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High-temperature CO_2 Sorption using Sintering-Resistant CaO/Saffil Fibres Sorbents Prepared by Precipitation Method

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Outline

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- **Introduction**
- **Material and Methodology**

  - Precipitation method and variables with a robust influence during the synthesis process.
- **Characterisation and Carrying Capacity Evaluation**

  - Techniques used for determination of the physicochemical properties
- **Results**

  - Morphology and microstructure analysis

  - Capture capacity

  - Residual reactivity of the CaO-based sorbents

  - Microstructural changes (sintering resistance)
- **Conclusion**

Introduction

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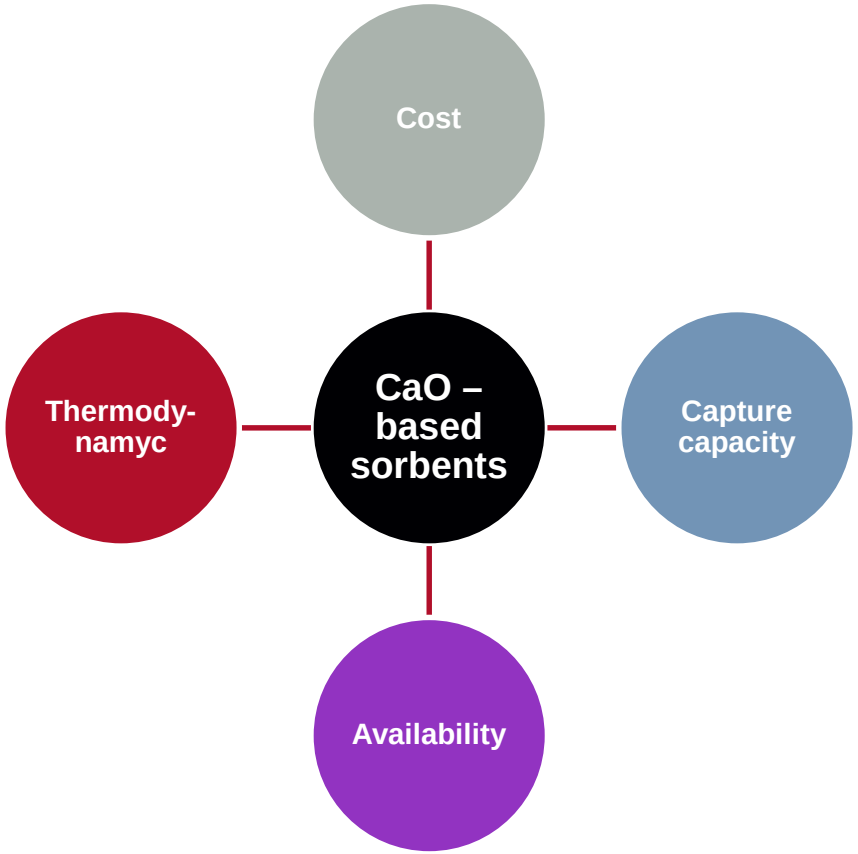
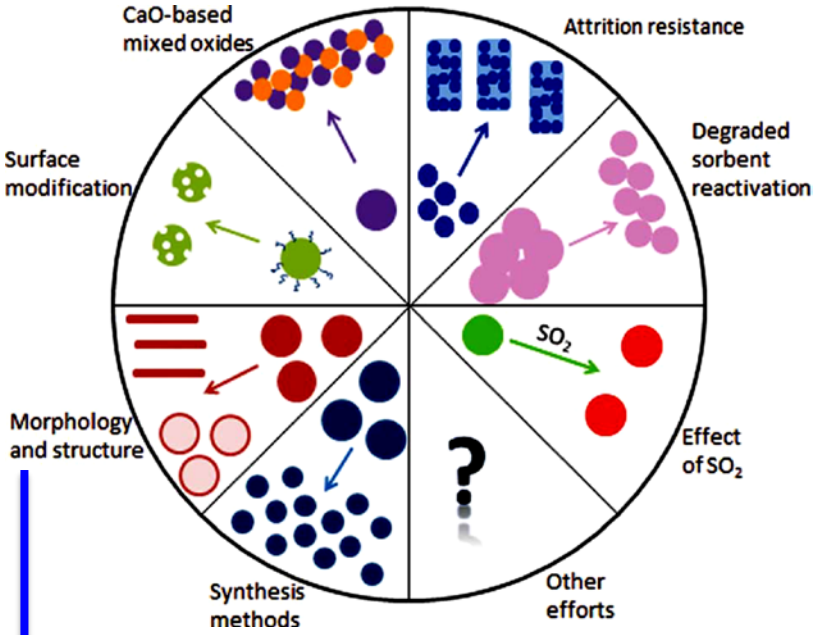
Advantages of CaO-based sorbents

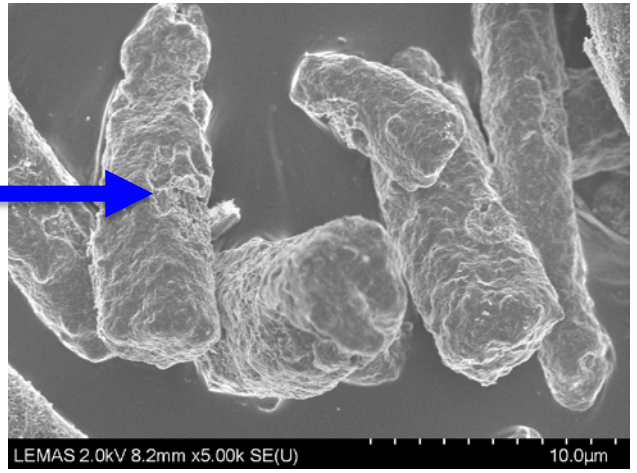


Attempts to improve the thermal and mechanical stability of CaO

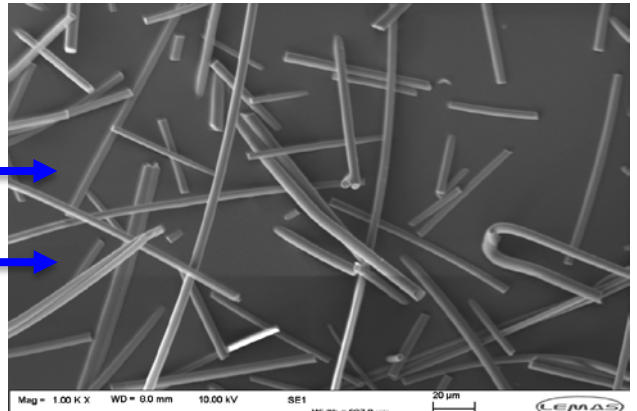


Ball, M. and M. Wietschel, International Journal of Hydrogen Energy, 2009. 34(2): p. 615-627.

CaO sintered by effect of the carbonation-calcination cycles



Saffil Fibres (Catalytic Grade)



Materials and Methodology

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Precipitation Method Via Urea

Materials: Calcium nitrate (CaO precursor), Saffil fibres (catalytic grade) and urea as precipitant

$Ca(NO_3)_2 \cdot 4H_2O$ + distilled water + saffil fibres

$Ca(NO_3)_2$ solution+ urea solution (6 mol/L)

- Both solutions will be added into a beaker and maintained at 85°C (pH=7).

Aging and rinsed 5 times

- The solid will be aged during 4 h, then, filtered and rinsed.

Drying

- The solid will be dried at 120°C overnight.

Thermal decomposition

- Calcination 850°C (4 h)

- CaO/Sf-25%-U
- CaO/Sf-15%-U
- CaO/Sf- 5%-U

Characterisation and Evaluation of Carrying Capacity

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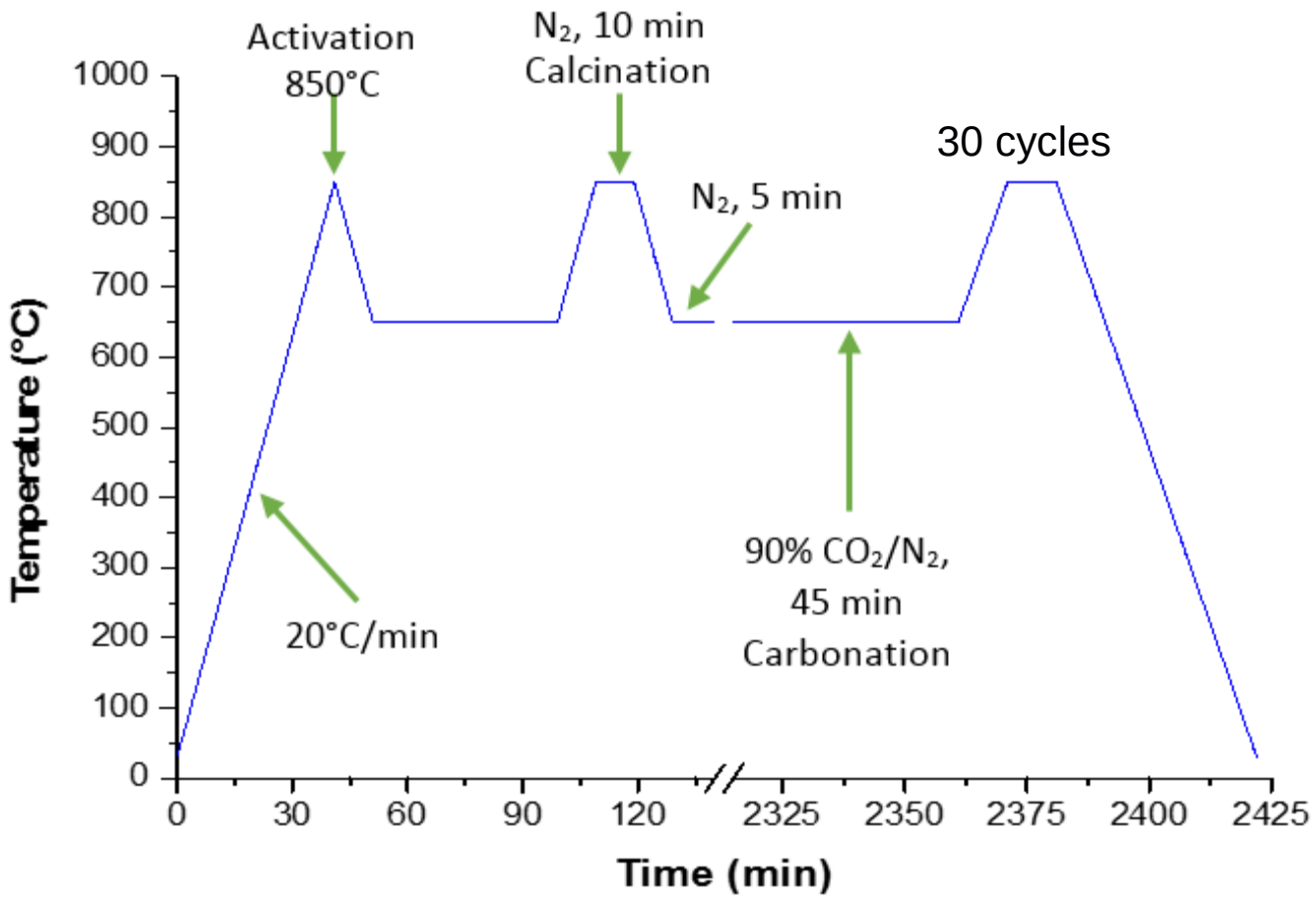
Techniques

- X-ray diffraction (**XRD**)
- Scanning electron microscopy – Energy dispersive X-ray spectroscopy (**SEM-EDS**)
- N_2 physisorption (**BET**)
- X-ray fluorescence (**XRF**)
- Thermogravimetric analysis (**TGA**)

Thermal Program for determination of the Carrying Capacity



Results and Discussion

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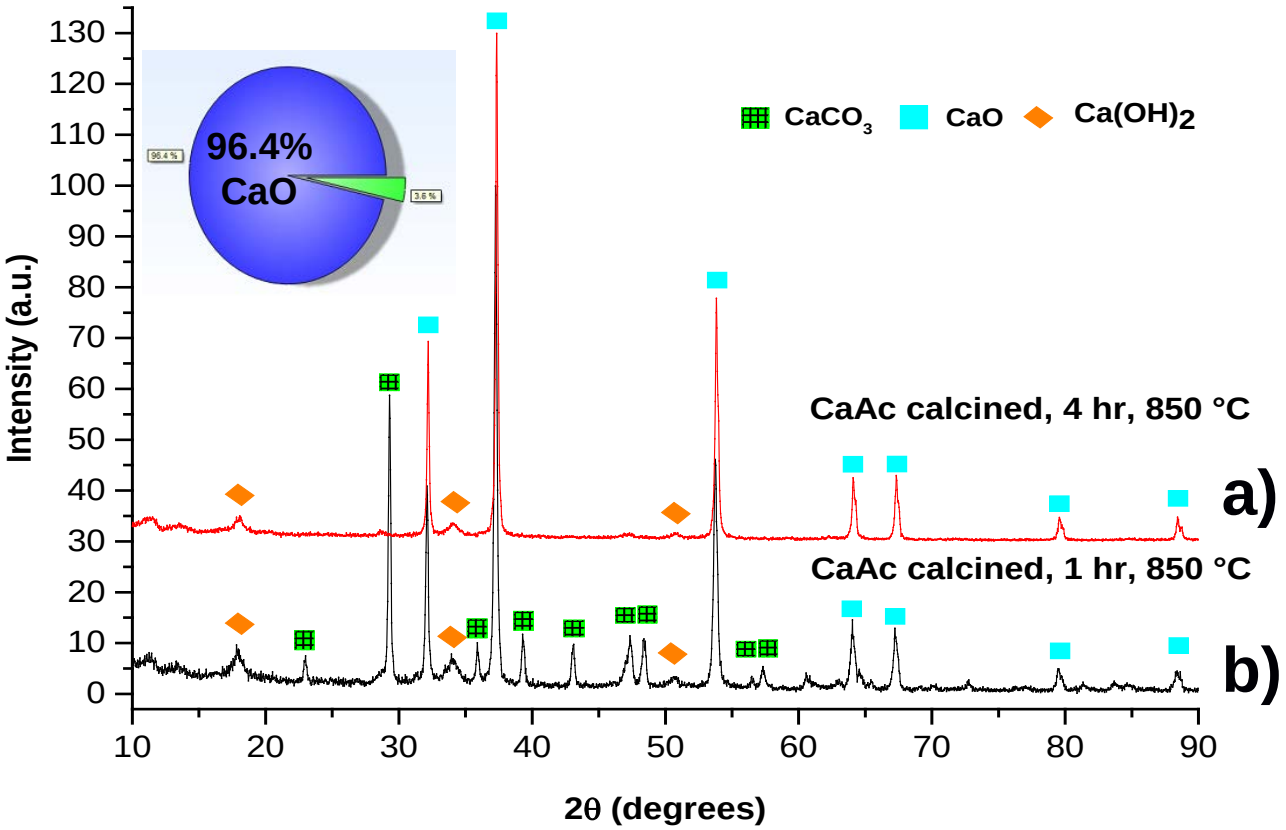
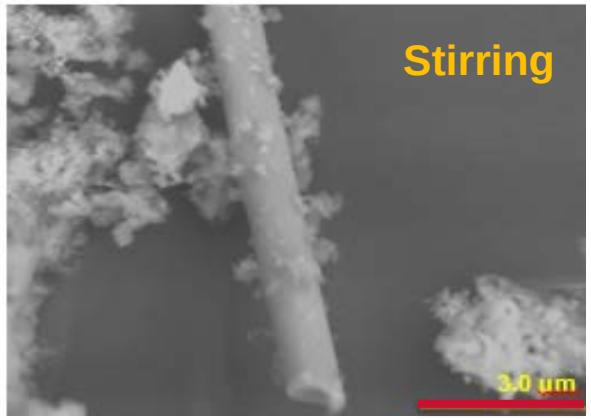
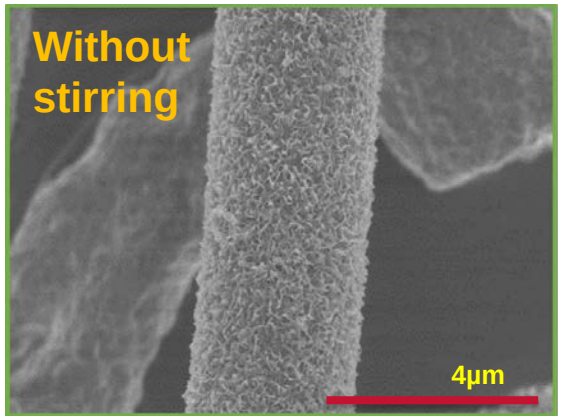
Synthesis Parameters

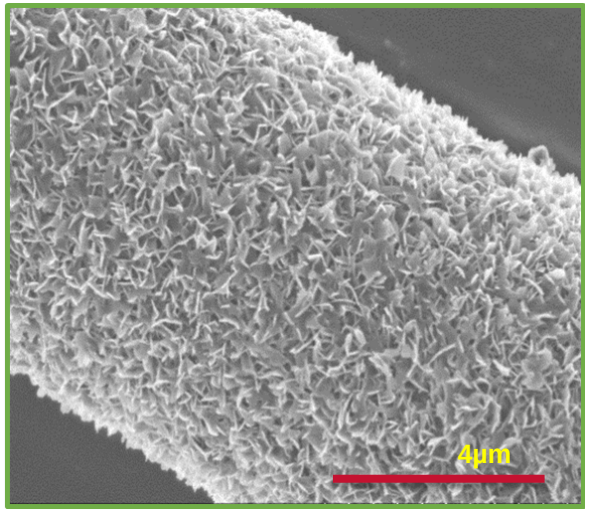


XRD patterns of the thermal decomposition of CaO at different exposure times.

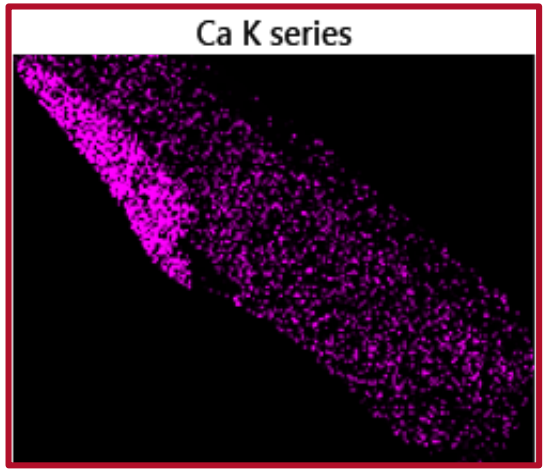
CaO-Based Sorbents Morphology







EDS Element Map



Characterization of the CaO-Based Sorbents

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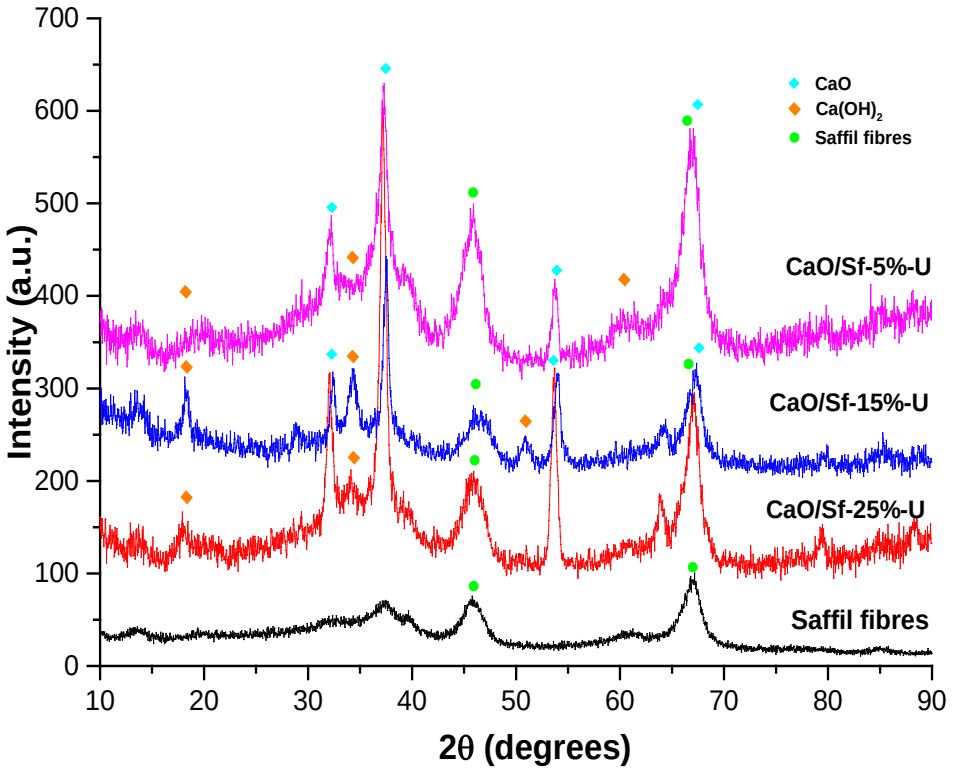
XRD Analysis for Phases Identification



XRD patterns of the CaO/Sf-%-U sorbents registered in a 2θ range between 10 to 90°.

X-Ray Fluorescence Elemental Composition of the CaO-Based Sorbents

CaO-based sorbent	CaO (%)	Al_2O_3 (%)	SiO_2 (%)
CaO/Sf-25%-U	25.9	71.16	2.94
CaO/Sf-15%-U	13.1	83.5	3.4
CaO/Sf-5%-U	4.8	91.5	3.7
Saffil fibres	-	95.7	4.3

Surface area (m^2/g)

CaO/Sf-25%-U	CaO/Sf-15%-U	CaO/Sf-5%-U	Saffil Fibres
96.2	112.8	123.2	138.5

Surface area as a function of CaO content (30%)

Carrying Capacity Measurements

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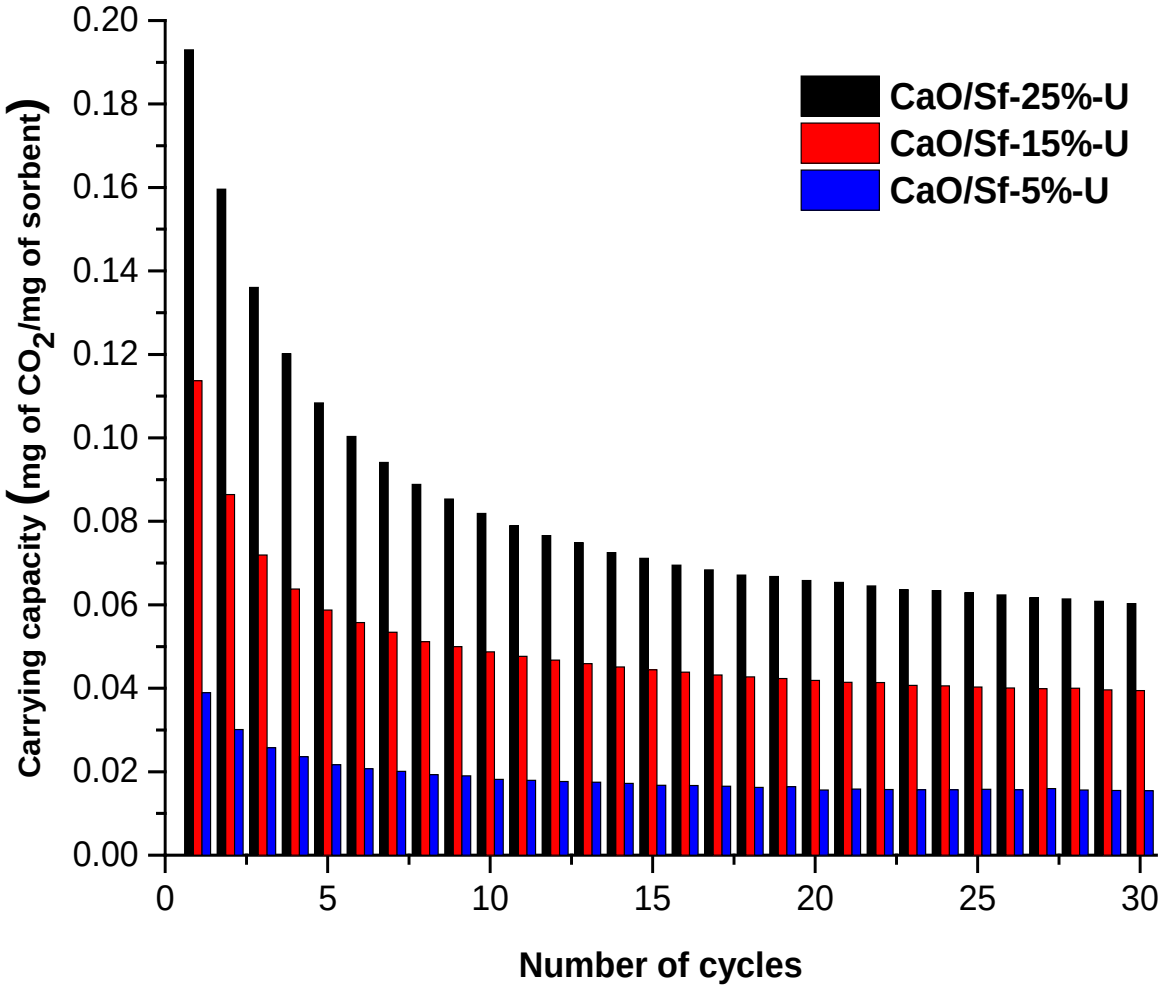

Forecasting of the Residual CO_2 Capacity

Semiempirical equation **(1)** proposed by Grasa et al. to predict the residual carrying capacity in CaO sorbents.

$$a_N = \frac{1 - a_\infty}{(1 + kN)^n} + a_\infty \qquad (1)$$

Double exponential model **(2)** used to forecast the residual reactivity of the CaO-based sorbents prepared by the precipitation method.

$$a_{cc,N} = A_1 * e^{-k_1 * N} + A_2 * e^{-k_2 * N} + a_r \qquad (2)$$

Residual Reactivity

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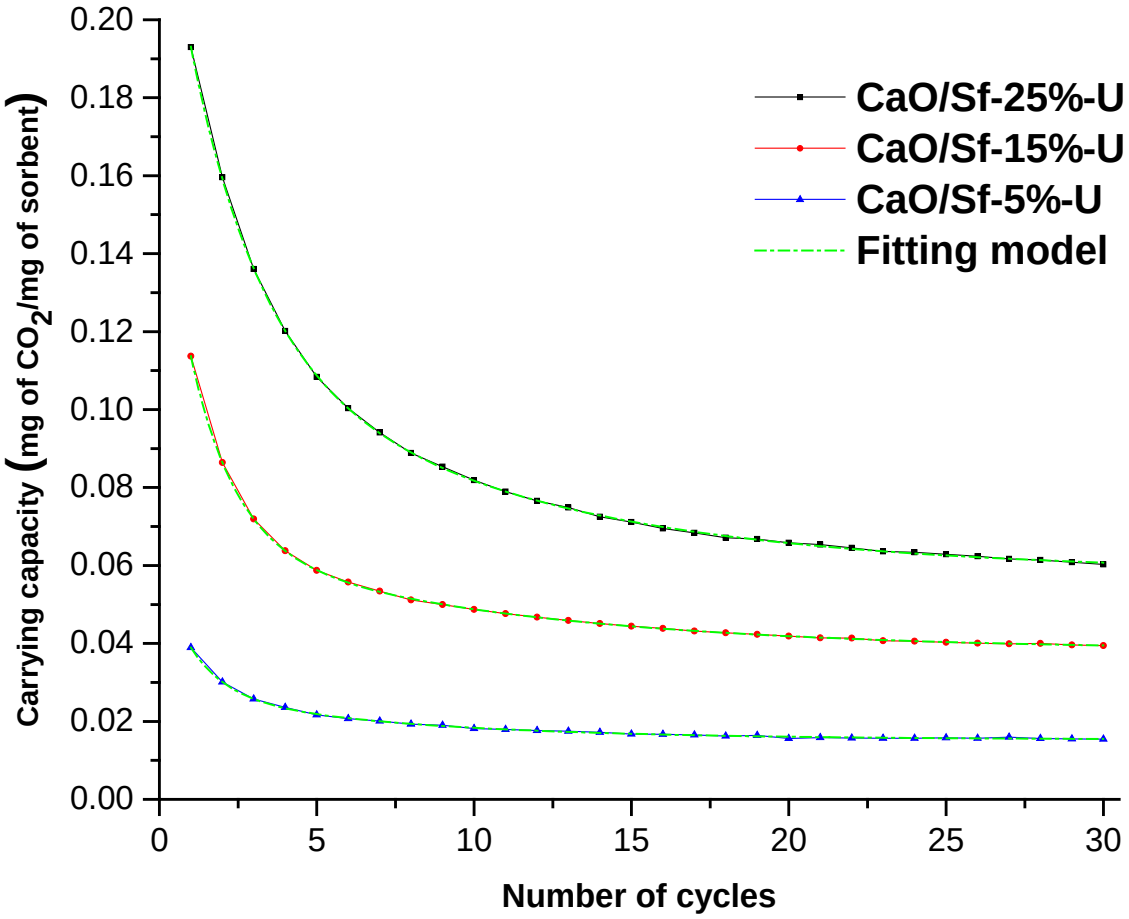
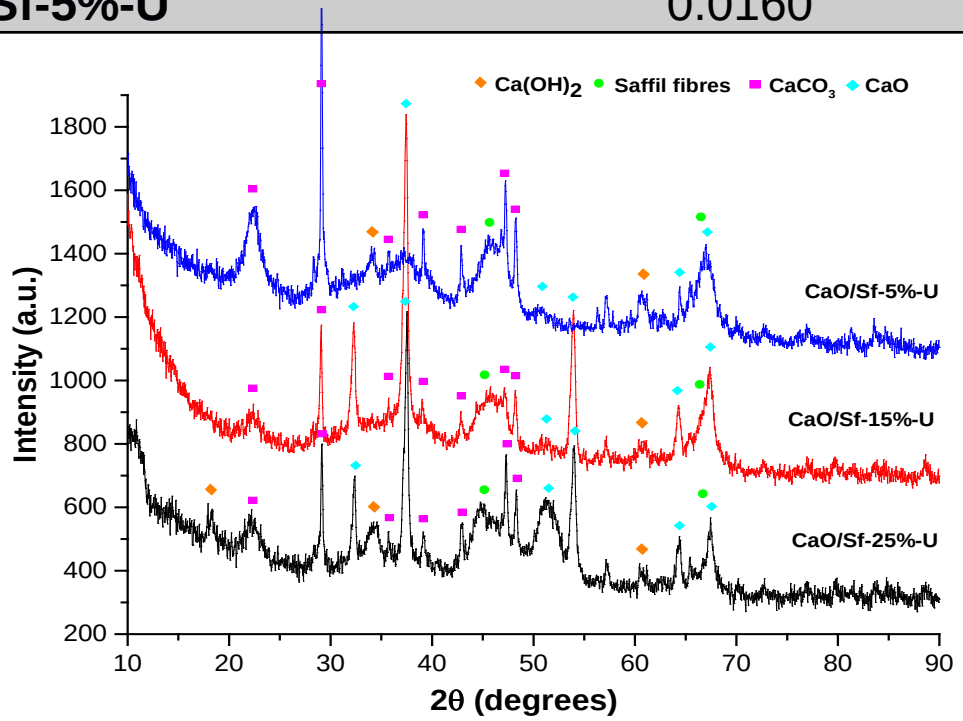


Sorbent	Residual reactivity (mg CO_2/mg Sorbent)
CaO/Sf-25%-U	0.0647
CaO/Sf-15%-U	0.0411
CaO/Sf-5%-U	0.0160

Determination of the residual reactivity in the CaO-based materials after a long number of cycles.



XRD patterns of CaO/Sf-%-U sorbents registered upon completion of the CO_2 capture test

Microstructural Changes

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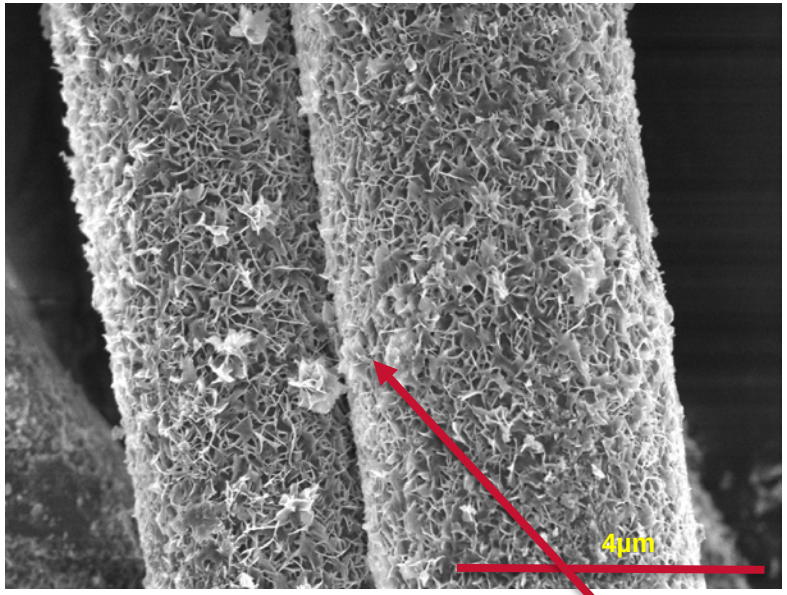
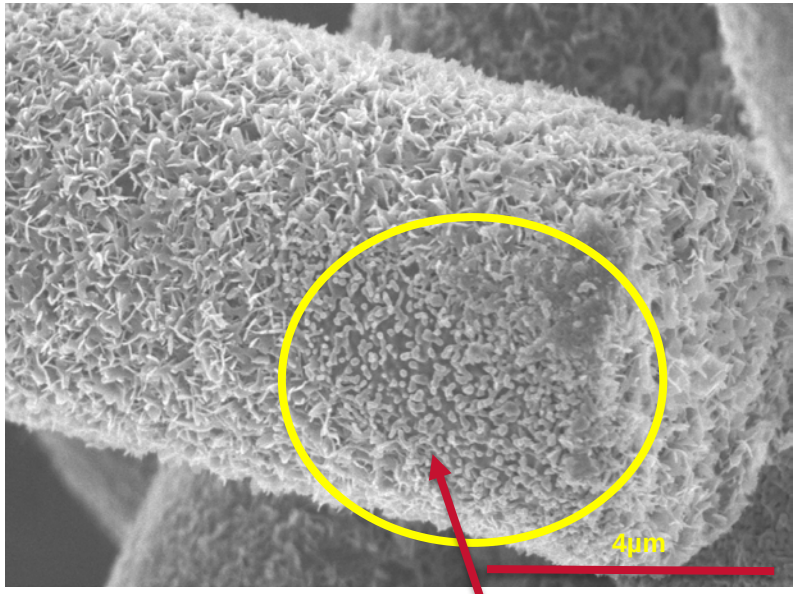
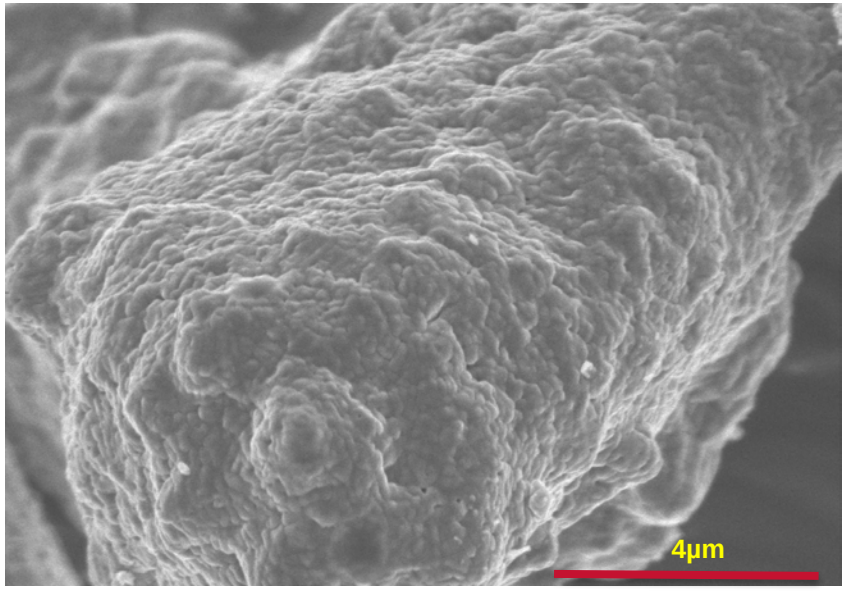
CaO/Sf-25%-U sorbent



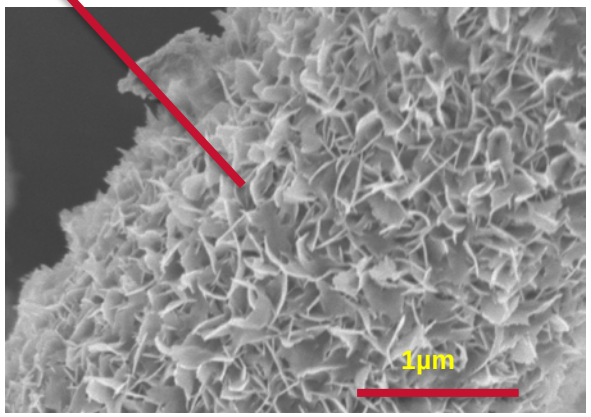
CaO/Sf-5%-U sorbent

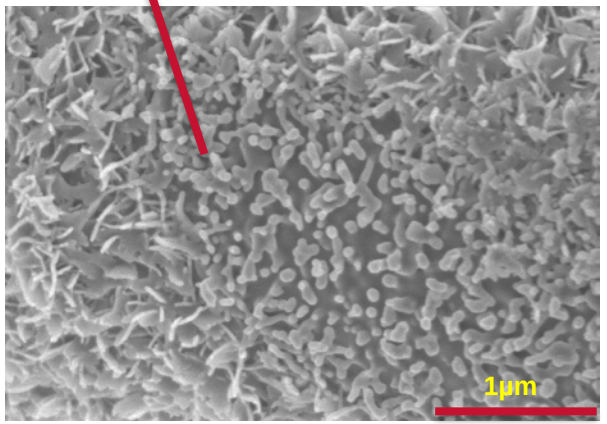


CaO aggregates



High thermal resistance by the incorporation of Saffil fibres and the structure adopted through the controlled deposition method.





Sintering of CaO by effect of temperature after 30 carbonation-calcination cycles

Conclusion

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- The sorbent impregnated with 25% of CaO presented the highest carrying capacity over the 30 carbonation-calcination cycles (0.195 mg of CO_2/mg of sorbent).
- The loss of reactivity was mainly associated with sintering of the CaO aggregates that grew out the surface of the fibrous support.
- The nanostructure (nanosheets) adopted by the CaO as a results of the precipitation method provide high thermal stability to the active phase even after the exposure to 30 continuous carbonation-calcination cycles.
- Saffil fibres as CaO support are conceived as a promising option to inhibit sintering of the active phase.

Acknowledgments

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