“CO_2 and SO_2 co-capture in a circulating fluidized bed carbonator reactor of CaO"

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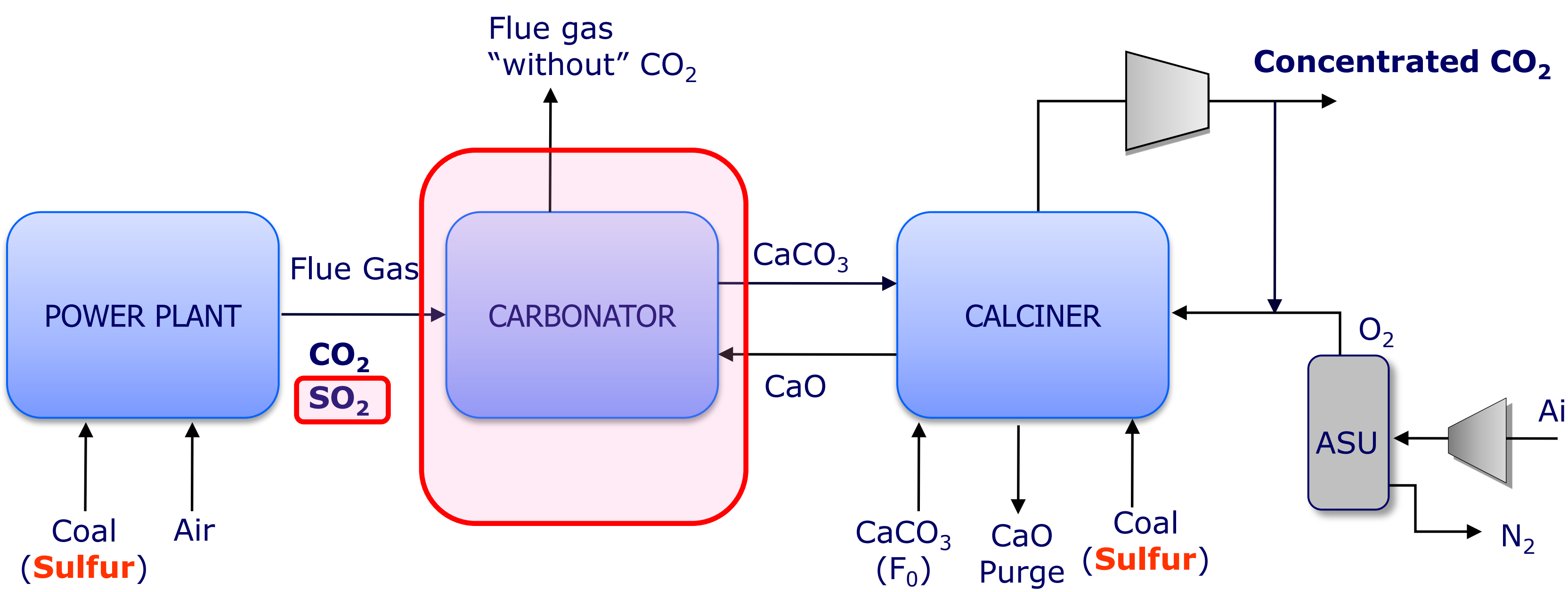
- Introduction
- Objectives
- Experimental
  - Thermogravimetric analysis
  - Small pilot plant of 30 kWt
- Results and discussion
  - Sulfation rates
  - SO_2 retention under carbonation conditions
- Conclusions

SO_2 on Ca-looping post-combustion systems



Reaction of CaO with SO_2:

- CaO is being used routinely as desulfurization agent in CFB combustors
- Main differences between SO_2 capture in CFBC and carbonator:
  - Range of temperatures
  - Range of conversion
  - Texture of CaO

Previous findings

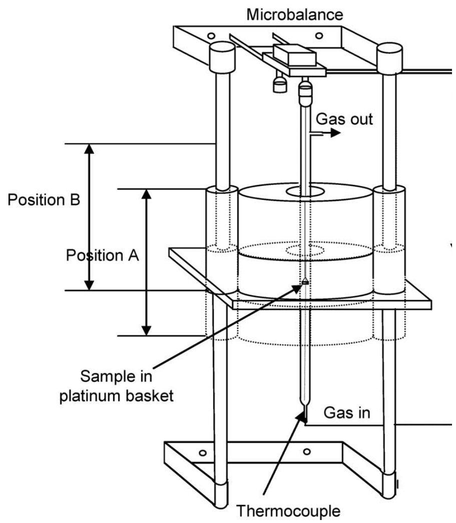
- SO_2 reduces maximum CO_2 carrying capacity
- Sulfation behavior of CaO is enhanced during cycling

¿Sulfation rates of cycled CaO at carbonation conditions and SO_2 capture efficiency?

- Introduction
- **Objectives**
  - **Determination of sulfation rates of cycled CaO particles under carbonation conditions**
  - **Study the SO_2 capture efficiency in a CFB carbonator**
- Experimental
- Results and discussion
- Conclusions

Experimental facilities

Thermo-gravimetric analyzer



Experimental conditions during TGA tests

- Mixtures of air/CO_2/SO_2
- Calcination: T=950 ºC, Air
- Carbonation: T=650 ºC, 10% CO_2 in air
- Sulfation: T=650 ºC, SO_2=500-3000 ppm
- Number of cycles up to 50
- Three different limestones

	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SiO_2	TiO_2
Compostilla	**0.16**	**89.7**	**2.5**	**0.46**	**0.76**	**<0.01**	**0.07**	**0.37**
Imeco	**0.10**	**96.1**	**0.21**	**0.05**	**1.19**	**0.01**	**1.11**	**<0.05**
Enguera	**0.18**	**98.9**	**<0.01**	**0.03**	**0.62**	**0.00**	**0.43**	**0.02**

30 kWt Pilot Plant at INCAR-CSIC

Main characteristics:

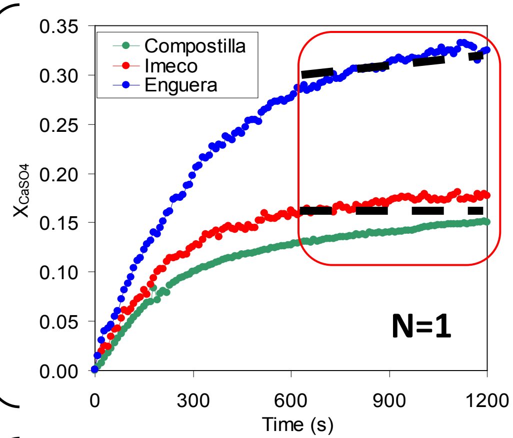
- Two CFB reactors (Height~6.5 m, diameter=100 mm)
- Electrically heated
- Measurement port (temperature, pressure, gas composition)
- Solid circulation measurements
- Solid samples characterization (TG analysis, C/S analyzer)

Experimental results: Sulfation rates

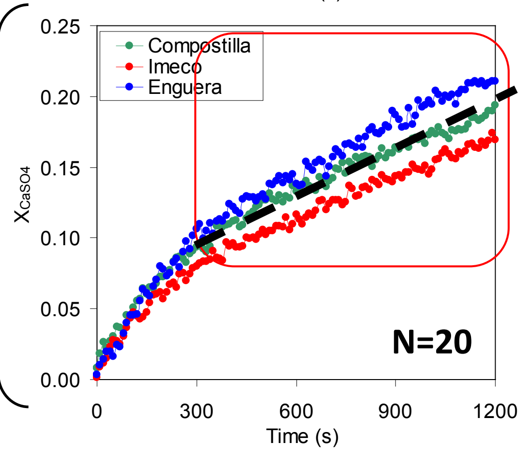
Effect of number of cycles on sulfation behavior

Sulfation conditions: T=650 ºC, SO_2=500 ppm$_v$

Fresh calcined limestone



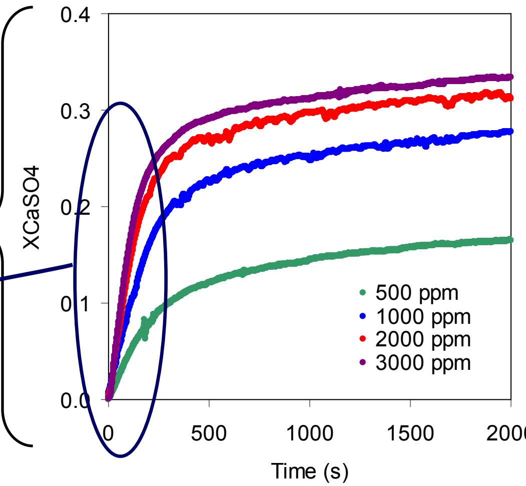
After 20 cycles



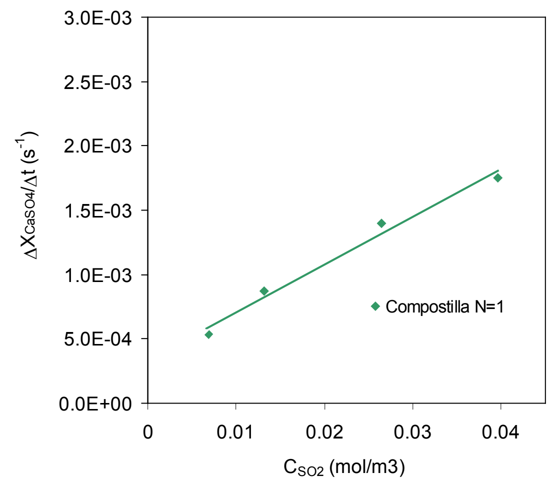
- **No pore plugging is present during sulfation of cycled particles up to reaction times of 20 min.**

Effect of SO_2 concentration on CaO sulfation

Compostilla limestone (N=1)



Determination of reaction order respect to SO_2



- **Results show that sulfation of CaO is a first reaction order**

Experimental results: Sulfation rates

Interpretation of experimental data: Application of the Random Pore Model

Chemically controlled reaction (k_s)

$$X = 1 - \exp\left(\frac{1 - \left(\frac{\tau}{2}\psi_N + 1 \right)^2}{\psi_N} \right)$$

$$\frac{1}{\psi}\left[\sqrt{1-\psi \ln(1-X)} - 1\right] = \frac{k_s S C t}{2(1-\varepsilon)}$$

General expression of RPM

$$\frac{dX}{dt} = \frac{k_s S C \sqrt{1-\psi \ln(1-X)}}{(1-\varepsilon)\left[1 + \frac{\beta Z}{\psi}\left(\sqrt{1-\psi \ln(1-X)} - 1\right)\right]}$$

1

2

Chemically/Diffusion controlled reaction (k_s, D)

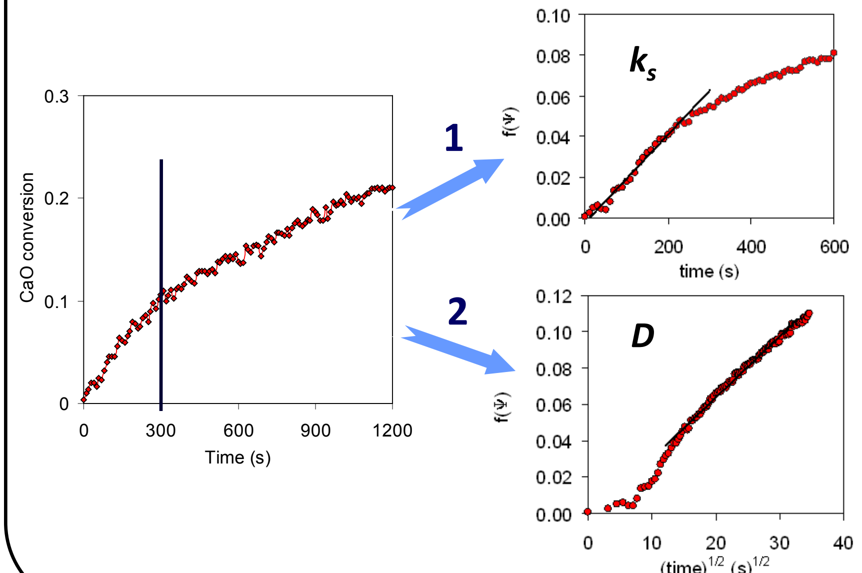
$$X = 1 - \exp\left(\frac{1}{\psi_N} - \frac{\left[\sqrt{1+\beta Z \tau} - \left(1 - \frac{\beta Z}{\psi_N}\right)\right]^2 \psi_N}{(\beta Z)^2} \right)$$

$$\frac{1}{\psi}\left[\sqrt{1-\psi \ln(1-X)} - 1\right] = \frac{S}{(1-\varepsilon)}\sqrt{\frac{D M_{CaO} C t}{2 \rho_{CaO} Z}}$$

Main model parameters:

- k_s: reaction rate of surface reaction
- D: effective product layer diffusion
- ψ: structural parameter

Derivation of reaction rate parameters



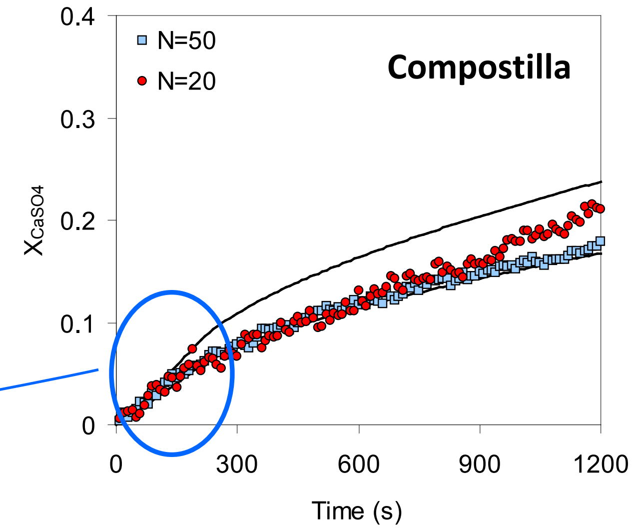
Experimental results: Sulfation rates

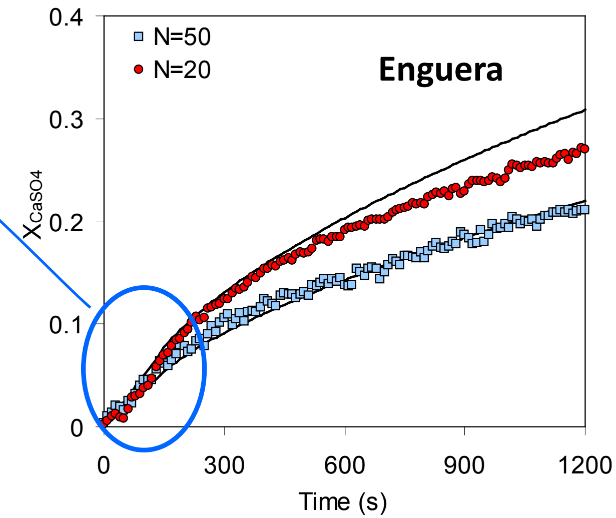
RPM model results

Reaction rate parameters for studied limestones

	Compostilla	Imeco	Enguera
k_{s0} (m^4/mols)	6.38E-06	7.31E-06	8.31E-06
E_{ak} (kJ/mol)	56	56	56
D_0 (m^2/s)	1.71E-05	1.49E-05	3.02E-05
E_{aD}(kJ/mol)	120	120	120
h (nm)	8.6	7.0	9.9

Comparison of experimental and calculated values using the RPM model





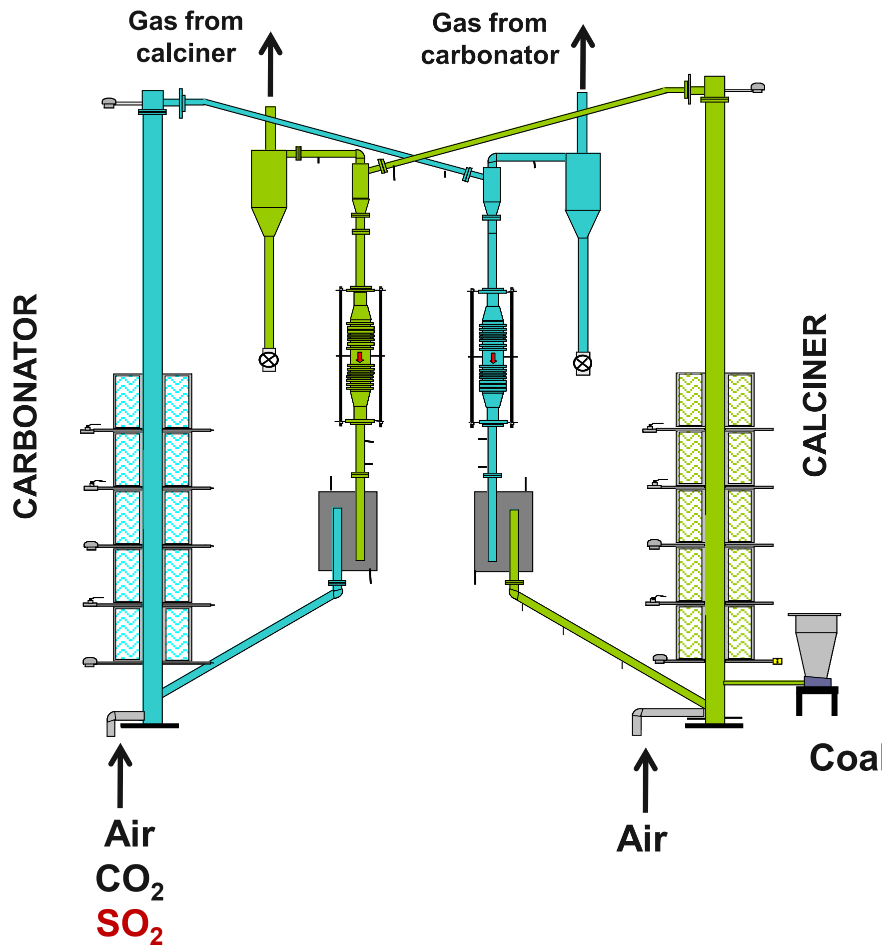
For practical application purposes in a Ca-looping, only the chemically controlled stage can be considered

$$\frac{dX}{dt} = \frac{k_s\, S\, C(1-X)\sqrt{1-\psi \ln(1-X)}}{(1-\varepsilon)}$$

- Introduction
- Objectives
- Experimental
  - Thermogravimetric analysis
  - Experiments in small pilot plant
- **Results and discussion**
  - Determination of sulfation rates
  - **SO_2 retention in a CFB carbonator in presence of CO_2**
- Conclusions

Experimental results: SO_2 retention in a circulating fluidized bed carbonator bed

30 kWt Pilot Plant at INCAR-CSIC



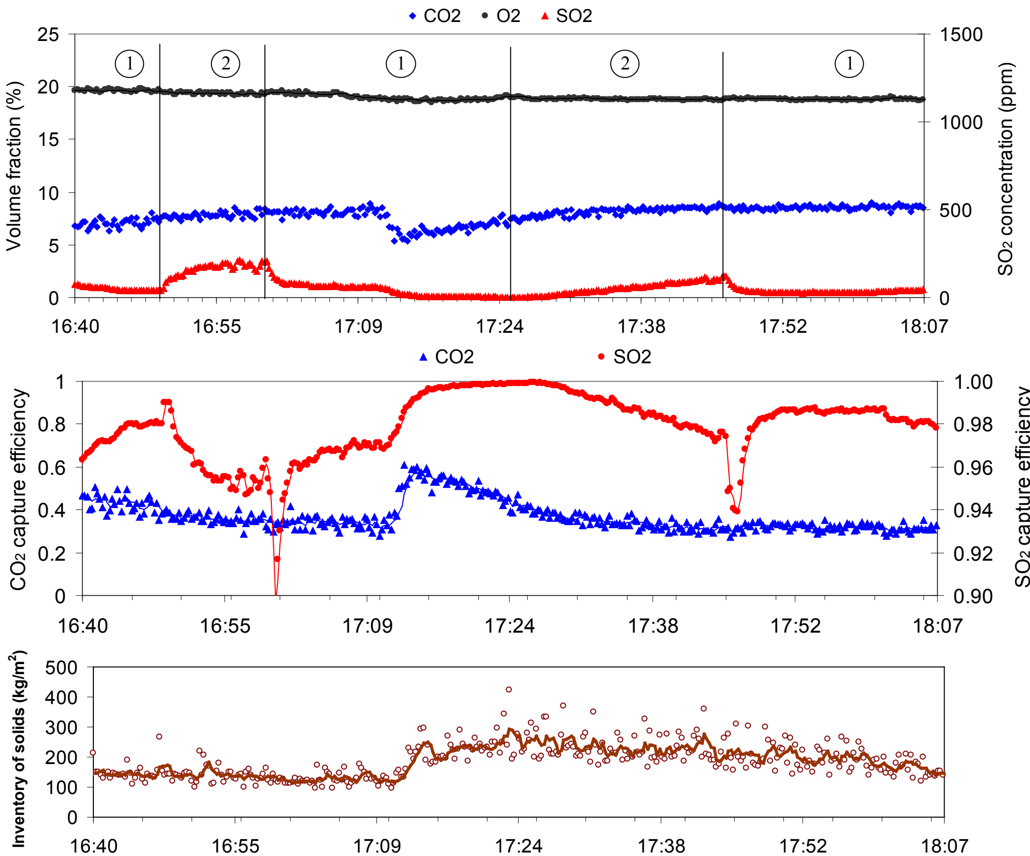
Experimental results: SO_2 retention in a circulating fluidized bed carbonator bed

EXAMPLE OF SO_2 CAPTURE EFFICIENCY

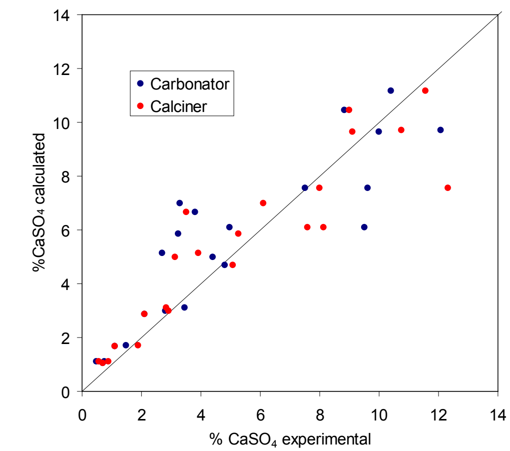
Experimental conditions*

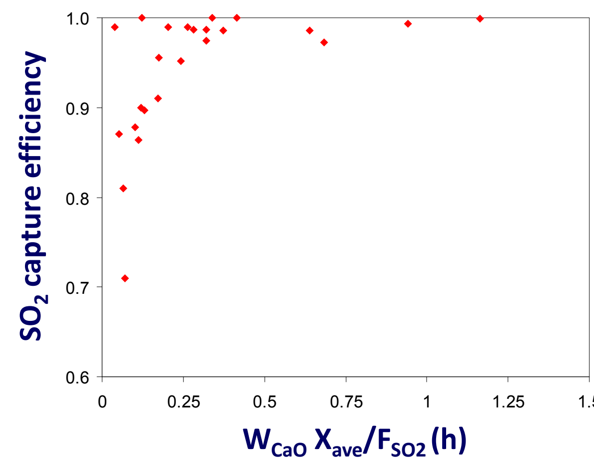
- ***Flow to carbonator:*** 19 m^3N/h
- u_{gas}=2.5 m/s
- ***CO_2 inlet concentration*** = 12%
- ***SO_2 inlet concentration***:
  1900 ppm (1)
  3800 ppm (2)
- ***Solid circulation*** = 1.9 kg/m^2s
- X_{sulf} = 0.08
- X_{max}-X_{carb} = 0.03
- $T_{carbonator}$ = 668 ºC

*Average values during experimental period shown



SO_2 mass balance during the experimental testing period





CONCLUSIONS

- Sulfation of CaO cycled particles proceeds through an initial chemically controlled step followed by a second period where chemical reaction and diffusion through the product layer are the controlling resistances.
- Sulfation of CaO has been found to be a first reaction order with respect to SO_2 under carbonation conditions.
- Cycled particles do not undergo pore plugging due to the growth of the $CaSO_4$ layer during sulfation (for reaction times up to 20 min).
- The random pore model has been used to study the sulfation behavior of three limestones. Good agreement between experimental and calculated values has been found confirming the suitability of this model to describe the sulfation reaction under both reaction regimes.
- Post-combustion Ca-looping carbonators can be effective reactors for capturing SO_2 from flue gases even for low inventories of solids.

“CO_2 and SO_2 co-capture in a circulating fluidized bed carbonator reactor of CaO"

Thank you for your attention

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- This work has been carried out as part of the FP7 “CaOling“ Project.

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