# CONTROL OF $NO_X$

## Why we should control NOx:

- NOx is one of the four major air pollutants and is the element primary element responsible for formation of photochemical smog.
- The first priority in designing a strategy to control nitrogen oxides is to protect human health.
- Nitrogen oxides are precursors to ozone (O3) formation, which can harm human health and vegetation.
- Finally, 30% of Acid Rains due to NOx which damages vegetation and aquatic ecosystems.

## Sources

- Atmospheric Nitrogen
- Nitrogen present in Fuel

## NOx control methods:

- Modification Design Condition
- Modification Operating Condition
- Treatment of effluent gases

## Modification Design Condition
## Low excess air combustion:

- For complete combustion about 10 to 20 % of excess air is needed.
- This excess air is sufficient for reacting with Nitrogen to form NOx .
- In this case 25% excess air produces 600 ppm of NOx and 1.4 % produces 175 ppm

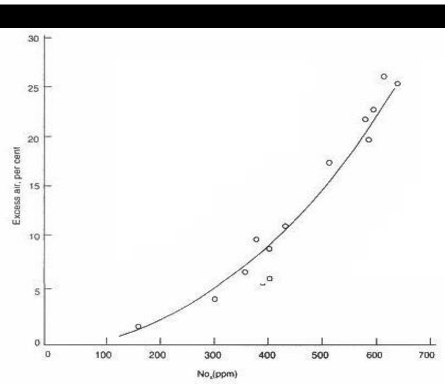
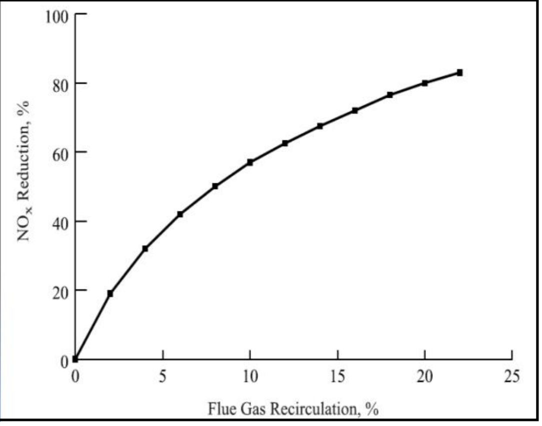



Fig. 6.12 NO formation as a function of excess air (ref. 14)

## 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, i.e., acts as a heat sink, and reduces the peak flame temperature.




## 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 NOx.

## 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.

## 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% NOx reduction can be achieved by injecting steam at a rate up to 20 to 30% of the fuel weight.

## Two stage combustion:

- Here , 90 to 95 % of total air required is provided at the bottom of the furnace.
- This is followed by the secondary air injection in the next furnace which provides complete combustion.
- In primary furnace incomplete combustion takes while in secondary furnace complete combustion takes place hence this leads to decrease in the total NOx output.

## Modification of Design Condition

- The burner configuration in the combustion chamber has a great influence in the formation of NOx.
- There are 2 basic furnace designs:
  - Tangential firing.
  - Horizontal firing.
- In the tangential firing the furnace itself is used as burner so that the flame and the combustion product rotating upward spiral around walls of the furnace.

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- This results in low peak flame temperature and consequently results in low NO emission.
- In the horizontal firing the flame is at right angle to the wall of the fire box.
- Fluidized bed combustion is used which is operated at 1050 C. Fluidized bed results in low combustion temperature.

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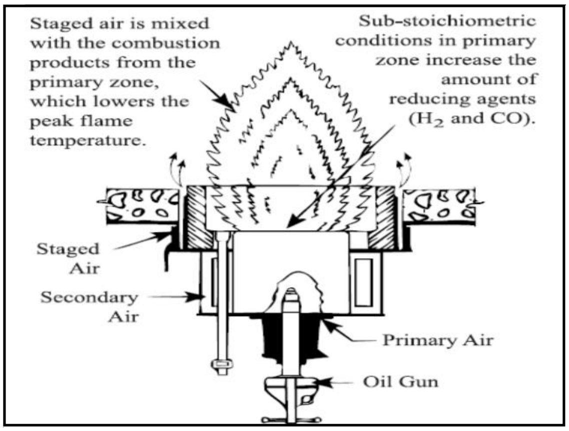
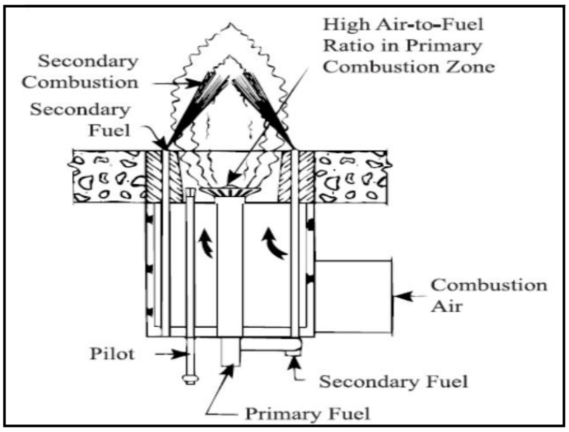
## Low Nox Burners

- Low-NOx burners are designed to stage either the air or the fuel within the burner tip.
- The principle is similar to overfire air (staged air) or reburn (staged fuel) in a furnace.
- With staged-air burners, the primary flame is burned fuel rich and the low oxygen concentration minimizes NOx formation.
- Additional air is introduced outside of the primary flame where the temperature is lower, thereby keeping the thermodynamic equilibrium NOx concentration low, but hot enough to complete combustion.




- Staged-fuel burners introduce fuel in two locations. A portion of the fuel is mixed with all of the combustion air in the first zone, forming a hot primary flame with abundant excess air. NOx formation is high in this zone.
- Then additional fuel is introduced outside of the primary flame zone, forming a low-oxygen zone that is still hot enough for kinetics to bring the NOx concentration to equilibrium in a short period of time.
- In this zone, NOx formed in the primary flame zone reverts back to nitrogen and oxygen.
- Low Nox burners can reduce NOx emissions by 40 to 65% from emissions produced by conventional burners.

## Effluent gas treatment method

- The practical methods for removal of NOx can be grouped in following:
  - Absorption by liquid
  - Adsorption by Solids
  - Catalytic reduction
    - Selective
    - Non selective
  - Electron beam irradiation

## Absorption by Liquids

- Water
- Hydroxide and Carbonate solution
- Sulphuric acid, Organic solution
- Moltan alkali carbonates and hydroxides

## Absorption by Alkaline Solution

- NaOH
- $Mg(OH)_2$

## Absorption by Lime

- Calcium Hydroxide
- $Ca(OH)_2 + 2NO_2 \longrightarrow Ca(NO_2)_2 + H_2O$
- $2H_2SO_4 + 3Ca(NO_2)_2 \longrightarrow 2CaSO_4 + 4\,NO + Ca(NO_3)_2 + 2H_2O$

## Absorption by $H_2SO_4$

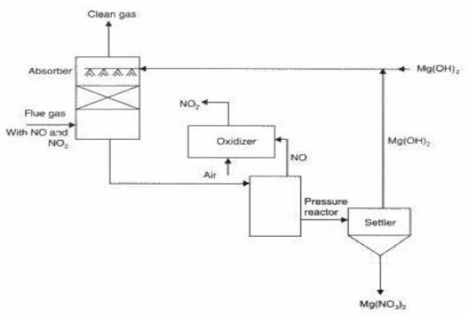
- It forms violet acid, $H_2SO_4NO$ and Nitrocyl sulphuric acid, $NOHSO_4$
- $NO + NO_2 + 2H_2SO_4 \longrightarrow 2NOHSO_4 + H_2O$

## Absorption by Liquids

- Absorption of NOx by Magnesium Hydroxide
- In this process the oxides of Nitrogen are absorbed by magnesium hydroxide liquor in absorption tower.
- The magnesium nitrate solution, leaving the absorber is taken to pressure reactor, where the nitrite is converted to nitrate.
- The by product NO is oxidized to NO2 and the liquid leaving the pressure reactor consisting Mg(NO3)2 or Mg(OH)2 is sent to settling chamber , where the nitrate is separated from hydroxide which is recycled to the absorption tower.

- The part of NO2 from the oxidizer is sent to the absorber to maintain equilibrium between concentration of NO & NO2, while the rest of NO2 is used for the production of HNO3.

## Absorption of NOx by Magnesium Hydroxide




## Adsorption by Solids

- Adsorbent which show some capacity for oxidizing NO to $NO_2$
- Activated Carbon, Silica gel, molecular sieves, ion exchange resins and certain metal oxides
- Activated carbon has a high adsorption rate and capacity compared to other materials.
- However regeneration may be problem.
- A potential fire and explosion hazard due to $O_2$ presence.
- Efficiency decreases with quantity of $O_2$ present
- Manganese oxide and alkalized ferric oxides show technical potential.
- The most promising adsorbent is ferrous salt

## Selective Noncatalytic Reduction (SNCR)

- Selective noncatalytic reduction uses ammonia ($NH_3$) or urea ($H_2NCONH_2$) to reduce NOx to nitrogen and water.
- The overall reactions using ammonia as the reagent are

$$2NH_3 + 2NO + \tfrac{1}{2}O_2 \leftrightarrow 2N_2 + 3H_2O \qquad 1600\text{–}1900^\circ F$$

$$2NH_3 + 2NO + O_2 + H_2 \leftrightarrow 2N_2 + 4H_2O \qquad 1300\text{–}1900^\circ F$$

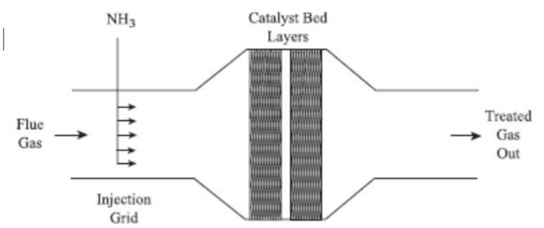
- No catalyst is required for this process; just good mixing of the reactants at the right temperature and some residence time.
- The key to this process is operating within the narrow temperature window.
- Sufficient temperature is required to promote the reaction.
- The presence of hydrogen in the flue gas, if there is a source of it such as dissociation of steam, increases the operable temperature range at the cooler end.

- SNCR produces about 30 to 50% NOx reduction.
- Some facilities that require higher levels of NOx reduction take advantage of the low capital cost of the SNCR system, then follow the SNCR section with an SCR system.
- Capital costs may be lower than an SCR system alone because the catalyst bed for the SCR can be smaller due to the lower Nox removal requirement for SCR after the SNCR system has removed a significant portion of the NOx.

## Selective Catalytic Reduction (SCR)

- 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.

- SCR operating considerations include ammonia storage and handling.
- Ammonia can be in either the anhydrous or aqueous form.
- A small amount of ammonia, about 5 to 20 ppm, will pass, or "slip," through the catalyst, which creates an emission of a small amount of a hazardous air pollutant in exchange for reducing NOx.




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

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

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

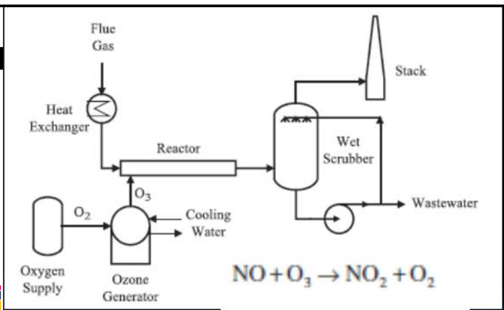
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

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

- A variety of catalyst types are used for SCR. Precious metals are used in the low temperature ranges of 350 to 550°F.
- Vanadium pentoxide supported on titanium dioxide is a common catalyst for the temperature range of 500 to 800°F.
- Zeolites, which are various alumino silicates, are used as high temperature catalysts in the range of 850 to 1100°F.

- Besides temperature, another catalyst issue is oxidation of $SO_2$ to $SO_3$ in flue gases from fuels that contain sulfur.
- $SO_3$ results in sulfuric acid mist emissions, which can create opacity that is expensive to control.
- Tungsten trioxide and molybdenum trioxide are catalysts that minimize sulfur oxidation.

## Low Temperature Oxidation with Absorption




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

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

$$N_2O_5 + H_2O \rightarrow HNO_3$$

## Electron Beam Irradiation

- 90% Sox and Nox removal
- NH3 is utilize
- Activated by electron beam irradiation
- No Catalyst required
- Dry Powder of Ammonium Sulphate and Ammonium nitrate sulphate
- Potential fertilizer feed stock