Nitrogen Oxides (NO_x) Control:

There are a number of oxides of nitrogen, including nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), nitrogen trioxide (N_2O_3), and nitrogen pentoxide (N_2O_5), that are referred to collectively as NO_x. The two oxides of nitrogen that are of primary concern to air pollution are NO and NO_2. NO is a colorless gas that is a precursor to NO_2 and is an active compound in photochemical reactions that produce smog. NO_2 is a reddish brown gas that gives color to smog and can contribute to opacity in flue gas plumes from stacks. NO_2 is a precursor to nitric acid, HNO_3, in the atmosphere and is a major contributor to acid rain, although less important than SO_2. Nitric acid contributes only one proton per molecule, while sulfuric acid has two protons per molecule, and mass emissions of sulfur compounds are larger than oxides of nitrogen.

Finally, NO_x and volatile organic compounds react photochemically in a complex series of reactions to produce smog, which includes ozone, NO_2, peroxyacetyl nitrate, peroxybenzoyl nitrate, and other trace oxidizing agents. By far the largest source of NO_x is combustion, although there are other industrial sources such as nitric acid manufacturing. The large amount of NO_x generated at coal-fired electric motor vehicles and other forms of transportation, including ships, airplanes, and trains, is pronounced. Preventing an increase in total NO_x emissions can be attributed to the increased use of NO_x controls, especially in automobiles and in industrial fuel consumption.

NO_x FROM COMBUSTION:

NO_x is generated during combustion from three mechanisms:

1- Thermal NO_x

2- prompt NO_x

3- Fuel NO_x

Understanding these mechanisms enables one to utilize control methods for NO_x emissions.

Thermal NO_x:

The thermal NO_x mechanism was first proposed by Zeldovich and involves radicals to produce the overall reaction of combining oxygen and nitrogen:

$$O_2 \leftrightarrow 2O \quad (1)$$
$$O + N_2 \leftrightarrow NO + N \quad (2)$$
$$N + O_2 \leftrightarrow NO + O \quad (3)$$
$$N_2 + O_2 \leftrightarrow 2NO \quad (4)$$

The overall reaction that produces NO_2 is

$$NO + ½\ O2 \leftrightarrow NO_2$$

Both thermodynamics and kinetics are important to the formation of thermal NO_x, so both concentration and temperature influence the amount of NO_x produced.

Prompt NO_x:

NO_x concentrations near the flame zone for hydrocarbon fuels demonstrate less temperature dependence than would be expected from the thermodynamic and kinetics considerations of the Zeldovich mechanism discussed above for thermal NO_x. Near the flame zone, radicals such as O and OH enhance the rate of NO_x formation. Hence, some NO_x will form despite aggressive controls on flame temperature and oxygen concentration.

Fuel NO_x:

Some fuels contain nitrogen, for example, ammonia or organically bound nitrogen in hydrocarbon compounds. For coal-fired burners, fuel NO_x typically falls in the range of 50%–70% of the total NO_x emissions. Nitrogen in the fuel reacts with oxygen regardless of the flame temperature or excess oxygen concentration in the combustion air. Carbon–nitrogen bonds are broken more easily than diatomic nitrogen bonds, so fuel NO_x formation rates can be higher than thermal NO_x. Combustion control techniques that aim at reducing thermal NO_x formation by reducing flame temperature may not be effective for fuels that have high nitrogen content.

CONTROL TECHNIQUES FOR NO_x Emissions:

Two primary categories of control techniques for NO_x emissions are (1) combustion controls and (2) flue gas treatment. Very often more than one control technique is used in combination to achieve desired NO_x emission levels at optimal cost.

COMBUSTION CONTROL TECHNIQUES:

A variety of combustion control techniques are used to reduce NO_x emissions by taking advantage of the thermodynamic and kinetic processes. Some reduce the peak flame temperature; some reduce the oxygen concentration in the primary flame zone; and one, reburn, uses the thermodynamic and kinetic balance to promote reconverting NO_x back to nitrogen and oxygen.

1- Low Excess Air Firing:

Combustors tend to be easier to operate when there is plenty of oxygen to support combustion, and operators like to adjust the air-to-fuel ratio to produce a stable and hot flame. By simply cutting back the amount of excess air, the lower oxygen concentration in the flame zone reduces NO_x production. Tuning the combustion air requires minimal capital investment, possibly some instrumentation and fan or damper controls, but it does require increased operator attention and maintenance to keep the system in optimal condition.

Depending on the prior operating conditions, combustion air tuning can produce NO_x reduction of 0%–25%. Applying advanced optimization systems at four coal-fired power plants resulted in NO_x emission reductions from 15% to 55%.

2- Overfire Air:

The primary flame zone can be operated fuel-rich to reduce oxygen concentration, then additional air can be added downstream. This overfire air provides oxygen to complete combustion of unburned fuel and oxidizes carbon monoxide to carbon dioxide, creating a second combustion zone. Because there is so little fuel in this overfire zone, the peak flame temperature is low. Thus, NO_x formation is inhibited in both the primary and overfire combustion zones.

3- Flue Gas Recirculation:

In this technique, some of the flue gas, which is depleted in oxygen, is recirculated to the combustion air. This has two effects: (1) the oxygen concentration in the primary flame zone is decreased and (2) additional nitrogen absorbs heat, that is, acts as a heat sink, and reduces the peak flame temperature.

4- Reduce Air Preheat:

Combustion air often is preheated in a recuperator with the heat from the flue gas. This conserves energy by recovering the heat in the flue gas. However, it also raises the peak flame temperature because the combustion air absorbs less heat from the combustor prior to reacting with the fuel. Reducing air preheat lowers the flame temperature to reduce the formation of thermal NO_x.

5- Reduce Firing Rate:

Peak flame temperature is determined by the complete heat balance in the combustion chamber, including radiant heat losses to the walls of the chamber. Reducing both air and fuel proportionately would result in the same flame temperature if only fuel, air, and combustion products were considered. However, reducing fuel and air in a fixed size chamber results in a proportionately larger heat loss to the chamber walls and peak flame temperature is reduced.

6- Water/Steam Injection:

Injecting water or steam into the combustion chamber provides a heat sink that reduces peak flame temperature. However, a greater effect is believed to result from the increased concentration of reducing agents within the flame zone as steam dissociates into hydrogen and oxygen. Compared to standard natural draft, in natural gas-fired burners, up to 50% NO_x reduction can be achieved by injecting steam at a rate up to 20%–30% of the fuel weight.

7- Burners out of Service:

In a large, multiburner furnace, selected burners can be taken out of service by cutting their fuel. The fuel is redistributed to the remaining active burners, and the total fuel rate is not changed. Meanwhile, combustion air is unchanged to all burners. This becomes an inexpensive way to stage the combustion air. The primary flames operate fuel-rich and depleted in oxygen, reducing NO_x formation. Test results on a coal-fired boiler demonstrated NO_x emission reduction of 15%–30%.

8- Reburn:

A second combustion zone after the primary flame zone can be established by adding additional hydrocarbon fuel outside of the primary flame zone. NO_x is reduced by reaction with hydrocarbon radicals in this zone. Overfire air is added after reburn to complete the combustion process at a low temperature flame. Results from five coal-fired boilers from 33 to 158 MW net capacities show NO_x reduction from baseline levels of 58%–77%.

Flue Gas Treatment Techniques:

1- Selective Noncatalytic Reduction:

Selective noncatalytic reduction (SNCR) uses ammonia (NH_3) or urea (H_2NCONH_2) to reduce NO_x to nitrogen and water. The overall reactions using ammonia as the reagent are as follows:

$$2NH_3 + 2NO_2 + \frac{1}{2} O_2 \leftrightarrow 2N_2 + 3H_2O \qquad 1600 - 1900^oF$$

$$2NH_3 + 2NO_2 + O_2 + H_2 \leftrightarrow 2N_2 + 3H_2O \qquad 1300 - 1900^oF$$

The intermediate steps involve amine (NH_i) and cyanuric nitrogen (HNCO) radicals. When urea is used, it first dissociates to the primary reactants of ammonia and isocyanic acid.

No catalyst is required for this process; just good mixing of the reactants at the right temperature and some residence time. The key to this process is operating within the narrow temperature window. Sufficient temperature is required to promote the reaction. At higher temperatures, ammonia oxidizes to form more NO, thereby wasting ammonia reagent and creating the pollutant that was intended to be removed. Above 1900°F, this reaction dominates:

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

2- Selective Catalytic Reduction:

A catalyst bed can be used with ammonia as a reducing agent to promote the reduction reaction and to lower the effective temperature. An SCR system consists primarily of an ammonia injection grid and a reactor that contains the catalyst bed. The following reactions result in reducing NO_x in an SCR system. Reaction 1 is dominant. Since the NO_2 concentration in the flue gas from combustion systems usually is low, then reactions in Equations 3 through 5 are not particularly significant to the overall NO_x reduction or to the reagent requirement.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad 1$$

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \qquad 2$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad 3$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \qquad 4$$

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \qquad 5$$

A variety of catalyst types are used for SCR. Precious metals are used in the low temperature ranges of 350°F–550°F. Vanadium pentoxide supported on titanium dioxide is a common catalyst for the temperature range of 500°F–800°F. Zeolites, which are various aluminosilicates, are used as high temperature catalysts in the range of 850°F–1100°F. SCR systems are capable of 70%–90% NO_x reduction. In the common power generation application of gas-fired turbines, less than 5 ppm NO_x at 15% O_2 can be achieved.

3- Low Temperature Oxidation with Absorption:

A recently commercialized, proprietary technology for NO_x removal is low temperature oxidation of NO_x species to highly soluble N_2O_5, followed by absorbing the N_2O_5 in a wet absorption tower. Ozone is used as the oxidizing agent for the reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad 1$$

$$NO_2 + O_3 \rightarrow N_2O_5 + O_2 \qquad 2$$

$$N_2O_5 + H_2O \rightarrow HNO_3 \qquad 3$$

Oxidation with ozone takes place at a low temperature of about 300°F, in the temperature range after the combustion air heater and/or economizer in a typical boiler. At high temperatures above 500°F, ozone decomposes rapidly. Ozone can be generated from either ambient air or pure oxygen. The absorption step is accomplished in a spray tower. Caustic is used to neutralize the nitric acid that is formed.

Kinetics is a key to this process. Oxidation of NO_2 is faster than oxidation of NO; therefore, NO_2 concentration is not increased. Also, competing oxidation reactions with CO and SO_2 in combustion exhaust gases are relatively slow and do not compete for ozone consumption.

$$CO + O_3 \rightarrow CO_2 + O_2 \qquad 4$$

$$SO_2 + O_3 \rightarrow SO_3 + O_2 \qquad 5$$

An advantage of this process over other downstream treatment processes is very high NO_x removal efficiency, with 99% removal being reported for an industrial boiler.

4- Catalytic Absorption:

A proprietary catalytic absorption technology called $SCONO_x$ also has been commercialized recently. The system utilizes a single catalyst for removal of both NO_x and CO. First, NO, CO, and hydrocarbons are oxidized to NO_2 and CO_2. Then NO_2 is absorbed in a coating of potassium carbonate on the catalyst.

$$2NO_2 + K_2CO_3 \rightarrow CO_2 + KNO_2 + KNO_3$$

After the carbonate coating has been depleted, it is regenerated by passing a dilute stream of hydrogen and carbon dioxide over the catalyst in the absence of oxygen.

$$KNO_2 + KNO_3 + 4H_2 + CO_2 \rightarrow K_2CO_3 + 4H_2O + N_2$$

The process can operate effectively at temperatures ranging from 300°F to 700°F. Significant advantages of this process include the simultaneous removal of CO, hydrocarbons, and NO_x to very low levels, and the lack of ammonia storage and emissions.

5- Corona-Induced Plasma:

Non-thermal plasma consists of ionized gas that can be generated by corona-discharge reactors or electron beams. Plasmas produce chemically active radicals that can oxidize NO to NO_2 and N_2O_5. As discussed above, these NO_x species are water soluble and can be removed by absorption.

Control of SO_x

We will focus primarily on sulfur dioxide emissions because they are the largest source of sulfur emissions and the primary contributor to acid rain. Other forms of sulfur emissions are H_2S, SO_3, and sulfuric acid mist.

Sulfur occurs naturally in fuels. In coal, it is bound as iron pyrite, FeS_2, mineral sulfates, elemental sulfur, and in organic compounds and mercaptans. High sulfur coals typically contain 2%–5% sulfur. Low sulfur coals have less than 1% sulfur. Besides burning coal, sources of sulfur emissions include petroleum refining, oil and gas production, sulfur and sulfuric acid manufacturing, ore smelting, waste incineration, and petroleum coke calcining.

Sulfur emissions as a source of air pollution can be avoided by using processes that remove sulfur from coal before it is burned. Washing coal removes some of the mineral sulfur, sometimes as much as 30%–50% of sulfur in coal. But washing can be a relatively costly process.

H_2S CONTROL

H_2S is a common pollutant in oil and natural-gas processing facilities. Many facilities have sulfur recovery units that convert H_2S to elemental sulfur using the Claus process. In this two-step process, a fraction of the H_2S is burned to SO_2. The combustion process must be carefully controlled to obtain the correct molar ratio of 2 moles of H_2S for every mole SO_2. The second step is to pass the mixture of H_2S and SO_2 over catalyst, where H_2S is oxidized and SO_2 is reduced to produce elemental sulfur by the reaction:

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

A 93%–97% sulfur recovery can be obtained with the Claus process.

SO_2 REMOVAL

A- Calcium-Based Reactions:

Limestone is an inexpensive rock that is quarried and crushed. It can be used directly as a reagent either in an aqueous slurry or by injection into a furnace, where the heat decarbonates the limestone. Quicklime is produced by calcining limestone, so quicklime is more expensive than limestone because of the high energy requirement for calcination.

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$$

Slaking or hydrating quicklime produces more expensive slaked or hydrated lime:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Wet limestone scrubbing produces calcium sulfite and calcium sulfate reaction products. Oxidation of sulfite to sulfate can be inhibited by adding emulsified sulfur, which forms the thiosulfite ion. Alternatively, oxidation can be enhanced by blowing air into the slurry in the reactor holding tank.

$$CaCO_3 + SO_2 + \frac{1}{2} H_2O \rightarrow CaSO_3 \bullet \frac{1}{2} H_2O + CO_2$$

$$2CaSO_3 \bullet \frac{1}{2} H_2O + 3H_2O + O_2 \rightarrow 2CaSO_4 \bullet 2H_2O$$

Wet lime scrubbing, lime spray drying, and hydrated lime processes also form a mixture of calcium sulfite and sulfate reaction products:

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 \bullet \frac{1}{2} H_2O + \frac{1}{2} H_2O$$

$$Ca(OH)_2 + SO_2 + O_2 + \frac{1}{2} H_2O \rightarrow CaSO_4 \bullet 2H_2O$$

B- Sodium-Based Reactions:

1. Wet Sodium-Based Scrubbers:

Either soda ash(Na_2CO_3) or caustic soda(NaOH) may be used as reagents. They produce a clear scrubber liquor solution with a high pH. The two reagents often are cost competitive with each other on a weight basis, although soda ash tends to be a little less expensive. Caustic soda and soda ash solutions can be used interchangeably in most scrubbers. Caustic soda typically is sold as a 50% solution with pricing on a dry ton NaOH basis. Soda ash is dissolved in water to make the scrubber liquor solution:

Na_2CO_3 (s) + H_2O → $2Na^+$ (aq) + $CO_3^=$ (aq) + H_2O

$CO_3^=$ (aq) + H_2O ↔ HCO_3^- (aq) + OH^-

Caustic soda typically is sold as a 50% solution, which eliminates the need for solid-handling equipment.

NaOH (s) + H_2O → Na^+ (aq) + OH^- + H_2O

The first step in alkaline scrubbers is absorption of SO_2 into the aqueous solution. The alkalinity keeps the following equilibrium reactions progressing to the right, which prevents buildup of sulfurous acid from limiting the solubility of gaseous SO_2:

SO_2(g) +H_2O ↔ H_2SO_3 (aq)

Sulfurous acid dissociates to form bisulfite or sulfite, depending on the pH:

H_2SO_3 (aq) ↔ HSO_3^- + H^+ ↔ $SO_3^=$ + $2H^+$

Therefore, the overall reactions with SO_2 produce a mixture of sodium sulfite, sodium sulfate, and sodium bisulfite. The exact proportions of the sulfur species depend on the pH and degree of oxidation. The simplified overall reactions are as follows:

$$2Na^+ + 2OH^- + SO_2 \rightarrow Na_2SO_3\,(aq) + H_2O$$

$$2Na^+ + 2OH^- + SO_2 + \tfrac{1}{2}\,O_2 \rightarrow Na_2SO_4\,(aq) + H_2O$$

$$Na^+ + OH^- + SO_2 \rightarrow NaHSO_3\,(aq)$$

2. Dry Sodium-Based Systems:

When exposed to heat, dry sodium bicarbonate decomposes to produce dry, high surface-area soda ash. The soda ash in turn reacts with SO_2. This can be achieved at moderate temperatures of 300°F–600°F, which is in the range of typical exhaust temperatures for many processes.

$$2NaHCO_3 + \text{heat} \rightarrow Na_2CO_3 + CO_2 + H_2O$$

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$