CHARACTERIZATION OF THE THERMOPHYSICAL PROPERTIES OF MOLTEN SALTS USED IN CSP PLANTS USING THE dT-HISTORY METHOD

Grover Viracochea[1,2], Abdiel Mallco[1,2], Mauricio Lague[1] and Carlos Pérez[3]

[1] Universidad de Antofagasta, Antofagasta (Chile)

[2] Solar Energy Research Center, Santiago (Chile)

[3] Instituto de energías Renovables, Morelos (Mexico)

Abstract

Accurate thermophysical characterization of molten salts is essential for the efficient design of thermal energy storage (TES) systems in concentrated solar power (CSP) plants. Differential scanning calorimetry (DSC), the standard method, uses millimeter-sized samples that may not be representative of the behavior of bulk material. This work presents a complete experimental protocol for the implementation of the dT-History method, a low-cost calorimetry technique based on the RC circuit analogy, to characterize a 130 g sample of solar salt (60% $NaNO_3$, 40% KNO_3). The methodology includes systematic calibration of the calorimeter components, followed by sample analysis. The results generated the specific heat curve cp as a function of temperature, successfully identifying the solid-solid (~105 °C) and solid-liquid (~220 °C) phase transitions. Although the results are qualitatively similar to the DSC data in the literature, a quantitative discrepancy in the transition temperatures was observed. It is concluded that the dT-History method is a validated and robust alternative, and it is postulated that the discrepancies observed are due to the use of a more representative sample size, capturing dT/dt thermal dynamics that DSC omits.

Keywords: Thermal Energy Storage (TES), Concentrated Solar Power (CSP), Molten Salts, dT-History Method, Calorimetry, Specific Heat, Solar Salt.

1. Introduction

The transition to renewable energy sources is a fundamental pillar of global decarbonization, and concentrated solar power (CSP) is emerging as a key solution for dispatchable power generation (Bauer et al., 2013). However, the economic viability of CSP plants depends critically on the efficiency of their thermal energy storage (TES) systems (Jayathunga et al., 2024). For high-temperature applications, molten salts, and in particular "Solar Salt," a mixture of 60% NaNO3 and 40% KNO3, have become the industry standard due to their thermal stability and low cost (Palacios et al., 2020).

Accurate and efficient design of TES systems requires precise knowledge of the thermophysical properties of these salts, especially their specific heat c_p (Parida and Basu, 2023). The standard method for this characterization has been Differential Scanning Calorimetry (DSC) (Abir et al., 2024). However, DSC has significant limitations: the inconsistent results reported in the literature are often attributed to the use of tiny samples (<10 mg), which may not be representative of the thermal behavior of the bulk material (Saoudi et al., 2021). This discrepancy between laboratory measurements and industrial performance is a critical knowledge gap (Caraballo et al., 2021).

To overcome the limitations of DSC, the T-History technique has gained recognition as a robust alternative that uses larger, more representative samples (on the order of grams) (Martínez et al., 2020). This work is based on the dT-History formulation, an analytical refinement based on detailed knowledge of the physics of the experimental device. This method offers the promise of a characterization more analogous to actual operating conditions (Moreno-Alvarez et al., 2010).

The objective of this article is to present and validate a complete experimental protocol for the implementation of the dT-History method in the characterization of Solar Salt. To this end, (1) the calibration procedure for the calorimeter components (container tube and steel as reference material) is detailed; (2) the protocol is applied to obtain the specific heat curve cp as a function of temperature; and (3) the results are validated by comparing them

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with DSC reference data, discussing the differences observed in phase transitions and the impact of the dT/dt thermal dynamics that this method manages to capture.

2. Experimental methodology

The methodology of this work is based on the dT-History method, a technique based on the analogy between heat transfer and RC electrical circuits. The objective is to determine the heat capacity C_1 and thermal resistance R_1 of the material sample. The experimental setup with the elements involved is shown in Figure 1.

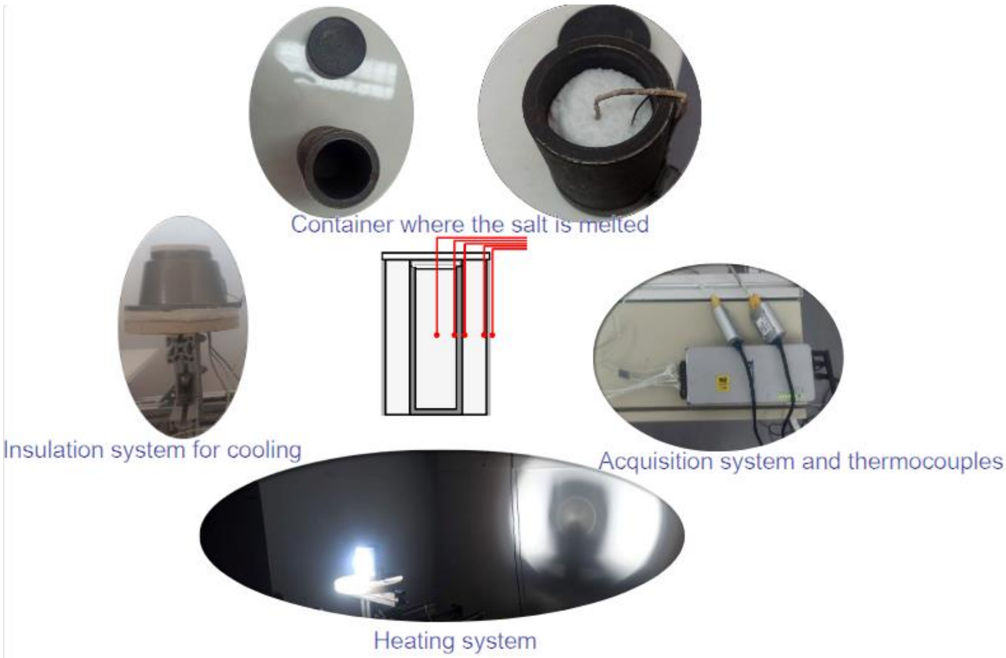

Figure 1: Diagram of the experimental setup for the thermal characterization of the heating and cooling of the solar salt sample.

The complete analytical model considers the system as a set of four coupled thermal components: the sample to be characterized C_1, R_1; the container tube C_2, R_2, exposed to irradiation from the simulator, which is the heat source during the heating stage.

The reference element or solid cylinder C_3, R_3, and the insulation system C_4, $\tilde{R}_4$, which interacts with the environment in the case of cooling, the equivalent thermal circuit for the analytical model can be seen in Figure 2.

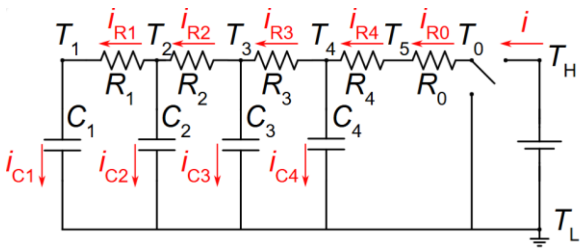

Figure 2: Equivalent thermal circuit for the experimental system based on the dT-History method.

The determination of C_1 and R_1 requires prior knowledge of the thermal parameters of the other components of the system C_2, R_2, C_3, R_3, C_4, $\tilde{R}_4$. Therefore, the experimental protocol was divided into three stages: characterization of the container tube with insulation, characterization of the reference element, and characterization of the salt sample.

For each characterization, representative equations based on the equivalent thermal circuit and electrical analogy are provided below:

$$\tau_{11}\dot{\theta}_1^* + \theta_1^* = \theta_2^* \quad \text{(eq. 1)}$$

$$\tau_{22}\dot{\theta}_2^* + \theta_2^* = \theta_3^* - \tau_{21}\dot{\theta}_1^* \quad \text{(eq. 2)}$$

$$\tilde{\tau}_{33}\dot{\theta}_3^* + \theta_3^* = -\left(\tilde{\tau}_{31}\dot{\theta}_1^* + \tilde{\tau}_{32}\dot{\theta}_2^*\right) \quad \text{(eq. 3)}$$

$$\tilde{\tau}_{44}\dot{\theta}_4^* + \theta_3^* = -\left(\tilde{\tau}_{41}\dot{\theta}_1^* + \tilde{\tau}_{42}\dot{\theta}_2^* + \tilde{\tau}_{43}\dot{\theta}_3^*\right) \qquad \text{(eq. 4)}$$

where $\tau_{ij}= R_i C_j$; $\tilde{\tau}_{44}=\tilde{R}_4 C_4$; $\tilde{R}_4=R_4+R_0$

2.1. Characterization of the Container Tube

To determine the C_2 and R_2 parameters of the container tube, a separate experiment was conducted. A stainless-steel tube was used in the setup for both the solar salt sample and the reference steel, with an inner diameter of 39.7 mm and a depth of 200.2 mm. For the measurement, K-type thermocouples were placed to measure T_2 (internal surface of the tube), T_3 (external surface of the tube), and T_4 (external surface of the insulator).

A solar simulator was used to heat the samples to the same temperature, and they were allowed to reach a steady state. Subsequently, cooling was performed from the maximum temperature reached.

Resistance R_2 was calculated using the laws of heat transfer in thermal circuit analogy for a hollow cylinder in a steady state. The characteristic time τ_{22} was obtained from the cooling process. Finally, C_2 was determined from $C_2= \tau_{22} / R_2$, where τ_{22} is obtained from the direct measurement of the internal and external temperatures of the steel container.

2.2. Characterization of the reference element

The characterization of the reference element used the same setup as the main experiment, but the solar salt sample was replaced by solid steel with a hole in the center to insert the thermocouple. The temperatures T_1, in the center of the solid steel, T_2 at the container-solid steel interface, and T_3 on the outer surface of the container were measured.

To obtain the characteristic reference time $\tilde{\tau}_{44}$ of the reference element, T_1 representing the center and T_2 representing the exterior were measured. The result of the experiment allows $\tilde{R}_4$ and C_4 to be solved.

2.3. Main Experiment Characterization of Solar Salt (60% $NaNO_3$ and 40% KNO_3)

Once the components of the calorimeter had been characterized, the main experiment was carried out using 78 g of $NaNO_3$ (99.5% purity) and 52 g of KNO_3 (99.28% purity) were used, which in terms of mass fraction represent 60% and 40% respectively of the eutectic mixture of solar salt, with 130 g of this contained in the stainless-steel tube.

The container-sample assembly was heated by the incidence of 4207.33 W m^{-2} irradiance from the solar simulator, which acts as a homogeneous heat source at T_H. Six K-type thermocouples were used: T_1 positioned in the center of the salt sample, T_2 located on the inner surface of the container, T_3 on the outer surface of the container, and the other three between the inner and outer insulation layers and the ambient temperature.

Heating was applied from 25°C to 545°C, followed by a cooling ramp. Temperature data were recorded every second (1 Hz) using an NI CDAQ-9191 data acquisition system and LabVIEW.

With the parameters C_2, R_2, C_3, R_3, $\tilde{R}_4$, C_4 known, and the experimental T-t curves T_1, T_3, T_4, the differential equations of the system were solved to obtain C_1, cp, and R_1 of the solar salt sample.

3. Results

Following the methodological protocol, the results are presented in two stages: the characterization of the calorimeter components and the uncertainty analysis.

3.1. Characterization of Calorimeter Components

Determining the properties of sample C_1, R_1 requires prior knowledge of the parameters of tube C_2, R_2, and reference material C_3, R_3. Solving the equations requires the temporal derivatives of the temperatures at the connection nodes between the surfaces. The temperature data measured every second, which is discrete in nature, is reworked to translate the equations into their finite difference form, and through them we calculate the time derivatives.

The thermal history curves for the heating and cooling of the 60% $NaNO_3$ and 40% KNO_3 sample are shown in the Figures, respectively.

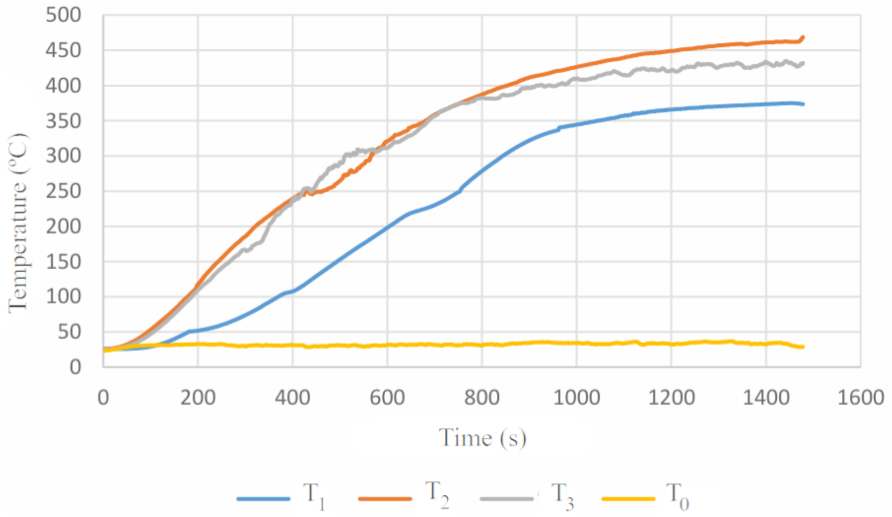

Figure 3: Thermal history curves of the experimental setup during heating.

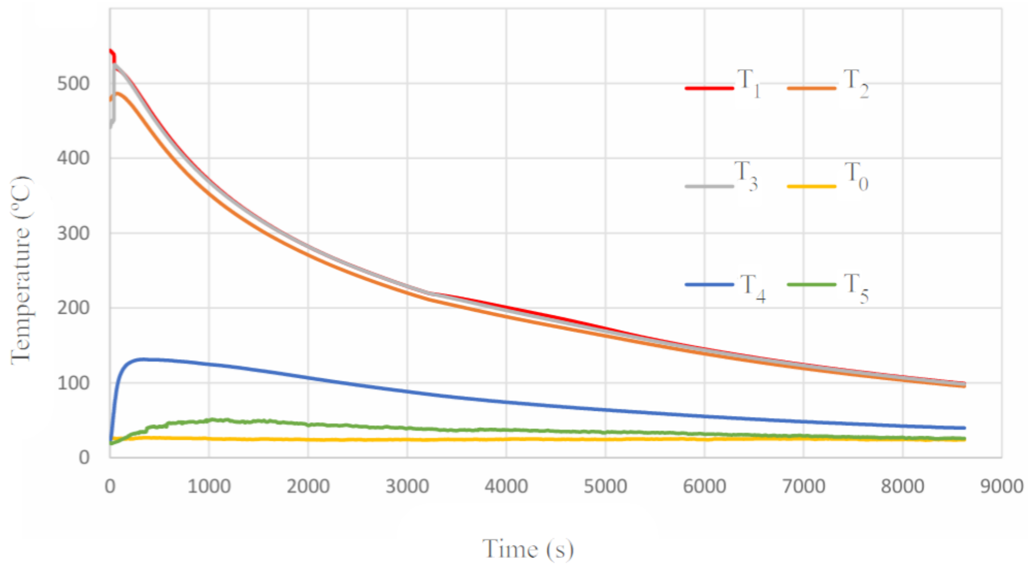

Figure 4: Thermal history curves of the experimental setup during cooling.

The results in the figure show two clear peaks corresponding to phase transitions:

1. Solid-Solid Transition: An interval of T_S=100 °C to T_L=115 °C was identified, with a maximum T_E peak at 108 °C.
2. Solid-Liquid Transition (Melting): An interval of T_S = 217 °C to T_L = 230 °C was identified, with a maximum T_E peak at 225 °C.

Figure 5 shows the specific heat-temperature curve c_{Pl} of cooling, showing the thermal hysteresis shift caused by subcooling.

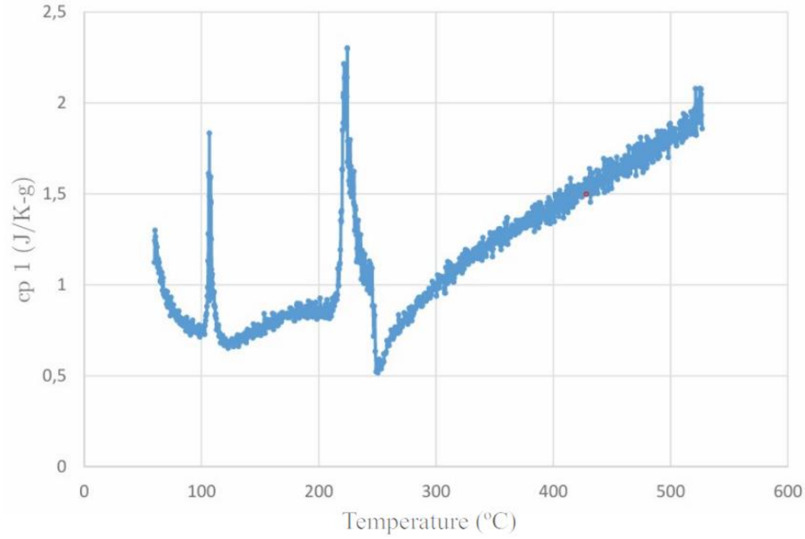

Figure 5: Specific heat curve obtained through modeling using the dT-History method, clearly showing the phase transition that occurs in the solar salt sample.

3.2. Uncertainty and Repeatability Analysis

Three identical experimental runs were performed to evaluate the repeatability of the method. The coefficient of variation (CV) was calculated as a function of temperature. The results show a CV of less than 1% in the sensible heat regions, increasing to a maximum of 3.2% only during the solid-solid phase transition.

The uncertainty of the c_{P1} calculation was evaluated using the coefficient of variation method on a moving average. The results indicate that the measurement uncertainty remains below 10% in the sensible heat zones, increasing significantly, as expected, at the phase transition peaks.

4. Conclusions

This study demonstrated the successful application of the dT-History method for the high-temperature calorimetric characterization of solar salt, composed of 60% by weight of NaNO3 (99.5% purity) and 40% by weight KNO3 (99.28% purity), validating the experimental protocol as a viable and economical substitute for standard calorimetry techniques.

The findings confirm that, while the specific heat curves cp obtained are qualitatively consistent with DSC reference data (Bonk and Bauer, 2022), our method captures a higher level of detail in the dynamics of the process, particularly the effect of the heat rate of change dT/dt.

Crucially, a consistent shift in phase transition temperatures (solid-solid and melting) was observed compared to the literature. We postulate that this discrepancy is not an error but reflects the actual thermal behavior of the material, a phenomenon that the large sample volume of our method can capture, unlike the micrograms analyzed in DSC.

The reliability of the protocol was confirmed by repeatability analysis, showing a coefficient of variation of less than 1% in the heat-sensitive zones and an overall measurement uncertainty of 5-10% outside the transitions. In addition, the method effectively quantified dynamic phenomena such as thermal hysteresis and subcooling during the cooling cycle.

It is concluded that the dT-History method is an accessible and scalable characterization tool. Its fundamental advantage lies in its ability to incorporate the temporal dependence of heat, allowing for a calculation of energy availability, not just its quantity. This level of detail is essential for accurate modeling and industrial design of future storage systems in CSP plants.

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