EFRC-NETL
Research on Carbon Capture
ARPA-E

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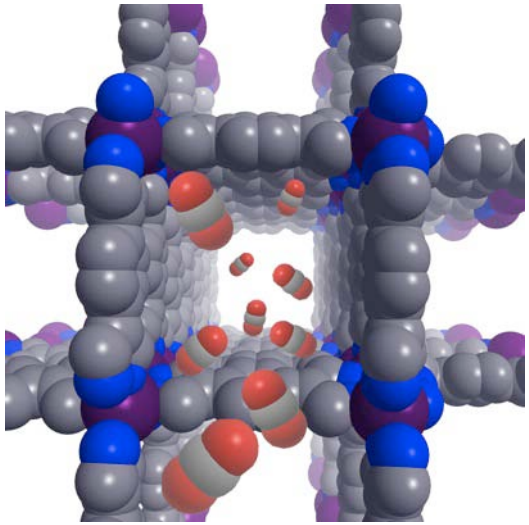
Center for Gas Separations
Relevant to Clean Energy Technologies

an Office of Basic Energy Sciences
Energy Frontier Research Center

Center for Gas Separations Relevant to Clean Energy Technologies

Berend Smit and Jeff Long (UC Berkeley)

The aim of this EFRC is to develop new strategies and materials that allow for *energy efficient* selective *capture* or *separation* of CO_2 from gas mixtures based on molecule-specific chemical interactions.



RESEARCH PLAN AND DIRECTIONS

Capture of CO_2 from gas mixtures requires the molecular control offered by nanoscience to tailor-make those materials exhibiting exactly the right adsorption and diffusion selectivity to enable an economic separation process. Characterization methods and computational tools will be developed to guide and support this quest.

High-Throughput Synthesis

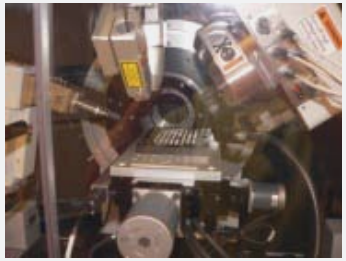
Highly-parallel, automated discovery of new MOFs

Automated Solid and Liquid Dosing

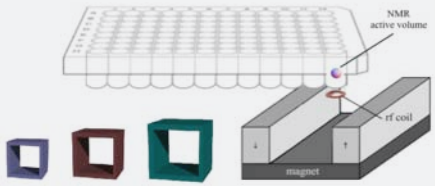
New Structure Types

High-Throughput Characterization

Rapid identification of new porous materials

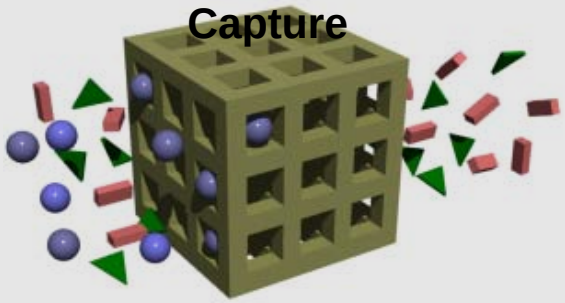


Powder X-ray Diffraction



NMR Porosity Screening

High-Throughput Discovery of Robust Metal-Organic Frameworks for CO_2 Capture



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arpa·e
Advanced Research Projects Agency • ENERGY

Wildcat Discovery Technologies

Steven S. Kaye

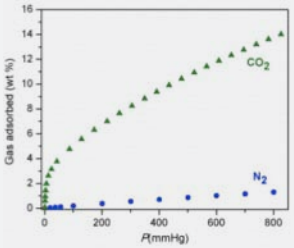
EPRI ELECTRIC POWER RESEARCH INSTITUTE

Abhoyjit S. Bhown

CO_2 Adsorption Screening

Rapid screening of CO_2 capture performance

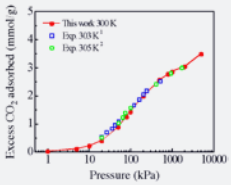
High-throughput Instrumentation

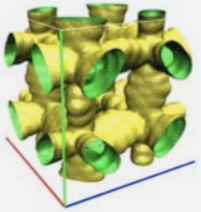


Adsorption Data

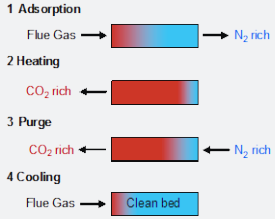
Computational Analysis

Data analysis, life cycle and sorbent performance analysis





Simulations



Sorbent Performance

Screening of capture materials

Li-Chiang, Joe Swisher, and Jihan Kim
(UC Berkeley/LBNL)

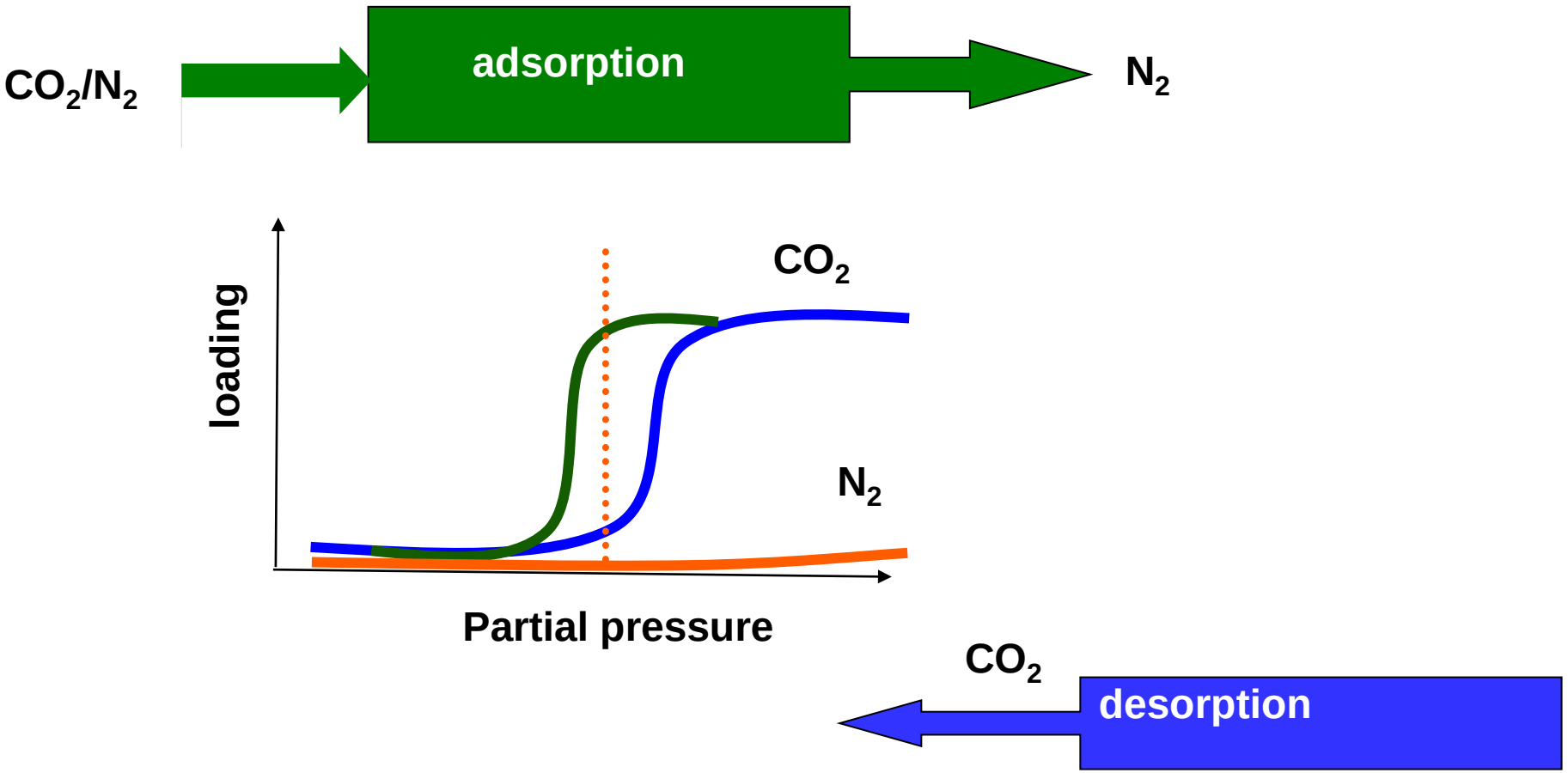
Richard Martin, Kuldeep Jariwala, and Maciej Haranzcyk
(LBNL)

Adam Berger and Abhoyit Bhown
(EPRI)

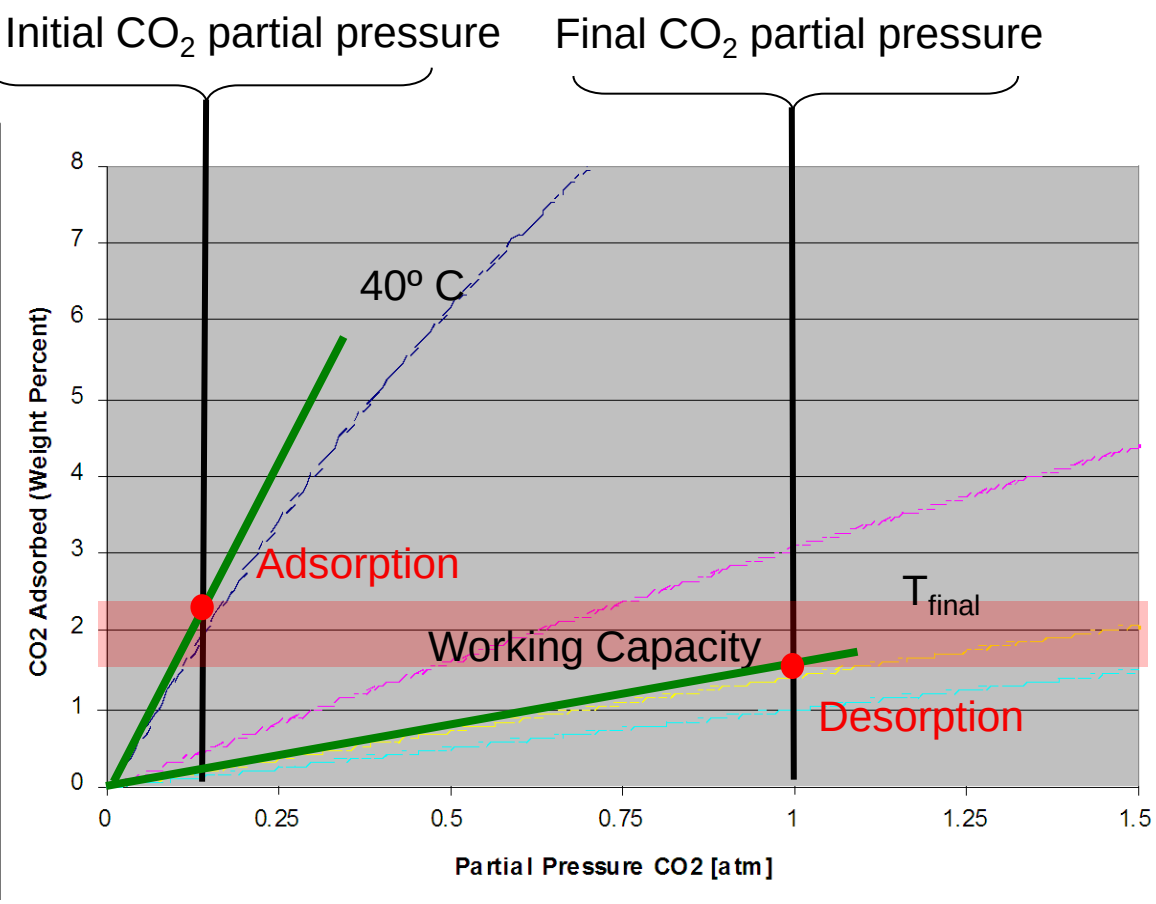
Support: DOE-BES/DOE-ARPA-e/DOE-NETL

Experiment: what happens we do if we bring EFRC – ARPA-e – NETL expertise together?

Separating CO_2



Working Capacity



Adsorption

- *Flue gas conditions: 14% CO_2 (40ºC and 1bar)*
- Partial pressure *CO_2 =0.14 atm*
- *N_2 very low*

Desorption:

- Final temperature and pressure

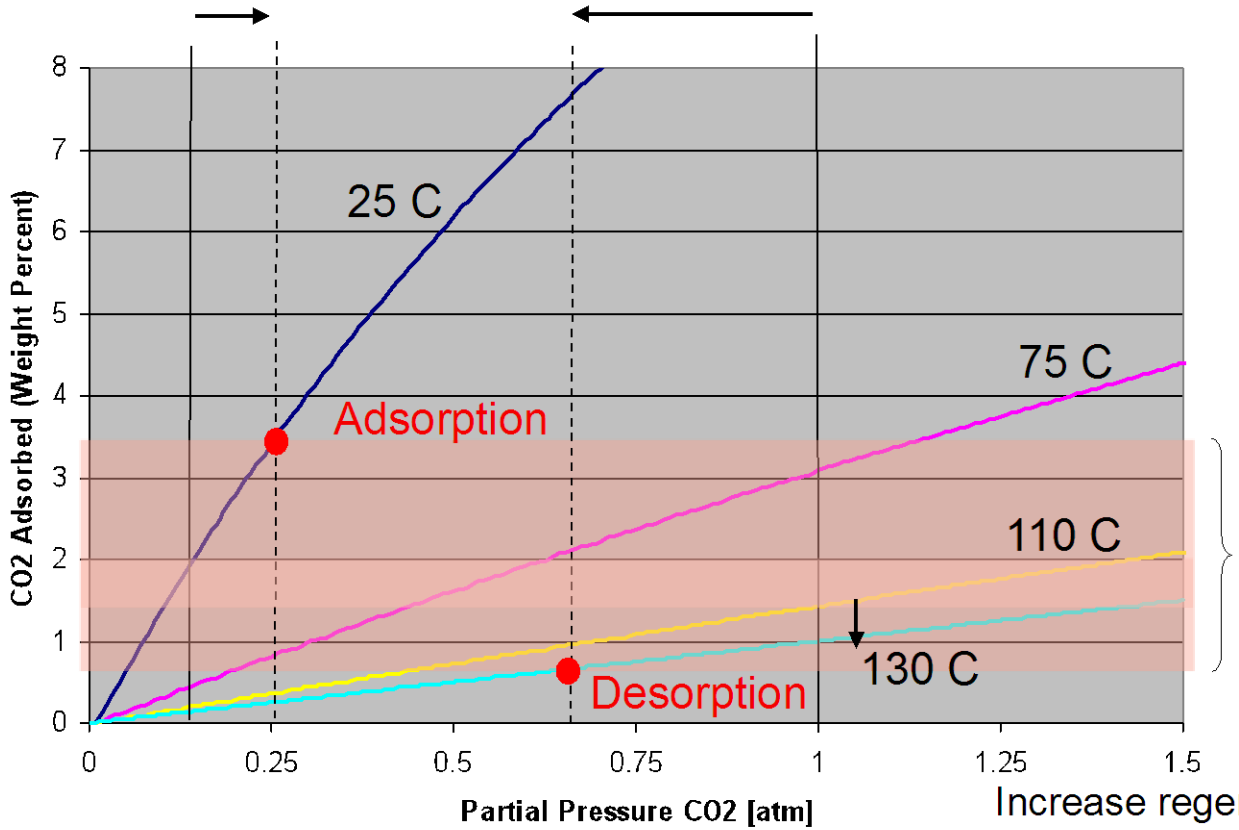
Working capacity

- Total amount of *CO_2* that can be removed

Optimizing the working capacity

Increase initial CO_2 partial pressure (feed compression)

Decrease final CO_2 partial pressure (vacuum or purge gas)



Working Capacity

Increase regeneration temperature (110 C to 130 C)

Adsorption:

- Decrease T
- Increase P

Desorption:

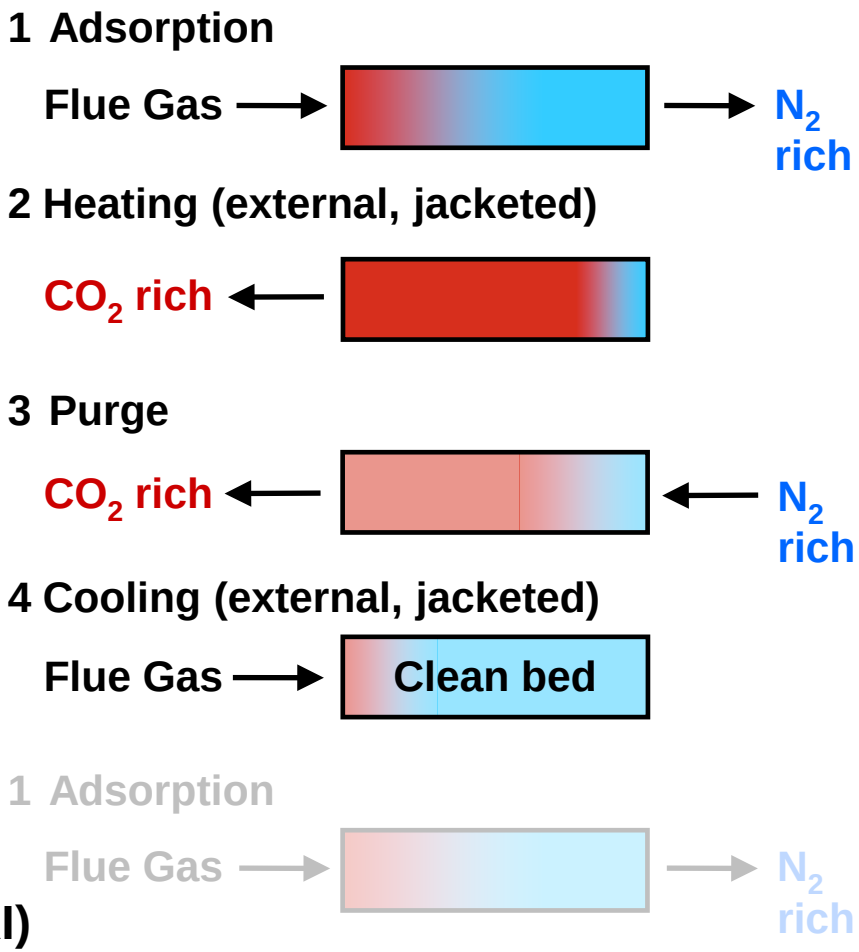
- Increase T
- Decrease P

What are the costs?

How does these relate to the materials?

Model for Screening Materials

- Calculate process independent performance characteristics of materials for CCS
- Fixed bed configuration
  - Temperature swing
  - Pressure swing
  - **Hybrid processes**
- **Equilibrium model**
  - No heat or mass transfer
  - Based on isotherms
- Uses difference in capacity between *adsorption / desorption* conditions



(Adam Berger and Abhoyit Bhown, EPRI)

Energy Calculation

Energy penalty for CCS can be roughly divided into the compression work and the heating energy:

- **Heating energy (Q):** heat necessary to regenerate a given sorbent:
  - Sensible heat: heats and cools bed. Provides driving force to produce CO_2
  - Desorption heat: desorbs CO_2 (equal to heat of adsorption, Δh).

$$Q = \left(\underbrace{C_p \rho_{sorbent} \Delta T}_{\text{Sensible heat requirement}} + \underbrace{\Delta h_{CO2} \Delta q_{CO2} + \Delta h_{N2} \Delta q_{N2}}_{\text{Desorption heat requirement}} \right) \Big/ CO_{2\,\mathrm{Produced}}$$

- **Compressor work (W_{comp}):** Work to compress CO_2 product to 150 bar (for transport)

Equivalent energy calculated by discounting the heat requirement by the Carnot efficiency to simulate the effect of taking steam from a steam cycle

$$W_{eq} = \left(0.75 Q \cdot \eta_{carnot} + W_{comp} \right)$$

Model Use

- The input of the model are:
  - Flue gas composition and conditions (1atm, 14% CO_2, 40ºC)
  - Mixture adsorption isotherms, heat capacity, heats of adsorption

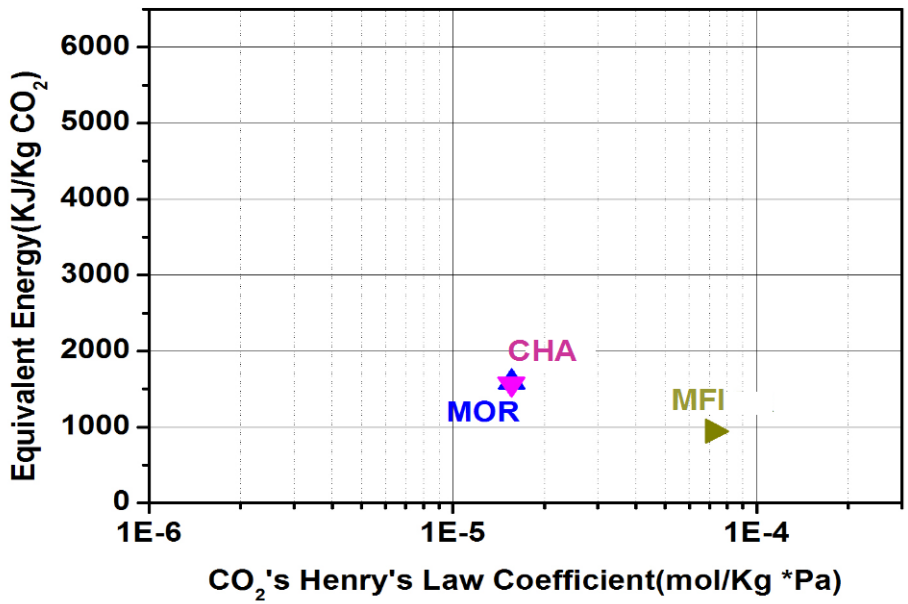
- For a given sorbent, we look at the equivalent energy for the whole range of regeneration temperatures and pressures to find the optimal process conditions for a given material

- This aims to be a fair process-independent metric for sorbents

- In this metric MEA solvents are 1065 kJ/kg CO_2 (a full scale design gives 1325 kJ/kg CO_2)

- **Conclusion of this work**:
  - The **best** all-silica structures are < 700kJ/kg CO_2

Zeolites for Carbon Capture



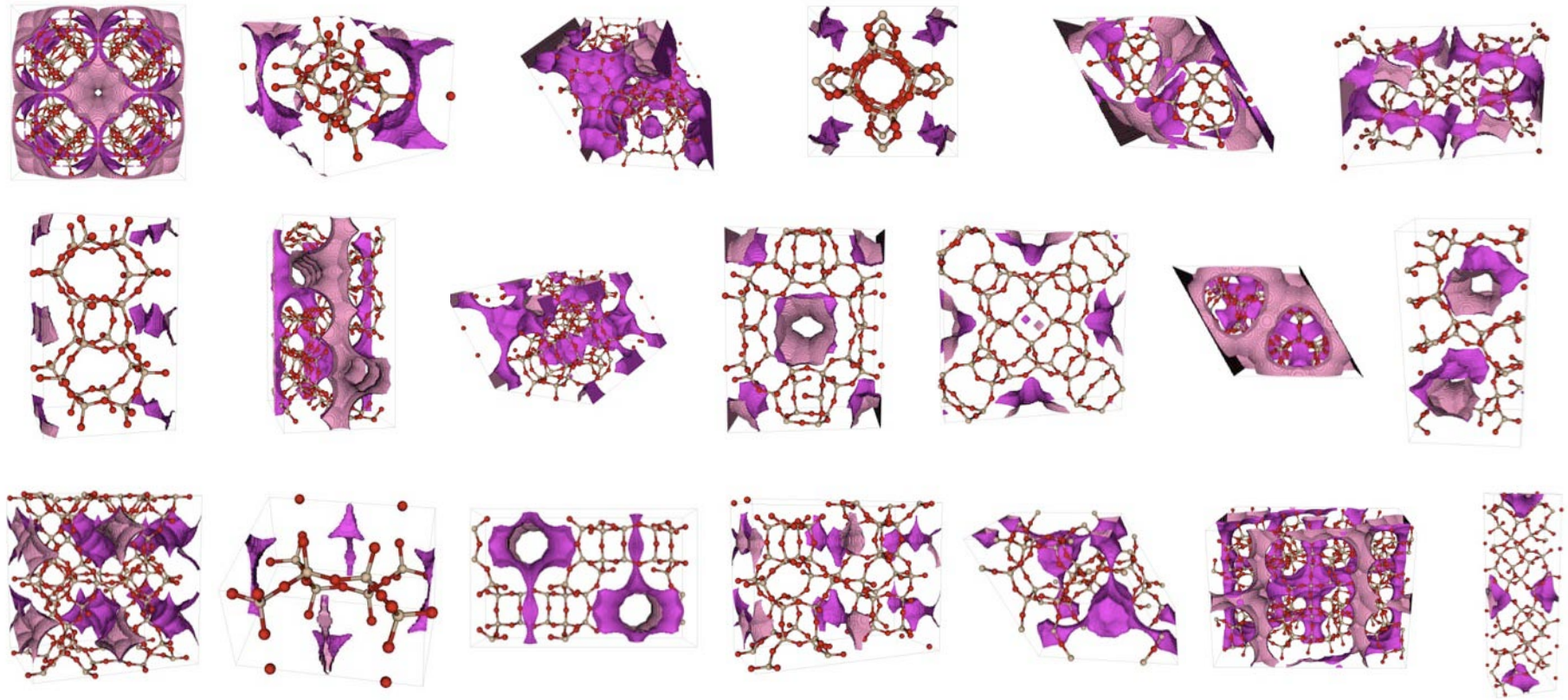
Equivalent Energy for those all silica structure with experimental data

What is the best structure?

What is the lowest energy?

IZA structures

Can we use molecular simulations to screen all possible structures?



Computation of mixture adsorption

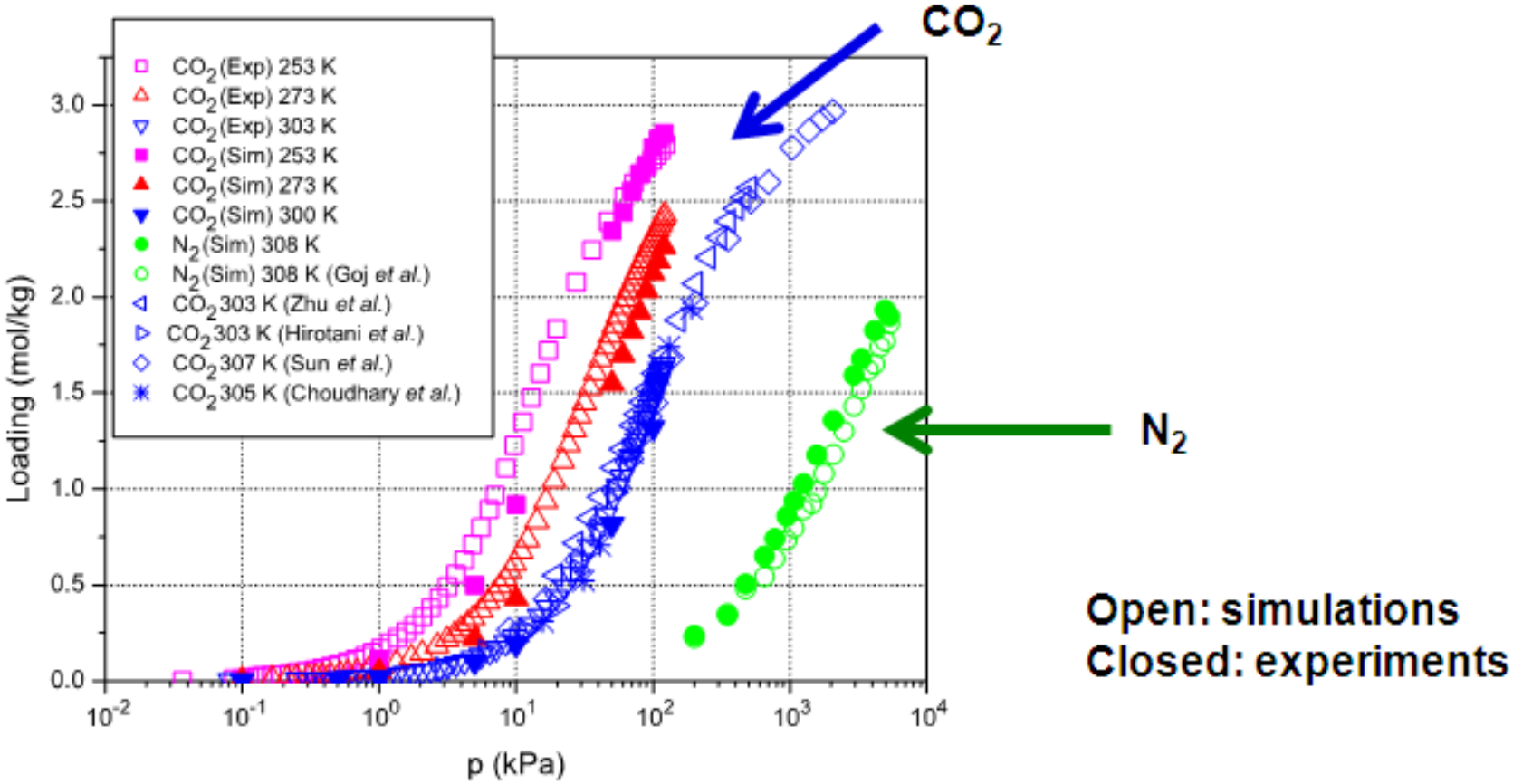
Model assumptions (best models available):

- Crystal structure zeolites
- Force-fields:
  - CO_2-CO_2 EMP2 force field
  - Lennard-Jones + Coulomb terms

Screening for carbon capture

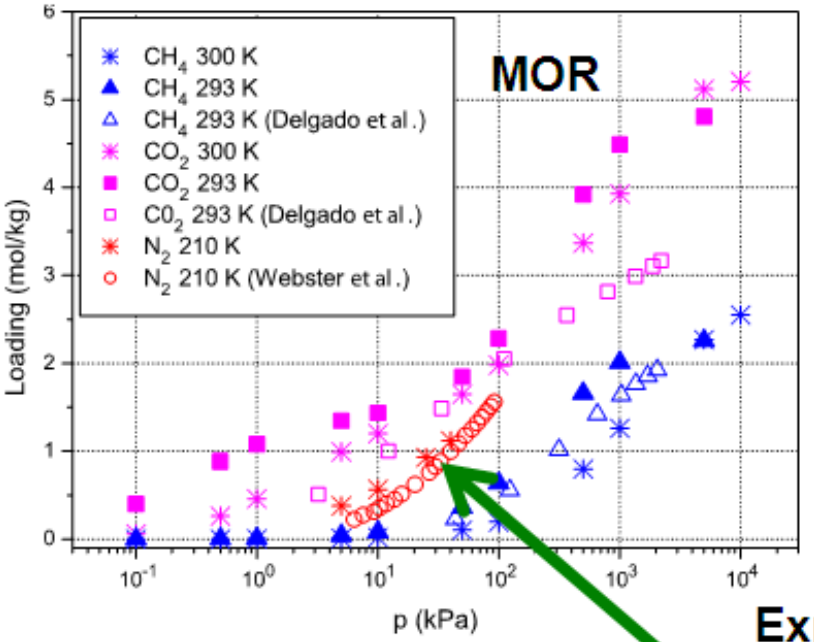
- Relatively low pressures
- Reduced set of data

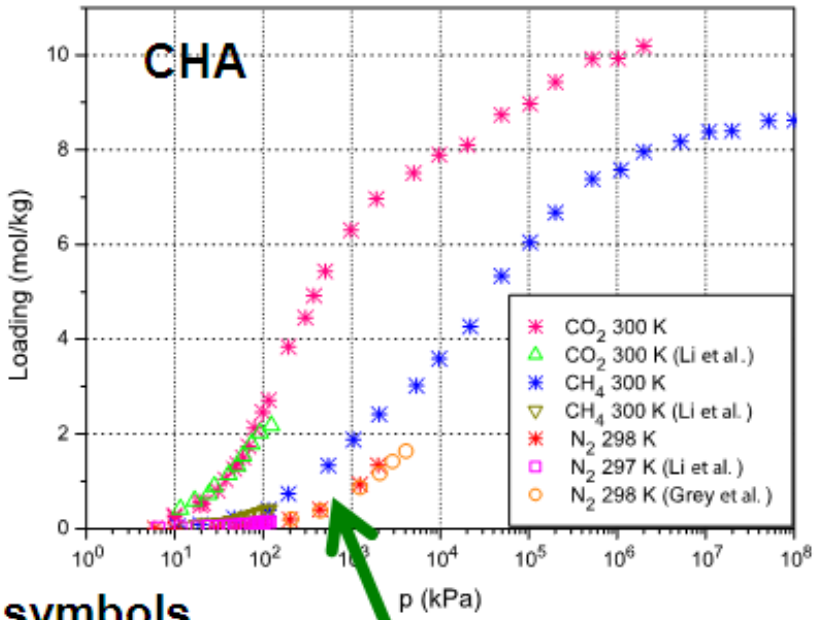
Comparison with experimental data (MFI)



(From: E. García-Pérez *et al.* Adsorption (2007) 13: 469–476)

Comparison with experimental data (MOR and CHA)





Exp: open symbols

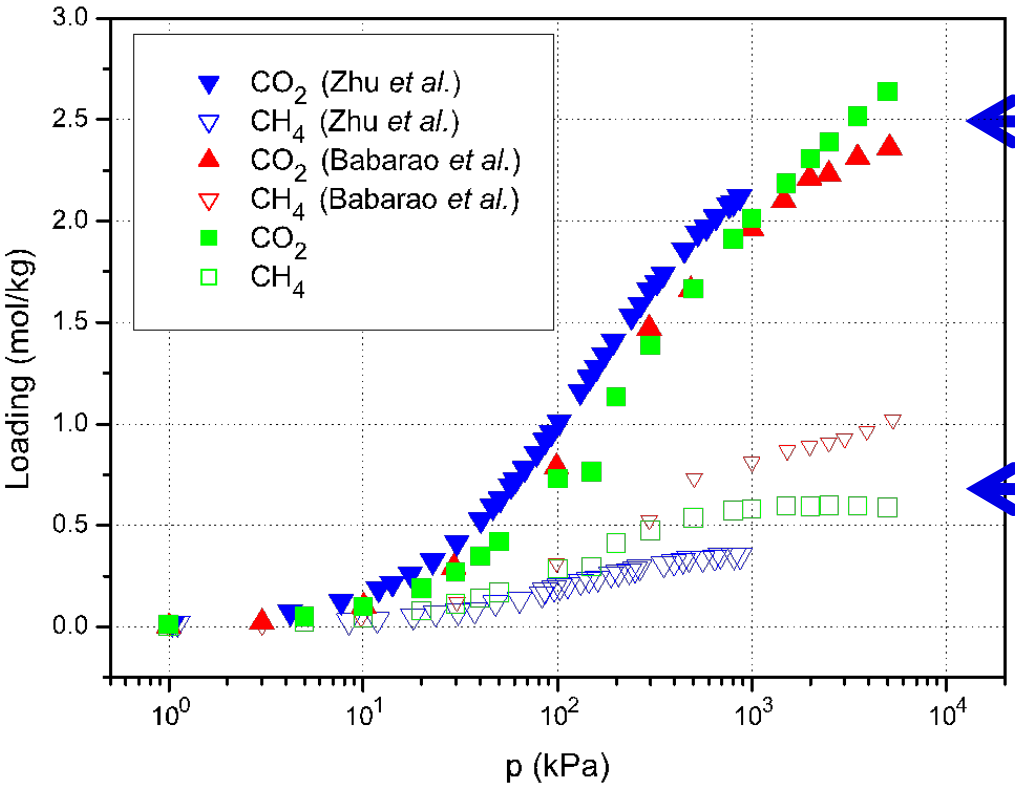
N_2

N_2

Conclusion: force fields gives a very reasonable prediction of the pure component isotherms of CO_2 and N_2 in different zeolites

(From: E. García-Pérez *et al.* Adsorption (2007) 13: 469–476)

Comparison with experimental mixture data (CH_4-CO_2 in MFI)



CO_2

Green: simulations
Rest: experiments

CH_4

Conclusion: force fields gives a very reasonable prediction of the mixture isotherms of CO_2 and CH_4 in MFI

(From: E. García-Pérez *et al.* Adsorption (2007) 13: 469–476)

Computation of mixture adsorption

Model assumptions:

- Crystal structure (rigid)
- Force-fields:
  - CO_2-CO_2 TraPPE force field
  - Lennard-Jones + Coulomb terms

Screening for carbon capture

- Relatively low pressures
- Reduced set of data

Screening

Screening for carbon capture:

- Complete isotherms: 10 days of CPU time per composition

- **Simplifications**:
  - IAST: only pure component isotherms
  - Pure components:
    - Flue gas: relatively low pressures: no need for predictions beyond 50bar
    - Single site Langmuir isotherm (2 parameters)

      - Henry coefficient:
      - Temperature dependence Henry coefficient: heat of adsorption ΔH
      - Dif model: largest diameter of an included sphere (of a free channel)

$$\frac{q}{q_0} = \frac{bP}{1 + bP}$$

density model

To determine the Langmuir adsorption isotherm

- Henry coefficient: simulations
- Heat of adsorption (gives temperature dependence of the Henry coefficient): simulations
- Maximum loading: chemoinformatics

$$\frac{q}{q_0} = \frac{bP}{1 + bP}$$

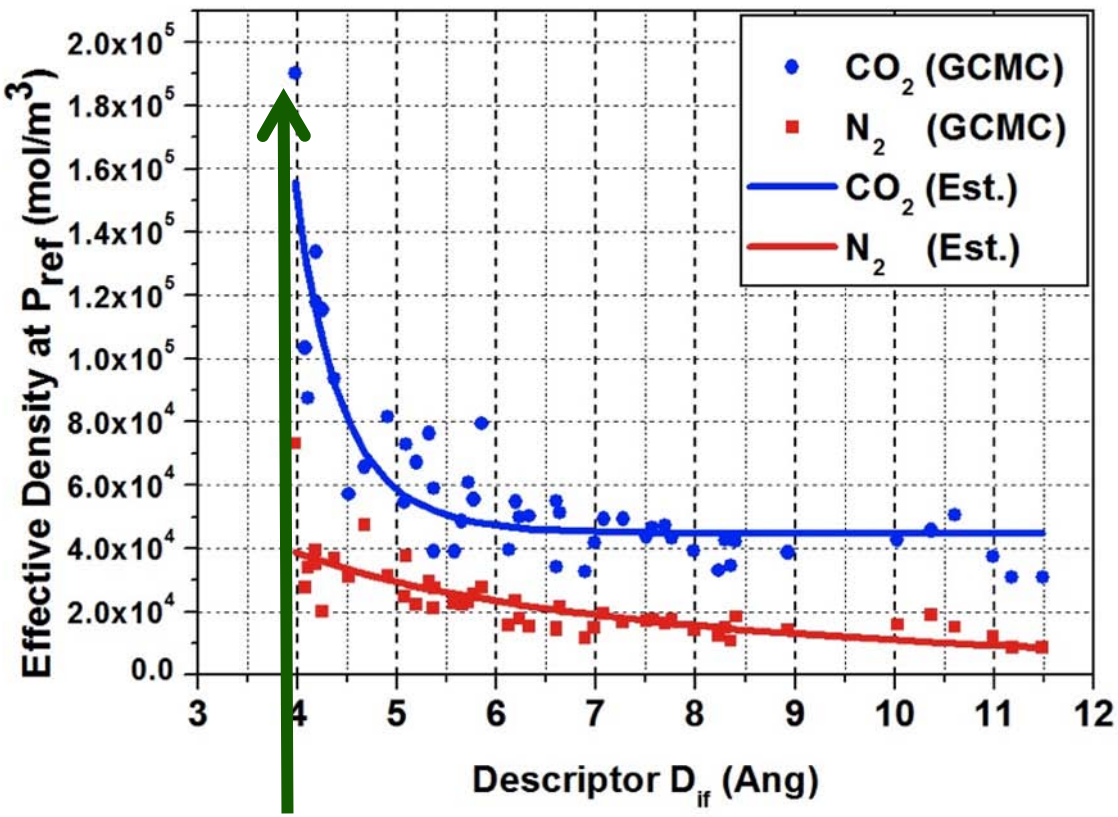
Maximum loading

- Very sensitive to details of the zeolite
- High pressure not very relevant

Is there an "ideal" effective density?

- Easy to compute the pore volume
- Pore volume x effective CO_2 density= loading

DIF model



CO_2 cannot enter

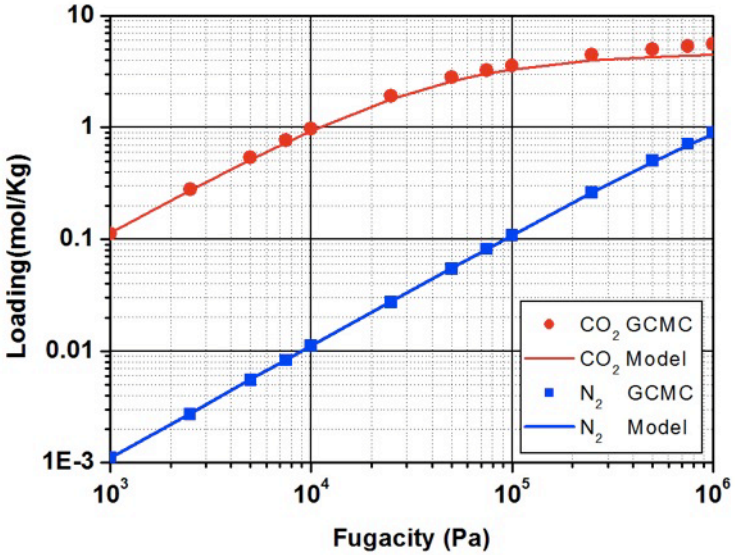
Is there an ideal density?

- Easy to compute: the pore volume
- Pore volume x ideal CO_2 density= loading at (50 bar and 300K)

Reasonable descriptor

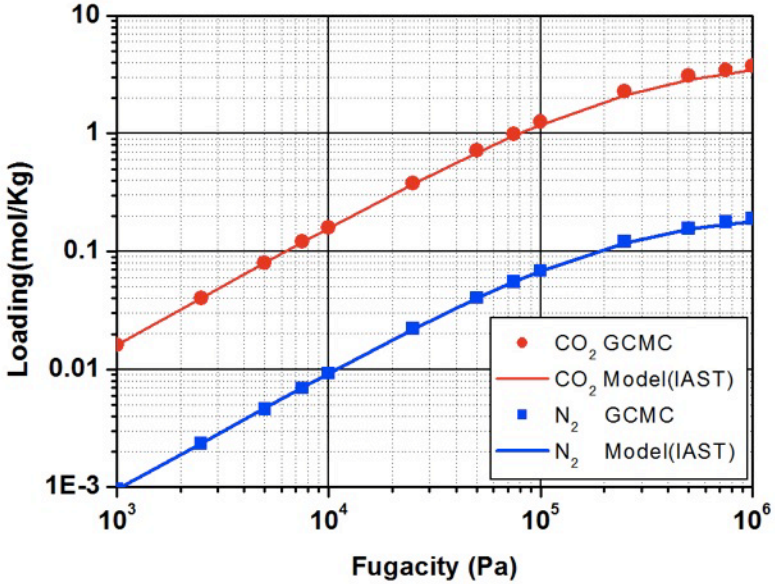
- DIF pore diameter: free sphere diameter
- Test with 50 zeolites

Test of the assumptions



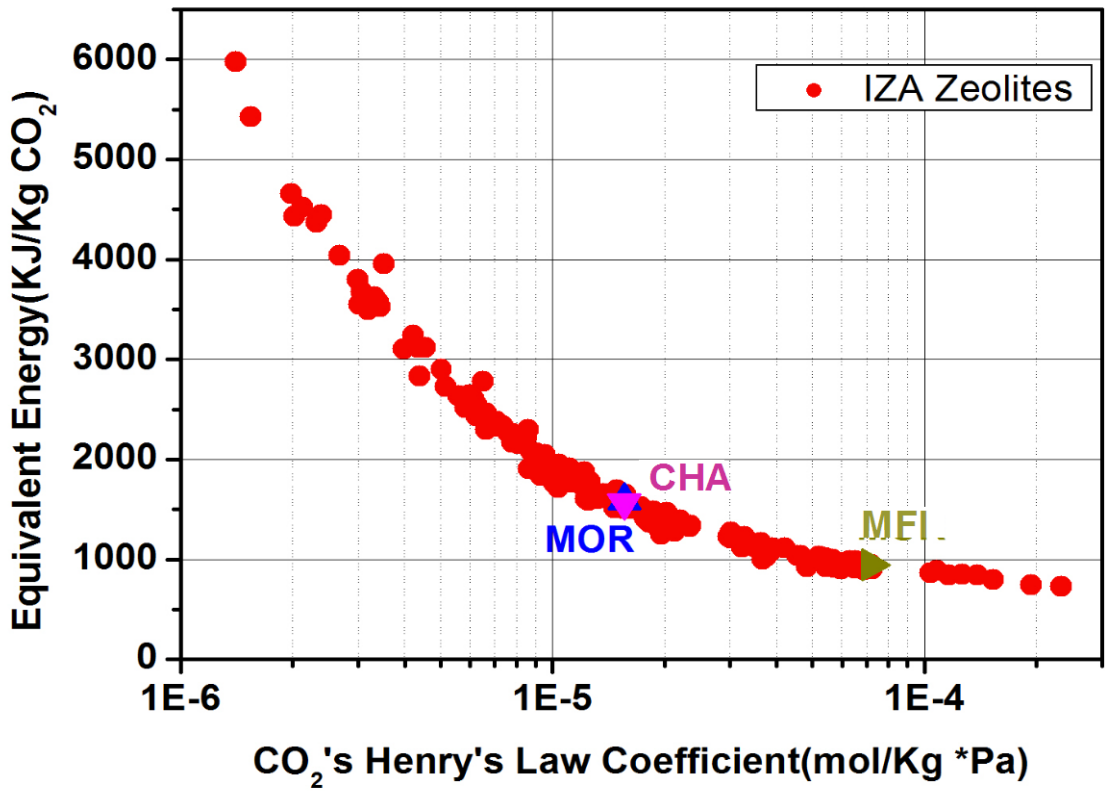
Pure components in SIV (300K)

14% CO_2/ 86% N_2 in SIV (300K)



Pure Isotherm at 300K (50 structures)	CO_2	N_2
Average R^2	0.869	0.920
Mixture(CO_2/N_2(14/86))	**Selectivity at 1bar**	**Loading at 1bar**
Relative Error(%)	8.30%	7.10%

Screening IZA data base

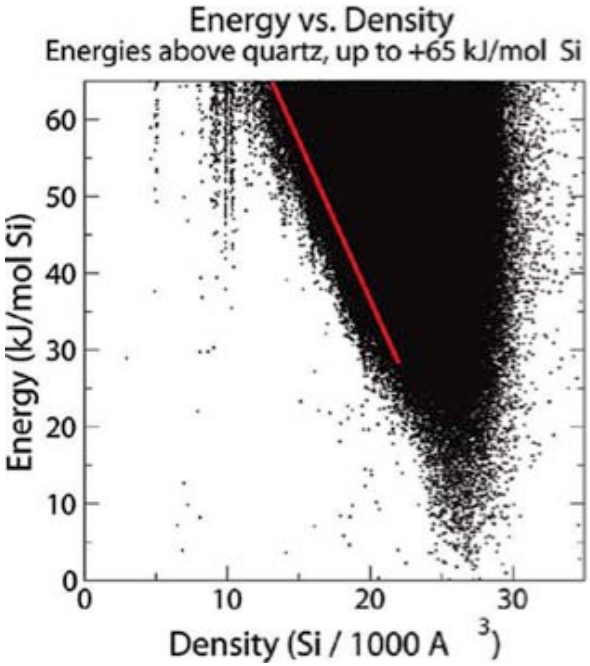


Are there structures with even a lower EE?

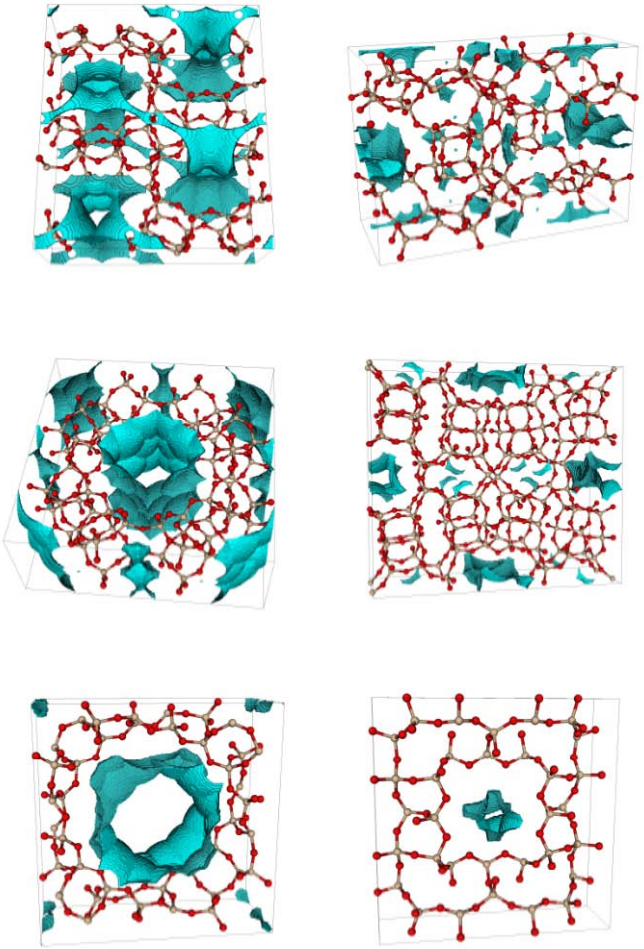
What is the best zeolite structure?

Hypothetical zeolites

~2.7M unique structures were enumerated, with roughly 10% within the +30 kJ/mol Si energetic band above R-quartz in which the known zeolites lie

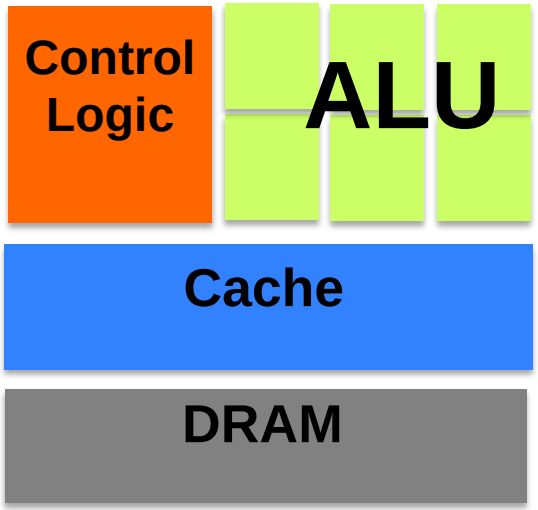


Deem et al. *J. Phys. Chem. C* 2009, *113*, 21353.



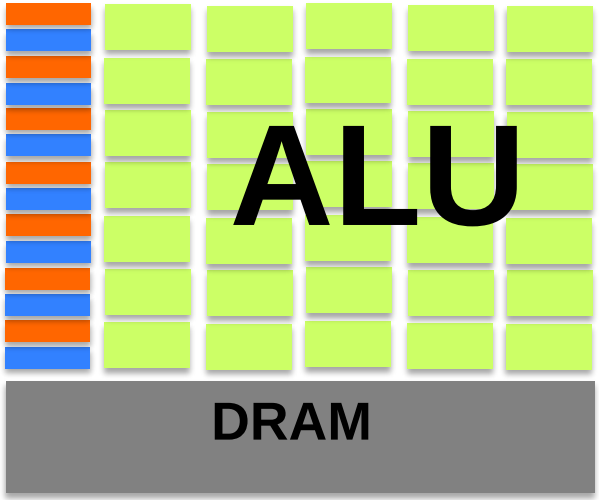
Screening 3 million structures: GPU calculations

CPU



- Less than 20 cores
- Designed for general programming

GPU



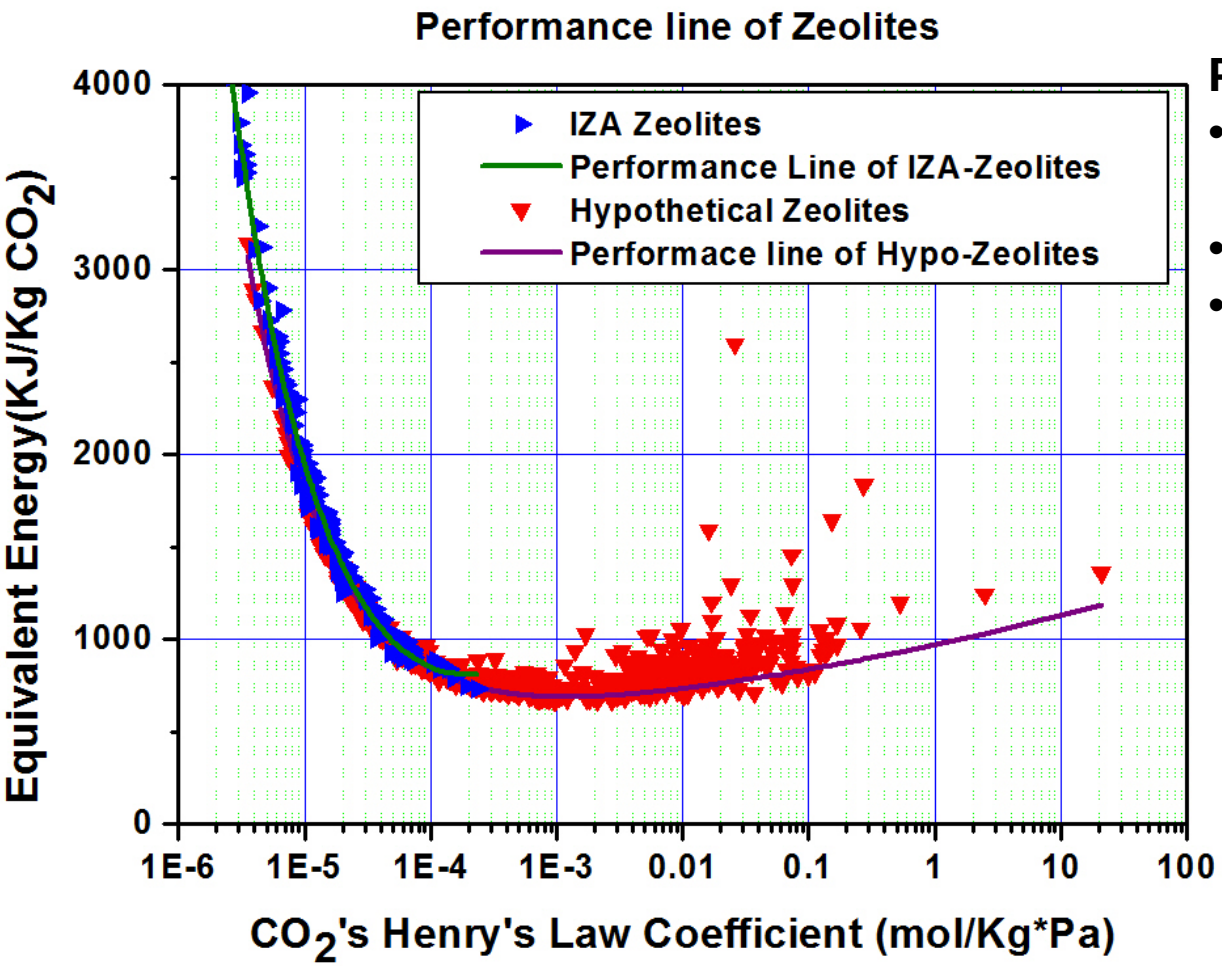
- More than 500 cores
- Optimized for SIMD (same-instruction-multiple-data) problems

30 minutes on a CPU, only 2 seconds on a GPU

These calculations 150 years for 5 million structures on one GPU; 2 weeks on 10 processors (which costs 30k$)

(Jihan Kim, LBNL)

All zeolites



Prescreening

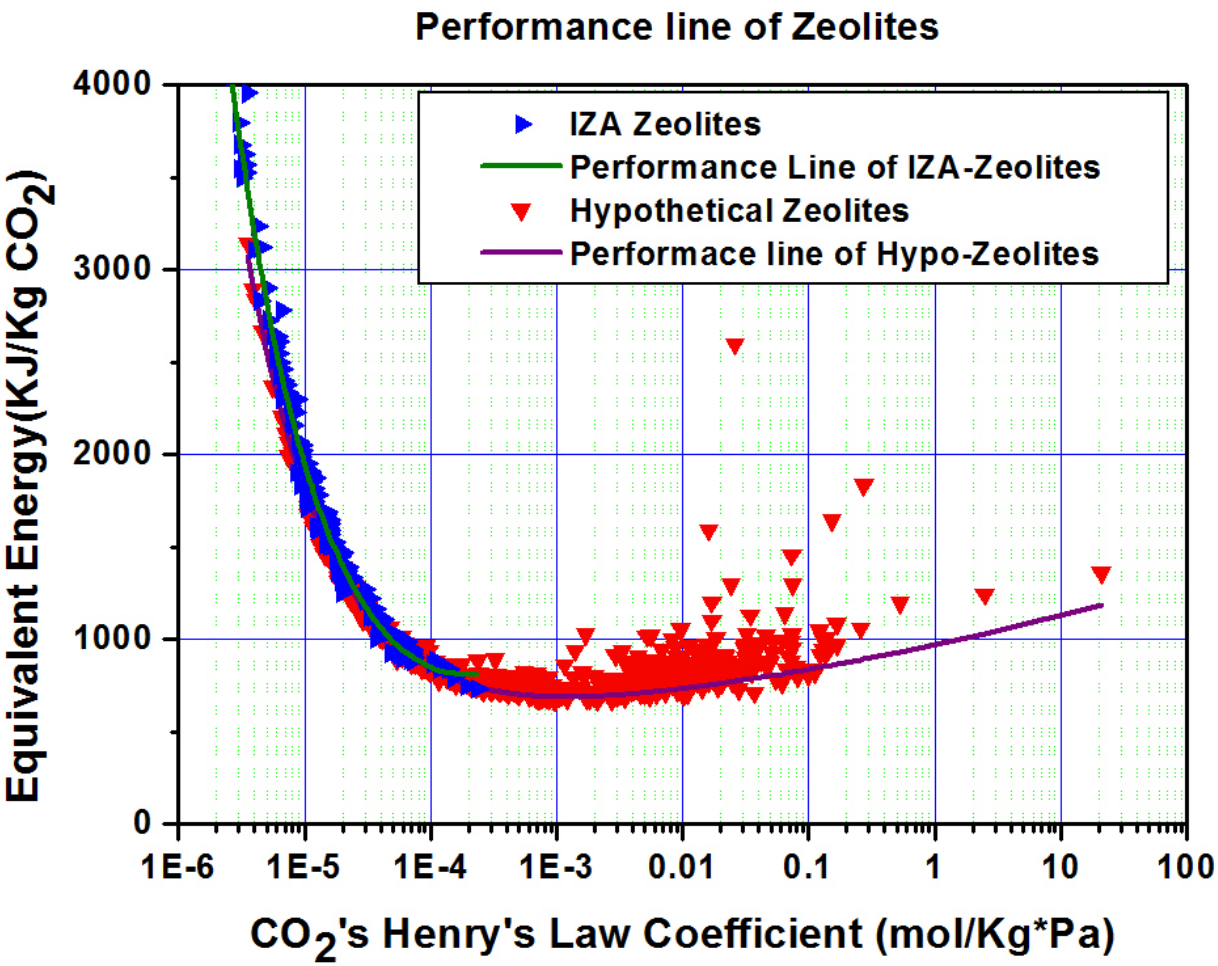
- Selectivity sufficient! Nitrogen Henry is very low
- Molecules need to enter
- Henry needs to be > 5.10^{-5}

Conclusion:

Minimum is 669kJ/kg CO_2

the structure is h8062759

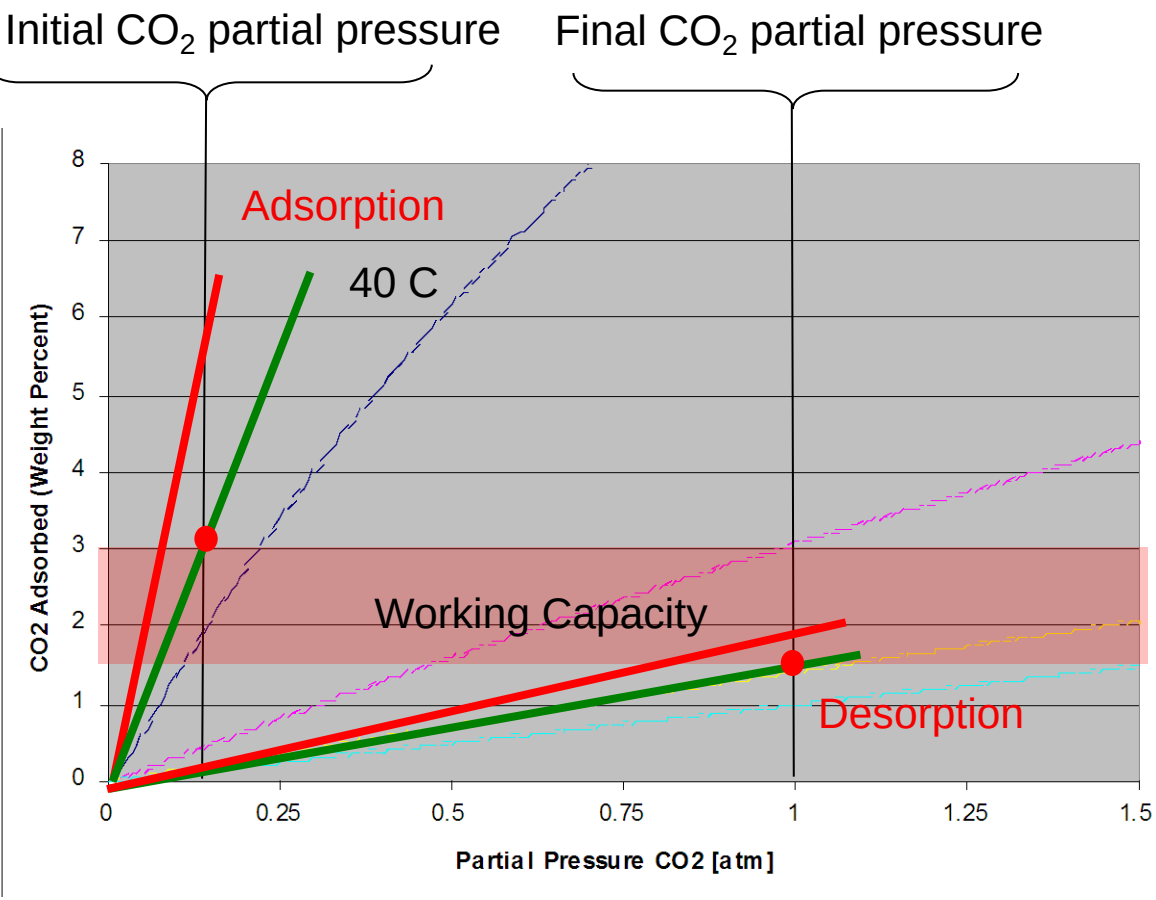
Increasing the Henry coefficient



Increasing the Henry coefficient

- Rapid decrease of the equivalent energy

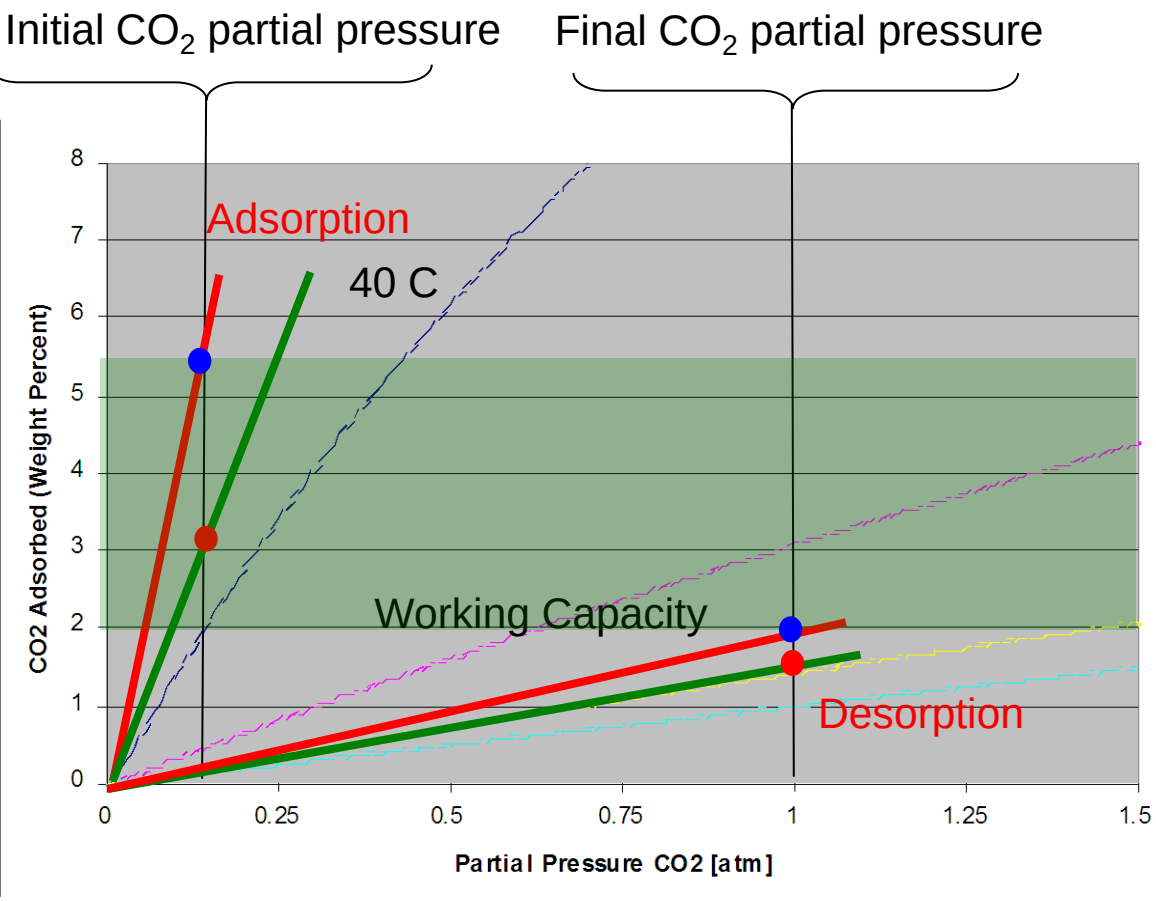
low Henry regime



Increasing Henry coefficient

- *Adsorption:* rapid increase of the working capacity
- *Desorption:* more modest decrease
- Higher heat of adsorption (helps)

Increasing the Henry coefficient

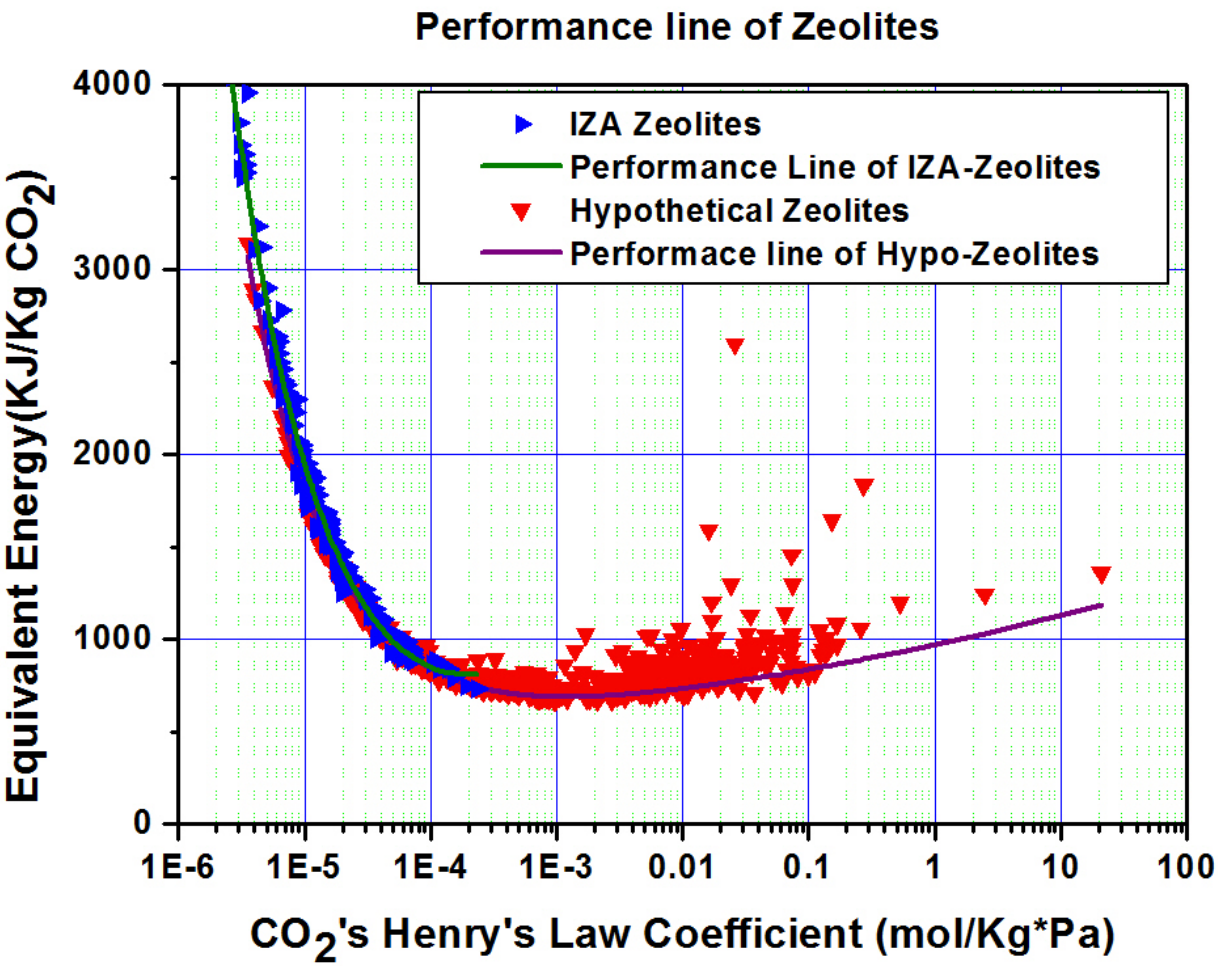


Increasing Henry coefficient

- Higher heat of adsorption
- *Adsorption:* rapid increase of the working capacity
- *Desorption:* more modest decrease

Large increase of the working capacity, without increasing the heating requirements much

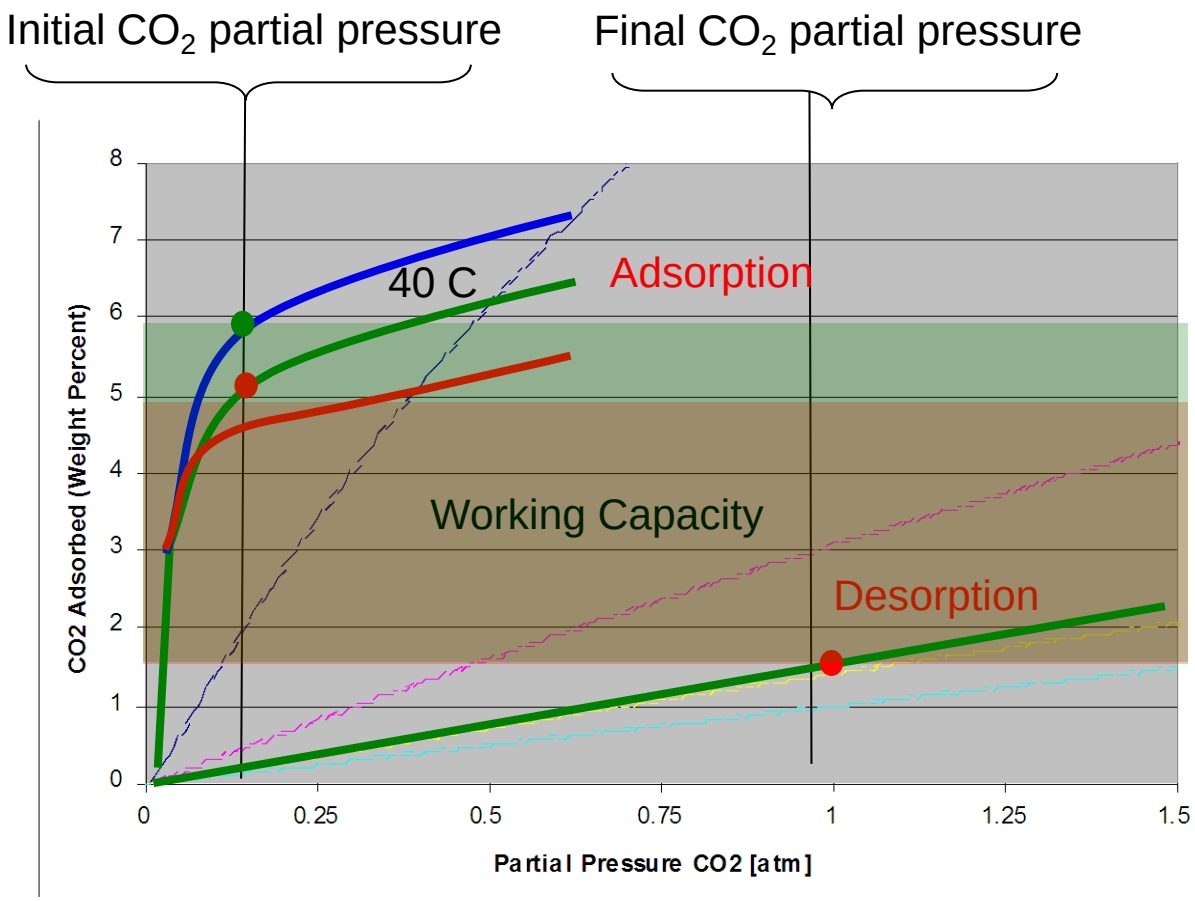
High Henry



High Henry regime

- Large difference between materials

High Henry regime

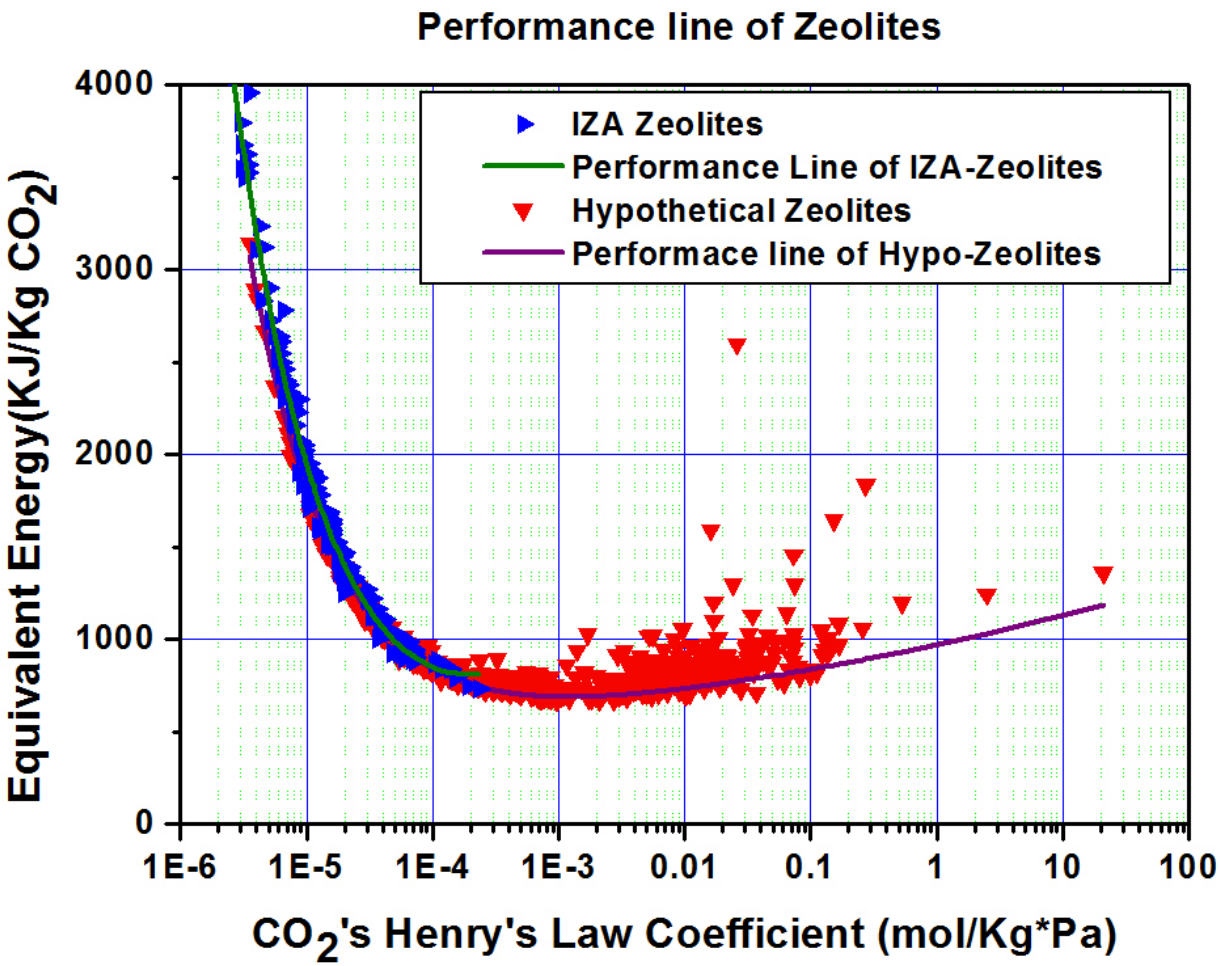


High Henry regime

- *Adsorption:* not in the Henry regime anymore: **pore volume** becomes important
- *Desorption:* in the Henry regime

Pore volume become an important additional variable ⇒ larger pore volume: higher working capacity

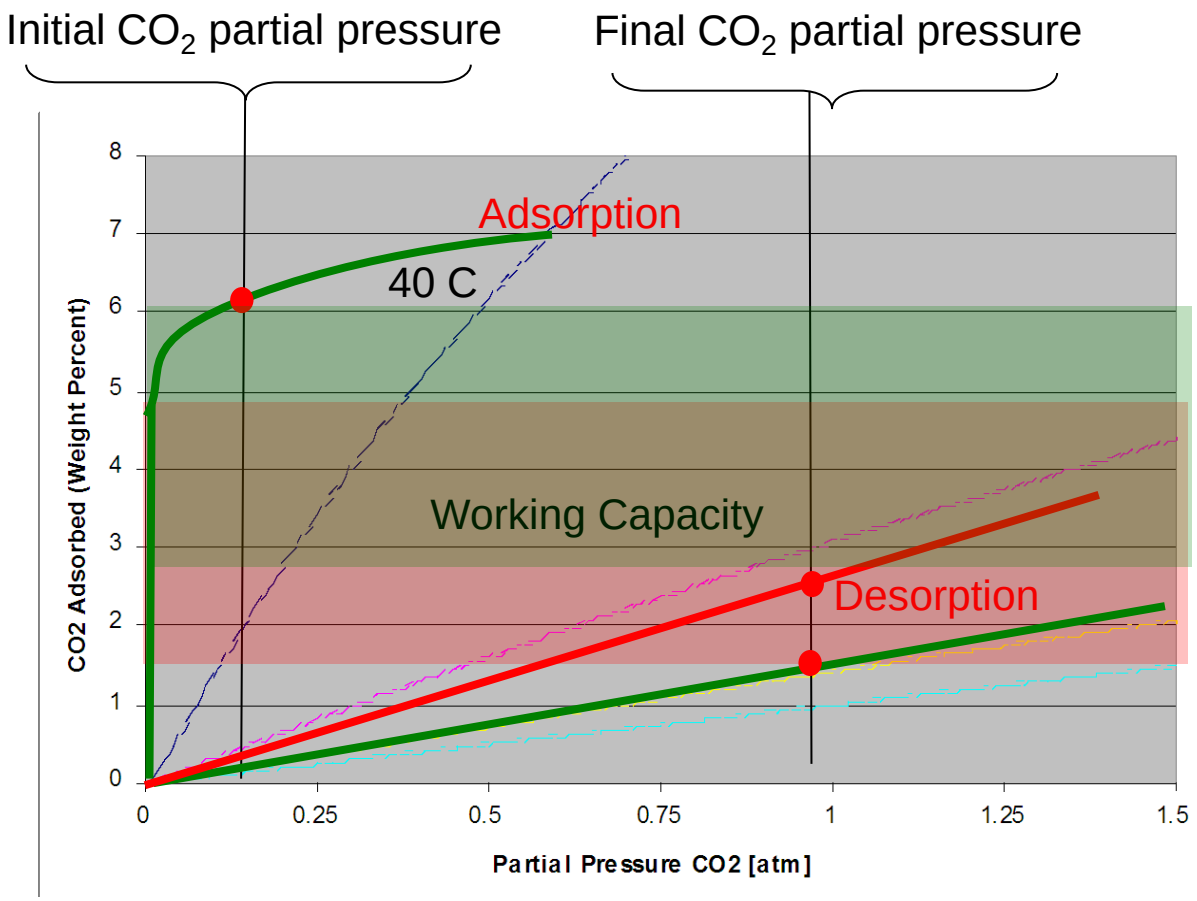
Very high Henry regime



Very High Henry regime

- Increase in equivalent energy

Very High Henry regime



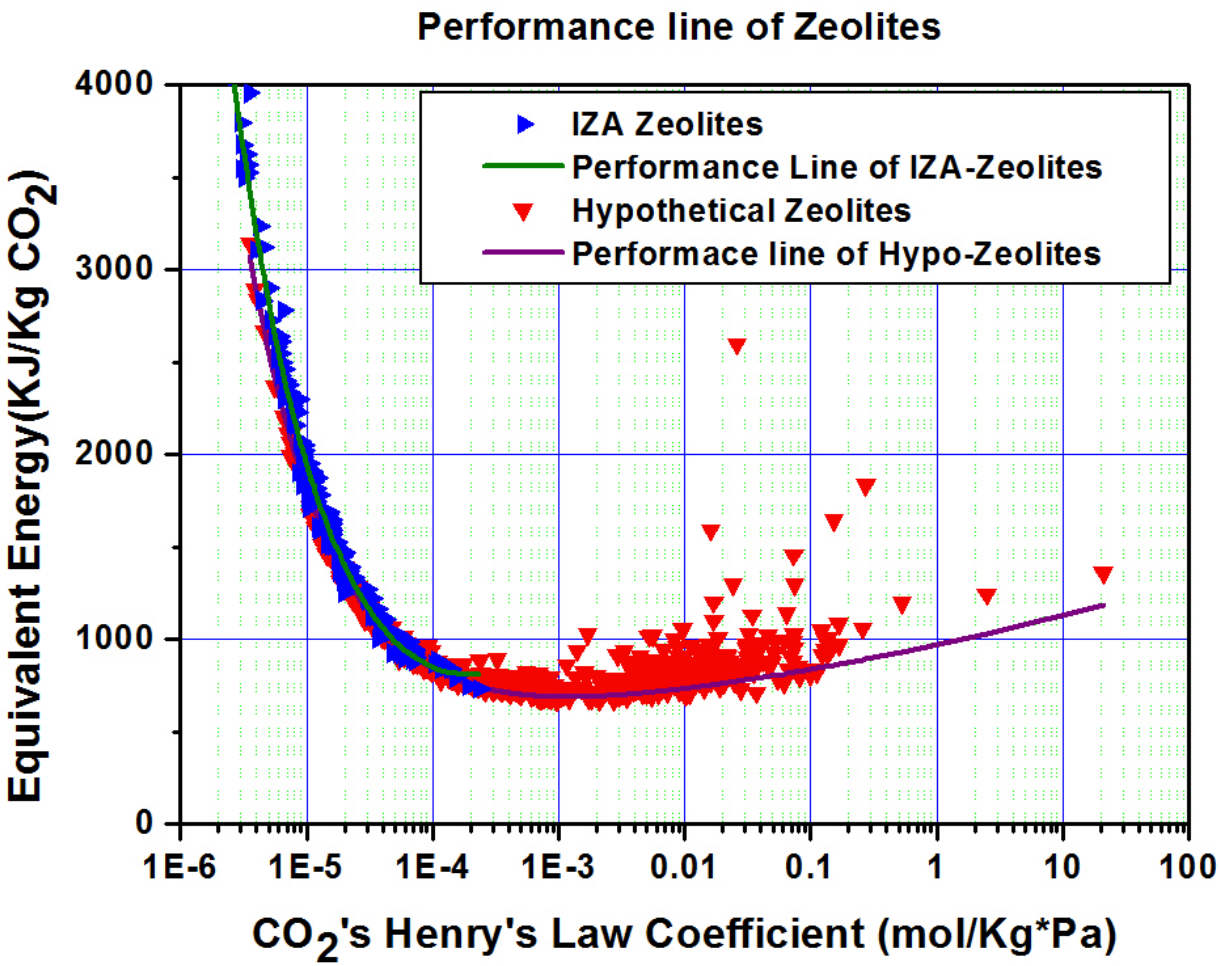
High Henry regime

- *Adsorption:* increase of the Henry has little effect; complete determined by the pore volume
- *Desorption:* in the Henry regime: hence higher Henry decreases the working capacity

Very high Henry gives an increase of the equivalent energy

<u>Conclusion:</u> There is an optimal Henry coefficient

The optimum



Very broad optimum: many structures

Broad maximum

Higher Henry

- Higher heat of adsorption
- Increase of the working capacity at the adsorption side
- Decrease of the working capacity at the desorption side

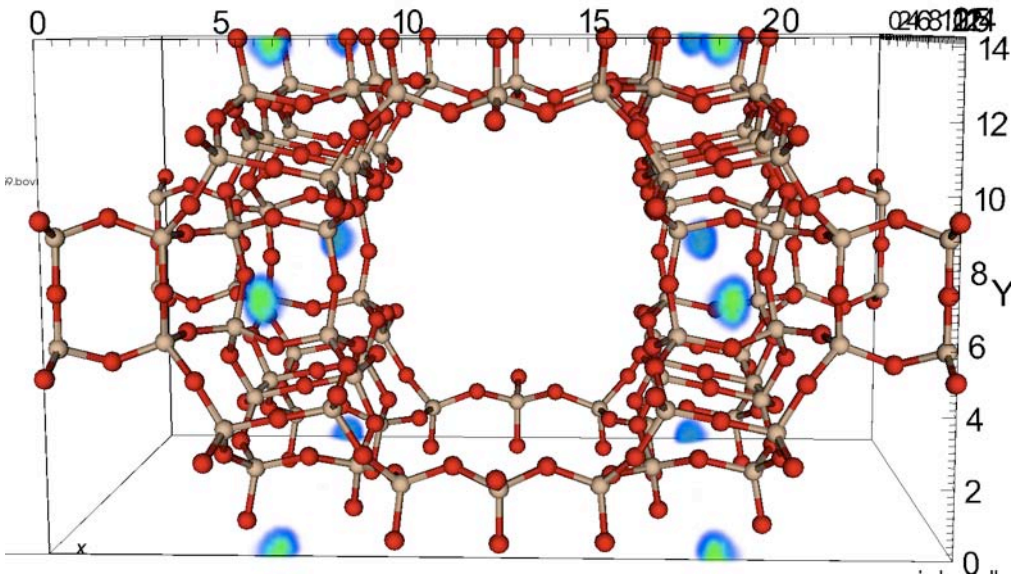
Energy

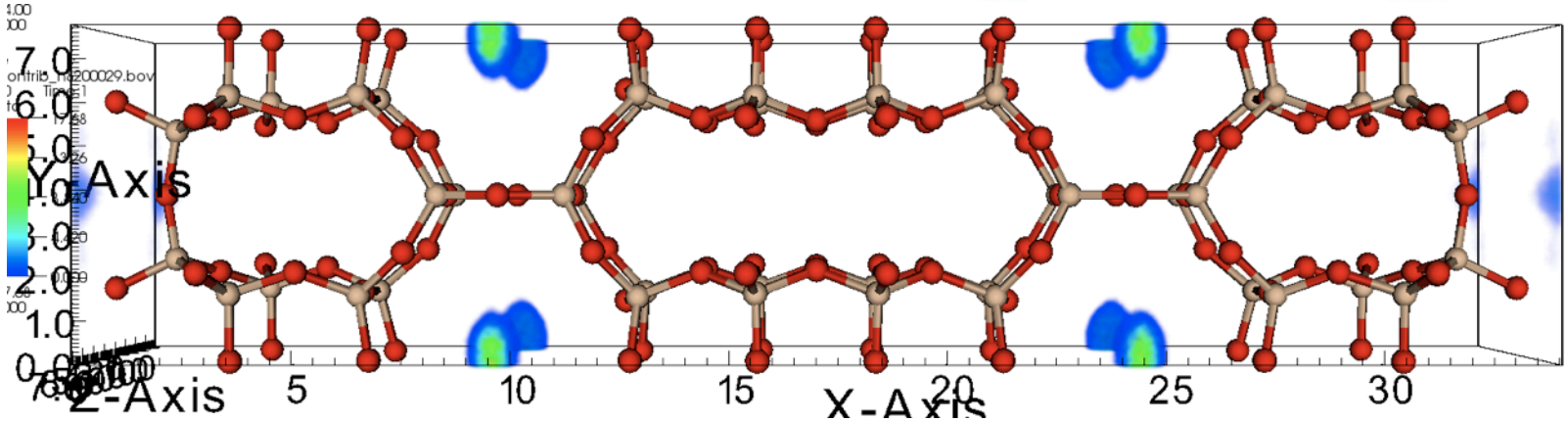
- ↑ Higher because of the desorption energy
- ↓↓ Effects tends to level out as the system goes out of the Henry regime and pore volume become more important
- ↑ Decrease of the working capacity at the desorption side

These cancellation effects give a broad minimum

Optimal structures: top 5

Framework Name	eq_energy(J/kg)
h8072795	668895.9962
h8200129	669379.4124
h8236159	671997.2134
h8287959	672932.2555
h8144128	674876.7077





Conclusions

- **Very large screening with a relevant metric is possible; benchmark for other systems**
- **The structure needs to have optimal sites.** There are **many** different ways of getting these: top 5 contains one, two, and three dimensional structures
- Structures will be made available through a website
- We have **not** been able to make very simple correlations: pore diameter, optimal sphere, similarity, etc. (if we would have been really smart …)
- Our model has MANY assumptions, but they can be improved (suggestions)
- Hypothetical zeolites: can they be made???
- Next: adding cations; Zifs, Ionic liquids, etc (suggestions)