EXPERIMENTAL APPROACHES TO ANALYSE THERMOPHYSICAL PROPERTIES OF THERMOCHEMICAL HEAT STORAGE MATERIALS

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OVERVIEW

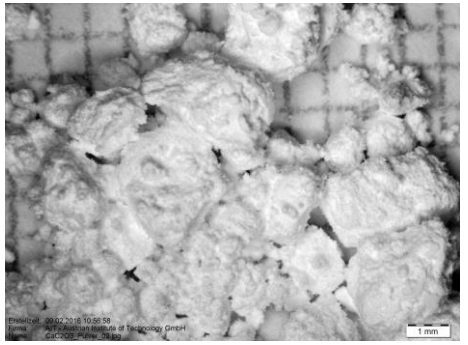
- Thermochemical Heat Storage – principle, requirements and materials
- SolidHeat Projects – objectives, partners and methods
- Experiments @ AIT
  - Preliminary STA experiments for further thermophysical characterisations
  - DSC experiments for apparent $c_p(T)$ measurements
  - THB experiments of powdery and liquid samples
  - LFA experiments on compacted, powdery and liquid samples
    - Liquid measurements and simulation
    - Powdery samples in 3 layer model
- Conclusion and Outlook

THERMOCHEMICAL ENERGY STORAGE - TCES

Principle

- Utilisation of the enthalpy of reversible chemical reactions or sorption effects
- Heat storage is charged as long as both reaction partners are separated and discharged when they are brought together

$$A(s,l) + B(g) \leftrightarrow AB(s,l)$$

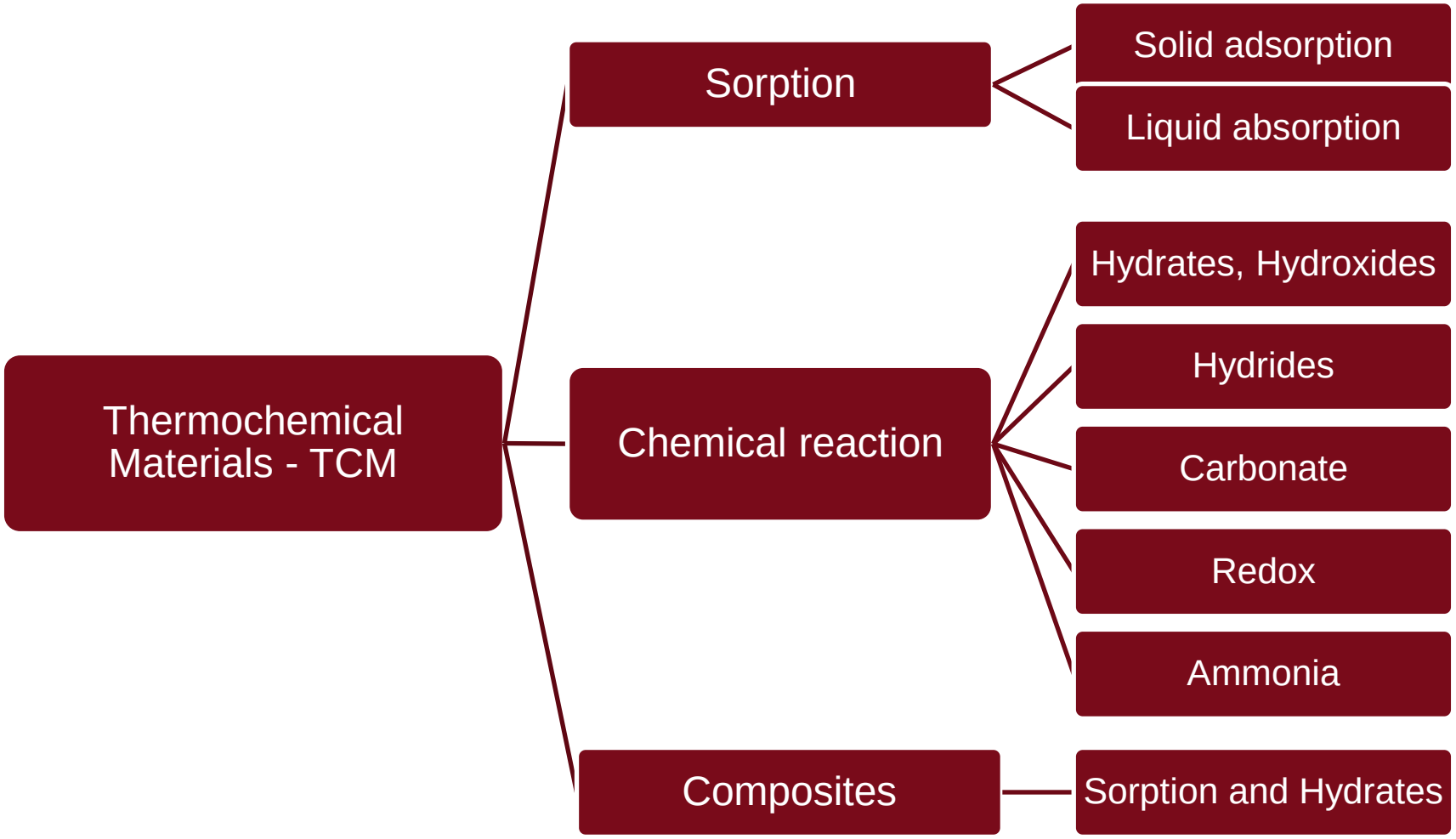


- Mainly in powder form but also liquids
- No heat loss to the environment in comparison to sensible and latent heat storage – no thermal insulation necessary

Requirements

- High energy density, reversible without side reactions, fast reaction rates (kinetics), easy to handle, economic

THERMOCHEMICAL MATERIALS FOR HEAT STORAGE APPLICATIONS - TCM



SOLIDHEAT PROJECTS

Project objectives

- Identify promising materials and reactions for TCES
- Characterization of physical and chemical properties
- http://solidheat.project.tuwien.ac.at/

Project Partners

- TU Wien institutes: Energy systems and thermodynamics, Applied Synthetic Chemistry, Chemical Engineering, Chemical Technologies and Analytics
- Academy of fine arts (XRF)
- Austrian Institute of Technology AIT

Methods

- STA (TGA-DSC), DSC, LFA, THB, XRD, XRF, FTIR, BET

Dissemination:

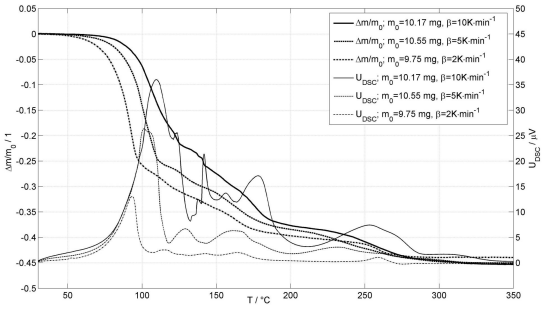
- Systematic search algorithm for potential thermochemical energy storage systems

- High temperature energy storage: Kinetic investigations of the CuO/Cu2O reaction cycle

TU WIEN SolidHeat
Thermochemical energy storage research consortium

EXPERIMENTS @ AIT

STA result



Measured quantities

Mass change and reaction enthalpies ΔH_r

- STA and TGA experiments

- Apparent specific heat capacity app. $c_p(T)$
  - hf-DSC experiments
- Effective thermal diffusivity and conductivity $a_{eff}(T)$, $\lambda_{eff}(T)$
  - LFA and THB experiments

DSC sensor

THB Sensor in compacted powder

LFA samples with peeled of graphite coating

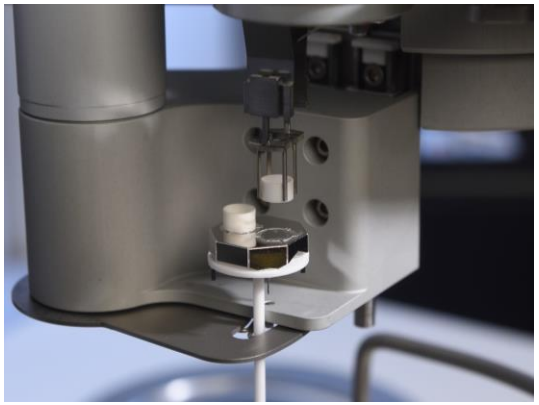
LFA sample with sputtered Au coating

LFA liquid sample holder

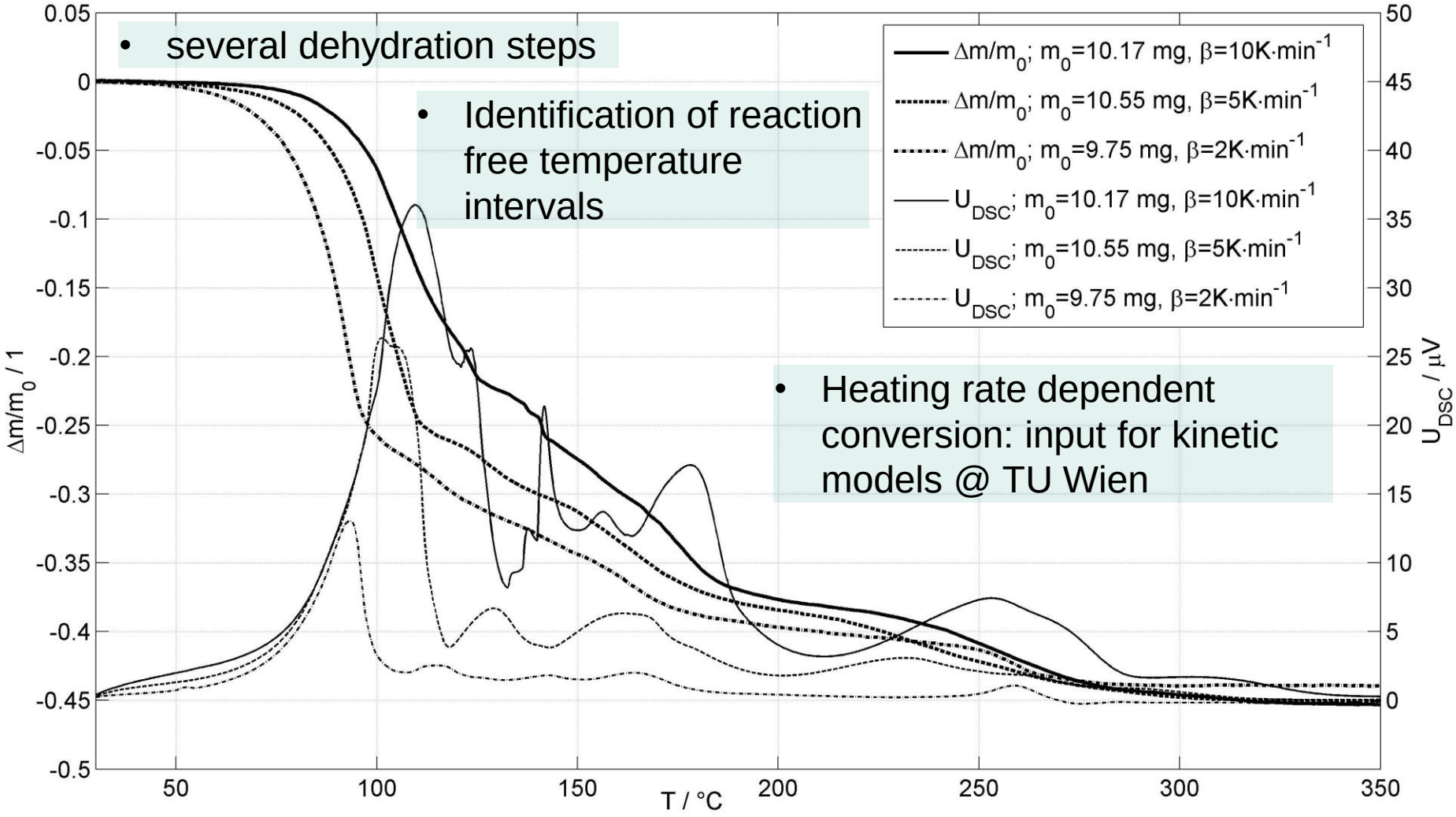
PRELIMINARY STA EXPERIMENTS

Preliminary STA experiments were conducted to identify:

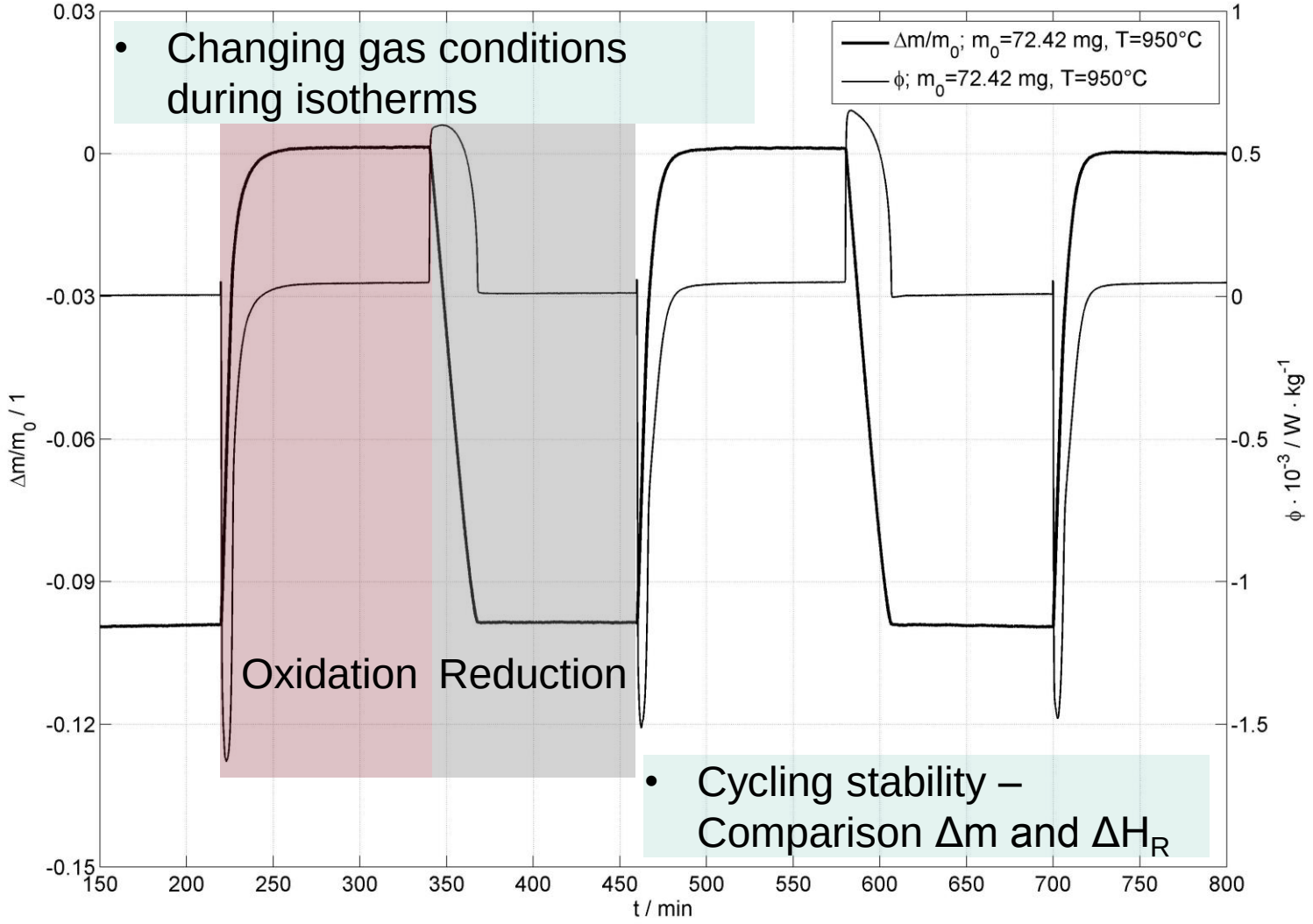
- Reaction free temperature intervals, educt or product exists at a certain temperature range
- Reaction rate of the measured conversion related to sample mass and applied heating rate
- Reaction enthalpies
- Cycling experiments for repeatability tests
- not expected results: degradation, phase transitions, etc.



SALT HYDRATE DEHYDRATION STA EXPERIMENT



METAL OXIDE REDOX CYCLING IN STA



DSC EXPERIMENTS

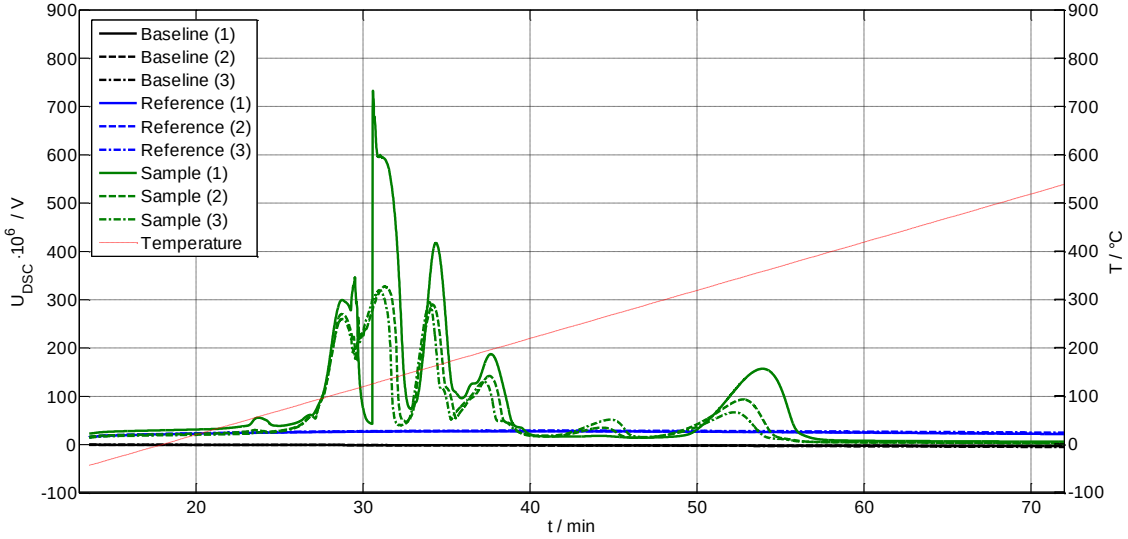
- Pure hf-DSC experiments in the identified reaction free temperature intervals
- Direction: AB(s,l) → A(s,l) + B(g)
- Measurement of educt and product in two consecutive cycles to avoid reaction with ambient gas conditions
- Sample form: compacted and loose powder
- Mass correction according preliminary STA results
- Repeatability tests by measuring at least 3 samples
- Measurement uncertainty evaluation based on GUM [1]

loose powder

compacted sample

[1] Guide to the expression of uncertainty in measurement - JCGM 100:2008 (GUM 1995 with minor corrections - Evaluation of measurement data)

SALT HYDRATE EXPERIMENT

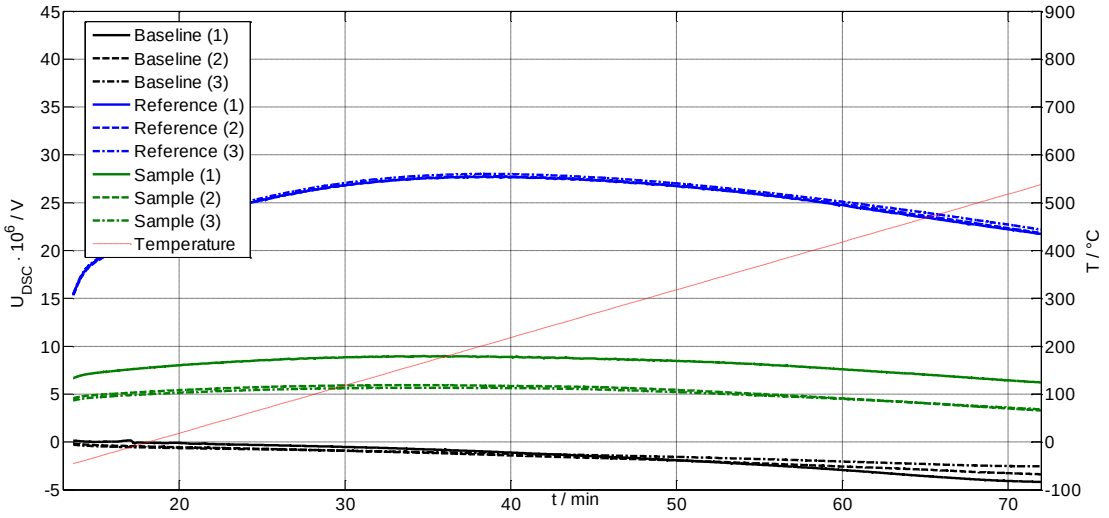


1st run

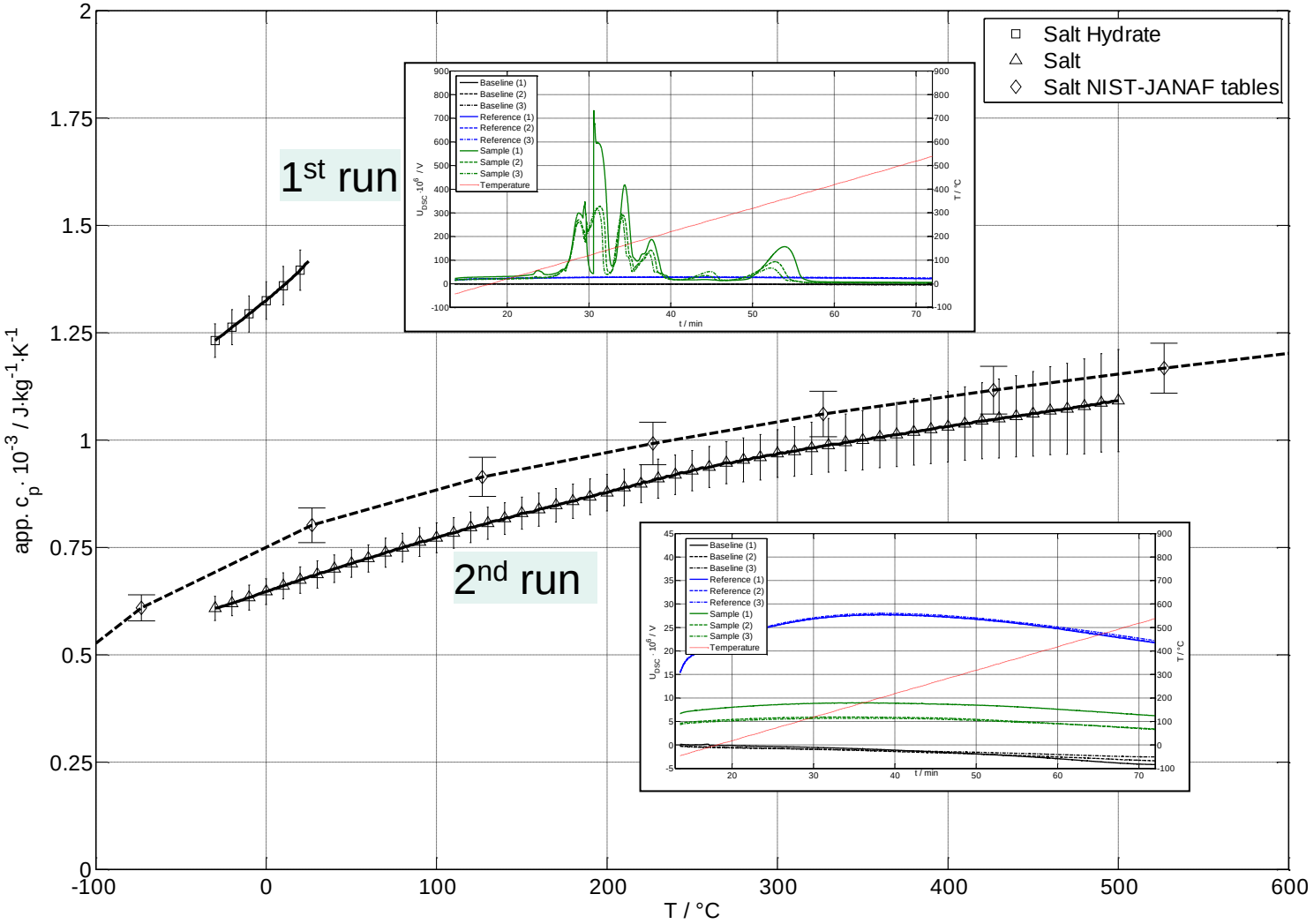
- Dehydrating the salt hydrate in the DSC (pierced lid Al crucibles)
- Cooling back to T_{start} using dry inert gas conditions

2nd run

- Measuring the pure salt using under the same experiment conditions
- Mass correction according the STA results



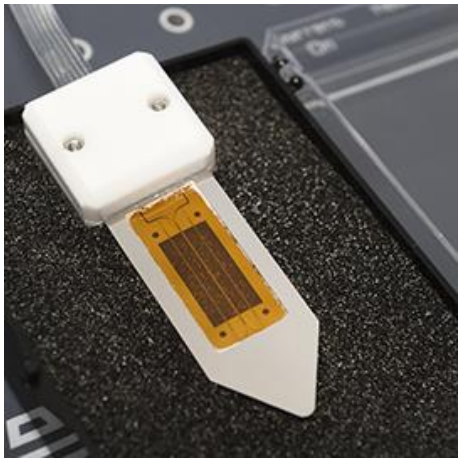
APPARENT SPECIFIC HEAT CAPACITY ANALYSIS



THB EXPERIMENTS

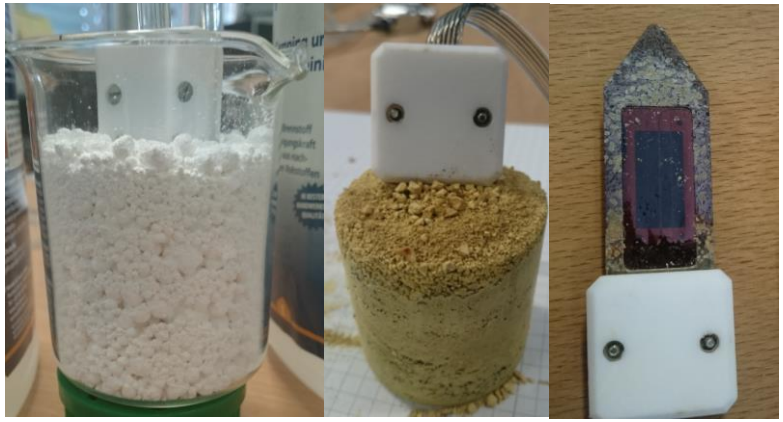
- Transient Hot Bridge Sensor with metal frame
- Sample form: powder & liquid
- Quantity: Thermal conductivity
- Lab oven with ambient gas conditions
- Temperature range 25 – 200°C (sensor limit)
- THB experiments direction:
  - AB(s,l) → A(s,l) + B(g) or direct A(s,l)

THB sensor



Calibration

Powder measurements

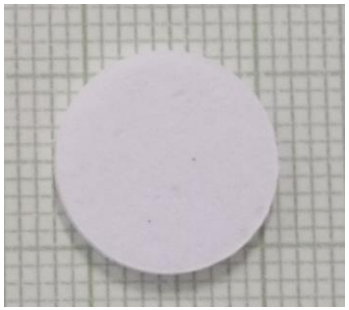


Lab oven

LFA EXPERIMENTS

- Light and Laser Flash
- Sample form: compacted solid, coated solid, liquid and powder containment powdery
- LFA experiments direction:
  - AB(s,l) → A(s,l) + B(g) or direct A(s,l)
- Repeatability tests by measuring at least 3 samples
- Measurement uncertainty evaluation based on GUM [1]

compacted cylinder

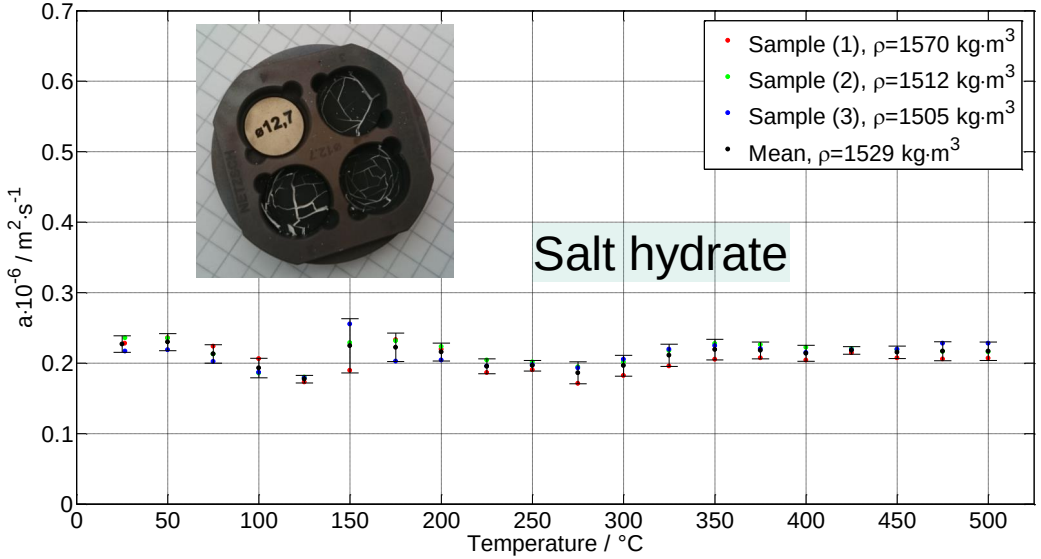


coated sample

liquid sample holder

powder sample holder

LFA RESULTS SALT HYDRATE

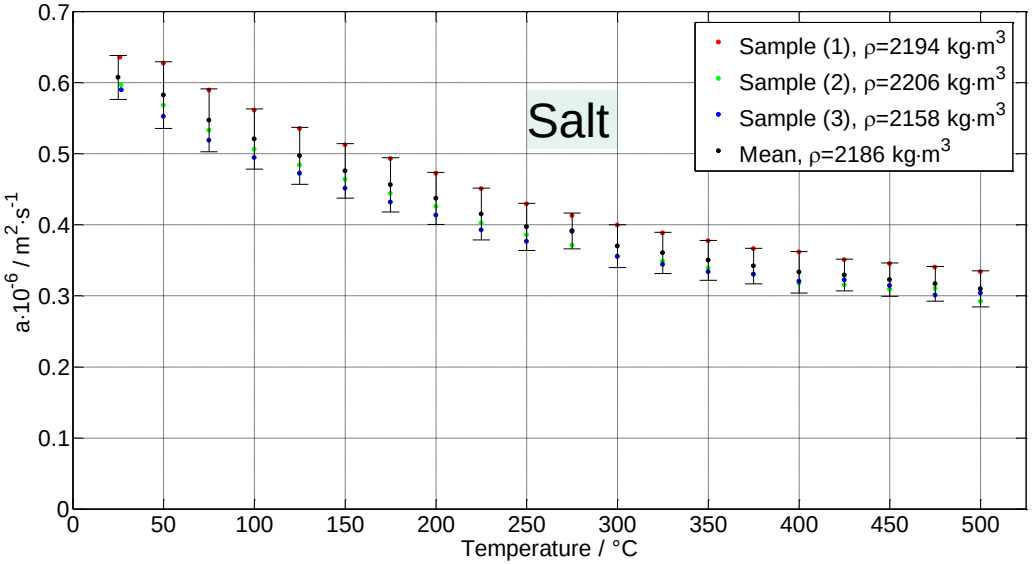


Starting from the hydrated salt

- Dehydrating destructs the compacted sample and the coating
- Thickness is changing
- Data usable before dehydrating reaction

Starting from the dehydrated salt

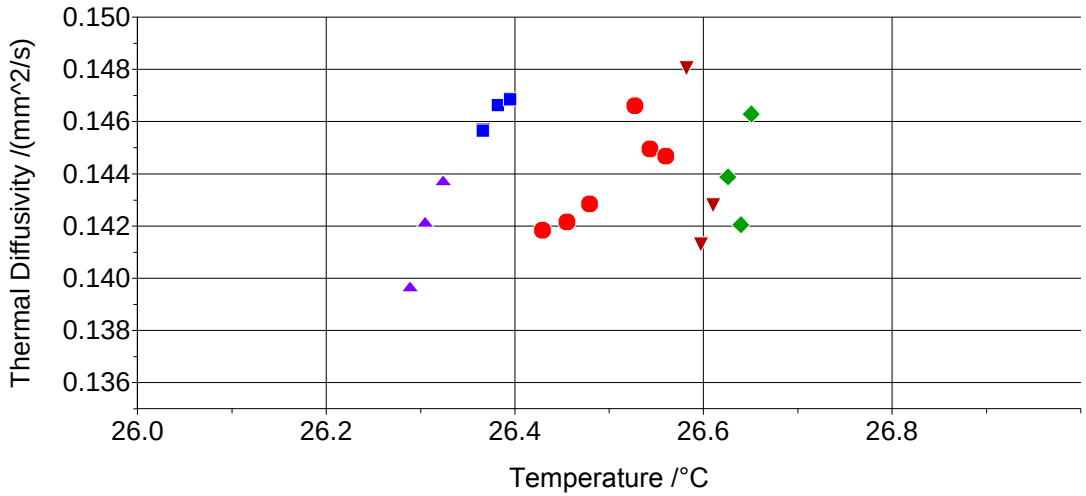
- Higher initial density
- Compact sample survives the measurement
- Data usable over whole measurement range



LFA EXPERIMENTS LIQUIDS

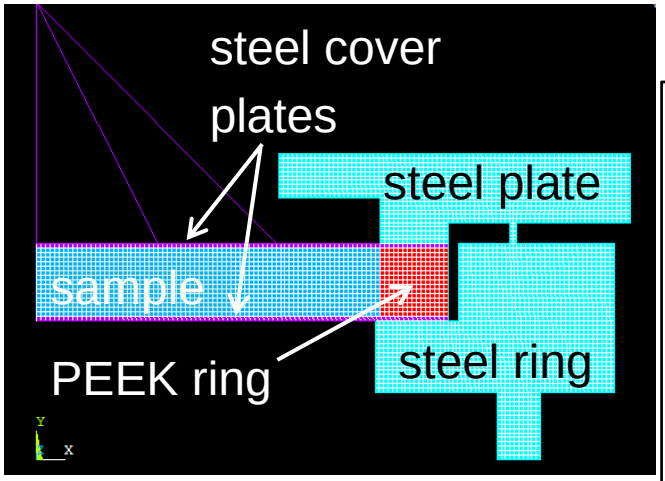
closed 3-layer sample holder

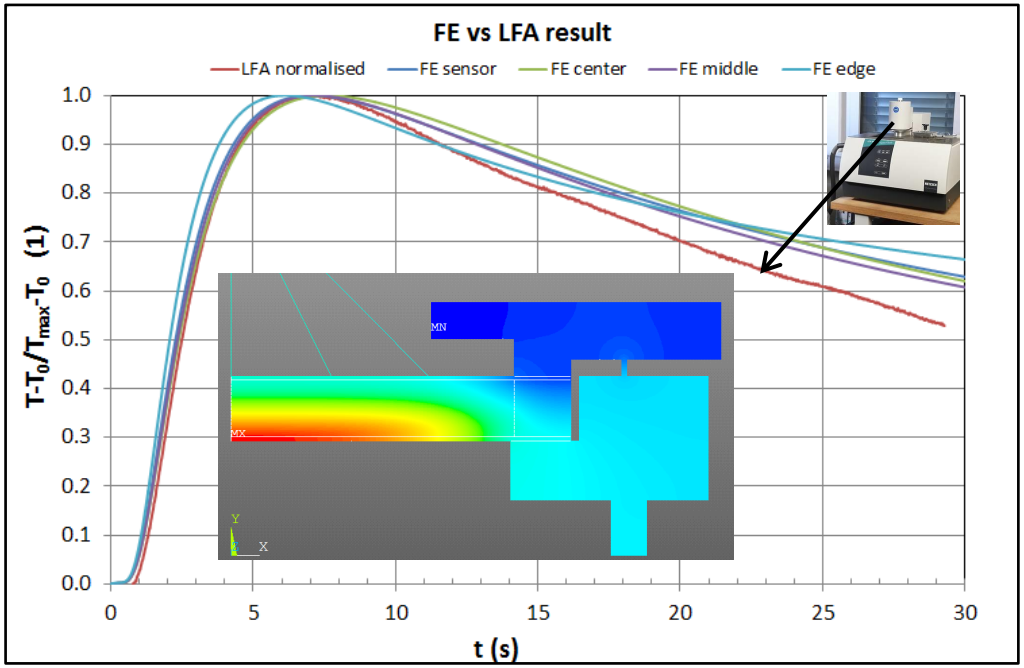
- Reference: H_2O a(25°C)=0.146 ·10^{-6} m²/s
- 3 Layer setup:
  - graphite coated steel cover plates
  - steel frame outside and PEEK ring inside
- 3 Layer LFA Model with heat loss
- LFA measurement on several samples with varying pulse energy, focus of the detector, range of model calculation
- Measured a=0,144 ·10^{-6} m²/s, σ=2,373·10^{-9} m²/s



LIQUID SAMPLE HOLDER FE MODELL

- Axially symmetric 2D FE Model
- Simulation with water compared to measurement data



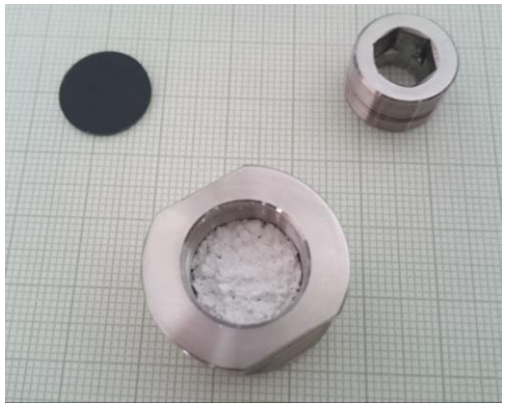


- different run time between center and edge
- ratio of λ_{PEEK} to λ_{sample} crucial ($\lambda_{PEEK} \sim 0{,}3\ Wm^{-1}K^{-1}$)

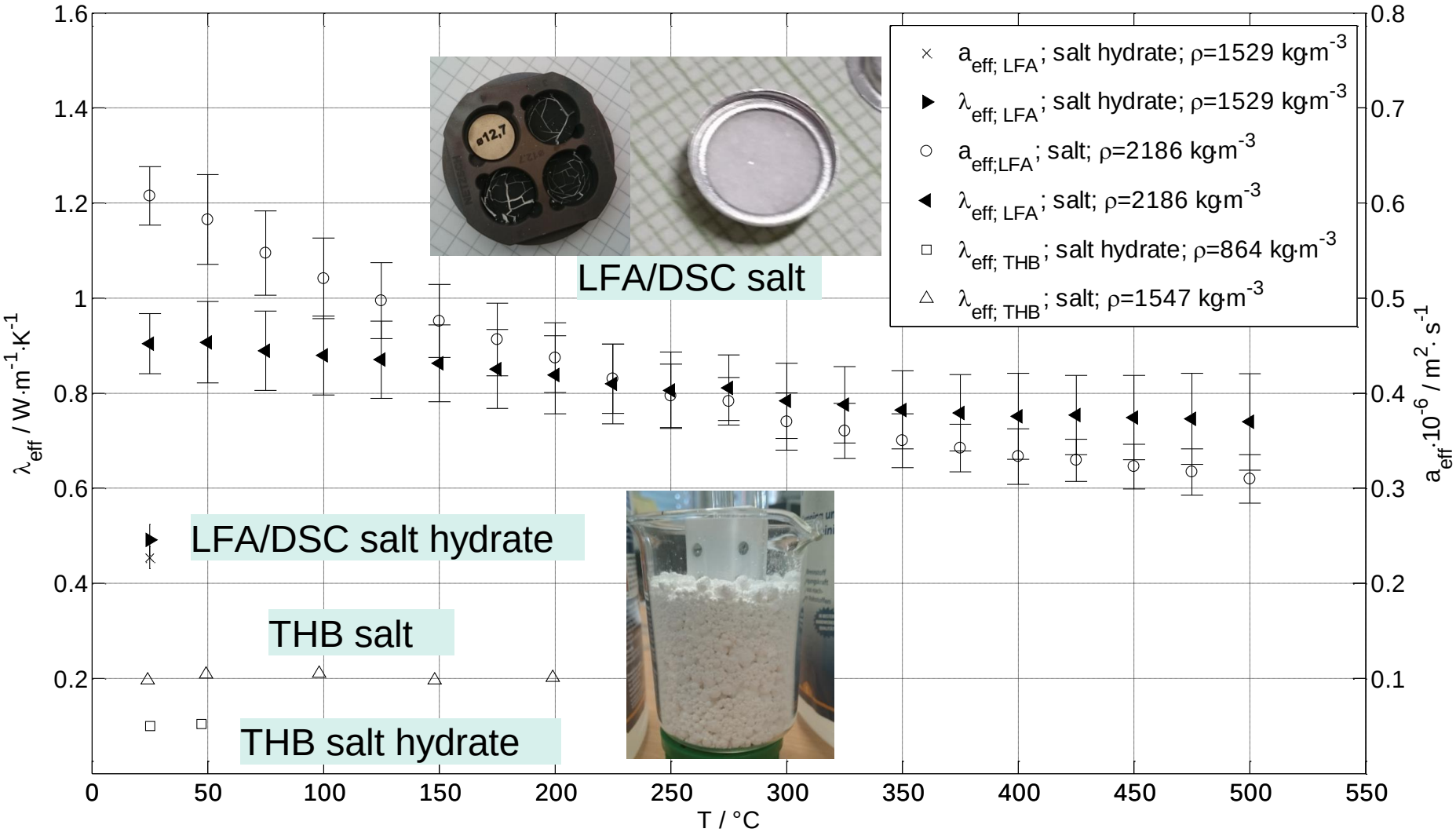
LFA EXPERIMENTS POWDER

- Powdery sample in special sample holder system
- 3 Layer setup:
  - graphite coated Al cover plates (d=1 mm)
  - steel frame with steel screw
- High pulse energy necessary due to thermal mass and low λ_{eff} off the powdery samples – small sample volume
- Measured a_{eff} depends on
  - Bulk density ρ_B of the packed bed
  - Constant sample thickness (deformation of Al cover plates)
  - λ of the used gas (λ_{He}=0.154 $W \cdot m^{-1} \cdot K^{-1}$, λ_{Ar}=0.018 $W \cdot m^{-1} \cdot K^{-1}$)
  - Particle form, contact area size, particle arrangement, imperfections in the bed…
- Further experiments and models on spherical powder with known properties and sample holder system

Sample holder system



EFFECTIVE THERMAL DIFFUSIVITY AND CONDUCTIVITY SALT HYDRATE RESULTS



CONCLUSION & OUTLOOK

- Preliminary STA tests are useful to identify reaction free temperature intervals, reaction enthalpies, cycling stability and not expected effects
- Evaluation of the apparent $c_p(T)$ of educt and product can be evaluated in one run using the hf-DSC
- λ_{eff} measurements of powders and liquids using THB can be done without much effort in sample preparation
- a_{eff} and λ_{eff} measurements of powders and liquids in the LFA need accurate sample preparation. Side effects of the used sample holder have to be taken into account.

- Further experiments on spherical powder with known properties using THB, LFA and HFM are planned.
- The impact of the LFA powder sample holder will be modeled and calculated.

THANK YOU!

Daniel Lager, 3.4.2017

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