

The Partial Removal of CO₂ from Flue Gases using Carbon recovered from PFA



The University of
Nottingham

*Nottingham Fuel
& Energy Centre*

**Dr.M.Cloke, Prof.C.E.Snape,
Prof.J.W.Patrick, Dr.E.Lester, Dr.K.Steel
Mr.K.M.Smith and Dr.T.C.Drage.**

*Nottingham Energy & Fuel Research Centre,
School of Chemical, Environmental and Mining
Engineering (SChEME), University of Nottingham,
University Park, Nottingham NG7 2RD*

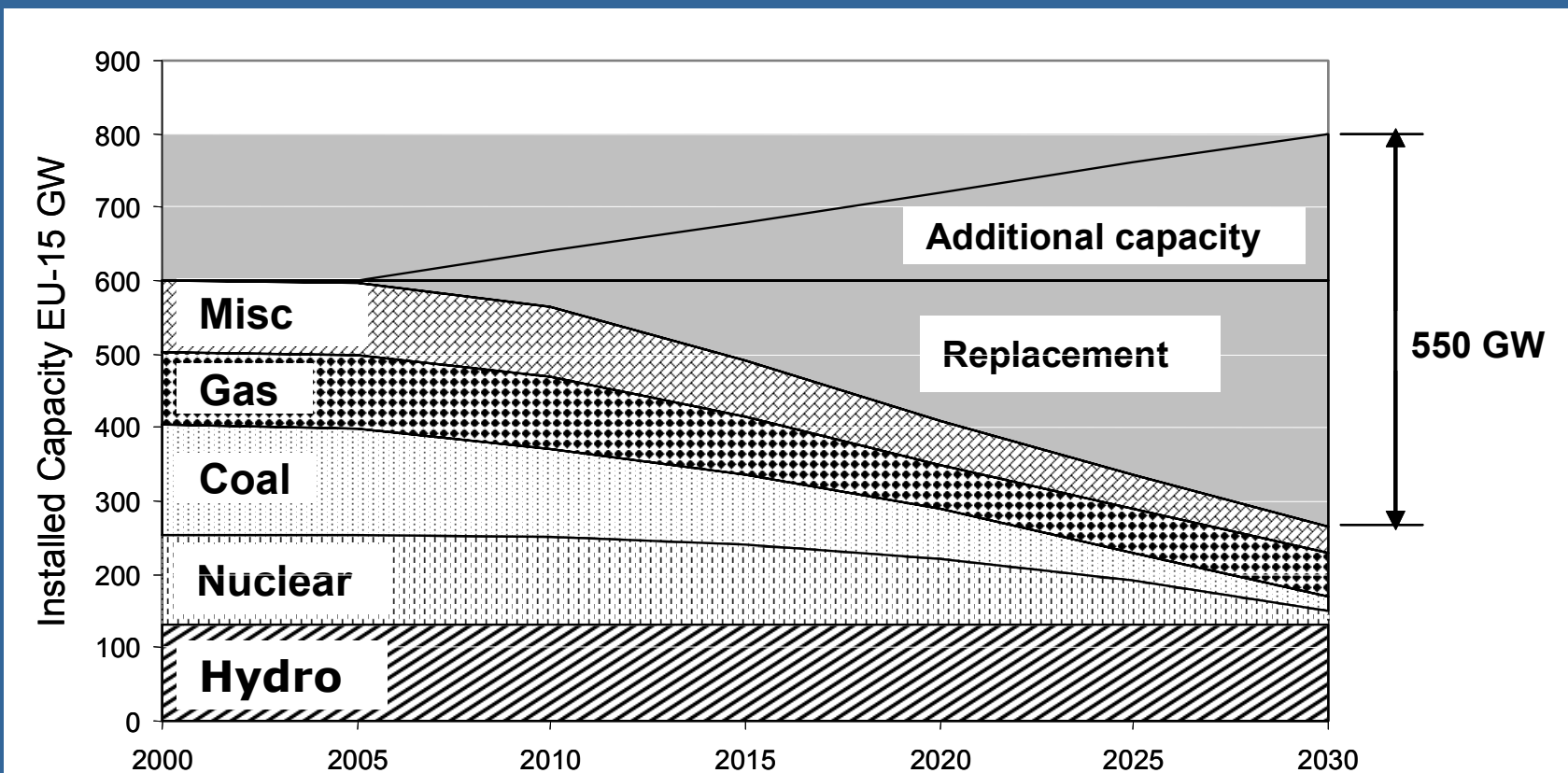
***British Coal Utilisation and Research Association
(BCURA), project B65 (October 2002 start).***

CO₂ Capture Research Nottingham Fuel and Energy Centre



- **BCURA**
 - The partial removal of CO₂ from flue gases using tailored coal derived carbons (B65)
- **Carbon Trust**
 - Developing Effective Adsorbent Technology for the Capture of CO₂ in Fossil Fuel Fired Power Plant (CT 2002-6-38-1-1)
- **Research Fund for Coal and Steel**
 - Assessment of Options for CO₂ Capture and Geological Sequestration (RFC-CR-03008)
- **DTI Cleaner Coal Technology Programme**
 - Impact of CO₂ Removal on Coal Gasification based Fuel Plants (Contract 60845900)
- **EPSRC Advanced Research Fellowship (Dr T. Drage)**
 - Developing Effective Adsorbent Technology for the Capture of CO₂ (EP/C543203/1)

Introduction: The Energy Future



- Fossil fuels will continue to dominate energy production for the foreseeable future
- CO₂ capture key to sustainable + competitive fossil fuel options

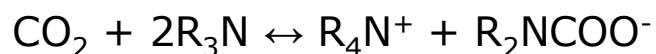
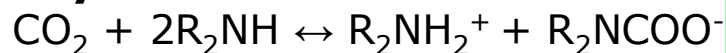
Introduction:

Why Adsorption?

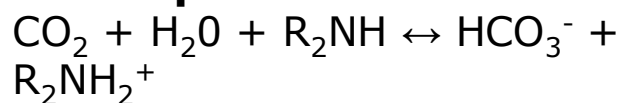
- Solvent Absorption (Chemical solvent MEA / Physical solvent Selexol™)
- Adsorption on a solid (Pressure or Temperature Swing Adsorption)
- Membranes
- Solvent assisted membrane demonstrated
- Cryogenics

Mechanism:

Dry



In the presence of OH



Adsorption:

Selective concentration of one or more gas components at the surface of a solid - Chemical best for CO_2

Advantages:

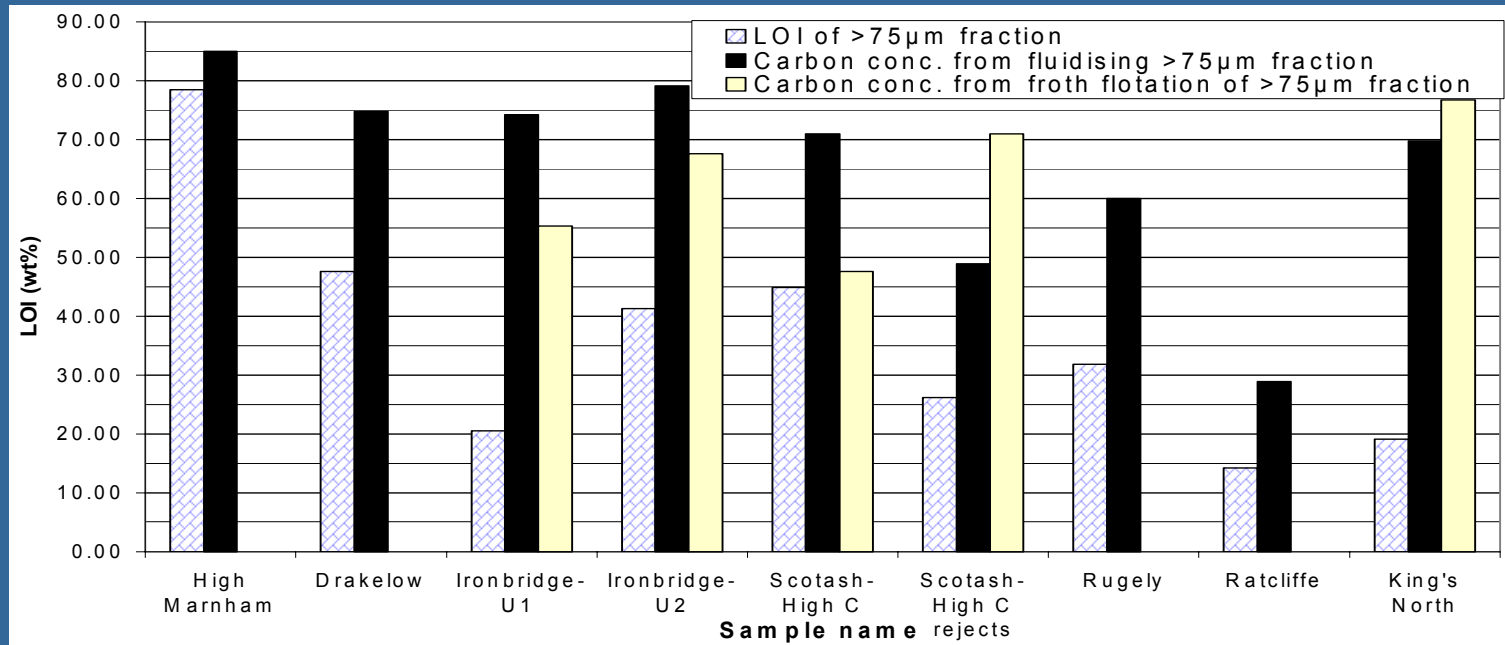
- Low regeneration energy
- Reduced Cost
- High amine density
- Contact efficiency
- Less sensitive to trace species (SO_2)

Aims and Objectives

Develop effective CO₂ adsorbents through the treatment of low cost coal derived carbons through the impregnation with basic amine polymers

- 1. Preparation and characterisation of carbon concentrates from pulverised fuel ash (PFA_CCs)**
- 2. Activation of carbon concentrates – to achieve optimum textural properties for adsorption**
- 3. Assessment of CO₂ uptakes of the adsorbents before and after impregnation with basic polymers**
- 4. Establishing suitable regeneration regimes and ascertain the lifetimes of the most effective adsorbents via multiple adsorption and regeneration**

1. Preparation of carbon concentrates from fly ash (PFA_CCs)



Aim: to recover most carbon from 9 PFAs:

- **Dry sieving** was the least effective of the beneficiation methods evaluated.
- **Demineralisation** was the most effective but was the most time consuming and the least practical for generating large quantities of PFA_CCs.
- **Incipient fluidisation** yielded PFA-CCs with higher carbon contents than those produced with **froth flotation**
- **Froth flotation** was the preferred method of beneficiation due to its ease of use and the relative ease with which it could generate PFA_CCs

2. Carbon Concentrate Activation

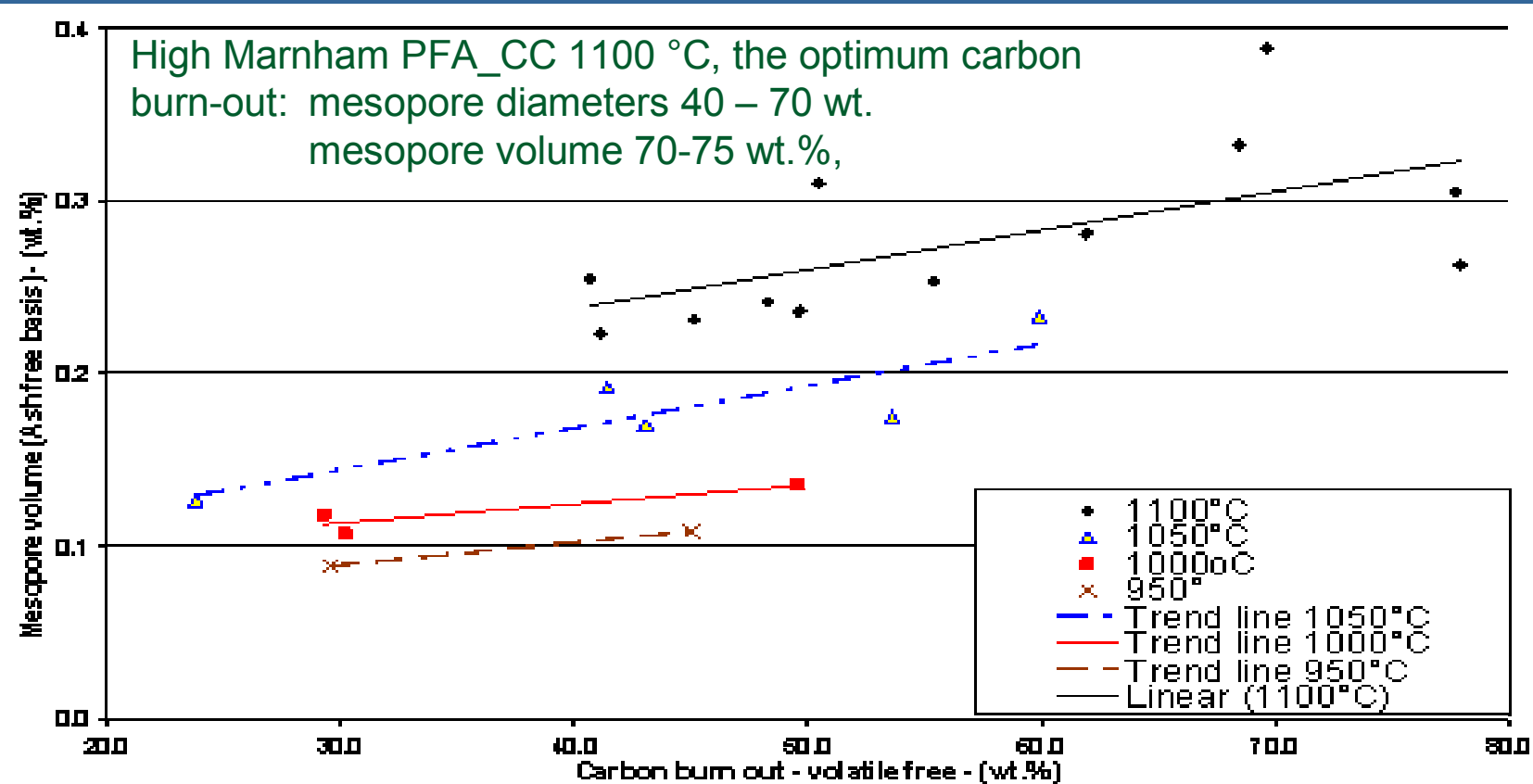
Optimal properties

- **Which porosity is best for amine impregnation?**
 - Crystalline mesoporous zeolite MCM-41 highly amenable to amine impregnation (Xu *et al.*, 2003)
 - Analysis of a range of proprietary silicas demonstrated a high mesopore volume and diameter are optimal to achieve optimum adsorption capacity
- **Need to generate high mesopore volume and diameter – Activation:**
 - Chemical : NaOH, KOH, K_2CO_3
 - Physical : Steam, CO_2

Xu, X., Song, C., Andresen, J. M., Miller, B. G. and Scaroni, A. W. (2003). Preparation and characterization of novel CO₂ "molecular basket" adsorbents based on polymer-modified mesoporous molecular sieve MCM-41, Microporous and Mesoporous Materials 62 (1-2), 29-45

2. Carbon Concentrate Activation

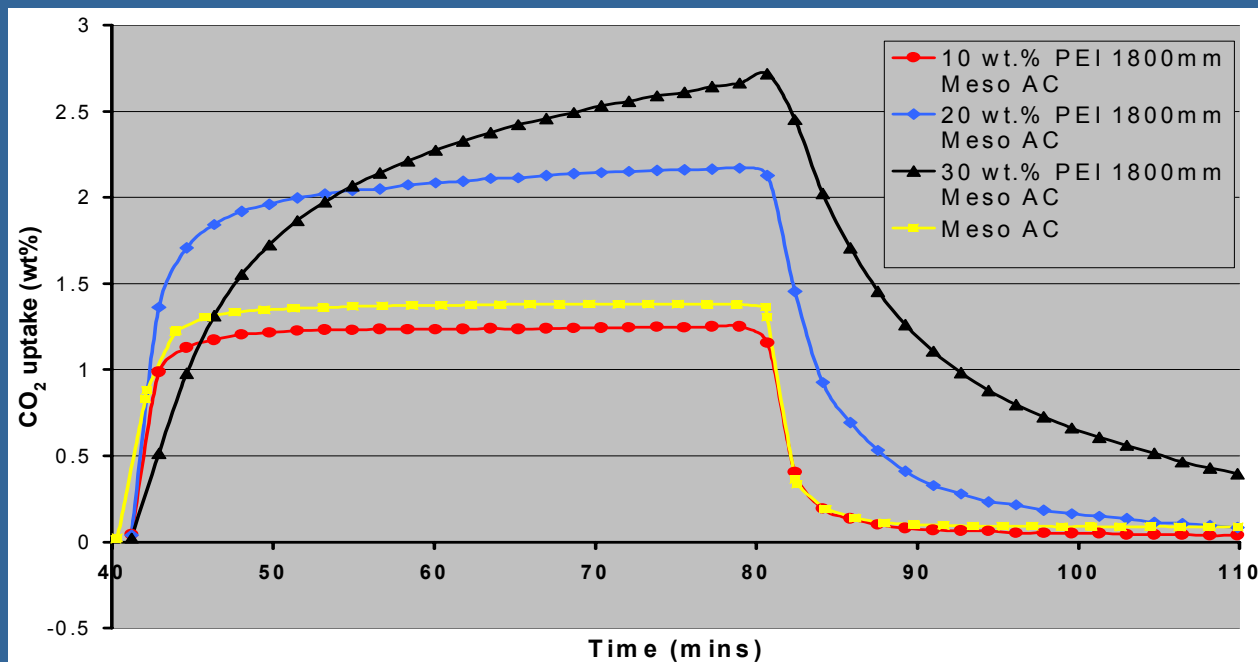
Optimal Properties



- **CO₂ activation (1100°C) the most effective of the three activation methods for generating mesoporosity**

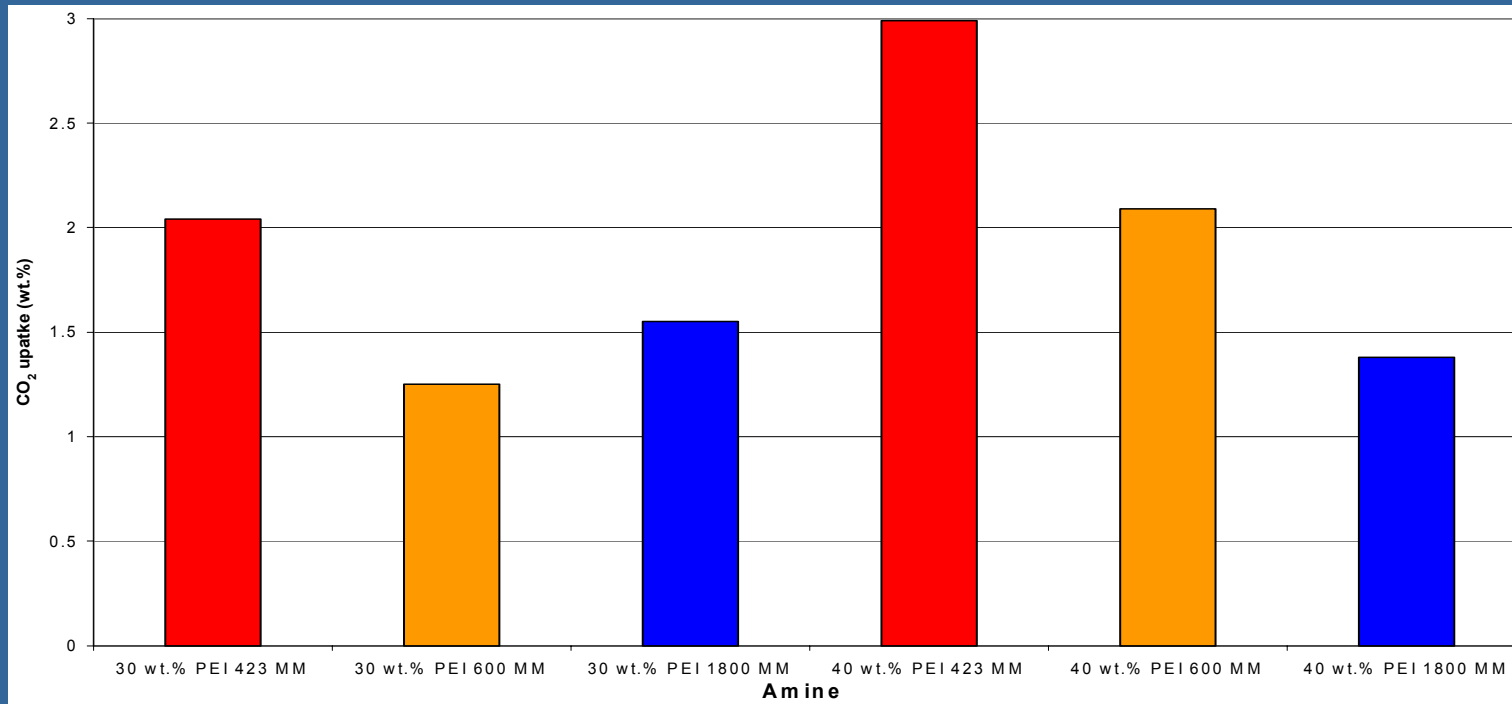
3. Equilibrium CO₂ adsorption Amine polymers

- **Polyethylenimine (PEI)** - $\text{NH}_2(\text{CH}_2\text{CH}_2\text{-NH})_n$
– 3 molecular mass forms used 1800, 600, 423
- **Diethanolamine (DEA)** - $(\text{C}_2\text{H}_4\text{OH})_2\text{NH}$
- **Tetraethylenepentaamineacrylonitrile (TEPAN)** -
 $(\text{CNCH}_2\text{CH}_2\text{NH-CNCH}_2\text{CH}_2\text{NH-})_n$



3. Equilibrium CO₂ adsorption

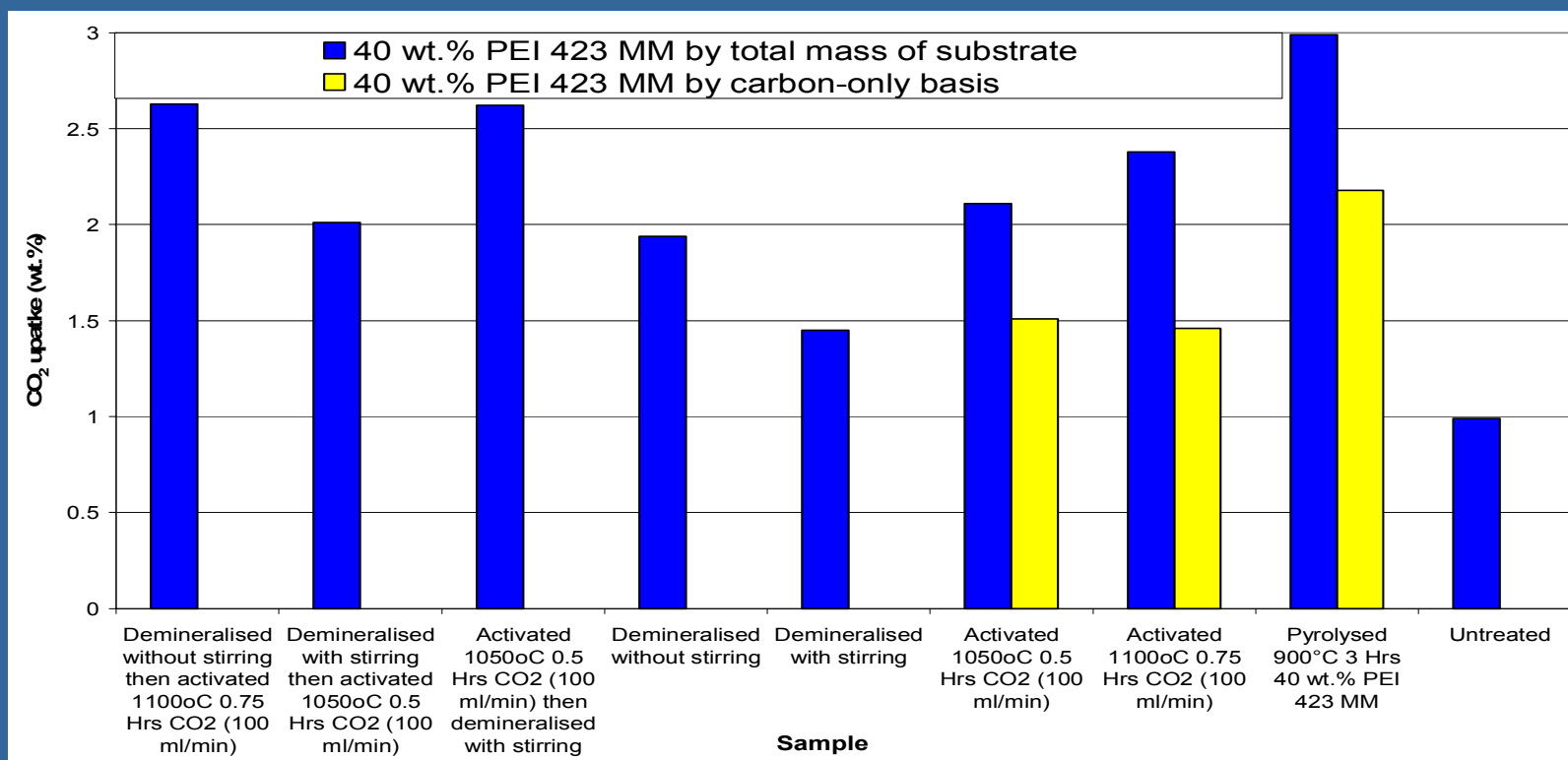
Effect of amine type on CO₂ uptake, 75°C, PFA-derived activated carbon at 40 wt.% loading



- **TEPAN** poorest CO₂ uptakes, lower ratio of amine groups to carbons: 1:4, vs 1:2 for PEI.
- **PEI 423 MM** best suited for PFA-derived substrates, i.e. low mesoporosities
- **The best CO₂ uptake - 4.7 wt.% at 75°C** using High Marnham PFA-derived substrate (pyrolysed form: 3 Hrs at 900°C, 75-710 µm size fraction) PEI 423 MM 40 wt.%

3. Equilibrium CO₂ adsorption

75 °C, PFA-derived activated carbon at 40 wt.% loading

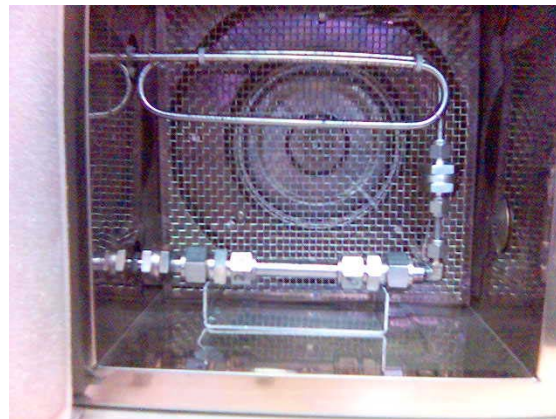
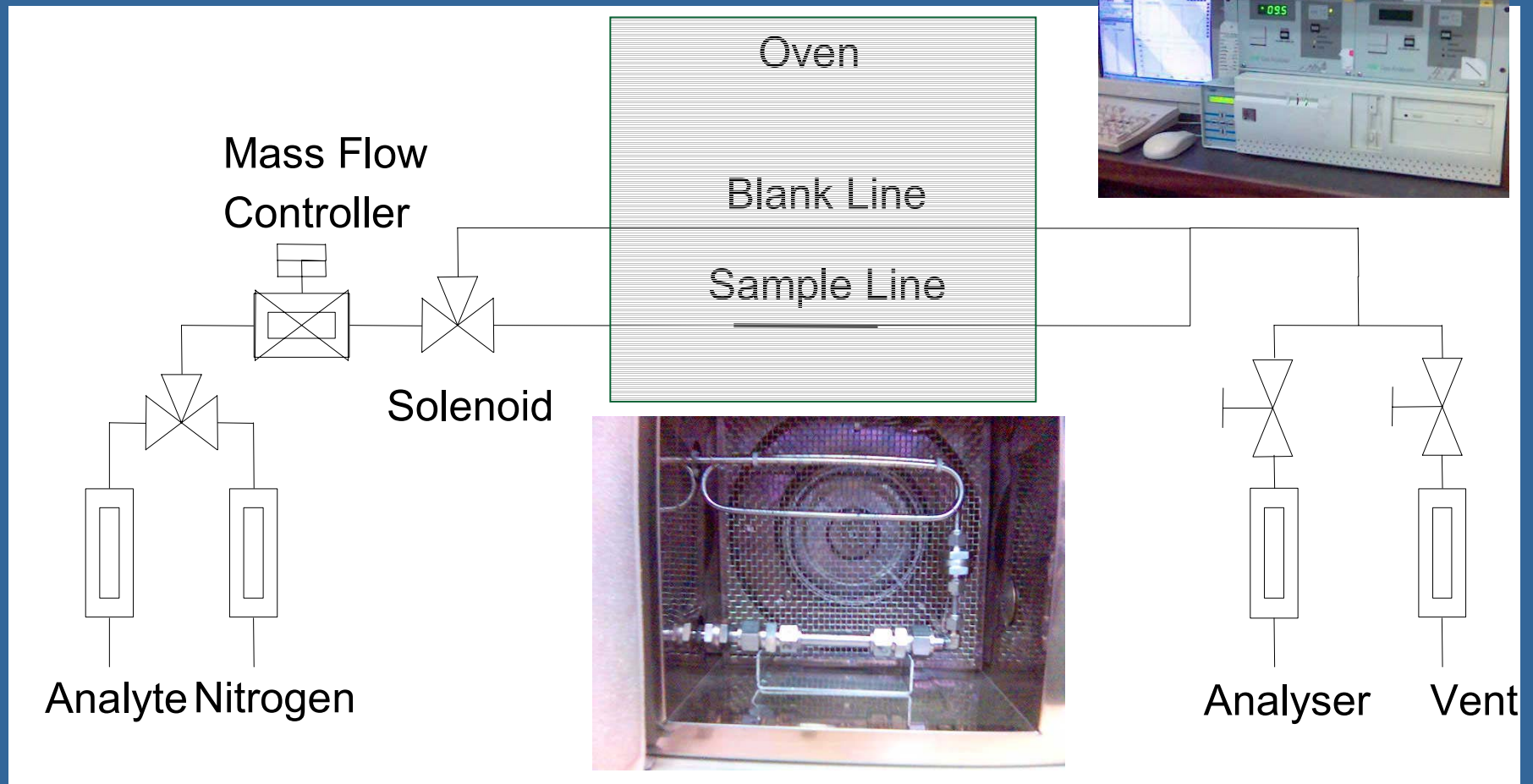


- Demineralisation after activation enhances adsorption capacity
- Pyrolysis of the PFA results in increased CO₂ adsorption capacity – this can be attributed to changes in surface chemistry allowing for more efficient adsorption of the PEI amine polymer

3. Simulated flue gas CO₂ adsorption

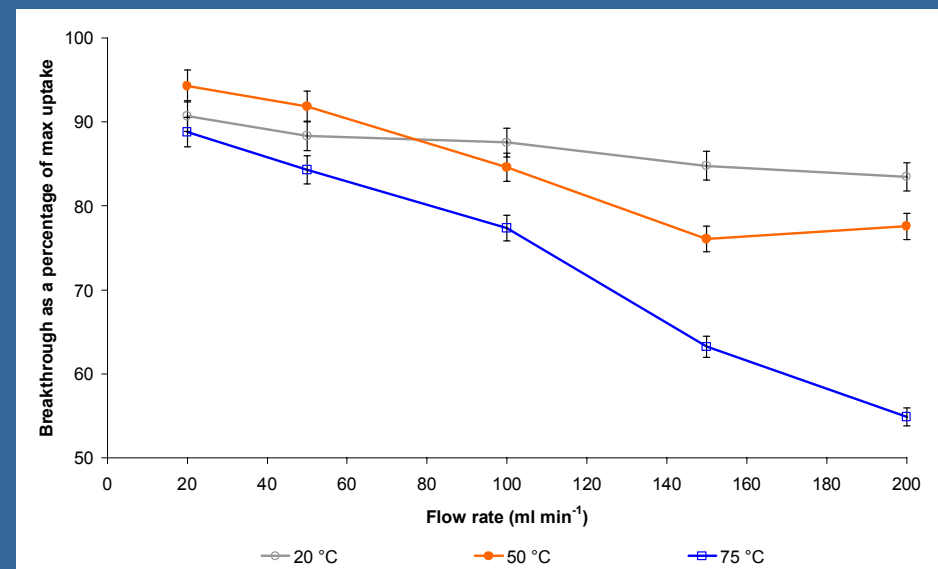
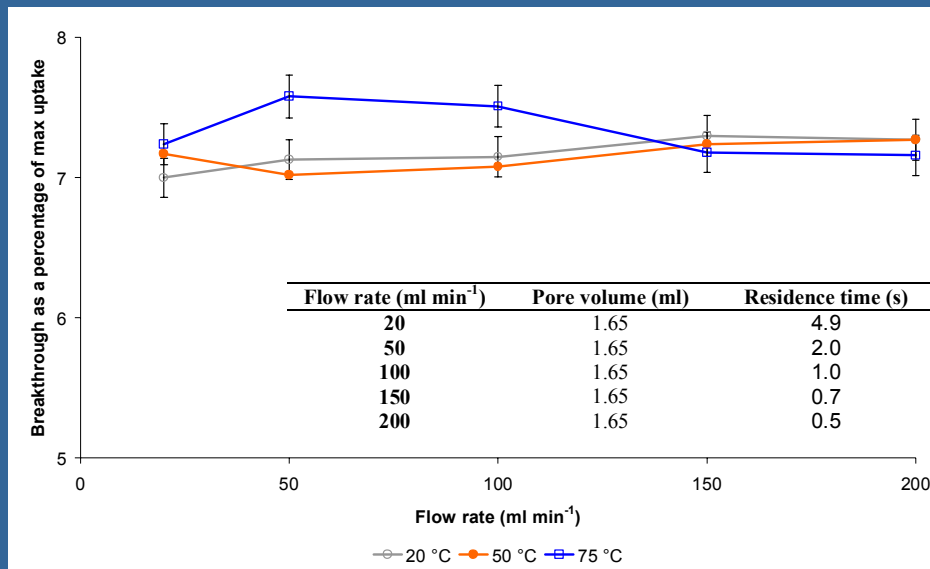
Dynamic adsorption rig

15% CO₂ ± 1000 ppm SO₂, balance N₂



3. Simulated flue gas CO₂ adsorption

Adsorption and breakthrough

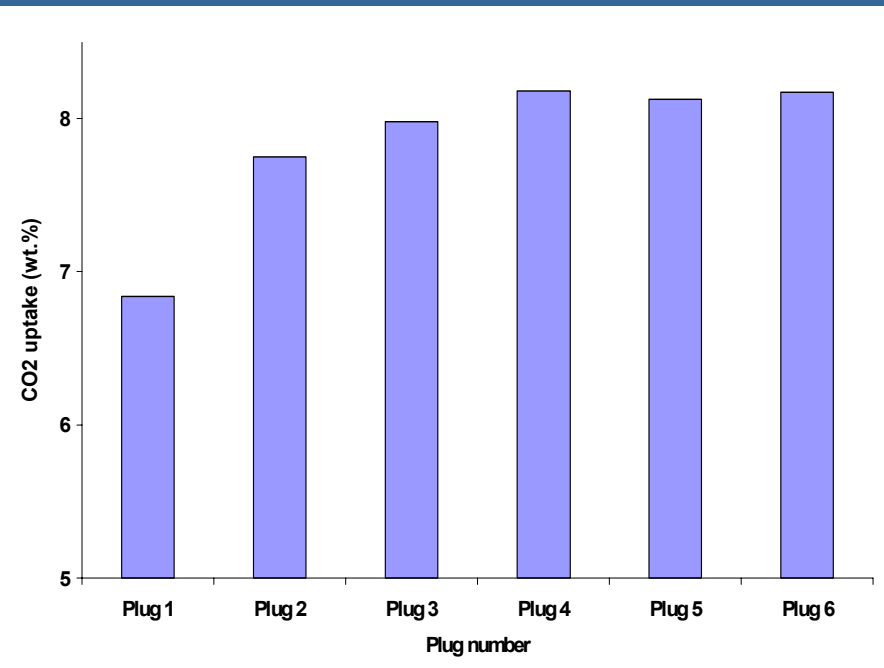
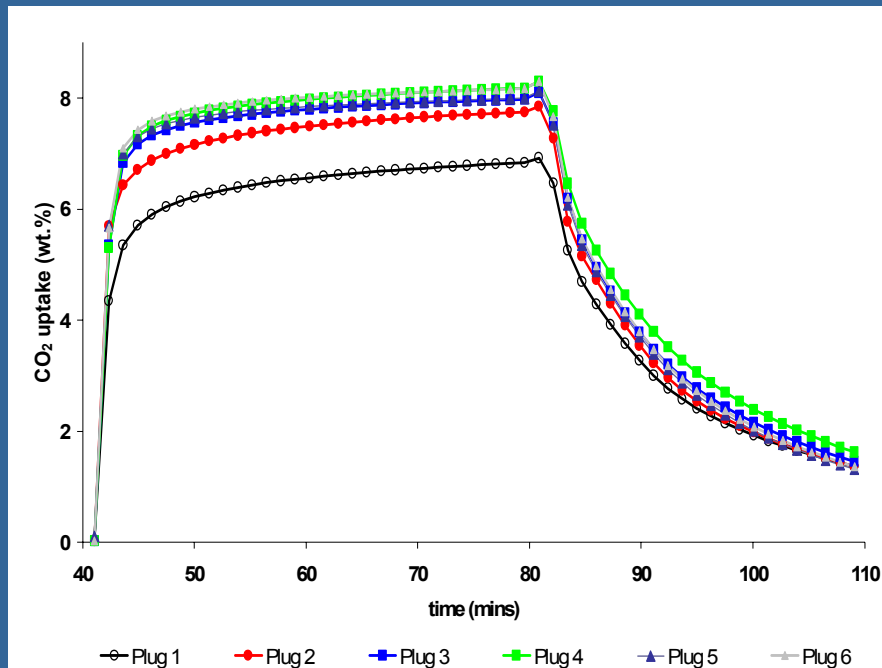


•Results for PEI based adsorbent:

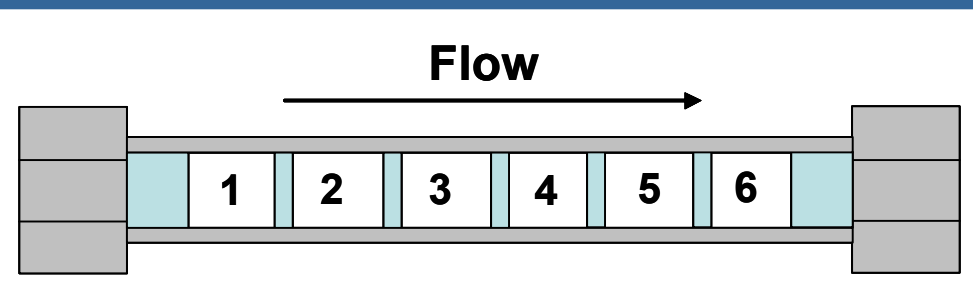
- Overall adsorption capacity not influenced by flow rate – approx 80% of that determined by TGA at equilibrium
- Breakthrough capacity high – only significantly decreasing at 75 °C
- Demonstrates adsorption on PEI to be rapid – low residence times

SO₂ analysis

Adsorption Capacity after contact with SO₂



- Adsorption capacity of the “front end” of the adsorbent reduced after contacting with SO₂
- Demonstrates SO₂ only penetrates the front end of the adsorbent bed



SO₂ analysis

TGA Analysis






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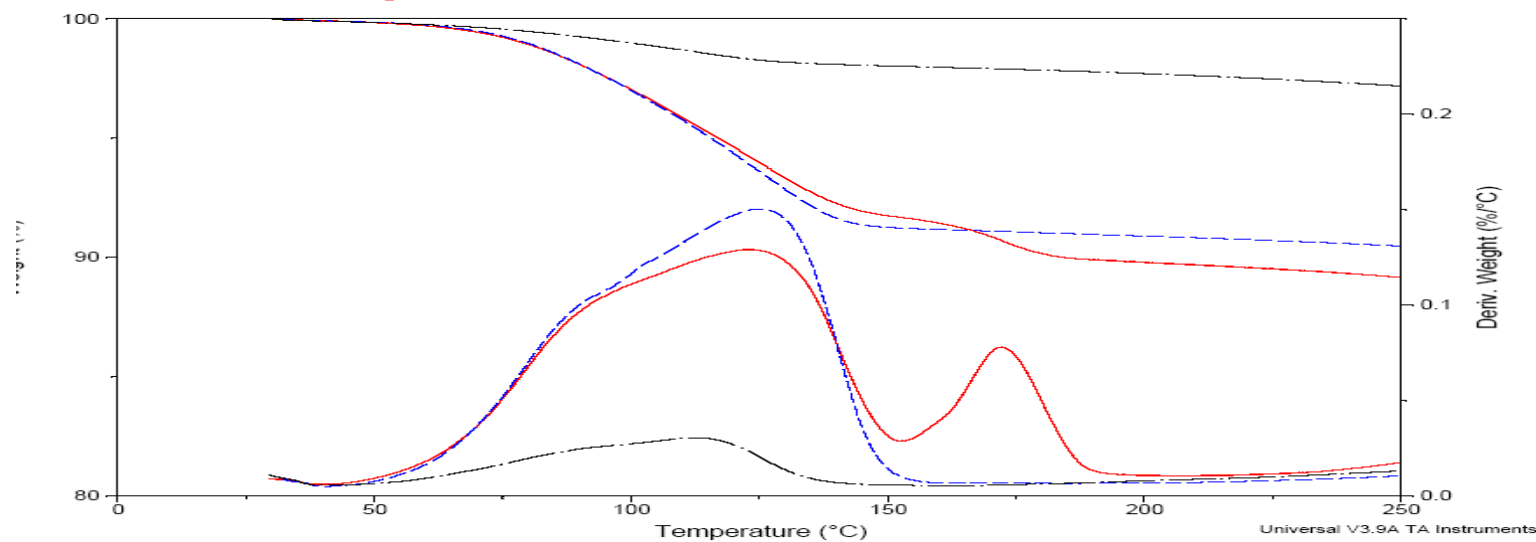
Mass Spec

CO₂

SO₂

Blank 
Front 
End 

TGA

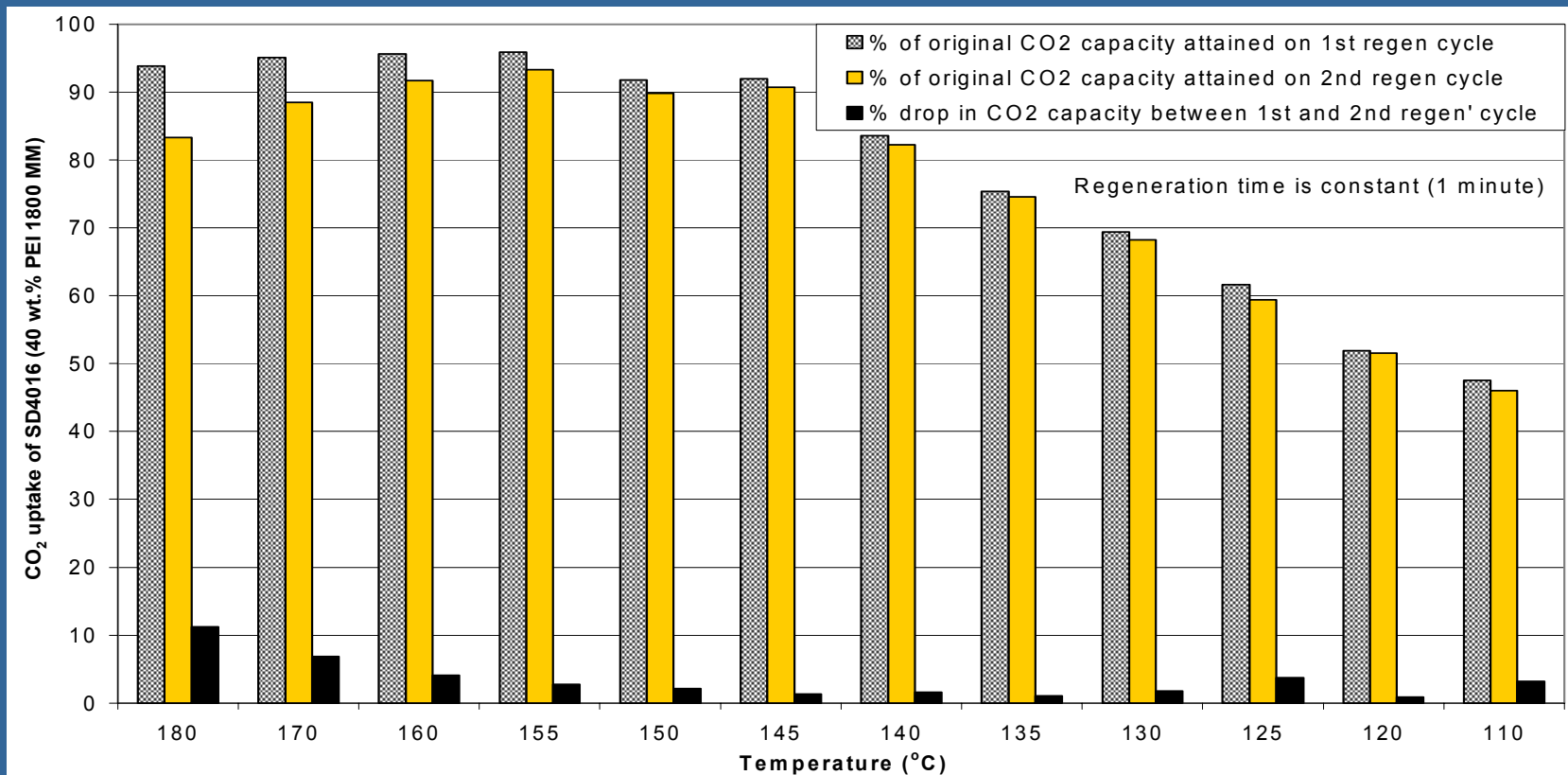


Universal V3.9A TA Instruments

4. Establishing Suitable Regeneration Regimes

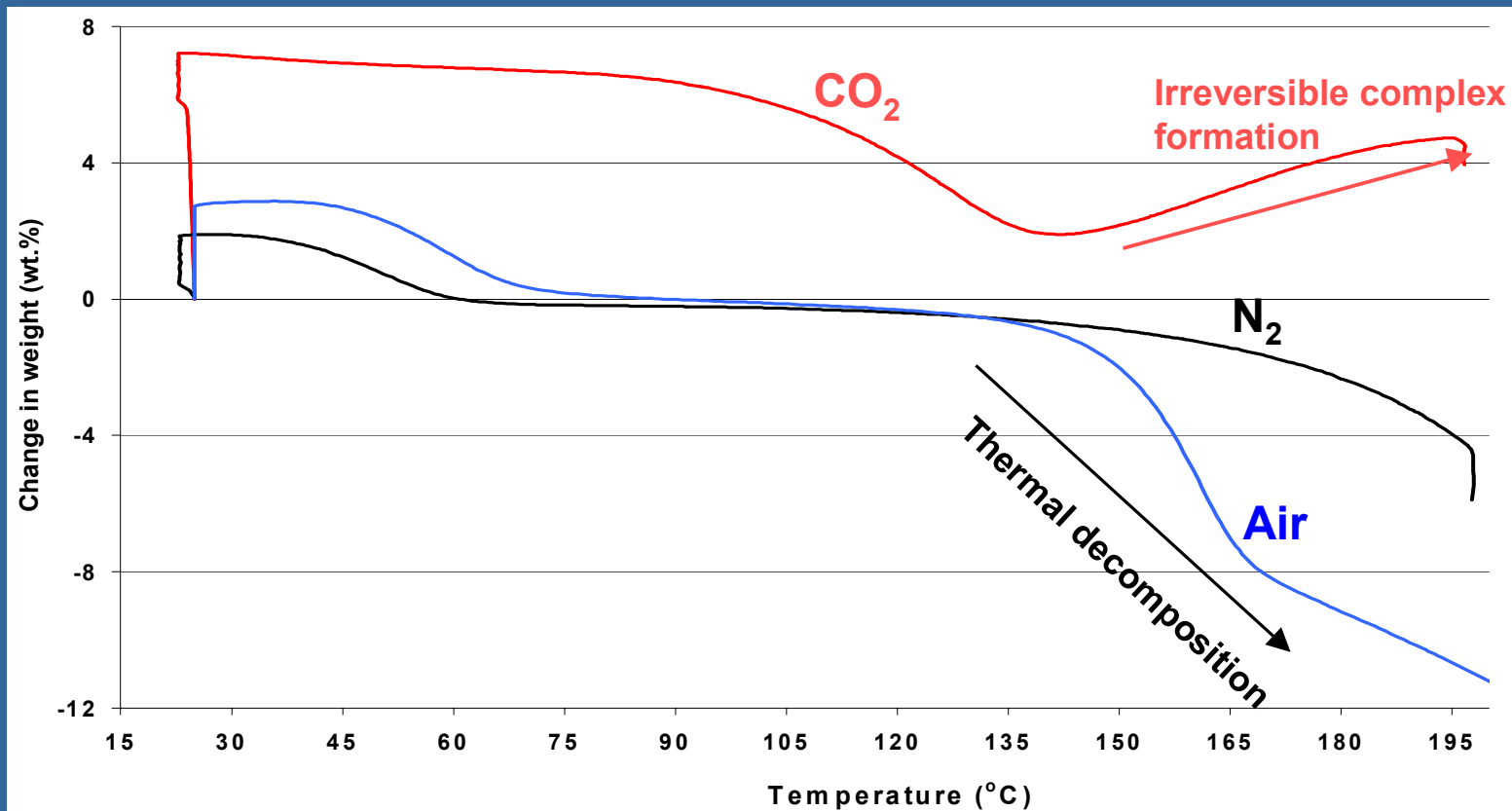
Effect of regeneration temperature

- 3 cycle TSA program under CO₂ (preceded by drying in N₂ for 30 mins):
 - Adsorption: 40 min, 75°C
 - Regeneration : Heating to regeneration temp at 15°C/min, 1 minute at regeneration temp, cooling at 10 °C/min to 75°C



4. Establishing Suitable regeneration Regimes

Effect of regeneration temp



- Possible dehydration of carbamate leading to urea formation proposed for irreversible complex
- Destruction of adsorbent can be avoided by steam stripping

Conclusions

- **PFA-polymer system offer significant increase in adsorption over standard physical adsorption**
- **PFA can be used as a CO₂ adsorbent if mesopore volume and diameter are maximised to achieve high CO₂ adsorption capacities**
- **Comparison between PFA and silica demonstrates silica to be preferred option:**
 - Greater density
 - Higher adsorption capacities
- **Demonstrated selected capture and desorption of SO₂**
- **PEI - reasonable thermal stability for repeated recycling**
 - irreversible complex formation can be overcome by steam stripping

BCURA funding helped to establish an international leading activity on adsorbents