Options for calcium looping for CO$_2$ capture in the cement industry


$^1$Italcementi, Bergamo, Italy
$^2$IKN GmbH, Neustadt, Germany
$^3$Agencia Estatal Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain
$^4$Politecnico di Milano, Milan, Italy
$^5$Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart, Stuttgart, Germany

2nd ECRA/Cemcap workshop:
Carbon Capture Technologies in the Cement Industry
Dusseldorf, 6-7 November 2017
WP12 participants

Institute of Power Plant and Combustion technology, University of Stuttgart

Spanish research council, INCAR-CSIC

Politecnico di Milano, Department of Energy

IKN,

Italcementi
Calcium Looping process fundamentals

CARBONATION

CaO + CO₂ → CaCO₃

~ 650°C

CO₂-lean flue gas

Flue gas (CO₂) (F_{CO₂})

CaCO₃

CaO (F_R)

Heat

CALCINATION

CaCO₃ → CaO + CO₂

~ 900°C

CO₂-rich gas to sequestration

CaCO₃ make-up (F₀)

CaO purge

Heat
Calcium Looping for CO$_2$ capture: history

- Continuously developed since 1998, mainly for application in power plants
- Several fluidized bed pilot facilities - demonstrated up to 1.7 MW

200 kW pilot at IFK, U. Stuttgart  
1 MW pilot at TU Darmstadt  
1.7 MW pilot at La Pereda (ES)
Calcium looping for cement plants

1. **Cement plant-power plant coupling**: CaO-rich spent sorbent from a CaL power plant as feed for the cement plant, as substitute of CaCO₃.

2. **Post-combustion “tail end” configuration**: CaL process is integrated in the cement plant with a conventional post-combustion capture configuration.

3. **Highly integrated CaL configuration**: the CaL process is integrated within the cement production process by sharing the same oxyfuel calciner.
Cement plant-power plant coupling

**POWER PLANT with CaL**

- **Bolier**
  - coal
  - air

- **Carbonator**
  - $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$
  - $F_{\text{CO}_2}$
  - $F_R$

- **Calciner**
  - $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
  - $F_0$
  - $\text{CO}_2$ to storage
  - $\text{CaO/ CaCO}_3$
  - $W_S$

**CEMENT PLANT**

- **Pre calciner**
  - raw meal preheater
  - fuel

- **Rotary kiln**
  - calcined raw meal
  - hot air
  - air

- **Clinker cooler**
  - clinker
  - fuel
  - air
Cement plant-power plant coupling

Substitution ratio (% of Ca fed to the cement kiln as CaO from the power plant)

<table>
<thead>
<tr>
<th>Substitution Ratio</th>
<th>Emitted CO2, cement plant</th>
<th>Emitted CO2, power plant</th>
<th>Avoided CO2, cement plant</th>
<th>Avoided CO2, power plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>97%</td>
<td>33.6</td>
<td>7.1</td>
<td>5.8</td>
<td>138.8</td>
</tr>
<tr>
<td>51%</td>
<td>17.9</td>
<td>22.8</td>
<td>7.1</td>
<td>123.1</td>
</tr>
<tr>
<td>31%</td>
<td>11.0</td>
<td>29.7</td>
<td>12.8</td>
<td>107.0</td>
</tr>
<tr>
<td>16%</td>
<td>5.8</td>
<td>34.9</td>
<td>19.2</td>
<td>85.3</td>
</tr>
<tr>
<td>9%</td>
<td>3.3</td>
<td>37.5</td>
<td>20.7</td>
<td>67.9</td>
</tr>
</tbody>
</table>

Calcium Looping CO$_2$ capture: Tail-end CaL configuration

General features of the process:

- Carbonator removes CO$_2$ from cement plant flue gas → Easy integration in existing cement
- Limestone partly calcined in Calcium Looping calciner → CaO-rich purge from CaL calciner used as feed for the cement kiln
- High fuel consumption (double calcination for the mineral CO$_2$ captured)
- Heat from fuel consumption recovered in efficient (~35% efficiency) steam cycle for power generation
- CFB CaL reactors: $d_{50}=100$-250 μm, vs. particle size for clinker production $d_{50}=10$-20 μm → CaL purge milled in the raw mill at low temperature
Calcium Looping CO₂ capture: Tail-end CaL configuration

Conducted Work:

- Parameter screening at 30 kW scale at CSIC (TRL5)
- Demonstration at semi-industrial scale (200 kW \text{th}) at IFK (TRL6)
- Process simulation and integration


Calcium Looping CO$_2$ capture: Tail-end CaL configuration

Active space time design rule:

1. $\tau_{\text{active}} = \frac{N_{\text{CaO}}}{\dot{N}_{\text{CO}_2}} f_a X_{\text{ave}}$

2. $\tau_{\text{active}} > 50 \frac{1}{s}$ for 90% CO$_2$ capture

$N_{\text{CaO}}$: molar amount of CaO in Carbonator
$\dot{N}_{\text{CO}_2}$: molar flow of CO$_2$ entering the Carbonator
$f_a$: sorbent fraction reacting in fast reaction regime
$X_{\text{ave}}$: average sorbent CO$_2$ carrying capacity
Demonstration at semi-industrial scale:

- High CO$_2$ capture up to 98 % demonstrated
- Favorable CaL operation conditions
  - reduced recycle train
  - high sorbent activity
- High CO$_2$ capture at carbonator inlet may cause problems of entrainment due to reduction of fluidization gas (~ -25 %)
Calcium Looping CO$_2$ capture: highly integrated configuration

General information:
- CaL calciner coincides with the cement kiln pre-calciner
- Calcined raw meal as CO$_2$ sorbent in the carbonator
- Sorbent has small particle size ($d_{50}=10$-$20$ μm) → entrained flow reactors


Calcium Looping CO$_2$ capture: highly integrated configuration

Conducted Work:
- TGA – sorbent characterization
- (Re)carbonation experiment in EF conditions
- EF oxyfuel calcination experiments
- Simulation of entrained flow Calcium Looping
- Preliminary process integration study
### Tail end vs. highly integrated configuration: preliminary H&M balance

<table>
<thead>
<tr>
<th></th>
<th>Cement plant w/o capture</th>
<th>Tail-end CaL</th>
<th>Integrated CaL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_0/F_{CO2}$</td>
<td>--</td>
<td>0.16</td>
<td>4.1</td>
</tr>
<tr>
<td>$F_{Ca}/F_{CO2}$</td>
<td>--</td>
<td>4.8</td>
<td>4.0</td>
</tr>
<tr>
<td>Carbonator CO$_2$ capture efficiency [%]</td>
<td>--</td>
<td>88.8</td>
<td>80.0</td>
</tr>
<tr>
<td>Total fuel consumption [MJ$<em>{LHV}$/t$</em>{clk}$]</td>
<td>3223</td>
<td>8672</td>
<td>4740</td>
</tr>
<tr>
<td>Rotary kiln burner fuel consumption [MJ$<em>{LHV}$/t$</em>{clk}$]</td>
<td>1224</td>
<td>1210</td>
<td>1180</td>
</tr>
<tr>
<td>Pre-calciner fuel consumption [MJ$<em>{LHV}$/t$</em>{clk}$]</td>
<td>1999</td>
<td>1542</td>
<td>3560</td>
</tr>
<tr>
<td>CaL calciner fuel consumption [MJ$<em>{LHV}$/t$</em>{clk}$]</td>
<td>--</td>
<td>5920</td>
<td>--</td>
</tr>
<tr>
<td>Net electricity production [kWh$<em>{el}$/t$</em>{clk}$]</td>
<td>-132</td>
<td>159</td>
<td>-164</td>
</tr>
<tr>
<td>Direct CO$<em>2$ emissions [kg$</em>{CO2}$/t$_{clk}$]</td>
<td>863.1</td>
<td>143.2</td>
<td>71.4</td>
</tr>
<tr>
<td>Indirect CO$<em>2$ emissions [kg$</em>{CO2}$/t$_{clk}$]</td>
<td>105.2</td>
<td>-123.5</td>
<td>128.7</td>
</tr>
<tr>
<td>Equivalent CO$<em>2$ emissions [kg$</em>{CO2}$/t$_{clk}$]</td>
<td>968.3</td>
<td>19.7</td>
<td>200.1</td>
</tr>
<tr>
<td>Equivalent CO$_2$ avoided [%]</td>
<td>--</td>
<td>98.0</td>
<td>79.3</td>
</tr>
<tr>
<td>SPECCA [MJ$<em>{LHV}$/kg$</em>{CO2}$]</td>
<td>--</td>
<td>3.26</td>
<td>2.32</td>
</tr>
</tbody>
</table>

Summary

- Project objectives
- The demo plant
- The consortium
- Work packages
Primary project objectives

The ultimate objective of CLEANKER is advancing the integrated Calcium-looping process for \( \text{CO}_2 \) capture in cement plants.

This fundamental objective will be achieved by pursuing the following primary targets:

- Demonstrate the **integrated CaL process** at TRL 7, in a new demo system connected to the operating cement burning line of the Vernasca 900.000 ton/y cement plant, operated by BUZZI in Italy.

- Demonstrate the **technical-economic feasibility** of the integrated CaL process in retrofitted large scale cement plants through process modelling and scale-up study.

- Demonstrate the **storage** of the \( \text{CO}_2 \) captured from the CaL demo system, through **mineralization** of inorganic material in a pilot reactor of 100 litres to be built in Vernasca, next to the CaL demo system.
Vernasca plant location
Primary project objectives

- TRL 1 – basic principles observed
- TRL 2 – technology concept formulated
- TRL 3 – experimental proof of concept
- TRL 4 – technology validated in lab
- TRL 5 – technology validated in relevant environment (industrially relevant environment in the case of key enabling technologies)
- TRL 6 – technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies)
- TRL 7 – system prototype demonstration in operational environment
- TRL 8 – system complete and qualified
- TRL 9 – actual system proven in operational environment; manufacturing in the case of key enabling technologies; or in space
Indicative configuration of the CLEANKER pilot

- **Entrained-flow carbonator**
- **Temperature about 400°C**
- **Temperature about 650°C**
- **GAS FROM PREHEATING TOWER**
- **CO2 TO THE PROCESS FILTER**

**TO THE PROCESS FILTER**

**MEAL TO PREHEATER**

**FUEL**

**OXYGEN**

**MEAL 1 t/h Tamb**

**Entrained-flow oxyfuel calciner**
Vernasca kiln preheater and rendering of CaL pilot
The consortium

5 EU member states + Switzerland

The CLEANKER project

Co-funded by the Horizon 2020 Framework Programme of the European Union
Work packages

WP1 - Management

WP2 – Demonstration system design

WP4 – Comparative characterization of raw meals for CaL

WP7 – Transport and storage

WP3 – Demonstration of CaL process

WP5 – Process integration and modelling

WP6 – Scale up, economics, LCA

WP8 – Exploitation

WP9 - Dissemination
Conclusions and Outlook

Ca-LOOPING PROCESS INTEGRATION OPTIONS:

1. Cement plant-power plant coupling:
   - Excellent expected performance
   - Easily retrofittable with low cost
   - Logistic problem: a very large power plant has to be built next to the cement plant

2. Post-combustion capture configuration:
   - Low uncertainty in the feasibility of the process (very similar to application in power plants)
   - Very high CO₂ capture expected
   - Two calciners are present in the system, leading to high fuel consumptions

3. Integrated CaL configuration:
   - High CO₂ capture efficiency without modifying rotary kiln operation (no need of kiln oxyfiring).
   - Higher thermal efficiency and lower fuel consumptions expected (compared to option 2)
   - New carbonator design and fluid-dynamic regime: fluid-dynamics, heat management and sorbent performance need validation
Thank you for your attention!

Acknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreements n. 641185 (Cemcap) and n. 764816 (Cleanker)

www.sintef.no/cemcap
Twitter: @CEMCAP_CO2

Disclaimer: The European Commission support for the production of this publication does not constitute endorsement of the contents which reflects the views only of the authors, and the Commission cannot be held responsible for any use which may be made of the information contained therein.