Energy Conversion and Management 167 (2018) 156–164

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Assessment of a novel ternary eutectic chloride salt for next generation high-temperature sensible heat storage

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ARTICLE INFO

Keywords:
High-temperature
Sensible heat storage
Melting point
Heat capacity
Mass loss
Molten salt

ABSTRACT

A novel ternary eutectic salt mixture for high-temperature sensible heat storage, composed of sodium chloride, potassium chloride and magnesium chloride (NaKMg–Cl) was developed based on a phase diagram generated with FactSage®. The differential scanning calorimetry (DSC) technique was used to experimentally validate the predicted melting point of the ternary eutectic composition, which was measured as 387 °C, in good agreement with the prediction. The ternary eutectic was compared to two binary salts formulated based on prediction of the eutectic composition by FactSage, but unfortunately DSC measurements showed that neither binary salt composition was eutectic. Nonetheless, the measured thermo-physical properties of the ternary and the two binary mixtures are compared. Liquid heat capacities of both the ternary and binary salts were determined by using DSC with sapphire as the standard reference. The average heat capacity of the ternary mixture was recorded as $1.18\,J\,g^{-1}\,K^{-1}$. The mass loss of the molten eutectic salts was studied up to 1000 °C using a thermogravimetric analyser in nitrogen, argon and air. The results showed a significant mass loss due to vaporisation in an open system, particularly above 700 °C. However, simulation of mass loss in a closed system with an inert cover gas indicates storage temperatures above 700 °C may be feasible, and highlights the importance of the design of the storage tank system. In terms of storage material cost, the NaKMg-Cl mixture is approximately 4.5 USD/kWh, which is 60% cheaper than current state-of-the-art nitrate salt mixtures.

1. Introduction

Concentrating solar power (CSP) with integral thermal storage is one of the most promising renewable energy technologies for non-intermittent production of electricity. The most important component in any thermal energy storage (TES) system is the storage media [1]. Molten salts are the widely preferred thermal storage media and heat transfer fluid (HTF) in CSP plants due to their good heat capacity, thermal stability and operating temperature range compatible with current generation steam power plants [2]. State-of-the-art CSP plants utilise nitrate and nitrite based molten salts as storage media. Solar salt, a mixture of sodium and potassium nitrate (60 wt% $NaNO_3$–40 wt% KNO_3), has been widely adopted in commercial parabolic trough and central tower power plants [3–5]. This salt has a melting point of 221 °C and is thermally stable up to about 600 °C. HITEC® salt (7 wt% $NaNO_3$–53 wt% KNO_3–40 wt% $NaNO_2$) is also utilised as a sensible heat storage medium, and has a melting point of 142 °C and maximum operating temperature of 530 °C [6–8].

With the objective of reducing the cost of power from CSP plants, there is presently a strong focus on deployment of high temperature (> 600 °C) power systems, with better power cycle efficiency. The current nitrate salt mixtures are not stable at temperatures above 600 °C, which precludes their usage for high-temperature power cycles (such as the supercritical CO_2 (sCO_2) Brayton cycle) that operate above this temperature [9–11], although a slight extension in the operating temperature is possible with meticulous atmospheric control [12]. Because of this temperature limitation, and in support of concurrent efforts to develop advanced power cycles, it is vital to develop new high-temperature molten salts with high thermal stability, acceptable thermo-physical properties, and low cost. For example, the recent U.S. Gen3 CSP Roadmap [13] is structured around the development of a sCO_2 Brayton power cycle operating between temperature limits 500 °C–700 °C. Power cycles may operate at even higher temperatures, for example, air Brayton cycles operate around 1100 °C and, in combined cycle mode, achieve very high thermal-to-electric conversion efficiency. When coupled to CSP, such plants typically consider air as the working fluid and solid media for thermal storage. Storage in a liquid at such high temperatures appears very challenging from the

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https://doi.org/10.1016/j.enconman.2018.04.100
Received 2 March 2018; Received in revised form 26 April 2018; Accepted 27 April 2018
0196-8904/

perspective of both the storage media itself and the containment material, and is beyond the scope of this work.

The possibility of utilising ternary carbonate mixtures, such as Li_2CO_3-Na_2CO_3-K_2CO_3, as a replacement for molten nitrates has been studied by several researchers [12,14,15]. Such a carbonate mixture succeeds in the areas of thermal stability (> 700 °C), good specific heat capacity, and acceptably low melting point (397 °C), but the presence of expensive Li_2CO_3 in the mixture reduces its viability for commercial application. In a state-of-the-art thermal storage system, the molten salt material accounts for approximately 50% of the total TES system costs [16]. Thus, development of a cost effective salt mixture is crucial. Chlorides are a potential replacement for nitrates due to their abundance, low cost and excellent thermal stability. Molten chloride mixtures have been used as coolants in nuclear power plants [17] and extensively used in other thermal processes. In recent years, mixtures with chloride salts abundant in nature, like NaCl, KCl, $MgCl_2$, $ZnCl_2$, $CaCl_2$, were developed and tested for thermal storage application [18–20]. Li et al. [20] analysed the ternary eutectic of NaCl–KCl–$ZnCl_2$ (NaKZn–Cl) based on three proportions reported in literature [21], and showed low melting temperatures between 199 °C and 210 °C. However, $ZnCl_2$ is relatively expensive (1850 USD/tonne[1]), and makes up between 60 and 75 wt% for the tested mixtures. The high proportion of $ZnCl_2$, plus its relatively high vapour pressure, hinders the prospects for commercialisation of this salt mixture.

In this paper, a ternary chloride salt system of NaCl, KCl and $MgCl_2$ (NaKMg-Cl) is explored for sensible heat storage applications. This combination of chloride salts has been proposed previously for latent heat storage [22], as a high-temperature coolant [17], and for sensible heat storage [23]. In recent work, Xu et al. [24] tested the properties of a supposedly eutectic ternary NaCl-KCl-$MgCl_2$ mixture based on proportions suggested in literature [25], but the results showed it was off eutectic. In the present work, the eutectic composition is predicted using FactSage®, and verified by testing. The thermo-physical properties of this ternary eutectic mixture are compared to two binary eutectics containing the same base salts, to analyse the merits of the ternary blend relative to the binary options. NaCl–$MgCl_2$ (NaMg–Cl) and KCl–$MgCl_2$ (KMg–Cl) were the binary salts considered in this study. The NaCl–KCl eutectic was neglected due to its predicted high melting temperature of 657 °C. A similar eutectic temperature was reported in the literature [26].

2. Experimental methodology

2.1. Material and salt preparation

The FactSage® software was used to estimate the eutectic composition of the ternary and three binary chloride salts. FactSage is a thermochemical modelling software package, and can be used to predict eutectic points, chemical properties and liquidus projections for an extensive set of chemical mixtures [27]. The base salts - NaCl (> 99% purity, ACS grade), KCl (> 99% purity, ACS grade) and $MgCl_2$ (> 98% purity, ACS grade) - were procured from Alfa Aesar and Sigma-Aldrich and stored in a glove box under nitrogen to avoid moisture absorption. To synthesise the mixtures, the required quantity of each base salt was weighed to match the eutectic composition predicted by FactSage. The salt mixtures were mixed with a mortar and pestle continuously for 30 min until the mixture became fine and visibly well mixed. Both the weighing and mixing processes were conducted in a glove box to avoid moisture absorption. Magnesium chloride ($MgCl_2$) is extremely hygroscopic, and it should be handled with utmost care to avoid moisture absorption [28,29]. The presence of water can lead to several hydrolyses and partial hydrolysis reactions [30]. The final products of the hydrolysis reaction at high temperature are magnesium oxide (MgO) and corrosive hydrochloric acid (HCl) gas [29–32]. Therefore, the presence of small quantities of metal oxide in the mixture is unavoidable. Removal of oxide impurities from magnesium salt requires a process that involves adding Cl_2 or HCl gas over the melt [28,29]. A wide range of reactions are possible during a thermal treatment of hydrated $MgCl_2$ [30]:

(1) Dehydration

$$MgCl_2.\ xH_2O(s) \rightarrow MgCl_2.\ (x-y)H_2O(s) + yH_2O(g) \quad (1)$$

$$MgCl_2.\ zH_2O(s) \rightarrow MgCl_2(s) + zH_2O(g) \quad (2)$$

(2) Thermal hydrolysis

$$MgCl_2.\ xH_2O(s) \rightarrow Mg(OH).\ Cl(s) + HCl(g) \quad (3)$$

(3) Dehydroxylation

$$Mg(OH).\ Cl(s) \rightarrow MgO(s) + HCl(g) \quad (4)$$

The usual reaction temperatures for dehydration, hydrolysis and dehydroxylation are below 200 °C, above 200 °C, and above 400 °C respectively [30].

2.2. Apparatus and procedure

A NETZSCH Pegasus 404 F3 DSC with a silicon carbide (SiC) furnace was used to perform initial characterization of salt samples and measure their melting points. Four continuous heating and cooling cycles were run for each sample. Fusion between the salts in the mixture was achieved during the first heating cycle, and the melting point determined from the three subsequent cycles.

A platinum-rhodium (Pt-Rh) furnace was used for accurate measurement of the specific heat capacity. Each sample of about 10 mg was loaded into an 85 µL graphite crucible. It was then covered with a lid, perforated by a small hole. Differential scanning calorimetry (DSC) tests were conducted with a 50 mL/min nitrogen purge at a heating rate of 10 °C/min and 20 °C/min for melting points and specific heat respectively. Specific heat capacities of the samples were determined using the ASTM E1269 standard, with sapphire as the reference material.

Two different tests were conducted to analyse the feasibility of utilising these salts at high temperature. Firstly, a thermogravimetric analysis (TGA) was carried out to evaluate the mass loss of the salt mixtures, where the salts were heated in a single cycle from room temperature to 1000 °C until significant mass loss was experienced. The salt samples were heated using a TA Instrument Q600 SDT TGA/DSC, at a heating rate of 10 °C/min in 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. Secondly, a thermal cycling test was carried out where the samples were heated and cooled in 100 cycles, between temperature limits of 500 °C and 700 °C. The thermal cycling test of the samples was conducted in a controlled atmosphere tube furnace with a continuous nitrogen purge. About 20 g of salt was placed in an alumina crucible, covered with a lid to minimise volatilization.

3. Results and discussions

3.1. Determination of eutectic point

The phase diagrams of NaKMg–Cl, KMg–Cl and NaMg–Cl salt mixtures, as predicted by FactSage, are presented in Figs. 1, 2 and 3, respectively. The eutectic temperature of the ternary chloride mixture was predicted to be 383 °C with the weight proportions of 24.5 wt% NaCl–20.5 wt% KCl–55 wt% $MgCl_2$. The eutectic temperatures of the

[1] 1850 USD/tonne based on personal communication with SQM Europe M.V. in October 2015.