Cryogenic Adsorption Equilibrium and Kinetics of CO_2 and CH_4 in zeolites

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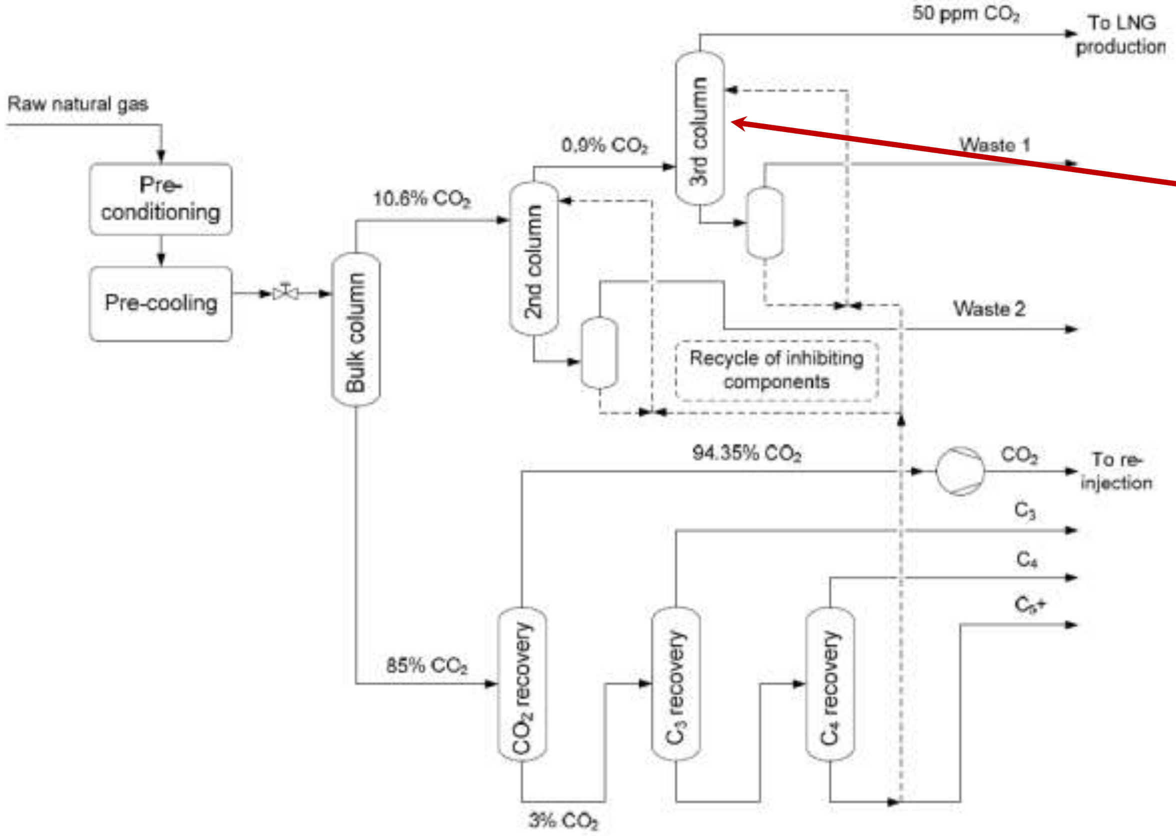
Outline

- Scope of the problem
- Concept of Temperature Swing Adsorption process
- Adsorption equilibrium
- Adsorption kinetic (batch system)
- Fixed-bed experiments
- Conclusions
- Acknowledgments

Scope of the work:

Cryogenic distillation for upgrading of natural gas is a multi-column for sequential removal of CO_2.



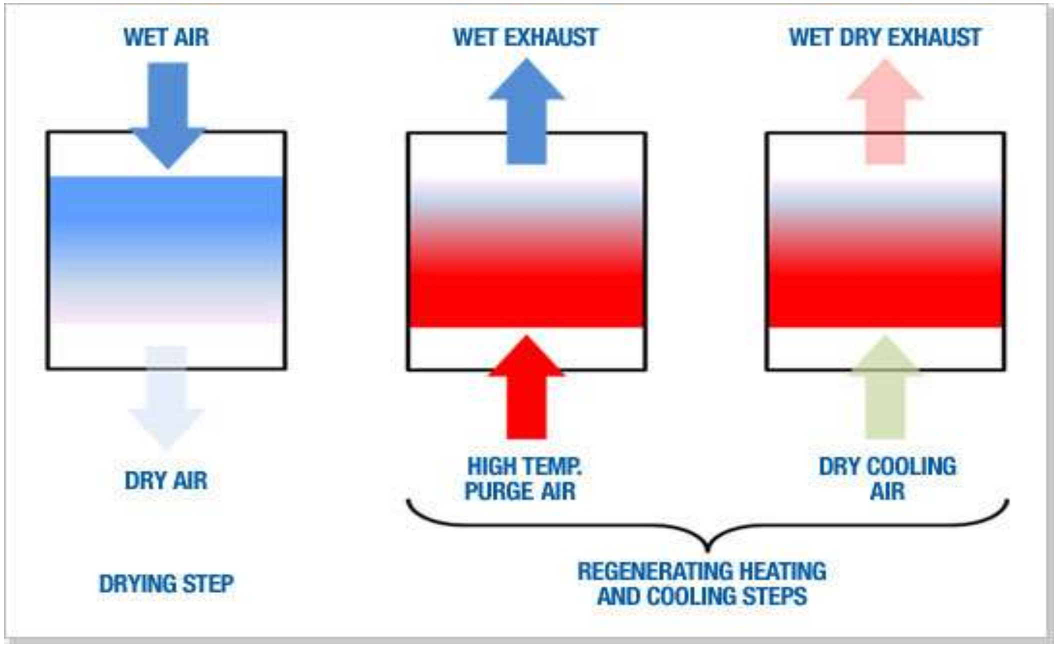
Question: can we replace this column by an adsorption process?

Conditions:
~1%CO_2 (rest CH_4)
P = 40 bar
T = -80ºC

Berstad, Nekså and Anantharaman, Energy Procedia, 2012, 26, 41-48

Temperature Swing Adsorption design

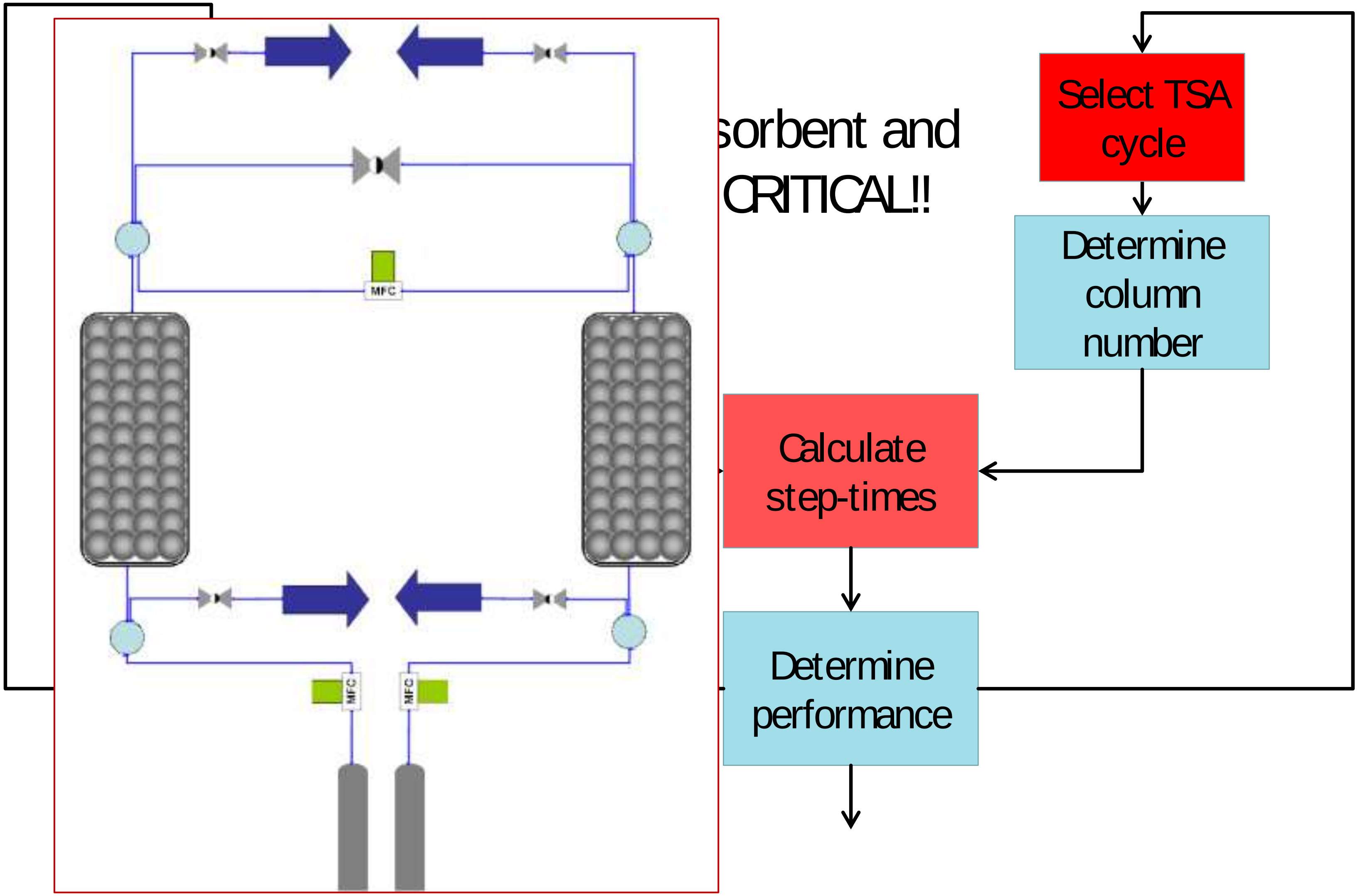
Before breakthrough of adsorbed species, the adsorbent (column) is "heated" with a hot stream of gas.



Heating / cooling can be directly (as shown) or indirectly with a hot fluid. In this application, the "hot fluid" can be at ambient temperature.

TSA require "strong" adsorption at low temperature that can be reverted with temperature increase → **zeolites should be ideal materials**

Process design sequence:



sorbent and
CRITICAL!!

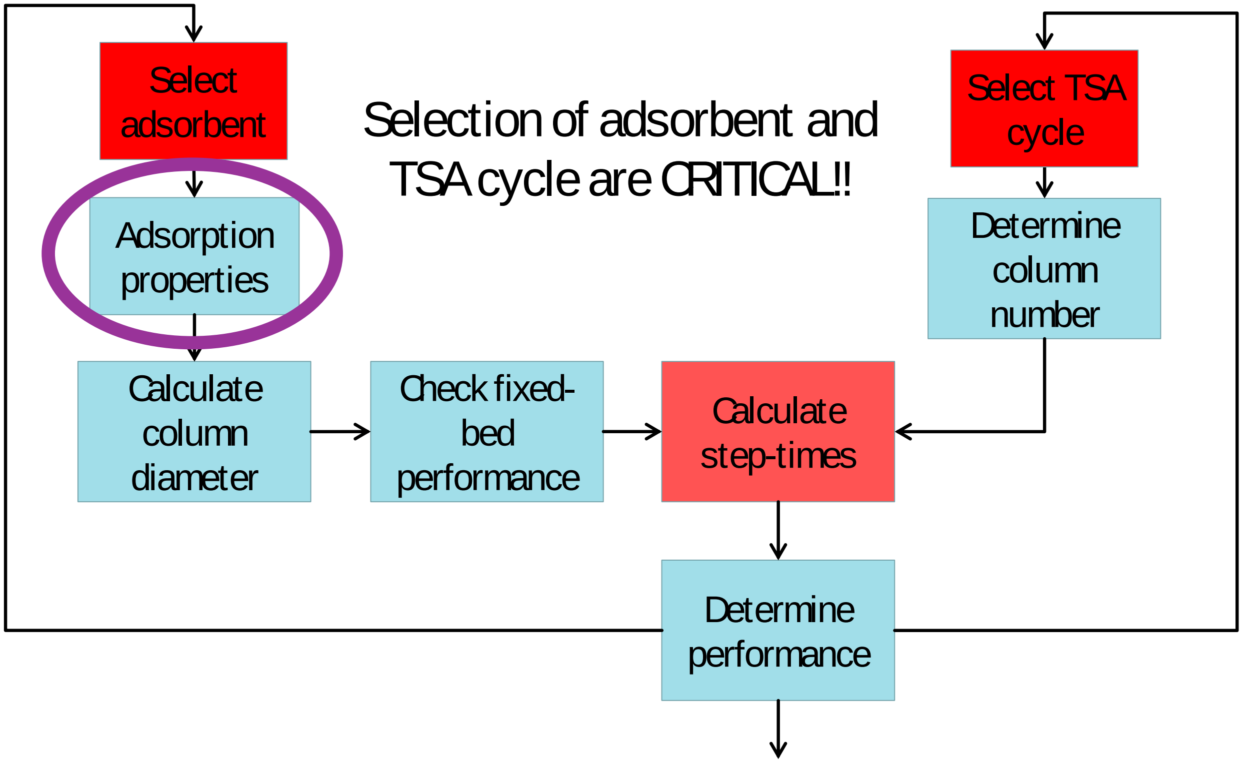
Select TSA cycle

Determine column number

Calculate step-times

Determine performance

Go back to the beginning:



Selection of adsorbent and TSA cycle are CRITICAL!!

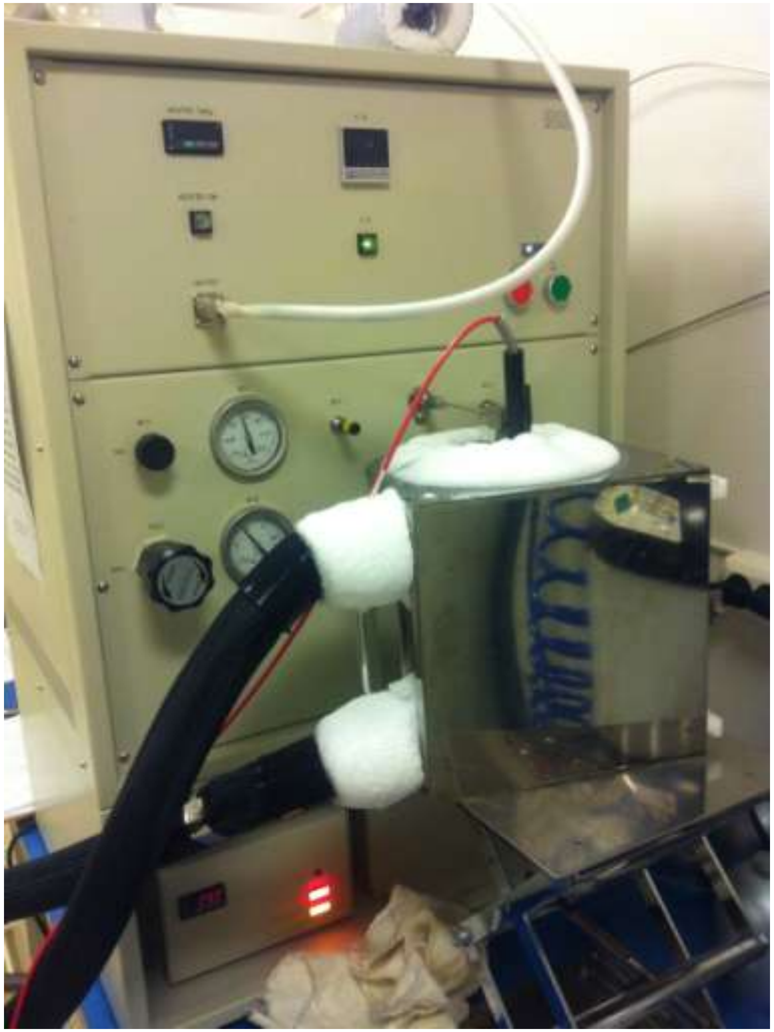
No adsorption equilibrium data available in literature for other materials than carbon molecular sieve (not proper material for TSA applications).

NEED TO MEASURE FUNDAMENTAL PROPERTIES TO DESIGN THE PROCESS…

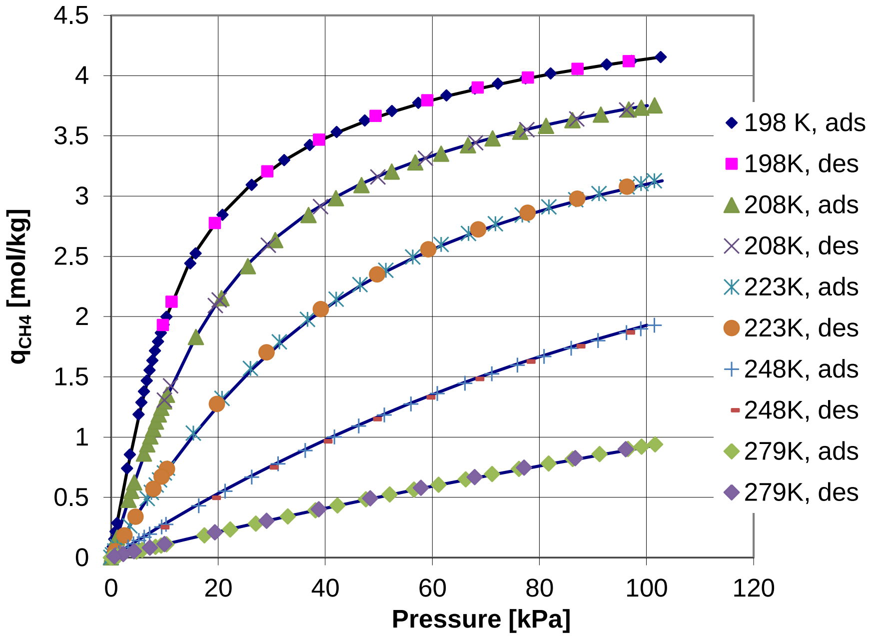
Experimental set-up:

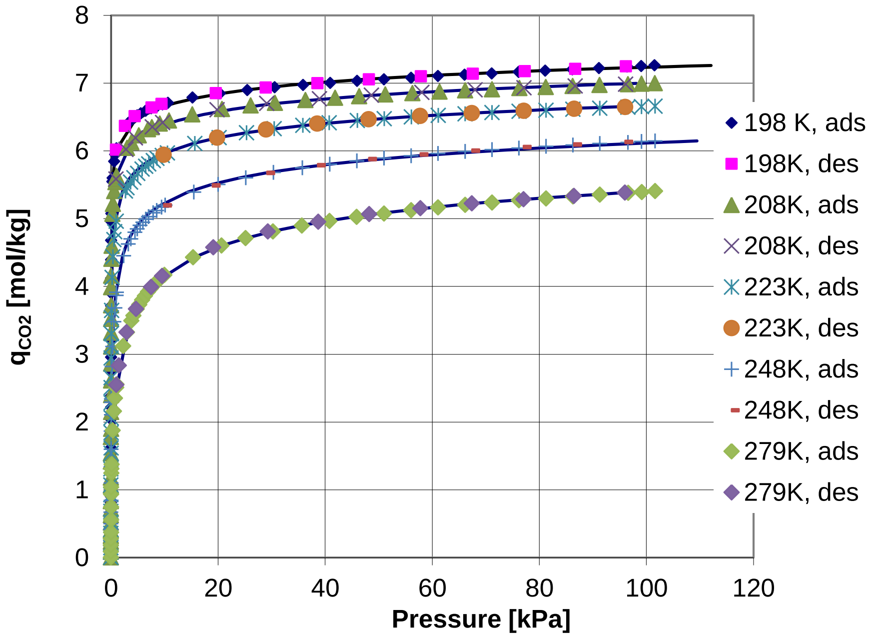
- Measurements were carried out in an automated Belsorp Max unit (Japan).
- The measurements might take very long time
  - Diffusion at low temperatures can be "tortuous"
  - Diffusion through pores of similar molecular size.
- The amount of CO_2 adsorbed can be high:
  - Only P and T are used so error can increase
  - Full regeneration was difficult
- We learned how to deal with a lot of ice…

- Low pressure Isotherms were measured at:
  - 198 K
  - 208 K
  - 223 K
  - 248 K
  - 279 K (~water temperature in North Sea).



Zeolite 13X: adsorption equilibrium

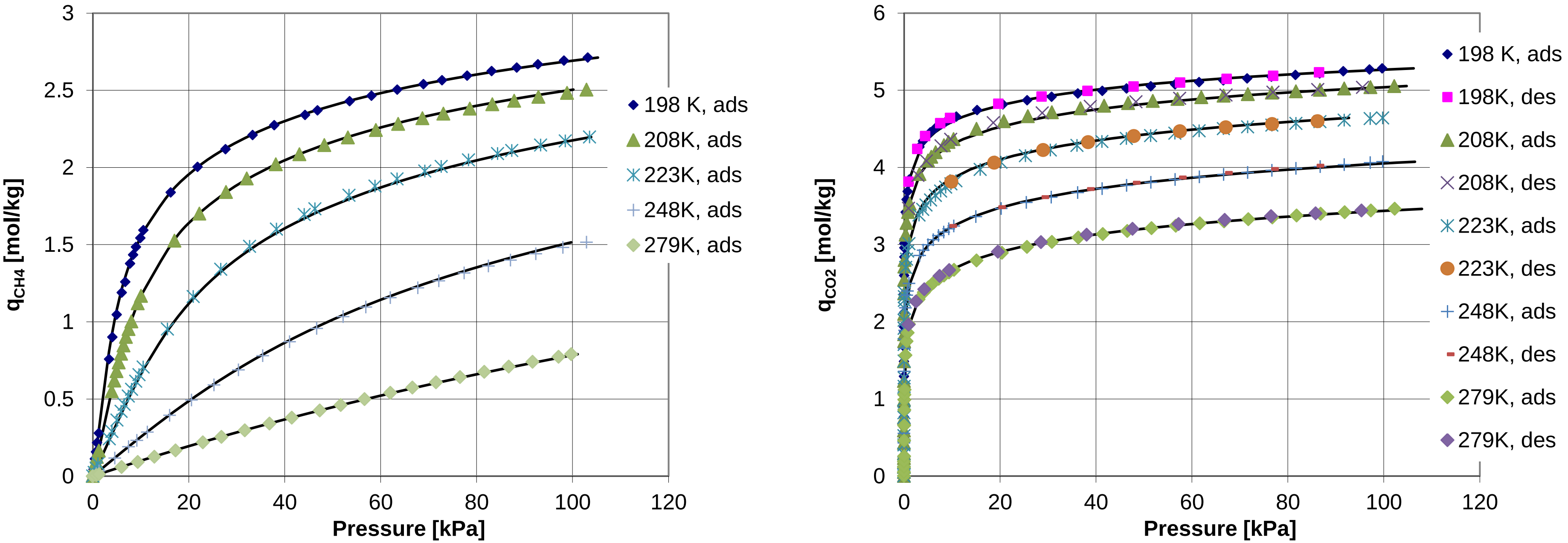




Adsorption of CO_2 is much more preferential than CH_4. Isotherms are very steep making it difficult to desorb and fully regenerate.

However, adsorption of CH_4 is considerable. Since pores are 7.8 Å, CH_4 has "free way to adsorb", generating a lot of heat. This makes it impossible the utilization of this adsorbent for an "efficient" TSA application.

Zeolite 4A : adsorption equilibrium



Adsorption of CO_2 is preferential than CH_4. Loadings of both gases are smaller than in zeolite 13X.

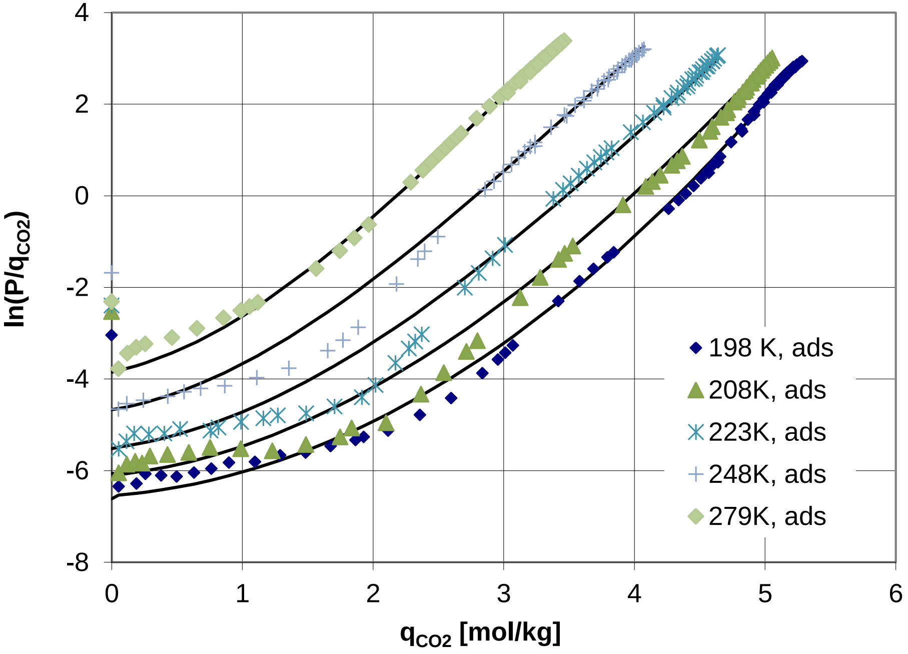
Adsorption of CH_4 is considerable, but potentially limited by pore size (pores close to the size of the molecule).

Adsorption of CO_2 very steep → difficult regeneration but good for TSA purposes

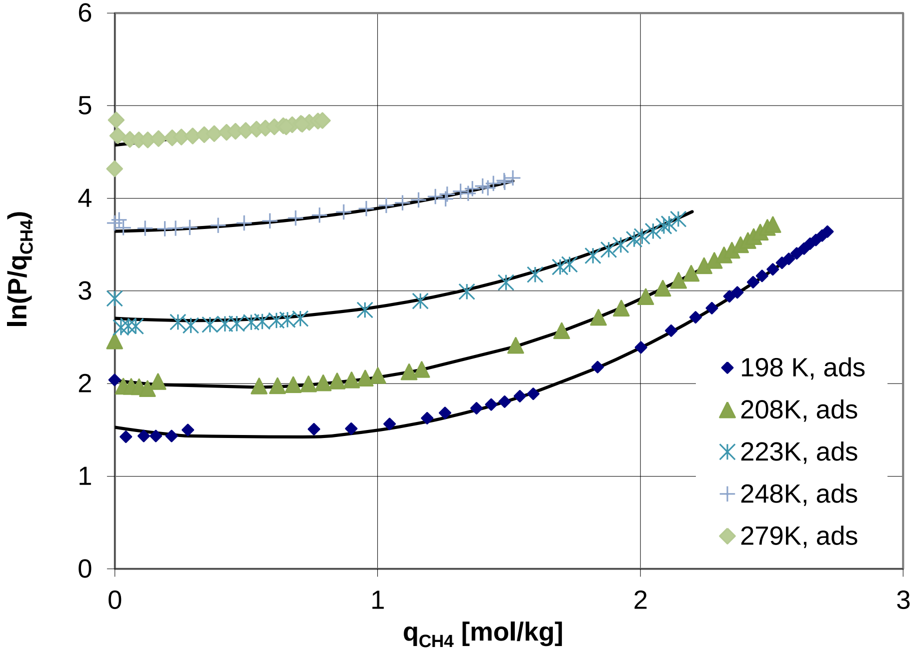
Zeolite 4A : adsorption equilibrium

- The results at low pressure with the "high accuracy" equipment show some deviation at very low pressures.
- The results are unique of their kind and will soon be published in literature. Taking into account the reproducibility tests, measurements took over three months.

CO_2 low-pressure "zoom"



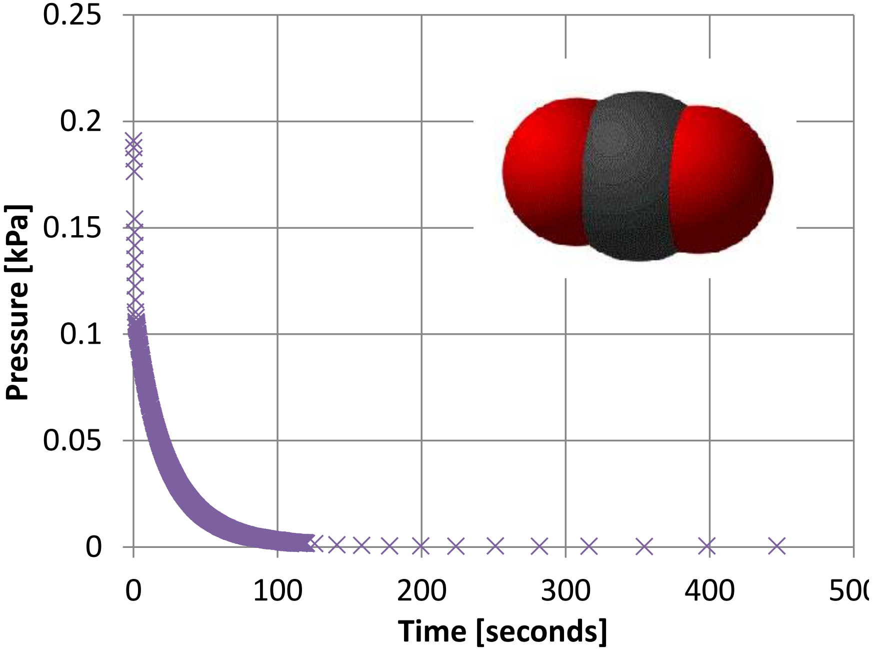
CH_4 low-pressure "zoom"



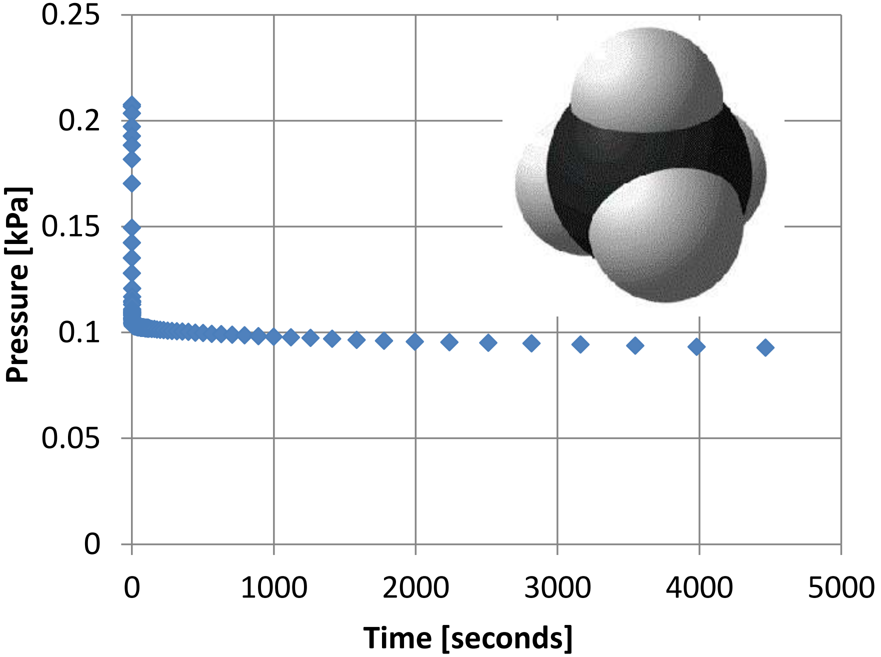
Zeolite 4A: diffusion at 198 K

- Carbon dioxide is fast to achieve adsorption equilibrium. Pressure goes very low increasing error of the first measurements.
- Each equilibrium point of methane takes at least 10000 seconds to be completed. Very delayed measurements.

Kinetic diameter 3.3 Å



Kinetic diameter 3.8 Å



Dynamic measurements

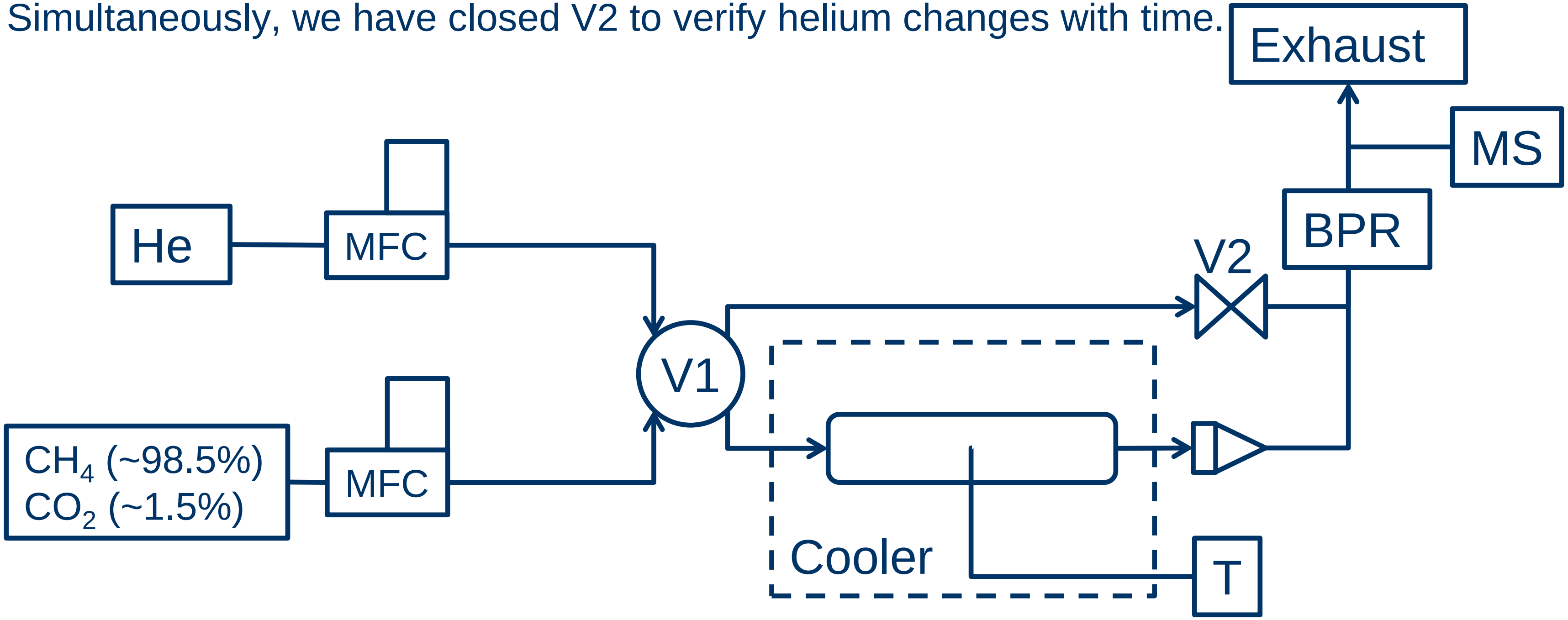
Experiments were carried out in a new unit to measure breakthrough curves using a small amount of sample. All dead volumes are minimized using short distances and 1/16" tubes.

Adsorption column:

Length: 97,5 mm; Diameter: 9,1 mm; Zeolite weight (humid): 3,7255 g

Before starting the experiments, helium was passing through the column and the mixture was passed through the bypass.

At t=0, we have changed the position of V1 so that the mixture goes through the column. Simultaneously, we have closed V2 to verify helium changes with time.



Mathematical model (dynamic)

System of partial differential equations

Material balances

Gas phase:
$$\frac{\partial}{\partial z}\left(\varepsilon D_{ax} C_{g,T} \frac{\partial y_i}{\partial z}\right) - \frac{\partial}{\partial z}\left(u_0 C_{g,i}\right) - \varepsilon \frac{\partial C_{g,i}}{\partial t} - (1-\varepsilon) a_p k_f \left(C_{g,i} - C_{s,i}\right) = 0$$

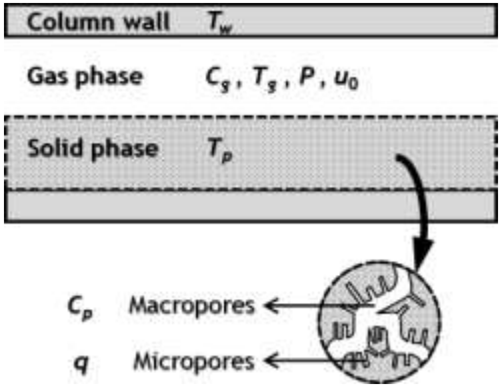
Solid phase:

Macropore
$$\frac{\partial \langle C_{m,i} \rangle}{\partial t} = \frac{\Omega_m D_{p,i}}{R_p^2}\left(C_{s,i} - \langle C_{m,i} \rangle\right) - \frac{\rho_p}{\varepsilon_p} \frac{\partial \langle \bar{q}_i \rangle}{\partial t}$$

Micropore
$$\frac{\partial \bar{q}_i}{\partial t} = \frac{\Omega_c D_{c,i}}{r_c^2}\left(q_i^* - \bar{q}_i\right)$$

Momentum balance

Ergun Equation:
$$-\frac{\partial P}{\partial z} = \frac{150 \mu (1-\varepsilon)^2}{\varepsilon^3 d_p^2} u_0 + \frac{1.75 (1-\varepsilon) \rho_g}{\varepsilon^3 d_p} |u_0| u_0$$



Ribeiro AM, Grande CA, Lopes FVS, Loureiro JM, Rodrigues AE. Chemical Engineering Science 2008;63:5258-5273.

Energy balances

Gas phase:
$$\frac{\partial}{\partial z}\left(\lambda \frac{\partial T_g}{\partial z}\right) - u_0 G_{g,T} C_p \frac{\partial T_g}{\partial z} + \varepsilon R_g T_g \frac{\partial G_{g,T}}{\partial t} - (1-\varepsilon) a_p h_f \left(T_g - T_p\right) - \frac{4 h_w}{d_{wi}}\left(T_g - T_w\right) - \varepsilon C_{g,T} C_v \frac{\partial T_g}{\partial t} = 0$$

Solid phase:
$$(1-\varepsilon)\left[\varepsilon_p \sum_{i=1}^{n} C_{m,i} C_{v,i} + \rho_p \sum_{i=1}^{n} \langle \bar{q}_i \rangle C_{v,ads,i} + \rho_p \hat{C}_{p,s}\right] \frac{\partial T_p}{\partial t} = (1-\varepsilon) \varepsilon_p R_g T_p \frac{\partial C_{m,T}}{\partial t} + \rho_b \sum_{i=1}^{n} (-\Delta H)_i \frac{\partial \langle \bar{q}_i \rangle}{\partial t} + (1-\varepsilon) a_p h_f \left(T_g - T_p\right)$$

Column wall:
$$\rho_w \hat{C}_{p,w} \frac{\partial T_w}{\partial t} = \alpha_w h_w \left(T_g - T_w\right) - \alpha_{w\ell} U \left(T_w - T_\infty\right) \qquad \alpha_w = d_{wi} / \left[e\left(d_{wi} + e\right)\right] \qquad \alpha_{w\ell} = 1 / \left[\left(d_{wi} + e\right) \ln\left(\left(d_{wi} + e\right) / d_{wi}\right)\right]$$

Adsorption isotherm model

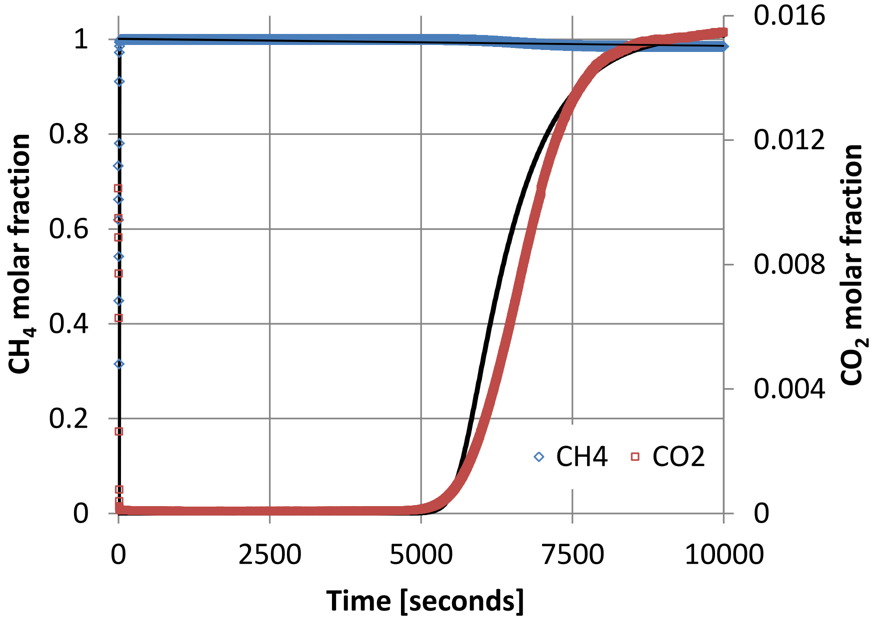
Virial isotherm
$$P = \frac{q}{K_H} \exp\left(\frac{2}{S} A q + \frac{3}{2 S^2} B q^2 + \ldots\right) \qquad A = \sum_{m=0}^{\infty} \frac{A_m}{T^m} \qquad B = \sum_{m=0}^{\infty} \frac{B_m}{T^m}$$

Virial extended isotherm
$$P_i = \frac{q_i}{K_{Hi}} \exp\left(\frac{2}{S} \sum_{j=1}^{N} A_{ij} q_j + \frac{3}{2 S^2} \sum_{j=1}^{N} \sum_{k=1}^{N} B_{ijk} q_j q_k\right) \qquad A_{ij} = \frac{\left(A_i + A_j\right)}{2} \qquad B_{ijk} = \frac{\left(B_i + B_j + B_k\right)}{3}$$

Van’t Hoff equation
$$K_H = K_\infty \exp\left(\frac{-\Delta H}{R_g T}\right)$$

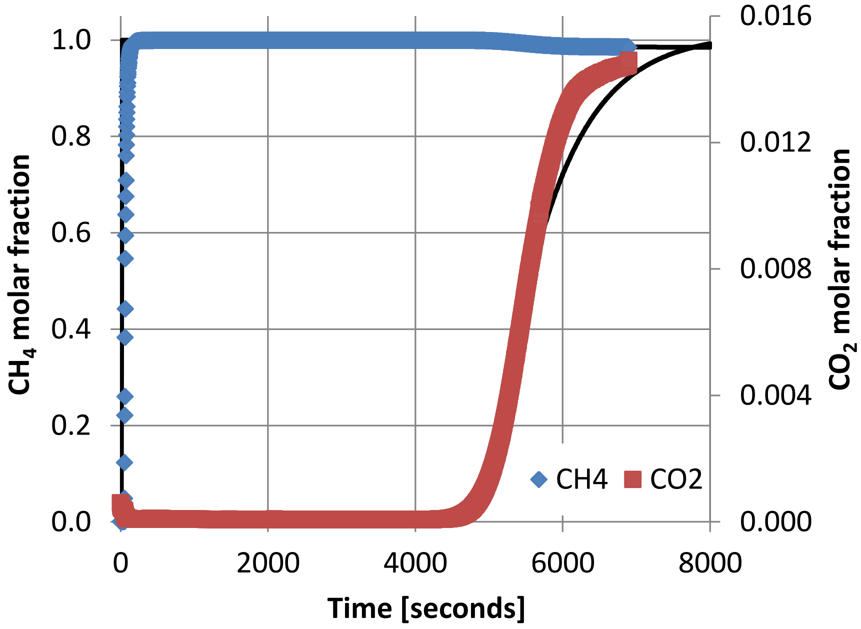
Dynamic measurements: results

Experiments were performed at 204 K and with total pressure of 1 bar and 10 bar. Different flowrates were used. Here we show two examples.



Experiment at 1 bar, 195 ml/min feed flow. Temperature variation was negligible.

Mathematical model predicts the breakthrough curve with good accuracy.



Experiment at 10 bar, 263 ml/min feed flow. Temperature variation was 1.5 K.

Mathematical model predicts the breakthrough curve with acceptable accuracy.

Conclusions:

- Fundamental data for adsorption of methane and carbon dioxide was measured under cryogenic conditions.
- Methane adsorption in zeolite 13X is very fast and might generate intense heat if used in a TSA process which makes this adsorbent not desirable for this application.
- Adsorption data of CO_2 indicates that the desorption might have to be carried out at slightly high temperature than sea water.
- Zeolite 4A practically excludes adsorption of methane at these conditions which is very desirable to avoid internal recycles in a TSA process.

Acknowledgments:

- This publication is based on the results from the research project “A Green Sea”, performed under the Petromaks program. The author(s) acknowledge the partners: Statoil, Gassco, Petrobras and the Research Council of Norway (200455/S60) for their support.