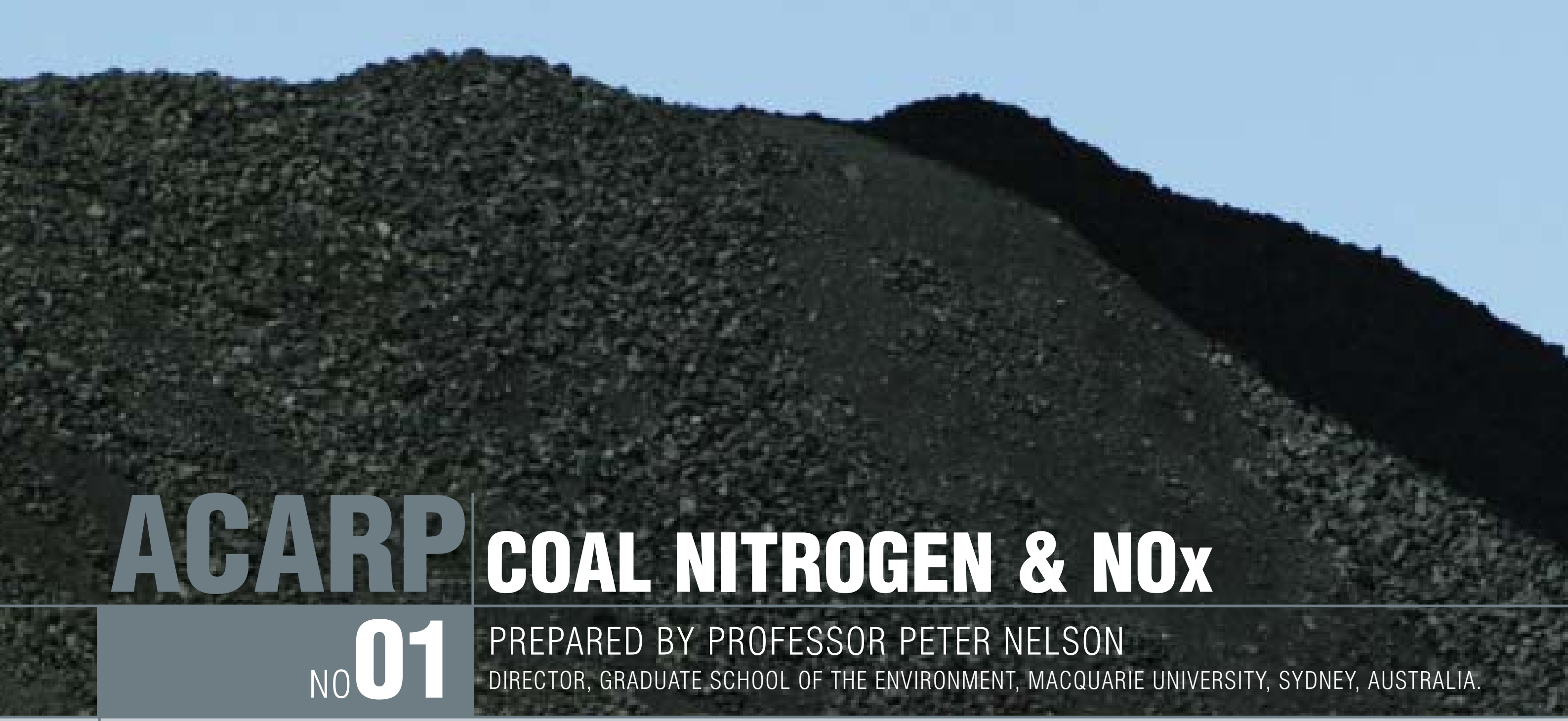

ACARP

COAL NITROGEN & NO_x

NO01

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OVERVIEW

Combustion of fossil fuels to produce power and for transportation is the major man-made source of NO_x and has resulted in large increases in NO_x emissions to the atmosphere since the mid nineteenth century. These emissions have significant environmental impacts on air quality, natural resource productivity, acidic deposition and biodiversity, global climate change and stratospheric ozone depletion. Coal combustion contributes to these emissions largely through conversion of N contained in the coal, but the extent of this conversion is a strong function of combustion conditions and plant design. **Coal N content alone is not a good indicator of potential NO_x formation.**

Under the conditions used in modern coal-fired plants to control NO_x, including air staging and low NO_x burners, lower emissions of NO_x are observed for coals which rapidly release coal N with the volatiles.

Careful control of the air/fuel ratio, and staging of the combustion air, results in conversion of most of this volatile N to N_2 rather than NO. Volatile matter (VM) content, or Fuel Ratio (FR = FC/VM), is likely to be a reasonable indicator of the volatile N release. **It follows that coals with high VM or low FR are likely to respond favourably to NO_x controls based on combustion modifications. A survey of Australian coals of fuel potential shows that most have FRs less than 2.5 and can be predicted to produce relatively low NO_x emissions in full scale plant.**

Emission limits on NO_x continue to be tightened worldwide. **An historical analysis of NO_x emission trends show major decreases from electricity production since the 1970s, much of it due to combustion modifications and flue gas treatment to reduce or remove NO_x.**

OXIDES OF NITROGEN (NO_x)

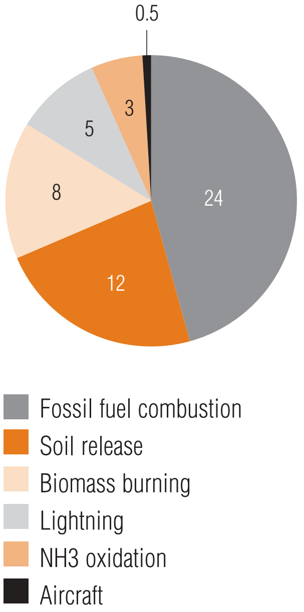

Figure 1: Global sources of NO_x Magnitude (Tg N per year)

SOURCES

There are at least ten different oxides of nitrogen, including NO, NO_2, NO_3, N_2O_4, N_2O_5 and the strong greenhouse gas N_2O. The commonly used shorthand form, NO_x is strictly equivalent to the sum of nitric oxide (NO) and nitrogen dioxide (NO_2).

Nitric oxide (NO) is formed in all combustion processes, in lightning strikes, and in denitrification processes in soils and plants. It follows that there are both natural and man-made sources of NO. It has been estimated that fossil fuel derived sources of N have increased from less than 1 Tg (1 Tg = 10^{12} g, or 10^6 tonnes) N per year in 1860 to approximately 25 Tg N per year in 2000 (Galloway *et al.* 2003). Figure 1 shows the magnitude of global sources of NOx and illustrates the dominance of combustion of fossil fuels as a source (Seinfeld and Pandis 1998).

FORMATION MECHANISMS AND ENVIRONMENTAL IMPACTS

The major reactive N species formed in combustion is NO. Smaller amounts of NO_2 are also formed, usually some 5-10% of the total NO_x.

The mechanism for formation of NO and NO_2 in combustion processes is complex; the complexity arises since NO can be produced by several pathways. These pathways are reasonably well understood, and for coal combustion the two most important are:

- **the thermal (or Zeldovich) route** in which atmospheric N_2 in the combustion air is converted to NO_x; and
- **the fuel NOx route** in which oxidation of nitrogen contained in the organic structures of the coal produces NO_x.

The relative contributions of thermal and fuel NO_x to total NOx varies with coal properties and combustion conditions. For many coals, fuel NO_x can contribute greater than 80% to the total emissions, but radiative properties of the ash can increase the thermal NO_x contribution for some coals. Nitrogen in coal is largely present in aromatic structures in the coal matrix (Nelson *et al.* 1992); these are converted to volatile N compounds such as HCN during the initial decomposition of the coal, or are combusted with the rest of the char (Ashman *et al.* 1998). **The relationship between coal nitrogen and NO_x formation is complex and no simple relationship with N content exists. Significant amounts of the coal nitrogen can be converted to N_2 in the combustion process, and the efficiency of this conversion is a complex function of boiler design parameters, combustion conditions and coal characteristics.**

An increase in emissions of reactive nitrogen and accumulation of the nitrogen in the environment contributes to many environmental problems (Galloway *et al.* 2003):

- production of tropospheric ozone and fine nitrate particles; exposure to these pollutants has been shown to have a range of health impacts;
- impacts on forest and grassland productivity when critical thresholds for N deposition are exceeded
- acidification and loss of biodiversity in lakes and streams in many parts of the world;
- eutrophication, hypoxia, loss of biodiversity and habitat destruction in coastal ecosystems;
- global climate change and stratospheric ozone depletion.

For this reason increasingly stringent controls have been developed for NO_x sources.

COAL PROPERTIES AND NO_x EMISSIONS

Coal N content is, in general, a poor guide to NO_x emissions from coals. In contrast to emissions of SO_2, where coal S content largely determines emissions, the amounts of NO_x formed from coal combustion depends on boiler design and operating conditions in addition to coal properties. A summary of these factors is given in Table 2.

Control of emissions of sulphur oxides is often achieved by the use of a coal of lower S content. In the case of N, however, there is much less justification for choosing coals on the basis of N content. Careful control of combustion conditions and boiler design can result in significant reductions in NO_x formation. These factors are more important in achieving lower emission standards than coal nitrogen content. There are, however, a number of factors which suggest that the search for a relationship between coal quality and emissions of NO_x will continue:

- in spite of the lack of a direct relationship, limitations in the allowable levels of coal nitrogen (usually less than 2.0 % N, dry ash free basis) have been imposed by pollution control agencies (in Japan, for example)
- there is considerable downward pressure on emission limits worldwide
- there are some recent results of large international research programs which show that even under staged combustion conditions (low overall NO_x emissions) there are demonstrable effects of coal quality on NO_x formation.

Our current understanding of NO_x formation from coal nitrogen during coal combustion is summarized by Glarborg *et al.* (2003). Extensive research at laboratory, pilot and full scale suggests that:

- Under staged combustion conditions, **NO_x formation can be related to the volatile matter content of the coal**[1] (see, for example, (Jones *et al.* 1995; Man *et al.* 1995; Kiga 1999)
- The nitrogen released in the volatiles can be effectively reduced to N_2 by control of the combustion stoichiometry (fuel lean conditions favour NO formation; fuel rich conditions favour N_2 formation)
- Rapid and extensive release of nitrogen with the volatiles is conducive to low NO_x formation (Sullivan and Whitehouse 2004)

Based on these observations, a coal characteristic likely to lead to lower NO_x emissions under staged combustion conditions is rapid release of coal N in the volatiles. **Hence, coals which exhibit higher volatile release will be favoured in terms of NO_x outcomes. Reject limits set on coal N contents alone can therefore be challenged on scientific grounds.**

Nitrogen release under high heating rate conditions is not routinely measured for the purpose of coal characterisation, but some measurements have been made (Baxter *et al.* 1996; Sullivan and Whitehouse 2004). A reasonable surrogate for this measurement is conventional volatile matter (VM), provided that:

- Volatile release at high heating rate and VM are related;
- N is released in a similar way to volatile matter

It remains to be determined what acceptable limits for coal volatile matter and N content are, given that there is a continuum in the potential NO_x emissions determined by the volatile N release and the N content.

In this context it is perhaps best to examine the Australian coal resource in light of typical reject limits for N content and fuel ratio (FC/VM)[2]. Figure 2 shows one possible means of addressing this issue. The coal data is drawn from NSW Joint Coal Board and Queensland Coal Board data (JCB and QCB 1987) for coals of fuel potential. Clearly the vast majority of Australian coals fall below the reject limits for N content and fuel ratio. **For those coals which fail the N content reject limit, but which still have acceptable fuel ratios, an argument could be made to use these in blends where the high VM content may have beneficial impacts on NO_x reduction.** *The purchasing policy of the biggest Japanese utility in relation to NOX removal, has been described by Ikuno (2002).*

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[1] In this case the volatile matter content would be most accurately represented by the high heating rate volatile release or the high heating rate nitrogen release, but conventional VM measurements do provide a guide to this

[2] Fuel Ratio (FR = FC/VM) is another indicator of volatile release, and is used in some locations as a coal reject limit; for example in Japan the typical Japanese Electric Power Company rejects coal with a FR > 2.5

COAL PROPERTIES AND NO_x EMISSIONS CONT.

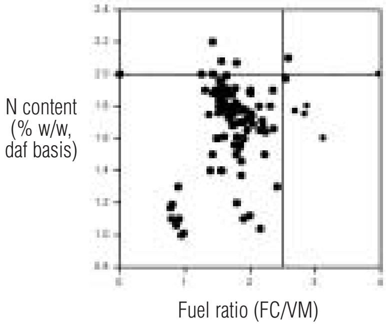

Figure 2: Relationship between fuel ratio (FC/VM) and N content for Australian coals of fuel potential, with typical reject limits for Japanese EPCs indicated (> 2.0% N; FR > 2.5)

As noted above NO_x formation in coal combustion is strongly influenced by furnace design and operating conditions. This dependence has been exploited by combustion engineers to develop burner and process designs which result in lower NO_x emissions. These include air staging, and low NO_x burners which are largely designed to effectively achieve staged air combustion. The success of these approaches in reducing NO_x relies on:

- rapid release of volatile nitrogen as HCN and NH_3 which burn under fuel rich conditions, encouraging formation of N_2, and hence minimising NO_x formation;
- char burn out on addition of second stage oxygen or over fire air (OFA).

An unfortunate consequence of air staging is that as NOx is reduced the amount of unburnt carbon in ash (UBC) often increases. Control then becomes a process of optimisation in which both NO_x and UBC have to be considered. Coal properties will also be important in determining the process of optimisation in so far as they determine coal reactivity and hence UBC.

Recent indications suggest that power station operators would like to extend the range of coals which can be burnt with acceptably low NO_x emissions and without increasing UBC unduly. Researchers at the Central Research Institute of the Electric Power Industry (CRIEPI) in Japan have, for example, studied the combustion characteristics of high-fuel ratio coals, extending to semi-anthracites with FR from 4.25 to 7.10 (Kurose *et al.* 2004). They find that both the conversion ratio of fuel nitrogen to NO_x and UBC formation increase with increasing fuel ratio.

Table 1: Some Factors affecting NOx emissions from pulverised coal-fired boilers (after Smouse et al (1994))

BOILER DESIGN FACTORS

- firing mode (front wall, opposed wall, tangential)
- capacity or maximum continuous rating (MCR, MWe or steam flow rate)
- burner type (pre-NSPS or low-NOx)
- number and capacity of burners
- burner zone heat release rate (plan, volume and basket)

BOILER OPERATING FACTORS

- load
- excess air or oxygen
- burner tilt
- burner swirl vane settings

COAL PROPERTY FACTORS

- volatile matter content
- fuel ratio (FC/VM)
- coal carbon-to-hydrogen ratio (C/H)
- nitrogen content

It's clear that knowledge of N chemistry under complex practical combustion conditions, and impacts of coal properties on that chemistry, will continue to be exploited to reduce NO_x emissions. It's also clear that coal nitrogen content is a poor guide to relative NO_x emissions for the reasons listed above. In Figure 3, NO_x emission levels for a suite of coals tested in a PF boiler simulation furnace under standard conditions are presented (ACIRL 1995). **There is clearly no correlation between coal nitrogen content and NO_x emissions under these conditions.**

NOx EMISSION LIMITS

National limits for NOx emissions vary from country to country, and often depend on the size of the plant and its age. Trends in emission standards have been reviewed by Sloss (2003). New approaches to control, such as load-based licensing and cap and trade economic instruments, are increasingly being used in addition to emission limits to reduce total emissions of pollutants such as NOx.

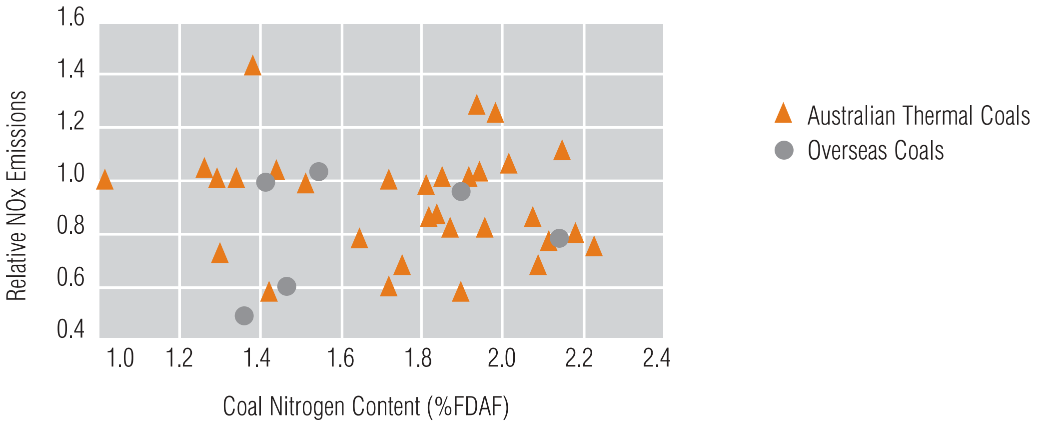

Figure 3: NOx emission levels for a range of coals tested in a boiler simulation furnace under standard conditions (from (ACIRL 1995))

NO_x CONTROL

CONTROL TECHNOLOGIES FOR NO_x EMISSIONS

Control techniques for NO_x in combustion systems can be conveniently divided into two general types:

- **Modifications to the combustion process, such as air and fuel staging, sometimes described as primary-side measures, and**
- **gas cleaning techniques based on ammonia injection into the flue, also known as secondary-side measures**

Both primary and secondary-side measures have been used commercially to control NO_x emissions. The most common combustion modification is air staging, often in the form of so-called low NO_x burners. By far the most common flue gas cleaning technique is selective catalytic reduction (SCR), but this is almost always installed in conjunction with primary-side measures such as low-NO_x burners.

Application of the most appropriate of these technologies is dependent on the degree of control to be achieved, and the cost. SCR can achieve the greatest reductions (it was required, for example, for attainment by hard coals of the German limit of 100 ppm when stringent controls were introduced in the 1980s) but the costs of the catalyst are very high. **Coal quality will have some influence on this technology, particularly sulphur content and the contents of trace elements which may act as poisons for the catalyst (alkali ions, particularly in sulphated form, arsenic and selenium).**

Air staging, particularly in the form of carefully designed low NO_x burners, can be used to reduce NO_x emissions substantially, and in some locations will be the preferred technique. Table 2 summarises key features of NO_x control technologies.

WORLDWIDE NO_x REDUCTIONS

There has been substantial investment in NO_x control technologies in Europe, Japan and the USA. Some very significant reductions in NO_x emissions from electricity production have been achieved as a result of:

- efficiency improvements
- increased use of nuclear and renewable energy
- fossil fuel switching (largely to natural gas), and
- combustion modifications and flue gas treatment

Historical data for NO_x emissions from electricity production in the EU are presented in Figure 4. **The data show very significant reductions (approximately 50%) in spite of large increases in electricity production. It also reveals that the major contribution to the reduction is through combustion modifications and flue gas treatment.**

Table 2: Summary of features of NOx control technologies

CONTROL TECHNIQUE	BASIS OF METHOD	REDUCTION (%)	COMMENTS/ LIMITATIONS
Air staging, low NOx burners	The fuel/air ratio is controlled to create a primary reducing zone close to the burner. Volatile N is released but due to lack of O_2 conversion to NO is reduced	30-70	• reduction in combustion efficiency • incomplete combustion leading to higher UBC in ash • fly ash disposal/sale problems • reducing conditions leading to corrosion
Fuel staging (reburning)	NO already formed is reduced by a secondary fuel (usually natural gas) added to a reducing zone	30-70	• careful optimisation of operating conditions required • cost of secondary fuel • mixing controlled
Selective catalytic reduction (SCR)	Catalyst promotes reaction between NO and added ammonia to produce N_2	80-90	• Poisoning, sintering, erosion • catalyst can oxidise SO_2 to SO_3 resulting in formation of corrosive ammonium salts • ammonia slip (emission) • cost and disposal of catalyst
Selective non-catalytic reduction (SNCR)	Same reaction as for SCR but at higher temperatures Rarely used for coal-fired systems	50-75	• temperatures and flow patterns must be very accurately known • mixing of NH_3 and NH_3 slip

CONCLUSIONS

1. The extent of the conversion of coal N to NOx is a strong function of combustion conditions and plant design; coal N content alone is not a good indicator of NOx emissions
2. Combustion modifications, including air staging and low NOx burners, result in lower emissions of NOx and coals which rapidly release coal N with the volatiles show the largest reductions.
3. Volatile matter (VM) content, or Fuel Ratio (FR = FC/VM), is likely to be a reasonable indicator of the volatile N release. Hence, coals with high VM or low FR are likely to respond favourably to NOx controls based on combustion modifications, provided of course that the high VM coals do not present any other technical difficulties in utilization.
4. A survey of Australian coals of fuel potential shows that most have FRs less than 2.5 and can be predicted to produce relatively low NOx emissions in full scale plant.
5. Emission limits on NOx continue to be tightened worldwide. Major reductions have been achieved through combustion modifications and flue gas treatment to reduce or remove NOx.

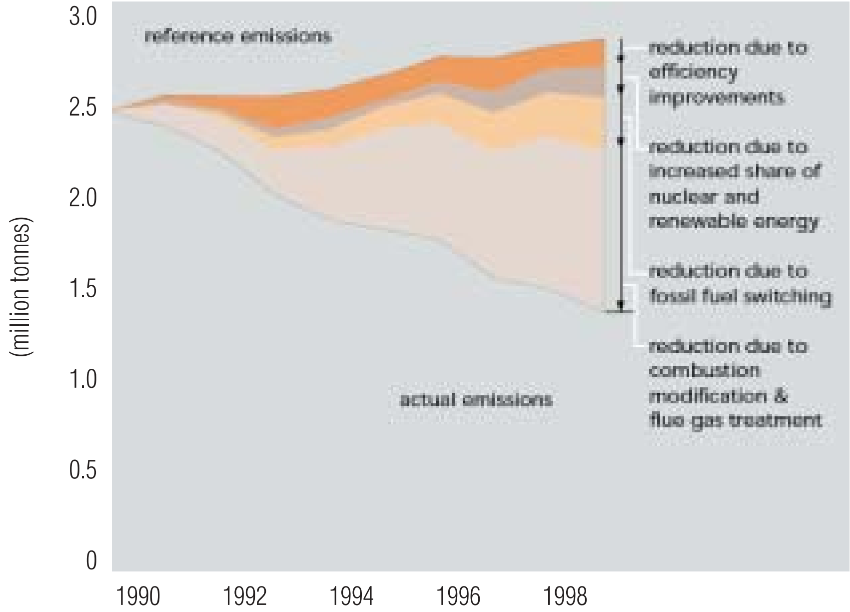

Figure 4: NOx emissions from electricity production in the EU

(Data from European Environment Agency report Environmental Signals 2002, available at: http://reports.eea.eu.int/environmental_assessment_report_2002_9/en/signals2002-chap05.pdf)

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