



International Conference on Concentrating Solar Power and Chemical Energy Systems,
SolarPACES 2014

Assessment of novel inorganic storage medium with low melting point

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Abstract

Thermal energy storage is essential to increase the efficiency of industrial processes by waste heat utilization and to enable future solar electricity generation by solar thermal power plants. Taking into account the need to reduce the emission of CO₂ and to save conventional energy both processes are indispensable.

However with the (direct) storage media used so far the range of applications is limited. Currently organic media are used which are not appropriate at high temperatures due to high vapor pressures, low flash points and low thermal stabilities. Those challenges can be tackled by using inorganic media. Yet applications are limited so far because state of the art inorganic storage materials cannot be used below 100 °C requiring expensive anti-freeze systems.

This paper presents a novel storage medium combining advantages of both organic media and state of the art inorganic media. This storage medium was developed by a novel method [1] and was assessed by the investigation of the most essential thermal properties, such as the heat capacity, viscosity, phase diagram around the eutectic point as well as the thermal stability. To get an idea about the thermal stability, state of the art TGA measurements were performed which suggested a higher thermal stability as compared to organic media.

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Peer review by the scientific conference committee of SolarPACES 2014 under responsibility of PSE AG

Keywords: direct storage medium; nitrate salts; thermal gravimetry analysis; phase diagram; liquidus temperature

1. Introduction

The raising world energy demand resulting in global warming and reduction of primary energy source requires optimization of energy consuming processes as well as rapid development of renewable energies. (Direct) sensible storage media are one of the most import elements to increase the efficiency of industrial processes and to allow the

dispatchability of thermal energy, thereby allowing thermal power to generate electricity on demand. However the efficient use of this methodology still requires optimization of the materials being involved in the conversion of the thermal energy into electricity. State of the art media suffer either low thermal stabilities and challenging handling due to high vapor pressure and low flash points in case that organic media are used or high solidification temperatures in the case that molten salts are used. By optimization of molten salts, with thermal stabilities exceeding those of oils, in terms of solidification temperature, the efficiency of the process can be enhanced. Particularly, periods with low solar radiation require low melting points of the (direct) storage medium to reduce freezing problems. Additionally, a reduction of the melting temperature also increases the usable temperature range which is proportional to the storage capacity.

Therefore, one trend in the latest development of thermal power storage media was to synthesize molten salts with reduced melting temperature while still featuring appropriate properties in terms of handling, toxicity and costs. For those reasons the research did focus on nitrate/nitrite salts.

A reduction in the melting temperature can usually be achieved by the addition of new ions to the salt. This tendency is based on a reduction of the chemical potential of the molten salt upon the addition of another component, resulting in a decreased intersection point of the temperature dependent chemical potential in the solid and liquid state as is shown in Fig. 1.

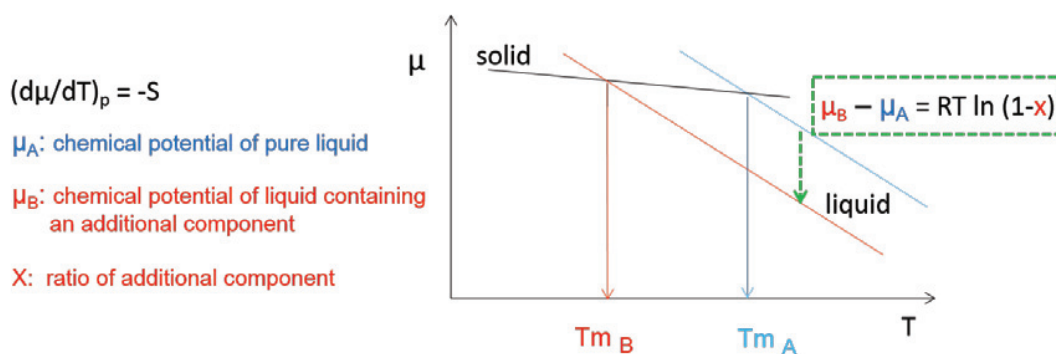


Fig. 1 Reduction of melting temperature following the addition of new components

Even though calculations are possible for ternary salts i.e. by FactSage, iphase diagrams of complex salt mixtures cannot be calculated accurately. Therefore experiments to find the appropriate composition are required. By using high throughput screening methods multiple component nitrate/nitrite salts with decreased solidification temperatures have been reported as shown in Table 1.

Table 1. Overview of alkali nitrate/nitrite salt systems for CSP.

Ions	Classification	Example and minimum melting temperature
2	Single salt	NaNO ₃ ~ 306 °C; KNO ₃ ~ 334 °C
3	Binary system, common anion	KNO ₃ -NaNO ₃ ~ 222 °C ("solar salt" system) [2,3,4,5,6]

4	Ternary reciprocal Ternary additive, common anion	K, Na // NO ₂ , NO ₃ ~ 142 °C (Hitec) [7,8,9,10,11,12,13,14] Ca(NO ₃) ₂ -KNO ₃ -NaNO ₃ ~ 130 °C (HitecXL) [15,16,17,18,19,20,21]
5	Quaternary additive, com. anion Quaternary reciprocal	Ca(NO ₃) ₂ -KNO ₃ -LiNO ₃ -NaNO ₃ ~ 105 °C [22] Li, Na, K // NO ₂ , NO ₃ ~ 80 °C [23]

As the melting temperatures of the novel salt formulations still exceed the temperatures reached in specific applications there was still need for the optimization of salt mixtures.

Thus, at DLR a novel method was used to develop a novel molten salt with a solidification temperature less than 100 °C, the molar composition of which is 31,16 % NO₂⁻, 20.55 % NO₃⁻, 14 % Li⁺, 9.6 % Na⁺, 21 % K⁺ and 3.6 % Ca²⁺ [1]. In this paper the salt is characterized by thermodynamic properties which are essential to assess its value as thermal storage medium. For the optimization not only the solidification point is of importance but also the thermal stability which correlates with the efficiency of connected processes and which increases the usable temperature range. The temperature range is directly proportional to the storage capacity. Therefore, a high thermal stability is essential and requires careful investigations. The second parameter directly affecting the storage capacity is the specific heat capacity which needs to be analyzed as well. Another property comes into play when launching the plant initially. In case of multicomponent salts the addition of the single components resulting in an accurate composition is challenging and therefore it is essential to test the melting properties close to the eutectic point by the characterization of phase diagrams. This allows to assess the effect of an altered composition on the solidification temperature. If the effect will be low the filling process can be simplified in a similar way as for the solar salt. Because the liquidus in the 40/60 wt% mixture deviates only by 20 K from the melting point of the eutectic composition (KNO₃: 54 wt%, NaNO₃: 46 wt%) , the storage tank can be filled with full packages, in the ratio 4:6, without the need of weighting the salt on site. Additionally knowledge of the viscosity is important to evaluate the feasibility of the pumping process.

Nomenclature

TGA	Thermogravimetry Analysis
MS	Mass Spectrometry
DSC	Differential Scanning Calorimetry
c _p	Heat capacity at constant pressure

2. Materials and methods

2.1. Measurement of the Heat Capacity and phase transitions

For the determination of the heat capacity as well as the phase transitions a commercial heat flux type differential scanning calorimeter (DSC) was utilized (Netzsch DSC404). This device is equipped with an intracooler and contains a constantan (CuNi) disc sensor. The heating rate was 10 K/min and the atmosphere was nitrogen (25 ml/min). The sample mass of approximately 15 mg was checked before and after the DSC measurements with a microbalance. Aluminum crucibles (mass of crucible: 61 mg) with a lid were used. Sapphire was utilized as heat capacity reference material. The 2nd cycle was used for analysis of the data. The temperature calibration was performed with the substances Hg, In, Sn, Bi and Zn.

2.2. Investigation of the thermal stability

The investigation of the thermal stability was examined by TG/MS measurements using a commercial system (Netzsch STA449). For those measurements a heating ramp of 2 K/min was used. The atmosphere was pure nitrogen. The gas flow rate was kept at 100 ml/min. The sample mass of around 30 mg was checked before and after the TG measurements with a microbalance to confirm mass losses. Platinum crucibles without a lid were used.

2.3. Determination of viscosity

For the measurement of the viscosity a commercial shear rheometer was utilized (Anton Paar MCR 501). This device is equipped with a cylinder of a diameter and height of 24 mm and with a distance between inner and outer cylinder of 1 mm. Measurements were performed at a torque of 500 μ Nm. The viscosity was determined up to 400 °C with a heating rate of 2 K/min.

3. Results and discussion

Previous work focused on the development of a new method to find nitrate/nitrite salts with a low solidification point in order to optimize sensible storage media especially in the case of direct storage media which means that the same medium is used in the pipes for the heat transfer. In the present paper we describe additional properties which are essential for effective thermal energy storage.

3.1. Thermal stability

High thermal stabilities are essential for high conversion efficiencies of connected processes and to increase the usable temperature range and thereby the storage capacities. Mass losses of the salt may occur due to three mechanisms: nitrite formation in the melt and oxygen (1) release, alkali metal oxide formation in the melt and nitrogen oxide release (2) as well as vaporization of the salts.

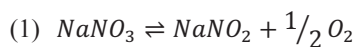


Fig. 2 shows results of TG measurements with concomitant analyses of the gaseous phase by a connected mass spectrometer.

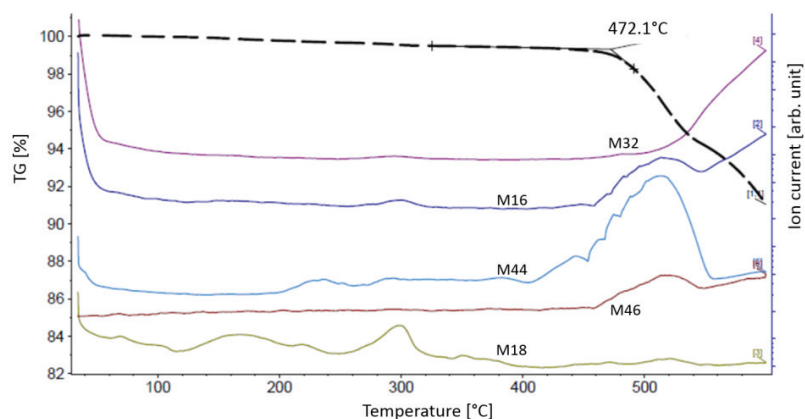


Fig. 2 TG/ MS results of Ca, Li, Na, K/NO₂, NO₃; the dashed line represents TG data, the remaining curves MS data

The initial mass loss of approximately 1 % at temperatures below 300 °C correlates with the release of water, as is shown by the signal in the MS with a mass of 18. The formation of oxygen with mass numbers of 16 and 32 as well as nitrogen oxide N_2O and NO_2 with a mass number of 44 and 46 only starts at temperatures of around 450 °C. The formation of those gases correlate with an onset of the TG curve at 470 °C. The heating rate was low with 2 K/min, for which the onset is close to decomposition temperatures measured with static experiments. Still dynamic TG measurements rather give semi-quantitative decomposition results and are best suited to compare the onset temperatures of different salts. Therefore the TG experiment was performed for solar salt at the same conditions. The result is shown in Fig. 3.

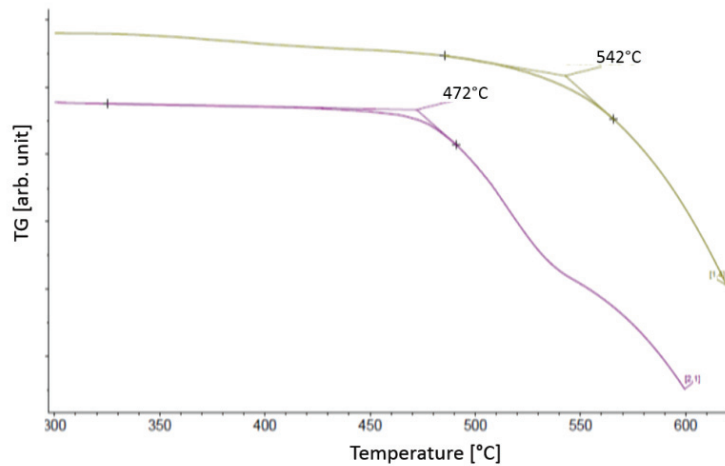


Fig. 3 TG measurements of solar salt (top) and the Ca, Li, Na, K/NO₂, NO₃ system (bottom) acquired with a heating rate of 2 K/min

The decrease in thermal stability relative to solar salt is 70 K, when measured and analyzed at the same conditions. The reduction in the upper operating temperature therefore is significantly less than the decrease in the solidification temperature (approximately 140 K, as is shown in Fig 4 and [5]), resulting in a larger usable temperature range and storage capacity of this salt formulation.

3.2. Heat capacity

The storage capacity Q , being defined as $Q = m c_p \Delta T$, not only is proportional to the usable temperature range but also to the heat capacity. Therefore the investigation of the heat capacity is important. Fig. 4 shows the heat capacity in the range of 65 °C to 230 °C.

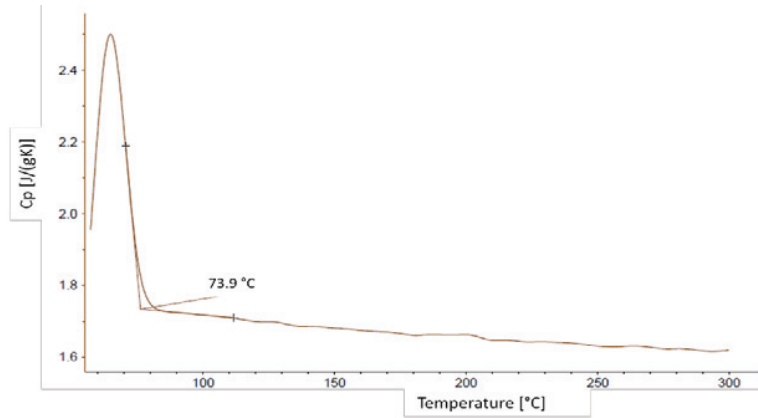


Fig. 4 Cp measurements of the Ca, Li, Na, K/NO₂, NO₃ system

The heat capacity of the new salt formulation is approximately 10 % higher than that of solar salt. Taking into account that the temperature range is increased by 23 % as well, the storage capacity even is increased by 35 %.

3.3. Viscosity

Besides the above mentioned thermal properties the viscosity is an important parameter for direct storage media applications with molten salt pumping. Therefore the viscosity of the novel salt formulation has been determined for temperatures ranging from the phase transition up to 400 °C as is shown in Fig. 5.

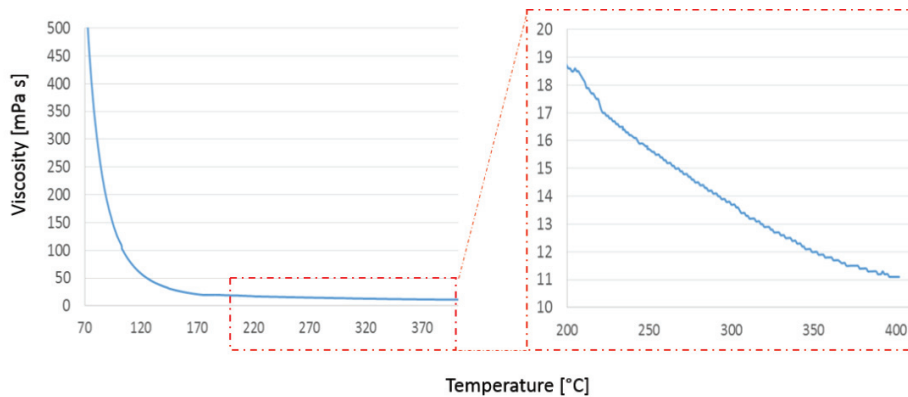


Fig. 5 (a) viscosity of Ca, Li, Na, K/NO₂, NO₃

The viscosity strongly depends on the temperature. At temperatures between 200 °C and 400 °C it is around 15 mPa s and roughly one order of magnitude higher than that of solar salt (Fig. 6). At temperatures close to the phase transition it reaches 500 mPa s. So far no investigations on the effect of the viscosity on the pumping process exist. Therefore this effect needs to be investigated in future.

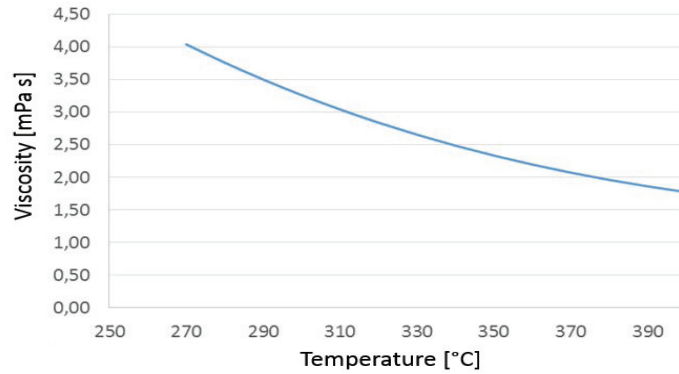


Fig. 6 Viscosity of solar salt as reported by [24]

3.4. Phase diagram close to the melting temperature

The investigation of the effect of a modified composition on the solidification temperature is essential to get an idea of the required precision of the storage filling process. Therefore selected slices of the multidimensional phase diagram close to the eutectic point were measured. The evolution of the liquidus temperature with increasing ratio of potassium and with increasing ratio of sodium is shown in Fig. 7 a) and b) respectively.

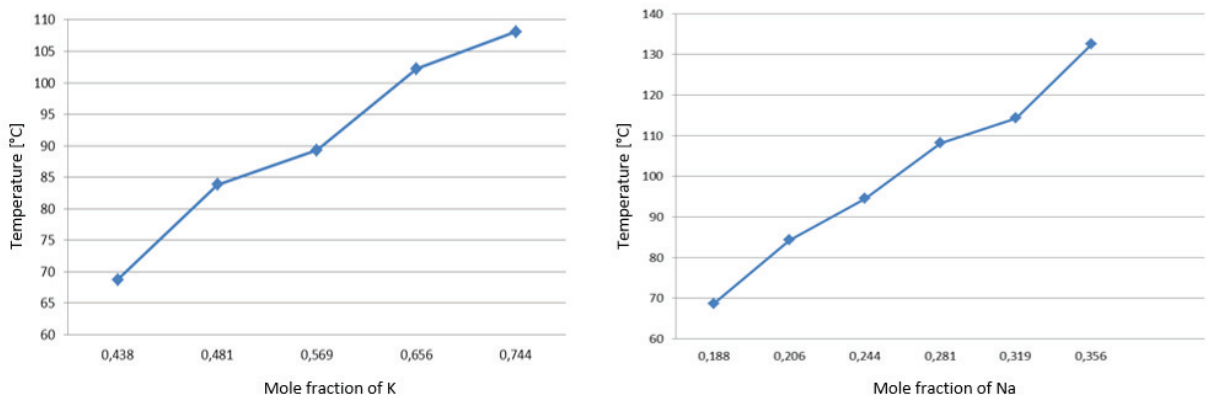


Fig. 7 Selected dimensions of the phase diagram of the Ca,Li,Na,K//NO₂,NO₃ system

The results show that in this multicomponent system the effect of the cation variation on the liquidus temperature is similar to the effect in the Na,K//NO₃ system (Fig. 8).

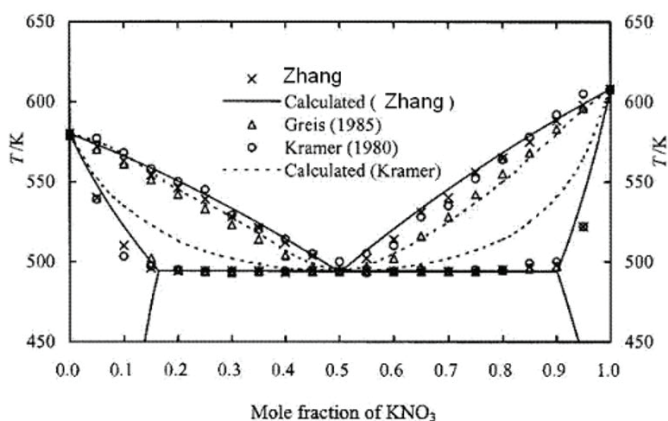


Fig. 8 Overview of different phase diagrams of the system $\text{KNO}_3\text{-NaNO}_3$ [5]

4. Summary and conclusion

The studies presented in this paper did characterize a novel nitrate/nitrite salt mixture to assess its utilizability as storage medium for thermal energy storage technology. It was shown by thermogravimetry with coupled gas analysis (MS) that even though the solidification point is close to ambient temperature, the thermal stability still exceeds $400\text{ }^\circ\text{C}$ in nitrogen atmosphere. Therefore this salt system allows high operating temperatures of a direct storage material reducing the requirement of elaborated anti-freeze systems significantly. Additionally, the increased usable temperature range increases the storage capacity by 23 %. Because the heat capacity of the novel salt is higher than that of the state of the art solar salt, the storage capacity is increased even up to 35 %.

Furthermore, phase diagrams of this system have been measured to assess the effect of an altered composition on the solidification temperature. It could be shown that the phase diagram close to the eutectic point when changing the ratio of potassium and of sodium is similar to that of solar salt. Thus the filling process does not requires specific measures.

Finally, the viscosity has been investigated which was shown to be one order of magnitude higher than the viscosity of solar salt for temperatures ranging from $200\text{ }^\circ\text{C}$ to $400\text{ }^\circ\text{C}$. For temperatures close to the eutectic point the viscosity approaches the operating limits of state of the art pumps. Overall the study presented in this paper shows that the storage capacity can be increased by the $\text{Ca, Li, Na, K//NO}_2, \text{NO}_3$ system as well as the efficiency of power plant process due to the increased thermal stability as compared to organic storage materials.

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