NO_x EMISSIONS PRODUCED WITH COMBUSTION OF POWDER RIVER BASIN COAL IN A UTILITY BOILER

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EXECUTIVE SUMMARY

Nitric oxide (and nitrous oxide) emissions from coal-fired utilities depend primarily on how the coal is burned and to a lesser extent on the nitrogen content of the coal itself, even though most of the NO_x produced originates from coal nitrogen. With a combination of tight, computerized combustion control, including controlling temperatures and the use of low-NO_x burners utilities should be able to meet the Clean Air Act Title IV NO_x limits. For tangentially fired boilers the limits are 0.45 lb/mm Btu (Phase I) and 0.40 lb/mm Btu (Phase II). For dry-bottom, wall-fired boilers the limits are 0.50 lb/mm Btu (Phase I) and 0.46 lb/mm BTU (Phase II). Compliance for phase I is January 1996; compliance for phase II is January 2000. Emission limits for these laws and regulations are expressed as equivalent NO₂ even though nitric oxide (NO), and to a much lesser extent nitrous oxide (N₂O), are the chemical species actually emitted. Local and regional regulatory agencies may place more stringent limits on utility NO_x emissions than the Title IV standards in an effort to meet ambient air quality standards, especially in ozone nonattainment areas.

Powder River Basin (PRB) coal offers an advantage for utilities meeting NO_x limitations because it is a more reactive coal and when burned in a utility boiler fitted with low-NO_x burner technology can produce 20% less NO_x than burning an eastern bituminous coal. While this may not seem like a major improvement, because the U.S. Environmental Protection Agency (EPA) has set Phase II limits near what low-NO_x burner and tight combustion control is technically capable of achieving, any improvement will help. This is providing, however, that the furnace is clean and well maintained, as a dirty furnace with slag buildup will result in higher burning temperatures and increased NO_x. Burning PRB coal can result in more furnace slag buildup than when burning eastern coals. This buildup is not easily removed with soot blowers; frequent cleaning with waterlances is required.

Nevertheless, in laboratory and in pilot plant demonstrations using more reactive, subbituminous coals NO_x emissions have been lower than those from bituminous coals. NO_x emissions lower than those from eastern coals have also been demonstrated in power plants burning PRB coal. The greater reactivity is related to the higher quaternary nitrogen functionality (compared with pyridinic and pyrolic nitrogen functionality) of subbituminous coal (including PRB coal), which produces less NO_x when burned in low-NO_x burners. The term "quaternary" does not mean a four-ring structure but refers to what is believed to be a six-ring structure containing nitrogen with oxygen as part of the ring. This report reviews laboratory and pilot plant work on NO_x emissions related to coal nitrogen structure, as well as the experience of utility with NO_x emissions burning PRB coal.

INTRODUCTION

The objective of this report is to estimate the NO_x emissions produced when Powder River Basin (PRB) coal is combusted in a utility boiler. The Clean Air Act regulations specify NO_x limits of 0.45 lb/mm Btu (Phase I) and 0.40 lb/mm Btu (Phase II) for tangentially fired boilers, and 0.50 lb/mm Btu (Phase I) and 0.46 lb/mm Btu (Phase II) for dry-bottom wall-fired boilers. The Clean Air Act regulations also specify other limits for other boiler types. Compliance for Phase I has been in effect since January 1, 1996. Compliance for Phase II goes into effect on January 1, 2000. Emission limits are expressed as equivalent NO₂ even though NO (and sometimes N₂O) is the NO_x species emitted during combustion. Regulatory agencies usually set even lower NO_x emission limits in ozone nonattainment areas.

In preparing this report, Western Research Institute (WRI) used published test results from utilities burning various coals, including PRB coal, using state-of-the art control technology for minimizing NO_x emissions. Many utilities can meet Clean Air Act NO_x emission limits using a combination of tight combustion control and low-NO_x burners and by keeping furnaces clean (i.e., no slag buildup). In meeting these limits, some utilities also report problems such as increased carbon in their fly ash and excessive furnace tube corrosion. This report discusses utility experience.

The theory of NO_x emission formation during coal combustion as related to coal structure and how the coal is combusted is also discussed. From this understanding, projections are made for NO_x emissions when processed PRB coal is combusted in a test similar to that done with other coals. As will be shown, there are a lot of conditions for achieving low NO_x emissions, such as tight combustion control and frequent waterlancing of the furnace to avoid buildup of deposits.

THEORY OF NO_x FORMATION DURING COMBUSTION

General Comments

Essentially all NO_x emitted during combustion of coal is nitric oxide (NO). Two important exceptions are (1) combustion of coal in fluidized beds and (2) urea injection into a coal-fired furnace, either of which results in some nitrous oxide (N₂O) which is emitted from the stack. The N₂O concentration in the stack resulting from normal combustion of pulverized coal is in the 1 to 5 ppm range compared with several hundred parts per million of NO, but N₂O concentration from fluidized bed combustion is in the 20 to 250 ppm range (Wójtowicz et al. 1993). Nitrogen dioxide (NO₂) is not formed during normal coal combustion but is formed later

when the stack gas is cooled and NO reacts with air oxygen. Rapid quenching of combustion products promotes large concentrations of NO₂ (Lin 1996). While the lifetime of NO and NO₂ may be in the order of days, N₂O is persistent in the atmosphere and is an important greenhouse gas. Regardless of the form of NO_x emitted, U.S. government regulations are in terms of equivalent NO₂.

Formation of NO_x is due to three mechanisms: (1) thermal NO_x, (2) prompt NO_x, and (3) fuel nitrogen. Coal nitrogen contributes between 50% to perhaps up to 95% of the total NO_x, depending on how the coal is burned. The NO_x derived from coal nitrogen may be either produced from homogeneous gas phase reactions through HCN and NH₃ intermediates or from heterogeneous reactions taking place on the coal char surface. To complicate the picture, NO produced from homogeneous reactions can be reduced to N₂ by contact with coal char carbon. At this time, it is not possible to predict NO_x emissions for a practical coal combustion situation based on solving individual reaction rate equations, even using computers, although there have been attempts reported in the literature. While the gas phase reaction rate constants have been worked out, the heterogeneous reactions taking place on the char surface have not been described for general situations. Reaction rates on char surfaces are strongly influenced by the mineral content, especially iron and trace metals.

Yang and Puri 1993 have published a list of reaction rate constants for 234 homogeneous gas phase reactions involving combustion of hydrocarbons and interactions with nitrogen. Additional rate constants are in Zabarnick 1992. Chen et al. 1996 have used these rate constants and derived a fuel-NO rate expression for the homogeneous gas phase combustion, applicable for reburning situations. Chen et al. 1996 also caution that formation and destruction rates of NO_x are the same magnitude as turbulent mixing rates, and the equilibrium assumption usually done to simplify the mathematics is inadequate when calculating NO_x concentrations. It is not possible with today's knowledge to fully describe coal combustion and predict a NO_x emission using mathematical relationships, mainly because of lack of information on heterogeneous reactions.

Thermal NO_x

Significant thermal NO_x only occurs at high flame temperatures (>2300°F or 1260°C). It is formed by reaction of oxygen and nitrogen in the air. Generation of thermal NO_x is exponentially dependent on temperature and square-root dependent on oxygen. Roughly 40 times the amount of NO_x is produced at 2700°F than at 2250°F, for example (Colannino 1993). Minimization of thermal NO_x involves reducing the peak flame temperature and lowering oxygen concentrations near the flame zone. Most thermal NO_x is formed at the portion of flame close to the burner, where oxygen and peak flame temperature is the highest. With good furnace and burner design, thermal NO_x formation during coal combustion can be kept very low. Thermal

NO_x formation during coal combustion becomes significant in tight furnaces such as with cyclone furnaces or furnaces with significant slag buildup, either of which result in higher temperatures.

Prompt NO_x

Prompt NO_x is formed from reaction of hydrocarbons with air nitrogen and oxygen. It is created from partial-combustion products such as CH· very close to the flame front, and forms at temperatures cooler than those for thermal NO_x. It is not possible with present burner technology to completely eliminate prompt NO_x; the first 15 to 20 ppm of NO_x generated during combustion of hydrocarbons, including coal, is due to prompt NO_x (Colannino 1993). The use of oxygenated fuels, such as methanol and ethanol, reduces prompt NO_x when burning gasoline. The primary NO_x formation route when burning natural gas is prompt NO_x.

Dupont et al. 1993 reviewed the formation of NO_x in natural gas flames, including publication of rate constants. The principal prompt NO_x route is through the reaction

which is followed by

The HCN converts to NO and N₂ (see reactions for HCN under coal nitrogen). The CH· is formed in the burning process (e.g. CH₄ + OH· → CH₃· + H₂O; CH₃· + OH· → CH₂· + H₂O; etc.).

Coal Nitrogen NO_x

When coal is combusted, the nitrogen portion is converted to nitric oxides and nitrogen gas. The fraction of NO_x nitrogen to total nitrogen in the coal depends primarily on how the coal is burned and to a relatively minor degree on the coal itself. Unlike thermal and prompt NO_x, coal nitrogen NO_x can form at temperatures as low as 700°C (1292°F). Cai et al. 1993 estimate that under conventional power station firing conditions, 15 to 30% of the coal nitrogen is typically converted to NO_x.

Coal is composed of a mixture of minerals and an organic portion called marcerals. Both are heterogeneous and differ widely among coals. Marcerals are composed of carbon, hydrogen, and oxygen atoms plus some sulfur and nitrogen bound in a macromolecular network, usually in

the form of aromatic ring clusters with small peripheral groups linked by bridges plus long-chain aliphatics. Marcerals may also contain unbound guest molecules. Coal can be physically separated into marceral components by density gradient centrifugation of the pulverized coal using cesium chloride solution as the flotation medium. Coal nitrogen exists in the marceral portion either as part of six-ring structures (pyridinic), five-ring structures (pyrrolic), quaternary, or as amino-type side chains. The distinction between quaternary and amino-type side chains is not really clear in the literature. Most of the references to amino-type side chains are for peats and European brown coals. The existence of amino-type side chains is neither confirmed nor disproven for U.S. coals, according to Kelemen et al. 1994, although some U.S. coals probably contain a small amount.

Using a technique called X-ray photoelectron spectroscopy, a number of researchers (e.g. Kambara et al. 1995; Kelemen et al. 1994) have determined the relative amounts of coal nitrogen in quaternary, pyrrolic, and pyridinic groups. The chemical structure of quaternary forms is not clear; Kelemen et al. 1994 have suggested (at least for Wyodak and Illinois No. 6 coals) that the quaternary-type nitrogen species may be pyridinic forms associated with oxygen functionalities that can be easily broken during mild pyrolysis. Examples of nitrogen forms for different coals are shown in Table 1.

Table 1. Nitrogen Functionality for Selected U.S. Coals

Coal	% N (dry, ash-free basis)	Proximate wt % volatile (dry basis)	Proximate wt % fixed C (dry basis)	% of total N as quaternary	% of total N as pyrrolic	% of total N as pyridinic
Roshell	1.1	43.5	51.4	11.6	59.2	29.2
Usibelli	0.9	48.8	43.0	14.2	52.8	33.1
Beulah Zap	1.15	44.9	46.5	16	59	25
Wyodak	1.12	44.7	46.5	15	60	25
Illinois No. 6	1.37	40.1	44.4	12	62	26
Blind Canyon	1.57	45.8	49.5	14	55	31
Pittsburgh No. 8	1.64	37.8	53.0	7	61	32
Pocahontas	1.33	18.6	76.6	3	64	33

The percentage of pyridinic nitrogen increases with coal rank. Lower ranked coals have a higher percentage of quaternary nitrogen. Quaternary nitrogen is the least stable, and pyridinic nitrogen is the most stable when the coal is heated.

When pulverized coal is combusted, a number of complicated reactions take place. Researchers studying pyrolysis and combustion of coal differ as to details, but basically the coal nitrogen is converted to ammonia (NH_3), hydrogen cyanide (HCN), and char nitrogen (char-N)

intermediates, which in turn are converted to nitric oxide (NO), nitrous oxide (N₂O), and nitrogen (N₂). Quaternary and amino-side chain nitrogen produce NH₃ as an intermediate, but pyridinic nitrogen produces char-N and HCN. The fate of pyrrolic nitrogen is less clear, but there is evidence (Kambara et al. 1995) that it produces mostly char-N and HCN and possibly some NH₃. Pyrolysis studies (Varey et al. 1996; Bassilakis et al. 1993) have also demonstrated that rapid heating and higher temperatures favor more HCN, but slower heating and lower temperatures favor more NH₃ as an intermediate. Wójtowicz et al. 1995 has found that pyrrolic nitrogen going through the HCN and char-N route is first converted to a pyridinic group and that char-N is a 6-ring structure mostly of carbon atoms but with the volatile component removed.

Nitrogen oxides and molecular nitrogen may be produced either as a homogenous, gas phase reactions or as heterogeneous reactions involving the coal char surface. The most important reactions on the char surface are

In the gas phase, fuel-lean conditions favor the formation of NO from HCN:

Fuel-rich conditions favor N₂ from HCN:

A similar set of reactions can be written for NH_3 , with fuel-lean conditions favoring NO and fuel-rich conditions favoring N_2 .

In addition, HCN can react with coal hydrogen in the coal pores to form NH_3 (Bassilakis et al. 1993). A slower coal heating rate allows more time for this reaction to take place. Rapid heating during pyrolysis produces more HCN, but slower heating produces more NH_3 .

In reburning schemes, a small amount of secondary fuel is injected into the products from the main combustion zone. The secondary fuel could be pulverized coal, but some utilities use natural gas, which does not contain fuel nitrogen. The natural gas portion typically represents 10 to 20% of the total fuel burned on a heat content basis. When natural gas is burned, hydrocarbon free radicals are formed, which react with NO produced in the primary combustion zone.

The HCN formed may then react to form N_2 under oxygen-lean conditions or it may reform NO if the oxygen concentration is too high.

Niksa and Cho 1996 of SRI International concluded after studying conversion of fuel nitrogen in pulverized coal flames that NO production shuts down if hydrocarbons are present but become the main coal-N conversion channel in their absence. The inception point for NO production is determined by consumption of O_2 among all fuel components including soot and char. As long as there are hydrocarbon radicals present, N_2 is the only stable product of fuel-N conversion.

German researchers (Spliethoff et al. 1996) studying coal reburning (also called fuel staging) reported that increased residence time in the primary zone reduces NOx emissions, leading to optimum reburning (minimum NOx) under fuel-lean conditions. They also reported that more reactive European brown coals produced less NOx emission than bituminous coals, and the NH_3 intermediate produced less NOx than the HCN intermediate, all under fuel staging conditions. As verified by other researchers, the authors found NOx emissions increase with temperature and with increased air. German utilities (Maier et al. 1994) have reduced NOx emissions by a factor of two (~400 ppm to ~200 ppm at 6% O_2) by using reburning.

Low-NOx burners work on the principle of controlling combustion by staging air introduction to the flame to ensure that the primary burning zone takes place under air-starved

(fuel-rich) conditions. The air is added in several stages and/or fuel is added in two stages to ensure that hydrocarbon radicals are present to react with nitric oxide without resulting in unburned carbon in the ash. Coal-fired utility (tangentially fired) boilers using low-NO_x burners have successfully reduced NO_x emissions to the 0.35 to 0.5 lb NO_x/mm Btu range.

Wang et al. 1996 has commented that low-NO_x burners have successfully reduced thermal and prompt and gas-phase, fuel-derived NO_x emissions but are not very successful in reducing the char-N component. Wang et al. 1996 estimate that 60 to 90% of the NO_x left after installation of low-NO_x burners originates from the char-N component. Cai et al. 1993 say the same, estimating 60 to 95% of NO originates from char-N when using low-NO_x burners. This compares with 60 to 80% NO_x emissions derived from gas phase reactions when low-NO_x burner technology is not used during pulverized coal combustion (Wang et al. 1994). The char-N can be combusted to N₂ or NO, and NO formed previously can be reduced by carbon char to N₂. Higher-ranked coals formed more NO from coal-N, and lower ranked coals formed more N₂, when different coal chars were combusted in an entrained flow test reactor. The authors (Wang et al. 1996) attributed this to a greater surface area (from volatiles leaving the coal), allowing NO to be reduced on the surface or in the pores of the char.

Varey et al. 1996 looked at NO formation during combustion of different coals in a temperature-programmed reactor using 20% oxygen and 80% helium as the combustion gas, with sampling of pyrolysis intermediates and NO directly above the sample. The NO-to-coal nitrogen ratio (NO/N) increased significantly with temperature at 50% burnoff. The authors classified the various coals into marcceral density fractions, with vitrinite being the most reactive and having the lowest temperature at 50% burnoff. Fusinite was the least reactive marcceral and had the highest temperature at 50% burnoff and highest NO/N. Vitrinite char was more reactive and led to a greater reduction of NO to N₂ on its surface. The Wyodak coal tested had a marcceral analysis of 89% vitrinite and 11% inertinite (another marcceral fraction) by volume.

Niksa and Cho 1996 found that char, soot, and noncondensibles burned simultaneously when a subbituminous coal (Dietz) was burned in a laboratory quartz tube flow reactor. A bituminous coal (Pittsburgh No. 8) char oxidation rate was slower. When the char oxidation rate is comparable to the noncondensable and soot oxidation rates, there are free hydrocarbon radicals to react with any NO produced previously.

Pease et al. 1993 of ABB Power Plant Laboratories (Windsor, Connecticut) advocate preliminary testing of coals in pilot plant setups to assess the impacts of utility coal switching from eastern to western low-sulfur subbituminous coals. The authors state that the higher combustion reactivity of subbituminous coal compared to bituminous can be advantageous from a carbon burnout standpoint under low NO_x firing applications.

Effect of Mineral Content on NO_x Emissions

The mineral content of the coal affects the NO_x emissions, especially the heterogeneous reactions taking place on the char surface during burning. The minerals act as catalysts promoting a particular conversion pathway rather than taking part directly. This is one area where reaction rate constants have not been determined, and therefore it is not possible with today's technology to develop a computer program to predict NO_x emissions for a given coal and burning configuration.

A high iron content promotes the conversion of coal nitrogen to N₂ rather than to NO, for example. Ohtsuka et al. 1993 and Mori et al. 1996 demonstrated that N₂ formation from coal nitrogen was greatly promoted when various pulverized coals were doped with iron from precipitated FeCl₃ solutions and pyrolyzed in a fluidized bed reactor. During pyrolysis tests in a helium atmosphere at 900°C, 50 to 60% of the coal nitrogen was converted to N₂ rather than HCN and NH₃ when the raw coal was doped with 3 to 7% iron, compared with about 3% conversion to N₂ without the iron. Even at 0.73 % iron, the amount of N₂ formed relative to HCN and NH₃ under pyrolysis conditions was 12 times that for a test run with no iron added. The nitrogen content of the chars with iron following pyrolysis was either the same or lower than chars produced without iron (depending on the coal).

Leppälähi et al. 1991 also found under pyrolysis conditions at 900°C that the presence of iron catalyzed the destruction of NH₃ and HCN from coal nitrogen, forming N₂; the authors also found that limestone or dolomite added to the raw coal catalyzed the destruction of HCN but not NH₃. At 800°C, iron was much less effective in catalyzing the destruction of NH₃ and HCN. The iron catalyst was added to the coal as ultrafine particles slurried in an acetone matrix and acetone evaporated. Silica or silicon carbide did not promote the conversion of NH₃ and HCN from coal pyrolysis to N₂.

The cationic mineral composition from ash analysis is presented in Table 2 for six different coals. In the original coal, the minerals are present as complexes containing carbonates, bicarbonates, chlorides, and sulfates, but the analyses are reported as equivalent oxides.

Table 2. Composition of Coal Ashes (weight percent expressed as equivalent oxide)

Coal	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅
Beulah Zap	27.5	14.2	9.9	2.8	27.4	5.9	10.8	1.0	0.4
Pittsburgh No 8	50.8	20.2	17.5	1.3	5.2	1.3	0.0	2.5	0.2
Illinois No 6	48.6	23.1	14.3	1.2	5.8	1.6	0.5	3.1	0.3
Indian Head	36.0	22.1	2.8	1.2	24.0	5.8	1.9	0.9	0.1
Martin Lake	33.4	19.0	10.4	1.2	29.4	5.9	1.5	0.4	0.0
Wyodak	41.2	20.0	4.6	2.0	24.1	5.3	1.0	0.5	0.8

Table from Novok et al. 1990.

There is little published work available on the effect of the mineral composition of a coal on NO_x emissions when the coal is burned. For example, on the basis of iron content, one would expect burning Illinois No 6 coal to result in lower NO_x emissions than burning Wyodak coal. In fact, pilot plant and utility data show that NO_x emissions are primarily affected not by the coal itself but by how the coal is burned and that burning Wyodak coal may even result in slightly lower NO_x emissions than Illinois No 6. This is because Wyodak is a relatively reactive coal with a relatively high quaternary nitrogen functionality.

Formation of N₂O from Coal Nitrogen in Fluidized Bed Combustors

Nitrous oxide (N₂O) is a persistent greenhouse gas and has been implicated in destruction of stratospheric ozone. According to Wójtowicz 1993, its half life is in the range of 150 to 160 years compared with 0.5 to 5 days for nitric oxide. Almost half of the stratospheric ozone loss is due to N₂O, and a doubling of N₂O concentration from its current level (as of 1990) of 310 parts per billion (ppb) could decrease stratospheric ozone by 12%.

Nitrous oxide (N₂O) emissions may be significant from fluidized bed combustors, with emissions in the range of 20 to 250 ppm. According to Åmand and Lechner 1993, the dominant N₂O pathway is through the HCN intermediate, as follows:

The NH₃ intermediate may also form some N₂O but the yield is smaller than from the HCN route.

Aho et al. 1993 report that high concentrations of N₂O will form if HCN is artificially introduced into a post flame environment at temperatures around 730 to 900°C, but relatively small amounts of N₂O are formed if NH₃ is introduced. Tullin et al. 1993 also add that N₂O can form from the oxidation of char in the presence of NO. Wójtowicz 1993 estimate that char-formed N₂O contributes about 10% of the total N₂O in fluidized bed combustion.

Nitrous oxide emissions are very much temperature dependent. Nitrous oxide (N_2O) emissions significantly decrease with increasing temperature but nitric oxide (NO) emissions significantly increase with temperature. At higher temperatures (Tullin et al. 1993), significant $\text{H}\cdot$ and $\text{OH}\cdot$ radicals are formed that destroy N_2O . Fluidized bed combustors operate at temperatures of 700 to 900°C compared with about 1200°C for pulverized coal furnaces; the corresponding N_2O emissions are typically 50 to 150 ppm for fluidized bed combustors compared with < 5 ppm for pulverized coal combustors. Graphs of N_2O and NO emissions for different coals are presented as a function of temperature in a paper by Collings et al. 1993. Higher ranked coals produce more N_2O than lower ranked coals, and North Dakota lignites produced more N_2O than Wyoming subbituminous coals. In their test, the fluidized bed combustor operated at 1120 K and 20% excess air combusting PRB coal, and 3.42% of the fuel nitrogen was converted to N_2O , 8.34% was converted to NO, and 88.2% was converted to N_2 .

Table 3. Major Researchers With Supporting Institutions and Publication Interests

Researchers	Supporting Institution	Publications/Interests
L.D. Smoot W. Chen T.H. Fletcher K.J. Bateman W.F. Wells A. U. Blackham C.R. Monson G.J. Germane	Brigham Young University, Provo, Utah	Global Fuel-NO Rate Expressions; NO reburning mechanisms; effect of pressure on oxidation rate of chars; relation between coal reactivity and structure; also paper (Blachkam) on combustion of large char particles; also paper (Monson and Germane 1993) on a high-pressure drop tube furnace for coal combustion studies.
F. Derbyshire	University of Kentucky, Lexington, KY	Changes in vitrinite structure of coal during thermal processing
S. Eser R.G. Jenkins C. Song H.H. Schobert	Amoco Research Center, Naperville IL; also Pennsylvania State Univ.	Changes in Wyodak and Illinois coals during heating in a helium atmosphere between 150 and 1000 psi (interest is in coal conversion processes, especially liquefaction)
S. Niksa S. Cho	SRI International, Menlo Park, CA	NOx formation in pulverized coal flames (experimental)
P.R. Solomon R. Bassilakis Y. Zhao M.A. Serio	Advanced Fuel Research, Inc., East Hartford, CN	Coal pyrolysis; published data on off-gases when heating bituminous and lignite in absence of air
B.R. Pease A.A. Levasseur O.K. Chow	ABB Power Plant Laboratories, Combustion Engineering Inc., Windsor CN	Assessment of coal fuel switching using a pilot plant; statement made, "The higher combustion reactivity of subbituminous coal compared with bituminous can be advantageous from a carbon burnout... under low-NOx firing applications."
K.S. Vorres	Argonne Nat. Lab, Argonne, IL	drying of Wyodak subbituminous and Beulah-Zap lignite coals

Researchers	Supporting Institution	Publications/Interests
W.P. Partridge Jr. N.M. Lauendeau	Purdue University, West Lafayette, IN	NO _x formation in diffusion flames
W.G. Willson S.A. Farnum M.E. Collings M.D. Mann B.C. Young	University of North Dakota, Grand Forks, ND	Williams noted that tars emitted under pressure during heat drying of lignites tend to coat the particle surface; Collings modeled N ₂ O emissions in circulating fluidized bed combustion; Mann reviewed N ₂ O emissions testing and abatement
O.I. Ogunsola	University of Alaska, Fairbanks, Alaska	Effect of thermal drying on oxygen functional groups in lignite (western Canada)
K. Zygourakis	Rice Univ., Houston TX	Effect of pyrolysis on coal macropore structure
T.L. Yeh T.C. Keener	University of Cincinnati, Cincinnati, OH	Use of a heated screw to achieve mild pyrolysis of an Ohio coal
S.R. Keleman M.L. Gorbaty	Exxon Research and Eng. Co., Annandale, NJ	Nitrogen forms in coal
B.A. Wong G.R. Gavalas R.C. Flagan	California Inst. of Tech., Pasadena, CA	Shrinking of porous coal particles during combustion
A. Atal Y.A. Levendis	Northeastern University, Boston, MA	Combustion behavior of coal and waste automobile tires
A.F. Sarofim S. Goel	Mass. Inst. of Tech., Cambridge, MA	NO and N ₂ O formation in fluidized beds; with C.J. Tullin et al. 1993, Chalmers Univ. of Technology, Göteborg, Sweden
D. Marlow S. Niksa	Stanford University, Stanford, CA	combustion of soot from coal
M. Nishioka	BCR Nat. Lab., Pittsburgh, PA	Coal structure (bituminous and lower rank)
J.O.L. Wendt J.B. Mereb	University of Arizona, Tucson, AZ	Reburning mechanisms for NO _x abatement (laboratory coal combustor)
D.S. Ross B.H. Loo	SRI International, Menlo Park, CA	Hydrothermal treatment of Wyodak coal
J. Crelling	Southern Illinois University, Carbondale IL	Release of nitrogen during combustion of coal chars (experimental)
W.I. Friesen O.I. Ogunsola E. Furimsky	CANMET, Devon, Alberta, Canada	Changes in low-rank coal pore structure and component upgraded by heating in a nitrogen atmosphere up to 500°C. another paper Furimski) of effect of iron mixed with subbituminous coal on NO _x formation.
C.M.H. Brereton C.J. Lim J.R. Grace	University of British Columbia, Vancouver, BC, Canada	Pitch and coal combustion in circulating fluidized bed combustors
A. Williams H.K. Chagger P.R. Goddard V. Dupont M. Pourkashanian A.B. Fuertes	University of Leeds, Leeds, UK	Modeling of NO _x formation during pulverized coal combustion; also interactions of SO ₂ and NO _x ; two papers by V. Dupont on NO _x formation in natural gas flames; paper by Fuertes on direct measurement of coal ignition temperatures

Researchers	Supporting Institution	Publications/Interests
M.J. Richardson	National Physics Laboratory, Teddington, UK	Specific heats of coals, cokes, and ashes
K.M. Thomas W.X. Wang S.D. Brown J.E. Varey C.J. Hindmarsh K. Grant B.M. Gibbs	University of Newcastle upon Tyne and University of London, UK.	NO release and reactivity of coal chars; also N ₂ O emissions from fluidized bed combustors; also detection of intermediate compounds in combustion and pyrolysis of coals
K.M. Laughlin D.G. Gavin G.P. Reed M.A. Dorrington	British Coal Corp., Cheltenham, UK	Nitrogen chemistry during pressurized fluidized bed combustion of coal
C.F.M. Coumbra I. Gulyurla H. Esparteiro	Instituto Superior Técnico, Lisboa Codex, Portugal	Mathematical model for predicting NO _x emissions in a 300 MWe front wall fired pulverized coal combustor; another paper on emissions from burning waste oil; two papers on NO and N ₂ O formation in fluidized bed combustors
J.P. Hämäläinen J.L. Tummavuori M.J. Aho Y. Lu J. Saastamoinen I. Hippinen	Technical Research Center of Finland, Jyväskylä, Finland; also Espoo, Finland	Formation of HCN and NH ₃ from European coals and peat; some papers consider effect of pressure; looked at effect of coal composition; devolatilization and char formation under pressurized fluidized bed conditions; also NO _x and N ₂ O formation and control
J. Leppälähi M.J. Aho P.M. Pirkonen	VIT Energy, Finland	literature review on nitrogen emissions from gasification of coal; also papers (Aho) on effect of pressure
H. Miettinen J.E. Johnsson L.-E. Åmand A. Jensen B. Leckner	University of Göteborg or Chalmers University of Technology, Göteborg, Sweden; Technical Univ. of Denmark, Lyngby, Denmark	N ₂ O emissions in fluidized bed combustors; also NO _x formation in pressurized fluidized bed combustors
A. Nordin L. Ericksson M. Öhman	University of Umeå, Umeå, Sweden	NO _x emissions and reduction in fluidized bed combustors
M.A. Wójtowicz J.R. Pels J.A. Moulijn W. Lin J. Andries	Delft Univ. of Technology, Delft, The Netherlands	Fate of coal nitrogen during pyrolysis and combustion; also papers on N ₂ O emissions in fluidized bed combustion; Lin modeled SO ₂ and NO _x emissions in fluidized bed combustion
D.J. Morgan J.P. Smart M.A. Wójtowicz	International Flame Research Foundation, The Netherlands	Multifuel reburning for NO _x reduction; another paper on N ₂ O emission control in fluidized bed combustors

Researchers	Supporting Institution	Publications/Interests
J.B. Illerup K. Dam-Johansen	Technical University of Denmark, Lyngby, Denmark	Characterization of a full-scale pulverized coal boiler (temperature, NO _x)
A. Kicherer H. Spliethoff H. Maier K.R.G. Hein U. Greul	University of Stuttgart, Stuttgart, Germany	Air-staging and reburning to reduce NO _x emissions from pulverized coal combustors (experimental, 0.5 MW test combustor)
B. Bonn G. Pelz H. Baumann	DMT-Institute for Cokemaking and Fuel Technology, Essen, Germany	N ₂ O formation in fluidized bed boilers
J.-R. Richard	Laboratory de Combustion et Systèmes Reactifs, Orleans Cedex, France	Effect of pressure on NO _x formation
P. Davini P. Ghetti	Pisa University, Pisa, Italy	Char surface area during combustion of pulverized coal particles
M.J. Lázaro J.V. Ibarra L.F. de Diego	Instituto de Carboquímica, Zaragoza, Spain	Release of nitrogen during combustion of coal chars in fluidized bed combustors
A. Karcz S. Porada J. Tomeczek H. Palugniok	Univ. of Mining and Metallurgy, Kraków, Poland; also Silesian Tech. Univ., Katowice, Poland	Pressure pyrolysis of coals; also properties of coal undergoing pyrolysis
Y. Ohtsuka H. Mori K. Asami H. Yamashita A. Tomita K. Nonaka T. Watanabe	Tuhoku University, Sendai, Japan	Distribution of nitrogen species emitted during pyrolysis of a subbituminous coal (effect of iron and mineral matter); effect of addition of iron catalyst to coal to improve N ₂ and lower NO; also paper (Yamashita et al 1993) on effect of char on reduction of NO.
S. Kambara T. Takarada Y. Yamamoto K. Kato	Idemitsu Kosan Co. Ltd, Chiba, Japan; Gumma University, Gumma, Japan	Relationship between coal-N and NO _x emissions; also (Kambara et al. 1995) relationship between functional forms of coal-N and NO _x precursors during rapid pyrolysis
P.F. Nelson M.D. Kelly	CSIRO, North Ryde, Australia	Conversion of coal-N to NO _x precursors under rapid heating
J.O. Chae Y.N. Chum	Inha University, Incheon, Korea	NO _x emissions, experimental two-stage combustor, pulverized coal

Comments: (1) listings do not include work on catalytic reduction of NO_x in the flue gas (e.g. by carbon, by injection of ammonia or urea, etc.), and (2) some papers on coal combustion or pyrolysis or drying, especially under pressure are included in this listing.

NO_x LAWS AND REGULATIONS FOR COAL-FIRED ELECTRIC POWER PLANTS

Clean Air Act of 1990

Two major sections of the Clean Air Act of 1990 affect maximum allowable NO_x emission limits from coal-fired power plants. The first section is contained in Title I Part A, Air Quality and Emission Limitations, and Part D, Plan Requirements for Nonattainment Areas. The second is under Title IV, Acid Deposition Control. Title IV section 407 sets specific NO_x limits from coal-fired boilers. Title I, Sections 107, 108, and 109 require the Environmental Protection Agency (EPA), referred to as the Administrator in the Clean Air Act, to set national ambient air quality standards and to review these standards every five years.

Areas of the country where ambient air quality standards are not met are called nonattainment areas for that pollutant. States must submit a plan to the EPA outlining how they will achieve attainment. Because large sources, such as utilities, are easier to target and control than many small sources, the result is that state or regional permitting agencies often set lower NO_x emission limits than that specified under Title IV Section 407.

1. Title IV, Acid Deposition Control, Section 407. Specific NO_x Limits

Section 407 of Title IV of the Clean Air Act establishes maximum allowable annual emissions for several classes of coal-fired boilers. There are two phases for compliance. Compliance for Phase I has been in effect since January 1, 1996. Compliance for phase II goes into effect January 1, 2000. Regulations are in 40 CFR Part 68. (See Table 4.)

Table 4. Phase I NO_x Emission Limits Specified in the Clean Air Act

Boiler Type	NO _x Emissions, lb/mmBtu
Tangentially Fired	0.45
Dry Bottom Wall-fired (except units applying cell burner technology)	0.50

The NO_x emissions listed in Table 5 are given as calendar year averages. Also, quarterly reports must be sent to the U.S. EPA. States may adopt an "emissions cap and trade" program in which utilities may over-control at one plant to offset emissions at another plant, providing that overall NO_x emissions are less than if each plant met the limits.

Table 5. Phase II NO_x Emission Limits
(Final Rule Published in Federal Register Dec. 19, 1996)

Boiler Type	NO _x Emissions, lb/mmBtu
Tangentially Fired	0.40
Dry Bottom Wall-fired (except units applying cell burner technology)	0.46
Wet-Bottom Wall-fired > 65 MW	0.84
Units Applying Cell Burner Technology	0.68
Cyclone > 155 MW	0.86
Vertically Fired	0.80

2. National Ambient Air Quality Standards

The three pollutants that affect NO_x emission limits set by regulatory agencies are NO_x, ozone, and particulates. Current and proposed national standards for these pollutants are listed in Table 6. The Clean Air Act requires the EPA to review national ambient air quality standards every five years and set new standards based on health considerations.

Table 6. National Ambient Air Quality Standards for NO_x , Ozone, and Particulates

Pollutant	Current Standards	New Standards Proposed Nov. 1996; rules finalized July 1, 1997
NO _x (as equivalent NO ₂)	0.053 ppm	0.053 ppm
ozone	120 ppb	80 ppb
particulates	annual average: 50 µg/m ³ daily maximum: 150 µg/m ³ particles regulated down to and including 10 µm	annual average: 15 µg/m ³ daily maximum: 50 µg/m ³ particles regulated down to and including 2.5 µm

Plans for meeting the proposed new standards are due in 2002 for particulates and 2000 for ozone, with full compliance due several years later.

The country is now in compliance with NO_x standards, but there are nonattainment areas for ozone and particulates. This will be especially true if the proposed standards take effect. Ozone is a component of smog produced when nitric oxides react with organic compounds in the air. The proposed 2.5 µm size limit for particulates is in the range of nitric oxide condensation products (the brown haze around some cities from volatile organics, sulfur dioxide, and nitric oxides). Although coal-fired power plants probably contribute 20% (source: Nescaum, in *Power* Feb. 1994) to ambient NO_x (compared with 45% from transportation sources and most of the remainder from agriculture fertilizers), it is easier for regulatory agencies to target a few large

sources than many small sources. In a December 13, 1996, press release, the EPA estimates that electric utilities contribute approximately 33% of the NOx emissions.

Another part (Title I, Part D) of the Clean Air Act that affects limits on power plant NOx emissions is Section 169A on visibility protection for Federal Class I areas (for example, Grand Canyon National Park). This is also related to the brown haze problem. The result may be more stringent emission limits for some facilities than if they were located in other parts of the country.

U.S. EPA Regulations (40 CFR Part 60.44)

The EPA regulations establish NOx emission limits by coal type rather than by the type of boiler. (See Tables 7 and 8.) All NOx emission rates are expressed in terms of equivalent NO₂ even though NOx is emitted typically as NO and sometimes as N₂O. State or regional permitting agencies may specify more stringent NOx limits than EPA regulations in order to meet ambient air quality standards in nonattainment areas. These are separate, stand-alone regulations from the Clean Air Act now in effect. The utility must meet whichever is most stringent.

If a mixture of coals or a mixture of coal and natural gas is used, the emission limit is prorated according to the heat value of the fuel. NOx emission limits for natural gas are either 0.10 or 0.20 lb/mm Btu, depending on the heating rate and size of the facility. Using natural gas as a reburning fuel in a coal-fired power plant is one of several methods available that effectively reduce NOx emissions. A utility employing this approach might derive 20% of the heating value from natural gas and 80% from coal, but the NOx reduction achieved may be more than offset by the more stringent EPA limit for coal alone.

Table 7. EPA NOx Emission Limits Specified in 40 CFR Part 60.44a for Utilities Combusting More Than 250 Million Btu/hr of Fossil Fuel

Coal Fuel Type	NOx Emission Limits, lb/mm Btu
gaseous coal-derived fuel	0.50
liquid coal-derived fuel	0.50
solid coal, anthracite	0.60
solid coal, bituminous	0.60
solid coal, subbituminous	0.50
solid coal, more than 25% lignite from North Dakota, South Dakota, or Montana combusted in a slag-type furnace	0.80
solid coal, more than 25% lignite from North Dakota, South Dakota, or Montana not combusted in a slag-type furnace	0.60
solid fuel derived from coal	0.50

Table 8. EPA NO_x Emission Limits Specified in 40 CFR Part 60.44b for Utilities Combusting Between 100 and 250 Million Btu/hr of Fossil Fuel

Coal or furnace type	NO _x Emission Limits, lb/mm Btu
mass-feed stoker	0.50
spreader stoker and fluidized bed combustion	0.60
pulverized coal	0.70
coal-derived synthetic fuels	0.50
lignite mined in North Dakota, South Dakota, or Montana and combusted in a slag-type furnace	0.80
other lignite or lignite not combusted in a slag-type furnace	0.60

A fuel-neutral NO_x emission limit of 0.15 lb/mm Btu under consideration by the EPA was shelved, at least for now. This limit would apply to utilities regardless of the kind of fuel. Critics pointed out that the limit was not fuel-neutral, as economics favored switching to natural gas. The limit could be met with coal only by applying very expensive technologies.

Determination of NO_x Emission Rates

Nitrogen oxide emission rates are measured using a continuous monitoring system (40 CFR Part 60.47a; 40 CFR Part 60 Appendix F, procedure 1), which has been calibrated according to method 7 procedures specified under 40 CFR 60 Appendix A: Test Methods. At least two data points are required each hour from which a 1-hour average is calculated, and data must be taken for at least 18 hours/day and 22 days per 30-day month. The numbers are converted from parts per million (ppm) to lb/mm Btu using procedures specified by Method 19 (also in 40 CFR Part 60, Appendix A). The utility then calculates a 30-day rolling average according to procedures specified under 40 CFR Part 49b.

The calculation of NO_x emission rates from ppm data first involves converting to pounds of NO_x per standard cubic feet (lb/scf) and then converting scf to 10⁶ Btu using an F factor. The procedures are specified by method 19 under 40 CFR Part 60 Appendix A. Method 19 allows the user to work in English or metric units, and calculate an F factor based on oxygen (dry basis), oxygen (wet basis), or carbon dioxide (dry or wet basis). For the purpose of illustration, the procedure for oxygen (dry basis) and in English units is described below.

1. The ppm NO_x on a water-free basis is converted to lb/scf by multiplying by 1.194×10^{-7} (dscf = dry standard cubic feet).

2. An F factor is calculated (Method 19 calls the oxygen-dry basis F factor F_d). The utility has the option of either using an F factor based on the type of coal burned or calculating an F factor from the coal ultimate analysis. (See Table 9.)

Table 9. F Factor for Converting dscf to mm Btu

Coal	F_d (units: dscf/ 10^6 Btu)
Anthracite	10,100
Bituminous	9,780
Lignite	9,860
Based on ultimate analysis	$F_d = 10^6 [3.64 (\%H) + 1.53 (\%C) + 0.57 (\%S) + 0.14 (\%N) - 0.46 (\%O)] / G$

where G = gross caloric value of fuel, Btu/lb.

3. The emission rate is calculated

$$E = C_d F_d [20.9 / (20.9 - \% O_{2d})]$$

E = NOx emission rate, lb/mm Btu

C_d = NOx concentration, lb/dscf

F_d = F factor based on oxygen, dry basis

$\%O_{2d}$ = volume percent oxygen on a water-free basis

POWER PLANT COMPLIANCE WITH NOx EMISSION LIMITS

General Comments

In a Dec. 13, 1996, press release, EPA estimates that 85 to 90% of the coal-fired power plants can meet Clean Air Act Title IV Phase II NOx emission limits by employing a combination of low NOx burners and good computerized combustion control. Some utilities have reported improvement by switching to a different coal. If regulatory agencies impose more stringent standards, then additional technologies may need to be used, such as reburning using natural gas or other fuel, selective catalytic reduction (SCR) or selective noncatalytic reduction (SNCR) technologies. More stringent requirements are based on the Clean Air Act Title I compliance (ground-level ozone and smog air quality) rather than on Title IV compliance (specific NOx emission limitations). There is a lot of competition among equipment vendors offering technologies promising low NOx emissions, and some have complained (Leone 1994) that promises of low emissions have encouraged regulators to set even lower NOx emissions as a

condition for power plants to obtain construction permits. This section reviews technologies used by new and existing power plants. Many plants use a combination of technologies.

Keeping the Furnace Clean

In a paper (Boocher 1995) presented at the 1995 International Joint Power Generation Conference, Joel Boocher of Diamond Power Specialty Co. said that NO_x emissions may be reduced by as much as 40% by cleaning the furnace of slag deposits. The several power plants participating in the study showed between 15% and 40% NO_x emission reduction after furnace cleaning with waterlances. Two of the plants used Powder River Basin coal. The slags produced from western coals were more tenacious and more resistant to wallblower cleaning than those of eastern coals. The furnaces were cleaned using a waterlance, which delivers high-pressure water through jets that travel along the tube wall. Heavy slag deposits in the furnace reduced local radiation heat transfer rates, and less heat transfer meant higher flue gas temperatures, as high as 3000°F (1650°C). The higher temperatures resulted in generation of significant thermal NO_x.

Hill 1996 of Dairyland Power Cooperative Inc., La Crosse, Wisconsin, reported better control over NO_x emissions by sootblowing in a 400-MW turbo-fired unit burning PRB coal with low-NO_x burners. The NO_x emissions were reduced from 0.6 to 0.3 lb/mm Btu in a test before and after cleaning. Following the test, waterlances that operate based on a measurement of heat flux in various regions of the waterwalls were installed at the J.P. Madgett station; each lance operates for five minutes every five or six hours. This system has been in operation since 1992.

Kind of Furnace

While switching furnaces may not be an option for utilities, it should be mentioned that the kind of furnace affects NO_x emissions and NO_x reduction capability. Furnaces with generous dimensions are more capable of minimizing NO_x formation and completing carbon dioxide burnout. Tight furnaces with high release rates are conducive to increased NO_x emissions. Operating temperatures in tight furnaces are generally higher, which leads to the formation of thermal NO_x. Wall-fired and tangentially fired units are more easily retrofitted with low-NO_x burners than cyclone or turbo furnaces. Circulating fluidized bed boilers inherently operate at lower temperatures and have lower NO_x emissions than pulverized coal boilers, but can emit some N₂ O. Cell burners (manufactured in 1950s and 1960s) rapidly mix pulverized coal and combustion air resulting in highly turbulent and efficient combustion, but NO_x emissions are high, typically 1.0 to 1.8 lb/mm Btu.

Coal Switching

Much has been published (Makansi 1994a; Kramerik and Rupinskas 1996; McComas and Morris 1995) on coal switching as a method of meeting Clean Air Act compliance for sulfur dioxide. Very little has been published on NO_x. Many utilities have switched to low-sulfur, western subbituminous coal as a method of compliance. Alternatives such as full scrubbing have disadvantages, for example, scrubbing may rob the utility 8% of its power production and there are scrubber solids disposal costs. Switching from eastern to Powder River Basin (PRB) coal also involves major modifications in coal handling, coal preparation, to the furnace itself, and ash handling. Makansi 1994a has documented experiences of several utilities in switching to PRB coal.

Documentation on NO_x is complicated by the fact that changes in coal also change combustion characteristics, and equipment must be optimized for burning that coal. There is mention of a reduction in NO_x emissions from an unnamed facility (Makansi 1994b) with low-NO_x burner technology installed when it switched from high-sulfur Illinois coal to PRB coal. When a utility switches from a high-sulfur coal to PRB coal, many other changes are made, so it is difficult to get a comparison based on the effect of a coal change only.

The University of North Dakota (Zygarlicke et al. 1995) compared the NO_x levels in parts per million of four different coals combusted in a bench-scale drop tube furnace, first under normal conditions and then under lower temperatures and low excess air conditions. Every effort was made to control temperatures, oxygen concentrations, and retention times so that the conditions were the same. See Table 11.

Table 11. Comparison of NO_x Emissions from Combusting Four Different Coals

Coal	Conventional Conditions (21% excess air, max temp 1530°C)	Lower Temperature and Excess Air Conditions (3% excess air, max temp. 1430°C)
Black Thunder Subbituminous	NO _x = 359 ppm	166
Rochelle Subbituminous	440	186
Illinois No. 6 Bituminous	527	262
Beulah Lignite	364	184

Tight Computerized Combustion Control

Optimized combustion control is essential (Makansi 1996a) in any power plant program designed to reduce NO_x emissions without loss in boiler performance. NO_x emissions reduction

is intimately tied to the complexities of combustion. Optimization includes use of computer software packages to precisely control stack oxygen readings ($\approx 3\%$ excess oxygen), air and fuel flows to each burner, stack emissions, and other parameters. An example is sequential process optimization, developed by Ultramax Corp., Cincinnati, Ohio, and enhanced by Electric Power Research Institute, which has been applied at a number of utilities (e.g. TVA, Georgia Power Co., Carolina Power and Light, Detroit Edison, Illinois Power Co., and Central & Southwest Services Inc.).

Using the Ultramax software, the TVA New Johnsonville Plant reduced NO_x emissions by 5 to 15%, which was enough to enable it to comply with the Phase I Clean Air Act Title IV limit of 0.45 lb/mm Btu without special low-NO_x burners. Under full-load optimization, the TVA units (T-fired) varied from 0.39 to 0.43 Btu/mm Btu. The Phase II limit, due in the year 2000, is 0.40 lb/mm Btu. Another software package is called neural-network-based, closed-loop, supervisory control (Neusight), developed by Pegasus Technologies Corp., Painesville, Ohio. After testing the Neusight package at its New Castle Unit 5, Pennsylvania Power and Light reported a 25% reduction in NO_x emissions, which was enough to enable it to meet limits set by state regulators without installing low-NO_x burners (Makansi 1996a). Another system is EPRI's Gnocis, which is undergoing testing (in 1996) at Alabama Power Co.'s Gaston Unit 4. A software package developed jointly by Lockheed Martin Control Systems and New York State Electric and Gas Co. (called InEC) is undergoing testing at an 85-MW tangentially fired unit at the Goudey Station. It should be mentioned that it takes months to achieve these results, even after the necessary modifications are installed to optimize the boiler.

Low-NO_x Burners

The use of low-NO_x burners is closely tied with optimum combustion control. Storm 1993 has listed the following ten prerequisites for optimum combustion:

1. The furnace exit flue gas must be oxidizing ($\sim 3\%$ excess oxygen).
2. Fuel fineness must be greater than 72% passing 200 mesh and less than 0.5% remaining on 50 mesh.
3. Fuel distribution must be within the range of $\pm 5\%$ to $\pm 10\%$ from burner to burner.
4. The primary air flow must follow a defined "ramp," usually with an air/fuel ratio of 1.8:1 at high pulverizer loads.
5. The primary air flows from each pulverizer must be measured and controlled for balance (within 10%) compared with other pulverizers.
6. Secondary air flow to each group of burners must be proportional (within 10%) to the fuel supplied to the individual burners.
7. Overfire air must be measured and controlled.

8. Fuel flow to the pulverizers must be measured and controlled to the best tolerances available.
9. Pulverized-coal line velocities must remain above minimum velocity at low loads to minimize fuel settling and line plugging.
10. The fuel rate to the pulverizers must be constant with smooth flow rate changes during boiler load changes.

Low-NO_x burners work on the dual principle that NO_x emissions are reduced by depressing combustion-zone temperatures and by delaying the admission of sufficient oxygen to complete combustion in an internally staged burner with overfire air ports (OAP), or with fuel staging. The major problem with low-NO_x burner retrofits is that they can easily leave unburned carbon in the ash. If unburned carbon remains in the ash, the power plant is not fully using the heat content of the fuel; also, the ash itself may be unsuitable for reuse applications, such as construction. To minimize unburned carbon, the burner equipment must be properly designed, and combustion control must be optimized. Examples of low-NO_x burner retrofits are presented in Table 12.

Table 12. Low-NO_x Burner Retrofit Coal-fired Utility Published Examples

Utility	Unit	Coal	Low NO _x Burner	NO _x Before Retrofit, lb/mm Btu, full load	NO _x After Retrofit, lb/mm Btu, full load
Black Hills P&L Co.	22-MW Simpson Unit 5 (front wall fired)	Wyodak coal	B&W DRB-XCL with OFA	1.1	0.37 (Makansi 1993)
Alabama Power Co.	248-MW Gaston Unit 2 (opposed wall fired)	Pyxis coal	B&W DRB-XCL with OFA	0.8	0.4 (Makansi 1993)
Public Service Co. of Colorado	100-MW Arapahoe Unit 5 (roof fired)	western bituminous	B&W DRB-XCL with OFA	1.15	0.4 (Makansi 1993)
Dayton Power & Light Co.	605-MW Stewart Unit 4 (opposed wall fired)	eastern bituminous	S-burners with OFA ports	1.17	0.53 (Makansi 1993)
Ohio Edison Co.	Sammis Unit 6 (cell burners)	eastern bituminous	B&W DRB-XCL with OFA	1.35	0.4 (Makansi 1993)
Southern Calif. Edison Co.	215-MW Mandalay Unit 1	natural gas or oil	S-burners with OFA ports	Gas: 0.18 (150 ppm); oil 0.22 (180 ppm)	Gas: 0.03 (25 ppm); oil 0.13 (105 ppm) (Makansi 1993)
Wisconsin P&L Co.	310 MW Oak Creek Unit 7	no inform.	Foster Wheeler Tangential Low-NO _x with fuel staging	0.68	0.35 (Morris and Sweeney 1995)
Wisconsin P&L Co.	100-MW Dewey Unit 2, Cyclone	eastern bituminous	S-burners with fuel staging	0.83	0.38 (Makansi 1993)

Utility	Unit	Coal	Low NOx Burner	NOx Before Retrofit, lb/mm Btu, full load	NOx After Retrofit, lb/mm Btu, full load
American Power Co.	600-MW Muskingum River Unit 5 Cell Burner	eastern bituminous?	Riley Stoker CCV	1.2 (1.0 to 1.8)	0.51 (see Penterson and Dorai 1995)
Georgia Power Co.	Yates Plant, several T-fired units	eastern bituminous?	ICL flame attached nozzle; Yates Units 6 & 7 with SOFA	Reductions of NOx of 40% typical; see Jones 1995	vendor guarantee meets 0.4 lb/mm Btu limit
Georgia Power Co.	Bowen Plant, several T-fired units	eastern bituminous?	ICL flame attached nozzle with SOFA	see Jones 1995a	vendor guarantee meets 0.4 lb/mm Btu limit
United Illuminating Co.	390-MW Bridgeport Harbor Unit 3 (T-fired)	Kentucky low-sulfur coal	ABB-CE Services TFS2000 sm R burner with OFA	0.55 to 0.66	exceeds 0.38 lb/mm Btu Connecticut limit (ozone non-attainment area); see Jones 1995b
Kentucky Utilities	517 MW Ghent Unit 1 (T-fired)	Kentucky bituminous 11400 Btu/lb	ABB-CE concentric with SOFA	0.539 (0.471 combustion control only)	0.37 (Gabrielson et al. 1995)
Housier Energy	each 116.6 MW Frank E. Ratts Units 1 & 2	not specified except low sulfur	Foster Wheeler with fuel staging	1.1 (Reynolds et al. 1995)	Unit 1: 0.48 Unit 2: 0.46
Duquesne Light Co.	Elrama Power Stat., Units 1 & 2 each 110 MW, Unit 3 120 MW	high volatile bituminous	Energy Systems Assoc. (Pittsburgh) with SOFA	0.8 (all units) (Bionda et al. 1995)	Unit 1: 0.44 Unit 2: 0.43 Unit 3: 0.42
Owensboro Municipal Utility	Elmer Smith Station, 151 MW Unit 1 (cyclone); 265 MW Unit 2 (T-fired)	Western Kentucky (3% S, 1.55% N, 11,000 Btu/lb)	International Combustion Concentric Firing with close coupled OFA and flame attached nozzle	Unit 2: 0.6 (Conn et al. 1995)	Unit 2: 0.37
PECO Energy Co.	160 MW Cromby Unit 1	Eastern bituminous	B&W PRB-XCL with OFA	0.61 to 1.0 (Trego et al. 1995);	0.44 (can get 0.34 with flyash carbon of 11.3%); regulatory limit 0.35
American Electric Power Service Co.	240 MW Glen Lyn Unit 6; 165 MW Conesville Unit 3 (both front wall fired)	Glen Lyn: SW Virginia; Conesville: Ohio coals	DB Riley Inc. CCV Burners (venturi) without OFA.	Glen Lyn: 0.50 to 0.53 Conesville: 1.1	Glen Lyn: 0.48 to 0.53 Conesville: 0.48 to 0.53 (Penterson and Dorman 1995)

Comments on burners: S-burner is a sliding damper burner with air measurement features; DRB-XCL is a dual-register burner with sliding damper of S-burner type marketed by Babcock & Wilcox; OFA means overfire air ports; fuel staging means that the fuel is split into two streams, each burning with a different stoichiometry; Riley Stoker Co. CCV burner is a controlled combustion venturi retrofit that uses neither OFA nor fuel staging; ICL (International Combustion Co. of Atlanta, GA) has also developed a low NOx burner with an option of separated overfire air (SOFA); the ABB C-E Services, Inc., Windsor, Conn. burner is described by Jones 1995b.

Several authors (Jones 1995b; Storm 1993) have emphasized that utilities cannot simply install low-NOx burners in an existing boiler and expect to see major reductions in NOx emissions. Experience demonstrates that burner retrofits require more precise combustion and fuel flow management than the original designs.

Foster Wheeler has summarized its field experience (Steitz and Cole 1996) with low-NOx burners in wall fired installations. The design of low-NOx burners is critical; the authors remark that even very minor changes in the discharge configuration of the nozzle design has resulted in NOx reductions on the order of 25-30%. Additional field experience with other low-NOx burners is summarized by Thompson et al. 1996.

Power magazine (a McGraw Hill publication) maintains a web site at where utilities can communicate their experience using low NOx burners (<http://www.powermag.com>; click under "LNB Challenge"). Some of this information is summarized in the public domain (Jones 1997). The two main problems that have surfaced using low-NOx burners are (1) excessive waterwall tube wastage and (2) increased carbon and fly ash. Both problems are related with the need to have a fuel-rich reducing atmosphere to convert fuel nitrogen to N_2 rather than NO. In an oxidizing atmosphere, protective scales are formed on the water tubes, which resist further corrosion. In a reducing atmosphere, sulfides and not oxides are formed; the sulfides form iron sulfides with the water tube surfaces. The result is excessive tube corrosion. Additionally, not all the fuel is burned in a reducing atmosphere, resulting in excessive carbon in the flyash. Unburned carbon in the flyash represents loss in heating value of the fuel and creates a flyash disposal problem. Load cycling exacerbates the problem because it changes the flue-gas composition and the oxidizing/reducing characteristics.

The problem is trying to maintain a tight balance between the need to have a fuel-rich reducing atmosphere for minimum NO formation but also have an oxidizing atmosphere to minimize tube wastage and unburned carbon in the flyash. Tight, computerized control of the fuel/air characteristics helps achieve the right balance, but judging from utility response (Jones 1997) it is not an easy thing to accomplish. For example, in a test (Trego et al. 1995) with a wall-fired unit, PECO could achieve 0.44 lb NOx/mm Btu at 3% carbon in their flyash (B&W DRB-LCL low-NOx burner) and 0.34 lb/mm Btu at 11.3% carbon in their flyash.

According to Pepco (Potomac Electric Power Co., Washington, D.C., cited by Jones 1997), the burning of coals containing more than 1.5% sulfur in low-NOx burners particularly results in excessive water tube corrosion. To minimize corrosion, Pepco is experimenting with chromized replacement panels and high-alloy weld overlays. Other utilities (e.g. Cinergy, Cincinnati, Ohio, also cited by Jones 1997) are also experimenting with tube chromizing and weld overlays and also diverting combustion air to the tube regions to help maintain oxidizing conditions. New York State Electric & Gas Co. (Bingham, NY) also has gone to the expense of

upgrading pulverizers to improve coal fineness by 30% and has further upgraded their low-NOx burners to a concentric firing system with SOFA. Better coal fineness improves char combustion and reduces the carbon content of water tube deposits (and therefore resulting in less sulfide corrosion). A lot more is involved than the expense of installing low-NOx burners and computerized combustion control. Utilities have challenged the U.S. EPA on the EPA-estimated costs (e.g. \$270/ton for wall-fired units and \$611/ton for tangentially fired units for phase I) for NOx controls.

The use of Powder River Basin coals may offer the benefit of reduced NOx emissions compared with burning eastern coals when using low-NOx burners. According to George Offen 1997, Electric Power Research Institute (EPRI) program manager for NOx emissions, utilities have reported a 20 to 30% decrease in NOx emissions compared with burning eastern coals, but the data are proprietary and cannot be released to non-EPRI members. The limited information in the public domain (*Power* magazine, the Internet, and Makansi 1993) indicates numbers of around 0.3 Btu/mm Btu (Dairyland Power Cooperative Inc.) or 0.38 lb/mm Btu (Black Hills Power and Light) with PRB coals and tangentially fired boilers compared with often higher numbers for eastern coals (Table 12). The EPA limit (phase II controls) is 0.4 lb/mm Btu.

From a coal analysis of nitrogen functional forms, the formulations presented in Kambara et al. 1995 show that burning Wyoming subbituminous coal with low-NOx burners should result in lower NOx emissions than burning eastern coals with low-NOx burners. However, it is necessary to keep the furnace clean using waterlances to remove any slag buildup, otherwise NOx concentrations will increase (Hill 1996). The lower sulfur content of PRB coals should also be beneficial in reducing water tube corrosion. The experiences of three utilities in switching from high-sulfur eastern coal to PRB coal are documented by Kramerick and Rupinkas 1995 and McComas and Morris 1995.

Natural Gas Co-Firing and Reburning

Natural gas co-firing is the combustion of natural gas with coal in the primary combustion zone of coal-fired boilers. In most co-firing applications, the natural gas contribution is limited to about 20% of the thermal input. The gas may be supplied by ignitors, warmup guns, or gas burners. Benefits are (1) increased capacity, (2) improved precipitator performance, (3) enhanced coal-switching capability, (4) reduced boiler startup and warmup times, and (5) reduced SO₂ and NOx emissions.

Reburning is a co-firing technology specifically directed towards reducing NOx emissions. In gas reburning, natural gas is injected into the boiler above the main heat-release zone to convert nitric oxide (NO) to molecular nitrogen. According to Swanekamp 1996, maximum NO

reduction is achieved when sufficient gas is added to create sub-stoichiometric conditions in the reburn zone; following the reburn zone, overfire air must be added to complete the process. Natural gas provides 15 to 20% of the heat input. Overall NO_x emissions are reduced by 50 to 75%, as shown in Table 13.

Selective Catalytic Reduction (SCR)

Ammonia is added to the flue gas to reduce NO_x to water and elemental nitrogen. The reaction normally proceeds at temperatures between 1600°F and 2200°F (871°C and 1204°C), but a catalyst is used to promote the reaction at a lower temperature. The technology can be used to achieve 90% and greater NO_x reduction in oil-fired or gas-fired units, which have a more confined heat release zone compared with coal-fired units. Still, up to about 70% NO_x additional removal has been achieved with coal-fired systems. An example is the 285-MW Chamber Works plant in Carney's Point, N.J., with an inlet NO_x flue gas concentration of 196 ppm, outlet NO_x of 73 ppm, catalyst temperature in the range of 570 to 750°F, and ammonia slip of 5 ppm. With gas turbine systems, NO_x emissions below 10 ppm (even below 7 ppm) are possible with SCR units.

Table 13. Published Examples of Gas Reburning

Utility	Unit	Coal	Baseline NO _x lb/mm Btu, full load	NO _x With Reburning, lb/mm Btu, full load
Illinois Power	71 MW Hennepin Unit 1 T-fired	high sulfur Illinois coal	0.75	0.245
City Water Light & Power	30 MW Lakeside Unit 7, Cyclone	not specified	0.95	0.344
Public Service Co. of Colorado	172 MW Cherokee Unit 3, wall-fired	Colorado low sulfur bituminous	0.73 baseline 0.48 with Foster Wheeler Low-NO _x fuel staging	0.26 (both gas reburning and low-NO _x burner)

From Folsom et al. 1996.

In a coal-fired unit, the SCR unit may be placed either between the economizer and air heater, between the particulate collection device and a flue-gas desulfurization unit, or after the flue-gas desulfurization unit. In a gas-turbine application, the SCR unit is typically placed within the heat recovery steam generator.

Several classes of catalysts may be used. One class is primarily aluminum oxide. Another formulation includes vanadium pentoxide (the active ingredient) and titanium dioxide or aluminum

oxide (a carrier) with tungsten trioxide (reduces unwanted SO_2 oxidation to SO_3). Two other classes of catalysts are based on iron oxide or activated carbon. One problem is the oxidation of sulfur dioxide to sulfur trioxide, which reacts with ammonia to form sticky ammonia salts. The salts blind catalyst surfaces and can also induce acid corrosion downstream. Other factors that reduce catalyst life are arsenic and lead from coal combustion. The size of the SCR unit and the amount of catalyst depend on the pitch (spacing from centers of adjacent openings). A smaller pitch means greater surface area within a confined flue duct space but greater potential for plugging. Another downside of a catalyst is it contributes to the pressure drop in the flue gas, which in turn results in increased fan power consumption.

Ammonia may be added as anhydrous or aqueous ammonia. The amount added is crucial. If too much is added, flyash may be contaminated with ammonium salts, making disposal or flyash reuse is impossible. The ammonia slip should be as low as possible (~ 3 to 5 ppm).

The Southern Electric International 245-MW Birchwood Station (in Virginia) is in an ozone nonattainment area and is permitted at 0.15 lb NOx/mm Btu. To achieve this low emission level, the facility uses a combination of good combustion control, low-NOx burners (ABB-CE Services TFS2000TM), and downstream SCR. ABB Combustion Engineering, Inc. is guaranteeing 0.1 lb/mm Btu after SCR, according to Makansi 1996b.

Another system (Cho and Snapp 1994) has been tested at the Keystone Cogeneration Plant in Logan Township, NJ, also in an ozone nonattainment area. The 230-MW Unit uses eastern bituminous coal with a heat content of 13054 Btu/lb (HHV). The Low-NOx burners (Foster Wheeler, internally fuel staged with overfire air) result in a furnace NOx emission of 0.27 lb/mm Btu. Injection of 27% aqueous ammonia and use of a plate catalyst (mfg. Siemens AG, Germany) reduces NOx emissions to 0.10 lb/mm Btu.

Selective Non-Catalytic Reduction (SNCR)

Anhydrous ammonia, aqueous ammonia, or urea is added to the furnace where temperatures are in the range of 1600 to 2000°F (871 to 1093°C). Urea dissociates to ammonia in the furnace. At temperatures above 2000°F (1093°C), additional NOx can form. At temperatures below 1600°F (871°C), the ammonia slip can be too high. Sometimes additives such as oxygenated hydrocarbons are blended with the ammonia or urea formulation to extend the temperature window. The formulation is injected at multiple ports to ensure uniform distribution in the flue gas and at the proper temperature window.

Sometimes both SNCR and SCR technologies are used, with the formulation injected at multiple ports, including the furnace, and a catalyst in the flue gas ductwork. Also, a stand-alone SNCR may be installed and a catalyst structure added later as a polishing step.

CONCLUSIONS

- The NO_x emissions that occur as a result of coal combustion depend primarily on how the coal is burned and only to a minor extent on properties of the coal itself. The NO_x emissions may be classified into (1) thermal NO_x, (2) prompt NO_x, and (3) NO_x originating from fuel nitrogen. The NO_x originating from coal nitrogen may be subdivided into (1) homogeneous reactions producing NO_x from HCN and NH₃ intermediates from coal volatiles and (2) heterogeneous reactions taking place on the coal char surface from char nitrogen. The combination of tight combustion control and use of low-NO_x burners at coal-fired utilities has been demonstrated as being successful in controlling thermal, prompt, and coal volatile (homogeneous phase) NO_x; the technologies are less successful in controlling NO_x from char nitrogen.
- In a December 1996 press release, the EPA estimated that 85 to 90% of the utilities can meet the Clean Air Act Phase II limitations on NO_x (e.g. 0.4 lb NO_x/mm Btu for tangentially fired boilers, other limits for other boiler configurations) under Title IV, Acid Deposition Control, using low-NO_x burners and tight combustion control. Available published data from utilities show that this limit is near the edge of what is possible, practically speaking, and that many utilities have experienced increased carbon in the flyash and increased fireside tube corrosion.
- Coal properties that affect NO_x emissions include nitrogen content of the coal, coal reactivity, and mineral makeup of the coal. While coal properties only affect NO_x emissions in a minor way compared to how the coal is burned, because the EPA emission limits are near the ragged edge of what tight combustion control and low-NO_x burners are capable of, any benefit will help.
- Based on (1) the relative proportions of quaternary, pyrolic, and pyridinic nitrogen functionality groups in the coal, and (2) the coal nitrogen, Powder River Basin coal is predicted to result in roughly 20% less NO_x emission than many eastern U.S. coals when burned in utility boilers employing tight combustion control and low-NO_x burners. Unpublished utility data from the Electric Power Research Institute also show roughly 20% less NO_x emission when switching to PRB coal.
- One warning is that utilities burning PRB coal can experience increased slag buildup, higher temperatures, and as a result, higher NO_x emissions. Frequent cleaning (e.g. use of waterlances at some utilities) is required for those situations.

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