Development of measurement setup for thermal conductivity at high temperatures using the parallel hot-wire

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Abstract. An experimental setup is built to determine the thermal conductivity of a mixture of KNO₃ and NaNO₃ with a ratio of 54-46m% which is used in high temperature thermal storage systems. The measurement principle is based on the transient parallel hot-wire method which is described in the standards NBN B 62-202 and ISO 8892-2. The setup is designed to measure the thermal conductivity around the melting temperature (<300°C). Measurements within the liquid region show faulty results caused by natural convection within the sample. The measured thermal conductivity within the solid region is 0.5466-0.5529W/mK close to the melting point and 0.7174W/mK at room temperature, which shows a decreasing thermal conductivity with increasing temperature in the solid region.

1. Introduction

The storage of thermal energy on a large scale will be an important contributor to the transition to green energy. Currently a lot of scientific research is being done on experimental testing [1] and modeling [2, 3] to design these thermal energy storage (TES) systems properly. Knowledge of accurate material properties of the used phase change material (PCM) is important, both when deriving correlations from experimental results as when using them in correlations for thermal models. The thermal conductivity of the PCM is one of these properties, which is dependent on the temperature.

Mixtures of salts are commonly used as PCM for high temperature applications [1]. The appropriate melting temperature can be set by the mixing ratio but also the material properties of the mixture dependent on this ratio. A frequently used mixture is NaNO₃ with KNO₃, which has a lower melting temperature than the pure components [4]. In the liquid region, the thermal conductivity of the pure salts NaNO₃ and KNO₃ has been investigated exhaustively in scientific literature. Nagasaka et al. [5] and Zhao et al. [4] summarized the data and concluded that discrepancies are present between the different studies, mostly caused by a non-negligible contribution of natural convection in the steady state measurement techniques. Continuing on this work, Zhao et al. [4] developed a theoretical model to predict the thermal conductivity of a liquid mixture of the salts, which is shown in equation (1) and has a predicted standard error of 4.15% in the investigated temperature range and mixture composition:

\[
\lambda = \lambda_A \left(1 - \left(\frac{b}{a}\right)^2 + \frac{b^2}{1 + \frac{\Delta \lambda}{\lambda_B} \frac{b}{2a}}\right)
\]

with \(b/a = (2v_B)^{1/3}\) (1)
where $\lambda$ is the thermal conductivity, $v$ is the volume fraction and subscripts A and B indicate the component with respectively the highest and lowest volume fraction in the mixture.

The investigated spectrum of the thermal conductivity of the KNO$_3$ and NaNO$_3$ mixture is however mostly applied to the fully molten state (e.g. in solar energy applications) [4] and as a result no data is available around the melting temperatures of the salt and also equation (1) cannot be used around the melting temperature. However, within the design of TES it is important to know the thermal properties around this melting temperature accurately. Therefore an experimental setup is designed within this paper to be able to measure the thermal conductivity of the molten salt in the solid and liquid state in a wider range and around the melting temperature.

An eutectic salt mixture of KNO$_3$ and NaNO$_3$ with a ratio of 54-46m% will be studied in this paper, which has a melting temperature of 222°C and is used in TES applications [1]. For this specific mixture, values from 0.485-0.445W/mK can be expected in the liquid region between 230-400°C according to Zhao et al. [4] and 0.46-0.51W/mK closer to the melting point according to Tamme et al. [6]. A decreasing thermal conductivity with increasing temperature is expected in the liquid region [4]. Within the solid region no data is available [6].

Based on the findings in literature [4, 5], it was decided to use a transient measurement technique, specifically the parallel hot-wire method. Within the following sections, first the measurement setup and methodology will be described. Then the measurement results of the thermal conductivity will be discussed and some issues related to the current setup are discussed.

2. Measurement methodology, setup and procedure

The hot-wire method is a standard transient technique based on the measurement of the temperature rise at a defined distance from a line heat source in the material. The temperature rise $\Delta T$ in a point of the material at a distance $r$ from the line heat source with a heat dissipation per length $q$ at a time $t$ after switching on the heat source, is given by equation (2). The thermal conductivity at a certain initial sample temperature can then be calculated with a least square fitting of the thermal conductivity $\lambda$ and thermal diffusivity $D$ on the measurement results. The heat capacity can also be calculated with this method from the determination of the thermal diffusivity, but is not investigated in this paper.

$$\Delta T(r,t) = \frac{q}{4\pi \lambda} Ei\left(-\frac{r^2}{4Dt}\right)$$

with $Ei$ the exponential integral, defined by $Ei(-x) = \int_{-x}^{\infty} \frac{e^{-u}}{u} du$.

The experimental setup is designed based on the standards NBN B 62-202 [7] and ISO 8892-2 [8]. A maximum temperature of 300°C was taken into account within the selection of the components and materials of the setup. An overview of the setup lay-out is shown in Figure 1 (left). In the middle of the width and height of the sample with dimensions $h \times w \times l$ of $128 \times 114 \times 230$mm, the hot junction of a thermocouple and hot-wire are placed along the length direction at a distance $r$ of 5mm ($\pm$1mm) from each other. A K-type thermocouple ($\pm$1°C) is used and the induced voltage due to a difference in temperature between hot and cold junction is measured with a voltage sensor (NI 9213). The absolute reference temperature $T_{\text{reference}}$ at the cold junction is measured with a PT100 and NI 9219. A Constantan alloy wire with a diameter of 0.2mm with a maximum operating temperature of 600°C and a length equal to the length of the sample is used as hot-wire. Two wires are welded at each end of the hot wire: one for an accurate measurement of the voltage (NI 9205 ±6.230 µV) over the hot-wire and a second for the power supply circuit. The latter consists of a power source, a current sensor ($\pm$10mA) to determine the power dissipated in the hot-wire and a switch to start the experiment at $t=0$.

An appropriate container from stainless steel was constructed to contain the salt sample both in solid and liquid state, which is shown in Figure 1 (right). The salt is provided as solid particles, which will decrease in volume when melting starts. To deal with this reduction, some extra space is added at the
top of the container resulting in a total height of 154mm. To remove the molten salt out of the container after an experiment, a screw cap is provided at the bottom of the container and the bottom is placed in a slope (1%/m) to remove as much salt as possible by gravity. After removing the screw cap, the molten salt flows into a reservoir which is placed underneath the container. When molten, the salt is electrically conductive and therefore, the hot junction of the thermocouple and hot-wire should be electrically insulated from the sample. Therefore both wires and connections are electrically insulated by a layer of polyamide tape towards outside the container. A suspension system for the thermocouple and hot-wire cables is provided in the container.

The container, reservoir, sample and parts of the measurement circuit which are resistant to the high temperatures are inserted in an electrically heated furnace which can reach 300°C. According to the ISO standard, temperature differences at any two points in the region occupied by the samples should not exceed 10°C [8]. These requirements are checked by measuring the air temperature in the surrounding of the sample. Furthermore, some additional thermocouples are added within the sample to check the temperature uniformity and stability.

Before the start of a measurement, the sample is heated to the desired temperature during a pre-test, which lasts until the temperature of the salt is stable within 0.036°C during one hour (dT/dt < 10^{-5}). This slope is later on used to correct the temperature during the measurement. Then the main-test starts, where the switch of the hot-wire circuit is closed and the temperature rise, voltage and current are being measured every second during one hour. This data is then used to determine the conductivity iteratively based on equation (2). Only the valid data (heat wave did not reach the outside of the sample) is used within this calculation, by determining the maximum test duration $t_e$ based on the calculated thermal diffusivity and equation (3):

$$t_e = \frac{h^2}{4D} \left( e^{\frac{1}{e^{2.131}}} \right)$$ and
$$z = \frac{1.056}{\ln(\frac{h}{r} + 0.365)}$$

3. Results and discussion

Initially measurements of the thermal conductivity were planned in the solid and liquid region around the melting point. However, for measurements within the liquid region, faulty results were obtained. This is probably caused by natural convection occurring within the sample in the container before and from the start of the measurements. To avoid this natural convection, a more uniform temperature should be provided within the furnace and shorter measurement times should be used [4]. Up till now only four measurements could be done within the solid region due to the long stabilization time of the sample
temperature (±48h). The results at three different temperatures are shown in Table 1 with the set heat dissipation, end time and temperature rise at the end of the test indicated. The measured thermal conductivities in the solid region where no natural convection can occur, were within the region of expectation. The measurement at 209°C was repeated and the deviation was smaller than 0.7%. Based on this preliminary results it is shown that within the solid region, a decreasing thermal conductivity occurs with increasing temperature. This is similar to the findings in literature for the liquid region [4].

Table 1. Thermal conductivity in solid region for eutectic mixture of KNO3 and NaNO3 (54-46m%)

| T (°C) | q (W/m) | tc (s) | T_end-T_start (°C) | λ (W/mK) |
|-------|---------|--------|--------------------|----------|
| 26.64 | 7.934   | 829    | 3.39°C             | 0.7174   |
| 199.35| 8.817   | 1800   | 4.66°C             | 0.5466   |
| 209.15| 8.823   | 1800   | 4.61°C             | 0.5489   |
| 209.02| 8.821   | 1800   | 4.60°C             | 0.5529   |

4. Conclusion
An experimental setup has been built to determine the thermal conductivity of a salt mixture of KNO3 and NaNO3 (54-46m%) around the melting temperature. The method is based on the transient parallel hot-wire technique and the design is based on the standards NBN B 62-202 [7] and ISO 8892-2 [8]. No valid measurements could be obtained within the liquid region due to the occurrence of natural convection. Four measurements of the thermal conductivity were done within the solid region. The measured thermal conductivity is between 0.5466-0.5529W/mK close to the melting point, which is in the region of expectation from literature. The thermal conductivity at room temperature is determined as 0.7174W/mK, and as a result a decreasing thermal conductivity is obtained with increasing temperature in the solid region. In a continuation of this work, more measurements are planned within the solid region to increase the spectrum of data. Further investigation will be done on the liquid region to be able to obtain valid results in this region.

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