Development of adsorbent technologies for pre and post-combustion CO_2 capture

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Introduction
Why adsorption?

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- The CO_2 capture step is projected to account for 75 % for the overall carbon capture and storage process.
- Post-combustion
  - Aqueous solutions of amines used by industry as adsorbents for acid gas (chemical solvents) and all commercial CO_2 capture plants use similar processes
  - Technologies require significant modification, ultimately leading to high capital and running costs
  - Typical energy penalty incurred by an MEA plant estimated 15 – 37 % of net output of plant (Herzog and Drake 1993)
- Pre-combustion
  - Use of physical absorption (ie Rectisol and Selexol)
  - Current physical absorption systems (eg. Selexol) large efficiency loss ca. 6% due to compressing the resultant CO_2.
- Need for the development of alternative low cost technologies to provide a more effective route for the capture and storage of CO_2 on a global scale.

Summary of Adsorption Research

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- Post-combustion capture
  - The Partial Removal of CO_2 from Flue Gases using Tailored Coal-Derived Carbons BCURA; Project B65 (2002-05)
  - Developing effective adsorbent technology for the capture of CO_2 in fossil fuel fired power plant. Carbon Trust; 2002-6-38-1-1 (2003-07)
  - Assessment of Options for CO_2 Capture and Geological Sequestration. RFCS; RFC-CR-03008 (2003-07)
  - Developing effective adsorbent technology for the capture of CO_2. EPSRC Advanced Research Fellowship, Dr T.C. Drage; EP/C543203/1 (2005-10)
- Pre-combustion capture
  - Impact of CO_2 removal on coal based gasification plants. Dti Cleaner Coal Technology Programme; Project 406 (2004 – 2005)
  - Hydrogen separation in advanced gasification processes. RFCS; RFC-PR-04032 (2006-09)

Introduction
Conditions for Capture

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	Pre-combustion capture (after water gas shift)[a]	Post-combustion capture[b]
Gas composition		
CO_2	35.5 %	15 – 16 %
H_2O	0.2 %	5 – 7 %
H_2	61.5 %	-
O_2	-	3 – 4 %
CO	1.1 %	20 ppm
N_2	0.25 %	70 – 75 %
SO_x	-	< 800 ppm
NO_x	-	500 ppm
H_2S	1.1%	-
Conditions		
Temperature	40 °C	50 – 75 °C
Pressure	50 – 60 bar	1 bar

As with solvent systems physical adsorption systems work for high pressure, whilst chemical amine systems are needed at atmospheric pressure

[a]Linde Rectisol, 7[th] European Gasification Conference; [b]Pennline (2000), Photochemical removal of mercury from flue gas, NETL

Post combustion capture

the need for chemical adsorbents

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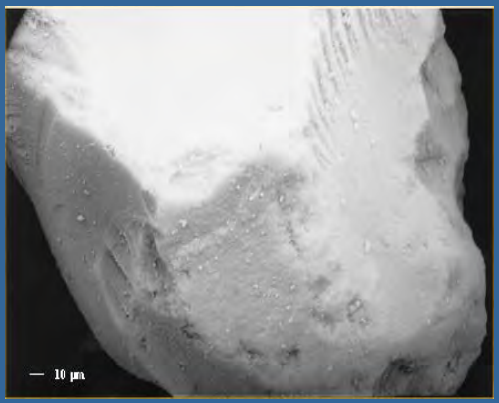
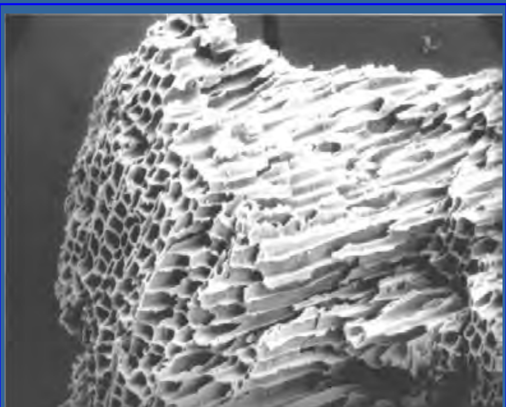
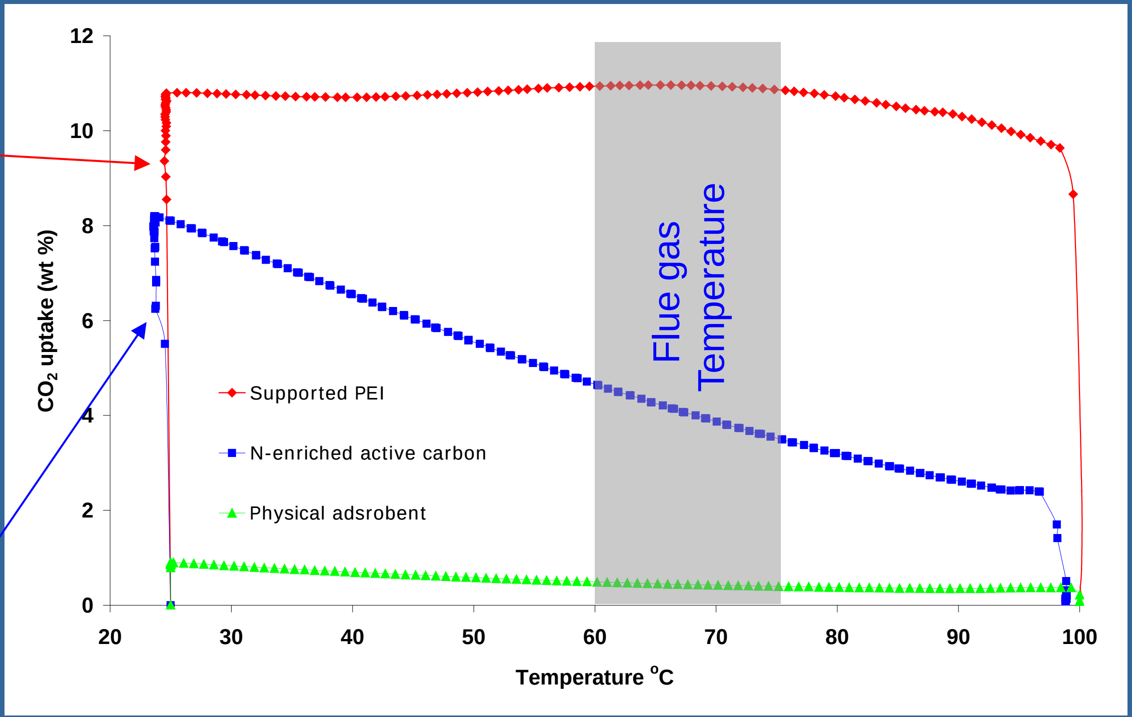
Supported-polyethylenimine



High N-content active Carbons[1,2]





Amine-CO_2 chemical adsorption

$CO_2 + 2R_2NH \leftrightarrow R_2NH + R_2NCOO^-$ <1>

$CO_2 + 2R_3N \leftrightarrow R_4N^+ + R_2NCOO^-$ <2>

$CO_2 + H_2O + R_2NH \leftrightarrow HCO_3^- + R_2NH_2^+$ <3>

[1] Drage, T.C., Arenillas, A., Smith, K., Pevida, C., Pippo, S., and Snape, C.E. (2007) Preparation of active carbons from the chemical activation of urea-formaldehyde and melamine-formaldehyde resins for the capture of carbon dioxide. Fuel, **86**, 22-31

[2] Arenillas, A., Drage, T.C., Smith, K.M, and Snape C.E. (2005). CO2 removal of carbons prepared by co-pyrolysis of sugar and nitrogen containing compounds. Journal of Analytical and Applied Pyrolysis, **74**, 298-306.

Adsorbent Capacities

Silica-PEI adsorbents

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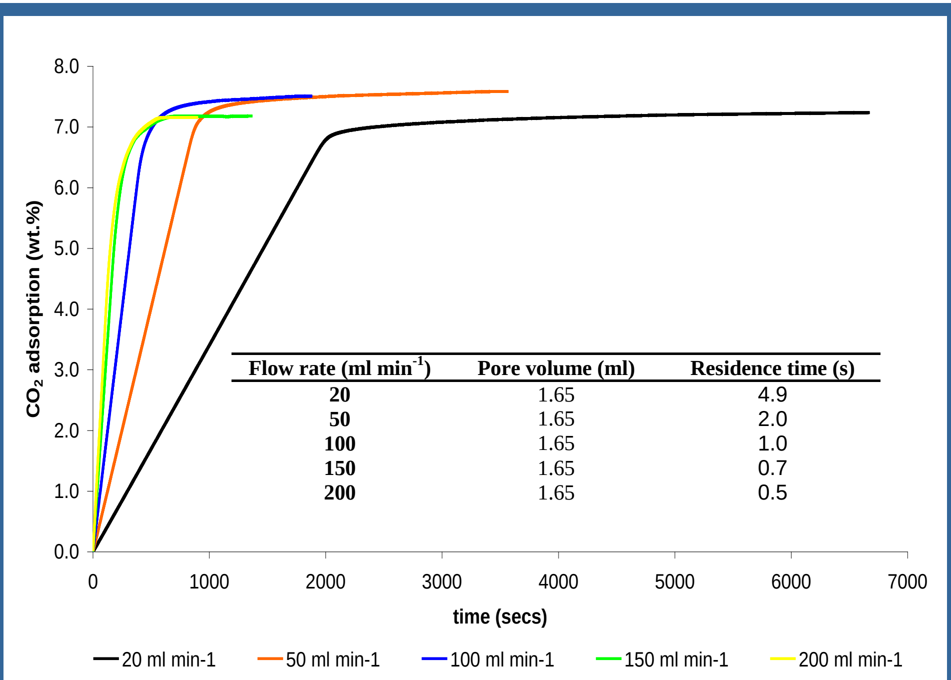
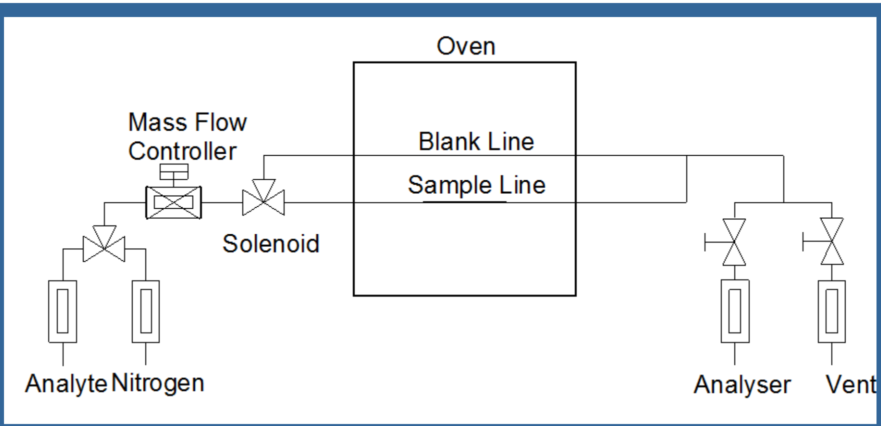


Flow rate (ml min^{-1})	Pore volume (ml)	Residence time (s)
20	1.65	4.9
50	1.65	2.0
100	1.65	1.0
150	1.65	0.7
200	1.65	0.5



- Adsorption capacities explored under equilibrium and dynamic conditions using simulated flue gases
- Simulated flue gas conditions capable of adsorbing CO_2 with high breakthrough capacities, requiring only short residence times
- Potential demonstrated for selective regeneration of other acid gases, for example SO_2

Adsorbent Regeneration

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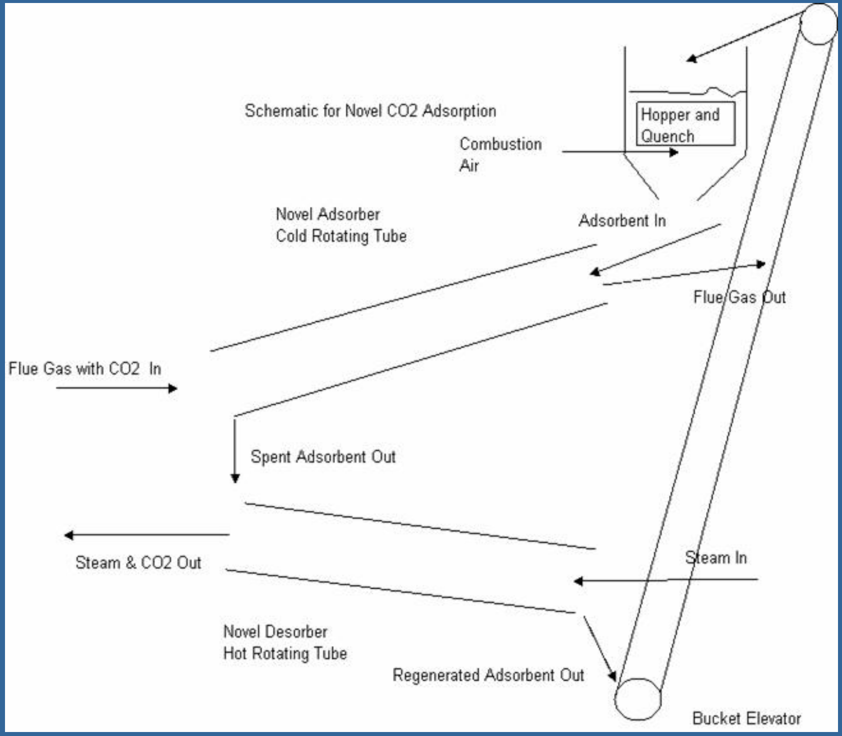
Efficient adsorbent regeneration is crucial

- To be economic the adsorbents will have to be regenerable. Energy required for regeneration will dictate the efficiency and economics of the process. Minimising temperature differential between adsorption / desorption cycles and stripping gas volumes are key to efficient operation.
- Regeneration strategy will influence adsorbent lifetime and replacement rate.



Two regeneration strategies tested to determine feasibility for scale-up:

- Thermal swing adsorption cycles over a range of time and temperatures in CO_2
- Using nitrogen as a stripping gas at elevated temperatures.

Regeneration

PEI based adsorbents - thermal

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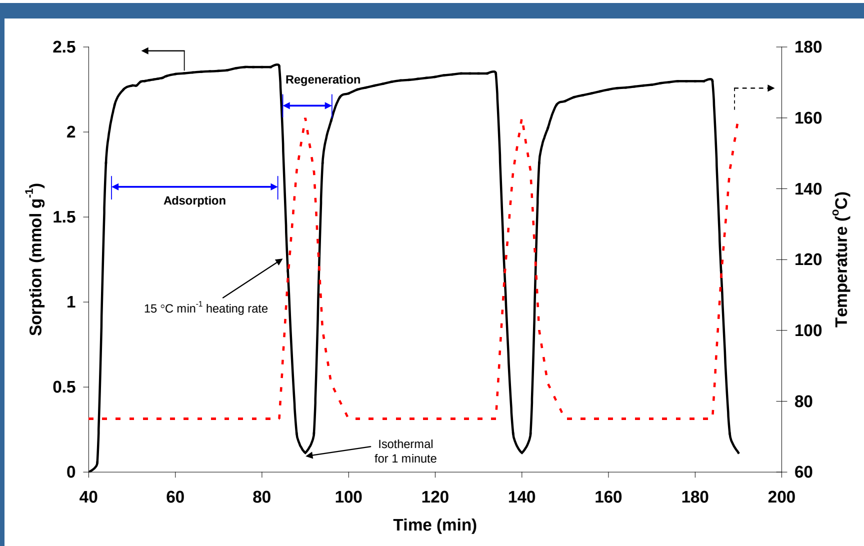
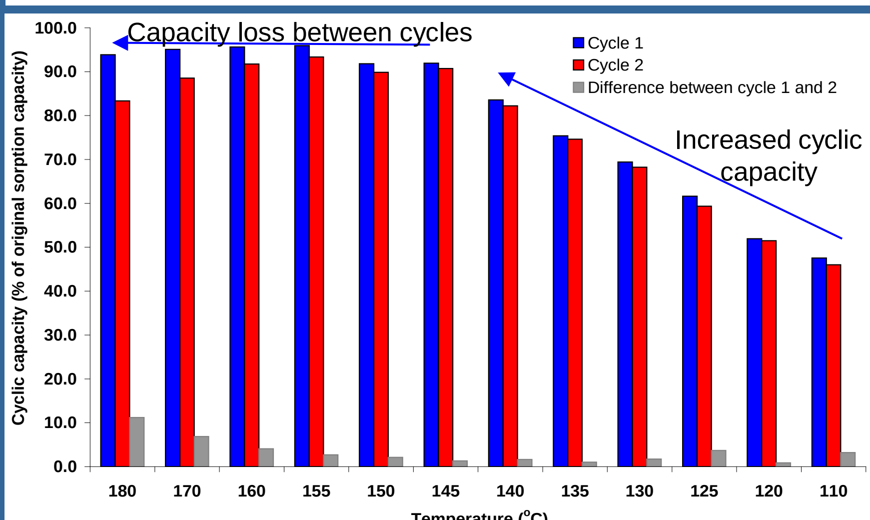
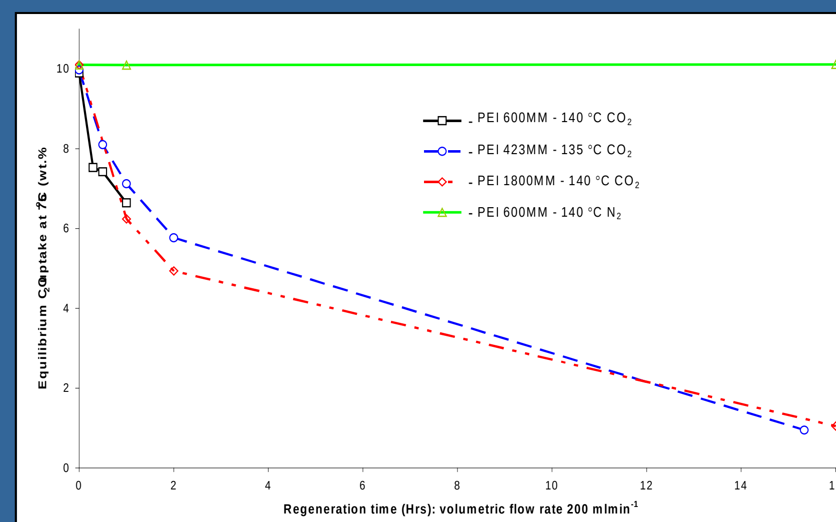


- Regeneration in a stream of pure CO_2 by temperature swing
- Cyclic capacity dependent upon temperature
- > 90 of sorption capacity recovered on cycling
- Problems arise with secondary reaction leading to short adsorbent lifetime





Regeneration
Secondary reaction

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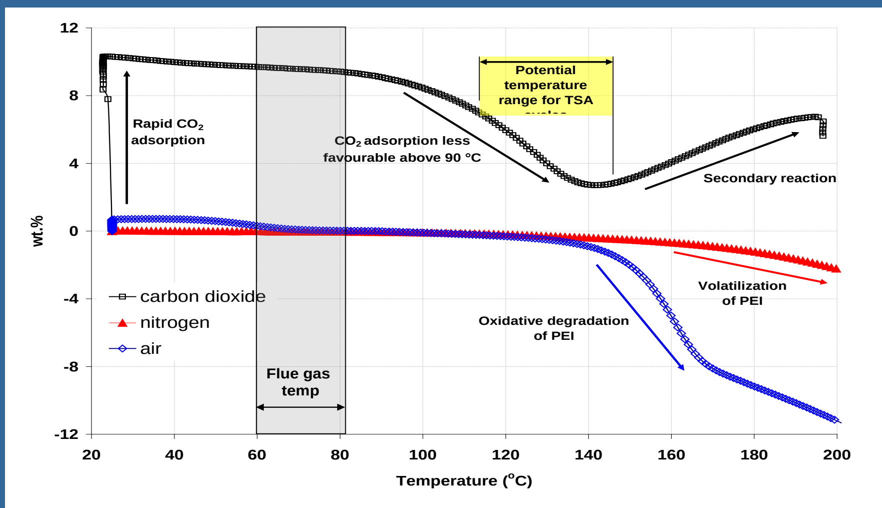
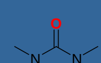
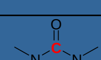
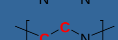
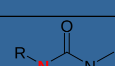
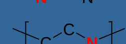
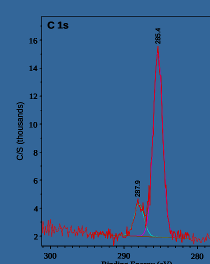
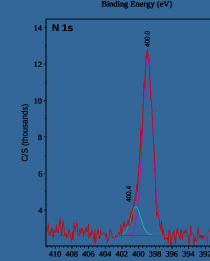
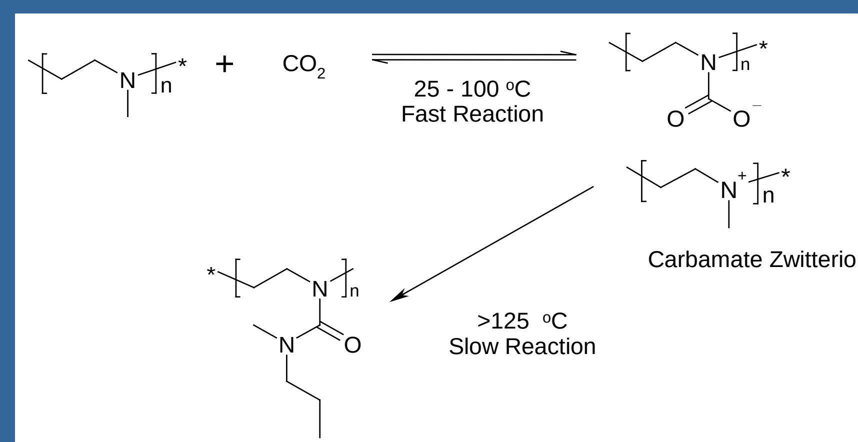


- ^{13}C NMR, XPS, elemental analysis, DRIFT used to identify secondary reaction product
- Reaction proposed to result in the formation of a urea type linkage

Element	Binding Energy	Intensity %	Assignment	Structure	Reference
Si	103.9	20	SiO_2 - inorganic support	SiO_2	[3]
O	532.0	29	SiO_2 - inorganic support. Good agreement between the ratio of Si and O_2	SiO_2	[3]
	530.8	1.5	Close match to urea / polyurea		[4]
C	287.9	5.3	Carbonyl carbon from urea fragment		[4]
	285.4	30.2	Matches carbon skeleton of polyethylenimine		[4]
N	400.4	1.8	Good match to nitrogen adjacent to a carbonyl group - such as polyurea		[4]
	400.0	10.5	Matches nitrogen of polyethylenimine		[4]







Regeneration
Stripping gas

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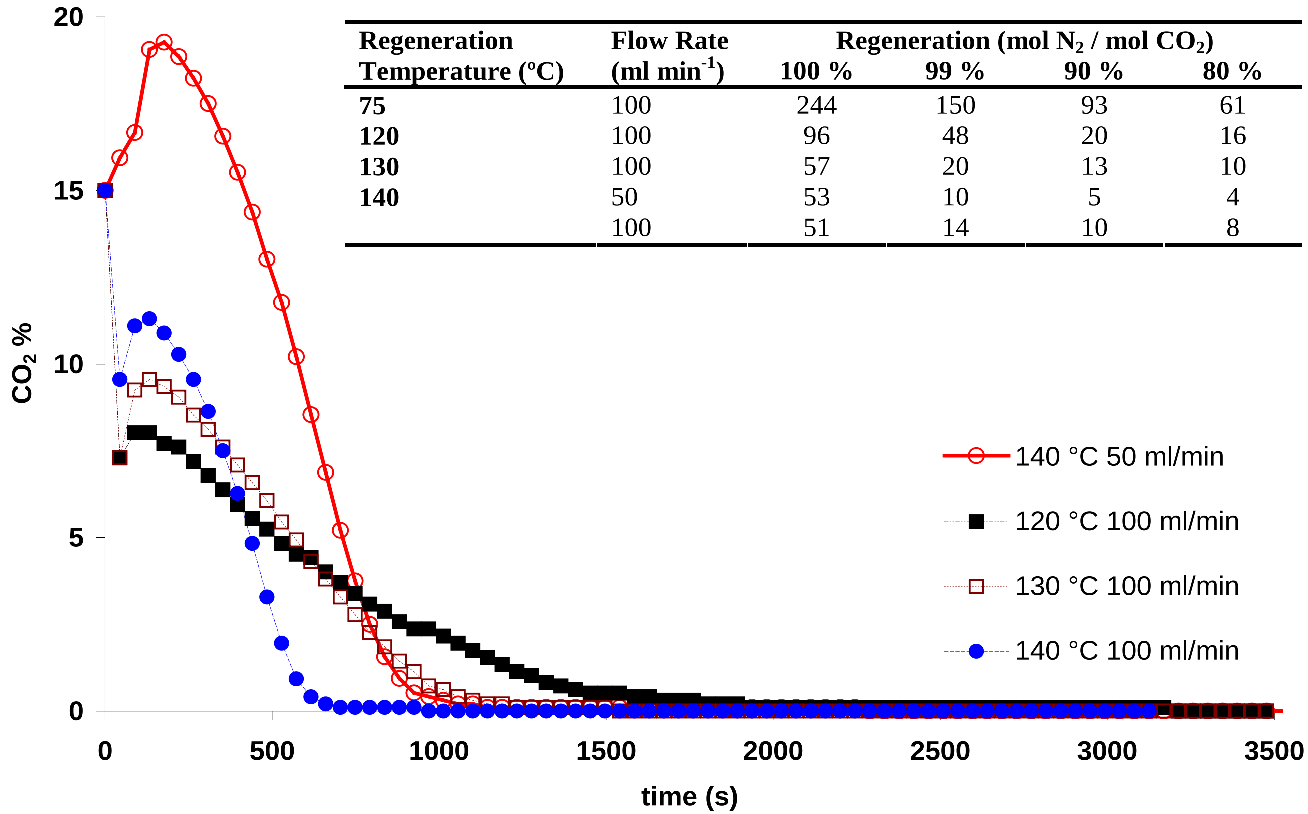

Regeneration Temperature (°C)	Flow Rate (ml min^{-1})	Regeneration (mol N_2 / mol CO_2) 100 %	99 %	90 %	80 %
75	100	244	150	93	61
120	100	96	48	20	16
130	100	57	20	13	10
140	50	53	10	5	4
	100	51	14	10	8

- Using nitrogen as stripping gas suggests potential for steam stripping as a method for sorbent regeneration

Post-combustion capture
economic studies

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Economic study* based on:

- 90 % CO_2 removal
- Pressure drop < 6 psi
- Use of enriched amine SBA-15 substrate
- Adsorption offers potential cost saving over MEA scrubber
- Fixed bed not viable due to large footprint
- Nottingham investigating novel moving bed design
- Minimising temperature difference between adsorption and regeneration key

Table 1. Comparison of CO_2 Capture Unit Performance

	Flowrate per Unit (acfm)	Absorber Units	Sorbent Mass (tonnes)	ΔP (psi)	Total Footprint (ft^2)
MEA Scrubber	250,000	8-10	N/A	3-6	9,000
Fixed Bed	50,000	96	1,500	6	86,000
Fluidized Bed	150,000	8	1,100	0.3	7,000
Novel Fixed Bed					
Case 5	150,000	8	3,500	2.2	7,400
Case 11	300,000	4	1,300	2.9	9,700

Table 2. Plant Performance and Economics with CO_2 Capture

	ID Fan Load (MW)	Solvent Pump (MW)	Gross Plant Size (MW)	COE (c/kWh)	COE Increase
MEA Scrubber	22	3	491	7.56	55%
Fixed Bed	25	N/A	483	6.39	31%
Fluidized Bed	6.5	N/A	465	6.88	41%
Novel Fixed Bed					
Case 5	16	N/A	474	6.93	42%
Case 11	19	N/A	478	6.34	30%

*Tarka et al., 2006, Prep. Pap.-Am. Chem. Soc., Div. Fuel. Chem. 51(1), 104.

Techno-Economic Study

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- Study based on a novel moving bed adsorber – realistic option to minimise pressure drop
- Technical study to remove CO_2 from 20% of flue gas flow
- Comparison made to plant without capture and MEA scrubber

Assumptions:

20% slip stream flow – 90% removal	:	31 kg/s of CO_2
Adsorbent capacity	:	9% w/w
Adsorbent requirement /sec	:	350.5 kg
Solid residence time	:	12 s
Regeneration steam temp	:	140 °C
Assumed steam flow (5 times CO_2 flow)	:	570 tonne/hr

- Conservative adsorption capacities and regeneration volumes assumed.
- Basic system considered in the first instance – no integration in terms of heat as would be used for a specifically designed process.

Conclusions

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- CO_2 regeneration of the adsorbent a trade off between efficient / rapid regeneration at sufficiently high temperature and thermostable complex formation (above 130 °C)
- TSA in an atmosphere of CO_2 not feasible due to short adsorbent lifetime
- Conditions for regeneration of PEI adsorbents must be carefully controlled to prolong adsorbent lifetime
- Adsorbent regeneration conditions are going to be critical when combined into any adsorber system.

- Future Work
  - Optimisation of steam regeneration cycles
  - Determination of adsorbent lifetime with steam present
  - Construct a test scale rig based on the novel moving bed adsorber (adsorption efficiency, attrition rates etc)

Acknowledgements

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