Overview of Carbon Capture Methods

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Understanding the Scale of CO$_2$ Capture

Let’s make useable products out of CO$_2$! Not a good idea... the only market that scales appropriately is the fuel market (the original source of CO$_2$!)

• Annual Worldwide Chemical Production – *millions* of tons
  – Sulfuric acid → 200
  – Ammonia → 122
  – Ethylene → 109

• Annual Worldwide CO$_2$ Emissions – *billions* of tons
  – Coal → 12.49 (primarily point-source)
  – Liquids → 11.27 (primarily distributed)
  – Natural Gas → 5.93 (both distributed and point-source)
Minimum Thermodynamic Work

\[ W_{\text{min}} = RT \left[ n_B^{CO_2} \ln(y_B^{CO_2}) + n_B^{B''CO_2} \ln(y_B^{B''CO_2}) \right] + RT \left[ n_C^{CO_2} \ln(y_C^{CO_2}) + n_C^{C''CO_2} \ln(y_C^{C''CO_2}) \right] \\
^{''} RT \left[ n_A^{CO_2} \ln(y_A^{CO_2}) + n_A^{A''CO_2} \ln(y_A^{A''CO_2}) \right] \]
Minimum Work for Various Applications

- CO₂ in air (380 ppm – 580 ppm)
- CO₂ in NGCC (5-8%)
- CO₂ in PCC (10-15%)
- CO₂ in IGCC (≈40-60%)
Sherwood Plot for Flue Gas Scrubbing

Next: How to Reduce the Cost of CC, Edward Rubin, Carnegie Mellon

*Calculations carried out using IECM, all cases assume 500-MW plant burning Appalachian bituminous, NGCC (477-MW) O&M + annualized capital costs are included in the cost estimates
## Cost and Scale

<table>
<thead>
<tr>
<th>Process</th>
<th>Price [$/kg]</th>
<th>Concentration [mole fraction]</th>
<th>Emissions [kg/day]</th>
<th>Cost [1000s $/day]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)-PCC</td>
<td>0.045</td>
<td>0.121</td>
<td>8.59 x 10(^6)</td>
<td>392</td>
</tr>
<tr>
<td>CO(_2)-NGCC</td>
<td>0.059</td>
<td>0.0373</td>
<td>3.01 x 10(^6)</td>
<td>178</td>
</tr>
<tr>
<td>SO(_x) (MS)</td>
<td>0.66</td>
<td>0.00127</td>
<td>8.94 x 10(^4)</td>
<td>59.6</td>
</tr>
<tr>
<td>SO(_x) (LS)</td>
<td>2.1</td>
<td>0.000399 (399 ppm)</td>
<td>2.32 x 10(^4)</td>
<td>50.4</td>
</tr>
<tr>
<td>NO(_x)</td>
<td>1.1</td>
<td>0.000387 (387 ppm)</td>
<td>1.11 x 10(^4)</td>
<td>12.5</td>
</tr>
<tr>
<td>Hg</td>
<td>22000</td>
<td>5 x 10(^{-9}) (ppb)</td>
<td>0.951</td>
<td>21.6</td>
</tr>
</tbody>
</table>

“the recovery of potentially valuable solutes from dilute solution is dominated by the costs of processing large masses of unwanted materials.”

- Edwin Lightfoot

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\(^1\)These can change based upon coal-type burned and scrubbing methods; \(^2\)EN Lightfoot, MCM Cockrem, What Are Dilute Solutions, Sep. Sci. Technol., 22(2), 165, 1987.
2nd-Law Efficiency Drops with Concentration

*Manuscript in preparation in collaboration w/ Kurt House, et al.*
How to Increase the $2^{nd}$-Law Efficiency?

Taking a closer look at absorption via MEA as an example:

1. Regeneration
2. Compression
3. Blower/Fan
4. Pumping

Can we establish targets based upon scientific limits? Should we reconsider the way in which we convert coal to energy?
Rethinking Coal to Energy

*with the vision of CC*

- Coal - 40% of the world’s electricity
- Carbon Capture was not an aspect of the original vision of heat extraction from coal oxidation to produce steam
- Advanced conversion methods may lead to increased CC efficiencies:
  - Chemical Looping – using metal oxides as the oxidation source to minimize “unwanted materials”
  - Integrated Gasification Combined Cycle – syngas ($\text{CO}_2 + \text{H}_2$ after WGS) production leading to an increased driving force for mass transfer and flexibility
  - Oxy-fuel Combustion – burning in oxygen (ASU)
  - Novel Approach: Integrating coal-to-energy conversion w/ storage

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1 LS Fan, Chemical Looping Systems for Fossil Energy Conversions, 2010 (OSU); 2 Chris Edwards (SU)
Traditional Separation Methods

- Absorption (most advanced → MEA)
- Adsorption
- Membrane Technology
- Hybrid Approaches
  - Contained-liquid membranes
  - Hollow-fiber sorbents

Expanding the CC Portfolio

- CO$_2$ Reduction Electrocatalysis
- Role of Algae in CC
CC in General: Mass Transfer is Key

Which is the limiting mass transfer step? Begin the research there.

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Carbonate versus Carbamate

1. Dissolution of \( \text{CO}_2 \) (physical)
2. Bicarbonate formation
   - \( \text{CO}_2: \text{amine} = 1 \)
   - Low heat of absorption
3. Carbamate formation
   - \( \text{CO}_2: \text{amine} = 0.5 \) (lower capacity)
   - High heat of absorption

Tertiary amine acts as a base catalyst, forming a H bond with water, weakening the OH bond and allowing for hydration of \( \text{CO}_2 \) to bicarbonate

More details to come: Nicola McCann, Kinetics of \( \text{CO}_2 \) Absorption, TU Kaiserslautern, Germany
Carbonic Anhydrase

- CA is a Zn-containing metalloenzyme
- Facilitates hydration and dehydration of CO₂
- Rate of reaction is up to 8 orders of magnitude faster than CO₂ binding in neutral water w/out catalyst
- Scalable?
- Can the dehydration act as a regeneration method to substitute the traditional heat requirement?

More details to come: Roger Aines, CC Using Small-Molecule Catalysts that Mimic CA, LLNL
Absorption (physical)

- Simple models → Rate of absorption
- Film Theory (Whitman, 1923 and Nernst, 1904 on “diffusion layer”)
  - No convection in the film
  - Dissolved CO\textsubscript{2} moves by only molecular diffusion
  - Rate of absorption = \( \frac{D_A}{\text{\text{\(A^* - A^0\)}}} \)
- Penetration Theory (Higbie, 1935)
  - Fluid is comprised of elements that get exposed to the gas interface for some amount of time
  - Assumes that every element of fluid is exposed to the interface for same length of time (\(\theta\))
  - Rate of absorption = \( 2 \left( A^* - A^0 \right) \sqrt{D_A} \)
- Surface-Renewal Theory (Dankwerts, 1951)
  - Average over a distribution of exposure times
  - Where \(s\) is the fraction of SA replaced w/ fresh liquid per unit time, rate of absorption =
  \[
  \left( A^* - A^0 \right) \sqrt{\frac{D_A}{\int_0^\infty e^{-s}\, dq}}
  \]
Absorption (chemical)

- Irreversible 2nd-order Reaction: $CO_2 + 2B \xrightarrow{k_2} CO_2B$
  - Assume that bulk $CO_2$ concentration = 0 (i.e., $A^0 = 0$)
- Rate of Absorption = $k_L A^* E$
- $EF \rightarrow$ factor by which absorption rate is increased by rxn
- Enhancement factor is a function of:
  
  \[
  \sqrt{M} = \sqrt{\frac{D_A k_2 B^0}{k_L}} \quad \text{and} \quad E_i = 1 + \frac{D_B B^0}{2D_A A^*}
  \]

- $E_i$ corresponds to instantaneous rxn
- Simplifying Criteria:
  1. Instantaneous rxn (fast rxn or $B^0 << A^*$): $\sqrt{M} > 10E_i$
  2. Pseudo-first order (slow rxn or $B^0$ undepleted): $\sqrt{M} < \frac{1}{2}E_i$
  3. Fast pseudo-first order rxn: If #2 is satisfied and $\sqrt{M} > 3$
  4. Checking these criteria can provide reasonable estimates on rates of absorption

More details to come: Ed Cussler, Mass Transfer is Key, UMN

Danckwerts, Gas-Liquid Reactions, 1970
Tunable Parameters in Absorption

• Rate of absorption
  ▪ Solubility of CO₂ in solution (Henry’s Law)
  ▪ Diffusion of CO₂ in solution
  ▪ Diffusion of B (reactant with CO₂) in solution
  ▪ Concentration of B in solution
  ▪ Rate constant of CO₂ with B in solution
  ▪ Liquid-phase mass-transfer coefficient of CO₂ in solution (physical)
  ▪ → influences mass transfer → extent of separation → tower design

• Heat of absorption
  ▪ Heat transfer properties of solvent

• Fluid properties
  ▪ Viscosity
  ▪ Vapor pressure
  ▪ Environmentally safe
  ▪ Low cost

• Can we assign targets based upon scientific limits?
Tunable Parameters in Adsorption

• Rate of adsorption
  ▪ Sorbent film resistance depending upon water vapor content
  ▪ Micro and mesopore diffusion
  ▪ Tortuosity
  ▪ Pore size distribution
  ▪ Surface area
  ▪ Steep breakthrough

• Heat of adsorption
  ▪ Heat transfer properties of sorbent

• Sorbent Lifetime and durability
  ▪ Regeneration cycles

• Can we assign targets based upon scientific limits?

More to come: ¹Doug Ruthven, CC by Adsorption: General Principles and Economics, UME

Carbon-Based Sorbents for CC

- Carbon nanotubes → high surface area substrates for amine functional groups
- Controllable pore size distribution
- Potential controllable tortuosity
- Mesopore → easier regeneration?
- Use quantum chemistry to generate charge profiles
- GCMC physical adsorption predictions
- Breakthrough experiments with bench-scale packed-bed experiments

Yangyang Liu and Abby Kirchofer
Cylindrical versus Slit pore

1. Stronger surface-surface interactions of CNT
2. Easier to form a second layer adsorption within a cylindrical pore

*Simulations carried out using GCMC in MUSIC (code developed by Snurr Group)
Tunable Membrane Parameters

• Do membranes have a place in PCC? What approaches exist to handle dilute systems?
• Flux
  ▪ Solubility of CO$_2$ in membrane (or some other component of gas mixture that may have a higher driving force)
  ▪ Diffusivity of CO$_2$ in membrane
  ▪ Permeability of CO$_2$ in membrane
• Selectivity toward CO$_2$
• Product purity and yield?
• Separator arrangement and varying compression stages?
• Can we assign targets based upon scientific limits?

More to Come: Richard Baker, Developing Membranes for CC (MTR)
**H₂-Selective Membranes**

- Quantum chemistry simulations
- For syngas application
- Pd-based alloys and Group V metals appear promising

**N₂/O₂-Selective Membranes**

- N₂ and O₂ are also able to catalytically dissociate across metal surfaces and diffuse atomically through interstitial crystal sites
- Use the solubility and diffusion parameters from the H₂-selective membrane field as targets
- Dope group V metals (reactive) to tune transport properties
- UHV (SLAC) and bench-scale experiments ongoing
As the Nitrogen is further from the Ru dopant, the binding strength increases
Recall H binding: O-site = -0.076eV; T-site = -0.280eV

Pauling-Scale Electronegativities: N = 3.04; V = 1.63; Ru = 2.2
Using kinetic Monte Carlo and various hopping mechanisms, diffusivity can be predicted.
Breakout-Session Questions
Breakout Session Groups

**Group 1: Performance Targets**
Tim Fout*, Mark Hartney, Karl Gerdes, Robert Perry

**Group 2: Absorption and Catalysis**
Roger Aines*, Ed Cussler, Nicola McCann, Rich Noble, Andy Peterson

**Group 3: Adsorption and Adsorption Processes**
Mike Arne*, Doug Ruthven, LS Fan, Holly Krutka

**Group 4: Membrane and Adsorption**
Richard Baker*, Shingo Kazama, Chris Jones, Randy Snurr

**Group 5: Systems and Optimization**
Tony Pavone*, Abhoyjit Bhown, Hamadri Pakrasi, Ed Rubin

*Person to report back breakout results in Panel Discussion*
Breakout Session Questions

Performance Targets

- Which criteria should GCEP include in a proposal solicitation as performance targets?

- For example, what performance targets would be game-changing over the next 10-50 years in terms of:
  - Energy Penalty
  - Water Use
  - Capital and Operating Cost
  - Lifetime
  - Materials
  - Scale/ Size/ Capacity
  - Reliability

- How do the targets change with scale?

- How should we account for variation in the rate of generation and capture in setting performance targets?

- What other metrics should we think about in addition to numbers for performance targets?
Breakout Session Question

*Quantifying the Scientific Limits*

Based on the criteria to be used in specifying performance targets (energy penalty, water, lifetime, etc.) for carbon capture systems:

- What are the most important technical parameters in your approach?
- Which performance targets can potentially be most impacted?

### Technical Parameters

<table>
<thead>
<tr>
<th>Absorption</th>
<th>Adsorption</th>
<th>Membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimal mass transfer coefficients (gas to liquids)</td>
<td>Optimal mass transfer coefficients (gas to adsorbed)</td>
<td>Optimal driving force</td>
</tr>
<tr>
<td>Absorption kinetics</td>
<td>Adsorption kinetics</td>
<td>Advanced configurations</td>
</tr>
<tr>
<td>Solvent pressure drop</td>
<td>Bed pressure drop</td>
<td>Selectivity</td>
</tr>
<tr>
<td>Solvent capacity</td>
<td>Sorbent capacity</td>
<td>Architecture</td>
</tr>
<tr>
<td>Heat of absorption</td>
<td>Heat of adsorption</td>
<td>Stability</td>
</tr>
<tr>
<td>Gas to liquid ratio</td>
<td>Diffusion resistance (pore size)</td>
<td>Optimal flux</td>
</tr>
<tr>
<td>Solvent losses and properties</td>
<td>Advanced adsorption process</td>
<td>Surface area</td>
</tr>
</tbody>
</table>
Breakout Session Questions

Systems and Optimization

- How can capture technologies best be integrated into energy conversion processes to achieve the desired performance targets?
- Are there other technologies or strategies for carbon capture systems that have not been discussed thus far? If so, what are they?
- What technologies could be developed that would result in high-pressure CO$_2$ as an end-product?
- What are the options for regeneration w/out the use of heat, i.e., dehydration via CA, inert gas purge or vacuum in desorption processes?
- What opportunities might there be for system optimization to benefit from these alternative approaches?
Extra Slide
Molecular N$_2$ adsorption energy

\[ E_{\text{ads}} (\text{eV/molecule}) = \frac{E(\text{surf}+\text{N}_2) - [E(\text{surf}) + E(\text{N}_2)]}{n(\text{N}_2)} \]

Metal-Organic Frameworks

- Nanoporous crystalline materials
- Composed of organic-bridging ligands coordinated to metal-based nodes to form a 3D extended network of uniform pores ranging from 3 to 20 Å
- Surface areas up to 5000 m²/g and high void volumes (55-90%)¹

A metal-organic framework consisting of cobalt atoms (purple) linked by an organic bridging ligand (1,4-benzenedipyrazolate, with nitrogen and carbon atoms shown in blue and grey, respectively) and CO₂ molecules (red-grey-red spheres).²

More to come: Randy Snurr, Design and Assessment of MOFs for CC, Northwestern

¹Tranchemontagne, D.J. and et al., Chem. Int. Ed., 47, 2-14, 2008; ²Deanna M. D'Alessandro/UC Berkeley
Consider Hybrid Approaches - *Isowork Plot* \([kJ/\text{mol } CO_2]\)