Thermo-physical properties of NaCl – Na_2CO_3 – NaOH as a high-temperature sensible heat storage medium

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Abstract

A novel ternary salt mixture composed of sodium chloride, sodium carbonate and sodium hydroxide (Na-Cl-CO_3-OH) was developed for high-temperature sensible thermal energy storage (HTSTES) application. The melting point and the heat capacity of the Na-Cl-CO_3-OH mixture was measured using a differential scanning calorimeter. The final melting temperature of the blend was estimated as 347.3°C. The average heat capacity of the blend was calculated as 1.50 J g^{-1} K^{-1} by following the ASTM standard E1269. The mass loss of the molten salt mixture was studied up to 1000°C using a thermogravimetric analyser in three different atmospheres, and the salt was found to be stable over 700°C. In terms of cost, Na-Cl-CO_3-OH mixture costs approximately 4.5 USD/kWh, around 60% less than the commercial “solar salt” nitrate salt mixture.

Keywords: Molten salt, sensible energy storage, thermophysical properties, mixed-anion.

1. Introduction

Thermal energy storage (TES) plays a vital role in the effective and efficient use of concentrated solar power (CSP) to provide steady output and meet intermittent electricity demands. The storage media is the most important component in any thermal energy storage (TES) system (Kuravi et al., 2013). Molten salts are extensively used thermal storage media and heat transfer fluid (HTF) in CSP plants due to their favourable thermo-physical properties. Current state-of-the-art CSP plants utilise “solar salt” (60 wt. % $NaNO_3$ – 40 wt. % KNO_3) and HITEC salt (53 wt. % KNO_3 – 40 wt. % $NaNO_2$ – 7 wt. % $NaNO_3$) for TES due to their acceptably low melting point and reasonable heat capacity (Ushak et al., 2015). Several recent CSP research programs have focused on developing high-temperature, and high-efficiency CSP plants incorporating advanced power cycles such as the supercritical Rankine, supercritical CO_2, and air-Brayton cycles. Selection of the HTF and TES media plays a crucial role in developing a modern CSP plant. The current generation molten salts (solar salt and HITEC) decompose around 600°C, which is insufficient for high-temperature power cycles (Gil et al., 2010; Kenisarin, 2010; Medrano et al., 2010), although a slight extension in the operating temperature is possible with meticulous atmospheric control (Olivares, 2012). Thus, development of new high-temperature molten salts with high thermal stability, specific heat capacity, reasonable melting point, and low cost is vital to support advanced power cycles. For the operating temperature range between 500°C and 700°C, mixtures of carbonates, chlorides, fluorides and hydroxides can potentially be exploited for high temperature sensible thermal energy storage (HTSTES). Several researchers attempted to develop HTSTES molten salt mixtures with carbonates (Olivares et al., 2012; Wu et al., 2011), chlorides (Wei et al., 2015), fluorides (Forsberg et al., 2007), and also mixed anions (Wang et al., 2015). Most of these mixtures had one or all of the following issues: (i) high melting point, (ii) low heat capacities, and (iii) an expensive salt component.

In this research work, a ternary salt mixture with a mixed anion configuration, and sodium (Na) cation (NaCl – Na_2CO_3 – NaOH), was developed based on the FactSage prediction reported by Gomez (Gomez, 2011) for latent heat storage. To the best of the authors’ knowledge, this mixture has not been investigated as a sensible heat storage media. In this research work, we assume the thermal storage system is in the ‘two-tank’ configuration, as shown schematically in Figure 1. Note, Figure 1 includes a heat exchanger between the storage tank and the receiver, which allows for a separate heat transfer fluid (HTF) in the receiver (such as sodium). This particular mixture is interesting for HTSTES because of three important factors: firstly, low predicted melting point with inexpensive materials; secondly, the use of sodium (Na^+) as the cation for all three salts, which allows compatibility with an elemental sodium HTF for direct-contact heat exchange (Venkataraman, 2017); and finally, presence of large proportion of NaOH augments the specific heat capacity of the molten salt mixture. The key thermo-physical properties, such as, melting point, heat capacity, and thermal stability of this

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ternary mixture were experimentally determined, and its commercial suitability for HTSTES application has been assessed.

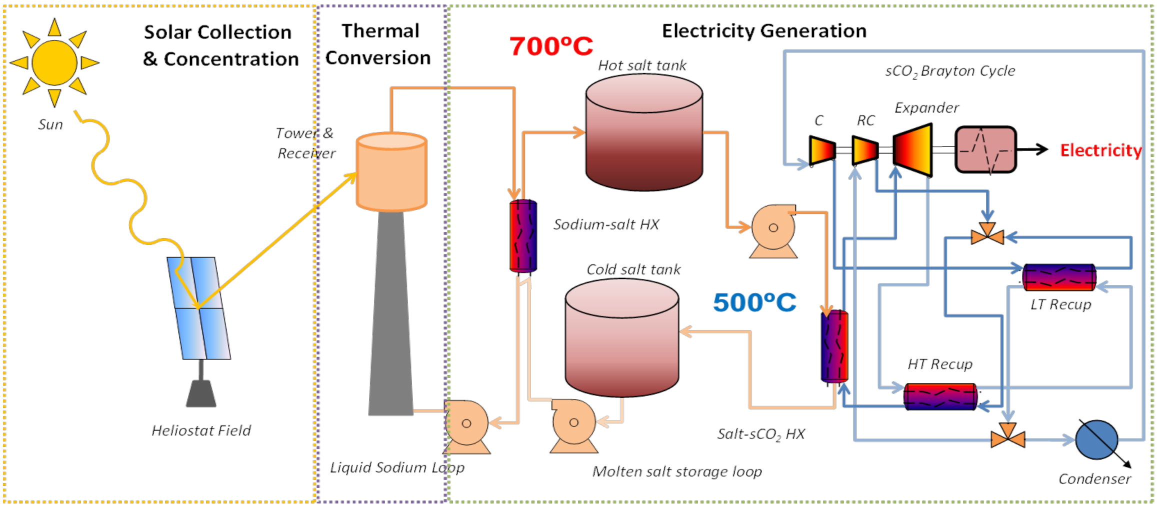

Fig. 1: Schematic diagram of proposed next-gen two-tank CSP power plant

2. Experimental procedure

A ternary mixture of NaCl – Na_2CO_3 – NaOH (Na-Cl-CO_3-OH) (mass ratio- 24.68:15.67:59.65) was synthesised. The three salts — NaCl (>99% purity, ACS grade), Na_2CO_3 (>99.5% purity, ACS grade), and NaOH (>98% purity) — were procured from Alfa Aesar and stored under nitrogen flow to avoid moisture absorption. The salt components were weighed in proportion to the FactSage prediction, then blended by hand-grinding inside a glove box using a mortar and pestle for 30 min.

The ground mixture was used directly in a Netzsch Pegasus DSC 404 to determine the melting point and heat capacity. Graphite crucibles with lids were utilised for the DSC experiments to attain faster heat transfer into the salt mixtures. The melting point and heat capacity measurements were conducted using SiC and Pt-Rd furnaces respectively at a heating/cooling rate of 10 °C/min and 20 °C/min respectively with 50 ml/min of nitrogen purge. The heat capacity of the sample was determined by following ASTM standard E1269 with a sapphire disk as the reference.

The mass loss of the salt mixture was tested using a Q600 SDT TG/DSC (TA instruments). Experiments were conducted from room temperature to 1000°C at a heating rate of 10°C/min in three different atmospheres (nitrogen, argon and air), at a flow rate of 50 mL/min. Each sample of about 5-10 mg was placed into an 85 µL alumina crucible and covered with a perforated lid.

3. Results and discussions

3.1. Determination of melting point

The melting point of the Na-Cl-CO_3-OH mixture was predicted as 320°C by FactSage. Fig. 1(a) shows the DSC curve with onset and peak melting temperatures, and multiple endothermic peaks suggesting that the mixture is off-eutectic. It is evident from Fig. 2 that complete melting of the ternary mixture takes place around 347.3°C. The freezing of the salt mixture begins at 325°C, and this difference between the melting and freezing temperatures is due to sub cooling. Four continuous heating and cooling cycles were run for each sample. The fusion between the salts in the mixture was achieved during the first heating cycle, and the melting point determined from the three subsequent cycles.

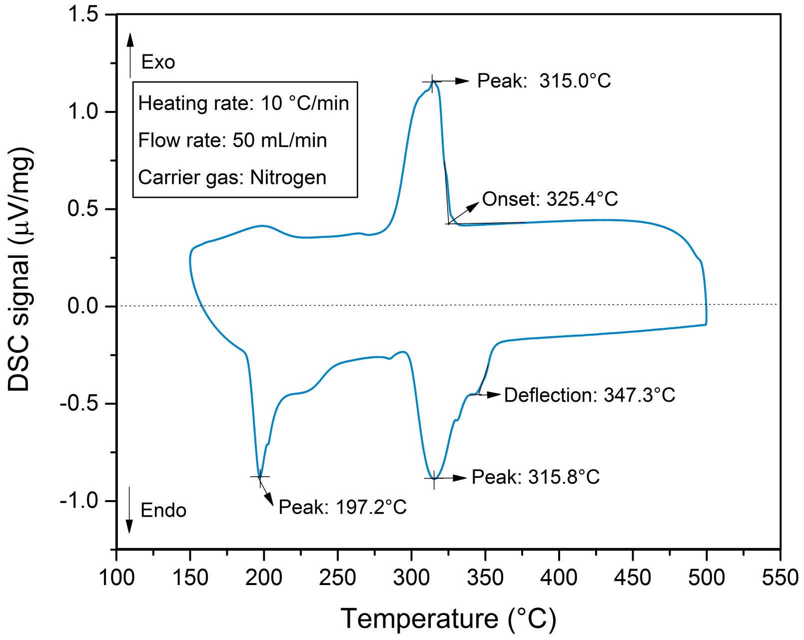

Fig. 2: Melting point analysis of Na-Cl-CO_3-OH mixture in a nitrogen atmosphere

3.2. Heat capacity measurement

The experimental measurement of specific heat capacity, c_p in the DSC followed the ASTM E1269 standard with a sapphire disk as the reference. The specific heat capacity measurement method was validated by correlating the heat capacity values obtained for a unary salt (NaCl) with the theoretical values (Chase-Jr, 1998) in the temperature range 400 – 600°C. The maximum variation between the experimental and theoretical values was less than ±2%, as presented in Fig. 3. The heat capacity of the mixed anion ternary was measured above the liquidus temperature between 450 and 600°C as shown in Fig. 4. The experiments were conducted in a nitrogen atmosphere at 50 mL/min, and measured over 10 heating-cooling cycles. The average heat capacity of the mixture is 1.508±0.005 J g^{-1} K^{-1}, which is similar to the commercial 'solar salt' mixture. Values for average specific heat capacity is first averaged across all 10 cycles, and then averaged across the measurement temperature range. The error value (±0.005) is the standard deviation from the mean of the temperature averaged values across the 10 heat capacity measurements. The liquid heat capacity values (J g^{-1} K^{-1}) of Na-Cl-CO_3-OH are fitted into a polynomial function for convenience of use. Polynomial regression is used to fit curves to the c_p data with good agreement, and therefore, within the nominated temperature ranges, specific heat capacity can be taken as follows:

$$c_p = aT^3 + bT^2 + cT + d \tag{1}$$

where temperature T is the salt temperature in °C and the coefficients are given in Table 1. The R^2 value from the regression analysis is also given.

Tab. 1: Polynomial coefficients for the heat capacity

Mixture	Validity	a	b	c	d	R^2
NaCl – Na_2CO_3 – NaOH	455 – 600	$-3E^{-7}$	0.000516	0.281139	52.45630	0.972

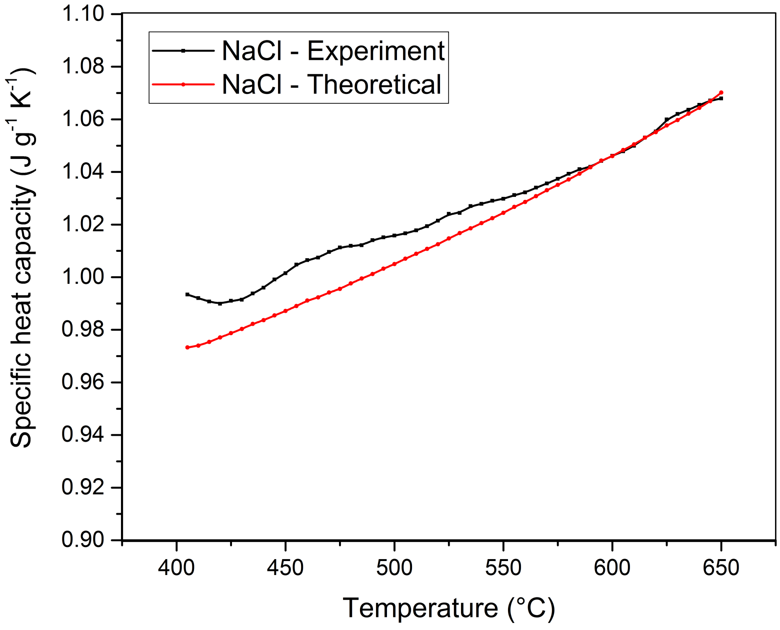

Fig. 3: Validation of heat capacity measurement with NaCl

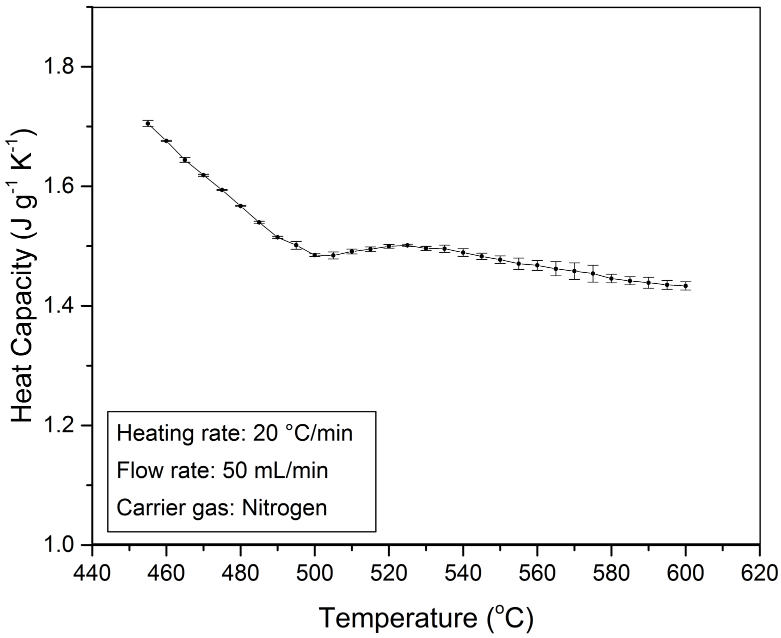

Fig. 4: Heat capacity measurement of Na-Cl-CO_3-OH mixture in a nitrogen atmosphere

3.3. Mass loss testing of the ternary mixture

Both thermal stability and mass loss due to vaporisation of the molten salt are important considerations for solar thermal application. Here we distinguish between the physical decomposition of the salt (thermal stability) and mass loss due to vaporisation caused by high vapour pressure. The mass loss of the salt mixture was measured in three different atmospheres with a flow rate of 50 mL/min using the DSC-TGA equipment. The experiments were conducted up to 1000°C from room temperature as shown in Fig. 3. An initial mass loss is observed due to evaporation of absorbed moisture during sample loading process. The tested salt mixture showed excellent stability over 700°C in inert atmospheres. In the presence of air, the ternary mixture reacts and increases in mass as shown in Fig. 5. This may be due to the interaction between NaOH and CO_2, leading to the formation of Na_2CO_3 (Zeman, 2007). Fig. 6 shows that pure liquid NaOH reacts with air at higher temperatures, causing a change in mass, which reaffirms the previous statement. It is evident from the tests, that the Na-Cl-CO_3-OH mixture shows promising thermal stability as a HTSTES media for modern high-temperature CSP plants.

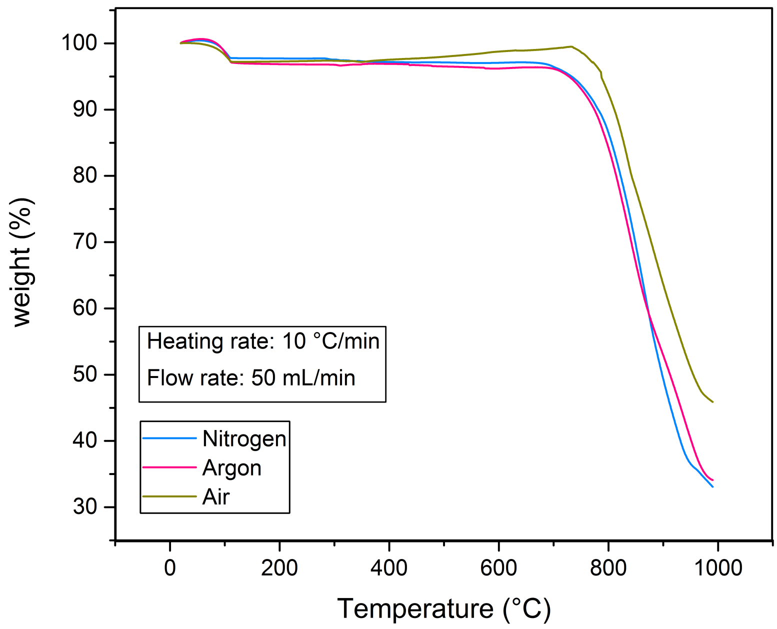

Fig. 5: Thermal stability of ternary mixture in three atmospheres

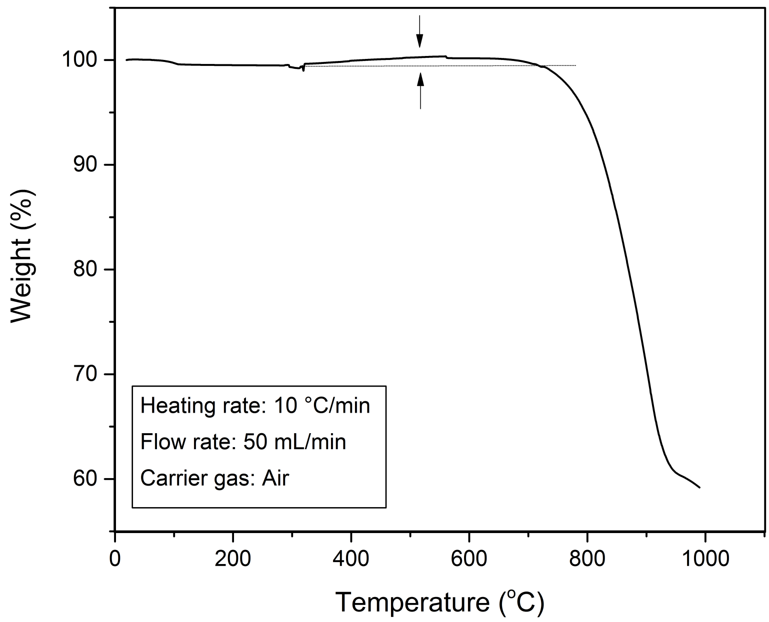

Fig. 6: Thermal stability of NaOH in air

3.3. Economic analysis

The cost of the storage media is one of the important parameter in the selection process. The costs of individual salt components considered in the study, as well as the reference case 'solar salt', are shown in Table 2. All the values shown in the table are adjusted to December 2016 currency using the PPI (producer price index) commodity data for industrial chemicals provided by Bureau of Labor Statistics (BLS) (BLS, 2016). The cost of each salt mixtures was calculated in terms of USD/tonne and USD/kWh, assuming operating temperature range between 500°C and 700°C. Prices were obtained from industrial suppliers. The total cost of the salt mixture was 390 USD/tonne and 4.5 USD/kWh, which is approximately 60% cheaper than the 'solar salt'.

Tab. 2: Cost of individual salts, as in Dec 2016. PPI: average Purchaser Price Index provided by (BLS, 2016)

Material	Cost (USD/tonne)	Source
NaCl	49	52 USD/tonne in Mar'16 (Industrial minerals, 2016). PPI = -6%
Na_2CO_3	324	320 USD/tonne in Sep'15 (Industrial minerals, 2016). PPI = 1%
NaOH	550	550 USD/tonne in Dec'16 (Alibaba, 2016)
Solar Salt	950	950 USD/tonne in Dec'16 (SQM, 2016)

4. Conclusion

The current state-of-the-art storage media decomposes around 600°C, and there is therefore a need for new storage media with thermal stability over 700°C to support modern high-efficiency CSP plants. In this research work, a new ternary mixture was developed and its thermo-physical properties evaluated for HTSTES applications. The molten salt mixture displayed acceptable melting point (<350°C), good heat capacity (1.50 J g^{-1} K^{-1}) and excellent thermal stability (>700°C). Most importantly, the ternary mixture was more economical (4.5 USD/kWh) that the nitrate 'solar salt' blend used in many current CSP plants. The experimental results indicate that Na-Cl-CO_3-OH mixture is a promising candidate for future HTSTES applications. The corrosion behaviour of containment materials and interacting surfaces is an important issue which needs to be addressed, before this mixed anion salt mixture can be recommended for use in high-temperature CSP systems.

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