Sodium nitrate thermal behavior in latent heat thermal energy storage: A study of the impact of sodium nitrite on melting temperature and enthalpy

Adrien Lomonaco, Didier Haillot, Eric Pernot, Erwin Franquet, Jean-Pierre Bédécarrats *

Univ. Pau & Pays Adour – EA1932 – LaTEP – Laboratoire de Thermique Energétique et Procédés, Rue Jules Ferry, BP7511, PAU F-64075, France

A B S T R A C T

Using direct steam generation in concentrated solar power plant leads to the development of new storage systems, which may include a latent heat thermal energy storage module. With this module, the behavior of the storage system matches the thermal behavior of the water used as heat transfer fluid. Sodium nitrate, which is already used in such lab-scale systems, is able to fulfill the conditions to assume the role of phase change material to store thermal energy. However, this material may evolve during its lifetime, either due to thermal decomposition or by corrosion phenomena, both leading to the reduction of nitrates to nitrites. Such evolution has been reported for the so-called "solar-salt" ($NaNO_3$–KNO_3 60:40 wt%), driving to the reduction of the melting temperature and latent heat. It is thus important to study the evolution of these properties in the case of sodium nitrate. The work proposed here aims to characterize sodium nitrate–nitrite mixture by differential scanning calorimetry for comparison with pure sodium nitrate (laboratory grade and industrial grade). Since the considered compounds are not at the eutectic composition, their melting does not occur at a fixed and single temperature. Thus, a calorimetric method using isothermal steps has been used in order to determine the evolution of involved energy during the melting of samples versus temperature for each sample. The results show the spreading of the melting over a range of temperature and the shifting of the liquidus to lower temperature when the sodium nitrite part increases. Moreover, a decrease in latent heat up to nearly 15% was observed.

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1. Introduction

The rise in energy generation by direct steam generation (DSG) in concentrated solar power (CSP) plant systems requires new design for thermal energy storage in order to decrease the production cost. Because up to 70% of the involved energy is transferred during the phase change of the water (which is the heat transfer fluid), it has been demonstrated that using a latent heat storage unit, combined with two sensible heat storage elements (low and high temperature) was a relevant solution for the DSG technology [1]. In this case the storage systems can follow the thermal behavior of the heat transfer fluid.

Among the various phase change materials (PCM), sodium nitrate $NaNO_3$ seems to be a good material for the latent heat storage of DSG systems. Its melting temperature corresponds to the range of running of the systems and its latent heat is relatively

high (178 $J\,g^{-1}$) [2]. Moreover it is a single component with a high commercial availability and is easier to manufacture than an eutectic salt such as for example the so-called "solar salt" ($NaNO_3$–KNO_3 60:40 wt%). However, it has been showed that $NaNO_3$ may change during its lifetime, either due to thermal degradation [3] or by corrosion of metallic materials in contact with the PCM [4,5], by the reduction of nitrates in nitrites.

Indeed, in the case of solar salt mixture for sensible heat storage, Kruizenga et al. [6] have highlighted an evolution to a mixture with a nitrite proportion up to 6 mol% (m%) at high temperature (680 °C), leading to the shifting of the melting point to lower temperatures and the reduction of the latent heat. If such effects are not limiting in the case of sensible heat storage, they would not be acceptable for a phase change material in a latent heat thermal energy storage system.

In the same way, Bauer et al. [3] compared thermograms for pure $NaNO_3$ and a $NaNO_3$–$NaNO_2$ (96–4 m%) mixture obtained by differential scanning calorimetry (DSC). They concluded in a reduction of the liquidus temperature by 6 K, showing that adding

Nomenclature			**Subscripts**		
B	baseline heat flow, (mW)		L	liquidus	
hf	heat flow, (mW)		M	melting	
L	enthalpy, ($J\,g^{-1}$)		onset	onset (temperature)	
t	time, (s)		S	solidus	
T	temperature, (°C)				
X	molar fraction				

sodium nitrite to sodium nitrate alters its thermal behavior. Unfortunately no calibration was used to perform these characterizations, and it is thus impossible to measure the effect of the sodium nitrite on latent heat.

The work presented here aims to complete the previously cited work by studying the impact of different molar fraction of sodium nitrite in sodium nitrate on thermal properties of the PCM. Thermal characterizations by DSC of $NaNO_3$–$NaNO_2$ compounds (2, 4 and 6 m%) have been performed according to "dynamic mode" and "step method". The evolution of liquidus temperature and latent heat with the growing proportion of sodium nitrite will be determined.

2. Materials and methods

2.1. Materials

Sodium nitrate–nitrite mixtures were prepared under nitrogen atmosphere to avoid that hygroscopicity of this material disrupts weighing. Sodium nitrate is provided by Acros Organics (purity 99.6%) and the sodium nitrite by Sigma Aldrich (purity 99.5%). Three different $NaNO_3$–$NaNO_2$ compositions were prepared: 98:2 m%, 96:4 m% and 94:6 m%. In order to ensure the accuracy of their preparation, these compounds were verified by ion chromatography and also by a spectrophotometric quantitative analysis (Griess method [7] adapted to our conditions). Finally industrial sodium nitrate – refined grade (purity 99.5%) provided by SQM was also characterized.

2.2. Methods

The determination of thermal properties of each compound was done using DSC. According to Höhne et al. [8], it consists in the measurement of the differences in the heat flow rate between a material and a reference sample while they are both subjected to the same controlled temperature program, a so-called ramp [9]. The differential heat flow is recorded as a thermogram, function of time and temperature. It is then possible to access to transition temperature or involved energy by processing this thermogram.

There is basically two kinds of Differential Scanning Calorimeters (DSC):

– Heat-flow DSC: the measured signal is proportional to the temperature difference between the sample and the reference, which are both in the same furnace. The heat flow rate is then accessible through an energy calibration, giving the relation between temperature difference and the energy involved [8,9].
– Power compensation DSC: sample and reference crucibles are in separated furnaces, which are both compelled to the same ramp. The resulting difference in heat flow between the furnaces is electrically compensated. The measured signal is proportional to this electrical power. The heat flow rate is determined by using an energy calibration [8].

In addition, there are different common techniques to characterize materials in DSC. Two of them, used in this work, are described below in Sections 2.2.2 and 2.2.3. These two modes differ in the shape of the ramp, using respectively constant and variable heating/cooling rates.

This work uses these two modes together for each sample, according to the following: dynamic characterizations have been made before and after each isothermal steps characterization, in the same run.

2.2.1. Experimental conditions

All characterizations were done with a power compensation calorimeter: Perkin Elmer Pyris Diamond DSC, associated with a three stages refrigerating machine. For each composition, three samples A, B and C were tested in 20 μL sealed aluminum pans, under nitrogen gas flow (30 mL min^{-1}). Each sample was weighted with a XP26 scale from Mettler-Toledo (accuracy $\pm$ 0.002 mg). All of the sample masses are detailed in Table 1.

The A and B samples masses have been taken close to each other, while the C sample mass has been taken voluntary different to ensure the independence of the result from the sample mass.

Before analysis, a necessary calibration in temperature and energy [10] was done for a temperature ramp rate of 5 K min^{-1} with mercury (purity 99.999%, $T_M = -38.834$ °C, $L_M = 11.469\,J\,g^{-1}$), indium (purity 99.99%, $T_M = 156.598$ °C, $L_M = 28.5\,J\,g^{-1}$) and tin (purity 99.9985%, $T_M = 231.928$ °C, $L_M = 60.22\,J\,g^{-1}$).

2.2.2. Dynamic mode

Dynamic method is the most classical method used for DSC characterization [9]. It consists in a temperature ramp with constant heating or cooling rates (typically in the range of 2–20 K min^{-1} [9,10]) with optional isothermal phases.

To illustrate this mode, an example of thermogram obtained with pure $NaNO_3$ is presented in Fig. 1.

In this thermogram, four phases can be noticed:

– Isotherm phase at low temperature (210 °C) during 5 min (1).
– Heating to high temperature (320 °C) at a constant rate of 5 K min^{-1} (2).
– Isotherm phase at high temperature (320 °C) during 5 min (3).
– Cooling to low temperature (210 °C) at a constant rate of 5 K min^{-1} (4).

During these phases, several thermal phenomena can be observed:

Table 1
Samples weight in mg (acc. $\pm$ 0.004 mg). The mixtures correspond to different $NaNO_3$–$NaNO_2$ compounds. The percentage is the molar fraction of $NaNO_2$.

Sample	NaNO₃ (ACROS) (mg)	NaNO₃ (SQM) (mg)	Mixture 2 m% (mg)	Mixture 4 m% (mg)	Mixture 6 m% (mg)
A	10.812	14.848	12.902	7.304	15.026
B	10.654	15.342	15.596	7.720	14.072
C	15.876	10.678	17.334	19.030	8.996