Enthalpy-temperature plots to compare calorimetric measurements of phase change materials at different sample scales

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Highlights

- Four PCM were investigated (RT58, bischofite, D-mannitol, and hydroquinone).
- Measurements at three scales (DSC, T-History, and pilot plant) were carried out.
- Sample volumes are ~15 µl (DSC), ~15 ml (T-History), and ~150 l (pilot plant).
- Tabular enthalpy changes within defined temperature ranges are difficult to compare.
- Enthalpy-temperature plots facilitate the interpretation of measured results.

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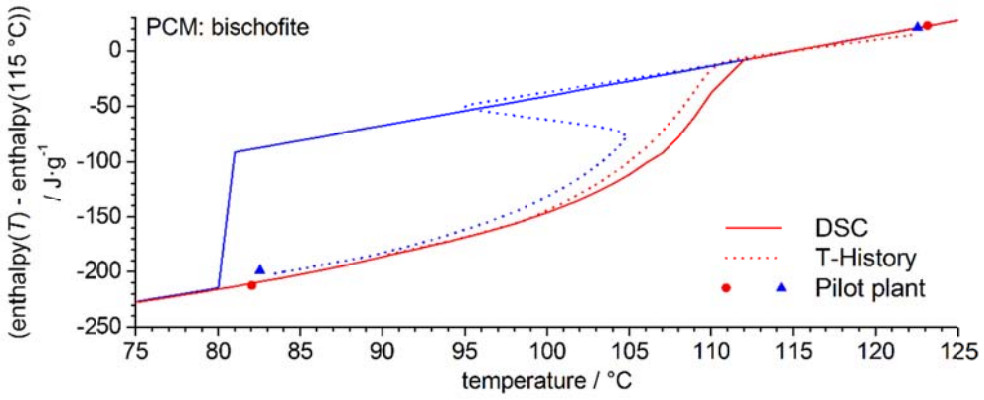
Graphical abstract



Abstract

Phase change materials (PCM) can provide high thermal energy storage capacities in narrow temperature ranges around their phase change temperature. The expectable maximum storage capacity of a PCM in a defined temperature range is equal to the enthalpy change in that range and can be determined via calorimetric measurements such as differential scanning calorimetry (DSC) or T-History calorimetry. T-History samples (~15 ml) are about 1000 times larger than DSC samples (~15 µl). Experiments in a pilot plant are performed to study the charging and discharging behaviour of even larger amounts of the PCM (~150 l). The common practise is to investigate PCM at one scale, rarely at two scales. In this work, the characterisation was carried out at three scales (DSC, T-History, and pilot plant) for four PCM (RT58, bischofite, D-mannitol, and hydroquinone). Thereby, the question arises how the enthalpy changes measured at different scales and under different conditions can be compared. In literature, the melting enthalpy is usually assigned to a single temperature without indicating the temperature range considered for evaluation. In very few instances, the enthalpy change within a defined temperature range is stated. In both cases, results measured under different conditions are difficult to compare. In this work, it is demonstrated that enthalpy-temperature plots facilitate the comparison and interpretation of measurements obtained under different experimental methods at different sample scales.

Keywords:

Thermal energy storage (TES); Latent heat storage; Phase change material (PCM); Storage capacity; Enthalpy curve; T-History

Nomenclature:

$h(T)$	mass-specific enthalpy curve/J·g^{-1}
$\Delta h_{\Delta Tc}$	mass-specific enthalpy change upon crystallisation within ΔT_c/J·g^{-1}
$\Delta h_{\Delta Tm}$	mass-specific enthalpy change upon melting within ΔT_m/J·g^{-1}
T_{in}	inlet temperature for measurements at pilot plant scale/°C
T_m	melting temperature/°C
T_{PCM}	PCM temperature during measurements at pilot plant scale/°C
ΔT_c	temperature interval for the determination of $\Delta h_{\Delta Tc}$/K
ΔT_m	temperature interval for the determination of $\Delta h_{\Delta Tm}$/K

Abbreviations:

AHE	air-HTF heat exchanger
DSC	differential scanning calorimetry
HTF	heat transfer fluid
PCM	phase change material
TES	thermal energy storage

1. Introduction

Thermal energy storage using phase change materials (PCM) provides high storage capacities in narrow temperature ranges. Most of the PCM used in applications are solid-liquid PCM storing heat or cold in repeated melting and crystallisation processes [1]-[3]. To select a suitable PCM for an application, the entire phase change has to take place within the temperature interval of the application. In the case of solid-liquid PCM, both melting and crystallisation have to be within the range of

charging and discharging temperature of the intended application. The storage capacity which is achieved in a storage unit is not an intrinsic material property but affected by the design of the storage and the conditions given by the application. The expectable maximum storage capacity of a PCM in a defined temperature range is equal to the enthalpy change upon melting or crystallisation in that temperature range and can be determined via calorimetric measurements such as differential scanning calorimetry (DSC) or T-History calorimetry [4]-[7]. DSC samples (~15 µl) are about 1000 times smaller than T-History samples (~15 ml). Therefore, T-History measurements are favoured over DSC measurements in the case of heterogeneous materials, materials with volume-dependent crystallisation behaviour, and non-congruently melting materials [6]. Experiments in a pilot plant are performed to study the charging and discharging behaviour of even larger amounts of PCM (~150 l, i.e. 10^7 times larger than DSC samples; hereinafter referred to as pilot plant scale). Measurements of such large quantities of PCM are of peculiar interest if the PCM is not encapsulated. In the case of encapsulated PCM, other experiments are required to study their applicability.

The common practise is to investigate PCM at one scale, rarely at two scales [6], [7]. In this study, four PCM (RT58, bischofite, D-mannitol, and hydroquinone) were investigated at three scales, namely via DSC, T-History, and at pilot plant scale. In this context, the question arises how to deal with different enthalpy measurements [8]. In literature, the melting enthalpy is usually assigned to a single temperature without indicating the temperature range considered for evaluation. In very few instances, the enthalpy change within a defined temperature range is stated [7]. In this work, enthalpy-temperature plots are demonstrated to be advantageous compared with tabular enthalpy changes within defined temperature ranges in order to compare measurements under different conditions at different scales [9]. The novelty of the paper is that it is the first time such a comparison is done in a consistent way. Preliminary results of this study were presented at a conference [10].

2. Materials and methods

2.1. Materials

For this study, materials were selected which have been investigated recently in the pilot plant test

facility of the University of Lleida. RT58 is a commercial paraffin which has been proposed for domestic hot water applications [11]. Bischofite is a mineral which precipitates in the evaporation ponds during the potassium chloride and lithium carbonate production process in Salar de Atacama, Chile. The main component of this by-product, about 95 wt%, is $MgCl_2 \cdot 6H_2O$ [12]-[14]. D-mannitol and hydroquinone are organic PCM which have been studied as solar thermal storage materials [15]-[21].

In the case of bischofite, which is naturally of technical grade, and RT58, a commercial PCM, materials of the same batch, i.e. of the same grade, were investigated at all three scales. It was not possible to carry out measurements of technical grade D-mannitol and hydroquinone from the same supplier via DSC and T-History, because D-mannitol and hydroquinone were not available anymore at the time of the laboratory scale measurements. Specifications of the investigated materials are given in Table 1. Indicated melting temperatures T_m and purities are provided by the suppliers.

Table 1

Specifications of investigated PCM as given by suppliers.

Material	Material class	Formula	T_m (°C)	Supplier	Purity (wt%)
RT58	Paraffin	n/s	53 – 59	Rubitherm	n/s
Bischofite	Salt hydrate	$MgCl_2 \cdot 6H_2O$ [c]	n/s	SALMAG	95 [c]
D-mannitol [a]	Sugar alcohol	$C_6H_{14}O_6$	167 – 169	Alfa Aesar	99
D-mannitol [b]	"	"	n/s	QUIMIVITA	96
Hydroquinone [a]	Phenol	$C_6H_6O_2$	172	Merck	≥99.5
Hydroquinone [b]	"	"	n/s	QUIMIVITA	95

[a] measured via DSC and T-History, [b] measured at pilot plant scale, [c] main component, n/s = not specified

Samples were prepared using the solid substances as purchased. DSC and T-History samples were prepared with a weighing accuracy of 0.01 mg and pilot plant samples with a weighing accuracy of 100 g. Sample masses of investigated materials are listed in Table 2.

Table 2

Sample masses used in DSC and T-History measurements and at pilot plant scale.

Material	m_{DSC} (mg)	$m_{T\text{-}History}$ (g)	$m_{pilot\ plant}$ (kg)
RT58	12.35	9.61	108
Bischofite	11.57	17.11	204
D-mannitol	4.76	11.07	160
Hydroquinone	9.86	15.36	170

2.2. DSC measurements

DSC measurements were carried out at ZAE Bayern using a TA Q2000 heat-flux DSC device which was calibrated with indium as recommended by TA Instruments. The sufficiency of the single point indium calibration was verified via additional measurements of gallium and biphenyl in terms of temperature, and distilled water in terms of enthalpy. The accuracy of enthalpy curves determined with this DSC device has been approved in various comparative studies, such as the round robin test of octadecane within IEA SHC Task 42 / ECES Annex 24 and its continuation IEA SHC Task 42 / ECES Annex 29 [22]. Based on the participation in Annex 24 / 29 and the authors' experience, the enthalpy can be measured via this DSC device with an accuracy of ±5%. A constant stream of nitrogen (50 ml·min^{-1}) was applied as flushing gas during the entire DSC measurements. Hermetically sealed alodined aluminium crucibles were used for DSC measurements.

According to the RAL testing regulations (RAL German Institute for Quality Assurance and Certification of PCM Gütegemeinschaft e.V. [23]), a temperature resolution of 1 K is required to indicate the enthalpy change upon melting and crystallisation. Therefore, DSC step measurements with temperature steps of 1 K were performed in this study. Using a heat-flux DSC in isothermal step mode, the ambience of PCM (placed inside a crucible) and reference (an empty crucible) is heated up and cooled down stepwise in given temperature intervals [24]-[27]. The PCM temperature follows the temperature step of the DSC oven with some time delay. Before the next temperature step can follow, the measured heat flow signal has to decrease to zero. The temperature resolution of the acquired data is equal to the step size. The heat flow signal of each step is integrated using a linear baseline and the cumulative sum is calculated for the determination of enthalpy curves.

Typical data of a DSC step measurement is shown in Fig. 1. To measure the melting and crystallisation curve of bischofite which melts around 105 °C, the ambient temperature was increased stepwise from 70 °C to 125 °C and decreased stepwise from 125 °C to 70 °C, respectively.

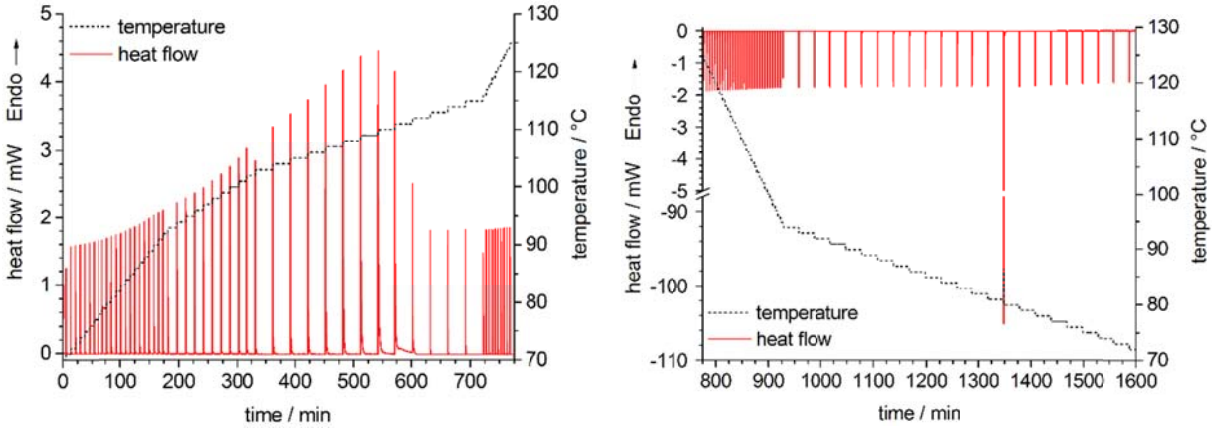


Fig. 1. DSC step measurement of bischofite consisting of a heating run (left) and a cooling run (right).

2.3. T-History measurements

T-History measurements were performed with a calorimeter which was designed and built at ZAE Bayern [28]. A top-view sketch of the calorimeter is shown in Fig. 2, left.

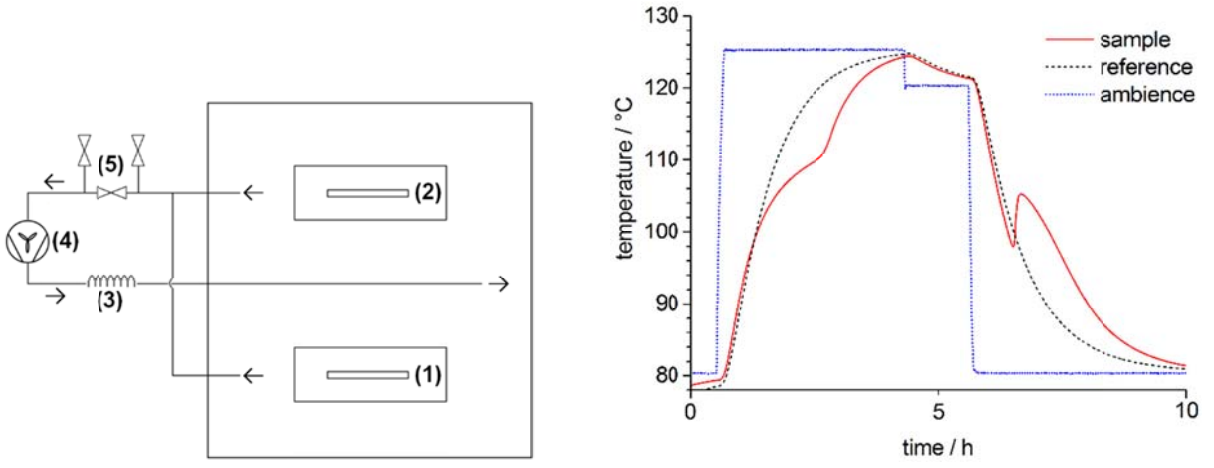


Fig. 2. Top-view sketch of the T-History calorimeter (left): PCM with insulation (1), reference with insulation (2). Further details are given in [4]; Temperature – time data of bischofite (red solid line), reference (black dashed line), and ambience (blue dotted line) during a T-History measurement (right).

In a T-History measurement, the PCM is exposed to constant charging / discharging temperatures instead of stepwise temperature increases or temperature ramps, as it is done in DSC measurements. The T-History calorimeter at ZAE Bayern can be used for the determination of enthalpy curves of samples of about 15 ml between 40 °C and 200 °C and was calibrated with indium, electrolytic copper, and three organic PCM [4]. Further information about the T-History method and technical details of the applied instrument can be found in literature [4], [26], [29], [30].

An example for typical temperature-time data measured via T-History is shown in Fig. 2, right. For the measurement of enthalpy curves of bischofite, the ambient temperature was changed from 80 °C to 125 °C in the case of melting, and from 120 °C to 80 °C in the case of crystallisation. Different temperature steps are required for heating and cooling due to the supercooling of bischofite and the fact that the first 15-30 minutes of each heating or cooling segment cannot be evaluated due to an unstable ambient temperature.

2.4. Measurements at pilot plant scale

The pilot plant facility used to experimentally test PCM was designed and built at the University of Lleida [13], [18]. This equipment consists of three main parts: the heating system, the cooling system, and the storage system (Fig. 3).

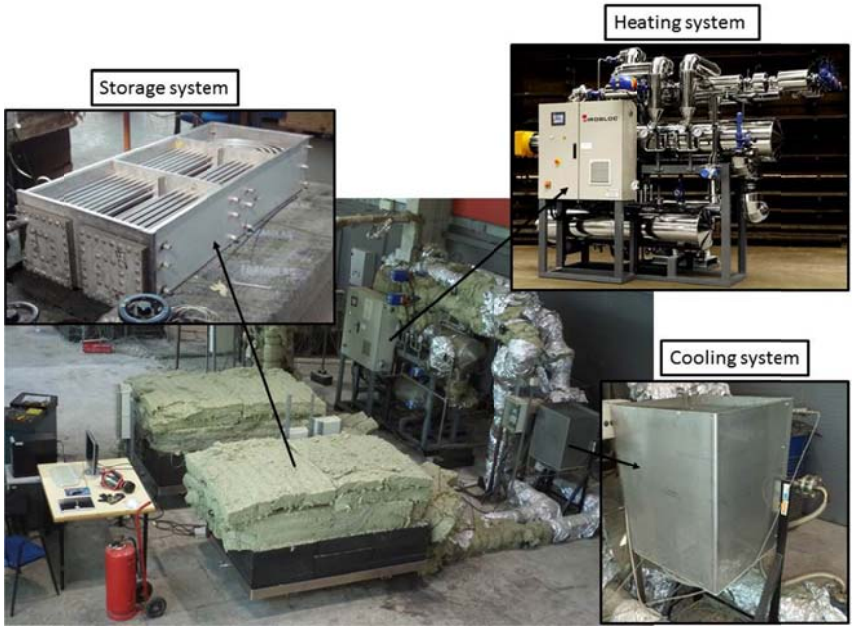


Fig. 3. Pilot plant facility built at the University of Lleida [13].

The heating system consists of a 20 kW_{th} electrical boiler supplied by the Pirobloc Company. The boiler heats up the heat transfer fluid (HTF) acting as the heating energy source during a charging process in a real installation. HTF flow rates between 0.3-3 $m^3 \cdot h^{-1}$ can be applied. The cooling system is based on a 20 kW_{th} air-HTF heat exchanger (AHE) which simulates the energy consumption by the user during a discharging process. The AHE was designed and built at the University of Lleida and it is based on the cross-flow heat exchanger concept. The heat exchange is carried out by circulating air at ambient temperature with a flow rate of 1800 $m^3 \cdot h^{-1}$ through a set of 50 fins and 56 tubes arranged in zigzags, inside which the HTF circulates.

The tank used to store the PCM and to realise the energy exchange between HTF and PCM consists of a shell-and-tube heat exchanger made of stainless steel. The insulated tank vessel has a volume of 154 l (145 l of which can be filled with PCM) and houses 49 tubes with an average length of 2.49 m. To have accurate data on the phase change temperatures of the PCM under investigation, 19 Pt100 temperature sensors with an accuracy of ±0.1 ºC are installed at different positions inside the tank. In the figures providing the measured data, the output of a sensor from the middle of the tank was considered as the PCM temperature. Due to this loss in temperature precision, only the overall amount of energy stored upon charging or discharging the storage tank can be calculated. Thus, the

temperature accuracy of enthalpy determination at pilot plant scale is lower compared with the two other calorimetric instruments which are operated and calibrated in a way that highly accurate enthalpy-temperature plots can be determined. Instead, the main objective of pilot plant measurements is to characterize the PCM together with the storage tank in terms of the storage capacity in a temperature range covering the entire phase transition, the achieved power output, and the stability upon repeated thermal cycling. Further information on the temperature measurement and data evaluation of measurements at pilot plant scale are given in literature [13].

3. Results and discussion

3.1. Temperature-time data measured at pilot plant scale

To measure the melting and crystallisation of RT58, the tank inlet temperature T_{in} was changed from 48 °C to 68 °C and vice versa, respectively. In the case of bischofite, 80 °C and 120 °C turned out to be appropriate, and for both D-mannitol and hydroquinone, 145 °C and 187 °C were applied as inlet temperatures. The temperature-time data measured at pilot plant scale for one heating-cooling cycle is shown in Fig. 4 (RT58 and bischofite) and Fig. 5 (hydroquinone and D-mannitol). The oscillation observed on the HTF temperature profile is due to the intrinsic configuration of the electrical heater [13].

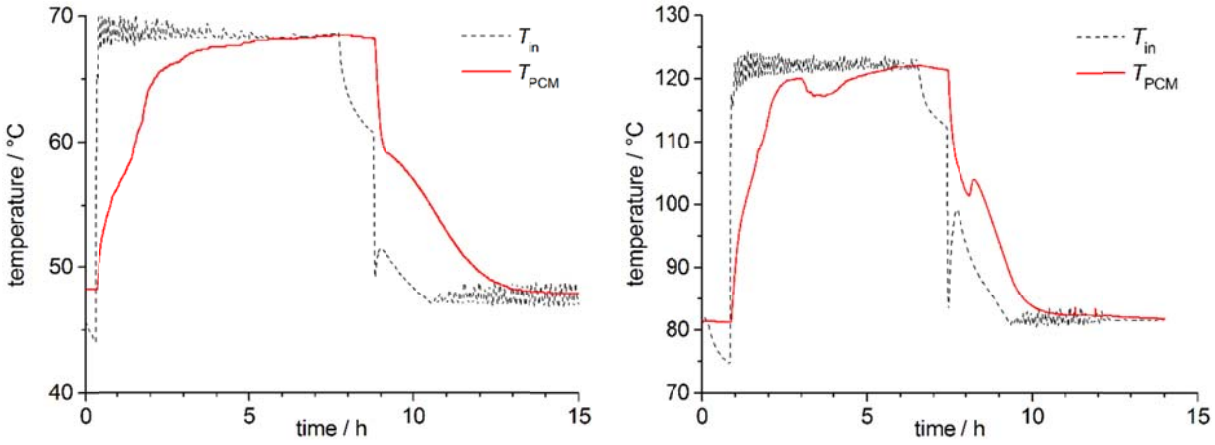


Fig. 4. Temperature-time data of melting and crystallisation of RT58 (left) and bischofite (right) at pilot plant scale. Tank inlet (T_{in}) and PCM (T_{PCM}) temperatures are plotted with dashed and solid lines, respectively.

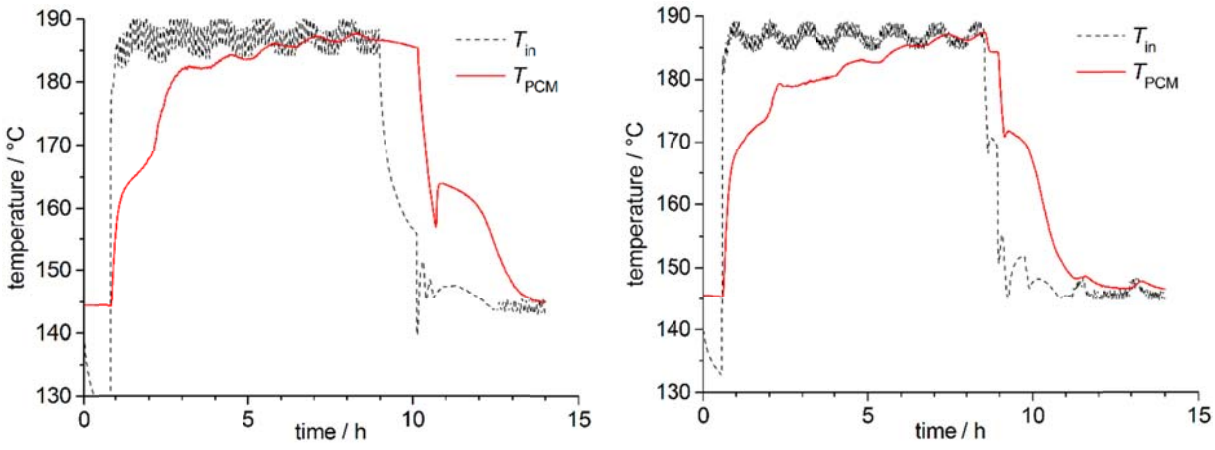


Fig. 5. Temperature-time data of melting and crystallisation of D-mannitol (left) and hydroquinone (right) at pilot plant scale. Tank inlet (T_{in}) and PCM (T_{PCM}) temperatures are plotted with dashed and solid lines, respectively.

3.2. Comparison of measurements via DSC, T-History, and at pilot plant using enthalpy-temperature plots

In this work, the results of the calorimetric measurements via DSC, T-History, and at pilot plant scale are given as enthalpy-temperature plots. Due to the different evaluation procedures, enthalpy-temperature plots are the only common graphical representation suitable for these methods. In the case of DSC and T-History, the measured results are given as continuous enthalpy curves h(T). At pilot plant scale, the total amount of energy stored / released upon melting or crystallization within a certain temperature range is calculated, which can be translated into enthalpy stored / released per kg PCM. Therefore, in the enthalpy-temperature plots, pilot plant measurements are indicated with two data points for heating and two data points for cooling.

If the thermal connection between PCM and DSC crucible or PCM and T-History sample container changes after first melting, the data of the first cycle differs from succeeding cycles. Thus, only the second cycle of each measurement is plotted and used to determine a suitable temperature range and the corresponding enthalpy changes therein. The fact that the first cycle needs to be disregarded when

measuring enthalpy curves with DSC is known from literature. However, this conclusion is not as well stated and known in the case of the T-History method. As observed in the experiments, the first cycle should also be disregarded. In the case of measurements at pilot plant scale, the stabilization of the PCM might need more than one cycle.

Red lines represent heating and blue lines represent cooling curves. Enthalpy curves measured via DSC and T-History are plotted with solid and dashed lines, respectively. Red circles and blue triangles indicate the enthalpy changes measured at pilot plant scale upon melting and crystallisation, respectively. In the plots, enthalpy curves measured via DSC and T-History and enthalpy changes measured at pilot plant scale were shifted to a common zero point located in the liquid state, which is denoted in the label of the enthalpy axis. Shifting to a common zero point in the liquid state is reasonable since the liquid state can be considered as identical from one cycle to another. The results for RT58 and bischofite are shown in Fig. 6 and the results for D-mannitol and hydroquinone in Fig. 7.

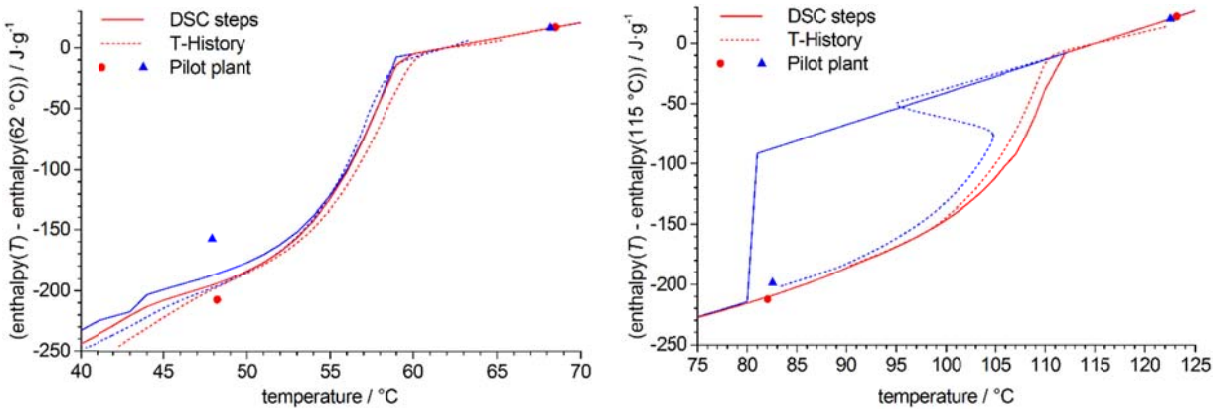


Fig. 6. Enthalpy curves of RT58 (left) and bischofite (right) measured via DSC in step mode (solid line) and T-History (dashed line). Red circles and blue triangles indicate the enthalpy changes measured at pilot plant scale upon melting and crystallisation, respectively.

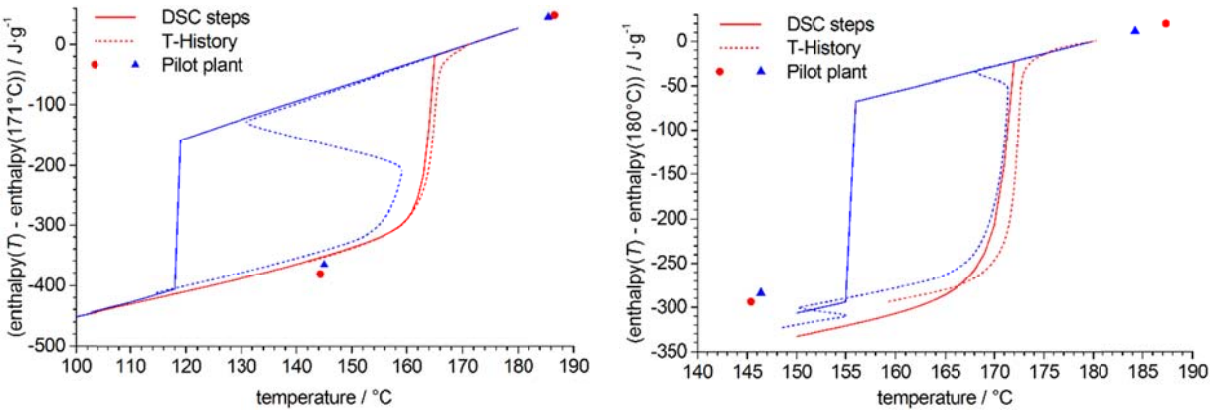


Fig. 7. Enthalpy curves of D-mannitol (left) and hydroquinone (right) measured via DSC in step mode (solid line) and T-History (dashed line). Red circles and blue triangles indicate the enthalpy changes measured at pilot plant scale upon melting and crystallisation, respectively.

The enthalpy curves measured via DSC and T-History indicate a volume-independent melting and crystallisation behaviour of RT58. Melting and crystallisation occur within a temperature range matching the specifications of the supplier (53–59 °C). In the case of bischofite, D-mannitol, and hydroquinone, a significant degree of supercooling is observed in DSC step measurements. After nucleation, the crystallisation evolves in a single temperature step. The supercooling of bischofite, D-mannitol, and hydroquinone in T-History measurements is reduced compared to DSC results. At pilot plant scale, a further reduction of the degree of supercooling compared to T-History data is observed (cf. Fig. 4 and Fig. 5). This trend was expected from own experience and literature [2], [6].

The enthalpy change of RT58 during the crystallisation at pilot plant scale is comparably low. Enthalpy curves of hydroquinone upon cooling measured via T-History indicate a second transition upon cooling between 155 °C and 150 °C (cf. Fig. 7, right), as described in a previous publication [6]. This additional transition was not observed in DSC or pilot plant measurements and might contribute to the comparably low enthalpy changes determined at pilot plant scale. Except for the crystallisation of RT58 at pilot plant scale and influence of the second transition of hydroquinone, enthalpy-temperature plots upon melting and crystallisation measured at different sample scales show a reasonable agreement.

3.3. Tabular comparison of enthalpy changes in defined temperature ranges

In order to show how difficult an evaluation of measurements under different conditions would have been without using enthalpy-temperature plots, enthalpy changes upon melting and crystallization within defined temperature ranges measured at the three scales are compared in Table 3.

Table 3

Enthalpy changes upon melting $\Delta h_{\Delta Tm}$ and crystallisation $\Delta h_{\Delta Tc}$ within defined temperature ranges ΔT_m and ΔT_c measured via DSC, T-History, and at pilot plant scale.

	RT58				Bischofite			
	ΔT_m (°C)	$\Delta h_{\Delta Tm}$ (J·g^{-1})	ΔT_c (°C)	$\Delta h_{\Delta Tc}$ (J·g^{-1})	ΔT_m (°C)	$\Delta h_{\Delta Tm}$ (J·g^{-1})	ΔT_c (°C)	$\Delta h_{\Delta Tc}$ (J·g^{-1})
DSC	52-62	167	52-62	162	75-115	228	75-115	227
T-History	52-62	170	52-62	167	90-115	186	90-115	183
Pilot plant	48-68	224	48-68	173	82-123	235	83-123	220
	D-mannitol				Hydroquinone			
	ΔT_m (°C)	$\Delta h_{\Delta Tm}$ (J·g^{-1})	ΔT_c (°C)	$\Delta h_{\Delta Tc}$ (J·g^{-1})	ΔT_m (°C)	$\Delta h_{\Delta Tm}$ (J·g^{-1})	ΔT_c (°C)	$\Delta h_{\Delta Tc}$ (J·g^{-1})
DSC	115-165	400	115-165	396	150-180	333	150-180	307
T-History	131-171	389	131-171	375	160-180	292	160-180	278
Pilot plant	144-187	428	145-186	409	145-187	314	146-184	295

The expectable maximum storage capacity of a PCM in a defined temperature range is equal to the enthalpy change in that range. Therefore, the enthalpy changes upon melting ($\Delta h_{\Delta Tm}$) and crystallisation ($\Delta h_{\Delta Tc}$) were determined within temperature ranges ΔT_m and ΔT_c, respectively. In the case of DSC and T-History measurements, temperature ranges were chosen which cover the entire phase change upon melting and crystallisation according to measured data (cf. Fig. 6 and Fig. 7). At pilot plant scale, only the overall amount of energy stored upon charging / discharging the storage tank is calculated enthalpy. Therefore, changes upon melting and crystallisation were evaluated considering a temperature interval which is approximately the range between the initial and final storage tank inlet temperatures (cf. Fig. 4 and Fig. 5). In the case of D-mannitol (cf. Fig. 7, left), the enthalpy curve measured via T-History upon heating was extrapolated to lower temperatures to determine the

309 enthalpy change. Thus, due to the different measuring methods and their specific evaluation
310 procedures, the temperature ranges ΔT_m and ΔT_c applied to calculate $\Delta h_{\Delta Tm}$ and $\Delta h_{\Delta Tc}$ vary
311 significantly.

312 Using a tabular comparison as shown in Table 3, it is not clear if the differences in $\Delta h_{\Delta Tm}$ and
313 $\Delta h_{\Delta Tc}$ between the different sample scales / measuring methods arise from the different temperature
314 ranges considered for evaluation or from an actual deviation in the measured enthalpy-temperature
315 data. For example, in the case of bischofite, enthalpy-temperature plots upon melting show a very
316 good agreement (cf. Fig. 6, right). Contrary, indicated enthalpy changes upon melting, $\Delta h_{\Delta Tm}$, in Table
317 3 exhibit a deviation of up to 21% comparing T-History data with measurements at pilot plant scale.
318

319 **4. Conclusions**

320 Four PCM from different material classes (RT58, bischofite, D-mannitol, and hydroquinone) were
321 investigated at three sample scales, namely via DSC, T-History, and at pilot plant scale.

322 To compare the enthalpy changes measured at different scales and under different conditions,
323 enthalpy-temperature plots were demonstrated to be advantageous compared with tabular enthalpy
324 changes within defined temperature ranges. Since the temperature range chosen to calculate the
325 expectable maximum storage capacity differs from method to method due to their different data
326 evaluation procedures, the comparison becomes difficult even if the temperature ranges are reported
327 next to the calculated enthalpy change. It is not clear if possible differences between the different
328 sample scales / measuring methods arise from the different temperature ranges considered for the
329 evaluation or from an actual deviation in the measured enthalpy-temperature data.

330 Except for the crystallisation of RT58 at pilot plant scale and influence of a second transition of
331 hydroquinone, enthalpy-temperature plots upon melting and crystallisation measured at different
332 sample scales show a reasonable agreement. However, relying on a tabular comparison of enthalpy
333 changes within defined temperature ranges, this conclusion cannot be drawn.
334

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