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A study of a eutectic salt of lithium nitrate and sodium chloride (87–13%) for latent heat storage

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A R T I C L E   I N F O

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A B S T R A C T

Latent heat storage in salt mixtures has attracted much attention as it can store a large amount of heat within a small temperature range in a small volume compared to sensible heat storage. In this paper, the eutectic salt of LiNO₃–NaCl (87–13%) was investigated to evaluate its potential for latent heat storage for medium temperature range applications (< 300 °C). The eutectic salt was prepared using the indirect mixing method. Its thermal properties including melting temperature and latent heat were measured over multiple cycles using Differential Scanning Calorimetry (DSC). The measurements show that the eutectic salt of LiNO₃–NaCl (87–13%) has a suitable melting temperature (around 220 °C) and a relatively high latent heat (> 290 kJ/kg). Its thermal decomposition temperature was tested using a Thermogravimetric Analyser (TGA). The salt mixture exhibits an excellent chemical stability below 400 °C with no changes after tests of multiple cycles with DSC and TGA. The main factors affecting the economic feasibility for this eutectic salt were also discussed.

1. Introduction

The industrial sector in the UK is one of the most energy-intensive sectors as it accounts for 25% of the final energy demand, of which 70% is heat production [1]. It is becoming increasingly important to use renewable energy resources and new technologies to make energy use more efficient and sustainable as well as to reduce CO₂ emissions. It is known that when producing heat for industrial processes there is also a penalty in terms of waste heat. The potential and technologies required for industrial waste heat reuse have been investigated and reported in the literature [2-5]. Based on temperature, the industrial waste heat sources can be divided into three groups: high-temperature (> 300 °C), medium-temperature (120 °C–300 °C) and low-temperature (< 120 °C). Compared to high-temperature waste heat, medium-temperature and low-temperature sources are more difficult to reuse due to the relatively low energy quality according to the second law of thermodynamics. Heat at such temperatures needs to be efficiently recovered, stored and transported for use.

Thermal energy storage using a salt mixture as PCM may play a key role in industrial medium-temperature waste heat storage because of its suitable phase change temperature and large heat storage capacity. Kenisarin [6] reviewed the investigations and developments of PCMs for thermal energy storage in detail, having summarised the thermophysical properties of hundreds of salt mixtures in the melting temperature range of 120–1000 °C, including fluorides, chlorides, hydroxides, nitrates, carbonates, vanadates, molybdates, metal alloys and other salts. He concluded that the hydroxide and nitrate materials have suitable phase change temperatures for applications in medium-temperature heat storage. In addition to suitable temperature and high latent heat storage capacity, reasonable thermal conductivity and good chemical characteristics including stability are needed. In this respect, the nitrate materials have a high potential.

Thermal properties investigations of salt mixtures have been carried out by researchers, mostly focuses on them being used as Heat Transfer Fluid (HTF), such as Solar Salt (NaNO₃–KNO₃ /60–40%) and Hitec Salt (KNO₃–NaNO₃–NaNO₂ /53–7–40%) [7,8] (All the percentages in this paper are based on mole percentages). Lopez et al. [9,10] reported that a eutectic salt of NaNO₃–KNO₃ (50–50%) having a melting temperature of 223 °C and a latent heat capacity of 106 kJ/kg. The mixture has several desirable characteristics for use as a PCM, such as good thermal and chemical stability, no phase segregation, low cost and low corrosion potential. Zhao et al. [11] tested a Ca(NO₃)₂–NaNO₃ mixture to determine its potential for latent heat storage. They concluded that a 3:7 mixture has a similar latent heat capacity to the commonly used Solar Salt (around 130 kJ/kg) but available at half the cost. However, the heat capacity of the material still was low for use in a latent heat storage system. The addition of LiNO₃ can lower the phase transition temperature and increase the latent heat capacity of the salt mixture.

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Roget et al. [12] reported that the eutectic mixtures of KNO₃-LiNO₃ and KNO₃-NaNO₃ have latent heat storage capacities of 178 kJ/kg and 155 kJ/kg respectively, which is useful for reducing the size of a thermal energy storage system. Wang et al. [13] found the ternary system of KNO₃-NaNO₃-LiNO₃ had good short-term and long-term thermal stability and reliability at temperatures below 435 °C. The phase transition temperatures of the ternary systems of KNO₃-NaNO₃-LiNO₃ with different component material proportions can be much lower than 200 °C, with some being lower than 150 °C.

For medium-temperature industrial waste heat storage, a PCM with a melting temperature in the range from 120 °C to 300 °C is of great interest. In this paper, results of experiments to evaluate the potential of a eutectic salt of LiNO₃-NaCl (87–13%) for use as a latent heat storage material for medium-temperature heat storage are reported. The thermal properties including melting temperature and latent heat of this salt over multiple cycles were investigated using Differential Scanning Calorimetry (DSC). Other thermal properties, such as cycle stability and specific heat capacity were also presented based on DSC and TGA measurements. Thermal conductivity was predicted using a verified method from literatures. To find the suitable materials contacting with the eutectic salt, a simple material compatibility test was carried out between the salt and some commonly used metals, such as copper, stainless steel 304 and stainless steel 316.

2. Material preparation

An indirect mixing procedure was used for the material preparation to get a homogeneously mixed eutectic salt with a uniform composition. LiNO₃ (99%, Technical, provided by Leverton–Clarke Ltd) and NaCl (99.5%+, AR, provided by Fisher Scientific) were heated at 150 °C for 30 min to fully evaporate all moisture from the samples. After drying the two components were weighed quickly, to minimise moisture being absorbed from the atmosphere which would distort the measured quantity of material. The measured quantities of materials were then dissolved in water separately to produce solutions which mixed together provided a homogeneous mixture with the required composition of salts. Subsequently the mixture was placed in an oven and kept at 150 °C until all of the water evaporated, leaving a crystal-like solid salt mixture. The crystal-like salt mixture was ground into a fine powder in a mortar using a pestle.

3. Methodology and results

3.1. Phase change temperature and latent heat

The thermal properties including phase change temperature and latent heat capacity were measured with a TA instruments Discover DSC [14]. The working temperature range of the DSC is from −180 °C to 725 °C. The precision of the temperature and enthalpy measurements is reported to be within ±0.005 °C and ±0.04% respectively. All of the tests were conducted under a pure nitrogen atmosphere. In the tests, a sample with a weight of 10–15 mg was heated from 50 °C to 250 °C then cooled back down to 50 °C at a constant heating/cooling rate. The cycle was repeated 10 times to minimise the effect of any absorbed moisture in the sample on the initial cycle. Two heating/cooling rates were used, 10 °C/min and 15 °C/min in order to evaluate the effect of heating/cooling rate on the materials measured thermal properties. The DSC test results for 10 cycles are shown in Fig. 1. The binary salt exhibits excellent charging and discharging in all cycles except for the first cycle which was affected by absorbed water. The phase change temperatures during heating and cooling were almost the same for the same heating/cooling rate. The average phase change temperatures measured during the charging processes were 221.65 °C and 219.92 °C respectively for the two heating/cooling rates, 10 °C/min and 15 °C/min. The measured average latent heat values were 316.5 kJ/kg and 296.5 kJ/kg.

3.2. Thermal repeatability

A PCM should have a stable phase change temperature and latent heat capacity even after a large number of thermal cycles, which is referred to as the materials thermal repeatability or stability. In the experiments the performed material was thermal cycled 51 times to examine the level of degradation that occurred in the materials thermal properties. During the cycles the eutectic salts were heated up and cooled down between 50 °C and 250 °C with a heating/cooling rate of 10 °C/min. The deviations in the measured melting temperatures and latent heat were calculated from the Eqs. (1) and (2), showing how much difference there is between each test result and the average value. Figs. 2 and 3 show the deviations of the melting temperatures and
latent heat in the test performed for the eutectic salt respectively. The eutectic salt showed very good repeatability for both melting temperature and latent heat, especially after the initial 2 cycles. The deviation of the measured melting temperatures was within ±0.4% and the deviation of latent heat was within ±1.5%, which is good for a salt mixture that is to be used as a PCM.

\[
T_n = \frac{T_n - \langle T \rangle}{\langle T \rangle} \quad 1 \leq n \leq 50
\]
(1)

\[
L_n = \frac{L_n - \langle L \rangle}{\langle L \rangle} \quad 1 \leq n \leq 50
\]
(2)

3.3. Thermal stability

The thermal stability of a PCM is another important parameter for selection of materials to be used in latent heat energy storage systems. It includes both the thermal stability under multiple heating/cooling cycles and the PCM thermal decomposition temperature, which sets the upper temperature limit for the material can be used in a practical application. A TA Instruments Discovery TGA [15] was used to test the thermal stability of the eutectic salt. The weight loss and temperature were recorded within an accuracy of 0.01% and 0.1 °C respectively. In the short-term thermal stability test, the sample was cyclically heated up and cooled down at a rate of 10 °C/min from 50 °C to 250 °C. The weight loss values for the first five cycles are shown in Fig. 4. It can be seen that the first cycle weight loss is about 10.6%. It is because of the moisture absorbed by the sample being evaporated. After the first cycle, the weight losses for the other four cycles are much smaller, and are even not visible from Fig. 4.

Fig. 5 shows the percentage weight losses of the eutectic salt of LiNO_3–NaCl (87–13%) for the 2nd to the 50th cycle. The percentage weight loss for each cycle is within 0.02% for all of these cycles and within 0.01% after the first 5 cycles. The total percentage weight loss for all the 50 cycles excluding cycle 1 is only 0.26%. Considering the weight loss recording accuracy of the TGA (being 0.01%), the eutectic salt shows good thermal stability in the cyclic tests and is suitable for medium-temperature latent heat storage applications.

For a heat storage material, the thermal decomposition temperature is a critical factor affecting its practical applications. A molten salt will lose its original thermal properties above the thermal decomposition temperature because most thermal decomposition processes are not chemically reversible. To determine the thermal decomposition temperature of the eutectic salt studied, a high temperature thermal stability test was undertaken using the TGA. The sample was placed in the TGA under an atmosphere of pure nitrogen and heated up from ambient temperature (20 °C) at a heating rate of 5 °C/min. Fig. 6 shows the percentage weight loss of the eutectic salt with time and temperature. It can be seen that the decomposition temperature of this material is between 400 °C and 450 °C. NaCl can tolerate higher temperatures; however, LiNO_3 decomposes at this temperature, as shown in Eq. (3). This decomposition temperature is sufficiently high above the application temperature that the material is suitable for medium-temperature heat storage.

\[
4\text{LiNO}_3 \rightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2
\]
(3)
3.4. Thermal conductivity

The thermal conductivity of materials used in thermal energy storage system is a key parameter in determining storage system geometry and rates of charge and discharge that can be realised. As the effects of thermal convection and long wave radiation at high temperatures cannot be determined from the DSC and TGA tests undertaken, a simple relationship from the literature is used to predict the thermal conductivity of the eutectic salt by the method of Zhao et al. [16].

\[
\lambda_{\text{binary salt}} = \lambda_a \times \left[ \frac{1 - \left( \frac{b}{a} \right)^2}{1 + \left( \frac{b}{a} - 1 \times \frac{\rho_a}{\rho_b} \right)^2} \right] \text{W/m/K}
\]

(4)

where, \( \frac{b}{a} = \left( \frac{\rho_B \times W_A}{\rho_A \times W_B} \right)^{1/3} \). \( \lambda_a \), \( \rho \) and \( W \) stand for thermal conductivity, density and weight percentage respectively. Gheribi et al. [17] proposed Eq. (5) to predict values for thermal conductivity of molten salts between the melting and boiling points.

\[
\lambda(T) = \lambda_{\text{ fus }} + \eta \times (T - T_{\text{ fus}}) \text{ W/m/K}
\]

(5)

where, \( \eta = -A_{\text{ fus }} \alpha_{\text{ fus }} (T_{\text{ fus }} + \frac{1}{4}) \). \( T_{\text{ fus}} \) is the melting temperature; \( \lambda_{\text{ fus }} \), \( \alpha_{\text{ fus }} \) and \( \eta_{\text{ fus }} \) are the thermal conductivity (W/m/K), thermal expansivity (K\(^{-1}\)) and Grueisen parameter (Dimensionless) at melting temperature. In their paper, Gheribi et al. [17] recommended \( \eta \) values for LiNO\(_3\) and NaCl. The parameters for use in Eq. (5) are listed in Table 1.

The densities of the salts are given by Smith and Petersen [18] to be:

\[
\rho_{\text{LiNO}_3} = 1.922 - 0.000556 \text{Tkg/m}^3
\]

(6)

\[
\rho_{\text{NaCl}} = 1.991 - 0.000543 \text{Tkg/m}^3
\]

(7)

The predicted thermal conductivity of the eutectic salt LiNO\(_3\)-NaCl (87–13%) when it is heated and melts is plotted in Fig. 7. It can be seen that the predicted thermal conductivity reduces slightly with increasing temperature. Below the safe operating temperature (under 400 °C), the thermal conductivity is predicted to be within the range of 0.57 W/m/K and 0.60 W/m/K. The thermal conductivity is higher than that of most organic materials used for phase change energy storage and even higher than some nitrate mixtures. However, it still is low for use as a thermal energy storage material. A higher thermal conductivity results in faster charging/discharging rates, to compensate for the low thermal conductivity heat transfer enhancement approaches will be required in the thermal storage system design, for example, adding high thermal conductivity particles or introducing a matrix of high thermal conductivity materials into the eutectic salt, or using advanced efficient heat exchanger structures. However, no matter which methods are used, the volumetric heat capacity and the cost of the whole system will be affected. Therefore, the development of optimal cost effective storage system designs will be essential.

4. Compatibility with commonly used metals

When used for heat storage a PCM is normally placed inside a vessel with heat transferred to and from the PCM through a series of heat transfer pipes/plates/fins or other heat exchangers. To provide good thermal conductivity, the heat transfer elements are made from commonly used metals, such as copper and stainless steel. It is essential when designing a system to know the compatibility of the studied eutectic salt with the metals used in the heat exchangers and vessel. Goods et al. [19] conducted a corrosion test of mixtures of NaNO\(_3\)-KNO\(_3\) with stainless steel 304 and 316 and found both stainless steels to be acceptable for high temperature (up to 570 °C) solar thermal applications. Kruizenga and Gill [20] studied the corrosion of molten nitrate salts with iron and stainless steel at very high temperatures of 600 °C. They found that the corrosion rates increased exponentially with the temperature. In this work, a simple corrosion test was performed to determine suitable metal, with copper, stainless steel 304 and stainless steel 316 tested. Similar sized metal samples of dimension 0.015 m by 0.005 m by 0.001 m were placed in the eutectic salt of LiNO\(_3\)-NaCl and the samples were put into a temperature controlled oven at 300 °C for two weeks (336 h). The photographs of the samples are presented in Fig. 8 after the test when the eutectic salt had cooled and solidified. It is obvious that the copper has suffered the most severe corrosion and is definitely not compatible with this salt and is not suitable for use in a thermal energy storage system with this material. Stainless steel 316 suffers the least corrosion and is the best choice for of construction material for heat exchanger and vessel. The simple corrosion test performed allows the selection of a metal suitable for use in an experimental scale test system to evaluate performance at

Table 1

Parameters for evaluation \( \lambda(T) \) for LiNO\(_3\) and NaCl.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T_{\text{ fus}} ) (K)</th>
<th>( \lambda_{\text{ fus}} ) (W/m/K)</th>
<th>( \eta ) (W/m/K(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO(_3)</td>
<td>527.15</td>
<td>0.5856</td>
<td>(-1.47 \times 10^{-4})</td>
</tr>
<tr>
<td>NaCl</td>
<td>1081.15</td>
<td>0.4923</td>
<td>(-2.11 \times 10^{-4})</td>
</tr>
</tbody>
</table>

Fig. 7. Predicted variation of thermal conductivity with temperature of the eutectic salt of LiNO\(_3\)-NaCl (87–13%).

Fig. 8. Photographs of samples of copper, stainless steel 304 and stainless steel 316 when immersed in the eutectic salt of LiNO\(_3\)-NaCl (87–13%) at 300 °C for two weeks: (a) prior to cooling; (b) after cooling to ambient.
lab scale. For practical applications however a much more precise and stringent corrosion test would be required to guarantee long term trouble free operation.

5. Conclusion

In this paper a eutectic salt of LiNO₃–NaCl (87–13%) was studied to determine its thermal properties and suitability for use as a PCM for medium-temperature latent heat storage. The measured melting temperature and latent heat capacity were around 220 °C and 300 kJ/kg respectively. The salt shows excellent thermal cycling repeatability and stability. The thermal decomposition temperature is between 400 °C and 450 °C, which is sufficiently above the application temperature to make it safe for the medium-temperature latent heat storage. The thermal conductivity of the molten salt was predicted to be between 0.57 W/m/K to 0.60 W/m/K. Although it is greater than several other PCMs, additional heat exchange arrangements will still be required to enhance the charging/discharging process. Corrosion test identified stainless steel 316 to be compatible with the eutectic salt and a suitable metal for the construction of the heat exchanger and storage vessel.

NaCl is available in large quantities at low commercial prices. Compared to other nitrates, LiNO₃ has no advantage in price. The demand for LiNO₃ is however increasing greatly and the technology for producing LiNO₃ is improving to meet this demand. According to a study by Zhao and Wu [21], LiNO₃ could be produced at much lower cost by producing it from lithium carbonate using nitric acid. The overall cost of a heat storage system does not only include the cost of the PCM but also the cost of the supporting systems and materials, such as the heat storage container and the heat exchanger. Due to the higher energy density a latent heat storage system is usually of a smaller size than a sensible heat storage system, which can compensate for the extra cost of required supporting materials. The operating temperatures of the eutectic salt of LiNO₃–NaCl (87–13%) studied are for a medium-temperature latent heat storage system application, the requirements for some of the supporting components will be lower than those for a sensible heat storage system with a comparable energy storage capacity and a larger operating temperature range, possibly leading to an overall cost reduction.

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