Applied Energy 112 (2013) 682–689

Contents lists available at SciVerse ScienceDirect

Applied Energy

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

Design of new molten salt thermal energy storage material for solar thermal power plant

Qiang Peng [a,*], Xiaoxi Yang [a,c], Jing Ding [b], Xiaolan Wei [a], Jianping Yang [a]

[a] *Key Laboratory of Enhanced Heat Transfer and Energy Conservation of the Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China*
[b] *School of Engineering, Sun Yat-sen University, 132 Waihuan Dong Road, Guangzhou High Education Mega Center, Panyu, Guangzhou 510006, PR China*
[c] *Guangdong Provincial Key Laboratory of Distributed Energy Systems, Dongguan University of Technology, Dongguan 523808, PR China*

HIGHLIGHTS

- New quaternary reciprocal system (K, Na/NO_2, Cl, NO_3) is prepared.
- This molten salt has a lower melting point.
- This new salt has excellent thermal stability.
- This salt mixture has a reduced cost.

ARTICLE INFO

Article history:
Received 28 August 2012
Received in revised form 21 October 2012
Accepted 22 October 2012
Available online 17 November 2012

Keywords:
Molten nitrate salt
Heat transfer fluid (HTF)
Eutectic mixture
Phase diagram calculation
Conformal ionic solution (CIS) theory
Solar thermal power

ABSTRACT

In order to obtain molten salt with lower melting point, higher thermal stability and reduced cost relative to previously available materials, a variety of molten salt mixtures of alkali nitrates are investigated by experimental methods. However, since measurements are generally expensive and time-consuming, it is of interest to be able to predict melting point and the component of multi-component systems by using the numerical methods. In this paper, eutectic point and component of a new kind of the quaternary reciprocal system (K, Na/NO_2, Cl, NO_3) are determined firstly by conformal ionic solution theory. Then thermal stability of the mixtures that show a lower melting point is measured by thermogravimetric analysis device. Experimental results show the agreement between measurements and calculations is found to be very good. This kind of molten salt has a lower melting point, 140 °C. It is thermally stable at temperatures up to 500 °C, and may be used up to 550 °C for short periods. Besides, this molten salt has a reduced cost relative to previous low-melting nitrate mixtures due to the elimination of cesium nitrate and lithium nitrate.

1. Introduction

Thermal energy storage (TES) technologies is a key factor in solar thermal power plants. Concentrating solar power (CSP) plants with TES can generate electricity when sunlight is not available, for example, during momentary cloud transients, which otherwise disrupt electricity generation and cause widely varying power output, and during evening hours when electricity is highly valued [1]. There are several types of HTF in TES system, among which molten salt has been widely studied due to its higher working temperatures (more than 500 °C) and heat capacity, lower vapor pressure and corrosivity, good thermal and physical properties even at elevated temperatures. For instance, increasing the maximum fluid output temperature of current CSP plants from 390 °C to 450–500 °C would increase the Rankine cycle efficiency of the power block steam turbine to the 40% range, compared to 393 °C with the current high-temperature oil and a cycle efficiency of 37.6%, thereby reducing the levelized energy cost by 2 cents/kW h [2,3]. At present, molten salts for heat transfer and energy storage mainly include nitrates, chlorides, fluorides and carbonates. The eutectics of fluoride salts may be utilized in space solar power and molten salt nuclear reactor because of their high heat storage capacity, but with the disadvantage of cost, material compatibility and toxicity [4–6]. Chlorides are attractive due to their high heat fusion and low cost although they are less attractive in terms of high corrosiveness [7]. Carbonates can be used for high temperature latent heat storage applications such as central receiver system, but with high viscidity and easy to decomposition [8,9]. The eutectics of nitrate or nitrite salts have the advantages

* Corresponding author. Tel.: +86 20 39332320; fax: +86 20 39332319.
E-mail address: peng.qiang@mail.scut.edu.cn (Q. Peng).

0306-2619/$ - see front matter Crown Copyright © 2012 Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apenergy.2012.10.048

Nomenclature

CIS	conformal ionic solution	HTF	heat transfer fluid
CSP	concentrating solar power	TES	thermal energy storage
DSC	differential scanning calorimeter	TGA	thermal gravimetric analysis

of low chemical reactivity, low corrosiveness and low cost [10]. Therefore, nitrates or nitrites are suitable for heat transfer and thermal storage material in solar thermal power plants.

There are several commercially available molten salt formulations, mixtures of nitrates or nitrites, and they also have been used for solar thermal systems. The binary solar salt mixture (60 wt.% $NaNO_3$–40 wt.% KNO_3) is used at the 10 MWe solar two central receiver project in California [11] and the indirect TES system for the Andasol plant in Spain [12]. It has the higher thermal stability (600 °C) and the lower cost, but also the higher melting point (220 °C). Hitec (53 wt.% KNO_3–7 wt.% $NaNO_3$–40 wt.% $NaNO_2$) has been used for decades in the heat treating industry. This salt has the lower melting point (142 °C). It is thermally stable at temperatures up to 454 °C, and may be used up to 538 °C for short periods [13]. However, a drawback of these molten salts as HTF is their relatively high melting point and limits the practical applications in CSP applications. A straightforward approach to identifying an improved HTF would be to add constituents to solar nitrate salt that depress the melting point significantly without compromising its properties. The eutectic temperature of $LiNO_3$, $NaNO_3$ and KNO_3 is 120 °C and a Hitec XL mixture of $Ca(NO_3)_2$, $NaNO_3$ and KNO_3 melts at about 133 °C [14]. Recently, some work have been done on more complex salt mixtures. Melting temperatures of the quaternary nitrate salts with Li, Na, K, and Ca cations are below 100 °C [15,16]. Eutectic points of salt mixtures with Li, Na, and K cations and nitrate/nitrite anions are below 80 °C [17–19]. The advanced mixtures consisting of a mixture of nitrate salts of lithium, sodium, potassium, cesium, and calcium have a low melting point of 65 °C [20]. A novel mixtures of inorganic salts with multi-component system (Li, Na, K, Ca/NO_3, NO_2, Cl) show a lower melting point of 53 °C [21]. However, the problems of these salts are the high proportion of nitrate salts of lithium, cesium improves the cost considerably and the addition of calcium nitrate generally increased density and viscosity. As we know, very large quantities (millions of kilograms) of HTF are required for energy storage in 100–200-MW power plants and entail high capital investment costs, so minimizing that cost while maximizing the HTF performance is paramount.

Generally speaking, phase behavior of higher order salt mixtures has been focused largely on experimental methods and directly measuring the phase transitions of a system of salts. However, since measurements are generally expensive, time-consuming and the difficulty of study increases very rapidly with the number of components, it is of interest to be able to predict thermodynamic properties of higher order systems from known theories by using available data for lower order systems. Thus that also is hope that the development of analytical equations which express the thermodynamic properties of multi-component solutions as simple polynomial functions in terms of mole fractions has permitted sophisticated thermodynamic calculations to be performed with the aid of digital computers [22]. Besides, the lack of information for the molten salt at high temperatures, as well as existing databases of thermodynamic salt properties are incomplete, some detailed material properties of the component may be estimated roughly here.

In this paper, in order to maximizing HTF performance while minimizing material cost, the quaternary reciprocal system (K, Na/NO_2, Cl, NO_3) is investigated to identify low melting (low liquidus temperature) mixtures. Firstly, the liquidus temperatures of the quaternary reciprocal system can be calculated a priori using the equations derived on the basis of the CIS theory [23,24]. Then, the mixtures that exhibit a lower melting point are determined to further testing for thermal stability using a thermogravimetric analysis (DSC–TGA) device, the Q600 SDT from TA Instruments (New Castle, Delaware). Approximately 15 mg of each mixture is loaded onto a graphite pan for TGA testing. A TGA heats a sample in a nitrogen environment and continuously measures the sample weight, which typically decreases at higher temperatures as the sample decomposes into gaseous products.

2. Theory

2.1. Calculation of phase diagram

A reciprocal quaternary system [25,26] is defined as one containing two different cations and three different anions (*A*, *B*/*X*, *Y*, *Z*). Even though such a system contains five different ions (A^+, B^+, X^-, Y^-, Z^-) and has six constituent salts (*AX*, *AY*, *AZ*, *BX*, *BY*, *BZ*). It is one restriction on the system, namely, the electroneutrality condition. Thus, one has six constituents, but only four independent components. The choice of the independent components can be arbitrarily made and should not affect the final expressions for the thermodynamic properties of mixing as long as the components contain the five different ions.

The composition of a reciprocal quaternary system *A*, *B*/*X*, *Y*, *Z* is conveniently plotted on a composition prism as shown in Fig. 1. The two triangular bases of the prism represent compositions in

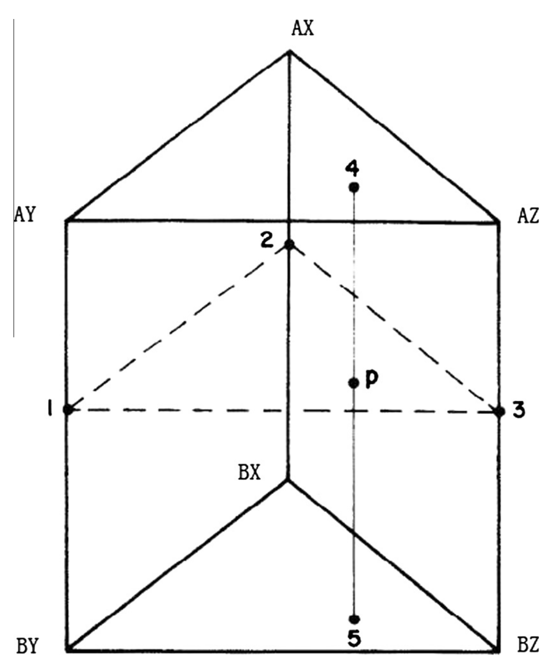

Fig. 1. Composition prism of a reciprocal quaternary system illustrating the geometrical basis of the CIS equation.