Carbon Composite Adsorbents for Post Combustion CO₂ Capture

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Lab Scale Study – Carbon Fibre Composites

Fabrication and Testing of Lab Size Honeycomb Carbon Fibre Composite Monoliths

Carbon Fibre (s) and Phenolic resin binding material

Slurry or Paste

Vacuum Moulded to honeycomb structure

Drying at 50-60°C and Curing at 130-150°C

Carbonised with inert gas at 650-850°C to pyrolize the resin

Activation at 650-950°C to achieve pore characteristics

Length: 80mm, Dia: 30mm, Number of Channels: 17

Fabricated (HMCFC)

Microscopic morphology

Molding equipment

3 processing furnaces

Adsorbent Testing Equipments

Adsorbent Characterisation  Breakthrough Test Rig with Lab Scale Adsorption Chamber
Solid Carbon Sorbent CO₂ Capture Technology

- Based on honeycomb carbon composite monoliths
  - Enable CO₂ capture with low pressure drop
  - Potentially low energy consumption for adsorbent regeneration
    - Lower heat capacity of solid adsorbents than liquid solvents
    - Physisorption - lower heat of CO₂ adsorption
    - Utilisation of flue gas waste heat for CO₂ desorption
  - Tolerant to moisture, SOₓ and NOₓ
    - Avoid flue gas pre-treatment prior to CO₂ capture; this is important as there are no FGD and SCR DeNOₓ facilities at coal fired power plants in Australia
Evolutionary Journey

Lab scale CO₂ capture (2006-2008)

• Proof-of-Concept
• Capture studies using simulated flue gas

Large scale CO₂ capture with regeneration (2009-2011)

• CO₂ capture combined with thermal and vacuum regeneration

CO₂ capture site trials (2011-2014)

• To evaluate CO₂ capture and regeneration under real flue gas conditions

Lab scale studies
Development of next generation carbon composite adsorbents (2010 – present)

Lab scale study
New regeneration process with enhanced heat transfer (2011 – present)
Large Scale Capture-Regeneration Studies

CF composites

Lab size adsorbent (Ø 30mm)

Large scale moulding unit for composite fabrication

Large size adsorbent (Ø 123 mm)

CO₂ adsorption Isotherms at 25 ⁰C

- 11.7 wt % at 760 mmHg
- 3.5 wt % at 114 mmHg (15% CO₂)

Large scale CO₂ capture-regeneration unit

- Two 2 meter long columns
- Repetitive capture & regeneration capability
- Thermal and vacuum swing regeneration

Summary of Large Scale Study Results

Adsorption Breakthrough Profile Showing CO$_2$ capture at Real Time

- CO$_2$ capture carried out at ambient temperature and pressure
- Simulated flue gas consisting of 13% CO$_2$, 5.5% O$_2$ and balance N$_2$
- CO$_2$ adsorption efficiency > 97% from adsorption breakthrough
• Residual CO$_2$ inside column after thermal regeneration
• Vacuum regeneration alone is ineffective
• Heating is essential to desorb CO$_2$
• Combined thermal and vacuum regeneration with pure product purge is most effective
• Very high purity of recovered CO$_2$
• CO$_2$ recovery > 95%

Site Trials of Prototype CO$_2$ Capture Unit

• **Objective**
  – to evaluate the stability of honeycomb CF composite monolithic adsorbents using the real flue gas at Vales Point Power Station
  – to test the effect of real flue gas characteristics on the operation and performance of the CO$_2$ capture unit

• **Site installation, commissioning and testing**

Opening of real flue gas to test unit for first time at Vales Point Power Station

Fully commissioned solid sorbent prototype unit at Vales Point power Station

Individual sensors to measure SOx, NOx, CO and CO$_2$ for accurate measurement
Site Trials of Prototype CO₂ Capture Unit (continued)

- **Site trial testing involving two main scenarios**
  - CO₂ capture performance with flue gas pre-treatment
  - CO₂ capture performance without flue gas pre-treatment

- **Process methodology adopted for site trials**

  - Flue gas without Pre-treatment
  - Caustic Scrubber System for Flue gas Pre-treatment
  - Adsorption/Gas capture
  - CO₂ Flushing
  - Thermal & Vacuum Swing Regeneration
  - Recovered CO₂ for Flushing
  - CO₂ Recovered from Fluegas

- **Performance of carbon composite solid adsorbents evaluated:**
  - Stability of adsorbents to real flue gas evaluated from over 200 tests
  - CO₂ removal performance
  - Solid sorbent performance to removal of other gases apart from CO₂
Results of Site Trials

- Adsorption & desorption: flue gas with pretreatment
Results of Site Trials (continued)

- Adsorption & desorption: flue gas without pretreatment
Results of Site Trials (continued)

- **Adsorbent stability**

![Graph showing adsorption and desorption efficiency over 200 runs]

- **Excellent stability** to real flue gas over 200 site tests
  - CO₂ adsorption efficiency consistently over 98%
  - CO₂ desorption efficiency between 90-95%.
Development of New-Generation Carbon Composite Adsorbents

Objective

- Enhance CO₂ adsorption capacity (smaller footprint, lower capital and operating costs)
- Lower the cost of adsorbents using local biomass waste and brown coals

New-generation carbon composite adsorbents

- Carbon nanotube (CNT) modified carbon composite monoliths
- Biomass derived carbon composites (HiPerCap WP2)
CNT Composites - Source of CNTs

- CPD & CCI are home made, Com the commercial product

![Images of CPD, CCI, and Com](image1.png)

Specifications of as-produced/as-received CNTs

<table>
<thead>
<tr>
<th>CNT samples</th>
<th>Diameter, $D$ (nm)</th>
<th>Length, $L$ (μm)</th>
<th>Alignment</th>
<th>Purity (%)</th>
<th>Aspect ratio, $L/D$</th>
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</thead>
<tbody>
<tr>
<td>CPD</td>
<td>10</td>
<td>300</td>
<td>highly aligned</td>
<td>99.8</td>
<td>30,000</td>
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<tr>
<td>CCI</td>
<td>80</td>
<td>1500</td>
<td>aligned, some branching</td>
<td>97</td>
<td>18,750</td>
</tr>
<tr>
<td>Com</td>
<td>10-20</td>
<td>5-15</td>
<td>very tangled</td>
<td>95</td>
<td>400-1,500</td>
</tr>
</tbody>
</table>
Preparation of CNT Composite Adsorbents

The current preparation method (physical activation with CO$_2$) is simpler and more economic than chemical activation (e.g. with KOH) and functionalisation with basic groups.
SEMMorphology

Morphology and macropore size distributions of CNT composites

Comparisons of CNT and CF composites

**CO₂ uptake at 25 °C**

- **CNT composite (Com-15)**
- **CF composite**
- **Resin alone derived carbon**

**Narrow micropore size distributions**

- **CNT composite (CCI-15)**
- **CF composite**
- **Resin alone derived carbon**

CNT composites exhibit much higher CO₂ adsorption capacities

- **CO₂ uptake**: 15.9 wt% at 25 °C and 1 bar, and 5.2 wt% at 25 °C and 0.15 bar
- **Up to 30% increase in CO₂ adsorption capacity at 25 °C and 1 bar**
- **Over 45% increase in CO₂ adsorption capacity at 25 °C and low CO₂ pressures (0.15 bar)**

CO\textsubscript{2} & N\textsubscript{2} uptake adsorption isotherms at 0 and 25 °C

Rates of CO\textsubscript{2} adsorption at 25 °C and 25 mmHg

- CO\textsubscript{2}/N\textsubscript{2} selectivity: 32.6 at 273 K and 19.8 at 298 K
- Fast adsorption kinetics observed in the CNT composites

Conclusions

• Porous carbon composite monoliths show great promise in post-combustion CO$_2$ capture.

• Site trials demonstrate the excellent stability of the carbon composite adsorbent towards real flue gas.

• New-generation CNT carbon composite adsorbents exhibit significantly enhanced CO$_2$ uptake particularly under low CO$_2$ pressures, which is of more relevance for flue gas applications.
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Thank you

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