Thermal characterization of sodium nitrate – sodium nitrite compounds for thermal storage applications.

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Abstract:

Thermal energy storage seems to be the most promising way to improve concentrated solar power plant efficiency. In the specific case of direct steam generation, where the working fluid changes of phase (liquid – vapor), a latent thermal energy storage system, fitting the working fluid behavior, appears to be the most suitable.
The sodium nitrate is a phase change material already used for latent thermal energy storage to store a high amount of energy at a fixed temperature: its melting temperature. However the fixed and single nature of this temperature is a direct consequence of the purity of the phase change material. Two steps are critical for this parameter: the manufacturing of the phase change material, where the purity depends on process, and the "life" of this material in industrial conditions where it may be altered through many processes, like thermal degradation or corrosion of metallic materials in contact with the phase change material. These mechanisms lead to the production of impurities, mainly sodium nitrite. It then becomes essential to determine the influence of this impurity on the thermal behavior of the sodium nitrate.
That is why the thermal characterization of pure $NaNO_3$ and of $NaNO_3$-$NaNO_2$ compounds has been done using the differential scanning calorimetry. Since the considered compounds are not at the eutectic composition, their melting does not occur at a fixed and single temperature. A calorimetric method using isothermal steps has been chosen in order to determine the involved energy during the melting of samples versus temperature. Pure sodium nitrate (laboratory grade) and different compounds of sodium nitrate – sodium nitrite (2%, 4% and 6% molar fraction), were experimentally studied. This work confirmed the spreading of the melting over a range of temperature and the shifting of the melting peak to lower temperature when the sodium nitrite part increases. A decrease in latent heat in a range of 12-14 % for the worst case, i.e. the 6 % molar compounds, was determined.

Keywords:

Differential scanning calorimetry, Isothermal Step Method, Latent thermal energy storage, $NaNO_3$+$NaNO_2$ compounds, Phase Change Materials.

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 working 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]. Indeed, in this case, the storage can follow the working fluid thermal behavior.

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. The melting temperature corresponds to the range of running of the systems (275-325 °C) and the 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 the PCM [4].

One of the likely consequences of this evolution, in the considered temperature range – *i.e.* near the phase change temperature, is the reduction of the sodium nitrate ion in sodium nitrite ion by corrosion mechanisms [5]. Bauer *et al.*, 2012 showed that adding sodium nitrite to sodium nitrate alters its thermal behavior [3].

The work presented here concerns the thermal characterization by differential scanning calorimetry, named hereinafter DSC, of sodium nitrate-nitrite compounds with an aim to assess the impact of the PCM composition on its thermal properties.

2. Materials and methodology

2.1. Materials

Sodium nitrate-nitrite compounds 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 by a spectrophotometric quantitative analysis: Griess test adapted to our conditions. Finally industrial sodium nitrate – refined grade (purity 99.5 %) provided by SQM was also characterized.

2.2. Methodology

The determination of thermal properties of each compound was done using DSC. According to Höhne *et al.* [6], 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* [7]. 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, as explained in *2.2.4. Results analysis.*

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 [6,7].
- 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. As heat-flux DSC, an energy calibration allows to access to the heat flow rate [6].

In addition to that, there are different common techniques to characterize materials in DSC. Two of them, used in this work, are described below in paragraphs *2.2.2. Dynamic mode* and *2.2.3. Isothermal step mode*. These two modes differ in the shape of the *ramp*, using respectively constant and variable heating/cooling rate.

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 refrigerating machine. For each composition, three samples A, B and C were tested in 20 µL sealed aluminum pans, under nitrogen gas flow (around 30 $mL.min^{-1}$). Each sample

was weighted with a XP26 scale from Mettler-Toledo (accuracy ± 0.002 mg). All of the sample masses are detailed in Table 1.

Table 1. Samples Weight in mg (acc. ± 0.002 mg)

Sample	*$NaNO_3$ (ACROS)*	*$NaNO_3$ (SQM)*	*Mixture 2%*	*Mixture 4%*	*Mixture 6%*
A	10.812 mg	14.848 mg	12.902 mg	7.304 mg	15.026 mg
B	10.654 mg	15.342 mg	15.596 mg	7.720 mg	14.072 mg
C	15.876 mg	10.678 mg	17.334 mg	19.030 mg	8.996 mg

The A and B samples masses have been taken close 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 [8] was done for a speed of 5°C.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 [7]. It consists in a temperature ramp with constant heating or cooling rate (typically in the range of 2 K.min^{-1} to 20 K.min^{-1} [7,8]) with optional isothermal phases.

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

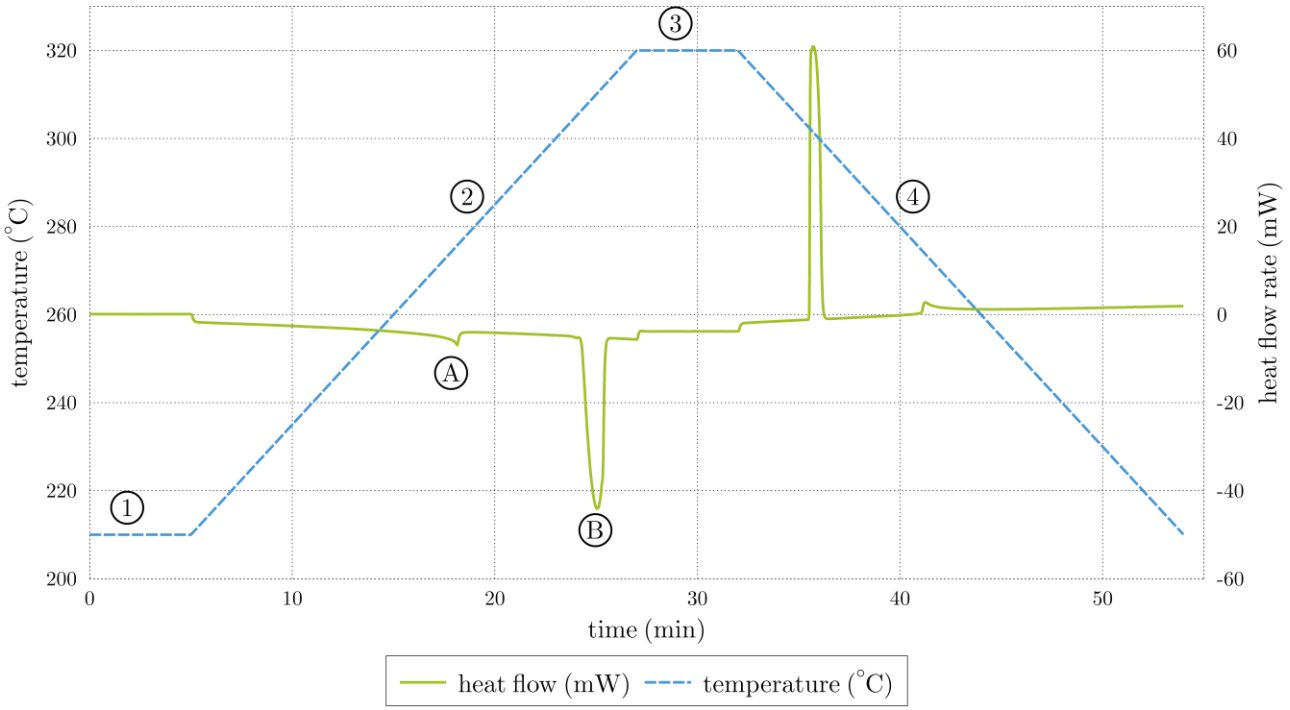


Fig. 1 – Sodium nitrate thermogram obtained by dynamic mode protocol

In this thermogram, four phases can be noticed:

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

During these phases, several thermal phenomena can be observed:

- The first (A) endothermic peak is related the known solid-solid transformation [3,9].
- The second one (B) corresponds to the melting [3] of the sodium nitrate.

- The third and fourth peaks are exothermic and respectively accords to the crystallization and the inverse solid-solid transformation.

2.2.3. Isothermal step mode

The isothermal step method consists in heating the sample and the reference stepwise in a temperature interval. The heat flow goes back to baseline between each step, ensuring the thermal equilibrium in each furnace and avoiding thermal gradient in sample. This procedure allows measuring the energy involved for each relevant step. This method is quite criticized because of the longest time of experimentation than dynamic mode, and the time consuming treatments of results [10]. In addition, the resolution in temperature depends on the size of the step. However Richardson [8], Castellón *et al.* [11] and Günther *et al.* [7] have shown that this mode seems to be more precise on some aspects than dynamic mode, avoiding thermal lag mainly due to thermal gradient in the sample. Another advantage is that the uncertainty in temperature is confined in the step size. Finally, this method is able to provide a confident enthalpy versus temperature curve, which is more useful than only two numeric values (onset temperature and involved energy) to define a phase transition [7], mainly in the case of random compounds of phase change materials as will be discussed later.

In this work the isothermal step method is applied both during heating and cooling. The "height" of the step is fixed and equals to 1°C throughout the experiment, implying 110 steps between low and high temperatures (respectively 210 and 320°C). The heating/cooling rate at each step is equal to 5°C.min^{-1}. An example of isothermal step mode performed on a pure sodium nitrate sample is showed in Fig 2.

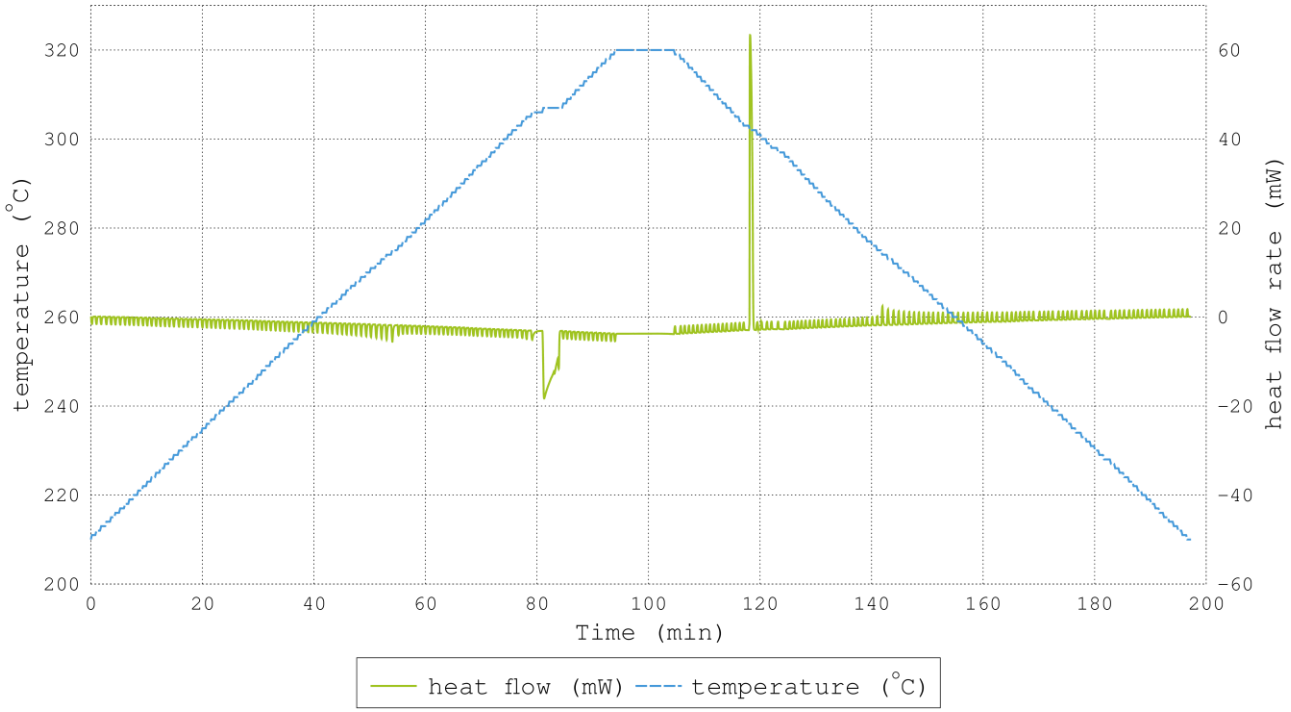


Fig. 2 – Sodium nitrate thermogram obtained by step mode protocol

In Fig. 2, we can observed that each step, during the heating (or cooling) sequence, gives rise to an endothermic (or exothermic) heat flow peak. These peaks are related to the amount of energy that must be supplied to the sample so that it follows the temperature program. So when the sample reaches the temperature of the phase change, the energy required is high, hence the highest peak is in this location.

It can also be seen that the "length" of each step (their duration) is not fixed. Indeed, it is the calorimeter command software which starts the beginning of the following step when heat flow is stabilized. This function decreases significantly the experiments duration.

2.2.4. Results analysis

Results analysis and treatment differ in dynamic and in isothermal step mode.

In dynamic mode, as illustrated in Fig. 3, the latent heat is obtained by integration of the endothermic signal occurring at the phase change during the heating sequence. The representative temperature of the transformation is obtained from the onset temperature determination, in accordance with the calibration.

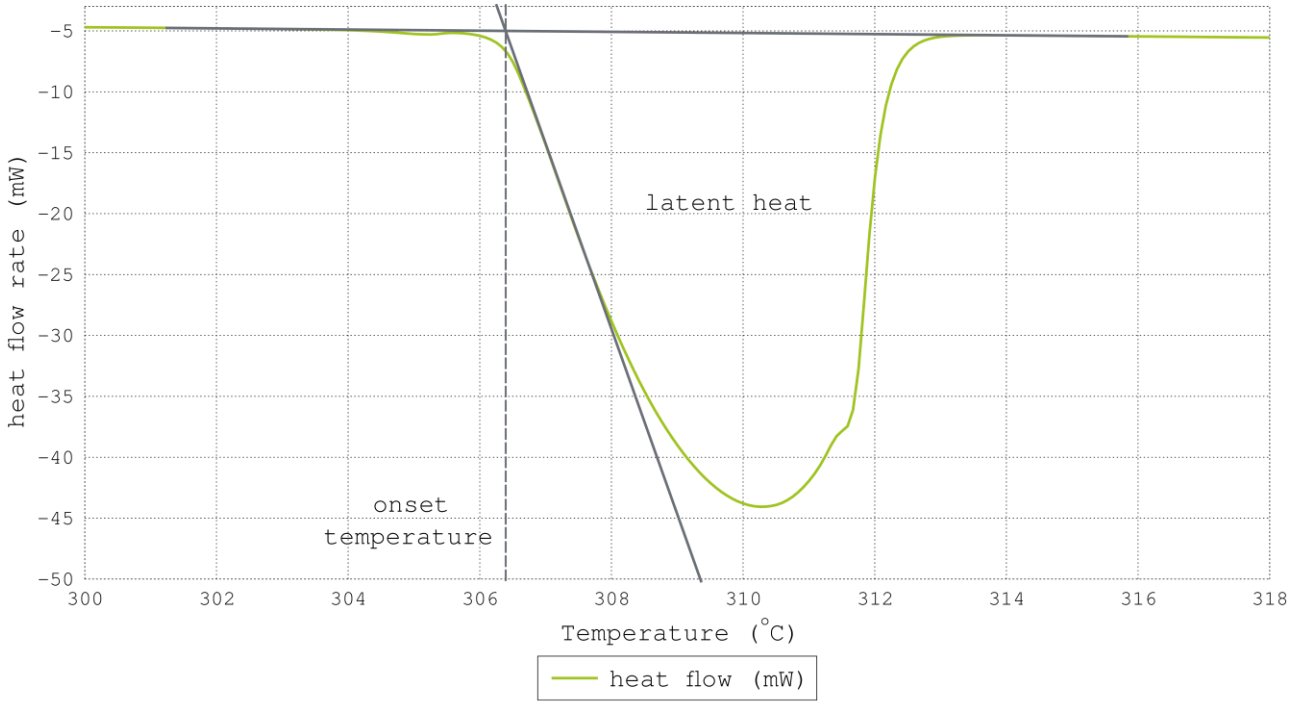


Fig. 3 – Melting temperature and latent heat determination in dynamic mode and for pure substance

However, if this value makes sense for the analysis of the melting temperature of a single sample (pure substance type, i.e. pure sodium nitrate from ACROS), it is not the same concerning the random concentration sodium nitrate/nitrite compounds, which present a progressive fusion. Physical signification of onset temperature is here most questionable, mainly because of inherent inertia effects in dynamic mode. Günther *et al*. [7] discussed the classical approach based on the two discrete values of melting temperature and latent heat to define a material, saying that a more useful way is to consider the function enthalpy versus temperature.

The isothermal step mode allows us to distinguish more distinctly the liquidus from the solidus temperature, the difference between these two temperatures forming the representative temperature range of the sample where the whole latent heat is exchanged. In addition, this mode allows us determining the enthalpy function versus temperature, meaningful in the case of non-pure substance, like random concentration nitrate/nitrite compounds.

Fig. 4 below presents an automatic processing tool developed in VBA on Excel to process these results.

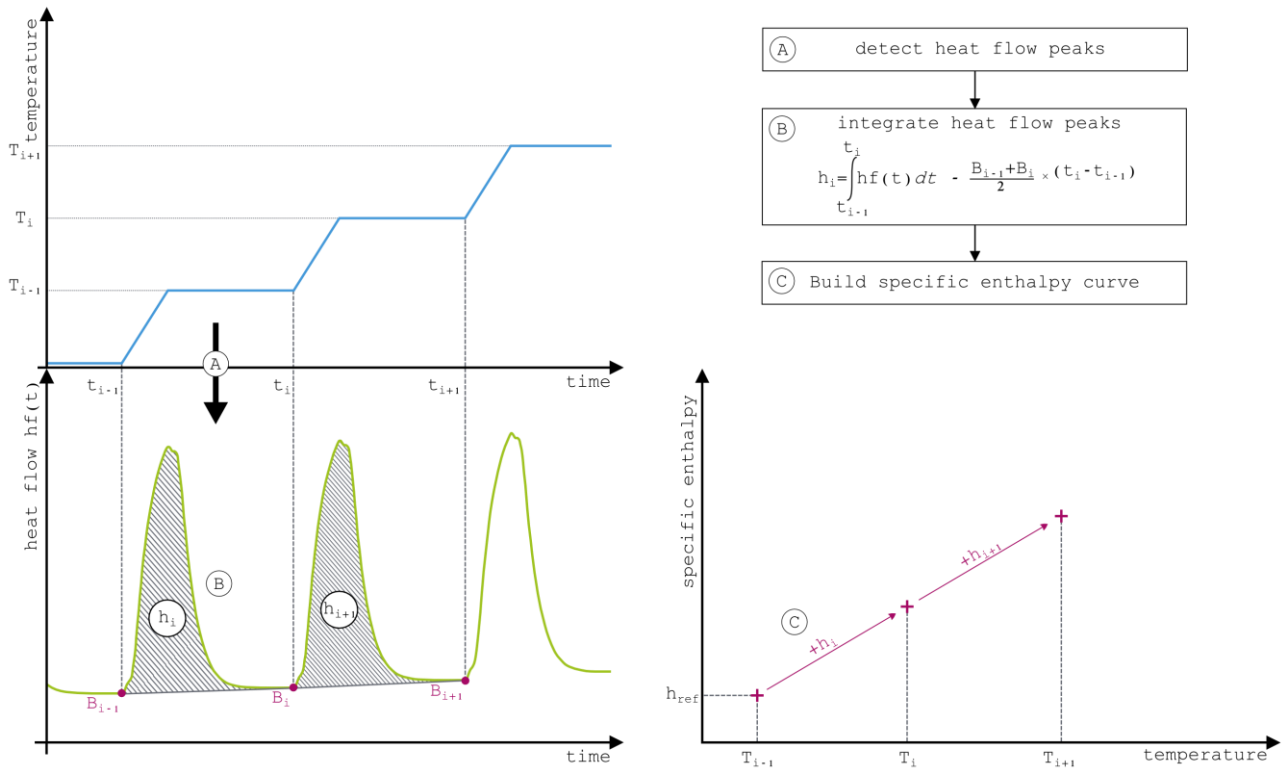


Fig. 4 – Processing tool illustration

This code allows us to detect (A) and integrate (B) each small peak in order to determine the involved energy for relevant steps. It then becomes possible to access to the sample enthalpy versus temperature by adding (C) successively the energy associated to each step starting from a reference enthalpy taken at a reference temperature. The program is able to determine the enthalpy versus temperature for heating phases as well as for cooling phases.

3. Results and discussions

For the sake of readability, only the arithmetical average value of results obtained for each material is presented. This average value is realized with six thermograms obtained for each material (3 samples, 2 experiments per sample).

Several observation can be made about Fig. 5. First, the onset temperature was measured only for pure substance namely ACROS sodium nitrate (T_{onset} = 306.6°C) and the SQM sodium nitrate (T_{onset} = 306°C). These values are in agreement with literature [3].

Then, these results show clearly an evolution of the thermal behavior of material while the proportion of sodium nitrite increases. First of all, the increase in sodium nitrite proportion leads to a shift of the melting peak to lower temperatures. In addition, we note that the higher the concentration in sodium nitrite is, the wider the peak is, phenomenon that reflects the emergence of a progressive fusion in a temperature range increasingly large.

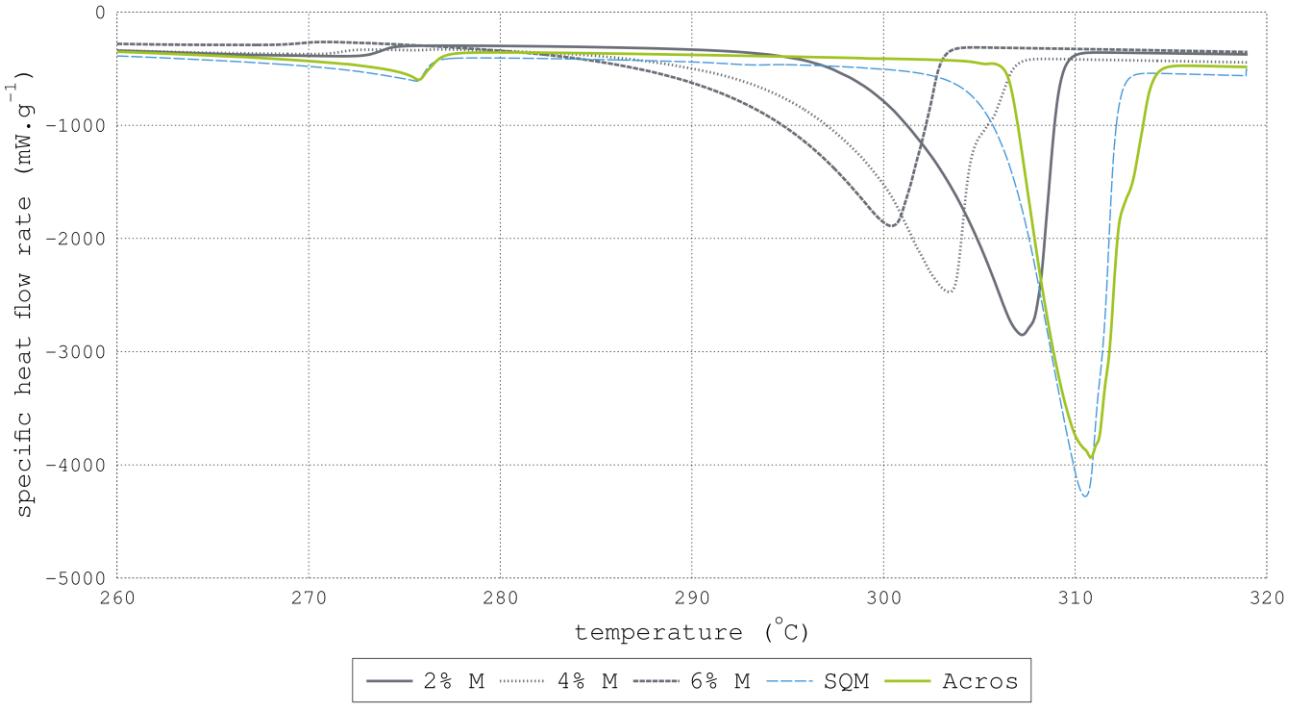


Fig. 5 – Average specific heat flow versus temperature for each material

It can also be noticed that concerning the sodium nitrate provided by SQM, results seem to show the behavior of a compounds with a slightly sodium nitrite proportion, contrary to the sodium nitrate provided by ACROS although the announced purity was very close (respectively 99.5% and 99.6%). The impurity composition may explain this difference: the presence of a small amount of sodium nitrite (0.02% depending on the certificate of analysis) in the material of SQM causes this slight drift of thermal behavior, while the material from ACROS is completely free of nitrite.

At last the energy involved at the melting of each sample has been determined and gathered in Table 2. For each material, we calculated the arithmetic average value and the standard deviation of measured latent heat.

Table 2. Synthesis of measured latent heat ($J.g^{-1}$) for characterized materials

	$NaNO_3$ (ACROS)		*$NaNO_3$ (SQM)*		*Mixture 2%*		*Mixture 4%*		*Mixture 6%*	
	1^{rst} cycle	*2^{nd} cycle*	*1^{rst} cycle*	*2^{nd} cycle*	*1^{rst} cycle*	*2^{nd} cycle*	*1^{rst} cycle*	*2^{nd} cycle*	*1^{rst} cycle*	*2^{nd} cycle*
A	176	177	174	174	162	161	159	158	155	148
B	177	177	173	173	163	161	159	156	152	146
C	178	177	173	173	161	161	164	-	153	146
Average value		**177**		**173.3**		**161.5**		**159.2**		**150**

These results show indubitably that the latent heat decreases with the increase in sodium nitrite proportion. So a drop of up to 15% of latent heat is observed when the sodium nitrite proportion reaches a concentration of 6% molar.

Results performed in isothermal step mode are gathered in Fig. 6 and confirm the observations made on the dynamic mode results.

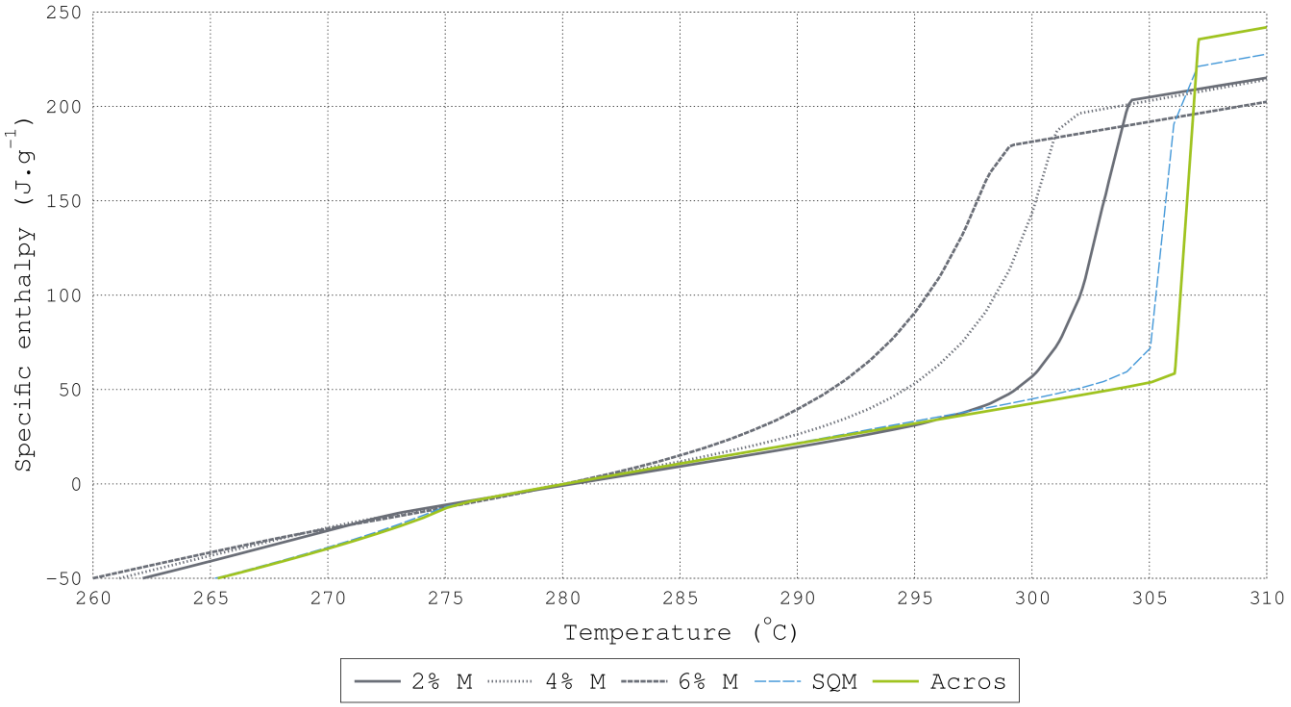


Fig. 6 – Average mass enthalpy versus temperature for each material (null enthalpy at 280°C)

In fact, we can easily notice the shifting of the melting temperature to lower temperatures when the concentration in sodium nitrite rises. In addition a spreading out of the enthalpy at the end of each melting can be noticed, resulting from the diminution of latent heat. Finally the softening slope corresponding to the fusion as the sodium nitrite proportion increases is a consequence of the progressive separation of solidus and liquidus temperature, according to the phase diagram of the literature [12].

Table 3 shows the synthesis of quantitative results from the exploitation of this data. It is important to highlight that the precision on measured temperature cannot exceed the step size (1°C). For example, when the temperature of the beginning of the melting is different from the melting end temperature for the laboratory grade sodium nitrate (ACROS), which is a pure substance, it should be interpreted as the melting takes place at a fixed temperature on the step where the low temperature is 306°C and the high temperature is 307°C. This restriction is inherent to the characterization program.

Table 3. Synthesis of latent heat ($J.g^{-1}$) and beginning (T_S, °C) and end (T_L, °C) temperature of the melting measured for each material

	$NaNO_3$ (ACROS)			***$NaNO_3$ (SQM)***			***Mixture 2%***			***Mixture 4%***			***Mixture 6%***		
	L_M	T_S	T_L	L_M	T_S	T_L	L_M	T_S	T_L	L_M	T_S	T_L	L_M	T_S	T_L
A	179	306	307	165	304	307	167	297	304	161	292	302	155	287	299
B	175	306	307	169	304	306	165	297	304	169	291	301	155	287	299
C	177	306	307	165	303	307	164	297	304	164	290	302	157	287	299
Av.	**177**			**166.3**			**165.3**			**164.6**			**155.6**		

Concerning the latent heat, the isothermal step mode result for pure $NaNO_3$ (ACROS) matches the dynamic mode result, according to the literature [3]. For the $NaNO_3$ (SQM), the latent heat is lower than the result of dynamic mode. For other results, latent heat values are globally larger than the ones obtained in dynamic mode, from around 5 $J.g^{-1}$. Globally it appears, on both results in dynamic and isothermal step mode, a drop of latent heat between the laboratory grade sodium nitrate (ACROS) and the 6 % molar fraction compounds.

The temperatures of the beginning of the melting decrease from 306 °C to 287 °C, representing a drop of nearly 20 °C between pure laboratory grade $NaNO_3$ and 6 % M compounds, while the temperatures of the end of melting decrease of 8 °C, from 307 °C to 299 °C. These values fit well with the phase diagram data available in literature, as shown in Fig. 7.

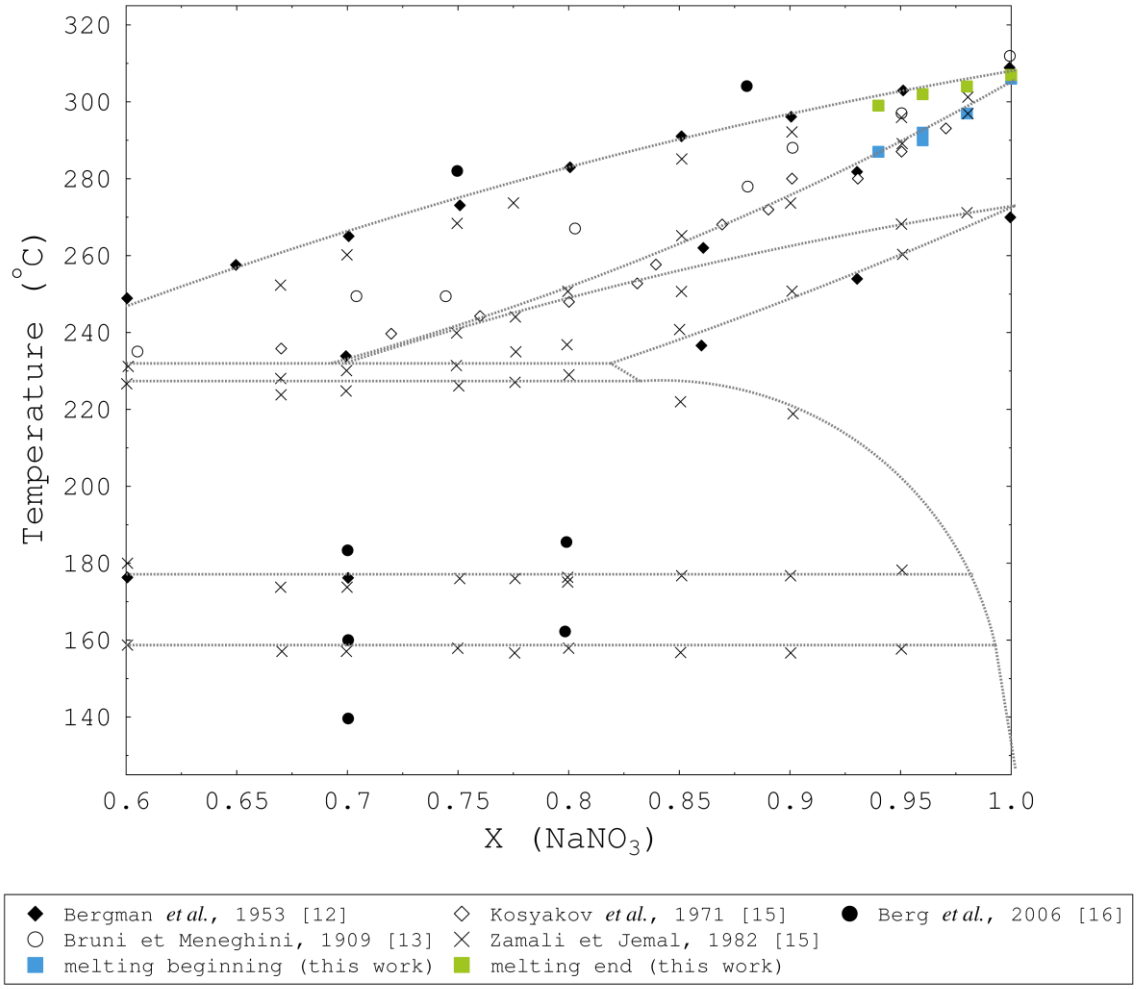


Fig. 7 – Sodium nitrate – sodium nitrite phase diagram adapted from [16]

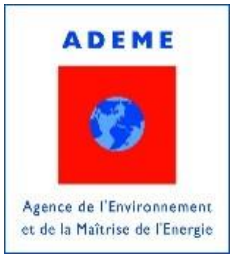
4. Conclusion

This work completes the previous literature results from Bauer et al. [3]. It confirmed the trend shown by these authors: the decreasing of the latent heat and the spreading of the melting over a temperature range when the sodium nitrite concentration raises. Characterizations presented here, add to these observations, quantitative information. Thus these results showed a decrease in latent heat in a range of 12-14 % for the worst case, i.e. the 6 % molar compounds. This work confirms the spreading of the melting over a range of temperature and the shifting of the melting peak to lower temperature when the sodium nitrite part increases, matching literature data [12-16]. In addition, by using the DSC experiments, we have been able to determine the enthalpy versus temperature. This information is very pertinent to be used in numerical models where the phase change material is used.

With an aim to use this PCM in a latent heat storage system, several consequences of these changes in the thermal behavior of the PCM are identified. Firstly, the reduction of the latent heat impacts directly the storage capacity, which decreases with the sodium nitrite part raise. Secondly the appearance of a progressive melting will modify the thermal exchange between the working fluid and the storage material. Finally the shifting of the melting to lower temperature will play on the storage and release temperature, which means a modification of all parameters of the thermodynamic cycle of the plant.

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Nomenclature

B baseline heat flow, (mW)

hf heat flow, (mW)

L enthalpy, ($J.g^{-1}$)

t temps, (s)

T temperature, (°C)

X molar fraction

Subscripts

L liquidus

M melting

onset onset (temperature)

S solidus

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