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# Volumetric Determination of Densities of Molten Salts for CSP Applications

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**Abstract.** The densities of molten salt mixtures are determined by direct volumetric measurements providing uniform thermal conditions, defined gas atmosphere above the sample and direct observation of the sample during the measurement. Three nitrate/nitrite salt systems are examined: $NaNO_3$-$KNO_3$ (40:60 by mass, solar salt), $KNO_3$-$NaNO_3$-$NaNO_2$ (53:7:40 by mass, Hitec) and two alternative compositions of $KNO_3$-$NaNO_3$-$Ca(NO_3)_2$ (45:7:48 and 43:15:42 by mass, Hitec XL) are examined. Linear fits of the density are presented derived from the experimental data.

**Keywords:** Density, Molten Salt

## 1. Introduction

Binary and ternary nitrate and nitrite salt mixtures are considered as next generation heat transfer fluids for parabolic trough systems at operating temperatures up to 550 °C. Precise data on several physical parameters are required for designing such systems. Literature data on densities of relevant candidate materials are so far not completely reported for the temperature ranges of interest.

The aim of this study is to determine the densities within the liquid range up to the stability limit using a volumetric technique. In contrast to alternative approaches like buoyancy (Archimedean) method [1] or volumetric tests like pycnometry [2] or expansion measurement with conductivity detection [3] the technique applied in this study is based on direct observation of the sample. Hence, any changes of the sample like bubble formation by decomposition is unambiguously detected. The sample is located within circulation air convection furnace ensuring isothermal conditions and allowing for defined gas conditions by flushing the furnace with the gas of interest.

## 2. Approach

Samples of molten salt are prepared from high quality salts ($NaNO_3$, Merck, Emsure, ACS, ISO, Reag. Ph. Eur. for analysis, 99.8%, $NaNO_2$, Merck, GPR RECTAPUR, ≥ 98%, $KNO_3$, Merck, Emsure, ISO, Reag. Ph. Eur. for analysis, 99.9%, $Ca(NO_3)_2$*4 $H_2O$, Merck, Emsure, ACS for analysis, 99.7%). The powders are melted at 300 - 350 °C for up to 24 hours to ensure complete mixing and dehumidification.

17 – 19 g of salt sample is filled into 10 ml measuring cylinders (Hirschmann Laborgeräte, Duran®, class A, brown graduation) which are located inside a convection furnace (Carbolite

HT 6/95) next to a calibrated Pt-100 sensor. The position of the meniscus of the liquid salt (see Figure 1) is determined with an endoscopic camera system (Schölly HT endoscope SO.HT.00xx with camera flexiscope IQ101).

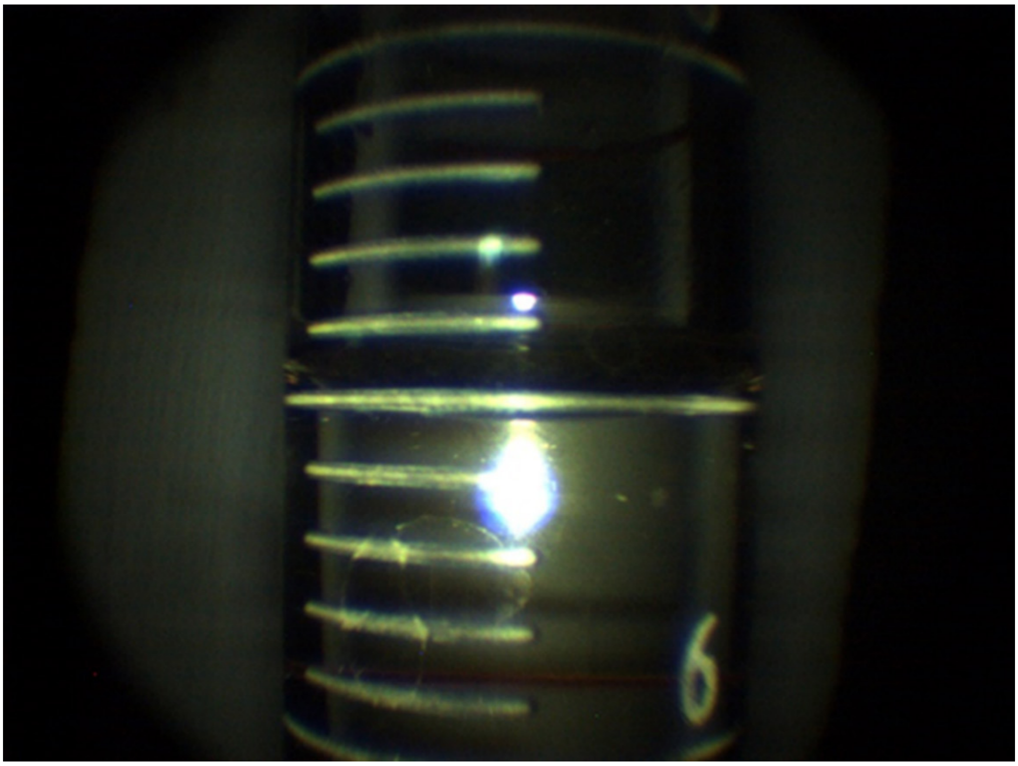


***Figure 1***. *View with an endoscopic camera system on a solar salt sample at 564 °C in a 10 ml measuring cylinder inside a convection furnace.*

Digital evaluation of the pictures allows for precise volumetric evaluation of the salt level. This is done at thermal steps starting above the melting point up to 600 °C and in steps back to the initial temperature with 2 – 3 K/min. Each target temperature is held at least for 15 min. Four mixtures of sodium nitrate ($NaNO_3$), sodium nitrite ($NaNO_2$), potassium nitrate ($KNO_3$) and calcium nitrate ($Ca(NO_3)_2$) have been tested (see Table 1).

***Table 1.*** *Salt mixtures tested in this study.*

| **Salt** | **Composition (mass fractions)** | **Melting point** |
|---|---|---|
| Solar salt | 40% $KNO_3$, 60% $NaNO_3$ | 221 °C [4] |
| Hitec | 53% $KNO_3$, 7% $NaNO_3$, 40% $NaNO_2$ | 142 °C [4] |
| Hitec XL (1) | 45% $KNO_3$, 7% $NaNO_3$, 48% $Ca(NO_3)_2$ | 131 °C [4] |
| Hitec XL (2) | 43% $KNO_3$, 15% $NaNO_3$, 42% $Ca(NO_3)_2$ | 140 °C [5] |

## 3. Results

All salts are examined up to temperatures when gas formation is vigorous and the salt seems to be boiling. Nevertheless, strictly linear decrease of salt volume is observed for all tested salts indicating no significant gas volume is in the fluid. This is likely due to the low viscosities at high temperatures of these liquids which facilitates fast separation of gas bubbles from the liquid.

For solar salt the densities determined with the volumetric measurement in this study deviate only less than 0.5% at 255 °C and about 1.7% at 595 °C from the data reported in [6] or [7] (see Figure 2).

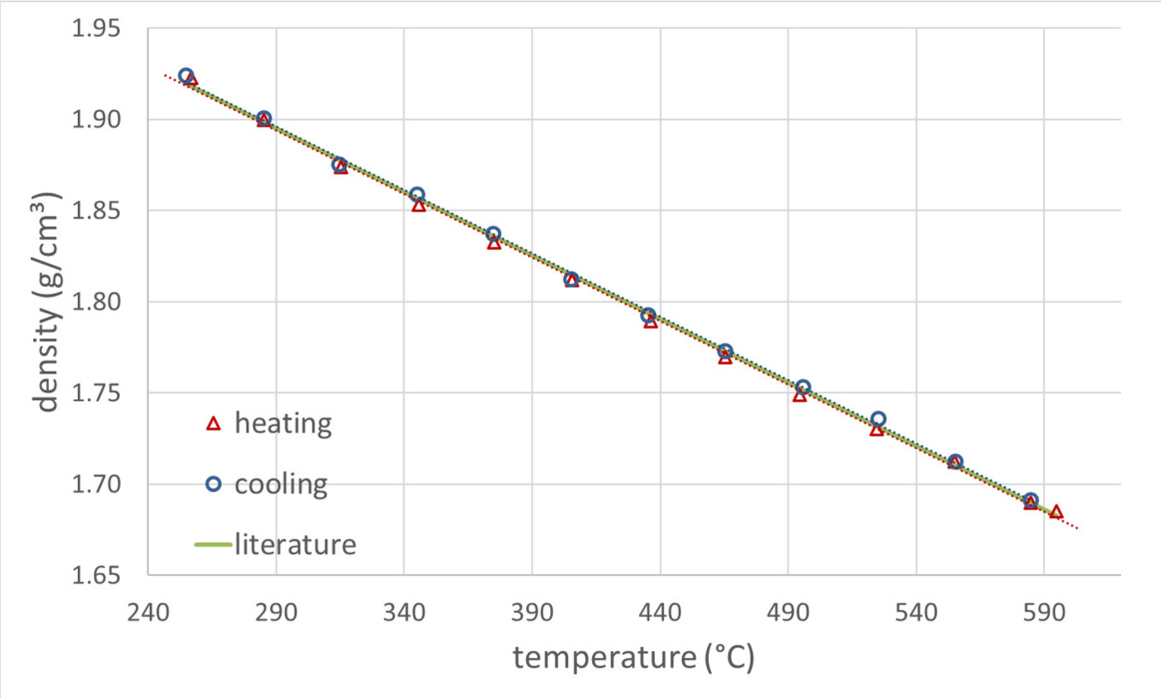


***Figure 2**. Density findings with solar salt during heating up (red triangles) and cooling down (blue circles) in comparison to literature data [6].*

Volumetrically determined densities of Hitec salt mixture deviate 1.6% at 175 °C and 2.3% at 565 °C in comparison to [1] (see Figure 3). The same incremental decrease is found at higher temperatures in this study like in [1].

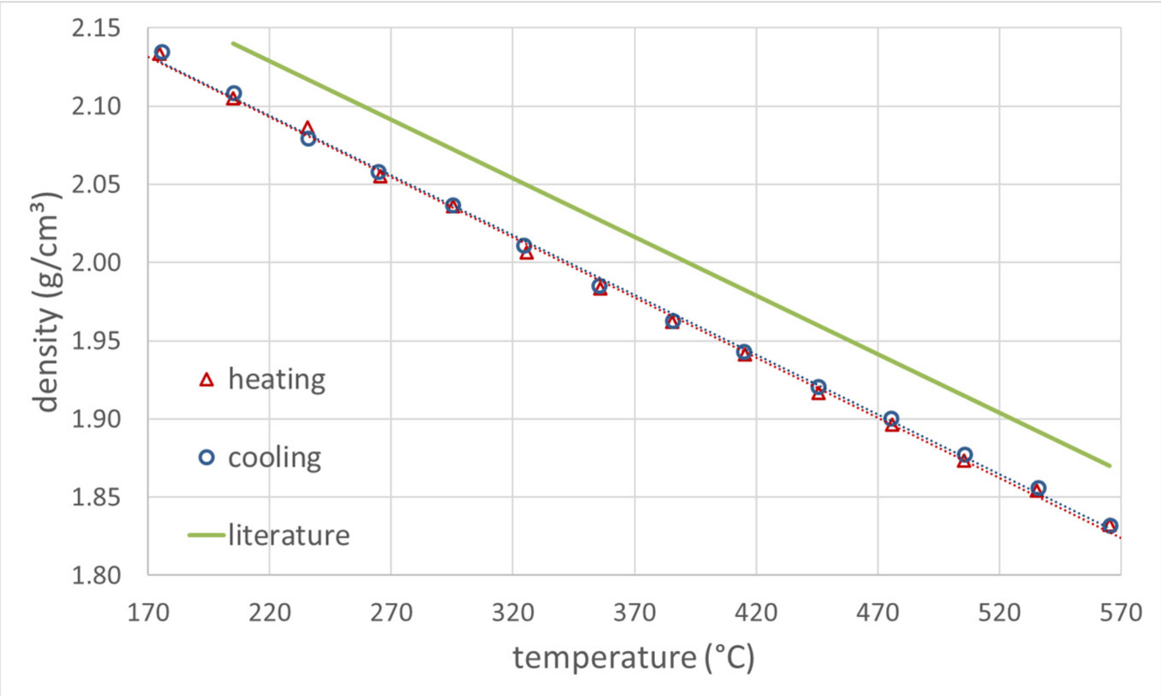


***Figure 3**. Density findings with Hitec salt during heating up (red triangles) and cooling down (blue circles) in comparison to literature data [1].*

Both versions of the Hitec XL mixture have almost equal densities (see Figure 4 and Figure 5). For salt version 1 no literature data have been found by the authors so far. Data for version 2 reported in [8] are 1.8% smaller at 120 °C and 1% higher at 510 °C.

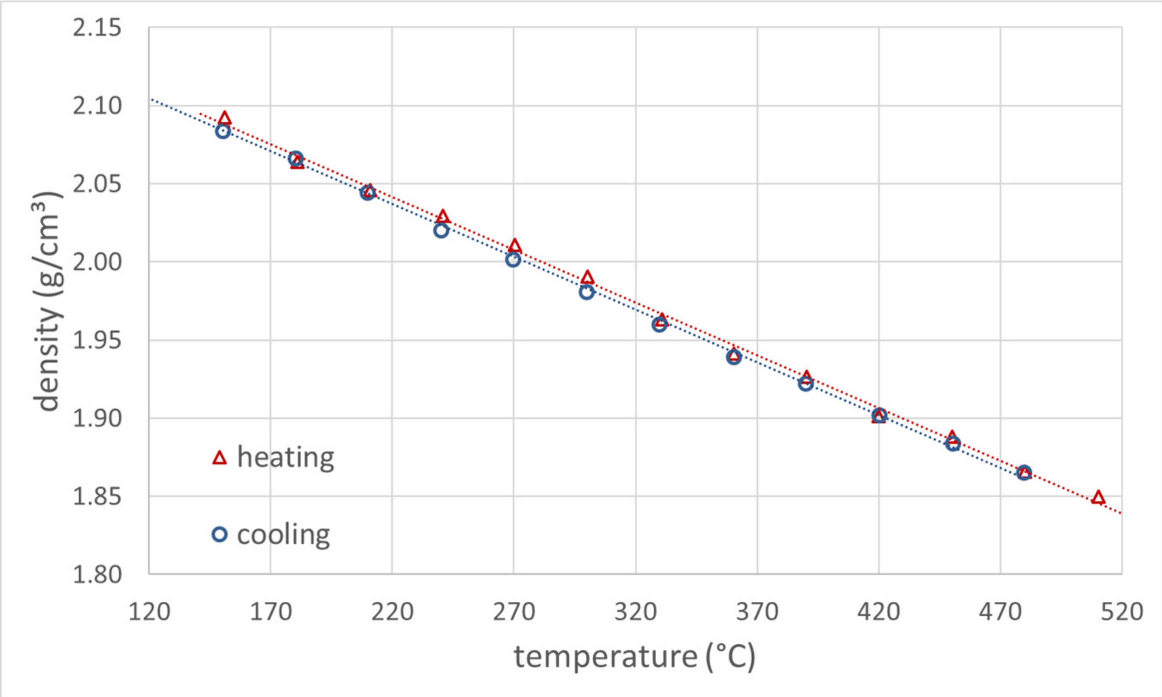


***Figure 4**. Density findings with Hitec XL salt (version 1) during heating up (red triangles) and cooling down (blue circles).*

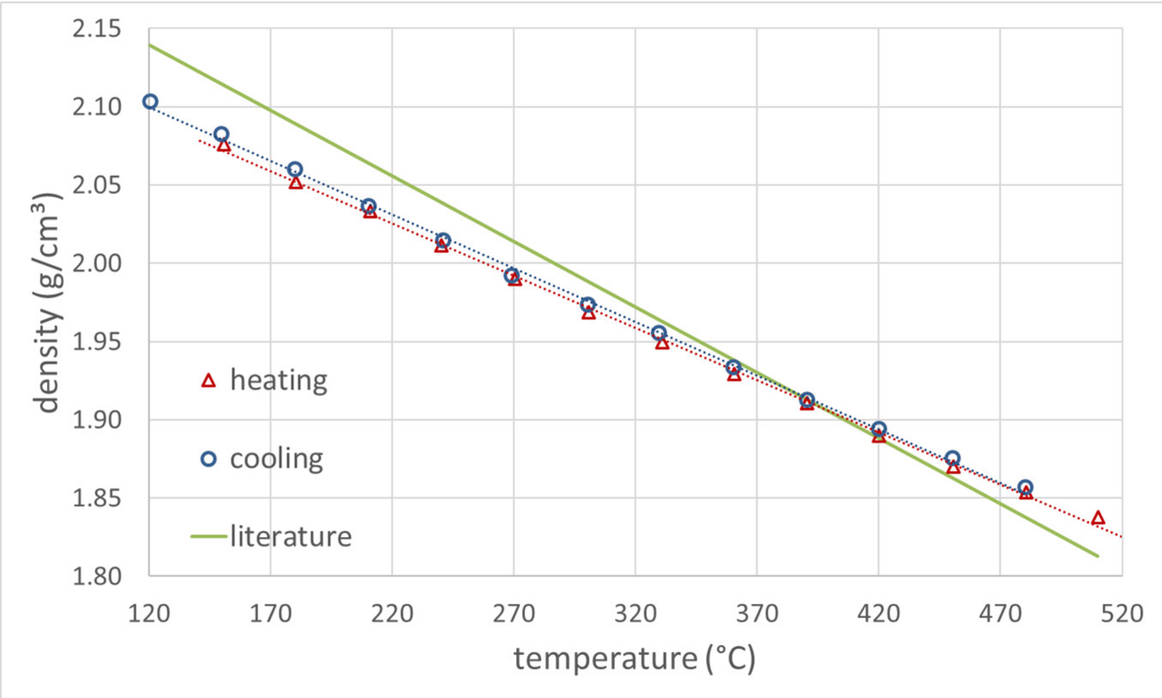


***Figure 5**. Density findings with Hitec XL salt (version 2) during heating up (red triangles) and cooling down (blue circles) in comparison to literature data [8].*

The relations of the densities determined with the volumetric measurement during heating up and cooling down are fitted to linear equations according to Table 2.

***Table 2.*** *Linear fit data and temperature ranges of the density measurements.*

| **Salt** | **Linear fit, d(g/cm³) =** | **Range (°C)** |
|---|---|---|
| Solar salt | 2.097 - 6.961 10-4 T(°C) | 255 – 595 |
| Hitec | 2.263 - 7.689 10-4 T(°C) | 175 – 565 |
| Hitec XL (1) | 2.187 - 6.723 10-4 T(°C) | 120 – 510 |
| Hitec XL (2) | 2.178 - 6.791 10-4 T(°C) | 120 – 510 |

## 4. Discussion

It could be shown that densities of liquid salts can be determined by direct volume measurements with the experimental set-up used in this study up to 600 °C. Although decomposition of nitrate salts give rise to vigorous gas formation no tendency to decreasing salt density is observed. This is as the gas volume within the fluid remains insignificant in this experiment as the gas forms as small bubbles which are quickly released.

First results on binary and ternary nitrate/nitrite molten salts agree well with literature data indicating that the method provides reliable results.

## Data availability statement

No additional data are available to this publication.

## Underlying and related material

No additional material is available to this publication.

## Author contributions

Christian Jung prepared the manuscript. Carsten Spenke supervised the experiment and the data acquisition for this paper.

## Competing interests

The authors declare that they have no competing interests.

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