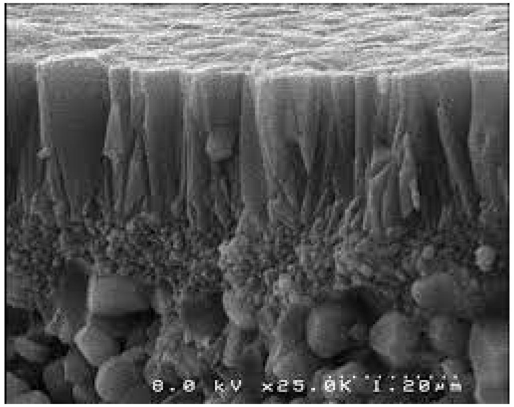
Zeolite membranes

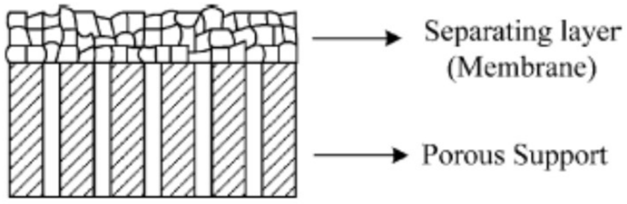


Applications : separation using membranes

↳ development of selective zeolite membranes

Zeolite membrane specifications ⇒ pure phases
⇒ particles of small sizes
⇒ uniform size distribution of particles

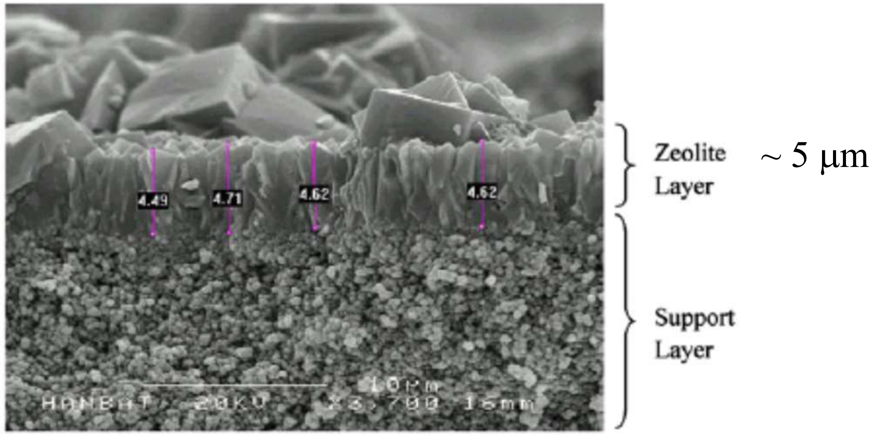
Most zeolite membranes are supported to ↗ mechanical strength



Support

Al_2O_3 tube, ∅ pores 5 - 200 nm

Stainless steel, ∅ pores 0.5 – 4 μm



Cross section

→ synthesis control difficult

↳ the presence of impurities ↘ the selectivity and the separative properties
↳ an heterogeneous crystallite size creates meso/macroporosity (⇒ induces leaks)

Applications : separation using membranes

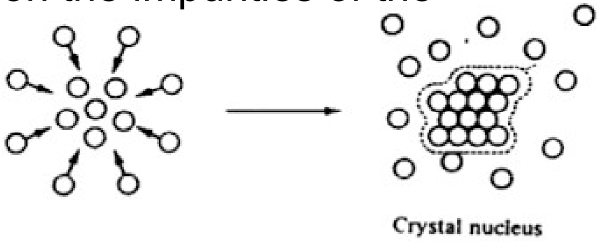
↳ Membranes preparation : nucleation - growth mechanism

- Control of the nucleation (germination) step

  germination = formation of crystal nuclei = heterogeneous process

  ⇒ The nuclei of the future crystalline phase form preferentially on the impurities of the system

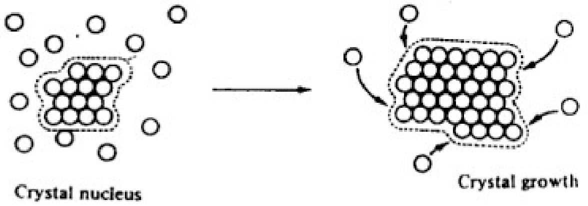
  ⇒ Support = impurity ⇨ the choice of the support is important

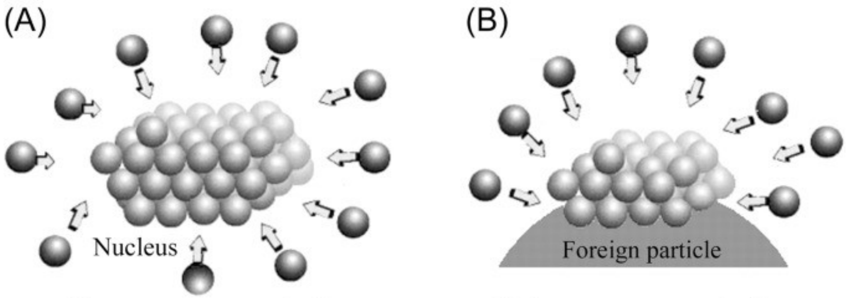


- Control of the growth step

  search for a continuous, homogeneous film

  ⇒ control of the deposition rate of reactive species on the substrate, T, H_2O content, [reagents]





Homogeneous nucleation

Heterogeneous nucleation

→ The presence of impurities ↘ the selectivity and the separation properties

→ A heterogeneous crystallite size creates meso and macroporosity

⇨ **Synthesis is difficult**

Membranes preparation

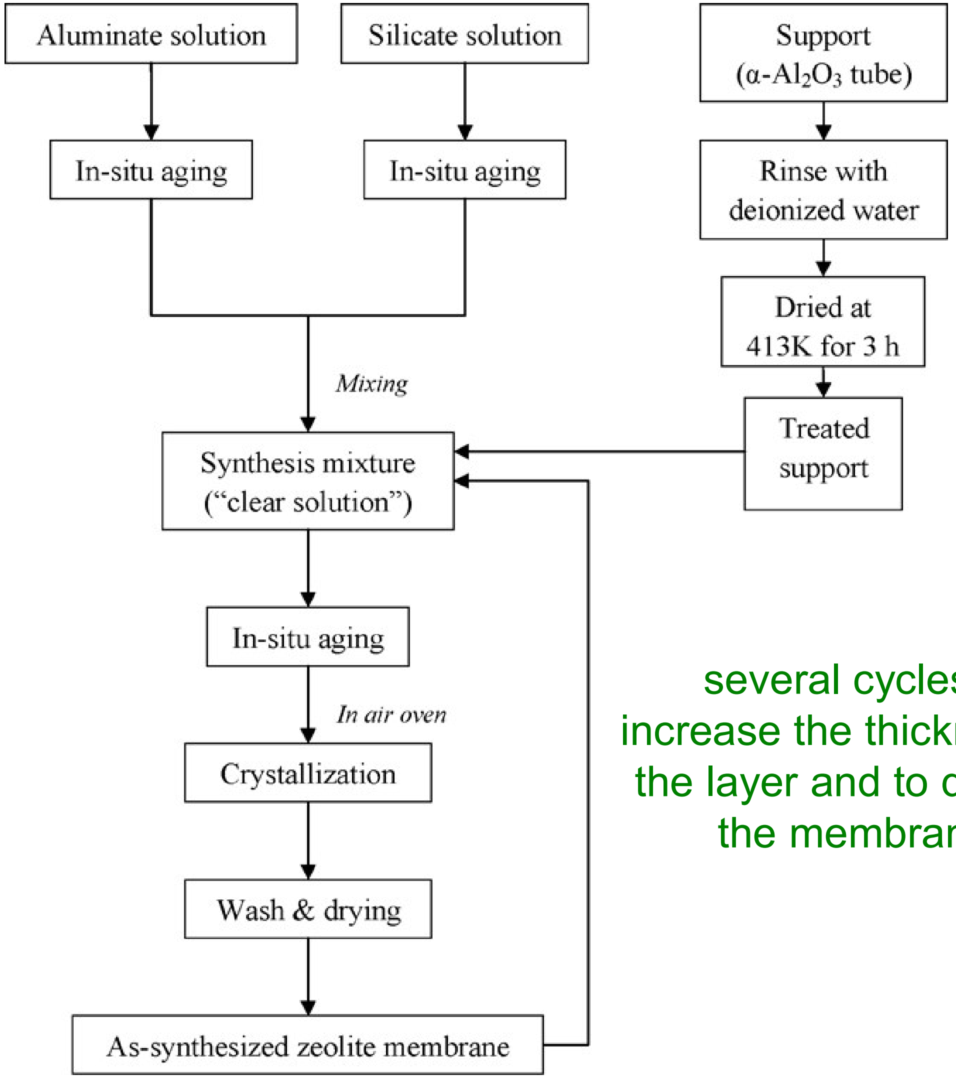
↳ Classical hydrothermal synthesis route

⇨ hydrothermal synthesis in the presence of the support

Disadvantages

- Low density membranes
- Long time synthesis (days)
- Frequent formation of impurities
  (nucleation step difficult to control)

  ⇒ reduced separation properties
- Crystalite size control difficult



Aluminate solution
In-situ aging
Silicate solution
In-situ aging
Mixing
Synthesis mixture
("clear solution")
Support
(α-Al_2O_3 tube)
Rinse with
deionized water
Dried at
413K for 3 h
Treated
support
In-situ aging
In air oven
Crystallization
Wash & drying
As-synthesized zeolite membrane

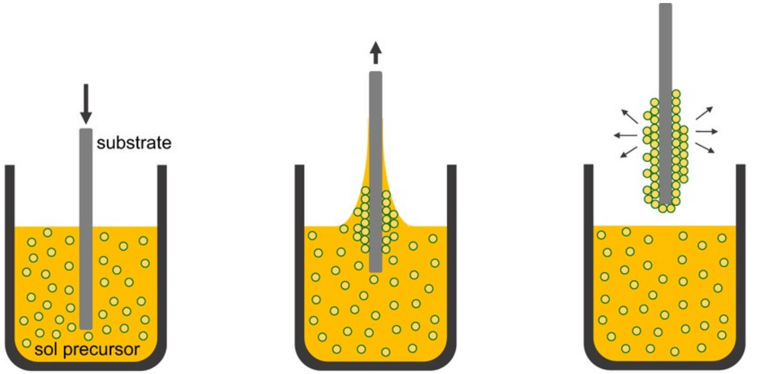
several cycles to
increase the thickness of
the layer and to densify
the membrane

Membranes preparation

⇘ Secondary growth synthesis of the material

1) Deposition of zeolite seeds on the support prior to hydrothermal synthesis

⇒ Deposition by dip-coating → a) Immersion of the substrate in a solution containing seeds
→ b) Formation of a continuous film on the surface of the substrate
→ c) Evaporation of the solvent: formation of crystal nuclei



a) dipping b) withdrawal c) evaporation

2) Hydrothermal synthesis on the support coated by the crystal nuclei

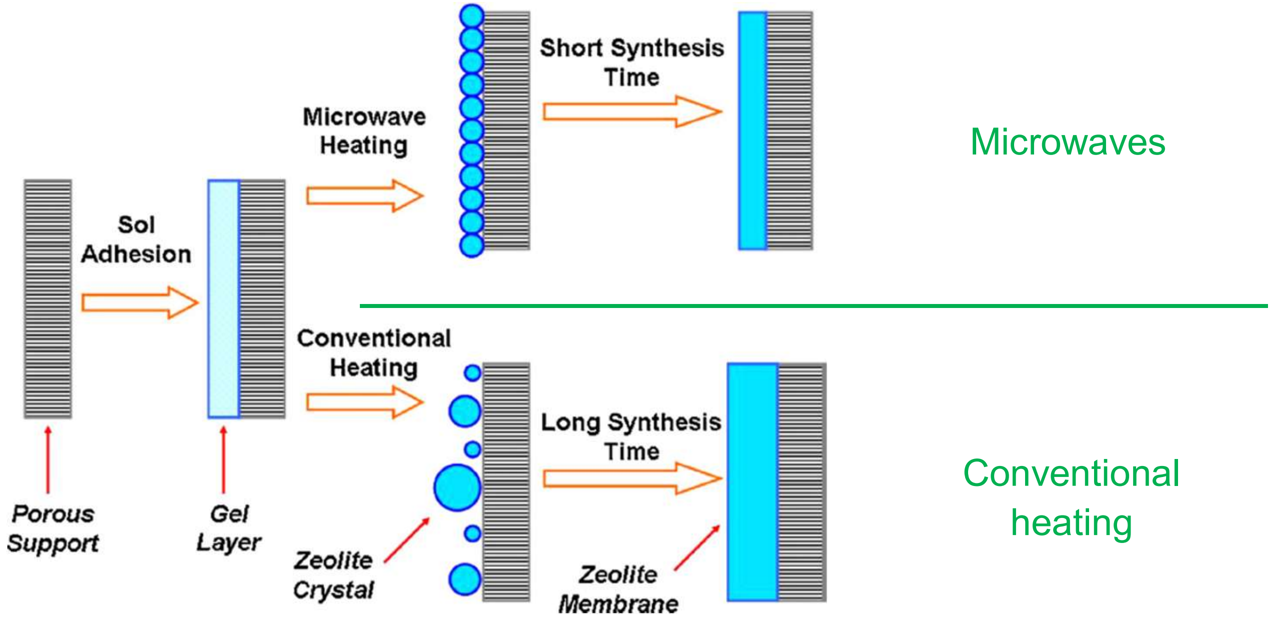
⇨ Better control of the membrane microstructure (crystal thickness and orientation)

⇨ Better reproducibility

} Control of the nucleation step = key step

Membranes preparation

↳ Microwave assisted synthesis



Advantages microwave synthesis vs conventional heating

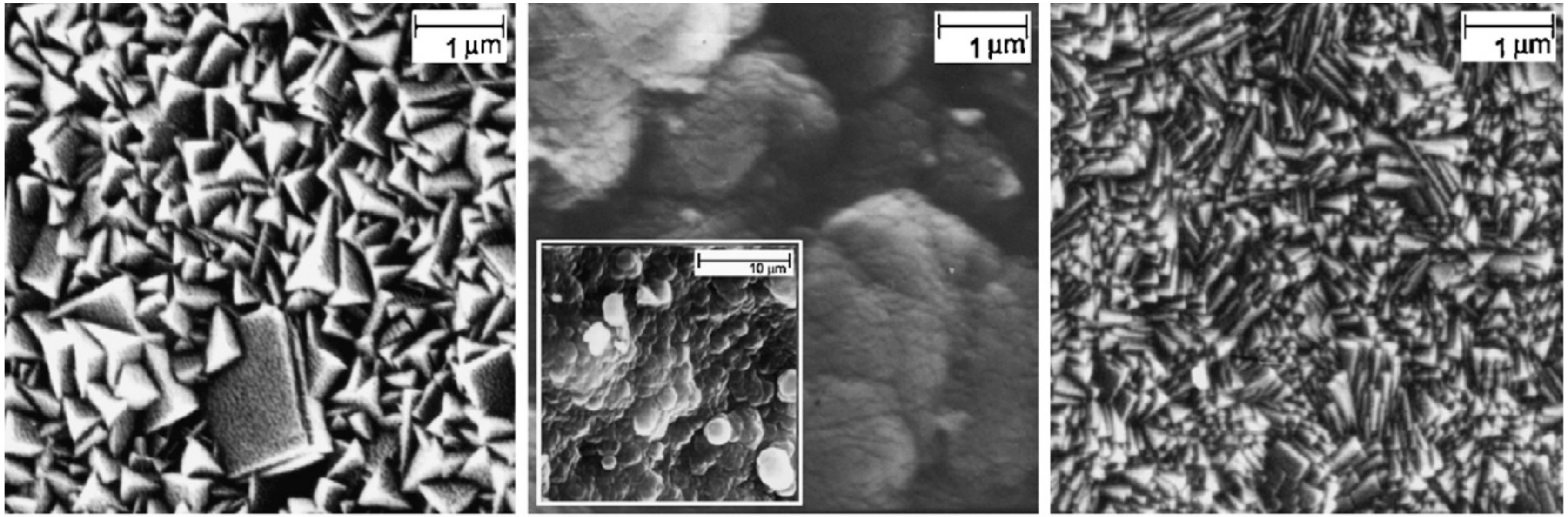
- Less time consuming (~ 10 min for crystallization) ⇒ no conduction or convection: direct transfer of microwave energy to the core of the material
- Formation of smaller crystallites which are better stacked on the surface of the support, because of a rapid crystallization ⇒ presence of fewer defects (↘ meso/macroporosity)
- Narrower pore size distribution ⇒ the thickness of the layer is well controlled
- High purity

⇒ Improved selectivity

Membranes preparation

↳ Microwave assisted synthesis vs conventional heating

NaA membrane



Hydrothermal synthesis
⬇
Micrometric size crystals

Pulsed microwave
⬇
Particules with no specific shape

Continuous microwave
⬇
Submicrometric size rystals

→ characterisation of the porosity by gas permeation (presence of defects ?)
→ Measure of BET surface area (S_{BET}) : characterisation of the microporosity

Application : separation on membranes

⇘ Efficiency criteria for membranes

⇨ Selectivity

It is expressed by a parameter called « retention » or by the « Separation Factor » : $\alpha_{A/B}$ (SF)

$$\alpha_{A/B} = \frac{\left(\frac{x_A}{x_B}\right)_{\text{permeate}}}{\left(\frac{x_A}{x_B}\right)_{\text{alimentationfeed}}}$$

x_A, x_B : molar ratios

⇒ The Separation Factor must be as high as possible

⇨ Productivity

It is expressed by a parameter called « flux »

It is the volume of fluid separated, per unit of membrane surface, per unit of time

→ in $L/m^2/h$

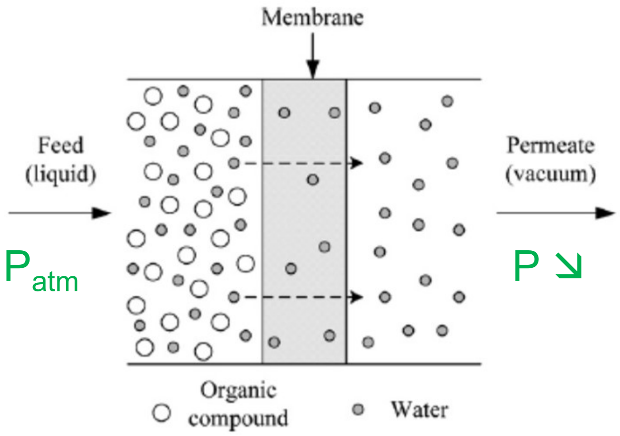
⇒ The Productivity must be as high as possible

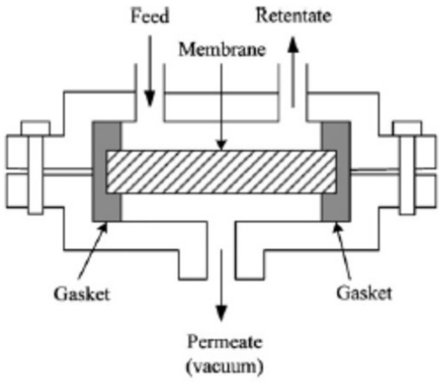
⇨ A good compromise must be found between the two factors

Application : separation on membranes

➥ Pervaporation (= pervaporative separation)

= process for the separation of liquid mixtures by partial vaporization through a membrane





Stainless steel module + 12m² Na-A

- Membrane = selective barrier between several phases
- A pressure difference (ΔP) is applied between both sides of the membrane
  → the phase able to pass through the membrane (size match) is vaporised, diffuses through the membrane and is recondensed into liquid phase ⇨ permeate
  → the mismatched phase remains in liquid form upstream

⇒ transfer possible due to the difference in vapour pressure of the compounds

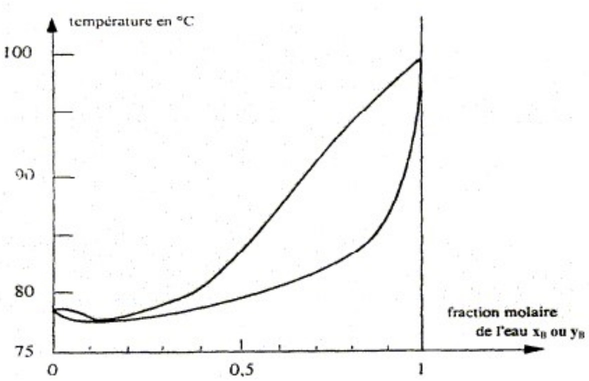
Ideal material: ⇨ good selectivity
⇨ high productivity (L/m²/h)

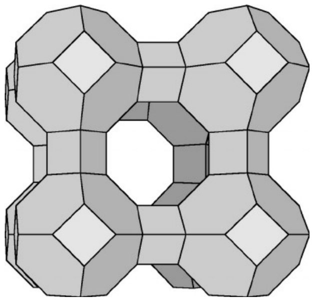
Application : separation on membranes

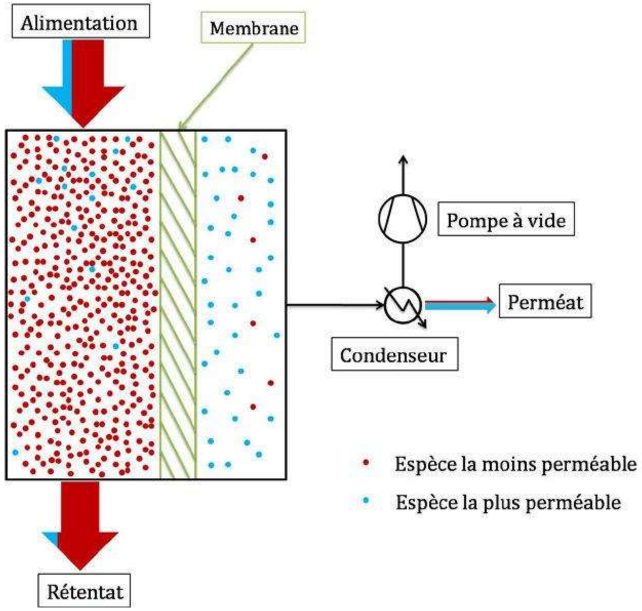
↳ Pervaporation : separation of water – ethanol mixtures

- Used in bio-ethanol production units
- Bioethanol production (by fermentation of sugars/starch) produces large amounts of aqueous ethanol solutions
- Absolute ethanol (99.9%) can be obtained by azeotropic distillation → long/difficult process (especially for constituentsif of close volatilities)

⇒ Possibility of separation by pervaporation on hydrophilic membranes







Ex : Na-A hydrophilic zeolite membrane

→ Adequate properties for H_2O diffusion

→ Obtention of absolute EtOH

→ Flux ~ 2.3 kg/m^2/h

Application : separation on membranes

↳ Pervaporation membranes

- **Advantages**

  - Low energy consumption compared to distillation (only the extracted liquid fraction is evaporated: 10 to 150 kWh/m^3)
  - Flexibility and compactness of the plant (can be easily adjusted)
  - High purity of the obtained products and absence of polluting emissions
  - Easy to operate and to control

- **Disadvantages**

  - The investment cost is high compared to other technologies (distillation, molecular sieve adsorption)
  - The choice of industrial membranes is insufficient : does not cover all types of separations
  - Many preliminary tests must be carried out before sizing
  - Membranes are very sensitive to variations in composition of the liquid

Application : separation by pervaporation

➯ Acetic acid / water mixture on a Sn-substituted MFI-type zeolite

- Polymeric hydrophobe membranes present poor performances for CH_3COOH/H_2O separation

  → Separation Factor α ~ 2

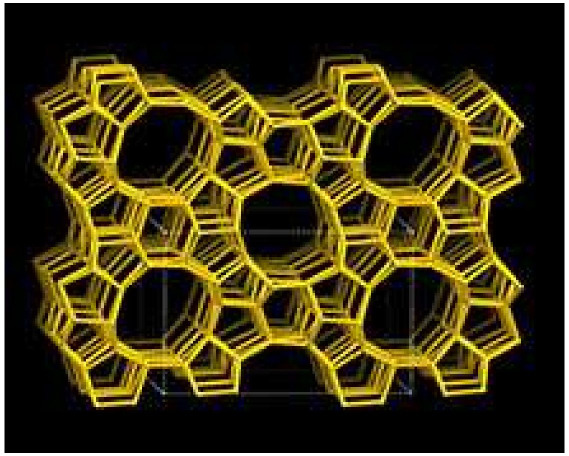
  → flux < 0.15 kg/m²/h

$$\alpha_{A/B} = \frac{\left(\frac{x_A}{x_B}\right)_{\text{permeate}}}{\left(\frac{x_A}{x_B}\right)_{\text{alimentationfeed}}}$$

- Aim of the study : comparison of the separation properties of :

  → a silicalite (MFI, Si/Al = ∞)

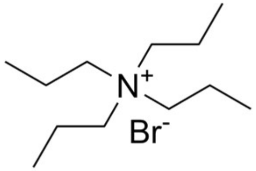
  → a Sn-substituted MFI



MFI view along [010]

⇒ Elaboration of MFI membranes supported on α-Al_2O_3 tubes

Hydrothermal synthesis route : TEOS + $SnCl_4,5H_2O$ + NaOH + TPABr



Si/Sn = ∞, 100, 50, 30 and 25

⇒ The substitution of Si by Sn led to an increase in hydrophobicity

Application : separation by pervaporation

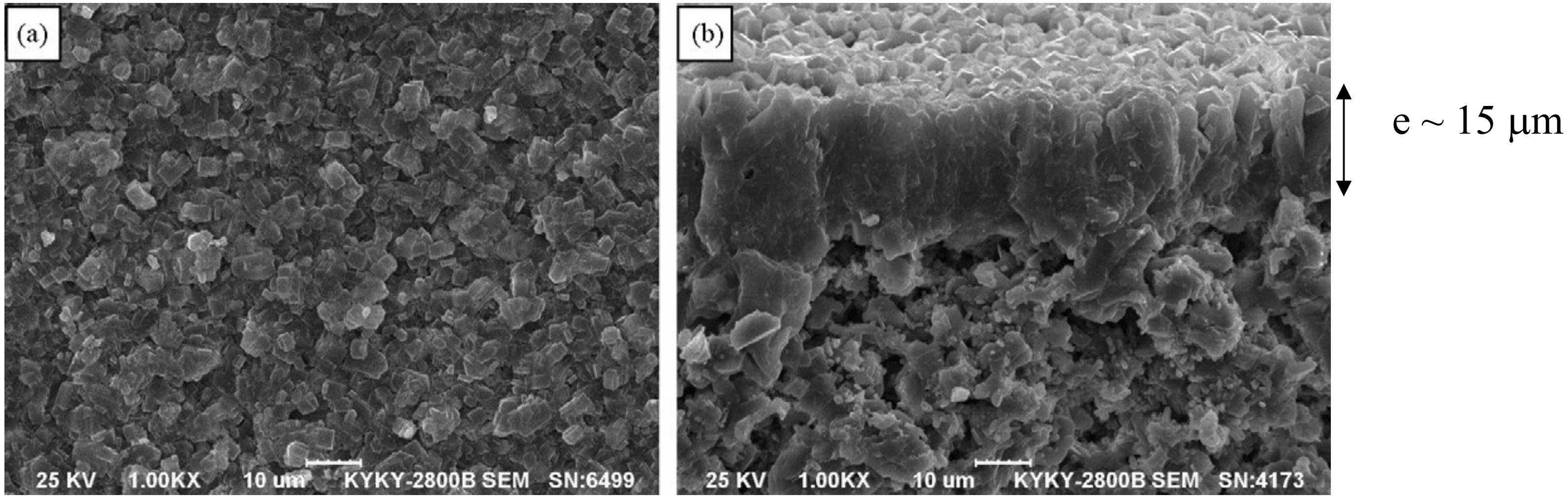
↳ Acetic acid / water mixture on a Sn-substituted MFI-type zeolite

Characterization of Si/Sn substitution :

→ FTIR : shift of the Sn-O vibration bands compared to Si-O ones

→ XRD : increase of the lattice parameters after substitution

→ SEM : high density of crystals, no crackings



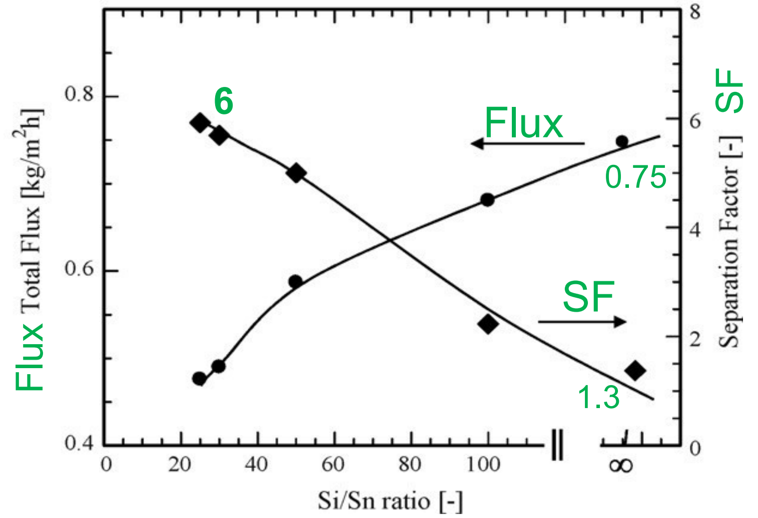
Surface Edge

Application : separation by pervaporation

➥Acetic acid / water mixture on a Sn-substituted MFI-type zeolite

- For silicalite (Si/Al = ∞) : SF ~ 1.3, flux ~ 0.75 kg/m^2/h

[CH_3COOH]
5 wt.%
70°C



$$SF = \alpha_{A/B} = \frac{\left(\frac{x_A}{x_B}\right)_{\text{permeate}}}{\left(\frac{x_A}{x_B}\right)_{\text{feed}}}$$

- When Si/Sn ↘ , the SF ↗

  ⇒ the increase in Sn content leads to a better separation

  ⇒ the increase in Sn content increases hydrophobicity

  ⇒ the zeolite does not retain H_2O

  ⇒ H_2O (permeate) is better separated from the acid

- When Si/Sn ↘ , the total flux ↘

  ⇒ the increase in Sn content increases hydrophobicity

  ⇒ the zeolite has a low affinity for H_2O

  ⇒ H_2O passes through it slowly

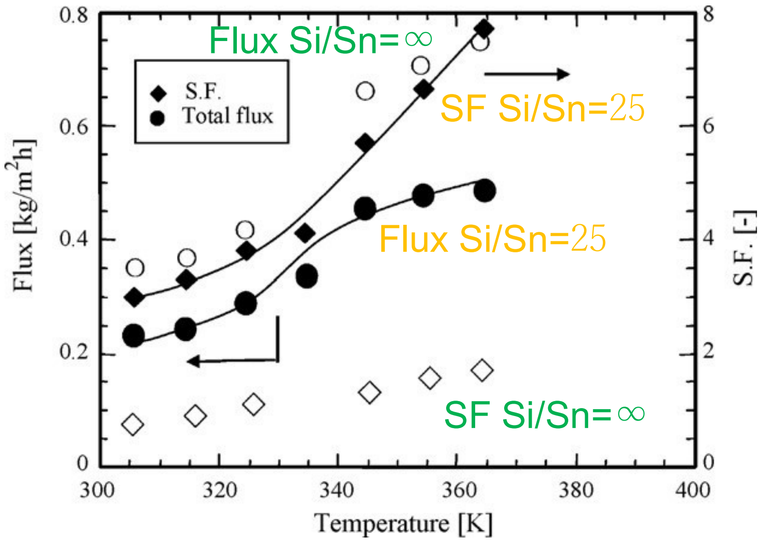
  ⇒ The separation kinetic is slow

When Si/Sn ↘, the separation is better but the kinetic of separation is slower

⇨ The Sn content is limited by the precipitation of SnO_2

Application : separation by pervaporation

↳ **Acetic acid / water mixture on a Sn-substituted MFI-type zeolite : <u>effect of T</u>**



Comparison Si/Sn = ∞ and Si/Sn = 25

(higher/lower ratios)

- When T ↗, Flux ↗

⇒ The diffusion rates of H_2O and CH_3COOH increase with the increase in T (thermal agitation)

- When T ↗, SF ↗

⇒ The diffusion rate of H_2O increases more then the one of CH_3COOH

⇨ for Si/Sn = 25 (5 wt.% CH_3COOH), the Sn-substituted MFI has a better performance (SF~ 6) than the silicalite (Si/Sn = ∞) and also than classical polymeric membranes

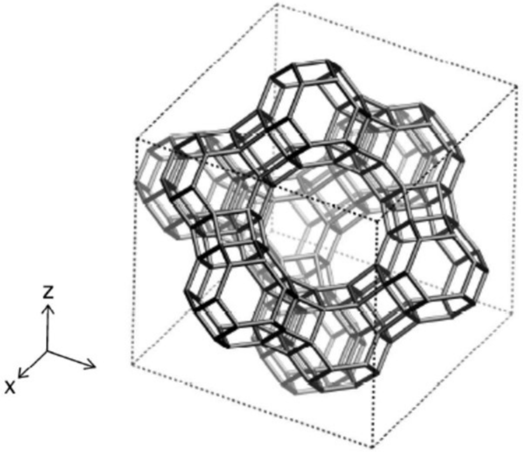
⇨ <u>However</u> : ↘↘ in performance as [CH_3COOH] ↗, which limits the applications

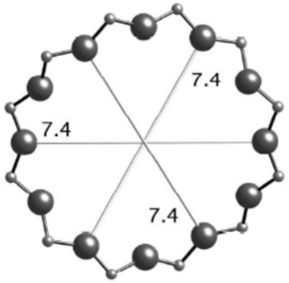
Adsorption / ozone decomposition coupling

↳ VOC adsorption and in-situ regeneration of zeolites by simultaneous O_3 adsorption

- Comparison of the adsorption properties of a faujasite (FAU) and a silicalite (MFI)
- Adsorption of toluene (1 $g.cm^{-3}$) and methyl ethyl cetone (2,15 $g.cm^{-3}$) present in a gaseous effluent

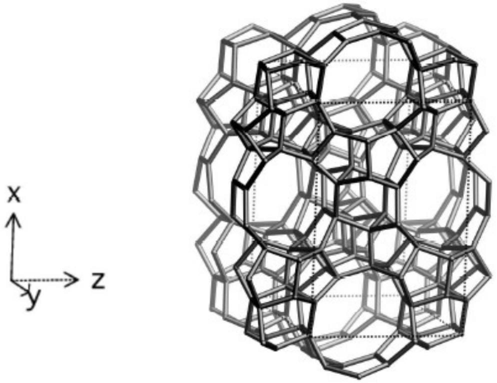
Faujasite
FAU

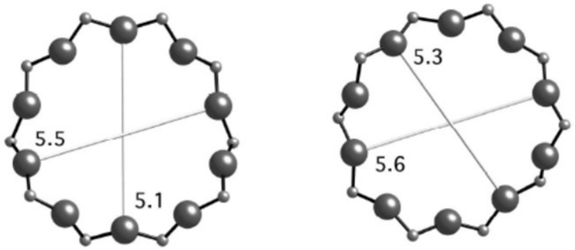




12T along [111]

Silicalite
MFI

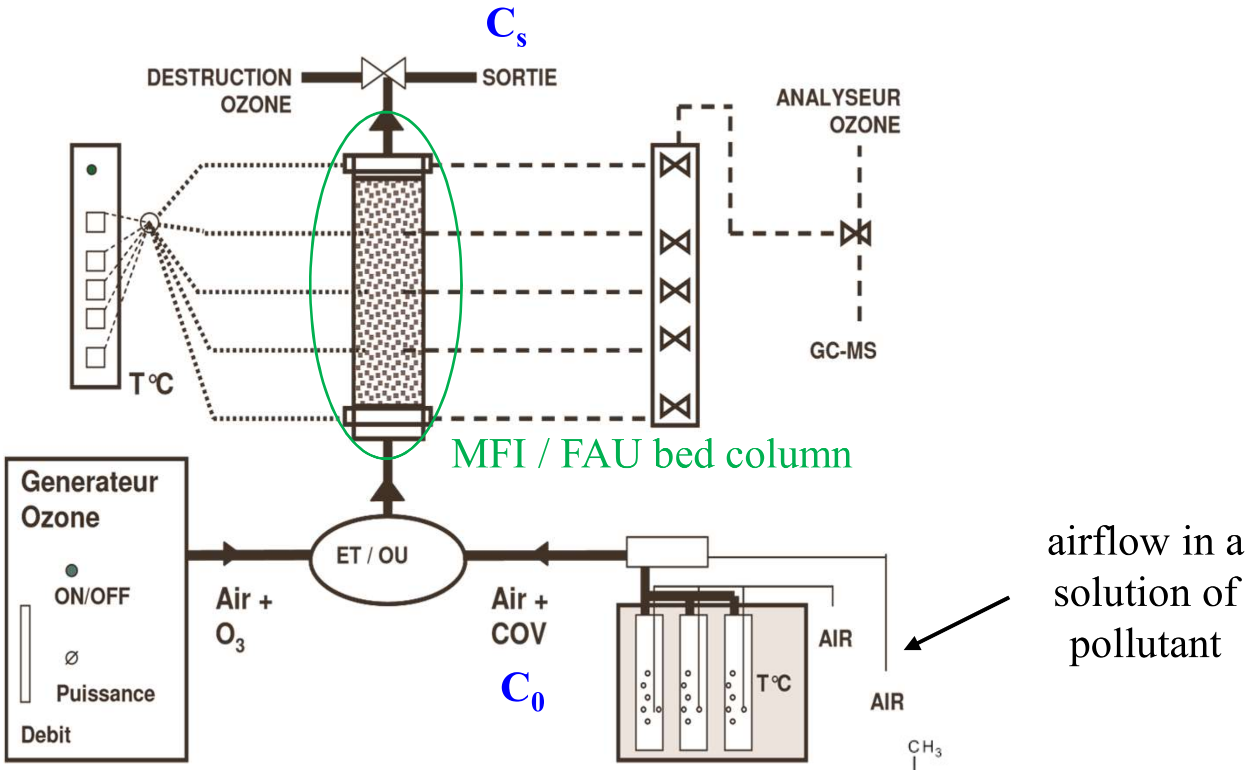




10T along [100] et [010]

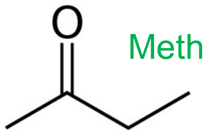
Adsorption / ozone decomposition coupling

- Experimental bench

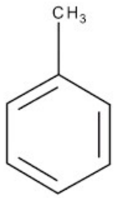


MFI / FAU bed column

airflow in a solution of pollutant



Methyl Ethyl Cetone
MEC

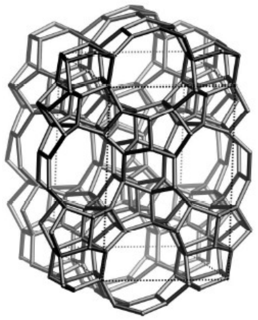


Toluene
TOL

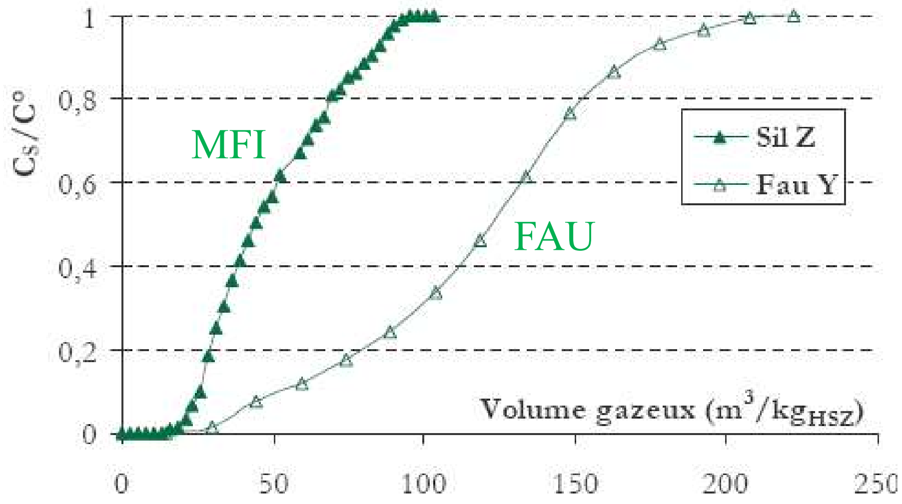
- Saturation of the zeolites by the gaseous effluent
- Study of the breakthrough curves : $C_s/C_0 = f$(Volume of gas treated per unit mass of adsorbent)

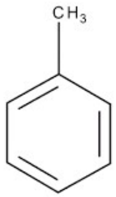
Adsorption / ozone decomposition coupling

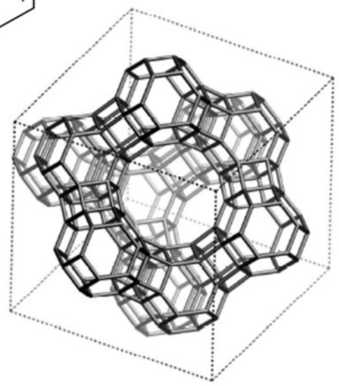
↳ Breakthrough curves of Toluene (“courbes de percée”)



MFI







FAU

Toluène : $C_0 = 1 g.m^{-3}$

⇨ Both zeolites present different adsorption properties

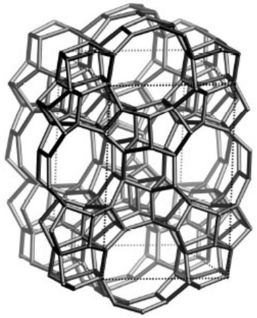
- Silicalite adsorbs toluene more rapidly (breakthrough more vertical)
- Silicalite is more quickly saturated ($V_{\text{gas at saturation}} \sim 100\ m^3.kg^{-1}$ vs $225\ m^3.kg^{-1}$)
- Qads (FAU) > Qads (MFI)

⇨ The cavity of FAU is more suitable for the adsorption of TOL than the channels of MFI

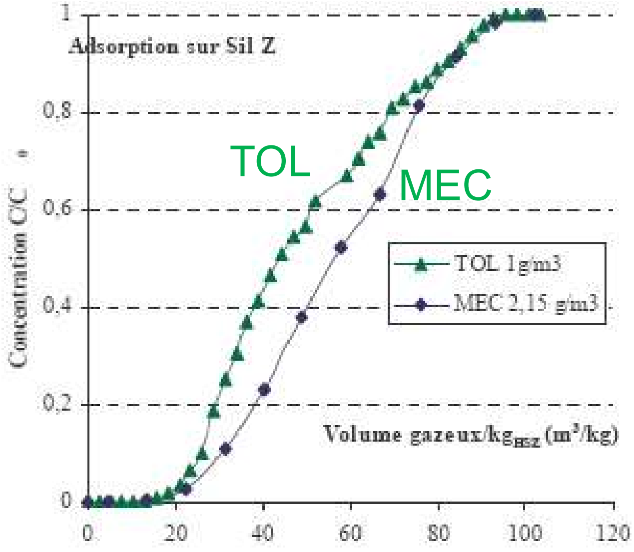
⇨ **Good match of shape**

Adsorption / ozone decomposition coupling

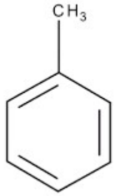
↳ Breakthrough curves of MEC and TOL on silicalite



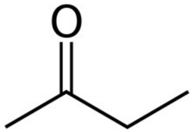
MFI



Breakthrough curves on silicalite



TOL



MEC

Silicalite adsorbs more MEC :

→ The saturation is obtained for a similar gas volume but for a more concentrated effluent (1 g.m^{-3} for TOL vs 2.15 g.m^{-3} for MEC)

⇨ The channels of MFI are more suitable for the adsorption de MEC than the cavities of FAU

⇨ **Good match of shape**

Adsorption / ozone decomposition coupling

↳ Zeolites regeneration

→ a dry air/O_3 (18 g.m^{-3}) flow is passed through the saturated adsorbent

→ Measurement of C_{O_3} et C_{VOC} at the outlet of the column

∀ zeolite ∀ VOC → highly exothermic reaction
→ formation of by-products : organic molecules + H_2O + CO_2
→ no trace of O_3 detected at the outlet of the column

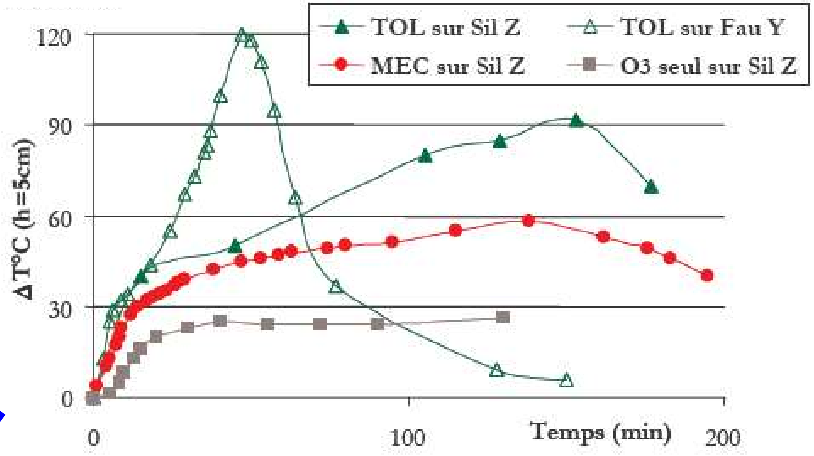
oxidation on the zeolite surfaces

Measure of the T ↗ during the oxidation by ozone

→ the more exothermic the reaction is

→ the more T ↗

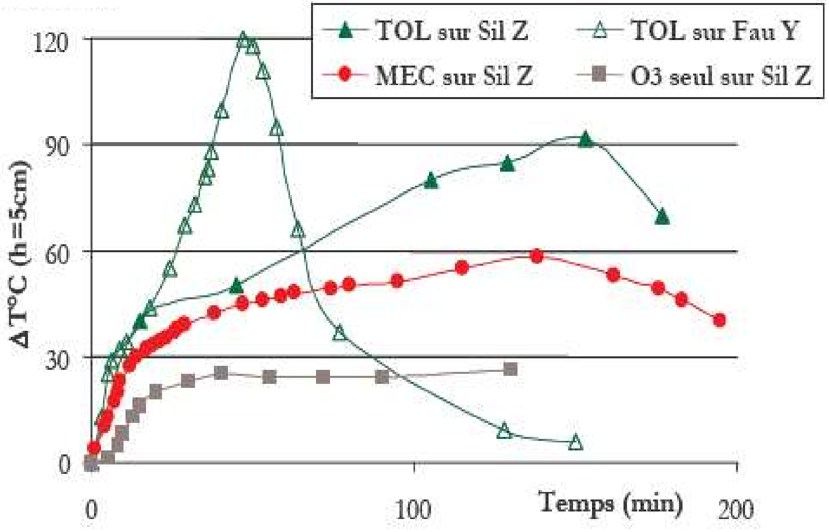
→ the more efficient the oxidation is



Concentration profiles inside the bed during ozonation of pristine and VOC-saturated zeolites

Adsorption / ozone decomposition coupling

⇘ Zeolites regeneration



Concentration profile inside the bed during ozonation of pristine and VOC-saturated zeolites

- For the oxidation of TOL on SIL (▲) and FAU (△) → different thermal effect
  → higher temperature increase for FAU

⇨ $\varnothing_{pores}$ FAU (~ 13 Å) > $\varnothing_{pores}$ MFI (~ 5-6 Å) : this favors the diffusion of reactants and products
⇨ V_{pores} FAU > V_{pores} MFI ⇒ FAU can adsorb a higher amount of VOC

- For the oxidation on silicalite (MFI) → lower T increase for MEC (●) than for TOL (▲)
  → incomplete oxidation and formation of stable by-products

- Detected by-products → TOL : oxalic, acetic, formic acids, formique and acetaldehyde
  → MEC : acetic acid, butan-2,3-dione

Adsorption / ozone decomposition coupling

➯ Reaction mechanisms (Toluene)

1st hypothesis – classical oxido-reduction mechanism

→ Adsorption of toluene onto the zeolite surface

→ O_3 = strong oxidizing gas ⇒ polluant's degradation by oxidation

2nd hypothesis- Radical mechanism

→ Adsorption of O_3 onto the Lewis acid sites of the surface (s : aluminium)

$O_3 + s = sO_3$ s = active site

→ Decomposition into O_2 and atomic active oxygen : $O^{\bullet}$

$$sO_3 = sO^{\bullet} + O_2$$

→ Decomposition of toluene by par atomic active oxygen

C_7H_8 (TOL) $+ 18\ O^{\bullet} = 7\ CO_2 + 4\ H_2O$ (detected by GC-MS)

⇨ Possibility of in-situ regeneration of the zeolite

⇨ Zeolites can be used for continuous pollution control

Adsorption by cationic exchange

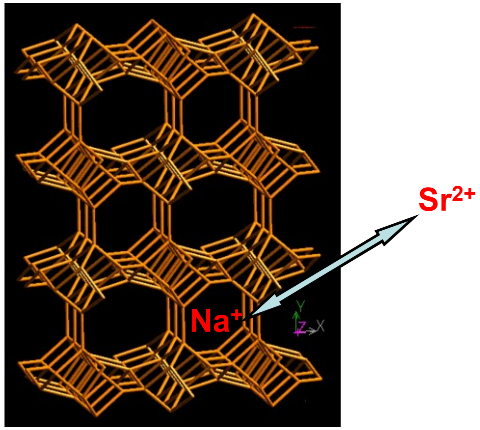
↳Treatment of aqueous nuclear effluents

- Removal of radioactive waste from nuclear power plant effluents before discharge into the environment

  → retention of ^{90}Sr, ^{137}Cs, ^{60}Co, ^{45}Ca by ionic exchange with the zeolite cations (Na^+, K^+) ⇨ size match

  → use of clinoptilolites and mordenites (good resistance to soil acidity)

  → zeolites containing « non-harmful » waste are burried



Clinoptilolite
10T et 8T
(natural, synthetic)

- reduction of radioactive contamination

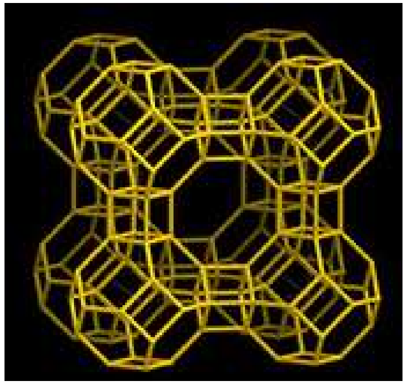
  → Three Mile Island, 1979

  → cleaning up after the Tchernobyl disaster, 1986
  (> 500 000 t)

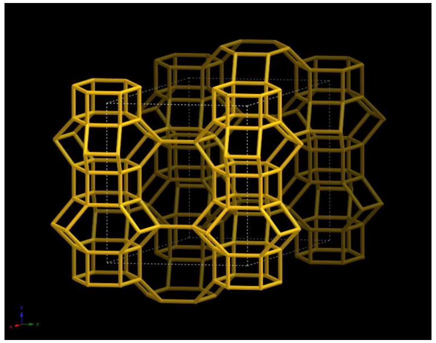
  → Limiting the pollution of the marine environment, Fukushima, 2011

Adsorption by cationic exchange

➩ Comparative adsorption of ^{137}Cs and ^{90}Sr on different zeolites



NaA (LTA)

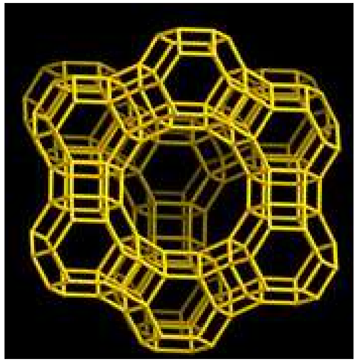


ERI

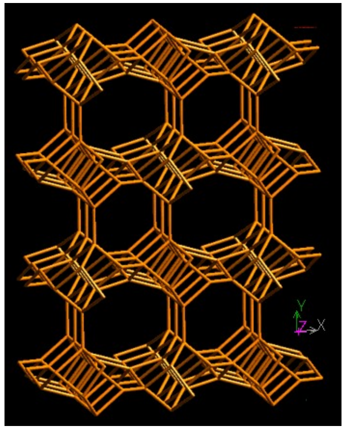
Zeolite	Si/Al	Structure	Ouverture
NaA	1	LTA	8T
NaX	1.25	FAU	12T
NaY	2.4		
Erionite	3.5	ERI	8T
Clinoptilolite	> 4	HEU	10T and 8T

synthetic

natural



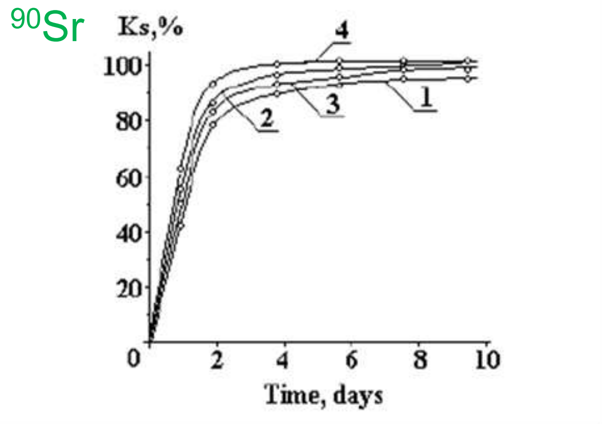
NaX/NaY (FAU)



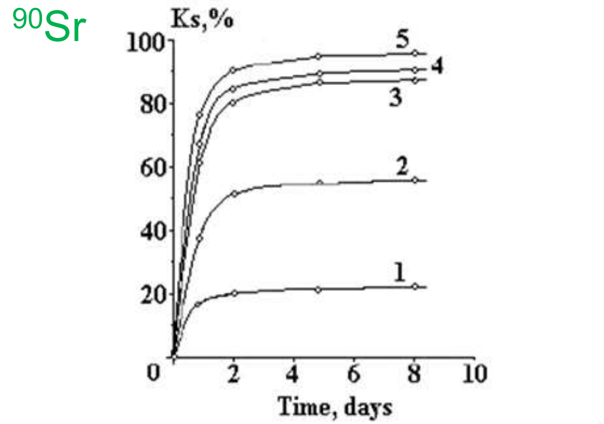
Clinoptilolite

Adsorption by cationic exchange

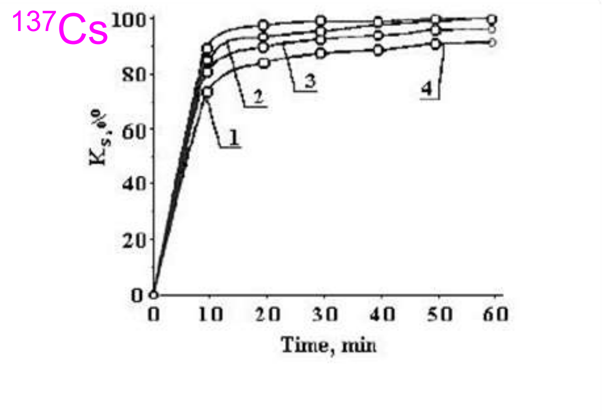
⇘ Adsorption kinetics



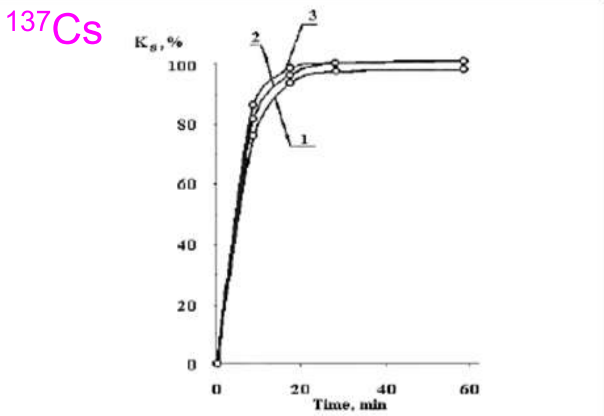
Adsorption ^{90}**Sr** sur erionite (1), NaY (2), NaA (3) et NaX (4) à pH = 7



Adsorption ^{90}**Sr** sur **clinoptilolite** à pH = 2 (1), 5 (2), 7 (3), 8,5 (4) et 11 (5)



Adsorption ^{137}Cs sur erionite (1), NaY (2), NaA (3) et NaX (4) à pH = 7



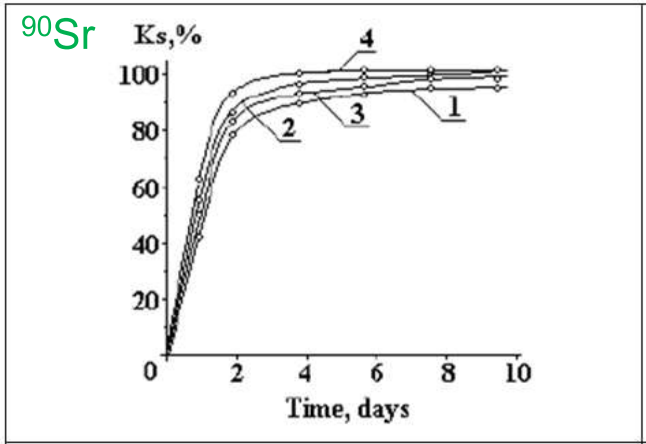
Adsorption ^{137}Cs sur **clinoptilolite** à pH = 2 (1), 7 (2) et 11 (3)

∀ zeolite, ∀ the pollutant ⇒ adsorption in 2 steps :

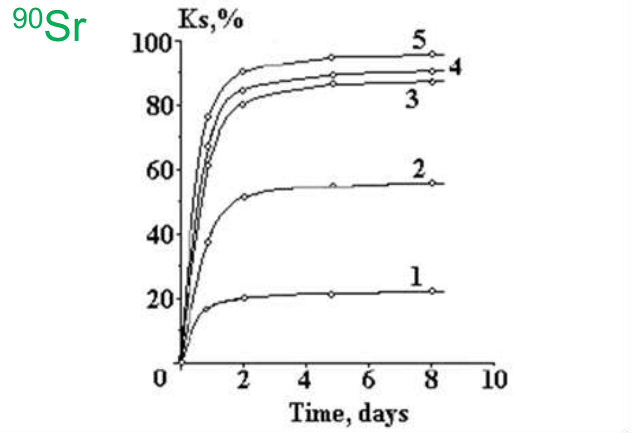
- 1st step, very quick → saturation of the sites by the polluant : fast diffusion due to accessible porosity
- 2nd step, slower → steric hindrance ⇒ decrease in diffusion speed

Adsorption by cationic exchange

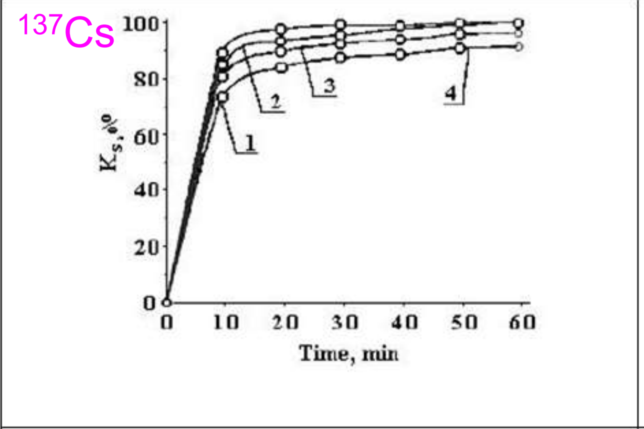
↳ Adsorption kinetics



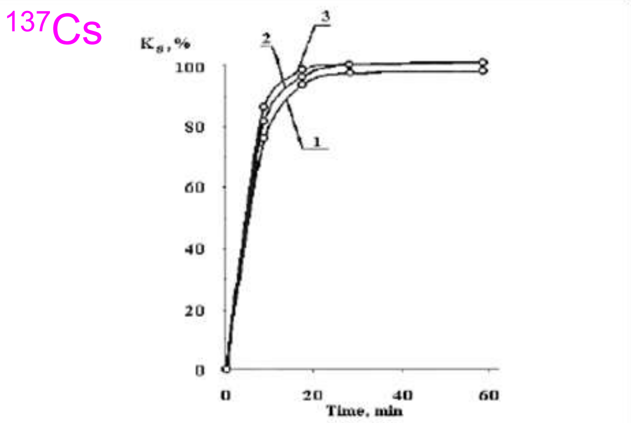
Adsorption ^{90}**Sr** sur erionite (1), NaY (2), NaA (3) et NaX (4) à pH = 7



Adsorption ^{90}**Sr** sur **clinoptilolite** à pH = 2 (1), 5 (2), 7 (3), 8,5 (4) et 11 (5)



Adsorption ^{137}**Cs** sur erionite (1), NaY (2), NaA (3) et NaX (4) à pH = 7



Adsorption ^{137}**Cs** sur **clinoptilolite** à pH = 2 (1), 7 (2) et 11 (3)

^{90}**Sr** **:** Adsorption equilibrium → 2 days for clinoptilolite
→ 4 days for the synthetic zeolites

^{137}**Cs** **:** ≠ adsorption phenomena : adsorption equilibrium reached more quickly (< 20 min) ∀ zeolite

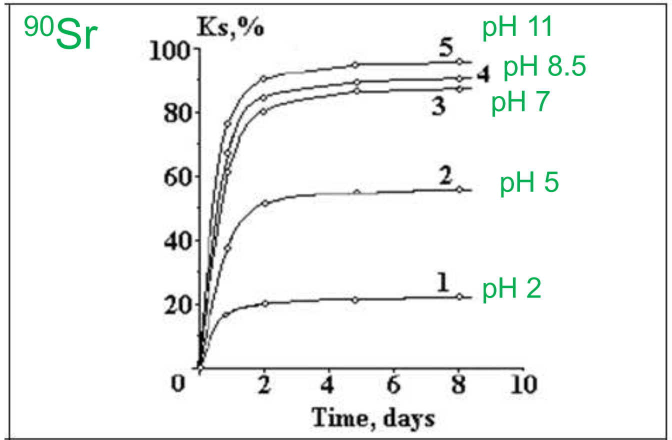
⇨ Adsorption of ^{137}Cs favored compared to ^{90}Sr

Diapositive 26

LR1 Laurence Reinert; 12/11/2024

Adsorption by cationic exchange

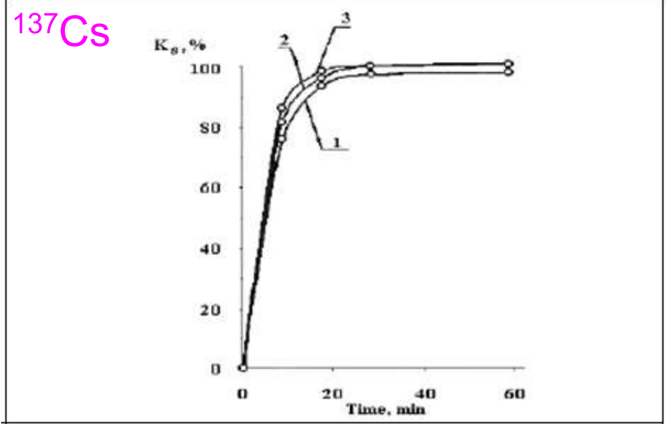
↳ Adsorption kinetics : effect of pH (clinoptilolite)



Adsorption ^{90}Sr sur clinoptilolite à pH = 2 (1), 5 (2), 7 (3), 8,5 (4) et 11 (5)

^{90}Sr → adsorption highly dependent of the pH of the initial solution

→ Maximal adsorption from pH 7



Adsorption ^{137}Cs sur clinoptilolite à pH = 2 (1), 7 (2) et 11 (3)

^{137}Cs : adsorption independent of the pH

⇨ adsorption sites different for Cs$^+$ and Sr^{2+}

- Acidic pH : competition between H$^+$ and Cs$^+$/Sr^{2+}

⇒ Protonation of the O$^-$ groups of the framework
⇒ ↘ of the negative charge of the framework
⇒ ↘ of the adsorption capacities

Adsorption by cationic exchange

↳ Adsorption mechanisms on clinoptilolite

- Qads **^{137}Cs** > Qads **^{90}Sr**

Or rSr^{2+} ~ 127 pm and rCs^{+} ~ 167 pm ⇒ $rCs^{+} > rSr^{2+}$

⇨ Sr^{2+} is probably adsorbed under an hydrated form ⇒ increase in ion size

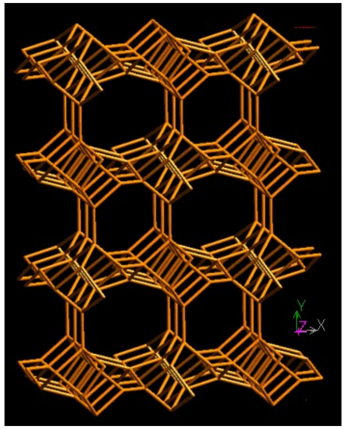
(Sr^{2+} : small and highly charged ⇒ PP ↗ ⇒ is easily surrounded by a hydration sphere)

⇨ Cs^{+} fits the 8T clinoptilolite cycle with the right size

- Clinoptilolite possesses a high Si/Al ratio

⇒ low charge compensation required

⇒ specific zeolite for low-charge cations



Clinoptilolite

⇨ Clinoptilolite is selective for low hydrated mono/divalents cations