

## Final report

### 1.1 Project details

<b>Project title</b>	IEA Task 42 Compact Thermal Energy Storage 2.periode
<b>Project identification (program abbrev. and file)</b>	Task 42
<b>Name of the programme which has funded the project</b>	EUDP
<b>Project managing company/institution (name and address)</b>	Department of Civil Engineering, Technical University of Denmark. Building 118, Brovej, DK-2800 Kgs. Lyngby, Denmark
<b>Project partners</b>	-
<b>CVR</b> (central business register)	30 06 09 46
<b>Date for submission</b>	29/02-2016

### 1.2 Short description of project objective and results

The aim of the project is, within the International Energy Agency SHC programme Task 42 project "Compact Energy Storage: Material Development and System Integration 2nd period", to evaluate the suitability of seasonal heat storages based on a salt hydrate with stable supercooling for solar heating systems which can fully cover new building's yearly heat demand.

Valuable knowledge on how to design compact long term heat storages has been gained. The project included cooperation with the Danish company Nilan A/S and the German company H.M. Heizkörper. These companies can utilize the gained knowledge in their efforts to develop improved compact long term heat storages. However, more research and development activities are needed before such heat storages will be economically attractive.

Projektformålet er dansk deltagelse i IEA SHC Programme Task 42 projektet "Compact Energy Storage: Material Development and System Integration 2nd period". I projektet vurderes egnetheden af kompakte sæsonvarmelagre baseret på et stabilt underafkølede salthydrat til solvarmeanlæg, som fuldstændigt kan dække det årlige varmebehov for bygninger.

Der er skabt værdifuld viden, som kan udnyttes til at designe kompakte langtidsvarmelagre. I projektet er der samarbejdet både med det danske firma Nilan A/S og med det tyske firma H.M. Heizkörper. Disse firmaer kan udnytte den viden der er skabt i projektet til at producere forbedrede kompakte langtidsvarmelagre. Der er dog behov for yderligere forsknings- og udviklingsarbejde før disse varmelagre kan blive økonomisk attraktive for forbrugere.

### 1.3 Executive summary

The main objective of the research was to expand the knowledge of heat of fusion storage utilizing stable supercooling of the salt hydrate sodium acetate trihydrate. Theoretical as well as experimental investigations on heat of fusion storages were carried out. Both small scale experiments to elucidate characteristics and melting/solidification behavior of the heat storage material and different additives as well as full scale experiments with differently designed heat storages with different compositions of sodium acetate trihydrate and different additives were carried out. Investigations of heat storages from the companies Nilan A/S and H.M. Heizkörper were included in the project.

Among other things the suitability of different heat storage materials consisting of sodium acetate trihydrate and different additives has been elucidated with regard to heat storage capacity, thermal conductivity and stability.

Reasons for failure of supercooling of sodium acetate trihydrate in differently designed full scale heat storage modules have been elucidated by means of experimental investigations. Additional investigations have documented how to design and operate full scale heat storage modules in such a way that stable supercooling is achieved.

Further, theoretical and experimental investigations have elucidated the thermal behavior of differently designed heat storage modules with different heat storage materials during charge and discharge. The investigations determined in this connection the importance of the contraction of the heat storage material during solidification. The contraction creates cavities in the solid salt hydrate resulting in decreased heat transfer within the solid phase of the heat storage material. The investigations also documented that a tall heat storage module with sodium acetate trihydrate and a thickening agent as additive works in a stable way.

Investigations of different principles for starting the solidification of the supercooled sodium acetate trihydrate were carried out in order to determine the most suitable solution.

The project showed that the principle of supercooling works in full scale: It is possible in full scale heat storages to store heat in long periods without heat loss.

Theoretical calculations with a simulation model for a solar heating system with a heat storage based on sodium acetate trihydrate with stable supercooling showed that it is possible for the solar heating system to cover the heat demand of low energy houses in Denmark completely.

The project results are valuable in connection with future development of compact long term heat storages. The project therefore forms an excellent basis for development of economically attractive long term heat storages with very low heat losses. Such heat storages can be used in different heating systems relying on different renewable energy sources.

#### **1.4 Project objectives**

The aim is, within the International Energy Agency SHC programme Task 42 project "Compact Energy Storage: Material Development and System Integration 2<sup>nd</sup> period", to evaluate the suitability of seasonal heat storages based on a salt hydrate with stable supercooling for solar heating systems which can fully cover new building's yearly heat demand.

The main problem of utilizing the storage principle is to achieve stable supercooling of the salt hydrate over long periods in units with large quantities of salt hydrate and in a design which allows for transferring heat to and from the salt hydrate at a high heat transfer rate. The first part of the research therefore focused on developing a storage unit design that allowed for this stable supercooling. During the research it was found that the storage needed to be operated without pressure changes inside the chamber for the salt hydrate. When the salt hydrate is heated it expands. This expansion caused pressures inside the storage unit and resulted in deformations. These pressure changes and deformations caused spontaneous solidification of the salt hydrate and supercooling failed. To avoid this pressure built up the storage units were designed with expansion volumes for the salt hydrate to expand and contract. This expansion was then connected to an external expansion vessel which allowed operating the storage without any pressure built-up and deformations. It was also elucidated that heating to temperatures above 80°C of all parts of the salt hydrate was required in order to achieve stable supercooling. In this was stable supercooling of the salt hydrate was achieved.

The second main problem was to stabilize the salt hydrate in terms of consistent and high heat content over a high number of heating and cooling cycles. The heat content of the salt hydrate was reduced due to the phenomena phase separation where the salt concentration of the storage changes in different levels of the storage due to the solubility of the salt in

water. Initially this problem was attempted solved by adding a little extra water to the salt and to keep the height of the chamber with the salt hydrate low, about 5 cm. This method reduced the problem of phase separation but the tests showed that the salt water mixture was not completely cycling stable and the heat released from the supercooled salt was reduced over repeated cycles.

Other additives than extra water to the salt hydrate were investigated and it was found that thickening agents were promising. Mixtures of the salt hydrate with thickening agents showed to have high and stable heat contents which can be released from the salt hydrate by solidification from a supercooled state. 220 kg salt with a thickening agent was successfully melted in a storage unit and was left in supercooled state for two months after which the solidification was triggered and the heat of fusion was released. There was no loss of heat over the long storage period compared to short storage periods and the mixture was stable over repeated heating and cooling cycles.

As the storage principle was proven the research went in the direction of optimising the salt hydrate mixture in terms of thermal conductivity. The thermal conductivity of the salt hydrate influence to a high extent the performance of the storage as it limits the heat transfer to and from the storage. The effect of adding highly conductive graphite particles was elucidated. The added graphite would separate out from the salt when it is in melted state due to density differences. Therefore, also the required quantity of thickening agent to keep the mixtures with uniformly distributed graphite particles at high temperatures was determined.

Parallel to the material optimization four heat storage units were installed in a demonstration system connected to solar collectors. The purpose of this was for the first time to demonstrate that melting and stable supercooling could be achieved with heat supplied from solar collectors and thereby showing that long term storage of heat from solar collectors was possible. This was achieved.

## **1.5 Project results and dissemination of results**

Experimental investigations were carried out on different scales. The characteristics of SAT (sodium acetate trihydrate) mixtures in sample sizes of 100-1300 g were investigated and optimized mixtures suggested. The performance of prototype heat storage units containing 100-220 kg SAT mixtures were investigated under laboratory conditions. A solar combi demonstration system elucidated the potential to achieve stable supercooling of storage units with SAT mixtures under realistic conditions with solar collectors as the heat source. Simulation software elucidated the potential thermal performance of a solar heating combi system for a single family house including heat storage units with SAT able to supercool. Comparisons between experimental investigations and numerical CFD calculations of heating and cooling including phase change of SAT in a small test unit were made.

The experimental setups and the reasoning for the path of development are described in the following sections.

### *Composites of sodium acetate trihydrate*

One of the key problems of utilizing sodium acetate trihydrate as a heat storage material is phase separation of the incongruently melting phase change material. Phase separation is caused by the fact that the solubility of sodium acetate in water at the melting point of 58 °C is not high enough to dissolve all the sodium acetate in the corresponding crystal water from the sodium acetate trihydrate composition. Melted SAT just above the melting point therefore consists of a saturated solution of sodium acetate dissolved in water and undissolved sodium acetate. The undissolved salt will settle to the bottom of the container if nothing is done to prevent it due to the density difference. When SAT suffering from phase separation solidifies all potential SAT crystals will not be formed due to the physical distance between the sodium acetate in the bottom of the container and the water it need to bind with in the top of the container. This reduces the heat of fusion in practice.

Another key problem of using PCM in heat storage is the relative low thermal conductivity of the PCM itself. The thermal conductivity affects how fast heat spreads in the PCM, especially

in the solid state and will therefore to a high extent influence the charge time and the discharge power of a PCM (phase change material) heat storage.

Both phase separation and low thermal conductivity may cause the PCM heat storage to perform worse than it potentially could. The possibility of developing composites of SAT with different additives has therefore been investigated. The research was focused on maximizing the heat content of SAT composites by reducing losses due to phase separation and elucidated a method to enhance the thermal conductivity of SAT composites.

#### *Heat content measurements*

The highest possible heat content of the supercooled SAT mixtures is desired in heat storages. The heat released after solidification of the supercooled SAT mixtures may be lower than the theoretical maximum due to the phase separation. This part of the investigations focused on developing SAT mixtures where the loss of heat storage potential due to phase separation was reduced. A variety of additives to the SAT was tested.

Adding extra water to the SAT may allow for all sodium acetate to be dissolved in the water at melted state and thereby possibly avoid phase separation. From studying the phase diagram of sodium acetate – water, it can be realized that a composition of approximately 42% water and 58% sodium acetate (SAT with 4% extra water) is required for all sodium acetate to be dissolved in the solution at the melting point of 58 °C. In supercooled state at 20 °C a composition of approximately 45% water and 55% sodium acetate (SAT with 10% extra water) is required for all sodium acetate to be dissolved.

Another solution for avoiding the loss from phase separation is adding thickening agents to the SAT. These additives increase the viscosity of the solution so that the anhydrous sodium acetate stays suspended in the solution and does not settle to the bottom. This allows potentially for formation of all SAT crystals after solidification when the sodium acetate stays near the water it need to bind with at crystallization. The thickening agents Carboxymethyl Cellulose (CMC) and Xanthan rubber were investigated as additives to SAT.

Figure 1 (a) shows a sample of SAT in supercooled state at ambient temperature which suffers from phase separation. A layer with crystals can be seen in the lower part of the glass jar and a transparent solution can be seen in the upper part of the glass jar. Figure 1 (b) shows a sample of SAT with 10% extra water in supercooled state at ambient temperature. The entire solution is transparent. Figure 1 (c) shows a sample of SAT thickened with 0.5% Xanthan rubber in supercooled state at ambient temperature. The anhydrous sodium acetate is suspended in the full height of the sample.

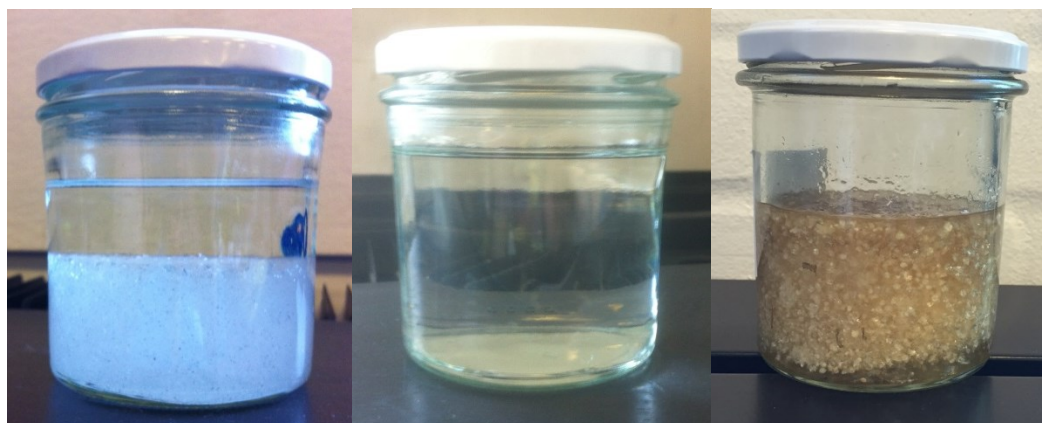


Figure 1. (a) SAT with phase separation. (b) SAT with extra water. (c) SAT with the thickening agent Xanthan rubber.

Samples with different percentages of extra water, CMC or Xanthan rubber were prepared in 350 mL glass jars closed with metal lids. A suitable mixing method was necessary when mixing the thickening agents especially Xanthan Gum into the SAT. The Xanthan rubber binds very fast with the water when it is mixed into the samples and jelly chunks were easily formed. To have the Xanthan rubber evenly dispersed in the composite, 90% of the SAT was melted in an oven; the remaining 10% of the SAT was in cold solid granular state mixed with the Xanthan rubber powder before it was added to the melted SAT little by little while stirring

with an overhead mixer. This ensured a uniform mixture. Unwanted air bobbles were easily trapped inside the mixture when stirring the thickened SAT composite in the melted state. Mixing was carried out carefully to avoid this.

The samples of the SAT composites of approximately 200 g each were melted in the oven at 80-90°C. The height of the PCM sample in the glass jars were 5 cm. After the heating they were placed in the ambient temperature at 20-25°C to cool down to supercooled state.

The samples were then placed in an insulated box and the solidification was initiated by dropping a SAT crystal into the supercooled composite. The temperature developments of the samples were recorded after the solidification.

Beforehand, heat loss coefficients of the glass jars placed in the insulated boxes were determined by having the glass jars with heated water as a reference material cool down to ambient temperature. When the heat loss coefficient of the glass jars in the box was determined, the heat content of the SAT samples could then be determined by recording the temperature development as they cool down.

Figure 2 shows an open box with insulation and hole for placing the glass jars.



Figure 2. Well insulated box for heat content measurements by heat loss method.

Both short and long periods in supercooled state were investigated for the SAT samples with extra water.

The theoretical heat content of supercooled SAT at 20°C without phase separation is 230 kJ/kg.

An example of the cooling down progress of a SAT mixture sample is shown in Figure 4. With temperature of approximately 80°C, a sample is placed in the in box. During the first 60 hours the sensible heat of the sample is released and the sample reached ambient temperature. At the 85th hour the solidification is initiated and the temperature increases. The heat generated from the solidification of the supercooled SAT sample is released during the following 40 hours.

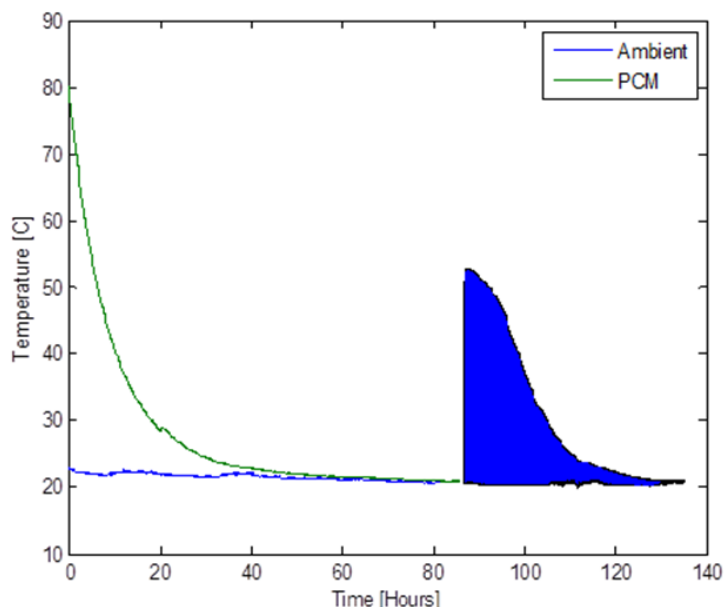


Figure 4. Temperature development of SAT composite sample inside insulated box.

The heat loss experiments showed that SAT (40% water, 60% sodium acetate) without additives suffering from phase separation released 162 kJ/kg of heat with short storage periods. With a storage period of 100 days the heat content was further reduced to 100 kJ/kg. Samples of SAT with 4% extra water (42% water, 58% sodium acetate) showed a heat content of 190 – 200 kJ/kg for short storage periods and approximately 160 kJ/kg for longer storage periods. Samples with SAT and 10% extra water (45% water, 55% sodium acetate) showed to have a heat content of 160 – 170 kJ/kg independent of the storage period. Samples of SAT with CMC or Xanthan rubber as thickening agents showed to have a heat content up to 215-220 kJ/kg for short and long storage periods. Mixtures of SAT with 0.3-1.0% Xanthan rubber or 0.4-2.0% CMC resulted in the highest heat content. The released heat after solidification of supercooled SAT samples with thickening agent was up to 95% of the theoretical potential. Further details and results are given in [1].

#### *Suspension of graphite in thickened SAT composites*

Low thermal conductivity of PCMs is a typical limitation when using PCMs in heat stores as it limits the heat transfer between the PCM and the heat transfer fluid. One solution for increasing the thermal conductivity of a PCM is to create composites with highly conductive additives. Many researchers have investigated the potential of graphite as additives to PCMs. Some researchers investigated the potential for impregnating graphite matrices with PCM. A more simple way is to make a PCM composite with small particles of graphite. In this case the PCM composites can easily be handled and filled into stores even with complex geometries. The characteristics of a PCM composite need to remain relatively homogeneous over its lifetime so that the performance is stable. If small sized particles are part of a PCM composite, it is necessary that the additive stays evenly distributed in the composite and does not settle to the bottom or float to the top of the container.

A suspension test for evaluating the ability of different quantities of thickening agents to suspend graphite particles in SAT composites has been carried out. Mixtures of SAT and graphite were placed on top of SAT composites with different percentages of thickening agents. The samples were heated to 90°C in an oven and the ability for the thickening agent to keep the graphite suspended on top was evaluated. It was assumed that if the graphite stayed suspended on top of the thickened composite, there was enough thickening agent to keep a uniform mixture. Carboxymethyl cellulose and Xanthan rubber were applied as thickening agents. Graphite powder and graphite flakes were used as the highly conductive compound in the investigations. Figure 4 shows three samples of thickened SAT with a SAT and graphite powder layer on top before being placed in the oven.



Figure 4. Three samples of SAT with thickening agent with a layer of graphite and SAT on top.

Figure 5 shows the SAT samples with 0.25%, 0.5% and 1% Xanthan rubber with graphite powder on top after 14 days in the oven at 90°C.



Figure 5. SAT samples with 0.25%, 0.5% and 1% Xanthan rubber with graphite powder on top after 14 days at 90°C.

Figure 6 shows the SAT samples with 1%, 2.5% and 5% CMC with graphite flakes on top after 14 days in an oven at 90°C.



Figure 6. SAT samples with 1%, 2.5% and 5% CMC with graphite flakes on top after 14 days at 90°C.

The suspension test showed that either 5% CMC or 1% Xanthan rubber was required for composites of SAT to keep graphite powder or graphite flakes suspended on top of the sample over a 14 days period at 90°C.

Further details are given in [2].

#### *Thermal conductivity and cavities of SAT composites*

The density of solid SAT is 1280 kg/ m<sup>3</sup> and the density of liquid SAT is 1450 kg/m<sup>3</sup>. This density difference between the solid and liquid PCM may cause cavities forming in the PCM

storage during solidification. These cavities may have an insulating effect reducing the effective thermal conductivity. The speed of which the solidification of the PCM takes place may also have an effect on the crystal structure as the PCM needs to contract in the process. When supercooled SAT solidifies the crystallization happens with a fast moving crystallization front from the point of nucleation. When SAT solidifies without supercooling the crystallization front moves slower as the heat is being released and the temperature drops below the melting point. The crystal structure and the denseness of the solid may affect the thermal conductivity of the SAT composite. In a heat storage the way the heat exchanger is designed and the cooling rate may therefore also affect the effective thermal conductivity of the PCM. The formation of cavities and the effective thermal conductivity of SAT in bulk size samples with 1.3 kg of SAT with different additives were investigated. Samples which had solidified from a supercooled state and samples which solidified without supercooling were compared. Composites with extra water, the thickening agents: carboxymethyl cellulose and Xanthan rubber plus graphite powder and graphite flakes were investigated. Figure 7 shows a 1.3 kg SAT sample with extra water as additive. The samples were prepared by heating the SAT composites in glass jars. One sample of each type of composite was let to supercool to ambient temperature after which the solidification was initiated by opening the jar and dropping a SAT crystal. Other samples of each type cooled down to ambient with the lid open and a SAT crystal was added when the melting temperature of the SAT of 58°C was reached to avoid supercooling. The solidified samples were removed from the glass jars and cut into three layers. The contraction and formation of cavities was observed and the thermal conductivity in the different layers was measured.

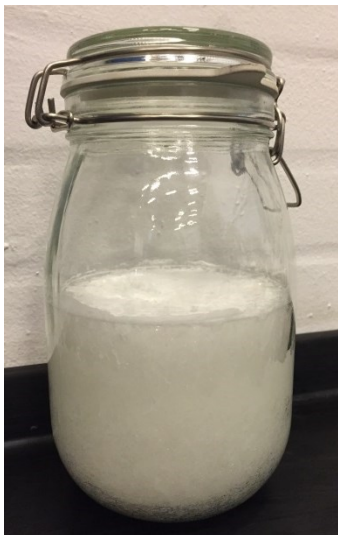


Figure 7. 1.3 kg SAT composite sample.

The thermal conductivities were measured with an ISOMET heat transfer analyzer from the company Applied Precision. Figure 8 shows the surface measuring probe on a layer of SAT composite.



Figure 8. Applied Precision surface probe for measuring thermal conductivity of SAT sample.



The location of cavities in the SAT composites after solidification varied depending on the type of additive and whether it solidified with or without supercooling. Single large cavities were typically formed away from the heat transfer surface in the samples without thickening agent and with CMC. When Xanthan rubber was used as thickening agent minor cavities were typically spread out in the PCM volume. Samples that had solidified from a supercooled state tended to form fewer and smaller cavities.

Figure 9 (a) shows a SAT sample with 1% CMC solidified without supercooling. Figure 9 (b) shows a sample of SAT with 1% CMC which solidified from supercooled state.

Figure 10 (a) shows a sample of SAT with 0.5% Xanthan rubber solidified without supercooling. Figure 10 (b) shows a sample of SAT with 0.5% Xanthan rubber which solidified from supercooled state.

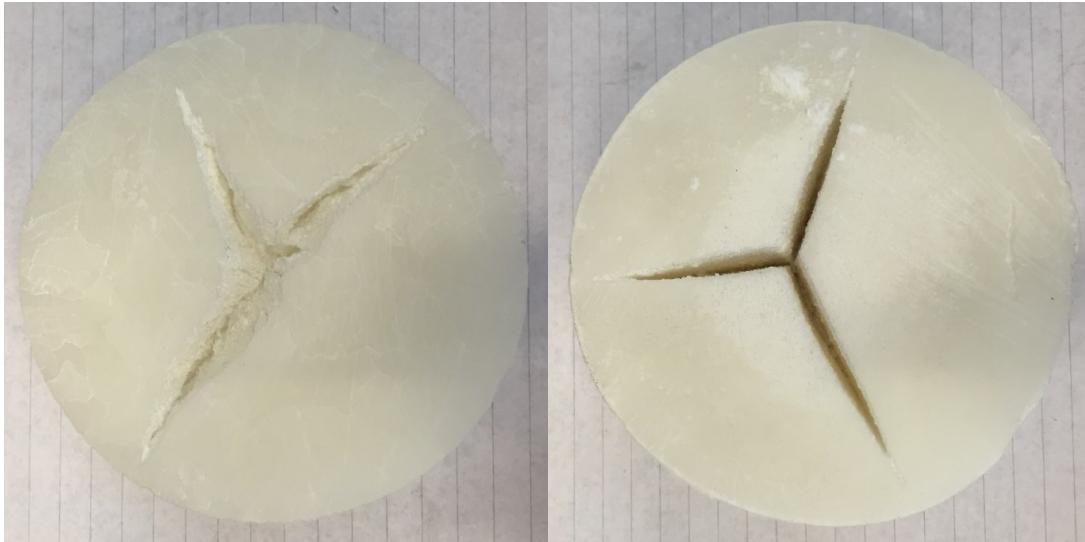


Figure 9. (a) SAT with 1% CMC solidified without supercooling. (b), SAT with 1% CMC solidified from supercooled state.

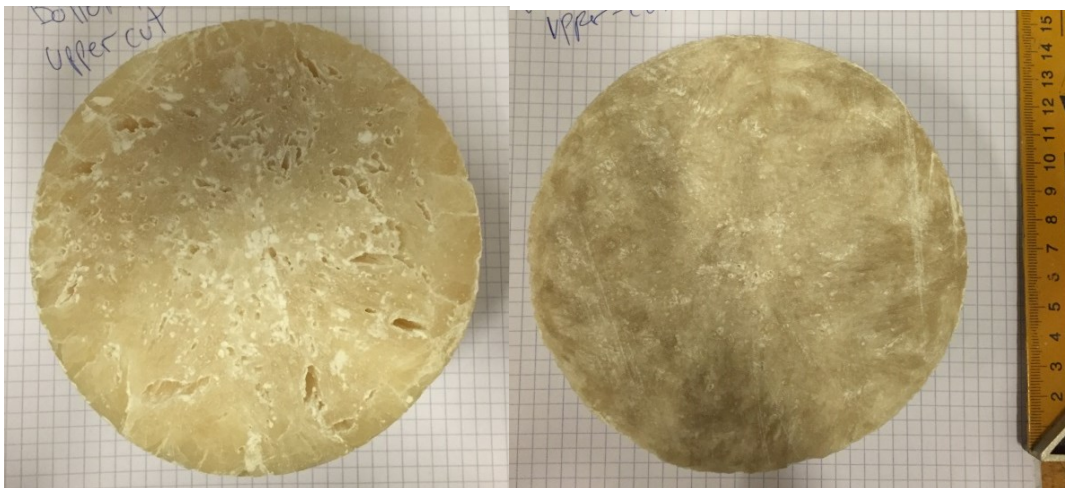


Figure 10. (a) SAT with 0.5% Xanthan rubber solidified without supercooling. (b) SAT with 0.5% Xanthan rubber solidified from supercooled state.

The measured thermal conductivity depended on whether the samples had solidified from supercooled state or without supercooling. In the solid parts of the SAT composites without graphite which had solidified without supercooling the thermal conductivity was up to 0.64-0.67 W/m K. The samples of SAT without graphite which had solidified from supercooled state had thermal conductivities of 0.56-0.65 W/m K. The spread out cavities in the samples of SAT with Xanthan rubber gave in practice significantly lower thermal conductivities due to the cavities working as thermal resistances.

Graphite flakes showed to increase the thermal conductivity in the SAT composites better than graphite powder. In SAT composites with Xanthan rubber and 5% graphite flakes the

thermal conductivity was up to 1.12 W/m K in the sample that solidified without supercooling and up to 0.95 W/m K in the sample that solidified from supercooled state.

Further details and results are given in [2].

### *Simulations and numerical calculations*

#### *Comparison of measurements on test unit with CFD calculations*

A box shaped test unit of steel with the dimensions 302 x 302 x 55 mm was filled with 4.6 kg of SAT with 4 % extra water (42% water, 58% sodium acetate). The steel box was heated and cooled under controlled conditions by placing it in a thermostatic bath. The temperatures of the surface and the temperature in the centre of the PCM were measured. Figure 11 shows the steel box with thermocouples attached.

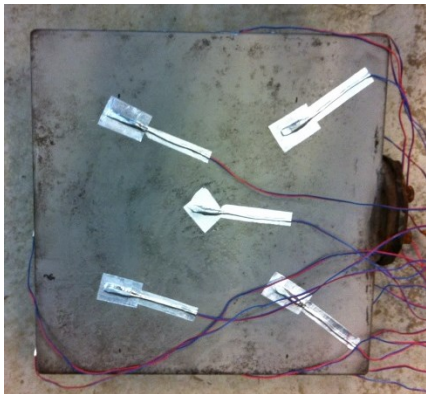


Figure 11. Steel unit containing 4.6 kg SAT with 4% extra water and thermocouples attached.

Figure 12 (a) shows the steel box placed in the thermostatic bath without water. Figure 12 (b) shows the thermostatic bath closed with lid and the controller.



Figure 12. (a) Steel unit placed the thermostatic bath. (b) Closed thermostatic bath with controller.

A computational fluid dynamics (CFD) model of the box was built up in Ansys fluent. The measured surface temperature was used as input parameters for the CFD model. The measured temperature development of the probe inside the steel box was compared to the calculated temperature of the probe tip by the CFD model.

Figure 13 shows part of the mesh of the CFD model of the steel box.

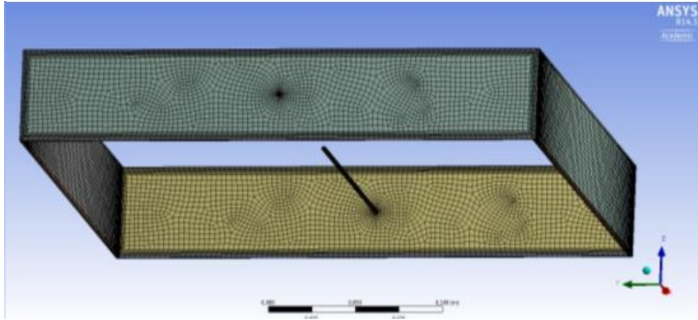


Figure 13. Part of mesh for CFD model of 302x302x55 mm steel box with SAT mixture.

Different heating and cooling scenarios were applied. Assumptions on formation of cavities affecting the heat transfer were made. The measured temperature in the centre of the box was compared to the calculated values by the CFD model.

The agreement between the CFD calculations and the measurement was excellent in the cases which did not include phase change of the PCM. In the case where phase change occurred some deviations were observed. In the CFD calculations the heating and melting happened faster than in the experiment. The reason may be the material properties of the SAT mixture used in the model. Especially the thermal conductivity may cause the deviation. Also the formation of cavities in the steel box may be different from what was expected and therefore gave larger resistance than assumed in the first case.

Figure 14 (a) shows the good agreement between the measured and calculated temperature development of the probe in the steel box when heated from 22°C to 52°C. Figure 14 (b) shows the poor agreement between the measured and calculated temperature development of the probe in the steel box when heated across the phase change from 22°C to 82°C.

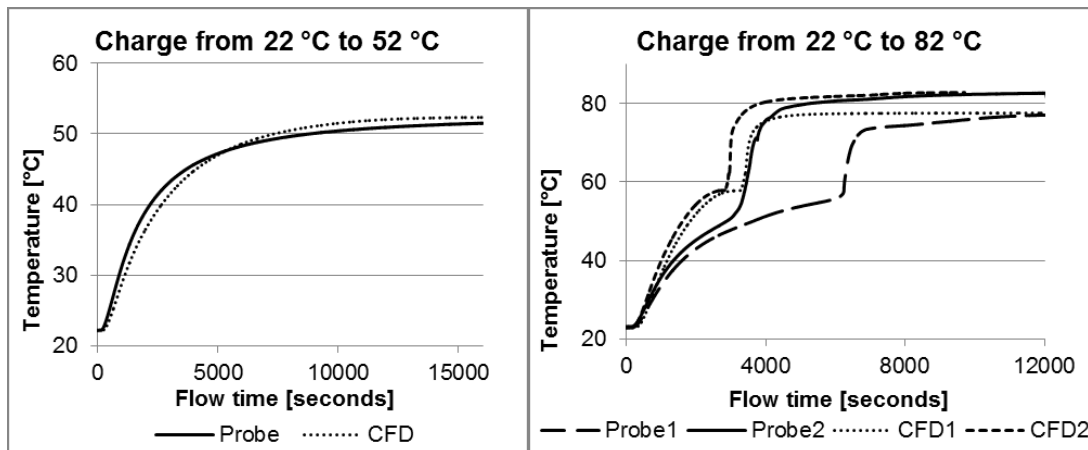


Figure 14. (a) Measured and calculated temperature development of probe in steel box heated from 22°C to 52°C. (b) Measured and calculated temperature development of probe in steel box heated from 22°C to 82°C.

Further details on the CFD model and the experiments are given in [3].

#### *TRNSYS system simulation*

A TRNSYS model of a solar heating combi system with PCM storage previously developed by Schultz et al. [4] was adapted to fit the dimensions of the flat heat storage unit prototypes with a PCM volume of approximately 150 L. The simulations were carried out for the system with 36 m<sup>2</sup> flat plate solar collectors facing south with a tilt of 75°, a 180 L domestic hot water tank, a space heating system and auxiliary heating. The solar collectors had a start efficiency of 0.82 and 1st and 2nd order heat loss coefficients of 2.44 W/(m<sup>2</sup> K) and 0.005 W/(m<sup>2</sup> K<sup>2</sup>). The daily hot water consumption was 99 L. The DHW temperature was 50°C and the cold water temperature was 10°C resulting in a yearly energy consumption of DHW of

1677 kWh. A space heating demand of 2008 kWh/year corresponding to the space heating demand of a passive house was assumed. The heat exchange capacity rate of the storage units was an input parameter to the TRNSYS model. Heat exchange capacity rate of the PCM storage units were varied to show the effect on the yearly system performance. Figure 15 shows that schematic of the system simulated in the TRNSYS model.

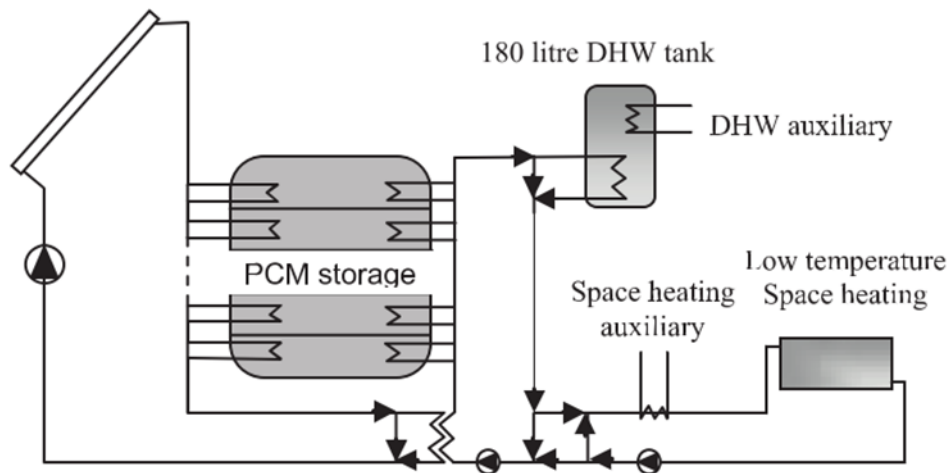


Figure 15. Schematic sketch of solar heating system in TRNSYS model.

The TRNSYS simulations showed that the heat exchange capacity rate (HXCR) had significant influence on the yearly solar fraction of a solar combi system with supercooled thermal energy storage. Figure 16 shows the yearly solar fraction of the simulated solar combi system with varying number of storage units and HXCR.

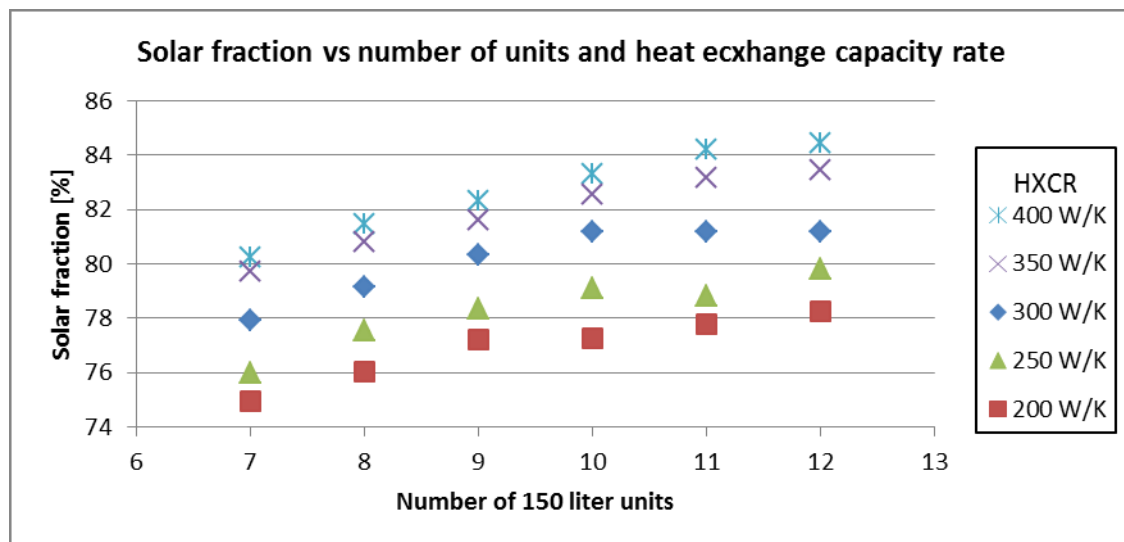


Figure 16. TRNSYS simulation results, effect of HXCR on solar fraction of solar combi system in single family house.

Further results are given in [5].

#### Prototype heat storage units

The SAT mixtures should be contained in a closed container to avoid loss of water vapour from the PCM when it is melted. Loss of water from the SAT mixtures will change its composition and most likely reduce the performance over time. Also a closed container will provide more stable supercooling as external particles will not enter and initiate nucleation.

It is also recommended to design the inner surfaces of the PCM chamber, which is in contact with the supercooled PCM, to be as smooth as possible. Cracks, joining segments or pene-

trating tubes poses a risk of uncontrolled solidification of the supercooled PCM. In a similar way as bending a metal disc with cracks will start the solidification in the pocket sized hand warmers [6], solidification could be started at cracks in the unit if affected by internal or external pressure changes or impacts.

The density difference between the liquid SAT and the solid SAT is approximately 12%. SAT expands when it melts. Preliminary investigations on early storage unit prototypes showed, that heating and melting SAT in a closed chamber caused deformations of the heat storage unit and sometimes leakage from the lids closing the PCM chamber due to a pressure built up. Consequently supercooling failed. It was necessary to implement means for allowing the SAT mixture to expand and contract with minimal pressure changes in the PCM chamber to achieve stable supercooling. Filling the PCM chamber of the storage units approximately 85% and connecting the air volume above the PCM to an external expansion device allowed for heating and melting the storage unit with only slight pressure built up. Thereby no deformations of the storage unit occurred and stable supercooling was achieved.

As the PCM needs to be fully melted to achieve stable supercooling, a heat exchanger that provides restively uniform heating and melting of the PCM is desired. The thermal conductivity of SAT is relatively low therefore the maximum distance between heat exchanger and PCM should be short to allow for faster complete melting of the PCM.

A number of barriers and problems for operation heat storage based on stable supercooling of sodium acetate trihydrate in a large storage unit are discussed in [5].

#### *Flat heat storage unit*

One heat storage unit design was developed at DTU together with Nilan A/S. The developed heat storage unit consisted of a flat PCM chamber with an internal height of 5 cm with heat exchangers on the outer surface of the PCM chamber. Manifolds were along the side of the unit and 14 parallel channels covered the top surface of the PCM chamber and 16 channels covered the bottom surface. In this way heat could be transferred through the PCM chamber walls into the PCM. The length on the storage unit was 240 cm and the width was 120 cm, see Figure 17. One unit was constructed in steel and another unit with the inner chamber in stainless steel. There is no risk of corrosion or chemical reactions happening with SAT in contact with steel and stainless steel [7].

An expansion chamber was located in one end of the unit to accommodate for the density change of the SAT. An external expansion vessel without pre-pressure or an inflatable plastic bag allow for the expansion of the PCM in the unit with minimal pressure built-up, see Figure 18.

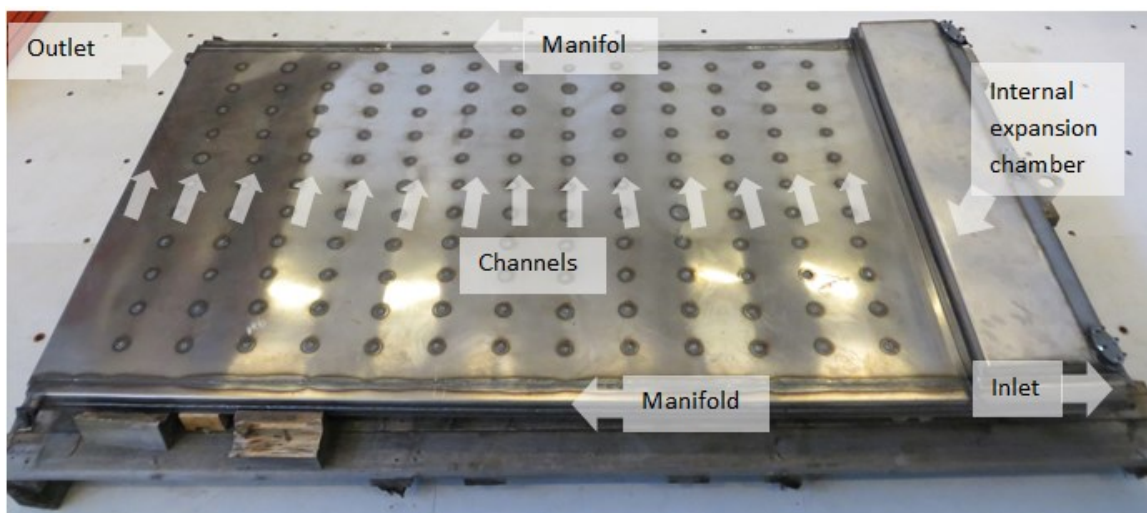


Figure 17. Flat heat storage unit with the dimensions 240 cm x 120 cm, internal expansion.

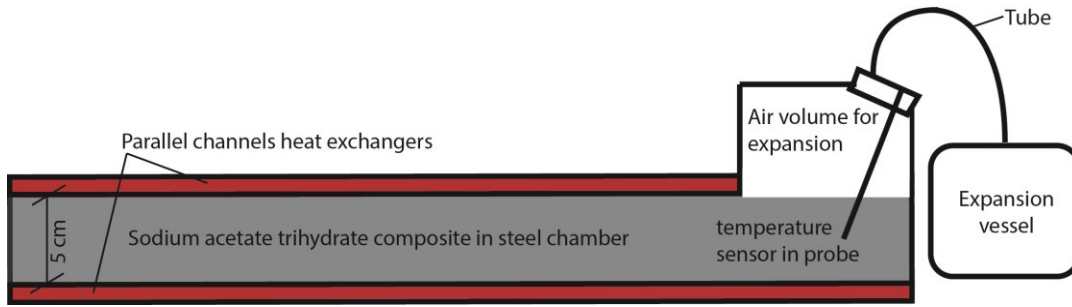


Figure 18. Principal diagram of flat heat storage unit with expansion.

The units were filled with 199.5 kg SAT with 9% extra water (44.8% water, 55.2% sodium acetate) and with 220 kg SAT with 1% CMC.

A 100 mL chamber was mounted on one side of the PCM chamber. When solidification was required, pressurized CO<sub>2</sub> was flushed through the chamber and as the CO<sub>2</sub> evaporated the nearby PCM was cooled to its maximum degree of supercooling of about -15°C [8]. This initiated the solidification of the supercooled PCM during laboratory testing.

Further details are given in [5] and [9].

#### *Cylindrical heat storage unit*

Two cylindrical heat storage units in stainless steel from the German company H.M. Heizkörper were tested. The units were 150 cm high. The diameter was 30 cm. The units were insulated with 4 cm expanded polypropylene. Figure 19 shows the cylinder with insulation. One of the units had inspection windows to observe the state of the PCM inside the unit if needed. The heat exchangers consisted on 16 tubes located in a circular formation running from top to bottom. Thin aluminium plates were attached to the tubes as fins to increase heat transfer. Figure 20 shows part of the steel tubes and the attached fins.



Figure 19. Cylindrical heat storage unit with insulation.



Figure 20. Internal heat exchanger of stainless steel pipes and aluminium fins.

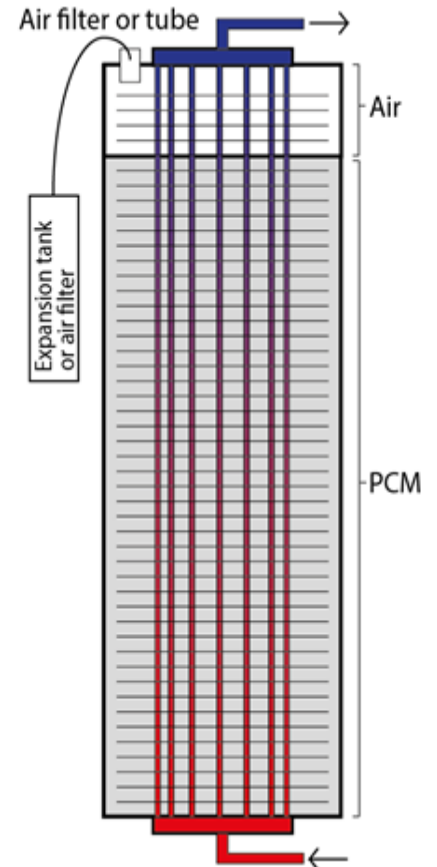


Figure 21. Principal diagram of PCM unit

The units were filled approximately 90% with PCMs to allow for the expansion. The units were tested with external expansion tanks and with an airfilter instead of the expansion. Figure 21 shows the principle diagram of the cylindrical unit with the expansion devices. The cylindrical units were tested with 91 kg water as a reference material; with 116 kg SAT with 6.4% extra water (43.5 % water, 56.5% sodium acetate) and with 116.3 kg SAT with 0.5% Xanthan rubber and 4.4% graphite powder. Paraffin oil was added to the PCM chamber of the unit with SAT, Xanthan rubber and graphite after some test cycles. This was done as an attempt to increase the heat transfer in the PCM when it was in solid phase. If oil filled the cavities formed during solidification of the PCM instead of air or vacuum it could enhance the heat transfer.

Further details are given in [10].

### *Storage unit test description*

The performance of PCM heat storage prototype units were investigated under controlled conditions in the heat storage test facilities to verify the working concept. The scale of the units represents a size which could be installed as part of a solar heating combi system in a single family house. The measured heat contents over a number of charge and discharge cycles are measured and compared to theoretical values.

The heat storage units were connected to a heat storage test facility. The test facility allowed for circulating water as the heat transfer fluid through the heat exchanger of the units and through an electric heating element and a heat exchanger for cooling. The power and temperatures for charge was set by a controller. The discharge power and temperature was controlled by adjusting the flow conditions of the heat sink side of the heat exchanger for the cooling. Flow rates were set by string values to represent desired test conditions.

The units were heated to a temperature of 80-90°C to ensure supercooling during cooling down. Preliminary investigations showed that a minimum temperature of the PCM of 80°C helped to achieve supercooling. The sensible heat was either actively or passively discharged from the units by cooling down to the ambient temperature of 20-25°C. After solidification the units were actively discharged to determine the heat released after a supercooled period. The units were charged with a high flow rate during a period long enough to ensure complete melting of the PCM and a minimum temperature in all parts of the storage units of 80°C. During discharge the flow rates were relatively low in order to have high temperature increase of the heat transfer fluid.

Five junction thermopiles based on copper/constantan type TT thermocouples with counter flow sensors measured the temperature difference across the inlet and outlet of the units. The accuracy of the temperature difference measured by the thermopile was 0.1 K. Absolute flow temperatures were measured with thermocouples. Temperatures on the outside of the units were measured at key locations. All thermocouples were copper/constantan type TT with accuracy of 0.5 K. In some cases the PCM temperature was determined by thermocouples in probes inserted into the PCM. The flow rate was measured by the inlet to the units with Clorius or Brunata HGQ1-R0 flow meters which had been calibrated to have an accuracy of  $\pm 1\%$  in the relevant flow range. Solartron cards with a PC were used to log the measurements at respective intervals. Figure 22 shows the principle of the heat storage test facility.

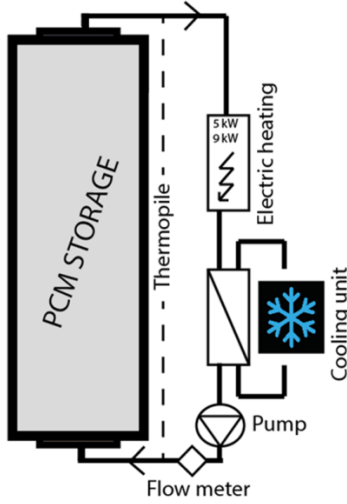


Figure 22. Principle diagram of heat storage test facility.

The charge and discharge powers  $\dot{Q}$  [W] when heating and cooling the units were determined by:

$$\dot{Q} = \dot{V} \cdot c_p \cdot \rho \cdot (T_i - T_o) \quad (1)$$

where  $T_i$  is the inlet temperature,  $T_o$  is the outlet temperature,  $\dot{V}$  is the volume flow rate of the heat transfer fluid measured at the inlet,  $c_p$  is the specific heat capacity of the heat transfer fluid at mean temperature between  $T_i$  and  $T_o$ ,  $\rho$  is the density of the heat transfer fluid at  $T_i$ .

The heat loss coefficients  $H_{loss}$  [W/K] of the storage units were measured by heating the units to a high stable temperature. The heat balance of the system was used to determine the heat loss experimentally, that is, the heat added to the system was equal to the heat loss, when the storage temperature was stable over a period. In this way a simplified heat loss coefficient with a constant value was determined by:

$$H_{loss} = \dot{Q} / (T_s - T_{amb}) \quad (2)$$

Where  $T_s$  is the mean temperature of the surface of the unit and  $T_{amb}$  is the ambient temperature. The heat loss coefficient for the storage unit was used when calculating the heat content of the unit based on the measured data. The heat content in the storage unit after a charge  $E_{charge}$  [J] or the heat discharged from the unit  $E_{discharge}$  [J] over a specific time period was determined by:

$$E_{charge/discharge}(t) = \int_0^t (\dot{Q} - H_{loss} \cdot (T_s - T_{amb})) dt \quad (3)$$

The heat content of the PCM per unit mass at a specific storage temperature  $T_s$  above a defined start temperature  $T_{start}$  excluding the specific heat of the tank material  $C_{unit}$  was calculated by the following expression:

$$E_{PCM}(T_s, T_{start}) = \frac{E_{charge/discharge}(T_s, T_{start}) - C_{unit} \cdot (T_s - T_{start})}{m} \quad (4)$$

Where  $E_{charge/discharge}(T_s, T_{start})$  is the measured heat content of the storage at a storage temperature  $T_s$  above a start temperature  $T_{start}$  and  $m$  is the mass of the PCM. This allows for comparing the heat content of the different PCMs disregarding the heat capacities of the unit material and comparing the measurement to a theoretical storage capacity of the PCMs with given sensible heat and latent heat.

The heat exchange capacity rate (HXCR) is an expression related to how fast heat is transferred between the heat transfer fluid and the heat storage material in the storage. It indicates how well the heat exchanger of the storage performs. The HXCR is affected by multiple



factors such as the storage temperature, the power charged to or discharged from the storage, the flow rate, the heat exchanger design and material properties. The heat exchange capacity rate was expressed by the following equation which can be derived from the heat transfer rate and log mean temperature difference.

$$HXCR = \dot{V} \cdot c_p \cdot \rho \cdot \ln \left( \frac{T_i - T_s}{T_o - T_s} \right) \quad (5)$$

A number of test cycles with each unit were carried out. This was to evaluate the cycling stability of the PCM material i.e. if the heat content in the first test cycles were similar to the heat content in the later test cycles or if it changed over the number of cycles. Also test cycles where the PCMs were kept in supercooled state for different periods were carried out to evaluate any potential heat loss over long storage periods. The performance of the different PCMs in the application sized units was determined so the heat content could be compared to the results from the investigations of heat content in the glass jars in the insulated boxes.

#### Measurement on flat units

The temperature development of a selected charge and discharge test cycle can be seen in Figure 23. During the charge period the temperature of the storage increased as more energy is stored in the unit. The unit is kept with a stable temperature of approximately 90 °C for a period. In this period the heat loss coefficient of the unit was determined to be 8 W/K. After the stable hot period the sensible heat was discharged. The PCM remained in liquid state and remained supercooled for approximately 3 days. After the supercooled period the solidification was initiated by the cooling technique and the latent heat released during solidification was discharged. Figure 23 also shows the thermal energy content of the unit throughout the test cycle.

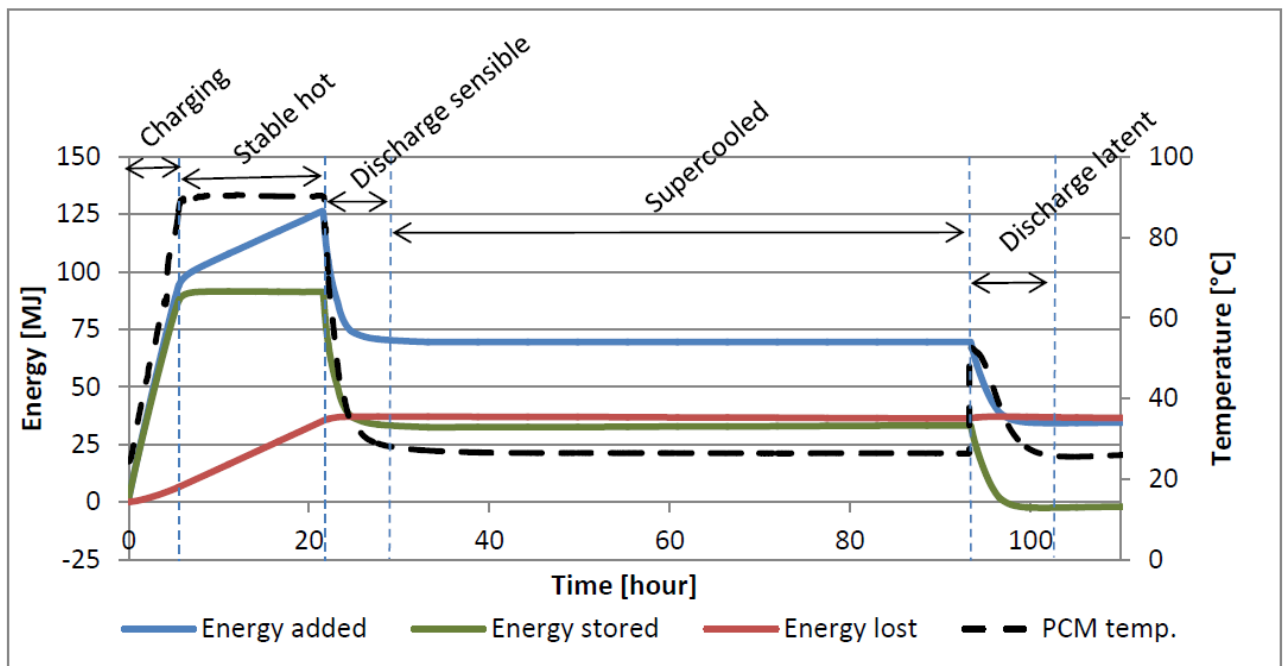


Figure 23. Test cycle with flat unit with SAT with 9% extra water.

The energy released after solidification of the supercooled SAT with 9% extra water was in the first test cycle 194 kJ/kg of PCM. In the 5th test cycle 188 kJ/kg was discharged. After 20 test cycles the measured energy content was 179 kJ/kg of PCM. The drop in heat content over the test cycles shows that the PCM mixture was not cycling stable. The heat content of the SAT with 9% extra water tested in this unit was slightly higher than what was expected from the heat content measurement of SAT with 10% extra water in the glass jars.

The energy released from the unit with SAT and 1% CMC after solidification from the super-cooled state was consistent around 205 kJ/kg of PCM over the six test cycles. The determined heat content in the glass jars with similar SAT mixtures was slightly higher than for the prototype unit tests.

The determined heat exchange capacity rate for the flat storage units during selected charges with similar charge powers are shown in Figure 24. It can be seen that the HXCR is higher for the bottom heat exchanger compared to the top heat exchangers. This is partly due to the larger heat transfer surface but possibly also due to better contact between PCM and heat exchanger in the bottom than in the top due to gravity. Also the buoyancy effect in the liquid PCM will favour the heat transfer of the bottom heat exchanger. It can also be seen that the HXCR is significantly higher for the unit with SAT and extra water compared to the unit with SAT and 1% CMC. This is due to less heat transfer by convection in the unit with CMC due to the fact that the PCM was thickened.

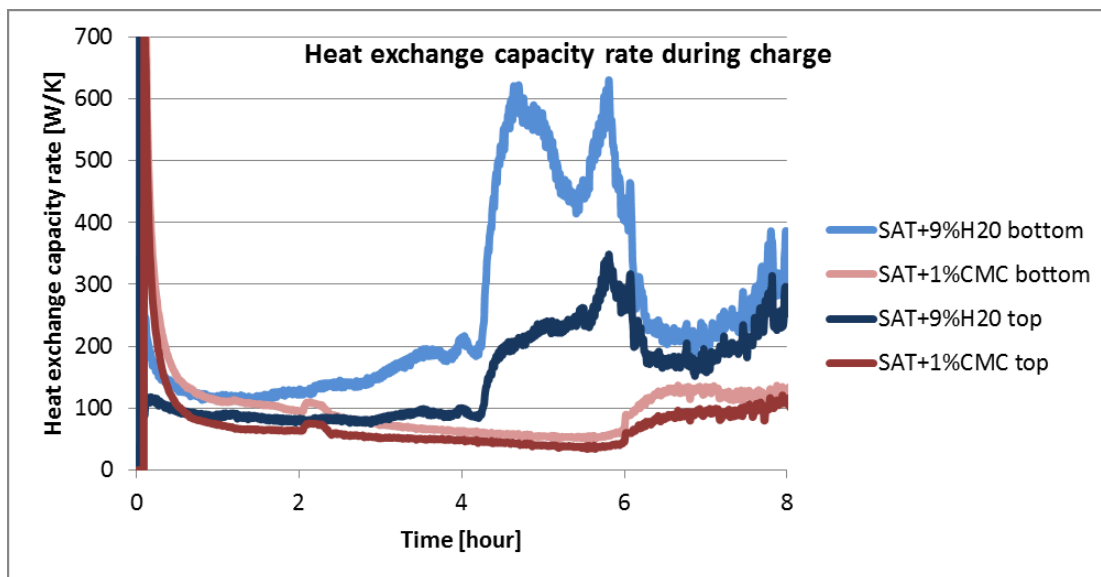


Figure 24. Heat exchange capacity rate during charge.

The unit with SAT and extra water was kept in supercooled state for up to 8 weeks and the unit with SAT and CMC was kept in supercooled state for up to 5 weeks before solidification was intentionally initiated and the units were discharged.

After solidification the discharge power of the modules peaked at approximately 5 kW in the beginning of the discharge. The heat transfer fluid temperature was raised from approximately 25°C to 45°C in the start of the discharge. This was with a flow rate of 2 l/min in each heat exchanger. A lower flow rate gave a 2-3 K higher outlet temperature. The PCM temperature after solidification peaked at 58°C in the SAT mixture with CMC whereas the PCM temperature in the SAT mixture with extra water peaked at 53°C.

Further details are given in [9].

#### *Measurements on cylindrical units*

Comparing the HXCR during charge of the cylindrical unit with the two different SAT mixtures showed similar tendency as for the flat storage units. The HXCR was significantly lower for the unit with the thickened SAT compared to the unit with SAT and extra water. Adding oil to the PCM chamber gave minimal improvement to the HXCR during charge. The amount of oil was however very small and larger amount of oil may show better improvements.

The released heat after solidification in the unit with SAT and 6.4% extra water was 177 kJ/kg in the first test cycles dropping to 140 kJ/kg after 17 test cycles. Severe phase separation was observed in the unit and the cause of the loss of heat storage potential. The heat content per kg SAT measured in the cylindrical unit was somewhat lower than for the flat

storage unit. This may indicate that the risk of phase separation is higher in a tall unit compared to a unit of lower height.

The heat released after solidification of the SAT mixture with Xanthan rubber was stable at 205-210 kJ/kg in the cylindrical storage unit over the 40 test cycles carried out. This was similar to the heat content measured in the flat unit with SAT thickened with CMC.

Figure 25 shows the theoretical thermal energy content of the SAT mixture with Xanthan rubber over a selected temperature interval. The theoretical energy content is shown with blue curves, where the dotted curve represents the supercooled state. Measurements from two selected test cycles where stable supercooling were achieved are also shown. The areas marked with circles are the states where the temperature of the storage and PCM was considered uniform and the comparison between the measurements and calculations area valid.

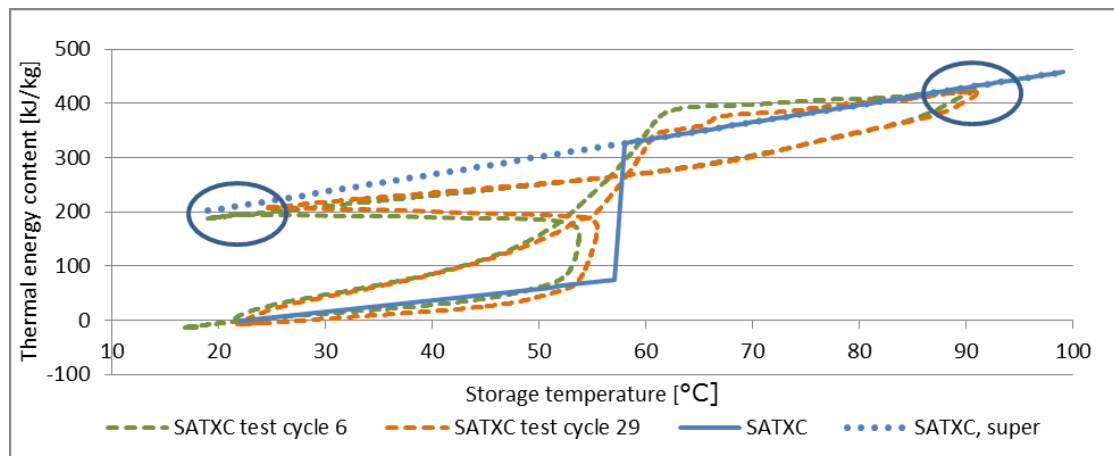


Figure 25. Theoretical and measured thermal energy content of SAT with Xanthan rubber in cylindrical unit.

In the cylindrical units, supercooling was unstable in most test cycles where solidification started spontaneously during the active or passive discharge of the sensible heat. Only short periods of stable supercooled PCM were achieved in the cylindrical units. Further details are given in [9].

### Demonstration system

Four flat heat storage modules were after the laboratory testing installed as a part of a full scale demonstration solar heating system in the solar heating test facilities at the Technical University of Denmark. Two of the modules are of black steel, two are of stainless steel. The heat storage material in the modules is sodium acetate trihydrate with different additives, see table 1. Whether it was possible to completely melt the SAT mixtures in the heat storage and thereafter achieve supercooling was investigated.

	Module 1	Module 2	Module 3	Module 4
Tank material	Carbon steel	Stainless steel	Carbon steel	Stainless steel
PCM composite	SAT + 1% CMC + 2% C + 5l Oil	SAT + 1% CMC	SAT + 1% H <sub>2</sub> O + 1% EDTA	SAT + 2 % EDTA
PCM mass	202 kg	220 kg	202 kg	158 kg

Table 1. Heat storage modules with heat storage materials. EDTA: Ethylene Diamine Tetracetic.

The main components of the demonstration system were 22.4 m<sup>2</sup> of evacuated tubular collectors, a 735 L tank in tank water buffer store and four flat heat storage units covered with insulation. Figure 26 shows a principle diagram of the demonstration system.

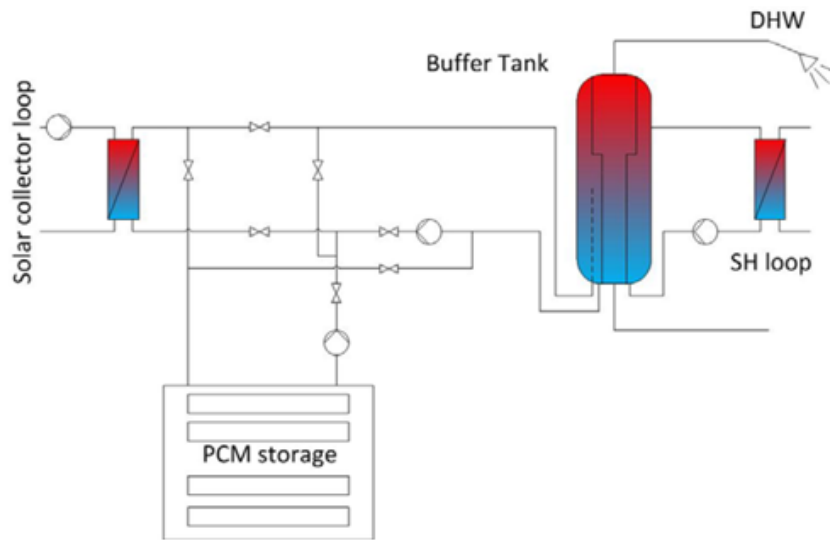


Figure 26. Principle diagram of demonstration system with PCM storage, pipes loops, water buffer storage.

Figure 27 (a) shows the 22.4 m<sup>2</sup> of solar collectors of the demonstration system which charge the PCM storage units. Figure 27 (b) shows the insulated water buffer storage for the demonstration system.



Figure 27. (a) Evacuated solar collectors for demonstration system. (b) 735 L water buffer storage for demonstration system.

Figure 28 shows the temperature development of the PCM temperature in one unit over a 12 days period in August 2015. With the heat from the solar collector the PCM temperature was increased from 25°C to 85°C over the first 3 days in Figure 28. Several units were heated in parallel. It would therefore be possible to heat the unit from 25°C to 85°C in one day if only one unit was charged. After the third day the unit was let to passively cool down to ambient temperature. After another 7 days the PCM inside the unit had reached 29°C and the solidification was intentionally initiated and discharged.

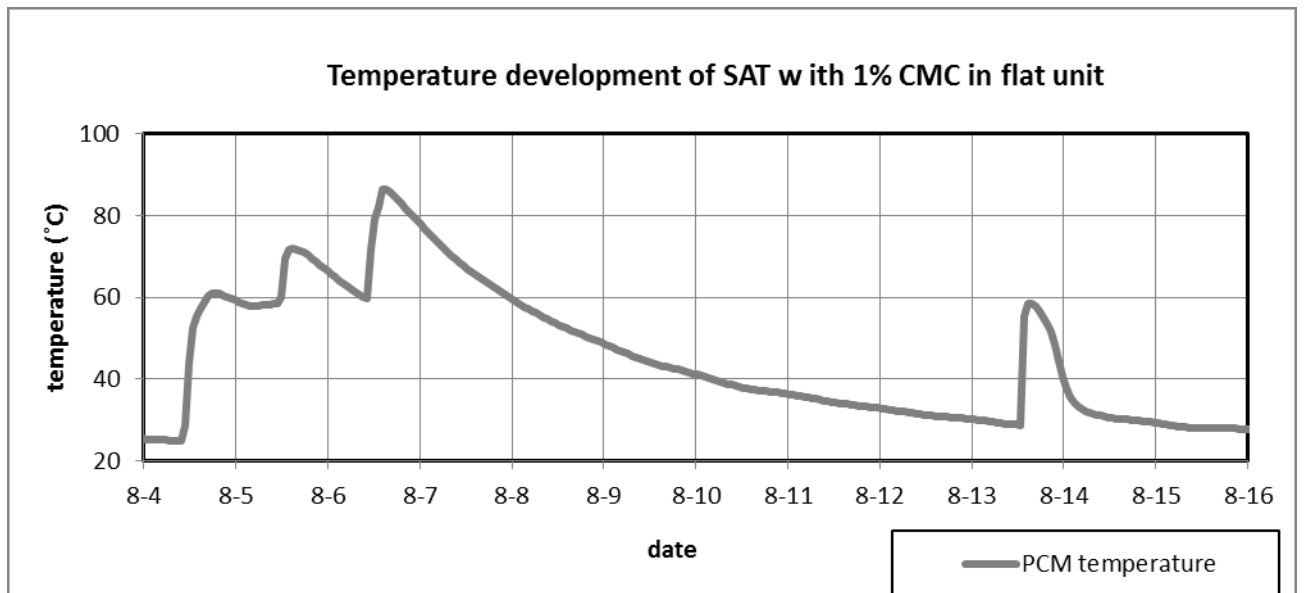


Figure 28. PCM temperature in flat heat storage unit charged with heat from solar collectors and cool down period.

Further details on the operation of the demonstration system are given in [11].

#### Dissemination of results:

The project results were disseminated through the PhD thesis:

"Compact seasonal PCM heat storage for solar heating systems", Mark Dannemand, Department of Civil Engineering, Technical University of Denmark.

Additional, 3 scientific journal articles were published with the findings:

1. Long term thermal energy storage with stable supercooled sodium acetate trihydrate, Mark Dannemand, Jørgen M. Schultz, Jakob Berg Johansen, Simon Furbo, *Applied Thermal Engineering*, Vol. 91 pp. 671–678, 2015, doi:10.1016/j.applthermaleng.2015.08.055.
2. Solidification behaviour and thermal conductivity of bulk sodium acetate trihydrate mixtures with thickening agents and graphite powder, Mark Dannemand, Jakob Berg Johansen, Simon Furbo, *Solar Energy Materials and Solar Cells*, Vol 145, Part 3, pp. 287–295, 2016, doi:10.1016/j.solmat.2015.10.038.
3. Experimental investigations on prototype heat storage units utilizing stable supercooling of sodium acetate trihydrate mixtures, Mark Dannemand, Janne Dragsted, Jianhua Fan, Jakob Berg Johansen, Weiqiang Kong, Simon Furbo, *Applied Energy*, Vol 169, pp. 72–80, 2016, doi:10.1016/j.apenergy.2016.02.038.

2 additional journal articles have been submitted to scientific journals and are currently under review:

4. Experimental investigations on cylindrical latent heat storage units with sodium acetate trihydrate composites utilizing supercooling, Mark Dannemand,

Jakob Berg Johansen, Weiqiang Kong, Simon Furbo, Submitted to Applied Energy.

5. Experimental investigations on heat content of supercooled sodium acetate trihydrate by a simple heat loss method, Weiqiang Kong, Mark Dannemand, Jakob Berg Johansen, Jianhua Fan, Janne Dragsted, Gerald Englmaier, Simon Furbo, Submitted to Solar Energy Materials and Solar Cells.

Results were also presented with conference papers at conferences:

1. Validation of a CFD model simulating charge and discharge of a small heat storage test unit based on a sodium acetate water mixture, Mark Dannemand, Jianhua Fan, Simon Furbo, Janko Reddi, ISES Solar World Congress 2013, Energy Procedia, 57 pp. 2451 – 2460, 2014, doi:10.1016/j.egypro.2014.10.254.  
Presented by poster
2. Laboratory test of a prototype heat storage module based on stable supercooling of sodium acetate trihydrate, Mark Dannemand, Weiqiang Kong, Jianhua Fan, Jakob Berg Johansen, Simon Furbo, International Conference on Solar Heating and Cooling for Buildings and Industry, SHC 2014, Energy Procedia, 70, pp. 172-181, 2015, doi:10.1016/j.egypro.2015.02.113  
Presented orally
3. Solidification Behaviour and Thermal Conductivity of Bulk Sodium Acetate Trihydrate Mixtures with Thickening Agents and Graphite Powder, Mark Dannemand, Jakob Berg Johansen, Simon Furbo, IEA ECES Greenstock conference 2015  
Presented by poster
4. Laboratory test of a cylindrical heat storage module with water and sodium acetate trihydrate, Mark Dannemand, Weiqiang Kong, Jakob B. Johansen, Simon Furbo, SHC 2015, International Conference on Solar Heating and Cooling for Buildings and Industry, Energy Procedia.  
Presented orally
5. Testing of PCM heat storage units with solar collectors as heat source, Gerald Englmaier, Mark Dannemand, Jakob B. Johansen, Weiqiang Kong, Janne, Dragsted, Simon Furbo, Jianhua Fan, International Conference on Solar Heating and Cooling for Buildings and Industry 2015, Energy Procedia .  
Presented orally
6. Laboratory Testing of Solar Combi System with Compact Long Term PCM Heat Storage, Jakob Berg Johansen, Gerald Englmaier, Mark Dannemand, Weiqiang Kong, Jianhua Fan, Janne Dragsted, Bengt Perers, Simon Furbo, SHC 2015, International Conference on Solar Heating and Cooling for Buildings and Industry. Energy Procedia  
Presented by poster
7. Thermal conductivity enhancement of sodium acetate trihydrate by adding graphite powder and the effect on stability of supercooling, Jakob Berg Johansen , Mark Dannemand, Weiqiang Kong, Jianhua Fan, Janne Dragsted, Simon Furbo, International Conference on Solar Heating and Cooling for Buildings and Industry, SHC 2014, Energy Procedia 2015, Volume 70, pp. 249-256  
Presented by poster
8. Applications of Compact Thermal Energy Storage, Wim van Helden, Motoi Yamaha, Christoph Rathgeber, Andreas Hauer, Nolwenn Le Pierres, Barbara Mette, Pablo Dolado, Mark Dannemand, Simon Furbo, Alvaro Campos-Celador, Ruud Cuypers, Andreas König-Haagen, Benjamin Fumey, Robert Weber, Rebekka Köll, SHC 2015, In-

ternational Conference on Solar Heating and Cooling for Buildings and Industry.  
Presented orally

9. Ageing stability of sodium acetate trihydrate with and without additives for seasonal heat storage, Weiqiang Kong, Mark Dannemand, Jakob Berg Johansen, Jianhua Fan, Janne Dragsted, Simon Furbo, ISES Solar World Congress 2015.  
Presented by poster

Results were presented orally at 6 IEA Task 42 experts meetings:

1. Fraunhofer-Institut für Solare Energiesysteme ISE, Germany, 15.04.2013 to 17.04.2013
2. National Institute of Chemistry, Slovenia, 02.10.2013 to 04.10.2013
3. National Institute of Applied Sciences (INSA), France, 28.04.2014 to 30.04.2014
4. CHUBU University, Japan, 08.10.2014 to 10.10.2014
5. Vienna University of Technology (TU Wien), Austria, 09.02.2015 to 11.02.2015
6. University of Zaragoza, Spain, 05.10.2015 to 07.10.2015

Additional conferences/workshops where project results were presented:

1. Intersolar Europe 2013, Munich, 17.06.2013 to 18.06.2013, orally
2. DTU energy conference 2013, poster
3. DTU workshop on compact long term heat storage, Kgs. Lyngby, January 28, 2016.  
Presentations from the workshop available on: on  
[http://www.byg.dtu.dk/Om\\_Instituttet/bygkonferencer/DTU\\_Byg\\_arrangementer/Compact-Heat-Storage-Workshop](http://www.byg.dtu.dk/Om_Instituttet/bygkonferencer/DTU_Byg_arrangementer/Compact-Heat-Storage-Workshop)

Finally, the investigations are presented by means of videos:

<https://www.youtube.com/watch?v=sLPrfG9btH0>

<http://videnskab.dk/miljo-naturvidenskab/hvordan-gemmer-vi-solens-varme-til-vinteren>

## **1.6 Utilization of project results**

Further development is needed to make the storage economically attractive to the market. The project results form an excellent basis for development of inexpensive reliable compact long term heat storage solutions. Such heat storage solutions can be used in different energy systems, which will be suitable for the future energy system with increased use of renewables.

No patents are expected from the research carried out at DTU.

Further, lectures presenting the project have been given in the solar energy courses at DTU, and several Bachelor projects, Master thesis projects and special courses have been carried out by DTU students.

An application for participation in the coming IEA SHC Task project "Material and component development for thermal storage systems" has been forwarded to the Danish Energy Agen-

cy's EUDP programme. If the application is accepted work together with industries will be carried out with the aim to develop economically attractive long term PCM heat storages for different applications.

## 1.7 Project conclusion and perspective

It can be concluded that the thermal conductivity of SAT can be increased by adding graphite to the PCM mixture. 1% Xanthan rubber or 5% CMC was required to keep a uniform composite where the graphite did not settle to the bottom of the sample container. Graphite flakes had a much better effect on increasing the thermal conductivity compared to graphite powder.

If SAT solidified from a supercooled state or if it solidified without supercooling affected the thermal conductivity of the bulk SAT composites. Solidification without supercooling resulted in a denser crystal structure with higher thermal conductivity and cavities formed away from the heat transfer area. Solidification from supercooled state resulted in fewer large cavities in the bulk SAT samples and a lower thermal conductivity. The type of thickening agent added to the SAT composites affected the formation of cavities.

Phase separation reduced the heat storage potential of SAT significantly. Adding water to the SAT can limit the loss in heat content of supercooled SAT due to phase separation. In large heat storage unit sizes the heat content is however reduced over repeated charge and discharge cycles. This was especially evident in a 1.5 m tall storage unit. SAT composites with the thickening agents CMC and Xanthan rubber showed to have a high stable heat content also over repeated charge and discharge cycles in the 1.5 meter tall storage unit.

The storage principle of utilizing stable supercooled sodium acetate trihydrate for long-term heat storage worked in heat storage unit sizes large enough for systems in single family houses. The supercooling in the tested prototypes units was however not stable in all cycles. Uncontrolled solidification occurred in a number of test cycles. This was caused by improper handling of the expansion, inner surface design of PCM chamber with cracks and operation of the units. In rigid storage units of steel and stainless steel it was necessary to operate the units with minimal pressure built up in the PCM chamber during charge and discharge due to risk on uncontrolled crystallization. An expansion volume inside the PCM chamber connected to an external expansion tank allow for having the SAT remain stable in supercooled state. Under laboratory test conditions prototype heat storage units were in supercooled state for up to two months after which the solidification was intentionally initiated and the latent heat of fusion discharged.

Simulations showed that the heat exchange capacity of the heat storage units had significant effect of the yearly performance of a combi solar heating systems of a single family house.

It was shown that the storage principle works but there is still room for improvements on different levels.

### *SAT composites:*

The SAT mixtures with thickening agents tested in the prototype units showed to have a heat content in the supercooled state of 205-210 kJ/kg which is 90% of the theoretical maximum heat content of SAT of 230 kJ/kg at 20°C. Further increasing the heat content may be possible by optimizing the ratio of the thickening agent in the SAT mixture or by refining the mixing method. As an alternative to the thickening agents, liquid polymers, additives with chelating effect or additives which increase the solubility of the sodium acetate in water may also be a solution.

One major drawback of using a thickening agent for solving phase separation in SAT is the increased viscosity which causes lower heat transfer by convection during charge. The liquid polymers as additives have the potential to reduce phase separation without increasing the viscosity of the PCM. In that case heat transfer during charge may be as high as for SAT. However, in the solidified state when discharging the SAT after a storage period, the PCM is entirely in solid state and the heat transfer is dominated by thermal conduction. In this case heat transfer of the SAT mixture with thickening agent and other additives may be the same. To increase the discharge power after solidification it is therefore necessary to increase the thermal conductivity of the PCM mixture. This could be by adding graphite to the PCM com-



posite. As the investigation showed it was required to thicken the SAT to keep the graphite suspended in the mixture. In this case the thickening agents solve both the phase separation problem and keeping the graphite suspended in the solution. Higher discharge powers after solidification may therefore be achieved in PCM mixtures with thickening agents and graphite compared to PCM composites with liquid additives. Graphite flakes showed to have a better effect on increasing the thermal conductivity compared to graphite powder. The size of the graphite flakes may show to have an influence of the effect or there may be other graphite additives which prove even better. This may be graphite fibers or expanded graphite. The performances of heat storage units in a solar heating system will to a high extend depend on the design of the systems, the supply of solar energy and the demand profiles. Whether the system as a whole will perform better with a higher heat transfer during the charge which will be possible with the liquid additives or if the system will perform better with a higher discharge power from the thickened PCM mixtures with graphite is a complex matter. Further simulations must clarify this but as the storage concept aims to deliver heat when solar energy is not available it is likely that higher discharge power is desired. Adding oil to the PCM chamber of a storage unit potentially increases the heat transfer as the oil fills in the gaps that are formed when the SAT solidifies and contracts. When the PCM is in liquid state the oil should float on top of the PCM. When PCM solidifies and contracts the oil should be sucked into the cavities formed in the PCM to increase heat transfer. When the PCM again is melted the oil should then again float to the top of the PCM to be ready for the next cycle. In a thickened PCM composite there is however a risk that the oil will not float to the top when the PCM is melted but stay trapped in the thickened PCM in a similar way as air bobbles are trapped. Oil as an effective way to enhance heat transfer in thickened PCM mixtures may therefore not be cycling stable over repeated test cycles. If a PCM mixture is thick enough to avoid phase separation and to keep graphite suspended and at the same time allows for oil to escape and float on top is unknown. In the research the general practice was to heat the SAT mixtures to 80°C to achieve the stable supercooling. Some more detailed investigations of the required temperature and heating duration to achieve the supercooling may be investigated. Especially SAT mixtures with additives could be investigated as the additives may influence this temperature requirement. If a lower temperature is required for stable supercooling, this will have an effect on system performance and gives more options for implementation of the heat storage technology.

#### *Heat storage unit designs*

The investigations showed that stable supercooling was not achieved in every test cycle with the tested prototype heat storage units. It is of course necessary that the supercooling is controlled in every cycle for such storage system. In some cases the supercooling failed in the first couple of test cycles and was afterwards achieved.

It was observed that in some cases the solidification of the SAT started from the bottom of the cylindrical unit. This was most likely due to the way the sides of the cylinder were joined with the bottom which formed a crevice or crack along the assembly line. Another critical point in the bottom of the cylinder was the location where the tubes for the heat exchanger penetrated the bottom. In both areas there was a risk of crystals being trapped under high pressure in the cracks and with a slight movement of the cylinder the trapped crystals could be released to initiate crystallization of the entire PCM volume. In the flat unit critical areas were when inner stabilizing supports of the PCM chamber were constructed where cracks could form between parts and when the lid closing the PCM chamber was in contact with the PCM. A design of the heat storage units and especially the inner surface of PCM chamber being smooth could possibly lead to increased supercooling stability. A coating on the inner surfaces could possibly eliminate the problem with cracks. Alternatively, if the PCM chamber was made from a softer material, the risk of high pressures at cracks causing crystallization may possibly be reduced.

It was shown that the stores needed some expansion devices to handle the expansion and contraction of the PCM without causing too high pressures and deformation of the units to obtain stable supercooling in the rigid storage units. An inner expansion volume connected to an external expansion device seemed to be working in many cases. In some cases, however, the tube connecting the internal and external expansion tanks was blocked after a number of

test cycles leading to spontaneous solidification. The blockage was possibly by SAT which had migrated from the storage to the tube. An integrated expansion device in the PCM unit could avoid the need for the external expansion device and eliminate the risks associated with that. An air volume in the PCM chamber where the expansion of the PCM could be taken up by compressing the air will most likely need to be impractically large to avoid too high pressures. A flexible membrane in the top of the storage unit above the PCM which could move as the PCM expanded and contracted could be a solution. This could be a solution when the storage units are of rigid material such as steel. Alternatively, the outer shell of the PCM chamber could be of a flexible material which could take up the density changes. An outer shell of a soft plastic material could be a solution. Plastic containers casted of softer material could possibly be made with smooth inner surfaces without any joining of parts where a potential crack could pose a risk of trapped crystals. This could be a design that supports more stable supercooling. A heat exchanger spiral with or without fins could be inserted to the PCM from the top of the container with the joining parts being in an air gap above the PCM.

In some cases the spontaneous solidification started from the top of the cylindrical unit and from the end of the flat unit with the expansion chamber. Nucleation possibly started at the upper surface of the PCM. This nucleation could be caused by airborne SAT crystals or other dust particles in the air inside the expansion volume. When these particles land on the PCM surface the solidification may start. Alternatively, particles or unmelted SAT crystals could be stuck on the inner surface of the PCM chamber above the supercooled SAT and at one point when they fall down and land on the surface of supercooled PCM and crystallization is initiated. If this is the case having a layer on top of the SAT mixture which neutralizes the particle causing the spontaneous crystallization may be a solution.

#### *Heat storage implementation*

It is clear that a high heat transfer rate between the PCM and the heat transfer fluid is of key importance in this storage. As argued the material properties of the PCM affect the heat transfer. However of equal importance is the heat exchanger design and system design. Smarter and possibly more complex designs of the heat exchangers should be considered to increase the performance of the storage units. More complex heat exchange designs are likely to be more costly therefore some parameter variation analysis optimizing the heat exchanger design and the PCM properties as well and the applications must be considered. Another consideration of implementing the storage is to have a water buffer store as part of the system. This buffer storage could cover the demands of a high discharge power over short time while the PCM storage units are discharged into the water buffer with lower power but with high temperatures over longer periods. In a system with a water buffer storage the demand for HXCR for the PCM storage may not be so high.

The cost of the storage units does naturally play a vital role for the extent of implementation. Considering the life time of the storage and the number of cycles over its lifetime, the storage should provide high heat storage capacity at a low cost. Where this type of storage is justifiable to install depend on the lifecycle cost of the full heating system of the house compared with alternative technologies. This storage principle may not prove economically feasible in areas with district heating. However, in more rural areas where few other sustainable energy sources are available this concept may be feasible.

The storage principle with supercooling of SAT is relatively simple. SAT is a simple low cost material which is easy to handle and there are low requirements for the containers. Potentially stores can therefore be designed in a simple way at a low cost, for instance of plastic. For the two investigated storage designs, the cost was significantly lower for the cylindrical unit compared to the flat unit due to the production methods and amount of material for the tanks. The main reason for designing the unit flat was to reduce the risk of phase separation but as this problem was solved with thickening agents even in tall units there is no longer incentive to design the units flat.

The number and sizes of the PCM storage units which has to form the PCM storage will depend on the demands of the system. What size water buffer storage will give the best performance and how it works with the PCM storage will depend on the system and demands. Optimizing this relationship including solar collector area is complex and can be done by simulations.

The scope of the project was to consider the heat storage as part of a solar heating system. The storage principle could possibly also be used combined with other technologies or in other systems. This could be combining the heat storage with heat pumps and utilizing periods with cheap electricity. Also future systems relying on solar heating and cheap electricity in winter are of interest, because the needed heat storage volume can be strongly reduced if the storage is heated during winter. Or it could be in applications which runs more but shorter cycles for example waste heat of industrial applications.

All in all the project results form an excellent basis for development of economically attractive compact long term PCM heat storages.

## **Annex**

Relevant links:

[http://www.byg.dtu.dk/Om\\_Instituttet/bygkonferencer/DTU\\_Byg\\_arrangementer/Compact-Heat-Storage-Workshop](http://www.byg.dtu.dk/Om_Instituttet/bygkonferencer/DTU_Byg_arrangementer/Compact-Heat-Storage-Workshop)

<https://www.youtube.com/watch?v=sLPrfG9btH0>

<http://videnskab.dk/miljo-naturvidenskab/hvordan-gemmer-vi-solens-varme-til-vinteren>

<http://task42.iea-shc.org/>

<http://comtes-storage.eu/>

<http://samssa.eu/>

<http://www.sotherco.eu/index.php>

<http://www.merits.eu/>

## **References**

- [1] Experimental investigations on heat content of supercooled sodium acetate trihydrate by a simple heat loss method. W. Kong, J. Berg Johansen, J. Fan, J. Dragsted, G. Englmair, S. Furbo. Paper submitted to Solar Energy Materials and Solar Cells.
- [2] Solidification behavior and thermal conductivity of bulk sodium acetate trihydrate mixtures with thickening agents and graphite. M. Dannemand, J. Berg Johansen, S. Furbo. Solar Energy Materials and Solar Cells 145, pp. 287-295, 2016.
- [3] Validation of a CFD model simulating charge and discharge of a small heat storage test module based on a sodium acetate water mixture. M. Dannemand, J. Fan, S. Furbo, J. Reddi. Energy Procedia 57, pp. 2451-2460, 2014.
- [4] System Simulation Report System: PCM with supercooling. A report of IEA Solar Heating and Cooling Programme – Task 32 Advanced storage concepts for solar and low energy buildings. Department of Civil Engineering, Technical University of Denmark, J. M. Schultz, 2008.
- [5] Long term thermal energy storage with stable supercooled sodium acetate trihydrate. M. Dannemand, J.M. Schultz, J. Berg Johansen, S. Furbo. Applied Thermal Engineering 91, pp. 671-678, 2015.
- [6] Solidification in Heat Packs: III. Metallic Trigger, AIChE J. 49, pp. 522-529. doi:10.1002/aic.690490222. M.A. Rogerson, S.S.S. Cardoso, 2003.
- [7] Immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 48 to 58C temperature range, Mater. Corros. 53, pp. 902-907.

Doi:10.1002/maco.200290004. L.F. Cabeza, J. Roca, M. Nogues, H. Mehling, S. Hiebler, 2002.

[8] Development of seasonal heat storage based on stable supercooling of a sodium acetate water mixture, in: *Energi Procedia*, pp. 1-10. S. Furbo, J. Fan, E. Andersen, Z. Chen, B. Perers, 2012.

[9] Experimental investigations on prototype heat storage units utilizing stable supercooling of sodium acetate trihydrate mixtures. M. Dannemand, J. Dragsted, J. Fan, J. Berg Johansen, W. Kong, S. Furbo. *Applied Energy* 169, pp. 72-80, 2016.

[10] Experimental investigations on tall cylindrical latent heat storage units with sodium acetate trihydrate composites utilizing supercooling. M. Dannemand, J. Berg Johansen, W. Kong, S. Furbo. Submitted to *Applied Energy*.

[11] Testing of PCM heat storage units with solar collectors as heat source. G. Englmair, M. Dannemand, J. Berg Johansen, W. Kong, J. Dragsted, S. Furbo, J. Fan. SHC 2015 Conference paper, Istanbul, Turkey, 2015.