CO$_2$ Capture by Aqueous Absorption/Stripping

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Outline

• Absorption/Stripping: THE technology
• MEA: not a bad solvent alternative
  – Stripper Energy favored by greater $\Delta H_{\text{abs}}$
  – Mass Transfer Requires Fast Kinetics
  – MEA Makeup and Corrosion Manageable
• Optimized systems approach 1.5 x ideal W
• Critical Opportunities & Needs for R, D, D, & D
• Now the time to plan Demo and Deployment
Capture by Aqueous Absorption
The Critical Technology

• For Coal Combustion
• in “existing” power plants
• that are an important, growing source of CO₂.
• Aqueous Absorption/Stripping is preferred
• because it is tail-end technology
What is the CO₂ Capture Market?

Coal Dominates CO₂ Emissions From Fossil Power Generation
As Percent of Coal-fired Generation Grows to 59% (2030)

75% of all coal related CO₂ production from existing coal-fired power generation.
TXU: an extreme example

• Current TXU CO$_2$ emissions
  – 60 MM ton/y from 16 plants
• 11 x 800 MW fossil plants in the next 5 years
  – 100 million ton CO$_2$/y
• Good for Texas and TXU
  – Capacity for growth
  – Replace expensive gas-fired capacity
  – TXU capital from deregulation
• Inconceivable in the next 5 years
  – IGCC, Oxycombustion
  – CO$_2$ Capture by absorption/stripping
• The prime market for retrofit CO$_2$ capture
Absorption/stripping = The technology

- Near Commercial
- Tail End Technology for Existing Plants
  - Oxycombustion and gasification are not.
- Expensive in $$ and energy
- By analogy to limestone slurry scrubbing
  - Expect significant evolutionary improvements
  - Do not expect major cost & energy reductions
  - Do not waste resources on step change R&D
System for CO₂ Sequestration

Coal → Boiler → ESP → FGD

10 atm stm

CaCO₃

3 atm stm

CaSO₄

Flyash

Abs/Str

Turbines

150 atm CO₂

Net Power

Disposal Well
MEA Absorption/Simple Stripping

Absorb
40°C
1 atm

Absorb

CO₂

12% CO₂
5% O₂
7% H₂O
40°C

SO₂, HCl, NO

Strip
117°C
2 atm

Strip

3 atm

Steam

CO₂

ΔT=5°C

Lean

Rich

ΔT=5°C

H₂O

Purge to Reclaim

30% MEA
(Monoethanolamine)
Aqueous Abs/Str: Near commercial

– 100’s of plants for treating H₂ & natural gas
  • MEA and other amine solvents
  • No oxygen

– 10’s of plants with combustion of natural gas
  • Variable oxygen, little SO₂
  • Fluor, 30% MEA, 80 MW gas, 15% O₂
  • MHI, KS-1, 30 MW, <2% O₂

– A few plants with coal combustion
  • Abb-Lummus, 20% MEA, 40 MW
  • Fluor, 30% MEA, 3 small pilots
  • CASTOR, 30% MEA, 2.5 MW pilot
  • MHI, KS-1, <1 MW pilot
Tail End Technology Ideal for Development, Demonstration, & Deployment

- Low risk
  - Independent, separable, add-on systems
  - Allows reliable operation of the existing plant
    - Failures impact only Capture and Sequestration
- Low cost & less calendar time
  - Develop and demonstrate with add-on systems
  - Not integrated power systems as with IGCC
    - Reduced capital cost and time
  - Resolve problems in small pilots with real gas
  - Demo Full-scale absorbers with 100 MW gas
    - Ultimately 500 MW absorbers
Other Solutions for Existing Coal Plants

- **Oxy-Combustion**
  - O₂ plant gives equivalent energy consumption
  - Gas recycle, boiler modification for high CO₂
  - Gas cleanup, compression including air leaks

- **Coal Gasification**
  - Remove CO₂ and burn H₂ in existing boiler
  - O₂ plant, complex gasifier, cleanup, CO₂ removal
  - H₂ more valuable in new combined cycle

- **Neither is Tail end**
  - Require higher development cost, time, and risk
Practical Problems

• Energy = 25-35% of power plant output
  – 22.5%, Low P stm, 30-50% of stm flow
  – 7%, CO₂ Compression
  – 3.5%, Gas pressure drop
  – $42/tonne CO₂ (0.7 MWh/CO₂ x $60/MWhr)

• Capital Cost  $500/kw
  – Absorbers same diameter as FGD, 50 ft packing
  – Strippers somewhat smaller
  – Compressors
  – $20/tonne CO₂ for capital charges & maint

• Amine degradation/environmental impact
  – $1-5/tonne CO₂
Analogy to CaCO$_3$ slurry scrubbing

- 1970 “Commercial” starting point
  - Only process “immediately” available
  - “Inappropriate” for government support
- Starting point was “too expensive”
  - Environmentally messy, solid waste unattractive
  - Initial applications even more expensive
  - Cost decreased with experience
- Alternative developments heavily funded
  - Regenerable FGD processes – too complex
  - Coal gasif/combined cycle – not tail end
  - Fluidized bed combustion – not tail end
- 2006 Commercial Generic Process
Aqueous Solvent Alternatives
MEA is hard to beat

• Stripper Energy Requirement
• Mass Transfer Rates
• Makeup and Corrosion
**Carbonate & Tertiary/Hindered Amines**

\[
\begin{align*}
\text{Carbonate} & \quad \text{Bicarbonate} \\
\text{CO}_3^- + \text{CO}_2 + \text{H}_2\text{O} & \leftrightarrow 2 \text{HCO}_3^- & 20 \text{ kJ/gmol} \\
\text{very slow} &
\end{align*}
\]

\[
\begin{align*}
\text{HO-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-OH} & \leftrightarrow \text{MDEAH}^+ + \text{HCO}_3^- \\
\text{CH}_3 & \quad 60 \text{ kJ/gmol, slow} \\
\text{Methyldiethanolamine (MDEA)} &
\end{align*}
\]

\[
\begin{align*}
\text{HO-CH}_2\text{-CH}_2\text{-NH}_2 + \text{CO}_2 & \leftrightarrow \text{AMPH}^+ + \text{HCO}_3^- \\
\text{CH}_3 & \quad 60 \text{ kJ/gmol, slow} \\
\text{2-Aminomethylpropanolamine (AMP, KS-1(?))} &
\end{align*}
\]
Primary and Secondary Amines
60-85 kJ/gmol, fast

2 HO-CH₂-CH₂-NH₂ + CO₂ ↔ HO-CH₂-CH₂-NH-COO⁻ + MEAH⁺
Monoethanolamine (MEA)
MEA Carbamate (MEACOO⁻)

2 NH₃ + CO₂ ↔ NH₂-COO⁻ + NH₄⁺
Ammonia

CH₂-CH₂
HN \[\langle\]
\[\rangle\]
NH + CO₂ ↔ +HPZ-COO⁻
Piperazine (PZ)
Components of Stripper Heat Duty
(mol stm/mol CO₂)

\[ S_{\text{rxn}} = \frac{H_{CO₂}}{H_{H₂O}} \]

\[ S_{H₂O} = \left[ \frac{H_{2O}}{CO_2} \right]_{\text{ABS}} EXP \left[ -\frac{(H_{CO₂} - H_{H₂O})}{R} \left( \frac{1}{T_{\text{ABS}}} - \frac{1}{T_{\text{STRIP}}} \right) \right] \]

\[ S_{\text{sens}} = \frac{C_p \left( T_{S,\text{Bot}} - T_{S,\text{Feed}} \right)}{H_{H₂O} A_T \Delta L \text{dg}} \]
Total Equivalent Work

\[ W = W_{eq} + W_{\text{comp}} \]

\[ W_{eq} = 0.75Q_{\text{reb}} \frac{T_{\text{reb}} + 10 - 40}{T_{\text{reb}} + 10 + 273} \]

\[ W_{\text{comp}} = RT \ln \left( \frac{100 \text{ atm}}{P_{\text{CO}_2} + P_{\text{H}_2\text{O}}} \right) \]
Total Equivalent Work for Generic Solvents
(Rich $P_{CO_2}^* = 2.5$ kPa at 40°C, $\Delta T = 10°C$)

Equivalent Work (kcal/gmol) vs. $\Delta H_{des}$ (kcal/gmol)

- Stripper at 1.6 atm
- Stripper at 0.3 atm
Mass Transfer with Fast Reaction

\[
\text{CO}_2 + 2\text{MEA} = \text{MEACOO}^- + \text{MEAH}^+
\]
Mass Transfer with Fast Reaction

\[ D_{CO_2} \frac{\partial^2 [CO_2]}{\partial x^2} - k_2 [Am] [CO_2] = 0 \]

\[ N_{CO_2} = \frac{\sqrt{D_{CO_2} k_2 [Am]}}{H_{CO_2}} (P_{CO_2,i} - P_{CO_2,b}^*) \]
\[ N_{CO_2} = k_g' (P_{CO_2,i} - P_{CO_2,b}^*) \]
Mass Transfer with Reaction in Wetted Wall Column

normalized flux (mol/Pa-cm\(^2\)-s)

Normalized flux vs \(P_{CO_2}^*\) (Pa)

- 5.0 M MEA
- 3.6 m K\(^+\)/0.6 m PZ
- 6.2 m K\(^+\)/1.2 m PZ
- 3.6 m K\(^+\)/0.0 m PZ

Conc. K\(^+\)/PZ
## Reagent Energy Properties

<table>
<thead>
<tr>
<th>Reagent</th>
<th>$\Delta H_{\text{abs}}$ (kJ/gmol)</th>
<th>$k_2$ at 25°C (M$^{-1}$s$^{-1}$)</th>
<th>Reagent m</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>84</td>
<td>6e3</td>
<td>7</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>60</td>
<td>0.35e3</td>
<td>10</td>
</tr>
<tr>
<td>PZ</td>
<td>84</td>
<td>100e3</td>
<td>2</td>
</tr>
<tr>
<td>MDEA</td>
<td>60</td>
<td>0.005e3</td>
<td>6</td>
</tr>
<tr>
<td>AMP</td>
<td>60</td>
<td>0.6e3</td>
<td>6</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>20</td>
<td>0.05e3</td>
<td>5</td>
</tr>
</tbody>
</table>
**MEA Makeup & Corrosion**

- **Degradation**
  - MEA Oxidizes to NH₃, aldehydes, etc
  - MEA Polymerizes at Stripper T
  - Optimize operating conditions, add inhibitors
  - Reclaim by evaporation to remove SO₄²⁻, NO₃⁻, Cl⁻, etc.

- **Volatility**
  - Use Absorber Wash Section

- **Corrosion**
  - Minimize Degradation
  - Add Corrosion inhibitors such as Cu⁺⁺
  - Use Stainless Steel, FRP
## Reagent Properties Affecting Makeup

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Cost $/lbmol</th>
<th>$P_{amine, 40C} \text{ atm x } 10^3$</th>
<th>Degradation</th>
<th>Corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>40</td>
<td>0.1</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>5</td>
<td>200</td>
<td>None</td>
<td>High</td>
</tr>
<tr>
<td>PZ</td>
<td>300</td>
<td>0.1</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>MDEA</td>
<td>300</td>
<td>0.003</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>AMP</td>
<td>500</td>
<td>$\approx 0.03$</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>40</td>
<td>0</td>
<td>None</td>
<td>High</td>
</tr>
</tbody>
</table>
Flowsheet Enhancements

• Absorber
  – Direct Contact Cooling & Intercooling
    • To get lower T
  – Split feed – to enhance reversibility

• Stripper
  – Minimum exchanger approach T
  – Internal Exchange
  – Multistage Flash, Multieffect Stripper
  – Multipressure, Matrix,
  – Vapor Recompression
**Energy for Separation & Compression to 10 MPa**

\[ W_{eq} \text{ of power production} = 150 \text{ kJ/gmol CO}_2 \]

<table>
<thead>
<tr>
<th>Separation Method</th>
<th>( W_{sep} )</th>
<th>( W_{comp} )</th>
<th>Total ( W_{eq} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Sep., (40(^\circ)C, 100 kPa) Isothermal Comp.</td>
<td>7.3</td>
<td>10.8</td>
<td>18.1</td>
</tr>
<tr>
<td>Ideal Membrane (40(^\circ)C) 75% ad. comp. in 5 stages</td>
<td>11.6</td>
<td>16.8</td>
<td>28.4</td>
</tr>
<tr>
<td>Baseline (7m MEA, 10(^\circ)C, 160 kPa)</td>
<td>20.7</td>
<td>13.8</td>
<td>34.5</td>
</tr>
<tr>
<td>Matrix (MDEA/PZ)</td>
<td>14.6</td>
<td>11.6</td>
<td>26.2</td>
</tr>
</tbody>
</table>
Needs for Capture Deployment

• Large Absorbers: different from FGD
  – Countercurrent Gas/liquid Distribution
    • 35 gal/mcf
  – Pressure drop
  – Capital cost of internals
  – Test and demonstrate at 100+MW

• Steam integration
  – Control systems for load following
  – Test at 100+MW

• Environmental impact & losses of solvent
  – Long term test at 1 MW
Opportunities for Capture R&D

• Better Solvents
  – Faster CO$_2$ Transfer: Blends with PZ, etc.
  – Greater Capacity – MEA/PZ, MDEA/PZ
  – Oxygen scavengers/Oxidation inhibitors

• Better Processes
  – Matrix, split feed
  – Reclaiming by CaSO$_4$/K$_2$SO$_4$ Precipitation

• Better contacting
  – Packing to get G/L area
Deployment Schedule

– 2007 - 0.5 MW pilot plant on real flue gas
  Demonstrate solvent stability & materials
– 2008 - 5 MW integrated pilot plant
  Compressor/stripper concepts
– 2010 – 100 MW Integrated module
  Energy integration and absorber design
– 2012 – 800 MW full-scale on CaCO$_3$
  Energy, multitrain, operation
– 2015 – Deployment on all plants
Conclusions

• Absorption/stripping is THE technology for existing coal-fired power plants
  – Expect 15-30% reduction in cost and energy
• The solvent should evolve from MEA
  – High $\Delta H$, fast rate, high capacity, cheap reagent
• Process & contactor enhancements expected
• Now time to plan technology demonstrations