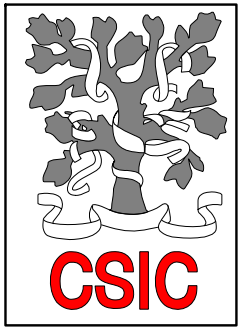
SULFATION RATES OF PARTICLES IN CaL REACTORS



J.M. Cordero, B. Arias, M. Alonso, J.C. Abanades

CSIC-INCAR
jmacod@incar.csic.es

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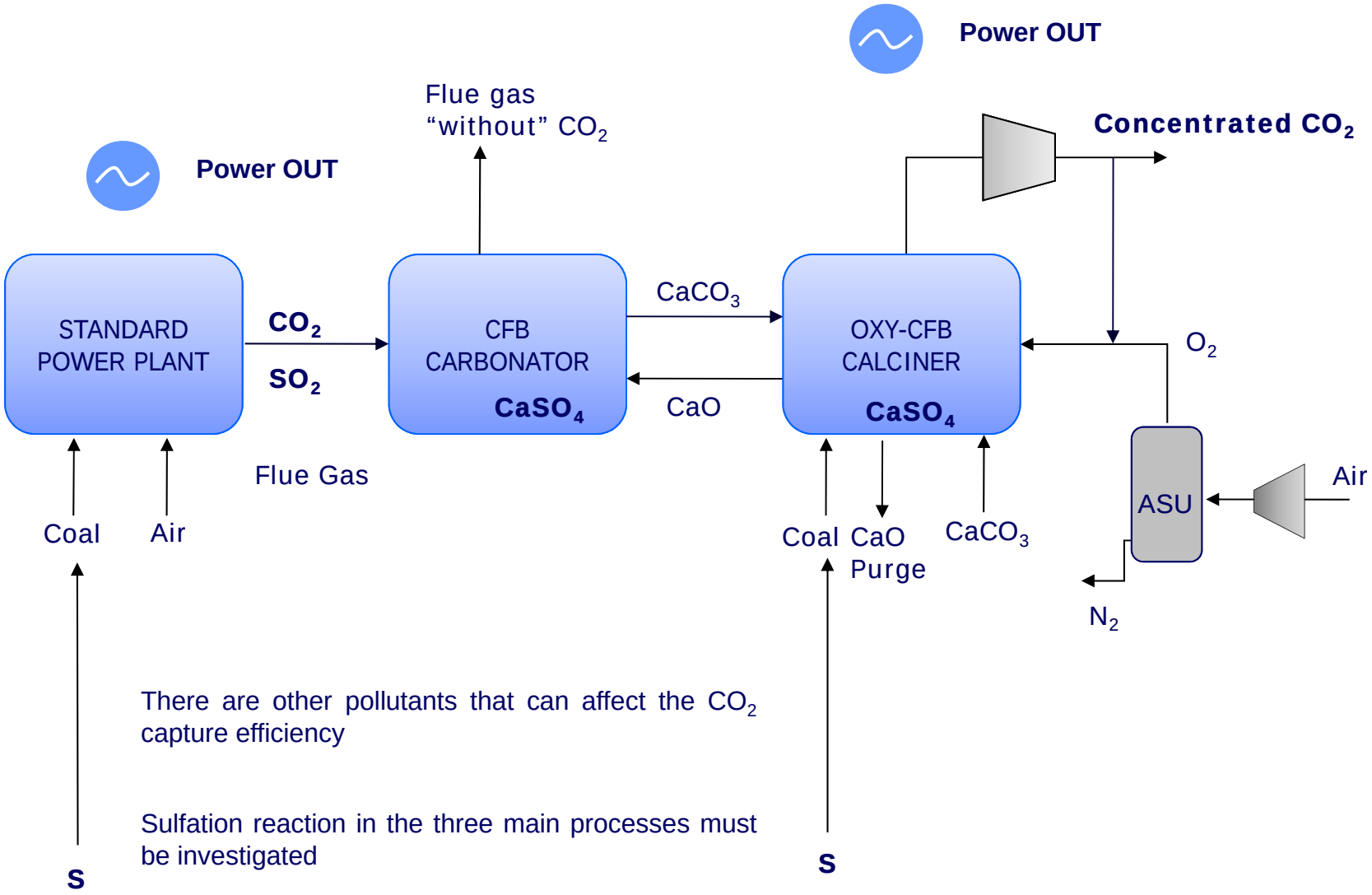
SO_2 capture in CaL post-combustion technologies: general sketch

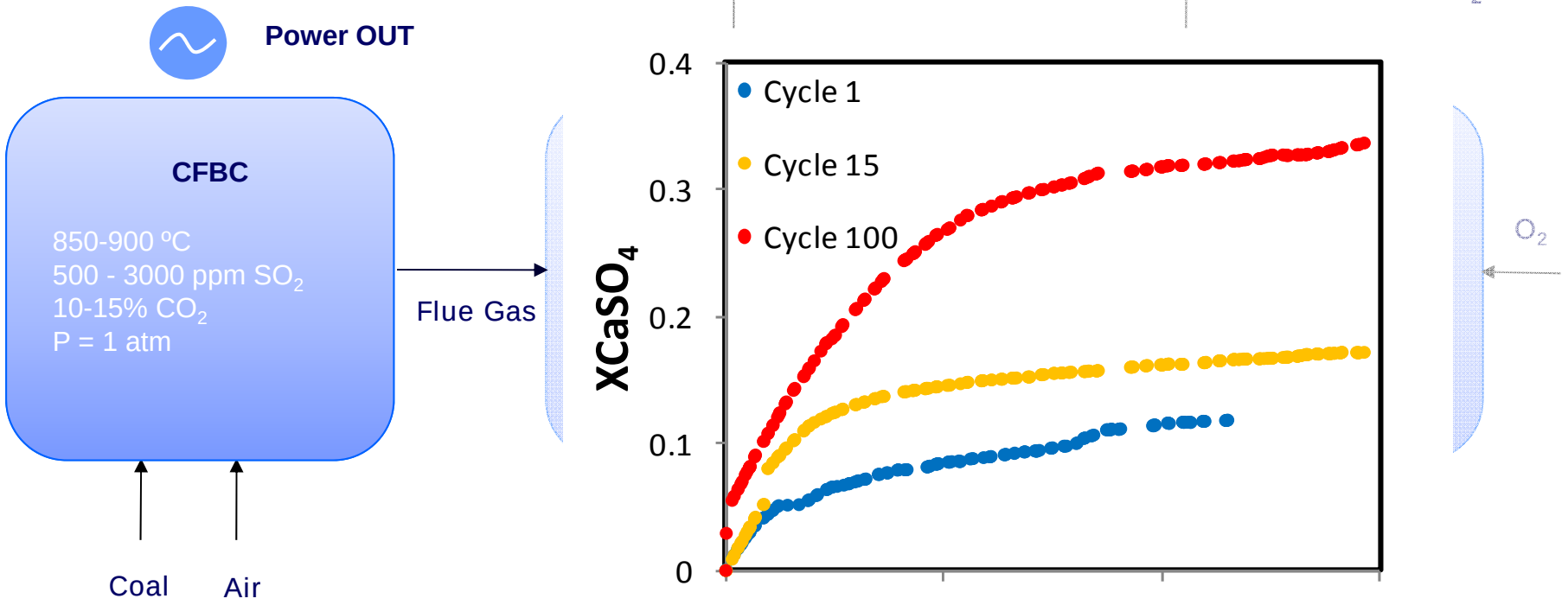


There are other pollutants that can affect the CO_2 capture efficiency

Sulfation reaction in the three main processes must be investigated

SO_2 capture in CFBCs

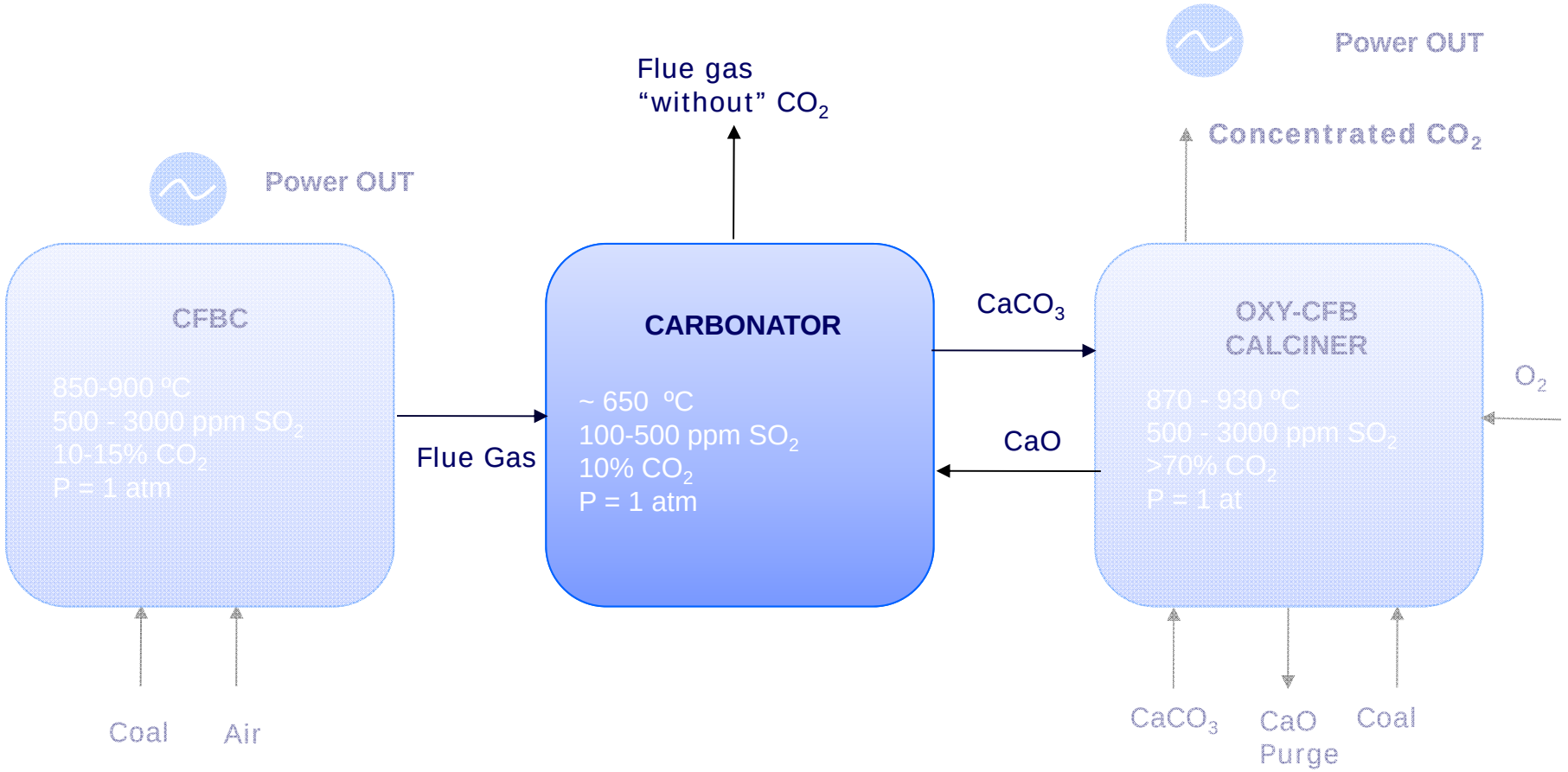
Sulfation is a "well known" reaction in CFBC environments
Several studies suggest that sulfation reactions will be enhanced when using CaL purges



T = 900 ºC
dp = 300-600 µm
2200 ppm SO_2

Grasa et al, *Ind. Eng. Chem. Res. 2008; 47:1630–1635*

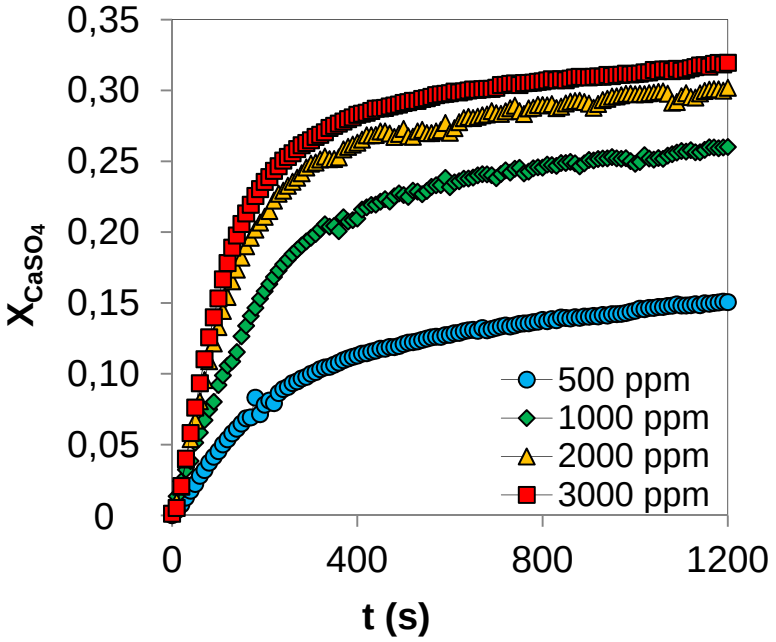
SO_2 capture in the CaL carbonator

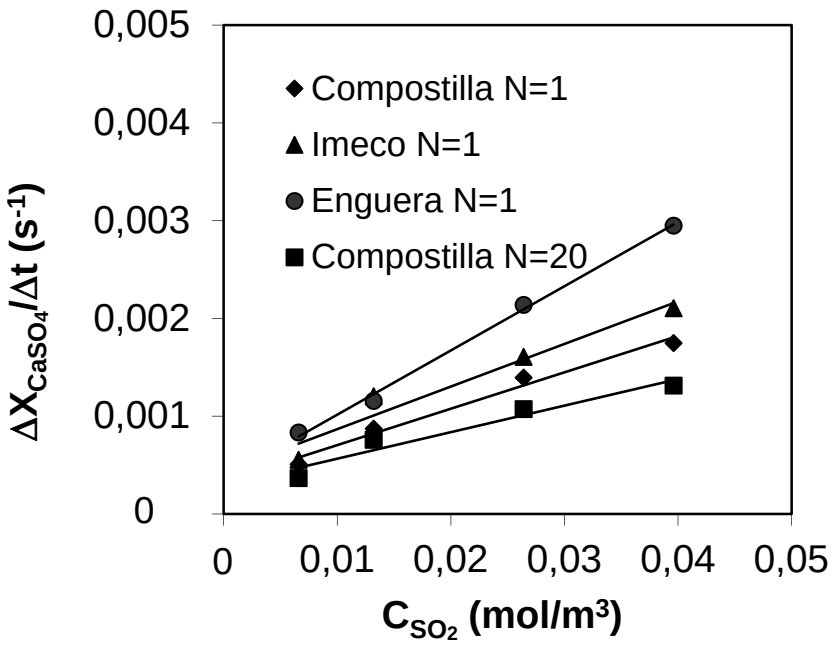


SO_2 capture in the CaL carbonator: effect of the SO_2 concentration

T = 650 ºC
dp = 63-100 µm
Gas phase = 500 ppm SO_2
Oxygen in all cases > 5%

SO_2 concentration effect over Compostilla limestone.



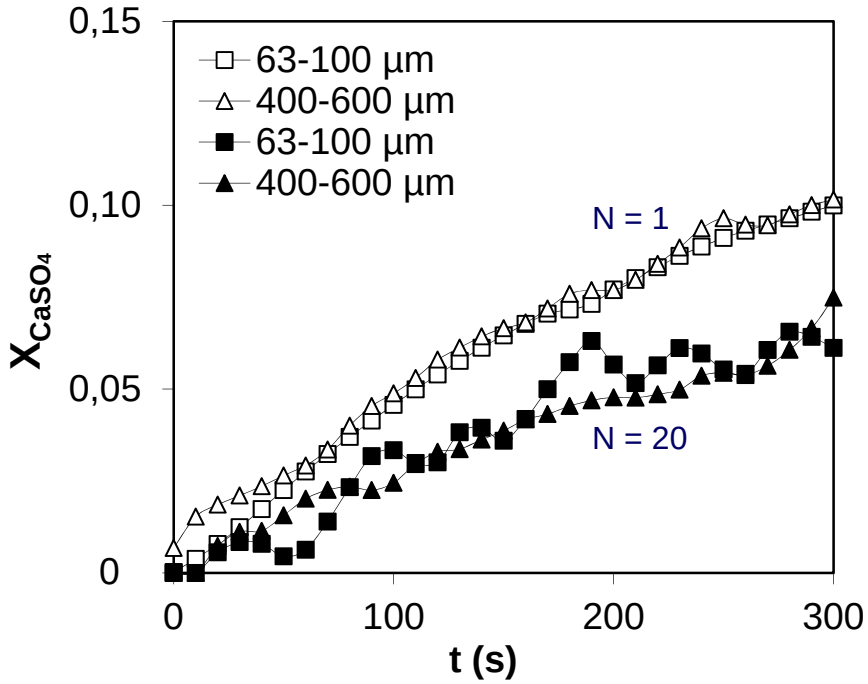


- The experimental procedure: sulfation after N cycles of calcination-carbonation.
- The initial rate of sulfation is clearly affected by SO_2 concentration.
- Apparent first order with respect to SO_2, maintained along cycles.

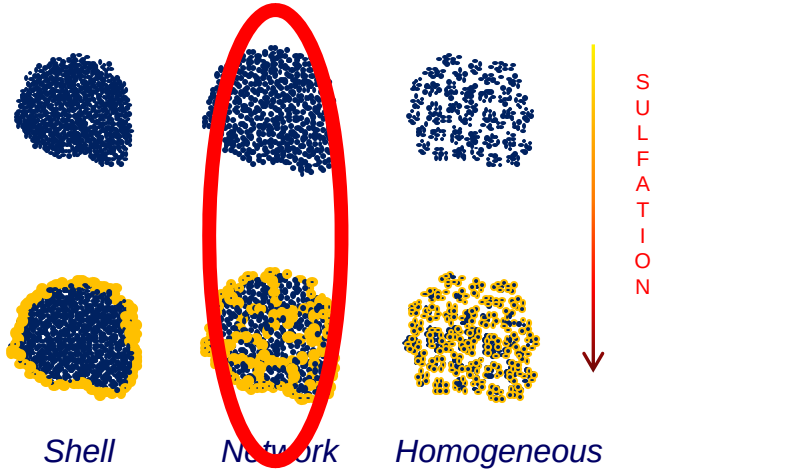
SO_2 capture in the CaL carbonator: effect of the particle size

T = 650 ºC
dp = 63-100 µm
Gas phase = 500 ppm SO_2
Oxygen in all cases > 5%

Effect of the particle size after the first calcination and 20 calcination/carbonation cycles for Compostilla limestone.



Constant concentration of $CaSO_4$ through the particle



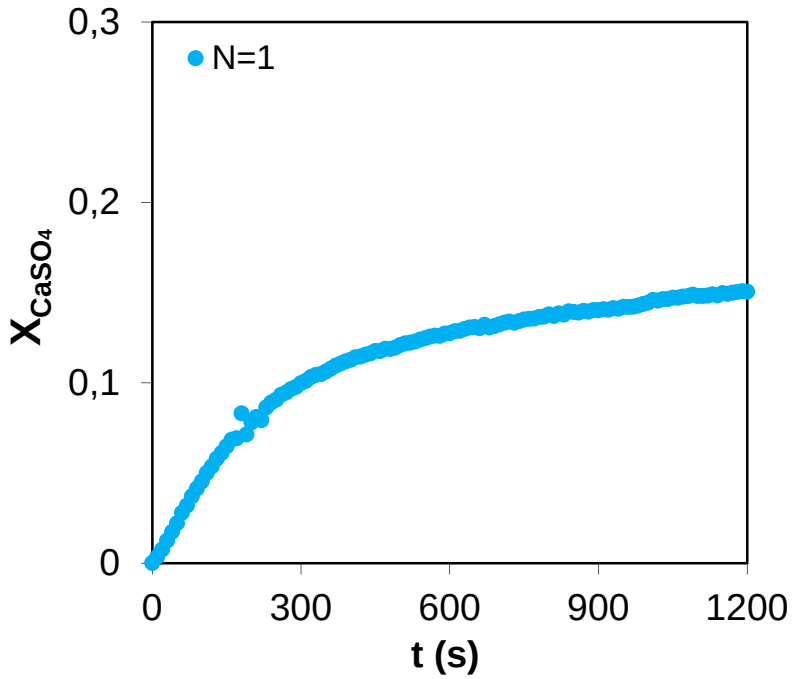
K. Laursen et al, *Fuel 2000; 79:153–163*

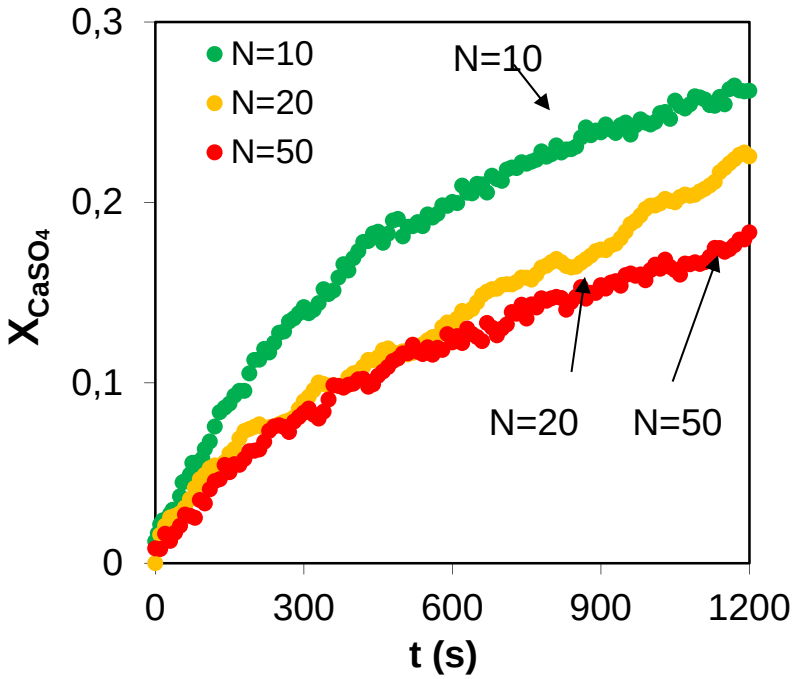
- Reaction rates similar to both sizes → homogeneous model of sulfation

SO_2 capture in the CaL carbonator: effect of N cycles

T = 650 ºC
dp = 63-100 µm
Gas phase = 500 ppm SO_2
Oxygen in all cases > 5%

Evolution of CaO conversion to $CaSO_4$ with time. Comparing the effect of the number of cycles.





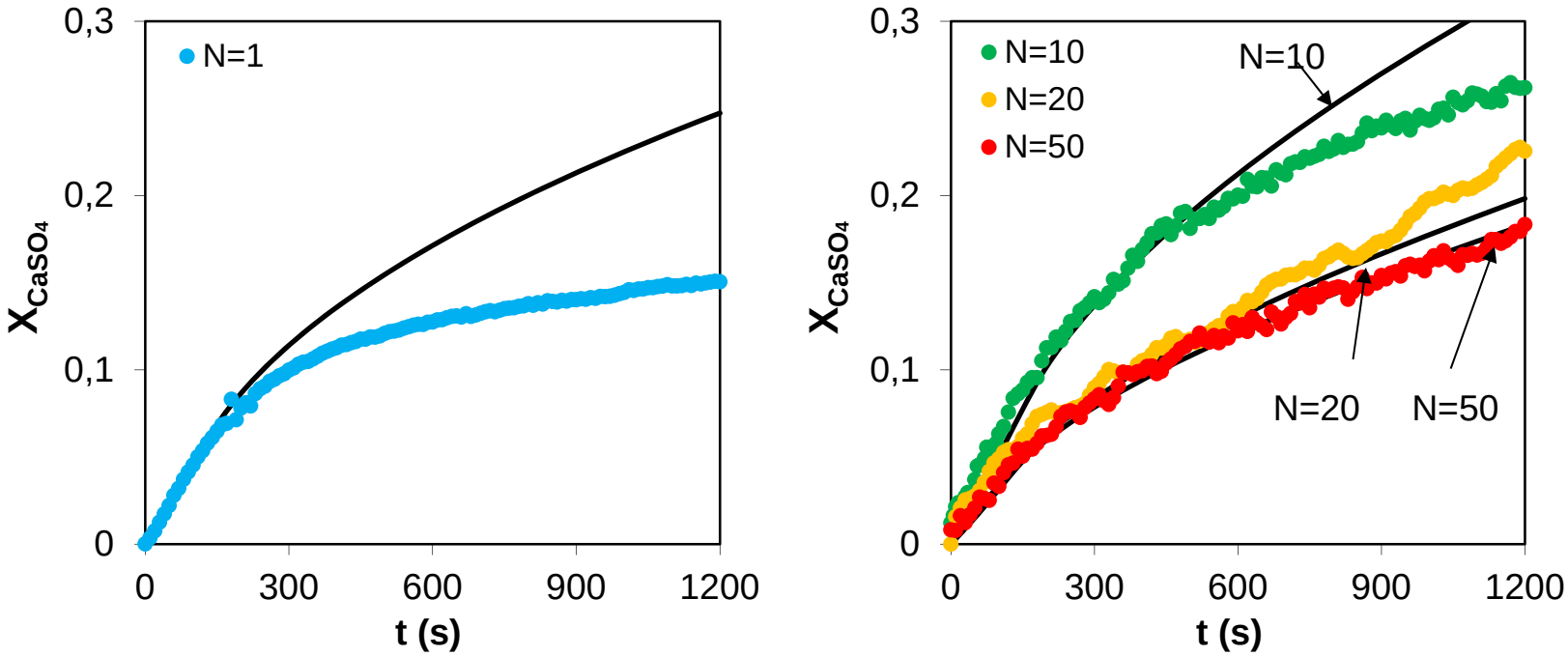
- For N = 1, sulphation rate falls sharply after 10 minutes of reaction, due to pore blockage.
- For N > 1, there is a smoother transition between fast and slow stages of reaction. This transition is due to the product layer diffusion, that produces a change of regime when the critical thickness is reached.

SO_2 capture in the CaL carbonator: fitting by the Random Pore Model

T = 650 ºC
dp = 63-100 µm
Gas phase = 500 ppm SO_2
Oxygen in all cases > 5%

B. Arias et al, *AIChE (in press)*

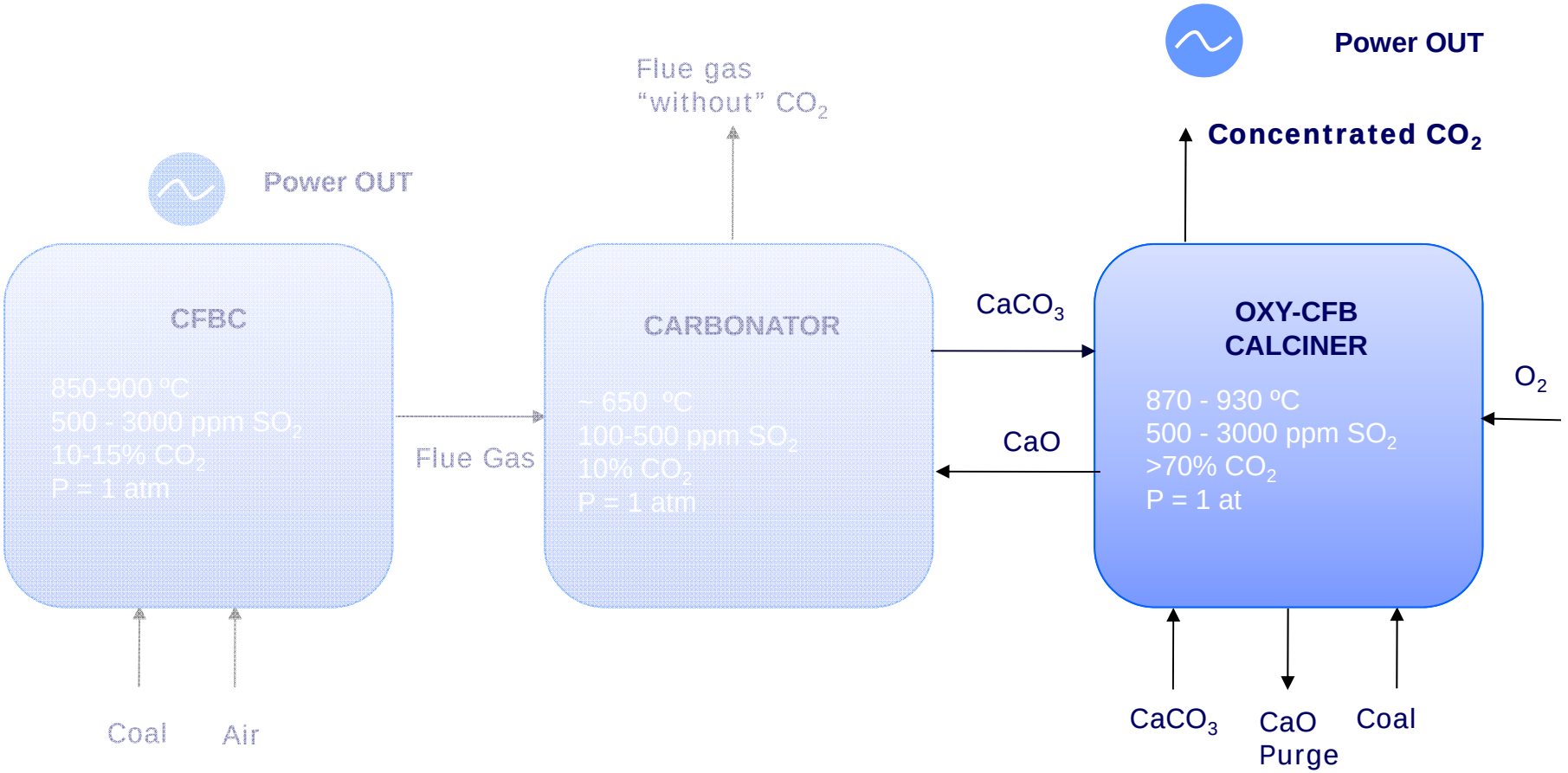
Comparison of the experimental values with those calculated for Compostilla limestone, for different number of cycles.



• For N = 1, the model only fits well from a conversion up to 0.1. From that value, the model overpredicts the results (pore blockage)

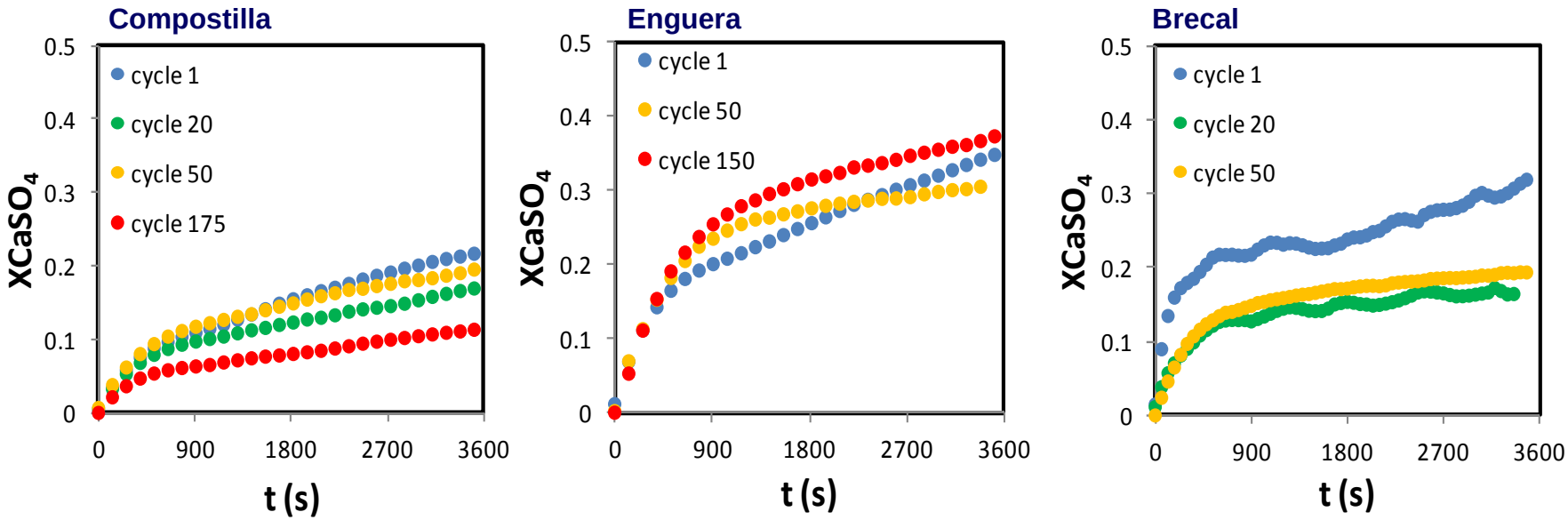
• For N = 50, the RPM fits well over all the range of conversion, showing that the product layer can full develop without any geometrical restriction.

SO_2 capture in the CaL calciner



Sulfation in the Oxy-CFB calciner: effect of N cycles

T = 930 ºC
dp = 63-100 µm
Gas phase = 500 ppm SO_2, 70% CO_2
Oxygen in all cases > 5%



- The sulfation pattern is different from that shown for CFBC conditions.
- The final conversion to $CaSO_4$ and the initial slope of the sulfation curves decreased generally with the cycles.
- Since the surface area S only can decrease while cycling, two scenarios are possible for both limestones:

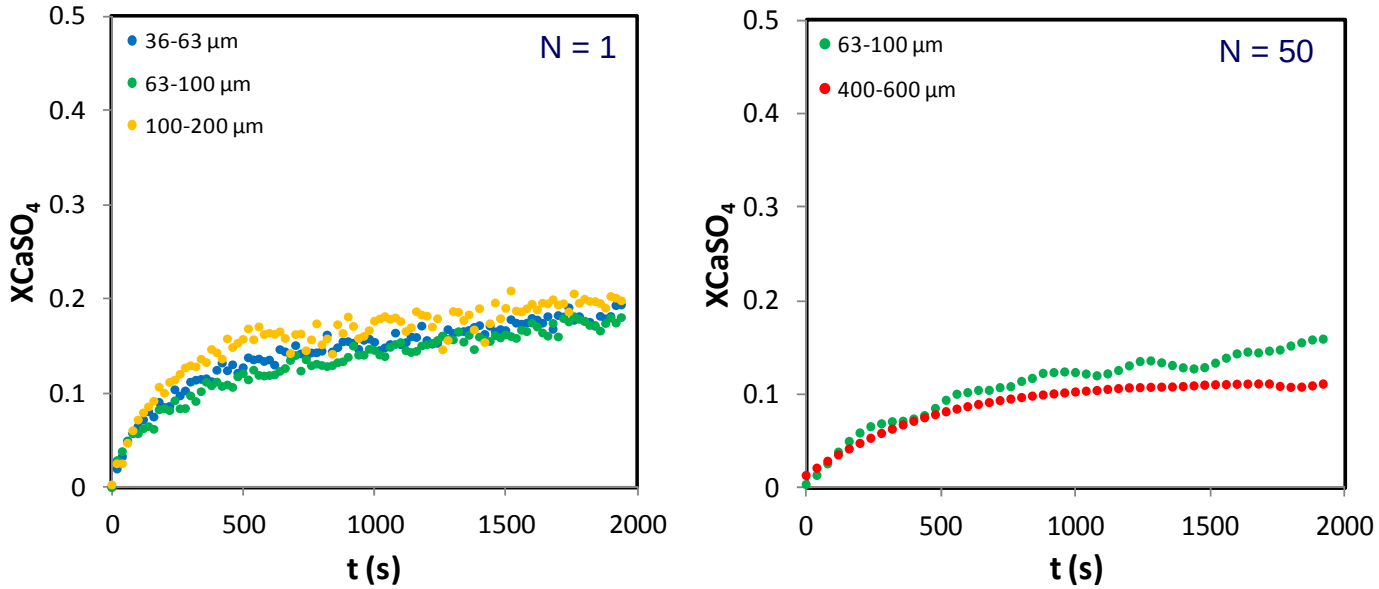
1. The sulfation pattern is homogeneous (pseudo-homogeneous) from the beginning.
2. The sulfation pattern starts being unreacted core, but between N = 1 and 20, it transforms into homogeneous.

For checking the sulfation pattern at oxy-CFB conditions, experiments varying the particle diameter were performed.

Sulfation in the Oxy-CFB calciner: effect of the particle size

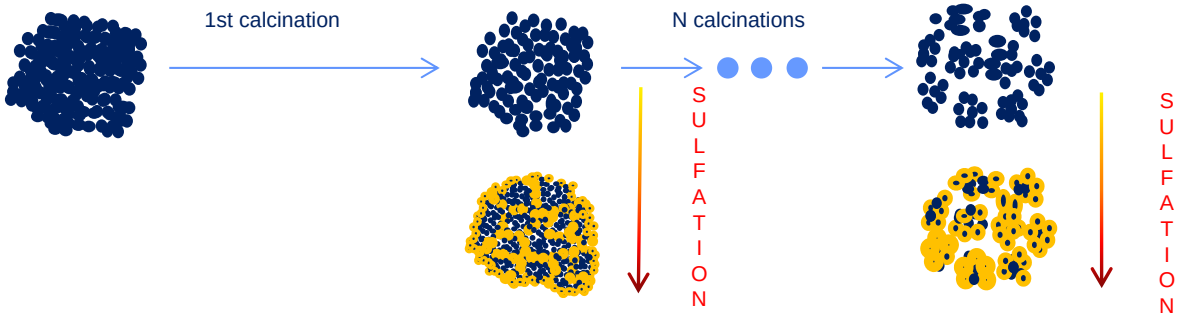
T = 930 ºC
dp = 63-100 µm
Gas phase = 500 ppm SO_2, 70% CO_2
Oxygen in all cases > 5%

Compostilla



• The initial rate of sulfation is similar whichever is the particle diameter and the number of cycle N, so:

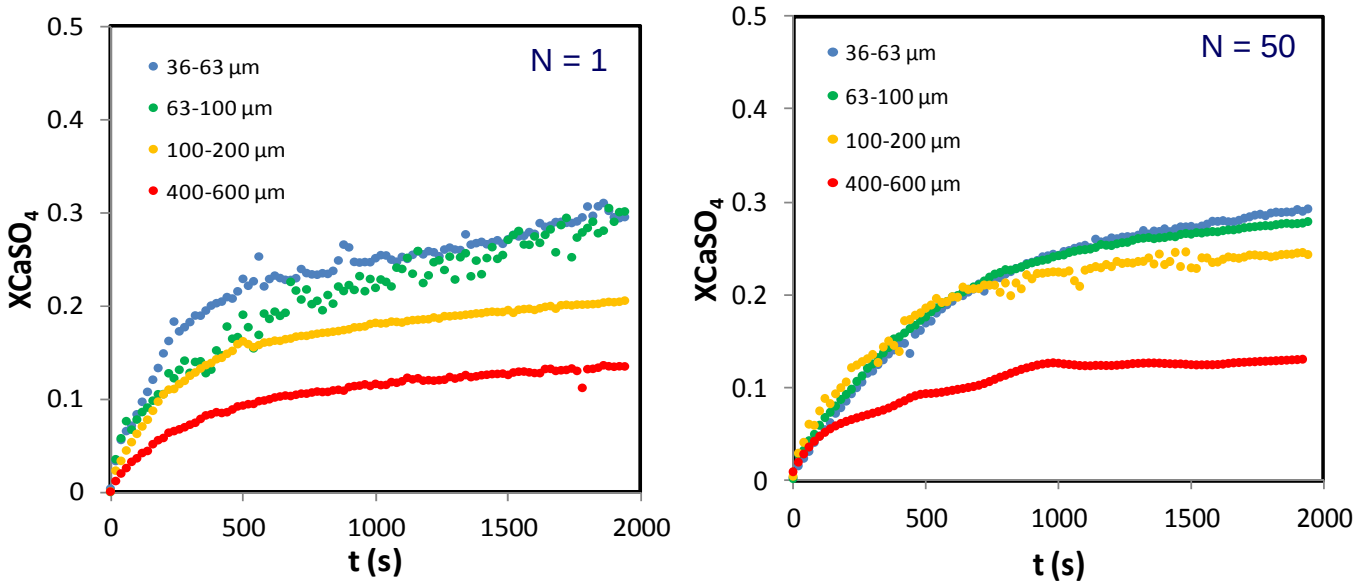
The sulfation pattern is pseudo-homogeneous from the beginning



Sulfation in the Oxy-CFB calciner: effect of the particle size

T = 930 ºC
dp = 63-100 µm
Gas phase = 500 ppm SO_2, 70% CO_2
Oxygen in all cases > 5%

Enguera



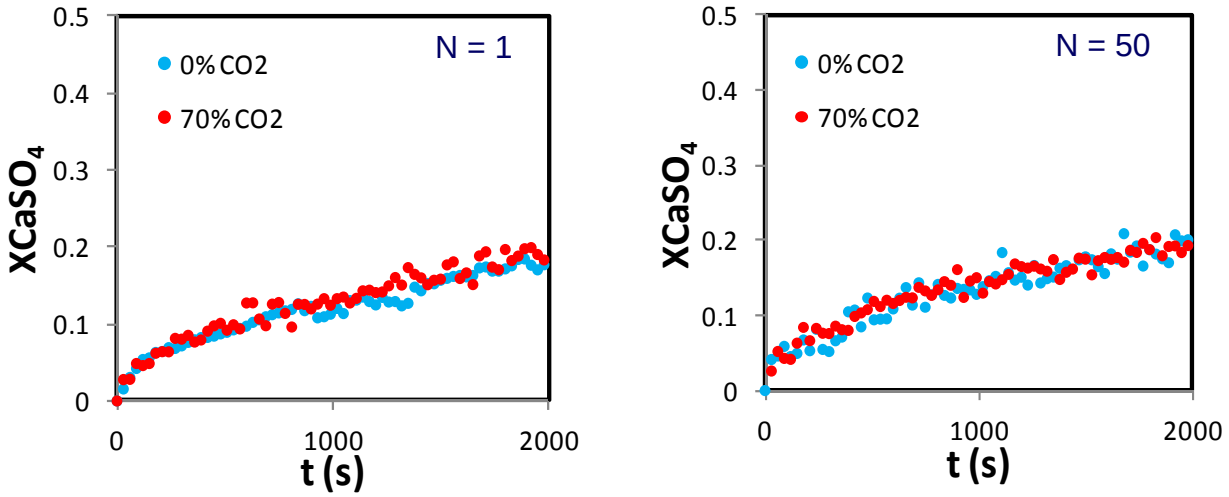
- The sulfation rate depends on the particle size, but:
- The three smaller particle sizes studied behavior is almost homogeneous for cycle 50 (initial slope).
- The larger particle size is always non homogeneous, on the contrary that occurred for Compostilla limestone.

Sulfation in the Oxy-CFB calciner: effect of the CO_2

T = 930 ºC
dp = 63-100 µm
Gas phase = 500 ppm SO_2, 70% CO_2
Oxygen in all cases > 5%

Comparison of the conversion curves under CO_2 atmosphere with those without CO_2

Compostilla

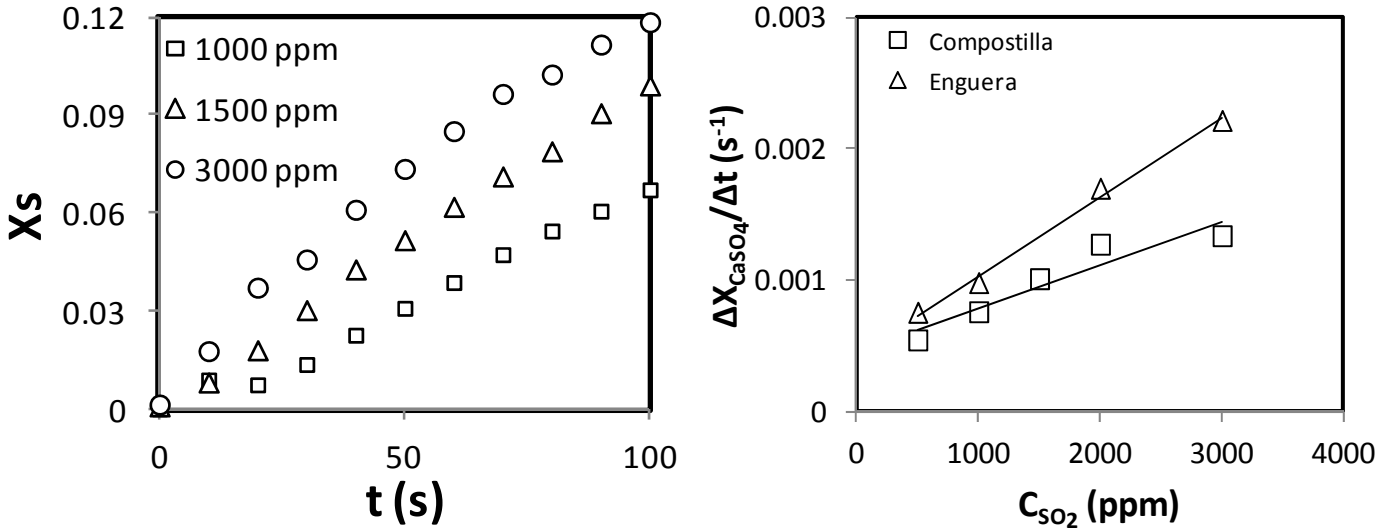


- Regardless of the limestone, CO_2 did not show important influence over the initial sulfation rate.
- The times and temperatures of exposition to sinterization are insignificant compared to the sulfation rate, so its effect is despicable.

Sulfation in the Oxy-CFB calciner: effect of the SO_2 concentration

T = 930 ºC
dp = 63-100 µm
Gas phase = 500 ppm SO_2, 70% CO_2
Oxygen in all cases > 5%

Enguera N = 50

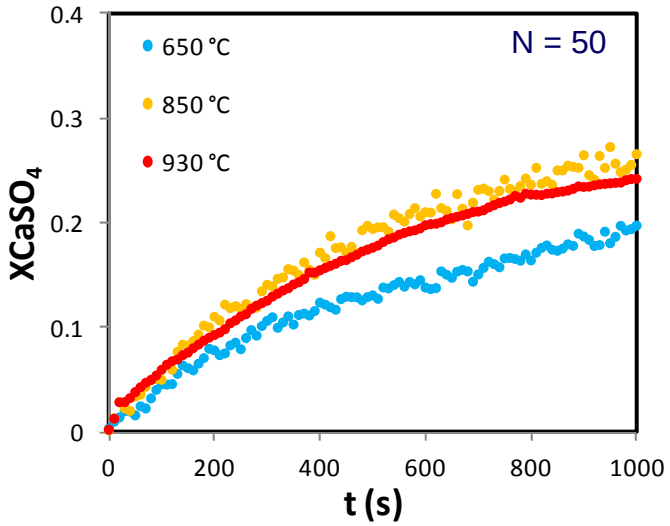


• The sulfation rate increases with SO_2 concentration in gas phase, as was expected, following an apparent first order.

SO_2 capture in CaL post-combustion technologies

T = 650, 850, 930 ºC
dp = 63-100 µm
SO2 concentration = 500 ppm SO_2 (balance in air)
Oxygen in all cases > 5%

Conversion to $CaSO_4$ curves for Enguera limestone.

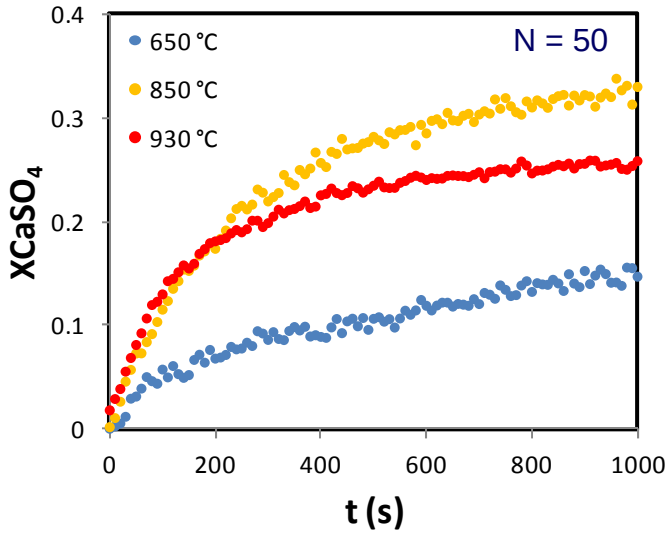


- At the view of the graphs, it appears that a change of mechanism is produced some point between 850-930 ºC. Supporting this:
- The conversion curve for 930 ºC is below the expected considering the others at lower temperature.
- The final conversion of the interval shows a maximum at 850 ºC.
- There is a number of explanations,
- Blockage of small pores due to improved kinetics (difficult → N = 50)
- Sintering at higher temperatures (short times)
- Change in sulfation mechanism
- Others

SO_2 capture in CaL post-combustion technologies

T = 650, 850, 930 ºC
dp = 63-100 µm
SO2 concentration = 2000 ppm SO_2 (balance in air)
Oxygen in all cases > 5%

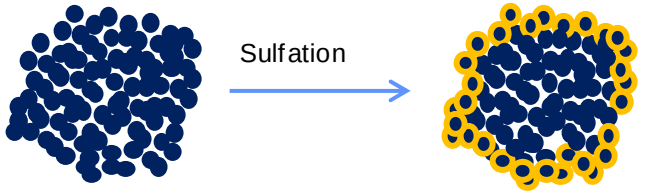
Conversion to $CaSO_4$ curves for Compostilla limestone.

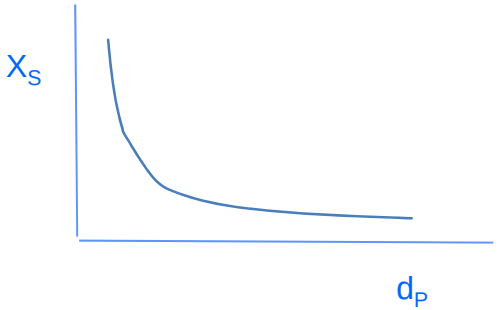


- For Compostilla limestone, the result was the same.

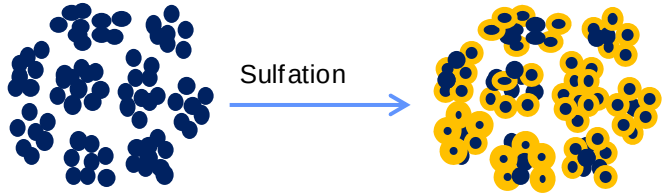
Sulfation patterns

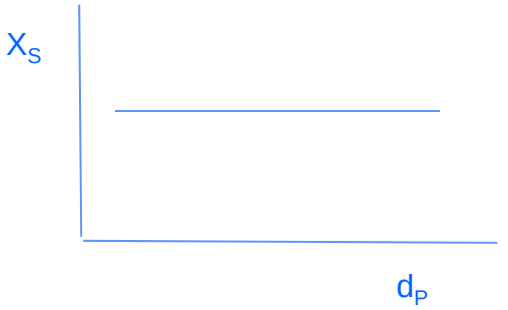
Non Homogeneous
(Unreacted Core)



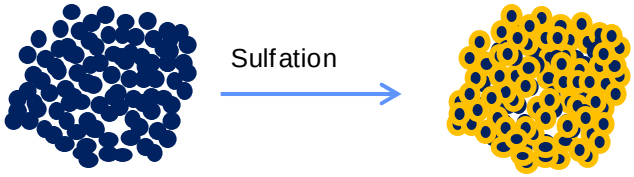


Pseudo-
Homogeneous
(Network)





Homogeneous



Unreacted Core: Grains separated by micropores. Only reacts the external surface area.

Network: Grains gathered together, only reacts the external surface area of this groups, remaining slightly or unsulfated their core.

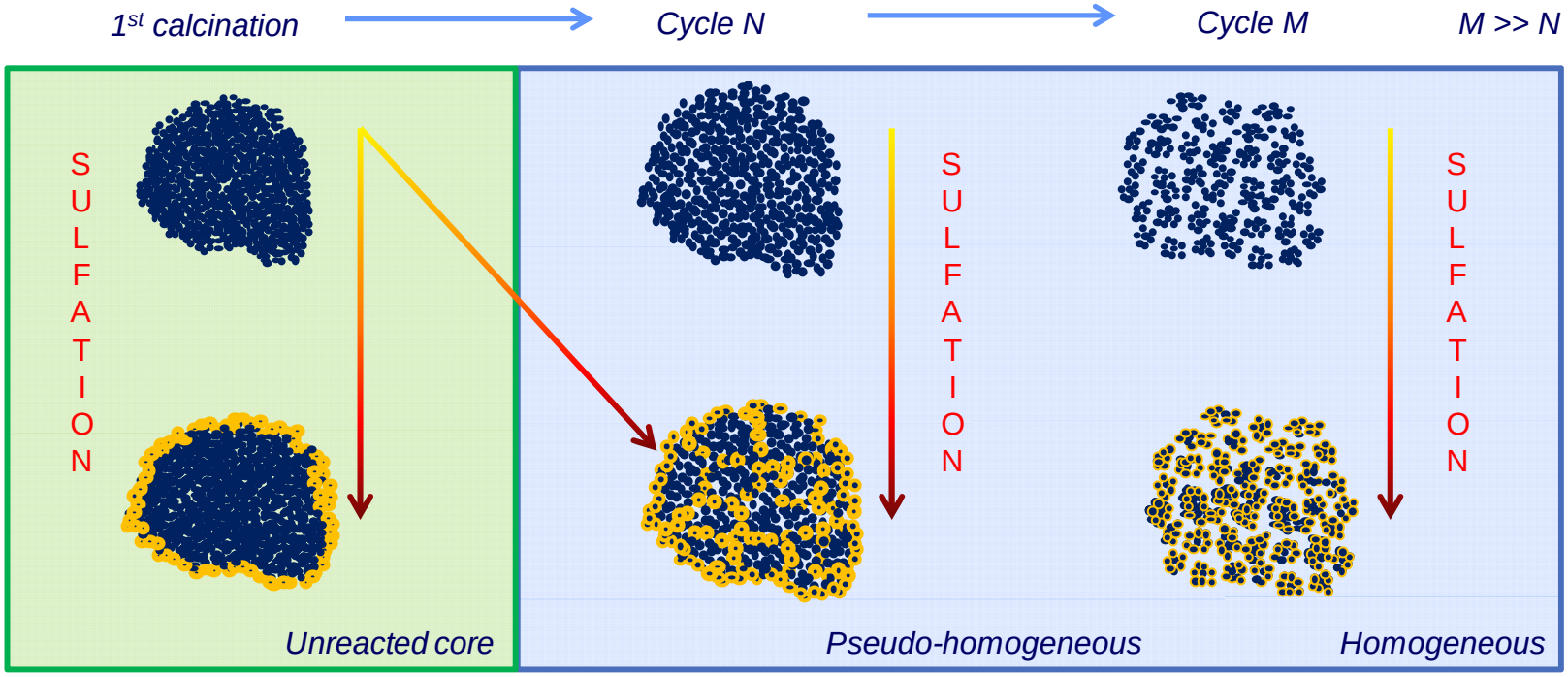
Homogeneous: The surface area of the particle reacts homogeneusly, independently of the radius position.

Sulfation patterns in CaL systems

Conditions of reaction
Operating conditions

Properties of the sorbent
Type of limestone
d_P

Modifications of the internal structure
Conversion (time of reaction)
N (normally N↑ , d_{pore}↑ and S↓)



Characteristic of some limestones, specially with low N , high particle size and reaction conditions typical of CFBCs and CFB calciners.

Common for all types of CaL particles with high N and dp below 200 µm, in all reactors.

Future work

- To study the use of the purge of the Ca-looping cycles in a combustor to capture the SO_2 before it enters the system of CO_2 capture. This means studying the sulfation reaction under the conditions that exist typically in combustors.

- To study the sulfation behavior of samples of sorbents from La Pereda power plant.

- To study the competence between carbonation and sulfation reactions carried at the same time: co-capture.

Conclusions

•The apparent order of reaction was one for sulfation reaction at carbonating and calcining conditions in the Ca-looping CO_2 capture systems.

• The CO_2 concentration did not affect the initial sulfation rates.

• The number of cycle, N, affects the pattern of sulfation, becoming it more homogeneous with higher N. Spent enough CaL sorbents will sulfate homogeneously in both carbonator, CFBC and calciner. For low values of N and moderate to high particle sizes, the pattern usually is unreacted core type for many limestones.

• The reactor that achieved a better conversion to $CaSO_4$ was the CFBC.

• The results indicate that the post-combustion Ca-looping carbonators and calciners would be effective reactors for capturing SO_2 from flue gases.

Acknowledgements

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• J.M.C. acknowledges a predoctoral research from FICYT.

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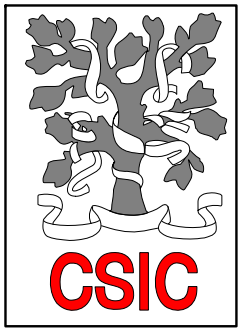

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CSIC-INCAR
jmacod@incar.csic.es

THANKS FOR YOUR ATTENTION

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