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OXIDES OF NITROGEN
Their Formation and Control
in
Stationary Sources

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INTRODUCTION

Over the last fifty years, a major concern of environmentalists, health care providers, national governments, and international organizations has been the unhealthy and destructive effects of air pollution. In this regard, much attention has been given to a primary pollutant of air - oxides of nitrogen (NO_x). The two most important oxides of nitrogen with respect to pollution are nitric oxide (NO) and nitrogen dioxide (NO_2). In the atmosphere, elevated concentrations of these gases contribute to the greenhouse effect and ozone depletion. In addition, they foster the formation of acid rain and photochemical smog. Lastly, not only do NO_x contribute directly to these atmospheric reactions, but they also participate in the production of secondary pollutants which have similar effects.

NO_x are produced and destroyed naturally as a part of the nitrogen cycle. Nitrogen in the form of N_2 makes up almost 80% of our atmosphere. Although it is a vital constituent of the biosphere, there are relatively few mechanisms by which molecular nitrogen can be fixed into a form which is accessible to living organisms. These mechanisms include lightning, microbial activity, fertilizer production, and combustion.

In soil, fixed nitrogen (manmade or naturally formed) is utilized by plants. When a plant dies, this material is reabsorbed into the soil. However, nitrogen compounds stored in plant material can be released as NO_x during biomass burning. Material from decomposing plants, animals and micro-organisms deposited millions of years ago have produced the fossil fuels - coal, oil and gas. These fuels are used for power and electricity generation today. Fossil fuel combustion in power stations, industry or the transport sector is a major source of NO_x in the atmosphere.

In the U.S., initial legislative efforts to control air pollution, including NO_x emissions, began with the passage of the Air Pollution Control Act of 1955. A modest beginning, the 1955 Act provided funding for research, but not control, of air pollution. Quantitative standards and emission limits were not instituted until the passage of the 1970 amendment to the 1963 Clean Air Act. The Environmental Protection Agency was tasked with establishing National Ambient Air Quality Standards (NAAQS) for all air pollutants as well as New Source Performance Standards (NSPS) for new industrial plants. The current NO_x NAAQS is a maximum annual concentration of 53 ppbv. Newly constructed utility plants greater than 73 MW in size must meet an NSPS of not more than 740 mg/m^3 (Sloss, 1991).

Since the passage of the 1970 amendment to the Clean Air Act in the United States, and similar legislation in Japan and Europe, many technologies have been developed and employed to reduce the amount of oxides of nitrogen emitted by both moving and stationary sources. The main focus of these efforts has been upon automobile exhaust emissions. Recently, however, attention has been turned to stationary sources, particularly power plants that burn fossil fuels (Boer et al., 1990). Utility plants account for about one-third of all the manmade nitric oxide emissions in the United States (EPA, 1988) and 25% of all manmade NO_x emissions (Sloss, 1991). This paper will discuss oxides of nitrogen and their effect on the environment; how they are formed in fossil-fueled power plants; how their formation can be prevented; and how, if formed, they are removed from combustion gases.

OXIDES OF NITROGEN

The stable gaseous oxides of nitrogen include nitrous oxide (N_2O), nitric oxide (NO), dinitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2), and dinitrogen pentoxide (N_2O_5). An unstable form, nitrogen trioxide (NO_3), also exists. Of these, the only ones naturally present in the atmosphere in any significant amount are nitrous oxide, nitric oxide, and nitrogen dioxide. Thus, these three gases are potential contributors to air pollution (Wark and Warner, 1981).

Nitrous Oxide

Nitrous oxide is an inert gas with anesthetic characteristics. It is a very stable compound with an atmospheric lifetime of well over a century. Its ambient concentration is 0.50 ppm, which is considerably below the threshold concentration for a biological effect. Nitrous oxide is relatively inert chemically, but is a strong infrared absorber. Thus, it contributes to the greenhouse effect. This phenomenon is the absorption by atmospheric gases of infrared radiation emitted by the earth. Greenhouse gases like nitrous oxide absorb this radiation and prevent some of the heat from escaping into space. As a result, average global temperature increases (Wark and Warner, 1981).

In the stratosphere (upper atmosphere), 90% of the nitrous oxide is decomposed by photolysis to release molecular nitrogen:

$$N_2O \xrightarrow{\text{light}} N_2 + O\cdot \qquad (1)$$

Approximately 5% of nitrous oxide reacts with the free oxygen radical to produce nitric oxide:

$$N_2O + O\cdot \rightarrow 2\ NO \qquad (2)$$

This reaction is the primary source of nitric oxide in the stratosphere. As will be discussed in the next section, nitric oxide destroys ozone in the upper atmosphere. Nitrous oxide therefore acts indirectly toward the depletion of stratospheric ozone (Lyon, 1989).

The remaining 5% of nitrous oxide is destroyed by the free oxygen radical to produce molecular nitrogen and oxygen:

$$N_2O + O\cdot \rightarrow N_2 + O_2 \qquad (3)$$

Nitric Oxide

Nitric oxide is a colorless gas with an ambient concentration of usually far less than 0.5 ppm. At this concentration, its biological toxicity in terms of human health is insignificant. However, it is a primary air pollutant, making up 90 to 95% of the NO_x emissions from fossil fuel combustion (Wark and Warner, 1981).

Nitric oxide is a precursor to the formation of nitrogen dioxide and is an active compound in photochemical smog formation as well. Its average lifetime in the troposphere (lower atmosphere) is short, only minutes or even seconds (Wark and Warner, 1981). It is rapidly oxidized to nitrogen dioxide by:

$$2\ NO + O_2 \rightarrow 2\ NO_2 \tag{4}$$

This occurs in the lower atmosphere where oxygen is readily available. The lifetime of nitric oxide can be longer in specific conditions such as those found in plumes from combustion sources where different chemical compounds are present (Wark and Warner, 1981).

Atmospheric nitric oxide can also react with the hydroperoxy radical ($HO_2\cdot$), a photochemical product of the hydroxyl radical and hydrogen atoms. This radical is normally present in urban air. The result is the release of the hydroxyl radical ($OH\cdot$):

$$NO + HO_2\cdot \rightarrow NO_2 + OH\cdot \tag{5}$$

The hydroxyl radical is highly reactive in the atmosphere and, through reaction, can change the chemical properties of many pollutants. When reacting with hydrocarbons, it produces organic peroxy radicals ($RO_2\cdot$). These, in turn, can contribute to photochemical smog and oxidize nitric oxide to nitrogen dioxide:

$$RO_2\cdot + NO \rightarrow RO\cdot + NO_2 \qquad (6)$$

In the upper troposphere and stratosphere, where oxygen is not abundant, nitric oxide reacts with ozone:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (7)$$

This reaction contributes to the depletion of the earth's protective ozone layer. In the upper atmosphere, ozone protects surface life by absorbing the sun's infrared radiation. Loss of ozone in the stratosphere leads to an increase in the amount of infrared radiation which reaches the earth's surface. This increase in radiation could, in turn, lead to an increased incidence of cancer in humans.

Since nitric oxide initiates reactions that produce air pollutants, the control of nitric oxide is an important factor in reducing air pollution (Wark and Warner, 1981).

Nitrogen Dioxide

Nitrogen dioxide is a reddish brown gas that is readily visible in sufficient amounts. For example, a concentration of one ppm of nitrogen dioxide probably would be detected by the human eye. As a direct result of this property, the nitrogen dioxide ambient air quality standard in California was set at 0.25 ppm on an hourly average (Wark and Warner, 1981).

The toxicological and epidemiological effects of nitrogen dioxide on human beings are not completely understood. As far as it is known, nitrogen dioxide is not a primary pollutant in the sense that it directly affects human health, unless the concentration is extremely high (Wark and Warner, 1981).

The major source of nitrogen dioxide in the atmosphere is a result of the rapid oxidation of nitric oxide as shown in equation (7). Although nitrogen dioxide is also a product of fossil fuel combustion, it accounts for only 5 to 10% of the NO_x measured immediately after combustion. The reconversion of nitrogen dioxide to nitric oxide can occur by photolysis. This reaction results in the formation of a free oxygen radical that can react rapidly with molecular oxygen to produce ozone:

$$NO_2 \xrightarrow{\text{light}} NO + O\cdot \tag{8}$$

$$O\cdot + O_2 \rightarrow O_3 \tag{9}$$

This reaction is enhanced in the presence of reactive hydrocarbons that are usually present in urban air (Builtjes and Stern, 1988). Ozone produced in the troposphere by this mechanism contributes to the greenhouse effect and is the major constituent of photochemical smog. It is a pollutant that is toxic to humans at high concentrations.

The combination of nitrogen dioxide with the hydroxyl radical produces nitric acid:

$$NO_2 + OH\cdot \rightarrow HNO_3 \tag{10}$$

Nitric acid is removed from the atmosphere by either wet or dry deposition and is a major contributor to rain acidification in polluted areas.

Dissolution of nitrogen dioxide and nitric oxide into water droplets can result in the formation of nitrous acid by two methods:

$$2\ NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \tag{11}$$

$$NO_2 + NO + H_2O \rightarrow 2\ HNO_2 \tag{12}$$

Nitrous acid can also contribute to acidification of rain.

NO_x and Other Pollutants

The majority of chemical reactions involving NO_x occur at ground level in urban areas where other reactive pollutants are present in relatively high concentrations. A large percentage of these reactions contribute to photochemical smog formation.

Ozone, a major pollutant in urban air, arises from photochemical reactions between NO_x and most hydrocarbons. Further reaction between nitrogen dioxide and ozone produces the nitrate radical ($NO_3\cdot$). This radical does not exist in measurable amounts during the day because it is rapidly dissociated by sunlight. During the night, however, concentrations may reach as high as 350 pptv (Builtjes and Stern, 1988).

An equilibrium exists between this radical, nitrogen dioxide, and dinitrogen pentoxide. The latter compound has, nonetheless, never been observed in ambient air due to a lack of sensitivity in measurement techniques. This occurs because rapid hydrolysis removes dinitrogen pentoxide from the atmosphere in the form of nitric acid in acidic deposition (Builtjes and Stern, 1988).

Nitric acid is also produced from the reaction between the hydroxyl radical and nitrogen dioxide (see reaction (10)). Nitric acid builds up over night in urban environments. At sunrise, photolysis releases hydroxyl radicals from volatilized hydrocarbons and nitric oxide into the atmosphere. These compounds combine to produce nitrous acid:

$$NO + OH\cdot \rightarrow HNO_2 \qquad (13)$$

Both nitric and nitrous acids act as storage media for the hydroxyl radical in urban air. This radical is so reactive, its atmospheric concentration is almost undetectable. In the absence of NO_x, its lifetime in the atmosphere is limited. When it combines with NO_x during the night, however, the hydroxyl radical's atmospheric residence time is, in effect, prolonged. At sunrise, the radical is released by photoylsis and thus has another opportunity to alter the chemical state of many atmospheric pollutants (Cox, 1982).

The production of peroxyacyl nitrate ($CH_3COO_2NO_2$) from NO_x and non-methane hydrocarbons occurs with concomitant production of ozone:

$$CH_3COO_2 + NO_2 + M \rightarrow CH_3COO_2NO_2 + M \qquad (14)$$

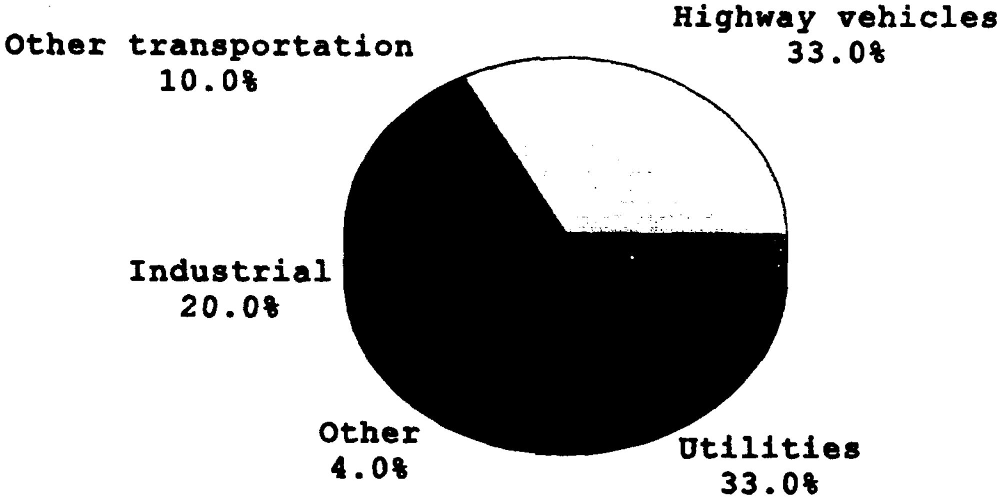
$$O + O_2 + M \rightarrow O_3 + M \qquad (15)$$

where M is a third catalytic molecular species. Peroxyacyl nitrate is ubiquitous. Its lifetime varies from a few hours to several months depending on the temperature; the lifetime of peroxyacyl nitrate is greater at lower temperatures. Accordingly, it dissociates as warmer air is encountered and releases nitrogen dioxide. In this manner, it may act as a storage and transport medium for NO_x by preventing its removal from the atmosphere via precipitation. Thus, it facilitates the transport of NO_x over longer distances (Singh, 1987).

Well over 90% of all the manmade NO_x that enters our atmosphere is produced by the combustion of various fuels (Boer et al., 1990). On a nationwide basis, roughly one-half of NO_x is from stationary sources (see Figure 1). The remainder is from mobile sources such as spark-ignition and compression-ignition engines in automobiles and trucks (Hjalmarsson, 1990).

In the 1970s, reducing NO_x emissions from mobile sources received a great deal of attention. As a result, all automobiles in the U.S. now have catalytic converters to minimize emitted pollution. Unfortunately, the same attention was not afforded to stationary sources of NO_x because stationary emitters had another, more serious, problem. Though they emitted NO_x, they emitted sulfur dioxide (SO_2) in even greater quantities. However, this situation has now changed. While sulfur dioxide emissions from stationary sources has decreased, NO_x emissions have continued to rise. Currently the amount of both pollutants

FIGURE 1. Sources of Manmade Nitric Oxide Emissions in the U.S. Adapted from EPA, 1988.



1990). In addition, the 1990 amendment to the Clean Air Act further limits the amount of NO_x which can be given off by all sources. Thus industries, particularly the power industry, are under much more pressure to reduce NO_x emissions.

NO_x FORMATION

Oxides of nitrogen cannot form without a source of nitrogen. In fossil-fueled utility plants, there are two sources of nitrogen. The first source is the fuel itself. The other source of nitrogen is the air used to burn the fuel.

Fuel NO_x

Although they consist primarily of hydrocarbons, most fossil fuels contain small amounts of nitrogen. As shown in Table 1, of the fossil fuels, coal generally produces the most nitrogen oxide emissions when burned. Furthermore, the nitrogen content of domestic coals ranges from 0.25 to 2.0% (Makansi, 1991). Obviously, NO_x emissions could be eliminated by not burning fossil fuels at all. In this regard, alternative energy sources, such as nuclear, hydroelectric, solar, and wind power, have been investigated. To date, these energy sources either have their own significant waste products, or are not practical for large scale energy production. As a result, coal-fired plants alone

TABLE 1. NO_x Emissions for Different Types of Fuel in Different Size Plants (Dry and La Nauze, 1990)

Fuel Type	**Unit Size, MW**	**NO_x emissions, ppm NO at 7% O_2**
Bituminous coal	65	40-260
Bituminous coal	226	23-4
Brown coal	65	80-120
Washery rejects	84	100
Petroleum coke	97	90-120
Wood waste	56	110-135

energy production ("Inventory ..., 1988). Coal-fired plants are, in fact, the single largest producer of electricity in the United States. The natural abundance of fossil fuel also ensures our reliance on it as an energy source into the foreseeable future (Caprioglio, 1991).

Fossil fuels are, and will continue to be, a primary source of energy in the United States. Switching to fuels lower in sulfur content is a logical step for reducing sulfur dioxide emissions because the sulfur content of coal can be directly related to sulfur dioxide emissions exiting the stack. Unfortunately, this is not the case with NO_x emissions. Coals with constant nitrogen content will exhibit widely varied NO_x emissions after combustion. Also unlike sulfur, nitrogen is not removable from fuel. No practical process for removing fuel-bound nitrogen is commercially available (Makansi, 1991).

Nonetheless, several properties of coal are known to be related to NO_x emissions. For instance, nitrogen, fixed-carbon, and volatile content are all known to influence NO_x emissions. Generally, as coal nitrogen and fixed-carbon content increase, NO_x production increases. The opposite is true for volatile content. High volatility usually correlates with low NO_x production, even in high-nitrogen-content coal (Makansi, 1991).

Physical characteristics may also affect NO_x production. Coal particle size may be a parameter which can be manipulated to control emission levels. Evidence suggests that use of smaller coal particle sizes can reduce NO_x emissions. Although micronized coal burns hotter, the higher temperature is compensated for by shorter residence times. Furthermore, combustion characteristics of very finely grained coal approach those for liquid fuels (Makansi, 1991).

Switching to coals with the most desirable characteristics is a logical step to take to reduce NO_x emissions. However, merely changing fuel types, by itself, does not reduce NO_x emissions sufficiently to meet current standards under the Clean Air Act (Makansi, 1991). More importantly, it does not prevent the formation of NO_x by the Zeldovich mechanism. As will be discussed, often more NO_x results from that set of chemical reactions than by the release of fuel-bound nitrogen.

Thermal NO_x

The primary constituents of air are oxygen and nitrogen. While the oxygen in air is required for combustion, the nitrogen is not. Nonetheless, under certain combustion conditions, reactions between gaseous oxygen and nitrogen can occur. At high temperature (greater than 1500°F), molecular oxygen may dissociate and become atomic oxygen:

$$O_2 + \text{heat} \rightleftharpoons 2\ O \qquad (16)$$

Atomic oxygen then combines with molecular nitrogen to form nitric oxide:

$$O + N_2 \rightleftharpoons NO + N \qquad (17)$$

Atomic nitrogen can also react with molecular oxygen to form nitric oxide:

$$N + O_2 \rightleftharpoons NO + O \qquad (18)$$

These reactions are known as the Zeldovich mechanism. The overall result of the Zeldovich mechanism may be written as follows:

$$N_2 + O_2 \rightleftharpoons 2\ NO \qquad (19)$$

Equilibrium concentrations of the products and the reactants are highly temperature dependent. The equilibrium expression for equation (19) has been determined to be:

$$K_{eq} = \frac{[NO]^2}{[N_2][O_2]} = 21.9e^{-43,200/RT} \tag{20}$$

where R is the universal gas constant and T is the temperature in degrees Kelvin (Wark and Warner, 1981).

In the combustion process, nitric oxide then may react to form nitrogen dioxide:

$$2\ NO + O_2 \rightleftharpoons 2\ NO_2 \tag{21}$$

The equilibrium constants for equations (19) and (21) vary dramatically with temperature. Tables 2 and 3 list the values of the equilibrium constants at various temperatures. As Table 2 shows, the Zeldovich mechanism is negligible at room temperature. Increasing temperature to 1500°K as in combustion, however, increases the equilibrium nitric oxide concentration by 10^{25}. In addition, almost all the NO_x produced in combustion is in the form of nitric oxide since the formation of nitrogen dioxide is not favored at 1500°K, as shown in Table 3.

Under typical combustion conditions, the partial pressure of molecular nitrogen is about 0.76 atm and the partial pressure of molecular oxygen is about 0.033 atm. Using these assumptions and

TABLE 2. Equilibrium Constants for the Formation of Nitric Oxide from Molecular Oxygen and Nitrogen. Adopted from JANAF, 1965.

	Temperature		
$N_2+O_2 \rightarrow 2NO$	(°K)	(°F)	K_{EQ}
$K_{EQ}=\frac{(pNO)^2}{(pN_2)(pO_2)}$	300	80	1.0×10^{-30}
	1000	1340	7.5×10^{-9}
	1200	1700	2.8×10^{-7}
	1500	2240	1.1×10^{-5}
	2000	3140	4.0×10^{-4}
	2500	4040	3.5×10^{-3}

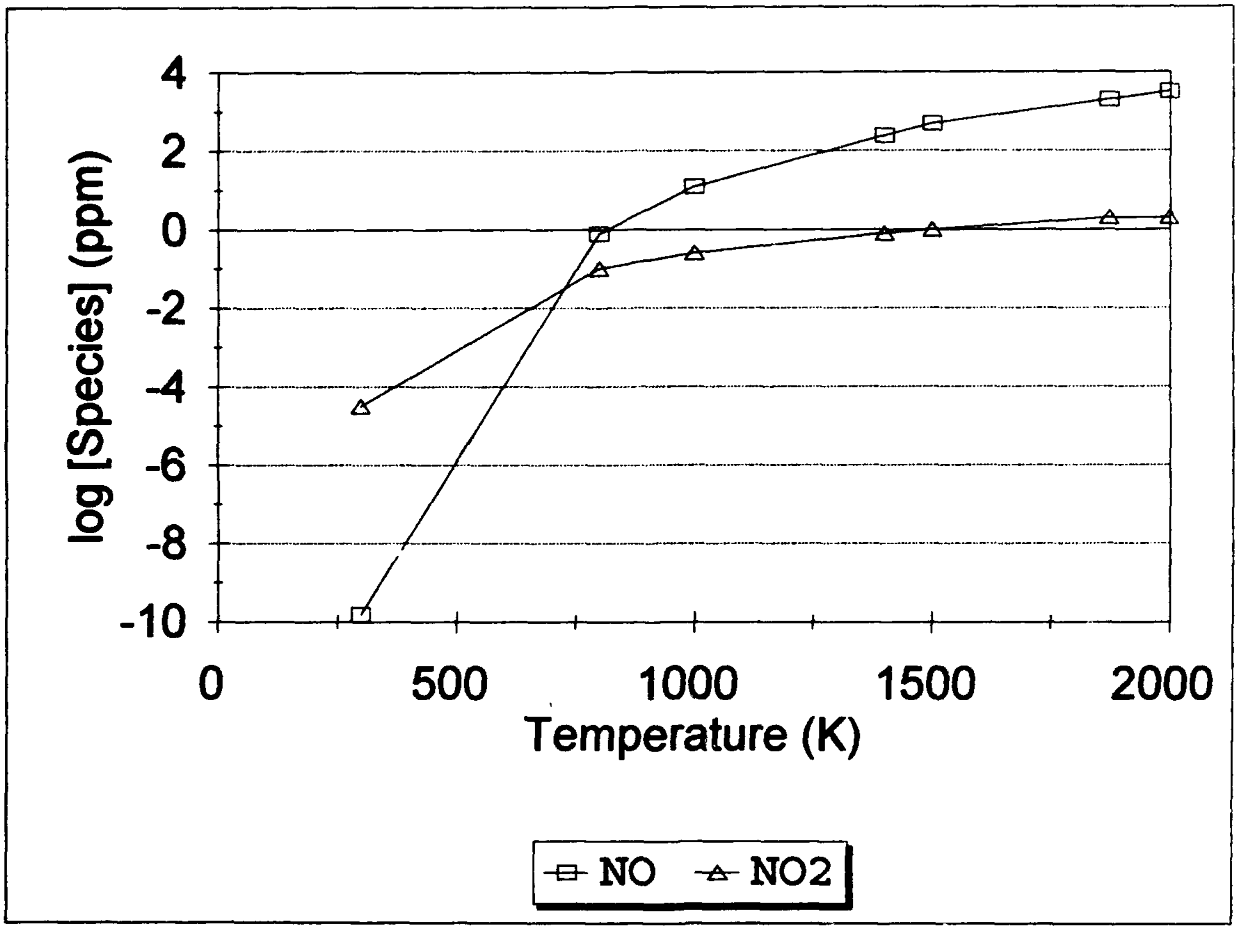
TABLE 3. Equilibrium Constants for the Nitric Oxide Oxidation Reaction to Nitrogen Dioxide. Adopted from JANAF, 1965.

	Temperature		
$2NO+O_2 \sim NO_2$	**(°K)**	**(°F)**	**K_{EQ}**
$K_{EQ}=\frac{(pNO_2)^2}{(pNO)^2(pO_2)}$	300	80	1.0×10^{12}
	500	440	1.4×10^{4}
	1000	1340	1.2×10^{-2}
	1500	2240	1.2×10^{-4}
	2000	3140	1.2×10^{-5}

the equilibrium equations in Tables 2 and 3, one can calculate the speciation of nitric oxide and nitrogen dioxide as a function of temperature. This speciation is shown in Figure 2.

Consequently, there are three important parameters in NO_x formation. These parameters are temperature, time, and available oxygen. Basically, at high temperatures (*e.g.*, greater than 1900°K), both thermodynamics and kinetics favor nitric oxide formation. Hence, peak temperatures should be avoided. Two ways of accomplishing this are avoiding high heat-release rates and achieving high heat-removal rates. One possible method of implementing these techniques is to keep the residence time at peak temperatures to a minimum. If the temperature in the combustion zone can be lowered, then reaction rates become the limiting factor. In this case, the temperature-time profile of the reacting mixture controls the ultimate composition of the flue gas as it leaves the furnace. Since equilibrium is not attained at these lower temperatures, the kinetics of formation is more important than the kinetics of decomposition. Consequently, the rate of formation of nitric oxide is suppressed, anda lower amount of nitrogen dioxide is ultimately formed (Wark and Warner, 1981).

FIGURE 2. Speciation of NO and NO2 as a Function of Temperature



To a large extent, the oxygen content of the reacting mixture determines the peak temperature. Although the stoichiometric air-to-fuel ratio leads essentially to the maximum possible combustion temperature, the peak equilibrium NO_x concentration occurs at a percentage of stoichiometric air somewhat greater than 100%. Accordingly, one approach to NO_x control is combustion at, or slightly less than, stoichiometric air (Wark and Warner, 1981). In other words, understanding the thermodynamics and kinetics of NO_x formation is critical for developing methods to reduce NO_x via combustion control systems.

COMBUSTION CONTROLS

By controlling combustion conditions, NO_x emission reductions of up to 50% can be achieved (White and Maibodi, 1991). Methods which reduce NO_x formation during combustion include: operating at a combustion temperature under 1300°C and reducing the furnace heat release rate; minimizing the residence time at high temperatures; and eliminating excess air from the combustion chamber.

Operational Measures

The primary operational technique for reducing NO_x is minimizing excess air in the combustion chamber. The goal of this technique is to provide sufficient oxygen for stoichiometric combustion of the fuel, but not enough to allow the formation of atomic oxygen at high temperatures as in equation (16). Radically reducing the amount of air, however, can result in incomplete and unstable combustion. The consequence of this situation is increased production of unburnt carbon in the fly ash and carbon monoxide in the combustion gases. Both of these products are pollutants and are as undesirable as NO_x.

To maintain optimal operating conditions for NO_x reduction, the burner must be constantly monitored to ensure that it continues to operate properly. For instance, when operating under close to stoichiometric conditions, air and fuel distribution must be as even as possible. Uneven distribution of either air or fuel can lead to zones of incomplete combustion in the reaction chamber. A furnace fouled by a coating of particulate matter can also increase NO_x production. Fouling increases operating temperature and thus enhances the Zeldovich mechanism. Variations in fuel content can degrade the performance of the system as well. Unfortunately, even good operational burner performance does not reduce NO_x emissions enough to meet current emission standards. Therefore, some form of post-combustion NO_x control is also usually required (Hjalmarsson, 1990).

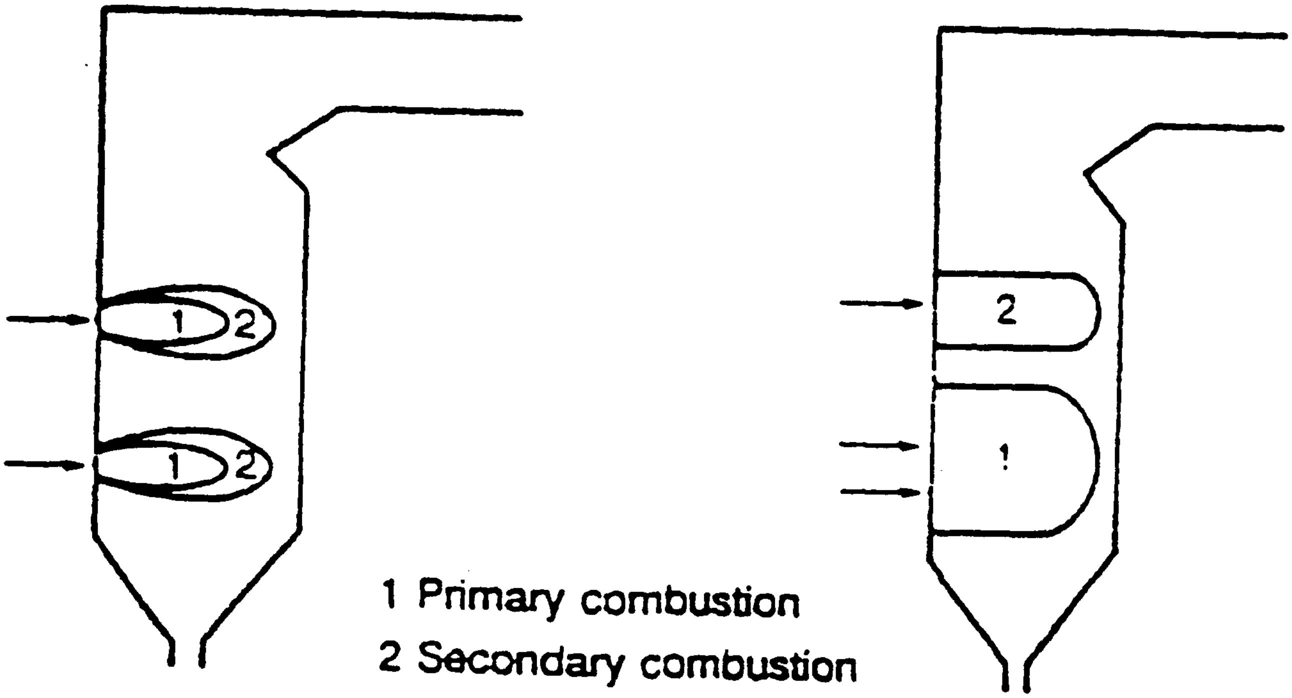
Design Measures

The proper design of a combustion system can significantly reduce NO_x production. Several different types of low NO_x burners are currently in commercial use. They are air staged burners and fuel staged burners.

Air Staging. Air staging operates under the principle of reducing the level of available oxygen in zones where it is critical for NO_x formation. The amount of fuel burned at peak temperature is also minimized. The air can be staged in the furnace, in the burner, or in both. The differences between a burner staging and a furnace staging are shown in Figure 3.

In air staging, the combustion process is split into two steps. In the combustion zone, where the high temperature required for NO_x formation exists, air is reduced. Combustion is completed when more air is added after the combustion zone. The additional air can be added above, below, or on the side of the flame. However, air is generally added in several locations to minimize spot areas of incomplete combustion. This prevents corrosion and slagging (deposition of vitrified particulate matter) in the furnace.

Figure 3. Air Staging in the Burner and the Furnace (Hjalmarsson, 1990).



a burner staging

b furnace staging

Air staging can also be accomplished in the burner. This technique is useful for retrofitting existing plants. Delayed combustion is achieved by varying the introduction of fuel and air. The amount of reactable oxygen is reduced in areas that are critical for NO_x generation. In addition, the quantity of fuel burned at peak temperature is diminished. By staging the addition of air, the fuel is devolatized at low stoichiometry. Under these conditions, fuel nitrogen is more likely to convert to molecular nitrogen than NO_x (Hjalmarsson, 1990).

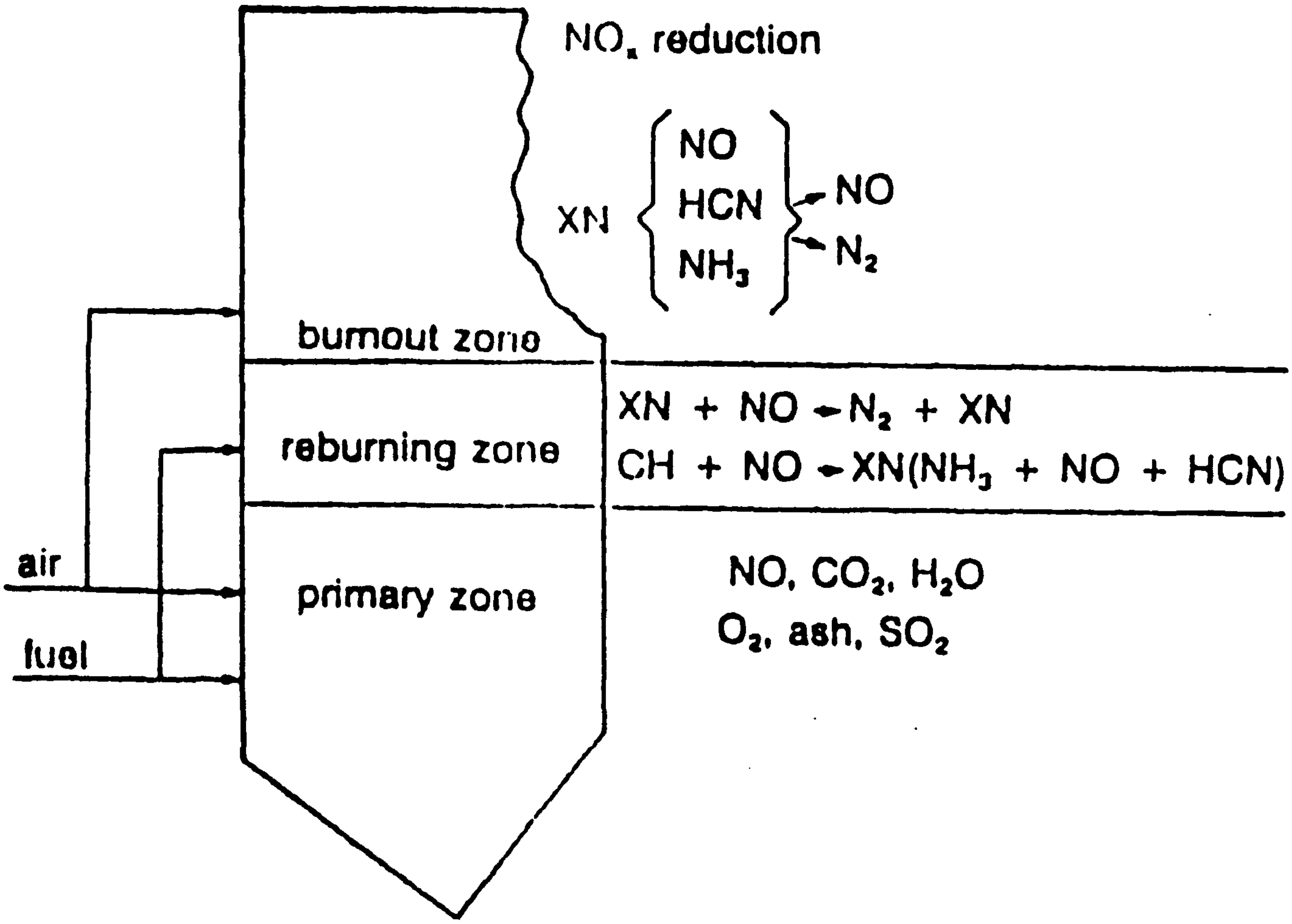
Fuel Staging. Fuel staging converts NO_x created during combustion back to molecular nitrogen. This conversion occurs in the combustion chamber. Fuel staging is accomplished by executing combustion in three zones. In the primary zone, the fuel is burned in an oxidizing or slightly reducing atmosphere. In the next combustion zone, secondary fuel is injected in a reducing atmosphere. As a result, hydrocarbon radicals are produced. These radicals react with nitric oxide which was produced in the primary combustion zone. The desired product of this reaction is molecular nitrogen. Nonetheless, other undesirable volatile nitrogen compounds such as ammonia may also be formed. Combustion is completed in the final, burnout, stage.

Only air is added in this zone. Figure 4 shows the principles of fuel staging.

For fuel staging to succeed, operational conditions must be optimized. For example, excess air should be minimized in the primary zone. In addition, the primary and secondary stages must be separate. This arrangement ensures complete combustion of the fuel. Fuel added in the secondary stage should be injected at as high a temperature as possible. At least 1200°C is required to avoid competing reactions and to ensure sufficient reaction time. Additionally, the secondary stage fuel must be able to easily mix and disperse with the primary combustion gases. Natural gas is often used as the reburning fuel because it has those characteristics. Furthermore, it has low nitrogen content, high energy intensity, facile ignition, and no requirement for a carrier gas (Hjalmarsson, 1990).

Control Systems. Due to their complexity, both air and fuel staging systems require automatic control on an increasing number of parameters. Moreover, the permitted operating range of those parameters is not very large. Operating outside optimal conditions in either system negates the intended NO_x emission reduction.

Figure 4. Principle of Fuel Staging in a Furnace (McCarthy et al., 1990).



Potential Problems. Low NO_x combustion and combustion modifications can cause several problems. For instance, operating conditions such as low combustion temperature and minimal excess air are not conducive to complete combustion. Incomplete combustion increases unburnt carbon in the fly ash. Unburnt carbon can make the fly ash less suitable for resale. If the fly ash cannot be reused, it becomes a hazardous waste problem.

Another problem associated with low NO_x combustion is the increased occurrence of slagging. Slagging reduces the efficiency of the system. It may also increase corrosion and thus shorten plant life. Low NO_x burners' major drawback are their inability to reduce NO_x emissions below legislative limits. While controlling combustion reduces NO_x emissions, some form of flue gas treatment is usually required in addition to the combustion controls (Hjalmarsson, 1990).

POST-COMBUSTION NO_x REMOVAL

There are three basic types of post-combustion control systems. They are selective catalytic reduction, non-selective catalytic reduction, and selective non-catalytic reduction. All three processes chemically reduce the nitrogen in NO_x to molecular nitrogen and water. Since roughly 80% of the earth's atmosphere is molecular nitrogen, the products of these treatment processes can be released directly to the atmosphere without further treatment.

A reduction process is selective if the reagent (usually ammonia) reacts only with NO_x and not with oxygen in the flue gases. Thus, in non-selective reduction processes, some reagent is wasted. While the most widely used NO_x removal processes employ catalysts, a few non-catalytic processes have been recently developed.

Selective Catalytic Reduction

The selective catalytic reduction process was invented in 1959 and has been refined greatly in the last 15 years (Boer et al., 1990). It is currently the dominant technology for NO_x reduction (Hjalmarsson, 1990). With this process, the concentration of NO_x is reduced by injecting ammonia into the flue gas in the presence of a catalyst. The overall reaction for the reduction of nitric oxide is:

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O \qquad (23)$$

The most noteworthy aspect of this reaction is the fact that all the end products are natural constituents of air and no further treatment is required (Boer et al., 1990). The ratio of ammonia to nitric oxide is 1:1. For this process to occur in flue gases, ammonia must be injected into the gas stream. The gases are passed over metal plates coated with a catalyst (Beeckman and Hegedus, 1991).

Catalyst. The catalyst is integral to selective catalytic reduction technology because it ensures that the ammonia reacts only with NO_x gases (Boer et al., 1990). Various materials for the catalyst have been tested. The types that are currently in operation are titanium oxide, zeolite, iron oxide, and activated carbon. Generally, the more active the catalyst, the less selective it is (Hjalmarsson, 1990). The most effective materials have been inorganic oxides and noble metals such as lead and platinum. While reactivity is of primary importance when selecting catalytic material, other properties are also considered. Hydrothermal and chemical stability, resistance to deactivation and abrasion, strength and extrudability are all desirable characteristics (Boer et al., 1990). Currently, the most common type of catalyst is vanadia or tungsten-vanadia on a porous anatase-type titania block.

Titanium oxide-based catalysts consist of activated titanium oxide. Vanadium and tungsten are added as further active components. The amount required depends on flue gas composition and operating conditions. Other additives contribute to an increased resistance to breakage and abrasion. Operating temperature for this catalyst is 270 to 400°C. The catalyst can be adapted to different circumstances by varying the mixture and the manufacturing process. For example, catalysts with a high vanadium oxide content have higher activity, which means higher NO_x reduction rates. However, they also have the disadvantage of higher oxidation rates for sulfur dioxide to sulfur trioxide (Hjalmarsson, 1990).

Zeolite is a porous crystalline solid which has a well defined pore system and a large internal surface area. It consists primarily of a variety of aluminum silicates. The zeolite can be manufactured in granular form and is then used as a bed-type catalyst. It can also be manufactured in monolithic layers in an extruded form. The catalyst can be reused in ceramic production thus eliminating the need for disposal of a hazardous waste. The working temperature for this catalyst is 300 to 430°C. It is possible to store large amounts of ammonia in the catalyst. This capability prevents an immediate increase in excess ammonia in the treated gases if there is an overdose (Hjalmarsson, 1990).

Iron oxide catalysts consist of iron oxide particles with a thin crystalline surface cover of iron phosphate. When the catalyst starts operation in the flue gases it undergoes a transformation and adjusts to the ambient conditions. During transformation, the catalyst converts sulfur dioxide to sulfate. Upon completion of this reaction, the specific area and pore size of the catalyst are changed and the catalyst is primed for nitrogen reduction. The transformation is completed after 50 to 300 hours of operation during which the activity of the catalyst will decrease by 20% or more (Hjalmarsson, 1990).

The iron oxide catalyst has a relatively high operating temperature of 380 to 430°C. The activity of the catalyst increases with increasing temperatures. On the other hand, a substantially greater volume of catalyst is required when iron oxide catalyst is used compared to conventional catalysts. This results in more layers of catalyst which are heavier and bulkier. Disposal of the catalyst is simple since it can be melted along with normal iron at a steel plant (Hjalmarsson, 1990).

Activated carbon may also serve as the catalyst material. It can be used for flue gas desulfurization and denitrification.

These processes may occur separately or in combination. When the process is used for desulfurization, the activated carbon acts as an adsorber for sulfur dioxide.

If the process is used only for NO_x removal, the carbon is placed in an end position, after the desulfurization system. There, the flue gases are reheated to approximately 120°C. Particulate matter must be removed from the flue gases before entering the activated carbon reactor to avoid build up and increase in pressure drop over the reactor. If the carbon is placed before the desulfurization system and the flue gases contain sulfur dioxide, there is a risk that ammonium sulfate may be formed. This chemical destroys the grains of the adsorber and causes clogging in the reactor. Thus, removal of residual sulfur dioxide is required before the NO_x treatment stage. Removal is accomplished by passing the flue gases into a two-stage reactor of activated carbon. The residual sulfur dioxide is removed through adsorption when the flue gases pass through the activated carbon in the first stage. Ammonia is then added to the flue gas before entering the second stage of the bed. Desorption of the sulfur-containing carbon is performed thermally by indirect heating at a temperature of 400 to 450°C. The sulfur-dioxide-rich gas from the desorber is not processed further, but is returned upstream of the desulfurization unit (Marnet, 1987).

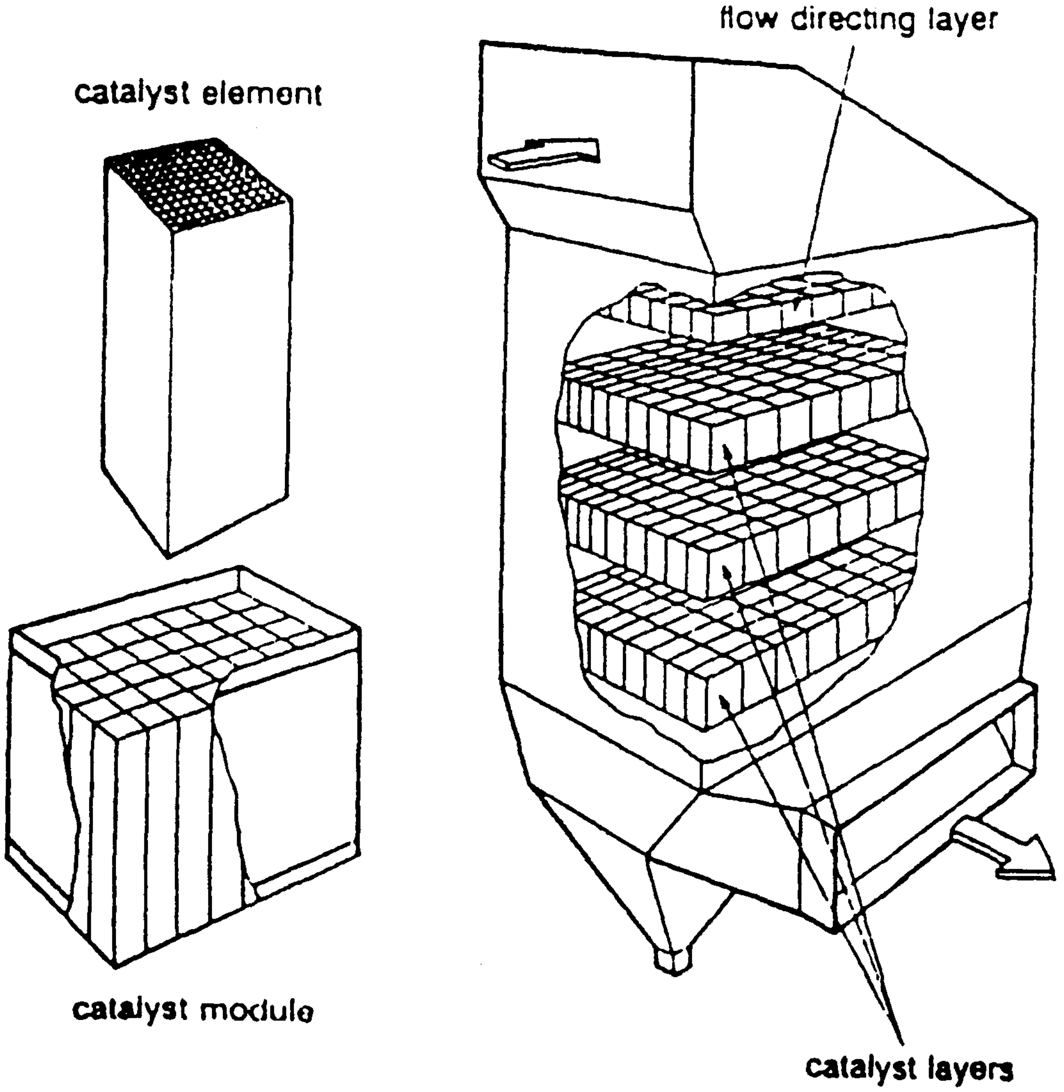
A denitrification rate of 80 to 90% has been obtained with the activated carbon process. This reaction depends on flue gas temperature and the moisture content of the flue gases. The optimal operating temperature is 80 to 100°C. Efficiency starts to decrease when the moisture content is over 7.5% and strongly decreases when over 12%. Heavy metals in the flue gas or dust are completely adsorbed on the carbon (Marnet, 1987).

Geometry. The catalysts used for coal-fired plants are designed mainly for parallel flow and can be characterized as one of two types, plates or extruded. Plate-type catalysts have a metal net as supporter onto which the active substance is applied. The plates can all be corrugated or can be a mixture of level and corrugated plates. Plate types have a higher resistance to deposition and erosion than block types and are mainly used for high dust installations. The key geometric parameter is the distance between plates.

The extruded, or block, type of catalyst is self-supporting and can be formed square or as a honeycomb. The principal parameter for a block is usually the wall thickness. The block itself is typically 70 to 100 cm long with a cross sectional area of 15 cm by 15 cm. It is formed into square channels 0.3 to 1.0 cm wide with walls 0.005 to 0.15 cm thick (Beeckman and Hegedus, 1991). Figure 5 shows a typical block catalyst.

Lifetime. At present, typical catalyst lifetime is three to four years (Boer et al., 1990). A catalyst may be deactivated by several mechanisms. For instance, physical deactivation is caused by the deposition of fly ash and undesirable ammonia byproducts such as ammonium bisulfate. The catalyst pores can be blocked by deposition of solids through capillary condensation or by small particles. Condensation can also be caused by ammonium bisulfate. The formation of ammonium bisulfate depends on the flue gas temperature, sulfur trioxide and ammonia concentration. Once ammonium bisulfate has been formed it may be decomposed by increased temperature. When the temperature is above 350°C, the conversion rate of sulfur dioxide to sulfur trioxide increases exponentially with temperature for most types of catalyst when they are placed upstream of desulfurization equipment. Fly ash contains water soluble substances. When the system is taken off line, it cools and water vapor condenses on the surfaces of the catalyst. The soluble constituents of the fly ash may then dissolve and reduce the activity of the catalyst (Hjalmarsson, 1990).

Figure 5. Typical Block Catalyst (Beeckman and Hegedus, 1991).



Hydrothermal sintering, the agglomeration of minerals caused by heating, can also cause fouling. High temperature is the reason for this problem. Sintering can destroy the micro-surface of the catalyst. In addition, catalyst pore volume may be reduced (Hjalmarsson, 1990).

Fly ash can physically abrade the catalyst surface, thus removing reaction sites. Uneven particulate concentration and size distribution can also cause erosion problems.

The catalyst may also be chemically deactivated by alkali or arsenic compounds, or alkaline earth oxides (Boer et al., 1990). Alkali ions such as sodium, potassium, calcium and magnesium can poison catalysts. When these elements are in sulfated form, they are particularly destructive. Fly ash with a sodium and potassium content as low as 4% by weight can cause catalyst poisoning (Hjalmarsson, 1990).

Arsenic in gaseous form has also been found to poison catalysts. Besides the arsenic content in coal, the type of firing and the calcium oxide content in the fly ash affect the concentration of arsenic in the flue gases. The first and most evident cases of catalyst poisoning were found under the special conditions arising in wet bottom boilers with ash recycling. The ash recycling leads to an enrichment of arsenic in the flue gases. The arsenic content in the flue gases can increase a thousand fold if all the fly ash is recycled. Selenium has been found to have the same poisonous effect on catalysts as arsenic (Hjalmarsson, 1990).

Ammonia Supply. Before the ammonia is injected into the flue gas, it is vaporized by either hot water or steam or, in small plants, by electricity. The evaporated ammonia is subsequently combined with air in a mixing chamber. A partial flow of the combustion air (approximately 1% by volume) is used for mixing. The mix consists of less than 5% ammonia. The combination of air and ammonia must also be thorough to produce an even concentration of ammonia. The pressure of the mixing air should also be monitored because the ammonia and air mixture is explosive in the region of 15 to 27% ammonia (Hjalmarsson, 1990).

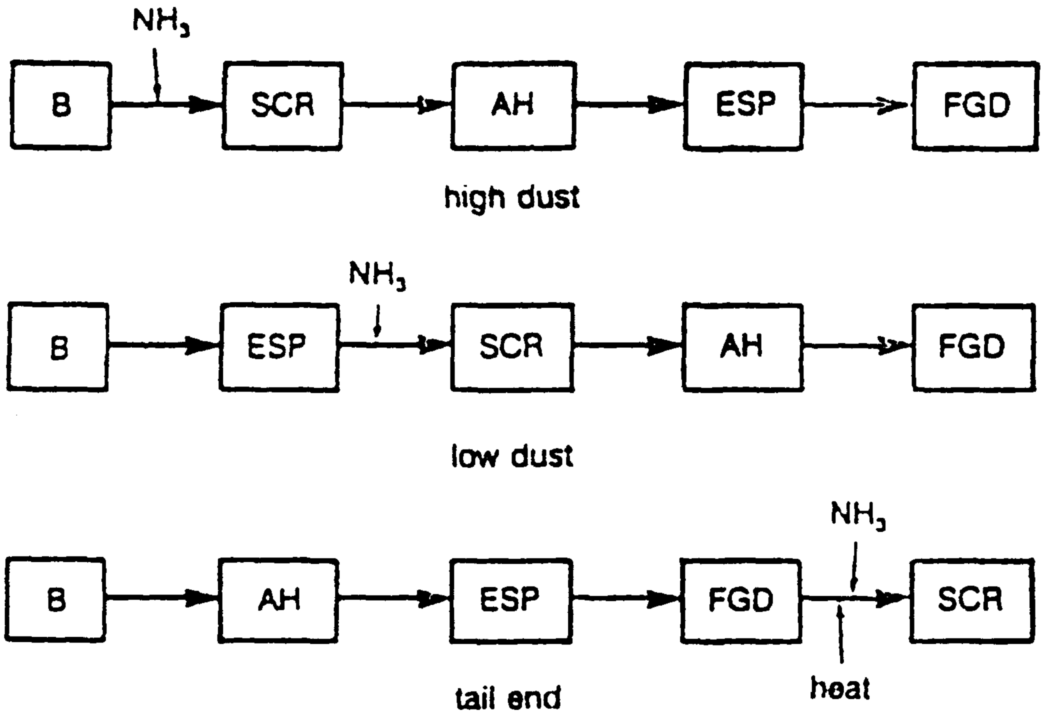
Ammonia injection is done through nozzles arranged in a grid pattern covering the whole flue gas duct. To enable high NO_x reduction and avoid any unreacted ammonia in the treated flue gases, the ammonia distribution must correspond to the NO_x concentration profile in the flue gases at the inlet of the catalyst. Injection precision is achieved by having plenty of individually controlled nozzles. A long mixing chamber for the flue gases and the ammonia is also beneficial (Hjalmarsson, 1990).

As an extremely toxic substance at high concentration, ammonia for the selective catalytic reduction must be carefully transported and handled. Ammonia in concentrated form can be stored either in pressurized tanks or in cooled tanks. Normally, pressurized systems are used to transport and store concentrated ammonia (Hjalmarsson, 1990).

Process Placement. The catalyst may be placed before or after removal of fly ash and sulfur dioxide gas. Placing the catalyst before the removal of other contaminants exposes the catalyst to abrasion and poisoning. On the other hand, the flue gases do not require costly reheating prior to passing through the catalyst (Boer et al., 1990).

When the catalyst is placed after electrostatic precipitators and sulfur dioxide removal equipment, it is less likely to suffer physical or chemical damage. Its life can thus be greatly extended. Additionally, the catalyst can have greater geometric surface area. However, while costs due to the catalyst are reduced, energy costs increase because reheating flue gases is necessary in this type of setup (Boer et al., 1990). Figure 6 shows the various ways the processes may be arranged.

Figure 6. Selective Catalytic Reduction Process Placement (Hjalmarsson, 1990).



B = boiler
AH = air preheater
ESP = electrostatic precipitator (or other particulate collector)
SCR = selective catalytic reduction
FGD = flue gas desulphurisation

Cost. Selective catalytic reduction of NO_x increases the cost of electricity by 5% (Gouker et al., 1989). The major costs associated with selective catalytic reduction are capital investment and operation. Both expenditures are directly related to catalyst performance and longevity. Proper catalyst design can minimize these costs (Boer et al., 1990).

The greatest disadvantage of selective catalytic reduction is its cost. About 50% of the total (capital and maintenance) cost of these NO_x reduction systems is associated with the catalyst (Boer et al., 1990). Catalysts are expensive and need to be replaced periodically. Nonetheless, it is one of the few technologies that can achieve greater than 80% removal of NO_x (White and Maibodi, 1991).

Non-Selective Catalytic Reduction

Non-selective catalytic reduction systems, also known as three-way conversion catalyst systems, reduce NO_x, unburnt fuel, and carbon monoxide at the same time. To operate correctly, the combustion process must be at an air-to-fuel ratio which is less than stoichiometric. Under this condition and in the presence of a catalyst, the oxides of nitrogen are reduced by the carbon monoxide, forming nitrogen and carbon dioxide (Campbell et al., 1991).

Non-selective catalytic reduction systems generally use the following reaction to reduce NO_x:

$$2\ CO + 2\ NO \rightarrow 2\ CO_2 + N_2 \tag{24}$$

catalyst used to promote this reaction is usually a mixture of platinum and rhodium. The catalyst operating temperature limits are 700 to 1500°F, with 800 to 1200°F being the most desirable. Temperatures above 1500°F result in catalyst sintering (Campbell et al., 1991).

Typical NO_x conversion ranges from 80 to 95% with corresponding decreases in carbon monoxide and unburnt carbons. Potential problems associated with non-selective catalytic systems include catalyst poisoning and inadequate control systems (Campbell et al., 1991).

Selective Non-Catalytic Reduction

While selective catalytic reduction has proven highly effective in decreasing NO_x emissions, it is an expensive process which costs \$60 to \$100 per kilowatt. Selective non-catalytic reduction, on the other hand, costs \$5 to \$15 per kilowatt

(Roberts, 1991). However, without a catalyst, NO_x reductions of only 30 to 40 percent are usually achieved (Kokkinos et al., 1991). In selective non-catalytic reduction, ammonia or aqueous urea is injected into the combustion gases. These chemicals may react with nitric oxide and oxygen in two ways. As with catalytic reduction, the first reaction is:

$$2\ NO + 4\ NH_3 + 2\ O_2 \rightarrow 3\ N_2 + 6\ H_2O \qquad (25)$$

The second possible reaction is:

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O \qquad (26)$$

Reaction (26) is clearly undesirable because its product is more nitric oxide. The variable that decides the dominant reaction is temperature. Below 870°C, neither reaction occurs significantly. Above 1200°C, reaction (26) dominates the system. Reaction (25), the desired process, predominates between 870°C and 1040°C. The optimal temperature is approximately 950°C (Campbell et al., 1991).

Aside from temperature, the selective non-catalytic reduction process is affected by the mixing of urea with the combustion gases. Other factors, such as boiler design, operating conditions, and urea process variables, do not affect the efficiency of NO_x removal (Kokkinos et al., 1991).

An alternative method of selective non-catalytic reduction is the proprietary NOxOUT Plus process. The developer, Nalco FuelTech, claims that the technique can achieve up to 80% reduction of NO_x emissions. The process involves injecting urea instead of ammonia, as well as other proprietary chemicals, into the flue gases. The system is suitable for retrofit, and like most selective catalytic reduction and selective non-catalytic reduction processes, may be combined with combustion modification (Roberts, 1991).

COMBINED SO_x AND NO_x REMOVAL

As previously discussed, one of the problems in post-combustion removal of NO_x is placement of the removal equipment in relation to desulfurization equipment. Both particulate matter and sulfur oxides can interfere with nitrogen reduction processes. By combining SO_x and NO_x removal into one process, this problem, and several others, can be resolved.

A variety of techniques for combined SO_x and NO_x removal have been explored. These processes can be divided into two groups: wet processes and dry processes. Dry removal methods use activated carbon, irradiation, integrated catalytic reduction and absorption, and spray drying. Wet methods use complexing ions, oxidation and absorption, ammonia and ozone, and nitric oxide and sulfuric acid. Wet methods are not in widespread commercial use, however, and they will not be discussed in this paper.

Activated Carbon

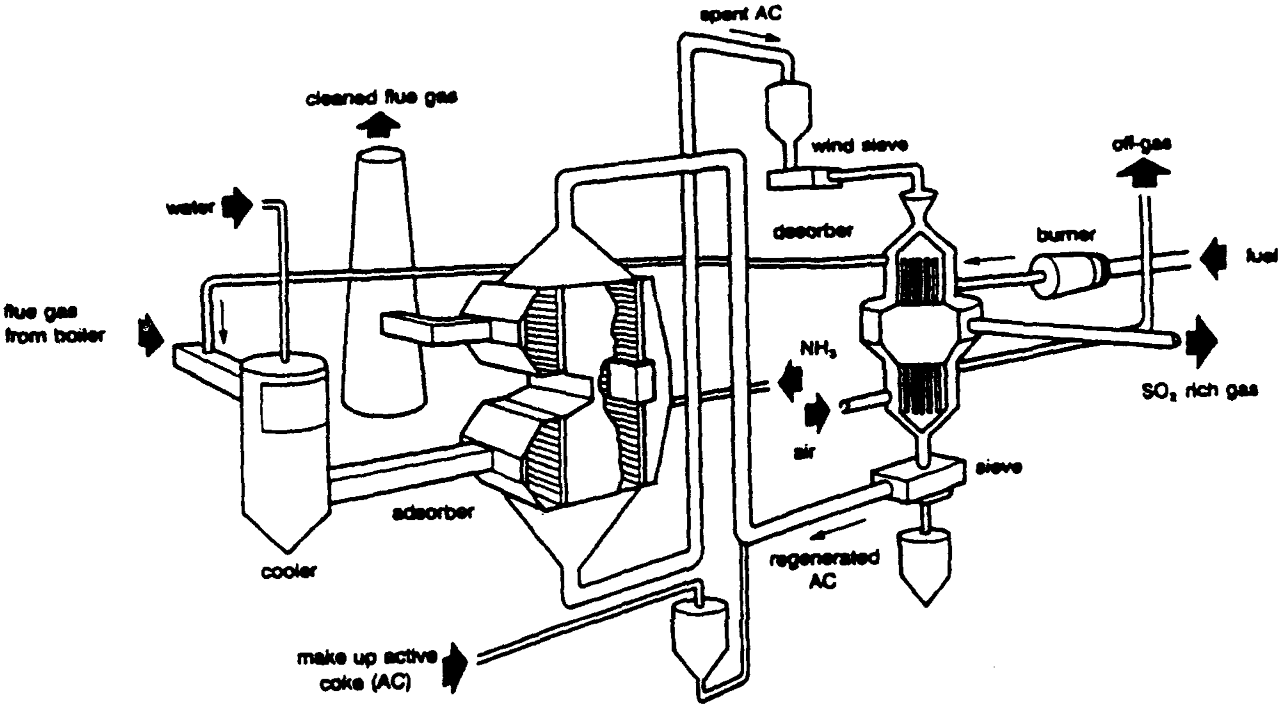
The activated carbon process can be used for flue gas desulfurization and flue gas denitrification separately or in combination. When used in combination, the flue gases from the particulate control system enter the first stage of the activated carbon bed at temperature of 90 to 150°C. Sulfur dioxide undergoes catalytic oxidation with the moisture in the flue gases to form sulfuric acid and the sulfuric acid is adsorbed on the activated carbon. Ammonia is then injected into the flue gases in a mixing chamber before the flue gases enter the second stage. In the second stage nitric oxide reacts catalytically with the ammonia to form molecular nitrogen and water. These processes take place in a reactor where the activated carbon is transported from top to bottom in the form of a moving bed while the gas flows across the layers, entering the first and lowest part of the bed (see Figure 7). Desorption of the sulfur-containing carbon is performed thermally by indirect heating at a temperature of 400 to 450°C. The sulfur dioxide rich gas thus obtained can be further processed to pure sulfur, sulfuric acid or liquid sulfur dioxide (Neumann, 1987). Removal of 98% for sulfur dioxide and up to 80 percent for NO_x have been obtained in pilot plants using this system (Hjalmarsson, 1990). The performance of activated carbon depends upon flue gas temperature, sulfur dioxide and NO_x inlet concentrations, quantity of activated carbon transferred, ammonia-to-sulfur dioxide ratio, volume of treated gas to volume of activated carbon, and ammonia-to-NO_x ratio.

In practice, activated carbon systems have had a number of operating problems. Overheating has been a problem in both the activated carbon and the desorber. Corrosion and plugging in the regenerator and the piping system have also been experienced. Additionally, uneven distribution in the adsorber also decreases operating efficiency (Hjalmarsson, 1990).

Catalytic Absorption

In combined catalytic absorption, flue gases from the particulate controller enter a catalyst reactor for NO_x reduction

Figure 7. Activated Carbon Process for Combined SO_x/NO_x Reduction, (Richter, 1989).



similar to those used in selective catalytic reduction plants. The flue gases are then heated to 400 to 420°C before entering another catalyst reactor for oxidizing sulfur dioxide to sulfur trioxide. In the presence of the sulfur catalyst, any ammonia slip from the nitrogen reduction process is oxidized to molecular nitrogen. The flue gases are further cooled by ambient air in a sulfuric acid condenser. The sulfuric acid is a saleable byproduct of the process. Both NO_x and sulfur dioxide are reduced by at least 95% (Hjalmarsson, 1990).

In addition to the tested technologies, there are a few emerging technologies under development such as electron beam irradiation and copper oxide flue gas desulfurization. These techniques can potentially remove 80 to 95% of sulfur oxides and 55 to 95% of NO_x (White and Maibodi, 1991). Irradiation uses electron beams as an energy source for excitation or the necessary ions to initiate the reduction reactions (Hjalmarsson, 1990).

COSTS

The cost of NO_x controls varies for many reasons. The main source of variation in costs is the technological basis for design. The first determination of cost is whether the system will be built into a new plant or retrofitted into an existing one. The size of the plant can affect both capital and maintenance expenditures. Another cost driver is strict regulatory requirements which may demand an expensive selective catalytic reduction system because this type of system can meet stringent standards most reliably. System byproducts can also influence the overall NO_x control price tag. If the byproducts are usable and saleable, pollution control costs may be defrayed. However, if the byproducts are another form of pollutant or hazardous waste, costs can only increase.

Generally speaking combustion measures are the least costly NO_x reduction technology. They achieve up to 50% removal efficiency. Selective non-catalytic reduction is more costly, but can reach up to 70 to 80% reduction of NO_x under favorable conditions. Selective catalytic reduction is significantly more expensive than the other systems because of the catalyst. Nevertheless, NO_x reduction rates of more than 90% are attainable. Moreover, as the technology is refined and dispersed, its price has dropped appreciably. The cost of current selective catalytic reduction systems is about one-third the cost of first generation systems (Hjalmarsson, 1990).

CONCLUSION

Oxides of nitrogen can be effectively eliminated from power plant flue gases by several techniques. Altering the combustion process is integral to minimizing NO_x emissions. However, the combustion process is the heart of power plant operations and must be built into the plant from the start. Nonetheless, some adjustment of existing plants can usually achieve a measurable, albeit small, reduction of NO_x emission (Campbell et al., 1991). The best results appear to be combining combustion control techniques with flue gas NO_x reduction. Usually, it is most cost effective to reduce the NO_x level as far as possible through combustion modification and thus keep down the reduction rate required for gas treatment.

Post-combustion treatment, on the other hand, is a relatively easy NO_x reduction method to retrofit on existing power plants. It is, furthermore, the only technique which sufficiently reduces NO_x to levels required by emission standards. These two facts explain why end-of-process NO_x treatment is so prevalent. Of the various methods of post-combustion NO_x removal, selective catalytic reduction is currently the choice removal mechanism because of decreasing costs, refinement of the technology, and high NO_x removal efficiency (Boer et al., 1990).

Combined desulfurization and denitrification processes are not yet in widespread commercial use. However, several combustion technologies show promising results and will probably proliferate as emission standards for both pollutants tighten.

An important consideration in the choice of emission control systems is to avoid producing new pollutants. For example, some systems create wastes that have a potential to leach, thus producing contaminated waste water. Others generate additional atmospheric emissions like ammonia or carbon dioxide. In the future, total optimization of the whole power plant will become essential. Both plant efficiency and emission control must be taken into account. Ultimately, the result will be the integration of combustion and emission controls.

APPENDIX A

UNIT ABBREVIATIONS

Abbreviation	**Unit**
atm	atmosphere
cm	centimeter
m	meter
mg	milligram
MW	megawatt
ppbv	parts per billion by volume
ppm	parts per million
pptv	parts per trillion by volume

APPENDIX B

SUMMARY OF REACTIONS

Nitrous Oxide Reactions in the Atmosphere

$$N_2O \xrightarrow{\text{light}} N_2 + O\cdot$$

$$N_2O + O\cdot \rightarrow 2\ NO$$

$$N_2O + O\cdot \rightarrow N_2 + O_2$$

Nitric Oxide Reactions in the Atmosphere

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

$$NO + HO_2\cdot \rightarrow NO_2 + OH\cdot$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$RO_2\cdot + NO \rightarrow RO\cdot + NO_2$$

Nitrogen Dioxide Reactions in the Atmosphere

$$NO_2 \xrightarrow{\text{light}} NO + O\cdot$$

$$O\cdot + O_2 \rightarrow O_3$$

Nitric Acid Production in the Atmosphere

$$NO_2 + OH\cdot \rightarrow HNO_3$$

Nitrous Acid Production in the Atmosphere

$$2\ NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

$$NO_2 + NO + H_2O \rightarrow 2\ HNO_2$$

$$NO + OH\cdot \rightarrow HNO_2$$

Peroxyacyl Nitrate and Ozone Production in the Atmosphere

$$CH_3COO_2 + NO_2 + M \rightarrow CH_3COO_2NO_2 + M$$

$$O + O_2 + M \rightarrow O_3 + M$$

The Zeldovich Mechanism

$$O_2 + \text{heat} \rightleftharpoons 2\ O$$

$$O + N_2 \rightleftharpoons NO + N$$

$$N + O_2 \rightleftharpoons NO + O$$

$$N_2 + O_2 \rightleftharpoons 2\ NO$$

Nitric Oxide - Nitrogen Dioxide Equilibrium

$$2\ NO + O_2 \rightleftharpoons 2\ NO_2$$

Nitric Oxide Reduction

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$$

$$2\ CO + 2\ NO \rightarrow 2\ CO_2 + N_2$$

$$2\ NO + 4\ NH_3 + 2\ O_2 \rightarrow 3\ N_2 + 6\ H_2O$$

Ammonia Oxidation

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$$

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