Thermische Speicherung von Solarenergie

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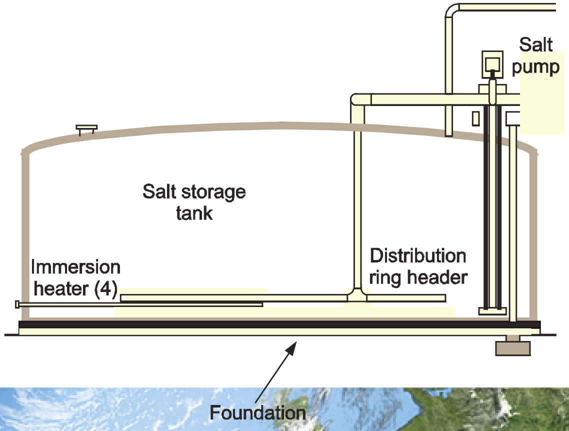
Thermal Energy Storage (TES) Activities at the Institute of Technical Thermodynamics

High temperature TES for CSP plants, CC plants, Adiabatic CAES, industrial process heat and CHP

- Sensible heat storage
  - Solids: Concrete, packed bed, regenerator
  - Liquids: Molten salt
- Latent heat storage (PCM-salt)
- Thermo-chemical storage



CeraStorE (*Competence Center for Ceramic Materials and Thermal Storage Technologies in Energy Research)*

Institute of Materials Research (WF)

WHIPOX (wound highly porous oxide composite)

Redox material development

Material aspects

Institute of Solar Research (SF)

Solar-powered thermochemical cylces

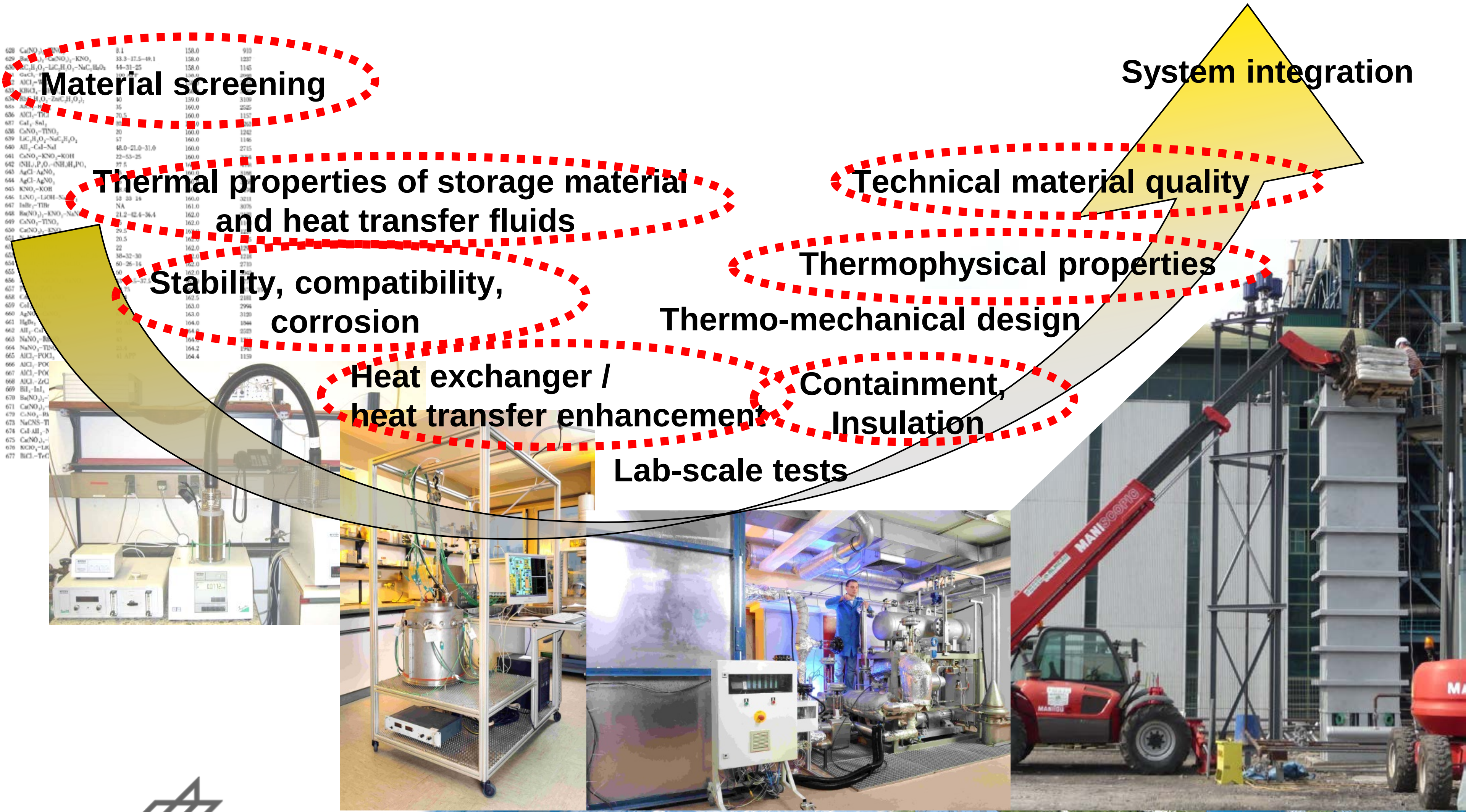
Thermochemical and molten salt aspects

Institute of Technical Thermodynamics (TT)

Thermochemical and molten salt heat storage

Importance of Material Research

Development Steps for Storage Systems



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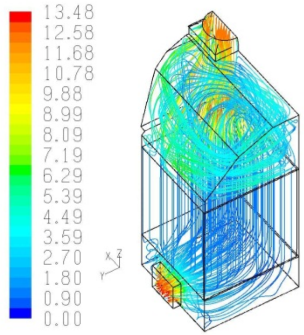
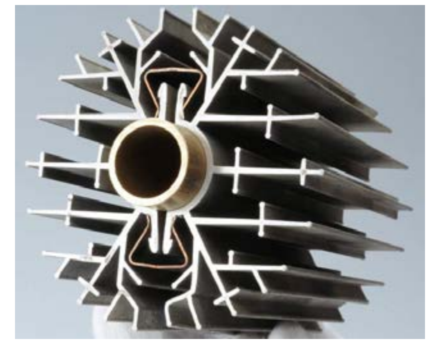
Materials and Sub-Components for Heat Storage

Storage material	Heat transfer fluid	Container	Heat exchanger
			
Water, natural rocks, ceramics, concrete salts, metal oxides	*Air, flue gas, water/steam, molten salt, thermal oil*	*Pressurized vessels, packed bed designs, corrosive media*	*Finned tubes, shell-and-tube heat exchanger*

Additional components: pumps, valves, connection pipes, insolation, foundation, instrumentation and control devices

Take away: TES requires more than storage material research

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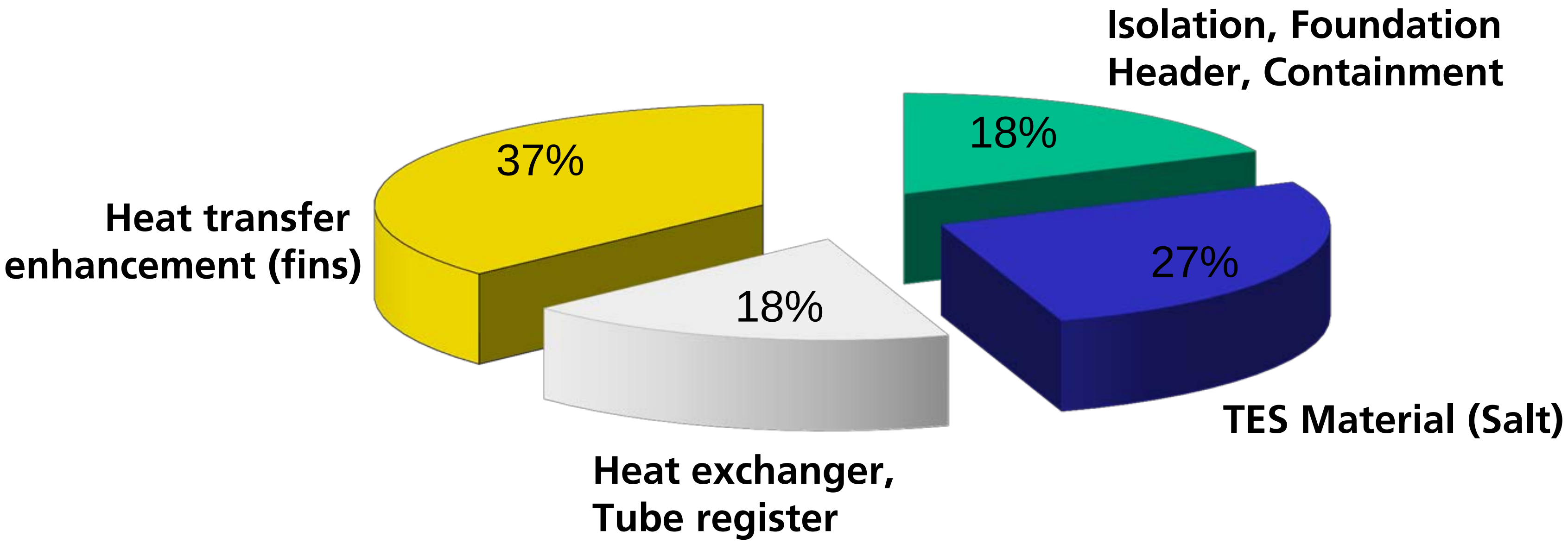
Impact of Specific Material Categories
Example: PCM storage with Nitrate Salts

Operated with water/steam HTF



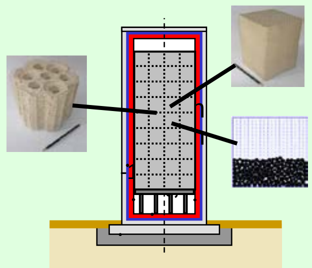
High-Temperature TES materials and technologies

Sensible heat

Solids

Concrete

Ceramics and rocks



Liquids

Molten salt

Pressurized water

Mixture of solids and liquids

Latent heat

Phase change

Solid-solid

Solid-liquid

Alkali nitrate/ nitrite salts

Chemical heat

Reactions

Gas-gas

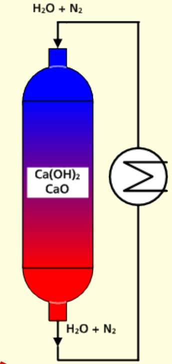
Liquid-gas (Absorption)

Solid-gas

$Ca(OH)_2/CaO/H_2O$

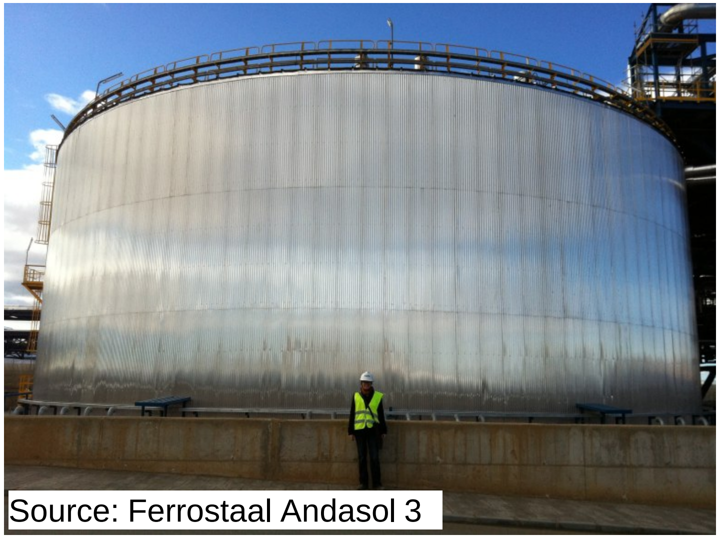
$CaCl_2/H_2O$

$Mn_2O_3/Mn_3O_4/O_2$



Molten Salt Storage

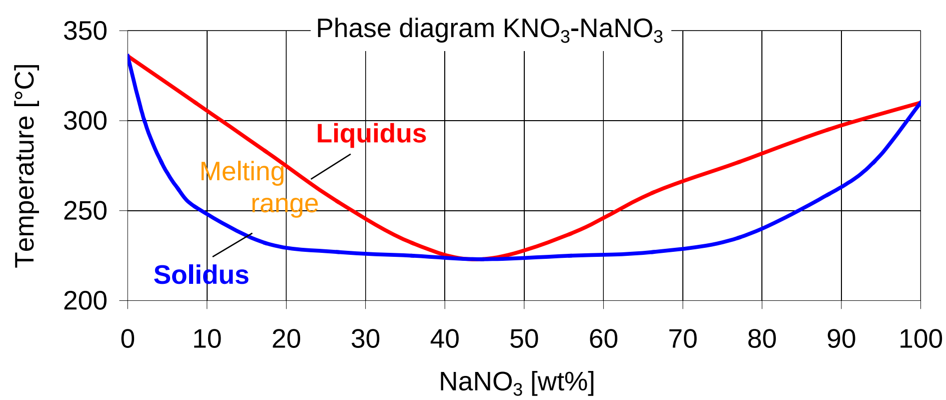
- Market status: Commercial CSP experience
  - 2-tank indirect concept, max. 390 °C (Andasol, 2009)
  - 2-tank direct concept, max. 560 °C (Gemasolar, 2011)
- Technology:
  - Decoupled thermal power and capacity; constant power
  - Boundaries set by current storage medium (temperature levels, costs)
- Research focus/challenges:
  - Development of alternative salt systems
    - Lower melting temperature to avoid freezing (< 140 °C)
    - Stability at higher temperatures (up to 700 °C)
  - Cost reduction – alternative tank design (e.g. Thermocline – single tank with filler)
  - Components and materials for higher temperatures



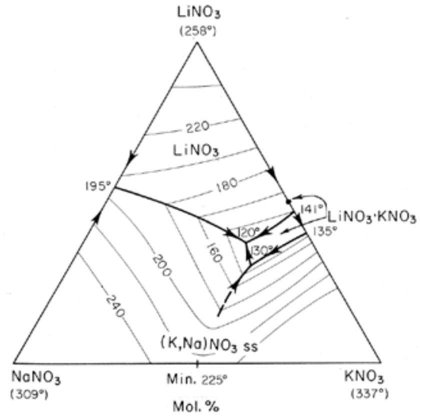
Source: Ferrostaal Andasol 3

Molten Salt Storage – Phase diagrams

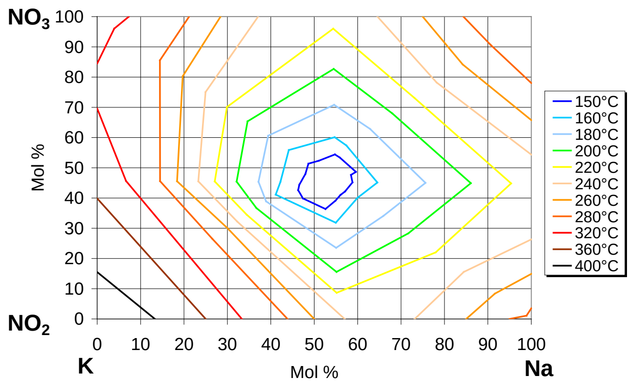
3 different Ions,
Binary system with common ion



4 Ions,
Additive
Ternary



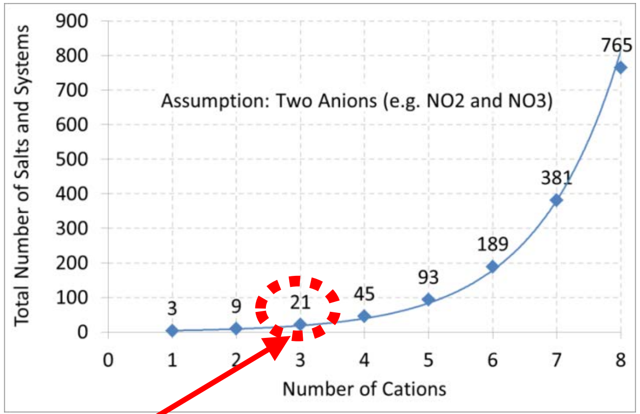
4 Ions,
Reciprocal
Ternary

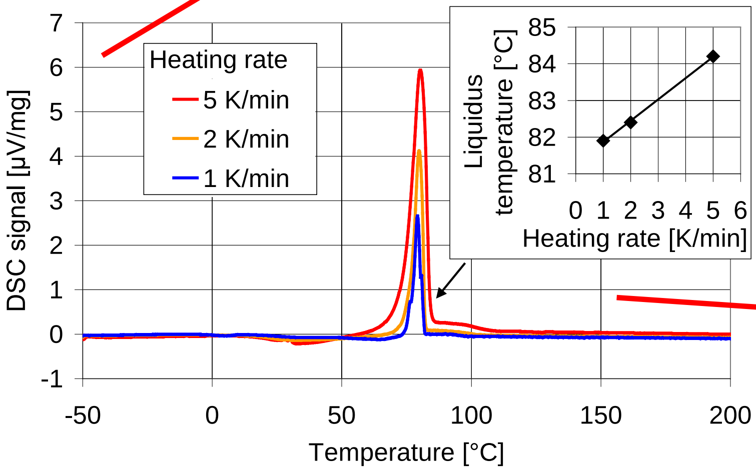


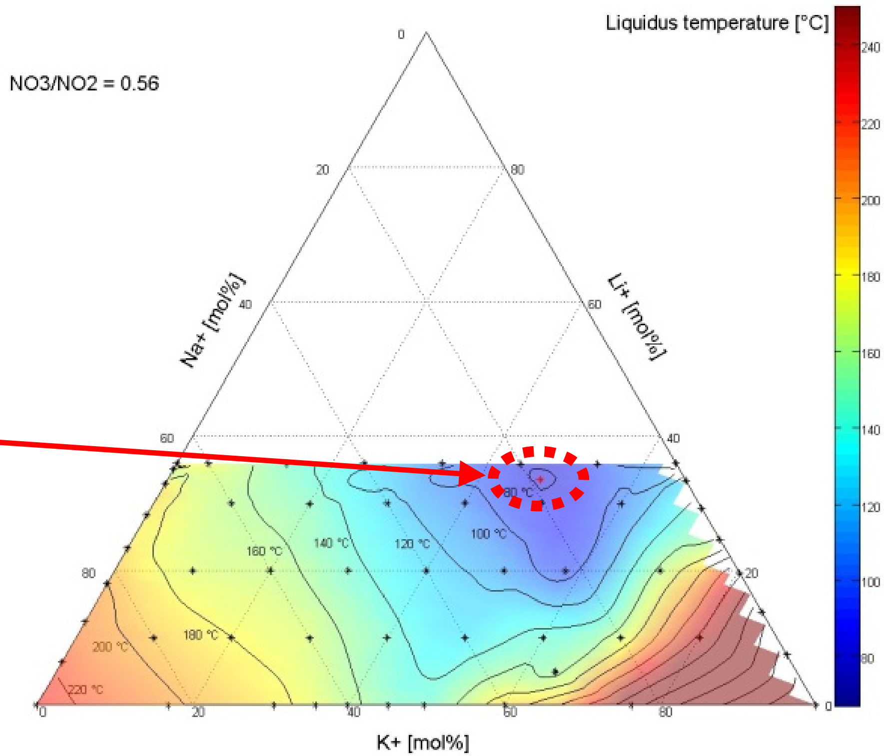
5 Ions, Additive **Quaternary**
(e.g. KNO_3-$NaNO_3$-$LiNO_3$-$Ca(NO_3)_2$)

5 Ions, Reciprocal **Quaternary**
(e.g. Li, Na, K // NO_2, NO_3, $T_{min} \approx 80$ °C)

Molten Salt Storage – Novel Salt Mixtures







Take away: Low melting temperature alkali nitrate/nitrite mixtures are feasible

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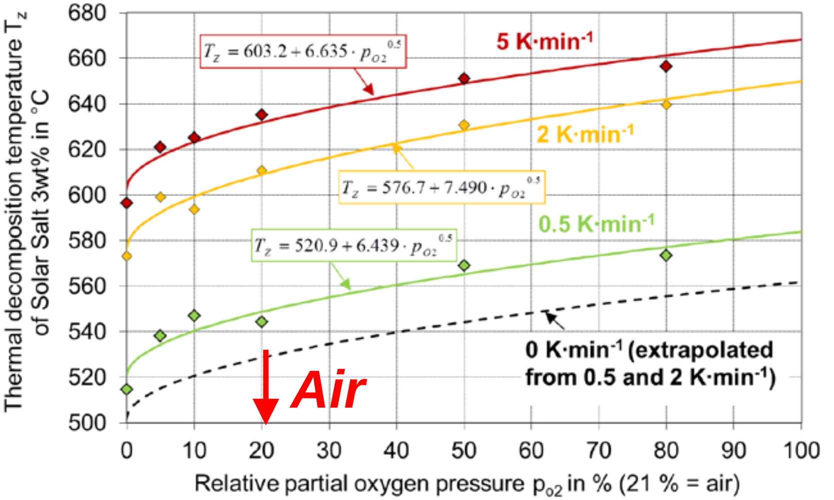
Na NO$_3$

Cation Anion

Molten Salt Storage – Solar Salt Stability



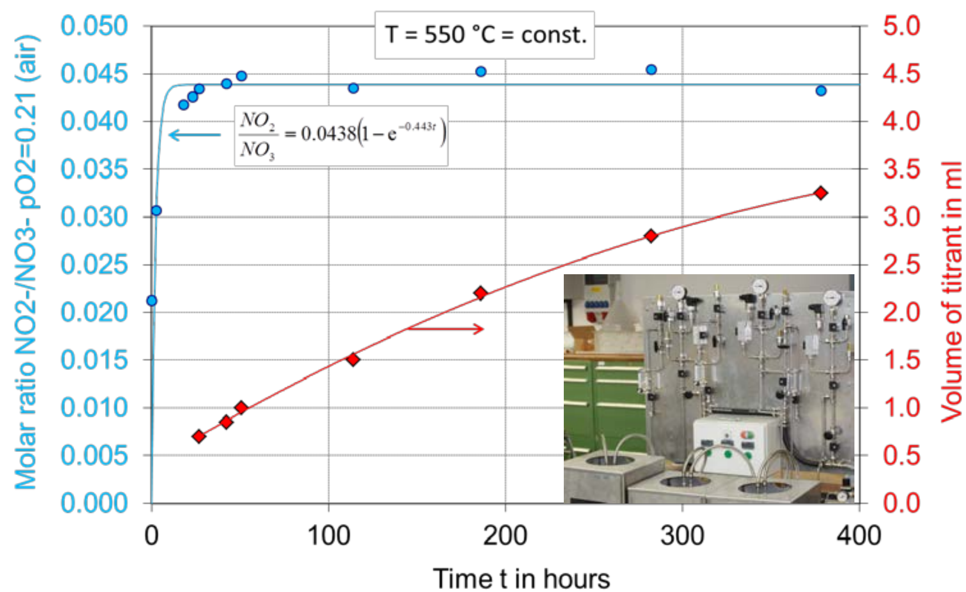
First decomposition reaction:

$NO_3^- \rightarrow NO_2^- + ½\ O_{2(gas)}$ (reversible)

Second decomposition reaction:

NO_3^- or $NO_2^- \rightarrow O^{2-} + NO_{x(gas)}$ or $N_{2(gas)}$

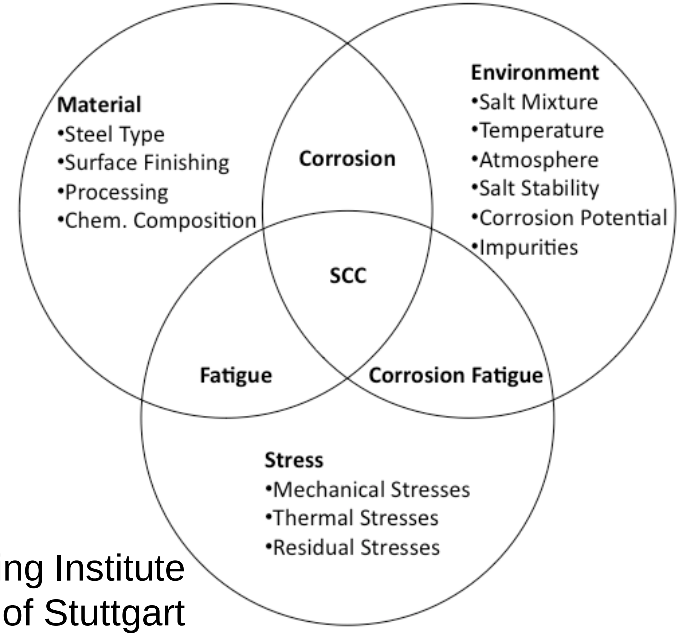
Other Side reactions with CO_2 and H_2O



Take away: Stability of nitrate salts depends on several parameters

Molten Salt Storage – Steel Corrosion with Nitrates

- Major structural alloys:
  - Low alloyed carbon steel (≤ 400° C)
  - Cr-Mo steel (≤ 500° C) (Cr-content up to about 9 wt%)
  - Stainless Cr-Ni steel (≤ 570° C) (with/without Mo, Nb, Ti alloying)
  - Ni-alloys (≤ 650° C) (i.e. Alloy 800)
- Corrosion aspects:
  - Nitrate salt impurities (e.g., chlorides)
  - Nitrate salt decomposition products
  - Solubility of chromium from oxide layer
  - Stress corrosion cracking (SCC)



Source: Materials Testing Institute (MPA), University of Stuttgart

Molten Salt Test Facility “Tesis”

- Technical figures:
  - 20 m³ Solar Salt
    (60 wt% $NaNO_3$ and 40 wt% KNO_3)
  - Temperature range 250 to 560 ° C
  - Mass flow rate up to 8 kg/s
- Research focus/challenges:
  - Molten salt storage concepts
    (e.g. single tank / thermocline)
  - Component tests
    (e.g. pumps, valves, receiver tubes, measurement & control)
    → industrial partners
  - Operational molten salt aspects

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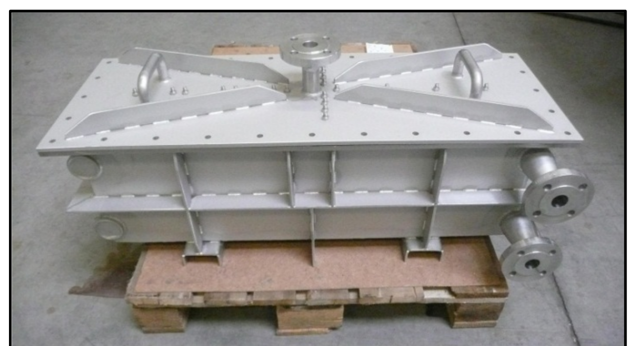
Thermo-chemical Heat Storage

- DLR Development status: Lab-test rigs
  - $Ca(OH)_2$ /CaO (300 – 700 ° C)
  - Salt hydrates, reference $CaCl_2$ (up to 200 ° C)
  - Metal oxides (up to 1000 ° C)
- Target applications: CSP, industrial heat recovery
- Technology:
  - Reversible Gas-Solid Reactions
  - High storage density
  - Loss-free and long-term storage feasible
  - Heat transformation possible
- Research focus/challenges:
  - Characterization of suitable material system
  - Complexity of heat and mass transfer with chemical reaction
  - Reactor designs
  - Separation of thermal power and capacity (movement of the reaction bed)


Source: DLR

Thermochemical $Ca(OH)_2/CaO$ storage

- Target applications:
  - CSP, industrial process heat
  - Temperatures 300 – 700 °C
- Technology
  - $Ca(OH)_2 + \Delta H \leftrightarrow CaO + H_2O$
  - Direct/indirect contact concepts
- Start of larger test rig in progress
- Research focus/challenges
  - Up-scaling of reactor design
  - Movement of the reaction bed
  - System modeling and process integration



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Summary and Conclusions

- Molten salt TES technology
  - Several parameters affect nitrate salt stability → no single limit
  - Tower systems require novel salts with stabilities up to 700 °C
  - Parabolic through systems require salts as fluids with a liquidus temperature as low as possible to avoid freezing

- Thermochemical TES technology offers unique advantages
  → Storage of educts/products at room temperature, heat transformation

- Diversity of fluids and storage materials in the high temperature range
  → Molten salt is **one** TES option among several others

- TES material development not only refers to improved storage materials, but also to material aspects in other components (e.g., containment)

Thank you for your attention !