Istituto di Ricerche sulla Combustione

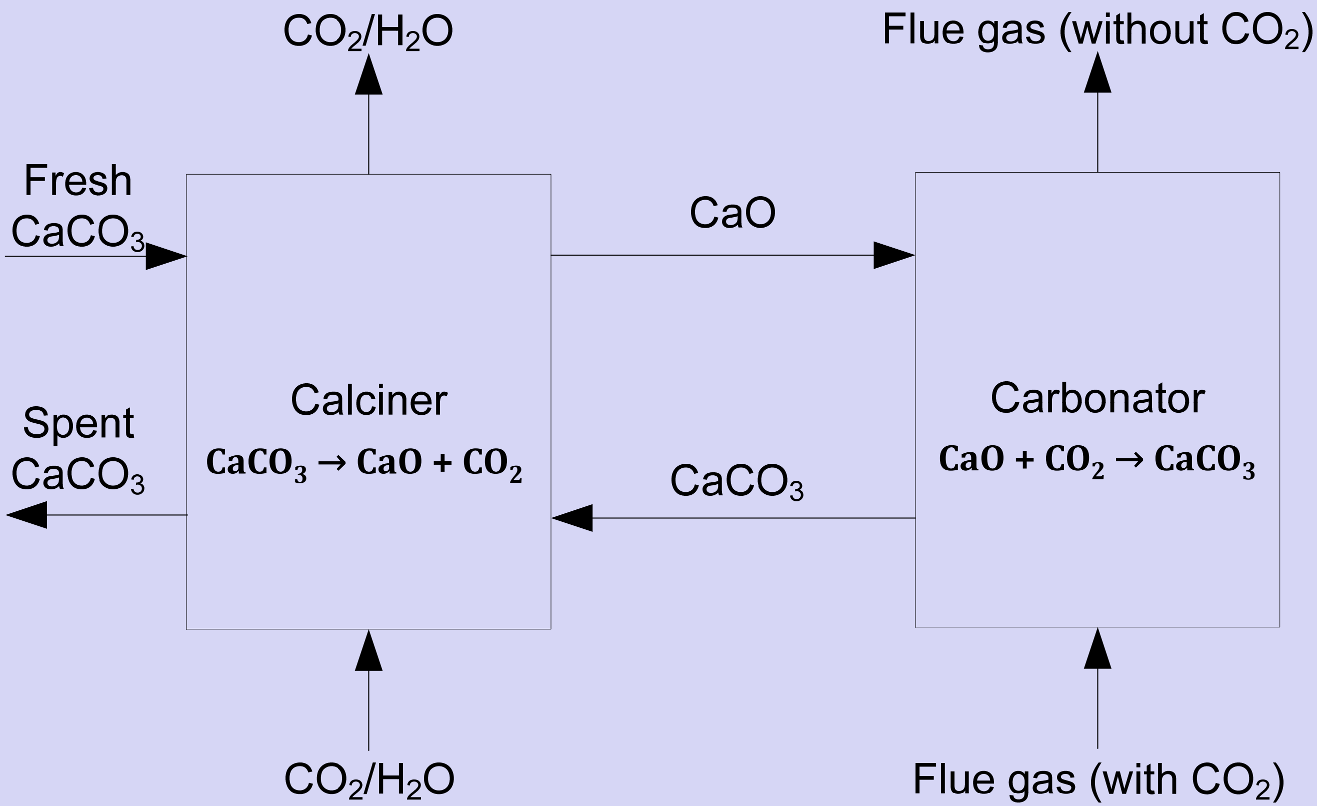
Università degli Studi di Napoli Federico II

The effect of an oxyfiring environment on the calcination stage of a Ca-looping process

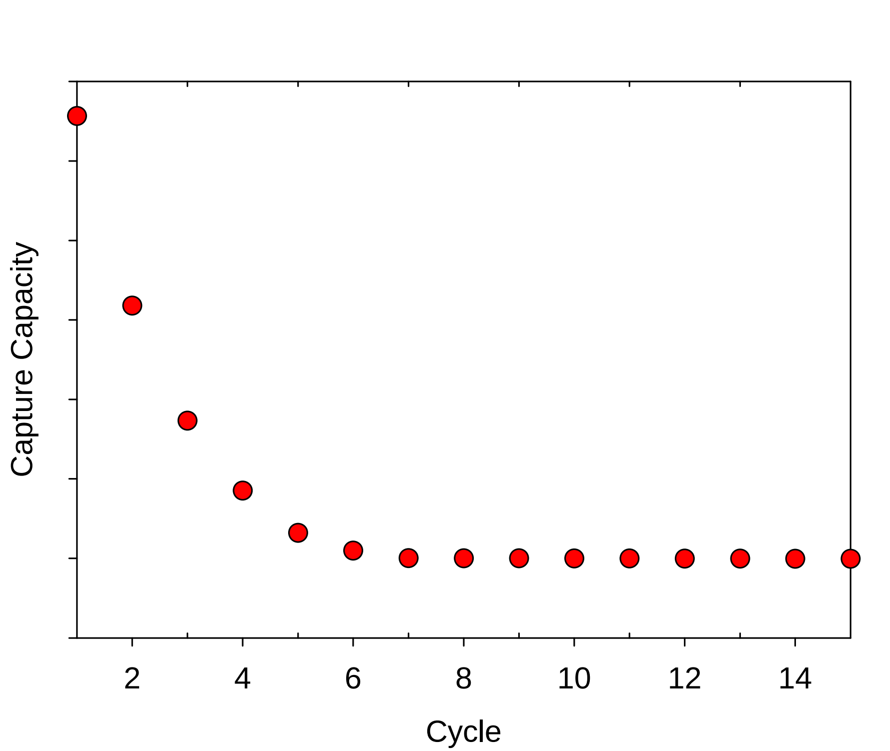
Antonio Coppola, Fabio Montagnaro, Piero Salatino and Fabrizio Scala

This work has been carried out in the framework of the European Commission – Research Fund for Coal and Steel Contract no. RFCR-CT-2010-00013 (CAL-MOD)

Calcium-Looping is a post-combustion technology which uses lime to capture carbon dioxide from flue gas



Calcium-Looping: Main Issues



Decay of CO_2 Capture Capacity of the sorbent:

- **Sintering**
- **Presence of SO_2 in the flue gas**

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4$$

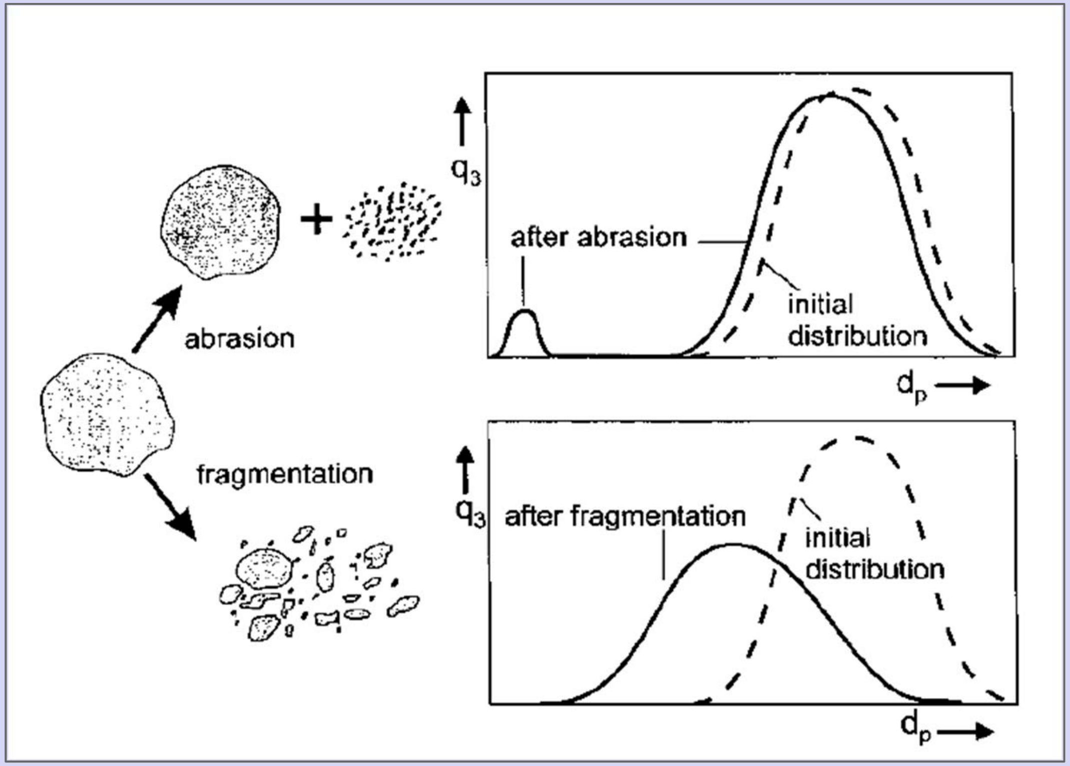
Calcium-Looping: Main Issues

Attrition/Fragmentation Phenomena

➢ Primary Fragmentation

➢ Secondary Fragmentation

➢ Attrition by Abrasion



Operating conditions in the calciner under oxy-firing conditions:

- ✓ High CO_2 concentration (> 70%)
- ✓ High temperature (> 900°C)
- ✓ Presence of SO_2 (from coal combustion)

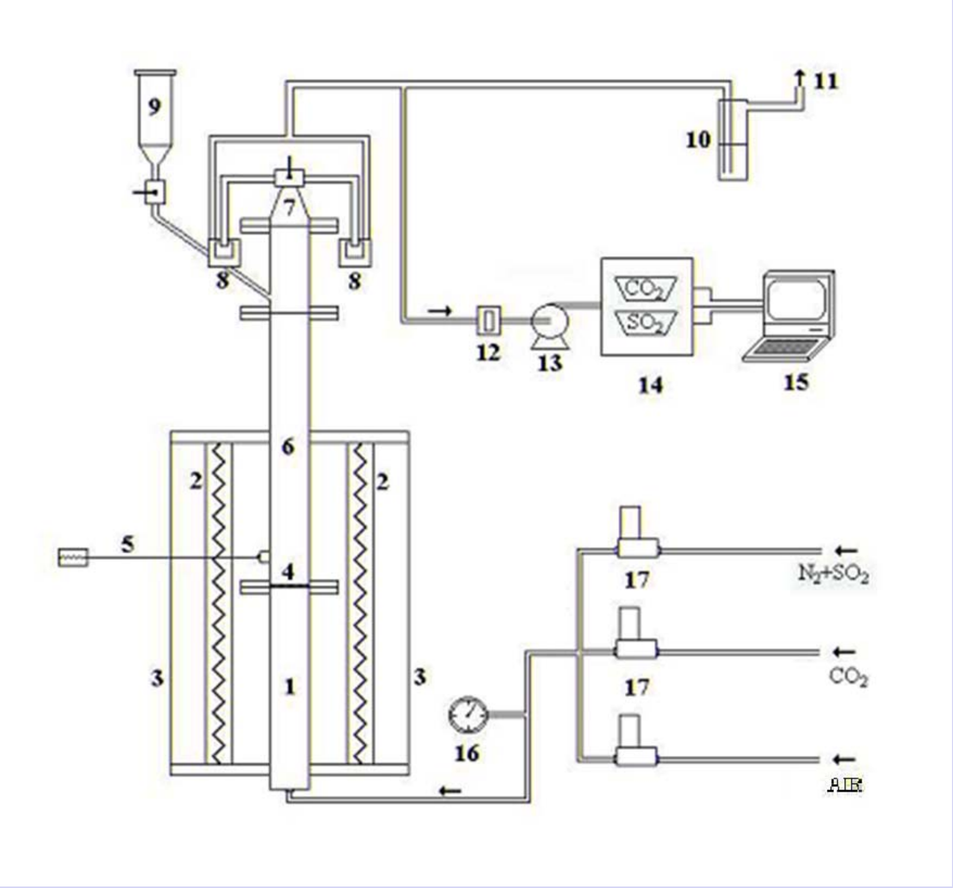
What is the effect of these conditions on CO_2 capture capacity and sorbent attrition?

Sorbents

Sample	Origin	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	TiO_2	LOI	Sum
Massicci	Italy	1.11	0.37	0.14	54.53	0.44	0.06	0.02	0.00	0.02	43.13	99.81
Schwabian Alb	Germany	3.51	0.50	0.18	53.64	0.51	0.08	0.02	0.00	0.02	41.94	100.39
EnBW	Germany	0.30	0.13	0.08	56.01	0.26	0.00	0.02	0.00	0.01	43.50	100.31
Xirorema Sand	Greece	0.83	0.26	0.36	55.13	0.56	0.00	0.01	0.00	0.02	42.87	99.22
Tarnow Opolski	Poland	1.73	0.34	0.39	54.04	0.94	0.00	0.02	0.00	0.02	42.64	100.11
Czatkowice	Poland	3.91	0.39	0.31	52.88	0.99	0.00	0.02	0.00	0.03	41.43	99.96

Limestone particle size = 0.4-0.6 mm

Experimental apparatus



40 mm ID

(1) gas preheating/premixing section;
(2) electrical furnaces;
(3) ceramic insulator;
(4) gas distributor;
(5) thermocouple;
(6) fluidization column;
(7) two-exit head;
(8) sintered brass filters;
(9) hopper;
(10) SO2 scrubber;
(11) stack;
(12) cellulose filter;
(13) membrane pump;
(14) gas analyzers;
(15) personal computer;
(16) manometer;
(17) mass flow meter/controller.

Effect of temperature and CO_2 in the calciner

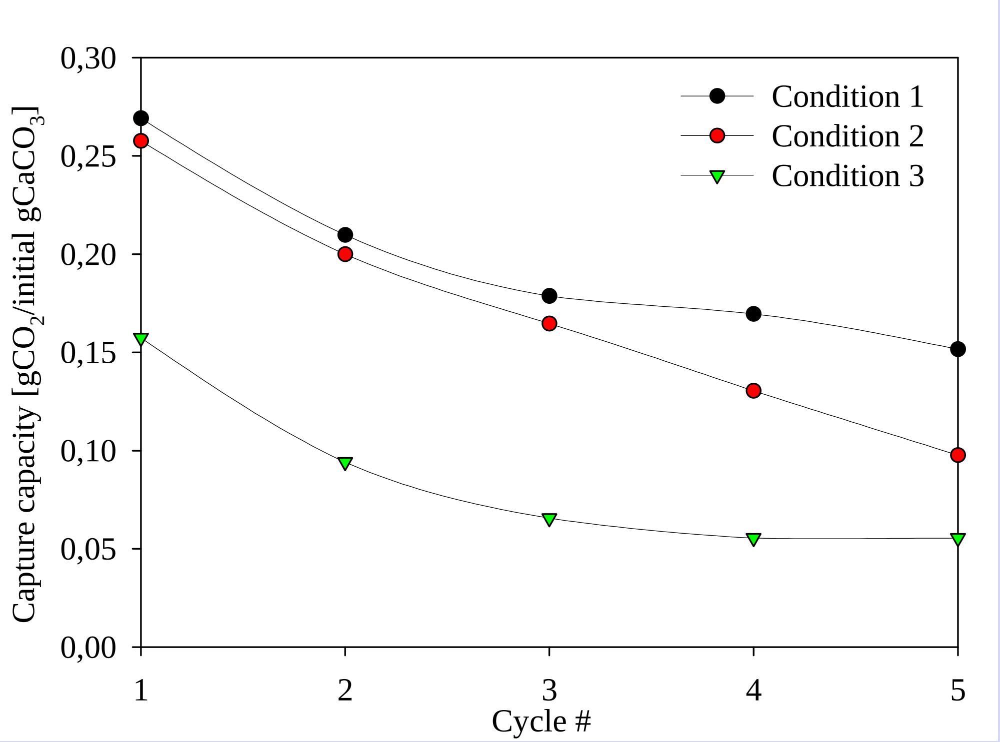
✓ Attrition of an Italian limestone during calcium looping cycles for CO_2 capture was studied in a lab-scale FB apparatus.

✓ Batch experiments under alternating calcination-carbonation conditions (5 cycles) were carried out.

✓ Attrition processes were characterized by following the modifications of bed sorbent PSD and the elutriation rates of fines throughout conversion over repeated cycles.

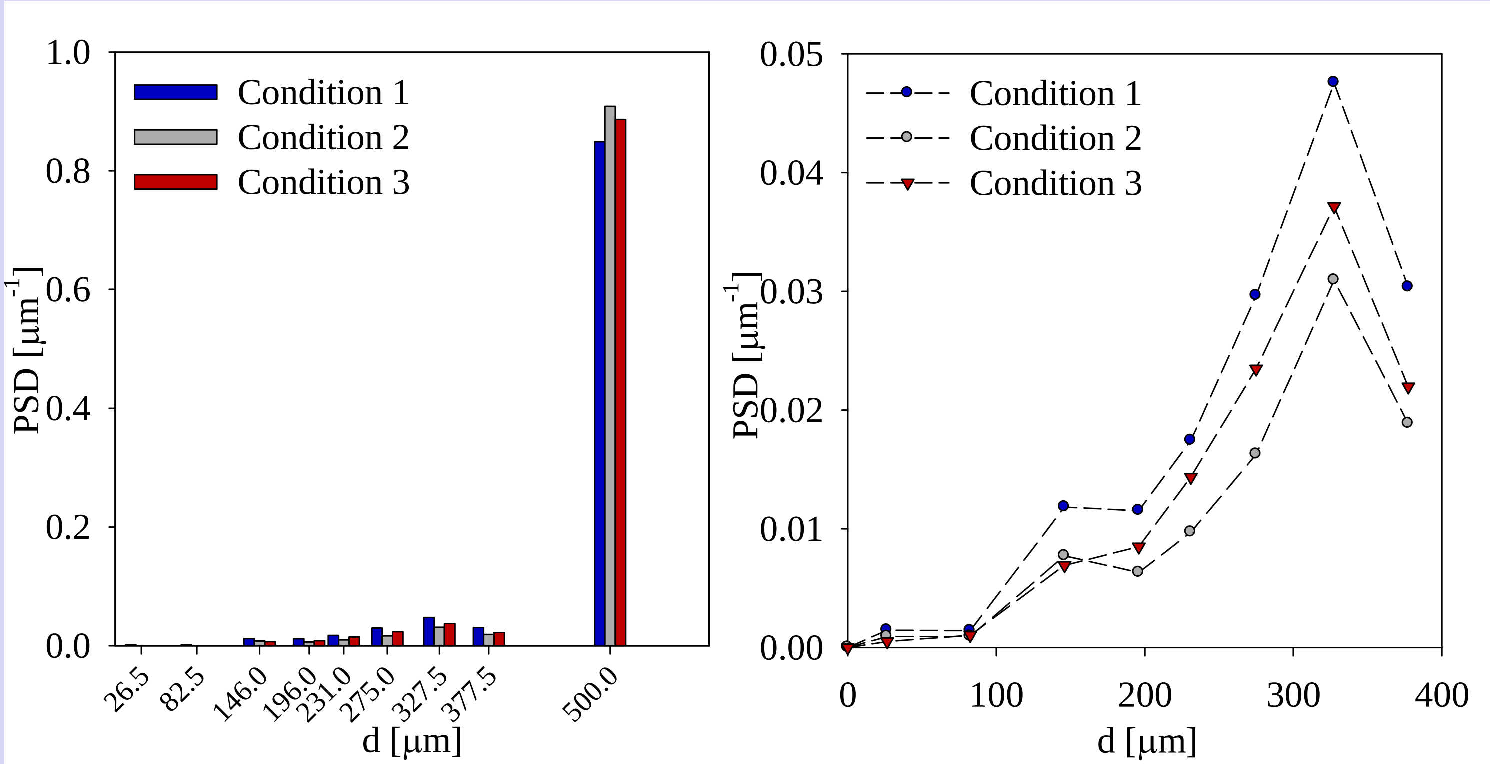
Calcination/Carbonation	Condition 1	Condition 2	Condition 3
Duration [min]	15/15	35/15	20/15
Temperature [C]	850/700	850/700	900/700
Inlet CO_2 [%v/v] (balance air)	0/16	20/16	44/16

Results: CO_2 capture capacity



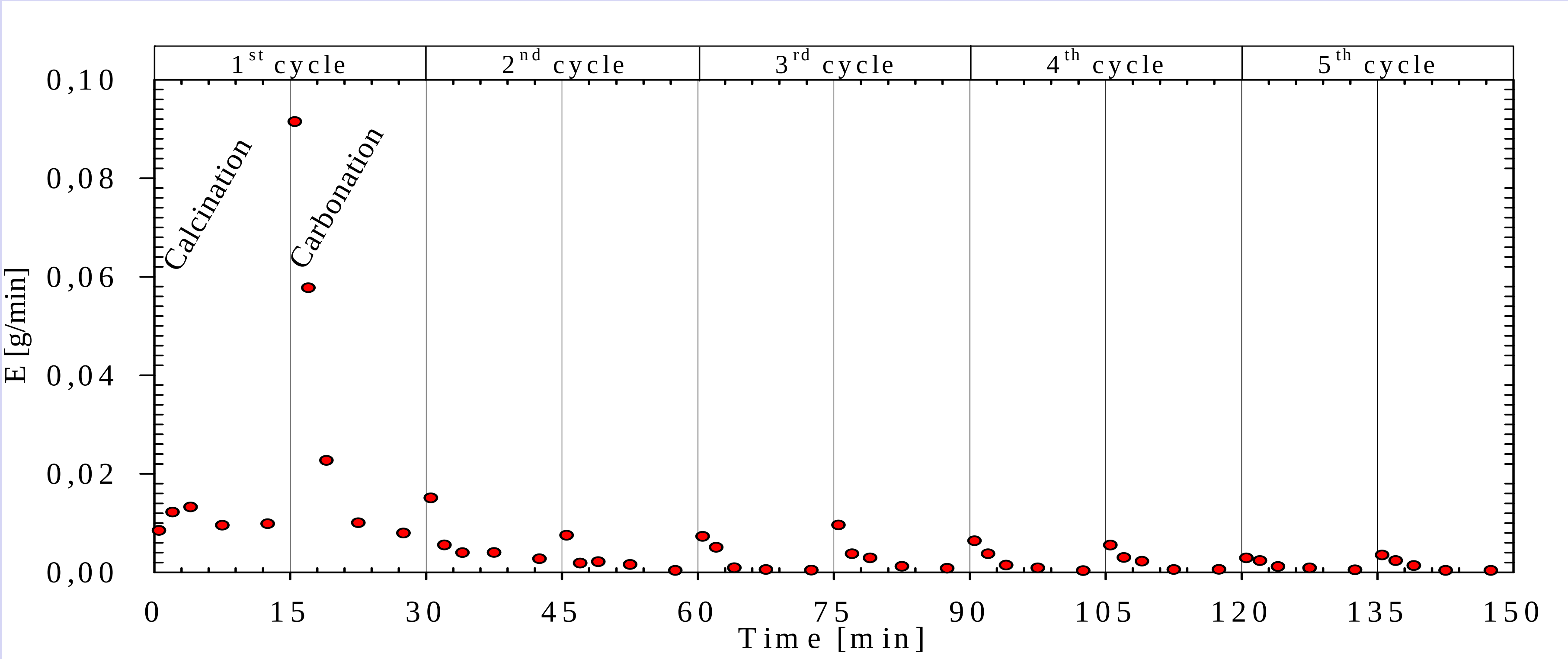
- **Highest capacity: Condition 1 (calcination in air);**
- **Slightly lower capacity: Condition 2 (calcination in CO_2);**
- **Lowest capacity: Condition 3 (calcination in CO_2 at higher temperature – 900°C).**

Results: PSD changes after 5th cycle

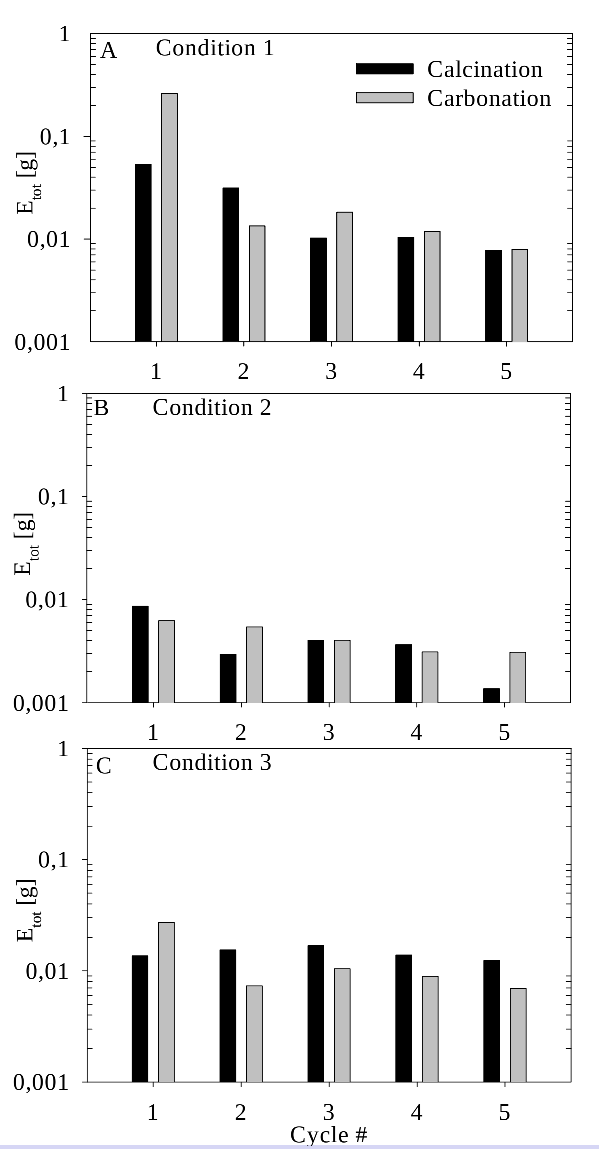


- **Tests carried out under the three experimental conditions showed the same qualitative trend.**

Results: Elutriation rate in Condition 1



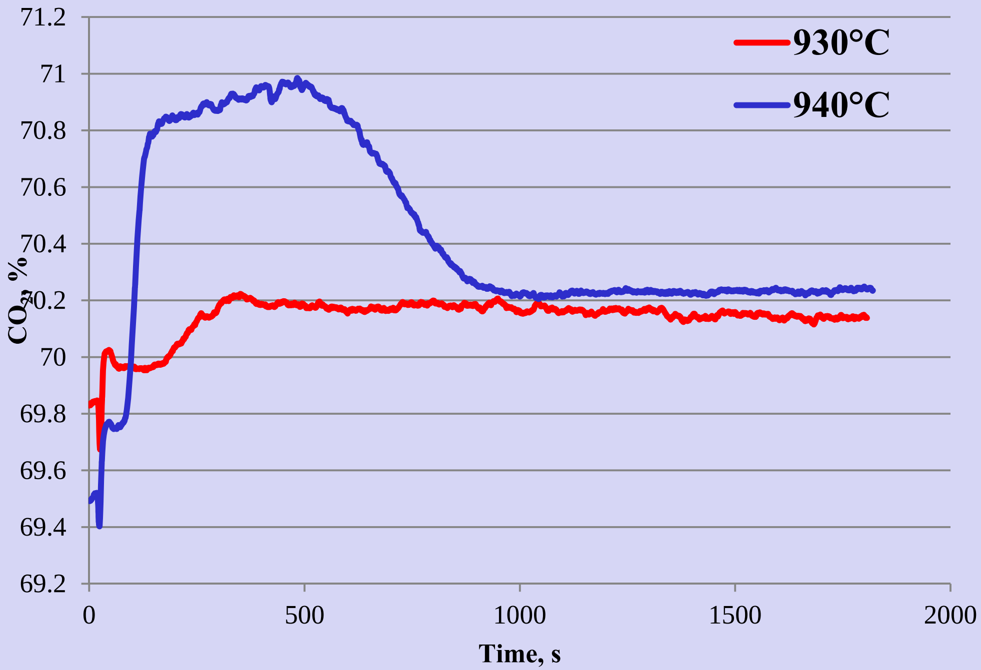
- **Fines elutriation rate decreases with the number of cycles;**
- **In each cycle the elutriation rate shows an initial peak, caused by a combination of rounding off, thermal shock and rapid release of CO_2 (only during calcination).**

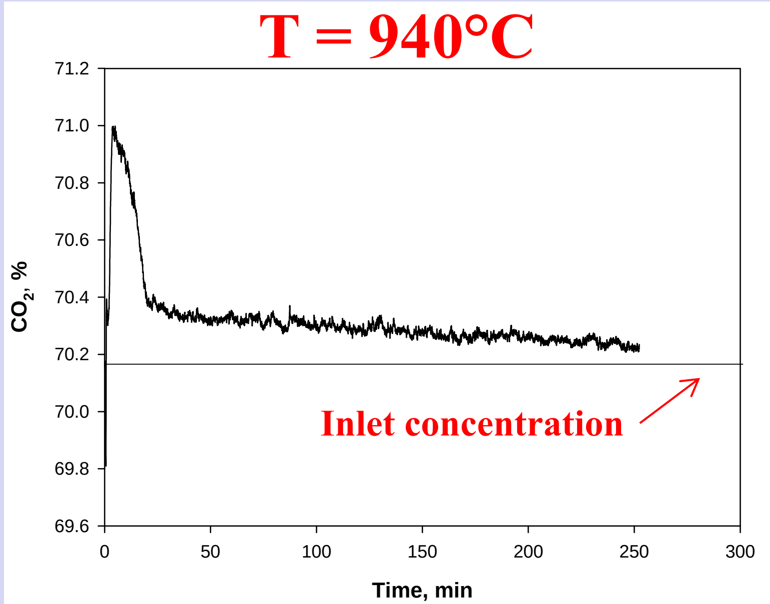


Results: Total amount of elutriated fines

- The largest amount of fines was obtained in the tests carried out in Condition 1;
- Fines generation was much smaller under Condition 2 (20% CO_2 during calcination);
- When the calcination temperature was increased at 900°C (Condition 3), a larger amount of fines was collected.

Calcination at high CO_2 concentration: explorative tests (Massicci limestone)





CO_2 = 70%

Tests under high temperature and CO_2 in the calciner

- ✓ Five calcination/carbonation cycles were carried out under all experimental conditions;
- ✓ An initial amount of 20 g of fresh limestone, sieved in the range 0.4-0.6 mm was fed to a bed consisting of 150 g of silica sand in the range 0.85-1.0 mm;
- ✓ The fluidizing velocities were 0.7 and 0.6 m/s in the calcination and in the carbonation stages, respectively;
- ✓ The progress of calcination/carbonation was followed by measuring the CO_2 concentration at the exhaust;
- ✓ The duration of each stage was such that calcination/carbonation was complete;
- ✓ After each step the bed was discharged, the limestone was separated from the sand by sieving, and its PSD was measured;
- ✓ During the runs the rate of fines generation was determined by measuring the amount of fines elutriated from the reactor by means of the brass filters.

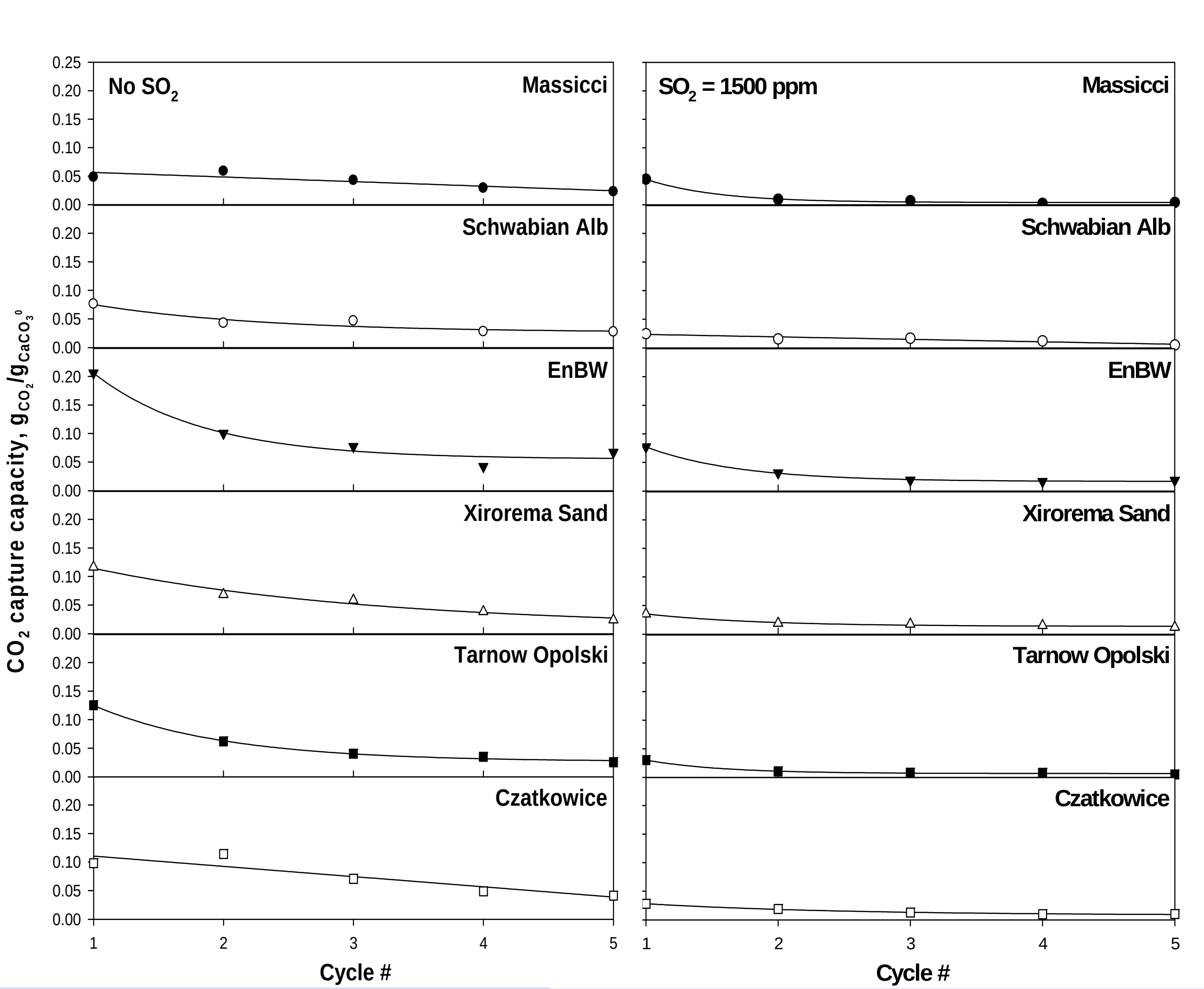
Experimental conditions

Calcination/Carbonation	Without SO_2	With SO_2
Duration [min]	20/15	20/15
Temperature [°C]	940/650	940/650
Inlet CO_2 [%v/v]	70/15	70/15
Inlet SO_2 [ppmv]	0/0	1500/1500

Materials: Limestones

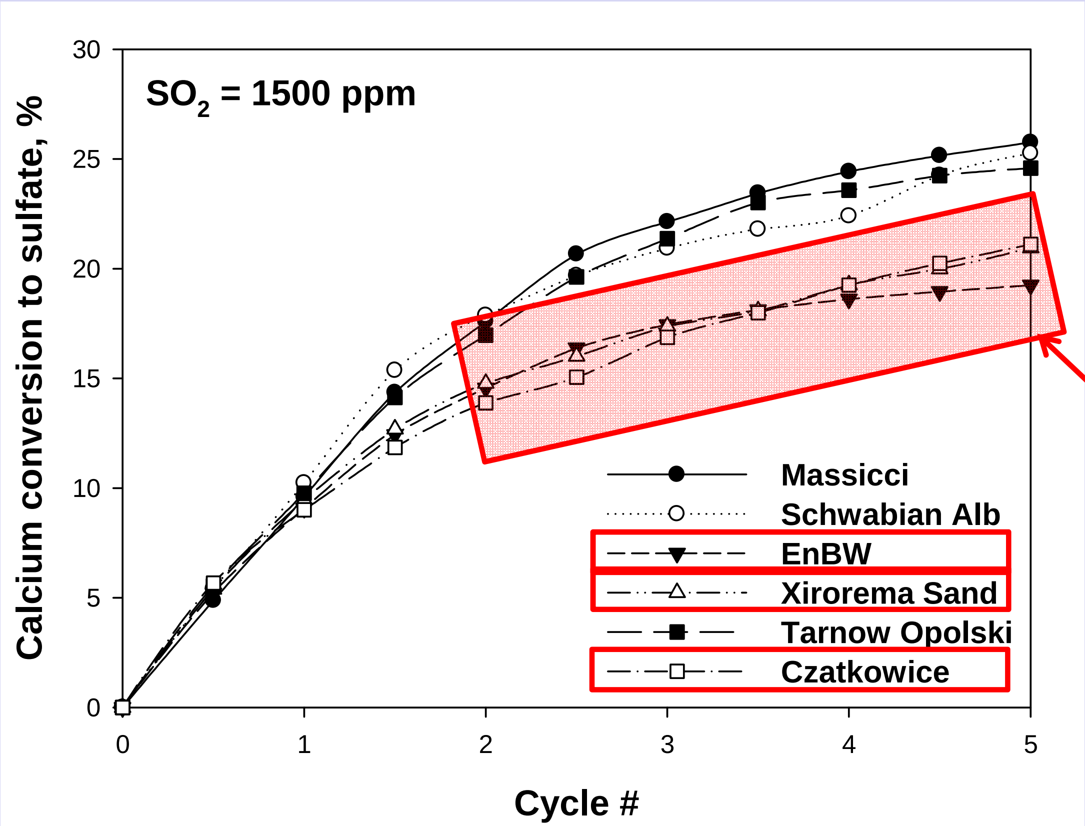
Sample	Origin
Massicci	Italy
Schwabian Alb	Germany
EnBW	Germany
Xirorema Sand	Greece
Tarnow Opolski	Poland
Czatkowice	Poland

Results: CO_2 Capture Capacity - CC



- Typical decay for all limestones (with and without SO_2);
- The residual CC - without SO_2 - is 0.02-0.07 $gCO_2/gCaCO_3°$ - lower values then Blamey et al. (2010) (0.1-0.2 $gCO_2/gCaCO_3°$) ;
- Higher decay of CC with SO_2 (0.004-0.07 $gCO_2/gCaCO_3°$);
- The presence of SO_2 does not alter the relative ranking of the six limestones:
  1. EnBW;
  2. Xirorema Sand;
  3. Czatkowice;
  4. Tarnow Opolski;
  5. Schwabian Alb;
  6. Massicci:

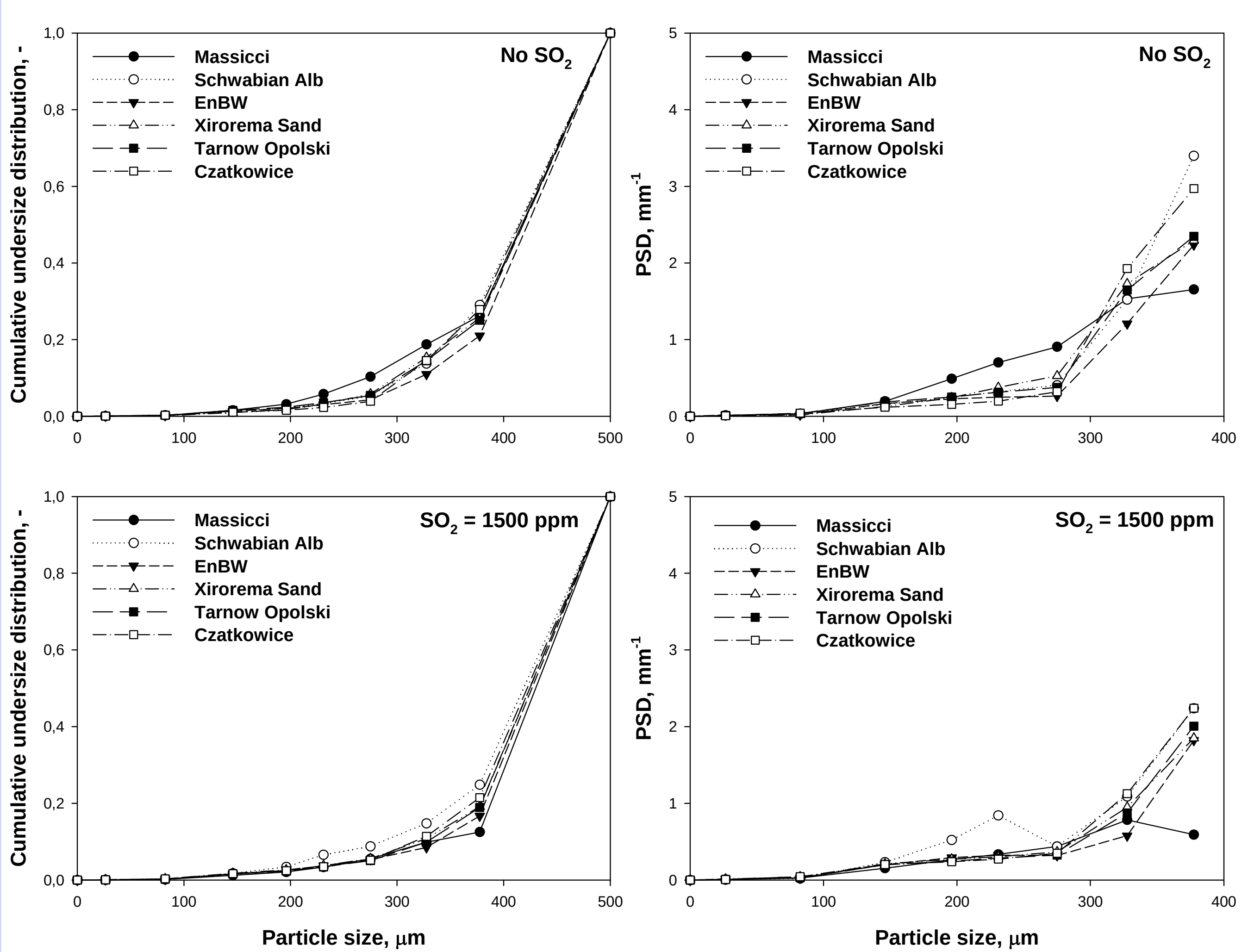
Results: Ca conversion to sulfate



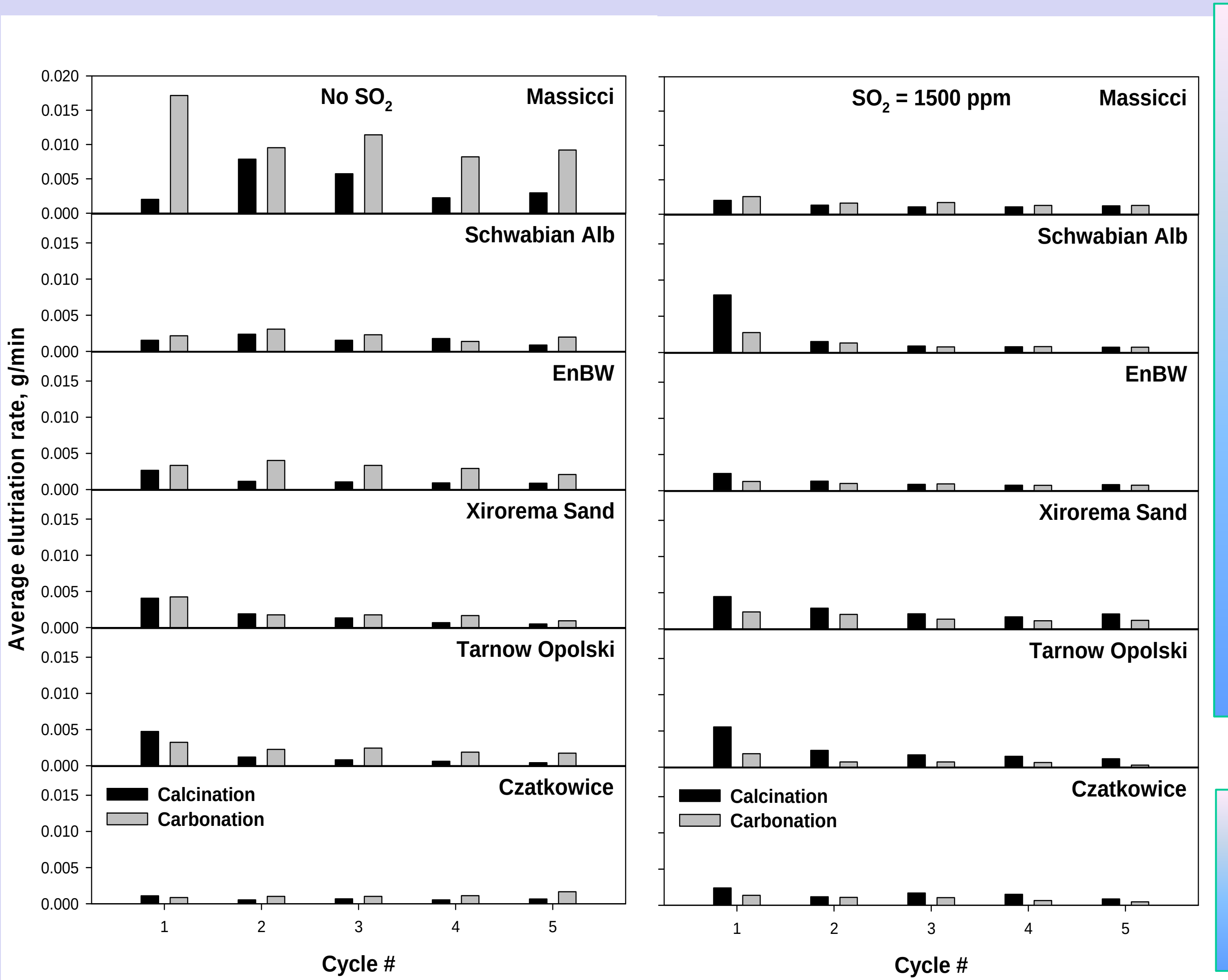
- Typical decay for all limestones (with and without SO_2);
- The residual CC - without SO_2 - is 0.02-0.07 $gCO_2/gCaCO_3°$ - lower values then Blamey et al. (2010) (0.1-0.2 $gCO_2/gCaCO_3°$) ;
- Higher decay of CC with SO_2 (0.004-0.07 $gCO_2/gCaCO_3°$);
- The presence of SO_2 does not alter the relative ranking of the six limestones:
  1. **EnBW;**
  2. **Xirorema Sand;**
  3. **Czatkowice;**
  4. Tarnow Opolski;
  5. Schwabian Alb;
  6. Massicci:

Results: Particle Size Distribution - PSD

- Similar shape for all limestones;
- Slight differences in the amount of the produced fragments;
- The presence of SO_2 appears to reduce the extent of fragmentation.
- Ranking:
    1. EnBW;
    2. Massicci;
    3. Tarnow Opolski;
    4. Xirorema Sand;
    5. Czatkowice;
    6. Schwabian Alb.



Results: Total amount of elutriated fines



In general, the amount of elutriated fines:

- decreases with the number of cycles;
- is approximately the same during tha calcination and the carbonation stage – Scala et al. 1997;
- is slightly lower when SO_2 is present.
- Ranking:
  1. Czatkowice;
  2. EnbW;
  3. Tarnow Opolski;
  4. Schwabian Alb;
  5. Xirorema Sand;
  6. Massicci

The estimated limestone loss rate is **0.3-0.5 %/h** - Charitos and coworkers (2010) found a value of 2%/h

Conclusions

- Results showed that the CO_2 capture capacity decreased with the cycles. The presence of a high CO_2 concentration during calcination (70%) and a high calcination temperature (940°C) determined a significant decrease of the sorbent capacity for all the cycles, most likely due to the enhancement of particle sintering.
- The analysis of the PSD of bed material over repeated calcination/carbonation cycles indicated that particle fragmentation was limited for all the limestones.
- The fines elutriation rate was relatively large only during the first cycle and decreased with the number of cycles, since the combined chemical-thermal treatment affected the particle structure making it increasingly hard.
- The presence of SO_2 had a detrimental effect on the CO_2 capture capacity of all limestones, while attrition was only slightly affected by the presence of SO_2.
- The residual CO_2 capture capacity after the first few cycles is of the order of 0.05 and 0.01 g_{CO2}/g_{CaCO3} without and with the presence of SO_2, respectively.
- The average limestone loss rate by elutriation can be estimated to be of the order of 0.5%/h under realistic conditions, and should not represent a process limitation.
- The overall ranking of the six limestones tested in this work (combining the capture capacity and attrition performance) was, from the best to the worst: EnBW, Czatkowice, Xirorema Sand, Tarnow Opolski, Schwabian Alb and Massicci.