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Project Summary

Sourcebook: NO$_x$ Control Technology Data

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Available information on control of NO$_x$ emissions from stationary combustion sources has been compiled to assist new source permitting activities by regulatory agencies. The sources covered are combustion turbines, internal combustion engines, non-utility boilers and heaters, and waste incinerators.

The report discusses the background of NO$_x$ formation in the combustion process, major NO$_x$ sources, and processes for NO$_x$ control. The current status of NO$_x$ control technology is discussed and applications to meet permitting requirements is detailed. Permitted NO$_x$ emission levels are summarized by combustion source, fuel type and control technology. Documentation includes references and contacts for further information.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Emission of NO$_x$ is an environmental issue which has been attracting increasing regulatory attention at the local, state, and Federal level. Concerns over ozone abatement and control, acid rain, the growth in stationary source combustion systems, and implementation of prevention of significant deterioration (PSD) increments for NO$_x$ have all contributed to the increased attention. A number of states, in addition to California, are now regulating (or are considering regulating) NO$_x$ emission sources stringently.

A wide variety of new and emerging NO$_x$ control technologies are being marketed in the U.S., as well as in Europe and Japan. The performance reported by vendors for many of these systems have not been well documented in the public literature. Little primary data are available to demonstrate the actual applicability and long-term operating performance of the current generation of NO$_x$ control technologies.

There is interest among state and local regulatory agencies as to the level of NO$_x$ control that can be achieved with current technology. State and local officials are not always familiar with some of the technologies currently being marketed and often have no basis for critically reviewing permit applications for major NO$_x$ emission sources. In some states, the permitting process has been slowed by the uncertainty over the availability and performance of NO$_x$. This has resulted in many requests to the U.S. Environmental Protection Agency (EPA) for assistance in the NO$_x$ control (BACT) area. As part of an effort to respond to these requests, EPA's Control Technology Center (CTC) initiated the current study to develop a reference book of information on NO$_x$ controls. This report is that book.

NO$_x$ Formation in Selected Combustion Sources

Combustion Turbines

Gas turbines are rotary internal combustion engines fueled by natural gas, diesel or distillate fuel oils (occasionally re-

sidual or crude oils). The basic gas turbine consists of a compressor, combustion chambers, and a turbine. The compressor delivers pressurized combustion air to the combustors at compression ratios of up to 20 to 1. Injectors introduce fuel into the combustors and the mixture is burned with exit temperatures up to 1100°C. The hot combustion gases are rapidly quenched by secondary dilution air and then expanded through the turbine which drives the compressor and provides shaft power. In some applications, exhaust gases are also expanded through a power turbine.

NO_x is the primary pollutant produced by combustion turbines. Factors affecting NO_x formation include turbine design, ambient conditions, turbine load, and fuel type. The design parameters that affect the production of NO_x in the combustor most significantly are combustor inlet temperature and pressure and the firing temperature. As predicted by the Zeldovich equations, NO_x emissions rise rapidly with increasing firing temperatures. NO_x formation is also directly related to combustor pressure: increased pressure results in increased NO_x emissions.

Turbine efficiency is determined largely by the combustor firing temperature and pressure. Therefore, turbine models with regenerators, which are used to increase efficiency by increasing the combustor inlet air temperature, have higher NO_x emissions than the same models without regeneration. Many cogeneration/combined-cycle systems also employ natural gas-fired duct burners for exhaust temperature control.

Turbine NO_x emissions change with changes in ambient temperature, pressure, and especially humidity. Increases in humidity have a quenching effect on the combustor zone peak temperature, thereby reducing thermal NO_x formation. The effect of temperature on NO_x emissions changes as humidity changes. At low humidity, NO_x levels increase with an increase in temperature. At high humidity, the effect on NO_x formation depends on the range over which the temperature changes. Increases in ambient pressure increase gas compressor outlet pressures which in turn increase NO_x emissions. For example, NO_x emissions from a turbine installed at an elevation of one mi (1.6km) above sea level decrease by about 10 % compared to a similar turbine operating at sea level.

Stationary Combustion (IC) Engines

Stationary reciprocating IC engines use two methods to ignite the fuel/air mixture in the combustion chamber: (1) compression ignition (CI) fueled by diesel oil or a combination of natural gas and diesel oil (dual), or (2) spark ignition (SI) fueled by natural gas or gasoline.

In CI engines, air is first compression heated in the cylinder, and the diesel fuel is injected into the hot air where ignition is spontaneous. In SI engines, combustion is spark initiated with the natural gas or gasoline being introduced either by injection or premixed with the combustion air in a carburetted system. Either 2- or 4-stroke power cycle designs with various combinations of fuel charging, air charging, and chamber design are available.

Due to the high flame temperatures and pressures of IC engines, most of the NO_x formed is thermal. As diesel fuel and natural gas are the predominate fuels for this source, little fuel NO_x is formed, except in engines that fire residual and/or crude oils. Formation of prompt NO_x is also negligible in CI engines which operate with large amounts of excess air.

When fuel is injected into the cylinder, it undergoes a series of reactions that lead to ignition. The time between the start of injection of the fuel and the start of combustion (as measured by the onset of energy release) is called the ignition delay. Initial combustion occurs around the periphery of the fuel jet, where the air/fuel ratio is close to the stoichiometric ratio.

During ignition delay, some of the fuel is pre-mixed with air and evaporates. After ignition occurs, the pre-mixed charge burns extremely rapidly, thereby quickly releasing energy. Most of the burning takes place as a diffusion flame after the pre-mixed charge has burned.

NO_x emissions are directly affected by the amount of pre-mixing which, in turn, is a function of the ignition delay. When the ignition delay is large, there is more pre-mixing and a greater energy release rate at the start of combustion. This generally leads to higher temperatures and, accordingly, higher NO_x emissions.

Non-Utility Boilers and Heaters

Industrial boilers are typically classified by the type of firing mechanism employed, the heat transfer mechanism, and the type of fuel fired. Firing mechanisms include burners, spreader-fed, or mass-fed. With burners, the fuel is injected into the boiler through a nozzle and burns while suspended within the boiler combustion chamber. Mass-fed and spreader-fed boilers are used for most solid fuel industrial boilers. They combust the fuel on a grate in the boiler.

Watertube is the most common mechanism used for heat transfer in industrial boilers. In watertube boilers, the water for steam generation is contained in banks of tubes suspended in the boiler combustion chamber and flue. Firetube boilers invert this configuration and pass hot flue gasses through tubes suspended in a water drum.

Industrial boilers are fired with a wide variety of fossil and nonfossil fuels, including natural gas, fuel oil, and coal. Nonfossil fuels fired in industrial boilers include wood, bark, agricultural waste, municipal waste, and industrial waste.

Many designs of fired heaters are available. All fired heaters have a radiant section, and most have a convection section. The radiant section is in the firebox and contains the burners and a single row of tubular coils. The primary heating of the feedstocks occurs in the radiant section. As the name implies, radiation is the primary method of heat transfer.

Combustion air preheaters are often used to improve the efficiency of a fired heater. In the air preheater, heat is transferred from the flue gas to the combustion air. Therefore, less heat is required to heat the combustion air which allows a greater proportion of the total heat released to be absorbed in the radiant section. Also, less fuel is required to reach the required combustion temperature. In addition, the preheater raises the adiabatic flame temperature above that of ambient air heaters.

NO_x emissions from boilers and fired heaters depend on such design and operating parameters as fuel type, burner type, combustion air preheat, firebox temperature, draft type, excess air level, and heater load.

The most important design parameter affecting NO_x emissions from a boiler/fired heater is fuel type (i.e., the nitrogen content of the fuel). Coal-firing and gas-firing can be expected to generate higher NO_x emissions per unit of energy input than comparable oil-fired units. In addition, fluctuations in fuel composition and heating value may affect NO_x emissions.

Another design factor having a large effect on NO_x emissions is burner type. Oil-fired burners differ primarily in the methods used to atomize the oil prior to combustion. Steam atomization is used almost exclusively in fired heaters. Steam-atomized oil burners can be divided into two categories: conventional and staged combustion air oil burners. Conventional oil burners have a single combustion zone in which all of the air is fed to the atomized fuel oil. Staged combustion air oil burners make use of at least two air injection sections. Decreased NO_x emissions are achieved with these burners by oper-

ating a primary air/fuel injection section at substoichiometric air conditions and injecting secondary air downstream of the primary section to complete combustion. The use of combustion air preheat increases the amount of NO_x formed by virtue of increased flame temperature. Increasing the degree of preheat will likewise increases NO_x emissions.

The firebox temperature required for a given application influences NO_x emissions because of the relation between firebox temperature and flame temperature. High firebox temperature applications are expected to have higher NO_x emissions. The fractional use of firebox capacity can reduce NO_x emissions by lowering firebox temperature. An increase in the excess air level of a fired heater under typical operating conditions results in an increase in NO_x emissions due to the resulting higher peak flame temperature.

Waste Incinerators

The most common type of refuse incinerator consists of a refractory-lined chamber with a grate upon which refuse is burned. Combustion products are formed by heating and burning of refuse on the grate. The most prevalent types of sewage sludge incinerators are multiple hearth and fluidized bed units. In multiple hearth units, the sludge enters the top of the furnace where it is first dried by contact with the hot, rising combustion gases, and then burned as it moves slowly down through the lower hearths. At the bottom hearth, any residual ash is then removed. In fluidized bed reactors, the combustion takes place in a hot, suspended bed of sand with much of the ash residue being swept out with the flue gas. Temperatures in a multiple hearth furnace are 300°C in the lower, ash cooling hearth; 750 to 1100°C in the central combustion hearths, and 550 to 650°C in the upper, drying hearths. Temperatures in a fluidized bed reactor are fairly uniform, from 675 to 800°C. In both types of furnace, an auxiliary fuel may be required either during start-up or when the moisture content of the sludge is too high to support combustion.

Influencing the production of fuel NO_x in an incinerator are the distribution of the combustion air (underfire versus overfire), the fuel nitrogen content, and the total excess air rates. Thermal NO_x formation rates increase with temperature, oxygen availability, heat release rate, and flue gas residence time at high temperature.

The relative contribution of fuel and thermal NO_x to the total NO_x emitted from an incinerator depends on the design and operation of the furnace and the nitrogen content of the refuse burned. Testing has demonstrated a seasonal increase in NO_x emissions during the summer months. It is theorized that the higher emissions are due to the higher nitrogen content of the fuel because the raw refuse contains more yard waste, which has a high nitrogen content. At temperatures less than 1100°C, typical of municipal solid waste incinerators, NO_x emissions are influenced mainly by oxidation of fuel nitrogen. Thus, generally, 75-80 % of the total NO_x emitted from incinerators may be fuel NO_x.

Combustion Control of NO_x

The key parameters controlling the rate of NO_x formation for a given fuel and combustor design are the local oxygen concentration, temperature, and time history of the combustion products. Each of these parameters, within the temperature range of NO_x formation, is determined by the system design and operation. The combustion system, therefore, determines the NO_x formed and represents the only control capability for reducing the rate of NO_x formation. Techniques concerned with reducing NO_x formation are applied in this region and are collectively referred to as "combustion controls." All other NO_x control techniques applied in downstream zones work to reduce the NO_x formed during combustion and are called post-combustion controls.

The combustion controls discussed below are grouped according to the following source categories: combustion turbines, IC engines, and other. Combustion turbine controls include dry control and wet injection. IC engine controls include injection timing retard, pre-ignition chamber combustion, air to fuel ratio, and wet injection. Controls applicable to other combustion sources (including boilers, process heaters, and municipal waste incinerators) include low excess air, low NO_x burners, overfire air, burners out of service, flue gas recirculation, reburn, reduced combustion air temperature, and derating/load reduction.

Combustion Turbine NO_x Control

Extensive progress has been made in commercializing dry low NO_x combustors for natural gas-fired gas turbine applications. NO_x reductions of up to 60 % have been achieved, and in special instances, reductions of over 80 % have been reported. Emissions in the range of 25-50 ppm at 15 % O_2 have been achieved for large, natural gas-fired heavy duty turbines. However, additional development is needed prior to commercialization of oil-fired applications.

Although combustors are proprietary, similarities among designs can be noted. The technologies are based on reducing the flame turbulence and intensity, enhancing the fuel/air mixing, and establishing fuel-lean zones in the combustor. They generally rely on staged combustion with the first stage used as a pilot burner followed by a second stage of multiple fuel injection nozzles. The second stage often burns a lean, premixed fuel/air mixture to ensure a uniform mixture and avoid high temperature regions in the combustor. The control of the two burner zones and the preparation and control of premix air complicate the combustor control systems. The control system can be based on using variable geometry, and/or variable air flow scheduling.

The principal requirements in using wet injection for NO_x reduction are to inject sufficient water or steam at the proper location in the flame envelope and, with appropriate dispersion, to reduce the peak flame temperature without degrading combustion efficiency. Although it is easier to ensure uniform mixing if steam is used, water can be effective as well.

The major factor affecting NO_x reduction is the water/steam-to-fuel ratio. The NO_x reduction achievable for a particular unit is directly related to the amount of water or steam which can be injected before serious impacting combustor performance. The impacts include flameouts, reduced thermal efficiency expressed as a heat rate penalty, large increases in carbon monoxide (CO) and hydrocarbon (HC) emissions, and pressure pulsations which result in significantly reduced combustor reliability. Higher corrosion rates may also be experienced. The highest ratio sustainable will vary depending on the tradeoff between NO_x, emissions and CO, and HC emissions and combustor design characteristics.

Water/steam can be injected in a variety of ways ranging from premixing with the intake air or fuel to injecting it directly into the combustor. The effectiveness of the method is a function of the atomization and mixing of the water/steam within the combustion charge. Wet injection is applicable to gas or liquid fuels.

Stationary IC Engine Controls

Ignition in a normally adjusted IC engine is set to occur shortly before the piston reaches its uppermost position (top dead center, or TDC). At TDC, the air or air/fuel mixture is at maximum compression. The timing of the start of injection or of the spark is given in terms of the number of degrees that the crankshaft must still rotate between this event and the arrival of the piston at TDC.

Retarding the timing beyond TDC, the point of optimum power and fuel consumption, reduces the rate of NO_x production. Retarding causes more of the combustion to occur during the expansion stroke, thus lowering peak temperatures, pressures, and residence times. Injection timing retard is an applicable control with all IC engine fuels.

The use of a pre-ignition chamber can improve fuel efficiency and reduce NO_x emissions. The system is designed to burn lean fuel/air mixtures. The fuel charge is introduced into the pre-chamber as a rich mixture and ignited by a spark plug. Since it burns in the absence of excess oxygen, NO_x formation is inhibited. This "torch" of burning fuel expands into the power cylinder where it thoroughly ignites a lean mixture at reduced temperatures. Therefore, combustion is completed in an overall lean mixture at temperatures which are adequate for combustion but below those where NO_x forms. This NO_x control is currently applied to gas-fired engines only.

In injection type engines, which include all diesel and many dual fuel and gas varieties, the air to fuel ratio for each cylinder can be adjusted by controlling the amount of fuel that enters each cylinder. These engines are therefore operated lean where combustion is most efficient and fuel consumption is optimum.

The most practical use of air-to-fuel ratio adjustment as a control technique is to change the setting toward leaner operation. The oxygen availability will increase but so will the capability of the air and combustion products to absorb heat. Consequently, the peak temperature will fall, resulting in lower NO_x formation rates. The limiting factor for lean operation is the increased emissions of HC at the lower temperatures.

Carbureted engines are beset by large variations in cylinder air-to-fuel ratios. Therefore, they must operate near the stoichiometric ratio to ensure that no individual cylinder receives a charge which is too lean to ignite.

As with combustion turbines, wet injection can reduce NO_x emissions from IC engines. Wet control effectiveness correlates inversely with excess air levels. Since wet controls reduce peak temperature by increasing the charge mass, the technique is more effective in a low excess air system than in one with much excess air and, hence, much thermal mass. Presumably, systems with high excess air absorb all the heat that can be transferred to a fluid in the short time between combustion and peak temperature. Because of difficulty of water injec-

tion, use of water/fuel emulsions is under development for IC engine applications, but not currently available.

NOₓ Control for Other Combustion Sources

There are two fundamental ways of controlling flame stoichiometry: regulating the overall fuel/air ratio supplied (low excess air), or gross staging of combustion (low NO_x burners, overfire air ports, removing burners from service, derating, reburn). In addition to being influenced by burner design and fuel/air stoichiometry, the flame temperature can be reduced from its peak value by the introduction of heat absorbing inerts (recirculated flue gas) or by reduction in the temperature of the combustion air supplied to the burners.

The NO_x combustion controls discussed below are applicable to all of the combustion sources grouped collectively as "other" including non-utility boilers, process heaters, and waste incinerators.

For all conventional combustion processes, some excess air is required to ensure that all fuel molecules can find and react with oxygen. In the low excess air (LEA) approach to NO_x control, less excess air (oxygen) is supplied to the combustor than normal. The lower O_2 concentration in the burner zone reduces the flame temperature and the formation of thermal NO_x. In the starved-air flame zone, fuel bound nitrogen is converted to nitrogen thus reducing formation of fuel NO_x. The limiting criteria which define minimum acceptable excess air conditions are increased emissions of CO and visible plume, and a reduction in flame stability.

New designs and most existing combustion operations will incorporate LEA firing as standard practice. LEA operation has an economic incentive since it results in increased fuel efficiency. The reduced airflow decreases the volume of combustion air to be heated, allowing more heat of combustion to be transferred, thus lowering fuel requirements for a given output. LEA operations may be used as the primary NO_x control method or in combination with other NO_x controls such as low NO_x burners, overfire air, or flue gas recirculation. LEA operations are applicable to all combustion sources/fuels.

Low NO_x burners control NO_x formation by carrying out the combustion in stages. These burners control the combustion staging at and within the burner rather than in the firebox. Low NO_x burners are designed to control both the stoichiometric and temperature histories of the fuel and air locally within each individual burner flame envelope. This control is achieved through design features which regulate

the aerodynamic distribution and mixing of the fuel and air.

As with overfire air, the burner staging delays combustion and reduces the peak flame temperature, thus reducing thermal NO_x formation. The sub-stoichiometric oxygen introduced with the primary combustion air into the high temperature, fuel nitrogen evolution zone of the flame core reduces fuel NO_x formation. Thus, low NO_x burners are effective for reducing NO_x emissions independent of fuel. There are two distinct types of designs for low NO_x burners: staged air burners and staged fuel burners.

Staged air burners have been in service since the early 1970s and were the first type of burner designed to specifically reduce NO_x emissions. They are designed to reduce flame turbulence, delay fuel/air mixing, and establish fuel-rich zones for initial combustion. The reduced availability of oxygen in the initial combustion zone inhibits fuel NO_x conversion. Radiation of heat from the primary combustion zone results in reduced temperature as the final unburned fuel gases mix with excess air to complete the combustion process. The longer, less intense flames resulting from the staged stoichiometry lower flame temperatures and reduce thermal NO_x formation. Staged air burners are effective with all fuels.

A more effective concept for NO_x reduction is staging of the fuel rather than the air. Staged fuel burners mix a portion of the fuel and all of the air in the primary combustion zone. The high level of excess air greatly lowers the peak flame temperature achieved in the primary combustion zone, thereby reducing formation of thermal NO_x. The secondary fuel is injected at high pressure into the combustion zone through a series of nozzles which are positioned around the perimeter of the burner. Because of its high velocity, the fuel gas entrains furnace gases and promotes rapid mixing with first stage combustion products. The entrained furnace gases simulate flue gas recirculation. Unlike the staged air burner, staged fuel burners are designed only for gas firing.

An overfire air (OFA) system uses conventional burners to introduce the fuel and sub-stoichiometric quantities of combustion air (primary air). The remaining combustion air (secondary air) is introduced approximately 1-3 of the distance down the firebox through overfire air ports. The overfire air system reduces NO_x formation by two mechanisms: (1) Staging the combustion air partially delays the combustion process, resulting in a cooler flame and suppressed thermal NO_x formation; and (2) staging of the combustion air also al-

lows deprivation of oxygen and less mixing of fuel and air in the combustion region where fuel nitrogen evolves, thereby reducing fuel NO_x formation. This method is effective with all fuels.

Burners out of service is a variation of the staged combustion technique for reduction of NO_x formation. It is a low cost retrofit NO_x control measure for existing fireboxes. Ideally, all of the fuel flow is diverted from a selected number of burners to the remaining firing burners. Since airflow is maintained unchanged among all the burners, a staged combustion effort is obtained. The fuel-admitting burners fire more fuel-rich than normal, with the remaining air required for combustion being admitted through the inactive burners. NO_x is reduced by decreasing the excess air available in the active burner zone. This reduces both fuel and thermal NO_x formation and, thus, is applicable to all fuels.

Reburn, also referred to as in-furnace NO_x reduction or staged fuel injection, is the only NO_x control approach implemented in the furnace zone – defined as post-combustion, preconvection section. Reburning involves passing the burner zone products through a secondary flame or fuel-rich combustion process. This process is designed to reduce NO_x formation without generating CO emissions. This NO_x control approach diverts a fraction of the fuel to create a secondary flame or fuel-rich zone downstream of the burner (primary combustion zone). Sufficient air is then supplied to complete the oxidation process. These reactions are NO_x forming as well as NO_x reducing. Laboratory results indicate that a maximum reduction in NO_x is achieved when the reburning zone stoichiometry is approximately 0.9 (90% theoretical air).

The burner pattern plus overfire air ports provides an existing, potential capability to implement the reburning NO_x control approach. In fact, the burners out of service mode of operation implemented on some units to achieve fuel-rich primary combustion may also result in partial reburning. LEA and flue gas recirculation (FGR) controls are combustion modification techniques often combined with reburning.

FGR is based on recycling a portion of cooled flue gas back to the primary combustion zone. The FGR system reduces NO_x formation by two mechanisms: (1) the recycled flue gas is made up of combustion products which act as inerts during combustion of the fuel air mixture (this additional mass is heated and lowers the peak flame temperature, thereby reducing

the amount of thermal NO_x formation); and (2) to a lesser extent, FGR also reduces thermal NO_x formation by lowering the oxygen concentration in the primary flame zone (the decrease in flame temperature alters the distribution of heat and lowers the fuel efficiency).

The recycled flue gas may be pre-mixed with combustion air or injected directly into the flame zone. Because FGR beneficial effects are limited to reduction of thermal NO_x, the technique is applied primarily to natural gas or distillate oil combustion. In these applications, the thermal NO_x component is virtually 100% of the total NO_x. The amount of recirculation is limited by flame stability. Typically, 15-20% is employed. FGR is more adaptable to new designs than as a retrofit application.

Other techniques discussed in the report include reduced combustion air temperature, derating, and load reduction.

Post-Combustion NO_x Control

This section describes NO_x reduction techniques applied downstream of the combustion zone to reduce the NO_x formed during the combustion process. The three post-combustion NO_x control technologies described include selective catalytic reduction (SCR), non-selective catalytic reduction (NSCR), and selective noncatalytic reduction (SNCR).

In the SCR process, ammonia (NH_3), usually diluted with air or steam, is injected through a grid system into the flue/exhaust gas stream upstream of a catalyst bed. On the catalyst surface, the NH_3 reacts with NO_x to form molecular nitrogen and water. Depending on system design, NO_x removal of 80-90% and higher is achievable. The reaction of NH_3 and NO_x is favored by the presence of excess oxygen (air-rich conditions). The primary variable affecting NO_x reduction is temperature. Optimum NO_x reduction occurs at catalyst bed temperatures between 300 and 400°C for conventional (vanadium or titanium-based) catalyst, and 240 and 265° for platinum catalysts. The catalyst selected depends largely on the temperature of the flue gas being treated. A given catalyst exhibits optimum performance within a temperature range of ±30°C. Below this optimum temperature range, the catalyst activity is greatly reduced, allowing unreacted NH_3 to slip through. Above 450°C, NH_3 begins to be oxidized to form additional NO_x. The NH_3 oxidation to NO_x increases with increasing temperature. Depending on the catalyst substrate material, the catalyst may be quickly damaged due to thermal stress at tempera-

tures in excess of 450°C. It is important, therefore, to have stable operations and thus uniform flue gas temperatures for this process to be an effective NO_x control.

A new family of zeolite catalysts has been developed and is in use in the U.S. These can function at higher temperatures than conventional catalysts. Zeolites are claimed to be effective over the range of 300 to 600°C, with the optimum temperature range states as 360 to 580°C. Ammonia oxidation to NO_x begins at around 450°C and is predominant at temperatures in excess of 500°C. Zeolites suffer the same performance and potential damage problems as conventional catalysts when used outside their optimum temperature range. In particular, at around 550°C, the zeolite structure may be irreversibly degraded due to loss of pore density. Zeolite catalysts have not been continuously operated commercially at temperatures above 510°C due to NH_3 oxidation to NO_x and potential damage to the catalyst.
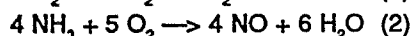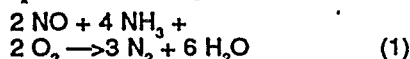
With zeolite catalysts, the NO_x reduction reaction takes place inside a molecular sieve ceramic body rather than on the surface of a metallic catalyst. This difference is reported to reduce the effect of particulates/soot, SO_2/SO_3 conversion, heavy metals, etc. which poison, plug, and mask metal catalysts. These catalysts have been in use in Europe since the mid-1980s, with approximately 100 installations on-stream. Process applications range from gas to coal fuel. Typically, NO_x levels are reduced 80-90%.

Non-selective catalytic reduction systems are often referred to as "three-way conversion" catalyst systems since they reduce NO_x, unburned hydrocarbon, and CO simultaneously. To operate properly, the combustion process must be with an air-to-fuel ratio slightly fuel-rich of stoichiometric. Under this condition, in the presence of the catalyst, the NO_x are reduced by the CO, resulting in nitrogen(N_2) and carbon dioxide (CO_2).

The catalyst used to promote this reaction is generally a mixture of platinum and rhodium. The catalyst operating temperature limits are 350 to 800°C, with 425 to 650°C being the most desirable. Temperatures above 800°C result in catalyst sintering.

Typical NO_x conversion ranges from 80-95 % with corresponding decreases in CO and HC. Potential problems associated with NSCR applications include catalyst poisoning by oil additives (e.g., phosphorous, zinc) and inadequate control systems.

There are two commercially available selective non-catalytic reduction processes. Thermal DeNO$_x$™ (TDN) developed by Exxon is an add-on NO$_x$ control technique which reduces NO$_x$ to N$_2$ without the use of a catalyst. The TDN process injects gaseous NH$_3$ to react with NO$_x$ in the air rich flue gas. The NH$_3$ and NO$_x$ react according to:

$$2 \, NO + 4 \, NH_3 + 2 \, O_2 \longrightarrow 3 \, N_2 + 6 \, H_2O \quad (1)$$

$$4 \, NH_3 + 5 \, O_2 \longrightarrow 4 \, NO + 6 \, H_2O \quad (2)$$

Temperature is the primary variable for controlling the selective reaction. In the temperature range of 870 to 1200°C, Reaction (1) dominates, reducting NO$_x$. Above 1200°C, Reaction (2) dominates, increasing NO$_x$ production. Below 870°C, neither reaction is of sufficient activity to either produce or destroy NO$_x$. NO$_x$ reduction performance is maximized in the relatively narrow temperature range of 870 -1040°C, with an optimum temperature of about 950°C. The 170°C reaction window can be lowered to a range of 700 - 800 °C by introducing hydrogen, a readily oxidizable gas.

Without using a catalyst to increase the reaction rates, adequate time at optimum temperatures must be available for the NO$_x$ reduction reaction to occur. Design considerations should allow ample residence time and good mixing in the required temperature range. Long residence times (>1 sec) at optimum temperatures will tend to promote relatively high performance even with less than optimum initial mixing or temperature/velocity gradients. However, when the NH$_3$ injection zone is characterized by low temperatures and/or steep temperature declines, a loss of process efficiency results.

The initial ratio of NH$_3$ injected to NO$_x$ concentrations is another parameter to control the process. Maximum NO$_x$ reductions (40-60%) require 1.5-2.0 NH$_3$/NO$_x$ injection ratios. At these ratios, significant concentrations of NH$_3$ can exit the convective zone, creating corrosive ammonium sulfates and/or a visible NH$_3$ or NH$_4$Cl stack plume. (Unreacted ammonia emissions from a Thermal DeNO$_x$™ system are usually higher than from SCR systems.)

Selection of the optimum NH$_3$ injection location also affects NO$_x$ reduction performance and NH$_3$ slip. In most Thermal DeNO$_x$ applications today, the injection grids are being replaced by wall injectors. The temperatures and velocity profiles will change significantly with load, requiring multiple NH$_3$ injection points to achieve the desired NO$_x$ reduction for a range of operating loads.

In the NOxOUT™ process, a urea type (or amine salt) compound is injected into the oxygen-rich upper furnace and/or high temperature convection section of a boiler to promote NO$_x$ reduction. The exact chemical mechanism is not fully understood, but involves the decomposition of urea – C(NH$_2$)$_2$O. The likely decomposition products include the amino(NH$_2$) groups. The reaction takes place at temperatures of 950 to 1650°C.

Originally developed for the Electric Power Research Institute (EPRI) in the late 1970s, the process is currently licensed by Fuel Tech where proprietary additives (that allow NO$_x$ reduction capability over a temperature range of 425-1150°C) have been developed. As with the other post-combustion NO$_x$ control systems, temperature is the primary control variable for the selective reactions. NO$_x$ reductions up to 80 % are achievable with this technology. The performance of the

urea injection process is limited by the time/temperature/flow characteristics of the flue gas. Residence time in the temperature window and the urea-to-NO$_x$ ratio impact the performance in a manner similar to Thermal DeNO$_x$. The NO$_x$ reduction capability is limited by mixing because the reaction times are relatively fast.

The capital costs associated with urea injection tend to be less than those of NH$_3$ injection. Urea is injected in liquid form, eliminating the need for a compressor. The hazards of NH$_3$ storage are also alleviated. The lower capital costs are offset, however, by higher operating costs; urea is more expensive than NH$_3$. The urea injection process may better accommodate changing conditions due to varying loads by altering the solution formulation, in addition to multiple injection points for varying temperature/load requirements.

NO$_x$ Control Applicability and Effectiveness

Table 1 summarizes the applicability of NO$_x$ controls discussed above for the four source categories considered. As shown in Table 1, combustion modifications and selective catalytic reduction have been applied universally . The report gives an extensive breakdown of technologies applied by combustion source and fuel and lists U.S., Japanese, and West German installations.

NO$_x$ permit limits for turbines are summarized in Table 2, by fuel type and control technology. Tables 3, 4, and 5 provide similar summaries for IC engines, boilers and heaters, and waste incinerators, respectively.

The full report is intended to be a handy desk reference for those involved in permitting of stationary NO$_x$ sources. An extensive vendor listing should provide easy access to updated information.

Table 1. NO$_x$ Control Technology Applicability [a,b]

Control Technology	Combustion Turbines	Stationary Combustion Engines	Boilers/ Heaters	Waste Incinerators
Combustion Controls[c]	X	X	X	X
Post-combustion Controls				
Selective catalytic reduction	X	X	X	X
Non-selective catalytic reduction		X		
Selective non-catalytic reduction			X	X

[a] Refer to full report for facility-specific data.
[b] Commercial applications in U.S., Germany, and Japan.
[c] Includes a variety of combustion techniques to reduce NO$_x$ formation in the combustion zone depending on the source: wet injection, timing retard, staged combustion, low excess air, burners out of service, flue gas recirculation, overfire air, dry combustion controls, reduced air preheat, clean burn, and derating.

Table 2. No$_x$ Control Levels - Combustion Turbines [a,b]

Control Technology	NO$_x$ Permits Limits (ppm NO$_x$ at 15% O$_2$, dry basis)		
	Natural Gas	Oil	Dual Fuel
Combustion Controls			
Wet injection	25-195		25-79 (gas)/40-129 (oil)
Dry low NO$_x$	32-188		
Post-combustion Controls			
Selective catalytic reduction	5-25[c]	10-25[d]	8-10 (gas)/12-18 (oil)[e]

[a] Refer to full report for facility-specific data.
[b] Commercial applications in U.S. and Japan.
[c] In combination with combustion controls.
[d] Units in Japan.
[e] Based on two units in Eastern U.S.

Table 3. NO$_x$ Control Levels-- Stationary Internal Combustion Engines [a,b]

Control Technology	NO$_x$ Permit Limits (g/hp-hr)		
	Natural Gas/ Dual Fuel	Oil	Other[c]
Combustion Controls	0.75-16.5 (~80-1,760 ppm)[d]	520-1,158 ppm[d]	1.5-2 (160 to 210 ppm)[d]
Injection timing retard Pre-ignition chamber combustion (clean burn) Air to fuel ratio Stratified charge Turbocharging Wet injection Derating			
Post-combustion Controls			
Selective catalytic reduction	70-90% (U.S.) 96-190 ppm[d]	90-150 ppm[d] (Japan)	
Non-selective catalytic reduction	1.0-1.5 (110 to 160 ppm)[d]		

[a] Refer to full report for facility-specific data.
[b] Commercial applications in U.S., West Germany, and Japan.
[c] Landfill gas, refinery gas, process gas, digester gas.
[d] At 15% O$_2$, dry basis.

Table 4. NO$_x$ Control Levels -- Boilers and Heaters [a,b]

Control Technology	NO$_x$ Emission Limits (ng/J)				
	Coal Conventional	Coal Fluid Bed	Wood	Gas	Oil
Combustion Controls[e]	73-258 (40-145 ppm)[d]	86-129 (50-75 ppm)[d]		7.7-43 (5-30 ppm)[d]	52-164 (30-100 ppm)[d]
Low excess air Overfire air Flue gas recirculation Low NO$_x$ burners					
Post-combustion Controls					
Selective catalytic reduction	60-250 ppm (Japan)	213 ppm (Germany site visit)		13-21.5 (10-15 ppm)[d] 15-30 (Japan)	25-50 ppm (Japan)
Selective non-catalytic reduction	<——43-114——————————> (25-65 ppm)[d]			21.5 (15 ppm)[d]	64.5 (40 ppm)[d]

[a] Refer to full report for facility-specific data.
[b] Commercial applications in U.S., West Germany, and Japan.
[e] May involve concurrent application of more than one technology.
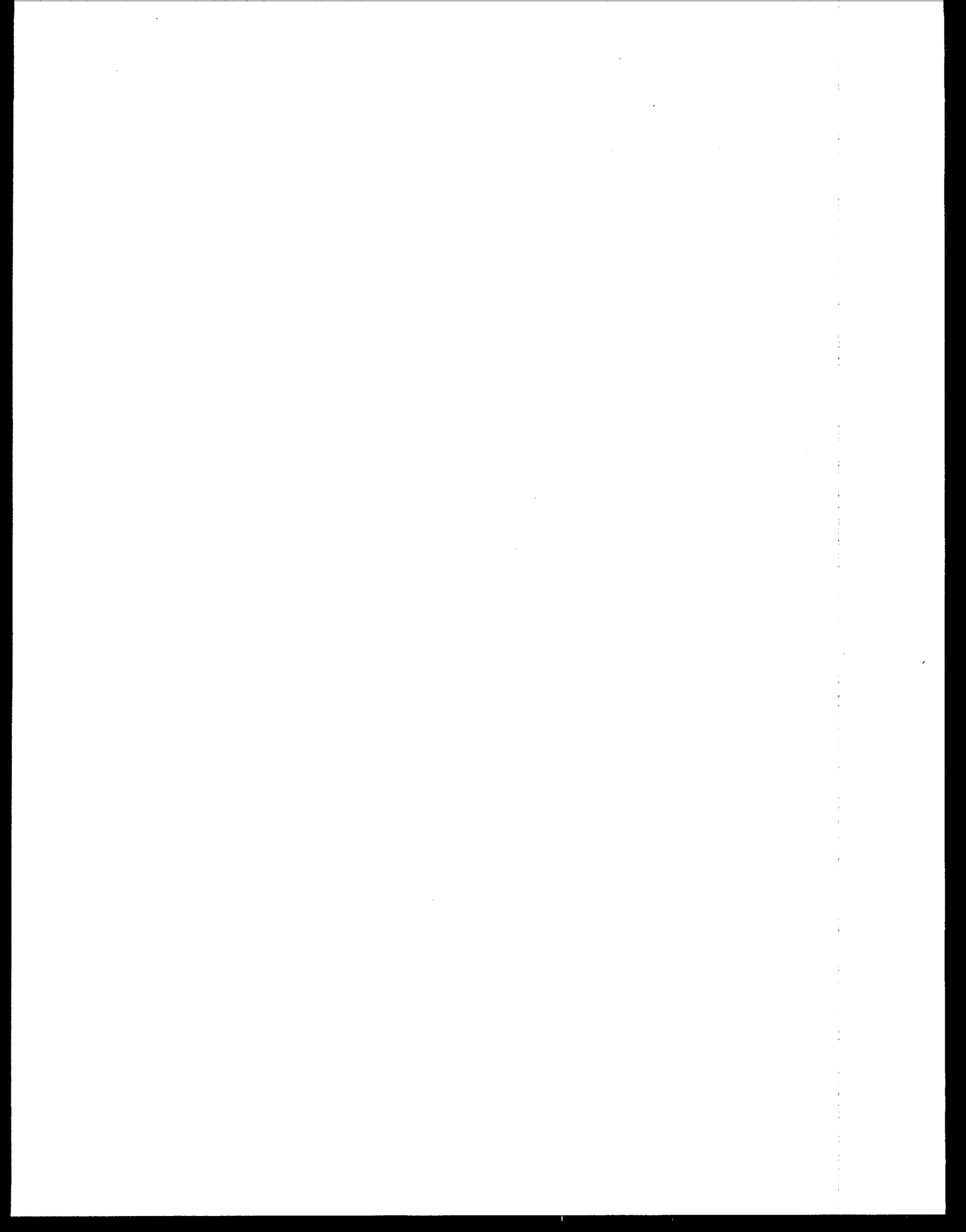[d] At 15% O$_2$, dry basis.

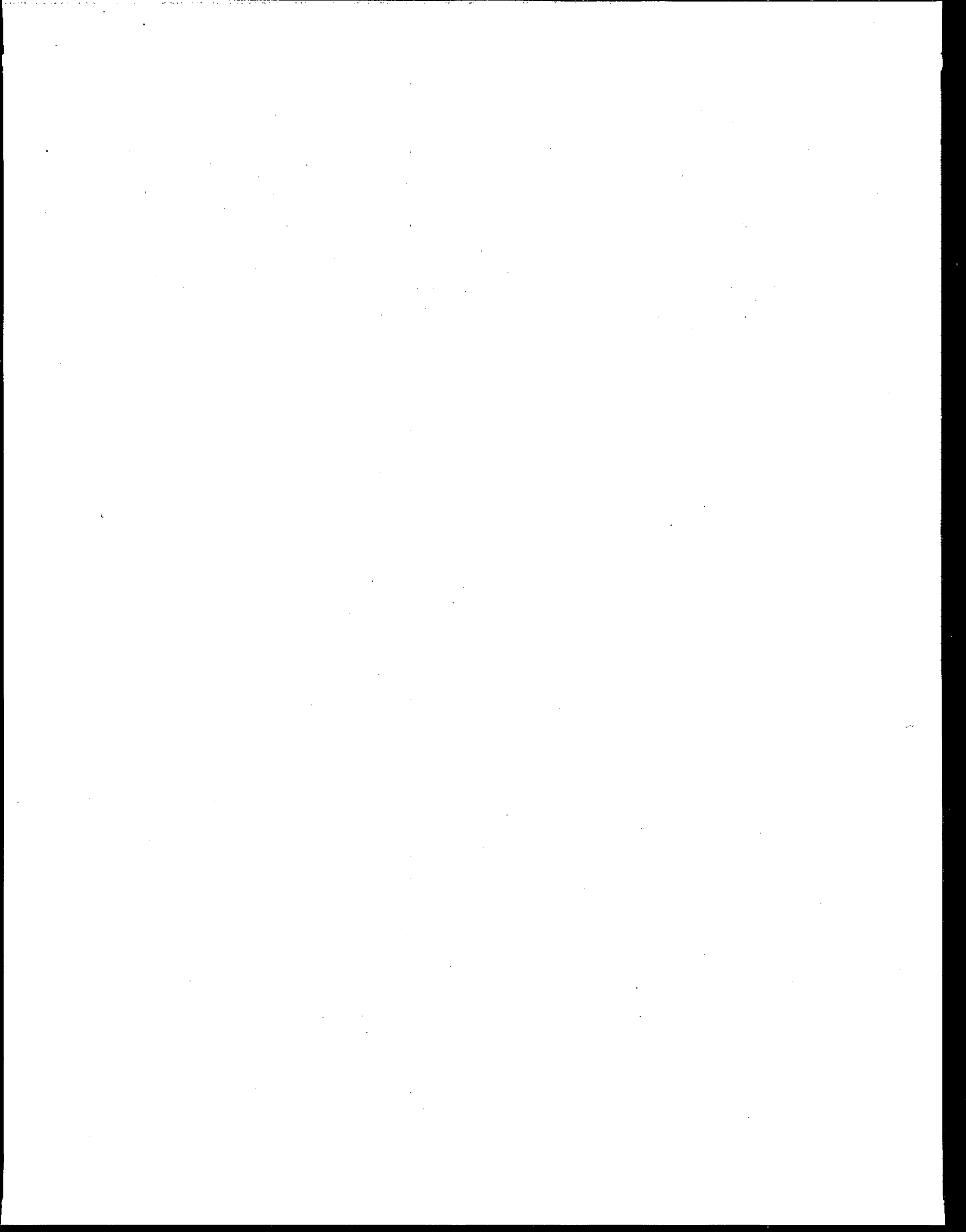*Table 5. NO$_x$ Control Levels—Waste Incineration* [a,b]

Control Technology	NO$_x$ Emission Limit (ng/J)
Combustion Controls	34-344
Boiler design	
Overfire air	
Post-combustion Control	
Selective catalytic reduction	< 21.5-43[c]
Selective non-catalytic reduction	32-146

[a] Refer to full report for facility-specific information.
[b] Commercial applications in U.S. and Japan.
[c] Japanese applications.

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