Experimental study of adsorption and desorption of carbon dioxide/nitrogen using microwave heating (MSA) on modified Metal Organic Frameworks (MOF’s) with graphene oxide

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Introduction and outlet of the presentation

Absorption

Cryogenic

Post-combustion

Adsorption

Membranes

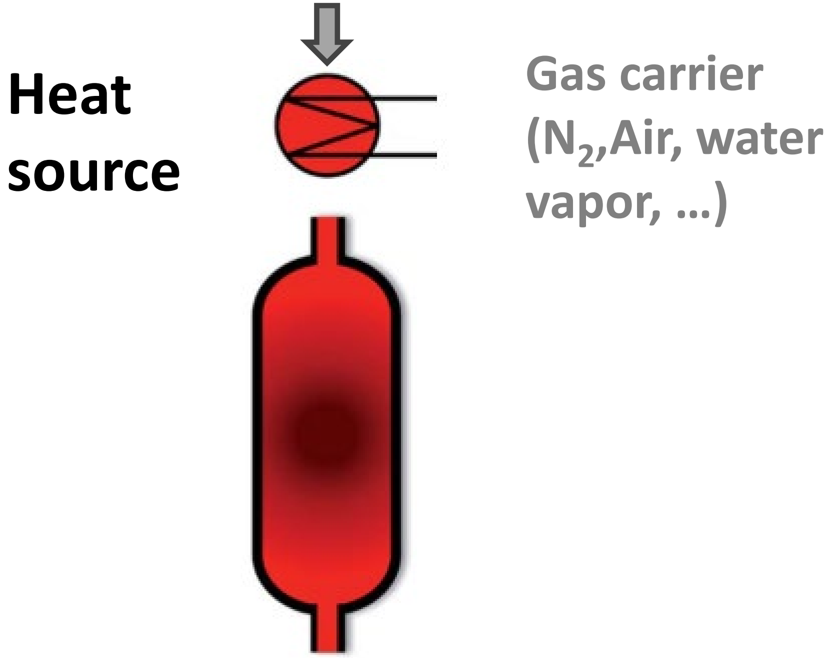
Adsorption capture:

- Easy of regeneration and so a potential lower energy consumption
- No use of toxic components
- A great adaptability
- Regeneration with pressure (PSA)
- Regeneration with temperature (**TSA**)

Microwave CO_2 capture study

Carbon Capture by Microwave Swing Adsorption

Conventional TSA



M. Muschi et al., J. Mater. Chem. A, 2021, 9, 13135 doi: 10.1039/D0TA12215G

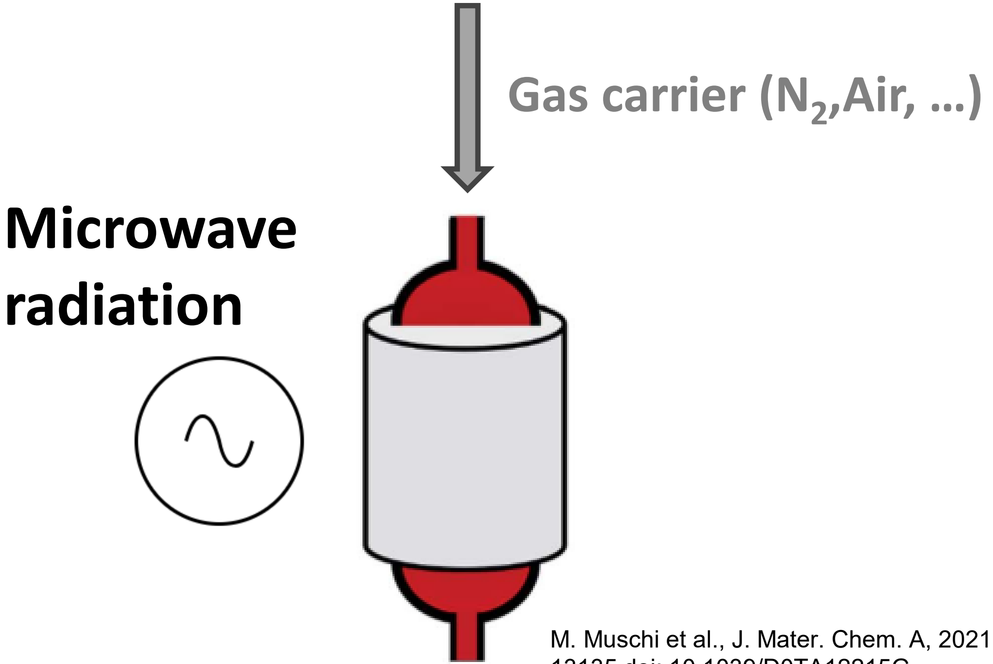
Pros

- Advanced regeneration
- Thermal energy

Cons

- Slow desorption kinetic

Microwave Swing Adsorption



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Pros

- Advanced regeneration
- Quick desorption kinetic

Cons

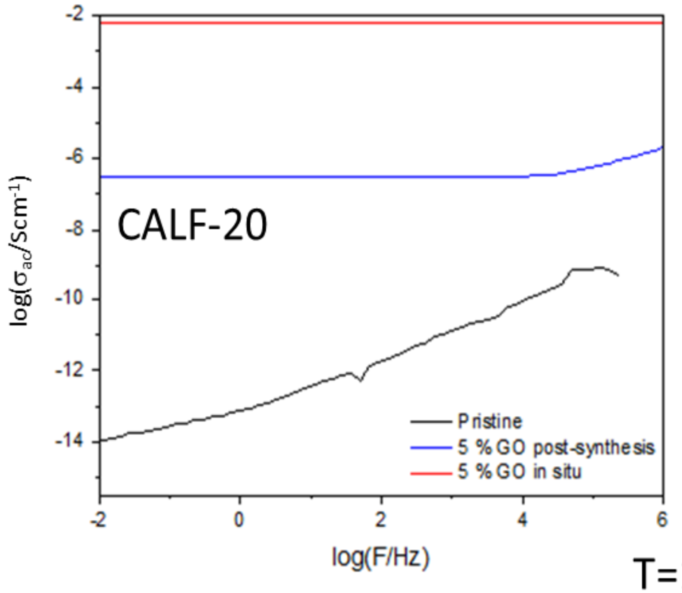
- Inhomogeneous heating
- Design of semiconductive adsorbent

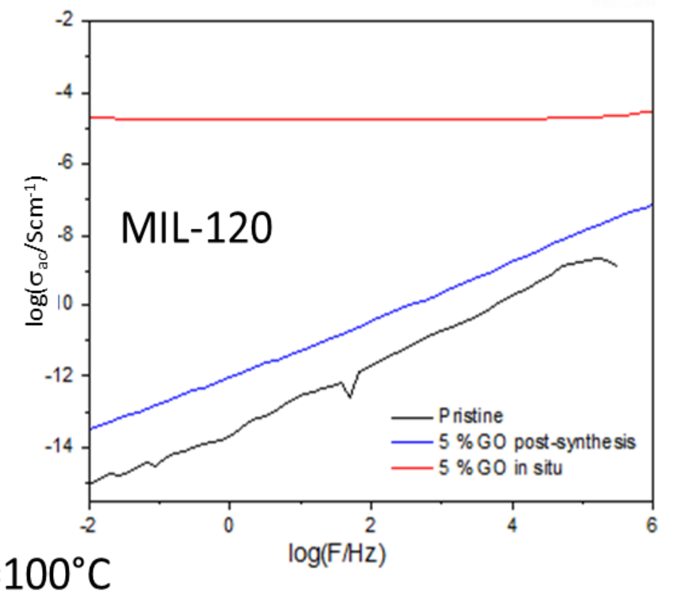
Adsorbent characterization

Required properties:

- ➢ Microwave absorption
- ➢ Thermal conductivity
- ➢ Maintaining the adsorption properties of the selected MOF's

Addition of **5%wt** of **G**raphene **O**xide (**GO**)



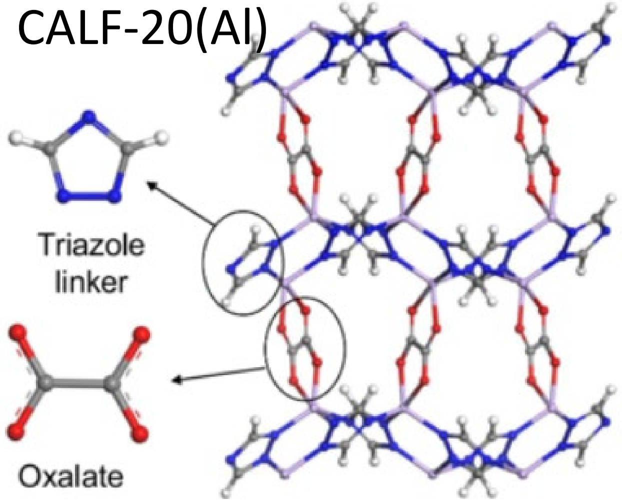


T=100°C

Composite properties:

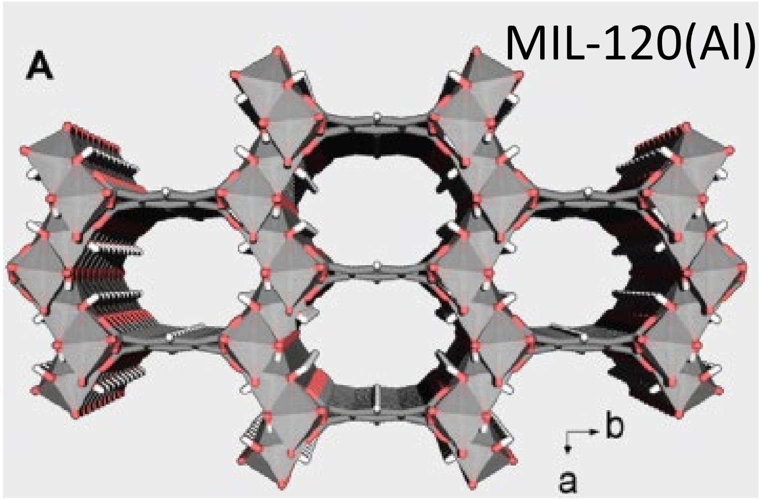
- ➢ CO_2 adsorption capacity of 1 – 2.5 mmol/g at T_{amb} and 0.15 bar
- ➢ Selectivity higher than 30
- ➢ Electrical conductivity 10^{-5} - 10^{-2} S/cm
- ➢ Good chemical/mechanical stability
- ➢ Shaping with Bentonite (10%wt)

CALF-20(Al)



R. Oktavian et al., Nature Communication, 2024, 15

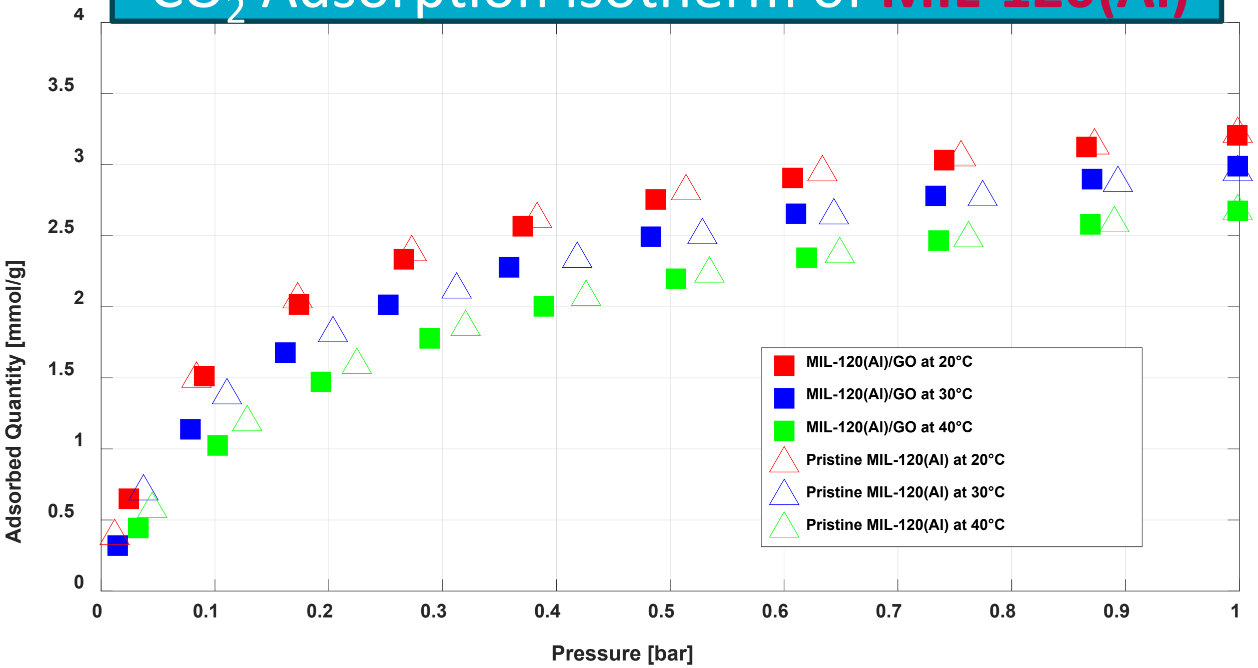
MIL-120(Al)



B. Chen et al., Adv. Sci., 2024, 11, 2401070

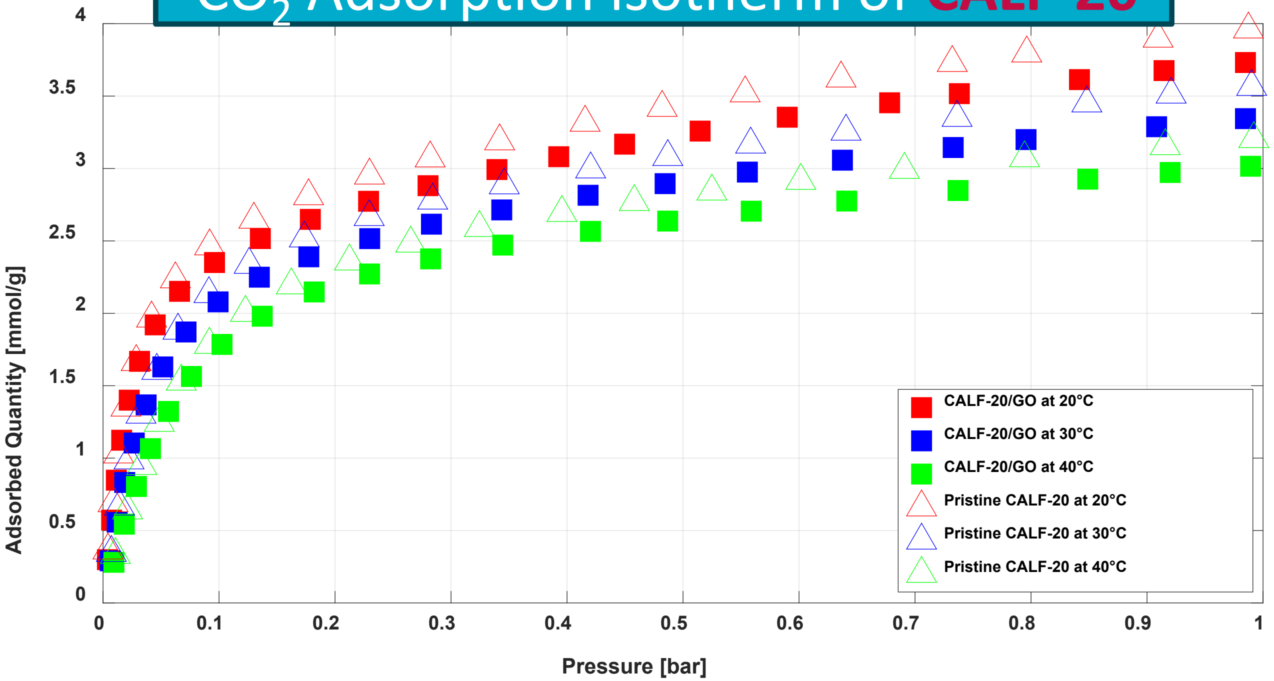
Adsorption capacity assessment

CO_2 Adsorption isotherm of MIL-120(Al)



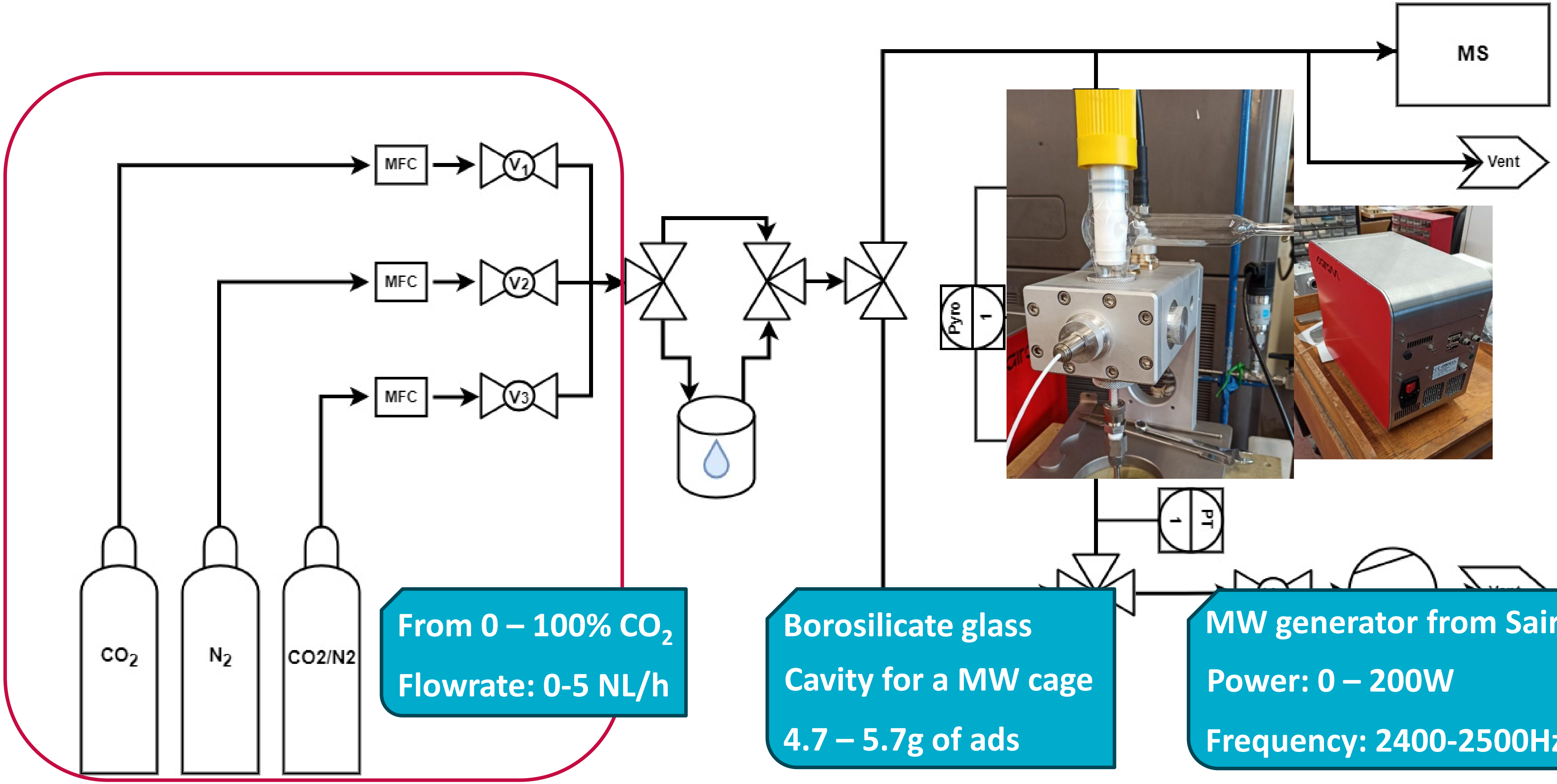
- Adsorption capacity at 30°C and 0.15 bar = 1.6 mmol/g
- No effect of the GO on adsorption capacity
- IAST Selectivity at 1 bar; 15%CO_2 and 30°C ≈ 90

CO_2 Adsorption isotherm of CALF-20



- Adsorption capacity at 30°C and 0.15 bar = 2.32 mmol/g
- Slight deterioration of adsorption capacity (around 6% loss)
- IAST Selectivity at 1 bar; 15%CO_2 and 30°C ≈ 260

Carbon Capture by Microwave Swing Adsorption

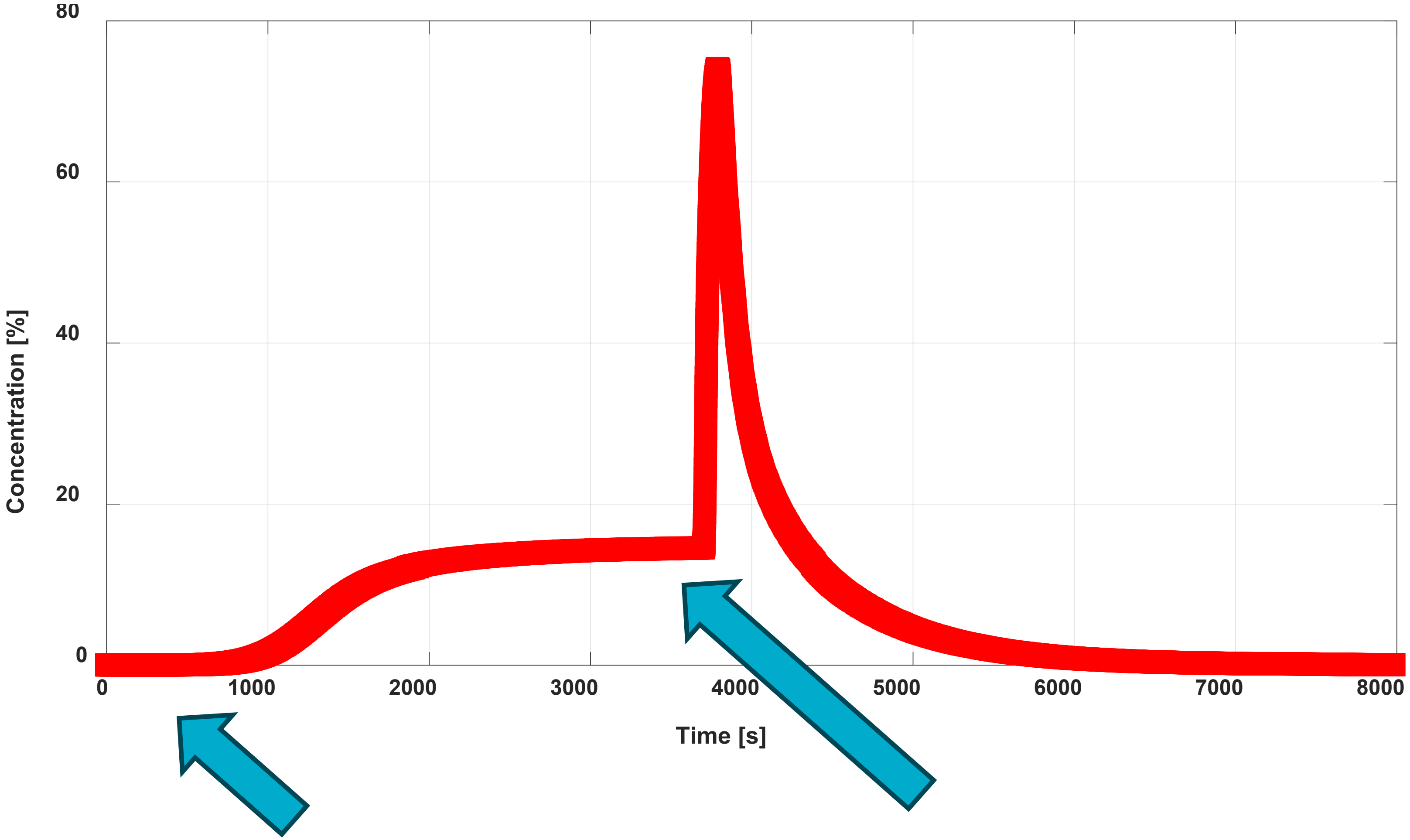


From 0 – 100% CO_2
Flowrate: 0-5 NL/h

Borosilicate glass
Cavity for a MW cage
4.7 – 5.7g of ads

MW generator from Sairem
Power: 0 – 200W
Frequency: 2400-2500Hz

Procedure for the MSA study



- Start of the adsorption with a 4 NL/h flowrate
- Start of the desorption (MW heating + N_2 flowrate)

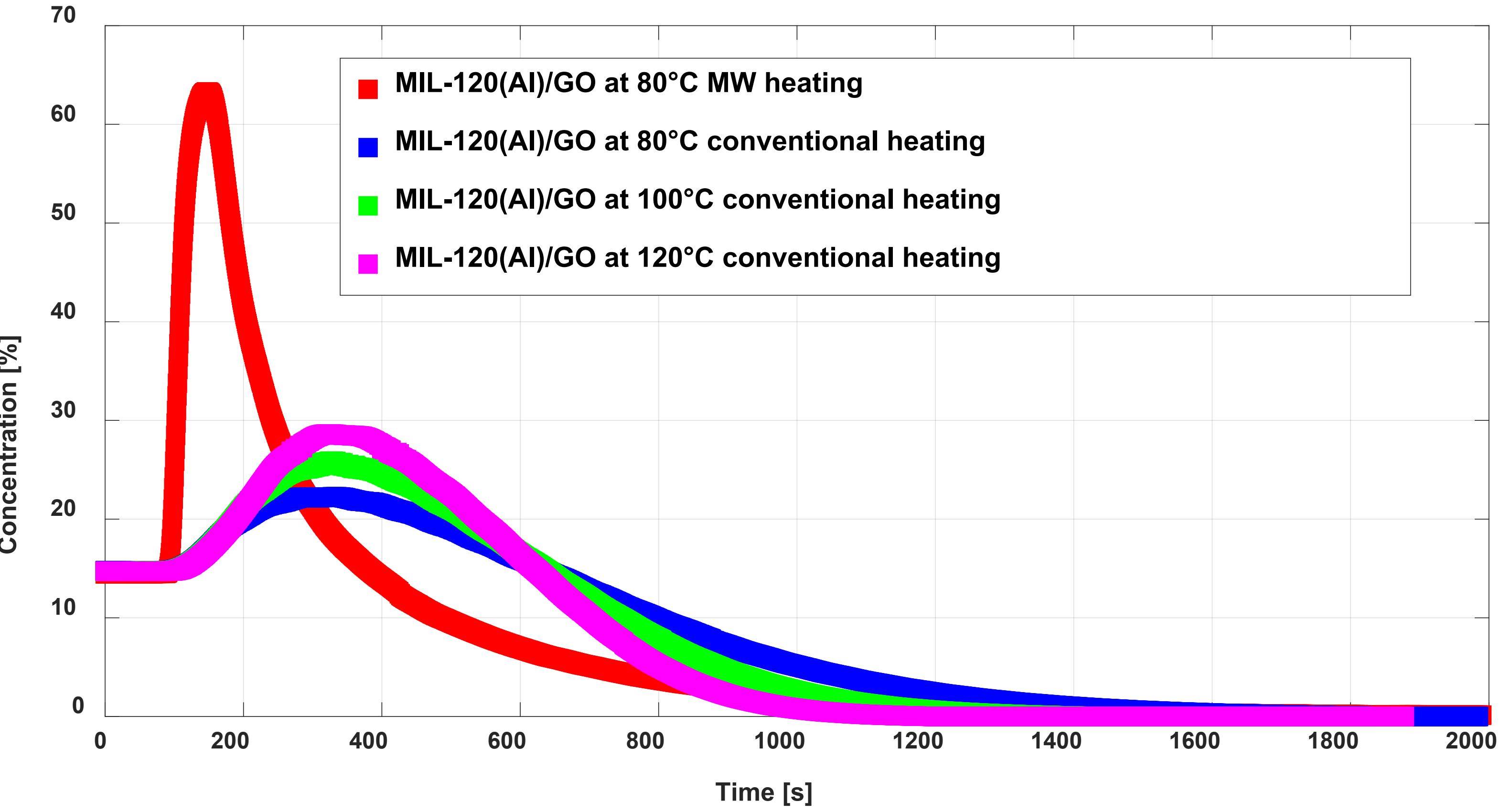
Measured parameters

- Outlet CO_2 and H_2O concentration
- Temperature inside the column
- Forward and reflected MW power

Studied parameters

- Inlet CO_2 and H_2O concentrations
- Desorption flowrate
- Desorption temperature

Carbon Capture by Microwave Swing Adsorption



Configuration:

- Conventional heating with an alumina column with corresponding dimensions, flowrates and temperature as the microwave heating

Results:

- Much quicker desorption with a microwave heating
- Stiffer and higher peak of CO_2 concentration
- Similar results already shown in previous study for MIL-91 (Ti) and UiO-66-btc (Zr)

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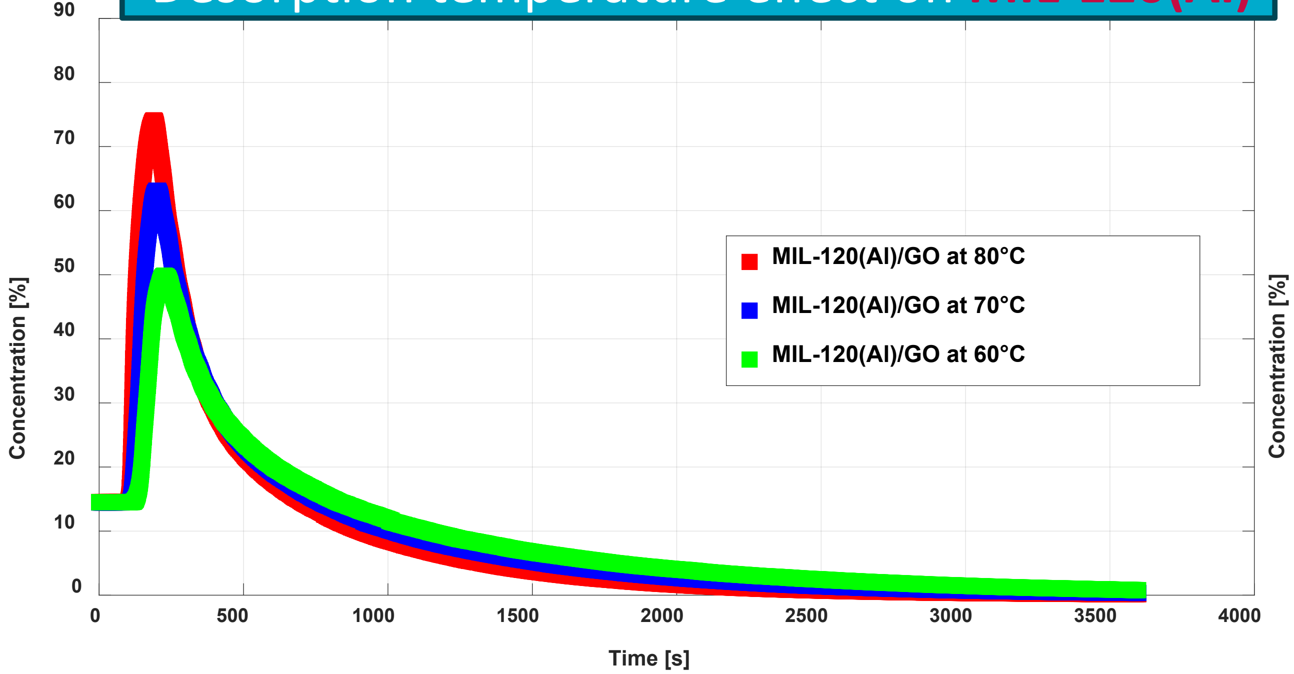
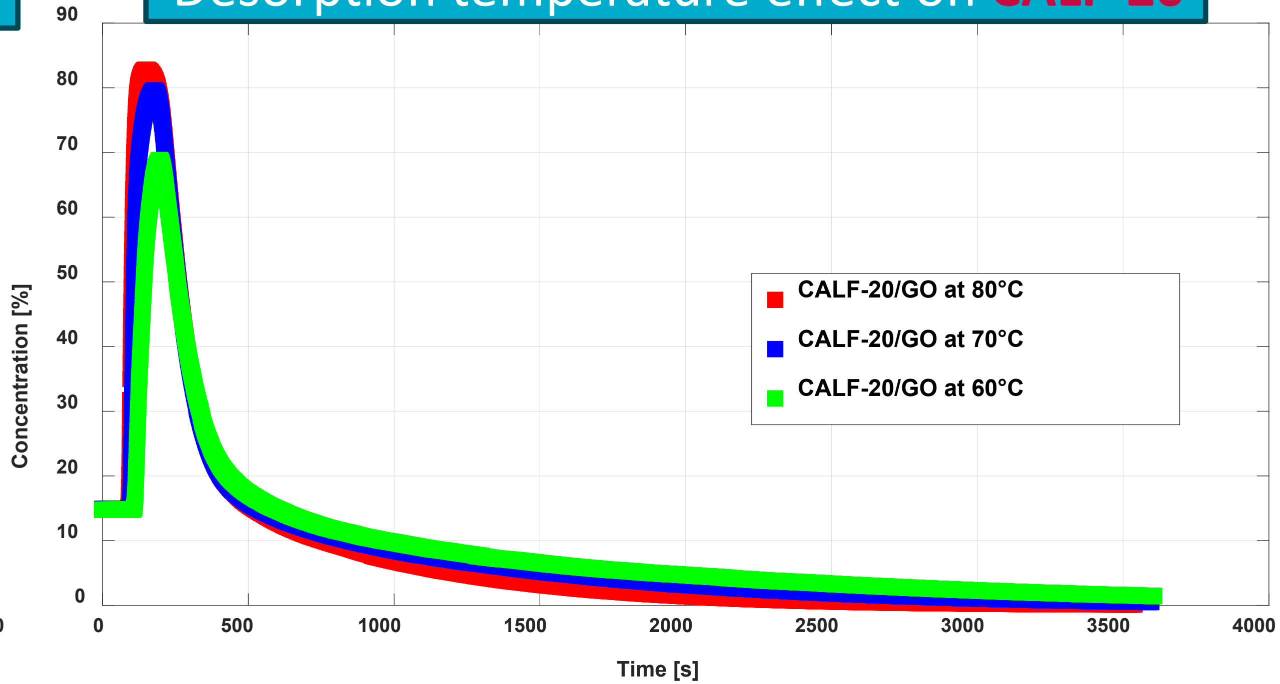
Screening of adsorption/MW desorption

Desorption temperature effect on **MIL-120(Al)**



Desorption temperature effect on **CALF-20**

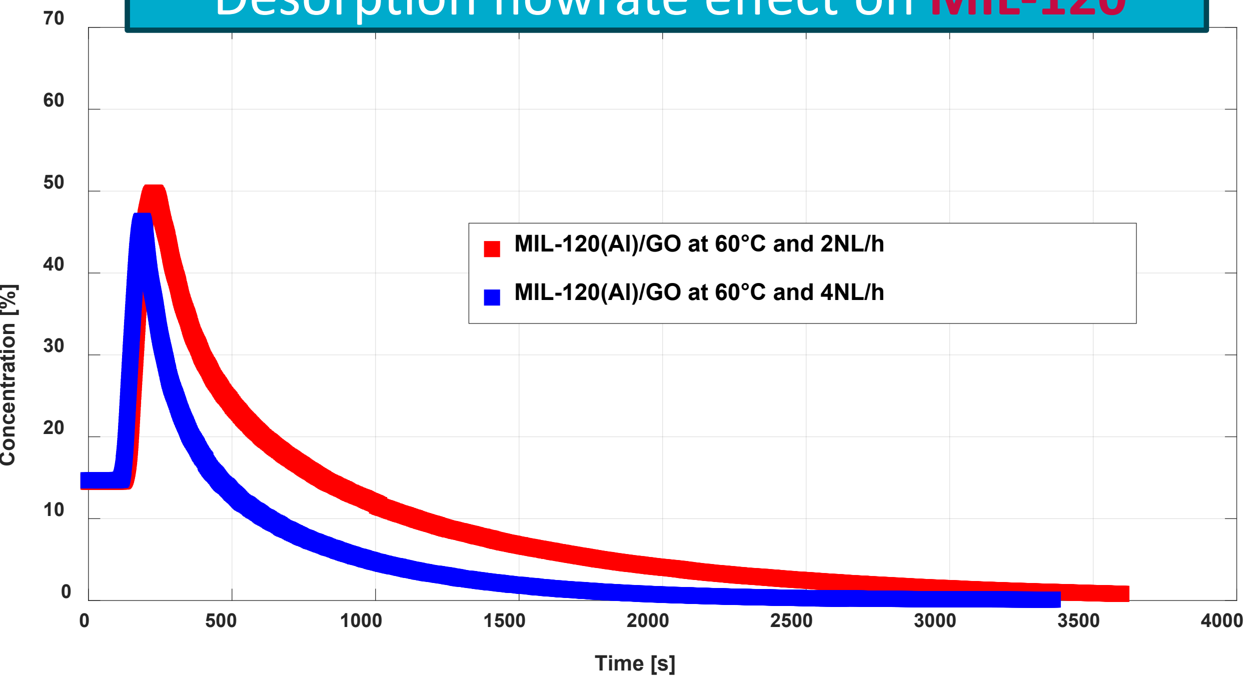


- Quicker desorption with the temperature
- More pronounced effect of the temperature

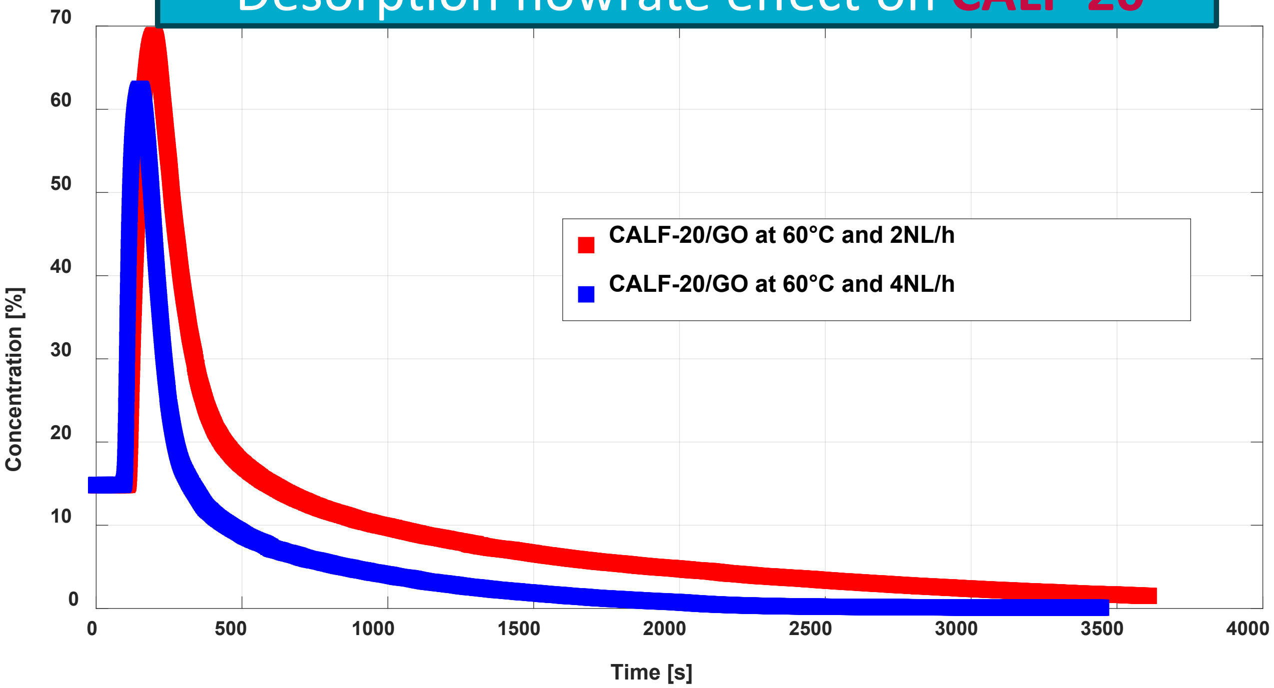
- Higher desorption peak
- Longer desorption time
- Smaller effect of the temperature
- Optimum around 70°C

Screening of adsorption/MW desorption

Desorption flowrate effect on **MIL-120**



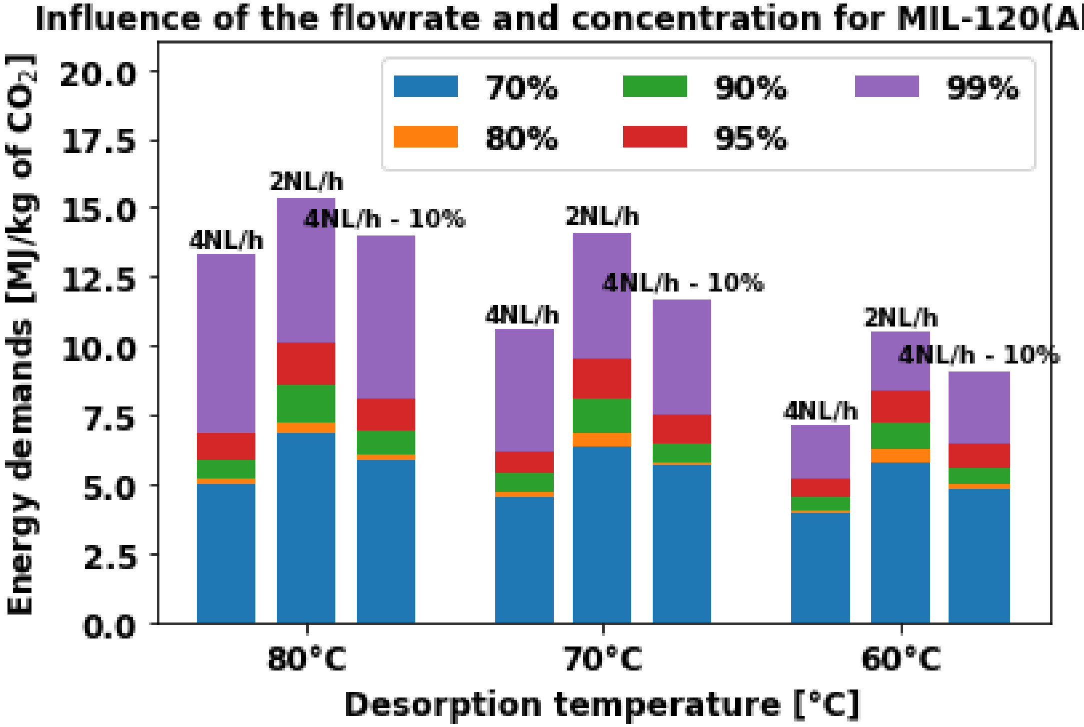
Desorption flowrate effect on **CALF-20**

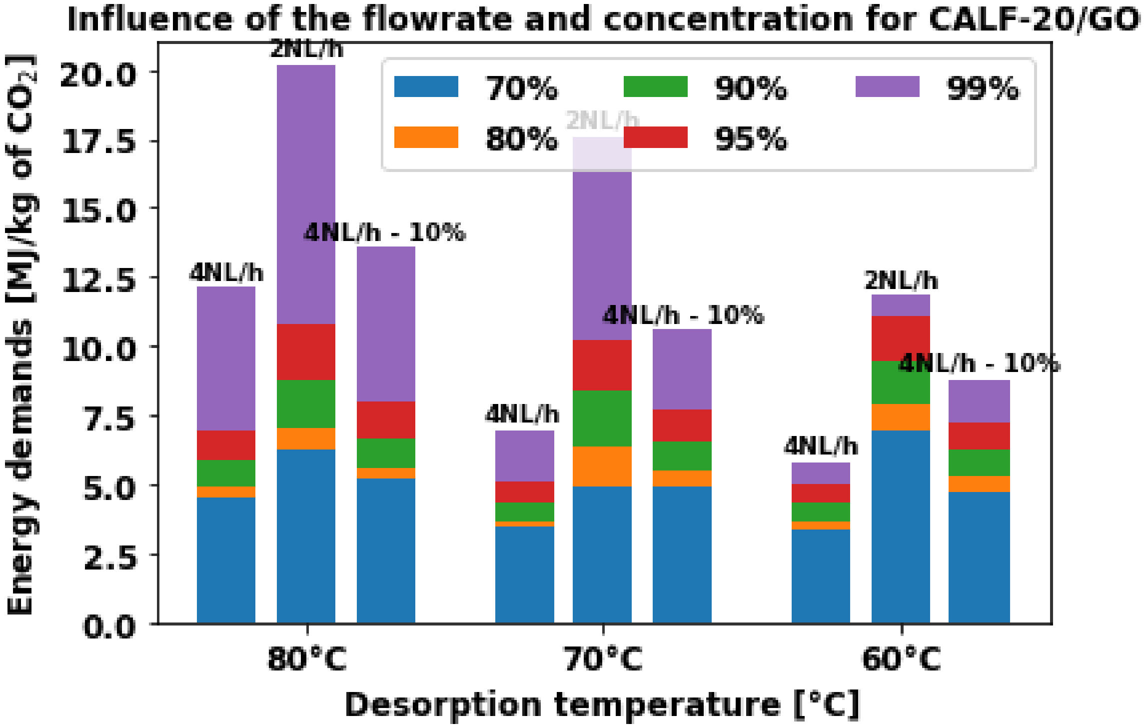


- Much quicker desorption with an increasing flowrate but smaller peak (more diluted CO_2)
- More pronounced effect of the flowrate than for the CALF-20

- Much quicker desorption with the flowrate but smaller peak (more diluted CO_2)
- Less pronounced effect of the flowrate than for the MIL-120 (Al)

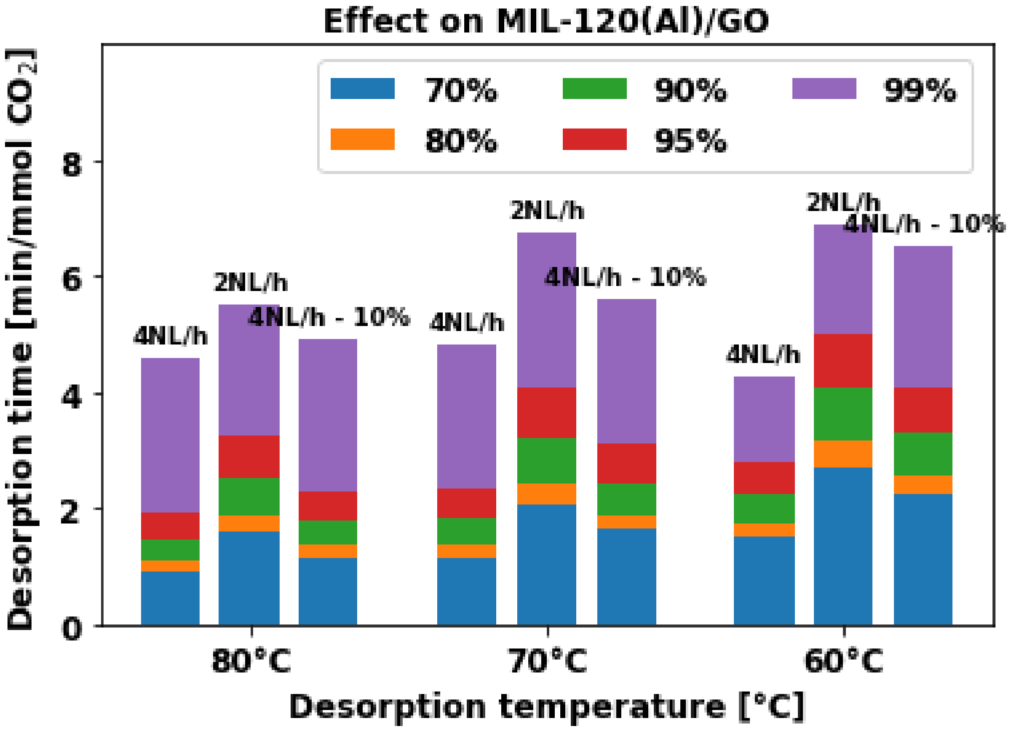
Energetic study – MW energy demands

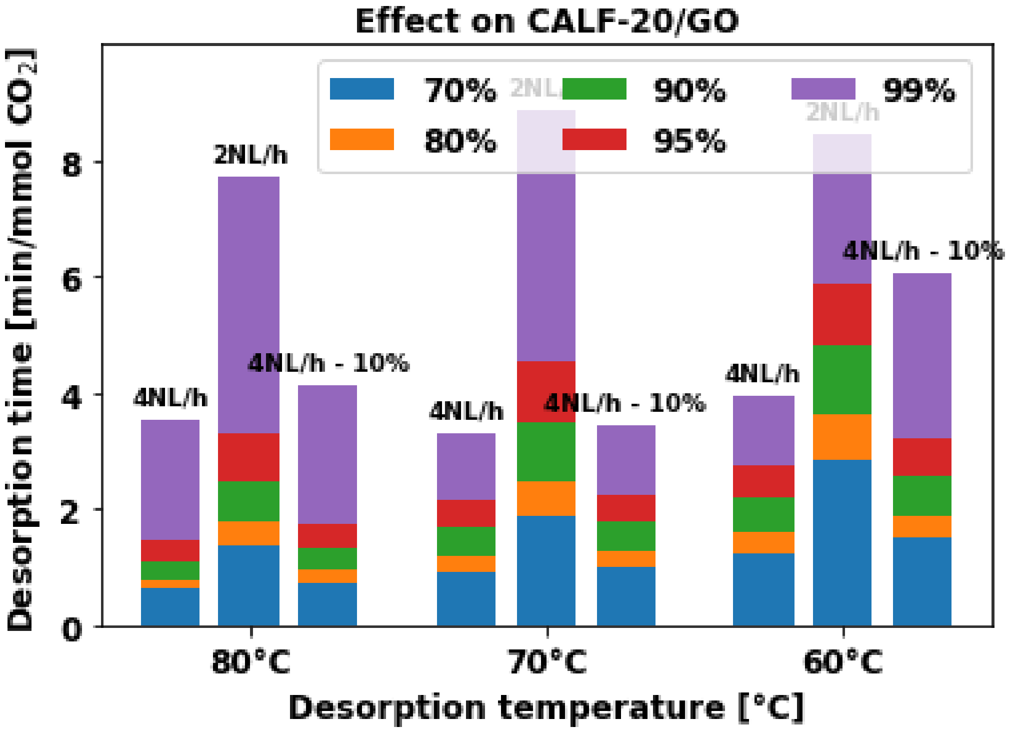




- Conventional carbon capture process does not regenerate all the adsorbent
- Recovering >95% of the adsorption capacity drastically increase the energy demands
- A bigger desorption flowrate decreases the energy demands
- The higher the saturation concentration, the more efficient the process is
- Q_{des} MIL-120(Al)/GO ≈ 6MJ/kgCO_2 >< Q_{des} CALF-20/GO ≈ 4MJ/kgCO_2 (90% recovery and 4NL/h)

Energetic study – desorption time

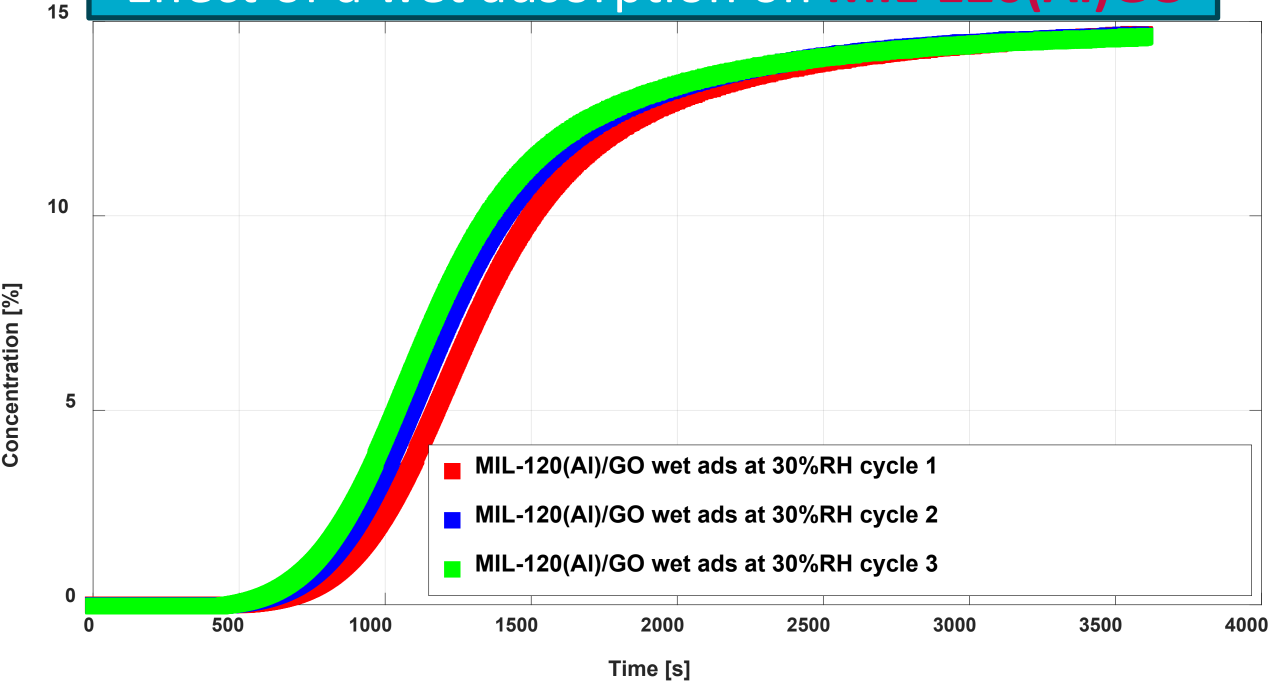




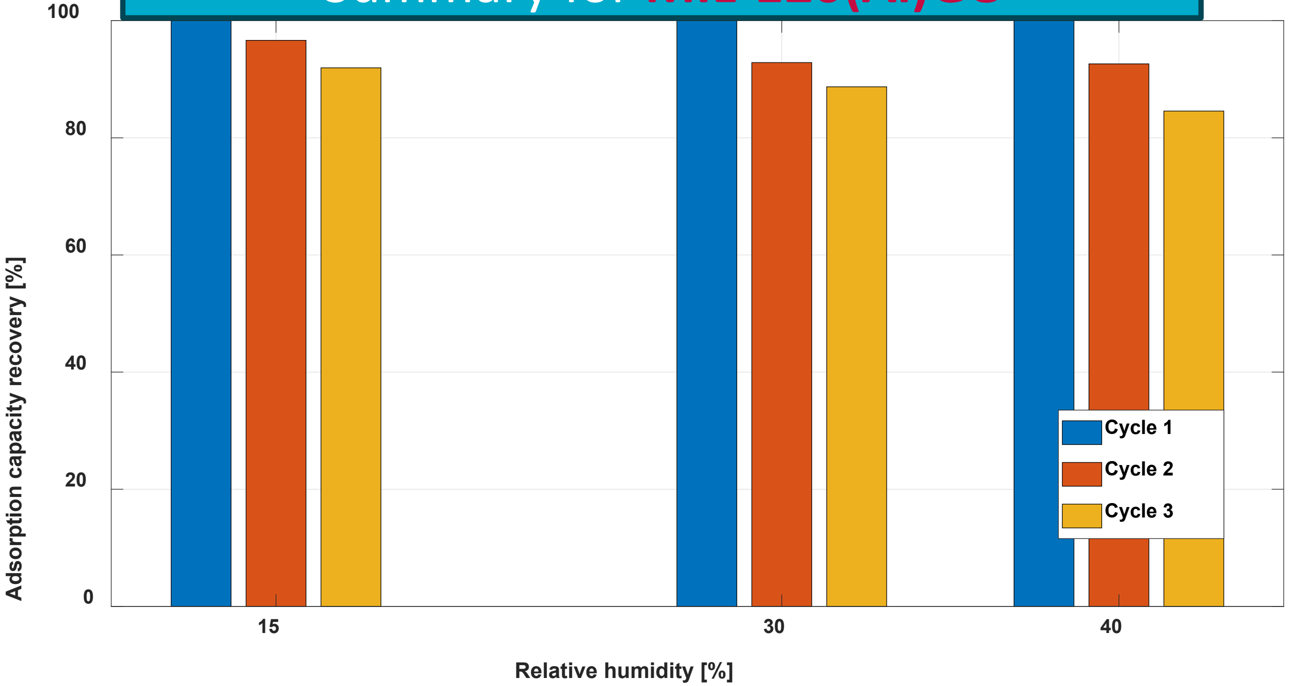
- A smaller desorption temperature looks better for the energy consumption, but it increases the desorption time
- A higher flowrate seems beneficial both for the desorption time and the energy but dilutes more the CO_2
- A lot of improvements are still to be made (higher flowrates, non fully saturated surface, …) to reduce the energy penalty

Cycling study of ads/des in humid conditions

Effect of a wet adsorption on **MIL-120(Al)GO**



Summary for **MIL-120(Al)GO**



- Carbon capture in wet conditions on the MIL-120 (Al)/GO decreases the adsorption capacity at each cycle (1h at 80°C for the desorption)
- The higher the relative humidity the stronger the effect
- Water removal on MIL-120 (Al) is significantly harder than for CALF-20
- A higher temperature is required which increases the energy consumption

Conclusions and Perspectives

- ➢ A lab-scale microwave pilot has been developed for carbon capture
- ➢ Microwave Swing Adsorption seems promising to drastically reduce the desorption time of TSA processes
- ➢ A selection of MOF’s have been made to synthesize a composite with graphene oxide for MW absorption namely CALF-20 and MIL-120 (Al) → New additives are in study
- ➢ A study of the adsorption/desorption behavior for both composites has been conducted to determine the influence of the desorption temperature, the flowrate and the gas concentration
- ➢ An energetic study shows promising results but that an optimum is yet to be found between the working capacity, the desorption conditions, the times of heating/cooling, … → an optimization of the cycling capture is in progress
- ➢ The carbon capture in humid condition has been firstly assessed, and a higher desorption temperature seems to be needed to recover the adsorption capacity → coupling water/MW is in study

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MOF's characterization

- S. Devautour-Vinot

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