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

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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.

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,

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Nomenclature

$h(T)$	Mass-specific enthalpy curve/J g^{-1}
$\Delta h_{\Delta T_c}$	Mass-specific enthalpy change upon crystallisation within ΔT_c/J g^{-1}
$\Delta h_{\Delta T_m}$	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 $\Delta h_{\Delta T_c}$/K
ΔT_m	Temperature interval for the determination of $\Delta h_{\Delta T_m}$/K

Abbreviations

AHE	Air-HT F heat exchanger
DSC	Differential scanning calorimetry
HTF	Heat transfer fluid
PCM	Phase change material
TES	Thermal energy storage

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.

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.

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

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)	$m_{pilotplant}$ (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

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.