U.S. DEPARTMENT OF ENERGY

High-Throughput Discovery of Robust Metal-Organic Frameworks for Carbon Dioxide Capture

Abhoyjit Bhown,[3] Maciej Haranczyk,[1] Steven Kaye,[2] Jeffrey Long,[1] Eric Masanet,[1] Jeffrey Reimer,[1] and **Berend Smit**[1]

[1]*Lawrence Berkeley National Laboratory (LBNL)*

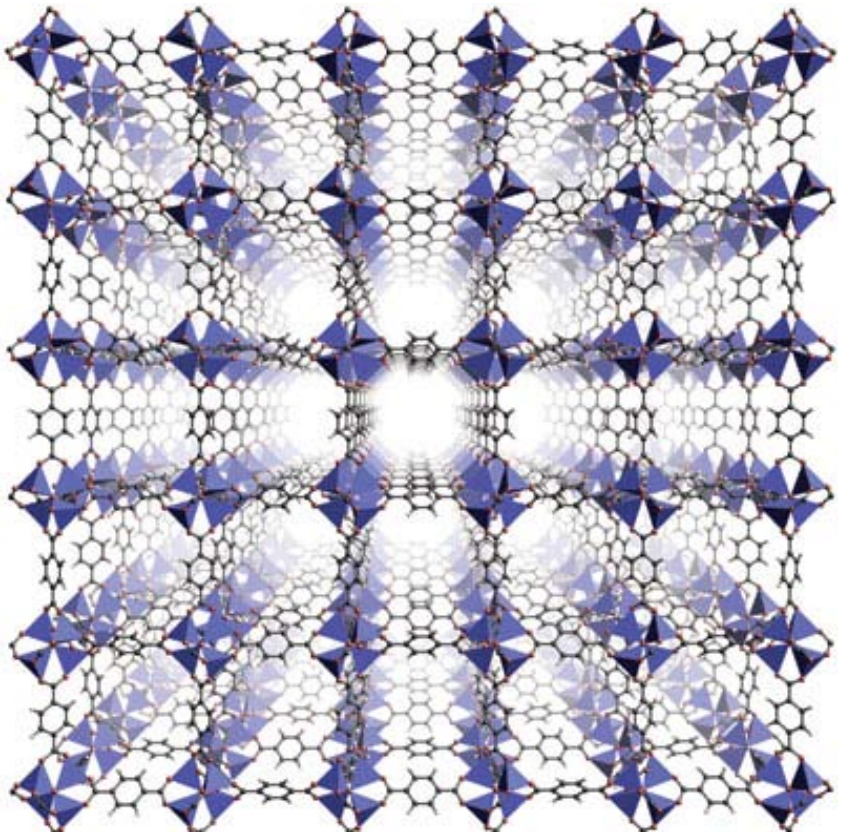
[2]*Wildcat Discovery Technologies*

[3]*Electric Power Research Institute (EPRI)*

Project started: 07/2010 (Wildcat), 09/2010 (LBNL), 12/2010 (EPRI)

Funding: $3.9M (ARPA-e), $1.0M (cost share)

Metal-Organic Frameworks



Zn_4O(1,4-benzenedicarboxylate)$_3$

MOF-5

BET surface areas up to 6200 m^2/g

Density as low as 0.22 g/cm^3

Tunable pore sizes up to 5 nm

BASF production on ton scale

Surface can be functionalized for selective CO_2 binding

Metal-Organic Framework Synthesis

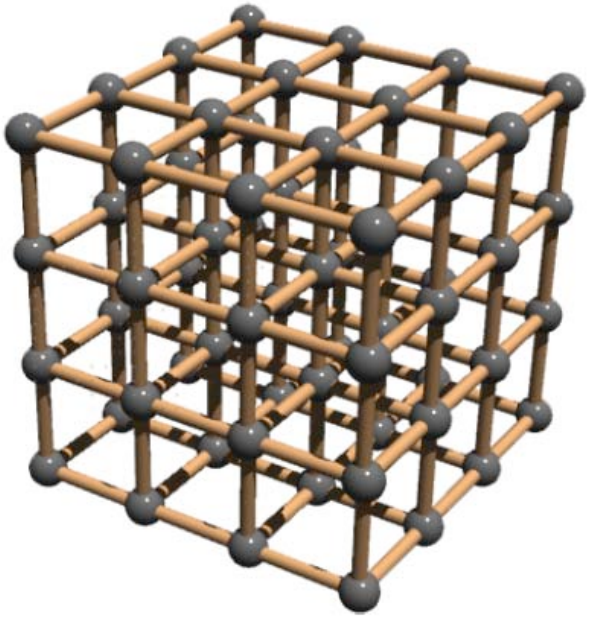
metal ion or cluster

+

organic linker

?

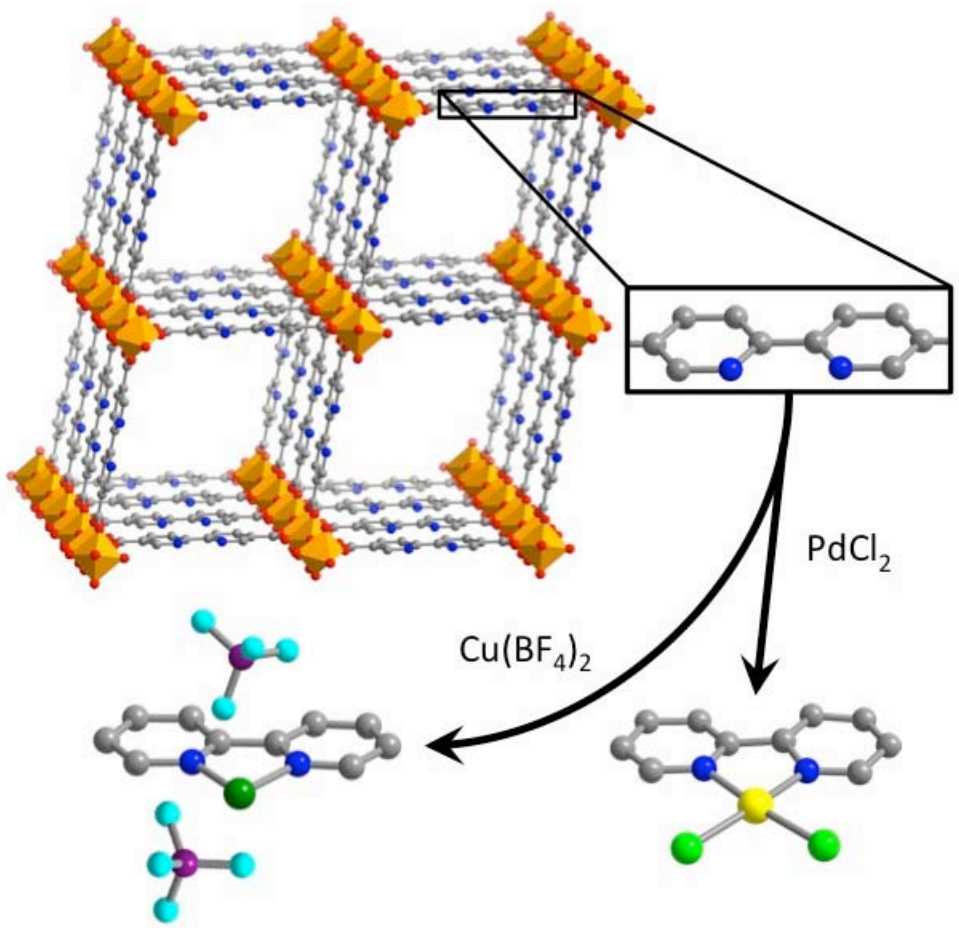
temperature?
reactant ratio?
solvent?
cosolvent?
acid/base added?



metal-organic framework (MOF)

- An enormous number of structures are possible; most are not highly porous
- Impossible to predict conditions leading to pure, crystalline target structure

Metal binding in an aluminum based metal-organic framework for carbon dioxide capture



- This lightweight, high surface area material based on inexpensive aluminum is stable to 350 °C.
- The compound shows great water stability, a necessity for flue gas CO_2 capture.
- Transition metals can be added to the framework by simply soaking the material in salt solutions.
- An added copper salt greatly increased CO_2 capacity and CO_2/N_2 selectivity.
- Small amounts of precious metal salts supported on this porous framework may be useful for catalysis applications.

Bloch et al, ***J. Am. Chem. Soc.* 2010**, *132*, 14382

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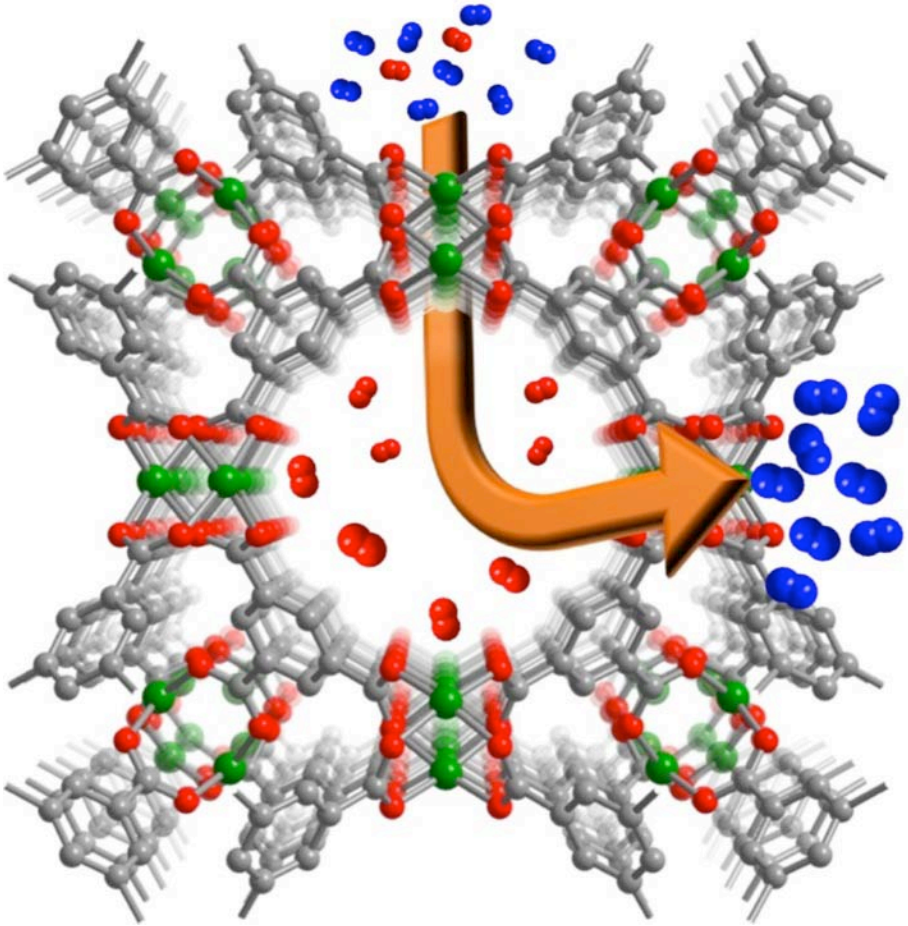
Nitrogen/oxygen separations in metal-organic frameworks for clean fossil fuel combustion



Murray et al, ***J. Am. Chem. Soc.* 2010**, *132*, 7856

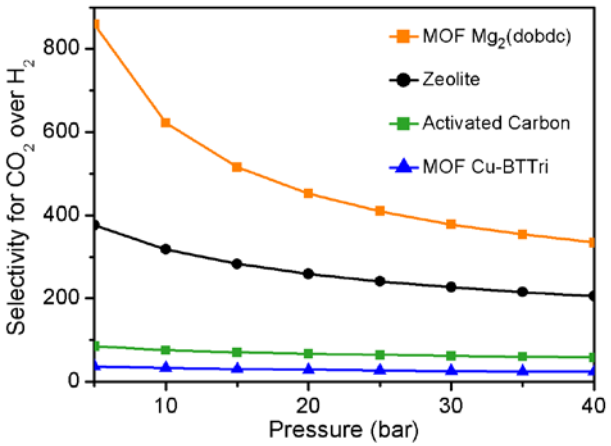
- Burning fossil fuels in the absence of nitrogen facilitates an easier capture of carbon dioxide from flue gas
- Metal-organic frameworks are 3-D materials containing metal ions and bridging organic linkers
- 2.5 grams of material (2040 m^2/g) has the same surface area as a football field
- Large pores (1 nanometer in diameter) allow fast diffusion of gas molecules
- Framework adsorbs 11 weight percent O_2 at room temperature but only 0.6 weight percent N_2
- Most of the adsorbed O_2 can be removed by simply heating the solid

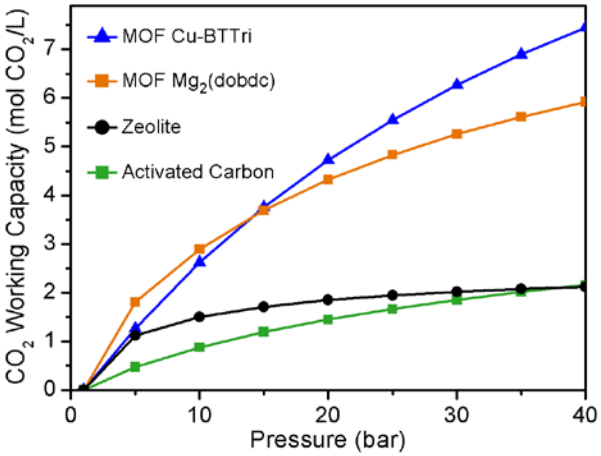
Center for Gas Separations Relevant to Clean Energy Technologies

an Office of Basic Energy Sciences

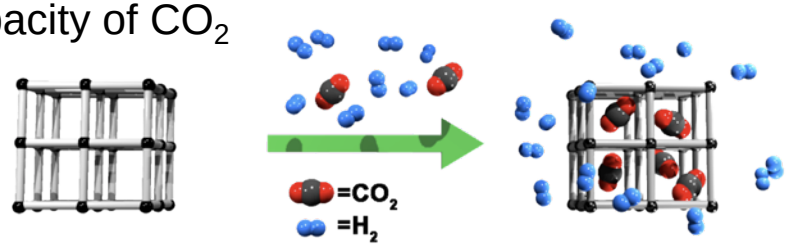
Energy Frontier Research Center

Metal-Organic Frameworks Capture CO_2 From Coal Gasification Flue Gas





- Gasifying coal generates H_2, which can be used to generate electricity, and CO_2, which can be sequestered.
- Metal-organic frameworks were studied for their CO_2/H_2 separation abilities. The following properties were tested:
  - High surface area
  - Flexible structure
  - Lewis acidic open metal sites
- Metal-organic frameworks with open metal sites, specifically Mg_2(dobdc) and Cu-BTTri, far outperformed others, as well as zeolites and activated carbons. This excellent performance can be quantified in terms of:
  - Selectivity
  - Working capacity of CO_2



Herm *et al.*, ***J. Am. Chem. Soc.* 2011**, DOI 1021/ja111411q.

Center for Gas Separations Relevant to Clean Energy Technologies

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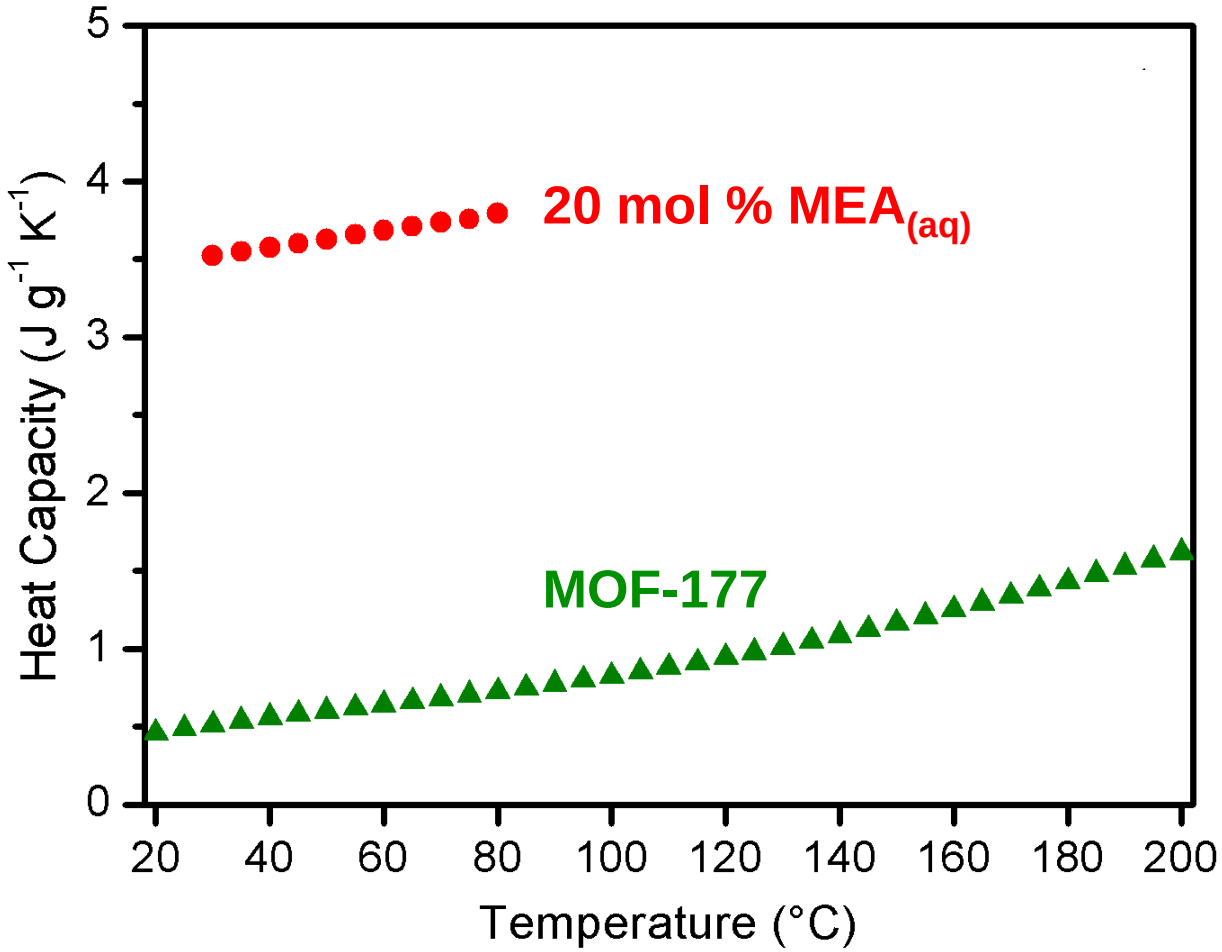
Reduced Heat Capacity



Project Mission

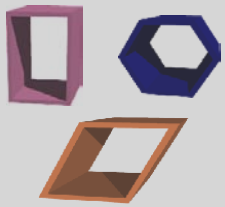
Develop and utilize high-throughput instrumentation for the discovery of robust, cost-effective metal-organic frameworks for the efficient capture of CO_2 from power plant flue gas.

Accelerated Discovery

High-Throughput Synthesis

Highly-parallel, automated discovery of new MOFs

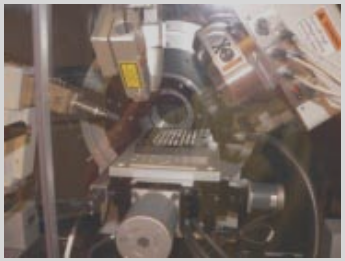
Automated Solid and Liquid Dosing



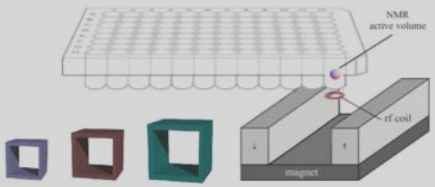
New Structure Types

High-Throughput Characterization

Rapid identification of new porous materials



Powder X-ray Diffraction

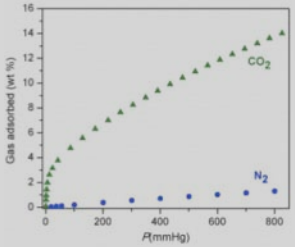


NMR Porosity Screening

CO_2 Adsorption Screening

Rapid screening of CO_2 capture performance

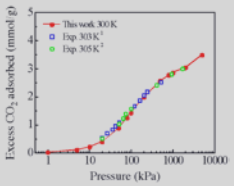
High-throughput Instrumentation

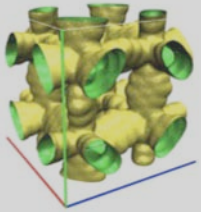


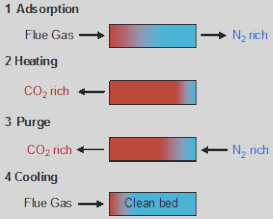
Adsorption Data

Computational Analysis

Data analysis, life cycle and sorbent performance analysis







Simulations

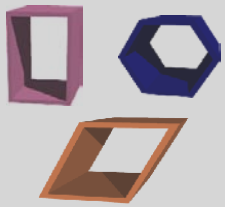
Sorbent Performance

Accelerated Discovery

High-Throughput Synthesis

Highly-parallel, automated discovery of new MOFs

Automated Solid and Liquid Dosing



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Rapid identification of new porous materials

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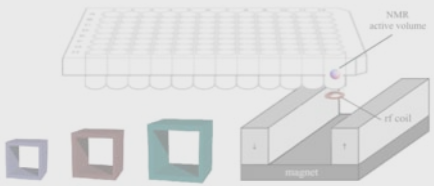

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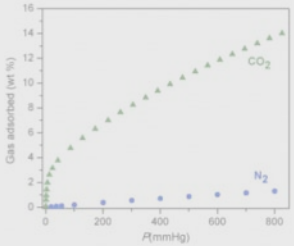
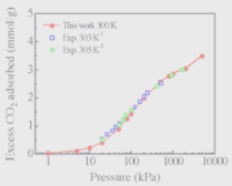
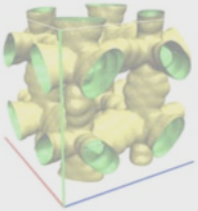


Adsorption Data

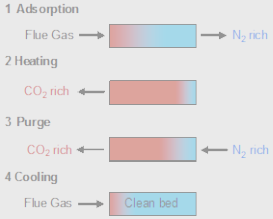
Computational Analysis

Data analysis, life cycle and sorbent performance analysis





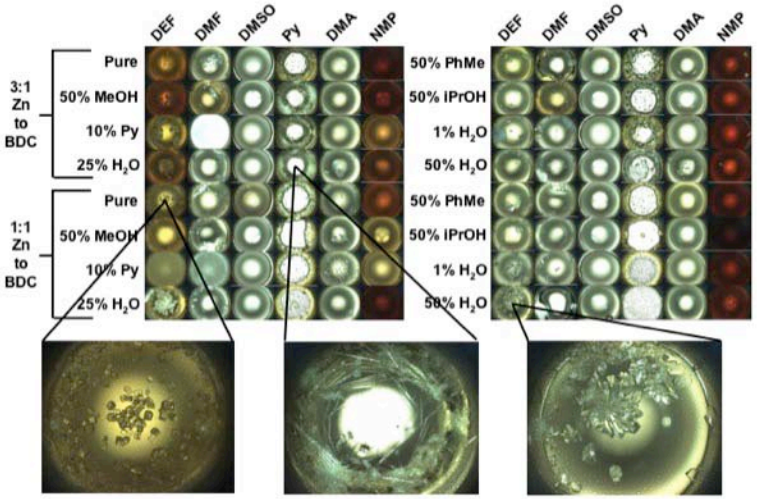
Simulations



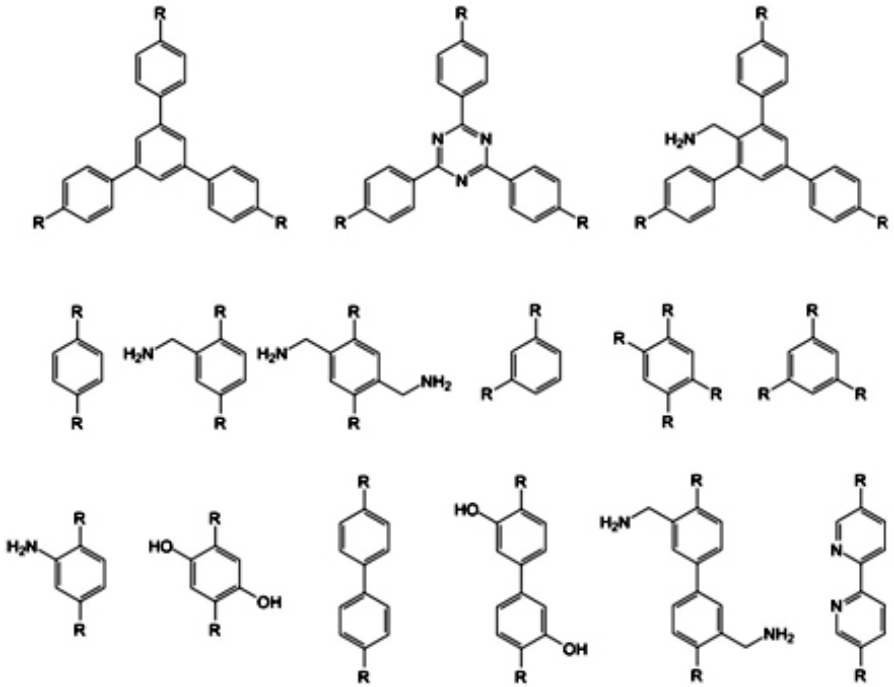
Sorbent Performance

High-Throughput Synthesis

Automated solid and liquid dispensing



Ligands synthesized and being screened

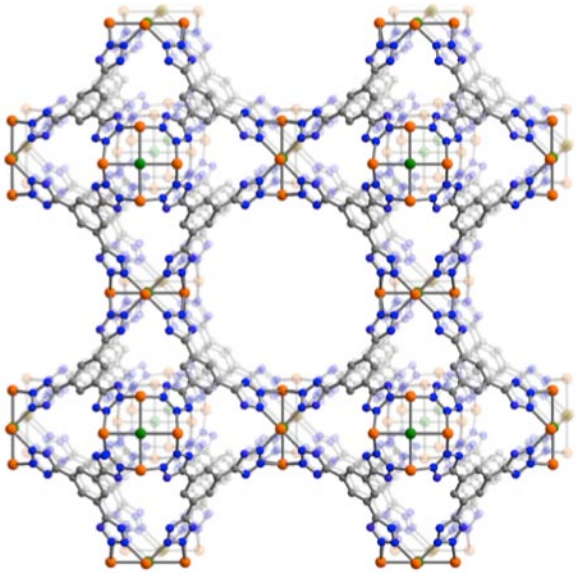


(R = carboxylate, pyrazole, triazole, imidazole, or tetrazole)

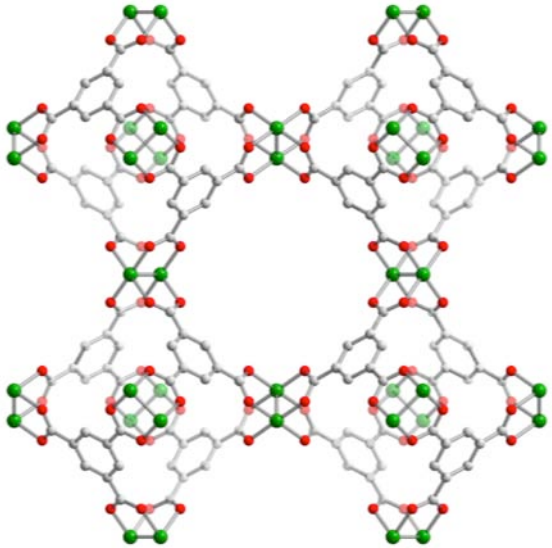
High-valent and main group metal ions

Mg^{2+}, Ca^{2+}, Al^{3+}, Ti^{4+}

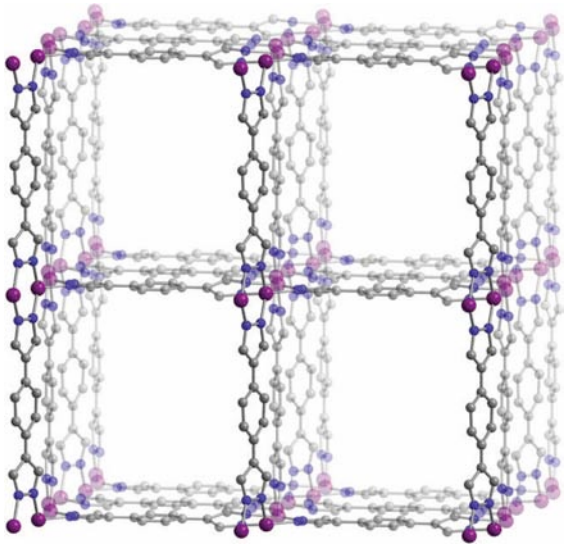
New Compounds Synthesized



$M_3[(M_4Cl)_3(BTT)_8]_2$
(M = Mg, Ca, Fe, Co)



$M_3(BTC)_2$
(M = Mn, Fe, Co, Zn)



M(BDP)
(M = Ca, Mn, Fe)

- Currently exploring optimal activation procedures for new compounds
- BTT- and BTC-based compounds should afford exposed metal cation sites
- BDP-based frameworks expected to show high thermal and chemical stability

Accelerated Discovery

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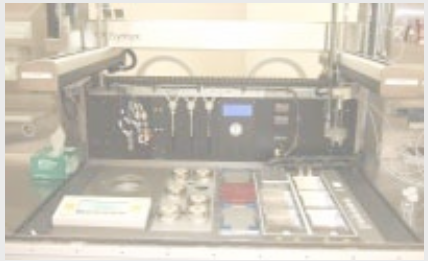
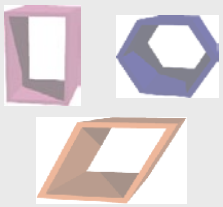


Automated Solid and Liquid Dosing



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Rapid identification of new porous materials

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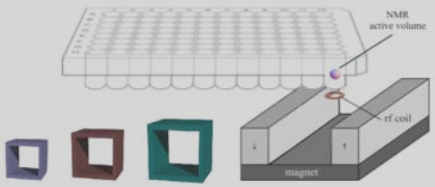
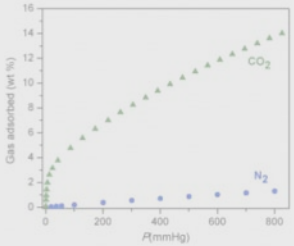


NMR Porosity Screening

CO_2 Adsorption Screening

Rapid screening of CO_2 capture performance

High-throughput Instrumentation



Adsorption Data

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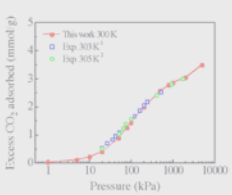
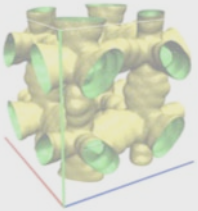
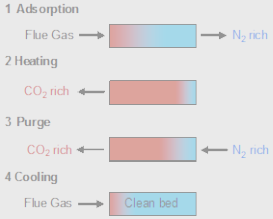
Data analysis, life cycle and sorbent performance analysis





Simulations



Sorbent Performance

High-Throughput Measurement of Surface Area

Challenge: high-throughput screening of surface area of MOFs

Techniques	BET (conventional)	NMR Relaxation (new)
Time-efficiency	Hours	Minutes
Preparation	N_2 gas (complicate)	Liquid solvent (simple)
		Easy to automate

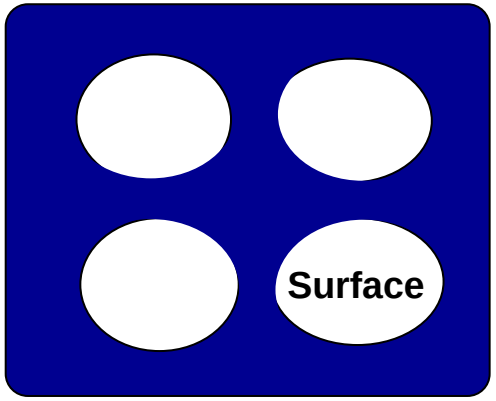
NMR Relaxation Theory:

NMR relaxation rate R of solvent molecules at particle surface is different from bulk

$$R = \rho_{surface} * S/V + R_{bulk}$$

The surface to volume ratio (S/V) is obtained

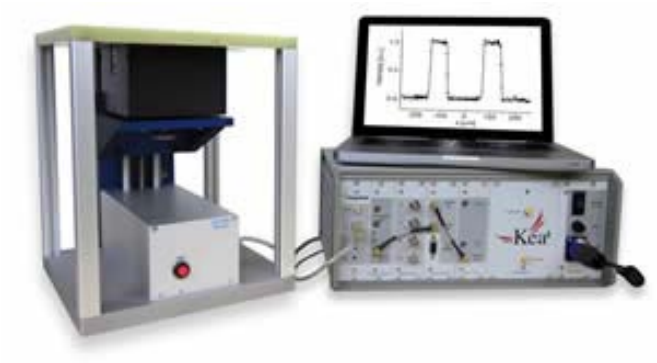
$$R_{bulk} < R_{surface}$$



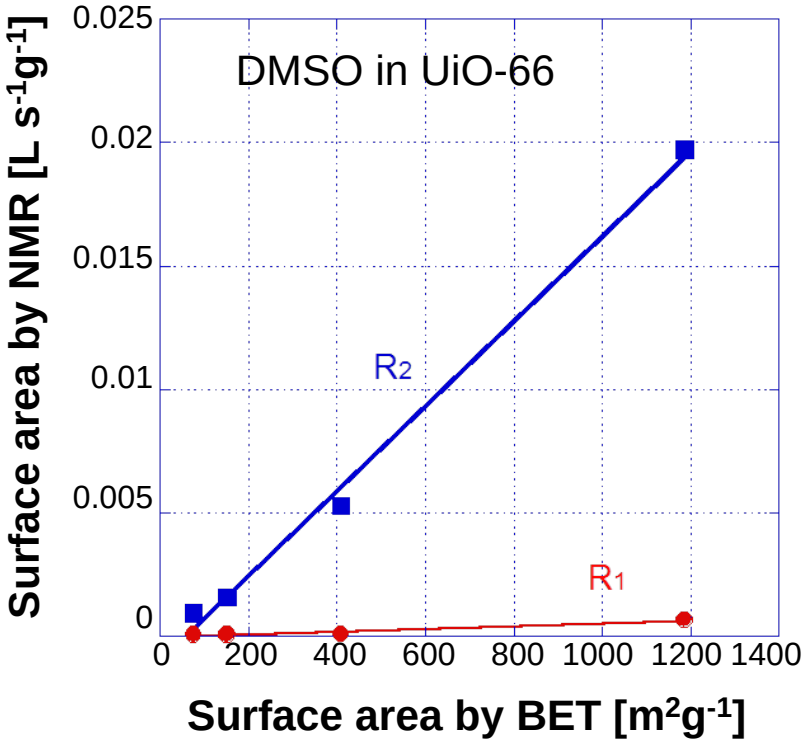
Bulk

High-Throughput Measurement of Surface Area

Novel device for NMR relaxation measurement



Single-sided NMR
(compare to traditional NMR)
Low cost
Compact
Easy for automation

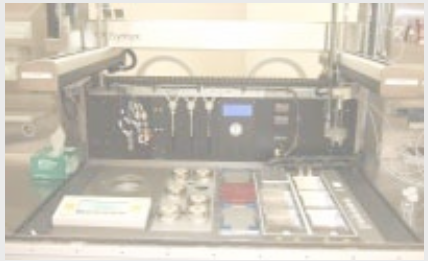


Demonstrated correlation of NMR relaxation with the surface area of MOFs

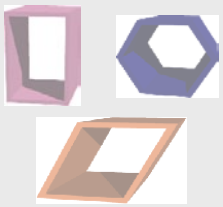
Accelerated Discovery

High-Throughput Synthesis

Highly-parallel, automated discovery of new MOFs



Automated Solid and Liquid Dosing

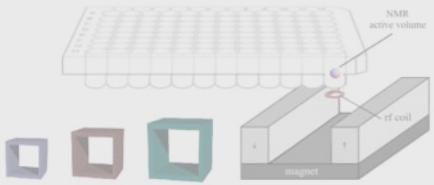


New Structure Types

High-Throughput Characterization

Rapid identification of new porous materials

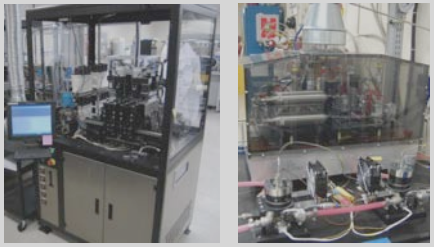
Powder X-ray Diffraction



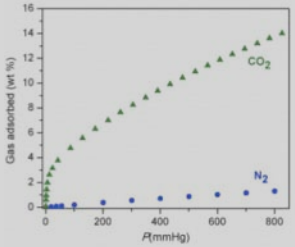
NMR Porosity Screening

CO_2 Adsorption Screening

Rapid screening of CO_2 capture performance



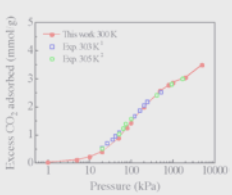
High-throughput Instrumentation

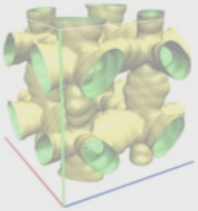


Adsorption Data

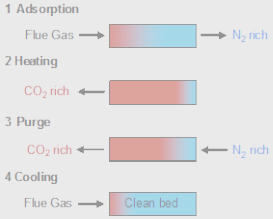
Computational Analysis

Data analysis, life cycle and sorbent performance analysis





Simulations



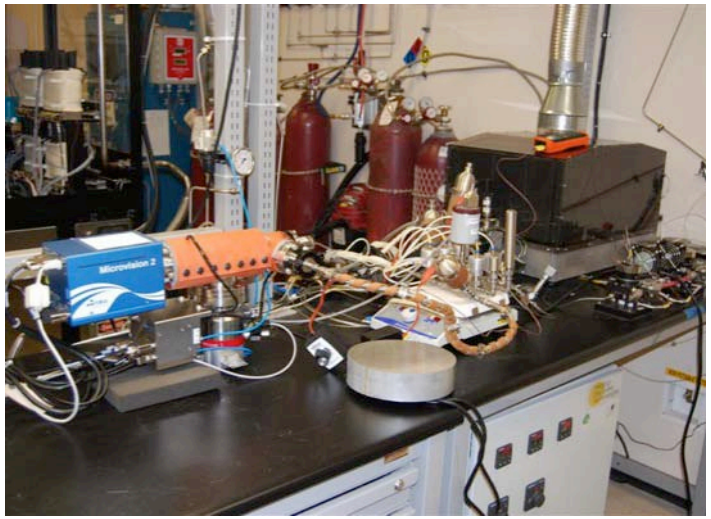
Sorbent Performance

High-Throughput Gas Sorption Analysis

Goals:

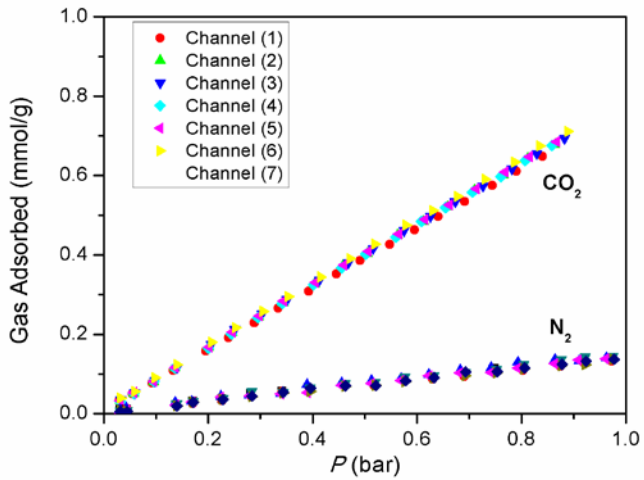
Develop high throughput adsorption measurement apparatus for fast screening

- Modify, install, and validate first-generation Wildcat high throughput adsorption apparatus
- Design, build, install, and validate second-generation Wildcat high throughput adsorption apparatus

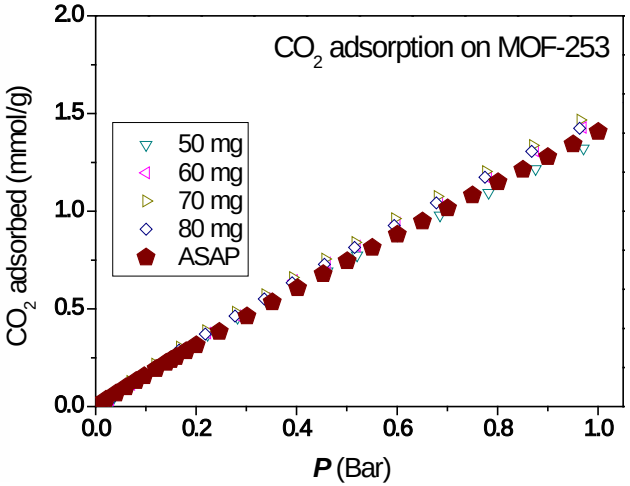


High-Throughput Gas Sorption Analysis

First generation system validation with MOFs



CO_2 and N_2 isotherms of ZIF-8

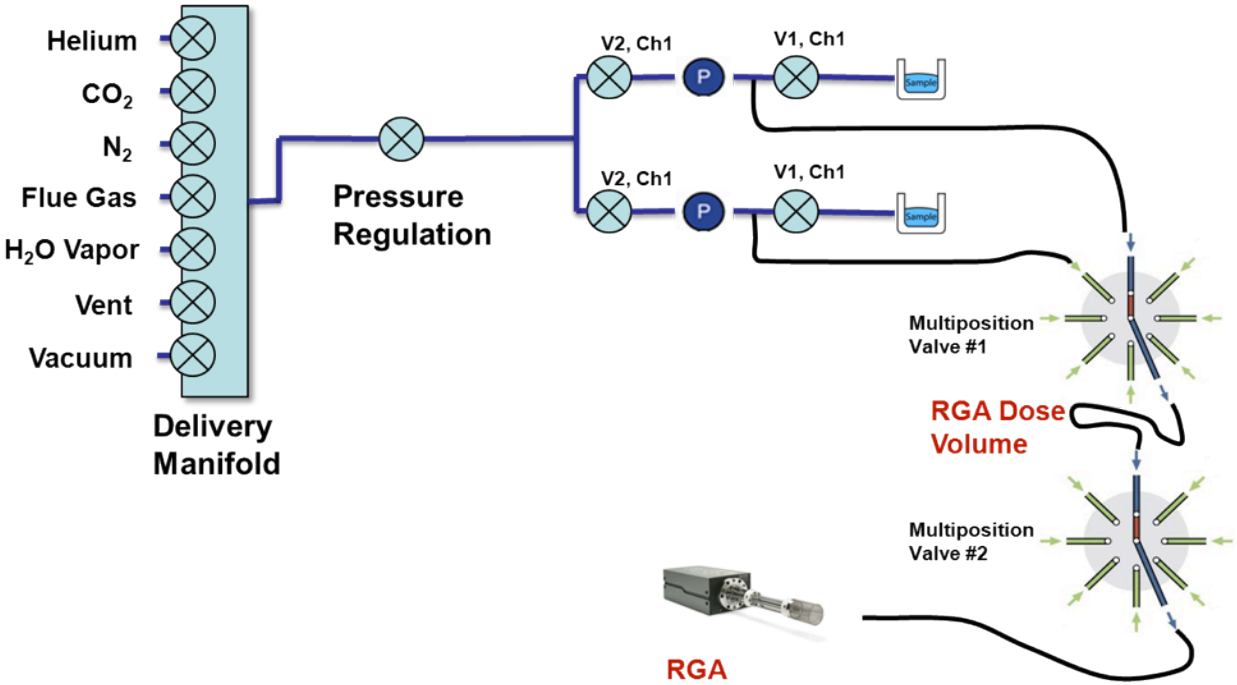


ASAP vs HT system

- Low-pressure CO_2 and N_2 adsorption isotherms
- 28 samples can be measured simultaneously

High-Throughput Gas Sorption Analysis

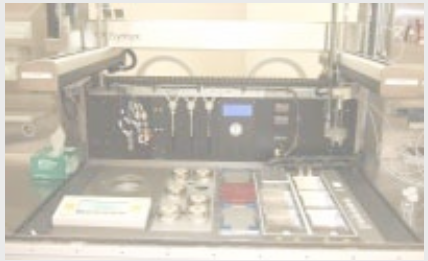
2nd Generation System Targets
- 28 channels
- Kalrez, metal and PCTFE seals
- 5-1300 mbar pressure range
- 200°C max. sample temperature
- High accuracy
- 2 µbar/min leak rate
- Integrated mass spectrometer
- Compatible with water vapor



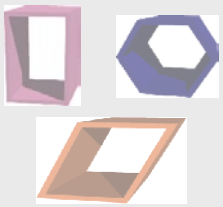
Accelerated Discovery

High-Throughput Synthesis

Highly-parallel, automated discovery of new MOFs



Automated Solid and Liquid Dosing

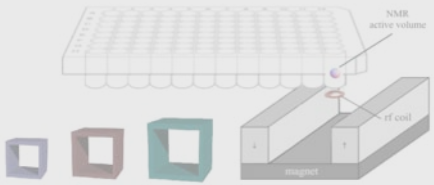


New Structure Types

High-Throughput Characterization

Rapid identification of new porous materials

Powder X-ray Diffraction

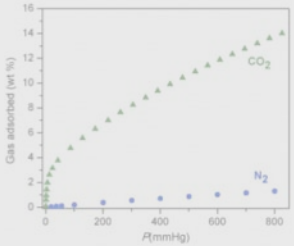


NMR Porosity Screening

CO_2 Adsorption Screening

Rapid screening of CO_2 capture performance

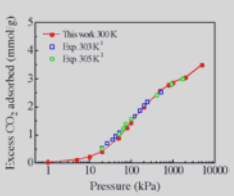
High-throughput Instrumentation

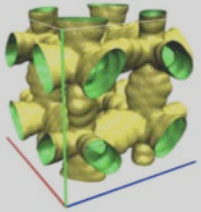


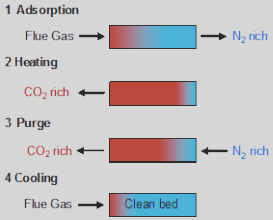
Adsorption Data

Computational Analysis

Data analysis, life cycle and sorbent performance analysis





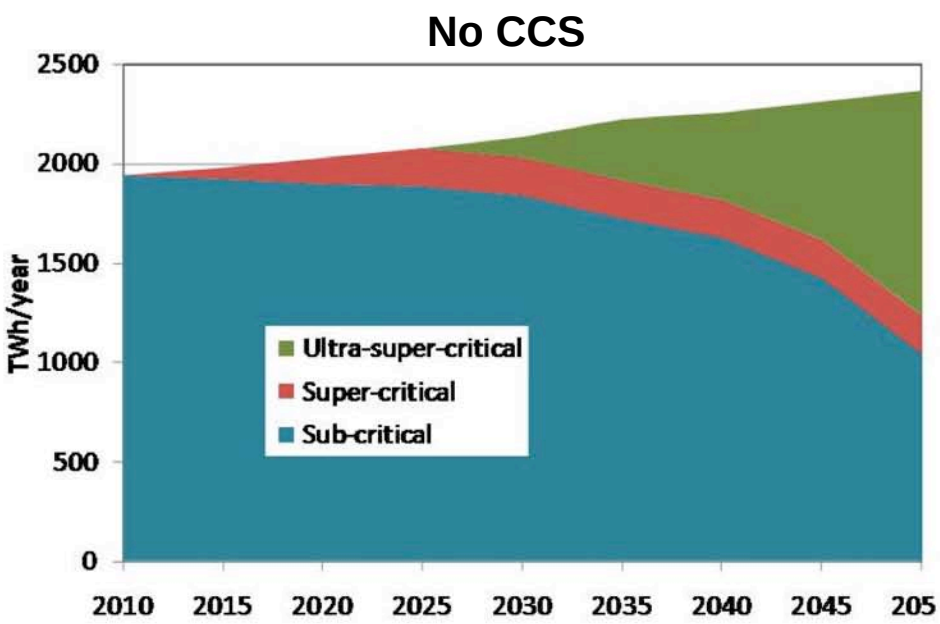


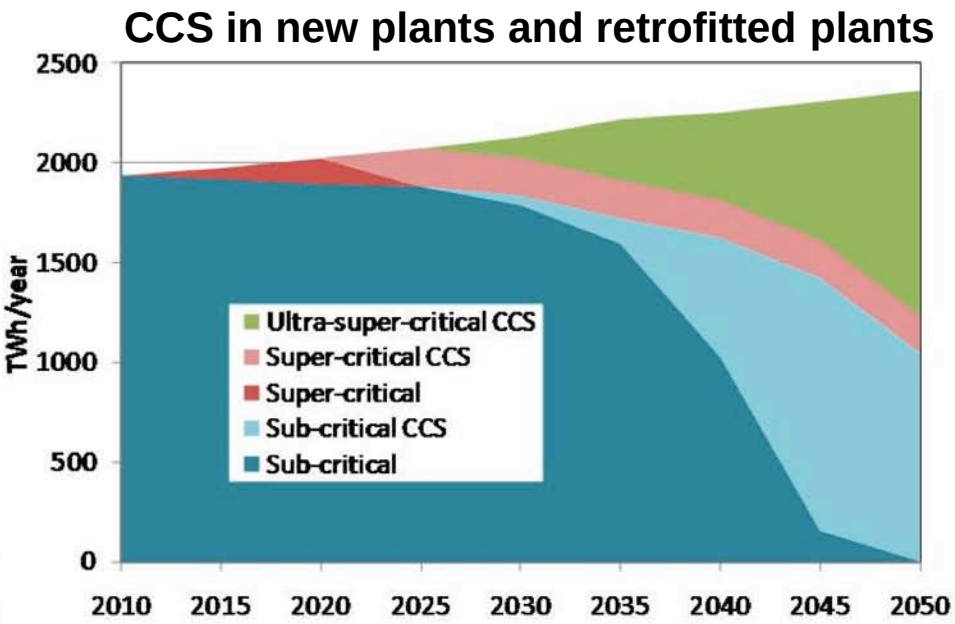
Simulations

Sorbent Performance

CCS Deployment Scenarios

- CCS deployment scenarios for US coal-fired power plant fleet through 2050
- Electricity demand based on EIA 2010 Annual Energy Outlook



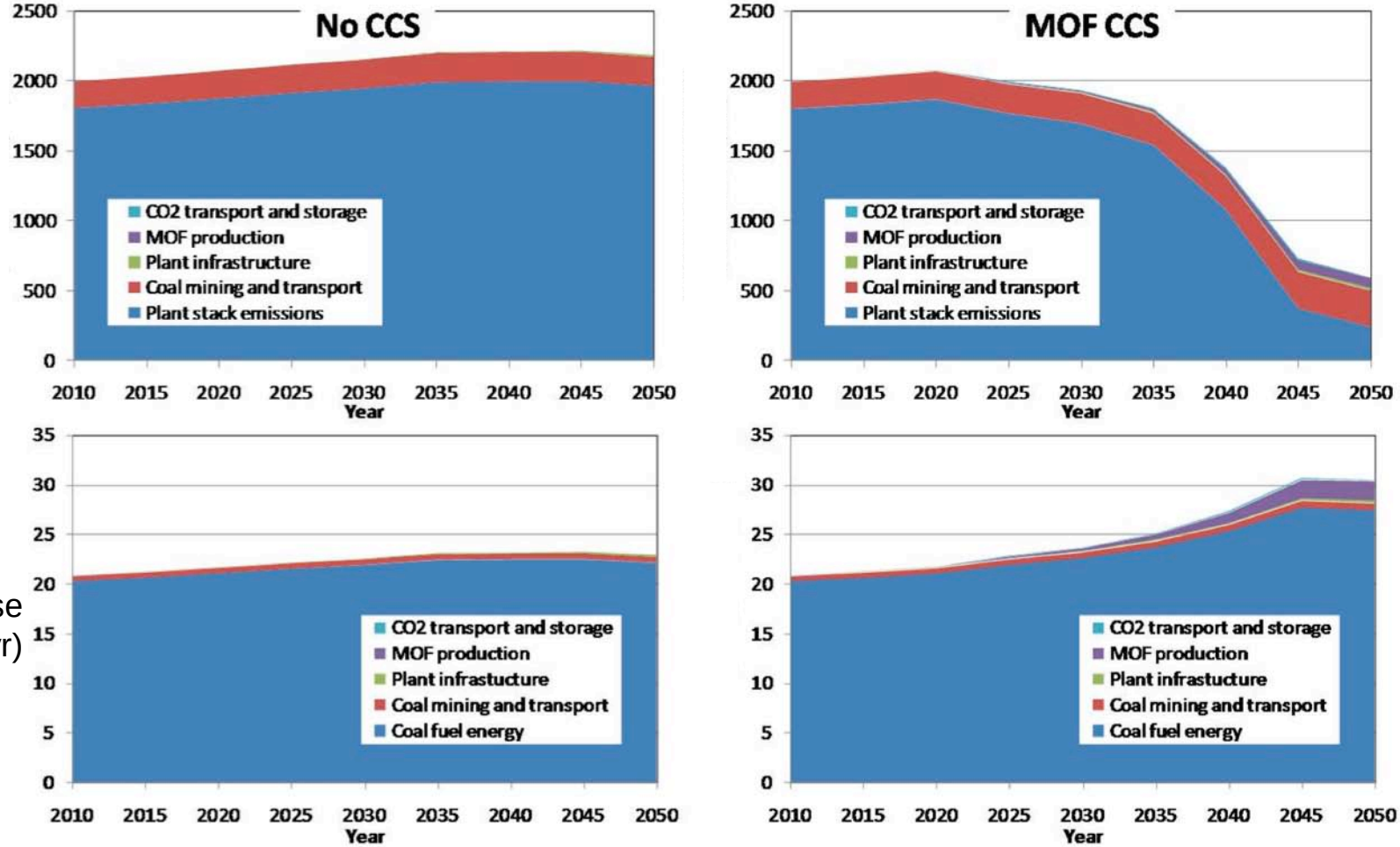


- Other scenarios (not shown) assumed other CCS deployment patterns

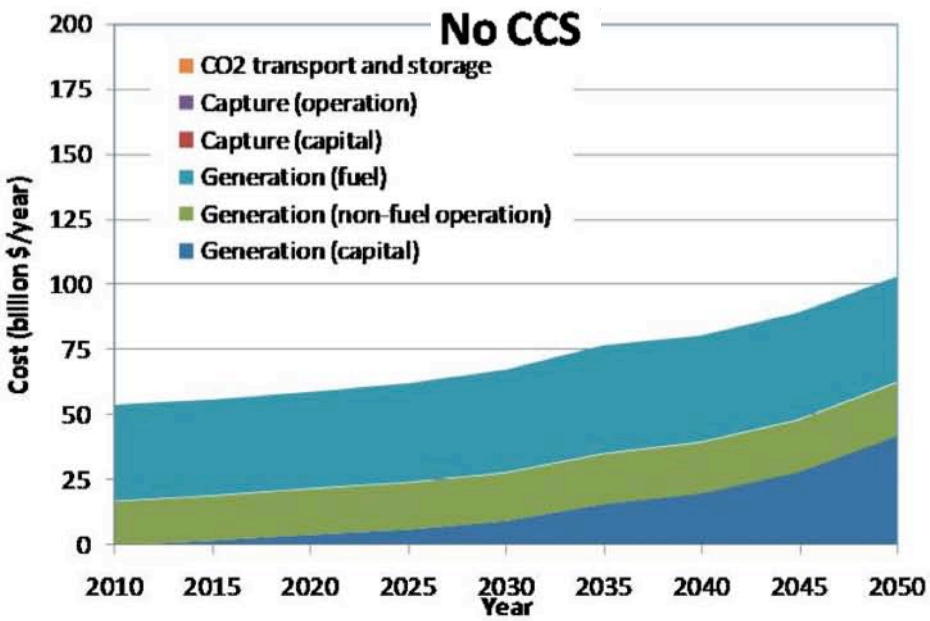
GHG Emissions and Primary Energy Use

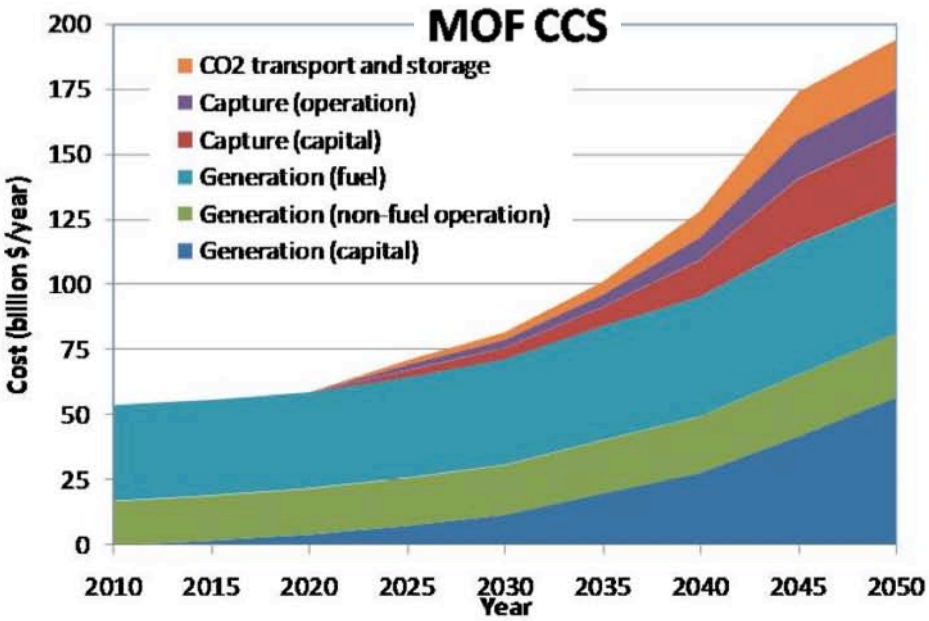
GHG emissions (million tCO_2e/yr)

Primary energy use (EJ/yr)



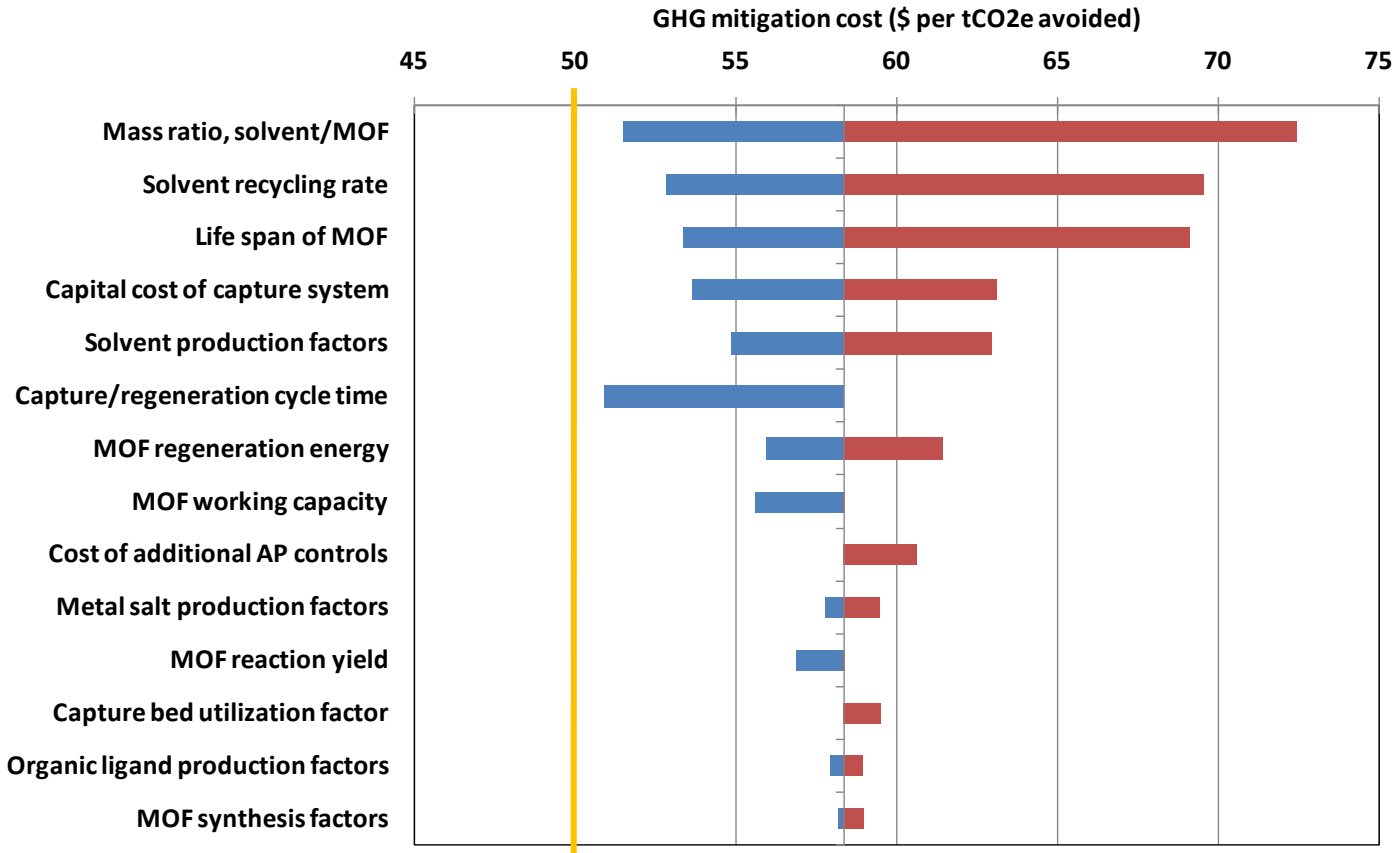
Preliminary Cost Estimate





- Estimated costs are in constant 2010 dollars

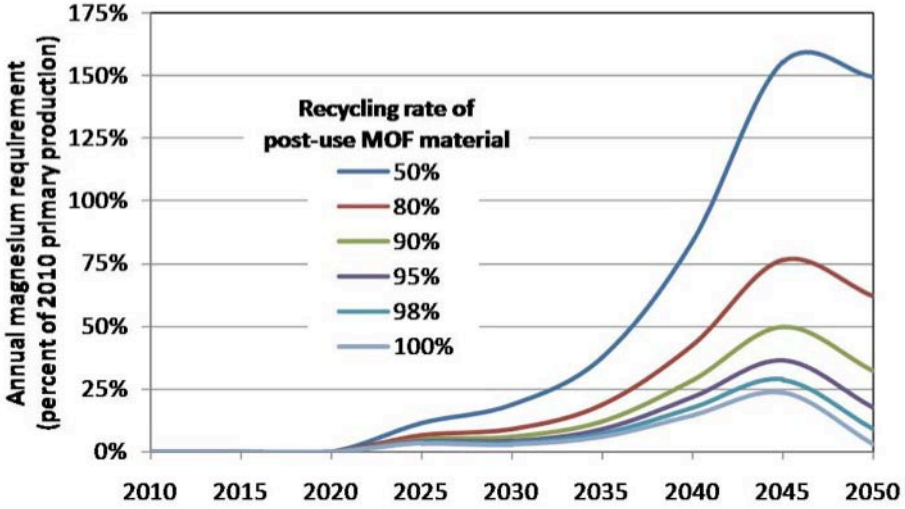
Sensitivity of GHG mitigation cost



- GHG mitigation cost is $58/tCO$_2$ under "base-case" MOF parameter values
- Optimization of critical parameters (e.g. solvent use, MOF life span, capture cycle time) can reduce MOF mitigation cost significantly

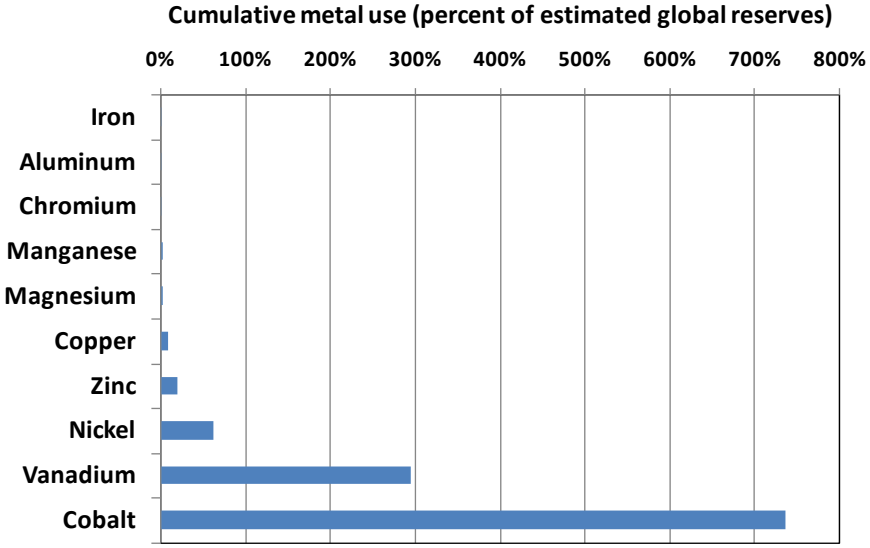
Mitigation cost of MEA CCS is estimated at $50/tCO$_2$

Metal requirements



- Rate of primary Mg use for *US* deployment of Mg-MOF-74 capture
- Expressed as percent of 2010 global Mg production
- Recycling of post-use MOF material will be necessary

- Cumulative metal use for *global* deployment of MOF CCS using different metals
- Assumes all MOFs have same performance and metal content as Mg-MOF-74, and 95% recycling
- Supply of some metals is constrained

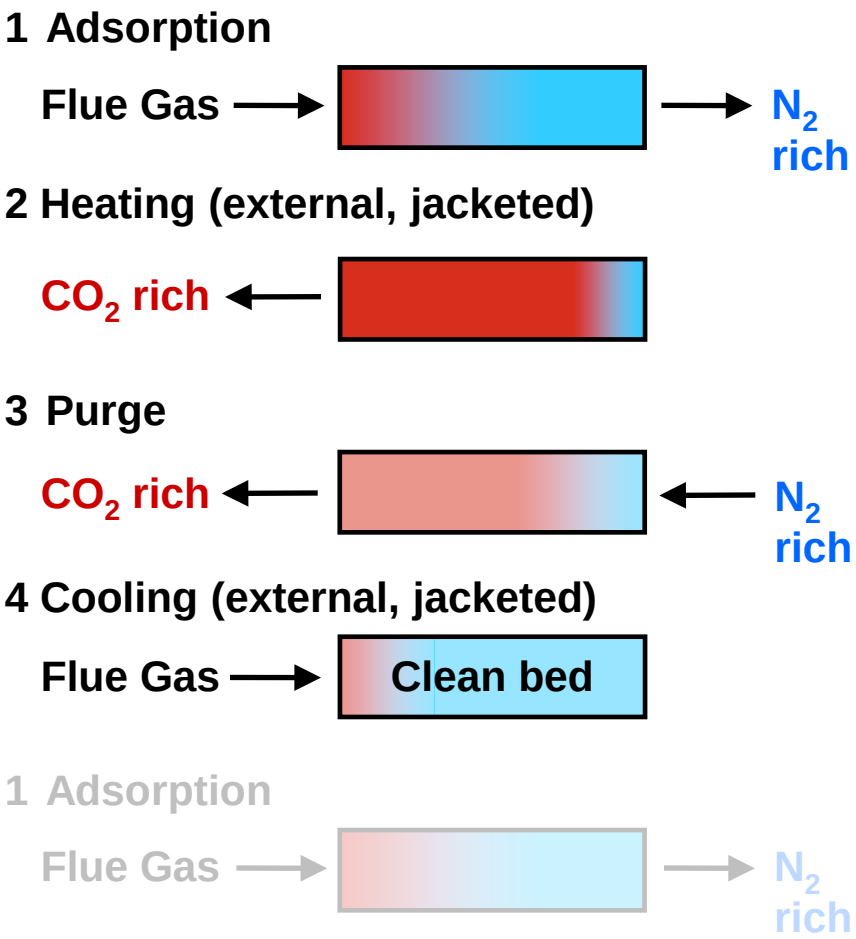


Model for Material Screening

Goal:

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



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).

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

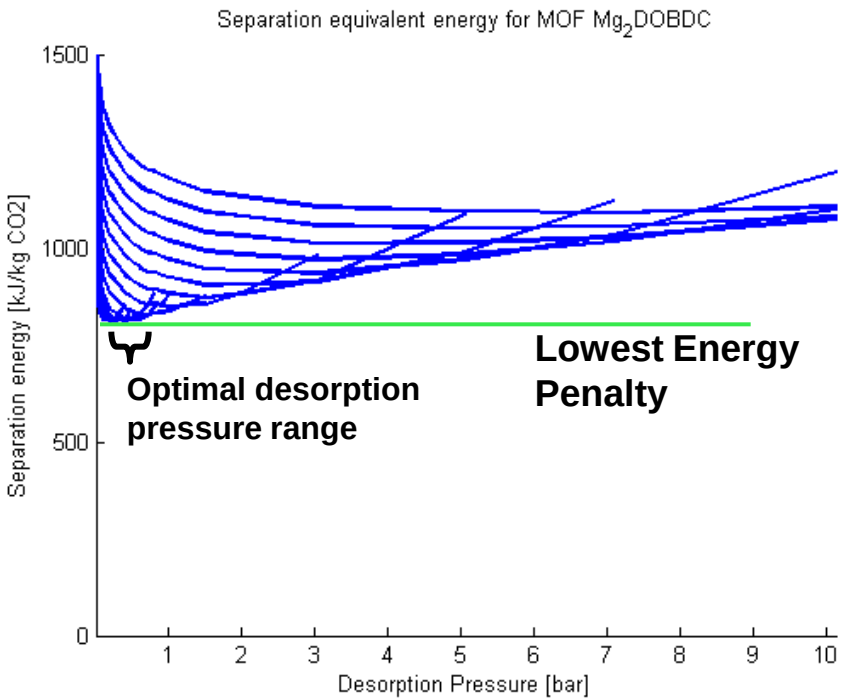
- **Compressor work (W_{comp}):** Work to compress CO_2 product to 150 bar (for transport)

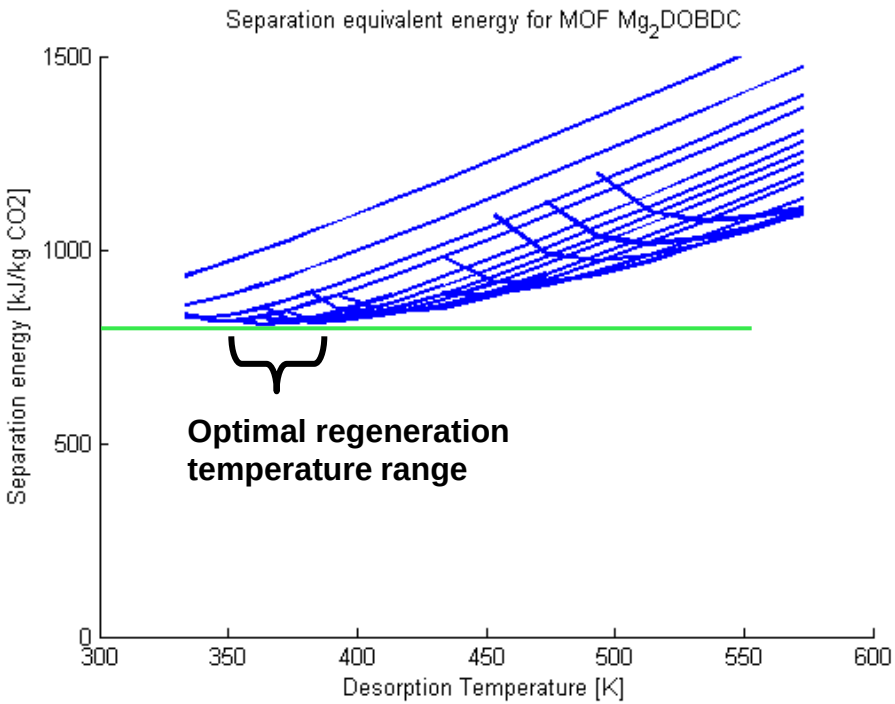
Equivalent energy calculated by discounting the heat requirement by the Carnot efficiency to simulate the effect of taking steam from a steam cycle

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

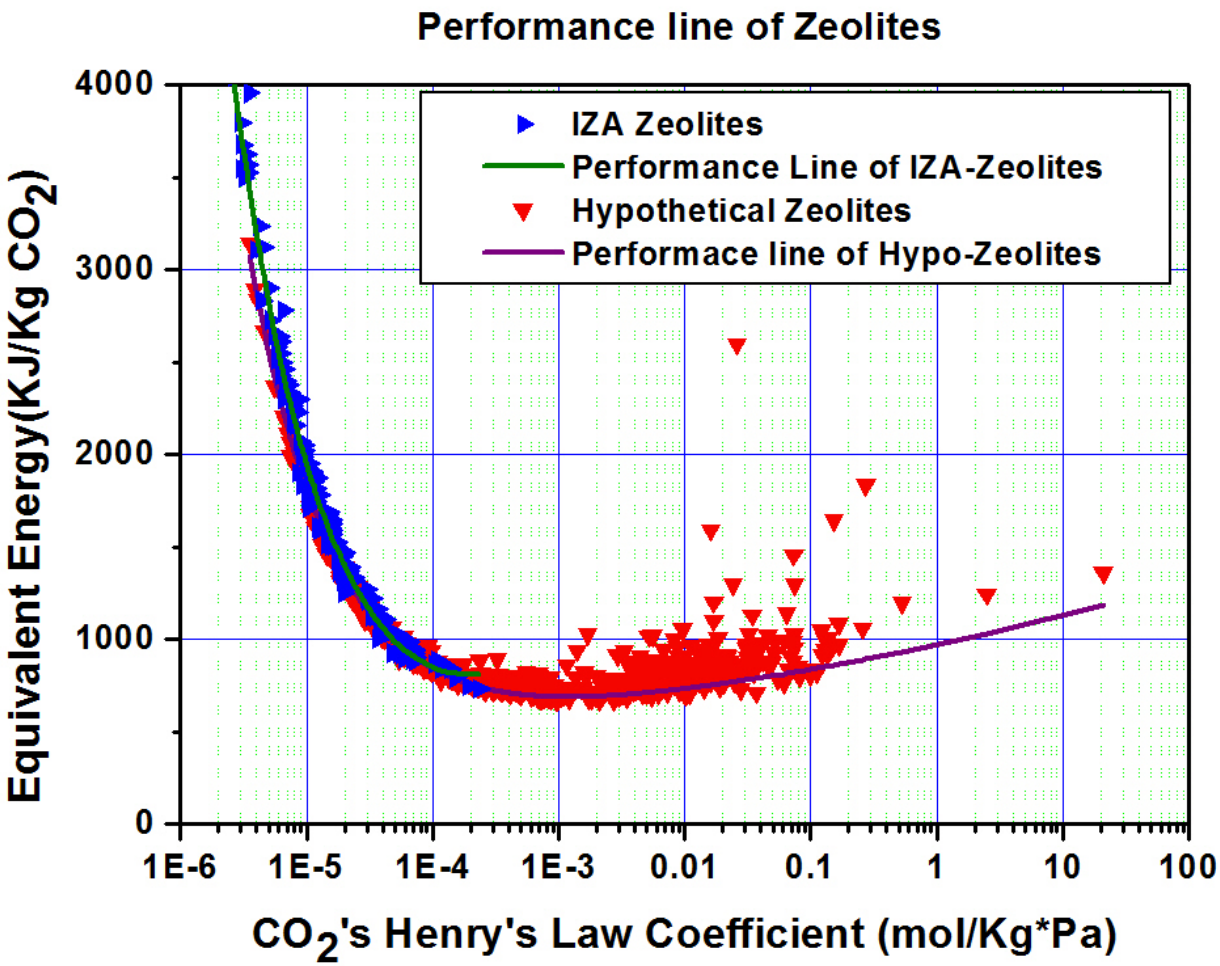
Model Use

- For a given sorbent, we look at the equivalent energy for the entire range of regeneration temperatures and pressures to find the optimal conditions
- This creates a process-independent metric for evaluating sorbents





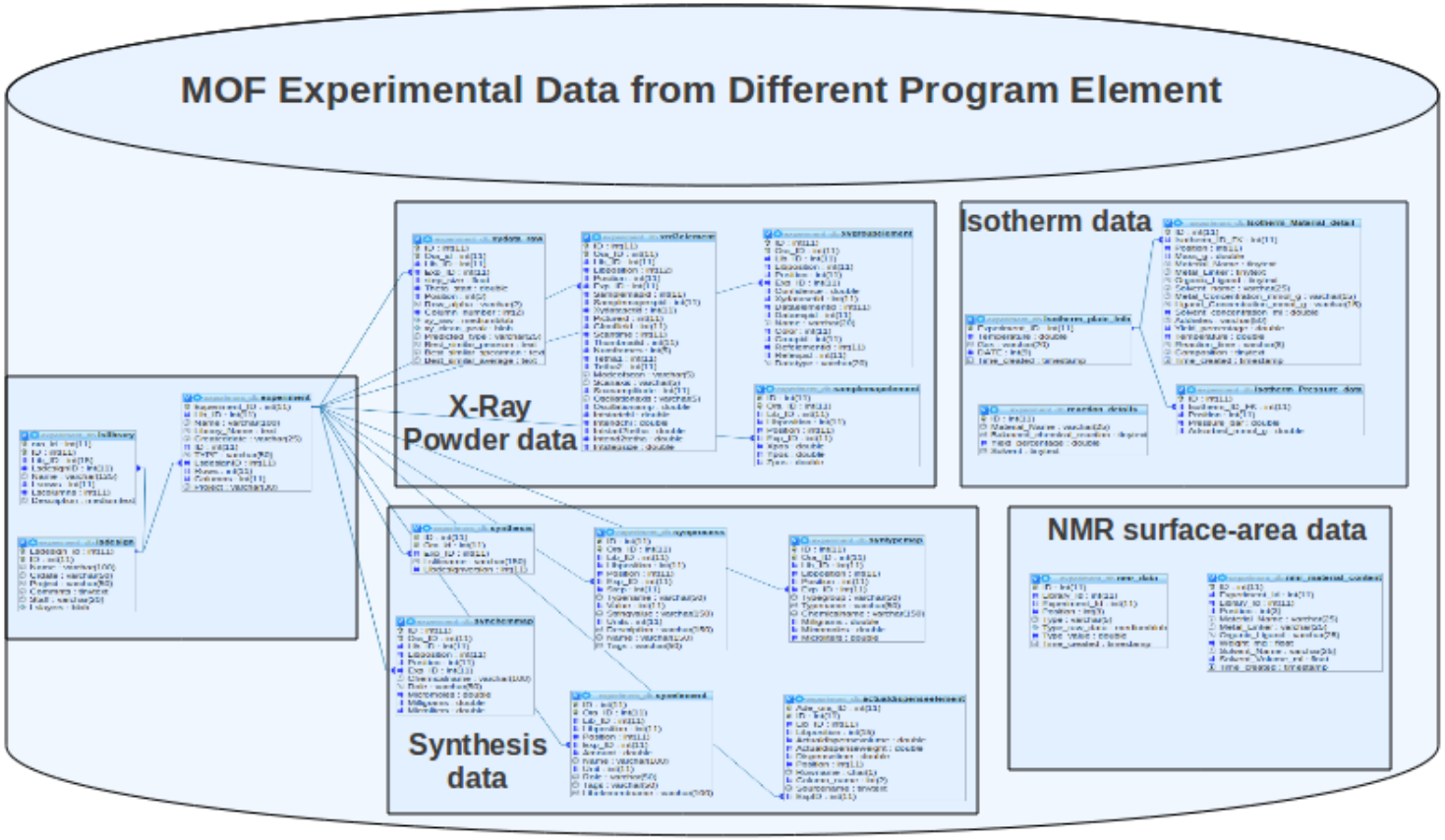
Screening >1M zeolites



Very broad optimum: many structures

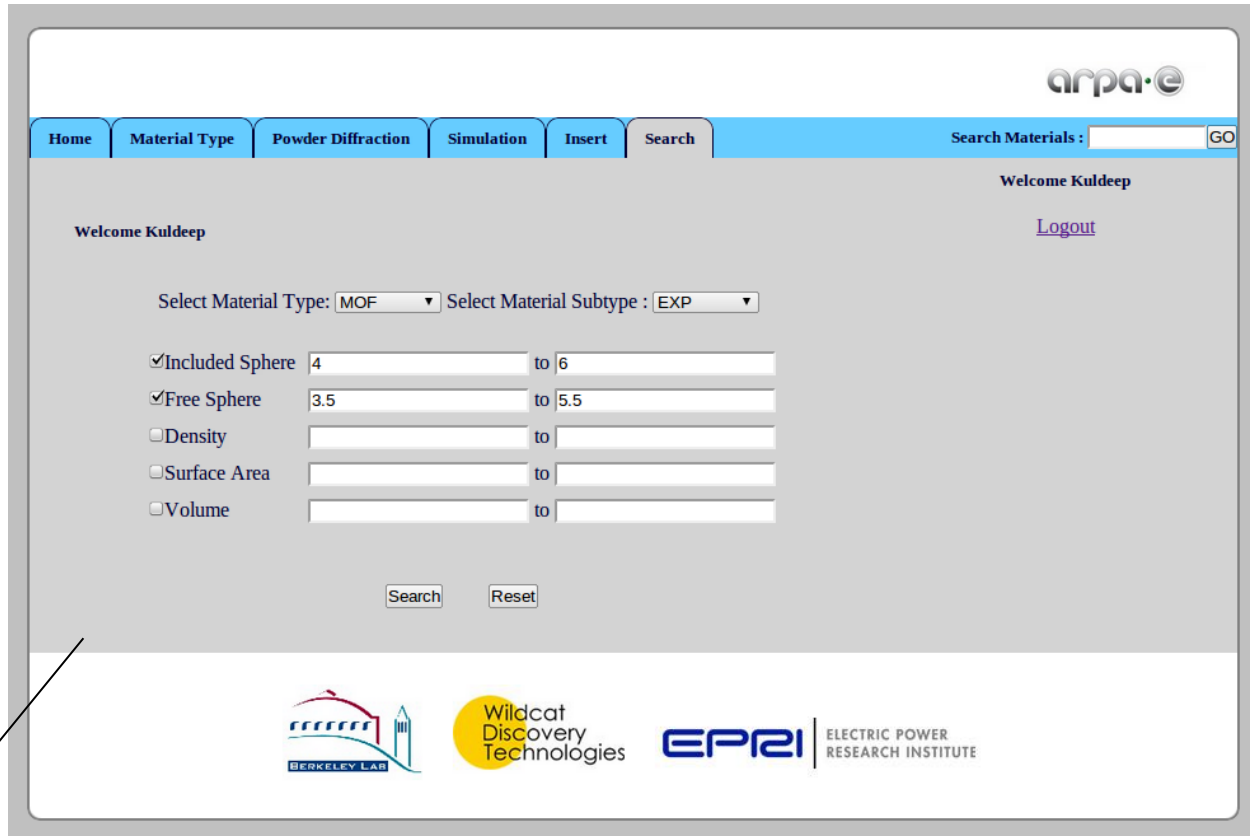
Materials Database

Database schema shows relations between stored data. The schema is optimized to avoid redundant data fields and search bottlenecks.



Material Database – Web interface

Options/typical tasks:
- **Insert data**
- **Search**
- **View search results**



Search page – Search for materials with requested geometrical properties:

Future Plans

- New metal-organic frameworks recognized by high-throughput powder x-ray diffraction will be screened for high CO_2 uptake
- Development of NMR method for pore size distribution analysis will be completed and high-throughput screening validated
- Second-generation adsorption instrument capable of testing 28 samples with a realistic flue gas mixture will be completed, validated, and implemented in screening
- Analysis of how best to utilize specific new frameworks in a capture process will be undertaken