OVERVIEW OF MOLTEN SALT STORAGE –
MATERIAL DEVELOPMENT FOR SOLAR THERMAL POWER PLANTS

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Denver

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Outline

- Introduction to Solar Energy and Thermal Energy Storage (TES)
- Data on state of the art storage material
- Development of new salts for higher storage capacity
Exploitation of solar energy

Availability of solar energy ↔ Demand for electrical power
⇒ impact of Thermal Energy Storage (TES)
Requirements on storage material

Storage capacity = $C_p \Delta T$

- For large storage capacity $\Delta T$ of usage should be large:
  - Low melting temperature
  - High thermal stability (additionally important for high efficiency)

- The heat capacity should be large
State of the art storage material: „solar salt“

- Definition: mixture of NaNO$_3$ and KNO$_3$ (60:40 wt%)

- Properties: ratio of NaNO$_3$/ KNO$_3$ is close to the eutectic mixture (→ low melting temperature)

- Thermophysical values are available:
  - Heat capacity
  - Thermal conductivity
Research on temperature stability

thermal decomposition reaction:

(1) \[ 2 \text{NaNO}_3 \rightleftharpoons 2 \text{NaNO}_2 + \text{O}_2 \]

(2) \[ 2 \text{NaNO}_2 \rightarrow \text{Na}_2\text{O} + \text{NO} + \text{NO}_2 \]

→ Determination of decomposition temperature can be reported by mass loss

→ Equilibrium constant of reaction (1) is given by:

\[ (\text{NaNO}_2/ \text{NaNO}_3) \times p\text{O}_2^{0.5} \]

→ Reaction (2) can be followed by determination of Na\textsubscript{2}O
Long term stability of solar salt

Solar Salt in synthetic air atmosphere in an open type system at 550 °C

\[
\frac{\text{NO}_2}{\text{NO}_3} = 0.0438 \left( 1 - e^{-0.44t} \right)
\]
Development of new salts

Aim: Increase of the storage capacity, given by: $C_p \cdot \Delta T$

(1) Increase of $C_p$
(2) Increase of $\Delta T$ (by lowering temperature of liquid-solid transition)

(1) Increase $C_p$ per volume (volumetric heat capacity):
   → can be estimated due to correlation of: atomic radii ↔ $C_{p_{\text{vol}}}$
**Atomic radii of salt components**

Salt: Cations and anions

<table>
<thead>
<tr>
<th>Li</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>Mg</td>
</tr>
<tr>
<td>K</td>
<td>Ca</td>
</tr>
<tr>
<td>Sr</td>
<td>Ba</td>
</tr>
</tbody>
</table>

Periodic table:

- **alkali element**
- **alkaline earth element**
- **halogenes**

Correlation elements $\downarrow$ atomic radii:
Systematic change of heat capacity

Volumetric heat capacity [MJ/(m³K)]

0 0.5 1 1.5 2 2.5 3 3.5 4 4.5
Li Na K Mg Ca Sr Ba

Variable cation

Alkali element Alkaline earth element

X⁺ F⁻ → Fixed anion: fluorine
X⁺ Cl⁻
X⁺ Br⁻
Development of new salts

Increase of the storage capacity, given by: $C_p^* \Delta T$

(1) Increase $C_p$

(2) Increase $\Delta T$ (by lowering temperature of liquid-solid transition)

→systematic screening/ creation of phase diagrams

<table>
<thead>
<tr>
<th></th>
<th>NO$_2$</th>
<th>NO$_3$</th>
<th>NO$_2$,NO$_3$</th>
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<tr>
<td><strong>Single salts and binary systems with common cation</strong></td>
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<tr>
<td>Ca</td>
<td>398 °C*</td>
<td>561 °C*</td>
<td>393 °C</td>
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<tr>
<td>K</td>
<td>440 °C</td>
<td>334 °C</td>
<td>316-323 °C</td>
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<td>Li</td>
<td>220 °C</td>
<td>254 °C</td>
<td>196 °C</td>
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<td>Na</td>
<td>275 °C</td>
<td>306 °C</td>
<td>226-233 °C</td>
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<td><strong>Binary systems with common anion and ternary reciprocal</strong></td>
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<td>Ca,K</td>
<td>185 °C</td>
<td>145-174 °C</td>
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<td>Li,Na</td>
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<td>126 °C</td>
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<td><strong>Ternary additive common anion and quaternary reciprocal</strong></td>
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<td><strong>Quaternary additive common anion and quinary reciprocal</strong></td>
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<td>Ca,K,Li,Na</td>
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<td>109 °C</td>
<td>N/A</td>
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Summary

- Overview of a commercial molten salt TES (thermal energy storage) system

- Examination of the thermal stability of nitrate salts

- Identification and characterisation of salt formulations with a high storage capacity/ low liquidus temperature