Salt/Zeolite Composite Materials for Thermochemical Energy Storage

Steffen Beckert
Roger Gläser

Institute of Chemical Technology
Universität Leipzig

Heat consumption and solar irradiation over the year

http://comtes-storage.eu/home/seasonal-heat-storage/
Outline

Thermochemical Heat Storage

Experimental Setup

Salt/Zeolite Composites

Numerical Modelling

Conclusion and Outlook
Thermochemical Heat Storage

Chemical Reaction
- Metallic Hydrides
- Carbonate Systems
- Hydroxide Systems
- Redox Systems
- Ammonia Systems
- Organic Systems

Absorption
- Hygroscopic salts
  - CaCl$_2$, MgCl$_2$, LiCl
  - MgSO$_4$
  - NaOH
  - LiBr
  - ...

Adsorption
- Silica Gels
- Metalaluminophosphates
- MOFs
- Zeolites

Current systems still cover a wide range of required conditions for a large area of application.
# Thermochemical Heat Storage

## Chemical Reaction
- Metallic Hydrides
- Carbonate Systems
- Hydroxide Systems
- Redox Systems
- Ammonia Systems
- Organic Systems

## Absorption
- Hygroscopic salts
  - CaCl₂, MgCl₂, LiCl
  - MgSO₄
  - NaOH
  - LiBr
  - ...

## Adsorption
- Silica Gels
- Metalaluminophosphates
- MOFs
- Zeolites

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**Recent Developments**

- Tailoring and Fine Tuning for Designated Applications
- Combination of Different Material Concepts
- Increasing the Heat Storage Density for Solar Applications

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Tailoring and Fine Tuning for Designated Applications (II)

- Reducing the regeneration temperature (solar applications < 120 °C)
- Decreasing the hydrophilic potential of the material
  - Aluminophosphates (AlPOs): AlPO₄
  - Silico-Aluminophosphates (SAPOs): (SiₓAlᵧPₓ)O₂
  - Zeolites: Variation of the Si/Al ratio during synthesis; Dealumination

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Si/Al ratio</th>
<th>T_max (DTG) in K</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaLSX</td>
<td>1</td>
<td>440</td>
</tr>
<tr>
<td>NaX</td>
<td>1.2</td>
<td>425</td>
</tr>
<tr>
<td>NaY</td>
<td>2.3</td>
<td>395</td>
</tr>
<tr>
<td>NaY(7)</td>
<td>7.4</td>
<td>375</td>
</tr>
<tr>
<td>NaY(11)</td>
<td>11.4</td>
<td>355</td>
</tr>
<tr>
<td>NaY(30)</td>
<td>30</td>
<td>345</td>
</tr>
</tbody>
</table>
Tailoring and Fine Tuning for Designated Applications (III)

- Salt/Zeolite Composites

![Graph showing change in heat storage density with salt content](image)

**Legend**
- ▲ MgCl₂/Na-MOR (Whiting 2014)
- ○ MgSO₄/Na-Y (Whiting 2013)
- ■ MgSO₄/Na-X (Whiting 2013)

**Graph Details**
- Change in Heat Storage Density / %
- Salt Content / wt.-%
- 0 5 10 15 wt.-%
- -30 0 30 60 90 %

**Data Points**
- 150 kW h m⁻³
- 800 kW h m⁻³ (thermodynamically)
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Thermochemical Characterization I

Dry Air

Sorption Chamber

Humidity Management
Operating Conditions and Measurement Uncertainty

- Temperature (both sorption and desorption): 30 … 180 ºC
- Humidity (30 ºC): <0.1 … 30 g kg\(^{-1}\), <0.2 … 42 mbar (40 ºC: 50 g kg\(^{-1}\), 74 mbar)
- Sample volume: 2 … 17 cm\(^3\) (e. g., ca. 1 … 12 g zeolite)
- “Material size”: ~0.2 … 17 mm (from grains over granulates to foams)
- Pressure: ambient pressure

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Measurement Uncertainty / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Loading Lift</td>
<td>6</td>
</tr>
<tr>
<td>Heat Storage Density</td>
<td>7</td>
</tr>
<tr>
<td>Water Sorption Enthalpy</td>
<td>5</td>
</tr>
<tr>
<td>Thermal Output Power</td>
<td>5-10</td>
</tr>
</tbody>
</table>
Typical Cycling Profile

![Graph showing temperature and humidity changes over time for different conditions.]

- **Temperature / °C**
- **Humidity / (g kg\(^{-1}\))**
- **Time / h**

- **T1 (Reactor Inlet)**
- **T2 (Bulk 1)**
- **T3 (Bulk 2)**
- **T4 (Bulk 3)**
- **T5 (Reactor Exit)**
- **T6 (Surrounding)**
- **X2 (Reactor Inlet)**
- **X4 (Reaktor Exit)**
Outline

1. Thermochemical Heat Storage
2. Experimental Setup
3. Salt/Zeolite Composites
4. Numerical Modelling
5. Conclusion and Outlook
Thermochemical Heat Storage with Salt/Zeolite Composites

Thermochemical Properties
Higher or Lower Heat Storage Density
Various Methods/Conditions

Composite Composition
FAU, LTA, MOR
+ MgSO$_4$, MgCl$_2$, CaCl$_2$

Characterization
Blocking of Zeolitic Micropores by Salt

Composite Salt/Zeolite + Water

Characterization
Structural, Textural Properties
(XRD, SEM, N$_2$ Sorption, Hg Intrusion)

Present Work
Salt/Zeolite Composites
FAU + MgSO$_4$, CaCl$_2$, LiCl
Variation of Salt Loading

Relation
of Thermochemical and Material Properties

Thermochemical Properties
Conditions Close to Application
Variation of Sorption Humidity

Literature
Binderless Zeolite Granulates

Zeolite Powder

Zeolite Granulate

CaCl\textsubscript{2} and MgSO\textsubscript{4} Composites: SEM

Salt is Predominantly Located Inside the Micropores (Salt Inclusion)

https://upload.wikimedia.org/wikipedia/commons/5/5f/Faujasite_structure_labeled_German.svg.
CaCl$_2$ Composites: XRD

![XRD diagram showing the diffraction patterns of CaCl$_2$ composites with different crystal forms and hydration levels.](image)

- 23CaCl$_2$/Ca-X
- 15CaCl$_2$/Ca-X
- 8CaCl$_2$/Ca-X
- Ca-X
- Na-X
- CaCl$_2$ / CaCl$_2$ $\cdot$ 2 H$_2$O
- CaCl$_2$ $\cdot$ 4 H$_2$O ($\alpha$) / ($\beta$)
- CaCl$_2$ $\cdot$ 6 H$_2$O
- Faujasite
Thermochemical Properties (MgSO\textsubscript{4}/Mg-X Composites)

- Included Salt Ions Can Not Be Hydrated
- Reduced Water Uptake

Humidity: ■ 3, ● 6, ▲ 9, ▼ 12, ◀ 15, ► 21 g kg\textsuperscript{-1}
Thermochemical Properties (CaCl$_2$/Ca-X Composites)

- Formation of a Salt Solution Above the Deliquescence Humidity (CaCl$_2$: ~8 g g$^{-1}$) within the Secondary Pore System
- Three Phase Equilibrium (Included Salt, Salt Solution, Water Vapor)
- Pore Volume Limits the Water Uptake

Humidity: ■ 3, ● 6, ▲ 9, ▼ 12, ◄ 15, ► 21 g kg$^{-1}$
Further Improvements: Ongoing Work

- Lower Deliquescence Humidity
- Larger Secondary Pore Volume
- Reducing the Inclusion
Experimentalist’s View

Microscopic Material Properties

- **Structure**
  - Intensity / arb. u.
  - 2θ / °

- **Texture**
  - Pore Volume / (10^-2 cm^3 cm^-3)
  - Salt Content / wt.-%

- **Thermochemical Material Properties**
  - Water Uptake / (g cm^-3)
  - Heat Storage Density / (kW h m^-3)

Macroscopic Material Properties

- **Water Uptake**
  - Salt Content / (mol mol^-1)

- **Heat Storage Density**
  - Salt Content / (mol mol^-1)

Application
General Aspects of Numerical Modelling

balance laws
- mass balance(s)
- linear and angular momentum balance(s)
- energy balance(s)
- entropy balance

material independent

constitutive relations
- mass transport (Darcy, Forchheimer, ...)
- heat transport (Fourier, radiation, ...)
- reaction/sorption equilibrium
  (van't Hoff, Dubinin, ...)
- reaction/sorption kinetics
  (linear driving force, logarithmic driving force, ...)
- state-dependencies
  (e.g. conversion-dependent heat capacity)
- mixture rules (effective properties of multiphase media)
- constraints (e.g. incompressibility)
  
material dependent

numerical method
- FEM
- FDM
- FVM
- ...

reference solutions
- analytical solutions
- manufactured solutions

numerical model

boundary and initial conditions

system dependent

experimental input

verification

simulation results

prediction

validation

different boundary/initial conditions

parameterisation experiments

inverse modelling

different boundary/initial conditions

physical insight and assumptions

physical modelling

numerics and implementation

validation & application

OpenGeoSys: Open Source Simulation Software for Multi-Physical Modelling

Dubinin-Polanyi Theory

- Adsorption Potential:
  \[ A_m = \frac{R}{M_{ads}} T \ln \frac{p_s}{p} \]

- Adsorbed Volume:
  \[ W(A_m) = \frac{C_{eq}(T)}{\rho_{ads}(T)} \]

Water Sorption Isotherm

Characteristic Curve

Experimental Input

Density Model

- Water Uptake / g g\(^{-1}\)
- Pressure / mbar
- 25 °C
- 50 °C
- 70 °C
- 100 °C
- 130 °C
- 150 °C
- 180 °C
- 200 °C
- 250 °C
## Adsorbate Density Models (I)

![Graph showing adsorbate density models](image)

Adsorbate density models used in the literature.

<table>
<thead>
<tr>
<th>References</th>
<th>Adsorbate density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Núñez [16]</td>
<td>Free liquid over entire temperature range</td>
</tr>
<tr>
<td>Nikolaev and Dubinin [18]</td>
<td>$Q_{\text{Ads}}(T) = \begin{cases} \text{free liquid} &amp; T \leq T_0 \ Q_{\text{Ads}}(T_0) - \frac{Q_{\text{Ads}}(T_0) - M}{T_c - T_0}(T - T_0) &amp; T &gt; T_0 \end{cases}$ with $T_0 = 373.15 , \text{K}$ (boiling point of water)</td>
</tr>
<tr>
<td>Cook and Basmadjian [19]</td>
<td>$Q_{\text{Ads}}(T) = \begin{cases} \text{free liquid} &amp; T \leq T_0 \ Q_{\text{Ads}}(T_0)[1 - \alpha_{T,\text{Ads}}(T_0)(T - T_0)] &amp; T &gt; T_0 \end{cases}$ with $T_0 = 373.15 , \text{K}$ (boiling point of water)</td>
</tr>
<tr>
<td>Mugele [15]</td>
<td>$Q_{\text{Ads}}(T) = \frac{Q_{\text{Ads}}(T_0)}{1 + \alpha_{T,\text{Ads}}(T_0)[T - T_0]}$ with $T_0 = 293.15 , \text{K}$ (room temperature)</td>
</tr>
<tr>
<td>Hauer [14]</td>
<td>$Q_{\text{Ads}}(T) = Q_{\text{Ads}}(T_0)[1 - 3.781 \times 10^{-4} , \text{K}^{-1} \cdot (T - T_0)]$ with $T_0 = 283.15 , \text{K}$</td>
</tr>
</tbody>
</table>

**Adsorbate Density Models (II)**

- **Desorption:**
  \[ T = 180 \, ^\circ\mathrm{C} \]
  \[ \rho_W = 0 \, \text{mbar} \]

- **Adsorption:**
  \[ T = 20 \, ^\circ\mathrm{C} \]
  \[ \rho_W = 10 \, \text{mbar} \]

\[ \Delta h = \Delta h^y + A_m - T\Delta s \]

<table>
<thead>
<tr>
<th>Adsorbate density model</th>
<th>Storage density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kW h m(^{-3})</td>
</tr>
<tr>
<td>Constant</td>
<td>153.5</td>
</tr>
<tr>
<td>Mugele [15]</td>
<td>158.0</td>
</tr>
<tr>
<td>Cook [19]</td>
<td>160.8</td>
</tr>
<tr>
<td>Núñez [16]</td>
<td>161.3</td>
</tr>
<tr>
<td>Hauer [14]</td>
<td>162.2</td>
</tr>
<tr>
<td>Nikolaev [18]</td>
<td>163.6</td>
</tr>
<tr>
<td>100 MPa [22]</td>
<td>163.8</td>
</tr>
<tr>
<td>Mean</td>
<td>160.5</td>
</tr>
</tbody>
</table>
Heat Storage Density – Numerical Modelling vs. Experiment

Desorption: $T = 110 \, ^\circ\text{C}$  \hspace{1cm} Adsorption: $T = 30 \, ^\circ\text{C}$

$p_W = 0.2 \, \text{mbar}$ \hspace{1cm} $p_W = 5.5 \ldots 33 \, \text{mbar}$

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Conclusions

Formation of a Salt Solution
Above Deliquescence Humidity
Higher Heat Storage Density

Salt Inclusion
Below Deliquescence Humidity
Lower Heat Storage Density

Composite
Salt/Zeolite + Water

Ion Exchange
Necessary Prior Impregnation

Outlook

Tuning the Composites
for the Use at Low Humidities
by, e.g., Salt Mixtures

Reduce Salt Inclusion
Lower Donnan-Potential
e.g., Less Hydrophilic Zeolites

Larger Secondary Pore Volume
for Increased Water Uptake Capability
and Increased Heat Storage Density
by Modifying of the Granulation Process

Regulation Strategies
Need to be Adapted to
Material Properties
Thank You for Your Attention