

# Enhancing the Thermal Stability of Solar Salt up to 600°C in Extended Lab-Scale Experiments

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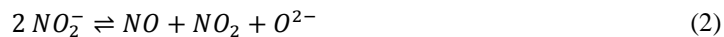
**Abstract.** Future trends push TES towards higher temperatures to increase solar-to-electricity conversion efficiency and novel storage materials are often considered the only viable option. To date these candidates suffer from either high costs (carbonate salts containing Li<sup>+</sup>) or severely attack structural materials (chloride salts) and are far from industrial implementation. An alternative approach is investigated in our work – the use of the classical Solar Salt with sophisticated gas management which selectively shifts the chemical equilibrium to the stable nitrate-side of the decomposition reaction. We demonstrate that the thermal stability of conventional Solar Salt (60-40wt % NaNO<sub>3</sub>-KNO<sub>3</sub>) is substantially increased when the storage system including the gas system is simply but effectively sealed. The key to this novel data is the unique feature of in-situ sample extraction and post-analysis that allows for a quasi in-situ determination of molten salt stability in terms of nitrite and oxide ion formation. Our investigations present clear evidence on the enhanced thermal stability at an experimental scale of about 100 g that is two magnitudes larger than conventional thermal analysis experiments.

## 1. INTRODUCTION

Thermal Energy Storage (TES) is a vastly growing complementary technique in the field of concentrating solar power, storage of industrial waste heat and bulk electro thermal energy storage (Carnot batteries).<sup>1</sup> The use of nitrate salts such as conventional Solar Salt (60-40wt % NaNO<sub>3</sub>-KNO<sub>3</sub>) has proven successful even for TES in the gigawatthour-scale. It serves as heat transfer fluid (HTF) and storage medium simultaneously but its operating temperature range is limited between 290 °C and 560 °C. The high temperature limit of the molten salt directly affects the volumetric storage capacity and the efficiency of the coupled steam cycle. The high temperature limit of Solar Salt has been investigated at different scales and there is a consensus, for commercial CSP projects, that under open atmospheres this limit is at around 565 °C. At this temperature it is assumed that decomposition reactions, reflected by changes in the molten salt chemistry are negligible. Accordingly, the thermo-physical properties and corrosiveness of the molten salt are thought to remain unchanged leading to the assumption that Solar Salt is *thermally stable* at this temperature. Decomposition reactions in nitrate salts are however of increasing interest above 560 °C.<sup>2-4</sup> One crucial reaction is the formation of the nitrate-nitrite equilibrium according to the anion reaction (1)<sup>3,5</sup>. The reaction can be observed at temperatures between 290 °C and 560 °C and at any scale and typically results in the formation of a stable nitrite-nitrate ratio over time.



The equilibrium depends on the oxygen partial pressure above the melt and on the applied temperature. Above 500 °C further decomposition of the nitrite ion to form oxide ions is known to occur.<sup>3</sup> Several reaction paths are feasible but all of them result in the formation of oxides of the type Na<sub>2</sub>O, Na<sub>2</sub>O<sub>2</sub> or K<sub>2</sub>O, depending on cation types, their composition and the exact molten salt temperature (see e.g. ref. <sup>6</sup>). Equation (2) shows one example for the (nitrite ion) decomposition which is commonly accepted within the community:



The evolution of (toxic) nitrous gases as decomposition products represents one of the major environmental and technical concerns, especially since currently large-scale, high-temperature TES systems (e.g. 560°C) based on

nitrate salts typically operate with an atmospheric gas cover with regular exchange of ambient air. Yet, the formation of the oxide ion species ( $O^{2-}$ ) also presents a concern since this species is supposed to aggravate corrosion and is accompanied by the release of harmful nitrous gases.<sup>7,8</sup> The irreversibility of the oxide ion formation reaction is ultimately the reason for the upper temperature limit of the nitrate salts. At 560 °C the rate of oxide ion formation is acceptably low and while it is commonly known that the rate increases with increasing temperature, the exact rate of oxide ion formation above 560 °C is still subject to investigations.<sup>5,9,10</sup>

Enhancing the thermal stability limit of Solar Salt can therefore be achieved when the rate of oxide ( $O^{2-}$ )- and nitrite ( $NO_2^-$ ) ion formation is controlled simultaneously. This can be obtained by basically two approaches: either by increasing the concentration of product gases formed in reaction (1) and (2) in the purge gas, or by simply sealing the storage system including the gas and thereby retaining decomposition gases in the storage tank. Using a closed system in terms of molten salt and cover gas increases the nominal concentration of gaseous oxygen and nitrous gases during formation of equilibrium states in eq. (1) and (2). The increasing partial pressure (or accumulation) of oxygen and nitrous gases could shift the equilibrium of the chemical reactions (1) and (2) to the left hand side. This would effectively result in higher nitrate- as well as lower nitrite- and oxide ion concentrations, thereby reducing changes of thermo-physical properties and at the same time reducing the concentration of corrosive species.

In this study we investigate the approach of closing a molten salt- including the gas system to demonstrate that the thermal stability limit of Solar Salt can be increased to at least 600°C, when the system is closed. Using a novel sample extraction method we are able to extract molten salts *in-situ* over the duration of all experiments from the purged and closed system. Using post-analysis methods this allows for a quasi-*in-situ* proof of a stable molten salt chemistry and a direct comparison of closed and purged storage configurations.

## 2. EXPERIMENTAL

Solar Salt was produced by mixing and subsequent melting of 60 wt%  $NaNO_3$  (>99%, Merck, Germany) and 40 wt%  $KNO_3$  (> 99 %, Merck, Germany). Melting was performed at 300 °C in an autoclave test rig that was also used for the isothermal experiment. A detailed description of the setup is described elsewhere.<sup>11</sup>

An autoclave test rig was used to perform individual experiments in the aforementioned purged and closed configuration in terms of molten salt and gas atmosphere (see Figure 1).

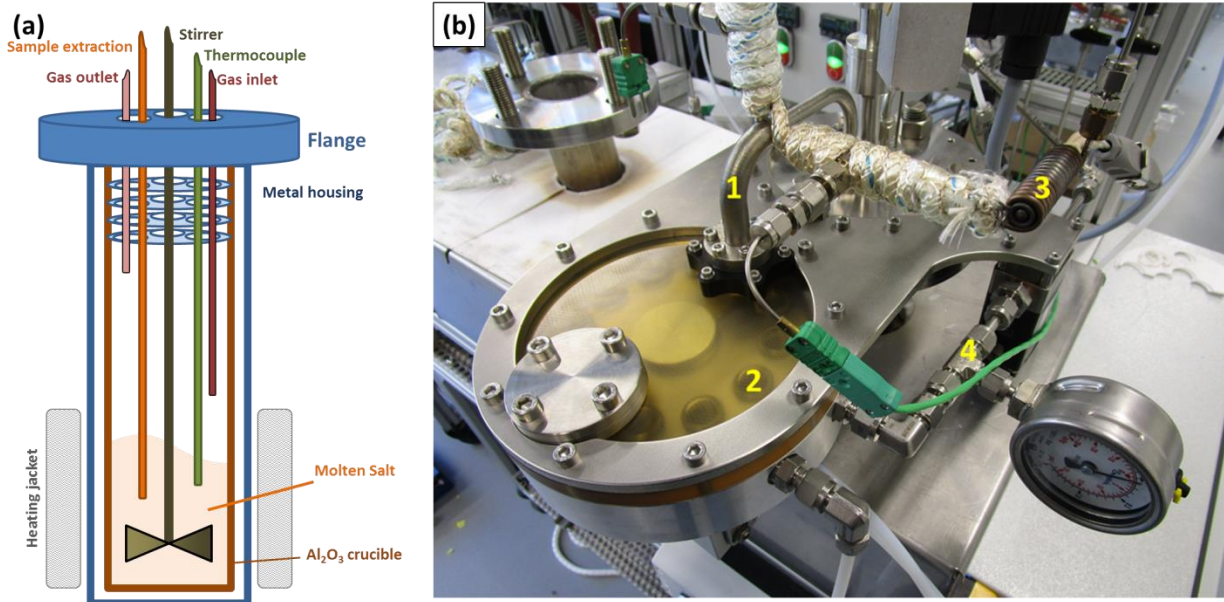


Figure 1 (a) Schematic of the autoclave test rig with autosampler used for storage experiments and (b) picture of the home-engineered autosampler featuring (1) a stand pipe, (2) a sample container, (3) trace heating connections and (4) gas supply of the autosampler.

The molten salt temperature is controlled while the pressure build-up in the closed cell was recorded during all experiments in closed configuration. In the open configuration a gas flow of 100 ml/min was purged over the top of

the melt containing either pure N<sub>2</sub> (5.0 grade) or mixtures of N<sub>2</sub> with O<sub>2</sub> (5.0 grade) at different oxygen partial pressures. A home-engineered autosampler (Figure 1 (b)) was used for in-situ sample extraction during operation in a closed system. Coupled with post-analysis of the molten salt samples, this allowed for *quasi in-situ* analysis of the molten salt chemistry during operation in a closed environment. Heart of the autosampler is the riser tube made of Inconel which allows sample extraction by applying a vacuum in the gas system of the Autosampler, which can temporarily be decoupled from the otherwise connected gas system of the autoclave. Molten Salt chemistry was analyzed in terms of nitrate, nitrite and oxide anion species using chromatography and potentiometric acid-base titration. The procedures are also described elsewhere in more depth.<sup>11</sup>

### 3. RESULTS & DISCUSSIONS

The molten salt chemistry of nitrate salts has been well discussed in the temperature range up to 560 °C.<sup>12-14</sup> Despite the interest in higher temperatures of operation, there is very limited work on nitrate salts, and Solar Salt operation in particular, beyond 560 °C.<sup>15-17</sup> Most noteworthy, Wei *et al.*<sup>15,16</sup> have quantified the amount of nitrous gases (NO and NO<sub>2</sub>) evolving from a 100 g-batch of Solar Salt at 550 °C and 600 °C and proposed that the direct decomposition of the nitrate ion was responsible NO<sub>x</sub>-formation.

At this elevated temperature the lab equipment must be specially designed to avoid molten salt creeping and evaporation, which become pronounced above 560 °C. Using specialized equipment in the lab-scale and thus by avoiding molten salt creeping and evaporation, the molten salt chemistry can reliably be determined even in temperature ranges where nitrate salts are expected to be unstable. All of which is supported by the relatively large lab-scale of the experiments (100-200 g of molten salt) compared to thermal analysis, which has proven successful in representing the nitrite-nitrate equilibrium in large scale (up to the MWh-scale of DLR's molten salt test facility TESIS).<sup>14</sup>

#### 3.1 Solar Salt Chemistry in a Purged System

The molten salt chemistry of Solar Salt has been measured in the 150 g – scale in classical *open* configuration, where a synthetic air gas is purged on top of the melt and the total pressure is 1 bar (atmospheric pressure). For the two temperature 560 °C and 600 °C the molten salt composition in terms of nitrate, nitrite and oxide ion content is shown in Figure 2. At 560 °C, which represents the state-of-the-art in Solar power tower plants, the initially pure nitrate melts form nitrite by the reversible equilibrium reaction (1) shown earlier. The equilibrium is ultimately reached due to the constant temperature and oxygen partial pressure (0.2 atm O<sub>2</sub>) in the purge gas. Only marginal concentrations of oxide ions are found over the course of the 500 h experiment indicating the decomposition of the nitrite ion according to reaction (2) can be neglected.

Increasing the temperature to 600 °C one can observe lower nitrate levels compared to 560 °C, as well as higher levels of nitrite and accumulating oxide ions. This indicates that

1. Equilibrium reaction (1) is shifted to the nitrite side due to the higher temperatures and
2. The nitrite ion decomposes steadily to form oxide ions.

While the shift of the nitrate-nitrite equilibrium presents no matter of concern (a change in thermal properties can be considered as small), the oxide ion formation is critical since increasing levels of oxide ions can promote corrosion drastically and lead to release of toxic nitrogen oxide gases.<sup>18,19</sup> When looking at Figure 2 it is immediately obvious the oxide ion concentration does not reach equilibrium but rather increases steadily indicating ongoing decomposition of the Solar Salt. Looking at the underlying decomposition reaction (2) this can be explained by the fact that all nitrous gases formed during decomposition are flushed out of the system by the purge gas stream. The setup with purge gas leads to a situation with low partial pressure of nitrous gases over the salt melt. Hence, equilibrium of reaction (2) is shifted to the right side and oxide ion formation continuously increases.

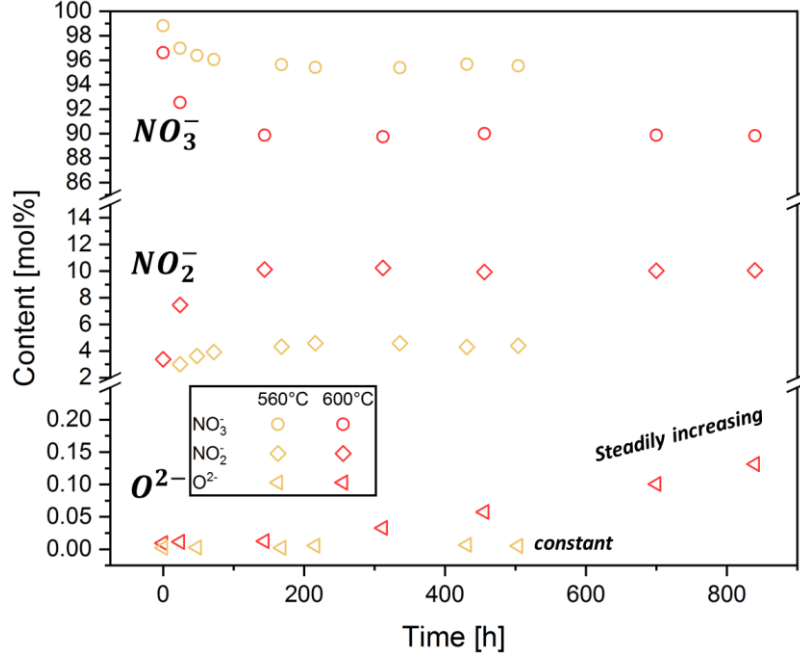


Figure 2 Molten Salt chemistry in terms of nitrate, nitrite and oxide levels in Solar Salt isothermally stored at 560 °C and 600 °C under a purge gas of synthetic air.

### 3.2 Solar Salt Chemistry in a Closed System

Different strategies could be employed to avoid high nitrite and oxide ion formation, or in other words shift the chemical equilibrium of the decomposition reactions (1) and (2) to the left hand side, at higher temperatures. Firstly, the concentration of gaseous oxygen and nitrous purge gases could be increased substantially. This would shift the equilibrium to lower nitrite and oxide ions levels, but require excessive gas handling on a large scale. Alternatively, the molten salt and gas system can operate as *closed* system. During equilibration of the molten salt chemistry all gases formed in reaction (1) and (2) would be retained in the system, their concentration would increase over time and push the overall equilibrium to the nitrate and nitrite side. Yet, one has to be aware that this procedure would go along with a certain pressure increase in the system due to the release of oxygen and nitrous gases.

Theoretically, the pressure increase can be predicted using the ideal gas law according to

$$\Delta P \cdot V_{Gas} = \Delta n_{Gas} \cdot R \cdot T_{Gas} \quad (3)$$

Where  $\Delta P$  is the monitored change in pressure,  $V_{Gas}$  is the volume of the gas phase,  $\Delta n_{Gas}$  is the molar change of the gas content,  $R$  is the gas constant (8.314 J/mol·K) and  $T_{Gas}$  the total volume of the experimental setup.  $V_{gas}$  was measured using a fluid-displacement method and was found to be highly reproducible ( $\pm 2\%$ ). Since the volume of the molten salt can be calculated with high accuracy from linear density estimations (see e.g. ref. <sup>4</sup> or <sup>20</sup>), the total gas volume ( $V_{gas} = V_{system} - V_{salt}$ ) can be derived. Given the isochoric nature of the experiment and the constant gas temperature, the relation appears to be purely based on the change in molar gas content and change in pressure (at low temperatures it is reasonable to assume that *only* the evolution of oxygen contributes to  $\Delta n_{Gas}$ ). Accordingly, eq. (3) and eq (1) can express the direct relation between change in pressure and the amount of oxygen evolved (which is known from the *change* in nitrite content) leading to eq. (4):

$$\Delta P(t) = \left[ \frac{1}{2} \cdot (x_{NO_2^-,t} - x_{NO_2^-,t=0h}) \cdot \frac{m_{Salt}}{M_{Salt}} \right] \cdot \frac{R \cdot T_{Gas}}{V_{Gas}} \quad (4)$$

Where  $x_{NO_2^-,t}$  is the molar nitrite content after a certain time  $t$  and  $x_{NO_2^-,t=0h}$  is the molar nitrite content immediately after closing the system,  $m_{Salt}$  is the mass of molten salt during the individual experiments and  $M_{Salt}$  is the molar mass of Solar Salt.

The storage of Solar Salt in purged vs closed configurations was tested in the 100-200 g scale. Results are compared to the open configuration (see subsection 3.1). Regarding the closed system, a first experiment was conducted where Solar Salt was heated to 550 °C (under synthetic air) and where the gas atmosphere and molten salt systems were sealed immediately when the molten salt reached 550 °C. The pressure increase in the cell was recorded (Figure 3) over time and molten samples were extracted before and after the experiment.

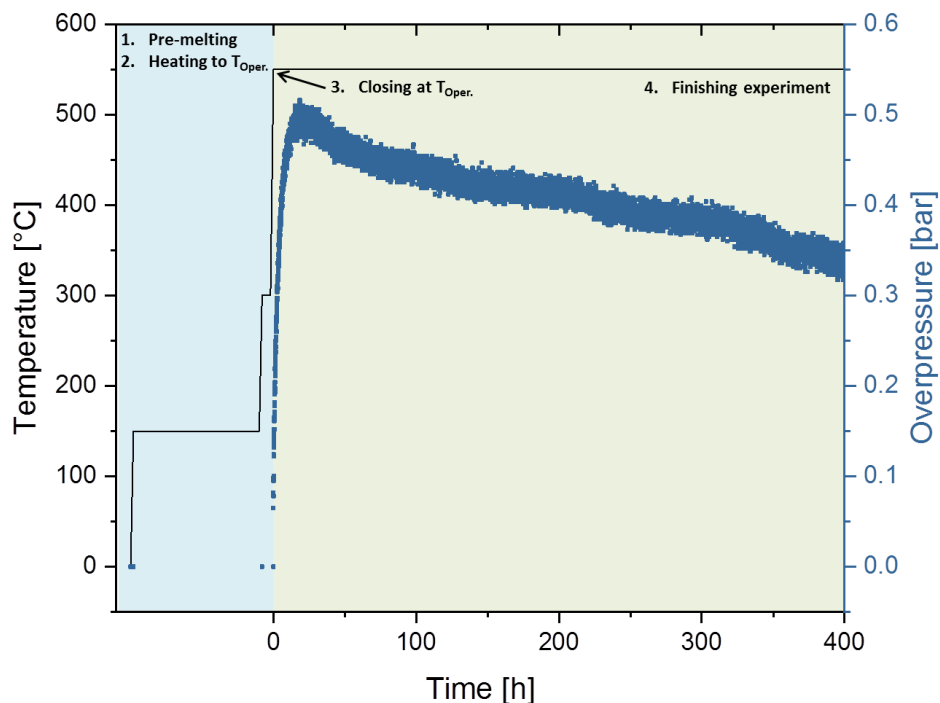


Figure 3 Temperature profile (black line) and pressure build (blue dots) of closed-type experiments over time in a system containing molten Solar Salt.

Figure 3 shows the pressure increase in the gas phase over the molten Solar Salt directly after *closing* the system. An immediate pressure increase can be detected which indicates the formation of gaseous species (temperature changes in the gas phase were not detected). Over the duration of the experiment (~350 h) the pressure decreases slightly (most likely due to leakage) before it is released at the end of the experiment (not shown). Molten salt analysis after the experiment yielded nitrite concentrations 2.8 mol% in an otherwise pure nitrate melt. The nitrite level is substantially lower than in the *open* experiment where levels of ~4 mol% are found. This indicates that the equilibrium of reaction (1) was effectively shifted to the (left) nitrate-side. Given the similar experimental boundary conditions compared to the *open* configuration (experiment in Figure 2) the molten salt chemistry of *open* and *closed* system can be compared.

From the experiment in the *closed* system we attempted to reproduce the measured pressure increase from the known change in nitrite content ( $x_{NO_2^-,t} - x_{NO_2^-,t=0h} = 2.8 - 1.7 = 1.1 \text{ mol}\%$ ). When calculating the theoretical change in pressure using a gas temperature of 550°C, the expected *change* in pressure would be  $\Delta P = 1.55 \text{ bar}$ , which is significantly higher than the *measured* pressure change in the experiment ( $\Delta P = 0.5 \text{ bar}$ ). Pressure effects from gas expansion due to changing gas temperatures or other heating/cooling sources can be excluded from additional experiments performed prior to this study (data not shown for clarity). Additional experiments were conducted to measure the gas temperature and it was found to be significantly lower than the salt temperature – typically in the range of 200-300 °C (depending on salt temperature and geometrical parameters of the setup). This is mainly attributed to the fact that only the lower part of the crucible is heated (see Figure 1) to avoid excessive salt creeping to the top of the setup

Consequently, the setup was optimized by implementing a heat shield for a constant gas temperature distribution. (schematically shown in Figure 1). In addition the temperature distribution inside the chamber was measured. It was

found that the distribution is very constant in different regions of the gas phase, indicating thermal equilibrium of the system.

In order to monitor the salt composition over the entire experiment a home-engineered autosampler, which allowed for continuous samples extraction even from the *closed* system, was built and utilized.

The same experiment in a *closed* system was repeated in this optimized autoclave test-rig at temperatures of 600 °C with a fresh Solar Salt batch. While in the purged configuration the nitrite and oxide levels are significantly increased at 600 °C (8.25 mol% and 0.121 mol%, respectively), they are substantially decreased in the *closed* system to levels of 6.52 mol% and 0.018 mol% (see data in **Fehler! Verweisquelle konnte nicht gefunden werden.**). The oxide ion concentrations remain very constant in the closed system while they steadily increase in the purged system. This indicates that decomposition reactions were suppressed in the closed configuration which is not the case on the purged system. We ascribe that to the fact that oxygen gas and nitrous gases, eventually formed when eq (1) and eq (2) reach equilibrium, are retained in the closed system and therefore push chemical equilibrium to the left side (higher stability of the nitrate ion).

Even more so the data showed that pressure build-up and nitrite formation occur simultaneously. This indicated that indeed the evolution of gaseous oxygen contributes to the pressure increase and that other effects are less relevant at this temperature.

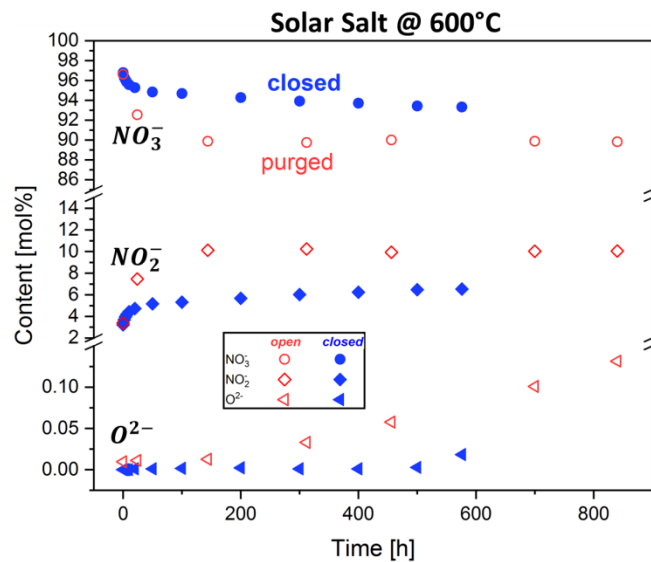


Figure 4 Molten Salt chemistry in Solar Salt at 600 °C in the classical *purged* and advanced *closed* configuration. Data for the *purged* system is the same as shown in Figure 2.

Table 1 Molten salt composition in open and closed configuration at 550°C and 600°C.

Experiment	$T_{\text{Salt}}$ [°C]	Concentration at $t_{\text{end}}$ [mol%]		
		Nitrate ( $\text{NO}_3^-$ )	Nitrite ( $\text{NO}_2^-$ )	Oxide ( $\text{O}^{2-}$ )
Solar Salt <i>classical</i>	550	95.80	4.20	-
Solar Salt <i>closed</i>	550	97.86	2.14	-
Solar Salt <i>classical</i>	600	91.63	8.25	0.121*
Solar Salt <i>closed</i>	600	93.33	6.52	0.018

\*: no equilibrium value reached, level still increasing

## Regeneration of Solar Salt at 600 °C in a Closed System

Additional experiments were conducted where certain levels of nitrite were added prematurely to the Solar Salt mixture, thereby decreasing the level of oxygen evolved during equilibration. An experiment with an initial nitrite content of 5 mol% was performed. The salt was heated to 600 °C under a purge gas containing 0.2 atm  $\text{O}_2$  and closed when reaching the desired salt temperature. After 1000 h the overpressure was released and the molten salt was cooled to room temperature where it was flushed with a purge gas containing a higher  $P_{\text{O}_2}$  of 0.8 atm. This was

supposed to actively push chemical equilibrium of eq. (1) to the left (nitrate) side. The salt was re-heated to-, and closed at 600 °C in an attempt to regenerate the molten salt. The pressure recorded during this 4-step experiment (#1 heating; #2closing; #3flushing; #4closing) is shown in Figure 5.

During heating of the Solar Salt to 600 °C two samples were extracted, one at 300 °C and one immediately before closing the system at 600 °C. Both samples exhibited a molar nitrite content of ~6.5 mol% indicating that the even the short time of heating is enough to start the formation of measurable nitrite content. During the first isothermal step (labelled #2 in Figure 5) the overpressure increases steadily and does not appear to reach a steady state. After 1000 h it reaches ~0.6 bar and the level of nitrite increased slightly to 7.45 mol%. This nitrite concentration is still somewhat lower than in the open system (8.25 mol%), but at the same time higher than during the first *closed* experiment at 600 °C (6.52 mol%). Nonetheless, after cooling the salt (necessary for extraction of a sample), flushing with oxygen-rich cover gas (0.8 atm O<sub>2</sub>), re-heating and closing at 600 °C we observe a pressure drop below ambient pressure (stage #4 in Figure 5). This indicates that a gas species, most likely O<sub>2</sub>, is consumed. The (negative) pressure stabilizes after ~100 h and, from the experiments presented earlier, it is reasonable to assume that chemical equilibrium is reached at this point. Consequently, the experiment was stopped and the nitrite content in the melt was measured. Indeed, the molar nitrite content had decreased to 6.98 mol% (while the nitrate content simultaneously increased) giving rise to the fact that melt had regenerated with the available O<sub>2</sub> to form nitrate. The pressure decrease can therefore be explained in terms of oxygen consumption and the reaction of nitrite ions to form nitrate.

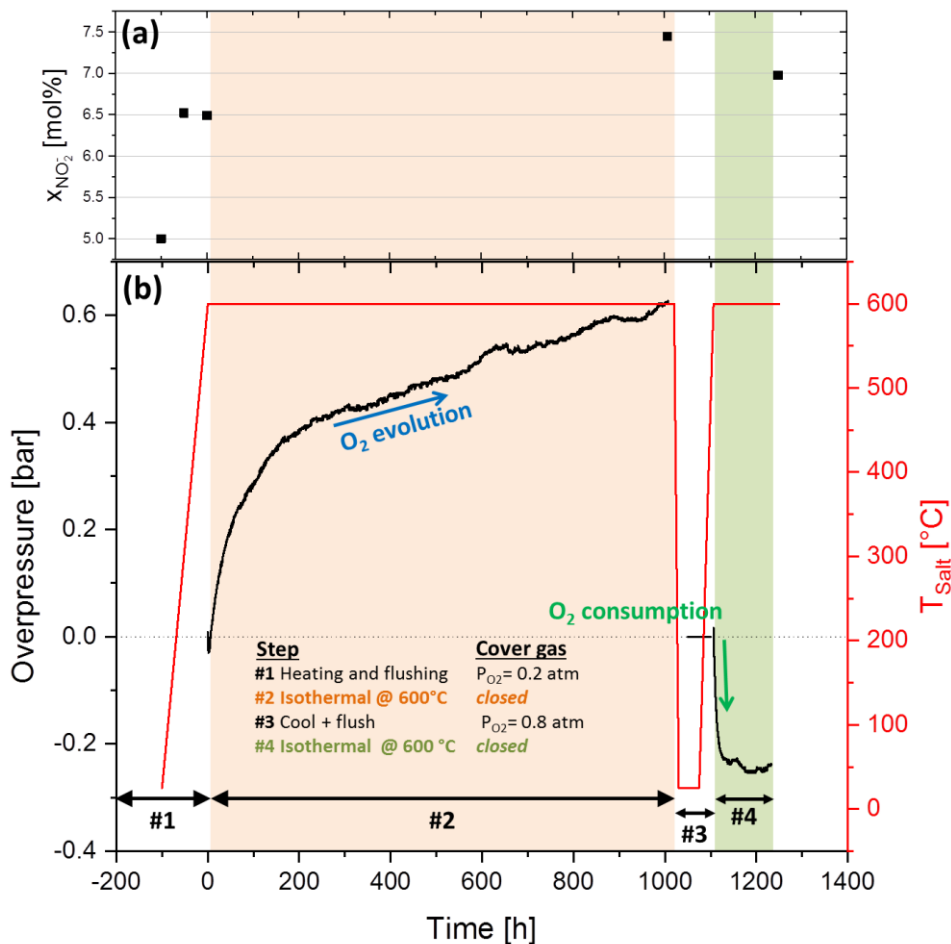


Figure 5 (a) Molar nitrite contents and (b) pressure recorded during a 4-step experiment with Solar Salt containing a starting nitrite content of 5 mol%. The experimental steps are indicated in part (b) of the figure.

## CONCLUSIONS

Our experiments demonstrate a stabilizing effect for Solar Salt operation in closed system configuration at 600 °C. The Reactive gases NO<sub>x</sub> and O<sub>2</sub> are retained within the system rather than being flushed out in an open container. Closing the storage systems would lead to significantly reduced decomposition reactions in terms of nitrite but especially oxide ion formation, re-opening the discussion on thermal energy storage systems at and above 600 °C with Solar Salt. We furthermore demonstrated that the pressure-build up is highly sensitive to the composition of molten salt at the start of the experiment and simultaneously the composition of the cover gas. As shown, certain combinations can even lead to the formation of a negative pressure if reactive gases regenerate the molten salt. The technical constraints related to pressurized system designs can therefore effectively be overcome if molten salt chemistry and cover gas composition are leveled out appropriately. Overall, it appears that the *closed* system design could enable higher Solar Salt operation temperatures.

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