NOx

Sources and Control Methods

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Specific sources of NO_x

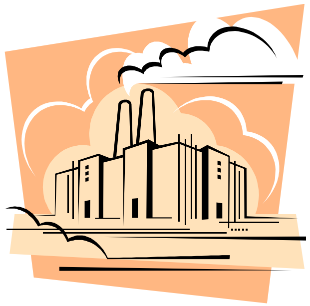
1. Combustion sources

- Automobiles
- Boilers
- Incinerators

2. High-temperature industrial operations

- Metallurgical furnaces
- Blast furnaces
- Plasma furnaces
- Kilns

3. Other sources



- Nitric acid plants
- Industrial processes that use nitric acid

NO_x Effects

- It is one of the main ingredients involved in the formation of ground-level ozone, which can trigger serious respiratory problems
- contributes to nutrient overload that deteriorates water quality
- contributes to atmospheric particles that cause visibility impairment most noticeable in national parks
- reacts to form nitrate particles, acid aerosols, as well as NO_2, which also cause respiratory problems
- contributes to formation of acid rain
- reacts to form toxic chemicals
- contributes to global warming

Characteristics of NOx compounds

NO – Nitric oxide

- Colorless and odorless gas
- Insoluble in water
- Toxic

NO_2 – Nitrogen dioxide

- Usually exists as a dimer compound (N_2O_4) at low ^0C
- Has distinct reddish-brown color
- Moderately soluble in aqueous liquids
- Toxic
- Contributes to brown haze that occurs with smog

NOx Regulation

NOx concentrations are relatively low in the atmosphere, so why are they regulated?

NO and NO_2 react rapidly with other compounds, creating ozone and other undesirable compounds. The NO and NO_2 may never reach high concentrations, but are creating other air pollutants.

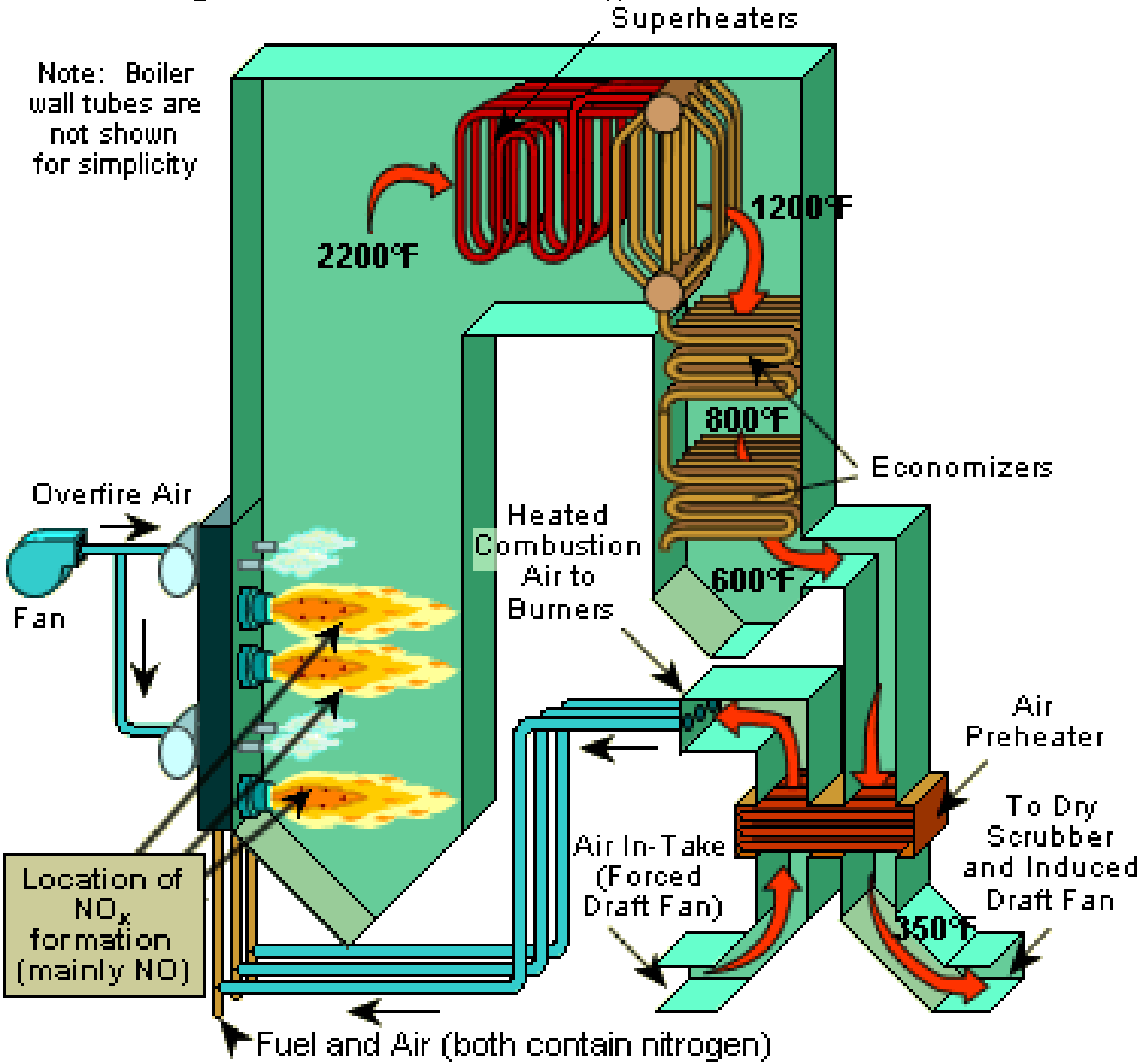
NO_x Formation

- Formed at elevated temperatures during combustion of fuel in the presence of air.
- Approximately 90 to 95% of the nitrogen oxides generated in combustion processes are in the form of nitric oxide (NO).
- Once in the atmosphere, the NO reacts in a variety of photochemical and thermal reactions to form NO_2.

- **Thermal NOx:** formed by reaction betweenN_2 and O_2 in the air; sensitive to temperature

- **Fuel (or Prompt) NOx:** formed from combustion of fuel containing organic nitrogen; dependent on local combustion conditions and nitrogen content in the fuel.

Not all of the fuel nitrogen compounds are released during combustion. Unlike sulfur, a significant fraction of the fuel nitrogen remains in the bottom ash or in the fly ash.



Location of No_x formation in a Boiler

Control Technologies & Techniques

NOx control technologies

- Primary – reduce the NOx produced in the primary combustion zone
  - Low NO_X burners (LNBs)
  - Overfire air (OFA)

- Secondary - reduce the NOx already present in the flue gas
  - Reburning
  - Selective non-catalytic reduction (SNCR)
  - Selective catalytic reduction (SCR)

NOx control Techniques

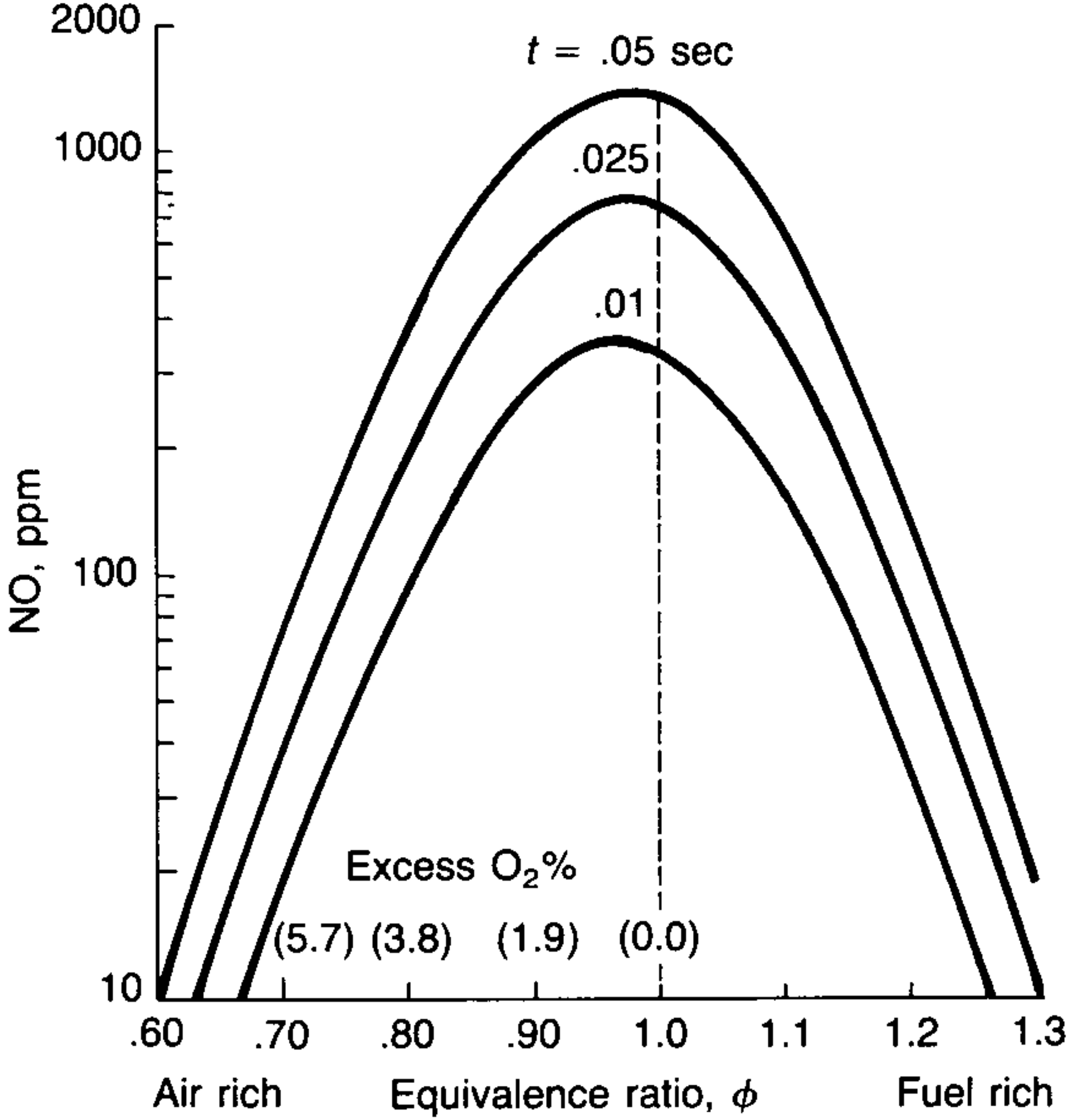
1. **Modify combustion to suppress NO_x formation**

   - Low excess air operation
   - Off-stoichiometric combustion
   - Flue gas recirculation
   - Natural gas reburning

2. **Reduce No_x to molecular nitrogen through controls (also known as flue gas treatment)**

   - Selective Non-Catalytic Reduction (SNCR)
   - Selective Catalytic Reduction (SCR)
   - Dry Sorption

Strategies for Combustion Modification



Reduce peak **temperatures** of the flame zone

Reduce gas **residence time** in the flame zone

Would wet scrubbers be a good control technique for NO_x emissions?

Wet scrubbers would *not* be a good control technique for NO_x emissions.

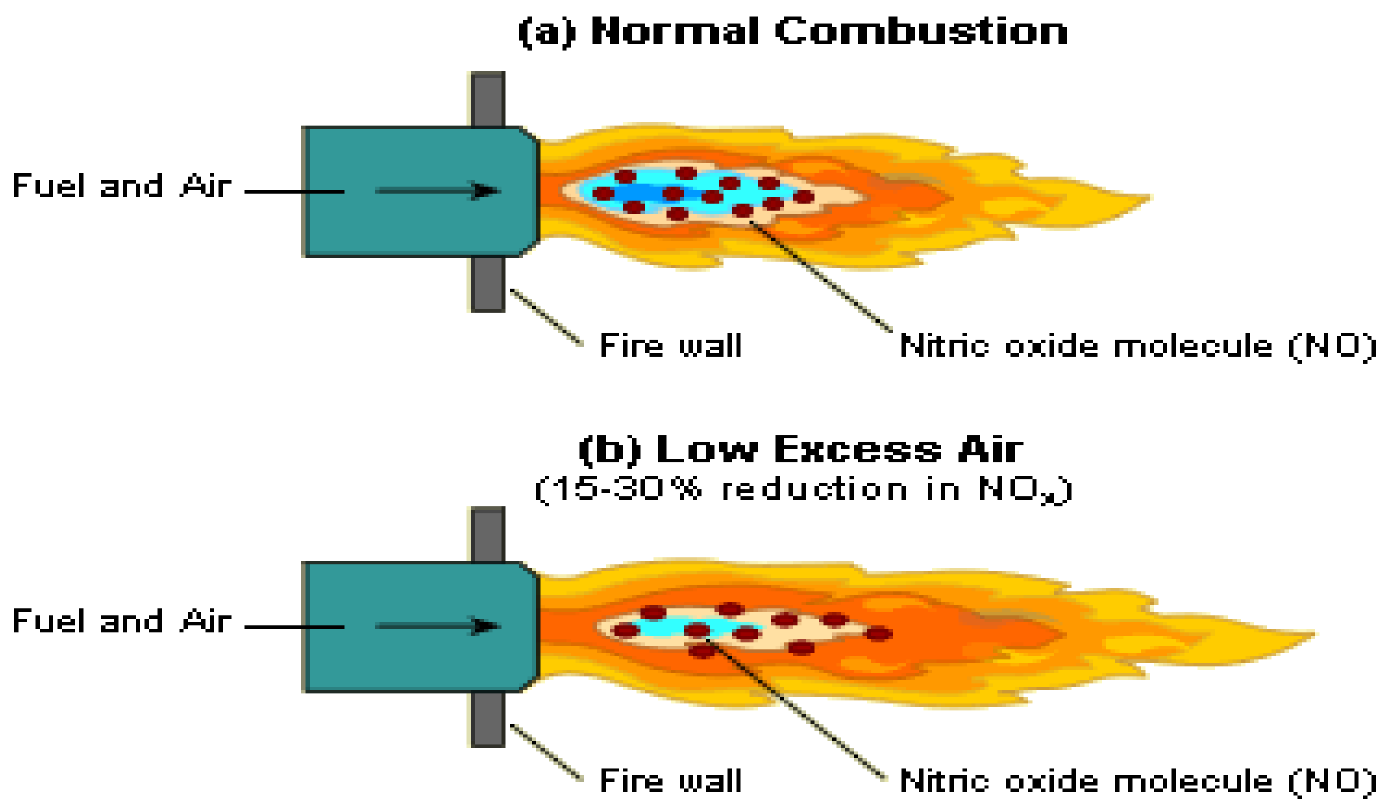
Reason

NO is mainly formed during the combustion process and NO_2 is formed in the atmosphere.
Since NO is insoluble in water, wet scrubbing would not work very well!

Combustion Modifications

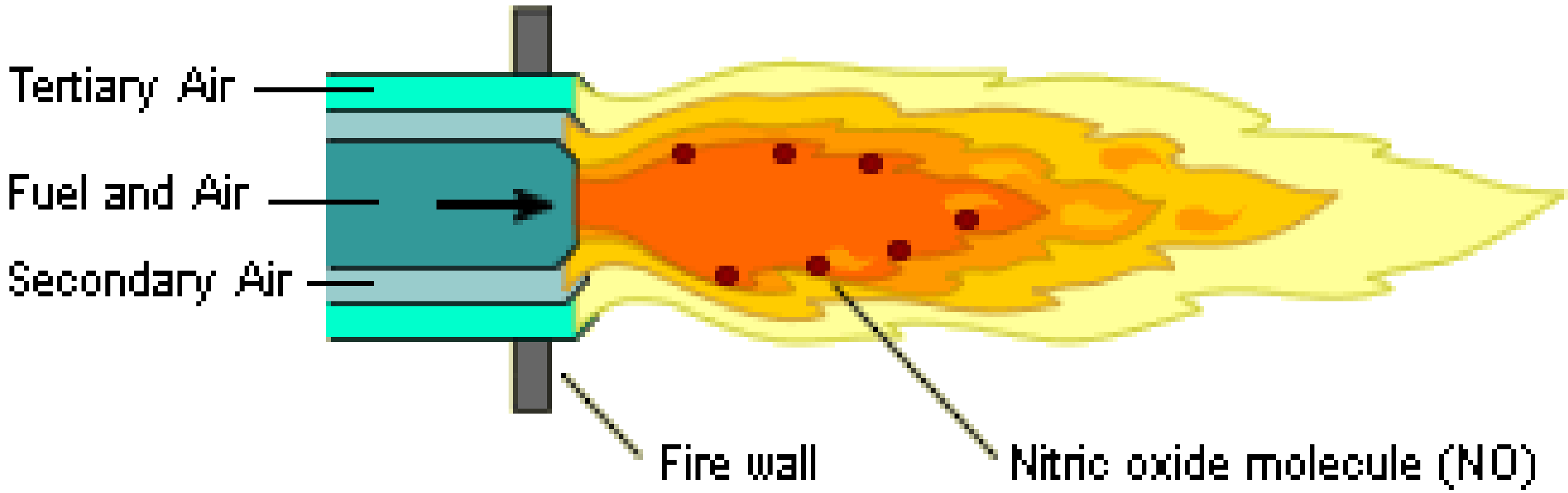
Low excess air operation: Involves a reduction in the total quantity of air used in the combustion process. By using less oxygen, the amount of NOx produced is not as great.

Figure 1. NO_x Formation under Normal Conditions and Low Excess Air

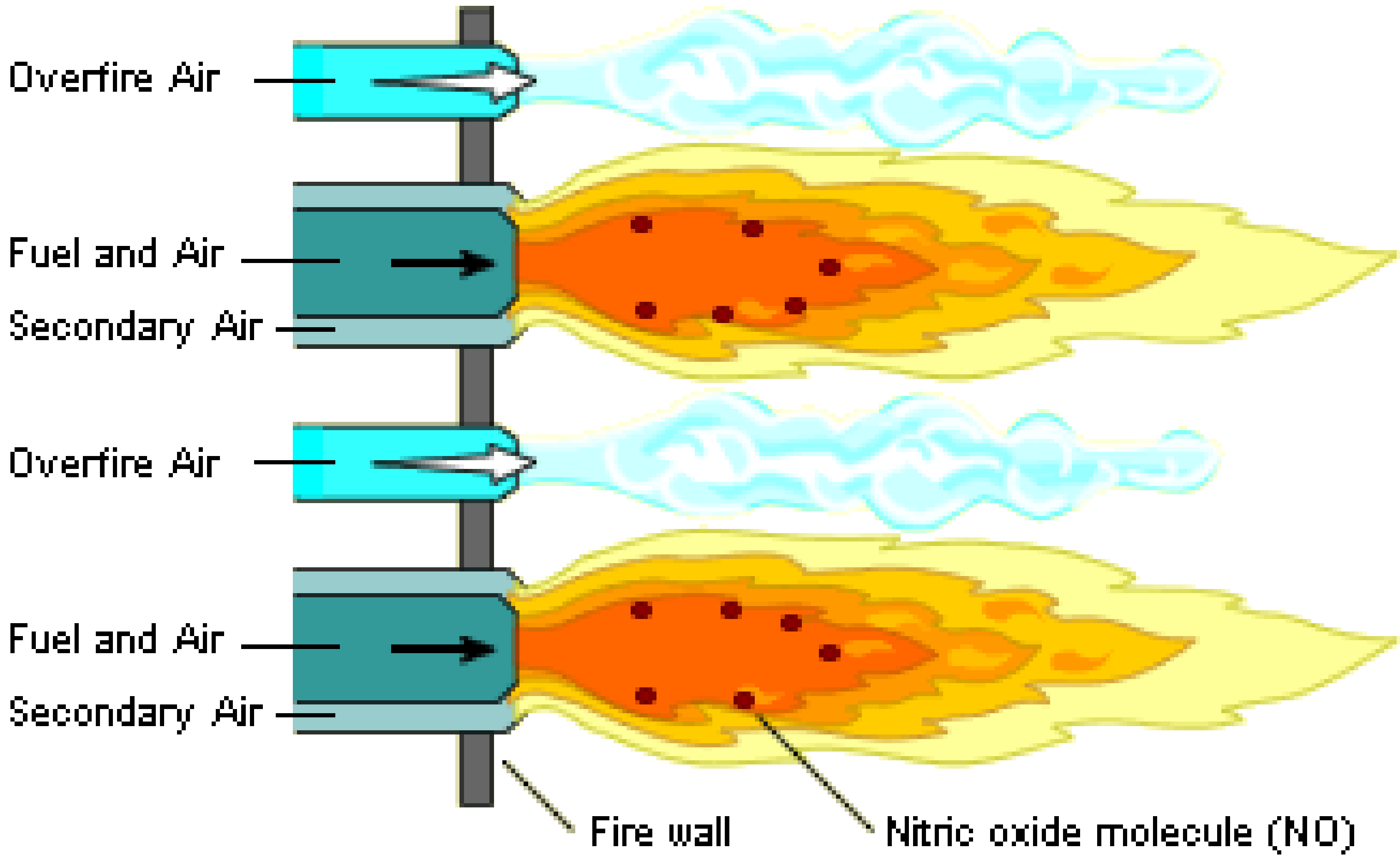


Off-stoichiometric combustion: Involves the mixing of the fuel and air in a way that reduces the peak gas temperatures and peak oxygen concentrations.

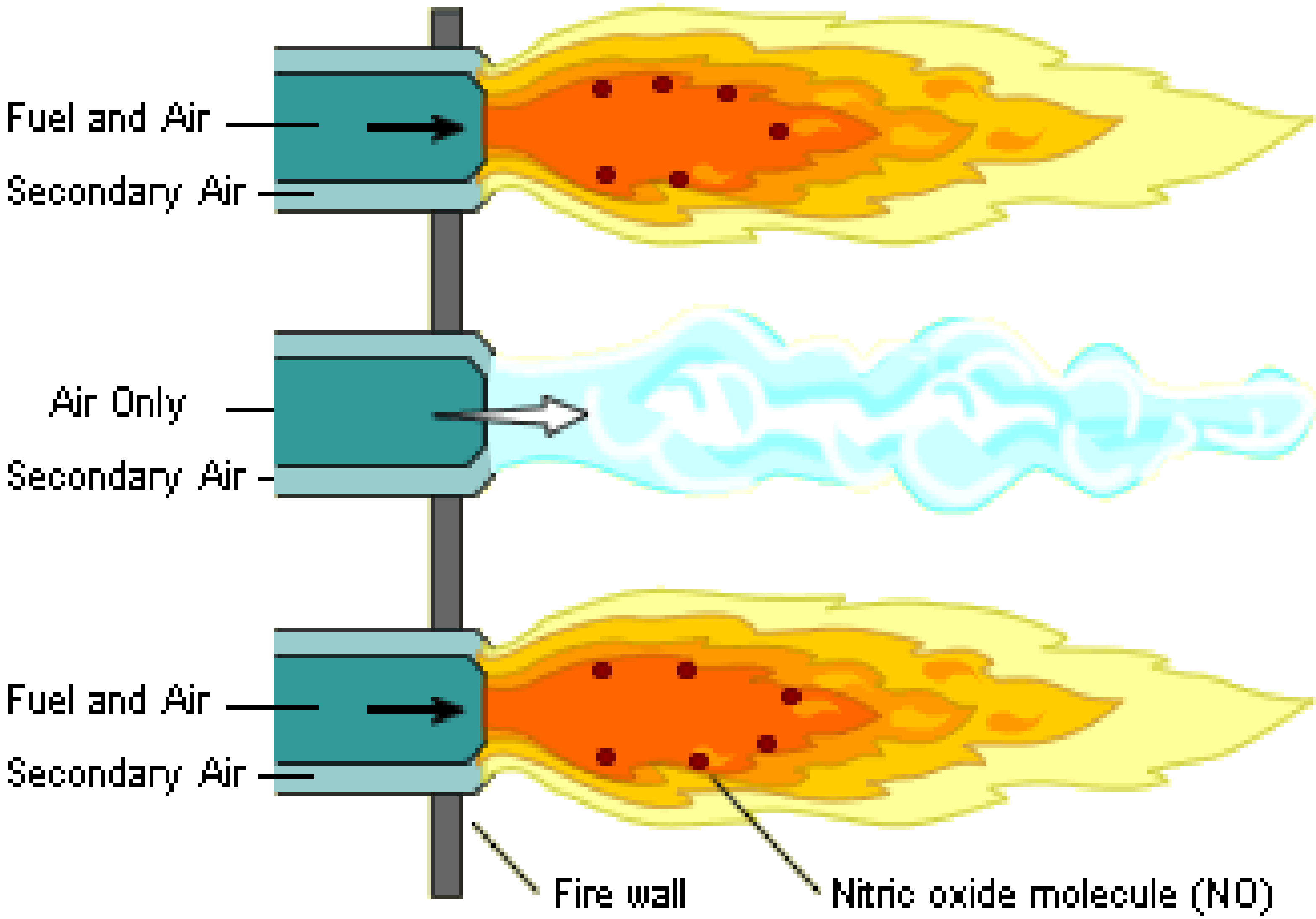
- ❑ **Low NOx burners**: Keeps temperatures down and dissipates heat quickly
- ❑ **Overfire air (OFA)**: Keeps mixture fuel rich and completes combustion process using air injection nozzles
- ❑ **Burners out of service (BOOS)**: Operates alternate burners in combustion zone as fuel rich, air rich, and air only



Off-Stoichiometric Combustion in Burner (Low No_x Burner)



Off-Stoichiometric Combustion (Overfire Air)



Off-Stoichiometric Combustion (Burners-Out-of-Service)

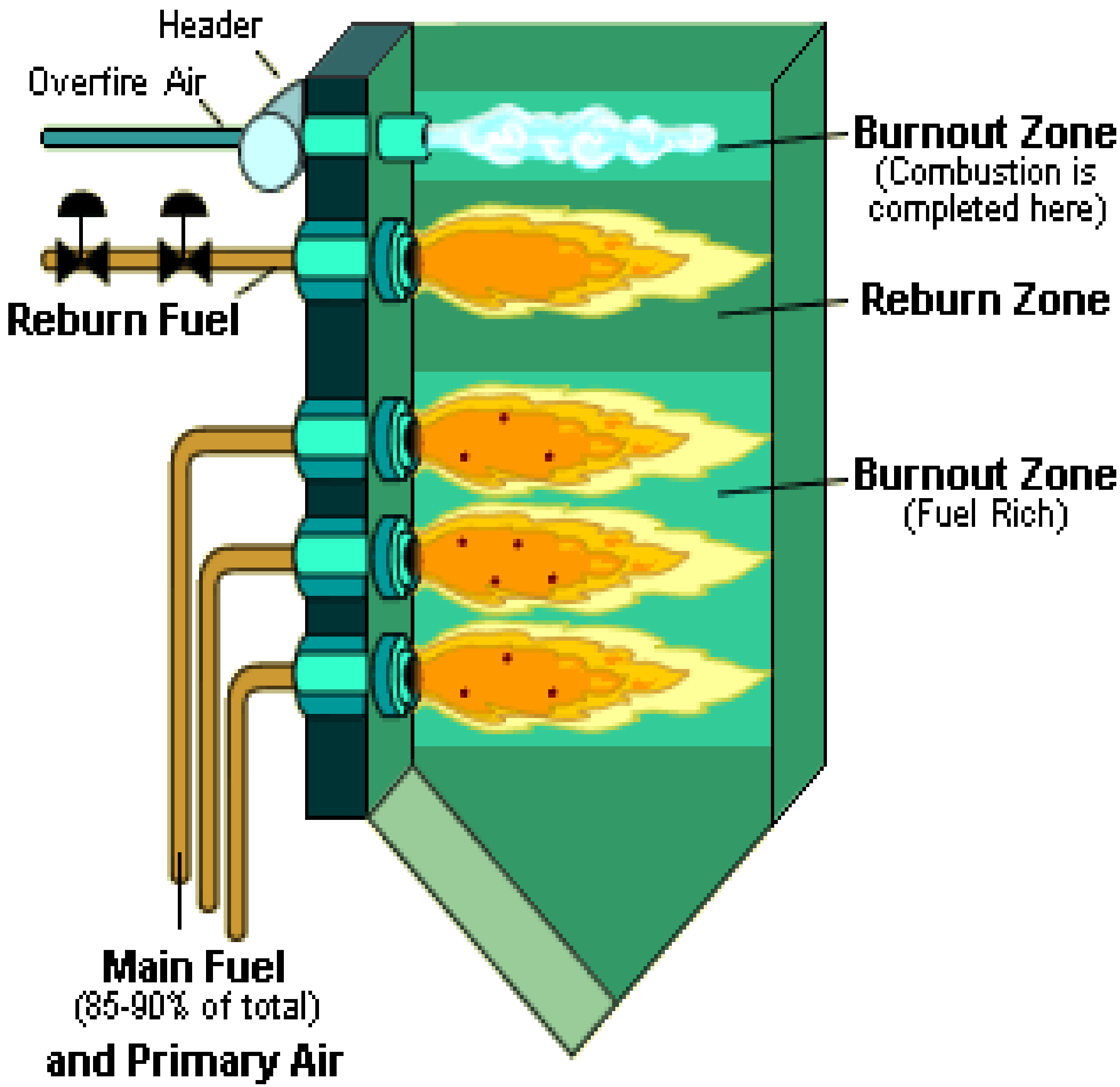
Flue gas recirculation

Involves the return of cooled combustion gases to the burner area of the boiler. Reduced temperatures produce less NOx. The process requires a recirculation fan and duct system.

Fuel Reburning

Involves the operation of the main burners in a boiler at very low excess air (fuel rich conditions).

A series of overfire air ports are used in this upper region to provide all of the air needed for complete combustion.



Fuel Reburning:

Add-On Controls (Flue Gas Treatment)

Selective non-catalytic reduction systems (SNCR)

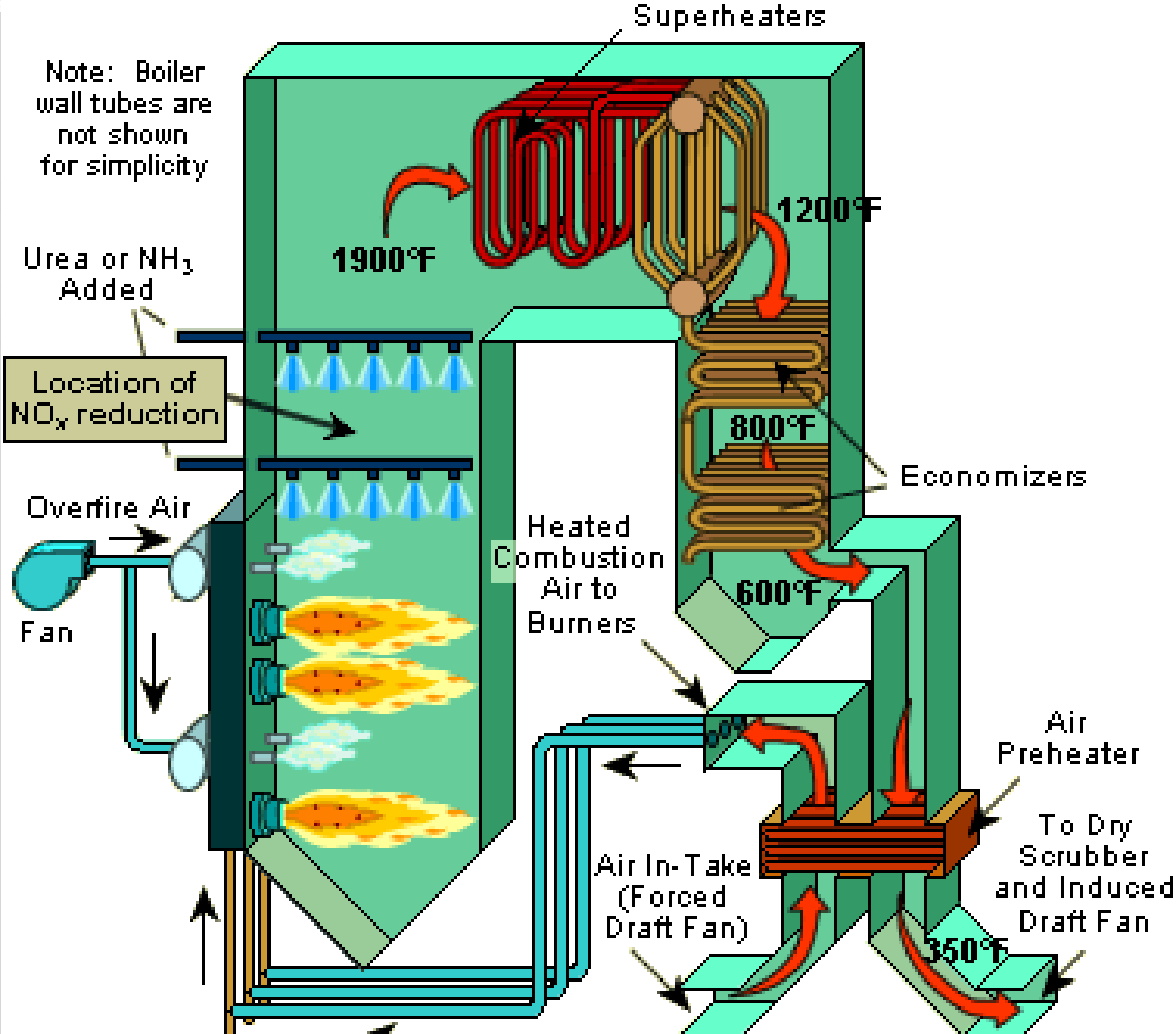
Involves the injection of ammonia (NH_3) or urea into the hot gas zone where reactions leading to reduction of nitrogen oxides can occur. The reactions are completed within the boiler, and no waste products are generated. There is a risk of ammonia (NH_3) being emitted into the atmosphere if temperatures are too low, however. SCNR systems are capable of reducing nitrogen oxides from 20 to 60%.

Selective Noncatalytic Reduction (SNCR) Reactions:

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

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

Above 1000 ^{o}C



Example SNCR System for No_x Control in a Boiler

Selective catalytic reduction (SCR)

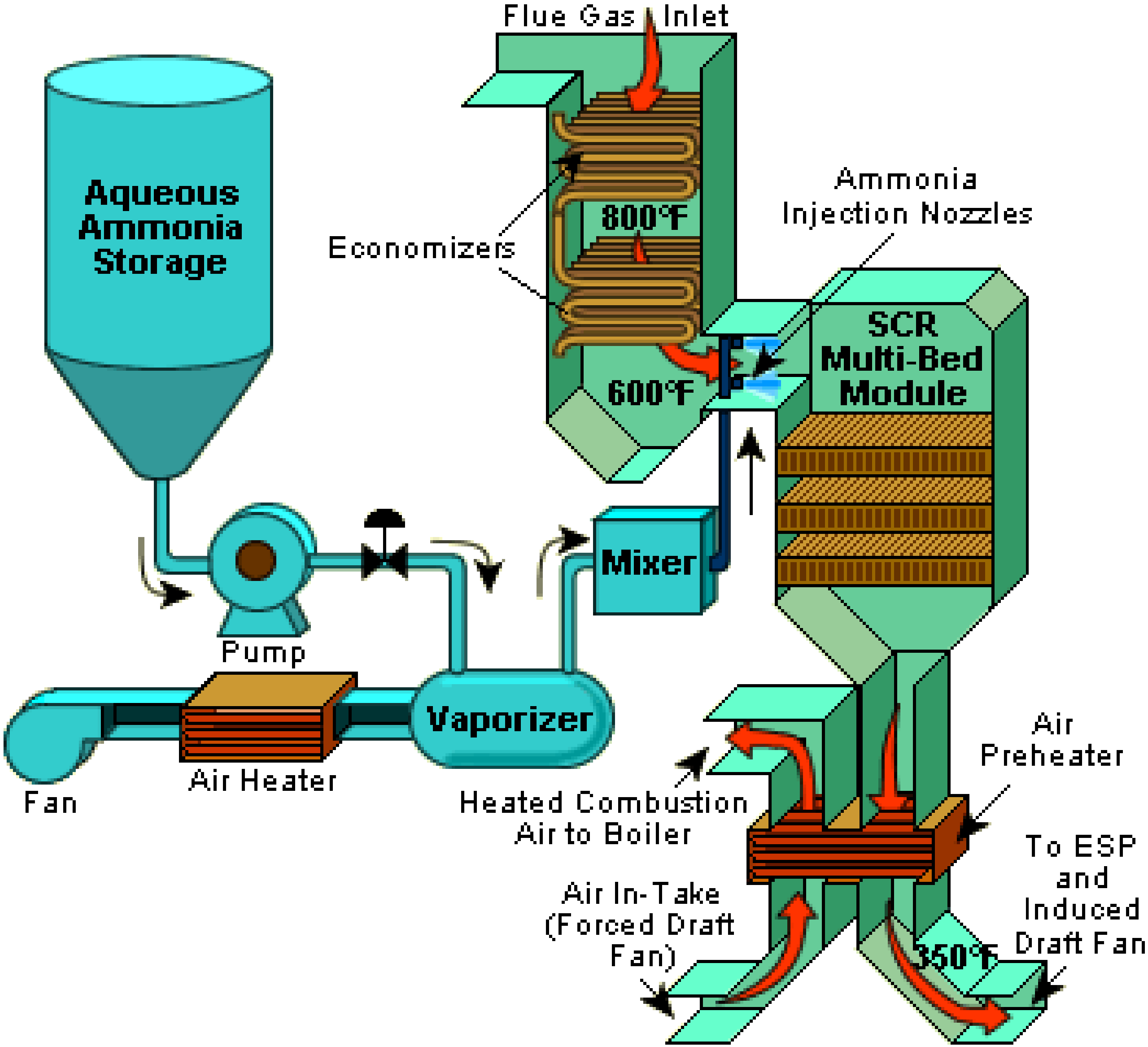
Involves using beds containing ammonia or urea to reduce nitrogen oxides to molecular nitrogen and water. Two or three catalysts (usually tungsten and vanadium) are arranged in honeycomb shapes in the beds so air can flow through. NOx reduction efficiencies ranging from 75 to 90% are possible when the amount of catalyst is sufficient, the catalyst is in good condition, the ammonia reagent flow is sufficient, and the ammonia is adequately distributed across the gas stream.

Selective Catalytic Reduction (SCR) Reactions

$$4NO + 4NH_3 + O_2 \xrightarrow{\text{TiO}_2 \text{ or } \text{V}_2\text{O}_5 \text{ supported catalyst}} 4N_2 + 6H_2O$$

$$2NO_2 + 4NH_3 + O_2 \xrightarrow{\text{TiO}_2 \text{ or } \text{V}_2\text{O}_5 \text{ supported catalyst}} 3N_2 + 6H_2O$$

Temperature ~ 300 - 400 ^{o}C



Exapmle SCR System for No_x Control in a Boiler

Dry Sorption

- Activated carbon (220 ~ 230 °C)
- Shell Flue Gas Treating System (~ 400 °C)

$$CuO + 0.5O_2 + SO_2 \rightarrow CuSO_4$$

$$4NO + 4NH_3 + O_2 \xrightarrow{\text{CuO or CuSO}_4\text{ as catalysts}} 4N_2 + 6H_2O$$

$$CuSO_4 + 2H_2 \rightarrow Cu + SO_2 + 2H_2O$$

$$Cu + 0.5O_2 \rightarrow CuO$$