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Effect of heating rates and composition on the thermal decomposition of nitrate based molten salts

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Abstract

A detailed analysis on the thermal degradation of nitrate based molten salts evaluating the influence of different impurities and heating rates in their maximum working temperature is presented. Determining the maximum operating temperature is of interest when searching for new heat transfer fluids (HTF) for high temperature solar thermal applications as it limits the thermodynamic efficiency of the power block. Thermogravimetric analysis is performed on potassium nitrate, sodium nitrate, sodium nitrite, the binary system Solar Salt, and the ternary Hitec. The kinetics of the thermal decomposition reactions are investigated through iso-conversional analysis. The effect of adding some common impurities such as NaCl and Na₂CO₃ on the multi-component nitrate salts is evaluated. It was found that impurities such as Na₂CO₃ can enhance the thermal stability of Hitec salt, leading to higher thermal decomposition temperatures. For solar salt, impurities such as NaCl can enhance the thermal stability of solar salt at 10K·min⁻¹, while adding Na₂CO₃ can have the opposite effect. For nitrate based molten salts used in TES and HTF systems in CSP a reduction on the purity required for the materials can present some operational advantages besides cost reduction.

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1. Introduction

The ability to store heat to produce power beyond daylight hours represents the main competitive advantage of Concentrated Solar Power (CSP) plants with respect to other types of renewable energy. Current thermal energy storage (TES) systems based on molten salts provide sufficient thermal energy to cover not only the natural intermittencies of the solar resource but also to produce power throughout the entire night (~ 15 hours) [1]. The highest temperature that can be achieved by the heat transfer fluid (HTF) and TES material determines the efficiency of the power plant and limits plant operation. Consequently, there is an endless quest for improved HTF and TES materials.

The lower and upper temperature practical limits of the molten salts used in CSP are determined by the melting temperature (T_m) and the maximum operating temperature (T_{max}), respectively. Commercial maximum operating temperatures are typically determined by the thermal decomposition process, but could also be determined by other factors such as testing conditions (atmosphere, crucible material, heating rate...), compatibility with containment materials, and thermal cycling requirements. For example, in a commercial project, the salt must have a thermal stability suitable for a life of 300,000 hours. Additionally, lowering the melting temperature is of interest in CSP because salts typically have high melting temperatures which require expensive heat tracing elements to maintain the salts in the molten state. Increasing the maximum operating temperature by improving the thermal stability of molten salts can allow the use of higher efficiency thermodynamic cycles, such as supercritical power generators and can improve the efficiency of the heat storage systems [2].

Solar salt (60% NaNO_3 , 40% KNO_3 by wt) can be used up to 565°C without significant degradation [3]. However, this upper temperature limit might vary slightly depending on the level and type of impurities present in the salts (which can change depending on the supplier), as well as the specific heating/cooling rates which can differ from one power plant to another. The different grades of purity can have great impact on both the specific cost of these materials and the lifetime of the fluid. It has been suggested that some commonly found impurities, such as sodium chloride, may increase the maximum operating temperature of molten salts [4,5]. The effect of sodium chloride on the viscosity of multi-component nitrate salts was studied briefly by Bradshaw [4]. Peng [5] also measured thermo-physical properties of nitrate based molten salts (KNO_3 , NaNO_3 , and NaNO_2) analyzing the effect of adding 5% (by wt.) of unspecific chlorides. A detailed analysis and, in some cases, the exact compositions tested are missing from these studies. Similarly, the solar literature typically reports tests performed at heating rates of 10 $\text{K}\cdot\text{min}^{-1}$. However, limited studies have been found that evaluate the effect of slower heating rates and impurities on the thermal decomposition of molten salts.

This paper presents a detailed analysis of the thermal degradation of the nitrate based molten salts, evaluating the influence of different impurities and heating rates on their maximum working temperature. Based on the thermogravimetric results at different heating rates, simplified kinetics can be obtained to improve our understanding of the decomposition processes.

2. Experimental methods

The solar salt was prepared from Technical Grade KNO_3 , NaNO_3 , and NaNO_2 without further purification (Thermosolar - Crystals, SQM Northamerica Corporation, Atlanta, GA). Na_2CO_3 and NaCl (Panreac Química S.L.U., Barcelona, Spain) were used as impurities. The impurity content was fixed to 5% in weight, a relatively high content to accentuate any effects.

The amount of salt prepared for each composition was 3g. Both compositions, with and without impurities, were prepared using the same method: firstly, prills from each component were milled and mixed in a mortar. The resulting powder was melted into a borosilicate beaker on a hot plate at 350°C. Once the content was in liquid state, it was homogenized by stirring manually. The resulting liquid was poured over the mortar for fast cooling. The resulting frozen product was milled again and the process described before was repeated three times (milling, mixing, melting) to guarantee homogenization.



Fig. 1. Sample preparation (Hitec)

Hitec salt (mixture of NaNO_3 – KNO_3 – NaNO_2 in 7–53–40 wt. %), solar salt (NaNO_3 – KNO_3 in 60–40 wt. %), and their components were tested as a reference fluids. Impurities found in their commercial compositions (Na_2CO_3 and NaCl) were added. The influence of the impurities on the thermal degradation was analyzed through thermogravimetric analysis (TGA).

For the thermogravimetric analysis a TGA/DSC1 from Mettler-Toledo was used. The calibration procedure was performed by using the melting temperatures of standard certified reference materials (CRMs) (In, Al, Au), at a heating rate of $10\text{K}\cdot\text{min}^{-1}$, resulting within the limits specified by the equipment manufacturer. Samples of 4 - 6 mg were introduced in $70\mu\text{l}$ alumina crucibles using nitrogen as inert gas in the thermal program. Samples were held at 300°C or 400°C (depending on the sample) for 20 minutes to ensure thermal stability before the dynamic temperature segment. The samples were then heated at different heating rates ($2.5, 5, 10, \text{ and } 20\text{ K}\cdot\text{min}^{-1}$) while recording the mass in order to characterize the thermal decomposition.

3. Results and discussion

The use of molten salts in high temperature solar thermal applications requires the definition of the decomposition temperature, this being one of the most important parameters which defines the practical operation temperature range. The higher the temperature operation range, the higher the thermal energy it is possible to store in the same amount of salt. Having a high operational temperature also implies higher thermal cycle efficiency within the power block. The maximum temperature or stability limit of the samples is usually defined as the temperature at which the sample has lost 3% of its initial weight [1,6]. This point, called T3, is usually calculated at a heating rate of $10\text{K}\cdot\text{min}^{-1}$ and is used at a laboratory scale to compare substances. However, T3 can vary depending on the experimental methods and conditions such as heating rate, crucible type or atmosphere.

Furthermore, molten salts are known to be complicated to characterize in laboratory conditions, due to their high hygroscopicity, high surface tension, high reactivity with crucible materials, and high melting temperatures, causing the melt to condense on unexpected surfaces of the measuring equipment [7]. This difficulty to measure salts can affect the reproducibility of results and experiments should be performed carefully to avoid sensor deterioration.

3.1. Pure components analysis (TGA)

When exposed to high temperature, alkali metals nitrate salts thermally decompose according to three different mechanisms [1]: a) nitrite formation in the melt and oxygen release, b) alkali metal oxide formation in the melt and nitrogen or nitrogen oxides release, and c) vaporization of the nitrate salts. There is only agreement on the first type of reaction which is governed by:



where gaseous oxygen is released as a decomposition product. The complexity of the secondary decomposition reaction comes from a superposition of different effects such as the decomposition of the intermediate nitrite formed, due to its lower decomposition temperature, and the formation of oxides in the melt [8].

Different reaction paths have been proposed by Stern [9] for the decomposition of NaNO_2 . However, experiments with continuous removal of the gas phase are governed by equation (2).



The dynamic measurements were preceded by an isothermal section to stabilize the sample temperature. This isothermal segment was varied for each component to ensure thermal decomposition occurred only during the heating ramp up to 1000°C. The temperature program used for the NaNO₃ sample degradation started with an isothermal at 400°C, which is below the temperature of the thermal decomposition of sodium nitrate, about 450°C [10]. However, to avoid the instability of NaNO₂ that appears above 330°C reported in [9], this first isothermal segment was lowered to 300°C in the NaNO₂ tests, ensuring no weight loss happened before the dynamic segment.

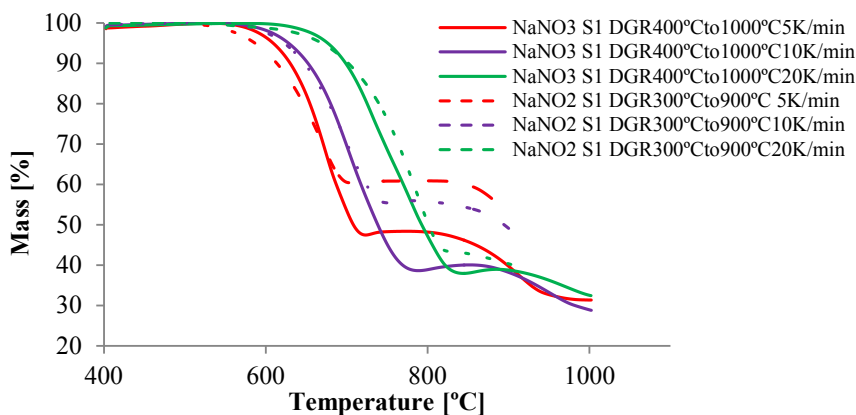


Fig. 2. Thermal decomposition of NaNO₃ and NaNO₂ for different heating rates

Fig. 2 shows the thermogravimetric curves for NaNO₂ and NaNO₃ at 5, 10 and 20K·min⁻¹ normalized by the initial mass. It can be seen that the heating rate has a strong effect on the measured decomposition temperature. Higher heating rates results in higher decomposition temperatures. This effect was observed in all the different samples. The measured decomposition temperatures (T3) are summarized in Table 1.

The thermal decomposition temperature T3 at different heating rates for NaNO₃ is in very good agreement with Bauer [1], 595.8°C for 5 K/min and 612.5°C for 10 K/min, indicating the procedure and the effect of heating rate on the decomposition temperature is being captured correctly. Some authors have emphasized the importance of the experimental conditions in obtaining repeatable results. The definition of the decomposition temperature together with experimental parameters such as atmosphere, gas flow, and crucible material, may lead to different results [8]. The performed measurements show lower T3 for NaNO₂ compared to the nitrates KNO₃ and NaNO₃, suggesting lower thermal stability for NaNO₂. This result is in agreement with Stern [9]. In contrast, results from Bauer [11] showed very similar thermal stabilities of NaNO₂ compared to nitrates KNO₃ and NaNO₃.

Table 1. Summary T3 for NaNO₃, NaNO₂, KNO₃, Hitec, Solar Salt

| Composition | T3 (°C) at 2.5K·min ⁻¹ | T3 (°C) at 5K·min ⁻¹ | T3 (°C) at 10K·min ⁻¹ | T3 (°C) at 20K·min ⁻¹ |
|-------------------|-----------------------------------|---------------------------------|----------------------------------|----------------------------------|
| NaNO ₃ | - | 595.8 | 612.8 | 661.6 |
| NaNO ₂ | - | 569.5 | 607 | 646.8 |
| KNO ₃ | 552.2 | 584.5 | 663.5 | - |
| Hitec | 532.6 | 571.6 | 603.6 | - |
| Solar Salt | - | - | 630 | - |

Comparing Hitec results to its pure components, our measurements indicate higher thermal stability for KNO_3 and NaNO_3 , but similar T3 temperature to that of NaNO_2 . Among the salts tested, Hitec was found to have the lowest thermal stability. These results disagree with Bauer [11] which found a different trend, with Hitec being more stable than KNO_3 , the most stable of its constituents.

The results at different heating rates can be linearly extrapolated to equilibrium conditions ($0\text{K}\cdot\text{min}^{-1}$). However, since T3 is not linear with heating rate it should only be considered as a rough estimate.

3.2. Hitec vs. Hitec+5% Na_2CO_3

The TGA curves obtained for Hitec at different heating rates were compared to results of a mixture of Hitec and 5% Na_2CO_3 , one of the main impurities found in its commercial composition. The degradation curves for three heating rates comparing Hitec and Hitec+5% Na_2CO_3 are presented in Fig.4. The T3 values obtained from these curves are summarized in Table 2.

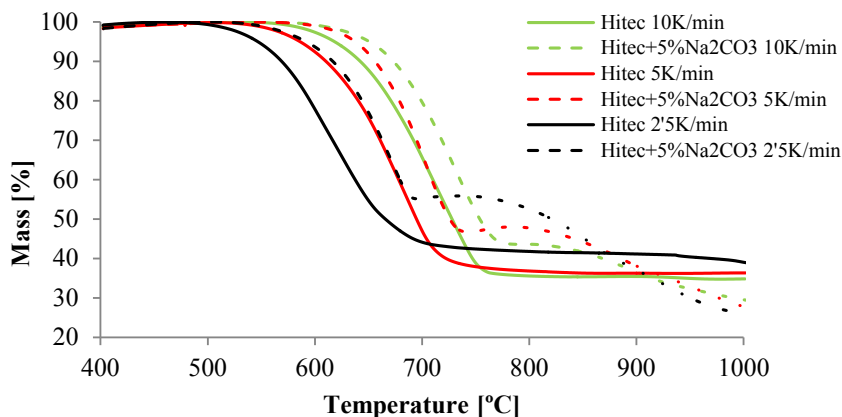


Fig. 3. Hitec salt vs. Hitec salt + 5% Na_2CO_3 at different heating rates

Fig. 3 suggests higher thermal stability for Hitec with 5% Na_2CO_3 than for the pure mixture, as the mass loss starts at a higher temperature than for the pure salt regardless of the heating rate. The degradation process is changed by the addition of impurities, showing a second step on the thermal decomposition not present for the main salt. Also, the residue at the end of the degradation is slightly lower for the salt with sodium carbonate.

Table 2. T3 for Hitec, Hitec with 5% Na_2CO_3 .

| Composition | T3 (°C) at $2.5\text{K}\cdot\text{min}^{-1}$ | T3 (°C) at $5\text{K}\cdot\text{min}^{-1}$ | T3 (°C) at $10\text{K}\cdot\text{min}^{-1}$ |
|-------------------------------------|--|--|---|
| Hitec | 532.6 | 571.6 | 603.6 |
| Hitec + 5% Na_2CO_3 | 575.4 | 625.1 | 635 |

TGA can provide simplified kinetic information based on heating rates. The non-isothermal TGA curves were analyzed and fitted to an Arrhenius decomposition reaction following the iso-conversional method described by Friedman [12]. This methodology allows the determination of the dependence of the apparent activation energy on the extent of conversion and permits reliable mechanistic conclusions to be drawn even though it calls for a large number of TGA experiments [13]. The decomposition process under study was found to fit a power law kinetic model (P2) ($f(\alpha) = 2 \cdot \alpha^{1/2}$), described in Eq. (3), similar to that of Janovik [13] with silver nitrate, for extent of conversion ($\alpha = (m - m_{\text{initial}}) / (m_{\text{final}} - m_{\text{initial}})$) in the range of $0.1 \leq \alpha \leq 0.7$. In equation (3) A is the pre-exponential factor, E_a is the activation energy, (in kJ/mole), R is the gas constant ($R = 8,311 \times 10^{-3}$ kJ/(mol·K)) and T is the absolute temperature.

$$\ln \left[\frac{d\alpha}{dt} \frac{1}{f(\alpha)} \right] = \ln(A) - \frac{E_a}{R \cdot T} \quad (\text{with } f(\alpha) = 2 \cdot \alpha^{1/2}) \quad (3)$$

The iso-conversional plots for Hitec and Hitec with 5%Na₂CO₃ are presented in Fig. 4, allowing the determination of the activation energy as a function of α .

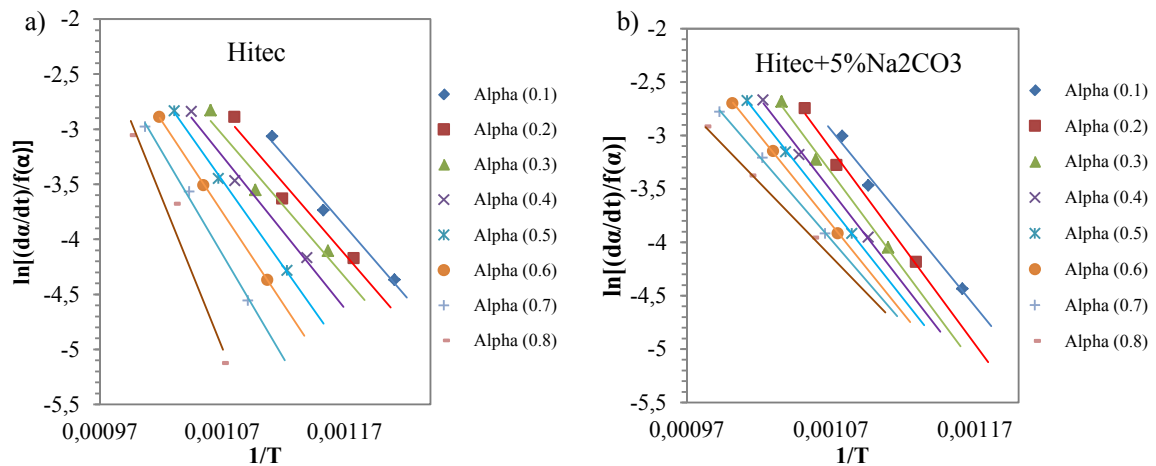


Fig. 4. Iso-conversional plots for a) Hitec and b) Hitec+5%Na₂CO₃

The apparent activation energy calculated as a function of the extent of conversion is presented in Fig. 5.

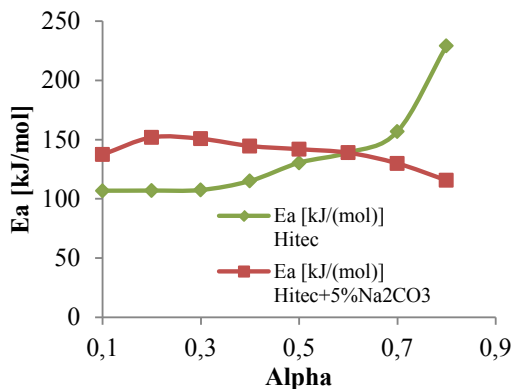


Fig. 5. Activation Energy for Hitec and Hitec+5%Na₂CO₃

Larger activation energy, E_a , signifies slower decomposition rates and therefore higher kinetic stability. Fig. 5 shows the activation energies obtained for Hitec and Hitec+5%Na₂CO₃, confirming that the addition of a small quantity of Na₂CO₃ increases the decomposition reaction activation energy, hence increasing the temperature at which a significant weight loss occurs.

As mentioned before, the main decomposition reaction in nitrate based salts is the partial dissociation of nitrate ion to nitrite ion and oxygen (Eq.1). According to Bradshaw [14] this initial decomposition reaction proceeds to approximately the same extent in ternary mixtures (such as Hitec) as in an equimolar binary mixture of NaNO₃ and KNO₃. Moreover, the decomposition at high temperature seems to be due to reactions of nitrite and nitrate that yield oxide ions. Olivares [15] mentions that the solubility of carbonate ions in nitrate salts can affect the concentration of oxygen ions and thus the main decomposition reaction. This may be a possible explanation for the stabilizing effect of sodium carbonate on Hitec as shown in Figs.4-5.

3.2.1. Solar Salt vs. Solar Salt+5%Na₂CO₃ vs. Solar Salt+5%NaCl

The thermal decomposition curves for solar salt and solar salt presenting two common impurities, NaCl and Na₂CO₃, at a constant heating rate of 10K·min⁻¹ are shown in Fig. 6. Two samples are shown for each case, demonstrating repeatability of the results. The T3 values for Fig.6 are summarized in Table 3.

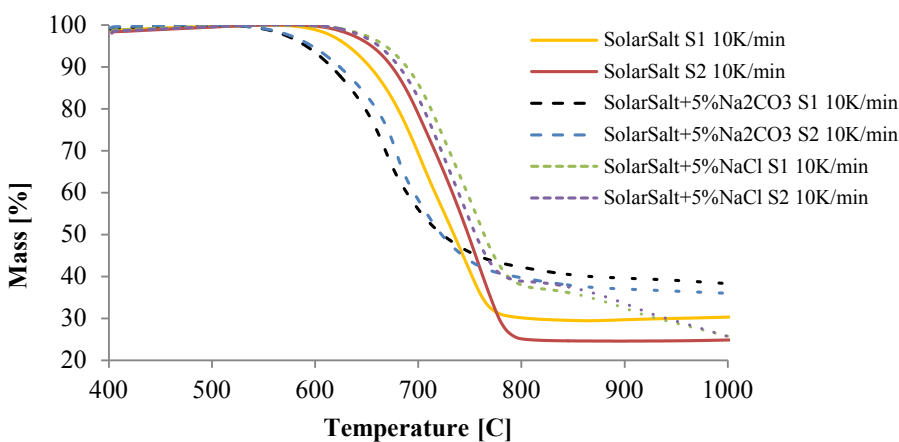


Fig. 6. Solar Salt at 10 K·min⁻¹: pure solar salt, solar salt + 5% Na₂CO₃, and solar salt + 5% NaCl

The effect of adding Na_2CO_3 to Solar Salt is quite the opposite than that of Hitec (Fig. 3); i.e. adding a small quantity of sodium carbonate accelerates the decomposition reaction. The average T3 for Solar Salt at a $10\text{ K}\cdot\text{min}^{-1}$ rate was found to decrease by 8% when 5% Na_2CO_3 was added (Fig. 6). This suggests the degradation mechanisms are different from those appearing with only sodium nitrate and nitrite.

On the other hand, adding 5% NaCl to solar salt resulted in an average increase of T3 of 3%. This trend is in agreement with previous work by Peng [4] who suggested adding unspecified chlorides into ternary nitrate salt would increase the optimum operating temperature from 500°C to 550°C .

Table 3. Sample 1, 2 and average T3 for Solar Salt, Solar Salt with Na_2CO_3 and Solar Salt with NaCl, at $10\text{ K}\cdot\text{min}^{-1}$

| Composition | S1 T3 ($^\circ\text{C}$) at $10\text{ K}\cdot\text{min}^{-1}$ | S2 T3 ($^\circ\text{C}$) at $10\text{ K}\cdot\text{min}^{-1}$ | Avg T3 ($^\circ\text{C}$) at $10\text{ K}\cdot\text{min}^{-1}$ |
|--|---|---|--|
| Solar salt | 619.4 | 641 | 630 |
| Solar salt + 5% Na_2CO_3 | 576.3 | 581 | 579 |
| Solar salt + 5%NaCl | 653 | 648.6 | 651 |

4. Conclusions

The thermal decomposition of molten nitrite/nitrates salt used for TES and HTF in CSP was measured for the pure components as well as the ternary mixture Hitec and the binary Solar Salt by thermogravimetric analysis (TGA) in nitrogen atmospheres between 400 and 1000°C , at a range of heating rates between 2.5 - $20\text{ K}\cdot\text{min}^{-1}$. The influence of the addition of impurities was evaluated as well as the effect of different heating rates on the maximum operating temperature. As expected lowering the heating rates correspond to lower degradation temperatures. The pure components analysis resulted in higher stability for nitrates compared to nitrites. Solar salt was found to present an intermediate stability (T3) similar to the average of its components. On the other hand, the thermal stability of Hitec was found to be similar to NaNO_2 , the component with lower stability.

It was found that impurities such as Na_2CO_3 can enhance the thermal stability of Hitec salt, leading to higher thermal decomposition temperatures. Specifically a 5% Na_2CO_3 increases the thermal decomposition temperature of Hitec by 30 - 50°C depending on the heating rate. For solar salt, impurities such as NaCl can enhance the thermal stability of solar salt (at $10\text{ K}\cdot\text{min}^{-1}$ the T3 is increased by 20°C on average), while adding Na_2CO_3 can have the opposite effect (at $10\text{ K}\cdot\text{min}^{-1}$ the T3 decreases by 50°C on average). For nitrate based molten salts used in TES and HTF systems in CSP a reduction of the purity required for the materials can present some operational advantages besides cost reduction. However, the consequences of increasing the chloride content can have severe detrimental effects on the corrosion characteristics of the salt.

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