Experimental Investigation of $CaO/Ca(OH)_2$ for Thermochemical Energy Storage – Commissioning of a 0.5 kWh Experimental Set-Up

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Agenda

- **Thermochemical Energy Storage – Basics and Material System**
- **Material System – Challenges**
- **Reactor and System Design**
- **Commissioning – First Results**
- **Conclusion and Outlook**

Thermochemical Energy Storage

Basics an Storage System

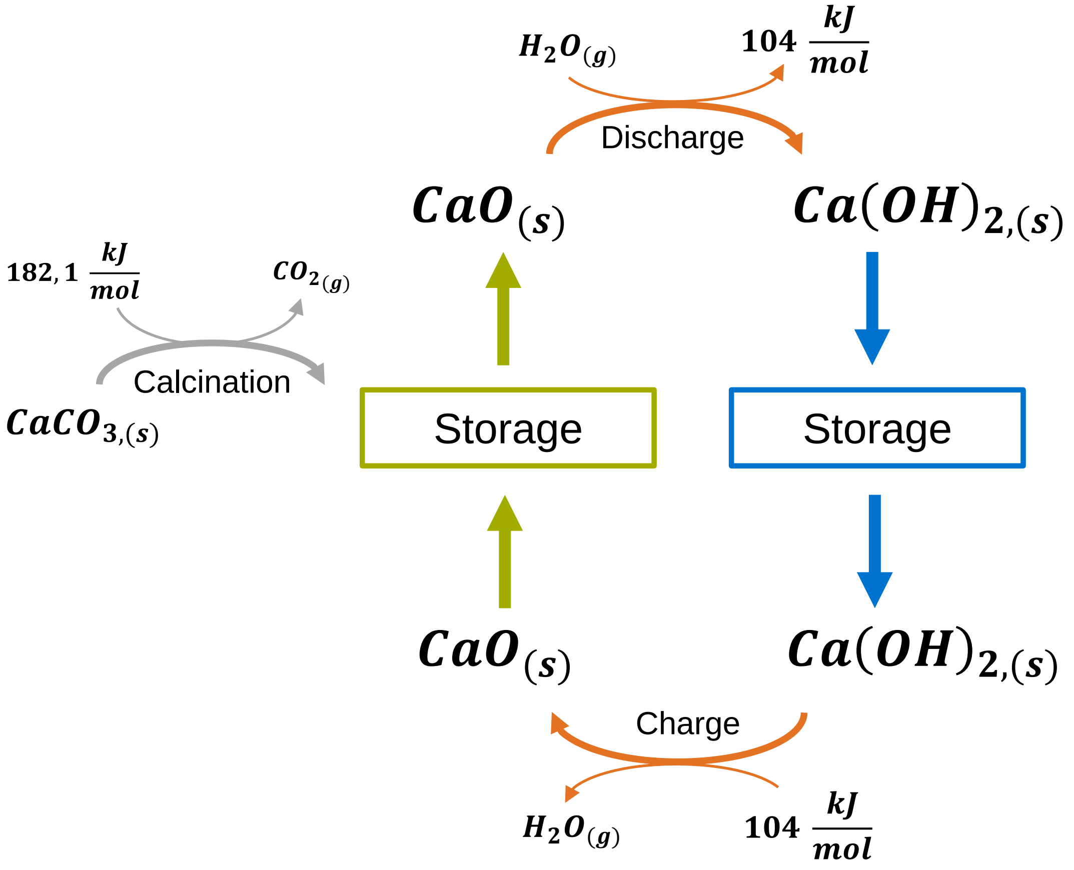
Principle: Heat storage in reaction enthalpy of gas-solid reaction

State of the art: Long term storage < 150 °C

Goal: (scalable) heat storage > 150°C, here: **400 °C – 600 °C**

Material System: Calcium Oxide – Calcium Hydroxide

Advantages[1]:
+ Cheap, abundant, Non-toxic
+ Theoretically no losses during storage period
+ High storage density
+ Decoupling of capacity and power[2,3]



Material System
Challenges

Challenges:

- Powdery material
- Agglomeration (in fixed bed)[4,5]
- **Heat transfer (limits power)[2]**

  → **Fluidized bed**

- **Mechanical material stability (limits process)[5,6]**

  → **Particle degradation/breakage**

Required process and analytic parameters include:

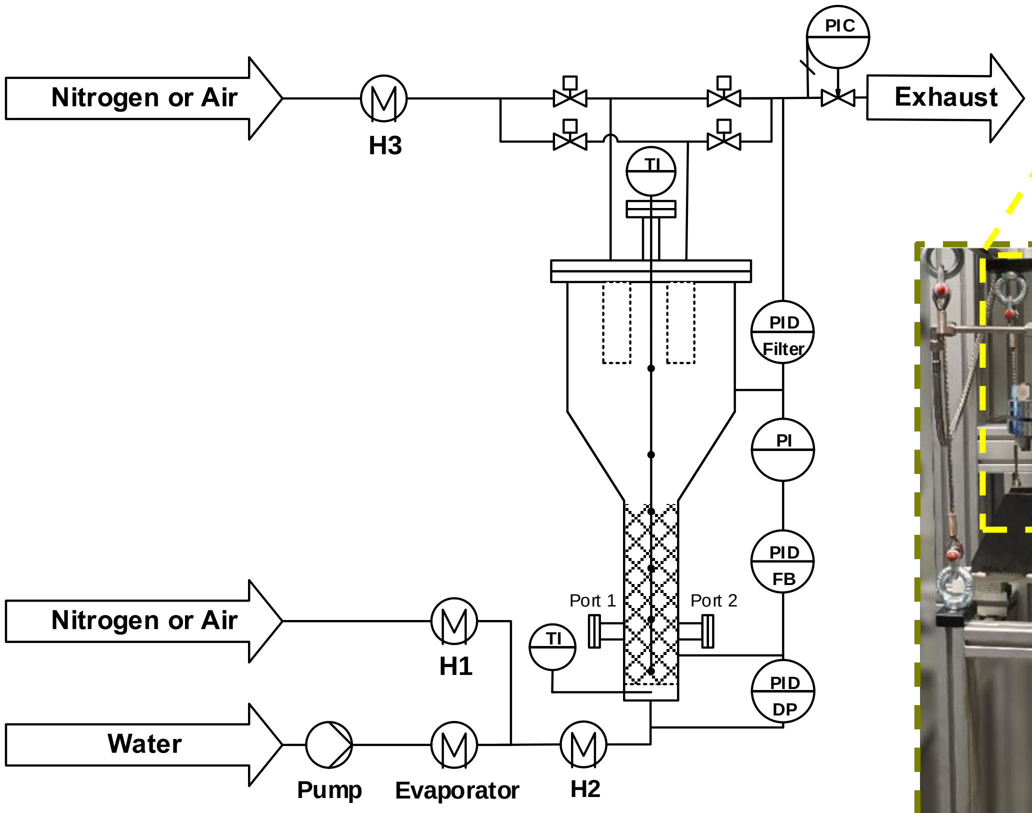
PSD, u_0, (Differential-)pressure, Temperature(-profile), Densities, Porosities …

Qualitative representation of particle degradation/breakage. Pictures for visualization only.[7]

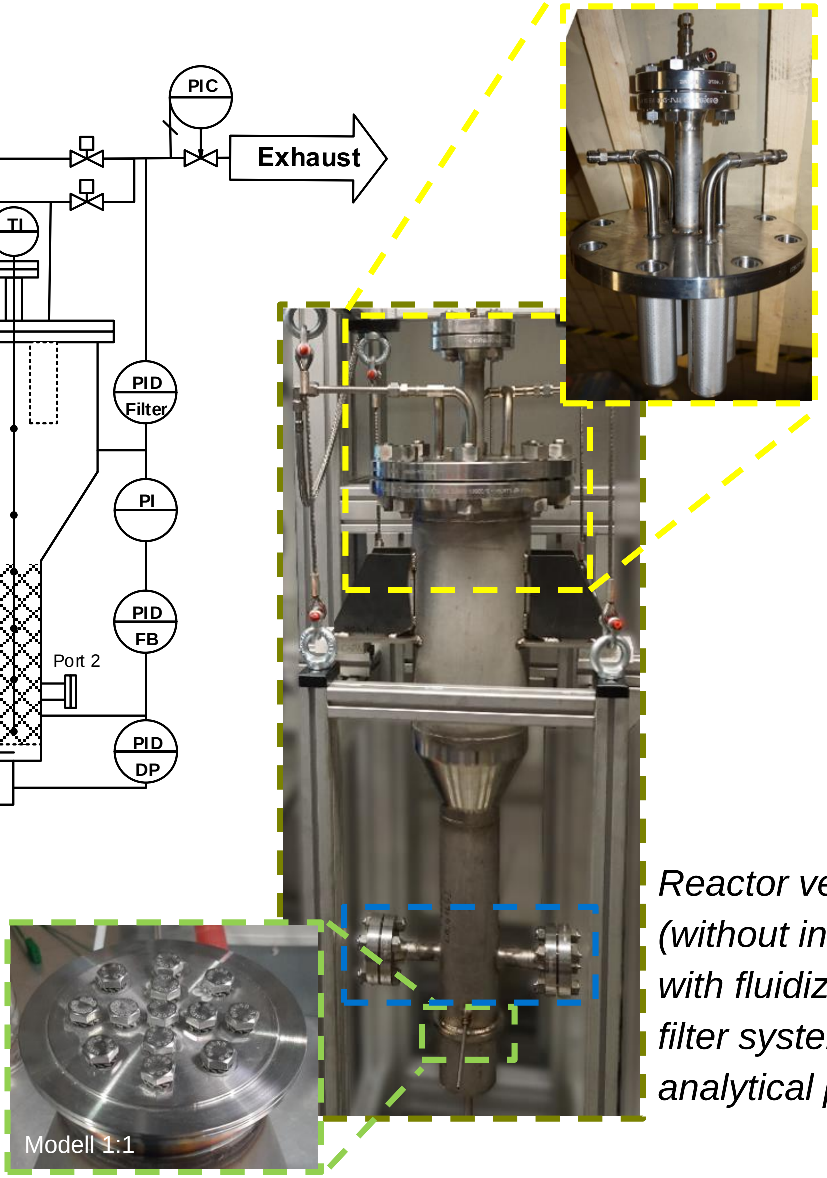
Cyclization

Reactor System and Design

- **Reaction zone:**
  - 1,8 L at d_i = 80 mm
  - 1,8 kg/h steam, u_0 = 0 - 30 cm/s
  - 850 °C, 4 bar_a
- **Analytics:**
  - 4x Temp. inside of fluidized bed
  - Absolute pressure
  - Differential pressure
- **Blowback Filter System**
- **Analytical Ports**
  (e.g. heat transfer probe)

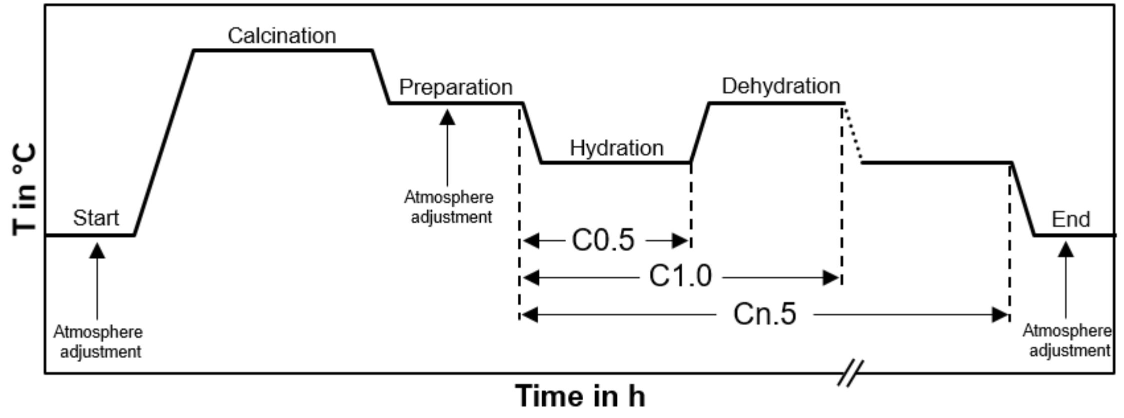


Process flowsheet of Setup

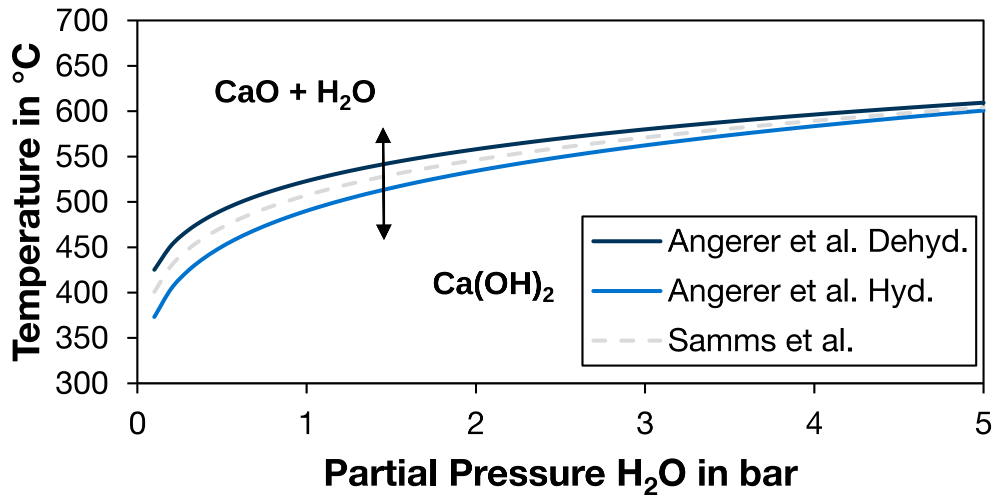


Reactor vessel (without insulation) with fluidization plate, filter system and analytical ports

Commissioning Procedure



Cyclization procedure



Apparent reaction equilibrium of $CaO/Ca(OH)_2$ according to Angerer et. al[3] *and theoretical equilibrium according to Samms et. al.* [8]

Parameters

$T_{set,Hyd.}$ = 456 °C

$T_{set,Dehyd.}$ = 586 °C

$T_{set,Kalz.}$ = 750 °C

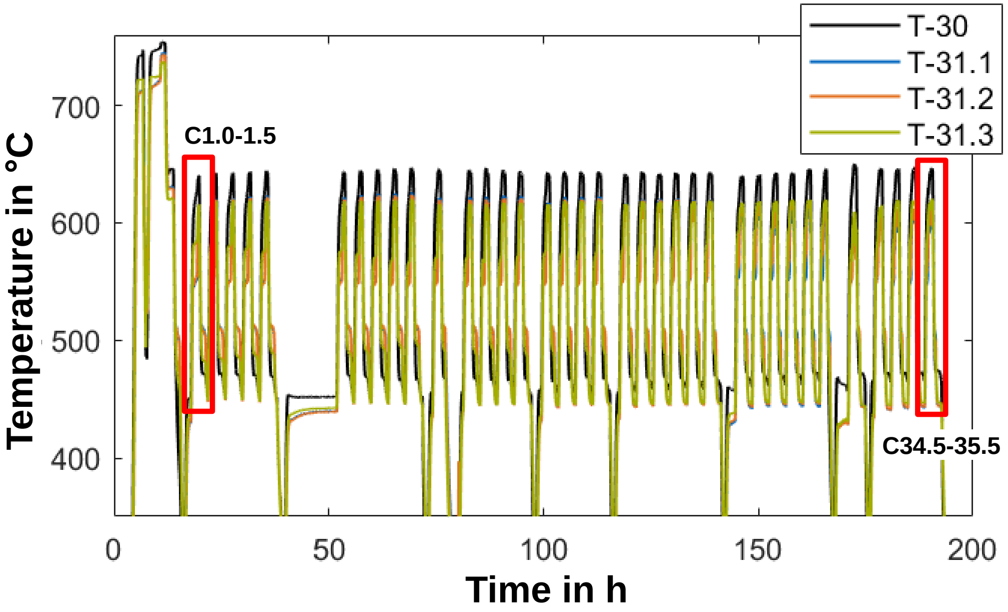
p_{set} = 1.4 bar_{abs}

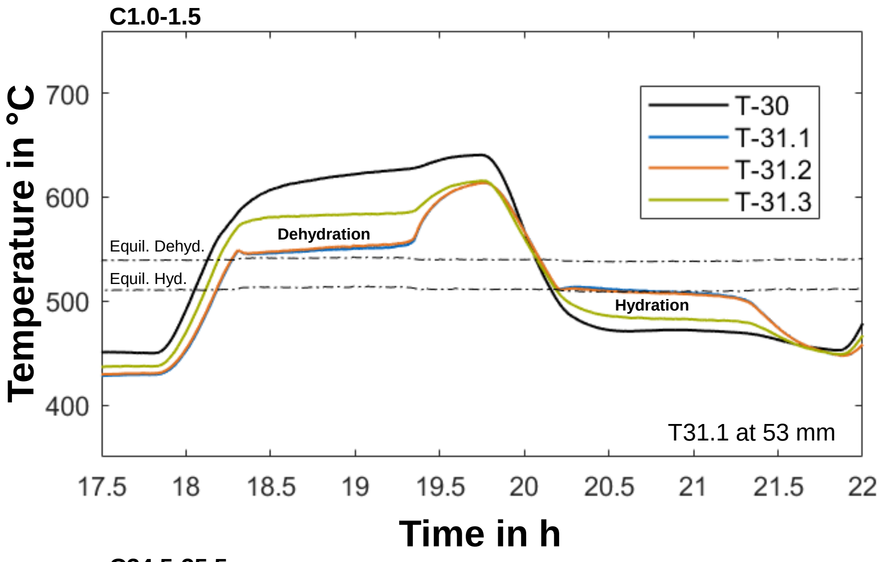
$\dot{m}_{H_2O}$ = 1.4 kg/h

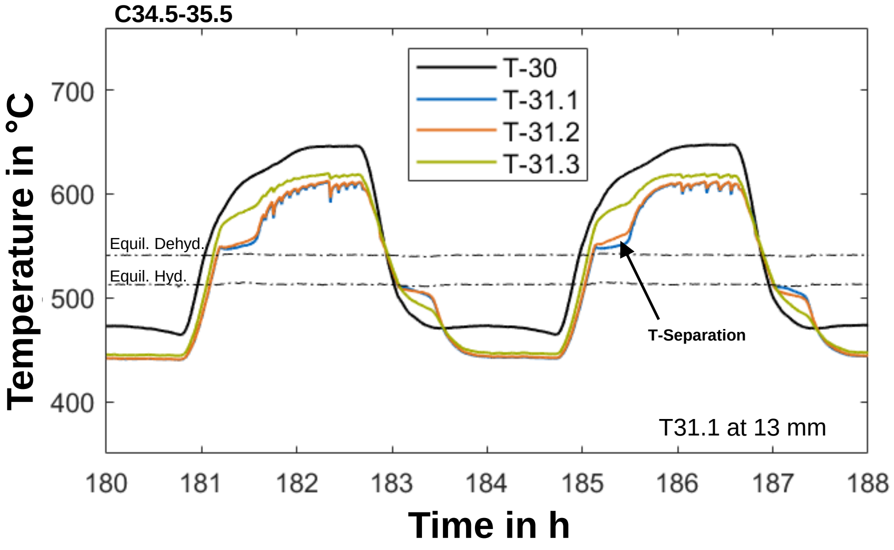
$CaCO_3$ – 800 g

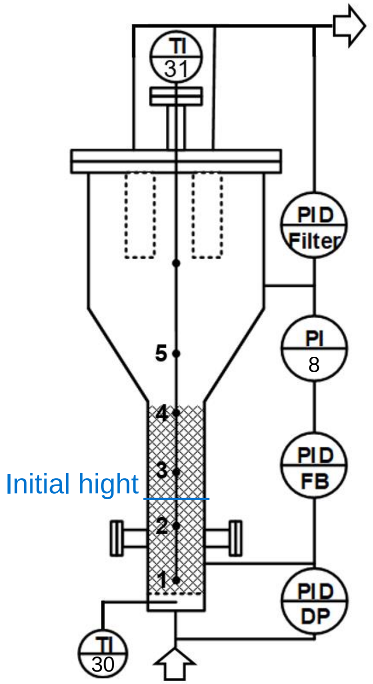
Commissioning – Results – Temperature

$CaCO_3$, Calc. in H_2O, $T_{set,Hyd.}$ = 456 °C, $T_{set,Dehyd.}$ = 586 °C, $T_{set,Kalz.}$ = 750 °C, p_{set} = 1.4 bar, m_{H20}= 1.4 kg/h, u_0 = 18.2 – 21.5 cm/s (at T_{set})







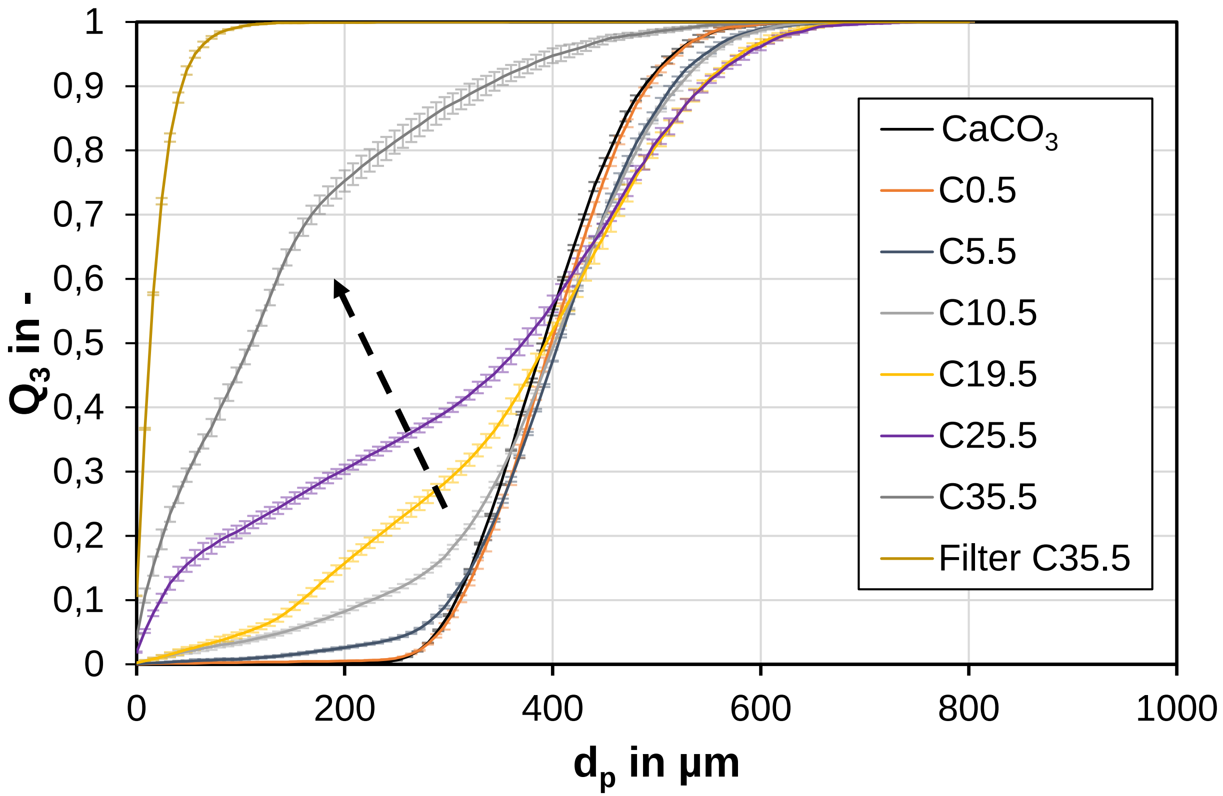


T-31.1: 10 mm – 100 mm
T-31.2: pos. T-31.1 + 80 mm
T-31.3: pos. T-31.2 + 80 mm

- Full conversion in every cycle (TGA)
- Good fluidization quality
- Reproducible reaction conditions

Commissioning – Results – PSD

$CaCO_3$, Calc. in H_2O, $T_{set,Hyd.}$ = 456 °C, $T_{set,Dehyd.}$ = 586 °C, $T_{set,Kalz.}$ = 750 °C, p_{set} = 1.4 bar, $\dot{m}_{H2O}$= 1.4 kg/h, u_0 = 18.2 – 21.5 cm/s (at T_{set})



- Particle breakage
- Loss of material from reaction zone
- Material in reaction zone still fluidizable
- No agglomeration in fluidized bed

→ Quantification of breakage
→ Handling of fines and Make-up

Conclusion

Challenges in thermochemical heat storage with $CaO/Ca(OH)_2$

- Poor heat conductivity limits power
- Particle breakage limits process

New experimental setup for long-term operation designed, built and commissioned successfully

- 1,8 L at d_i = 80 mm, 1,8 kg/h steam, u_0 = 0 - 30 cm/s, 850 °C, 4 bar_a, several temperature and (differential-)pressure measurements, analytical ports

Result

- Successful operation of 35.5 storage cycles, remaining material is fluidizable
- Handling of fines (discharge from fluidized bed, backflow to windbox)

Thank you for your attention!

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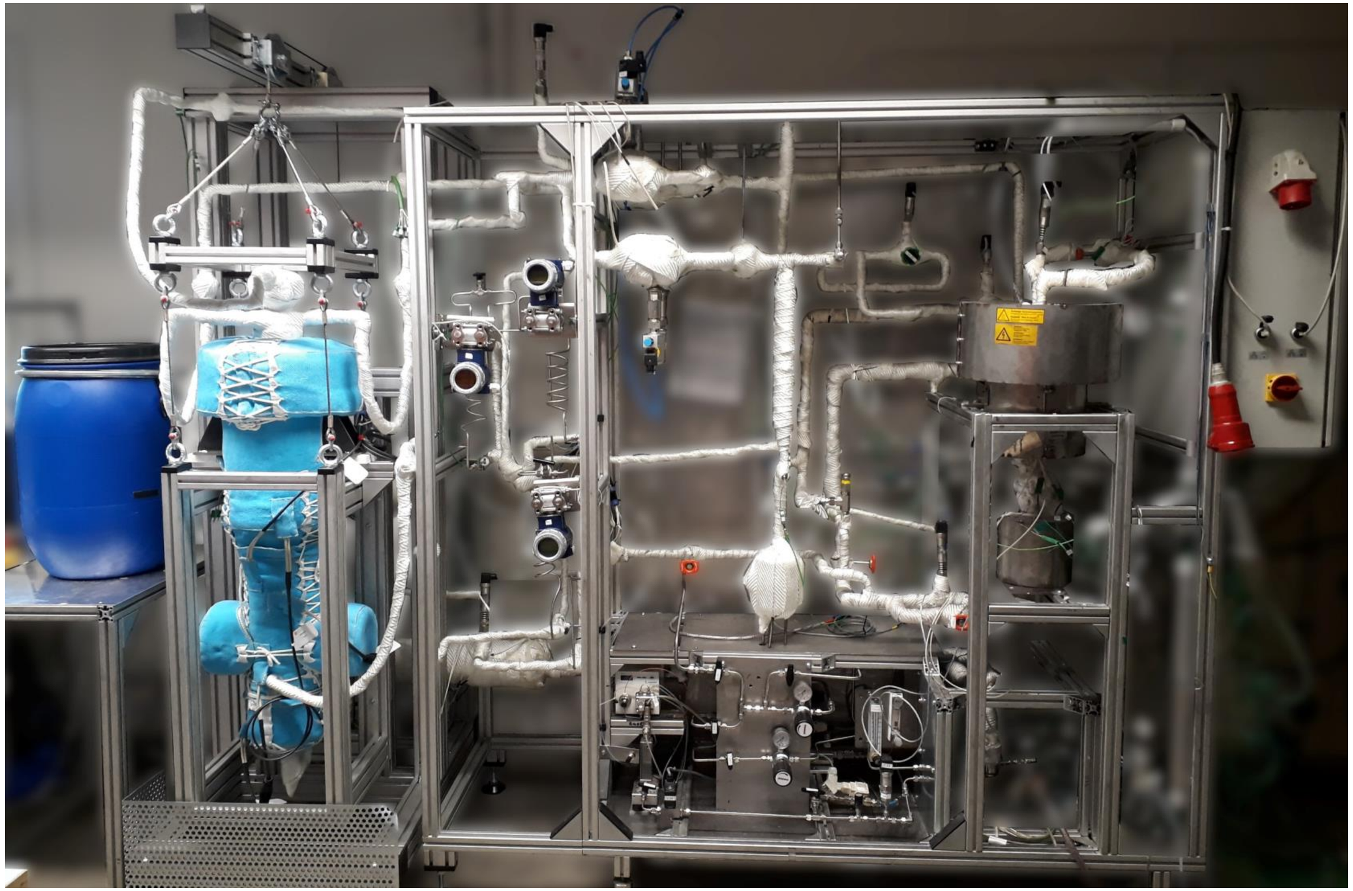

Experimental setup ready for operation

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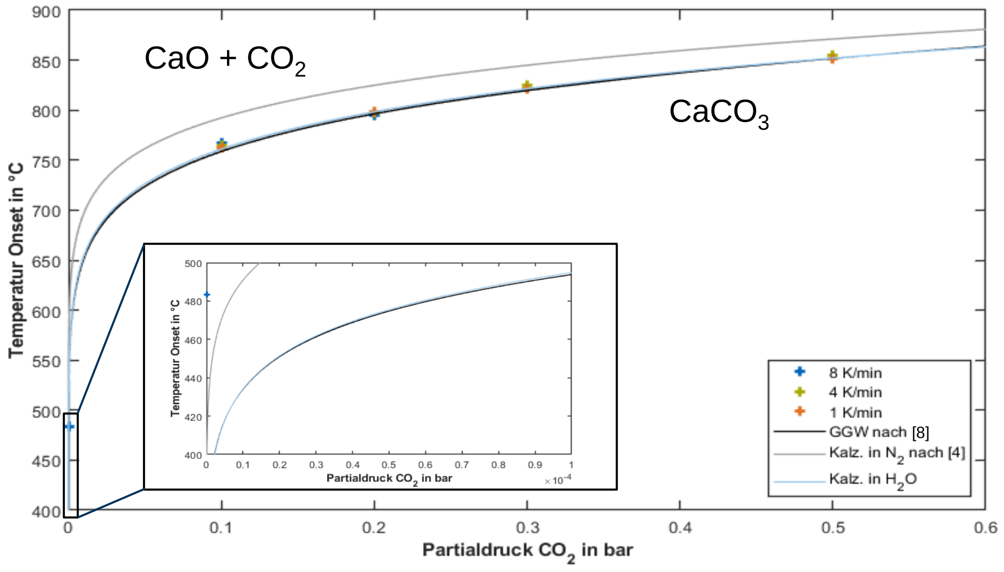
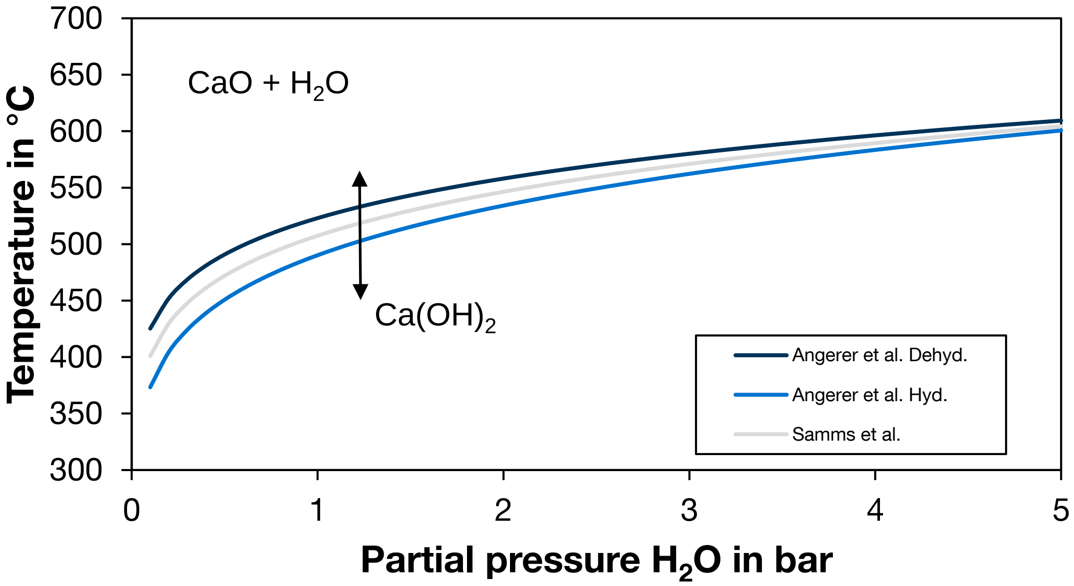
Comparison of Materials for Heat storage

	kWh/kg	kWh/m³	factor	€/kWh (material)
hot water*	0.06	58	1	0.025
sand sensible**	0.06	89***	1.5	0.25
molten salt sensible**	0.10	190	3.2	5 - 10
molten salt latent	0.06	100	2	10 - 15
$CaO/Ca(OH)_2$ thermochemical	**0.40**	**385/330*** **	**6.6/5.7**	**0.15**
hardcoal	6.9	2775	56	0.007

* average temperature difference = 50 K, ** average temperature difference = 250 K, *** related to achievable technical bulk densities

Chemical Equilibrium $CaCO_3/CaO/Ca(OH)_2$





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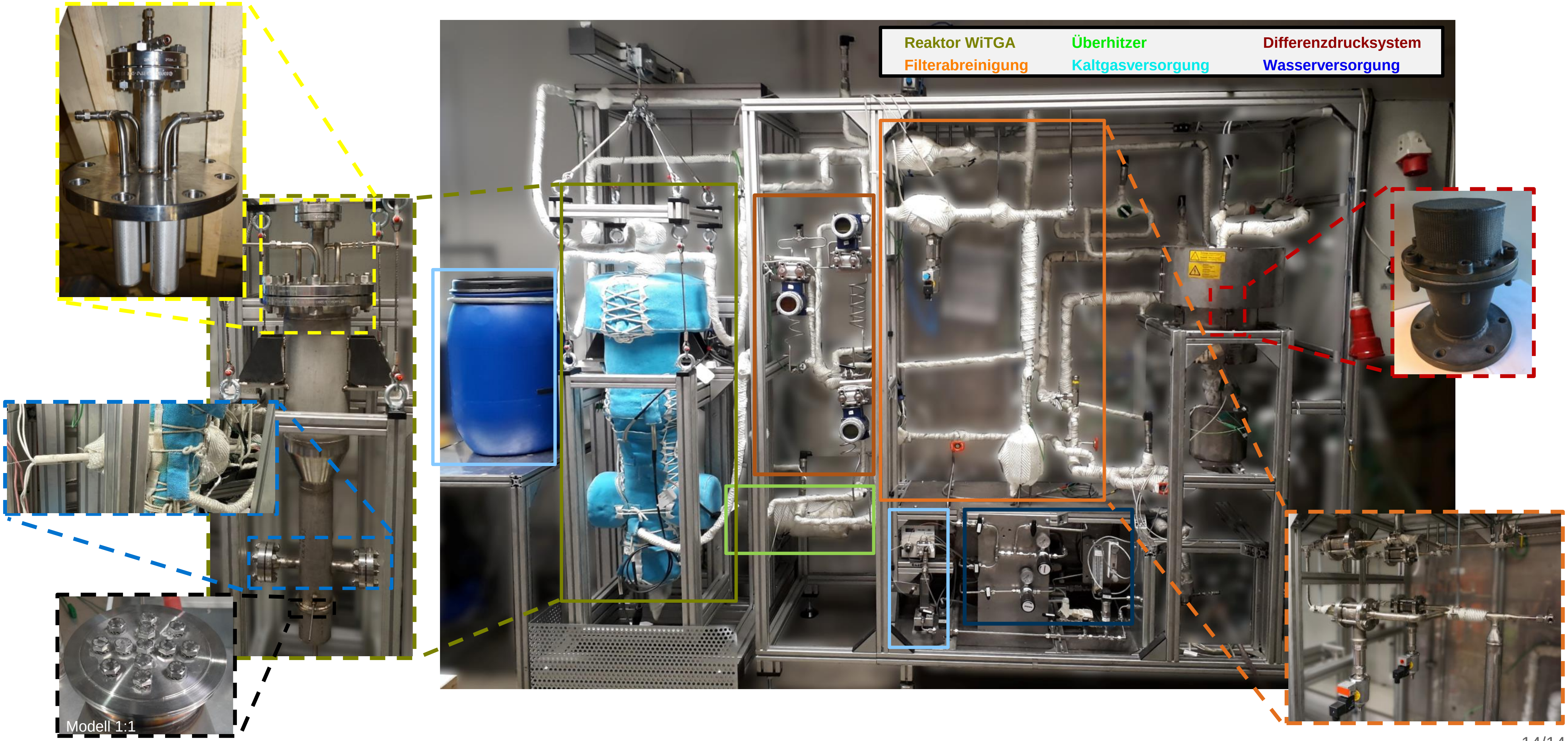
Full experimental Setup



Process parameters

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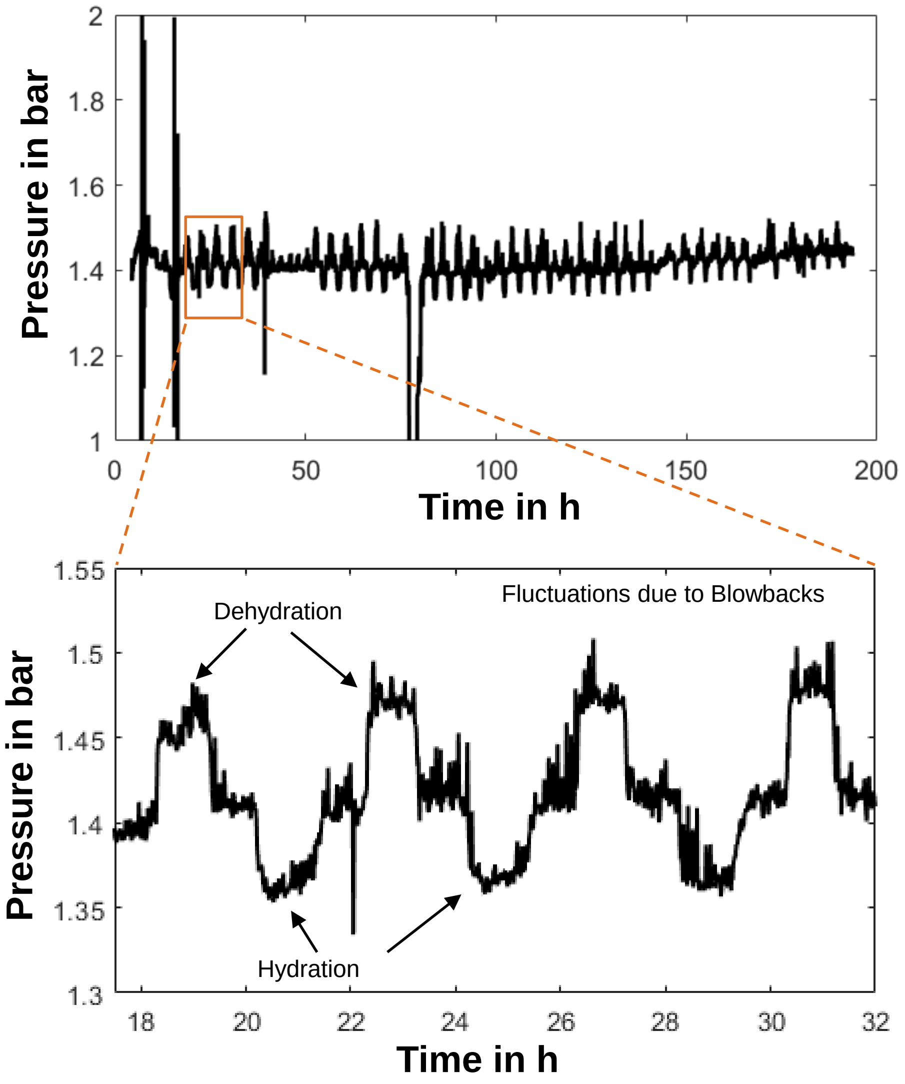
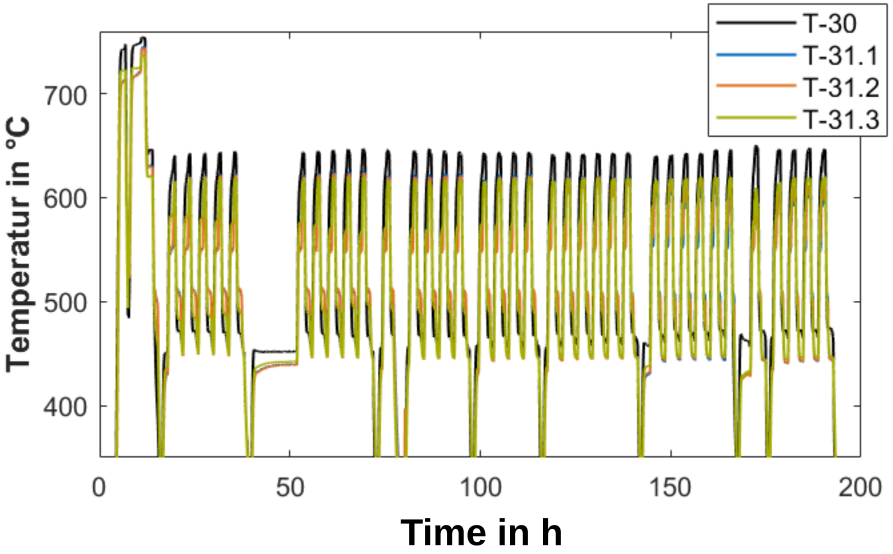
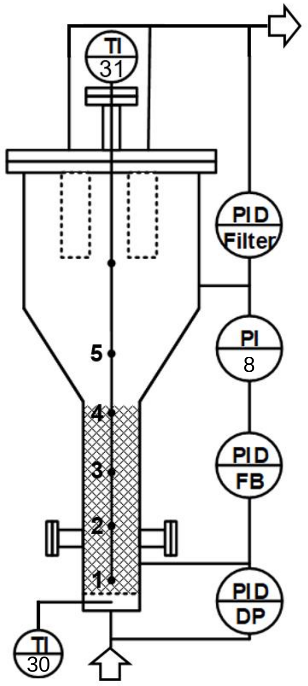






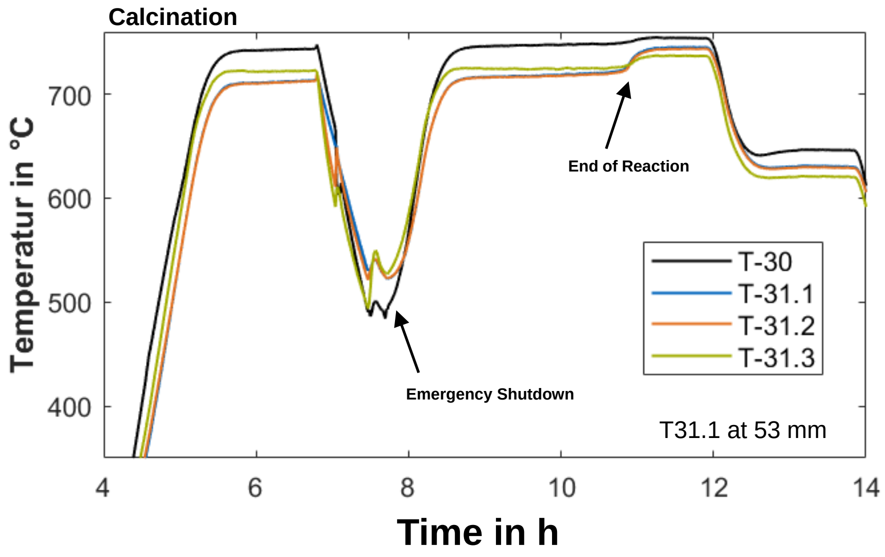
T-31.1: 10 mm – 100 mm
T-31.2: pos. T-31.1 + 80 mm
T-31.3: pos. T-31.2 + 80 mm

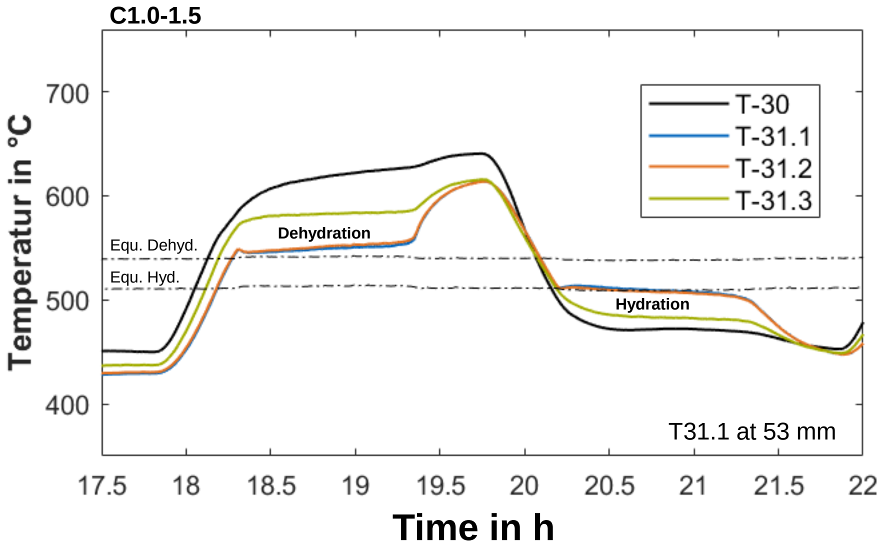
→ Blowback filtration system works

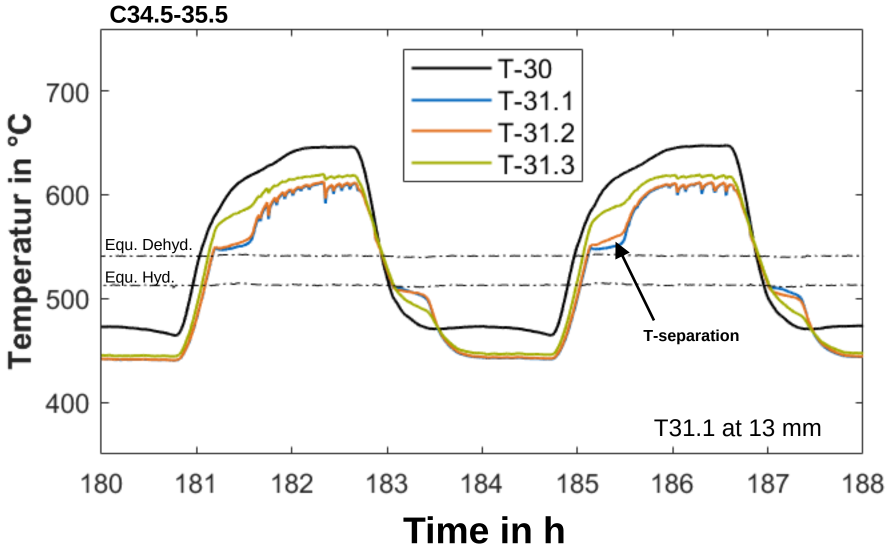
→ Controlled reproducible reaction conditions

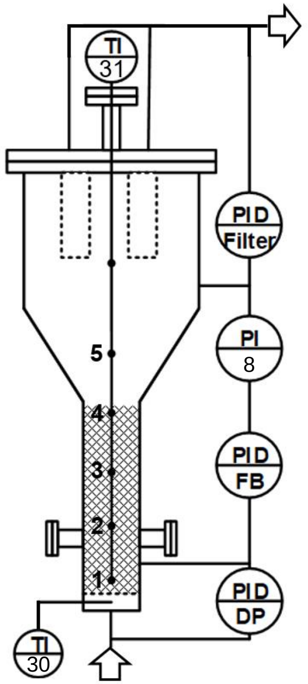
Temperatures

$CaCO_3$, Kalz. in H_2O, $T_{set,Hyd.}$ = 456 °C, $T_{set,Dehyd.}$ = 586 °C, $T_{set,Kalz.}$ = 750 °C, p_{set} = 1.4 bar_{abs}, $\dot{m}_{H2O}$= 1.4 kg/h, u_0 = 18.2 – 21.5 cm/s (bei T_{set})









T-31.1: 10 mm – 100 mm
T-31.2: pos. T-31.1 + 80 mm
T-31.3: pos. T-31.2 + 80 mm

- Reaction plateaus
- Good fluidization quality (T31.1 and 31.2 identical)
- Reaction temp. equals $T_{app.\ GGW,\ [4]}$
- from C33.5 on T-31.1 und T-31.2 start to separate (here loss of material in FB)

→ Hight measurement via thermocouples
→ Material loss

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