Experimental Characterization of Reactor Operation for the Calcium Looping CO$_2$ Capture process

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1. The 10 kW\textsubscript{th} Calcium Looping DFB facility

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  - C:\\ F B B R e g e n e r a t o r \ (> 900 \, ^{\circ}C) \\
  - (3.2 \text{ m, } \phi 114 \text{ mm})
  - \text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2 \\
  - \Delta H = +178 \text{ kJ/mol}

- 
  - \text{CFB Carbonator } 600-700 \, ^{\circ}C \\
  - (12.4 \text{ m, } \phi 71 \text{ mm})
  - \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \\
  - \Delta H = -178 \text{ kJ/mol}

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  - \text{C-fuel/ O}_2 \text{ & CO}_2

- 
  - \text{Power Plant flue gas (10%-15% vol. CO}_2\)
2. Experimental parameters

**Regenerator**
1. Temperature: 850 - 900°C
2. **O₂** inlet concentration: 21 - 40 %
3. **Partial CO₂** pressure: < 0.3 bar
   **Sorbent Pre-calcination:** For 1h at 900 °C

**Carbonator**
1. Temperature: 630-700 °C
2. **CO₂** Inlet concentration: 11-15%
3. Calcium looping ratio (F\(_{Ca}\)/F\(_{CO₂}\)): 3-23
4. **Carbonator contacting mode:**
   - Circulating Fluidized Bed (CFB)
     - Velocity: 4-6 m/s
   - Bubbling Fluidized Bed (BFB)
     - Velocity: 0.5-1.2 m/s
5. **Two limestones:** Swabian Alb A & B
6. **Two PSDs:** 0.1-0.3 mm & 0.3-0.6 mm
7. **Simplifications:** No **SO₂**, steam and sorbent make-up flow addition
3. Process Characterization
   a. Chemical sorbent degradation (theory)

   • Average grain & Sorbent particle regions:
     a. Sintered \((1-X_{\text{max}})\)
     b. Converted to CaCO\(_3\) \((X_{\text{carb}})\)
     c. Free active CaO \((f_a)\):
       \[
       f_a = X_{\text{max}} - X_{\text{carb}}
       \]

   • The maximum carbonation conversion \((X_{\text{max}})\) decays with carbonation-calcination cycles \((N)\) due to sintering

   • An equivalent concept to cycles for continuous conditions is the cumulative sorbent specific CO\(_2\) loading \(L(t)_{\text{CO2}}\):

   \[
   L(t)_{\text{CO2}} = \int \frac{F_{\text{CO2}} E_{\text{CO2}} dt}{n_{\text{Ca,total}}}
   \]

   \(F_{\text{CO2}}\): Inlet molar flow of CO\(_2\) to carbonator (mol/h)
   \(E_{\text{CO2}}\): CO\(_2\) capture efficiency (-)
   \(n_{\text{Ca,total}}\): Total Ca mol in the whole system
3. Process Characterization

a. Chemical degradation (results)

- The $X_{\text{max}}$ decreases with increasing CO$_2$ loading ($L(t)_{\text{CO}_2}$, mol$_{\text{CO}_2}$/mol$_{\text{CaO}}$)

- Regarding low sorbent CO$_2$ loading, i.e. $L(t)_{\text{CO}_2} < 1.5$ mol$_{\text{CO}_2}$/mol$_{\text{CaO}}$:
  - $X_{\text{max}}$ measured is 12-18 %
  - $X_{\text{max}} > 30$ % was expected from thermobalance curve

  ⇒ Reason may be that pre-calcination (residence time: 1h) causes sintering

- Regarding high CO$_2$ loading values of i.e. $L(t)_{\text{CO}_2} > 3$ mol$_{\text{CO}_2}$/mol$_{\text{CaO}}$:
  - Both decay curves match

- The $L(t)_{\text{CO}_2}$ can characterize the sorbent decay for the given conditions

CFB carbonator, $T_{\text{carb}} = 650$ °C, inlet CO$_2$ conc. = 15 %vol., BFB regenerator, $T_{\text{reg}} = 900$ °C, $P_{\text{CO}_2} < 0.3$ bar, Swabian Alb A
3. Process Characterization

b. Regenerator operation (theory)

What is the metric for regenerator performance?

- The regenerator efficiency:
  \[ \eta_{\text{reg}} = \frac{X_{\text{carb}} - X_{\text{calc}}}{X_{\text{carb}}} \]

- When \( X_{\text{reg}} = 0 \) → \( \eta_{\text{reg}} = 1 \) and when \( X_{\text{carb}} = X_{\text{reg}} \) → \( \eta_{\text{reg}} = 0 \)

Why is it important?

- Through carbonator mass balance:
  \[ \frac{E_{\text{CO}_2}}{X_{\text{carb}}} = \frac{F_{\text{Ca}}}{F_{\text{CO}_2}} \eta_{\text{reg}} \]

- A kinetic situation \( (E_{\text{CO}_2}, X_{\text{carb}}) \) is possible for a constant \( F_{\text{Ca}}/F_{\text{CO}_2} \eta_{\text{reg}} \)

✓ The calcium looping ratio \( (F_{\text{Ca}}/F_{\text{CO}_2}) \) needed is minimized when \( \eta_{\text{reg}} = 1 \)!
3. Process Characterization

b. Regenerator operation (results)

- $X_{\text{carb}}$: carbonation conversion of solids entering the regenerator
- $r_{\text{reg}}$: the sorbent residence time

$\Rightarrow$ The regenerator efficiency ($\eta_{\text{reg}}$) decreases with increasing $X_{\text{carb}}/r_{\text{reg}}$

- At 900 °C and $P_{\text{CO}_2} < 0.3$ bar:
  - At $X_{\text{carb}}/r_{\text{reg}} < 2.5$ 1/h, then $\eta_{\text{reg}} > 90 \%$
  - At $X_{\text{carb}}/r_{\text{reg}} > 6$ 1/h, then $\eta_{\text{reg}} < 50 \%$

- Residence time > 3 min for any design needed
- The ratio $X_{\text{carb}}/r_{\text{reg}}$ characterizes the $\eta_{\text{reg}}$ for given temperature, partial pressure of CO$_2$
For constant temperature & inlet CO$_2$ concentration:

- The CO$_2$ capture efficiency is influenced by:
  - **The particle reaction rate:**
    \[
    \frac{dX_{\text{carb}}}{dt} \sim (X_{\text{max}} - X_{\text{carb}})^{2/3}
    \]
  - Dependant on:
    - The actual carbonation conversion ($X_{\text{carb}}$)
      - The $X_{\text{carb}}$ is inversely proportional to $F_{\text{Ca}}/F_{\text{CO}_2}$
    - The maximum carbonation conversion ($X_{\text{max}}$), dependant on $F_{0}/F_{\text{CO}_2}$
  - **The carbonator space time ($\tau$)**
    \[
    \text{Spacetime}(\tau) = \frac{\text{moles Ca in Carbonator}}{\text{moles CO}_2 / h \text{ entering the Carbonator}} = \frac{n_{\text{Ca}}}{F_{\text{CO}_2}} \text{ in h}
    \]
  - **Active space time combines $\tau$ and reaction rate:**
    \[
    \tau \text{ active} = \tau \cdot (X_{\text{max}} - X_{\text{carb}}) = \tau \cdot f_a
    \]
3. Process characterization

c. Carbonator operation (results)-The characteristic factor of active space time

- For a gas-solid contacting mode (BFB or CFB) the $\tau_{active}$ is:
  - the characteristic factor in regard to the carbonator $E_{CO2}/E_{eq}$

- For same active space time value:
  - CFB carbonators (INCAR-CSIC & IFK) result to better $E_{CO2}/E_{eq}$ values than the BFB carbonator.
    - Because the BFB carbonator exhibits bad gas-solid contacting

- All data sets exhibit a critical active space time value above which $E_{CO2}/E_{eq} > 90 \%$ is obtained
  - CFB carbonator→critical $\tau_{active}$ of 0.01 h, while the BFB carbonator→critical $\tau_{active}$ is 0.05 h

Inlet CO$_2$ conc. = 11-17 %, $T_{carb} = 634-660 \degree C$, $X_{max} = 0.08-0.23$

Source: Rodríguez et al., Energy Procedia, GHGT10 conference
4. Conclusions (I)

• Chemical sorbent degradation
  ✓ $L(t)_{CO2}$ characterizes sorbent decay at given conditions, during DFB mode operation
  – At $L(t)_{CO2} < 1.5 \, \text{mol}_{CO2}/\text{mol}_{CaO}$, the $X_{max}$ is 12-18 %, less than expected from TGA
  – At $L(t)_{CO2} > 3 \, \text{mol}_{CO2}/\text{mol}_{CaO}$, the $X_{max}$ decay follows the expected TGA curve

• Regenerator performance:
  – For constant regenerator temperature and partial pressure of CO$_2$:
    ✓ The ratio of the incoming sorbent carbonation conversion ($X_{carb}$) and regenerator residence time ($r_{reg}$) characterizes-defines the regeneration efficiency
      ✓ An $X_{carb}/r_{reg} < 2.5 \, 1/h$ leading to $\eta_{reg} > 90\%$ should be considered for any new design
4. Conclusions (II)

- **Carbonator performance**
  - The active space time ($\tau_{active}$) is the carbonator characteristic factor
    - $\Rightarrow$ BFB carbonator: $\tau_{active} > 0.05$ h $\rightarrow E_{CO2}/E_{eq} > 90 \%$
    - $\Rightarrow$ CFB carbonator: $\tau_{active} > 0.01$ h $\rightarrow E_{CO2}/E_{eq} > 90 \%$
    - Increasing $F_{Ca}/F_{CO2}$ increases carbonation reaction rate and therefore $E_{CO2}$
      - $\Rightarrow$ BFB carbonator: $F_{Ca}/F_{CO2} > 12 \rightarrow E_{CO2}/E_{eq} > 90 \%$
      - $\Rightarrow$ CFB carbonator: $F_{Ca}/F_{CO2} > 9 \rightarrow E_{CO2}/E_{eq} > 90 \%$

- **Future scaling up of the calcium looping process is feasible in Dual Fluidized Beds**
- **Scale up can be based on proposed characteristic factors**
Thank you for your attention.
Questions?
3. Process Characterization
Carbonator operation (results)-The key parameters of F\textsubscript{Ca}/F\textsubscript{CO2} and X\textsubscript{max}

- \( \frac{E_{CO2}}{E_{eq}} \) increases with \( F_{Ca}/F_{CO2} \)

\[ \Rightarrow \text{From mass balance: } \frac{X_{carb}}{F_{Ca}/F_{CO2}} \sim \frac{1}{F_{Ca}/F_{CO2}} \]

- The reaction rate is proportional to:

\[ \frac{dX_{carb}}{dt} \sim (X_{max} - X_{carb})^{2/3} \sim f_a^{2/3} \]

 Increasing \( F_{Ca}/F_{CO2} \) increases the carbonation rate & thus \( \frac{E_{CO2}}{E_{eq}} \)

**CFB carbonator, inlet \( CO_2 \) conc. = 11.3 %vol, \( T_{carb} = 650 \, ^\circ C \),
Swabian Alb A, dp= 0.3-0.6mm

- Even for very sintered particles (\( X_{max} = 8\text{--}10\% \)) when using a CFB carbonator:

\[ F_{Ca}/F_{CO2} > 9 \rightarrow \frac{E_{CO2}}{E_{eq}} > 90 \]

\[ \checkmark \text{ Similar to what has been considered in steam cycle-economical studies} \]
3. Process Characterization
Carbonator operation (results)-The key parameters of \( \frac{F_{\text{Ca}}}{F_{\text{CO}_2}} \) and \( X_{\text{max}} \)

- For the same \( \frac{F_{\text{Ca}}}{F_{\text{CO}_2}} \) value higher \( \frac{E_{\text{CO}_2}}{E_{\text{eq}}} \) is obtained for higher \( X_{\text{max}} \)

  ✔ Increasing \( X_{\text{max}} \) means increment of the carbonation rate & thus \( \frac{E_{\text{CO}_2}}{E_{\text{eq}}} \)

\[
\frac{dX_{\text{carb}}}{dt} \sim \left( X_{\text{max}} - X_{\text{carb}} \right)^{2/3} \sim f_a^{2/3}
\]

- When \( \frac{F_{\text{Ca}}}{F_{\text{CO}_2}} \), \( \frac{E_{\text{CO}_2}}{E_{\text{eq}}} \) are defined:

  \( \Rightarrow X_{\text{max}} \) is a function of \( \frac{F_0}{F_{\text{CO}_2}} \)

  (Hawthorne 2008; Rodríguez 2010)

CFB carbonator, inlet \( \text{CO}_2 \) conc. = 11.3 %vol, \( T_{\text{carb}} = 650 \degree \text{C} \),

Swabian Alb A, dp= 0.3-0.6mm

✔ \( \frac{E_{\text{CO}_2}}{E_{\text{eq}}} \) is set by the pair \( \frac{F_{\text{Ca}}}{F_{\text{CO}_2}} \) & \( X_{\text{max}} \)

✔ \( \frac{E_{\text{CO}_2}}{E_{\text{eq}}} \) of 90 % can be achieved by a combination:

  \( \Rightarrow \) of „low“ \( \frac{F_{\text{Ca}}}{F_{\text{CO}_2}} \) and „high“ \( X_{\text{max}} \), e.g.: (3, 15.8 %)

  \( \Rightarrow \) of „high“ \( \frac{F_{\text{Ca}}}{F_{\text{CO}_2}} \) and „low“ \( X_{\text{max}} \), e.g.: (16, 6.0 %)
3. Fluid-Dynamic Characterization

- The carbonator flow is defined by:
  - Pressure drop profile
  - Solid fraction profile: $\varepsilon = \frac{l}{\rho g \Delta}$

- The carbonator consists of 3 regions:
  - A dense region ($\varepsilon_s = 0.1-0.2$)
  - A lean region ($\varepsilon_s = 0.01-0.03$)
  - An exit region ($\varepsilon_{s \text{ exit}} > \varepsilon_{s \text{ lean}}$)

- The entrainment was found to be:
  - 15-20 kg/m²s

✓ The $\varepsilon_s$ values, gas-solid contacting modes of the regions influence axial CO₂ capture
✓ 80% of the CO₂ capture is within the dense region
✓ A cone valve was used to control the calcium looping rate between carbonator and regenerator

Carbonator riser, $u_0 = 5.75$ m/s, inventory = 3.9 kg, $\Delta P = 98$ mbar, $dp = 0.3-0.6$ mm
4. Kinetic Characterization
b. Mechanical degradation (results)

- **Moderate attrition behaviour:**
  - $d_{50}$ reduces from 340 µm to 325 µm after pre-calcination
  - Reason is the mild mechanical stresses of BFB pre-calcination
  - Further minor decrease to 300 µm after 8 h of operation
  - Reason may be that sintering during pre-calcination increases sorbent mechanical strength

![Particle Size Distribution](chart.png)

- **Cumulative size distribution**
  - psd after 8 h operation
  - psd after first calcination
  - psd of raw limestone

Particle Size Distribution of initial Swabian Alb A limestone, of material after pre-calcination with residence time of > 1 h and after 8 h of operation

- **Pre-calcination is considered industrially with a CaCO$_3$ pre-calciner**

- **The attrition rate found is 2 %wt./h, corresponding to a make-up flow $F_0/F_{CO2}$ of 0.04**
  - Since a make-up flow of $F_0/F_{CO2} > 0.08$ is feasible to maintain chemical activity: **Attrition values reported here are not a process limitation**