

Overview of molten salt technology in the CSP sector - state of the art and current research

Euchemsil 2022 - 28th Euchem conference on Molten Salts & Ionic Liquids
5.6-10.6.2022, Patras, Greece

7.6.2022, Dr. Thomas Bauer



Knowledge for Tomorrow



Contents

- **Systems:** CSP and other applications
- **Components:** thermal energy storage and power related components
- **Materials:** nitrate and chloride Molten Salt
- Summary and conclusions



Systems and applications



Energy related application and R&D of molten salt technology

• **Concentrated Solar Power (CSP)**

- improve existing molten salt plants
- new/improved components
- develop novel CSP configuration



reduce Levelized Cost of Electricity (LCOE)

- Add storage (and power-to-heat) to **conventional steam power plants**
 - ...for flexibility (special interest for combined heat and power)
 - ...to include renewables (e.g., repurposing of coal plants, attach CSP)
- New **electrical storage** solutions
 - Power-to-heat-to-power (PtHtP) and Pumped thermal energy storage (PTES)
 - Adiabatic compressed air energy storage (A-CAES)
 - Molten metal battery with salt electrolyte ←
- **Nuclear** (e.g, molten salt reactor, waste heat treatment)

Presentation ID 85
Thursday 9:30 h
Wenjin Ding

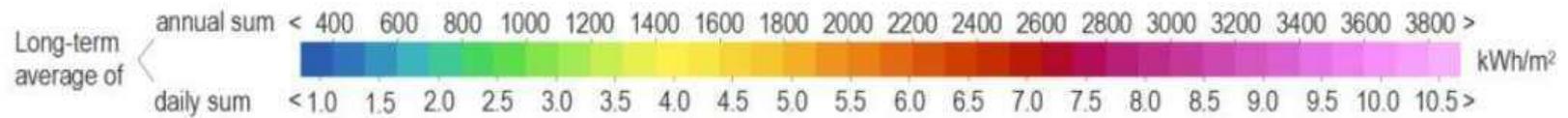
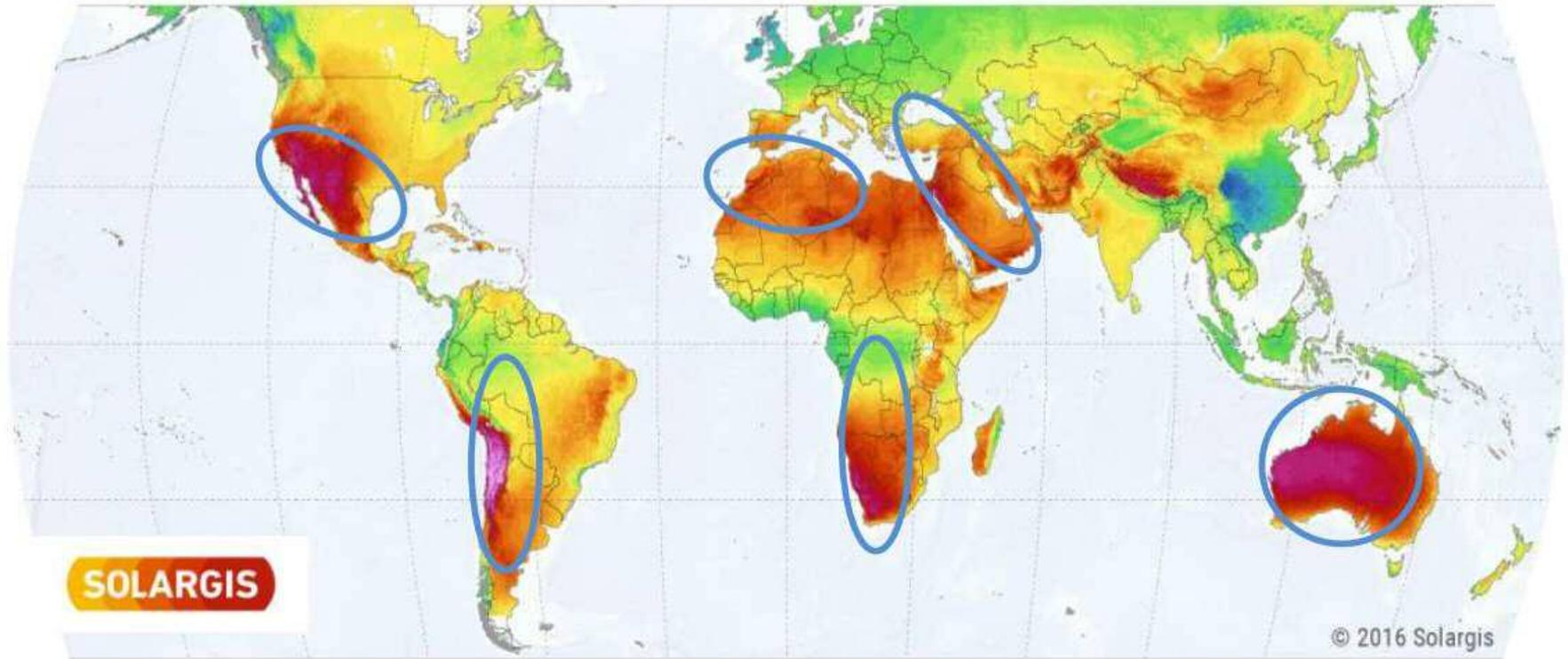
• **Industrial process heat**

- improve existing molten salt systems for process heat control
- develop novel concepts with power-to-heat and molten salt storage



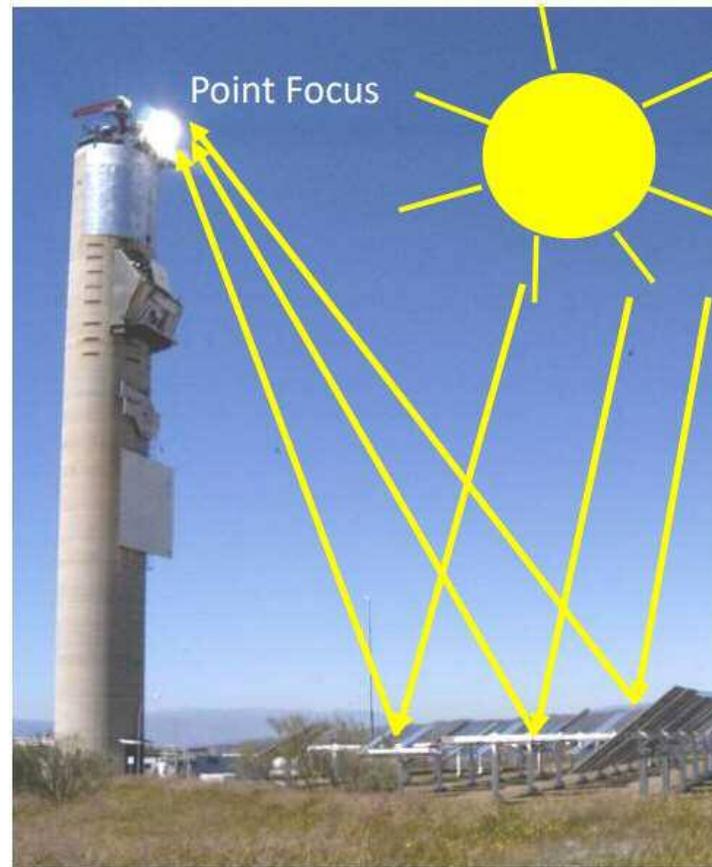
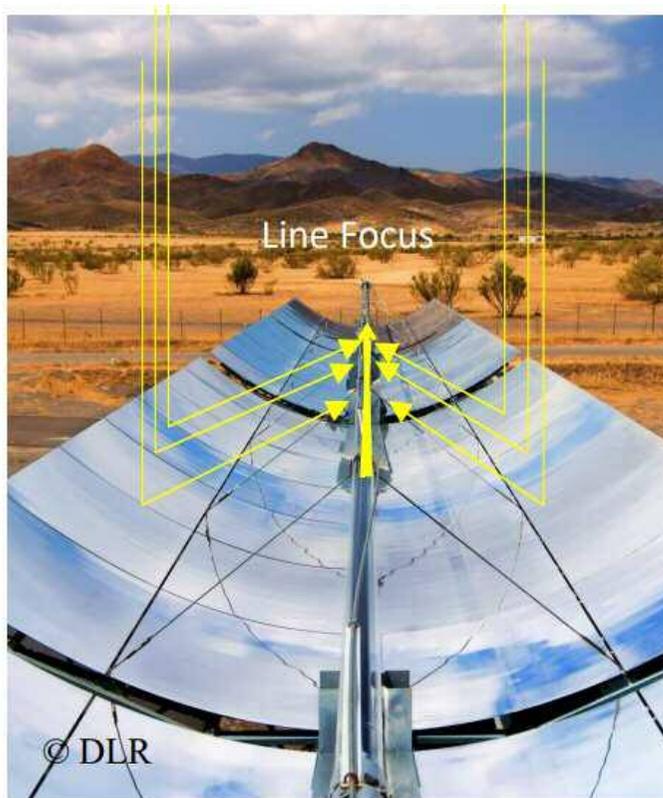
Concentrated Solar Power (CSP)

DIRECT NORMAL IRRADIATION



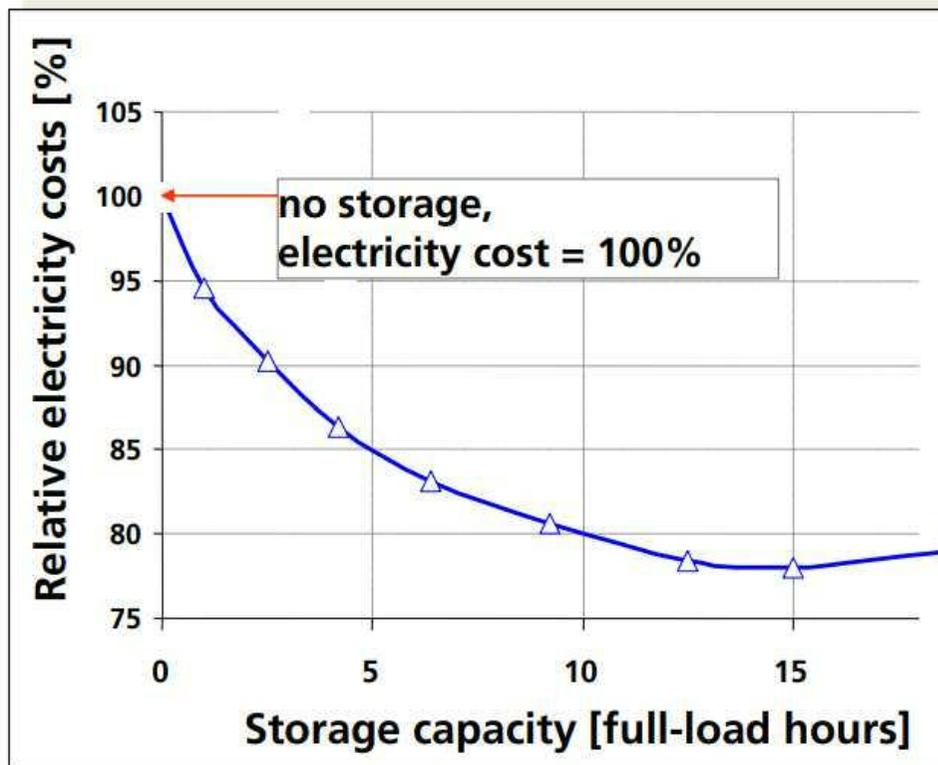
Concentrated Solar Power (CSP)

Trough vs. tower



Concentrated Solar Power (CSP)

Thermal energy storage = more operating hours = cost reduction

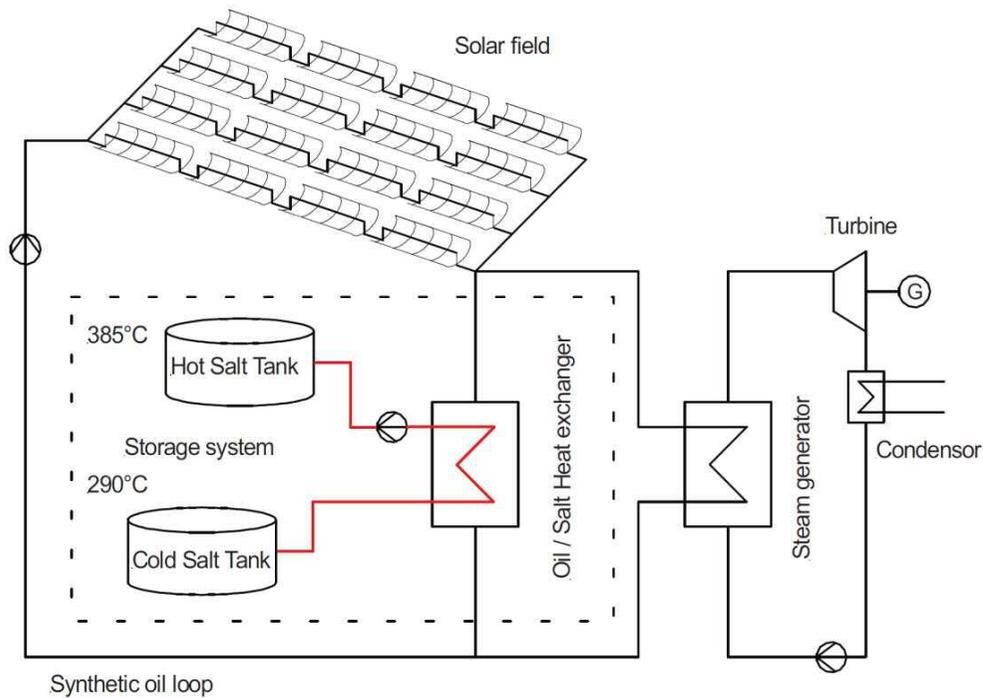


* assuming specific investment costs for the storage of 10 Euro/kWh

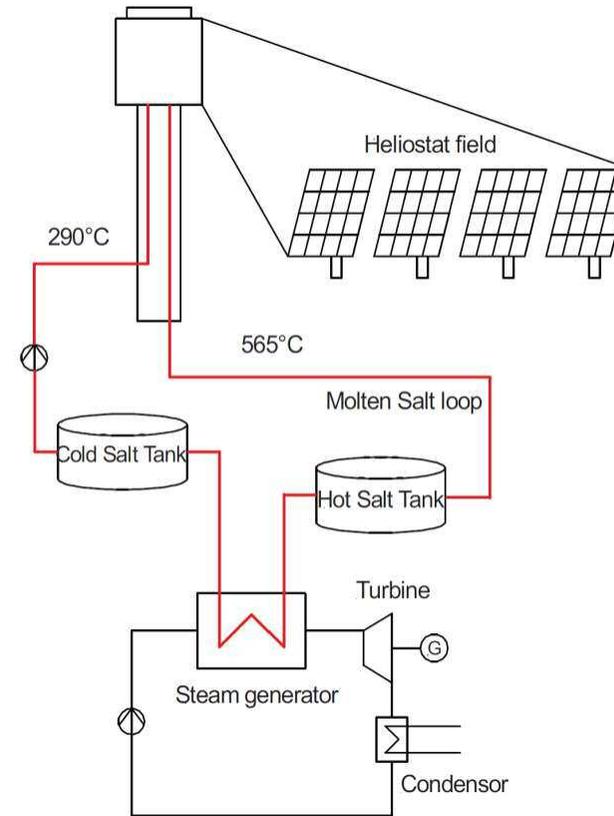


Concentrated Solar Power (CSP)

Two-tank: trough vs. tower



Direct storage system
for solar tower systems
(Storage medium = HTF)



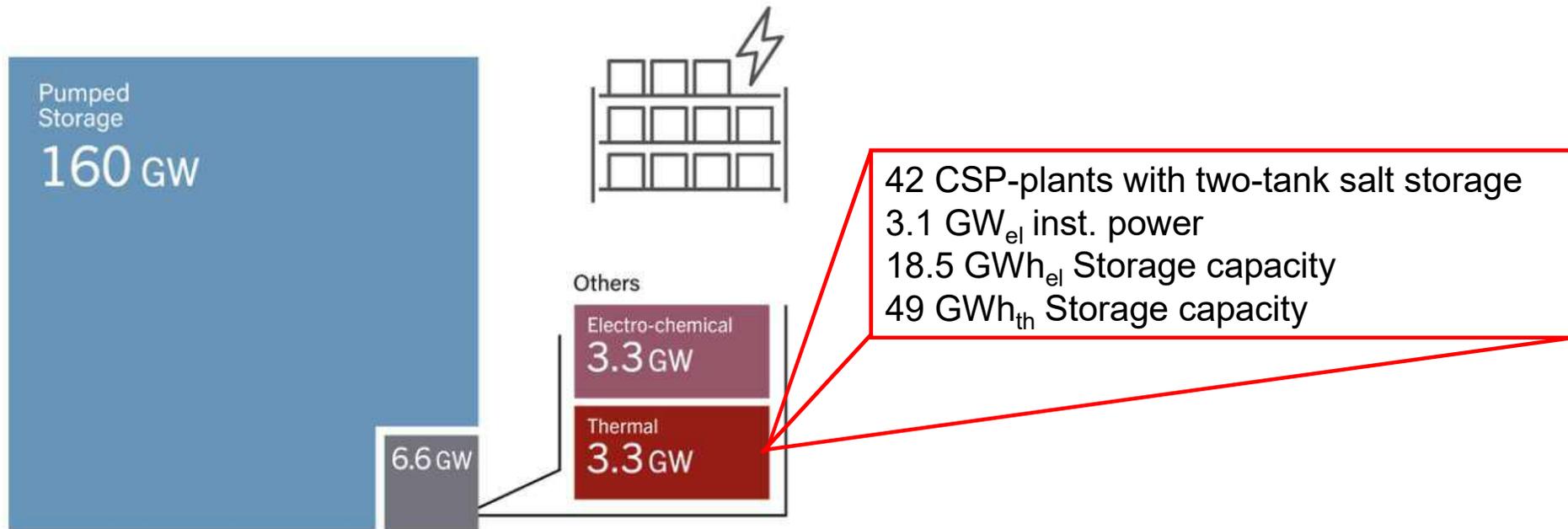
Indirect storage system
for parabolic trough systems
(Storage medium \neq receiver HTF)



Concentrated Solar Power (CSP)

Installed global capacity for grid-connected storage

Utility-Scale Energy Storage Capacity, Selected Technologies, 2018



Note: Numbers should not be compared with prior versions of this figure to obtain year-by-year increases, as some adjustments are due to improved or revised data. The category of electro-mechanical storage has been excluded due to limited global data availability.

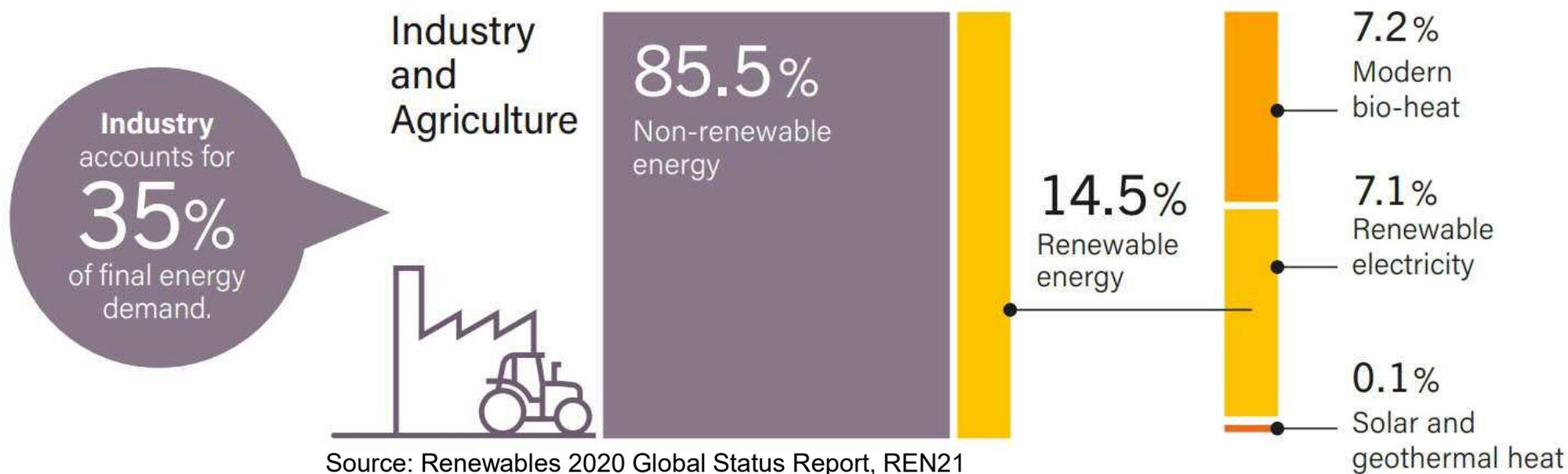
Source:

- REN21 Renewables 2019 Global Status Report
- <https://www.protermosolar.com/proyectos-termosolares/proyectos-en-el-exterior/>



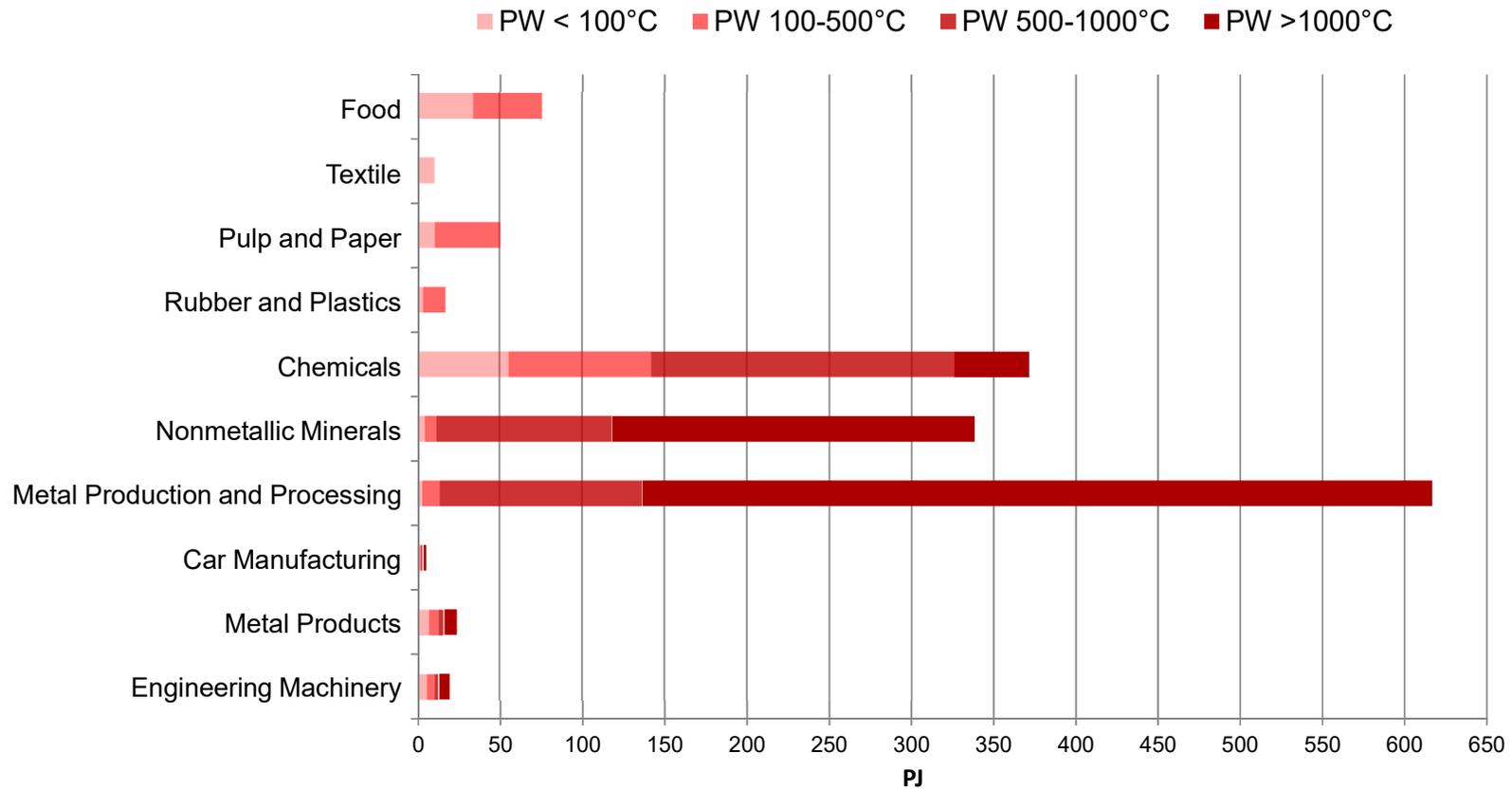
Industrial process heat

World renewable share of total final energy consumption in industry & agriculture in 2017



Industrial process heat

Temperature levels and process heat demand in Germany



Source: M. Nast, DLR 2010



Industrial process heat

Step-by-step path to future climate-neutral supply

5. Alternative energy carrier
(e.g. green H₂)

4. Grid-support with electrothermal storage
(e.g. Power-to-Heat with storage)

3. Electrification of industrial processes
(e.g. Power-to-Heat, heat pumps)

2. Use of renewable heat sources
(e.g. solar thermal)

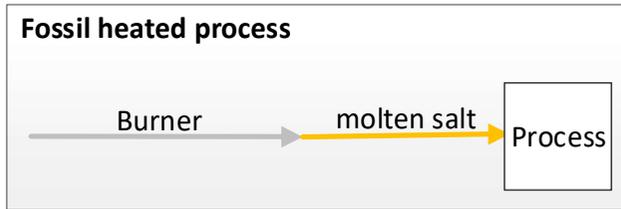
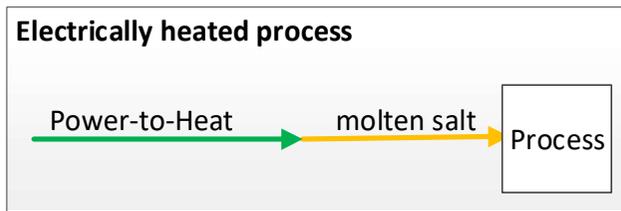
1. Increasing energy efficiency
(e.g. waste heat utilization, storage, combined heat & power)



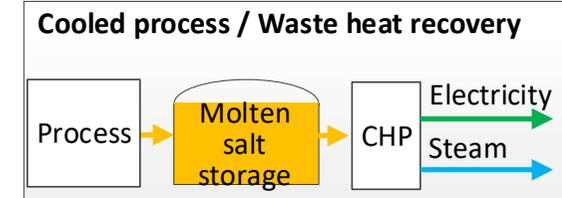
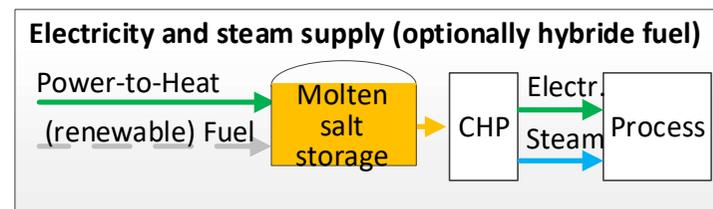
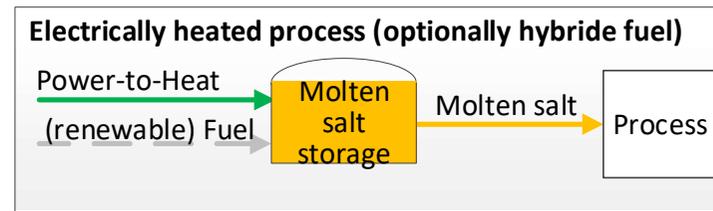
Industrial process heat

Molten salt utilization

State-of-the-art

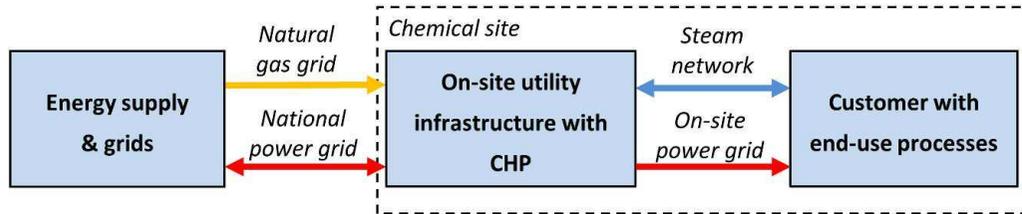


Novel concepts



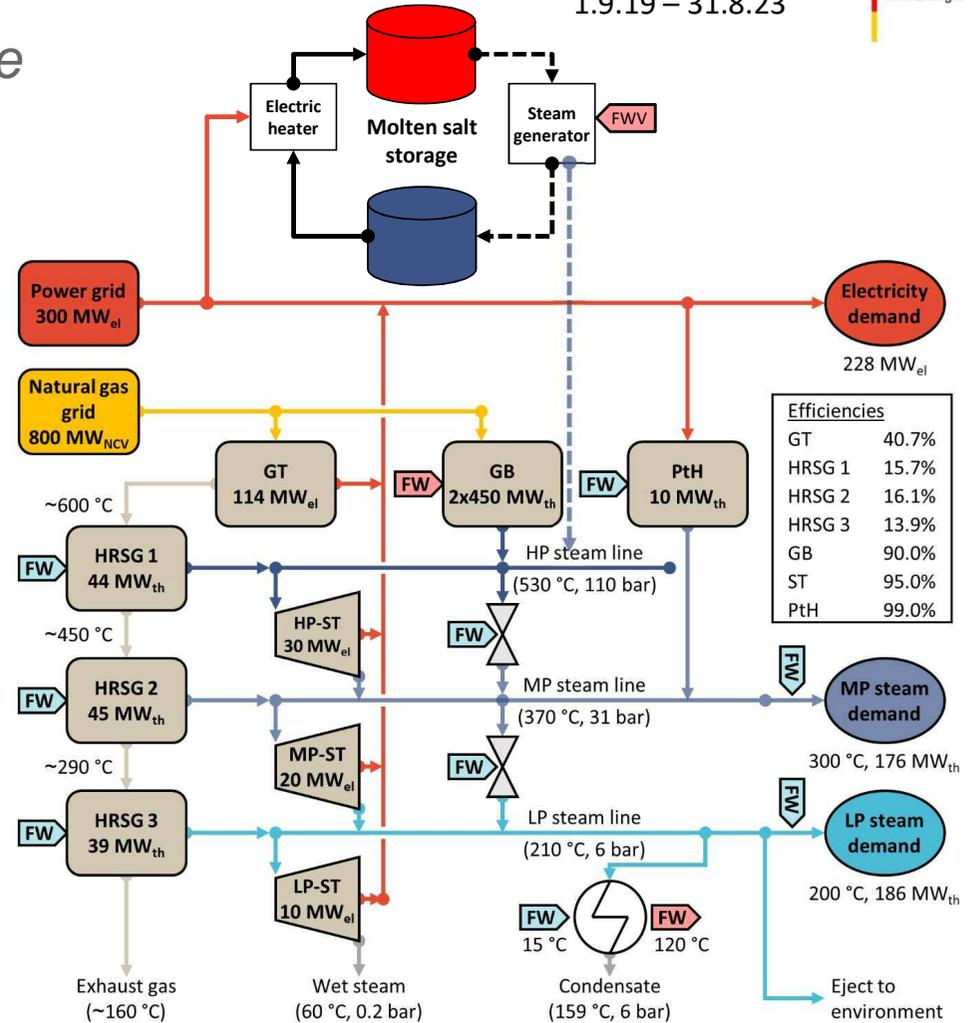
Industrial process heat

Concept for integration of molten salt storage



Project: TranSTES-Chem
 FKZ 03ET1646A-E
 1.9.19 – 31.8.23

Gefördert durch:
 Bundesministerium für Wirtschaft und Energie



Deutsches Zentrum für Luft- und Raumfahrt e.V.
 in der Helmholtz-Gemeinschaft



Components



Component related R&D

• Storage

- Improvement of existing two-tank technology
- Development of single-tank technology

• Power related components

- Solar receivers/absorber
- Electrical heater
- Combustion heater
- Heat exchanger and steam generators

• Subcomponents

- Pumps and valves
- Connections (seals, hoses, flanges)
- Auxiliary heating
- Measurement equipment (temperature, pressure, flow and level)

• Fundamental research, e.g.

- Freezing and re-melting
- Heat transfer aspects



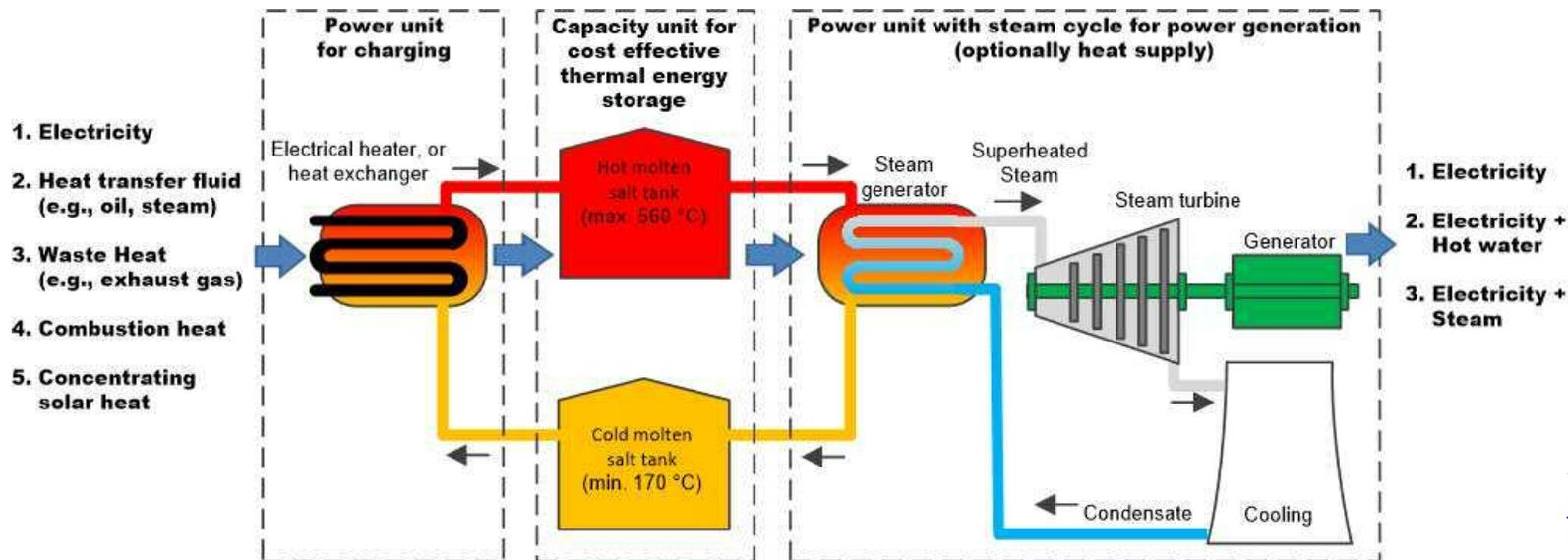
Overview of high-temperature thermal energy storage technologies

	Solid media			Ruths	Molten Salt		PCM
Min. tank number	1	1	2	1	2	1	1
Storage material	Ceramics	Natural stone	Ceramic particles	Pressurised water	Nitrate salt liquid	Nitrate salt & Natural stone	Nitrate salt solid/liquid
Energy density in kWh/m ³	75 - 200	75 - 200	100-200	Up to 100	40-120 (with void vol.)	80 – 240	50 - 200
Typ. Temperature	400-1600 °C	200-800 °C	400-800 °C	150-230 °C	170-560 °C	170-560 °C	130-330 °C
Typ. Heat transfer fluid	Gas	Gas	Particle with HX	Saturat. steam Pressur. water	Salt with HX to superh. steam	Salt with HX to superh. steam	Steam, max. superh. 330 °C
Max. Capacity	1000 MWh	N/A	N/A	30 MWh	4000 MWh	N/A	N/A
Technol. readiness	TRL 5 – 9	TRL 4 – 6	TRL 3 – 4	TRL 8 – 9	TRL 5 – 9	TRL 3 – 5	TRL 3 – 5
Example figure							



Overview and components of molten salt technology

1. Large-scale storage for CSP-Plants demonstrated
2. **Inexpensive** sensible heat storage from 290 °C to 560 °C in molten salt (non-toxic, non-flammable) in large-scale **unpressurized** tanks
3. Separated heat exchanger for **constant** power
4. Potential to transfer technology from CSP to new applications fields



Source:
<https://doi.org/10.1002/cite.202000137>
(open access)



Examples of commercial two-tank storage systems



Andasol systems in Spain

- 50 MW_{el}
- Storage capacity: 1,000 MWh (8h)
- 2 tanks: 34 m Ø, 14 m high
- 28,000 t of nitrate salts



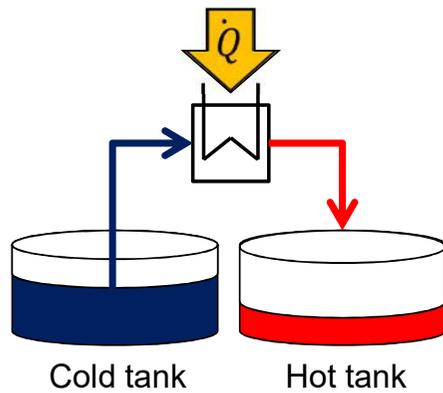
Largest system Solana in US

- 280 MW_{el}
- Storage capacity: 6h / ~4000 MWh
- 12 tanks: 37 m Ø, 15 m high
- 125000 tons of salt

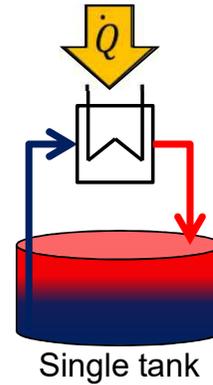


Single-tank storage technology - overview

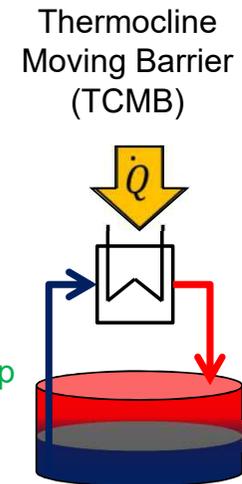
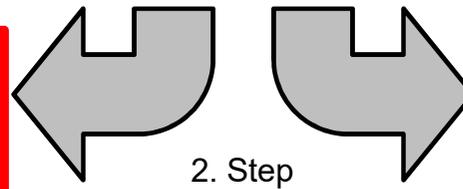
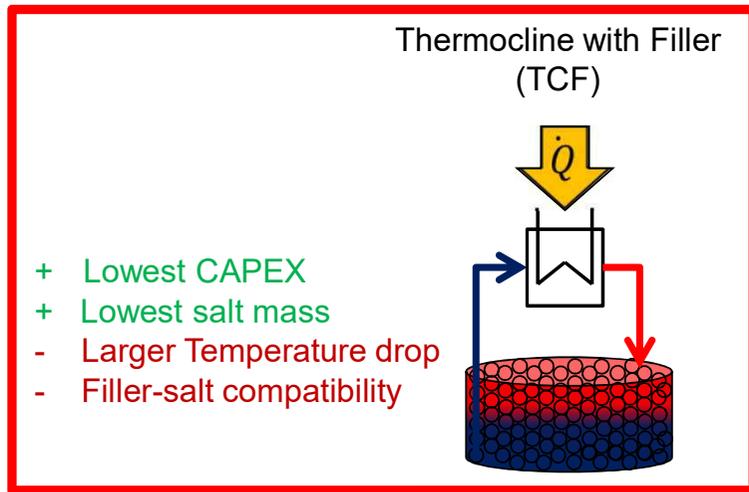
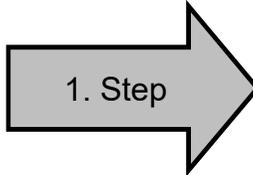
2-Tank (state-of-the-art)



Thermocline (TC)



- + Lower CAPEX
- + Smaller footprint
- + Lower gas exchange
- Temperature drop
- Larger salt mass
- Tank design with ΔT



Single-tank storage technology– R&D aspects

Aim:

- Demonstration of single-tank thermocline concepts with filler

Research topics:

- Compatibility between filler and salt
- Heat & mass transfer
- Thermomechanics, up-scaling (packed bed, tank stress)
- Operational aspects (start-up, repair)
- System integration

Results:

- 9 thermal cycles under realistic boundary conditions performed
- World's largest demonstration with 4 MWh_{th} for 290/560 °C

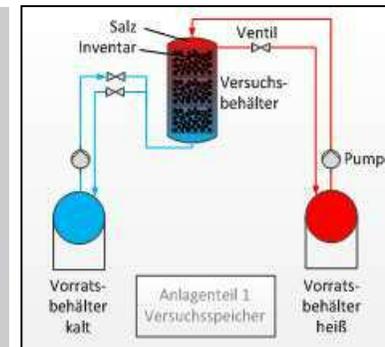
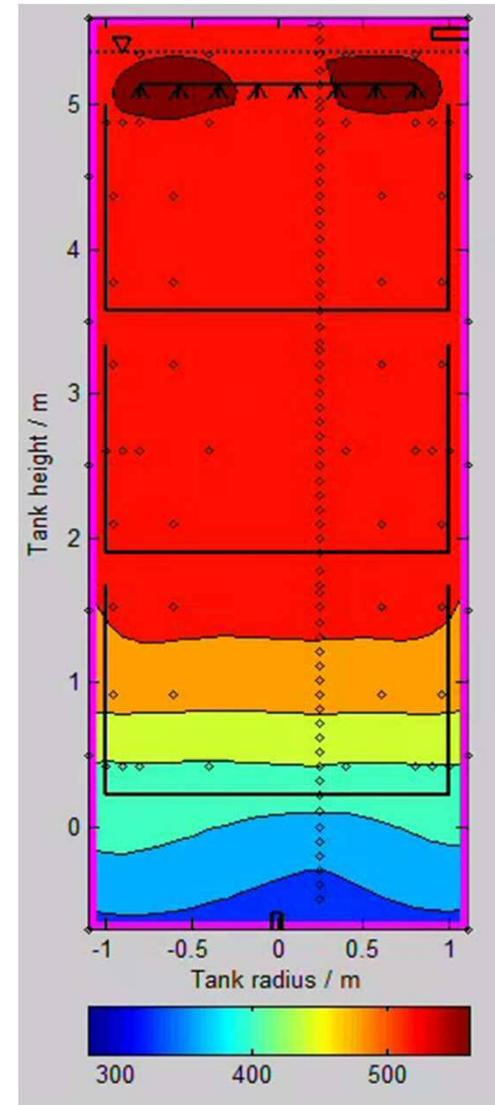
Potential

- Sandia and DLR estimations: 20-40% CAPEX TES reduction

Source:

- Odenthal et al. (2019) <https://doi.org/10.1063/5.0028494>

- Klasing et al. (2020) <https://doi.org/10.1115/1.4046463>



Materials



Material related R&D

- **Solar Salt as standard solution**
 - Salt mixtures with **lower melting temperature**
 - Salts and methods for **higher operation temperature**
 - **Metallic corrosion and compatibility of molten salt with other materials**
-
- **Fundamental research:**
 - Thermophysical properties
 - Molecular dynamic modeling
 - Nano-additives
 - Thermodynamic data
 - ...



High-temperature heat transfer fluids for CSP

	Thermal Oil (Biphenyl / Diphenyl ether)	Molten Salt (Solar Salt, Hitec, Hitec XL)	Molten Metal (Sodium)	Water/Steam	sCO ₂	Air	Particles
Typ. Max. Temp.	400 ° C	560 ° C	650 ° C	550 ° C	700 ° C	700 ° C	800 ° C
Freezing Temp.	-10° C	140-250 ° C	98 ° C	0 ° C	no risk	no risk	no risk
Pressure	Medium	Medium	Medium	High	High	Low	Low
HX heat transfer	Medium	Medium	High	Medium	Medium	Low	Low
Vol. heat capacity	Medium	High	Medium	Low	Low	Low	Medium
Flammability	Yes	No	Yes	No	No	No	No
Storage Solution	HX+MS	Direct MS	HX+MS	PCM+MS; Ruths	Solid media; PCM	Solid media	Direct particles
Line-focusing Relevance	Standard	Niche markets	Not relevant	Niche markets	R&D	Not relevant	Not relevant
Point-focusing Relevance	Not relevant	Standard	R&D	Interest faded	R&D	R&D	R&D

HX = Heat exchanger; MS = Molten salt; PCM = Phase change material



Solar Salt as “the standard solution”

- Composition

- Eutectic: NaNO_3 (46wt%)- KNO_3 (54wt%)
- “Solar Salt”: NaNO_3 (60wt%)- KNO_3 (40wt%)

- Properties

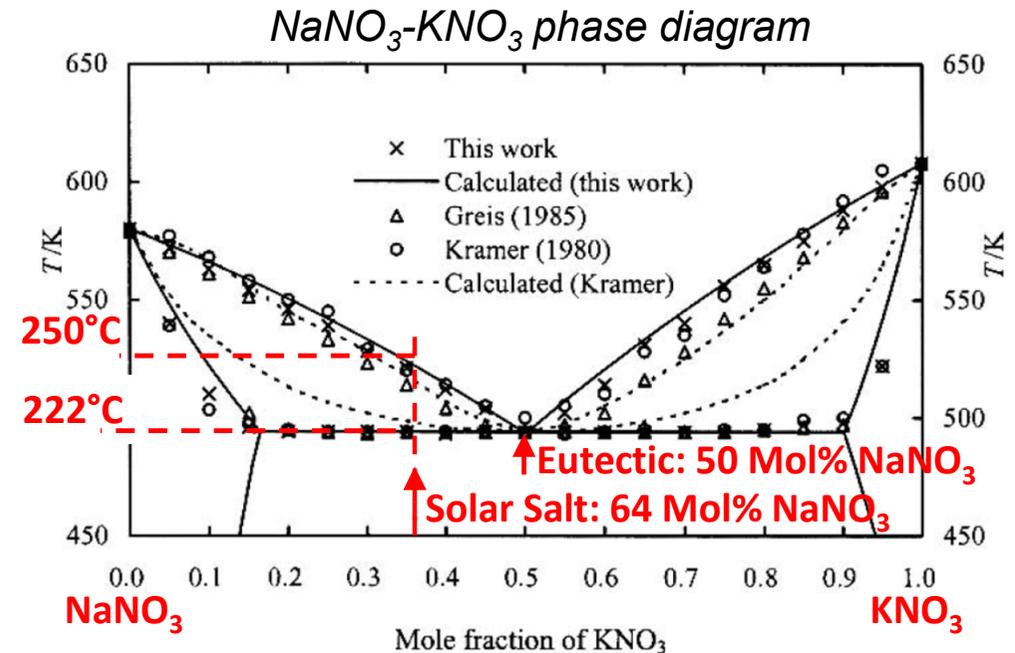
- Zavoico et al. (2001) Report SAND2001-2100
- Bonk, A. et al. (2018) <https://doi.org/10.1016/j.pecs.2018.02.002>

- Production

- “**Mined nitrates**”, e.g.,
Caliche Ore and Solar Brines in Chile
- “**Synthetic nitrates**”
via Haber–Bosch process and mined KCl

- Utilization

- Process industry (500 °C, as HTF and for heat treatment for decades)
- CSP trough plants (390 °C with N_2 blanket as storage medium)
- CSP tower plants (560 °C with air blanket as HTF and storage medium)



Source:

Rogers, D. (1982) <https://doi.org/10.1021/je00030a017>

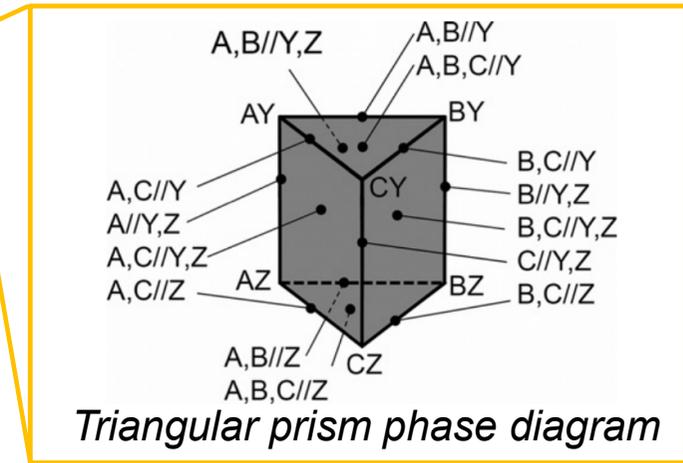
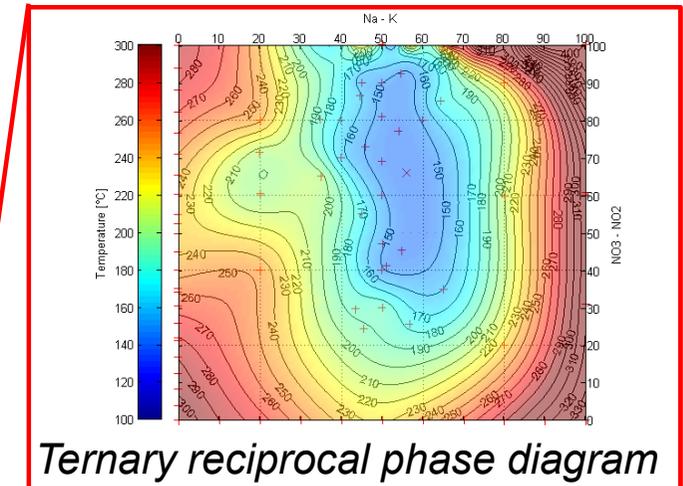
Zhang, X. (2003) <https://doi.org/10.1361/105497103770330091>

Berg, R. (2004) <https://doi.org/10.1039/B403260H>



Reduction of melting temperature by salt mixture

Ion No.	System Classification	Example System with T_m	Develop. Status
2	Single salt	NaNO ₃ 306 °C; KNO ₃ 334 °C	State-of-the-art
3	Binary system, common anion	K,Na//NO ₃ 222 °C (“Solar Salt” system)	State-of-the-art
3	Binary system, common cation	Na//NO ₂ ,NO ₃ 230 °C	State-of-the-art
4	Ternary additive, common anion	Ca,K,Na//NO ₃ ~ 130 °C (HitecXL)	State-of-the-art
4	Ternary reciprocal	K,Na//NO ₂ ,NO ₃ 142 °C (Hitec)	State-of-the-art
5	Quaternary additive, com. anion	Ca,K,Li,Na//NO ₃ 90-110 °C	Novel [88,90]
5	Quaternary reciprocal	Li,Na,K//NO ₂ ,NO ₃ ~ 80 °C	Novel [88,89,93]
6	Quinary reciprocal	Ca,Li,Na,K//NO ₂ ,NO ₃ ~ 70 °C (DLR)	Novel [92]
6	Quinary additive, com. anion	Ca,Cs,Li,Na,K//NO ₃ ~ 65 °C	Novel [90]
7	Senary reciprocal	Ca,Li,Na,K//Cl,NO ₂ ,NO ₃ ~ 53 °C	Novel [91]



Source: Bauer et al. (2013)
<https://doi.org/10.1016/B978-0-12-398538-5.00020-2>



Molten Salts – R&D at lower temperatures

	LiNaK Nitrate	Hitec	HitecXL
Composition	LiNO ₃ -KNO ₃ -NaNO ₃ (30-52-18 wt%)	KNO ₃ -NaNO ₂ -NaNO ₃ (53-40-7 wt%)	Ca(NO ₃) ₂ -KNO ₃ -NaNO ₃ (42-43-15 wt%)
Melting temperature	~120 °C	~140 °C	~140 °C
Max. temperature	450-550°C (air)	450-550°C (N ₂)	450-550°C (air)
Avg. heat capacity	~1.6 J/(g·K)	~1.55 J/(g·K)	~1.4 J/(g·K)
Density	1.7-1.95 g/cm ³	1.7-1.95 g/cm ³	1.9-2.1 g/cm ³
Price	Higher	Medium	Lower
Water Hazard Class	1	3	1
Related experience	LiNO ₃ -KNO ₃ process industry	HTF process industry	New

Source:

- Bonk et al. (2018) <https://doi.org/10.1016/j.pecs.2018.02.002>



Molten Salts – R&D at higher temperatures

	LiNaK Carbonate	MgNaK Chloride	Controlled Solar Salt
Composition	K_2CO_3 - Li_2CO_3 - Na_2CO_3 (35-32-33 wt%)	$MgCl_2$ -KCl-NaCl (57-21-22 wt%)	$NaNO_3$ - KNO_3 (60-40 wt%)
Melting temperature	397 °C	385 °C	~250 °C
Max. temperature	650-700 °C	700-750 °C	600-650 °C
Avg. heat capacity	~1.6 J/(g·K)	~1.1 J/(g·K)	~1.5 J/(g·K)
Density	~2 g/cm ³	1.6 – 1.75 g/cm ³	1.7-1.9 g/cm ³
Price	High	Low	Middle
Related experience	Molten carbonate fuel cell (MCFC)	Next generation nuclear reactor	CSP up to 560 °C

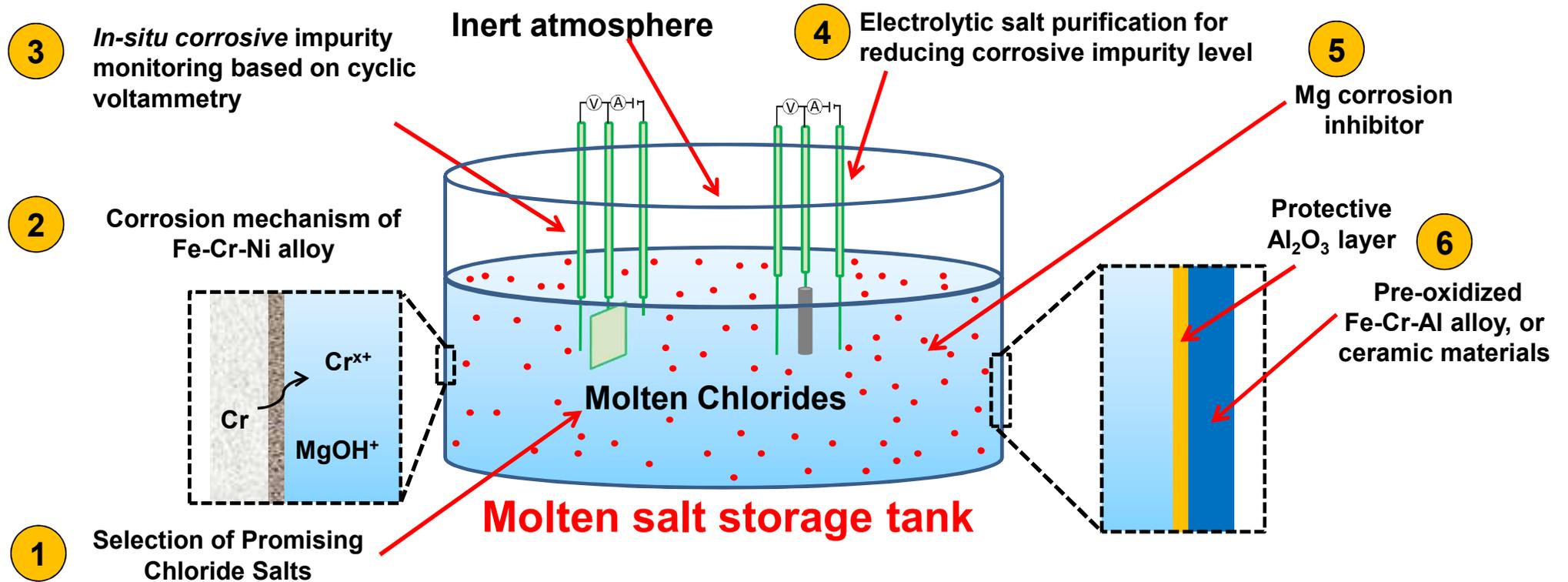
Source:

- Villada et al. (2021) <https://doi.org/10.1016/j.solmat.2021.111344>
- Turchi et al. (2018) <https://doi.org/10.1016/j.solener.2018.01.063>
- Mehos et al. (2017) Report NREL/TP-5500-67464
- Bonk, et al. (2020) <https://doi.org/10.1016/j.apenergy.2020.114535>



MgNaK Chloride - material development

**Presentation
ID 89 – this session
Qing Gong**

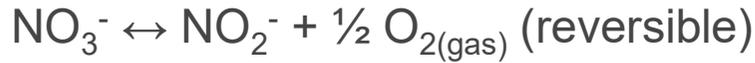


Source:
C. Villada & W. Ding* (2021) <https://doi.org/10.1016/j.solmat.2021.111344>



Controlled Solar Salt

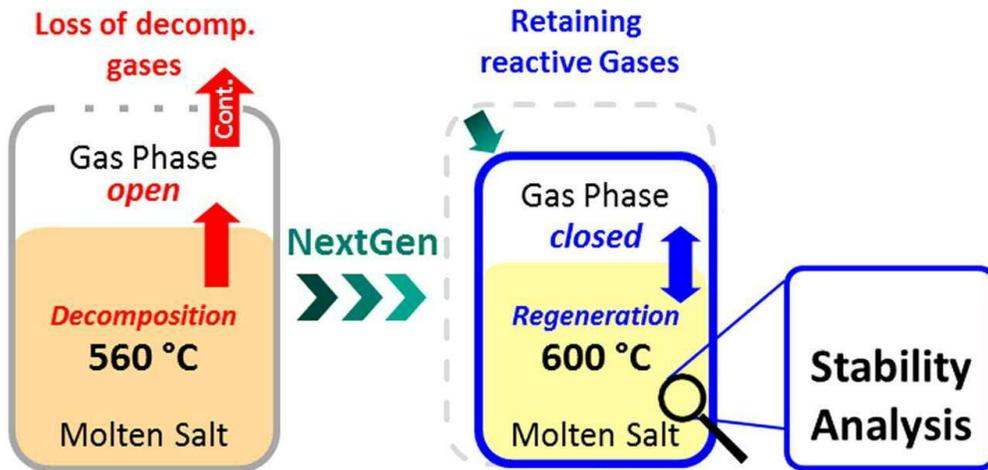
First decomposition reaction



Second decomposition reaction

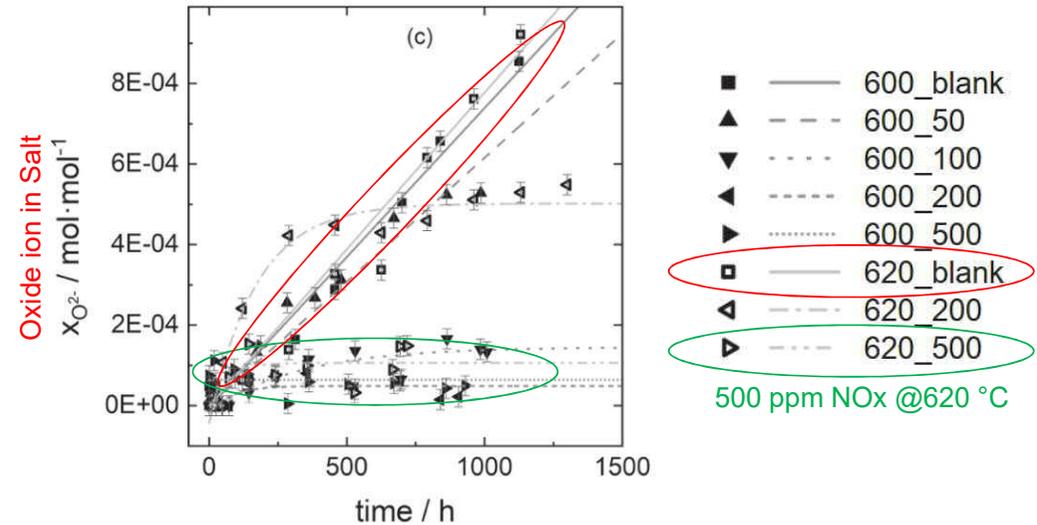


Oxide ions (can dissolve in melt)



Source: A. Bonk et al. (2020)
<https://doi.org/10.1016/j.apenergy.2020.114535>

Presentation ID 105 – this session Alexander Bonk

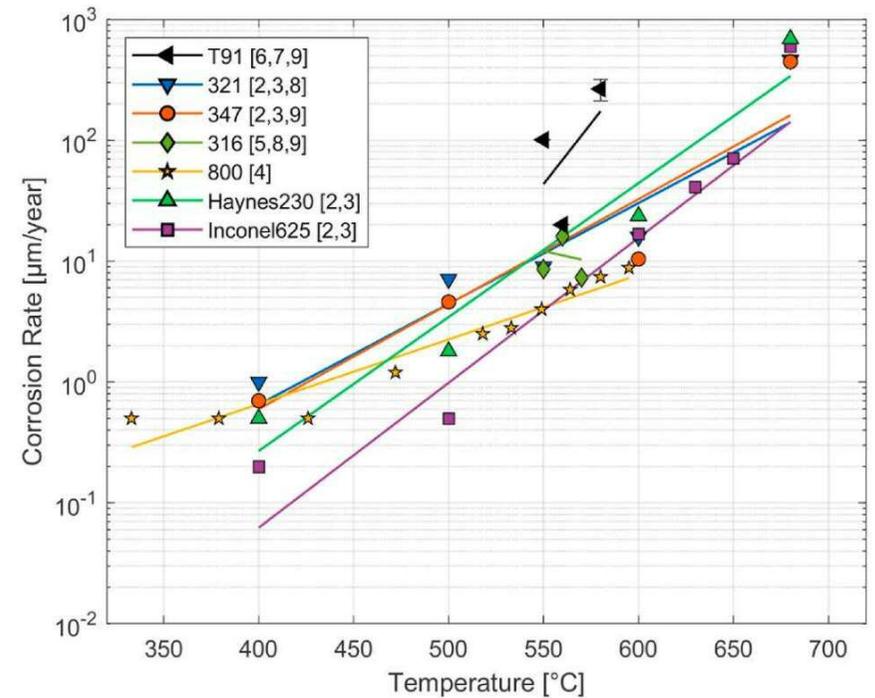
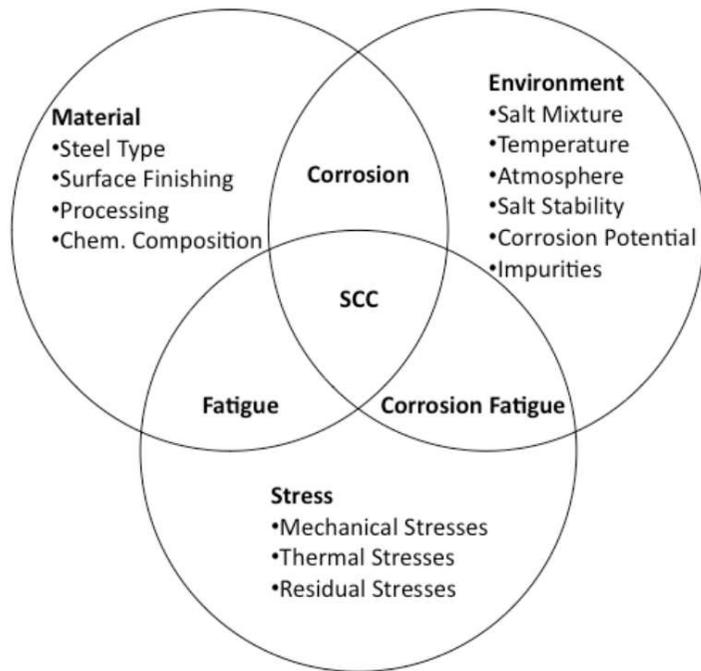


Source: V. Sötz et al. (2020)
<https://doi.org/10.1016/j.solener.2020.09.041>



Alloys and corrosion for Solar Salt

- Low-alloyed carbon steel
- Stainless Cr-Ni steel
(with/without alloying elements Mo, Nb, Ti,...)
- Ni- and Ni-based alloys



[2] A. Kruizenga – SAND2013-8256

[3] A. Kruizenga – SAND2013-2526

[4] R.W. Bradshaw, Corrosion 43 (3), 1987

[5] S.H. Goods – SAND94-8211

[6] P. Audigié, AIP Conf. Proc. 2017

[7] P. Audigié, Surf. Coat. Tech, 2018, 349

[8] A. Gomes, SolMat, 2019, 177

[9] A. Bonk, SolMat, 2019, 203

Source: Sutter, F. et al. (2021)

<https://doi.org/10.1016/j.solmat.2021.111331>



Summary and conclusion

Materials

- Low-temperature salts to replace thermal oil in line-focusing plants
- High-temperature salts to increase the performance of point-focusing plants

Components

- Two-tank storage as established solution up to 560 °C
- Capital cost reduction by single-tank storage with filler
- Further improvement of several other components feasible (e.g. heat exchanger, pumps, valves,...)

Applications and system integration

- Concentrated solar power: molten salt as established storage and heat transfer medium
- Industrial process heat: existing niche processes and potential new power-to-heat applications
- Other potential fields: conventional steam plants, nuclear, new electrical storage solutions

Further information on CSP molten salt technology: <https://doi.org/10.1002/cite.202000137> (open access)



Thank You

German Aerospace Center (DLR)
Institute of Engineering Thermodynamics
Department Thermal Process Technology
Linder Höhe, Building 26
51147 Köln, Germany

Thomas Bauer, Dr. (Northumbria University, UK)
Team leader - Thermal Systems for Fluids
Telephone +49 2203 601-4094
thomas.bauer@dlr.de
www.DLR.de/tt www.DLR.de/tt/tsf



Knowledge for Tomorrow