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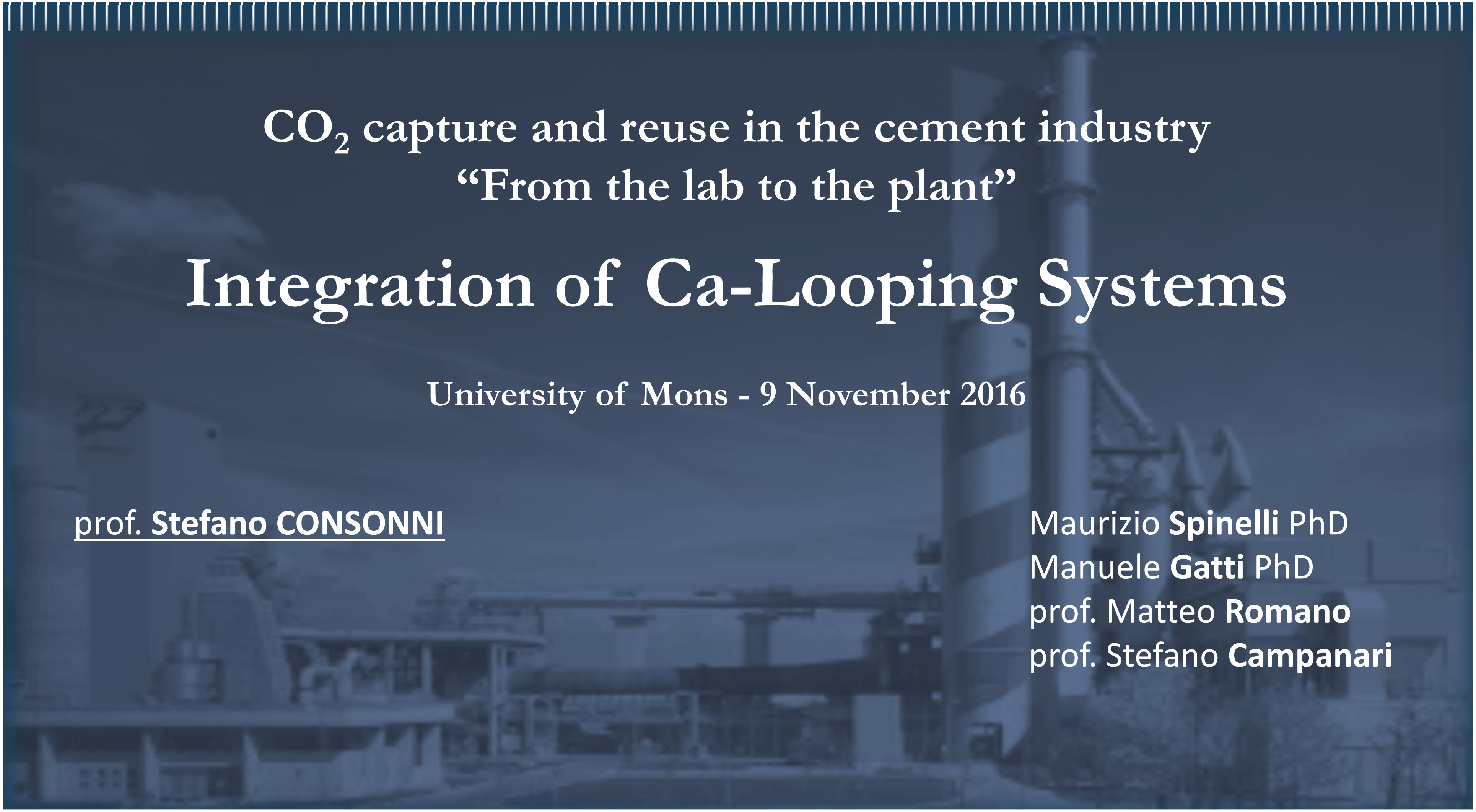

CO$_2$ capture and reuse in the cement industry
"From the lab to the plant"

Integration of Ca-Looping Systems

University of Mons - 9 November 2016

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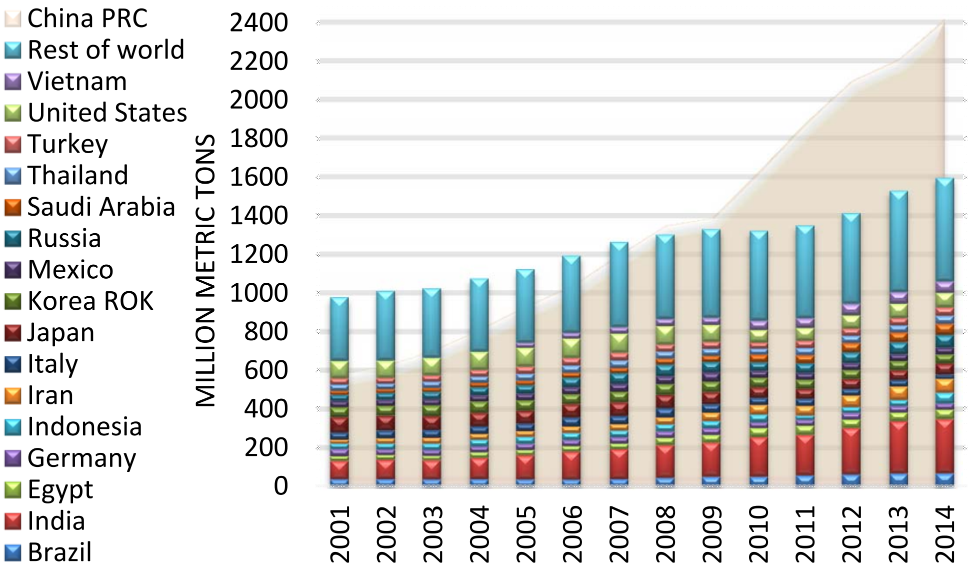
Why CCS in cement plants?

- ✓ Strong production increase worldwide (>250% in the last 15 years)
- ✓ High CO_2 emissions per unit product (~850g_{CO2}/kg_{CK})
- ✓ Globally, cement industry is responsible for the 5% of the total anthropogenic CO_2 emissions from stationary sources

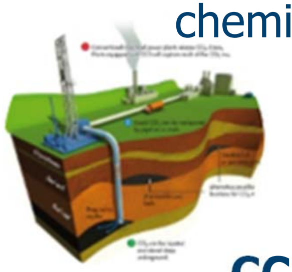


Several CO_2-reduction measures are currently available:

Efficiency increase *E.g: Additional preheating stage efficient electric engines*

Alternative fuels *E.g: Use of biomass and other carbon neutral fuels*

Alternative cement *E.g: MgO-based clinker (low temperature, low CO_2 process)*



Differently from other industrial process, most of CO_2 emission comes from chemical processes and not from fuel combustion

CCS is essential for a deep reduction of both the CO_2 generated by combustion and $CaCO_3$ calcination

✓ Outline

- ✓ Calcium Looping technology (CaL)
- ✓ CaL applications for CCS in cement plants
- ✓ Synergy process between CaL power plant & cement plant
- ✓ Tail-end CaL option in cement plants
- ✓ Integrated CaL option in cement plants
- ✓ Entrained flow carbonator model

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Ca-Looping technology

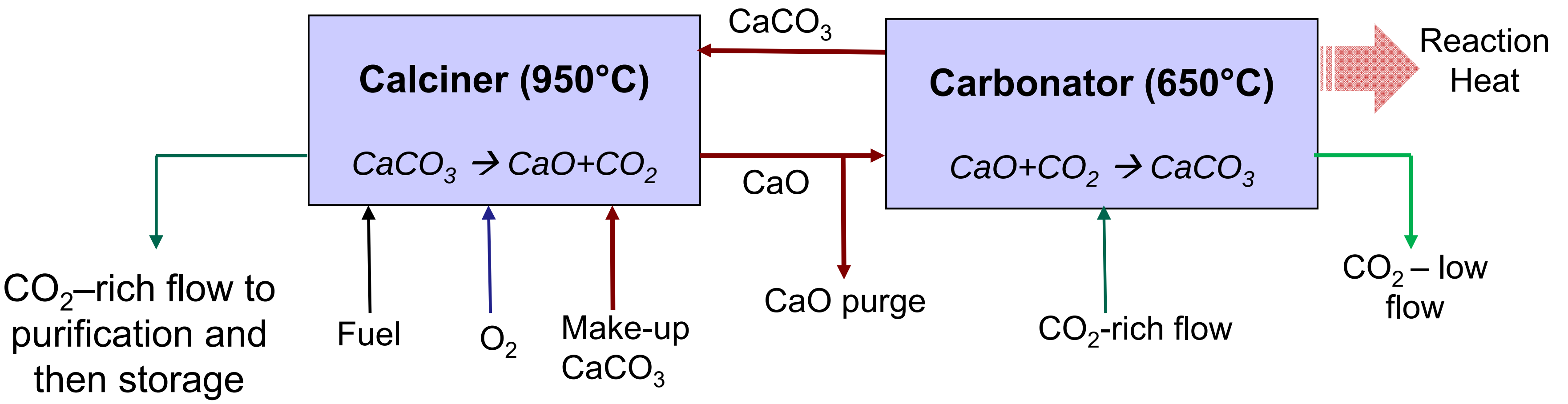
The Calcium Looping concept

- ✓ CO_2 capture by Calcium Looping comprises two basic steps
- ✓ 1) Capture diluted CO_2 by calcium oxide (CaO) to form calcium carbonate ($CaCO_3$):

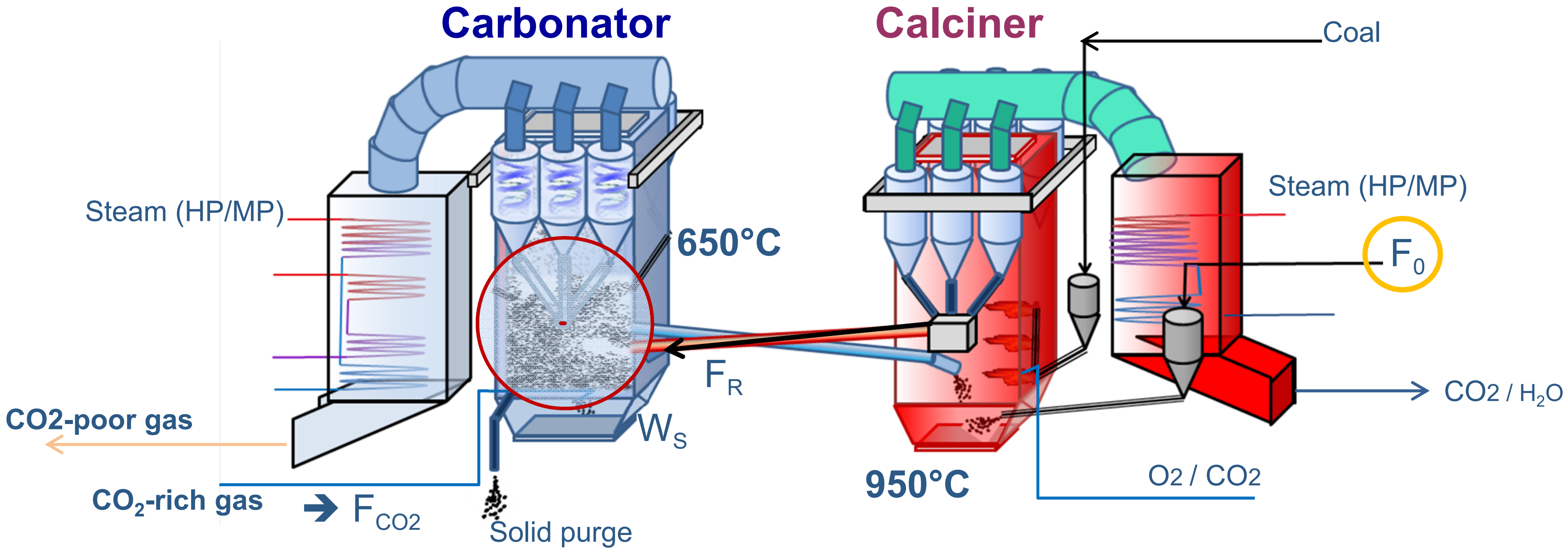
$$CaO_{(S)} + CO_{2(G)} \rightarrow CaCO_{3(S)} \quad \Delta h_R = -179 \text{ kJ mol}^{-1}$$

At atmospheric pressure this **Carbonation** reaction takes place around 650°C with the release of a significant amount of heat, which can be used in a steam cycle

- ✓ 2) Release highly-concentrated CO_2 by **oxy-fuel Calcination** at about 950°C. Liquid CO_2 for storage is obtained by purifying the flow generated in the calciner.
- ✓ The same **CaO keeps looping across the Carbonator and the Calciner**, with a fraction being purged to maintain adequate reactivity



Calcium looping with CFB reactors – key parameters



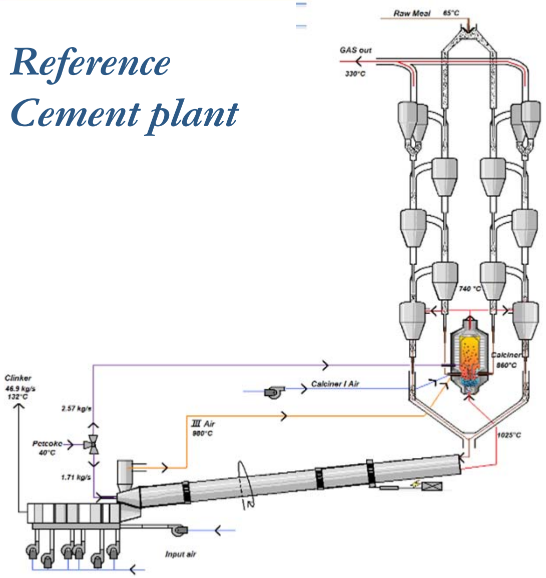
- **F_0/F_{CO2} (Limestone make-up)** = mol ratio {fresh $CaCO_3$ flow to carbonator} / {CO_2 in the exhaust gases entering the carbonator}; make-up is needed to keep high sorbent reactivity and extract sulphur and other impurities; high make-up gives higher CO_2 capture rates but also higher energy consumption
- **F_R/F_{CO2} (Sorbent recycle rate)** = mol ratio {CaO recirculated across reactors} / {CO_2 in the exhaust gases entering the carbonator}; this ratio gives the excess of sorbent with respect to stoichiometric conditions
- **W_S/V_G (solid inventory)** = ratio {solids in carbonator / { vol flow rate of gas};

High F_R/F_{CO2} and low F_0/F_{CO2} maximize CO_2 capture while minimizing waste sorbent

Ca-Looping in cement plants

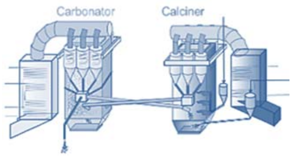
Ca-Looping application for power production and CCS in cement plants

Reference Cement plant



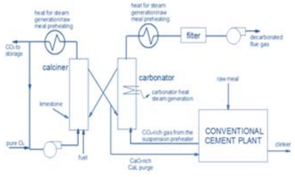
CaL-I

1) Synergy between cement plant and power plant with Ca-Looping reactors



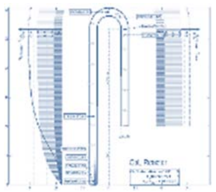
CaL-II

2) Tail-end application of Ca-Looping process in the cement plant;



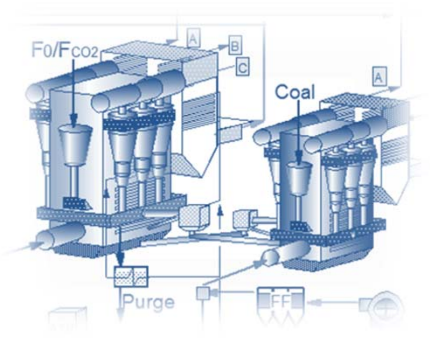
CaL-III

3) Integrated Ca-Looping process in cement plant

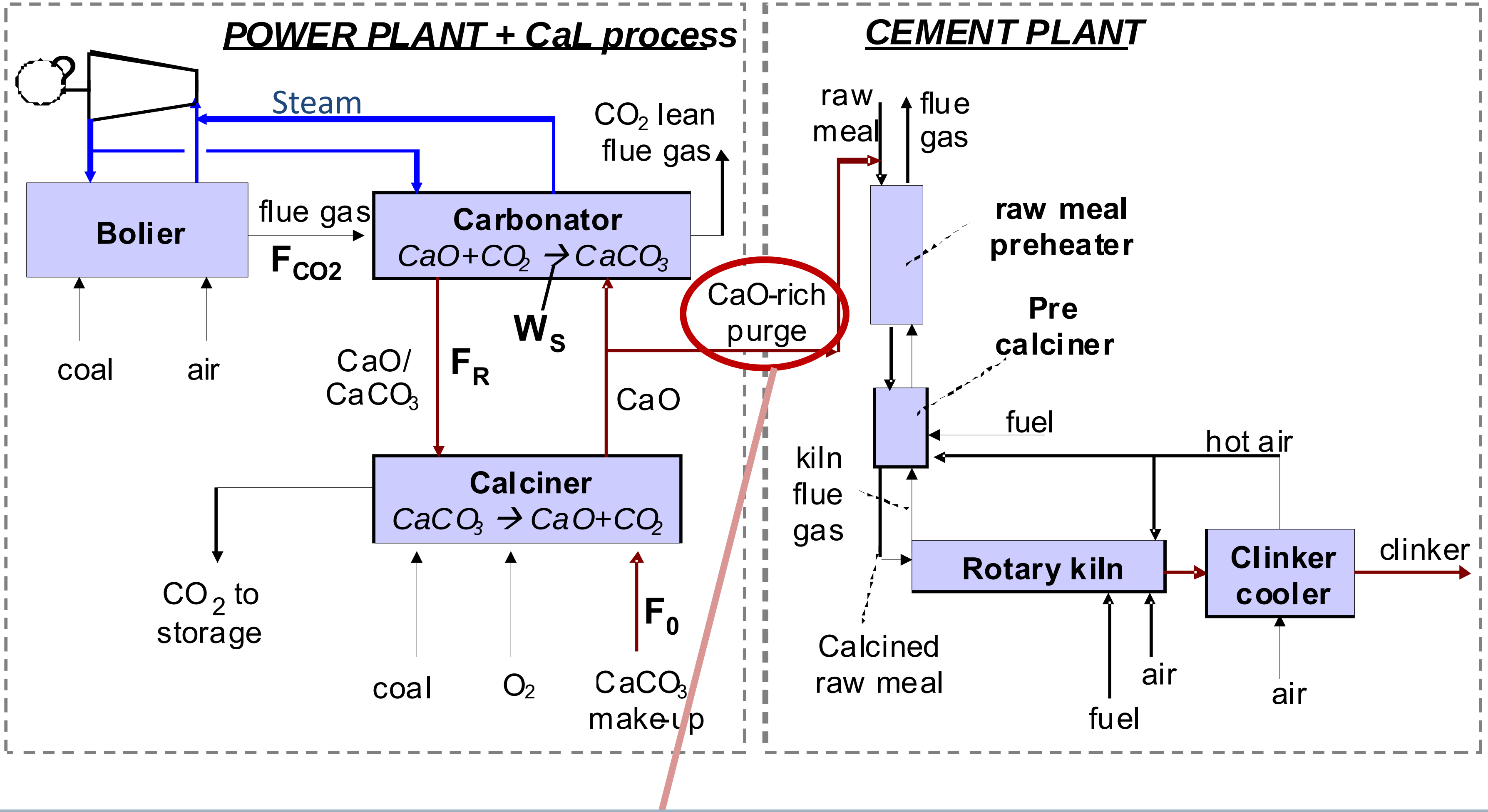


- ✓ Complete process simulations (GS-Aspen) & models for Carbonator and MCFC (Matlab and Fortran) ➔ techno-economic analysis
- ✓ All the proposed processes are compared with the reference CCS option (oxycombustion)

Synergy process between a cement plant and a CaL power plant



Synergy process concept: cement plant fed by power plant purge



Process integration: solid purge from power plant fed to cement plant as **calcined raw meal** → strong reduction in fuel consumption, CO_2 emission and costs

Cement plant off design operation: substitution rate

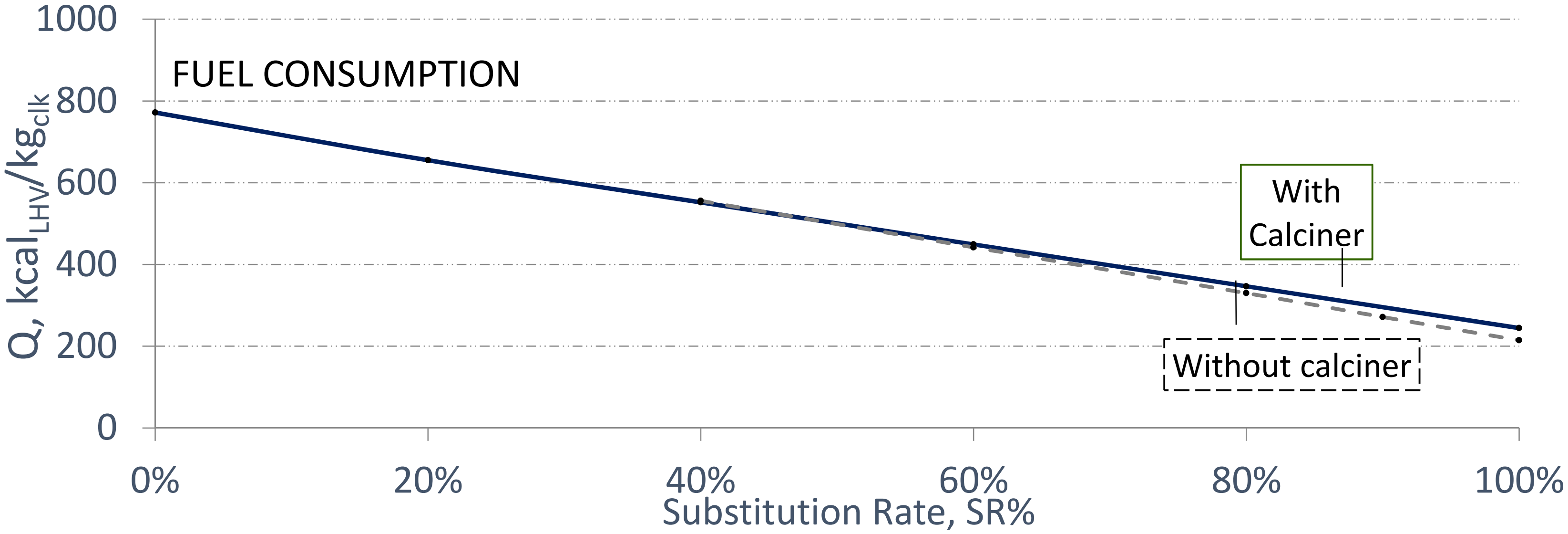
Effects of feeding CaO-rich CaL purge:

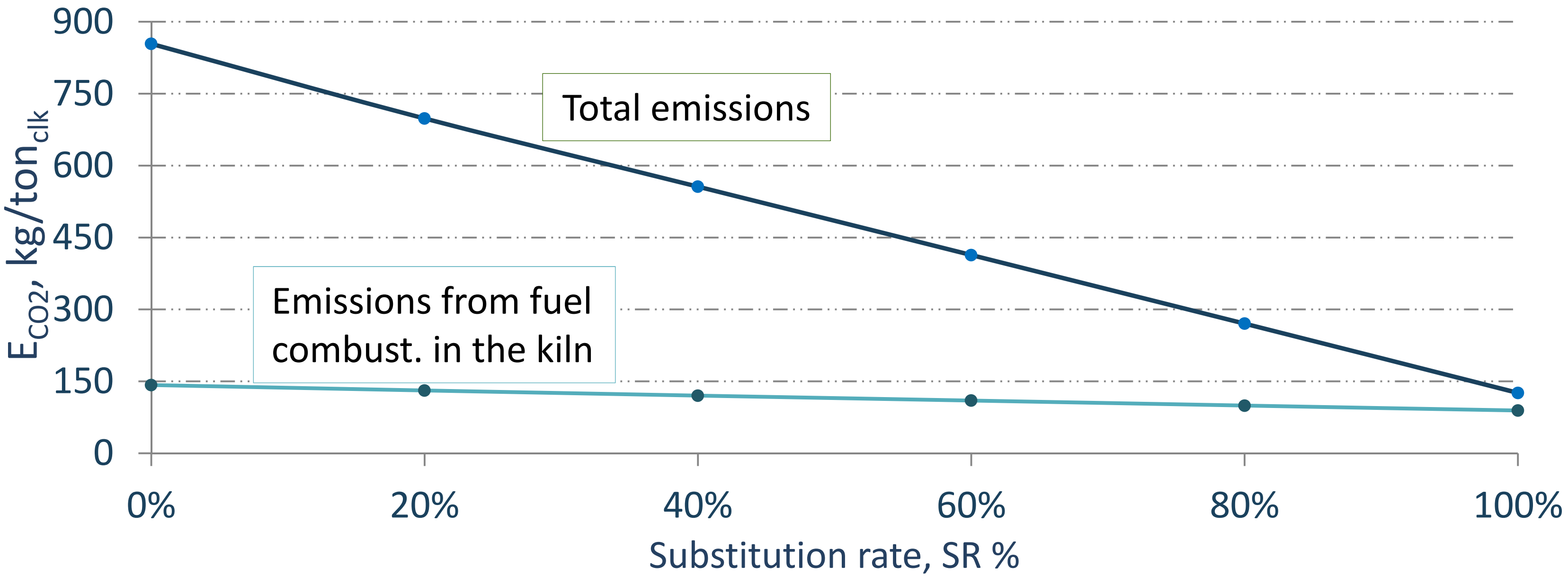
- Reduction of fuel consumption for limestone calcination
- Reduction of CO_2 emission from fuel oxidation and calcination
- Reduction of gas and solid flow rate in the suspension preheater

Integration level defined by the substitution rate (SR):

$$SR = \frac{moles\ of\ CaO\ from\ CaL\ purge}{total\ moles\ of\ Ca\ fed\ to\ the\ plant}$$

Effect of different SR: fuel consumption and CO_2 emissions





Cement plant off design operation: substitution rate

Effects of feeding CaO-rich CaL purge:

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Integration level defined by the substitution rate (SR):

$$SR = \frac{moles\ of\ CaO\ from\ CaL\ purge}{total\ moles\ of\ Ca\ fed\ to\ the\ plant} \rightarrow \boxed{SR_{Max}=f(Ash,S\ in\ purge)}$$

<u>Maximum substitution rate limited</u> by the presence of solids species other than $CaO/CaCO_3$, i.e. fuel ash and $CaSO_4$ in the CaL purge

➔ Important influence of composition of fuel used in the calciner of the CaL process

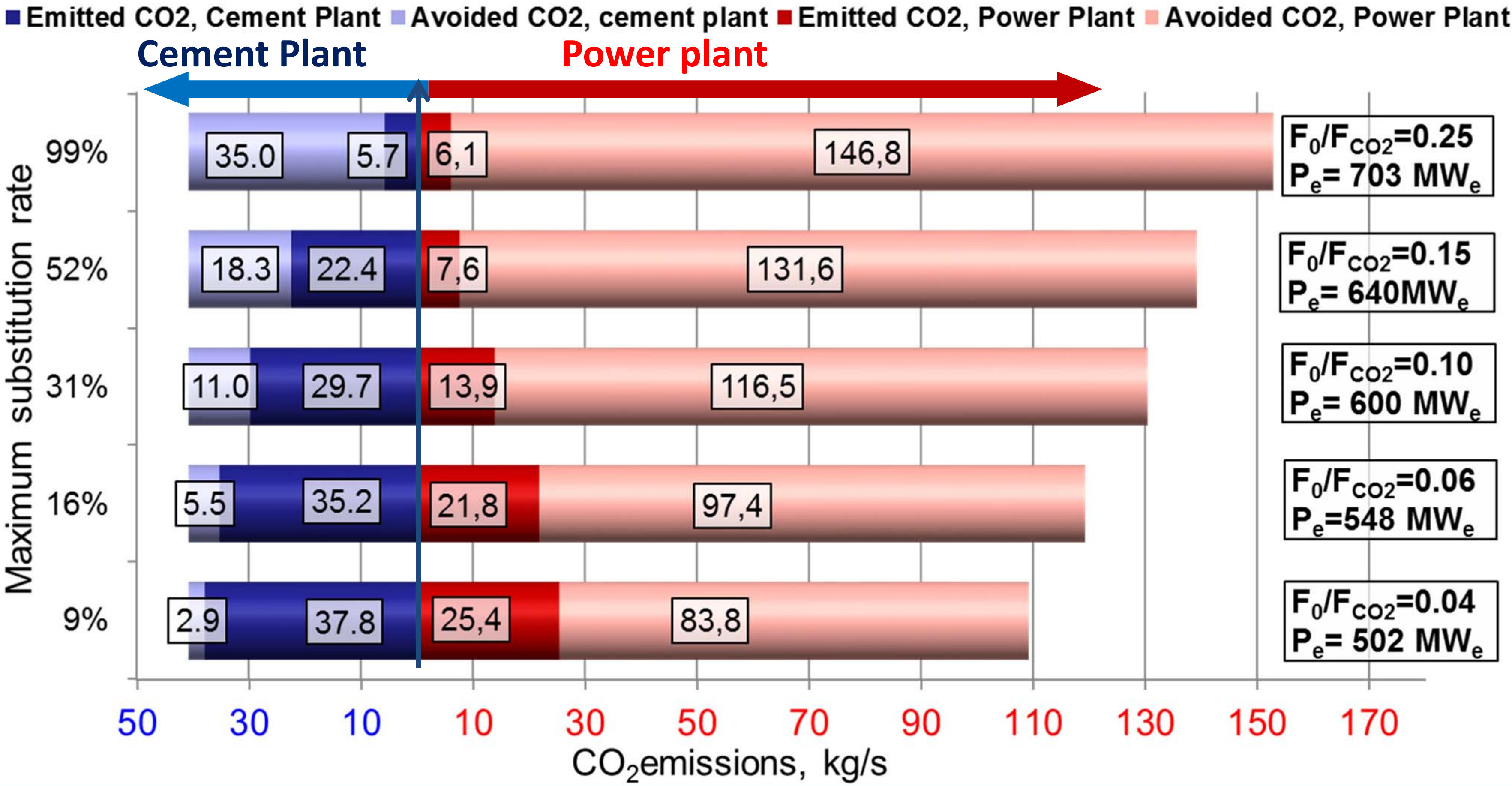
➔ SRmax determined by comparing the CaL purge composition with ISO-substitution rate maps

➔ Cases with lower F_R/F_{CO2} lead to higher purity purge and may be preferred

Synergy process – Results (i): power plant size & CO_2 avoided

Simulation criteria: Fixed size for the cement plant (4100 tpd)
Variable size for the power plant, determined by the maximum substitution rate

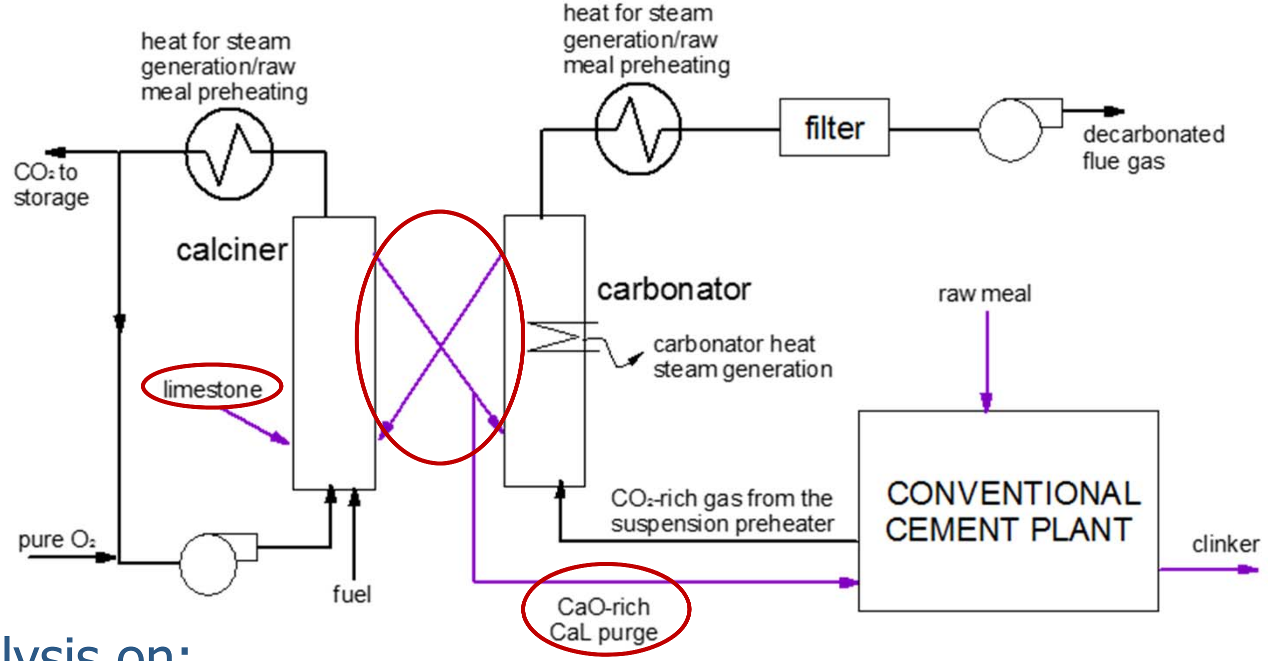
(F_0/F_{CO2} variable, $F_R/F_{CO2}=6$, $W_S/G_G=150$ kg/(m^3/s))



Tail-end CaL application in cement plant

Tail-end CaL application in cement plant

Downstream Calcium looping CO_2 capture section based on two interconnectec fluidized bed reactors (carbonator-calciner) fed by a pure $CaCO_3$ stream.



Sensitivity analysis on:

➔ Integration level (IL): fraction of raw meal substituted with the CaL purge➔ depends on F_0 (moles of fresh $CaCO_3$ introduced in the CaL system)

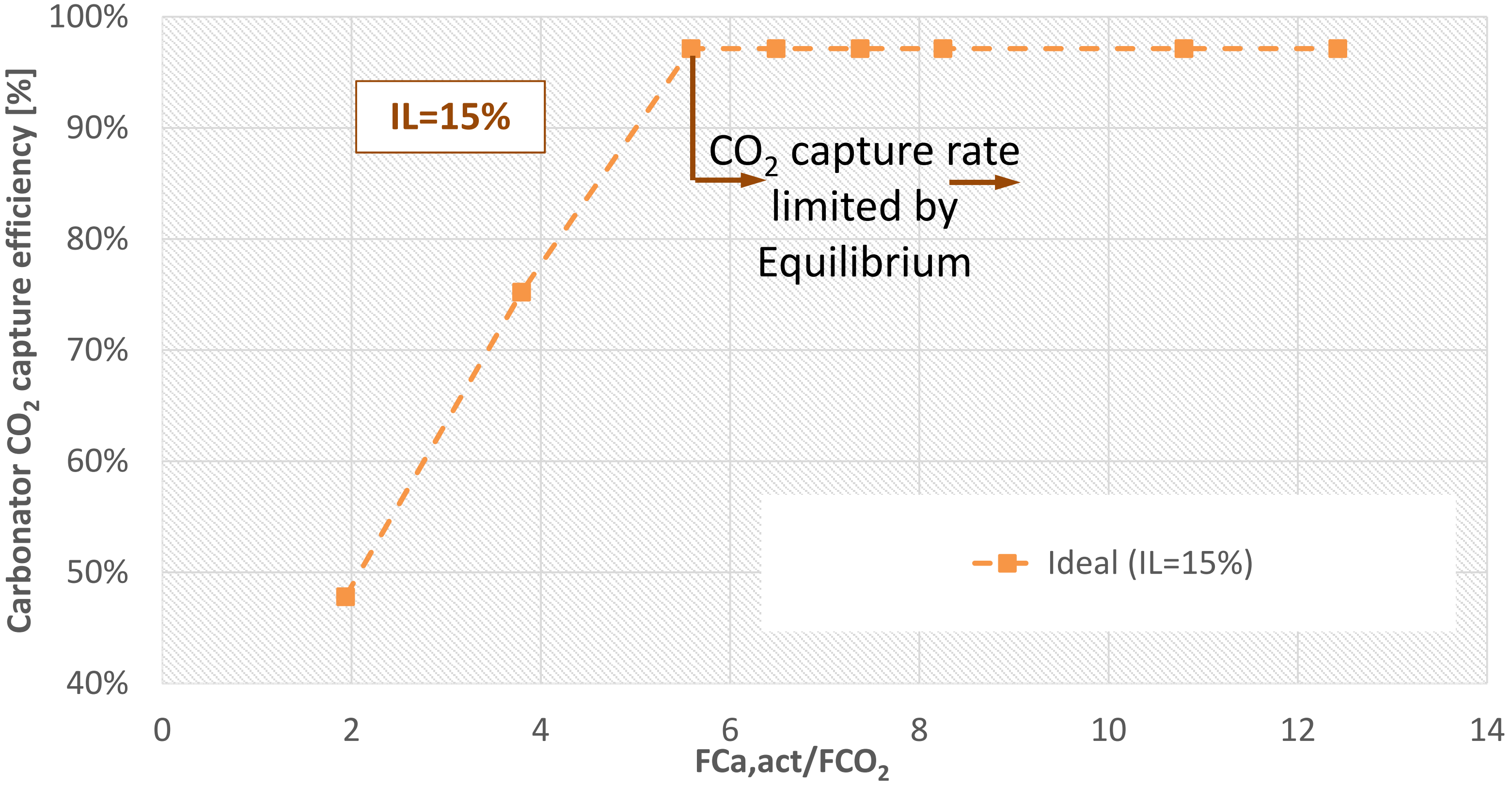
➔ $F_{Ca,Act}$ amount of active sorbent circulating between carbonator and calciner.

Simulation tools: ➔ Matlab for carbonator model
➔ GS for the integrated CaL/cement production process

Tail end CaL: results (i) – CO_2 capture efficiency

Ideal/real CO_2 capture efficiency as a function of $F_{ca,act}/F_{CO2}$ and IL:

- Ideal ➔ assuming that CaO particles achieve their maximum average conversion;
- Real ➔ calculated by carbonator model, which takes into account the operating conditions (geometry, inventory) and the effects of sulfur species and coal ash (Carbonator: h=40 m, v_s=5 m/s, W_s=1000 kg/m²).



- Low $F_{Ca,act}$: CO_2 capture limited by conversion; High $F_{Ca,act}$: limited by equilibrium.
- The higher IL, the higher the sorbent reactivity and the CO_2 capture rate

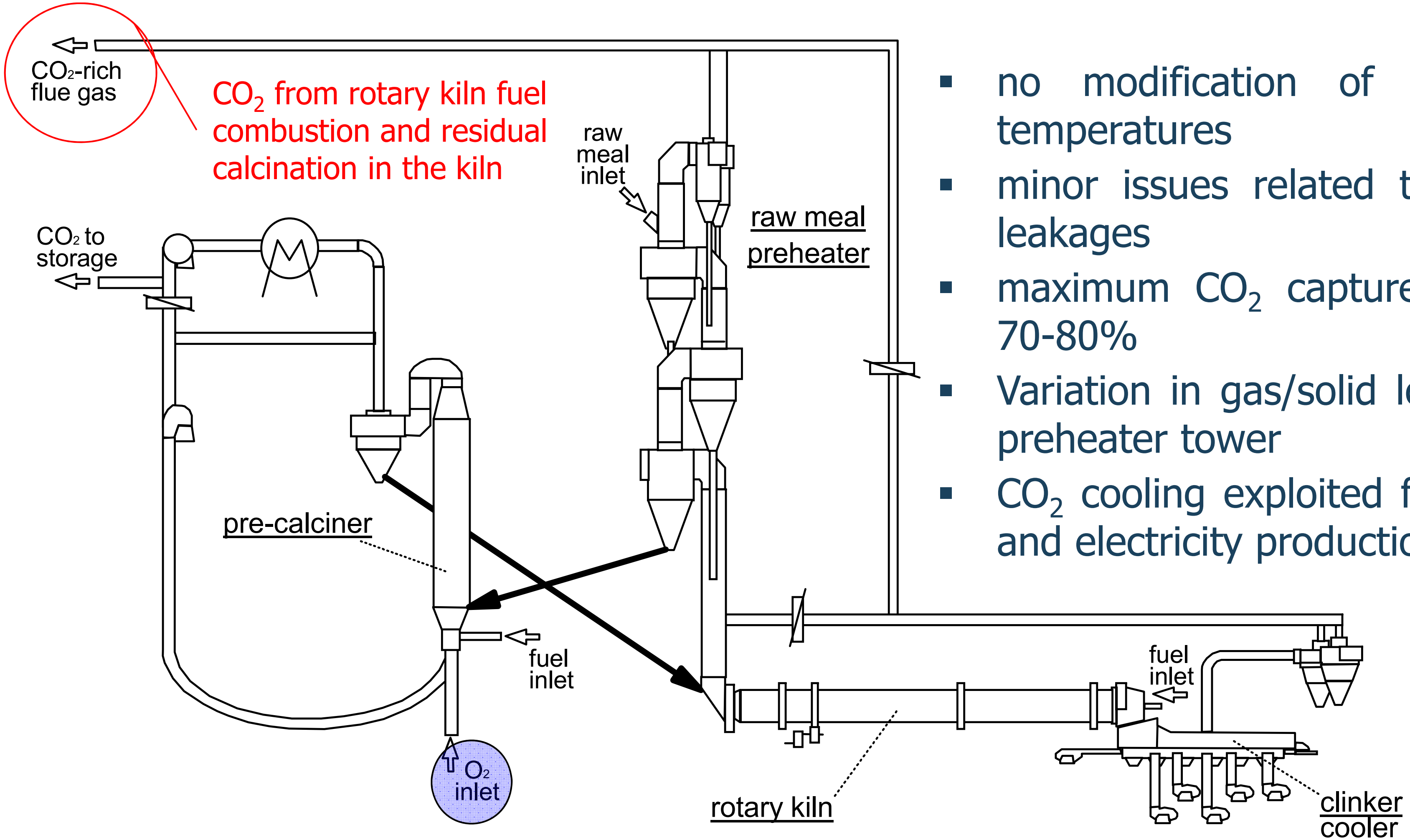
Tail end CaL: results (ii) – selected case (IL=20%, F_{Ca}/F_{CO2}=5)

	Reference cement plant without CO_2 capture	Tail-end CaL configuration with CFB reactors
Integration level [%]	--	**20**
F_0/F_{CO2}	--	**0.16**
$F_{Ca,act}/F_{CO2}$	--	**4.8**
Carbonator CO_2 capture efficiency [%]	--	**88.8**
Total fuel consumption [MJ_{LHV}/t_{clk}]	3223	**8672**
Rotary kiln burner fuel consumption [MJ_{LHV}/t_{clk}]	1224	**1210**
Pre-calciner fuel consumption [MJ_{LHV}/t_{clk}]	1999	**1542**
CaL calciner fuel consumption [MJ_{LHV}/t_{clk}]	--	**5920**
Electric balance [kWh_{el}/ t_{clk}]		
Gross electricity production	--	**579**
ASU consumption	--	**-117**
CO_2 compression	--	**-146**
Carbonator and calciner fans	--	**-25**
Cement plant auxiliaries	-132	**-132**
Net electric production	-132	**159**
Direct CO_2 emissions [kg_{CO2}/t_{clk}]	863.1	**143.2**
Indirect CO_2 emissions [kg_{CO2}/t_{clk}]	105.2	**-123.5**
Equivalent CO_2 emissions [kg_{CO2}/t_{clk}]	968.3	**19.7**
Equivalent CO_2 avoided [%]	--	**98.0**
SPECCA [MJ_{LHV}/kg_{CO2}]	**--**	**3.26**

Integrated CaL application in cement plant

Partial oxyfuel (Lafarge) and direct CaL (PoliMI) concepts

Lafarge process consists in the conversion of calciner to oxyfuel operation, obtaining rich-CO_2 exhausts which can be cooled and stored.



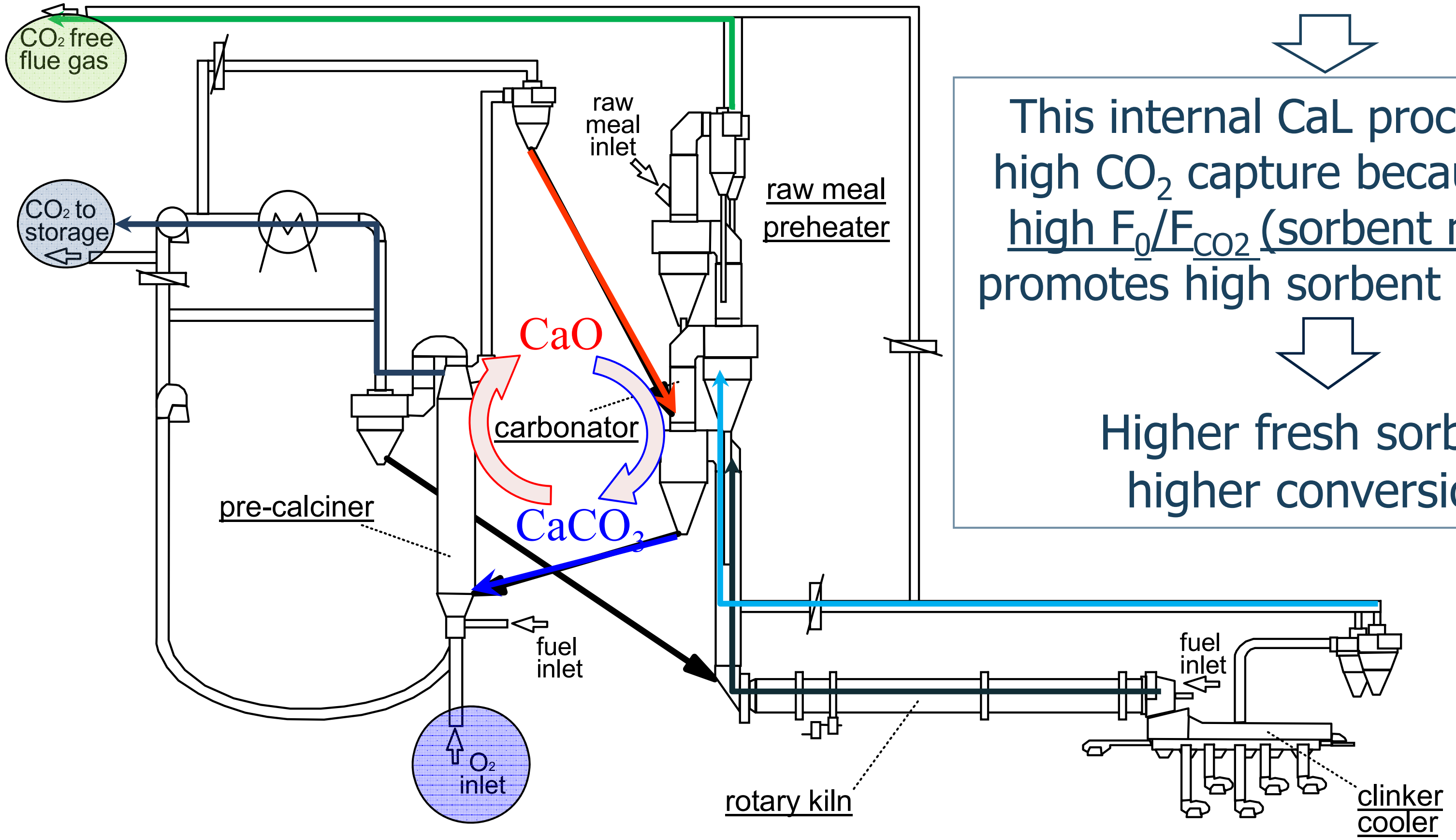
- no modification of the kiln temperatures
- minor issues related to air in-leakages
- maximum CO_2 capture rate of 70-80%
- Variation in gas/solid loading in preheater tower
- CO_2 cooling exploited for steam and electricity production

Partial oxyfuel (Lafarge) and direct CaL (PoliMI) concepts

Extension of the Lafarge concept: oxyfuel calciner is required also in this case

Only flue gases from kiln and III air (from clinker cooler) are fed to the preheater, without flowing through the calciner.

A portion of the calcined raw meal is injected in the suspension preheater (entrained flow carbonator), where CaO can act as sorbent of the CO_2 in the kiln flue gas



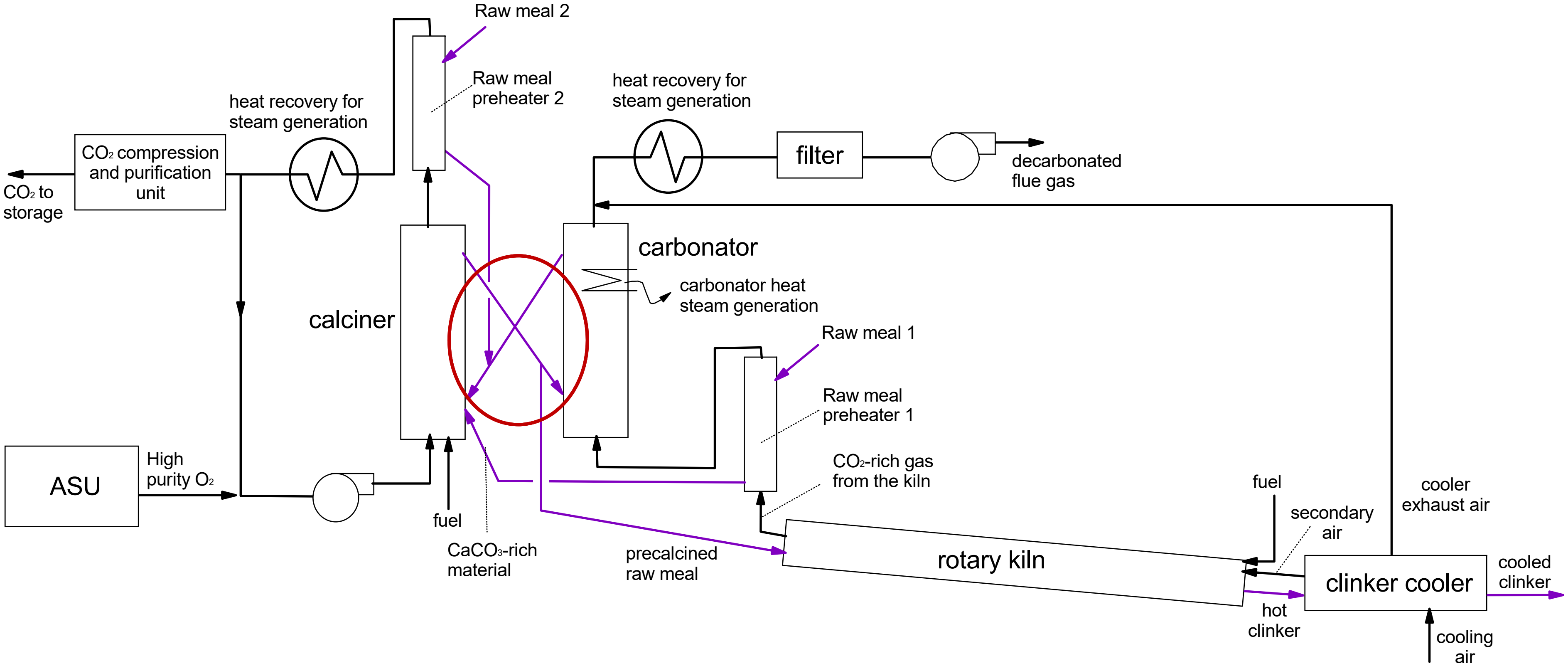
⇩

This internal CaL process gives high CO_2 capture because of the high F_0/F_{CO2} (sorbent make-up) promotes high sorbent conversion

⇩

Higher fresh sorbent, higher conversions

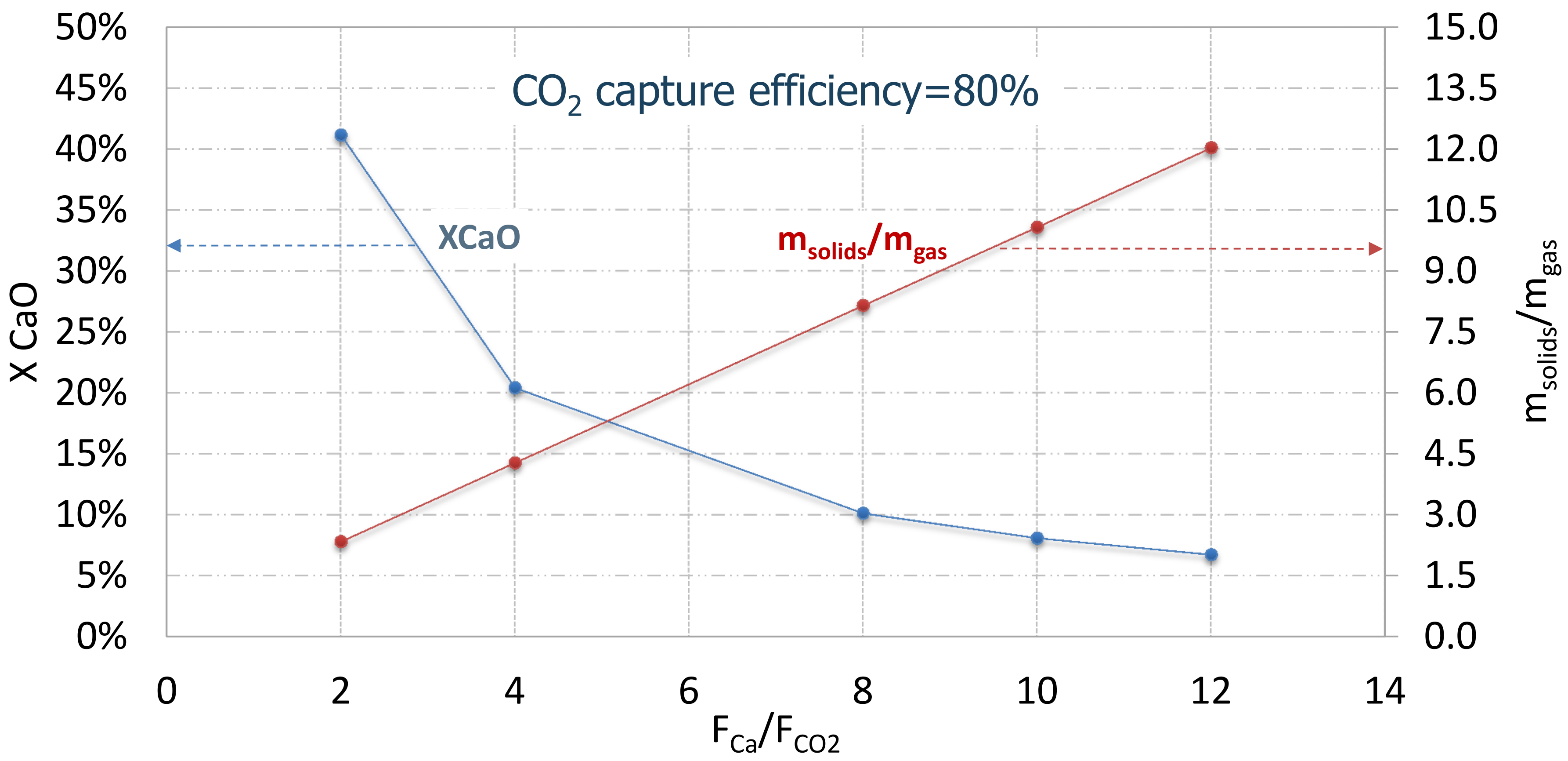
Integrated CaL application in cement plant



Sensitivity analysis on:

➔ $F_{Ca,Act}$ amount of active sorbent circulating between carbonator and calciner ➔ the sorbent conversion and the solid loading are tuned for reaching 80% of CO_2 capture ratio

Integrated CaL results(i): solid loading & conversion



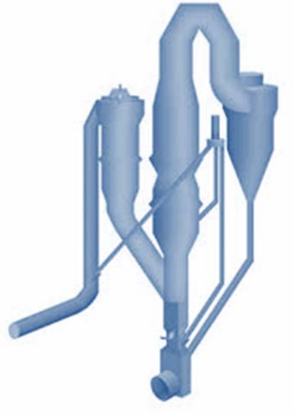
Sensitivity analysis on:

➔ $F_{Ca,Act}$ amount of active sorbent circulating between carbonator and calciner ➔ the sorbent conversion and the solid loading are tuned for reaching 80% of CO_2 capture ratio

Integrated CaL: results (ii) – selected case (X_{CaO}=20%)

	Reference cement plant without CO_2 capture	Tail-end CaL configuration with CFB reactors	integrated CaL configuration with EF reactors
Integration level [%]	--	20	**100**
F_0/F_{CO2}	--	0.16	**4.1**
$F_{Ca,act}/F_{CO2}$	--	4.8	**4.0**
Carbonator CO_2 capture efficiency [%]	--	88.8	**80.0**
Total fuel consumption [MJ_{LHV}/t_{clk}]	3223	8672	**4740**
Rotary kiln burner fuel consumption [MJ_{LHV}/t_{clk}]	1224	1210	**1180**
Pre-calciner fuel consumption [MJ_{LHV}/t_{clk}]	1999	1542	**3560**
CaL calciner fuel consumption [MJ_{LHV}/t_{clk}]	--	5920	
Electric balance [kWh_{el}/ t_{clk}]			
Gross electricity production	--	579	**163**
ASU consumption	--	-117	**-73**
CO_2 compression	--	-146	**-111**
Carbonator and calciner fans	--	-25	**-11**
Cement plant auxiliaries	-132	-132	**-132**
Net electric production	-132	159	**-164**
Direct CO_2 emissions [kg_{CO2}/t_{clk}]	863.1	143.2	**71.4**
Indirect CO_2 emissions [kg_{CO2}/t_{clk}]	105.2	-123.5	**128.7**
Equivalent CO_2 emissions [kg_{CO2}/t_{clk}]	968.3	19.7	**200.1**
Equivalent CO_2 avoided [%]	--	98.0	**79.3**
SPECCA [MJ_{LHV}/kg_{CO2}]	**--**	3.26	**2.32**

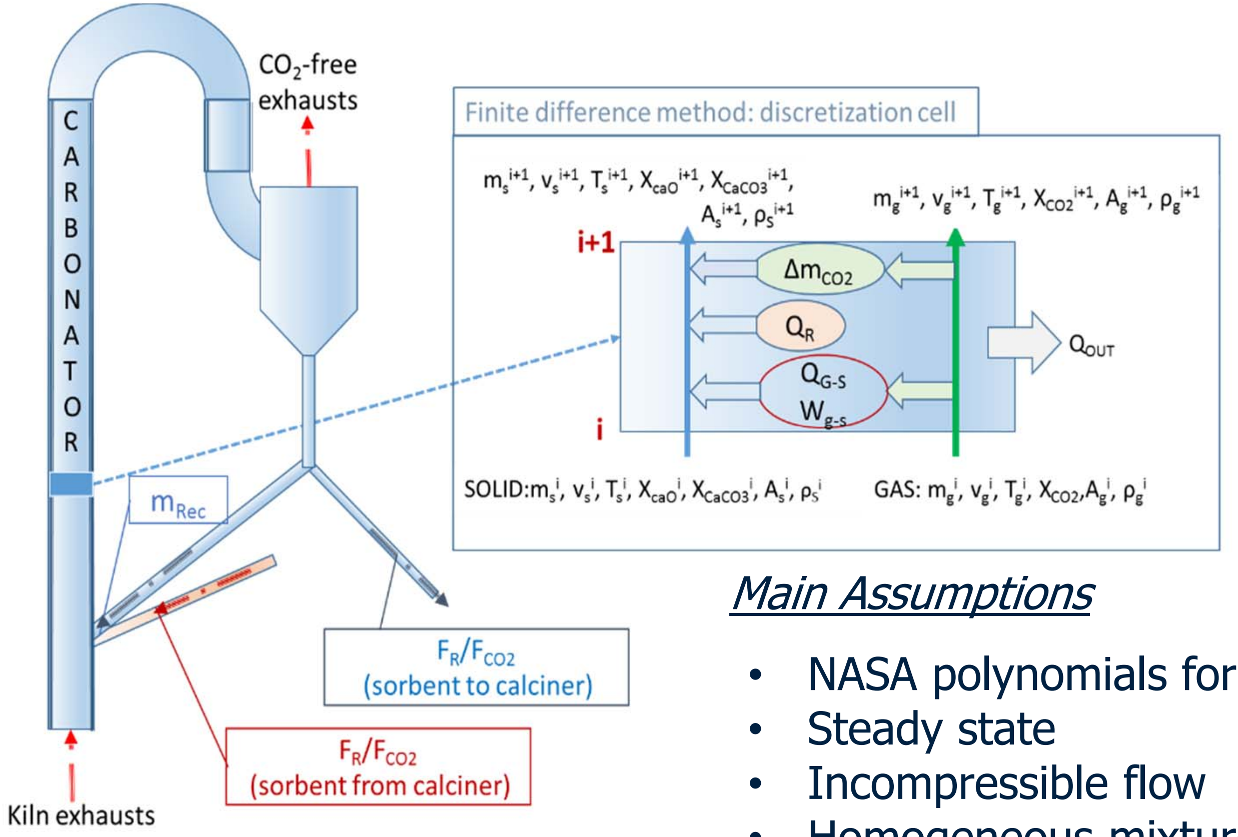
Entrained flow carbonator model



Entrained flow CaL carbonator modeling

Dilute reactor is the most suitable option for the cement plant CaL application, because of the **experience** with entrained flow technologies and the **low particle size**.

A simple, finite-difference model (axial discretization) has been developed to solve mass, momentum and energy equations and evaluate the potential CO_2 capture rate.



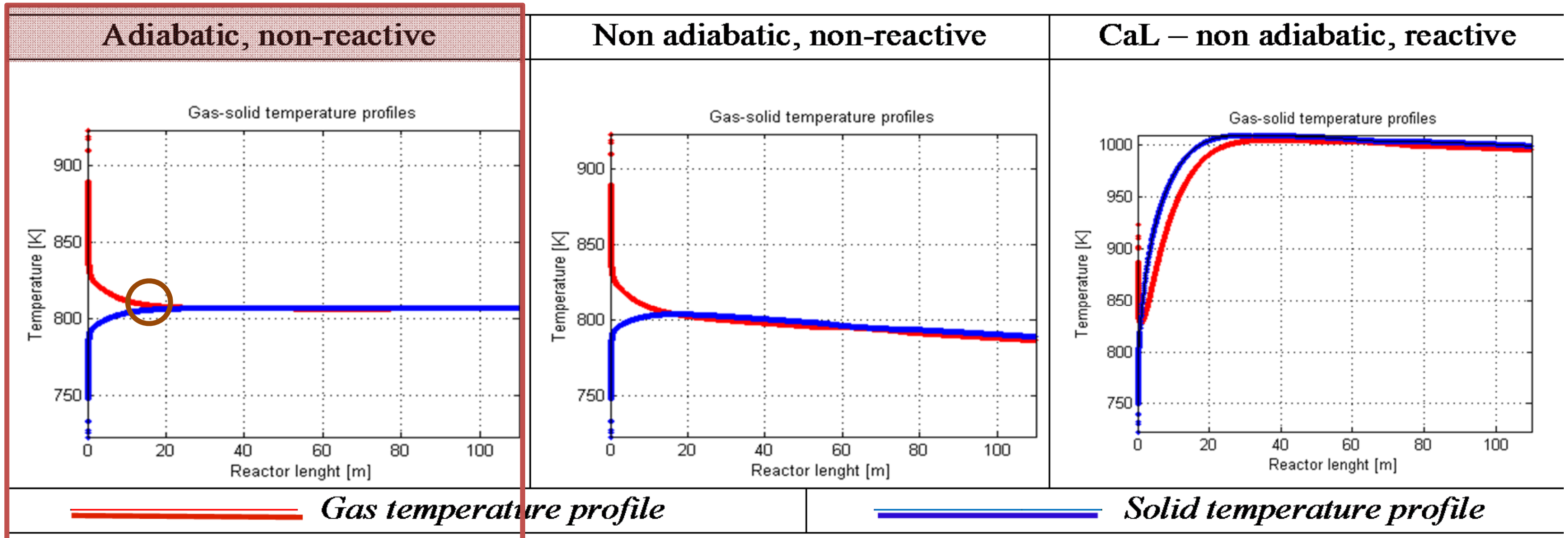
- CaL kinetics
- Gas-solid drag ➔ velocities
- Interphase heat transfer
- External heat transfer
- Pressure losses
- Fluid-dynamic check
- Internal sorbent recycle

Main Assumptions

- NASA polynomials for gas /solid TDN properties
- Steady state
- Incompressible flow
- Homogeneous mixtures
- Mass transfer effect neglected (low *Da* numbers)

EF Carbonator model – Temperature profiles

Temperature profiles along reactor axis: influence of operating conditions



Very high gas-solid heat transfer rates in the first section (high slip velocities)

⇩

Temperature equilibrium reached in around 15 meters

Very low external heat transfer rate (ΔT=15-20°C)

⇩

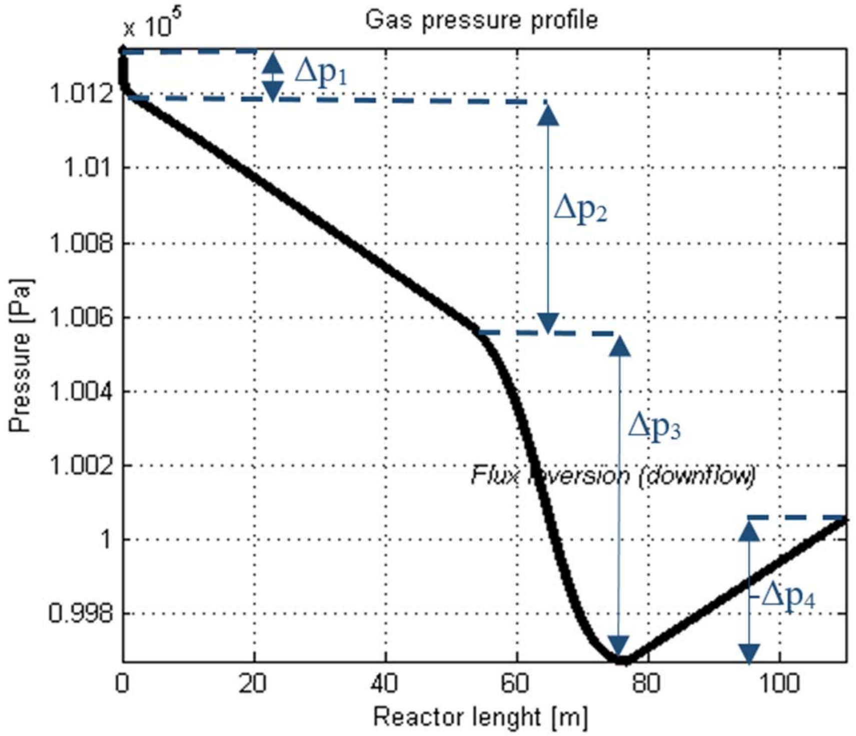
Heat transfer improvement due to particles is negligible

Strong effect of reaction heat (released only in the solid phase)

⇩

The effect of slip velocity is more evident

EF Carbonator model – pressure profile



Pressure profile along reactor axis ➔(4 different trends)

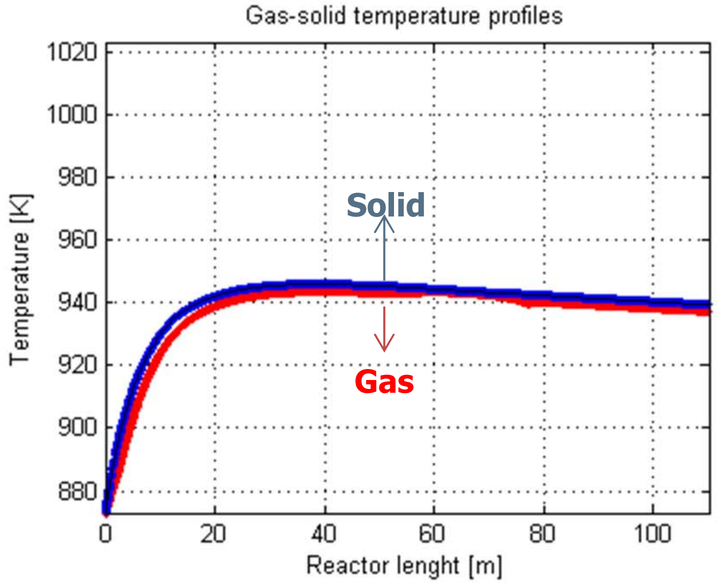
Δp_1➔ solid acceleration;

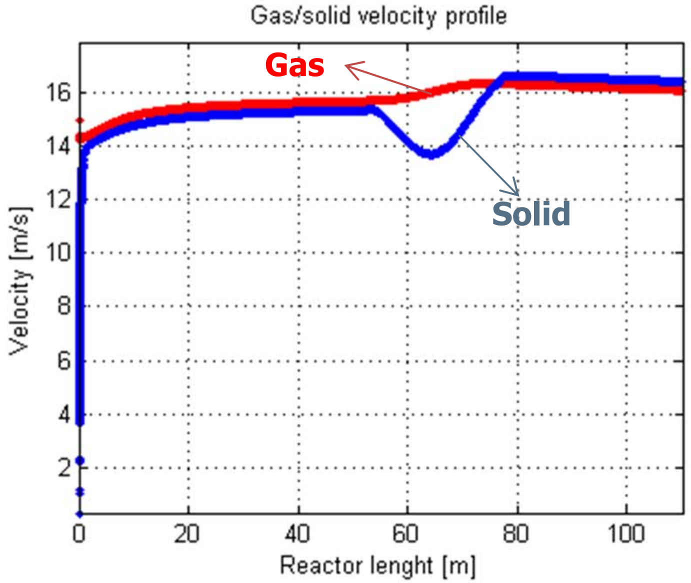
Δp_2➔ solid hold-up and wall friction;

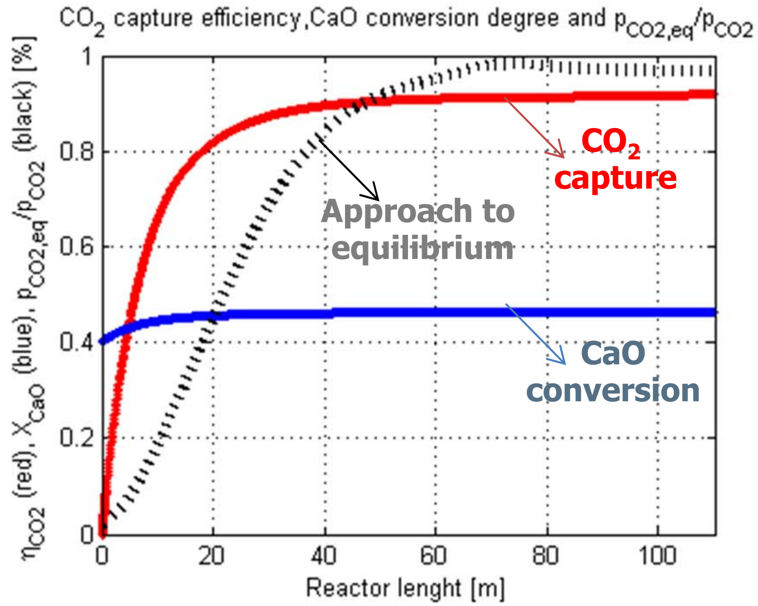
Δp_3➔ concentrated pressure loss (curvature);

Δp_4➔ pressure increase in descending section.

EF Carbonator model – CO_2 capture efficiency







Results from preliminary model in:
Spinelli M.: «Advanced technologies for CO_2 capture and power generation in cement plants", PhD dissertation, 2016.

Ongoing activities and further research needs

Ongoing activities:

- Improvement on the entrained-flow carbonator model by better fluid-dynamic and heat transfer correlations from literature
- Improvement of the kinetic model based on sorbent performance from lab tests
- Assess the configuration and performance of the heat recovery steam cycle
- Perform preliminary economic analysis of the process

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Further research needs:

- Validate the entrained-flow carbonator performance at pilot scale, connected with an oxyfuel calciner.
- Validate the chemical, fluid-dynamic and thermal model based on pilot tests
- Improve process models and economic analysis based on knowledge from pilot tests.

Thank you
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