CO₂ capture by Adsorption Processes: From Materials to Process Development to Practical Implementation

Paul A. Webley
Dept. of Chemical Engineering
Talloires, July 2010

Outline

- Adsorption for Post-Combustion CO₂ Capture – PVSA or TSA or TVSA?
- Materials development – synergy with process and adsorbent assessment
- Lab and Pilot scale Post Combustion Experimental Work
- Field Demonstrations
- Conclusions
Post Combustion Flue Gas Conditions and Challenges – T,P,Flow

<table>
<thead>
<tr>
<th></th>
<th>PC(black)+FGD</th>
<th>PC(brown)</th>
<th>NGCC</th>
<th>Oxyfuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Flow (kg/s)</td>
<td>600</td>
<td>790</td>
<td>1000</td>
<td>180</td>
</tr>
<tr>
<td>Volume flow (m³/hr)</td>
<td>2.2 x 10⁶</td>
<td>3.0 x 10⁶</td>
<td>3.8 x 10⁶</td>
<td>0.5 x 10⁶</td>
</tr>
<tr>
<td>Pressure (barg)</td>
<td>~ 0.05</td>
<td>~ 0.05</td>
<td>~ 0.05</td>
<td>~ 0.05</td>
</tr>
<tr>
<td>Temperature(°C)</td>
<td>~ 90</td>
<td>~ 90</td>
<td>~ 90</td>
<td>~ 170</td>
</tr>
</tbody>
</table>

- Volume flows VERY large (pressure drop)
- Pressures very low (no driving force)
- Temperatures relatively high (for adsorption)

Post Combustion Flue Gas Conditions and Challenges - Composition

<table>
<thead>
<tr>
<th></th>
<th>PC(black)+FGD</th>
<th>PC(brown)</th>
<th>NGCC</th>
<th>Oxyfuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>71</td>
<td>60</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>12.6</td>
<td>12</td>
<td>3.4</td>
<td>62.6</td>
</tr>
<tr>
<td>Water</td>
<td>11.1</td>
<td>24</td>
<td>6.9</td>
<td>31.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>4.4</td>
<td>3</td>
<td>13.8</td>
<td>4.5</td>
</tr>
<tr>
<td>SO₂</td>
<td>~200ppm</td>
<td>~200ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOx</td>
<td>670 ppm</td>
<td>25 ppm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- CO₂ concentration ranges from 12-63% (wet basis)
- High water content
- SOx, NOx, ash, heavy metals, etc present
Commercial Adsorption based CO₂ Systems

- CO₂ Recovery from COREX Gas–Saldanha Steel, South Africa
- 360,000 Nm³/h feed rate (15psig, 30%CO₂)
- 2xVPSA trains
- Each has 12 vessels and 4 vacuum pump sets
- Worlds largest VPSA

CO₂ Capture: Program at Monash University

- Materials development:
  - Good working capacity & good selectivity
  - Insensitive to moisture
  - Operable at above ambient temperature
  - There is a strong relationship to the process cycle

- Process development
  - Cycle development
  - Structured adsorbents
  - Energy integration

- Solution of engineering issues
PSA or TSA?

- Throughput (kg CO2/day/kg adsorbent)

\[
\frac{kg \ CO2}{day \ \cdot \ kg \ ads} = \frac{kg \ CO2}{kg \ ads. \ cycle} \cdot \frac{cycles}{day} \approx \frac{WC_{CO2}}{\tau}
\]

- TSA provides large WC at the expense of cycle time unless innovative rapid cycling systems are developed
- PSA provides smaller WC but can provide much shorter cycle time
- Large throughput, bulk separation tends to favor PSA, eg. O2VSA, H2PSA etc.
- PTSA??? (yes)

Adsorbent Requirements from Process Operation

- Minimal compression of flue gas! – vacuum operation => need large WC between 0 and 1 atm
- Regeneration of the adsorbent is where the energy is needed – put energy into CO2, not N2, not solid material (minimal N2 adsorption, minimal T swing)
- Difference between adsorption and desorption for CO2 compared to other gases is key
- Large adsorption amount is not necessarily better
- Interaction of species is important (impurities)
Adsorbent Isotherms

CO2 Adsorption Isotherms at 25°C

13X
WC, CO2 ~ 1.6

Screening Problem

• Which adsorbent is “best” over a particular operating region and what is this operating region (can we solve the inverse problem)?
• By how much will improvements in adsorbent reduce capture cost (or particular interest to sponsors!)?
• Should improvements be aimed at CO₂ capacity, N₂ capacity, heat of adsorption, etc?
• Cannot simulate processes for every possible adsorbent – too time-consuming.
Quick Assessment – “First Order” effects

- Need to consider adsorption P,T and desorption P,T of CO₂ required to meet purity constraints
- Need to consider adsorption P,T and desorption P,T of N₂ (selectivity)
- Need to consider temperature change on adsorption/desorption (isothermal vs adiabatic)
- Need to capture effect of isotherm shape on pressure profile and hence power
- Ideally, should include kinetics – however, initial goal is to permit equilibrium evaluation

Capacity for CO₂ – effect of temperature

- Heat of adsorption (exothermic) leads to reduction in working capacity since adsorbent T increases on adsorption and decreases on desorption
- Instead of isotherm only, need to look at adiabat

\[
\frac{dn}{d(yP)} = \frac{\partial n}{\partial yP} \left( \frac{Q}{C_v} \right)
\]

\[
\frac{dT}{d(yP)} = \frac{\partial n}{\partial yP} \left( \frac{\partial n}{\partial T} \right)_{yP}
\]
Example T-swing during CO2VSA process

![Graph showing temperature over time for different conditions](image)

**Development of Proposed Parameter**

- Consider 1kg adsorbent with feed gas of known composition and specified pressure and temperature
- Perform adiabatic pump-down calculation tracking composition, temperature, moles removed (CO₂ and N₂) and energy consumed
- Derive CO₂ working capacity (WC\(_{CO2}\)), N₂ working capacity (WC\(_{N2}\)), working selectivity (WS=WC\(_{CO2}\)/WC\(_{N2}\)), and specific energy (E\(_{CO2}\)=energy/mole CO₂ removed)
- Repeat for a range of operating temperatures and pressure ratios
- Very easy and fast calculations
Basis for Comparison

- 3 adsorbents: NaX, NaY, Activated Carbon,

<table>
<thead>
<tr>
<th>ADSORBENT</th>
<th>ZERO LOADING ΔH(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaX</td>
<td>44.4</td>
</tr>
<tr>
<td>NaY</td>
<td>37.0</td>
</tr>
<tr>
<td>AC</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Isotherms for CO$_2$

CO2 Adsorption Isotherms at 25C
Isotherms for N₂

Comparison of Isothermal and Adiabatic Working Capacity (Yf=0.1)

- Isothermal working capacity exceeds adiabatic working capacity by several factors
- Adsorbent requirement scales directly with CO₂ working capacity
- Adiabatic working capacity has a maximum unlike isothermal working capacity
Comparison of Isothermal and Adiabatic Working Selectivities (Yf=0.1)

- Isothermal working selectivity exceeds adiabatic working selectivity by several factors
- Adsorbent purity and recovery scales with CO₂ working selectivity
- Both show a maximum but at different locations

Comparison of adsorbents – Adiabatic Working Capacity (Yf=0.15)
Comparison of adsorbents – Adiabatic Working Selectivity (Yf=0.15)

Comparison of Energy Required
Ranking depends on which parameter to chose

- WC and WS suggests NaX is superior for $T > 300$, NaY superior for $T < 300$
- AC shows lowest regen. energy
- Ultimate ranking should reflect capture cost relative to a base case (NaX) (trend at least!)
- Capture Cost depends on capital (use $1/WC_{CO2}$ as a surrogate) and power (use WS as a surrogate). Both also depend on recovery (use WS as surrogate)

“Capture Figure of Merit” or CFM

- Must necessarily be approximate since relative contributions to capital and operating are site specific
- Need 2 parameters to truly reflect each situation
- For a given ratio of capital : power costs, we combine the parameters into a single CFM:

\[
CFM \propto \frac{WC \times WS}{E}; \quad \text{Relative CFM} = \frac{CFM}{CFM_{\text{ref}}}
\]
How well does it perform?

- Rigorous PSA simulations conducted with 3 adsorbents
- Ranking of overall performance compared with CFM prediction
- Assume capital contributes ~50% towards overall capture cost

Performance of Adsorbents based on CFM

![Graph showing performance of adsorbents based on CFM over temperature range 300-400K]
Selection of Operating Temperature based on CFM

NaX Performance Based on CFM over temperature range 300-400K

Laboratory and Pilot Scale Work

- Vacuum Swing Cycle with multiple beds
- Minimum pressurization of feed gas
- Evacuation of beds to low pressure (< 10kPa)
- Energy is used on recovered stream only, not on total feed stream
- Cyclic process to ensure longevity of adsorbent
Process Development and Testing

- **Experimental pilot scale plant**
  - provides “real” operating data validates process simulations
    - 3 beds, 1m x 8 cm i.d.
- **Simulation**
  - allows prediction of the effect of operating and design variables
    - in-house simulation tools

---

PSA Cycle Design: Nine step cycle (product purge)

<table>
<thead>
<tr>
<th>ITEM</th>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>Step 4</th>
<th>Step 5</th>
<th>Step 6</th>
<th>Step 7</th>
<th>Step 8</th>
<th>Step 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed 1</td>
<td>I</td>
<td>II</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td>V</td>
<td>VI</td>
<td>VII</td>
<td>VII</td>
</tr>
<tr>
<td>Bed 2</td>
<td>VI</td>
<td>VII</td>
<td>VII</td>
<td>I</td>
<td>II</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td>V</td>
</tr>
<tr>
<td>Bed 3</td>
<td>III</td>
<td>IV</td>
<td>V</td>
<td>VI</td>
<td>VII</td>
<td>VII</td>
<td>I</td>
<td>II</td>
<td>II</td>
</tr>
</tbody>
</table>
Performance Data for 6 and 9 step VSA cycles

<table>
<thead>
<tr>
<th>Performance</th>
<th>6-step Cycle no purge</th>
<th>9-Step cycle with purge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity, %</td>
<td>82~83</td>
<td>90~95</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>60~80</td>
<td>60~70</td>
</tr>
<tr>
<td>Power, kW/TPDc</td>
<td>4-8</td>
<td>8~12</td>
</tr>
<tr>
<td>Power, MJ/kg CO2</td>
<td>0.35 to 0.7</td>
<td>0.7 to 1.0</td>
</tr>
</tbody>
</table>

Cycle can be optimised for specific feed gas - adsorbent combinations

Water: Not just an “impurity”

- Will our existing adsorbent (13X) tolerate high concentrations of water?
- What is the impact on process performance (purity, recovery, power) of high humidity flue gas streams?
- Can we operate at elevated temperature?
- If water adversely affects CO2 capture plant performance, can we “protect” the adsorbent?
- What is the impact of impurities (SOx, NOx for post combustion, NH3, H2S for pre-combustion) on adsorbents?
Water and Impurities - Multilayers

Current P/VSA process currently undergoing testing at a Power Plant

- Multi-step cycle with 3 beds including two pressure equalizations, heavy and light rinse, heavy purge effluent recycle
- Up to 1 TPDc
- Capable of “deep” vacuum (1-2 kPa)
- Wash tower will remove impurities and reduce water level.
Demonstration Plant in fabrication shop

Demonstration Plant
Conditions – Flue Gas & Adsorbent

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>NaX</th>
<th>Sorbead WS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>UOP</td>
<td>BASF-Engelhard</td>
<td></td>
</tr>
<tr>
<td>Mass in each column (3:1), kg</td>
<td>25.00</td>
<td>9.15</td>
<td></td>
</tr>
<tr>
<td>Mass in each column (9:1), kg</td>
<td>29.96</td>
<td>3.66</td>
<td></td>
</tr>
<tr>
<td>Price, US$/kg</td>
<td>11.18</td>
<td>7.10</td>
<td></td>
</tr>
<tr>
<td>Water capacity, wt% sat</td>
<td>28</td>
<td>&gt;34</td>
<td></td>
</tr>
<tr>
<td>Structure</td>
<td>Crystalline</td>
<td>Amorphous</td>
<td></td>
</tr>
</tbody>
</table>

CO₂, % | 12 |
O₂, % | 8 |
CO, ppm | 40 |
NOx, ppm | 170-250 |
SOx, ppm | 60-270 |
H₂O, % | ~10 |

Pressure Profiles with Simple Cycle (no Purge)

![Graph showing pressure profiles over time](image-url)
Preliminary Results

6-step without purge (Actual plant)
  Purity: ~71%
  Recovery: ~60%

6-step without purge (Simulation with void volume)
  Purity: ~70%  Recovery: 75%

9-step with purge (Simulation with low void volume)
  Purity: 96%  Recovery: 75%

Power consumption: 12kW/TPD ~ 1 MJ/kg CO₂ captured

Engineering Issues

- Ash carryover from wash tower
- Water condensation in adsorption vessels
- Corrosion & Blockage in feed blower
- Large void space dilutes product % CO₂
- Partial fluidization at high gas velocity
- Main capture plant disruption
Water Condensation – reduces pumping capacity

Void Volumes

Simulations indicate a drop in purity of 5-10%
Conclusions

- CO2 Capture using adsorption processes is technically feasible but issues remain
  - Scale-up is significant challenge
  - Advantages of no waste, very limited water use
  - Very simple process
  - Significant improvements can be made using advanced adsorbents but must be careful of water and other impurities

- Adsorbent development must carefully consider the relationship to the process