

AN OVERVIEW OF TECHNOLOGIES FOR REDUCTION OF OXIDES OF NITROGEN FROM COMBUSTION FURNACES

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Abstract

This overview examines the different technologies available for reducing NO_x emissions from combustion furnaces. For each of the general types of NO_x emission controls (combustion control and post-combustion control), the characteristics of the individual technologies are identified, including a description of the features impacting their selection and implementation. A range of the level of NO_x emissions control provided and the capital costs associated with implementing each individual technology are presented.

The implementation of NO_x control on a furnace should start with tuning the combustion process to achieve optimum firing conditions. The other controls required will depend on the specifics of the furnace design, the arrangement of the facility, and the extent of emissions control required. The specific NO_x control technologies applied should be tailored to the requirements of the furnace. The use of multiple NO_x control technologies may provide the most economical and timely control solution.

Background

Oxides of nitrogen (NO_x) emissions are a known precursor to formation of ozone and acid rain and can react with volatile organic compounds to form photo-chemical smog. Standards for the control of NO_x have been established as part of the Clean Air Act (40CFR60 Subpart D) starting in 1977. These standards, referred to as New Source Performance Standards (NSPS), were intended to promote the use of the air pollution control technologies in new generating units. New units located in non-attainment areas for NO_x emissions will be required to meet lowest achievable emission rates (LAER), a standard based on the capabilities of emissions control technology. New units located in attainment areas for NO_x emissions will be subject to Prevention of Significant Deterioration (PSD) rules and required to install the best available control technology (BACT), as defined by a project specific assessment taking into account the cost, health and environmental impact, and control technology energy requirements. These standards affect all types and sizes of stationary furnaces, excepting the smallest (< 10 million Btu/hr). The application of these standards to existing stationary sources depends on the application of the New Source Review (NSR) standards based on the extent of furnace modifications, a matter of current litigation by the Department of Justice and the federal Environmental Protection Agency (EPA).

Three other sources of NO_x emissions regulations have been enacted that affect combustion furnaces. Title IV to 1990 Clean Air Act Amendment (CAAA) specified a two phase approach for the reduction of NO_x emissions from existing electric utility furnaces. This program includes annual reductions in the emissions levels. The second source of controls on NO_x emissions results from the need to comply with federal ozone standards. In identified ozone non-

attainment areas, NO_x emissions controls regulations apply to furnaces based on state specific non-compliant regions. Finally, NO_x emissions controls for the existing stationary sources in the ozone transport region are being enacted via the NO_x SIP (State Implementation Plan) Call. Under this requirement, each state is required to provide EPA with a plan for controlling NO_x emissions to satisfy the state-wide emissions cap. A NO_x trading program is an integral part of this emissions control approach. The development of the NO_x SIPs for each state is an on-going process.

Tables 1 and 2 summarize the emissions limits specified under these various NO_x emission control regulations. The ozone non-attainment specifications in Table 2 are based on the regulations imposed by the State of Texas. These limits are typical of those enacted in other states. These regulatory limits have and continue to require furnace owners to select and implement NO_x control strategies on both new and existing furnaces. An understanding of the features and costs of the various NO_x reduction technologies available is important to continuing operation of stationary furnaces.

Table 1. New Source Performance Standards NO_x Emissions Limits

Fuel Type	NO _x Emissions Limits (lbs/MMBtu)		
	New Source Performance Standards (NSPS)		
	>250 MMBtu/hr (Electric Utility)	> 100 MMBtu/hr (Industrial)	10 MMBtu/hr to 100 MMBtu/hr
Gas from coal	0.20	n.a.	0.20 – 0.80
Other Gas	0.50	0.10 – 0.20	
Liquid from coal	0.50	n.a	
Liquid from shale oil	0.50	n.a	
Other liquid	0.30	0.10 – 0.20	
Distillate oil	0.30	0.10 – 0.20	
Residual oil	0.30	0.10 – 0.20	
Coal-derived	0.50	0.50 – 0.80	
Coal from SD, ND, or MT	0.80		
Subbituminous coal	0.50		
Bituminous coal	0.60		
Anthratic coal	0.50		
All other fuels	0.60	n.a	

Table 2. Clean Air Act Amendment and Ozone Attainment NO_x Emissions Limits

Furnace Type	Title IV Limits (lbs/MMBtu)	NO _x SIP Call (lbs/MMBtu)	Ozone Non-attainment Region Texas* (lbs/MMBtu)
Utility boilers: Wall fired	0.46	0.15	0.020 – 0.060
Tangentially fired	0.40	0.15	
Heaters and furnaces	n.a	0.15	0.025 – 0.036
Industrial boilers	n.a	0.15	0.020 – 0.089

*Latest TCEQ Proposal to EPA

A number of technologies for reducing NO_x emissions have been developed and are commercially available for stationary combustion sources such as steam boilers, process heaters, and other “fired” equipment. This paper provides information on the technical basis for selecting and utilizing the most common NO_x control technologies. In particular, it provides an overview of the features and costs of commonly available NO_x control techniques. The paper does not cover the many developmental NO_x control technologies. An appendix providing background on the mechanisms of NO_x formation is also included.

NO_x Control Approach

The control of NO_x emissions are generally achieved using two approaches:

- Combustion controls; and
- Post-combustion controls;

Combustion controls reduce the level of NO_x emissions by altering or modifying the firing conditions under which combustion is achieved. Each of the combustion control technologies are based on achieving have one or more of three primary objectives: 1) lower the flame temperature; 2) create a fuel rich condition at the maximum flame temperature; or 3) lower the residence time under which oxidizing conditions exist. The efficiency of the combustion process and CO emissions are often affected by the implementation of combustion controls. In general, combustion controls are the least cost approach for obtaining an initial reduction in the uncontrolled NO_x emissions on any stationary furnace.

Post-combustion controls reduce the level of NO_x emissions by converting the NO_x formed during combustion to nitrogen (N₂) gas. The chemical reactions required to convert the NO_x to N₂ are applied downstream of the combustion zone. These techniques introduce a reagent into the flue gas stream to selectively react with the NO_x. The reaction may be completed either with or without the use of a catalyst.

Often it is necessary to combine two or more combustion and post-combustion controls to achieve the desired level of NO_x reduction. The purpose of combining control techniques is to increase the overall NO_x reduction achieved and provide the most economic overall control for each installation. It should be noted that when used in combination, the effectiveness of multiple techniques is not additive. Each application must be evaluated to determine the most effective combination of technologies to achieve the desired result.

Combustion Controls

A summary of the combustion control technologies that have been demonstrated for combustion furnaces is provided in Table 3. The technologies are divided into two categories:

- Control Technologies: Approaches that provide substantial reductions in NO_x emissions
- Trim Technologies: Low cost approaches that provide only limited reductions.

The table lists the NO_x reduction achieved by each technology as a percentage of NO_x reduction prior to the implementation of the combustion control. The capital costs, both per ton of NO_x emissions removed and per kW of production, are also listed in Table 3. Each of the combustion control technologies is discussed separately below.

Table 3. Summary of Combustion Control Technologies

NO _x Emissions Control Technology	Application	NO _x Reduction (%)	Capital Cost	
			\$/Ton	\$/kW
Control Technologies				
Low NO _x Burners –Oil & Gas	Boilers/Process Heaters	40-60	125-250	2-4
Low NO _x Burners – Coal	Boilers	40-60	300-500	5-10
Over Fire Air (close coupled)	Boilers	30-50	200-450	4-7
Over Fire Air (separated)	Boilers	40-60	250-500	5-10
Reburn	Coal Fired Boilers	40-50	500-800	10-12
Induced Flue Gas Re-circulation (existing fan)	Boilers/Process Heaters (Internal)	30-40	200-300	3-5
Forced Flue Gas Re-circulation (additional fan)	Boilers	40-50	300-500	5-10
Water/Steam Injection	Boilers/Process Heaters	20-25	100-150	2-3
Trim Technologies				
Burners Out of Service	Boilers/Process Heaters	10-15	N/A	N/A
Fuel Biasing	Boilers/Process Heaters	10-20	N/A	N/A
Low Excess Air	Boilers/Process Heaters	5-15	N/A	N/A

The capital cost ranges shown in Table 3 represent industry average values. However, the capital costs will also vary depending on the specific type of fuel, the capacity of boiler or heater, and the physical layout of the furnace installation. In general, coal-fired furnaces have slightly higher costs for implementing combustion controls compared to gas-fired or oil-fired furnaces. As the size of the furnace increases, economies of scale are realized.

Low NO_x Burners

In this combustion control technology, fuel and air are staged across the burner. A specific installation design can stage these combustion components either separately or in combination. The staging in the low NO_x burner results in “fuel-lean” and “fuel-rich” combustion zones in the furnace. In the “fuel-lean” zones, the combustion temperature is lowered, reducing the production of NO_x emissions. Both the temperature and oxygen concentrations are lowered in the “fuel-rich” zones.

A modern low NO_x burner for oil/gas firing is shown in Figure 1.



Courtesy:
Todd Combustion

Figure 1. Modern Low NO_x Burner for Oil/Gas Fuels

With air staging, normally 75-85% of the air is supplied to the primary combustion zone along with all of the required fuel. This creates a “fuel-rich” flame zone where the formation of NO_x is retarded due to sub-stoichiometric (i.e. lack of oxygen to achieve complete combustion of the hydrocarbons in the fuel) combustion conditions. The sub-stoichiometric conditions limit NO_x formation by reducing the combustion temperature and limiting the amount of oxygen available for NO_x production. The remainder of the air is injected outside the primary combustion zone to complete the combustion of the fuel. Low NO_x burners relying on staged air typically achieve NO_x reductions of 40–50 % in gas-fired furnaces and 30-40% for oil-fired and coal-fired furnaces.

A low NO_x burner designed for fuel staging works the opposite of air staging. In the primary combustion zone, about 60-70 % of the fuel is injected with all of the air. Although excess oxygen is available, NO_x formation is retarded due to the low combustion temperature. The remainder of the fuel is injected downstream of the primary combustion zone. Prompt NO_x formation (see Appendix) is also reduced due to the highly oxidizing conditions across the burner. Staged fuel can reduce NO_x formation by up to 60% for gas-fired boilers and heaters. Fuel staged low NO_x burner applied to coal or oil-fired furnaces requires the use of Reburn technology, (see discussion on Reburn technology below).

For oil-fired and gas-fired furnaces, the existing burners can often be converted in-place to a Low NO_x burner design. The capital cost for this conversion is in the range of \$50 - \$100 per ton per year of NO_x reduced, or in terms of cost per kW, \$1-2. Implementing low NO_x burners on a coal-fired furnace requires replacement of the burners..

Contemporary low NO_x burners can safely operate with NO_x emissions as low as 30 - 50 ppmv. “Ultra-low NO_x” burners, offered by a number of vendors, can achieve NO_x emissions of less

than 10 ppmv in certain gas-fired applications. Ultra-low NO_x burners generally pre-mix significant amounts of fuel and air, prior to injection into the furnace combustion zone. Extreme care must be exercised when operating ultra low NO_x burners to avoid hazardous operating conditions and the tolerance on operating limits to achieve the design NO_x emissions are very tight. Cost and performance data for ultra-low NO_x burners are not presented herein.

Over Fire Air (OFA)

In this technique a controlled portion of the total combustion-air flow, typically 10-20%, is directed through over-fire ports located above the highest elevation of burners in the furnace. The removal of the air flow from the burners results in a fuel rich primary combustion zone to limit the NO_x formation. The combustion of the CO produced in the primary combustion zone is completed using the air supplied by the over-fire air ports. In most cases, new furnace penetrations are required to implement an over-fire air system in an existing furnace.

Two types of over-fire air systems can be used to accomplish NO_x emission reductions; close-coupled over-fire air (COFA) and separated over-fire air (SOFA) systems. COFA systems are typically implemented by adding air injectors immediately above the existing furnace burners. Overfire air is supplied from the top of the existing windbox. As shown in Figure 2, the over-fire air ports are located immediately above the primary combustion zone. This approach minimizes the changes required to implement the over-fire-air system. However, the approach limits the time available to complete initial combustion prior to the introduction of the OFA and will result in NO_x reductions of 30 to 50%.

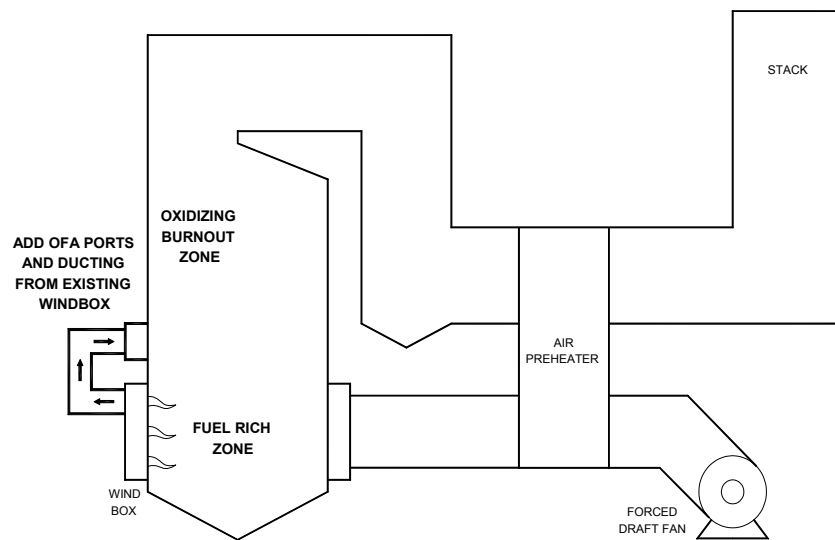


Figure 2. Close-coupled Over-fire Air System (COFA)

Higher NO_x reductions will be achieved by increasing the separation of the over-fire air ports from the primary combustion zone and increasing the air velocity through the ports. This technique, known as SOFA, is illustrated in Figure 3. NO_x reductions of 40 to 60 % may be

achieved with this arrangement. In some cases, an effective SOFA system requires the addition of a fan to provide sufficient mixing velocity to the over-fire air.

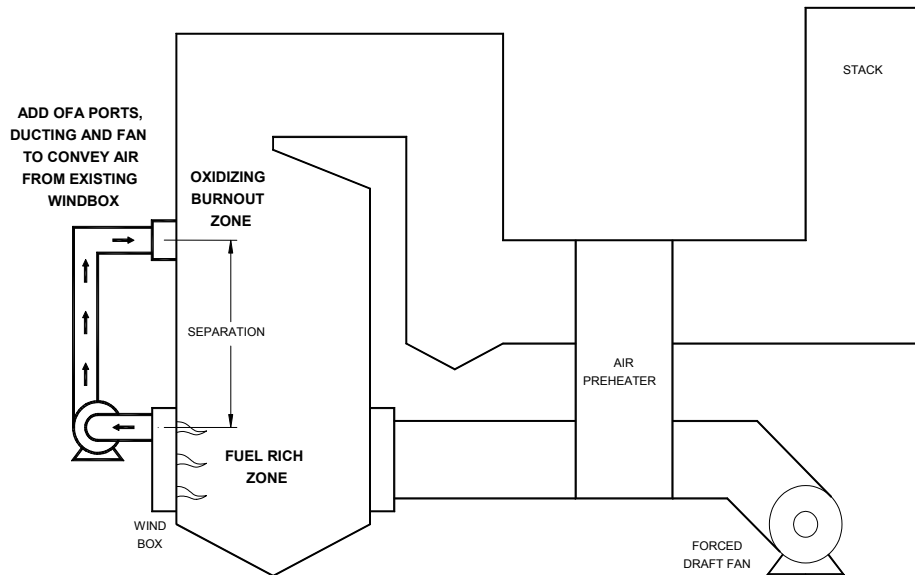


Figure 3. Separated Over Fire Air System (SOFA)

The effectiveness of over-fire air systems depends on adequate mixing of the injected air with the primary combustion products. The port location, number, spacing, geometry, pressure drop and furnace dimensions all must be considered in designing the over-fire air system. The installed forced draft fan capacity and effect on structural integrity of the furnace walls are also important considerations when designing an over-fire air installation.

Over-fire air systems may cause increases in CO emissions and will change the temperature distribution in the furnace section. As with other combustion control techniques, the design of the system must balance the required NO_x control with the existing design of the furnace heat transfer surfaces and the residence time in the furnace for complete combustion. Typically, computational fluid dynamic (CFD) modeling is used in combination with field data to optimize the over-fire air port location and sizing. Overall furnace heat transfer modeling is also required to evaluate the impact of specific port locations on the furnace heat transfer performance.

Reburn

Reburn was developed as a NO_x combustion control technique primarily for use on coal-fired furnaces. This technique involves splitting the combustion zone by installing a second level of burners above the primary combustion zone. Typically up to 25% of the total heat input is injected into this “Reburn” zone to create a fuel rich condition in the primary combustion zone. In the reburn zone, NO_x formed in the combustion zone is partially reduced to elemental

nitrogen. The formation of additional NO_x is limited due to the lower oxygen concentrations and lower combustion temperature in the reburn zone.

Most installations employing reburn for NO_x control have used natural gas as the reburn fuel above a coal-fired combustion zone, as shown in Figure 4. However, micronized coal has also been used as the reburn fuel. Reburn combustion control requires significant changes to the design of the furnace and the additional operating expense of the reburn fuel. It offers the potential advantage of improved unburned carbon, also known as loss of ignition (LOI), and CO emission control.

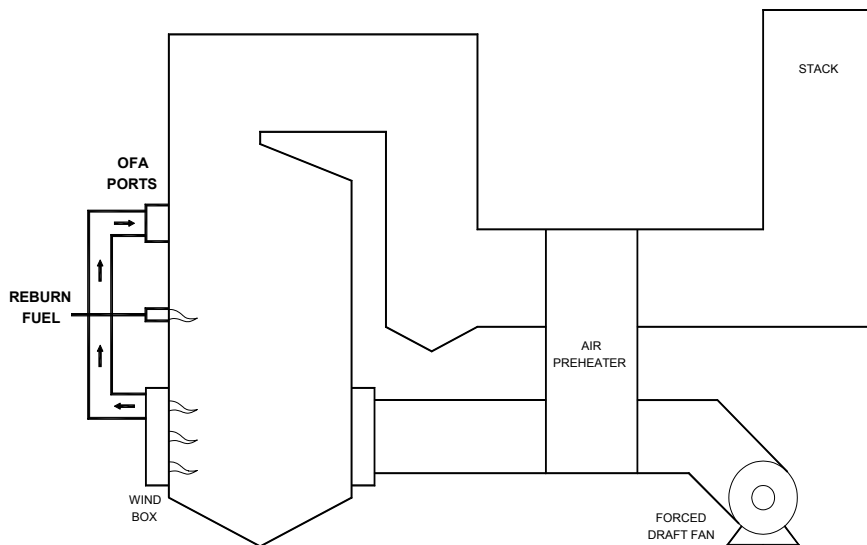


Figure 4. Natural Gas Reburn System

As shown in Figure 4, over-fire air ports are installed above the reburn zone to provide for complete combustion.

Flue Gas Re-circulation (FGR)

This method of combustion control uses flue gas recycled from the stack and mixed with combustion air to reduce the oxygen content of the combustion air and cool the flame. The target percentage of the total combustion air flow to be replaced with recirculated flue gas is typically 10-15%. This control technique has been used with gas-fired and oil-fired furnaces.

Figure 5 illustrates a common scheme for flue gas recirculation for NO_x emissions control. A flue gas recirculation fan is used to transport the recirculated flue gas to the furnace windbox from the stack. The recirculation fan provides sufficient pressure to ensure adequate mixing of the flue gas with the combustion air in the windbox prior to reaching the burners.

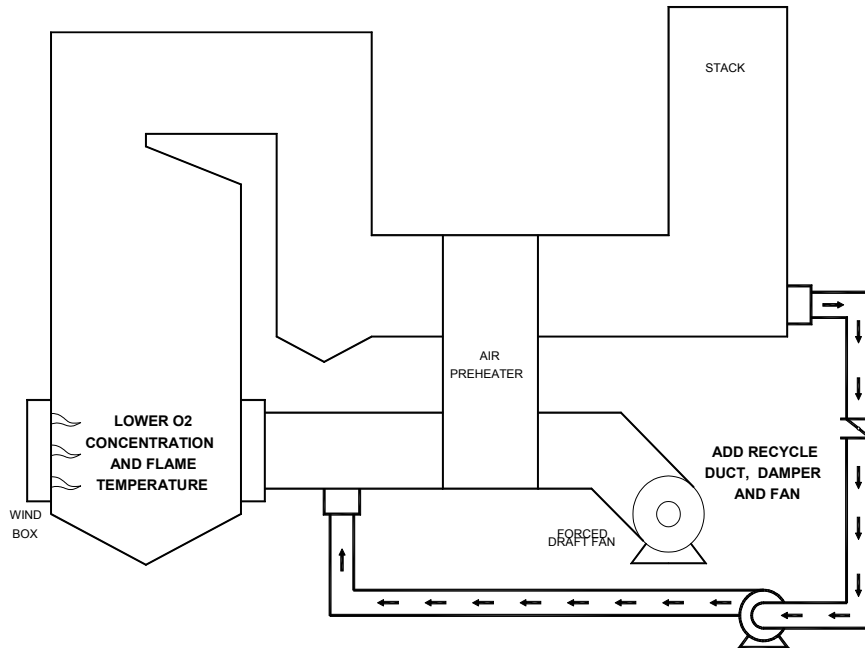


Figure 5. Flue Gas Recirculation

Induced Flue Gas Recirculation (IFGR), illustrated in Figure 6, is an increasingly popular means for transporting recirculated flue gas. This technique utilizes any spare capacity in the existing forced draft air fan to transport the flue gas into the combustion air duct. This eliminates the need for an additional fan. The flue gas recirculation duct runs from the stack to the inlet of the forced draft fan and flue gas recirculation flow rate is controlled by means of a damper.

Another variation of this concept which is applicable to gas-fired furnaces, introduces the flue gas directly into the combustion flame zone to enhance the cooling effect. This approach requires that a separate flue gas ductwork be routed to the burner front. The flue gas can be transported either using a flue gas recirculation fan or an eductor operated with fuel flow. The mixture of fuel and FGR is then burned in specially sized gas tips. This method creates a low BTU fuel that burns “cooler” than fuel not mixed with flue gas, which minimizes NO_x formation.

Burners Out of Service (BOOS)

Burners out of service is a simple technique to achieve NO_x reductions of around 15% in multiple burner level furnaces with multiple levels of burners. In this technique fuel flow is isolated from selected burners and only air passes through the burners, as depicted in Figure 7. The balance of the fuel required to maintain the unit firing rate is redirected to other burners. This technique provides for air and fuel staging in the combustion zone. Depending on the capacity margins in the existing burner design, a slight furnace de-rate penalty may result. The specific capacity of the pulverizers will also affect the implementation of this technique in coal-fired furnaces.

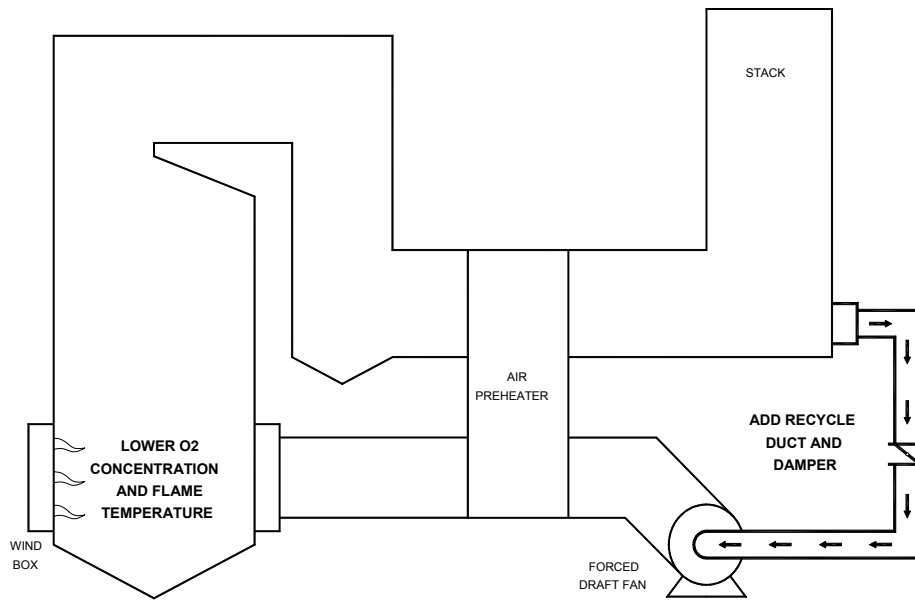


Figure 6. Induced Flue Gas Recirculation

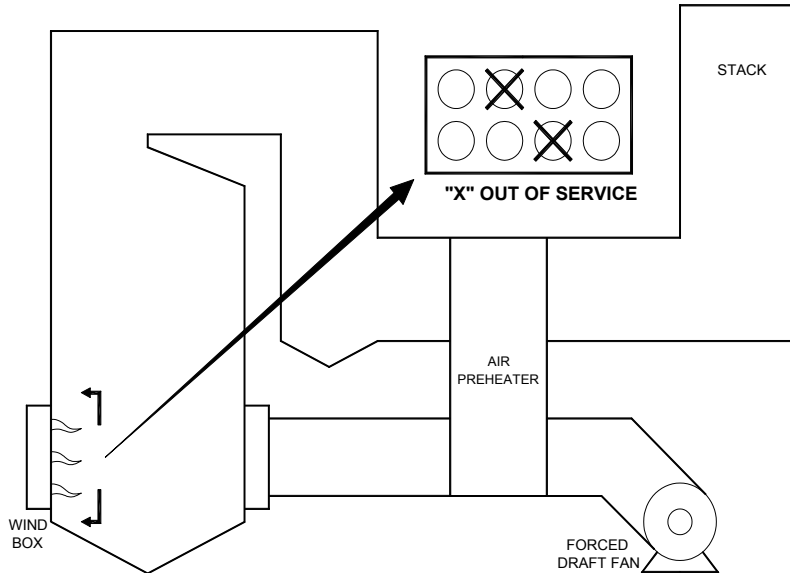


Figure 7. Burners Out of Service (BOOS)

This technique has been applied successfully on many industrial and utility boilers in the US. Higher CO emissions and O₂ imbalances may result from this technique. These conditions can be minimized by appropriate selection of the burners removed from service.

Fuel Biasing

Fuel biasing is another relatively simple combustion control technique for achieving modest NO_x reductions. In this technique, the furnace is divided into upper and lower combustion zones. The lower zone is operated fuel-rich to reduce the NO_x formation. The upper zone is operated fuel-lean to complete CO burnout. The total quantity of fuel supplied to the boiler remains the same as before fuel biasing. The specific amount of fuel supplied to the upper burners depends on the unit load with more effective biasing possible at lower loads. The extent of the fuel biasing that can be implemented depends on the design of the burners and in coal-fire units the capacity of the pulverizers.

NO_x reductions of up to 20% may be achieved with fuel biasing.

Low Excess Air

Low excess air is a combustion control strategy used to improve furnace combustion efficiency that will also contribute to NO_x reductions. The reduction in combustion zone oxygen that results from reducing the excess air will cause an appreciable reduction in the NO_x emissions. The objective is to operate the furnace at the lowest excess air level that provides safe, efficient, and complete combustion. The effectiveness of the furnace heat transfer surfaces will also be impacted affected by minimizing the excess air since this reduces the total flue gas flow.

Low excess air is essentially a burner optimization strategy that should be part of normal furnace operation. However, it may require process control tuning and combustion testing to identify the optimal operating point given the current fuel characteristics and furnace condition. No significant capital outlays for new or modified hardware are required to implement this combustion control technology.

Combustion Tempering

Combustion tempering, which utilizes the injection of water or steam injection into the combustion zone to reduce the firing temperature, has been traditionally associated with minimizing NO_x emissions from combustion turbines. However, this combustion control technology has also been applied to furnaces. Adding water or steam in the combustion zone can suppress NO_x formation by up to 25%. Water injection in a furnace is depicted in Figure 8.

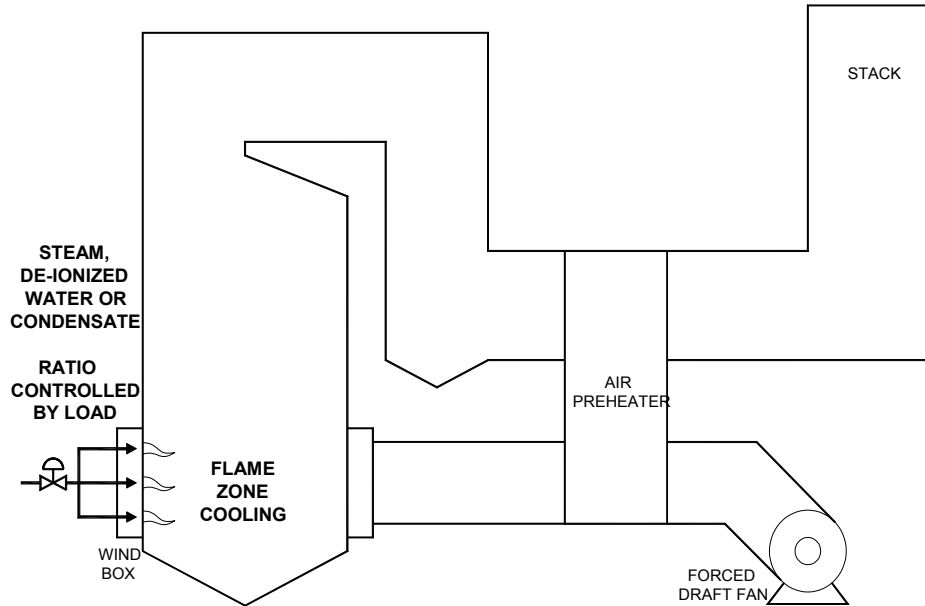


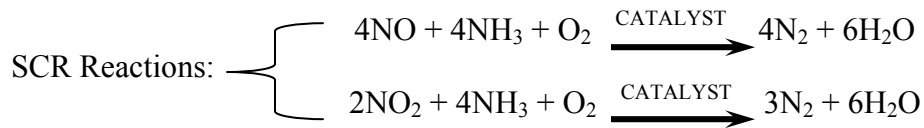
Figure 8. Water Injection (Combustion Tempering)

Successful implementation of water/steam injection requires properly injecting the fluid into the combustion zone. The size and velocity of the droplets determines where in the combustion zone the temperature is affected. This normally requires targeting the highest temperature areas of the combustion zone based on predictions from computational fluid dynamics (CFD) modeling of the burner flame. This method is somewhat effective in oil-fired and coal-fired furnaces but has been applied more effectively in gas-fired furnaces.

The implementation of water/steam injection to control NO_x emissions has several significant disadvantages. Carbon monoxide and un-burned hydrocarbons increase, especially at low loads. Fuel consumption increases by as much as 5% to make up for the heat of vaporization of the water. If steam injection is utilized, about 50% higher mass rate is required compared to water injection and there is the inherent loss of energy required to produce the steam. Additionally, water that has been extensively treated is lost out the stack.

Post Combustion Control

Post combustion technologies for the reduction of NO_x are: (1) selective non-catalytic reduction (SNCR) and (2) selective catalytic reduction (SCR). Each of these technologies requires the introduction of a reagent, such as ammonia or urea that will “selectively” react with NO_x. This reaction occurs in the presence of oxygen. The following simplified chemistry summarizes the reactions involved in the post combustion controls to convert NO_x to elemental nitrogen:



It should be noted that the reactions for the SNCR process and the SCR process are very similar. However, there are significant differences in the flue gas temperatures and technologies to implement each of these post combustion control technologies.

Most furnaces using post combustion technologies to control NO_x emission use urea or ammonia in an aqueous solution of less than 20%. This complicates the design of the delivery system for the reagent but minimizes the safety issues involved with permitting, storing, and handling the reagent. When urea is used, it is broken down as part of the flue gas reactions to produce the ammonia necessary to complete the reaction.

Table 4 provides a summary of the effectiveness and relative costs for these technologies. The table lists the NO_x reduction achieved by each technology as a percentage of the NO_x prior to the implementation of the combustion control. The capital costs, both per ton of NO_x emissions removed and per kW of furnace production, are also listed in Table 4. Each of these post combustion control technologies is discussed separately below.

Table 4. Summary of Post-Combustion Control Technologies

Control Technology	Application	NO _x Reduction (%)	Capital Cost	
			(\$/Ton)	(\$/kW)
SNCR	Boilers/Process Heaters	40-60	500 - 1000	10 - 20
SCR	Boilers/Process Heaters	80 - 90	1000 – 10,000	20 - 200

The capital cost ranges shown in Table 4 represent industry average values. However, the capital costs will also vary depending on the specific type of fuel, the capacity of the boiler or heater, and the physical layout of the stationary furnace installation. In general, coal-fired furnaces have slightly higher costs for implementing post combustion controls compared to gas-fired or oil-fired furnaces. As the size of the furnace increases, economies of scale are realized.

Selective Non-Catalytic Reduction (SNCR)

Selective non-catalytic reduction involves the injection of the reagent into a region where the gas temperature is in the range of 1500 to 2100°F. As shown in Figure 9, the specific temperature window is important. At lower flue gas temperatures, the reaction rate will decrease resulting in higher levels of NO_x and increased ammonia slip (un-reacted ammonia). At higher flue gas temperatures, not only will the effectiveness of the reagent reaction with NO_x be diminished but increased NO_x levels may occur due to the oxidation of the reagent.

The objective of the system is to deliver the required reagent in the temperature window described as the plateau in Figure 9 with sufficient residence time for the required reaction to occur. The minimum residence time required is one second. The required temperature window and residence time are typically available in the upper and backpass sections of the furnace. In order for the reagent to reach the temperature window available in a typical furnace design, the injection of the reagent must precede the plateau temperature range to achieve the desired reduction. The design of the reagent injector and the specific injection locations are therefore an important part of the SNCR system design. The time for any carrying medium to vaporize and the breakdown of urea to occur are important considerations in design of the system.

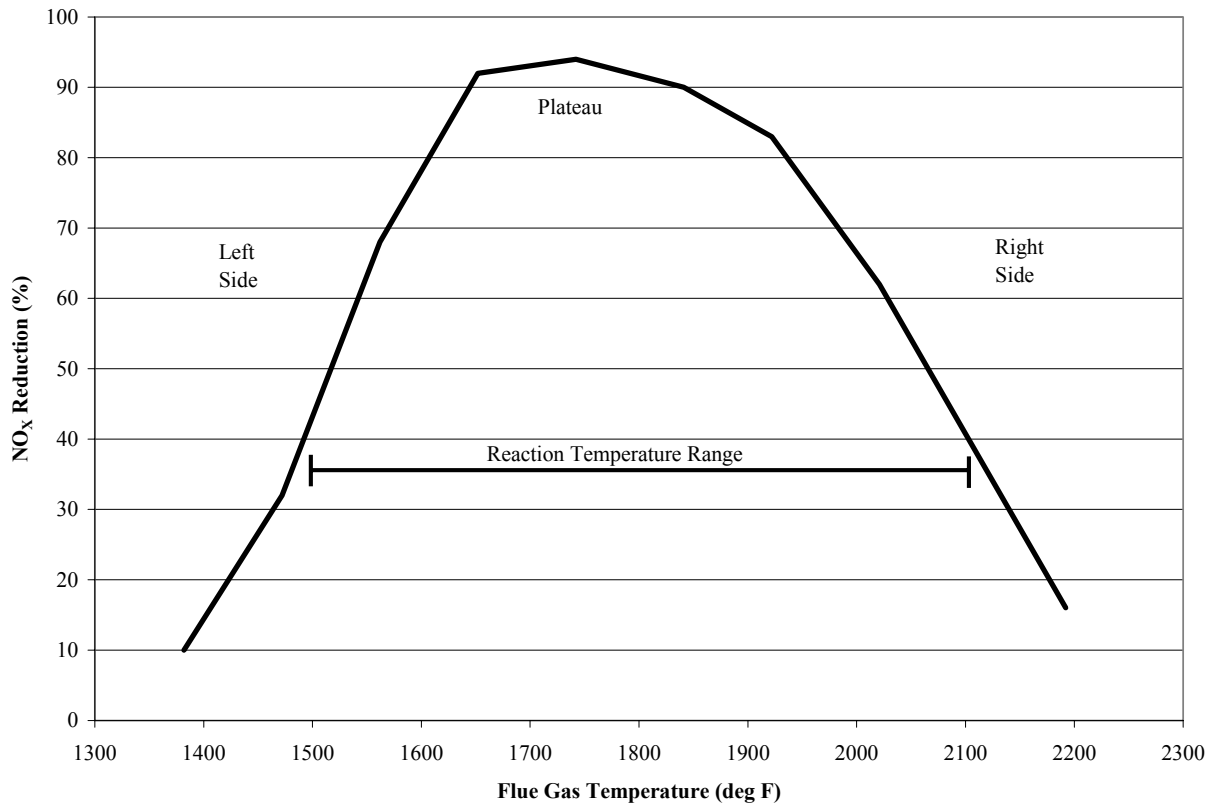


Figure 9. Typical SNCR Operating Curve

The required ratio of reagent to NO_x are typically in the range of 2:1 at a minimum and 4:1 at a maximum on a mole to mole basis. The specific ratio depends on the temperature and acceptable reagent slip. The curve shown in Figure 9 is for a 2:1 reagent ratio.

Complete coverage of the flue gas in the furnace requires that multiple injection nozzles be used in the SNCR design. Multiple injection ports can be provided either by install multiple injectors or using retractable lances with multiple nozzles. The optimal distribution of the reagent is to match the distribution of the NO_x produced during combustion. The non-uniform nature of the NO_x distribution places a premium on flexibility in the injector design used with an SNCR system. To maximize NO_x reduction and minimize reagent slip, it is often necessary to vary the injection rate to each nozzle location as boiler load changes.

Figure 10 describes the arrangement of a typical SNCR system. The system includes provisions to mix the reagent and the carrying medium, usually water or compressed air. The specific droplet size and dispersion pattern from the injector will depend on the type and pressure of the carrying medium used. As previously discussed, the reagent may or may not be vaporized in an SNCR system. The temperature of the flue gas is typically sufficient to vaporize the reagent in the furnace.

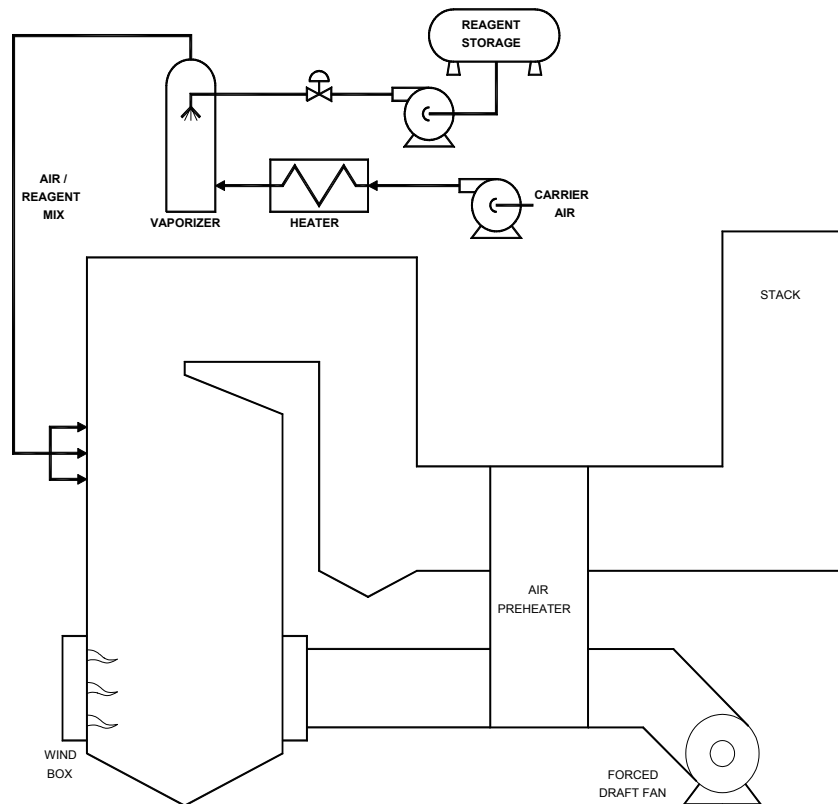


Figure 10. Selective Non-Catalytic Reduction

An emerging technology that is a unique application of SNCR is rich reagent injection (RRI). This technology involves the injection of the reagent into a region where the flue gas is fuel rich (i.e., no excess oxygen) and the temperature is in the range of 2400 to 3000°F. The objective of the system is to deliver the required reagent to the fuel rich zones in the temperature window with sufficient residence time for the required reaction to occur. The system is used with an over-fire air system to produce the required fuel rich combustion zone. The combustion process is completed in a burnout zone located sufficiently downstream of the fuel rich combustion zone to allow the reactions to be complete. Figure 11 illustrates the arrangement of the RRI system in a typical furnace. The reagent handling system required is similar to the system shown for the SNCR system in Figure 10.

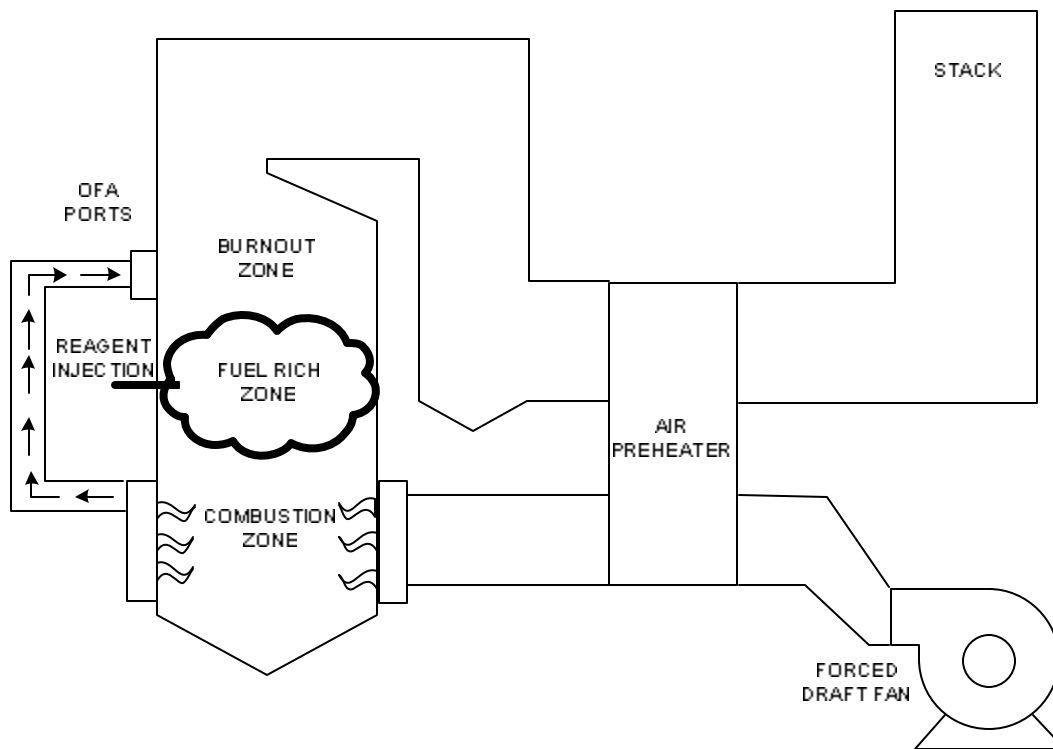


Figure 11. Rich Reagent Injection

The theoretical efficiency of the RRI process of greater than 90% can not be achieved in practical applications due to the complexity and non-uniformity of the combustion zone in a typical furnace. In typical field installations, RRI has demonstrated the capability to reduce NO_x emissions up to 60 % from the levels produced with over-fire air alone. However, significant production of NO_x will occur if the reagent is introduced into an oxygenated area of the combustion zone. Further, the high temperatures make distribution of the reagent to all fuel rich zones difficult. Finally, the high temperature, high corrosive environment of the fuel rich zone makes reliable injector design difficult.

It should be noted that any use of RRI must be combined with over-fire air to maintain a reliable fuel rich combustion zone. The cost is somewhat higher than SNCR, due to the added cost for the over-fire air. This approach has advantages for the more difficult coal fired applications.

Selective Catalytic Reduction (SCR)

Selective catalytic reduction technology is based on a selective reaction between the reagent and NO_x on the surface of a catalyst. These reactions occur at much lower flue gas temperatures than either the RRI or SNCR technology reactions. However, the specific temperature range for the catalytic reaction depends on the type of catalyst used. Most SCR catalysts are a blend of titanium oxide and vanadium oxide. Noble metal blends of platinum and palladium have also been developed as catalysts but are more expensive. Typical reagents are urea and ammonia. The ratio of reagent to NO_x is 1.5:1 on a molar basis.

There are three types of catalyst design, which are differentiated by the temperature at which the reaction occurs: (1) Low Temperature, (2) Conventional, and (3) High Temperature. The temperature range for conventional SCR catalyst is 650 - 850°F. Low temperature catalysts operate in the range of 350 - 500°F. High temperature catalysts operate in the range of 850 - 1200°F. Low temperature catalysts are normally located between the air pre-heater and the stack. High temperature catalysts are primarily used for combustion turbine applications and are not applicable to stationary furnaces.

A typical conventional SCR system is depicted in Figure 12. Conventional catalyst systems are located between the convection section and the air preheater in typical furnace applications. Due to the lower flue gas temperatures, the use of a vaporizer is required to distribute the reagent in the flue gas. A grid of injection nozzles in the flue gas is used to achieve the required reagent distribution. The size of the SCR catalyst is controlled by the residence time requirements for the reduction reactions. Typically a vessel similar in size to the volume of the furnace is required to reduce the flue gas velocity sufficiently for the required residence time.

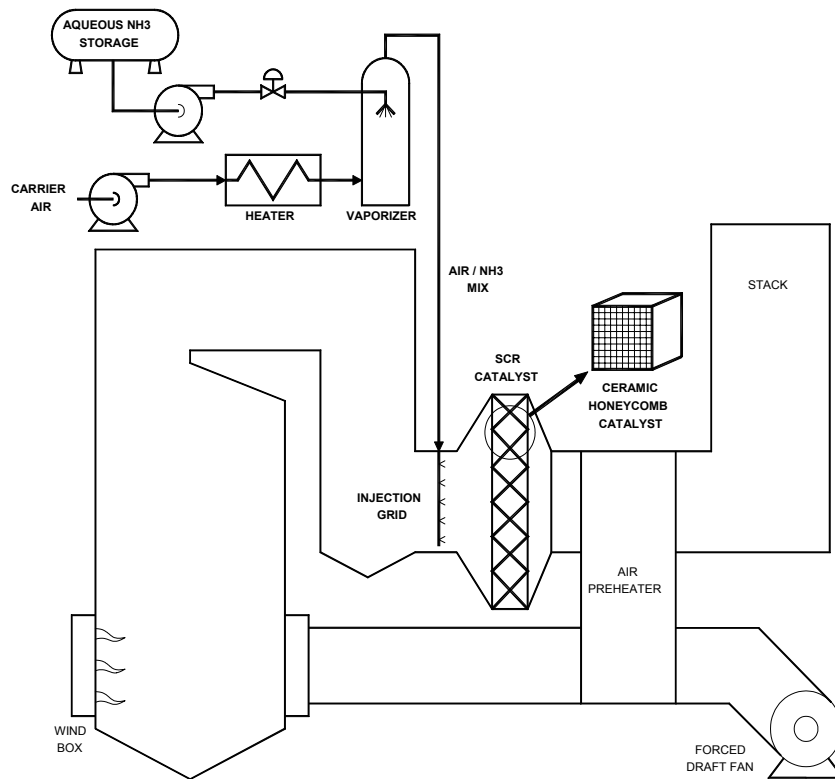


Figure 12. Selective Catalytic Reduction (SCR)

The surface of the catalyst included in a SCR system must be kept clean to maintain its effectiveness. This typically requires the installation of a washing or sootblowing system as part of the SCR installation. The catalyst must also be protected from poisoning by constituents in the flue gas. For example, the arsenic present in trace amounts in much of the coal burned in the

United States has complicated the application of SCR systems to control NO_x emissions. When the catalyst is out of service, special humidity and temperature controls are also required to maintain the catalyst effectiveness. Periodic replacement of the catalyst is also required. This significantly increases the operating cost for a typical SCR.

The presence of sulfur in the flue gas can promote the formation of ammonium bisulfate. This requires the use of additional reagent. In addition the ammonium bisulfate will condense and foul heat transfer surfaces downstream of the catalyst. The catalyst will also increase the oxidation of SO₂ to SO₃. Increased SO₃ concentrations have resulted in sulfuric acid stack plumes at some SCR installations. In some cases, this has required the installation of additional controls to eliminate the stack plume.

Combining Control Technologies

In the past, standards for NO_x emissions control have allowed furnace operators to effectively utilize the NO_x technologies discussed above on an individual basis. However, with the exception of SCR Systems, individual NO_x control techniques can not provide the NO_x reductions required to meet current and emerging emission limits. This has led furnace operators to pursue the implementation of multiple control technologies. For individual furnaces implementation of multiple NO_x combustion control techniques can provide reduction levels of up to 65-70%..

The effectiveness of multiple combustion control techniques is not directly additive. For example, if LNB and OFA are used together on a coal fired boiler, the total reduction in NO_x would be 60 to 65%, not the 70% or greater reduction which would be predicted by the simple addition of the reduction achievable by each technique on its own. This is because the combustion control techniques are essentially targeting the same sources of NO_x formation. In practice, combined combustion control techniques can achieve NO_x reductions of up to 65 – 70%.

Combining combustion with post combustion control technologies such as SNCR has the potential to provide reductions equal to the 90% reduction levels achievable with the SCR process alone. Combining control technologies has several advantages over stand-alone SCR installations, including the ability to install the NO_x controls in phases consistent with the regulatory requirements.

Even in the case of SCR technology, the application of additional NO_x control techniques can have significant benefits. For example, implementation of combustion control techniques with the SCR can significantly reduce the size and operating costs for the SCR. This is possible since the extent of the reduction required from the SCR is reduced by the use of the combustion control technologies. Similarly, the combination of SNCR and SCR technologies, known as Hybrid NO_x Controls, has been shown to provide benefits in reducing the cost and size of the NO_x controls. Hybrid NO_x technology can achieve NO_x reductions in excess of 95% with minimum ammonia slip.

Due to the fact that SCRs require large volumes of catalyst, reducing the size of any SCR installation is a significant issue for most furnace retrofit. Usually the available space for the addition of emissions control equipment is limited and there may be a need at some installations to add emissions control equipment to control other pollutants. This further illustrates advantage of combining technologies to minimize the size of the SCR installation to allow for future changes.

Conclusions

The increasing requirements for reduction on NO_x emissions from combustion furnaces require the development of a control strategy to identify the most effective approach for each installation. The characteristics of the furnace design, unit operating practices, and presence of any existing NO_x controls should be considered in determining the most cost-effective solution. The challenge, however, is not solely reducing NO_x levels, but achieving the necessary emissions control while maintaining unit performance and safety.

The following guidelines should be considered when selecting NO_x emissions controls:

- Significant NO_x reductions can be achieved by tuning (burners and process controls) the combustion process. This should be the starting point for any NO_x reduction program. It also has the added benefits of increasing combustion efficiencies and enhancing any of the combustion modification approaches that may be applied.
- The specific requirements and schedule for the implementation of NO_x emissions controls for the specific furnace should be identified. A phased approach, including the use of NO_x emissions credits to mitigate the implementation schedule, can provide an economical NO_x emissions control approach.
- The effectiveness of combining lower cost combustion controls with post combustion controls should be evaluated as an overall control strategy to achieve the desired NO_x reduction at the lowest cost.
- Available plant area should be evaluated to determine the feasibility of installing equipment necessary to address all emissions control requirements (including sulfur oxides, particulates, and Mercury) prior to selecting a specific NO_x control approach.

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APPENDIX A FORMATION OF OXIDES OF NITROGEN IN STATIONARY FURNACES

At the flue gas temperatures encountered during combustion in stationary furnaces, typically 2800° F to 3600° F, virtually all of the NO_x formed exists as NO, nitrogen oxide. This NO is formed by one of three mechanisms:

- Thermal NO_x: result of high temperature dissociation and chain reaction of elemental nitrogen and oxygen from the air during combustion. Thermal NO_x is formed in the flame envelope.
- Prompt NO_x: a reaction of free radicals in a fuel rich flame zone. Prompt NO_x is formed in specific fuel rich areas of the flame envelope.
- Fuel NO_x: oxidation of nitrogen compounds chemically bound in liquid and solid fuels or as a separate component in gaseous fuels. Fuel NO_x may be formed when fuel bound nitrogen is in an oxidizing environment at temperatures above 1800°F. These conditions may exist throughout the furnace.

Figure A-1 shows the equilibrium versus actual NO concentrations for both Thermal NO_x and Prompt NO_x reactions. The equivalence ratio is the ratio of fuel to air in the combustion process. An equivalence ratio of one represents stoichiometric combustion conditions. An equivalence ratio less than one indicates that the combustion occurs under oxidizing conditions. An equivalence ratio greater than one indicates reducing conditions for the combustion. The lines plotted on Figure A-1 indicate the NO_x concentration for both equilibrium and experimental measurement at a combustion temperature of 3002° F.

The experimental data shows that equilibrium conversions of NO_x are not achieved under oxidizing conditions. Conversely, under reducing (slightly fuel rich) conditions, conversions of elemental nitrogen to NO_x approach equilibrium. At high equivalence ratios, the experimental conversion exceeds the equilibrium conversion. In the experimental methane combustion process, a combination of thermal and prompt mechanisms occurs during combustion. This accounts for the fact that equilibrium conversions are exceeded in the high equivalence ratio cases. It also illustrates that Thermal NO_x conversion is rate limited and Prompt NO_x conversion is equilibrium limited.

Based on equilibrium considerations, Thermal NO_x from the dissociation of elemental nitrogen and subsequent reaction with oxygen could reach levels as high as 3,000 to 4,000 ppmv. In furnace combustion, concentrations this high are not achieved. Typically the “uncontrolled” levels of Thermal NO_x are in the range of 100 to 200 ppmv. The Thermal NO_x conversion does not approach equilibrium due to limited reaction time in the furnace at the elevated temperatures. The rate of Thermal NO_x formation is also dependent on the concentration of oxygen available at the high temperature conditions.

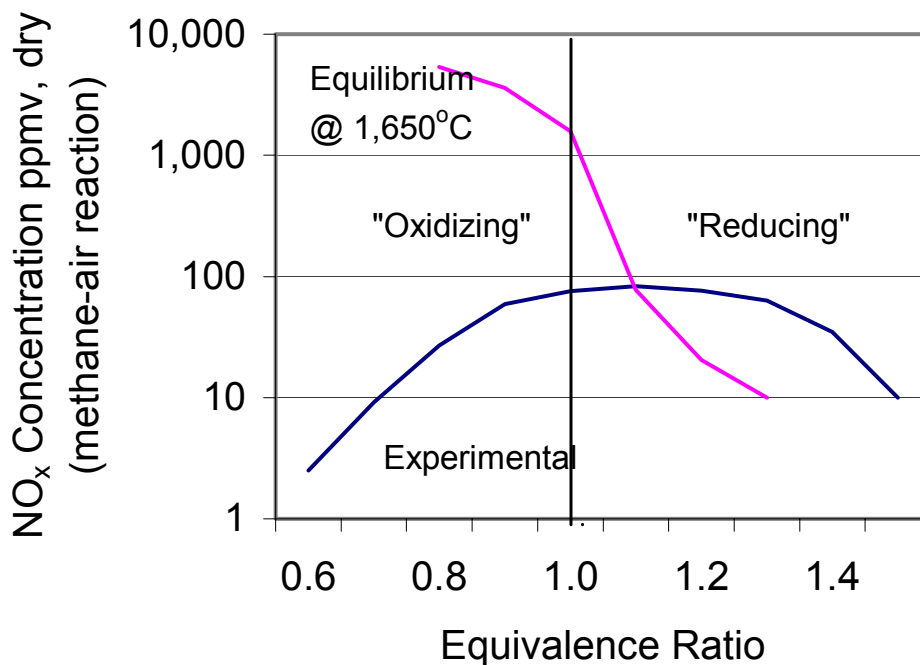


Figure A-1. Experimental vs. Equilibrium NO_x Formation of Methane-Air Combustion

Under the necessary conditions (excess fuel and high temperature), the concentrations of Prompt NO_x can be as high as those achieved from either Thermal NO_x or Fuel NO_x. However, this reaction occurs under partially fuel rich conditions where nitrogen is first decomposed by a hydrocarbon radical (CH) to form hydrogen cyanide (HCN). HCN reacts with oxygen-containing hydroxo- (OH-) radicals to form NO_x. Equilibrium considerations lead to the conclusion that the Prompt NO_x mechanism is not rate limited, since it is not unusual to achieve concentrations that are 60 to 80 percent of equilibrium conversions.

The formation of Fuel NO_x depends on the concentration of chemically bound nitrogen in the fuel and the local concentration of oxygen in the combustion zone. Formation of Fuel NO_x can occur at temperatures as low as 1800° F. Under oxidizing conditions, the extent of Fuel NO_x formation is a primarily a function of the bound nitrogen concentration in the fuel. Depending on the temperature and oxygen concentration, up to one-third of the bound nitrogen in the fuel will be converted to NO_x.

Each of these three mechanisms affects the overall formation of NO_x in the furnace. The type of fuel, the type of burner(s) and the conditions in the combustion zone each influence the uncontrolled NO_x concentrations. Table A-1 summarizes uncontrolled NO_x concentrations for typical stationary furnace designs.

Table A-1. Typical Furnace Uncontrolled NO_x Emissions

Fuel	Nitrogen in Fuel (%)	Uncontrolled NO_x (ppm)
Natural Gas	0	150 - 200
Fuel Oil - No. 6	0.9	250 - 300
- No. 2	0.2	100 - 150
Bituminous Coal	1.2 to 2.0	400 - 800
Subbituminous Coal	1.0 to 1.3	300 - 800

The uncontrolled NO_x concentrations reported in Table A-1 were all reported for combustion with 3.0% excess oxygen for the combustion process.

For all fuels, Thermal NO_x is the most important factor in determining the total NO_x concentration. Furnace volume and excess oxygen greatly affect the concentration of Thermal NO_x produced. Small furnace volumes require increased burner zone heat release, which will increase the Thermal NO_x formation for a given fuel.