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Investigation of the $Ca(NO_3)_2$–$NaNO_3$ mixture for latent heat storage

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A B S T R A C T

In this paper, calcium nitrate and sodium nitrate are mixed in different molar ratios to form a cheap phase change material. The result shows that these binary mixtures all have exothermic peaks at around 220 °C, and the observed enthalpy increases with the $NaNO_3$ ratio. Further study indicates that although $Ca(NO_3)_2$ and $NaNO_3$ are mixed in different proportions, the mixture always first melts in the eutectic composition. Different $Ca(NO_3)_2$ and $NaNO_3$ ratio will lead to different amount of eutectic production, thereby resulting in different observed enthalpy. The sample with $Ca(NO_3)_2$ and $NaNO_3$ molar ratio of 3:7 shows the best heat storage performance. Specific heat capacity, compatibility and thermal conductivity are also measured in the paper. The cost of the 3:7 mixture is only about half of solar salt, but they have a similar latent heat storage capacity. Overall, this mixture shows a good application advantage.

1. Introduction

Energy is the foundation of human existence and development. With the improvement of human life, the demand for energy keeps increasing. It becomes more and more urgent to develop renewable energy, and concentrated solar power (CSP) is considered as a candidate to replace the conventional one [1]. Thermal storage system is very important to efficiently use the solar energy, since it solves the time mismatch between solar energy supply and electricity demand [2]. Sensible heat storage technology has a relatively mature application in solar energy, but its rather low thermal capacity leads to considerable volumes units. Therefore researchers try to find out a more efficient solution to thermal energy storage, and latent heat storage is supposed to be the choice because it stores 5–14 times [3] more heat per unit volume than the sensible one.

Theoretically, any material adsorbing or releasing heat when changing its phase could be used as latent heat storage material. However, much more considerations make a big deal when it comes to practical application. An ideal phase change material should including following properties: suitable phase transition temperature, high latent heat of transition, high thermal conductivity, long-term stability, low corrosivity, low toxicity, low cost and so on [4]. There is no such material meeting all these conditions; therefore compromise must be made when choosing phase change materials. Zabla et al. [3] listed over 150 materials used in research as phase change materials and about 45 commercially available. Kenisarin [5] focused on high-temperature phase change materials and more details of inorganic salts were given. Sameer et al. [6] considered Al–Si alloys as PCM to store thermal energy because of its high heat of fusion and thermal conductivity. Ge et al. [7] recommended nano/micio-structured composite materials as a direction for future. Among all the feasible materials, inorganic salts are considered as the first choice for its wide temperature range of utilization, low vapor pressure, satisfactory physical properties and low unit cost [8].

In fact, most salts in the review papers on phase change materials are initially developed as heat transfer fluids. They are called molten salts, which mean that they work in liquid phase. Especially, solar salt (60 wt% $NaNO_3$–40 wt% KNO_3) and Hitec Salt (53 wt% KNO_3, 40 wt% $NaNO_2$ and 7 wt% $NaNO_3$) have been widely used as heat transfer fluid and heat storage material [9]. As heat transfer fluids, the required properties mainly focus on low viscosity, low melting point, and high upper limit temperature. From the point of view of heat storage, the aforementioned salts belong to the sensible storage, and most current researches mainly concentrate on this field. Peng [10] developed multi-component molten salts composed of KNO_3, $NaNO_2$ and $NaNO_3$ with 5% additive A of chlorides and found that the additive A can lower freezing point, and loss of nitrite content and deterioration time of molten salts are reduced at the same time. Zhao [11] developed a class of ternary nitrate salt mixtures consisting of 50–80 wt% KNO_3, 0–25 wt% $LiNO_3$ and 10–45 wt% $Ca(NO_3)_2$, which have a melting point lower than 100 °C. As latent heat storage materials, salts work in both solid and liquid phases.The required

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properties are suitable melting point matching its heat source and high heat of fusion. Besides, other properties such as chemical stability, compatibility, thermal expansion, and thermal conductivity are also important in practice. However, more details are still absent. Only melting point and heat of fusion are listed for most phase change materials in the review papers. Furthermore, a heat storage system always needs a tremendous amount of heat storage material. For example, the quantity of molten salts in the Solar Two's heat storage system is 1.5 million tons [12] so that the economic cost plays a key role in its practice applications.

According to the Carnot's principle, the higher temperature of the heat source leads to the greater energy conversion performance. However, the high temperature technology asks for great costs for the building and the maintenance due to corrosion phenomena [13]. As a result, the low temperature and low cost solar thermal storage technology would be competitive. The temperature range between 200 and 300 °C is considered to be important for solar energy systems [14]. Table 1 shows the representative salts melting below 300 °C which are collected from the review papers. These salts can be divided into three categories. One contains lithium, but lithium is too expensive to apply as heat storage materials. The second group contains alkali, which has strong chemical activity and easily leads to deterioration. The third group consists of chloride or nitrite, which is corrosive or toxic. So there are still few options for us to choose a kind of economical and reliable latent heat storage medium.

Nitrate is widely considered as suitable phase change material for latent heat storage in solar energy. Bauer et al. [15] analyzed the detail of $NaNO_3$ for latent heat storage. Jung et al. [16] used KNO_3 as phase change material to estimate the heat transfer rate and the transient temperature variation in the heat pipe heat exchanger. Iverson et al. [17] studied the thermal and mechanical properties of solar salt, Hitec Salt and a low melting point quaternary salt (2.3 wt% KNO_3, 39.4 wt% $Ca(NO_3)_2$, 12.1 wt% $NaNO_3$, and 6.1 wt% $LiNO_3$) for latent heat storage. Roget et al. [13] investigated the KNO_3–$LiNO_3$ and KNO_3–$NaNO_3$–$LiNO_3$ eutectics for latent heat storage in a low-temperature solar power plant. As mentioned above, these mixture salts are initially developed as heat transfer fluid and they have a low melting point or high upper limit temperatures, but such good performance as heat transfer fluids is not much helpful for the latent heat storage capability. In addition their prices may not be cheap enough. Protsenko et al. [18] studied the temperature-composition phase diagram for $Ca(NO_3)_2$–$NaNO_3$ and some thermal properties such as electrical conductance, density, and surface tension were also measured. Perhaps this mixture does not perform well as heat transfer fluid; therefore no further investigation was carried out. Since the prices of $Ca(NO_3)_2$ and $NaNO_3$ are lower than other nitrates, their mixture may have an advantage in the practice applications in latent heat storage. To our knowledge, no publication in the open literature has clearly reported its application in latent heat storage. In this paper, $Ca(NO_3)_2$ and $NaNO_3$ are mixed in order to make an economic latent heat storage material. Some important thermal properties such as enthalpy of its solid–liquid transition, cycle stability, specific heat capacity, thermal conductivity and compatibility are also measured. After overall considerations, this eutectic is a kind of competitive latent heat storage material.

Table 1
Summary of molten salts below 300 °C.

Materials (mol%)	Melting point (°C)	Heat of fusion (kJ/kg)
$LiNO_3$	253	373
(28.5–28.9)LiCl–(43.5–44.5)CsCl–(13.7–14.1)KCl–(13.3–13.5)RbCl	256 ± 2.5	375–380
59.15LiCl–40.85$Ca(NO_3)_2$	270	167
63LiOH–38LiCl	264	437
65.5LiOH–34.5LiCl	274	339
[a]33$LiNO_3$–67KNO_3	133	170
[a]29$LiNO_3$–17$NaNO_3$–49.4KNO_3–4.6$Sr(NO_3)_2$	105	110
[a]58.1$LiNO_3$–41.9KCl	166	272
[a]57$LiNO_3$–43$NaNO_3$	193	248
50NaOH–50KOH	169–171	202–213
30LiOH–70NaOH	210–216	278–329
20NaOH–80$NaNO_2$	230–232	206–252
73NaOH–27$NaNO_2$	237–238	249–295
87.3NaOH–6.1NaCl–6.6Na_2CO_3	291	283
[a]87$LiNO_3$–13NaCl	208	369
86.3$NaNO_3$–8.4NaCl–5.3Na_2SO_4	287	177
[a]53KNO_3–40$NaNO_2$–7$NaNO_3$	142	80

[a] Weight percent.

2. Materials and preparation

The molten salts mixtures are prepared from $Ca(NO_3)_2 \cdot 4H_2O$ (purity > 99%) and $NaNO_3$ (purity > 99%) manufactured by Sinopharm Chemical Reagent Co., Ltd. They are weighted and mixed together in molar ration from 1:9 to 9:1 in ceramic crucibles. Then they are put into a heating furnace. Due to the low melting point of $Ca(NO_3)_2 \cdot 4H_2O$ (about 40 °C), it soon dissolves into liquid state, and absorbs $NaNO_3$ to form a homogeneous transparency phase. Then the mixture liquid is stirred to mixing uniformity.To keep the mixture dried, it is put back to the furnace and kept at 300 °C for 5 h. Finally the products are naturally cooling down and kept in a dryer prior to the thermal analysis.

3. STA tests of different mixture samples

The melting temperature, heat of fusion and cycle stability are all measured by the Simultaneous Thermal Analyzer (STA 8000, PerkinElmer), which offers real-time measurement and analysis of sample weight change and heat flux. The instrument is calibrated by indium and zinc. The heat flux signal is a relative value. As the endothermic peak size depends on the basis line and the amount of the sample, its concrete numerical value is meaningless. Therefore, it is not shown in the figures below.

The materials used in the preparation are first tested by the STA. The sodium nitrate is heated from 120 °C to 350 °C at 10 °C/min heating rate under N_2 purging of 20 mL/min. The curve is shown in Fig. 1. Its melting point and heat of fusion measured by STA are 302.06 °C and 175.65 kJ/kg. The relative errors are 1.6% and 0.76% to the date of published literature shown in Table 2. The smaller endothermic peak in Fig. 2 is solid–solid transition, which is also mentioned in published literature [19]. From the above tests, it can be seen that this instrument is accurate and reliable.

The $Ca(NO_3)_2 \cdot 4H_2O$ is heated from ambient temperature to 350 °C. As the STA curve shown in Fig. 2a, Peak 1 is the melting peak, and Peaks 2 and 3 are dehydration peaks. This sample is then heated from 350 °C to 750 °C at 10 °C/min heating rate. As shown in Fig. 2b, it can be found that when the temperature exceeds 500 °C, decomposition as well as phase transition comes to calcium nitrate. Hence, pure calcium nitrate is not suitable for latent heat storage.

Since the melting point of eutectic is generally lower than that of its components, it is supposed that melting peak would appear below 300 °C. The nine different molar ration samples are heated from 120 °C to 350 °C at 10 °C/min heating rate under N_2 purging of 20 mL/min. As the mixtures are good at hygroscopicity and imperfect lattice may also arise in the preparation process, the first STA curves fluctuate disorderly. Therefore the samples are reheated several times to make sure that water is totally removed; then the curves become smooth and have high reproducibility.