nitrogen concentrations. Once HCN is formed, it decays back through NH_3 to NO and N_2 by the global sequence shown in Fig. 6.4.

The detection of HCN, NH_3 and NO_2 reveals that the Zel'dovich mechanism cannot quantitatively predict total NO concentrations in swirling, natural gas diffusion flames. Despite the complexity of the chemistry, the Zel'dovich mechanism appears to be the major contribution to NO_x concentrations for this case. However, the formation of HCN in the fuel-lean zone confirms that it is impossible to completely avoid prompt NO formation and NO decay in gaseous hydrocarbon diffusion flames.

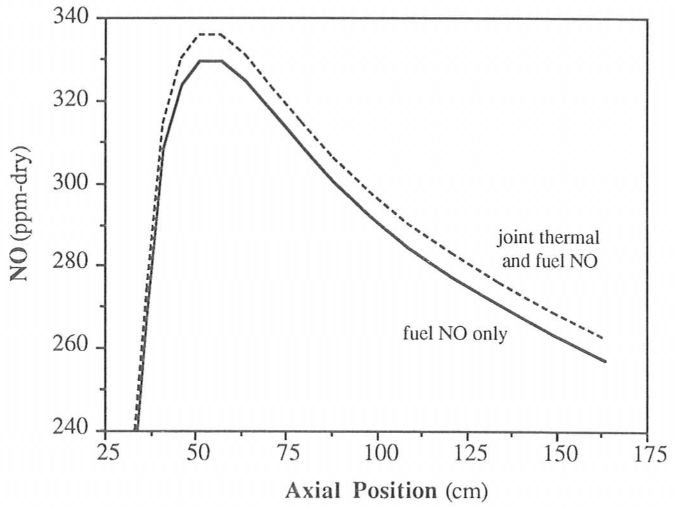
Joint thermal NO and fuel NO comparisons. When the thermal NO mechanism was jointly solved with the global fuel NO mechanism, the impact on total NO concentrations was less that the sum of the individual mechanisms. An incremental difference of less than 10 ppm NO was predicted for both the bituminous and subbituminous combustion cases (see Fig. 6.13). The main explanation for this result is the decay of thermal NO by fuel-nitrogen intermediates but also includes competition for oxygen atoms. This finding matches the observation of Pershing and Wendt (ref. 58) who showed that thermal NO concentrations in their laboratory-scale combustor were less than 5% of the total NO at reactor temperatures below 2200 K. By separately predicting fuel NO and thermal NO, the appropriate NO_x abatement strategy can be identified.

6.4 NITROGEN OXIDE CONTROL TECHNOLOGIES

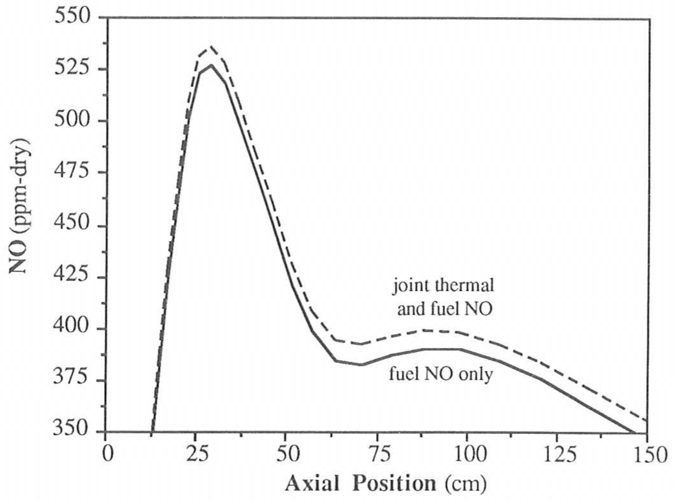
6.4.1 Strategies

In order to comply with regulations for nitrogen oxides emissions, various abatement strategies have been developed. These strategies can be broken down into three categories; 1) modification of the combustion configuration, 2) injection of reduction agents into the flue gases, and 3) treatment of the flue gas by post-combustion denitrification processes. A compilation and discussion of current stationary combustion NO_x control systems, including those available by commercial manufacturers and those presently being developed by private and government research organizations, is given by the International Energy Agency (IEA, see refs. 114, 115). A determination of the most effective and least-cost abatement technology depends on specific boiler firing conditions and the mandated emission limits. A combination of technologies may be needed. Figure 6.14 shows a composite drawing of an industrial coal fired boiler and illustrates the point of application of the various abatement techniques. A summary of the achievable emission rates for the various NO_x control technologies is presented in Table 6.6.

It is obvious that the selection of the pollution control system must also include the impact on boiler efficiency since many of the changes affect the fuel oxidation process. The large variety of combustion configurations and different fuel types requires that the abatement strategy be applied on a case-by-case basis. There is no guarantee that a particular alternative will achieve the desired control level due to the complex interrelations among fluid dynamics, chemistry, and energy transport processes. Even the scale-up of new configurations from pilot plant performance data can miss projected abatement levels. For this reason, an application of theoretical and practical experience is prudent when developing the appropriate nitrogen oxide abatement strategy.



a. Wyoming subbituminous coal combustion case



b. Utah bituminous coal combustion case

Fig. 6.13 Joint thermal and fuel nitric oxide mechanism prediction of nitric oxide concentrations for coal combustion cases.

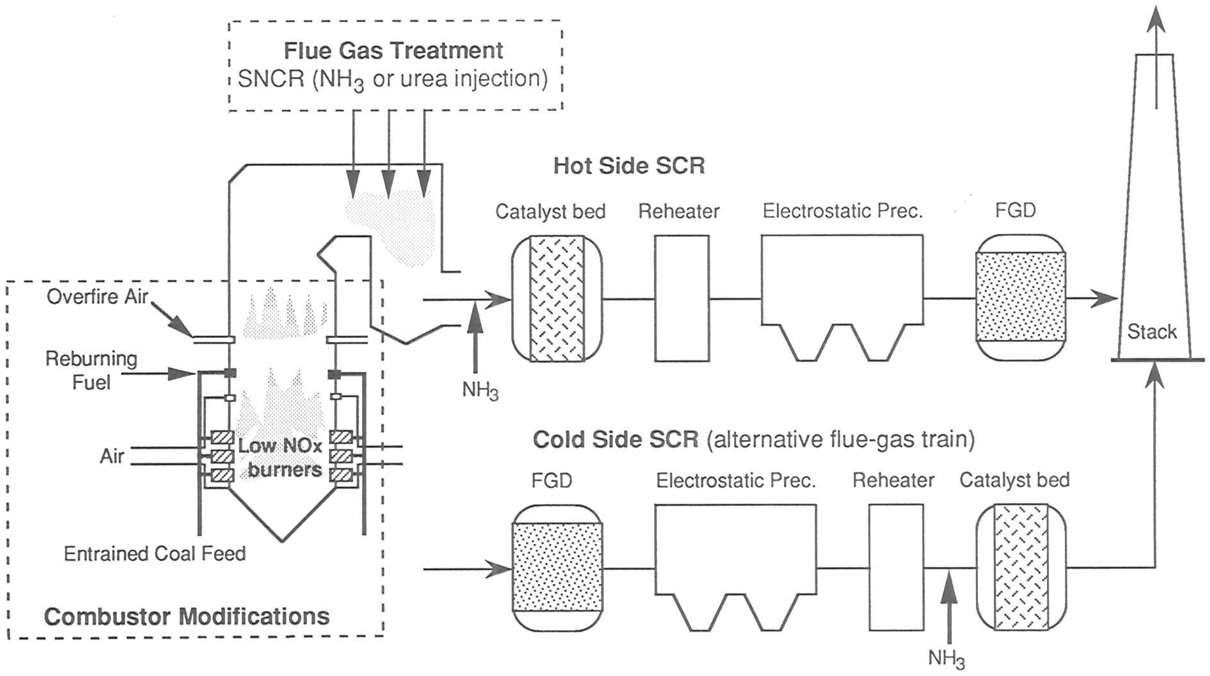


Fig. 6.14 Schematic drawing of NO_x abatement control technologies and their point of application. SNCR = Selective Non-Catalytic Reduction; SCR = Selective Catalytic Reduction; FGD = Flue Gas Desulfurization.

TABLE 6.6

Achievable emissions reduction for selected stationary combustion NO_x control technologies

Abatement Technology	Percentage NO_x Reduction Possible Coal[114]	 Nat. Gas [116]	 Resid. Oil[116]	Advantages[116]	Disadvantages[116]
Low excess air	0-15%	0-15%	0-20%	No significant capital cost, increased boiler efficiency	Oxygen trim system requires maintenance
Flue gas recirculation	0-5%	10-30%	5-20%	Retrofits are usually possible, can easily be combined with other technologies, very effective in reducing thermal NO	Requires high-temperature duct work and fans, higher capital cost than staged air or staged fuel to achieve equal or greater emissions reductions
Air staging	10-50% 30% typical	30-40%	30-40%	Low to moderate operating costs, can be adapted to existing boilers by taking selected burners out of service	May not be applicable to package boilers, access for secondary air ports may not be available
Fuel staging or low NO_x burners	30-75% 50 % typical	30-40%	30-40%	Low capital costs, retrofits normally possible, low operating and maintenance costs	Some increase in static pressure, may require package boilers to operate at a lower rate
Low NO_x burners and air staging and/or fuel staging	25-80% 70% typical	-	-	Highest reduction efficiency without resort to flue-gas treatment technologies, retrofit of existing combustors normally possible	May require boiler to be taken off line for an extended period during retrofit, may require package boilers to operate at reduced rates

TABLE 6.6 (continued)

Achieveable emissions reduction for selected stationary combustion NO_x control technologies

Abatement Technology	Percentage NO_x Reduction Possible			Advantages[116]	Disadvantages[116]
	Coal[114]	Nat. Gas [116]	Resid. Oil[116]		
Ammonia injection	40-90% 75% typical	40-70%	30-70%	Lower capital costs than SCR	Potential formation of fine particulates, potential NH_3 emissions, moderate to high costs, sensitive to temperature, catalyst poisoning possible
Urea or cyanuric acid injection	30-70%				
Selective catalytic reduction	60-95% 90% typical	70-90%	70-90%	Achieves lowest emission rate, can be retrofitted to most combustors	Highest capital cost, potential for NH_3 emissions, increased pressure drop, potential for catalyst poisoning
Combined NO_x/SO_x	NO_x: 50-95% SO_x: 50-95%	-	-	Joint removal of NO_x and SO_x, often a salable by-product is produced	High capital cost, most technologies only in developmental stage, solid or liquid waste disposal may be required

6.4.2 Combustion Modification Approaches

The formation of nitrogen oxides strongly depends on temperature conditions, and oxygen availability; both are influenced by the combustor design and firing configuration. Conventional boiler designs are classified as wall-fired, cell units, tangentially-fired, cyclone, and stoker-fired boilers. Wall-fired boilers consist of rows of burner nozzles through which air and/or fuel are injected. Cell units employ a different type of wall-fired design with the burners arranged in clusters along the boiler wall. In a tangentially-fired boiler, the burners are located in the corners and directed off-center to produce rotation of the bulk combustion zone gas. This assures a well mixed condition throughout the boiler. Cyclone boilers are equipped with one or more smaller combustion chambers (cyclones) which burn the fuel at high turbulence and temperatures (1900-2150 K). They are designed to reduce fuel preparation costs (only coal crushing is required), furnace size, and fly ash in the flue gas. Stoker-fired boilers are not generally used for power generation but are used for heating and steam production by industry.

The chief objective of boiler operations is to achieve maximum conversion of the fuel to products in order to gain the highest possible thermodynamic efficiency. This objective can be accomplished by thoroughly mixing the oxidizing air and fuel and by increasing the excess air. In part, well-mixed conditions are achieved by the air which is used to pneumatically transport classified coal and also to atomize fuel oil. Preheating the oxidizing air is also used in conventional designs to improve the thermal efficiency.

Unfortunately, the well-mixed, high-temperature, and high excess-air conditions which promote efficient oxidation of the fuel constituents also favor the production of nitric oxide. The relative inertness and insolubility of nitric oxide makes flue gas treatment more difficult than for sulfur oxide removal. Consequently, it is often easier to intervene right at the point of fuel combustion to avoid the formation of nitrogen oxides and their precursors. Modifications to conventional combustion configuration hardware can reduce nitrogen oxide emissions from 50-80%. They are the simplest and least expensive alternatives to apply. Modifications recognized as being technically viable in reducing nitrogen oxide emissions include:

1. Low excess air
2. Flue gas recirculation
3. Staged air combustion
4. Staged fuel combustion

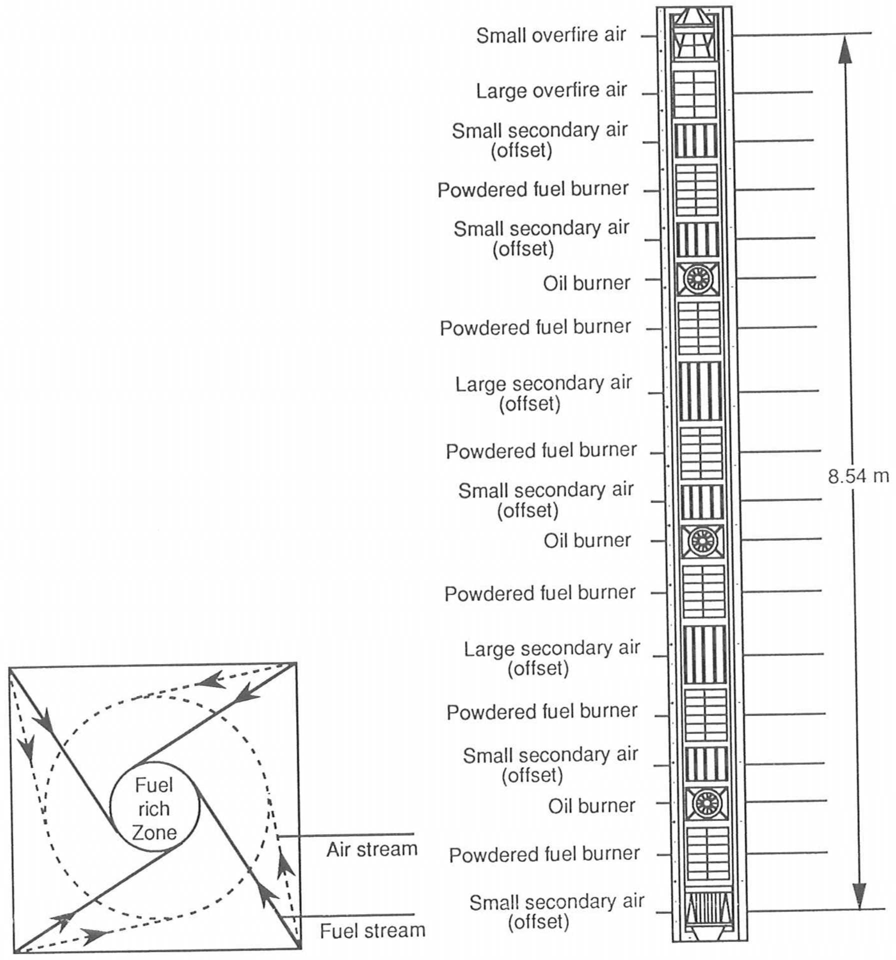
Operating with lower excess air is achieved without any retrofit modifications and may reduce nitrogen oxide emissions up to 15% in some, but not all, combustors. Lowering the excess air often improves the thermal efficiency since higher excess air, while serving to reduce hydrocarbon emissions, also acts as a thermal diluent. The tradeoffs in combustion efficiency and nitrogen oxide reductions must be monitored to achieve the best air-to-fuel ratio. Already most boilers, including pre-NSPS boilers, have implemented low-excess air practices.

The purpose of flue gas recirculation is two-fold; 1) to dilute the inlet oxygen concentration and 2) to lower the combustion zone temperature. Flue gas recirculation primarily affects thermal NO but has little influence on fuel NO. Also the high cost of equipment and operating costs (recirculation blowers) make this modification generally unattractive. In fact, very few facilities have retrofitted or designed boilers with flue gas recycle capability.

Air staging and fuel staging are very effective in controlling nitrogen oxide emissions. In concept, air and fuel staging can be accomplished by advanced burner design (aerodynamic staging) or by externally injecting the air and/or fuel at optimal elevations throughout the boiler. Over-fire air is one form of external air staging and has been successfully implemented in wall-fired boilers to achieve nitrogen oxide reduction of up to 30%. Typically 25% of the air is redirected from the primary combustion zone to an elevation above the fuel burners as shown in Fig. 6.14. Overfire air has the advantage of reducing nitrogen oxides without sacrificing boiler efficiency; however, thermal NO formation may result in the region of overfire air. Most applications of overfire air have been made to new facilities although retrofit applications are proposed for a number of existing facilities.

Air staging is accomplished in tangentially fired boilers by alternating fuel-rich and fuel-lean zones at different levels in the combustion zone. Another technique is to divert part of the combustion air along the boiler wall, thus establishing a concentric envelop of air rotating around a fuel-rich core. Figure 6.15 illustrates these concepts. Staged fuel operation (reburning) involves injecting fuel into more than one combustion zone in the boiler. The objective is to inject a sub-stoichiometric part of the fuel with the bulk of the combustion air in the primary combustion zone. This produces a very fuel-lean zone which reduces the formation of thermal NO by lowering the peak temperature; however, the potential for formation of fuel NO may be increased. In the secondary combustion zone where reburning fuel is added, the overall air-to-fuel ratio is maintained fuel-rich. Fuel fragments are produced which react with NO producing HCN (see reactions 6.31 and 6.32). Subsequently, HCN favors reduction to N_2 under the prevailing fuel-rich conditions. Final air addition is then employed to burn out the unoxidized hydrocarbons at lower temperatures that do not favor thermal NO formation.

Fuel staging is particularly effective for abating fuel NO formation in oil and coal-fired boilers. The most effective reburning fuels are volatile, low-nitrogen-containing fuel oils and natural gas, although coal has been successfully applied in some pilot-scale tests. A 40-60% reduction in nitrogen oxide emissions can be achieved by reburning. One combustor that is a prime candidate for fuel staging is the cyclone combustor since most modifications to the cyclone chambers are counter productive.



(a) Fuel and air directional firing

(b) Schematic diagram of burner box modified for low NO_x firing

Fig. 6.15 Basic arrangement of burners and fluid motion of a low NO_x concentric (corner-fired) firing system. (Illustration used with permission from ref. 11).

Advanced low-NO_x burners have been developed and tested by a number of boiler manufacturers and utilities (ref. 114). The general purpose of low NO_x burners is to aerodynamically stage the air and/or fuel. Variation in the momentum of the fuel and air streams, in the swirl of the streams, and in the angle of injection of the streams, affects the mixing and combustion pattern and retards the formation of both thermal and fuel NO. The majority of nitrogen oxides formed in coal flames occurs as the fuel nitrogen, which is released with the volatiles, is oxidized. Fortunately, the chemistry controlling nitrogen oxide formation is slower than the fuel oxidation rates. Thus, the aim of low-NO_x burners is to establish a fuel-rich zone of low temperature where the volatiles are oxidized but not the fuel nitrogen constituents. This zone is followed by gradual mixing of air into the outer fringes of the flame to burnout the char and soot. Figure 6.16 illustrates the basic anatomy of a low-NO_x burner which is incorporated with degrees of variation in commercially available burners.

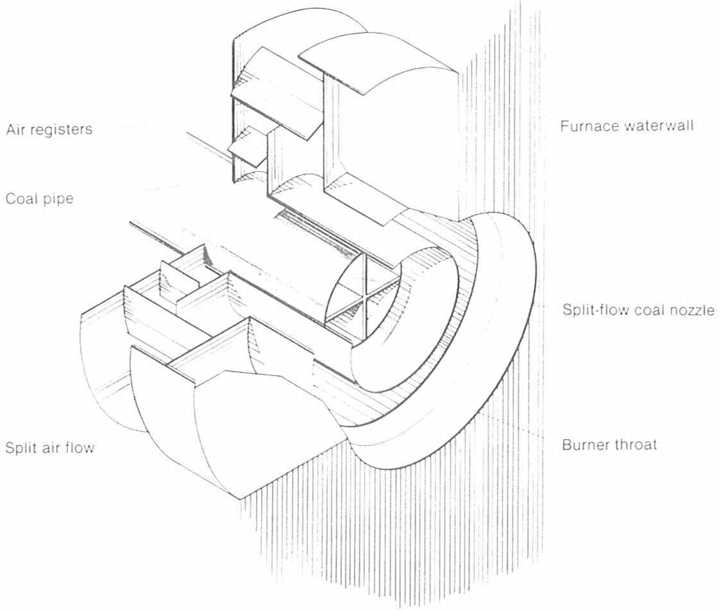


Fig. 6.16 Basic anatomy a of low-NO_x burner. (Figure used with permission from EPRI, ref. 116).

Low-NO_x burner concepts also apply to fuel-oil and natural gas combustors. Changes in the design which affect fuel oil atomization and the positioning of the flame stabilizer can impact the combustion pattern and lower the production of nitrogen oxides. Also, the amount of pre-mix air and swirl imparted to both the fuel and the oxidizing air are important burner-design parameters. Long diffusion flames favor low thermal NO formation but unfortunately prompt NO may be increased in fuel-rich zones of the flame.

6.4.3 Injection of Chemical Reductants

(i) *Overview.* Under the right conditions, nitrogen oxides can be converted to nitrogen and water by injecting chemical reductants into the combustion flue gases. This technique involves, "selective non-catalytic" homogeneous reactions with the decomposition products of the injected compounds. Ammonia is the chemical reductant used in a well-established commercial process pioneered in the early 1970's (ref. 117). Other compounds which have been successfully tested include cyanuric acid, $[(HOCN)_3]$, hydrazine hydrate (N_2H_4) solutions, urea $[CO(NH_2)_2]$, and methanol (refs. 118, 119).

Factors which determine the effectiveness of nitrogen oxide removal by reducing agents include the temperature of the flue gas, injection rate and mixing efficiency, and the composition of the flue gas. Injection jets are designed to achieve rapid and thorough dispersion of the reductant at the optimum temperature. Flue gas radicals initiate decomposition of the chemicals to nitrogen-containing intermediates which then selectively react with NO to form N_2. Thus, the presence of moisture in the exhaust gas, or certain additives such as hydrogen and hydrogen peroxide, may enhance the initiation of reduction reactions.

Normally, there is a narrow temperature range which is conducive to the reduction reactions. At excessive temperatures, the nitrogen intermediates will be oxidized and produce additional nitrogen oxides. At lower temperatures, undesired amounts of the injectant can slip through the process and be emitted with the nitrogen oxides. In some cases, the unreacted injectant can react with the nitrogen oxides to form undesirable particulate matter (*eg.*, NH_4NO_3 and $(NH_4)_2SO_4$ aerosols).

(ii) *NO_x Reduction by Ammonia.* Research efforts have succeeded in elucidating the chemical kinetics of ammonia decomposition and reaction with nitric oxide to the point where the process is virtually predictable (ref. 117). This knowledge, coupled with practical experience in a variety of commercial combustors, has allowed nitrogen oxide reduction efficiencies of around 75% to be obtained. Some retrofit applications have achieved in excess of 90% removal of NO.

The reaction sequence for NO_x reduction by ammonia is summarized in Fig. 6.17. It is obvious that the principal nitrogen intermediate, NH_2, either reduces NO or is competitively converted to NO. The $NH_2 + O$ reaction has a high activation energy; thus, higher temperatures are required for this reaction pathway to be favorable. When the temperature is too low, the reaction of NH_3 with oxygen atoms and hydroxl radicals is slow, allowing NH_3 to slip. The optimum temperature window for selective reduction of NO ranges from approximately 1250 K to 1400 K.

Ammonia reduction of nitric oxide is only effective when excess oxygen is available to produce oxygen atoms. In fact, the process can be inhibited by increasing the NH_3 concentration above the O_2 concentration or by increasing the moisture content of the flue gas. The presence of moisture can inhibit NO reduction at low temperatures by competing for the oxygen atom. At higher temperatures, moisture competes with the oxidation of NH_2 and inhibits NO formation. The combination of effects results in an increase of the optimum temperature.

Additives such as hydrogen and hydrogen peroxide tend to lower the optimum temperature window by reacting with molecular oxygen to produce oxygen atoms and a hydroxl radical:

$$H + O_2 \leftrightarrow O + OH \tag{6.37}$$

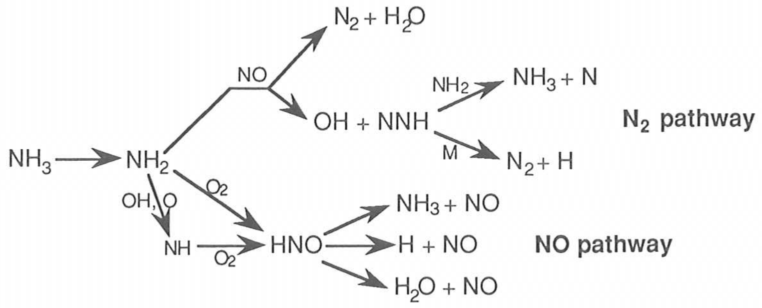


Fig. 6.17 Mechanism of nitric oxide (NO) reduction in the flue gas by ammonia (NH_3) injection. (Figure used with permission from ref. 117).

This obviously accelerates the conversion of NH_3 to NH_2.

(iii) *Urea and Cyanuric Acid Injection.* The selection of cyanuric acid as a chemical reductant resulted from recognizing that HNCO could be involved in a series of reactions that would remove NO (ref. 34). When cyanuric acid is injected into the exhaust stream it rapidly decomposes to form isocyanic acid (HNCO) which further decomposes in high temperatures to NH, NH_2, and N_2O. At lower temperatures, surface reactions are required to decompose isocyanic acid. The optimum temperature window ranges from 1000 K to 1200 K (ref. 119).

The detailed chemistry of urea with NO is not completely understood, but the reaction path is dependent of the thermal decomposition products. It is suggested that urea might decompose into NH_3 and HNCO and thus follow either or both the ammonia or isocyanic acid reaction paths. Figure 6.18 shows the major steps in the reaction sequence for NO reduction by ammonia, urea and cyanuric acid. Once NH_3 or NH_2 is formed, the chemistry can branch according to the reactions shown in Fig. 6.17.

(iv) *Nitrous Oxide Formation by Injected Chemicals.* One major disadvantage of flue gas treatment by chemical reductants is the potential formation of byproduct nitrous oxide (N_2O). In view of the increased concern over N_2O emissions, this is an undesirable by-product. A joint experimental and theoretical study conducted recently concluded that all chemical injectants, including NH_3, produce N_2O as a byproduct depending on the amount of reductant used and the conditions at the point of injection (ref. 120). Ammonia produced the least concentrations of N_2O while cyanuric acid produced the highest concentrations. Under some conditions, a molecule of N_2O may be formed for every molecule of NO removed by cyanuric acid (ref. 26). Nitrous oxide emissions due to urea injection were found to be in between the levels produced by NH_3 and cyanuric acid. These observations coincide with the chemistry illustrated in Fig. 6.18.

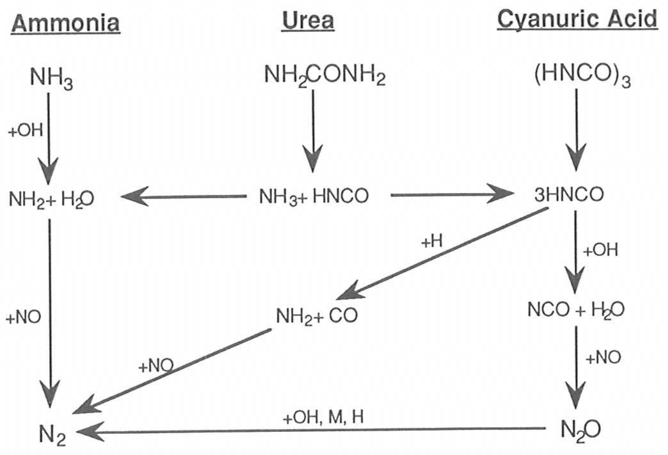


Fig. 6.18 Major paths for selective catalytic reduction of nitrogen oxides by chemical reductants injected into the flue gases. (Figure adapted with permission from ref. 120)

6.4.4 Catalytic Reduction of Nitrogen Oxides

The most effective technology for removing nitrogen oxides from combustion gases is selective catalytic reduction (SCR). Selective catalytic reduction involves introduction of ammonia prior to the catalyst bed as shown in Fig. 6.14. The catalyst can be placed in different positions in the flue gas flow as long as the gas temperature is appropriate for the type of catalyst used. Practical applications in Japan and Germany have obtained removal efficiencies approaching 90% (refs. 121, 122). Non-selective catalytic reduction, in which hydrogen or hydrocarbons in the flue gas act as reducing agents, has also been researched but has not achieved the same level of success as SCR.

The basic SCR catalyst types that have been researched and are commercially available are discussed in detail elsewhere (refs. 114, 122). These include noble metals (Pt, Pd, RU/Al_2O_3, and Pt/Al_2O_3), metal oxides (Fe_2O_3/Cr_2O_3, V_2O_5/TiO_2, $V_2O_5/MoO_3/WO_3/Al_2O_3$) and zeolite (synthetic mordenites). Each catalyst exhibits a unique optimum operating temperature and NH_3-to-NO_x ratio. The optimum operating temperature ranges from 500-700 K. At low temperatures, the reaction efficiency drops off while the catalyst is prone to sintering at excessive temperatures. Typically, the catalyst bed will be placed upstream of the electrostatic precipitator or baghouse to take advantage of the hot flue gas. However, a problem exists for fouling and plugging in the catalyst bed by fly-ash particulates. Flue gas products such as SO_3 can also combine with ammonia to form corrosive ammonium bisulfate $(NH_4)_2SO_4$.

Most metal-based catalysts are subject to a decrease in activity during operation. Catalyst poisons which deactivate the reaction sites include alkaline and alkaline-earth oxides or arsenic compounds. Sulfur oxides can also deactivate certain metal oxide catalysts and can reversibly inhibit noble metal catalysts. A catalyst activity loss of 20% per year is considered normal for most combustion clean-up applications.

Selective catalytic reduction requires the highest capital and operating costs, despite many recent technological advances in catalyst support geometries, and ammonia injection control. However, because of more stringent standards, SCR may become the most viable technology for nitrogen oxide removal.

6.4.5 Combined NO_x/SO_x Combustion Gas Treatment Technologies

Numerous processes have also been proposed in recent years for combined denitrification and desulfurization of combustion flue gases. Although the majority of these processes remain at the research level, a few are commercially available and have been implemented by full-scale combustion facilities (refs. 114, 123). Most of the NO_x/SO_x removal processes are considered expensive and may only be considered as more stringent standards become mandatory for new and existing facilities.

Combined NO_x/SO_x flue gas treatment processes are generally classified as wet or dry. Wet processes normally utilize absorption with complexation, reduction, or oxidation chemistry, while the dry processes include catalytic decomposition, absorption by activated carbon beds, spray drying, and electron-beam irradiation.

One innovative, NO_x/SO_x post-combustion concept involves streamer corona discharge to produce radical species in the flue gas. The chemistry proposed by various researchers is based on the interaction of electrons with molecular species, giving rise to atomic oxygen, nitrogen and amine radicals. In the presence of ammonia and water, the radicals lead to the reduction of nitrogen oxides and SO_2, proceeding through reactions included in the ammonia-NO_x reduction mechanism and other ionic and free radical reactions. However, in the absence of ammonia and water, NO_x emissions can be further exacerbated. The reactions leading to removal of SO_2 and NO by streamer corona discharge are discussed in detail elsewhere (ref. 124).

Another scheme proposes denitrification of the flue gas using regenerable mixed oxide sorbents (*eg.*, Na_2O, Co_3O_4, and Fe_2O_3). This process involves the sorption of nitrogen oxides onto porous sorbents which can be thermally regenerated upon saturation. The concentrated gas stream is then treated by standard catalytic reduction methods. An in-depth description on the removal of nitric oxide from flue gas using mixed oxide sorbents has been published (ref. 125).

6.5 MECHANISMS OF SULFUR OXIDES FORMATION

Sulfur oxides are formed in stationary combustors from the sulfur entering with the fuel. Natural gas is sulfur-free with the exception of trace amounts of odor additives such as mercaptans. However, both fuel-oil and coal commonly contain significant amounts of sulfur. The amount of sulfur in fuel oils depends on the quality of the specific petroleum and the refining and blending process. Heavy fuel oils, which are blends of the distillation bottoms (residuum) and lighter distillates, contain approximately 4 weight percent sulfur. Lighter blends of fuel oil can have a very low sulfur composition (< 0.1 weight percent). The sulfur content of coal varies from 0.2 to 11 weight percent, depending on rank and the environmental conditions during the coalification process. Sulfur oxide emissions can be reduced substantially by simply converting from high to low sulfur coal. For certain coals, the sulfur content can be reduced by cleaning the coal prior to burning it.

It is generally accepted that there are three forms of sulfur in coal (ref. 126); 1) organic sulfur thought to be thiophene (hetero-aromatic compounds), sulfides, and thiols, 2) pyritic sulfur (FeS_2) and/or marcasites, and 3) sulfates such as calcium or iron salts. Both the organic and inorganic sulfur phases undergo significant chemical transformations during coal devolatilization. An understanding of the kinetic mechanisms and chemical speciation is currently emerging from research studies. Correlations for the distribution of sulfur species among solid (char), liquid (tar), and gaseous phases have already been published (refs. 127-129). The yields of these phases and the distribution of early volatiles between H_2S and COS have been measured and fit to models.

Sulfur-containing pollutants formed by burning fossil fuels include SO_2, SO_3, H_2S, COS, and CS_2. Under normal boiler operating conditions, with overall excess oxygen being used, virtually all of the sulfur is oxidized to SO_2 and small quantities of SO_3 (refs. 130, 131). When coal is gasified, the sulfur predominantly remains as reduced forms of H_2S, COS, and CS_2 (132, 133). The reactions of sulfur species in coal flames are numerous and complex. The simplified reaction scheme in Fig. 6.19 has been suggested as the basis of a model to predict sulfur formation (ref. 131).

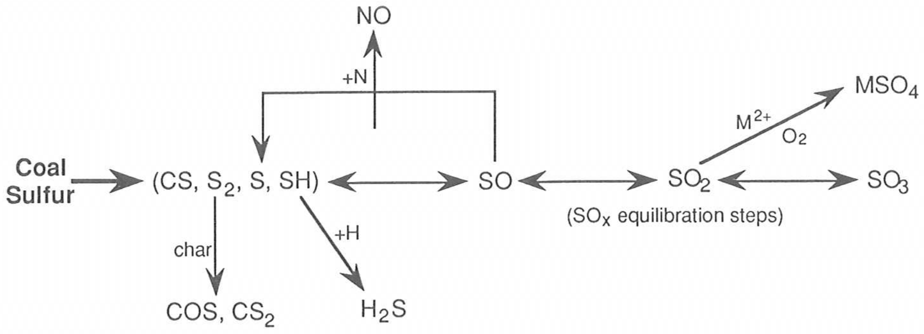


Fig. 6.19 Simplified reaction mechanism for the conversion of coal sulfur to sulfur-containing pollutants. (Figure adapted with permission from ref. 131)