U.S. DEPARTMENT OF ENERGY | Office of Science

Post-Combustion CO_2 Capture: Beyond 2020

Basic Energy Sciences Advisory Committee
November 5, 2009

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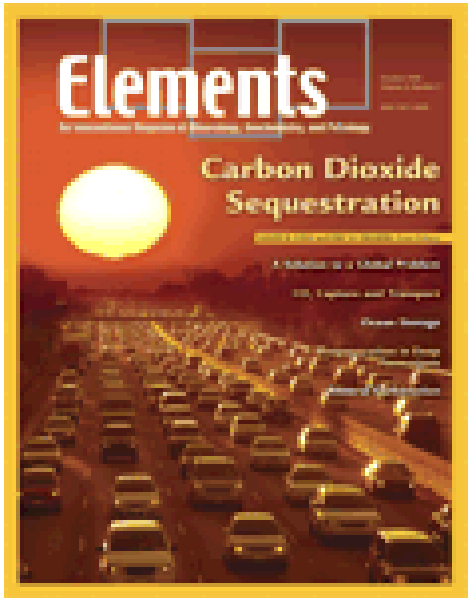
Office of Basic Energy Sciences

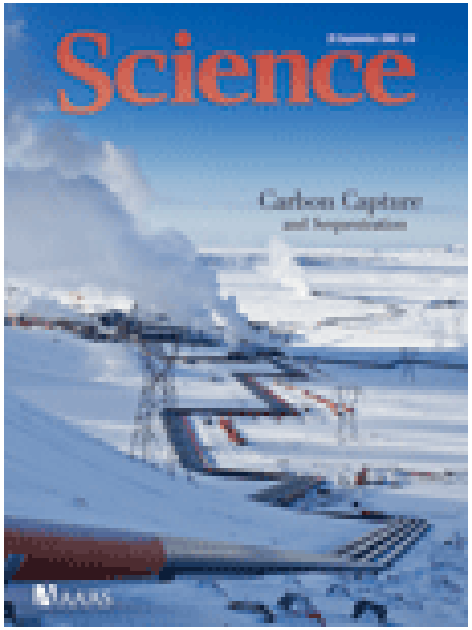
Outline

- Post-combustion Capture: Background and Challenges
- Carbon Capture 2020 Workshop
  - held Oct 5th and 6th, University of Maryland
- Carbon Capture Beyond 2020

Carbon Capture and Sequestration



Oct. 2008, Volume 4, Number 5
Perspective by Dr. Steven Koonin, Under Secretary For Science



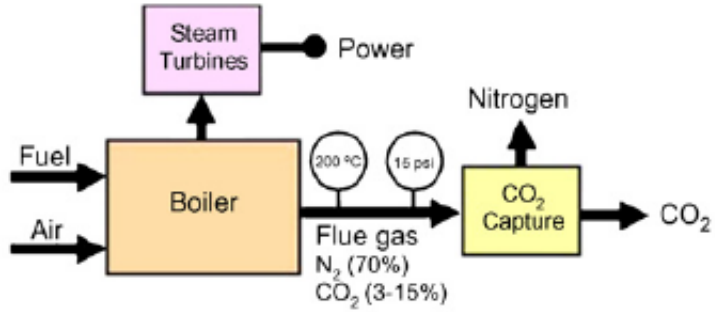
25 September 2009, Vol 325, Issue 5948
Perspective by Dr. Steven Chu, Secretary of Energy

Carbon Capture

Challenges

- Low CO_2 concentration
- High energy for regeneration

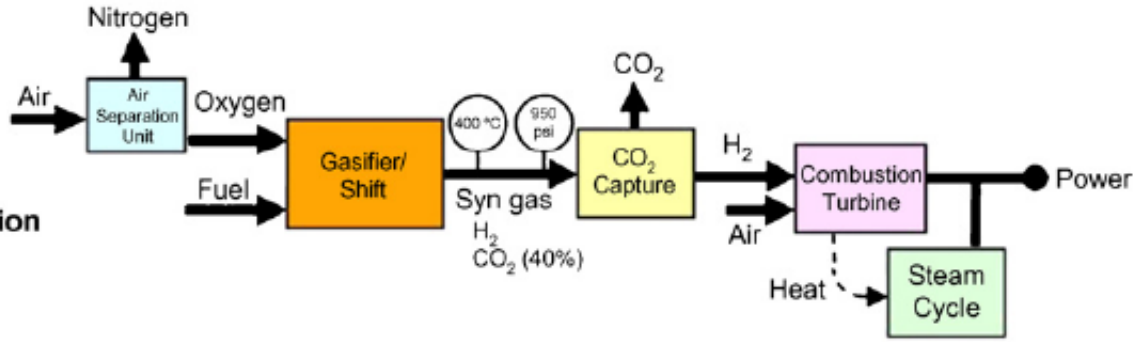
Post-Combustion



- Build new plants
- Oxygen production – expensive (chemical looping and ion transport membranes)

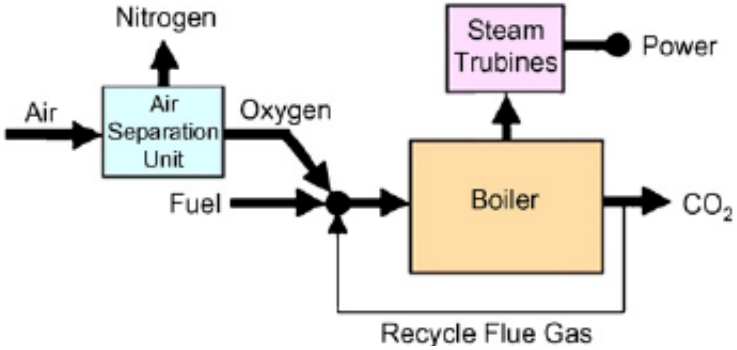
Pre-Combustion

IGCC



- Air Separation Units consume considerable energy
- Expense - corrosion resistant materials

Oxy-Combustion



INTERNATIONAL JOURNAL OF GREENHOUSE GAS CONTROL 2 (2008) 9–20

Carbon Capture Goals
DOE Fossil Energy

- *By 2020*
  - *have available for commercial deployment, technologies that achieve:*
    - *90% CO_2 capture*
    - *< 35% increase in COE (cost of electricity)*

Source: DOE Fossil Energy (FE)

Challenge - Scale

- ~30 Giga tons of Anthropogenic CO_2 produced globally in 2004
  - Requires 13.5 million Houston Astrodomes at atmospheric pressure*
- CO_2 from US electricity 2006 – only 1.05 million Houston Astrodomes

*From: George C. Marshall Institute Policy Outlook, June 2008.

Status of Current Technology

- Amines
  - Monoethanolamine (MEA) or amine blends - MEA with methyldiethanolamine (MEDA) or sterically hindered amines
  - NH_3
  - Can be aqueous solution in post-combustion
- Chilled ammonia (35 F)
  - ammonium carbonate to ammonium bicarbonate

- Advantages - amines
  - Selective, reversible, nonvolatile and somewhat inexpensive
- Disadvantages - amines
  - Corrosive, degrade esp. with O_2 or SO_2 present, require large thermal energy for stripping
  - NH_3 – less energy to strip but toxic vapor to deal with

Post-Combustion Capture

Conundrum

- To remove CO_2 from flue gas selectively and rapidly ⟶ strong chemical bond
- To strip the CO_2 from scrubber with little energy need ⟶ weak chemical bond

10 – 15 % CO_2
Predominately N_2
1 atm.
H_2O
Trace or more SO_x, NO_x

Flue gas

5% of efficiency loss

Scrubbing

Materials Challenges

Absorb/adsorb fast
High selectivity vs. N_2
Desorb fast
Chemically stable
Physical properties stable
(Viscosity, mechanical integrity)
Non-corrosive
CHEAP

Science

Build knowledge base that will provide guidance for rational design of next generation sorbents

Stripping

CO_2 + Steam

33% loss

CO_2

H_2O

ΔT (Steam)

60% of efficiency loss

Carbon Capture 2020 Workshop

- Joint FE (lead) and BES October Workshop

- Workshop Goals
  - Communicate status so that the research community understands:
    - The scale and nature of the problem that needs to be addressed
    - What parameters need to be defined for research activities
    - The potential of new ideas emerging from basic research
    - The status of existing Fossil Energy capture research
  - Produce a roadmap for a coordinated effort that will impact carbon capture by 2020
    - Identify ongoing research projects that could be connected to applied research goals
    - Propose and critique a numeric modeling approach to quickly assess the full-scale performance of new concepts

- http://www.netl.doe.gov/publications/proceedings/09/CC2020/index.html

- Held Oct 5th and 6th, University of Maryland

Carbon Capture 2020: Overview

- Welcome
  - *Dr. James J. Markowsky – Assistant Secretary, Office Fossil Energy*
    Dr. William F. Brinkman – Director, Office of Science
- Background talks
  - FE, NETL and BES
  - Overview of EFRCs – Berend Smit, Director: *Center for Gas Separations Relevant to Clean Energy Technologies, UC-Berkeley*
  - Background talks – Oxy-fuel combustion, Power Plant Configurations and Models for CC Scale-up
- Breakout Sessions & Poster Session
  - Solid sorbents – MOFs, ZIFs
  - Liquid adsorbents/solvents
  - Membrane Concepts
  - Cross-cutting
  - Chemical and Biological analogues

Recommendations from Breakout Sessions

- Solid Sorbents
  - Further development of Carbon Capture technologies needs industry wide communication and collaboration on projects (Academia, DOE, Industry).
  - Determine materials performance targets: Thermodynamics, kinetics, capacity, requirements, cost, etc.
- Liquid Solvents
  - Specific details and challenges for several types
  - For BES/FE collaboration : Going from atoms and molecules to thermodynamic design and functions
- Membranes – identified technical barriers for different classes
  - Work presently constrained by existing materials
  - Lack of common measure to rank or to identify how far new materials are from optimum

Recommendations from Breakout Sessions

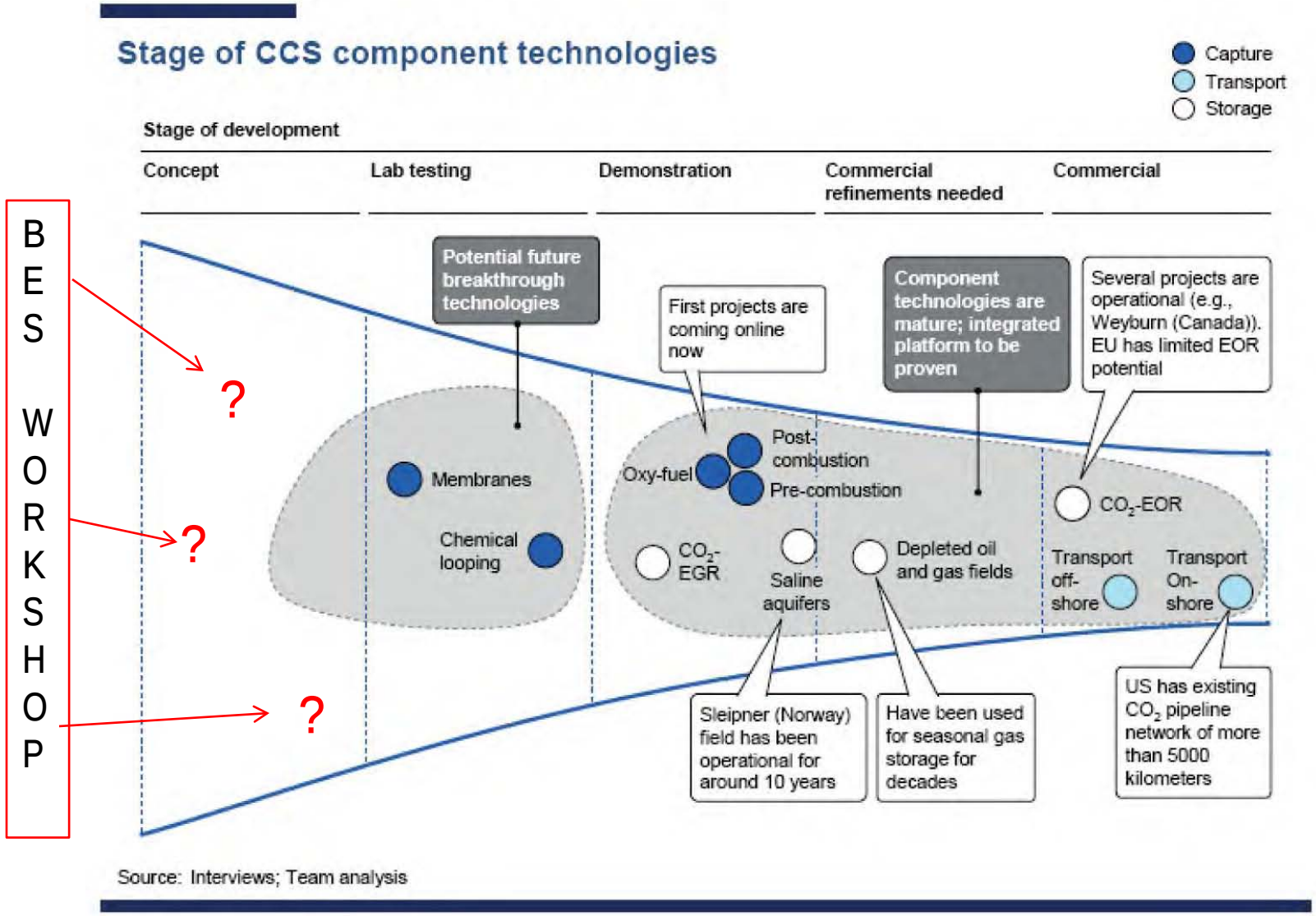
- Cross-cutting
  - Good assessment of different areas – chemical looping, computation and modeling, oxy-fuels etc.
  - Communication: Find ways to build a broader and more cohesive carbon capture community, including sub-communities

- Chemical and Biological Analogues
  - Considered challenges for algae, carbonic anhydrase mimetics, biological analogue for oxygen production
  - Falls into BES domain

Next - Carbon Capture: Beyond 2020

- Joint by BES (Lead) and FE
- Goal - Identify priority research directions for the challenges beyond 2020
- Run like a Basic Research Needs Workshop
  - Plenary talks on technical and scientific challenges
  - Breakout panels focused on development of priority research directions
  - Crosscutting panel focused on identification of grand challenge science themes
  - Dedicated report writers to ensure rapid progress on written report
- Co-Chairs
  - Paul Alivisatos – Lawrence Berkeley National Lab, UC-Berkeley
  - Michelle Buchanan – Oak Ridge National Laboratory
- Venue in the DC area
- Held February or early March

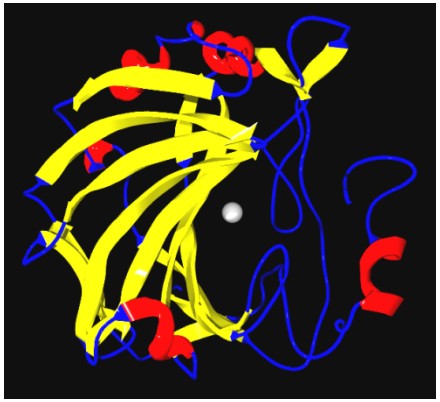
Research to Commercialization: CCS Pipeline



Source: McKinsey & Company (2008), Carbon Capture and Storage: Assessing the Economics

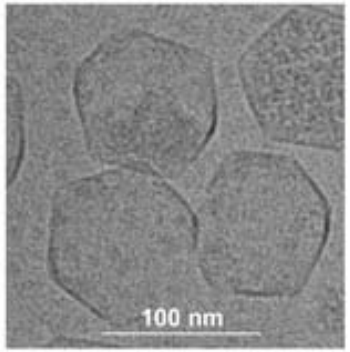
Biology and CO_2

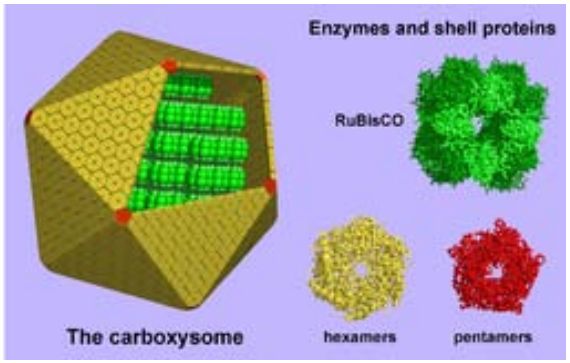
- Nature and CO_2
- Plants
  - Deal with dilute CO_2 (not efficiently)
  - Carbonic Anhydrase - in plants – increases CO_2 concentration
  - RuBisCO – plant enzyme converts CO_2 to sugar – 3 CO_2/sec



Ribbon diagram of human carbonic anhydrase with Zn atom in center

- Bacteria
  - Carboxysome - concentrates CO_2 levels to increase chemical transformation
  - Strategy: Concentrate, isolate and transform



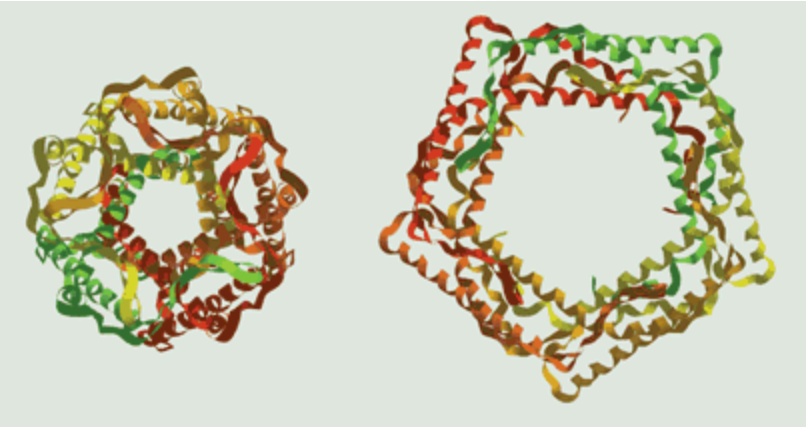


Carboxysomes – protein bacterial organelles on left is electron microscope image, on right is model of structure

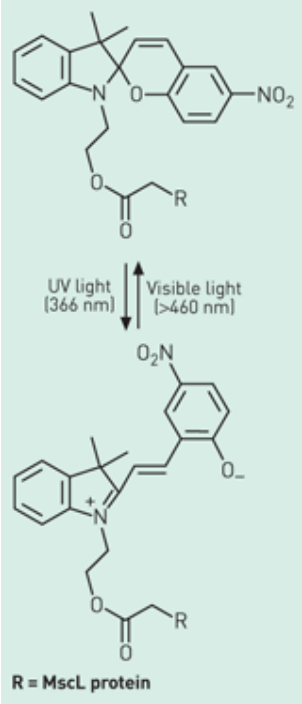
Source: http://en.wikipedia.org/wiki/File:Carbonic_anhydrase.png and http://en.wikipedia.org/wiki/Carboxysome

Nature's Triggers

- While nature does not deal with CO_2 ideally for post-combustion capture – can provide hints for non-thermal triggers
  - Ecoli have a channel protein that opens and shuts with pressure –
    - Has been modified to open and shut with light[1]



Channel proteins modified with spiropyran opens or closes channel with light.



Reversible spiropyran photo-switch.

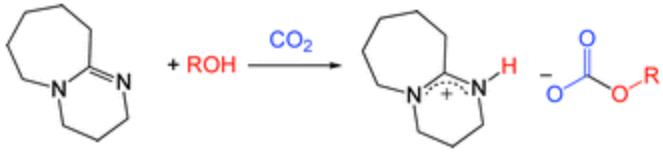
  - Synapses electrical field triggers release of neurotransmitter

[1]Source – *Science,* 2005, *309*,755, Copied from C&E News report http://pubs.acs.org/cen/news/83/i31/8331notw1.html

Novel Approaches: Base + Alcohol

Alternate science approach may offer a better pathway in the future - Heldebrant, PNNL

- Eliminate water and H bonding – reduces energy of stripping
  - Lower specific heat of organic liquids
    - Same strip temperature, considerable energy savings
- Organic amidine or biological guanidine base plus alcohol
  - Binds CO_2 – reversed with heat
  - Higher binding capacity for CO_2 than commercial MEA (monoethanolamine)
    - Design base to minimize hydrogen bonding – more energy savings



    - Demonstrated uptake in 50% CO_2/ 50% N_2 , strip 90 to 130 C
    - Issue - water form bicarbonate salt of base – strips MEA temperature

Source: Heldebrant et al. *Energy Procedia,* 1 (2009) 1187-1195

Summary

- Carbon Capture: Beyond 2020
  - Goal: Identify priority research directions for the challenges beyond 2020
- Fundamental science needs to advance existing approaches more rapidly
- Need for new approaches and materials that would require significantly less parasitic energy

- Thank you
- Questions?

Backup Information

Key Characteristics for CO_2 Capture (Post-Combustion)

- Perform in presence of water (steam) and trace contaminants including SO_x and NO_x, etc.
- Temperature stability over a wide temperature range
- If Solid sorbent – mechanical stability, If liquid – no viscosity change
- Sustainable
- High selectivity for CO_2 over N_2
- Work in dilute streams (10% CO_2)
- Rapid kinetics for capture (scrubbing) and regeneration (stripping)
- Non-corrosive
- High cycle life
- Low energy regeneration (stripping)
- Be utilized at unprecedented scale - Cheap

Science – Beyond 2020

- CO_2 sorbent that can be stripped with minimal energy
  - Look to Nature for ideas on triggers but unlikely to be a biological solution
  - Electrical, electrochemical, pressure, light, pH, phase change (liquid crystal)*
  - Nanoscale approaches

- Build the knowledge base to facilitate a rationale design of sorbents from first principles
  - Advanced computational modeling and theory - First-principles methods for capture and release of nonpolar molecules
  - Advanced characterization tools, including those supported by BES, to
    - Identify structure of binding sites
    - Understand kinetics and thermodynamics of sorption/desorption in realistic conditions
  - New chemistries for advanced sorbents
    - New sorbents
    - Synthesis

*Source: *Advanced Post-Combustion CO_2 Capture*, prepared for Clean Air Task Force, Howard Herzog, Jerry Meldon and Alan Hatton

Approaches Under Development

- Newer Materials
  - ZIFs – zeolite imidazole frameworks
    - Imidazoles increase selectivity
    - Non silicates – resistant to degradation from steam
  - Membranes – functionalized with amines or other groups to enhance selectivity (>200), increase cycle life
    - Chemical functionalization of polymer can increase selectivity beyond what is achieved with size separation
    - Fibrous membranes coated with amines (glass or carbon fiber mesh)
  - Poly (ionic liquids)
    - Some have higher sorption than ionic liquids
    - Avoid viscosity increases seen with some ionic liquids
  - Ion Engineering – amines in ionic liquids (65% cost savings over water)

Source: *Advanced Post-Combustion CO_2 Capture*, prepared for Clean Air Task Force, Howard Herzog, Jerry Meldon and Alan Hatton

Current BES Related Research

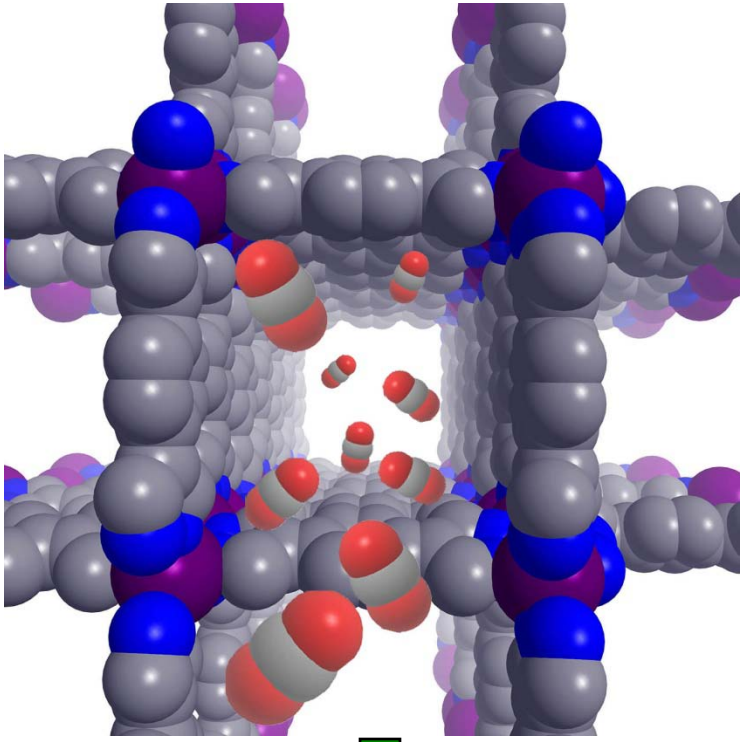
- Directly related (EFRC funding) – CO_2 from N_2
  - Zeolitic imidazolate framework (ZIFs) , metal organic frameworks (MOFs), membranes for separation
  - Synthesis, characterization, computation/modeling
- CO_2 Binding/Separation
  - Often from CH_4
  - MOFs, ZIFs
  - Polymer membranes
  - Computation, theory, modeling
- Hydrogen – Binding and Separation
  - H_2 sorbents
  - Inorganic clathrates, MOFs
  - Membranes
- Separation Sciences, Materials, Theory & Computation
  - Membrane synthesis
  - Transport
  - Theory and Computation

EFRC: Gas Separations for Clean Energy Technologies: (Smit, Berkeley)

Synthesis: Generate high surface area MOFs & self-assembled synthetic biomimetic polymer films

Characterization: Atomic-level structural characterization - before and after exposure to gas, accurate means of assessing the selectivity, kinetics, and thermodynamics of gas adsorbate binding – use to test computational models

Computational Separations: Strong computational component - understand chemical interactions at a molecular level, guide synthetic efforts



Goal: New strategies and materials for *energy efficient* selective *capture* or *separation* of CO_2 from gas mixtures based on molecule-specific chemical interactions

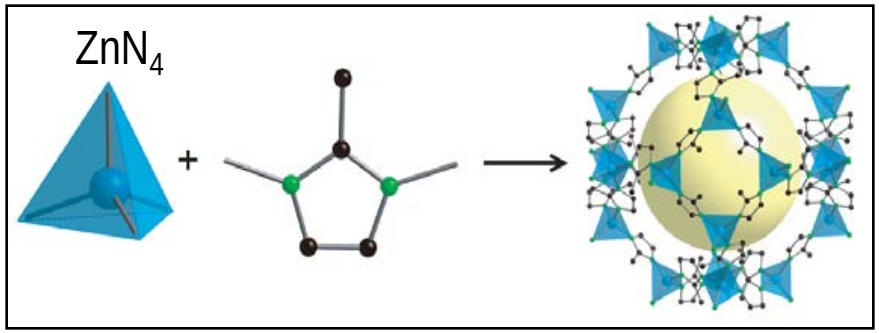
EFRC: Molecularly Engineered Energy Materials (Ozolins, UCLA)

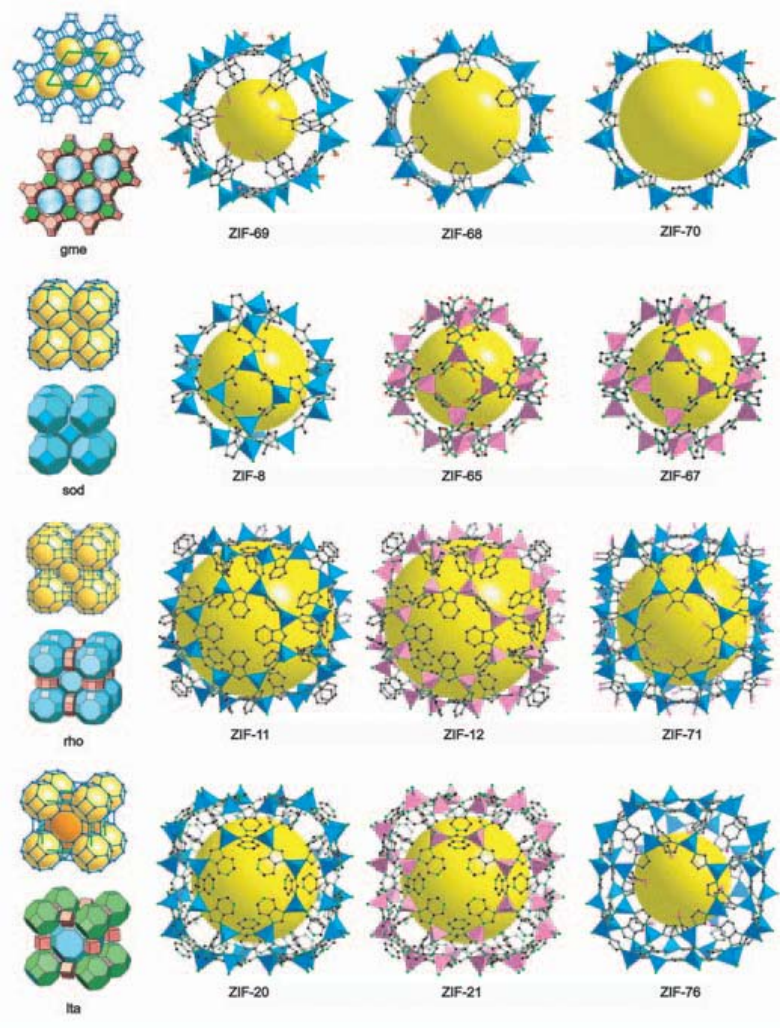
Capture is 1/3 of this EFRC: Novel ZIFs for gas separation including CO_2 capture

Yaghi – Synthesis, characterization

Asta – Electronic structure calculations

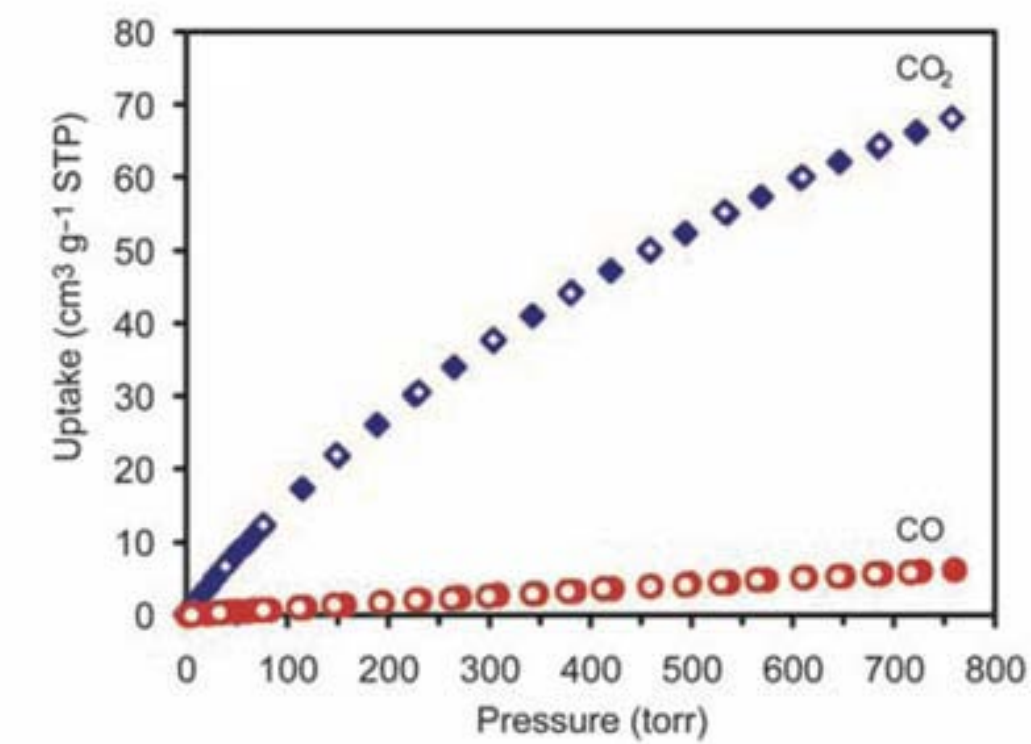
Laird & Houndonougbo – Monte Carlo Simulations

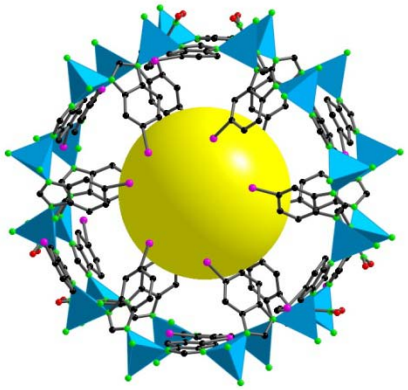




CO_2 Uptake in ZIF-69

Separate CO_2 from CO
- Surface areas to 1970 m^2/g
- Stable to 390 °C, 1 liter ZIF-69 holds ~83 liters of CO_2 at 273 K



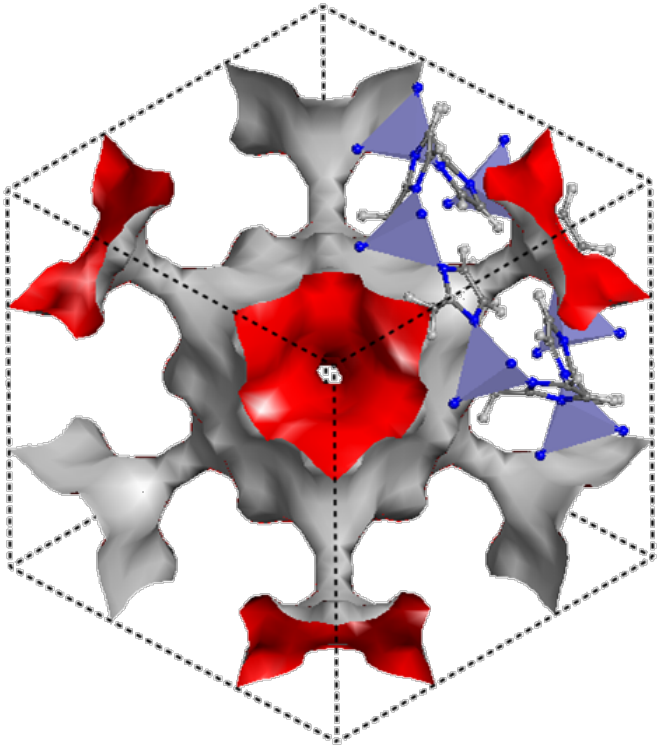


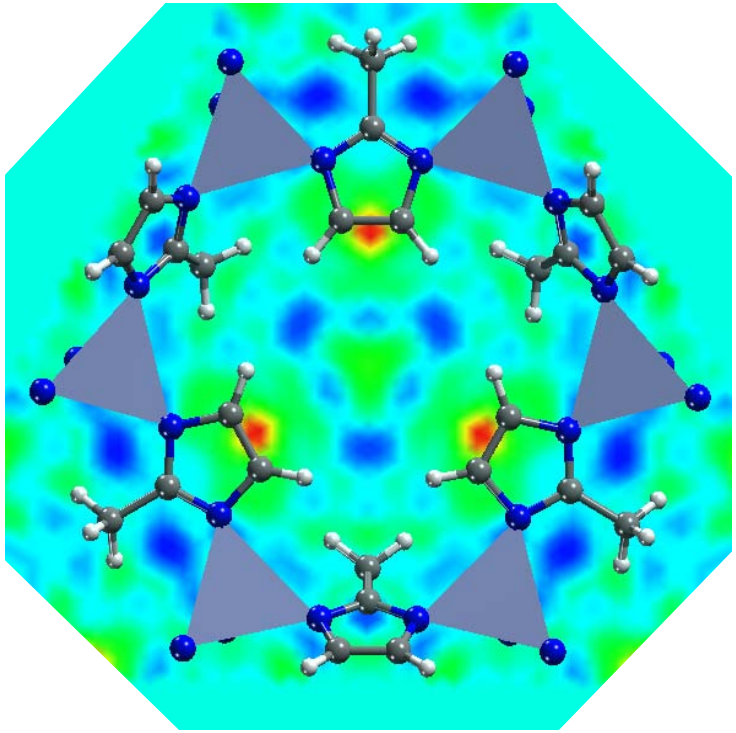
cbIM

Gas adsorption isotherms of CO (red) and CO_2 (blue) into ZIF-69 at 273 K. Uptake and release are represented by solid and open symbols, respectively. ZIF-69 has been shown to have substantially greater uptake capacity for CO_2 over CO.

Yaghi's group, UCLA, *SCIENCE* VOL 319 15 FEBRUARY 2008

Where Does Hydrogen Go in ZIFs? Apply Technique to CO_2





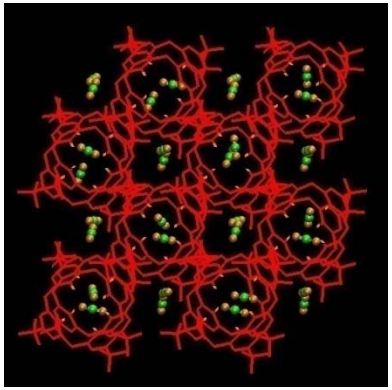
Calculated isosurface in ZIF-8

- Available nanopore volumes are connected by narrow channels

Difference Fourier analysis, showing the main-H_2 absorption sites in ZIF-8 are near the top of C-C bond of the linker and NOT the metal center

From: Taner Yildirim, U Penn and NIST

Examples of BES-Supported Projects in Theoretical and Computational Modeling



PNNL: Dang et al

One interpretation: Computer simulations show that at ambient temperatures, CO_2 molecules require ~ 4 times more energy than average to desorb. *Novel Strategies for selective heating may be necessary*.

Computational studies of load dependent guest dynamics and free energies of inclusion for CO_2 in low density p-*tert*-butylcalix[4]arene at loadings up to 2:1.

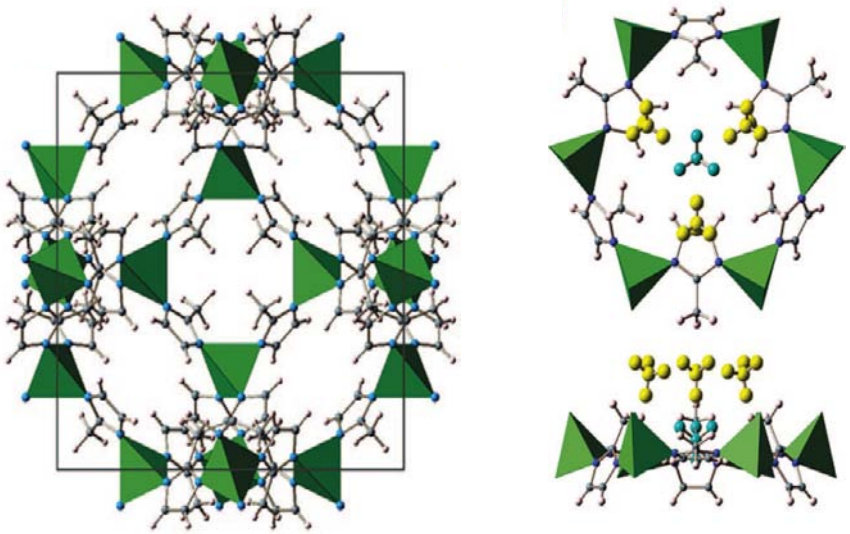
John L. Daschbach, Xiuquan Sun, Tsun-Mei Chang, Praveen. K. Thallapally, B. Peter McGrail, and Liem X. Dang. *J. Phys. Chem. A, Vol. 113, No. 14, 2009*

Theoretical and Computational Chemistry (Start FY09): Modeling CO_2 capture and separation in zeolitic imidazolate frameworks (Wisconsin, Schmidt)

- Molecular Level Mechanism of CO_2 adsorption?
- Specificity of CO_2 over N_2 ?
- Mechanism for CO_2/N_2 Selectivity in ZIFs ?
- Thermal and Solvent Stability?

Neutron Diffraction

- Studied CD_4 absorption in a ZIF with a deuterated methyl imidazolate linker.



- Structure of ZIF
  - Changes with sorption
  - Changes with temperature
- Identify binding sites
  - Primary and stronger binding site - imidazolate
  - Secondary and weaker site - center

Note: This can be used with CO_2 since the organic linkers in the ZIF can be deuterated

Source: Yildirim - J. Phys. Chem. C, Vol. 113, No. 7, 2009

NIST Center for Neutron Research

ARPA-E Projects for Carbon Capture

- Lehigh University $566,641
  - Bethlehem, PA *Carbon Capture* Electric field swing adsorption for carbon capture using high surface area conductive solid carbon sorbents. Uses electric fields to change the interaction of molecules on a surface, capturing and then releasing the CO2 using far less energy than current approaches
- Nalco Company (Argonne National Laboratory) $2,250,487
  - Naperville, IL *Carbon Capture* An electrochemical process for CO2 capture using Resin-Wafer Electrodeionization. Uses pH changes to adsorb and desorb CO2 from flue gas without energy intensive, costly processes such as heating or a vacuum.
- Ohio State University (PSRI, CONSOL Energy, Inc., Shell/CRI, The Babcock and Wilcox Company) $5,000,000
  - Columbus, OH *Carbon Capture* Syngas Chemical Looping (SCL) to convert coal or biomass into electricity while efficiently capturing the CO2. Has successfully been demonstrated at laboratory scale; this project will scale it up to a pilot plant at the National Carbon Capture Center.
- Porifera Inc. (University of California Berkeley, LLNL) $1,077,992
  - Hayward, CA *Carbon Capture* Carbon nanotubes integrated into polymer membranes to increase the flux of CO2 capture membranes by two orders of magnitude. Could enable much less expensive carbon capture from coal plants.
- United Technologies Research Center (Hamilton Sundstrand, CM-Tech, Inc., Worley-Parsons, Columbia University) $2,251,183
  - East Hartford, CT *Carbon Capture* Synthetic enzymes for capturing CO2 from coal plant flue gas streams. Uses a synthetic form of the enzyme carbonic anhydrase, which our bodies use to remove CO2. Could dramatically reduce the cost of carbon capture.