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An experimental study of a non-eutectic mixture of KNO_3 and $NaNO_3$ with a melting range for thermal energy storage

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HIGHLIGHTS

- Enhanced capacities are possible by using anhydrous salt mixtures in the melting range.
- As a suitable binary salt mixture was sodium nitrate and potassium nitrate identified.
- A distribution of the enthalpy of fusion within the melting range was determined.
- Cyclic stabilities of the selected salt mixture were measured.
- The effect of dimension on the cyclic stability was examined in various test rigs.

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ABSTRACT

Thermal energy storage is a key technology for reduced cost solar thermal power generation. This high-temperature application requires storage operation above 100 °C. Possible options are sensible, latent and thermochemical heat storages. A combination of sensible and latent heat storage seems a promising option for thermal energy storage with an increased specific heat capacity. Salt mixtures with a melting range as opposed to a melting point combine the effects of both latent and sensible heat storage. These provide the possibility of utilizing not only latent but in addition sensible heat during the melting and solidification process. The present paper focuses on a binary mixture of 30 wt.% potassium nitrate (KNO_3) and 70 wt.% sodium nitrate ($NaNO_3$). The measurement systems include a differential scanning calorimeter, a melting point apparatus, a custom-built adiabatic calorimeter and a lab-scale storage unit. The sample masses ranged from about 20 mg to 156 kg. Tests with the lab-scale storage unit indicate that salt mixtures with a melting range may be successfully utilized in large-scale applications.

1. Introduction

Thermal energy storage systems are one possibility for solar thermal power plants to compensate temporary divergences between the availability of sunlight and the demand for electricity. During periods of high solar insolation, more heat may be produced than is required for electricity generation. Therefore, some of the heat transfer fluid is diverted to the storage system and heats the thermal storage material. In order to produce electricity on demand in the concentrating solar power (CSP) plant during a period of low solar insolation, the heat transfer fluid can be heated by discharging the storage system. Another application for high-temperature storage is the storage of process heat in industrial plants. Heat that is discharged in an industrial batch process can be stored in a temporary buffer storage unit. Later, the available heat can be utilized for the same or another industrial process with a suitable temperature level. The choice of the appropriate storage material depends on various aspects. They include the type of heat transfer fluid, the temperature level and the storage capacity, as well as the charge and discharge power.

A favourable storage material for a two-phase heat transfer fluid such as water/steam system is an isothermal energy storage material. Phase change materials (PCM) are able to store latent heat at nearly isothermal conditions and can fulfil this demand. A single-phase heat transfer fluid is optimally paired with a sensible heat storage material that is able to store heat in the desired temperature range.

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Nomenclature

$c_{p,salt}$	average isobaric specific heat capacity of the salt in kJ/(kg K)
$c_{v,oil}$	average isochoric specific heat capacity of the oil in kJ/(m^3 K)
m_{salt}	salt mass in kg
ΔT_{salt}	temperature rise between start and end of loading in K
ΔT_{oil}	temperature difference between oil inlet and oil outlet in K
t	time for loading in h
$\dot{V}_{oil}$	volumetric flow rate of oil in m^3/h

The focus of this work is the development of an improved storage material for sensible heat from a single-phase heat transfer fluid such as thermal oil or superheated steam. The amount of stored sensible heat in storage materials such as ceramics, concrete and molten salt simply increases with the temperature of the material. Salt mixtures with a melting range as opposed to a melting point not only utilize sensible heat storage, but they additionally utilize latent heat in the form of the enthalpy of fusion. The advantage of combined sensible and latent heat storage is a high energy density as compared to simple sensible heat storage materials. In other words, the combined storage of sensible and latent heat is a promising option for increasing the energy density of storage materials.

The underlying principle is that a binary salt mixture with a non-eutectic composition both solidifies and melts over a temperature range as opposed to at a fixed temperature. A eutectic composition has its melting temperature at the minimum of a binary eutectic system. In this work, the term melting range describes the region of phase transition where solidified salt crystals and molten salt co-exist in equilibrium. With increasing temperature during the charging process, the fraction of molten salt becomes larger because the charged heat is stored as enthalpy of fusion. This paper presents a material investigation of an anhydrous non-eutectic binary salt mixture consisting of 30 wt.% potassium nitrate and 70 wt.% sodium nitrate. That material is analyzed with respect to its suitability as a heat storage material. The work focused on the investigation of the distribution of the enthalpy of fusion in the melting range and phase separation phenomena with repeated partial melting and solidification cycles (cyclic stability). Various test facilities measuring sample masses from 20 mg to 156 kg were used.

2. The salt mixture KNO_3–$NaNO_3$

Salt mixtures of sodium nitrate and potassium nitrate are well known. These mixtures are industrially used as raw material in heat treatment baths and in solar thermal power plants as a heat transfer fluid [1] or a heat storage medium [2]. For example, a salt mixture of sodium nitrate and potassium nitrate is used as the thermal energy storage material in the solar power plant Andasol 1 with a storage material mass of 28 000 kg. That non-eutectic binary salt mixture consists of 60 wt.% $NaNO_3$ and 40 wt.% KNO_3 and solidifies in the temperature range of 222 °C to about 240 °C. With a cold tank temperature of 291 °C and a hot tank temperature of 384 °C, the salt mixture is only used in the liquid phase in this installation [1]. Setting the lower temperature limit safely above 240 °C in the thermal storage unit is necessary to avoid local solidification.

For latent heat applications, Tamme et al. selected the eutectic mixture of the binary system KNO_3–$NaNO_3$ due to its favourable properties in terms of handling, cyclic stability and costs [3]. These advantages more than compensated the lower storage density in comparison with other candidate materials such as alkali metal chlorides and hydroxides. Another major disadvantage of the selected salt mixture is its low heat conductivity [4]. For example, research activities of Lopez et al. [5] investigate the use of expanded natural graphite for increasing the low heat conductivity and in theoretical studies of Kurnia et al. [6], the applications of an improved design using heat transfer structures and the use of multiple PCMs are discussed.

In the present paper, we investigate a non-eutectic salt mixture consisting of 70 wt.% sodium nitrate and 30 wt.% potassium nitrate (i.e. 73.5 mol% $NaNO_3$ and 26.5 mol% KNO_3). This mixture has a larger melting range (220–260 °C) than the salt mixture used in the solar plant Andasol 1. In the following, some information about the phase diagram is provided.

2.1. Phase diagram of $NaNO_3$–KNO_3

Valuable overviews of the salt mixture $NaNO_3$–KNO_3 have been given by Rogers and Janz [7], Berg and Kerridge [8] and Zhang et al. [9]. An extensive review of measurements concerning the general type of the phase diagram $NaNO_3$–KNO_3 was reported by Jriri et al. [10]. The KNO_3–$NaNO_3$ phase diagram is also found in the FactSage Ftsalt salt database [11]. Two types of thermochemical databases are the basis of the FactSage software package [12]. Kramer and Wilson studied the binary phase diagram of KNO_3 and $NaNO_3$ using a differential scanning calorimeter (DSC) and additionally delivered an overview of the distribution of the heat of fusion in the melting range depending on the composition of the mixture [13]. Wiedemann and Bayer also studied the phase diagram of KNO_3–$NaNO_3$ and the distribution of the heat of fusion in the melting range in a thermo-microscopy unit with DSC [14].

The salt mixtures consisting of KNO_3 and $NaNO_3$ undergo a solid–solid transition at around 110 °C [10]. However, the solid–solid transition was not considered in the work presented here. The system has a minimum melting temperature of 223 °C (54 wt.% KNO_3 and 46 wt.% $NaNO_3$) [5]. The exact shape of the solidus line is still under discussion [8]. The latest investigations of the solidus line indicate a salt mixture with a flat solidus line [9]. Measured thermophysical values for the eutectic composition of KNO_3–$NaNO_3$ have been summarized by Bauer et al. [15].

2.2. Investigated salt mixture

Fig. 1 shows a part of the KNO_3–$NaNO_3$ phase diagram and the composition of the investigated salt mixture.

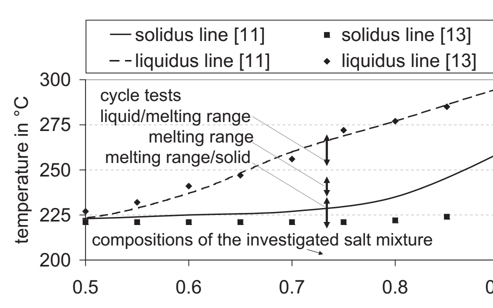

Fig. 1. Details of the phase diagram KNO_3–$NaNO_3$ with the investigated mixture based on data from Kramer and Wilson [13] and the FactSage FTsalt salt database [11].