SECOND GENERATION CALCIUM LOOPING SYSTEM WITH BIOMASS COMBUSTION IN THE CALCINER

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OUTLINE

Description of standard and 2nd generation CaL systems

Process simulation assumptions

Performance results and conclusions
Standard post-combustion CaL process

Benefits of Ca-looping

- Low energy penalty / low cost per ton CO₂ captured
- Low cost sorbent precursor
- Purge of CaO: synergies with cement industry and others (i.e. desulfurization)
- Pre-treatment of flue gas no needed (SO₂ co-capture)
- Benefits and limitations of large scale CFBCs (including oxy-CFB)
Standard post-combustion CaL process

STANDARD Ca LOOPING CONFIGURATION:
✓ Oxy-fuel combustion in the calciner
✓ Natural limestone used a sorbent precursor
✓ Circulating fluidized bed combustors

Disadvantages of oxy-fuel combustion in the calciner:
- Energy penalty due to oxygen production (~200 kWhe/tO₂)
- Large investment cost
- Low flexibility to load changes

Improvements of Ca-looping:
- Advanced process configurations without oxy-combustion
  (i.e. Indirect heat transfer through metallic walls/heat pipes, high temperature solid heat carriers ...)
- Second generation CaL processes (Reducing heat demand in the calciner)
**HEAT DEMAND IN THE CALCINER**

- Calcination of CaCO$_3$
- Sensible heat of recycled CO$_2$
- Sensible heat of circulating solids

**Minimize or reduce CO$_2$-recycle:**
- 20% REDUCTION by increasing oxygen contents up to 80%v.
- Less oxygen needed (less OPEX)
- Smaller ASU and calciner sizes (less CAPEX)

**Effect of O$_2$ in the comburent on calciner heat demand in a CaL standard scheme**

CaO$_2$: Calcium looping CO$_2$ capture technology with extreme oxy-coal combustion conditions in the calciner
European Union RFCS project: 2014-2017

Demonstration in a pilot (2-3 MW$_{th}$) of ultra-rich O$_2$ calcination technology

*$T_{carb}=650^\circ$C, $T_{calc}=910^\circ$C,$X_{ave}=0.15$, $X_{carb}=0.11$; $T_{comburent}=300^\circ$C
Second generation post-combustion CaL process

HEAT DEMAND IN THE CALCINER

- Calcination of CaCO₃
- Sensible heat of recycled CO₂
- Sensible heat of circulating solids

- Increase the temperature of the solids entering into the calciner
- Improve the activity of the solid

Improve sorbent activity by means of recarbonation:
- No energy penalty associated
- No influence on sorbent mechanical properties
- No need of additional reagents in the process
- Less limestone consumption (less OPEX)

The sorbent activity increases up to 8-10 net points due to recarbonation

Diego et al. 2016. Experimental testing of a sorbent reactivation in La Pereda 1.7 MW_th calcium looping pilot plant Int. J. Greenhouse Gas Control, 50, 14-22
Second generation post-combustion CaL process

2^{ND} GENERATION Ca LOOPING CONFIGURATION:
- Pure oxygen used in the calciner
- Sorbent improvement by means of recarbonation

- Contribute to negative CO\textsubscript{2} emission factors
- Avoid typical operational problems (corrosion and deposition in heat exchange surfaces, reduction of unburnt emissions, minor organic emissions ultimately captured in the CPU...)}
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Description of standard and 2nd generation CaL systems

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Process modeling – General assumptions

STANDARD & 2nd GENERATION Ca LOOPING CONFIGURATIONS

Existing CFB air-fired SC plant
✓ \( \eta_{net} = 43.3\% \)
✓ 1000 MW\(_{th}\) fuel input
✓ FG with 14\% CO\(_2\)

CARBONATOR & CALCINER
✓ Reactor models implemented
✓ RPM kinetic model for the carbonation reaction
✓ CO\(_2\) carrying capacity decay law (\( \rightarrow X_{ave} \))
✓ 99 \% SO\(_2\) capture efficiency

CALCINER
✓ 95\% calcination efficiency
✓ 3.5\% O\(_2\) at outlet

Power plant

Carbonator

Flue gas with low CO\(_2\) to stack

Calciner

CO\(_2\) recycle

Condensate

ASU

Oxygen

Air

Flue gas

Coal

Limestone

Purge

CO\(_2\)

Existing CFB air-fired SC plant

CPU

AIR SEPARATION UNIT
✓ 95\% O\(_2\) purity (Ar,N\(_2\))
✓ Consumption: 200 kWh/t\(_{O2}\)
Process modeling – General assumptions

**STANDARD & 2\textsuperscript{nd} GENERATION Ca LOOPING CONFIGURATIONS**

- CO\textsubscript{2} COMPRESSION AND PURIFICATION UNIT
  - Single flash auto-refrigerated process
  - Vent gas containing 3-4% inlet CO\textsubscript{2}
  - \(\approx 115 \text{ kWh/ton}_{\text{CO}_2}\)

- Existing CFB air-fired SC plant
  - \(\eta_{\text{net}}=43.3\%\)
  - 1000 MW\textsubscript{th} fuel input
  - FG with 14% CO\textsubscript{2}

**CARBONATOR & CALCINER**
- Reactor models implemented
- RPM kinetic model for the carbonation reaction
- CO\textsubscript{2} carrying capacity decay law \((\rightarrow X_{\text{ave}})\)
- 99 % SO\textsubscript{2} capture efficiency

<table>
<thead>
<tr>
<th>Power plant</th>
<th>Coal</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carb</td>
<td>CO\textsubscript{2} for transport</td>
<td>20 bar 30°C</td>
</tr>
<tr>
<td>Drier</td>
<td>Vent gas</td>
<td>-54°C</td>
</tr>
<tr>
<td>Multi-flow HX</td>
<td>Knock-out drum</td>
<td>-45°C</td>
</tr>
<tr>
<td>IC compressor</td>
<td>pump</td>
<td>89 bar</td>
</tr>
<tr>
<td>IC compressor</td>
<td>150 bar</td>
<td>23°C</td>
</tr>
</tbody>
</table>

**AIR SEPARATION UNIT**
- 95% O\textsubscript{2} purity (Ar,N\textsubscript{2})
- Consumption: 200 kWh/t\textsubscript{O2}

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Romano, M.C. *Int. J. Greenhouse Gas Control*, 2013, 18: 57-97

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[Diagram of process flow with labels and symbols]
Process modeling – General assumptions

2ND GENERATION Ca LOOPING CONFIGURATION

Flue gas with low CO₂ to stack

Carbonator

Re-carbonator

Calciner

Purge

Limestone

Oxygen

Biomass

CO₂ recycle

Condensate

Power plant

Coal

Air

Flue gas

Air

Oxygen

ASU

CPU

RE-CARBONATOR

- CaCO₃ content: X_{carb,R} = 0.02 + X_{ave,R}
- Excess CO₂ [i.e. +50% over that needed for (X_{carb,R} - X_{ave,R})]

Diego et al. 2014. *I&EC Research* 53, pp. 10059 - 10071
HEAT RECOVERY IN THE Ca LOOPING SCHEMES

Flue gas with low CO₂ to stack

T_{carb} – 100°C

CO₂

Calciner

T_{calc} – 350°C

350-60°C

CO₂ recycle

25-200°C

Condensate

ASU

Air

Oxygen

Coal

Limestone

Purge

T_{calc} – 150°C

Power plant

Air-fired SC plant 433 MW

Coal

Air

Energy

Flue gas
HEAT RECOVERY IN THE Ca LOOPING SCHEMES

USC STEAM CYCLE

✓ Heat recovered in the EVA, ECO, SH, RH
✓ Some of the HP & LP FWH replaced

Romano, M.C. Int. J. Greenhouse Gas Control, 2013, 18: 57-97
Process modeling – Operating conditions

STANDARD CaL SCHEME

- Carbonator CO₂ capture efficiency: 90%
- Carbonator temperature: 650°C
- Calciner temperature: 910°C
- Fuel in the calciner: high-rank coal (0.7% S, 3% H₂O and 6% ash; LHV=33 MJ/kg)
- Oxygen content in the oxidant: 40%v.
- Ratio F₀/F₃: 0.12 (0.6 kg /kg coal existing PP)
- CO₂ carrying capacity decay law typical for limestone (Xₙ ≈ 7-8%)

SECOND GENERATION CaL SCHEME

- Carbonator CO₂ capture efficiency: 80%
- Carbonator temperature: 690°C
- Calciner temperature: 890°C
- Fuel in the calciner: woody biomass (0.02% S, 15% H₂O and 1% ash; LHV=16 MJ/kg)
- Oxygen content in the oxidant: 95%v.
- Ratio F₀/F₃: 0.05 (0.3 kg /kg coal existing PP)
- Improved CO₂ carrying capacity decay law due to recarbonation (Xₙ ≈ 16-17%)

OUTLINE

- Description of standard and 2nd generation CaL systems
- Process simulation assumptions
- Performance results and conclusions
Simulation results

<table>
<thead>
<tr>
<th></th>
<th>STANDARD CaL</th>
<th>SECOND GENERATION CaL</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maximum CO₂ carrying capacity (X&lt;sub&gt;ave&lt;/sub&gt;) [%]</strong></td>
<td>12.5</td>
<td>19.9</td>
</tr>
<tr>
<td><strong>Solid circulation at carbonator inlet [kg/m²·s]</strong></td>
<td>6.4</td>
<td>3.4</td>
</tr>
<tr>
<td><strong>CaSO₄ / Ash content at carbonator inlet [%wt]</strong></td>
<td>7.3 / 5.1</td>
<td>5.2 / 2.5</td>
</tr>
<tr>
<td><strong>Kg limestone/kg total fuel to the plant [-]</strong></td>
<td>0.35</td>
<td>0.14</td>
</tr>
<tr>
<td><strong>Global CO₂ capture ratio (inc. CPU) [%]</strong></td>
<td>92.6</td>
<td>85.4</td>
</tr>
<tr>
<td><strong>Heat demand in the calciner (LHV-based) [MW]</strong></td>
<td>976.1</td>
<td>620.3</td>
</tr>
<tr>
<td><strong>Fraction of energy to the calciner [%]</strong></td>
<td>49.1</td>
<td>38.3</td>
</tr>
<tr>
<td><strong>Steam cycle net electric output [MWₑ]</strong></td>
<td>434.0</td>
<td>280.1</td>
</tr>
<tr>
<td><strong>Carbonator &amp; calciner fans [MWₑ]</strong></td>
<td>-19.0</td>
<td>-17.7</td>
</tr>
<tr>
<td><strong>ASU [MWₑ]</strong></td>
<td>-57.4</td>
<td>-39.0</td>
</tr>
<tr>
<td><strong>CO₂ compression and purification unit [MWₑ]</strong></td>
<td>-71.0</td>
<td>-56.0</td>
</tr>
<tr>
<td><strong>Net plant electric efficiency [%]</strong></td>
<td>36.7</td>
<td>37.0</td>
</tr>
<tr>
<td><strong>Specific CO₂ emissions [kg&lt;sub&gt;CO₂&lt;/sub&gt;/MWhₑ]</strong></td>
<td>66.5</td>
<td>134.0</td>
</tr>
<tr>
<td><strong>CO₂ emission factor [kg&lt;sub&gt;CO₂&lt;/sub&gt;/MWhₑ]</strong></td>
<td>66.5</td>
<td>-219.4</td>
</tr>
<tr>
<td><strong>Cost of Electricity (COE) [$/MWhₑ]</strong></td>
<td>80.0</td>
<td>78.8</td>
</tr>
<tr>
<td><strong>Avoided Cost (AC) [$/ton CO₂ avoided]</strong></td>
<td>34.8</td>
<td>23.1</td>
</tr>
</tbody>
</table>

Conclusions

- An optimized Ca-Looping system (2\textsuperscript{nd} generation) including sorbent reactivation by recarbonation and a pure oxy-fuel combustion in the calciner has been simulated.
- Heat demand in the calciner can be significantly reduced in the 2\textsuperscript{nd} generation Ca-Looping system with respect to standard Ca-Looping configuration.
- Limestone consumption can be reduced by more than 50\% compared to a standard Ca-Looping system.
- The electric efficiency for the 2\textsuperscript{nd} generation Ca-Looping system is slightly improved compared to the standard Ca-Looping system.
- A negative CO\textsubscript{2} emission factor results if biomass is used as fuel in the calciner, which results in a great reduction of the CO\textsubscript{2} avoided costs.
SECOND GENERATION CALCIUM LOOPING SYSTEM WITH BIOMASS COMBUSTION IN THE CALCINER

THANK YOU FOR YOUR ATTENTION
Detailed studies by CSIC

Effect of recarbonation on $X_{ave}$ – TG experiments

The residual activity doubles during 5 min in pure CO$_2$

$X_N = a_1 f_1^{N+1} + a_2 f_2^{N+1} + b$

Maximum average CO$_2$ carrying capacity

$X_{ave} = \sum_{N=1}^{N=\infty} r_N \cdot X_N = (F_0 + F_{Ca} r_0) f_{calc} \left( \frac{a_1 f_1^2}{F_0 + F_{Ca} f_{carb} f_{calc} (1 - f_1)} + \frac{a_2 f_2^2}{F_0 + F_{Ca} f_{carb} f_{calc} (1 - f_2)} + \frac{b}{F_0} \right) - \frac{F_S}{F_0}$


Pilot experiments with recarbonation

The sorbent activity increases by 8-10 net points thanks to recarbonation

Grasa et al. 2014. I&EC Research 28, pp. 4033 - 4042
Cost analysis

Economic parameters used:

\[ COE = \frac{TCR \cdot FCF + FOM}{CF \cdot 8760} + VOM + \frac{FC}{\eta_{Plant}} \]

\[ AC = \frac{COE_{capture} - COE_{reference}}{(CO_2/kWh_e)_{reference} - (CO_2/kWh_e)_{capture}} \]

Total capital requirements of whole CaL system

\[ TCR_{Cal} = (TCR_{reference} + TCR_{CPU}) \cdot (1 - H_{CaL}/H_{total}) + (TCR_{Oxy-CFB} + TCR_{Recarb} + TCR_{CC}) \cdot H_{CaL}/H_{Total} \]

Economic assumptions

<table>
<thead>
<tr>
<th>Economic assumptions</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCR_{ref} ($/kWe)</td>
<td>1900</td>
</tr>
<tr>
<td>TCR_{oxy} ($/kWe)</td>
<td>2800</td>
</tr>
<tr>
<td>TCR_{CC} ($/kWe)</td>
<td>280</td>
</tr>
<tr>
<td>TCR_{CPU} ($/kWe)</td>
<td>180</td>
</tr>
<tr>
<td>TCR_{RECARB} ($/kWe)</td>
<td>280</td>
</tr>
<tr>
<td>Fuel costs ($/GJ)</td>
<td>3</td>
</tr>
<tr>
<td>Limestone costs ($/t)</td>
<td>10</td>
</tr>
<tr>
<td>Capacity factor</td>
<td>0.85</td>
</tr>
</tbody>
</table>