

## OBJECTIVES

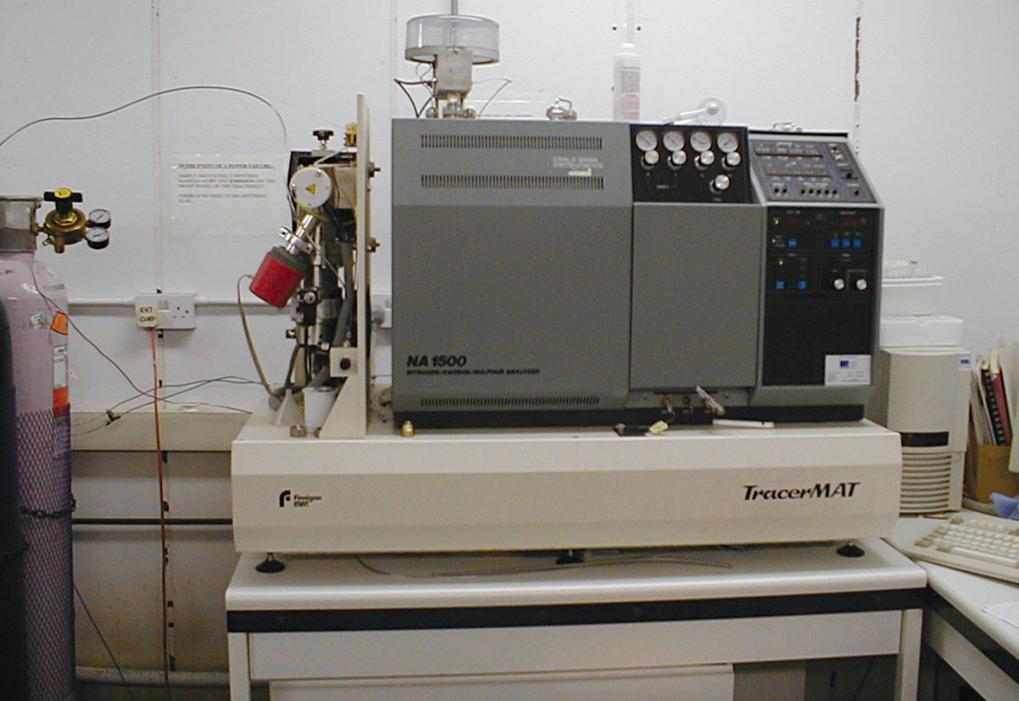
The main aim of the project was to develop a nitrogen-stable isotope measurement technique for NO<sub>x</sub> and to ascertain whether it can be used to determine the relative contributions of fuel and thermal NO<sub>x</sub> during coal combustion. The specific objectives were to:

- To design suitable substrates for adsorbing NO<sub>x</sub> in flue gases.
- To establish the isotopic values for fuel and thermally-derived NO<sub>x</sub> with samples from test rigs.
- To apply the experimental approach to larger facilities and to assess the data obtained for improving existing combustion models.

## SUMMARY

Suitable substrates for adsorbing sufficiently high concentrations of NO<sub>x</sub> 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<sub>y</sub>-ZrO<sub>2</sub>) and iron supported on active carbon (Fe/AC).

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<sub>x</sub> 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. The nitrogen stable isotope ratios ( $\delta^{15}\text{N}$ ) 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.



EA-IRMS system – determining nitrogen stable isotope ratios of  $\text{NO}_x$

The  $\delta^{15}\text{N}$  for fuel  $\text{NO}$  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  $\text{NO}$ , which is not the case for high temperature PF combustion where char is the major source for high volatile coals. Indeed, the first PF  $\text{NO}$  samples analysed displayed a relatively wide range of uncorrected  $\delta^{15}\text{N}$  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  $\text{NO}$ , together with variations in fuel  $\text{NO}$  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  $\text{NO}$  occurs in the formation of char with the possibility of further fractionation being associated with char combustion.

A nitrogen-free Fe/AC was then prepared with Mn as a promoter using an innovative procedure starting with sugar and was used to collect further thermal/prompt and actual PF  $\text{NO}_x$  samples from the 1 MW test facility. The isotopic data required no background corrections and indicated thermal/prompt  $\text{NO}_x$  collected during start-up burning diesel has a  $\delta^{15}\text{N}$  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)  $\text{NO}_x$  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  $\text{NO}_x$  were collected from the 1 MW test facility with and without over fired air. The  $\delta^{15}\text{N}$  values of these samples were in the range +5.5-7.5 ‰ and, if the reference points are taken as -6.5 ‰ and +15 ‰ for thermal/ prompt and fuel  $\text{NO}$ , respectively, this suggests that approximately 50% of the  $\text{NO}$  arises from prompt/thermal mechanisms. Indeed, this is consistent with the unstable smoky flame that was observed during the sampling period. Ways to incorporate the nitrogen stable isotope data into combustion models have been considered and plans have been made to develop the approach further.

## BACKGROUND

There is a continuing need to reduce  $\text{NO}_x$  emissions from pulverised coal-fired (PF) boilers. In PF combustion,  $\text{NO}_x$  is generated from both nitrogen in coal (fuel N) and from the nitrogen in air, the latter encompassing both thermal and prompt  $\text{NO}_x$  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<sub>x</sub> formation. It is considered that fuel N accounts for the majority of NO<sub>x</sub> from PF combustion but, to help guarantee combustor performance and aid combustion modelling through a better understanding of NO<sub>x</sub> formation pathways, means to quantify the contributions of fuel and thermal/prompt NO<sub>x</sub> are likely to prove valuable.

Atmospheric stable nitrogen isotope measurements on NO<sub>2</sub> (precipitated as nitrate) suggest that significant differences may exist between the <sup>15</sup>N to <sup>14</sup>N ratios for NO<sub>x</sub> derived from coal and that from transport fuel sources, 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.

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

Atmospheric nitrogen is the standard and  $\delta^{15}\text{N}$  values reported for NO<sub>2</sub> 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  $\delta^{15}\text{N}$  of the NO which, in terms of minimising sample size and maximising throughput is best achieved using an elemental analyser linked to an isotope ratio mass spectrometer (EA-IRMS).

## SORBENT DEVELOPMENT

Several gram batches of manganese/zirconia (MnO<sub>y</sub>-ZrO<sub>2</sub>)<sup>2</sup>, KOH treated  $\gamma$  alumina<sup>3</sup> and a number of active carbon-supported iron oxide sorbents<sup>4-6</sup> (Fe/AC, some with promoter metals such as cerium, Ce) were prepared. All these have been tested in a laboratory facility using a model gas mixture containing

650 ppm NO, 10% v/v CO<sub>2</sub> and 5% v/v O<sub>2</sub> and is generated by mixing the air with the special gas mixture purchased.

Table 1 and Figure 1 indicated that the NO sorption capacities at breakthrough are higher for the Fe/AC samples investigated than for the MnO<sub>y</sub>-ZrO<sub>2</sub>, this could arise from the considerably higher surface areas of the active carbon sorbents. However, the breakthrough capacity of 0.22 mmol g<sup>-1</sup> under the test conditions of for the MnO<sub>y</sub>-ZrO<sub>2</sub> 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<sub>y</sub>-ZrO<sub>2</sub>. The performance of the KOH treated  $\gamma$  alumina was not as good as those achieved for the MnO<sub>y</sub>-ZrO<sub>2</sub> and Fe/AC sorbents.

| Absorbents                              | Capacity at breakthrough, mmol/g |
|---|----------------------------------|
| Fe/AC                                   | 0.73                             |
| Ce-Fe/AC                                | 1.08                             |
| Ce-Fe/AC-Al <sub>2</sub> O <sub>3</sub> | 0.75                             |
| Fe-Mn/AC-ZrO <sub>2</sub>               | 0.73                             |
| Cu/AC                                   | 0.74                             |
| Ce-Cu/AC                                | 0.87                             |
| MnO <sub>y</sub> /ZrO <sub>2</sub>      | 0.22                             |

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

It was found that both for the MnO<sub>y</sub>-ZrO<sub>2</sub> and Fe/AC sorbents can be regenerated by calcination without any loss in the capacity achieved at the breakthrough point under the test conditions.

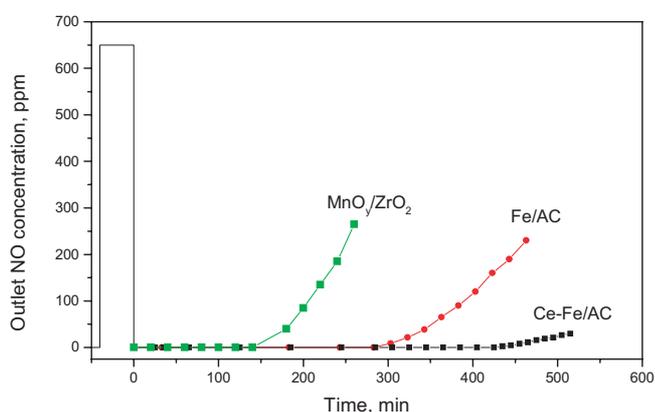


Figure 1. A comparison of the profiles for NO adsorption on MnO<sub>y</sub>/ZrO<sub>2</sub> and two of the activated carbon supported Fe sorbents. (Conditions: Internal diameter of tube reactor: 0.6 cm; bed length: 15 cm, flow rate: 200 ml/min; Inlet NO concentration: 650 ppm)

Given that the NO<sub>x</sub> uptake levels are inherently higher for Fe/AC than the MnO<sub>y</sub>-ZrO<sub>2</sub> sorbents and the latter still give a significant background contribution (although this can be corrected), it was decided to explore whether a low N content active carbon could be either purchased or synthesised in house. 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. This was first dehydrated in concentrated sulphuric acid to produce a char-like porous solid. This was then washed using excess distilled water, dried and then carbonised at 650°C to yield the sugar-based char, which was subsequently activated at 1000°C in a flow of CO<sub>2</sub>. For 100 g of sugar, about 15~20 g of activated carbon can be obtained from this procedure.

To achieve high NO<sub>x</sub> 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. Any use of nitrogen-containing chemicals should be avoided or at least minimised for NO<sub>x</sub> sorbents, so 'pre-treatment' in KMnO<sub>4</sub>/KOH solution was used instead to

achieve pre-oxidation of carbon material and the enhanced simultaneous dispersion of metal (Mn) oxides. 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<sub>2</sub>, are compared in Figure 2. The highest breakthrough capacity with the new Fe-Mn/AC catalyst had a Fe:Mn ratio of 1:1 which corresponds to a nitrogen uptake as NO of over 1.5% in the absence of SO<sub>2</sub>.

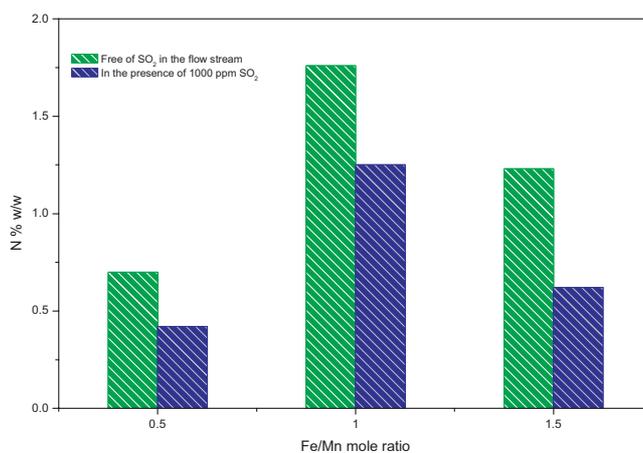


Figure 2. A comparison of nitrogen content achieved at NO breakthrough point for different Fe-Mn/AC sorbent with varying Fe-Mn ratios

## ISOTOPIC DATA FOR COALS AND CHARS

A number of coals from the UK and elsewhere were analysed. The δ<sup>15</sup>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 close to +2 ‰. Therefore, due to the similarity in δ<sup>15</sup>N values for the major internationally traded coals investigated, no major variations are expected in fuel NO<sub>x</sub> values due to the nitrogen in the coals used. The nitrogen stable isotope ratios of chars prepared in the drop-tube reactor are more positive (isotopically enriched) than those of the coals and range from +3 to +7 ‰. However, extent of the isotopic fractionation roughly decreases with increasing reactivity. For the two least reactive coals, the extent

of isotopic fractionation increases with burnout. Thus, it would appear that much of the isotopic fractionation that can occur between coal nitrogen and fuel NO emanates from the formation of char, although further fractionation could arise during char combustion.

## ISOTOPIC DATA FOR NO<sub>x</sub> SAMPLES

The overall average for all thermal/prompt NO<sub>x</sub> samples collected from the 1 MW test facility 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<sub>x</sub>. Taking a value of +2 ‰ for the diesel, this would make the mean for thermal/prompt NO<sub>x</sub> 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<sub>x</sub> samples collected can be taken as -6.5 to -8.5 ‰. This range of values compares to values of -14 ‰ reported 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  $\delta^{15}\text{N}$  values for more thermal/prompt combustion regimes.

The first set of PF NO samples analysed from the 1 MW facility displayed a wide range of values with an overall uncorrected mean of  $6.9 \pm 2.0$ . These variations probably 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 rates of devolatilisation and char reactivity occur. Despite the variation encountered and the uncertainty over applying reliable background corrections to these samples collected with the zirconia and N-containing carbon adsorbents, 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 indicated by the isotopic ratios for the chars.

The high value of +15 ‰ for the first sample collected with the N-free adsorbent from the 1 MW test facility 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 reported from an actual PF plant and (ii) samples collected with the early N-containing adsorbent, which if corrected would increase considerably to approximately + 4.5-10 ‰.

The isotopic values for the second set of NO<sub>x</sub> 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.

## CONCLUSIONS AND FUTURE WORK

This project has established a simple and robust experimental protocol for collecting and determining the stable isotope ratios of NO<sub>x</sub> from flue gas. The protocol is much more convenient and rapid than that used in the only other reported study where flue gas NO<sub>x</sub> has been sampled for determining isotopic ratios.

Knowledge of the proportions of fuel and thermal/prompt NO<sub>x</sub> formed during PF combustion would enable the relative rates of the sequence of reactions involved in NO<sub>x</sub> 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<sub>3</sub>, 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.

To continue developing the experimental approach, the main priorities are:

- To ascertain the  $\delta^{15}\text{N}$  values for more combustion regimes operating in thermal mode to help establish the most reliable values thermal/prompt NO<sub>x</sub> for PF combustion, as already described.
- To establish protocols for determining fuel NO<sub>x</sub> values for individual coals.

Once these have been achieved, the procedure can then be considered as a means to resolve NO<sub>x</sub> emanating in the environment from PF combustion and transport fuels.

## COST

The total cost of the project was £220,000 with the Department of Trade and Industry contributing £110,000 (50%). The balance of the project funding was provided by the participants.

## DURATION

2 years – March 2001 to February 2003

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