Carbon Composite Adsorbents for Post Combustion CO_2 Capture

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Lab Scale Study – Carbon Fibre Composites

Fabrication and Testing of Lab Size Honeycomb Carbon Fibre Composite Monoliths

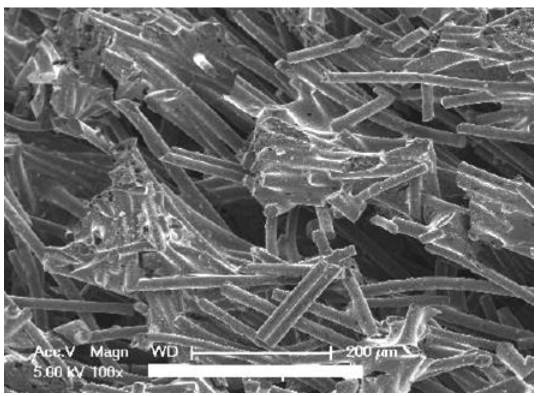
Molding equipment

3 processing furnaces

1. Carbon Fibre (s) and Phenolic resin binding material
2. Slurry or Paste
3. Vacuum Moulded to honeycomb structure
4. Drying at 50-60ºC and Curing at 130-150ºC
5. Carbonised with inert gas at 650-850ºC to pyrolize the resin
6. Activation at 650-950ºC to achieve pore characteristics

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

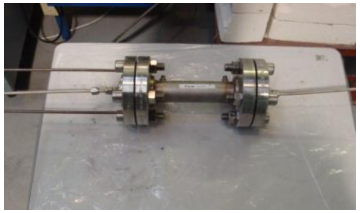
Fabricated (HMCFC)



Microscopic morphology

Adsorbent Testing Equipments

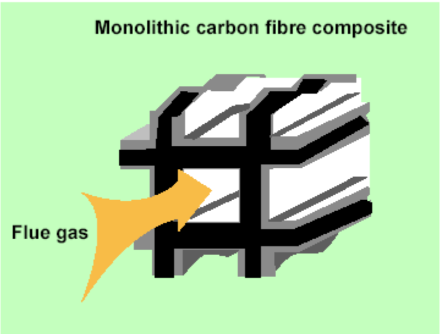
Adsorbent Characterisation



Breakthrough Test Rig with Lab Scale Adsorption Chamber

Solid Carbon Sorbent CO_2 Capture Technology

- Based on honeycomb carbon composite monoliths
  - ✓ Enable CO_2 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 CO_2 adsorption
    - Utilisation of flue gas waste heat for CO_2 desorption
  - ✓ Tolerant to moisture, SO_x and NO_x
    - Avoid flue gas pre-treatment prior to CO_2 capture; this is important as there are no FGD and SCR $DeNO_x$ facilities at coal fired power plants in Australia



Evolutionary Journey

Lab scale CO_2 capture (2006-2008)

Large scale CO_2 capture with regeneration (2009-2011)

CO_2 capture site trials (2011-2014)

NEXT

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

- CO_2 capture combined with thermal and vacuum regeneration

- To evaluate CO_2 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

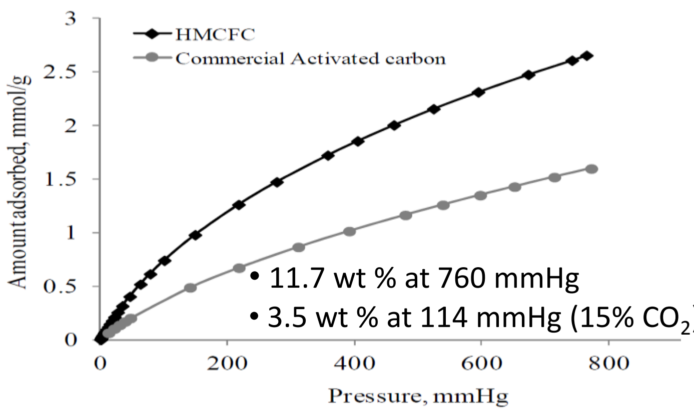
CF composites

Lab size adsorbent (Ø 30mm)

Large size adsorbent (Ø 123 mm)

Large scale moulding unit for composite fabrication

CO_2 adsorption Isotherms at 25 °C



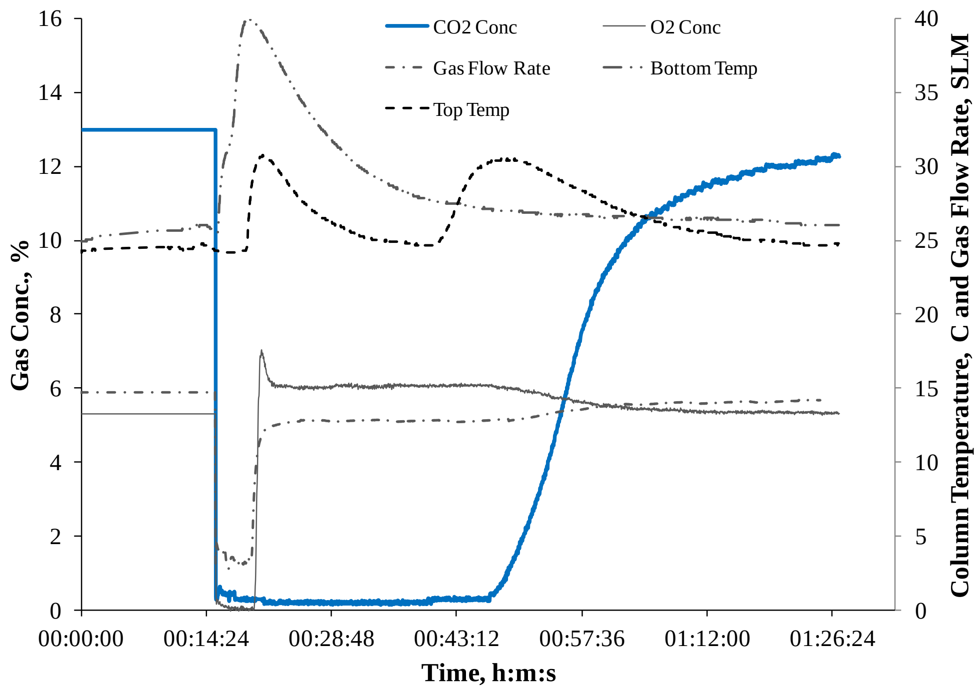
Large scale CO_2 capture-regeneration unit

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

R. Thiruvenkatachari, S. Su et al., *International Journal of Greenhouse Gas Control*, 2013, 13, 191-200.

Summary of Large Scale Study Results

Adsorption Breakthrough Profile Showing CO_2 capture at Real Time

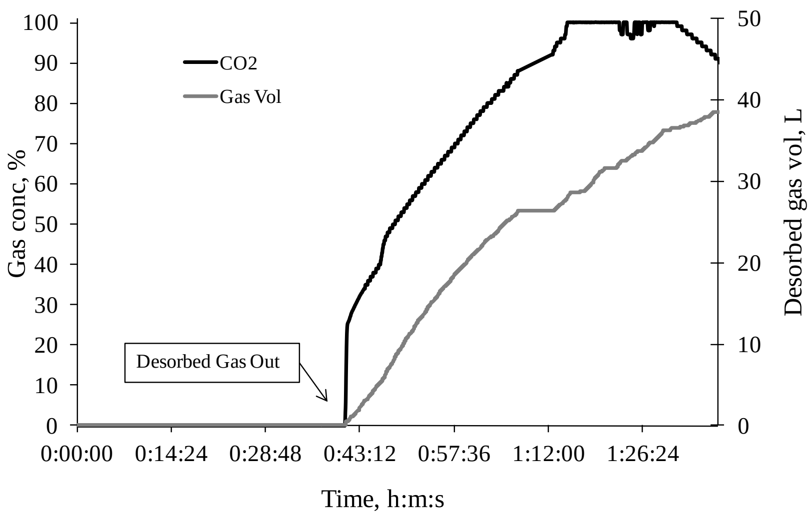


- CO_2 capture carried out at ambient temperature and pressure
- Simulated flue gas consisting of 13% CO_2, 5.5% O_2 and balance N_2
- CO_2 adsorption efficiency > 97% from adsorption breakthrough

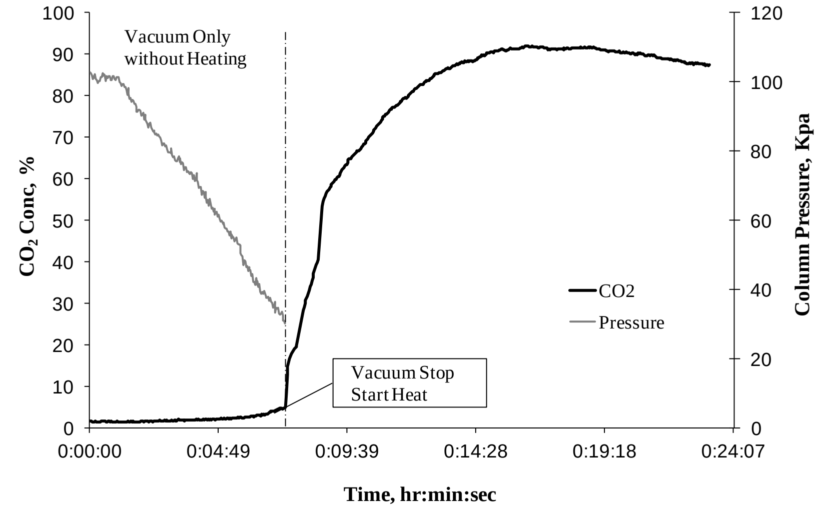
R. Thiruvenkatachari et al., *International Journal of Greenhouse Gas Control*, 2013, 13, 191-200.

Thermal and Vacuum Regeneration

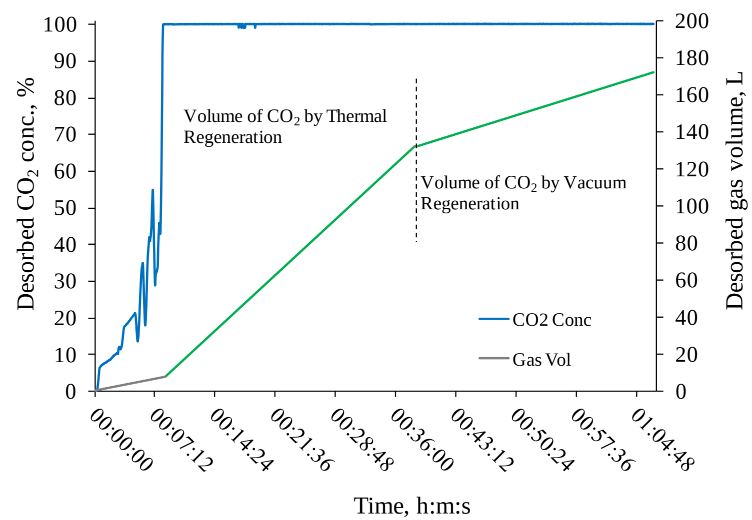
Individual Thermal Regeneration



Vacuum Regeneration



Combined Thermal and Vacuum Regeneration



- 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%

R. Thiruvenkatachari, S. Su et al., *International Journal of Greenhouse Gas Control*, 2013, 13, 191-200.

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

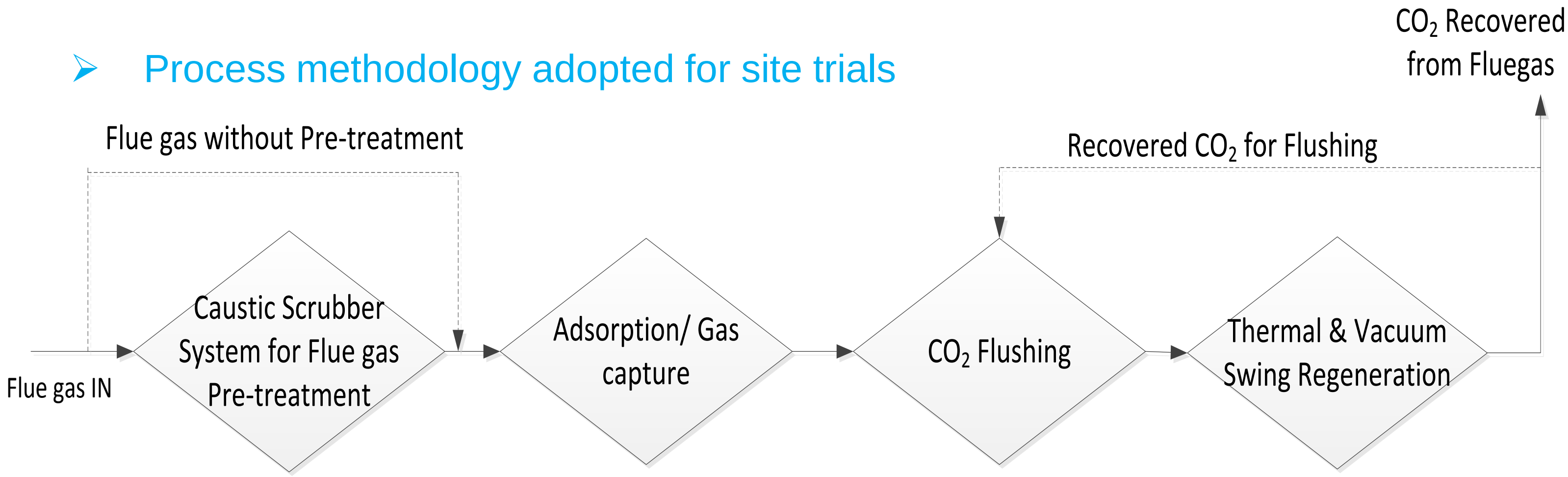
Fully commissioned solid sorbent prototype unit at Vales Point power Station

Individual sensors to measure SOx, NOx, CO and CO_2 for accurate measurement

Site Trials of Prototype CO_2 Capture Unit (continued)

- **Site trial testing involving two main scenarios**
  - CO_2 capture performance with flue gas pre-treatment
  - CO_2 capture performance without flue gas pre-treatment

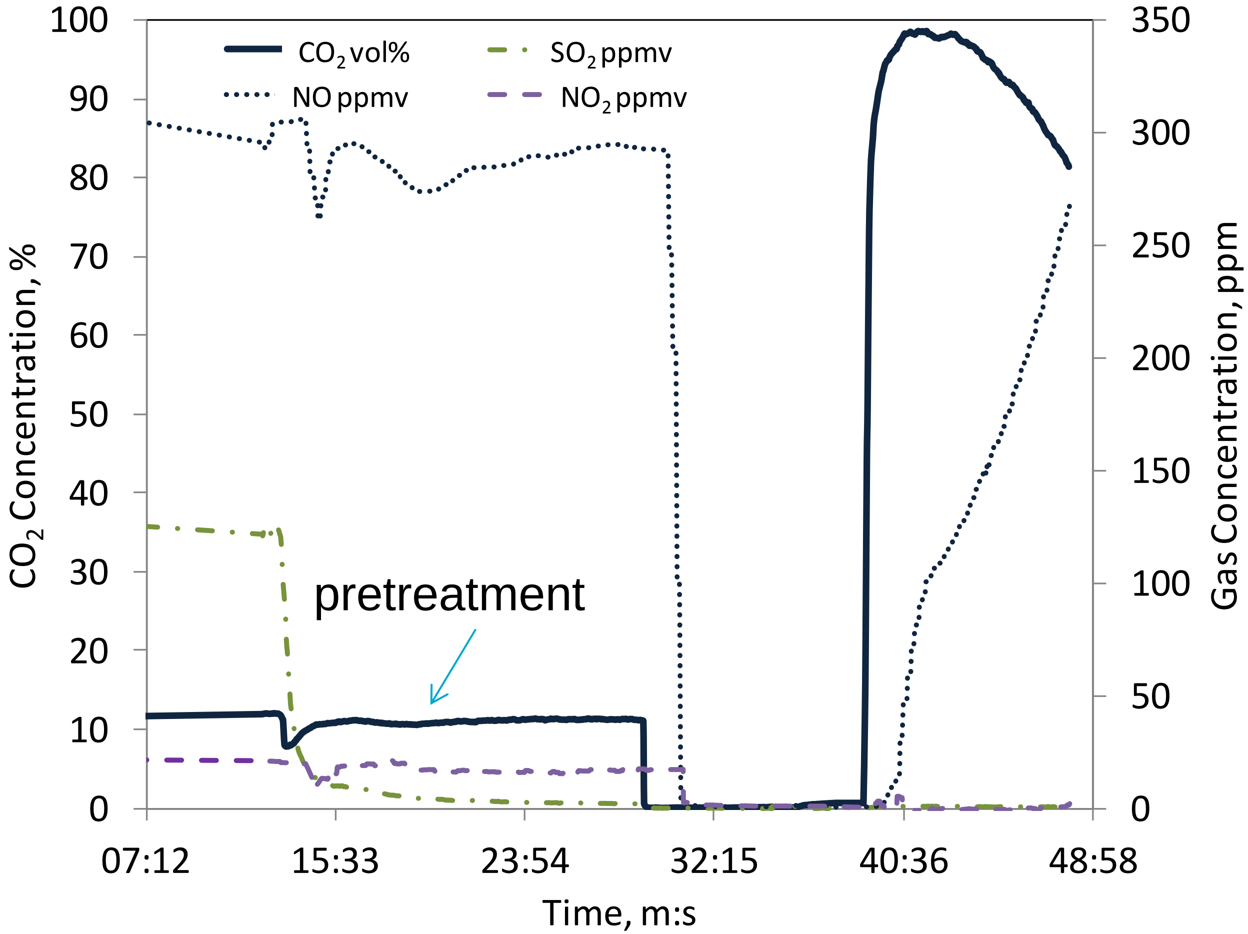
- Process methodology adopted for site trials



- **Performance of carbon composite solid adsorbents evaluated:**
  - Stability of adsorbents to real flue gas evaluated from over 200 tests
  - CO_2 removal performance
  - Solid sorbent performance to removal of other gases apart from CO_2

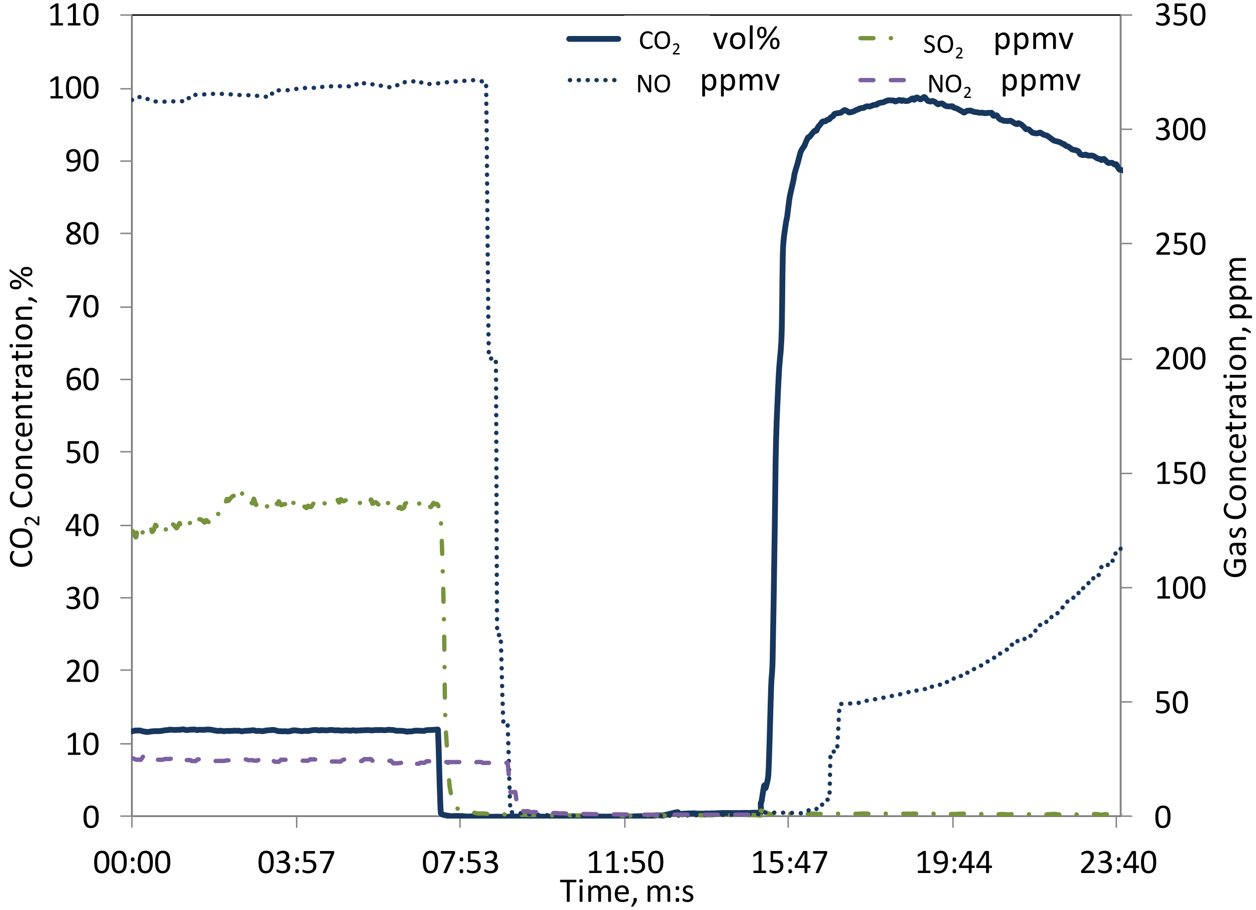
Results of Site Trials

❖ Adsorption & desorption: flue gas with pretreatment



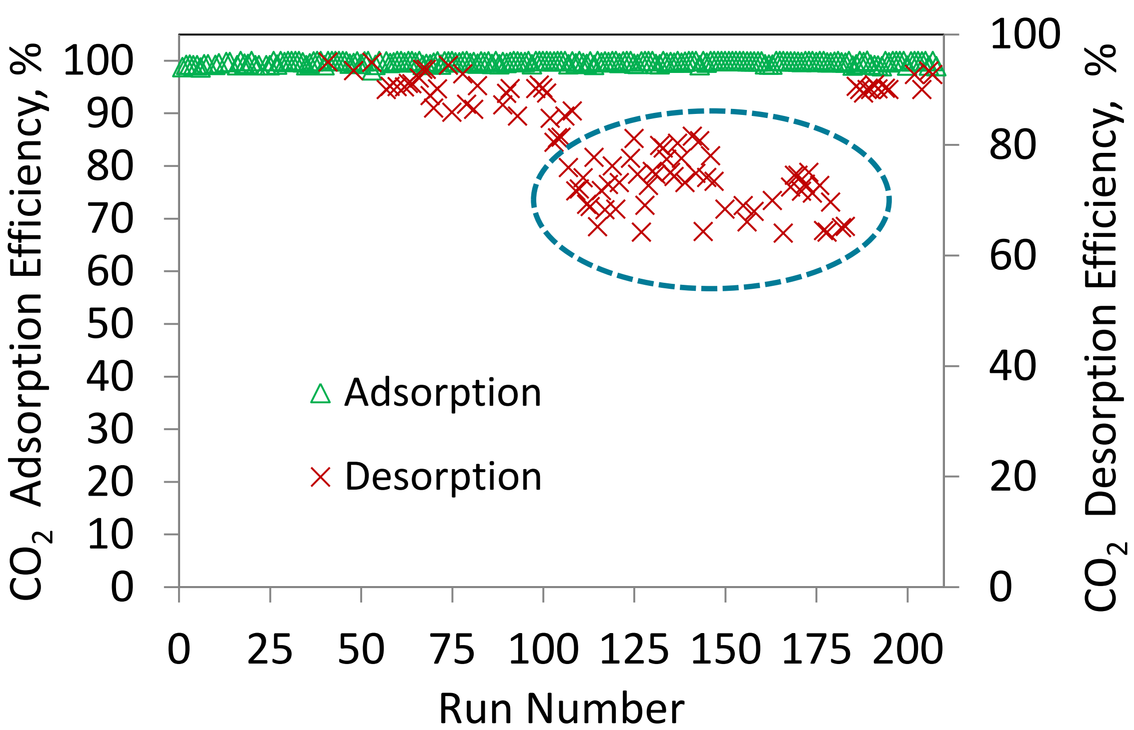
Results of Site Trials (continued)

❖ Adsorption & desorption: flue gas without pretreatment



Results of Site Trials (continued)

❖ Adsorbent stability



- **Excellent stability** to real flue gas over 200 site tests
  - CO_2 adsorption efficiency consistently over 98%
  - CO_2 desorption efficiency between 90-95%.

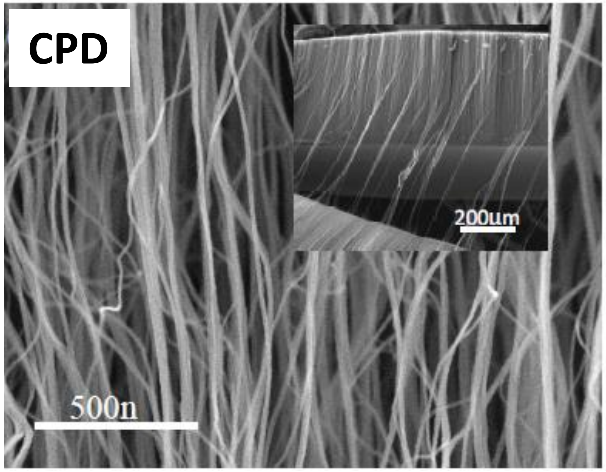
Development of New-Generation Carbon Composite Adsorbents

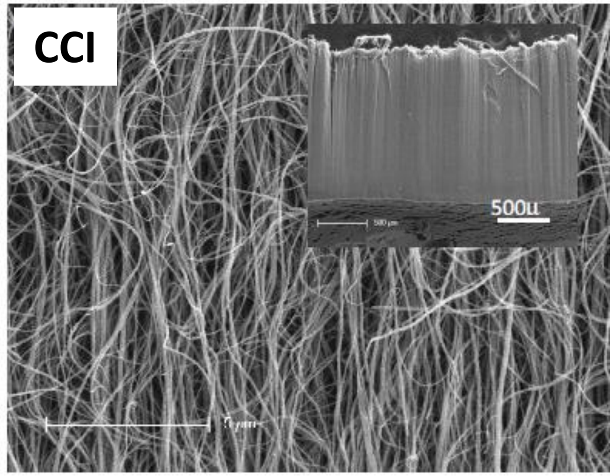
- **Objective**
  - Enhance CO_2 adsorption capacity (smaller footprint, lower capital and operating costs)
  - Lower the cost of adsorbents using local biomass waste and brown coals

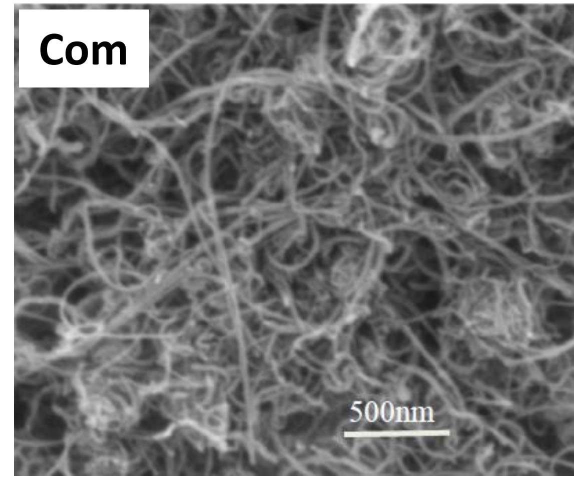
- **New-generation carbon composite adsorbents**
  - Carbon nanotube (CNT) modified carbon composite monoliths
  - ***Biomass derived carbon composites (HiPerCap WP2)***

CNT Composites - Source of CNTs

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



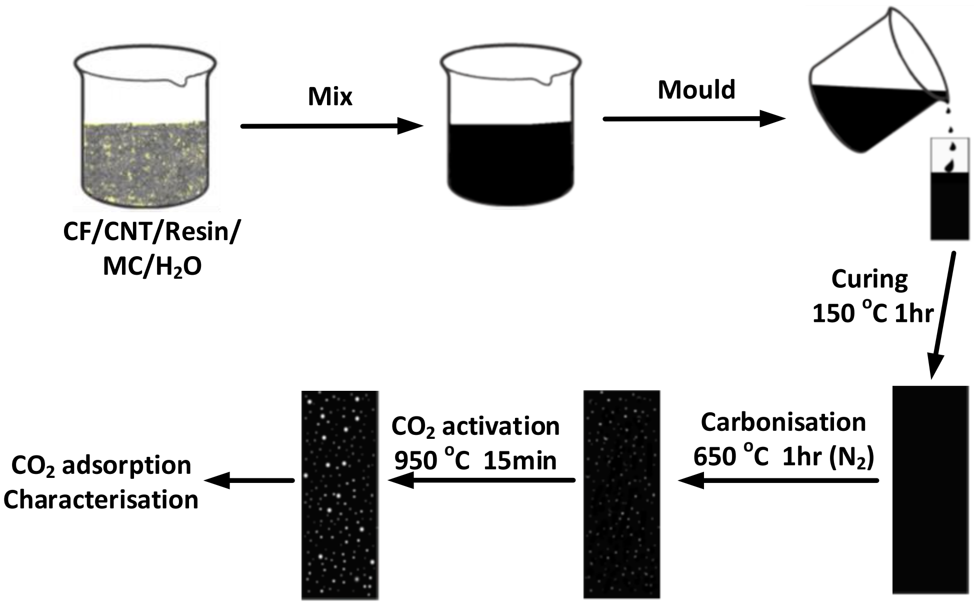




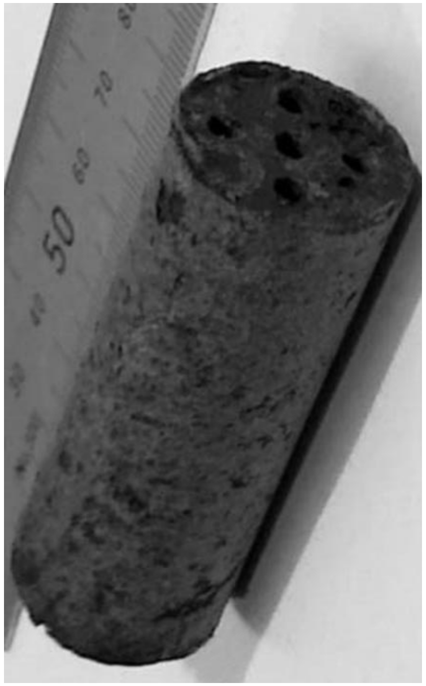
Specifications of as-produced/as-received CNTs

CNT samples	Diameter, *D* (nm)	Length, *L* (μm)	Alignment	Purity (%)	Aspect ratio, *L/D*
CPD	10	300	highly aligned	99.8	30,000
CCI	80	1500	aligned, some branching	97	18,750
Com	10-20	5-15	very tangled	95	400-1,500

Preparation of CNT Composite Adsorbents



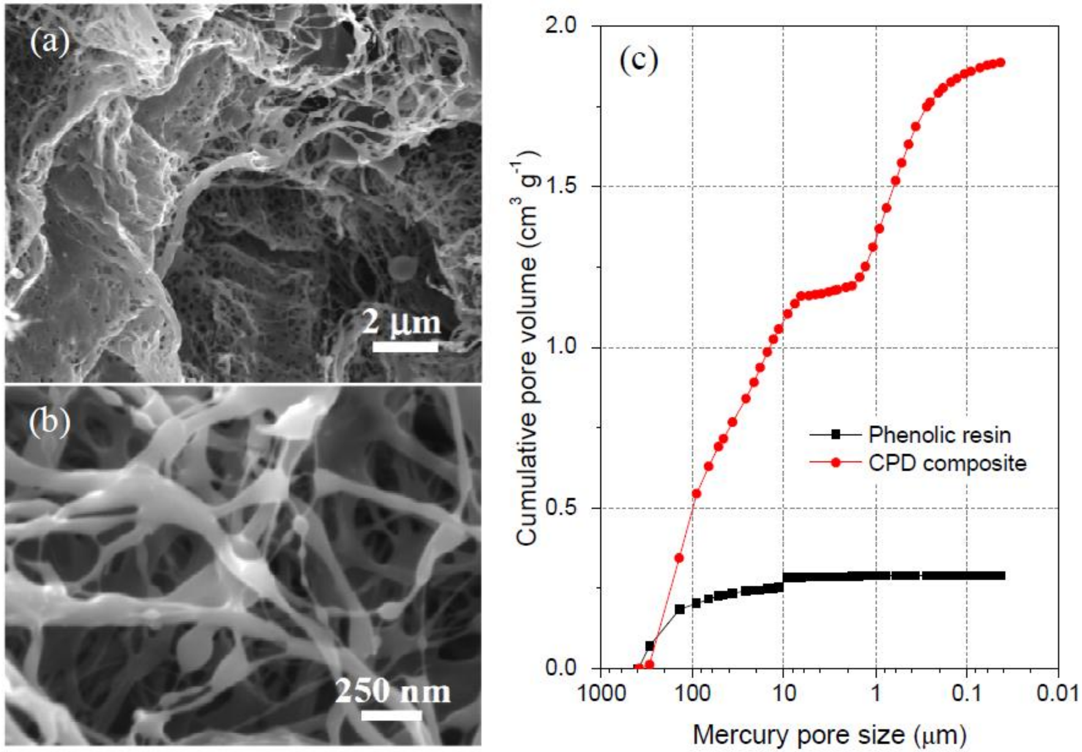
Schematic of composite preparation procedures

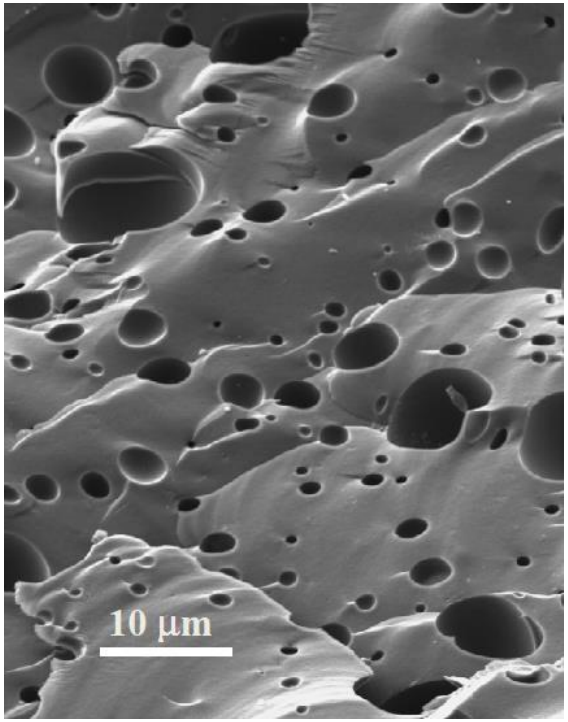


Prepared CNT composite monolith

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

SEM Morphology





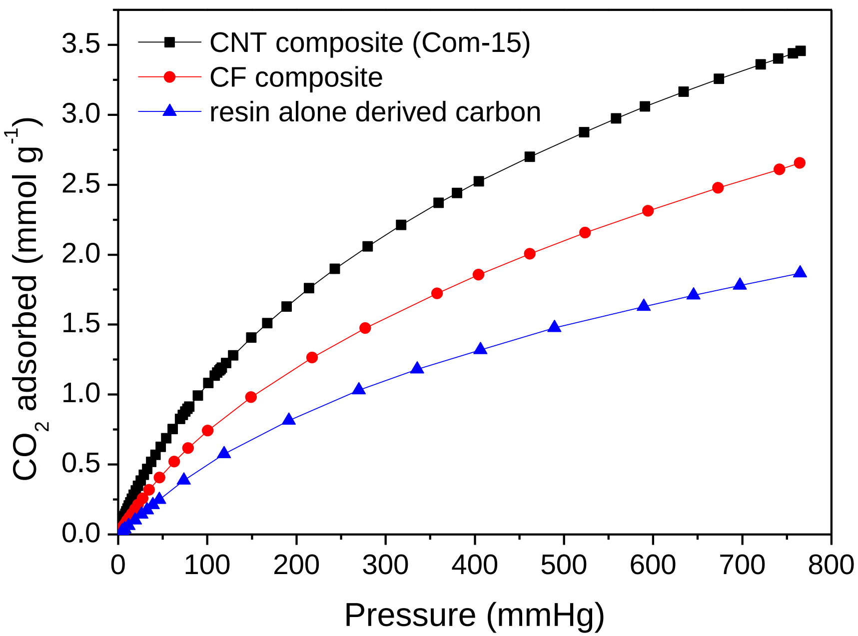
Morphology and macropore size distributions of CNT composites

Morphology of activated phenolic resin

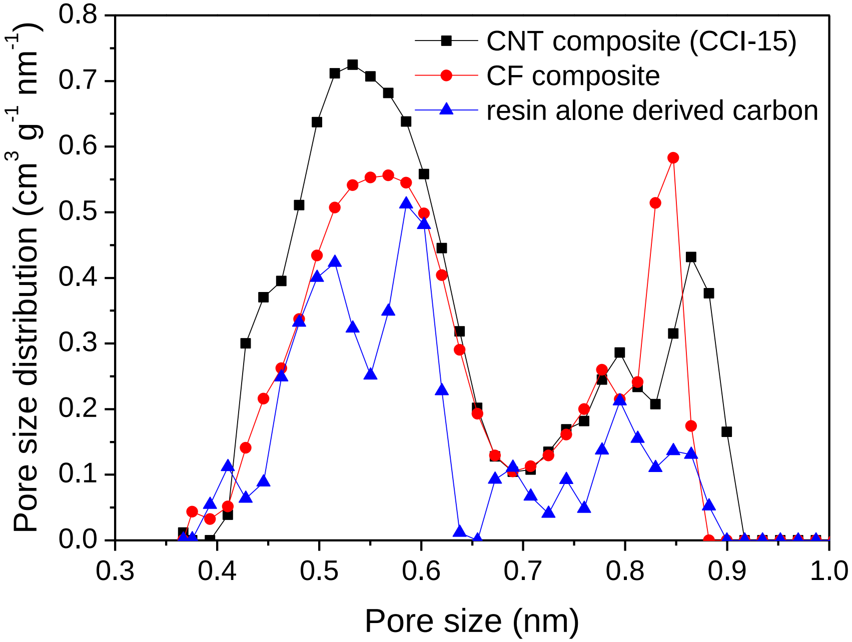
Y. Jin, S. Hawkins, C. Huynh, S. Su, *Energy Environ. Sci.*, 2013, 6, 2591-2596.

Comparisons of CNT and CF composites

CO_2 uptake at 25 °C



Narrow micropore size distributions



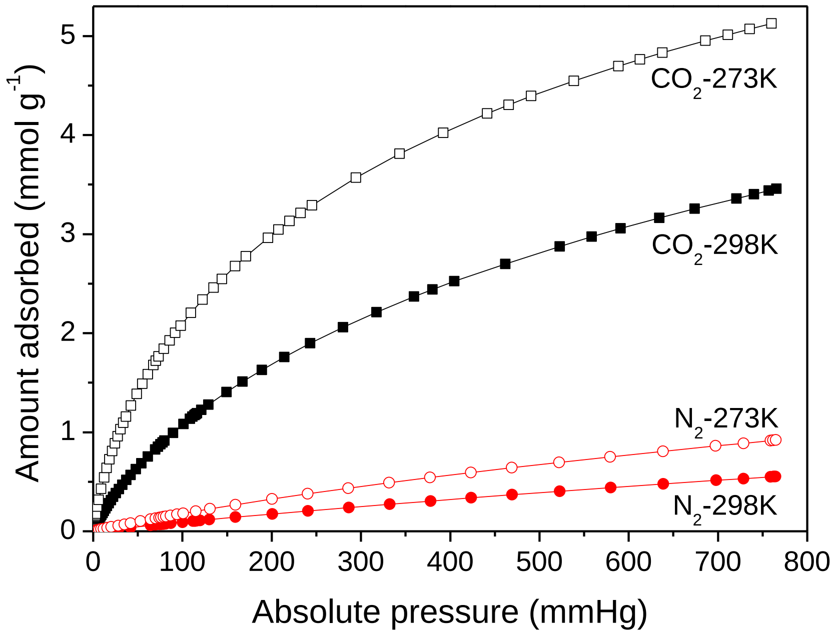
CNT composites exhibit much higher CO_2 adsorption capacities

- *CO_2 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 CO_2 adsorption capacity at 25 °C and 1 bar*
- *Over 45% increase in CO_2 adsorption capacity at 25 °C and low CO_2 pressures (0.15 bar)*

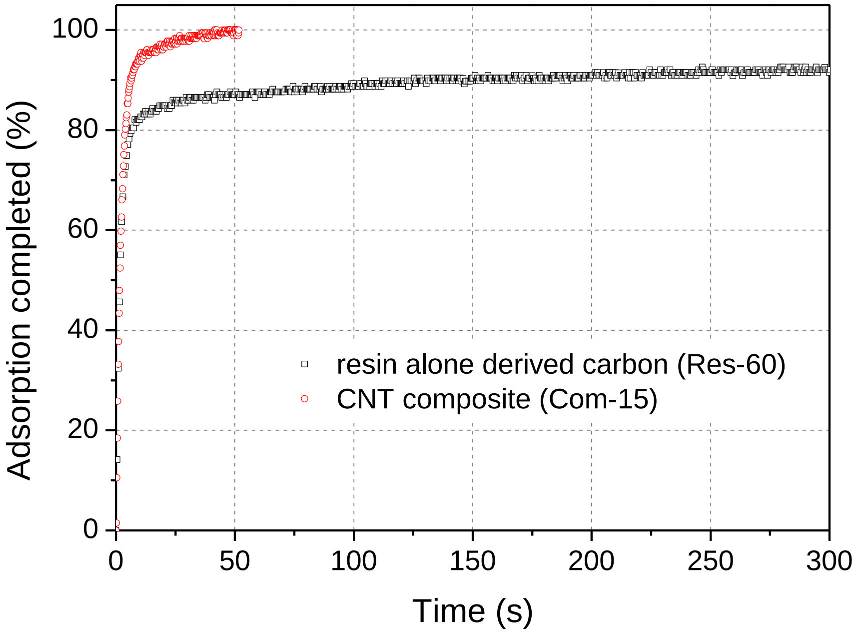
Y. Jin, S. Hawkins, C. Huynh, S. Su, *Energy Environ. Sci.*, 2013, 6, 2591-2596.

Adsorption Selectivity & Kinetics

CO_2 & N_2 uptake adsorption Isotherms at 0 and 25 °C



Rates of CO_2 adsorption at 25 °C and 25 mmHg



- CO_2/N_2 selectivity: 32.6 at 273 K and 19.8 at 298 K
- Fast adsorption kinetics observed in the CNT composites

Y. Jin, S. Hawkins, C. Huynh, S. Su, *Energy Environ. Sci.*, 2013, 6, 2591-2596.

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.

Acknowledgements

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  - Coal Innovation NSW for the site trials of prototype CO_2 capture unit at the Vales Point power station
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Thank you

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