

Progress in Research and Development of Molten Chloride Technology for Large-Scale Thermal Energy Storage at $\geq 700^{\circ}\text{C}$

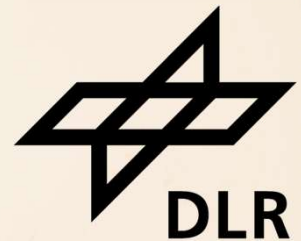
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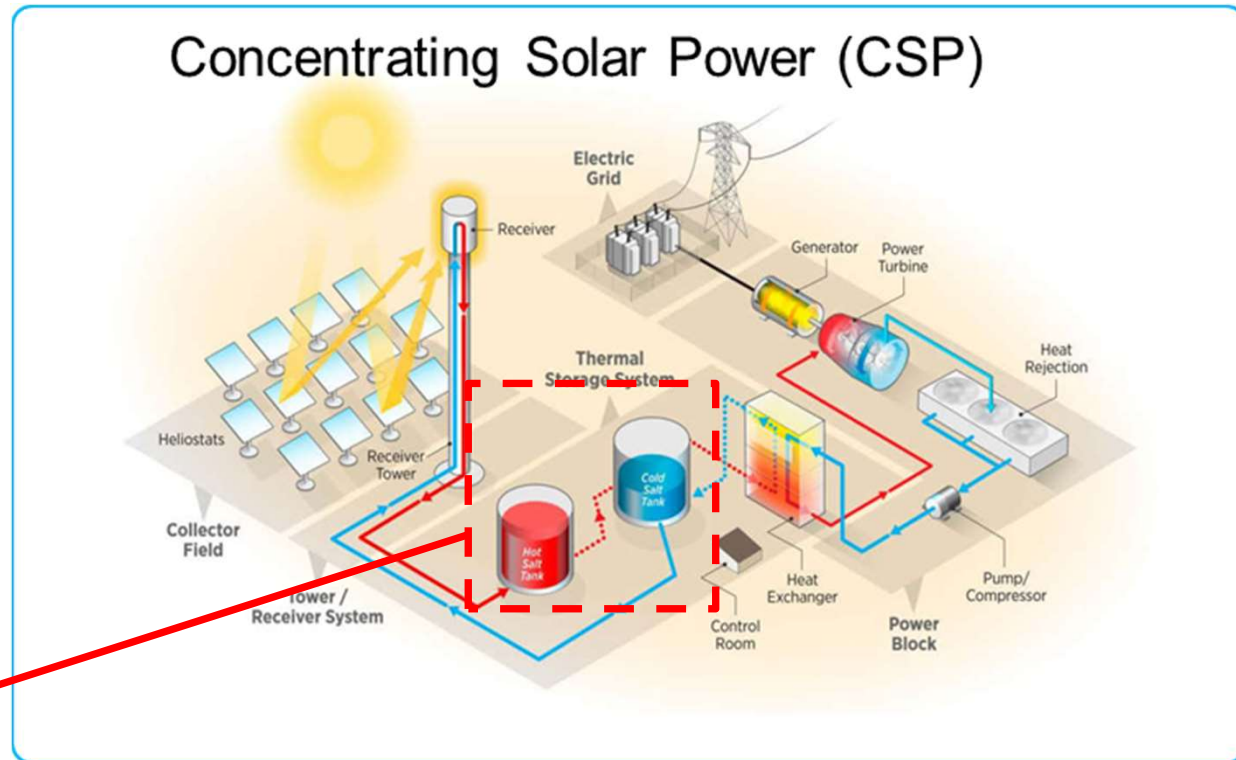


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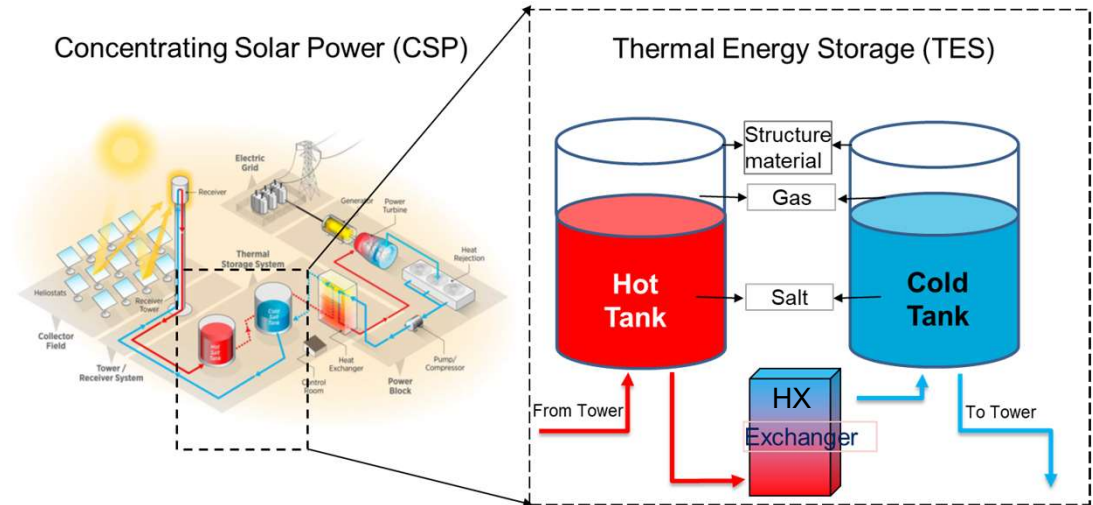
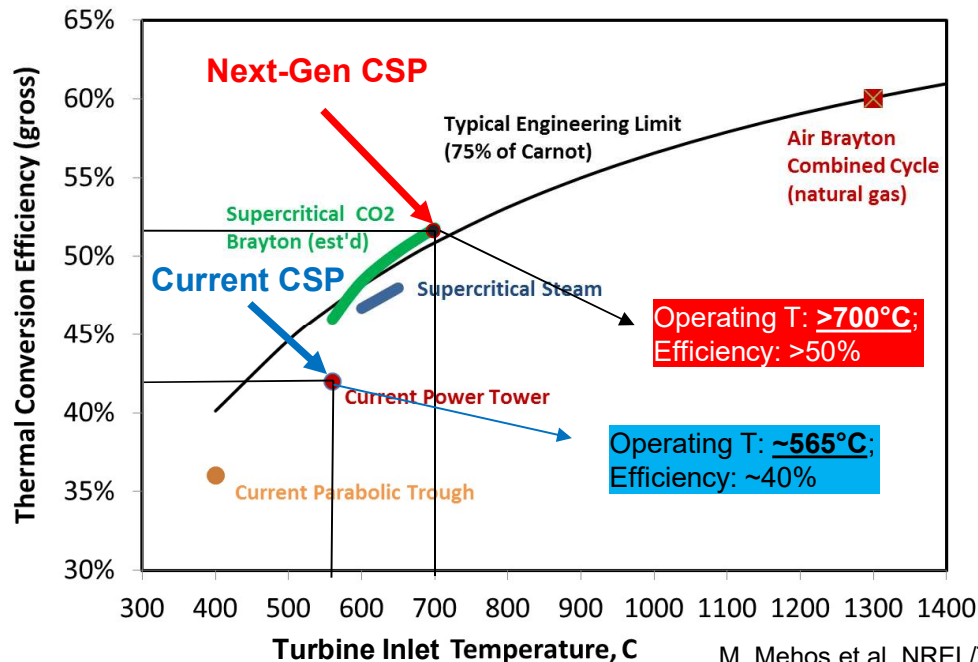
- **Background & Motivation**
- Corrosion Control of Molten Chloride Heat Storage and Transfer
- Process Upscaling of Molten Chloride Heat Storage and Transfer
- Summary

Molten salt TES for CSP



- **>7 GW CSP, >60 GWh_{th}** molten salt TES in operation
- Molten salt TES (**290-565°C**): **~2.5 GWh_{th}** for 10-hour storage of a 100MW_{el} CSP, **~20 000 tons nitrate salts**
- Low CAPEX of molten salt TES: **20-33 \$/kWh_{th}**

Molten Chloride TES for Advanced Thermal Power Plants



$T_{\text{hot}} 565^{\circ}\text{C}$ (Nitrate) $\rightarrow >700^{\circ}\text{C}$ (Chloride)

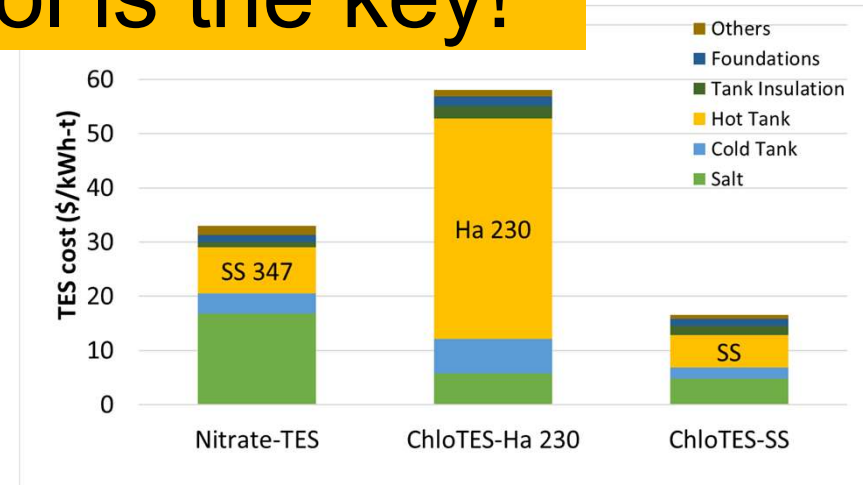
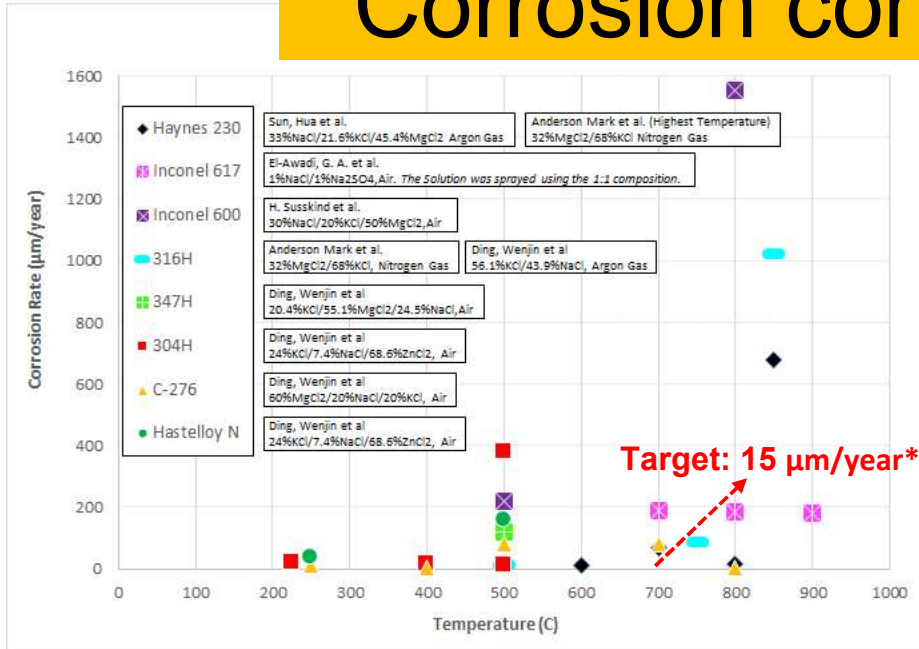
M. Mehos et al. NREL/TP-5500-67464, 2017.

Turchi, Craig. "Concentrating solar power: current cost and future directions." Colorado: National 32 (2017).

- **Next-Gen CSP:** advanced power cycle (e.g., sCO_2 Brayton) with higher efficiency $>50\%$ \rightarrow higher turbine inlet temperature $\geq 700^{\circ}\text{C}$ \rightarrow higher TES temperature $>700^{\circ}\text{C}$
- **But state-of-the-art commercial Nitrate-TES:** $\text{NaNO}_3\text{-KNO}_3$ 60-40 wt.% (Solar Salt), limited to 565°C by thermal decomposition
- **Chloride-TES** with operating temperature of $>700^{\circ}\text{C}$ with excellent thermal stability of $>1000^{\circ}\text{C}$

Main Challenges for Next-Gen Chloride-TES

Corrosion control is the key!



Nitrate-TES cost: 20-33 \$/kWh_{th}
 Chloride-TES with Ha 230 hot tank: 58\$/kWh_{th}
Estimated Chloride-TES with SS hot tank: ~15\$/kWh_{th}

1st challenge: Severe corrosion of molten chlorides

2nd challenge: Affordable structural materials

- **Severe corrosion of alloys in molten chlorides** due to corrosive impurities (e.g., OH⁺) formed by hydrolysis
- **Ni-based alloys needed for hot tank** if corrosion control is not achieved → **High TES cost**
- **Fe-based alloys** used for hot tank under successful corrosion control (Chloride TES-cost ~15\$/kWh_{th})

C. Turchi et al. NREL/TP-5700-79323, 2021. M. Mehos et al. NREL/TP-5500-67464, 2017. *Target of DOE: Garcia-Diaz BL, et al. J.S.C. acad. sci.. 2016; 14(1): 4.

R&D of Chloride-TES at DLR

Corrosion control system (CCS)

Inert atmosphere

4

Electrolytic salt purification for reducing corrosive impurity level

5

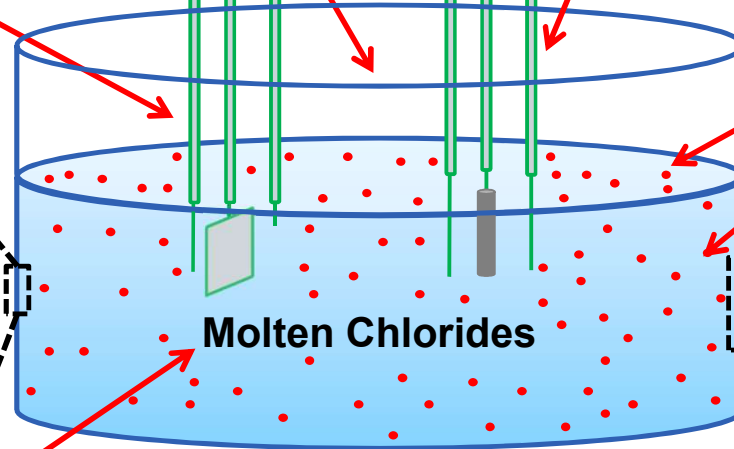
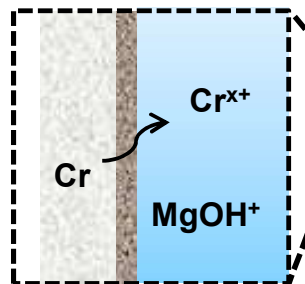
Mg corrosion inhibitor

3

In-situ corrosive impurity monitoring based on cyclic voltammetry

2

Corrosion mechanism of Fe-Cr-Ni alloy



Molten salt storage tank

Protective Al₂O₃ layer

Pre-oxidized Fe-Cr-Al alloy

6

Corrosion resistant structural materials (alloys and ceramics)

1

Selection of promising chloride salts & salt properties of selected MgCl₂-NaCl-KCl

Process upscaling

7

Process upscaling (salt purification, loop and key components)



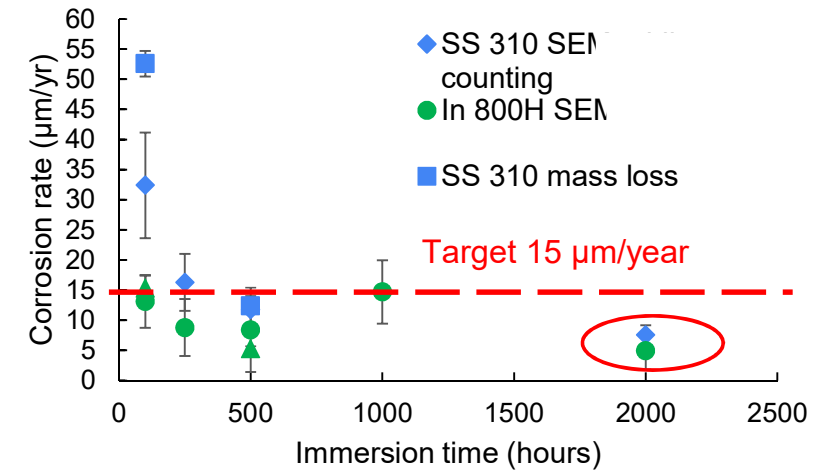
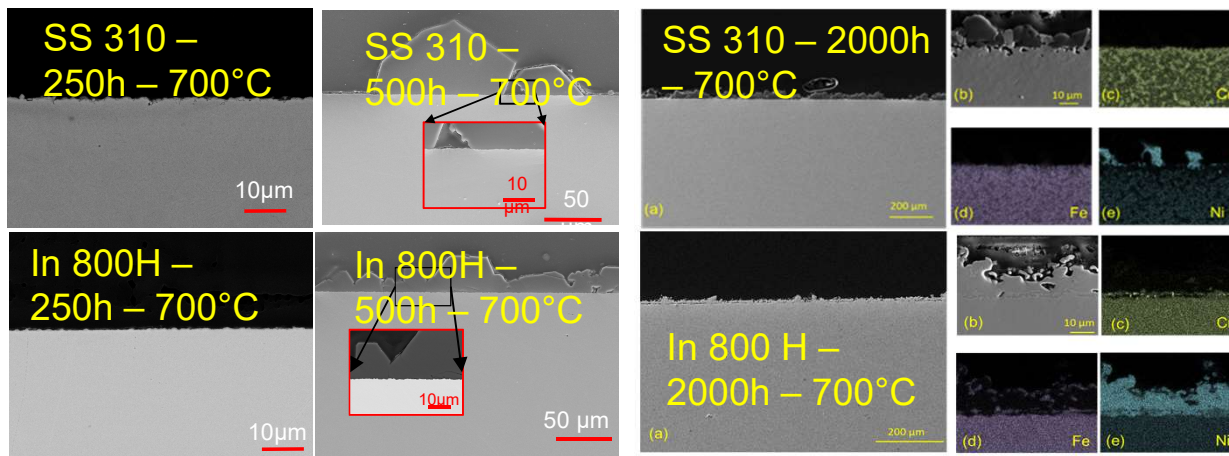
W. Ding*, et al., *FCSE* **2018**, 12(3): 564–576.
 W. Ding* & T. Bauer, *Engineering*, **2021**, 7(3): 334-347.
 C. Villada, W. Ding*, et al. *SOLMAT*, **2021**, accepted.
 W. Ding*, et al., *SOLMAT*, **2018**, 184: 22–30.
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 W. Ding*, et al., *SOLMAT*, **2019**, 193:298-313.
 *Patent filing: DE 10 2021 131 250.7 (2021)
 Q. Gong, et al., *Applied Energy*, **2022**, 324, 119708
 Q Gong, et al., *SOLMAT*, **2023**, 253, 112233

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5 Mg Corrosion Inhibitor – Breakthrough by DLR



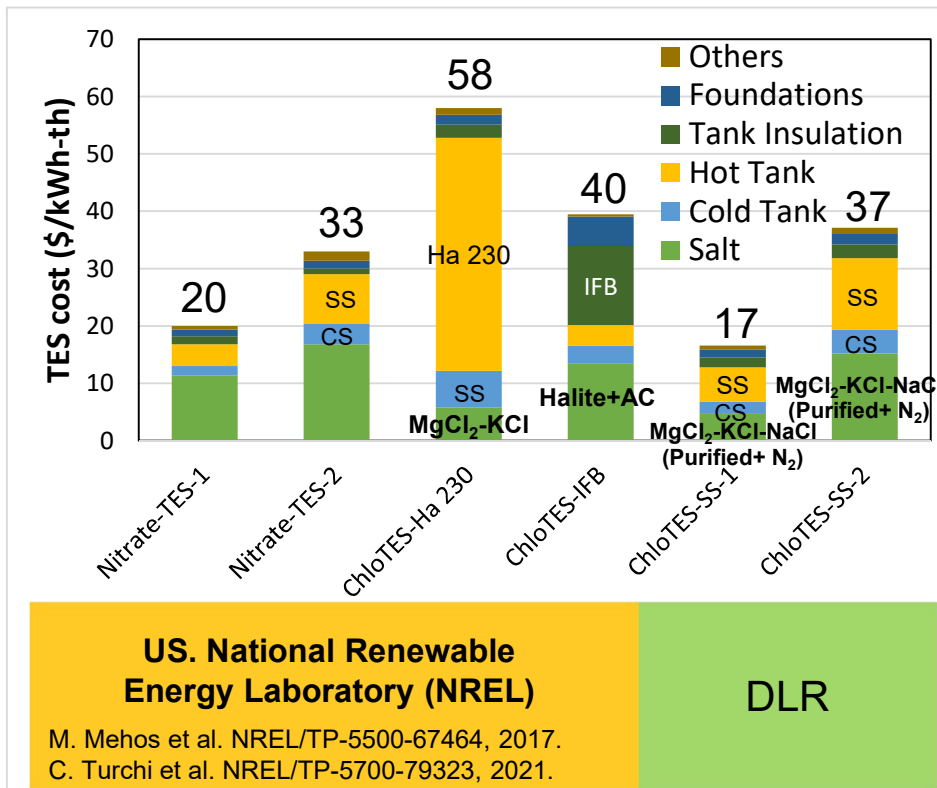
- Salt purified with Mg at 700°C in a patented process*
- **Static immersion tests in purified molten salt at 500-800°C under Ar (up to 2000h):** Almost no corrosion layers and Cr-depletion of Fe-based steels were observed
- Corrosion rate based on microstructural analysis (SEM) and mass loss: **<15 µm/year for SS 310 and In 800H at 700°C; <15 µm/year for P91 at 500°C**
- **Breakthrough*:** Experimental proof that Fe-based steels reach the target of **<15 µm/year** at 500 and 700°C

*Patent: DE 10 2021 131 250.7 (2021)

Q. Gong, T. Bauer, W. Ding, et al., Applied Energy, 324, 119708 (2022)
Q Gong, T Bauer, W Ding, et al., SOLMAT, 253, 112233 (2023)

5 Mg Corrosion Inhibitor –

Competitive low TES-cost based on molten chlorides and Fe-based steels



- Commercial Nitrate-TES cost estimated by NREL: **20 to 33 \$/kWh_{th}**
- Estimation cost of chloride-TES with insulating fire bricks (IFB) or Ha 230 as hot tank by NREL (corrosion control not achieved): **40 to 58 \$/kWh_{th}**
- Competitive low cost of chloride-TES** using Fe-based steels estimated by DLR (corrosion control achieved): **17 to 37 \$/kWh_{th}**

Ha: Hastelloy for hot tank
 SS: stainless steel for hot or cold tank
 CS: Carbon steel for cold tank

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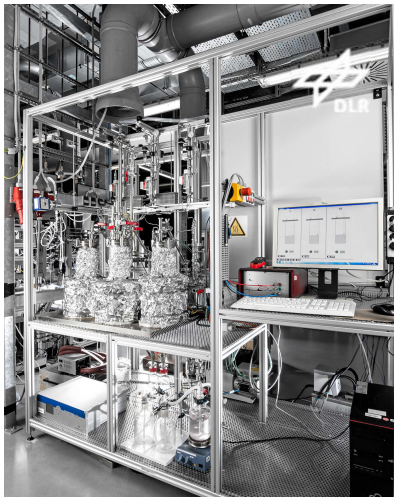


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7 Process Upscaling of Chloride-TES



Achieved



Materials research with <1 kg salt: corrosion control, structural materials pre-selection, ... (TRL 1-3)

Ongoing



Upscaling with ~100 kg salt: salt purification and corrosion control loop tests, structural materials selection (TRL 4-5)

Target



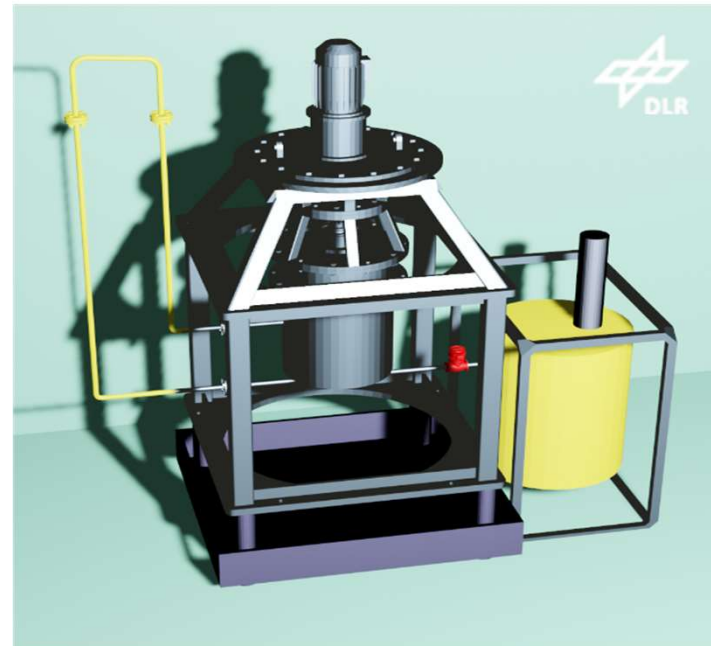
Pilot plant with ~100t salt & component testing (TRL 6-7)



Industry-application (TRL 8-9)

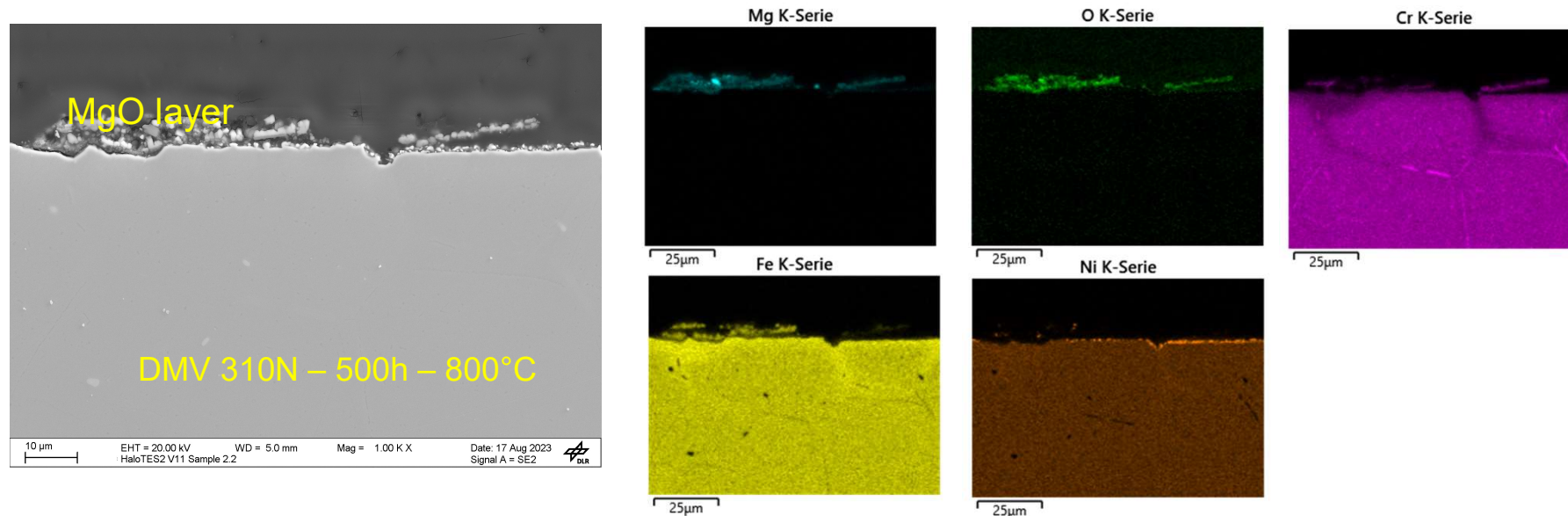
DLR seeks industrial and academic partners for upscaling

Molten Chloride Test Facility (MOCTEF) of DLR



- **Under construction** and will be operated soon
- **Two test units:** one for salt purification, one for pumped loop tests close to conditions in real applications
 - ~100 kg $\text{MgCl}_2\text{-NaCl-KCl}$ is used
 - Conventional stainless steels as structural materials
 - Designed test temperatures $>700^\circ\text{C}$
- **Highlights:** patented corrosion control system, salt and gas phase in-situ analysis, ...

Corrosion Test of DMV 310N in Purified Salt at 800 °C



- Pre-test*: 500h static immersion test **at 800°C** in salt purified with MOCTEF salt purification unit
- Corrosion rate (CR) via mass loss: **<50 µm/year**
- Chromium depletion depth ~ **10 µm** (mainly at crystal boundaries)
- 2000h static molten salt immersion and gas tests at 800°C are done and the results (**CR <15 µm/year**) will be published soon, while loop test in MOCTEF at >700°C is planned.

*H Barot, oral presentation in Enerstock Conference 2024, Lyon France, 2024.

Summary



- Molten chloride heat storage and transfer (MOC-HEST) with working temperatures up to 800°C has promising applications in next-gen CSP plants.
- Safe production of CSP plants with molten salt TES under corrosion control is vital.
- Corrosion control technologies in lab-scale have been developed for MOC-HEST.
- Stainless steels ($CR < 15 \mu\text{m}/\text{year}$) can be used as the main structural materials in MOC-HEST under corrosion control.
- Process upscaling of MOC-HEST to 100 kg-scale with pumped loop is ongoing.

Thanks for your attention & Welcome to contact us!

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DLR Smart Technology for Molten Salt Health Assessment (SmaTeAs)

Why is Molten Salt Health Assessment Important for Safe Operation?



Molten salt health problem leads to

- Piping and tank leakage by salt corrosion
- Failure of key components like molten salt pump, valve, receiver, e-heater, etc. by salt corrosion
- Change of key thermal properties (e.g., melting point) by salt decomposition
- Huge economic losses caused by downtime of power plants, e.g., Concentrated Solar Power (CSP) plants (>150 k\$/day for a 100MW CSP)

Molten Salt Corrosion in Chemical Boilers. Source: <https://www.chemicalboiler.com/forensicengineering/molten-salt-corrosion/>

Overview of DLR Possible Solutions for Safe Operation




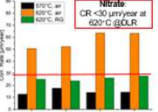
1. Salt Monitoring
Permanent & rapid monitoring of salt health changes by electrochemical in-situ sensors

2. Salt Auto-sampling & Analysis
Permanent and accurate long-term salt sampling record with minimum personnel resources

3. Salt Level/Filling detection
Reliable binary signal to detect existence of molten salt for process control

2a. Salt sampling at site → **2b. Salt analysis in lab**
High precision salt analysis for service life monitoring (corrosivity of salt towards steel)
Free salt sample analysis by DLR

DLR Expertise in Molten Salt

100 tons molten salt TESIS facility

- Continuous operation of DLR TESIS facility with approx. 100 tonnes of nitrate salt @560 °C since Jan. 2019
- Successful corrosion control of commercial nitrate salts (620 °C) and chloride (700 °C) with DLR solutions

https://nbi.org/10_1016/j.cors.2023.111700

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Flyer on DLR molten salt safe operation solutions