SOLAR HEATING & COOLING PROGRAMME
INTERNATIONAL ENERGY AGENCY

Task 58 / Annex 33
Subtask 3P
Deliverable 2

Experimental devices to investigate degradation of PCM

IEA SHC TASK 58 / ES ANNEX 33 | "Material Development for Compact Thermal Energy Storage"

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Contents

1 Contributors

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2 Introduction

Deliverable 2 of Subtask 3P is a collection of questionnaires regarding experimental devices that are used by the experts of Task 58 / Annex 33 to investigate the degradation of Phase Change Materials (PCM). Three types of experiments are considered: Tests on degradation of PCM over thermal cycling (type I), tests on degradation of PCM with stable supercooling (type II), and tests on degradation of phase change slurries (type III).

As the content of this deliverable is intended to be published as a peer-reviewed paper, the questionnaires are presented without further discussion in this document.

3 Questionnaires

3.1 Type I: Tests on degradation of PCM over thermal cycling

In the case of solid-liquid PCM, heat is stored and released under repeated melting and solidification processes, also referred to as thermal cycles. In order to assess the suitability of a PCM for a thermal storage application, testing its thermal properties (e. g. melting temperature and melting enthalpy) under repeated thermal cycling taking service conditions into account is crucial.

Testing device: “CIEMAT AGH”

Contact: Rocío Bayón

Description

Thermal cycling oven under air atmosphere, controlled heating & cooling rate, sample temperature monitoring, various samples at the same time with different sizes

Picture / scheme

Set-up outside

Oven inside

Min. Temperature [°C]	Max. Temperature [°C]
Room temperature	*350 ºC*
Typical heating rate [K/min] *1-20*	Typical cooling rate [K/min] *1-20*

Typical temperature profile

Cycles at two temperature levels with transition via linear ramps. ΔT above-below melting temperature depending on the specific application.

Tests at constant temperature (ΔT) above melting point.

Typical number of cycles per day [1/d]	Max. sample volume [ml]
1 cycle/day	*60 - 100*
PCM in contact with *air*	Sample container material *Glass beaker, glass tube, ceramic crucible*

Measured data

*T*emperature-time curve for the sample and oven

Stability checked via…

Comparison of temperature-time curves of different cycles

DSC measurements after a certain number of cycles or time

Sample mass monitoring after certain number of cycles or time

References (articles, presentations, etc.)

R. Bayón, M. Biencinto, E. Rojas, N. Uranga. STUDY OF HYBRID DRY COOLING SYSTEMS FOR STE PLANTS BASED ON LATENT STORAGE. To be presented at ISEC conference in Graz, October 2018.

M.M. Rodríguez-García, E. Rojas, R. Bayón, Test campaign and performance evaluation of a spiral latent storage module with Hitec® as PCM, Solar Heating and Cooling Conference 2017, Abu Dhabi, November 2017. Accepted for AIP Conference proceedings

Comments

These tests should be performed under conditions as close as possible to service conditions. They should be considered only as preliminary stability test without any long-term behavior extrapolation.

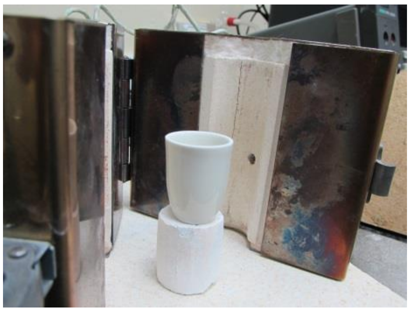
Testing device: “CIEMAT HDR”

Contact: Rocío Bayón

Description

Thermal cycling oven under air atmosphere, controlled heating and natural cooling, sample temperature monitoring, only one sample

Picture / scheme

Set-up outside	Oven inside
	

Min. Temperature [°C]	Max. Temperature [°C]
Room temperature	*500 ºC*

Typical heating rate [K/min]	Typical cooling rate [K/min]
1-20	*natural*

Typical temperature profile

Cycles at two temperature levels with transition via linear ramps. ΔT above-below melting temperature depending on the specific application.

Tests at constant temperature (ΔT) above melting point.

Typical number of cycles per day [1/d]	Max. sample volume [ml]
1 cycle/day	*10*

PCM in contact with	Sample container material
air	*ceramic crucible*

Measured data

*T*emperature-time curve for the sample

Stability checked via…

Comparison of temperature-time curves of different cycles

DSC measurements after a certain number of cycles or time

Sample mass monitoring after certain number of cycles or time

References (articles, presentations, etc.)

R. Bayón, M. Biencinto, E. Rojas, N. Uranga. STUDY OF HYBRID DRY COOLING SYSTEMS FOR STE PLANTS BASED ON LATENT STORAGE. To be presented at ISEC conference in Graz, October 2018.

M.M. Rodríguez-García, E. Rojas, R. Bayón, Test campaign and performance evaluation of a spiral latent storage module with Hitec® as PCM, Solar Heating and Cooling Conference 2017, Abu Dhabi, November 2017. Accepted for AIP Conference proceedings

Comments

These tests should be performed under conditions as close as possible to service conditions. They should be considered only as preliminary stability test without any long-term behavior extrapolation.

Testing device: "CIEMAT SUBMA"

Contact: Rocío Bayón

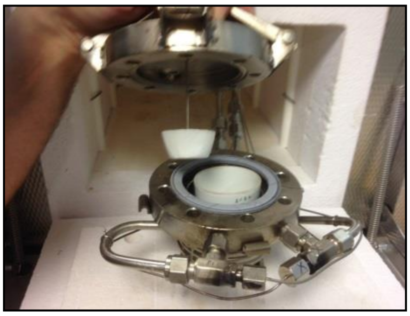
Description

Thermal cycling device inside a furnace, controlled heating and natural cooling, sample temperature monitoring, only one sample, different atmospheres are possible.

Picture / scheme

Set-up outside +furnace

Set-up inside



Min. Temperature [°C] *Room temperature*	Max. Temperature [°C] *500 ºC*
Typical heating rate [K/min] *1-20*	Typical cooling rate [K/min] *natural*

Typical temperature profile

Cycles at two temperature levels with transition via linear ramps. ΔT above-below melting temperature depending on the specific application.

Tests at constant temperature (ΔT) above melting point.

Typical number of cycles per day [1/d] *1 cycle/day*	Max. sample volume [ml] *60*
PCM in contact with *Air, N_2, Ar or other*	Sample container material *ceramic crucible*

Measured data

*T*emperature-time curve for the sample

Stability checked via…

Comparison of temperature-time curves of different cycles

DSC measurements after a certain number of cycles or time

Sample mass monitoring after certain number of cycles or time

References (articles, presentations, etc.)

M.M. Rodríguez-García, R. Bayón, E. Rojas, Stability of D-mannitol upon melting/freezing cycles under controlled inert atmosphere, Energy Procedia 91 (2016) 218–225. https://doi.org/10.1016/j.egypro.2016.06.207.

Comments

These tests should be performed under conditions as close as possible to service conditions. They should be considered only as preliminary stability test without any long-term behavior extrapolation.

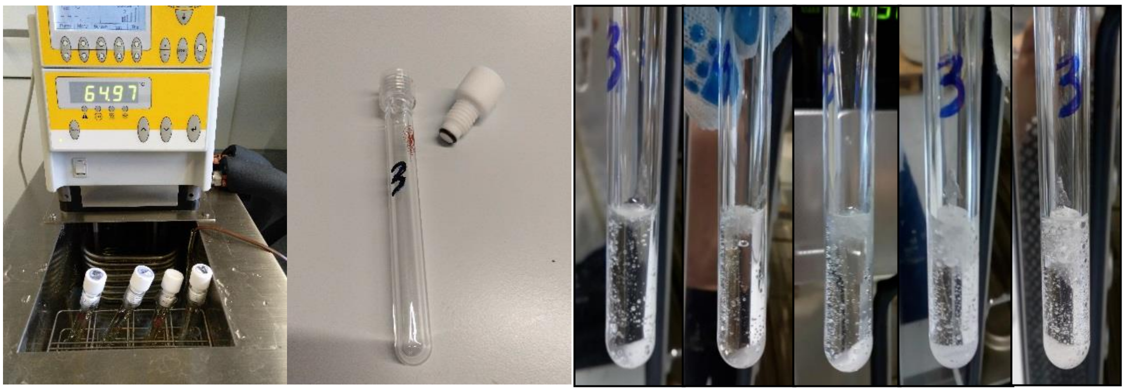
Testing device “EHU”

Contact: Gonzalo Diarce

Description

We use an own-made arrangement comprised by a thermostatic bath and airtight tubes. The samples are inserted inside the tubes and these are immersed into the thermostatic bath, which uses a silicone oil as a heat transfer fluid. The tubes are made by glass and include a nylon screwed cap with an O-ring sealing that ensures tightness. They can handle pressures up to 10 bar. The usual sample size is around 5 g, although tubes with variable dimensions can be employed. The arrangement and configuration is flexible and it is adapted to the PCM under study and the kind of degradation expected. The temperature program usually comprises consecutive heating and cooling cycles if physical phase segregation is expected. When the material under study might undergo thermal decomposition, then the program normally consists of submitting different samples to a constant temperature. The samples are extracted after different periods of time and analyzed. The analysis depends on the type of behaviour expected. Several complementary techniques are used. Variations on the thermal behaviour (storage capacity, melting temperatures and others) are evaluated by DSC. Visual control is kept by periodic imaging. Additional information is obtained by X-Ray diffraction, FTIR, liquid chromatography and others.

Picture / scheme



Min. Temperature [°C] -45 ºC	Max. Temperature [°C] *200 ºC*
Typical heating rate [K/min] *Depending on the feature under analysis*	Typical cooling rate [K/min] *Depending on the feature under analysis*

Typical temperature profile

Depending on the feature under analysis. Thermal cycles or constant temperatures can be employed.

Typical number of cycles per day [1/d] *Variable*	Max. sample size [g] *5*
PCM in contact with… *Air (normally). Other gases (N2, Ar, etc) can be introduced by the use of a controlled atmosphere chamber*	Sample container material *Normally glass. Metallic containers have been also used*

Measured data

Temperatures of the thermostatic bath. The inside temperature of the samples could be also controlled by introducing a thermocouple inside a “sacrified” sample.

Stability checked via…

DSC, optically, X-Ray Diffraction, FTIR.

Testing device “HSLU”

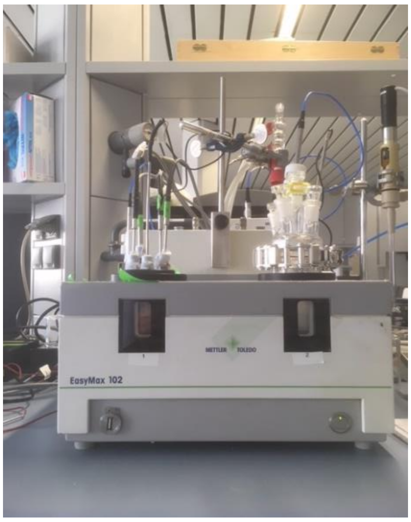
Contact: Oliver Fellmann, Rebecca Ravotti

Description

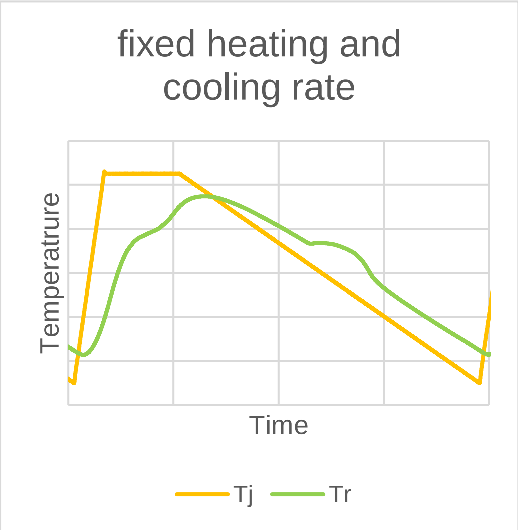
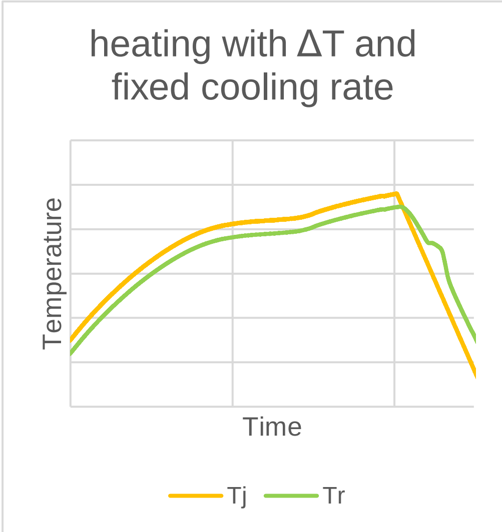
Easymax 102; cycling device and synthesis station; two heating chambers with various adapters allowing the measurement with one to five vessels (1x100ml, 3x25ml, 5x8ml) per chamber; magnetic or mechanical stirring. However, the Easymax 102 only contains one temperature sensor per chamber. Therefore, an external logging device to record the temperature of the other vessels is used.

Different heating and cooling rates can be applied, either using a fixed rate or by controlled heating so that a ΔT between measured inside temperature and the temperature of the jacket is not exceeded. If more than one vessel per chamber is applied, only heating by rate is possible.

Picture / scheme



Min. Temperature [°C]	Max. Temperature [°C]
-40	*180*
Typical heating rate [K/min]	**Typical cooling rate [K/min]**
10	*0.5*

Typical temperature profile	
 	
Typical number of cycles per day [1/d] *10*	Sample volume [ml] *1x100 ml, 3x25 ml, 5x8 ml*
PCM in contact with… *air*	Sample container material *glass*
Measured data *Temperature, reaction enthalpy, heat transfer coefficient, specific heat*	
Stability checked via… *Optical appearance of PCM; comparison of temperature-time curves of different cycles; DSC measurements after a certain number of cycles*	

Testing device "LAMTE"

Contact: Dominic Groulx

Description

PCM Thermal Cycler; simultaneous cycling of 8 samples within a similar range of phase transition temperature.

Uses two cartridge heaters embedded in an aluminum block as heat sources, and four thermoelectric coolers for cooling of the system.

Picture / scheme

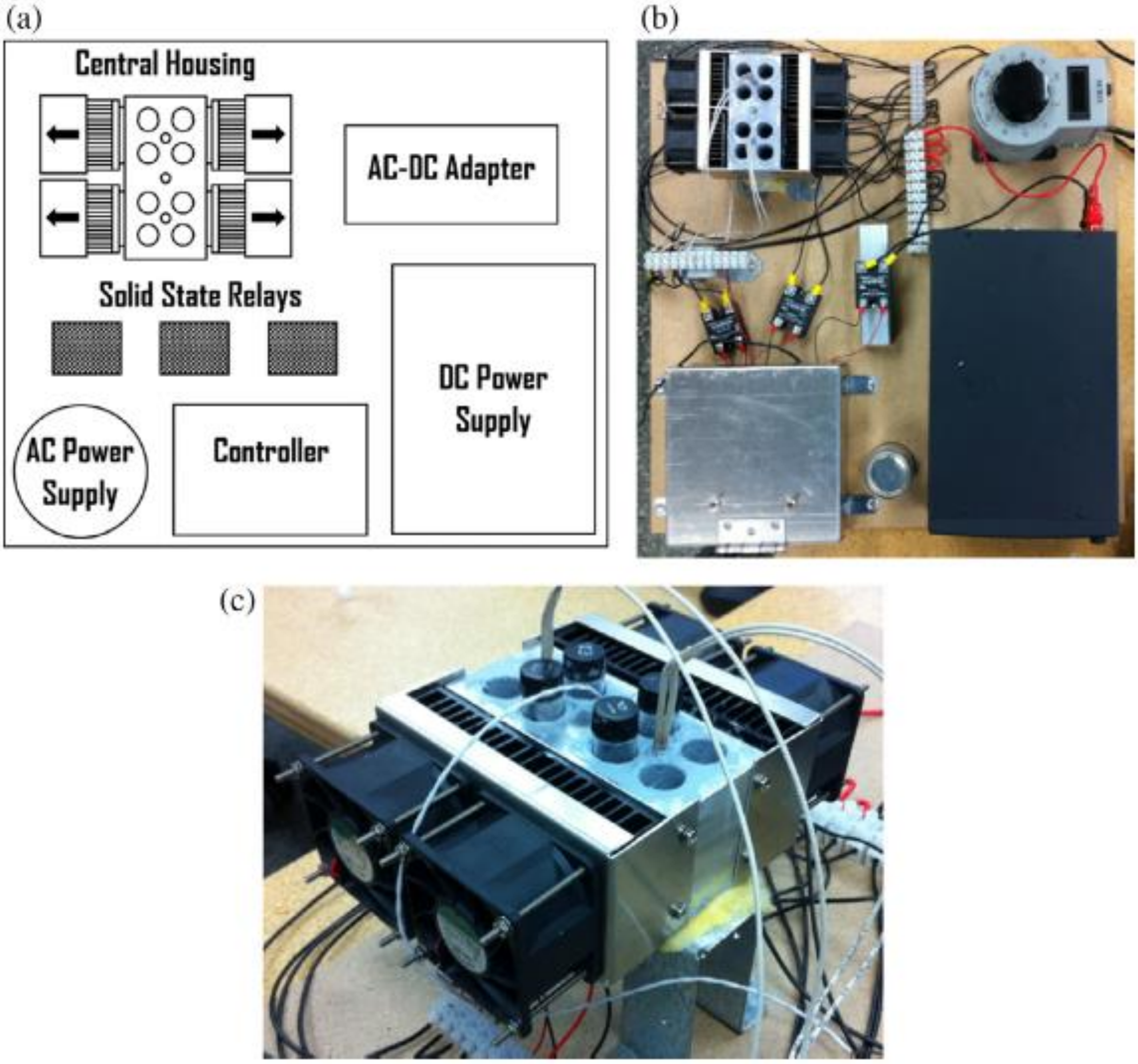
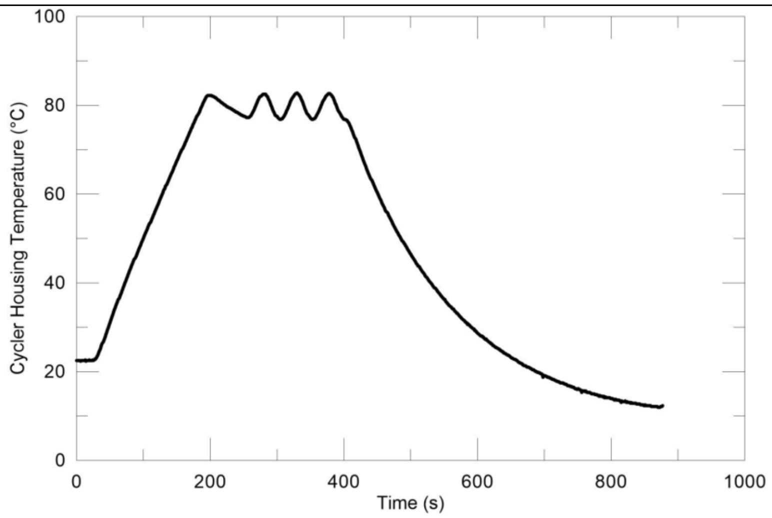


Fig. a) Schematic diagram showing the various components of the thermal cycler general assembly, b) photograph of the actual experimental setup, and c) photograph of the housing unit with the heating and cooling elements and vials containing PCMs [1].

Min. Temperature [°C]	Max. Temperature [°C]
-5	*125*
Typical heating rate [K/min]	Typical cooling rate [K/min]
13	*7*

Typical temperature profile



Typical number of cycles per day [1/d] *Up to 140 cycle per day (1,000 cycle a week).*	Sample volume [ml] *3 - 6*
PCM in contact with… *Aluminum, with thermal grease between Aluminum and the PCM vial to reduce thermal resistance to conduction.*	Sample container material *Dram vial with a 15-425 threaded PTFE/Silicone liner cap*

Measured data

T(t) saved on an SD card during the cycling and can be inspected at the end of the process.

Stability checked via…

DSC testing looking at the latent heat of transition and the onset of meting temperature of the cycled PCM (compared to the original pre-cycled PCM), with cycled PCM tested after every 500 or 1000 cycles.

References (articles, presentations, etc.)

[1] KAHWAJI, S., JOHNSON, M.B., KHEIRABADI, A.C., GROULX, D., WHITE, M.A. (**2016**) *Stable, low-cost phase change material for building applications: The eutectic mixture of decanoic acid and tetradecanoic acid,* Applied Energy, v.168, p.457-464.

Modeling of the system for design:

[2] C. KHEIRABADI, A., GROULX, D. *Design of an Automated Thermal Cycler for Long-term Phase Change Material Phase Transition Stability Studies*. in *COMSOL Conference 2014*. 2014. Boston, MA (USA).

Paper published with results from the setup [1], and:

[3] KAHWAJI, S., JOHNSON, M.B., KHEIRABADI, A.C., GROULX, D., WHITE, M.A. (**2017**) *Fatty acids and related phase change materials for reliable thermal energy storage at moderate temperatures,* Solar Energy Materials and Solar Cells, v.167, p.109-120.

[4] KAHWAJI, S., JOHNSON, M.B., KHEIRABADI, A.C., GROULX, D., WHITE, M.A. (**2018**) *A comprehensive study of properties of paraffin phase change materials for solar thermal energy storage and thermal management applications,* Energy, v.162, p.1169-1182.

Comments

A complete report about design, construction, equipment needed, etc, was also written and presented to the industrial partner (Intel). This report can be shared with interested groups.

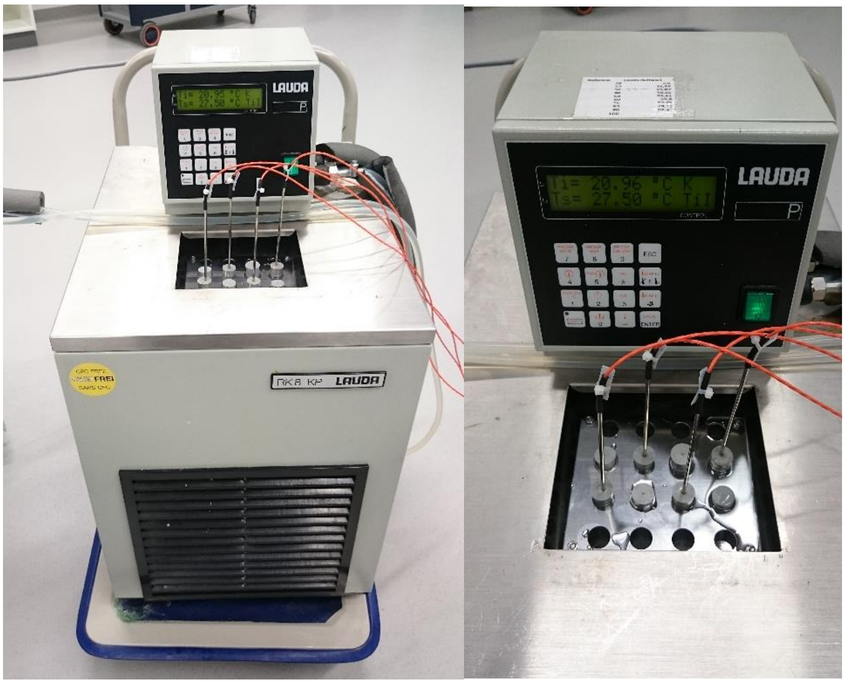
Testing device “LTTT”

Contact: Stephan Höhlein, Andreas König-Haagen

Description

Thermal cycling device with 4-channel PT100 data logger (expandable)

Picture / scheme



Min. Temperature [°C] *0 °C (water)* *-20 °C (oil)*	Max. Temperature [°C] *90 °C (water)* *180 °C (oil)*
Typical heating rate [K/min] *variable*	Typical cooling rate [K/min] *variable*

Typical temperature profile

One temperature level above and one below phase-change temperature. Rapid change between the temperature levels.

Typical number of cycles per day [1/d] *variable*	Max. sample volume [ml] *~ 10 … ~ 100 (depending on chosen container)*
PCM in contact with… *air*	Sample container material *glas, plastics, metals*

Measured data

T(t)

Stability checked via…

temperature-time curves of different cycles; DSC measurements after defined cycles

Testing device “UDL-GREiA I”

Contact: Luisa F. Cabeza, Gabriel Zsembinszki

Description

GeneQ BIOER TC-18/H(b) thermal cycler allows to perform thermal cycles from room temperature up to 100 °C using samples of PCM and other materials, to determine the stability of the samples over time. It simulates the melting and solidification cycles of real applications. The thermal cycler allows to place 18 samples at the same time in 0.5 ml eppendorfs. The eppendorf must not be filled completely because only the lower part will be subjected to heating and cooling cycles. It is recommended to fill 2/3 parts of the eppendorf.

Picture / scheme

Min. Temperature [°C] *4*	Max. Temperature [°C] *99.9*
Typical heating rate [K/min] *50*	Typical cooling rate [K/min] *50*

Typical temperature profile

Many different temperature profiles can be experimented depending on the aim of the study.

Typical number of cycles per day [1/d] *100*	Max. sample volume [ml] *18×0.5*
PCM in contact with… *Eppendorf, which is in contact with the metallic part of the device*	Sample container material *Polypropylene*

Stability checked via…

DSC, TGA analysis, FT-IR

References (articles, presentations, etc.)

- *Navarro, L, Solé, A, Martín, M, Barreneche, C, Olivieri, L, Tenorio, JA, Cabeza, LF. Benchmarking of useful phase change materials for a building application. Energy and Buildings 2019;182:45-50.*

Testing device “UDL-GREiA II”

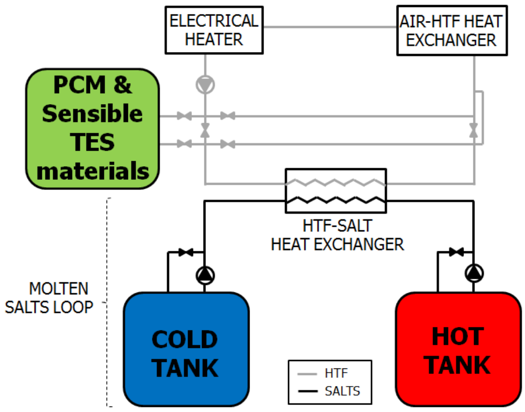
Contact: Luisa F. Cabeza, Gabriel Zsembinszki

Description

The University of Lleida pilot plant was built to accurately test different thermal energy storage (TES) systems working with latent or sensible heat storage materials. This facility is composed by an electrical boiler of 24 kWe to heat up the heat transfer fluid (HTF) acting as energy source during the charging process, different storage tanks containing phase change material (PCM), and an air heat exchanger of 20 kWe to cool down the HTF acting as energy consumption. All the piping that connects the different devices of the pilot plant are insulated using rock wool and the bottom of the storage tanks are insulated with foamglass and refractory cement to minimize the heat losses to the surroundings. Two different HTF were tested in the pilot plant facility: the synthetic oil Therminol VP-1 and the silicone fluid Syltherm 800.

A data acquisition system consisting of all the temperature, pressure and flow rate sensors as well as the different dataloggers and a personal computer, was integrated in the facility to measure and register the HTF flows, HTF pressures, and HTF and PCM temperatures in the boiler and storage tank, respectively.

Picture / scheme



Min. Temperature [°C] *20*	Max. Temperature [°C] *400*
Typical heating rate [K/min] *1.0*	Typical cooling rate [K/min] *Not available.*

Typical temperature profile

Many different temperature profiles can be experimented depending on the aim of the study.

Typical number of cycles per day [1/d] *1*	Max. sample volume [ml] *154,000*
PCM in contact with… *Stainless steel 316L*	Sample container material *Stainless steel 316L*

Measured data

Temperature, pressure, flow rate

Stability checked via…

DSC, TGA analysis, FT-IR

References (articles, presentations, etc.)

- *Oró, E, Gil, A, Miró, L, Peiró, G, Álvarez, S, Cabeza, LF. Thermal energy Storage Implementation Using Phase Change Materials for Solar Cooling and Refrigeration Applications. Energy Procedia 2012;30:947-56.*
- *Gil, A, Oró, E, Castell, A, Cabeza LF. Experimental analysis of the effectiveness of a high temperature thermal storage tank for solar cooling applications. Appl Therm Eng 2013;54: 521-27.*

- *Gil, A, Oró, E, Miró, L, Peiró, G, Ruiz, A, Salmerón, JM, Cabeza LF. Experimental analysis of hydroquinone used as phase change material (PCM) to be applied in solar cooling refrigeration. Int J Refrig 2014;39:95-103.*
- *Peiró G, Gasia J, Miró L, Cabeza LF. Experimental evaluation at pilot plant scale of multiple PCMs (cascaded) vs. single PCM configuration for thermal energy storage. Renew Energy 2015;83:729–36.*
- *Prieto C, Miró L, Peiró G, Oró E, Gil A, Cabeza LF. Temperature distribution and heat losses in molten salts tanks for CSP plants. Sol Energy 2016;135:518–26.*
- *Peiró G, Gasia J, Miró L, Prieto C, Cabeza LF. Experimental analysis of charging and discharging processes, with parallel and counter flow arrangements, in a molten salts high temperature pilot plant scale setup. Appl Energy 2016;178:394–403.*
- *Gasia J, de Gracia A, Peiró G, Arena S, Cau G, Cabeza LF. Use of partial load operating conditions for latent thermal energy storage management. Appl Energy 2018;216:234–42.*
- *Peiró G, Prieto C, Gasia J, Jové A, Miró L, Cabeza LF. Two-tank molten salts thermal energy storage system for solar power plants at pilot plant scale: lessons learnt and recommendations for its design, start-up and operation. Renew Energy 2018;121:236–48.*
- *Gil, A, Peiró, G, Oró, E, Cabeza LF. Experimental analysis of the effective thermal conductivity enhancement of PCM using finned tubes in high temperature bulk tanks. Appl Therm Eng 2018;142: 736-44.*
- *Gasia J, de Gracia A, Zsembinszki G, Cabeza LF. Influence of the storage period between charge and discharge in a latent heat thermal energy storage system working under partial load operating conditions. Appl Energy 2019;235:1389–99.*

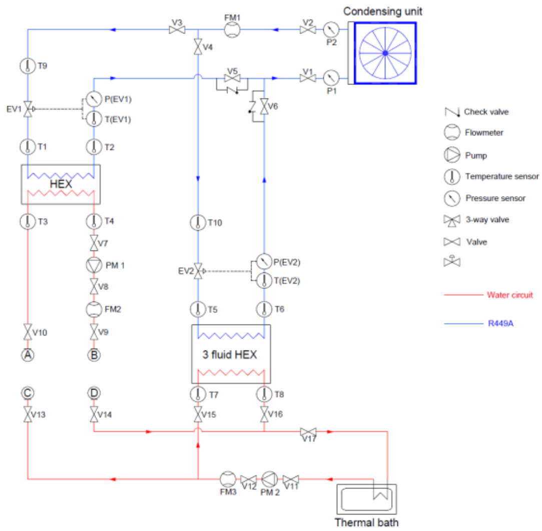
Testing device “UDL-GREiA III”

Contact: Luisa F. Cabeza, Gabriel Zsembinszki

Description

This experimental set-up of the GREiA lab at the University of Lleida was built to test the behaviour of different types of heat exchangers and thermal energy storage tanks, which are usually innovative components of different European projects. Both charging and discharging of the thermal energy storage modules can be performed, by means of two separate circuits: one cooling circuit connected to a variable capacity condensing unit, and one heating circuit connected to a thermal bath. There is the possibility to connect the heating bath to a water storage tank to increase the thermal inertia and provide a more stable water temperature to the heat exchangers.

Picture / scheme



Min. Temperature [°C]	Max. Temperature [°C]
-10	*80*
Typical heating rate [K/min]	Typical cooling rate [K/min]
0.5	*1.0*

Typical temperature profile

Many different temperature profiles can be experimented depending on the aim of the study.

Typical number of cycles per day [1/d]	Max. sample volume [ml]
2	*8,000*
PCM in contact with…	Sample container material
Aluminium, stainless steel	*Aluminium, stainless steel*

Measured data

Temperature, pressure, flow rate

Stability checked via…

DSC, TGA analysis, FT-IR

Testing device “ZAE”

Contact: Christoph Rathgeber

Description

Thermal cycling device; simultaneous measurement of 3 samples with similar melting temperatures

Picture / scheme

Min. Temperature [°C]	Max. Temperature [°C]
-30	*220*
Typical heating rate [K/min]	Typical cooling rate [K/min]
1	*1*

Typical temperature profile

two temperature levels for melting and freezing, e.g. 50 °C and 20 °C; transition via linear ramps, typically 1 h

Typical number of cycles per day [1/d]	Max. sample volume [ml]
2	*60*
PCM in contact with…	Sample container material
air	*glass, stainless steel*

Measured data

T(*t*)

Stability checked via…

photographs during cycling; comparison of temperature-time curves of different cycles; DSC measurements after a certain number of cycles

References (articles, presentations, etc.)

Rathgeber, C., Grisval, A., Schmit, H., Hoock, P., & Hiebler, S. (2018). Concentration dependent melting enthalpy, crystallization velocity, and thermal cycling stability of pinacone hexahydrate. Thermochimica acta, 670, 142-147.

Testing device “ISE Peltier”

Contact: Stefan Gschwander, Thomas Haussmann

Description: *Multiple Peltier Test Rig*

Flexible Peltier test rig for cycling in the temperature range -30°C to 200°C. Up to 16 Peltier modules with a max heating and cooling power of 30W each and a surface of 65x65mm can be flexible combined in x and z direction. Each Peltier modul has two Peltier elements. One on the bottom and one on top. The upper Peltierelements are single point fixed to compensate non parallel surfaces. The contact pressure of the upper Peltier element con be controlled by pressurized air.

Up to eight individual temperature controllers are used to control the temperature of samples. Peltier elements can be individually attached to each controller. Temperature profiles are composed of basic segments. Basic segments are: sudden temperature change, ramp or isotherms. Heating and cooling rate can be defined individually. Sample crucibles are designed as needed. Solid samples like construction materials can be tested without additional crucible. In line stability check is not foreseen. External Check with DSC, optical inspection or others is necessary.

Picture / scheme

Peltier Test rig

Min. Temperature [°C] *-30*	Max. Temperature [°C] *200*
Typical heating rate [K/min] *adjustable, depending on setup*	Typical cooling rate [K/min] *Adjustable, depending on setup*

Typical temperature profile

Programmable Profiles: temperature jump, Ramp, Isotherm

Typical Program: switching between temperature limits above and below melting range

Typical number of cycles per day [1/d] *Up to 24*	Max. sample volume [ml] *Not defined, typical 10-100ml*
PCM in contact with… *Crucible material or containment*	Sample container material *Raw materials: typical stainless steel, chosen as necessary*

Measured data

- *Temperatures of the PCM (middle or surface)*
- *Temperature of Peltier surface*

Stability checked via…

- External stability check, e.g. with DSC

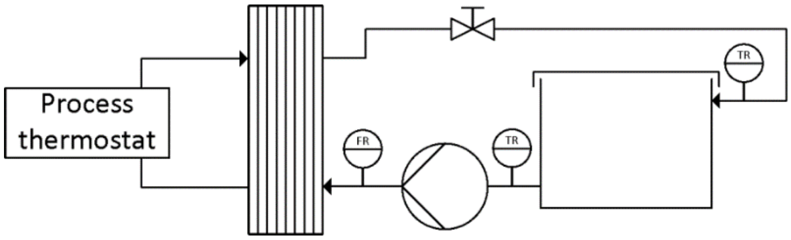
Testing device “ISE macrocapsules”

Contact: Stefan Gschwander, Thomas Haussmann

Description *Macro Capsule Cycling Test Rig*

The test facility consists of an open bath in which the encapsulated PCM samples are located in and circulated with tap water as a heat transfer fluid. The flow rate can be adjusted manually by means of a pump with a downstream restriction. The bath temperature can be controlled by a thermostat, which supplies heat to the test circuit by a heat exchanger. Temperature sensors at the flow and return line of the bath as well as a volume flow sensor allow thermal balancing of the heat stored in the PCM macro-capsules.

Picture / scheme



Min. Temperature [°C]	Max. Temperature [°C]
-10	*80*
Typical heating rate [K/min] *~1 K/min (depends on PCM and macrocapsule)*	Typical cooling rate [K/min] *~1 K/min (depends on PCM and macrocapsule)*

Typical temperature profile

Temperature steps are set, which are repeated cyclically. The set temperatures depend on the PCM used and are usually set 5 K below and above the melting temperature of the PCM.

Typical number of cycles per day [1/d]	Max. sample volume [ml]
10 (depends on PCM and macrocapsule)	*22 L bath volume*
PCM in contact with…	Sample container material
Macrocapsule material (metal, polymer)	*Polystyrene*

Measured data

- *Temperature at feed and return line of the bath*
- *Volumetric flow sensor*

Stability checked via…

- *Repeating optical inspection of the macrocapsules (reflected light microscope)*
- *Gravimetric analysis*
- *DSC analysis of the encapsulated PCM*

References

BIEDENBACH, M., KLÜNDER, F., GSCHWANDER, S. (2018). Investigations on the stability of metallic cans for PCM macro-encapsulation. International Institute of Refrigeration (IIR). https://doi.org/10.18462/iir.pcm.2018.0053

Testing device "LGCgE / Fluxmetric bench"

Contact: Laurent Zalewski, Noé Beaupéré

Description

The Fluxmetric bench (Figure 1) is a thermal cycling device used to impose temperature ramps on both larger sides of a parallelepipedic Polymethyl methacrylate (PMMA) sample containing PCM (Figure 2). Temperature ramps are applied thanks to exchanger plates each of which is connected to a refrigerated/heating circulators controlled by a computer, example of temperature ramps are presented in Figure 3. The four smaller faces of the sample are insulated so as to minimize lateral heat losses (Figure 2). In its current configuration, the container is filled with 270 ml of PCM. This configuration allows to limit convective flow when the PCM is in liquid state. A heat fluxmeter incorporating a T-type thermocouple is placed on each side of the PMMA sample in order to calculate the energy balance at each heat cycle and to identify the melting and solidification temperatures. Between each temperature ramp, an isothermal step is imposed to return to an equilibrium (isothermal state and heat flux = 0) (Figure 4). For each fusion, the latent heat is estimated by subtracting the sensible energy stored (stored by PMMA and PCM) from the total stored energy measured by heat fluxmeters.

For example, multiple heating and cooling ramps (Figure 3) have been imposed on Sodium Acetate Trihydrate (SAT / CH3COONa.3H2O) to study its ageing by following the variation in the amount of latent heat involved in each melting phase change. On the other hand, at each cooling ramp, the temperature of the stochastic solidification (or degree of supercooling) can be identified. The decrease in the amount of latent heat is related to the ageing of the PCM (Figure 5a). For each cooling ramp by observing the peak of heat flux at the moment of crystallization, the degree of supercooling can be estimated (Figure 5b). The curves below are coming from BEAUPERE's PhD work on SAT [1].


Figure 1: Fluxmetric bench


Figure 2: PMMA sample containing PCM with the lateral heat fluxmeters before installation in the insulation

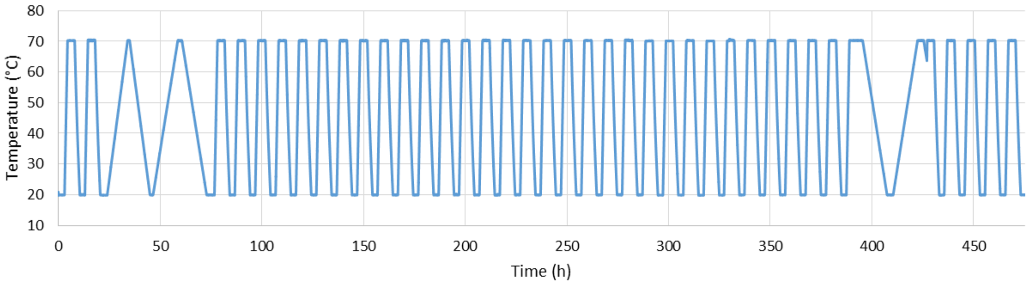


Figure 3: Feasible series of temperature ramps imposed on the sample

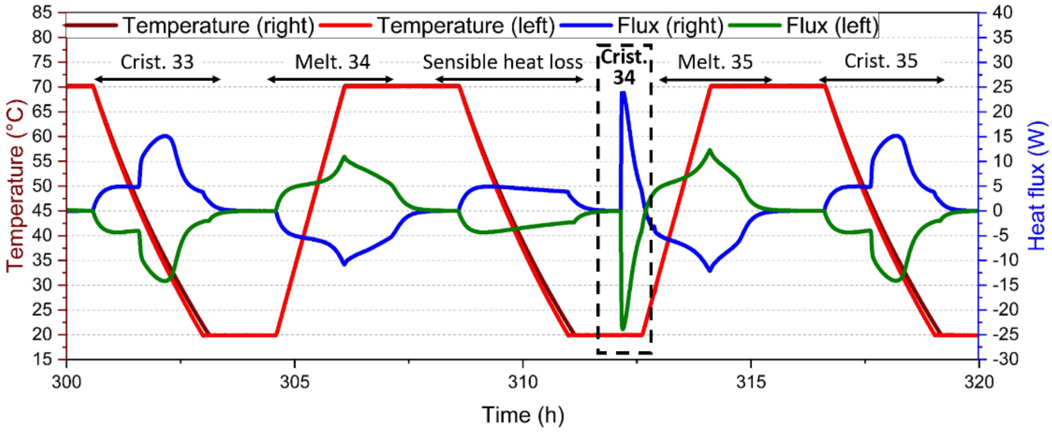


Figure 4: Ramps of temperature and heat fluxes measurements

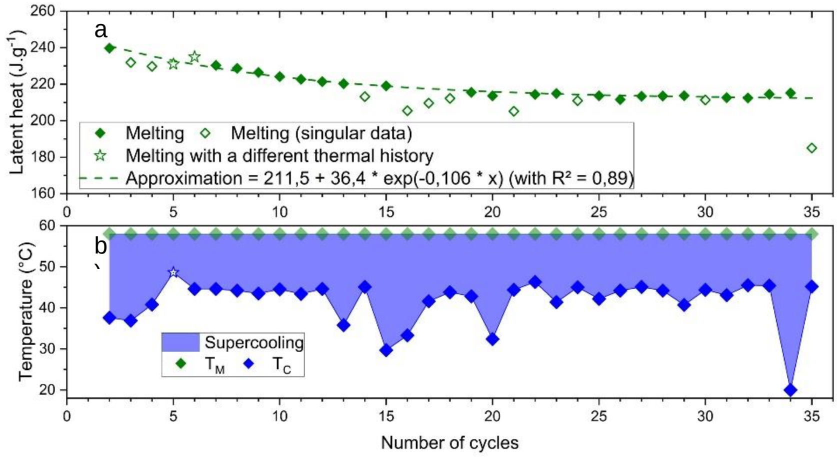


Figure 5: Evolution of latent heat and the solidification temperature vs number of cycles

References

[1] BEAUPERE Noé, Pilotage de la libération de chaleur et étude du vieillissement de matériaux à changement de phase, PhD, Université d'Artois/CEA Grenoble, 11/2019.

3.2 Type II: Tests on degradation of PCM with stable supercooling

A concept for medium and long-term thermal energy storage is to utilize the ability of certain PCM to be stored as a liquid in the supercooled state. As investigated by Englmair et al. [1] and Desgrosseilliers [2], application of sodium acetate trihydrate (SAT) in closed containers permits the use of its sensible heat capacity after melting while preserving its heat of fusion at room temperature in a state of stable supercooling. The result is a thermal energy storage capacity that can be used on-demand by controlled initialization of crystallization. To investigate the stability of PCM with stable supercooling, dedicated test procedures are required. In addition to temperature-time profiles of regular thermal cycling tests, both degree and duration of supercooling are parameters of interest.

[1] Englmair, G., Jiang, Y., Dannemand, M., Moser, C., Schranzhofer, H., Furbo, S. & Fan, J. (2018). Crystallization by local cooling of supercooled sodium acetate trihydrate composites for long-term heat storage. Energy and Buildings, 180, 159-171.

[2] Desgrosseilliers, L. (2016). Design and evaluation of a modular, supercooling phase change heat storage device for indoor heating, Dalhousie University.

Testing device “DTU heat loss method”

Contact: Gerald Englmair, Mark Dannemand

Description

T-history method: Testing of the heat content of (supercooled) PCM material in large sample size (200 g).

Picture / scheme

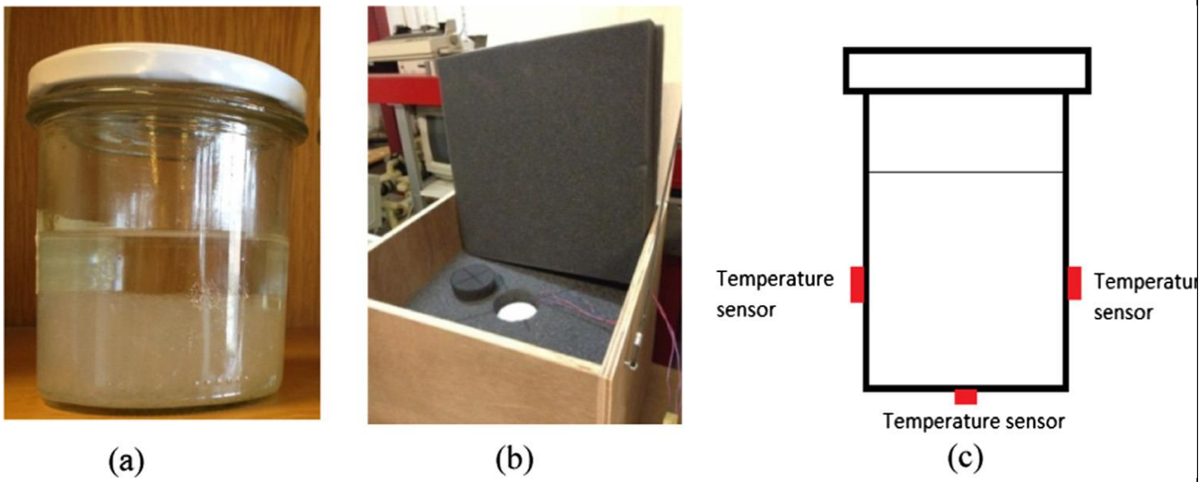


Fig. : (a) Glass jar with lid, (b) the well-insulated box, (c) locations of temperature sensors.

Min. Temperature [°C]	Max. Temperature [°C]
20	*90*

Typical heating rate [K/min]	Typical cooling rate [K/min]
1 (forced convection in oven)	*natural cooling*

Typical temperature profile

a) Heat-up in oven (20°C to 90°C)
b) Cool-down to ambient temperature (about 20°C) → when supercooling applied
c) Controlled crystallization in insulated chamber → when supercooling applied
d) Measurement of cool-down temperature curve (figure below)

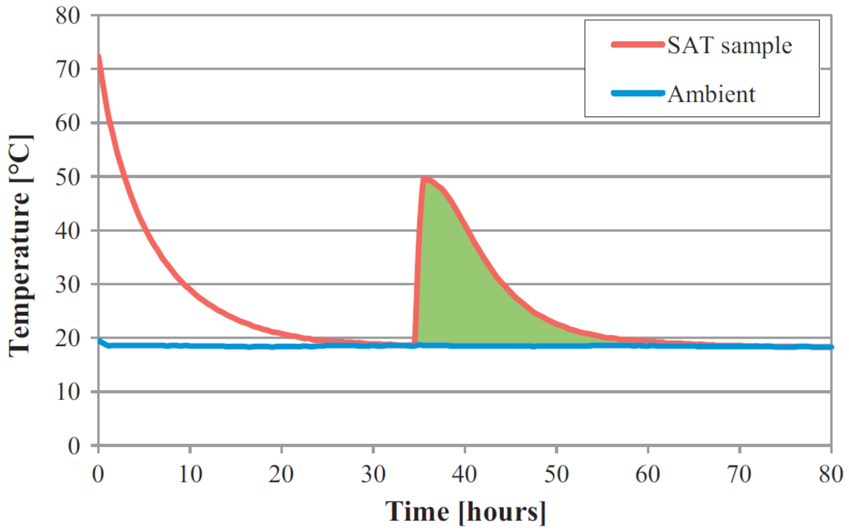


Fig.: An example of cooling process of PCM.

Typical number of cycles per day [1/d]	Max. sample size [g]
0.25 with supercooling *0.5 without supercooling*	*200*

PCM in contact with… *Glass and air*	Sample container material *Glass jar (metal lid)*
Measured data *Temperature profile during material solidification; Ambient temperature.*	
Stability checked via… *Comparison of samples:* • *Heat content via comparison of sample material with known properties (e.g. water, oil).* *Cyclic stability via comparison of samples with different heat storage cycles applied or with different material composition (screening for stabilizing additives).*	
References (articles, presentations, etc.) *W. Kong, M. Dannemand, J.B. Johansen, J. Fan, J. Dragsted, G. Englmair, S. Furbo, Experimental investigations on heat content of supercooled sodium acetate trihydrate by a simple heat loss method, Sol. Energy 139 (2016) 249–257.*	
Comments *Applied temperatures (heat-up, ambient temperature) should be in accordance to aimed application conditions.*	

Testing device “DTU full scale”

Contact: Gerald Englmair, Mark Dannemand

Description

Full scale heat storage prototype testing.
- Cyclic PCM stability in contact to PCM container material.

Picture / scheme

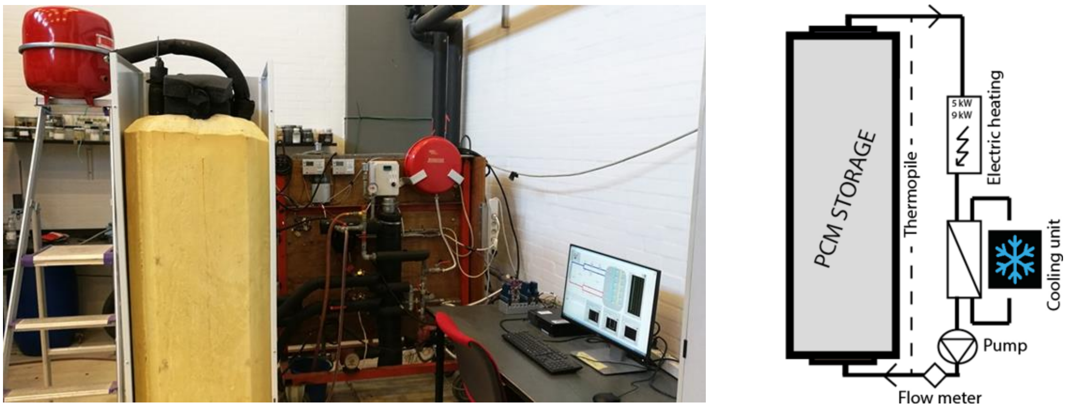


Fig.: PCM heat storage test facility at DTU BYG (left); Schematic of charge and discharge loop (right).

Min. Temperature [°C]	Max. Temperature [°C]
20	*90*
Typical heating rate [K/min] *1 (depending on the storage prototype)*	Typical cooling rate [K/min] *0.5 (depending on the storage prototype)*

Typical temperature profile

e) Charge (20°C to 90°C)
f) Cool-down to ambient temperature (about 20°C) → when supercooling applied
g) Controlled crystallization → when supercooling applied
h) Discharge to ambient temperature (about 20°C)

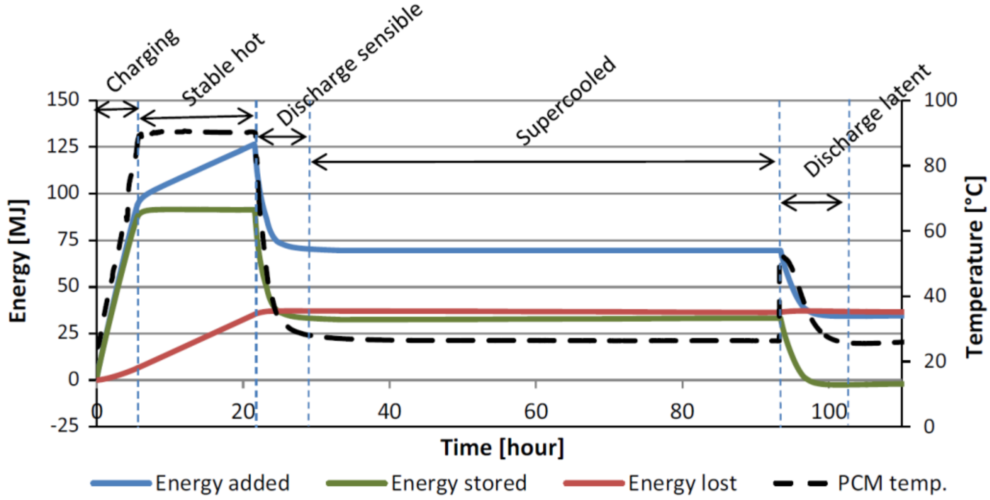


Fig.: Temperature profile of a test cycle with supercooling of PCM.

Typical number of cycles per day [1/d]	Max. sample volume [ml]
0.2 with supercooling *0.4 without supercooling*	*100,000 – 200,000*
PCM in contact with…	Sample container material

PCM container material(s)	*Typically metal or polymers*

Measured data

- *Heat transfer fluid: temperatures (flow, return), volume flow rate, temperature difference (in-out).*
- *Ambient temperature*
- *Heat storage surface temperature*

Stability checked via…

Comparison of the heat store´s energy content in repeated storage cycle.

Heat losses must be experimentally determined for each heat storage prototype.

References (articles, presentations, etc.)

M. Dannemand, J. Dragsted, J. Fan, J.B. Johansen, W. Kong, S. Furbo, Experimental investigations on prototype heat storage units utilizing stable supercooling of sodium acetate trihydrate mixtures, Appl. Energy 169 (2016) 72–80.

M. Dannemand, J.B. Johansen, W. Kong, S. Furbo, Experimental investigations on cylindrical latent heat storage units with sodium acetate trihydrate composites utilizing supercooling, Appl. Energy 177 (2016) 591–601.

Comments

The same testing device (setup) can be used for testing performance characteristics of PCM heat stores.

Testing device "DTU multiple storage"

Contact: Gerald Englmair, Mark Dannemand

Description

Multiple (10) identical heat storage units (water storage with sodium acetate trihydrate as PCM) subject to repeated heating and cooling cycles with various temperature levels. Focus is on effect of temperature levels and duration of charge on the supercooling stability and spontaneous solidification.

Picture / scheme

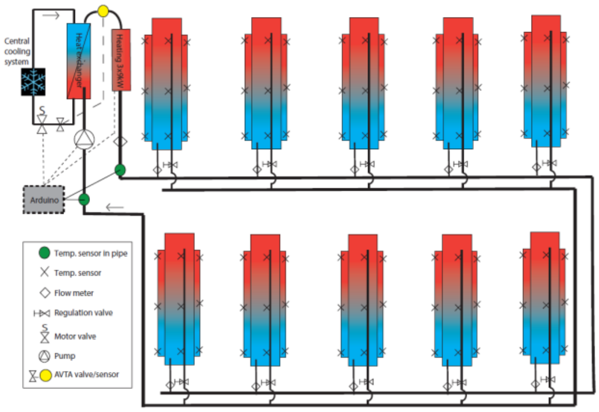


Fig.: PCM heat storage test facility at DTU BYG (left);
Schematic of charge and discharge loop (right).

Min. Temperature [°C]	Max. Temperature [°C]
8	*93*
Typical heating rate [K/min]	Typical cooling rate [K/min]
0.15	*3 - 4*

Typical temperature profile

- i) Charge in periods 8 to 16 hours 10°C to 90°C
- j) Discharge to 10-30°C
- k) 72 hours observation period, looking for spontaneous crystallization of the supercooled PCM
- l) Intentional initialization of solidification and discharge (10-30°C)

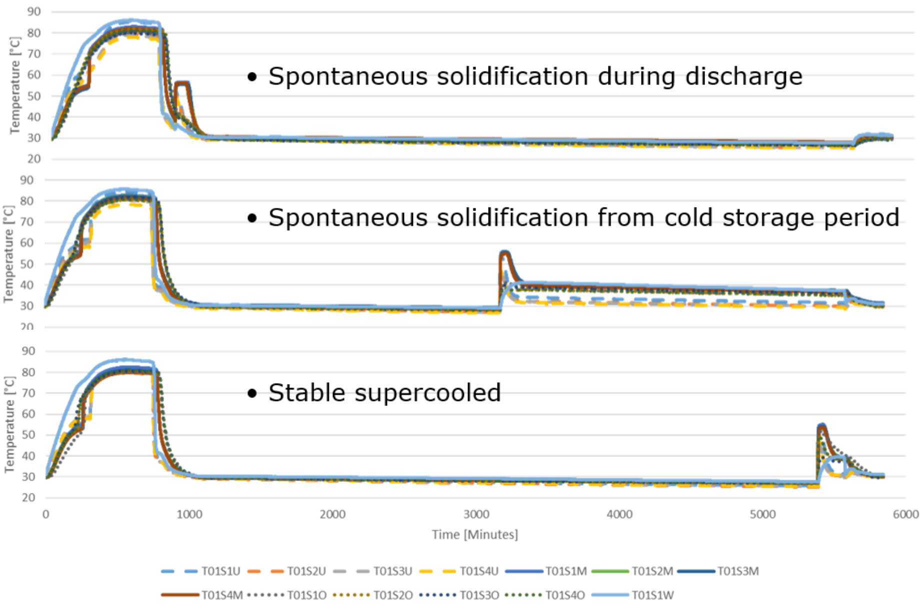


Fig.: Temperature profiles of test cycles with supercooling of PCM.

Typical number of cycles per day [1/d] *0.25*	Max. sample volume [ml] *10 * 30,000*
PCM in contact with… *PCM container / air*	Sample container material *Stainless steel*
Measured data • *Heat transfer fluid: temperatures (flow, return), volume flow rate, temperature difference (in-out).* • *Ambient temperature* • *Heat storage surface temperature*	
Stability checked via… *Observation of temperature development in test cycle*	

References (articles, presentations, etc.)

Dannemand, M., & Furbo, S. (2018). Supercooling stability of sodium acetate trihydrate composites in multiple heat storage units. Refrigeration Science and Technology, 2018-, 227–231. https://doi.org/10.18462/iir.pcm.2018.0031

Dannemand, M., Schultz, J. M., Johansen, J. B., & Furbo, S. (2015). Long term thermal energy storage with stable supercooled sodium acetate trihydrate. Applied Thermal Engineering, 91, 671–678. https://doi.org/10.1016/j.applthermaleng.2015.08.055

3.3 Type III: Tests on degradation of phase change slurries (PCS)

Phase change slurries (PCS) are fluids containing PCM and a carrier fluid. A PCS is stable if the emulsified or encapsulated PCM droplets do not degrade during operation, e.g. due to an agglomeration of droplets or a PCM leakage in the case of capsules. Among others, the stability of PCS depends on the investigated sample and particle size and the applied flow rate. Performance validation of PCS is carried out with self-built experimental devices that provide application-oriented charging and discharging conditions.

Testing device “ISE PCS”

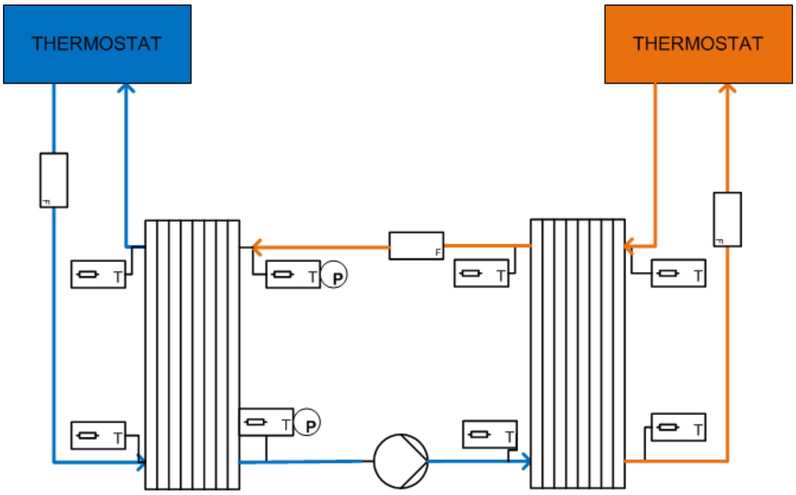
Contact: Stefan Gschwander, Thomas Haussmann

Description

Phase Change Slurry (PCS) Cycling Test Rig

In principle, the test setup consists of two heat exchangers which are connected in a test circuit (called secondary circuit). The heat exchangers each have a heating and a cooling thermostat, which act as heat source and heat sink (here called primary circuit). In the primary circuit it is possible to determine the transferred heat flux (and heat amount) using a volume flow sensor (MID) and temperature sensors at the flow and return flow of the two heat exchangers in the primary circuit. In the secondary circuit, the PCS to be tested is conveyed using a centrifugal pump. The PCS is heated or cooled to an adjustable target temperature (and thus the PCM contained is melted or crystallized). The volume flow in the secondary circuit can be monitored using a volume flow meter (MID). The cooling heat exchanger is additionally equipped with pressure sensors at the flow and return flow which determine the pressure loss of the slurry via the heat exchanger. This pressure difference can also be used to determine the degradation of the slurry, since in a degraded PCS the dispersed PCM is present as a free phase in the slurry and suggessively blocks the cooling/heat exchanger.

Picture / scheme



Min. Temperature [°C]	Max. Temperature [°C]
-10	*80*
Typical heating rate [K/min]	Typical cooling rate [K/min]
~140 K/min @ 200L/h	*~100 K/min @ 200L/h*

Typical temperature profile

<table>
<tr><td colspan="2">Constant temperature at the output of the heating and cooling heat exchanger in the secondary circuit. Temperature level depends on the melting point of the PCM in the PCS.</td></tr>
<tr><td>Typical number of cycles per day [1/d]
~1,300 @ 200 L/h</td><td>Max. sample volume [ml]
3,500</td></tr>
<tr><td>PCM in contact with…
Slurry test setup: PCM only in contact with water (continuous phase)</td><td>Sample container material
Heat exchangers: stainless steel
Piping: stainless steel
Pump: ceramic impeller</td></tr>
<tr><td colspan="2">Measured data
- Temperatures at the flow and return flow of the heating and cooling heat exchanger in the primary and secondary circuits
- Volume flows in both primary circuits and in the secondary circuit
- Pressure loss in the secondary circuit of the cooling heat exchanger</td></tr>
<tr><td colspan="2">Stability checked via…
- Pressure loss of the cooling heat exchanger (live)
- Regular sampling of samples (~50 mL) which are analysed by particle size analysis, DSC and viscosity.</td></tr>
</table>

References (articles, presentations, etc.)

Niedermaier, S., Biedenbach, M., Gschwander, S. (2016). Characterisation and Enhancement of Phase Change Slurries. Energy Procedia, 99, 64–71. https://doi.org/10.1016/j.egypro.2016.10.098

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