Development of Ca-Based Sorbent for High-Temperature CO_2 Capture

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CanmetENERGY

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PCCC2

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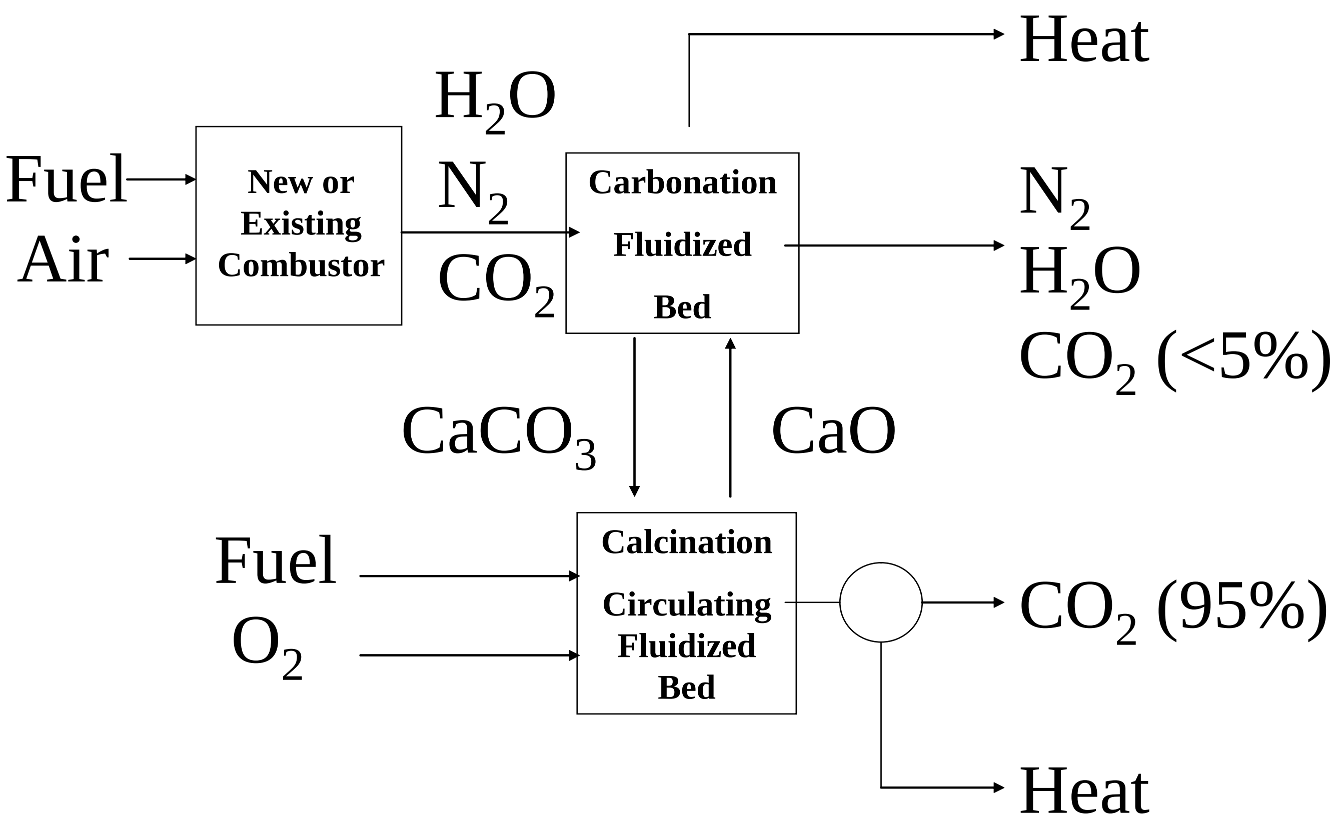
Carbon Capture and Sequestration (CCS)

- >30% of anthropogenic carbon dioxide is released from large stationary energy sources such as fossil-fuel-fired power plants
- 15% CO_2 in flue gas – direct compression, liquefaction, transport, and storage are not economically competitive
- NEW TECHNOLOGIES: rely on concentrated CO_2 stream (>90% CO_2)

- SCENARIOS FOR CONCENTRATED CO_2:
  - pre-combustion CO_2 capture
  - oxy-fuel combustion (chemical looping)
  - post-combustion CO_2 capture (calcium looping)

Calcium Looping Cycles (CaLC)



$$CaCO_3 \leftrightarrow CaO + CO_2$$

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Calcium Looping

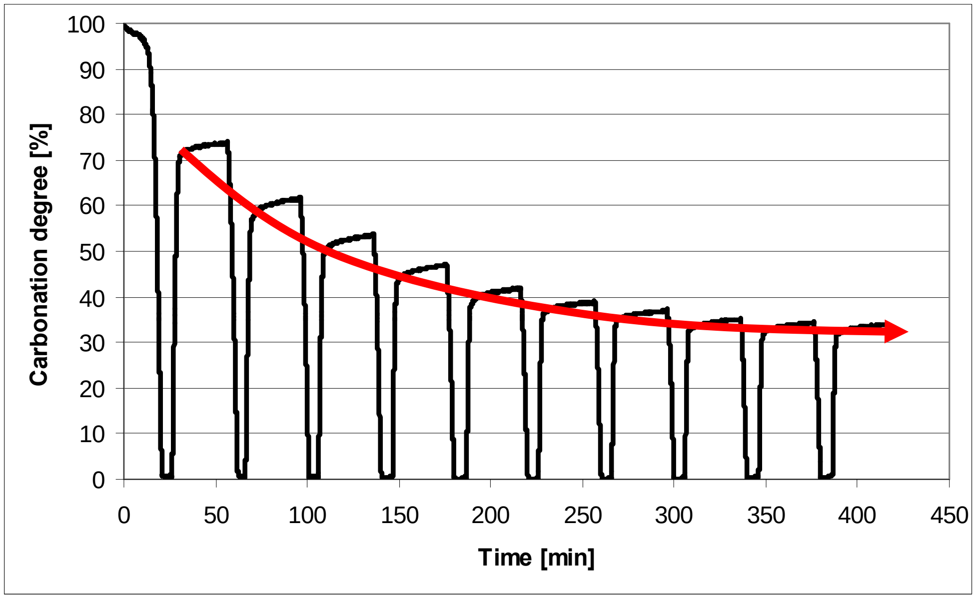
- Advantages

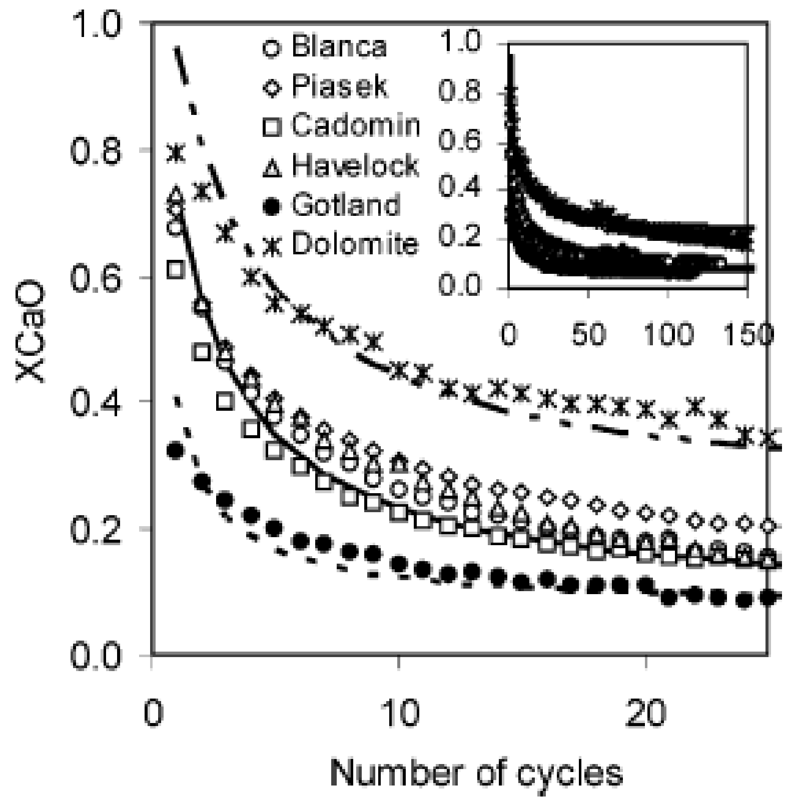
- Inexpensive sorbent (limestone ($CaCO_3$), ~$10/ton)
- The main components commercially available
- Low projected costs for CO_2 capture (~$20/ton CO_2 avoided)
- Environmentally benign

- Challenges:

- **Decay of CO_2 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 CO_2 stream is corrosive – purification required**

Sorbent Decay





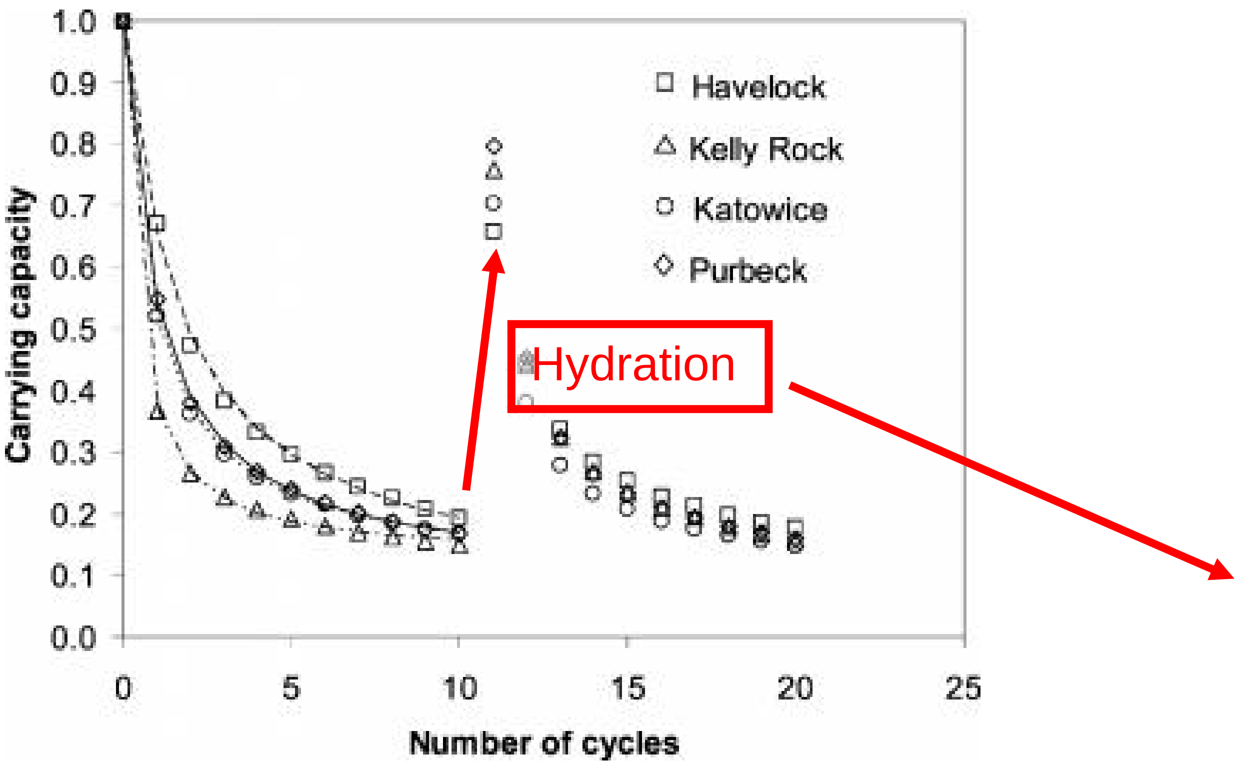
- Sintering: available surface area decreases

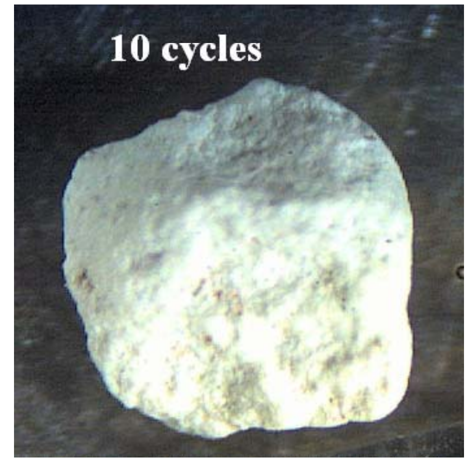
Changes in morphology:

- 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.

Grasa and Abanades, Ind. Eng. Chem. Res. 45, 8846-8851, 2006

Reactivation of CaO by Steam





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

<u>*Wu et al., Energy & Fuels, 24, 2768-2776, 2010*</u>

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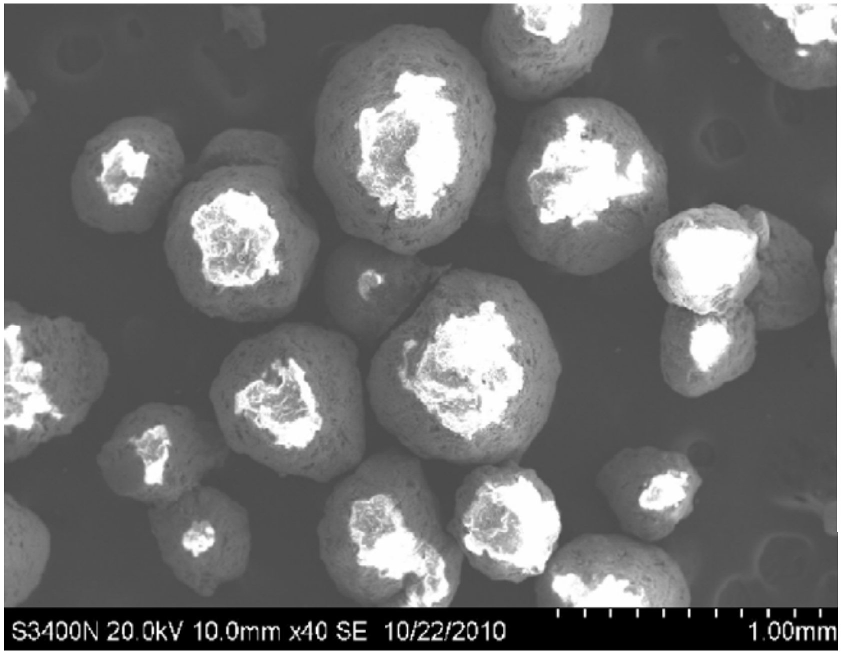
Pelletization

Binder: Calcium aluminate cements

- commercially available and relatively inexpensive
- improves mechanical strength
- improves CO_2 carrying activity

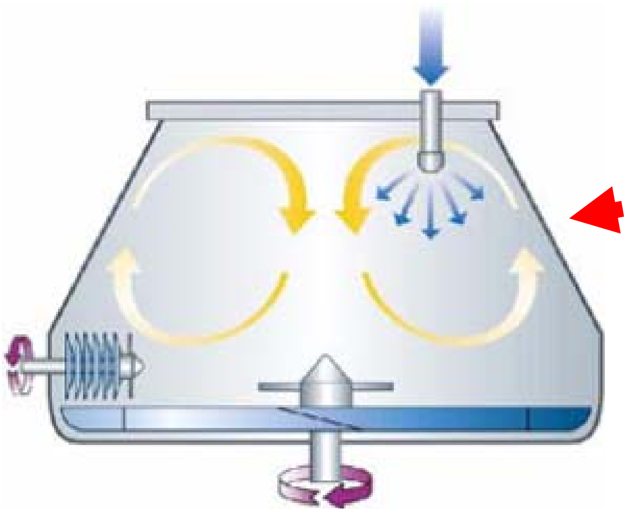
Pellets made by hand



Pellets made by the pelletizer

Mechanical Pelletization

Spray water



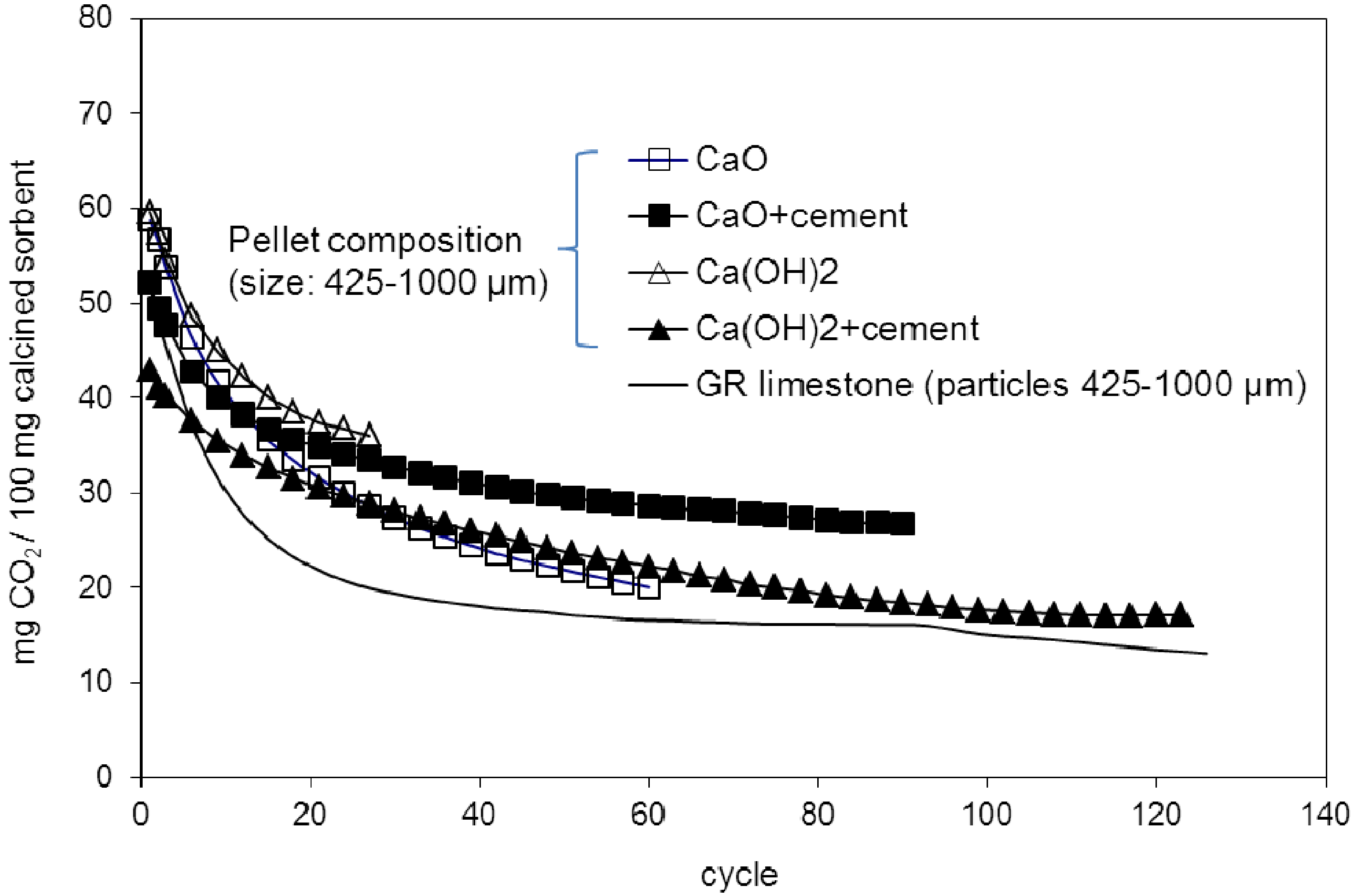
Pellet size is controlled by an agitator (bottom) and a chopper (side)

Pelletizer

Material for Pelletization

- CaO, $Ca(OH)_2$ powder
  - < 30 µm, from Graymont limestone
- Binder: CA-14 cement powder
  - 71% Al_2O_3, 28% CaO

Performance of Pellet Sorbents



Carbonation:
800 °C,
25% CO_2
Calcination:
800 °C, N_2

- Pellet sorbents performed better as compared to original limestone (same particle size)

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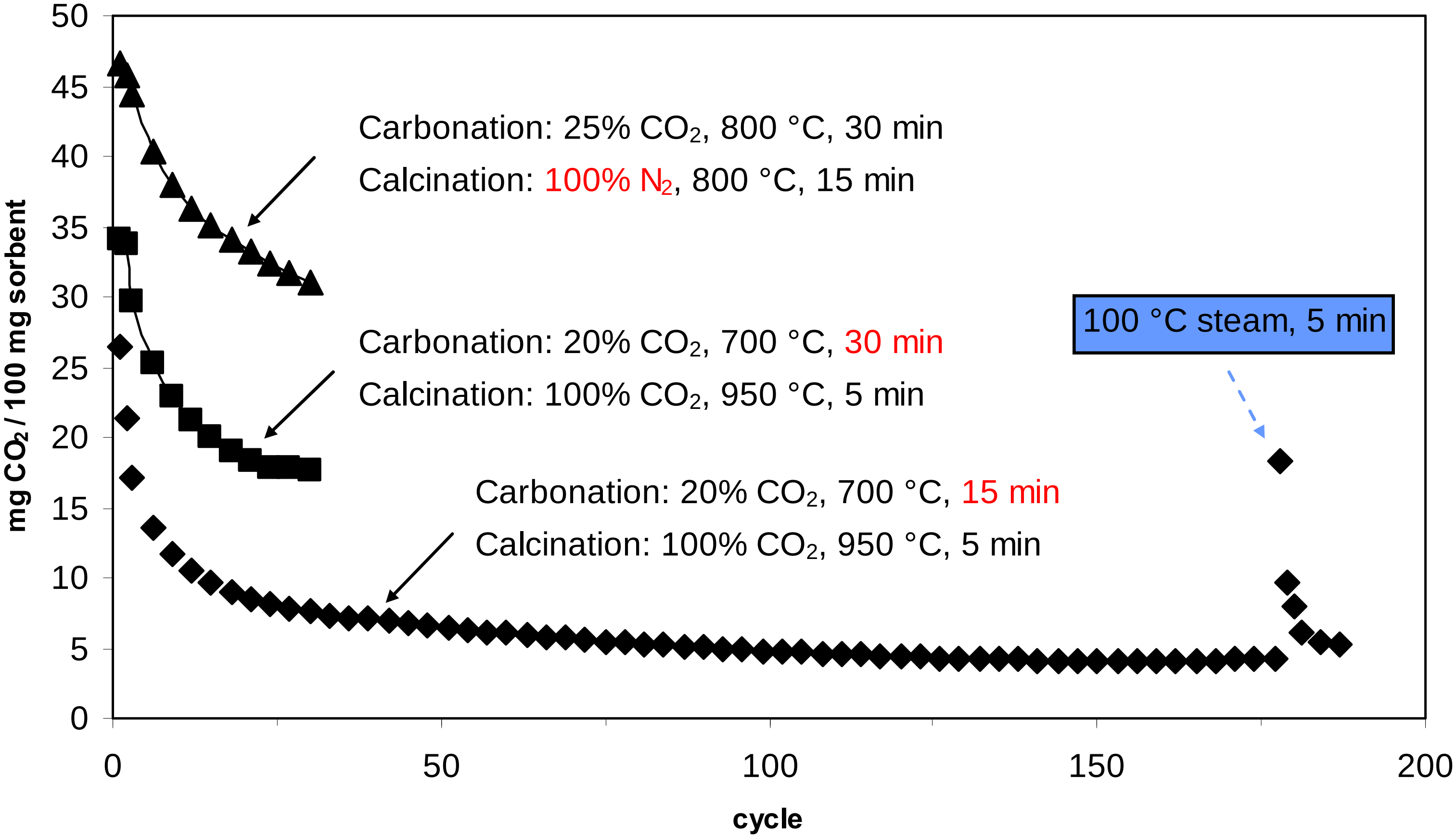
Effect of Cyclic Conditions

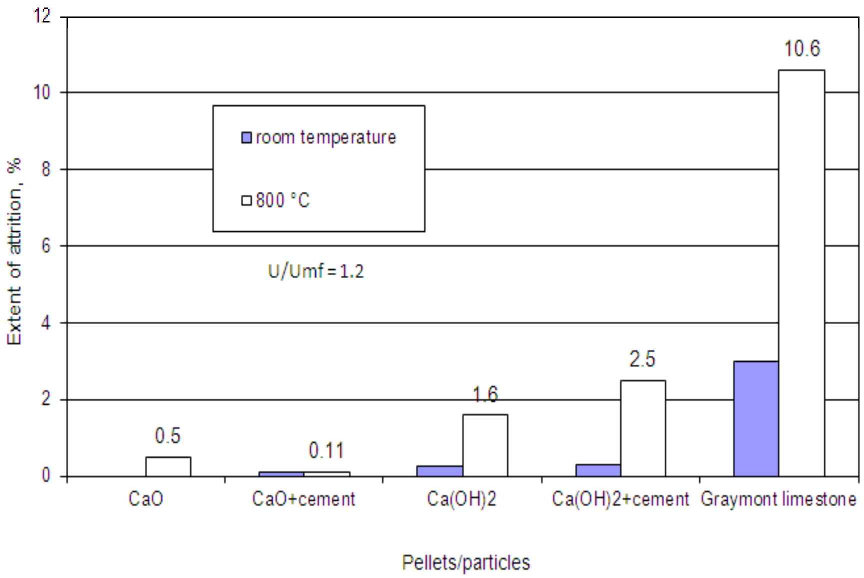


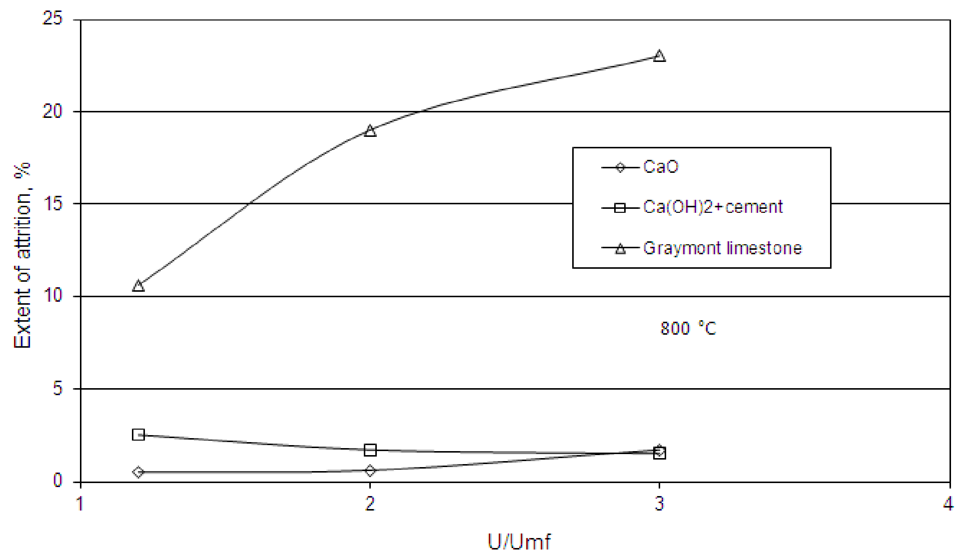
- Pellet: $Ca(OH)_2$ + cement, 425-1000 µm
- Longer carbonation period and calcination in N_2 increase CO_2 uptake capacity

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

Extent of Attrition (2-h Mass Loss, %)





- Mass loss of pellet sorbents not significant compared to limestone, even at high temperature

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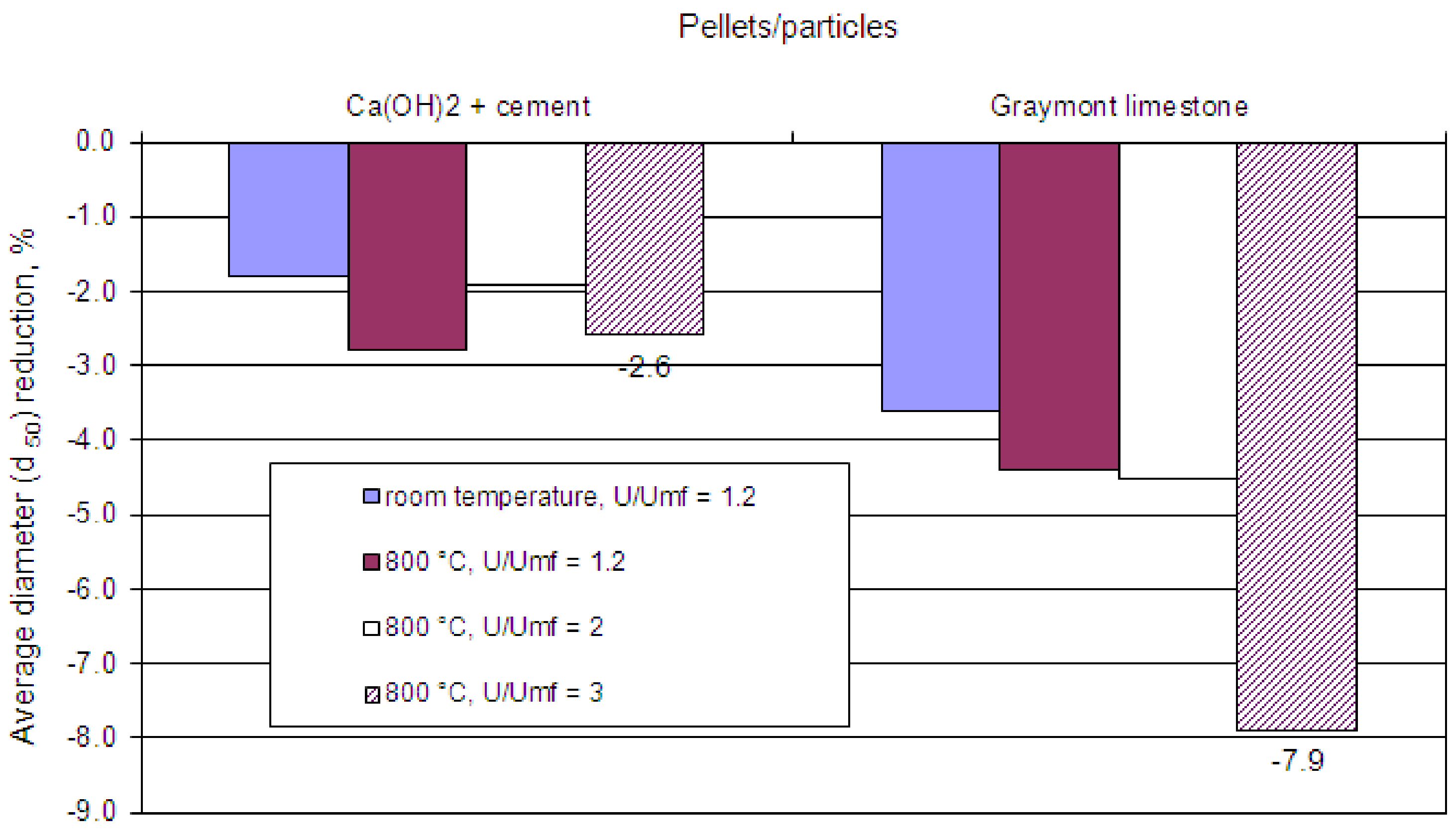
Particle Size (d_{50}) Reduction



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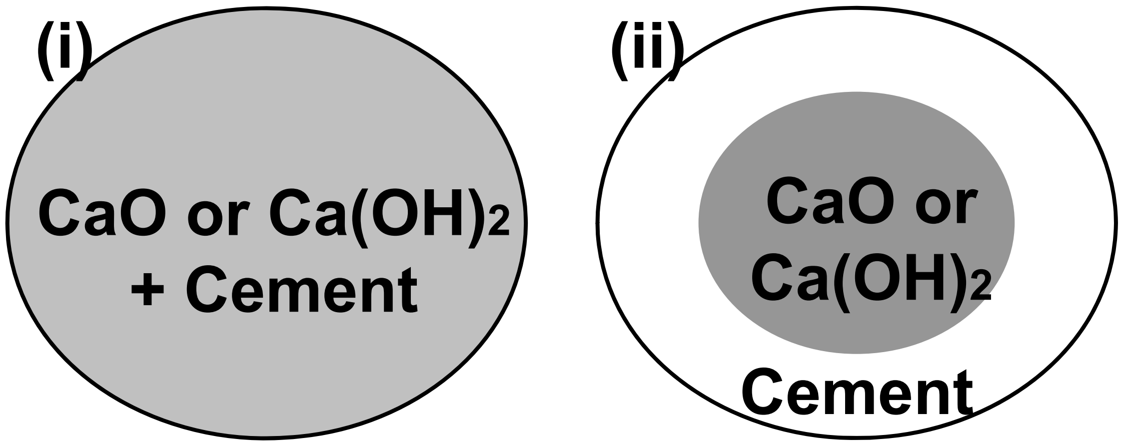
Benefits of Pelletization

- Enhanced CO_2 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)



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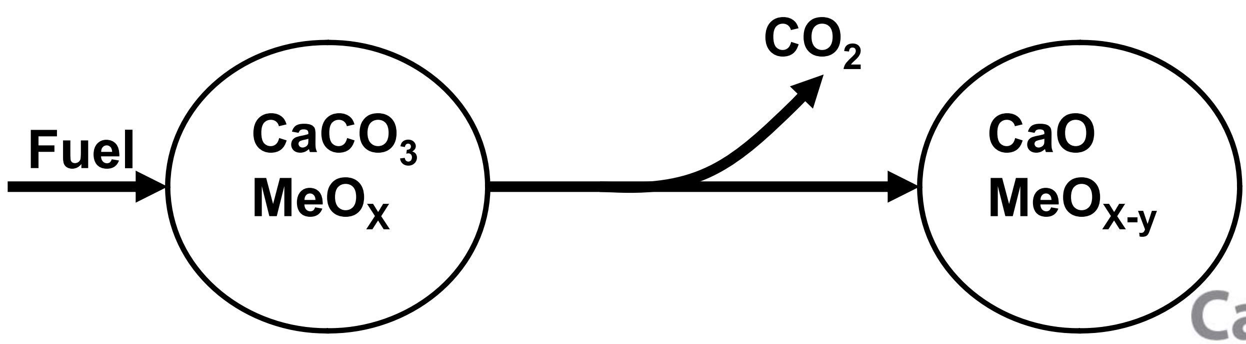
Integration of CaL with CLC

The main criteria considered for oxygen carriers:

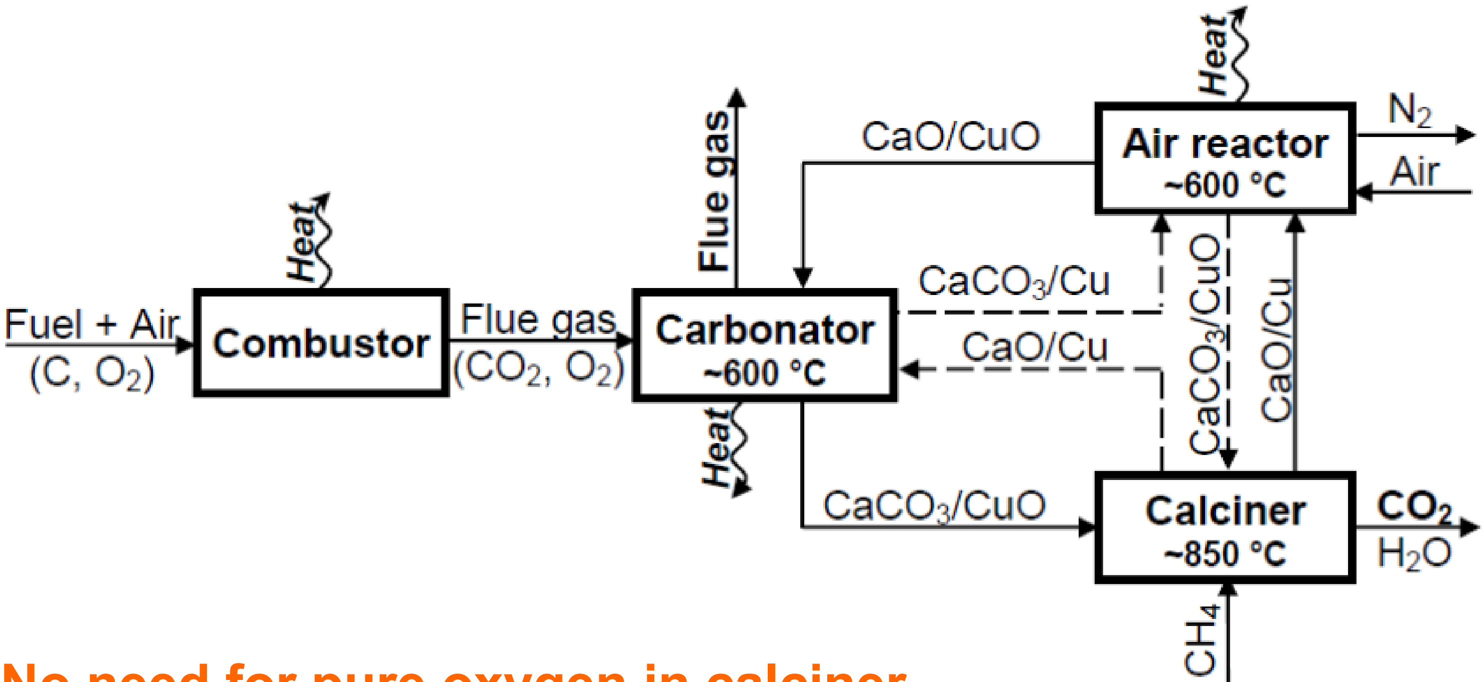
- oxygen transport capacity
- reactivity
- the reversibility of oxidation/reduction
- selectivity in reaction with fuel
- mechanical strength (to be used in FBC)
- melting point
- toxicity

The main parameter - Heat released during reduction



Integration of CaL with CLC

$CaCO_3$ + 179 kJ/mol = CaO + CO_2
4CuO + CH_4 = 4Cu + CO_2 +2H_2O + 211.6 kJ/mol



No need for pure oxygen in calciner

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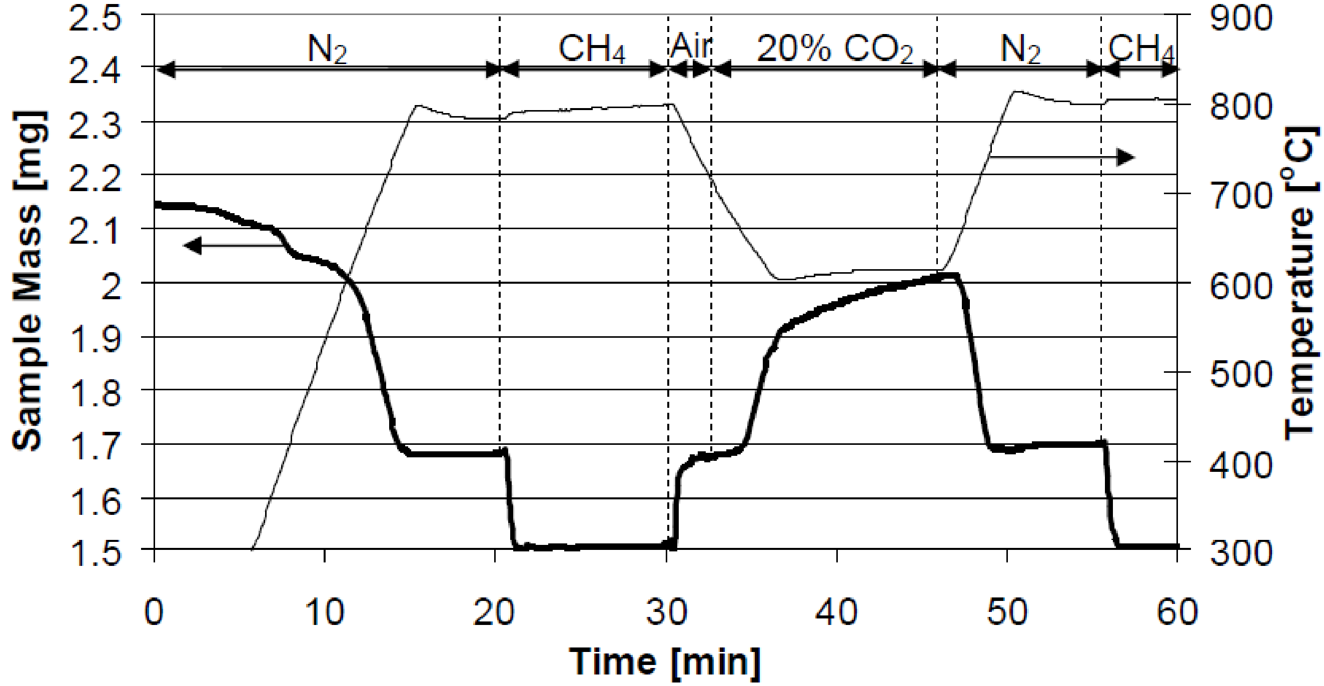
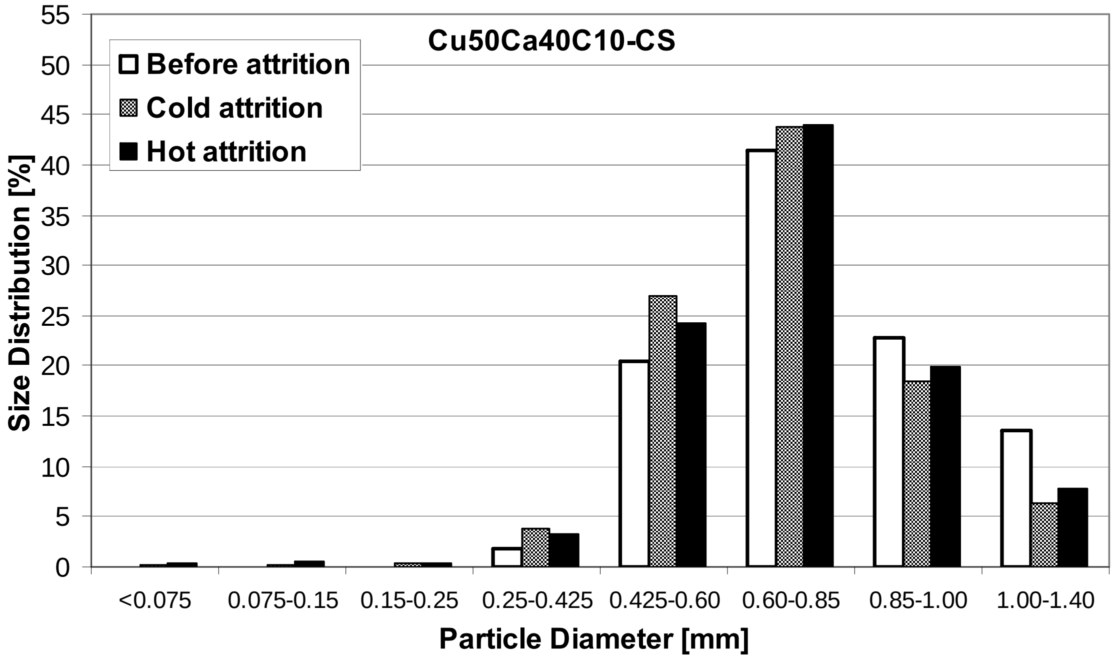
Integration of CaL with CLC



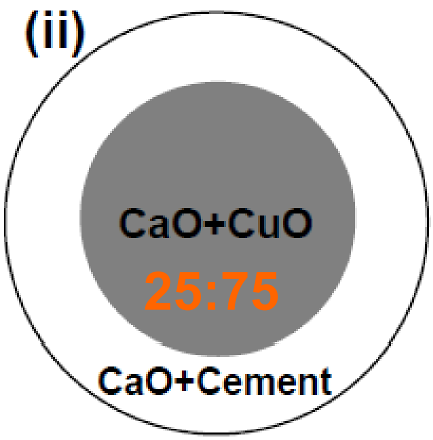
Calcination/reduction/oxidation/carbonation cycle of CaO/CuO-based pellets

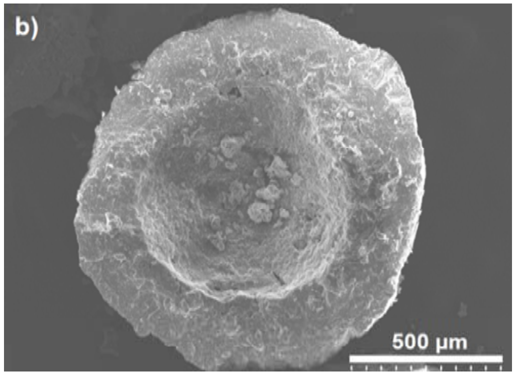
- Up to 10 cycles tested
- CO_2 carrying activity shows typical decay
- O_2 carrying activity is stable

Integration of CaL with CLC



Attrition test in a BFBC





- Pellets are resistant to attrition in FBC
- Core-in-shell pattern

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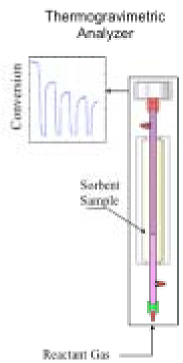
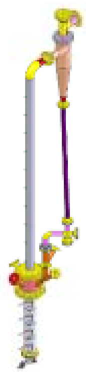
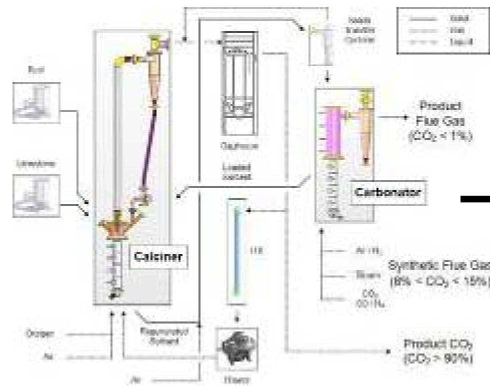
Looping Technology Development







CanmetENERGY Analytical

CanmetENERGY 0.1 MW_{th}

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Caoling / Foster Wheeler 1.7 MW_{th}

Imperial College London

FOSTER WHEELER

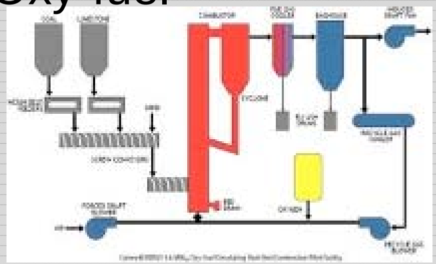
uOttawa

lut.fi

grupohunosa

endesa generación

Oxy-fuel



CanmetENERGY / Foster Wheeler 0.8 MW_{th}

Foster Wheeler 30 MW_{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
- $CaO/CuO/Al_2O_3$ composites were prepared and tested
- Benefits of integration of CaL with CLC
  - No need for pure oxygen
  - Concentrated CO_2 stream is oxygen-free
  - Steam released during reduction of CuO by CH_4 lowers calcination temperature

Conclusions (cont'd)

- Benefits of $CaO/CuO/Al_2O_3$ 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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