The University of Nottingham
Nottingham Fuel & Energy Centre

The Partial Removal of CO_2 from Flue Gases using Tailored Coal-Derived Carbons

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The Partial Removal of CO_2 from Flue Gases using Tailored Coal-Derived Carbons

Executive Summary

At present, liquid amine scrubbers are used for removing CO_2 from gas streams. Estimated losses in overall efficiency are in the region of 10% points (i.e. from *ca.* 40 to 30% for supercritical water PF combustion). Indeed, 75–80% of the total cost of capturing and storing 90% of the CO_2 from a power plant is attributable to the capture and compression stage, hence a substantial lowering of the cost of capture would represent a major advance in realising the goal of making CO_2 containment economically viable. As a result of these high energy losses, technologies other than amine scrubbing are now being considered for CO_2 capture, including oxyfuel combustion, chemical looping and adsorption. Due to their high surface areas and micro- and meso-pore volumes, which can be tailored to meet specific requirements, activated carbons possess relatively high CO_2 adsorption capacities; hence they should be an effective means for capturing CO_2 from flue gases. However, since CO_2 adsorption predominately involves physical mechanisms, uptakes are low pressures are generally not that high. Their use for this purpose is further hampered by their high sensitivity to temperature - at the temperatures commonly associated with power plant flue gases (50-120^oC), their adsorption capacity drops dramatically. Consequently, for their use to be made feasible, their modification by appropriate treatments is required. Indeed, the focus of this project is the treatment of low-cost coal-derived carbons through impregnation with basic chemicals giving a high affinity for CO_2. To assess the base impregnated carbon concentrates, extensive comparisons have been made with corresponding mesoporous silicas. Given that the regeneration and lifetimes of basic adsorbents are not heavily dependent on the substrate used, the silica-based systems have also been used to provide the results on these aspects of the research.

The Nottingham Fuel & Energy Centre has established a major research programme on adsorbents for CO_2 capture in both PF combustion and gasification. Regarding PF combustion, the BCURA award was used to facilitate matching funding to be obtained from the Carbon Trust. The BCURA-supported research investigated low-cost carbons as substrates for bases while the Carbon Trust programme has enabled mesoporous silicas to be developed. Overall, the anticipated benefit from the research is to establish adsorption as a potentially competitive means of capturing CO_2 from power plant flue gases.

The specific objectives listed in the proposal were as follows.

1. Prepare carbon concentrates from fly-ash using laboratory techniques already developed and obtain breeze from carbonisation (0-4 months).
2. Characterise the active carbons by BET surface area, other standard adsorption tests (e.g. phenol, methylene blue) microscopic techniques (4-7 months).
3. Activation of the carbon concentrates and breeze with steam or CO_2 at different temperatures and times (7-10 months).
4. Preparation of functionalised active carbons by impregnation with basic polymers (10-14 months).
5. Testing of the parent and tailored activated carbons in terms of CO_2 uptake compared with commercially available activated carbons (14-28 months) to determine the improvement achieved with immobilized amines (14-26 months).
6. Establishing suitable regeneration regimes (pressure swing and thermal) for selectively removing CO_2 and other acid gases, namely HCl and SO_2, during desorption for the most effective sorbents (26-32 months).
7. Ascertaining the lifetimes of the most effective adsorbents via multiple adsorption and regeneration tests (32-36 months).

The principal conclusions of the research relating to the specific objectives are now described.

Preparation and characterisation of carbon concentrates fly ash (PFA_CCs) Dry sieving was the least effective of the beneficiation methods evaluated. Demineralisation was the most effective but was the most time consuming and the most expensive. In general, incipient fluidisation yielded PFA-CCs with higher carbon contents than those produced with froth flotation, but because of its ease of use and the relative high speed with which it could generate PFA_CCs, froth flotation was the preferred method of beneficiation.

Activation of the carbon concentrates The most desirable characteristics in a substrate for amine impregnation are a high mesopore volume and mesopore diameter. Thus, the primary objective of the activation studies was to ascertain the optimum conditions for attaining these structural characteristics from PFA_CCs. NaOH was a better chemical activation reagent than either KOH or H_3PO_4: a PFA_CC:NaOH ratio of 1:1, coupled with an activation temperature of 800°C yielded the best substrates. Contrary to claims made in the literature, CO_2 activation was found to be more effective than steam activation. Its success was however contingent on the use of a high temperature: i.e. 1100°C: at this temperature the optimum carbon burn-out for generating high mesopore diameters was 40 – 70 wt.%. The optimum carbon burn-out for maximising the mesopore volume was ca. 70-75 wt.%.

Assessment of equilibrium CO_2 uptakes of the sorbents The higher the molecular mass (MM) of the basic polymer, polyethylenimine (PEI), the lower the loading a substrate can sustain before becoming saturated with the amine: beyond the saturation loading, there is a decline in the CO_2 uptake of the resulting sorbent. Of the three PEIs investigated, the one with the lowest MM (423) was the best suited for PFA-derived substrates, i.e. substrates with relatively low mesoporosities. At high loadings - 50 wt.% and above, the amine, tetraethylenepentaamineacrylonitrile (TEPAN) was more effective than the PEI, but these loadings engendered excessive stickiness in the sorbents. The best CO_2 uptake achieved at 75°C using a PFA-derived substrate was 4.7 wt.%. This utilised a PEI loading of 40 wt. % and the substrate comprised the pyrolysed form (3 Hrs at 900°C) of the 75-710 µm size fraction of the High Marnham sample. For the preparation of PEI-impregnated PFA_CC and PFA_ACC substrates, water can be used as a substitute for methanol without any significant effect on in the quality of the resulting sorbents. Ultimately, demineralisation represents the optimum route towards engendering a high receptivity to amine impregnation from PFA_CC and PFA_ACCs: work published in the literature has demonstrated that a PEI loaded demineralised PFA_CC can attain CO_2 uptakes up to 9.4 wt.% at 75°C: the shortfall with the CO_2 uptakes achieved here can be explained by differences in the PFA_CC used.

Dynamic testing of the adsorbents The key towards attaining breakthrough capacities that approach parity with the equilibrium uptakes is to maximise the residence time. However, even at relatively low residence times less than 1 s, PEI-loaded sorbents can attain breakthrough CO_2 uptakes that correspond to *ca.* 80 % of the equilibrium capacity. At 75°C and under a gas flow of 85 % N_2, 15 % CO_2 (by volume), the best PFA_CC based sorbent performed less well than its silica based counterpart, but it achieved *ca.* two thirds (4.7 wt.%) of the silica based sorbent's total CO_2 uptake and ca. three fifths (3.4 wt.%) of the breakthrough CO_2 uptake. When SO_2 is present in the flue gas, PEI-loaded substrates adsorb the SO_2 in the region closest to the gas inlet. Exposure to SO_2 exacerbates the reduction in CO_2 uptake engendered by the standard temperature swing adsorption (TSA) regeneration process. However, the sorbent's lifetime can potentially be conserved by the insertion of a sacrificial sorbent bed between the sorbent and the gas inlet.

Regeneration and life time testing All of the PEI amines, when exposed to CO_2, irreversibly gain mass at temperatures in excess of *ca.* 135°C, possibly as a result of the dehydration of the ammonium carbamate formed through the adsorption of CO_2 upon PEI, thus generating urea. This therefore inhibits the use of TSA when CO_2 is deployed as the stripping gas. Indeed, following the

equivalent of sixty 1 minute regeneration cycles (performed in the TGA), the measured drop in the CO_2 adsorption capacity of a PEI 1800 MM impregnated substrate was ca. 32 wt.% at 140°C. It has been demonstrated that PEI-loaded sorbents respond well to TSA conducted with nitrogen as the stripping gas, thus it is probable that steam could function as a viable alternative to CO_2, given CO_2's limitations as a stripping gas.

Significance of the findings The findings have resulted in the following.

1. The preparation of PEI-impregnated substrates for CO_2 adsorption to be optimised.
2. The effect of a range of activation conditions on mesopore volume and CO_2 uptake to be assessed.
3. To enable the CO_2 equilibrium adsorption capacities of a range of silica and carbon base-impregnated substrates to be rationalised in terms of the amount of base used and the mesopore volume of the substrate.
4. A simple dynamic test facility has been constructed to assess conditions where much of the CO_2 equilibrium uptake can be translated into breakthrough capacity in a fixed-bed as a basis for larger-scale tests.
5. Suitable temperature swing regeneration conditions have been identified for PEI-impregnated substrates: although most of the CO_2 can be desorbed at 150°C, the use of a CO_2 atmosphere leads to irreversible uptake and therefore, steam stripping, which was simulated here using nitrogen as a sweep gas, is likely to be the most effective strategy.

F**uture R&D direction** The findings for the base-impregnated PFA_CCs and their activated counterparts and the comparisons drawn the corresponding mesoporous silicas have indicated that mesopore volume is the key to achieving high CO_2 adsorption capacities. Thus, to develop base-impregnated substrates for CO_2 capture from flue gas, silicas are the preferred option. Further, silicas have the advantage of being denser than carbons and thus give vastly higher CO_2 uptakes on a volumetric basis. In terms of further development, PEI would appear to have reasonable thermal stability for repeated recycling, the main disadvantage is that it forms a stable complex with CO_2 at elevated temperatures and, for stripping, steam will need to be used giving an additional separation step (as in amine scrubbers). As part of the Carbon Trust project, a large batch (several kg) of a silica-PEI adsorbent will be prepared to demonstrate that the water-based preparation can readily be scaled up and to provide sufficient sample for tests with actual flue gas using a slip stream from the 1 MW rig at E.ON UK. The capture of SO_2 selectively over CO_2 means that the PEI-based adsorbents, depending upon economics, be extremely effective for reducing acid gases down to extremely low levels after flue gas desulphurisation for CO_2 removal in amine scrubbers.

Overall, the BCURA support has helped considerably in establishing an international leading activity on adsorbents which is likely to continue based on the results described. The beneficiaries of this research effort are the power generation industry who will need to actively assess alternative technologies to amine scrubbing in the quest to reduce the costs of CO_2 capture. . Further, physical adsorbents are being investigated for CO_2 capture in gasification at high partial pressures (DTI Cleaner Coal Technology Programme, project lead by Jacobs Consultancy).

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1 Introduction and objectives

Increasing awareness of the influence of greenhouse gases on global climate change has led to recent efforts to develop strategies for the reduction of carbon dioxide (CO_2) emissions from coal utilisation. Along with improved efficiency from supercritical steam cycles and partial biomass substitution, the strategy that is receiving the most attention for pulverised fuel (PF) combustion involves the capture of CO_2 and its long-term storage underground. At present, liquid amine scrubbers are used for removing CO_2 from gas streams. However, they have a large cost attached to both their purchase and operation, a flaw that is in part due to their requirement that concentrations of SO_x and NO_x in the flue gases must first be lowered to almost negligible levels upstream of the scrubbers. Amine scrubbers also place a heavy energy demand on the power plant, the lowered efficiency of which negates the effectiveness of the scrubbers. Estimated losses in overall efficiency are in the region of 10% (i.e. from *ca*. 40 to 30% for supercritical steam PF combustion). Indeed, 75–80% of the total cost of capturing and storing 90% of the CO_2 from a power plant is attributable to the capture and compression stage (David, 2000), hence a substantial lowering of the cost of capture would represent a major advance in realising the goal of making CO_2 sequestration economically viable. As a result of these high energy losses, technologies other than amine scrubbing are now being considered for CO_2 capture, including oxyfuel combustion, chemical looping and adsorption.

With their high surface areas and micro- and meso-pore volumes, which can be tailored to meet specific requirements, activated carbons possess relatively high CO_2 adsorption capacities; hence they should be an effective means for capturing CO_2 from flue gases. However, since CO_2 adsorption predominately involves physical mechanisms, uptakes at low pressures are generally not that high. Their use for this purpose is further hampered by their high sensitivity to temperature - at the temperatures commonly associated with power plant flue gases (50-120^oC), their adsorption capacity drops dramatically. Consequently, for their use to be made feasible, their modification by appropriate treatments is required. Thus, the focus of this project is the treatment of low-cast coal-derived carbons through impregnation with basic chemicals giving a high affinity for CO_2.

The use of amines for enhancing the CO_2 adsorption capacity of meso- and micro-porous solids has already been demonstrated. Of particular note is the work of (Gray, *et al.*, 2003), Filburn, et al., (2002), Birbara, *et al.* (1999), (Birbara, *et al.*, 2002), (Birbara and Naletta, 1994b), (Birbara and Naletta, 1994a), (Satyapal, *et al.*, 2001) and Xu, et al., (2003b). Of the different amine compounds investigated by these researchers, the most efficacious in enhancing the CO_2 sorption capacity of the substances upon which they have been impregnated have been PEI (polyethylenimine), DEA (diethanolamine) and TEPAN (tetraethylenepenta amineacrylonitrile). However, the research to date has not identified how base-impregnated adsorbents would be regenerated nor given any indication of their lifetimes under PF flue gas conditions. A potential advantage of adsorption compared to amine scrubbing is that residual acid gases, notably SO_2 and HCl, which result in amine solvent loss during scrubbing, could, as a consequence of their stronger acidity, be removed prior to CO_2.

The Nottingham Fuel & Energy Centre has established a major research programme on adsorbents for CO_2 capture in both PF combustion and gasification. Regarding PF combustion, the BCURA award was used to facilitate matching funding to be obtained from the Carbon Trust. The BCURA-supported research investigated low-cost carbons as substrates for bases while the Carbon Trust programme has enabled mesoporous silicas to be developed. Further, RFCS support (ASSOCODS) has enabled special activated carbons with high nitrogen contents for enhancing CO_2 capture to be developed. Overall, the anticipated benefit from the research is to establish adsorption as a potentially competitive means of capturing CO_2 from power plant flue gases.

The specific objectives of the BCURA project defined the proposal were as follows.

8. Prepare carbon concentrates from fly-ash using laboratory techniques already developed and obtain breeze from carbonisation (0-4 months).
9. Characterise the active carbons by BET surface area, other standard adsorption tests (e.g. phenol, methylene blue) microscopic techniques (4-7 months).
10. Activation of the carbon concentrates and breeze with steam or CO_2 at different temperatures and times (7-10 months).
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12. Testing of the parent and tailored activated carbons in terms of CO_2 uptake compared with commercially available activated carbons (14-28 months) to determine the improvement achieved with immobilized amines (14-26 months).
13. Establishing suitable regeneration regimes (pressure swing and thermal) for selectively removing CO_2 and other acid gases, namely HCl and SO_2, during desorption for the most effective sorbents (26-32 months).
14. Ascertaining the lifetimes of the most effective adsorbents via multiple adsorption and regeneration tests (32-36 months).

The results and discussion section is organised to reflect these objectives. For the purposes of brevity, the acronyms PFA_CC and PFA_ACC have been used for PFA-derived carbon concentrates and PFA derived activated carbon concentrates respectively. Other key acronyms employed in this report include MM for molecular mass and PFA for pulverised fuel ash. To assess the base impregnated PFA_CC and PFA_CC samples, extensive comparisons were made with the corresponding mesoporous silicas. Given that the regeneration and lifetimes of basic adsorbents are not heavily dependent on the substrate used, the silica-based systems have also been used to provide the results on these aspects of the research. The procurement and testing of the silicas constitutes part of the Carbon Trust funded project, and therefore all results pertaining to the silicas reported in this document are commercially sensitive.

The initial supervisors of the project were Dr. Cloke and Prof. Snape but, following Dr. Cloke's secondment to the Malaysia campus of the University of Nottingham, Dr. Snape became the principal supervisor and Dr. Steel became a co-supervisor. The research has largely been carried out by Karl Smith, a Ph.D student with contributions from Dr. Trevor Drage (employed on both Carbon Trust and BCURA contracts). However, Dr. Drage has been successful in obtaining an EPSRC Advanced fellowship and, in recognition of the prestigious award, he has also acted as co-supervisor for the latter stages of the project. Dr. Irons replaced Dr. Gibb as the industrial supervisor for the final year of the project.

2 Experimental/Methodology

In this section the principal experimental methods employed in the preparation, analysis and characterisation of the substrates and sorbents utilised in this project are described.

2.1 Beneficiation techniques:

2.1.1 Incipient fluidisation

Incipient fluidisation of the particles was performed using an open ended, hollow glass tube ca. 6 cm in diameter, one end of which narrowed into a cone. The tube was mounted vertically, the cone end facing downwards. A porous frit spanned the cross-sectional area of the tube immediately above the cone section, upon which the PFA to be beneficiated was placed. The orifice end of the cone was connected to a compressed air line: by manipulating of the flow rate of the air issuing

from the air line, a point could be reached at which the fluid pressure loss across the bed of particles was equal to the apparent weight of the particles per unit area of the bed (Particle Technology Research Group, 2001), whereupon the bed of PFA was said to be in a state of incipient fluidisation (Yin, 2002). Under these conditions the low-density carbon fractions which had accrued at the top of the bed could then be removed by means of a suction device. A diagram depicting how incipient fluidisation was deployed is shown in Figure 1.

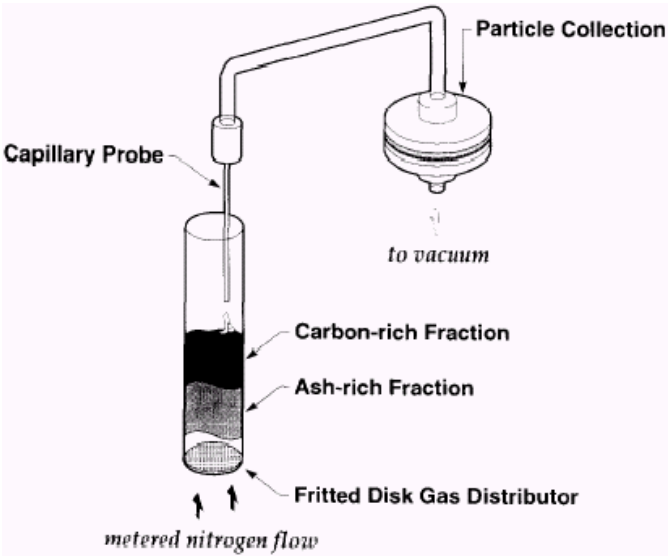

Figure 1: Diagram of fluidisation rig (Hurt and Gibbins, 1995)

2.1.2 Froth flotation

PFA_CCs were prepared with froth flotation by weighing 700 g of PFA into a container and then filling the container with the quantity of water necessary to reach a level ½ inch from its lip (3.5 litres). Between 0.3 ml and 0.6 ml of n-dodecane was added to the slurry, which was then agitated but not aerated. Between 0.1 ml and 0.5 ml was subsequently added – the amount added was the minimum required to generate a froth. The mixture was then aerated and agitated and the froth was collected over a series of 60 second periods. At the conclusion of each collection period 0.3 ml of n-dodecane was added to the slurry. Once the colour of the froth began to turn from black to grey, the process was terminated and the carbon recovered from the froth dried and then analysed.

2.1.3 Demineralisation

The demineralisation of the PFA samples entailed removing their mineral content through the application of the reagents hydrofluoric acid (HF) and hydrochloric acid (HCl). The demineralisation procedure comprised two distinct stages: In the first stage the PFA was mixed with HF. An approximate ratio of 10 ml HF per gram of ash (on a carbon free basis) was used. 50 ml HF, diluted in 150 ml of water, and hence 5 g of ash (i.e. the non-organic component of the PFA) were the maximum quantities used in a single test. The mixture of HF, water and PFA was mixed at a temperature of ca. 60°C for 6 hours. Subsequently, the treated PFA was recovered by filtration. In the second stage, the F^+ ions generated were mopped by mixing 30 ml of HCl, diluted in 170ml of water, with the recovered PFA at 60^{o}C. The material remaining was recovered by filtration.

2.2 Surface area analysis - N_2 adsorption isotherms

The surface area, meso- and micro- pore volumes and average pore diameter of the substrates were calculated from adsorption and desorption isotherms. These were produced using an ASAP 2010 unit, the function of which was to measuring the volume of N_2 adsorbed on and desorbed from the specimens under investigation over a range of pre-selected pressures from near-vacuum to ca.

atmospheric pressure at a temperature of 77 K. The pressure was increased incrementally to produce the adsorption isotherm, and then reduced incrementally to obtain the desorption isotherm (Perry, 2003). The carbons were degassed at 115°C prior to their surface area being measured.

The value for the surface area was obtained using the multi-point BET equation, and used points obtained within the relative pressure range 0.05-0.35 (the range of values also deployed by Zhang, *et al.* (2003)) on the adsorption branch of the isotherm.

The mesopore cumulative pore volume and diameter was found using the multipoint BJH (Barrett-Joyner-Halenda) equation - the BJH method has previously been used to find the mesopore volume of activated PFA carbon by Maroto-Valer, *et al.*, (1999) and Zhang, *et al.* (2003). The pores sizes 2nm and 50nm were taken as the limits between micro- and mesopores, and meso- and macropores, respectively, in accordance with the IUPAC nomenclature (Sing, *et al.*, 1985). The micropore volume was measured using the t-plot method, the use of which is described by Greg and Sing (1982).

2.3 LOI: Carbon content

For this report, the loss on ignition (LOI) test served as the principal method of determining the carbon content of the samples. A generally accepted method for estimating the carbon content of PFA (ASTM, 1996), the LOI test consisted of igniting a PFA sample in a muffle furnace at 750–950°C and measuring the change in its dry mass this engendered: the LOI was given as the percentage loss in mass of the sample. Essentially, the loss on ignition (LOI) of a sample refers to its combustible content, i.e. its organic content, most of which is carbon. The precise conditions employed n this project were 800ºC (± 10ºC) with a time period of ca. 1 Hr.

2.4 Physical activation: CO_2

The bulk of the CO_2 activation runs were conducted using a horizontal tube furnace. The samples, which were 3.0 g in weight, were placed on a crucible fabricated from firebrick, which was in turn positioned in the centre of the reactor: the reactor was a hollow, open ended quartz tube. The reactor was suspended n the horizontal tube furnace, with the sample sited within the heating zone.

The reactor was sealed on either end with a silicone bung. Each of the bungs was pierced by a stainless steel, ¼" pipe which ran through their centre: these pipes were connected to, variously a vent and a gas supply line. Activation runs entailed passing N_2 through the gas supply line at a flow rate of 100 ml/min whilst the furnace was heated to the activation temperature. Once the activation temperature was reached, the injected flow of gas was switched to CO_2 whilst the flow rate was maintained at 100 ml/min. Upon reaching the end of the activation period, the gas flow was reverted to N_2 and the furnace was cooled by the injection of compressed air.

2.5 Chemical activation

For this report, the use of phosphoric acid (H_3PO_4), sodium hydroxide (NaOH) and potassium hydroxide (KOH) for developing the pore stricture of PFA_CC through chemical activation was investigated and evaluated. The same method was used for each of these reagents: 2 g of the CC_PFA was added to 100 ml of distilled water (50 g of water was used for every gram of PFA) into which was then inserted the weight of reagent necessary to achieve the requisite ratio of reagent to CC_PFA. The resulting slurry was stirred and heated using a heater-stirrer at ca. 85°C until almost all of the water had been evaporated. Subsequently, the mixture was transferred to a crucible, whereupon it was dried overnight at ca. 105°C before being activated. The activation step entailed heating the mixture for a set time period at 900°C within a quartz tube held in a horizontal

tube furnace. Throughout the activation step the sample was kept under a flow of nitrogen (200 ml/min stp). A heating rate of 10°C/min, i.e. 600°C/hr was used to reach the activation temperature.

Subsequent to activation the sample was placed into a 250 ml solution of 0.5N HCl, which was then stirred and heated at 85°C using a heater/stirrer for 30 minutes. The solution was then filtered to recover the sample and was subsequently washed in distilled water until pH neutral conditions were achieved before being dried overnight at ca. 105°C. In instances where after the HCl washing treatment the samples still returned pHs in excesses of 7 the samples were washed with a further 250 ml of 0.5 N HCl and were again washed in distilled water.

2.6 Amine preparation and impregnation

All of the PEI amines were obtained from chemical suppliers. TEPAN was made from a combination of tetraethylenepentamine (TEPA) and acrylonitrile (AN, also known as propenenitrile CH_2=CHCN). It was prepared according to a method devised by Birbara, *et al.* (2002) which entailed mixing 1 mole of TEPA and 2.3 moles of AN mixing for 1 hr at 50°C. The mm of AN is 53 g and the mm of TEPA is 189.3 g, so to make TEPAN 3.22 g of AN was mixed with 5 g of TEPAN.

The method used to impregnate amines into the tested substrates was adapted from the method used by Xu, *et al.* (2003a) to load PEI and PEG into mesoporous silica.

Weights of 0.056, 0.125, 0.333 and 0.75 g corresponding to loadings of 10, 20, 40 and 60 wt.% respectively, were individually dissolved in 4 g of methanol and subsequently shaken for 15 minutes at room temperature. 0.5 g of substrate was then added to each mixture and shaken for a further 30 minutes at room temperature. In cases where the quantity of substrate available was limited, 0.25 g of substrate was used, in which case the chemical weights added to give the necessary loadings were halved, as was the loading of methanol. The resulting slurries were dried in a vacuum oven for 16 hours at 70 °C and a pressure of 700 mmHg. The ratio of methanol to substrate was 8:1 by weight, which was chosen because Xu *et al.* (2003a) found it to be the optimum ratio. Where larger quantities of sorbent were required, the masses of substrate and amine were scaled up accordingly.

2.7 Determination of equilibrium CO_2 adsorption capacities

Two distinct methods were used for ascertaining the equilibrium CO2 uptakes of the samples: an isothermal method and a temperature-ramp method. Both were conducted using a Perkin-Elmer thermogravimetric analyser (TGA).

The isothermal tests were generally conducted at 75°C and first entailed placing ca. 10 mg of the sample into an alumina crucible. This was then loaded into the TGA, whereupon it was dried by being heated at 20°C min^{-1} to 100°C: this temperature was maintained for 30 minutes, during which time the sample was kept under N_2 gas at a flow rate of 20 ml min^{-1}. The temperature was then decreased to 75°C and the gas flow, whilst being kept at a steady flow rate of 20 ml min^{-1}, was shifted from N_2 to CO_2. These conditions were sustained for 40 minutes, whereupon, in order to study the desorption behaviour of the samples, the gas flow was reverted to N_2.

The temperature-ramp method followed the isothermal template, except that subsequent to the drying stage, the temperature was decreased to 25°C, whereupon the N_2 gas flow was switched to CO_2. These conditions were maintained for 2 hrs, after which time the temperature was increased at a rate of 0.25 °C min^{-1} to 100 °C or 200 °C.

2.8 Thermal stability

To ascertain the thermal stability of the amines in their raw and impregnated states, they were subjected to a TGA program which essentially entailed heating the substances from room temperature to 800°C at 15 °C/min in a stream of nitrogen: the change in weight the heating engendered was monitored throughout the heating program. Prior to the heating program initiating, the samples were dried in the TGA for 40 minutes at 105^{o}C under nitrogen.

2.9 Dynamic testing of sorbents under simulated flue gas conditions

Figure 2 is a schematic representation of the rig used to assess how the sorbents performed under different dynamic conditions, and moreover under conditions analogous to those associated with flue gases. The rig also facilitated the appraisement of the impact of the packing of the sorbent upon its performance.

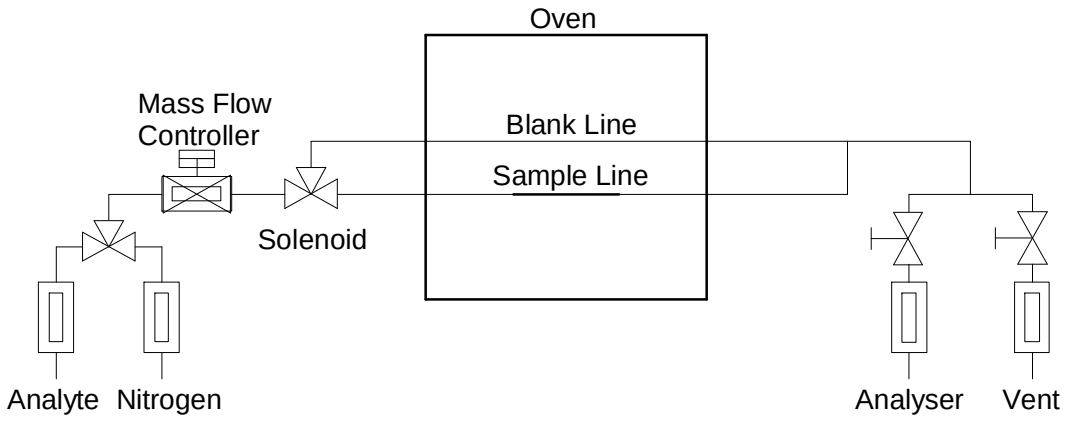

Figure 2: The configuration of the rig for operation in the first phase of sorbent testing

The mechanism by which the rig measured the CO_2 adsorption capacity of the sorbent involved the utilisation of a bypass line. The principle behind this mechanism revolved around first measuring the conc. of CO_2 in the analyte stream through the 'blank' line - i.e. the sorbent by-pass line - and then measuring the conc. of CO_2 in the analyte stream after it has passed through the sample line, i.e. the sorbent under analysis; the analyte is the gas under analysis.

The blank line contains no sorbent therefore it should have a negligible effect upon the conc. of CO_2 in the feed stream. The reading on the CO_2 meter (analyser) produced from the blank line was therefore taken to be the baseline concentration of CO_2 in the analyte stream. The difference in concentration between the sample line and the blank line was hence used to calculate the CO_2 adsorption capacity of the sample.

To determine the effect of SO_2 upon a sorbent and moreover the SO_2 adsorption capacity, a special gas mixture formulated by BOC was used as the analyte: the composition of this gas mixture was 15 % CO_2 (by volume), 1000 ppm SO_2 with the balance comprising N_2.

To measure the quantity of SO_2 adsorbed by the sorbent, as the analyte exited from the CO_2 analyser it was bubbled through a beaker of distilled water, the pH of which was logged at regular intervals with a pH meter. The quantity of SO_2 adsorbed was thus inferred from the change in the water's pH; the calculation was formulated from a calibration procedure. This entailed comparing the rate of decline in the water's pH engendered by the SO_2-containing mixture when it was passed directly into the beaker of distilled water, with the rate of decline caused by a gas that was entirely devoid of SO_2 but otherwise was of identical composition.

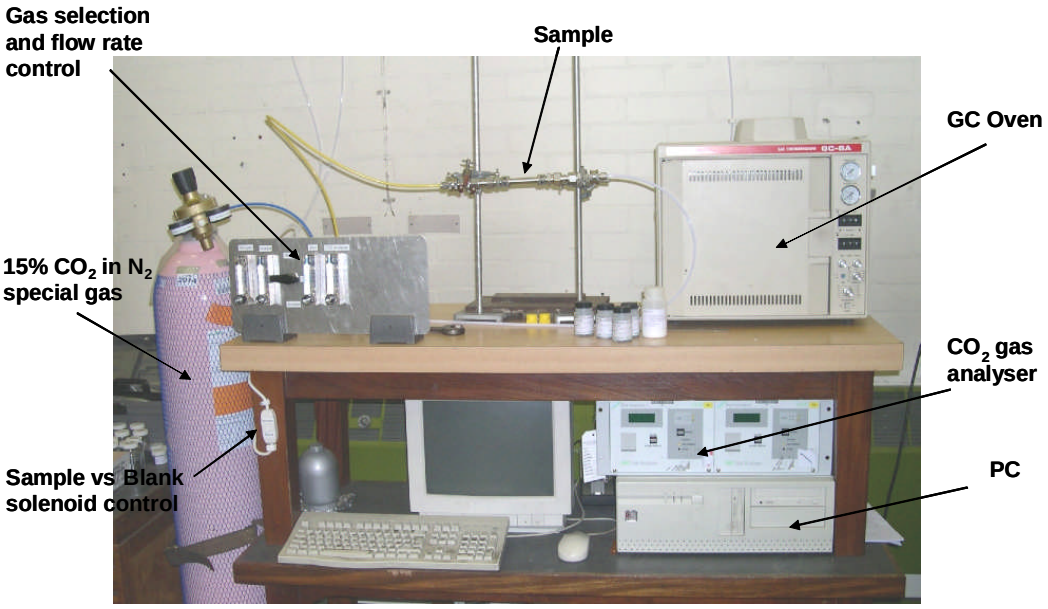

Figure 3: A photograph of the simulated flue gas rig

2.10 Regeneration

2.10.1 TGA

The optimum conditions for regenerating sorbents with temperature swing adsorption (TSA), where CO_2 served as the regeneration purge gas, was found using the TGA by the following method:

The sample was first dried for 30 min in N_2 at 100℃ and then subjected to the standard CO_2 uptake measurement procedure, which comprised exposing the sorbent to a flow of CO_2 (20 ml/min) for 40 min at a temperature of 75°C. Immediately subsequent to this, the sorbent was subjected to a regeneration cycle: this consisted of heating the sorbent at 15 ^{o}C/min to the designated regeneration temperature, holding the sorbent at this temperature for the proscribed regeneration time and then cooling the sample back to 75°C. The sorbent was then subjected to two more 75°C adsorption cycles, which were intersected by another regeneration cycle.

The regeneration temperatures studied spanned 100 °C - 180 °C. Throughout the whole analysis, bar the preliminary drying stage, the gas flowing over the sample was CO_2 and its flow rate was 20 ml/min. Figure 4 shows the profile obtained from such an analysis - in this instance the regeneration temperature is 160 °C.

The new CO_2 adsorption capacity of the sample following each regeneration cycle was found by deducting the change in the weight (wt .%) of the sample at the start of the succeeding adsorption cycle from the change in the weight (wt. %) of the sample at the end of the succeeding adsorption cycle: Figure 4 illustrates the position of these points.

2.10.2 Dynamic rig

The method used to regenerate the sorbents with the dynamic rig via TSA, with CO_2 acting as the regeneration purge gas, entailed first the allowing the sorbent to reach its equilibrium CO_2 uptake at the designated temperature and analyte flow rate - typically these were 75°C and 100 ml/min respectively. The analyte flow was then switched to CO_2, the gas flow rate was set at 200 ml/min and the temperature of the oven heating the sorbent was immediately ramped up to the designated

regeneration temperature: 100 seconds was the time interval allocated to the temperature ramp stage. Upon reaching the regeneration temperature, the sorbent was left under these operating conditions for the proscribed regeneration time, and then the gas flowing through the rig was switched to N_2, its flow rate was lowered to 100 ml/min and the oven was cooled back to the temperature at which the sorbent's equilibrium uptake would be assessed: the period of time assigned to this cooling stage was 300 seconds. Subsequently, the standard adsorption capacity measurement procedure was executed.

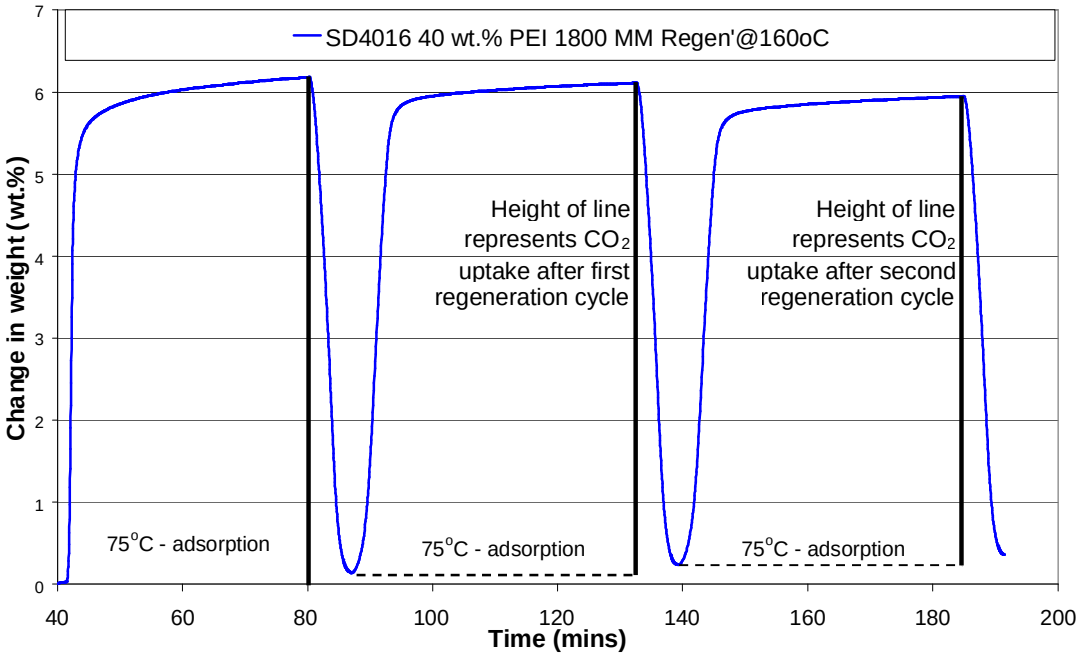

Figure 4: TSA profile for 2 40 wt.% PEI 1800; each regeneration cycle, bar the time taken to reach the regeneration temperature and return to the adsorption temperature, is 1 minute in duration

Due to the CO_2 meter's inability to measure CO_2 concentration's greater than 20 wt.%, it was not possible to directly assess the quantity of CO_2 desorbed when CO_2 was deployed as the purge gas. Thus, the primary measure of the sample's amenability to regeneration was the percentage drop regeneration engendered in the sorbent's equilibrium CO_2 adsorption capacity.

3 Results and discussion

Prior to describing the major outcomes of this project, and in accordance with the directives issued for producing the final BCURA report, the authors wish to report here that the primary objectives outlined in the introduction have each been achieved. In short: CO_2 sorbents have been produced from substrates which were created through the beneficiation and activation of PFA; the substrates have been extensively characterised, had their performance compared with commercially available substrates and been tested under simulated flue gas conditions; the optimum conditions for their regeneration have been determined and they have been subjected to life time testing.

3.1 Beneficiation: Preparation of high carbon substrates from PFA

A suite of nine samples of PFA were used. These were characterised using a combination of dry sieving and the LOI test: the results of this characterisation are presented in Table 1.

3.1.1 Dry sieving

In general, the larger particles of PFA contain a larger percentage of unburned carbon by mass than the smaller particles. Consequently, dry screening by sieving can be used as a rough (Soong, *et al.*, 2002) or primary (Ghafoori, *et al.*, 1999) method for beneficiating PFA. Dry sieving coupled with determination of the LOI of each of the generated size fractions also serves as an effective tool for gauging the distribution of un-burnt carbon in the sample. For the dry sieving investigations conducted as part of this study the sieve sizes 106, 75, 53 and 38 µm were employed. The data collected from the dry-sieving investigations is displayed below in Table 1.

Table 1: LOI of PFA samples and distribution by mass and LOI of their constituent size fractions

	Dry sieving results					LOI	LOI	LOI	LOI	LOI
	% (wt.)	% (wt.)	% (wt.)	% (wt.)	% (wt.)	% (wt.)	% (wt.)	% (wt.)	% (wt.)	% (wt.)
Sample	106 µm	106 µm < 75 µm	53 µm < 75 µm	38 µm < 53 µm	<38 µm	106 µm	75 µm < 106 µm	53 µm < 75 µm	38 µm < 53 µm	<38 µm
High Marnham- U1 BZ pptors	27.59	14.99	11.71	7.41	38.29	77.8	73.4	58.7	36.7	11.1
Drakelow	3.80	2.80	5.60	7.30	79.50	50.9	45.2	29.1	19.4	4.9
Ironbridge- U1	4.60	3.40	5.70	10.00	76.30	27.1	11.7	8.8	8.5	4.4
Ironbridge- U2	5.24	4.78	8.25	12.66	69.02	44.0	31.2	23.0	17.1	8.1
Scotash- High C from STI	4.25	3.37	6.35	8.86	77.19	52.4	40.3	40.8	36.3	22.6
Scotash- High C rejects from STI	29.60	12.70	16.70	13.00	28.00	40.3	8.0	3.9	1.6	2.0
Rugely	3.82	4.02	5.61	8.94	77.62	41.1	20.4	13.3	9.4	3.2
Ratcliffe	19.00	13.00	15.00	12.00	41.00	18.9	9.6	7.2	5.9	4.1
Kings North	24.98	16.09	22.96	15.03	20.94	30.90	17.06	5.80	1.60	0.73

Figure 5 shows the LOI of each of the PFA samples and moreover the contribution each size fraction makes to the samples' LOI, i.e. how the carbon content of each PFA sample is distributed between its constituent size fractions. As shown on Figure 5, the High Marnham sample, with an LOI of 46%, has an unburned carbon content significantly larger than the other samples.

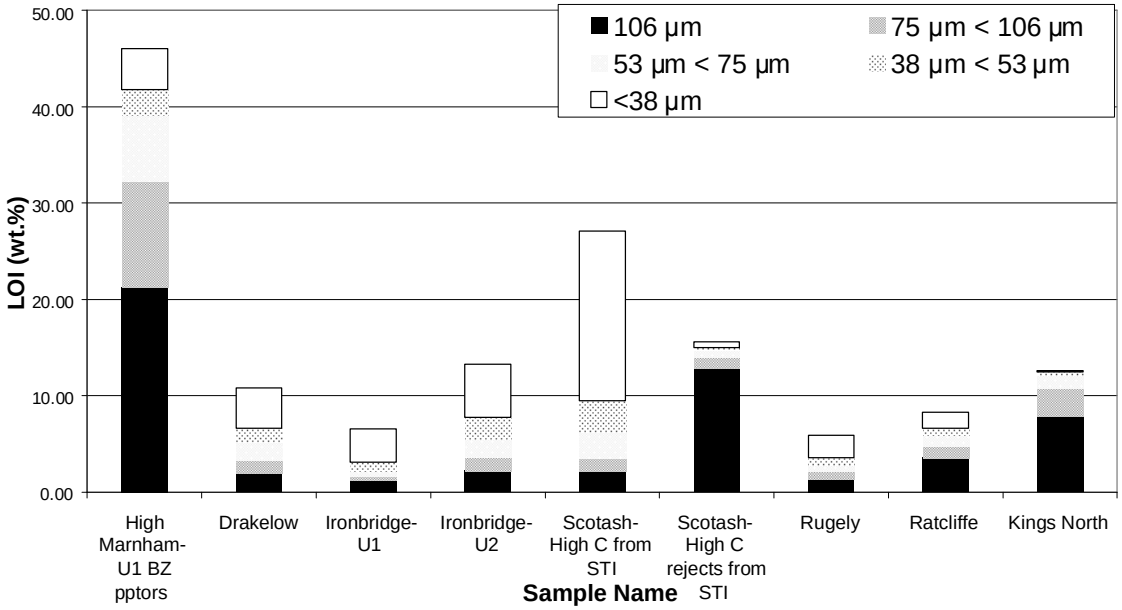

Figure 5: LOI of the samples and the contribution made by the samples' constituent size fractions

The two Scotash samples are respectively the rejected and accepted streams from a triboelectrostatic process used to concentrate the carbon-rich fraction of PFA. The LOIs of these two samples, 15.6 and 27.1 w.% respectively, are consequently higher than the LOIs of the

Drakelow, Ratcliffe, Rugely and Ironbridge samples, which were not specifically selected for their high carbon content. Hence, the LOIs of the Drakelow, Rugely and Ironbridge samples are more akin to the LOIs that would be typically be expected from PFA (i.e. they are under 15 wt.% range).

The actual LOI of each of the constituent size fractions of the PFA samples is shown in Figure 6. Discounting the Ironbridge Unit 1, Rugely, Kings North and Ratcliffe samples, Figure 6 shows that dry sieving was successful in achieving PFA-derived carbons with LOIs in excess of 40 wt.%. While this figure is too low for the carbons produced from this method to be suitable for use in their unaltered state in the project, it does at least demonstrate that size classification can serve as an effective preliminary/screening tool for the preparation of PFA_CCs from PFA.

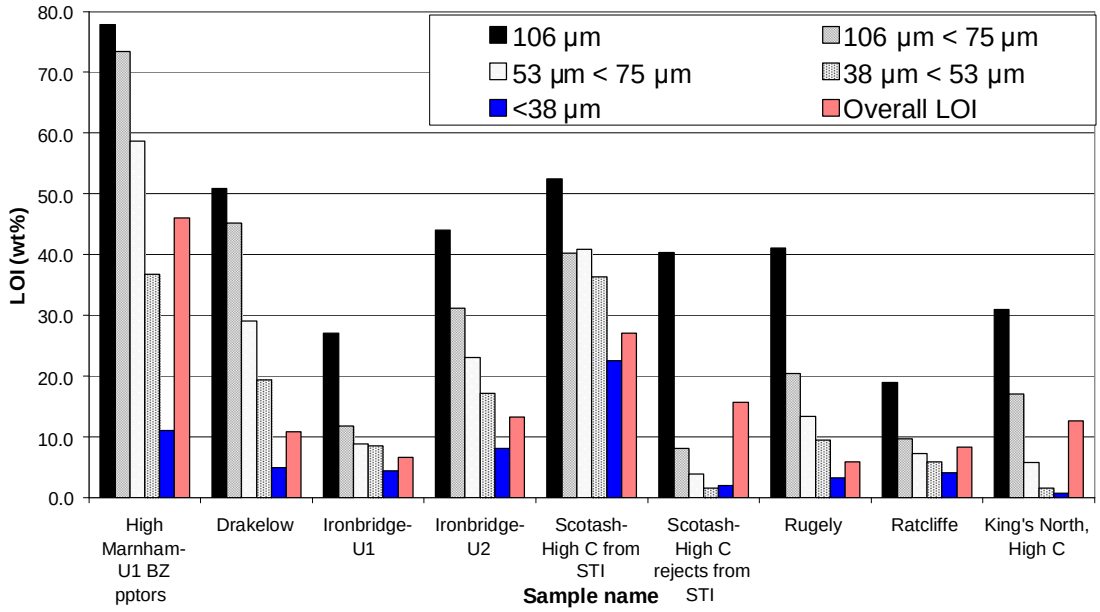

Figure 6: LOI of each of the samples' constituent size fractions

3.1.2 Incipient fluidisation

The carbon-rich fraction of PFA is of a lower density than the mineral-rich fraction, therefore PFA is amenable to beneficiation by means of density separation. Incipient fluidisation is one such process, and involves applying an upward flow of air to a bed of PFA. The air flow rate is fine tuned to a point at which the fluid pressure loss across the bed of particles is equal to the apparent weight of the particles per unit area of the bed (Particle Technology Research Group, 2001), (Yin, 2002). Under these conditions, the fluidised bed can be said to be acting in a manner that is analogous to that of a liquid at rest. Hence the low-density carbon fractions 'float' to the top of the bed and the high-density ash particles 'sink' to the bottom. The carbon-rich fraction that accumulates at the top of the bed can then be collected

Incipient fluidisation was used to beneficiate the +75 µm fractions of each the PFA samples were beneficiated using. The results of these experiments into the efficacy of incipient fluidisation are shown in Figure 7. It is apparent from Figure 7 that incipient fluidisation can function highly effectively, producing carbon concentrates with LOIs in excess of 70 wt.% from six (i.e. two thirds) of the samples subjected to this method of beneficiation.

The chief drawback of incipient fluidisation was that removing the top-fraction with the suction device was a rather difficult and laborious process: firstly because it required that the sample be pre-treated through the removal of its sub 75 µm fraction; secondly as the actual process of performing the technique was, in comparison with froth flotation, highly labour intensive.

3.1.3 Froth flotation

Froth flotation is a physicochemical process that separates particles on the basis of their ability to adsorb or repel water and air. PFA is amenable to beneficiation by froth flotation because its carbon-rich fraction is hydrophobic whilst its mineral-rich fraction is largely hydrophilic (Luttrell, 2002).

The beneficiation of PFA by froth flotation comprises three stages (Luttrell, 2002):

- Addition of liquid to the PFA and the subsequent conditioning of the resulting slurry with appropriate reagents (usually a collector, the function of which is to increase the hydrophobic nature of the carbons, and a frother, which generates a froth following the injection of air into the slurry).
- Injection of finely disseminated air bubbles through the slurry - the carbon-rich fraction thus adheres to the bubbles and rises to the surface, whilst the mineral-rich fraction remains in suspension.
- Collection of the carbon-rich froth and discharge of the mineral-rich liquid.

Three different froth flotation techniques were investigated. These were evaluated with a PFA sample obtained from Ratcliffe, which had an LOI of approximately 5.6 wt.%. The first technique, which used a combined collector and frother formulated specifically for the beneficiation of coals mined from Wellbeck colliery, proved ineffective. The second treatment, which was based upon the patented method devised by Hwang (1993) fared little better. The third, which utilised N-dodecane ($CH_3(CH_2)_{10}CH_3$) as the collector and MIBC (methyl isobutyl carbonate) as the frother proved however to be far more efficacious and thus was used to produce all the PFA_CC samples described in this project as being produced by forth flotation.

Grinding was investigated as a means of raising the yield of carbon recovered from froth flotation. 750 g of sample 6 (Scotash High C Rejects) was ground in a ball mill for one minute. Froth flotation of the resulting PFA yielded a slight increase in the LOI of the >75 µm and 38-75 µm fractions from 66 to 71 wt.% and 52 to 58 wt.% respectively, although this was at the expense of the overall yield of carbon in these fractions. Furthermore, there was a significant increase in the quantity of carbon recovered in the <38 µm fraction, to the extent that more carbon was recovered than was present in the parent fraction. Evidently, one of the consequences of grinding the PFA had been to downsize the larger carbon particles, thus causing a shift in their distribution from the large size fractions into the <38 µm size fraction.

Figure 7 provides a comparison of froth flotation and incipient fluidisation in terms of their ability to generate high purity unburned carbons from PFA. Where figures are not presented for the carbon concentrates generated from the samples, this is because froth flotation was either unsuccessful (Drakelow), deemed unnecessary due to the already high carbon content of the PFA (High Marnham), not possible because there was insufficient PFA available (Rugely) or because of time limitations (Ratcliffe).

Evidently, the success of froth flotation is very much dependent upon the nature of the PFA, with the LOI of the >75 µm size fraction of the recovered carbon concentrates ranging from 77 wt.% (King's North) to 47 wt.% (Scotash High C). Although incipient fluidisation was, in some cases at least - the Ironbridge and Scotash high C samples - found to function more efficaciously than froth flotation, its use as a tool of generating substrates was ultimately vetoed; the principal driving force behind this decision was its labour intensive nature: the time taken to use incipient fluidisation to generate an acceptable quantity of PFA_CC from a PFA sample exceed by a significant margin the time taken to generate the same quantity of material through froth flotation.

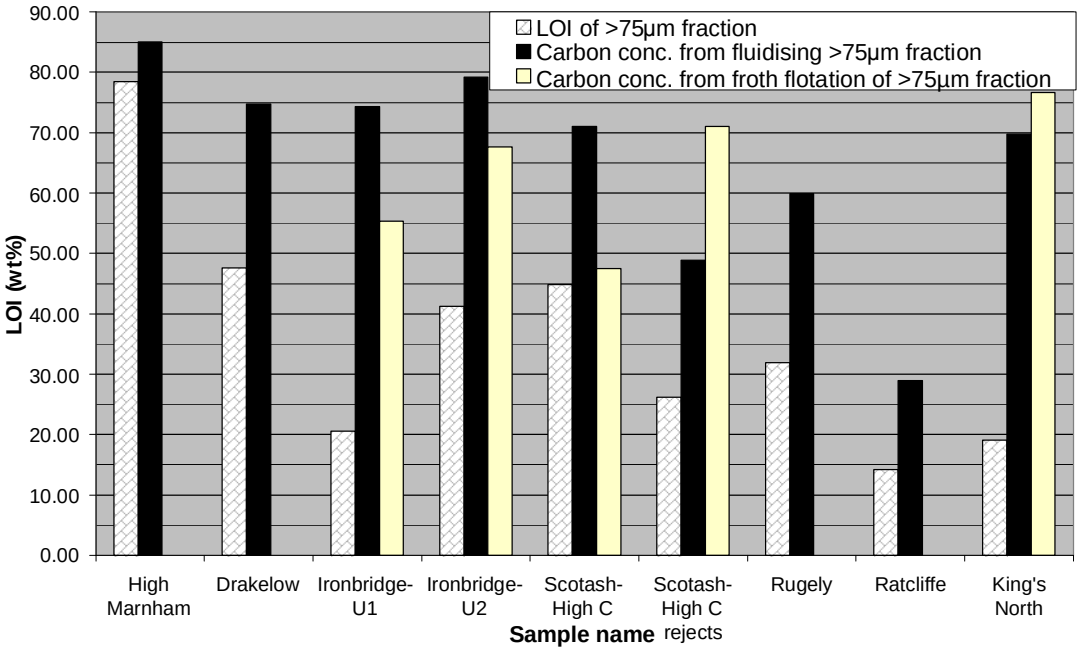

Figure 7: A comparison of the LOIs of the >75µm fraction recovered from froth flotation and incipient fluidisation.

3.1.4 Demineralisation

Demineralisation was conducted using HF, the function of which was to react with the aluminosilicates in the mineral matter, largely forming AlF_2^+, AlF_3 and SiF_4 (Steel, et al., 2001) and HCl: this was used to dissolve the insoluble fluoride compounds and Fe present in the pyrite (FeS_2) remaining in the HF-treated PFA (Steel and Patrick, 2001).

Two PFA_CC samples were demineralised, the 75-710 µm size fraction of the High Marnham PFA sample, and the 75-710 µm size fraction of the PFA_CC prepared by froth flotation of the Kings North Sample: the former had an LOI of 79 wt.%, the latter an LOI of 76 wt.%. The LOI of the PFA_CCs recovered from the demineralisation of these samples was ca. 99 wt.%. Thus, demineralisation was found to be a highly effective means of beneficiation.

One observation made which raised concerns about the viability of demineralisation as a tool for preparing substrates from PFA was that it engendered a noticeable reduction in the generated concentrates' particle size. It was feared that this diminution in particle size could adversely affect the amenability to impregnation of any substrates produced from these materials. Thus, to ascertain whether this reduction could be averted, the demineralisation experiments described were repeated but in the absence of any stirring.

The outcome of this investigation as regards to the effect of stirring on the size of the materials demineralised was quantified by using Malvern Size analysis, the results of which are shown in Figure 8. Clearly, Figure 8 shows that performing demineralisation without stirring was highly effective as a means of circumventing particle size reduction. Moreover, LOI measurements of the treated samples found that forgoing stirring did not comprise the efficacy of the demineralisation process.

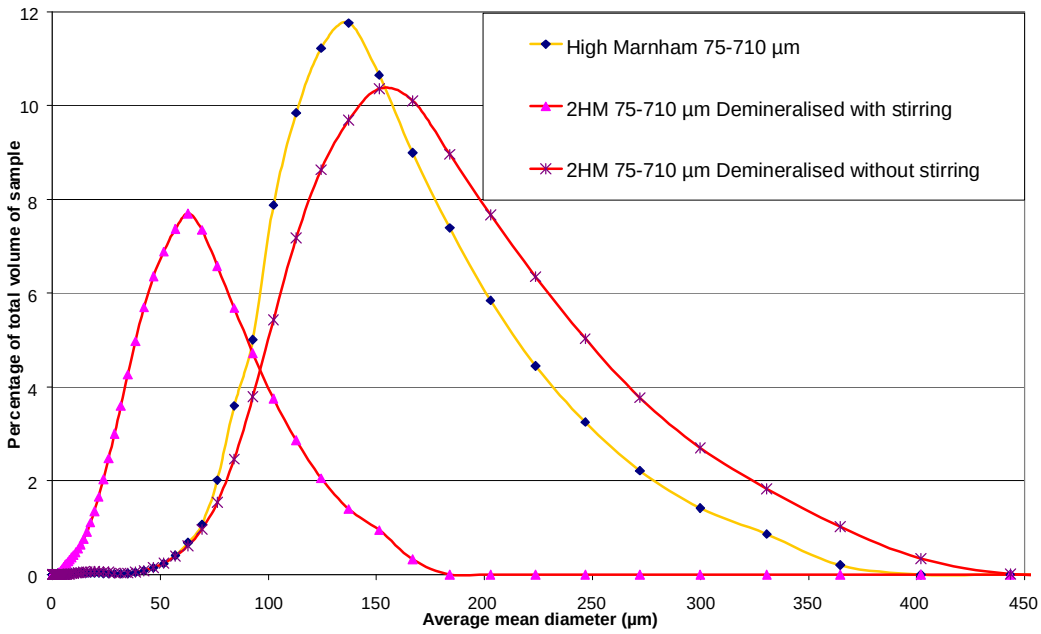

Figure 8: Effect of demineralisation with and without stirring on the particle size distribution of the 75-710 µm size fraction of the High Marnham PFA

The consequences of coupling demineralisation with activation for the purpose of making high quality PFA_ACC substrates are presented in sections 3.4.3 and 3.5.2. The principal conclusions from the beneficiation studies were:

- 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, but because of its ease of use and the relative rapidity with which it could generate PFA_CCs, ultimately, froth flotation was the preferred method of beneficiation.

3.2 Amine assessment

Five amines were selected as candidate reagents for developing CO_2 sorbents from PFA-derived substrates. The amines selected were diethanolamine (DEA, MM 105), tetraethylenepentaamineacrylonitrile (TEPAN, MM 311) and polyethyleneimine (PEI) 1800 MM (branched), PEI 600 MM (branched) and PEI 423 MM (linear).

The first stage of the investigation entailed characterising the amines in terms of their CO_2 capture uptake at 75 ℃ and their thermal stability. The former analysis was necessary to demonstrate that utilising the amines in their raw form to capture CO_2 was not practical; the latter analysis was essential in order to vet the candidate amines on their ability to withstand the temperatures associated not only with flue gases but also with thermal swing adsorption (TSA) - i.e. regeneration.

Figure 9 displays the CO_2 uptakes of the candidate amines in a flow of CO_2 at 75^{o}C: these results were obtained using the standard CO_2 uptake measurement program detailed in section 2.7. The two principal conclusions that may be drawn from Figure 9 are that there is a strong relationship between the MM of the PEI amines and the rate at which they adsorb CO_2 - the higher the MM, the lower the CO_2 uptake - and furthermore the amines, in their raw state, exhibit neither a high CO_2 uptake nor a high rate of CO_2 absorption. The latter finding corroborates the central tenet of this

project, which is that the optimum method of deploying amines in CO_2 capture applications lies in coupling them with an appropriate substrate, as demonstrated by Xu, et al. (2002).

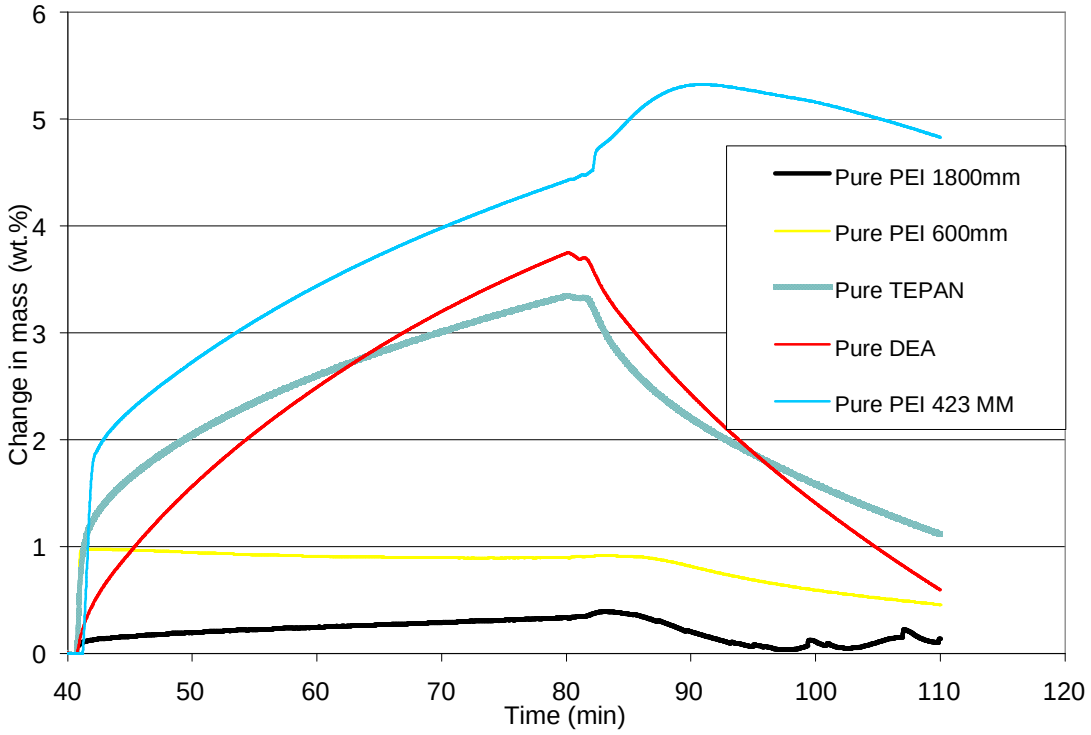

Figure 9: Uptake of the candidate amines at 75 °C

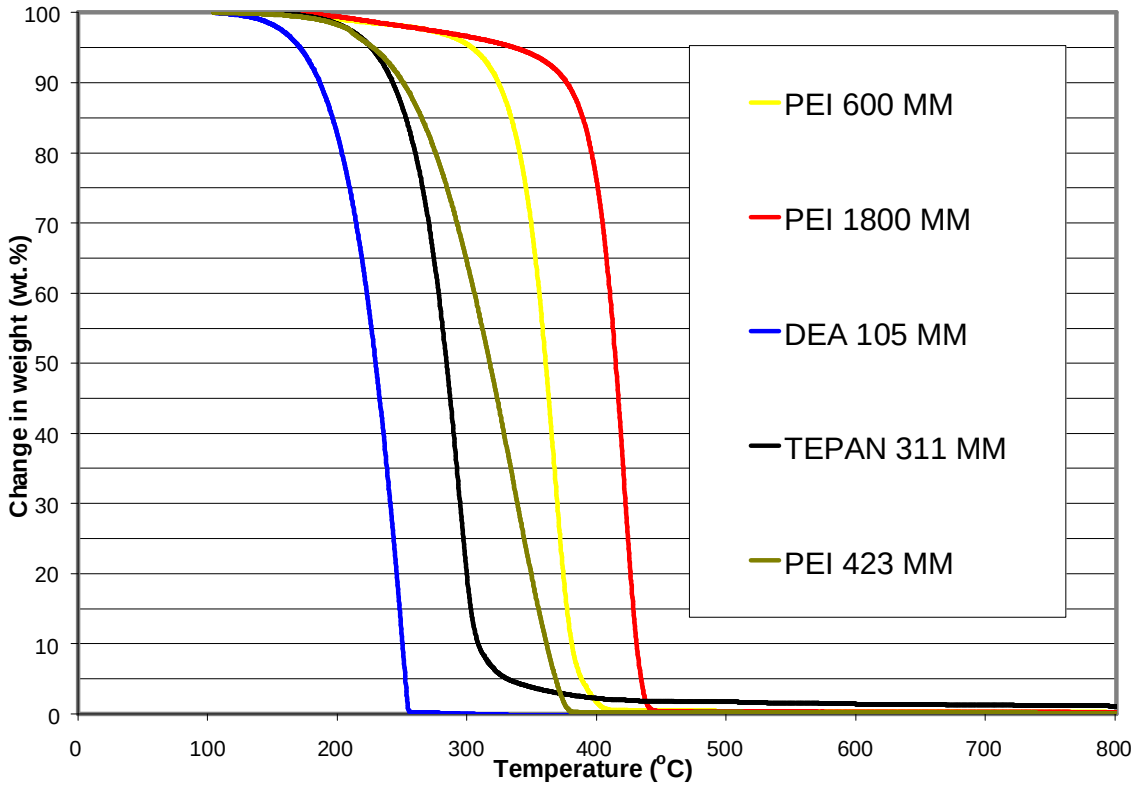

Figure 10: Thermal stability in a flow of nitrogen of DEA, TEPAN and PEI

Figure 10 shows the results of the analysis of the thermal stability of the amines, from which can be surmised that the lowest MM form of PEI (423 MM) has a considerably lower thermal stability than the 600 MM form of PEI, which in turn has a lower thermal stability than its high MM (1800) counterpart: the temperatures at which these amines began to exhibit a rapid fall in mass were 230, 300 and 360°C respectively. Thus, it was found that there was a broad correlation between the MMs of the amines and the temperatures at which they began to decompose. Accordingly, as befits their lower MM, DEA and TEPAN exhibited a sharp drop in mass at lower temperatures than PEI. These temperatures were ca. 210°C and 170°C for TEPAN and DEA respectively.

Subsequent to the evaluation of DEA's thermal stability, the decision was made to eliminate DEA from the list of candidate amines: it was felt that it's instability would jeopardise its viability for deployment at flue gas temperatures.

3.3 Utilisation of mesoporous silicas to determine optimum pore structure characteristics of substrates

As highlighted in the introduction, the crystalline mesoporous zeolilte MCM-41, was found to be the substrate most amenable to amine impregnation (Xu, *et al.*, 2002). Consequently, if substrates that could rival the efficacy of mesoporous silicas were to be produced from PFA_CC, it was essential to ascertain what pore structure characteristics particular to mesoporous silicas rendered them effective as substrates. Determining these characteristics would thus facilitate the tailoring of the activation process with the creation of these pore characteristics in mind.

To ascertain which pore structure characteristics were most desirable, five (non-crystalline) mesoporous silicas supplied by Ineos Silicas, of differing pore structures but which otherwise were identical, were impregnated with PEI 1800 MM and then assessed in terms of their CO_2 capture ability.

The pore structure characteristics of the silicas, which were calculated from N_2 adsorption/desorption isotherms measured at 77 K, are presented in Table 2. The equilibrium CO_2 uptake at 75°C of the impregnated silicas was assessed via the standard TGA program.

An examination of Figure 11 reveals that at low loadings of PEI, i.e. 10-20 wt.%, the disparity between the measured uptakes of CO_2 is slight. The impregnated silicas only begin exhibiting pronounced differences in their CO_2 uptakes at the 40 wt.% loading, which, with the exception of 4, whose extremely low mesopore volume rendered it ineffectual as a substrate, represents the optimum loading for the silicas. At this loading it is apparent that 1 is by far the most amenable to impregnation, achieving a CO_2 uptake of 11 wt.%, whereas 2, 3 and 5 only adsorb ca. 8 wt.% of CO_2.

Silica Ref No.	Surface area (m^2/g)	Cumulative BJH Pore Volume of mesopores (cm^3/g)	Cumulative BJH mesopore surface area (m^2/g)	Average pore diameter (nm)	BJH average mesopore diameter (nm)
1	283.4	1.88	491.9	15.3	15.3
2	519.2	2.23	672.9	16.8	13.2
3	398.5	1.23	527.1	12.0	9.3
4	173.9	0.01	8.1	2.3	4.4
5	108.6	0.93	125.6	9.6	29.6

Table 2: The pore structure characteristics of the silicas

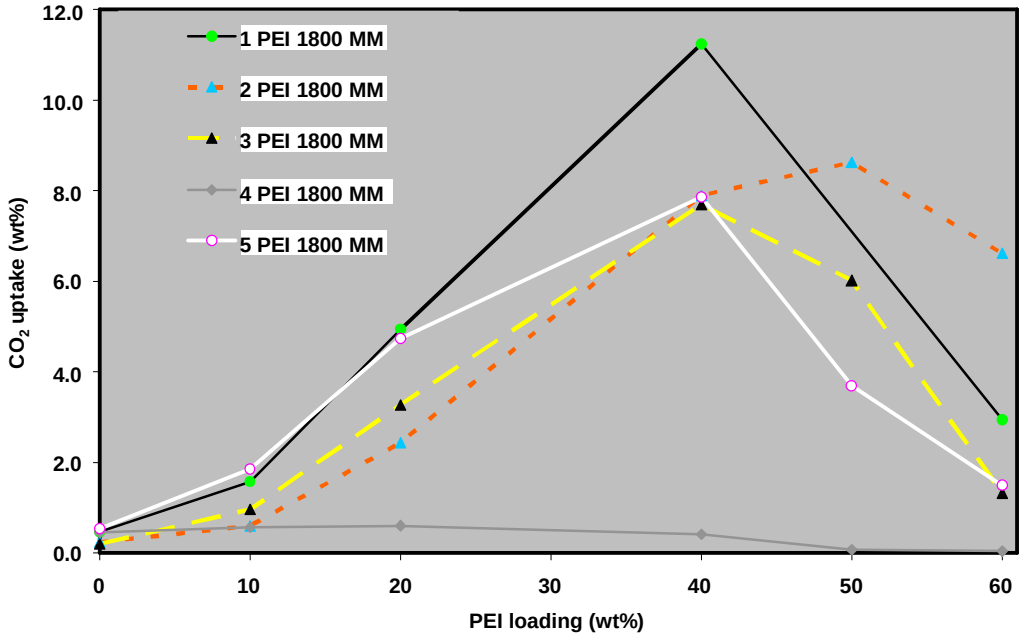

Figure 11: The CO_2 uptake at 75°C of the silicas at different loadings of PEI 1800 MM

In order to deduce which qualities of silica 1 made it superior to the other silicas a comparison was made between its pore structure characteristics and the pore structure characteristics of the other silicas. Looking at Table 2, it is first apparent that neither the mesopore surface area, nor the overall surface area are the dominant factor, as in both instances at least two of the other silicas have higher values for these variables. Rather, it appears that the most important feature is the combination of a high mesopore volume and high mesopore diameter. Although silica 2 has a higher mesopore volume than silica 1 and silica 5 has a higher average mesopore diameter, it is silica 1 which boasts the combination of a relatively high mesopore volume and a high average mesopore diameter.

To conclude, the most desirable characteristics in a substrate for base impregnation are both a high mesopore volume and a high mesopore diameter

3.4 Activation

As explained in section 3.3, the key objective of activating the generated PFA_CC substrates was to develop their meso-porosity, thus improving their amenability to impregnation with amines and therefore facilitating their use in the manufacture of CO_2 sorbents.

3.4.1 Chemical activation

Chemical activation is a process in which the raw material is physically mixed with the activation reagent and then heated in an inert atmosphere to a temperature sufficient to react the raw material with the activation reagent: thus the carbonisation/pyrolysis and activation steps proceed simultaneously (Hayashi, *et al.*, 2002). In the reaction that an activation agent undergoes with carbon, it generally reacts with the more reactive sites of the carbon lattice, converting the reacted carbon into the form of CO_2 or a carbonate which can then be removed post-activation. This selective removal of carbons results in the development of the lattice's pore structure.

It was found that of the three reagents assessed, NaOH was the most effective in terms of its ability to generate a combination of a high mesopore volume and diameter. However, its efficacy as an

activation tool was severely inhibited by its high corrosiveness: the crucibles used to contain the NaOH:PFA mixtures sustained severe corrosion, in some cases leading to contamination of the samples through their being bonded to the crucibles. The KOH activation procedure was observed to have a similarly pernicious effect upon the crucibles: the results of the KOH activation runs are given in the April-September 2004 BCURA report pertaining to this project.

Another major drawback of chemical activation with NaOH was its poor repeatability, as a consequence of which, the NaOH activation procedure is still in the process of being optimised. Hence, at the time of writing it has only been applied to the 75-710 µm size fraction of the High Marnham PFA sample. Table 3 displays all of the results generated to date using NaOH activation and the aforementioned PFA sample.

Ratio of NaOH to CC_PFA	Mass CC_PFA (g)	Activation temperature (oC)	Activation time (hrs)	BET surface area (m2/g)	Average pore diameter (nm)	BJH ave pore diameter (nm)	Cumulative Pore Volume of mesopores (cm3/g)
1:1	2	800	1	51.0	8.1	14.8	0.197
3:1	2	800	1	138.9	5.2	7.1	0.194
2:1	2	800	1	38.0	4.1	9.5	0.040
1:1	2	800	1	58.3	5.4	11.2	0.101
1:1	2	800	1	44.3	3.2	9.0	0.024
1:1	2	800	2	58.2	6.0	13.2	0.152
1:1	2	850	1	46.8	4.2	9.5	0.054
1:1	2	900	1	51.9	5.5	8.2	0.099

Table 3: Pore structure characteristics as determined at 77 K by N_2 adsorption and desorption isotherms of the PFA_ACC substrates generated by NaOH activation of the 75 – 710 µm size fraction of the High Marnham sample

Once it has been decided which combination of activation time and temperature to use, the optimum chemical activation procedure will be applied to other PFA_CC samples, the intention being to establish whether a better degree of mesoporosity can be attained through the careful selection of the characteristics of the PFA_CC material.

3.4.2 Physical action: steam

The steam activation of PFA_CC proved to be an extremely troublesome process, with the various problems experienced stemming from the difficulty of safeguarding that the flow of steam through the reactor did not become impeded, thus inducing a pressure build-up: the usual consequence of such a build-up would be the premature termination of the experiment through the formation of a leak in the reactor. Several different rig designs were employed in a bid to try and circumvent these difficulties, but with only limited success, and details of the these rigs and the outcome of the activation runs conducted with them are available in the BCURA 6th monthly reports submitted over the course of this project.

The best mesopore volume and average mesopore diameter achieved from the standard test sample - the 75-710 µm size fraction of the High Marnham sample - through steam activation was 0.16 cm^3/g and 6 nm respectively, which on an ash and volatile free basis become 0.24 cm^3/g and 2.96 nm: the decline in mesopore engendered by the subtraction of the contribution of the ash fraction is attributable to the high measured mesopore diameter of the ash fraction (*ca.* 17 nm). More success in terms of the generation of a high mesopore volume and diameter from the standard PFA_CC - the 75-710 µm size fraction of the High Marnham sample - was achieved through CO_2 activation and chemical activation.

The relative low mesopore volumes obtained with the steam activation is probably due to the unreactive nature of the PFA_CC used here: in the literature steam activation has been reported as achieving relatively high mesopore volumes from PFA_CCs. Assuming that the generation of

PFA_ACCs with a high mesopore diameter and volume is feedstock dependent, the emphasis of this project was placed upon ascertaining how the sorbents fared under simulated flue gas conditions.

3.4.3 Physical activation: CO_2

Initial attempts to activate samples with CO_2 had been made using a vertical, fluidised activation reactor. The results obtained from this rig are available in the October – March 2005 BCURA report. Shortly after the completion of said report the utilisation of the activation reactor had to be arrested owing to the break-down of the vertical tube furnace used to heat it. Consequently, recourse had to be made to a horizontal activation reactor: all of the results presented in this section were obtained using this activation method.

After considerable testing, it was found that contrary to reports in the literature - these asserted that CO_2 activation promoted the generation of microporosity over mesoporosity - CO_2 activation could in fact be employed to generate mesoporosity. However, that was only possible when high temperatures were employed, with 1100℃ proving to be the most efficacious. One drawback was that subsequent to each high temperature activation, it was observed that there was a small reduction in the efficacy of the next activation run performed with the rig. Presumably, this phenomenon was a consequence of a diminution in the properties of the activation furnace's thermocouple, precipitated in all likelihood by the preternaturally high activation temperatures employed. Investigations at temperatures in excess of 1100°C were thus precluded.

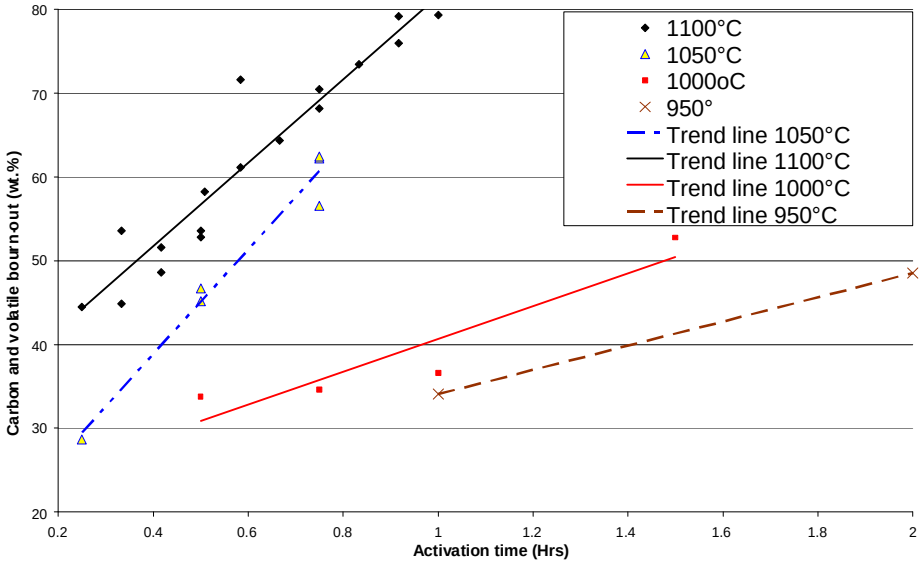

Figure 12: Effect of activation time and temperature on carbon and volatile burnout of 75-710 µm size fraction of the High Marnham sample activated in a horizontal tube furnace with CO_2 at a flow rate of 100 ml/min

Figure 12 presents the relationship between burnout and activation time for each of the activation temperatures employed. The parent material is the 75 – 710 µm size fraction of the High Marnham PFA sample. With regard to the observation made that the efficacy of the activation process deteriorates with the use of the activation furnace, if the time intervals of 0.5, 0.75, and 0. 92 Hrs are considered for the 1100℃ activation temperature, it is evident from Figure 12 that the range in carbon burn-outs of the samples produced in each time interval is relatively large. Chronological analysis of the samples reveals that for each given activation period, the samples activated most recently have the lowest burn-out, thus supporting the afore-mentioned conclusion pertaining to the degenerative effect of each 1100℃ activation run.

Figure 13 shows that a high activation temperature is conducive to the generation of a high mesopore volume from a PFA_CC. The carbon burnout of ca. 70-75 wt.%, which at 1100°C equates to an activation time of between 0.8 and 1 hrs, appears to be most effective. However, as stated earlier, a high mesopore diameter plays an equally critical role in determining the amenability of a substrate to amine impregnation.

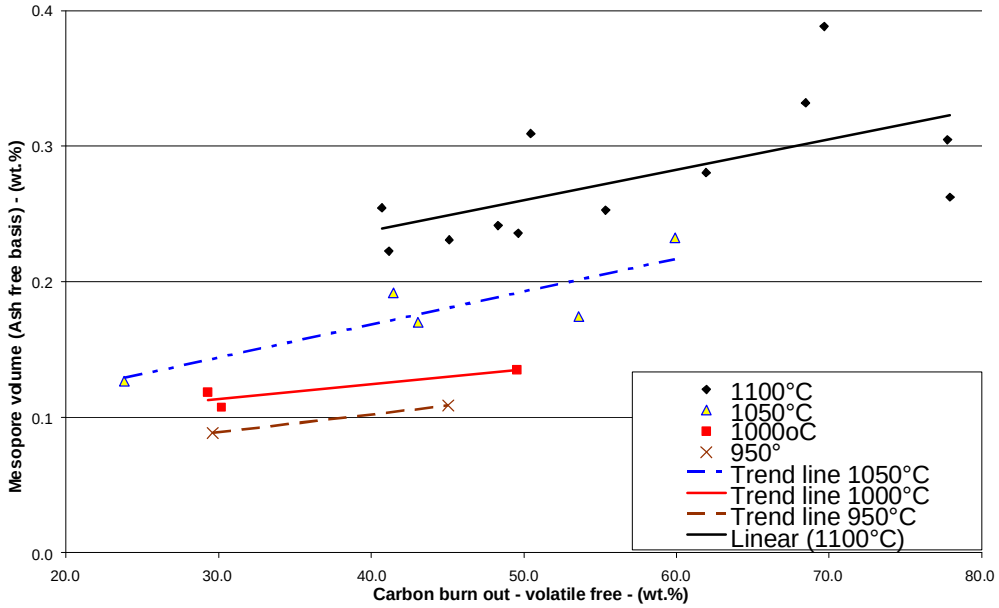

Figure 13: Effect of carbon burn out and temperature on mesopore volume of the 75-710 µm size fraction of the High Marnham sample activated in a horizontal tube furnace with CO_2 at a flow rate of 100 ml/min

Figure 14 shows the relationship between carbon burn-out, activation temperature and the mesopore diameter of the activated samples. It is apparent that the relationship between average mesopore diameter and burn-out is not as linear as the relationship between mesopore volume and burn-out, with the largest mesopore diameters being generated at 1100°C using burn-outs which range between 40 and 70 wt.%.

Only one other PFA sample has been activated with CO_2, the sample in question being the 75-710 µm size fraction of the PFA_CC recovered from the froth flotation of the Kings North sample, the LOI of which is 76.4 wt.%. The details of this sample's response to activation are given in Table 4, which is to be found in section 3.5.2.

The principal conclusions from the activation studies are as follows.

- Contrary to claims made in the literature, CO_2 activation can be employed to generate high mesoporosity from PFA_CC. Moreover, it was found to be more efficacious than steam activation. Its success was however contingent on the use of a high temperature: i.e. 1100°C.
- For the High Marnham PFA_CC, at 1100°C, the optimum carbon burn-out for generating high mesopore diameters was 40 – 70 wt.%. The optimum carbon burn-out for maximising the mesopore volume was ca. 70-75 wt.%, which at 1100°C equated to an activation time of between 0.8 and 1 Hrs.
- Ultimately, CO_2 activation was the most efficacious of the three activation methods considered, thus it was selected as the principle technique for generating PFA_ACC materials.

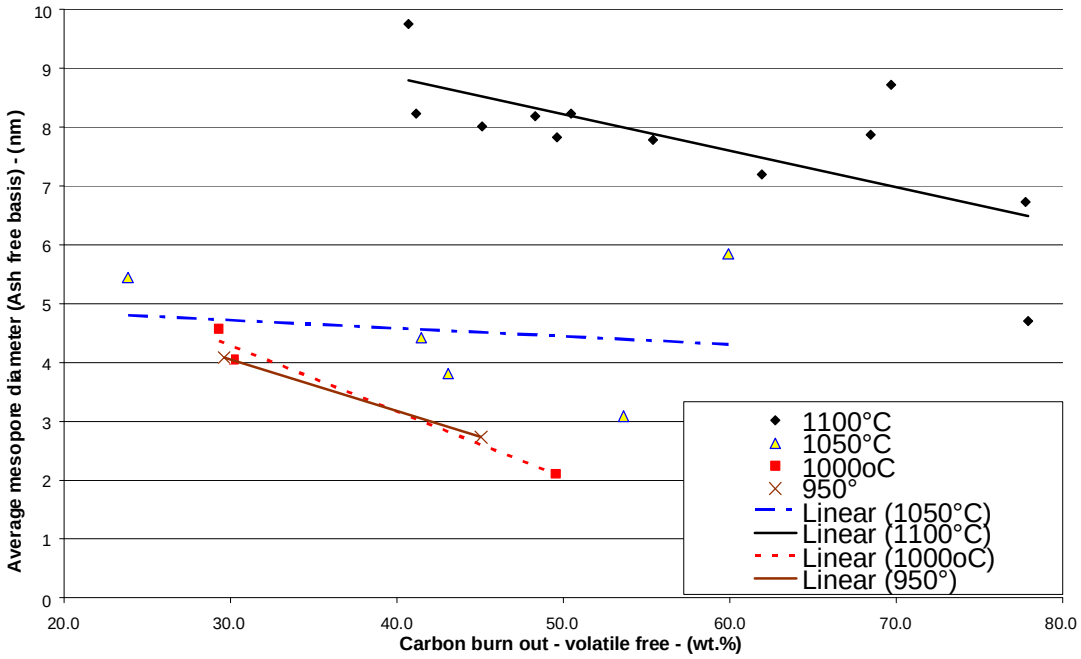

Figure 14: Effect of carbon burn out and temperature on mesopore diameter of 75-710 µm size fraction of the High Marnham sample activated in a horizontal tube furnace with CO_2 at a flow rate of 100 ml/min

3.5 Equilibrium CO_2 adsorption capacities at 75°C

3.5.1 Impregnated silicas: Amine loading optimisation and influence of MM of PEI on CO_2 uptakes

Having established which characteristics were most desirable in candidate substrates for amine impregnation, it was necessary to quantify how effective each of the candidate amines would be at attaining high CO_2 uptakes from the reference substrate – mesoporous silica – and moreover the loadings at which they behaved most efficaciously. Consequently, a series of sorbents were produced using silica 2 – see Table 2 – and each of the candidate amines, with the loadings of the amines applied being 20, 30, 40, 50 and 60 wt.%.

The standard TGA program was used to assess the CO_2 uptake of the sorbents at 75°C. The results from this study are displayed in Figure 15. Considering first the PEI group of amines, what Figure 15 shows is that at the loadings of 20, 30 and 40 wt.%, they do not exhibit any significant differences in their CO_2 uptakes. However, it is apparent that at a loading of 50 wt.%, PEI 600 and PEI 423 attain a far greater CO_2 uptake than PEI 1800. To verify whether this pattern was not just particular to this mesoporous silica, i.e. 2, the CO_2 uptake at 75°C of sorbents made using the amine loadings deployed in Figure 15 but with a mesoporous silica of a slightly different pore structure, i.e. 5, (the structural characteristics of both 2 and 5 are given in Table 2) was also measured.

As Figure 16 shows, in general, the same pattern was observed, in that PEI 423 MM and PEI 600 outperformed PEI 1800 at the 50 wt.% loading. It can thus be surmised that the superior performance of PEI 423 and PEI 600 at the 50 wt.% loading is a consequence of their lower MMs. PEI 1800 evidently attains its optimum loading at 40 wt.%; beyond this loading all of the substrate's pores large enough to accommodate PEI 1800 are saturated. PEI 600 and PEI 423, on the other hand, owing to their smaller size, are presumably able to access pores which are inaccessible to the PEI 1800 molecule. Consequently, the substrates tested can support higher loadings of these two amines before reaching their saturation point.

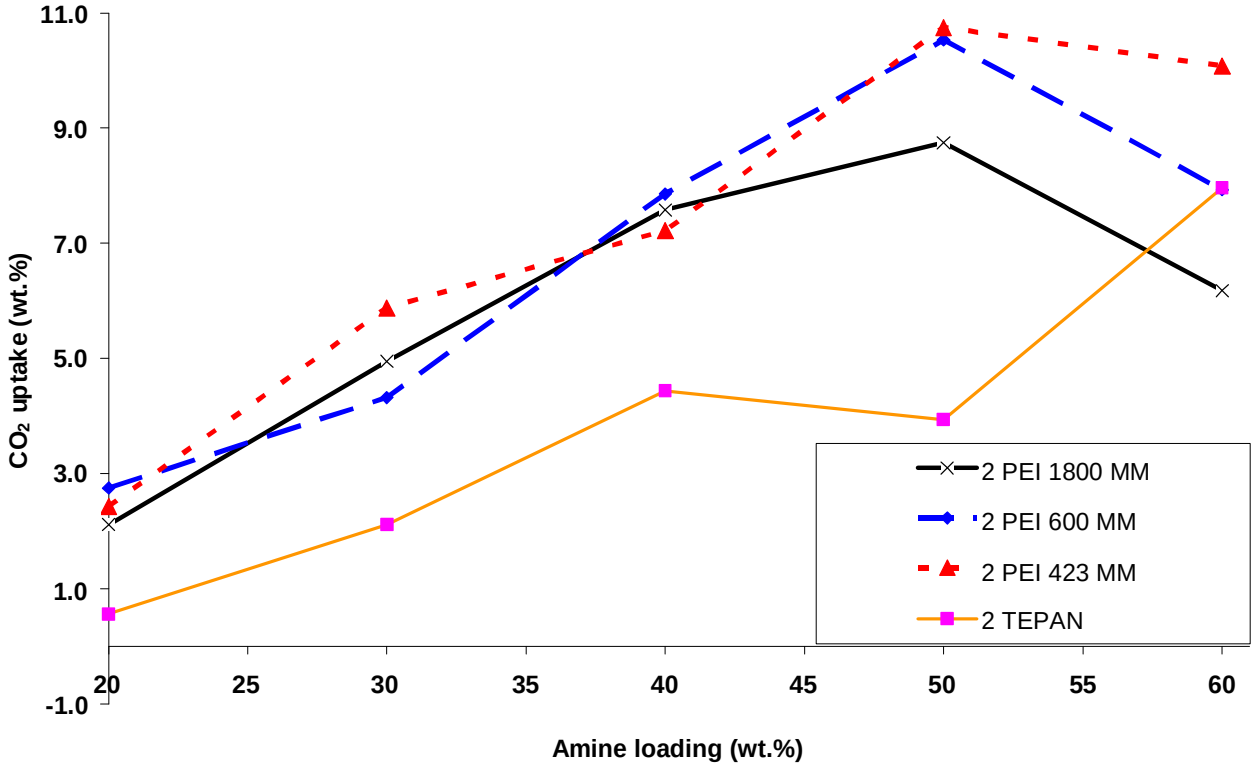

Figure 15: CO_2 uptake of 75°C of sorbents made using the mesoporous silica 2, TEPAN and the three forms of PEI

However, whereas at a loading of 50 wt.%, PEI 600 and PEI 423 yielded the same CO_2 uptake from silica 2, when impregnated into silica 5, PEI 423 significantly outperformed PEI 600, as shown in Figure 16. It is probable that 5 adsorbed more CO_2 when loaded with PEI 423 MM rather than with PEI 600 MM because of its particular pore structure characteristics. Referring to Table 2, it can be seen that 5 has a lower average pore diameter than 2, and thus it is probable that 5 possesses a significant number of pores which are too small to accommodate PEI 600 but are able to support PEI 423.

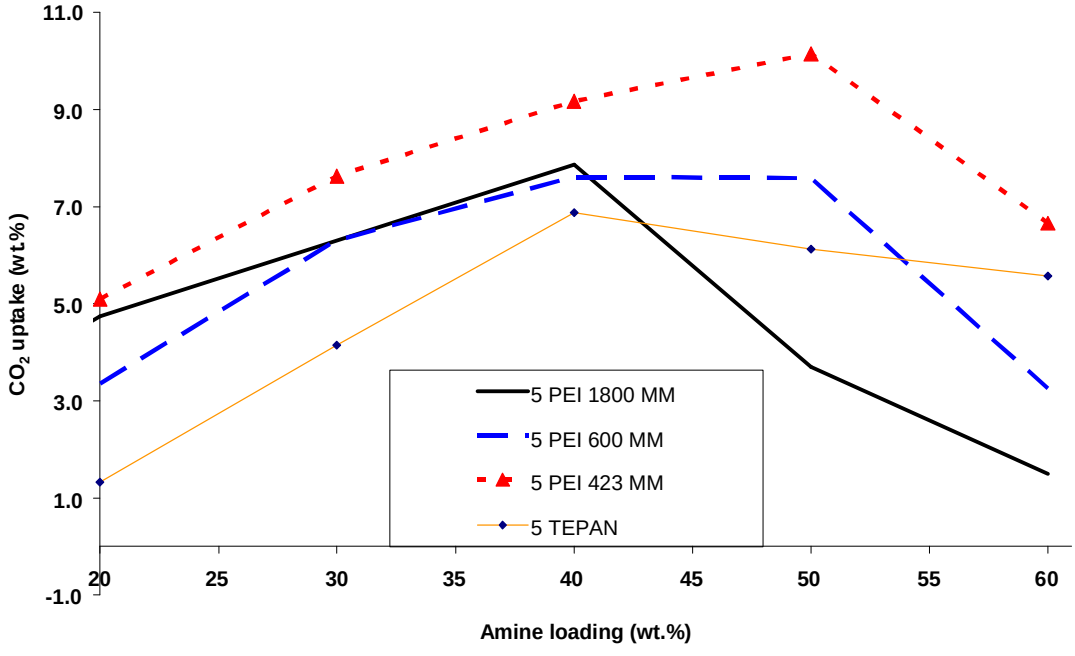

Figure 16: CO_2 uptake of 75ºC of sorbents made using a mesoporous silica 5 and the three forms of PEI under investigation

As regards the performance of TEPAN, Figure 16 shows that 5 reaches its saturation point with TEPAN at a loading of 40 wt.%. Considering Figure 15, 2 also appears to reach its TEPAN saturation point at a loading of 40 wt.%, but then shows an unexpected upturn at a 60 wt.%. This could be due to experimental error, and hence these results are to be repeated. These anomalous data points aside, it is apparent that TEPAN achieves the poorest CO_2 uptakes of the amines studied. This can be attributed to its lower ratio of CO_2-attracting amine groups to carbons: 1:4, as opposed to the amine to carbon ratio of ca. 1:2 for PEI. It is interesting to note however that as with PEI 423 MM, at the 40 and 50 wt.% loadings TEPAN yields a higher CO_2 uptake from 5 than from 2.

3.5.2 Equilibrium CO_2 adsorption capacities at 75°C of impregnated PFA-derived substrates

Prior to impregnating the PFA-derived substrates, it was first necessary to demonstrate that at 75°C they did not adsorb CO_2 to a satisfactory degree. Thus, an arbitrarily selected PFA_ACC, and for the purposes of comparison, a commercially made activated phenolic resin, each had their equilibrium CO_2 uptake at 75°C assessed. Their uptakes were 0.04 wt.% and 1.38 wt.% respectively. Clearly these sorbents are not competitive with the uptakes achieved using the base impregnated silicas, or, as is explicated in this section, the base impregnated PFA_CCs and PFA_ACCs, thus verifying the supposition that base impregnation is required to produce effective sorbents from PFA-derived substrates.

A preliminary finding from the activation optimisation program was that the attainment of a mesopore volume and diameter from the candidate PFA_CC samples that stood comparison with those of the best performing silicas was not a realistic possibility. The decision was therefore made to ascertain whether it might still be possible to achieve competitive CO_2 uptakes from low mesopore volume and diameter PFA-derived substrates through the careful selection of the amine and amine loading used in the impregnation step.

For this specific investigation, a PFA_ACC produced by activating the 75-710 μm size fraction of the High Marnham sample (LOI 79 wt.%) for 2 Hrs at 900°C under CO_2 at a flow rate of 100 ml/min in the vertical fluidised activation rig was used as the test substrate. This substrate was selected on the basis that it was reasonably representative of a PFA_ACC with a low mesopore volume and mesopore diameter, these being 0.04759 cm^3/g and 7.9454 nm respectively.

Loadings of 20, 30, 40 and 50 wt.% of the amines PEI 1800 MM, PEI 600 MM, PEI 423 MM and TEPAN were applied and the CO_2 uptakes of the resulting substrates were measured at 75°C using the standard TGA program: these CO_2 uptakes are shown in Figure 17.

Figure 17 shows that at a 20 wt.% loading, PEI 1800 MM achieves ca. three times the CO_2 uptake of PEI 423 and PEI 600; TEPAN was not analysed at this loading. At 30 wt.%, PEI 1800 and PEI 600 attain very similar CO_2 uptakes, although again PEI 1800 has the higher uptake, and TEPAN occupies the midway point between PEI 423 and the two larger PEI molecules At a 40 wt.% loading, however, TEPAN becomes the best performing amine and PEI 423 now attains the highest CO_2 uptake of the three PEI molecules. This pattern is repeated at the 50 wt.% loading. It could be hypothesised therefore that the mechanisms by which the amines interact with the substrate alters between the 30 and 40 wt.% loadings; this could be related to the fact that at the 40 wt.% and 50 wt.% loadings the impregnated PFA_ACC begins to exhibit excessive stickiness; owing to their greater mesoporosity, the silicas investigated generally did not become ‘sticky’ until loadings of 50 or 60 wt.% were applied.

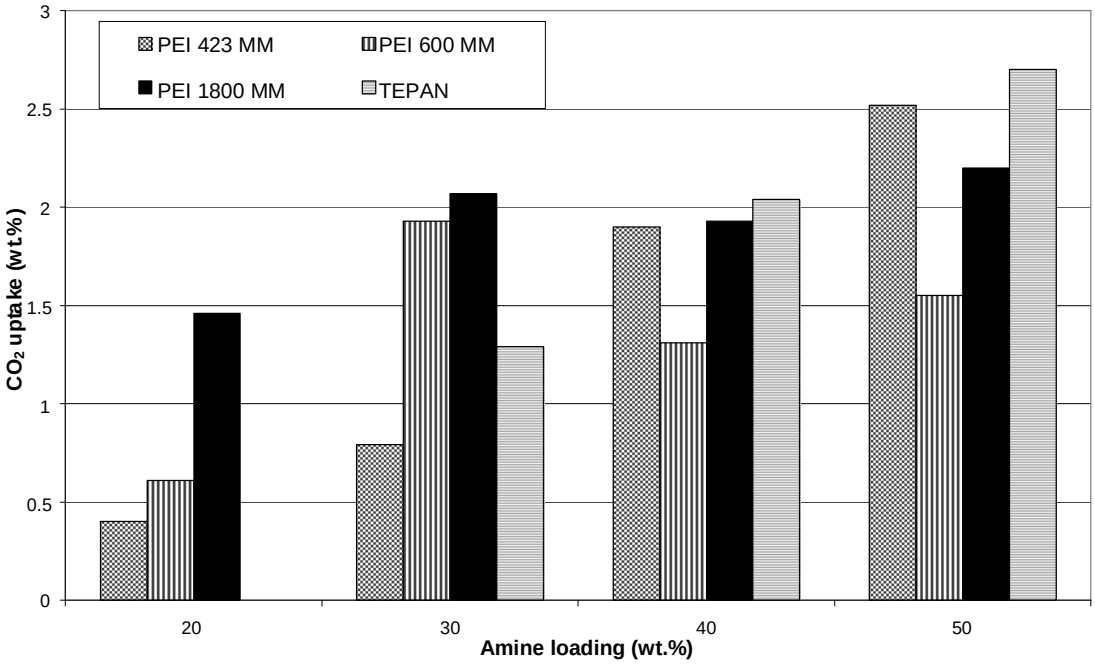

Figure 17: CO_2 uptake at 75°C by 75-710 µm fraction of High Marnham PFA activated in a flow of CO_2 under fluidised conditions at a flow rate of 100 ml/min at 900°C for 2 Hrs

In an attempt to try and fathom a plausible explanation for the almost arbitrary behaviour depicted in Figure 17, the three PEI molecules were loaded at what were judged to be the crucial loadings of 30 and 40 wt.% into a more efficacious PFA_CC derived substrate. This substrate, although again derived from the 75-710 µm size fraction of the High Marnham sample (LOI 79 wt.%), had been pyrolysed at 900°C for 3 hrs. Despite having an even lower mesopore volume than its activated counterpart, it had been shown to respond well to a loading of PEI 423 MM of 40 wt.%.

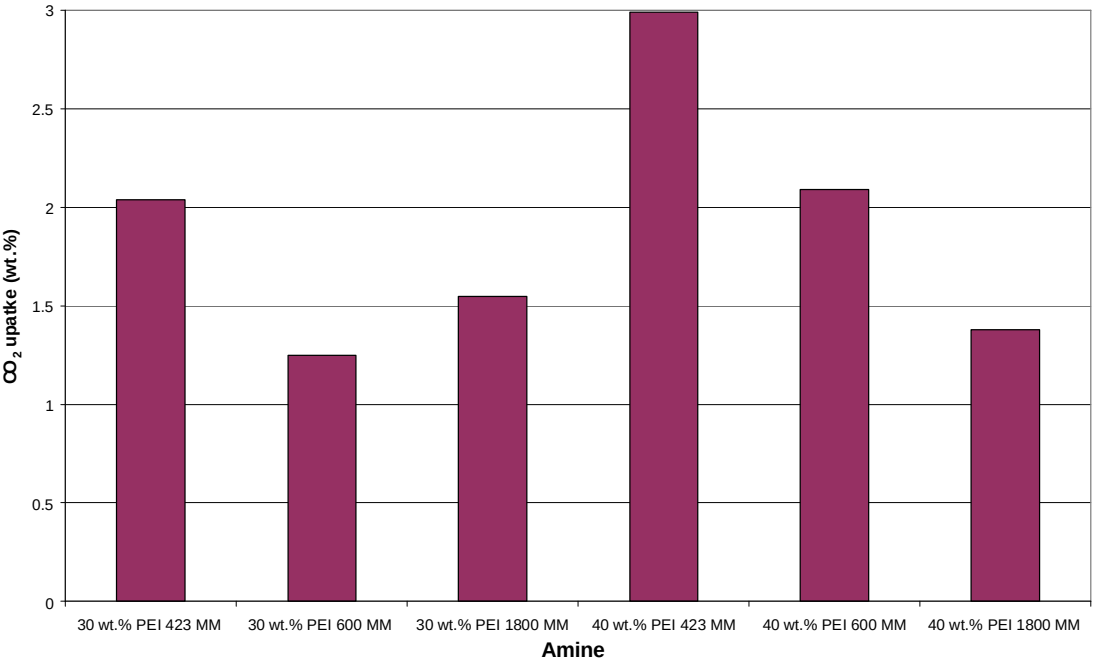

Figure 18: CO_2 uptake at 75°C by 75-710 µm fraction of High Marnham pyrolysed in a flow of N_2 at a flow rate of 100 ml/min at 900°C for 3 Hrs

The CO_2 uptakes of these PEI impregnated PFA_CC substrates are given in Figure 18. For this substrate, the amines responded in a manner more in keeping with their MM, with the CO_2 uptakes

at 40 wt.% showing a clear correlation with the MM of their respective amines. However, at the loading of 30 wt.%, whilst PEI 423 MM still yielded the best CO_2 uptake, PEI 1800 MM performed more strongly than PEI 600 MM.

Overall, it would seem that for substrates of low mesoporosity the interaction between the amine and the substrate is not purely governed by the conventional parameters of mesopore volume and diameter. Ultimately though, of the three PEI amines, PEI 423 MM is the best suited for substrates with relatively low mesoporosities – the amenability of the PFA_ACC substrate to impregnation is so poor as to render its influence on the forming of the afore mentioned conclusion redundant. As regards the use of TEPAN, so far nothing conclusive has been yielded from this study.

Another noteworthy issue on the subject of amine-loaded PFA_CC and PFA_ACC substrates is that of stickiness. Even for the relatively effective PFA_CC substrate shown in Figure 18, at a loading of 40 wt.%, the samples do begin to exhibit considerable stickiness. It is therefore clearly imperative to find a compromise between maximising the CO_2 uptake whilst minimising the stickiness of the sorbents. However, to counter the natural inference from this which is that for PFA_CC derived substrates, only a loading of 30 wt.% PEI loading should be deployed, these results were not obtained from the best PFA_ACC obtainable, hence for the purposes of screening substrates, a loading of 40 wt.% should continue to be used.

In the literature it has been reported that the addition of polyethylene glycol (PEG) can enhance the CO_2 uptake of sorbents produced by the impregnation of PEG into a substrate. To ascertain whether this might prove the case two parallel studies were conducted, one into whether PEG could enhance the CO_2 uptake of silicas, the other into whether PEG could enhance the CO_2 uptake of PFA. What emerged from this study is that PEG has a beneficial effect when used in conjunction with PFA_CC and PFA_ACC, i.e. substrates with a low mesoporosity, but is detrimental to the CO_2 uptakes of sorbents made with a high mesoporosity.

As expounded in section 3.4.3, the highest mesopore volume and diameters attained for the 75-710 µm size fraction of the High Marnham sample through the use of physical activation with CO_2 were yielded using a horizontal activation rig at a temperature of 1100 °C and a CO_2 flow rate of 100 ml/min. To establish whether the enhanced mesopore diameters and mesopore volumes of the PFA_ACCs achieved by these means would confer upon them a greater receptivity to PEI impregnation, they were loaded with PEI 423 MM and their CO_2 uptake at 75°C was subsequently measured and compared with other substrates which had likewise been loaded with PEI 423 MM.

The loading of PEI 423 MM applied to each of the substrates investigated in this study was 40 wt.% In order to account for the fact that amongst the substrates under investigation, there was a considerable variation in their ash content, the PEI 423 MM wt .% loading was applied on a carbon-only as well as on a total substrate mass basis.

The substrates under investigation included those produced by activating with CO_2 the 75-710 µm fraction of the Kings North PFA_CC produced by froth flotation (LOI 76.4 wt.%). In addition, substrates that had variously been subjected to demineralisation applied before and after activation and with and without the use of stirring were also assessed. Furthermore, substrates which had been pyrolysed at 900℃ for three hours and substrates that not been subjected to any chemical, thermal or physical treatment were analysed.

The pore structure details, preparation conditions and calculated carbon content of the substrates are given in Table 4 and the CO_2 uptakes at 75°C of the High Marnham and Kings North derived substrates are presented in Figure 19 and Figure 20 respectively.

Parent material and size fraction (FF = PFA-CC recovered from froth flotation)	Demineralisation details	Carbon content (wt.%)	Activation agent	Activation temp (°C)	Activation time (hrs)	PEI loading of sorbent (wt.%)	PEI loading on carbon only basis (wt.%)	BET surface area (m^2/g)	Average pore diameter (nm)	BJH ave pore diameter (nm)	Cumulative Pore Volume of mesopores (cm^3/g)
								All values given on a volatile & ash free basis			
High Marnham 75-710	Demin pre-act without stirrer	99.2	CO_2	1100	0.75	40		170.5	4.2	7.5	0.152
High Marnham 75-710	Demin pre-act with stirrer	99.6	CO_2	1050	0.5	40	-	187.7	3.7	7.2	0.122
High Marnham 75-710	Demin post-act with stirrer	99.6	CO_2	1050	0.5	40	-	166.1	4.2	8.0	0.149
High Marnham 75-710	Demin without stirrer	99.6	NONE	-	-	40	-	Still to be analysed			
High Marnham 75-710	Demin with stirrer	99.6	NONE	-	-	40		Still to be analysed			
High Marnham 75-710	Not demineralised	67.4	CO_2	1050	0.5	40	-	191.4	3.6	6.8	0.192
High Marnham 75-710	Not demineralised	67.4	CO_2	1050	0.5	31.0	40	191.4	3.6	6.8	0.192
High Marnham 75-710	Not demineralised	52.6	CO_2	1100	0.75	40	-	225.9	4.6	7.9	0.332
High Marnham 75-710	Not demineralised	52.6	CO_2	1100	0.75	26.0	40	225.9	4.6	7.9	0.332
High Marnham 75-710	Not demineralised	78.1	N_2	900	3	34.2	40	64.2	3.0	7.0	0.039
High Marnham 75-710	Not demineralised	78.1	N_2	900	3	40	-	64.2	3.0	7.0	0.039
High Marnham 75-710	Not demineralised	79	NONE	-	-	40	-	61.3	2.9	6.8	0.039
King's North FF 75-710	Not demineralised	76.1	N_2	900	3	40		Still to be analysed			
King's North FF 75-710	Not demineralised	76.1	N_2	900	3	33.7	40	Still to be analysed			
King's North FF 75-710	Not demineralised	76.7	NONE	-	-	40		Still to be analysed			
King's North FF 75-710	Not demineralised	76.7	NONE	-	-	33.8	40	Still to be analysed			
King's North FF 75-710	Not demineralised	59.3	CO_2	1100	0.75	40		362.9	1.6	2.9	0.182
King's North FF 75-710	Not demineralised	59.3	CO_2	1100	0.75	28.3	40	362.9	1.6	2.9	0.182

Table 4: Pore structure characteristics and impregnation details of the substrates used to prepare the sorbents shown in Figure 19

The foremost conclusion that can be made from a cursory examination of Figure 19 and Figure 20 is that pyrolysis appears to be the most effective of the various methods assessed for making PFA_CC substrates amenable to impregnation. This finding runs counter to the expected outcome, which would be that the most mesoporous of the samples would prove most receptive to impregnation. Moreover, it might reasonably be assumed that the demineralised samples would exhibit the greatest CO_2 uptakes following their impregnation, as they have by a considerable margin the highest carbon content - the study is predicated on the assumption that only the carbon fraction of the PFA, owing to its porous nature, influences the amenability to impregnation of the substrate. However, the pyrolysed sample outperformed even the demineralised samples.

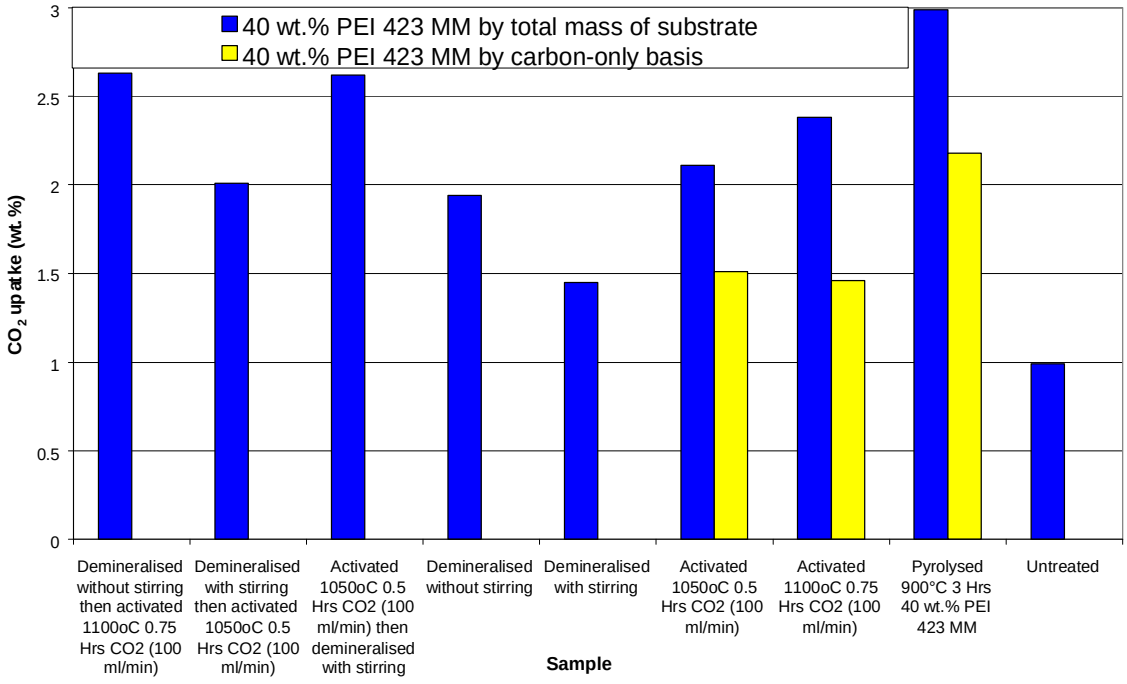

Figure 19: CO_2 uptakes at 75°C of PEI 423 MM impregnated substrates produced from the 75-710 µm size fraction of the High Marnham PFA substrates described in Table 4

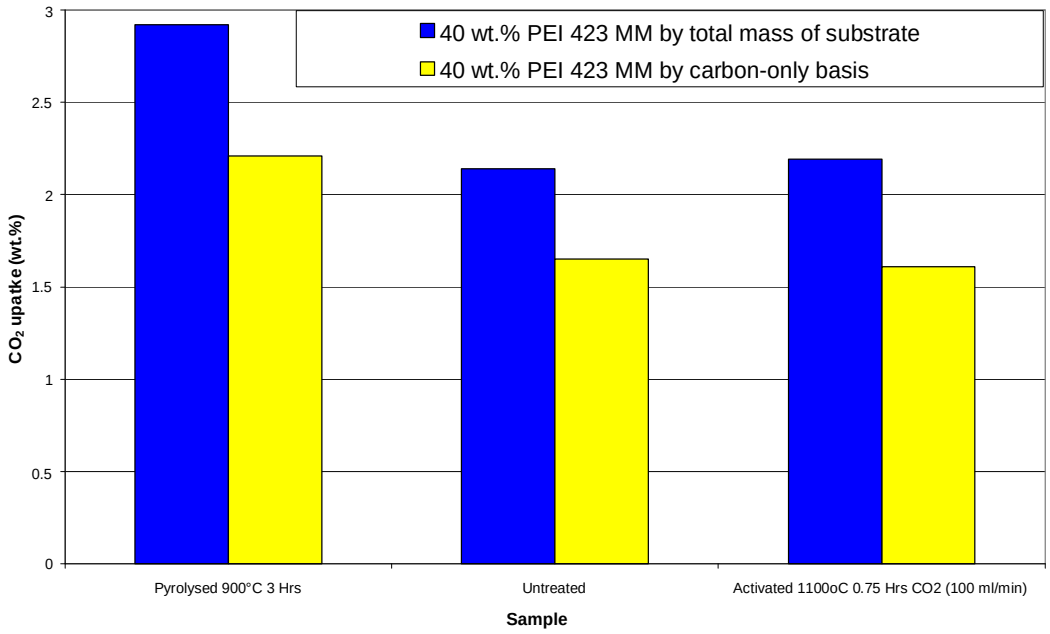

Figure 20: CO_2 uptakes at 75°C of PEI 423 MM impregnated substrates produced from the 75-710 µm size fraction of the Kings North PFA_CC produced by forth flotation described in Table 4

Before though this finding is taken as being incontrovertible proof that PFA carbon, irrespective of what treatment method is deployed to boost its mesoporosity, is of insufficient quality to be utilised as a substrate for PEI impregnation, it should be noted that work published in the literature has demonstrated that a PEI loaded PFA_CC can attain a CO_2 uptake of 9.4 wt.% at 75°C. This work was conducted by Zhang, *et al.* (2004): their investigations comprised loading PEI into samples of CC_PFA that had been either: demineralised, activated, demineralised and oxidised, demineralised and activated, or demineralised and both oxidised and activated.

Zhang, *et al.* (2004) found that the sample which responded best to impregnation with PEI had been subjected solely to demineralisation. They proposed that the high effectiveness of demineralisation was a consequence of its enlargement effect upon the pore diameter of the samples, thus facilitating the incursion of the loaded PEI. The shortfall between the CO_2 uptake achieved using the demineralised substrates deployed in this study and those utilized by Zhang, *et al.* (2004) lies in the difference between their respective mesopore volumes: the best sample formed by Zhang, *et al.* (2004) had a mesopore volume of 0.702 m^2/g, which was five times greater than the mesopore volume of the most mesoporous demineralised PFA_CC tested in this investigation.

Returning to the issue of what information can be gleaned from Figure 19 and Figure 20, what perhaps could be surmised is that the ash-component of these two PFA_CC samples does in fact contribute to their amenability to PEI impregnation. This conclusion is drawn from the observation that the CO_2 uptake of the impregnated pyrolysed sample exceeds that of the demineralised samples, even those which have been activated and hence have a considerably higher mesopore volume and mesopore diameter. It is quite probable that the pyrolysis treatment applied has some form of effect upon the surface chemistry of the ash fraction, imparting it with a high affinity for PEI. The chemical composition and surface chemistry of the ash fraction is however unknown, therefore it is not at present possible to verify this speculative explanation.

What is also worthy of note from Figure 19 is that the sample demineralised without stirring exhibits a higher CO_2 uptake than its agitated counterpart, and this pattern of behaviour manifests itself in the activated as well as the non-activated forms of these demineralised PFA_CC samples.

It would therefore appear that as suggested in 3.1.4, there is a definite minimum size for substrates that are to be made into CO_2 sorbents by PEI impregnation.

What also emerges from Figure 19 is that activation renders the carbon fraction more amenable to PEI impregnation: the activated demineralised samples all outperform the samples that have only been demineralised. Another conclusion that may be drawn from Figure 19 is that demineralisation subsequent to activation results in a substrate that functions far more efficaciously than a substrate that is demineralised prior to activation.

The principal conclusions from the equilibrium uptake measurements are as follows.

- Of the three PEI amines, PEI 423 MM is the best suited for substrates with relatively low mesoporosities. At high loadings, (50 wt.% and above) TEPAN, is more effective than PEI 423 MM but these loadings engender excessive stickyness in the sorbents.
- Demineralisation subsequent to activation results in a substrate that functions far more efficaciously than a substrate that is demineralised prior to activation.
- There is a minimum size for candidate substrates, but this has yet to be quantified.
- The ash-component of the two PFA_CC samples tested positively contributed towards their amenability to PEI impregnation following the samples' pyrolysis.
- Ultimately, demineralisation represents the optimum route towards engendering a high receptivity to amine impregnation from PFA_CCs: work published in the literature has demonstrated that a PEI loaded demineralised PFA_CC can attain a CO_2 uptake of 9.4 wt.% at 75°C (Zhang, *et al.* 2004): the shortfall between the CO_2 uptakes achieved here and those attained by Zhang, *et al.* (2004) can be explained by differences in the PFA_CC used: PFA, and moreover its unburned carbon is highly heterogeneous, therefore it is vital that PFA_CC substrates be selected primarily on the basis of the nature of their unburned carbon

3.5.3 Evaluation of effect of solvent type on efficacy of the impregnation method

To ascertain whether water might present itself as a viable alternative to methanol as the solvent of choice for the dissolution of the amine during the amine loading process, six sorbents were prepared using an PFA_ACC (High Marnham, 75-710 μm) as the substrate and the amines PEI 423, PEI 600 and PEI 1800; for each of these amines two sorbents were produced, one for which water has been used for the dissolution of the amine, the other methanol. The ratio of solvent to substrate was 8:1 (by mass) and the loading of the amine was 30 wt.%.

The motivation behind establishing whether water could supplant methanol as the solvent in choice was its lower cost. Curiously, what emerged from the results of this investigation, which are displayed in Figure 21, is that the higher the MM of the amine (i.e. PEI), the stronger the performance of water in relation to methanol. Overall however, the differences between the CO_2 uptakes of the sorbents made from the two solvents were too small to be of any great significance. Work done previously into the effect of using water rather than methanol as the solvent with mesoporous silica acting as the substrate has yielded similar outcomes; consequently, it can be reasonably concluded that the choice of solvent has a relatively minor effect upon the CO_2 uptake of the resulting sorbent. Further work, using a wider range of substrates and amine loadings (i.e. 20 and 40 wt.%), should be performed to quantify more precisely what differences there are.

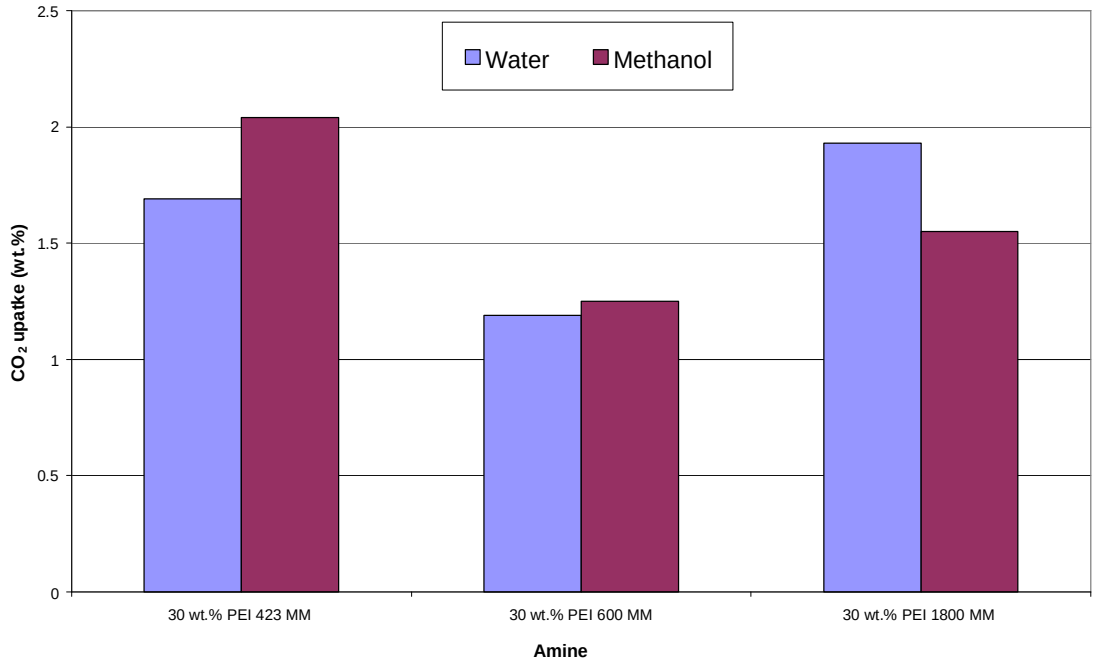

Figure 21: Comparison of the effect of the solvent type on the CO_2 uptake of sorbents prepared from PEI and a PFA-CC (High Marnham, 75- 710 μm) pyrolysed for 3 Hrs at 900°C

3.6 Dynamic testing: assessment of sorbents under simulated flue gas conditions

In order to assess how the manufactured sorbents would function under simulated flue gas conditions a rig was designed and constructed that would not only assess how the sorbents' CO_2 uptake would be affected by flue gas conditions, but also evaluate the effect of packing density upon the sorbents' performance.

Work on the rig was partitioned into several key areas, which were assessing:

- the performance of PEI-loaded substrates using a CO_2/N_2 mixture at different flow rates and temperatures
- the performance of sorbents using a $SO2/CO_2/N_2$ mixture
- the regeneration of sorbents using TSA
- the performance of sorbents using different packing densities
- the performance of sorbents using a humidified CO_2/N_2 mixture

As with the work on optimising the regeneration regime, it was decided to conduct much of the initial research using sorbents produced from mesoporous silica substrates. Again, this is because in principal the resistance of a sorbent to potentially pernicious operating conditions is primarily a function of the amine and not of the substrate.

3.6.1 Performance of PEI-loaded substrates using a CO_2/N_2 mixture at different flow rates and temperatures

Figure 22 shows the effect that temperature and flow rate have upon equilibrium (maximum) CO_2 uptake of a mesoporous silica (2) impregnated with a loading of 40 wt.% PEI 1800, where the simulated flue gas comprises a 15% CO_2, 85% N_2 (by volume) mixture and the sorbent weight is 3g. The best CO_2 uptake achieved is ca. 7.5 wt.%, which was achieved at a flow rate of 50 ml/min and a temperature of 75°C. Encouragingly, none of the combinations of temperature and flow rate examined here resulted in the sorbent's CO_2 uptake falling below ca. 7 wt.%

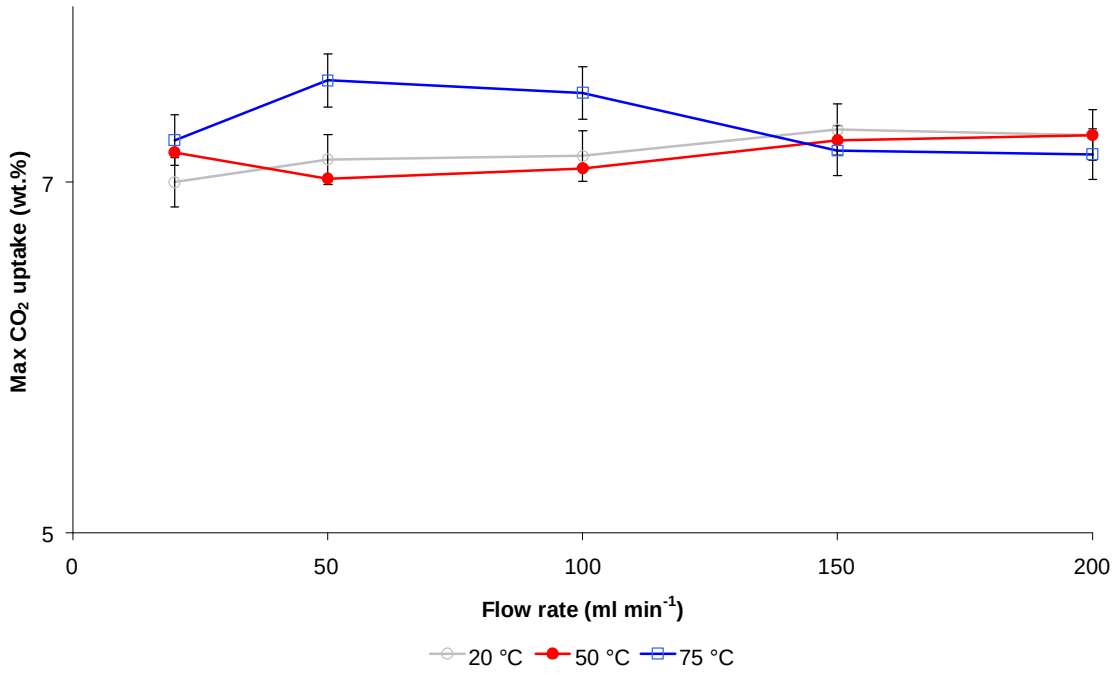

Figure 22: Effect of flow rate and temperature on total CO_2 uptake of a mesoporous silica (2) impregnated with a PEI 1800 loading of 40 wt.%: the gas comprises 15 % CO_2, 85 % N_2 by volume

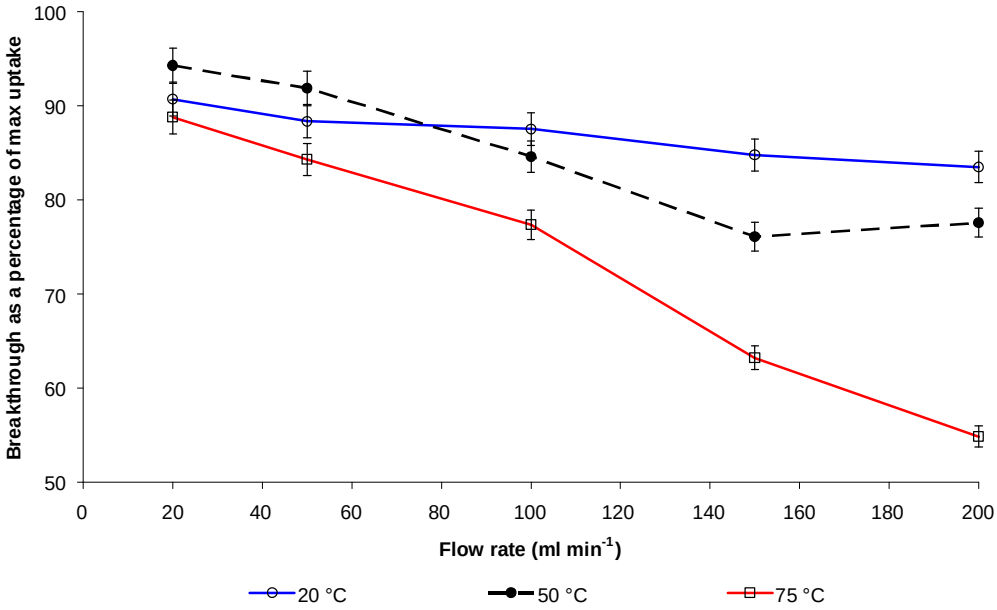

Figure 23: Effect of flow rate and temperature on the breakthrough CO2 uptake of a mesoporous silica impregnated with a PEI 1800 loading of 40 wt.%: the gas comprises 15 % CO_2, 85 % N_2 by volume

However, what is of primary concern is not the maximum CO_2 uptake achievable but rather the breakthrough CO_2 uptake - this represents the total quantity of CO_2 the sorbent can adsorb before it begins to exhibit a decline in its performance under the extant operating conditions. Figure 23 shows the breakthrough CO_2 uptake as a percentage of the total CO_2 uptake achieved by the sorbent described in Figure 22. It is evident that there is a negative correlation between the breakthrough CO_2 uptake and the gas flow rate, and moreover this correlation becomes more pronounced with increasing temperature. The lowest flow rate used, 20 ml min^{-1}, is clearly the most efficacious at ambient conditions but, at 50°C, a flow rate of 100 ml min^{-1}, corresponding to a residence time of

ca. 1 s, does not result in any significant loss of performance. Such as a short residence time is encouraging for scale-up.

Figure 24 presents the results of an analysis of the effect that the PEI MM has upon the saturation CO_2 uptake of the silica. It strongly suggests that PEI 423 MM and PEI 600 MM both out-perform PEI 1800 MM. However, it should be pointed out that the silica used for PEI 1800 MM is different to that used for PEI 600 and 423 MM thus these results cannot be held to be conclusive. Work is presently underway to establish whether small changes in the pore structure of the silica support can indeed have any effect on the breakthrough and equilibrium CO_2 uptakes: it has been posited that small differences in the pore volume of the sorbent may affect its CO_2 uptake through altering the residence time of the sorbate.

Figure 25 shows the influence that the PEI MM has upon the breakthrough CO_2 uptake of the PEI loaded silicas whose equilibrium uptakes are displayed in Figure 24. Curiously, the CO_2 breakthrough uptake of the silicas loaded with low MM PEI molecules does in general appear to comprise a far smaller proportion of the equilibrium (max) CO_2 uptake than that observed for the PEI 1800 MM loaded silica. However, as is evident from the chart, the validity of these results does appear to be somewhat dubious, as for both the PEI 600 and PEI 423 MM loaded silicas, the downward trend in the breakthrough CO_2 uptake is rather incongruously punctuated by the measured CO_2 uptake for the 100 ml/min flow rate. Evidently, these tests need to be repeated to verify these findings.

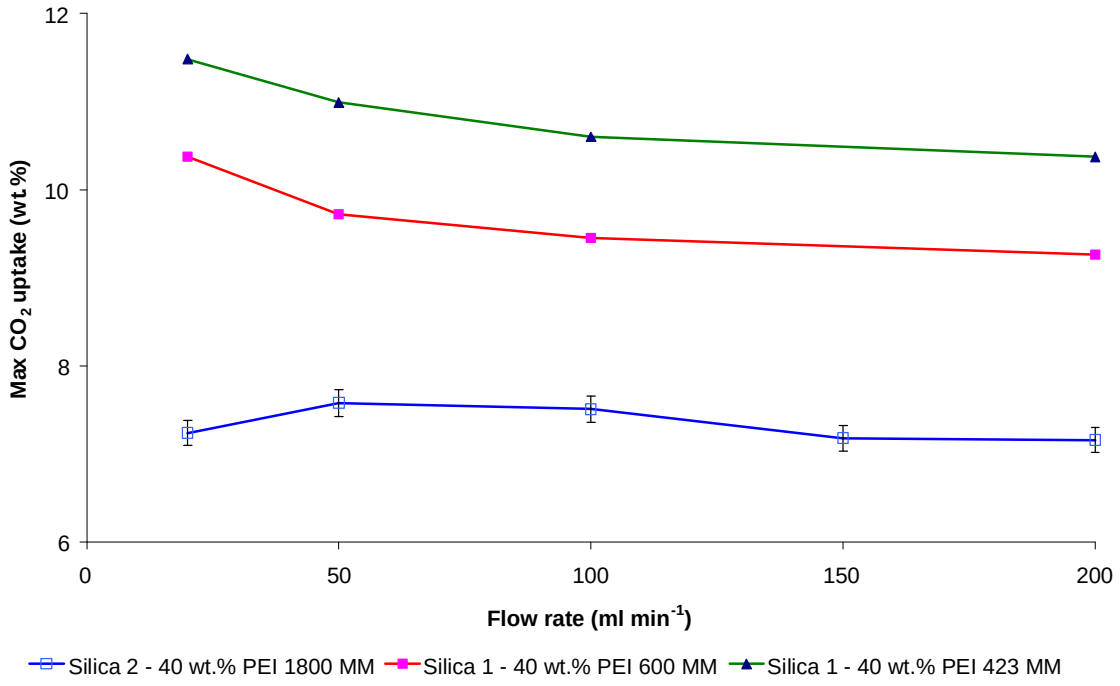

Figure 24: Effect of flow rate and PEI MM on the equilibrium CO_2 uptake at 75°C of sorbents in a 85 % N_2 15 % CO_2 mixture within the dynamic rig.

Thus far, one amine impregnated PFA_CC sample has been assessed with the dynamic flue gas rig using a gas comprising 15 % CO_2 and 85% N_2 (by volume). The substrate was pyrolysed for 3 hrs at 900°C under a stream of N_2 and was selected on the basis of it having found to be relatively amenable to PEI impregnation. Owing to its low density, the quantity of sorbent analysed in the rig was only 1.9 g. The results of this analysis, along with the results attained under the same operating conditions for the PEI-impregnated silica described in Figure 23 are given in Table 5.

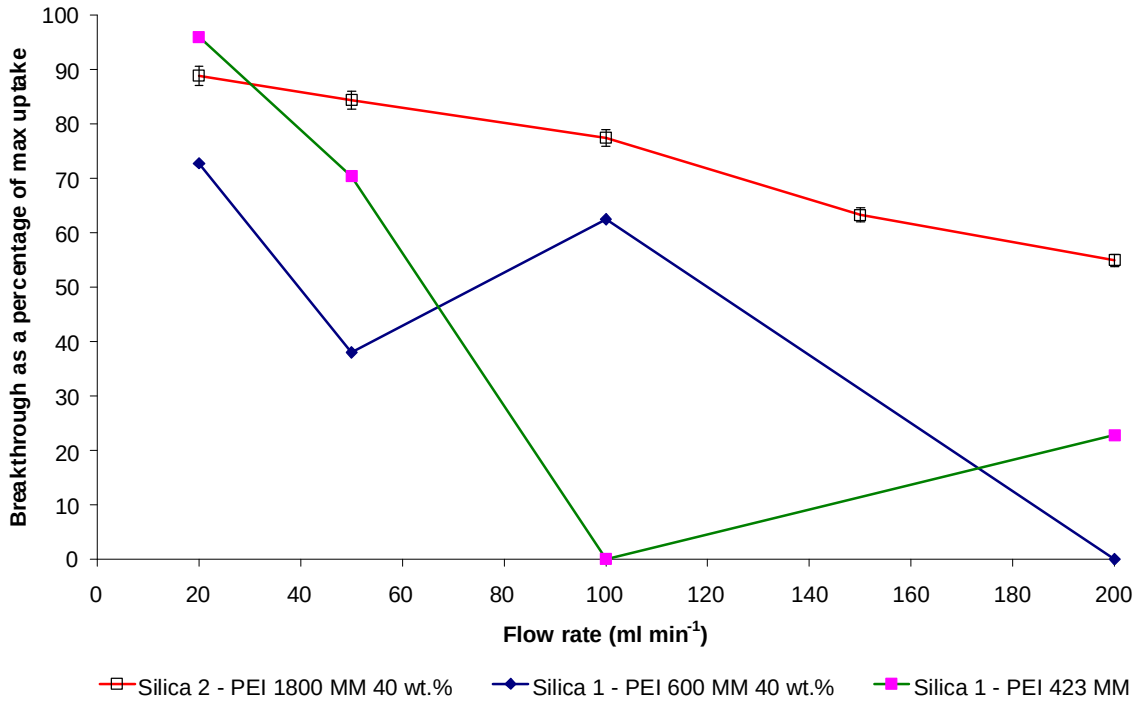

Figure 25: Effect of flow rate and PEI MM on CO_2 breakthrough uptake at 75°C: these results were obtained with the dynamic rig, the gas comprised a 85 % N_2 15 % CO_2 mixture

Substrate	Substrate preparation conditions	Amine impregnated in substrate	Dry mass of sorbent analysed in rig	Amine loading (wt.%)	Gas flow rate (ml min^{-1})	Total CO_2 uptake (wt.%)	Break-through CO_2 uptake (wt.%)	Breakthrough as a % of the total CO_2 uptake
Mesoporous silica (2)	None	PEI 1800 MM	3	40	100	7.5	5.8	77.3
High Marnham 75-710µm PFA	3 Hrs 900oC in N_2	PEI 423 MM	1.9	40	100	4.7	3.4	71.9

Table 5: Results of comparison of CO_2 uptake at 75°C of amine impregnated silica and PFA_CC in the dynamic flue gas rig

At this juncture, attention should be drawn to the fact that the PFA_CC sorbent tested here is in essence the same at the sorbent tested in section 3.5.2, and yet the quantity of CO_2 adsorbed reported here (4.7 wt.%) was one third greater than the quantity of CO_2 adsorbed by the sorbent tested in section 3.5.2: i.e. 3 wt.%. This CO_2 uptake of 4.7 wt.% was moreover replicated when the sorbent was tested in the TGA.

The explanation for this disparity stems from the observation that following the preparation of the sorbents, there was a film clearly visible upon the interior surface of the sample bottles. This film consisted of the fraction of the impregnated amine which accrues as a residue on the sides of the sample container. Nitrogen analysis of the sorbents revealed that the fraction of the impregnated amine which accrued as a residue, rather than adhering itself to the substrate, was a function of the ratio of the container volume to the combined volume of the substrate and solvent.

Thus, the sorbent prepared in section 3.5.2, was produced using 0.25g of substrate and a container with a volume of 15 ml. The sorbent made for the dynamic rig on the other hand was fabricated with ca. 1.5 g of the substrate. As the ratio of methanol:substrate (by weight) was maintained at 8:1, a larger container for the rig sorbent's preparation was required, thus a 30 ml sample bottle was utilised. Hence, the solvent used for the 0.25 g substrate and the 1.5 g substrate occupied ca. 13.3 wt.% and 40 wt.% respectively of their respective sample bottle volumes. Evidently, the stronger performance of the sorbent prepared for the dynamic rig was a consequence of a greater proportion of the impregnated amine adhering to the substrate rather than to the sides of the container. Hence,

it is recommended that the volume of the sorbet bottle volume should be kept as close as is practicable to the volume of the solvent which is to be added during the sorbent preparation stage.

Returning to the issue of the performance of the sorbent under dynamic conditions, although, as would be expected, the PFA_CC based sorbent performed less well than its silica based counterpart, achieving ca. two thirds of the total CO_2 uptake and ca. three fifths of the breakthrough CO_2 uptake, the disparity between the CO_2 uptakes of the two sorbents was not so great as to suggest that the PFA_CC based sorbents can not be made competitive with the mesoporous silicas.

However, the PFA_CC based sorbent, due to its much lower density (*ca*. 0.2 g/cm^3, as opposed to ca. 0.6 g/cm^3 for the silica based sorbent), occupied more of the sample tube (*ca.* 9 cm^3 – the silica based sorbent occupied ca. 5 cm^3) therefore it is likely that the gas would have had a longer residence time, which might account for its relatively strong performance. However, as the void volume of the impregnated PFA_CC is not actually known the sorbents can not be directly compared in terms of the residence time of the gas. Future work needs to look into the effect of the packing density through using a range of different sorbent masses in the sample tube.

- To conclude, the key towards attaining breakthrough capacities that approach parity with the uptakes achieved at equilibrium is to maximise the residence time. However, even at relatively low residence times, i.e. at a flow rate of 100 ml/min, PEI-loaded sorbents can attain breakthrough CO_2 uptakes that correspond to ca. 80 % of the equilibrium capacity.

3.6.2 Rig analysis of performance of sorbents using a SO2/CO_2/N_2 mixture

The effect that the presence of SO_2 had on the performance of sorbents made from PEI loaded substrates was evaluated using the dynamic flow rig: a mesoporous silica impregnated with a 40 wt.% loading of PEI 1800 MM served as the sorbent, the analysis gas comprised a 15 % CO_2, 85% N_2 (by volume), 1000 ppm SO_2 gas mixture. Again, the rationale behind using a mesoporous silica rather than a PFA-derived carbon was that the sorbent's response to contact with SO_2 was a function of the impregnated amine, rather than the substrate.

The data collected from this investigation indicated that initial contact with SO_2 did not diminish the CO_2 uptake of a fresh sorbent. However, the results also suggested that prolonged exposure to SO_2 in the gas stream over a number of consecutive TSA cycles could exacerbate the reduction in the sorbent's CO_2 uptake engendered by the standard TSA regeneration process.

Figure 26 shows the results of the investigation from which this conclusion was derived. It charts how the equilibrium uptake of CO_2 at 75ºC in a pure stream of CO_2 increases with increasing distance from the gas inlet port of the sorbent bed: the measurements were taken subsequent to the sorbents being saturated in the SO_2-containing gas and then being regenerated in N_2 at 100°C. Evidently this deterioration is a consequence of the SO_2 being adsorbed by the first part of the sorbent it comes in contact with. Moreover, this decline was paralleled by a discolouration of the front end of the sorbent. Future work will need to see whether this SO_2 can be desorbed in order that the sorbent might be successfully regenerated.

Perhaps the principle conclusion that can be drawn from SO_2's propensity towards accumulating in the front of the bed is that if this sorbent was deployed in an industrial setting, then it would comprise two beds placed in series: the front end bed would be a *sacrificial bed* used to denude the gas of SO_2; the second bed would be used to capture CO_2. It is important to note here that the dramatic reduction in the sorbent's lifetime engendered by SO_2 would be unlikely to be seen if the sorbent was used to capture CO_2 from PF flue gases: PF flue gases typically have a SO_2 conc. of 100 ppm, rather than the 1000 ppm used here.

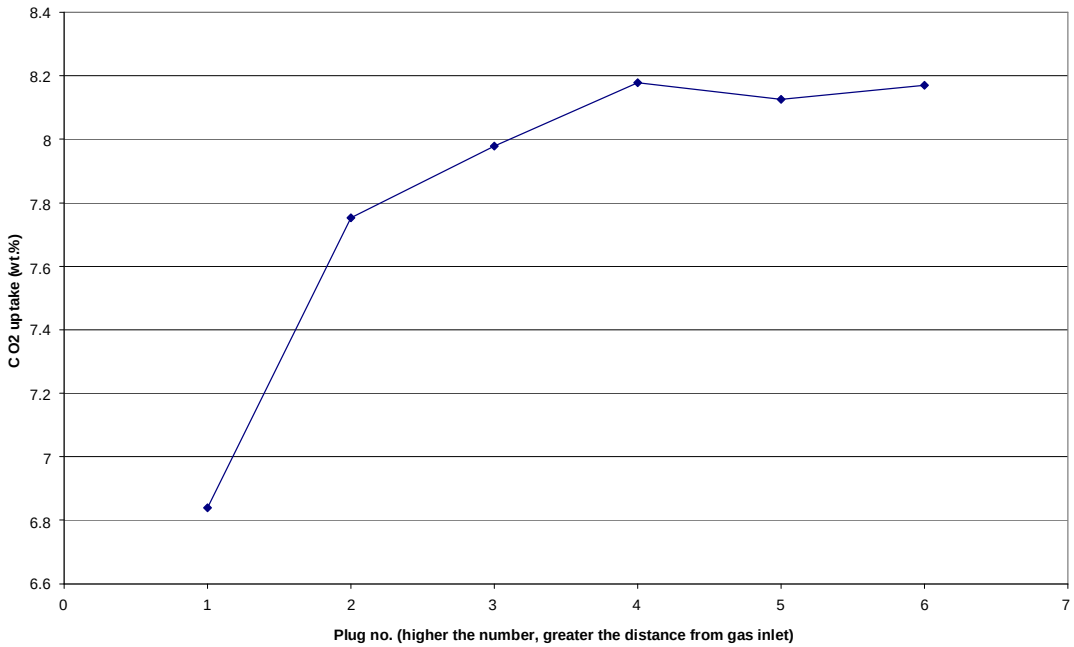

Figure 26: Relationship between the CO_2 uptake measured using the standard 75°C TGA program and the distance along the length of a sorbent (silica 2 40 wt.% PEI 1800 MM) from the gas inlet subsequent to a standard adsorption cycle at 75°C (the gas is 15 % CO_2, 85 % N_2 (by volume), 1000 ppm SO_2) with the gas flow set at 100 ml/min and a regeneration cycle (100°C in N_2) performed on the simulated flue gas rig

To complement the work on elucidating how the presence of N_2 and SO_2 in the gas stream affects the CO_2 uptake of amine-impregnated substrates, it is recommended that for future work the effect of adding humidity to the simulated gas flow be investigated.

3.7 Regeneration: TSA regime

Temperature swing adsorption (TSA) analyses were conducted using a series of sorbents that had been fabricated by impregnating a mesoporous silica - 2 – with a 40 wt.% loading of each of the four candidate amines under investigation. The decision to use a mesoporous silica and not a PFA_ACC as the test substrate was made on the basis that the amenability of an amine-impregnated substrate to regeneration is primarily a function of the amine rather than the substrate and moreover due to it higher CO_2 uptake, the silica-based sorbent would exhibit a greater sensitivity to small changes in regeneration conditions, thus facilitating an examination of the regeneration process's niceties.

It has already been demonstrated in the literature that CO_2 can be desorbed from PEI-loaded substrates through exposure to a flow of N_2. This method of regeneration does however have the major drawback of diluting the liberated CO_2, thus defeating the aim of the CO_2 capture process. It is therefore probable that if the sorbents are deployed on an industrial scale, then either TSA, pressure swing adsorption (PSA) or a combination thereof will constitute the regeneration method of choice.

In essence, TSA entails heating up a sorbent saturated with the gas to be recovered – in this case CO_2 – to the temperature at which the bonds holding the adsorbate to the sorbent are broken, thus facilitating the adsorbate's recovery. TSA is usually conducted in the presence of a purge gas. For this study, the two candidate purge gases were CO_2 and steam, the former because it would not adulterate the liberated CO_2 and the latter because the steam deployed could be easily isolated from the recovered CO_2 through cooling.

The evaluation of the use of TSA to regenerate the sorbent, with steam acting as the purge gas - i.e. steam stripping – was not possible with the TGA employed in this project. Neither was it possible to use the TGA to appraise the efficacy of PSA. Whilst it was possible to asses this form of TSA using the dynamic testing rig, the functionality necessary to facilitate its assessment has yet to be installed. TSA using CO_2 as the purge gas was however assessable using the TGA. Consequently, in order to determine the optimum regeneration conditions under this regime, a series of studies was conducted in which the effect that the duration and temperature of the regeneration stage were evaluated.

The first phase of this investigation entailed ascertaining which regeneration temperatures maximised the quantity of CO_2 desorbed without compromising the integrity of the sorbent. Figure 27 shows the results from the first, exploratory phase of this investigation, in which PEI 1800 MM was the amine impregnated into the silica; the CO_2 uptake achieved after the first and second regeneration cycles is expressed as a percentage of the initial CO_2 uptake achieved by the sorbent. Figure 27 shows that the most pressing issue pertaining to regeneration process's optimisation is the imperative to reconcile the dual needs of regenerating the sample at a temperature high enough to maximise the quantity of CO_2 desorbed, but low enough to minimise the degradation of the amine.

Figure 27 indicates that for PEI 1800 MM, the optimum temperature of regeneration appears to lie within the 150-135^{o}C temperature zone. Above this region, although the CO_2 uptake achieved after the 1st regeneration cycle is at its highest (between 90 and 95 % of the original CO_2 uptake), the decline in the CO_2 uptake between successive regeneration cycles is such that the sorbent would be unable to withstand a large number of adsorption/regeneration cycles without exhibiting an appreciable drop in its performance.

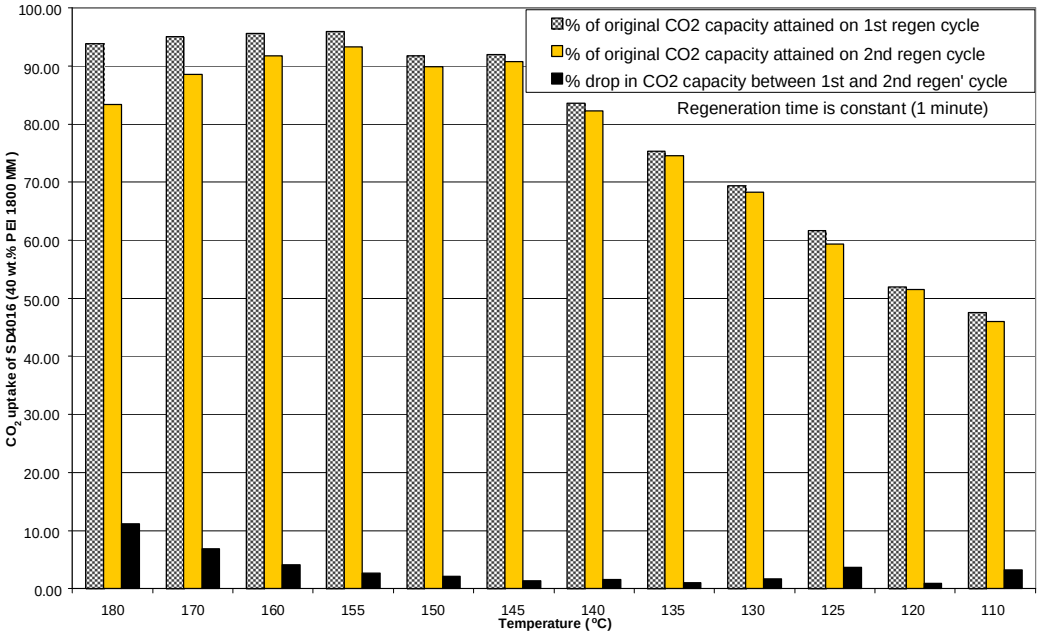

Figure 27: Regeneration of silica 2 impregnated with PEI 1800 MM at a loading of 40 wt.% over two 1 minute regeneration cycles: adsorption cycle length and temperature are 40 mins and 75^{o}C respectively

Below 135^{o}C, there is a significant decline in the recovered CO_2 adsorption capacity following the first regeneration cycle, and while the decline over successive regeneration cycles is not excessively high, the initial drop is too great for the use of these regeneration temperatures to be practical.

To ascertain whether the efficacy of the lower regeneration temperatures (i.e. 145^{o}C and below) might be improved by increasing the length of the regeneration cycle, thus affording more time for the desorption of CO_2, the analyses conducted over the 120 -145 ^{o}C range were repeated using

regeneration times of two and three minutes. The results of the effect of this extension of the regeneration time are shown in Figure 28.

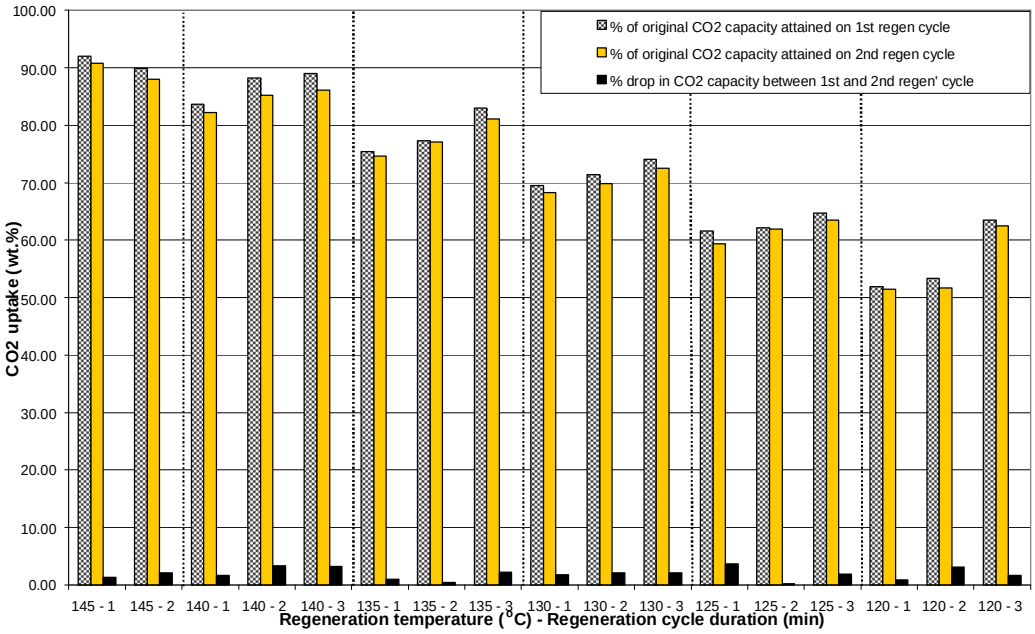

Figure 28: Regeneration of 2 40 wt.% PEI 1800 MM over the 120-145 °C temperature range using regeneration times of 1, 2, and 3 minutes: adsorption cycle length and temperature are 40 mins and 75°C respectively

Bar the temperature of 145°C, Figure 28 shows that increasing the regeneration time does improve the ensuing CO_2 adsorption capacity of the sorbent. However, and with the exception of the regeneration temperature of 120°C, not to a degree that would justify the doubling or tripling of the regeneration time. Figure 28 provides compelling evidence that the range in strength of the physical bonds formed between CO_2 and the PEI molecule is quite broad, with some of these bonds being cleaved at 120°C, but others requiring temperatures in excess of 140°C.

As shown in Figure 10, PEI 1800 MM remains thermally stable in a N_2 atmosphere below ca. 250°C, therefore it seemed clear that the pernicious effect exercised upon the amine's CO_2 uptake by regeneration temperatures in excess of 140°C was not a consequence of thermal decomposition. In order to ascertain why temperatures above 140°C were degrading the sorbent, the PEI 1800 MM loaded silica was subjected to a slow heating regime in the TGA. This entailed drying the sorbent at 100°C for 40 minutes under N_2 and then exposing it a flow of CO_2 (20 ml/min) for 2 hrs at room temperature, following which it was heated at a rate of 0.25 °C/min to 200°C. This experiment was repeated using variously N_2 and air as a substitute for CO_2. The data collected from this experiment is presented in Figure 29.

The most noteworthy part of Figure 29 is the 135-145°C temperature region of the sorbent's CO_2 profile. Below this region, the sorbent performs in a manner that corresponds with the expected pattern: at room temperature, the sorbent adsorbs a high quantity of CO_2, whereupon, upon being heated, it begins to lose mass as the bonds between the adsorbed CO_2 and the sorbent become less stable, with their being a marked increase in the rate of CO_2 desorption at the 90-110°C temperature region. However, what then unfolds at the 135-145°C mark is a buckling of the trend towards there being an ever increasing loss in mass with a rise in temperature: rather, the amine in fact begins to gain mass.

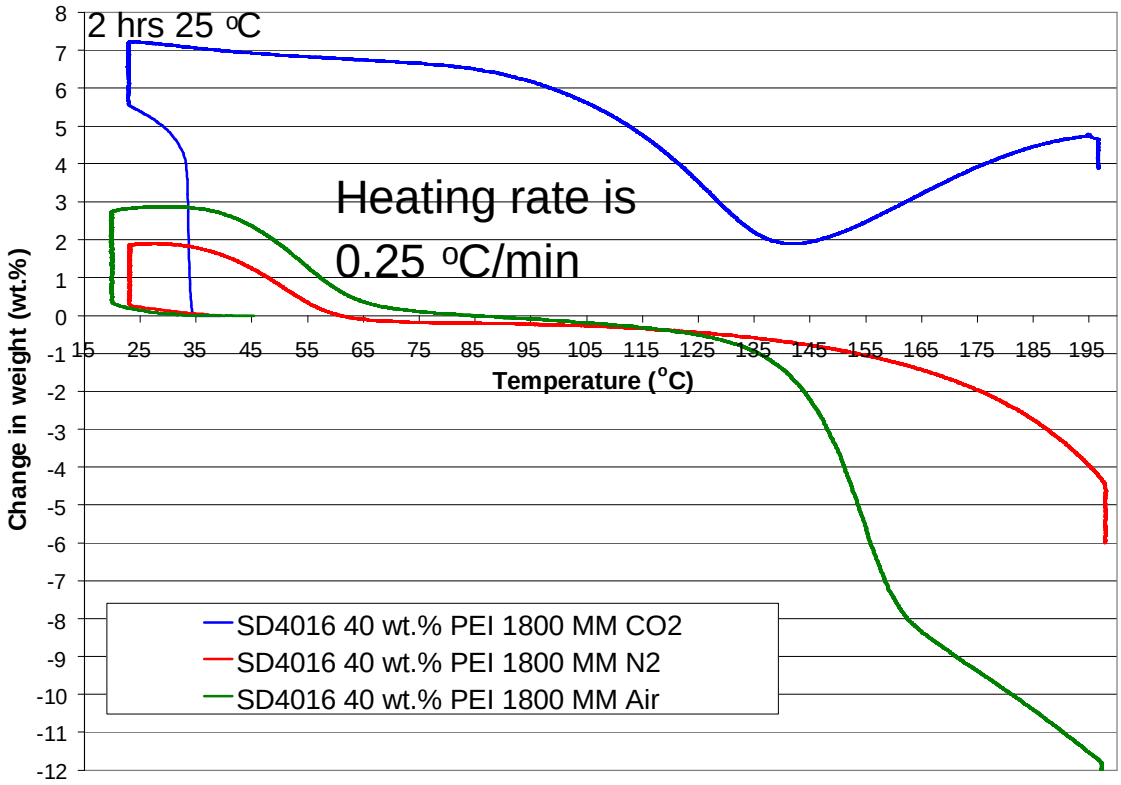

Figure 29: Effect of heating in variously CO_2, N_2 and air on the weight of a 40 wt.% PEI 1800 MM loaded silica

Currently, an irrefutable explanation for this contrarian behaviour can not be given. However, a consultation of the available literature on amine-CO_2 reactions has led to the postulation that this phenomenon is caused by the dehydration of the ammonium carbamate formed through the adsorption of CO_2 upon PEI, thus leading to the formation of urea. This hypothesis is supported by the observation that the PEI-coated silica turns orange at temperatures in excess of 140°C, which is consistent with urea formation. Further work needs to be conducted to verify this supposition.

3.8 Lifetime testing

In essence, the lifetime of a sorbent can be defined as the number of times it can be regenerated without exhibiting an appreciable drop in its performance. A fundamental element of this project therefore comprised ascertaining whether the sorbents made through the amine impregnation method would have lifetimes of a length that was sufficient to make them commercially viable.

3.8.1 TGA analysis using TSA as the regeneration method

The sorbent lifetimes were assessed by subjecting them to a regeneration cycle that was 60 minutes in length, making here the assumption that a single sixty minute regeneration cycle was broadly analogous to subjecting the sorbent to 60 one minute regeneration cycles. The sorbents were also subjected to 60 minute regeneration cycles performed in flows of N_2 and air: each 60 minute regeneration cycle was bordered by a standard 40 minute 75°C adsorption cycle. The results of the experiments conducted using PEI 1800 MM loaded silica as the sorbent are shown in Figure 30.

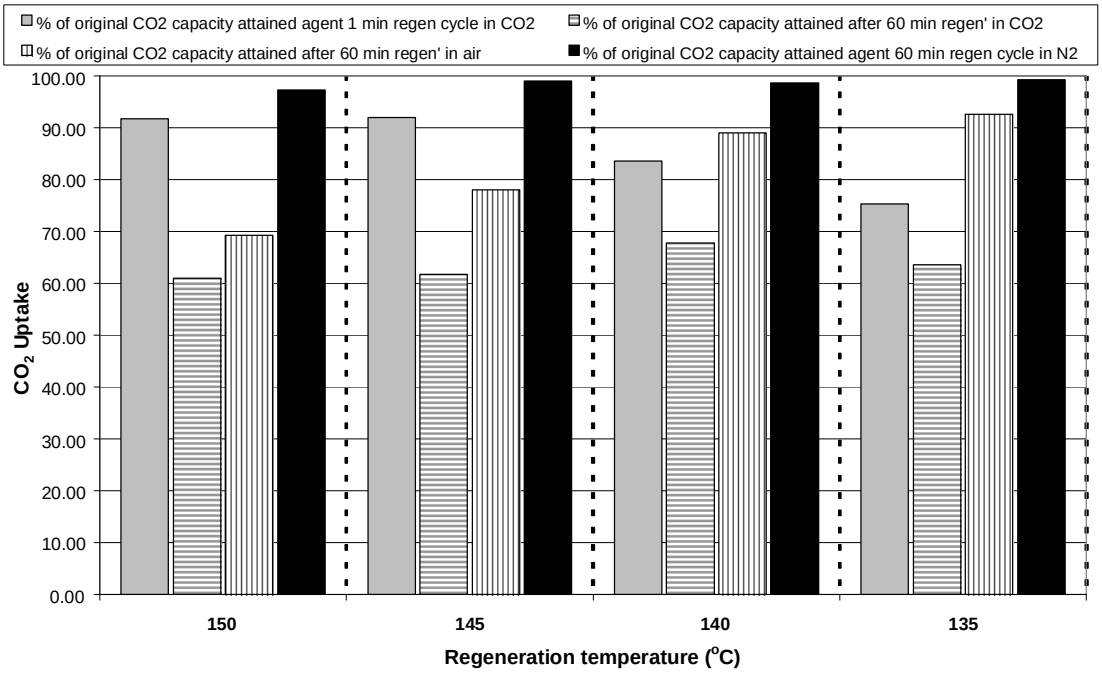

Figure 30: Comparison of CO_2 uptake of 2 impregnated with a loading of 40 wt.% PEI 1800 MM after regeneration for 1 minute in CO_2 and 60 minutes in, variously CO_2, N_2 and air.

Figure 30 shows that as expected, as the regeneration temperature falls, the disparity between the CO_2 uptakes attained after, respectively a 1 minute regeneration cycle and a 60 minute cycle, narrows, i.e. lower regeneration temperatures are less destructive. Thus, it could be concluded that 140^oC is the optimum regeneration temperature as it yields the highest CO_2 uptake after a 60 minute regeneration cycle, i.e. it exhibits the most resistance to the equivalent of 60 1 minute regeneration cycles.

As regards the effect of regenerating the sorbent in air and N_2, Figure 30 shows that for N_2, the decline in the CO_2 uptake of the sorbent engendered by the 60 minute regeneration cycle is minimal. This therefore indicates that within the 135-150^oC temperature range the loss of mass of the amine through its evolution and decomposition is not significant. However, it is clear that above 140^oC, the regeneration cycles performed in air induce a marked drop in the sorbent's CO_2 adsorption capacity. This indicates that above 140^oC, PEI 1800 MM becomes vulnerable to oxidation.

All of the tests described in this section have also been applied to sorbents comprising of silicas loaded with 40 wt.% loadings of PEI 600, PEI 423 MM and TEPAN. When subjected to the slow heating program in the TGA, both PEI 600 MM and PEI 423 MM loaded silicas exhibited the same response to CO_2 displayed by the PEI 1800 MM loaded silica in Figure 29. The optimum regeneration temperatures for PEI 600 and PEI 423 MM were 135 °C and 130 °C respectively. TEPAN responded best to a regeneration temperature of ca. 120 °C.

3.8.2 Rig analysis using TSA as the regeneration method

Figure 31 shows how PEI loaded silicas saturated with CO_2 adsorbed from a 85 % N_2, 15 % CO_2 gas mixture flowing at 100 ml/min, responded to different exposure times to CO_2 at elevated temperatures in the dynamic testing rig. It is clear, firstly, that a regeneration time of 15 minutes or less can restore the CO_2 capacity of PEI 423 MM and PEI 600 MM loaded substrates to over 75% of their original capacity. Evidently, prolonged exposure to CO_2 at the regeneration temperatures used here (140°C for PEI 600 MM, 135°C for PEI 423 MM) had a strong degenerative effect on the

sorbents, but lowering the regeneration temperatures deployed by 5 or 10 °C may prove sufficient to avoid this diminution.

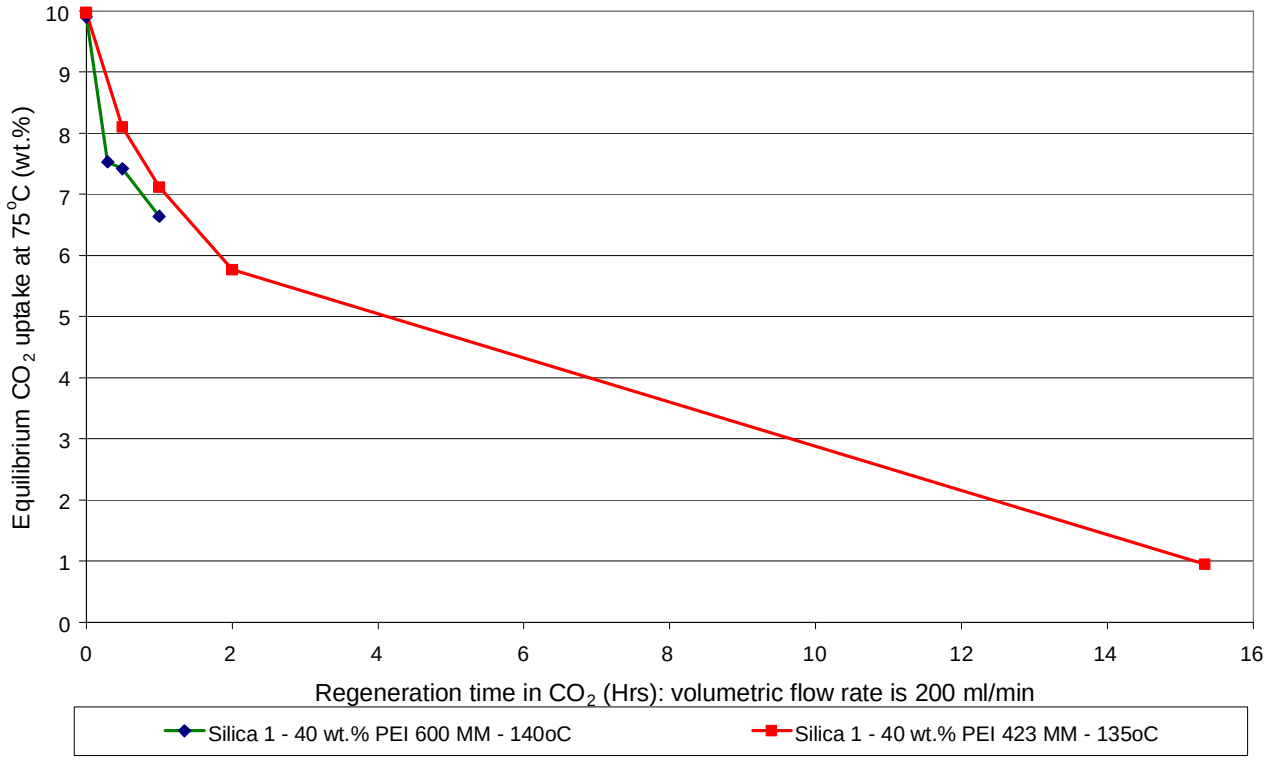

Figure 31: Effect of time on the regeneration of sorbents in a flow of CO_2 using the dynamic rig: gas used for adsorption is 85 % N_2, 15 % CO_2

- To conclude, all of the PEI amines, when exposed to CO_2, irreversibly gain mass at temperatures in excess of *ca.* 135°C, possibly as a result of the dehydration of the ammonium carbamate formed through the adsorption of CO_2 upon PEI, thus generating urea. This therefore inhibits the use of temperature swing adsorption (TSA) when pure CO_2 is deployed as the stripping gas. However, it has been demonstrated that PEI-loaded sorbents respond well to TSA when nitrogen is deployed as the stripping gas, thus TSA should be achievable with steam stripping.

4 Conclusions and future research directions

The specific conclusions from each of the key elements of the research programme are as follows.

1) Beneficiation

1.1) Dry sieving was the least effective of the beneficiation methods evaluated. Demineralisation was the most effective but was the most time consuming and the most expensive. In general, incipient fluidisation yielded PFA-CCs with higher carbon contents than those produced with froth flotation, but because of its ease of use and the relative rapidity with which it could generate PFA_CCs, froth flotation was the preferred method of beneficiation.

2) Activation

2.1) The most desirable characteristics in a substrate for amine impregnation are a high mesopore volume and mesopore diameter. Thus, the primary objective of activation was to ascertain the optimum conditions for attaining these structural characteristics from PFA_CCs.

2.2) NaOH was a better chemical activation reagent than either KOH of H_3PO_4: a PFA_CC:NaOH ratio of 1:1, coupled with an activation temperature of 800°C yielded the best substrates.

2.3) Contrary to claims made in the literature, CO_2 activation was found to be more efficacious than steam activation. Its success was however contingent on the use of a high temperature: i.e. 1100°C: at this temperature the optimum carbon burn-out for generating high mesopore diameters was 40 – 70 wt.%. The optimum carbon burn-out for maximising the mesopore volume was ca. 70-75 wt.%.

2.4) Ultimately, CO_2 activation was the most efficacious of the three activation methods

3) Assessment of equilibrium CO_2 uptakes of prepared sorbents

3.1) When deployed in conjunction with the silicas, TEPAN achieved the poorest CO_2 uptakes of the amines studied. This can be attributed to its lower ratio of CO_2-attracting amine groups to carbons: 1:4, as opposed to the amine to carbon ratio of ca. 1:2 for PEI.

3.2) The higher the MM of the PEI molecule, the lower the loading a substrate can sustain before becoming saturated with the amine: beyond the saturation loading, there is a decline in the CO_2 uptake of the resulting sorbent.

3.3) Of the three PEI amines, PEI 423 MM was the best suited for PFA-derived substrates, i.e. substrates with relatively low mesoporosities. At high loadings - 50 wt.% and above – TEPAN was more effective than PEI 423 MM, but these loadings engendered excessive stickiness in the sorbents.

3.4) The best CO_2 uptake achieved at 75°C using a PFA-derived substrate was 4.7 wt.% This utilised a PEI 423 MM loading of 40 wt.% and the substrate comprised the pyrolysed form (3 Hrs at 900°C) of the 75-710 µm size fraction of the High Marnham sample

3.5) For the preparation of PEI-impregnated PFA_CC substrates, water could be used as a substitute for methanol for the dissolution of the PEI.

3.6) Demineralisation subsequent to activation yielded better substrates that those produced by applying demineralisation prior to activation

3.7) There is a minimum size for candidate substrates, but this has yet to be quantified.

3.8) Ultimately, demineralisation represents the optimum route towards engendering a high receptivity to amine impregnation from PFA_CCs: work published in the literature has demonstrated that a PEI loaded demineralised PFA_CC can attain a CO_2 uptake of 9.4 wt.% at 75°C (Zhang, *et al.* 2004): the shortfall between the CO_2 uptakes achieved here and those attained by Zhang, *et al.* (2004) can be explained by differences in the PFA_CC used: PFA, and moreover its unburned carbon is highly heterogeneous, therefore it is vital that PFA_CC substrates be selected primarily on the basis of the properties of their unburned carbon.

4) Dynamic testing

4.1) The key towards attaining breakthrough capacities that approach parity with the equilibrium uptakes is to maximise the residence time. However, even at relatively low residence times, i.e. at a flow rate of 100 100/min, PEI-loaded sorbents can attain breakthrough CO_2 uptakes that correspond to ca. 80 % of the equilibrium capacity.

4.2) At 75°C and under a gas flow of 85 % N_2, 15 % CO_2 (by volume), the best PFA_CC based sorbent performed less well than its silica based counterpart, but its performance demonstrated that further optimisation of the PFA-derived substrates could yield substrates competitive with mesoporous silica: the PFA_CC achieved ca. two thirds (4.7 wt.%) of the silica based sorbent's total CO_2 uptake and ca. three fifths (3.4 wt.%) of the breakthrough CO_2 uptake.

4.3) When SO_2 is present in the flue gas, PEI-loaded substrates adsorb the SO_2 in the region closest to the gas inlet. Exposure to SO_2 exacerbates the reduction in CO_2 uptake engendered by the standard TSA regeneration process. However, the sorbent's lifetime can

potentially be conserved by the insertion of a sacrificial sorbent bed between the sorbent and the gas inlet.

5) Regeneration and life time testing

5.1) All of the PEI amines, when exposed to CO_2, irreversibly gain mass at temperatures in excess of *ca*. 135°C, possibly as a result of the dehydration of the ammonium carbamate formed through the adsorption of CO_2 upon PEI, thus generating urea. This therefore inhibits the use of temperature swing adsorption (TSA) when CO_2 is deployed as the stripping gas.

5.2) It has been demonstrated that PEI-loaded sorbents respond well to TSA conducted with nitrogen as the stripping gas, thus it is probable that steam could function as a viable alternative to CO_2, given CO_2's limitations as a stripping gas.

5.3) For TSA conducted with CO_2, utilising a regeneration cycle of 1 minute in duration, the optimum regeneration temperature for a PEI 1800 MM impregnated substrates is ca.135-140°C region. The optimum regeneration temperatures for PEI 600, PEI 423 MM and TEPAN were ca. 135 °C, 130 °C and 120 °C respectively.

5.4) Following the equivalent of sixty 1 minute regeneration cycles (performed in the TGA), the measured drop in the CO_2 adsorption capacity of a PEI 1800 MM impregnated substrate was *ca*. 32 wt.% at 140°C.

The results reported here for the base-impregnated PFA_CCs and their activated counterparts and the comparisons drawn with the corresponding mesoporous silicas have indicated that mesopore volume and diameter is the key to achieving high CO_2 adsorption capacities. Thus, to develop base-impregnated substrates for CO_2 capture from flue gas, silicas are the preferred option. Further, silicas have the advantage of being denser than carbons and thus give vastly higher CO_2 uptakes on a volumetric basis. In terms of further development, PEI would appear to have reasonable thermal stability for repeated recycling, the main disadvantage is that it forms a stable complex with CO_2 at elevated temperatures and, for stripping, steam will need to be used, necessitating an additional separation step (as in amine scrubbers). As part of the Carbon Trust project, a large batch (several kg) of a silica-PEI adsorbent will be prepared to demonstrate that the water-based preparation can readily be scaled up and to provide sufficient sample for tests with actual flue gas using a slip stream from the 1 MW rig at E.ON UK. The capture of SO_2 selectively over CO_2 means that the PEI-based adsorbents, depending upon economics, can be extremely effective for reducing acid gases down to extremely low levels after flue gas desulphurisation for CO_2 removal with amine scrubbers.

Overall, the BCURA support has helped considerably in establishing an international leading activity on adsorbents which is likely to continue based on the results described. Further, physical adsorbents are being investigated for CO_2 capture in gasification at high partial pressures (DTI Cleaner Coal Technology Programme, project lead by Jacobs Consultancy).

5 Publications arising from the project

Snape, C. E., Smith, K. M., Arenillas, A., Drage, T.C., (2004), Comparison of two different approaches for enhancement of CO_2 removal by adsorption, Fuel Chemistry Division Preprints, 49 (2)

Arenillas, A., Smith, K. M, Drage, T. C., Snape, C. E. (2005), CO_2 capture using some fly ash derived materials, Fuel, in press, 2005

Smith, K. M,, Arenillas, A., Drage, T. C., Snape, C. E. (2005), Comparison of two different approaches for enhancement of CO_2 removal from flue gas with carbon adsorbents.

(i) Proceedings of Second International Conference on Clean Coal Technologies for our Future (CCT2005), 10-12 May 2005**,** Sant'Elmo Beach Hotel Conference Centre, Sardinia, Italy and

(ii) Proceedings of International Symposium International Symposium Moving Towards Zero Emission Plants, Leptokarya Pieria, Greece, 20-22 June 2005.

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