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"Post-combustion CO_2 capture by Ca-looping"

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CO_2 Capture Group

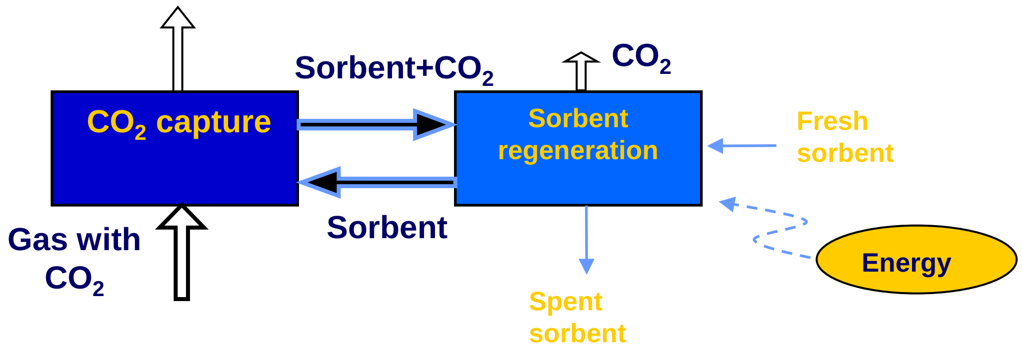
National Institute of Coal (INCAR-CSIC)

Workshop on Mathematical Modelling of Combustion

23-25 May, Santiago de Compostela, Spain

- **What is Ca-looping?**
  - Ca-looping for post-combustion CO2 capture: description of the process
  - Status of the technology
- **Modelling work:**
  - Particle models
  - Reactor models

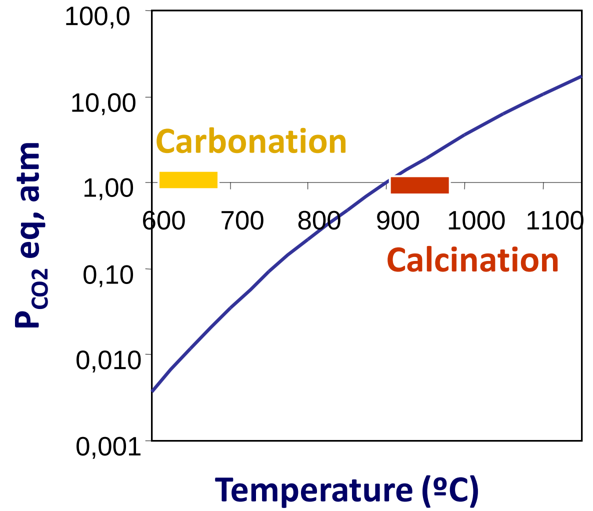
CO_2 capture using solid sorbents



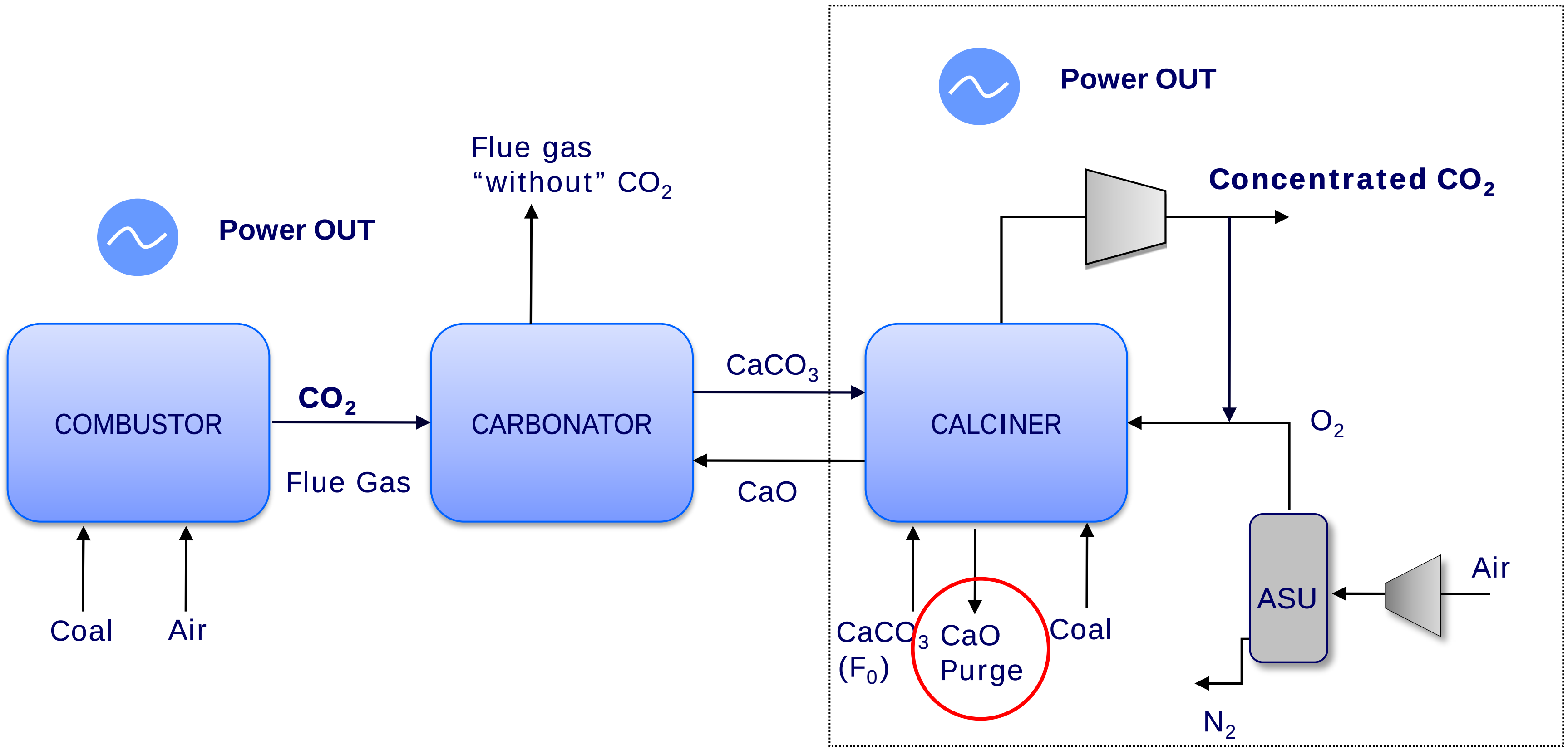
Use of lime as sorbent

Lime *Limestone*

$$CaO + CO_2 \longleftrightarrow CaCO_3$$



Advantages of Ca-looping versus other post-combustion technologies

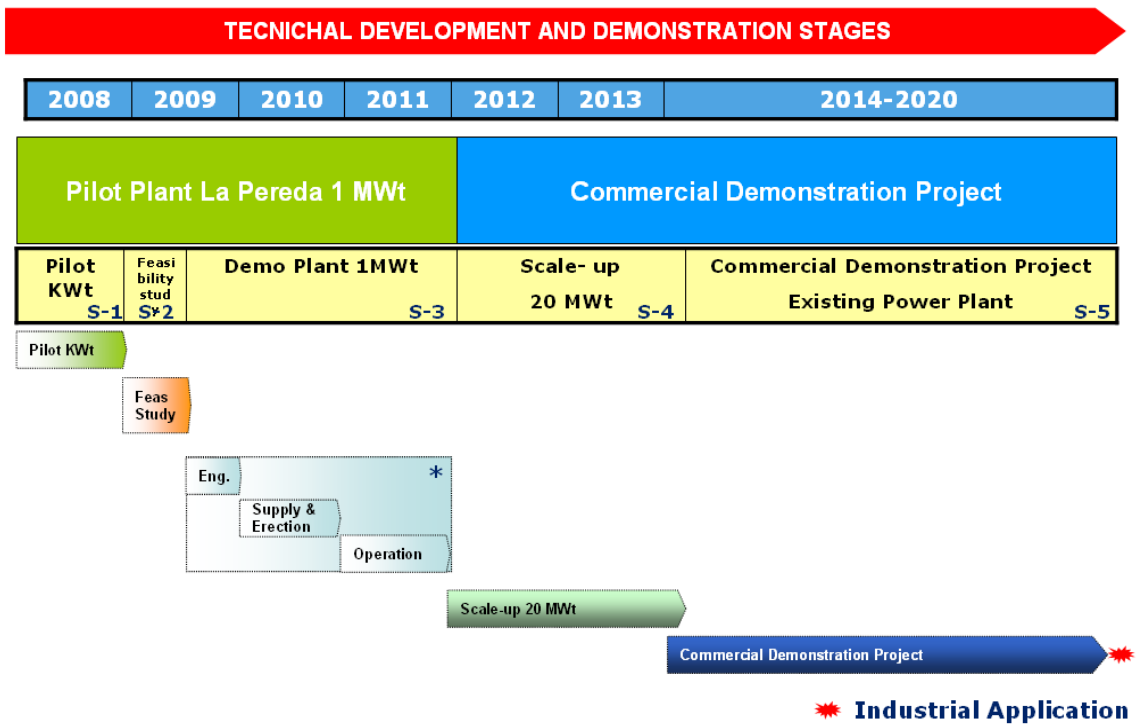


Some advantages of Ca-looping:

- Low energy penalty
- Purge of CaO: synergies with cement industry
- Pre-treatment of flue gas no needed

- Classification of CO_2 capture technologies:
  - Near commercial (amines, oxy-fuel combustion, pre-combustion)
  - Emerging technologies

Roadmap proposed for the development post-combustion CO2 capture with Ca-looping



FOSTER WHEELER

endesa generación

grupohunosa

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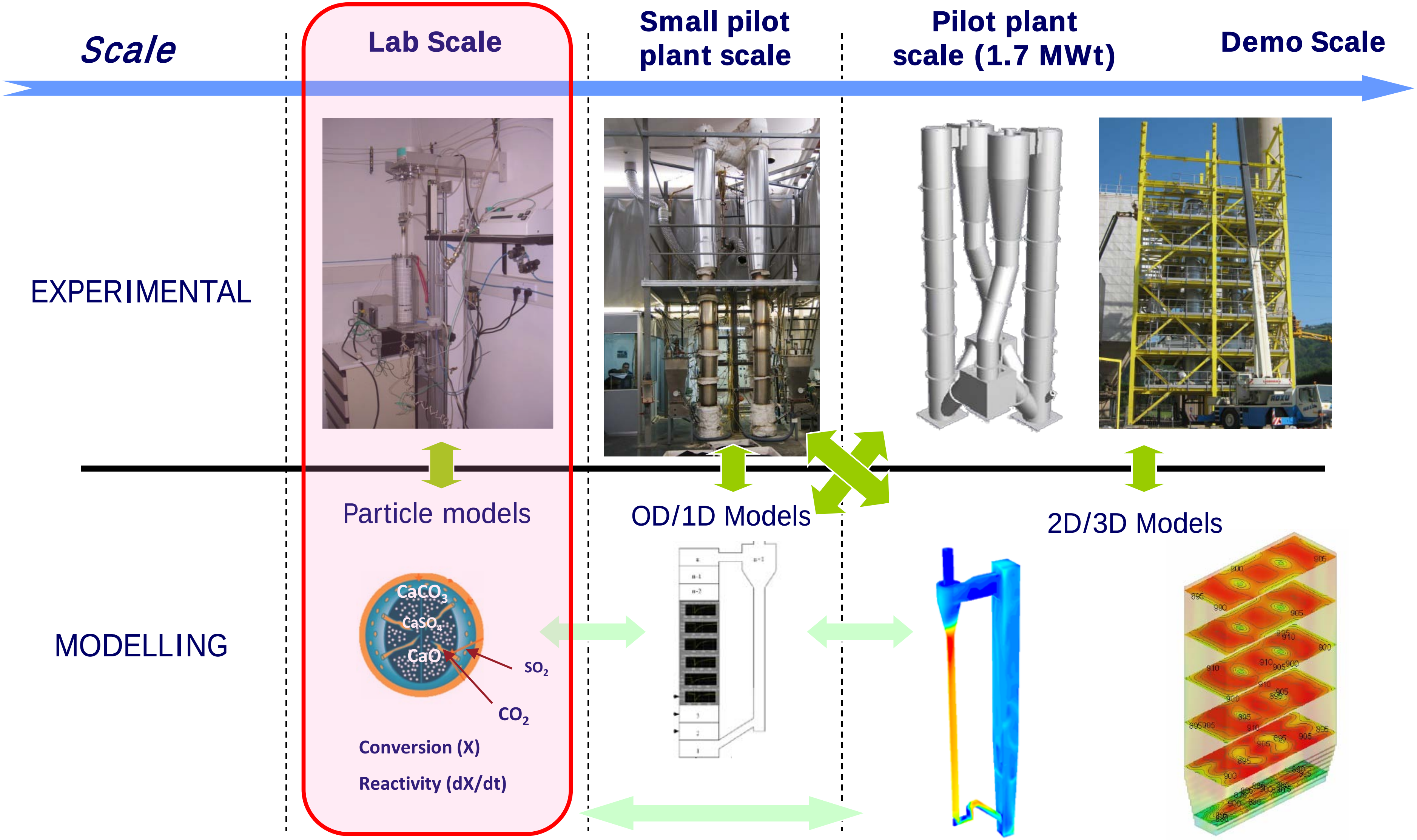
Post-combustion CO2 capture using Ca-looping

- **What is Ca-looping?**
  - Ca-looping for post-combustion CO2 capture: description of the process
  - Status of the technology

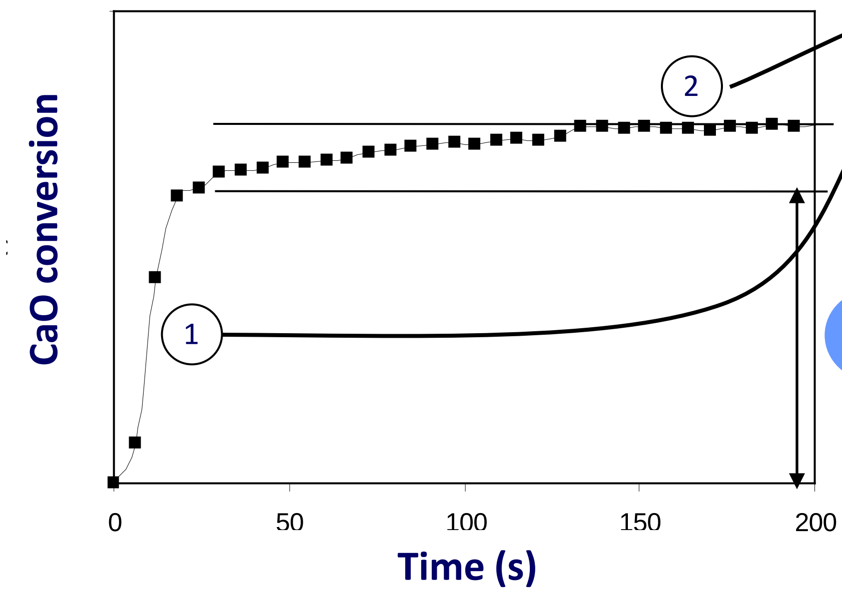
- **Modelling needs:**
  - Particle models
  - Reactor models

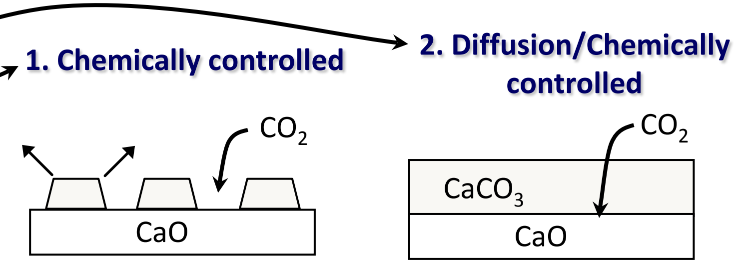
Post-combustion CO2 capture using carbonate looping



Particle Models: CaO conversion to $CaCO_3$

Typical conversion of CaO particles to $CaCO_3$





X_N → Maximum CO_2 carrying capacity under the chemical fast reaction regime

Reaction rate kinetics: Random Pore Model

$$\frac{dX}{dt} = \frac{k_s S_o C_s (1-X)\sqrt{1-\Psi\ln(1-X)}}{(1-\varepsilon_o)\left[1+\frac{\beta Z}{\Psi}\left(\sqrt{1-\Psi\ln(1-X)}-1\right)\right]}$$

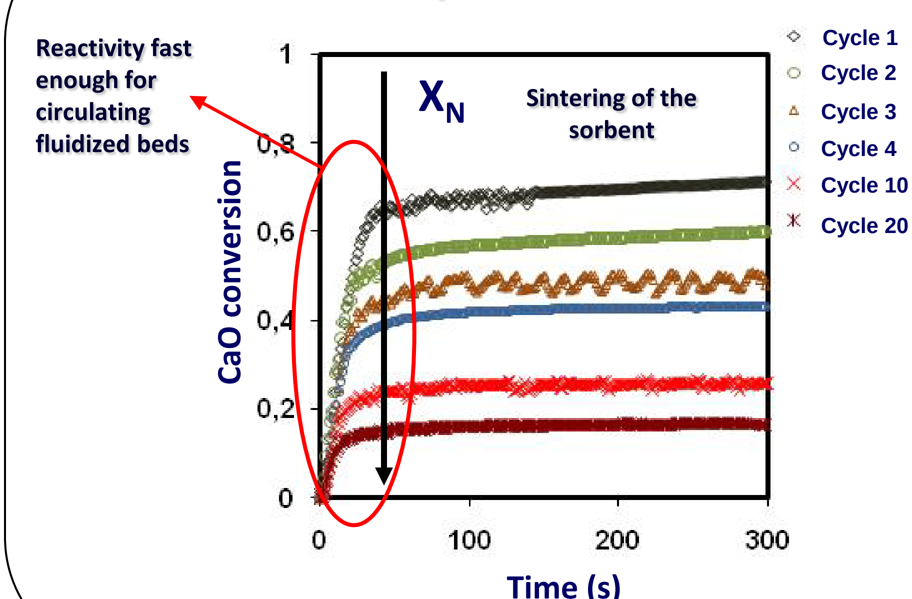
Kinetic parameters

k_{so} (m^4/kmol.s)	E_{ak} (kJ/kmol)	Do (m^2/s)	E_{aD}(kJ/kmol)
0.54×10^{-5}	20.3×10^{3}	3.85×10^{-6}	160×10^{3}

Changes of textural properties during cycling

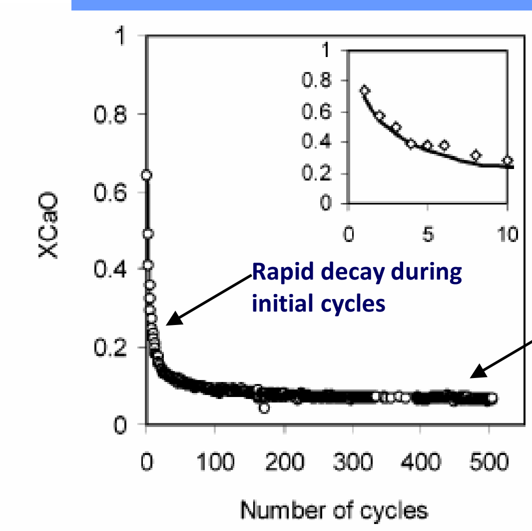
Ref: *Grasa et al. AIChE Journal, 2009, (55) 1246-1255*

Effect of number of cycles on sorbent conversion



Average activity of the solid in a Ca-looping

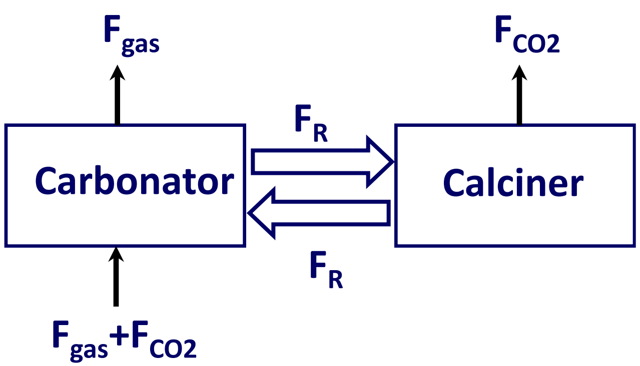
Sorbent decay conversion



Carbonation: 650 ºC
Calcination:850 ºC

K=0.52
Xr=0.075

Continuous system: Particles with different number of cycles



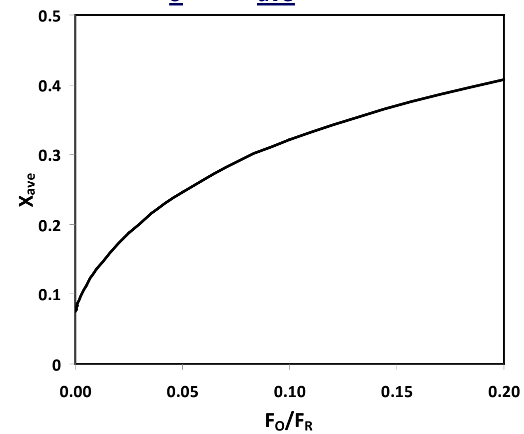
Average activity of the particles in the system

$$X_{ave} = \sum_{N=1}^{\infty} r_N X_N$$

$$X_N = \frac{1}{\frac{1}{1-X_r} + kN} + X_r$$

$$r_N = \frac{F_0 F_R^{N-1}}{(F_0 + F_R)^N}$$

Effect of F_o on X_{ave}



$F_{CO2\ capt} = F_R * X_{ave}$

Strategies of operation:

- Low Xave and high FR
- High Xave and low FR

Other aspect to consider:

- Presence of SO_2 in the Ca-looping
- Partial carbonation and calcination of the sorbent

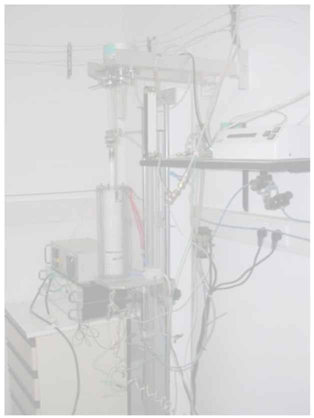
Ref: *Grasa et al. Ind. Eng. Chem. Res. 2006, 45:8846-8851*
Abanades, Chemical Eng. Journal 2002, 90: 303-306
Rodríguez et al. Chemical Eng. Journal, 2010, 156: 388-394

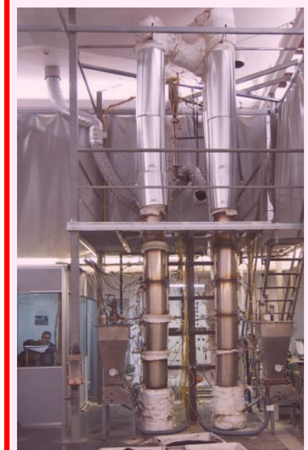
Post-combustion CO2 capture using carbonate looping

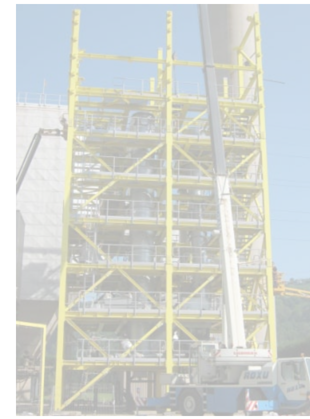
Scale

Lab Scale	Small pilot plant scale	Pilot plant scale (1.7 MWt)	Demo Scale

EXPERIMENTAL

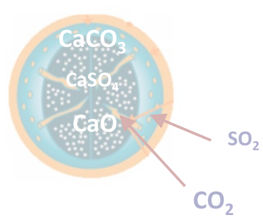






MODELLING

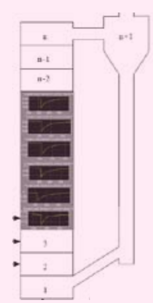
Particle models



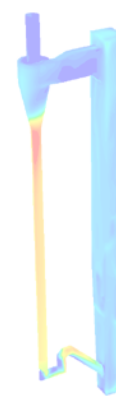
Conversion (X)

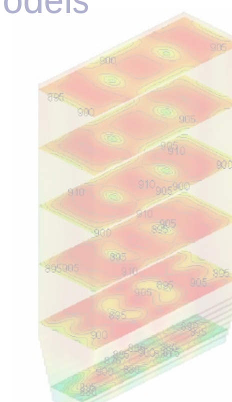
Reactivity (dX/dt)

OD/1D Models



2D/3D Models

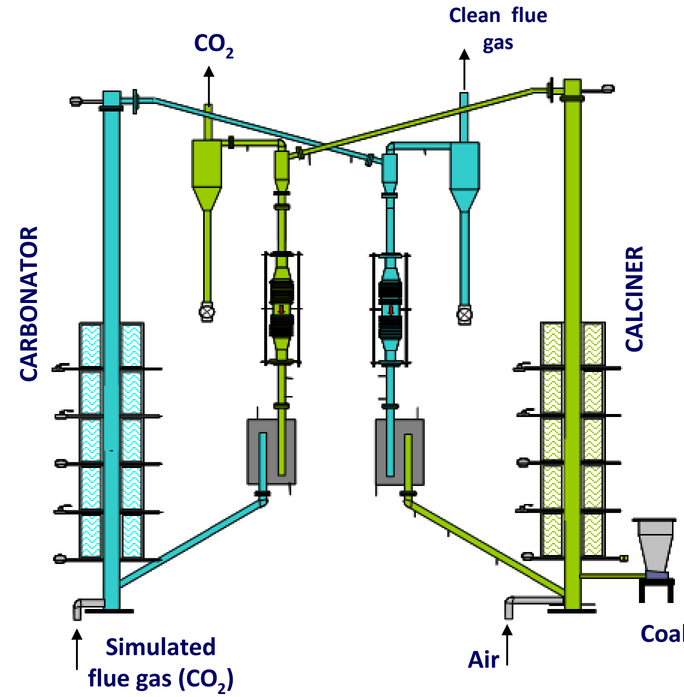




Small pilot-plant facility: Description

Small pilot plant at INCAR-CSIC (30 kWt)

Two interconected circulating fluidized beds



Main features:

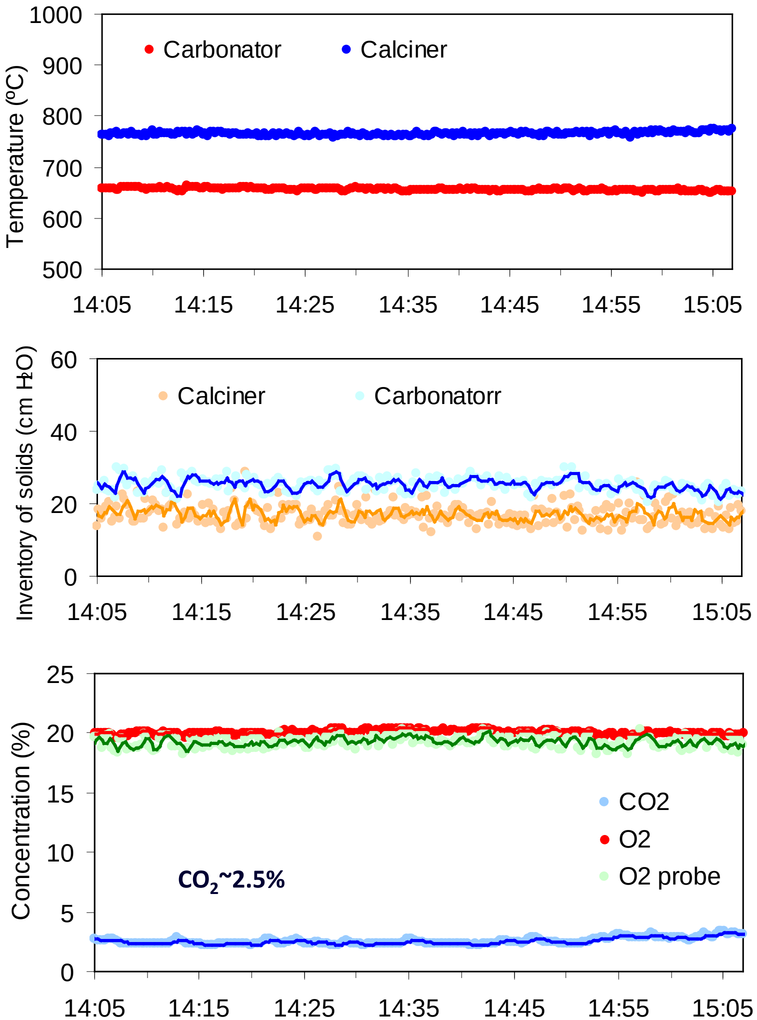
- Two CFB reactors (Height~6.5 m, diameter=100 mm)
- Electrically heated
- Measurement port (temperature, pressure, gas composition)
- Solid circulation measurements
- Solid samples characterization (TG analysis, C/S analyzer)

Small pilot-plant facility: Experimental results

Steady state:

Defined as the situation where carbonator and calciner temperature, pressure drops, inlet gas flows and outlet gas concentration remain constant for a period of time of at least 10-20 minutes.

Q_T= 19 m^3/h, ν_{CO2} = 0.12, X_{ave}= 0.08



Ref: *Rodriguez et al. AIChE J 2011, 57 (5) 1356-1366*

Some measured experimental parameters:

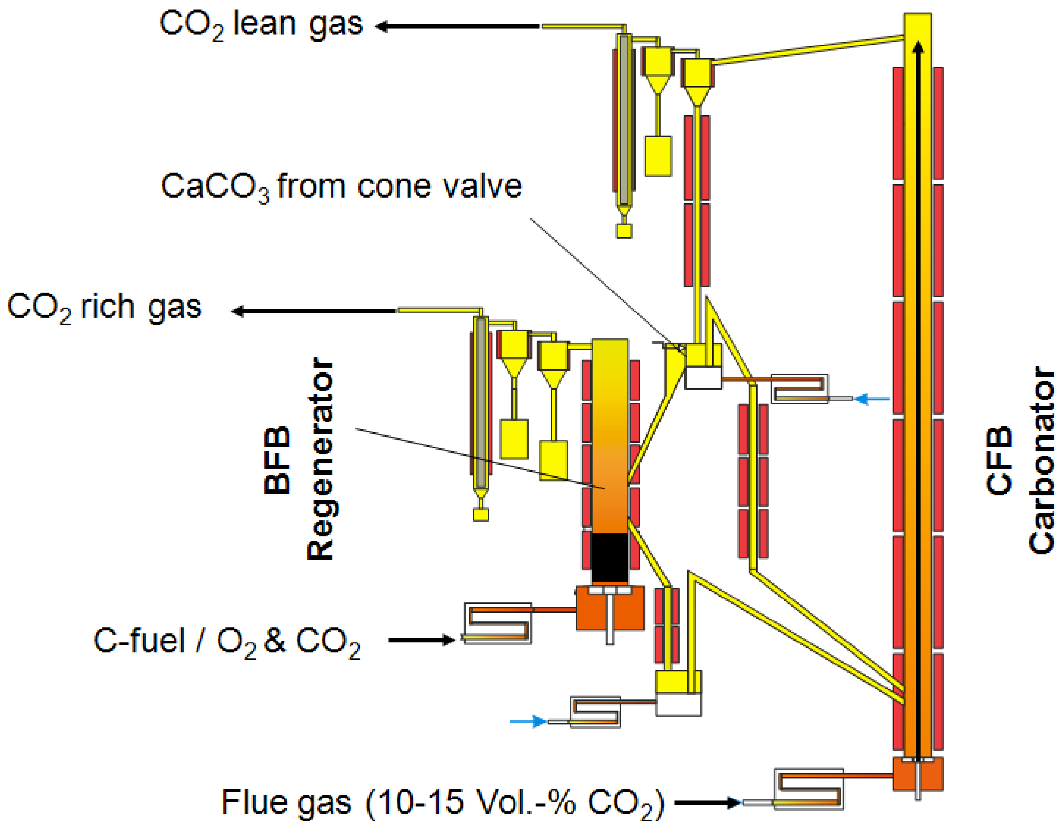
- Average carbonation temperature
- Inventory of solids
- Inlet CO_2 concentration and total flow
- Outlet CO_2 concentration
- Carbonate content of entering and exiting solids
- Average CO_2 carrying capacity of solids
- Solid circulation rates

Main achievements:

- Has completed 450 h of operation
- Max. CO_2 capture efficiency: 97 %
- Absorption capacity up to 7 molCO_2/m^2s)

Model validation in two experimental facilities: IFK and CSIC

Description of the IFK (University of Sttutgart) 10 kW_{th} facility



Main features:

- A CFB (height=12m) and a BFB
- Electrically heated
- Measurement ports (temperature, pressure, gas composition)
- Solid circulation measurements
- Cone vale to control sorbent flow between reactors
- Posibility of oxy-fuel combustion in the BFB calciner

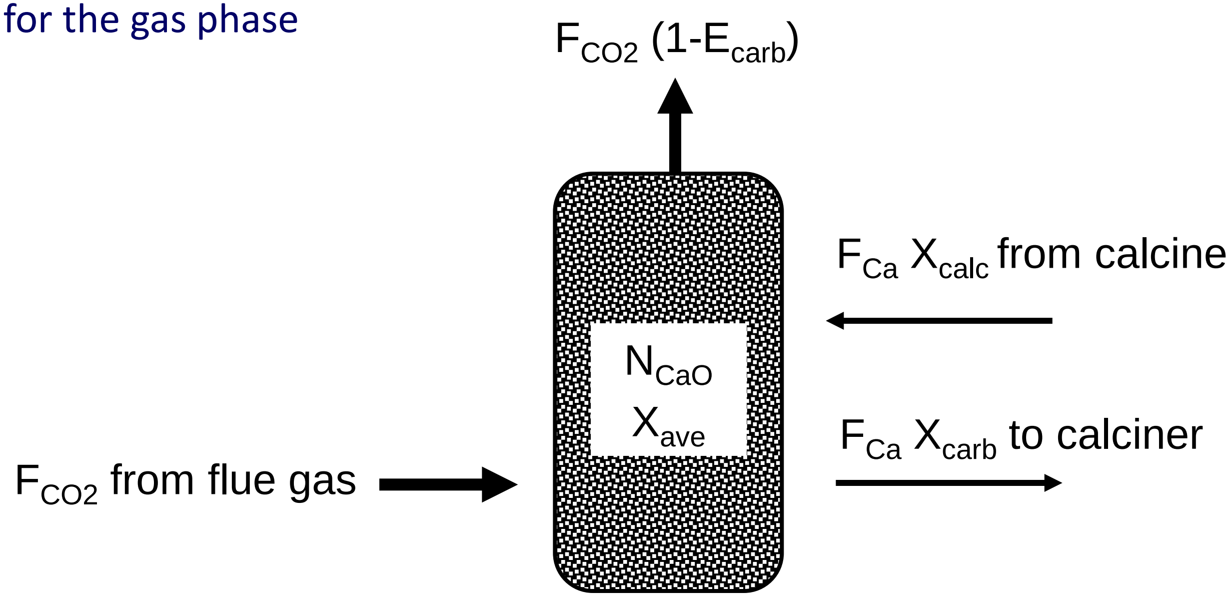
Ref: *Charitos et al. Int. J. Green. Gas. Con., 2010, (4) 776-784*

Carbonator reactor

Initial assumptions carbonator reactor:

- Instantaneous and perfect mixing of the solids
- Plug flow for the gas phase

$$\text{Carbonation efficiency}\,(E_{carb}) = \frac{F_{CO2\ \ in} - F_{\ \ CO2\,in}}{F_{CO2\,in}}$$



Overall mass balance in the carbonator

CO_2 reacting with CaO in the bed **=** **CO_2 removed from the gas phase** **=** **$CaCO_3$ formed in the circulating stream of CaO**

Ref: *Rodriguez et al. AIChE J 2011, 57 (5) 1356-1366*

Post-combustion CO2 capture using carbonate looping

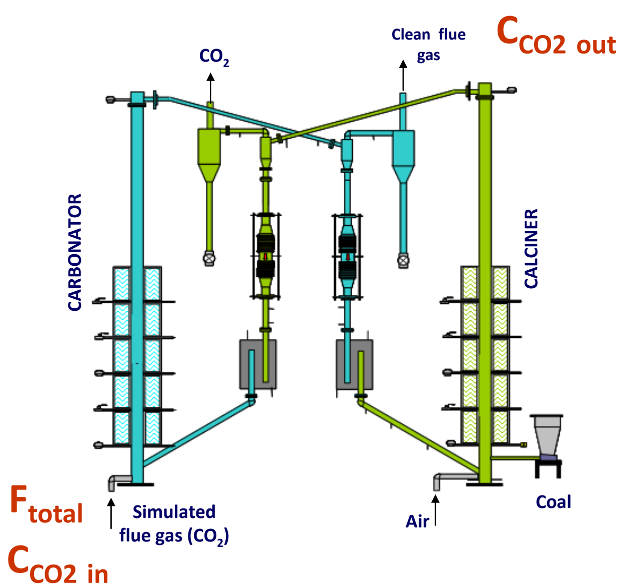
CO_2 mass balance in the system

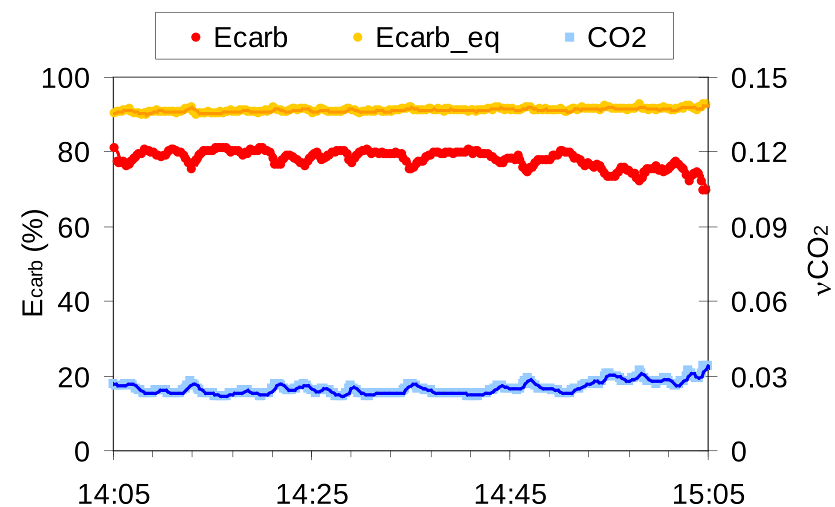
CO_2 reacting with CaO in the bed **=** CO_2 removed from the gas phase **=** $CaCO_3$ formed in the circulating stream of CaO

$$\text{Carbonation efficiency}\,(E_{carb}) = \frac{F_{CO2\ \ in} - F_{\ CO2\,in}}{F_{CO2\,in}}$$

***Continuous measurement of E_{carb} during an experimental run*:**

- **Flue gas fed to the carbonator**
- **CO_2 concentration at the inlet and exit of the reactor**





T_{carb} = 655 ºC, W_{Ca} = 260 kg/m^2, n_{CO2} = 0.12, X_{ave}= 0.08

Post-combustion CO2 capture using carbonate looping

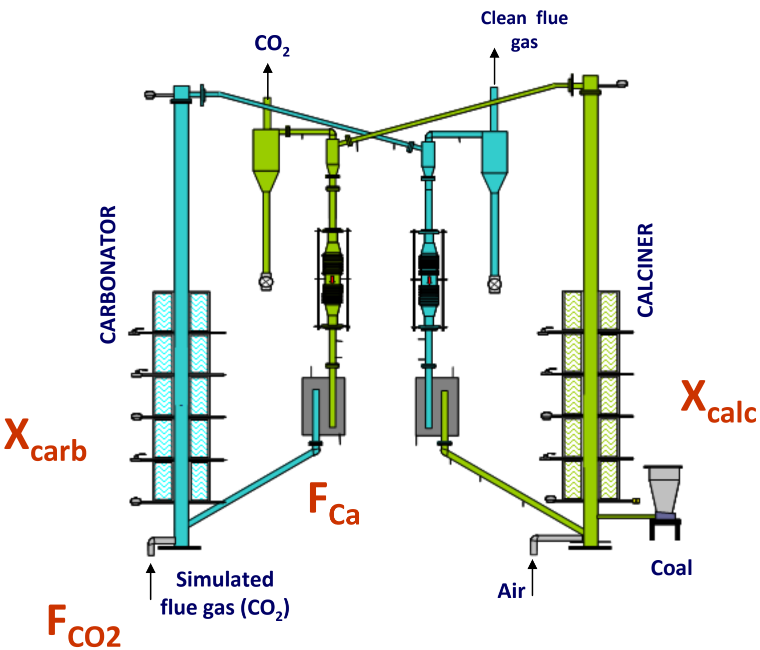
CO_2 mass balance in the system

CO_2 reacting with CaO in the bed **=** CO_2 removed from the gas phase **=** $CaCO_3$ formed in the circulating stream of CaO

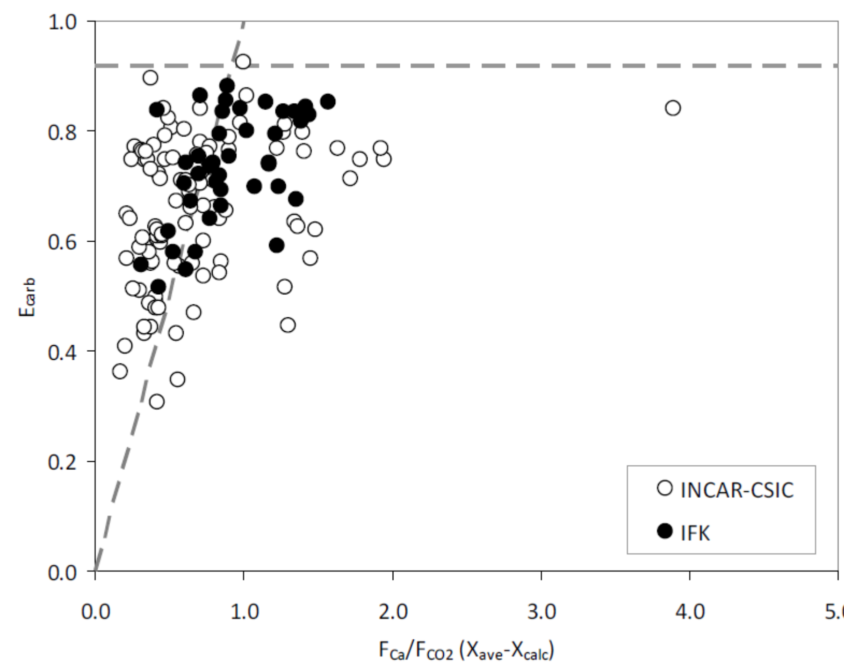
$$\begin{pmatrix} CaCO_3 \text{ formed in the} \\ \text{circulating stream of CaO} \end{pmatrix} = F_{Ca}\left(X_{carb} - X_{calc}\right)$$

$$F_{CO_2}\, E_{carb} \le F_{Ca}\left(X_{ave} - X_{calc}\right)$$

Experimental measurement



Supply of active flow of CaO



Ref: *Rodriguez et al. Energy Procedia 2011, (4) 393-401*

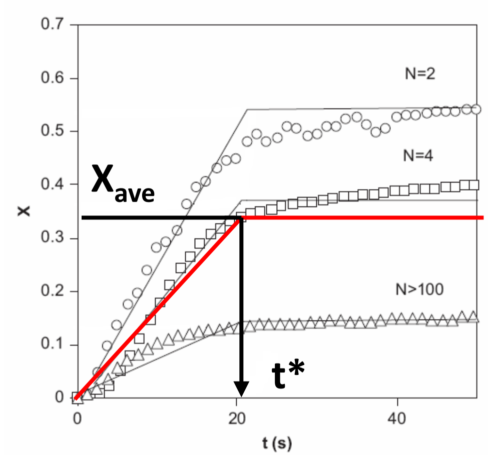
Post-combustion CO2 capture using carbonate looping

CO_2 mass balance in the system

CO_2 reacting with CaO in the bed = **CO_2 removed from the gas phase** = **$CaCO_3$ formed in the circulating stream of CaO**

$$\begin{pmatrix}\text{CO2 reacting with}\\ \text{CaO in the bed}\end{pmatrix} = N_{Ca\,Active}\left(\frac{dX}{dt}\right)_{reactor}$$

Simplified reaction rate



$$r_{ave} = \begin{cases} \dfrac{X_{ave}}{t^*} & \text{if } t < t^* \\ 0 & \text{for } t > t^* \end{cases}$$

$$r_{ave} = k_s X_{ave}\left(\overline{f_{CO2}} - f_e\right)$$

Particles reacting in the carbonator

$$N_{Ca\,Active} = N_{Ca}\, f_a$$

$$f_a = \left(1 - e^{-\frac{t^*}{\tau}}\right)$$

$$\tau = \frac{N_{Ca}}{F_{CaO}}$$

Ref: *Alonso et al. Chem. Eng. Journal, 2009, (64) 883-891*

Post-combustion CO2 capture using carbonate looping

CO_2 mass balance in the system

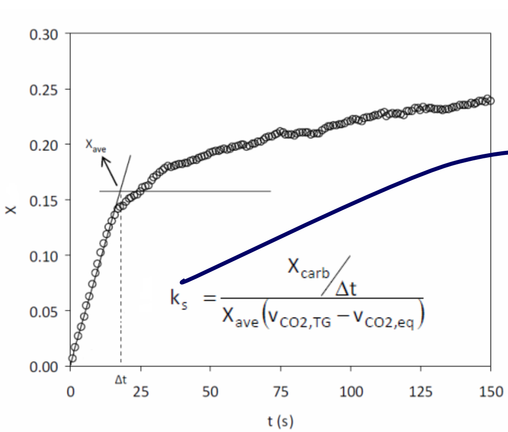
CO_2 reacting with CaO in the bed **=** CO_2 removed from the gas phase **=** $CaCO_3$ formed in the circulating stream of CaO

Comparison of CO_2 capture efficiencies and CO_2 removal rates in the reactor

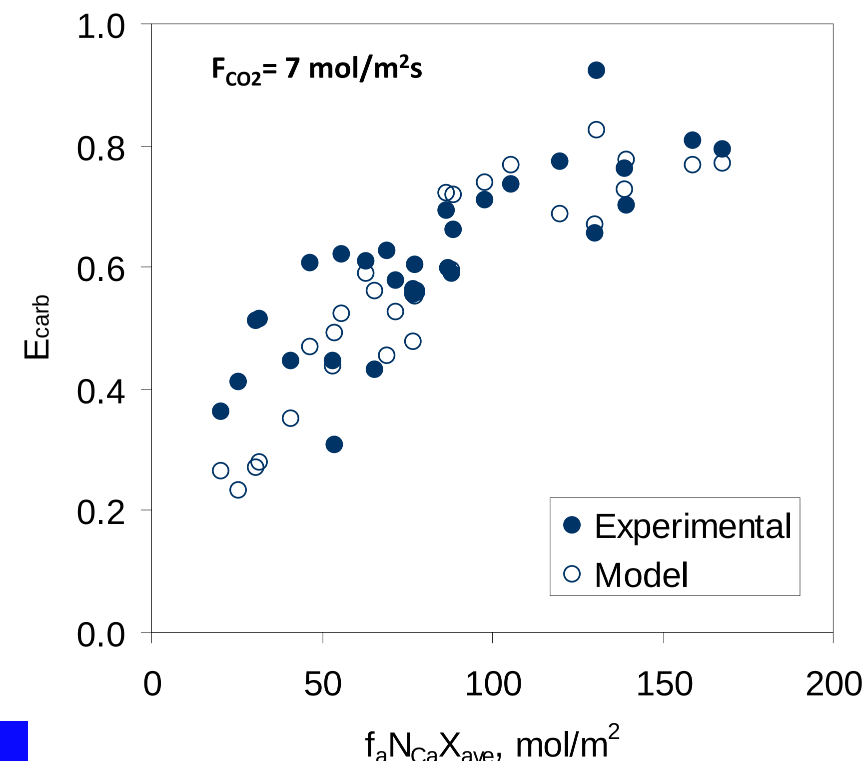
$$E_{carb} = \frac{N_{Ca}\, f_a\, \varphi k_s\, X_{ave}\left(\overline{f_{CO2} - f_e}\right)}{F_{CO2}}$$

Apparent reaction rate

Experimental determination of ks

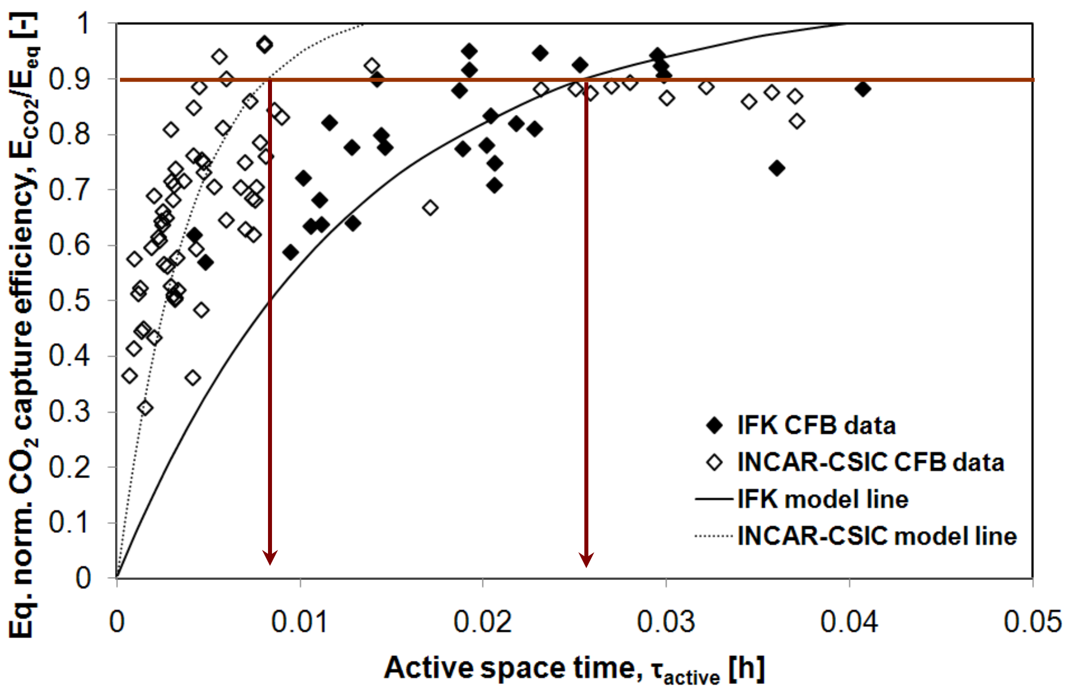


φ close to unity



The CO_2 capture in the reactor is controlled mainly by the kinetics of the carbonation reaction

Model validation in two experimental facilities: IFK and CSIC



$$E_{carb} = \tau_{active}\,\varphi k_s \left(f_{CO2} - f_e\right) = \frac{N_{Ca} f_a \varphi k_s X_{ave} \left(f_{CO2} - f_e\right)}{F_{CO2}}$$

Active space time

$$\tau_{active} = \frac{N_{CaO}}{F_{CO2}} f_a X_{ave}$$

Critical active space time at which

E_{CO2}/E_{eq}>90%:

Experimental data:

Inlet CO_2 Vol. % = 11.4 for IFK &16.5 for INCAR-CSIC

T_{carb}= 634-660 °C, $X_{max,ave}$= 0.08-0.23

Main differences between both series of experimental and calculated data

- Different inlet CO2 concentration (11.4% IFK, 16.5% INCAR)
- Different limestone (IFK limestone less reactive, k_s=0.20s^{-1})

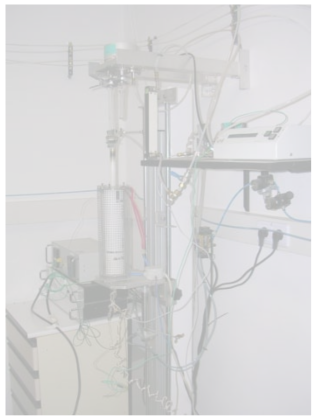
Ref: *Charitos et al. Ind. Eng. Chem. Res. Submitted for publication. Common paper between IFK and INCAR-CSIC*

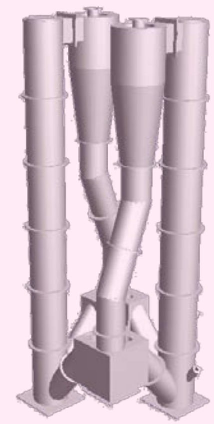
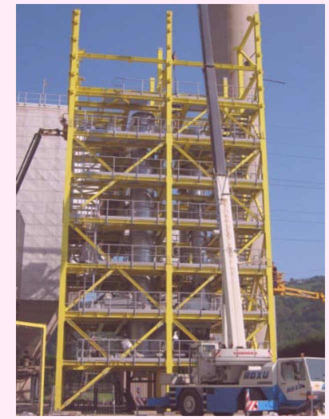
Post-combustion CO2 capture using carbonate looping

Scale

Lab Scale	Small pilot plant scale	Pilot plant scale (1.7 MWt)	Demo Scale

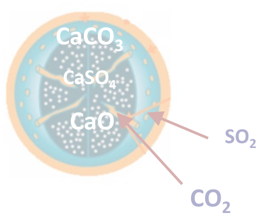
EXPERIMENTAL



MODELLING

Particle models

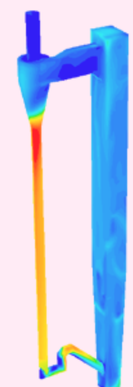
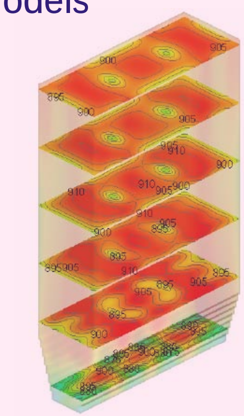


Conversion (X)

Reactivity (dX/dt)

OD/1D Models

2D/3D Models

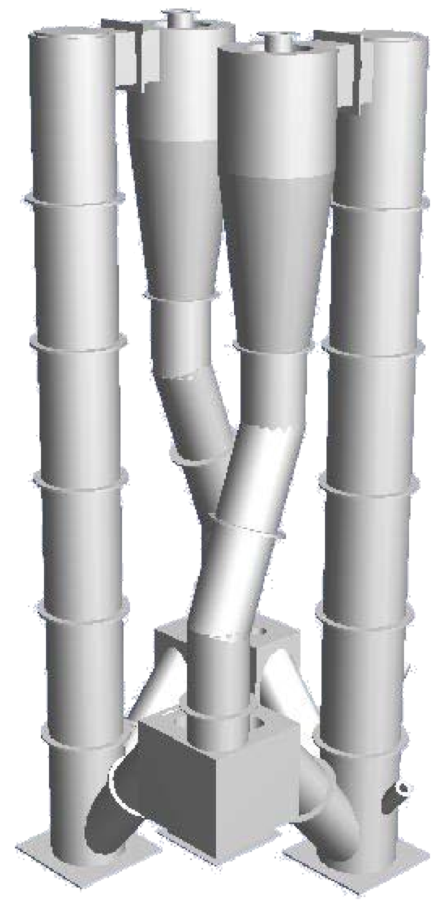
Next steps in Ca-looping development: 1.7 MWt pilot plant

FP7 "CaOling" Project:
Development of postcombustion CO2 capture with CaO in a large testing facility: "CaOling"

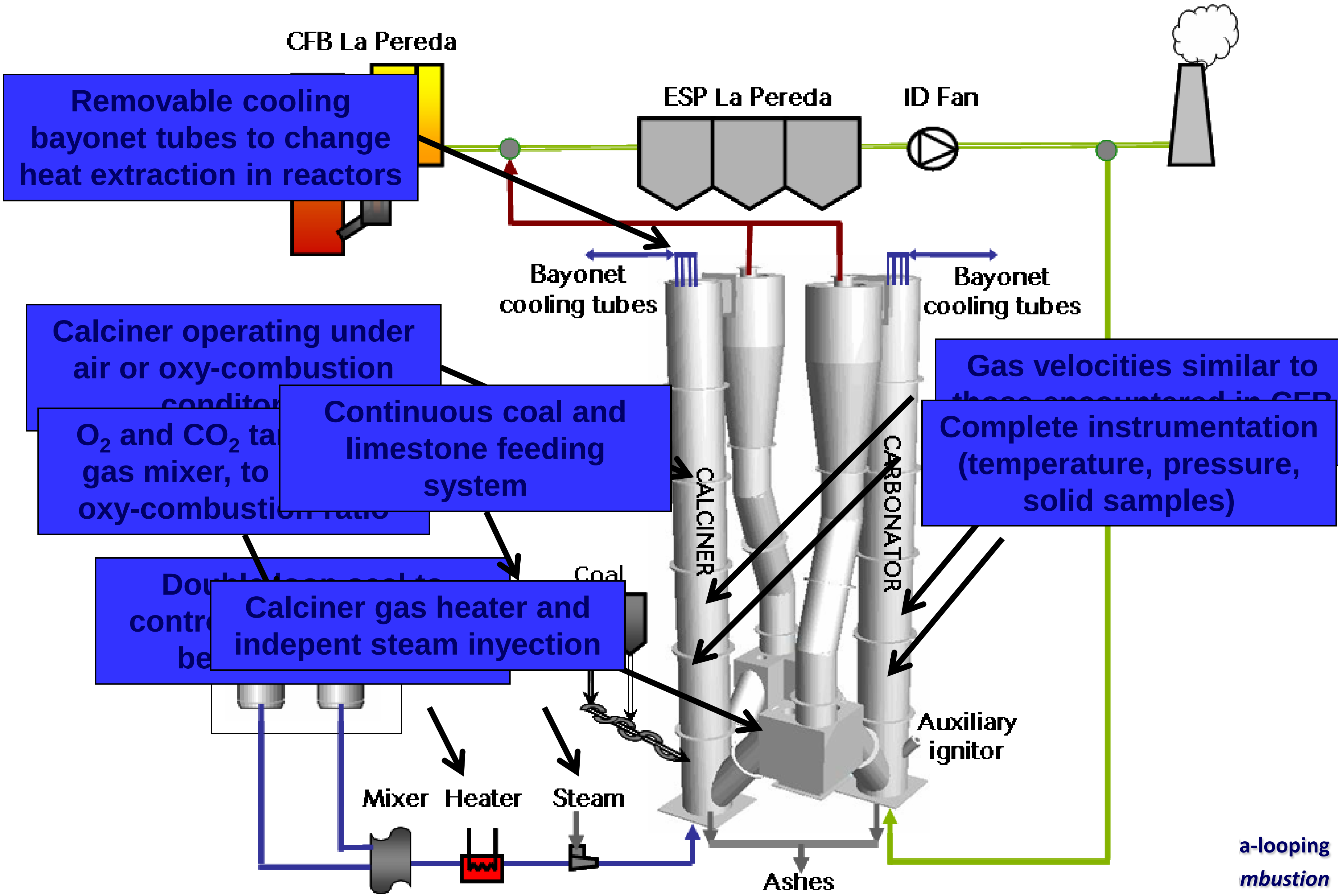
Main objective:

To advance in the experimental validation of the carbonate looping cycle (at a 1 MWt scale range) and demonstrate that this is a low cost, highly energy efficient CO_2 capture technology, suitable for retrofitting coal combustion power plants

Operation will start in September 2011



Next steps: 1.7 MWt pilot plant

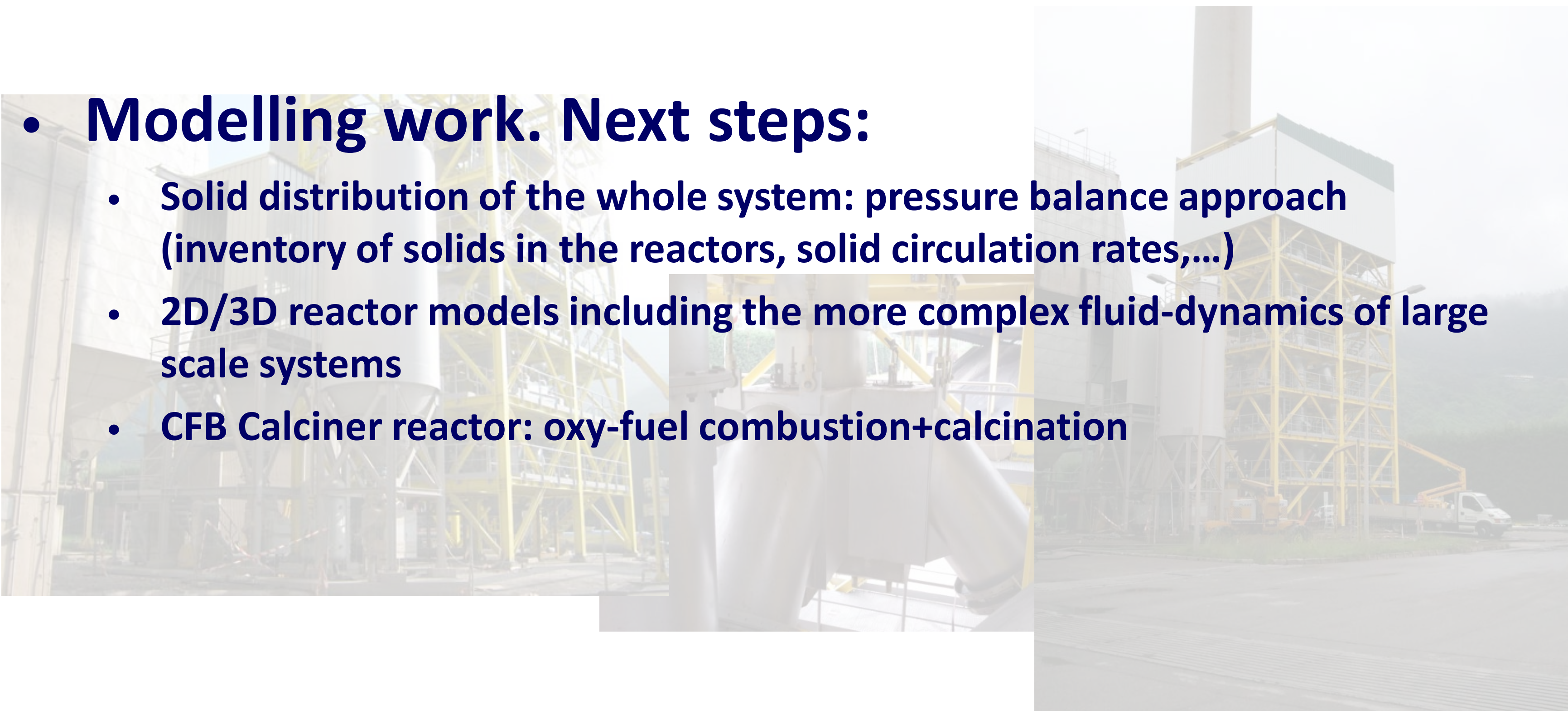


a-looping
mbustion

Next steps: 1.7 MWt pilot plant

SOME OBJECTIVES:

- To gain the necessary design data and experience for rapid scale-up of the technology, building experimentally validated models from the careful interpretation of results produced from lab-scale prototypes and from the experimental campaigns in a 1 MW test facility.
- To evaluate and optimise the concept in operating conditions equivalent to large-scale industrial units and integrated in a commercial plant. To analyse the controllability and stability of the process
- To find the optimum set of operating conditions to minimize sorbent make-up flow cost (calcination temperatures, O_2/CO_2 ratios in the calciner, requirement for steam in the carbonator and calciner, best suitable approach for SO_2 capture, etc).



- **Modelling work. Next steps:**
  - Solid distribution of the whole system: pressure balance approach (inventory of solids in the reactors, solid circulation rates,…)
  - 2D/3D reactor models including the more complex fluid-dynamics of large scale systems
  - CFB Calciner reactor: oxy-fuel combustion+calcination

Conclusions/Remarks

- Postcombustion Calcium Looping is a rapidly developing technology successfully characterized at small pilot plant scale.
- A simple carbonator reactor model (CSTR for solids and PF for gas) is shown to fit reasonably well the available results in CFB mode of operation.
- The model highlights the importance of sufficient solid inventories and solid circulation rates for a given activity of the solids and a given flow of flue gases entering the carbonator.
- The extrapolation of results to large scale CFB carbonator reactors anticipates capture efficiencies over 90% in operating at realistic conditions (similar to those present in commercial CFBC units) even with CaO particles in their residual activity after 10s to 100s of carbonation-calcination cycles.
- Carbonation efficiency correlates well with active space time, which combines the main carbonation operation parameters.
- A flexible experimental facility has been constructed in La Pereda Power Plant (Spain) aiming to validate Calcium Looping technology in the 1MWs size.

"Post-combustion CO_2 capture by Ca-looping"

Thank you for your attention

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- This work has been carried out as part of the FP7 "CaOling" Project.
- Special thanks to IFK (Prof. Scheffknecht) for permission to use some of their data and figures in this presentation.

Workshop on Mathematical Modelling of Combustion

23-25 May, Santiago de Compostela, Spain