Use of activated carbon in the synthesis of highly active and stable sol-gel CaO sorbents for CO_2 capture

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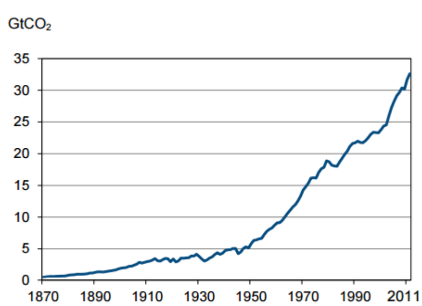
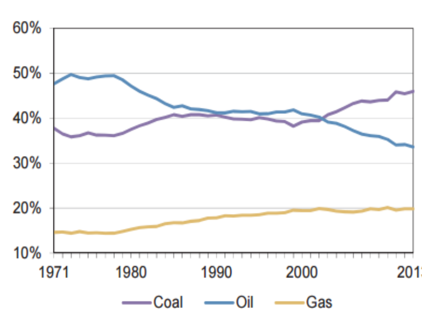
Motivation

Trend in CO_2 emissions from fossil fuel combustion:



Fuel shares in global CO_2 emissions:



Source: IEA, CO_2 EMISSIONS FROM FUEL COMBUSTION Highlights, 2015.

Carbon Capture Technologies

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Options to reduce CO_2 Emissions:

- **Reducing energy intensity** – Requires efficient use of energy.

- **Reducing carbon intensity** – Use of carbon-free fuel, requires switching to using non-fossil fuels such as hydrogen and renewable energy.

- **Enhancing the capture of CO_2** – Development of technologies to capture and storage of CO_2.

http://www.rsc.org/

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Carbon Capture Technologies

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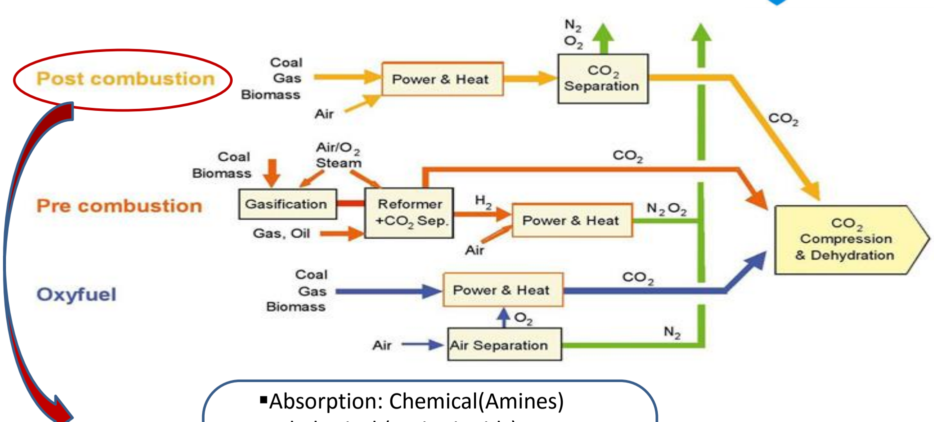

- Absorption: Chemical(Amines) and Physical (Ionic Liquids)
- Cryogenic distillation
- Membranes
- Adsorption
- Biofixation of microalgae
- **Ca looping technology**

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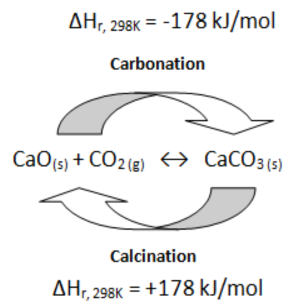
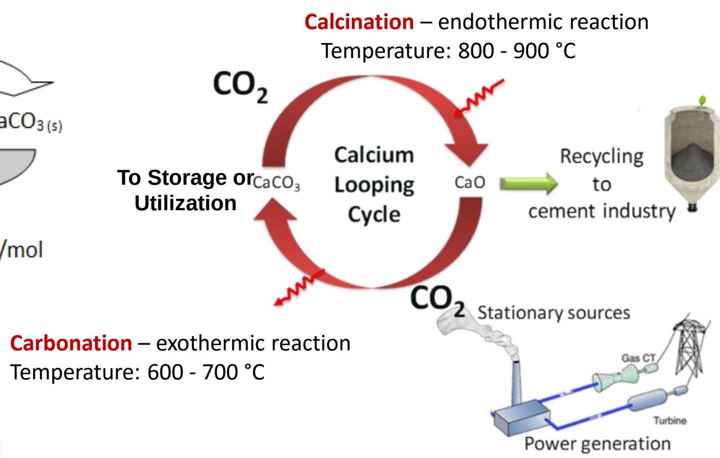
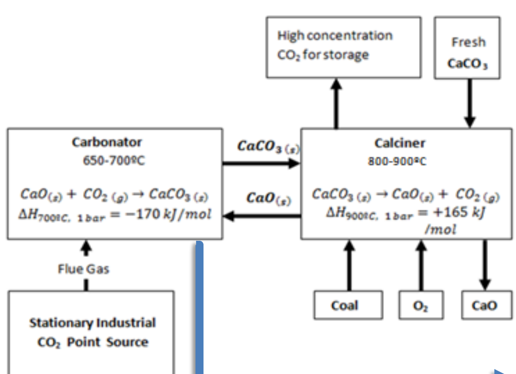
Post-Combustion Calcium Looping Technology

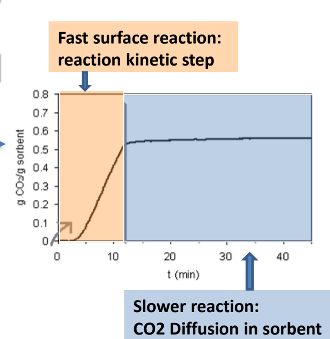
Reversible Reaction: carbonation-calcination





Post-Combustion Calcium Looping Technology





Post-Combustion Calcium Looping Cycle

Advantages

- Initial high and fast uptake of CO_2 from flue gas
- Use of cheap and nontoxic sorbents (lime or other Ca-based)
- Purge of CaO: synergies with cement industry
- Pre-treatment of flue gas is not needed
- High adsorption capacity for CO_2 at high temperature
- Production of a pure CO_2 stream for utilization or storage
- Lower energy penalty and operating costs than other post-combustion capture technologies.

Drawbacks

- Sorbent activity and stability lost with increasing number of carbonation/calcination cycles can be caused by:
  - sintering of CaO sorbent may occur during high-temperature calcination, causing the sorbent deactivation due to grain growth and pore shrinkage or blockage
  - ash fouling
  - competing reactions (e.g. sulfur)

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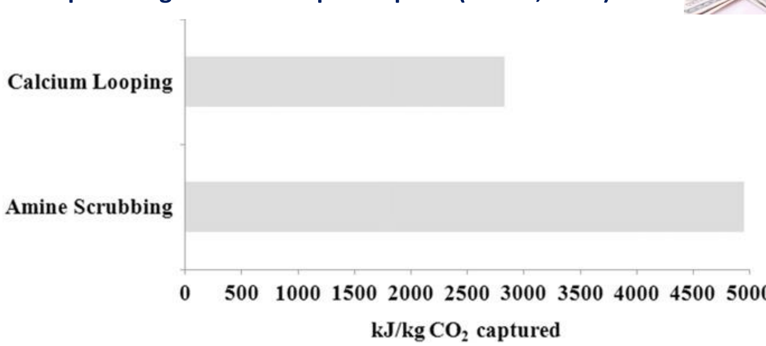
Energy Penalty

Calcium looping process currently being tested experimentally in bench- and pilot-scale plants worldwide:
promising alternative to amine scrubbing approach (efficiency penalty 8-12.5%), as it leads to the projected efficiency penalty of 6–8% upon integration to the power plant (Hanak, 2015).



Source: K. Vatopoulos, E. Tzimas, Journal of Cleaner Production, 32 (2012) 251-261

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Efficient sorbents for Ca Looping: challenges!

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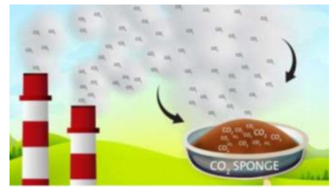

http://phys.org/partners/american-chemical-society/

- **High adsorption capacity,**
- **High selectivity,**
- **High calcium oxide content,**
- **Non deactivating cyclic operation,**
- **Good mechanical resistance to attrition,**
- **Economically viable!**

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Enhancing the capture of CO_2 by Sol-Gel CaO-based sorbents

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- **Sol-Gel Synthesis and Characterization of CaO-based Sorbents:** without and with Activated Carbon as structuring.

- **Effect of the temperature in calcination and the amount of Activated Carbon (AC) added during synthesis:** CO_2 Sorption Capacity and stability of CaO-based Sorbents.

⇩

- **High CO_2 Sorption Capacity**
- **Non deactivating along the carbonation/calcination cycles**

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Sol-Gel Synthesis

Materials:

- Citric acid monohydrate as complexation agent ($C_6H_8O_7.H_2O$)(molar ratio acid/Ca= 1:1)
- Distilled water as solvent (molar ratio H_2O/Ca= 120:1)
- Calcium nitrate tetrahydrate as calcium precursor
- Activated Carbon (Norit GAC 1240 plus)as structuring
  - 0 mg
  - 250 mg
  - 500 mg
  - •2°C/min

Wet gel Preparation

$C_6H_8O_7.H_2O$ + Distilled Water

Solution at 60°C: $Ca(NO_3)_2.4H_2O$ + Activated Carbon

Oven Drying

Oven at 130 °C- 14 hr

Without Carbon

Activated Carbon

Calcination:
750°C or 850 ° C

Without Carbon

With Carbon

Santos, E.T., Alfonsin, C., Chambel, A.J.S., Fernandes, A., Soares Dias, A.P., Pinheiro, C.I.C., Ribeiro, M.F. (2012) Investigation of a stable synthetic sol-gel CaO sorbent for CO2 capture. Fuel, 94, 624-628.

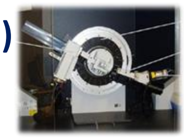
Sol-Gel Synthesized Sorbents

Calcination temperature (°C)	Heating rate in calcination (°C/min)	Amount of AC (mg/2g wet sol-gel)	Identification of fresh samples
750	2	0	SGα
		250	SGα_AC_250
		500	SGα_AC_500
850	2	0	SGβ
		250	SGβ_AC_250
		500	SGβ_AC_500

Characterization of Sol-Gel Synthesized

- **Nitrogen adsorption**

- **X-ray diffraction (XRD)**



- **Thermogravimetric analysis (TGA)**

- **Scanning electron microscopy (SEM)**

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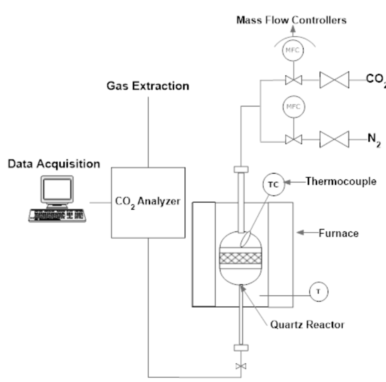
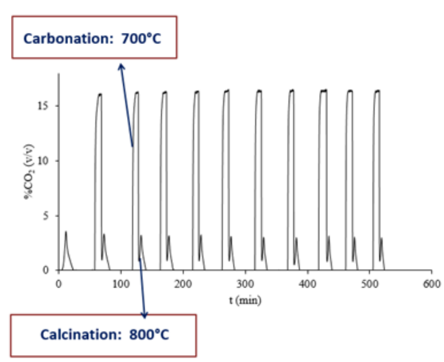
Experimental CO_2 Capture Unit



Quartz fixed bed reactor
$m_{sorbent}$ = 0.5 g

Calcination: 800°C (100% N_2 (v/v))
Carbonation: 700°C (15% CO_2 (v/v)+ 85% N_2(v/v))



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CO_2 Carrying Capacity of Sorbents

Carbonation conversion of CaO in the sorbent at cycle I (%)

$$X_i = \frac{n_{iCO_2} \times W_{CO_2}}{m_0 x_{CaO}} \times \frac{W_{CaO}}{W_{CO_2}} \times 100\%$$

X_i: carbonation conversion of CaO in the sorbent at cycle I (%)

n_{iCO_2}: amount of CO_2 absorbed by the CaO-based sorbent at cycle I (mol)

W_{CaO} : molecular weight of CaO (g/mol)

W_{CO_2} : molecular weight of CO_2 (g/mol)

m_0: sorbent sample mass (g)

x_{CaO}: CaO mass composition in the sorbent sample determined by calcination until 900 °C on the TGA (g)

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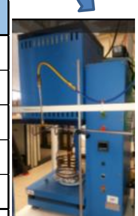
Sol-Gel Sorbents CO_2 capture tests

Calcination temperature (°C)	Heating rate in calcination (°C/min)	Amount of activated carbon (AC) (mg)	Identification of used samples
750	2	0	SG α_10 Cycles
			SG α_20 Cycles
		250	SGα_AC_250_10 Cycles
			SGα_AC_250_20 Cycles
		500	SGα_AC_500_10 Cycles
850	2	0	SGβ_10 Cycles
		250	SGβ_AC_250_10 Cycles
		500	SGβ_AC_500_10 Cycles



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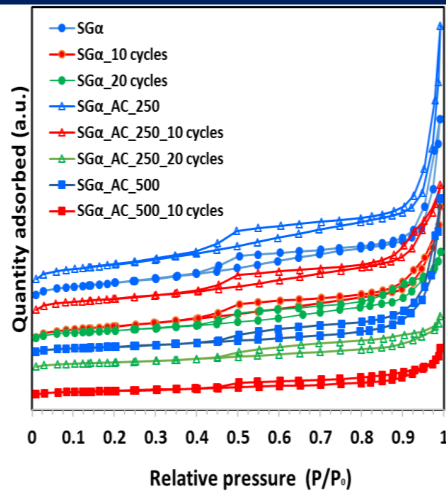
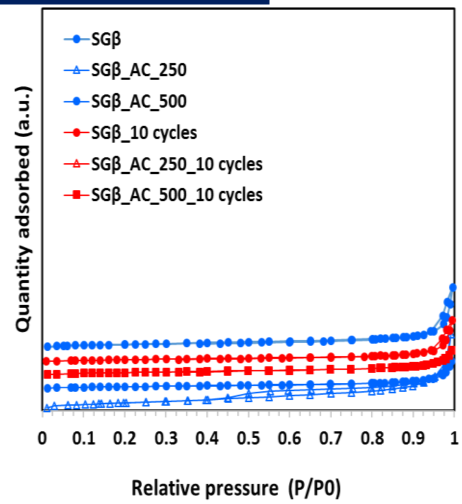
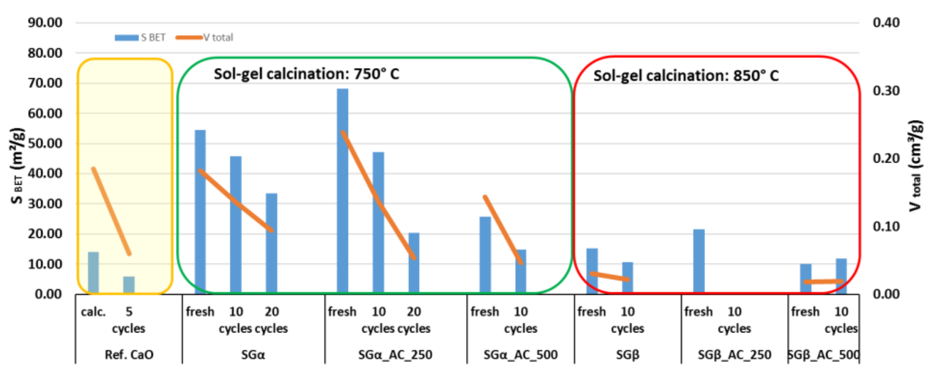
Characterization: N_2 sorption of Sol-Gel sorbents





- **SGα (synthesis calcination = 750°C) → Type IV adsorption isotherms**
- **SGβ (synthesis calcination = 850°C) → Type II adsorption isotherms**

Characterization: N_2 sorption of Sol-Gel sorbents



Ref. CaO was obtained through commercial $CaCO_3$ calcination at 800 °C during 8h

Characterization: Pore Size Distribution

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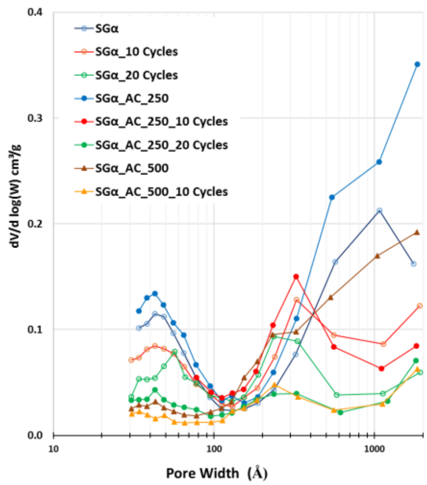

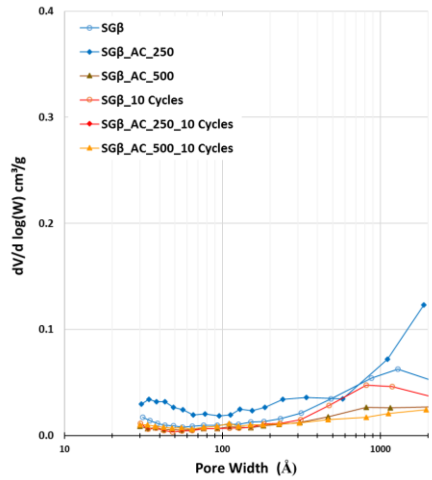

- *mainly mesoporous structure*
- *decrease of pore size along the calcination-carbonation cycles*
- *unimodal distribution (macropores presence need be evaluated by an alternative technique)*

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Characterization: XRD of Sol-Gel sorbents

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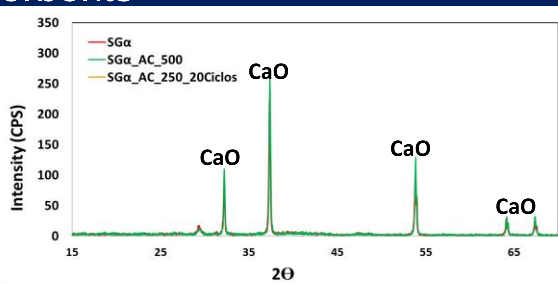

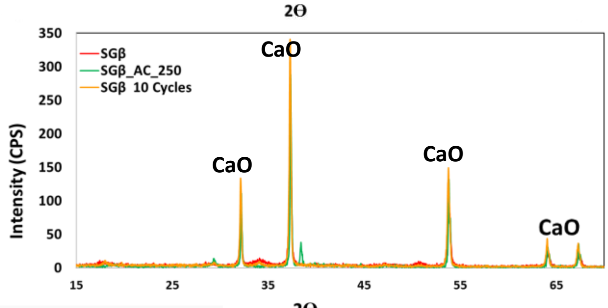

CaO is the main mineralogical compound identified in fresh samples with and without activated carbon and also in the used samples

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Characterization: SEM of Sol-Gel sorbents

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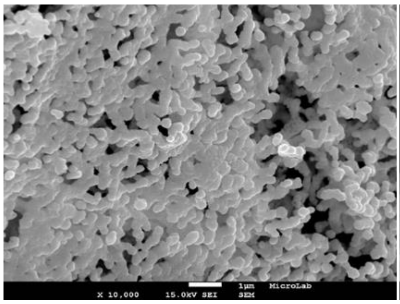
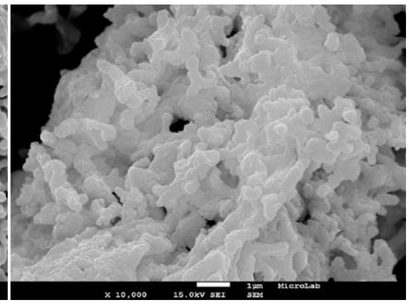
SGα **SG α_10 Cycles**





- **SGα sorbent presents a coral shape and some cavities which correspond to the CO_2 release during the synthesis calcination**
- **After 10 Cycles the amount of cavities decrease and some agglomeration is observed**

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Characterization: SEM of Sol-Gel sorbents

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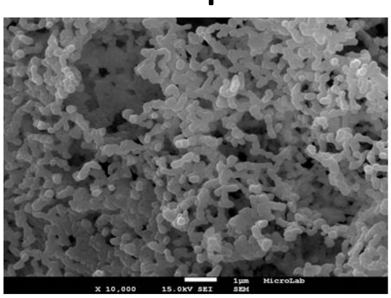
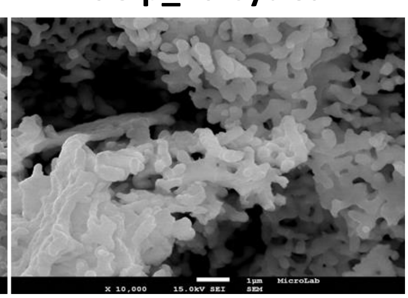
SG β **SG β_10 Cycles**





- **The morphology of the SGβ and used sorbents (after 10 Cycles) calcined at 850°C are similar with the sorbents calcined at 750°C during the synthesis**

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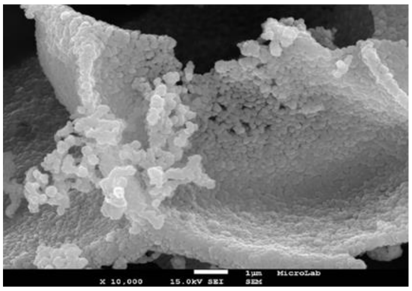
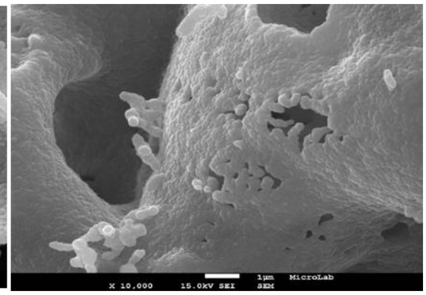
Characterization: SEM of Sol-Gel sorbents

SGα_AC_250 **SGα_AC_250_10 Cycles**

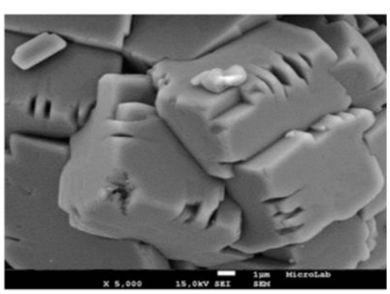


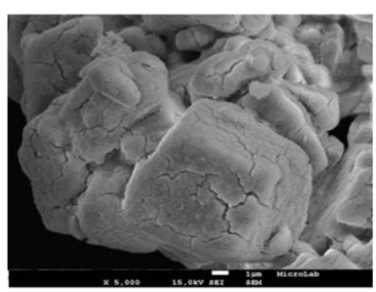


- **In SGα _AC_250 sorbent is observed some cavities formed due the burning of activated carbon during the sorbent synthesis → this promotes a major porosity of the sorbent**
- **After 10 cycles the sorbent maintain the same structure**

Characterization: SEM of $CaCO_3$ commercial sorbent

$CaCO_3$ **$CaCO_3$_10 Cycles**





- **The $CaCO_3$ is constituted by non porous compact aggregates of cubic particles (average particles diameter 30 µm)**
- **After 10 cycles a deformed cracked structure is observed**

Sorbents CO_2 Capture Capacity

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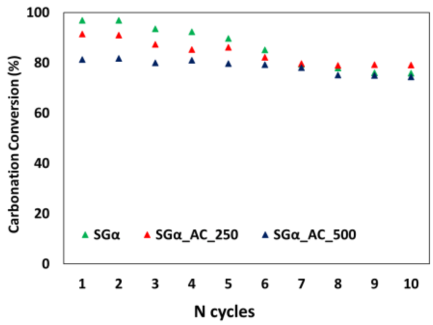
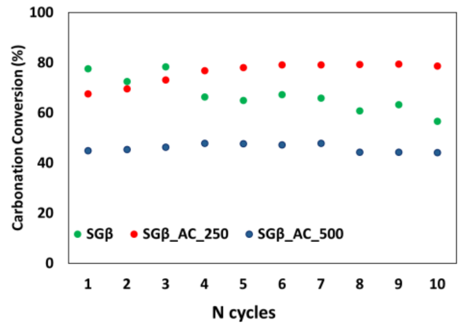
Sol-gel calcination: 750 °C



Sol-gel calcination: 850 °C



- **CO_2 carrying capacity is higher for sol-gel sorbents calcined at 750 °C during the synthesis**
- **The initial CO_2 carrying capacity is higher for sorbents synthetized without activated carbon, but comparatively with the sorbents synthetized with activated carbon the decrease of conversion along the cycles is more accentuated**

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Sorbents CO_2 Capture Capacity

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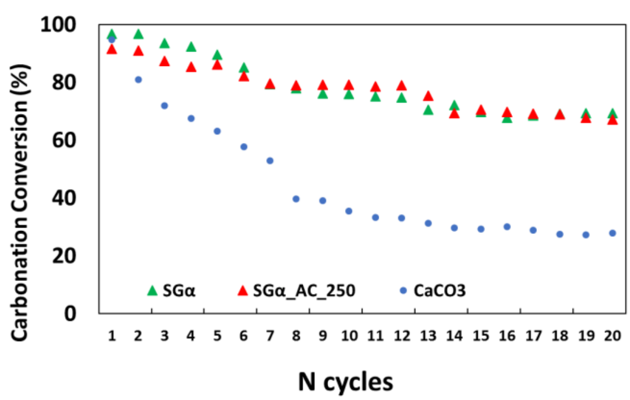

- **After 20 Cycles the CO_2 carrying capacity of SGα sorbent without or with 250 mg of activated carbon is similar and significantly higher than the observed for commercial $CaCO_3$**

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Conclusions

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Perspectives

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Acknowledgements

Project ***Carbon Emissions Reduction in the Cement Industry***

(PTDC/AAG-MAA/6195/2014) funded by *Fundação para a Ciência e Tecnologia* (FCT)

THANK YOU FOR YOUR ATTENTION

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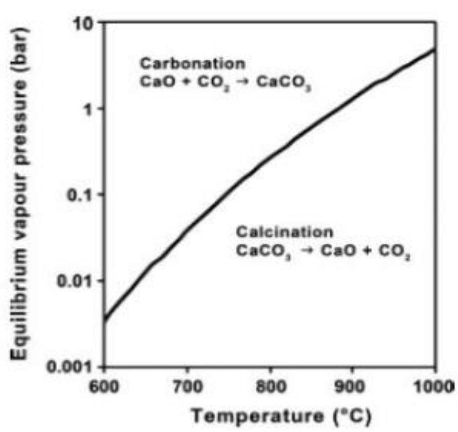
Post-Combustion Calcium Looping Technology



Equilibrium vapour pressure of CO_2 over CaO function of the temperature

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