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Solar Facilities for the European Research Area

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Author(s)	ENEA: E. Veca, N. Corsaro, C. Felici, G. Giorgi
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....	Salvatore Sau (ENEA)	…………………………..

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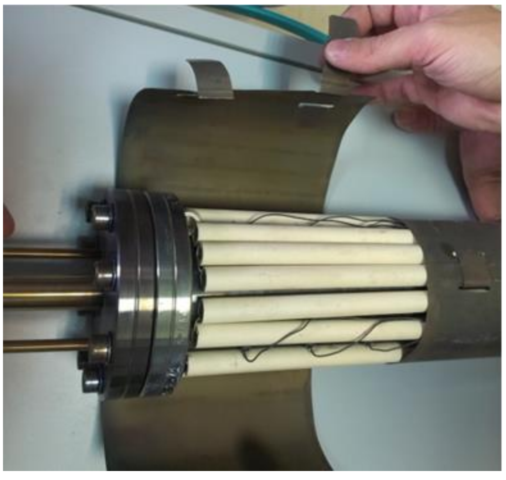
Table of contents

INTRODUCTION

This report presents the results of the experimental tests of the thermal decomposition of the HITEC XL mixture, the tests were performed in a small tubular reactor for five different temperatures data in the range 375-515°C.
Molten nitrate salts composition is 15% $NaNO_3$ – 42% KNO_3 – 43% $Ca(NO_3)_2$ by weight, the tubular reactor is equipped with impellers, it can contains about 1.5 kg of molten salts and there are also the mass flow controllers to measure the air flow in the inlet and outlet. Moreover there is a pressure gauge and there are also several thermocouples for the temperature measurement . On the outlet stream was measured the concentrations of oxygen and nitrogen by using chromatography.
The object of the present study is to validate the experimental setup by isothermal lab-scale tests
performing also a qualitative analysis, regarding the thermal decomposition of the mixture. The results provide qualitative information about the early stage of the thermal decomposition, but it's no possible to predict long term performance of the molten mixture. This mixture was selected to test the experimental facility, because it is one of the most commonly employed transfer and storage fluid, and its chemical stability was already investigated (see references).

EXPERIMENTAL SET UP

The small stain steel reactor was manufactured in order to study the thermal decomposition of molten salts for solar thermal power applications. The dimensions of the reactor are din=66mm dext=70mm H=310 mm and the material is made of AISI 316. The drawing in fig.2 describes the air diffuser, the impellers with the electrical motor and the valve plug to empty the reactor and it is surrounded by external insulation. It can contains about 1.5 kg of molten salts, there are also the mass flow controllers to measure the air flow in the inlet and outlet sections. The heating element is a heating resistance made of kanthal that can reaches 800°C, see figure 1. The reactor is equipped with instrumentation for the acquisition of the temperature, pressure and air flow of all the data, see figure 3. Inside the reactor there are three thermocouples tubes positioned at 120 degrees from the other at 3 different radial distance.



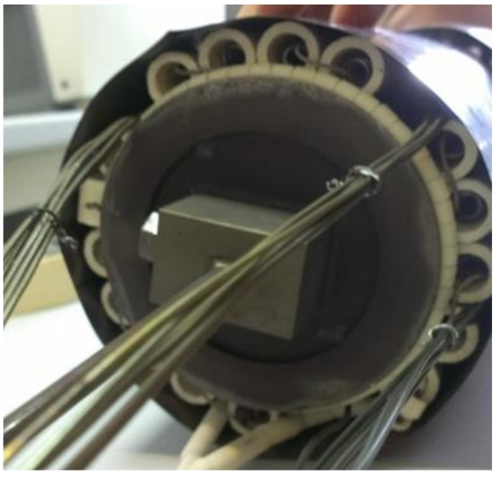


Figure 1. Details of the electrical heating resistance positioned along the wall of the reactor.

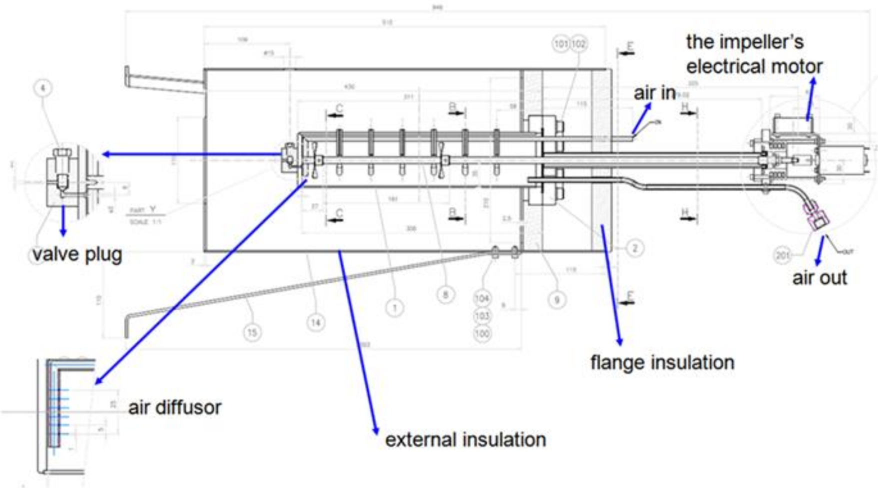


Figure 2. Tubular reactor the manufacturer's drawing.

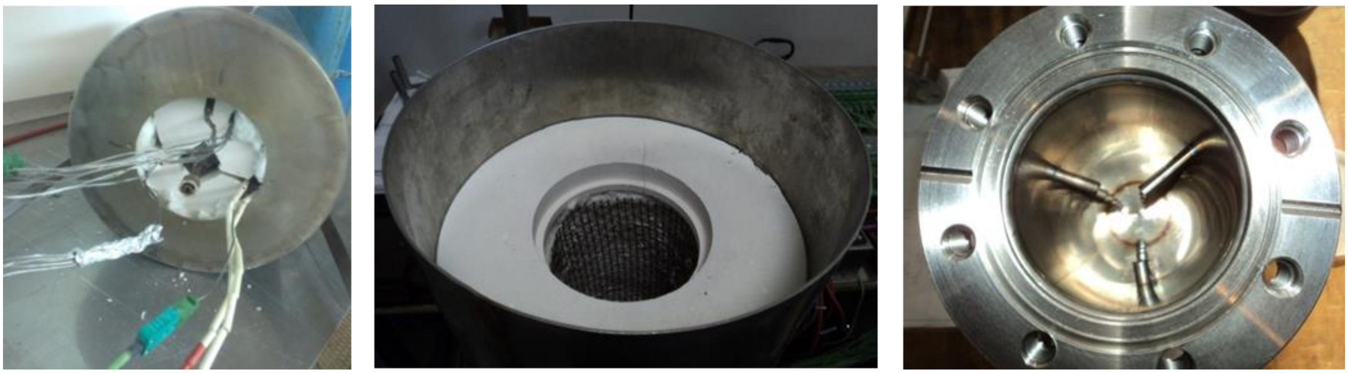
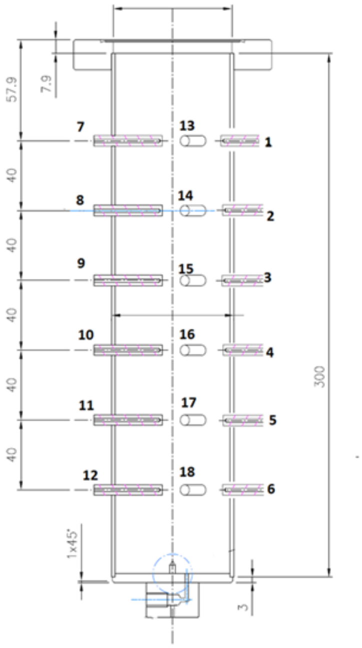


Figure 3. On the left hand side the details of the reactor, the bottom and the top. On the right hand side the detail of the thermocouple tubes.

Figure 4. The experimental setup, the reactor with the instrumentation for the acquisition and the trap positioned upstream the mass flow for the water condensation.



Termocouples positions		
n.	height[mm]	radius [mm]
1	250	25
2	210	25
3	170	25
4	130	25
5	90	25
6	50	25
7	250	7
8	210	7
9	170	7
10	130	7
11	90	7
12	50	7
13	250	15
14	210	15
15	170	15
16	130	15
17	90	15
18	50	15

Figure 5. The distribution of the thermocouple tubes in the reactor and the table of the radial distances and relative heights.

RESULTS AND DISCUSSION

Nitrate salts can degrade by numerous processes

1. $MNO_3 \Leftrightarrow MNO_2 + \frac{1}{2}O_2$
2. $5\ MNO_2 \rightarrow 3MNO_3 + M_2O + N_2$
3. $M_2O + \frac{1}{2}O_2 \rightarrow M_2O_2$
4. $\frac{1}{2}M_2O_2 + \frac{1}{2}O_2 \rightarrow MO_2$
5. $Ca(NO_3)_2 \Leftrightarrow CaO + NO_2 + NO + O_2$

The second reaction is the only major decomposition process as suggested by others (see references) even if numerous modes of decomposition appear to be active; N_2 and NO_x are generated as products of decomposition along with 0_2.

Chemical stability tests were performed by melting 1.6 kilograms of HITEC XL in stainless steel reactor, after that the molten salts were heated to 290°C up to 375°C and successively up to higher temperatures,410°C, 445°C, 480°C, 515°C, and kept at each constant temperature for several hours. The air flow leaving the reactor is sampled by the gas chromatograph during the thermal decomposition tests of the Hitec XL for 5 temperature values between 375°C to 515°C.
During the experimental tests, 3ml/min of air were pumped into the reactor to make the temperature uniform. About 100 hectograms of the mixture were lost in the gas phase. The results are described in figure 7, for the data at lower temperatures (375°C, 410°C), the oscillation of the flow rate of oxygen and nitrogen is around zero. For higher temperatures (445°C, 480°C) the flow rate of nitrogen goes down to negative values. This can be attributed to the accumulation of oxygen released by the mixture of salts inside the system.
Figure 7 shows the variation of the flow rate measured entering and exiting the system for the whole duration of the test. It is clear that nitrogen evolution is relevant above 450°C, according to
the literature, and this behavior is also confirmed by nitrogen oxides production detectable around 500°C, see figure 4. The reactions involved in the decomposition are the 1,2,4. After the experimental campaign the salt was sampled and analyzed by acid-basic titration and it presents an oxide percentage (weight O2- with respect to the final weight of the mixture) of 0.2%, this means an high degradation rate. Since Na and K nitrates are stable up to 550°C (see references) the oxide presence is due to the formation of CaO. The figures 9-14 show the mean temperature value, the black line, together with the standard deviation, the blue line, moreover beside the temperature field during the temperature ramps.

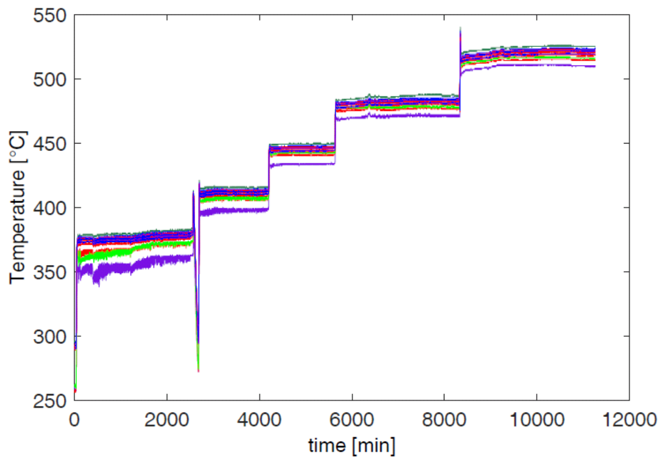


Figure 6. The temperature program of the experimental tests.

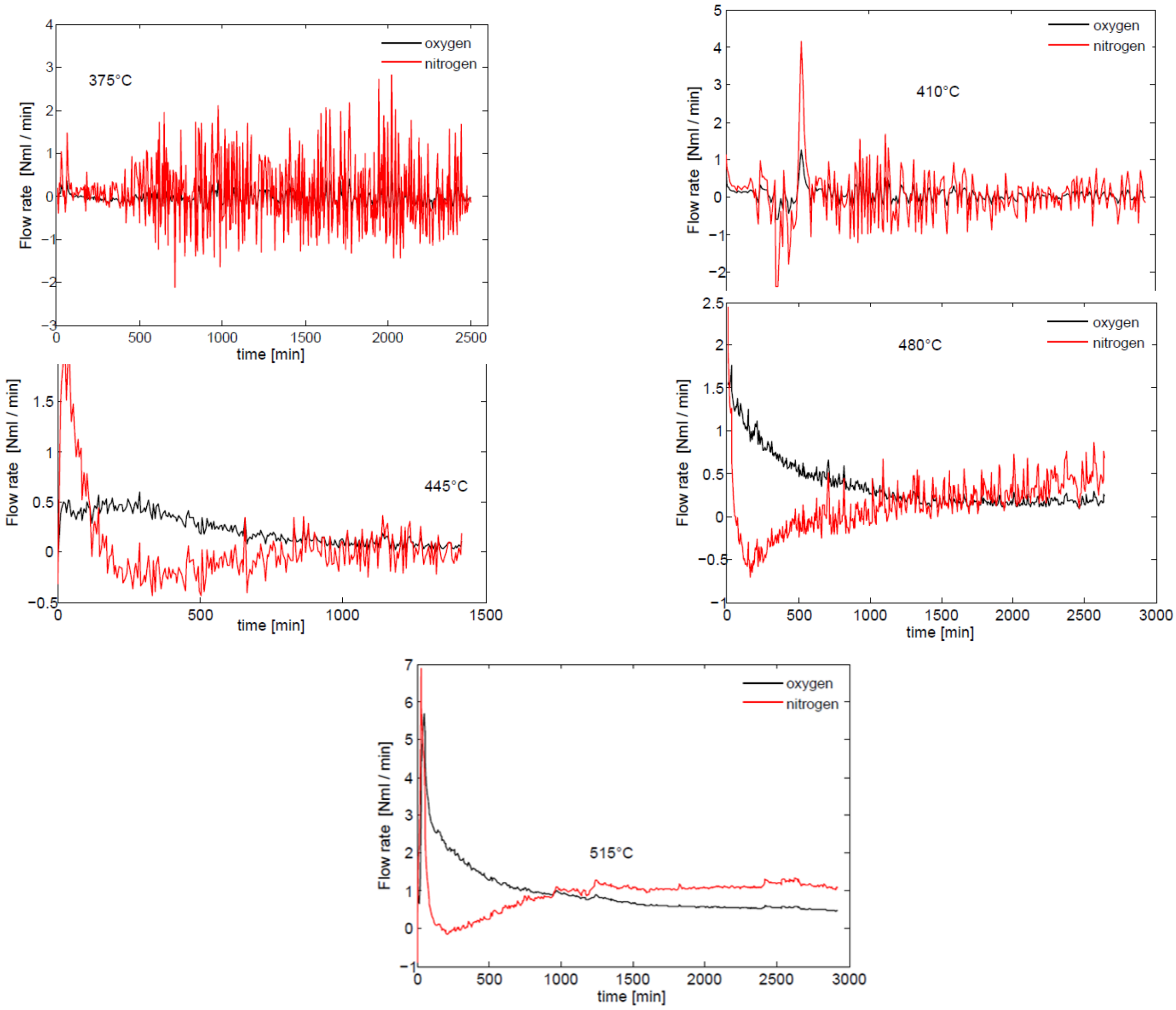


Figure 7 The experimental flow rate measured in the inlet and outlet sections of the system for the whole duration of the test.

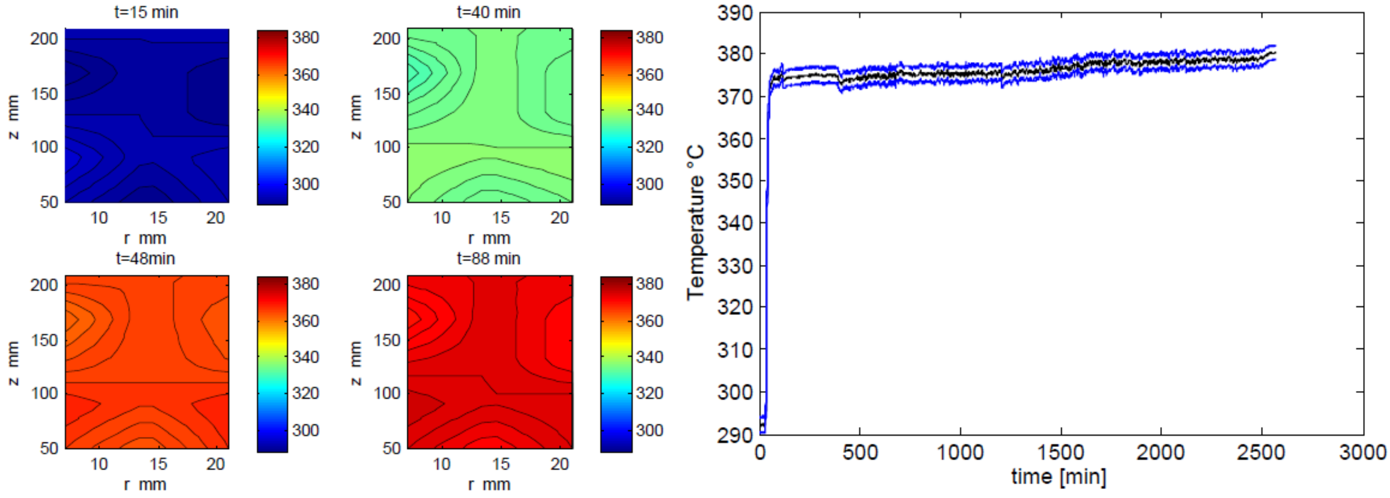


Figure 8. The mean temperature value over time and the temperature field both at 375°C.

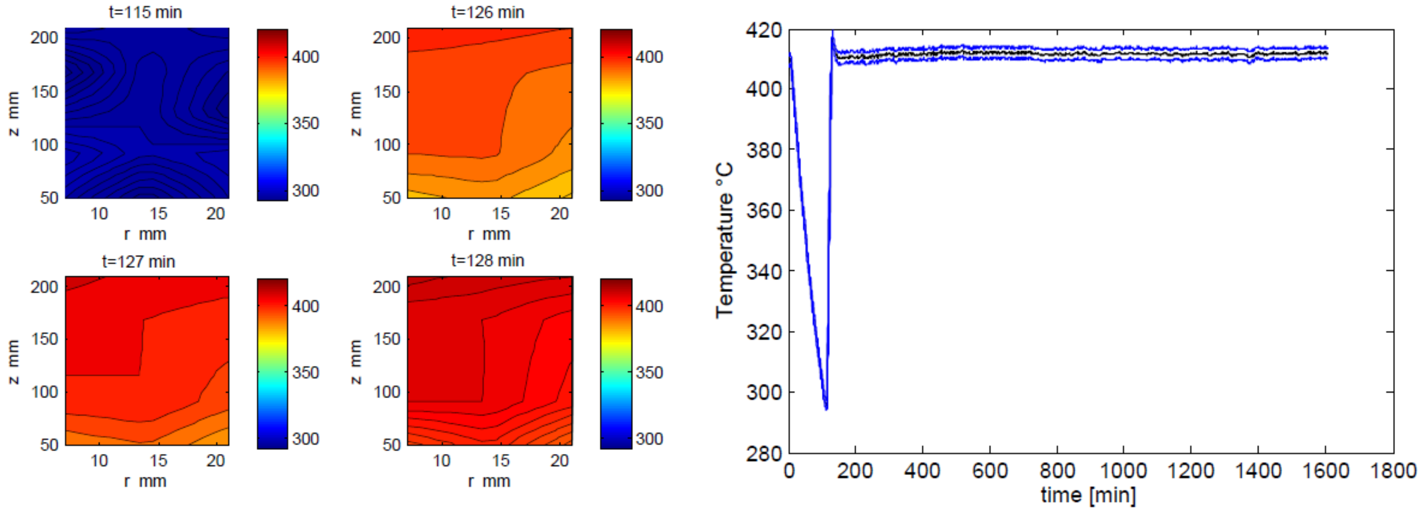


Figure 9. The mean temperature value over time and the temperature field both at 410°C.

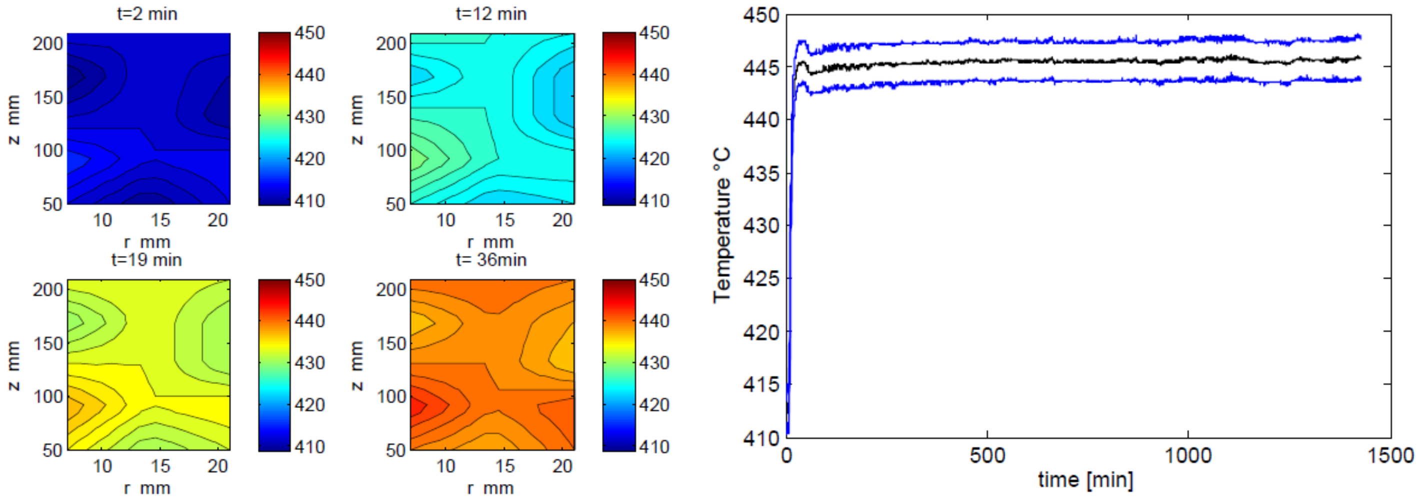


Figure 10. The mean temperature value over time and the temperature field both at 445°C.

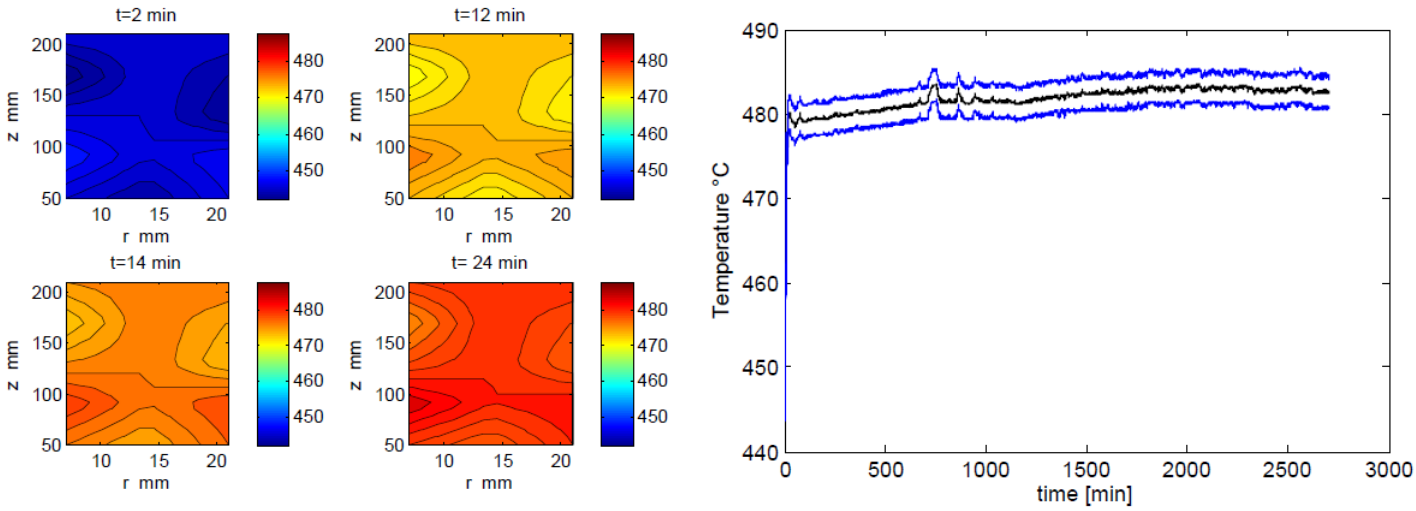


Figure 11. The mean temperature value over time and the temperature field both at 480°C.

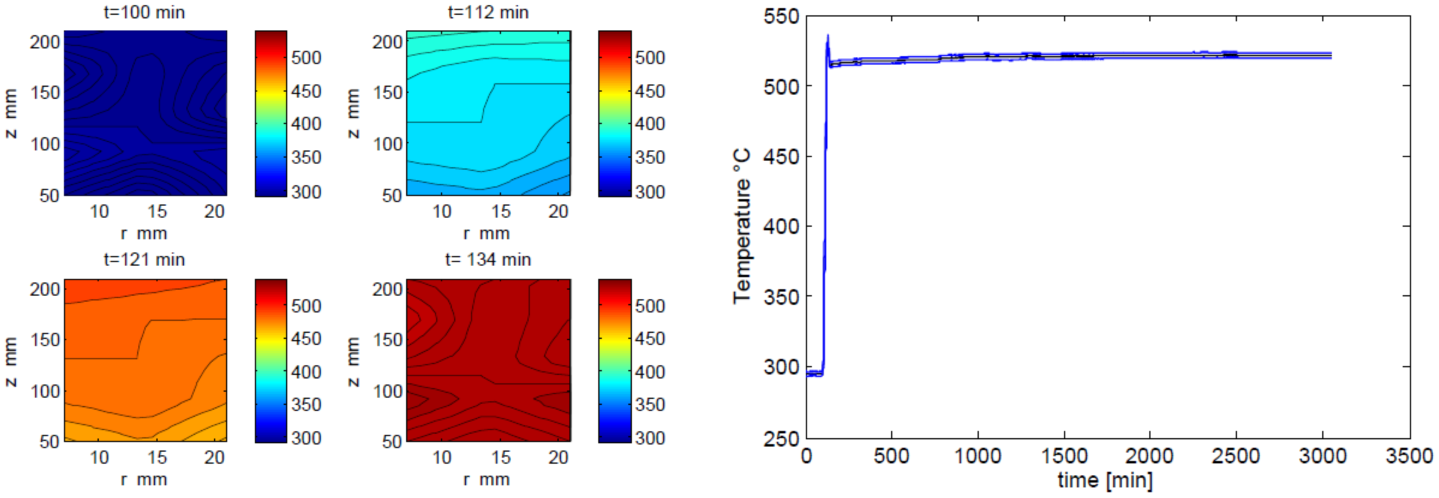


Figure 12. The mean temperature value over time and the temperature field both at 515°C.

CONCLUSIONS

To summarize, the described experimental set-up has demonstrated to be a valuable tool for following in real time the change in composition of thermal fluids. Although a molten nitrate was used to test the feasibility of the system, the same methodology can be employed for other inorganic mixtures.

The advantage of the system are the maintenance of isothermal conditions, the accuracy in the measurements of temperature and produced gas composition, and the possibility to sample directly analyse the melt.

In the near future, several molten fluids will be tested, in order to improve the knowledge about the chemical stability of heat transfer and storage materials for CSP.

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