CO_2 capture and storage by natural zeolites

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Introduction

In the last decades, the valorization of the solid organic waste has received growing interest.

The **waste treatment** has increased the attention towards a **new renewable energy carrier: the biogas**.

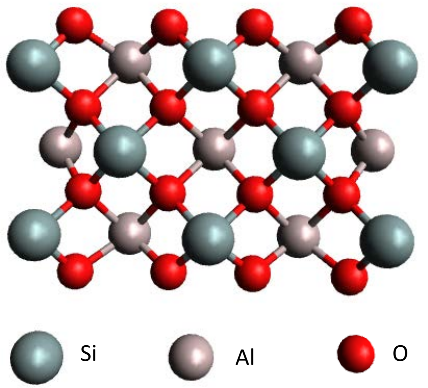
The biogas has different composition depending on the solid waste (i.e., CH_4=65%, CO_2=30%, H_2O=1.9%, N_2=1.8%, H_2S=0.6%, O_2=0.5%, mercaptans=0.2%).

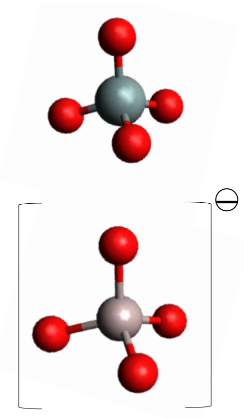
Since the CO_2 amount is not negligible, it must be captured because it is one of the significant contributors to the greenhouse effect.

Introduction

Over the years, several technologies were developed to abate **CO_2**. However, the actual capture systems are not low-cost, and the research is focusing on other possible technologies.

In this scenario, **zeolites** could be an **interesting solution**. These materials are characterized by **[SiO_4]** and **[AlO_4]$^-$** with **three-dimensional structure**. Thanks to this structural conformation, the zeolite can create cavities with different pores dimensions: micropores, mesopores (2 nm < d < 50 nm) or macropores (d > 50 nm).





A material with these physico-chemical properties could have application for several environmental applications, like water, soil and air decontamination.

Khraisheh, M., et al. (2020). *Journal of Environmental Management*, 255.
Colella, C. (2007). *In Studies in Surface Science and Catalysis.* Elsevier Inc.

Introduction

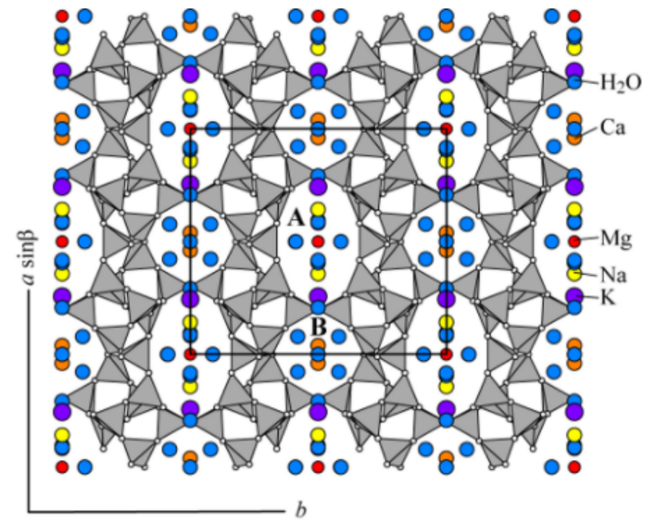
- Among the **zeolites**, the **natural** ones have received interest in academia and industry because of their **potential applications** and **low-cost** compared with the commercial (synthetic) zeolites.

- In particular, the **clinoptilolite** is the most used natural zeolite. This material can adsorb CO_2 by Van der Waals forces, and the modification of the chemical composition (i.e., by means ion exchange method) may increase the CO_2 adsorption capacity.

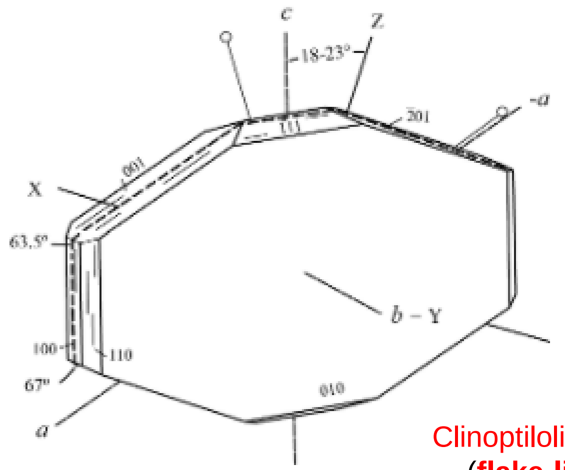
- It was demonstrated that the capacity of CO_2 removal by clinoptilolite follows the following orders: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$.

Clinoptilolite

$(NaKCa)_4(Al_6Si_{30}O_{72})\cdot 24H_2O$



The crystal structure of clinoptilolite-Na (Agoura, California) with cation positions from the refinement of Koyama and Takéuchi (1977). Typically clinoptilolite contains 4 to 7 cations per unit cell (Deer *et al.* 2004).



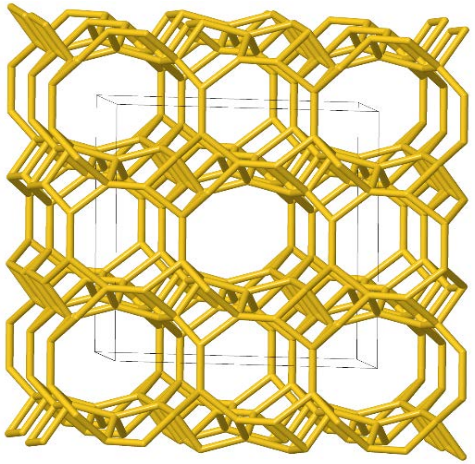
Clinoptilolite particle shape (**flake-like structure**)

Siriwardane, R.. V. et al. (2003). *Energy and Fuels*, 17(3), 571–576.
www.iza-online.org/natural/Datasheets/Clinoptilolite/clinoptilolite.htm

Materials and methods

Clinoptilolite powder was provided by Zeolado (Greece)

The clinoptilolite structure by the International Zeolite Association



N_2 Physisorption at -196°C

N_2 Physisorption Property	Clinoptilolite
BET Surface Area ($m^2\ g^{-1}$)	37
Total Volume ($cm^3\ g^{-1}$)	0.14

EDS Analysis

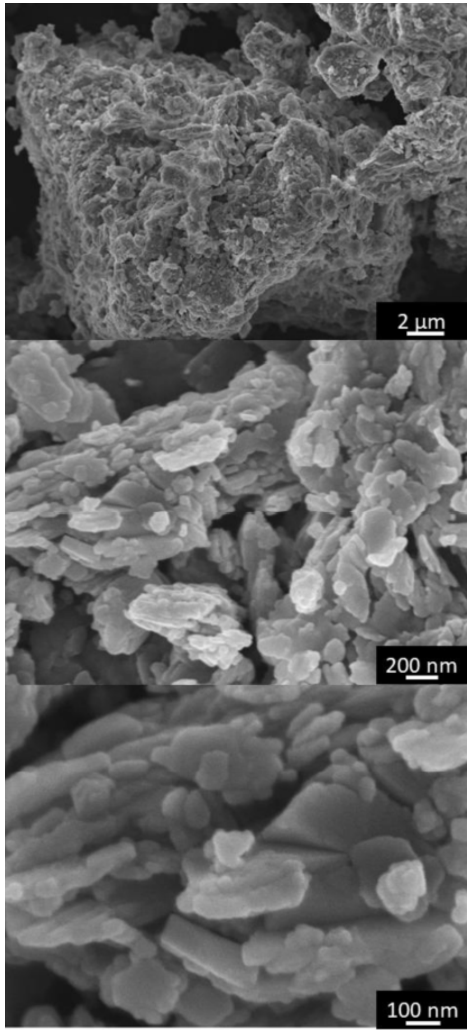
Compositions per unit cell.
Elemental concentrations given as no. of atoms/unit cell.

Elements	Cation Content / mmol g^{-1}
Si	23.55
Al	4.92
Fe	0.20
Ca	0.50
Mg	0.32
Na	0.12
K	0.78

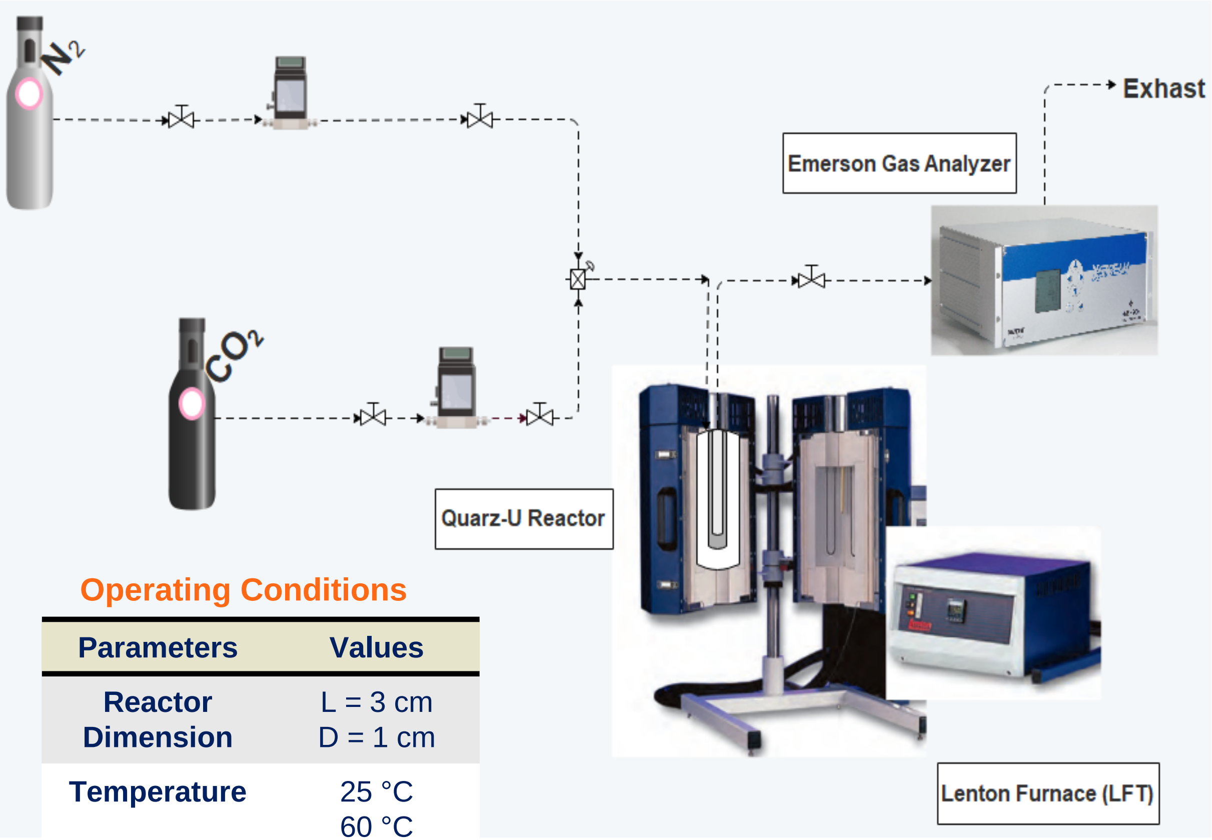
Si/Al = 5

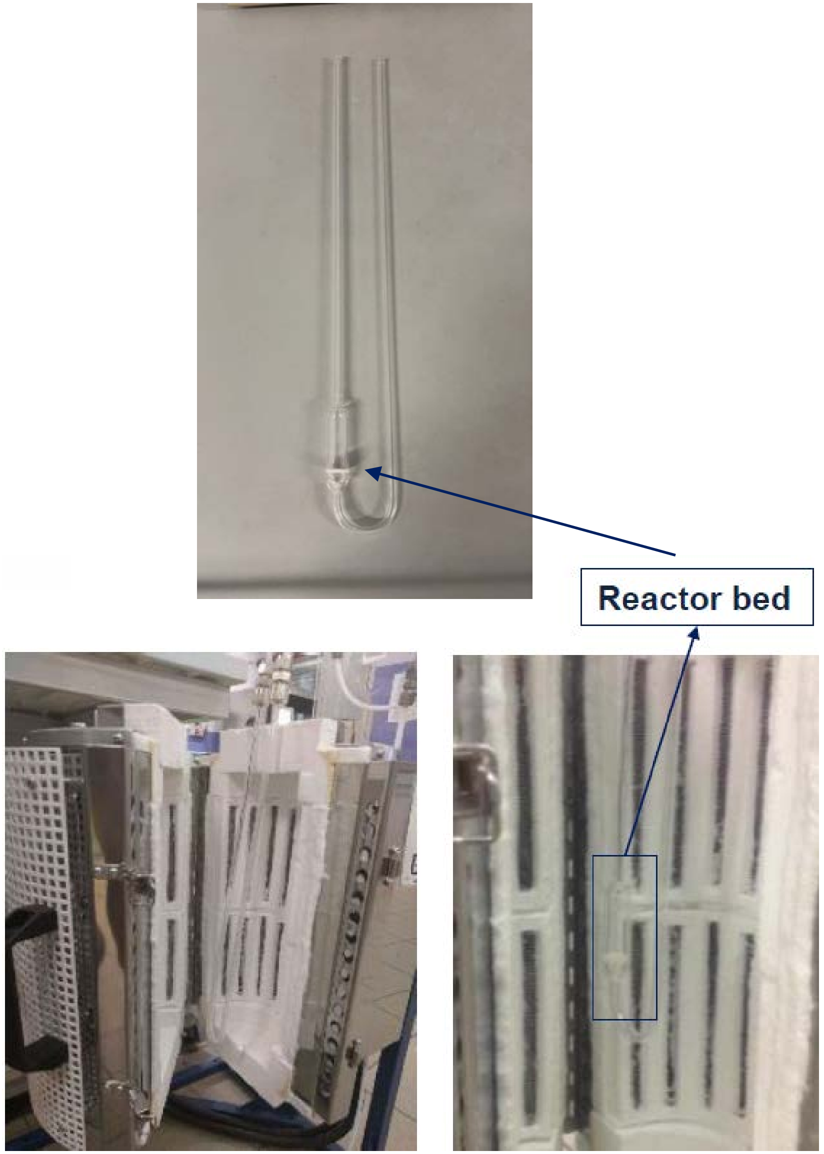
Theoretical clinoptilolite formula $(NaKCa)_4(Al_6Si_{30}O_{72})\cdot 24H_2O$

FESEM Images



Experimental set-up





Operating Conditions

Parameters	Values
Reactor Dimension	L = 3 cm D = 1 cm
Temperature	25 °C 60 °C 90 °C 150 °C
Pressure	1 bar
CO_2 /N_2	10 vol %
Flow	40 ml/min

Adsorption tests

- The CO_2 capture was performed at different temperatures, in the range 25 – 150 °C. Before the tests, the clinoptilolite was pretreated at 400 °C for 2 h with N_2 flow.

- The results are reported in Figure 1 and Table 1. As a whole, the CO_2 adsorption capacity decreases as the temperature increases (Figure 1A).

- The clinoptilolite presents good adsorption capacity at low temperature (2.2 $mmol_{CO2\ adsorbed}\ g^{-1}_{clino}$). Moreover, the clinoptilolite is stable for two consecutive runs (Figure 1B).

Table 1. CO_2 absorbed ($mmol_{CO2\ adsorbed}$) over the clinoptilolite mass at 25, 60, 90 and 150 °C.

Temperature (°C)	25	60	90	150
CO_2 adsorbed ($mmol_{CO2\ adsorbed}\ g^{-1}_{clino}$)	2.2	1.8	1.3	0.7

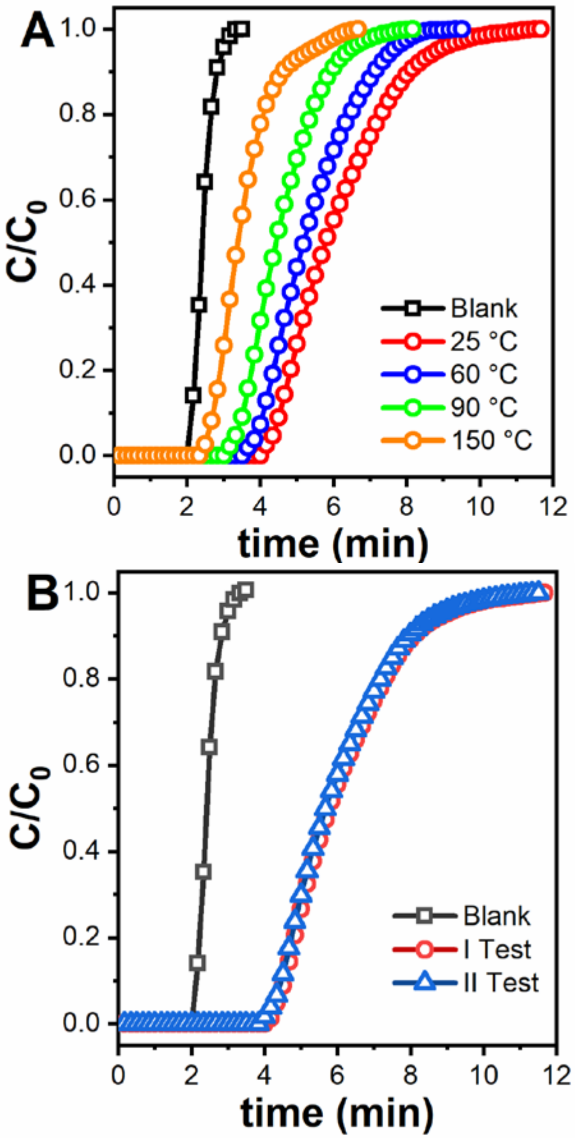


Figure 1. A) CO_2 capture over the time at different temperatures and B) stability tests (at 25 °C) for two consecutive runs on clinoptilolite powder

Adsorption tests

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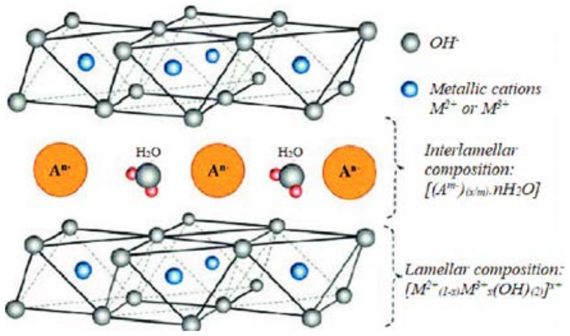
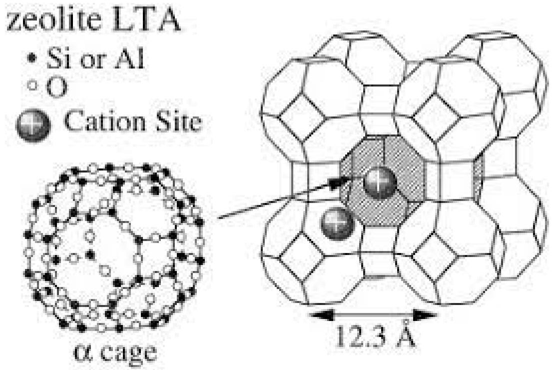
- Moreover, the clinoptilolite was compared with other CO_2 capture materials, as the hydrotalcite and the Linde Type A (LTA) zeolites.



Hydrotalcite structure, Salomao et al., 2013



LTA structure, Takehito N. et al. 2001

- At **25 °C**, the <u>most performing</u> catalysts are **Na- CaLTA samples**, respectively, 3.1 and 3.3 $mmol_{CO2\ adsorbed}\ g^{-1}_{adorbent}$.

- However, at a higher temperature (**150 °C**), the most interesting catalyst is **clinoptilolite** (0.7 $mmol_{CO2\ adsorbed}\ g^{-1}_{adorbent}$), and the worst performances are represented by the hydrotalcite (0.4 $mmol_{CO2\ adsorbed}\ g^{-1}_{adorbent}$).

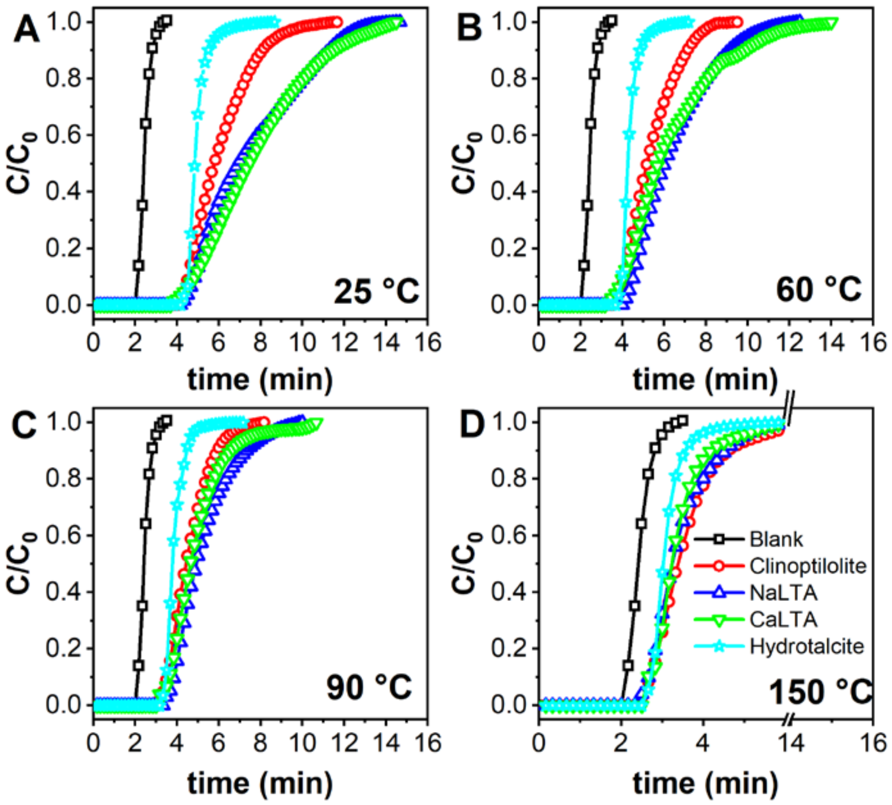


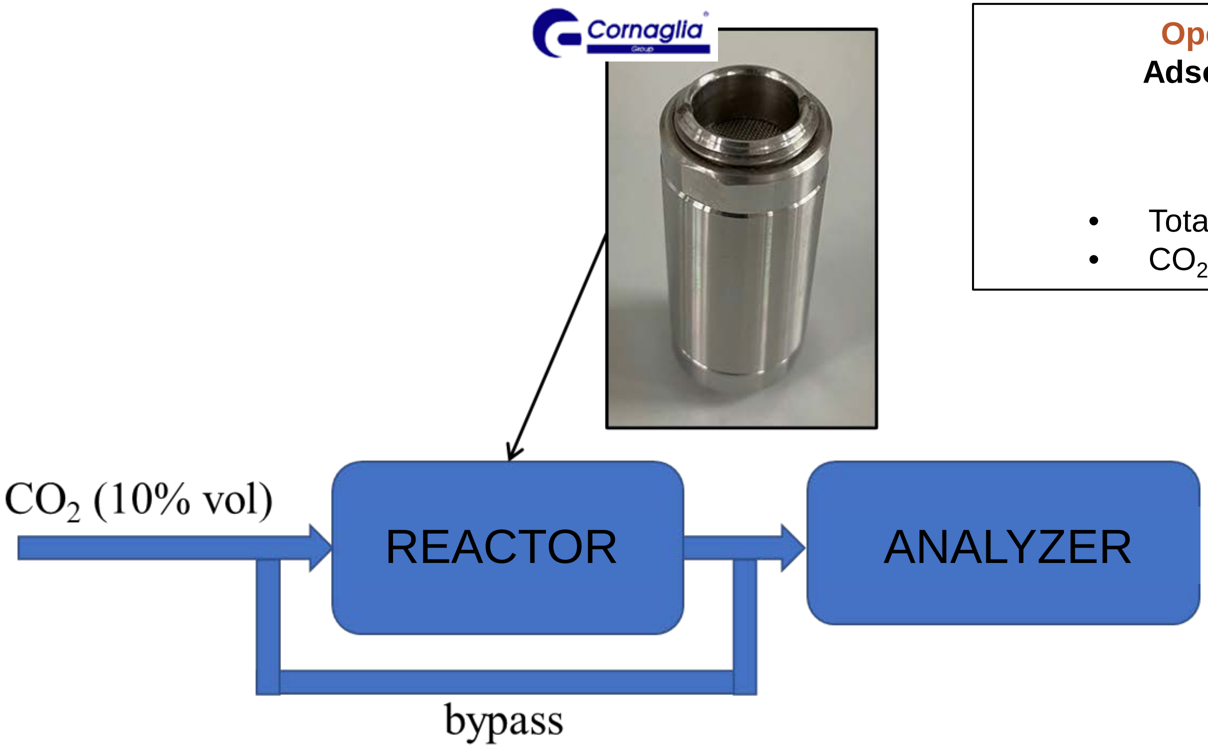
Figure 2. A) CO_2 capture at 25 °C, B) 60 °C, C) 90 °C and D) 150 °C over the time.

Salomão R et al. (2013) Interceram — refractories manual I/2013: 187—191.
Nakano, T. Et al. (2001). *Journal of magnetism and magnetic materials*, 226, 238-240.

Conclusions

- In conclusion, the **clinoptilolite** is an interesting (sustainable) material that can be used for the CO_2 capture at relatively high temperature since it is less affected by the variation of the temperature, compared to LTA-type zeolite and hydrotalcite.

Future perspectives



CO_2 capture scheme by a cartridge.

Operating conditions

Adsorbent mass: 6.18 g

$$\frac{W}{F} = 7.5\ \frac{g \cdot min}{l}$$

- Total flow = 824 ml/min
- CO_2= 10% vol. balanced with N_2

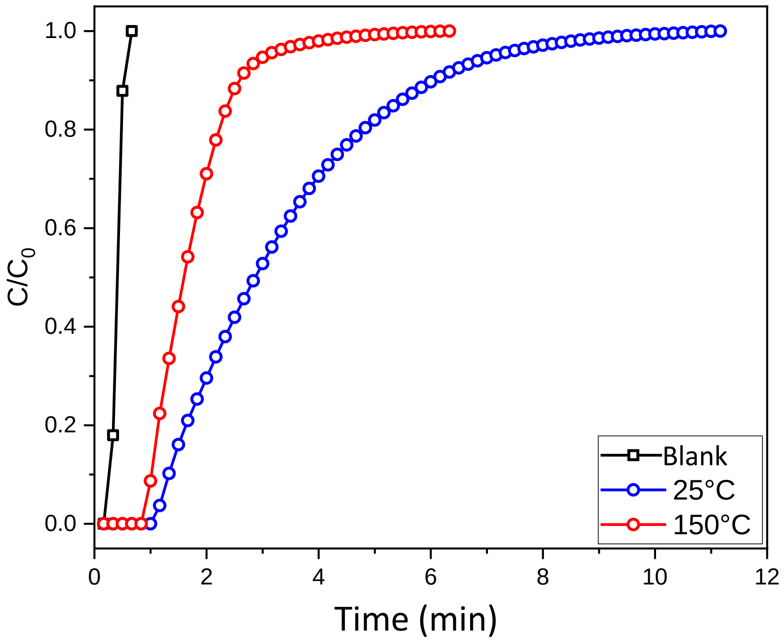


Figure 3. CO_2 capture by the clinoptilolite at 25 °C and 150 °C over the time

Table 2. CO_2 absorbed ($mmol_{CO2\ adsorbed}$) over the clinoptilolite mass at 25 and 150 °C.

Sample	Temperature (°C)	CO_2 adsorbed (mg/g)	CO_2 adsorbed (mmol/g)	Pressure losses (mBar)
Clinoptilolite	**25**	**79**	**1.8**	**4**
	150	**36**	**0.8**	**10**

Future perspectives

CO_2 adsorption over LTA-materials (cartridge tests).

Synthesis and characterizations of new materials for CO_2 capture: hierarchical systems (powder and cartridge tests).

Acknowledgment

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Thank you for your kind attention

Any questions?

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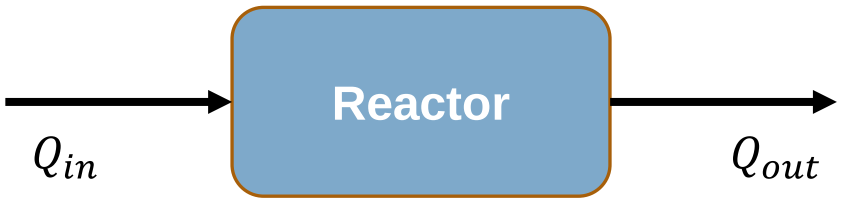
Supporting information

Supporting information

$$V_{CO2_{adsorbes}} = \int_{t_0+\Delta t}^{t_f} \left(1 - \frac{C_{CO2_{out}}}{C_0}\right) d(Q_{out} t) \quad (1)$$

$$Q_{out} = Q_{in} \left(\frac{1-y_{CO2}}{1-y_{CO2}\frac{C_{CO2_{out}}}{C_0}}\right) \quad (2)$$



$$n_{CO2_{out}}(t) = \frac{y_{CO2} PV}{RT} \quad (3)$$

Adsorption capacity: $\alpha_{zeolite} = \frac{n_{CO2_{adssorbed}}}{m_{zeolite}}$

Where:

- C_{CO2} is the vol. concentration of CO_2 recorded by the analyzer;
- Q_{out} $\left[\frac{m^3}{s}\right]$ is the vol. flux out from the reactor;
- y_{CO2} CO_2 molar ratio in the reactor inlet;
- C_0 is the CO_2 concentration in the inlet;
- Δt $[s]$ is the delay time of the instrument.

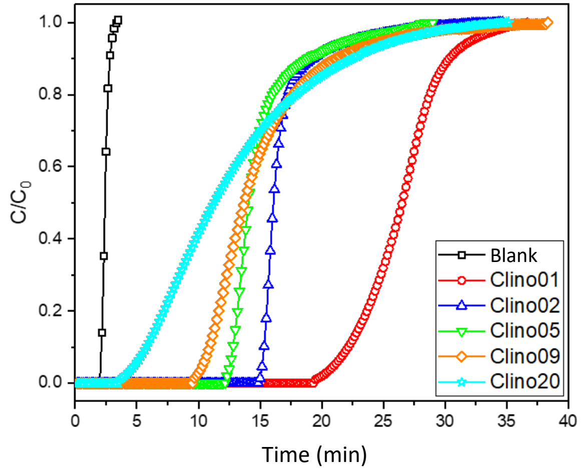
Supporting information

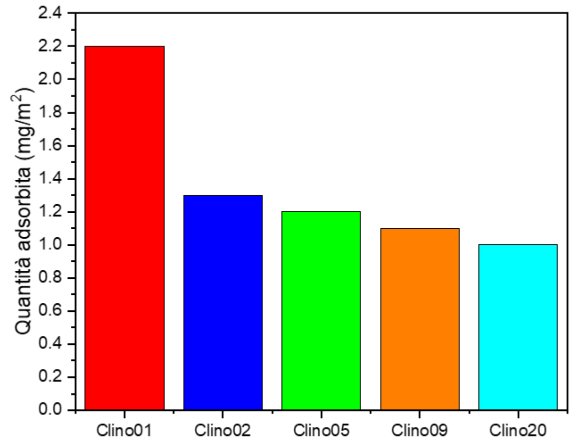
	NaClino	CaClino	Hydrotalcite
SSA[a] (m^2g^{-1})	43	48	282
Pores volume (cm^3g^{-1})	0.24	0.21	0.22
t-plot (cm^3g^{-1})	0.006	0.006	0.01

[a] Evaluated by BET method

Supporting information

Effect of the average particle's dimensions





Clinoptilolite	Temperature (°C)	CO_2 adsorbed (mg/g)	CO_2 adsorbed (mmol/g)
Clino01 (0.15mm)	**20**	**99**	**2.2**
Clino02 (0.21-0.50mm)	20	58	1.3
Clino05 (0.50-0.90mm)	20	51	1.2
Clino09 (0.90-2.50mm)	20	47	1.1
Clino20 (2.00-3.15mm)	20	43	1

Supporting information

Cartridge dimensions