# Salt/Zeolite Composite Materials for Thermochemical Energy Storage

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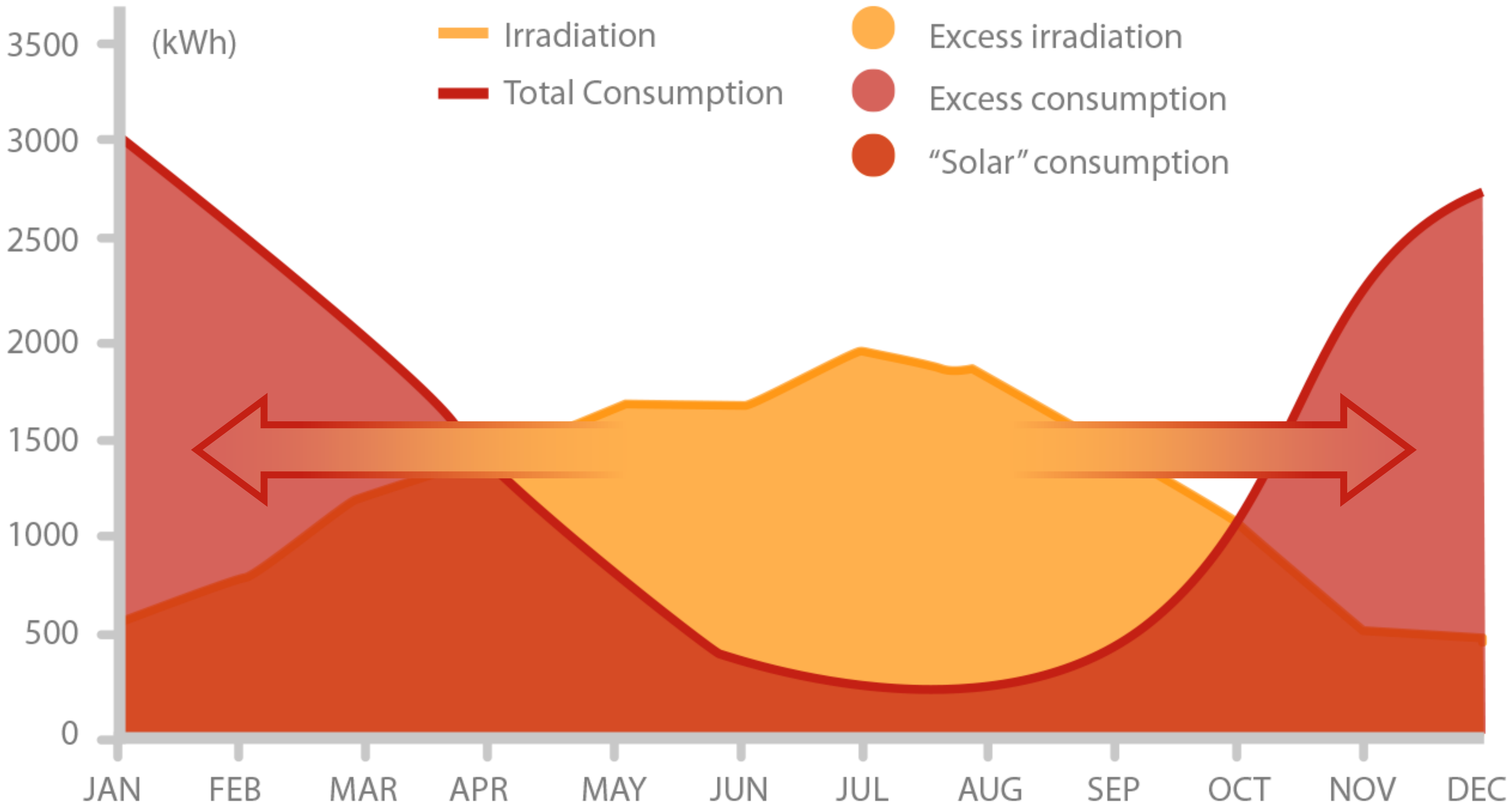
*Symposium „Dynamische Sorptionsverfahren“*
*Leipzig, May 30, 2017*

# Heat consumption and solar irradiation over the year




http://comtes-storage.eu/home/seasonal-heat-storage/
http://diepresse.com/home/panorama/klimawandel/741165/Waerme-in-den-Winter-retten (Patrick Pleul)

# Outline

- Thermochemical Heat Storage

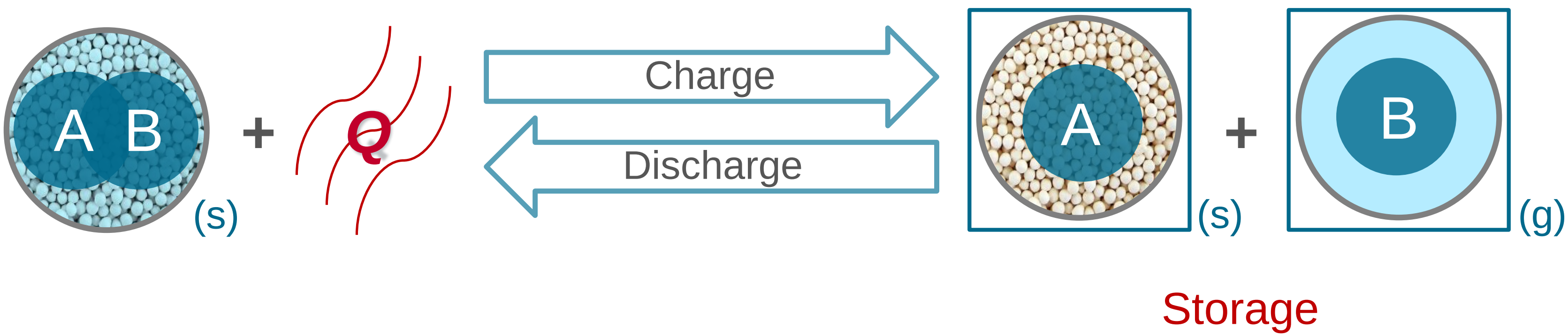
- Experimental Setup

- 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.

P. Pardo, A. Deydier, Z. Anxionnaz-Minvielle, S. Rougé, M. Cabassud, P. Cognet, Renew. Sust. Energ. Rev. 32 (2014) 591-610; P. Tatsidjodoung, N. Le Pierrès, L. Luo, Renew. Sust. Energ. Rev. 18 (2013) 327-349.

# Thermochemical Heat Storage

## Chemical Reaction
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  - LiBr
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## Adsorption
- Silica Gels
- Metalaluminophosphates
- MOFs
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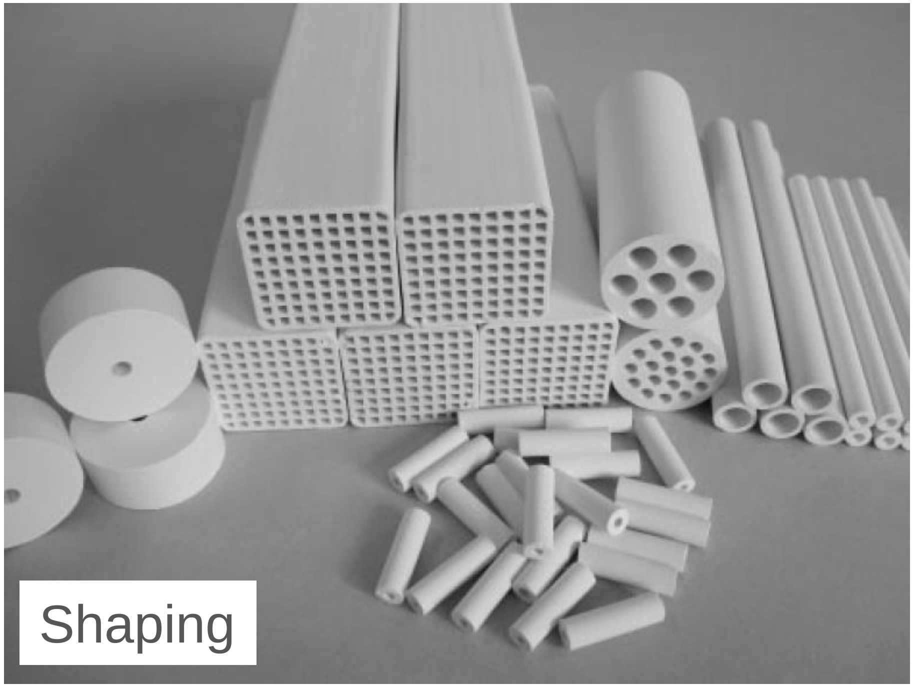
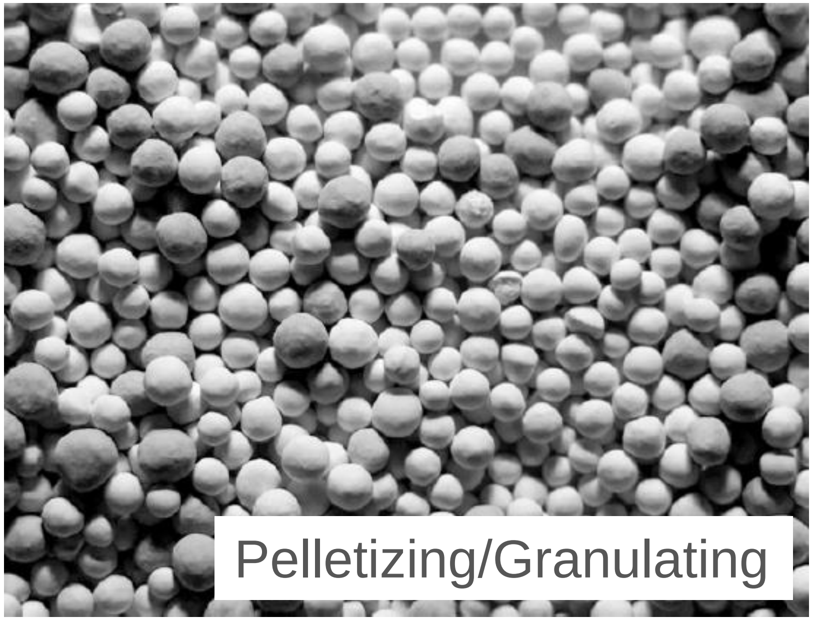
**Recent Developments**

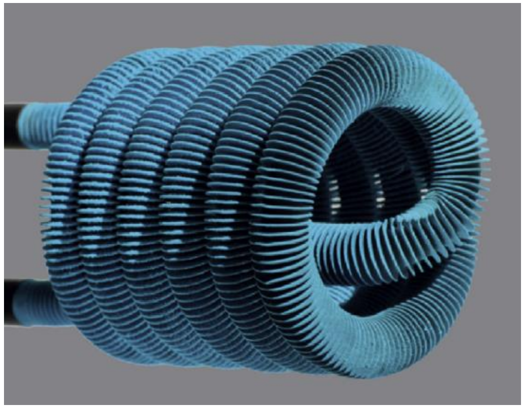
- **Tailoring and Fine Tuning for Designated Applications**
- **Combination of Different Material Concepts**
- **Increasing the Heat Storage Density for Solar Applications**

P. Pardo, A. Deydier, Z. Anxionnaz-Minvielle, S. Rougé, M. Cabassud, P. Cognet, Renew. Sust. Energ. Rev. 32 (2014) 591-610; P. Tatsidjodoung, N. Le Pierrès, L. Luo, Renew. Sust. Energ. Rev. 18 (2013) 327-349.

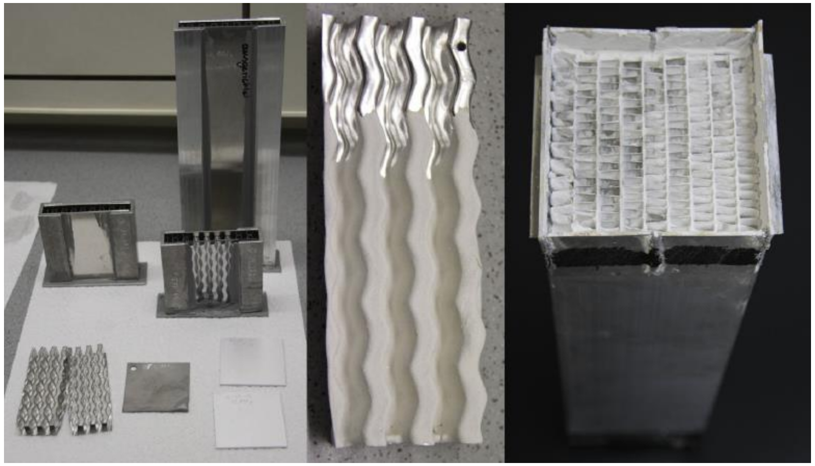
# Tailoring and Fine Tuning for Designated Applications (I)



Coatings



K. Schumann et al., Chem. Ing. Tech. 86 (2014) 106-111; Microporous Mesoporous Mater. 154 (2012) 119-123; G.M. Munz et al., Appl. Therm. Eng. 61 (2013) 878-883; S.K. Henninger et al., Renew. Energ. (2016) DOI: 10.1016/j.renene.2016.08.041.

# Tailoring and Fine Tuning for Designated Applications (II)

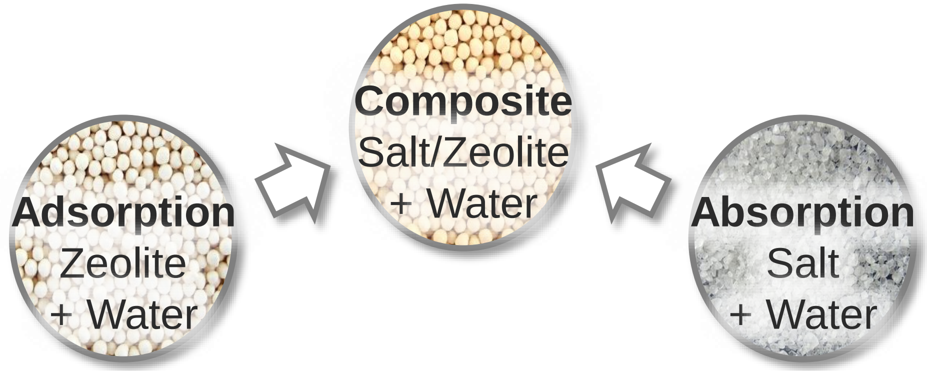
- Reducing the regeneration temperature (solar applications < 120 ºC)
- Decreasing the hydrophilic potential of the material
  - Aluminophosphates (AlPOs): $AlPO_4$
  - Silico-Aluminophosphates (SAPOs): $(Si_xAl_yP_z)O_2$
  - Zeolites: Variation of the Si/Al ratio during synthesis; Dealumination

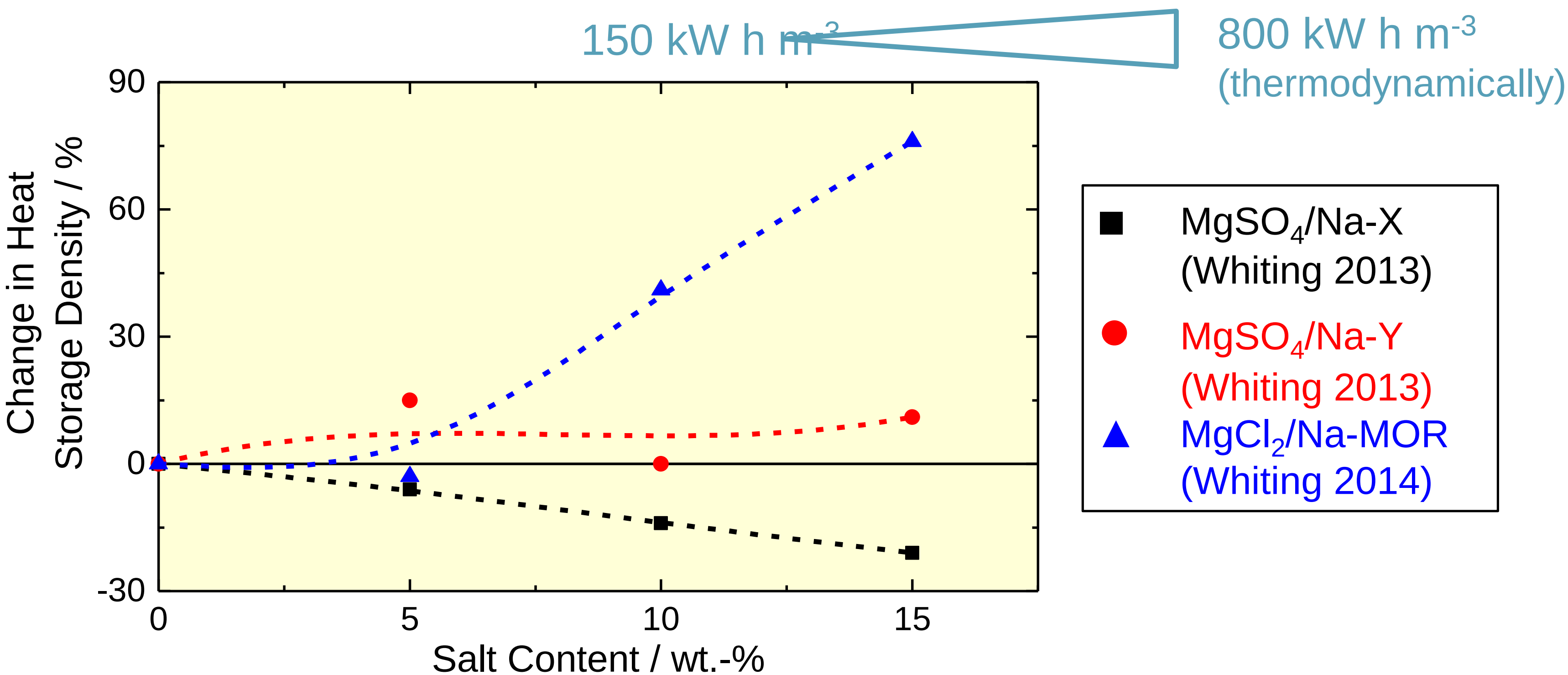
| Sample | Lattice Si/Al ratio | $T_{max}$ (DTG) in K |
|---|---|---|
| NaLSX | 1 | 440 |
| NaX | 1.2 | 425 |
| NaY | 2.3 | 395 |
| NaY(7) | 7.4 | 375 |
| NaY(11) | 11.4 | 355 |
| NaY(30) | 30 | 345 |

J. Jänchen, H. Stach, U. Hellwig, in: Studies in Surface Science and Catalysis, 2008, pp. 599–602; T.H. Herzog, J. Jänchen, E.M. Kontogeorgopoulos, W. Lutz, Energy Procedia 48 (2014) 380-383.

# Tailoring and Fine Tuning for Designated Applications (III)

- Salt/Zeolite Composites





G.T. Whiting, D. Grondin, S. Bennici, A. Auroux, Sol. Energy Mater. Sol. Cells 112 (2013) 112–119.
G.T. Whiting, D. Grondin, D. Stosic, S. Bennici, A. Auroux, Sol. Energy Mater. Sol. Cells 128 (2014) 289–295

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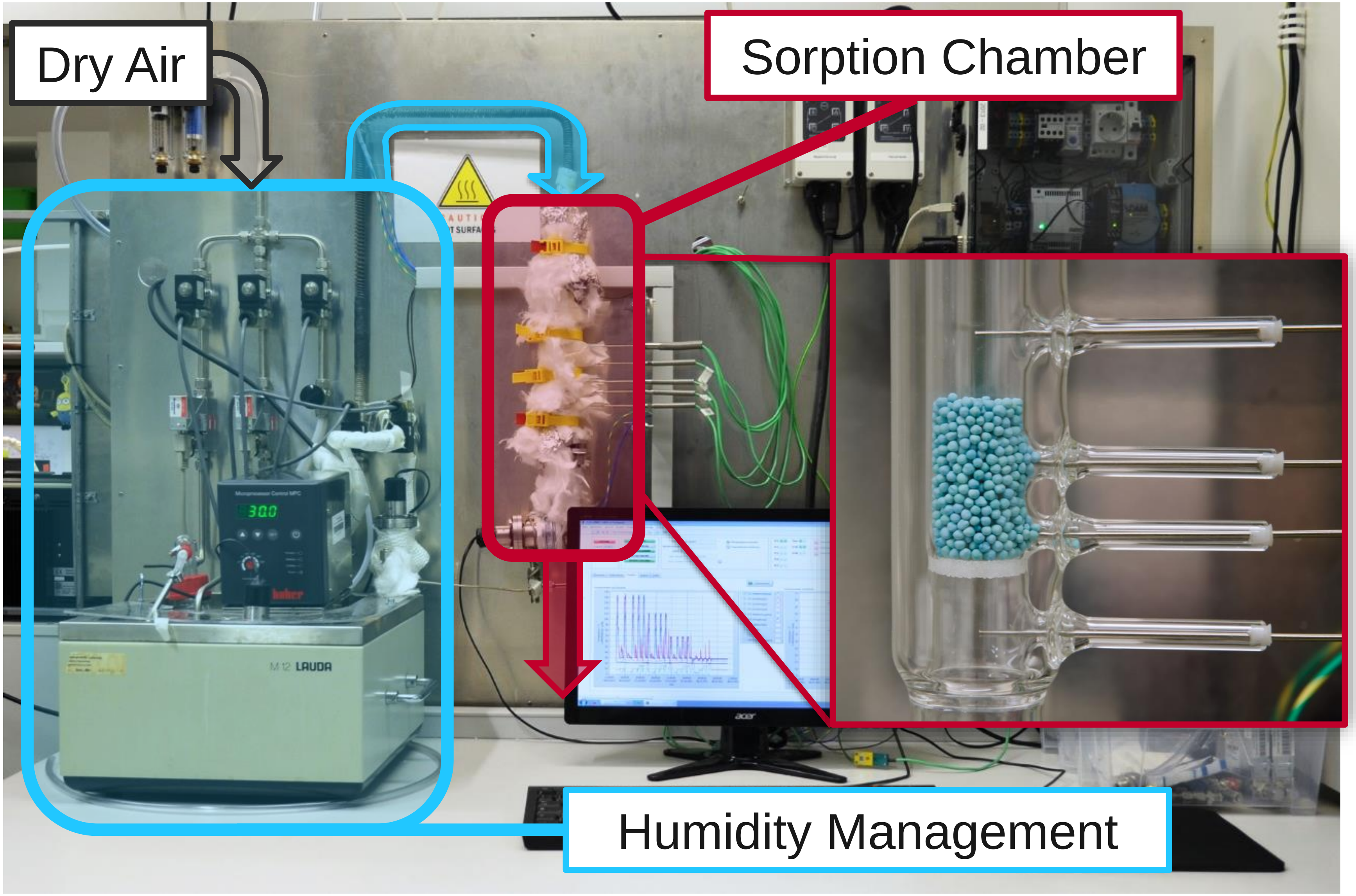
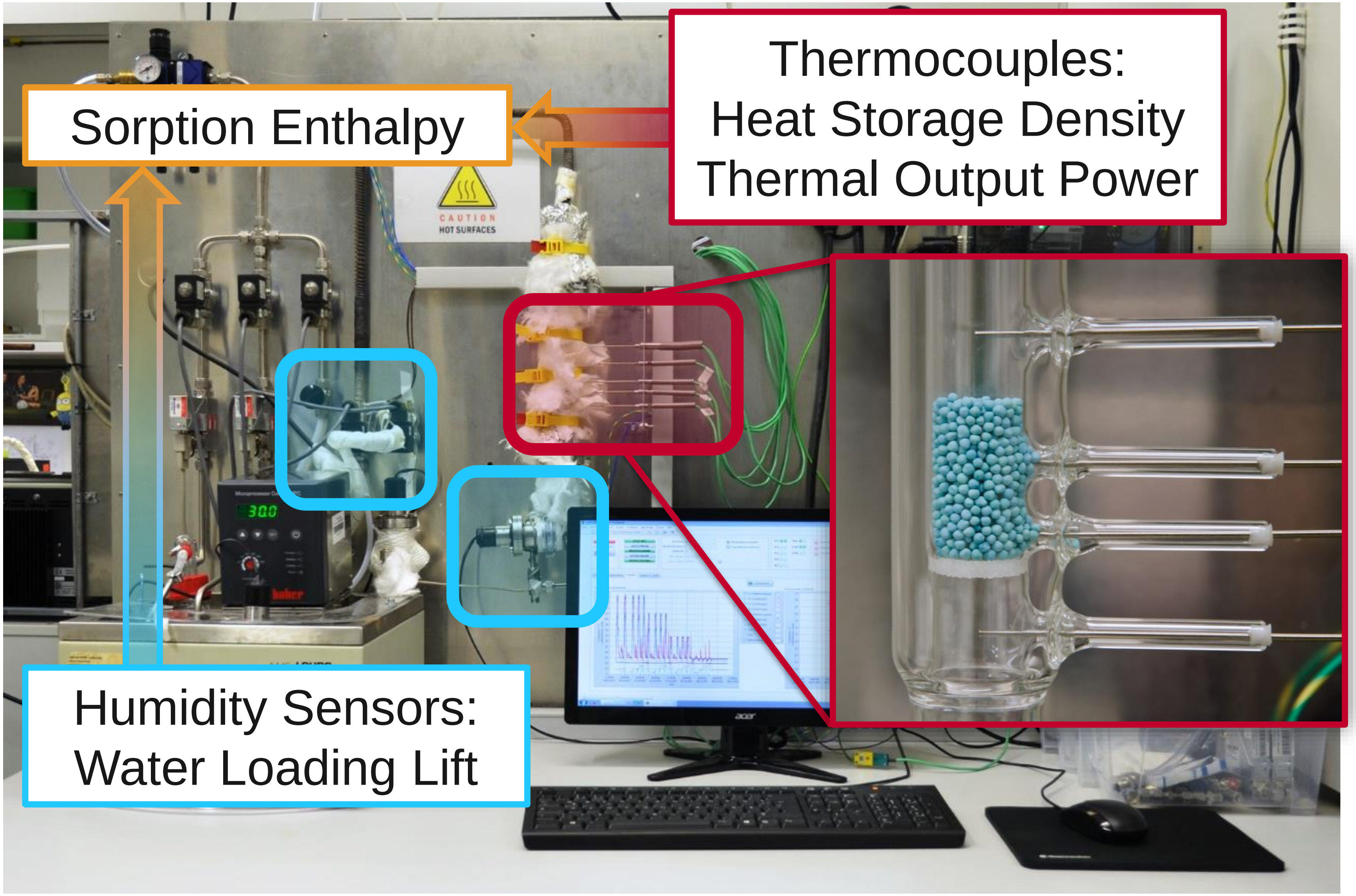
# Thermochemical Characterization I



# Thermochemical Characterization II

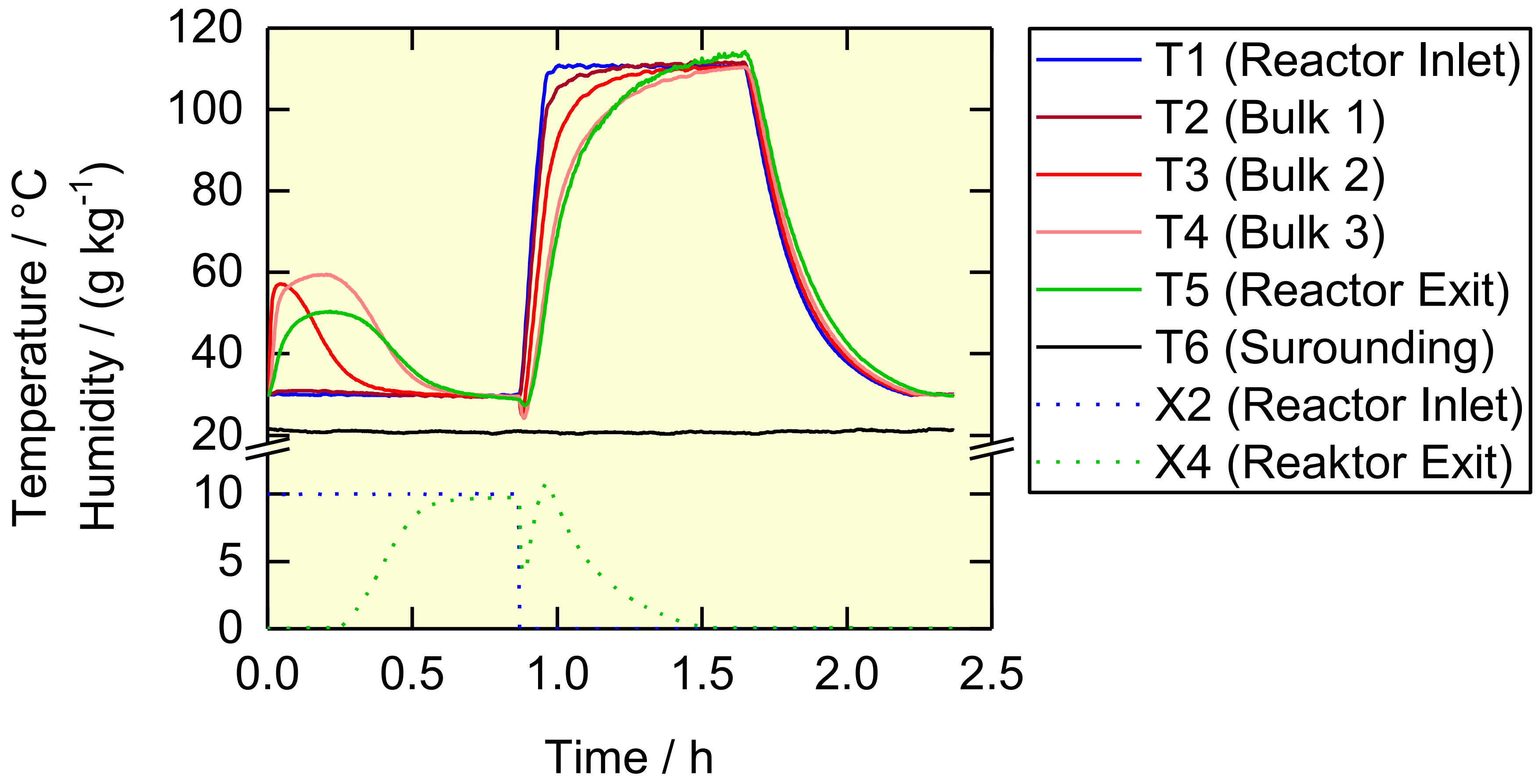


# Operating Conditions and Measurement Uncertainty

- 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

| Parameter | Measurement Uncertainty / % |
|---|---|
| Water Loading Lift | 6 |
| Heat Storage Density | 7 |
| Water Sorption Enthalpy | 5 |
| Thermal Output Power | 5-10 |

# Typical Cycling Profile



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# Thermochemical Heat Storage with Salt/Zeolite Composites

**Literature**

**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


**Present Work**

**Salt/Zeolite Composites**
FAU + $MgSO_4$, $CaCl_2$, LiCl
Variation of Salt Loading

**Relation**
of Thermochemical and
Material Properties

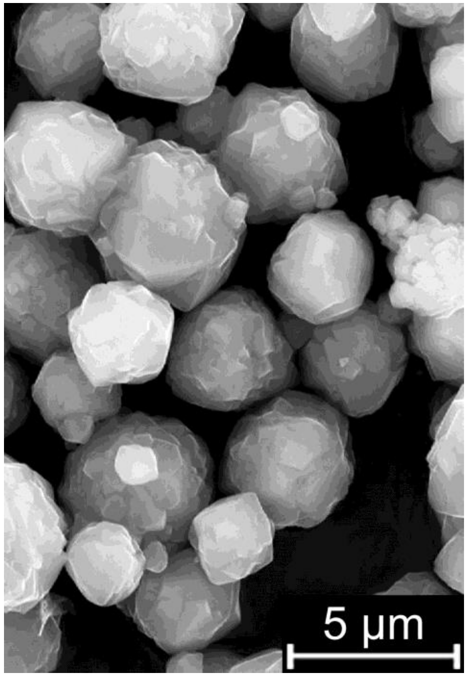
**Characterization**
Structural, Textural Properties
(XRD, SEM, $N_2$ Sorption, Hg Intrusion)

**Thermochemical Properties**
Conditions Close to Application
Variation of Sorption Humidity

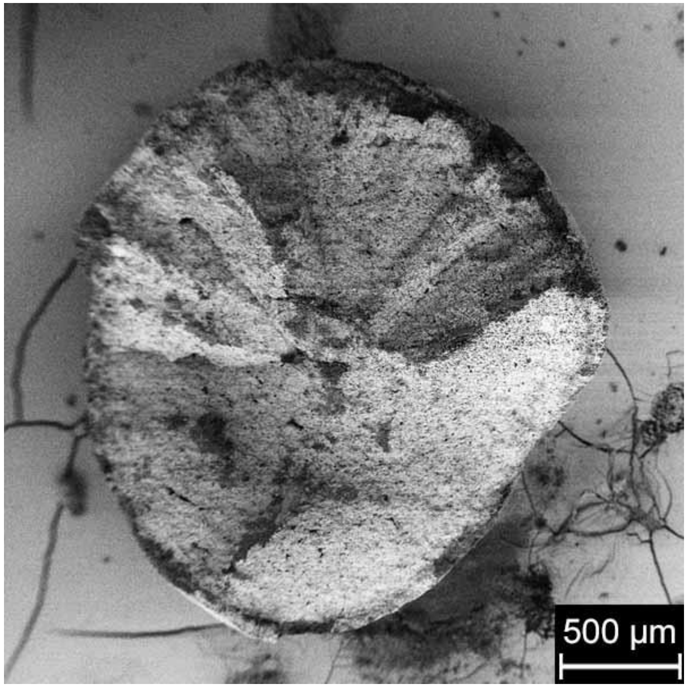
S. Hongois, F. Kuznik, P. Stevens, J.J. Roux, Sol. Energy Mater. Sol. Cells 95 (2011) 1831-1837.
G.T. Whiting, D. Grondin, D. Stosic, S. Bennici, A. Auroux, Sol. Energy Mater. Sol. Cells 128 (2014) 289-295.
G. Whiting, D. Grondin, S. Bennici, A. Auroux, Sol. Energy Mater. Sol. Cells 112 (2013) 112-119.

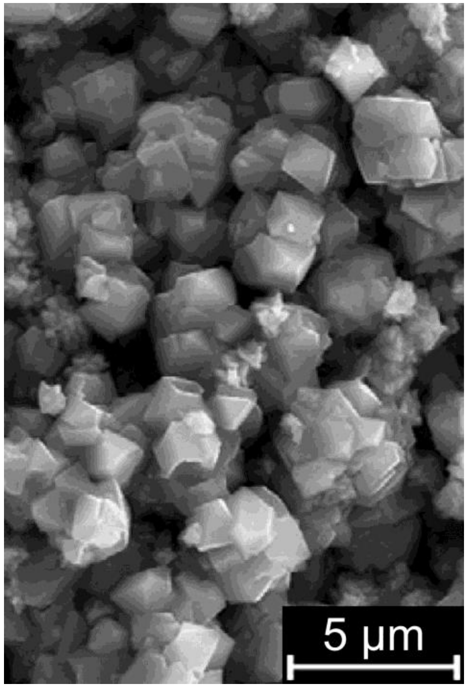
# Binderless Zeolite Granulates

## Zeolite Powder




## Zeolite Granulate

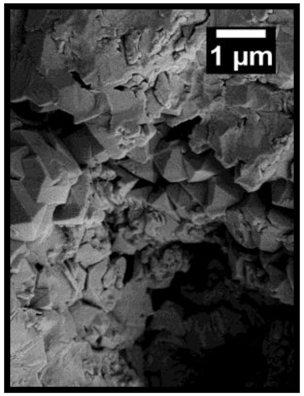


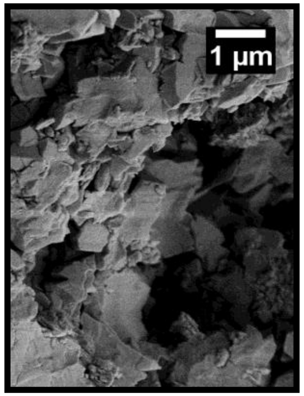

K. Schumann, B. Unger, A. Brandt, F. Scheffler, Micropor. Mesopor. Mats. 154 (2012) 119-123.

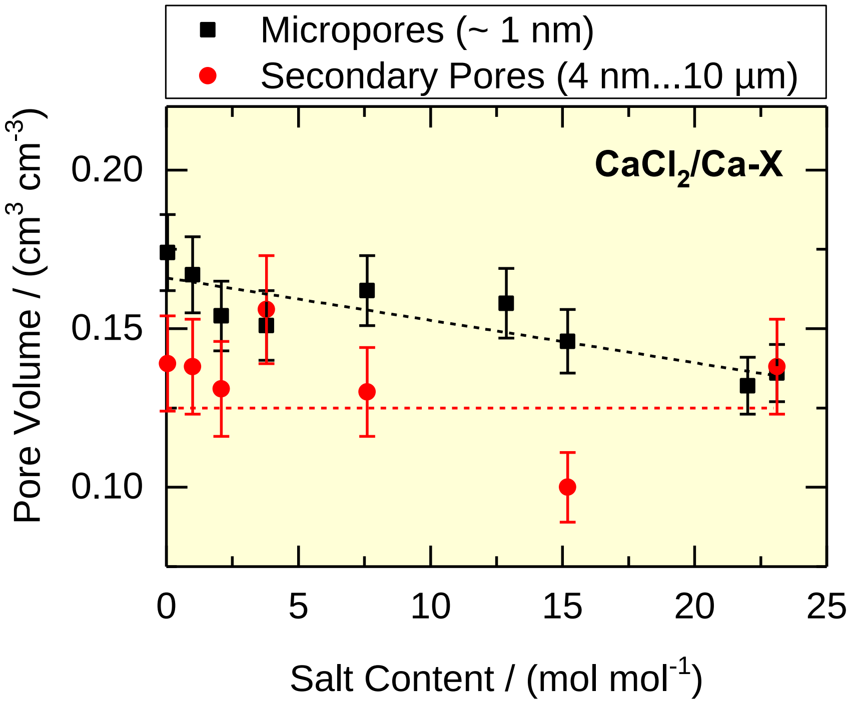
# $CaCl_2$ and $MgSO_4$ Composites: SEM

Ca-X

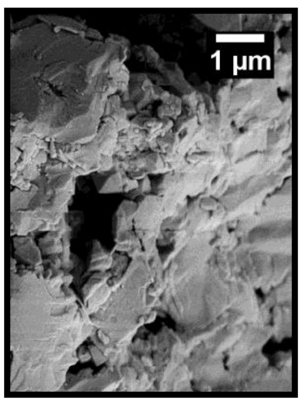



23$CaCl_2$/Ca-X

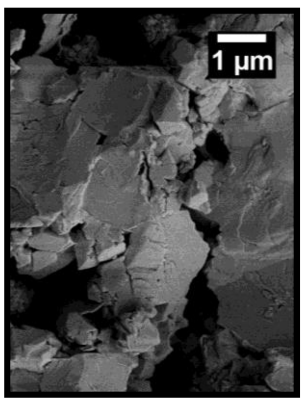


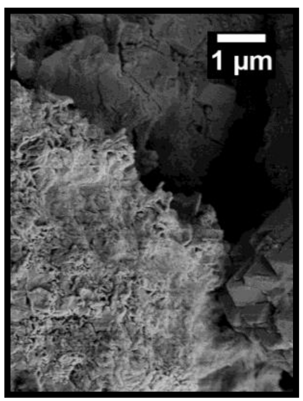

Mg-X

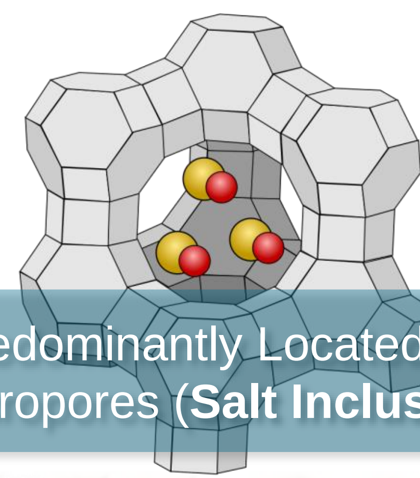



14$MgSO_4$/Mg-X




24$MgSO_4$/Mg-X

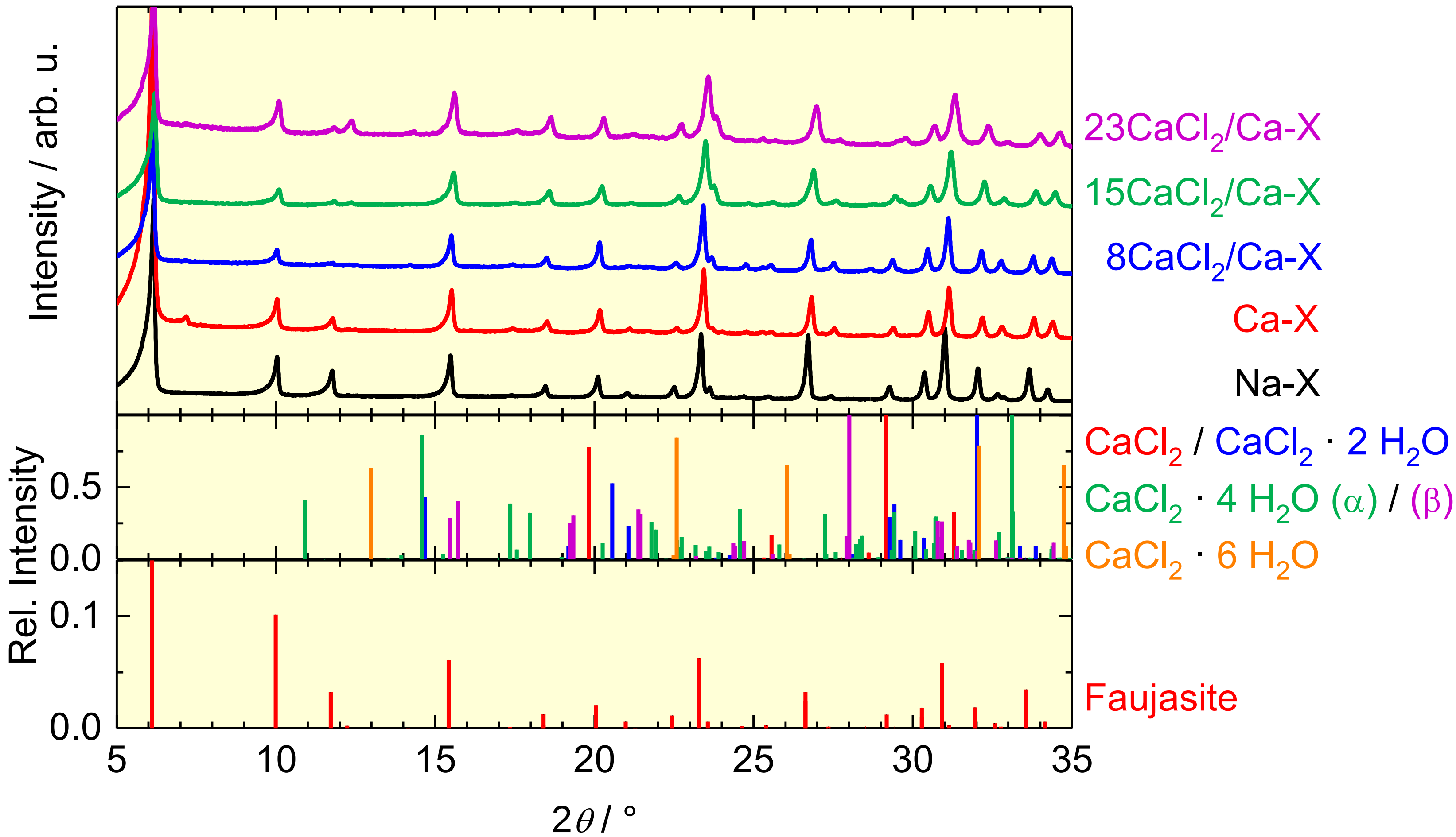


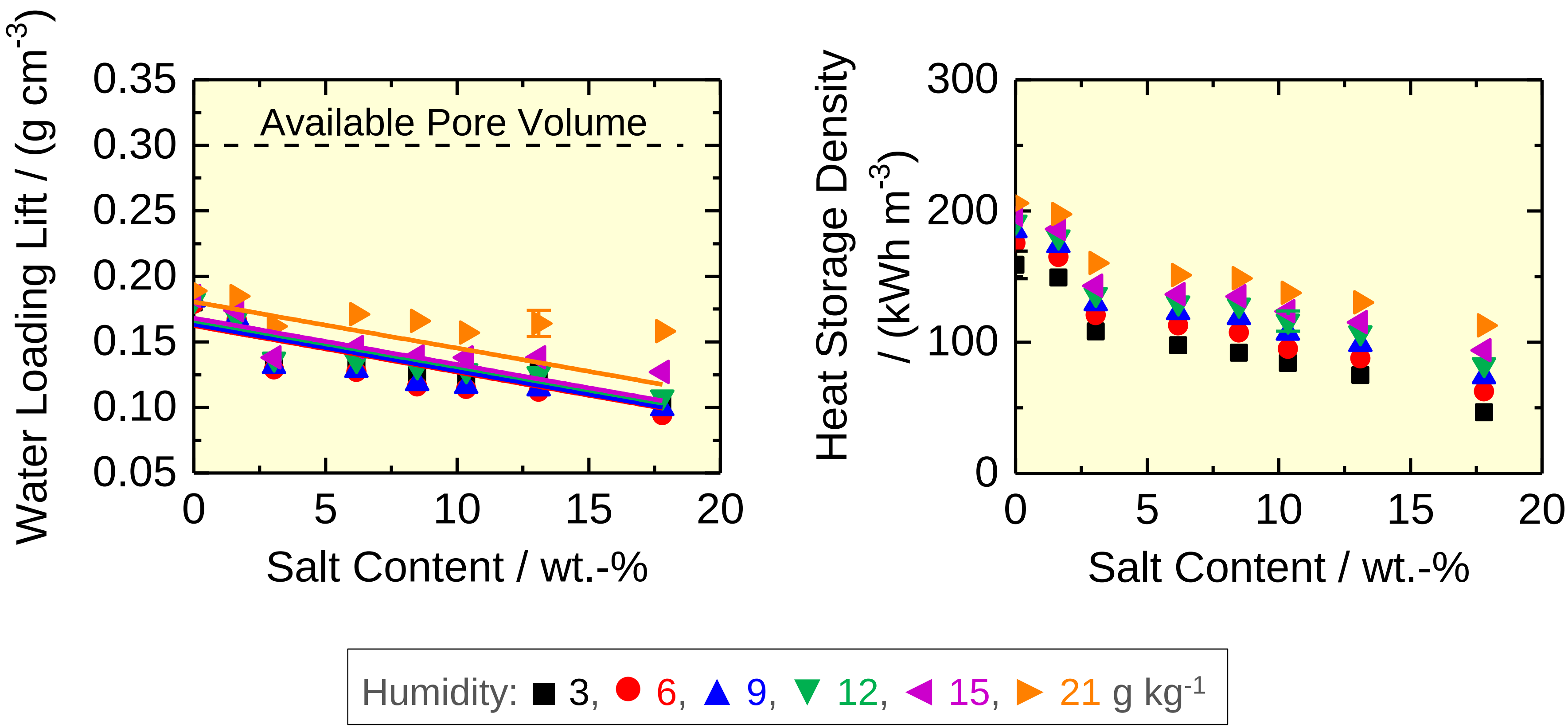
Salt is Predominantly Located Inside the Micropores (**Salt Inclusion**)

https://upload.wikimedia.org/wikipedia/commons/5/5f/Faujasite_structure_labeled_German.svg.
R.M. Barrer, W.M. Meier, J. Chem. Soc. (1958) 299-304.
R.M. Barrer, A.J. Walker, Trans. Faraday Soc. 60 (1964) 171-184.

# $CaCl_2$ Composites: XRD

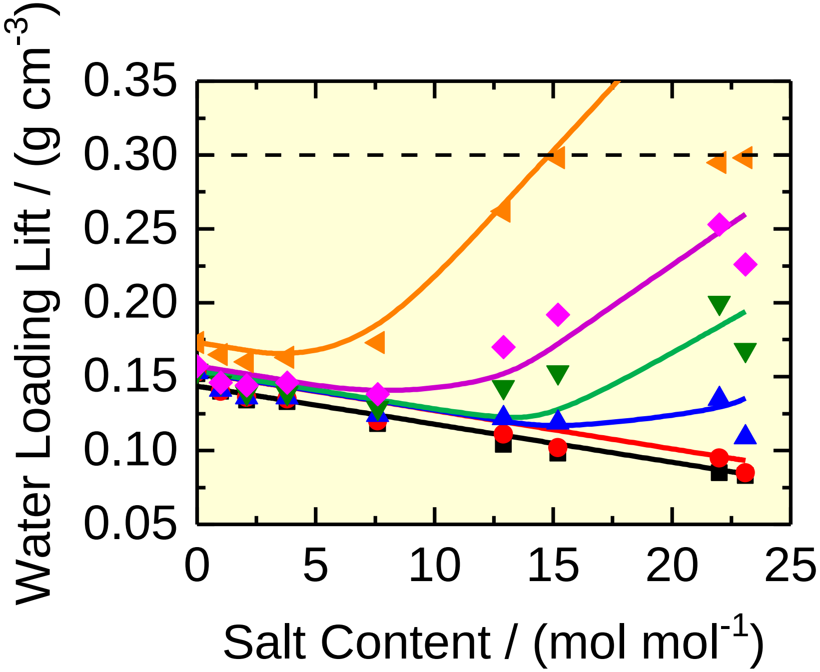


# Thermochemical Properties ($MgSO_4$/Mg-X Composites)




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

# Thermochemical Properties ($CaCl_2$/Ca-X Composites)

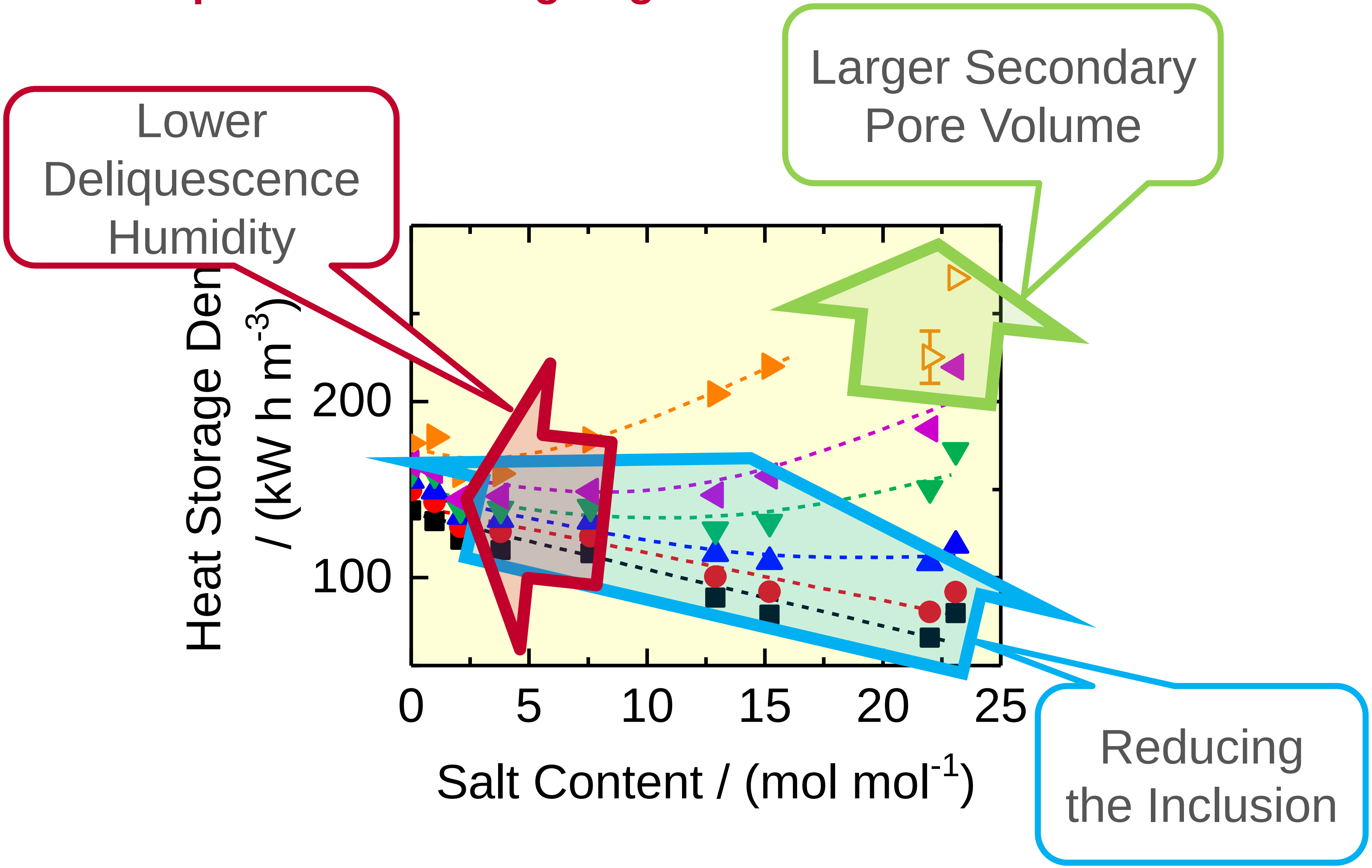




Humidity: ■ 3, ● 6, ▲ 9, ▼ 12, ◀ 15, ▶ 21 g $kg^{-1}$

- 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

# Further Improvements: Ongoing Work



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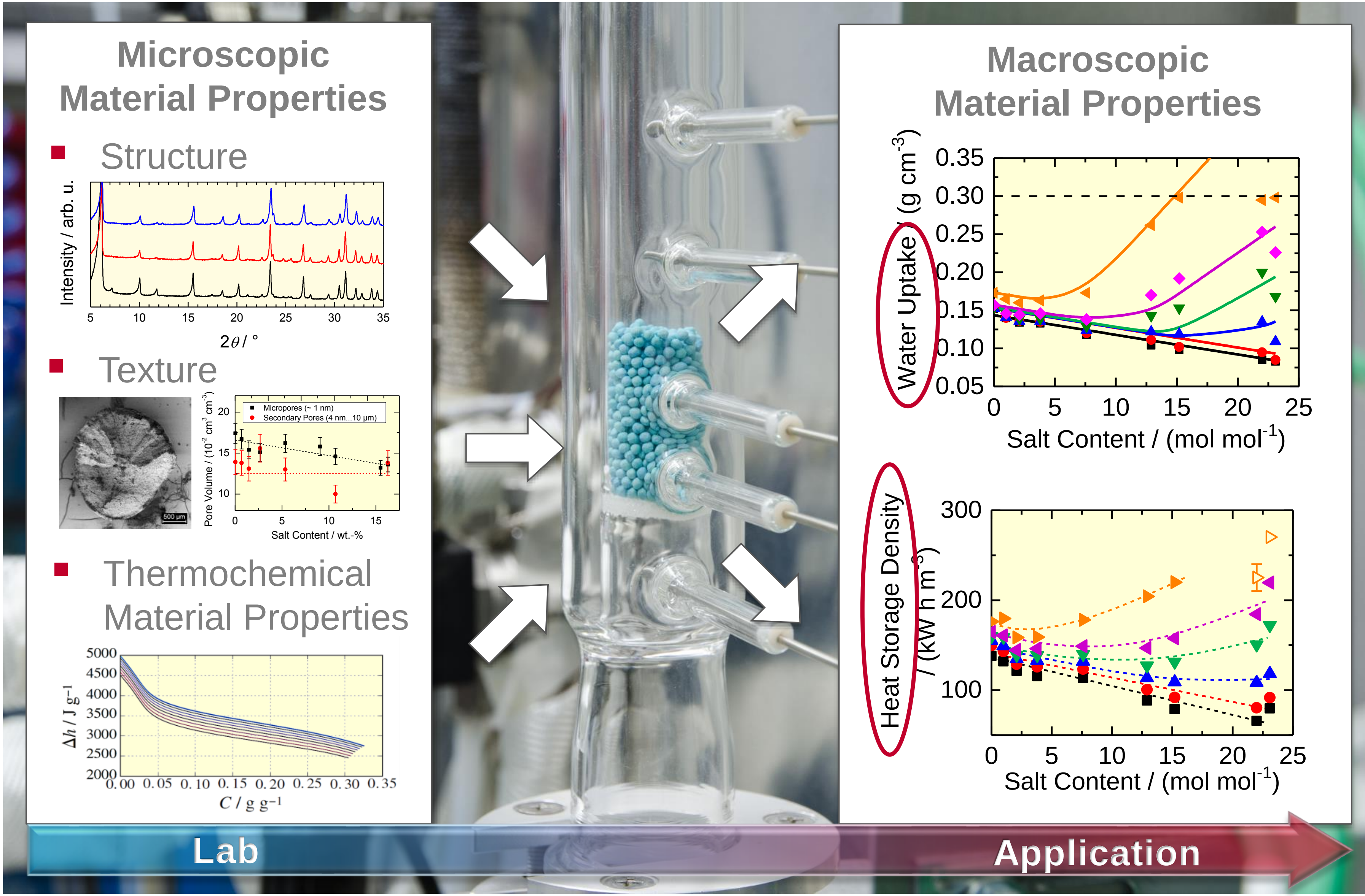
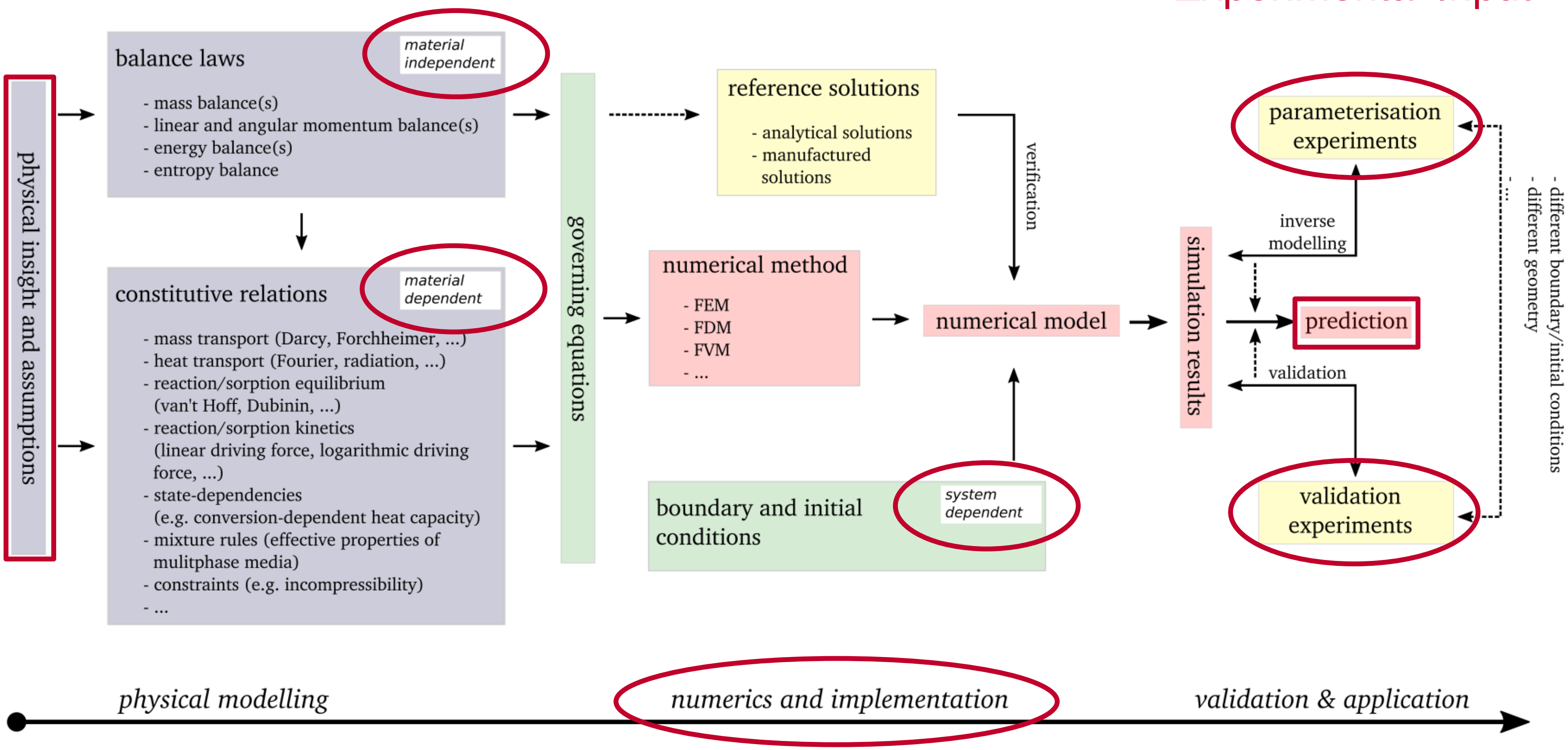
# Experimentalist's View



# General Aspects of Numerical Modelling

Experimental Input




**OpenGeoSys:** Open Source Simulation Software for Multi-Physical Modelling

T. Nagel, S. Beckert, C. Lehmann, R. Gläser, O. Kolditz, Appl. Energy 178 (2016) 323-345; H. Shao, T. Nagel, C. Roßkopf, M. Linder, A. Wörner, O. Kolditz, Energy 60 (2013) 271-282; T. Nagel, H. Shao, A.K. Singh, N. Watanabe, C. Roßkopf, M. Linder, A. Wörner, O. Kolditz, Energy 60 (2013) 254-270.

# Dubinin-Polanyi Theory

- Adsorption Potential:

$$A_m = \frac{R}{M_{\mathrm{Ads}}} T \ln \frac{p_s}{p}$$

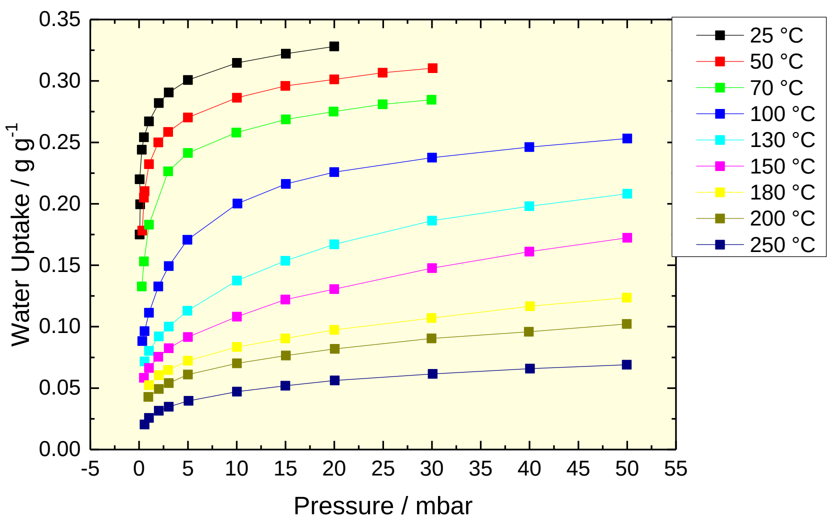
Output          Experimental Input

- Adsorbed Volume:

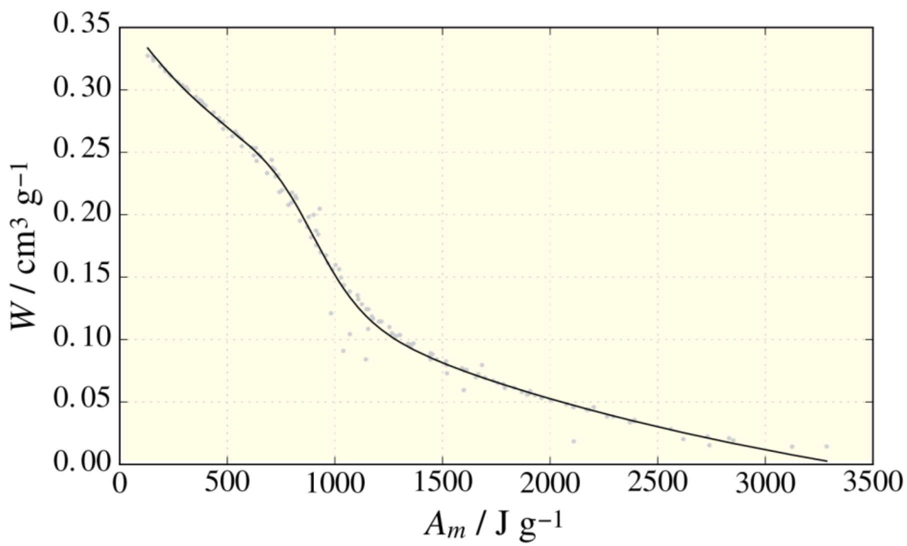
$$W(A_m) = \frac{C_{\mathrm{eq}}(T)}{\rho_{\mathrm{Ads}}(T)}$$

Density Model

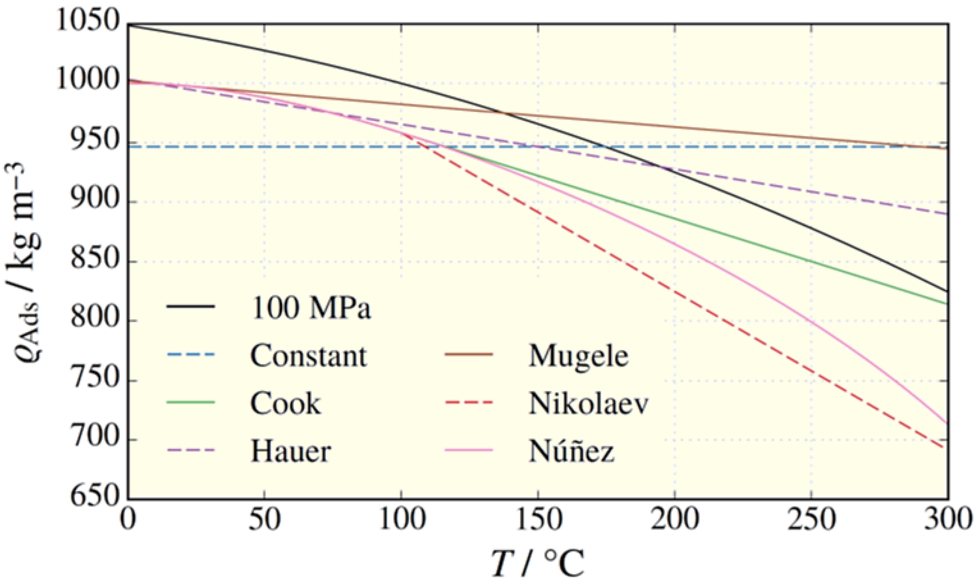
Water Sorption Isotherm




Characteristic Curve



# Adsorbate Density Models (I)



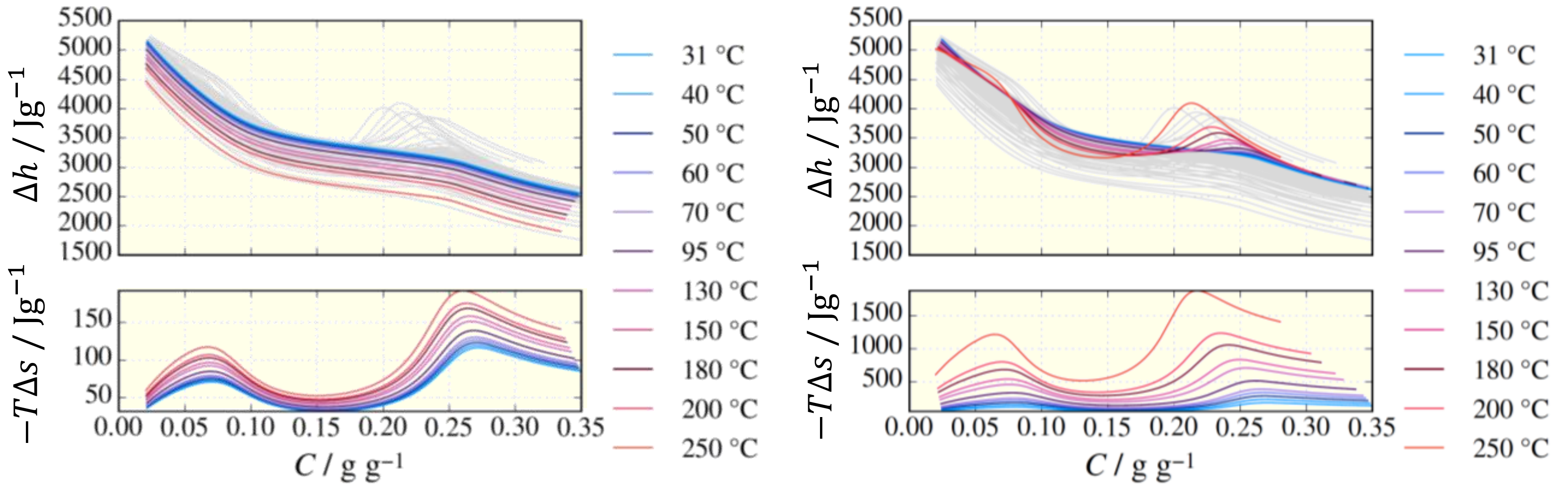

Adsorbate density models used in the literature.

| References | Adsorbate density | |
|---|---|---|
| Núñez [16] | Free liquid over entire temperature range | |
| Nikolaev and Dubinin [18] | $\varrho_{\mathrm{Ads}}(T) = \begin{cases} \text{free liquid} & T \leqslant T_0 \\ \varrho_{\mathrm{Ads}}(T_0) - \frac{\varrho_{\mathrm{Ads}}(T_0) - M/b}{T_c - T_0}(T - T_0) & T > T_0 \end{cases}$ | (4) |
| | with $T_0 = 373.15$ K (boiling point of water) | |
| Cook and Basmadjian [19] | $\varrho_{\mathrm{Ads}}(T) = \begin{cases} \text{free liquid} & T \leqslant T_0 \\ \varrho_{\mathrm{Ads}}(T_0)[1 - \alpha_{T,\mathrm{Ads}}(T_0)(T - T_0)] & T > T_0 \end{cases}$ | (5) |
| | with $T_0 = 373.15$ K (boiling point of water) | |
| Mugele [15] | $\varrho_{\mathrm{Ads}}(T) = \frac{\varrho_{\mathrm{Ads}}(T_0)}{1 + \alpha_{T,\mathrm{Ads}}(T_0)[T - T_0]}$ | (6) |
| | with $T_0 = 293.15$ K (room temperature) | |
| Hauer [14] | $\varrho_{\mathrm{Ads}}(T) = \varrho_{\mathrm{Ads}}(T_0)[1 - 3.781 \cdot 10^{-4}\ \mathrm{K}^{-1} \cdot (T - T_0)]$ | (7) |
| | with $T_0 = 283.15$ K | |

T. Nagel, S. Beckert, N. Böttcher, R. Gläser, O. Kolditz, Energy Procedia 75 (2015) 2106-2112, C. Lehmann, S. Beckert, R. Gläser, O. Kolditz, T. Nagel, Appl. Energy (2015) DOI: 10.1016/j.apenergy.2015.10.126.

# Adsorbate Density Models (II)

$$\Delta h = \Delta h^{v} + A_m - T\Delta s$$




(a) Mugele [14]  (b) Núñez [15]

- Desorption:
  $T$ = 180 ºC
  $p_W$ = 0 mbar

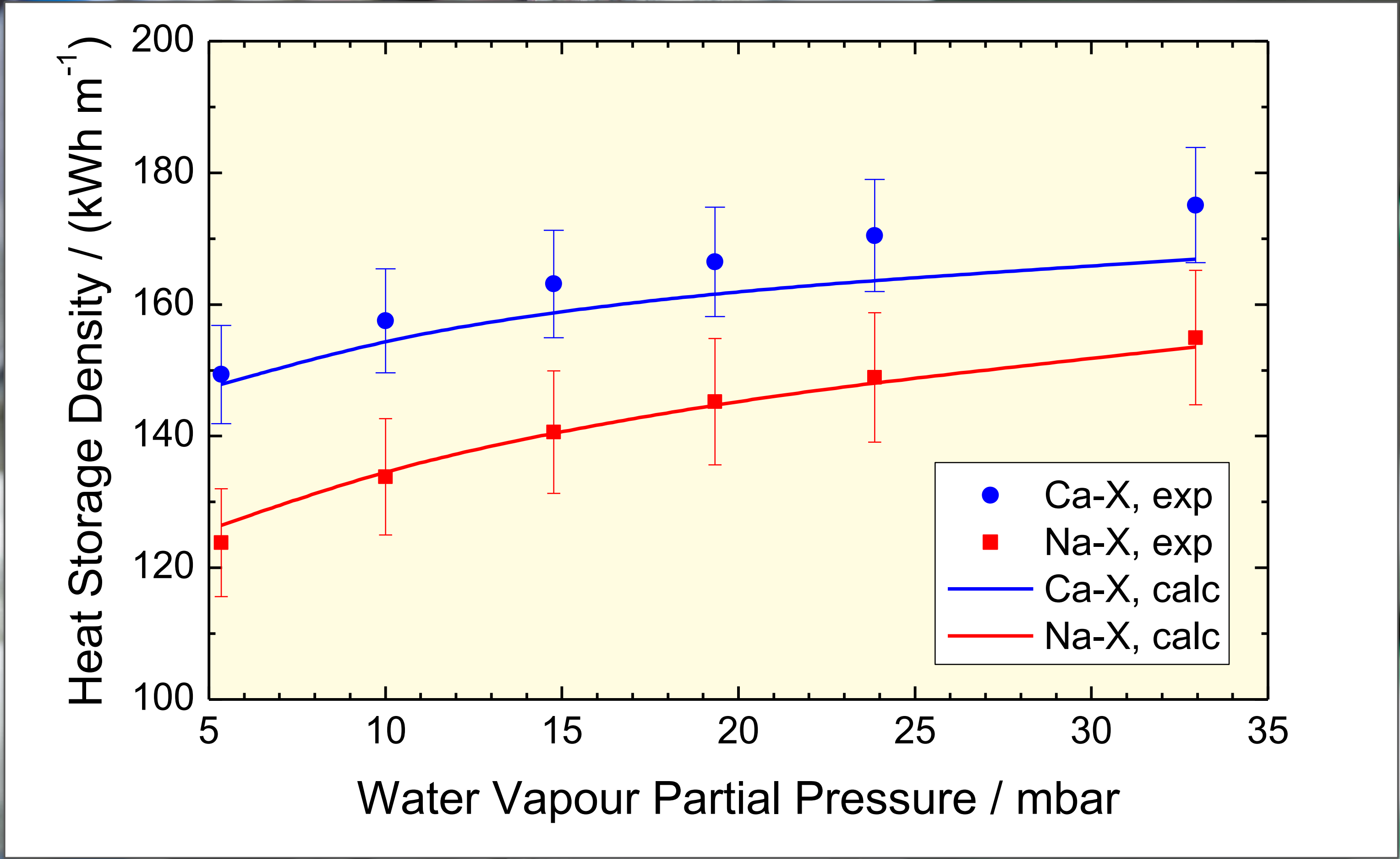
- Adsorption:
  $T$ = 20 ºC
  $p_W$ = 10 mbar

| Adsorbate density model | Storage density | |
|---|---|---|
| | kW h $m^{-3}$ | % |
| Constant | 153.5 | 95.7 |
| Mugele [15] | 158.0 | 98.5 |
| Cook [19] | 160.8 | 100.2 |
| Núñez [16] | 161.3 | 100.5 |
| Hauer [14] | 162.2 | 101.1 |
| Nikolaev [18] | 163.6 | 101.9 |
| 100 MPa [22] | 163.8 | 102.1 |
| Mean | 160.5 | 100.0 |

# Heat Storage Density – Numerical Modelling vs. Experiment

Desorption: $T$ = 110 ºC, $p_W$ = 0.2 mbar

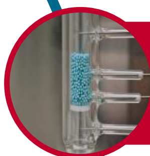
Adsorption: $T$ = 30 ºC, $p_W$ = 5.5 … 33 mbar




C. Lehmann, S. Beckert, T. Nonnen, J. Möllmer, R. Gläser, O. Kolditz, T. Nagel, accepted for publication in Energy Procedia (2017)

# Outline


Thermochemical Heat Storage


Experimental Setup


Salt/Zeolite Composites


Numerical Modelling


Conclusion and Outlook

# Salt/Zeolite Composites: Conclusions and Outlook

**Ion Exchange**
Necessary Prior Impregnation

**Salt Inclusion**
*Below* Deliquescence Humidity
*Lower* Heat Storage Density

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


## Conclusions

## Outlook

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

**Regulation Strategies**
Need to be Adapted to
Material Properties

**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

Gefördert durch:

Bundesministerium
für Wirtschaft
und Energie

aufgrund eines Beschlusses
des Deutschen Bundestages

PtJ Projektträger Jülich
Forschungszentrum Jülich

ENERGIESPEICHER
Forschungsinitiative der Bundesregierung

UNIVERSITÄT LEIPZIG

A TRADITION OF
CROSSING BOUNDARIES

CWK BAD KÖSTRITZ

Vaillant

itw

EnErChem (FKZ: 03ESP402)

# Thank You for Your Attention