which can be corrected mathematically after the measurement [1]. It moves the measured baseline to zero. The method requires isothermal sections before and after each heating and cooling ramp and it has to be ensured that thermal equilibrium is reached within these isothermal sections. Figure 1 shows the effect of this baseline correction for the example of an enthalpy curve.

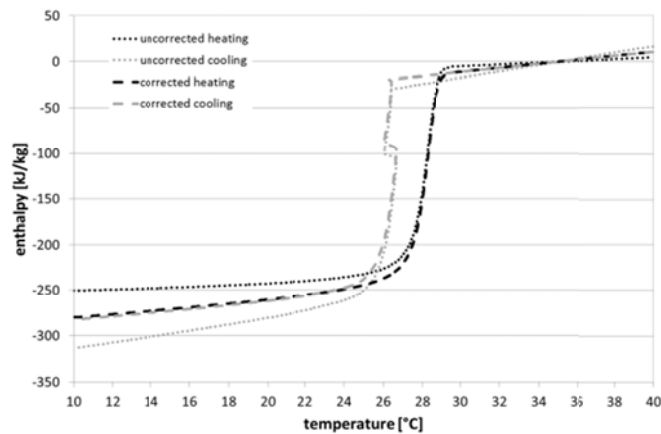


Figure 1: Effect of baseline correction

The overall procedure developed for the DSC measurement of PCMs consists of five elements:

1. Heating and cooling rate test to determine suitable heating and cooling rates for the PCM to be measured. This is done by using the PCM to be characterized and applying heating and cooling rates starting from fast rates (e.g. 10 K/min) and slowing down the heating and cooling rates of consecutive cycles by halve the previous.
2. Calibration of the DSC by using 3 different calibration materials covering the desired temperature range (e.g. water, gallium and indium). The calibration has to be done with the determined heating rate.
3. Measurement of the empty crucible using the determined heating and cooling rates.
4. Sample measurements by applying the sample to the crucible (apply the same sample mass as for the heating rate test) using the determined heating rate.
 - Four measurement cycles have to be applied
 - Three samples have to be measured
5. Analysis of data
 - If necessary, baseline correction (displacement to zero heat flow)

-Subtraction of heat flow signal measured with empty crucible from sample measurement
 -data evaluation, computation of enthalpy curves

A more detailed description for the procedure is available on [4].

In addition to the procedure a database is available to upload PCM data which is measured according to the standard [4]. The database provides an overview table of all PCMs being stored (Figure 2). By choosing a PCM all relevant measurement parameter are available (onset temperature, integration limits for the given heat of fusion, sample mass, heating rate, etc) as well as the measured data which is provided as ASCII table for download (Figure 3).

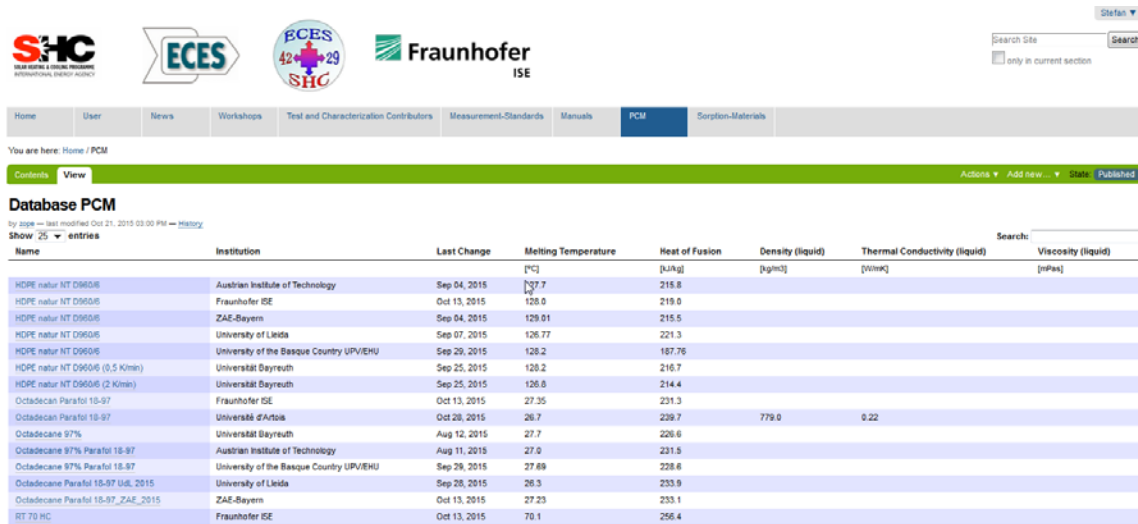


Figure 2: Screenshot overview table PCM web-database

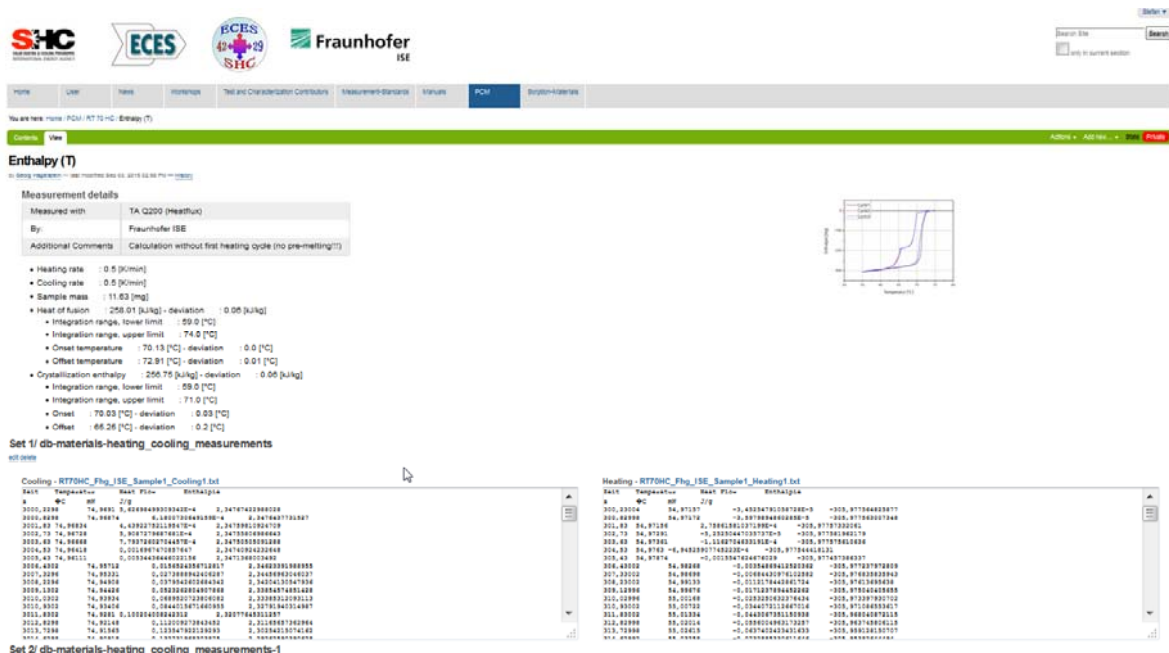


Figure 3: Screenshot database, example PCM dataset

3. Results

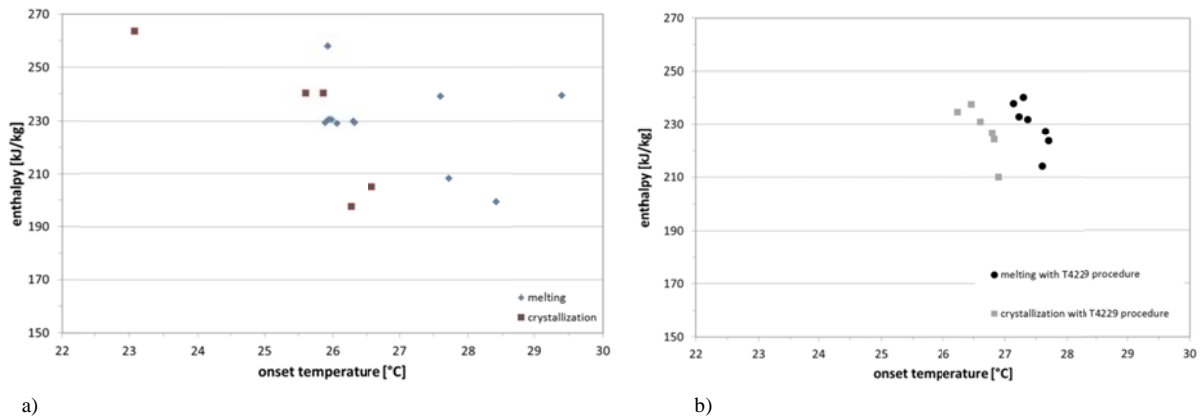


Figure 4: Comparison of heat of fusion, heat of crystallization plotted against the onset temperatures, left: Results of the first RRT without any definition, right: after applying the procedure developed in ECES Annex 29 and IEA-SHC Task 42.

Figure 4a shows the comparison of results obtained by the first RRT done without any definition. The results applying the new DSC procedure to the Parafol 18-97 is plotted in Figure 4b. With the defined DSC procedure the mean value and standard deviation over all values plotted in Figure 4b is for the onset temperature for melting 27.43 ± 0.22 °C and for the onset of crystallization is 26.64 ± 0.25 °C, the mean value for the heat of fusion is 229.68 ± 8.9 kJ/kg.

Figure 5a/b depicts enthalpy curves for the results shown in Figure 4b. The results plotted in Figure 5a reveal a very good agreement in temperatures during melting as well as for the enthalpy. More results are presented in Figure 5b in comparison to the MT DSC 1 results plotted already in Figure 5a. All three additionally plotted measurements are done with slower heating rates then in a) which might be a reason for the deviations. Other deviations arise from different analyses, e.g. one result doesn't consider the sensible heat in the enthalpy curve.

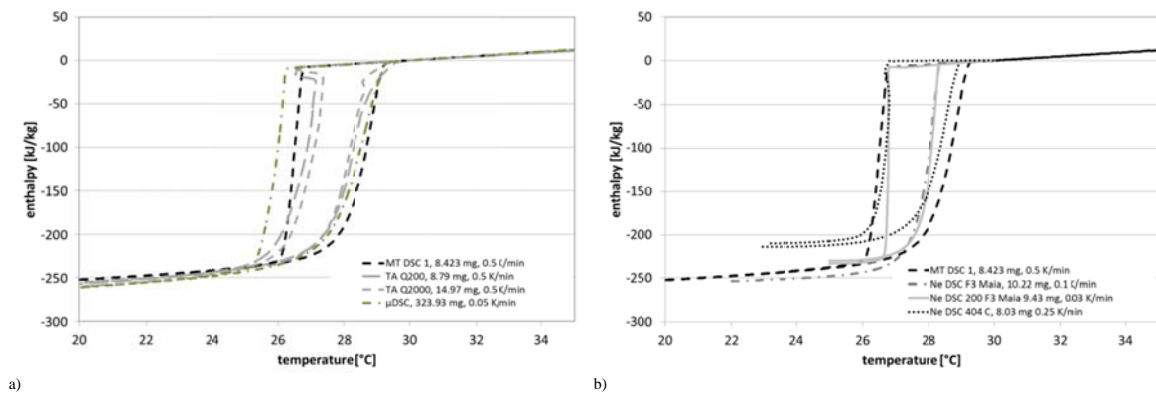


Figure 5: Results from Figure 4b shown as enthalpy curves.

DISCUSSION

The RRT results show a clear reduction of deviations for the DSC results due to the standard procedure developed. The determination of suitable heating and cooling rates for the characterization is the basis to measure a temperature close to the real sample temperature. For the measured Parafol 18-97 the the reduction of deviations is quite good applying a heating rate at 0.5 K/min when using a heat-flux DSC if a sample mass of around 10 mg is measured. Much lower heating and cooling rates have to be applied if the sample mass is higher. The Micro DSC (manufacturer Setaram) is a calvet DSC and requires a sample mass of around 300 mg which leads to a very slow heating rate of 0.05 K/min to meet the heating rate test

requirements. Due to the defined procedure results fit quite well with the others despite these differences in technology and sample mass.

While the Micro DSC is designed to measure with low heating rates, other DSCs might run at the lower limit of their resolution. It is essential to consider the DSC's specification when applying the procedure.

The RRT revealed also that a standardized calibration is necessary to gain good agreement of results for enthalpy as well as for temperature. It is advisable to calibrate by using several calibration materials and to choose calibration materials which show melting temperatures lower and higher than the PCM's melting temperature to avoid extrapolation. The calibration has to be done using the heating rate which is determined via the heating rate test and applied to the PCM sample.

The correction of baselines is another important step to increase the quality of the measurement results. Some DSC show a baseline drift which makes a comparability of results impossible as this drift is different for every DSC as well as might be different in every measurement. The baseline correction method can eliminate the effect of this baseline drift if the drift linear.

The results presented here show very good agreement if it was possible to apply the complete measurement procedure as well as using the recommended analyses. The results presented in Figure 4b and Figure 5ab show good agreement especially for temperatures measured in the melting process. The results for crystallization show larger deviation (Figure 5) due to the statistical behavior of nucleation. Very small deviations can be found for the onset values of the melting peak which is determined to $27.43\text{ }^{\circ}\text{C} \pm 0.22\text{ K}$ as mean value and standard deviation of all measurements (Figure 4b). The standard deviation of 0.22 K seems to be an acceptable value considering the different shapes of the measured curves. The determined mean value of onset temperature is a bit lower than the values provided by NIST for pure Octadecane [5]. Nist proclaims melting temperatures in the range between $27.85\text{ }^{\circ}\text{C}$ and $28.35\text{ }^{\circ}\text{C}$. The mean value for the heat of fusion measured in this work is determined to $229,62\text{ kJ/kg} \pm 8.9\text{ kJ/kg}$ considering all results, just considering the results shown in Figure 5a it is $232.45\text{ kJ/kg} \pm 4.32\text{ kJ/kg}$ which is again lower than the values given by NIST ($236.15 - 241.65\text{ kJ/kg}$). These differences might be due to impurities of the used Parafol 18-97. The differences in enthalpy between 20 and $30\text{ }^{\circ}\text{C}$ which is plotted in Figure 5a are less than 10 kJ/kg .

4. Conclusion

The characterization of PCMs using DSC instruments requires a careful procedure to achieve reliable results. The comparison of measurements done for the same material at different institutions using different DSC revealed significant differences without applying a standardized measurement procedure. The measurements done during the development showed that the procedure has to include the calibration, the measurement of the sample and the data analysis, as well. An accurate calibration using the heating rate which will be applied to the sample is essential for the characterization of PCM via DSC. It is also essential to measure PCM with a slow heating and cooling rate. Suitable heating and cooling rates have to be determined by applying a heating and cooling rate test as described. An offset and a drift of the baseline can be eliminated by an analysis with correction of the baseline.

The DSC procedure includes: I) the determination of the required heating and cooling rate, II) the calibration of the DSC device under consideration of the determined heating and cooling rate, III) the measurement itself and IV) the data analysis and representation. The procedure is available at [4].

The developed database provides the possibility to uploading, storing and providing high quality PCM-data. It is designed to store measurement data which have been done according the defined DSC procedure. This means that for every measured PCM datasets of three samples and at least three cycles each have to be stored. The user of the data has the possibility to assess the quality of the data and to consider deviations and to compare different material characteristics on a common basis. In general the database addresses users which are doing research on PCM and storages as well as development of PCM systems. In the near future more standard procedure for the characterization of PCMs will be developed. Comparative measurements of thermal conductivity have been just started as well as the characterization of flow behavior and viscosity via rheometers.

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Advanced numerical modelling techniques to tune the properties of heat storage materials for optimal reactor performance

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Heat storage materials like thermo-chemical materials (TCM) and phase change materials (PCM) can be successfully used for long-term heat storage in the built environment and/or industry, dependent on their loading temperatures, energy densities, power densities and recyclability. To gain more insight into the heat and mass transfer processes taking place in these materials during charging and discharging, numerical modeling is needed ranging from the molecular- and micro-scale up to the macro- and reactor-scale. A review of the activities within the working group A3 in the framework of IEA SHC Task 42 / ECES Annex 29 (Task 4229) related to different level modeling and simulations is given here. As an example of activity for developing and testing numerical models to understand and optimize material behavior, we will investigate MgCl₂ hydrates. Molecular models are used to check the effect of water vapor pressure on hydrolysis and dehydration reaction. The results of the water diffusivity in the crystalline structure can further be used to higher level models in the working group and in a later stage to optimize specific properties of the storage materials with respect to their usage.

Keywords: multi-scale simulations, thermochemical materials, molecular simulations

1. Introduction

Within the framework of IEA-SHC Task 42 and IEA-ECES Annex 29, the activities in the Numerical Modeling working group are aimed at developing and testing numerical models that help to understand and optimise the material behaviour and the dynamic behaviour 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. The Working Group includes the following activities: a) Micro-scale modeling, b) Meso-scale modeling, c) Macro-scale modeling, d) Multi-scale approach, e) Thermo-mechanical modeling, f) Reactor models. The knowledge of the thermodynamic properties and the dynamical behavior of all the materials and the components is the basis for the design of a storage device and the different level numerical models can help to understand how the limiting parameters can or should be adapted for the assigned task, reducing the number of time consuming and cost intensive experiments.

1.1. Molecular investigation of salt hydrates

An example is given in this overview, focusing as starting point on molecular investigation of salt hydrates. Magnesium salt hydrates are potential candidate materials for seasonal heat storage systems. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ are particularly interesting due to their high energy storage densities (roughly 2-3 GJ=m³[1]) and their wide availability. Magnesium salts serve as excellent thermochemical heat storage materials, however the performances of such systems are dependent on the material properties and the kinetics of hydration and dehydration reactions. Apart from the crystal structure and composition, the surface defects and dislocations show a large impact on the hydration/dehydration behavior[1]. MgSO_4 hydrates are known to exhibit slow kinetics and the presence of meta-stable states[2]. MgCl_2 hydrates show faster kinetics, but the hygroscopic chloride salts tend to form a gel-like material during hydration or the formation of a solution[2].

Besides, the dehydration of MgCl_2 hydrates is usually accompanied by hydrolysis reaction with the release of HCl, which can potentially damage the material as well as the equipment, and makes the material also less suitable for use in the built environment.

The information about the possibility of the hydrolysis reaction, and its preference over dehydration remains ambiguous and the characterization of the dehydration process which is essential for utilisation.

1.2. Macro-encapsulated latent thermal energy storage

Within the contributing project MALATrans a macro-encapsulated latent thermal energy storage system is being designed. To study the melting and solidification processes within the macro capsules a detailed numerical model is developed. Implemented in the OpenFOAM framework this model is capable of predicting the influence of the settling of the solid phase change material (PCM), the natural convection taking place in the liquid regime of the PCM and the air phase locked above the PCM. Due to the high numerical effort of this model simplified models are needed to study the influence of the heat transfer fluid (HTF) flow around the capsules and the overall behaviour of the storage unit. To investigate the latter strongly simplified computational fluid dynamics (CFD) models as well as 2-D and 1-D system models are evolved. In addition a exergetic evaluation method is developed to predict the optimization limit and the influence of different material parameters on the performance of the storage unit itself and on the overall system [4]. In the following the detailed CFD model as well as the strongly simplified CFD models are discussed more explicitly.

1.3 Numerical models to simulate the thermal performance of PCM-air heat exchangers

Uncertainty studies applied to theoretical models are a practice that allows an analysis of the behavior of the model, calculating the uncertainty in the model outputs induced by the uncertainty in the inputs. This improved knowledge of the theoretical model against these changes helps to know what are the most critical factors as model inputs and, therefore, indicates what should be more controlled in its determination or measurement. In the field of computer simulation of thermal energy storage (hereafter TES) systems by phase change materials (hereafter PCM) that exchange heat with air, it can get to work with important input data uncertainties. Most of these uncertainties are related to the value of air temperature or the airflow at the inlet of the TES unit but so are the properties of the PCM

1.4 CFD models for material and thermophysical properties of PCM storage systems

Development of new applications in the storage field has increased the needs for numerical predictions, be it for the design or the operating management of the associated technologies. To summarize, these calculations can either concern the material and the corresponding thermophysical properties or the whole system and its global features. In the first case, numerical calculations are coupled with some measurements through an inverse technique so as to determine the properties of the material. In the same time, a parametric analysis is also conducted. Then these properties, and the possible uncertainties linked to the key parameters obtained from the parametric analysis, are used to simulate a storage and observe the deviations in function of the input parameters.

2. Methods and Results

2.1 Molecular Dynamics with incorporated chemical reactions for TCM heat storage

Molecular simulations help us to understand the processes which occur at the microscopic level, and hence to describe the transitions between microscopic and macroscopic quantities. In this method, the atoms are considered as point masses and their trajectories are described by the equations of motion, in which they interact with each other through their inter-atomic potential. In order to model reactions in molecular dynamics a reactive force field (ReaxFF) is proposed [3]. ReaxFF was developed to bridge the gap between quantum mechanical and empirical force field based computational chemical methods. The total potential energy is a linear combination of various energy contributions, as given below: $E_{system} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{coa} + E_{C2} + E_{triple} + E_{tors} + E_{conj} + E_{H-bond} + E_{vdW} + E_{Coulomb}$.

The amount of dehydration is calculated by creating a spherical control volume (CV) around the center of mass of the crystal inside the simulation box. The amount of each of the particles N_i inside the control volume is counted at every iteration. The diffusivity is calculated using the Green-Kubo method. The Green-Kubo method uses the velocity autocorrelation function to compute the diffusivity.

2.2 CFD models for melting/solidifications in macrocapsules

For the detailed CFD model the Volume of Fluid (VOF) [5] approach is applied. The phase change process is accounted for by an enthalpy method with source term [6] and a variable viscosity method (VVM) [7]. The governing equations are as follows:

Mass conservation

$$\frac{\partial \alpha}{\partial t} + u \cdot \nabla \alpha + \nabla \cdot (\alpha(1 - \alpha)u_c) = 0 \quad (1)$$

Momentum conservation

$$\frac{\partial(\rho u)}{\partial t} + \rho u \cdot (\nabla u) = \nabla p + \mu_{eff} \Delta u + \rho \beta (T - T_{ref}) \quad (2)$$

Energy conservation

$$\frac{\partial(\rho c_p T)}{\partial t} + \nabla \cdot (\rho u c_p T) = k \Delta T - \gamma \left[\frac{\partial(\rho \alpha_{PCM} L)}{\partial t} + \nabla \cdot (\rho u \alpha_{PCM} L) \right] \quad (3)$$

Where α_{PCM} is the liquid fraction of the PCM, $(1 - \alpha)$ is the PCM fraction within the capsule and L is the phase change enthalpy.

A first step of simplification leads to a single phase PCM system with no gas phase and a second step of simplification to a model where the PCM capsules are implemented via a source term in the energy equation heating or cooling the HTF.

2.3 Numerical model for thermal performance of PCM-air heat exchangers

The starting point of this paper is the numerical model developed to simulate the thermal performance of PCM-air heat exchangers [1]. A sketch of the TES unit is shown in Fig. 1. The solid-liquid PCM is paraffinic based, commercially available, plate-shape aluminum macro encapsulated [9].

Thus, in this study the following goals have been set:

- a) To analyze the behavior of the theoretical model to modifications in the input variables/parameters;
- b) To identify the most critical factors acting as inputs in the model;

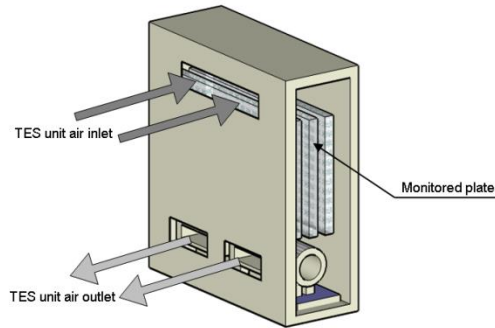


Fig. 1. TES unit sketch, the PCM-air heat exchanger.

For the current study, the following parameters that introduce uncertainty in the results, were considered and classified into three groups:

- Material properties (parameterized h - T curve, and thermal conductivity curve);
- Air conditions at the inlet of the TES unit (temperature and airflow);
- Geometric parameters (PCM plate thickness and width of the air gap between plates).

The determination of the thermophysical properties of PCM has several accepted methodologies (differential scanning calorimetry or DSC, T-history, adiabatic calorimetry). In any case, the results of these measurements are not always consistent between different authors [10]. Because of the importance of both, the enthalpy and the thermal conductivity curves as functions of temperature, these two properties are to be considered for this analysis. Thus, the importance of the knowledge of the material properties is studied. To facilitate the analysis of the results a parameterization of the h - T curve is proposed. This kind of curves can be described by a sigmoidal function. The advantage of using such a parameterization is that it allows defining parameters that can be associated with the most characteristic aspects of the h - T curve.

As shown in Fig. 2 the following associations of the curve parameters can be taken:

h_s , the value of enthalpy in solid phase (just before the start of the solid-liquid phase change);

h_l , the enthalpy in the liquid phase (just after finishing the solid-liquid phase change);

ΔT , amplitude of the thermal window (corresponding to the temperature range in which the PCM is changing phase);

T_{cl} , average phase change temperature of PCM.

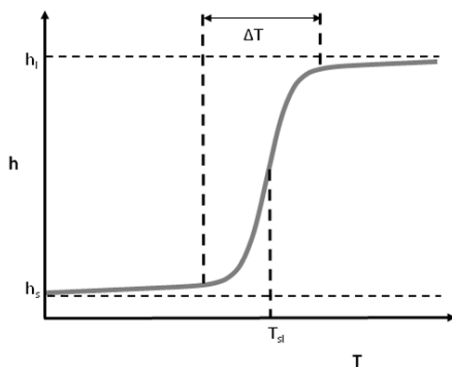


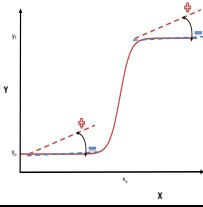
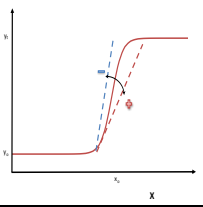
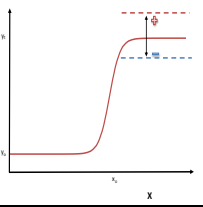
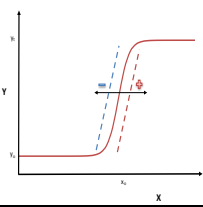
Fig. 2. Generic sigmoidal function applied to an enthalpy-temperature curve.

However, for a better agreement of the parameterized curve with that one obtained in the laboratory, the sigmoidal function is combined with a linear function. Thus, a new parameter is considered. The parameter

b is associated with the slope of the curve in all-liquid phase and all-solid phase (sensible heat). The setting is as shown in Eq. (1). The range of uncertainty assumed for all these parameters is shown in Table 1. The confidence level is 97.5%.

$$h = bT + h_s + \frac{h_l - h_s}{1 + e^{\frac{T - T_{sl}}{\Delta T}}} \quad \text{Eq. 1}$$

Table 1. Parameters setting of the enthalpy-temperature curve

Parameter	b	ΔT	hl	Tsl
Related with	Slope of the sensible heat part	Thermal window	Latent heat	Taverage of phase change
Reference value	3 kJ/(kg·K)	0.9 °C	170 kJ/kg	27 °C
Uncertainty	± 15 %	± 0.2 °C	± 20 kJ/kg	± 1 °C
Effect on h-T curve				

2.4 Numerical methods for material and thermophysical properties of PCM storage systems

The calculations are based on the classical balance equations written in the context of fixed grid methods [11, 12, 13, 14]. In the conductive regime, it thus corresponds to the classical energy equation:

$$\rho \frac{\partial h}{\partial t} = \vec{\nabla} \cdot (\lambda \vec{\nabla} T)$$

In the convective regime, one considers an incompressible flow of a Newtonian fluid with Boussinesq approximation:

$$\vec{\nabla} \cdot \vec{V} = 0$$

$$\rho \left(\frac{\partial \vec{V}}{\partial t} + \vec{V} \cdot \vec{\nabla} \vec{V} \right) = -\vec{\nabla} P + \vec{\nabla} \cdot (\mu \vec{\nabla} \vec{V}) - A \vec{V} + \rho \beta (T - T_{\text{ref}}) \vec{g}$$

$$\rho \left(\frac{\partial h}{\partial t} + \vec{V} \cdot \vec{\nabla} h \right) = \vec{\nabla} \cdot (\lambda \vec{\nabla} T)$$

With the porosity function

$$A = -C \frac{(1 - Y_l)^2}{Y_l^3 + q}$$

This set of partial differential equations is solved directly using a finite volume method, either explicitly or implicitly, or is implemented in the C++ OpenFOAM environment.

3. Results

3.1 Molecular dynamics results

The simulations show that both H₂O and some HCl are released during dehydration, whereas the Mg atoms remain inside the crystal at all times. The results of the simulations indicated the number of each type of atoms inside the control volume (with radius RCV = 50 Å) during dehydration at 450K and 550K . Comparing the results for the two different temperatures, it can be seen that at 550 K more H₂O is released and also slightly more HCl. This result is consistent with the results obtained from the equilibrium analysis. The dehydration behaviour at 450 K for different water vapour pressure was analysed in three different cases. The number of added water molecules to the vacuum space is for (a) 0, for (b) 300 and for (c) 600. From the three simulations, it follows that the dehydration kinetics decreases if the H₂O pressure is increased.

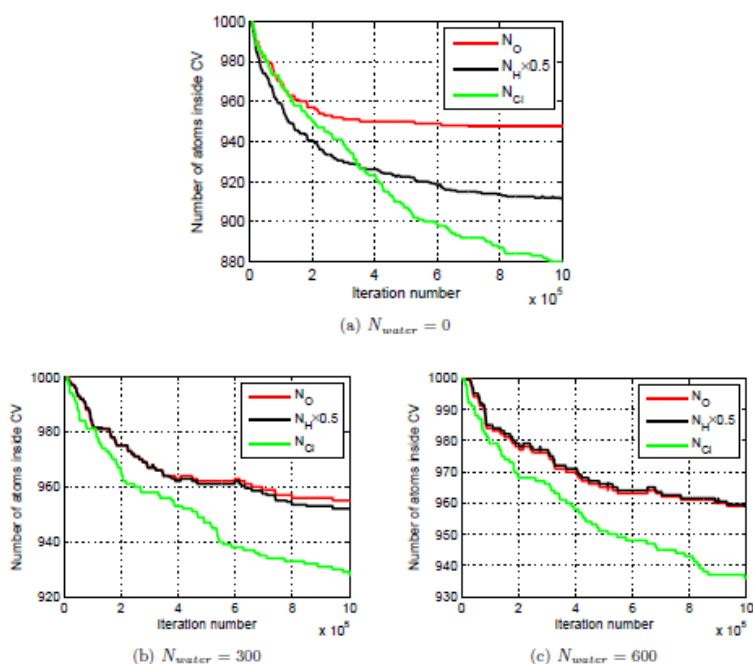


Fig 3. Number of atoms in the control volume during dehydration at 450 K. The number of added water molecules to the vacuum space is for (a) 0, for (b) 300 and for (c) 600.

The diffusivity of water out of the crystal is also measured for three different cases. It is already mentioned that a higher water vapor pressure results in less water evaporated from the crystal. It is found that indeed the highest diffusivity is found at the lowest water vapor pressure, and vice versa, the lowest diffusivity at the highest water vapor pressure. In Table 4.2, the water diffusivity is calculated for two different radii of the control volume. A control volume radius of 25 Å contains mostly the core of the crystal, while a radius of 30 Å also accounts for surface effects. Comparing both cases, it can be seen that the diffusivity increases towards the surface of the crystal. Namely, the atoms are less constrained at the surface and hence they move more freely, resulting in a higher diffusivity.

Case	N_{water}	$p_{\text{H}_2\text{O}}$	Diffusivity $R_{CV} = 25 \text{ \AA}$	Diffusivity $R_{CV} = 30 \text{ \AA}$
Case 1	$N_{\text{water}} = 0$	$p_{\text{H}_2\text{O}} = 0 \text{ mbar}$	$3.4e^{-9} \text{ m}^2/\text{s}$	$3.7e^{-9} \text{ m}^2/\text{s}$
Case 2	$N_{\text{water}} = 300$	$p_{\text{H}_2\text{O}} = 20 \text{ mbar}$	$9.0e^{-10} \text{ m}^2/\text{s}$	$1.2e^{-9} \text{ m}^2/\text{s}$
Case 3	$N_{\text{water}} = 600$	$p_{\text{H}_2\text{O}} = 40 \text{ mbar}$	$8.5e^{-10} \text{ m}^2/\text{s}$	$1.1e^{-9} \text{ m}^2/\text{s}$

3.2 Numerical models results for melting/solidifications in macrocapsules

Figure 4 shows a comparison of results of the detailed CFD model with experimental results for the melting of PCM RT 35 HC Paraffin with initially 303 K and a boundary wall temperature of 315 K. The geometry is a 40x40x40 mm cuboid and initially 75% capsule volume are filled with PCM.

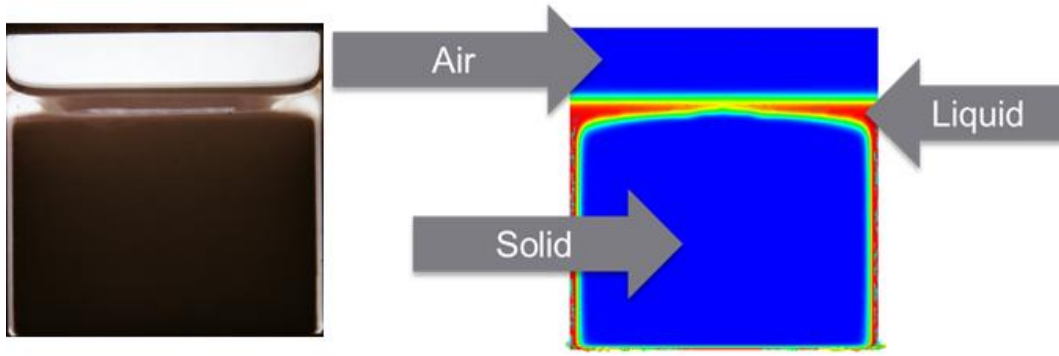


Figure 4: Melt front of a capsule filled with PCM and Air.

The heat transfer rate of the lower wall starts equal to that of the side walls and due to close contact melting it increases to almost 90 % of the overall heat transfer rate. In addition it is found that the influence of the locked air phase can be satisfyingly considered by an one-phase model with an appropriate boundary condition at the top wall. A comparison of the melting time for different capsule geometries with constant volume yields that a cuboid is favourable over a cylinder and a sphere.

Parallel to the heat transfer modelling the pressure drop and flow distribution within a storage unit is simulated. Whereas on the left hand side of Figure 5 a detailed fluid flow approach is applied, there is a packed bed porosity approach for modelling the permeability of the heat transfer fluid in the sphere packing on the right hand side. The results depict that the pressure drop within the storage unit will be very small, but care has to be taken to avoid a bypass flow at the outer walls.

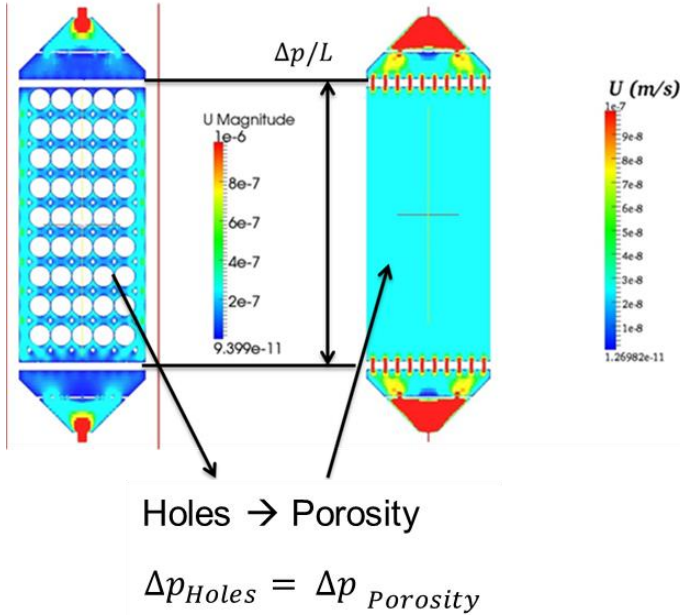


Figure 5: Flow distribution within a lab scale storage unit

These strongly simplified CFD models are also taken to implement the source term accounting for the thermal energy stored in the capsules. This source term is implemented as a function of the enthalpy within the capsule and the HTF temperature. Validating these models is work in progress.

3.3 Numerical model for thermal performance of PCM-air heat exchangers

Figure 6 shows the influence of these parameters in the solution of both the average heat rate expressed in terms of SRC and also indicates the source of each of these parameters. Analyzing the results regarding heat rate, it can be observed that the most influential parameter among the PCM properties is the average phase change temperature (furthermore being the most influential of all considered factors): the lower the temperature, the higher the average heat rate. This result is expected, while decreasing the average phase change temperature, the temperature gradient between the air and the PCM is more pronounced and therefore increasing both the maximum exchanged heat rate and the average heat rate (provided that the PCM is not melted in less than one hour). It can also be observed the importance of the parameter h_l (associated with the latent heat of the PCM in the parameterization of the h-T curve). These results emphasize the importance of a careful determination of the PCM enthalpy-temperature curve or its tuning. On the other hand, the analysis stresses the importance of both the inlet air temperature and the air flow. The air temperature is a crucial factor because in many cases designers will use temperature data from the given area where the TES unit is going to be located (hourly values recorded at a weather station and used as representative values for the specific location) what may become a significant source of error. Regarding the air flow, as it is strongly linked to the convection coefficient, its weight in the heat transfer process is substantial. Thus, it becomes another source of error to consider. From the results, the effect in the responses of reducing the associated uncertainty with the relevant parameters was also tested.

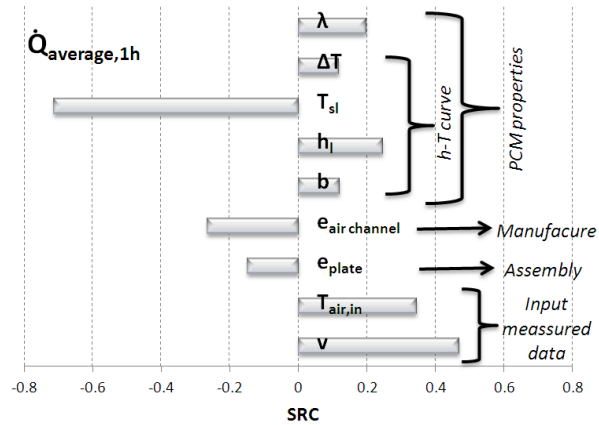


Figure. 6. SRC representation for each of the analyzed factors in the response $\dot{Q}_{average,1h}$

3.4 Numerical results for material and thermophysical properties of PCM storage systems

After the inversion process, one may be capable to determine the enthalpy function of some material [12] and its possible evolution during thermal cycling, as plotted in Fig 7.

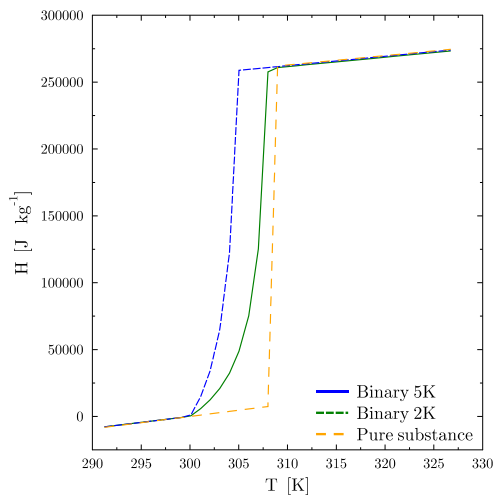
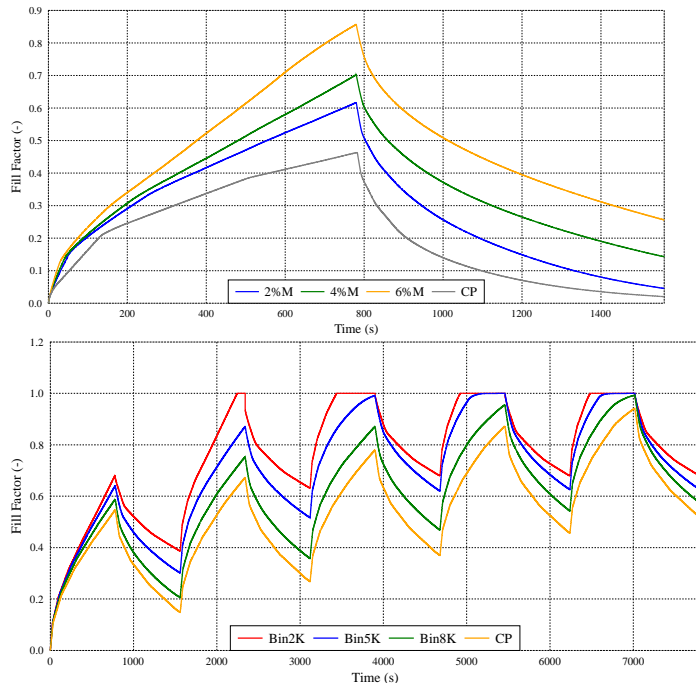


Figure 7. Enthalpy functions obtained with the inverse process during lifetime of a PCM

Given these thermophysical properties, the goal is then to calculate the impact on the performances of a thermal storage (all the others parameters being obviously kept constant) for different cycle [14, 15]. On Figure 8 are shown the fill factor temporal evolution, this one giving a good overview of the amount of energy available in the storage and permitting also to study the charge/discharge dynamics and therefore the input/output powers of the storage.



a) One cycle

b) Five cycles

Figure 8. Temporal evolution of the fill factor for various cycles using the different enthalpy functions corresponding to the PCM evolution with time

4. Conclusions and recommendations

An overview of all the numerical modelling techniques available on the micro-, meso- and macro-scale within the working group and the results from molecular to the larger scale modelling is outlined in the paper.

For the molecular modelling, the MD simulations for a particular system (MgCl₂ hydrates) results show a similar trend with those found from the thermodynamic equilibrium analysis. A higher water vapor pressure counteracts both the dehydration and the hydrolysis reaction, whereas a higher temperature increases the amount of dehydration and hydrolysis. However quantitatively, also some differences are observed. It was predicted that hydrolysis occurring from the di-hydrate was unlikely under the conditions of a heat storage system, while the MD simulations show that, up until a certain water vapor pressure (20-40 mbar), HCl is formed. A comparison of the MD results for three different water vapor pressures, also showed that a higher water vapor pressure ensures a higher crystal density, a more crystalline structure and a lower diffusivity of water.

In the case of the Numerical model for thermal performance of PCM-air heat exchangers, we have analyzed the importance of the variables that introduce uncertainty into the simulations run with the theoretical model. This study can be performed on a larger number of input variables/parameters that potentially provide uncertainty (PCM mass, fan power, roughness of the plate, material properties and characteristic parameters of the case, other PCM properties). Once you have a theoretical model developed, the methodology is worth to assess not only the accuracy of the model inputs but also state which are the more influencing factors for your model at system level, therefore marking the most relevant properties of the storage material (if considered in the model) to further tune.

From the numerical results of material and thermophysical properties of PCM storage systems, it is clear that some deviation may occur if the enthalpy function does not perfectly fit the real behavior of the material. This may arise first if the thermophysical characterization of the PCM is not correctly conducted, and therefore it is clear that this step has to be further investigated and improved so as to define reliable

methods. Secondly, such a bias could also come from the degradation of the product during its lifetime, independently of the precision of the characterization method, and consequently one has either to search for very stable materials (which may be difficult) or to determine the temporal evolution of the thermophysical properties, which is solely done and should thus be also further investigated.

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SHC 2015, International Conference on Solar Heating and Cooling for Buildings and Industry

IEA SHC Task 42 / ECES Annex 29 – Working Group B:

Applications of Compact Thermal Energy Storage

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Abstract

The IEA joint Task 42 / Annex 29 is aimed at developing compact thermal energy storage materials and systems. In Working Group B, experts are working on the development of compact thermal energy storage applications, in the areas cooling, domestic heating and hot water and industry. The majority of application projects were in the field of room heating and domestic hot water. In this article, an overview is given of a large number of applications. The storage technologies used in the applications are latent heat storage, open and closed solid sorption, liquid sorption and salt hydrates and composites thereof. On a broad front, a lot of progress was made in the development of components and systems, providing knowledge and experience regarding the design, numerical modeling, building, testing and economical assessing of components and storage systems. Most important findings are that the interaction of storage materials with the materials of components can be deciding for the technical feasibility, that a number of components, like reactor, heat exchangers and evaporators are less understood than initially thought and need more

development, that the inclusion of storage materials in systems generate new challenges like the occurrence of non-condensable gases and thermo-mechanical effects and that standardized and simplified system approaches are needed.

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Keywords: themal energy storage, applications; PCM; TCM;

1. Introduction

Within the Working Group B (Applications) of the IEA joint Task 42 /Annex 29, a large number of experts from more than 20 research organisations work on applications of compact thermal energy storage technologies. Application fields are cooling, room heating/domestic hot water and thermal storage for industry. The main challenges in the development of applications are in finding an optimal connection between the storage material and the other materials, the components and the system configuration. The problems to be solved are in the area of materials compatibility, like corrosion protection, prevention of side reactions and cycling stability; in the area of component design, with heat and mass transfer optimisation; and in the area of system design with control strategies and cost minimisation.

Thermal storage for cooling applications is the most advanced. There are numerous examples of ice storage systems, running to get a higher system performance or to enable a shift of electricity consumption from daytime to nighttime. Challenges in these systems are the integration of novel PCM with somewhat higher melting temperatures than water and the system optimisation in connection with electricity grids and heating networks.

Most application developments in T4229 are in the area of thermal energy storage for room heating and domestic hot water preparation. Here, there is a broad collection of storage technologies and system concepts being developed and tested. Phase change materials and thermochemical materials are applied as active material in open and closed systems.

A third field of application is in the transportation of residual or waste heat to a remote user by compact thermal storage technologies. Due to scaling effects, this application is first developed for industrial users.

In the Task 42 / Annex 29, special attention is paid to the collaboration between materials researchers and system engineers. A compact thermal energy storage material only has value in a certain application, and the application will imply certain design conditions on the storage material. A first step towards a better collaboration and interaction is for system engineers to understand how materials researcher evaluate the properties of a storage material, and for materials experts to understand the practical implications of integrating material into a storage system. In the Task, work is done to couple the material properties to system performance, although this in most cases is far from straightforward. For sorption storage technologies, an approach was set up using 4 typical operating temperatures with which the operation boundary conditions are determined and the performance of a storage material in an application can be determined [Hauer2015].

Given a certain application, it is necessary to have a common basis for determining the performance of different storage technologies. To this end, a design has been made of a set of Key Performance Indicators KPI's of compact thermal energy storage for seasonal storage. In future, these KPI's will be a valuable tool for comparison of different thermal storage concepts.

In the next chapters, a number of developments that were undertaken by experts from the Task 42 /Annex 29 are shortly described. Although numerous, these are not all the system concepts or technologies developed in connection to the Task. They give, however, a good view of all the developments presently underway including the challenges that are connected to them.

2. Low temperature storage applications

In the Task 42 /Annex 29 the division between application areas was determined by the typical operational temperature ranges: low, medium and high temperature. A low temperature, the typical application is cooling, with temperatures below 20 °C. Medium temperature applications are room heating and domestic hot water, with temperatures between 20 °C and 100 °C. Above 100 °C, the industry applications are situated.

Two developments in the low temperature application field will be described: a latent heat storage in a solar thermally driven cooling and heating system, and a very large ice storage system for building cooling in Japan.

2.1. Solar Heating and Cooling with Absorption Chiller and Latent Heat Storage; ZAE Bayern

The latent heat storage is integrated into a thermal solar heating and cooling system and supports the dry air cooler in the heat rejection system on hot days during summertime to ensure a constant cooling water return temperature of 32 °C. The charged heat is dissipated to the ambient during off peak hours or nighttime when more favorable ambient conditions are available. In wintertime the latent heat storage serves as an additional low temperature storage to buffer solar surplus at constant storage temperatures, leading to low collector temperatures and thus high solar gain. Calcium chloride hexahydrate with a melting temperature of about 29 °C is used as PCM and a propylene glycol - water mixture as heat transfer medium [Helm2014].

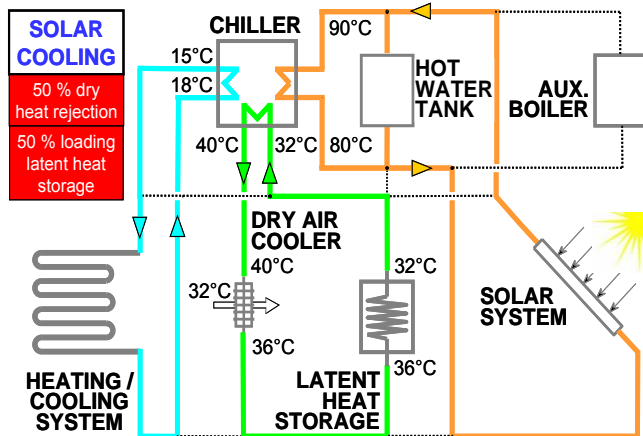


Figure 1: System scheme of the solar heating and cooling installation at ZAE Bayern

The heat storage material (Calcium chloride hexahydrate) has a volume of 1 m³, and the gross volume incl. the storage container accounts for 1.9 m³. The realized storage capacity between 22 and 36 °C is 83 kWh. In the case of discharging, 14 kW peak power can be extracted from the storage.

During the monitoring period the two latent heat storage modules have undergone over 800 loading and unloading cycles under real conditions. Due to the use of the latent heat storage the cooling water return temperature did not exceed 33.5 °C despite dry air cooling and ambient temperatures above 32 °C. In heating mode about 15 % of the overall heat demand has been provided by the latent heat storage.

2.2. Cooling of building; Nagoya Station; Chubu University

Ice thermal storage systems have been popular thermal energy storage systems in Japan since mid-90s. More than 10 thousand systems varying from small ones to huge ones are installed. This example is a district heating and cooling (DHC) facility for an area where the world's largest station building is situated. This DHC adapts the Eco friendly heat supply system which saves energy by combination of "Ice storage system (electricity)" and waste heat

from the “Cogeneration system (Natural gas)”. Energy management is adopted to enhance energy efficiency by continuous analysis of operational data.

As cooling demand in the summer time is at a high plateau from 11:00 to 18:00, by discharging the cold heat stored at night time, the system could reduce the operation hours of the chillers and contribute to energy saving. The electricity demand curve resulted to be flat. Its value is around 3 to 4 MW contributing to load levelling and reduction of operational cost.

The objective of the system is to shave the peak to off-peak hours and take advantage of the tariff difference between day and night. By producing ice at night time utilizing low cost night time electricity and using it to produce cold water in the daytime, this Ice Storage System contributes to cost reduction and load levelling. The facility has ice storage tanks of 1,266 m³ with 49GWh capacity.

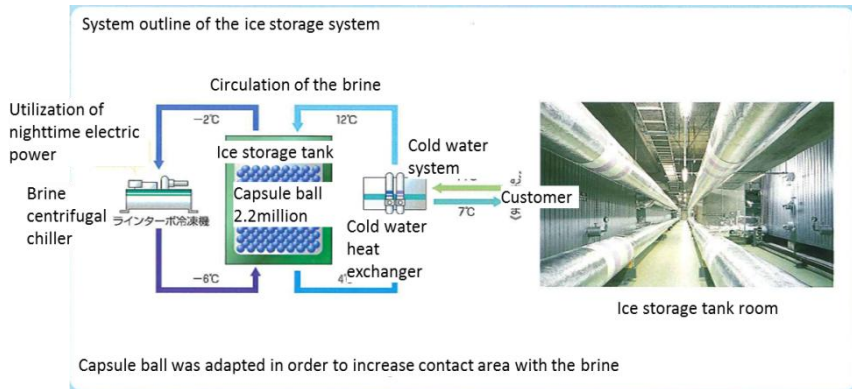


Figure 2: Schematic diagram of the ice tank storage system and photo of the storage tank room

3. Medium temperature storage applications

Typically, the medium temperature applications have the function to provide room heating, domestic hot water or both. In this area, most developments take place with a variety of storage technologies. These range from phase change, solid and liquid sorption to salt hydrate systems.

3.1. Closed absorption system with sodium hydroxide; EMPA and HSR-SPF

In Line B of the EU financed project COMTES a heat storage system based on absorption of vapor by a liquid in a closed process is developed. The working pair is aqueous sodium hydroxide (NaOH-H₂O) and water. In the project a demonstrator was built, functioning as a hybrid system [Fumey2013]. It is composed of hot water tanks as sensible heat storage for short term storage of several days and an absorption heat storage unit for long term storage of weeks and months. The complete system is built into a shipping container on which solar thermal vacuum tube collectors are installed for solar heat harvesting. The Figure 3 shows the outside of the container and the collector field. The absorption system consists of a power unit in the form of a heat and mass exchanger connected to a capacity unit made up of three tanks containing the sorbent NaOH-H₂O in its charged and discharged state as well as the sorbate water. Sorbent and sorbate are pumped to and from the heat and mass exchanger with gear pumps in both the charging and discharging process steps.



Figure 3: Picture of the demonstrator container from the outside with the vacuum tube collector field.

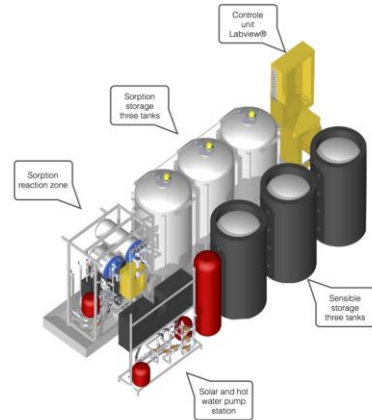


Figure 4: CAD picture of the hybrid system indicating components and function.



Figure 5: Picture of the demonstrator heat and mass exchanger connected to the storage tanks.

The design of the required heat and mass exchanger for desorption and absorption has proven to be challenging. For the sake of a compact build, a single unit for both process steps was pursued [Daguenet-Frick2015]. The falling film tube bundle approach followed in this development has shown poor power performance in the absorption (discharging) process [Fumey2015]. In contrast to this, in the desorption (charging) process power performance according to design calculations was reached. Nevertheless the desired concentrations in absorption as well as desorption were not reached. This is essential for a high system energy density. In the continuation of this work, the concept of a single unit combining the discharging and the charging process steps has to be reconsidered and possibly rejected. In case of the combined evaporator and condenser unit the concept can be followed.

3.2. Solid sorption solar seasonal storage; AEE INTEC, ITW, TH Wildau, Vaillant

In the EU funded project COMTES, in Development Line A, a system is developed, tested and optimized that is based on closed sorption of a solid material. The used working pair is zeolite 13XBF and water. In a first phase the heat and mass transfer in a prototype vessel with about 180 kg of zeolite was numerically modelled and experiments were carried out to validate the model. With this model, the heat exchanger geometry for the two larger vessels (each 1000 litres, 705 kg zeolite) was optimised. The system was built up, containing also 16 m² of vacuum tube

solar collectors, an evaporator/condenser heat exchanger and a separate vessel to contain the condensed water. During the system tests, a computer model emulates the actual heating and domestic hot water demand of a single family house, using the actual weather data and a standard tap water pattern. With the experimental system set up, different control strategies have been tested and a number of parameters (mostly heat loss coefficients) of the system have been determined. The first tests revealed a record storage density for this size of storage of 180 kWh/m³ of bulk material. Since October 2015, a half-year test is started with fully charged vessels, with the aim to assess the system performance in ‘winter’ mode.

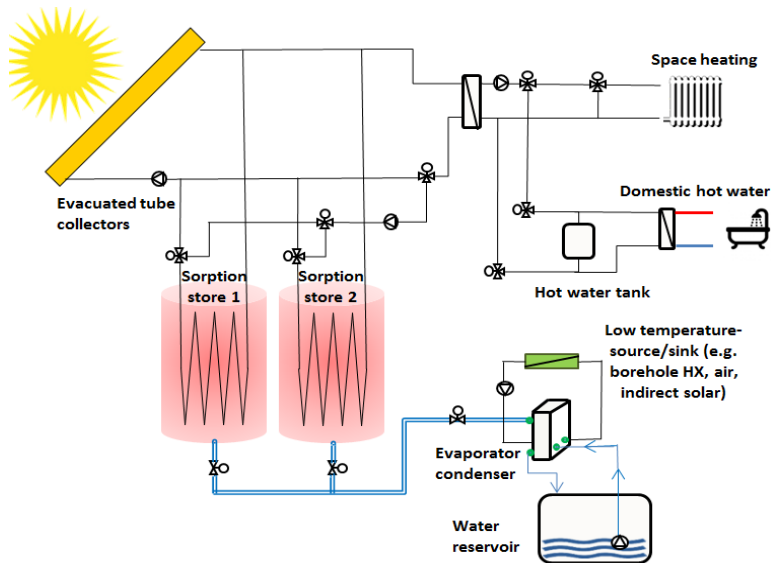


Figure 6: System schematic of the seasonal solar thermal storage system at AEE INTEC.

Figure 7: Picture of the PROSSIS2 prototype: in front, the water storage tank, in glass: the solution storage tank, above: the reactor

In the design and experiments of the storage system, it became clear that one of the major items that need further research and optimisation is the evaporator/condenser unit. Especially the evaporation process of water under low pressures is still too little understood.

3.3. PROSSIS2, LOCIE laboratory, CNRS-USMB

This experimental study develops a closed absorption process using LiBr-H₂O solution for building space heating. The developed system is composed of a reactor and two tanks, one to store the liquid LiBr solution and the other to store liquid water (Figure 7). It functions at low pressure, around 10 mbar. The system works in a discontinuous process (charge in summer and discharge in winter), consequently two reversible flat falling-film heat exchangers are situated inside the reactor where one heat exchanger operates as a desorber and the other as a condenser in the charging period or as an absorber and an evaporator in the discharging period, respectively [Huaylla2014], Huaylla2015]. Experimental tests have been carried out using a solution volume of 60 litres and covering a concentration range between 54% and 60% [mLiBr/mSol]. Results indicate that a heating power of up to 1.5 kW can be obtained in the discharging mode (Figure 8). An optimization of the system performance is envisaged through the improvement of the liquid wetting at the heat exchanger surfaces since in the described tests the percentages of wetted surface were between 30% and 70%. Tests conditions at higher concentrations will be experimented, to weigh the interest of crystallisation of the solution in the storage tank on the storage density. Other working couples will also be tested, as LiBr is quite expensive and could certainly not be used in a real-scale system.

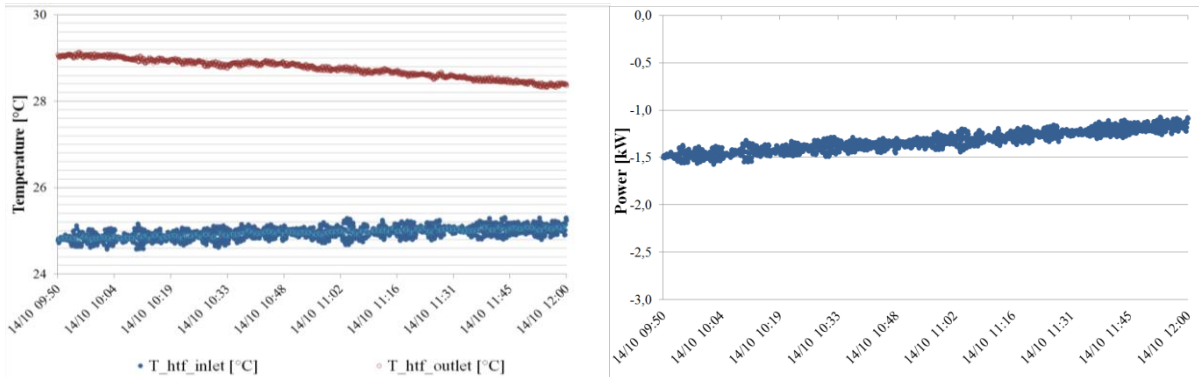


Figure 8: Example of experimental results: (left) temperature evolution of the heat transfer fluid (htf) at the absorber and (right) corresponding exchanged power, during a discharging phase.

3.4. Thermochemical storage demonstration system for space heating and DHW; MERITS project, TNO

MERITS is an R&D project supported by the European FP7 program with the aim to build a prototype of a compact rechargeable thermal battery. Such a product would offer a new solution for improved use of renewable sources for domestic heating, cooling and hot water appliances and thus greatly contribute to the European ambition of an energy-neutral built environment by 2050.

The project is carried out by four research institutes (TNO, VITO, Tecalia, Fraunhofer ISE), two universities (Ulster University, University of Lleida), two SME's (De Beijer RTB, Zonne-Energie Nederland BV), and two industries (Mostostal, Glen Dimplex). The team works with novel high energy density thermochemical materials that can supply required heating, cooling and domestic hot water for a dwelling with up to 100% renewable energy sources (e.g. the sun) throughout the year. The key development issues are:

- The delivery of heat on different dedicated temperature levels for heating, cooling and domestic hot water
- The tailoring to the requirements of individual dwellings
- The design and development of a dedicated solar collector
- The integrated design for the components and enhanced thermo-chemical materials, including the control system

Currently, the prototype of the MERITS setup [Jong2014] is being assembled in Warsaw for demonstration of a fully functional compact rechargeable heat battery (based on Na_2S as working salt hydrate [Roelands2015]), including heating, cooling and domestic hot water (Figure 9). Furthermore the project includes the development of business models and market strategies to foster market take-up before 2020. More information on MERITS is available on the public website “www.MERITS.eu”.

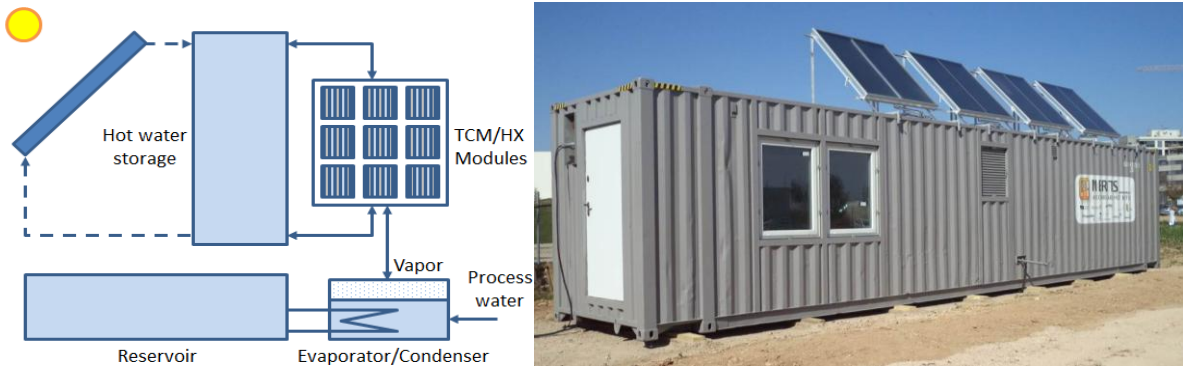


Figure 9: MERITS system setup (left) and MERITS heat battery demonstrator container (right) at the University of Lleida

3.5. FlowTCS, ITW

A long term thermal storage based on an open sorption process with zeolite and salt impregnated zeolite has been developed, set up and tested on a test rig. The sorption storage is characterized by an external reactor concept. A separation is made between the reactor with approximately 30 l of zeolite storage material and the material storage reservoir (in lab test: 200 l storage material volume). This concept enables a high flexibility concerning storage capacity (defined by the size of the material storage reservoir) and thermal power (defined by the reactor operation). The reactor (Figure 10) is designed as a quasi-continuous cross flow reactor. The storage material slowly flows down through the reactor led by gravity. Via a rotary feeder, which controls the mass flow through the reactor, the storage material is discharged. The air flows in cross flow to the material and transports the heat and water vapour into or out of the reactor. During discharge of the sorption storage the heat released in the reactor is transported to the heating system / buffer store via an air to water heat exchanger. For charging of the sorption storage the air is heated up in the air to water heat exchanger. The heat is delivered by solar thermal collectors or any other heat source. An air to air heat exchanger is integrated into the reactor unit for heat recovery.

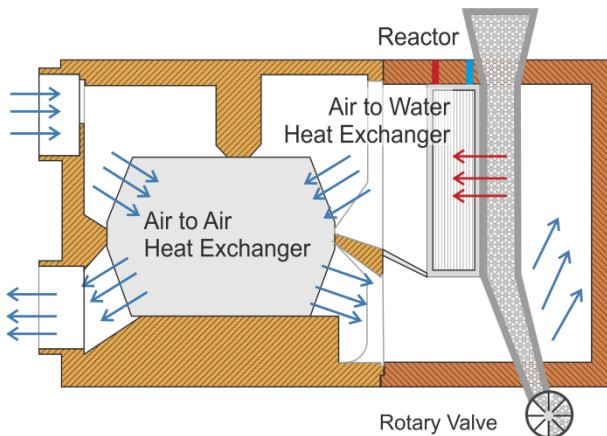


Figure 10: Reactor unit of the sorption storage: discharging mode

The charge and discharge of the developed sorption storage has been investigated on a so called Hardware In the Loop (HIL) test rig. The charge and discharge process was operated fully automatically (e.g. the control and regulation of the material and air flow). Zeolite and salt impregnated zeolite beads have been used as storage material. Different experiments have been conducted by varying the humidity of the air flow (5 g/kg ... 11 g/kg)

and by varying the heat demand of the heating system (400 W ... 1400 W), see Figure 11 and Figure 12. The high thermal performance of the sorption storage could be demonstrated: The temperature lift observed inside the reactor and the thermal power delivered to the heating system are close to the theoretical values. Furthermore, when leaving the reactor, the material was completely loaded (discharge of the sorption storage) or regenerated (charging of the sorption storage). Hence, the energy storage density of the material was fully utilised. The first results show the high potential of the developed storage concept. Research is ongoing to further optimize the sorption storage (e.g. more compact, less heat losses and lower charging temperature) and to proof the concept in a demonstration plant.

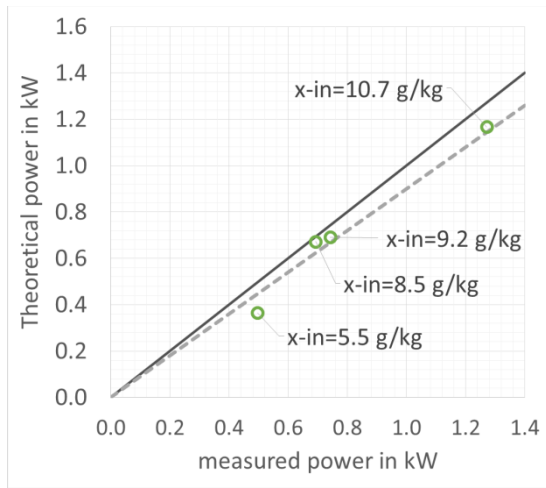


Figure 11: Thermal power delivered to the heating system as a function of the theoretical thermal power

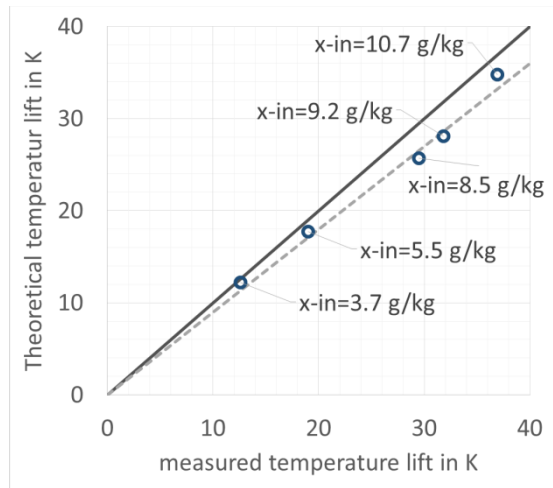


Figure 12: Temperature lift in the reactor as a function of the theoretical temperature lift.

3.6. STAID project, Seasonal Thermochemical Heat Storage in Buildings; CETHIL

Electric peak load is an important problem for electricity suppliers in industrial countries. In France, the critical peak load lasts about 2 h, at the end of the day, between 18 h and 20 h. The use of a storage system during consumption peaks, by punctual discharges, contributes to smooth the load curve and avoids the use of the most polluting power plants throughout the peak.

The purpose of the system developed in this study is to shave the peak by reducing the heating part of the demand. The heat required for space heating depends on the building location and constructive mode. But, relying on standards, it is possible to evaluate the maximum peak load for a low energy building. Focusing on Europe, it is possible to evaluate the mean values of the peak load for space heating, i.e. 20 W m^{-2} for a low energy building. Assuming a single-family house of 100 m^2 , the specification requirements for the heat released is 2 kW during 2 h equivalent to 4 kWh of energy stored.

The thermal energy storage system (TESS) will be integrated in the ventilation system of the building. Thus, the TESS is designed to be an open-system. The principle of the system integration is given in Figure 13. During desorption (i.e. charge), air coming from the building or from outside is heated using a heat source like solar air collectors or an electrical heater, provided that the dehydration temperature is reached. Then the air is sent through the reactor to dehydrate the material. The airflow leaving the reactor can also be used to heat fresh air coming from the exterior with the help of a heat exchanger. During sorption (i.e. discharge), moist air is extracted from the building and passes through the reactor. The water contained in the moist air is used for the hydration of the material. The hot air leaving the reactor is used to heat fresh air.

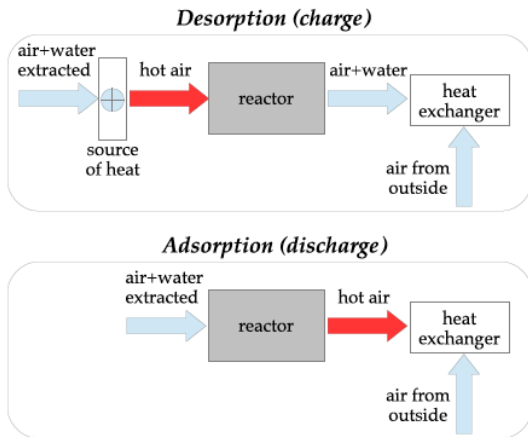


Figure 13: System integration with storage and release phases

Figure 14: Picture of the experimental prototype

Zeolite is the material used in the reactor, 80kg. Dealing with the price criteria, Na-X has finally been selected even if a lower heat of hydration than Na-Y (difference about 5%). The whole system consists of two sub-reactors and ducts to drive the airflow into the reactors. The length of the reactors upstream and downstream ducts is ten times their diameter in order to allow a correct measurement of the airflow. Of course an end user system should be more compact. A picture of the reactor is given in Figure 14. Table 1 shows the experimental conditions during the tests.

Test number	Dehydration		Hydration			Configuration
	T [°C]	Flowrate [m ³ h ⁻¹]	Hr [%]	T[°C]	Flowrate [m ³ h ⁻¹]	
1	180	180	70	20	180	parallel
2	180	180	70	20	180	serial
3	120	180	70	20	180	parallel
4	120	180	50	20	180	parallel
5	180	120	70	20	120	parallel

Table 1: Experimental conditions of the tests

Figure 15 shows the evolution of sensible power generated by the TESS according to the test cases. The serial configuration (test 2) is reaching a higher maximum power than the equivalent parallel configuration (test 1). This feature is due to the thermal mass of the second reactor requiring energy from the first one in serial configuration. Hence, serial configuration is not suitable as the maximum power is not constant. Comparing tests 1 and 3, we can observe that decreasing the dehydration temperature leads to decrease the energy but with the same sensible power: duration of maximum is lower for test 3 than for test 1. The maximum power value is 2250 W. The comparison between test 3 and 4 shows the influence of the relative humidity since for test 3 it has been set to 70 % while this value is 50 % for test 4. Thus, the sensible power decreases to 1550 W and the hydration phase is about an hour longer. The results from test 5 show the influence of decreasing the airflow rate to 120 m³ h⁻¹ both for hydration and dehydration phases. Hence, the released energy is the same as test 1 but with a lower maximum power: 1500 W against 2250 W. The hydration phase in this configuration lasts 9 h at the maximum power and decreases to 0 W after 14 h.

The aim of this work was to develop and to characterize a zeolite thermal energy storage system to supply at least 2000 W sensible heating power during 2 h. The experimental results show that it is possible with the designed open

reactor, which provided 2250 W during 6 h, namely 27.5 W kg⁻¹ of material. The reactor size can even be reduced to really meet the requirement of 2 h.

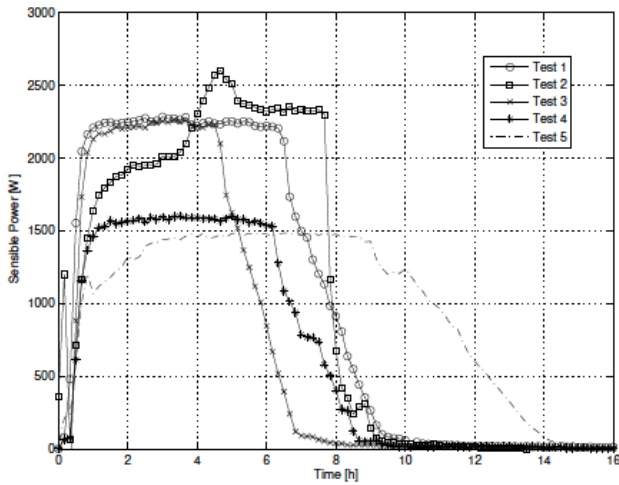


Figure 15: Sensible power generated by the TESS

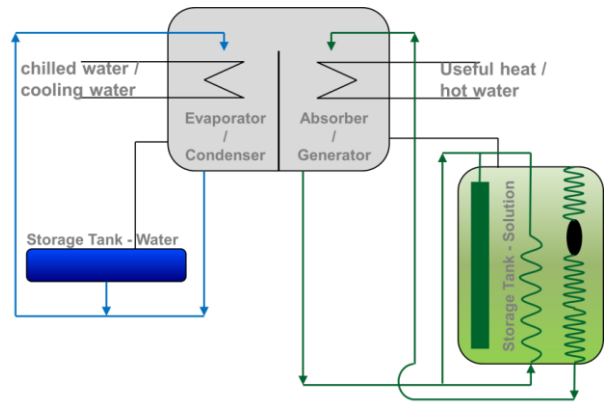


Figure 16: Scheme of the ZAE Bayern thermochemical heat storage using aqueous LiBr solution

3.7. Thermochemical heat storage using aqueous LiBr solution; ZAE Bayern

A thermochemical heat storage operating equivalent to an absorption heat pump, see Figure 16. Utilising solar heat (simulated by a gas-fuelled boiler) to charge the storage (i.e. to concentrate the lithium bromide solution by stripping water); during discharging, low temperature heat is used to evaporate the previously stripped water and the vapor is absorbed into the solution, decreasing the concentration of salt and releasing heat which can be used for low temperature heating. The charging power of the system is 6 kW, with charging/discharging temperatures of 70/30 °C; The storage has a total net volume of 0.5 m³ storage material, with 85 kWh storage capacity.

3.8. Long term heat storage with stable supercooled sodium acetate trihydrate; DTU

Sodium acetate trihydrate can be melted by solar energy in the summer. The melted salt can be cooled down to ambient temperature in its liquid phase without solidifying. Utilizing this supercooling effect the heat storage has no heat loss for a period when it rests at ambient temperature. When heat is needed solidification is started and the temperature in the salt increases to the melting temperature of 58 °C. The heat can be discharged and utilized. Figure 17 illustrates the principle by means of the heat content of sodium acetate trihydrate in the temperature interval from 20°C to 90°C. Different heat storage modules have been tested, both in laboratory heat storage test facilities and as part of a laboratory demonstration system consisting of 22.4 m² solar collectors, a PCM heat storage consisting of 4 modules as shown in Figure 18 and Figure 19 and a buffer tank [Dannemand2015a].

The main challenges of the concept are to achieve stable supercooling, reliable activation of solidification, sufficiently high heat exchange capacity rates to and from the heat storage, high enough heat content of the heat storage and long term stability of the heat storage with the high heat content [Dannemand2015b].

The ongoing test of the demonstration system will hopefully elucidate that the challenges have been tackled, [Berg2015].

Based on the knowledge gained in the projects it is hopefully possible in the future to develop economically attractive compact long term PCM heat storages.

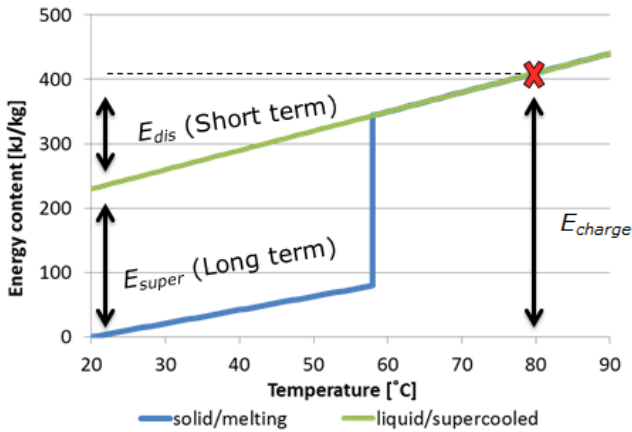


Figure 17: Heat content of sodium acetate trihydrate in the temperature interval 20°C-90°C.

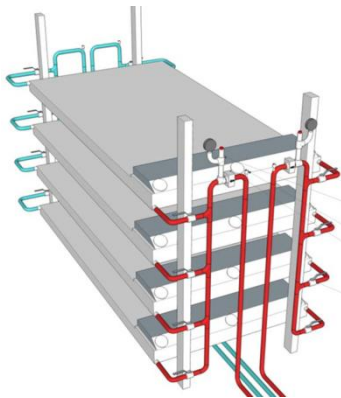


Figure 18: Sketch of PCM heat storage with four modules for the demonstration system.



Figure 19: PCM heat storage with four modules for the demonstration system.

3.9. PCM in building construction (radiant floor) or in HVAC systems; University of Zaragoza

The project has the aim to implement a thermal energy system (TES) with phase change materials (PCM) system in several applications: the energetic optimization in buildings with the use of PCM in their construction, and the study of the improvement of HVAC systems because of the use of PCM. For this purpose, adequate materials to the studied applications have been searched, and their most important thermophysical properties have been evaluated. All these data will improve the data base available within the research group. Later, the systems have been designed and a prototype of some of them have been built. Simulation has been used as a tool to extrapolate the results to other climates, applications, etc. Finally, an energetic and exergetic evaluation has been done to show the contribution to the energy demand and to the reduction of the ambient impact, also an economic viability analysis has been done. In the next steps, the life cycle analysis will be used to improve the systems.

The technical characteristics of one of the studied systems are: Storage capacity 6.8 kWh/per cycle; 132 kg of PCM; 250 kg overall system mass. First applications foreseen are free cooling or temperature maintenance in rooms (i.e. telecom shelters or similar)

During the project, several challenges came up: trade-off between material properties and system design is a feature (a better designed heat exchange system but with worse PCM -in terms of melting enthalpy and thermal conductivity-, can lead to better thermal performance). To turn some of the PCM based TES solutions more economically feasible, finding low cost PCM can be an issue. Further details can be found in [Lazaro2009], [Dolado2011] and [Mazo2012].

3.10. Under floor PCM for residential heating; Chubu University

PCM containers are installed under the floor of a residential house, see Figure 21. The system will take advantage of the electricity tariff difference between day and night [Lun2015]. The phase change material applied is paraffin wax with 25 °C melting temperature. The material is packed in a container of 300 x 300 x 20 mm and is installed in wooden boxes. 90 containers which contain 90 kg of PCM in total were connected in series under the floor of the house. During night time when discount tariff is offered, an air conditioner is in operation, charging the PCM containers. From 7:00 in the morning, a fan is turned on to circulate the air through the house for discharging. Demonstration houses are built in Nagano city and Aichi prefecture in Japan.

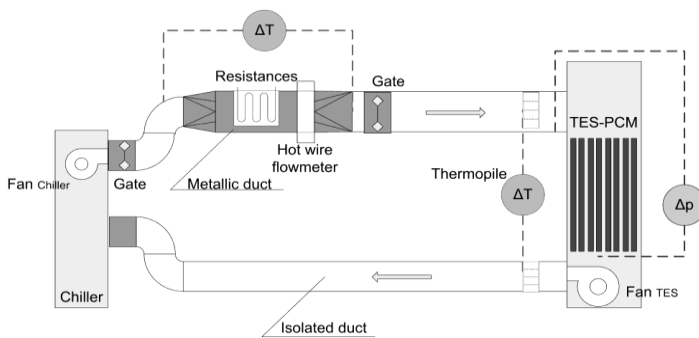


Figure 20: Experimental setup to test real scale PCM-Air TES systems.

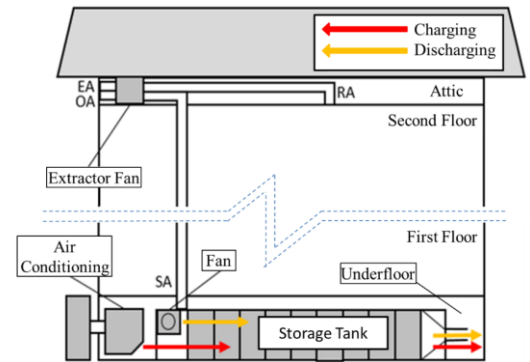


Figure 21: Schematic of the underfloor PCM storage system

3.11. Compact latent heat TES for micro-cogeneration plants; University of the Basque Country

The aim of the project is to develop a modular latent heat thermal energy storage system based on plates for its integration within micro-cogeneration (micro-CHP) plants. The plates are made of hollow aluminium filled with PCM. The HTF (water) flows in laminar regime through the spaces between the parallel plates exchanging heat with the PCM by the plate surfaces. The plates are grouped in stacks as it can be seen in Figure 22. The modular nature of the stacks of plates makes the solution very suitable for applications with different constraints, such as volume, capacity, power, maximum admissible discharging time, etc. The solution can be also integrated in other intermittent applications, for example thermal solar, waste heat, etc.

Figure 23 represents the integration of the latent heat TES system within the micro-CHP plant. It is placed in series at the return from the consumption (space heating and domestic hot water DHW). Thus, the system stores the surplus heat that is not consumed by the user, storing at full load at those moments with the micro-CHP operating with no demand. It can be seen that the domestic hot water (DHW) production has priority over the heating load, being produced by a plate heat exchanger. More information about the latent heat TES system and the integration into micro-CHP plants can be found in [Campos-Celador2013] and [Campos-Celador2014].

RT60 PCM by Rubitherm GmbH was selected as the latent storage medium with a phase change around 60°C. The design parameters are the following: 4.1 kW charging (at 65°C), 3.4 kW discharging (at 50°C); and 0.3 m³ volume with about 7.2 kWh capacity. Though experiments have been done at laboratory scale, the full scale LHTES

prototype is currently under construction. The plate based latent heat TES system prototype will be included in a micro-CHP plant and tested under real operation conditions.

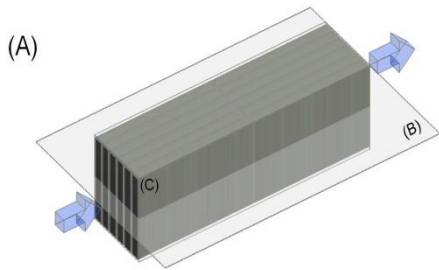


Figure 22: Schematic view of a stack consisting of 12 plates (6 in parallel and 2 in series)

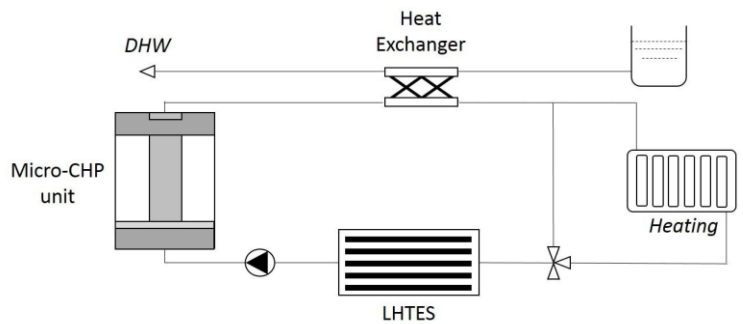


Figure 23: Schematic view of the latent heat TES integration within the micro-CHP installation

4. Storage applications for industry

4.1. Mobile sorption heat storage for industrial waste heat recovery, ZAE Bayern

A zeolite sorption storage, mounted on a semi-trailer, is charged using heat from a waste incineration plant, and driven to an industrial drying process in about 8 km distance, where the heat is released, substituting natural gas. The storage is charged by applying a hot airstream to the system, thus drying the zeolite. Discharging mode requires a moist airstream, which is dried and heated up by passing through the packed bed of zeolite. The operation conditions determine the water content of the zeolite at the charging and discharging cycle, which are important parameters for the energy capacity of the storage. Low invest costs, a short distance between charging and discharging station, a high energy capacity of the storage, and a customer with an almost constant annual heat demand are required to operate a mobile sorption storage system competitively [Kronauer].

The input temperatures to the storage are 250 °C and 60 °C for charging and discharging, respectively. A peak power of 300 kW can be provided for about 8 hours during discharging. Each storage container contains 22 m³ of heat storage material. The storage capacity under the given reference conditions is 4,600 kWh per container.

4.2. Development of macro-encapsulated latent heat storage for the transport of heat, University of Bayreuth

The latent thermal energy storage system is designed for mobile applications. It consists of a 20 feet long ISO container that is transportable with motor trucks.

Table 2: Key parameters of the previous storage container

Inlet temperature (charging/discharging)	90 / 40 °C
Discharging power (final/initial)	50 / 350 kW
Storage capacity (between 40 and 90 °C)	2300 kWh

Based on an already existing design with the key parameters shown in Table 22, an improved storage unit is evolved. For a considerably higher charging and discharging power the heat exchanger surface is increased by macro encapsulation see Figure 25. The range of applications of this mobile latent heat storage device is highly expanded by applying PCM with melting temperatures between 70 °C and 150 °C and the utilization of thermally stable metallic encapsulation materials [Hohlein2016]. Heat sources are for instance industrial waste heat. The

previous storage system based on sodium acetate tri-hydrate with its low melting point of 58 °C is suitable only for the supply of few specific heat sinks, e.g. for heating swimming pool water. The new system will be able to provide heat at a temperature level suitable for process heat applications.

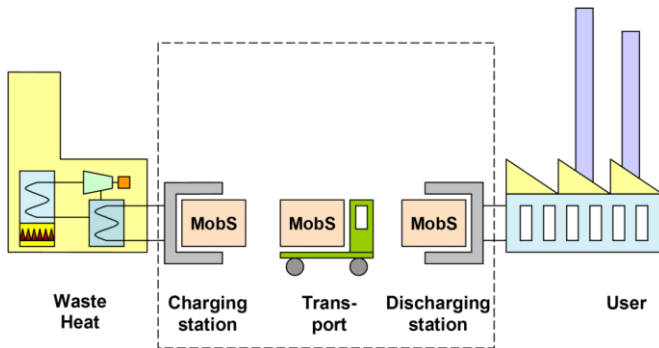


Figure 24: Principle of mobile sorption heat storage in industrial waste heat recovery



Figure 25: Macroscopic encapsulated PCM for mobile latent thermal energy storage of University of Bayreuth

5. Conclusions

One of the main elements in the work of T4229 was the further development of system applications for compact thermal energy storage in three temperature fields: low temperatures for cooling, medium temperatures for room heating and domestic hot water and high temperatures for industry. A large number of groups worked on these applications and their work provided inputs for validation of numerical models and boundary conditions for the further and more targeted development of materials.

Considerable progress was made on a broad range in the development of components and systems, providing knowledge and experience regarding the design, numerical modeling, building, testing and economical assessing of components and storage systems. The vast amount of knowledge and experience that was gained by the different projects, lead to the following conclusions.

The interaction between the storage materials and the materials of the system components can be deciding for the technical feasibility of the combination. Therefore, more targeted development of components should be done in combination with the storage material.

A number of components appeared to be less understood than initially thought. This concerns especially reactors, heat exchangers and evaporators for water under low pressure. These components need targeted attention for further research and development.

The inclusion of storage materials in components or systems generate new challenges like the occurrence of non-condensable gases and thermomechanical effects. To circumvent or prevent these, novel technologies have to be sought and applied in the components design.

Especially for thermochemical technologies, new technologies to determine the state of charge of the storage need to be developed.

In order to obtain a better comparison between system performance of different technologies, more standardized and simplified system approaches are needed.

Additionally, long term testing under real operating conditions (high level integration) will be fundamental for the implementation of novel TES approaches. This will have to assess the interaction between the TES system and the rest of the components through the lifespan of the whole application.

And in general, the development of all components and system configurations should be more aimed at cost reduction of the final system.

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IEA SHC Task 42 / ECES Annex 29 – A simple tool for the economic evaluation of thermal energy storages

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Abstract

Within the framework of IEA SHC Task 42 / ECES Annex 29, a simple tool for the economic evaluation of thermal energy storages has been developed and tested on various existing storages. On that account, the storage capacity costs (costs per installed storage capacity) of thermal energy storages have been evaluated via a Top-down and a Bottom-up approach. The Top-down approach follows the assumption that the costs of energy supplied by the storage should not exceed the costs of energy from the market. The maximum acceptable storage capacity costs depend on the interest rate assigned to the capital costs, the intended payback period of the user class (e.g. industry or building), the reference energy costs, and the annual number of storage cycles. The Bottom-up approach focuses on the realised storage capacity costs of existing storages. The economic evaluation via Top-down and Bottom-up approach is a valuable tool to make a rough estimate of the economic viability of an energy storage for a specific application. An important finding is that the annual number of storage cycles has the largest influence on the cost effectiveness. At present and with respect to the investigated storages, seasonal heat storage is only economical via large sensible hot water storages. Contrary, if the annual number of storage cycles is sufficiently high, all thermal energy storage technologies can become competitive.

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Keywords: Sensible heat storage; Latent heat storage; Thermochemical heat storage; Storage capacity costs

1. Introduction

Heat and cold storage are key technologies for increasing energy efficiency and a more extensive utilisation of renewable energy sources. A major barrier to the development of thermal energy storage (TES) technologies is cost uncertainty [1]. In order to make a rough estimate of the economic viability of an energy storage for a specific application, a simple tool was developed, which consists in determining the maximum acceptable storage capacity costs via a Top-down approach and the realised storage capacity costs via a Bottom-up approach.

Nomenclature

ANF	annuity factor / a^{-1}
i	interest rate
INC	investment costs / €
n	payback period / a
N_{cycle}	number of storage cycles per year / a^{-1}
REC	reference energy costs / $\text{€} \cdot \text{kWh}_{\text{en}}^{-1}$
SC	storage capacity / kWh_{cap}
SCC_{acc}	maximum acceptable storage capacity costs / $\text{€} \cdot \text{kWh}_{\text{cap}}^{-1}$
SCC_{real}	realised storage capacity costs / $\text{€} \cdot \text{kWh}_{\text{cap}}^{-1}$

2. Methods

2.1. Top-down approach

The Top-down approach assumes that the cost of energy supplied by the storage should not exceed the costs of energy from the market[†] (hereinafter referred to as REC = reference energy costs). Following this assumption, the maximum acceptable storage capacity costs (hereinafter referred to as SCC_{acc}) are calculated from the discount rate of storage capital i , the payback period of the investment n , the number of storage cycles N_{cycle} , and the reference energy costs [2]. To simplify the evaluation, this analysis neglects operating costs and changes in the cost of energy production over time. Detailed information about the storage technology or implementation are not required for this approach.

Using the interest rate assigned to the capital costs and the payback period, the present value annuity factor ANF can be calculated to determine the present value of the energy storage capital. ANF as a function of payback period n and interest rate i can be calculated via Eq. (1):

$$ANF = \frac{(i+1)^n \cdot i}{(i+1)^n - 1} \quad (1)$$

Interest rate i and payback period n depend on the user. Three classes of users are referred to in the following discussion. In the *industry* sector, high interest rates of 10% and above and short payback periods of 5 years and below are usual. For *building* applications, moderate interest rates of 5% and longer payback periods of 15 – 20

[†] Communicated e.g. by Dr. Rainer Tamme, German Aerospace Center (DLR), in many presentations since 20 years.

years are acceptable. In addition, one might also assume a user that can tolerate even longer payback periods of 25 years and low interest rates of 1%. The latter user class has probably political or ecological reasons for the investment and is hereinafter referred to as *enthusiast*. In Figure 1, the annuity factor ANF is plotted as a function of the payback period n for interest rates of 10% (red solid line) indicating *industry*, 5% (blue dashed line) indicating *building*, and 1% (green dotted line) indicating *enthusiast*.

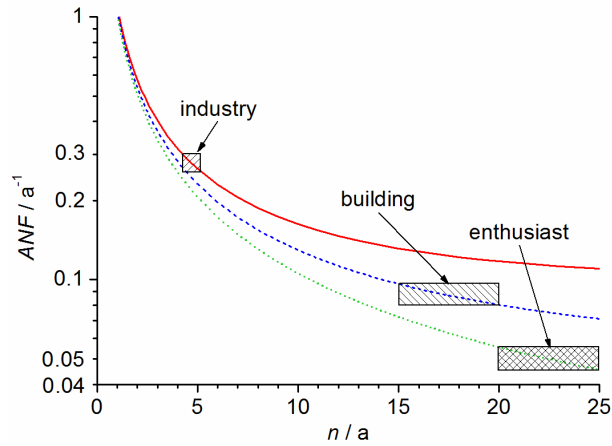


Figure 1. Annuity factor ANF as a function of payback period n for three user classes (industry $i = 10\%$, building $i = 5\%$, and enthusiast $i = 1\%$); framed regions indicate acceptable annuity factors for these user classes.

In the *industry* sector, a payback period of 5 years yields an ANF of about 0.26. Therefore, a range of ANF from 0.25 to 0.30 is considered as storage capacity cost annuity for industrial users. In the *building* sector, ANF are within 0.07 – 0.10, and in the case of *enthusiasts*, consequently, low ANF between 0.04 and 0.06 can be achieved.

The maximum acceptable storage capacity costs SCC_{acc} , calculated in € per kWh installed storage capacity ($\text{€}\cdot\text{kWh}_{cap}^{-1}$), are simply the product of the substituted reference energy costs REC , given in € per kWh energy ($\text{€}\cdot\text{kWh}_{en}^{-1}$), and the number of storage cycles per year N_{cycle} divided by the annuity factor ANF :

$$SCC_{acc} = \frac{REC \cdot N_{cycle}}{ANF} \quad (2)$$

Eq. (2) neglects operating costs and changes of REC over the payback period. Nevertheless, this analysis illustrates the relationship between acceptable storage capacity costs, the frequency of storage handling, and the costs of reference energy that is substituted by the storage system.

Similar to ANF , a range is considered for REC . As the focus of this work is to evaluate the costs of thermal energy storages, REC given in Table 1 correspond to heat or cold supply costs. Table 1 summarises the economic boundary conditions of the three user classes that are taken into account in the Top-down evaluation.

Table 1. Economic boundary conditions: costs of substituted reference energy REC and storage annuity factor ANF calculated via Eq. (1).

User class	$REC / \text{€}\cdot\text{kWh}_{en}^{-1}$		ANF / a^{-1}	
<i>Industry</i>	0.02	0.04	0.25	0.30
<i>Building</i>	0.06	0.10	0.07	0.10
<i>Enthusiast</i>	0.12	0.16	0.04	0.06

As an aid to orientation, expectable ranges for the costs of substituted reference energy REC and the storage annuity factor ANF are considered. In this way, a high and a low cost case are analysed for each user class. The high

case considers the max. REC and the min. ANF , and the low case the min. REC and the max. ANF , respectively. Future changes of the reference energy costs REC can be taken into account by adjusting the values of REC given in Table 1 appropriately, e.g. by considering average REC for the intended payback period. According to Eq. (2), SCC_{acc} is proportional to REC and, hence, an increase in REC will cause a similar increase in SCC_{acc} . Operating costs should be taken into consideration if they are not negligible compared to the capital costs. Especially in the case of mobile storages, operating costs are expected to have a significant influence on the economic viability. To consider operating costs requires a modification of the Top-down approach. According to the procedure outlined above, the Top-down approach calculates the costs per storage capacity. However, if operating costs have to be included, the costs per stored energy have to be determined, for instance on an annual basis.

2.2. Bottom-up approach

The Bottom-up approach focuses on the realised storage capacity costs of existing storage systems (hereinafter referred to as SCC_{real}). To investigate particular storages, a questionnaire was developed which inquires among other technical parameters both actual and expectable investment costs INC of the storage divided into costs of the heat storage material, costs of the storage container or reactor, and costs of the charging/discharging unit. For the Bottom-up approach, sensible heat storage, latent heat storage via PCM, and thermochemical heat storage including sorption storage have been investigated. Besides commercially available storage systems, innovative prototypes which are subject of ongoing research have been analysed [3]. The realised storage capacity costs SCC_{real} are simply the investment costs INC divided by the installed storage capacity SC :

$$SCC_{real} = \frac{INC}{SC} \quad (3)$$

INC sums up heat storage material costs, storage container or reactor costs, and cost of charging and discharging device. As in the case of SCC_{acc} , SCC_{real} are calculated in € per kWh installed storage capacity ($€ \cdot kWh_{cap}^{-1}$).

3. Results

The maximum acceptable storage capacity costs SCC_{acc} for the three user classes calculated via Eq. (2) are plotted as a function of the annual number of storage cycles N_{cycle} in Figure 2.

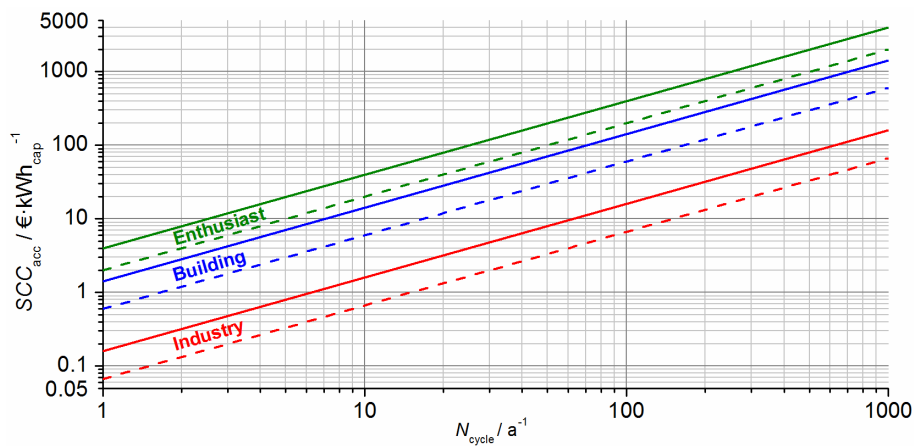


Figure 2. Maximum acceptable storage capacity costs SCC_{acc} for three user classes as a function of storage cycles per year N_{cycle} : enthusiast high/low case (green solid/dashed line), building high/low case (blue solid/dashed line), and industry high/low case (red solid/dashed line).

Solid lines indicate the high case of each user class and dashed lines the low case, respectively. A double-

logarithmic scale was chosen to visualize both SCC_{acc} of long-term storages with only few cycles per year and short-term storages with several hundred cycles per year. The results of the Top-down evaluation as shown in Figure 2 indicate that, for a fixed cycle period N_{cycle} , SCC_{acc} depend on the user’s economic environment. The low case of the industry sector and the high case of enthusiasts differ by a factor of about 60 in costs. Short-term storage with several hundred storage cycles per year, however, allows several hundred times higher storage costs because of the larger energy turnover.

For reasons of clarity, the comparison of SCC_{acc} (Top-down approach) with SCC_{real} (Bottom-up approach) is split up into four figures: long-term storages (Figure 3), hot-water storages up to 30 m³ storage volume (Figure 4), and short-term storages (Figure 5 and 6). Relevant specifications of the investigated storage systems are listed in Table 2.

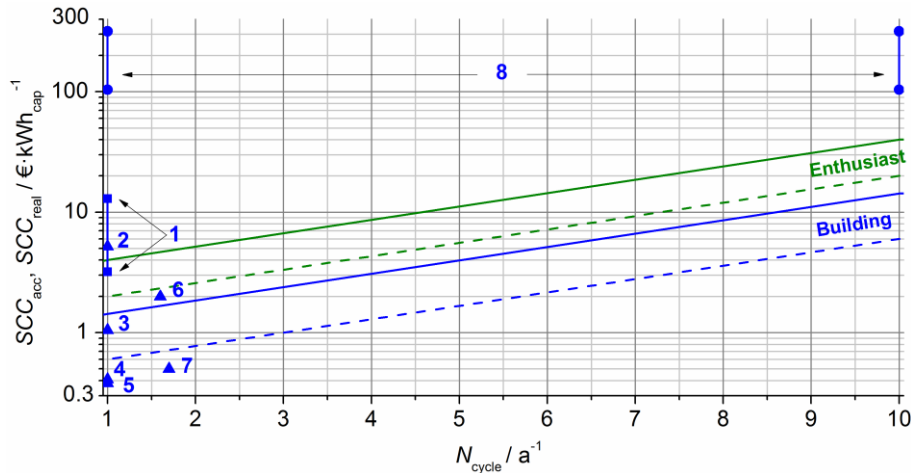


Figure 3. Maximum acceptable storage capacity costs (SCC_{acc}) and realised storage capacity costs (SCC_{real}) for long-term storages.

Seasonal TES with max. 2 cycles per year requires storage capacity costs below 3 €·kWh_{cap}⁻¹ in the building and below 0.4 €·kWh_{cap}⁻¹ in the industry sector, respectively. With respect to the storages under investigation, seasonal TES is only economical via large sensible hot water storages (cf. systems 3 – 7, Figure 3).

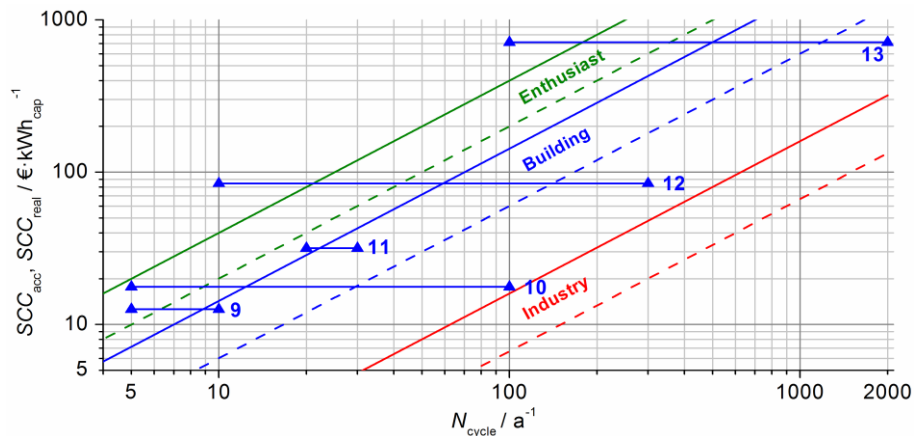


Figure 4. Maximum acceptable storage capacity costs (SCC_{acc}) and realised storage capacity costs (SCC_{real}) for hot water storages up to 30 m³ storage volume.

In the case of hot-water storages up to 30 m³ storage volume, the *building* sector is usually targeted. However, these storage can become financially attractive for *industrial* applications if N_{cycle} is sufficiently high. Since these

storages can be integrated in a variety of systems, exemplary ranges are indicated for N_{cycle} . The storage capacity SC of the storages 9 – 13 is calculated for the maximum technically permissible temperature ranges indicated in Table 2. To evaluate the economics under application conditions, these temperature ranges have to be adjusted.

On the other hand, in the case of short-term storages, storage systems are intended for either *industry* or *building*. Among the investigated short-term storages, systems 14 – 17 and 18 – 26 have been developed for *industry* and *building* applications, respectively.

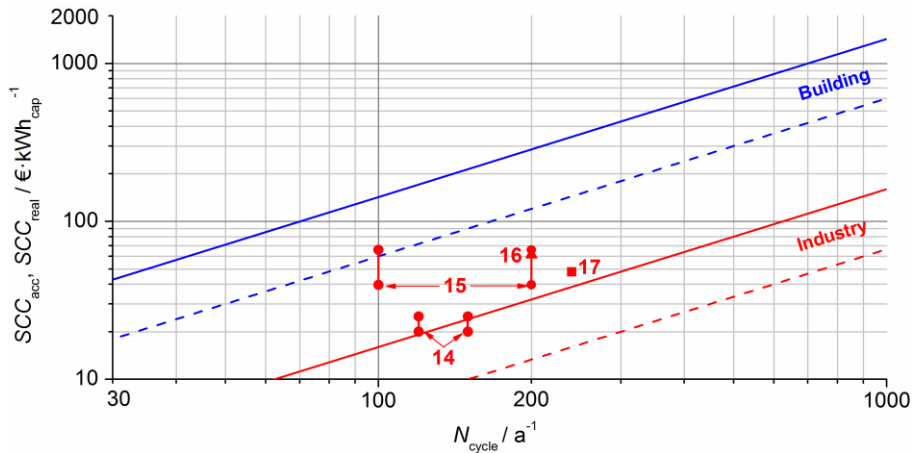


Figure 5. Maximum acceptable storage capacity costs (SCC_{acc}) and realised storage capacity costs (SCC_{real}) for industrial short-term storages.

Considering the investigated short-term storages for industrial applications (cf. Figure 5) it turns out that ice storages (system 14) are cost-effective, and other technologies are within reach.

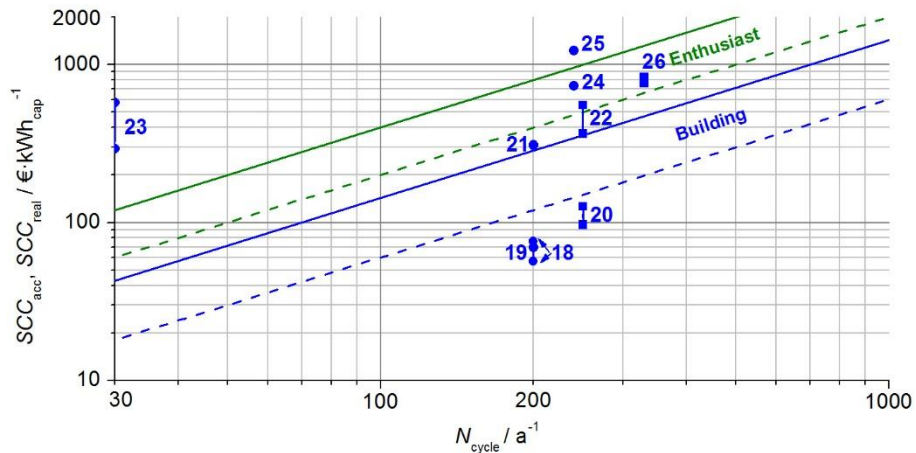


Figure 6. Maximum acceptable storage capacity costs (SCC_{acc}) and realised storage capacity costs (SCC_{real}) for short-term storages in buildings.

In the case of the systems 1, 8, 14, 15, 18, 20, 22, 23 and 26, cost ranges are given for SCC_{real} indicating the interval between actual costs (upper limit) and expectable costs that can be achieved in the near future (lower limit). The mobile PCM storage (system 15) is intended to be operated for 100 – 200 cycles per year with a storage capacity between 1,500 and 2,500 kWh depending on the degree of optimisation.

INC of the large water storages 2-7 are DMC (direct material costs) of the installed systems. INC of the commercial water storages 9-13 are list prices [4]. In the case of the other investigated systems, INC correspond to DMC of prototypes or estimated DMC and, therefore, numbers are roughly rounded. In addition, most of these prototypes are subject of ongoing research and, hence, at a lower TRL with higher investment costs.

Table 2. Specifications of thermal energy storages investigated via Bottom-up approach: annual number of storage cycles N_{cycle} , investment costs INC , installed storage capacity SC , realised storage capacity costs SCC_{real} .

Storage system (Institution)	Description	$N_{\text{cycle}} / \text{a}^{-1}$	$INC / \text{€}$	$SC / \text{kWh}_{\text{cap}}$	$SCC_{\text{real}} / \text{€} \cdot \text{kWh}_{\text{cap}}^{-1}$
1: NaOH storage (Empa)	NaOH sorption; seasonal storage for domestic applications	1	8,000 – 32,400	2,500	3.2 – 13.0
2: Ottruppgård, 1995 (PlanEnergi)	Hot water; 1,500 m ³ ; 35 – 60 °C	1	225,500	43,500	5.18
3: Sunstore 2, 2003 (PlanEnergi)	Hot water; 10,000 m ³ ; 35 – 90 °C	1	671,100	638,000	1.05
4: Sunstore 3, 2013 (PlanEnergi)	Hot water; 60,000 m ³ ; 10 – 90 °C	1	2,671,100	6,960,000	0.38
5: Sunstore 4, 2012 (PlanEnergi)	Hot water; 75,000 m ³ ; 10 – 90 °C	1	2,281,900	5,570,000	0.41
6: Ackermannbogen (ZAE Bayern)	Hot water; 6,000 m ³ ; 20 – 90 °C	1.6	942,400	472,400	1.99
7: Attenkirchen (ZAE Bayern)	Hot water + borehole heat exchanger; 7,000 m ³ ; 10 – 90 °C	1.7	327,300	654,600	0.50
8: SAT storage [5, 6] (DTU, Univ. Graz)	Supercooled sodium acetate trihydrate, seasonal storage modular system	1 – 10	2,700 – 4,120	13 – 26	104 – 317
9: VSI – 30 m ³ (ZAE Bayern, Hummelsberger GmbH)	Vacuum super insulated hot water storage; 30 m ³ ; 5 – 95 °C	5 – 10 ^a	37,888	3,020	12.5
10: allSTOR VPS/3 2000/3-7 (Vaillant GmbH)	Hot water; 2,000 l; 5 – 95 °C	5 – 100 ^a	3,559	202	17.6
11: VSI – 5 m ³ (ZAE Bayern, Hummelsberger GmbH)	Vacuum super insulated hot water storage; 5 m ³ ; 5 – 95 °C	20 – 30 ^a	15,962	504	31.7
12: actoSTOR VIH RL 500-60 (Vaillant GmbH)	Hot water; 500 l; 5 – 110 °C	10 – 300 ^a	4,953	58.7	84.4
13: actoSTOR VIH CL 20 S (Vaillant GmbH)	Potable water; 20 l; 10 – 70 °C	100 – 2000 ^a	965	1.35	715
14: Ice storages (Cristopia)	Storages with nodules filled with water/ice; installations in Europe	120 – 150	-	-	20 – 25
15: NaOAc mobile storage (Univ. Bayreuth, LaTherm)	Mobile PCM storage (sodium acetate trihydrate); 40 – 90 °C	100 – 200	99,000	1,500 – 2,500	39.6 – 66.0
16: Dual media storage (ZAE Bayern, Gießerei Heunisch)	Sensible storage; stone + heat transfer oil; up to 300 °C	200	400,000	6,500	61.5
17: MobS (ZAE Bayern)	Mobile sorption heat storage (2x14 t zeolite); industrial waste heat recovery	240	440,000	9,200	47.8
18: SolarHeatCool+PCM (ZAE Bayern)	1 m ³ PCM storage (CaCl ₂ ·6H ₂ O); 22 – 36 °C	200	4,700 – 6,300	83	56.6 – 75.9
19: TubeICE (VITO)	Modular PCM tubes (Salt hydrate + graphite); 30 – 70 °C	200	900	13	69.2
20: Dishwasher (ZAE Bayern)	Dishwasher with sorption drying (1.5 kg zeolite)	250	29 – 38	0.3	96.7 – 127
21: RT58 storage (VITO)	0.2 m ³ PCM storage (RT58); 30 – 70 °C	200	1,850	6	308

22: LiBr storage (ZAE Bayern)	Sorption storage (aqueous LiBr solution); domestic applications	250	31,000 – 47,000	85	365 – 553
23: PCM-Air [7, 8] (Univ. Zaragoza)	Free-cooling; PCM-Air heat exchanger; RT27 as PCM	30	2,000 – 3,900	6.8	294 – 574
24: VDSF (Univ. Lleida)	Free cooling; ventilated double skin facade + PCM (SP21)	240	5,133	7	733
25: Hydroquinone storage (Univ. Lleida)	Solar applications; hydroquinone as PCM; 145 – 187 °C	240	16,768	13.7	1,223
26: RT60 storage [9] (Univ. Basque Country UPV-EHU)	Plate based PCM storage (RT60) for a domestic micro-CHP installation	330	5,500 – 6,000	7.2	764 – 833

^a storages can be integrated in a variety of systems with different N_{cycle}

In order to identify major cost drivers and cost reduction potentials for the investigated storages, the composition of the investment costs *INC* has been analysed. Figure 7 illustrates how *INC* of the thermal energy storages under investigation are divided into costs of the heat storage material itself and costs of the surrounding container or reactor incl. charging/discharging device. If available, both actual (a) and expectable (b) costs are given.

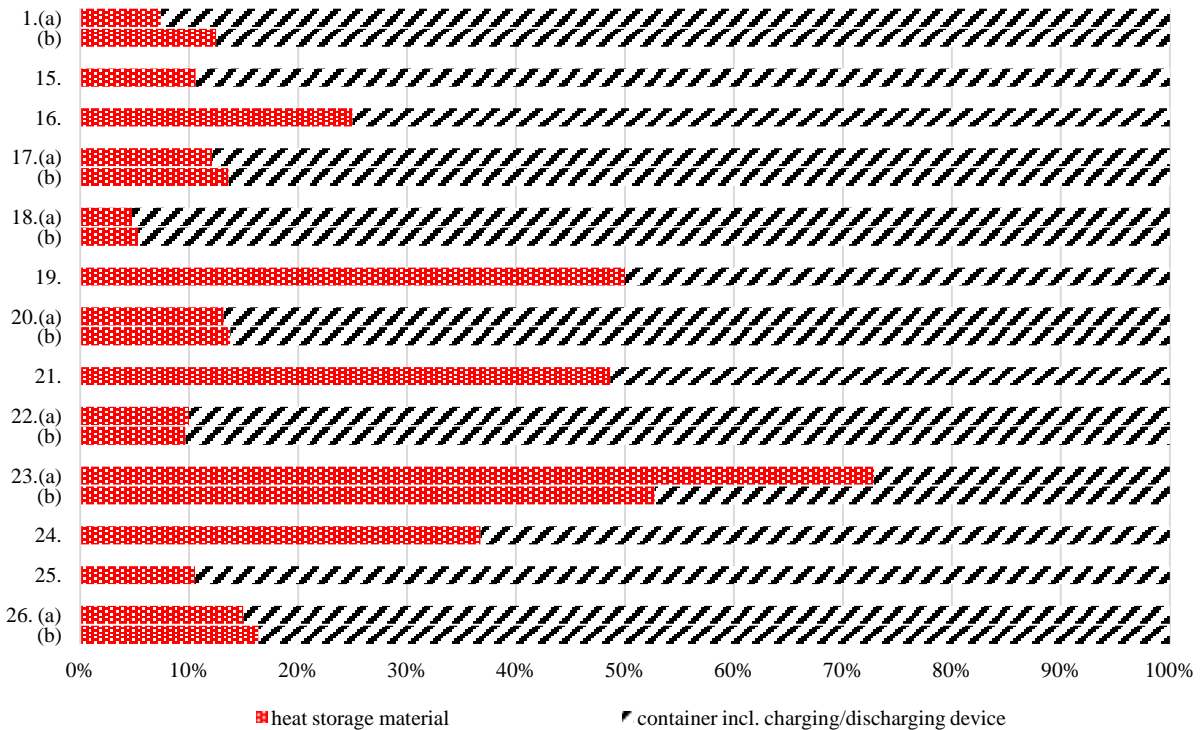


Figure 7. Actual (a) and expectable (b) Investment costs *INC* of the thermal energy storages under investigation divided into costs of the heat storage material and costs of the container incl. charging/discharging device.

In the majority of cases, the costs of the container incl. charging/discharging device exceed the costs of the heat storage material by far. For 9 out of 13 investigated storages, the costs of the heat storage material account for 25% or less of the total *INC*. Just in one case, the costs of the heat storage material account for more than 50% of *INC*. The composition of both actual and expectable investment costs indicates the significant potential to reduce storage costs by developing cost-effective storage containers and charging/discharging devices.

4. Discussion

The Top-down approach indicates some important findings in thermal energy storage economics that have often been ignored. First, for a fixed storage period, the maximum acceptable storage costs depend on the user's economic environment (e.g. *industry* or *building*) due to variances in payback period, discount rate, and costs of reference energy from the market. Second, the annual number of storage cycles has by far the largest influence on the maximum acceptable storage capacity costs and the cost effectiveness of storages. Third, scenarios exist under which most storage technologies are economical. In this case, systems should be compared with regard to physical and technical attributes.

The Bottom-up approach has been applied to analyse the costs of 26 thermal energy storages. Contrary to commercial water storages, several innovative storages are subject of ongoing research and, hence, their corresponding costs are roughly estimated. The comparison of SCC_{acc} and SCC_{real} indicates that, at present, seasonal storage is only economical using large hot water storages; other technologies require at least an order of magnitude reduction in costs. That implies that the development of storage systems which allow a high annual number of storage cycles is economically favourable over seasonal storages with exactly one cycle per year. In addition, the Bottom-up analysis showed that a major fraction of the investment costs of the investigated storages are not costs of the heat storage material itself but costs of the storage container or reactor incl. charging/discharging unit. Therefore, R&D activities on cost-effective TES systems have to consider both cost-effective heat storage materials and cost-effective storage container or reactor components.

The economic evaluation via Top-down and Bottom-up approach is not limited to thermal energy storage, it can also be applied to e.g. electrical energy storage. In this case, REC corresponds to the costs of electricity.

5. Conclusions

A simple tool for the economic evaluation of thermal energy storages via a Top-down and a Bottom-up approach has been developed and tested on various existing storages. This tool provides a rough estimate of the economic viability of an energy storage for a specific user and application. The main finding is that the number of storage cycles per year has the largest influence on the maximum acceptable storage capacity costs (costs per installed storage capacity). At present and with respect to the storages under investigation, seasonal TES is only economical via large sensible hot water storages. Contrary, short-term storages with several hundred cycles per year allow several hundred times higher costs because of the larger energy turnover. If the annual number of storage cycles is sufficiently high, all TES technologies can become economically competitive and systems should be compared with regard to physical and technical attributes.

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The responsibility for the content of this publication is with the authors.

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