
Nitrogen Oxide Air Emission Impacts and Controls

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TECHNICAL BULLETIN

NITROGEN OXIDES (NO_x), WHY AND HOW THEY ARE CONTROLLED

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Nitrogen Oxides (NO_x), Why and How They Are Controlled

Prepared by

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CORRECTION NOTICE

This document, EPA-456/F-99-006a, corrects errors found in the original document, EPA-456/F-99-006. These corrections are:

Page 8, fourth paragraph: “Destruction or Recovery Efficiency” has been changed to “Destruction or Removal Efficiency;”

Page 10, Method 2. Reducing Residence Time: This section has been rewritten to correct for an ambiguity in the original text.

Page 20, Table 4. Added Selective Non-Catalytic Reduction (SNCR) to the table and added acronyms for other technologies.

Page 29, last paragraph: This paragraph has been rewritten to correct an error in stating the configuration of a typical cogeneration facility.

Page 30, Internal Combustion Reciprocating Engines: A sentence has been added to the end of this section to refer the readers to Table 13 for more information;

Page 41, third through seventh paragraphs: These paragraphs were renumbered to correct for a numbering error (numbers 6 and 7 were used twice).

FORWARD

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Nitrogen Oxides (NO_x), Why and How They Are Controlled

*When we try to look only at one thing in Nature,
we find it connected to everything else.*

John Muir

Nitrogen oxides (NO_x) are a very interesting and important family of air polluting chemical compounds. This bulletin explains why NO_x are important air pollutants and how NO_x are formed and react in the atmosphere. This bulletin also discusses the principles on which all NO_x control and pollution prevention technologies are based; available NO_x technologies for various combustion sources; and performance and cost of NO_x technologies..

WHY SHOULD WE CONTROL NO_x?

NO_x represent a family of seven compounds. Actually, EPA regulates only nitrogen dioxide (NO₂) as a surrogate for this family of compounds because it is the most prevalent form of NO_x in the atmosphere that is generated by anthropogenic (human) activities. NO₂ is not only an important air pollutant by itself, but also reacts in the atmosphere to form ozone (O₃) and acid rain. It is important to note that the ozone that we want to minimize is tropospheric ozone; that is, ozone in the ambient air that we breathe. We are not talking about stratospheric ozone in the upper atmosphere that we cannot breathe. Stratospheric ozone protects us and the troposphere from ionizing radiation coming from the sun.

EPA has established National Ambient Air Quality Standards (NAAQS) for NO₂ and tropospheric ozone. The NAAQS define levels of air quality that are necessary, with a reasonable margin of safety, to protect public health (primary standard) and public welfare (secondary standard) from any known or anticipated adverse effects of pollution. The primary and secondary standard for NO₂ is 0.053 parts per million (ppm) (100 micrograms per cubic meter), annual arithmetic mean concentration.

Tropospheric ozone has been and continues to be a significant air pollution problem in the United States and is the primary constituent of smog. Large portions of the country do not meet the ozone NAAQS and thereby expose large segments of the population to unhealthy levels of ozone in the air. NO₂ reacts in the presence of air and ultraviolet light (UV) in sunlight to form ozone and nitric oxide (NO). The NO then reacts with free radicals in the atmosphere, which are also created by the UV acting on volatile organic compounds (VOC). The free radicals then recycle NO to NO₂. In this way, each molecule of NO can produce ozone multiple times.⁴⁰ This will continue until the VOC are reduced to short chains of carbon compounds that cease to be photo reactive (a reaction caused by light). A VOC molecule can usually do this about 5 times.

In addition to the NO₂ and Ozone NAAQS concerns, NO_x and sulfur oxides (SO_x) in the

atmosphere are captured by moisture to form acid rain. Acid rain, along with cloud and dry deposition, severely affects certain ecosystems and directly affects some segments of our economy. All of these facts indicate an obvious need to reduce NO_x emissions. However, to successfully do so, we must understand the generation and control of the NO_x family of air pollutants.

WHAT IS A NITROGEN OXIDE?

Diatomic molecular nitrogen (N₂) is a relatively inert gas that makes up about 80% of the air we breathe. However, the chemical element nitrogen (N), as a single atom, can be reactive and have ionization levels (referred to as valence states) from plus one to plus five. Thus nitrogen can form several different oxides. Using the Niels Bohr model of the atom, valence state relates to the number of electrons which are either deficient (positive valence) or surplus (negative valence) in the ion when compared with the neutral molecule. The family of NO_x compounds and their properties are listed in Table 1.

Table 1. Nitrogen Oxides (NO_x)

Formula	Name	Nitrogen Valence	Properties
N ₂ O	nitrous oxide	1	colorless gas water soluble
NO N ₂ O ₂	nitric oxide dinitrogen dioxide	2	colorless gas slightly water soluble
N ₂ O ₃	dinitrogen trioxide	3	black solid water soluble, decomposes in water
NO ₂ N ₂ O ₄	nitrogen dioxide dinitrogen tetroxide	4	red-brown gas very water soluble, decomposes in water
N ₂ O ₅	dinitrogen pentoxide	5	white solid very water soluble, decomposes in water

Oxygen ions are always at valence minus 2. Depending upon the number of oxygen ions (always balanced by the valence state of nitrogen), NO_x can react to either deplete or enhance ozone concentrations. The nitrogen ion in these oxides really does a dance in which it has (at different times) various numbers of oxygen ions as partners. Nitrogen changes its number of partners when it changes its ionization energy level. This happens whenever NO_x: (1) is hit with a photon of ionizing radiation (UV or a shorter wavelength light); (2) is hit with enough photons that together transfer enough energy to change its ionization level; (3) is catalyzed; (4) is stimulated sufficiently by thermal (IR) energy; (5) reacts with a chemically oxidizing or reducing radical (an ionized fragment of a molecule); or (6) reacts with a chemically oxidizing or reducing

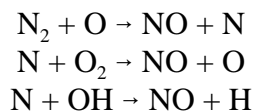
ion (an atom with unbalanced electrical charge).

When any of these oxides dissolve in water and decompose, they form nitric acid (HNO₃) or nitrous acid (HNO₂). Nitric acid forms nitrate salts when it is neutralized. Nitrous acid forms nitrite salts. Thus, NO_x and its derivatives exist and react either as gases in the air, as acids in droplets of water, or as a salt. These gases, acid gases and salts together contribute to pollution effects that have been observed and attributed to acid rain.

Nitrous oxide (N₂O), NO, and NO₂ are the most abundant nitrogen oxides in the air. N₂O (also known as laughing gas) is produced abundantly by biogenic sources such as plants and yeasts. It is only mildly reactive, and is an analgesic (i.e., unlike an anaesthetic you still feel pain, but you feel so good that you just don't mind it). N₂O is an ozone depleting substance which reacts with O₃ in both the troposphere (i.e., below 10,000 feet above sea level) and in the stratosphere (50,000 - 150,000 feet). N₂O has a long half-life, estimated at from 100 to 150 years.

Oxidation of N₂O by O₃ can occur at any temperature and yields both molecular oxygen (O₂) and either NO or two NO molecules joined together as its dimer, dinitrogen dioxide (N₂O₂). The NO or N₂O₂ then oxidizes quickly (in about two hours) to NO₂. The NO₂ then creates an ozone molecule out of a molecule of oxygen (O₂) when it gets hit by a photon of ionizing radiation from sunlight. N₂O is also a "Greenhouse Gas" which, like carbon dioxide (CO₂), absorbs long wavelength infrared radiation to hold heat radiating from Earth, and thereby contributes to global warming.

Emissions of NO_x from combustion are primarily in the form of NO. According to the Zeldovich equations, NO is generated to the limit of available oxygen (about 200,000 ppm) in air at temperatures above 1,300°C (2,370°F). At temperatures below 760°C (1,400°F), NO is either generated in much lower concentrations or not at all. Combustion NO is generated as a function of air to fuel ratio and is more pronounced when the mixture is on the fuel-lean side of the stoichiometric ratio⁵⁰ (the ratio of chemicals which enter into reaction). The Zeldovich equations are:



Except for NO from soils, lightning and natural fires, NO is largely anthropogenic (i.e., generated by human activity). Biogenic sources are generally thought to account for less than 10% of total NO emissions. NO produces the same failure to absorb oxygen into the blood as carbon monoxide (CO). However, since NO is only slightly soluble in water, it poses no real threat except to infants and very sensitive individuals.

NO₂ is present in the atmosphere and in acid rain. It produces nitric acid (HNO₃) when dissolved in water. When NO₂ reacts with a photon to make O₂ become O₃, NO₂ becomes NO. This NO is then oxidized within hours to NO₂ by radicals from the photo reaction of VOC. Therefore, our

present ozone concentration is the product of both NO_x and VOC pollution.

Dinitrogen trioxide (N₂O₃) and dinitrogen tetroxide (N₂O₄) exist in very small concentrations in flue gas. However, they exist in such low concentrations in the atmosphere that both their presence and their effect are often ignored. N₂O₄ is two NO₂ molecules joined together (another dimer) and reacts like NO₂; so, the presence of N₂O₄ may be masked by the more abundant NO₂.

Dinitrogen pentoxide (N₂O₅) is the most highly ionized form of nitrogen oxide. It is generated in air in a very small concentration, unless it is emitted from a process (such as a nitric acid production facility) that is specifically designed to generate it. N₂O₅ is highly reactive, and forms nitric acid (HNO₃) when it decomposes in water.

Some experts feel that NO₂ is a good surrogate for NO_x because NO is rapidly converted to NO₂, and N₂O has such a long life because it is not highly reactive. Others feel that due to their role in forming ozone, both NO and NO₂ should be considered NO_x. Still others feel that all nitrogen oxides (including N₂O) need to be regulated. NO and NO₂ are certainly the most plentiful forms of NO_x and they are largely (but not exclusively) from anthropogenic sources. N₂O is largely biogenic, and as such is not subject to regulation. For environmental purposes, using the concentration of NO₂ as a surrogate for the concentration of NO_x has seemed to suffice, for it is the precursor for ozone.

WHERE DOES NO_x COME FROM?

Automobiles and other mobile sources contribute about half of the NO_x that is emitted. Electric power plant boilers produce about 40% of the NO_x emissions from stationary sources.³⁴ Additionally, substantial emissions are also added by such anthropogenic sources as industrial boilers, incinerators, gas turbines, reciprocating spark ignition and Diesel engines in stationary sources, iron and steel mills, cement manufacture, glass manufacture, petroleum refineries, and nitric acid manufacture. Biogenic or natural sources of nitrogen oxides include lightning, forest fires, grass fires, trees, bushes, grasses, and yeasts.¹ These various sources produce differing amounts of each oxide. The anthropogenic sources are approximately shown as:

Mobile Sources	Electric Power Plants	Everything Else
50%	20%	30%

This shows a graphic portrayal of the emissions of our two greatest sources of NO_x. If we could reduce the NO_x emissions from just these two leading categories, we might be able to live with the rest. However, don't expect either of these categories to become zero in the foreseeable future. We cannot expect the car, truck, bus, and airplane to disappear. The zero-emission car is still on the drawing board and not on the production line. Also, social customs will have to change before consumption of electricity can be reduced.

In all combustion there are three opportunities for NO_x formation. They are:

1. Thermal NO_x - The concentration of “thermal NO_x” is controlled by the nitrogen and oxygen molar concentrations and the temperature of combustion. Combustion at temperatures well below 1,300°C (2,370°F) forms much smaller concentrations of thermal NO_x.

2. Fuel NO_x - Fuels that contain nitrogen (e.g., coal) create “fuel NO_x” that results from oxidation of the already-ionized nitrogen contained in the fuel.

3. Prompt NO_x - Prompt NO_x is formed from molecular nitrogen in the air combining with fuel in fuel-rich conditions which exist, to some extent, in all combustion. This nitrogen then oxidizes along with the fuel and becomes NO_x during combustion, just like fuel NO_x. The abundance of prompt NO_x is disputed by the various writers of articles and reports - probably because they each are either considering fuels intrinsically containing very large or very small amounts of nitrogen, or are considering burners that are intended to either have or not have fuel-rich regions in the flame.

HOW DOES NO_x AFFECT THE ENVIRONMENT?

Because NO_x are transparent to most wavelengths of light (although NO₂ has a brownish color and the rare N₂O₃ is black), they allow the vast majority of photons to pass through and, therefore, have a lifetime of at least several days. Because NO₂ is recycled from NO by the photo reaction of VOC to make more ozone, NO₂ seems to have an even longer lifetime and is capable of traveling considerable distances before creating ozone. Weather systems usually travel over the earth’s surface and allow the atmospheric effects to move downwind for several hundred miles. This was noted in EPA reports more than twenty years ago. These reports found that each major city on the East coast has a plume of ozone that extends more than a hundred miles out to sea before concentrations drop to 100 parts per billion (ppb). Another report cited the same phenomenon for St. Louis. Therefore, this problem was not just on the sea coast. Since ozone in clean air has a lifetime of only a few hours, this phenomenon is a measure of the effect and the persistence of both VOC and NO_x.

Differences in the distance estimates between the emission of NO_x and the generation of ozone may be related to differences in plume transport (wind) speeds as well as other meteorological and air quality factors. It is important to note that, under the right conditions, power plant plumes may travel relatively long distances overnight with little loss of VOC, NO and NO₂. These pollutants can thus be available to participate in photochemical reactions at distant locations on the following day.⁴¹ Figure 1 shows a map of NO_x concentration drawn by the Center for Air Pollution Impact and Trend Analysis (CAPITA) at Washington University in St. Louis and reported to the Ozone Transport Assessment Group, a national workgroup that addressed the problem of ground-level ozone (smog) and the long-range transport of air pollution across the Eastern United States. OTAG was a partnership among the EPA, the Environmental Council of the States (ECOS) and various industry and environmental groups with the goal of developing a thoughtful assessment and a consensus agreement for reducing ground-level ozone and the

pollutants that cause it. The animated version of Figure 1 shows the trajectory of NOx emissions moving with the weather over an 8 day period.

Figure 2 is a map of ozone concentration that shows the same trajectory over the 8 day period. The animated version shows concentrations of both NOx and ozone moving with the weather for several hundred miles.⁵

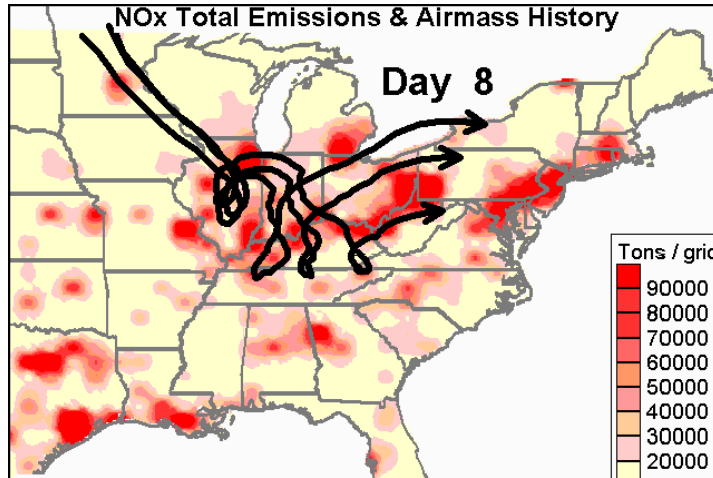


Figure 2 NOx Map

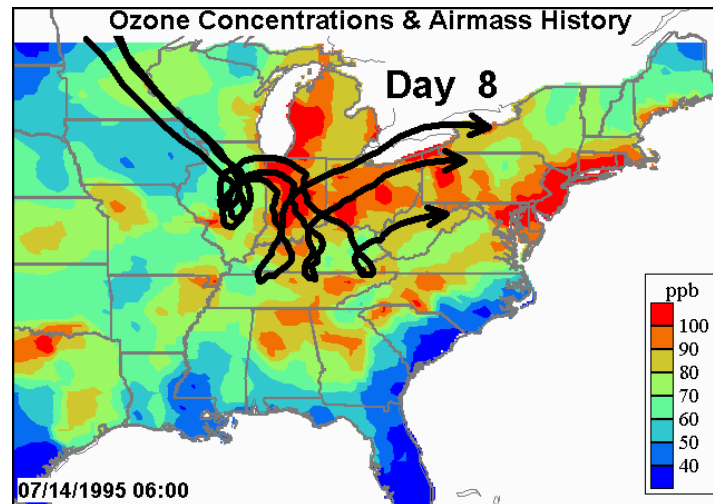


Figure 3 Ozone Map

Ozone is the primary constituent of smog. Between 1970 and 1990, we in the United States have tried to control ozone primarily by controlling the emissions of VOC. However, we have had mixed results, for although some areas reduced their VOC emissions and attained their ozone goals, others have not. It now appears that the communities that failed to meet their ozone goals

may not be completely at fault, for they appear to be affected by NO_x and VOC emissions in the air coming to them. To meet the ozone NAAQS, EPA must now regulate emissions of NO_x regionally.

ARE THERE OTHER NO_x RELATED ISSUES?

Yes. Nutrient enrichment problems (eutrophication) occur in bodies of water when the availability of either nitrates or phosphates become too large. As a result, the ratios of nitrogen to phosphorus, silicon, and iron and other nutrients are altered. This alteration may induce changes in phytoplankton, produce noxious or toxic brown or red algal blooms (which are called “red tides”), or stimulate other plant growth. The algal blooms and plant growth produce a shadow and cause the death of other plants in the water, which depletes the oxygen content of the water (hypoxia) when the plants die, sink, and decay. Such eutrophication can make the bottom strata of water uninhabitable for both marine animals (such as fish and shellfish) and aquatic plants. It can progress to virtually the complete depth of the water. It is estimated that between 12% and 44% of the nitrogen loading of coastal water bodies comes from the air.⁴⁰ Inland lakes are also affected in this way.

Another dimension of the problem is that high temperature combustion can convert sulfur in fuel to SO₂ and SO₃. While SO₂ is toxic and forms sulfurous acid when dissolved in water, SO₃ is both toxic and hygroscopic (moisture absorbing) and forms sulfuric acid by combining with moisture in the atmosphere. SO₂ and SO₃ form sulfites and sulfates when their acids are neutralized. Both of these acids can form solid particles by reacting with ammonia in air. SO₂ and SO₃ also contribute to pH (acidity) changes in water, which can adversely affect both land and aquatic life. Therefore, both NO_x and SO_x from combustion can kill plants and animals.

CAPITA has shown that there are about equal amounts by weight of sulfate/sulfite, nitrate and organic particles making up 90% of Particulate Matter less than 2.5 microns in aerodynamic diameter (PM-2.5). This was confirmed by Brigham Young University researchers. The Six Cities Study, published in the *New England Journal of Medicine* in 1990, has shown that illness and premature death are closely correlated with the amount of PM-2.5 in the air. Therefore, there is epidemiological data indicting nitrogen oxides, sulfur oxides, and/or organic compounds as PM-2.5 aerosols. There is currently no evidence that separately examines the health effects of each of these substances. PM-2.5 usually appear as smog, smoke, white overcast, haze, or fog which does not clear when air warms up. Brown smog is colored by nitrogen dioxide.

Because the nitric acid, sulfurous acid and sulfuric acid react with ammonia in air to form solid crystals that are much smaller than 2.5 microns and can be nucleation sites for particle growth, we need to be concerned about each of these pollutants. Some research indicates that even insoluble particles much smaller than 2.5 microns in size can exhibit severe toxic effects.³⁸ The smallest particles that have shown toxicity have a diameter of about 3% to 5% of the wavelength of any color of visible light. Therefore, these particles are too small to even scatter light and cannot even be detected optically.

Acid deposition occurs from airborne acidic or acidifying compounds, principally sulfates (SO_4^{-2}) and nitrates (NO_3^{-1}), that can be transported over long distances before returning to earth. This occurs through rain or snow (wet deposition), fog or cloud water (cloud deposition), or transfer of gases or particles (dry deposition). While severity of damage depends on the sensitivity of the receptor, acid deposition and NOx “represent a threat to natural resources, ecosystems, visibility, materials, and public health.”(section 401(a)(1) of the Clean Air Act).⁴⁰

WHAT ABATEMENT AND CONTROL PRINCIPLES APPLY?

NOx abatement and control technology is a relatively complex issue. We shall try to provide a structure to the spectrum of NOx pollution prevention and control technologies by first giving the principles that are used. Then we shall describe the more successful pollution prevention and emission control technologies and strategies.

Please note that abatement and control of NOx from nitric acid manufacturing and “pickling” baths differs from abatement and control at combustion sources. Combustion sources all have NOx in a large flow of flue gas, while nitric acid manufacturing plants and pickling baths try to contain the NOx. Wet scrubbers (absorbers) can control NOx emissions from acid plants and pickling, and can use either alkali in water, water alone, or hydrogen peroxide as the liquid that captures the NOx.³ The wet scrubber operates by liquid flowing downward by gravity through a packing medium, opposed by an upward flow of gas. Scrubbers operate on the interchange of substances between gas and liquid. This requires that the height of the absorber, type of packing, liquid flow, liquid properties, gas properties, and gas flow should collectively cause a scrubber to have the desired control efficiency. Chapter 9 of the OAQPS Control Cost Manual provides guidance on the application, sizing, and cost of these scrubbers (referred to as gas absorbers). Also, Table 16 in this Bulletin presents some information for non-combustion NOx sources. Other than that, non-combustion NOx sources are not addressed in this Bulletin.

For combustion sources, this Bulletin defines abatement and emission control principles and states the Destruction or Removal Efficiency (DRE) that each successful technology is capable of achieving. The effectiveness of pollution prevention measures in reducing NO and NO₂ generation also is expressed in terms of relative DRE; i.e., the amount NOx generation is reduced by using a prevention technology compared to NOx generation when not using that technology. Then, specific boiler types and combustion systems and applicable NOx technologies for each system are discussed. Finally, the cost of these technologies is considered.

Many new combustion systems incorporate NOx prevention methods into their design and generate far less NOx than similar but older systems. As a result, considering DRE (even a relative DRE) for NOx may be inappropriate. Comparing estimated or actual NOx emissions from a new, well-designed system to NOx emitted by a similar well-controlled and operated older system may be the best way of evaluating how effectively a new combustion system minimizes NOx emissions.

Table 2 lists principles or methods that are used to reduce NOx. Basically there are six

principles, with the seventh being an intentional combination of some subset of the six.

Table 2. NOx Control Methods ^{6,7}

Abatement or Emission Control Principle or Method	Successful Technologies	Pollution Prevention Method (P2) or Add-on Technology (A)
1. Reducing peak temperature	Flue Gas Recirculation (FGR) Natural Gas Reburning Low NOx Burners (LNB) Combustion Optimization Burners Out Of Service (BOOS) Less Excess Air (LEA) Inject Water or Steam Over Fire Air (OFA) Air Staging Reduced Air Preheat Catalytic Combustion	P2 P2 P2 P2 P2 P2 P2 P2 P2 P2 P2
2.Reducing residence time at peak temperature	Inject Air Inject Fuel Inject Steam	P2 P2 P2
3. Chemical reduction of NOx	Fuel Reburning (FR) Low NOx Burners (LNB) Selective Catalytic Reduction (SCR) Selective Non-Catalytic Reduction (SNCR)	P2 P2 A A
4. Oxidation of NOx with subsequent absorption	Non-Thermal Plasma Reactor Inject Oxidant	A A
5. Removal of nitrogen	Oxygen Instead Of Air Ultra-Low Nitrogen Fuel	P2 P2
6. Using a sorbent	Sorbent In Combustion Chambers Sorbent In Ducts	A A
7. Combinations of these Methods	All Commercial Products	P2 and A

Method 1. Reducing Temperature -- Reducing combustion temperature means avoiding the stoichiometric ratio (the exact ratio of chemicals that enter into reaction). Essentially, this technique dilutes calories with an excess of fuel, air, flue gas, or steam. Combustion controls use different forms of this technique and are different for fuels with high and low nitrogen content.

Control of NO_x from combustion of high nitrogen content fuels (e.g., coal) can be understood by the net stoichiometric ratio. Control of the NO_x from combustion of low nitrogen fuels (such as gas and oil) can be seen as lean versus rich fuel/air ratios. Either way, this technique avoids the ideal stoichiometric ratio because this is the ratio that produces higher temperatures that generate higher concentrations of thermal NO_x.

Combustion temperature may be reduced by: (1) using fuel rich mixtures to limit the amount of oxygen available; (2) using fuel lean mixtures to limit temperature by diluting energy input; (3) injecting cooled oxygen-depleted flue gas into the combustion air to dilute energy; (4) injecting cooled flue gas with added fuel; or (5) injecting water or steam. Low-NO_x burners are based partially on this principle.^{8,9,10} The basic technique is to reduce the temperature of combustion products with an excess of fuel, air, flue gas, or steam. This method keeps the vast majority of nitrogen from becoming ionized (i.e., getting a non-zero valence).

Method 2. Reducing Residence Time -- Reducing residence time at high combustion temperatures can be done by ignition or injection timing with internal combustion engines. It can also be done in boilers by restricting the flame to a short region in which the combustion air becomes flue gas. This is immediately followed by injection of fuel, steam, more combustion air, or recirculating flue gas. This short residence time at peak temperature keeps the vast majority of nitrogen from becoming ionized. This bears no relationship to total residence time of a flue gas in a boiler.

Method 3. Chemical Reduction of NO_x – This technique provides a chemically reducing (i.e., reversal of oxidization) substance to remove oxygen from nitrogen oxides. Examples include Selective Catalytic Reduction (SCR) which uses ammonia, Selective Non-Catalytic Reduction (SNCR) which use ammonia or urea, and Fuel Reburning (FR). Non-thermal plasma, an emerging technology, when used with a reducing agent, chemically reduces NO_x. All of these technologies attempt to chemically reduce the valence level of nitrogen to zero after the valence has become higher.¹¹ Some low-NO_x burners also are based partially on this principle.

Method 4. Oxidation of NO_x -- This technique intentionally raises the valence of the nitrogen ion to allow water to absorb it (i.e., it is based on the greater solubility of NO_x at higher valence). This is accomplished either by using a catalyst, injecting hydrogen peroxide, creating ozone within the air flow, or injecting ozone into the air flow. Non-thermal plasma, when used without a reducing agent, can be used to oxidize NO_x. A scrubber must be added to the process to absorb N₂O₅ emissions to the atmosphere. Any resultant nitric acid can be either neutralized by the scrubber liquid and then sold (usually as a calcium or ammonia salt), or collected as nitric acid to sell to customers.^{12, 49}

Method 5. Removal of nitrogen from combustion -- This is accomplished by removing nitrogen as a reactant either by: (1) using oxygen instead of air in the combustion process; or (2) using ultra-low nitrogen content fuel to form less fuel NO_x. Eliminating nitrogen by using oxygen tends to produce a rather intense flame that must be subsequently and suitably diluted. Although Method 2 can lower the temperature quickly to avoid forming excessive NO_x, it cannot

eliminate nitrogen oxides totally if air is the quench medium. Hot flue gas heats the air that is used to quench it and this heating generates some thermal NO_x. This method also includes reducing the net excess air used in the combustion process because air is 80% nitrogen. Using ultra-low-nitrogen content fuels with oxygen can nearly eliminate fuel and prompt NO_x.¹³

Method 6. Sorption, both adsorption and absorption -- Treatment of flue gas by injection of sorbents (such as ammonia, powdered limestone, aluminum oxide, or carbon) can remove NO_x and other pollutants (principally sulfur). There have been successful efforts to make sorption products a marketable commodity. This kind of treatment has been applied in the combustion chamber, flue, and baghouse. The use of carbon as an adsorbent has not led to a marketable product, but it is sometimes used to limit NO_x emissions in spite of this. The sorption method is often referred to as using a dry sorbent, but slurries also have been used. This method uses either adsorption or absorption followed by filtration and/or electrostatic precipitation to remove the sorbent.

Method 7. Combinations of these methods -- Many of these methods can be combined to achieve a lower NO_x concentration than can be achieved alone by any one method. For example, a fuel-rich cyclone burner (Method 1) can be followed by fuel reburn (Method 3) and over-fire air (Method 1). This has produced as much as a 70% reduction in NO_x.⁵⁵ Other control technologies that are intended to primarily reduce concentrations of sulfur also strongly affect the nitrogen oxide concentration. For example, the SO_x-NO_x-RO_x-Box (SNRB) technology uses a limestone sorbent in the flue gas from the boiler to absorb sulfur. This is followed by ammonia injection and SCR using catalyst fibers in the baghouse filter bags. The sulfur is recovered from the sorbent and the sorbent regenerated by a Claus process. This has demonstrated removal of up to 90% of the NO_x along with 80% of the SO_x.^{39, 42} EBARA of Japan reported that an electron beam reactor with added ammonia removed 80% of the SO₂ and 60% of the NO_x for a utility boiler in China.⁵⁴ FLS Milo and Sons reported at the same symposium that 95% of the SO₂ and 70%-90% of the NO_x were removed in several demonstrations of their SNAP technology, which is based upon an aluminum oxide adsorber with Claus regeneration.⁵⁶

WHAT ABATEMENT TECHNOLOGIES ARE AVAILABLE?

In this report existing NO_x abatement technologies are divided into two categories, external combustion applications (e.g., boilers, furnaces and process heaters) and internal combustion applications (e.g., stationary internal combustion engines and turbines). These categories are further subdivided into pollution prevention (which reduces NO_x generation) and add-on control technologies (which reduces NO_x emissions).

EXTERNAL COMBUSTION

For external combustion applicable technologies are shown in Table 3 (based on Table 2 in *Select the Right NO_x Control Technology*, Stephen Wood, Chemical Engineering Progress, January 1994).

Table 3. External Combustion NO_x Limiting Technologies

Technique	Description	Advantages	Disadvantages	Impacts	Applicability
Less Excess Air (LEA)	Reduces oxygen availability	Easy modification	Low NO _x reduction	High CO Flame length Flame stability	All fuels
Off Stoichiometric a. Burners Out of Service (BOOS) b. Over Fire Air (OFA)	staged combustion	Low cost No capital cost for BOOS	a. Higher air flow for CO b. high capital cost	Flame length Fan capacity Header pressure	All fuels Multiple burners for BOOS
Low NO _x Burner (LNB)	Internal staged combustion	Low operating cost Compatible FGR	Moderately high capital cost	Flame length Fan capacity Turndown stability	All fuels
Flue Gas Recirculation (FGR)	<30% flue gas recirculated with air, decreasing temperature	High NO _x reduction potential for low nitrogen fuels	Moderately high capital cost and operating cost Affects heat transfer and system pressures	Fan capacity Furnace pressure Burner pressure drop Turndown stability	All fuels Low nitrogen fuels
Water/Steam Injection	Reduces flame temperature	Moderate capital cost NO _x reduction similar to FGR	Efficiency penalty Fan power higher	Flame stability Efficiency penalty	All fuels as Low nitrogen fuels
Reduced Air Preheat	Air not preheated, reduces flame temperature	High NO _x reduction potential	Significant efficiency loss (1% per 40 °F)	Fan capacity Efficiency penalty	All fuels Low nitrogen fuels
Selective Catalytic reduction (SCR) (add-on technology)	Catalyst located in the air flow, promotes reaction between ammonia and NO _x	High NO _x removal	Very high capital cost High operating cost Catalyst siting Increased pressure drop Possible water wash required	Space requirements Ammonia slip Hazardous waste Disposal	All fuels

Table 3. External Combustion NO_x Limiting Technologies

Technique	Description	Advantages	Disadvantages	Impacts	Applicability
Selective Non-Catalytic Reduction (SNCR) (add-on technology) a. urea b. ammonia	Inject reagent to react with NO _x	a. Low capital cost Moderate NO _x removal Non-toxic chemical b. Low operating cost Moderate NO _x removal	a. Temperature dependent NO _x reduction less at lower loads b. Moderately high capital cost Ammonia storage, handling, injection system	a. Furnace geometry Temperature profile b. Furnace geometry Temperature profile	All fuels
Fuel Reburning	Inject fuel to react with NO _x	Moderate cost Moderate NO _x removal	Extends residence time	Furnace temperature profile	All fuels (pulverized solid)
Combustion Optimization	Change efficiency of primary combustion	Minimal cost	Extends residence time	Furnace temperature profile	Gas Liquid fuels
Catalytic Combustion	Catalyst causes combustion to be at low temperature	Lowest possible NO _x	Very high capital cost High operating cost Catalyst siting	Space requirements Disposal	Gas Liquid fuels
Non-Thermal Plasma	Reducing agent ionized or oxidant created in flow	Moderate cost Easy siting High NO _x removal	Fouling possible Ozone emission possible	Uses electrical power	All fuels
Inject Oxidant	Chemical oxidant injected in flow	Moderate cost	Nitric acid removal	Add-on	All fuels
Oxygen instead of Air	Uses oxygen to oxidize fuel	Moderate to high cost Intense combustion	Eliminates prompt NO _x Furnace alteration	Equipment to handle oxygen	All fuels
Ultra-Low Nitrogen Fuel	Uses low -nitrogen fuel	Eliminates fuel NO _x No capital cost	Slight rise in operating cost	Minimal change	All ultra-low nitrogen fuels

Table 3. External Combustion NO_x Limiting Technologies

Technique	Description	Advantages	Disadvantages	Impacts	Applicability
Use Sorbents (add-on technology) in: a. Combustion b. Duct to Baghouse c. Duct to Electrostatic Precipitator	Use a chemical to absorb NO _x or an adsorber to hold it	Can control other pollutants as well as NO _x Moderate operating cost	Cost of handling sorbent Space for the sorbent storage and handling	Add-on	All fuels
Air Staging	Admit air in separated stages	Reduce peak combustion temperature	Extend combustion to a longer residence time at lower temperature	Adds ducts and dampers to control air Furnace modification	All fuels
Fuel Staging	Admit fuel in separated stages	Reduce peak combustion temperature	Extend combustion to a longer residence time at lower temperature	Adds fuel injectors to other locations Furnace modification	All fuels

EXTERNAL COMBUSTION: POLLUTION PREVENTION METHODS

LESS EXCESS AIR (LEA)

Excess air flow for combustion has been correlated to the amount of NO_x generated. Limiting the net excess air flow to under 2% can strongly limit NO_x content of flue gas. Although there are fuel-rich and fuel-lean zones in the combustion region, the overall net excess air is limited when using this approach.⁴³

BURNERS OUT OF SERVICE (BOOS)

Multiple-burner equipment can have part of an array of burners with some “burners out of service” (not feeding fuel, but supplying air or flue gas). This allows the burners around them to supply fuel and air to air or flue gas flowing from the BOOS. The result is combustion by stages with temperature always lower than when all burners are in service. Thus, thermal NO_x is lower. The degree to which NO_x generation is reduced depends upon the spatial relationship of the BOOS to the other burners.⁴⁴

OVER FIRE AIR (OFA)

When primary combustion uses a fuel-rich mixture, use of OFA completes the combustion. Because the mixture is always off-stoichiometric when combustion is occurring, the temperature is held down. After all other stages of combustion, the remainder of the fuel is oxidized in the over fire air. This is usually not a grossly excessive amount of air.

LOW NO_x BURNERS (LNB)

A LNB provides a stable flame that has several different zones. For example, the first zone can be primary combustion. The second zone can be Fuel Reburning (FR) with fuel added to chemically reduce NO_x. The third zone can be the final combustion in low excess air to limit the temperature. There are many variations on the LNB theme of reducing NO_x. The LNB has produced up to 80% DRE.^{17,18, 32,33} This can be one of the least expensive pollution prevention technologies with high DRE. LNB have had problems with designs that had flame attaching to the burners, resulting in a need for maintenance. We believe that these design problems should now be a thing of the past.

FLUE GAS RECIRCULATION (FGR)

Recirculation of cooled flue gas reduces temperature by diluting the oxygen content of combustion air and by causing heat to be diluted in a greater mass of flue gas. Heat in the flue gas can be recovered by a heat exchanger. This reduction of temperature lowers the NO_x concentration that is generated. If combustion temperature is held down to below 1,400°F, the thermal NO_x formation will be negligible.⁵⁰

WATER OR STEAM INJECTION

Injection of water or steam causes the stoichiometry of the mixture to be changed and adds steam to dilute calories generated by combustion. Both of these actions cause combustion temperature to be lower. If temperature is sufficiently reduced, thermal NO_x will not be formed in as great a concentration.

REDUCED AIR PREHEAT

Air is usually preheated to cool the flue gases, reduce the heat losses, and gain efficiency. However, this can raise the temperature of combustion air to a level where NO_x forms more readily. By reducing air preheat, the combustion temperature is lowered and NO_x formation is suppressed. This can lower efficiency, but can limit NO_x generation.

FUEL REBURNING (FR)

Recirculation of cooled flue gas with added fuel (this can be natural gas, pulverized coal, or even oil spray) causes dilution of calories, similar to FGR, and primary combustion temperature can be lowered. Also, when added as a secondary combustion stage, the presence of added fuel chemically reduces newly generated NO_x to molecular nitrogen. Added fuel is only partially consumed in reducing NO_x and burning is completed in a later stage using either combustion air nozzles or over-fire-air. This technique has been demonstrated to be effective with residence times from 0.2 seconds to 1.2 seconds and has achieved up to 76% DRE.¹⁷

COMBUSTION OPTIMIZATION

Combustion optimization refers to the active control of combustion. In a natural gas fired boiler, by decreasing combustion efficiency from 100% to 99%, NO_x generation dropped to a much more acceptable level.^{14,15} For coal-fired boilers a 20% to 60% reduction in NO_x has been experienced. These active combustion control measures seek to find an optimum combustion efficiency and to control combustion (and hence emissions) at that efficiency. Another approach uses a neural network computer program to find the optimum control point.¹⁶ Still another approach is to use software to optimize inputs for the defined output.^{52,53}

One vendor decreases the amount of air that is pre-mixed with fuel from the stoichiometric ratio (ratio that produces the hottest flame) to lengthen the flame at the burner and reduce the rate of heat release per unit volume. This can work where the boiler tubes are far enough away from the burner. Carbon monoxide, unburned fuel, and partially burned fuel that result can then be subsequently oxidized in over-fire-air at a lower temperature. Combustion must be optimized for the conditions that are encountered. 50% DRE has been reported.¹⁴

AIR STAGING

Combustion air is divided into two streams. The first stream is mixed with fuel in a ratio that

produces a reducing flame. The second stream is injected downstream of the flame and makes the net ratio slightly excess air compared to the stoichiometric ratio. DRE up to 99% have been reported.⁵¹

FUEL STAGING

This is staging of combustion using fuel instead of the air. Fuel is divided into two streams. The first stream feeds primary combustion that operates in a reducing fuel to air ratio. The second stream is injected downstream of primary combustion, causing the net fuel to air ratio to be only slightly oxidizing. Excess fuel in primary combustion dilutes heat to reduce temperature. The second stream oxidizes the fuel while reducing the NO_x to N₂. This is reported to achieve a 50% DRE.⁵¹

OXYGEN INSTEAD OF AIR FOR COMBUSTION

An example of this is a cyclone burner where the flame is short and intense. Excess fuel air or steam, injected just after the combustion chamber per Method 2 is sufficient to rapidly quench the flue gas to below NO_x formation temperature. Combustion can then be completed in over-fire air. Oxygen can now be separated from air at a low enough cost to make this economical.¹³ This technique has reduced NO_x by up to 20%²³ in burners using conventional fuel. This technique also is usable with low-NO_x burners to prevent the prompt NO_x from being formed.

INJECTION OF OXIDANT

The oxidation of nitrogen to its higher valence states makes NO_x soluble in water. When this is done a gas absorber can be effective. Oxidants that have been injected into the air flow are ozone, ionized oxygen, or hydrogen peroxide. Non-thermal plasma generates oxygen ions within the air flow to achieve this. Other oxidants have to be injected and mixed in the flow. Nitric acid can be absorbed by water, hydrogen peroxide, or an alkaline fluid. Calcium or ammonia dissolved in the water can make an alkaline fluid that will react with nitric and sulfuric acids to produce a nitrate or sulfate salt that can be recovered. Alternatively, using water or hydrogen peroxide to absorb NO_x can provide nitric acid for the commercial market.

CATALYTIC COMBUSTION

Use of a catalyst to cause combustion to occur below NO formation temperatures can provide a suitable means of limiting temperature. This technique is not used often because it is very load sensitive. However, where it is used, catalytic combustion can achieve less than a 1 ppm concentration of NO_x in the flue gas.

ULTRA-LOW NITROGEN FUELS

These fuels can avoid NO_x that results from nitrogen contained in conventional fuels. The result can be up to a 70% reduction in NO_x emissions.⁴³ Now there are ultra-low-nitrogen liquid fuel

oils. These oils contain 15-20 times less nitrogen than standard No. 2 fuel oil. This oil is now commercially available and competitively priced. Ultra-low-nitrogen oil is most frequently used in Southern California where the air pollution is particularly a problem. Natural gas can be considered a low-nitrogen fuel. Coke (the quenched char from coal) can also be an ultra-low-nitrogen fuel because nitrogen in the volatile fraction of the coal is removed in making coke.

NON-THERMAL PLASMA

Using methane and hexane as reducing agents, non-thermal plasma has been shown to remove NO_x in a laboratory setting with a reactor duct only 2 feet long. The reducing agents were ionized by a transient high voltage that created a non-thermal plasma. The ionized reducing agents reacted with NO_x and achieved a 94% DRE. There are indications that an even higher DRE can be achieved. A successful commercial vendor uses ammonia as a reducing agent to react with NO_x in an electron beam generated plasma. Such a short reactor can meet available space requirements for virtually any plant. The non-thermal plasma reactor could also be used without reducing agent to generate ozone and use that ozone to raise the valence of nitrogen for subsequent absorption as nitric acid.

EXTERNAL COMBUSTION: ADD-ON CONTROL TECHNOLOGY

Add-on controls are applicable to a broad range of sources and fuels. This differs from the pollution prevention techniques listed above in that the prevention techniques must be adapted to the circumstances of their use.

SELECTIVE CATALYTIC REDUCTION (SCR)

SCR uses a catalyst to react injected ammonia to chemically reduce NO_x. It can achieve up to a 94% DRE³⁴ and is one of the most effective NO_x abatement techniques. However, this technology has a high initial cost. In addition, catalysts have a finite life in flue gas and some ammonia “slips through” without being reacted. SCR has historically used precious metal catalysts, but can now also use base-metal and zeolite catalysts. The base-metal and zeolite catalysts operate at much different temperatures than the precious metal catalysts.¹¹

SELECTIVE NON-CATALYTIC REDUCTION (SNCR)

In SNCR ammonia or urea is injected within a boiler or in ducts in a region where temperature is between 900°C and 1100°C. This technology is based on temperature ionizing the ammonia or urea instead of using a catalyst or non-thermal plasma. This temperature “window” – which is reported differently by various authors -- is important because outside of it either more ammonia “slips” through or more NO_x is generated than is being chemically reduced. The temperature “window” is different for urea and ammonia. Reduction of the NO_x by SNCR can have up to a 70% DRE.^{23,35,43}

SORPTION – BOTH ADSORPTION AND ABSORPTION

Several methods are used to inject and remove adsorbent or absorbent. One method sprays dry powdered limestone into the flue gas. The limestone then reacts with both sulfuric acid and nitric acid. There also is a spray dryer approach that sprays a slurry of powdered limestone and aqueous ammonia into the flue gas. The limestone preferentially reacts with the sulfur while the ammonia preferentially reacts with the NO_x. In-duct injection of dry sorbents is another example of this technique and can reduce pollutants in three stages: (1) in the combustion chamber, (2) in the flue gas duct leading to the baghouse, and (3) in the flue gas duct leading to the electrostatic precipitator. The by products formed by sorption are gypsum (calcium sulfate) that is sold to make wallboard, and ammonium nitrate that can be sold to make either an explosive or a fertilizer. Sorption is reported to have up to a 60% DRE.^{23, 31} Another version uses carbon injected into the air flow to finish the capture of NO_x. The carbon is captured in either the baghouse or the ESP just like other sorbents. There are many absorbents and adsorbents available.

COMBINED TECHNOLOGY APPROACHES

Very seldom is only one method or principle used alone. The choice depends upon the type of combustion system, type of boiler or other energy conversion device, and type of fuel used. Available technologies will be narrowed by consideration of turndown ratio, stability of combustion, availability or access to burners, air supply controls, fuel impurities, and cost among other factors.

There are many examples and here are a few of them. Selective catalytic reduction of NO_x to N₂ can be followed by selective oxidation of sulfur dioxide to sulfur trioxide. Then sulfuric acid is formed followed by scrubbing sulfuric acid from the flue gas.³⁰

LNB can be used in conjunction with SCR or SNCR to achieve a greater overall DRE than any of these can achieve alone. Water/steam injection can be used with SCR to achieve a DRE greater than SCR can achieve alone. Fuel reburning and SCR can be used together as well as separately, to get the maximum NO_x reduction.⁵⁷

INTERNAL COMBUSTION

Now we turn to internal combustion, which usually occurs at elevated pressures. Again, we divide the technologies between pollution prevention techniques and add-on technologies. This is shown in Table 4.

These techniques can be used in combination. Pollution prevention techniques do not have to be used separately. Add-on techniques could be used sequentially after a pollution prevention technique when they do not impose conflicting demands on the process.

Table 4. Internal Combustion NOx Limiting Technologies

Pollution Prevention	Add-On Control
Low-NOx Burners (LNB)	Selective Catalytic Reduction (SCR)
Steam/Water Injection	Selective Non-Catalytic Reduction (SNCR)
Catalytic Combustion	Non-Selective Catalytic Reduction (NSCR)
Air-Fuel Ratio and Ignition Type	Non-Thermal Plasma
Pre-Stratified Charge	
Lean Burn	

INTERNAL COMBUSTION: POLLUTION PREVENTION METHODS

LOW NO_x BURNERS (LNB)

Combining the use of LNB with closely controlled air/fuel ratio and water/steam injection can yield emissions as low as 10 ppm from gas turbines.⁴⁶

STEAM/ WATER INJECTION

To reduce combustion temperature, steam or water can be mixed with the air flow. This lowers combustion temperature to below 1,400°F to limit NO_x generation to about 40 ppm.⁴⁶ This can cause the concentration of CO and unburned hydrocarbons emitted from a turbine to be increased. However, these can be burned by either a catalyst bed, afterburner, or another stage of combustion. This otherwise wasted fuel and heat can also be recovered in co-generation boilers.

CATALYTIC COMBUSTION

A catalyst is used to react fuel with air at a lower temperature than normal combustion at which generation of significant amounts of NO_x does not occur. Emissions under 1 ppm NO_x have been reported.⁴⁶ However, if this combustion is for a turbine, turbine efficiency may depend upon achieving a higher temperature. When a catalyst is present, you also need to assure that NO_x will not be formed at the combustion temperature that results.

This technology has a relatively high capital and operation and maintenance cost because there is both a substantial initial investment and a replacement cost for the catalyst. The need for replacement and, therefore, replacement cost are usually driven by impurities in the fuel. However, catalytic combustion generates possibly the lowest level of thermal NO_x.

AIR-FUEL RATIO AND IGNITION TYPE

For internal combustion reciprocating engines, retardation of injection or spark ignition, or an air-fuel ratio that departs from stoichiometric conditions will reduce peak temperature. Lower peak temperature will limit the amount of NO_x formation. This technique can achieve up to 50% control efficiency.^{19, 48}

When a three-way catalyst is used for spark ignition engines, exhaust gas must have no more than 0.5% oxygen. This technique can be up to 98% effective.

The use of plasma ignition (an alternating current or AC system) instead of a direct current (DC) spark ignition system can also allow a greater fuel-lean departure from the stoichiometric ratio. NO_x emissions from internal combustion engines using plasma ignition have been reported to be reduced by up to 97%.^{20,21, 45}

Delaying injection of fuel in a compression ignition (diesel) engine can reduce the NO_x emissions. The amount of this reduction will depend upon the engine, valving, and fuel. Excessive timing retard can cause combustion instability or misfire.⁴⁸ However, some claims of high effectiveness are to be found with ostensibly excessive retard.

PRE-STRATIFIED CHARGE (PSC)

PSC refers to an engine equipped with a pre-combustion chamber that receives a rich enough air/fuel mixture to ignite dependably. This pre-combustion chamber fires a jet of flame into the main combustion chamber (cylinder). The main combustion chamber has a fuel-lean mixture that needs pre-combustion flame to ignite it reliably. The injected flame also produces a swirl in the main combustion chamber that acts like stratified charge combustion. This dependably ignites the lean main cylinder mixture. The PSC can achieve NO_x emissions of 2 grams/horsepower-hour (g/hp-hr) or 140 ppm.⁴⁸

LEAN BURN

Natural gas fueled engines that operate with a fuel-lean air/fuel ratio are capable of low NO_x emissions. These can achieve less than 1.0 gram/brake horsepower-hour according to the RACT-BACT-LAER Clearinghouse (RBLC) (<http://www.epa.gov/ttn/catc>, then select RBLC).

INTERNAL COMBUSTION ADD-ON CONTROL TECHNOLOGY

SELECTIVE CATALYTIC REDUCTION (SCR)

As with boilers, SCR can be used to obtain up to a 90% DRE of NO_x. When used with a LNB or steam/water injection, NO_x can be reduced to 5-10 ppm.⁴⁶ With compression ignition engines, zeolite catalysts achieve a DRE of 90+%, while base-metal catalysts can achieve a 80% to 90% DRE.⁴⁸

NON-SELECTIVE CATALYTIC REDUCTION (NSCR)

NSCR is the same technique used in automobile applications as a three-way catalytic converter. It does not require injection of a reducing agent because it uses unburned hydrocarbons as a reducing agent. The catalyst requires that exhaust have no more than 0.5% oxygen. This technique uses a fuel rich mixture that, combined with back pressure from exhaust flow through the catalyst, increases the brake specific fuel consumption of the engine. However, NO_x control of 90% to 98% can be achieved.⁴⁸

NON-THERMAL PLASMA REACTORS

This approach uses a non-thermal plasma to ionize ammonia, urea, hexane, methane or other reducing agents injected into a flue gas. Combined with the effect of temperature, non-thermal plasma ionizes the reducing agent that reacts with nitrogen oxides achieving a 94% DRE. This decreases the amount of reducing chemicals that “slips” through unreacted.^{20,44} The use of non-thermal plasma was developed to ionize pollutants and act as a catalyst to control NO_x in diesel exhaust.³⁶

DO FUELS AND COMBUSTION TYPE AFFECT ABATEMENT?

Yes they do. Here again, we find a spectrum of types, almost enough to make every gas turbine, internal combustion engine, boiler, or furnace seem unique. The type of fuel can vary with the vein of the mine from which coal was obtained, the well in the oilfield from which crude oil came, the refinery for petroleum based fuels, or the supplier of natural gas. Thus the concentration of impurities will vary between sources, refineries, and suppliers. Even “natural gas” (methane) may contain some “supplier gas” (propane, butane, and carbon monoxide) which will cause the composition of “natural gas” to vary.

The type of combustion system (low-NO_x burner, over-fire air, tangential firing, wall firing, etc) also will sometimes limit options. Each type of boiler, each type of fuel, each combustion system, and each construction of a boiler puts constraints on what is possible. It is not possible to treat each combination of combustion system and fuel in detail in this Technical Bulletin; however, we will try to show the picture while painting with broad strokes.

The choice of fuel and combustion system often depends upon: (1) what can or cannot be adjusted; (2) whether ducts are suitable for sorption; (3) what the effect on boiler maintenance will be; (4) the temperature profile in the flow; (5) how the combustion system can be modified; (6) what types of burners can be used; and (7) what can either be added or modified. The list does not end there, but continues. Let us consider some fuels with these limitations in mind.

SOLID FUELS

In burning a solid fuel (such as coal), combustion control is achieved by first getting the primary burner to gasify the volatile fraction of a fuel. The volatile fraction is carried away from char by

air flow, oxidized in the air flow, and becomes flue gas. Char needs more combustion air to burn and provide further heat, part of which is used to volatilize additional fuel. To control combustion temperature, you traditionally would limit combustion air through the char fraction. The volatile fraction is oxidized in over-fire-air or a secondary stage of burner and must have its air separately controlled. The balance of combustion air between these stages must be adjusted for composition of fuel being used, boiler loading, and transient loads. Because all of these parameters will vary continually, provisions to make balancing adjustments dynamically are recommended.

Pulverized coal can be burned similar to oil. The flame is usually well defined and, depending on particle size, char may remain in suspension in flue gas throughout burning. The volatile fraction burns in air even as char is burned. If the particles are too coarse, char will continue burning on its trajectory after leaving the flame, but will stop burning at some point. The trade jargon for this is “unburned carbon (UBC),” “carbon in the ash (CIA),” or “loss of ignition (LOI).” These terms refer to carbon in char that does not burn along the trajectory. UBC is minimized by grinding particles finer and classifying particles so that larger ones are returned to the roller mill or grinder. Particles will become fly ash if they are small enough. UBC ranging from 0.5% to 5% is considered acceptable. Therefore, particle size at ignition is important. The major concerns are to control stoichiometry and combustion temperature to minimize unburned carbon in ash.

Biomass is another solid fuel, but burning biomass char is less of a concern than with coal. Biomass cannot be pulverized to small particles, but can burn to ash in a short time. As with the burning of all char, ash and fly ash are problems, but can be treated with a slag tap or ash pit, baghouse, and/or electrostatic precipitator.

LIQUID FUELS

Liquid fuels burn like the volatile fraction of solid fuel provided that the droplets are small enough. Liquid fuels usually have less nitrogen content than solid fuels. Combustion of liquids and gases can be controlled much more readily than char from solid fuel because combustion is less dependent on the history of the past few minutes of demand. Combustion is also completed essentially without residual ash. The fuel-air ratio can be used to control combustion temperature and can be adjusted to minimize NO_x generation. The flame can be well-defined and combustion is essentially completed within the flame. Therefore, burning oil or liquid-from-coal or liquid-from-gas is different from burning coal because there is usually less nitrogen in the fuel, a lack of char, complete burning within the flame and a lack of ash.

SEMI-SOLID FUELS

Semi-solid fuels are residuals from refineries. They are not clean burning like distillates and often are not even liquid at room temperature. Many impurities typically found in crude oil are concentrated in semi-solid residual fuel. These fuels can contain more nitrogen than coal, but usually contain less sulfur.⁵⁰ Therefore, semi-solid fuels are intermediate between coal and oil. They often have somewhat less impurities than coal (although they can have more impurities),

but they do produce ash.

GAS FUEL

Natural gas is desulfurized before it is sent in a pipeline. Therefore, natural gas has almost no sulfur, essentially no impurities, and no ash. The only thing that varies is heat content per cubic meter. This variance is caused by natural gas producers supplementing natural gas with propane, liquified petroleum gas (butane), carbon monoxide, or other gaseous fuel. As a result, air to fuel ratio must be controllable to allow for changes in the stoichiometric ratio.

COMBUSTION SYSTEMS

To take advantage of a specific NO_x abatement technology, a combustion system must either have certain features in place, or needed system modifications must be technically and economically feasible. Therefore, when identifying applicable pollution prevention and emission control technologies, we must first consider combustion system design. The major types of combustion systems are shown in Table 5.²³

Table 5. Common Combustion Systems

Type of Combustion Unit	Fuel
Dry bottom boilers - wall-fired, front-fired or opposed-fired	pulverized coal, gas, or liquid
Dry bottom boilers - tangentially fired	pulverized coal, gas, or liquid
Wet bottom (slag tap) boilers - cyclone-type burners	pulverized coal, gas, or liquid
Fluidized bed	coal
Stokers with traveling grate.	crushed coal
Stokers with spreader grate	crushed coal.
Gas turbines	gas and liquid
Internal combustion engines	gas and liquid

Each NO_x abatement technology has different implementations, development histories, and, therefore, commercial status. Selection of a technology must occur after an engineering study to determine technical and economic feasibility of each NO_x technology. This includes how each technology can be implemented and its cost. Options may be limited by inability to adjust combustion system air flow appropriately, ducts that are at the wrong temperature, or ducts that

are too short to provide adequate mixing. These problems can be solved, but may require too much modification to make them economical.

DRY BOTTOM BOILERS - WALL-FIRED, FRONT-FIRED or OPPOSED-FIRED

Dry bottom pulverized coal, gas, and liquid fuel wall-fired boilers have used low-NOx burners to inject fuel and air from lower walls. Front-fired boilers have burners on one wall. Opposed-fired boilers have burners on front and back walls. These boilers typically use methods that reduce peak temperature, reduce residence time at peak temperature, or chemically reduce NOx (Methods 1, 2 & 3). These methods are used for large utility boilers in which combustion efficiency is all-important. NOx oxidation with absorption and removal of nitrogen (Methods 4 and 5) represent newer technologies that may be applied in the future. Using a sorbent (Method 6) is already in use for some boilers. See Table 6 for NOx technologies used for dry bottom wall-fired, front-fired or opposed-fired boilers.

Table 6: NOx technologies currently used for dry bottom wall-fired, front-fired or opposed-fired boilers.

NOx Abatement Method	Techniques Now Available	Efficiency
1. Reducing peak temperature	Flue Gas Recirculation (FGR) Natural Gas Reburning (NGR) Low NOx Burners (LNB) Combustion Optimization Burners Out Of Service (BOOS) Over Fire Air (OFA) Less Excess Air (LEA) Inject Water or Steam Reduced Air Preheat	50-70%
2.Reducing residence time at peak temperature	Air Staging of Combustion Fuel Staging of Combustion Inject Steam	50-70%
3. Chemical reduction of NOx	Selective Catalytic Reduction (SCR) Selective Non-Catalytic Reduction (SNCR) Fuel Reburning (FR) Low NOx Burners (LNB)	35-90%
4. Oxidation of NOx with subsequent absorption	Inject Oxidant Non-Thermal Plasma Reactor (NTPR)	60-80%
5. Removal of nitrogen	Ultra-Low Nitrogen Fuel	No Data
6. Using a sorbent	Sorbent In Combustion Chambers Sorbent In Ducts	60-90%

DRY BOTTOM BOILERS - TANGENTIALLY FIRED

Dry bottom pulverized coal, gas, or liquid fuel tangentially-fired boilers use jets from each corner of a furnace to inject fuel and combustion air in a swirl. The injected mix of fuel and combustion air forms a fireball in the center of the boiler. This firing configuration is used in medium sized utility and large industrial boilers. This combustion technique holds flame temperatures down (Method 1). In addition, chemical reduction of NO_x (Method 3) is frequently used. NO_x oxidation (Method 4) techniques may be used in the future. Sorbents (Method 6) are already used for some boilers. See Table 7 for NO_x technologies used for dry bottom tangentially fired boilers.

Table 7: NO_x technologies currently used for dry bottom tangentially fired boilers.

NO _x Abatement Method	Techniques Now Available	Efficiency
1. Reducing peak temperature	Flue Gas Recirculation (FGR) Natural Gas Reburning (NGR) Over Fire Air (OFA) Less Excess Air (LEA) Inject Water or Steam Reduced Air Preheat	50-70%
2.Reducing residence time at peak temperature	Air Staging of Combustion Fuel Staging of Combustion Inject Steam	50-70%
3. Chemical reduction of NO _x	Selective Catalytic Reduction (SCR) Selective Non-Catalytic Reduction (SNCR) Fuel Reburning (FR)	35-90%
4. Oxidation of NO _x with subsequent absorption	Non-Thermal Plasma Reactor (NTPR)	60-80%
5. Removal of nitrogen	Ultra-Low Nitrogen Fuel	No Data
6. Using a sorbent	Sorbent In Combustion Chambers Sorbent In Ducts	60-90%

WET BOTTOM (SLAG TAP) BOILERS

Wet bottom (slag tap) boilers use cyclone burners to create an intense flame. The flame is so hot that it melts ash, which then becomes slag that must be removed via a slag tap. These boilers are known to have higher NO_x generation because combustion temperature is so high. As a result, this high temperature combustion technique is not widely used because the NO_x concentration necessarily must be greater. Removal of non-fuel nitrogen as a reactant from the combustion process (Method 5) applies here. Reducing residence time at peak temperature, chemical

reduction of NO_x, and NO_x oxidation with absorption (Methods 2, 3 & 4) also apply to this combustion system. In addition, some slag tap boilers may be using sorbents (Method 6). There are recent reports that reducing peak temperature (Method 1) so that ash just melts has been used. See Table 8 for NO_x technologies used for slag tap boilers.

Table 8: NO_x technologies currently used for wet bottom (slag tap) boilers.

NO_x Abatement Method	Techniques Now Available	Efficiency
1. Reducing peak temperature	Flue Gas Recirculation (FGR) Natural Gas Reburning (NGR) Over Fire Air (OFA) Less Excess Air (LEA) Inject Water or Steam Reduced Air Preheat	30-70%
2.Reducing residence time at peak temperature	Air Staging of Combustion Fuel Staging of Combustion Inject Steam	20-50%
3. Chemical reduction of NO _x	Selective Catalytic Reduction (SCR) Selective Non-Catalytic Reduction (SNCR) Fuel Reburning (FR)	35-90%
4. Oxidation of NO _x with subsequent absorption	Non-Thermal Plasma Reactor (NTPR)	60-80%
5. Removal of nitrogen	Use Oxygen Instead Of Air Ultra-Low Nitrogen Fuel	No Data
6. Using a sorbent	Sorbent In Combustion Chambers Sorbent In Ducts	60-90%

FLUIDIZED BED

Fluidized bed combustion occurs in a bed of crushed coal that has air flowing upward through it to make coal particles behave like a fluid. Boiler pipes can be either submerged in the bed or exposed to the hot gases after they leave the bed. The fluidized bed is temperature controlled (Method 1). The bed also is a chemically reducing region in which available oxygen is consumed by carbon (Method 3) that reduces ionization of nitrogen. Excess air is injected (Method 2) over the fluidized bed to complete combustion of CO and other burnables. This allows for the addition of pulverized limestone (Method 6) to coal in the fluidized bed. Sulfur oxides then react with the limestone to form gypsum, a marketable product. Gypsum must be separated from the ash. As a result, NO_x generation can be essentially limited to prompt NO_x and fuel NO_x. See Table 9 for NO_x technologies used for fluidized bed combustion units.

Table 9: NOx techniques currently used for fluidized bed combustion.

NOx Abatement Method	Techniques Now Available	Efficiency
1. Reducing peak temperature	Flue Gas Recirculation (FGR) Natural Gas Reburning (NGR) Over Fire Air (OFA) Less Excess Air (LEA) Reduced Air Preheat	No Data
2.Reducing residence time at peak temperature	Inject Steam	No Data
3. Chemical reduction of NOx	Selective Catalytic Reduction (SCR) Selective Non-Catalytic Reduction(SNCR) Fuel Reburning (FR)	35-90%
4. Oxidation of NOx with subsequent absorption	Non-Thermal Plasma Reactor (NTPR)	60-80%
5. Removal of nitrogen	Ultra-Low Nitrogen Fuel	No Data
6. Using a sorbent	Sorbent In Combustion Chambers Sorbent In Ducts	60-90%

STOKERS WITH TRAVELING GRATE

Stokers with traveling grate cause the coal to move as it burns. Thus, char combustion is in one zone while volatiles are liberated and combusted in another zone. These stokers are commonly used with industrial boilers that are smaller than utility boilers. Reducing peak temperature, chemical reduction of NOx, and sorbents (Methods 1, 3 & 6) usually are applied. Perhaps NOx oxidation (Method 4) also will apply in the future. See Table 10 for NOx technologies used for stokers with traveling grates.

STOKERS WITH SPREADERS

Stokers with spreaders throw coal over the grate in a controlled manner. Coal is crushed, but particles are typically larger than pulverized coal. Therefore, combustion of volatiles begins while coal is in flight and combustion of char occurs on the grate. This system is used with somewhat larger boilers than stokers with traveling grates. It can be used in power plants, but this combustion system is used mainly for industrial boilers. Like stokers with traveling grates, reducing peak temperature, chemical reduction of NOx, and sorbents (Methods 1, 3, and 6) usually are applied. Perhaps NOx oxidation (Method 4) also will apply in the future. See Table 11 for NOx technologies used for stokers with Spreader grates.

Table 10: NO_x technologies currently used for stokers with traveling grates.

NO_x Abatement Method	Technique Now Available	Efficiency
1. Reducing peak temperature	Flue Gas Recirculation (FGR) Natural Gas Reburning (NGR) Combustion Optimization Over Fire Air (OFA) Less Excess Air (LEA) Inject Water or Steam Reduced Air Preheat	35-50%
2.Reducing residence time at peak temperature	Air Staging of Combustion Fuel Staging of Combustion	50-70%
3. Chemical reduction of NO _x	Selective Catalytic Reduction (SCR) Selective Non-Catalytic Reduction (SNCR) Fuel Reburning (FR)	55-80%
4. Oxidation of NO _x with subsequent absorption	Inject Oxidant Non-Thermal Plasma Reactor (NTPR)	60-80%
5. Removal of nitrogen	Ultra-Low Nitrogen Fuel	No Data
6. Using a sorbent	Sorbent In Combustion Chambers Sorbent In Ducts	60-90%

GAS TURBINES

Gas turbines use the Brayton Cycle with a burner to raise temperature of gas after compression and before expansion through the turbine. Turbines mainly use reducing peak temperature and reducing residence time (Methods 1 and 2) approaches to limit NO_x emissions. Because addition of particles to air flow entering the turbine would accelerate erosion of turbine blades, sorbents (Method 6) could only be applied after the expansion in the turbine. NO_x reduction (Method 3) has been used to treat exhaust gases. Many turbine operators claim that they use “good combustion practices” that do reduce the particles that produce visible emissions (which they equate with pollution), but say nothing about the NO_x emissions which are not visible.

Cogeneration units use a gas turbine to generate electricity and provide preheated combustion air for a boiler. Gas turbine exhaust is typically 10-15% oxygen and can be used to provide combustion air for a low pressure boiler. That boiler can be used to provide steam for another turbine, a process heater, a space heater, or some combination of these. If a steam turbine is used to generate electricity, it may constrain what can be done. Sorbent particles can be introduced to a flow after it leaves a gas turbine in order to control NO_x. There has also been some success in reducing NO_x concentrations when burning biomass fuels in a boiler. See Table 12 for NO_x technologies used for gas turbines.

Table 11: NOx technologies currently used for stokers with spreader grates.

NOx Abatement Method	Technique Now Available	Efficiency
1. Reducing peak temperature	Flue Gas Recirculation (FGR) Natural Gas Reburning (NGR) Low NOx Burners (LNB) Combustion Optimization Over Fire Air (OFA) Less Excess Air (LEA) Inject Water or Steam Reduced Air Preheat	50-65%
2.Reducing residence time at peak temperature	Air Staging of Combustion Fuel Staging of Combustion Inject Steam	50-65%
3. Chemical reduction of NOx	Selective Catalytic Reduction (SCR) Selective Non-Catalytic Reduction (SNCR) Fuel Reburning (FR)	35-80%
4. Oxidation of NOx with subsequent absorption	Inject Oxidant Non-Thermal Plasma Reactor (NTPR)	60-80%
5. Removal of nitrogen	Ultra-Low Nitrogen Fuel	No Data
6. Using a sorbent	Sorbent In Combustion Chambers Sorbent In Ducts	60-90%

INTERNAL COMBUSTION RECIPROCATING ENGINES

Internal combustion engines use air-to-fuel ratio and ignition/injection timing to control maximum temperature and residence time. This can reduce the concentration of NOx that is generated by reducing peak temperature (Method 1). Valve timing adjustments can reduce residence time at peak temperature (Method 2) to control NOx formation. Chemical reduction of NOx (Method 3) is used in catalytic converters to reduce NOx to N₂. Some stationary engines use both Method 3 and NOx oxidation (Method 4). A non-thermal plasma reactor was developed for treatment of diesel exhaust, but is not yet marketed to our knowledge. A plasma ignition system allows greater freedom in the air-fuel ratio and the ignition timing of spark ignition engines. See Table 13 for NOx technologies used for stationary internal combustion engines.

WHAT DOES NOx ABATEMENT AND CONTROL COST?

The cost of NOx abatement and control has been changing rapidly with dramatic reductions in recent years. Table 14 gives the 1993 cost as given in the Alternative Control Techniques

Table 12: NOx technologies currently used for gas turbines.

NOx Abatement Method	Technique Now Available	Efficiency
1. Reducing peak temperature	Natural Gas Reburning (NGR) Low NOx Burners (LNB) Inject Water or Steam Reduced Air Preheat Catalytic Combustion	70-85%
2.Reducing residence time at peak temperature	Air Staging of Combustion Inject Steam	70-80%
3. Chemical reduction of NOx	Selective Catalytic Reduction (SCR) Selective Non-Catalytic Reduction (SNCR) Fuel Reburning (FR) Low NOx Burners (LNB)	70-90%
4. Oxidation of NOx with subsequent absorption	Non-Thermal Plasma Reactor (NTPR)	No Data
5. Removal of nitrogen	Ultra-Low Nitrogen Fuel	No Data
6. Using a sorbent	Sorbent In Ducts	60-90%

Table 13: NOx technologies currently used for stationary internal combustion engines.

NOx Abatement Method	Technique Now Available	Efficiency
1. Reducing peak temperature	Air/fuel Ratio Timing of Ignition/Type of Ignition Pre-Stratified Combustion	20-97%
2.Reducing residence time at peak temperature	Valve Timing	No Data
3. Chemical reduction of NOx	Selective Catalytic Reduction (SCR) Non-Selective Catalytic Reduction (NCSR)	80-90%
4. Oxidation of NOx with subsequent absorption	Non-Thermal Plasma Reactor (NTPR)	80-95%
5. Removal of nitrogen	Ultra-Low Nitrogen Fuel	No Data
6. Using a sorbent	Sorbent In Exhaust Ducts Adsorber in fixed Bed	60-90%

Table 14. 1993 Costs of NOx Controls

	Cost of NOx Controls in 1993 Dollars					
Control	Low -Cap.	High -Cap.	Low - Oper.	High -Oper.	Low	High
Device	\$/MMBTU	\$/MMBTU	\$/MMBTU	\$/MMBTU	\$/ton	\$/ton
LNB	650	8,300	340	1,500	240	4,300
LNB + FGR					650	7,630
SNCR	1,600	3,300	680	1,200	N/A	N/A
(1994 ESTIMATE)					700	1,300
SCR	2,400	20,000	1,500	5,800	1,810	10,900
(1994 ESTIMATE)					500	2,800

Document NOx Emissions from Industrial/Commercial/Institutional Boilers (EPA 453/R-94-022).

The EPA Region III Low-NOx Control Technology Study in 1994 said that low-NOx burners had both beneficial effects on operating costs and detrimental effects on the burners, their life expectancy, and the boilers in which they were installed. Coal quality and some boiler designs caused NOx to remain high even after low-NOx burners were in place. Capital costs ranged from \$1.91 to \$54.24 per kW. Operating costs ranged from -\$23,000 (a profit) to \$1,113,750 per year. Thus, no reliable cost estimates could be obtained regarding low-NOx burner operation. Coal quality, boiler capacity, and burner design were among the variables influencing this cost. Many plants could not even give an estimate. SNCR cost between \$700 and \$1,300 per ton of NOx reduced. SCR cost between \$500 and \$2,800 per ton of NOx reduced.²⁵ However, cost per ton of NOx removed for all technologies is apparently becoming smaller.

These costs vary by control technique; type of fuel; grade of fuel; size of boiler, engine or turbine; type of boiler, or turbine; and other factors. Other costs were also changing with time. Therefore you need to examine the costs of these NOx control technologies for a specific application and at a particular time.

These preliminary cost estimates will also be further reduced as operating experience is gained, competition sharpens, and design iterations eliminate the high-maintenance or life-shortening features. Confidence in this view of the future is based upon reports that some users of low-NOx burners had already seen in 1994 that operating costs could be reduced to make the changeover yield a net profit. SCR and SNCR costs may also have declined further, since there is now competition for these technologies.

This analysis was supported by 1997 cost figures. These are presented in Table 15. This table is from the Analyzing Electric Power Generation Under the CAAA²⁶. It appears that competition and improved designs are still driving the costs downward. The Table was presented in that publication and is presented here for your convenience.

Table 15. 1997 Costs of NOx Controls

Analyzing Electric Power Generation Under the CAAA -- Cost Estimates ²⁶						
Boiler Type	Control Type	Capital Cost	Fixed O & M	Variable O& M	% Control	
		\$/kW	\$/kW/yr	mils/kWh		
Wall Fired	LNB w/o OFA	16.8	0.25	0.05	67.5	
Wall Fired	LNB w/ OFA	22.8	0.35	0.07	67.5	
Tang-Fired	LNB w/ OFA	32.3	0.49	0	47.3	
Tang-Fired LNB w/ SOFA		34.7	0.53	0	52.3	
Tang Fired LNB w/ BOFA		46.7	0.71	0.02	57.3	
Cell Burners	Non Plug-In Comb. Ctl.	22.8	0.34	0.07	60	
Cyclone	Coal Reburning	70.7	1.07	0.25	50	
Wet Bottom	NOx Comb. Ctl.	9.6	0.14	0.05	50	
Vert. Fired	NOx Comb. Ctl.	10.8	0.17	0.05	40	
	SCR -Low NOx Rate	69.7	6.12	0.24	70	
	SCR- High NOx Rate	71.8	6.38	0.4	80	
	SNCR-Low NOx Rate	16.6	0.24	0.82	40	
	SNCR-Cyclone	9.6	0.14	1.27	35	
	SNCR-High NOx Rate	19	0.29	0.88	35	
	Nat.Gas Reburn-Low	32.4	0.49		40	
	Nat.Gas Reburn-High	32.4	0.49		50	

Note that in Table 8 the following acronyms are used:

LNB is low-NOx burner
 OFA is closed coupled overfire air
 SOFA is separate over fire air

BOFA is both close coupled and over fire air
 Comb. Ctl. is combined controls

The Institute of Clean Air Companies also suggests that in 1999 SCR will cost \$50 - \$80 per kW for retrofit to units, which relates to \$400-\$1800 per ton of NOx that is destroyed.³⁴ Their cost estimate for SNCR ranges from \$5-\$15 per kW, which relates to \$400-\$2000 per ton of NOx that is destroyed.³⁵ Cost-effectiveness does not correlate with boiler capacity alone - other variables such as type and quality of fuel, type of boiler, SNCR/SCR design, etc enter into the analysis.

While the "Performance of Selective Catalytic Reduction on Coal-fired Steam Generating Units" study was for Germany, it cited a recent cost range for SCR from \$52 to \$77 per kW with retrofit units tending to have lower costs. Thus, the costs in Germany were very similar to costs in the U.S.A., except that retrofit costs usually are greater in the United States.

Table 16, Unit Costs for NOx control Technologies for Non-Utility Stationary Sources, is from the report "Ozone Transport Rulemaking Non-Electricity Generating Unit Cost Analysis." The report was prepared for EPA by the Pechan-Avanti Group. It indicates efficiencies and cost estimates for various NOx technologies for the year 2007. This appears to be a conservative estimate of efficiency and cost. Efficiencies indicated in the table tend to be lower than currently demonstrated efficiencies. Costs were based on historical information and, therefore, should be high estimates because NOx technology costs appear to be declining over time. The table was included here to indicate the relative efficiency and cost of NOx technologies for specific types of combustion systems.

The Alternative Control Techniques Document NOx Emissions from Stationary Reciprocating Internal Combustion Engines contains cost algorithms for the pollution prevention techniques and control technology applied to internal reciprocating engines. Costs for NOx elimination run from \$250/ton to \$1,300/ton for engines larger than 1,000 horsepower. For smaller engines the cost runs from \$400/ton to over \$3,500/ton.

ARE THESE METHODS SUFFICIENT?

YES, these methods are sufficient to meet the present goal of reducing NOx emissions 2 million tons below 1980 emissions.⁴⁷ The goal appears to be set at a level that can be achieved based on the state of NOx technology in 1996. However, we will have to see whether achieving our present goal provides the needed relief. A still more stringent set of standards may become necessary at sometime in the future.

As a high-technology nation and with a large urban and suburban population, we depend on automobiles, buses, airplanes, railroads, and trucks for transportation. We also depend upon electric power for computers, lights, air conditioning, and commerce. Therefore, we seem caught in a dilemma, for, while we depend on transportation, vehicles produce most of our NOx. While we also consume electric power as part of our market economy, electric power generation also generates over 40% of our NOx from stationary sources in 1995.³⁴

We also need to generate less NOx without regard to the ionization level of the nitrogen. In 1999, we are currently not capable of doing that. Therefore, we must do the best that we can,

Table 16: Unit Costs for NO_x Control Technologies for Non-Utility Stationary Sources

Source Type/Fuel Type	Control Technology	Percent Reduction (%)	Ozone Season Cost Effectiveness (\$1990/ton)	
			Small*	Large*
ICI Boilers - Coal/Wall	SNCR	40	1,870	1,380
ICI Boilers - Coal/Wall	LNB	50	3,490	2,600
ICI Boilers - Coal/Wall	SCR	70	2,910	2,450
ICI Boilers - Coal/FBC	SNCR - Urea	75	1,220	910
ICI Boilers - Coal/Stoker	SNCR	40	1,810	1,350
ICI Boilers - Coal/Cyclone	SNCR	35	1,480	1,110
ICI Boilers - Coal/Cyclone	Coal Reburn	50	3,730	710
ICI Boilers - Coal/Cyclone	NGR	55	3,730	710
ICI Boilers - Coal/Cyclone	SCR	80	1,840	1,560
ICI Boilers - Residual Oil	LNB	50	940	1,020
ICI Boilers - Residual Oil	SNCR	50	5,600	1,950
ICI Boilers - Residual Oil	LNB + FGR	60	2,670	920
ICI Boilers - Residual Oil	SCR	80	3,460	1,840
ICI Boilers - Distillate Oil	LNB	50	2,810	4,950
ICI Boilers - Distillate Oil	SNCR	50	10,080	3,520
ICI Boilers - Distillate Oil	LNB + FGR	60	5,960	1,810
ICI Boilers - Distillate Oil	SCR	80	6,480	3,460
ICI Boilers - Natural Gas	LNB	50	1,950	1,560
ICI Boilers - Natural Gas	SNCR	50	8,400	2,930
ICI Boilers - Natural Gas	LNB + FGR	60	6,110	1,420
ICI Boilers - Natural Gas	OT + WI	65	1,620	760
ICI Boilers - Natural Gas	SCR	80	5,190	2,770
ICI Boilers - Wood/Bark/Stoker	SNCR - Urea	55	2,090	1,430
ICI Boilers - Wood/Bark/FBC	SNCR - Ammonia	55	1,660	1,210
ICI Boilers - MSW/Stoker	SNCR - Urea	55	2,610	1,830
ICI Boilers - Process Gas	LNB	50	1,950	1,560
ICI Boilers - Process Gas	LNB + FGR	60	6,110	1,420
ICI Boilers - Process Gas	OT + WI	65	1,620	760
ICI Boilers - Process Gas	SCR	80	4,990	2,570
ICI Boilers - Coke	SNCR	40	1,870	1,380
ICI Boilers - Coke	LNB	50	3,490	2,600
ICI Boilers - Coke	SCR	70	2,910	2,450
ICI Boilers - LPG	LNB	50	2,810	4,950
ICI Boilers - LPG	SNCR	50	10,000	3,440
ICI Boilers - LPG	LNB + FGR	60	5,960	1,810
ICI Boilers - LPG	SCR	80	6,240	3,220
ICI Boilers - Bagasse	SNCR - Urea	55	2,090	1,430
ICI Boilers - Liquid Waste	LNB	50	940	1,020
ICI Boilers - Liquid Waste	SNCR	50	5,560	1,910
ICI Boilers - Liquid Waste	LNB + FGR	60	2,670	920
ICI Boilers - Liquid Waste	SCR	80	3,320	1,710
Internal Combustion Engines - Oil	IR	25	1,840	1,160

Source Type/Fuel Type	Control Technology	Percent Reduction (%)	Ozone Season Cost Effectiveness (\$1990/ton)	
			Small*	Large*
			Internal Combustion Engines - Oil	SCR
Internal Combustion Engines - Gas	IR	20	2,430	1,320
Internal Combustion Engines - Gas	AF RATIO	20	3,730	900
Internal Combustion Engines - Gas	AF + IR	30	3,430	1,080
Internal Combustion Engines - Gas	L-E (Medium Speed)	87	890	N/A
Internal Combustion Engines - Gas	L-E (Low Speed)	87	4,000	1,500
Internal Combustion Engines - Gas	SCR	90	5,547	1,075
IC Engines - Gas, Diesel, LPG	IR	25	1,840	1,160
IC Engines - Gas, Diesel, LPG	SCR	80	4,690	1,850
Gas Turbines - Oil	Water Injection	68	3,080	1,540
Gas Turbines - Oil	SCR + Water Injection	90	4,240	1,860
Gas Turbines - Natural Gas	Water Injection	76	3,590	1,750
Gas Turbines - Natural Gas	Steam Injection	80	2,490	1,190
Gas Turbines - Natural Gas	LNB	84	1,170	240
Gas Turbines - Natural Gas	SCR + LNB	94	4,850	1,140
Gas Turbines - Natural Gas	SCR + Steam Injection	95	3,750	1,570
Gas Turbines - Natural Gas	SCR + Water Injection	95	5,040	2,060
Gas Turbines - Jet Fuel	Water Injection	68	3,080	1,540
Gas Turbines - Jet Fuel	SCR + Water Injection	90	4,240	1,860
Process Heaters - Distillate Oil	LNB	45	8,290	2,320
Process Heaters - Distillate Oil	LNB + FGR	48	10,130	4,000
Process Heaters - Distillate Oil	SNCR	60	6,210	3,230
Process Heaters - Distillate Oil	ULNB	74	5,110	1,450
Process Heaters - Distillate Oil	SCR	75	18,970	12,520
Process Heaters - Distillate Oil	LNB + SNCR	78	7,160	3,630
Process Heaters - Distillate Oil	LNB + SCR	92	18,770	10,910
Process Heaters - Residual Oil	LNB + FGR	34	8,330	3,290
Process Heaters - Residual Oil	LNB	37	6,010	1,690
Process Heaters - Residual Oil	SNCR	60	3,730	2,050
Process Heaters - Residual Oil	ULNB	73	3,080	860
Process Heaters - Residual Oil	LNB + SNCR	75	4,730	2,510
Process Heaters - Residual Oil	SCR	75	10,560	7,170
Process Heaters - Residual Oil	LNB + SCR	91	11,170	6,550
Process Heaters - Natural Gas	LNB	50	5,250	4,290
Process Heaters - Natural Gas	LNB + FGR	55	7,610	5,890
Process Heaters - Natural Gas	SNCR	60	5,560	3,740
Process Heaters - Natural Gas	ULNB	75	3,580	2,870
Process Heaters - Natural Gas	SCR	75	24,840	16,760
Process Heaters - Natural Gas	LNB + SNCR	80	6,960	5,080
Process Heaters - Natural Gas	LNB + SCR	88	23,880	16,500
Process Heaters - Process Gas	LNB	50	5,250	4,290
Process Heaters - Process Gas	LNB + FGR	55	7,610	5,890
Process Heaters - Process Gas	SNCR	60	5,560	3,740
Process Heaters - Process Gas	ULNB	75	3,580	2,870
Process Heaters - Process Gas	SCR	75	24,840	16,760
Process Heaters - Process Gas	LNB + SNCR	80	6,960	5,080
Process Heaters - Process Gas	LNB + SCR	88	23,880	16,500

Ozone Season				
Cost Effectiveness (\$1990/ton)				
Source Type/Fuel Type	Control Technology	Percent Reduction (%)	Small*	Large*
Process Heaters - LPG	LNB	45	8,290	2,320
Process Heaters - LPG	LNB + FGR	48	10,130	4,000
Process Heaters - LPG	SNCR	60	6,210	3,230
Process Heaters - LPG	ULNB	74	5,110	1,450
Process Heaters - LPG	SCR	75	18,970	12,520
Process Heaters - LPG	LNB + SNCR	78	7,160	3,630
Process Heaters - LPG	LNB + SCR	92	18,770	10,910
Process Heaters - Other Fuel	LNB + FGR	34	8,330	3,290
Process Heaters - Other Fuel	LNB	37	6,010	1,690
Process Heaters - Other Fuel	SNCR	60	3,730	2,050
Process Heaters - Other Fuel	ULNB	73	3,080	860
Process Heaters - Other Fuel	LNB + SNCR	75	4,730	2,510
Process Heaters - Other Fuel	SCR	75	10,560	7,170
Process Heaters - Other Fuel	LNB + SCR	91	11,170	6,550
Adipic Acid Manufacturing	Thermal Reduction	81	1,000	1,000
Adipic Acid Manufacturing	Extended Absorption	86	210	210
Nitric Acid Manufacturing	Extended Absorption	95	840	840
Nitric Acid Manufacturing	SCR	97	1,010	1,010
Nitric Acid Manufacturing	SNCR	98	940	940
Glass Manufacturing - Container	Electric Boost	10	17,050	17,050
Glass Manufacturing - Container	Cullet Preheat	25	2,240	2,240
Glass Manufacturing - Container	LNB	40	4,040	4,040
Glass Manufacturing - Container	SNCR	40	3,320	3,320
Glass Manufacturing - Container	SCR	75	4,550	4,550
Glass Manufacturing - Container	OXY-Firing	85	10,960	10,960
Glass Manufacturing - Flat	Electric Boost	10	5,540	5,540
Glass Manufacturing - Flat	LNB	40	1,660	1,660
Glass Manufacturing - Flat	SNCR	40	1,380	1,380
Glass Manufacturing - Flat	SCR	75	1,490	1,490
Glass Manufacturing - Flat	OXY-Firing	85	4,530	4,530
Glass Manufacturing - Pressed	Electric Boost	10	20,910	20,910
Glass Manufacturing - Pressed	Cullet Preheat	25	1,930	1,930
Glass Manufacturing - Pressed	LNB	40	3,570	3,570
Glass Manufacturing - Pressed	SNCR	40	3,080	3,080
Glass Manufacturing - Pressed	SCR	75	5,170	5,170
Glass Manufacturing - Pressed	OXY-Firing	85	9,310	9,310
Cement Manufacturing - Dry	Mid-Kiln Firing	30	1,110	1,110
Cement Manufacturing - Dry	LNB	30	1,340	1,340
Cement Manufacturing - Dry	SNCR - Urea Based	50	1,280	1,280
Cement Manufacturing - Dry	SNCR - NH3 Based	50	1,490	1,490
Cement Manufacturing - Dry	SCR	80	6,850	6,850
Cement Manufacturing - Wet	Mid-Kiln Firing	30	1,010	1,010
Cement Manufacturing - Wet	LNB	30	1,260	1,260
Cement Manufacturing - Wet	SCR	80	5,840	5,840
Iron & Steel Mills - Reheating	LEA	13	3,160	3,160
Iron & Steel Mills - Reheating	LNB	66	720	720
Iron & Steel Mills - Reheating	LNB + FGR	77	900	900

Source Type/Fuel Type	Control Technology	Percent Reduction (%)	Ozone Season Cost Effectiveness (\$1990/ton)	
			Small*	Large*
Iron & Steel Mills - Annealing	LNB	50	1,350	1,350
Iron & Steel Mills - Annealing	LNB + FGR	60	1,790	1,790
Iron & Steel Mills - Annealing	SNCR	60	3,130	3,130
Iron & Steel Mills - Annealing	LNB + SNCR	80	3,460	3,460
Iron & Steel Mills - Annealing	SCR	85	8,490	8,490
Iron & Steel Mills - Annealing	LNB + SCR	90	9,070	9,070
Iron & Steel Mills - Galvanizing	LNB	50	1,170	1,170
Iron & Steel Mills - Galvanizing	LNB + FGR	60	1,370	1,370
Municipal Waste Combustors	SNCR	45	2,140	2,140
Medical Waste Incinerators	SNCR	45	8,570	8,570
Space Heaters - Distillate Oil	LNB	50	2,810	4,950
Space Heaters - Distillate Oil	SNCR	50	10,000	3,440
Space Heaters - Distillate Oil	LNB + FGR	60	5,960	1,810
Space Heaters - Distillate Oil	SCR	80	6,240	3,220
Space Heaters - Natural Gas	LNB	50	1,950	1,560
Space Heaters - Natural Gas	SNCR	50	8,330	2,860
Space Heaters - Natural Gas	LNB + FGR	60	6,110	1,420
Space Heaters - Natural Gas	OT + WI	65	1,620	760
Space Heaters - Natural Gas	SCR	80	4,990	2,570
Ammonia - NG-Fired Reformers	LNB	50	1,950	1,560
Ammonia - NG-Fired Reformers	SNCR	50	8,330	2,860
Ammonia - NG-Fired Reformers	LNB + FGR	60	6,110	1,420
Ammonia - NG-Fired Reformers	OT + WI	65	1,620	760
Ammonia - NG-Fired Reformers	SCR	80	4,990	2,570
Ammonia - Oil-Fired Reformers	LNB	50	940	1,020
Ammonia - Oil-Fired Reformers	SNCR	50	5,560	1,910
Ammonia - Oil-Fired Reformers	LNB + FGR	60	2,670	920
Ammonia - Oil-Fired Reformers	SCR	80	3,320	1,710
Lime Kilns	Mid-Kiln Firing	30	1,110	1,110
Lime Kilns	LNB	30	1,340	1,340
Lime Kilns	SNCR - Urea Based	50	1,280	1,280
Lime Kilns	SNCR - NH3 Based	50	1,490	1,490
Lime Kilns	SCR	80	6,850	6,850
Comm./Inst. Incinerators	SNCR	45	2,140	2,140
Indust. Incinerators	SNCR	45	2,140	2,140
Sulfate Pulping - Recovery Furnaces	LNB	50	1,950	1,560
Sulfate Pulping - Recovery Furnaces	SNCR	50	8,330	2,860
Sulfate Pulping - Recovery Furnaces	LNB + FGR	60	6,110	1,420
Sulfate Pulping - Recovery Furnaces	OT + WI	65	1,620	760
Sulfate Pulping - Recovery Furnaces	SCR	80	4,990	2,570
Ammonia Prod; Feedstock Desulfurization	LNB + FGR	60	6,110	1,420
Plastics Prod-Specific; (ABS) Resin	LNB + FGR	55	7,610	5,890
Starch Mfg; Combined Operations	LNB + FGR	55	7,610	5,890

Source Type/Fuel Type	Control Technology	Percent Reduction (%)	Ozone Season Cost Effectiveness (\$1990/ton)	
			Small*	Large*
By-Product Coke Mfg; Oven Underfiring	SNCR	60	3,130	3,130
Pri Cop Smel; Reverb Smelt Furn	LNB + FGR	60	1,790	1,790
Iron Prod; Blast Furn; Blast Htg Stoves	LNB + FGR	77	900	900
Steel Prod; Soaking Pits	LNB + FGR	60	1,790	1,790
Fuel Fired Equip; Process Htrs; Pro Gas	LNB + FGR	55	7,610	5,890
Sec Alum Prod; Smelting Furn/Reverb	LNB	50	1,350	1,350
Steel Foundries; Heat Treating Furn	LNB	50	1,350	1,350
Fuel Fired Equip; Furnaces; Natural Gas	LNB	50	1,350	1,350
Asphaltic Conc; Rotary Dryer; Conv Plant	LNB	50	5,250	4,290
Ceramic Clay Mfg; Drying	LNB	50	5,250	4,290
Coal Cleaning-Thrml Dryer; Fluidized Bed	LNB	50	3,490	2,600
Fbrglass Mfg; Txtle-Type Fbr; Recup Furn	LNB	40	4,040	4,040
Sand/Gravel; Dryer	LNB + FGR	55	7,610	5,890
Fluid Cat Cracking Units; Cracking Unit	LNB + FGR	55	7,610	5,890
Conv Coating of Prod; Acid Cleaning Bath	LNB	50	5,250	4,290
Natural Gas Prod; Compressors	SCR	20	5,547	1,075
In-Process; Bituminous Coal; Cement Kiln	SNCR - urea based	50	1,280	1,280
In-Process; Bituminous Coal; Lime Kiln	SNCR - urea based	50	1,280	1,280
In-Process Fuel Use; Bituminous Coal; Gen	SNCR	40	1,420	1,060
In-Process Fuel Use; Residual Oil; Gen	LNB	37	6,010	1,690
In-Process Fuel Use; Natural Gas; Gen	LNB	50	5,250	4,290
In-Proc; Process Gas; Coke Oven/Blast Furn	LNB + FGR	55	7,610	5,890
In-Process; Process Gas; Coke Oven Gas	LNB	50	5,250	4,290
Surf Coat Oper; Coating Oven Htr; Nat Gas	LNB	50	5,250	4,290
Solid Waste Disp; Gov; Other Incin; Sludge	SNCR	45	2,140	2,140

NOTE: *Small source cost per ton values are used to estimate control costs for all sources with 1995 NO_x emissions below 1 ton per day. If the ozone season daily 1995 baseline NO_x value is 1 ton or more, the cost per ton value for large sources is used.
N/A = not applicable. The population of medium speed gas-fired IC engines are all considered small.

and hope that we can endure while looking for the discovery and cost-reduction of the “better technology” that is capable of meeting the goal of sustainability. The reference literature suggests that the leading edge of pollution prevention and control technology in 1999 is capable of about 94%-99% control of NO_x or 1 ppm-5 ppm of NO_x.^{27,28}

As we all know, the leading edge technology always costs more because engineering has not yet shifted from feasibility to cost-reduction, and competition in the technology is not fully developed. Therefore, we can expect technology to be more affordable with time and to also improve its capability. We should expect to see the goal change with time as the technology advances, and as the achievable goal becomes both more stringent and more economically feasible. At one time, the capabilities that we now have seemed beyond imagining, and the costs seemed prohibitive. We live in an interesting time when the NO_x pollution prevention, abatement, and control technology is becoming more capable and more affordable.

CONCLUSIONS

1. Different fuels require different combustion, abatement and control techniques. Different coals have a varying content of volatile ingredients. The nitrogen content of fuel is important, as are the content of sulfur, lead, mercury and other contaminants. Ultra-low nitrogen content fuels have been developed and are already cost competitive. Thus, we can achieve some control of NO_x from the lowered concentration of nitrogen in the fuel without investing in changed burner designs.²⁹
2. The design of the boiler, internal combustion engine, or gas turbine has a major effect on the operation. NO_x formation tends to increase with an increase in boiler capacity, because larger boilers tend to have more intense combustion with higher combustion temperatures and longer residence time for flue gases. The same appears to be true of engines and turbines.
3. Staging of the combustion is implicit in several pollution prevention techniques. Tandem application (or use of hybrid control technology) of NO_x control techniques (first SNCR, then SCR in the duct, and then sorption before the ESP which is referred to as “polishing”) have been used to achieve an overall reduction of 90+% in NO_x and 80% in SO_x, even without using low-NO_x burners to lower NO_x generation.
4. Combustion of natural gas and petroleum distillates can be controlled in much the same way as pulverized coal. The major differences between coal and natural gas or oil are that gas and oil: (1) generally are lower in sulfur and ash; (2) usually are lower in nitrogen; and (3) probably are lower in lead and mercury. Thus, gas and oil do not deactivate a catalyst used in Selective Catalytic Reduction (SCR) at the same rate that coal or semi-solid fuels do.
5. The semi-solid petroleum products can actually have higher levels of sulfur, nitrogen and other impurities than coal. They do not have as much char or ash as coal, but have more than the lighter distillates.

6. We should expect the declining cost trend of control technology to continue as operating experience is gained, firing techniques are adapted to fuels, design flaws are corrected, and new designs appear. We should expect to see costs become less as they are driven down by competition between suppliers of successful technologies.
7. NO_x control technology appears capable of more than just meeting EPA's present goal and this should provide emission credits that can be traded to those firms that choose to continue emitting poorly controlled emissions. The sale of these credits by those that over-corrected for the present goal should further offset any net costs in adopting these control technologies.
8. Commercially available NO_x control systems are already available. The availability of these technologies was part of the basis of the recent NO_x SIP Call and Title IV regulations.
9. There has been an economic incentive to make combustion more efficient and to innovate ways to control nitrogen oxides. However, the amount of time and money that must be invested for a full-scale test of a strategy is significant. Acceptance requires that a technology be tried and succeed before a larger scale test is even contemplated. This delays acceptance of improved techniques.
10. There seems to be no control technology which is clearly superior for all combustion systems, boilers, engines, or fuels. Lacking a clear winner, one must select fuels and control technology either from among those already proven, or from a growing number of new and promising ideas.
11. The end of the search for control technologies is not yet in sight, and the search must continue. Past research must of necessity give ambivalent answers, because there are so many conflicting factors. However, at under \$150 per ton of NO_x prevented and with up to 80% control efficiency, the low-NO_x burner, where applicable, appears to be among the least expensive emission control technologies. SCR is more expensive, but can obtain up to 94% control efficiency. SNCR can be adopted without the initial cost of catalyst, although it is somewhat less effective. LNB, SCR and SNCR are all viable technologies across a wide spectrum of applications.
12. Research and development will have to continue to seek more effective answers and try to balance them against cost and efficiency. The cost will decrease as technology advances, operating experience is gained, competition becomes sharper, design flaws are corrected, and better designs become available. Reliability can only be gained with time. Cost will be reduced with time and experience. We also must expect that the level of pollution prevention and control technology effectiveness will improve with time.

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16. ABSTRACT The purpose of this document is to educate people about nitrogen oxides, how they are formed, the danger that they represent, and how emissions can be controlled. This knowledge is needed to make an informed choice of the control technology that is to be used.		
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nitrous oxide, nitric oxide, nitrogen dioxide, dinitrogen pentoxide, nitrous acid, nitric acid, ozone, volatile organic compounds, VOC, generation, pollution prevention, control technology, control technologies, emission control, acid rain, combustion, boilers, gas turbines, internal combustion engines, cost of emission controls, air pollution	air pollution control technology, combustion, pollution prevention, nitrogen oxides, boilers, internal combustion engines, diesel engines	
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