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NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

**A REVIEW OF NO<sub>x</sub> EMISSION CONTROL  
STRATEGIES FOR INDUSTRIAL BOILERS,  
KRAFT RECOVERY FURNACES, AND LIME  
KILNS**

**SPECIAL REPORT 99-01**

**APRIL 1999**

## **Acknowledgments**

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### **PRESIDENT'S NOTE**

A final USEPA rule requiring 22 states and the District of Columbia to submit State Implementation Plan (SIP) revisions for achieving significant reductions in nitrogen oxides or "NO<sub>x</sub>" was published in the October 27, 1998, *Federal Register*. The 22 states have until September 30, 1999, to prepare these revisions. All emission controls required by the states must be implemented by May 1, 2003. Electric utility plants and large fossil fuel-fired industrial boilers and turbines with over 250 x 10<sup>6</sup> Btu/hr heat input capacity are likely the main sources that would be subject to control requirements, although each state is free to formulate its own NO<sub>x</sub> reduction program.

This report is intended to serve as a background document to assist member companies in responding to proposed SIP revisions, especially relative to the technical feasibility of implementing various NO<sub>x</sub> control requirements. Besides providing a review of the fundamentals of NO<sub>x</sub> formation during combustion, this report identifies limitations of applying NO<sub>x</sub> control technologies developed primarily for fossil fuel-fired electric utility boilers to industrial boilers. Also, important differences in NO<sub>x</sub> generation, emissions, and control resulting from the use of biomass and biomass-derived fuels are pointed out. A combination of factors including (1) the uniqueness of biomass boilers and kraft recovery furnaces, (2) the swing nature of most boilers used at forest products industry (FPI) manufacturing facilities, (3) the unproven nature of NO<sub>x</sub> control technologies when applied to FPI combustion devices, and (4) the high cost of NO<sub>x</sub> control for such units, makes it unlikely that any but the largest fossil fuel-fired boilers can be controlled for significant NO<sub>x</sub> emission reduction in a cost-effective and technologically proven manner.

A handwritten signature in black ink, appearing to read "Ron Yeske", is positioned above the printed name.

Ronald A. Yeske

April 1999



# **A REVIEW OF NO<sub>x</sub> EMISSION CONTROL STRATEGIES FOR INDUSTRIAL BOILERS, KRAFT RECOVERY FURNACES, AND LIME KILNS**

SPECIAL REPORT NO. 99-01  
APRIL 1999

## **ABSTRACT**

Fundamentals of NO<sub>x</sub> formation are reviewed, especially as they apply to biomass and biomass-derived fuel combustion. Currently available technologies for industrial source NO<sub>x</sub> emission control and their applicability to forest products industry combination and bark boilers, recovery furnaces, and lime kilns are discussed. Limitations of applying techniques suitable for base-loaded, fossil fuel-fired boilers to industrial boilers that operate in a swing mode are identified. Other limitations, such as those related to furnace design and dimensions, need to handle chemicals such as ammonia and urea at a mill site, uniqueness of wood combustion NO<sub>x</sub> formation, and extremely high costs per ton of NO<sub>x</sub> removed for most forest products industry boilers, are reviewed. Most kraft recovery furnaces already operate in a manner that results in minimal NO<sub>x</sub> generation, and the existing practice of staged liquor combination is seen to be the most effective NO<sub>x</sub> control strategy. Lime kiln NO<sub>x</sub> emissions are extremely variable; the causes for this variation are unclear at the present time. The burning of stripper off-gases containing ammonia, while having the potential for NO<sub>x</sub> formation by oxidation of the NH<sub>3</sub>, is most likely not a source of additional NO<sub>x</sub> emissions since combustion temperatures at the point of introduction of these gases are not high enough to bring about oxidation. Application of NO<sub>x</sub> control strategies should take into account the predominantly "fuel NO<sub>x</sub>" nature of biomass and biomass-derived fuel combustion units.

## **KEYWORDS**

fuel NO<sub>x</sub>, thermal NO<sub>x</sub>, biomass, black liquor, staged combustion, wood residue, SCR, SNCR, combustion modification, LNB, OFA, costs, cost effectiveness

## **RELATED NCASI PUBLICATIONS**

Technical Bulletin No. 646 (February 1993). *Emission factors for NO<sub>x</sub>, SO<sub>2</sub> and volatile organic compounds for boilers, kraft pulp mills, and bleach plants.*

Technical Bulletin No. 636 (July 1992). *An analysis of kraft recovery furnace NO<sub>x</sub> emissions and related parameters.*

Technical Bulletin No. 455 (April 1985). *Volatile organic carbon emissions from wood residue fired power boilers in the Southeast.*

Atmospheric Quality Improvement Technical Bulletin No. 111 (January 1981). *A study of nitrogen oxides emissions from large kraft recovery furnaces.*

Atmospheric Quality Improvement Technical Bulletin No. 109 (September 1980). *A study of wood-residue fired power boiler total gaseous non-methane organic emissions in the Pacific Northwest.*

Atmospheric Quality Improvement Technical Bulletin No. 107 (April 1980). *A study of nitrogen oxides emissions from lime kilns.*

Atmospheric Quality Improvement Technical Bulletin No. 105 (December 1979). *A study of nitrogen oxides emissions from kraft recovery furnaces.*

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## **A REVIEW OF NO<sub>x</sub> EMISSION CONTROL STRATEGIES FOR INDUSTRIAL BOILERS, KRAFT RECOVERY FURNACES, AND LIME KILNS**

### **1.0 BACKGROUND**

In the October 27, 1998, Federal Register, USEPA published a 183-page final rule requiring 22 eastern states to submit State Implementation Plan (SIP) revisions to reduce NO<sub>x</sub> emissions. According to USEPA, the reductions would help minimize ozone formation resulting from the long range transport of one of ozone's major precursors, oxides of nitrogen. Ground-level ozone formation results from photochemical reactions involving NO<sub>x</sub> and VOC emissions. States subject to the NO<sub>x</sub> reduction requirements would be Alabama, Connecticut, Delaware, Georgia, Illinois, Indiana, Kentucky, Maryland, Massachusetts, Michigan, Missouri, New Jersey, New York, North Carolina, Ohio, Pennsylvania, Rhode Island, South Carolina, Tennessee, Virginia, West Virginia, and Wisconsin. For each of these states, USEPA has set a target reduction total amount of NO<sub>x</sub> (in tons) for point sources which would have to be achieved by May 2003. NO<sub>x</sub> emission reductions are based on the May 1 through September 30 ozone season.

The targets were established using sophisticated photochemical air quality simulation models. The models, which examined ozone formation over the eastern half of the U.S. during four different multi-day July ozone episodes (in 1988, 1991, 1993, and 1995), showed significant NO<sub>x</sub> emission reductions would be effective in lowering peak ground level ozone concentrations over broad regions. Various emission reduction strategies which considered the type, location, and magnitude of both NO<sub>x</sub> and VOC emission sources were examined with the models. In these evaluations, USEPA focused on the state-by-state NO<sub>x</sub> emission reductions that would be needed for most areas in the eastern U.S. to achieve attainment with the 8 hour average ozone ambient air quality standard in the year 2007. Although 37 states were included in the modeling effort, USEPA concluded NO<sub>x</sub> emissions from 15 of the states did not significantly impact maximum ozone concentrations in the region.

The due date for the 22 states to submit the SIP revisions to achieve these NO<sub>x</sub> reductions is September 30, 1999. All controls required by the states must be implemented by May 1, 2003. A cost criterion of \$2000 per ton of NO<sub>x</sub> reduction was used to determine which types of sources should be subject to control requirements. USEPA concluded that electric utilities and industrial boilers (>250 x 10<sup>6</sup> Btu/hr heat input capacity) should be the primary candidates for lowered NO<sub>x</sub> emissions, and believes reductions from these sources are the most cost-effective that can be achieved, with average costs under \$2000 per ton of NO<sub>x</sub> removed. Other types of sources, including smaller industrial boilers, pulp mill recovery furnaces, and lime kilns, were determined to likely have NO<sub>x</sub> control costs exceeding \$2000/ton. However, it will be up to the individual states to decide on the specific control requirements for each stationary NO<sub>x</sub> emission source.

In the 22 states, there are a large number of forest products manufacturing facilities, many of which operate combustion units that are potential candidates for NO<sub>x</sub> controls. These facilities will need to ensure the technical feasibility and cost-reasonableness of any proposed new NO<sub>x</sub> emission restrictions. Mills with large coal- and oil-burning boilers will especially need to begin examining the costs and technical feasibility of various NO<sub>x</sub> control measures such as fuel switching, boiler combustion modifications, and add-on controls. Mills planning to install new boilers with heat input capacities of 100 x 10<sup>6</sup> Btu/hr or greater will also need to meet the recently promulgated New Source Performance Standards (NSPS) for NO<sub>x</sub> emissions from these units. More details on this regulation are presented in Section 2.0.

This report provides a review of the fundamentals of  $\text{NO}_x$  formation during combustion and the currently available technologies for controlling industrial source  $\text{NO}_x$  emissions, especially as they pertain to the major  $\text{NO}_x$  emitting sources within the forest products industry (FPI) which include fossil fuel-, wood- and combination wood-fired boilers, kraft recovery furnaces, and lime kilns. Many FPI combustion units burn fuels of biomass origin. It is hoped that a clear understanding of what causes  $\text{NO}_x$  to form in these units and a review of currently available proven technologies for  $\text{NO}_x$  control for these units will be of help to mills facing possibly more stringent  $\text{NO}_x$  control measures in the future.

For industrial fossil fuel-fired boilers, a description of proven  $\text{NO}_x$  emission control techniques are extracted mainly from three sources: (1) a technical support document for proposed revisions to NSPS Subpart Db  $\text{NO}_x$  emission standards (USEPA 1997), (2) a USEPA summary of  $\text{NO}_x$  control technologies (USEPA 1992a), and (3) the Wisconsin Nitrogen Oxide Emission Reduction Cost Study report (WDNR 1989). The Subpart Db background document (USEPA 1997) provides a characterization of all industrial boilers as of 1995, discusses various nitrogen oxides emission control techniques for coal-, oil- and natural gas-fired industrial boilers and gives 1995 control cost estimates for applying proven  $\text{NO}_x$  control technologies to model industrial boilers. The WDNR study specifically recommends  $\text{NO}_x$  control technologies for five major industrial boiler categories: (1) stokers, coal-fired, (2) pulverized, coal-fired, (3) cyclones, coal-fired, (4) packaged, natural gas-fired, and (5) packaged, No. 6 oil-fired. This study also provides 1988 cost estimates for implementing  $\text{NO}_x$  emissions control for the five boiler categories. The control cost estimates for model industrial boilers given in the USEPA support document (USEPA 1997) and the recommendations for proven full-scale  $\text{NO}_x$  control technologies for industrial fossil fuel-fired boilers given in both the USEPA report and the WDNR report are reproduced here.

For forest products industry sources, including wood- and combination wood-fired boilers, kraft recovery furnaces, and lime kilns, the status and applicability of  $\text{NO}_x$  emissions control are discussed mainly based upon work carried out by NCASI and other researchers. As there exists only limited experience on  $\text{NO}_x$  emissions control for wood and combination wood-fired boilers, the discussion revolves mainly around the suitability of various  $\text{NO}_x$  control options currently available for fossil fuel combustion sources.

## **2.0 LEVEL OF $\text{NO}_x$ CONTROL REQUIRED FOR NEW INDUSTRIAL BOILERS**

It is perhaps instructive to first consider the level of  $\text{NO}_x$  control required to be implemented on a newly constructed boiler based on the recent NSPS. As mentioned above, USEPA revised  $\text{NO}_x$  emission limits contained in the Subpart Db NSPS which apply to industrial boilers with heat input capacities of  $100 \times 10^6$  Btu/hr or greater in September 1998. Table 1 shows the revised emission limits for various types of boilers. These apply to all boilers for which construction started after July 9, 1997. All limits are 30-day rolling averages. Limits for natural gas and distillate oil-fired boilers were left essentially unchanged from the earlier NSPS Subpart Db standards promulgated on June 19, 1984, while limits for coal and residual oil were lowered significantly. The basis for the revised standards for coal- and residual oil-fired boilers is the application of combustion modifications and selective catalytic reduction (SCR) flue gas treatment, although USEPA claims that selective non-catalytic treatment (SNCR) may be sufficient for residual oil-fired units. Although no specific limits were promulgated for boilers firing wood residues, any boiler firing more than 10% of any fossil fuel on an annual basis is subject to the  $\text{NO}_x$  emission limit for the fossil fuel. Thus boilers firing coal or oil with wood would have a limit of  $0.2 \text{ lb}/10^6 \text{ Btu}$ .

**Table 1.** NO<sub>x</sub> Emission Factors and NSPS for Industrial Boilers  
(>100 x 10<sup>6</sup> Btu/hr heat input)

Fuel Type	NO <sub>x</sub> Emissions		Percent Reduction Required
	AP-42 <sup>a</sup> (lb/10 <sup>6</sup> Btu)	1998 Subpart Db NSPS (lb/10 <sup>6</sup> Btu)	
Natural Gas	0.17 - 0.28 <sup>b</sup>	0.10 - 0.20 <sup>c</sup>	29 to 41
Residual Oil	0.28 - 0.45 <sup>b</sup>	0.20	29 to 56
Distillate Oil	0.13 - 0.28	0.10 - 0.20 <sup>c</sup>	23 to 29
Coal			
Pulverized	0.58-1.36 <sup>b</sup> <sub>0.55</sub>	0.20	66 to 85
Spreader Stoker		0.20	64
Fluidized Bed	0.61 <sup>d</sup>	0.20	67
Mass Feed Stoker	0.30-0.38	0.20	33-47
Wood			
Fuel Cell	0.042 <sup>e</sup> (0.00-0.17)	none	NA
Stoker Boilers	0.167 (0.07-0.40)	none	NA <sup>f</sup>
FBC Boilers	0.22	none	NA

<sup>a</sup> uncontrolled emission factors; used 1020 Btu/ft<sup>3</sup> gas, 150,000 Btu/gal oil, 12,500 Btu/lb coal & 4,500 Btu/lb as-fired wood in conversions

<sup>b</sup> lower factor for tangentially fired boilers

<sup>c</sup> lower factor for low and higher factor for high heat release rates

<sup>d</sup> bubbling bed

<sup>e</sup> NO<sub>x</sub> emissions from fuel cells operating within the forest products industry are typically > 0.2 lb/10<sup>6</sup> Btu; a review of the AP-42 factors may thus be warranted

<sup>f</sup> note that wood-fired boilers firing > 10% fossil fuel are subject to limits for fossil fuel; also note that NO<sub>x</sub> formation during wood combustion is primarily a function of wood nitrogen content

Table 1 also presents the uncontrolled NO<sub>x</sub> emission factors for typical industrial boilers as given in USEPA's AP-42 document (USEPA 1996). The final column gives the range of expected percentage reductions in NO<sub>x</sub> emissions from uncontrolled levels for boilers subject to the revised NSPS. Uncontrolled NO<sub>x</sub> emissions from wood-fired boilers are also shown in Table 1 (USEPA 1996). Besides boilers firing biomass or fossil fuels, kraft recovery furnaces and lime kilns constitute the two other major sources of NO<sub>x</sub> emissions in a typical kraft pulp mill. In NCASI Technical Bulletin No. 636 (NCASI 1992), NO<sub>x</sub> emissions from several kraft recovery furnaces and lime kilns were reported to range from 0.08 to 0.20 lb/10<sup>6</sup> Btu for recovery furnaces (average 0.13 lb/10<sup>6</sup> Btu) and from 0.01 to 1.12 lb/10<sup>6</sup> Btu for lime kilns (average 0.27 lb/10<sup>6</sup> Btu), respectively.

### 3.0 FUNDAMENTALS OF NO<sub>x</sub> FORMATION FROM FUEL AND LIQUOR COMBUSTION

This section provides a brief review of how oxides of nitrogen are formed during fuel and spent liquor combustion. Oxides of nitrogen formed during combustion comprise both NO and NO<sub>2</sub>. Typically, nearly 90% to 95% of the total NO<sub>x</sub> is NO due to kinetic limitations in the oxidation of NO to NO<sub>2</sub> (Bosch and Janssen 1988). USEPA's AP-42 document (USEPA 1996) suggests one use 95% for the NO fraction of all NO<sub>x</sub> formed from fossil fuel combustion, the rest being NO<sub>2</sub>. NO<sub>x</sub> formed during combustion is a function of fuel composition, the operating mode, and the basic design of the boiler and combustion equipment. In industrial boilers and furnaces, NO<sub>x</sub> is formed either as "fuel NO<sub>x</sub>" or as "thermal NO<sub>x</sub>."

Fuel NO<sub>x</sub> is formed during the combustion of all fuels containing "bound" nitrogen. Bound nitrogen is contained in solid/liquid fuels such as coal, No. 6 oil, wood residues, black liquor, secondary and deinking sludges, and also in certain non-condensable gases containing nitrogenous substances such as ammonia. The fraction of bound nitrogen converting to NO<sub>x</sub> depends on the fuel and its nitrogen content, a general trend being the lower the fuel nitrogen content, the higher the fraction converted to NO<sub>x</sub>. Fuel NO<sub>x</sub> is more sensitive to stoichiometry than to thermal conditions. The oxidation of fuel-bound nitrogen to NO is rapid and occurs on a time scale comparable to the energy release reactions during combustion (USEPA 1997). Approaches to reducing fuel NO<sub>x</sub> therefore mainly focus on creating a "fuel-rich" zone and reducing the availability of oxygen. Traditional thermal treatments such as flue gas recirculation and water/steam injection do not reduce NO<sub>x</sub> emissions from fuel nitrogen.

Thermal NO<sub>x</sub> is formed at high temperatures by thermal fixation of molecular nitrogen in the combustion air. It is formed in the high temperature, post-flame region of a combustion system. Thermal NO<sub>x</sub> is controlled by the reduction of temperature, oxygen and nitrogen concentrations, and residence time. Of these four factors, temperature is the most important. The rate of NO<sub>x</sub> formation increases exponentially above about 2800°F flame temperature. Due to a high activation energy needed for a critical reaction in the thermal NO<sub>x</sub> mechanism sequence, thermal NO<sub>x</sub> formation is "time dependent" and only occurs after the energy release reactions have equilibrated (i.e., after combustion is "complete") (USEPA 1997). Thus, temperature quenching is a valid technique for thermal NO<sub>x</sub> control. NO<sub>x</sub> formation during combustion of natural gas and distillate oils occurs mainly by the thermal NO<sub>x</sub> mechanism.

There is ample evidence in the literature suggesting NO<sub>x</sub> formation in wood-fired boilers and wood-derived spent liquor-fired furnaces is predominantly by the fuel NO<sub>x</sub> mechanism. During red alder combustion, Winter et al. (1989) observed that neither temperature (800°C, 1000°C, and 1200°C) nor moisture content of the wood fuel (10% and 45%) had any significant effect on the conversion of nitrogen evolved from the fuel to NO, leading to the conclusion that fuel N content and overall excess oxygen were the only key parameters controlling NO<sub>x</sub> formation. However, empirical studies have found NO<sub>x</sub> to vary inversely with fuel moisture content, although the magnitude of this correlation is less significant than with other operating conditions such as excess air, air staging and heat release rate (Stultz and Kitto 1992). Winter et al. (1989) also observed that NO emissions increased over threefold when red alder (0.76% N) or peat (1.18% N) was burned as compared with Douglas fir (0.18% N). Junge (1980) also concluded that NO<sub>x</sub> formation in bark boilers is by the fuel NO<sub>x</sub> mechanism. Tests in an industrial spreader-stoker pilot facility gave average emissions of 0.11 lb NO<sub>x</sub>/10<sup>6</sup> Btu for Douglas fir (0.10% N) and 0.21 lb NO<sub>x</sub>/10<sup>6</sup> Btu for eastern pine mix (0.22% N). The author concluded higher levels of fuel nitrogen will generate higher levels of NO<sub>x</sub> for fixed combustion conditions.

In 1992, NCASI carried out a detailed investigation of kraft recovery furnace  $\text{NO}_x$  emissions and related parameters (NCASI 1992). This study concluded that temperatures in the lower furnace under normal operating conditions are likely not high enough to result in  $\text{NO}_x$  formation by the thermal  $\text{NO}_x$  mechanism pathway.  $\text{NO}_x$  formation by the fuel  $\text{NO}_x$  mechanism pathway is perhaps the most dominant mechanism just as for wood-fired boilers. Several other researchers (Nichols and Lien 1993; Nichols and Thompson 1993; Veverka et al. 1993; Martin et al. 1994; Adams et al. 1992; Osborne 1992) have since confirmed this finding that only a minor part of the  $\text{NO}$  in recovery furnace emissions is thermal  $\text{NO}$ , the majority being fuel  $\text{NO}$  or nitrogen oxide formed as a result of the oxidation of organically bound nitrogen in black liquor. Aho et al. (1994) studied the behavior of fuel nitrogen in black liquor combustion. From data on  $\text{NO}_x$  emissions from several full-scale recovery furnaces, they concluded that the one main variable in determining  $\text{NO}_x$  levels in a furnace is the liquor type. Combustion of birch liquors, which had the highest N content of four different liquors burned, gave the highest levels of  $\text{NO}_x$ . In a recent study, Forssen et al. (1997) conclude that (a) 70% to 80% of the black liquor N is released during devolatilization as gaseous nitrogen species, mainly ammonia and  $\text{N}_2$ , and the oxidation of  $\text{NH}_3$  is perhaps the main contributor to the overall  $\text{NO}$  in normal black liquor firing, and (b) nearly 20% to 30% of the liquor nitrogen will be bound in the char residue much of which will remain as a reduced nitrogen species in the salt residue or smelt.

#### **4.0 $\text{NO}_x$ CONTROL TECHNIQUES FOR INDUSTRIAL FOSSIL FUEL-FIRED BOILERS**

There are two principal methods of industrial boiler  $\text{NO}_x$  emissions control, viz., (1) combustion modification and (2) flue gas treatment. Combustion modifications are often associated with improving boiler performance. Flue gas treatment can occur both within the boiler and at several points along the path of the flue gas from the boiler to the stack. Other pre-combustion techniques such as fuel denitrogenation to reduce "fuel  $\text{NO}_x$ " have shown little promise.

##### **4.1. Combustion Modifications**

Combustion modifications are the most common, commercially available means of controlling  $\text{NO}_x$  emissions from fossil fuel-fired boilers. These can be brought about either by effecting relatively simple modifications of operating conditions or by incorporating more elaborate modifications of the combustion facility. Retrofit applications of  $\text{NO}_x$  controls by combustion modification usually proceed in several stages. First, fine tuning of combustion conditions by lowering excess air and adjusting burner settings and air distribution may be attempted. Next, minor modifications such as biased burner firing or burners out of service may be implemented. Finally, if further reductions are desired, other retrofits such as installation of overfire air ports, flue gas recirculation systems, and/or low- $\text{NO}_x$  burners may be employed (USEPA 1992a).

Combustion modifications can be categorized under five areas: (1) low excess air (LEA), (2) staged combustion, (3) temperature reduction technologies, (4) low  $\text{NO}_x$  burners (LNB) and (5) in-furnace destruction.

##### **4.1.1 Low Excess Air in the Flame Zone (LEA)**

By reducing the amount of excess air, and therefore excess oxygen, in the local flame zone, moderate reductions in  $\text{NO}_x$  emissions may be possible. Operating the burners with low excess air (<5 % for oil and gas-fired boilers) results in lower  $\text{NO}_x$  emissions (both fuel and thermal  $\text{NO}_x$ ) and higher boiler efficiencies. Unfortunately, low excess air operation has proven to yield only moderate  $\text{NO}_x$  reduc-

tions, if any (Wood 1994). Ten percent to 20%  $\text{NO}_x$  reduction is believed feasible by LEA for every 1% reduction in furnace  $\text{O}_2$  levels (Makanski 1988). However, this technique is limited by the production of smoke, high  $\text{CO}$  emissions and possibly other problems within the boiler itself such as increased fouling and corrosion due to the reducing atmosphere (Jones, 1994). LEA is not in widespread use as a  $\text{NO}_x$  control technique for industrial boilers, but it is used for energy conservation (Jones 1994).

#### 4.1.2 *Staged Combustion or Off-Stoichiometric Combustion*

Staged combustion or off-stoichiometric combustion is one of the oldest modification techniques for  $\text{NO}_x$  control. By diverting a portion of the total amount of air required through separate ports, generally located above the burners, a “fuel-rich” zone is created (also known as air staging [AS]). The fuel-rich conditions result in lower peak temperatures and thus, lower thermal as well as fuel nitrogen-generated  $\text{NO}_x$ . Staged combustion can be accomplished by various in-furnace techniques such as (a) overfire air (OFA), (b) burners out of service (BOOS) and (c) biased burner firing (BBF) or air/fuel mixing, each of which are described briefly below. These techniques are generally applicable to larger, multiple burner, combustion devices (Wood 1994).

**(a) Overfire Air (OFA)** — In OFA about 10% to 20% of the combustion air flow is directed to separate air ports located downstream of the burners. This modification is more attractive in original designs than in retrofit applications because of cost considerations, including cost of additional ductwork, furnace penetrations, extra fan capacity, and physical obstructions that make retrofit difficult in some installations (USEPA 1992a). When implemented, 15% to 30%  $\text{NO}_x$  reductions with OFA alone are expected (Makanski 1988). OFA is a very effective technique for  $\text{NO}_x$  reduction, especially for tangentially fired boilers (USEPA 1992a), and may be used with all fuels and most combustion systems, including stoker/grate units (Jones 1994). Operational problems resulting from OFA can include decreased combustion efficiency and deterioration of final steam conditions.

**(b) Burners Out of Service (BOOS)** — BOOS is a relatively simple technique used mostly in retrofit situations (suspension-fired coal and oil/gas-fired boilers) wherein multiple burners exist and fuel flow is blocked to an upper level of burners, allowing only air to pass through these. To avoid flame stability and vibration problems, the number of burners taken out of service should not exceed 25% (USEPA 1991). Operational problems resulting from BOOS can include corrosion and soot/slag formation (USEPA 1991).

**(c) Biased Burner Firing** — In biased burner firing (BBF), also known as air/fuel mixing or fuel biasing, the furnace is divided into a lower, fuel-rich zone and an upper fuel-lean zone to complete the burnout. This technique has been proven only for oil/gas-fired utility boilers (Makanski 1988). A 20% reduction in  $\text{NO}_x$  can be expected.

#### 4.1.3 *Temperature Reduction Technologies*

Several  $\text{NO}_x$  reduction technologies employ some method of reducing peak flame temperatures to minimize thermal  $\text{NO}_x$  formation. These include (a) flue gas recirculation (FGR), (b) reduced air preheat, (c) steam and water injection, and (d) decreased load.

**(a) Flue Gas Recirculation (FGR)** — In FGR, a portion of the combustion flue gas is brought into the combustion zone (up to 20% of the flue gas). The flue gas acts as a heat sink, lowering the combustion zone temperature, which results in lower thermal  $\text{NO}_x$ . High capital expenditures are



necessary to install new ductwork, recirculation fans, devices to mix flue gas with combustion air, etc. Flue gas is typically taken from a stack breaching at about 300°F to 400°F and mixed with the secondary combustion air (wind box). As only thermal NO<sub>x</sub> can be controlled by this technique, it is especially effective only in oil and gas-fired units. In fact, FGR is probably the most effective and least troublesome system for NO<sub>x</sub> reduction for gas-fired combustors (Wood 1994). A 20% to 30% reduction in NO<sub>x</sub> is expected (Makanski 1988). FGR is most effective when used in conjunction with air and/or fuel staging (Jones 1994). Once the favored option for industrial-boiler NO<sub>x</sub> control, this is no longer the case due to a better understanding of the high capital costs and FGR fan and O&M costs involved in addition to loss of boiler efficiency (Jones 1994). FGR is more adaptable to new designs than as a retrofit application (USEPA 1992a).

**(b) Reduced Air Preheat (RAP)** — By lowering the amount of combustion air preheat the primary combustion zone peak temperature is lowered, hence resulting in lower thermal NO<sub>x</sub> emissions. The energy penalty usually makes this option unfavorable (Yaverbaum 1979). A rule of thumb is a 1% efficiency loss for each 40°F reduction in preheat (Wood 1994). As in FGR, RAP only lowers thermal NO<sub>x</sub>, and thus is economically attractive for only natural gas and distillate fuel oil combustion (USEPA 1992a).

**(c) Steam and Water Injection** — Flame quenching by the addition of steam or water in the combustion zone is an effective control technology for oil/gas-fired burners, although a significant energy penalty could ensue. Oil/water emulsions can realize a similar response as steam/water injection (Jones 1994). Suppression of NO<sub>x</sub> formation up to 70% in gas turbines is believed feasible (Makanski 1988).

**(d) Decreased Load** — A reduction in the percentage of rated capacity leads to lower “volumetric heat release rates” in the boiler, and correspondingly lower flame temperatures and NO<sub>x</sub> formation. Wasted load capacity is a definite disadvantage. Reduced mass flow can also cause improper fuel-air mixing during combustion, creating carbon monoxide and soot emissions (USEPA 1992a).

#### 4.1.4 *Low NO<sub>x</sub> Burners (LNB)*

LNBs are designed to mix fuel and air in a controlled pattern that sustains local fuel-rich regions, keeps the temperatures down and dissipates heat quickly. By controlling the mixing of the fuel and air, the combustion process can be initiated at the burner throat and the zone of complete combustion can be varied in the furnace chamber, resulting in elongated flames as compared to short, intense flames. Virtually all of the boiler and burner vendors have developed LNB for retrofit (Makanski 1988). Both staged air and staged fuel combustion principles are employed in LNBs. Combustion modification with LNBs is used in both gas/oil-fired and coal-fired units. A full LNB retrofit can be expected to reduce NO<sub>x</sub> levels by about 50% (Makanski 1988). Flame containment, specifically sidewall and/or rear-wall flame impingement, is a challenge in the smaller boilers, particularly in a high-space-heat-release-rate package boiler.

Considered a modification of the low NO<sub>x</sub> burner, *slagging combustors* involve high temperature combustion of coal in an air-deficient chamber. Ash is removed as a liquid slag and NO<sub>x</sub> formation is suppressed. The gasified coal is then combusted in the existing furnace cavity. Owing to their similarity of combustion characteristics with that of cyclone-fired coal boilers (coal ash removed as liquid slag) slagging combustors are thought to be particularly good for retrofitting the latter (Makanski 1988).

#### 4.1.5 *In-Furnace Destruction*

Also known as “reburning,” “off-stoichiometric combustion” or “fuel staging,” in this technique from 10% to 20% of the total fuel input is diverted to a second combustion zone downstream of the primary zone (Makanski 1988). The fuel in the fuel-rich secondary zone acts as a reducing agent, reducing NO formed in the primary zone to  $N_2$ . Low nitrogen containing fuels such as natural gas and distillate oil are typically used for reburning to minimize further  $NO_x$  formation. For example, the METHANE DeNOX reburning process uses the injection of natural gas together with recirculated flue gases (for enhanced mixing) to create an oxygen-rich zone above the combustion grate. Overfire air is then injected at a higher furnace elevation to burn out the combustibles (Loviska et al. 1998). This process is claimed to yield between 50% and 70%  $NO_x$  reduction and be suitable for all solid fuel-fired stoker boilers (coal, biomass, municipal solid waste, RDF, etc.). However, it has only been demonstrated on one municipal waste combustor (Abbasi et al. 1998) and one 60 MWe stoker coal-fired unit (Loviska et al. 1998) in the United States. The Institute of Gas Technology (IGT), which developed this process, has plans to apply METHANE DeNOX to a pulp and paper mill wood residue-fired boiler while increasing the feed of waste treatment plant residuals to the boiler from 1.5% to 5.0% of heat input.

## 4.2 **Flue Gas Treatment**

The selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) processes are among the only proven, viable post-combustion flue gas treatment processes. Several other more advanced processes are currently being developed, some awaiting results of pilot stage results and others awaiting the passage of more stringent  $NO_x$  control laws whereby their full-scale use can be put to the test.

### 4.2.1 *Selective Non-Catalytic Reduction (SNCR)*

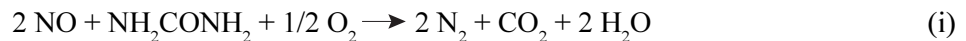
SNCR involves the injection of urea, ammonium hydroxide, anhydrous ammonia, or aqueous ammonia into the furnace exit region where the flue gas is in the range of 1,600°F to 1,900°F (USEPA 1997).  $NO_x$  is reduced to  $N_2$  and  $H_2O$ . One concern about this process is its ability to perform adequately under changing load and fuel conditions (Jones 1994). The thermal DeNO<sub>x</sub> process relies on the injection of ammonia and the  $NO_x$  OUT process relies on the injection of urea into the boiler. Both ammonia and urea bring about gas phase reduction of  $NO_x$  to nitrogen. A portion of the NO reduction by SNCR systems, usually around 5%, is due to transformation of NO to  $N_2O$ , which is a global warming gas (USEPA 1998).

(a) **Thermal DeNO<sub>x</sub>** — The thermal DeNO<sub>x</sub> process, developed and marketed by Exxon Research and Engineering Company (Hurst 1983), selectively reduces  $NO_x$  to molecular nitrogen and water by using ammonia injection into the air-rich flue gas in the temperature range of 1600°F to 2200°F, temperatures typically found in the upper portions of the furnace (superheater section or before air preheater). The actual chemical mechanism of the process is quite complex, involving 31 significant chemical reactions (Hurst 1983).  $NO_x$  reduction as high as 60% to 70% has been achieved in some industrial applications. The reduction efficiency is affected by the  $NH_3$  feed rate relative to  $NO_x$  concentrations, by the degree of flue gas thermal stratification in the ammonia injection section, and by the flue gas residence time within the appropriate temperature window.

The reaction predominates around a temperature of 1740°F (USEPA 1981). For temperatures above 2000°F, the injected ammonia is oxidized to NO, and for temperatures below about 1560°F the reaction proceeds slowly and the NO reduction falls off drastically, resulting in significant ammonia

slippage (USEPA 1981). The ammonia must be diluted with air or steam to allow for good mixing. The injection is usually accomplished by using a multiport injection grid to allow for varying flue gas temperatures due to boiler load swings. Problems with  $\text{NH}_3$  injection include ammonia slippage, fouling of air preheater surface by ammonium sulfate/biosulfate formation and maintaining optimum reaction temperatures (USEPA 1981).

**(b)  $\text{NO}_x$  OUT** — Research into the injection of urea (solid or aqueous solution) in a manner similar to ammonia was first carried out by the Electric Power Research Institute (DePriest et al. 1989). Known as the  $\text{NO}_x$  OUT process, it is receiving increased attention on account of both the reduced cost and reduced danger of handling urea as compared with ammonia. Also, it is believed that urea/water injection parameters can be more easily matched to furnace temperature, providing better load-following capability and resulting in reduced hardware requirements such as injection grids (Makanski 1988). The  $\text{NO}_x$  OUT process is based upon the following chemical reaction that occurs in the temperature range of 1700°F to 2000°F (Muzio and Anand 1976).

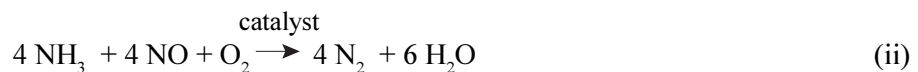


The problems of ammonia slippage and heat transfer surface fouling with byproduct formation also exist with the  $\text{NO}_x$  OUT process.

Six factors directly affect the performance of urea- or  $\text{NH}_3$ -based SNCR systems (USEPA 1997). These are inlet  $\text{NO}_x$  level, temperature, mixing, residence time, reagent-to- $\text{NO}_x$  ratio, and fuel sulfur content. Lower inlet  $\text{NO}_x$  concentrations reduce the reaction kinetics and hence the achievable  $\text{NO}_x$  emissions reductions. As mentioned above, temperatures below the desired window result in ammonia emissions (slip), and temperatures above the desired window result in  $\text{NH}_3$  being oxidized to  $\text{NO}_x$ . Mixing becomes an important consideration in regions distant from an injection nozzle where the level of turbulence is reduced and stratification of the reagent and flue gas will probably be a greater problem especially at low boiler loads (USEPA 1997). Residence time becomes important to allow the desired reactions to go to completion. Small, packaged, watertube boilers and boilers with varying steam loads are therefore difficult applications for SNCR (USEPA 1997). As higher than the theoretical  $\text{NH}_3$ : $\text{NO}_x$  ratios are generally required to achieve desired  $\text{NO}_x$  emission reductions, a trade-off exists between  $\text{NO}_x$  control and the presence of  $\text{NH}_3$  in the flue gas. Finally, in the case of high sulfur fuels, excess  $\text{NH}_3$  can react with sulfur trioxide to form ammonium sulfate salt compounds that deposit on downstream equipment leading to plugging and reduced heat transfer efficiencies.

#### 4.2.2 Selective Catalytic Reduction (SCR)

The SCR process also uses ammonia injection but the reduction reactions are carried out on the surface of a catalyst operating at temperatures between 450°F and 750°F. The following overall reactions are known to occur on the catalytic surface:



The active compound which promotes the  $\text{NH}_3$ - $\text{NO}_x$  reaction may be composed of a precious metal (e.g., Pt, Pd), a base metal oxide, or a zeolite (USEPA 1997). Precious metal catalysts are used in clean fuel applications and at lower temperatures than the base metal oxide or zeolite catalyst. The most common base metal oxide catalysts are vanadium/titanium based, with  $\text{V}_2\text{O}_5$  as the active material and  $\text{TiO}_2$  as the support material. The zeolite catalysts are stable over a wider temperature window than other types of catalysts. Optimum  $\text{NO}_x$  reduction occurs at catalyst bed temperatures between 600°F and 750°F for conventional (vanadium or titanium-based) catalyst types, and between 470°F and 510°F for platinum-based catalysts (USEPA 1991). An ammonia to  $\text{NO}_x$  ratio of 1:1 has typically reduced  $\text{NO}_x$  by 80% to 90% with a leak rate of less than 20 ppm (USEPA 1981). The reactor is usually located between the boiler and air preheater.  $\text{NO}_x$  control efficiencies are typically in the range of 70% to 90%, depending on type of catalyst, amount of  $\text{NH}_3$  injected, the initial  $\text{NO}_x$  level, and the age of the catalyst.

The performance of an SCR system is also affected by six factors (USEPA 1997). These are  $\text{NO}_x$  level at SCR inlet, flue gas temperature,  $\text{NH}_3$ -to- $\text{NO}_x$  ratio, fuel sulfur content, gas flow rate, and catalyst condition. For SCR, when inlet  $\text{NO}_x$  concentrations fall below 150 ppm the reduction efficiencies decrease with decreasing  $\text{NO}_x$  concentrations (USEPA 1997). Each type of catalyst has an optimum operating temperature range. Temperatures below this range result in ammonia emissions (slip) and temperatures above the desired range result in  $\text{NH}_3$  being oxidized to  $\text{NO}_x$ . For up to about 80%  $\text{NO}_x$  reduction efficiencies, a 1:1  $\text{NH}_3$ : $\text{NO}_x$  ratio is sufficient. For higher efficiencies, higher reagent to  $\text{NO}_x$  ratios are required which may result in higher  $\text{NH}_3$  slip. In the case of high sulfur fuels excess  $\text{NH}_3$  can react with sulfur trioxide to form ammonium sulfate salt compounds that deposit and foul downstream equipment. SCR application experience in the case of medium-to-high sulfur fuels is limited. For a given flue gas flow rate, the catalyst structural design should be chosen so that the residence time needed for the reduction reactions to take place on the catalyst surface is achievable. Catalysts degrade over time due to poisoning, fouling, thermal stress, erosion by particulate, etc.  $\text{NO}_x$  removal decreases as the catalyst gets deactivated. Catalysts are a major component of the cost of SCR.

SCR is considered a high-efficiency removal device. Today, SCR has become a common feature of new gas-turbine cogeneration and combined cycle systems in the US (Jones 1994). Major problems with SCR processes include corrosion due to higher flue gas acid dew points, and formation of solid ammonium sulfate and ammonium bisulfate, particularly in high sulfur oil-fired or coal-fired boilers. These could deposit on the air preheater surface to reduce heat transfer efficiencies. Ammonia slippage is also a potential problem. Due to poisoning by trace metals or erosion by fly ash, catalysts lose activity over time. Although a proven technology for larger units (>20 MW), it is not in widespread use for smaller industrial boilers. In fact, as of 1995 none of the industrial boilers in the United States was equipped with the SCR process (USEPA 1997).

#### **4.2.3 Other FGT Processes - $\text{SO}_2$ - $\text{NO}_x$ Removal**

DePriest et al. (1989) reviewed several other flue gas treatment processes that were under consideration nearly a decade ago. These processes typically had the goal of finding lower cost alternatives to SCR for  $\text{NO}_x$  control and conventional FGD for  $\text{SO}_2$  control. These technologies, primarily targeted at removing both  $\text{SO}_2$  and  $\text{NO}_x$  from the flue gas stream, may be classified under six categories. To date, none of these technologies has resulted in full-scale applications intended for significant  $\text{NO}_x$  reductions from combustion sources.

**(a) Solid Adsorption/Regeneration** — These processes use a recirculating solid sorbent material to remove  $\text{SO}_2$  and  $\text{NO}_x$  from the flue gas. They include (1) the UOP/PETC Fluidized-Bed

Copper Oxide Process, (2) the Rockwell Moving Bed Copper Oxide Process, (3) the NOXSO process, (4) the Mitsui/BF Activated Coke Process, (5) the Sumitomo/EPDC Activated Char Process, and (6) the Sanitech Nelsorbent SO<sub>2</sub>/NO<sub>x</sub> Control Process.

**(b) Irradiation of the Flue Gas** — High-energy electrons from electron accelerators, pulsed corona discharge, UV and microwave radiation are used in these processes to produce reactive species and subsequently oxidize SO<sub>2</sub> and NO<sub>x</sub> to their respective acids. Usually located after particulate control devices these processes often involve ammonia injection after the reactor, with ammonium compounds separated in a second control device.

**(c) Wet Scrubbing** — These processes either oxidize the NO to NO<sub>2</sub> and then scrub with an absorbing medium, or use additives to enhance solubility of NO in the medium. Processes in this category include (1) the Saarberg-Holter Iron Chelate Scrubbing Process, (2) the Argonne/Dravo ARGONNOX Process, (3) the Dow Electrochemical Regeneration Process, (4) the Dow Polychelant/Ultrafiltration Process, (5) the PETC Electrodialysis Process, and (6) the California (Berkeley) Ferrous Cysteine Process.

**(d) Gas/Solid Catalytic Operations** — In these processes hot flue gases prior to the air preheater are passed through a fixed bed catalytic reactor. The NO<sub>x</sub> is reduced to N<sub>2</sub>, while the SO<sub>2</sub> may be converted to either sulfuric acid or sulfur. Included are (1) the Haldor Topsoe WSSA-SNO<sub>x</sub> Process, (2) the Degussa DESONOX Process, (3) the B&W SO<sub>x</sub>/NO<sub>x</sub>/RO<sub>x</sub>/BO<sub>x</sub> (SNRB) Process, (4) the Parsons Flue Gas Cleanup Process, and (5) the Lehigh University Low-Temperature SCR Process.

#### **4.3 Applicability of Proven NO<sub>x</sub> Control Technologies for Utility Boilers to Industrial Boilers**

Much of the operating experience gained on fossil fuel-fired boiler NO<sub>x</sub> emissions control has been on utility boilers. As of 1995, industrial boilers subject to the earlier Subpart Db NSPS NO<sub>x</sub> limits included eight coal-fired fluidized bed combustors (FBC), four oil-fired boilers, and 31 natural gas-fired boilers (USEPA 1997). Five of the coal-fired FBCs used only combustion controls (CC), while the remaining three were equipped with SNCR. Three of the four oil-fired boilers used CC while the fourth controlled NO<sub>x</sub> by restricting operating hours. NO<sub>x</sub> emission controls on the 31 natural gas-fired boilers ranged from good combustion practice to using SNCR. None used SCR.

##### **4.3.1 Applicability of Combustion Modification NO<sub>x</sub> Control Technologies**

Industrial boilers typically operate with widely varying steam loads. On average, across the industrial spectrum, a mean capacity utilization factor of 45% to 55% is estimated (CIBO 1993). Even recently installed cogeneration and independent-power facilities are predicated on dispatch schedules dictated by the utility purchasing the power (Jones 1994). NO<sub>x</sub> reduction measures are particularly difficult to implement in small, low-capacity facilities because (a) residence time is limited and often inadequate for applying overfire air (OFA) without excessive loss of thermal efficiency or induced smoking, (b) relatively small furnace dimensions limit combustion modifications that increase flame length and tend to cause the flame to impinge on tube walls, (c) peak boiler efficiency and minimized NO<sub>x</sub> emissions occur close to minimum flue-gas O<sub>2</sub> content, which is at the threshold of smoke or combustible-emissions formation, (d) steam is used far more effectively in industrial applications than in conventional electric utility plants and consequently, basing emission limits on boiler heat input or volume of flue gas does not properly credit efficiency (Jones 1994).

The Council of Industrial Boiler Owners prepared a NO<sub>x</sub> RACT (Reasonably Available Control Technologies) guidance document (CIBO 1993) which summarized the problems associated with developing RACT rules for industrial boilers as follows:

- The industrial boiler population is diverse – no specific type is prevalent.
- There is very little hard NO<sub>x</sub> emissions data from existing industrial systems.
- The variability of emissions from a unit, type system or class of units, can be extreme.
- Projection of system trends is impractical; therefore, emissions may have to be considered on a unit by unit basis.
- Most industrial stoker fired units installed prior to 1987 were equipped with only one or two rows of overfire ports, and a maximum of 10% to 20% total air, an arrangement designed to optimize combustion efficiency, *not* to control NO<sub>x</sub> emissions.
- Bottom-supported stoker units are virtually impossible to retrofit with a new overfire air arrangement.
- Inherent system variability requires that a 30-day rolling average be the standard for industrial boilers.

In written comments to the Maine Department of Environmental Protection, Sonnichsen (1994) of CARNOT included the following reservations when applying utility NO<sub>x</sub> control experience to industrial boilers:

- The greatest difference between utility boiler operations and power boiler operations is the fluctuating steam demand characteristic of pulp and paper mill power boiler operations. Normally, power boilers continuously adjust fuel firing rates and excess air levels. Even with the most sophisticated combustion controls, it is neither practical nor safe to continuously maintain minimum levels of excess air. Consequently, power boilers have higher NO<sub>x</sub> emissions.
- Fuel biasing on an industrial boiler subject to rapid and excessive load swings could result in too rich or lean firing conditions, which can lead to flame stability problems and explosive conditions.
- Windbox flue gas recirculation (FGR) could be considered for use on oil-fired boilers. Its application, however, can be limited by (1) the windbox and boiler fans' capacities, (2) increased boiler bank tube wall erosion, and (3) the potential for severe damage from changes in convection heat transfer and boiler water circulation patterns.
- The application of low NO<sub>x</sub> burners (LNB) is often limited by the longer flames produced as a consequence of improved air distribution control. While there is generally ample room for LNB flames in utility furnaces, their use on the smaller power boilers can result in flame impingement on furnace walls, leading to tube wall overheating and mechanical failure. Flame impingement can also result in premature flame quenching and increased soot and CO emissions.

- Unlike utilities, which can specify the nitrogen content of their large oil purchases, most mills cannot make this specification.

Even within the family of industrial boilers there are considerable differences in the design of various types of boilers and therefore the applicability of certain NO<sub>x</sub> control technologies. For example, considerable differences exist in the heat removal rates between a grate-fired boiler for wood residue or coal combustion and a packaged boiler for oil or gas combustion. The grate boiler is designed for staged combustion since a large amount of the combustion air is introduced above the grate fire. Also, the size of the grate furnace compared to a similar packaged boiler is two to three times greater. The net result is that there is more heat absorption in a grate-fired boiler resulting in lower thermal NO<sub>x</sub> formation. When applied to packaged boilers, both air staging and flue gas recirculation, recommended NO<sub>x</sub> control techniques for oil and gas combustion, will increase the burner flame length requiring added furnace length to avoid flame impingement on the furnace walls.

#### **4.3.2 *Applicability of SNCR NO<sub>x</sub> Control Technology***

As previously mentioned, the use of the SNCR process in a packaged boiler would require having access to a temperature window between about 1700°F and 2000°F in which to inject the ammonia or urea. Controlling flue gas temperatures in the convective section of a package or even grate boiler over the entire range of operating loads the boiler is expected to experience will be very difficult to achieve. Boilers in the pulp and paper industry rarely operate under base loaded conditions. Consequently, the location of the desired temperature window is expected to change constantly. Accurate, instantaneous temperature measurement, as well as the ability to accurately adjust the location of the injection nozzle, would be necessary. Ammonia slip would be a recurring problem associated with the application of the SNCR process to industrial boilers with fluctuating loads.

#### **4.3.3 *Applicability of the SCR NO<sub>x</sub> Control Technology***

Since the selective catalytic reduction process also involves the injection of ammonia within a fairly narrow range of temperatures, albeit a lower range than for the SNCR process, the problems described for the SNCR process relative to fluctuating loads in pulp mill industrial boilers and resulting ammonia slip are equally relevant here. In addition, an important factor that further restricts the use of the SCR process to most industrial boilers is the large loss in energy efficiency that would result from the need to reheat the exhaust gases. Exhaust gases exiting the economizer sections of these boilers are typically in the range of 250°F to 350°F, while the desired temperature range for the SCR process is between 450°F and 750°F.

### **4.4 *Proven Full-Scale NO<sub>x</sub> Control for Industrial Fossil fuel-fired Boilers – The WDNR Study***

As part of the NO<sub>x</sub> Emission Reduction Cost Study (WDNR 1989), the Wisconsin Department of Natural Resources conducted a comprehensive study of industrial boiler NO<sub>x</sub> control, including both technical and economic evaluations. Only technologies proven in full-scale demonstration (mostly utilities) were considered. The results of this study may be relevant even today, and hence they are presented here. Industrial boilers in Wisconsin were found to belong to one of the following five major categories, viz., (1) coal-fired stokers, (2) pulverized coal, (3) coal-fired cyclones, (4) packaged, natural gas-fired, and (5) packaged, No. 6 oil-fired. The criteria for choosing technologies for specific boiler applications were based upon (a) evaluations of field demonstrations and (b) cost effectiveness of process implementation.

A summary of optimum NO<sub>x</sub> control technologies, NO<sub>x</sub> removal or reduction capabilities, commercial availability and any associated problems with these technologies for the five boiler categories considered in the WDNR study (WDNR 1989) is shown in Tables 2 to 6, respectively. In all cases, although the SCR process offered the highest percent NO<sub>x</sub> reduction, for reasons previously mentioned in this paper, the SCR process is not yet considered to be a cost-effective and demonstrable technology in the United States, at least not for the smaller industrial boilers.

Table 2 shows that a combination of FGR and OFA is effective for moderate NO<sub>x</sub> reduction in stoker-fired boilers. Further reductions could be achieved by installing the thermal DeNO<sub>x</sub> or NO<sub>x</sub> OUT process. On account of the difficulty in modifying the combustion chamber, reburning with natural gas is the only combustion modification option feasible with cyclone-fired coal boilers. Fifty percent to 60% NO<sub>x</sub> reduction with reburning and 60% to 70% reduction with the two SNCR processes are feasible (Table 3). Low NO<sub>x</sub> burners are the leading technologies for pulverized coal boilers (Table 4). The SNCR processes offer 60% to 70% reduction capability, only marginally better than boilers fitted with the LNBs (about 50%). LNB with FGR offers the highest percent reduction of NO<sub>x</sub> for natural gas-fired packaged boilers (Table 5). Finally, Table 6 shows that a new NO<sub>x</sub> reduction technology, low NO<sub>x</sub> with relatively large substoichiometrically fired precombustor, offers the best promise for No. 6 fuel oil-fired, industrial boilers.

In its technical support document to the proposed revisions to the Subpart Db NO<sub>x</sub> (USEPA 1997), USEPA summarizes the types of NO<sub>x</sub> controls demonstrated or applicable for new fossil fuel-fired industrial boilers. This summary is presented in Table 7. According to USEPA, low NO<sub>x</sub> burners (LNB) and LNB with overfire air (OFA) are applicable to all conventional (pulverized) coal-fired, gas-fired and oil-fired boilers, air staging is applicable to coal-fired fluidized bed combustors (FBC) and spreader stokers (SS), flue gas recirculation (FGR) is applicable to natural gas- and oil-fired industrial boilers, and flue gas treatment techniques such as SNCR or SCR are applicable to all fossil fuel-fired units. However, in the United States, SNCR has been applied to only a few industrial boilers and SCR has been applied to none.



**Table 2. NO<sub>x</sub> Control for Stoker-fired Industrial Boilers (Bituminous or Sub-bituminous Coal) (WDNR 1989)**

Control Techniques	NO <sub>x</sub> Reduction	
	Percent	Commercial Availability and Comments
FGR	40 to 45	Available. Increased operating cost and significant capital cost.
LEA	10 to 20	Available. Baseline O <sub>2</sub> levels of 9% are reduced to 6.5 to 7%. Danger of grate overheating, clinker formation, corrosion, high CO emission. Can be combined with OFA and FGR.
OFA	5 to 10	Available. Danger same as LEA. Could be applied very effectively with FGR and LEA.
NH <sub>3</sub> injection	60 to 70	Available. Problems – NH <sub>3</sub> slip, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> deposit. Multiple injection ports needed for swinging loads –High operational cost. Narrow temperature window of operability.
Urea injection	60 to 70	Available. Same as NH <sub>3</sub> injection. Wider temperature window than ammonia injection.
SCR	80 to 90	Available. Extremely high capital and operating costs. NH <sub>3</sub> slip and (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> deposit on catalyst surfaces. Catalyst deactivation by coal contaminants.

Notes: 1. NO<sub>x</sub> emissions for stokers are lower than for pulverized coal. Both chain grate spreader stoker and underfeed stokers were considered.

2. A combination of FGR and OFA is effective for moderate reduction.

3. The thermal DeNO<sub>x</sub> and NO<sub>x</sub>OUT processes can be added to augment FGR and OFA.

**Table 3. NO<sub>x</sub> Control for Cyclone-Coal-Fired Industrial Boilers (WDNR 1989)**

Control Techniques	NO <sub>x</sub> Reduction	
	Percent	Commercial Availability and Comments
Reburning natural gas	50 to 60	Under development. Up to 30% of coal heat input replaced by natural gas. Danger of unburned CO and HC in the flue gas.
NH <sub>3</sub> injection	60 to 70	Available. Problems – NH <sub>3</sub> slip, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> deposit. High operational cost. Narrow temperature window.
Urea injection	60 to 70	Available. Same as NH <sub>3</sub> injection.
SCR	80 to 90	Available. Extremely high capital and operating costs. Problems include NH <sub>3</sub> slip, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> deposit on catalyst surfaces and catalyst deactivation by coal contaminants.

Notes: 1. Cyclone boilers are characterized by high uncontrolled NO<sub>x</sub> emissions.

2. Combustion chamber design modifications are very difficult to accomplish.

**Table 4. NO<sub>x</sub> Control for Pulverized-Coal-Fired Industrial Boilers (WDNR 1989)**

Control Techniques	NO <sub>x</sub> Reduction	
	Percent	Commercial Availability and Comments
LNB	50	Commercial available. Relatively high capital investment for boiler modifications.
Reburning	50 to 60	Under development. Danger of unburned natural gas, CO and HC in the flue gas.
NH <sub>3</sub> injection	60 to 70	Available. NH <sub>3</sub> slip, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> deposit. High operational cost. Narrow temperature window.
Urea injection	60 to 70	Available. Same as NH <sub>3</sub> injection.
SCR	80 to 90	Available. Extremely high capital and operating costs. Problems include NH <sub>3</sub> slip, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> deposit on catalyst surfaces and catalyst deactivation by coal contaminants.

Note: Leading technologies for pulverized coal boilers (wall and tangentially fired) are low NO<sub>x</sub> burners.

**Table 5. NO<sub>x</sub> Control for Natural Gas-Fired, Packaged Industrial Boilers (WDNR 1989)**

Control Techniques	NO <sub>x</sub> Reduction	
	Percent	Commercial Availability and Comments
LNB W/LEA	5 to 10	Commercially available. Danger of unburned HC and CO in the flue gas.
LNB W/FGR	60 to 75	Commercially available. Increased operational cost for fans. Increased flame length may cause flame instability and affect super-heater performance.
LNB W/AS	10 to 15	Commercially available. Danger of unburned HC and CO in flue gas. Possible flame impingement.
LNB W/fuel	15 to 20	Commercially available. Danger of unburned HC and staging CO. Increased flame length.
NH <sub>3</sub> & urea	50 to 60	Commercially available. Several boiler design constraints to apply urea and NH <sub>3</sub> injection for package boilers.
SCR	80 to 90	Available. High capital and operating cost.

Note: NO<sub>x</sub> emissions are lower as thermal NO<sub>x</sub> is the only formative mechanism.

**Table 6. NO<sub>x</sub> Control for No. 6 Oil-Fired, Industrial Boilers (Packaged, Watertube) (WDNR 1989)**

Control Techniques	NO <sub>x</sub> Reduction	
	Percent	Commercial Availability and Comments
LNB W/LEA	5 to 10	Commercially available. Danger of unburned HC and soot formation. Flame instability.
Low NO <sub>x</sub> with relatively large substoichiometrically fired precombustor	70	In a final development state. Tested in full scale. Requires space in front of the boiler.
NH <sub>3</sub> & urea injection	50	Commercially available. Several boiler design constraints to apply urea and NH <sub>3</sub> injection for package boilers.
SCR	70 to 80	Commercially Available. SCR Difficulties include <u>plugging and catalyst deactivation.</u>

Note: NO<sub>x</sub> emissions are greater from residual oil compared with distillate oil and natural gas boilers.

**Table 7. NO<sub>x</sub> Emission Control Technologies For New Fossil Fuel Industrial Boilers (USEPA 1997)**

NO <sub>x</sub> Control Options	Fuel Applicability
Combustion control techniques	
Low NO <sub>x</sub> burners for conventional boilers	Coal, natural gas, oil
Low NO <sub>x</sub> burners + overfire air for conventional boilers	Coal, natural gas, oil
Air staging for fluidized bed combustion boilers	Coal
Air staging for spreader stoker boilers	Coal
Flue gas recirculation	Natural gas, oil
Flue gas treatment techniques	
Selective noncatalytic reduction	Coal, natural gas, oil
Selective catalytic reduction	Coal, natural gas, oil

## 5.0 USEPA CONTROL COST DATA FOR INDUSTRIAL FOSSIL FUEL-FIRED BOILERS

In the background technical document for the revised Subpart Db NO<sub>x</sub> emissions standards, USEPA also presented control technology costs for instituting various types of NO<sub>x</sub> emissions control on fossil fuel-fired industrial boilers (USEPA 1997). Summary annualized costs and incremental cost effectiveness ranges from this document are reproduced for various model boilers in Tables 8 and 9, respectively. Table 8 shows the cost of installing combustion controls for NO<sub>x</sub> emissions on industrial fossil fuel-fired boilers ranges from 0% to 2% of the net cost of generating steam in the boiler. When combustion controls are augmented by SNCR, the total cost rises to between 4% and 16% of the steam cost. Finally, when SCR is used along with combustion controls the total cost increases appreciably to between 10% and 48% of the steam cost. Table 9 gives estimates for incremental cost effectiveness in \$/ton NO<sub>x</sub> removed. When applying SCR to industrial boilers after combustion controls have been implemented, the incremental cost effectiveness estimates are seen to be extremely high, ranging from \$5,900 to \$49,800 per ton of NO<sub>x</sub> removed. Incremental cost effectiveness estimates for applying SNCR to boilers after combustion control implementation are also high, ranging from \$1,720 to \$32,140 per ton of NO<sub>x</sub> removed. In the July 1997 *Federal Register* proposal (*FR* 62 [131] 36948-36963), USEPA explains the wide range in the cost and cost effectiveness estimates as follows: “The main differences between industrial steam generating units and utility steam generating units are that industrial steam generating units tend to be smaller and tend to operate at lower capacity factors. The differences between industrial and utility steam generating units would be reflected in the cost impacts of the various NO<sub>x</sub> control technologies. Smaller sized and lower capacity factor units tend to have a higher cost on a per unit output basis.”

**Table 8.** Summary of Annualized Costs for Model Boilers<sup>a</sup> (EPA 1997)

Fuel Type	Furnace Type <sup>b</sup>	Size (MM Btu/hr)	CC <sup>c</sup>		CC + SNCR <sup>c</sup>		CC + SCR <sup>c</sup>		
			\$/yr	%	\$/yr	%	\$/yr	%	
Coal	PC	250	40,040	1	286,530	9	997,740	33	
		500	59,020	1	384,460	6	1,605,070	27	
		1,000	87,010	1	538,850	4	2,756,820	23	
	FBC	100	0	0	173,170	14	NA	NA	
		250	0	0	227,480	8	NA	NA	
		500	0	0	287,410	5	NA	NA	
		1,000	0	0	375,780	3	NA	NA	
	Spreader Stoker	100	0	0	184,580	15	583,440	48	
		250	0	0	256,000	8	960,920	32	
		500	0	0	344,540	6	1,551,210	26	
	Residual Oil	Field-erected Watertube	100	23,970	2	197,060	16	461,860	38
			250	40,040	1	265,600	9	668,940	22
500			59,020	1	341,770	6	972,550	16	
1,000			87,010	1	453,320	4	1,522,790	13	
Packaged Watertube		100	23,970	2	197,060	16	461,860	38	
		250	40,040	1	265,600	9	668,940	22	
Distillate Oil/ Natural Gas	Field-erected Watertube	100	0	0	168,910	14	418,880	35	
		250	0	0	215,110	7	581,250	19	
		500	0	0	261,830	4	818,200	14	
		1,000	0	0	324,470	3	1,245,120	10	
	Packaged Watertube	100	23,970	2	194,400	16	443,210	37	
		250	40,040	1	258,940	9	622,310	21	

<sup>a</sup> The data presented represents annualized costs for the range of boiler sizes at a capacity factor of 0.30. Annualized cost expressed as a percentage of steam cost; steam cost based on \$6 per 1000 lb steam; and 1,300 Btu of heat input per lb of steam generated.

<sup>b</sup> PC = Pulverized Coal; FBC = Fluidized Bed Combustion; <sup>c</sup> CC = Combustion Control; SCR = Selective Catalytic Reduction; SNCR = Selective Non-Catalytic Reduction

**Table 9. Model Boiler Incremental Cost Effectiveness Ranges<sup>a</sup> (USEPA 1997)**

Fuel Type	Furnace Type <sup>b</sup>	Control Technology Comparisons <sup>c</sup>	Incremental Cost Effectiveness (\$/ton)
Coal	PC	CC vs. Baseline	240 - 440
		CC + SNCR vs. CC	1,720 - 3,375
		CC + SCR vs. CC	6,350 - 9,110
		CC + SCR vs. CC + SNCR	14,070 - 18,040
	FBC	CC vs. Baseline	0
		CC + SNCR vs. CC	2,860 - 13,180
		CC + SCR vs. CC	NA <sup>d</sup>
		CC + SCR vs. CC + SNCR	NA
	Spreader Stoker	CC vs. Baseline	0
		CC + SNCR vs. CC	2,100 - 5,620
		CC + SCR vs. CC	5,900 - 11,100
		CC + SCR vs. CC + SNCR	12,250 - 20,240
Residual Oil	Field-erected Watertube	CC vs. Baseline	740 - 2,030
		CC + SNCR vs. CC	2,930 - 13,870
		CC + SCR vs. CC	7,190 - 21,920
		CC + SCR vs. CC + SNCR	14,280 - 35,350
	Packaged Watertube	CC vs. Baseline	640 - 960
		CC + SNCR vs. CC	7,230 - 13,870
		CC + SCR vs. CC	12,600 - 21,920
		CC + SCR vs. CC + SNCR	21,540 - 35,350
Distillate Oil/ Natural Gas	Field-erected Watertube	CC vs. Baseline	0
		CC + SNCR vs. CC	6,170 - 32,140
		CC + SCR vs. CC	14,180 - 49,800
		CC + SCR vs. CC + SNCR	29,190 - 79,250
	Packaged Watertube	CC vs. Baseline	2,030 - 3,040
		CC + SNCR vs. CC	11,110 - 21,620
		CC + SCR vs. CC	18,460 - 33,240
		CC + SCR vs. CC + SNCR	30,730 - 52,600

<sup>a</sup>The data presented represents the incremental cost effectiveness at a capacity factor of 0.30 for the range of boiler sizes 250, 500 and 1,000 MMBtu/hr for PC boilers; 100, 250, 500 and 1,000 MMBtu/hr for FBC and field-erected boilers; 100, 250 and 500 MMBtu/hr for spreader stoker boilers; and 100 and 250 MMBtu/hr for packaged boilers.

<sup>b</sup>PC = Pulverized Coal; FBC = Fluidized Bed Combustion;

<sup>c</sup>CC = Combustion Control; SNCR = Selective Noncatalytic Reduction; SCR = Selective Catalytic Reduction.

<sup>d</sup>NA = Not Applicable

## **6.0 NO<sub>x</sub> CONTROL TECHNIQUES FOR KRAFT PULP MILL SOURCES OTHER THAN FOSSIL FUEL-FIRED BOILERS**

When compared to other industries' facilities, forest products industry facilities are somewhat unique in that they burn a significant quantity of wood and wood-derived fuels. Also, the combustion sources in pulp and paper mills, such as recovery furnaces and lime kilns, are unique to this industry. For example, from data in NCASI files, of the total thermal energy generated at 16 kraft mills to make bleached paperboard, energy derived from wood residue (bark and hogged fuel) combustion ranged from 0% to 32% , averaging about 15%, and energy derived from black liquor combustion ranged from 39% to 70%, averaging about 49%. Thus, on average, nearly 65% of the energy required at a kraft mill to make bleached paperboard is derived from biomass fuels. Consequently, the NO<sub>x</sub> control issues faced by this industry are very different from those of others. This section discusses the potential for NO<sub>x</sub> formation and NO<sub>x</sub> emissions control in wood- and combination wood-fired boilers, kraft recovery furnaces, and kraft pulp mill lime kilns. Also included is a discussion on potential NO<sub>x</sub> emissions resulting from the burning of foul condensate stripper off-gases (SOG).

### **6.1 NO<sub>x</sub> Emissions and Control Techniques for Wood and Combination Wood-Fired Boilers**

NO<sub>x</sub> emissions resulting from wood residue combustion are typically low compared to emissions from coal or oil combustion. This is so because fuel NO<sub>x</sub> is the dominant NO<sub>x</sub> formation mechanism for most biomass combustion, and typical fuel wood N contents are far less than for coal or residual oil. In one study the mean N content of 14 hardwood tree species was found to be about 0.17%, while the mean for 16 softwood tree species was about 0.13% (NCASI 1992). By comparison, for typical anthracite coals, the N contents range from 0.2% to 1.8%, for typical bituminous coals, they range from 1.0% to 1.7%, and for typical sub-bituminous coals, they range from 0.7% to 1.5% (USEPA 1997). Typical N contents in nos. 4 to 6 fuel oils range from 0.3% to 2.2% (USEPA 1997). In addition, the heating values of wood residues are typically far less than those of coal and oil.

There are a few wood species that have N content as high as 0.5% to 1%. Examples of such species are red alder and some types of aspen. Typically, "juvenile" wood species will contain higher levels of N than the "older growth" species since the bark and foliage comprise a higher fraction of the overall tree and nitrogen tends to concentrate more in bark and foliage than in the stem of a tree. Finally, some boilers at the wood products manufacturing facilities are fired with board trim or sanderdust. Such boilers can have a high potential for NO<sub>x</sub> emissions due to the relatively high N concentrations in urea formaldehyde resins contained in the product. Particleboard and medium density fiberboard residuals may have nitrogen contents up to 3%.

The impact on NO<sub>x</sub> emissions from boilers firing wood residues in combination with other fossil fuels such as coal, oil, or natural gas is not well understood. In general, the contribution by thermal NO<sub>x</sub>, formed only when fossil fuels are burned, to overall NO<sub>x</sub> would be expected to be reduced. This is because a reduction is expected in the maximum combustion temperature when the lower heat value wood residue fuel is burned with the higher heat value fossil fuel. Recent test results showing reduction in NO<sub>x</sub> emissions in a coal-wood residue combination boiler as the fraction of wood was increased were attributed to yet another factor, viz., the higher fuel volatility (expressed as the volatile to fixed carbon ratio) of wood residue compared to coal (Battista et al. 1998). The high volatility of the biofuels promotes early ignition in a fuel-rich regime of the flame, creating internal fuel staging and NO<sub>x</sub> reduction (Battista et al. 1998).

Evidence of using combustion controls to reduce NO<sub>x</sub> emissions from wood or combination wood-fired boilers is generally lacking. For stoker and fluidized bed combustor wood-fired units, USEPA's AP-42 document suggests overfire air ports may be used to lower NO<sub>x</sub> emissions by staging the

combustion process (USEPA 1996). However, details of boilers where such modifications have been made and evidence of  $\text{NO}_x$  reductions obtained thereby are not yet available. Preliminary indications of  $\text{NO}_x$  reductions achieved in coal and MSW stoker-fired boilers by the IGT reburning process METHANE DeNOX were alluded to earlier. Most wood residue-fired spreader stoker and fuel cell boilers inherently practice staged combustion by the use of overfire air (with the possible exception of some certain older Dutch oven boilers). Some  $\text{NO}_x$  reduction can be achieved by optimizing staged combustion at full loads, but this cannot be sustained when the boilers are operated at lower loads. Lower emissions of  $\text{NO}_x$  observed from some wood-fired spreader stoker units are likely a result of several factors, including the use of low excess air, optimum staged combustion, low nitrogen content fuels and steady load patterns. With load swings, high excess air is needed to minimize CO emissions, and thus additional  $\text{NO}_x$  reductions cannot be expected.

The use of SCR technology on combination wood-fired boilers would be considered technically infeasible based on the fact that post particulate removal flue gas temperatures are typically significantly lower than those desired for this application (450°F to 750°F). Reheating flue gases in these boilers to bring them within the desired temperature window would result in significant energy penalties. There is limited evidence in the literature that post-combustion  $\text{NO}_x$  emission control by the SNCR process can be applied to wood and combination wood-fired boilers. One vendor states the  $\text{NO}_x$ OUT SNCR process has been successfully applied for post combustion flue gas  $\text{NO}_x$  emissions control on several wood-fired electric-generating units ranging from 130 to 500 x 10<sup>6</sup> Btu/hr with target  $\text{NO}_x$  reductions typically around 50% (NALCO 1998). At least six pulp and paper industry combination boilers burning (a) oil/bark/biomass, (b) paper sludge, (c) paper, (d) fiber waste, (e) bark/gas, and (f) bark/coal/gas were reported to have installed the  $\text{NO}_x$ OUT process (NALCO 1998). An instance of post-combustion  $\text{NO}_x$  emission control using ammonia injection in a 100% wood-fired industrial boiler was first reported in 1987 (Makanski 1987). Ammonia injection was used to reduce  $\text{NO}_x$  emission from 35% to 70% for ammonia-to- $\text{NO}_x$  molar ratios between 0.4 and 3.0. More recently, Abrams (1998) reported on problems experienced with an ammonia injection system installed on a newly constructed wood residue boiler for  $\text{NO}_x$  emissions control. While the manufacturer had guaranteed a  $\text{NO}_x$  emission limit of 0.042 lb/10<sup>6</sup> Btu, the boiler was unable to meet this guarantee unless operated at less than half load. Even then, reducing  $\text{NO}_x$  to near permitted limits consumed considerably more ammonia than anticipated, leading to the formation of a visible ammonium chloride salt plume.

## 6.2 $\text{NO}_x$ Emissions and Control Techniques for Kraft Recovery Furnaces

As previously noted, just as for wood residue combustion,  $\text{NO}_x$  emissions from black liquor combustion in kraft recovery furnaces are also expected to result strictly from the “fuel  $\text{NO}_x$ ” mechanism pathway. The highest temperatures measured in the recovery furnace, usually in the lower furnace region, range from about 1800°F to 2400°F. These are much lower than would be essential for appreciable  $\text{NO}_x$  formation by the thermal  $\text{NO}_x$  pathway (>2,800°F). Hence, due to the dominance of fuel  $\text{NO}_x$  formation pathways, factors that would minimize thermal  $\text{NO}_x$  formation by minimizing peak gas temperatures in the lower furnace, such as the firing of lower solids content liquors, effecting changes in combustion air temperature and pressure, changes in burner design and position, liquor temperature and density, perhaps have only a limited role in controlling  $\text{NO}_x$  formation.

A detailed investigation into the origins of kraft recovery furnace  $\text{NO}_x$  emissions and related parameters by NCASI concluded that black liquor N content was perhaps the most important factor affecting  $\text{NO}_x$  emissions from kraft recovery furnaces (NCASI 1992). Excess oxygen in the zone where the bulk of liquor combustion takes place was considered the second most important factor for  $\text{NO}_x$



formation. While very little can be done to affect the liquor nitrogen content, staged air combustion, which is already integral to the operation of most recovery furnaces, is perhaps the best strategy for minimizing  $\text{NO}_x$  formation in kraft recovery furnaces. The precise distribution of combustion air between primary, secondary and, if relevant, tertiary or quaternary air levels is most likely quite furnace-specific. Forssen et al. (1998) studied the influence of various operating conditions on  $\text{NO}$  formation in the recovery furnace. Using both laboratory experiments and kinetic modeling studies, the authors conclude  $\text{NO}$  is formed from the oxidation of ammonia produced during liquor droplet devolatilization, and this oxidation is strongly dependent on the temperature and number of stages in which the air is mixed with the devolatilized gases. The authors implied that additional air feed levels in the upper furnace may aid in minimizing  $\text{NO}_x$  formation, although no full-scale test results were used to support this conclusion.

The abovementioned NCASI report on recovery furnace  $\text{NO}_x$  emissions (NCASI 1992) contained long-term continuous emissions monitoring data for  $\text{NO}_x$  emissions from several kraft recovery furnaces. These data showed the  $\text{NO}_x$  emissions fell within a fairly narrow range for each furnace, in spite of apparent, significant day-to-day changes in furnace operating behavior as suggested by the corresponding, widely fluctuating data for  $\text{SO}_2$  and  $\text{CO}$  emissions. This lack of significant variability in a given recovery furnace's  $\text{NO}_x$  emissions would suggest most furnaces already use the concepts of staged combustion optimally, and the differences observed between one mill's furnace  $\text{NO}_x$  emissions and another's are mainly a result of the differences between their black liquor N contents. Another point to consider when effecting a change in operating conditions in a kraft recovery furnace is the resulting effect on emissions of compounds such as total reduced sulfur compounds,  $\text{CO}$  and other criteria pollutants ( $\text{SO}_2$  and  $\text{VOC}$ ) which often respond more significantly when reconfiguring the distribution of combustion air.

Relative to flue gas treatment as an  $\text{NO}_x$  control option, SNCR is not considered technologically feasible for kraft recovery furnaces (Kravett and Hanson 1994). This conclusion was based on the fact that a recovery furnace is a complex chemical reaction system and any disruption of the delicate reaction chemistry could potentially damage the furnace, impact the quality of the product, or otherwise unacceptably affect the system. Also, like industrial boilers, kraft recovery furnaces operate at varying loads which makes it difficult to inject the SNCR reagent within the desired temperature window. Several technological limitations also come to bear when one considers the installation of an SCR system on a recovery furnace including (a) potential for plugging and fouling of the SCR catalyst, (b) potential for fouling of the ESP, (c) ammonia handling and ammonia slip emissions issues, (d) potential for increased particulate emissions, (e) creation of a new hazardous waste (spent catalyst), and (f) potential significant energy penalty (Kravett and Hansen 1994).

In a recent paper, Janka et al. (1998) compared field experiments for recovery furnace  $\text{NO}_x$  reduction using (a) air staging, (b) the SNCR method, and (c) an oxidation-reduction scrubber. Working primarily with large Scandinavian furnaces they conclude that air staging, which primarily involves adding a quaternary air level in a large furnace, could potentially result in up to a 30%  $\text{NO}_x$  reduction. The SNCR method, while applicable to achieve up to a 60%  $\text{NO}_x$  reduction, would cost several million dollars for storing, feeding, and control systems for the SNCR agent. Insufficient details on the O-R scrubber make the efficacy of this application difficult to judge at the present time. In summary, the use of quaternary air may be useful in achieving marginal  $\text{NO}_x$  reductions in certain large or newly designed furnaces, while the reservations for use of SNCR mentioned above appear to be still valid.

In a summary assessment of control technologies for reducing nitrogen oxide emissions from non-utility point sources and major area sources, USEPA stated " $\text{NO}_x$  emissions from recovery boilers do

not generally result from thermal oxidation of nitrogen in the air. Oxidation of fuel nitrogen, which appears to be the dominant mechanism for recovery boiler  $\text{NO}_x$  formation, can be sensitive to furnace temperature, however. Changes in the process, such as low excess air and air staging, may reduce  $\text{NO}_x$  emissions in some cases. SNCR may be applicable as a post-process reduction technique. It should be noted, though, that most recovery furnaces already operate with relatively low excess air with little room for significant improvement. While some gains can be achieved in the newer (larger) furnaces, the use of these techniques may also result in increases in  $\text{SO}_2$  and CO emissions and can foul and plug the convection passes, increase acid deposition, and result in production losses” (USEPA 1998).

### 6.3 $\text{NO}_x$ Emissions and Control Techniques for Kraft Pulp Mill Lime Kilns

Lovblad et al. (1993) reviewed  $\text{NO}_x$  emissions from three Swedish lime kilns burning different fuels including tall oil, fuel oil, methanol, turpentine, bark and wood powder, bark gasifier pyrolysis gases, and non-condensable gases from pulping and condensate stripping areas of a pulp mill. Correlations between the fuel type and  $\text{NO}_x$  emissions generally reflected the N contents of the fuels. In one kiln, the  $\text{NO}_x$  emissions correlated well with the combustion temperature. Such a relationship was also observed in the case of one kiln during a 1980 NCASI study (NCASI 1980). Some authors have reported an increase in observed  $\text{NO}_x$  emissions from kilns when burning non-condensable gases (Lovblad et al., 1993; Kiiskila 1990). However, the causes for this increase are not clear. Burning NCGs may require an increase in the amount of excess air used for combustion or may require certain combustion flame adjustments to be made to accommodate the NCG burning so as to continue to meet the strict TRS emission limits generally imposed on lime kilns. Besides potential nitrogenous substances present in the NCGs that may oxidize to  $\text{NO}_x$ , these other factors may also influence  $\text{NO}_x$  emissions.

Fossil fuels burned in a kraft pulp mill lime kiln typically comprise only about 10% of the total energy expended to make the pulp or paper product. Fossil fuels such as natural gas or residual fuel oil are typically burned in the kiln to generate the bulk of the energy required for calcination of the lime mud. Lime kilns are designed to recover “reburned” lime or CaO by calcining the  $\text{CaCO}_3$ -containing lime mud with hot combustion gases resulting from fossil fuel combustion. No heat recovery occurs in the kiln, and kiln gases typically exit at about 450°F prior to being treated by a wet scrubber or ESP for particulate emission control. As such, the design of the lime kiln precludes the use of post-combustion  $\text{NO}_x$  reduction techniques such as SNCR and SCR. Only combustion control techniques valid for other fossil fuel-fired combustion units outlined earlier would be applicable to lime kiln  $\text{NO}_x$  emissions control. However, no systematic study of  $\text{NO}_x$  formation and  $\text{NO}_x$  emission reduction in lime kilns has been conducted in the U.S., possibly due to the need to operate the kiln within a fairly narrow temperature range to achieve proper lime moisture content. In a Best Available Control Technology (BACT) analysis conducted on a new lime kiln in 1997, the use of low  $\text{NO}_x$  burners was determined to be technically infeasible due to complexities resulting in poor efficiency, increased energy usage, and decreased calcining capacity (NCASI 1998).

More importantly, though, it is not clear why  $\text{NO}_x$  emissions measured from various lime kilns in the United States vary as much as they do. Table 1 showed that uncontrolled  $\text{NO}_x$  emission factors for natural gas and residual oil combustion in industrial boilers ranged from 0.17 to 0.25 lb/10<sup>6</sup> Btu and from 0.28 to 0.45 lb/10<sup>6</sup> Btu, respectively. In a 1980 NCASI study  $\text{NO}_x$  emissions measured from six lime kilns, four burning residual oil and two burning natural gas, ranged from as low as 0.07 lb/10<sup>6</sup> Btu to as high as 1.12 lb/10<sup>6</sup> Btu, averaging about 0.42 lb/10<sup>6</sup> Btu (NCASI 1980). Including these six kilns NCASI reported  $\text{NO}_x$  emissions from 14 kilns burning either natural gas or residual oil ranged

from as low as 0.01 to as high as 1.12 lb/10<sup>6</sup> Btu, averaging about 0.27 lb/10<sup>6</sup> Btu (NCASI 1993). Although never demonstrated, low NO<sub>x</sub> emissions from certain lime kilns could be a result of some of the NO<sub>x</sub> formed in the flame zone being captured downstream by the fine lime dust or in the wet alkaline scrubber, or in the case of kilns which also treat stripper off-gases (SOGs), the ammonia present in such SOGs could serve as a reducing agent converting some of the NO<sub>x</sub> present to N<sub>2</sub>. Alternately, high lime kiln NO<sub>x</sub> emissions may result either from the oxidation of nitrogenous substances in the treated SOGs or from the different ways in which excess combustion air is manipulated in the flame zone of a lime kiln in order to maintain adequate control of the regulated total reduced sulfur (TRS) compound emissions. In conclusion, while traditional NO<sub>x</sub> control techniques such as use of low NO<sub>x</sub> burners could no doubt be applied to lime kilns, the wide range in existing lime kiln NO<sub>x</sub> emission data suggest clearly that NO<sub>x</sub> control strategies for each kiln have to be evaluated on a case-by-case basis. Minimizing the use of excess air, while staying within regulated limits for TRS compounds, may be the most viable NO<sub>x</sub> control technique applicable to lime kilns.

#### 6.4 NO<sub>x</sub> Emissions from Kraft Pulp Mill Incineration of NCGs and SOGs

In a kraft pulp mill, SOGs result from the stripping of foul condensates. This practice is expected to become increasingly common, especially as mills begin to respond to the recently promulgated "Cluster Rule." Kraft foul condensates can contain significant levels of ammonia in addition to methanol and other VOCs which will be stripped off when the condensates are subject to steam stripping. If the SOGs are not subjected to methanol treatment (i.e., methanol removal) prior to incineration, or if the separated methanol is burned along with the SOGs in a boiler, lime kiln, or thermal oxidizer, significant NO<sub>x</sub> emissions can potentially result from oxidation of the NH<sub>3</sub> present in the SOGs. These emissions would be in addition to the NO<sub>x</sub> emissions expected from burning of fossil fuels and/or the SOG VOC content. In tracking the fate of nitrogen in a kraft mill chemical recovery process, Kymalainen et al. (1998) conclude "the stripping of foul condensates to be the main exit point for ammonia in the recovery process, the amount of this ammonia nitrogen being very significant and corresponding almost to a typical NO<sub>x</sub> emission of a recovery furnace."

Limited measurement data in NCASI files on foul condensate ammonia concentrations appear to support this conclusion. Ammonia concentrations in foul and steam-stripped condensates from two kraft pulp mills ranged from 140 to 170 ppm and from 1.7 to 2.2 ppm, respectively. Thus, over 98% of the NH<sub>3</sub> present in the foul condensates was stripped, presumably ending up in the SOGs. Each mill had a pulping capacity of about 1500 tpd, and the amount of NH<sub>3</sub> stripped ranged from about 28 to 50 lb/hr. If the SOGs contained all the stripped NH<sub>3</sub> and if the NH<sub>3</sub> in the SOGs were assumed to completely oxidize to NO<sub>x</sub> during treatment, NO<sub>x</sub> emissions ranging from 1.2 to 2.1 lb/ton pulp would have resulted. This would be comparable to NO<sub>x</sub> emissions from typical kraft recovery furnaces. In an NCASI study, NO<sub>x</sub> emissions from 11 kraft recovery furnaces ranged from 1.8 to 3.9 lb/ton pulp, averaging about 2.3 lb/ton (NCASI 1992).

However, it is not clear as to what extent the ammonia to NO<sub>x</sub> conversion occurs in various incineration devices and what baseline level of NO<sub>x</sub> can be expected when burning concentrated pulp mill NCGs and the combustible constituents in SOGs (such as methanol). As discussed earlier in section 4.2.1 (a), when injected in gases within a temperature window of about 1600°F to 2200°F, ammonia reduces NO<sub>x</sub> to N<sub>2</sub>. Below about 1600°F, ammonia most likely remains unreacted, leading to the so-called "ammonia slip." Above about 2000°F to 2200°F, the injected ammonia mostly oxidizes to NO<sub>x</sub>. Thus, in cases where SOGs are treated in boilers or lime kilns, if temperatures in the zone of SOG introduction exceed 2200°F, the ammonia present in the SOGs will likely completely oxidize to NO<sub>x</sub>. If, however, the SOGs are introduced in zones where temperatures are below about 2000°F, the

ammonia is likely to either remain unreacted or even participate in the reduction of  $\text{NO}_x$  already present in the combustion gases.

Limited data on  $\text{NO}_x$  emissions from burning of SOGs in dedicated thermal oxidizers currently available to NCASI suggest that while the presence of SOGs could lead to increased  $\text{NO}_x$  emissions, this increase is much less than that corresponding to complete conversion of ammonia to  $\text{NO}_x$ . Stack test data for  $\text{NO}_x$  emissions from 15 TRS thermal oxidizers were obtained by NCASI during a 1995 survey, and these averaged about 0.3 lb/ton pulp (NCASI 1997). However, it was unclear how many of these oxidizers were burning SOGs along with other NCGs. Bloom (1998) reported  $\text{NO}_x$  emissions from three oxidizers burning SOGs ranged from 176 to 225 ppm. However, other details such as gas flow rate, pulping rate, etc. were not provided, making it difficult to convert these emissions to a lb per ton pulp basis. Recent test data corresponding to a southeastern U.S. kraft pulp mill thermal oxidizer which treats pulp mill NCGs including SOGs showed  $\text{NO}_x$  emissions to be about 0.32 lb/ton pulp. After modifications in the manner in which the SOGs were introduced into the oxidizer were made, additional tests were carried out, and these changes resulted in  $\text{NO}_x$  emissions to be further reduced to below 0.2 lb/ton pulp.  $\text{NO}_x$  emission test data from another southeastern U.S. kraft pulp mill thermal oxidizer burning concentrated NCGs and SOGs showed a strong relationship between  $\text{NO}_x$  emissions and the excess air used in the oxidizer (as measured by the stack  $\text{O}_2$  concentration).  $\text{NO}_x$  emissions were as low as 0.01 lb/ton pulp at 1.0%  $\text{O}_2$  to as high as 0.79 lb/ton pulp at 13.2%  $\text{O}_2$  in the stack. Most thermal oxidizers operate at temperatures below about 1600°F, making it quite likely that much of the  $\text{NH}_3$  in the SOGs treated in these oxidizers will remain unreacted and no net increase in  $\text{NO}_x$  emissions will result from the ammonia content itself. Also, since most thermal oxidizers burning SOGs are equipped with a wet scrubber for  $\text{SO}_2$  removal, the unreacted ammonia is expected to be removed in such a scrubber. In conclusion,  $\text{NO}_x$  emission control strategies for units burning SOGs in a kraft mill should take the above anomalies into consideration.

## 7.0 SUMMARY

This report reviewed the current state of understanding of how  $\text{NO}_x$  is formed during combustion of fossil and biomass fuels. For fossil fuel-fired boilers, brief descriptions of techniques for reducing  $\text{NO}_x$  formation by installing various combustion modifications, as well as for reducing  $\text{NO}_x$  emissions by installing SNCR and SCR flue gas treatment systems, were provided. The limitations of applying  $\text{NO}_x$  control technologies, currently proven mainly for utility fossil fuel-fired boilers, to fossil fuel-fired and biomass fuel-fired industrial boilers were outlined. The uniqueness of  $\text{NO}_x$  emissions from combustion units typically present in a kraft pulp and paper mill, including wood and combination wood-fired boilers, kraft recovery furnaces and kraft pulp mill lime kilns and the potential for their control, were discussed. The complexities surrounding the burning of stripper off-gases and concentrated NCGs in boilers, lime kilns, and dedicated thermal oxidizers were also highlighted.

USEPA's recommendations of proven  $\text{NO}_x$  control technologies applicable to fossil fuel-fired industrial boilers as laid out in the technical support document for its recently promulgated revisions to the NSPS Subpart Db  $\text{NO}_x$  emission limits and the results of a 1989 Wisconsin DNR study that evaluated several  $\text{NO}_x$  emission reduction or removal technologies for all industrial boilers in the state of Wisconsin were presented. Control cost estimates derived in the Subpart Db supporting document were also presented for model industrial boilers. These estimates provided costs for combustion control (CC), CC with SNCR, and CC with SCR for various coal-fired, gas-fired, and oil-fired industrial boilers.

Based upon available information the following key observations were made:

- The use of low NO<sub>x</sub> burners with secondary air appears to be a viable NO<sub>x</sub> control technology for all fossil fuel-fired industrial boilers. However, flame impingement is a valid concern in small, packaged boilers.
- Flue gas recirculation may be applicable to natural gas- and oil-fired industrial boilers. However, windbox capacities, tube wall erosion and damage from changes in water circulation patterns should be considered.
- SNCR can theoretically be applied to industrial boilers firing any combination of coal, oil, natural gas, or biomass. However, several limitations unique to industrial boilers such as swinging loads, availability of the correct temperature window for NH<sub>3</sub> or urea injection, inadequate mixing, and excessive ammonia slip need to be considered.
- Swinging steam loads, problems with ammonia slip, catalyst deterioration and pluggage, significant costs and generally a lack of demonstrated experience with industrial boilers in the United States would likely rule out application of SCR technology to most industrial boilers.
- Swinging steam loads also limit the amount of NO<sub>x</sub> reduction that can be achieved in stoker-fired industrial boilers through limiting excess air.
- Optimizing combustion conditions by manipulating the combustion air is likely the most effective NO<sub>x</sub> control technique for kraft recovery furnaces, although the improvements are expected to be marginal. Most recovery furnaces are already operated with optimum staged combustion.
- While combustion modifications offer the best NO<sub>x</sub> control strategy in lime kilns, NO<sub>x</sub> formation and reduction mechanisms in kilns are not well understood. As such, they need to be investigated on a case-by-case basis.
- The potential for NO<sub>x</sub> emissions from burning untreated stripper off-gases in certain kraft mill combustion systems needs to be considered in future mill NO<sub>x</sub> emissions and inventory exercises.

Overall, the importance of recognizing that the nitrogen content of all biomass fuels, including wood residues, spent pulping liquors, and waste treatment plant residuals, is the most important contributing factor towards NO<sub>x</sub> formation and emissions cannot be understated. NO<sub>x</sub> control strategies for units burning biofuels should revolve around control of fuel NO<sub>x</sub> and not thermal NO<sub>x</sub>.

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