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Basic properties of eutectic chloride salts NaCl-KCl-$ZnCl_2$ and NaCl-KCl-$MgCl_2$ as HTFs and thermal storage media measured using simultaneous DSC-TGA

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ABSTRACT

Concentrated solar power (CSP) technologies tend to work at high temperatures for better energy efficiency, which need high temperature heat transfer fluids (HTF) and thermal storage. A good HTF should have low melting point and be thermally stable at high temperatures. A thermal storage medium needs a high heat capacity in order to store more energy in per unit of mass or volume. The objective of this work is to study the basic thermophysical properties of several eutectic molten salts for HTF and thermal storage media, which can work at upper limit temperatures of 850 °C. The eutectic salts are mixtures by NaCl-KCl-$ZnCl_2$, and by NaCl-KCl-$MgCl_2$, respectively. The heat capacity, melting point, and heat of fusion of the eutectic salts at different temperatures were measured using Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) simultaneously. Details of the measurements and obtained experience of operating the equipment are provided in the work. For each of the eutectic salts multiple samples were tested to check repeatability and to minimize random errors. In theoretical analysis, mixing rules from literature was used to estimate the heat capacity of the new HTFs, which showed good agreement with experimental data.

1. Introduction

The world demand for energy has been always increasing, while many economic and environmental issues have risen up through the years due to the use of fossil fuels. Concerns about the global temperature rise as a consequence of fossil fuel consumption become a driving force for development of technologies of renewable energies that are environmental friendly, sustainable, and secure. Solar power has been introduced a couple of decades ago as a clean energy source, but practically it has not been considered economically competitive enough compared to fossil fuels. Compared to conventional fossil-fuel-based thermal power plant, photovoltaic solar power production is limited to sunny time only. During nights and cloudy days the solar power is not available. One solution for this problem is the concentrated solar thermal power (CSP) and thermal storage. If the system is capable of storing solar thermal energy and continuously generating electricity during the nights, the overall cost-effectiveness can be significantly increased.

Through a decade of development, concentrated solar power (CSP) technologies tend to work at higher temperatures, which correspondingly need a high temperature heat transfer fluid (HTF) to transmit the heat from solar concentrator to power plants. At the same time, the HTF should also be used as thermal storage material, if possible. Therefore, a heat transfer fluid (HTF) has to meet some basic requirements for both heat transfer and thermal energy storage in CSP plants, which include:

(1) *Less expensive.* Studies show that the main portion of costs in a CSP plant with a two-tank thermal energy storage system is due to heat transfer fluid and thermal storage system costs (IRENA, 2012; Kuravi et al., 2013). Fig. 1 shows the distribution of the cost of components in a CSP plant in the current technology, where the cost of salt contributes a significant part, which is due to the need of thermal energy storage.
(2) *Low melting point.* If the HTF freezes at a high temperature, freeze protection can be more difficult. This imposes extra maintenance and operating costs during the nights and cold weather (Kearney et al., 2003). Therefore, molten salts with sufficiently lower melting points are preferred in a concentrated solar power plant.
(3) *High boiling point.* Low vapor pressure at high temperature is needed for a HTF, so that the fluid can work at high temperatures but at low vapor pressures as a liquid. Most of the current molten salts in solar power plants work below a temperature of 600 °C. In order to

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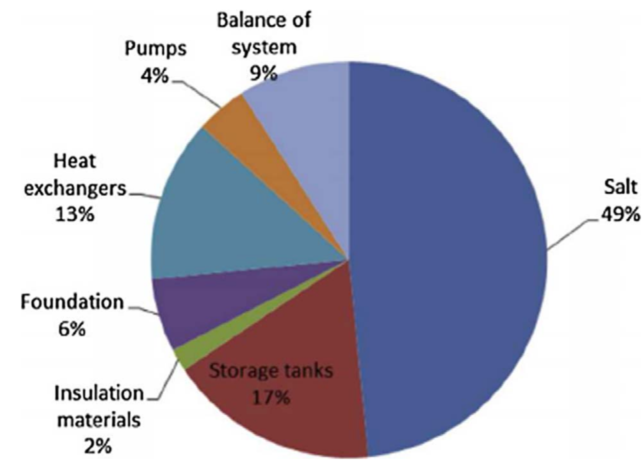

Fig. 1. HTF (salt) shares a dominant portion of the cost in a modern CSP plant with two-tank thermal energy storage (IRENA, 2012; Kuravi et al., 2013).

further increase the efficiency of a CSP plant, we need to raise the operating temperature of the HTF, while still keep its low melting point and low vapor pressure (Kearney et al., 2003). Low vapor pressure of the HTF at high temperatures is also important to the reduction of the cost of pressure vessels (Bauer et al., 2012).

(4) Chemical stability. It is important to use a HTF which is chemically stable at high temperatures and also imposes less corrosion to pipes and containers.
(5) Good thermophysical properties. In order to guarantee an efficient heat transfer between the solar concentrator and HTF, thermophysical properties of the HTF should meet some basic requirements.

As mentioned in Fig. 1, when the HTF is also used for thermal storage, a huge amount is needed. Therefore, the cost of the material is a big issue to be concerned. Oils were used in the early stage as HTFs for CSP technology because of their low melting point and appropriate thermal properties (Brosseau et al., 2006). However, due to the limited working temperature, oil-based HTFs cannot be used for temperatures above 400 °C (Casati et al., 2013). Giostri et al. (2012) compared four different CSP plants and concluded that using synthetic oil as a HTF limits the operating temperature and thermal efficiency. Solar Salts®, as alternative for synthetic oils, can improve the thermal efficiency of parabolic-trough-based CSP for more than 6%. Thermal storage using the same salt is typically added in such a system (Giostri et al., 2012). The effects of cost reduction using Solar Salts® and two-tank thermal storage compared to synthetic oil were reported in Kearney et al. (2003); Llorente Garcia et al. (2011). There are variety of types of molten salts HTF which may provide the possibility to further raise the solar field output temperature. High freezing point of the molten salts (than that of oils) is associated with a higher cost to the system. However, the results (Kearney et al., 2003; Llorente Garcia et al., 2011) show that if a 6 h daily storage is added to the system, one can observe a 14% reduction in electricity costs. The most remarkable advantage of a system working with salt is the higher operating temperature and hence higher overall efficiency than that of using oils.

With the addition of one extra salt component on the basis of Solar Salts®, HitecXL® was introduced as a eutectic ternary molten salt HTF to have lower melting point. Since the HitecXL® salt contains ionic calcium, there is concern about the chemical stability of the nitrate salts that contains calcium. Therefore, Solar Salts® are still popularly used today in CSP systems that have solar concentration towers.

Carbonate salts have been considered for HTF; however, they are not chemically stable when temperature is high, and are also corrosive (Kuravi et al., 2013; Brosseau et al., 2005; Pacheco et al., 2002). A few studies (Kuravi et al., 2013; Fathollahnejad et al., 1993) have shown that fluoride salts are possible candidates for HTFs. Mixtures of sodium, magnesium, lithium, and potassium fluoride salts are thermally stable at temperatures from 680 to 730 °C (Fathollahnejad et al., 1993). However, fluoride salts are relatively toxic compared to many other molten salts (Kuravi et al., 2013; Fathollahnejad et al., 1993). Liquid metals are another group of candidates for HTFs. They have wide operating temperature range and low melting point (Pacio et al., 2013; Pacio and Wetzel, 2013). The most important concern about liquid metals is that they are heavy and more expensive than other heat transfer fluids, and corrosion to metal pipes and containers is also a big concern.

Table 1 is an overall comparison among all materials that are considered as HTFs in CSP. These materials can be classified as three groups, organic HTF, molten salts, and liquid metals.

Through several years of screening study in the present research team, eutectic salts by mixture of NaCl, KCl, ZnCl2 and MgCl2 have

Table 1
A summary of heat-transfer fluids and major properties for thermal storage application.

Heat transfer fluid	Melting point (°C)	Maximum operating temperature (°C)	Flammable/toxic	Corrosive	Ref.
Synthetic oil (Therminol)	15	400	Flammable	Not-corrosive	Pacheco et al. (2002)
Mineral oil (Xceltherm)	10	300	Flammable	Not-corrosive	Pacheco et al. (2002)
Silicon oil	40	400	Flammable/ explosive	Not-corrosive	Pacheco et al. (2002)
Solar salt®	220	600	Non-flammable	Low degree Corrosive	Kearney et al. (2003)
HitecXL®	120	450	Non-flammable	Low degree Corrosive	Kearney et al. (2003)
Hitec®	142	535	Non-flammable	Low degree Corrosive	Kearney et al. (2003)
Calcium carbonate	290	400	Not stable	Corrosive	Kuravi et al. (2013); Pacheco et al. (2002)
Eutectic ternary mixture ($CaNO_3 + NaNO_3 + KNO_3$)	160	500	Stable up to 460 °C	Low degree Corrosive	Kuravi et al. (2013)
Eutectic ternary mixture ($LiNO_3 + NaNO_3 + KNO_3$)	120	600	Stable up to 550 °C	Corrosive	Kuravi et al. (2013)
Liquid lead–bismuth eutectic (LBE)	125	1670		Corrosive	Pacio et al. (2013)
Liquid Na	98	883	Very reactive	Corrosive	Pacio et al. (2013); Pacio and Wetzel (2013)
Sn	232	2687	Stable	Corrosive	Pacio and Wetzel (2013)
Ternary mixture (NaCl-KCl-$ZnCl_2$)	204–229	850	Non-flammable Non-toxic Stable up to 1000 °C	Low degree Corrosive	Li et al. (2016); Zhang and Li (2017)