Evaluation of 1 MW\textsubscript{th} long-term pilot testing of the carbonate looping process

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Outline

- Introduction
- Experimental
- Results
- Conclusion
Introduction

Process scheme

- Reversible reaction: 
  \[ \text{CaO} + \text{CO}_2 \xleftrightarrow{} \text{CaCO}_3 \]
- Sorbent = limestone: cheap, abundant, non-toxic, environmentally friendly
- Utilization of heat at high temperature (→ highly efficient steam cycle)
- Challenges:
  a) Attrition (loss of fines)
  b) Deactivation of CaO

**CARBONATOR**

- Temperature: \( T = 650 \, ^\circ\text{C} \)
- Reaction: \( \text{CO}_2 + \text{CaO} \rightarrow \text{CaCO}_3 + \text{Heat} \)

**CALCINER**

- Temperature: \( T = 900 \, ^\circ\text{C} \)
- Reaction: \( \text{CaCO}_3 + \text{Heat} \rightarrow \text{CO}_2 + \text{CaO} \)

Flue gas from power plant

Depleted flue gas

Make-up

Flue gas from power plant

\[ \text{CO}_2 \] to purification and compression

Purge

Recirculated \[ \text{CO}_2 \]

Coal

\[ \text{O}_2 \] (from ASU)
1 MW_\text{th} pilot plant

Reactors

<table>
<thead>
<tr>
<th></th>
<th>Carbonator</th>
<th>Calciner</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner diameter</td>
<td>600 mm</td>
<td>400 mm</td>
</tr>
<tr>
<td>Outer diameter</td>
<td>1.3 m</td>
<td>1.0 m</td>
</tr>
<tr>
<td>Height</td>
<td>8.7 m</td>
<td>11.4 m</td>
</tr>
</tbody>
</table>

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1 MW\textsubscript{th} pilot plant

Configuration
1 MW<sub>th</sub> pilot testing
Steady-state operation

\[ T_{\text{carb,avg}} = 655 \, ^\circ\text{C}, \quad W_{S,\text{carb}} = 550 \, \text{kg/m}^2, \quad LR = 17 \]

\[ E_{\text{carb}} = 70 \% \]

\[ X_{\text{sulph}} \quad X_{\text{carb}} \]

\[ 0.02 \quad 0.04 \quad 0.06 \]

\[ 0.002 \quad 0.004 \quad 0.006 \quad 0.008 \]

\[ 0 \quad 0.02 \quad 0.04 \quad 0.06 \quad 0.08 \quad 0.1 \quad 0.8 \quad 1 \quad 1.6 \quad 2.4 \quad 3.2 \quad 4 \]

\[ 0 \quad 5 \quad 10 \quad 15 \quad 20 \quad 25 \quad 30 \quad 35 \quad 40 \quad 45 \quad 50 \quad 55 \quad 60 \quad 65 \quad 70 \quad 75 \quad 80 \quad 85 \]

Time [h]
Oxy-calcination, $T_{\text{calc,avg}}=860$ °C, pulv. lignite
1 MW<sub>th</sub> pilot testing

Steady-state operation

Oxy-calcination, $T_{\text{calc,avg}}=860$ °C, pulv. lignite

- Higher temperatures in riser region $900 – 930$ °C
  - Required for full sorbent calcination

- Lower temperatures in bottom region $840 – 900$ °C
  - Incoming cold sorbent from carbonator
1 MW$_{th}$ pilot testing
CO$_2$ mass balance closure

CO$_2$ removed from the gas phase
= CaCO$_3$ formed in the circulating solids

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Average reactor temperature

- Maximum capture at equilibrium possible
- Influence of flue gas conditions (wet/dry)
- Highest capture rates at approx. 650/670 °C average carbonator temperature achievable

Equilibrium Curve for 14 % \( \text{vol} \) CO\(_2\) inlet concentration

- Wet flue gas
- Dry flue gas
1 MW\textsubscript{th} pilot testing

- Hard coal; Messinghausen (d\textsubscript{50} \sim 180 \mu m)

![Graph showing particle size distribution and various process stages such as Filters, Fresh Limestone, Loop Seals, and Separation due to Carbonator.](image)
1 MW$_{th}$ pilot testing

**PSD**

- Hard coal; Istein ($d_{50}$ ~ 220 µm)

![Graph showing particle size distribution](image)

Accumulate through fraction [-]

Particle size [µm]

- Filters
- Fresh Limestone
- Loop Seals
- Attrition
Fuel particle size

- Colombian hard coal
  - Sulphur 0.6 \%_{mass}
  - Ash 14.3 \%_{mass}
  - \(d_{50}\) 45 \(\mu m\) / 1,500 \(\mu m\)

- Comparable make-up rate

- Messinghausen limestone

\[
\begin{align*}
\text{Mass fraction [\% mass]} & \\
\text{d}_{50} = 45 \text{ mm} & \\
\text{d}_{50} = 1,500 \text{ mm} & \\
\text{ash} & \\
\text{CaSO}_4 &
\end{align*}
\]
### Fuel type

<table>
<thead>
<tr>
<th></th>
<th>HC</th>
<th>LG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Ash</td>
<td>5.9</td>
<td>1.7</td>
</tr>
<tr>
<td>(d_{50})</td>
<td>45</td>
<td>35</td>
</tr>
</tbody>
</table>

- Comparable make-up rate
- Messinghausen limestone

![Graph showing mass fraction of ash and CaSO₄](image)

**Hard coal**

- Sulphur: 0.3 g/MJ
- Ash: 5.9 g/MJ
- \(d_{50}\): 45 \(\mu m\)

**Lignite**

- Sulphur: 0.1 g/MJ
- Ash: 1.7 g/MJ
- \(d_{50}\): 35 \(\mu m\)
1 MW$_{th}$ pilot testing

Summary

- Successful long-term pilot testing under realistic operating conditions
  - Steady-state testing periods up to 70 h with chemical stability in operating points
  - High CO$_2$ capture rates during long-term tests ($E_{\text{carb}} > 80\%$, $E_{\text{total}} > 90\%$)
  - Realistic operating conditions

- Influence of different fuel types and their preparations
  - Fuel composition influences amount of inactive material (gypsum, ash)
  - Fuel preparation and reactor design have to be harmonized

- Particle size distribution depending on limestone and setup

- Resilient scale-up data acquired
Questions?

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300\text{ kW}_\text{th} \text{ indirectly heated CaL pilot plant}

1\text{ MW}_\text{th} \text{ CaL pilot plant}

CaL/CLC test facility at TUD
1 MW\textsubscript{th} pilot testing

TGA

- Carbonator inlet samples from two different campaigns
- Two different operation conditions; difference only the used limestone
- Influence of steam on activity
- Messinghausen has an higher activity than Istein due to its higher porosity
1 MW\textsuperscript{th} pilot plant

Impressions

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1 MW\textsubscript{th} pilot testing

Summary

- 4 comprehensive SCARLET test campaigns
  - Hard coal: September/October 2015 (#1) & January/February 2016 (#3)
  - Lignite: November/December 2016 (#2) & March/April 2016 (#4)
- >1,200 hours in CO\textsubscript{2} capture mode
- Continuous long-term operation in steady-state

<table>
<thead>
<tr>
<th>№</th>
<th>Fuel type</th>
<th>Sorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1a</td>
<td>hard coal</td>
<td>coarse</td>
</tr>
<tr>
<td>#1b</td>
<td>hard coal</td>
<td>pulverized</td>
</tr>
<tr>
<td>#2</td>
<td>lignite</td>
<td>pulverized</td>
</tr>
<tr>
<td>#3a</td>
<td>hard coal</td>
<td>pulverized</td>
</tr>
<tr>
<td>#3b</td>
<td>hard coal</td>
<td>coarse</td>
</tr>
<tr>
<td>#4a</td>
<td>lignite</td>
<td>pulverized</td>
</tr>
<tr>
<td>#4b</td>
<td>lignite</td>
<td>coarse</td>
</tr>
</tbody>
</table>

Messinghausen: d\textsubscript{50} \approx 180 \textmu m
Istein: d\textsubscript{50} \approx 215 \textmu m
1 MW\textsuperscript{th} pilot testing  
**Carbonator parameter**

Thermogravimetric analysis (TGA) of sorbent from pilot tests

\[ X_{\text{ave}} = \frac{\text{mol}_{\text{CaCO}_3}}{\text{mol}_{\text{Ca}}} \]

- Reaction in the fast regime predominant
- TGA testing w and w/o H\textsubscript{2}O started
- Strong influence of steam presence
Gas analysis for CO$_2$ profile

Exemplary CO$_2$ reactor concentration profile

CO$_2$ conc. [vol,dry]

Relative reactor radius $r/R$

Gas extraction probe
**1 MW\textsubscript{th} pilot testing**

**Active Space Time**

\[
F_{\text{CO}_2} \times E_{\text{carb}} = n_{\text{Ca}} \times \left( \frac{dX_{\text{carb}}}{dt} \right)
\]

\[
E_{\text{carb}} = \frac{n_{\text{Ca}}}{F_{\text{CO}_2}} \times \left( \frac{dX_{\text{carb}}}{dt} \right)
= \frac{n_{\text{Ca}}}{F_{\text{CO}_2}} f_{\text{active}} k_s X_{\text{ave}} (v_{\text{CO}_2} - v_{\text{eq}})
\]

\[
\tau_{\text{active}} = \frac{n_{\text{Ca}}}{F_{\text{CO}_2}} f_{\text{active}} X_{\text{ave}}
\]

\[
E_{\text{carb}} = k_s \tau_{\text{active}} (v_{\text{CO}_2} - v_{\text{eq}})
\]

\[
\left( \frac{dX_{\text{carb}}}{dt} \right) = k_s X_{\text{ave}} (v_{\text{CO}_2} - v_{\text{eq}})
\]

\[
f_{\text{active}} = 1 - e^{-\frac{t^*}{n_{\text{Ca}}/F_{\text{Ca}}}}
\]

\[
t^* = \frac{X_{\text{ave}} - X_{\text{calc}}}{(dX/dt)_{\text{reactor}}} = \frac{X_{\text{ave}} - X_{\text{calc}}}{k_s X_{\text{ave}} (v_{\text{CO}_2} - v_{\text{eq}})}
\]