Status on molten nitrate salts above 600 °C

03.12.2021, **Molten Salts 2021**, online

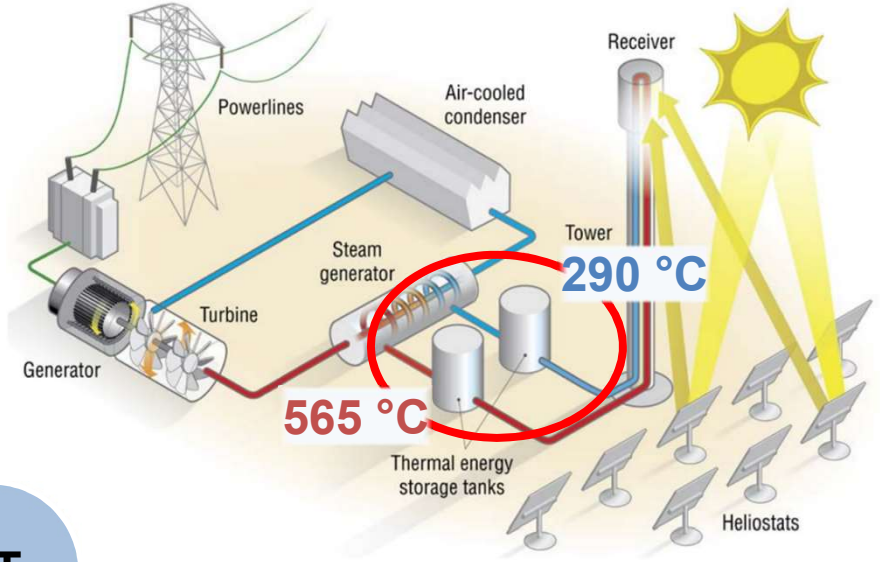
Julian Steinbrecher, Alexander Bonk, Markus Braun, Andrea Hanke, Thomas Bauer

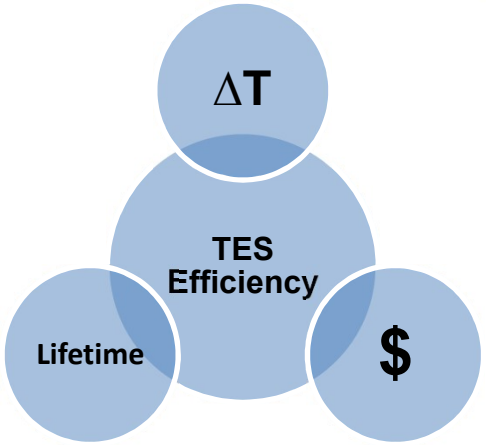
DLR

State of the art

Thermal energy storage for CSP application

DOE, U. "The Year of Concentrating Solar Power." US Department of Energy (2014).





→ Hot Tank 620 °C
→ Lower LCOE
→ Increased efficiency

Research group Thermal Systems for Fluids (TSF) at the DLR

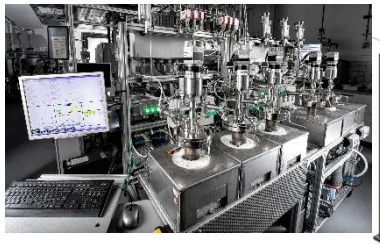
10 mg

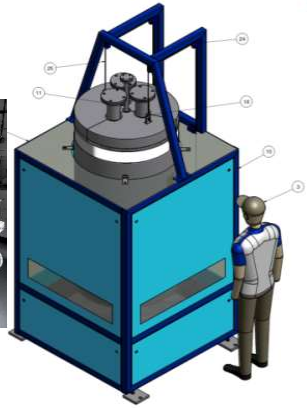
10 000 ton

"... value chain research..."

Material aspects

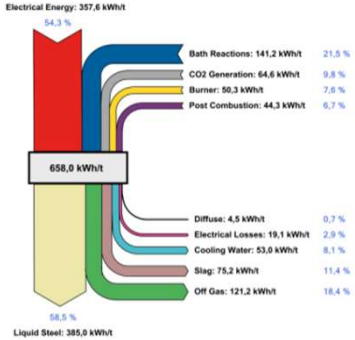
Process technology (Upscaling)





Components

System aspects



What are we dealing with?

Solar Salt

$(Na, K)NO_3$

High temperature decomposition

T > 565 °C

$$NO_3^- \rightleftharpoons \frac{1}{2}O_2 + \mathbf{NO_2^-} \rightleftharpoons \mathbf{O^{2-}} + NO_x$$

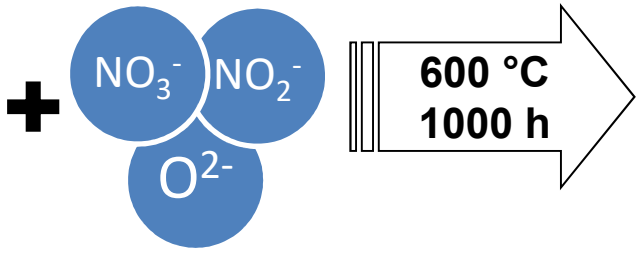
Accumulation of nitrite (NO_2^-) and oxide (O^{2-}) ions over time

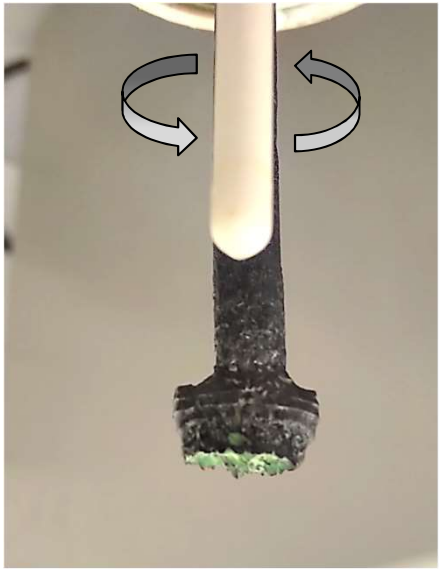
Is there a problem?

NO_2^- → Lower melting point

O^{2-} → Corrosive

Stirrer before the experiment





“Stirrer” after the experiment

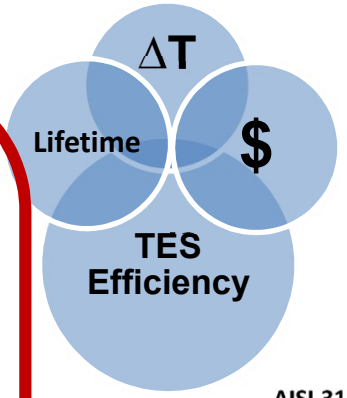
Careful parameter selection and experiment monitoring is necessary

The mission: Solar Salt chemistry above 600 °C

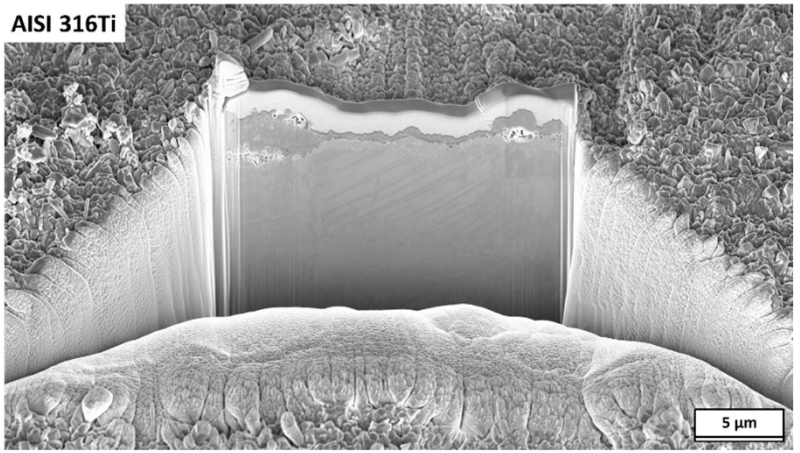
Molten Salt Stability

Temperature, partial pressure, salt composition

Equilibration



Corrosion Experiment



Bonk A., *Solar Energy Materials and Solar Cells* **2019**, *203*, 110162.

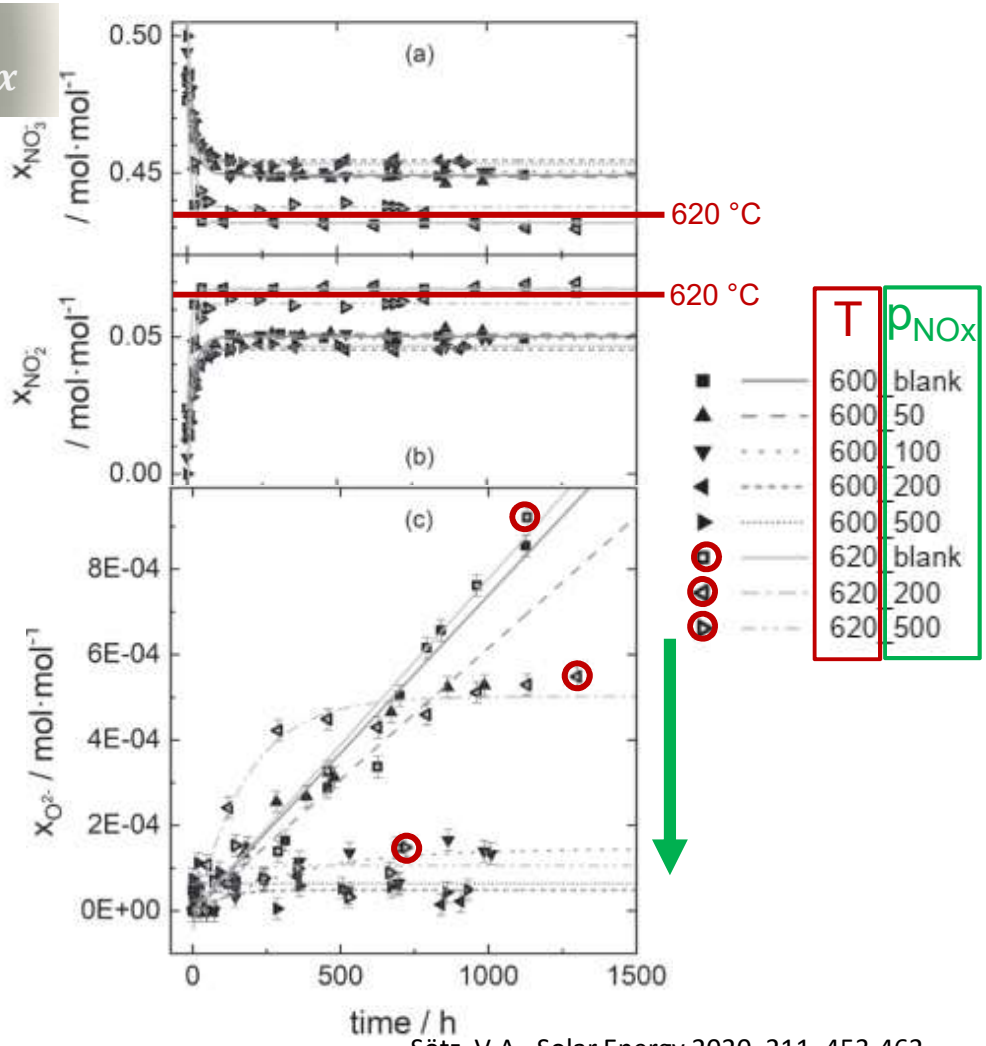
Molten salt stabilization at 600 and 620 °C

$$NO_3^- \rightleftharpoons \frac{1}{2}O_2 + NO_2^- \rightleftharpoons O^{2-} + NO_x$$

Experimental Design:

- Isothermal at 600/ 620 °C
- Salt composition monitoring
- Purge gas control
  - Oxygen (20 vol%)
  - Nitrous Gas (NOx)

→ To prevent oxide ion (O^{2-}) formation, nitrous gas (NOx) is <u>necessary</u> for molten salt stabilization



Sötz, V.A., Solar Energy 2020, 211, 453-462.

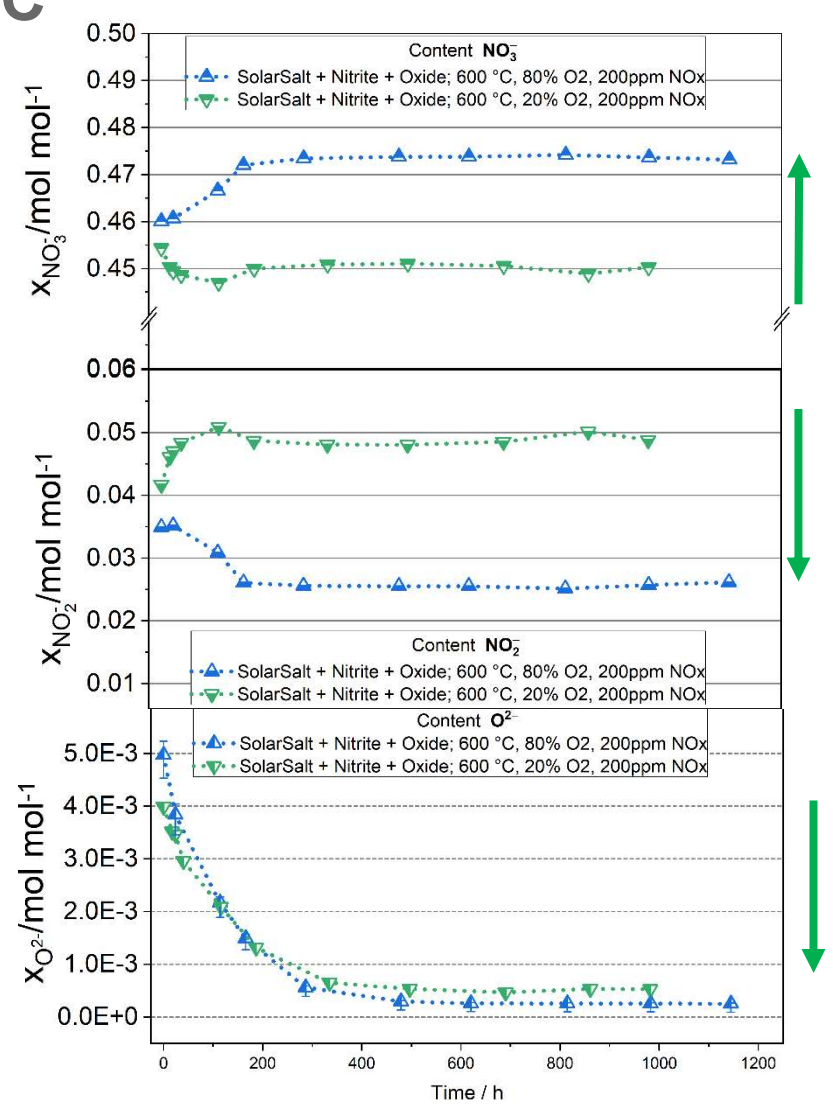
Molten salt regeneration at 600 °C

$$NO_3^- \rightleftharpoons \frac{1}{2}O_2 + NO_2^- \rightleftharpoons O^{2-} + NO_x$$

Experimental design:

- “aged” Solar Salt (+ nitrite, oxide)
- Isothermal at 600 °C
- Salt composition monitoring
- Purge gas control
  - Oxygen (20% / 80 %)
  - Nitrous Gas (NOx)

→ An oxide ion (O^{2-}) rich molten salt can be regenerated with adequate gas management



Steinbrecher, J., Materials 2021, 14. DOI:10.3390/ma14195664

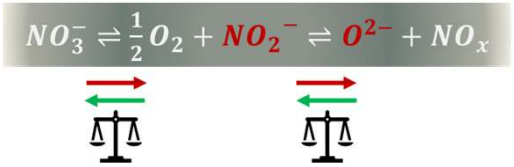
High temperature ~~decomposition~~ control

T > 565 °C

$$NO_3^- \rightleftharpoons \frac{1}{2}O_2 + NO_2^- \rightleftharpoons O^{2-} + NO_x$$

Stable Solar Salt at 600 °C and above

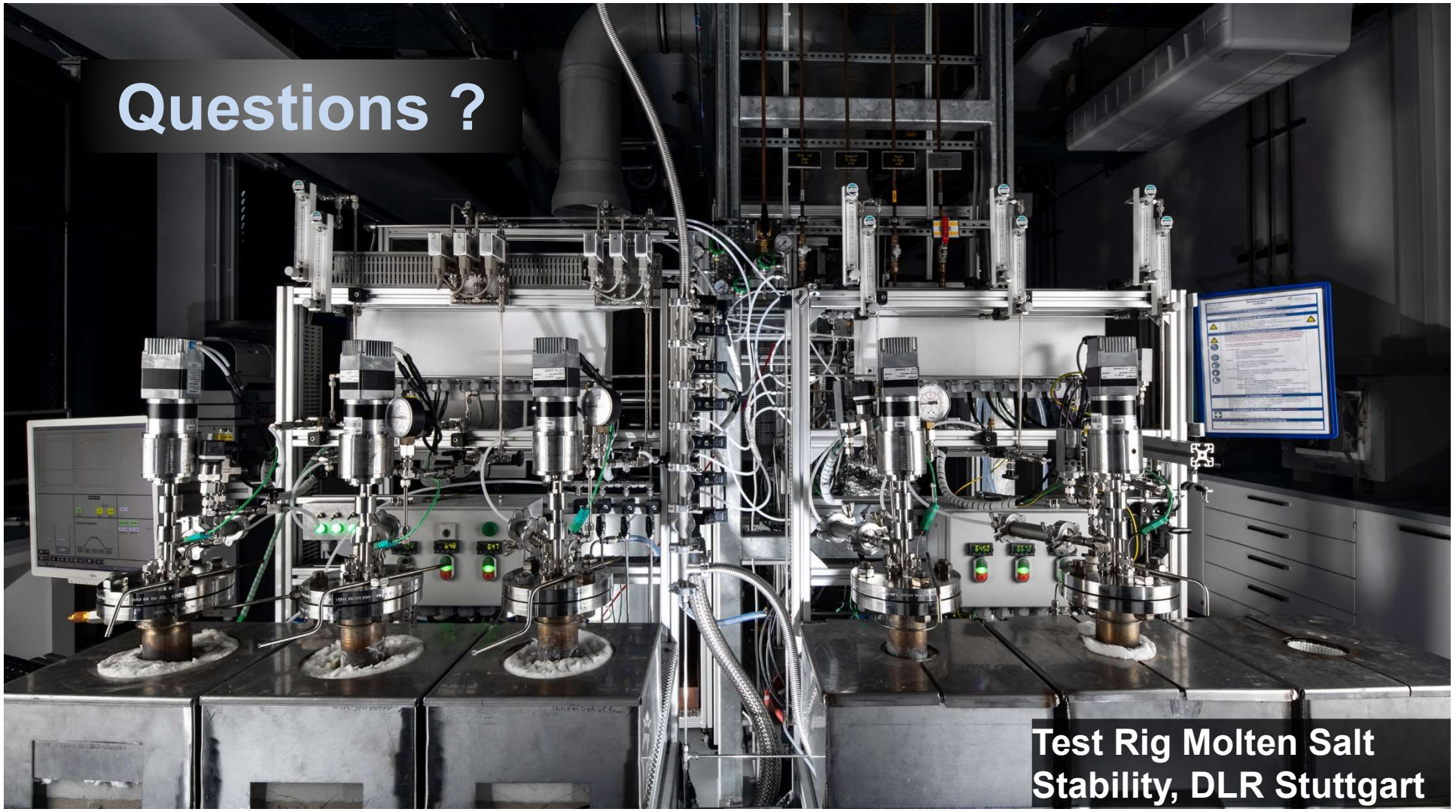
- First data the stabilization of Solar Salt at 620 °C in terms of ion conten (NO_3^-, NO_2^- and O^{2-}).
- First data on the regeneration of an “aged” Solar Salt with active gas management (O_2 and 200 ppm NOx).
- Temperature increase (for nitrate salt TES) is **not** advisable without simultaneously controlling the gas atmosphere.
- Future Work:
  Development of a liquid – gas reaction mechanism (model), high temperature corrosion experiment with gas phase control



Federal Ministry for Economic Affairs and Energy

FKZ: 03EE5043A

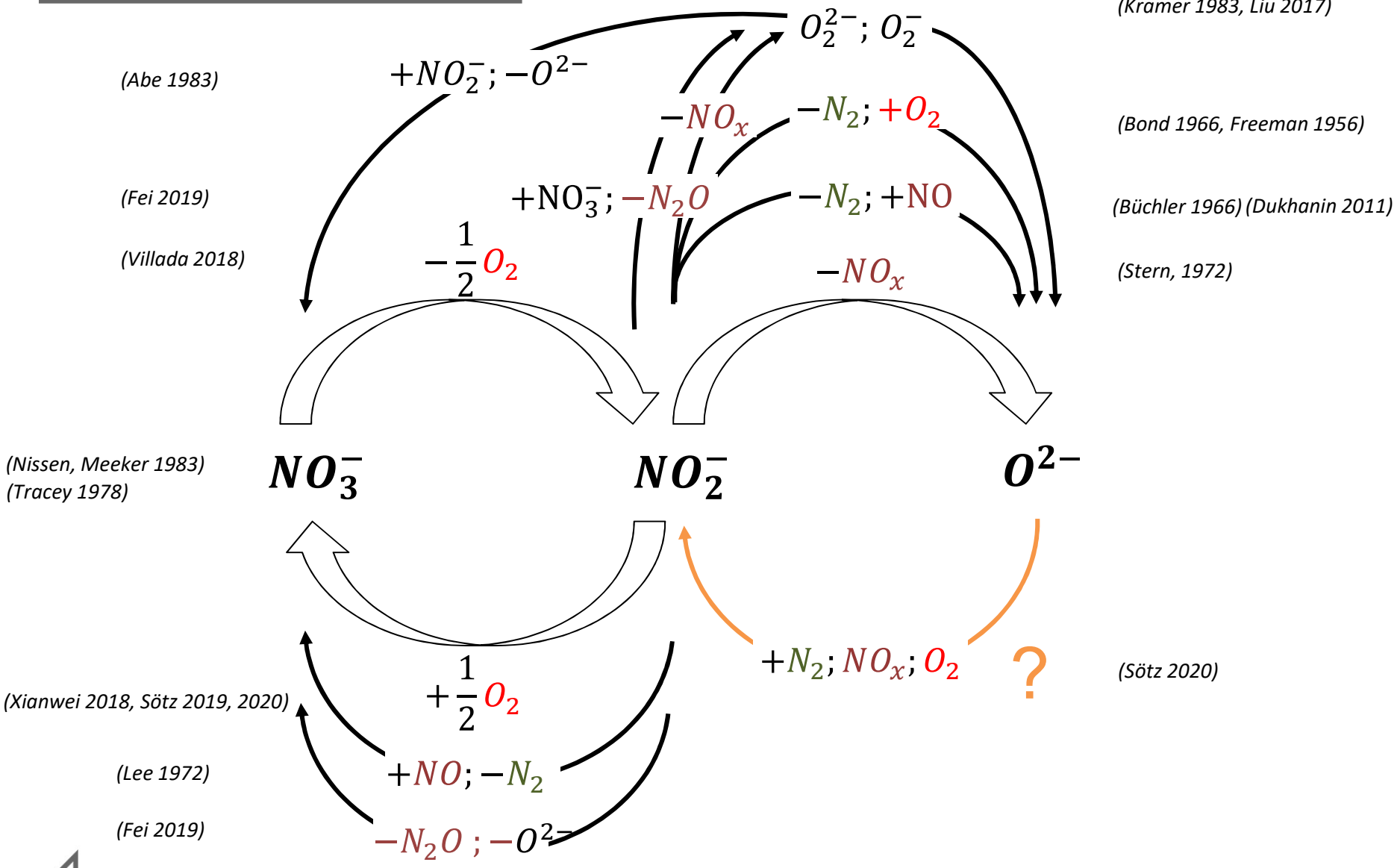
Questions ?



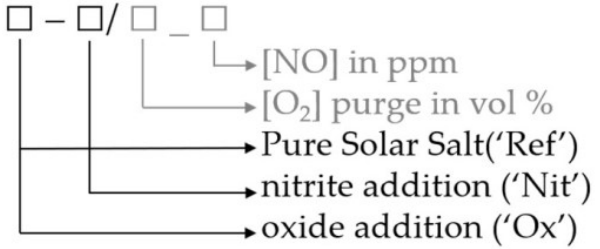
Test Rig Molten Salt Stability, DLR Stuttgart

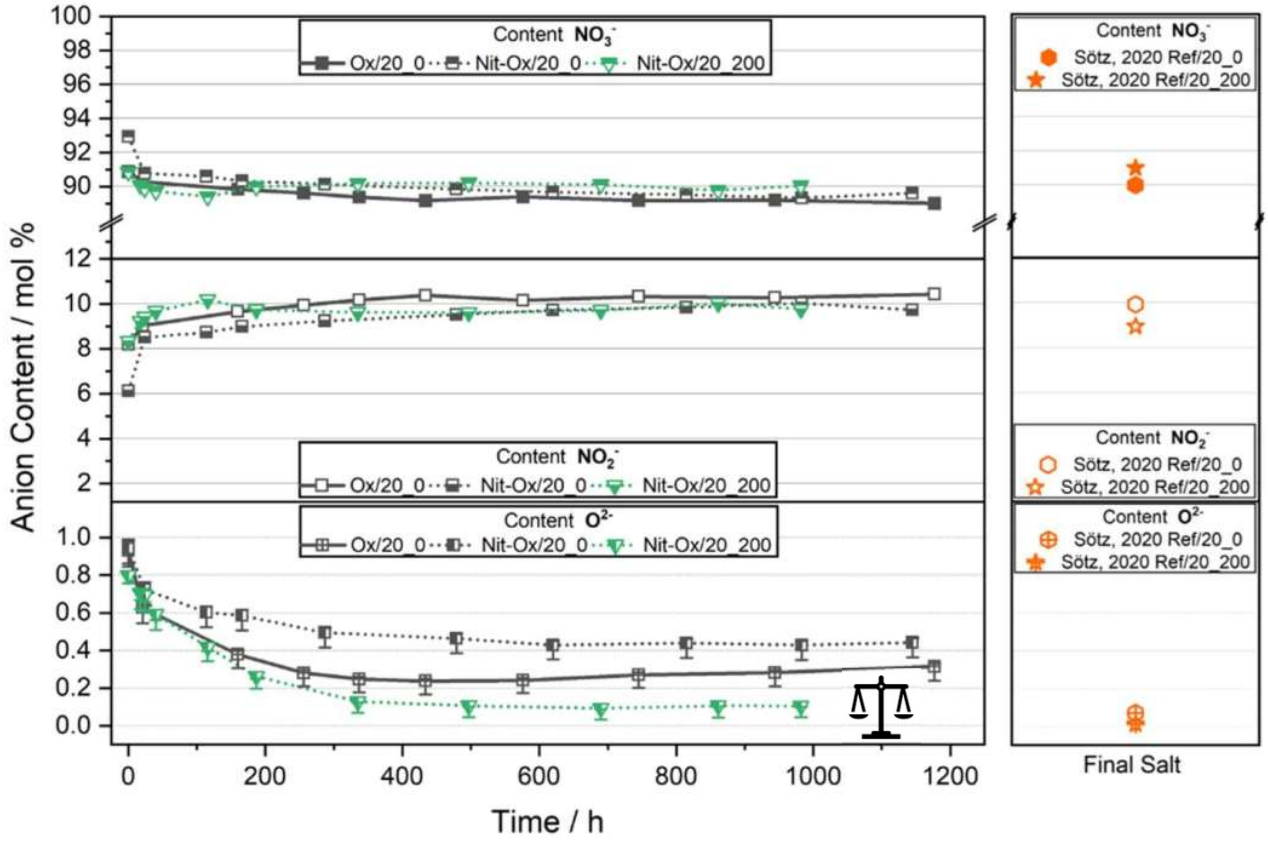
DLR

Nitrate Salt Equilibria



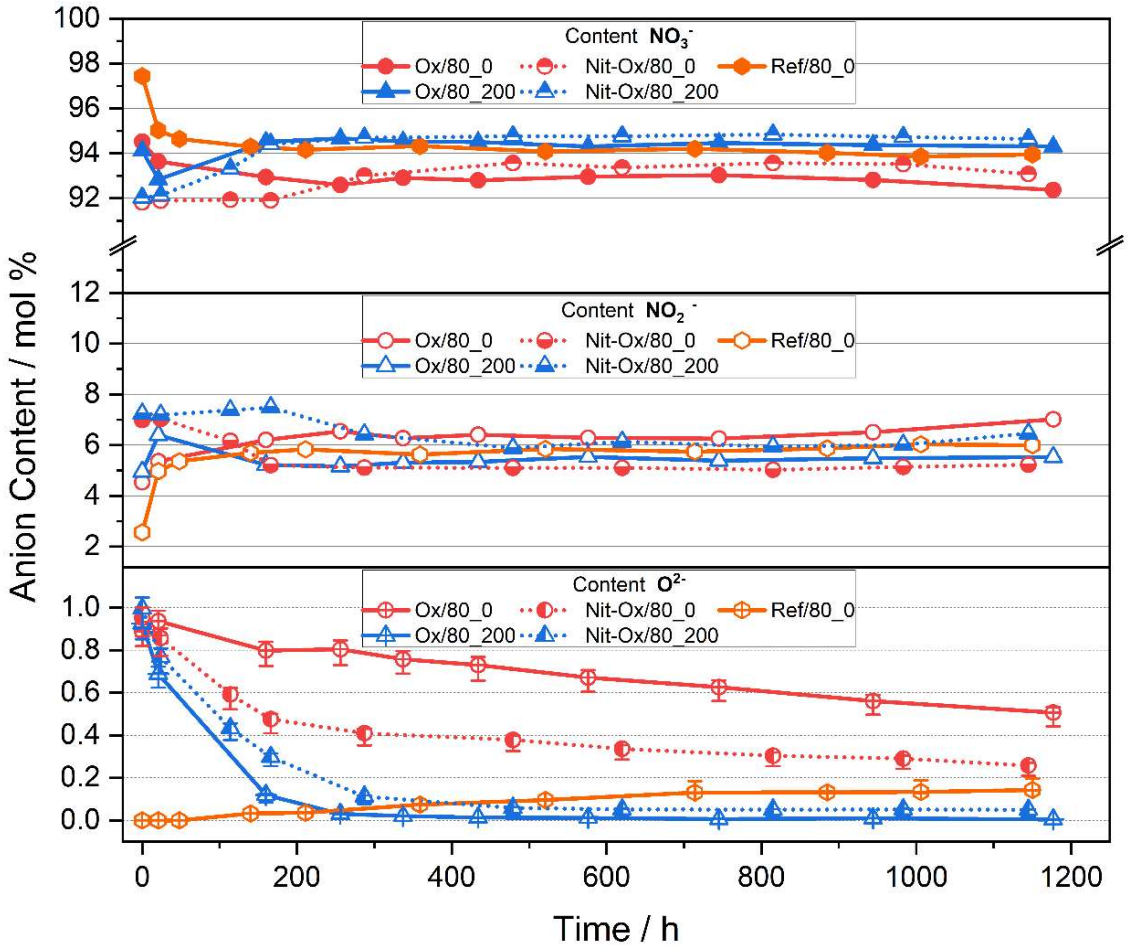
Steinbrecher, J.; Bonk, A.; Sötz, V.A.; Bauer, T. Investigation of Regeneration Mechanisms of Aged Solar Salt. ***Materials*** **2021**, *14*.





Steinbrecher, J.; Bonk, A.; Sötz, V.A.; Bauer,
Investigation of Regeneration Mechanisms of A
Salt. ***Materials*** **2021**, *14*.

□ – □/ □ _ □
- [NO] in ppm
- [O_2] purge in vol %
- Pure Solar Salt('Ref')
- nitrite addition ('Nit')
- oxide addition ('Ox')



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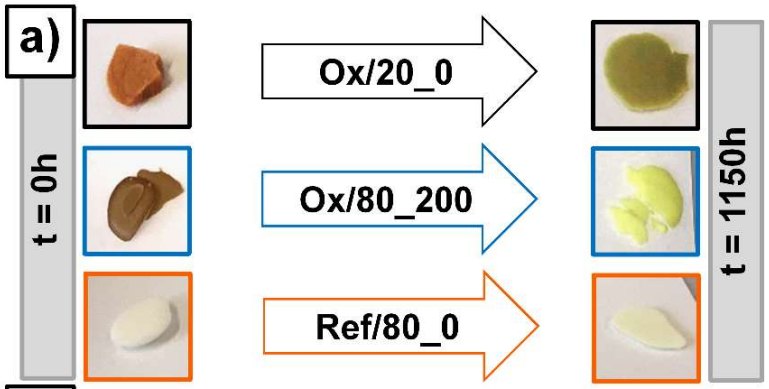
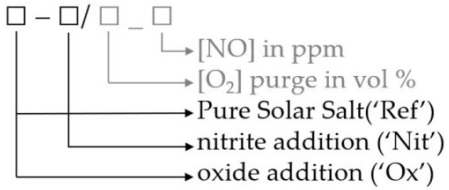
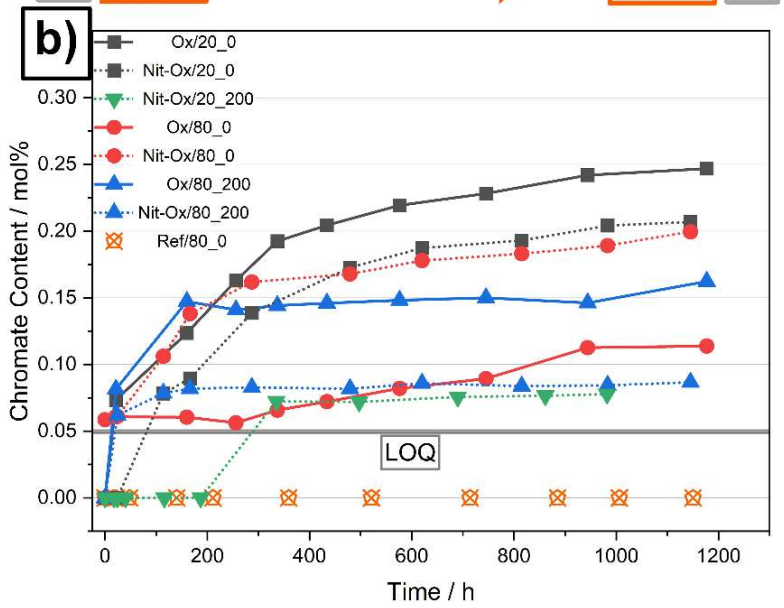
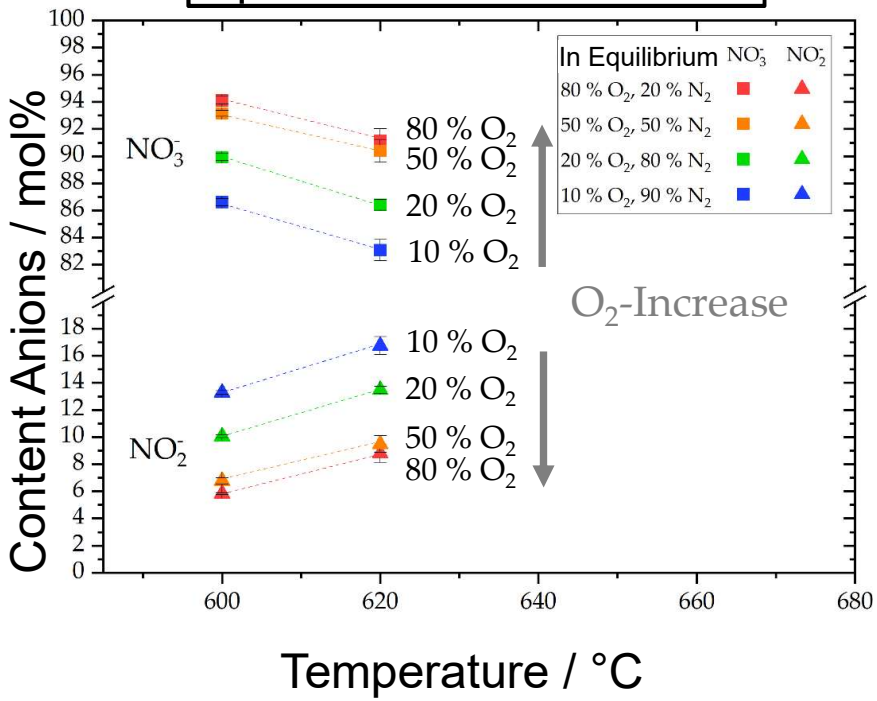




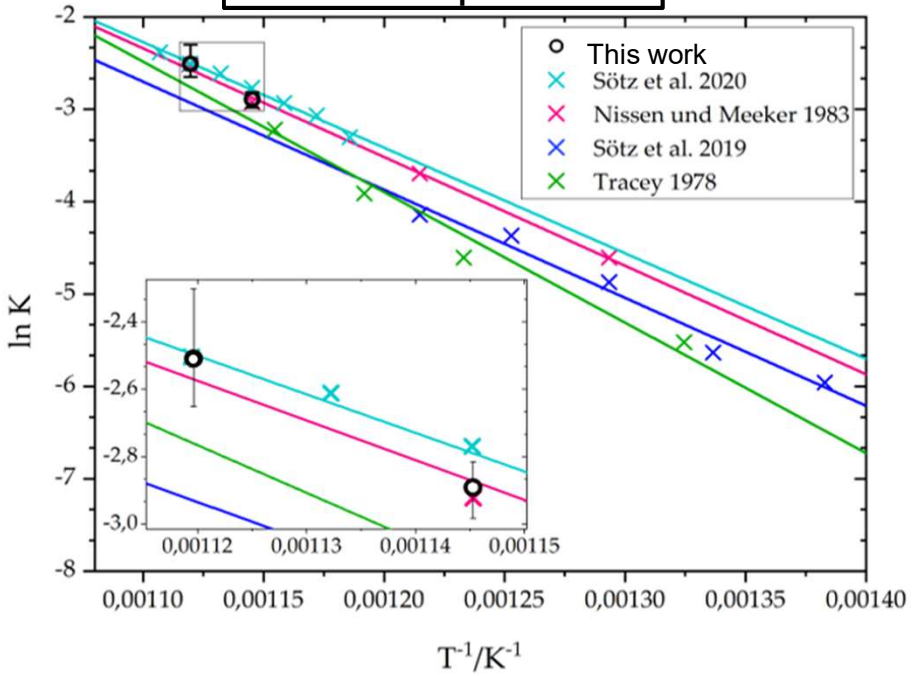


Recap 2021: Solar Salt Chemistry - **Oxygen**

Equilibrium concentrations



Van't Hoff plots of K

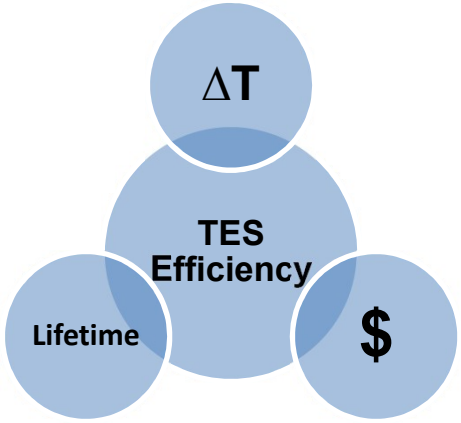


$$K_P = \frac{[NO_2^-]pO_2^{\frac{1}{2}}}{[NO_3^-]} = \exp(-\frac{\Delta G_R^\circ}{RT})$$

$$NO_3^- \rightleftharpoons \frac{1}{2}O_2 + NO_2^- \rightleftharpoons O^{2-} + NO_x$$

Upcoming Tasks

→Salt Stability at 620 °C (650 °C) with **NO_2, N_2O**



→Experiments with **overpressure** (>1 bar)

→Salt decomposition **modeling** based on our equilibrium data

→**Corrosion** Experiment of prominent Steel samples (at 620 °C) under NOx gas atmosphere