

# Options for calcium looping for CO<sub>2</sub> capture in the cement industry

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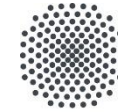
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# WP12 participants

Institute of Power Plant and Combustion technology,  
University of Stuttgart



**University of Stuttgart**  
Institute of Combustion and  
Power Plant Technology

Spanish research council, INCAR-CSIC



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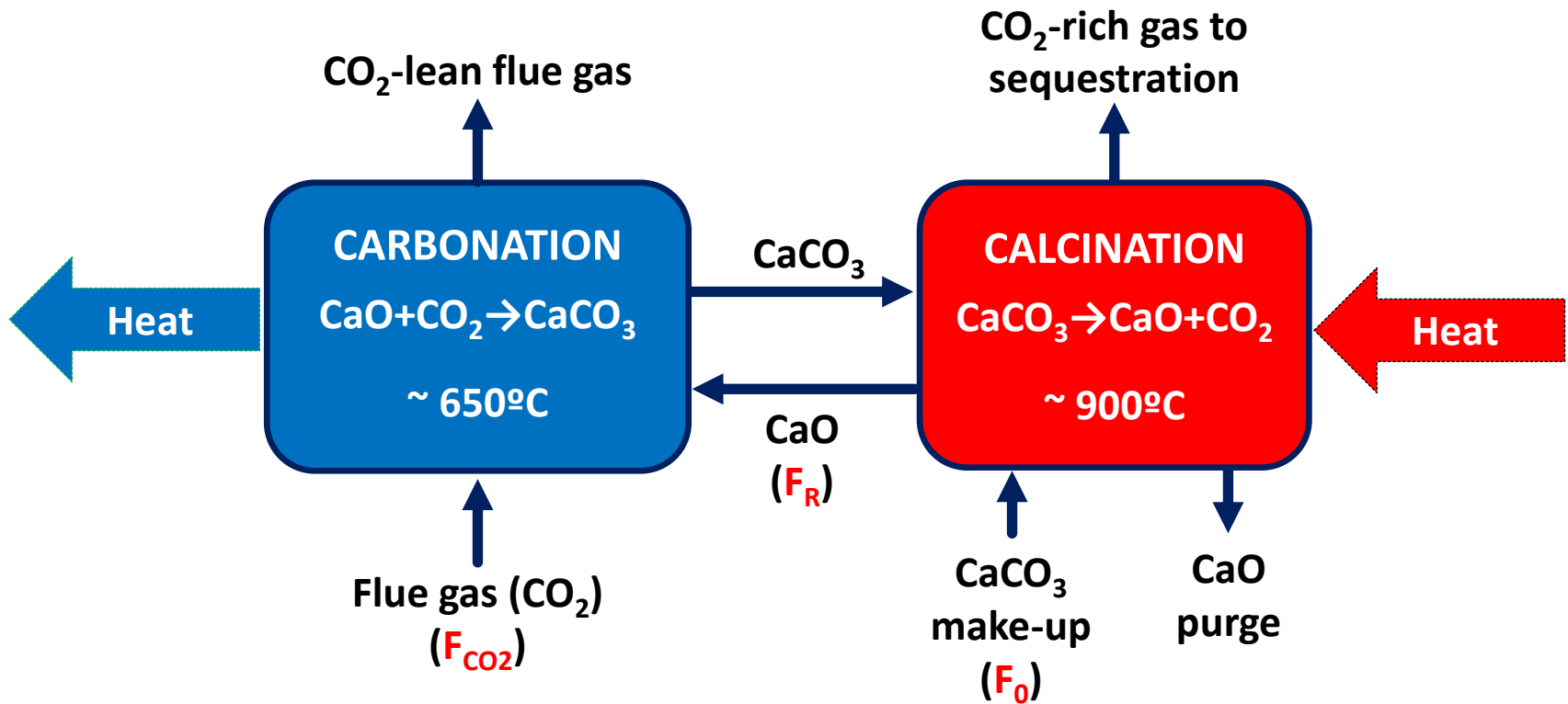
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# Calcium Looping process fundamentals



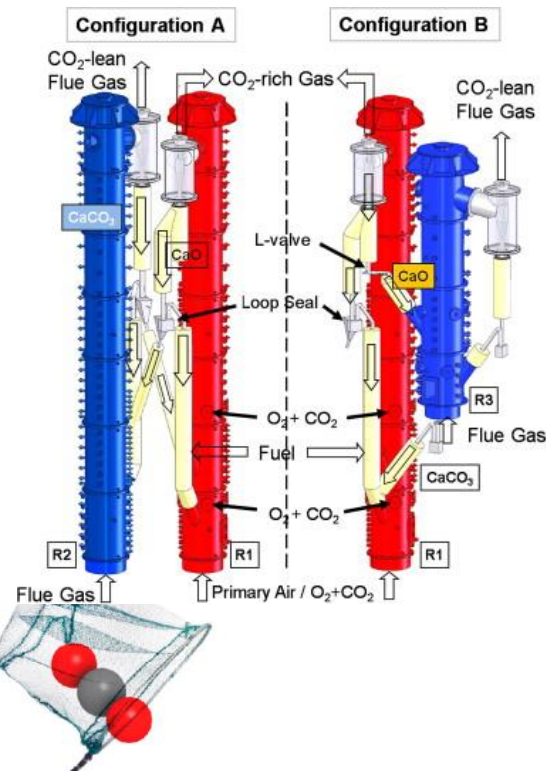
# Calcium Looping for CO<sub>2</sub> capture: history

- Originally proposed by Shimizu et al., 1999. A twin fluid-bed reactor for removal of CO<sub>2</sub>. Chem. Eng. Res. Des., 77.
- 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)



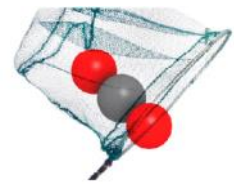
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# Calcium looping for cement plants

1. Cement plant-power plant coupling: CaO-rich spent sorbent from a CaL power plant as feed for the cement plant, as substitute of  $\text{CaCO}_3$
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

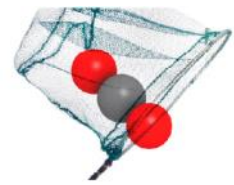
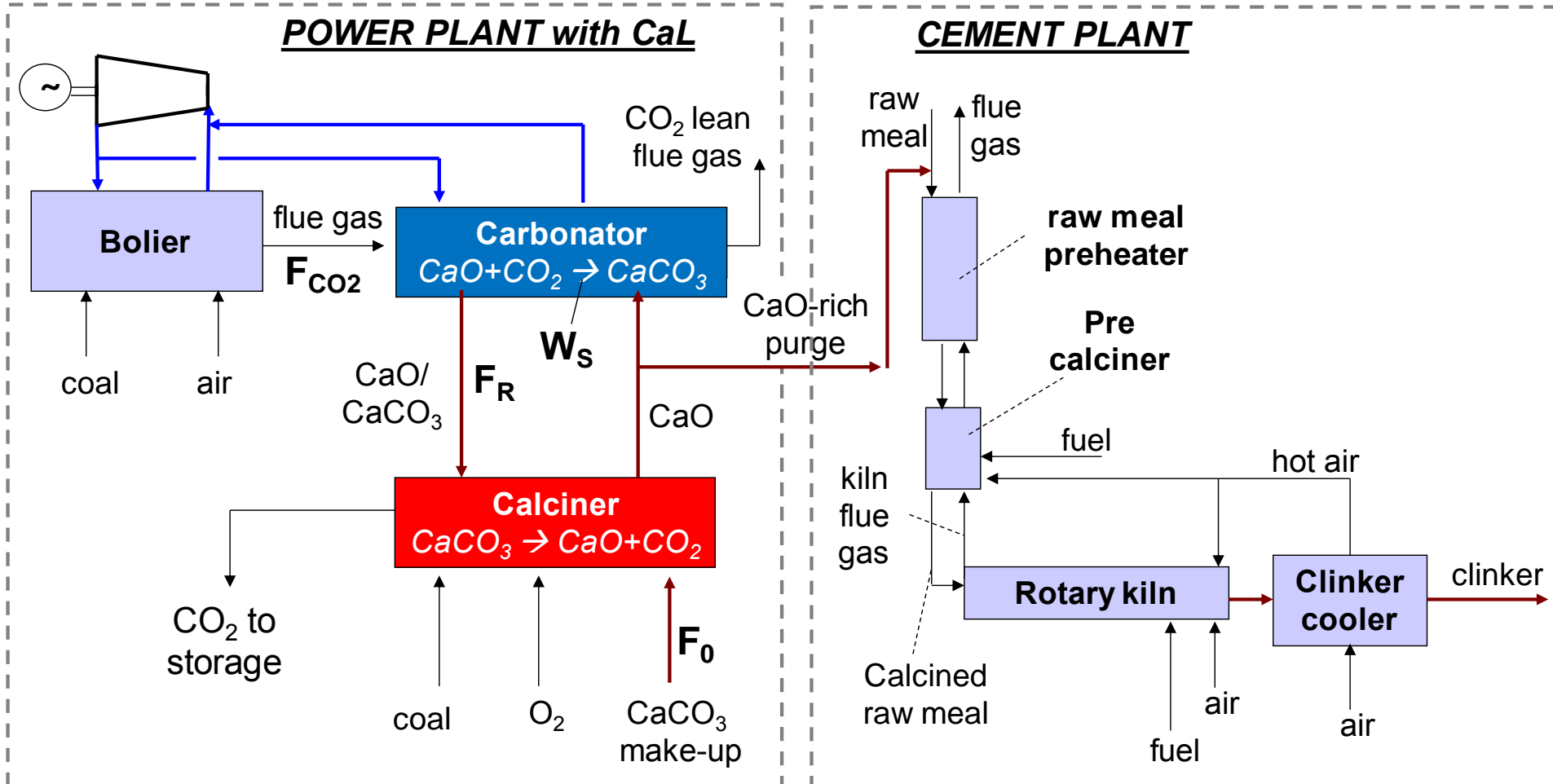


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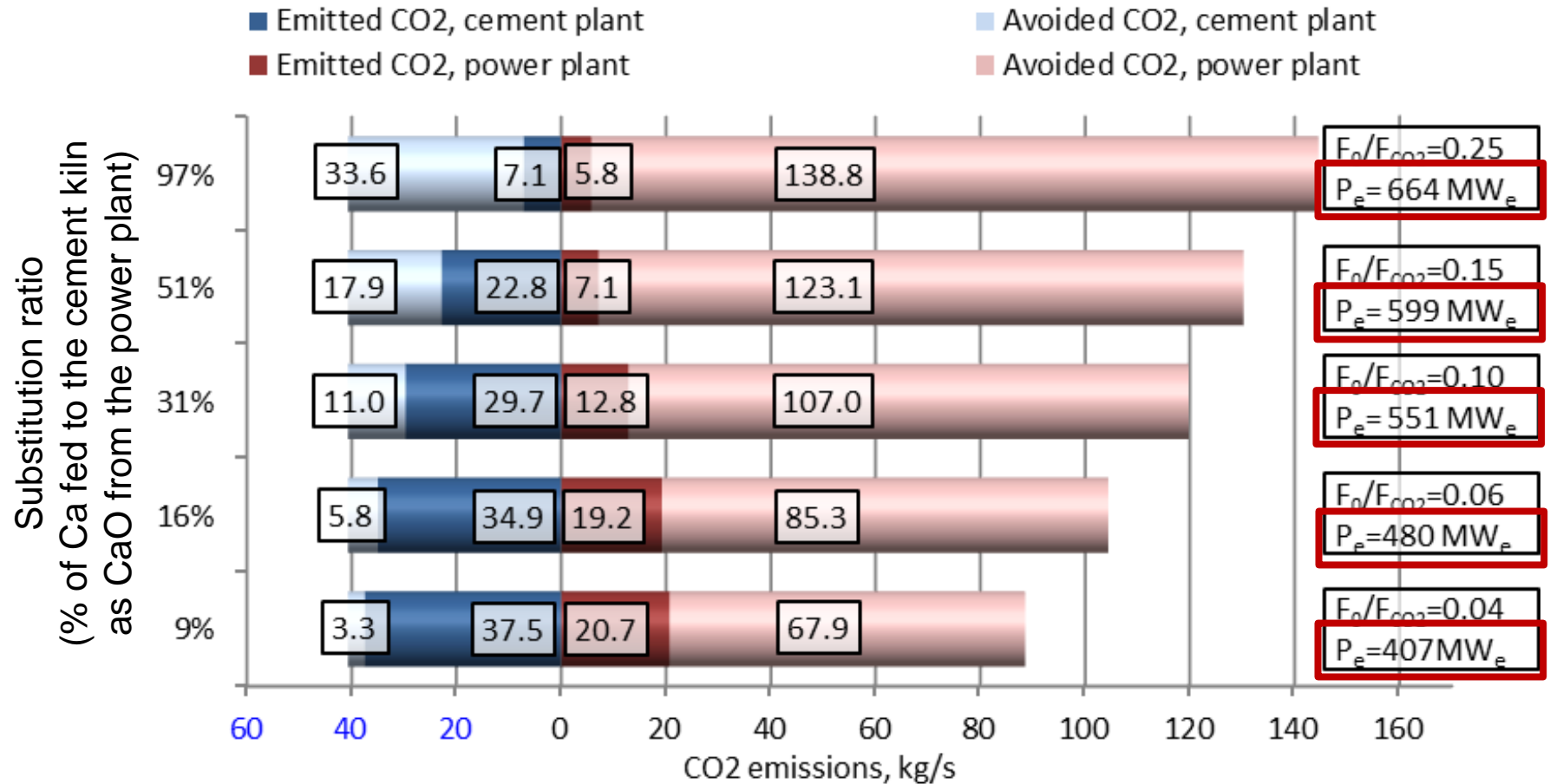
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# Cement plant-power plant coupling



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# Cement plant-power plant coupling



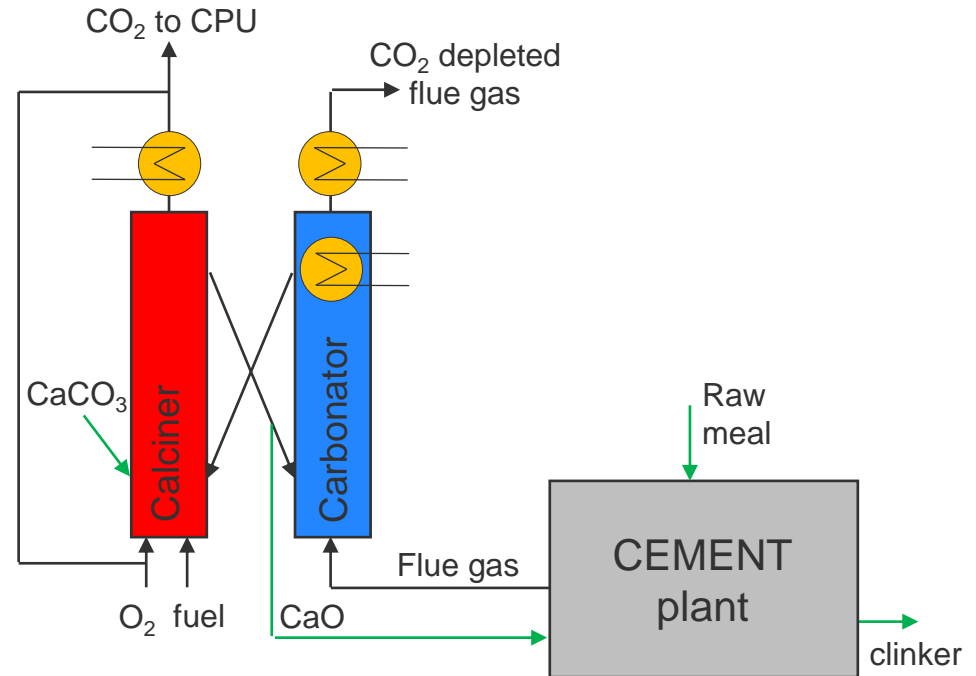
Romano M.C. et al., 2013. The calcium looping process for low CO<sub>2</sub> emission cement and power. *Energy Procedia*, 37, 7091-7099.

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# Calcium Looping CO<sub>2</sub> capture: Tail-end CaL configuration

## General features of the process:

- Carbonator removes CO<sub>2</sub> 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<sub>2</sub> captured)
- Heat from fuel consumption recovered in efficient (~35% efficiency) steam cycle for power generation
- CFB CaL reactors:  $d_{50}=100-250\ \mu\text{m}$ , vs. particle size for clinker production  $d_{50}=10-20\ \mu\text{m}$  → CaL purge milled in the raw mill at low temperature



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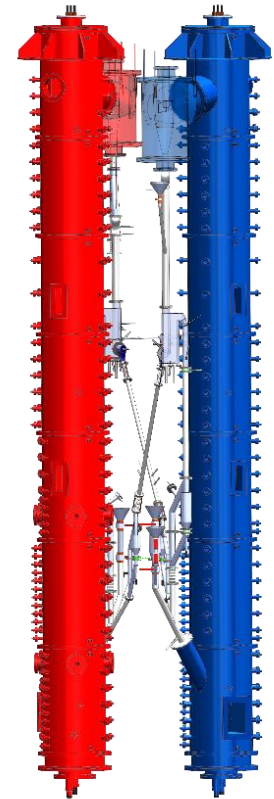
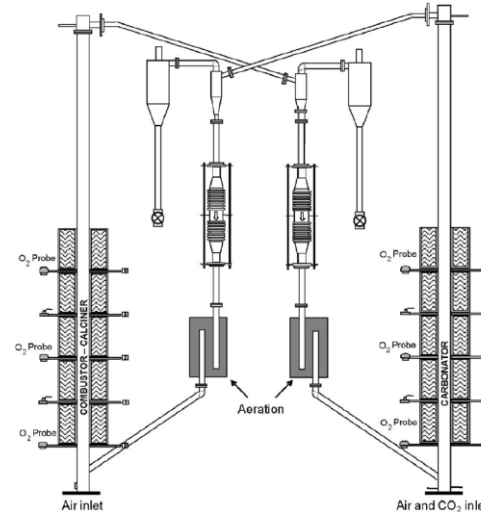
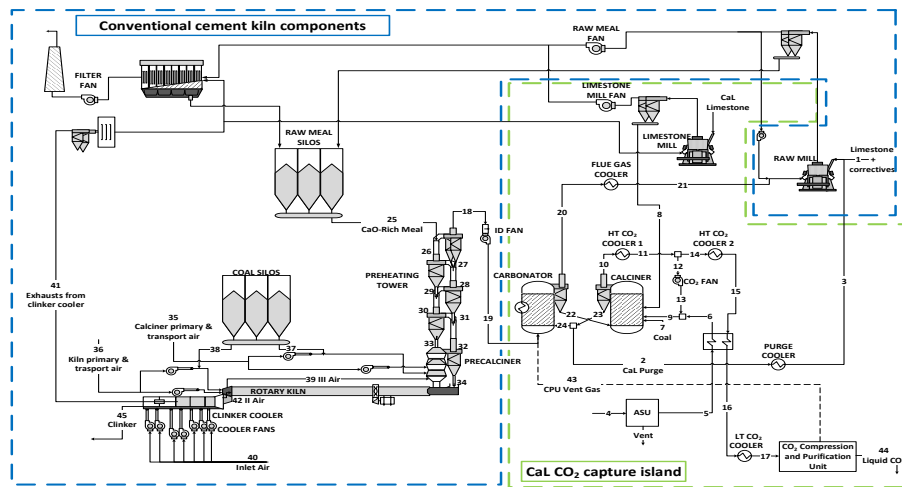




# Calcium Looping CO<sub>2</sub> capture: Tail-end CaL configuration

## Conducted Work:

- Parameter screening at 30 kW scale at CSIC (TRL5)
- Demonstration at semi-industrial scale (200 kW<sub>th</sub>) at IFK (TRL6)
- Process simulation and integration



Arias et al., 2017. CO<sub>2</sub> Capture by CaL at Relevant Conditions for Cement Plants: Experimental Testing in a 30 kW Pilot Plant. *Ind. Eng. Chem. Res.*, 56, 2634–2640.

Hornberger et al., 2017. CaL for CO<sub>2</sub> Capture in Cement Plants – Pilot Scale Test. *Energy Procedia*, 114, 6171–6174.

Spinelli et al., 2017. Integration of CaL systems for CO<sub>2</sub> capture in cement plants. *Energy Procedia*, 114, 6206–6214.

De Lena et al. Process integration of tail-end CaL for CO<sub>2</sub> capture in cement plants. *Int J Greenh Gas Control*. In press.

# Calcium Looping CO<sub>2</sub> capture: Tail-end CaL configuration

Active space time design rule:

- $$\tau_{active} = \frac{N_{CaO}}{\dot{N}_{CO_2}} f_a X_{ave}$$

$f_a X_{ave}$

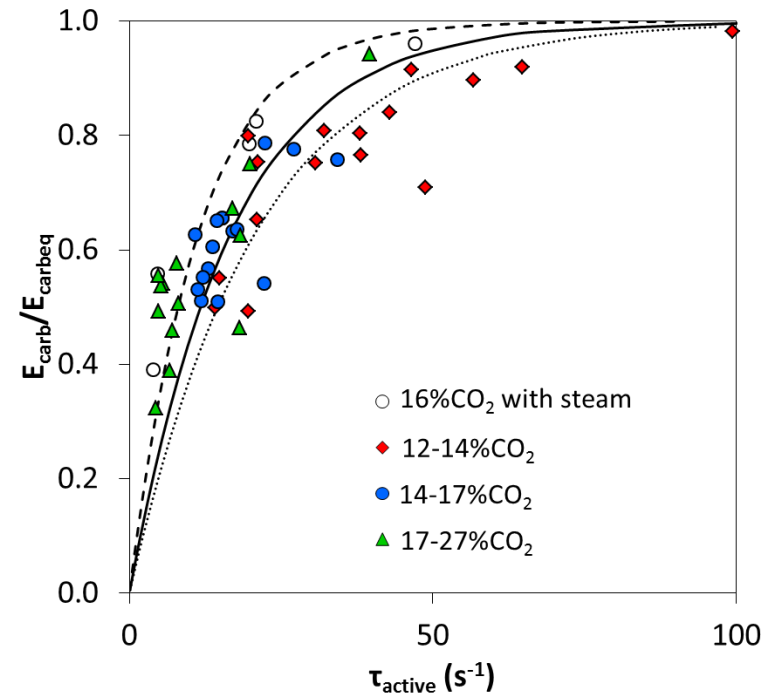
Amount of active sorbent in the bed
- $$\tau_{active} > 50 \frac{1}{s}$$
 for 90 % CO<sub>2</sub> capture

$N_{CaO}$ : molar amount of CaO in Carbonator

$\dot{N}_{CO_2}$ : molar flow of CO<sub>2</sub> entering the Carbonator

$f_a$ : sorbent fraction reacting in fast reaction regime

$X_{ave}$ : average sorbent CO<sub>2</sub> carrying capacity

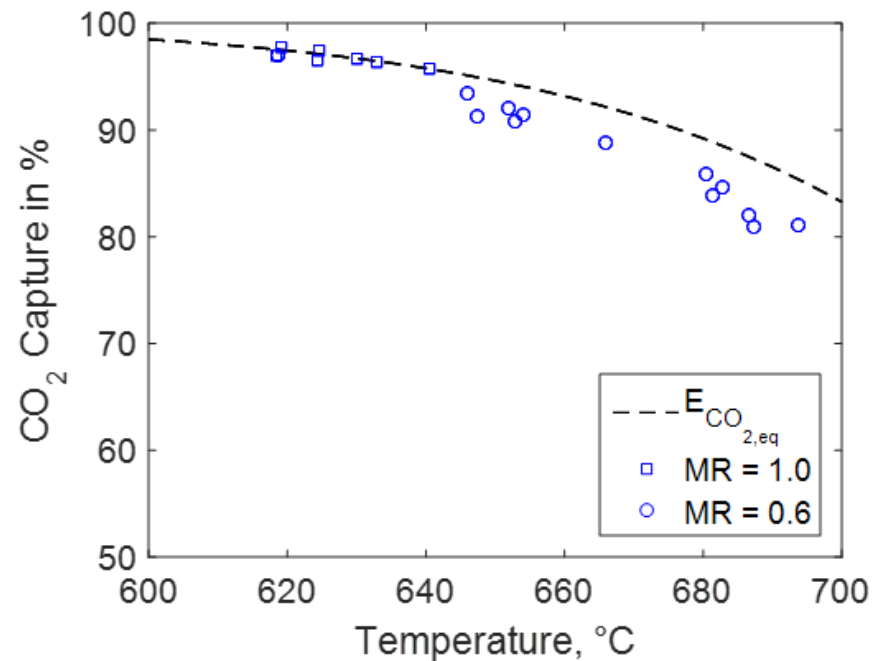


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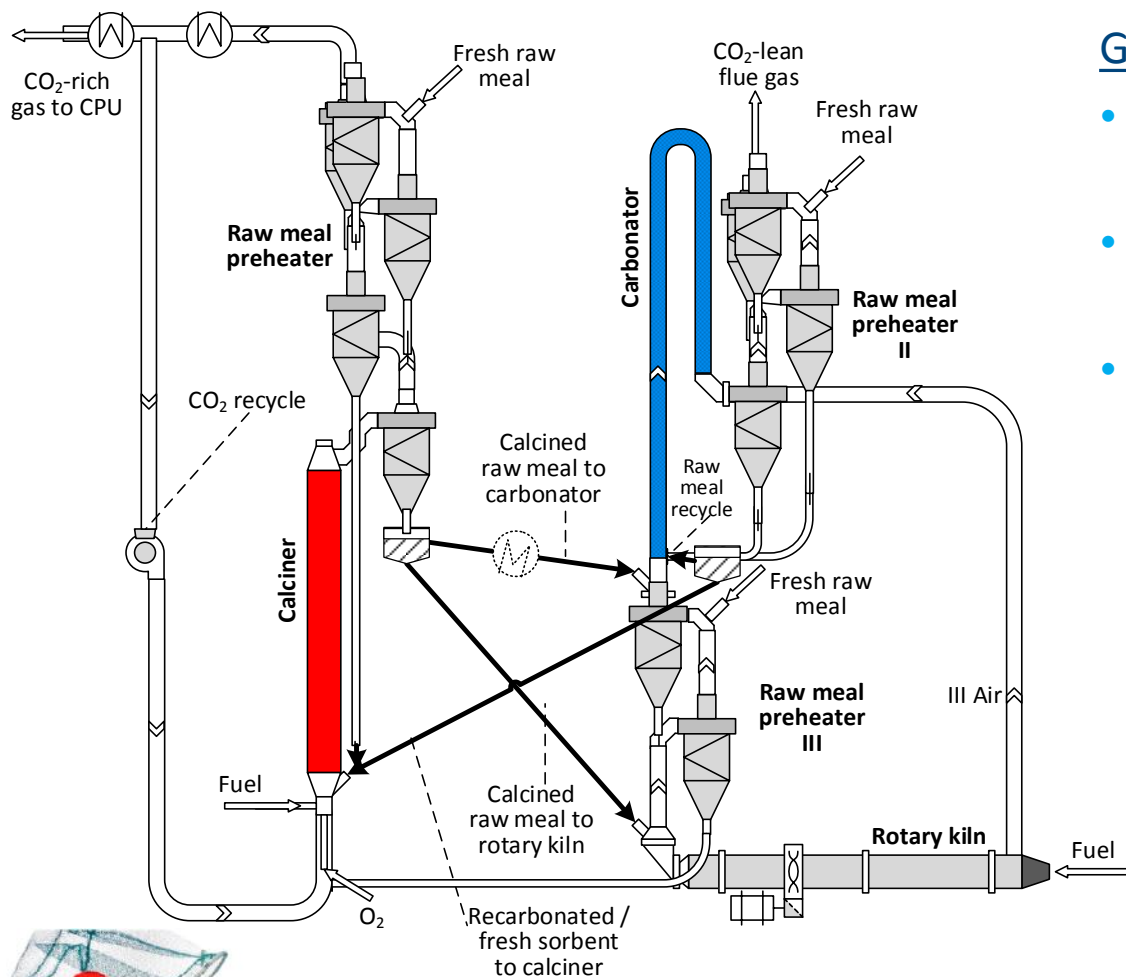
# Calcium Looping CO<sub>2</sub> capture: Tail-end CaL configuration

## Demonstration at semi-industrial scale:

- High CO<sub>2</sub> capture up to 98 % demonstrated
- Favorable CaL operation conditions
  - reduced recycle train
  - high sorbent activity
- High CO<sub>2</sub> capture at carbonator inlet may cause problems of entrainment due to reduction of fluidization gas (~ -25 %)



# Calcium Looping CO<sub>2</sub> capture: highly integrated configuration



## General information:

- CaL calciner coincides with the cement kiln pre-calciner
- Calcined raw meal as CO<sub>2</sub> sorbent in the carbonator
- Sorbent has small particle size ( $d_{50}=10-20 \mu\text{m}$ ) → entrained flow reactors

*Marchi M.I., et al., 2012.* Procedimento migliorato per la produzione di clinker di cemento e relativo apparato. *Patents MI2012 A00382 and MI2012 A00382.*

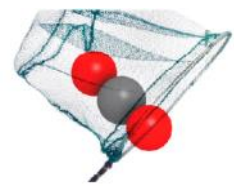
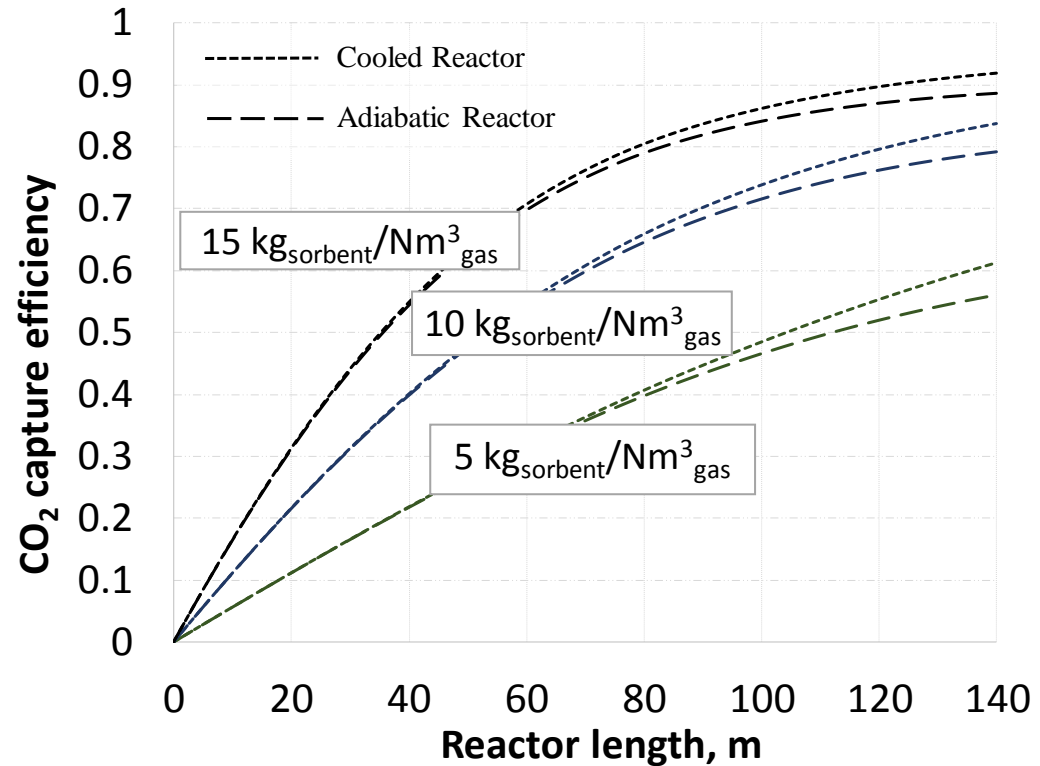
*Romano et al., 2014.* The calcium looping process for low CO<sub>2</sub> emission cement plants. *Energy Procedia, 61, 500-503.*

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# Calcium Looping CO<sub>2</sub> 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

	Cement plant w/o capture	Tail-end CaL	integrated CaL
$F_0/F_{CO_2}$	--	0.16	4.1
$F_{Ca}/F_{CO_2}$	--	4.8	4.0
Carbonator CO <sub>2</sub> capture efficiency [%]	--	88.8	80.0
<b>Total fuel consumption [MJ<sub>LHV</sub>/t<sub>clk</sub>]</b>	3223	8672	4740
Rotary kiln burner fuel consumption [MJ <sub>LHV</sub> /t <sub>clk</sub> ]	1224	1210	1180
Pre-calciner fuel consumption [MJ <sub>LHV</sub> /t <sub>clk</sub> ]	1999	1542	3560
CaL calciner fuel consumption [MJ <sub>LHV</sub> /t <sub>clk</sub> ]	--	5920	
<b>Net electricity production [kWh<sub>el</sub>/t<sub>clk</sub>]</b>	<b>-132</b>	<b>159</b>	<b>-164</b>
Direct CO <sub>2</sub> emissions [kg <sub>CO2</sub> /t <sub>clk</sub> ]	863.1	143.2	71.4
Indirect CO <sub>2</sub> emissions [kg <sub>CO2</sub> /t <sub>clk</sub> ]	105.2	-123.5	128.7
Equivalent CO <sub>2</sub> emissions [kg <sub>CO2</sub> /t <sub>clk</sub> ]	968.3	19.7	200.1
Equivalent CO <sub>2</sub> avoided [%]	--	98.0	79.3
<b>SPECCA [MJ<sub>LHV</sub>/kg<sub>CO2</sub>]</b>	--	3.26	2.32

*Spinelli M. et al., 2017. Integration of Ca-Looping systems for CO<sub>2</sub> capture in cement plants. Energy Procedia, 114, 6206-6214.*

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Dusseldorf, 6-7 November 2017

## The CLEANKER project

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F. Canonico<sup>d</sup>, S. Consonni<sup>b,c</sup>

Calcium Looping  
for cement industry  
decarbonization



<sup>a</sup> Italcementi, Heidelberg Group

<sup>b</sup> LEAP

<sup>c</sup> Politecnico di Milano

<sup>d</sup> Buzzi Unicem



- **Project objectives**
- **The demo plant**
- **The consortium**
- **Work packages**





The ultimate objective of CLEANKER is advancing the integrated Calcium-looping process for CO<sub>2</sub> 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 CO<sub>2</sub> 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



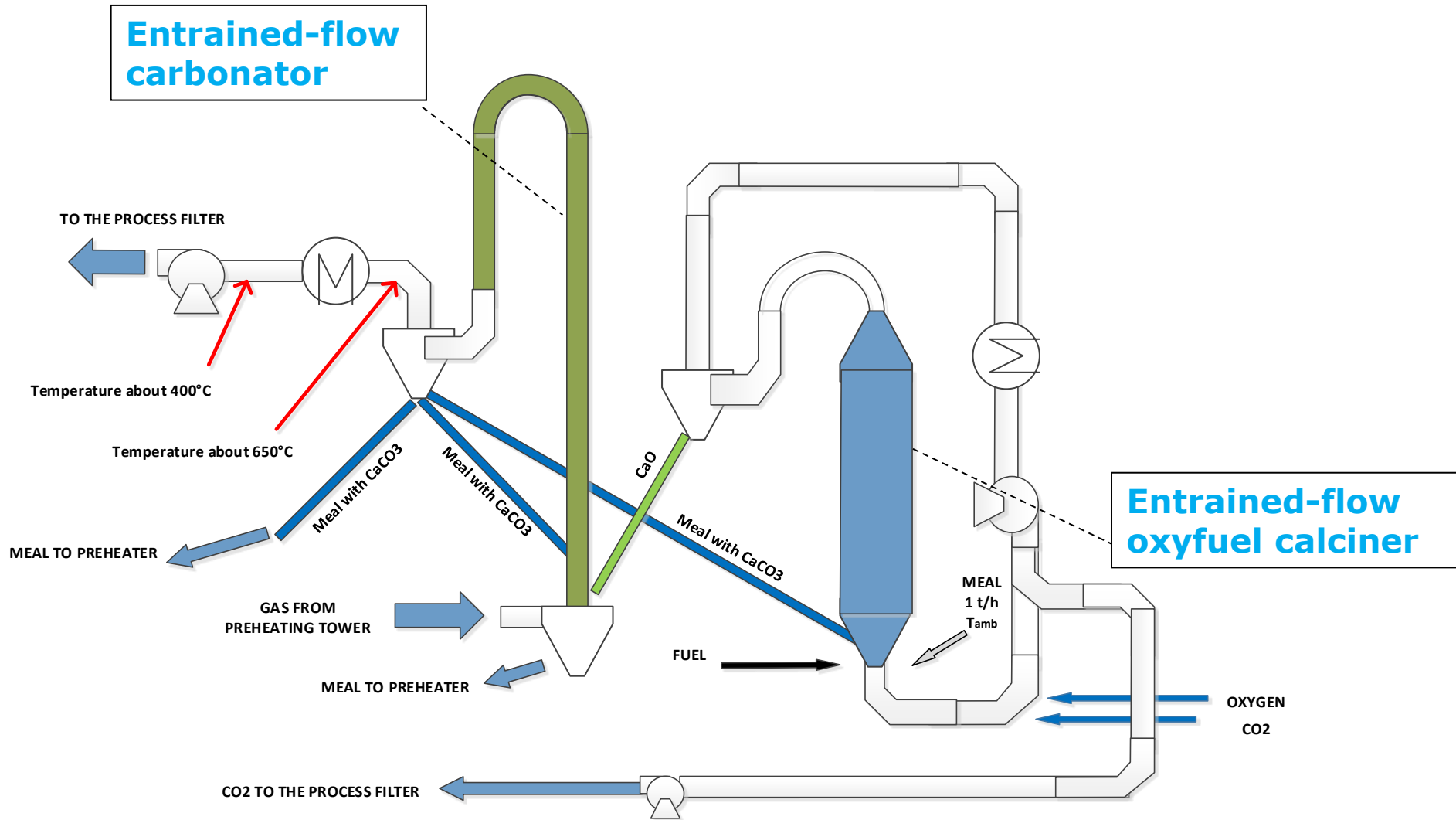
# Primary project objectives

- 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 (actual manufacturing in the case of key enabling technologies; or in space)

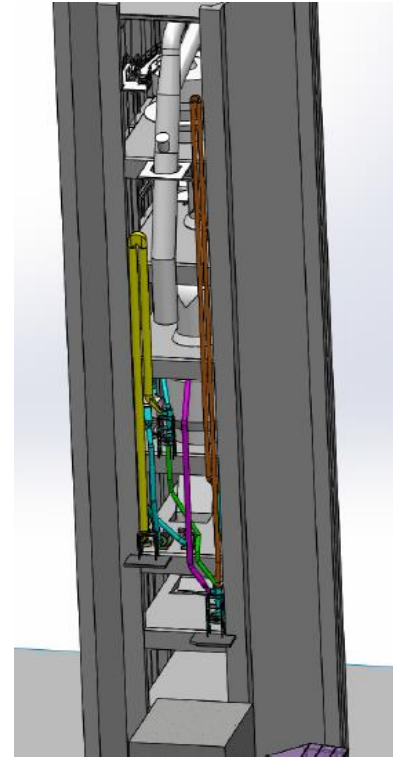
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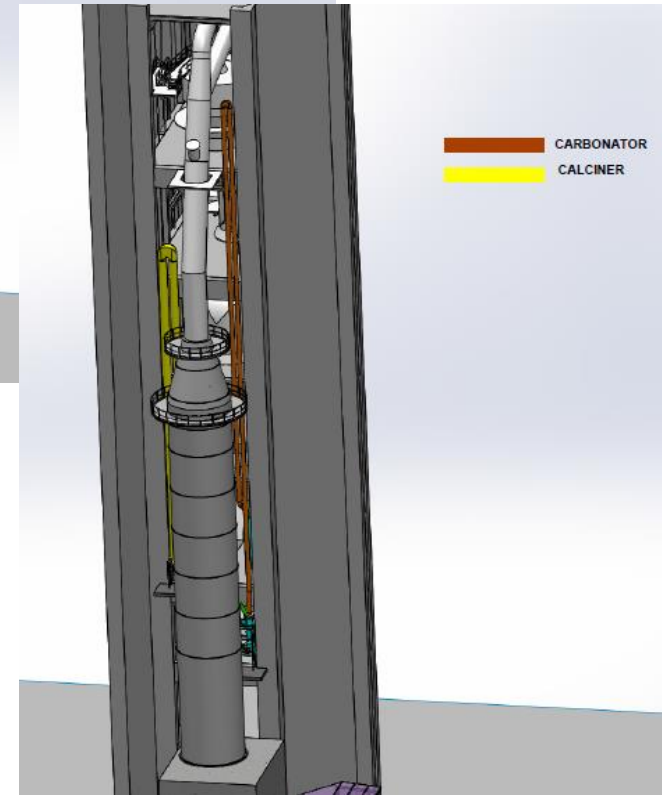
# Indicative configuration of the CLEANKER pilot



# Vernasca kiln preheater and rendering of CaL pilot



- CARBONATOR
- CALCINER
- PH 2nd stage TAKE-OFF
- CaO to CARBONATOR

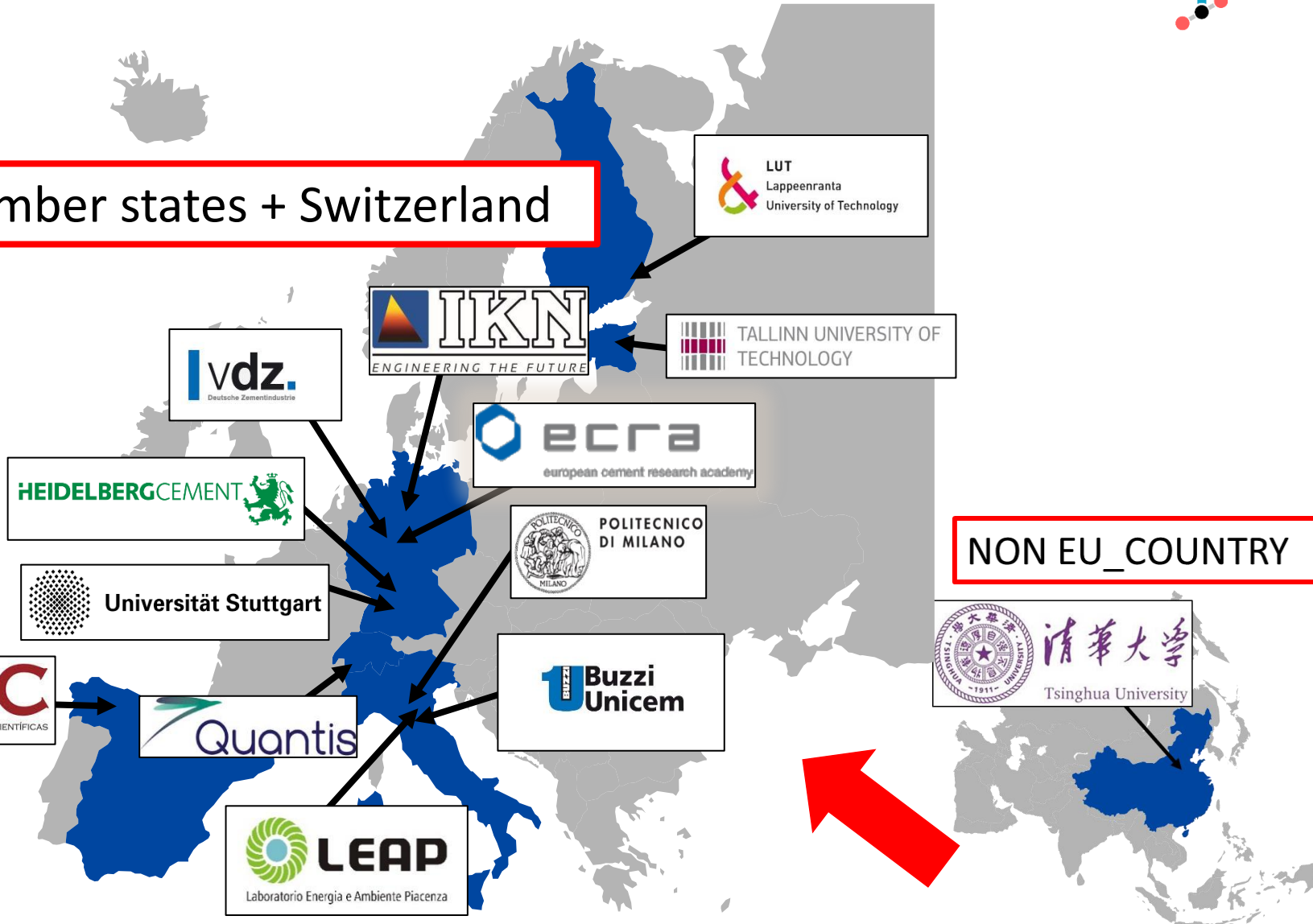


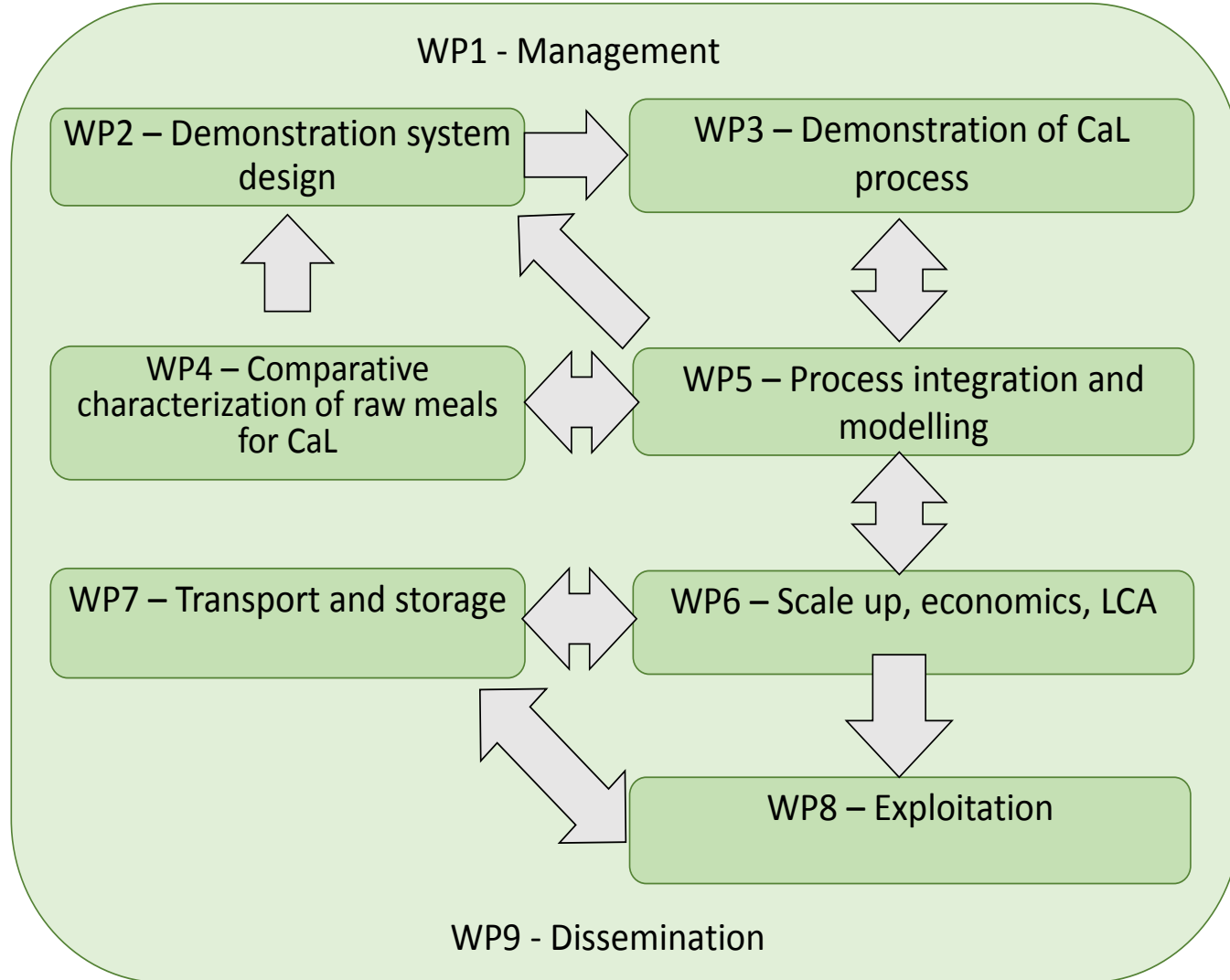
- CARBONATOR
- CALCINER



# The consortium

5EU member states + Switzerland








# 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 CO<sub>2</sub> capture expected 
- Two calciners are present in the system, leading to high fuel consumptions 

### 3. Integrated CaL configuration:

- High CO<sub>2</sub> 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**

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