



CALCIUM LOOPING CAPTURE IN THE CEMENT INDUSTRY – CEMCAP CONCLUSIONS

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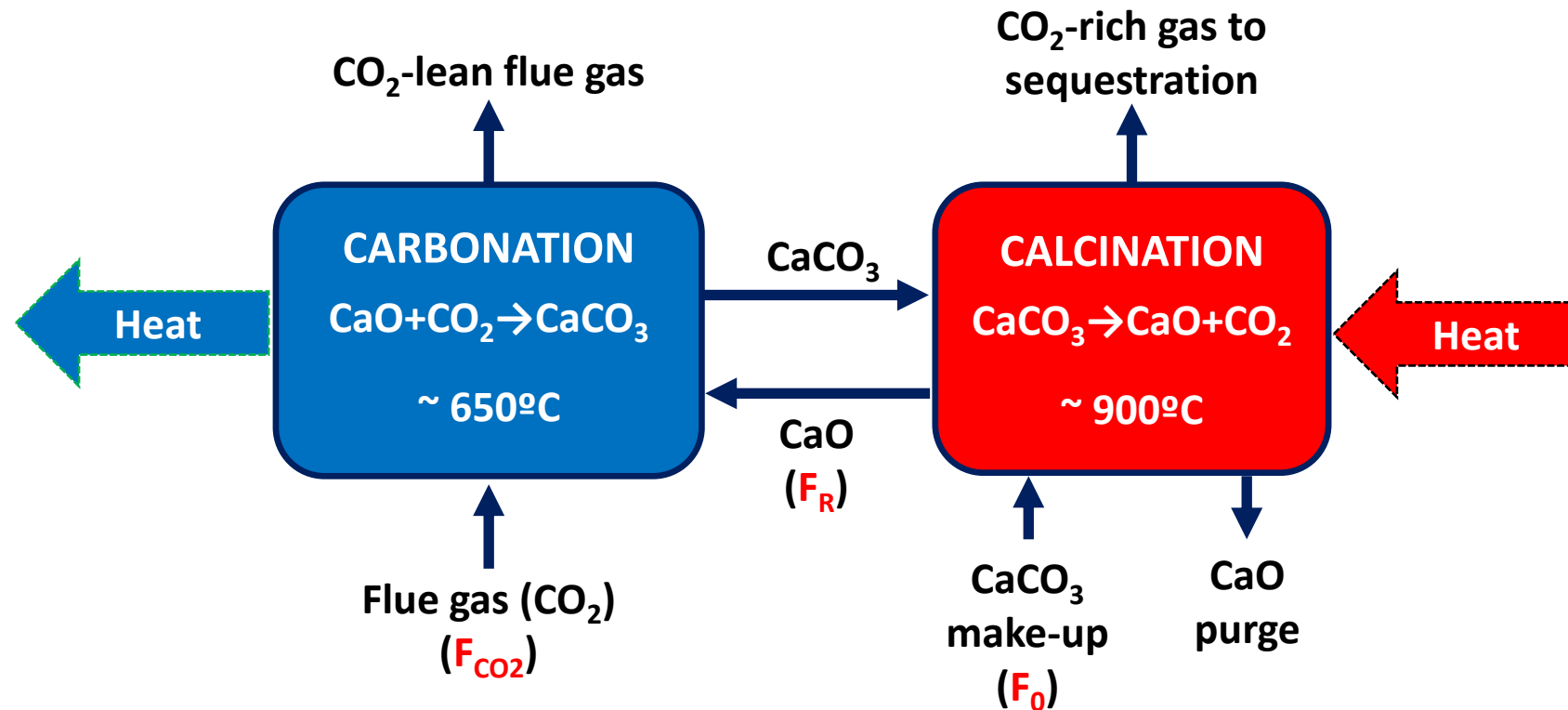
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Calcium Looping process fundamentals



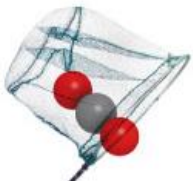
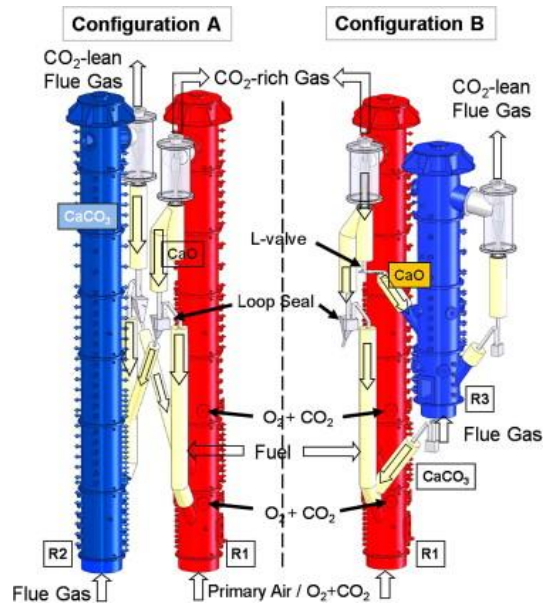
Calcium Looping for CO₂ capture: history

- Originally proposed by Shimizu et al., 1999. A twin fluid-bed reactor for removal of CO₂. 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)



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 CaCO_3

CEMCAP focus

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

CLEANKER focus

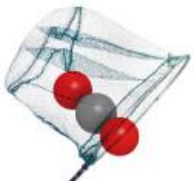
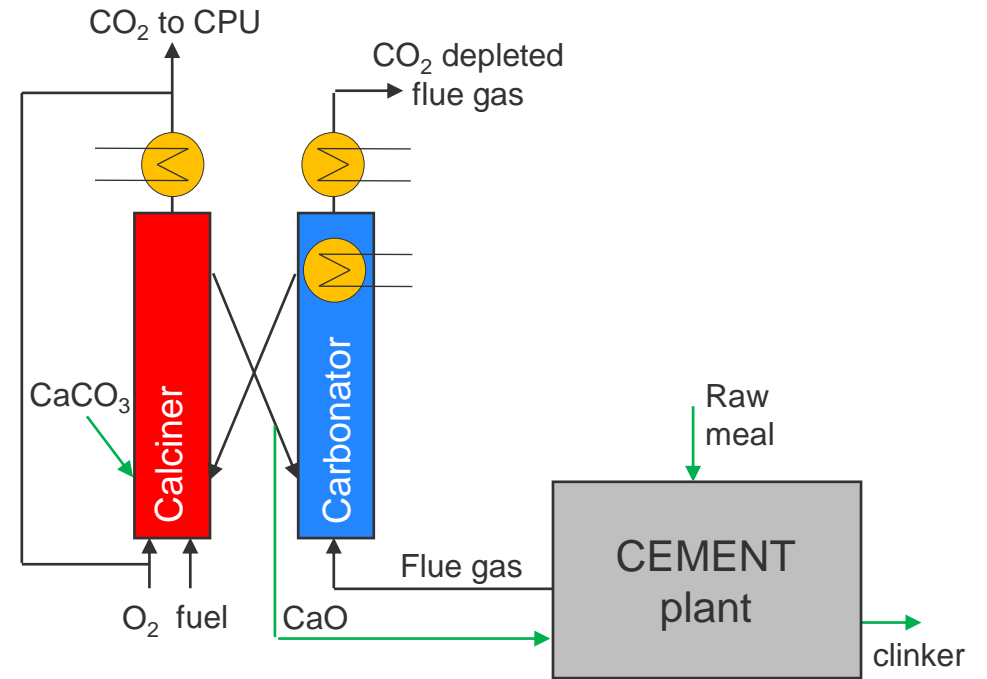
3. Integrated CaL configuration: the CaL process is integrated within the cement production process by sharing the same oxyfuel calciner



Calcium Looping CO₂ capture: Tail-end CaL configuration

General features of the process:

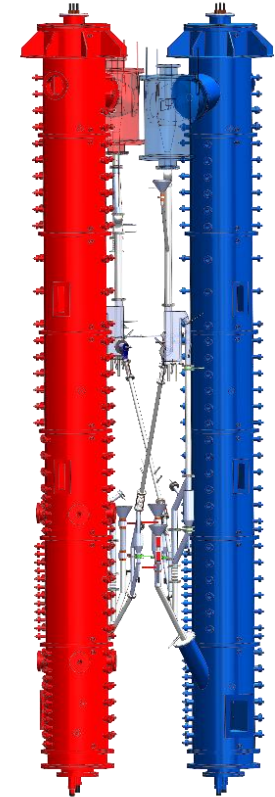
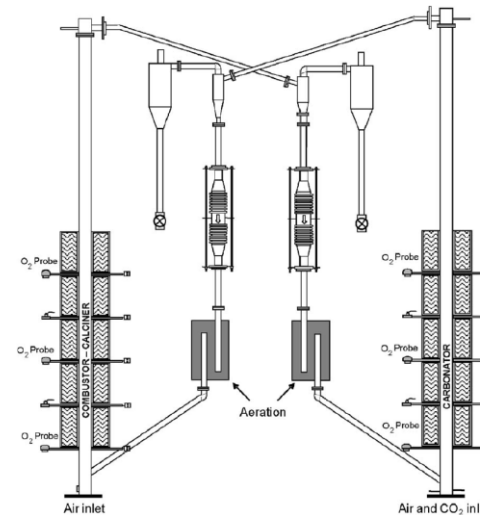
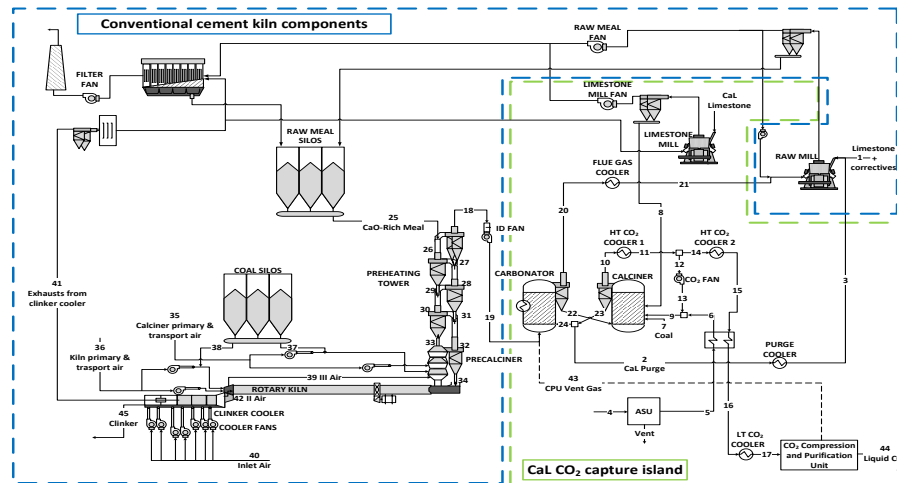
- Carbonator removes CO₂ from cement plant flue gas
→ Easy integration in existing cement
- Limestone partly calcined in Calcium Looping calciner
→ CaO-rich purge from CaL calciner used as feed for the cement kiln
- High fuel consumption (double calcination for the mineral CO₂ captured)
- Heat from fuel 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



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_{th}) at IFK (TRL6)
- Process integration study and techno-economic analysis



Arias et al., 2017. CO₂ 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 CO₂ Capture in Cement Plants – Pilot Scale Test. *Energy Procedia*, 114, 6171–6174.

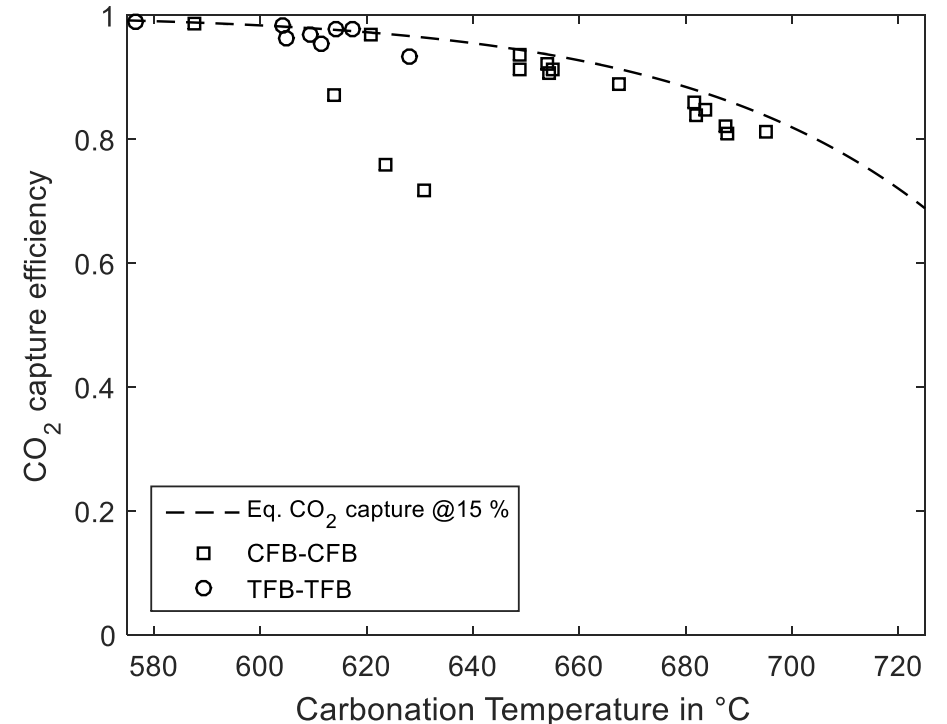
Spinelli et al., 2017. Integration of CaL systems for CO₂ capture in cement plants. *Energy Procedia*, 114, 6206-6214.

De Lena et al., 2017. Process integration of tail-end CaL in cement plants. *Int J Greenh Gas Control*. 67, 71-92.

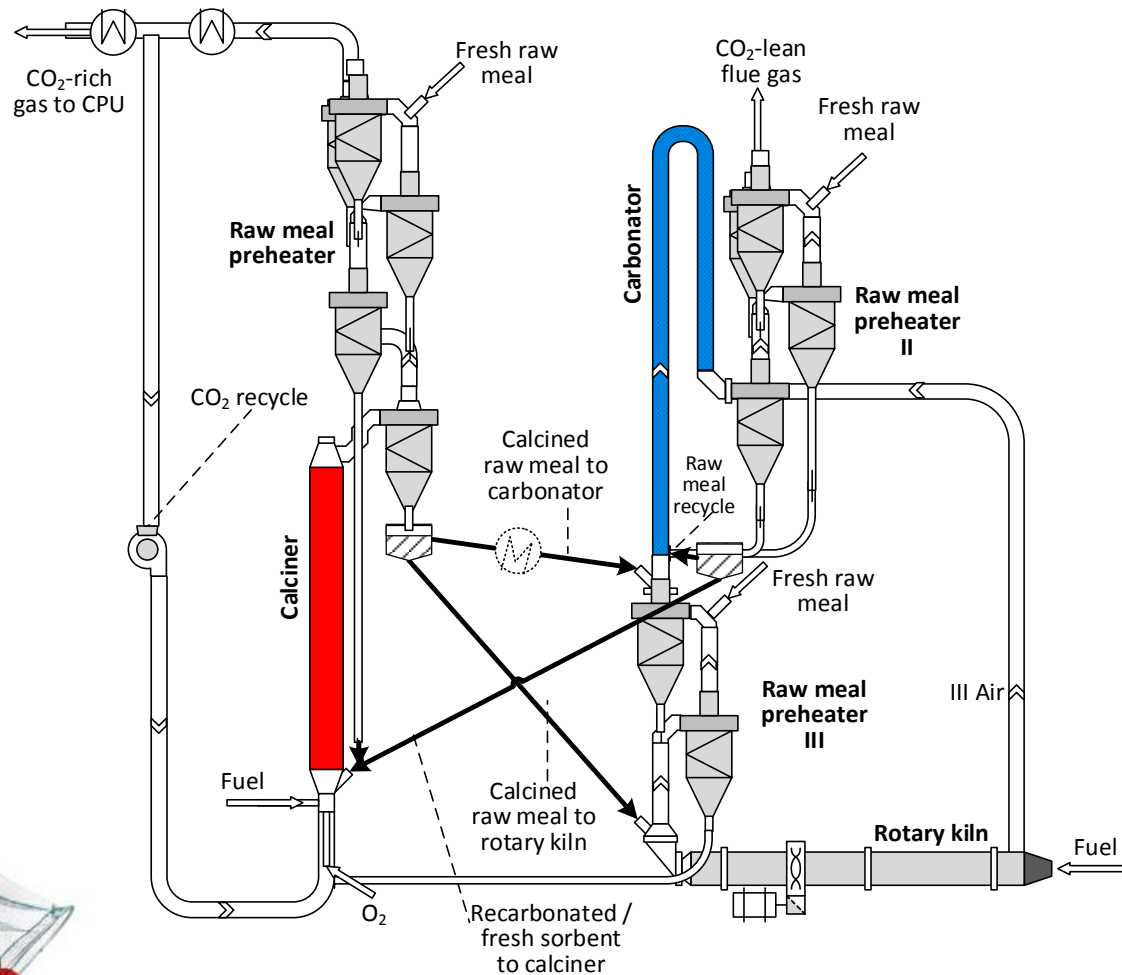
Calcium Looping CO₂ capture: Tail-end CaL configuration

Demonstration at semi-industrial scale:

- High CO₂ capture up to 98 % demonstrated in TRL6 facility
- The CaL design parameters for cement plant applications are in good agreement with the design parameters for power plant operation.
- Tail-end CaL ready for demonstration at TRL7-8.



Calcium Looping CO₂ capture: integrated configuration

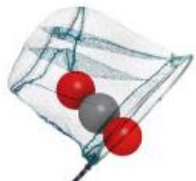


General information:

- CaL calciner coincides with the cement kiln pre-calciner
- Calcined raw meal as CO₂ 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.*

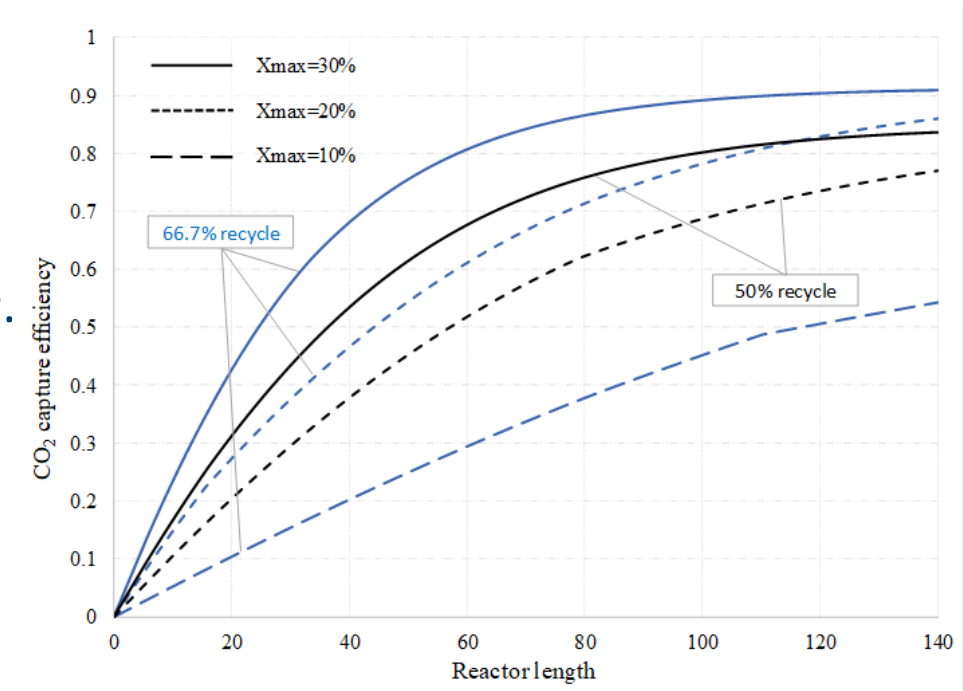
Romano et al., 2014. The calcium looping process for low CO₂ emission cement plants. *Energy Procedia, 61, 500-503.*



Calcium Looping CO₂ capture: integrated configuration

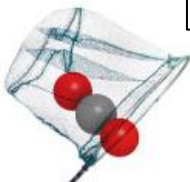
Development of integrated CaL concept using entrained flow calciner/carbonator:

- 1D carbonator modelling showed possibility of achieving high capture efficiency with solids/gas ratio of $\sim 10 \text{ kg/Nm}^3$.
- Belite formation in calciner may cause a decrease of the sorbent CO₂ carrying capacity.
- Demonstration of chemistry and fluid-dynamics of the reactors in industrially relevant conditions needed.



Alonso et al., 2018. Capacities of Cement Raw Meals in Calcium Looping Systems. *Energy & Fuels*, 31, 13955–13962.

Spinelli et al., 2018. One-dimensional model of entrained-flow carbonator for CO₂ capture in cement kilns by calcium looping process. *Chemical Engineering Science*, 191, 100-114.



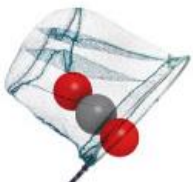
Mass and energy balance

	Cement plant w/o capture	Tail-end CaL (20% integration)	Tail-end CaL (50% integration)	Integrated CaL
Carbonator CO₂ capture efficiency [%]	--	88.8	90.0	82.0
Total fuel consumption [MJ_{LHV}/t_{clk}]	3240	8720	7100	5440
Rotary kiln fuel consumption [MJ _{LHV} /t _{clk}]	1230	1220	1220	1150
Pre-calciner fuel consumpt. [MJ _{LHV} /t _{clk}]	2010	1550	850	4290
CaL calciner fuel consumpt. [MJ _{LHV} /t _{clk}]	--	5950	5040	
Net electricity consumpt. [kWh_{el}/t_{cem}]	97	-81	42	117
Direct CO₂ emissions [kg_{CO2}/t_{clk}]	865	119	79	55
Indirect CO₂ emissions [kg_{CO2}/t_{clk}] *	35	-29	15	46
Equivalent CO₂ emissions [kg_{CO2}/t_{clk}]	900	90	94	101
Equivalent CO₂ avoided [%]	--	90.0	89.5	88.8
SPECCA [MJ_{LHV}/kg_{CO2}] **	--	4.42	4.07	3.16

* Evaluated with the average EU-28 electricity mix: $\eta_e = 45.9\%$, $E_{CO_2,e} = 262 \text{ kg/MWh}$

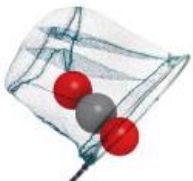
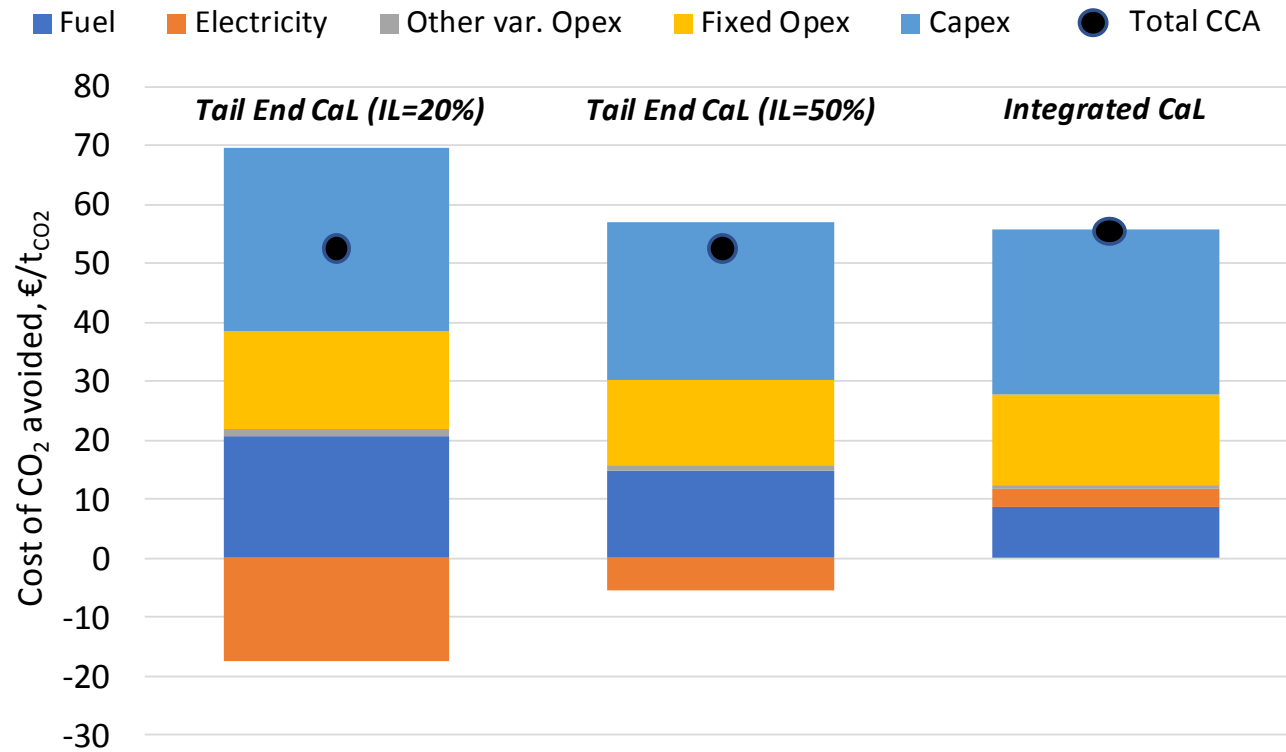
** Specific primary energy consumption for CO₂ avoided

De Lena et al., 2017. Process integration of tail-end CaL in cement plants. Int J Greenh Gas Control. 67, 71-92.



Economic analysis




Cost of CO₂ avoided = 50-55 €/t_{CO2}, mainly due to Capex.






Conclusions and outlook

Ca-LOOPING PROCESS INTEGRATION OPTIONS:

1. Post-combustion capture configuration:

- Low uncertainty in the technical feasibility 
- Very high CO₂ capture expected 
- Two calciners are present in the system, leading to high fuel consumptions 

2. Integrated CaL configuration:

- High CO₂ capture efficiency without modifying rotary kiln operation (no need of kiln oxyfiring). 
- Higher thermal efficiency and lower fuel consumptions 
- New carbonator design and fluid-dynamic regime: fluid-dynamics, heat management and sorbent performance need validation 

– Competitive cost of CO₂ avoided. 



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