



NEW STORAGE LATENT AND SENSIBLE  
CONCEPT FOR HIGH EFFICIENT CSP PLANTS



Schweizerische Eidgenossenschaft  
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## **Deliverable D3.8 - Report on Lithium mixtures**

### **ABSTRACT**

One of the main objectives of Work package 3 was the development of new salt mixture compositions with improved thermal performance for thermal energy storage, thus contributing to the overall storage efficiency of the CSP plant.

Assessment of thermal stability and thermal cycling resistance of a Li-based ternary mixture containing nitrates of lithium, sodium and potassium was carried out under subtask 3.2.2 and the results are reported in the present deliverable D3.8.

After a short review on relevant properties of molten salts to be taken into account in TES applications, particularly on the utilization of lithium in the mixtures, the experimental work carried out at LNEG and DLR is described. The results are discussed and compared to those obtained on a Ca-containing mixture studied under subtask 3.2.1.

The research carried out was focused on a  $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$  eutectic mixture, which has a very low melting point (near  $120^\circ\text{C}$ ), which promotes stability at low temperatures and avoids risk of freezing in the "cold tank" of the thermal energy storage plants. After selection of working temperature range through TG/DTA-DSC and short-term thermal tests, long-term isothermal tests at  $490$  and  $470^\circ\text{C}$  were carried out up to  $5000$  and  $4000$  h, respectively, as well as thermal cycling tests between  $150$  and  $480^\circ\text{C}$  ( $900$  h at the higher temperature). The evaluation of the salt stability was assessed by determination of thermal properties as well as chemical analysis for identification of possible transformations occurred.

Results can be summarized as follows:

- The  $\text{Li-Na-K-NO}_3$  mixture can be considered thermally stable at  $470^\circ\text{C}$ , with low nitrate decomposition and low oxide and carbonate formation;
- Nitrates and nitrites content were stabilized with around  $98.5$  and  $0.6 - 0.7$  mol%, respectively, from  $2500$  h;



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- Oxides and carbonates content were stabilized with around 0.1 and 0.8 mol%, respectively, from 2500 h;
- Lithium nitrate is the less chemically stable constituent of the mixture;
- Selective decomposition of the lithium nitrate into carbonate over time was observed at temperature of 490°C, according to the sequence  $\text{LiNO}_3 \rightarrow \text{Li}_2\text{O} \rightarrow \text{Li}_2\text{CO}_3$  and solid lithium carbonate was identified in the bottom of the crucible; the same was not found at 470°C.
- Working temperature during long term cycling is proposed to range between 150 and 470 °C ( $\Delta T = 320$  °C).
- As compared with a Ca-bearing mixture, also tested in the project, the Li-bearing mixture allows working at lower temperature, it decomposes earlier, and has a quite similar working temperature range (320°C vs. 330°C).

To the authors knowledge, this was the first study on long-term (>1000 h) thermal stability of lithium containing nitrate salt ternary mixtures for thermal energy storage application at high temperature.