

MEASUREMENT OF THE ENTHALPY OF PCM

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ABSTRACT

The main characteristic of phase change materials (PCM) is the enthalpy-temperature relation that determines the heat storage capacity. This relation is determined experimentally using calorimetric methods. PCM are particularly difficult samples because of their outstanding thermal mass, but also because they are often heterogeneous materials, or show volume dependent effects. Therefore, obtaining representative calorimetric data is not guaranteed by applying standard methodology, and uncommented measurement data can easily be misunderstood. An improved methodology in the measurement and interpretation of calorimetric data will help to avoid misunderstandings among and between researchers, producers and consumers of PCM. We show in this paper the reasons for uncertainty in calorimetric measurements of PCM, and explain in theory and with examples how to quantify and reduce them.

1. BACKGROUND

PCM are used to store thermal energy, i.e. heat or cold, in a small temperature range with high efficiency. The storage capacity is determined by the enthalpy curve and the usable temperature range, where the stored heat $Q(T)$ is

$$Q(T) = \int c_p dT = h(T) + h_0 \quad (1)$$

PCM show superior storage density compared to sensible heat storage materials, such as concrete or water, when used in a small temperature interval around the phase change temperature. The exact slope of the enthalpy curve $h(T)$ has to be known to quantify the storage capacity and thus the potential advantage of PCM.

In reality, many PCM have a melting range and the phase change does not occur at one fixed temperature only. In Figure 1, the enthalpy curve of an ideal PCM is sketched together with the curve of a more realistic PCM.

An ideal PCM can be mathematically characterized by four scalar values, namely the specific heat c_p of solid and liquid phases, the phase change enthalpy Δh and the melting temperature T_m . A real PCM is better represented by the function $h(T)$. The precise determination of this function is the goal of calorimetry of PCM.

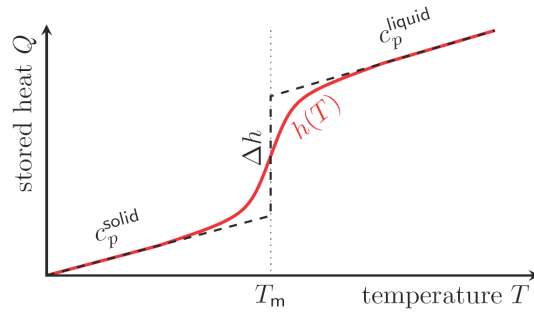


Figure 1: Slopes of the enthalpy curves of an ideal (dashed) and a real PCM (solid), schematic.

2. POTENTIAL PROBLEMS IN CALORIMETRY OF PCM

Basics of calorimetry

In general, calorimetry is the measurement of heat effects. Heat effects become detectable macroscopically only in thermal non-equilibrium, which is therefore required for any calorimetric measurement. The heat uptake or release of a material of mass m and specific heat c_p is given by

$$\Delta Q = m \cdot c_p \cdot \Delta T \quad (2)$$

Here, Δ refers to two thermodynamic states, i.e. two temperature levels, and the equation relates only the initial and final heat contents.

As to the dynamics of the heat flow, considering heat conduction only, it is determined by the thermal resistance R and the temperature difference between two places x_1 and x_2

$$\dot{Q} = \frac{1}{R} \cdot [T_{x_1}(t) - T_{x_2}(t)] \quad (3)$$

In one place (x_1), the temperature is controlled by the instrument according to a temperature program. The temperature at the other place (x_2) is a reaction to this program, and is determined among other by the sample properties. The thermal resistance characterizes the whole heat transfer path. In a calorimetric measurement, this path is typically composed of parts of the instrument and parts of the sample itself. The overall thermal resistance is given by

$$R = \sum_i \frac{\Delta x_i}{\lambda_i A_i} + \sum_j \frac{1}{\alpha_j A_j} \quad (4)$$

where A denotes the cross section area, λ the thermal conductivity of the individual sections Δx of the heat flow path, and α the heat transfer coefficient at intersections.

In a measurement, a minimum value of ΔQ is required in order to be detectable with good precision. The time required for the measurement – which is a main factor of the measurement cost – is thus determined by material properties (m , c_p , λ), instrument properties (A , α) and measurement variables (temperature program $T_{x_1}(t)$). This is essential for the following discussion; more detailed information on calorimetry can be found readily in literature such as [1][2].

Precision of a calorimetric measurement

The property that is detected in most calorimetric measurements is the temperature. While the uncertainty of a temperature sensor can be very low, typically below 0.1 K, the crucial question is what exactly this measured temperature corresponds to.

In Figure 2, the temperature profile of a sample during heating and cooling is sketched.

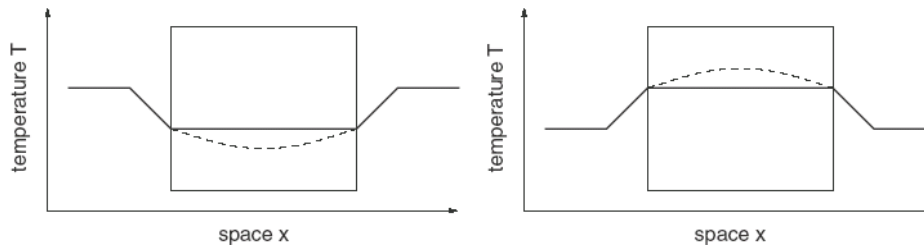


Figure 2: The inner state of the sample is different for heating (left) and cooling (right) although the same temperature is detected on its surface.

While heat flows to or from the sample, a gradient is formed inside it (dashed line). During heating, the temperature inside the sample is below the external temperature, and during cooling it is above. In lack of detailed information about this gradient, the sample temperature is assumed constant (solid line). With a thermo sensor placed at the surface of the sample, the sample temperature is overestimated in the case of heating, and underestimated it in the case of cooling. If the sensor were at a different place, the effect could be reversed but not eliminated without knowing the exact temperature profile.

In order to keep this thermal gradient effect small, low heating and cooling rates, low thermal resistance and small sample geometry are required. Unfortunately, these parameters cannot all be changed without negative side effects.

First, low heating and cooling rates lead to undesired long measurement times as we have lined out before. Also, in many instruments, to improve temperature measurement precision, not absolute but temperature differences are detected, which become very small in the case of small heating and cooling rates. Then, the signal noise increases and signal precision is lost. Second, the thermal resistance is not determined by the setup of the experiment alone, but also by the thermal properties of the sample material. Therefore, it cannot be adapted as desired. Third, the sample geometry cannot be reduced at will for many materials, particularly PCM, as we will show in the next section.

Specific problems in calorimetry of PCM

The introduced basic considerations about precision in a calorimetric measurement of course also apply for calorimetry of PCM. In fact, in the case of PCM, several limitations are particularly severe and lead to a complex situation.

PCM are chosen for their high heat effect, i.e. the heat capacity of PCM in the range of their phase change is outstanding compared to other materials. The factor c_p in equation (2) is thus very large, which corresponds to a long measurement time. While this is not a feature as such, also the thermal resistance of most PCM is high, in particular when compared to metals that are used as standard materials in calorimetry. A high thermal resistance R again leads to a

long measurement time. Finally, most PCM contain additives, are compound materials or show volume dependent effects such as phase separation or subcooling, and thus require a large sample volume to assure that the sample is representative for the bulk material. This means that the factor m in equation (2) is large, which again leads to a long measurement time.

Altogether, the combination of specific properties of PCM makes them something like a worst case sample for calorimetry. Problems that might be insignificant for other materials, including calibration standards, are significant for PCM. In addition, the slope of the enthalpy curve of real PCM being unknown, mathematical corrections that could be applied for pure materials are not applicable to PCM.

Determination of uncertainty in calorimetry

A measurement report is complete only when it includes the declaration of the uncertainty. When the sample temperature is misestimated as lined out above, how can the temperature precision of the measurement be quantified? There are basically two solutions to this problem.

The first solution is to take advantage of the opposite gradients when heating and cooling as sketched in Figure 2. When the enthalpy curve of the sample is measured during heating as well as during cooling, the real curve is found between the two measurement results. The smaller the thermal gradient, the closer are the two curves.

The second solution is to use a stepwise heating and cooling with isothermal segments between the steps to allow thermal equilibrium to establish within the sample. The maximum internal gradient is then confined to the step size. The uncertainty in temperature is thus in any case limited to the step size and can be accordingly adapted to the required precision.

If measured heating and cooling enthalpy curves are not as close as expected, the influence of measurement parameters on the measurement results should be checked by carrying out the measurement with different heating and cooling rates or step programs. If the difference between heating and cooling curves remains, this could be an indication of subcooling or thermal hysteresis. In any case, heating and cooling curves should be included in the measurement report.

3. MEASUREMENT OF ENTHALPY CURVES OF PCM

Now that the sources of problems in calorimetry of PCM and possible solutions are identified, we show with three examples how these principles apply to different calorimeters.

Steps method using a differential scanning calorimeter

With a differential scanning calorimeter (DSC), different heating and cooling rates as well as stepwise heating and cooling can be carried out. From our point of view, the steps method is preferable for PCM, because it offers the same precision for all sample materials without lengthy testing and adaption process [3]. We use the smallest possible step size for our instrument, 1K, which assures a satisfactory temperature resolution. The temperature precision of the sensors in a calibrated instrument is at least 0.1K.

In Figure 3, the result of a DSC measurement of a PCM using the step method is shown.

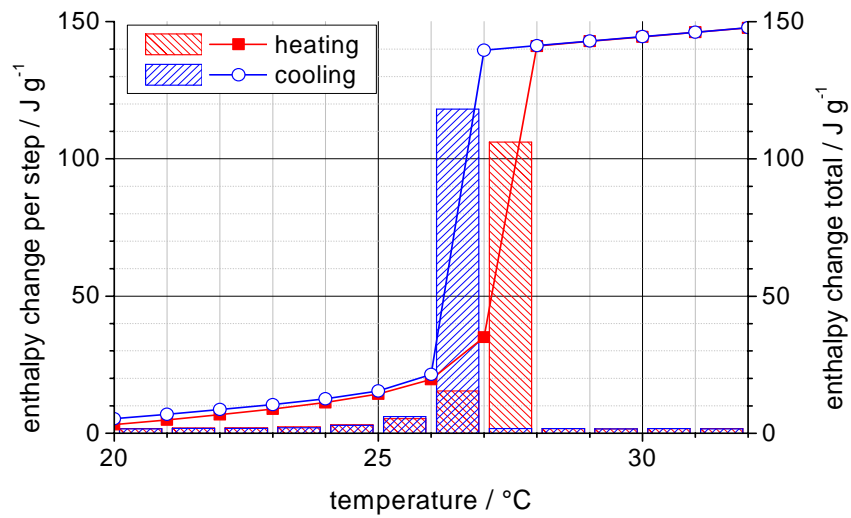


Figure 3: Result of a DSC measurement using the steps method.

From this graph, the heat storage potential of this PCM can easily be read. The PCM exhibits its phase change within a narrow temperature range around 27°C both for heating and cooling. The bars mark the 1K-steps of the measurement and thus the temperature resolution of the enthalpy curve. The overall enthalpy change during heating and cooling between 20°C and 30°C is almost the same, proving high precision in the enthalpy value.

While the DSC is a standard instrument, the step method requires a somewhat sophisticated programming, evaluation and data representation, i.e. skilled personal. Moreover, the DSC sample size is very small and only suitable for pure PCM where a sample of typically 20 μ l is representative for the bulk material.

T-history-method

The T-history method was developed for calorimetry of larger samples, typically of test tube size (approx. 15 ml). Two identical tubes, one containing the sample and the other one a reference substance, are exposed to a sharp change in surrounding temperature. The temperature versus time curves of the sample and the reference are recorded simultaneously. A typical heating segment of a T-history measurement is shown in Figure 4.

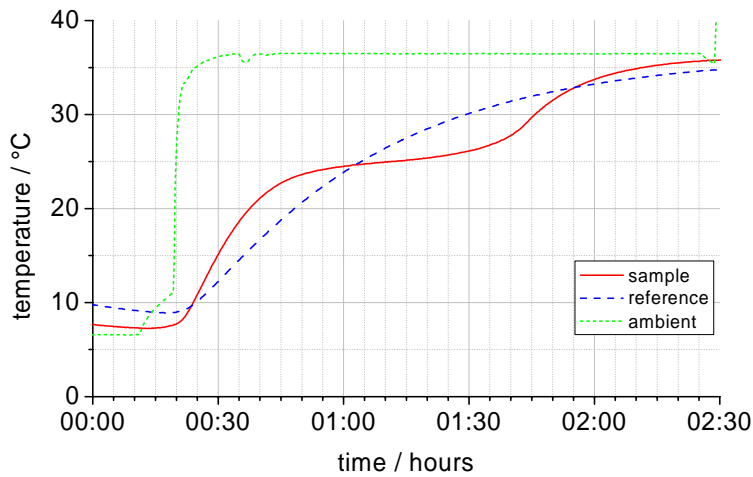


Figure 4: Typical heating segment of a T-history measurement

From the temperature curve and thermal data of the reference, the heat flow to the ambient is determined and applied to the sample. From this, the enthalpy change in the sample is determined as a function of temperature [4].

The T-history method does not directly force a heating rate on the sample as does the DSC. Instead, the sample slowly adopts its temperature to the constant ambient temperature via a large thermal resistance between ambient and sample (part of the instrument). The heating or cooling speed of the sample therefore is not constant during a T-history measurement, as can be seen in Figure 4. The main variable measurement parameter is the ambient temperature level. Temperature levels at different distances above and below the phase change temperature of the PCM are used to vary the heating and cooling speed. In Figure 5, the results of T-history measurements with different ambient temperatures are shown.

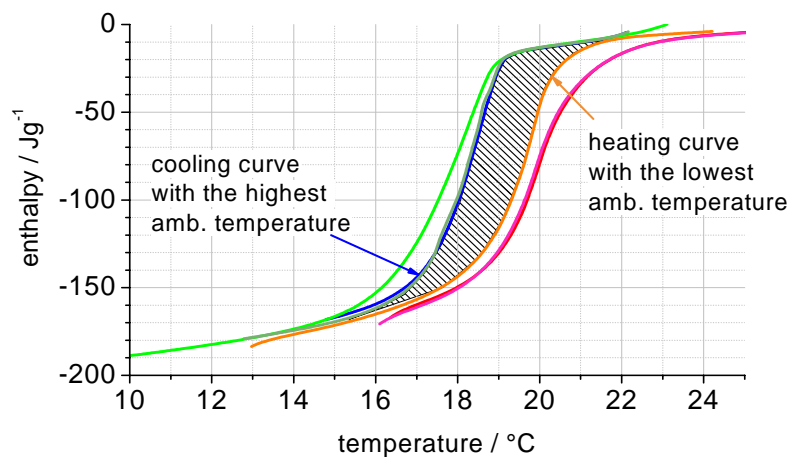


Figure 5: The resulting enthalpy curves of a set of T-history heating and cooling measurements limit the region of the real enthalpy curve.

The cooling curve with the highest ambient temperature and the heating curve with the lowest ambient temperature correspond to the smallest temperature gradient inside the sample and

thus limit the region of the enthalpy curve at isothermal conditions. The other heating and cooling curves illustrate the effect of an increased gradient: the end of the phase change is shifted toward higher temperatures for heating and toward lower temperatures for cooling.

Due to the large sample size, the T-history method can be applied also to compound or other inhomogeneous PCM and PCM with significant subcooling. In our T-history installation, we achieve temperature accuracy of about $\pm 1\text{K}$ and accuracy in the enthalpy of about $\pm 10\%$ [5]. The T-history installation is not a commercial instrument, but it can be assembled from standard laboratory equipment.

Air flow apparatus

A third calorimeter, which is designed for measurements on encapsulated, macroscopic PCM objects in an air stream, is the “air flow apparatus”. Its general setup is sketched in Figure 6.

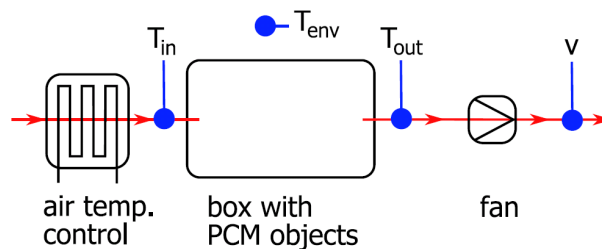


Figure 6: Sketch of the air flow apparatus.

Air from the environment is conditioned and blown through a box that contains the PCM objects. The temperature is measured at the box inlet and outlet, and the air flow is quantified by a flow meter. The heat effect of the box content is determined, subtracting heat losses to the environment as quantified by reference measurements. The box in the installation at ZAE Bayern has a capacity of about 20 liters for the PCM objects.

Here, a considerable gradient within and between the individual PCM objects cannot be avoided. Also, the temperature sensor is relatively far away from the PCM. Therefore the temperature resolution of the measurement is low. This method is however suitable to verify the overall heat content of large PCM objects within the application temperature range, and to check the performance of the PCM objects in an air based storage system. In Figure 7, a comparison with T-history data is shown, proving a good agreement.

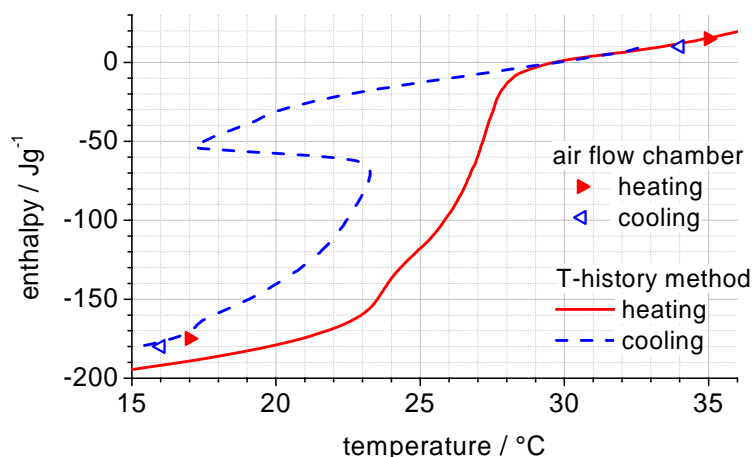


Figure 7: Results of a T-history and air flow measurement on one material.

4. CONCLUSIONS

Calorimetry of PCM has to cope with a demand for high precision and temperature resolution on the one hand, and some particularly difficult material parameters on the other hand. If the measurement results depend on the measurement parameters, they are not identical with the material properties. Then, the use of the acquired data in an application, which means in a different setup with respect to the sample geometry and heating rate, is erroneous. We have shown in this paper how the requirements can be met and introduced two methods to assure in practice a good quality of measurement. With the help of three different types of calorimeters, the problems and solutions were illustrated and discussed.

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