QTHERM

ENHANCING QUEENSLAND'S THERMAL COAL INDUSTRY

The Significance of Coal Nitrogen in the Combustion Process

DEPARTMENT OF MINES AND ENERGY

PREFACE

This report, commissioned by the Q*THERM* Program, was compiled by the Australian Combustion Technology Centre a business unit of the independent Australian Coal Research Laboratories.

Input to this review was provided by the Queensland Department of Minerals and Energy and various company technical representatives. It has been undertaken in response to requests from some coal producers, who have been seeking to clarify apparent technical anomalies, with regard to the use of nitrogen content in coal as a means of regulating emissions of oxides of nitrogen.

This report summarises the role played by each of the major contributors to the emissions of NO_x in the combustion process. It highlights both the poor correlation between NO_x emission levels and nitrogen content in coal and, the influence of power plant design and operating patterns on the resulting NO_x emission levels.

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THE SIGNIFICANCE OF COAL NITROGEN IN THE COMBUSTION PROCESS

EXECUTIVE SUMMARY

The factors which affect emissions of oxides of nitrogen (NO_x) resulting from the combustion of coal include boiler design and operating features, the use of flue gas clean-up technologies and the properties of the coals being used.

Power plant design and operating patterns have a major influence on the resulting NO_x emission levels. It has been demonstrated that with modern NO_x reduction technologies, low NO_x emission levels can be achieved with all coals. The use of flue gas clean-up, involving selective catalytic reduction, can typically reduce NO_x emission levels by 90%. The use of these technologies in combination, has resulted in typical NO_x emissions levels being reduced to less than 60 ppm, in a number of utility power plants firing a wide range of coals (Refer to p8).

The influence of coal properties on NO_x emission levels is not well defined. While it is clear that several factors influence NO_x formation, the roles and interaction of such factors as nitrogen partitioning (between the volatiles and chars), nitrogen functionality, coal rank, coal nitrogen content and volatile content in the formation of NO_x are not well understood, despite an enormous amount of scientific research over a number of decades. What has been demonstrated repeatedly however, is that the selection of coals on the basis of coal nitrogen content is an inappropriate and ineffective means of restricting NO_x emissions. The selection of coals should be the sole preserve of the generating utility who have the best understanding of the influence of their combustion plant design and operation on the level of NO_x emissions. Furthermore, the continued use of coal nitrogen as a controlling specification for coal supplies to an expanding utility market will not only fail to limit NO_x emission levels but will also result in the limitation on the development of new coal resources. This could be expected to lead to a tighter supply market with increased competition for the available supplies. In this context, the environmental regulations should focus on limiting the level of gaseous emissions of NO_x, and not on the coal nitrogen content.

1. INTRODUCTION

As countries around the world become increasingly more industrialised, increasing levels of concern on the part of regulatory authorities and other sectors of the community are being raised regarding the associated levels of atmospheric pollution. The use of coal for electric power generation is regarded as a major source of atmospheric pollution, especially in relation to the generation of oxides of sulphur (SO_2) and nitrogen (NO_x). These gases, formed during the combustion of hydrocarbon fuels, contribute to *photochemical smog*, *acid rain* and the *greenhouse effect*. It is essential for the benefit of both the coal industry and the community in general that the most effective means of monitoring and minimising emissions be employed.

The generation of oxides of sulphur resulting from coal combustion can be predicted with reasonable accuracy from the coal properties, and there is a single dominant oxide formed as the combustion product, viz. sulphur dioxide (SO_2). The generation of oxides of nitrogen, on the other hand is far more complex, with several possible nitrogen products. Species such as molecular nitrogen (N_2), nitric oxide (NO), nitrogen dioxide (NO_2) and nitrous oxide (N_2O) are the possible products of many different and competing reactions during the combustion process (Davidson, 1994). Historically, there has been an incorrect perception that coal nitrogen content could be used as a predictor of NO_x emissions. The precise nature of the chemical reactions in which NO_x is produced however, is not yet clearly defined or well understood by the scientific community. Furthermore, boiler design and gas-clean up technology have developed to the extent that emission levels of less than 60 ppm can now be achieved in modern pulverised-fuel (PF) fired power stations firing a wide variety of coals. This, and the fact that a simple relationship between NO_x emission levels and coal nitrogen content has not been able to be demonstrated after more than 20 years of scientific research in this area renders the use of coal nitrogen-related restrictions inappropriate for coal selection. Such a restriction not only fails to contribute to the control of NO_x, but also restricts the range of coals available to the utility by rendering large economic resources unavailable for development. (In Queensland alone, the reserves of coal in this category are estimated to exceed 5 billion tonnes, and could be developed to yield in excess of 20 million tonnes per annum.)

2. TECHNICAL DATA

2.1 Atmospheric Effect of Oxides of Nitrogen

It is widely recognised that NO_x has undesirable atmospheric effects, being a contributor to acid rain, photochemical smog and the greenhouse effect. In reference to fossil fuel combustion, the term "NO_x" is generally considered to include nitric oxide (NO) and nitrogen dioxide (NO_2), although nitrous oxide (N_2O) is also a product of the combustion process. In addition to the combustion of coal, NO_x is generated from the combustion of natural gas and petroleum products, motor vehicles, the combustion of biomass, fertilisers and natural sources.

2.2 Factors which Influence NO_x Emissions from Coal Combustion

2.2.1 General

NO_x emissions resulting from coal combustion (principally in coal-fired power generating plant) are governed by several factors which can be classified in three broad categories including:

a) Boiler design
b) Operating conditions of plant
c) Use of flue gas clean-up (de-NO_x plant)
d) Coal properties

2.2.2 Boiler Design

Boiler design and burner configuration have a major influence on NO_x emission levels. Physically larger furnaces (for a given energy input) have low furnace heat release rates which lead to decreased levels of NO_x. The use of air-staged burners and over-fire air, both of which discourage the oxidation of nitrogen by the existence of sub-stoichiometric conditions in the primary combustion zone, also lead to lower levels of NO_x. Firing configuration (ie. tangentially-fired, horizontally opposed fired, etc) can also influence NO_x emission levels.

2.2.3 Boiler Operational Parameters

In general, NOx emission levels increase with increasing load (due to increased peak flame temperatures) and increasing excess oxygen content. The choice of in-service mills/burners can also have a major effect on NOx emissions as it provides the opportunity to vary the peak flame temperature within the furnace.

Excess air level has a profound effect on NOx emission levels irrespective of the type of boiler or the nature of the firing system. In general, decreasing the level of excess air decreases NOx emissions. The extent to which excess air levels can be reduced in practice however, will be governed by other combustion considerations including possible reduced combustion efficiency and possible increased tendency for furnace slagging to occur.

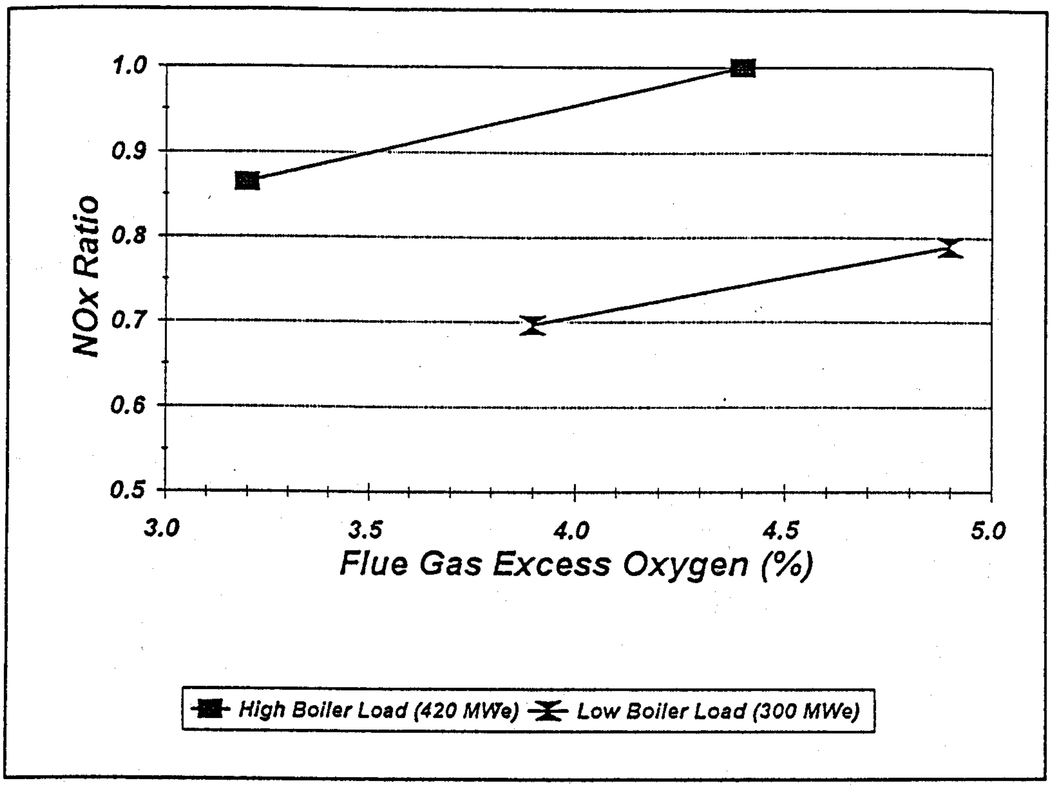


Figure 1 **Effect of Excess Oxygen on NOx Emissions at Liddell Power Station**

Figure 1 shows the effect of excess air variations on NOx emissions for a 500 MWe tangentially-fired boiler at Liddell Power Station in New South Wales, Australia, firing a high nitrogen (2.13% daf) domestic Hunter Valley coal (Cives and Holcombe, 1992). Results are shown for two boiler loads, viz. 450 MWe and 300 MWe. For the data presented, all other operational parameters were the same. The figure shows the influence of excess oxygen level and boiler load on NOx emission levels. As the figure shows, substantial reductions in NOx at both boiler loads (up to almost 15%) were achieved with modest variations in excess oxygen levels. For all cases of boiler operation at reduced O2, there was no evidence of deterioration in other aspects of combustion performance.

Figure 2 shows the response of NOx emissions to variations in excess air from boilers at Bayswater Power Station (660 MWe) firing the same high nitrogen Hunter Valley coal referred to above (Cives and Holcombe, 1992). Again the same strong dependency of NOx emission levels on excess oxygen content is evident. A 48% increase in NOx emission levels was found to result from an increase in excess oxygen level form 2.5% to 4.0%. The removal of over-fire air at 3.5% excess oxygen resulted in a 64% increase in NOx compared to the level measured at 2.5% excess oxygen

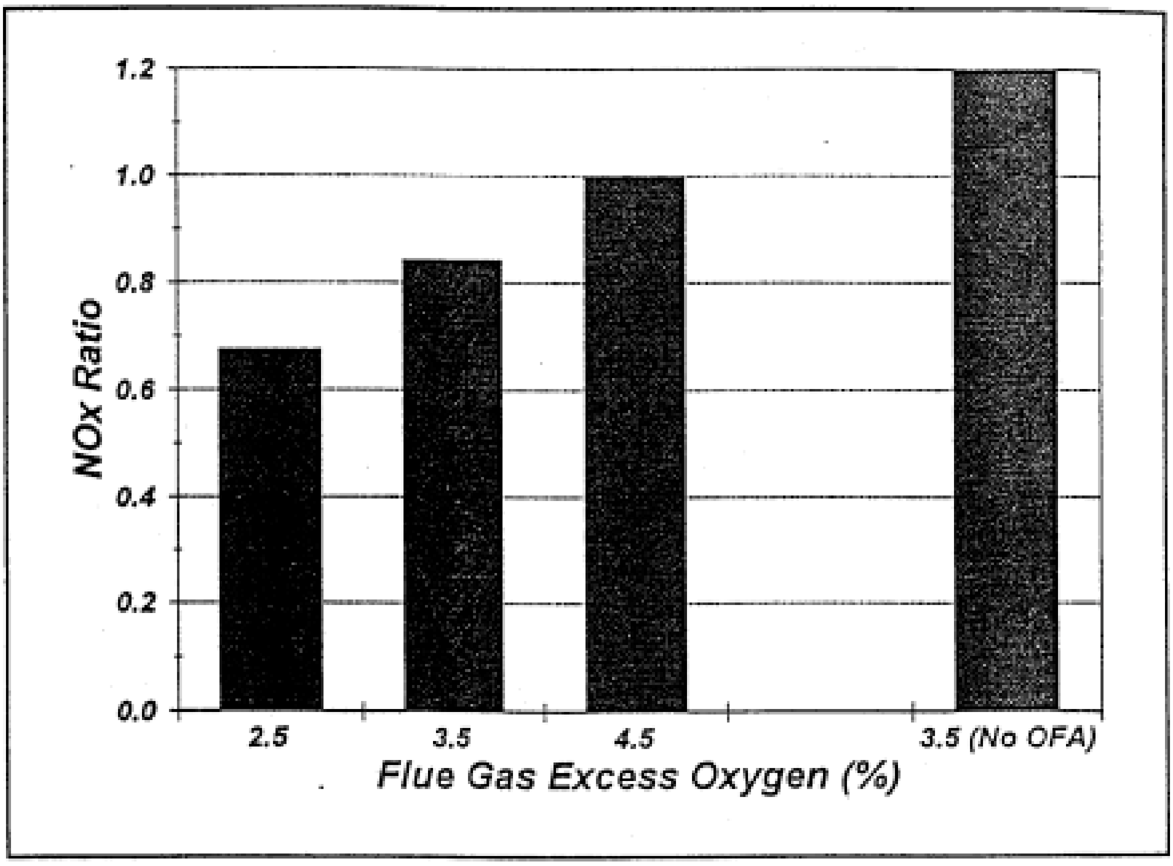


Figure 2 Effect of Excess Oxygen and Over-Fire Air on NOx Emissions at Bayswater Power Station

The use of over-fire air is proven and well-established as a NOx-reduction technique. It employs the same strategy as air-staging in which the oxidation of nitrogen is discouraged by the existence of sub-stoichiometric conditions in the primary combustion zone. Morrison (1980, cited in Dacey, 1984) reports that the use of over-fire air can achieve reductions in NOx emissions of 10-35%, without any deleterious effects on boiler efficiency.

Figure 3 shows the results of utilising over-fire air for NOx control for a tangentially-fired boiler (520 MWe) (Marshall and Selker, 1978). As the figure shows, an trend of increasing NOx-reduction with increasing over-fire air damper opening was observed, with NOx levels measured 45% lower at 100% damper opening, compared to when no over-fire air was used.

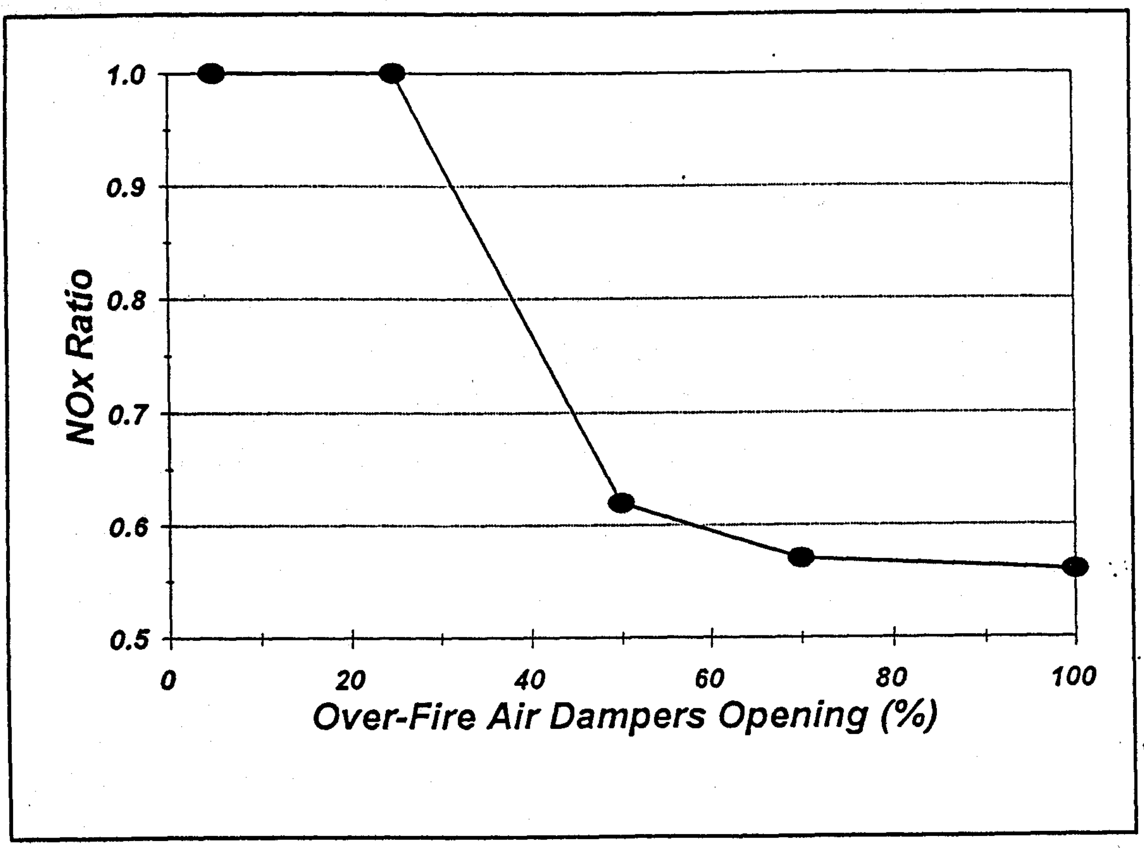


Figure 3 **Effect of Over-Fire Air on NOx Emissions (Marshall and Selker, 1978)**

2.2.4 Flue Gas Clean-Up

The use of post-combustion NO_x removal (typically using selective catalytic reduction, SCR) is the most effective NO_x reduction option. While combustion modifications alone have been found to reduce NO_x emissions, by as much as 70% (Makansi, 1993), flue gas treatment can increase the overall level of NO_x reduction to values in excess of 90%. Chubu Electric Power Company's Hekinan Power Station is fitted with SCR de-NO_x equipment such that stack emissions of NO_x do not exceed 45 ppm.

Selective catalytic reduction, which involves the injection of ammonia into the flue gas, converts NO_x to nitrogen and water in the presence of a catalyst, is the most capital expensive NO_x reduction technique but also, by far the most effective.

2.2.5 Coal Properties

Despite the intuitive appeal of having a simple relationship which would allow the estimation of NO_x emission levels from coal nitrogen content (just as SO_2 emission levels can be estimated with reasonable accuracy from coal sulphur content), the fact remains that such a relationship has not been revealed despite the abundance of research work which has been conducted in this area over many years. Davidson (1994), following a review of fundamental research in this area, states that:

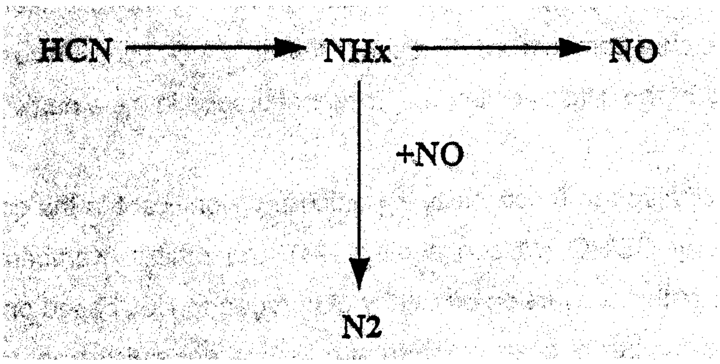
"The chemistry of the formation of nitrogen oxide combustion products from the nitrogen in the coal is complex and not yet understood."

This is not surprising given the number of coal properties which potentially impact on NO_x generation. The following paragraphs attempt to summarise the current level of understanding of the role of coal properties in the formation of NO_x from coal combustion. It is important to note that the influences of the different properties is very much inter-related, and as such, it is difficult to examine the influence of individual properties in isolation.

Combustion of Coal Volatiles (Unsworth et al, 1991):

NO_x is predominantly formed from the combustion of volatile coal nitrogen liberated during pyrolysis in PF flames. In many coals, nitrogen is present predominantly as stable aromatic ring structures, and the extent to which these are ruptured during pyrolysis, allowing the nitrogen to be evolved with the volatiles, has been found to be a function of volatile matter content. Among the products of pyrolysis are HCN, NH_3, NO and nitrogenous tars. The tars breakdown to small species fairly quickly. The fraction of nitrogen that is vaporised increases with temperature, and both this and the distribution of products depends on the coal type and the particle size. The gas phase species are subsequently oxidised to NO or N_2. As shown in the figure below, the amount of NO formed is dependent on the extent to which the alternative reactions of the NH_x species take place, ie. to be either:

a) Oxidised to NO, or
b) Reacted with NO to form N_2.



Under utility boiler conditions, a maximum of around 50% of volatile fuel nitrogen may be converted to NO but, as with atmospheric nitrogen, conversion is strongly influenced by the mixing in the flame, owing to the dependency on temperature and stoichiometry.

Combustion of Coal Char:

The conversion to NO of the nitrogen released as the char burns, is small (<20%) in comparison to the NO produced during the volatile combustion. This is probably because the NO can be reduced (to N_2) by carbon under the rich conditions that occur inside the burning char particles. The NO produced during char combustion is important however, as NO_x formation from the volatile fuel nitrogen can be minimised by promoting devolatisation in zones of high temperature under reducing conditions, a principle which is successfully exploited in low-NO_x (ie. air-staged) burner technology.

Nitrogen Functionality:

The major structures of nitrogen in coal are:

a) The six-membered heterocyclic ring structure - *pyridine*.
b) The five-membered ring - *pyrrole*.
c) The primary aromatic amine, $C_6H_5NH_2$.

While the influence of nitrogen functionality on NO_x emissions is not yet clearly defined, it has been found by a number of investigators that the pyrrolic-type nitrogen structures are considerably less stable, and therefore more likely to react and oxidise to form NO_x than the pyridinic-type structures (Davidson, 1994), a factor which has been found to have influence on NO_x generation from both volatile and char combustion. The coal nitrogen content, in isolation, gives no indication of the relative proportions of the different nitrogen functional groups in the a particular coal.

The issue of nitrogen functionality is particularly significant in the context of Australian coals. Studies conducted by CSIRO (Nelson et al, 1991) and others (Kambara et al, 1993,) have found that predictions of the conversion efficiency of nitrogen to NO_x based on the correlations of pilot scale test results of a number of coals of different rank, are not satisfactory for the prediction of NO_x emissions from Australian coals. In this study, coals of the same nitrogen content and volatile content have been found to produce different amounts of volatile nitrogen when pyrolysed. It has been suggested (Nelson et al, 1991) that the relative amounts of pyrrolic and pyridinic nitrogen may explain this difference in behaviour. The importance of nitrogen functionality and its possible influence on NO_x emissions has also been highlighted in work conducted by Idemitsu (1995).

Coal Rank:

Test work conducted at the International Flame Research Foundation (Phelan and Flament, 1983) suggests that lower rank coals have a tendency to produce more NO_x than higher rank coals having the same nitrogen content. This is consistent with the findings of Chen et al (1992), and Nelson and Kelly (1993) both of which have found that lower VM (ie. higher rank) coals released less nitrogen (for subsequent oxidation to NO_x) than higher VM, lower rank coals. It has been postulated that this may be due to the increased stability of the nitrogen functional groups with the increased aromaticity of higher rank coals.

Coal Nitrogen Content:

Some experimental results may suggest that NO_x emissions correlate with total coal nitrogen content, however the dependency is very weak and heavily influenced by other factors. Other factors may be of similar or greater influence, and may cause the nitrogen dependence to be obscured. Studies by Thompson and Stainsby (1993), Idemitsu Kosan (1995), *ACIRL* Limited (unpublished) and Shell Research (Fortune, undated) have indicated that coal nitrogen content has no simple influence on NO_x emission level which can be predicted with any accuracy.

Figure 4, which shows the relationship between NO_x emissions and coal nitrogen content determined for a range of coals (Australian and non-Australian) tested by *ACIRL* Limited in pilot scale combustion test equipment with no NO_x reduction strategies employed, demonstrates that similar levels of NO_x emissions have been measured from the combustion of low nitrogen and high nitrogen coals. Not only do the results demonstrate the fact that there is no correlation between coal nitrogen and NO_x, they also show that the influence of coal properties is considerably less than that of plant design features which can achieve reductions in NO_x emissions of up to 90%.

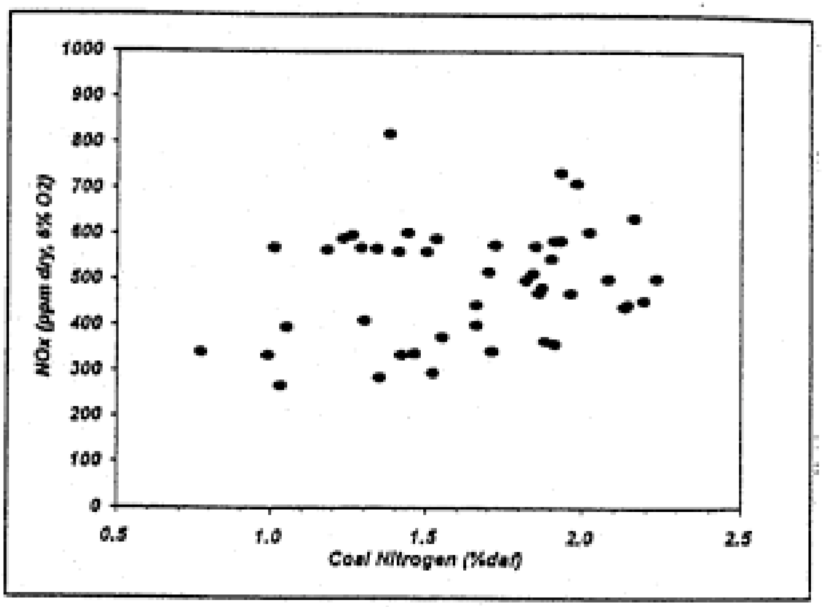


Figure 4 Relationship between NO_x Emissions and Coal Nitrogen Content (*ACIRL* Limited)

Coal Volatile Matter Content:

A broad trend of increasing NO_x with volatile matter has been observed, by some researchers. For bituminous coals, higher volatility is associated with higher flame temperatures which would tend to increase the conversion of fuel nitrogen and atmospheric nitrogen to NO. The higher temperature would also cause a higher proportion of the fuel nitrogen to be emitted in the volatiles, where the conversion would be greater than if it were oxidised in char. The development of boiler and burner technology has, however, been successful in negating these effects on NO_x generation.

This influence of VM led to the prediction of NO_x emission levels using rather simplistic equations (Pohl, 1983). Studies by Nelson et al (1991) however have demonstrated that predictions based on VM and coal nitrogen content are not valid.

3. SUMMARY

The factors which affect NO_x emission levels can be summarised as follows:

a) The influence of power plant design and operating patterns has a major influence on the resulting NO_x emission levels. It has been demonstrated that with modern NO_x reduction technologies, low NO_x emission levels can be achieved with all coals. Furthermore the influence of plant design and operation on NO_x emission levels is much more clearly defined and understood than that of coal properties.

b) The use of flue gas clean-up, involving selective catalytic reduction, can typically reduce NO_x emission levels by 90%.

c) The influence of coal properties on NO_x emission levels is not well defined. While it is clear that several factors influence NO_x formation, the roles and interaction of such factors as nitrogen partitioning (between the volatiles and chars), nitrogen functionality, coal rank, coal nitrogen content and volatile content in the formation of NO_x are not well understood. As such, the use of coal nitrogen content as a predictive tool for NO_x emission levels is totally invalid.

4. CONCLUSIONS

Over the last forty years, the combination of modern boiler design philosophy and flue gas clean-up technology has seen NO_x emission levels reduced from in excess of 1000 ppm to less than 60 ppm, a level achieved in a number of utility power stations firing a wide range of coals. The influence of coal properties on NO_x emissions, despite an enormous scientific research effort, has not yet been sufficiently well defined to allow the prediction of NO_x emission levels from these properties. What has been demonstrated repeatedly however, is that the selection of coals on the basis of coal nitrogen content is an inappropriate and ineffective means of restricting NO_x emissions. The selection of coals should be the sole preserve of the generating utility who have the best understanding of the influence of their combustion plant design and operation on the level of NO_x emissions. Furthermore, the continued use of coal nitrogen as a controlling specification for coal supplies to an expanding utility market will not only fail to limit NO_x emission levels but will also result in the limitation on the development of new coal resources. This could be expected to lead to a tighter supply market with increased competition for the available supplies. In this context, the environmental regulations should focus on limiting the level of gaseous emissions of NO_x, and not on the coal nitrogen content.

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