Particle Properties of CaO/$Ca(OH)_2$ Throughout Cyclisation in a Fluidized Bed for Thermochemical Energy Storage – Consequences for Fluidization

Leander Morgenstern[1], Elija Talebi[1], S. Ohmstedt[1], F. Kerscher[1] and H. Spliethoff[1]
[1]*Chair of Energy Systems, Technical University of Munich, Boltzmannstr. 15, 85748 Garching b. München, Germany*

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Agenda

Motivation

Fluidization Characterization

Experimental Procedure

Results

Thermochemical Energy Storage

Basics

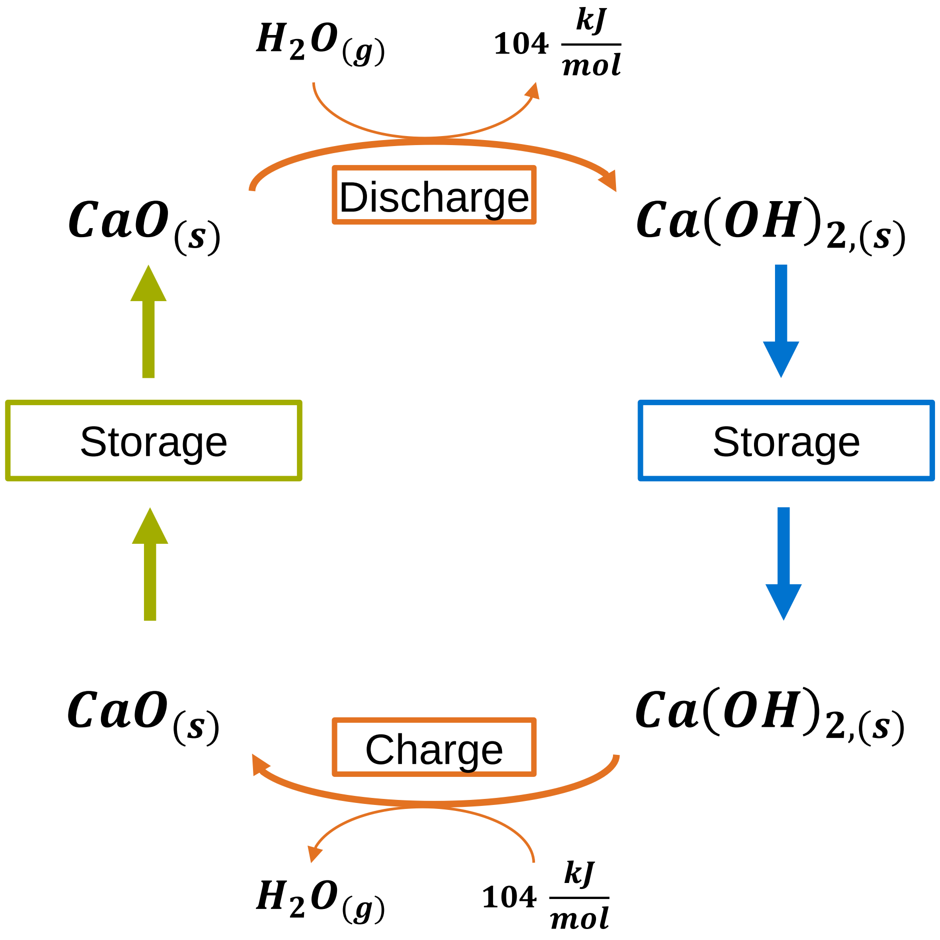
Principle: Heat storage in reaction enthalpy of gas-solid reaction

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

Material System: Calcium Oxide – Calcium Hydroxide

Advantages[Ren. a. Sust. En. Rev. 32 (2014): 591-610]**:**

+ Cheap, abundant, Non-toxic
+ Theoretically no losses during storage period
+ High storage density: **0.40 kWh/kg - 385/330 kWh/m³**
+ Decoupling of capacity and power[978-3-8439-1085-9; 978-3-8439-4729-9]



Material System

Challenges

Challenges:

- Powdery material
- Agglomeration (in fixed bed)[978-3-8439-1085-9; 978-3-8439-4729-9]
- **Heat transfer (limits power)**[J.of En. Res. Tech. 140 (2018) 40]

→ **Fluidized bed**

- **Mechanical material stability (limits process)**[978-3-8439-4729-9; FKZ: 03ET7025]

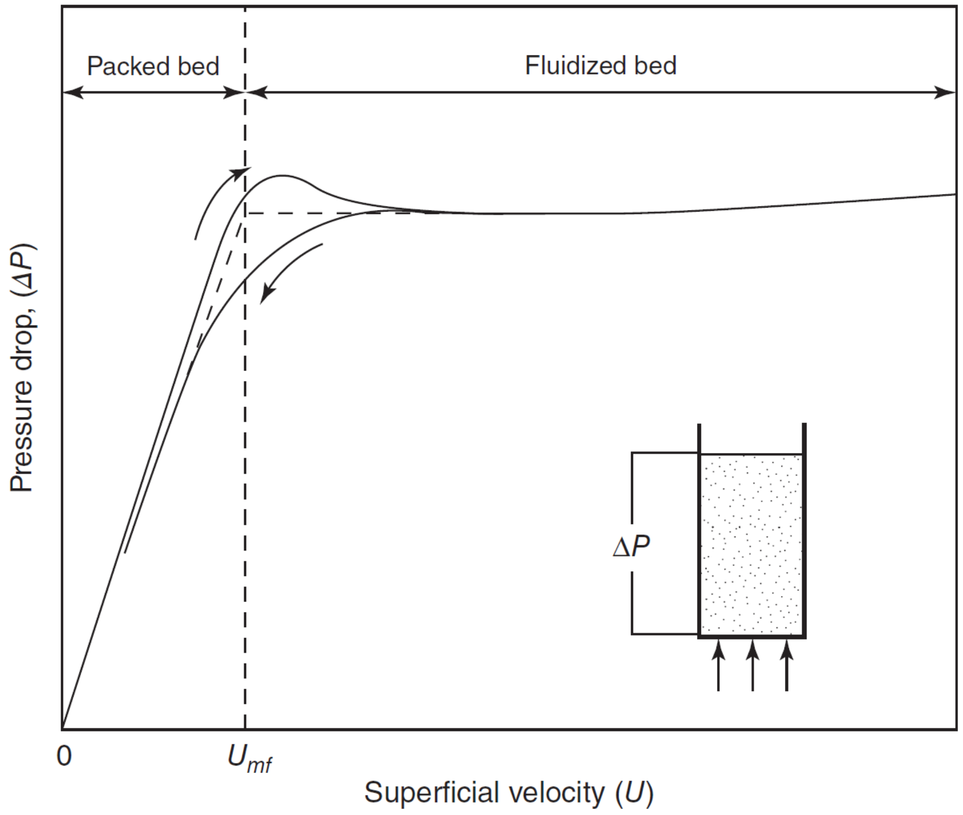
→ **Particle degradation/breakage**

Qualitative representation of particle degradation/breakage. Pictures for visualization only.[Talebi et al, FBC24, 2022]

Cyclization

Fluidization

What is it we need to know?



Graphical identification of the minimum fluidization velocity u_{mf} (from Grace, 2020, ISBN: 978-3-527-69947-6)

Fluidization of $Ca(OH)_2$ with $d_{3,2}$ = 148 µm and u_{mf} = 0.012 m/s at u_0 = 0.150 m/s in Nitrogen.

Characterization of Particles for a Fluidized Bed

What is it we need to know?

1. Fluidizability and Fluidization Regime → Geldart-Classification

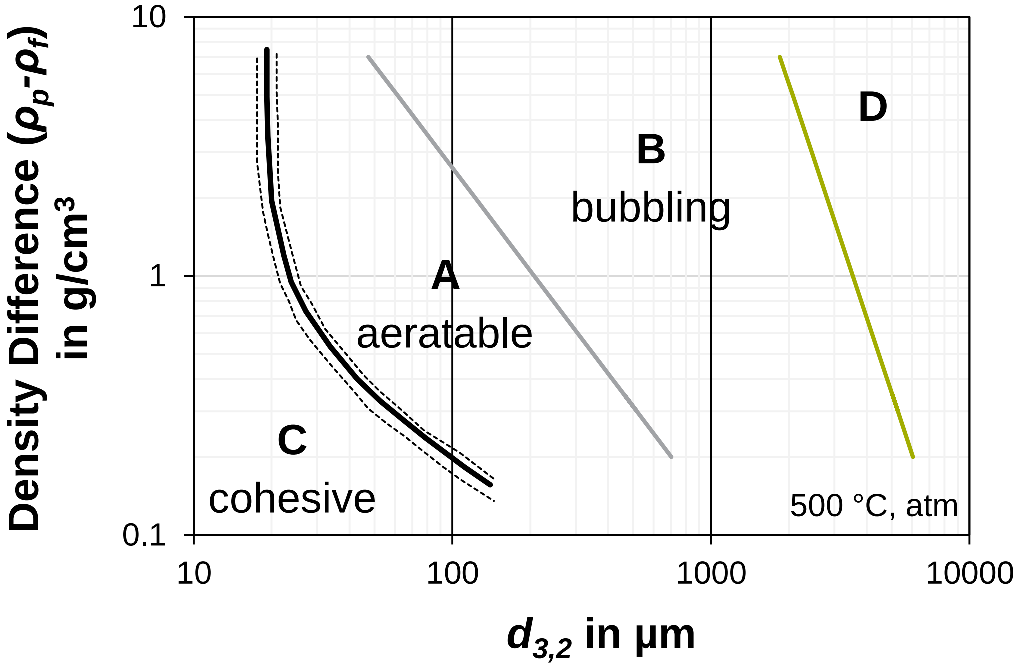
   PSD ($d_{3,2}$), particle/bulk/tapped density, sphericity

2. Minimal/terminal fluidization velocity u_{mf}, u_t

   theoretical vs. experimental examination

3. Porosity of the fluidized bed: ε, ε_{mf}, ε_b …

   bed expansion during operation



Geldart-Diagram at 500 °C, atm. pressure with air as fluidization gas according to Grace 2020 (ISBN: 978-3-527-69947-6) *and Geldart 1976 (CONF-761109-8)*

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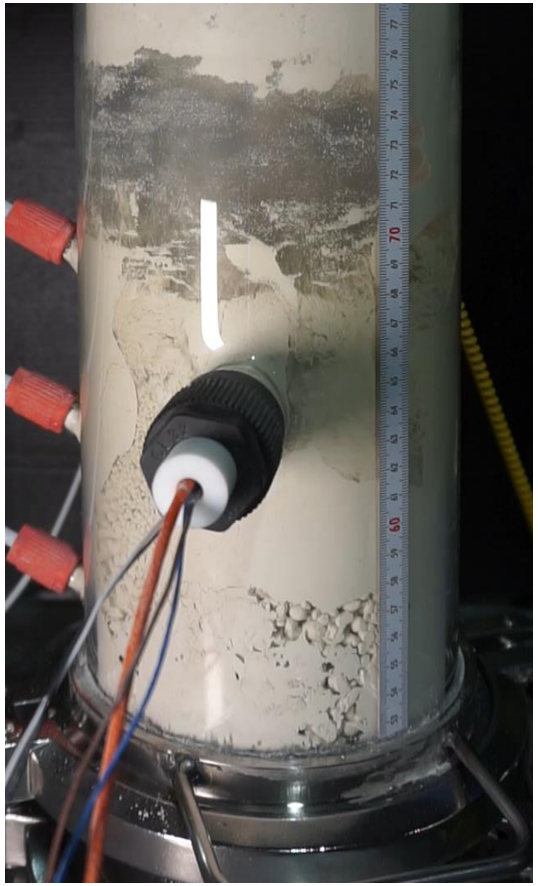
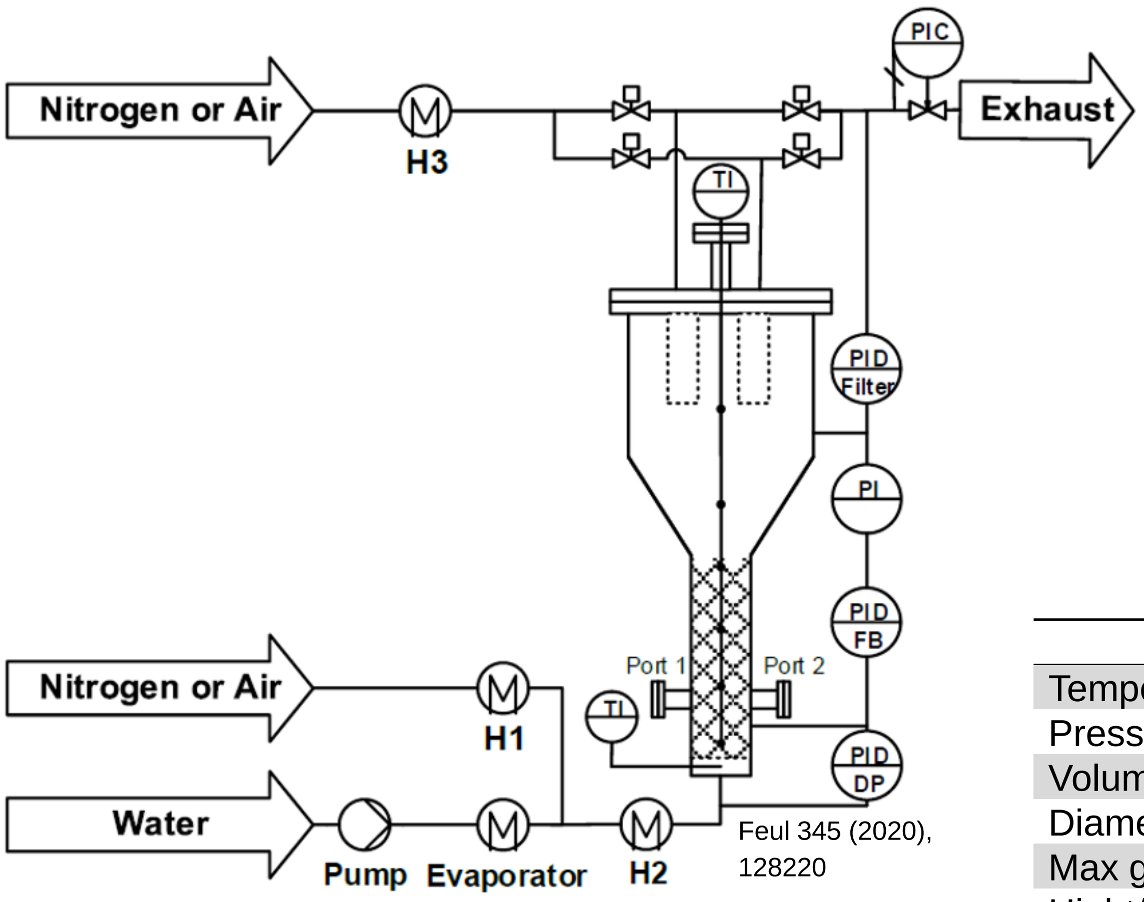


Fluidization of $Ca(OH)_2$ with $d_{3,2}$ = 36 µm and u_{mf} < 0.02 m/s at u_0 = 0.150 m/s in Nitrogen.

Lab and Pilot Scale Reactors

Experimental Set-Ups



Feul 345 (2020), 128220

Vessel Laboratory Reactor

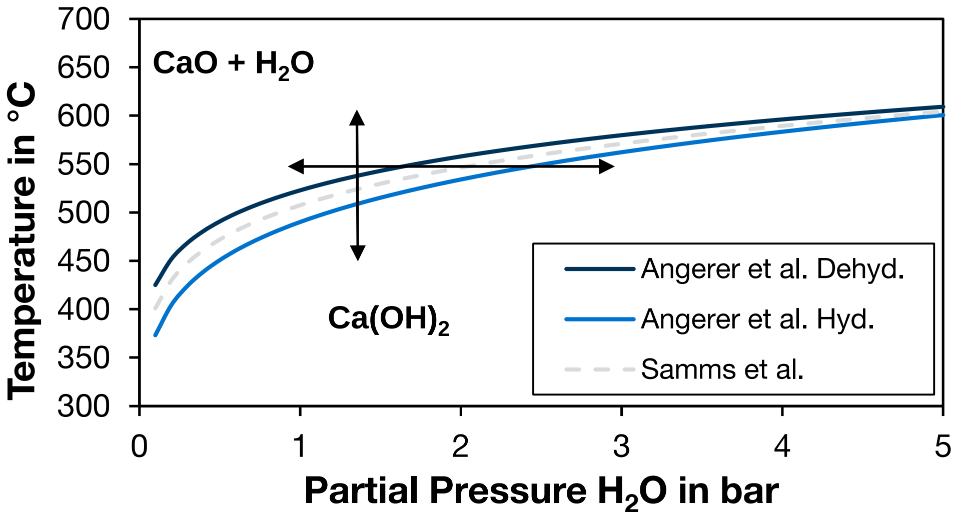
Feul 345 (2020), 128220

Vessel FluBEStoR

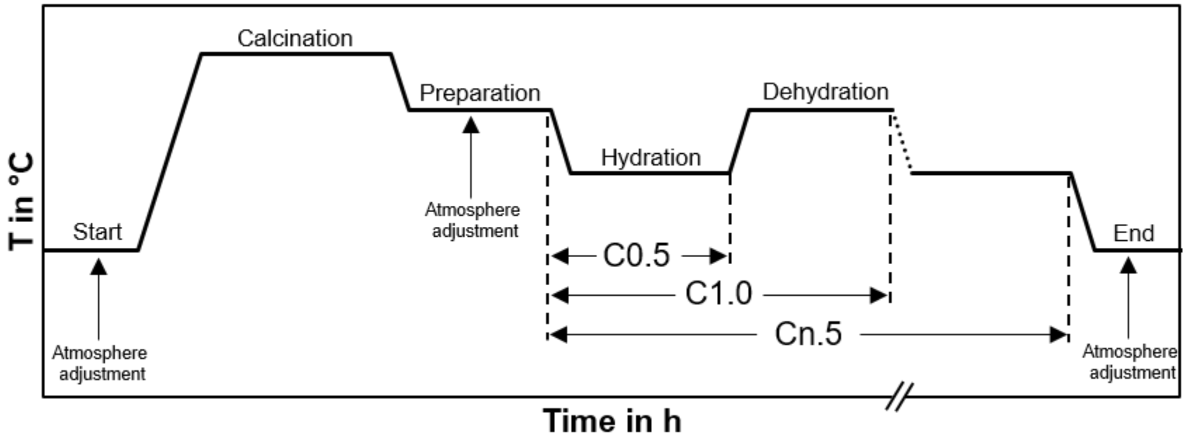
Parameter	Laboratory Reactor	FluBEStoR
Temperature TS	850 °C	700 °C
Pressure PS	4 bar	6 bar
Volume V_{FB} (V_{total})	1.8 L (7.7 L)	30 L (120 L)
Diameter Fluidized Bed	80.8 mm	254 mm
Max gas velocity (300 °C, 1bar)	0.25 mm	0.4 mm
Hight/Diameter of FB	4	2.4

Cyclisation of the Storage Material

Experimental Procedure



Apparent reaction equilibrium of $CaO/Ca(OH)_2$ according to Angerer et. al[En. Rep. 4 (2018) 507-519] *and theoretical equilibrium according to Samms et. al*[J. of Ap.Chem., 1968, 18. Jg., Nr. 1, S. 5-8].

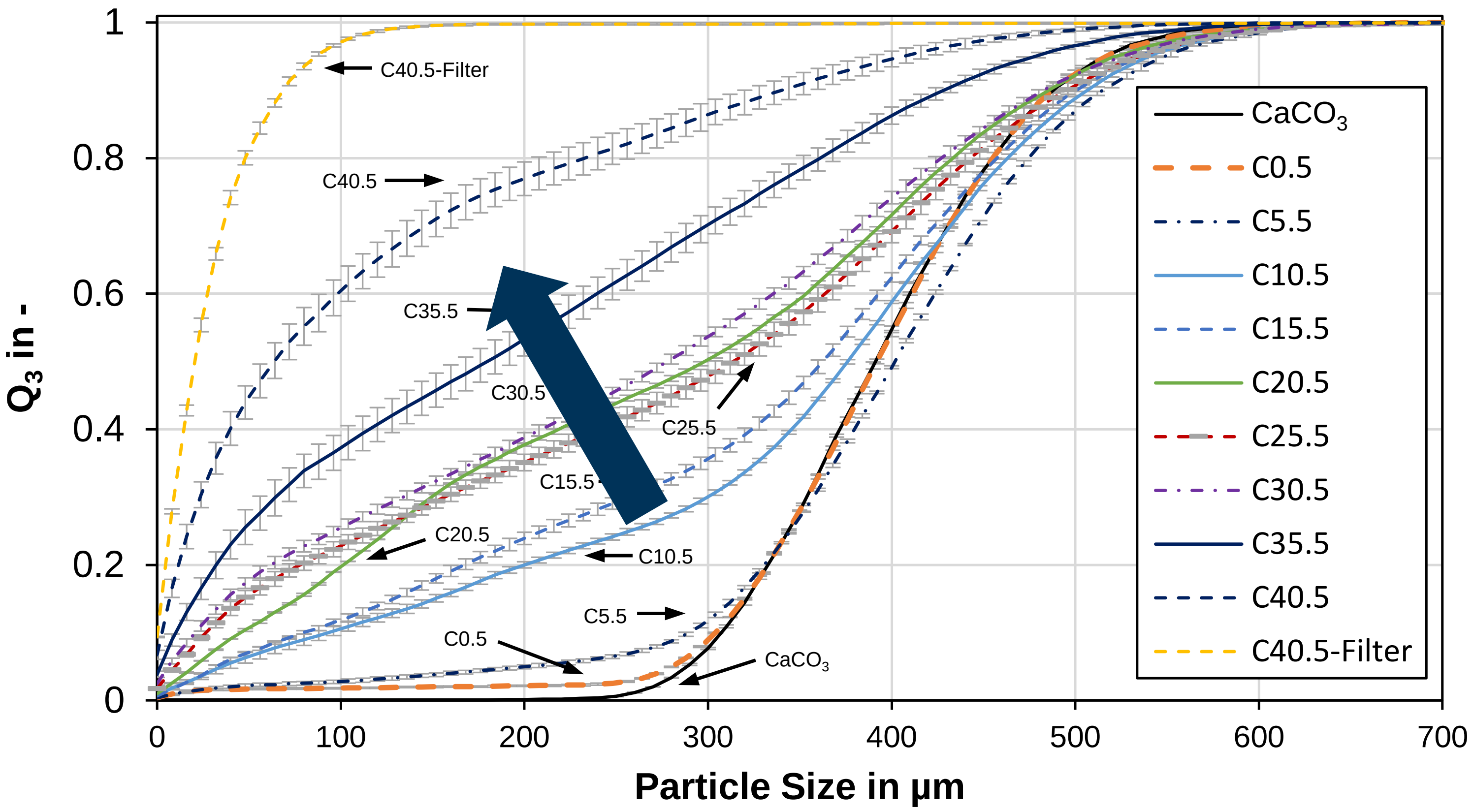


Experimental procedure for cyclisation of the storage material[Feul 345 (2020),128220]

- Material: 250 - 400 µm $CaCO_3$, 0.8 or 26.4 kg
- 700 °C (Calc.), 456 °C (Hyd.), 586 °C (Dehyd.)
- u_0 = 15 cm/s

Cyclisation – Change in Particle Size Distribution

Results



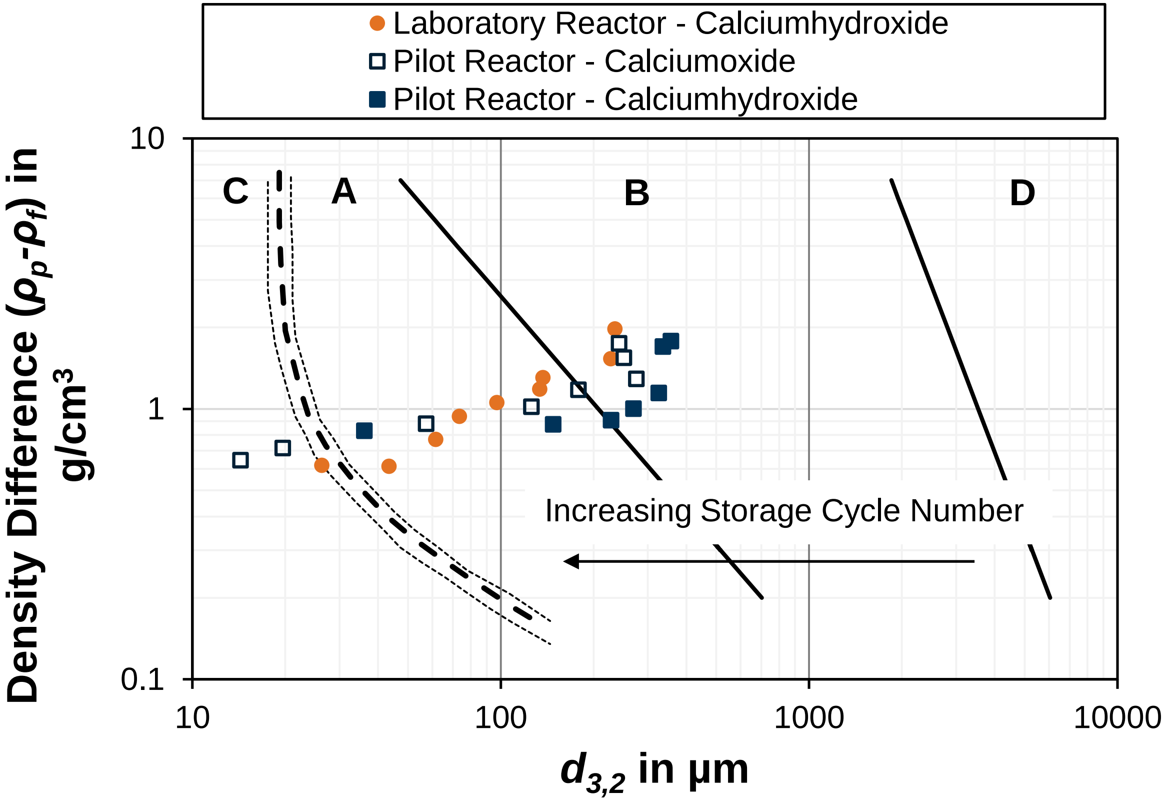
Particle size distribution as a function of storage cycle number given as Q_3. Raw material is $CaCO_3$ (indicated). All other samples are analyzed as $Ca(OH)_2$. (Feul 345 (2020), 128220)

Sauter Mean Diameter $d_{3,2}$ is the diameter of a sphere that has the same surface to volume ratio as the respective particle bulk.

$$d_{3,2} = \frac{d_V{}^3}{d_s{}^2},\ d_V = \sqrt{\frac{A_p}{\pi}},\ d_p = \left(\frac{6V_p}{\pi}\right)^{1/3}$$

Classification According to Geldart

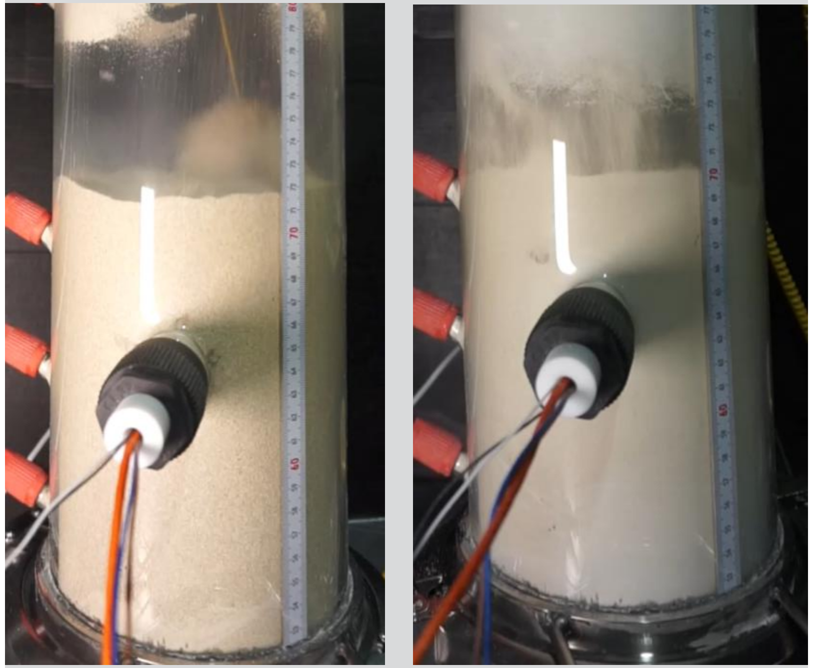
Results



Geldart diagram adapted from [Pow. Tech. 1973, 7 (5), 285-292] for transition A-B and B-D, evaluated for water vapor at 500°C and 1.5 bar and from [ISBN: 978-3-527-69947-6] for the C-A transition. Results on cyclisation of CaO/Ca(OH)$_2$ in pure steam [Feul 345 (2020), 128220].

Cycled Ca(OH)$_2$ at 0.15 m/s

$d_{3,2}$ = 355 µm, h_{WS} = 316 W/m²K | $d_{3,2}$ = 148 µm, h_{WS} = 191 W/m²K

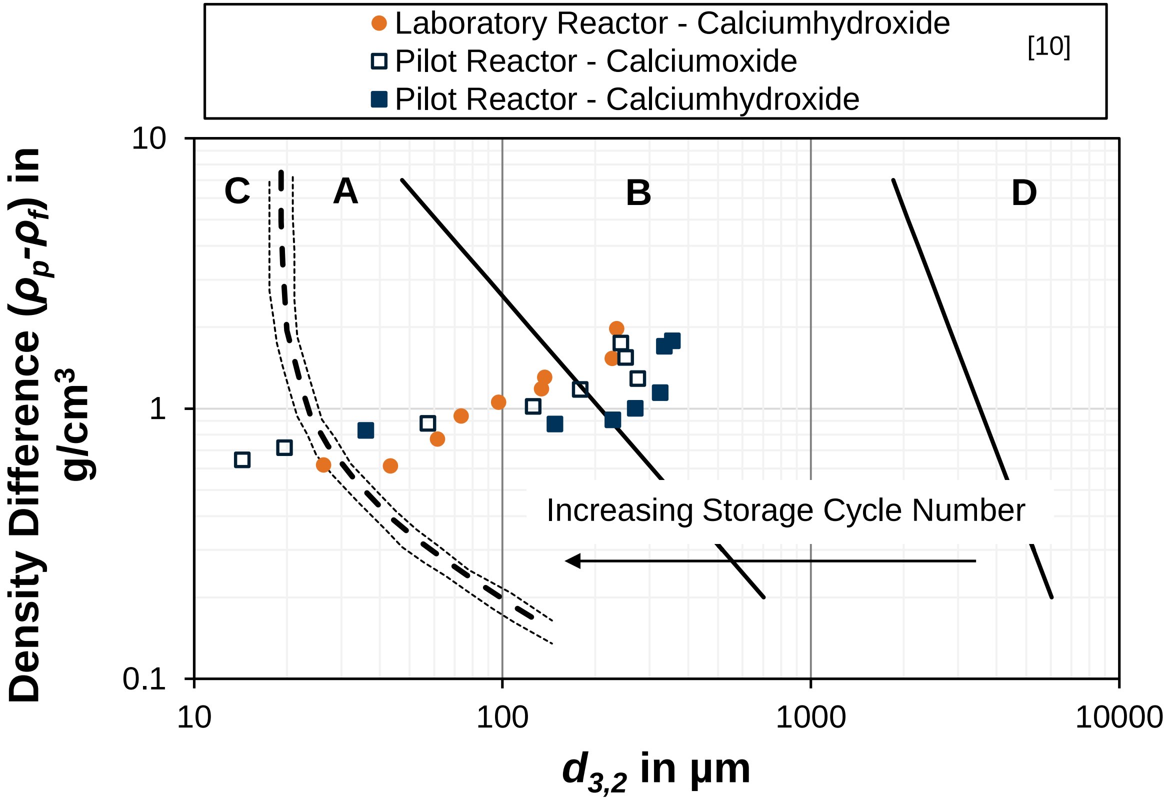


Fluidization test Rig described by Becker [978-3-8439-4729-9]

Samples of varying $d_{3,2}$ tested in a fluidization test rig.

Minimal Fluidization Velocity and Porosity

Results



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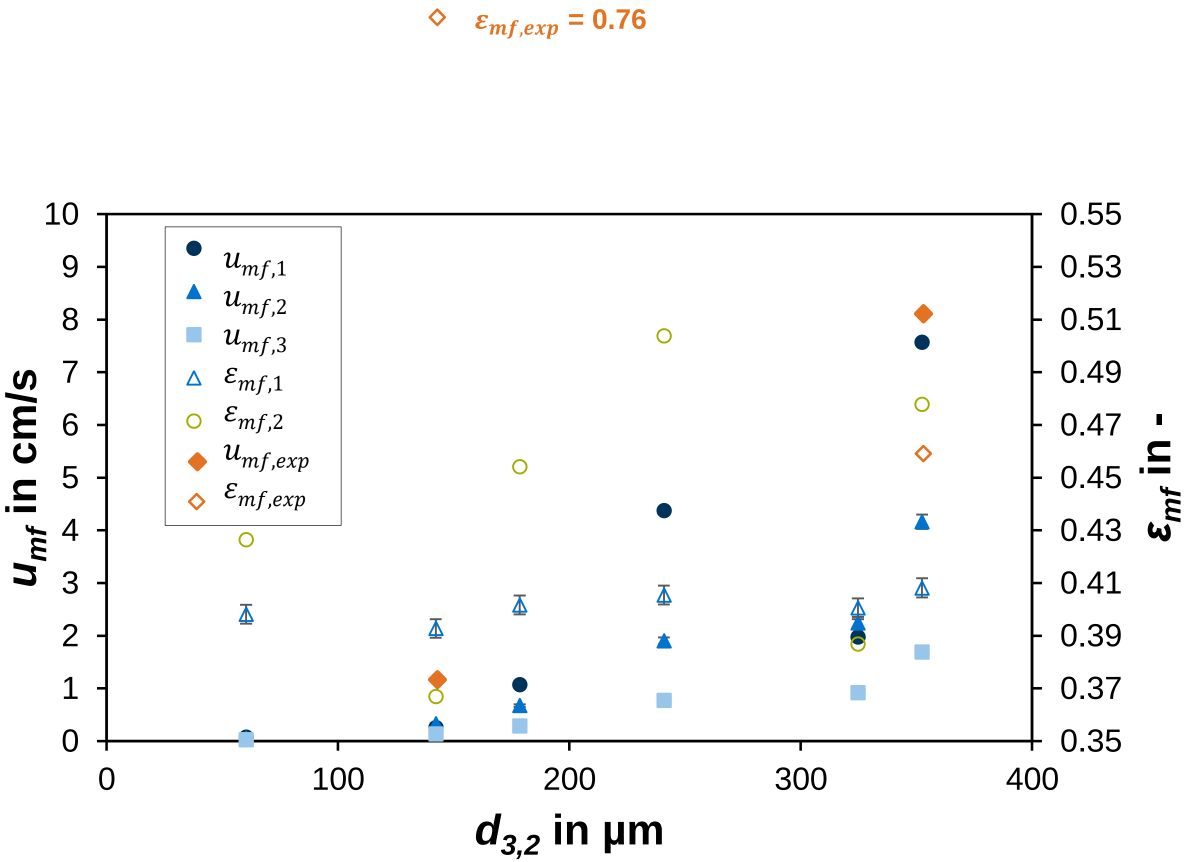

Theoretical minimal fluidization velocity calculated according to Kunii and Levenspiel (**$u_{mf,1}$** and **$u_{mf,2}$**, [9780409902334]) and Anantharaman et al. (**$u_{mf,3}$**, [Pow. Tech. 2018, 323, 454-485]). For **$u_{mf,1}$** the theoretical bed porosity **$\varepsilon_{mf,1}$** according to **$\varepsilon_{mf,2}$= ε_0=1-ρ_{bulk}/ρ_p** [ISBN: 978-3-527-69947-6] and for **$u_{mf,2}$** the **$\varepsilon_{mf,2}$** according to Gibson et al [Chem. Eng. Res. a. Des. 2018, 135, 103-111].

Summary

- Thermochemical Energy Storage utilizing **$CaO/Ca(OH)_2$** is promising for applications at **400 °C - 600 °C**
- Fluidization technology necessary due to **low heat conductivity**
- **Characterization of storage material** breakage throughout storage cycles
- Significant influence on **fluidization properties** needs to be and is **accessed experimentally**

Freeboard and off-gas-system of the pilot-scale reactor FluBEStoR

Thank you for your attention!

Leander Morgenstern, M.Sc.

leander.morgenstern@tum.de

www.epe.ed.tum.de/en/es

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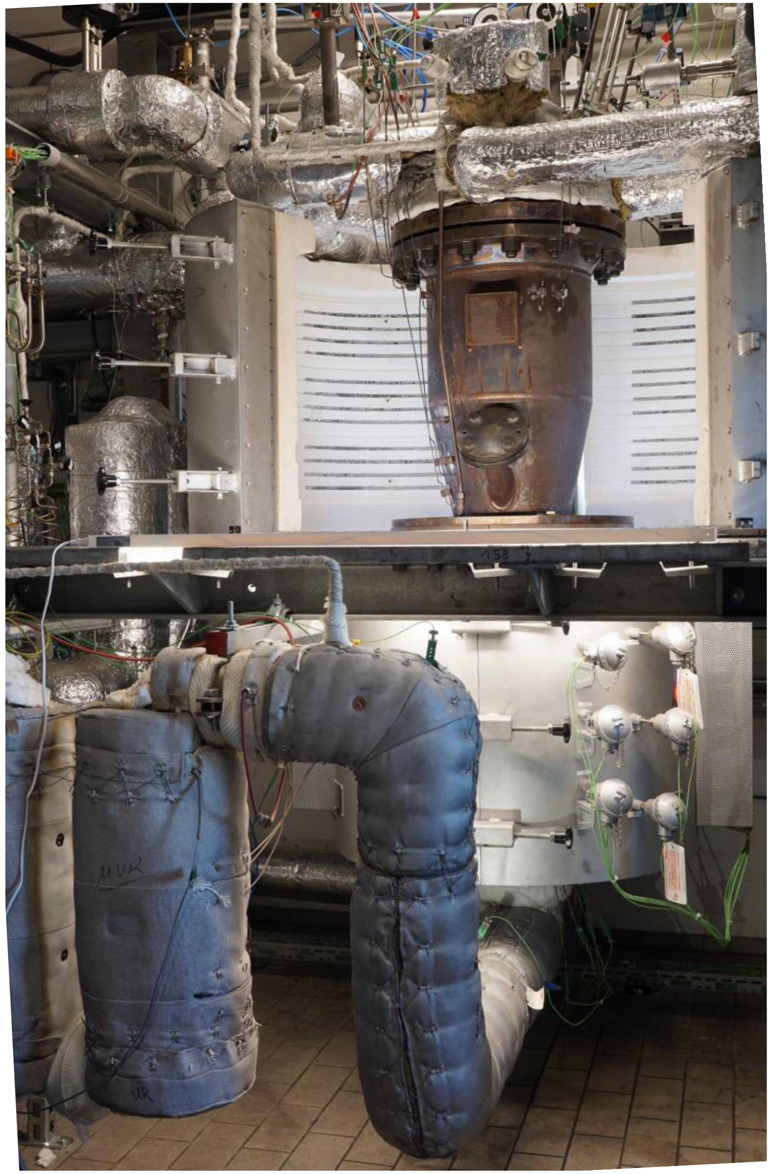

Pilot-Scale Reactor FluBEStoR