Development of Ca-Based Sorbent for High-Temperature CO₂ Capture

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PCCC2
Carbon Capture and Sequestration (CCS)

- >30% of anthropogenic carbon dioxide is released from large stationary energy sources such as fossil-fuel-fired power plants

- 15% CO₂ in flue gas – direct compression, liquefaction, transport, and storage are not economically competitive

- NEW TECHNOLOGIES: rely on concentrated CO₂ stream (>90% CO₂)

- SCENARIOS FOR CONCENTRATED CO₂:
  - pre-combustion CO₂ capture
  - oxy-fuel combustion (chemical looping)
  - post-combustion CO₂ capture (calcium looping)
Calcium Looping Cycles (CaLC)

Fuel $\rightarrow$ New or Existing Combustor $\rightarrow$ Carbonation Fluidized Bed $\rightarrow$ Heat

Air $\rightarrow$ N$_2$, CO$_2$ $\rightarrow$ N$_2$, H$_2$O, CO$_2 (<5\%)$

Fuel $\rightarrow$ CaCO$_3$ $\rightarrow$ CaO $\rightarrow$ CO$_2 (95\%)$

O$_2$ $\rightarrow$ Calcination Circulating Fluidized Bed $\rightarrow$ CO$_2 (95\%)$

CaCO$_3 \leftrightarrow$ CaO + CO$_2$
Calcium Looping

- **Advantages**
  - Inexpensive sorbent (limestone (CaCO₃), ~$10/ton)
  - The main components commercially available
  - Low projected costs for CO₂ capture (~$20/ton CO₂ avoided)
  - Environmentally benign

- **Challenges:**
  - Decay of CO₂ carrying activity (sintering)
  - Loss of sorbent due to attrition and elutriation
  - Sulphation of CaO-based sorbent
  - Need for pure oxygen (cryogenic separation from air is expensive)
  - Produced CO₂ stream is corrosive - purification required
**Sorbent Decay**

- **Sintering**: available surface area decreases

Changes in morphology:
- A large number of small pores are eliminated and a small number of large pores become even larger.
- Small intraparticle grains disappear and the CaO material is transferred to neighboring grains, making the large grains even larger.

Reactivation of CaO by Steam

- Significant increase in activity after reactivation
- Fragile sorbent particles after reactivation

Wu et al., Energy & Fuels, 24, 2768-2776, 2010
Pelletization

Binder: Calcium aluminate cements
- commercially available and relatively inexpensive
- improves mechanical strength
- improves CO\(_2\) carrying activity
Mechanical Pelletization

Spray water

Pellet size is controlled by an agitator (bottom) and a chopper (side)

Pelletizer

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Material for Pelletization

- CaO, Ca(OH)$_2$ powder
  - < 30 µm, from Graymont limestone

- Binder: CA-14 cement powder
  - 71% Al$_2$O$_3$, 28% CaO
Pellet sorbents performed better as compared to original limestone (same particle size)
Effect of Cyclic Conditions

- Pellet: Ca(OH)$_2$ + cement, 425-1000 µm
- Longer carbonation period and calcination in N$_2$ increase CO$_2$ uptake capacity

Carbonation: 25% CO$_2$, 800 °C, 30 min
Calcination: 100% N$_2$, 800 °C, 15 min

Carbonation: 20% CO$_2$, 700 °C, 30 min
Calcination: 100% CO$_2$, 950 °C, 5 min

100 °C steam, 5 min
Attrition Test

- 2-in dia. small bubbling fluidized bed
  - Sorbent size 425-1000 µm
  - 2-h test in air
  - Room temperature and 800 °C
- Extent of attrition (mass loss) and particle size distribution (PSD) were determined
Mass loss of pellet sorbents not significant compared to limestone, even at high temperature.
Particle Size ($d_{50}$) Reduction

![Bar chart showing particle size reduction for Ca(OH)2 + cement and Graymont limestone. The reduction is shown for different temperatures and U/Umfd ratios.](image_url)
Benefits of Pelletization

- Enhanced CO₂ carrying activity
- More resistant to attrition
- Spent sorbent can be used for pelletization
- Reactivation, reformulation and remaking of spent pellets
- **PELLETIZATION PROCEDURE ENABLES ADDITION OF OTHER MATERIALS:**
  - Catalysts
  - OXYGEN CARRIERS (Integration of CaL with CLC)

(i) CaO or Ca(OH)₂ + Cement

(ii) CaO or Ca(OH)₂ Cement
Integration of CaL with CLC

The main criteria considered for oxygen carriers:
- oxygen transport capacity
- reactivity
- the reversibility of oxidation/reduction
- selectivity in reaction with fuel
- mechanical strength (to be used in FBC)
- melting point
- toxicity

The main parameter - Heat released during reduction
Integration of CaL with CLC

\[ \text{CaCO}_3 + 179 \text{ kJ/mol} = \text{CaO} + \text{CO}_2 \]

\[ 4\text{CuO} + \text{CH}_4 = 4\text{Cu} + \text{CO}_2 + 2\text{H}_2\text{O} + 211.6 \text{ kJ/mol} \]

No need for pure oxygen in calciner
Integration of CaL with CLC

Calcination/reduction/oxidation/carbonation cycle of CaO/CuO-based pellets

- Up to 10 cycles tested
- CO$_2$ carrying activity shows typical decay
- O$_2$ carrying activity is stable
Integration of CaL with CLC

- Pellets are resistant to attrition in FBC
- Core-in-shell pattern
Looping Technology Development

CanmetENERGY / Foster Wheeler 30 MW\textsubscript{th}

CanmetENERGY

Analytical

0.1 MW\textsubscript{th}

CanmetENERGY

0.1 MW\textsubscript{th}

Caoling / Foster Wheeler

1.7 MW\textsubscript{th}

Foster Wheeler

30 MW\textsubscript{th}
Conclusions

- The pellet samples showed better reactivity over original limestone sorbent in long-term repeated cycles.
- The total loss of mass during attrition test was not significant, even at high temperatures. However, the particle size (d50) reduced significantly in hot attrition test.
- Integration of CaL with CLC is under investigation at CanmetENERGY.
- CaO/CuO/Al₂O₃ composites were prepared and tested.
- Benefits of integration of CaL with CLC:
  - No need for pure oxygen
  - Concentrated CO₂ stream is oxygen-free
  - Steam released during reduction of CuO by CH₄ lowers calcination temperature.
Conclusions (cont’d)

- Benefits of CaO/CuO/Al₂O₃ composites
  - Mechanical strength – can be used in FBC
  - Can be prepared in a core-in-shell form
  - Heat necessary for calcination is released in same particle
  - CaO can act as CuO/Cu support – no need for another support
  - Catalysts can be added in pellets – for sorption-enhanced reforming
Thank You!

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