Development of Stable Isotopic Ratio Measurement – Apportioning of Fuel and Thermal NOx

by

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Development of stable nitrogen isotope ratio measurements to apportion fuel and thermal NO_x in coal combustion (project 231)

Summary

The main aims of the project have been to develop a nitrogen-stable isotope measurement technique for NO_x and to ascertain whether it can be used to determine the relative contributions of fuel and thermal NO_x during coal combustion at high temperatures. Suitable substrates for adsorbing sufficiently high concentrations of NO_x from flue gas streams to facilitate the reliable measurement of the nitrogen stable isotope ratios were developed, the substrates encompassing both manganese oxide supported on zirconia (MnO_y-ZrO_2) and iron supported on active carbon (Fe/AC, first milestone completed October 2001).

Nitrogen stable isotope measurements were conducted on a number of thermal/prompt (diesel) and actual (coal) PF NO samples collected from the 1 MW test facility at Powergen and fuel NO_x samples from the fluidised-bed (FB) combustor at the Caledonian paper mill in Ayrshire, together with measurements on a range of pyrolysis and combustion chars obtained from a drop-tube reactor (second milestone completed, August 2002). The nitrogen stable isotope ratios ($\delta^{15}N$) of the thermal/prompt NO samples analysed occur across a relatively narrow range with a mean below 0 ‰ the value for atmospheric nitrogen, although reliable background corrections could not be applied at this stage. The $\delta^{15}N$ for fuel NO samples collected from the fluidised bed combustor also occur close to 0 ‰, albeit again without reliable background corrections. In FB combustion, the volatile nitrogen (HCN) is the principal precursor of the fuel NO, which is not the case for high temperature PF combustion where char is the major source for high volatile coals. Indeed, the first PF NO samples analysed displayed a relatively wide range of uncorrected $\delta^{15}N$ values (*ca.* + 4.5-10 ‰) with an overall mean of 7.3 ‰. It is considered that these variations reflect different proportions of fuel and thermal NO, together any variations in fuel NO isotopic ratios that might reflect the rates that devolatilisation and char combustion occur. Compared to the nitrogen stable isotope ratios of coals, which are generally all close to 2 ‰, those of the chars analysed lie in the range of 3-7 ‰, indicating that much of the isotopic fractionation that can exist between coal nitrogen and fuel NO occurs in the formation of char with the possibility of further fractionation being associated with char combustion.

After completing the second milestone, a nitrogen-free Fe/AC was prepared with Mn as a promoter using an innovative procedure starting with sugar and this was used to collect further thermal/prompt and actual PF NO_x samples from the 1 MW test facility. The isotopic data required no background corrections and indicated thermal/prompt NO_x collected during start-up burning diesel has a $\delta^{15}N$ of close to -6.5 ‰ compared to close to +15 ‰ for the actual PF sample analysed. Thus, differences of up to *ca.* 20 ‰ can exist between thermal and PF fuel (char) NO_x isotopic values, which augers well for the further development of the approach. During the final phase of the project, the performance of the N-free Fe-Mn/AC adsorbent was optimised and further samples with possible varying proportions of fuel and thermally derived NO_x were collected from the 1 MW test facility with and without over fired air. The $\delta^{15}N$ values of these samples were in the range +5.5-7.5 ‰ and, if the reference points of -6.5 ‰ and +15 ‰ for thermal/prompt and fuel NO, respectively, for the first set of samples can be assumed as being applicable here, this suggests that approximately 50% of the NO arises from prompt/thermal mechanisms. Indeed, this is consistent with the unstable smoky flame that was observed during the sampling period. Finally, to achieve the third milestone, ways to incorporate the nitrogen stable isotope data into combustion models have been considered and, due to the success of this project, plans have been made to develop the approach further. The main priorities now are to establish protocols for determining the fuel NO_x values for individual coals and to help establish the most reliable values thermal/prompt NO_x for PF combustion. Once this has been achieved, the procedure can then be considered as a means to resolve NO_x emanating from PF combustion and transport fuels in the environment.

1 Introduction

There is a continuing need to reduce NO_x emissions from pulverised coal-fired (PF) boilers. In PF combustion, NO_x is generated from both nitrogen in coal (fuel N) and from the nitrogen in air, the latter encompassing both thermal and prompt NO_x involving (i) the direct reaction of nitrogen with oxygen and (ii) the reaction of nitrogen with hydrocarbon radicals to generate HCN that then leads to NO_x formation. It is considered that fuel N accounts for the majority of NO_x from PF combustion but, to help guarantee combustor performance and aid combustion modelling through a better understanding of NO_x formation pathways, means to quantify the contributions of fuel and thermal/prompt NO_x are likely to prove valuable. Atmospheric stable nitrogen isotope measurements on NO_2 (precipitated as nitrate) suggest that significant differences may exist between the ^{15}N to ^{14}N ratios for NO_x derived from coal and that from transport fuel sources [1], which predominantly is formed from air nitrogen via the thermal and prompt mechanistic pathways. Ratios are reported in differences of parts per thousand (permil, ‰), i.e.

$$\boldsymbol{d}^{15}N = \left(\frac{(^{15}N/^{14}N)_{sample}}{(^{15}N/^{14}N)_{standard})} - 1 \right) \times \left(10^3\right)$$

Atmospheric nitrogen is the standard and $\delta^{15}N$ values reported by Heaton [1] for atmospheric NO_2 were *ca.* – 2 to -13‰ for transport fuels and + 5‰ for coal-fired power stations.

At the commencement of the project, no nitrogen isotopic data had been reported directly for NO from coal combustion due to the problems of first adsorbing the NO and then determining the $\delta^{15}N$ of the NO which, in terms of minimizing sample size and maximizing throughput is best achieved using an elemental analyzer linked to an isotope ratio mass spectrometer (EA-IRMS). The main aim of the project was to develop a nitrogen-stable isotope measurement technique for NO_x and to ascertain whether it can be used to determine the relative contributions of fuel and thermal NO_x during coal combustion. The specific objectives were to:

- (i) to design suitable substrates for adsorbing NO_x in flue gases;
- (ii) to establish the isotopic values for fuel and thermally-derived NO_x with samples from test rigs; and
- (iii) to apply the experimental approach to larger facilities and to assess the data obtained for improving existing combustion models.

The three specific milestones for the two-year R&D programme were as follows.

1. Developing suitable substrates for adsorbing sufficiently high concentrations of NO_x from flue gas streams to facilitate the reliable measurement of the nitrogen stable isotope ratios, the substrates encompassing both manganese oxide supported on zirconia (MnO_y-ZrO_2) and iron supported on active carbon (Fe/AC, milestone completed October 2001, section 2.1). Later in the project, a nitrogen-free Fe/AC was prepared (section 2.1) and this has been used to collect thermal/prompt and actual PF NO_x samples from the 1 MW test facility (milestone 3, section 2.5). As will be described, the isotopic data obtained with this adsorbent required no background/blank corrections.

2. Determining the isotopic values for fuel and thermally derived NO_x samples from the facilities at Mitsui Babcock and Powergen, together with those for chars from devolatilisation experiments (milestone completed August 2002, sections 2.3 and 2.4). Fuel NO_x samples were collected from the fluidised-bed (FB) combustor at the Caledonian paper mill in Ayrshire by Mitsui Babcock and nitrogen stable isotope measurements have been obtained for (i) the thermal and fuel NO_x samples, (ii) the actual coal NO samples collected on the 1 MW facility at Powergen and (iii) a selection of coals and pyrolysis and combustion chars obtained from a drop-tube reactor.

3. Making measurements on the 1 MW test facility operating with different total NO_x concentrations and different proportions of fuel and thermally derived NO_x (sections 2.5 and 2.6, milestone completed, February 2003). Ways to incorporate the nitrogen stable isotope data into combustion

models have been considered, and, due to the success of this project, plans have been made for further development of the approach (section 2.6).

It is worth stressing that thermal NO can only be sampled during the start-up period on PF test facilities, such as the 1 MW burner at Powergen, where diesel is burned, typically for up to 2 hours prior to coal feeding commences (milestones 2 and 3). After completing the second milestone and to better achieve the third and final milestone, a thorough understanding has been achieved of background and sample blank corrections in the EA-IRMS instruments used for the nitrogen stable isotope measurements (section 2.2 and Appendices 1-3).

2. Technical Progress

2.1 Sorbent development

2.1.1 Manganese/zirconia and first active carbon sorbents The most promising sorbents for investigation were identified from a literature review and these are listed in Table 1. The objective has been to achieve NO_x loadings corresponding to over 0.1% nitrogen which provides sufficient sensitivity for the nitrogen stable isotope measurements. Several gram batches of manganese/zirconia (MnO_y-ZrO_2)[2], KOH treated γ alumina[3] and a number of active carbon-supported iron oxide sorbents[4-6] (Fe/AC, some with promoter metals such as cerium, Ce). All these have been tested in a laboratory facility (Figure 1) using a model gas mixture containing 650 ppm NO, 10% v/v CO_2 and 5% v/v O_2 and is generated by mixing the air with the special gas mixture purchased. Some tests have been conducted at elevated temperatures and, at ambient temperature, diluting the model gas mixture in air to vary the NO concentration.
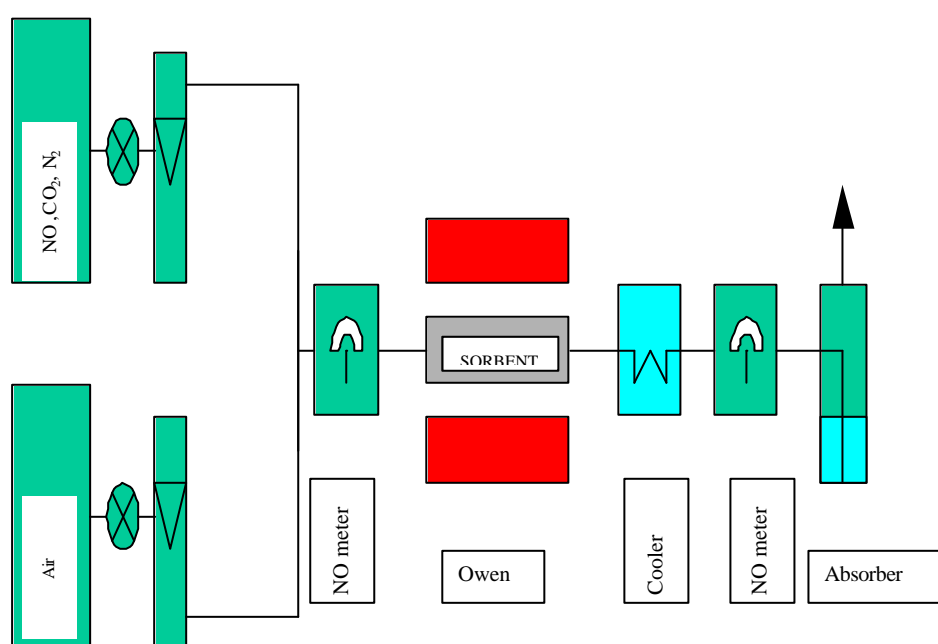
Figure 1 Schematic of the NO sorption experimental test rig.

Table 1 summarises the findings for the most effective sorbents tested in terms of the time required before breakthrough of NO occurred under the standard test conditions at ambient temperature. The amount of NO adsorbed at the point of breakthrough and, in some cases, BET surface areas are also listed. Figure 2 presents a comparison of the NO outlet concentration against time for the MnO_y-ZrO_2, normal Fe-AC and Fe-AC promoted with Ce sorbents.

Table 1 and Figure 2 indicated that the NO sorption capacities at breakthrough are higher for the Fe/AC samples investigated than for the MnO_y-ZrO_2, this could arise from the considerably higher surface areas of the active carbon sorbents. However, the breakthrough capacity of 0.22 mmol g^{-1} under the test conditions of for the MnO_y-ZrO_2 sorbent corresponds to *ca*. 0.6 % w/w of NO (corresponding to *ca*. 0.3% w/w of N) which is considerably higher than the initial target of *ca*. 0.1% w/w N. The Ce-promoted Fe/AC (*ca*. 2.5% w/w Fe) has the highest breakthrough capacity corresponding to *ca*. 1.0 % N. However, although the sorption capacities are clearly higher for the Fe/AC samples investigated, it is probable that, when determining the stable isotope ratios of the sorbed NO, the active carbon could well give a larger background nitrogen signal than the MnO_y-ZrO_2. The performance of the KOH treated γ alumina was not as good as those achieved for the MnO_y-ZrO_2 and Fe/AC sorbents in terms of NO sorption being incomplete at the outset with about a 20% breakthrough of NO.

Table 1 A comparison of NO adsorption from the model gas mixture on different absorbents under dynamic conditions (bed length: 15 cm; temperature: ambient; flow rate: 200 ml/min; Inlet NO concentration: 650 ppm)

Absorbents	**Capacity at breakthrough, mmol/g**	Breakthrough time, min	BET surface area, m^2/g
Activated carbon(AC)	--	--	961
Fe/AC	0.73	283	--
Ce-Fe/AC	1.08	424	715
Ce-Fe/AC-Al_2O_3	0.75	304	--
Fe-Mn/AC-ZrO_2	0.73	305	--
Cu/AC	0.74	284	--
Ce-Cu/AC	0.87	335	829
MnO_y/ZrO_2	0.22	143	197
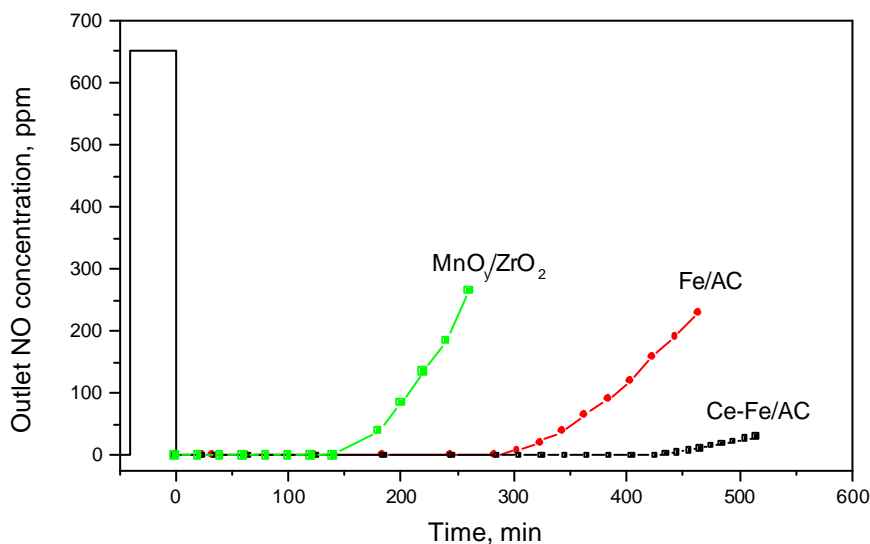
Figure 2 A comparison of the profiles for NO adsorption on MnO/ZrO_2 and two of the activated carbon supported Fe sorbents under dynamic conditions

*(*Conditions: Internal diameter of tube reactor: 0.6 cm; bed length: 15 cm, flow rate: 200 ml/min; Inlet NO concentration: 650 ppm)

The actual equilibrium sorption capacities are going to be considerably higher than the capacities at break through just described. However, in actual sampling, it is important to use the sorbent only until breakthrough

occurs, since after this point, isotopic fractionation effects may be evident between the adsorbed and non-adsorbed NO. As expected, breakthrough times decrease with increasing temperature (Figures 3 and 4) and, therefore, actual sampling will be conducted at ambient temperature. Also, reducing the bed volume had the expected effect of reducing the breakthrough time; reducing the amount of sorbent from 7 to 2 g for decreased the breakthrough time from 400 to 50 min. for MnO_y-ZrO_2 with the set of conditions used described in Figure 3. Keeping the actual amount of NO passing over the sorbent constant but increasing the gas velocity by mixing the test gas with air for MnO_y-ZrO_2 (i.e. decreasing the NO concentration) had only a relatively small influence on the breakthrough time.
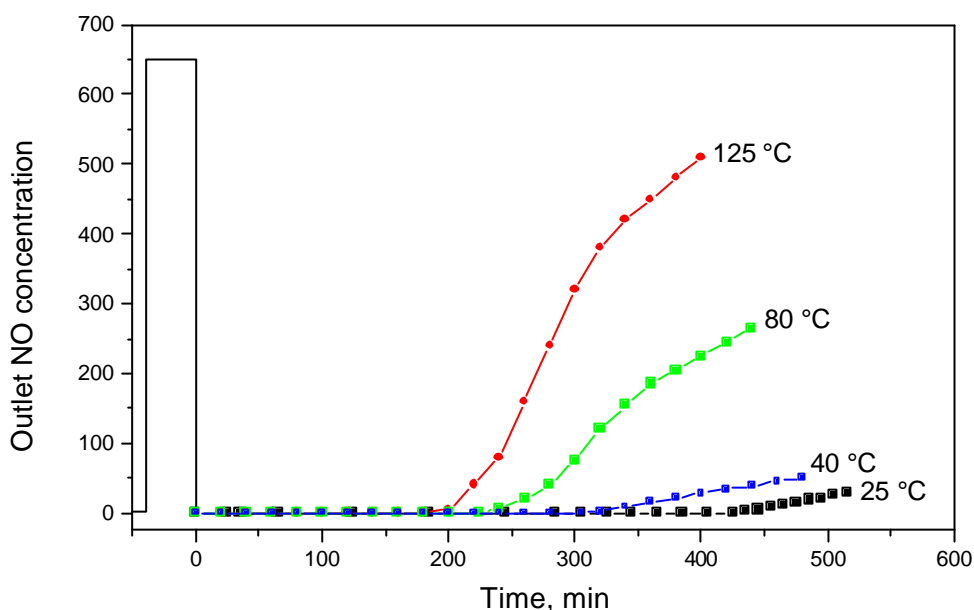

Figure 3 Temperature-dependency of NO adsorption for the Ce-Fe/active carbon sorbent
(Conditions: internal diameter of tube reactor: 0.6 cm; bed length: 15 cm, flow rate: 200 ml/min; inlet NO concentration: 650 ppm)
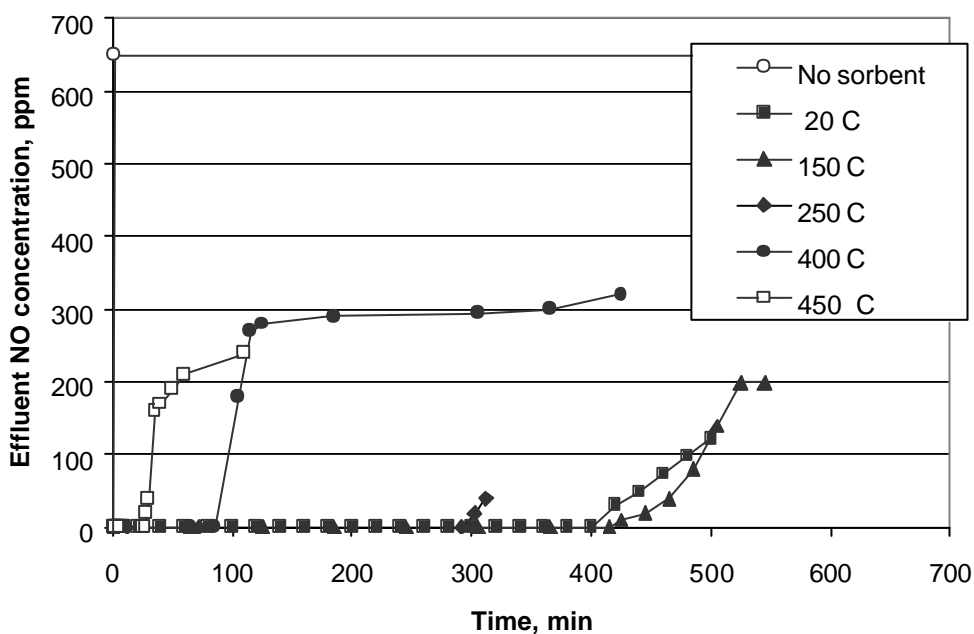

Figure 4 Comparison of NO sorption by the MnO_y ZrO_2 at different temperatures

(Gas flow rate: 100 cm^3 min^{-1} air +100 cm^3 min^{-1} gas mixture - NO: 0.13 %, CO$_2$:13.1 %, N$_2$: 86.7 % , bed length 15 cm , bed diameter: 9 mm. mass of sorbent:7.3 g)

It has been found that both for the MnO$_y$-ZrO$_2$ and Fe/AC sorbents can be regenerated by calcination without any loss in the capacity achieved at the breakthrough point under the test conditions (Figure 5).
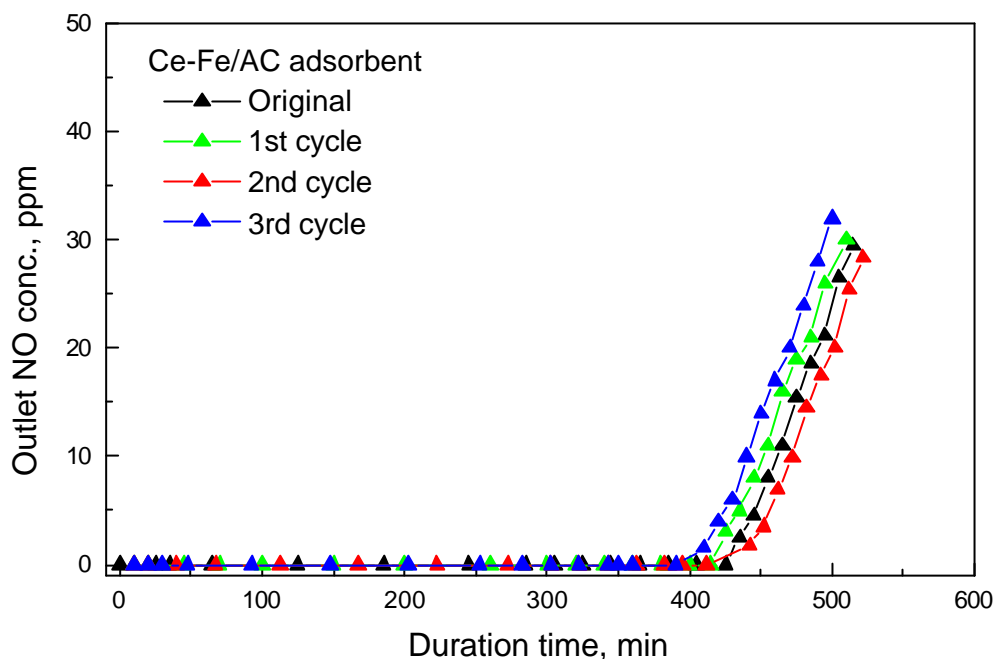

Figure 5 Breakthrough curves for Ce-Fe/AC adsorbent after repeated regeneration

Adsorption conditions: 1) Sorbent bed dimension: 15 × 0.5 (i.d) cm; 2) Flow rate: 200 ml/min; 3) Inlet NO/O$_2$ concentration: 650 ppm /12.5 % v/v; 4) Temperature: 25 °C

Regeneration (desorption): 1) 25 to 600 °C (1hr) at a rate 40 °C/min in helium atmosphere (200 ml/min)

For actual flue gas conditions, both adsorbents can adsorb sufficiently high quantities of NO for subsequent nitrogen stable isotope analysis, particularly after base solution is used to remove SO$_2$ and a stream of pure oxygen to increase the flue gas content to over 10% were incorporated into the sampling rig. The maximum nitrogen uptakes achieved during sampling were 0.4–0.8 % w/w for fuel NO and 0.1–0.2 % w/w for thermal NO (section 2.4), these levels being considerably higher than the initial target of 0.1% nitrogen for isotopic analysis at SUERC. However, background nitrogen levels were appreciable (0.1-0.2 % for active carbon), even for the zirconia system and this limited the accuracy of the first series of isotopic measurements made (section 2.4).

2.1.2 Nitrogen-free active carbon sorbent Given that the NO$_x$ uptake levels are inherently higher for Fe/AC than the MnO$_y$-ZrO$_2$ sorbents and the latter still give a significant background contribution (although this can be corrected, appendix 1), it was decided to explore whether a low N content active carbon could be either purchased or synthesised in house. As for the AC used thus far, the N contents of commercial active carbons (presumed to be prepared from biomass) were in the range 0.1-0.2%. Therefore, it was decided to prepare a carbon starting with carbonising sugar to obtain the lowest possible background N content.

Granulated white sugar purchased from a local supermarket was used. For the first preparation, about 200 g of this sugar was first dehydrated in ~ 250 ml concentrated sulfuric acid to produce a char-like porous solid. This solid material was then washed using excess distilled water and dried in an air-blown oven at 60°C. The

dried solid material was then carbonised at 650°C for about 3 hours in a fixed-bed reactor to yield the sugar-based char, which was subsequently activated at 1000 °C in a flow of CO_2 (~90 min.) in order to obtain the final sugar-based activated carbon product. For 100 g of sugar, about 15~20 g of activated carbon can be obtained from this procedure.

To achieve high NO_x absorption capacities, however, activated carbon materials often need to be pre-oxidised, generally using boiling concentrated nitric acid, in order to enhance the dispersion of metal oxides. Bearing in mind that a nitrogen-free NO_x sorbent is required, any use of nitrogen-containing chemicals should be avoided or at least minimised. The use of 'pre-treatment' in $KMnO_4/KOH$ solution in our protocol developed for preparing the unique N-free sorbent benefits from a combination of a pre-oxidation of carbon material and the enhanced simultaneous dispersion of metal (Mn) oxides. The sugar-based AC material was first treated in 0.2 N $KMnO_4$/0.5 N KOH solution for about 5 hrs and, subsequently, the same volume of 0.5M N $Fe_2(SO_4)_3$ solution was poured into the mixture. The pH of the new mixture was controlled at 12 and the mixture was then stirred for 5 hrs before it was filtrated, washed with distilled water and dried at 120°C. The dried raw sorbent material was then calcined at 500°C for 10 hrs to obtain the final Fe-Mn/AC sorbent.

Following the initial preparation, the procedure was improved as follows. Pre-oxidation using $KMnO_4$/ KOH solution and the ratio of Fe/Mn used both play important roles in determining the NO_x breakthrough capacity of this sorbent, the use of an over-saturated $KMnO_4$ solution is superior to the 0.2 N $KMnO_4$ used initially for carbon pre-oxidation. The adsorption characteristics and breakthrough capacities of the Fe-Mn/AC sorbents in the laboratory test facility with varying Fe/Mn mole ratios, with/without the presence of SO_2, are compared in Figure 6 and 7. The Fe/Mn ratios quoted in both figures are not necessarily the actual ratio of iron and manganese coated onto the carbon surface but the ratios mixed in the first place. As can be seen from Figures 6 and 7, the highest breakthrough capacity with the new Fe-Mn/AC catalyst with a Fe:Mn ratio of 1:1 which corresponds to a nitrogen uptake as NO of over 1.5% in the absence of SO_2. The lowest breakthrough capacity was obtained with a Fe:Mn ratio of 0.5 which still gave a nitrogen uptake as NO of over 0.7% in the absence of SO_2. As found for the other AC sorbents, the presence of 1000 ppm SO_2 in the flue gas mixture reduced breakthrough times by between 30 and 50% (Figures 6 and 7). Besides the improved sorbent performance, the preparation is also much less labour-intensive than used earlier.
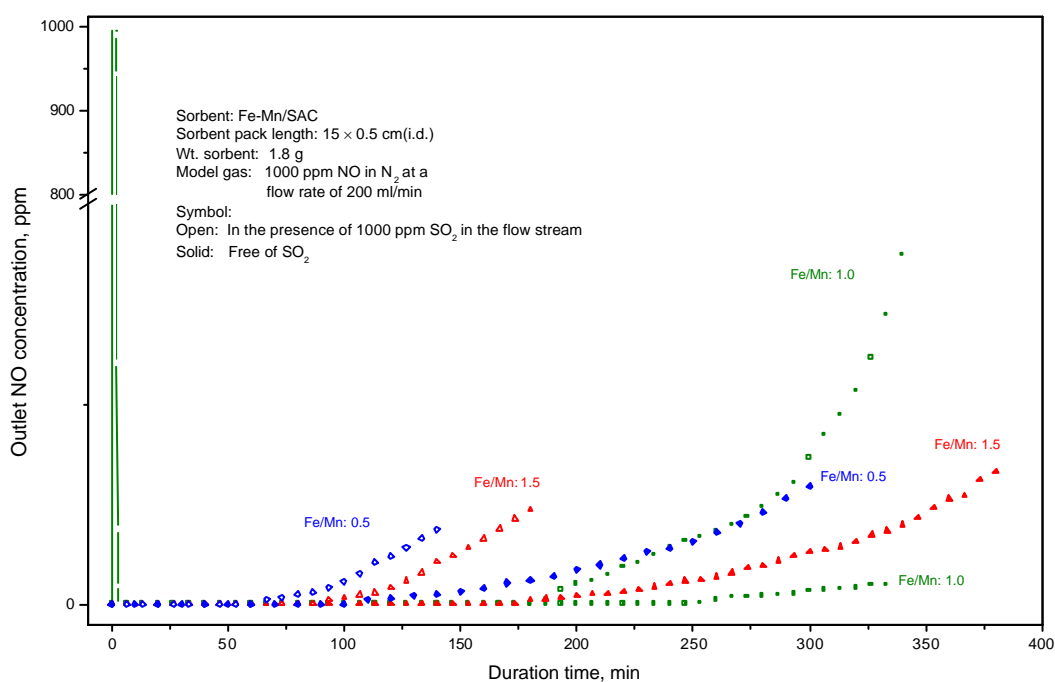
Figure 6 NO breakthrough curves for the nitrogen-free Fe-Mn/AC sorbent with varying Fe/Mn ratios.

A 100 g batch of the Fe-Mn/AC sorbent was prepared to sample NO in the final sampling campaign on the PF test facility at Powergen under controlled combustion conditions, with and without over-fired air (milestone 3). This sample is mixture of the 15-20 g samples prepared with Fe:Mn rats of 0.5:1, 1:1 and 1.5:1 for the laboratory tests carried out. For this bulked sample, the sugar-derived active carbon was pre-oxidised using $KMnO_4$/ KOH solution.
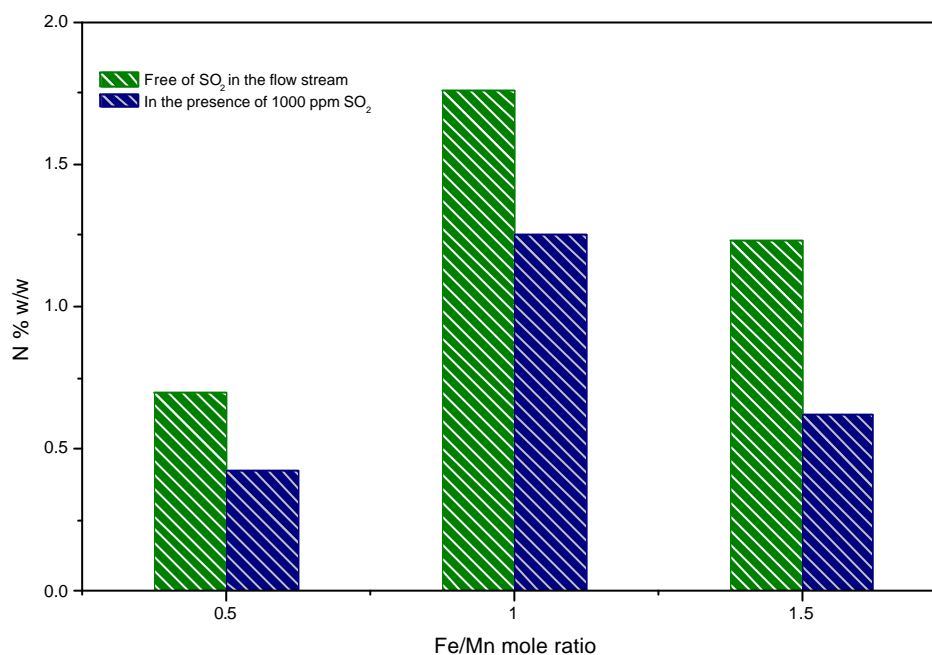
Figure 7 A comparison of nitrogen content achieved at NO breakthrough point for different Fe-Mn/AC sorbent with varying Fe-Mn ratios.

2.2 Blank sample and background corrections

These corrections are considered in Appendices 1-3 for the two EA-IRMS systems used during this investigation. In essence, three potential sources of background signal can be envisaged: firstly the background with no sample being delivered from the carousel and the system clean. Secondly, the blank signal, which in addition to clean system blank, might build up during a run because of ash from previous samples and could be transient or more continuous in nature. Finally, the organic nitrogen background from the adsorbent itself. In terms of the absolute nitrogen content measured, the system blank is insignificant. A variable transient arises from the combustion catalyst and this corresponds to 0.01-0.02 % (Appendix 1). For the N-free Fe/Mn adsorbent, the background nitrogen level is *ca*. 0.01-0.02 %, no more than from the combustion catalyst and typically less than 10% of the nitrogen adsorbed as NO during sampling (Appendix 2). Background N levels for the MnO_y-ZrO_2 sorbents were *ca*. 0.06 %, possibly arsing from the nitrate salts used in the preparation. Clearly, both in terms of lower background and higher uptake, the N-free Fe/Mn sorbent is preferred.

2.3 Nitrogen stable isotope measurements on coals and chars

A number of coals from the UK and elsewhere have been analysed and the nitrogen stable isotope ratios are listed in Table 2. The $\delta^{15}N$ values all occur over the relatively narrow range of + 1-4 ‰ with the range being

even smaller for the UK coals with all the values being to +2 ‰. Therefore, due to the similarity in $\delta^{15}N$ values for the major internationally traded coals investigated, no major variations are expected in fuel NO_x values due to the nitrogen in the coals used.

A drop tube furnace system used to prepare the chars was developed at PowerGen and was designed by Severn Furnaces Ltd to provide a means of producing reasonable quantities of char sample at similar conditions to those of a commercial PF boiler. This means using heating rates of the order of 10^4 to 10^5 ^{o}C/sec, and low oxygen levels (0-10%) when simulating the first few hundred milliseconds. Table 3 lists the nitrogen stable isotope ratios for a series of partially combusted chars prepared at different residence times (200, 400 and 600 ms) in the drop-tube reactor from three different coals. Pyrolysis chars from each coal were prepared in the drop tube reactor and these were then fed back into the reactor using an atmosphere containing 5 % oxygen. Two separate char samples were analysed for each residence time. Of the 3 coals investigated, the Indonesian coal (Kaltima Prima) is the most reactive and Pocahontas (USA) the least. Similarly, Table 3 lists the stable nitrogen isotopic ratios for a Spanish coal, a pyrolysis char and four combustion chars obtained at high levels of burnout.

Table 2 A summary of stable nitrogen isotopic values for a selection of coals.

Coal and description	$d^{15}N$, ‰	Analytical confidence (s)/Replicates
Blair Athol, Australia	1.6	0.5/4
Ensham, Australia	1.5	0.3/3
Gedehoop, South Africa	1.4	0.7/6
Irui, Brazil (high ash, high vol.)	3.8	0.3/6
Polish coal	2.6	0.1/3
Prodeco, Colombia (high vol.)	0.6	0.2/4
N. Dakota lignite, USA	2.2	0.3/4
Marrowbone, (USA, high vol.)	2.5	0.1/3
Walter, USA (low vol., Alabama)	1.4	0.2/4
Daw Mill, UK	2.6	0.3/5
Harworth, UK	1.8	0.1/4
Gascoigne Wood, UK	2.6	0.3/5

Table 3 Nitrogen stable isotope ratios for combustion chars prepared in a drop tube reactor from 3 coals

SAMPLE		N CONC % w/w	$\delta^{15}N$ ‰Air	Replicates
1. Oreganal	200 ms	2.04	3.9	4
(Colombia)	400 ms	1.39	5.0	4
	600 ms	0.59	5.7	5
2. Kaltima Pr.	200 ms	2.07	3.1	4
	400 ms	2.07	4.0	3
	600 ms	1.03	3.4	4
3. Pocahontas	200 ms	1.25	5.8	4
	400 ms	0.99	6.6	4
	600 ms	0.82	6.5	4

Table 4 Nitrogen stable isotope ratios of a Spanish coal, a pyrolysis char and three combustion chars prepared in a drop tube reactor (two replicates)

SAMPLE	N CONC % w/w	$\delta^{15}N$ ‰Air
1. Coal	2.20	2.5
2. Pyrolysis char	2.65	4.5
3. Combustion char, 86 % burnout.	1.98	6.0
4. Combustion char, 93 % burnout.	1.48	5.6
5. Combustion char, 95 % burnout.	5.3	5.3
6. Combustion char, 97 % burnout.	5.5	5.5

In all cases, the nitrogen stable isotope ratios of the chars are more positive (heavier) than those of the coals and range from +3 to 7 ‰. However, Table 3 indicates that the isotopic fractionation is roughly in the order Pocahontas > Oreganal > Kaltima Prima, which is the opposite trend to that in reactivity. For the two least reactive coals, the extent of isotopic fractionation increases with burnout (*cf.* 600 with 400 and 200 ms chars in Table 2 for Pocahontas and Oreganal). The data for the Spanish coal reveals that the nitrogen stable isotope ratios of combustion chars obtained at high levels of burnout do not change markedly (Table 4). In conclusion, it would appear that much of the isotopic fractionation that can occur between coal nitrogen and fuel NO (see following) emanates from the formation of char, although further fractionation could arise during char combustion.

2.4 First suite of NO_x samples collected on 1 MW test facility and samples from fluidised-bed combustor

More than 20 samples, including both thermal and fuel NO_x samples were collected using the MnO_y-ZrO_2 and Ce promoted Fe/AC-based adsorbents. Note that significant background corrections are required for these adsorbents and that these samples were collected before the N-free Fe-MN/AC adsorbent had been developed. The procedure used for sampling is quite similar to that used in laboratory, but some modifications were required. The first modification involved the use of base (KOH) solution to wash out the acid gases after it was observed that the relatively high contents of SO_x and CO (both up to 1500 ppm) and other possible products in the flue caused significant deactivation to both MnO_y-ZrO_2 and Ce promoted Fe/AC-based adsorbents. The acid wash also removes NO_2 but NO_2 levels are relatively small being typically below 3% of those for NO. Secondly, it was found that, as a result the oxygen concentration of the flue gas is being lower than in the laboratory gas mixture, breakthrough times were significantly shorter, especially for the Ce-Fe/AC system since there was insufficient oxygen to oxidise the NO for NO_2 for adsorption as nitrate. Therefore, a stream of pure oxygen was introduced into the flue gas to make the oxygen concentration in the range of 11-17%.

Details on the samples collected where appreciable NO uptakes were achieved are given in Appendix 2. The thermal NO_x samples were collected during start-up periods where the 1MW facility was solely fed with fuel oil, which contains little nitrogen. Start-up periods were typically 2 hours before coal was fed for the remaining duration of the tests. The increases in nitrogen content for the sorbents due to NO uptake (Table A2.1) were estimated from the NO_x levels in the flue gas. In most cases, this increase was between 0.1 and 0.2 %, which corresponds to an uptake of 0.2-0.4% NO. Higher uptakes were achieved for some of the actual PF (coal) samples (Table A2.1) due to the longer sampling periods. For the Ce-Fe/AC sorbents, the estimated background nitrogen contents were *ca*. 0.2%, in close agreement with that determined using the isotope ratio mass spectrometer. For the samples collected during the periods where coal was burned, the flue gas NO_x concentrations were considerably higher (Table A2.1) and as a result the adsorbed NO_x levels was also higher with nitrogen contents for the Ce-Fe/AC sorbents being as high as 0.4-0.8%.

Six samples were collected by Mitsui Babcock from the FB combustor at the Caledonian paper mill in Ayrshire using 2 g of sorbent, four using MnO_y-ZrO_2 and two using carbon. The carbon samples were collected in parallel with two of the MnO_y-ZrO_2 samples. The flow rate of conditioned flue gas was 0.4

l/min. and the NO concentration was close to 1000 ppm. However, the concentration of N_2O, which using a model gas mixture was shown not taken up by the AC adsorbents, can be taken as being approximately a maximum one third of that for NO. In all cases, the uptake of NO corresponded to approximately 0.1 % w/w of nitrogen.

The results for the thermal/prompt NO samples using the Fe/AC system are presented in Table A2.2 with duplicate or triplicate determinations being conducted on each sample. Overall, the mean thermal NO_x value from is 0.1 ± 1.6 ‰, suggesting that limited isotopic fractionation is associated with the formation of thermal NO, atmospheric nitrogen having the reference value of 0 ‰. However, closer inspection of the data suggests that the nitrogen concentration measured decreases with increasing sample size and this clearly affects the magnitude of the background correction that should be applied. Although due to this major uncertainty, no correction has been applied. However, given the positive $d^{15}N$ value of the active carbon, any correction is going to reduce the thermal to below 0 ‰.

The results from the fuel NO_x samples from the FB combustor are presented in Table A2.3. Given the large variations in the nitrogen isotopic ratios for the actual NO and background nitrogen for the MnO_y-ZrO_2 sorbents, the Fe/C sorbent is considered to be the most reliable where similar values being obtained for the two samples analysed (mean of 0.8 ‰). Applying a background correction (with the calculated NO uptake of 0.1 % nitrogen) for the carbon will reduce the mean value to below 0 ‰. Since over 90% of the NO emanates from the fuel [7], FB combustion was chosen initially to provide "reference" fuel NO samples. However, compared to high temperature PF combustion, a high proportion of the NO emanated from the volatiles in FB combustion where HCN is the main nitrogen-containing species. The stable isotope ratios for the chars analysed (3 to 7 ‰, compared to *ca*. 2 ‰ coals, Tables 2-4) indicate that those for the volatiles are going to be lighter than zero (i.e. negative). Thus, the large difference between the nitrogen isotopic ratios for FB and actual PF NO samples can be attributed to the fact that the NO for latter is formed primarily from burn out of the char. In conclusion, NO from FB combustion cannot be considered as a "reference" point for fuel NO arising from PF combustion.

The four PF NO samples analysed display a wide range of values with an overall uncorrected mean of 6.9 ± 2.0 ‰ (Table A2.4). It is considered that these variations reflect the different proportions of fuel and thermal NO, together with the variations in fuel (char derived) NO isotopic ratios as a function of the rate that the formation reactions (rates of devolatilisation and char reactivity) occur. Despite the variation encountered and the uncertainty over applying reliable background corrections, these values nevertheless indicate that a large difference does exist between the nitrogen stable isotope ratios for thermal/prompt NO and fuel NO, although the latter is influenced considerably by reaction rates, as suggested by the isotopic ratios for the chars.

2.5 Thermal/prompt and actual PF NO_x samples collected with the nitrogen-free Fe/AC adsorbent

2.5.1 First sample set Given the success of the first sampling campaign with the 1 MW facility at Powergen, it was decided to use facility for the subsequent measurements, as opposed to a larger facility or the NRTF rig at Mitsui Babcock (who had already contributed by sampling at the Caledonian paper mill specifically to collect fuel NO from FB combustion). Firstly, a thermal/prompt and an actual PF NO_x sample were collected in duplicate from burning Daw Mill coal. Details on the duplicate samples and the blank adsorbent analysed using the Europa EA-IRMS with 4 determinations being carried out for each of the NO_x samples can be found in Appendix 3 (Table A3.1). For the 8 replicate analyses, the mean $d^{15}N$ was -6.2 ± 0.9 ‰ for the thermal/prompt NO_x sample and being 14.8 ± 1.5 ‰ for the actual PF sample.

These NO_x isotopic measurements using the "N-free" Fe-Mn/AC adsorbent, represent the most reliable conducted thus far. The measurements indicate that differences of up to *ca*. 20 ‰ can exist between thermal and PF fuel (char) NO_x isotopic values, which extremely augurs well for the further development of the approach (section 1.6).

2.5.2 Second sample set Details of the set of samples collected in which Thoresby coal was burned with and

without over fired air are presented in Table A3.2. Due to the approximate time of one hour required to collect sufficient NO with the flow rate and concentrations in the flue gas, it was only possible to collect combined samples with and without over fired air for all the excess oxygen levels used, since these were switched every 15 minutes. Samples were collected in duplicate (designated A and B) by splitting the gas stream as for the first set of samples. As well as Thoresby coal, samples were also collected for an 80:20 blend of Thoresby coal and petroleum coke. Details on the instrument blank and actual measurements are also given in Appendix 3. Replicate measurements have been performed on all the samples collected and the averaged results from these analyses are presented in Table 5.

The thermal samples display some variability in their mean values, although the agreement for the duplicate samples is excellent for 2 out of the 3 pairs. The average nitrogen contents for the thermal samples collected are reasonably constant at 0.24 ± 0.03 (n = 6). The overall average is -6.9 ± 3.1‰ where the mean value for each experiment is used to calculate the overall average and 1s. This overall average is similar to that of -6.2 ± 0.9 ‰ obtained for the first set of samples collected. These thermal values will be discussed further in the following section.

It is readily apparent that the duplicate samples (a and b) for the actual PF (fuel) samples usually show reasonable agreement except for F090103/a and /b (coal/pet. coke blend)) at 4.2 ± 0.4 and -1.6 ± 0.2, and T090103/2A and 12B at -7.7 ± 0.3 ‰ and -3.6 ± 0.4 ‰. The overall average of the 3 samples collected for the coal (averaging the a and b for each sample is 6.4 ± 1.1 ‰ where the 1s error reflects the spread of the mean values for each experiment that arises from the different combustion conditions. The significance of the differences between the 3 samples is discussed in the following section, but suffice it say that a smoky flame was observed during the sampling period and that the sample collected without over-fired air is isotopically heavier (F070103/1, mean of 7.5 ‰, Table 5) than those collected with the over-fired air on (F070103/2 and 3, mean values of 5.7 and 5.9 ‰).

Table 5 Nitrogen stable isotopic data for the second set of thermal/prompt and actual PF NO$_x$ samples collected with the nitrogen-free Fe-MN/AC adsorbent

Sample Number	Type	% Nitrogen	d^{15}N (‰Air)	n
F070103/1a	Fuel (Coal)	0.58 ± 0.07	8.0 ± 1.3	3
F070103/1b	Fuel (Coal)	0.53 ± 0.02	7.0 ± 0.8	3
F070103/2a	Fuel (Coal)	0.41 ± 0.02	5.6 ± 1.0	3
F070103/2b	Fuel (Coal)	0.38 ± 0.03	5.8 ± 0.3	3
F070103/3a	Fuel (Coal)	0.31 ± 0.00	6.8 ± 0.7	3
F070103/3b	Fuel (Coal)	0.32 ± 0.02	5.1 ± 0.6	3
F070103/4	Fuel (Coal)	0.17 ± 0.03	3.7 ± 0.8	2
F090103/a	Fuel (0.8 Coal/ 0.2 Coke)	0.70 ± 0.03	4.2 ± 0.4	
F090103/b	Fuel (0.8 Coal/ 0.2 Coke)	0.54 ± 0.03	-1.6 ± 0.2	3
T070103/1a	Thermal	0.29 ± 0.01	-10.4 ± 1.0	2
T070103/1b	Thermal	0.23 ± 0.02	-10.6 ± 0.9	2
T090103/1a	Thermal	0.27	-4.7 ± 0.1	½
T090103/1b	Thermal	0.22 ± 0.01	-4.6 ± 0.1	2
T090103/2a	Thermal	0.20 ± 0.00	-7.7 ± 0.3	2
T090103/2b	Thermal	0.23 ± 0.01	-3.6 ± 0.4	2
Thoresby coal		0.72 ± 0.02	5.3 ± 0.8	2

For the other sample collected with the over-fired air off, F070103/4, the mean was 3.7 ± 0.8 ‰. Due to the significant disagreement between the duplicate a and b samples for the coal/pet. coke mixture, these values will not be considered further. However, the low average value of + 1.3 ‰ suggests a high thermal/prompt

contribution to the NO (see section 1.6). The $\delta^{15}N$ values for the latter two samples are in fact lower than that of Thoresby coal (Table 5) which qualitatively indicates a high input from thermal/prompt NO_x, plus some of the NO possibly arising from volatile-N (see following).

2.6 General discussion and future work

2.6.1 Isotopic data for thermal/prompt NO samples The overall average for all thermal/prompt NO_x samples is close to -6.5 ‰ using the N-free sorbent, although there is some variability. No attempt was made to apply a correction for the small amount of nitrogen (0.05%) present in the diesel. If all of this were converted to NO, this would account for up to 20% of the total NO_x collected (120-150 ppm, Appendix 3). Taking a value of +2 ‰ for the diesel, this would make the mean for thermal/prompt NO_x lie close to −8.5 ‰. Given the uncertainty over how much of the diesel N is converted to NO, the overall average for thermal/prompt NO_x samples collected can be taken as -6.5 to −8.5 ‰. This range of values compares to values of −14 ‰ reported by Kiga et al. [7] when methane was burned in a drop tube reactor. These variations could arise from the differences in fuel and reactor type between the two studies and indicate the need to ascertain the $\delta^{15}N$ values for more combustion regimes operating in thermal mode to help ascertain the most reliable values thermal/prompt NO_x for PF combustion.

2.6.2 Isotopic data for PF combustion samples The high value of +15 ‰ for the first sample collected with the N-free adsorbent would suggest that this is prominently fuel-derived, given the highest values for the drop-tube char analysed previously from high volatile bituminous coals were +6 ‰. This value compares with (i) +12-14 ‰ for samples collected from an actual PF plant by Kida et al. [8] and (ii), if corrections could be applied to the samples collected with the early N-containing adsorbent, these would increase considerably to approximately + 4.5-10 ‰.

The isotopic values for the second set of NO_x samples collected with the N-free adsorbent were +5.7-5.9 ‰ and +7.5 ‰ with and without over fired air. If the reference points of −6.5 ‰ and +15 ‰ for thermal/prompt and fuel NO, respectively, can be assumed as being applicable here (this might be the case since the fuel values are coal dependent), this suggests that approximately 50% of the NO arises from prompt/thermal mechanisms with a slightly lower proportion when the air was over fired. Indeed, this observation is consistent with the unstable smoky flame that was observed during the sampling period. Alternatively, volatile N in the form of HCN could have been converted directly to NO under these conditions. In conclusion, the data for sample suites analysed here have indicated that nitrogen stable isotopic ratios of NO from PF combustion is likely to vary widely. Although some of the variance is due to the differences in isotopic fractionation that occurs in going from coal-N to char-N and finally to fuel NO, it is considered that varying proportions of thermal/prompt and fuel NO_x have a major bearing, as demonstrated for these samples.

2.6.3 Input of information into combustion models Knowledge of the proportions of fuel and thermal/prompt NO_x formed during PF combustion would enable the relative rates of the sequence of reactions involved in NO_x formation to be determined. Further, an overall nitrogen isotopic balance for individual coals could be established involving the collection of volatile species including tar, HCN and NH_3, together with char, from devolatilisation tests in a drop tube reactor or other appropriate regime. This would also improve modelling since the isotopic shifts observed would reflect the relative rates of the elementary series of reactions leading to each N-containing species. Indeed, the measurements conducted here have given an initial indication that increased rates of devolatilisation reduce the isotopic differences between coals and their resultant chars. In conclusion, the ability to determine proportions of fuel and thermal/prompt NO_x, together with conducting nitrogen isotopic balance for devolatilisation and subsequent char burn out will lead to considerable improvement sin the predictive capability of models currently in use.

2.6.4 Project achievements and future work This project has established a simple and robust experimental protocol for collecting and determining the stable isotope ratios of NO_x from flue gas. The protocol is much more convenient and rapid than that used by Kida et al. [8] in the only other reported study where flue gas NO_x has been sampled for determining isotopic ratios. These workers used gas bags that contained oxidising solutions to convert NO to nitrate which was subsequently reduced to nitrogen gas for isotopic analysis. The

results obtained from this study have indicated significant isotopic differences of up to *ca*. 20 ‰ exist between thermal/prompt and fuel NO$_x$. However, although the stable isotopic ratios of thermal NO$_x$ samples were relatively constant, as mentioned earlier, there is a need to ascertain the δ^{15}N values for more combustion regimes operating in thermal mode to help ascertain the most reliable values thermal/prompt NO$_x$ for PF combustion. Rather than use diesel as has here during start-up on the 1 MW rig, other fuels need to be tested, possibly including volatiles from coal, and collecting NO by pure thermal reactions both to better understand and measure representative values for thermal and prompt NO$_x$.

As described earlier, significant variations in δ^{15}N values have been found for fuel NO$_x$ analysed. Although it is considered that differing proportions of thermal/prompt and fuel NO$_x$ have a major bearing, these variations have been shown to also arise in part from differences in the rate of devolatilisation and subsequent char burn out and the extent of conversion of char-N to NO. Char nitrogen becomes isotopically heavier with decreasing rate of devolatisation (increasing rank). However, the extent of char burn out does not seem to have a major effect on the isotopic values. Since some of the actual PF samples analysed were isotopically heavier still than the char samples analysed, this suggests that further isotopic fractionation occurs and this is going to be dependent on the extent of conversion of Char-N to N$_2$ and NO. The lighter isotope would be favoured in forming dinitrogen, meaning that any NO formed is going to be isotopically heavier.

Clearly, to continue developing the experimental approach, probably the main priorities are:

(i) to ascertain the δ^{15}N values for more combustion regimes operating in thermal mode to help establish the most reliable values thermal/prompt NO$_x$ for PF combustion, as already described; and

(ii) to establish protocols for determining fuel NO$_x$ values for individual coals.

Once these have been achieved, the procedure can then be considered as a means to resolve NO$_x$ emanating in the environment from PF combustion and transport fuels. Indeed, preliminary discussions with the dfT will be held for investigating the feasibility of the technique for apportioning environmental NO$_x$ emissions from transport and power generation.

Conceivably, establishing fuel NO$_x$ values for individual coals could be achieved in a drop-tube reactor to combust chars under an inert gas/oxygen atmosphere. If this approach were to be adopted, the effect of variables, such as temperature would need to be ascertained. Further, as mentioned earlier, overall nitrogen isotopic balances for devolatilisation and burn-out would be beneficial for improved modelling through the isotopic shifts reflecting the relative rates of the elementary series of reactions leading to each N-containing species. Future research along these lines would provide the basis for determining quantitatively determining the proportions of fuel and thermal/prompt NO$_x$ for PF combustion to build on the achievements of this research in:
- (i)   determining a protocol for collecting and determining the stable isotope ratios of NO$_x$ from flue gas;
- (ii)   demonstrating that large differences exist between actual PF and thermal NO$_x$ samples and;
- (iii)   ascertaining that the significant variations in δ^{15}N values found for the fuel NO$_x$ samples analysed arise in part from differences in the rate of devolatilisation and subsequent char burn out and the extent of conversion of char-N to NO, as well as varying proportions of fuel and thermal/prompt NO$_x$ being formed.

2. Overall Planning and Objectives Summary

In terms of the planning chart, the work completed in the past 24 months has addressed fully all the activities listed in the initial proposal. The development of suitable sorbents was completed by the end of the first year (activity a in proposal) and the adsorbents were improved further during the second year. The second activity involved collecting the thermal and actual coal NO$_x$ samples for isotopic analysis. Having determined the isotopic values of fuel and thermal NO and also having analysed a range of chars, all the experimental work

was completed for activities b and c in the initial proposal and to achieve the second milestone. Indeed, some work has also been completed on activity d to determine the nitrogen stable isotope values of actual PF NO samples ahead of schedule. During the final quarter of the project to complete activity d, further PF NO samples were collected using known combustion conditions from the 1 MW test facility to investigate the variance in the samples analysed thus far. Due to the success of the earlier sampling campaign, this facility was preferred to the NRTF at Mitsui Babcock. The potential use of information on the proportions of fuel and thermal/prompt NO_x to improve combustion modelling was assessed to complete activity e (by Mitsui Babcock, in conjunction with the University of Nottingham).

There were no changes from the overall plan in relation to the planned milestone achievements (Table 6).

3. Expenditure

The total expenditure has been £220k and has been completely broadly in line with the estimates for each activity in the initial proposal.

4. Exploitation/Publication of Results

The findings thus far on the development of the adsorbents and the determination of the nitrogen stable isotope ratios of fuels and thermal NO_x was presented at the 4th UK Coal Science Conference (September, 2002) and have also been presented at the forthcoming Spring American Chemical Society meeting, Div. of Fuel Chemistry Symposium on "Advances in Techniques for Analytical Characterisation in Fuel Chemistry" in New Orleans (March 2003, ref. 9). An abstract has been accepted for the 2003 International Conference on Coal Science (Cairns, November 2003). These communications are forming the basis for publications in refereed journals, namely Energy & Fuels and Carbon.

Table 6 Planned milestone achievements

Milestone No.	Completion Date predicted as per milestone schedule in Offer Letter	Date for issue of milestone deliverable	Current planned date for submission of payment claim
1. Sorbent development.	9 months, Nov. 2001	8 months, Oct. 2001	March 2002 (submitted)
2. Determination of isotopic values for fuel and thermally derived NO_x samples. In addition, determination of isotopic values for chars from the devolatilisation experiments.	15 months, May 2002	18 months, August 2002 (but, including some information for milestone 3)	November 2002 (submitted)
3. Samples with different proportions of fuel and thermally derived NO_x will have been analysed. The potential of the new information for improving combustion models will have been assessed. Plans for further research will have been made.	24 months, February 2003	24 months, February 2003	April 2003 (submitted July 2003)

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APPENDIX 1

Background nitrogen levels in EA-IRMS for the Europa 20:20 instrument

A1.1 Introduction Nitrogen stable isotopic data have been collected mainly using Europa 20-20 and Tracermat systems. At least three potential sources of background signal can be envisaged: firstly the background with no sample being delivered from the carousel and the system clean. Secondly, the blank signal, which in addition to clean system blank, might build up during a run because of ash from previous samples and could be transient or more continuous in nature (arsing from the combustion catalyst). Finally, the organic nitrogen background that arises from the sorbent itself obviously needs to be ascertained. This appendix considers errors for the Europa 20:20 syatem and those for the Tracermat system are considered in Appendix 2, together with the isotopic data obtained using the N-free Fe/Mn AC.

Considering the clean system blank, in a normal run a sample size is used that will deliver an ion beam intensity at m/z 28 (i.e. $^{14}N_2^+$) of between 1 and 2 x 10^{-7}A. A series of 8 blank m/z 28 measurements were conducted at the same time that the Powergen (PG) samples were analysed with a mean intensity of 1.4 ± 0.9 x 10^{-10} A. Although the isotopic composition of this blank cannot be reliably measured because of the low intensity of the m/z 29 ($^{15}N^{14}N^+$) beam, it is immediately obvious that the contribution from the clean system is negligible (*ca*. 0.1%). Measurements to date have provided no evidence for the background intensity building up during the analysis of a batch of samples.

The background corrections for the MnO_y-ZrO_2 sorbents and combustion catalyst used are considered in the following sections. In general, the commercial carbons investigated gave absolute nitrogen contents of *ca*. 0.1%.

A1.2 Background levels for MnO_y-ZrO_2 sorbents To probe the background (blank) nitrogen levels and the corrections required to measured isotopic data for the sorbents (using typically 20 mg), 4 regenerated MnO_y-ZrO_2 samples designated 1, 3, 5 and 6 were used (Table A1.1). The blank nitrogen levels (0.06 to 0.07 %N) should allow fairly reliable measurement of its isotopic composition. The total ion beam intensities were typically 10^{-8} A. It is clear that usable blank data have been obtained, but the variation (especially in isotopic composition) is intriguing. Therefore, a new experiment was devised in which the sample weight was varied in a sequential manner, with a high enough sample weight used to give the prospect of reliable isotope ratio measurements. Regenerated Sample MnO_y-ZrO_2 1 was used (as having the highest scatter in isotope data, Table A1.1) and the results are presented in Table A1.2.

Table A1.1 Isotopic ratios and nitrogen contents for regenerated MnO_y-ZrO_2 sorbents

Sample	n	% N	$\delta^{15}N$ ‰
Regenerated MnO_y-ZrO_2 1	4	0.065±0.006	21.1±3.8
Regenerated MnO_y-ZrO_2 3	4	0.065±0.006	19.7±2.8
Regenerated MnO_y-ZrO_2 5	4	0.068±0.005	20.4±1.8
Regenerated MnO_y-ZrO_2 6	4	0.065±0.006	23.8±2.3

Table A1.2 Effect of varying sample weight for one of the regenerated MnO_y-ZrO_2 sorbents (no. 1)

Weight, mg	Total beam, 10^{-9}A	% N	$\delta^{15}N$ ‰
15.7	8.63	0.07	22.10
19.6	9.43	0.06	18.16
26.6	11.7	0.06	15.40
24.8	12.0	0.06	17.57
20.7	9.82	0.06	21.11
15.7	8.14	0.06	23.89

This is an excellent linear correlation between sample weight and ion beam intensity where:

Beam intensity (10^{-9} A) = 0.34 Weight (mg) +3.0.
R = 0.9732 (>99% for n=6).

It is likely that the linear relationship will not, in reality, extrapolate to low sample weights; that is of no strong concern here. The four analyses of sample 1 from the first experiment (Table A1.1) plot close to the relationship calculated above, and the six (in total) measurements on sample sizes of close to 20 mg give an indication of the scatter to be expected: n=6, mean sample weight 20.1±0.4 mg, mean beam intensity (9.9±0.5) x 10^{-9} A, and a coefficient of variation of 5.5%. Note that the significant intercept on the extrapolated line can account for high and systematically variable % N values for low sample weights, whereas the data are relatively constant for large samples, as can be seen.

The isotope ratios vary widely; a range of close to 10 ‰ from 15.4 to 23.9 ‰ is observed. However, the variation is systematic with larger samples having lower isotope ratio values. Let the hypothesis that there are two components to the blank, each with a constant isotopic composition be examined. Then by mass and isotope balance:

$$M_T = M_1 + M_2 \qquad M = \text{mass} = \text{beam intensity} \qquad T = \text{total measured.}$$

$$M_T\, \delta_T = M_1\delta_1 + M_2\delta_2 \text{ where } \delta \text{ is the respective isotopic ration}$$
$$= M_1\delta_1 + (M_T - M_1)\, \delta_2$$
$$\text{and } \delta_T = \frac{M_1}{M_T}(\delta_1 - \delta_2) + \delta_2$$

In a system in which M_1 is constant (but M_T varies) the above equation predicts a linear relationship between the measured isotopic composition (δ_T) and the inverse of the ion beam intensity ($1/M_T$); the intercept of the line is δ_2, the isotopic composition of the variable contribution blank and the slope is the constant $M_1(\delta_1-\delta_2)$. For the data in Table 2, regression gives:

$$\delta^{15}N = 178\ (1/\text{Beam}) +1.4$$

with the units of 1/Beam being 10^9 A^{-1}. The correlation coefficient is r=0.889 which for n=6 is significantly above the 95% confidence level. The two component model described here thus fits the data reasonably well, although the physical nature (i.e. identity) of the two blank components remains elusive; the isotopic composition of the component which is strongly related to sample weight is close to 0‰, whereas the constant component has a high isotope ratio. Furthermore, the analysis lends confidence to estimating the contribution and isotopic composition of the blank for typical 10 mg samples of MnO_y-ZrO_2 as close to 6 x10^{-9} A with $\delta^{15}N$ of about +30‰. For 15 mg samples, the corresponding figures are 8 x10^{-9} A and 24 ‰. For 20 mg samples where the measured N content is 0.06%, this includes $ca.$ 0.04% from the sample and 0.02% from the constant background component (Tables A1.1 and A1.2).

A1.3 Contribution from combustion catalyst In the blank experiments, it has consistently been observed that plots of sample weight (mg) versus total beam give linear relationships with a common intercept of around 3 nanoamps, whereas the system blank is typically only one tenth of this. The origin of this residual 3nA signal has remained enigmatic. The system blank was determined by dropping an empty tin capsule into the reaction chamber of the autoanalyser. During analysis of samples and absorbent blanks, the material is accompanied by approximately 20 mg of vanadium pentoxide as an oxidant. The question then arises as to whether this chemical could be the source of, or induce, a processing blank over and above the system blank represented by the tin capsule plus autoanalyser plus mass spectrometer. To test this, we carried out the following experiments.

Firstly, the system blank with and without tin capsules was monitored. Total beams of 0.2 to 0.3 nA were

recorded, as usual (Table A1.3, zero sample weight). Secondly, the total beam was measured when the tin capsule contained varying amounts of vanadium pentoxide. This showed (see data for group 1 in Table 3) that there is a linear relationship between total beam and the weight of vanadium pentoxide with an intercept at the system blank of 0.2 nA:

$$\text{Total beam (nA)} = 0.139 \text{ Weight (mg)} + 0.20$$

TableA1. 3 Measurement of blanks for system plus vanadium pentoxide

Weight, mg	Total Beam, 10^{-10}A	Apparent d^{15}N ‰	Comment
0	1.66	-52.1	With tin
0	2.64	38.5	
0	2.17	-279.9	
0	2.34	89.4	
0	2.03	117.5	
			Mean 2.17 x 10^{-10}
Group 1			
40	7.39	33.8	
5.5	9.73	3.04	
11.0	17.7	8.39	
7.4	12.2	62.0	
6.3	10.6	49.0	
5.0	9.43	15.3	
1.0	3.25	13.7	
3.9	7.46	-65.2	
2.1	4.83	33.9	
1.8	4.55	149.2	
12.7	19.7	1.5	
15.9	24.2	22.0	
20.7	31.1	29.4	
18.4	26.6	31.1	
17.0	25.7	22.7	
0	2.44	-202.6	No tin
0	2.29	104.5	
0	2.40	81.6	
0	2.38	-84.9	
0	2.33	-55.2	
			Mean 2.37 x 10^{-10}
0	1.90	-180.3	With tin
0	1.85	-43.1	
0	1.69	-179.8	
0	1.90	-74.2	
			Mean 1.84 x 10^{-10}

Note that for 20 mg, the predicted total beam is 3 nA.

To investigate whether this process blank was due to nitrogen-bearing species (or indeed other volatiles contributing to m/z 28 after reaction in the elemental analyser), an aliquot of vanadium pentoxide was degassed in vacuo at 200°C overnight, and repeated the experiment. The results were entirely consistent with those of the previous experiment:

$$\text{Total beam (nA)} = 0.134 \text{ Weight (mg)} + 0.20 \text{ indicating a very high degree of reproducibility.}$$

To investigate the possibility that the process blank at m/z 28 generated by adding vanadium pentoxide is specific to the Elemental Microanalysis-originated batch of reagent that has been used in all NO_x experiments, an unopened bottle was procured from an alternative supplier and repeated the first experiment. This material has a considerably higher process blank. It is concluded that the origin of the 3 nA intercept in the absorbent blank total beam versus weight experiments was the 20 mg or so of vanadium pentoxide routinely used and that modest degassing prior to use does not reduce the problem. The isotope data is not discussed because of unreliability related due to low beam intensities. Clearly, as the NO_x uptake achieved increases, the importance of the combustion catalyst contribution diminishes.

Table A2.1 Details of NO_x samples collected on 1 MW test facility and fluidised-bed combustor

Sample no.	Bed dimensions –cm /duration of sampling (min)	Flue gas composition	Estimate of % N for sorbent
Thermal NOx sampling			
5	7.5 × 0.45 /62	*NO, 99-121 ppm*; CO_2, 13.5%; SO_2, 100 ppm; CO, 25 ppm; O_2, 1-2%; Flow rate: 200~250 ml/min	0.096 ~ 0.12
6	10.0 × 0.45 /47	*NO, 99-121 ppm*; CO_2, 13.5%; SO_2, 100 ppm; CO, 25 ppm; O_2, 1-2%; Flow rate: 200-250 ml/min	0.058~0.07
10	11 × 0.45 /120	*NO.110-120 ppm*; CO_2, 9.5%; SO_2, 50 ppm; CO, 10 ppm; O_2, 8.0%; Flow rate: 250 ml/min	0.17 ~ 0.19
11	10 × 0.45 /120	*NO 110-120 ppm*; CO_2, 9.5%; SO_2, 50 ppm; CO, 10 ppm; O_2, 8.0%; Flow rate: 250 ml/min	0.19~0.21
17	10 × 0.40 /148	*NO, 110-120ppm*; CO_2, 9.5%; SO_2, 100-130 ppm; CO, 10 ppm; O_2, 7.9%; Flow rate: 200 ml/min	0.24 ~ 0.26
18	10 × 0.4 /148	*NO ,110-120 ppm*; CO_2, 9.5%; SO_2, 100-130 ppm; CO, 10 ppm; O_2, 7.9%; Flow rate: 200 ml/min	0.19~0.21
19 (ZrO₂ based ads.)	10 x 0.6 /56 *(breakthrough)*	*NO ,140-150 ppm*; CO_2, 9.5%; SO_2, 100-130 ppm; CO, 10 ppm; O_2, 7.9%; Flow rate: 200 ml/min	0.098~0.11
Coal NOx sampling			
7	15 × 0.55 /120	*NO, 320-460 ppm*; CO_2, 15 %; SO_2, 470~550 ppm; CO, 25 ppm; O_2, 1-4%; Flow rate: 200-250 ml/min	0.24~0.34
8 (ZrO₂ based ads.)	10 × 0.55 /70 *(breakthrough)*	*NO, 320-460 ppm*; CO_2, 15 %; SO_2, 470~550 ppm; CO, 25 ppm; O_2, 1-4%; Flow rate: 200-250 ml/min	0.14~0.20
No. 9	15 × 0.55 /117	*NO, 270-290 ppm*; CO_2, 15 %; SO_2, 470~550 ppm; CO, 25 ppm; O_2, 1-2%; Flow rate: 200-250 ml/min	0.25~0.33
No.13 (ZrO₂ based ads.)	7 × 0.55 /181	NO, 170-220 ppm; CO_2, 15 %; SO_2, 350-400 ppm; CO, 10 ppm; O_2, 1-4%; Flow rate: 150-200 ml/min	0.17~0.25
No. 14	10 × 0.55 /65 *(breakthrough)*	NO, 170-220 ppm; CO_2, 15 %; SO_2, 350-400 ppm; CO, 10 ppm; O_2, 1-4%; Flow rate: 250 ml/min	0.09~0.12
No. 15	15 × 0.45 /245	*NO, 170-260 ppm*; CO_2, 17 %; SO_2, 350-400 ppm; CO, 10 ppm; O_2, 1-4%; Flow rate: 250-350 ml/min	0.43 ~0.65
No. 16	10×0.4 /205	*NO, 170-260 ppm*; CO_2, 17 %; SO_2, 350-400 ppm; CO, 10 ppm; O_2, 1-4%; Flow rate: 180-220 ml/min	0.58 ~0.80
No.20	10 × 0.5 /65	*NO, 500-650 ppm*; CO_2, 15 %; SO_2, 500-700 ppm; CO, 15 ppm; O_2, 2-4%; Flow rate: ~200 ml/min	0.27~0.35
No.21	10 × 0.5 /65. *(breakthrough)*	*NO, 500-650 ppm*; CO_2, 15 %; SO_2, 500-700 ppm; CO, 15 ppm; O_2, 2-4%; Flow rate: ~200 ml/min	0.23~0.29

*Notes: 1. If not stated, the adsorbent used for sampling is Ce-Fe dispersed AC adsorbent.

2. An extra 10−13% v/v of O_2 was introduced into flue gas, making the final O_2 concentration in the flue gas to 11−17% v/v.

3. The duration time quoted may not necessarily be the breakthrough time if not indicated.

4. The flue gas compositions quoted are typical for each sampling run, but the CO concentration can vary irregularly

reaching up to 2000 ppm where performance of the adsorbents was affected adversely.

Table A2.2 Thermal NO measurements using Fe/C sorbents

SAMPLE NO.	WEIGHT mg	ION BEAM 10^{-7}A		N CONC % w/w	Measured δ^{15}N ‰Air
PG5	49.1	1.82	0.20	2.08	
	30.8	2.13	0.38	1.28	Uncorrected mean δ^{15}N 1.7 ± 0.6
PG6	55.5	1.88	0.18	0.24	
	28.0	1.51	0.29	0.27	Uncorrected mean δ^{15}N 0.26 ± 0.2
PG10	24.2	1.97	0.47	-1.64	
	10.0	1.19	0.63	-0.99	
	13.1	1.60	0.66	-0.05	Uncorrected mean δ^{15}N –0.9 ± 0.8
PG11	39.6	2.10	0.31	-2.35	
	20.9	1.67	0.44	-1.60	Uncorrected mean δ^{15}N –2.0 ± 0.5
PG18	23.2	1.71	0.41	1.87	
	10.2	0.95	0.51	1.11	Uncorrected mean δ^{15}N 1.5 ± 0.5

Table A2.3 Fuel NO measurements

Sample No./Type	Uncorrected means δ^{15}N ‰ Air	Corrected means δ^{15}N for Fe/C, ‰ Air
Sample 1 (ZrO$_2$)	14.0 ± 1.0 (n=3)	
Sample 2 (Fe/C)	0.5 ± 0.5 (n=4)	-0.7)
Sample 3 (ZrO$_2$)	0.7 ± 0.7 (n=3)	) –0.65 ± 0.7
Sample 4 (Fe/C)	1.1 ± 0.5 (n=4)	-0.4)
Sample 5 (ZrO$_2$)	6.2 ± 0.4 (n=4)	
Sample 6 (ZrO$_2$)	7.1 ± 1.3 (n=4)	

Sample 1 was collected in parallel to sample 2 and, similarly, sample 4 with sample 5. The MnO$_y$-ZrO$_2$ adsorbents caused problems previously in the Tracermat system, but less severe problems were encountered in the Europa system with deposits.

Table A2.4 PF (coal) NO measurements using Fe/C sorbents

SAMPLE	WEIGHT mg	ION BEAM 10^{-7}A		N CONC % w/w	δ^{15}N ‰AIR
PG7	18.1	1.38	0.42	6.83	
	13.2	1.51	0.62	6.69	
				Uncorrected mean δ^{15}N 6.8 ± 0.1	
PG15	16.7	1.86	0.62	10.57	
	7.9	1.55	1.07	8.29	
	8.1	1.40	0.92	9.07	
	7.7	1.48	1.03	9.86	
				Uncorrected mean δ^{15}N 9.4 ± 0.9	
PG20	29.4	2.27	0.43	4.70	
	11.3	1.48	0.71	4.28	
				Uncorrected mean δ^{15}N 4.5 ± 0.2	
PG21	9.3	1.22	0.72	7.51	
	14.9	1.44	0.52	6.22	
	10.2	1.19	0.63	6.89	
				Uncorrected mean δ^{15}N 6.9 ± 0.6	

APPENDIX 3

Details on nitrogen stable isotope measurements obtained using the N-free Fe/Mn-AC

First sample set Duplicate samples and the blank sorbent analysed using the Europa EA-IRMS with 4 determinations being carried out for each of the NO_x samples can be found in Appendix 3. System blanks were measured before and after each set of replicates for the five samples. Eight measurements were attempted on the sorbent blank but the second high weight sample did not drop out of the carousel (identifying a common problem with sample weights in excess of 20 mg) giving 7 analyses in total. The results are presented in Table A3.1. The total beam intensity for these analyses did not vary systematically with sample weight but averaged $(3.1 \pm 0.4)\ 10^{-9}$ A; this compares to an average system blank of $(1.9 \pm 1.0)\ 10^{-10}$ A over the course of the entire experiment. The system blank is thus only 6% of the sorbent blank.

For four replicates of sample 13-08-02/1A – thermal, the mean %N was (0.125 ± 0.006) and the mean $d^{15}N$ was -6.2 ± 1.3‰ (Table 4). The average total beam was of $1.96 \pm 0.004\ 10^{-8}$A means that the sorbent blank represents 16% of the sample total beam. No correction was made here. For the four replicates of 13-08-02/1B thermal, the mean %N was 0.09 ± 0.00 and the total beam of $1.44 \pm 0.04\ 10^{-8}$A meant that the sorbent blank represents 21.5% with a mean $d^{15}N = -6.1 \pm 0.5$ ‰. The two mean values for thermal samples 1A and 1B are indistinguishable, supporting the decision not to correct for the blank. Note also that a value of 3×10^{-9} A is the common intercept of the other sorbent blank experiments where total beam was plotted against weight. This indicates that the N content of the sorbent is insignificant (considerably below 0.01 %). For the 8 replicates of the thermal NO_x samples, the mean $d^{15}N$ was -6.2 ± 0.9 ‰.

For four replicates of sample 13-08-02/2A-PF, the mean %N was $0.23\ (\pm 0.00)$ and mean $d^{15}N$ was 14.5 ± 0.5 ‰ (Table 4). The mean total beam intensity was $3.78 \pm 0.18\ 10^{-8}$ A so the sorbent blank represents 8 %. For 13-08-02/2B--PF, the mean %N was (0.19 ± 0.01) with $d^{15}N$ of 15.1 ± 2.1‰. The mean total beam intensity was $3.14 \pm 0.1\ 10^{-8}$ A so the sorbent blank represents 10%. Again, no correction has been made here and again the means for PF samples 2A and 2B are isotopically indistinguishable, with the overall average from the eight measurements being 14.8 ± 1.5 ‰.

Second sample set Details of the set of samples collected in which Thoresby coal was burned with and without over fired air are presented in Table A3.2. Due to the approximate time of one hour required to collect sufficient NO with the flow rate and concentrations in the flue gas, it was only possible to collect combined samples with and without over fired air for all the excess oxygen levels used, since these were switched every 15 minutes. Samples were collected in duplicate (designated A and B) by splitting the gas stream as for the first set of samples. As well as Thoresby coal, samples were also collected for an 80:20 blend of Thoresby coal and petroleum coke.

The measurements were carried out on the Tracermat IRMS. Thirty measurements were made of the instrument blank at m/z 28, reported as total peak area (volt seconds VS). The mean value was 0.29 ± 0.49 (1s) and it is apparent that values are generally relatively low (± 0.4) with occasional (about 17%) exceptional values up to 2.05. To assess the blank contribution from the oxidising reagent V_2O_5, known from previous work to be problematic with the EUROPA 20/20 mass spectrometer, the m/z 28 peak area and $d^{15}N$ were measured for a series of reagent blanks (tin capsule plus V_2O_5) at V_2O_5 weights ranging from 3.5 mg to 16.9 mg (typical weights of V_2O_5 are between 5 and 10 mg). The data are presented in Table A3.3.

There is no strong correlation between m/z 28 Peak area and weight of V_2O_5 (r = 0.3620 for n = 10) suggesting that the procedure adopted for this phase of analysis will not require differential blank correction depending on weight of reagent V_2O_5. With one exception out of the ten analyses, the mean $d^{15}N$ is rather constant at 15.7 ± 1.5‰ (1s, n = 9) and is not correlated with the 28 Peak Area (r = -0.1954, n = 9). Since typical peak area signals for the actual samples are between 7 and 33, and since at least duplicate measurements have been made in all cases whereby sporadic high (i.e. around a Peak Area of 2VS as opposed to around 1VS or below) blank contributions would likely be identified, in the analysis of the new data

no blank corrections will be applied.

Table A3.1 Nitrogen stable isotopic data for the first set of thermal/prompt and actual PF NO$_x$ samples collected with the nitrogen-free Fe/AC adsorbent from the 1 MW test facility burning Daw Mill coal

Sample	Weight mg	Total Beam A	% N	d^{15}N ‰ air	Blank before	Blank after
1. sorbent blank	10.8	3.87 10^{-9}	0.02	37.1	1.50 10^{-10}	
2. sorbent blank	16.0	3.13 10^{-9}	0.01	-0.7		
3. sorbent blank	20.9	2.73 10^{-9}	0.01	-4.1		
4. sorbent blank	24.9	3.16 10^{-9}	0.01	-12.0		
5. sorbent blank	20.4	3.18 10^{-9}	0.01	13.2		
6. sorbent blank	15.7	2.98 10^{-9}	0.01	28.0		
7. sorbent blank	10.4	2.68 10^{-9}	0.02	7.1		2.20 10^{-10}
1. 13-08-02/1A Thermal	20.7	1.95 10^{-8}	0.12	-4.7	4.62 10^{-10}	
2. 13-08-02/1A Thermal	19.5	1.94 10^{-8}	0.13	-5.6		
3. 13-08-02/1A Thermal	19.5	1.93 10^{-8}	0.13	-7.5		
4. 13-08-02/1A Thermal	20.9	2.02 10^{-8}	0.12	-7.0		1.80 10^{-10}
1. 13-08-02/1B Thermal	19.6	1.42 10^{-8}	0.09	-6.7	1.80 10^{-10}	
2. 13-08-02/1B Thermal	20.1	1.49 10^{-8}	0.09	-5.6		
3. 13-08-02/1B Thermal	21.1	1.43 10^{-8}	0.09	-6.1		
4. 13-08-02/1B Thermal	19.3	1.41 10^{-8}	0.09	-6.1		1.80 10^{-10}
1. 13-08-02/2A PF	19.1	3.52 10^{-8}	0.23	15.1	1.80 10^{-10}	
2. 13-08-02/2A PF	21.2	3.90 10^{-8}	0.23	14.5		
3. 13-08-02/2A PF	20.8	3.89 10^{-8}	0.24	13.8		
4. 13-08-02/2A PF	20.5	3.82 10^{-8}	0.23	14.4		1.20 10^{-10}
1. 13-08-02/2B PF	20.8	3.41 10^{-8}	0.21	18.1	1.20 10^{-10}	
2. 13-08-02/2B PF	19.9	3.06 10^{-8}	0.19	14.4		
3. 13-08-02/2B PF	20.0	3.06 10^{-8}	0.19	14.8		
4. 13-08-02/2B PF	20.5	3.04 10^{-8}	0.19	13.2		1.04 10^{-10}

Table A3.2 Details of second set of thermal/prompt and actual PF NO$_x$ samples collected with the nitrogen-free Fe/AC adsorbent from the 1 MW test facility burning Thoresby coal (07-01-03 and 09-01-03)

No. Sample	Type of NO	Conditions	Estimated N% w/w
T070103/1A	Thermal	Wt. Sorbent: 1.25 g Flow: 300 ml/min; NO: 120 ~ 140 ppm O$_2$: 5~7% v/v CO$_2$: 13.3% v/v, CO: 240 ppm SO$_2$: 20 ppm	0.18
T070103/1B	Thermal	Wt. Sorbent: 1.25 g Flow: 300 ml/min NO: 120 ~ 140 ppm O$_2$: 5~7% v/v CO$_2$: 13.3% v/v, CO: 240 ppm SO$_2$: 20 ppm	0.18
F070103/1A	Fuel (Thoresby coal)	Wt. Sorbent: 1.3 g Flow: 220 ml/min NO: 350 ~ 480 ppm O$_2$: 2~3.7% v/v CO$_2$: 21-23% v/v, CO: 25 ppm SO$_2$: 2000-2600 ppm **(Over fired air mode Off)**	0.3~0.5
F070103/1B	Fuel (Thoresby coal)	Wt. Sorbent: 1.3 g Flow: 220 ml/min NO: 350 ~ 480 ppm O$_2$: 2~3.7% v/v CO$_2$: 21-23% v/v, CO: 25 ppm SO$_2$: 200-2600 ppm **(Over fired air mode Off)**	0.3~0.5
F070103/2A	Fuel (Thoresby coal)	Wt. Sorbent: 1.3 g Flow: 260 ml/min NO: 240-440 (typical 330) ppm O$_2$: 1~4% v/v CO$_2$: 21-23% v/v CO: ~ 20ppm, SO$_2$: 1700 ~ 2200 ppm **(Over fired air mode ON)**	0.3 ~ 0.5
F070103/2B	Fuel (Thoresby coal)	Wt. Sorbent: 1.3 g Flow: 260 ml/min NO: 240-440 (typical 330) ppm O$_2$: 1~4% v/v CO$_2$: 21-23% v/v CO: ~ 20ppm, SO$_2$: 1700 ~ 2200 ppm **(Over fired air mode ON)**	0.3~0.5
F070103/3A	Fuel (Thoresby coal)	Wt. Sorbent: 1.3 g Flow: 260 ml/min NO: 270-310 (typical 290) ppm O$_2$: 1~4% v/v CO$_2$: 21-23% v/v CO: ~ 17ppm, SO$_2$: 1700 ~ 2000 ppm **(Over fired air mode ON)**	0.3 ~0.4
F070103/3B	Fuel (Thoresby coal)	Wt. Sorbent: 1.3 g Flow: 260 ml/min NO: 270-310 (typical 290) ppm O$_2$: 1~4% v/v CO$_2$: 21-23% v/v CO: ~ 17ppm, SO$_2$: 1700 ~ 2000 ppm **(Over fired air mode ON)**	0.3~0.4
F070103/4	Fuel (Thoresby coal)	Wt. Sorbent: 2.7 g Flow: 500 ml/min NO: 210-310 ppm, O$_2$: 1~4% v/v CO$_2$: 21-23% v/v ppm **(Over fired air mode ON)**	0.09 ~ 0.14
T090103/1A	Thermal	Wt. Sorbent: 1.15 g Flow: 300 ml/min; NO: 120 ~ 150 ppm O$_2$: 5~7% v/v CO$_2$: 10% v/v, CO: 17 ppm SO$_2$: 130 ppm	0.14 ~0.18
T090103/1B	Thermal	Wt. Sorbent: 1.15 g Flow: 300 ml/min; NO: 120 ~ 150 ppm O$_2$: 5~7% v/v CO$_2$: 10% v/v, CO: 17 ppm SO$_2$: 130ppm	0.14~0.18
T090103/2A	Thermal	Wt. Sorbent: 1.2 g Flow: 280 ml/min; NO: 140 ~ 150 ppm O$_2$: 5~7% v/v CO$_2$: 10% v/v, CO: 17 ppm SO$_2$: 130 ppm	~ 0.11
T090103/2B	Thermal	Wt. Sorbent: 1.2 g Flow: 280 ml/min; NO: 140 ~ 150 ppm O$_2$: 5~7% v/v CO$_2$: 10% v/v, CO: 17 ppm SO$_2$: 130ppm	~ 0.11
F090103/A	Fuel (80% coal (Thoresby)/20% pet coke blend)	Wt. Sorbent: 1.8 g Flow: 200 ml/min; NO: 470 ~ 680 ppm O$_2$: 2~5% v/v CO$_2$: 21-23% v/v, CO: 21-30 ppm SO$_2$: ~2500ppm **(Over fired air mode ON)**	0.6 ~ 0.9
F090103/B	Fuel (80% coal (Thoresby)/20% pet coke blend)	Wt. Sorbent: 1.8 g Flow: 200 ml/min; NO: 470 ~ 680 ppm O$_2$: 2~5% v/v CO$_2$: 21-23% v/v, CO: 21-30 ppm SO$_2$: ~2500ppm **(Over fired air mode ON)**	0.6 ~ 0.9

*1. All flue gas compositions are quoted as the primary values before the introduction of 10% O_2
 2. The flue gas was washed in a KOH solution and dried with a mixture of solid KOH/silica before mixing and passing through the sorbent.
 3. The sorbent used was the Fe-Mn dispersed sugar-derived activated carbon material.

Table A3.3 Reagent blank measurements for V_2O_5 on the Tracermat mass spectrometer

Weight V_2O_5 (mg)	28 PEAK AREA (VS)	$d^{15}N$ (‰ Air)
3.5	0.76	15.4
5.0	1.96	15.2
6.1	1.21	13.2
6.7	1.28	17.5
8.0	0.60	18.1
8.8	1.30	16.5
11.8	0.91	14.1
14.1	2.67	15.1
16.0	1.98	16.0
16.9	1.10	28.0