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Adsorption as a tool for design of new adsorbents and processes

Cécile Daniel

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Adsorption as a tool for design of new adsorbents and processes

Dr Cécile DANIEL, Ircelyon

Kyoto, 22/10/2020

Experimental parameters

Components

1: Adsorption

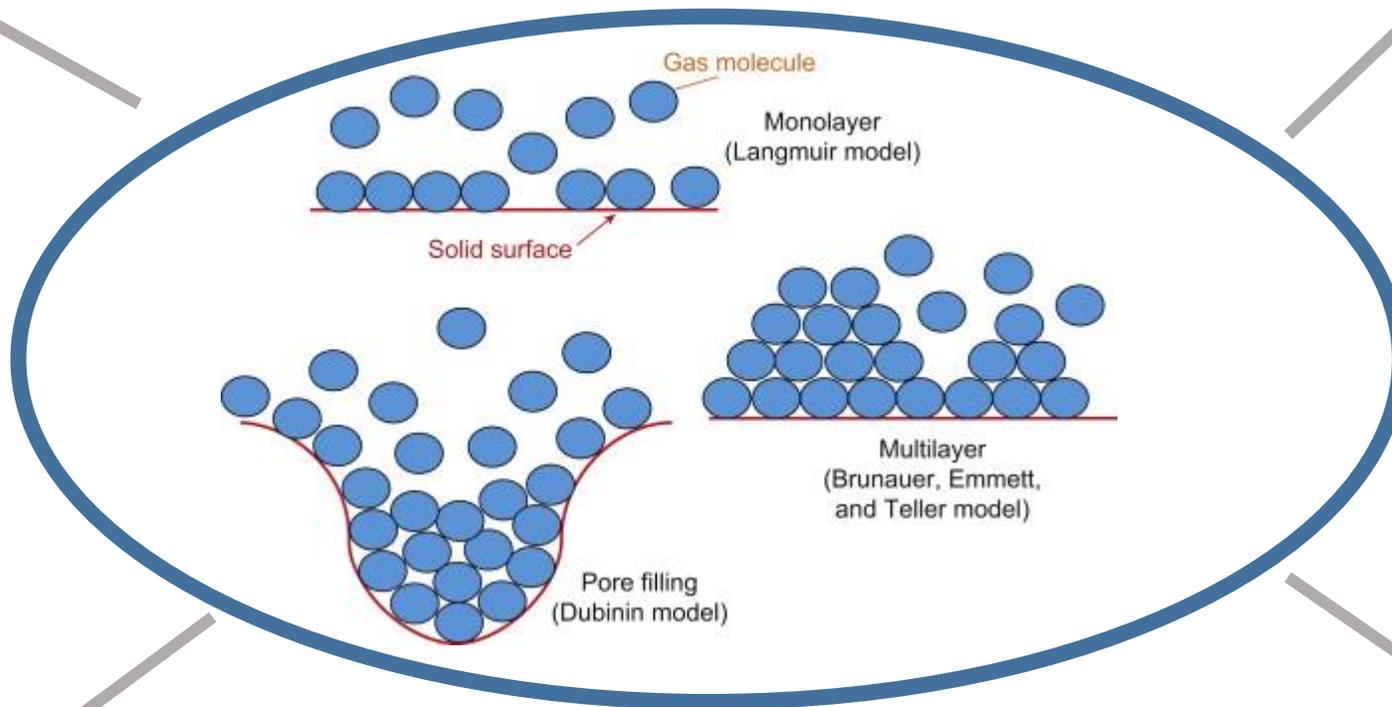
2 and more: Coadsorption

Fluid phase

gas

vapor

liquid



Method

Static

Dynamic

Pressure

1 bar

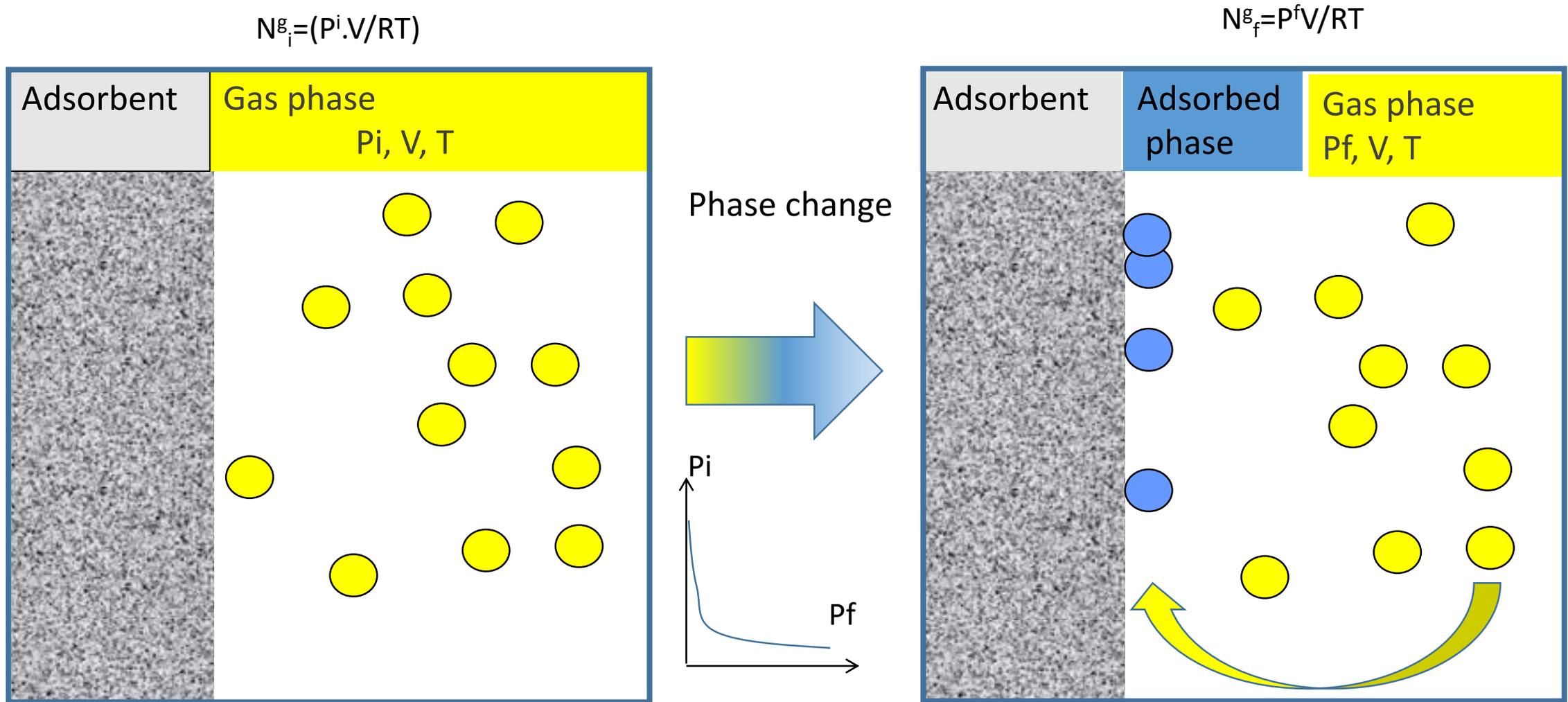
30... 200 bar

Temperature

...77K

...0 TO 80°C

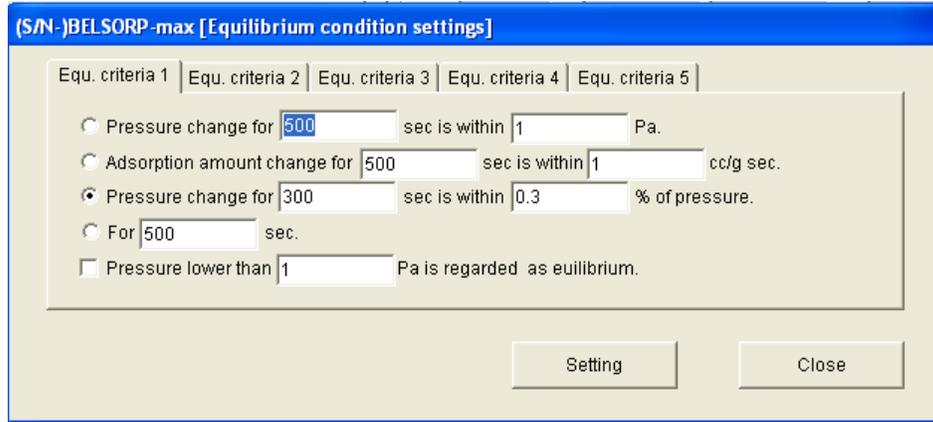
Static measurements in a closed vessel



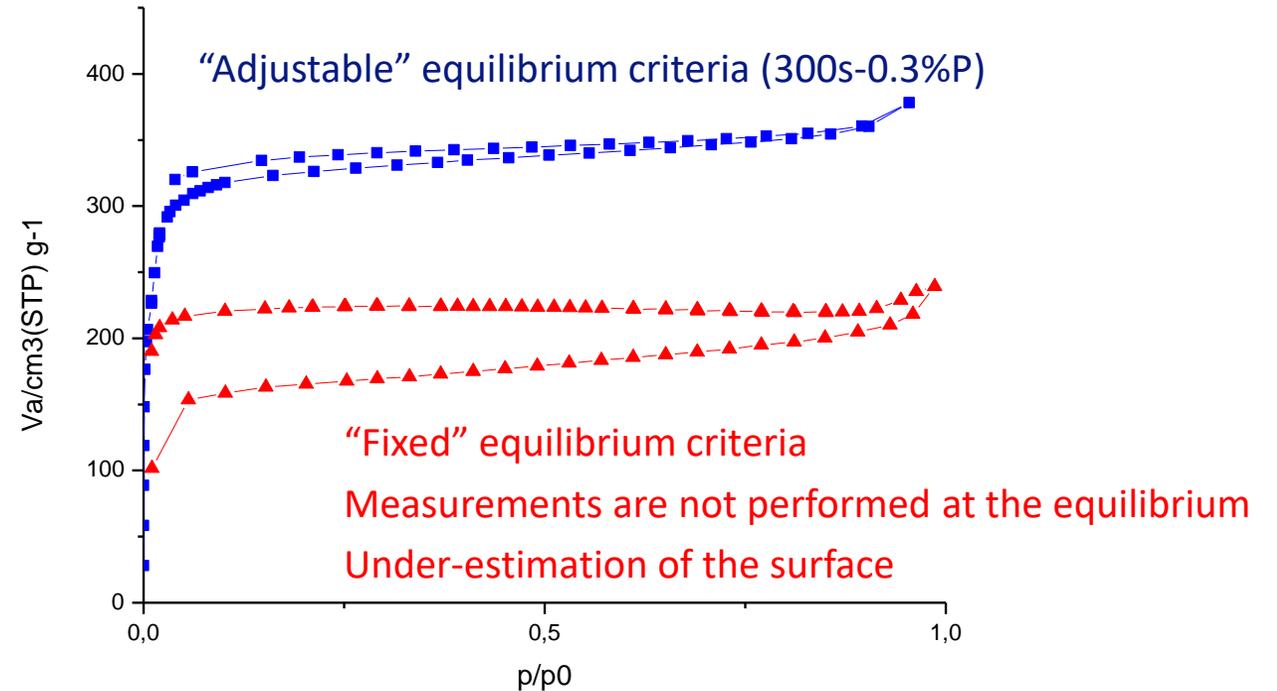
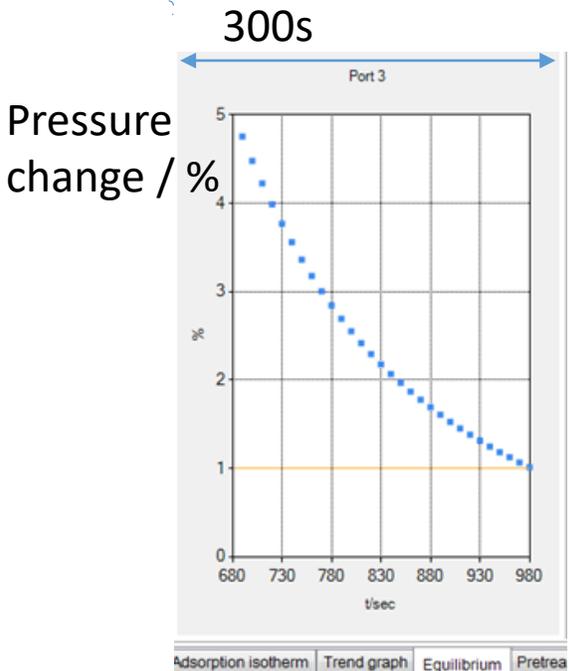
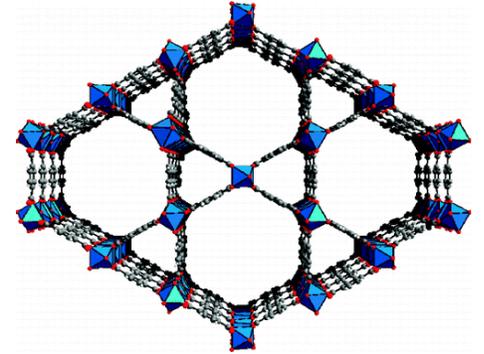
Ideal gas, isothermal

$$N_{ads} = (P_i - P_f) \cdot V / RT$$

Adsorption isotherm: equilibrium criteria



MIL-68-In
(Extremely slow up-take)

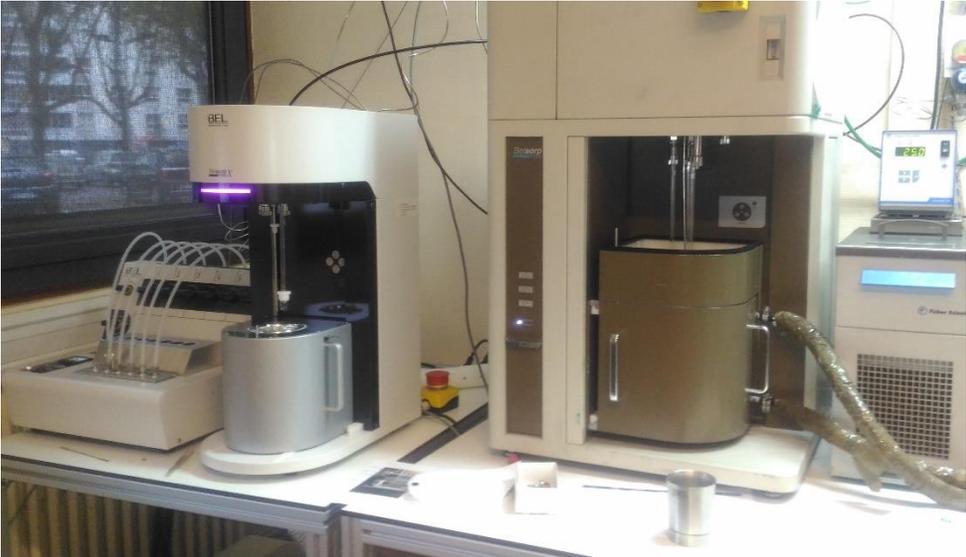


CNRS facilities in Lyon

Static adsorption equipments (MICROTRAC BEL)



Belsorp Mini



Belsorp MiniX

Belsorp Max



Belsorp HP # 30 bar



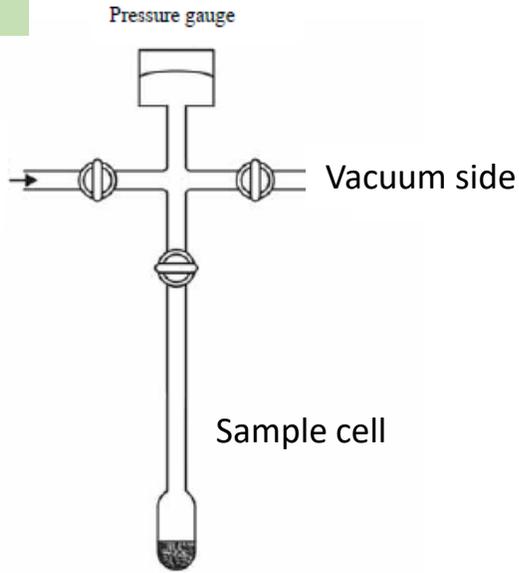
Belsorp Max 2

Static versus dynamic

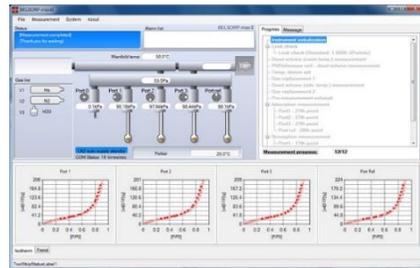
STATIC

Single component

ADSORPTION



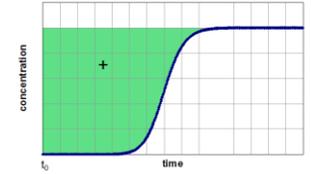
- Ideal conditions
- Under vacuum
- Pures gases: a single component
- Accurate amounts
- Adapted to Screening: MULTIPORT INSTRUMENTS



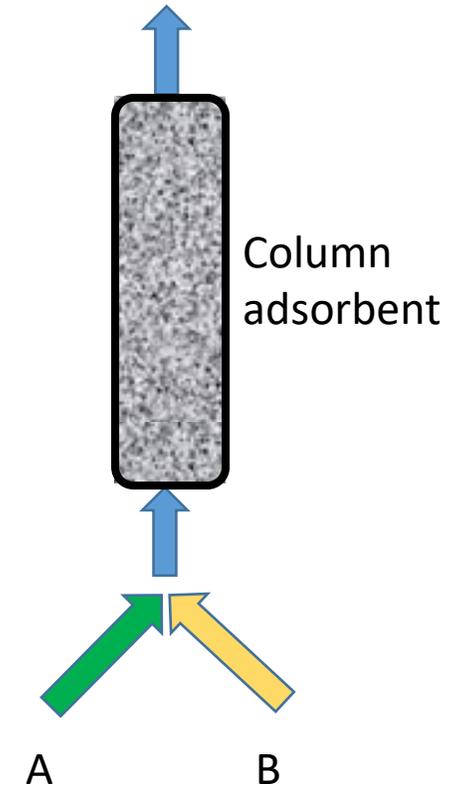
DYNAMIC

ADSORPTION
AND
COADSORPTION

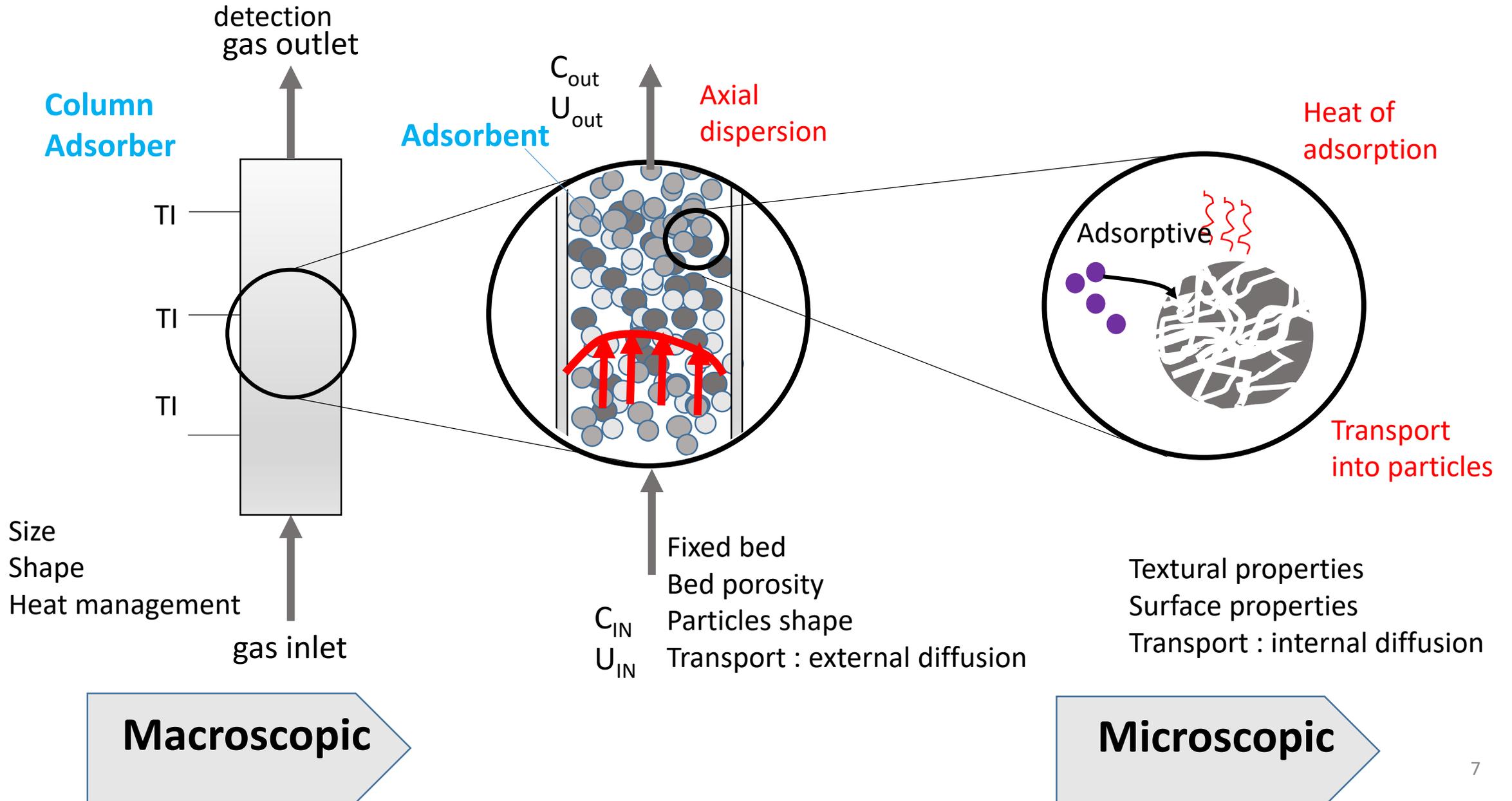
- Real conditions:
- Under flow
- gas mixture possible
- Selectivity & hydrodynamic
- Integrated amounts
- Specific detection required



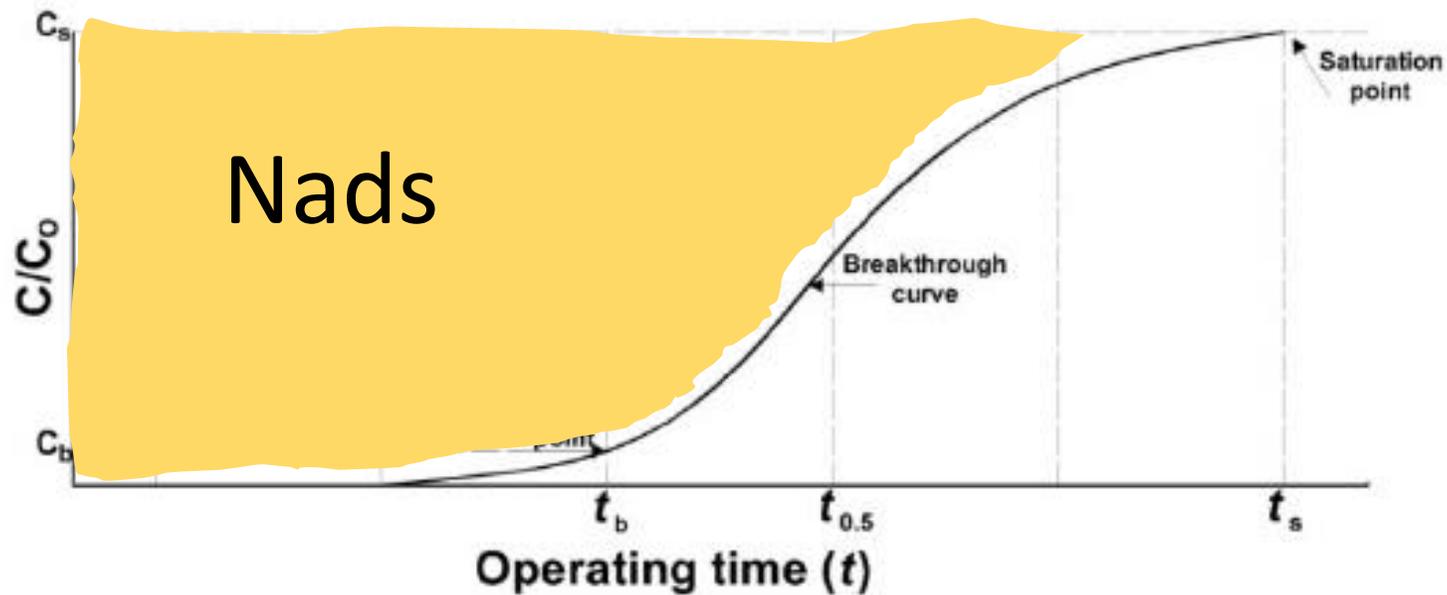
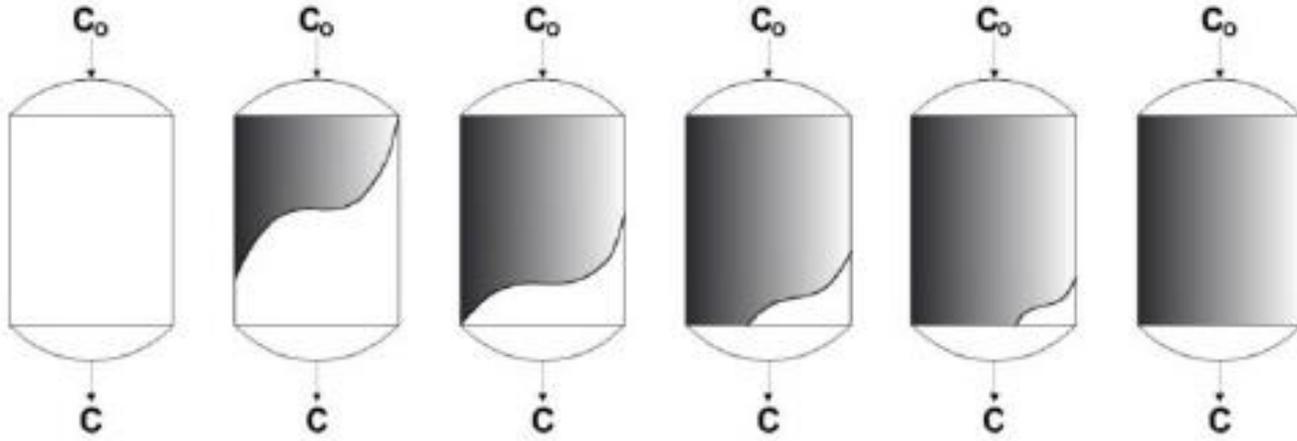
Detection



Dynamic experiments : multiscale process



Breakthrough experiment



Quantification : Integration

$$\int \varphi(t).dt = Nads$$

Dynamic experiments : Keys for reliable measurements

Chemical engineering basics:



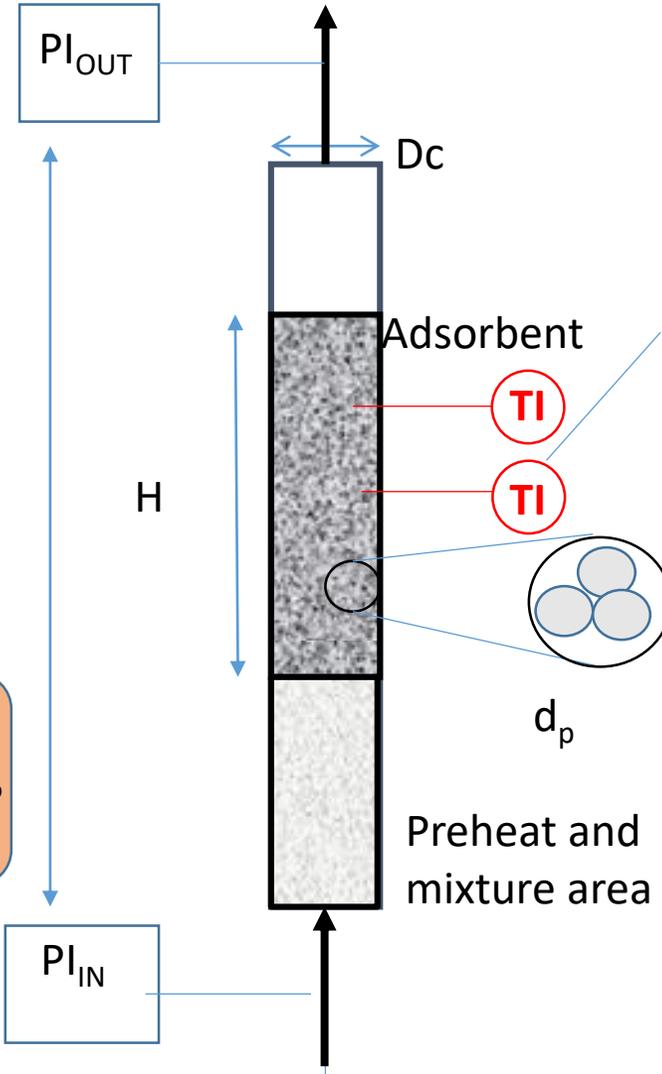
$$H/d_p \gg 50$$

$$H/D_c \gg 5$$

$$D_c/D_p \gg 10$$

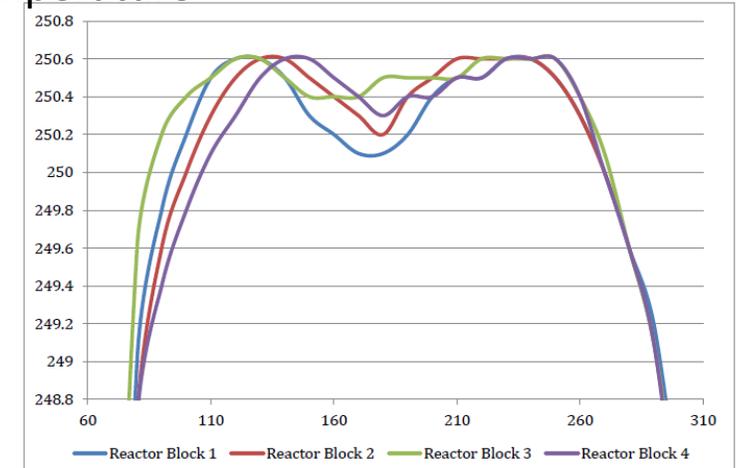
ΔP Pressure drop

Limit pressure drop
100m bar pressure drop @1 bar = 10% deviation!



Adsorption is exothermic =>
Check fixed bed temperature : Hot points
Measure axial profile of temperature

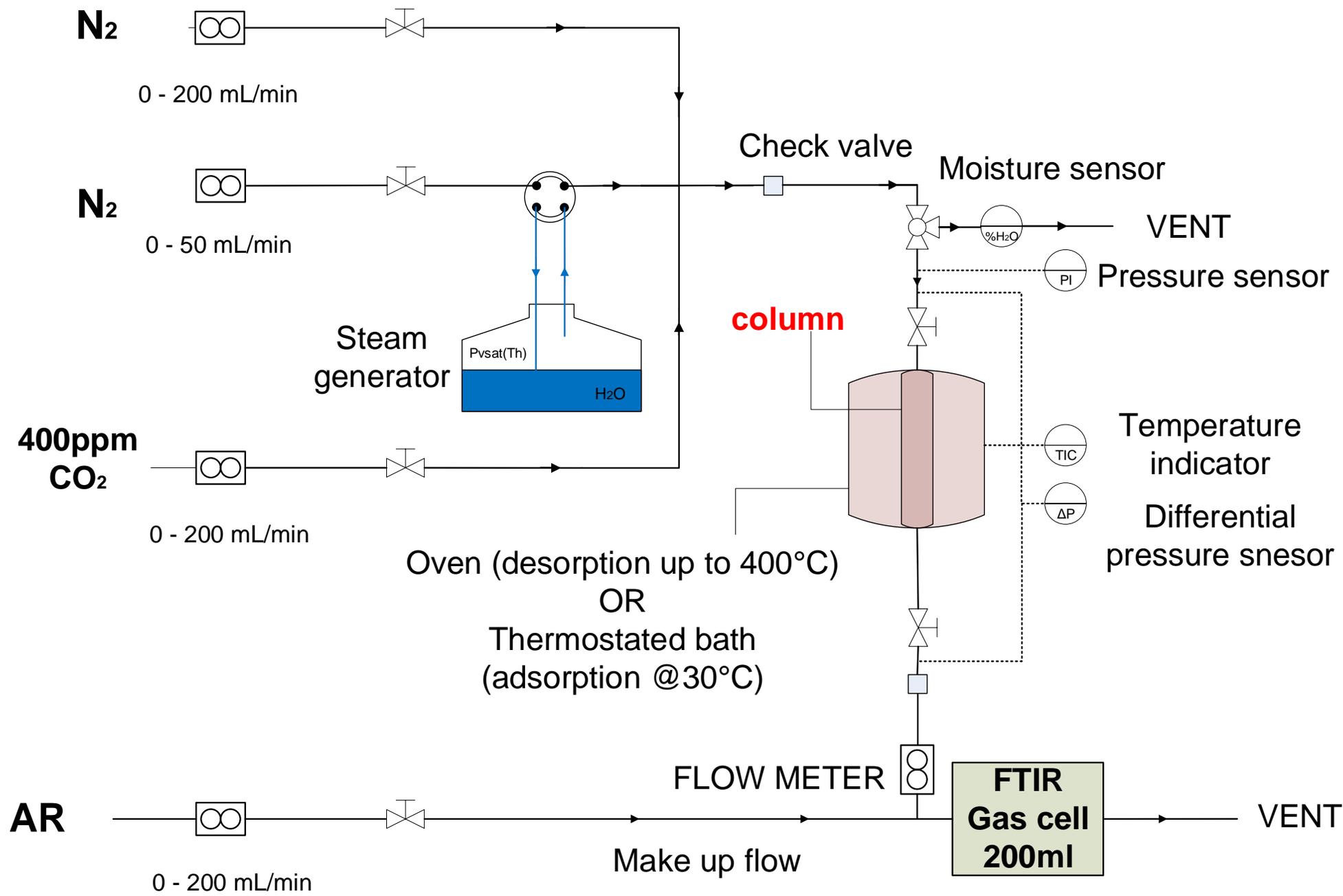
Temperature



Isothermal zones @250°C

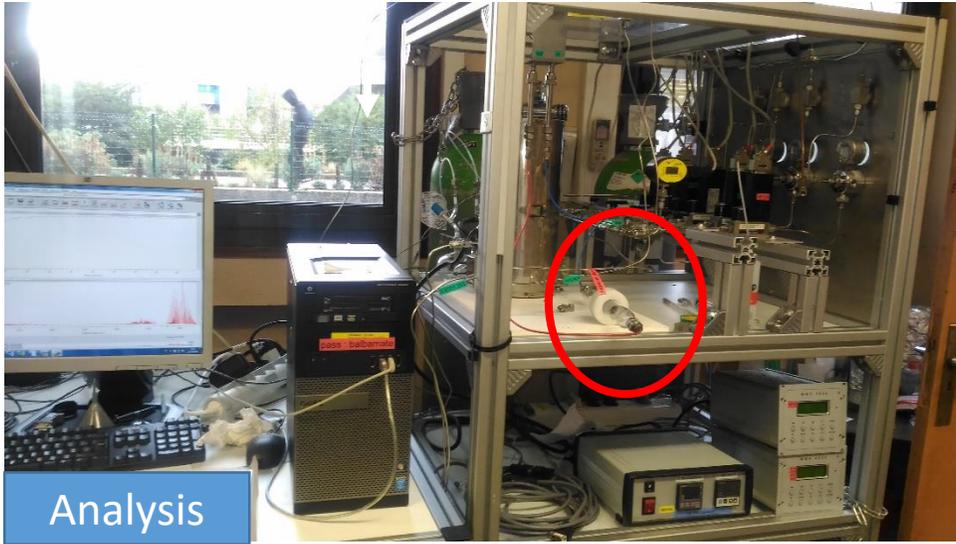
Axis length (cm)

Dynamic experiments : breakthrough equipment



CNRS facilities in Lyon

Dynamic measurements: home-made instruments



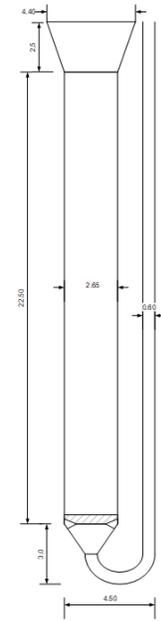
Powder breakthrough

#100mg



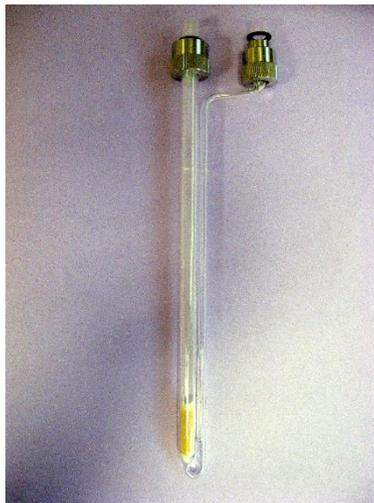
Pellets breakthrough

#10g



Reactor height = 23cm

Fixed bed height = 7mm



For each application scale a new design is required !
-Mass flow
-reactor(s)
-oven(s)



Cases studies

	Static	Dynamic
<ul style="list-style-type: none"> ▪ Measurements of porosity of composites <ul style="list-style-type: none"> -H₂O isotherms vs N₂ isotherms 	✓	
<ul style="list-style-type: none"> ▪ Screening of adsorbents at ppm level <ul style="list-style-type: none"> -Very low pressure isotherms 	✓	
<ul style="list-style-type: none"> ▪ Selection of adsorbents for a process <ul style="list-style-type: none"> -Henry vs IAST vs breakthrough 	✓	✓
<ul style="list-style-type: none"> ▪ Evaluation of Heat of adsorption at low pressure 		
<ul style="list-style-type: none"> ▪ Coadsorption with water <ul style="list-style-type: none"> ▪ Case of CO₂ capture ▪ Case of NH₃ adsorption 	✓	✓ ✓

Measurement of porosity : N₂ @77K

Shaped MOF : the CAU-10-H case



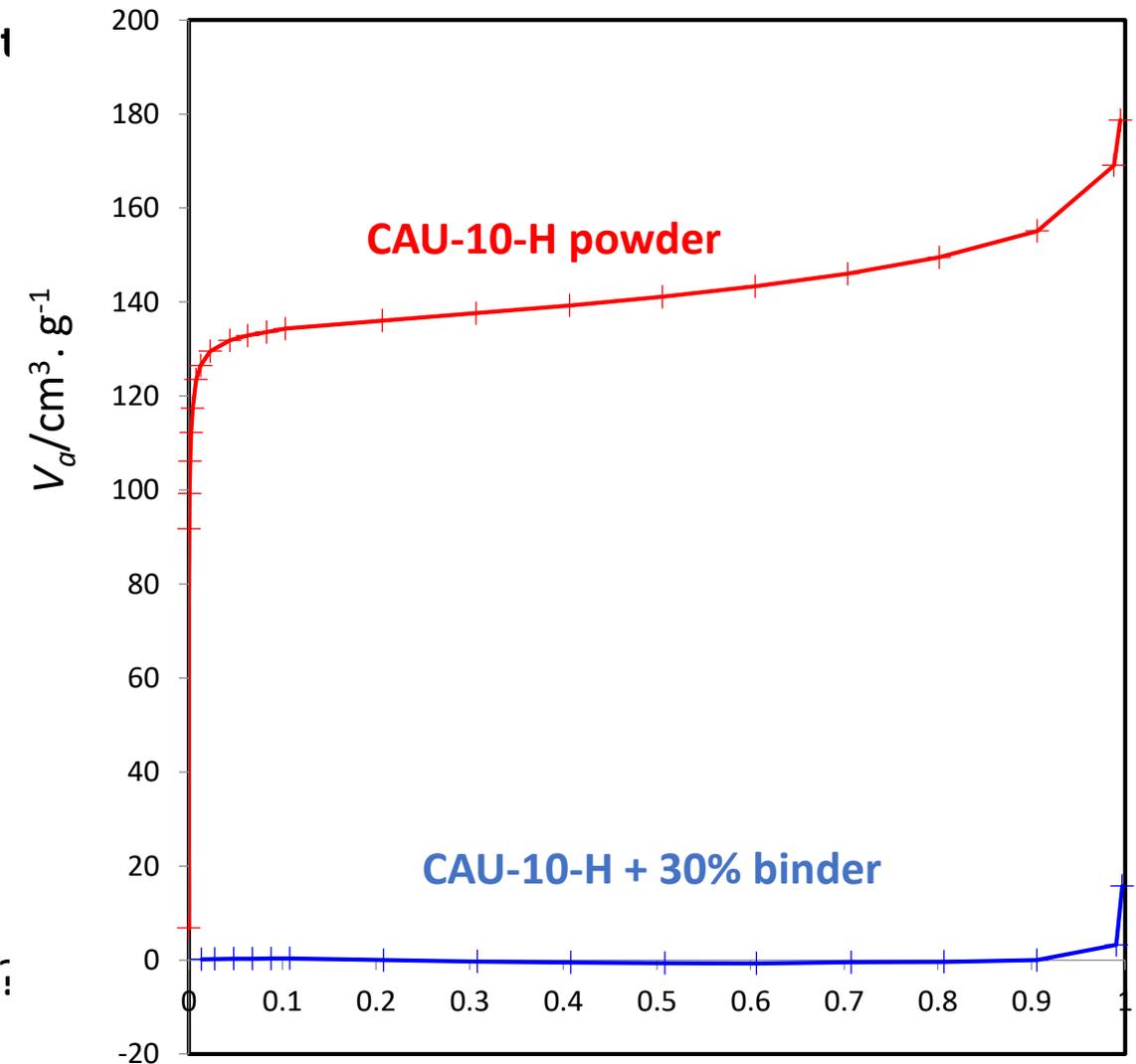
ProDIA

PROduction, control and DEMonstration of structural adsorption Applications (ProDIA)

- CAU-10-H: Al-based MOF
- Powder too fine to be densified
- Compression results in highly friable pellets: need to use a binder
- CAU-10-H + a silicone-based binder (70/30wt%),
 - Leads to an homogeneous and tough coating (1mm)
 - Easy to grind and shape again by pelletization,

BUT ... → Porosity not accessible at 77K (SSA = 1m².g⁻¹) ???

N₂ adsorption isotherm @77K



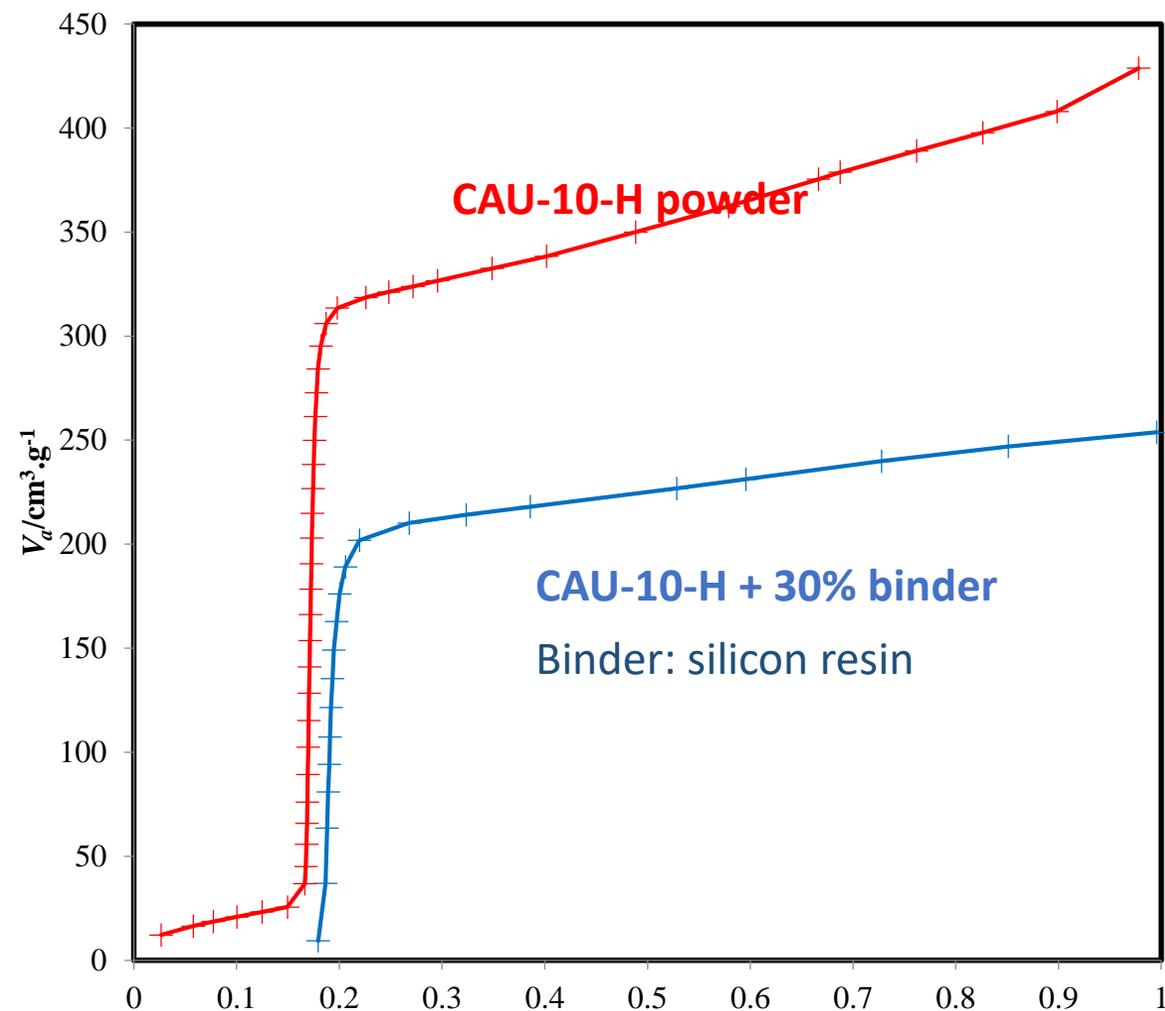
Measurement of porosity : H₂O @303K

Shaped MOF : the CAU-10-H case

- Porosity accessible at 303K to H₂O and comparable to CAU-10-H powder (-30%).
- Porosity not accessible at 77K to N₂ : pores are blocked by the binder

H₂O isotherm @30°C enables to check porosity

H₂O adsorption isotherm @303K



Screening of new adsorbents : Xe capture at ppm level

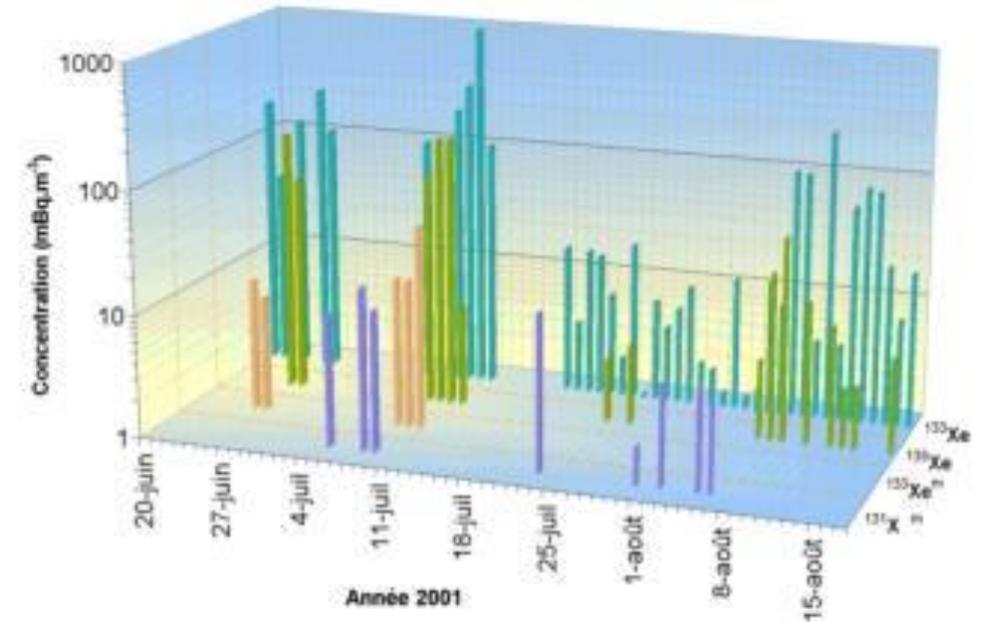
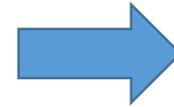
-Context: Comprehensive *nuclear* Test ban Treaty (CTBT)

-**SPALAX (CEA)** : on site Radio Xenon survey around nuclear sites by **Continuous separation and monitoring of radio Xenon**

Xe in air
87 ppb



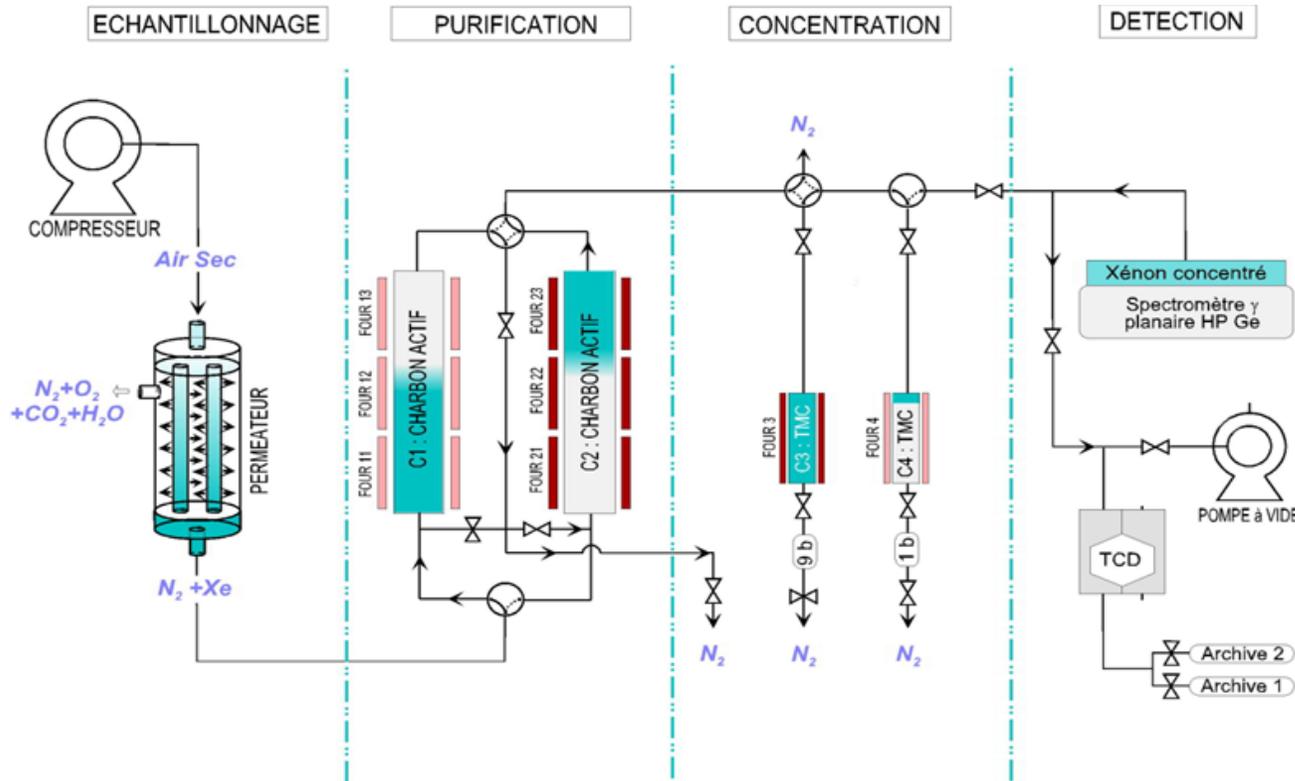
SPALAX: Super-concentrator of Xe: enrichment of 3.5 million times from Xe sampled



Analysis of 4 radioactive isotopes of xénon (^{131m}Xe , ^{133}Xe , ^{133m}Xe , ^{135}Xe),

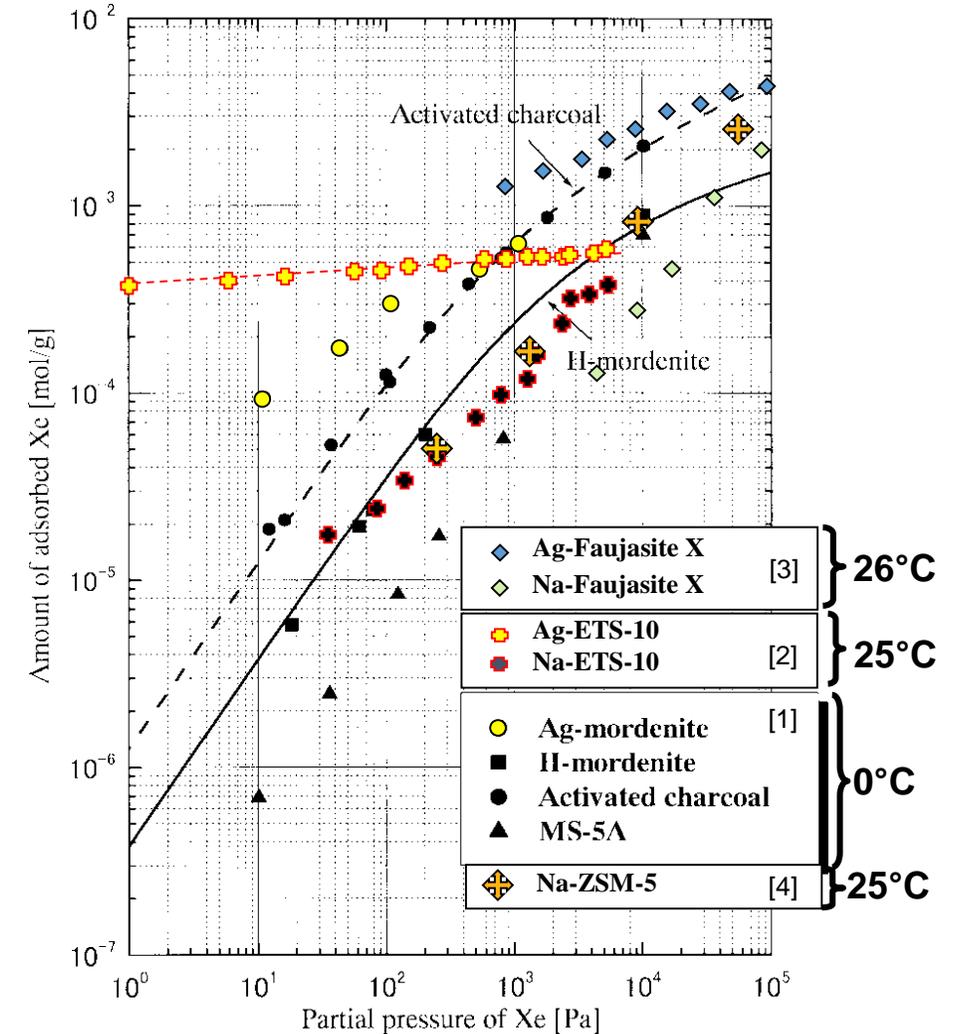
SPALAX

Process diagramm [5]



SoA

- Need of new adsorbents with wider heat of adsorption
- Reduction of adsorbent column volume in SPALAX

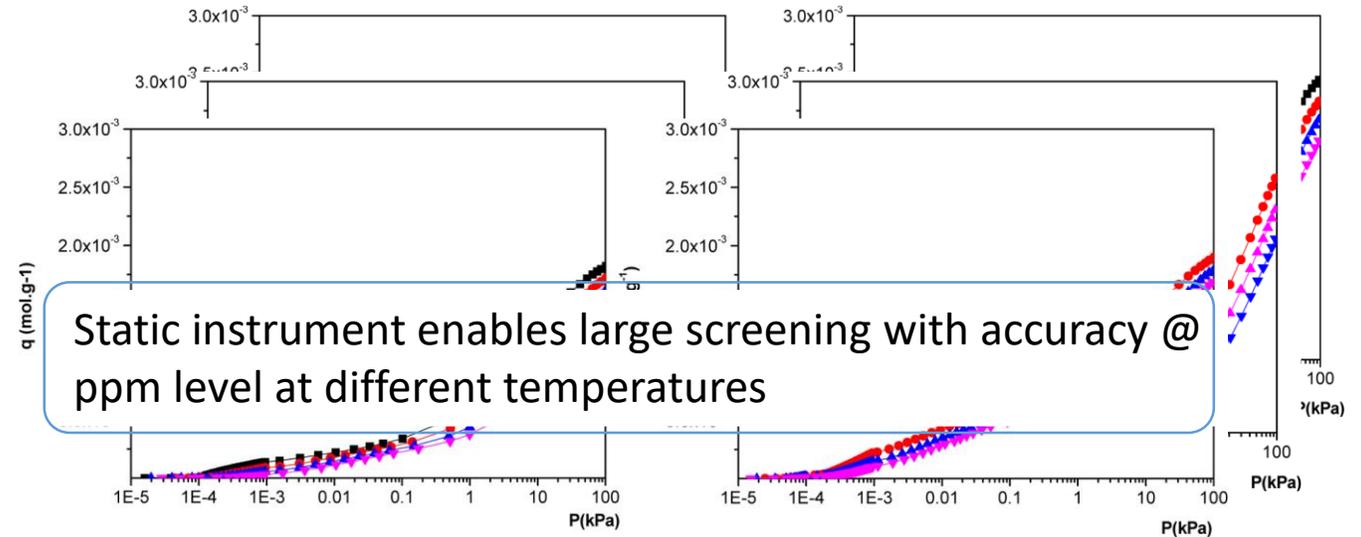


[1] K. Munakata, et al.. J. Nucl. Sci. Tec. **40** 9 (2003) p. 695
 [2] S.M. Kuznicki, et al.. J. Phys. Chem. C **111** 4 (2007) p. 1560
 [3] R. Grosse, et al., J. Phys. Chem. **95** (1991) p. 2443
 [4] Q.Chen , et al. J. Phys. Chem. **96** (1992) p. 10914
 [5] J.-P. Fontaine *et al.*, J. Environ. Radioact. **72**, 129-135, 2004

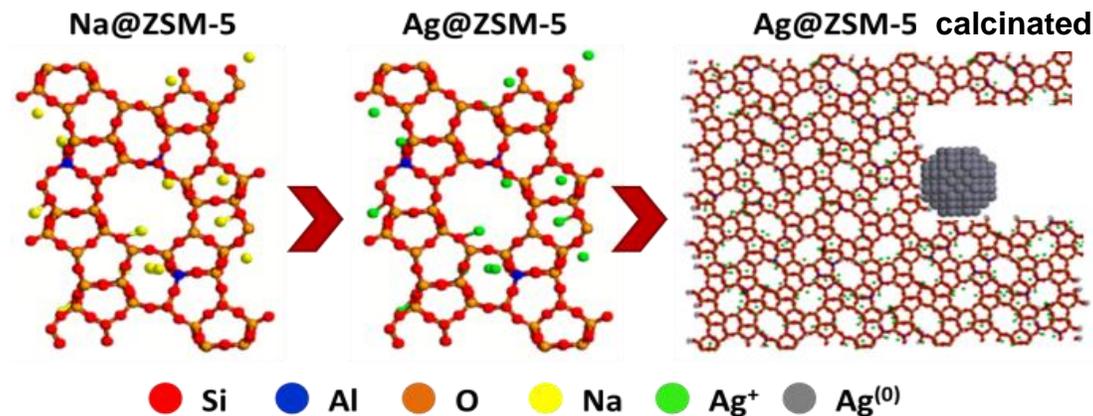
Screening of new adsorbents for Xe capture at ppm level

Screening of zeolites

sample	parent zeolite	structure
NaAgX	NaX	FAU
AgX	NaX	FAU
NaAgY	NaY	FAU
AgY	NaY	FAU
NaAg-PZ2-25	Na-ZSM-5 (25)	MFI
Ag-PZ2-25	Na-ZSM-5 (25)	MFI
NaAg-PZ2-40	Na-ZSM-5 (40)	MFI
Ag-PZ2-40	Na-ZSM-5 (25)	MFI
NaAg-PB	Na-Beta	Beta
Ag-PB	Na-Beta	Beta



✓ Identification of Ag-ZSM5 zeolite [1]

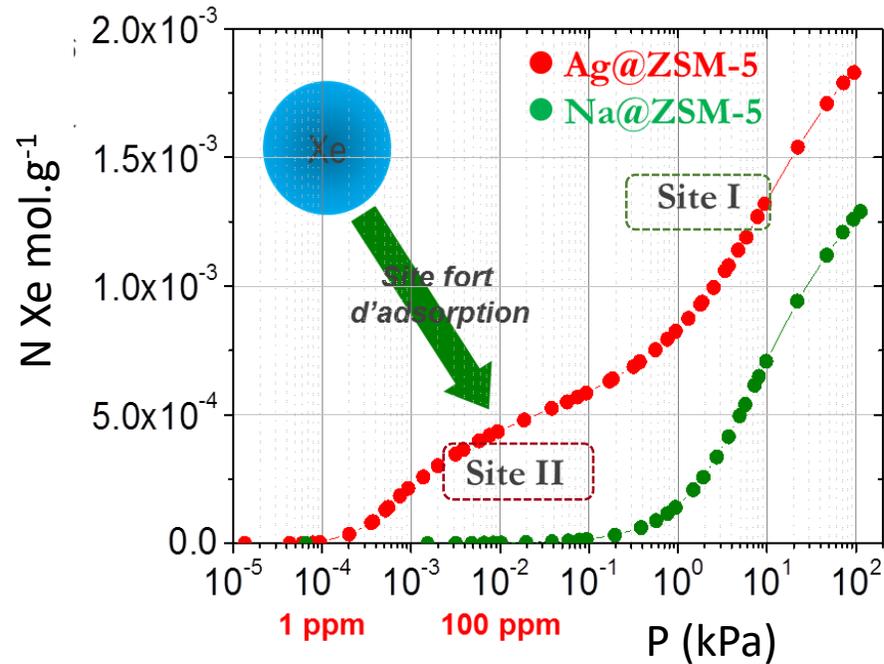


-Best adsorbent for rare gas
-Reduction of bed size from on order of magnitude

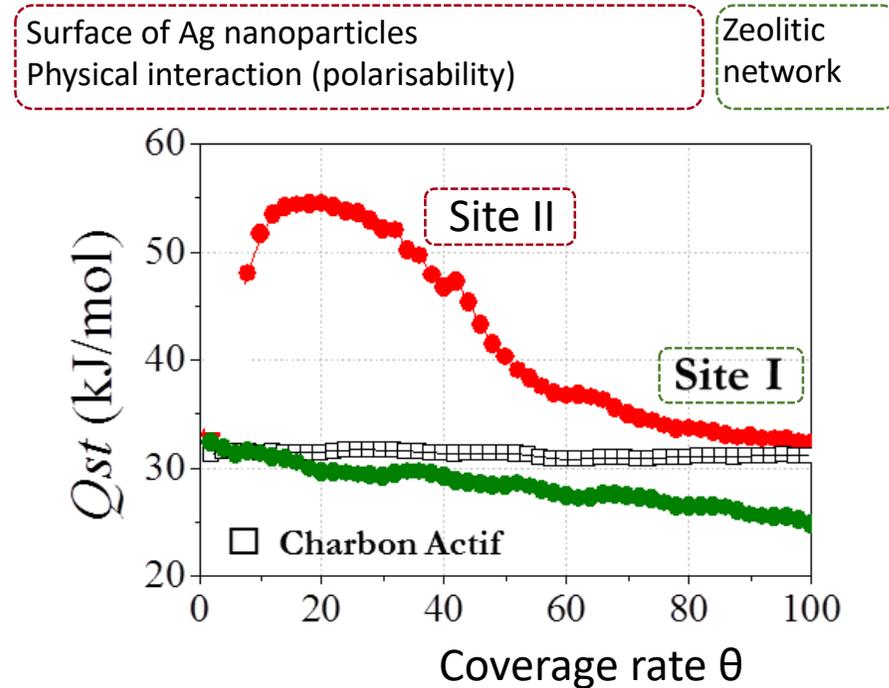
[1] C. Daniel *et al.*, J. Phys. Chem. C 117, 15122–15129, 2013

Adsorption of Xe on Ag@ZSM5: dual-site mechanism

Xe adsorption isotherms on Ag@ZSM-5 [1]



Heat of adsorption of Xe on Ag@ZSM-5 [2]



2 sites of adsorption
Strong sites of adsorption @ low concentration (1ppm-100ppm)

[1] C. Daniel *et al.*, J. Phys. Chem. C 117, 15122–15129, 2013

[2] L. Deliere *et al.*, J. Phys. Chem. C 118, 25032–25040, 2014

Selection of adsorbent for a process



Adsorbent choice:

- Stability
- Volumic mass
- Cost
- **Capacity**
- **Selectivity**

How to predict

Capacity ?

N adsorbed
Mol.g⁻¹

Selectivity A/B ?

$$S_{AB} = \frac{(x_A/x_B)}{(y_A/y_B)}$$

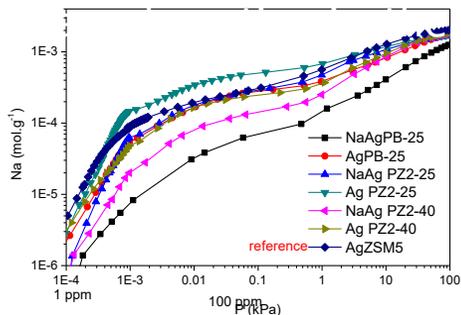
Molar ratio in adsorbed phase

Molar ratio in gas phase

Adsorption isotherms

- easy measurements
- high throughput
- ideal

Coadsorption



Prediction by gaz mixture models

Henry

- low partial pressure
- does not take into account coadsorption

Ideal Adsorbed Solution Theory (IAST)

- predict mixed-gas adsorption isotherms from a set of pure-component adsorption isotherms
- takes partially into account coadsorption

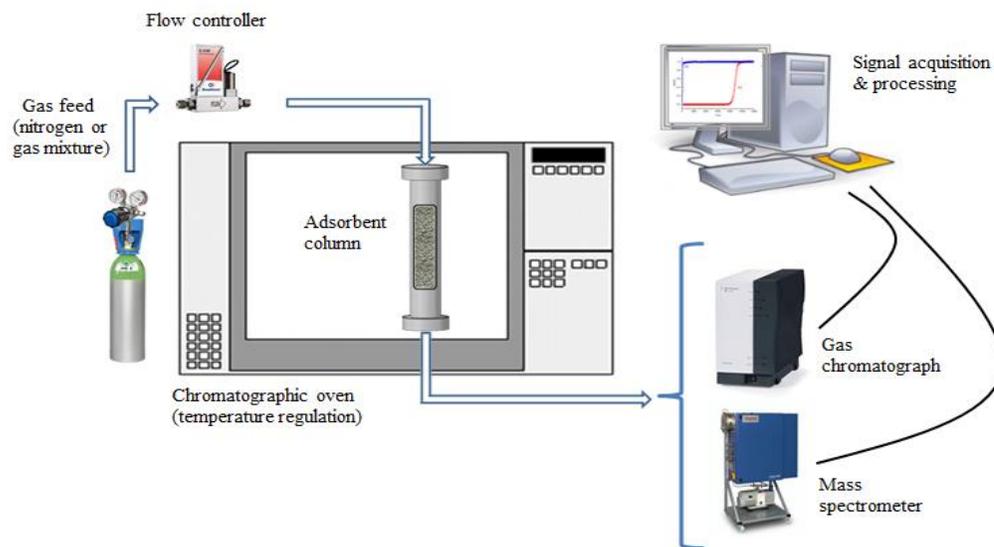
Evaluation methods for adsorbents: breakthrough

Case study : Separation of Xe and Kr in N_2 for gas separation in nuclear fuel reprocessing plant

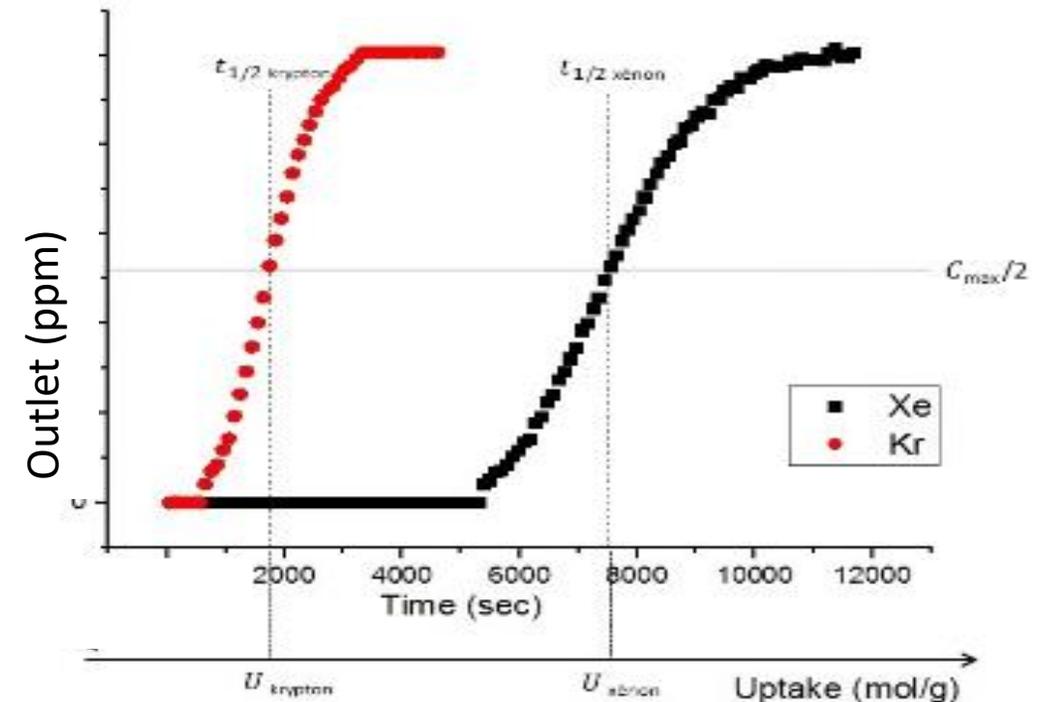
-Mixture : 400ppm Xe / 40ppm Kr in N_2

- Adsorbents : Active carbon (Ac) and Silver-exchanged zeolite

Dynamic flow apparatus

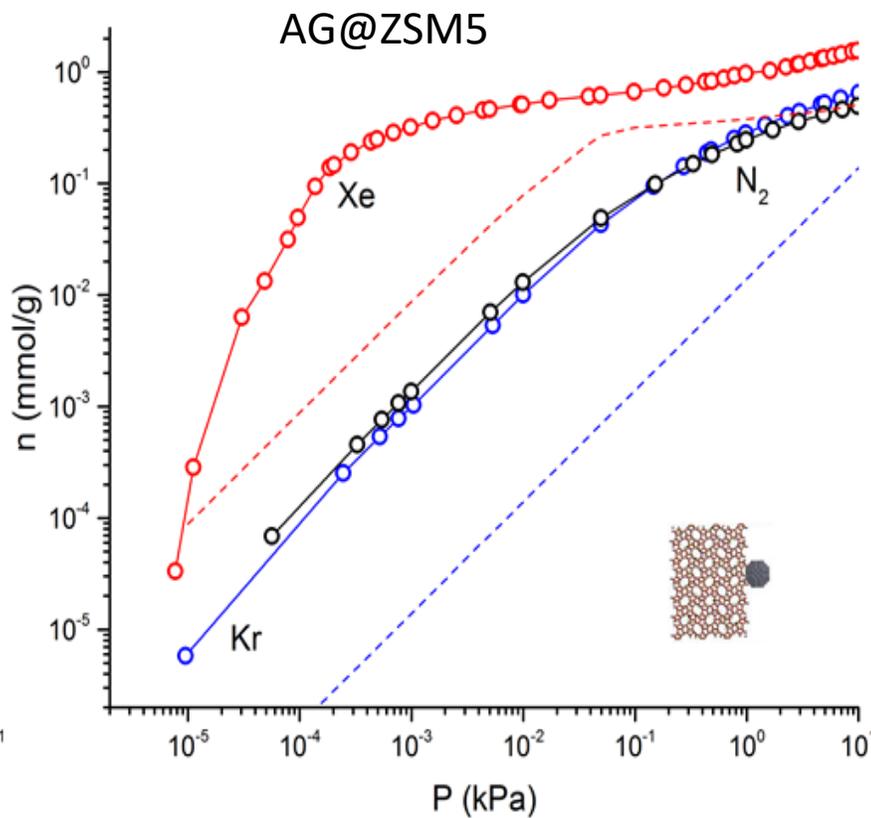
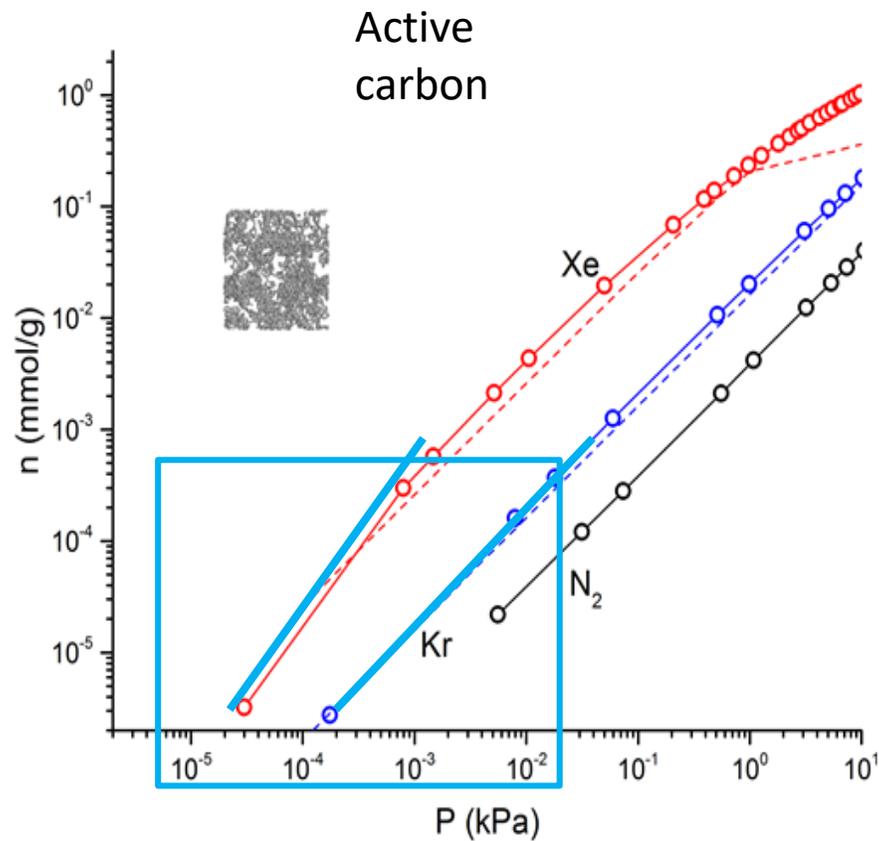


Breakthrough results under 400ppm Xe / 40ppm Kr



Evaluation methods for adsorbents : adsorption isotherms

—○— Isotherms
 - - - IAST Isotherms



Henry's regime

$N \sim H \cdot P$

Henry's selectivity:

$$S_{AB} = H_A / H_B$$

Evaluation methods for adsorbents : prediction of capacities and selectivities [1]

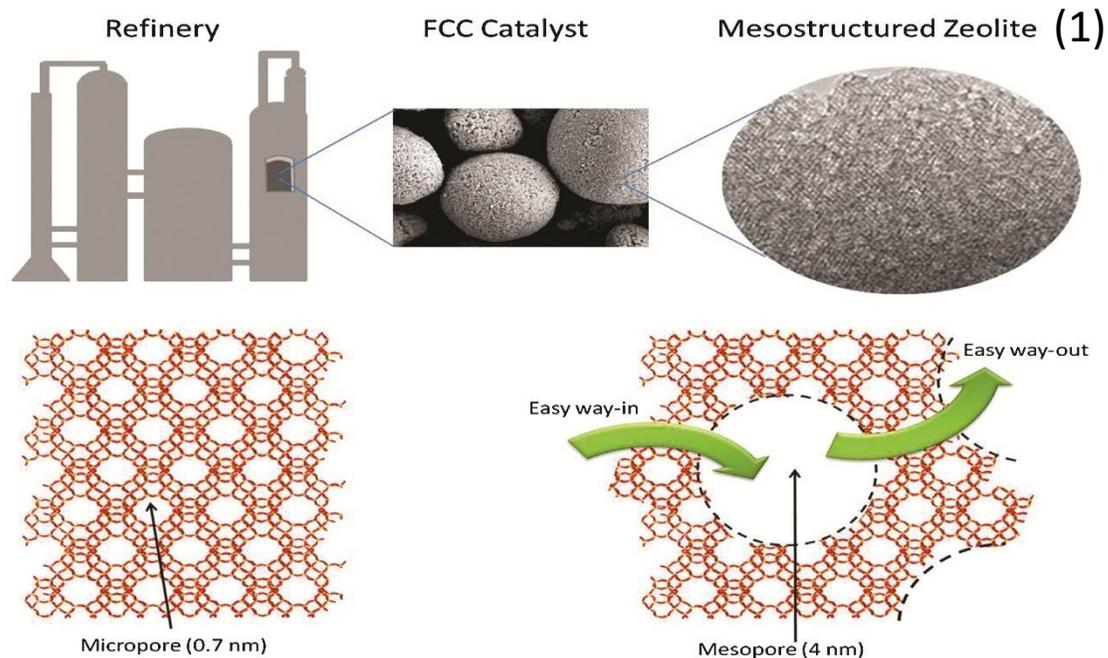
Adsorbent	capacities						selectivities		
	Henry N Xe (*1e-4) mol.g ⁻¹	Henry N Kr (*1e-7) mol.g ⁻¹	IAST N Xe (*1e-4) mol.g ⁻¹	IAST N Kr (*1e-7) mol.g ⁻¹	BKTH N Xe (*1e-4) mol.g ⁻¹	BKTH N Kr (*1e-7) mol.g ⁻¹	S _H	S _I	S _B
AC	0.16	0.79	0.1	0.67	0.11	1.9	20	15	6
Ag@ZSM5	98	34	2.3	0.58	2.4	2.5	296	403	142

(*)

(*) -Selectivity of 100 means Xenon purity @99.9%

- Breakthrough = true measurements
- Henry's law allows to discriminate selective adsorbent in this case
- good adequation with IAST for capacities of Ag@ZSM5

Fluid catalytic cracking: hierarchical zeolite

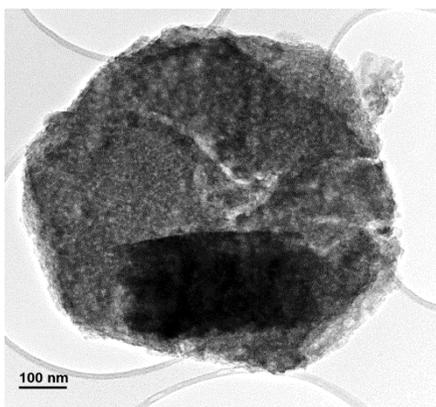


H-USY-0 -Y zeolite from Zeolyst, having Si/Al=15 ->

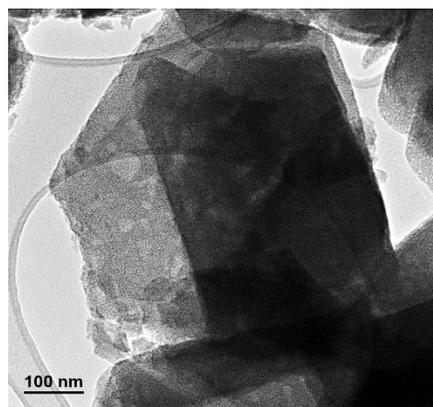


- **H-USY-1** : First sample prepared via templating method (CTAB in NH_4OH solution ²)
- **H-USY-2** : Second sample prepared via templating method (CTAB in TMAOH solution ³)

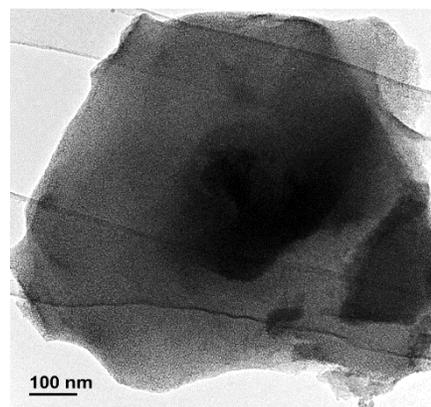
H-USY-0



H-USY-1



H-USY-2



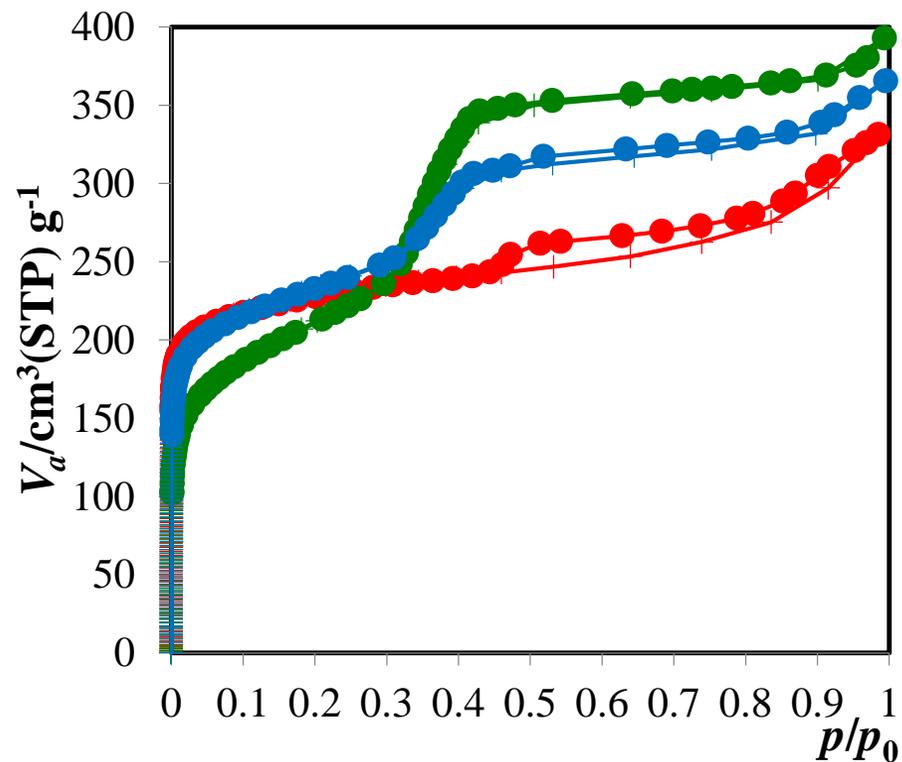
¹ J. Garcia-Martinez et al , Chem. Comm. 48,97, 2012

² J. Garcia-Martinez et al., Catal. Sci. Technol., 2012, 2, 987–994

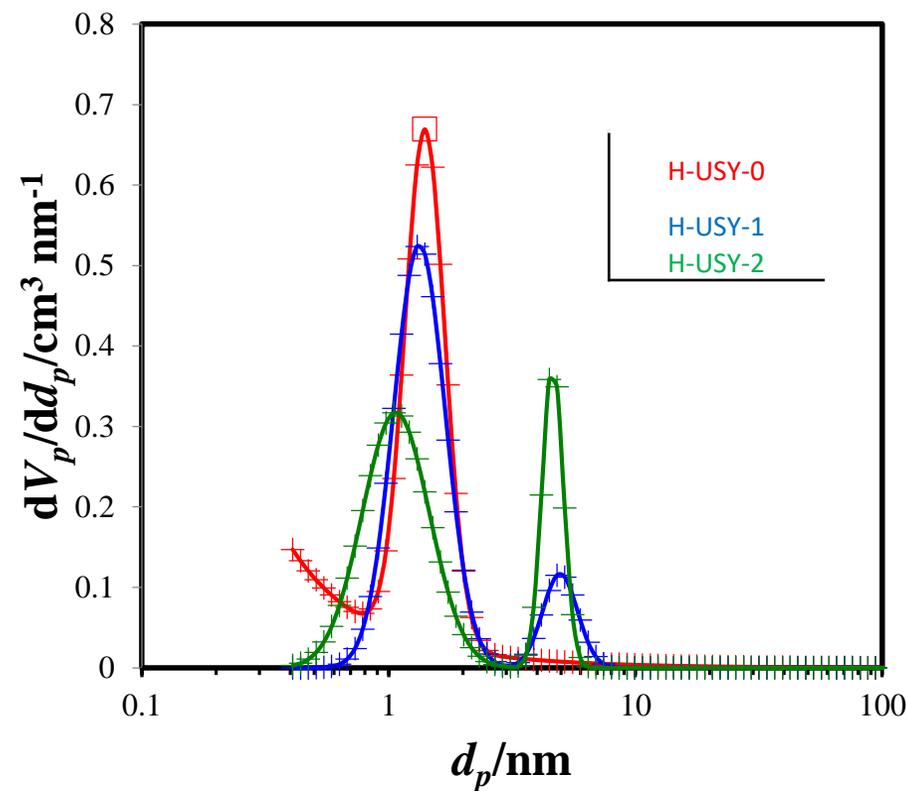
³ C. Gérardin et al., Chem. Commun., 2010, 46, 7840–7842

FCC: hierarchical zeolite with bimodal pore size

N₂ isotherms at very low pressure



Pore size distribution (NLDFT)



Catalyst	S _{BET} ^a [m ² .g ⁻¹]	V _{micro} ^b [cm ³ .g ⁻¹]	V _{meso} ^c [cm ³ .g ⁻¹]	V _{total} ^d [cm ³ .g ⁻¹]
H-USY-0	869	0.30	0.15	0.45
H-USY-1	827	0.28	0.22	0.50
H-USY-2	709	0.23	0.32	0.55

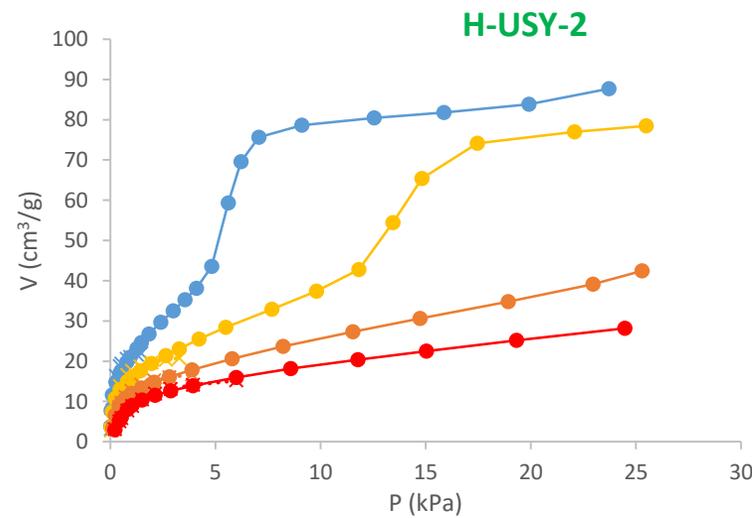
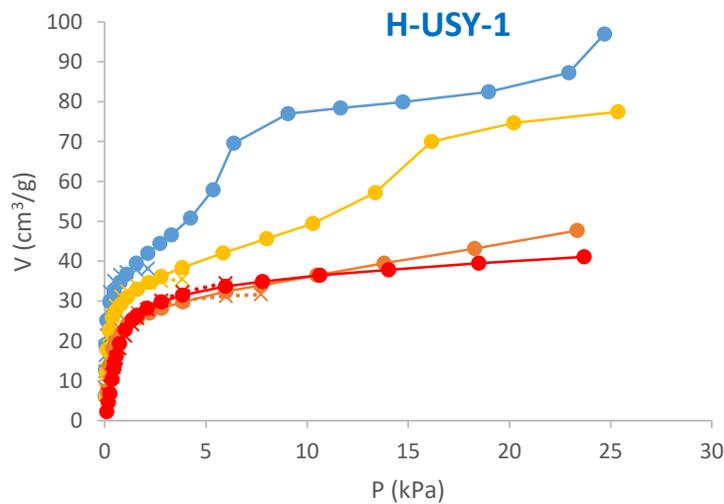
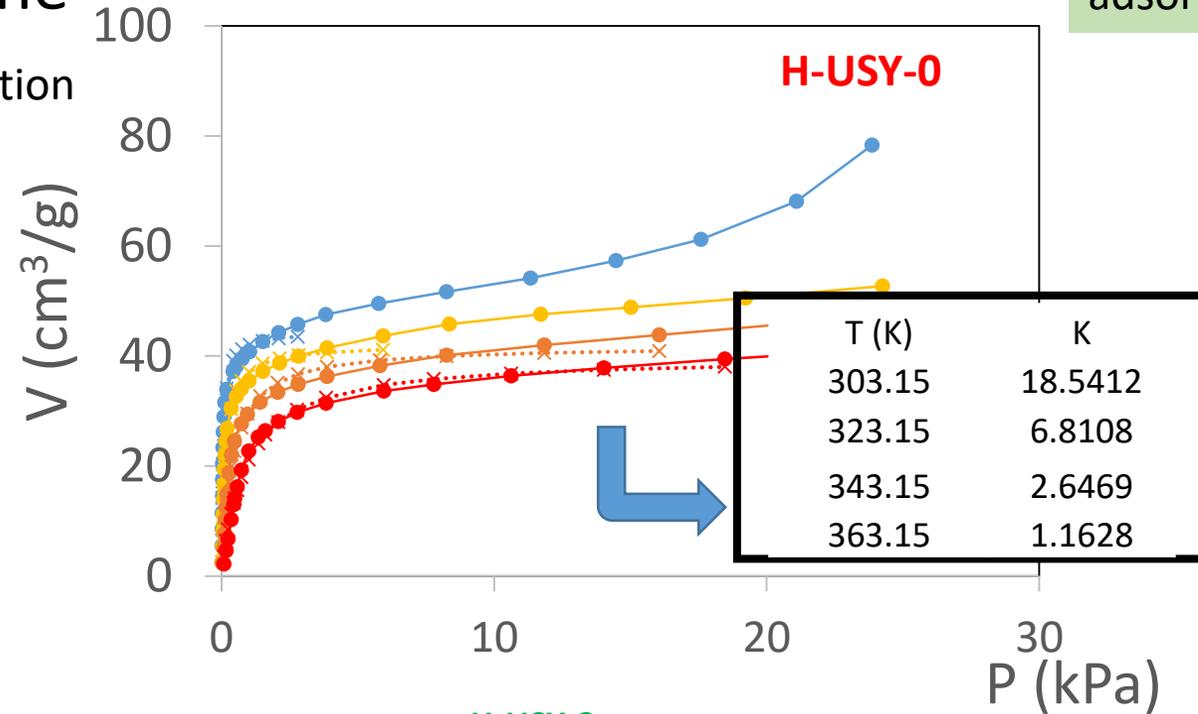
FCC: Heat of adsorption of n-hexane

Heat of adsorption (3)

Isothermes of n-Hexane @30, 50,70, 90°C: Vapor adsorption

The adsorption data are fitted with Langmuir model:

$$V = \frac{V_{\max} \times K \times P_e}{1 + K \times P_e}$$



Catalytic cracking of n-hexane: kinetic model

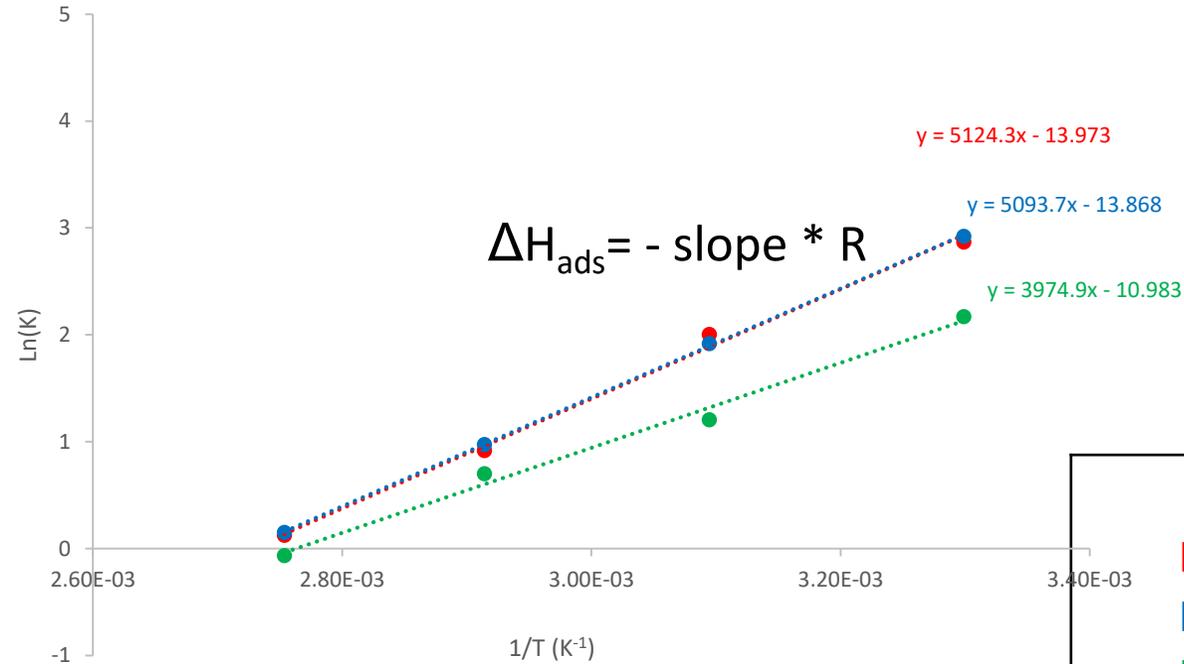
Heat of adsorption (4)

Heat of adsorption can be evaluated from adsorption equilibrium data by the following equation:

$$K = K_0 \times e^{\frac{-\Delta H}{RT}}$$

K from fitted isotherms

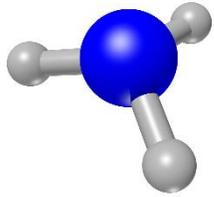
T (K)	K
303.15	18.5412
323.15	6.8108
343.15	2.6469
363.15	1.1628



	ΔH_{ads} (kJ/mol)
H-USY-0	-42.6
H-USY-1	-42.3
H-USY-2	-33.0

Rate of n_hexane cracking: $r = k \cdot K \cdot [C_6H_{14}] \cdot \theta$

Ammonia air purification filters



- high-risk chemicals used in manufacturing facilities
- possible spreading in conflict (tank attacks)

SoA on adsorbent for ammonia capture:

Adsorbent	DRY conditions	Wet conditions
impregnated activated charcoal with sulphuric or phosphoric acid	--	+++
zeolite	+++	-----
MOF: CuBtC, Zr-based mof	?	?

Gas masks equipped with type K filter cartridges



➔ Needs for new adsorbents Shaping ?

Ammonia air purification filters: experimental

Specifications:

Measure adsorption of NH_3 and H_2O

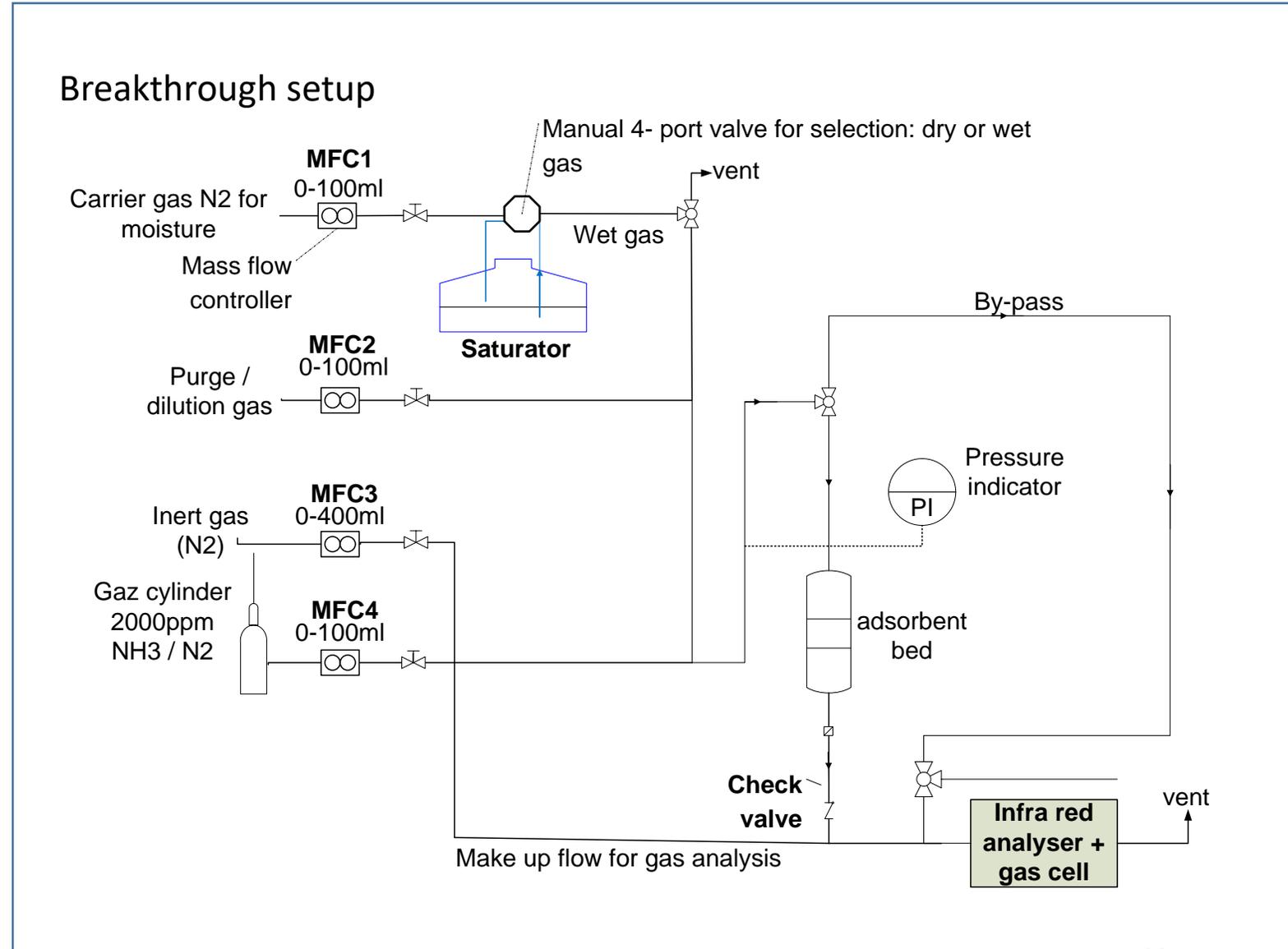
⇒ Coadsorption

⇒ Fast and accurate analysis for NH_3 and water

⇒ REAL CONDITIONS

CONDITIONS:

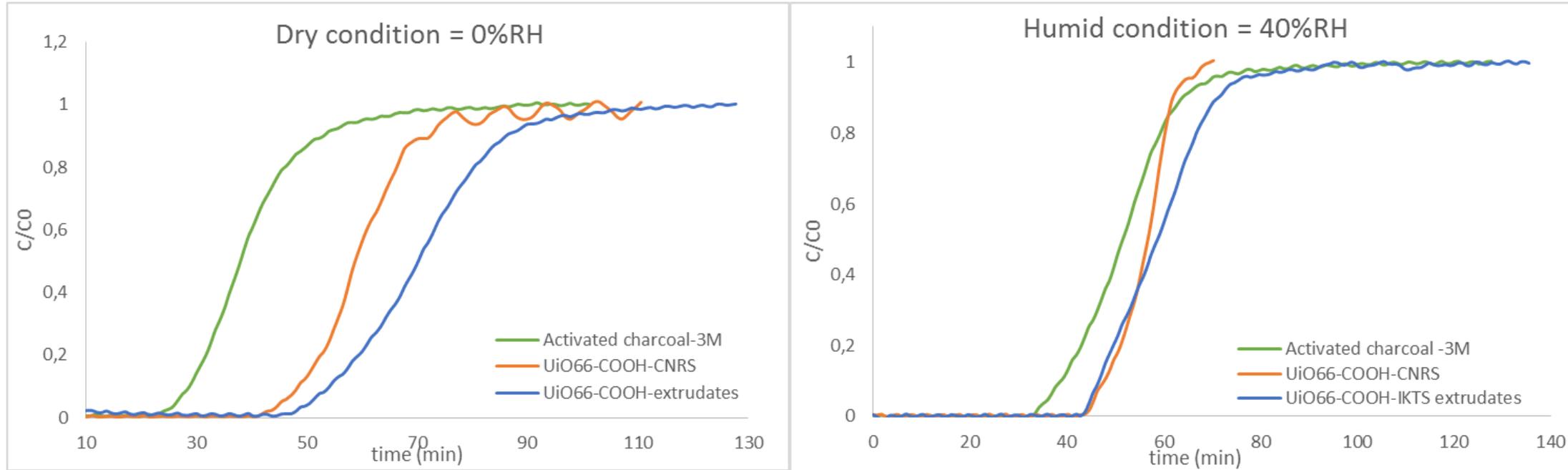
- 1200 ppm ammonia
- 40% HR
- Volume bed # 0.15cm³
- Time breakthrough < 1h
- Temperature 30°C



Ammonia air purification filters: breakthrough results



Tests @Iso volume of adsorbent, not at iso-weight

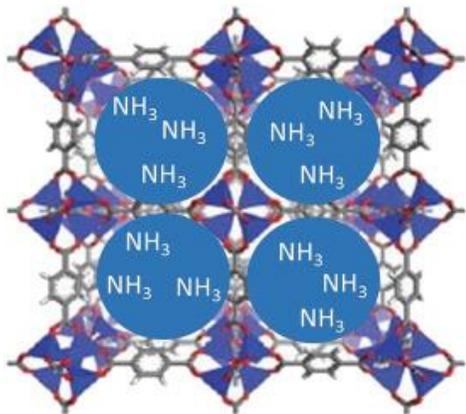
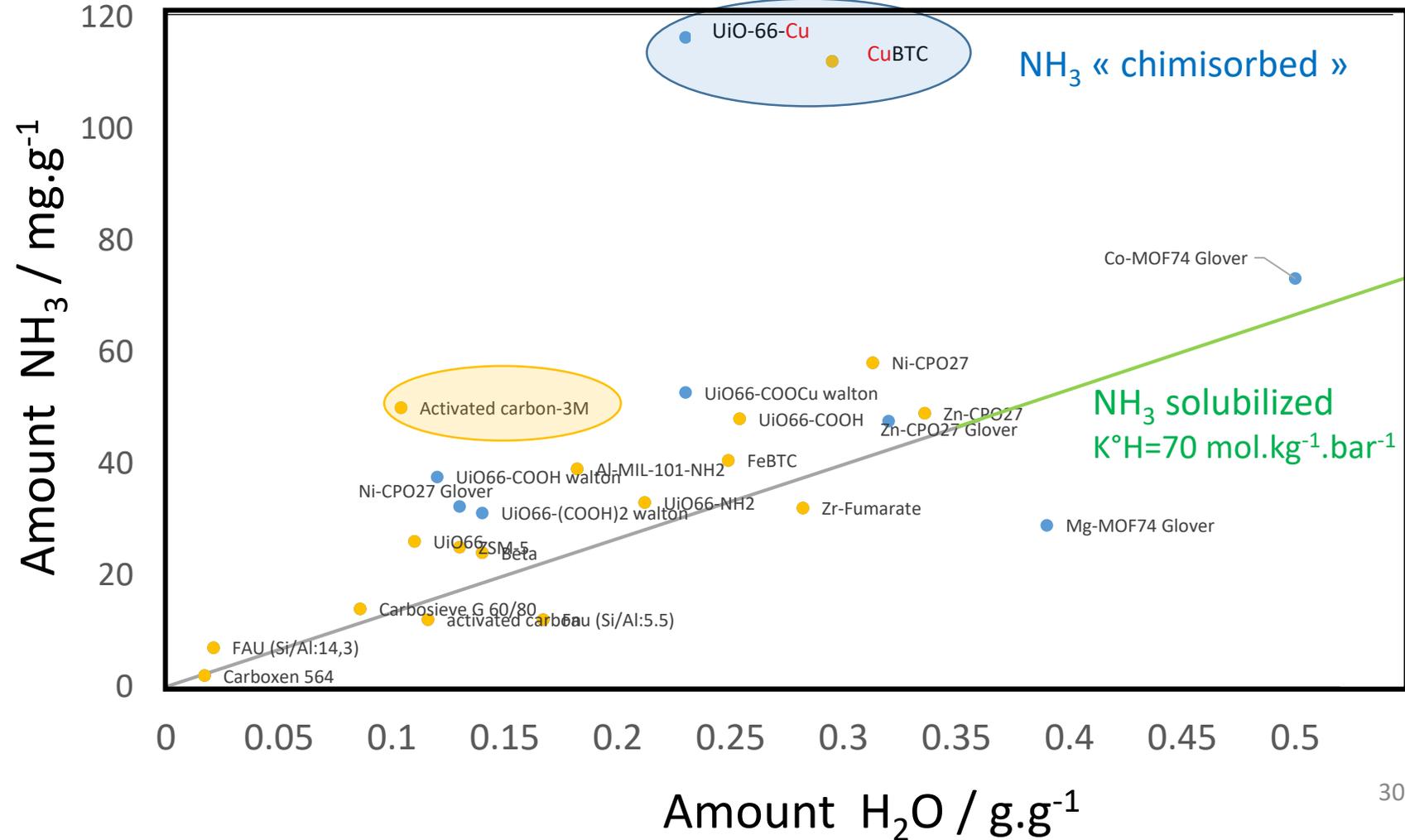


Adsorbent	Ammonia adsorption amount ^[1] (mg/cm ³)	
	0% RH	40% RH
Extrudates	40	34
AC-3M	23	29

[1] Khabzina et al, Ind. & Eng. Chemistry research, 57, 24, 8200-8208, 2018

Ammonia air purification filters: mechanism ?^[1]

Benchmark @1200 ppm NH₃, 40% RH

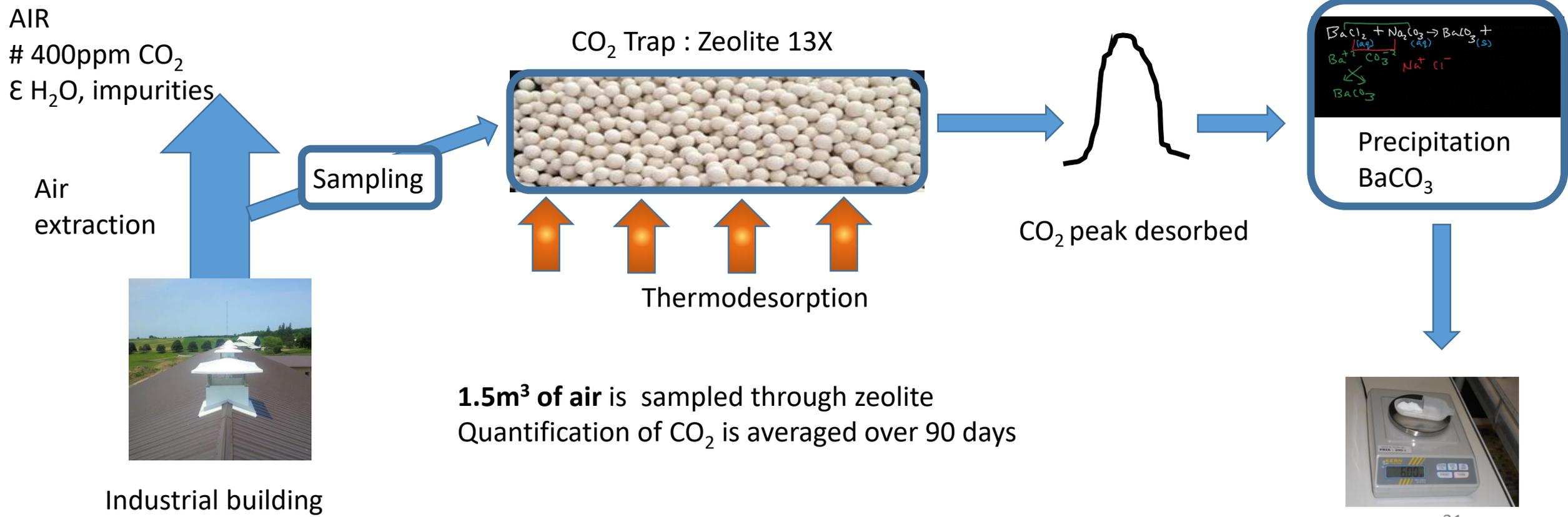


-Solubilisation of ammonia in water confined in micropores

[1] Khabzina et al, Micro. Mesoporous materials, 265 ,143-148, 2018

CO₂ quantification in extraction vent

- 2016: Current regulation makes CO₂ quantification mandatory for Company XX
- Issue : Reproducibility of measurements over 90 days sampling

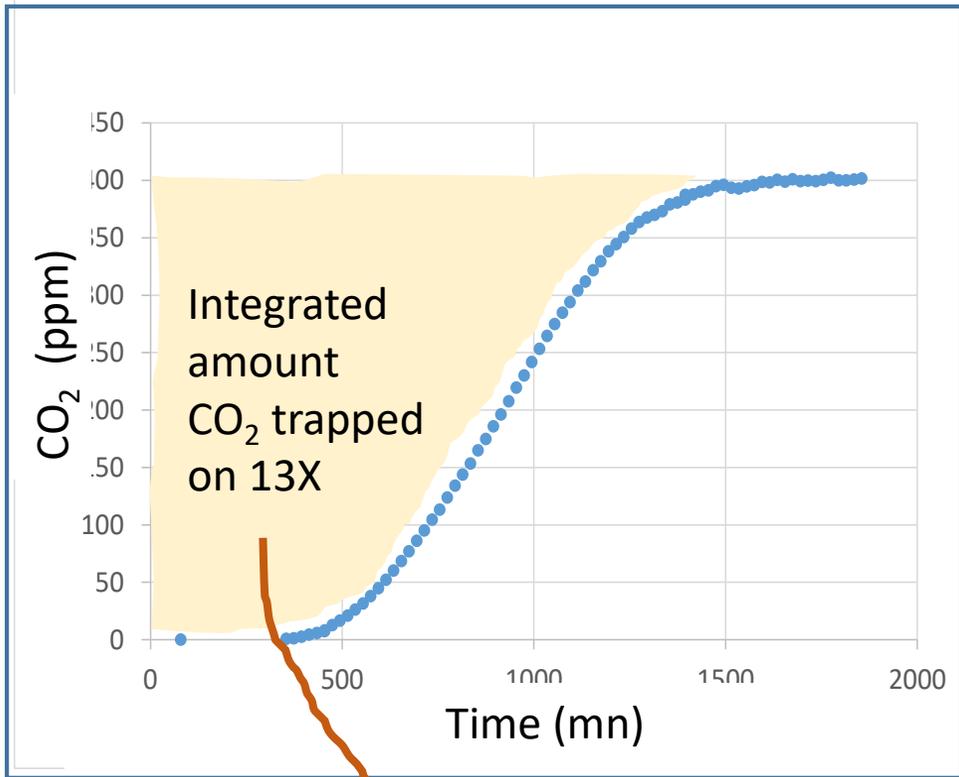


CO₂ quantification in extraction vent : model conditions

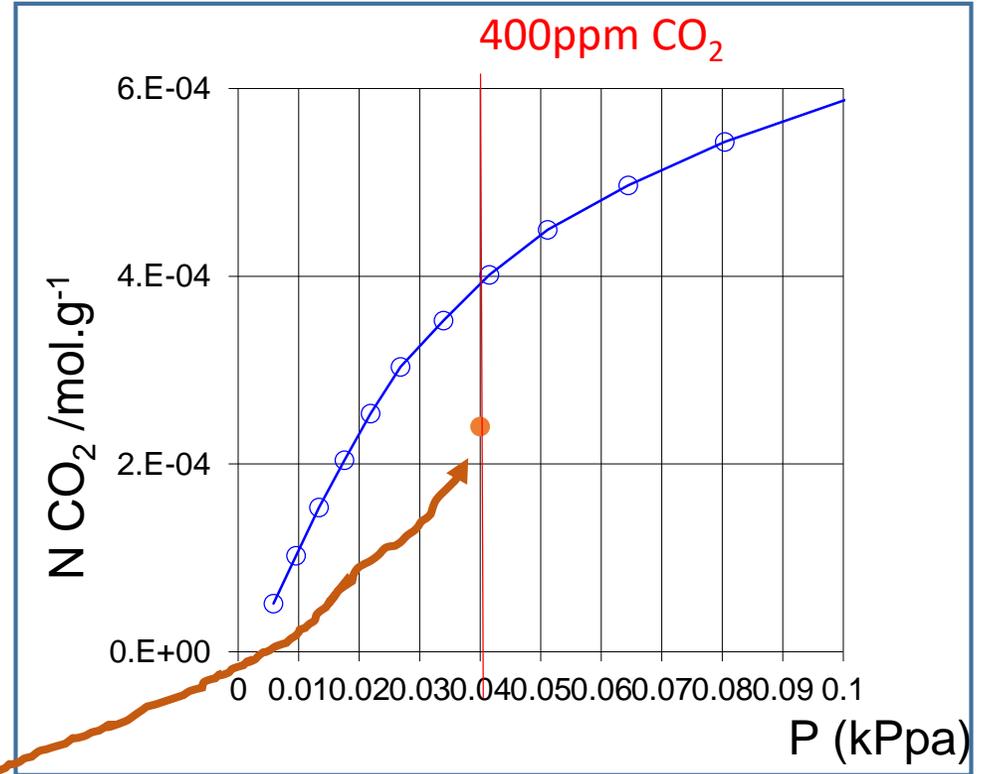
BREAKTHROUGH

10g dry zeolite 13X / 400ppm CO₂

Scale 1/30



ADSORPTION ISOTHERM @25°C

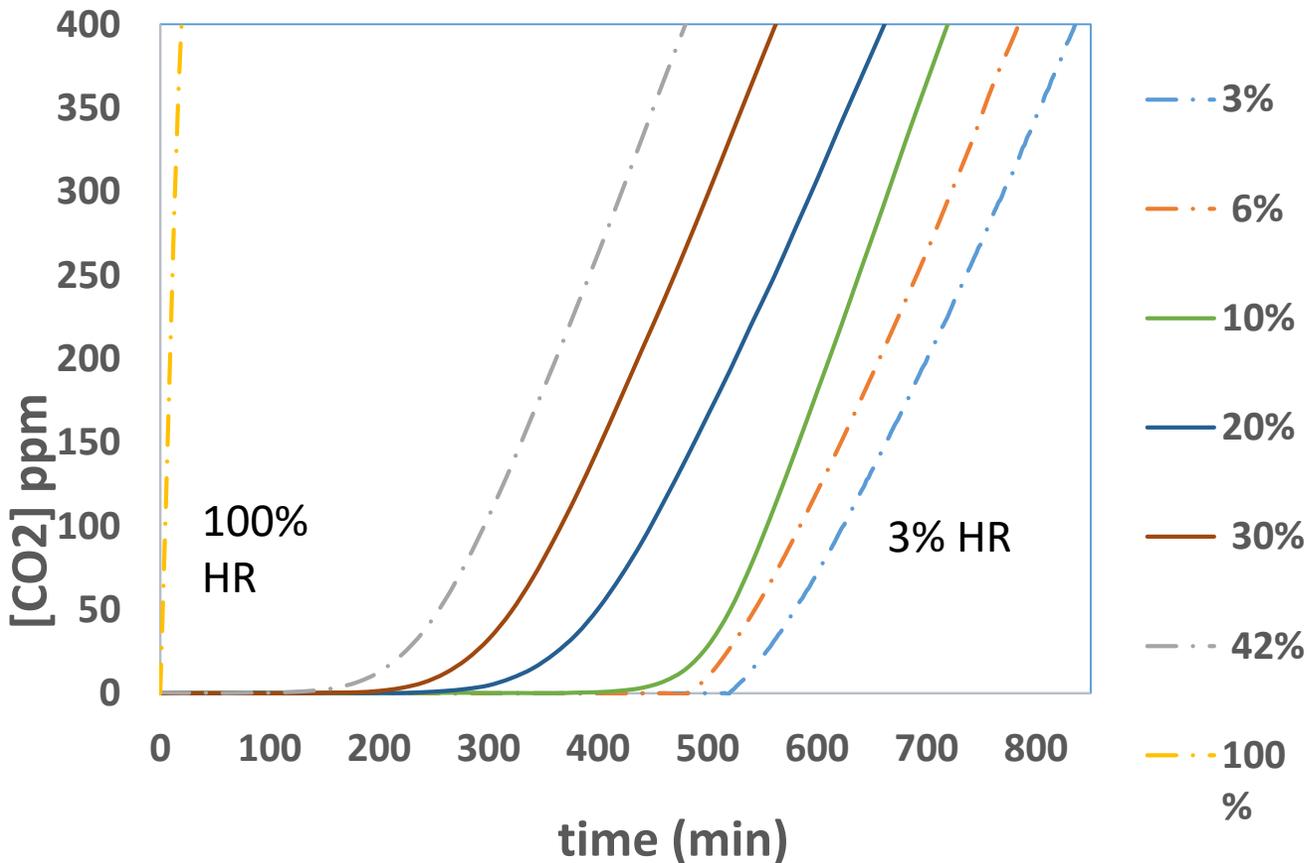


Under flow coadsorption is possible (contaminant, H₂O...)

CO₂ quantification in extraction vent : true conditions measurements

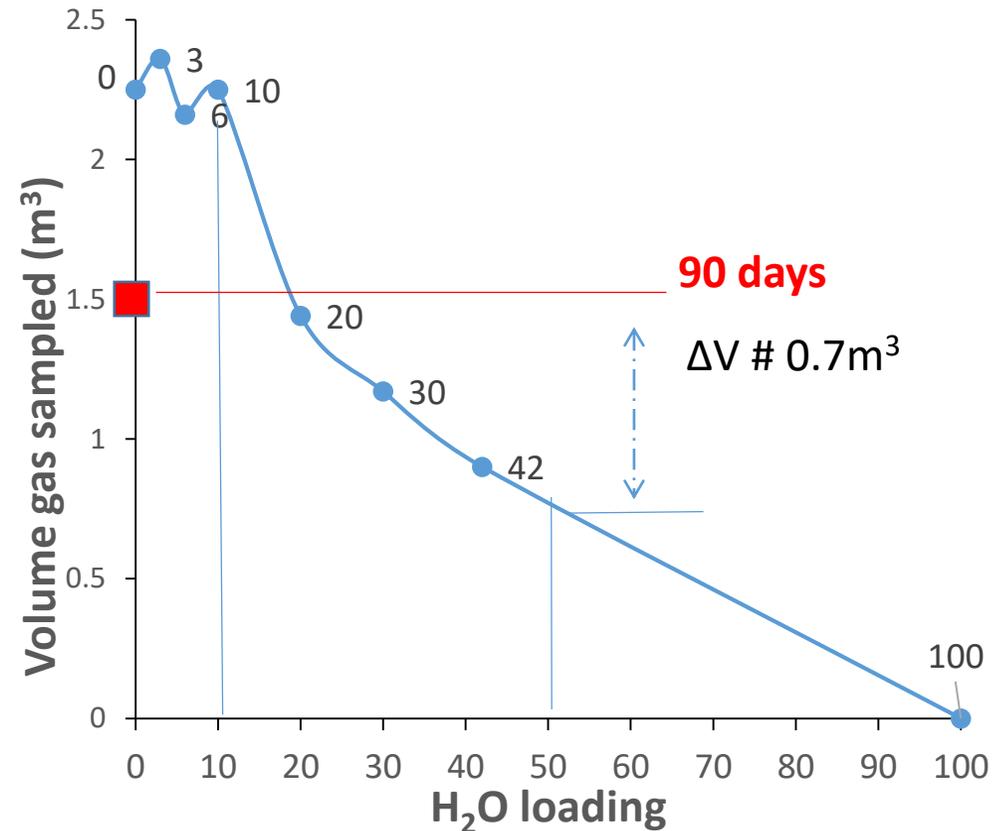
Breakthrough on wet zeolite

H₂O loading



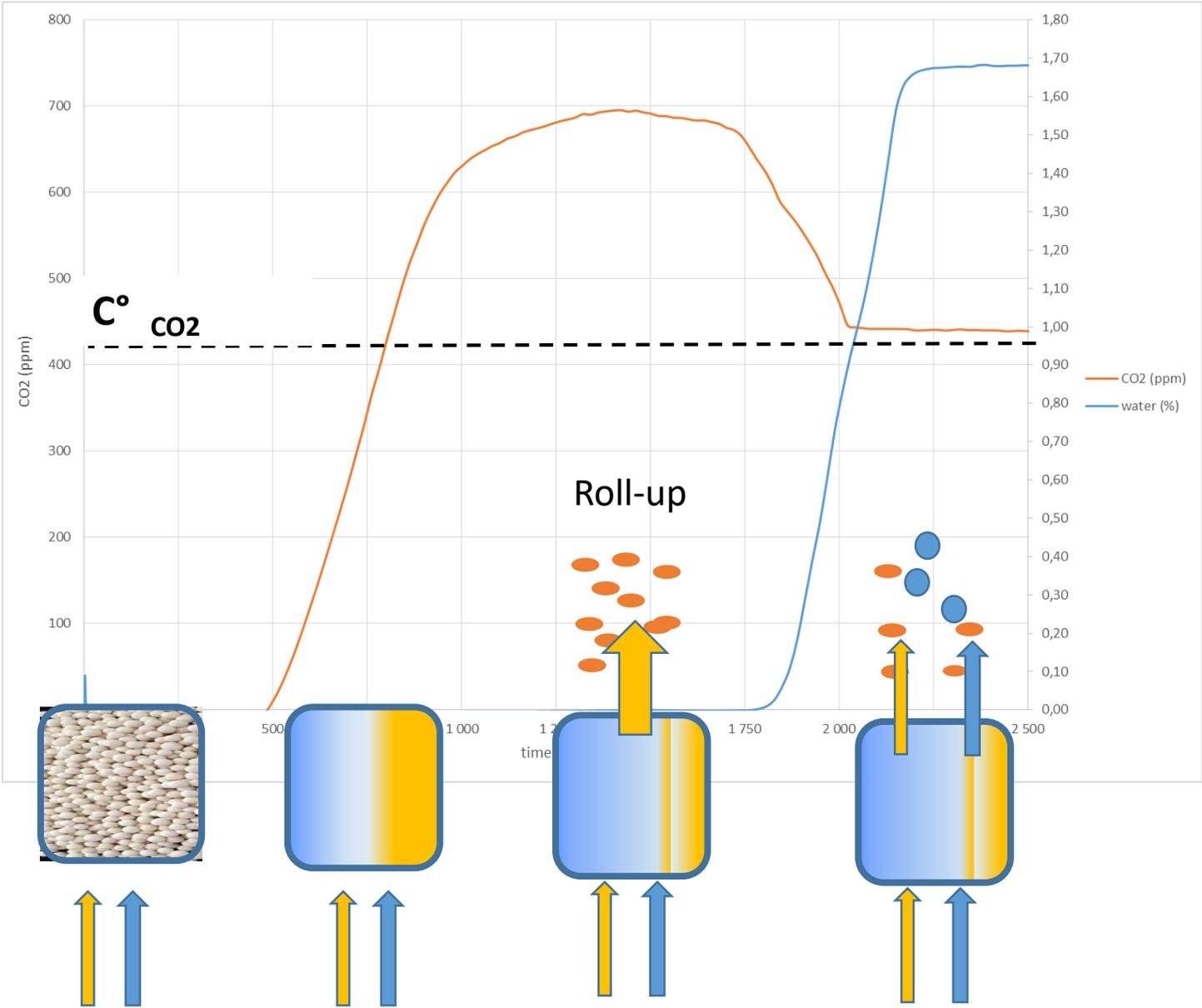
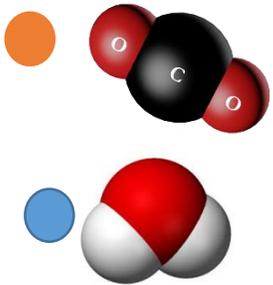
The CO₂ storage capacity of the zeolite drastically drops if the zeolite is wet

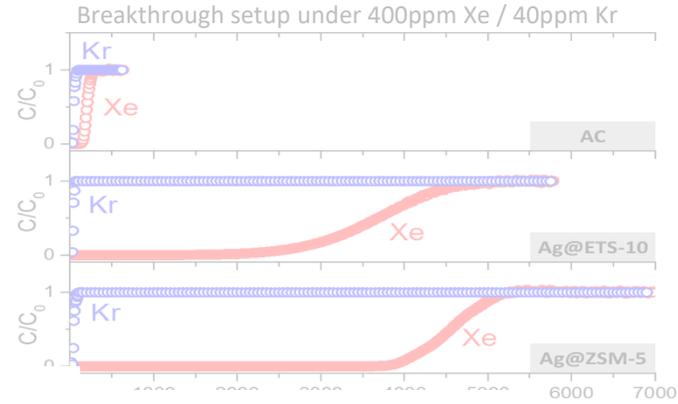
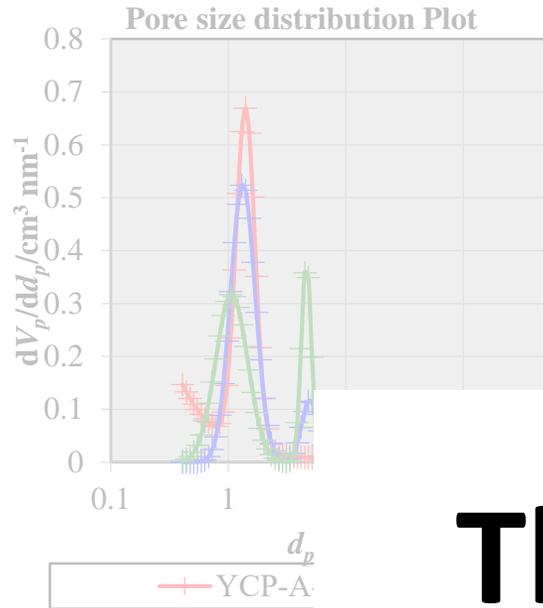
Process : Operation point



In protocol 1.5m³ of air is sampled over 90 days
True value may drop to 0.7m³ if air is wet !

CO₂ quantification in extraction vent: rollup effect





Thanks for your kind attention!

