

Burning Fossil Fuels – how do we evaluate their net impact on climate?

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Contents

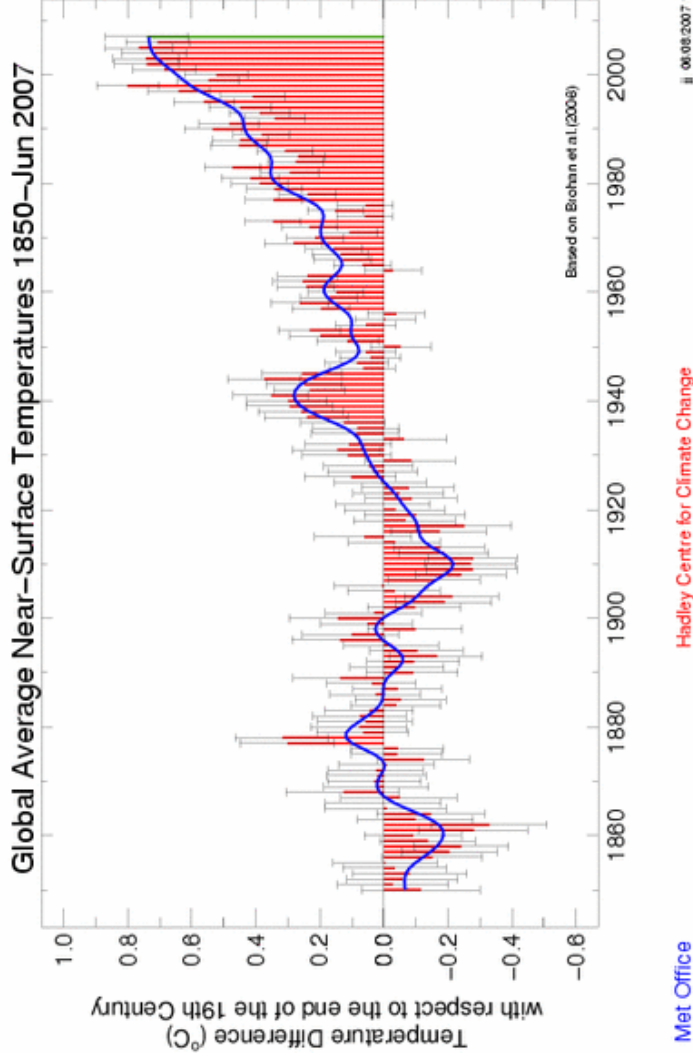
- A bit of background
- Comparing the emissions – the Kyoto Way
- Beyond Kyoto?
- Aviation – an extreme example
- Carbon capture and storage

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Intergovernmental Panel on Climate Change 2007 Assessment:

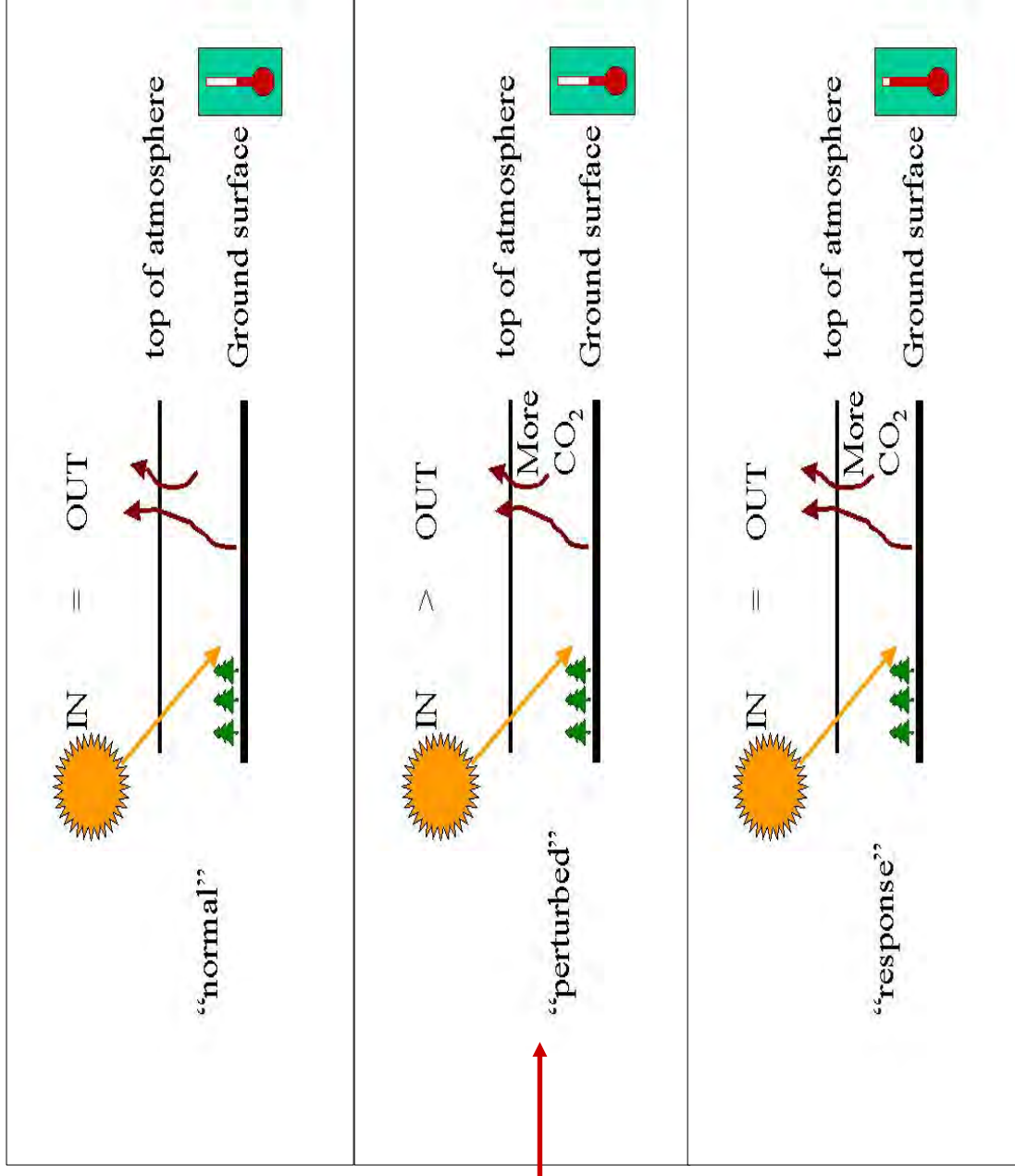
**"Warming of the
climate system is
unequivocal ..."**



"most of the observed increase in globally averaged temperatures since the mid-20th century is **very likely** due to the observed increase in anthropogenic greenhouse gas concentrations"

What *is* radiative forcing (of climate change)?

Forcing is the perturbation of the planetary radiation budget in absence of (almost!) any other change



Utility of radiative forcing

$$\Delta T \approx \lambda \Delta F$$

ΔT is *global-mean surface temperature change* (K)

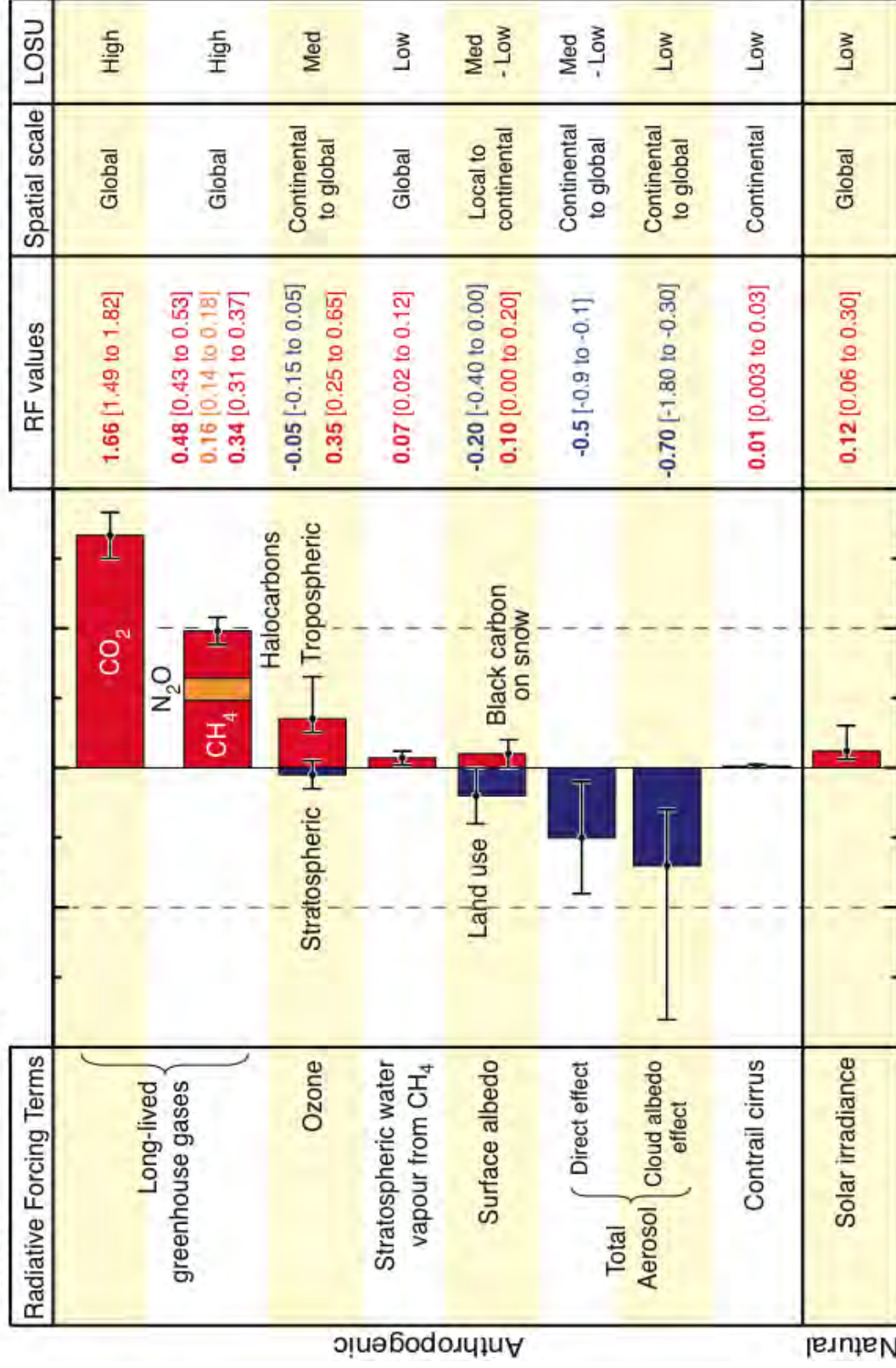
ΔF is *global-mean radiative forcing* (Wm^{-2})

λ is the poorly known *climate sensitivity parameter*
($\text{K}(\text{Wm}^{-2})^{-1}$)

Radiative forcing gives useful first order estimate of climate effect without resort to a complex climate model, and sidesteps uncertainty in climate sensitivity

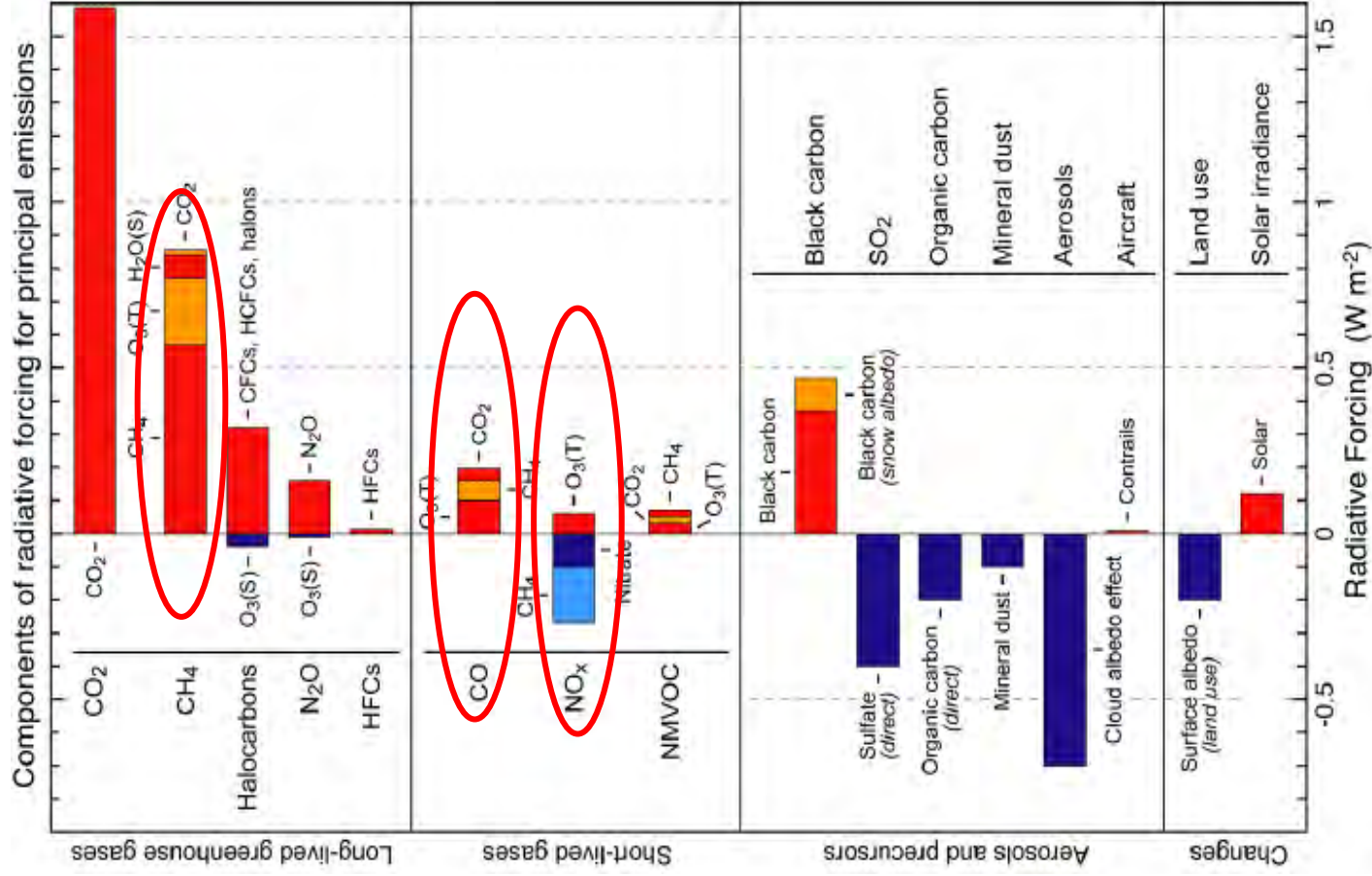
Global Mean Radiative Forcings

Panel A.



©IPCC 2007: WG1-AR4

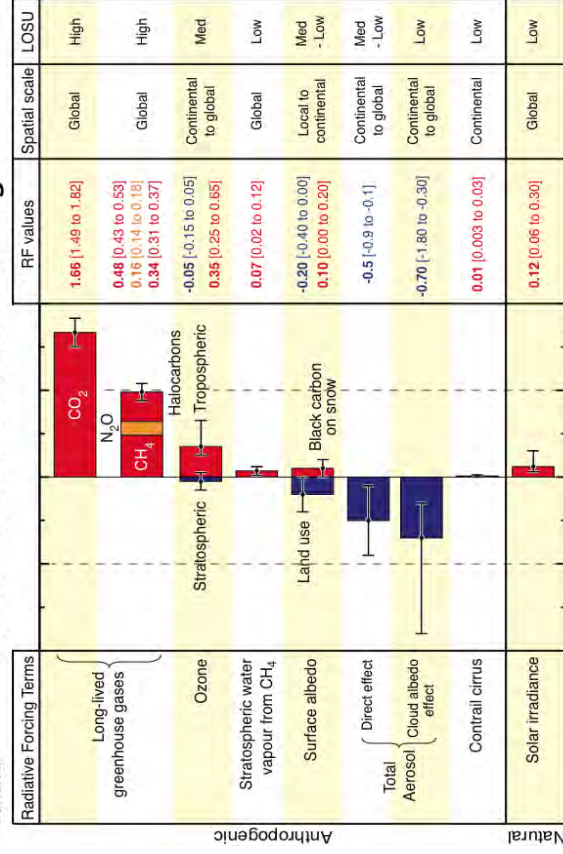
IPCC, 2007



A different view
of forcing, based
on *emissions*

Note methane,
CO, NO_x

Global Mean Radiative Forcings



©IPCC 2007: WG1-AR4

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UN Framework Convention on Climate Change, 1992

- UNFCCC requires that we stabilise atmospheric concentrations “at a level that would prevent *dangerous* anthropogenic interference with the climate system”
- Comprehensive approach: “measures should cover *all relevant sources*, sinks and reservoirs” and be “*cost effective*”

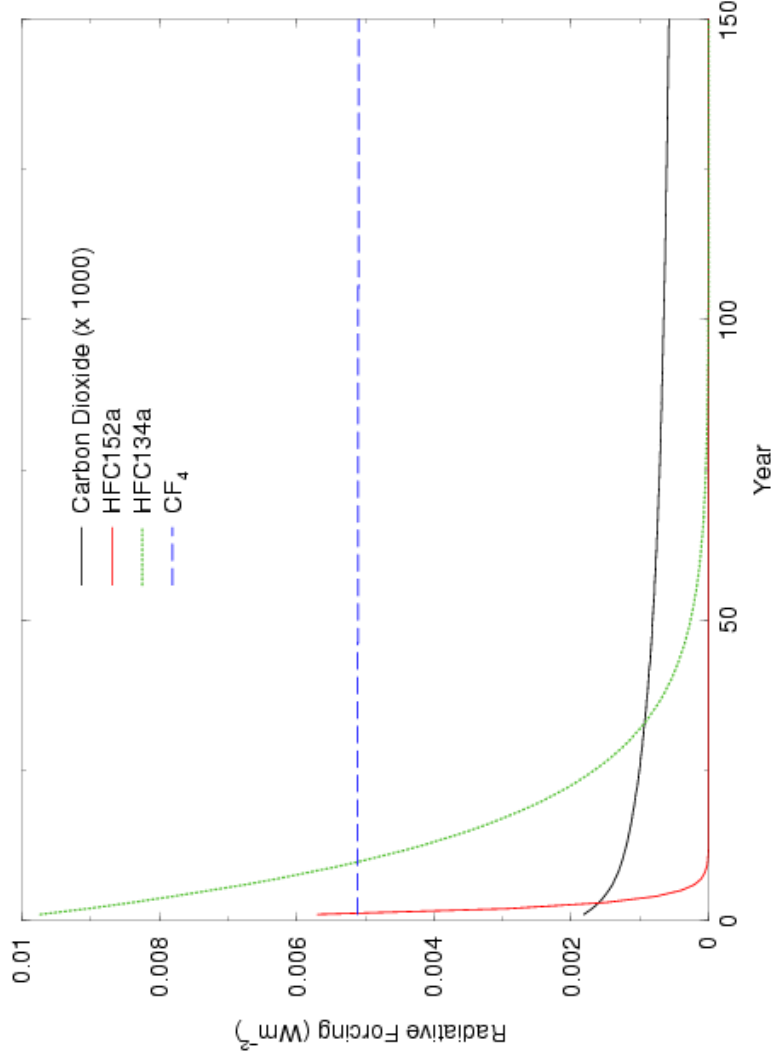
<http://unfccc.int>

Kyoto Protocol to UNFCCC, 1997

- The Kyoto Protocol commits signatories to control emissions of a range of gases: CO₂, CH₄, N₂O, HFCs, PFCs, SF₆
- Requires method to put emissions on a common scale
- Kyoto uses the Global Warming Potential (GWP) with a 100-year time horizon.
Widely accepted by the user community

What is the GWP?

Time-integrated radiative forcing following a pulse emission of a gas, normally relative to pulse emission of CO_2 .



But relative effect depends on choice of “time horizon” ... for CH_4 GWP varies from 72 for 20 years, to 25 for 100 years, to 8 for 500 years.

What kind of “equivalence” does the GWP give?

- Equivalence of emission reductions in GWP terms does not (necessarily) lead to equivalence in temperature change
- GWP is just one possible metric; it may not be the best – but what does “best” mean?

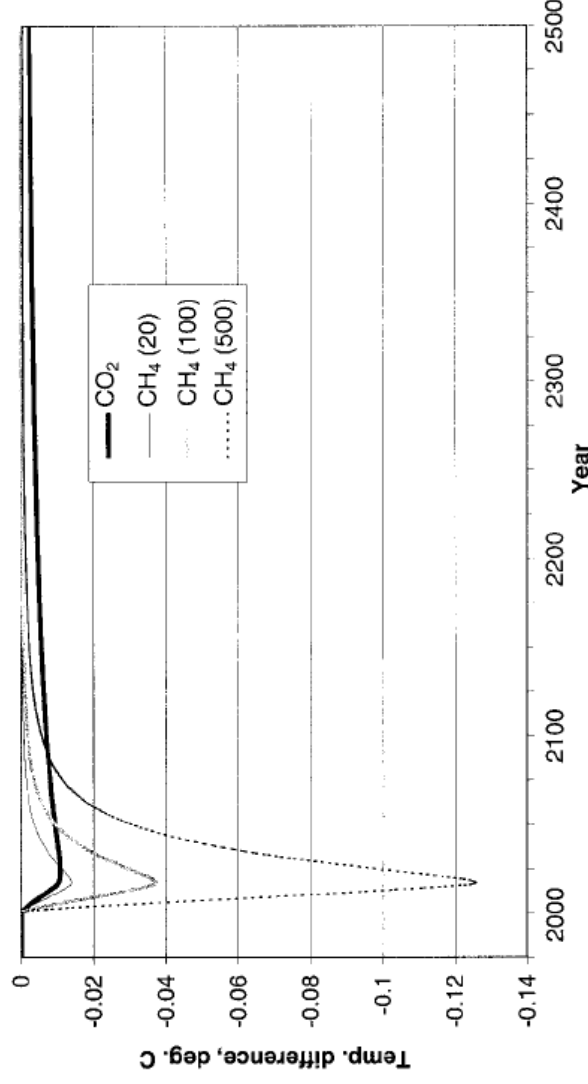


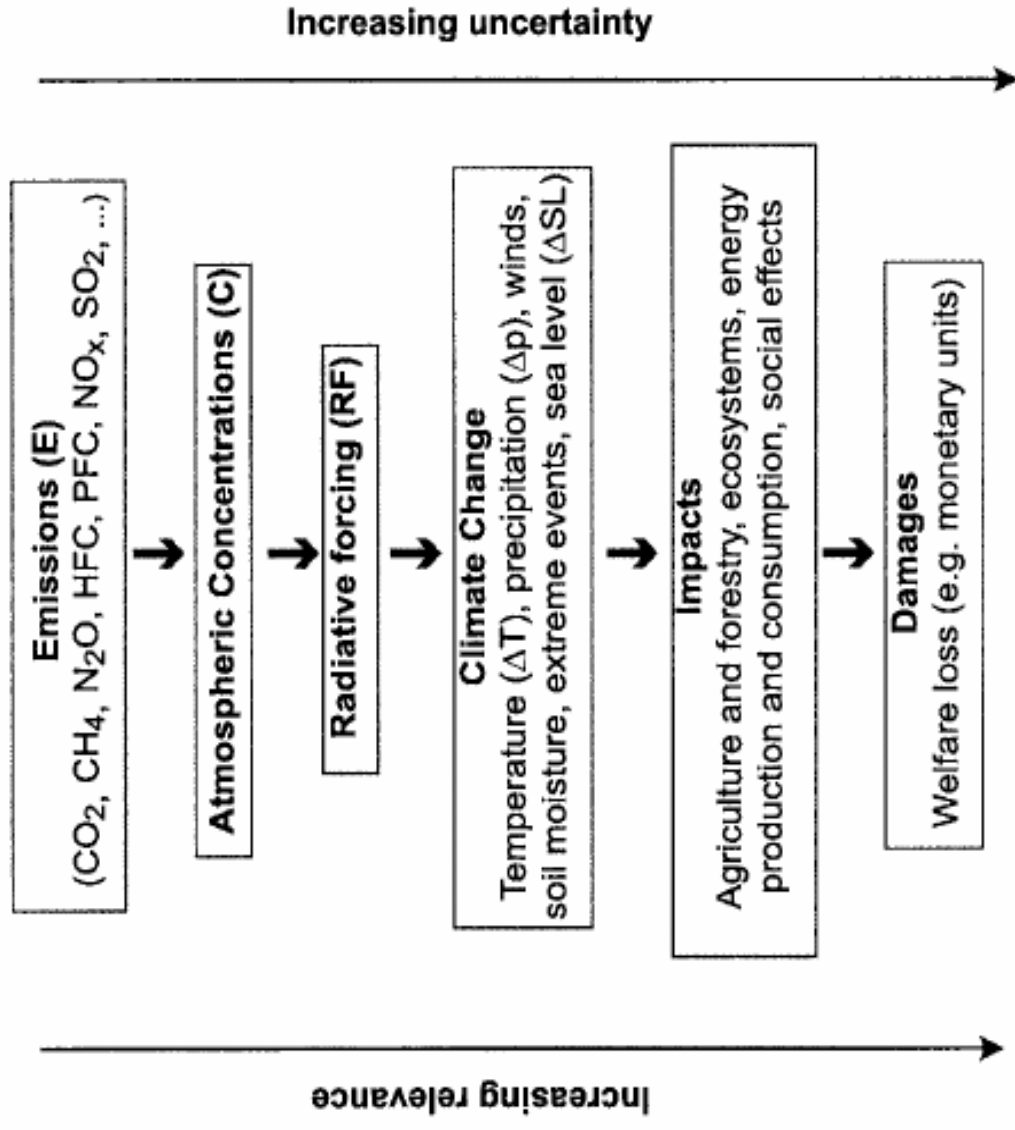
Figure 4. Temperature responses to sustained changes in emissions of CO₂ and CH₄ in terms of ‘CO₂-equivalents’ for various time horizons. The reductions are assumed to last for 15 years.

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Choice of climate impact

Trade-off:
relevance
VS.
certainty
&
feasibility



Choices for metrics

- What parameter? e.g. Δ forcing, Δ temperature, Δ sea-level, Δ damage ($\propto \Delta T^n$), or (d/dt) of these?
- What emission? Pulse, sustained,...?
- Value at a given time or integrated over a given "time horizon"?
- "discounted" so that changes in near-future are more important than changes in far-future ($\propto e^{-rt}$)?

The above choices affect decisions as to whether to it is best to cut short-lived or long-lived gases

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How aircraft can alter climate

- Carbon dioxide (CO_2) – “easy!”

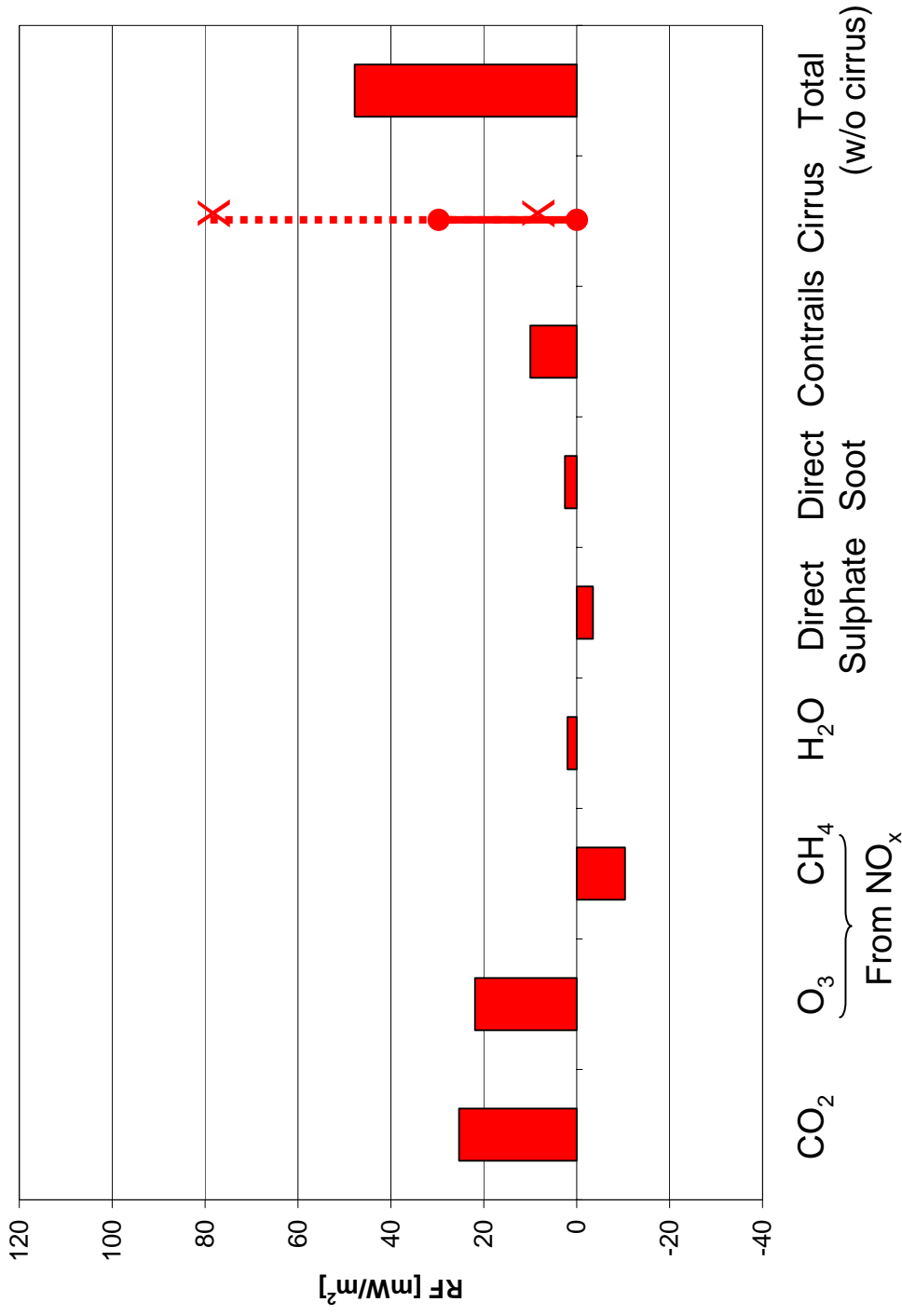
And the “non- CO_2 ” effects:

- Oxides of nitrogen – complicated!
- Contrails – uncertain!
- Aviation-induced cirrus – ugh!
- ...



- Massive range of different timescales
- And how do we compare one emission versus another when they are so different?

Radiative forcing from aircraft

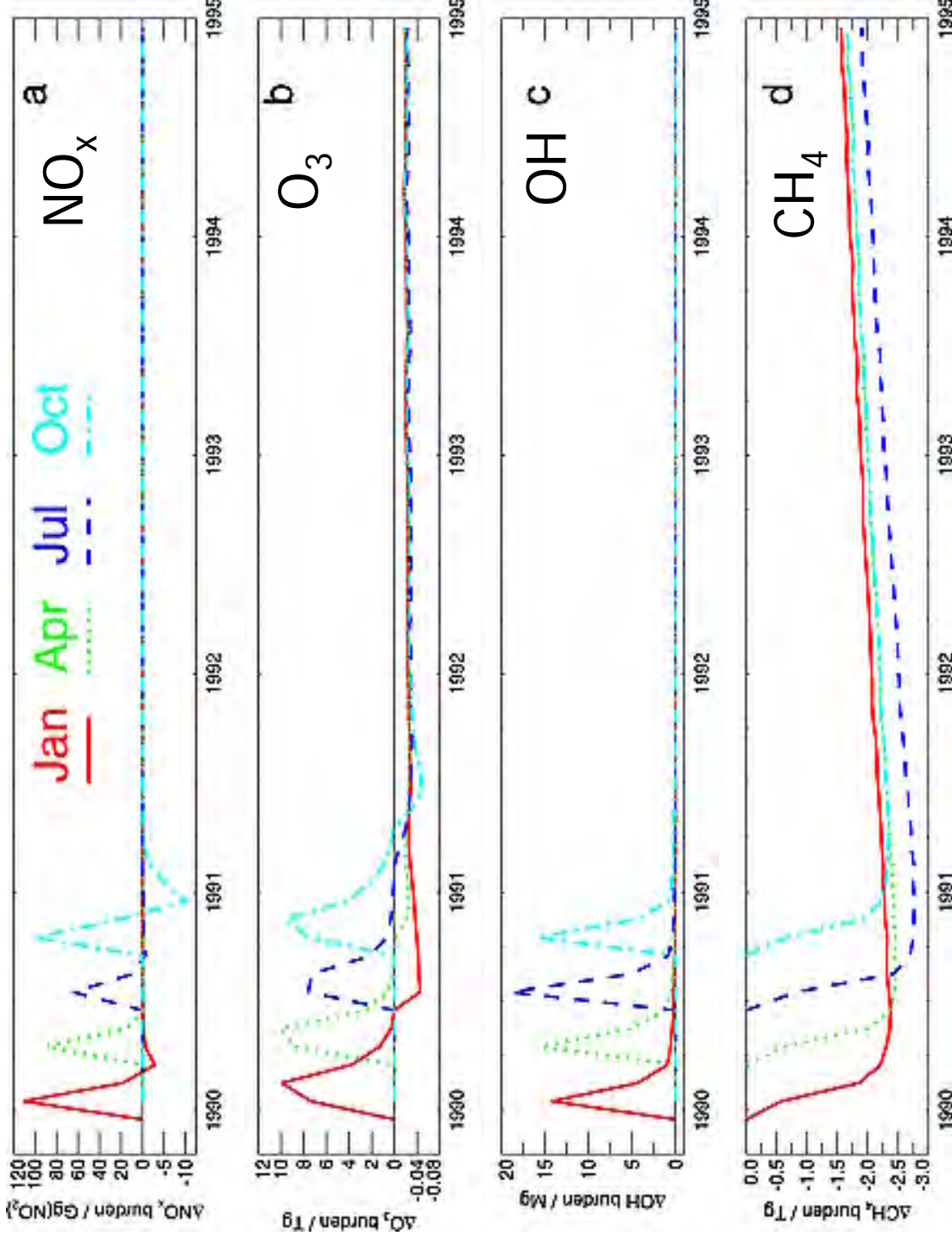


Level of scientific understanding

Good Fair Fair Fair Fair Fair Poor

Sausen et al 2005

Ozone-methane compensations due to NO_x aircraft emissions



Evolution of pulse emissions of aviation – offsets between ozone and methane (from Stevenson et al., J.Geophys.Res., 2004)

Oxides of nitrogen (NO_x)

- NO_x emissions lead to ozone *formation* – a greenhouse gas
- But *destroy* methane ... another greenhouse gas
- Which also leads to ... etc.
- The effect depends strongly on the height and location of the aircraft
- The ozone effect is mostly in northern hemisphere – the methane effect is global – to what extent do they really cancel?

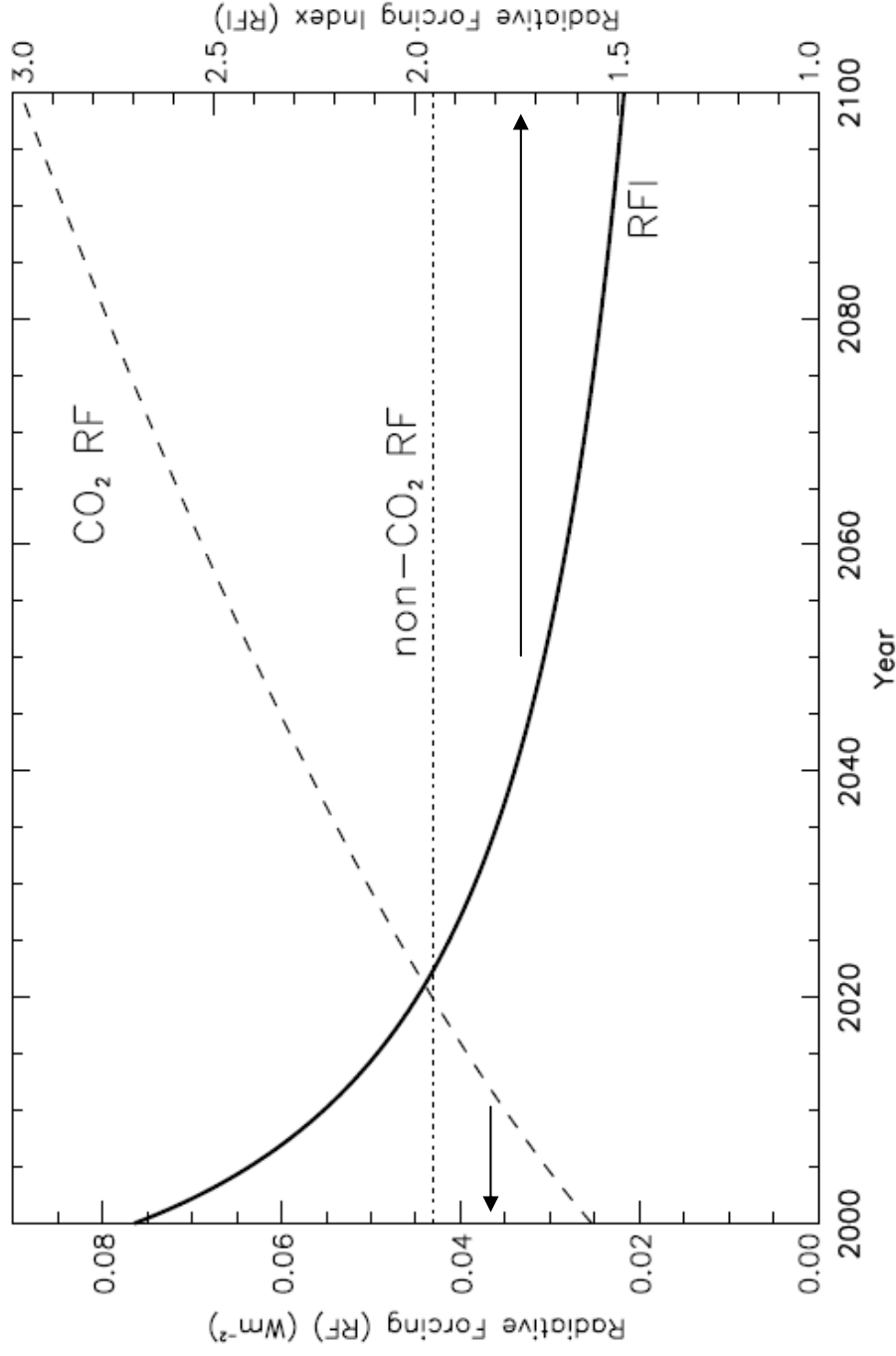
Contrails

- Different types ... short-lived and persistent
- Formation depends *strongly* on atmospheric conditions
- Quite subtle changes in altitude or location of aircraft can have big effects on contrail formation
- Contrails reflect sunlight (cooling) and trap infrared energy (warming) – makes calculating the net effect difficult
- Inadequate observations of some important contrail properties – extent, thickness, ...

The aviation multiplier ... the radiative forcing index (RFI)

- Some legislators and carbon-offset companies suggest multiplying the CO₂ emitted by aircraft by some factor – the so-called RFI - (e.g. 2.7) to account for the non-CO₂ effect
- Is this a “safe” thing to do? The non-CO₂ effects are short-lived, unlike the CO₂ effect
- “Equity” with other sectors?

Test of the RFI concept ...



Other forcings quickly in equilibrium – but CO_2 continues to rise

A tentative attempt at a "rational" aviation weighting

Time horizon (2000 start) (year)	CO ₂	CH ₄ and O ₃		Contrail	CO ₂
	AGWP	NET	AGWP	AGWP	EWF
1	0.25	1.94	1.8	1.8	16
20	2.65	0.34	1.8	1.8	1.8
100	9.15	-0.038	1.8	1.8	1.2
500	29.9	-0.038	1.8	1.8	1.1

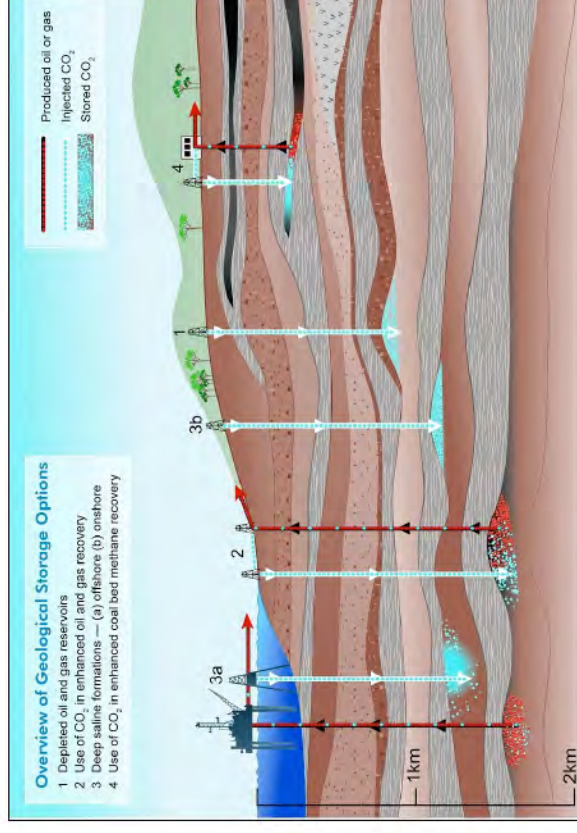
Units of AGWP are $10^{-14} \text{ W m}^{-2} \text{ kg CO}_2^{-1} \text{ year}$. The appropriate CO₂ Emission-Weighting Factor (EWF) for the total aviation effect at the given time horizon is given in the last column. This is the sum of the middle three columns divided by the CO₂ AGWP.

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Carbon Capture and Storage

With thanks to my collaborators: **Emma Stone** (now University of Bristol) and **Jason Lowe** (Hadley Centre, Met Office (Reading)) – all figures from Stone et al. (submitted 2007)



(IPCC 2005)

Problem

- Carbon capture and storage requires energy! i.e. the generation of a given amount of energy from fossil-fuel means extra CO₂ is produced
- But CO₂ will leak out of its storage reservoirs
- **Can we be sure that CCS doesn't lead to *increased* CO₂ in the atmosphere?!**

Approach

- Couple together three simple models:

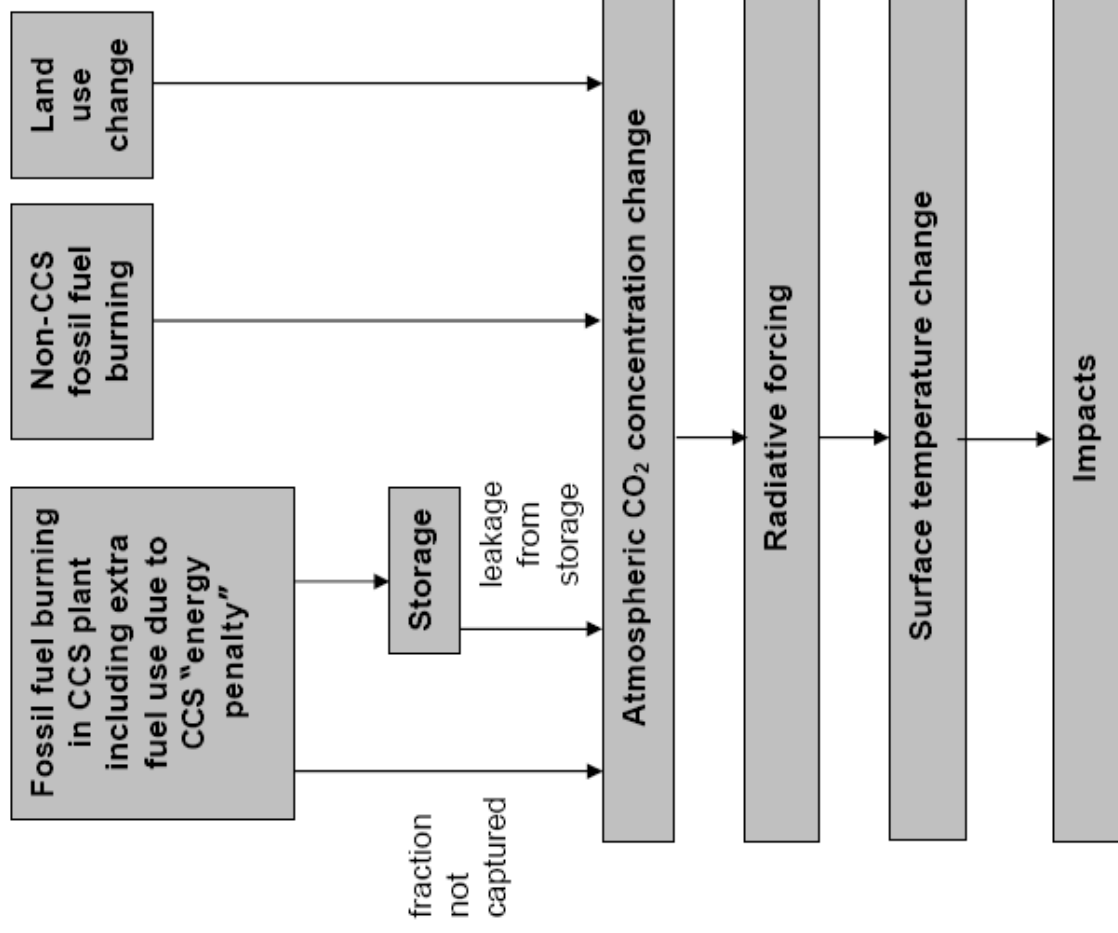
A carbon capture model

A carbon cycle model

A climate model

- Search parameter space of uncertainties

...



Key inputs to CCS model

- *Energy penalty*: fractional increase in CO_2 production for a given energy generation due to implementation of CCS
- *Fraction of CO_2 captured*: in an individual CCS plant, how much of the CO_2 is actually captured, rather than emitted directly to the atmosphere?
- *Leakage rate of CO_2 from reservoir (or transmission to reservoir)*: Express as a time constant in years ... and assume steady rather than catastrophic loss

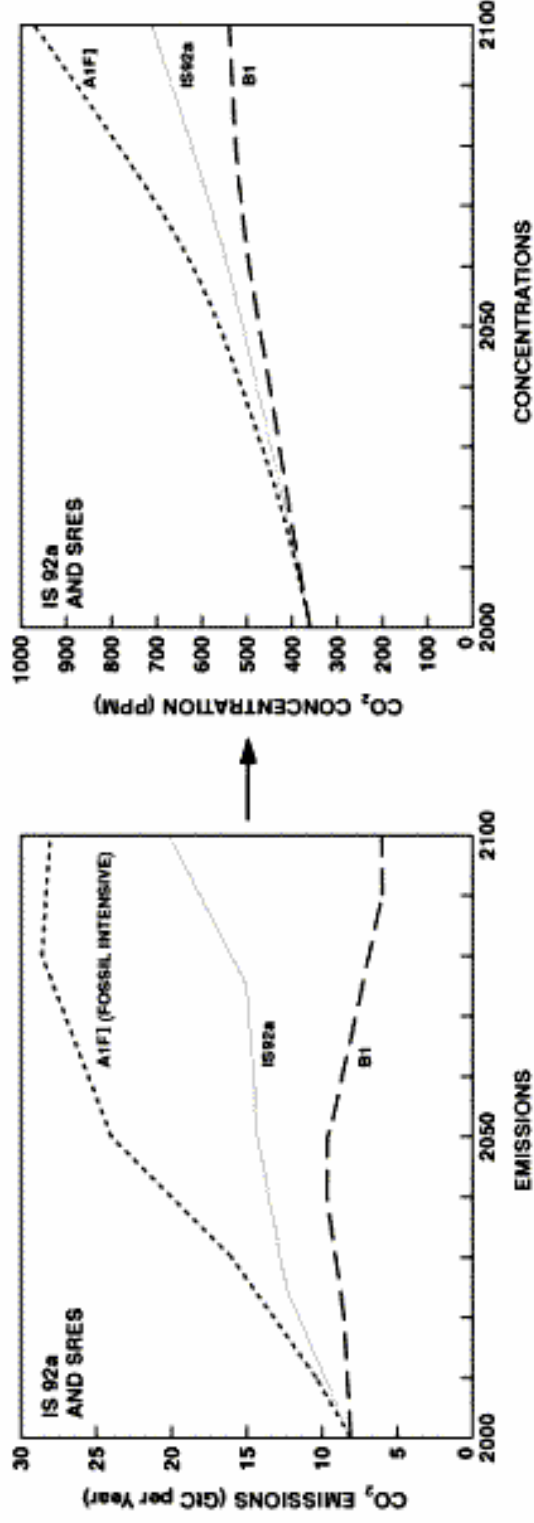
We assume a single value for each and ignore the fact that these will be time dependent as technology improves ...

Chosen Parameter Space

Retention time, τ (years)	Energy penalty, α	Fraction of fossil fuel emissions released from a single CCS plant, β	Fraction of global fossil fuels emissions subject to CCS, γ
10	0.10	0.05	0.25
40	0.25	0.1	0.50
100	0.40	0.15	
500			
1000			

Emission scenarios

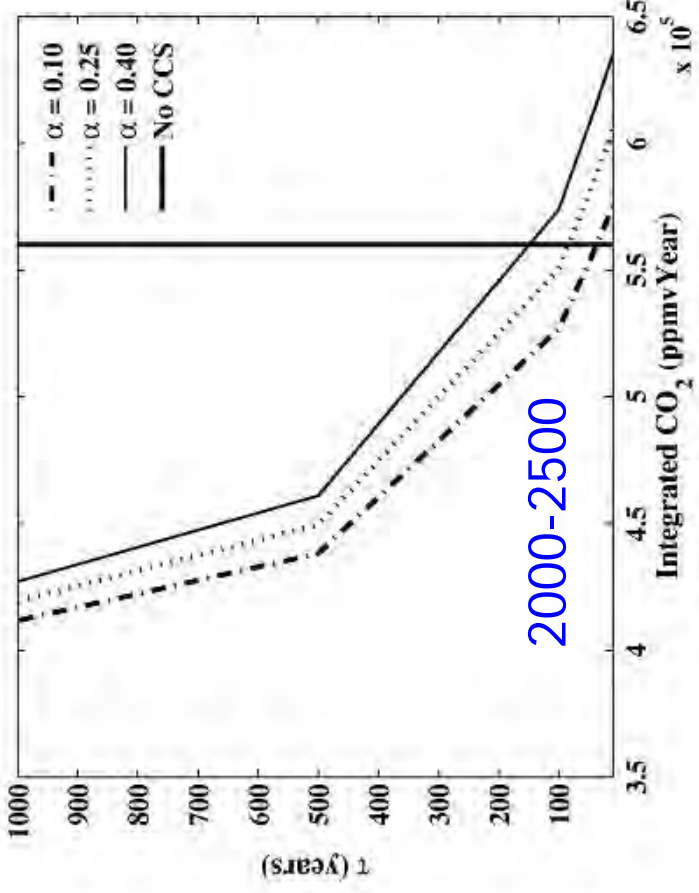
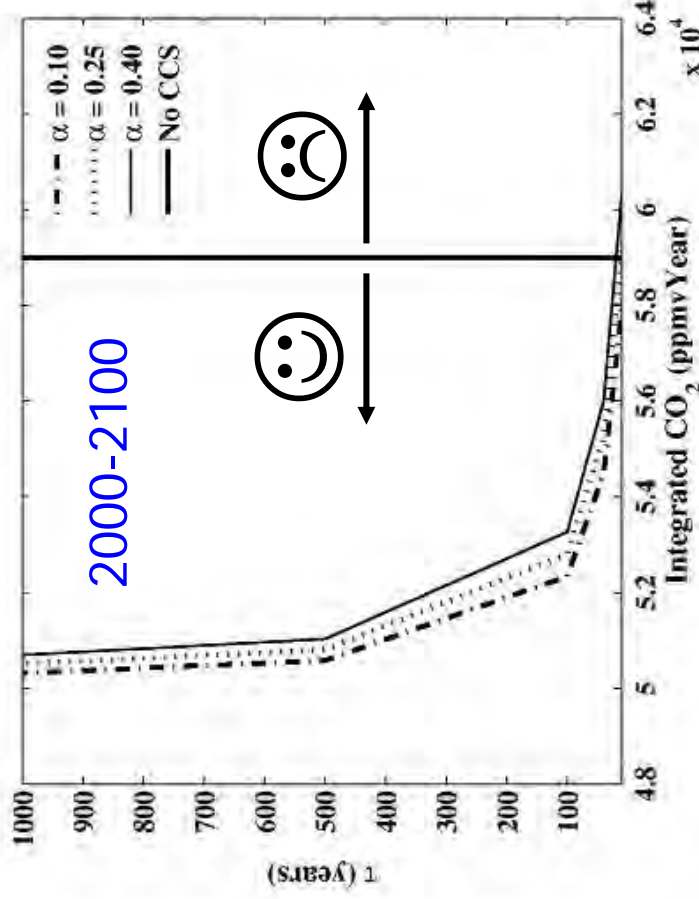
Need to specify the background emission scenario on which the CCS operates – assume two quite “extreme” cases – a fossil-fuel intensive world and a “greener” world from IPCC scenarios



How do we measure effectiveness of CCS?

- Need to choose timescale ... here we use 2000-2100 and 2000-2500 (!)
- Need to choose metric ... we use time-integrated CO₂ concentration, time-integrated radiative forcing and time-integrated temperature change (and compare calculations with and without CCS)

Integrated CO₂



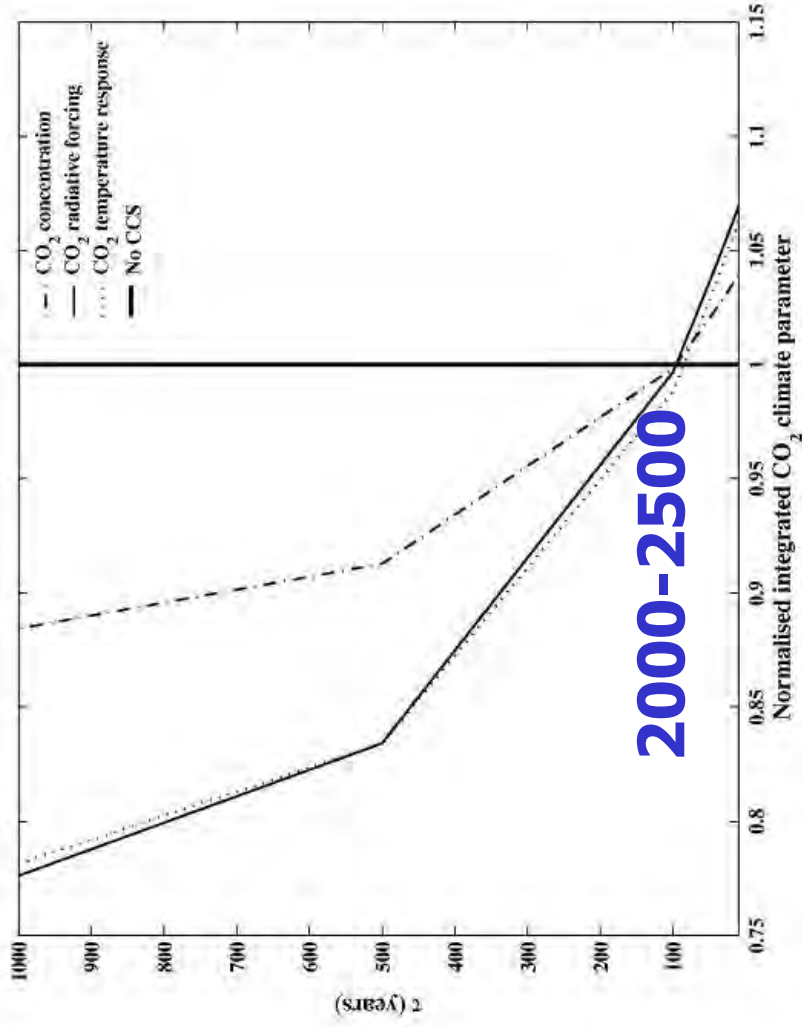
α is the energy penalty

Benefit of increase in retention time decreases with retention time

For the longer time period, greater retention times are necessary for break-even

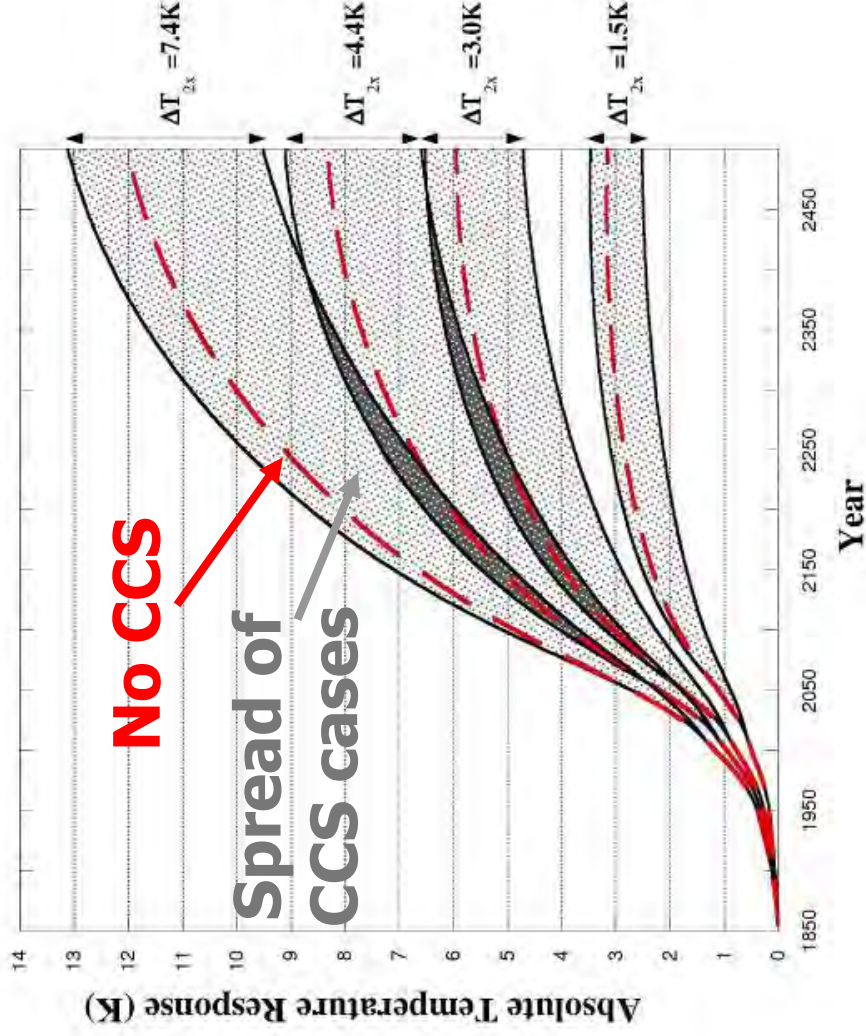
Impact of using other metrics

- Little impact on the “break-even” reservoir retention time, but the perceived fractional benefit varies.



Effect of uncertainty in climate sensitivity

- Example of “fossil intensive” scenario
- Over shorter time periods, almost all CCS cases are beneficial – less so, over long time periods
- Absolute benefit depends on climate sensitivity (and on emissions scenario)



Break-even retention times (in years) for 2000-2500 integrated CO₂

Scenario		Alpha	
	<i>0.1</i>	<i>0.25</i>	<i>0.40</i>
A1FI	36	83	125
B1	42	96	144

Obviously, the greater the energy penalty, the more stringent conditions there are on reservoir leakage

Conclusions

- In general, no clear consensus on which metrics are to be used to compare different emissions – nor obvious choice of which “time horizon” is appropriate
- For CCS, our *simple* model indicates that provided reservoir times are greater than about 200 years, CCS should be beneficial

*Future Energy: Chemical Solutions
12-14 September, 2007*

RSC | Advancing the
Chemical Sciences

Carbon sequestration in sediments containing ferric iron

September 13, 2007

Susana Garcia and
M. Mercedes Maroto-Valer

School of Chemical and Environmental Engineering,
Nottingham, United Kingdom



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Outline

Introduction

- Carbon dioxide capture and storage (CCS)
- CO₂ geological storage
- Estimates of CO₂ storage costs

Part 1

- Ferric-iron bearing sediments
- Objectives
- Study samples

Part 2

- Research plan
- Novel experimental set-up and methodology
- Preliminary results

Conclusions



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CO₂ capture and geological storage

1. Capture from a large point source
2. Injection into suitable deep rock formations



A **FOUR STEP** PROCESS:

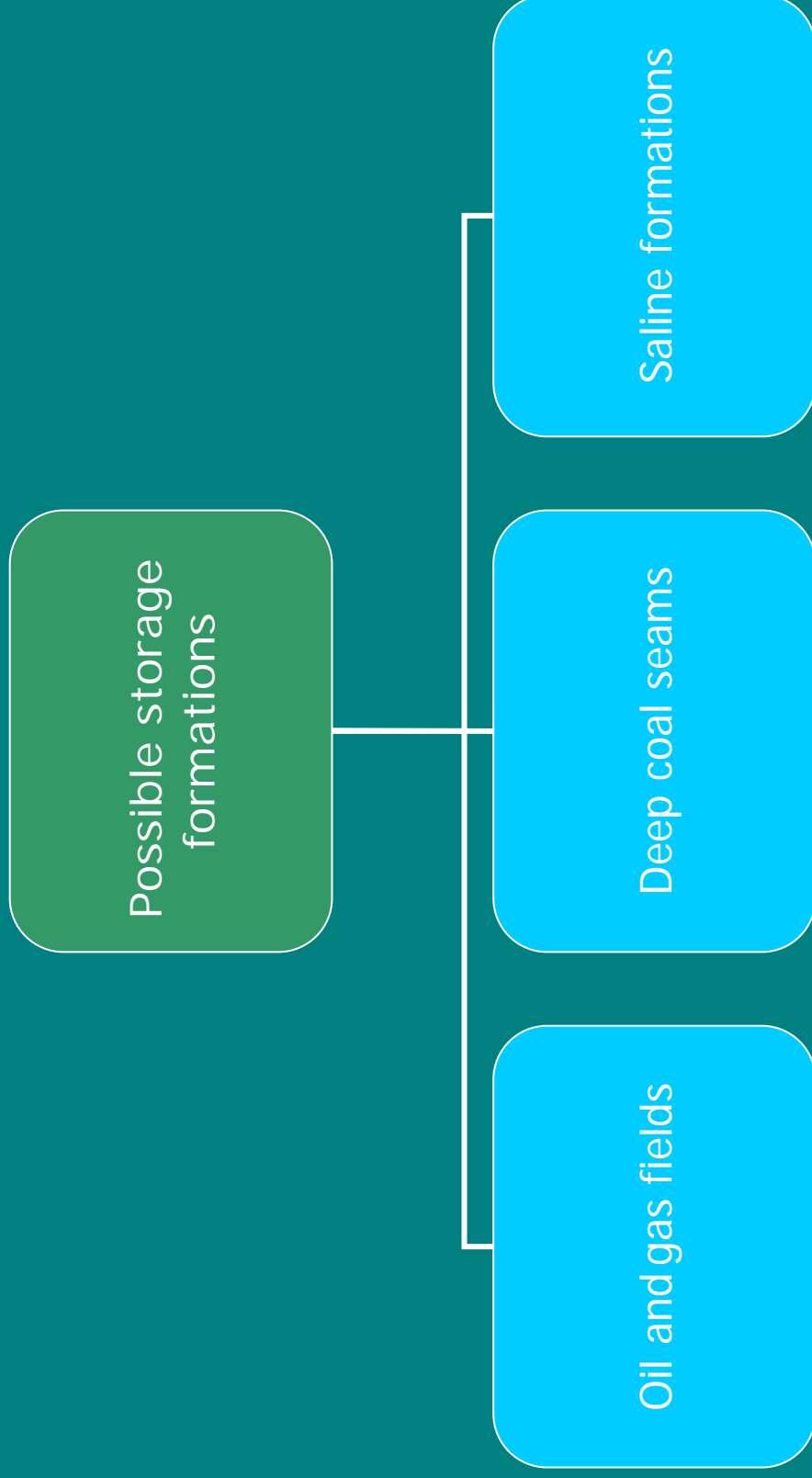


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CO₂ Geological Storage



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Global capacity of geological reservoirs

Emissions from combustion of fossil fuels = 22 Gt CO₂/year

Reservoir type	Lower estimate of storage capacity (GtCO ₂)	Upper estimate of storage capacity (GtCO ₂)
Oil and gas fields	675 ^a	900 ^a
Unminable coal seams (ECBM)	3-15	200
Deep saline formations	1,000	Uncertain, but possibly 10 ⁴

^a These numbers would increase by 25% if 'undiscovered' oil and gas fields were included in this assessment.

Source: IPCC Special Report on CCS, 2005

Estimates of CO₂ storage costs

Option	Representative Cost Range (US\$/tonne CO ₂ stored)	Representative Cost Range (US\$/tonne C stored)
Geological - Storage ^a	0.5-8.0	2-29
Geological - Monitoring Ocean ^b	0.1-0.3	0.4-1.1
Pipeline Ship (Platform or Moving Ship Injection)	6-31 12-16	22-114 44-59
Mineral Carbonation ^c	50-100	180-370

^a Does not include monitoring costs.

^b Includes offshore transportation costs; range represents 100-500 km distance offshore and 3000 m depth.

^c Unlike geological and ocean storage, mineral carbonation requires significant energy inputs equivalent to approximately 40% of the power plant output.

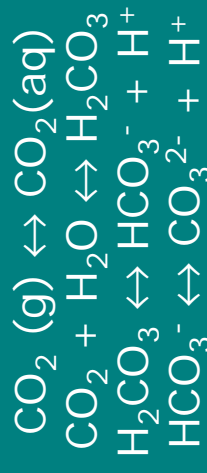
Source: IPCC Special Report on CCS, 2005

CO₂ Geological Storage

- CO₂ storage mechanisms in geological formations

Physical trapping: Hydrodynamic trapping

Geochemical trapping:



1. Solubility trapping \rightleftharpoons

2. Mineral trapping \rightleftharpoons




- Sediments considered so far:

Ca-bearing arkosic

Mg-bearing illitic

FeI-bearing glauconitic

Ferric-iron bearing sediments

- Their potential usage has been suggested lately (*Palandri, J.L. et al, 2005*)
 - Advantages versus sediments considered so far:
 - Widespread geographic distribution and great thickness
 - High porosity and permeability
 - Less expensive/less energy demanding CO₂ capture process
- 
- SO₂
- Reductant agent needed for the process to take place



Acid gas injection

- Acid gas: mixture of H_2S and CO_2 with minor amounts of hydrocarbon gases
- It occurs at 44 different locations across the Alberta Basin (Alberta and British Columbia)



Mature and safe technology

HOWEVER...

- It has not been developed as a CO_2 sequestration approach
- More research is needed



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Reaction of CO₂-SO₂ gas mixtures with ferric iron and water

- Dissolution process



- Reduction process



- Carbonation process



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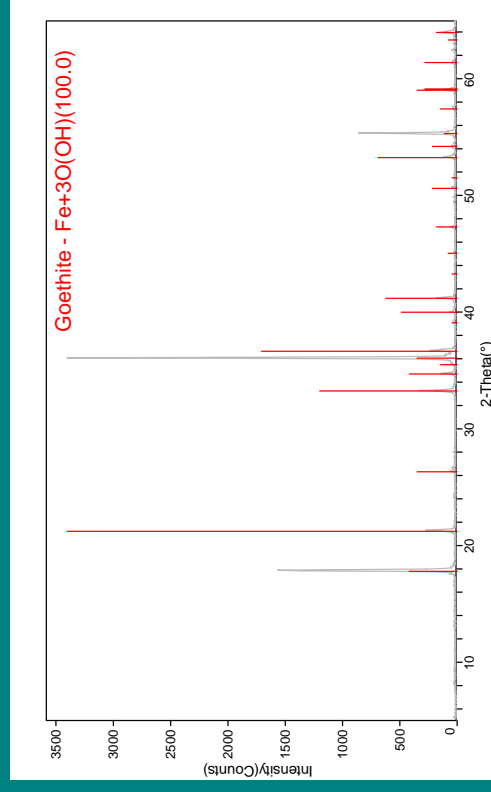
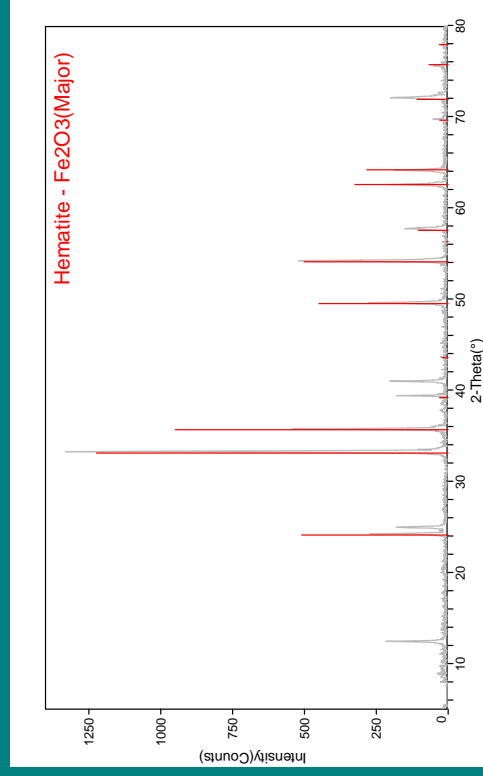
Objectives

- Laboratory studies to proof the ferric-iron bearing sediments potential for CO₂ underground storage
- Experimental set-up design to run tests under different geochemical conditions
- Research plan and development of the methodology



Study samples

- Previous researchers: Hematite sample from Gerais mines (Brazil)
- This research:
 - Hematite sample from Shishen mine (South Africa)
 - Goethite sample from El Paso County, Colorado (US)
 - Future samples: olivine, serpentine, granite and sandstone



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Research plan

Theoretical equilibrium geochemical simulations

Laboratory studies:

1. Reductive dissolution of iron oxides

CO₂/SO₂ ratio (boiler, experiment, stoichiometric)

Reaction time (1 day, 1 week, others)

Solids concentration (25g/L, 67g/L, 100g/L)

Reaction temperature (50°C, 100 °C, 150 °C)

Reaction pressure (100 bar, 200 bar, 350 bar)

Particle size (<38 µm, 38-150 µm, 150-300 µm)

2. Carbonation conditions

3. Optimization of reductive dissolution and carbonation processes



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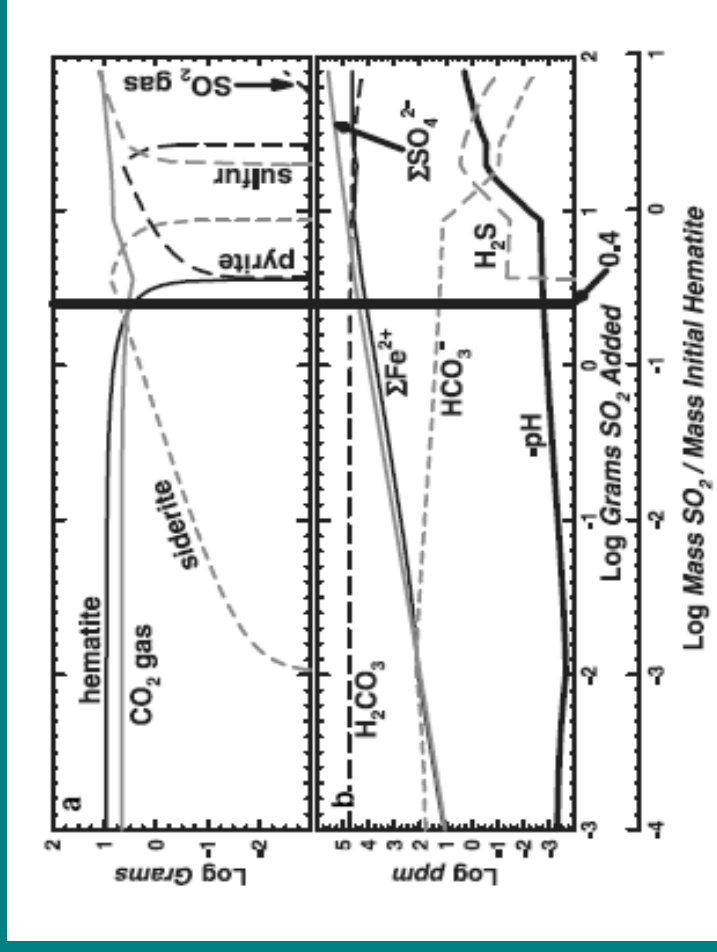
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Theoretical equilibrium geochemical simulations

Computer program: Chiller

Compute reaction path in geologic systems by changing one of the systems variables incrementally and re-computing equilibrium at each step.

Follow-up of work by
Palandri J.L, Rosenbauer
R.J. and Kharaka Y.K.



Results summary from simulation at 150°C and 300 bar of the CO₂-SO₂ reaction with 10 gr of hematite in 156 gr of 1.0M NaCl brine using 14 gr (excess) CO₂ (Palandri J.L. et al, 2005)

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Previous experimental work

- **Experimental apparatus**

Autoclave containing a flexible Au-Ti reaction cell with ~ 200 ml total volume.

- **Experimental conditions**

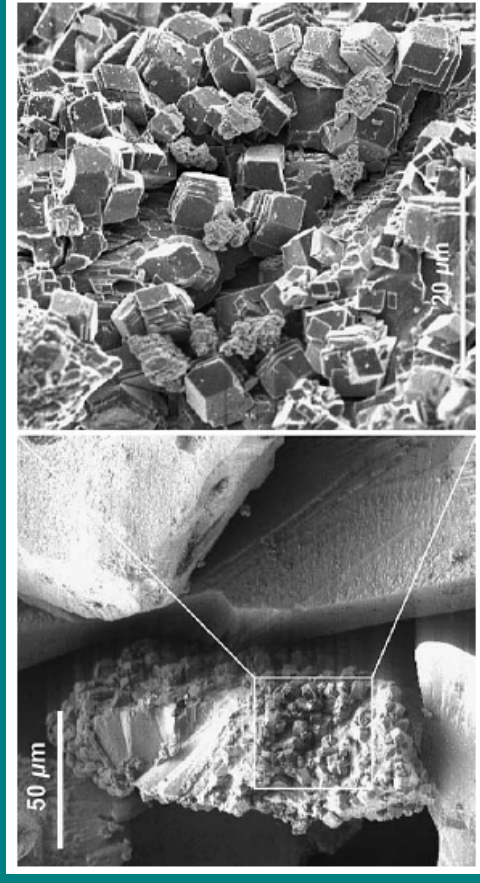
Temperature = 150°C

Pressure = 300 bar

CO₂/SO₂ ratio ~ 9:1

Brine volume (1.0 m NaCl) = 150 ml

Solids concentration = 67 g/L



Experimental results, solids: siderite on etched hematite (Palandri J.L. et al, 2005)

Only **ONE** experiment reported so far ...

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CO₂/SO₂ ratios

• Boiler ratio

	By Mass		By Volume	
	From boiler	Stack	From boiler	Stack
CO ₂	17.527%	17.159%	11.765%	11.340%
N ₂	70.204%	68.559%	73.987%	71.137%
Ar	1.188%	1.160%	0.878%	0.845%
O ₂	6.531%	6.374%	6.030%	5.795%
H ₂ O	4.447%	6.739%	7.291%	10.879%
SO ₂	0.101%	0.009%	0.046%	0.004%
HCl	0.002%	0.000%	0.002%	0.000%
	100.000%	100.000%	100.000%	100.000%
0.68% Sulphur Coal				



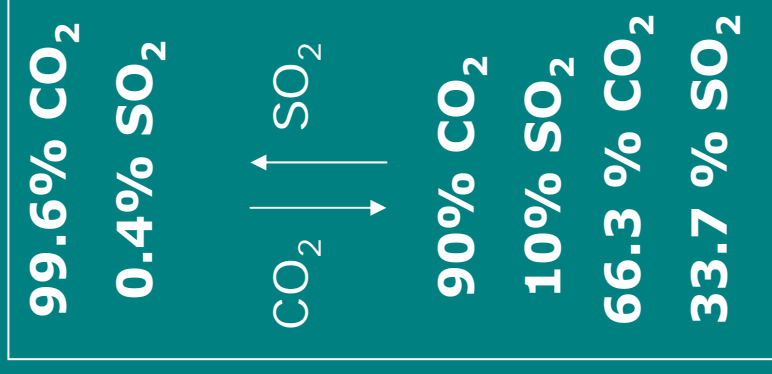
• Experiment ratio

CO₂/SO₂ ~ 9:1



• Stoichiometric ratio

2 mol CO₂
1 mol SO₂



AND...What about the SO₂ needed?

Significant limitation: Flue gas typically contains less than 5%wt SO₂

Various options to overcome the problem:

1. Targeted sediments must contain other divalent metals (e.g., Ca, Mg, Fe^{II}).
2. Reduced S-bearing waste gas derived from other industrial processes could be added to the waste gas stream, e.g., H₂S from sour natural gas processing.



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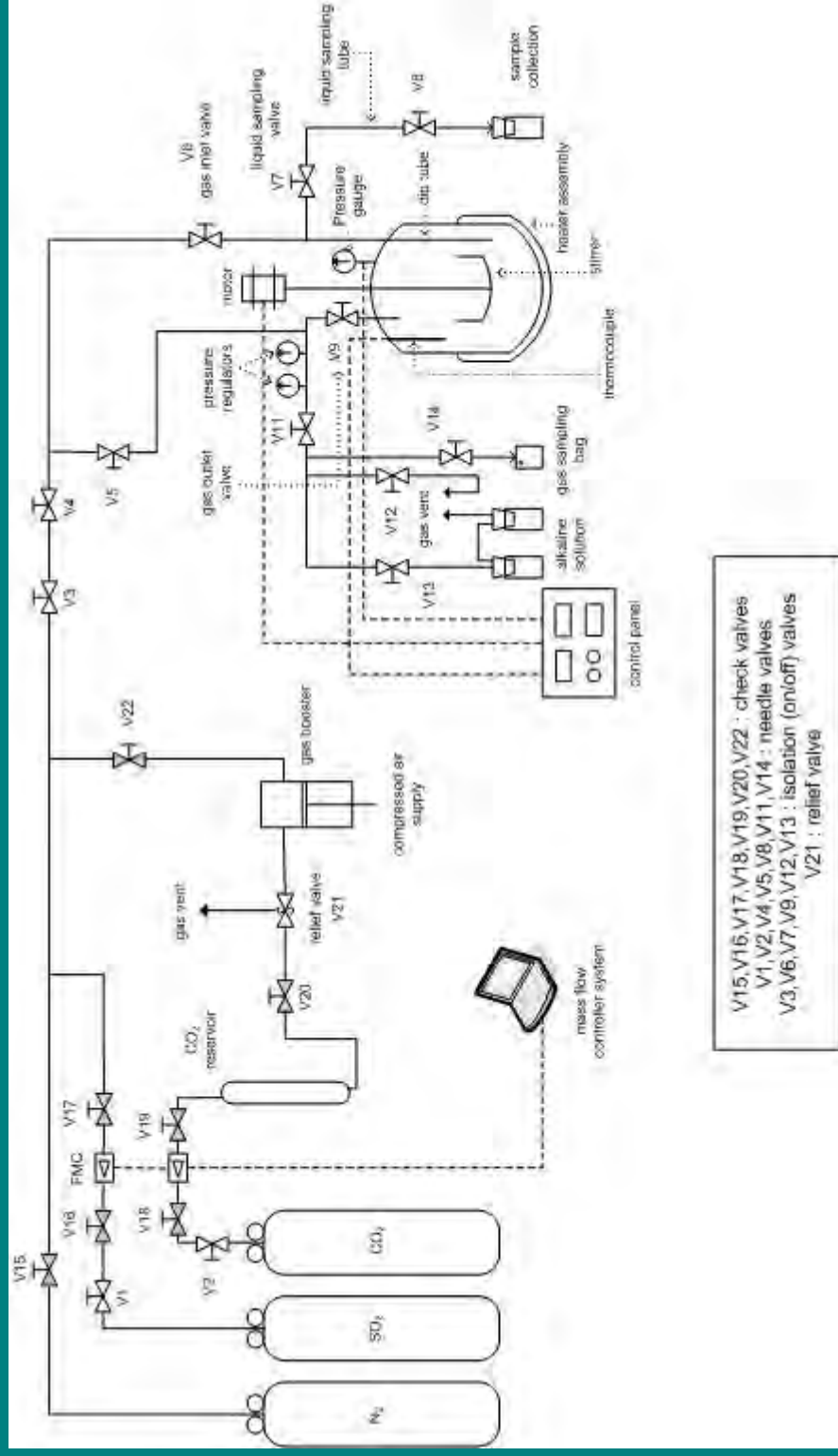


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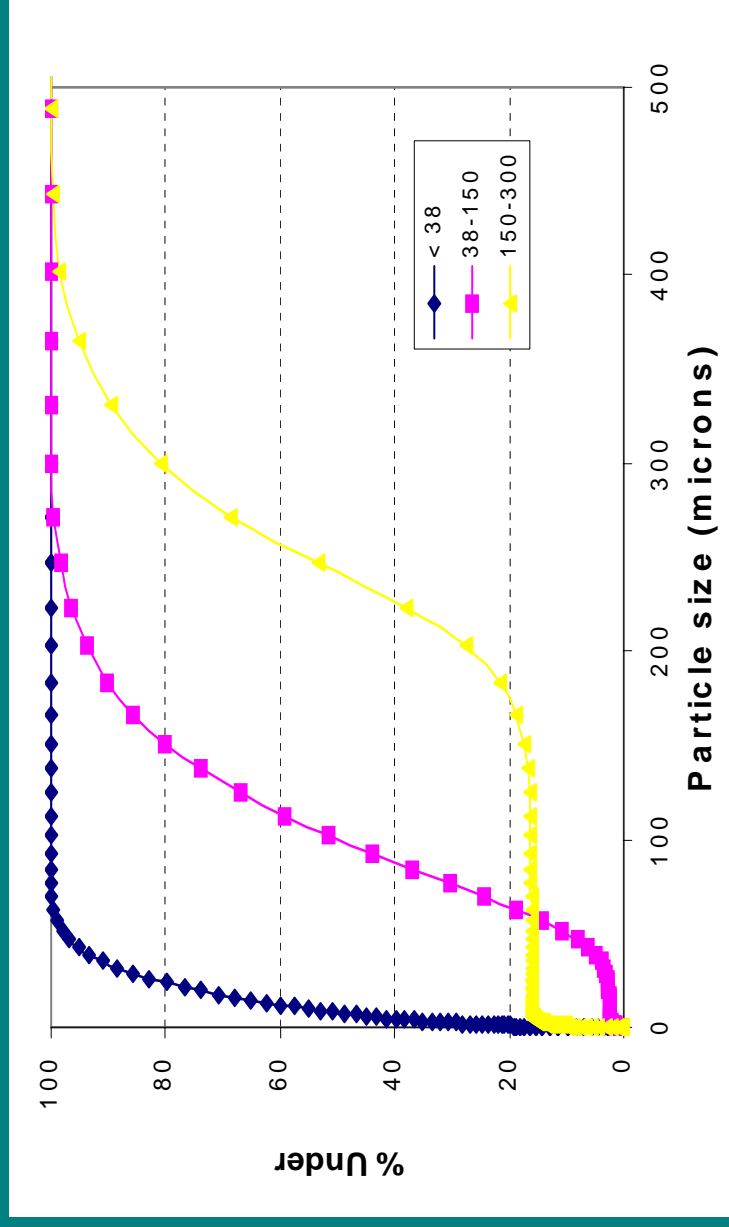
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Novel experimental set-up and methodology



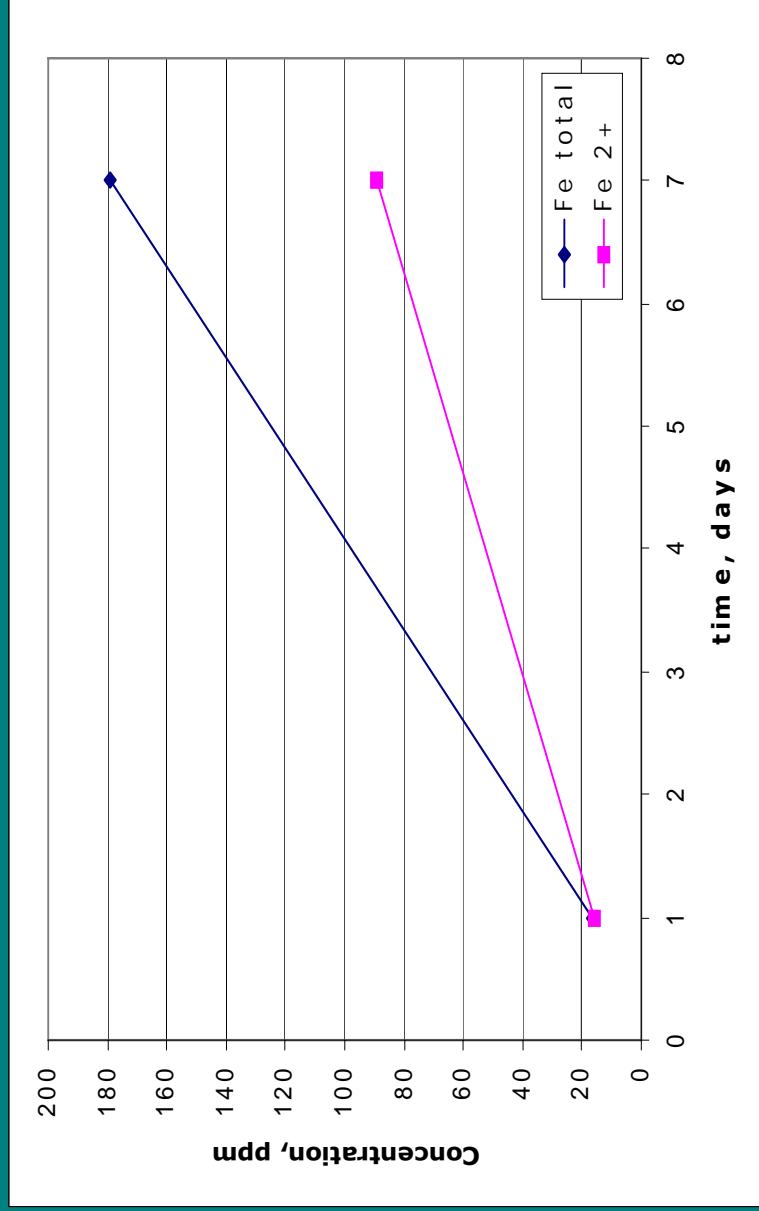
Preliminary results

Particle size distribution



Preliminary results

Experimental conditions			
T = 100 C P = 269 bar particle size = 38x150 100% CO2 solids concentration = 25 g/L stirring speed = 350 rpm			
time, days	final pH	mass removal, wt %	
1	5.25	1.5	
7	5.43	5	



Conclusions

- Experimental work is needed to assess the ferric-iron bearing sediments potential to become effective reservoirs for underground CO₂ storage.
- A state-of-the-art experimental set-up has been designed and assembled to test previous theoretical work.
- Different iron oxide samples have been obtained and characterized as well as other silicate samples already considered for CO₂ sequestration.
- This research will provide empirical and novel data concerning CO₂/SO₂ injection into saline aquifers with different rock formations.
- Data will help validation of the different geochemical simulations already conducted within the acid gas injection research field.



Acknowledgements

The work presented within this paper was supported by the School of Chemical and Environmental Engineering at the **University of Nottingham**.

The authors would also like to thank **R. Rosenbauer** and **J. Palandri** for their support in this research.



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Amine scrubbing for CO₂ capture from power plant flue gas

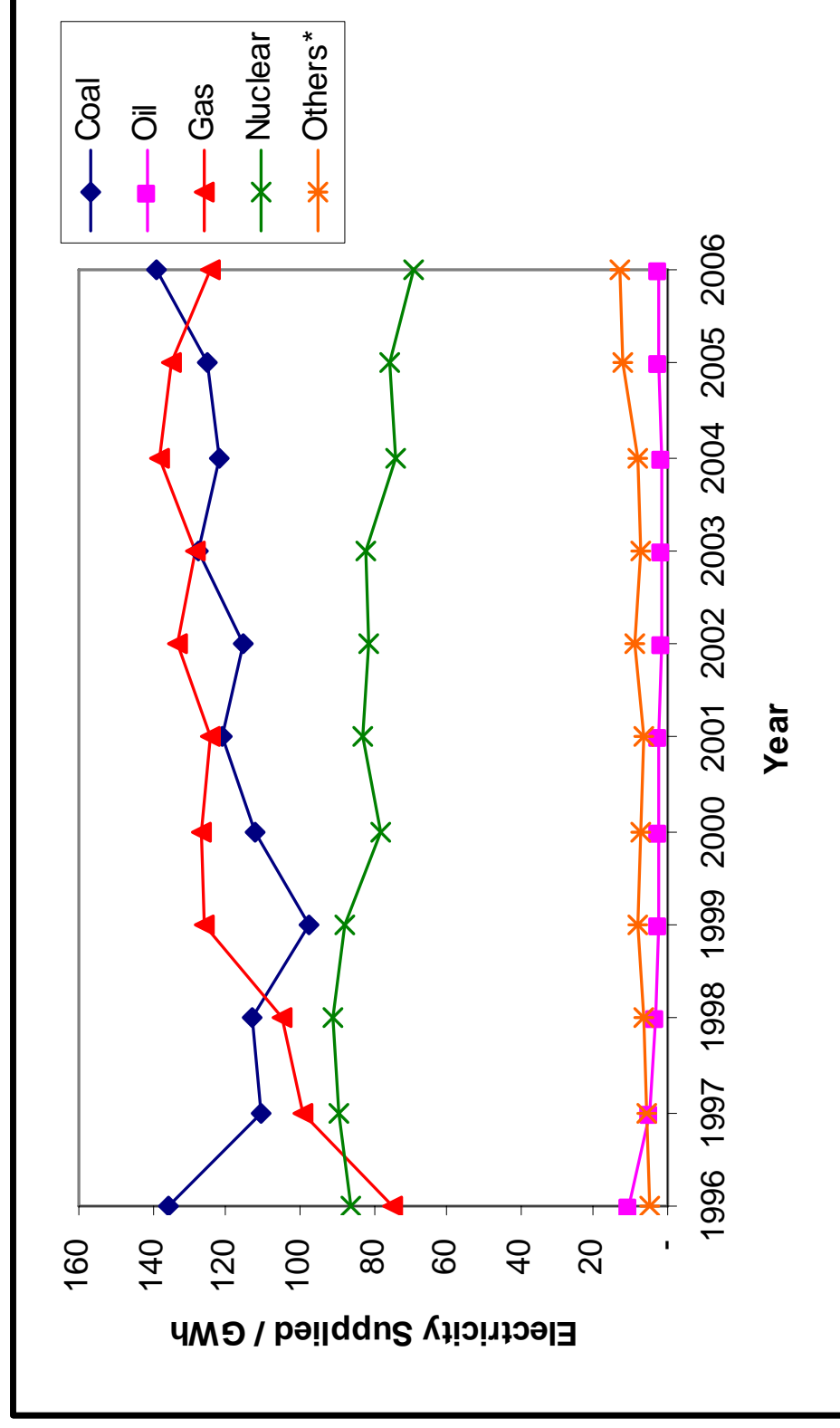
Nick Booth

Future Energy: Chemical Solutions
12-14th September 2007

Overview

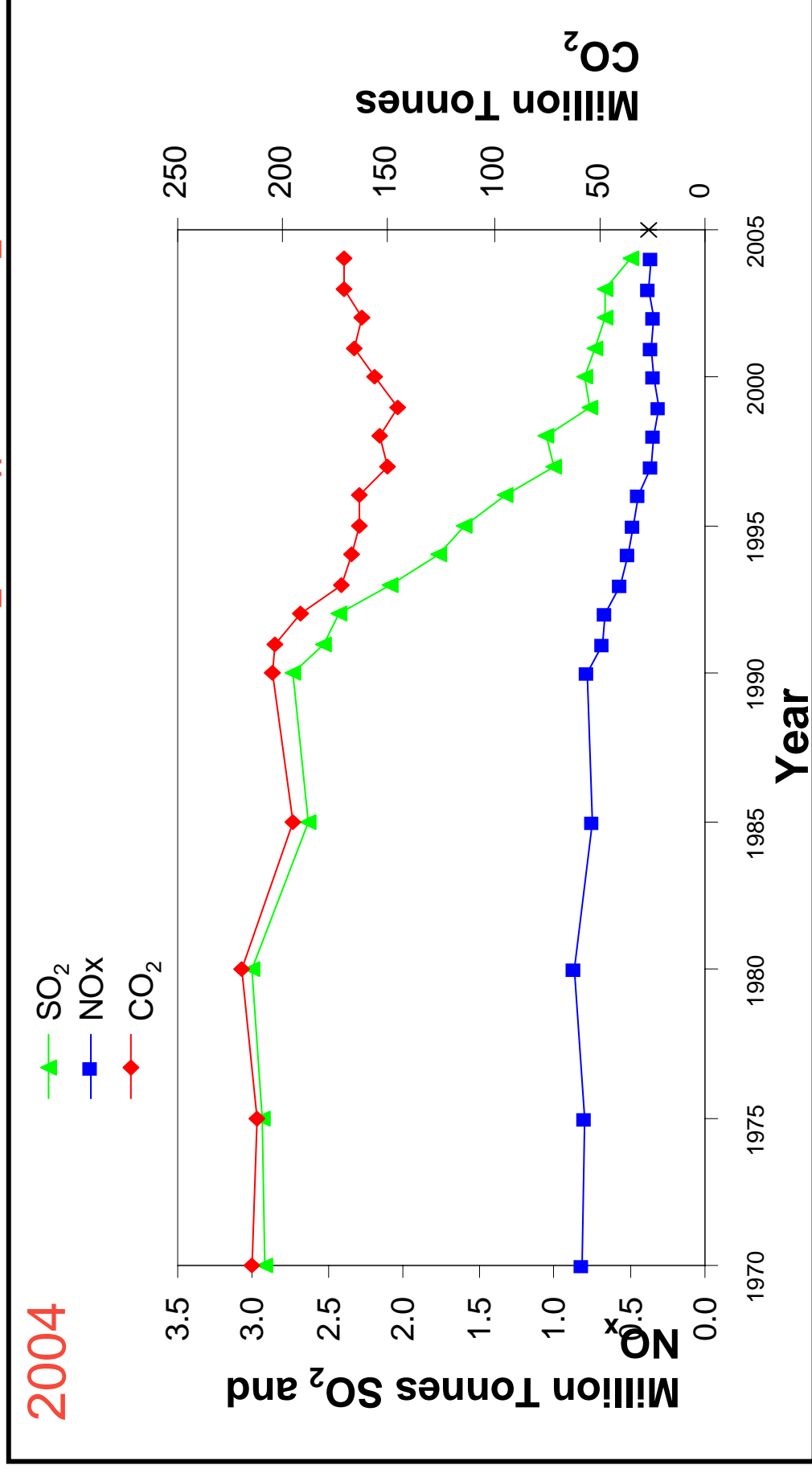
- UK Electricity production by fuel type
- Reducing power station CO₂ emissions
 - Track 1: Efficiency
 - Track 2: Carbon capture and storage
- Amine scrubbing process and chemistry
- Advantages and challenges
- Development activities
- Conclusions

UK electricity supply 1996 – 2006 by fuel type



Source: http://stats.berr.gov.uk/energystats/dukes5_6.xls

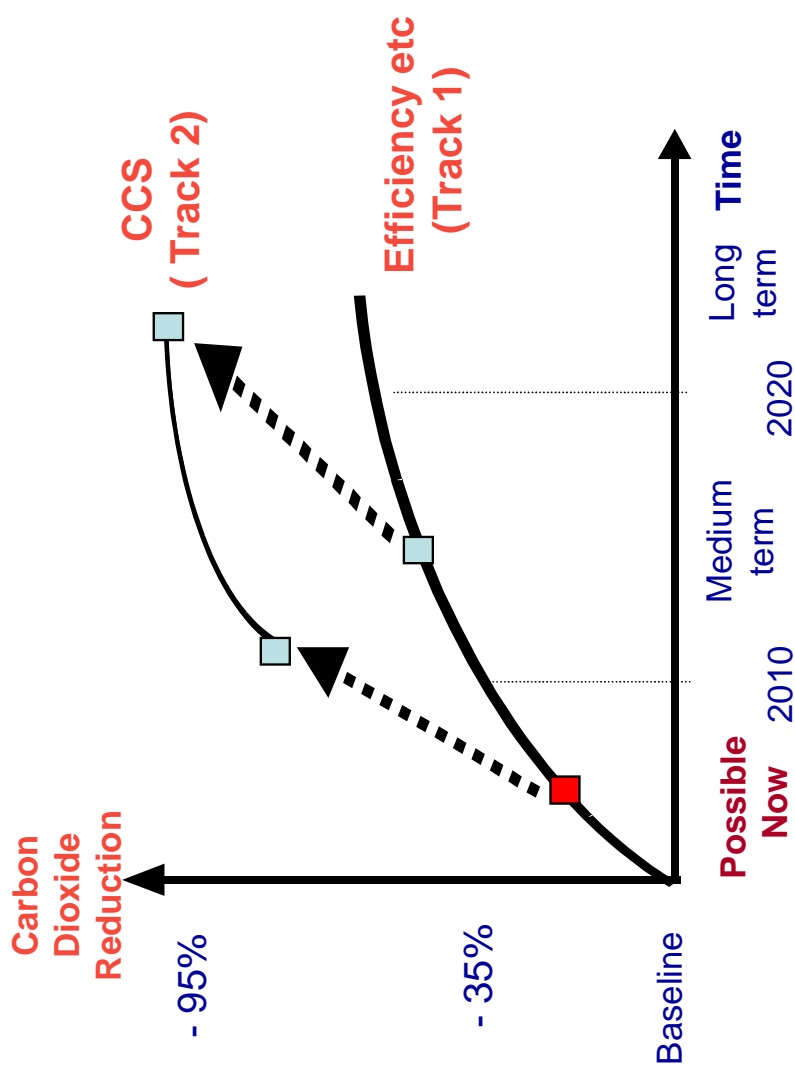
UK power station emissions of SO₂, NO_x and CO₂ 1970-2004



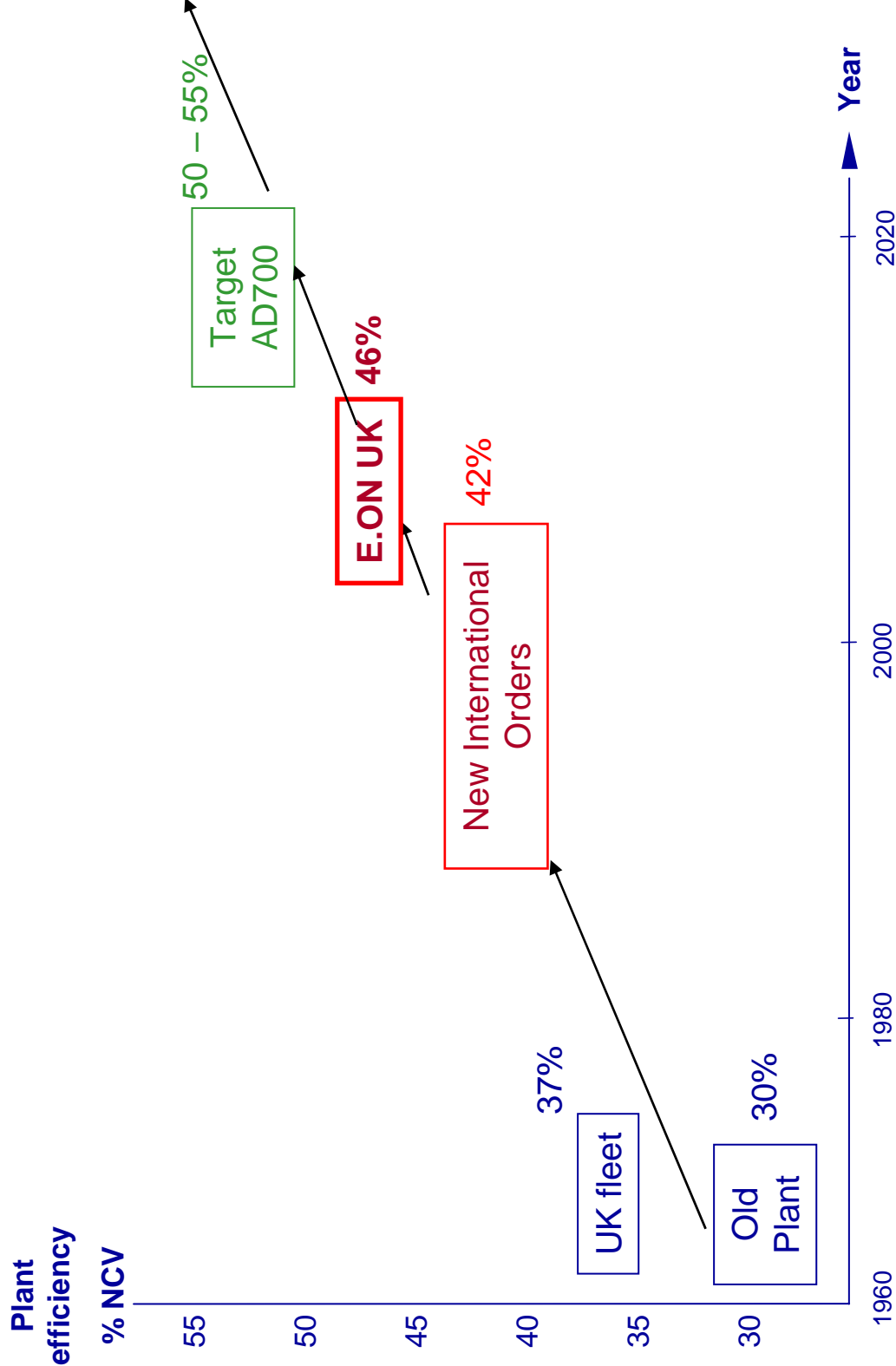
Carbon dioxide abatement from fossil fuels

Twin track Approach:

- Track 1
 - Fuel switch
 - Biomass
 - Efficiency improvements
- Track 2
 - Carbon Capture and Storage Technology



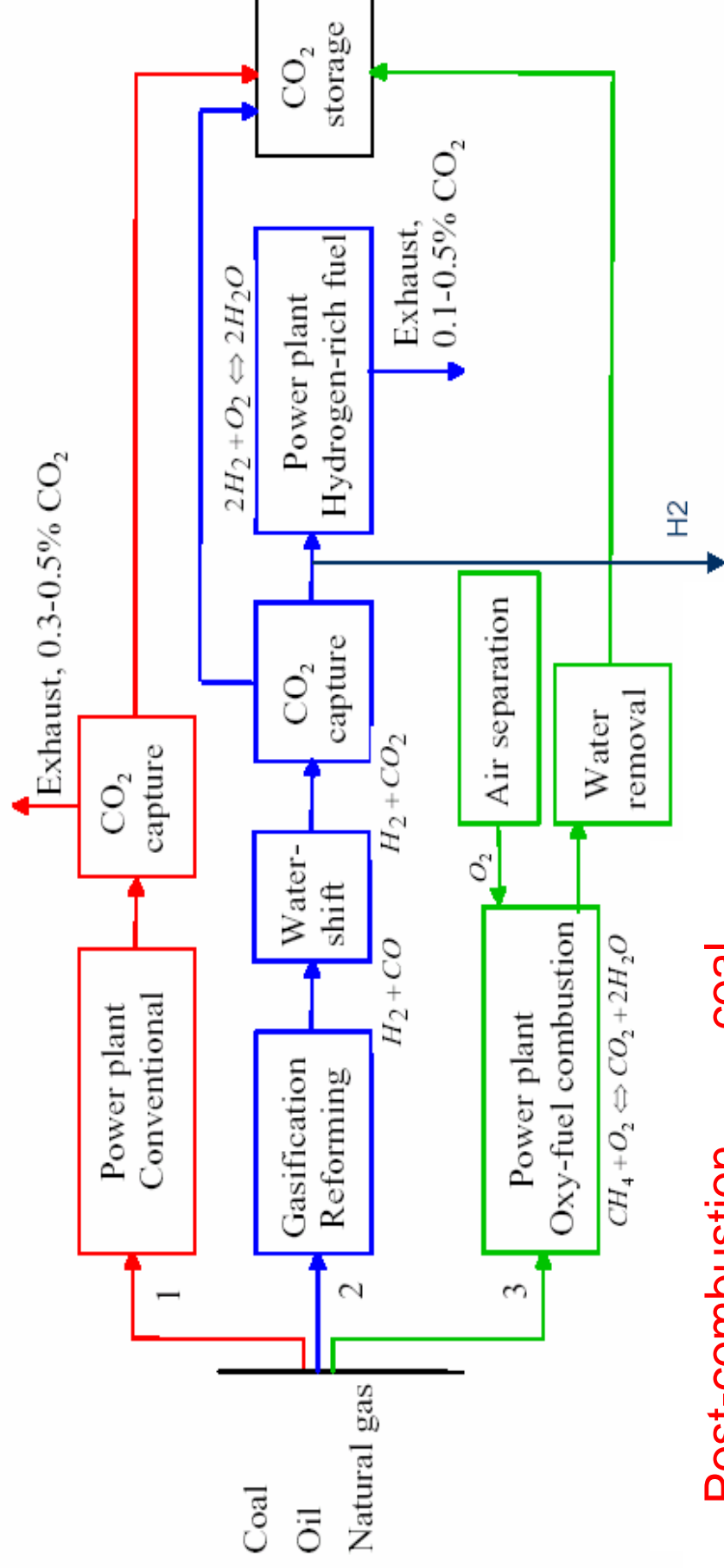
Track 1: Efficiency Improvement - Coal fired plant



Kingsnorth 5 & 6 – Artist's Impression (expected ~2013)



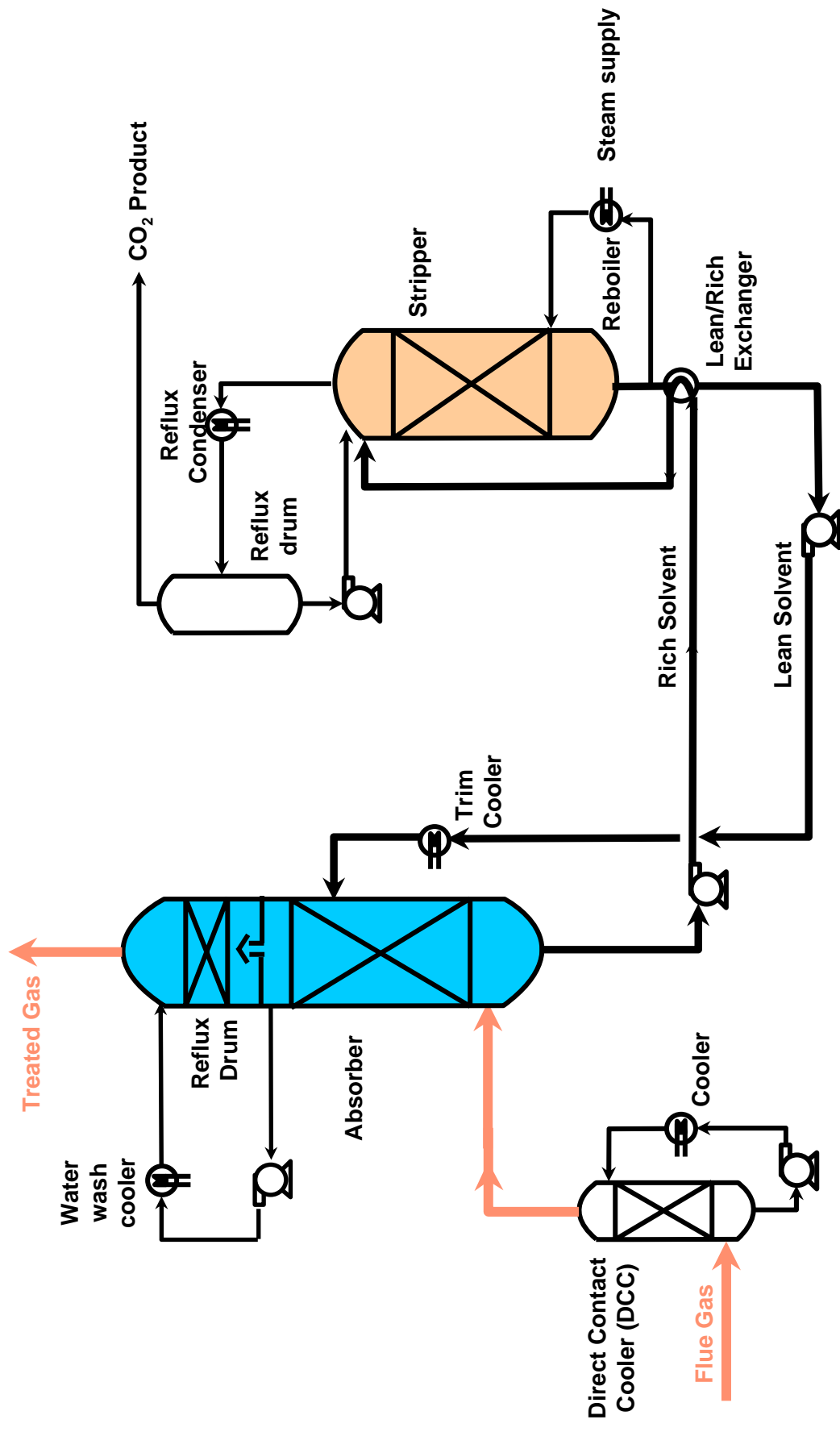
Track 2: Options for power plant CO₂ capture



1. Post-combustion — coal
2. Pre-combustion — coal, natural gas
3. Oxy-fuel — coal

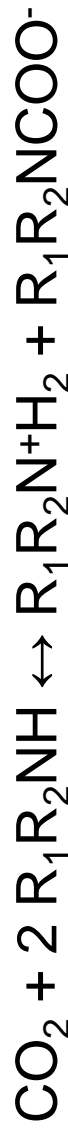


Amine Scrubbing for CO₂ Capture



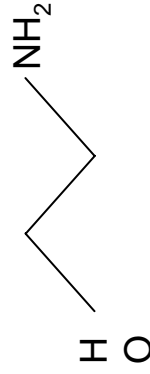
Process Chemistry

- Primary and secondary amines react directly with CO₂

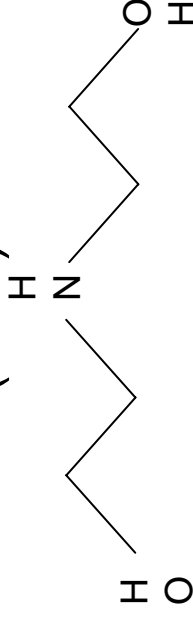


then, $\text{R}_1\text{R}_2\text{NCOO}^- + \text{H}_2\text{O} \leftrightarrow \text{R}_1\text{R}_2\text{NH} + \text{HCO}_3^-$ [but $K \ll 1$]

- Monoethanolamine (MEA) – primary amine



- Diethanolamine (DEA) – secondary amine

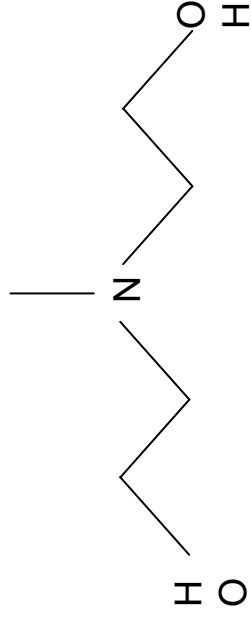


Process Chemistry

- Tertiary amines react indirectly with CO₂
- Base catalysed hydrolysis of CO₂



- Methyl diethanolamine (MDEA) – tertiary amine



Process Chemistry

- Reaction rate and reaction enthalpy for common amines

	Reaction rate	Reaction Enthalpy	Stoichiometry
	constant	kJ/mol	mol/mol
MEA	~ 7000	90	0.5
DEA	~ 1000	80	0.5
AMP	~ 700	75	1
MDEA	~ 7	60	1

Amine scrubbing advantages and disadvantages

- Advantages
 - 70+ years of experience with industrial gas streams
 - Retro-fit to existing and new conventional plant
 - Bypass
 - Pure CO₂ stream for storage
 - One of most developed CO₂ capture options (1000te/day)
- Challenges
 - High energy penalty (~10% points)
 - High cost - capital and operating
 - Footprint
 - Scale-up (13,000te/day)
 - Corrosion & degradation (SO₂, O₂, particulate, etc)

Development activities

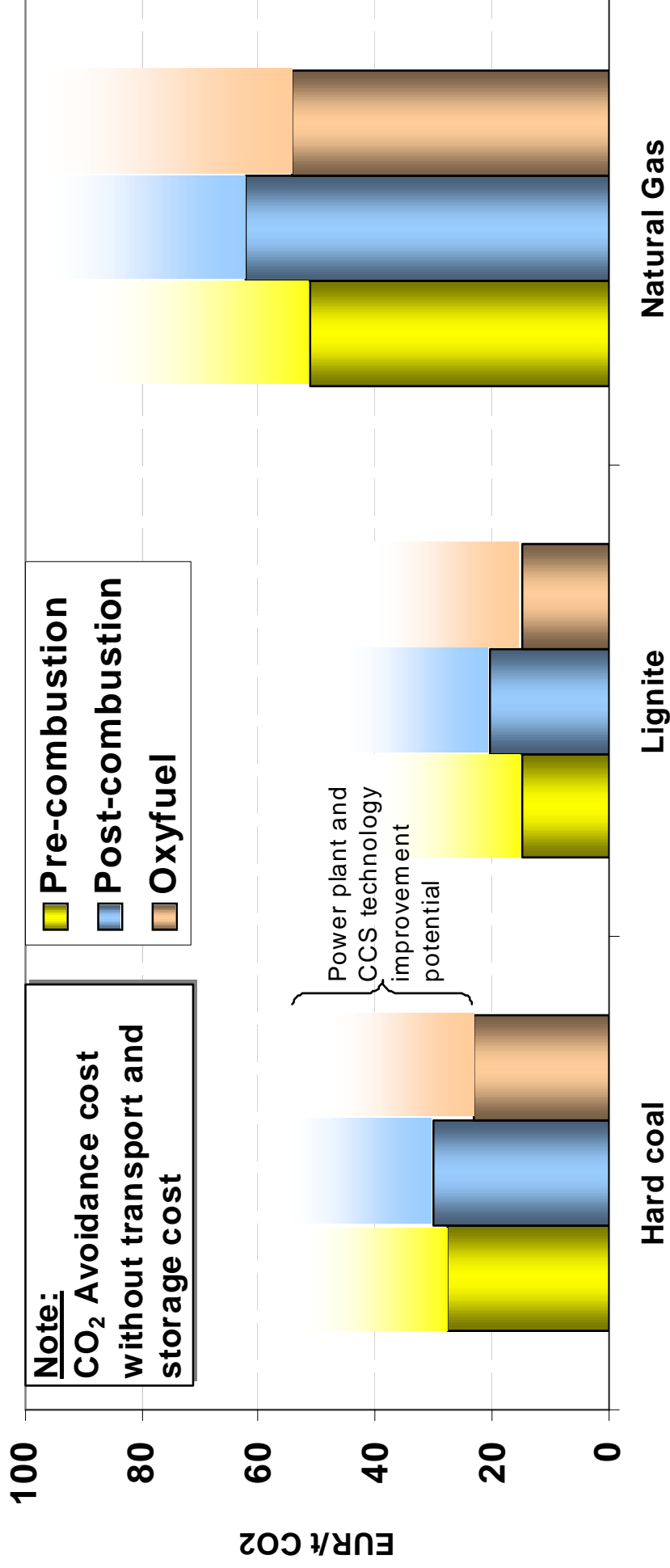
- Issues to address
 - Cost and energy penalty – advanced amines/reagent and engineering
 - Power plant integration – gas path and heat/steam
 - Corrosion – new materials
 - Degradation – flue gas pre-treatment
 - Scale-up – build & operate pilot, demo, full scale plants
- E.ON UK activities
 - CASTOR EU project – www.co2castor.com
 - International Test Centre (ITC) sponsor – www.co2research.ca
 - CAPRICE EU/Global project – www.caprice-project.eu
 - Ammonia process demonstration – E.ON Nordic/Alstom
 - 6te/day CO₂ pilot plant - E.ON Benelux
 - Others...

Conclusions – Amine scrubbing of CO₂

- Ongoing requirement for fossil fuel fired power plant
- Cleaner fossil fuel plant technically feasible
- Two track approach to reducing CO₂ emissions
 - Track 1: Efficiency, fuel selection (35% reduction)
 - Track 2: Carbon capture and storage (90-95% reduction)
- Amine scrubbing is a leading capture option, but needs
 - Amine chemistry development
 - Engineering development
 - Scale-up
 - Integration into power plant
- Leading technologies at similar stage of development and demonstration
- Uncertainty over cost of carbon capture technologies
- Uncertainty over future value/cost of carbon credits

Comparison of Costs Associated with CO₂ Capture Technologies

Expected CO₂ avoidance cost for large-scale power plants in operation by



Source: Technology Platform Zero Emission Power

Development of adsorbent technologies for pre and post-combustion CO₂ capture



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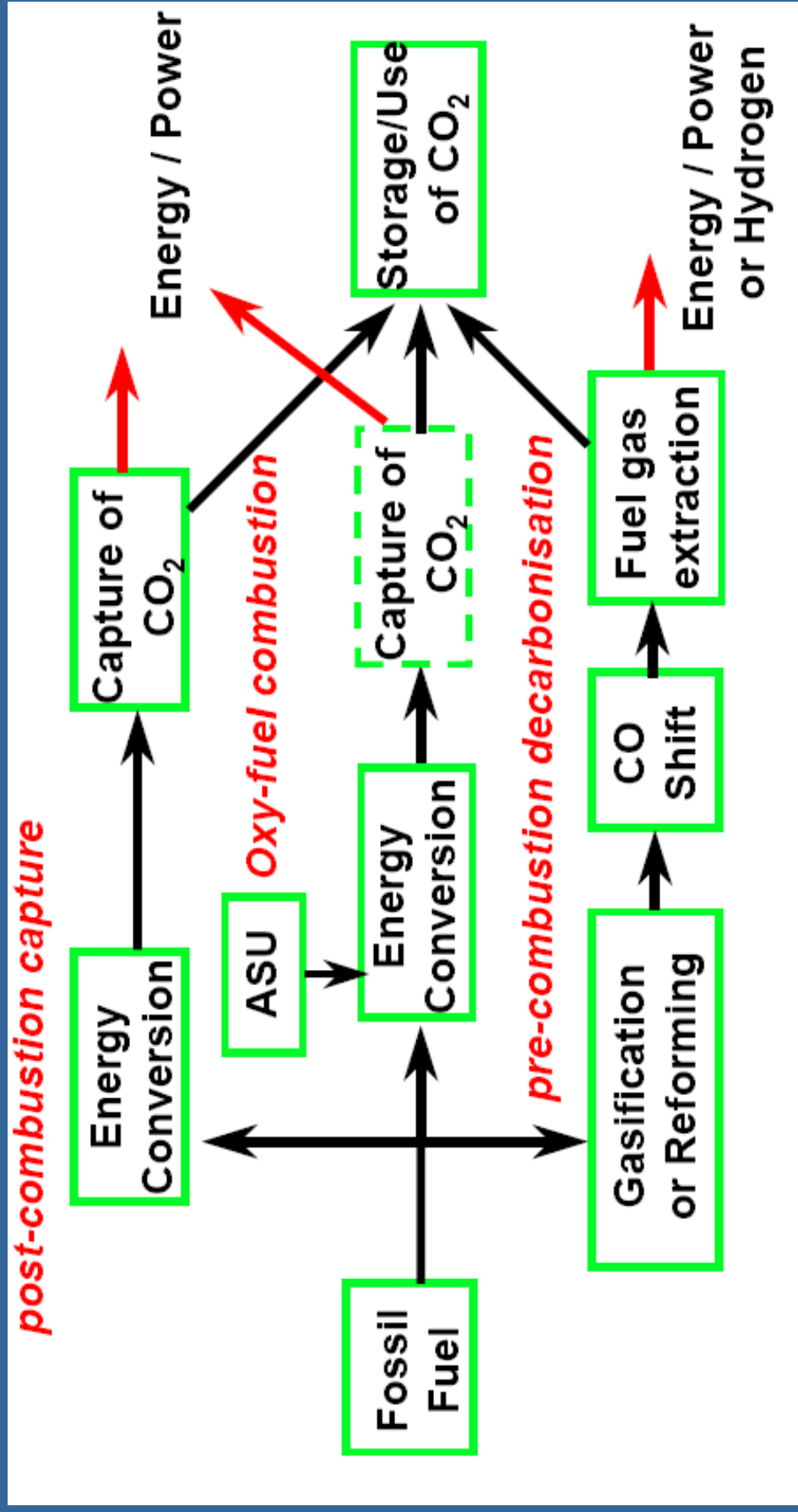
**Trevor C. Drage¹, Ana Arenillas², Cova Pevida²
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Options for CCS



Introduction

Why adsorption?

- The CO₂ 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 CO₂ 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 CO₂.
- Need for the development of alternative low cost technologies to provide a more effective route for the capture and storage of CO₂ on a global scale.

Summary of Adsorption Research

- Post-combustion capture
 - The Partial Removal of CO₂ from Flue Gases using Tailored Coal-Derived Carbons BCURA; Project B65 (2002-05)
 - Developing effective adsorbent technology for the capture of CO₂ in fossil fuel fired power plant. Carbon Trust; 2002-6-38-1-1 (2003-07)
 - Assessment of Options for CO₂ Capture and Geological Sequestration. RFCS; RFC-CR-03008 (2003-07)
 - Developing effective adsorbent technology for the capture of CO₂. EPSRC Advanced Research Fellowship, Dr T.C. Drage; EP/C543203/1 (2005-10)
- Pre-combustion capture
 - Impact of CO₂ 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

	Pre-combustion capture (after water gas shift) ^a	Post-combustion capture ^b
Gas composition		
CO ₂	35.5 %	15 – 16 %
H ₂ O	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 ₂ S	1.1%	-
Conditions		
Temperature	40 °C	50 – 75 °C
Pressure	50 – 60 bar	1 bar

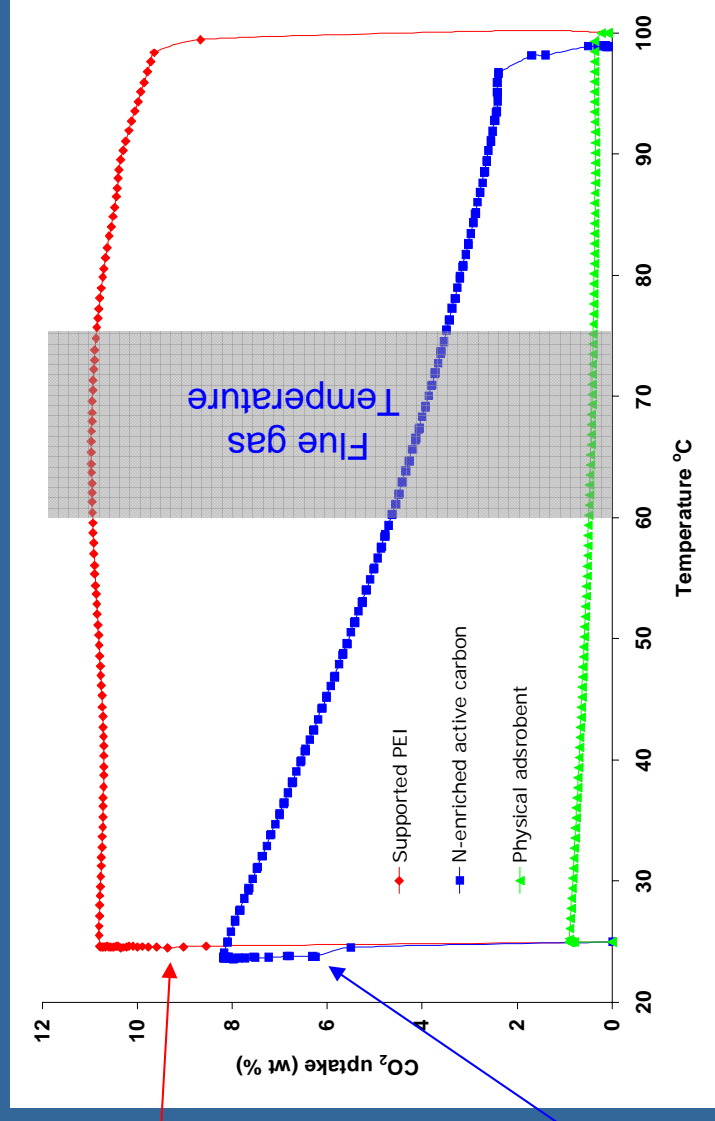
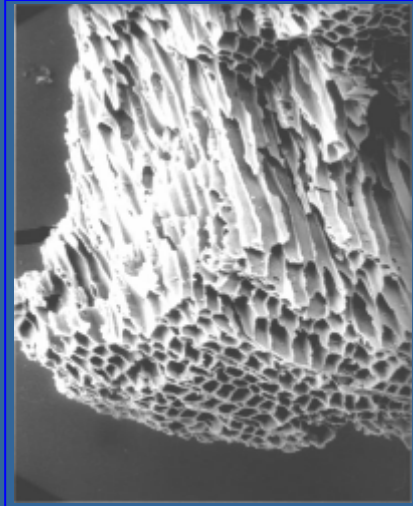
As with solvent systems physical adsorption systems work for high pressure, whilst chemical amine systems are needed at atmospheric pressure

Post combustion capture the need for chemical adsorbents

Supported-polyethylenimine



High N-content active Carbons^(1,2)



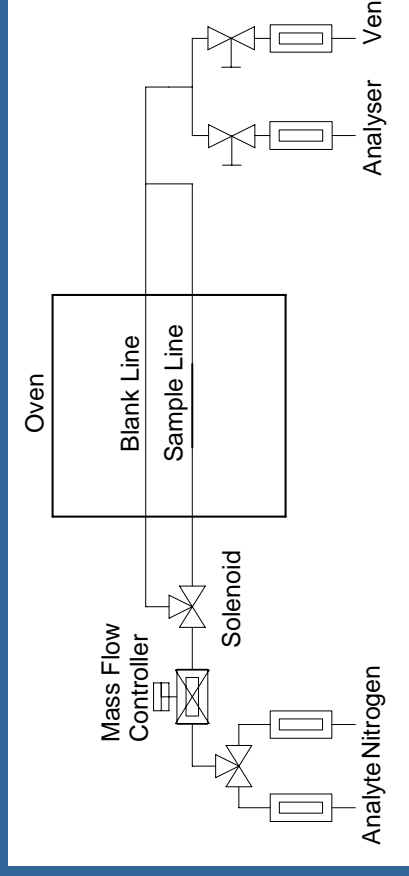
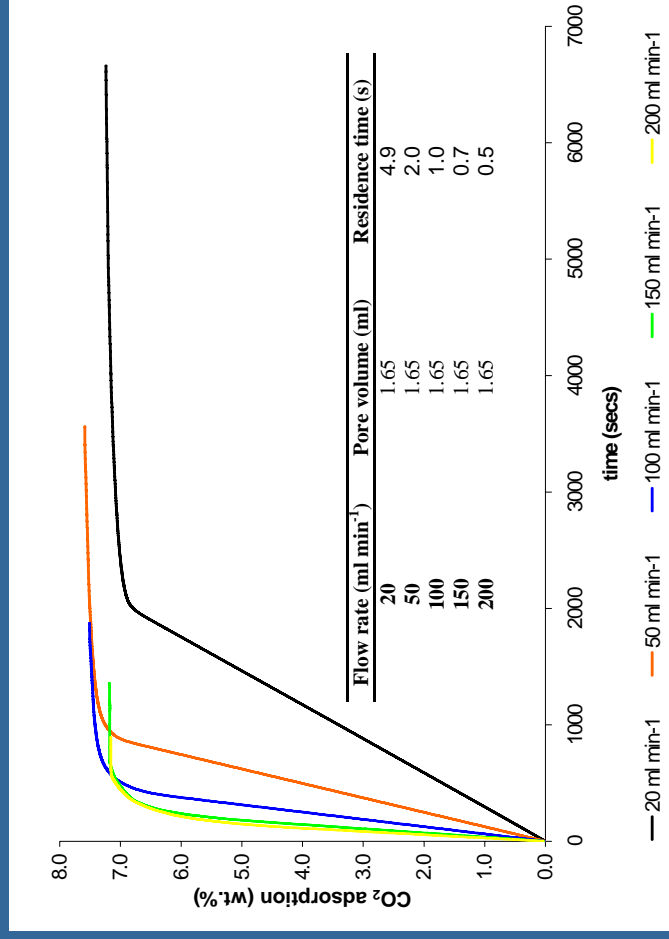
Amine-CO₂ chemical adsorption



⁽¹⁾ Drage, T.C., Arenillas, A., Smith, K., Pivida, 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



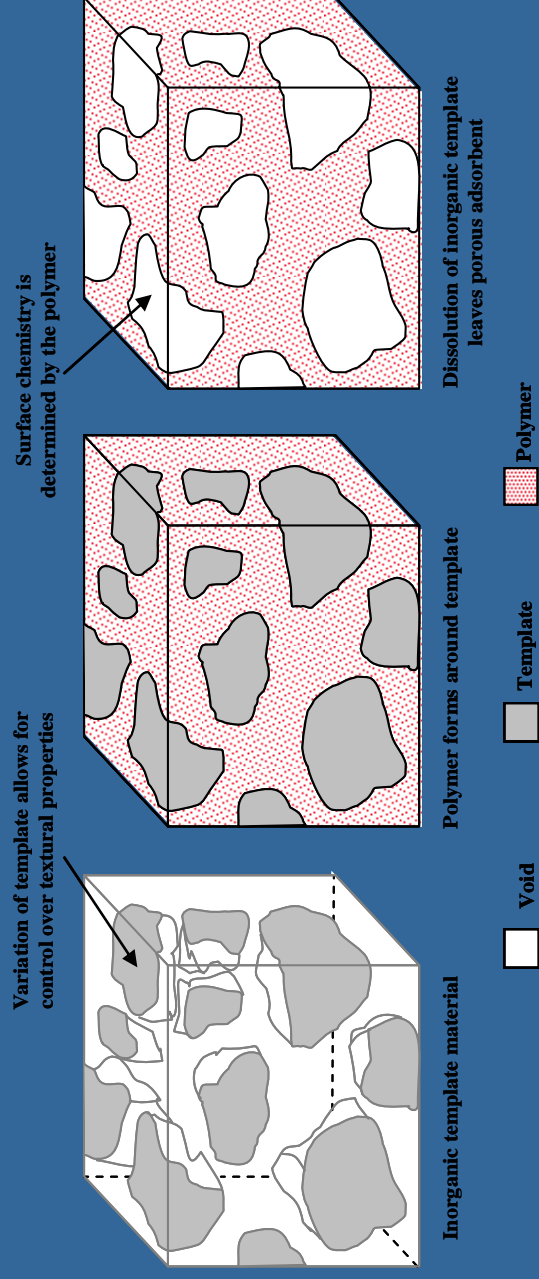
- Adsorption capacities explored under equilibrium and dynamic conditions using simulated flue gases
- Simulated flue gas conditions capable of adsorbing CO₂ with high breakthrough capacities, requiring only short residence times
- Potential demonstrated for selective regeneration of other acid gases, for example SO₂

Templated adsorbent synthesis



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- Increasing sorption capacity key for overall plant efficiency
- Combining stability and textural properties of activated carbons with chemistry of PEI based adsorbents
- Minimises water uptake from flue gas

Textural Properties

- Tailored pore geometry
- Surface area

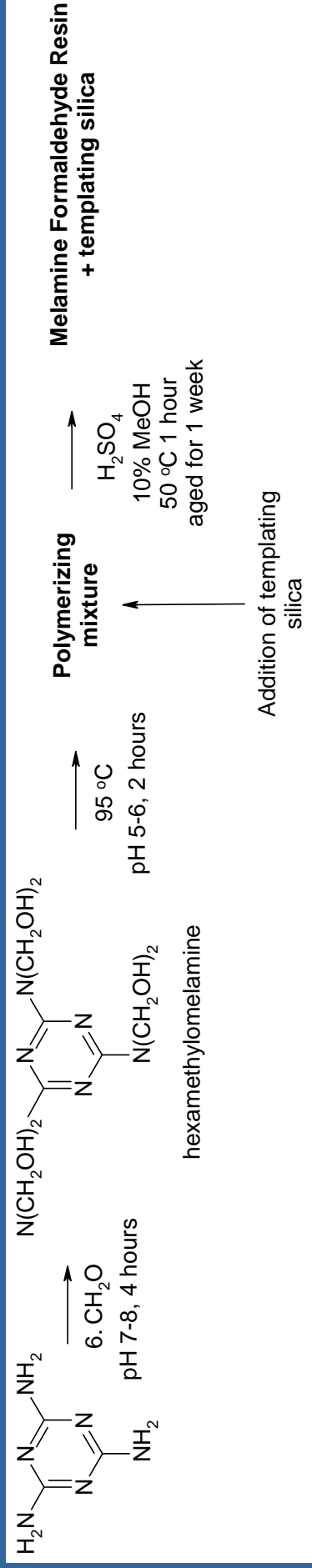
Surface Chemistry

- Wide range of amine polymers
- Amine polymers with OH groups

... Leading to

- Enhanced adsorption potential
- Generic Adsorption Technology
- Superior stability

Templated MF resin synthesis



Template - two types of fumed silica used (with and without CTAB surfactant):

7 nm

14 nm

Silica to melamine ratios used

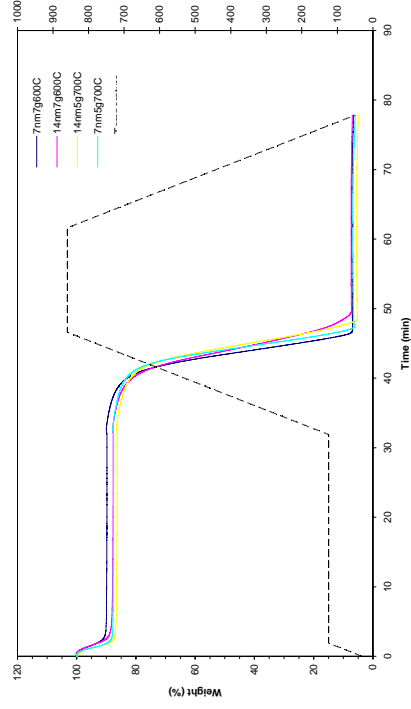
1:1 (5g)

1.4:1 (7g)

Thermal treatment – polymers analysed without heating and after carbonisation at 400, 500, 600 and 700 °C

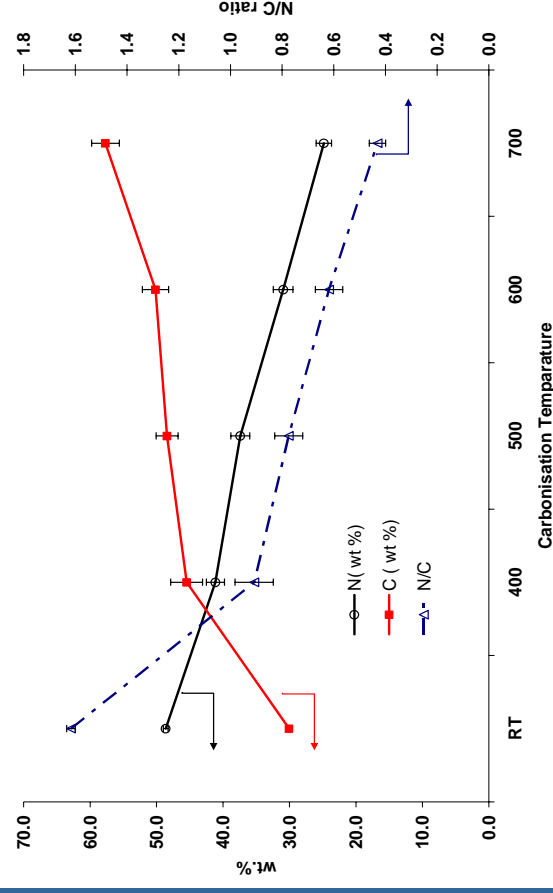
Template removal - 10% NaOH solution

Elemental Composition



- Template Removal – Loss on ignition analysis used to confirm >90% removal of silica template
- Materials have high N content as expected for MF resin source
- N and H decrease with carbonisation, concomitant increase in C

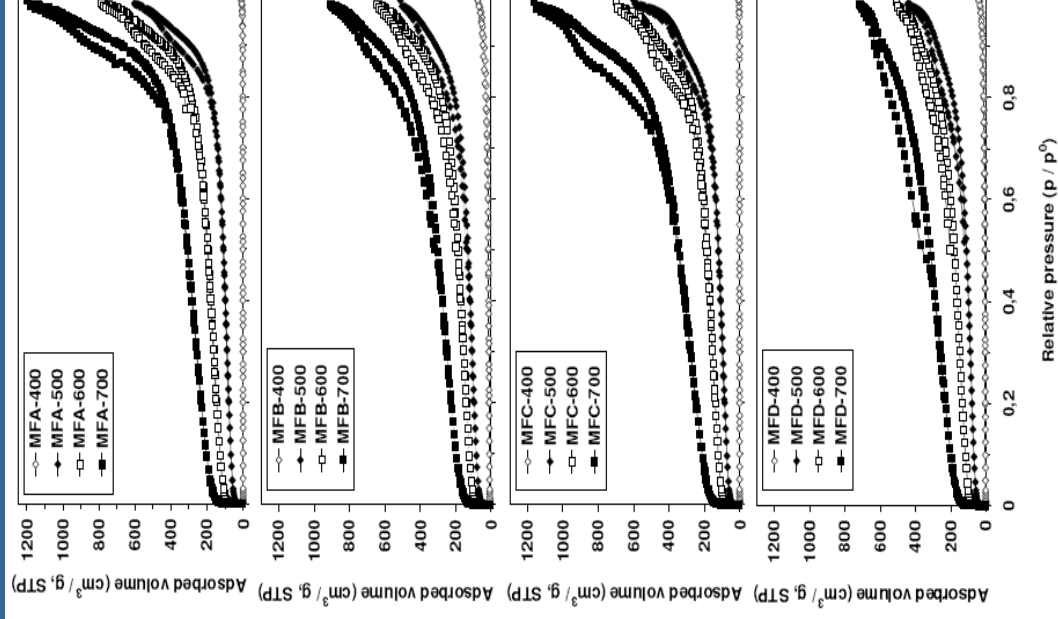
Carbonisation temperature	Sample	N (wt %)	C (wt %)	H (wt %)	N/C
RT	7nm5g	48.5	30.1	3.9	1.6
	7nm7g	48.8	30.0	3.7	1.6
	14nm5g	48.2	30.2	3.8	1.6
	14nm7g	49.0	30.0	3.6	1.6
400	7nm5g	39.2	48.1	2.9	0.8
	7nm7g	41.4	46.8	3.4	0.9
	14nm5g	42.0	44.1	3.0	1.0
	14nm7g	42.0	42.9	3.0	1.0
500	7nm5g	38.5	46.8	2.6	0.8
	7nm7g	35.4	50.4	2.2	0.7
	14nm5g	37.4	49.2	2.0	0.8
	14nm7g	38.4	47.3	2.1	0.8
600	7nm5g	29.1	52.8	1.8	0.6
	7nm7g	30.4	50.5	1.8	0.6
	14nm5g	31.9	48.8	1.8	0.7
	14nm7g	32.4	48.6	1.7	0.7
700	7nm5g	23.3	59.9	1.5	0.4
	7nm7g	24.7	56.6	1.4	0.4
	14nm5g	25.7	58.8	1.3	0.4
	14nm7g	25.7	55.4	1.4	0.5



Textural Properties

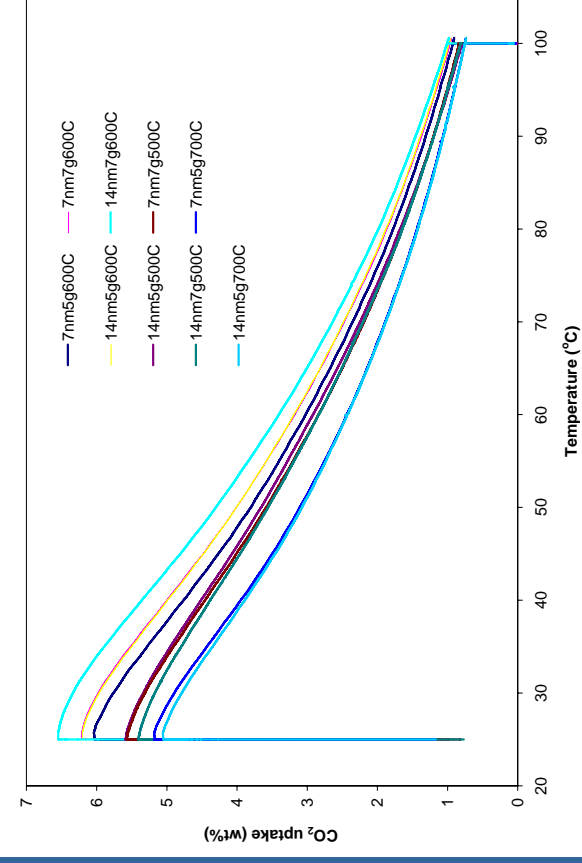
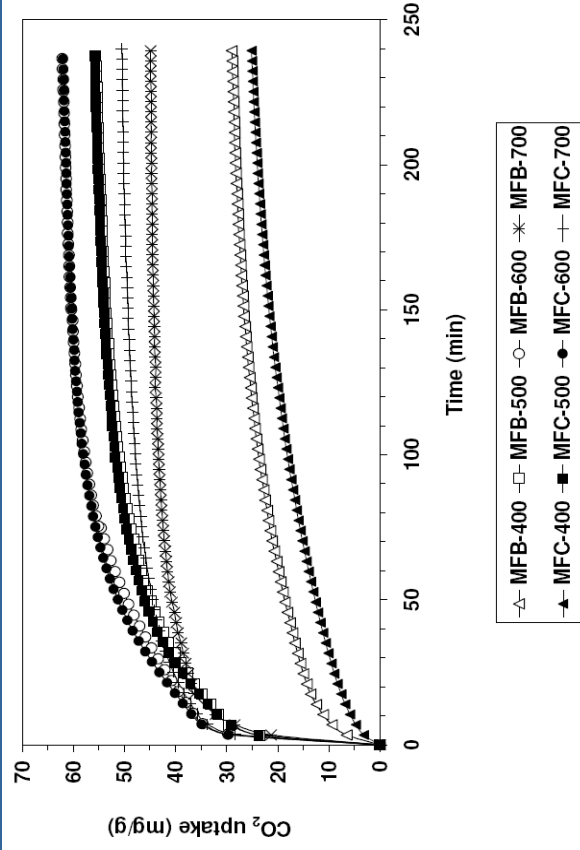
Silica size (nm)	Silica: melamine	Carbonisation Temperature (°C)	S_{BET} (m^2/g)	V_{pores} (cm^3/g)
7	1	-	28	0.01
		400	30	0.007
		500	276	0.69
		600	516	0.93
		700	819	1.45
7	1.4	-	31	0.05
		400	32	0.08
		500	330	0.62
		600	487	0.79
		700	777	1.17
14	1	-	36	0.001
		400	28	0.003
		500	294	0.84
		600	485	0.84
		700	852	1.47
14	1.4	-	35	0.05
		400	15	0.04
		500	279	0.50
		600	471	0.84
		700	800	0.99

- Micro and mesoporosity developed
- Surface areas not developed for non-pyrolysed samples
- Surface area and pore volume increases with carbonisation temperature



Adsorption

Rate and Influence of temperature

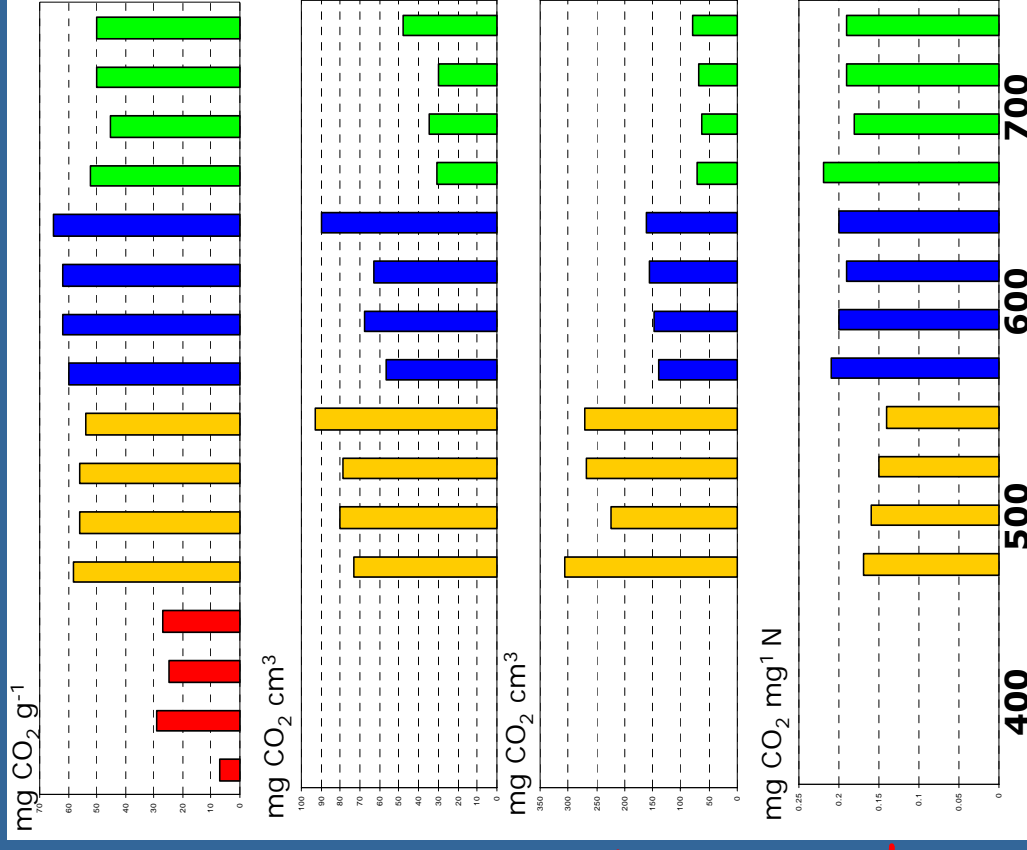


- Rate of adsorption varies for different activation temperatures – adsorption rate fastest for 700 °C activation.
- Adsorption capacity decreases with temperature (25 – 100 °C, 100% CO₂, 0.25 °C min⁻¹ ramp)
- Performance better than some physical adsorbents – especially at elevated temperatures.

Adsorption Results

What controls capacity?

- **Overall adsorption capacities**
 - Highest from carbonisation at 600 °C
 - Independent of template
- **Normalised to V_P**
 - Activity decreases with activation temperature
 - Pore volumes greatest for 700 °C activation
 - Capacity controlled by both textural and chemical properties
- **Normalised to $V_P - V_{MESO}$**
 - Further evidence for chemical influence
 - Negative relationship with micropore volume not expected
- **Normalised to N content**
 - Nitrogen content not key control on capacity
 - Nitrogen functionality altered by activation – higher temperature reduces basicity (XPS underway)
- **Adsorption a compromise between textural and chemical properties.**



Activation Temperature (°C)

Problem with pK_a polymer types

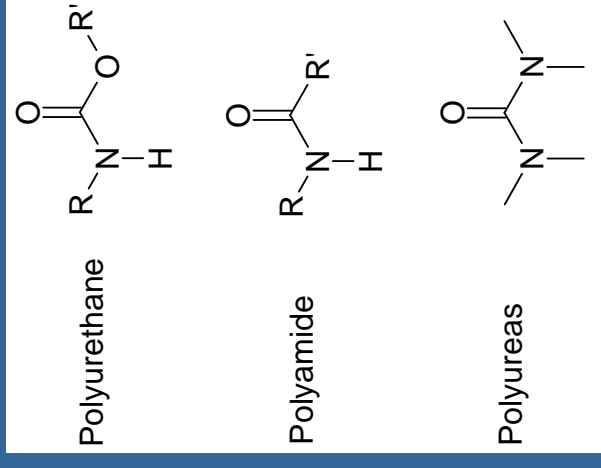
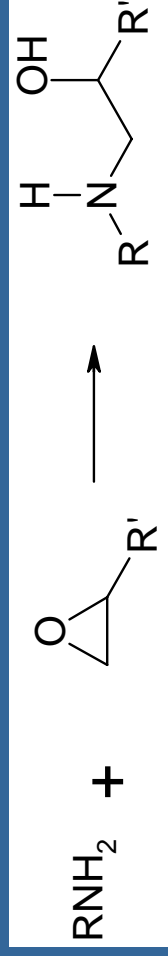


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Compound	pK _a	Chemical Structure	pK _a	Chemical Structure	pK _a
	11.0		10.7		10.7
			9.3		5.3
			4.6		0
			-1.0		

- From results it is clear that the presence of nitrogen alone is insufficient and that more basic nitrogen is required
- Nitrogen within melamine-formaldehyde resin has a low pK_a as a result of adjacent functional groups.
- Most common nitrogen containing polymers are linked via an amide group
- One possible solution is epoxy-resins
- New polymer and synthesis methods being explored



Adsorbent Regeneration

Efficient adsorbent regeneration is crucial

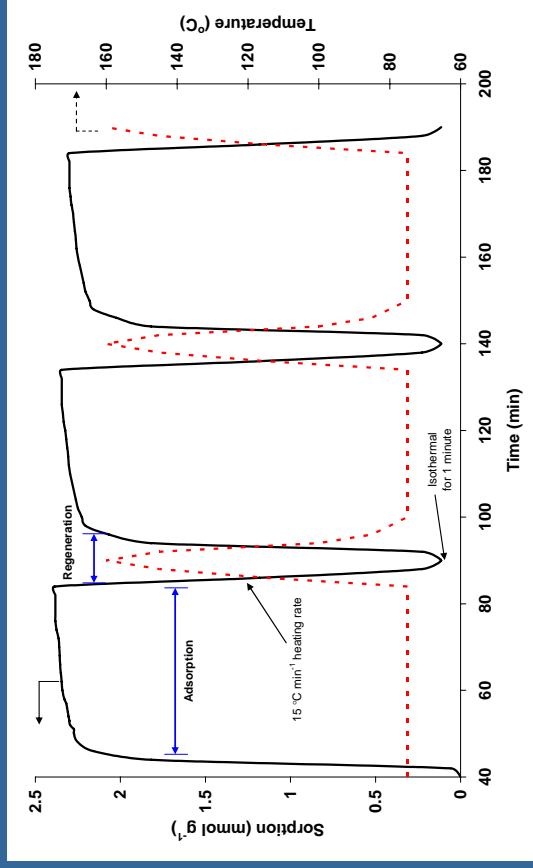
- To be economic the adsorbents will have to be regenerable. Energy required for regeneration will dictate the efficiency and economics of the process. Minimising temperature differential between adsorption / desorption cycles and stripping gas volumes are key to efficient operation.
- Regeneration strategy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

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

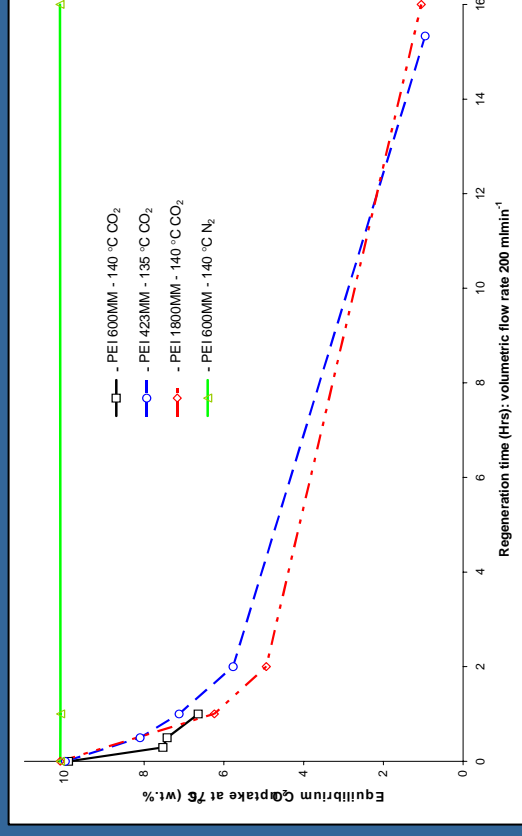
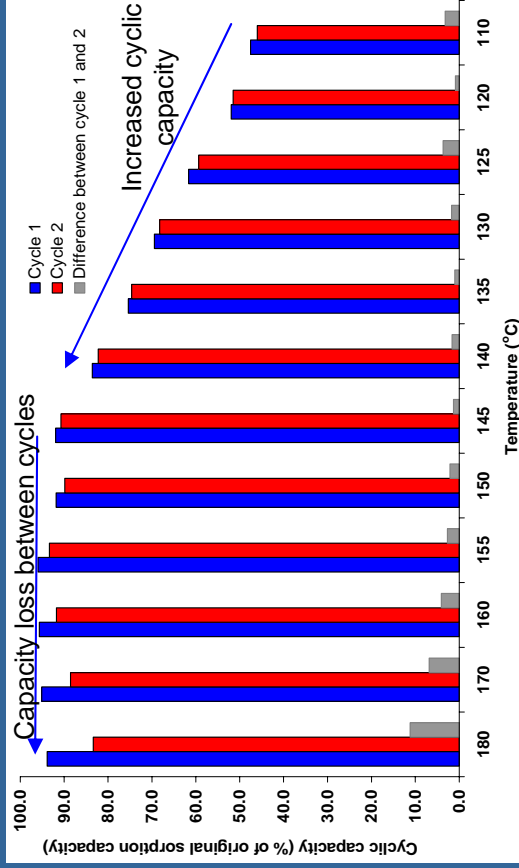
- Thermal swing adsorption cycles over a range of time and temperatures in CO₂
- Using nitrogen as a stripping gas at elevated temperatures.

Regeneration

PEI based adsorbents - thermal



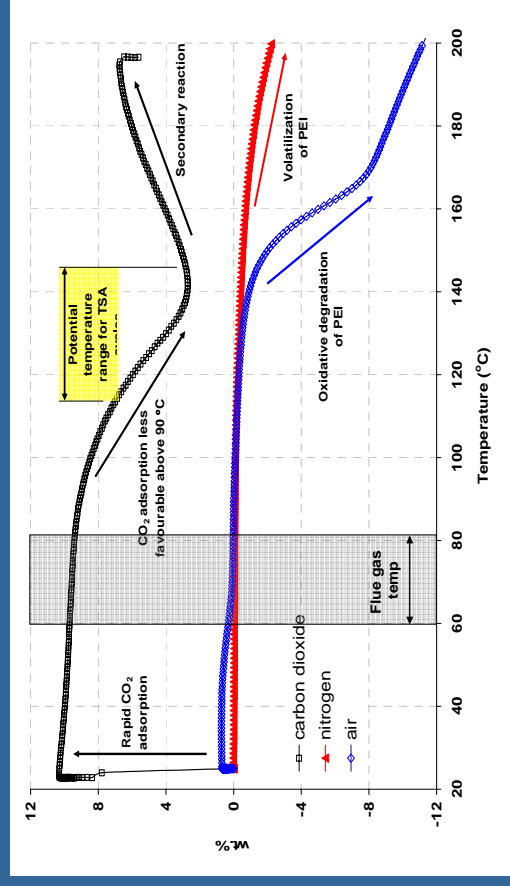
- Regeneration in a stream of pure CO₂ by temperature swing
- Cyclic capacity dependent upon temperature
- > 90 of sorption capacity recovered on cycling
- Problems arise with secondary reaction leading to short adsorbent lifetime



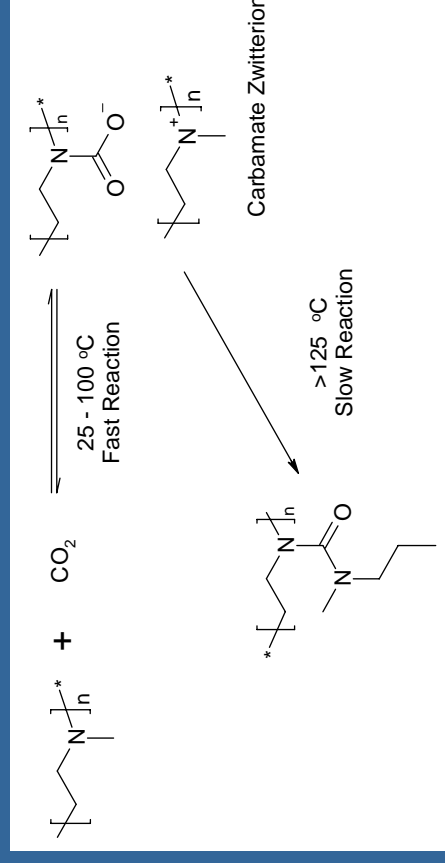
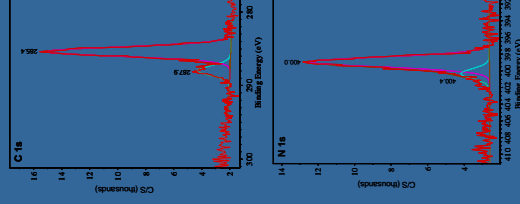
Regeneration

Secondary reaction

- ^{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



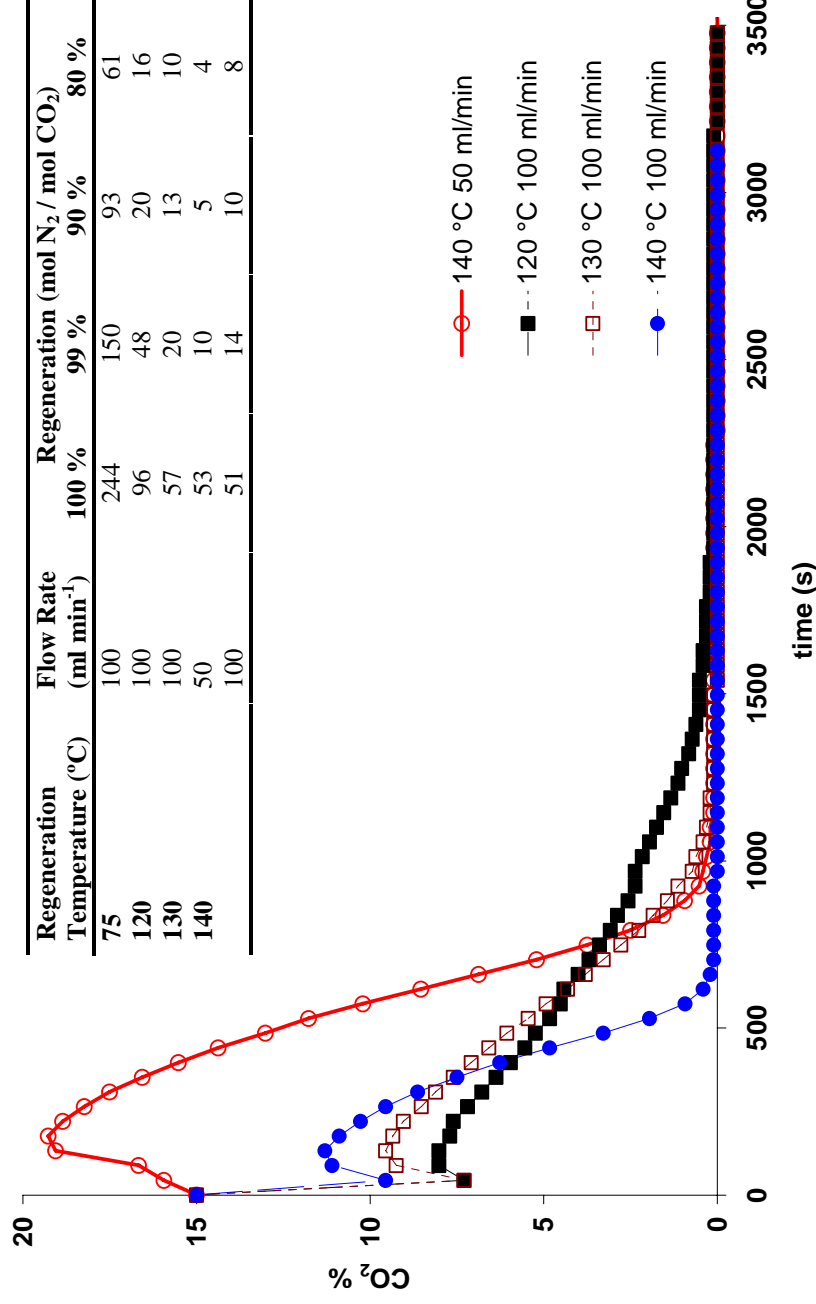
Element	Binding Energy	Intensity %	Assignment	Structure	Reference
Si	103.9	20	SiO ₂ - inorganic support	SiO ₂	[3]
O	532.0	29	SiO ₂ - inorganic support. Good agreement between the ratio of Si and O ₂	SiO ₂	[3]
	530.8	1.5	Close match to urea / polyurea		[4]
C	287.9	5.3	Carbonyl carbon from urea fragment		[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



- 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 % CO₂ 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
- Novel radial flow fixed bed reactor capable of providing best economic performance
- Nottingham investigating novel moving bed design

Table 1. Comparison of CO₂ 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

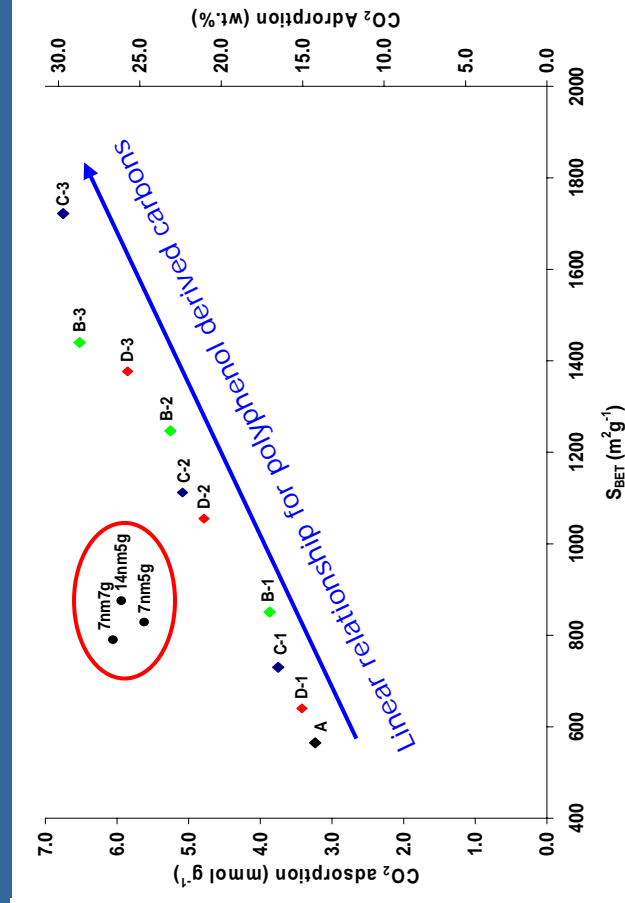
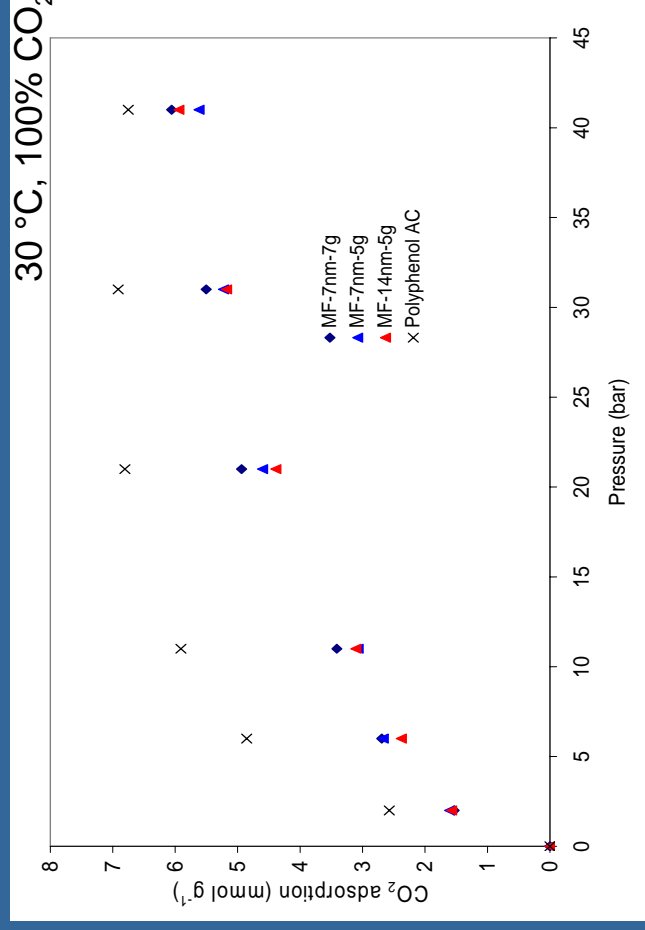
Table 2. Plant Performance and Economics with CO₂ Capture

	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.

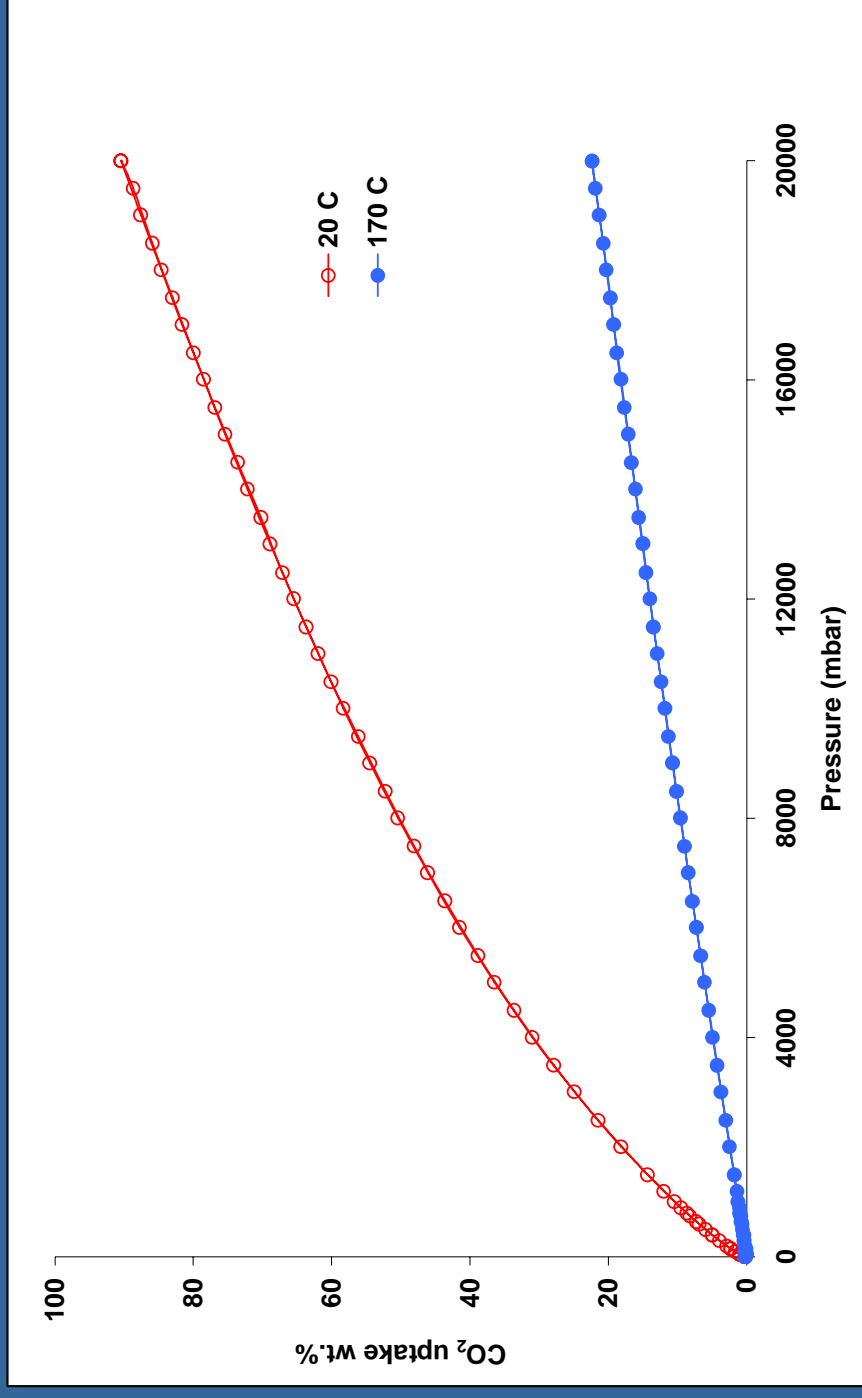
Pre-Combustion Capture

Surface chemistry or textural?



- High pressure adsorption explored as a method for pre-combustion capture
- MF derived carbons activated at 700 °C have excellent performance, different trend compared to polyphenol derived ACs
- Enhanced performance at lower SA may increase volumetric capacity
- Different isotherm shape – potentially useful for other applications

CO₂ uptake IGA – AC3000



Extensive de-gas
100 % CO₂

- IGA allows thermal swing regeneration to be performed
- Activated PAN – high adsorption capacity
- Large potential for thermal swing regeneration

Pre-combustion economics

- Based on a conservative adsorption capacity of 12 wt. %
 - Basic economic costing using fixed bed adsorption with pressure swing regeneration has potential economic benefits over current physical solvent systems
 - More detailed analysis of adsorption capacity under dynamic conditions required
- Advantage of adsorbents is the ability to produce CO₂ at relatively high pressure, even a pressure of 10 bar would have a significant impact in reducing CO₂ compressor cost and power requirements (100 bar for transportation)
- Moreover, if higher (20+ %) adsorption capacities can be achieved, TSA cycles can potentially be employed leading to significant benefits as CO₂ can be recovered at 30 – 40 bar.
- System has the potential to become a viable alternative in the future for bulk CO₂ removal

Conclusions

- Range of successful adsorbents developed for both pre and post-combustion capture
- Both techniques maximising adsorption capacity key to decrease amount of adsorbent required and regeneration time
- Regeneration of post-combustion capture more complicated due to the chemical nature of the adsorbents
- Pre-combustion capture has great potential if TSA can be used for regeneration of adsorbents and the production of pure CO₂ at high pressure
- Both pre and post-combustion capture offer potential economic and efficiency benefits over current solvent systems

Acknowledgements

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 - BCURA
 - The Research Fund for Coal and Steel (RFC-CR-03008)
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