# Nitrogen Oxides: Pollution Prevention and Control

The first priority in designing a strategy to control nitrogen oxides is to protect human health. Human health impacts appear to be related to peak exposures to nitrogen oxides ( $NO_x$ ). In addition to potentially damaging human health, nitrogen oxides are precursors to ozone ( $O_3$ ) formation, which can harm human health and vegetation. Finally, nitrogen oxides contribute to acid deposition, which damages vegetation and aquatic ecosystems.

The extent to which NO<sub>x</sub> emissions harm human health depends on ground-level concentrations and the number of people exposed. Source location can affect these parameters. Gases emitted in areas with meteorological, climatological, and topographical features that favor dispersion will be less likely to concentrate near the ground. However, some meteorological conditions, such as inversion, may result in significantly higher ambient levels. Sources away from population centers will expose fewer people to harmful pollution. Plant siting is a critical feature in any air pollution management strategy. However, due to the dispersion of nitrogen oxides that may contribute to ozone formation and acid deposition far from the source, relying on plant siting alone is not a recommended strategy. The long-term objective must be to reduce total emissions.

Effective control of NO<sub>x</sub> emissions will require controls on both stationary sources and mobile transport sources. Each requires different strategies. This guideline focuses on control strategies for stationary sources (primarily fossil-fuel-fired electricity-generating plants).

# Limiting Emissions from Stationary Sources

Nitrogen oxides are produced in the combustion process by two different mechanisms: (a) burning the nitrogen in the fuel, primarily coal or heavy oil (fuel NO<sub>x</sub>); and (b) high-temperature oxidation of the molecular nitrogen in the air used for combustion (thermal NO<sub>x</sub>). Formation of fuel NO<sub>x</sub> depends on combustion conditions, such as oxygen concentration and mixing patterns, and on the nitrogen content of the fuel. Formation of thermal NO<sub>x</sub> depends on combustion temperature. Above 1,538°C (2,800°F), NO<sub>x</sub> formation rises exponentially with increasing temperature (Stultz and Kitto 1992). The relative contributions of fuel NO<sub>x</sub> and thermal NO<sub>x</sub> to emissions from a particular plant depend on the combustion conditions, the type of burner, and the type of fuel.

Approaches for controlling  $NO_x$  from stationary sources can address fuel  $NO_x$ , thermal  $NO_x$ , or both. One way of controlling  $NO_x$  emissions is to use low-nitrogen fuels. Another is to modify combustion conditions to generate less  $NO_x$ . Flue gas treatment techniques, such as selective catalytic reduction (SCR) processes, can remove  $NO_x$ .

## Choice of Fuel

Coals and residual fuel oils containing organically bound nitrogen contribute to over 50% of total emissions of  $NO_x$ , according to some estimates. The nitrogen content of U.S. coal ranges between 0.5% and 2% and that of residual fuel oil between 0.1% and 0.5%. In many circumstances, the most cost-effective means of reducing  $NO_x$  emissions will be to use low-nitrogen fuels such as natural gas. Natural gas used as fuel can emit 60% less  $NO_x$  than coal and virtually no particulate matter or sulfur oxides.

## **Combustion Control**

Combustion control may involve any of three strategies: (a) reducing peak temperatures in the combustion zone; (b) reducing the gas residence time in the high-temperature zone; and (c) reducing oxygen concentrations in the combustion zone. These changes in the combustion process can be achieved either through process modifications or by modifying operating conditions on existing furnaces. Process modifications include using specially designed low-NO<sub>x</sub> burners, reburning, combustion staging, gas recirculation, reduced air preheat and firing rates, water or steam injection, and low excess air (LEA) firing. These modifications are capable of reducing NO<sub>x</sub> emissions by 50 to 80%. The method of combustion control used depends on the type of boiler and the method of firing fuel.

#### **Process Modifications**

New *low-NO<sub>x</sub>* burners are effective in reducing NO<sub>x</sub> emissions from both new power plants and existing plants that are being retrofitted. Low-NO<sub>x</sub> burners limit the formation of nitrogen oxides by controlling the mixing of fuel and air, in effect automating low-excess-air firing or staged combustion. Compared with older conventional burners, low-NO<sub>x</sub> burners reduce emissions of  $NO_x$  by 40–60%. Because low- $NO_x$  burners are relatively inexpensive, power utilities have been quick to accept them; in fact, low-NO<sub>x</sub> burners are now a standard part of new designs. Capital costs for low-NO<sub>x</sub> burners with overfire air (OFA) range between US\$20 and US\$25 per kilowatt (Bounicore and Davis 1992; Kataoka, personal communication, 1994).

Unfortunately, low-NO<sub>x</sub> burners are not suitable for reducing NO<sub>x</sub> emissions from cyclonefired boilers, which emit large quantities of NO<sub>x</sub>, due to their high operating temperatures. Because combustion takes place outside the main furnace, the use of low-NO<sub>x</sub> burners is not suitable for these applications (Bounicore and Davis 1992). However, reburning technology can reduce NO<sub>x</sub> emissions.

*Reburning* is a technology used to reduce  $NO_x$ emissions from cyclone furnaces and other selected applications. In reburning, 75–80% of the furnace fuel input is burned in the furnace with minimum excess air. The remaining fuel (gas, oil, or coal) is added to the furnace above the primary combustion zone. This secondary combustion zone is operated substoichiometrically to generate hydrocarbon radicals that reduce to nitrogen the nitrogen oxides that are formed. The combustion process is then completed by adding the balance of the combustion air through overfire air ports in a final burnout zone at the top of the furnace.

Staged combustion (off-stoichiometric combustion) burns the fuel in two or more steps. Staged combustion can be accomplished by firing some of the burners fuel-rich and the rest fuel-lean, by taking some of the burners out of service and allowing them only to admit air to the furnace, or by firing all the burners fuel-rich in the primary combustion zone and admitting the remaining air over the top of the flame zone (OFA); see Cooper and Alley 1986). Staged combustion techniques can reduce NO<sub>x</sub> emissions by 20–50%. Conventional OFA alone can reduce emissions of NO<sub>x</sub> by 30%, and advanced OFA has the potential of reducing them still further, although potential for corrosion and slagging exists. Capital costs for conventional and advanced OFA range between US\$5 and \$10 per kilowatt (Bounicore and Davis 1992).

Flue gas recirculation (FGR) is the rerouting of some of the flue gases back to the furnace. By using the flue gas from the economizer outlet, both the furnace air temperature and the furnace oxygen concentration can be reduced. However, in retrofits FGR can be very expensive. Flue gas recirculation is typically applied to oil- and gasfired boilers and reduces  $NO_x$  emissions by 20– 50%. Modifications to the boiler in the form of ducting and an energy efficiency loss due to the power requirements of the recirculation fans can make the cost of this option higher than for some of the in-furnace  $NO_x$  control methods.

Reduced air preheat and reduced firing rates lower peak temperatures in the combustion zone, thus reducing thermal  $NO_x$ . This strategy, however, carries a substantial energy penalty. Emissions of smoke and carbon monoxide need to be controlled, which reduces operational flexibility.

*Water or steam injection* reduces flame temperatures and thus thermal  $NO_x$ . Water injection is especially effective for gas turbines, reducing  $NO_x$ emissions by about 80% at a water injection rate of 2%. For a gas turbine, the energy penalty is about 1%, but for a utility boiler it can be as high as 10%. For diesel-fired units, 25–35% reductions in  $NO_x$  emissions can be achieved using waterfuel mixtures.

#### Modifications in Operating Conditions

*Low-excess-air firing (LEA)* is a simple, yet effective technique. Excess air is the amount of air in excess of what is theoretically needed to achieve 100% combustion. Before fuel prices rose, it was not uncommon to see furnaces operating with 50–100% excess air. Currently, it is possible to achieve full combustion for coal-fired units with less than 15–30% excess air. Studies have shown that reducing excess air from an average of 20% to an average of 14% can reduce emissions of NO<sub>x</sub> by an average of 19% (Cooper and Alley 1986).

Techniques involving low-excess-air firing, staged-combustion, and flue gas recirculation are effective in controlling both fuel  $NO_x$  and thermal  $NO_x$ . The techniques *of* reduced air preheat and reduced firing rates (from normal operation) and water or steam injection are effective only in controlling thermal  $NO_x$ . These will therefore not be as effective for coal-fired units, since about 80% of the  $NO_x$  emitted from these units is fuel  $NO_x$ .

#### Flue Gas Treatment

*Flue gas treatment (FGT)* is more effective in reducing  $NO_x$  emissions than are combustion controls, although at higher cost. FGT is also useful where combustion controls are not applicable. Pollution prevention measures, such as using a high-pressure process in nitric acid plants, is more cost-effective in controlling  $NO_x$  emissions. FGT technologies have been primarily developed and are most widely used in Japan and other OECD countries. The techniques can be classified as selective catalytic reduction, selective noncatalytic reduction, and adsorption.

Selective catalytic reduction (SCR) is currently the most developed and widely applied FGT technology. In the SCR process, ammonia is used as a reducing agent to convert  $NO_x$  to nitrogen in the presence of a catalyst in a converter upstream of the air heater. The catalyst is usually a mixture of titanium dioxide, vanadium pentoxide, and tungsten trioxide (Bounicore and Davis 1992). SCR can remove 60–90% of  $NO_x$  from flue gases. Unfortunately, the process is very expensive (US\$40–\$80/kilowatt), and the associated ammonia injection results in an ammonia slipstream in the exhaust. In addition, there are some concerns associated with anhydrous ammonia storage.

Selective noncatalytic reduction (SNCR) using ammonia- or urea-based compounds is still in the developmental stage. Early results indicate that SNCR systems can reduce NO<sub>x</sub> emissions by 30-70%. Capital costs for SNCR are expected to be much lower than for SCR processes, ranging between US\$10 and US\$20 per kilowatt (Bounicore and Davis 1992; Kataoka, 1992). Several dry adsorption techniques are available for simultaneous control of  $NO_x$  and sulfur oxides  $(SO_x)$ . One type of system uses activated carbon with ammonia  $(NH_3)$  injection to simultaneously reduce the NO<sub>x</sub> to nitrogen  $(N_2)$  and oxidize the SO<sub>2</sub> to sulfuric acid  $(H_2SO_4)$ . If there is no sulfur in the fuel, the carbon acts as a catalyst for NO<sub>x</sub> reduction only. Another adsorption system uses a copper oxide catalyst that adsorbs sulfur dioxide to form copper sulfate. Both copper oxide and copper sulfate are reasonably good catalysts for the selective reduction of NO<sub>x</sub> with NH<sub>3</sub>. This process, which has been installed on a 40-megawatt oil-fired boiler in Japan, can remove about 70% of NO<sub>x</sub> and 90% of SO<sub>x</sub> from flue gases (Cooper and Alley 1986).

## **Applications of NO<sub>x</sub> Control Systems**

For *coal-fired boilers* (which accounted for a major portion of all utility  $NO_x$  emissions), the most widely applied control technologies involve combustion modifications, including low-excess-air firing, staged combustion, and use of low- $NO_x$ burners. For *oil-fired* boilers, the most widely applied techniques include flue gas recirculation, in addition to the techniques used for coal-fired units. For *gas-fired units*, which in any case emit 60% less  $NO_x$  than coal-fired units, the primary control technologies include flue gas recirculation and combustion modifications. Finally, for *diesel plants*, the common technologies are watersteam injection, and SCR technology.

Table 1 summarizes the  $NO_x$  reduction rates that are normally achieved through combustion modifications and flue gas treatment systems.

### Recommendations

The most cost-effective methods of reducing emissions of  $NO_x$  are the use of low- $NO_x$  burners

Coal	Oil	Gas	
10–30	10–30	10–30	
20–50	20–50	20–50	
n.a.	20-50	20–50	
n.a.	10–50	n.a.	
30–40	30–40	30–40	
60-90	60–90	60-90	
n.a.	30–70	30–70	
	10-30 20-50 n.a. n.a. 30-40 60-90	10-30 10-30   20-50 20-50   n.a. 20-50   n.a. 10-50   30-40 30-40   60-90 60-90	10-30 10-30 10-30   20-50 20-50 20-50   n.a. 20-50 20-50   n.a. 10-50 n.a.   30-40 30-40 30-40   60-90 60-90 60-90   60-90 60-90 60-90

Table 1. NO<sub>x</sub> Removal Efficiencies for Combustion Modifications and Flue Gas Treatment (percentage reduction in NO<sub>x</sub>)

n.a. Not applicable.

and the use of low nitrogen fuels such as natural gas. Natural gas has the added advantage of emitting almost no particulate matter or sulfur dioxide when used as fuel. Other cost-effective approaches to emissions control include combustion modifications. These can reduce  $NO_x$  emissions by up to 50% at reasonable cost. Flue gas treatment systems can achieve greater emissions reductions, but at a much higher cost.

Table 2 shows applications of NO<sub>x</sub> abatement technologies.

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Technique	Boiler		Metal	Petro- leum	Sinter-	Cement calci-	Glass		Waste inciner-	Nitric acid	Internal combus-		
	Large/	51	heating	heating	ing	nation	melting	Coke		manu-	tion	Gas	
	medium	Small	furnace	furnace	furnace	furnace	furnace	oven	furnace	facture	engine	turbine	Diesel
Low excess air	•	•	•	•	U	•	•	М					
Two-stage combustion													
(including off-stoichio-													
metric combustion)	•	М	•	•									
Flue gas recirculation	•	М	М			U		Μ			М	М	
Water/steam injection													
(including emulsion fuel)	М	U	U	М							М	Μ	Μ
_ow-NO <sub>x</sub> burners	•	•	М	•			U						
Selective catalytic													
reduction	М		U	М	U	U	U	Μ		Μ	U	U	Μ
Nonselective catalytic													
reduction	U			U		М				Μ			
Noncatalytic reduction	М			U			U						
Net-chemical scrubbing	М		U	U	U				U	Μ			
Other: change of temperatu	ıre		М			• (Use p	re-			• (Use h	nigh-		
profile; nonsuspension						heaters	3			pressu	ire		
preheater kiln						and pro	э-			proces	ss)		
						calcine	ers)						

# Table 2. Applicability of NO<sub>x</sub> Abatement Technologies, by Type of Facility and by Technique

*Notes:* • indicates high reliability; M, some points must be taken into account in the case of actual application; U, under study in a test plant. *Source:* Adapted from OECD 1983 (verified as current).