

Environmental  
Compliance  
Navigator

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# NO<sub>x</sub> – Sources, Regulation, and Control – A Close Look



*Prepared for:*

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# AGENDA

- **Nitrogen in the Atmosphere**
- **Where Do Nitrogen Oxides Come From?**
- **Why Do We Regulate Nitrogen Oxide Emissions?**
- **How Are Nitrogen Oxide Emissions Regulated?**
- **How Are Nitrogen Oxide Emissions Controlled?**
- **A Look Ahead - Trends**

# Nitrogen in the Atmosphere

## Nitrogen exists in the atmosphere in various forms:

- **Diatomic nitrogen ( $\text{N}_2$ )** – 78% of the atmosphere by volume and very stable
- **Nitric oxide ( $\text{NO}$ )** – ppbv levels – rapidly oxidized in the atmosphere to  $\text{NO}_2$
- **Nitrogen dioxide ( $\text{NO}_2$ )** – 10-200 ppbv – fairly rapidly oxidized in the atmosphere to  $\text{NO}_3^-$
- **Nitrate radicals ( $\text{NO}_3^-$ )** – pptv levels, transient – hydrolyzes to  $\text{HNO}_3$  – acid rain
- **Nitrous oxide ( $\text{N}_2\text{O}$ )** – currently about 337 ppbv, atmospheric lifetime over 10 years
- **Other nitrogen oxides ( $\text{N}_2\text{O}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$ )** – pptv levels, transient
- **Ammonia ( $\text{NH}_3$ )** – variable concentration from 1-5 ppbv, atmospheric lifetime of 2-3 wks

# Where Do Nitrogen Oxides Come From?

In general, nitrogen oxides in the atmosphere arise for the combination of atmospheric nitrogen and atmospheric oxygen. The  $\text{N}\equiv\text{N}$  bond in atmospheric  $\text{N}_2$  is very strong, so significant energy input is required to break it and form oxides.

## Natural $\text{NO}_x$ sources:

- Lightning
- Wildfires
- Volcanoes



## Anthropogenic $\text{NO}_x$ sources:

- Fuel combustion sources – stationary and mobile
- Industrial furnaces (e.g. blast furnaces, cement kilns, glass furnaces, nitric acid plants and incinerators)



# Why Do We Regulate Nitrogen Oxide Emissions?

## Nitrogen oxides in the atmosphere cause multiple adverse effects:

NO/NO<sub>2</sub> causes impairment of respiratory function in humans from direct exposure:

- inflammation and coughing
- increased incidence of asthma
- immunosuppression affects

Ground level ozone (O<sub>3</sub>) formed from NO<sub>x</sub>, VOC and UV causes:

- impaired respiratory function from direct exposure and increased incidence of asthma
- smog formation
- oxidative damage to forests and agricultural products

Fine particulate matter (PM<sub>2.5</sub>) formed from NO<sub>x</sub> causes:

- respiratory and cardio-vascular function impairment in humans
- reduced atmospheric visibility

Acid precipitation (NO ⇌ NO<sub>2</sub> ⇌ NO<sub>3</sub><sup>-</sup> ⇌ HNO<sub>3</sub>) causes:

- surface water ecological impacts
  - lower pH
  - nutrient eutrophication
- acid damage to forests, agriculture and the built environment

Greenhouse gas (N<sub>2</sub>O) contributing to climate change (GWP roughly 300 times CO<sub>2</sub>)

# How Are Nitrogen Oxide Emissions Regulated?

- **National Ambient Air Quality Standards (NAAQS)**
- **Reasonably Available Control Technology (RACT) Rules**
- **Acid Rain Program (ARP)**
- **Cross State Air Pollution Rule (CSAPR)**
- **New Source Performance Standards/Emission Guidelines (NSPS/EG)**
- **New Source Review (NSR)**
- **Mobile Source Emission Standards**
- **Regional Haze – Clean Air Visibility Rule**
- **Transportation and General Conformity**
- **National Environmental Policy Act (NEPA)**

# How Are Nitrogen Oxide Emissions Regulated?

## National Ambient Air Quality Standards (NAAQS)

- **Nitrogen Dioxide (NO<sub>2</sub>)**
  - ◆ 1-hour Primary Standard: 100 ppbv
  - ◆ Annual Primary and Secondary Standard: 53 ppbv
- **Ozone (O<sub>3</sub>)**
  - ◆ 8-hour Primary and Secondary Standard: 70 ppb
- **Fine Particulate (PM<sub>2.5</sub>)**
  - ◆ Annual Primary Standard: 9 µg/m<sup>3</sup>
  - ◆ Annual Secondary Standard: 15 µg/m<sup>3</sup>
  - ◆ 24-hour Primary and Secondary Standard: 35 µg/m<sup>3</sup>

NAAQS drive source category-specific regulations and stationary source permitting

**Affected Sources: Stationary and mobile sources of nitrogen oxides**



# How Are Nitrogen Oxide Emissions Regulated?

## Reasonably Available Control Technology (RACT)

Establishes emission control performance standards for existing major stationary sources of non-attainment pollutants or their precursor pollutants

- NO<sub>2</sub> non-attainment areas: existing major sources of NO<sub>x</sub> must apply RACT
- Ozone (O<sub>3</sub>) non-attainment areas: existing major sources of NO<sub>x</sub> and VOC must apply RACT
- Fine particulate (PM<sub>2.5</sub>) non-attainment areas: existing major sources of PM<sub>2.5</sub>, NO<sub>x</sub> and SO<sub>2</sub> must apply RACT

RACT performance levels are driven by the NAAQS and non-attainment status of an Air Quality Control Region (AQCR)

**Affected Sources: Existing, major stationary sources of non-attainment pollutants/precursors**

# How Are Nitrogen Oxide Emissions Regulated?

## Acid Rain Program (ARP)

- First national cap-and-trade system for air emissions – mandated by Title IV of the 1990 Clean Air Act Amendments
- Requires controls of acid rain precursors sulfur dioxide ( $\text{SO}_2$ ) and nitrogen oxides ( $\text{NO}_x$ ), from large stationary sources, through a system of allowance trading - market-based incentives to reduce pollution
- Reduction in  $\text{SO}_2$  and  $\text{NO}_x$  pollution have also produced collateral benefits including reductions in fine particles ( $\text{PM}_{2.5}$ ) and ground-level ozone ( $\text{O}_3$ )

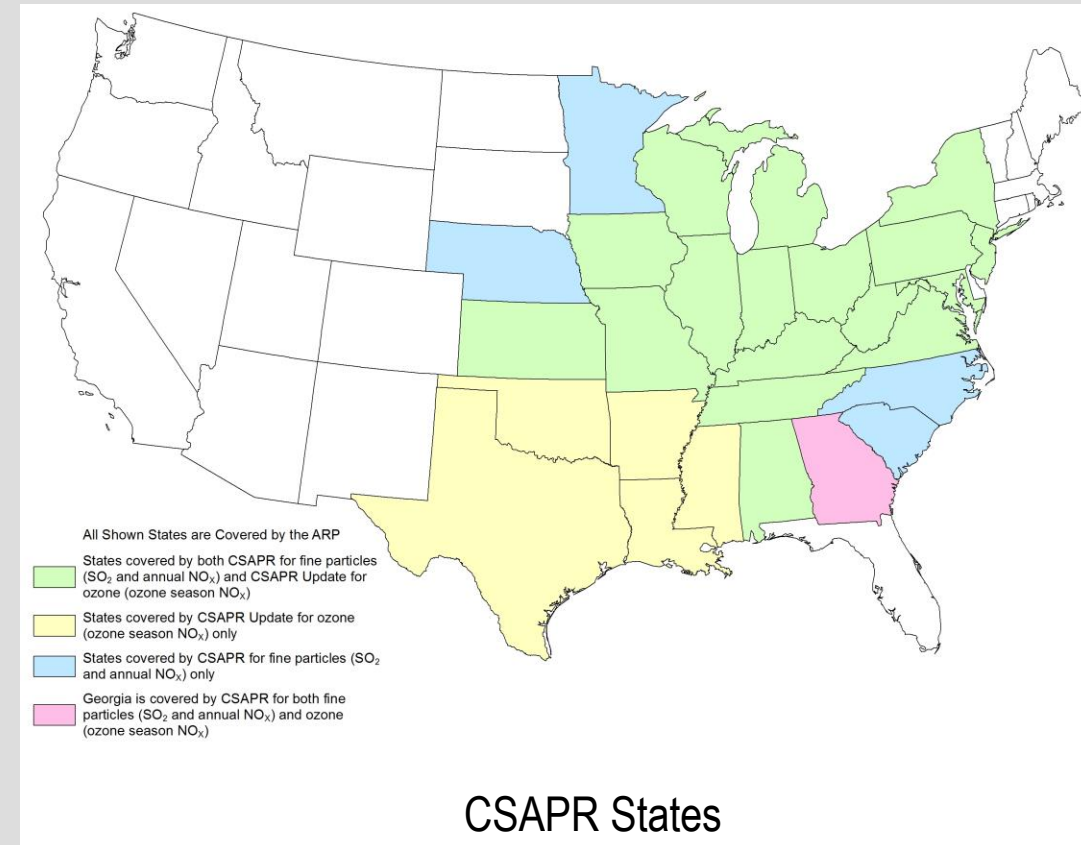


**Affected Sources: Fossil fuel burning power stations**

# How Are Nitrogen Oxide Emissions Regulated?

## Cross State Air Pollution Rule (CSAPR)

- A cap-and-trade program to limit interstate transport of emissions of  $\text{NO}_x$  and  $\text{SO}_2$  that contribute to harmful levels of fine particle matter ( $\text{PM}_{2.5}$ ) and ozone ( $\text{O}_3$ ) in downwind states.
- Requires 28 states in the eastern United States to reduce  $\text{SO}_2$ , annual  $\text{NO}_x$  and ozone season  $\text{NO}_x$  emissions from fossil fuel-fired power plants that affect the ability of downwind states to attain and maintain compliance with  $\text{PM}_{2.5}$  and  $\text{O}_3$  NAAQS.



**Affected Sources: Fossil fuel burning power stations**

# How Are Nitrogen Oxide Emissions Regulated?

## New Source Performance Standards/Emission Guidelines (NSPS/EG)

### Examples:

- **40 CFR Part 60 Subpart Da** – *Standards of Performance for Electric Utility Steam Generating Units*: NO<sub>x</sub> emission limits range from 0.2 lb/MMBtu for gaseous fuel to 0.5-0.8 lb/MMBtu for various grades of coal
- **40 CFR Part 60 Subpart F** – *Standards of Performance for Portland Cement Plants*: NO<sub>x</sub> emissions are limited to 1.5 lbs per ton of clinker on a 30-day rolling average
- **40 CFR Part 60 Subpart G/Ga** – *Standards of Performance for Nitric Acid Plants*: NO<sub>x</sub> emissions are limited to 1.5 kg per metric ton of acid produced for plants constructed on or before 10/14/2011 or 0.5 lbs per short ton of acid produced for plants constructed, reconstructed or modified after 10/14/2011
- **40 CFR Part 60 Subpart J/Ja** – *Standards of Performance for Petroleum Refineries*: NO<sub>x</sub> emissions are limited to 80 ppmdv at 0% excess air on a 7-day rolling average basis for plants constructed, reconstructed or modified after 5/14/2007
- **40 CFR Part 60 Subpart KKKK** – *Standards of Performance for Stationary Combustion Turbines*: NO<sub>x</sub> emissions are limited 15 to 150 ppm at 15% O<sub>2</sub> or 54 to 1,100 ng/J of useful output, depending on size, age, fuel and location

**Affected Sources: New, modified or reconstructed (NSPS) and existing sources (EG) of CAPs**

# How Are Nitrogen Oxide Emissions Regulated?

## New Source Review

Major stationary sources and stationary sources making major modifications are subject to permitting under prevention of significant deterioration (PSD) and non-attainment new source review (NNSR).

- PSD sources must apply Best Available Control Technology (BACT) and demonstrate acceptable ambient impacts from forecasted emissions through modeling
- NNSR sources must apply Lowest Achievable Emission Rate (LAER) technology and provide emission offsets at more than 1:1

Example: A major source of  $\text{NO}_x$  making a major modification in an area attainment for  $\text{NO}_2$  but non-attainment for ozone ( $\text{O}_3$ ), would need to:

- ◆ apply BACT for  $\text{NO}_2$  and demonstrate acceptable impacts
- ◆ apply LAER for  $\text{NO}_x$  and provide external offsets for  $\text{NO}_x$  emissions

**Affected Sources: New and existing major emitting stationary sources of NSR pollutants**

# How Are Nitrogen Oxide Emissions Regulated?

## Mobile Source Emission Standards for On- and Off-road Vehicles

### 40 CFR:

Part 79	Registration of Fuels and Fuel Additives
Part 80	Regulation of Fuels and Fuel Additives
Part 85	Control of Air Pollution from Mobile Sources
Part 86	Control of Air Pollution from New and In-Use Highway Vehicles and Engines
Part 87	Control of Air Pollution from Aircraft and Aircraft Engines
Part 88	Clean Fuel Vehicles
Part 89	Control of Emissions from New and In-use Non-road Compression Ignition Engines
Part 90	Control of Emissions from Non-road Spark Ignition Engines
Part 91	Control of Emissions from Marine Spark Ignition Engines
Part 92	Control of Air Pollution from Locomotives and Locomotive Engines
Part 94	Control of Emissions from Marine Compression Ignition Engines



**Affected Sources: On-road and non-road vehicles**

# How Are Nitrogen Oxide Emissions Regulated?

## Regional Haze – Clean Air Visibility Rule

- Program goal is to achieve natural background visibility conditions (pristine, pre-industrial age) in all 156 Class I (National Parks and Wilderness Areas) by 2064, by reducing emissions of fine particulate matter and its precursor pollutants
- Requires Best Available Retrofit Technology (BART) for certain industrial facilities emitting visibility reducing pollutants, including  $\text{NO}_x$ , that:
  - ◆ were built or reconstructed between August 7, 1962 and August 7, 1977
  - ◆ have the potential to emit more than 250 tpy of visibility-impairing pollutants



**Affected Sources: 26 source categories including utility and industrial boilers, large industrial plants such as pulp mills, refineries and smelters**

# How Are Nitrogen Oxide Emissions Regulated?

## Transportation and General Conformity

- Conformity is intended to ensure that federal actions do not:
  - ◆ cause new violations of air quality standards
  - ◆ worsen existing violations of standards
  - ◆ delay timely attainment of the NAAQS in non-attainment/maintenance areas
- If aggregate direct and indirect emissions exceed de minimis thresholds, conformity must be determined through mitigation and/or modeling  
Example: A Federal Action in a SERIOUS ozone non-attainment area with annual NO<sub>x</sub> emissions exceeding 50 tons would require mitigation (offsets)

**Affected Sources: Federal Actions in non-attainment and maintenance areas**



# How Are Nitrogen Oxide Emissions Regulated?

## National Environmental Policy Act (NEPA)

### Federal Actions must be assessed for their effects, including:

- ◆ Land Use
- ◆ Air Quality
- ◆ Noise
- ◆ Geology, Topography, & Soils
- ◆ Water Resources
- ◆ Biological Resources and Ecosystems
- ◆ Cultural Resources
- ◆ Visual/Aesthetic Resources
- ◆ Socioeconomics
- ◆ Environmental Justice
- ◆ Infrastructure, including Transportation
- ◆ Hazardous and Toxic Materials and Wastes
- ◆ Recreation

Example: A federal action including a major source of NO<sub>x</sub> emissions could be assessed using New Source Review tools and the impacts mitigated as with General Conformity

**Affected Sources: Federal Actions**

# How Are Nitrogen Oxide Emissions Controlled?

Anthropogenic  $\text{NO}_x \equiv \text{NO} + \text{NO}_2$ , is generally formed by high-temperature fuel combustion, via three possible pathways:

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## Thermal $\text{NO}_x$

formed by oxidation of nitrogen in combustion air with oxygen in combustion air – generally the largest contributor to anthropogenic  $\text{NO}_x$  and manageable by both combustion and post-combustion controls

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## Fuel $\text{NO}_x$

oxidation of nitrogen present in a fuel – generally more of a problem with solid fuels – must be controlled by post-combustion controls

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## Prompt $\text{NO}_x$

formed by a different mechanism involving organic combustion radicals – a lesser contributor to overall  $\text{NO}_x$  and only controllable with post combustion controls.

# How Are Nitrogen Oxide Emissions Controlled?

Nitrogen oxide emissions from stationary and mobile sources are generally either prevented from forming or reduced before release.

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## Combustion Control

- Low Excess Air
- Flue Gas Recirculation
- Low NO<sub>x</sub> Burners
  - ◆ Staged Air Combustion
  - ◆ Staged Fuel
- Water or Steam Injection
- Reburning
- Exhaust Gas Recirculation

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## Post-Combustion Control

- Selective Noncatalytic Reduction (SNCR)
- Selective Catalytic Reduction (SCR)
- Nonselective catalytic reduction (NSCR)

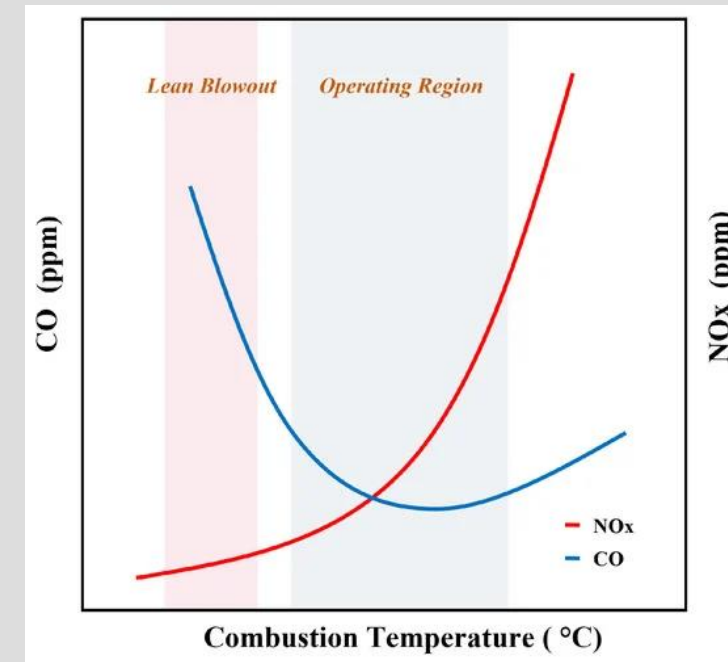
# How Are Nitrogen Oxide Emissions Controlled?

## Combustion Control – Low Excess Air

- Reduces available oxygen, peak flame temperature and thermal  $\text{NO}_x$  formation
- Also improves thermal efficiency of combustion units
- Must be balanced to ensure efficient (complete) combustion – low CO
- By itself, provides 10-20%  $\text{NO}_x$  reduction

## Combustion Control – Flue Gas Recirculation

- Reduces available oxygen, peak flame temperature and thermal  $\text{NO}_x$  formation by returning 10-30% of flue gas to the combustion chamber
- Suitable for large industrial boilers and furnaces
- Must be carefully controlled to ensure efficient (complete) combustion – low CO
- Can provide 15+%  $\text{NO}_x$  reduction



# How Are Nitrogen Oxide Emissions Controlled?

## Combustion Control – Low NO<sub>x</sub> Burners

- Provides staged combustion to reduce peak flame temperature, high-temperature residence time and thermal NO<sub>x</sub> formation
- Can provide 20-50% reduction in NO<sub>x</sub> emissions
- When used in conjunction with FGR, ultra-low NO<sub>x</sub> burners (UNLB) can achieve low single digit ppm NO<sub>x</sub> concentrations

## Combustion Control – Water or Steam Injection

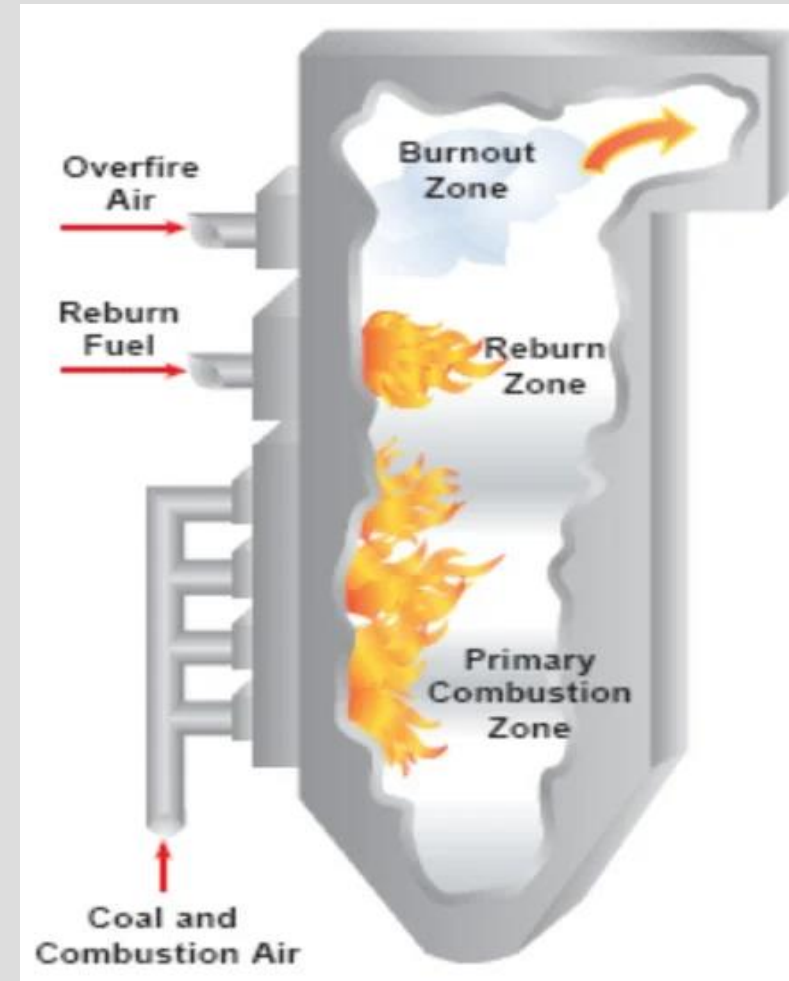
- A method of controlling NO<sub>x</sub> emissions from combustion turbines, still in use with older models
- Water or steam injected into the combustor reduces peak combustion temperature and thermal NO<sub>x</sub> formation
- Capable of reducing NO<sub>x</sub> emissions by from 60 – 80%
- Largely superseded in new combustion turbines by dry low-NO<sub>x</sub> combustor designs



# How Are Nitrogen Oxide Emissions Controlled?

## Combustion Control – Reburning

- Provides staged combustion to reduce high-temperature residence time under oxidizing conditions and thermal  $\text{NO}_x$  formation
- Must commonly used with large industrial or utility plant boilers, where natural gas is injected above the main combustion zone for a fuel like pulverized coal, followed by tertiary combustion air injection
- The reburn fuel typically contributes 15-20% of the gross fuel heat input
- Reburning can provide 50-70% reduction in  $\text{NO}_x$  emissions
- Use is waning as coal-fired boilers are retired



# How Are Nitrogen Oxide Emissions Controlled?

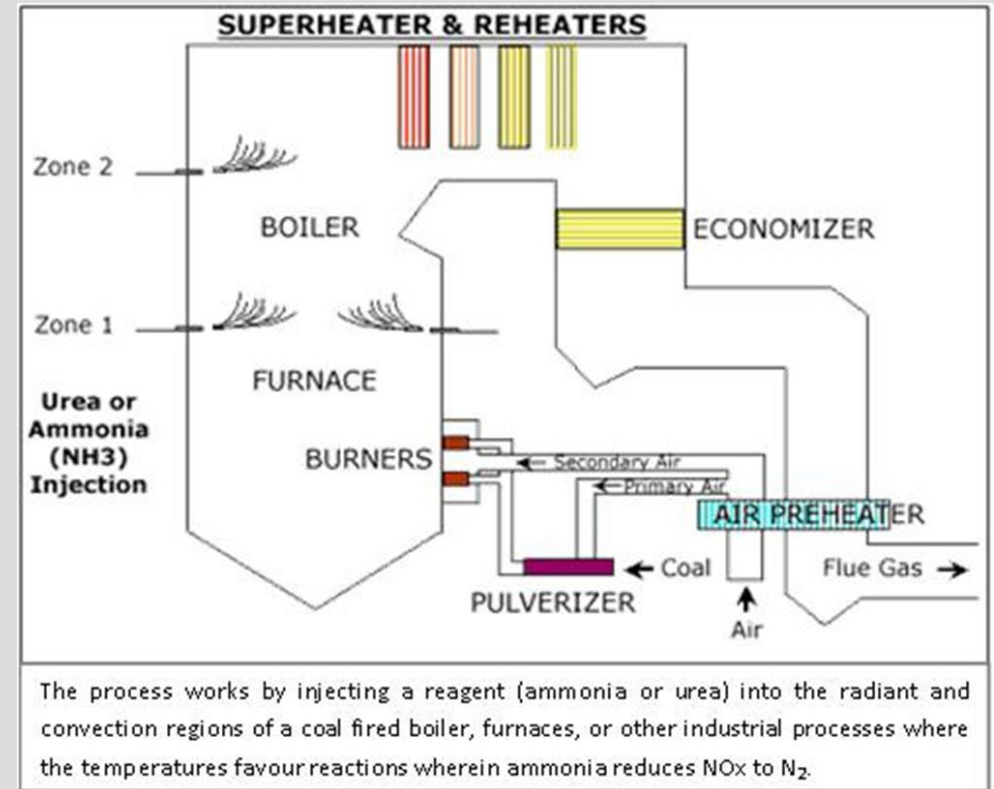
## Combustion Control – Exhaust Gas Recirculation (EGR) for Reciprocating Internal Combustion Engines

- As with FGR for stationary external combustion systems, EGR returns a portion of the exhaust gases (10-20%) to the intake side of the engine, tempering the combustion reaction to lower flame temperatures and reduce  $\text{NO}_x$  formation
- Can provide 10-20% reduction in  $\text{NO}_x$  emissions
- EGR must be properly controlled to:
  - ◆ minimize reduction of engine power and efficiency
  - ◆ minimize potential increase in CO and UHC emissions

# How Are Nitrogen Oxide Emissions Controlled?

## Post-Combustion Control – Selective Non-Catalytic Reduction (SNCR)

- Ammonia or urea is injected into boiler/furnace or ducts in a region where temperatures are between 900°C and 1,000°C
- Ammonia is ionized – reacts with  $\text{NO}_x$  to reduce to  $\text{N}_2$
- Temperature window is crucial for  $\text{NO}_x$  control – outside of this window either:
  - ◆ Ammonia “slip” (emissions) increase, or
  - ◆ More  $\text{NO}_x$  is generated.
- SNCR  $\text{NO}_x$  control efficiencies range from 20 and 70%
- Advanced SNCR utilizes real-time diagnostics and controls to optimize performance and can further improve  $\text{NO}_x$  reduction performance by 20% over SNCR

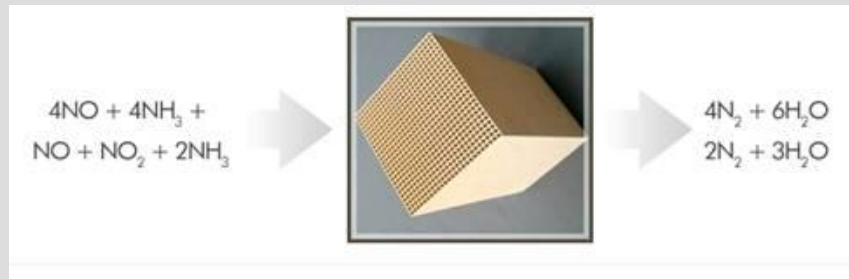




# How Are Nitrogen Oxide Emissions Controlled?

## Post-Combustion Control – Selective Catalytic Reduction (SCR)

- Ammonia or urea is injected into exhaust gas at between 200°C and 600°C, upstream of a catalyst – V, Mo, W, precious metals, or zeolites on a ceramic substrate
- Ammonia is ionized – reacts with NO<sub>x</sub> to reduce to N<sub>2</sub>

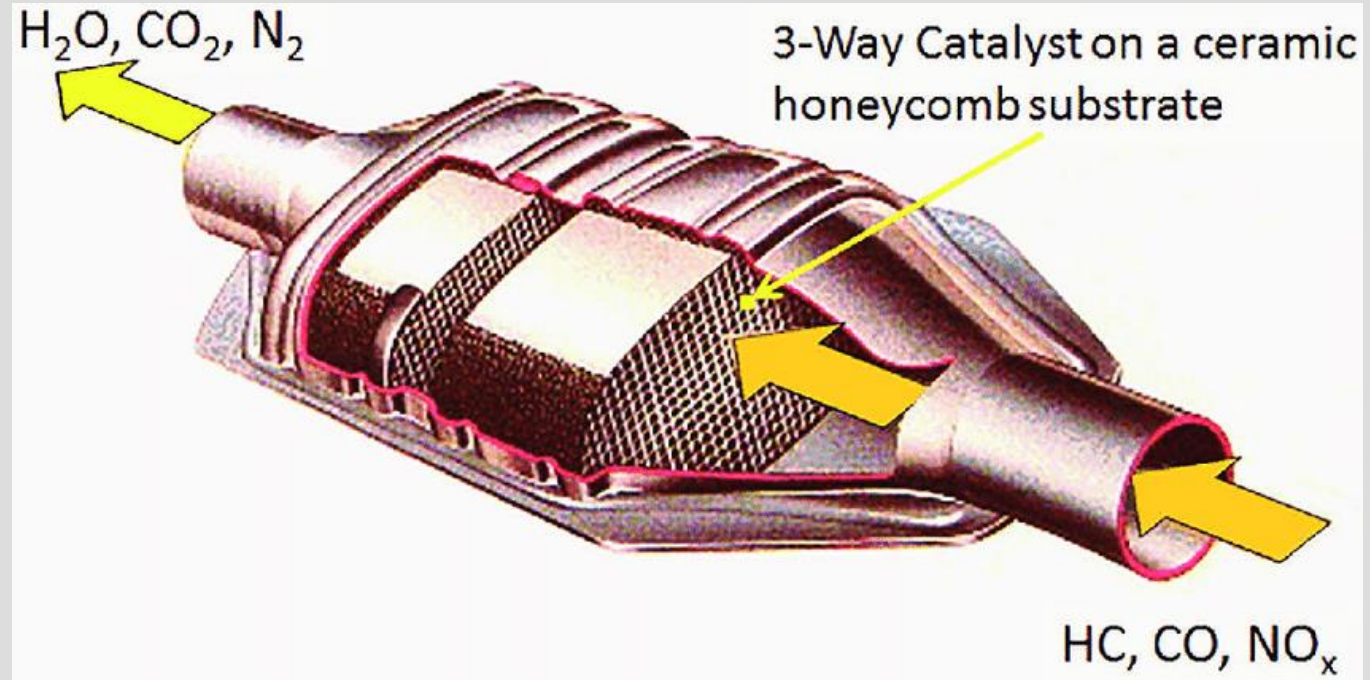


- Temperature window is crucial for NO<sub>x</sub> control – outside of this window either:
  - ◆ Ammonia “slip” (emissions) increase, or
  - ◆ More NO<sub>x</sub> is generated.
- SCR NO<sub>x</sub> control efficiencies range from 70 and 95+%
- Lower operating temperatures make SCR feasible for more processes than SNCR, but catalyst increases first cost

# How Are Nitrogen Oxide Emissions Controlled?

## Post-Combustion Control – Non-Selective Catalytic Reduction (NSCR) – Catalytic Converters on Vehicle Exhaust

- Reduces  $\text{NO}_x$ , CO, and UHC emissions by both reduction and oxidation reactions
- Operating temperature ranges from  $400^\circ\text{F}$  and  $1400^\circ\text{F}$
- Catalysts are generally noble metals (Pt, Pd, Rh) on ceramic substrate
- Control efficiencies range from 80 and 90%



# A Look Ahead - Trends

**Stationary sources of NO<sub>x</sub> have been heavily regulated and that class of sources is changing in important ways:**

- Large coal-fired power plant boilers are being retired and replaced by natural gas-fired power plants based on combustion turbine technology, significantly reducing the NO<sub>x</sub> emissions per net MWh of output.
- Combined heat and power (CHP), often natural gas-based, is proliferating in industrial and academic settings, reducing aggregate NO<sub>x</sub> emissions over THP
- Fossil fuel-fired power plants are being supplanted by renewable energy power plants (wind, solar PV, hydro, grid-scale storage, etc.), eliminating air emissions
- Control technologies (SNCR, SCR, FGR, ULNB) are being widely implemented, significantly reducing NO<sub>x</sub> emissions from existing stationary sources
- Industrial, commercial and residential buildings are increasingly being electrified, eliminating fuel combustion

# A Look Ahead - Trends

## Mobile (fuel-burning) sources have been heavily regulated and are also changing in ways that reduce/eliminate NO<sub>x</sub> emissions:

- Hybrid electric and battery electric vehicles are proliferating
- Charging infrastructure is growing rapidly to support HEV and BEV use
- Alternative forms of transportation are being facilitated
- Transit systems are increasingly electrified or using lower emission fuels
- Teleworking options are reducing commuting emissions
- Alternative shore power (ASP) at marine terminals eliminates “hoteling” emissions
- Electrification of cargo handling equipment at marine terminals
  - ◆ gantry cranes
  - ◆ drayage trucks
  - ◆ locomotives
- Electrification of passenger gates, GSE, and GAVs are reducing airport emissions

# Questions?

***Thank You!***

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