Validation of a real-scale high-temperature calorimeter – lessons learned

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In order to characterise the cyclic evolution of thermophysical properties of metallic latent thermal energy storage systems, application scale can be a significant factor. Therefore, new setups and measurement procedures for real-scale and high-temperature calorimetry are needed. In this study we tried to validate a novel device and procedure regarding trueness and precision (in terms of repeatability). It is shown, why the chosen validation approach was not satisfying and recommendations to avoid severe mistakes in a validation routine are presented.

The novel calorimetric procedure was performed with a known reference sample consisting of 4.5 kg Aluminium as metallic Phase Change Material in an AISI 316Ti hollow cylindrical container. The procedure, consisting of a stepwise heating half cycle with active cooling fluid flow followed by a controlled cooling half cycle, was performed five times between 100 °C and 680 °C under identical conditions. The aim of the procedures is to determine the specific heat capacity at different temperatures, the specific heat of fusion and peak onset and offset temperatures. In order to evaluate the reliability of these results, characteristic quality numbers were evaluated: The recovery rate *RR* for trueness, the coefficient of variation V_k for precision and the method capability index C_{mk} for accuracy. The recovery rate *RR* is the ratio between the mean value of all results $\bar{x}$ and the expected true value (a reference value) x_{Ref}:

$$RR = \frac{\bar{x}}{x_{Ref}} \cdot 100\%$$

The coefficient of variation V_k is the ratio between the standard deviation σ and $\bar{x}$. It is calculated from all measurement results x_i and the number of measurements *n*:

$$V_k = \frac{\sigma}{\bar{x}} \cdot 100\% \text{ with } \sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

The method capability index C_{mk} depends on $\bar{x}$, the standard deviation σ and a chosen specification limit *SL*:

$$C_{mk} = \frac{\bar{x} - SL}{3\sigma}$$

For *SL* a deviation of 10 % was chosen. C_{mk} gives information about the position of the mean value in relation to this allowed tolerance center. It is only valid for normally distributed values.

In this study only four of the five measurements were used for evaluating these characteristic quality numbers, because of differences during the phase change. For determining the specific heat of fusion C_{mk} = 3.67 was found (*RR* = 106 %, V_k = 1.36 %). That means, that the measurement procedure is suitable to determine the specific heat of fusion in the allowed tolerance limit.

For determining the specific heat capacity $C_{mk} < 1$ was found, which means, that the measured values are not distributed within the allowed range. C_{mk} even tends to decrease for lower temperatures.

The too low C_{mk} value results from a low precision. However, this does not imply, that the proposed procedure itself is not suitable, but can also result from the reference sample changing its properties over cycling. It is assumed, that the reference sample changed its properties due to solubility between Aluminium from the mPCM and different elements (like Iron, Chromium, …) from the housing component. Therefore, it is not a suitable reference sample anymore. Thus, calorimetric procedures are in any case to be validated with stable reference samples. The design and setup of such a stable reference sample was found to be the main challenge of high temperature metallic latent thermal energy storage systems, due to the potentially high reactivity of liquid metals at high temperatures.