Demonstration of Calcium Looping CO\textsubscript{2} capture for cement plants at semi industrial scale

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Fundamentals of Calcium Looping CO₂ capture from cement plants
Calcium Looping CO$_2$ capture

$$CaCO_3 \rightleftharpoons CaO + CO_2 \quad \Delta_R H = +178.2 \frac{kJ}{mol}$$

- Solid sorbent cycle process
- CO$_2$ capture by cyclic calcination and carbonation of CaCO$_3$/CaO
- Efficient energy recuperation because of high temperature level
Calcium Looping CO$_2$ capture process

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\]

Definitions

- Sorbent activity: \( X_{avg} = \frac{M_{CO_2}}{M_{Sorbent}} \)
- Make-Up ratio: \( \frac{\dot{N}_{CaO,fresh}}{\dot{N}_{CO_2,Carb,in}} \)
- Looping ratio: \( \frac{\dot{N}_{CaO,trans}}{\dot{N}_{CO_2,Carb,in}} \)
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Clinker manufacturing process

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]

- Cement production constitute ~5-8% of global anthropogenic CO\(_2\) emissions
- CO\(_2\) emissions:
  - 60% by raw materials
  - 40% by fuel
- Synergies between clinker manufacturing and CaL CO\(_2\) capture by solid and energy integration possible
Tail-end Calcium Looping CO₂ capture from cement plants

- Easy retrofitability
- CO₂ capture by carbonation and oxy-fuel calcination

Increasing integration level (X_{IL}) leads to:
- Increase make-up to CaL system
- Increase sorbent activity
- Reduced CO₂ load (Cal oxy-fuel calcination)
- Overall fuel consumption increases
- Electricity production (CO₂ neutral)

\[ X_{IL} = \frac{\dot{N}_{CaO,cal}}{\dot{N}_{CaO,clinker}} \]
Methodology / experimental set-up
Fluidized Bed Research Facilities – MAGNUS

200 – 230 kW<sub>th</sub> pilot scale facility (3 reactors)

Bubbling bed reactor (1x)
- diameter: 330 mm
- height: 6 m

Circulating fluidized bed reactor (2x)
- diameter: 200 mm
- height: 10 m

Possible reactor configuration: CFB-CFB, BFB-CFB

Hot flue gas recirculation for oxy-fuel combustion

Gas analysis (CO<sub>2</sub>, O<sub>2</sub>, CO, SO<sub>2</sub>, NO<sub>x</sub>, CH<sub>4</sub>, H<sub>2</sub>, C<sub>x</sub>H<sub>y</sub>)

No electrical heating (heated by combustion)
Experimental conditions

- CO₂ flue gas concentration: 15 – 33 vol%
- Volume Flow: up to 180 Nm₃/h (~ 0.1 % of cement plant flue gas)
- Make-up flow/ratio: up to 50 kg/h / 1 mol_{CaO}/mol_{CO₂}

<table>
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<tr>
<th>Limestone</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Others</th>
<th>CO₂</th>
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<tbody>
<tr>
<td>Western Germany</td>
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<td>0.4</td>
<td>1.2</td>
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*detemined by TIC

<table>
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<tr>
<th>Coal</th>
<th>C</th>
<th>H</th>
<th>O*</th>
<th>N</th>
<th>S</th>
<th>Ash</th>
<th>H₂O</th>
<th>H_i</th>
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<tbody>
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<td>Columbian I</td>
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<td>4.9</td>
<td>12.3</td>
<td>1.9</td>
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<td>Columbian II</td>
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<td>5.3</td>
<td>14.4</td>
<td>1.6</td>
<td>1.1</td>
<td>9.13</td>
<td>7.4</td>
<td>28.09</td>
</tr>
</tbody>
</table>

wf: water free; waf: water and ash free; ad: air dried

*calculated by difference
Results and discussion
Results and discussion – Sorbent CO₂ carrying

- Sorbent capacity depends strongly on make-up ratio ("sorbent age")
- At lower make-up ratios sorbent activity of carbonator samples significantly higher than calciner samples
- Hydration during cooling of samples higher for carbonator samples indicates structural during carbonation
Results and discussion – CO₂ capture performance

- Higher CO₂ concentration at lower integration levels leads to reduced looping ratios
- Limitation of CO₂ capture by incoming amount of (active) CaO
  - CO₂ capture increases with looping ratio
  - Stronger improvement of CO₂ capture with looping ratio at higher integration level
Results and discussion – CO₂ capture performance

- CO₂ capture up to 98 % achieved due to high sorbent activity
- Limitation of CO₂ capture by calcination-carbonation equilibrium at higher integration levels
- No influence on CO₂ capture efficiency at higher integration levels (i.e. make-up ratios)

![Carbonator CO₂ capture efficiency vs looping ratio at enhanced integration levels](image-url)
Conclusion
Conclusion

• Synergies between clinker manufacturing and Calcium Looping CO$\text{}_2$ capture due to use of common feedstock (CaCO$_3$)

• Different integration levels (15% to 65%) for a tail-end Calcium Looping cement plant system has been assessed

• Calcium Looping CO$\text{}_2$ capture for cement application has been investigated at IKF’s 200 kW$_{th}$ Calcium Lopping pilot plant achieving CO$\text{}_2$ capture efficiencies up to 98%

• Sorbent’s CO$\text{}_2$ carrying capacity improves with increasing integration level (i.e. make-up)

• For lower integration levels a significant improvement of CO$\text{}_2$ capture with increasing looping ratio was found, while for higher integration levels the CO$\text{}_2$ capture was limited by the carbonation equilibrium
Thank you for your attention!

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www.sintef.no/cemcap
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Thank you!

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