Molten Chloride Salt TES for Next-Generation CSP Plants: R&D Progress in Corrosion Control and Process Upscaling

Dr. Wenjin Ding[1], MSc. Hem Barot[1], Dipl.-Ing. Ralf Hoffmann[1], Dr. Thomas Bauer[2]

1. Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Stuttgart, Germany
2. Institute of Engineering Thermodynamics, DLR, Cologne, Germany

30th SolarPACES Conference

October 8-11, 2024 in Rome, Italy

SolarPACES
Concentrating Solar Power, Thermal, and Chemical Energy Systems

October 8-11, 2024
Rome, Italy

30th SolarPACES Conference

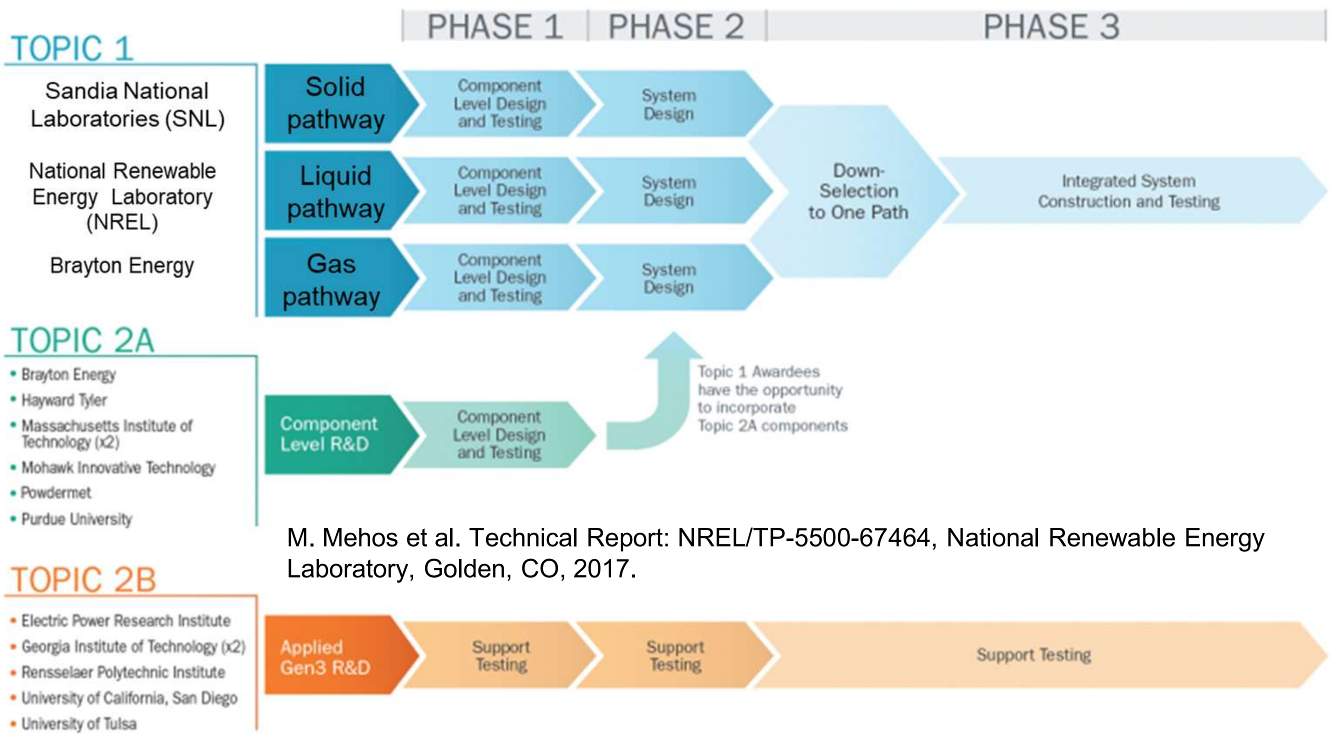
DLR

Contents

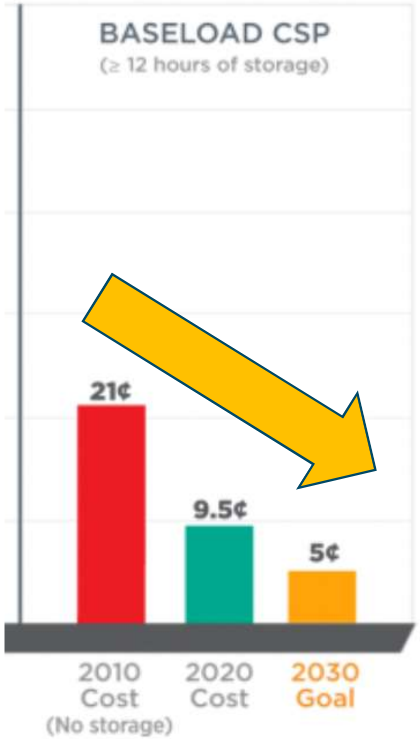
- Background of Next-Gen CSP and Chloride-TES
- Corrosion Control of Chloride-TES
- Process Upscaling of Chloride-TES

BACKGROUND OF NEXT-GEN CSP AND CHLORIDE-TES

Next-Gen CSP Plants under R&D



M. Mehos et al. Technical Report: NREL/TP-5500-67464, National Renewable Energy Laboratory, Golden, CO, 2017.



Gen3 CSP (Next-Gen CSP) of DOE SunShot 2030 since 2018

Three pathways under R&D:

- Solid pathway
- **Liquid pathway (molten salt/liquid metal)**
- Gas pathway

DOE CSP Target in 2030:

- Low LCOE (≤5 ¢/kWh$_e$) for baseload CSP (≥12 hours of storage)

2030 CSP Scenarios to Achieve LCOE of 5¢/kWh

Compared to Benchmark 2018, main achievements are required for the target LCOE of 5¢/kWh*

- Higher power-cycle efficiency (≥40%, better ≥50%)
- Lower Power block cost (≤ $900/kW)
- Lower solar field cost (≤ $70/m^2)
- Lower thermal energy storage (TES) cost (≤ $15/kWh)

If **higher power-cycle efficiency** is achieved*

- Higher costs of key components and subsystems (e.g. power block, solar field, tower and thermal storage) are acceptable

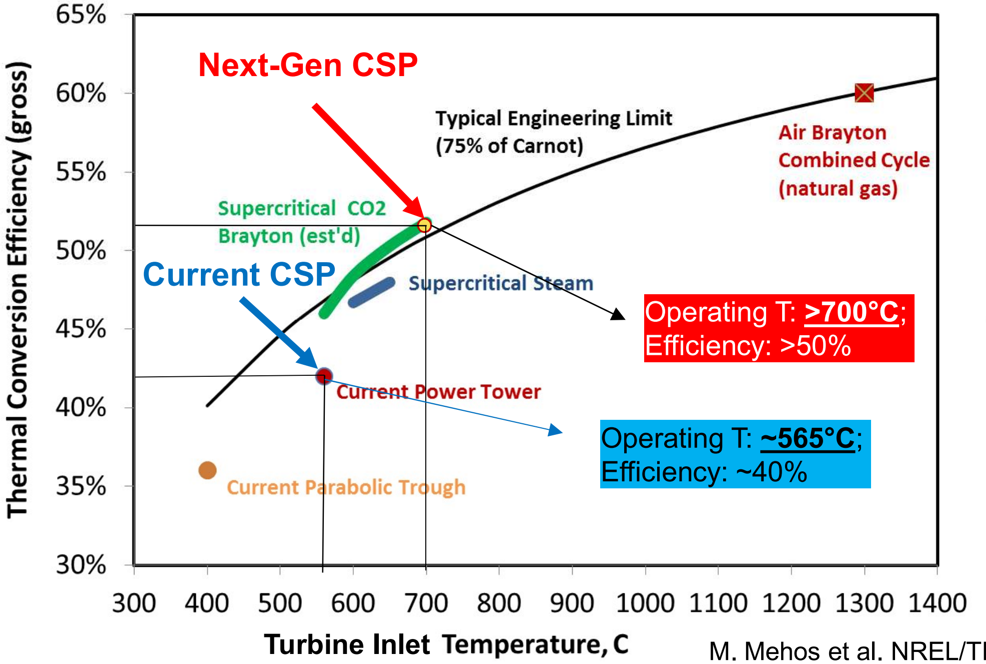
Table IV. Benchmark parameters for a 100 MW CSP system with 14 hours thermal storage.[36]

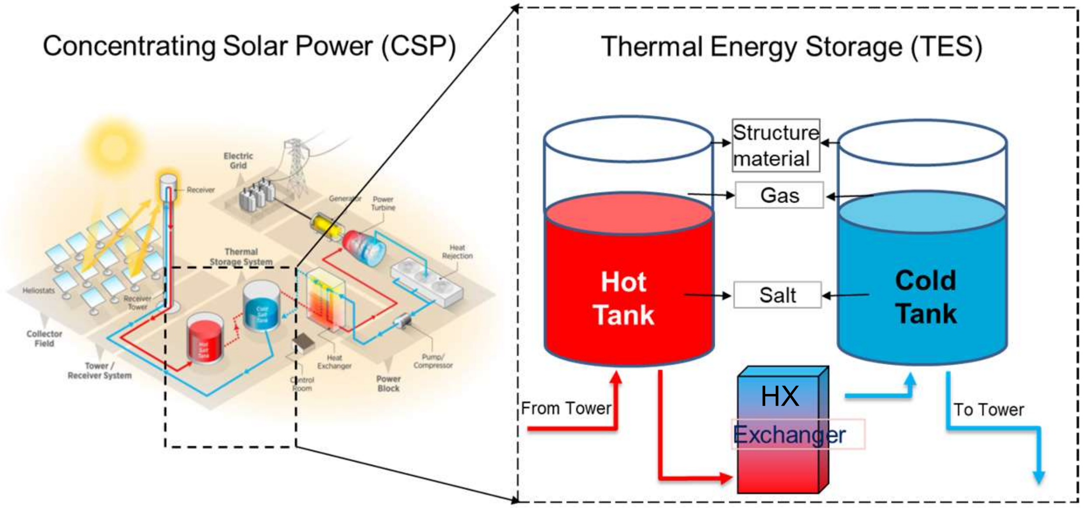
Parameter	2018 Benchmark[37,38]	2030 Low-Cost	2030 Balanced	2030 High-Performance
Net power-cycle efficiency	37%	40%	50%	55%
Rated thermal power	730 $MW_{thermal}$	675 $MW_{thermal}$	540 $MW_{thermal}$	491 $MW_{thermal}$
Power block cost	$1330/$kW_{ac\text{-}gross}$	$700/$kW_{ac\text{-}gross}$	$900/$kW_{ac\text{-}gross}$	$900/$kW_{ac\text{-}gross}$
Solar field cost	$140/m^2	$50/m^2	$50/m^2	$70/m^2
Site preparation cost	$16/m^2	$10/m^2	$10/m^2	$10/m^2
Tower and receiver cost	$137/$kW_{thermal}$	$100/$kW_{thermal}$	$120/$kW_{thermal}$	$120/$kW_{thermal}$
Thermal storage cost	$22/$kWh_{thermal}$	$10/$kWh_{thermal}$	$15/$kWh_{thermal}$	$15/$kWh_{thermal}$
Levelized O&M cost[39]	$9/$kW_{thermal}$-yr	$6/$kW_{thermal}$-yr	$7/$kW_{thermal}$-yr	$7/$kW_{thermal}$-yr
Levelized capacity factor	68.9%	69.2%	70.7%	71.0%
LCOE (2019 US$)[40]	**9.8¢/kWh**	**5.0¢/kWh**	**5.0¢/kWh**	**5.0¢/kWh**

Target in 2030: LCOE (≤5 ¢/kWh_e) for baseload CSP

*https://www.energy.gov/eere/solar/articles/2030-solar-cost-targets

Molten Chloride Salt TES for Next-Gen CSP Plants



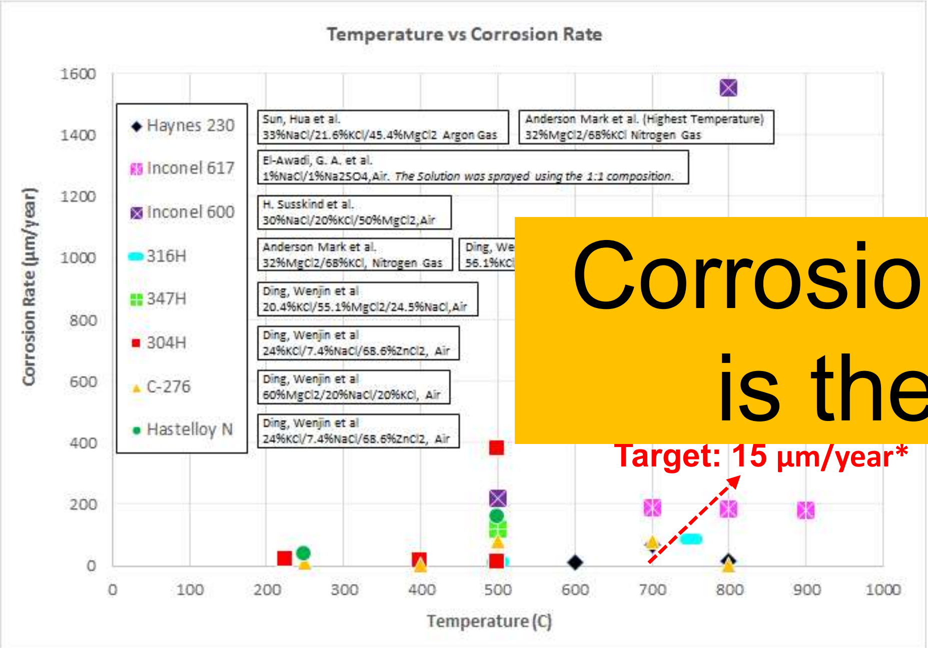


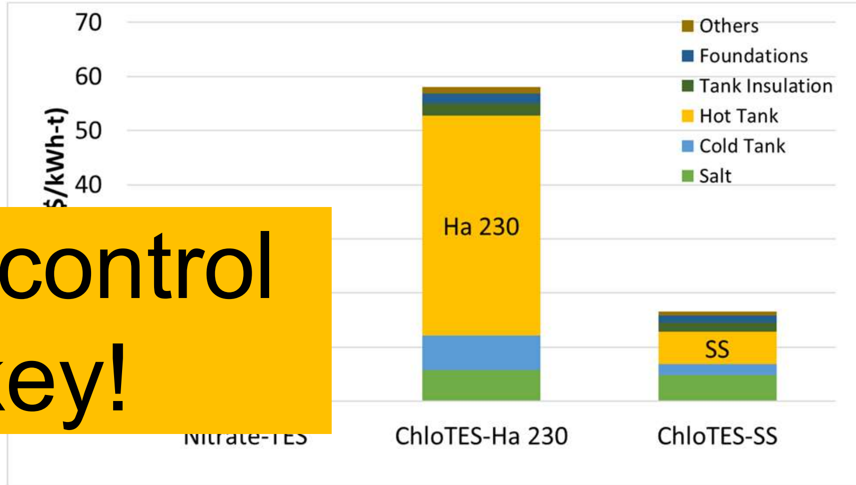
T_{hot} 565°C (Nitrate) → >700°C (Chloride)

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%** **→ higher turbine inlet temperature ≥700 °C → higher TES temperature >700 °C**
- **But state-of-the-art CSP with commercial Nitrate-TES**: $NaNO_3$-KNO_3 60-40 wt.% (Solar Salt), limited to **565 °C** by thermal decomposition
- **Chloride-TES with operating temperature of >700 °C** with excellent thermal stability of >1000°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 corrosion control (**Chloride TES-cost $~15/kWh$_{th}$**)

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

R&D of Chloride-TES at DLR

Corrosion control system (CCS)

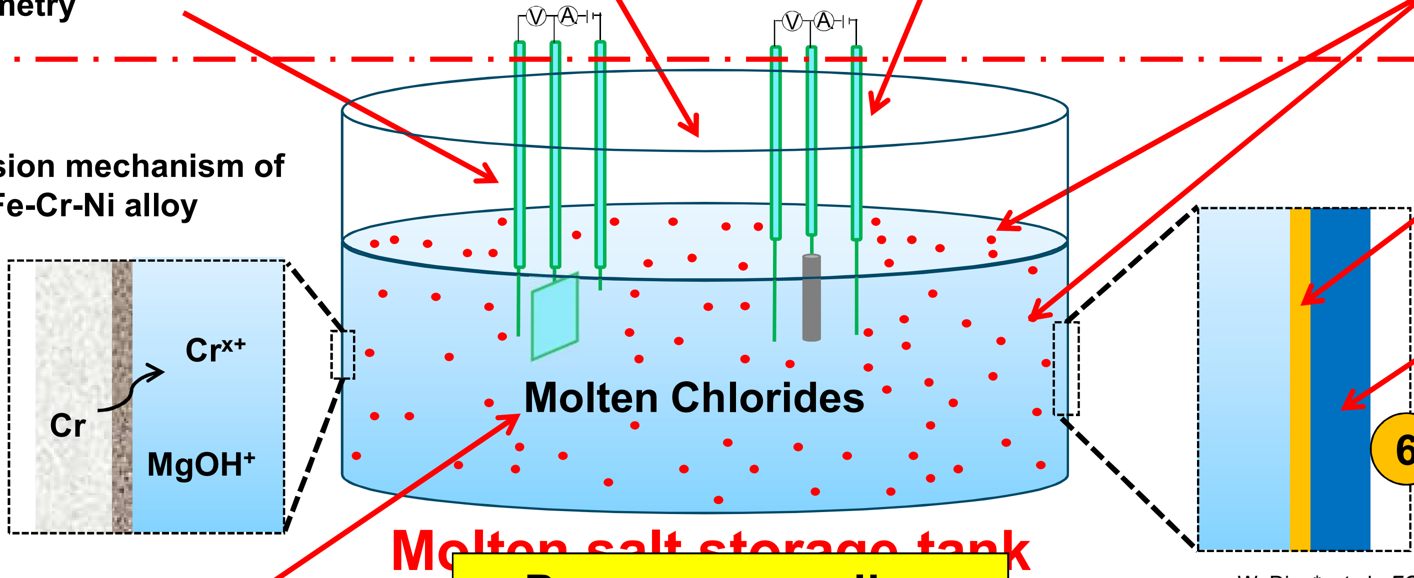
3 *In-situ* corrosive impurity monitoring based on cyclic voltammetry

Inert atmosphere

4 Electrolytic salt purification for reducing corrosive impurity level

5 Mg corrosion inhibitor

2 Corrosion mechanism of Fe-Cr-Ni alloy



Protective Al_2O_3 layer

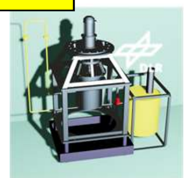
Pre-oxidized Fe-Cr-Al alloy

6 Corrosion resistant structural materials (alloys and ceramics)

1 Selection of promising chloride salts & salt properties of selected $MgCl_2$-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.
W. Ding*, et al., *J. Energy Storage*, **2018**, 15: 408–414.
W. Ding*, et al., *SOLMAT*, **2019**, 199: 8-15.
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

R&D of Molten salt TES at DLR

10 mg – 1 kg

100 kg

100-1000 ton

>10000 ton

"... value chain research..."

Material

Process technology (Upscaling)

DLR test facility TESIS

Component testing & pilot plant

CSP research site in Evora/Portugal

System integration

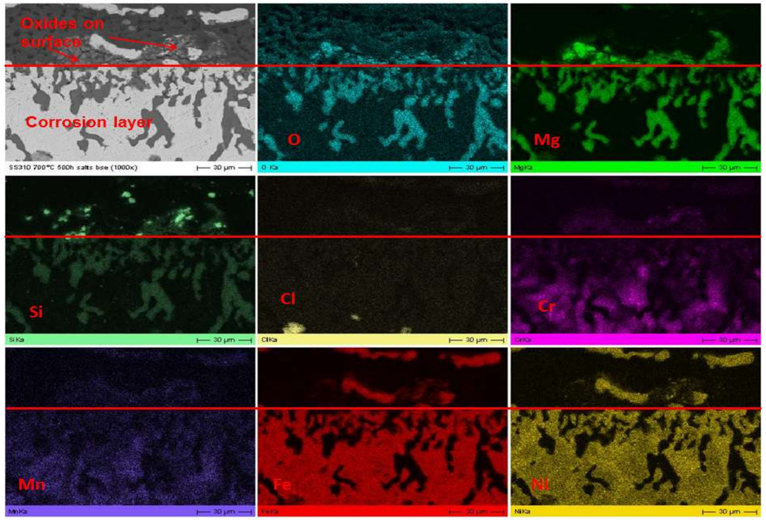
R&D from material to system level

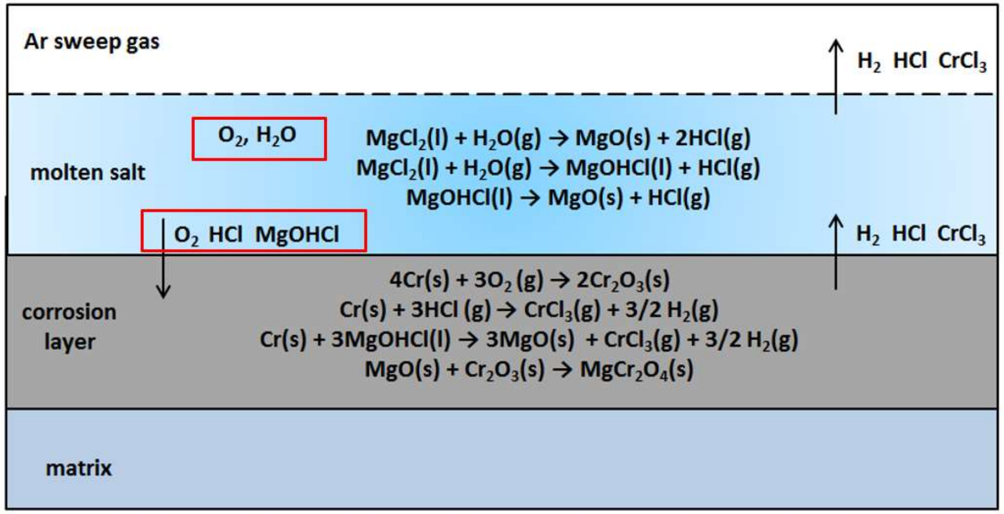
- Materials: focusing on nitrate/nitrite salts and chloride salts
- Upscaling and component testing: salt purification, corrosion control; Molten salt pump, HX, …
- System: Molten salt TES used in CSP, Carnot battery, …

CORROSION CONTROL OF CHLORIDE-TES

② Proposed corrosion mechanism

SS 310 in MgNaK chloride (700°C, 500 h)





- Large amount of Mg and O detected in corrosion layer
- $MgCr_2O_4$ and MgO detected in oxides on surface

Corrosion mechanisms proposed by DLR:

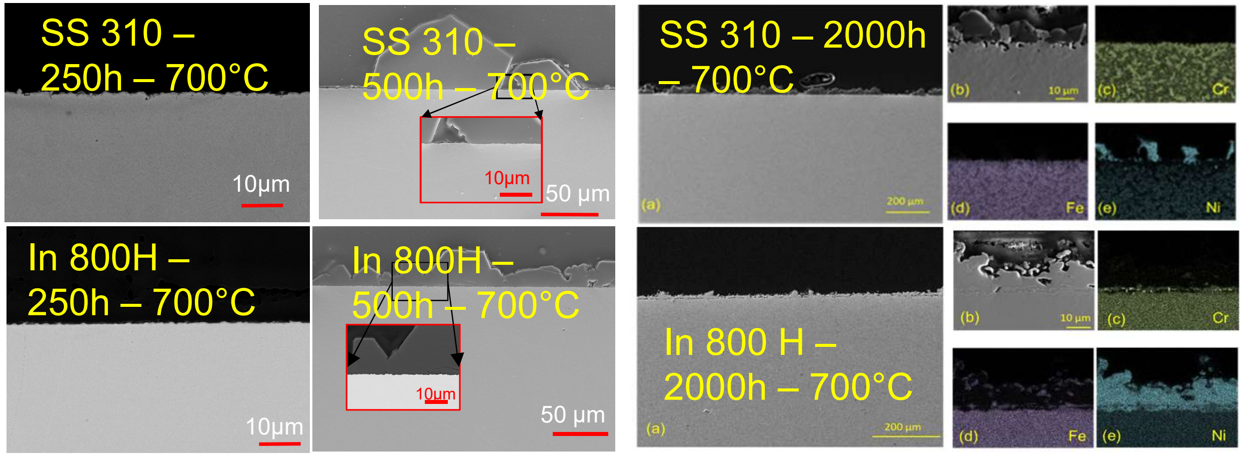
- Cr dissolved preferentially
- Corrosion is driven by impurities mainly **MgOHCl**

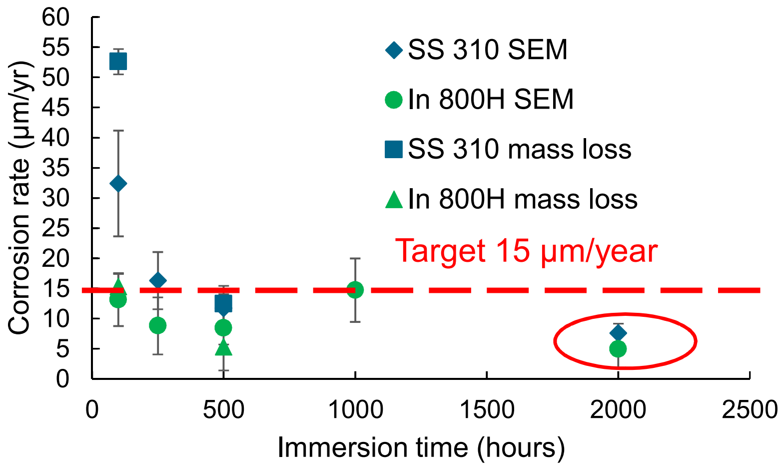
- Corrosive impurities: H_2O, O_2, HCl, MgOHCl (high solubility in molten chlorides)
- Corrosion products: $MgCr_2O_4$, MgO, $CrCl_3$
- Corrosion control by controlling concentration of impurities

Karlsruhe Institute of Technology

W. Ding, A. Weisenburger, et al., *SOLMAT*, **2018**, 184: 22–30.

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

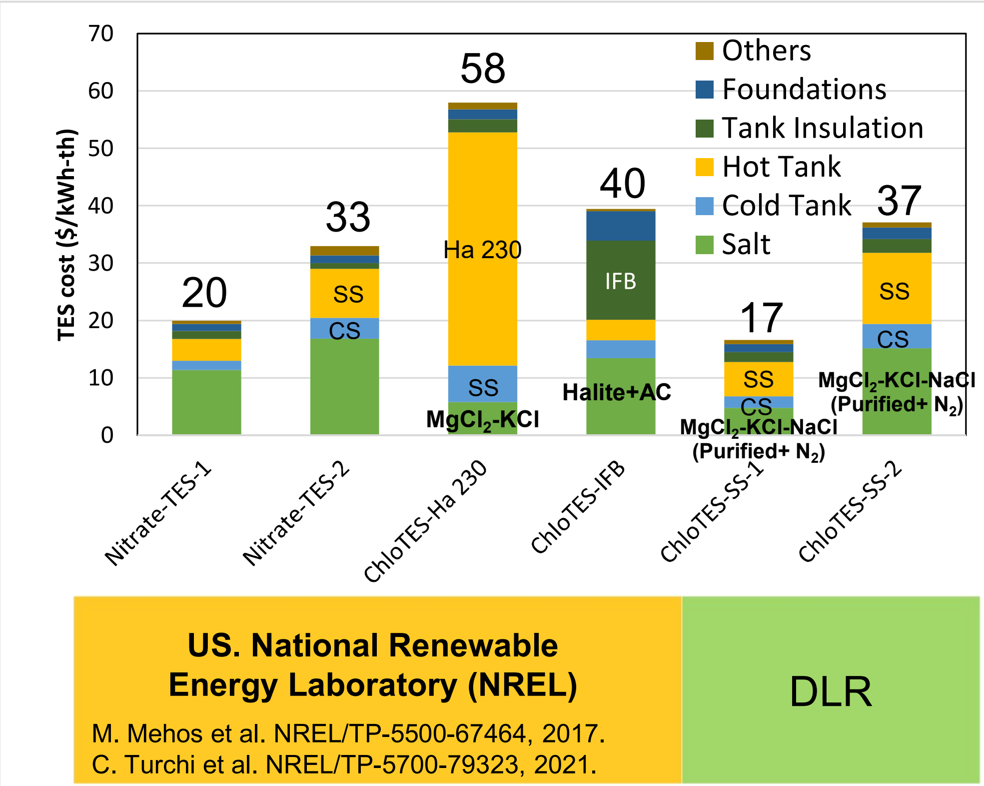
*Patent filing: DE 10 2021 131 250.7 (2021)
Q. Gong, T. Bauer, W. Ding, et al., Applied Energy, 324, 119708 (2022) Q Gong, T Bauer, W Ding, et al., SOLMAT, 253, 112233 (2023)

5

Mg Corrosion Inhibitor –

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

DLR



Q. Gong, W. Ding, et al., Applied Energy (2022).

- 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}$**

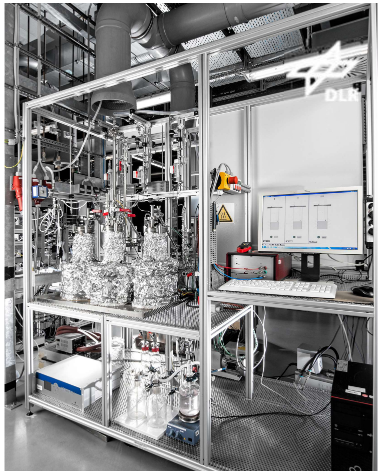
Ha: Hastelloy for hot tank
SS: stainless steel for hot or cold tank
CS: Carbon steel (or similar price alloy like P91) for cold tank

PROCESS UPSCALING OF CHLORIDE-TES

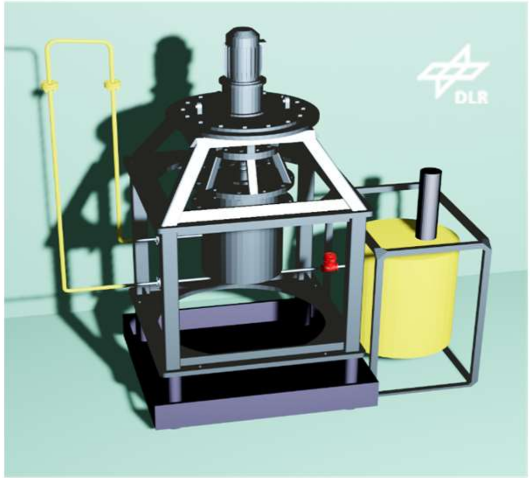
7 Process Upscaling of Chloride-TES

DLR

Achieved | **Ongoing** | **Target**



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



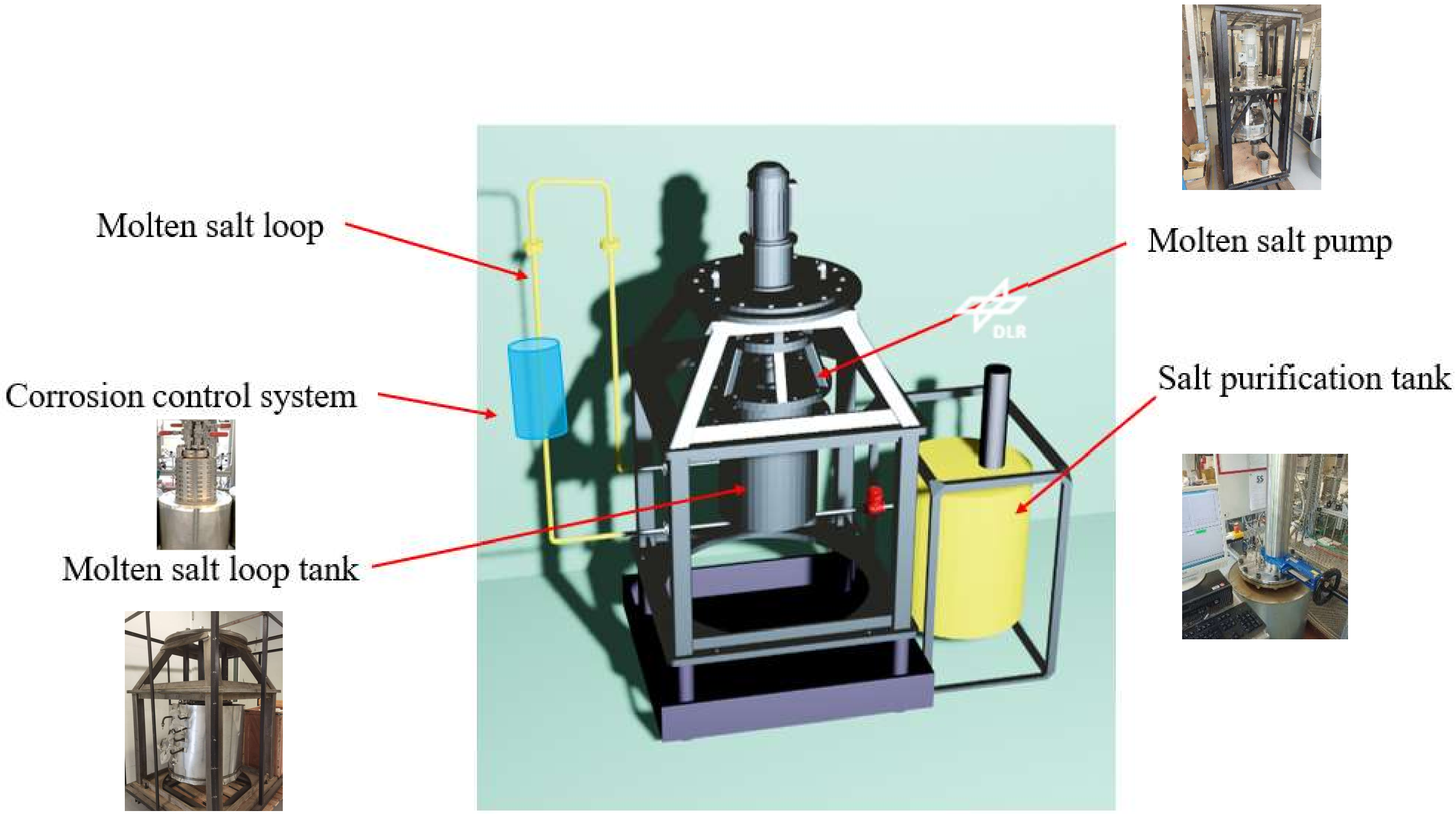
Upscaling with ~100 kg salt: salt purification and corrosion control loop tests, structural materials selection (TRL 4-5)

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

Industry-application (TRL 8-9)

DLR seeks industrial partners for upscaling

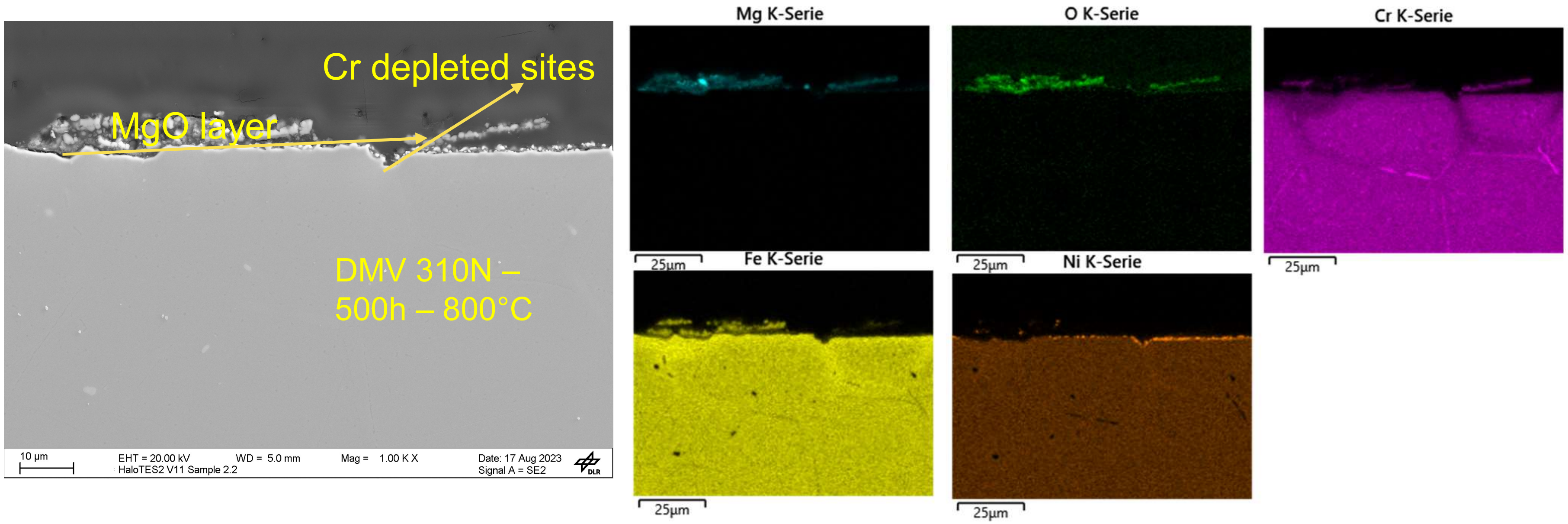
7 Molten Chloride Test Facility (MOCTEF) of DLR



- **Under construction** and will be operation in the starting of 2025
- **Two test units**: one for salt purification, one for loop tests close to conditions in real applications.
  - ~100 kg $MgCl_2$-NaCl-KCl is used
  - Designed test temperatures >700°C
- **Highlights**: patented corrosion control system, salt and gas phase in-situ analysis, …

7

First results –
Corrosion test of DMV 310N in purified salt at 800 °C



- First test*: 500h static immersion test **at 800°C** in salt purified with MOCTEF salt purification unit in kg-scale
- Corrosion rate via mass loss: < **50** µm/year
- Chromium depletion depth: ~ **10** µm (mainly at crystal boundaries)

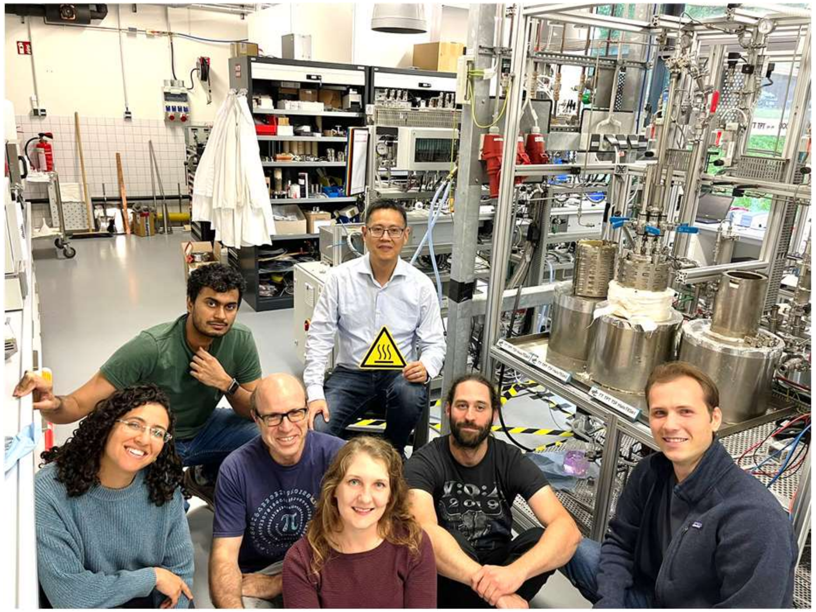
- 2000h static immersion test at 800°C is ongoing, while loop test in MOCTEF at >700°C is planned.

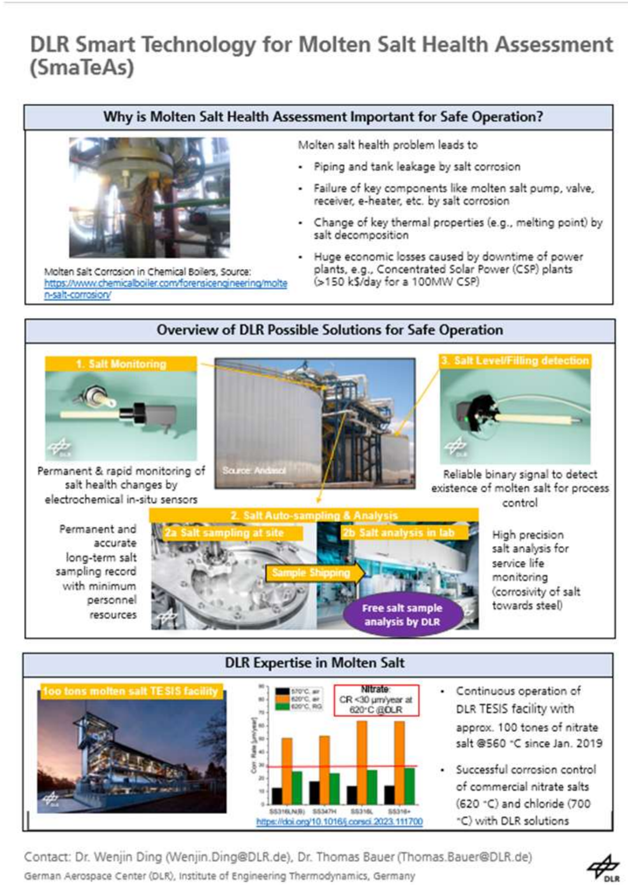
*H Barot, oral presentation in Enerstock Conference 2024, Lyon France, 2024.

Thanks for your Attention!

Dr. Wenjin Ding: Wenjin.Ding@dlr.de

Acknowledgement:
This work is performed in the project funded by DLR **Department of Technology Marketing**: Smart Technologies for Molten Salt Health Assessment in Long-Duration Energy Storage Systems (**SmaTeAs**), and the DAAD-DLR fellowship project.





DLR Smart Technology for Molten Salt Health Assessment (SmaTeAs)

Why is Molten Salt Health Assessment Important for Safe Operation?

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

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)

Overview of DLR Possible Solutions for Safe Operation

Permanent & rapid monitoring of salt health changes by electrochemical in-situ sensors

Reliable binary signal to detect existence of molten salt for process control

Permanent and accurate long-term salt sampling record with minimum personnel resources

High precision salt analysis for service life monitoring (corrosivity of salt towards steel)

DLR Expertise in Molten Salt

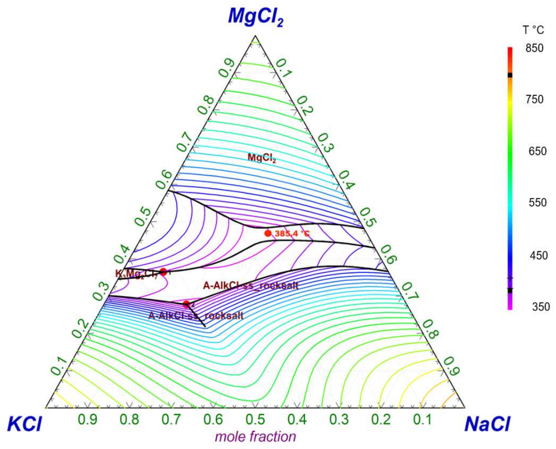
https://doi.org/10.1016/j.corsci.2023.111700

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

Contact: Dr. Wenjin Ding (Wenjin.Ding@DLR.de), Dr. Thomas Bauer (Thomas.Bauer@DLR.de)
German Aerospace Center (DLR), Institute of Engineering Thermodynamics, Germany

The flyer on DLR molten salt health assessment solutions can be found at DLR exhibition stand!

1 Promising $MgCl_2$+KCl+NaCl and its Salt Properties



After screening, **$MgCl_2$-KCl-NaCl salt mixture (<0.35 USD/kg, <3 USD/kWh$_{th}$)*** is selected for TES at **420-800°C**. Following considered:

- **Thermal properties** of single chlorides,
- Hydrates phases (**hygroscopicity** to lead severe **corrosion**),
- **Large-scale prices** of single chlorides,
- **Vapor pressures** of single chloride salts (cost of tanks),
- **Melting temperatures** of eutectic salt mixtures (freezing risk).

- **Salt properties** for engineering this salt are recommended**.

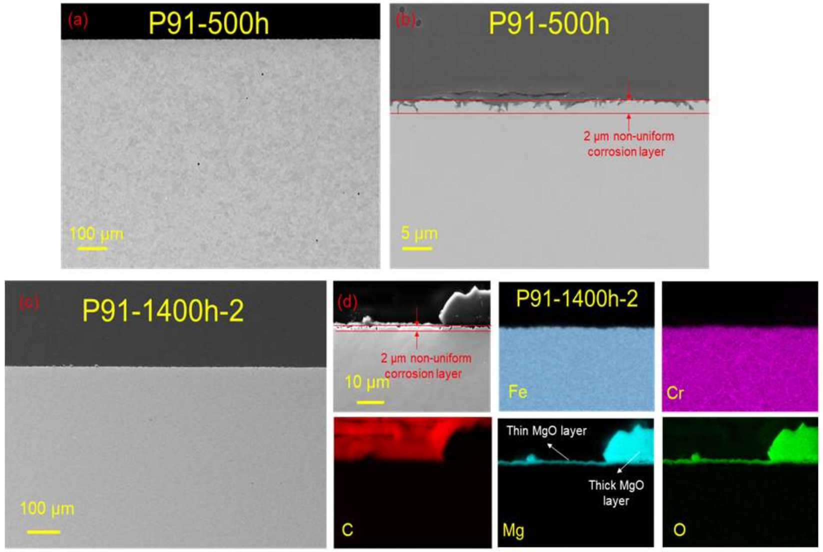
$MgCl_2$+KCl+NaCl		Recommendation**
Salt composition		Eutectic 47.1-22.7-30.2 mol. % (56.5-21.3-22.2 wt.%)
Min. melting temperature (°C)	T_m	385
Min. working temperature (°C)	T_{min}	420
Max. working temperature (°C)	T_{max}	800
Vapor pressure (kPa)	p_v	700-1000°C: $3.1\times10^{-08}\cdot e^{0.0214\cdot T(°C)}$ 400-700°C: <0.1, 800°C: 1
Heat capacity (J/g °C)	c_p	1.10 (420-800 °C)
Density (g/cm³)	ρ	1.76-1.60 (420-800°C), $1.94-4.2\times10^{-4}T(°C)$
Thermal conductivity (W/(m °C))	λ_l	0.47-0.42 (420-800°C), $0.53-1.32\times10^{-4}\cdot T(°C)$
Dynamic viscosity (mPa s)	η	6.01-1.51 (420-800°C) $27.728\,e^{-0.00364\,T(°C)}$

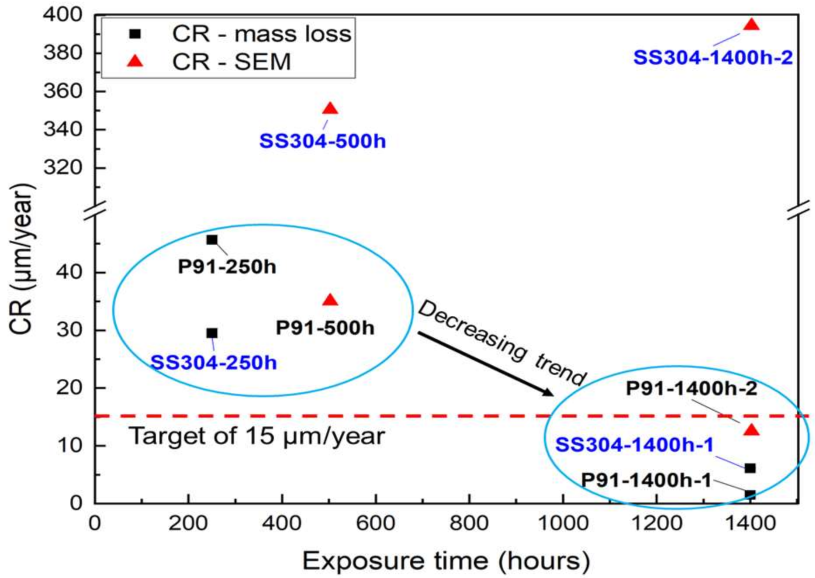
*W. Ding, et al., SolarPaces **2018**.
C. Villada, W. Ding*, et al. *Solar Energy Materials & Solar Cells*, **2021, 232(1):111344.

C. Villada, W. Ding, et al., Front. Energy Res. **2022**, 10:809663.

5

Mg Corrosion Inhibitor – Structural materials for cold parts





- Salt purified with Mg at 700°C
- **>2 months immersion tests at 500°C**: Almost no corrosion layers and Cr-depletion were observed
- Corrosion rate based on microstructural analysis (SEM) and mass loss: **<15 µm/year for P91 at 500°C**
- Experimental proof that **low-cost Fe-based steels** reach the target of **<15 µm/year** at 500°C

Q Gong, T Bauer, W Ding, et al., Solar Energy Materials and Solar Cells 253, 112233 (2023)