Binary Sodium/Lithium Nitrate Molten Salt Systems for Industrial Waste Heat of Medium Temperature

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Potential molten salts mixture

<table>
<thead>
<tr>
<th>PCMs</th>
<th>Melting temperature (°C)</th>
<th>Latent heat (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCl₂ – NaCl – KCl</td>
<td>203</td>
<td>*</td>
</tr>
<tr>
<td>NaOH – Na₂CO₃</td>
<td>210</td>
<td>*</td>
</tr>
<tr>
<td>KNO₃ (54%) – NaNO₃ (46%)</td>
<td>222</td>
<td>~100</td>
</tr>
<tr>
<td>NaNO₃ – NaNO₂</td>
<td>226 - 233</td>
<td>*</td>
</tr>
<tr>
<td>Ca(NO₃)₂ (45%) – NaNO₃ (55%)</td>
<td>230</td>
<td>~110</td>
</tr>
<tr>
<td>Ca(NO₂)₂ – NaNO₂</td>
<td>200 - 223</td>
<td>*</td>
</tr>
<tr>
<td>Ca(NO₂)₂ – LiNO₃</td>
<td>235</td>
<td>*</td>
</tr>
<tr>
<td>LiNO₃ (12%) – NaNO₃ (18%) – KNO₃ (70%)</td>
<td>200</td>
<td>*</td>
</tr>
<tr>
<td>LiNO₃ (57%) – NaNO₃ (43%)</td>
<td>193</td>
<td>248</td>
</tr>
<tr>
<td>LiNO₃ (49%) – NaNO₃ (51%)</td>
<td>194</td>
<td>265</td>
</tr>
<tr>
<td>LiNO₃ (87%) – NaCl (13%)</td>
<td>208</td>
<td>360</td>
</tr>
<tr>
<td>LiNO₃ (45%) – NaNO₃ (47%) – Sr(NO₃)₂ (8%)</td>
<td>200</td>
<td>199</td>
</tr>
</tbody>
</table>

*: unknown

Two binary mixtures, sample 1, NaNO₃ – LiNO₃ (51% – 49%) and sample 2, NaNO₃ – LiNO₃ (43% – 57%), were studied to find their potential of being a suitable PCM for latent heat storage in industrial waste heat recovery.

1. An appropriate melting temperature (just under 200 °C)
2. A relatively high latent heat (over 240 kJ/kg)
Thermal properties and repeatability

Figure 1 Effects of heating/cooling rate on phase change process, NaNO$_3$ – LiNO$_3$ (51% – 49%)

1. A larger effect on onset solidification points than onset melting points
2. Onset melting points were almost the same but a little lower with a higher heating/cooling rate
3. A lower heating/cooling rate resulted in a smoother phase change curve and a narrow phase change transition range.
Thermal properties and repeatability

Same effects were found on sample 2 as sample 1.

Figure 2 Effects of heating/cooling rate on phase change process, NaNO$_3$ – LiNO$_3$ (43% – 57%)
Thermal properties and repeatability

The samples were tested in DSC between 50 °C and 300 °C by a heating/cooling rate of 10 °C/min for 51 times. All the results exclude first cycle. The deviations of the melting temperatures and latent heat were calculated from:

\[ T_D = \frac{T_n - T_{\text{average}}}{T_{\text{average}}} \quad 1 \leq n \leq 50; \quad L_D = \frac{L_n - L_{\text{average}}}{L_{\text{average}}} \quad 1 \leq n \leq 50 \]

Figure 3: Deviation of the melting temperatures from the average value in the test

The average melting temperatures of the binary systems were **193.87 °C** (194 °C in the reference) and **193.27 °C** (193 °C in existing references) respectively.
Thermal properties and repeatability

(a) NaNO$_3$ – LiNO$_3$ (51% – 49%)

(b) NaNO$_3$ – LiNO$_3$ (43% – 57%)

Figure 4: Deviation of the latent heat from the average value in the test

The average latent heat of the samples was 261.7 kJ/kg (265 kJ/kg in the reference) and 244.1 kJ/kg (248 kJ/kg in existing references).

NaNO$_3$ – LiNO$_3$ (51% – 49%) showed a better repeatability. For NaNO$_3$ – LiNO$_3$ (43% – 57%), the deviation of melting temperatures was within ± 0.5% and the deviation of latent heat was within ± 4%, which is still considered to be good as a PCM.
Thermal stability

The test was carried out in TGA between 120 °C and 300 °C by a heating/cooling rate of 15 °C/min for 50 times, excluding first cycle.

(a) NaNO$_3$ – LiNO$_3$ (51% – 49%)
(b) NaNO$_3$ – LiNO$_3$ (43% – 57%)

Figure 5: Weight loss of the binary systems for 51 heating/cooling cycles between 120 °C and 300 °C

In first cycle, the huge weight losses were attributed to the loss of moisture. In the subsequent 50 thermal cycles, the weight losses were negligible comparing with the first cycle.
Thermal stability

(a) NaNO$_3$–LiNO$_3$ (51% – 49%)
(b) NaNO$_3$–LiNO$_3$ (43% – 57%)

Figure 6: Weight loss percentage of the binary systems for each cycle excluding cycle one

The binary system of NaNO$_3$–LiNO$_3$ (51% – 49%) showed a better thermal stability than NaNO$_3$–LiNO$_3$ (43% – 57%). The binary system with less LiNO$_3$ had a better thermal stability. After 50 cycles, the total weight losses of the binary systems were 0.28% for NaNO$_3$–LiNO$_3$ (51% – 49%) and 0.33% for NaNO$_3$–LiNO$_3$ (43% – 57%) respectively, both of which are considered to be very good.
Chemical stability

The mixtures were kept isothermal at 120 °C for 10 minutes to evaporate the moisture as much as possible. Then, they were heated by a heating rate of 15 °C/min and kept isothermal at each constant temperature, such as 250 °C, 300 °C, 350 °C, 400 °C, 450 °C and 500 °C, for 3 hours to get their weight losses.

Figure 7: Weight loss of the binary systems for long-term thermal stability experiment

(a) NaNO₃ – LiNO₃ (51% – 49%)
(b) NaNO₃ – LiNO₃ (43% – 57%)
There were less weight losses for both binary systems below 400 °C.

At 500 °C, there were large increasing weight losses for both mixtures. The binary systems had been decomposing at 500 °C.

Generally speaking, NaNO₃ – LiNO₃ (51% – 49%) showed a better chemical stability than NaNO₃ – LiNO₃ (43% – 57%).

The binary systems both worked well below 450 °C but best below 400 °C, which meets the requirement of the medium temperature industrial waste heat storage.

Table 2 Weight loss percentage of the two binary systems at each isothermal temperature

<table>
<thead>
<tr>
<th></th>
<th>250 °C</th>
<th>300 °C</th>
<th>350 °C</th>
<th>400 °C</th>
<th>450 °C</th>
<th>500 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO₃ – LiNO₃ (51% – 49%)</td>
<td>0.015%</td>
<td>0.0146%</td>
<td>0.041%</td>
<td>0.218%</td>
<td>1.031%</td>
<td>7.430%</td>
</tr>
<tr>
<td>NaNO₃ – LiNO₃ (43% – 57%)</td>
<td>0.040%</td>
<td>0.016%</td>
<td>0.052%</td>
<td>0.279%</td>
<td>1.188%</td>
<td>8.802%</td>
</tr>
</tbody>
</table>
Specific heat capacity

Based on DSC test results, the specific heat, \( C_p \), can be calculated from: \( C_p = \frac{q}{\beta} \), where \( q \) is the unit heat flow (w/g) and \( \beta \) is the heating rate (ºC/min).

Figure 8: Specific heat capacity as a function of temperature between 150 ºC and 300 ºC without phase change process.

(a) NaNO\(_3\) – LiNO\(_3\) (51% – 49%)  
(b) NaNO\(_3\) – LiNO\(_3\) (43% – 57%)
Specific heat capacity

The operating temperature of the medium temperature industrial waste heat storage is between 150 °C and 300 °C, thus the specific heat capacity tendency between these temperature ranges is of great interest.

The test results represented that the specific heat capacity of molten NaNO₃ – LiNO₃ (51% – 49%) was up to 2.12 kJ/kg·K until 300 °C. For molten NaNO₃ – LiNO₃ (43% – 57%), the specific heat capacity was up to 2.33 kJ/kg·K.

For the current studied binary systems, the sensible heat storage capacity after melting until 300 °C could be over 190 kJ/kg for molten NaNO₃ – LiNO₃ (51% – 49%) and over 210 kJ/kg for molten NaNO₃ – LiNO₃ (43% – 57%), which can not be neglected.
Economic evaluation

1. The commercial price of NaNO$_3$ is around $0.41$/kg [1]

2. The commercial price of LiNO$_3$ is $4.32$/kg [2].

3. In that case, the prices for these two binary systems are $2.32$/kg for NaNO$_3$ – LiNO$_3$ (51% – 49%) and $2.64$/kg for NaNO$_3$ – LiNO$_3$ (43% – 57%), respectively.

4. LiNO$_3$ could be much cheaper by converting from lithium carbonate with nitric acid[2].

5. A latent heat storage system has a smaller size than a sensible heat storage system, which reduces the cost of the supporting materials.

6. The operating temperature of the current studied latent heat storage system is between 150 °C and 300 °C, the requirements for some supporting components are lower, comparing to some sensible heat storage system with a large operating temperature range.


Thank you!