



High-temperature stability of nitrate/nitrite molten salt mixtures under different atmospheres



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HIGHLIGHTS

- New methodology was proposed to evaluate the thermal stability of molten salts.
- Long-term thermal stability was determined for molten nitrate/nitrite mixtures.
- The effect of nitrogen-oxygen atmospheres on nitrate molten salts was studied.
- Solar Salt and lithium mixtures are stable under both, nitrogen-oxygen atmosphere.
- Hitec molten salt is stable only under nitrogen atmosphere.

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ABSTRACT

Molten salts are widely used as thermal energy storage media in the Concentrating Solar Power (CSP) technologies. The melting point and the thermal stability of the salt determine the applicable temperature range of the storage system. The focus of this paper is to evaluate the effect of different gas atmospheres on the thermal stability of binary Solar Salt and two ternary salt mixtures containing lithium nitrate (Lithium mixture) and sodium nitrite (Hitec). The isothermal stability experiments were carried out at 550 °C during 500 h and the results show that the initial decomposition reaction of nitrate to nitrite depends strongly on the gas atmosphere. It is observed that changes in the nitrate-nitrite-ratio are the key parameters influencing the melting temperatures of the salt mixtures. For example, for experiments with oxygen in the atmosphere a large increase of the liquidus temperature of the Hitec mixture was observed. Metal oxides are formed during the irreversible decomposition of nitrite-ions but are found to affect the solidus and liquidus temperature of the salt mixtures only marginally. No carbonate formation was detected according to titration analysis of the salt mixtures in our experiments due to the absence of carbon dioxide in the atmosphere.

1. Introduction

Thermal energy storage is an indispensable component when regarding issues of managing energy considering the discontinuity of the energy supply and demand [1,2]. The storage can be either in the form of sensible heat by using solid or liquid storage media, latent heat storage by using phase change materials or thermochemical storage through chemical reactions [3–5]. Sensible heat storage liquids including oil-based fluids, pressurized water and, molten salts are widely used high-temperature media. For dispatchable operating Concentrated Solar Power (CSP) systems involving thermal energy storage, molten salts are the most common option as storage media, whereas parabolic trough systems most commonly utilize thermal oil as heat transfer fluid.

Molten salts are challenging due to undesired freezing events when exposed to room temperature, however, advantages of molten salt compared to thermal oil include low costs, high thermal stabilities, and low vapor pressures [6,7]. The maximum operation temperature of thermal oil (currently around 400 °C [6]) limits the Rankine cycle efficiency of the power block. From a thermodynamic point of view, higher operation temperatures of the parabolic trough field are desirable to increase the power block efficiency. In future, molten salt could operate at temperatures up to 550 °C as heat transfer fluid in trough or linear Fresnel systems [6,8]. This could increase the Rankine cycle efficiency of the power block of a trough plant from 37.6% to 40% by using molten salts instead of thermal oil [9]. Furthermore, there are some capital cost savings feasible for the molten line-focusing

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installations. Expensive synthetic thermal oil can be replaced by cost-efficient molten salts. Also, state-of-the-art systems with thermal oil as heat transfer fluid and molten salt storage systems show some power block efficiency losses due to temperature differences in the heat exchanger during charging and discharging. Projects in the MW scale such as Andasol 1, 2 and 3 (each 50 MW electrical power) have been operating in the last years in Spain [10]. In these cases, indirect 2-tank storage systems use thermal oil as heat transfer fluid, a heat exchanger from thermal-oil to molten salt and a thermal energy storage system with molten salt.

Parabolic trough systems with molten salt as heat transfer fluid and heat storage medium fully avoid this heat exchanger with capital cost savings and efficiency benefits in the power cycle [11]. Besides, the direct concept has been deployed using molten salts as the working fluid in both, parabolic trough and central receivers, also known as solar tower [12–14]. At present, parabolic trough collectors occupy more than 82% of the global CSP installations [15]. However, solar power tower systems are more preferred in future trends since higher efficiencies can be achieved converting heat into electricity at higher temperatures as commercially tested in installed solar power plants such as Gemasolar 20 MW [16].

The sensible heat storage concept considers the amount of energy stored as the mass of storage material, the specific heat capacity and the temperature change ($Q = mc_p\Delta T$) [3], making the operating temperature range of molten salts an important factor in the development of these systems. Salt mixtures which operate in a storage system with a larger ΔT reduce the amount of salt and hence the capital costs of a thermal energy storage system.

Among nitrate salt mixtures used as heat storage media, Solar Salt and Hitec are the most commonly used [17,18]. Solar Salt is a binary mixture of 40 wt% KNO_3 -60 wt% NaNO_3 and it is inexpensive compared to other storage fluids, although it starts to solidify at about 250 °C, the typical minimum operation temperature is about 290 °C and the maximum operating temperature given in the literature is 585 °C [3]. Hitec is a ternary mixture of 53 wt% KNO_3 -7 wt% NaNO_3 -40 wt% NaNO_2 with a melting point of 142 °C [3], however the operating temperature is limited by the atmosphere used, for example to a maximum operating temperature under air of around 454 °C in long-term use and up to 528 °C in short-term use [10,19]. Nevertheless, the main challenge in Hitec salt is the prevention of nitrite oxidation by oxygen since this salt contains 40 wt% NaNO_2 making it necessary to protect the salt above 300 °C with inert gas [20]. The development of new molten salt mixtures with melting temperatures lower than those currently used for TES applications is indispensable for future more powerful CSP plants. Therefore, other nitrates such as LiNO_3 have been added to these mixtures in order to decrease the melting temperature, thereby increasing the working temperature range [17,21]. For example, the eutectic mixture composed of 52 wt% KNO_3 -18 wt% NaNO_3 -30 wt% LiNO_3 exhibits a melting point of 120 °C [22] and can be used up to 550 °C according to Bradshaw in the absence of atmospheric CO_2 [23]. The advantages of using ternary mixtures in CSP plants are the low risk of freezing compared to Solar Salt, since ternary mixtures have considerably lower liquidus temperatures [9]. Molten salt mixtures with lower melting temperatures compared to Solar Salt could reduce the risk of freezing and decrease thermal losses due to lower standby operation. Hence, for CSP systems larger temperature differences between the cold and hot tank of the thermal storage system improves the efficiency by extending the operating temperature range, as well as a higher output temperature in the solar field increases the efficiency of the power block by minimizing operation losses [24,25]. It is known that the heat transfer fluid temperature rise in the collector field can increase up to a factor of 2.5 for a plant with salt [26,27].

Thermal stability of the salt mixtures is an important challenge at high temperatures; therefore, many studies investigate the decomposition of nitrate salts. Therein, understanding the thermal decomposition mechanisms, mainly given by the reaction in Eq. (1) and the

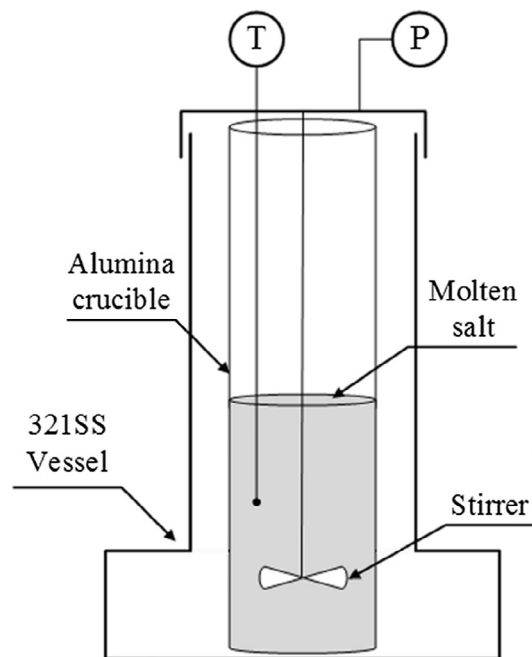


Fig. 1. Schematic of the experimental setup used for isothermal stability experiments.

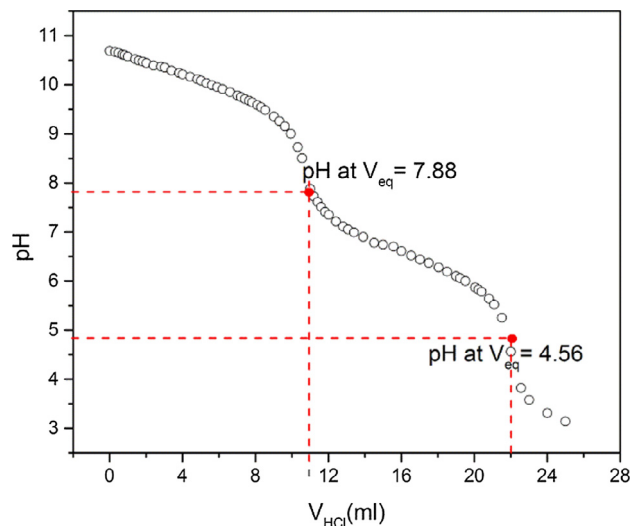


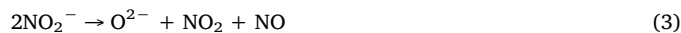
Fig. 2. Acid-base titration calibration curve of Na_2CO_3 with 0.01 mol/l HCl solution.

equilibrium constant (K_1) in Eq. (2), has been a major goal [28].



$$K_1 = [\text{NO}_2^-](\text{P}_{\text{O}_2})^{1/2}/[\text{NO}_3^-] \quad (2)$$

Subsequently, secondary decomposition reactions of the intermediate nitrite formed and the oxides in the melt may occur according to Eq. (3) [19,29].



Isothermal storage data are rare, and the salt chemistry of nitrate salt systems is still not fully understood under isothermal conditions. As a consequence further research is important to determine the nitrate and nitrite content which depend strongly on the atmosphere used as well as the composition of the salt, temperature and other experimental conditions [30].

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