

REINHOLD ENVIRONMENTAL Ltd.



# **2017 NO<sub>x</sub>-Combustion-CCR Round Table Presentation**

February 27 & 28, 2017, in Cleveland, OH / Hosted by FirstEnergy

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# Advanced Oxidation Catalysts for Gas Turbines

February 28<sup>th</sup> 2017

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Johnson Matthey Stationary Emissions Control

[www.jmsec.com](http://www.jmsec.com)



Johnson Matthey

EMISSION CONTROL TECHNOLOGIES



# Stationary Emissions Control (SEC) - Overview

## Catalyst and System Technologies Portfolio:

- Selective Catalytic Reduction (SCR)
- CO and VOC Oxidation
- Hg Oxidation
- Ammonia Slip Control



Waste Incineration Plants



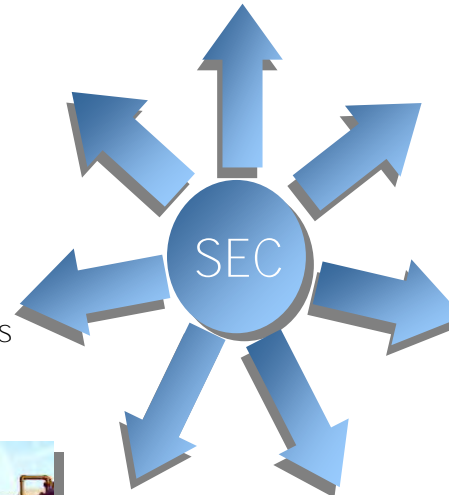
Power Plants



Gas Turbines



Industrial Processes



Stationary Engines



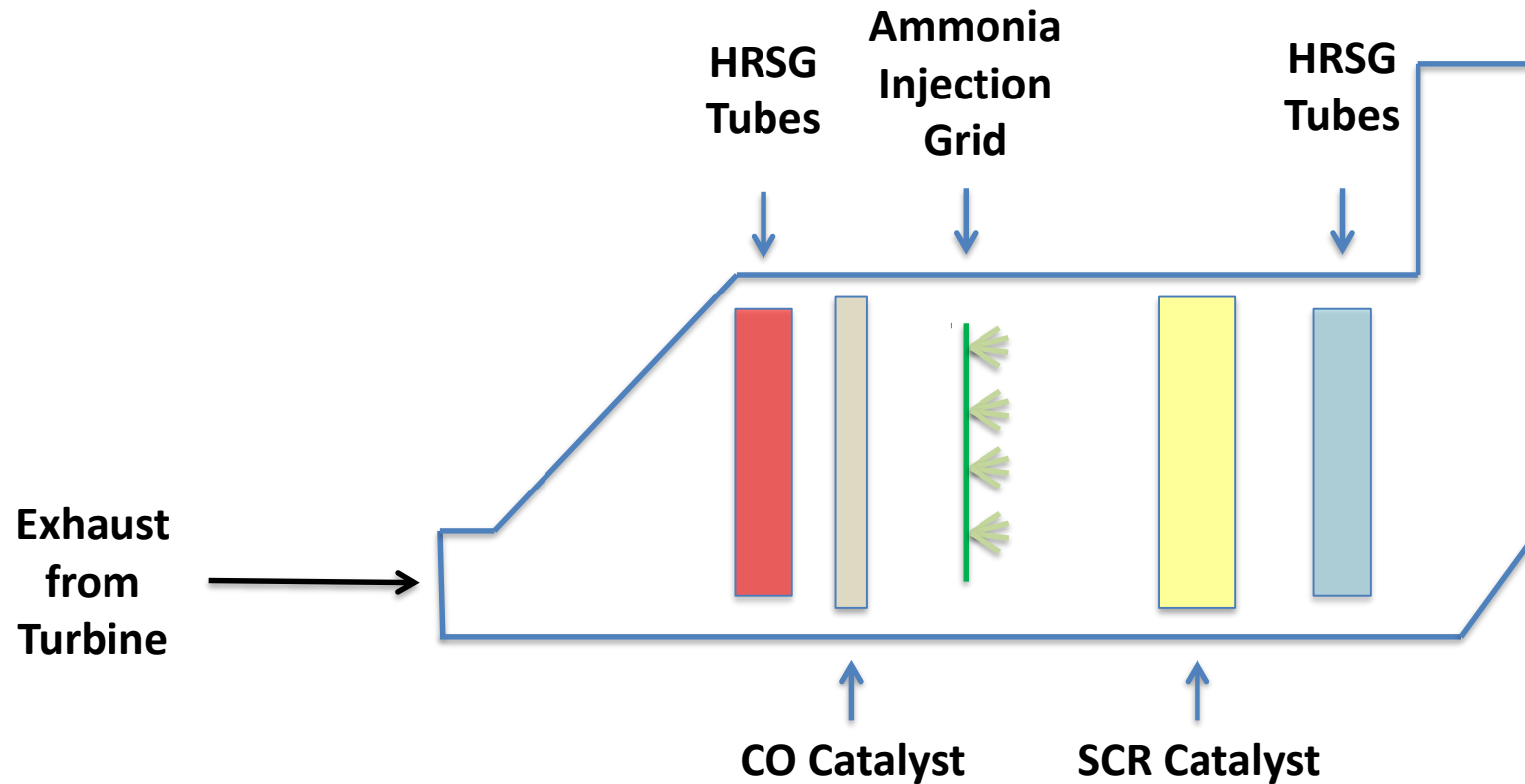
Boilers



Marine Engines



# After Treatment Layout Within Heat Recovery Steam Generator (HRSG)



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# Advances in CO Oxidation Catalyst Technology



# Typical Gas Turbine Emission Requirements

Fuel = NG or ULSD

CO Reduction

- 50 - 95+% Range
- 80 - 90% Typical

VOC Reduction

- 0 – 70% Range
- 0 – 50% Typical

NOx Reduction

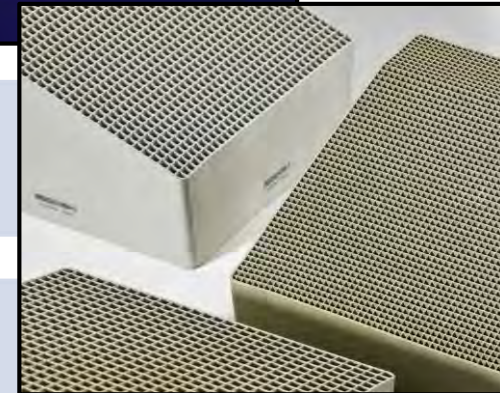
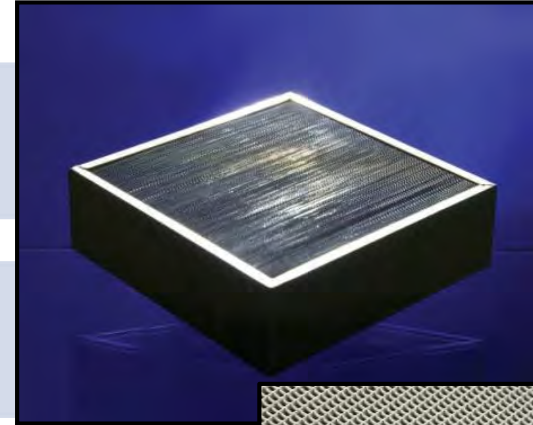
- 80 - 90% Typical
- 2ppm – 5ppm NH<sub>3</sub> Slip Typical

Pressure Drop

- ≤1.0in H<sub>2</sub>O Typical (CO Catalyst)
- ≤2.5in H<sub>2</sub>O Typical (SCR Catalyst)

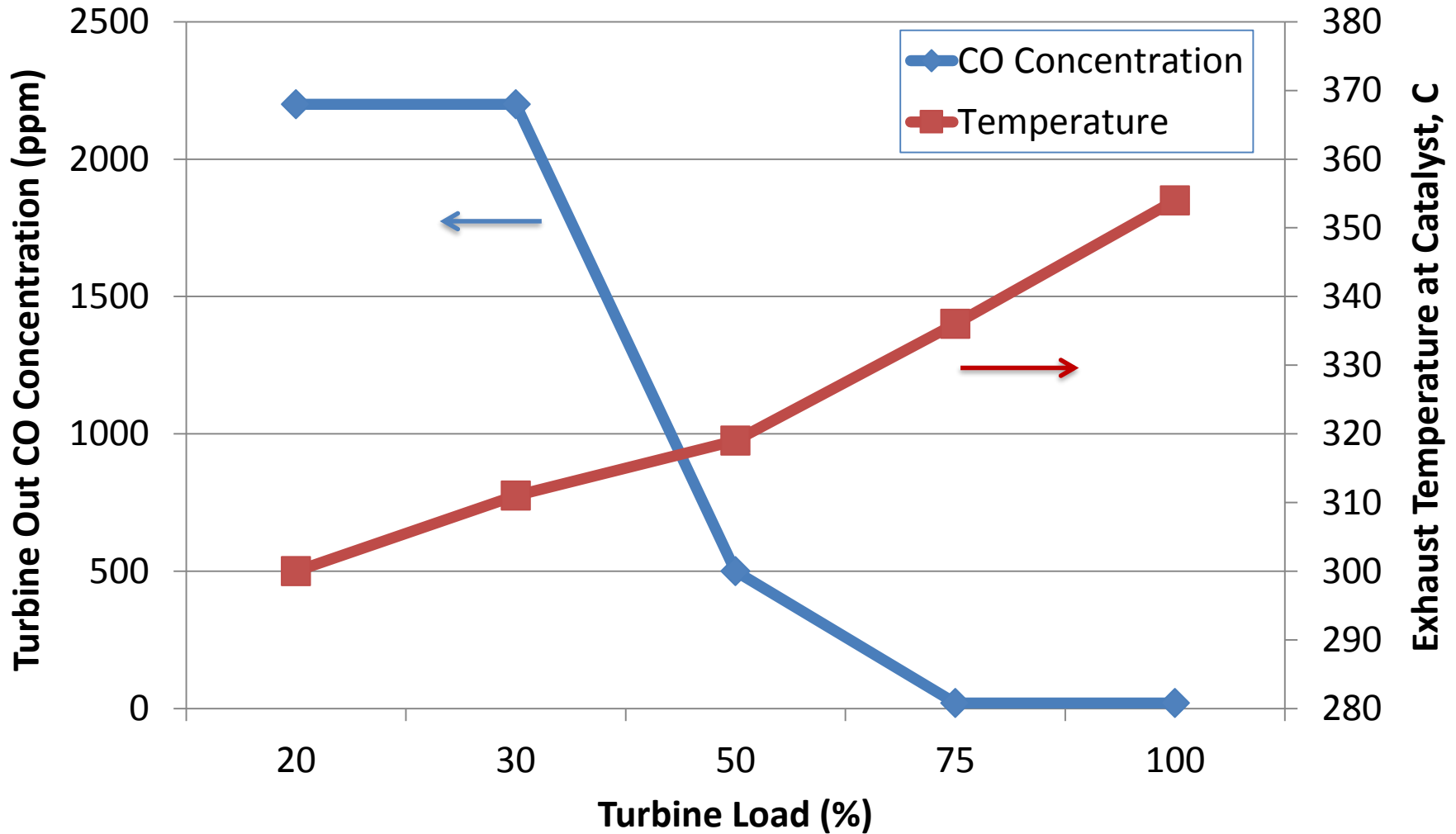
Performance Guarantee Period

- 3 years or 5 years Typical



# CO Emissions High / Temperatures Low at Low Loads

High CO conversion required to allow low load operation

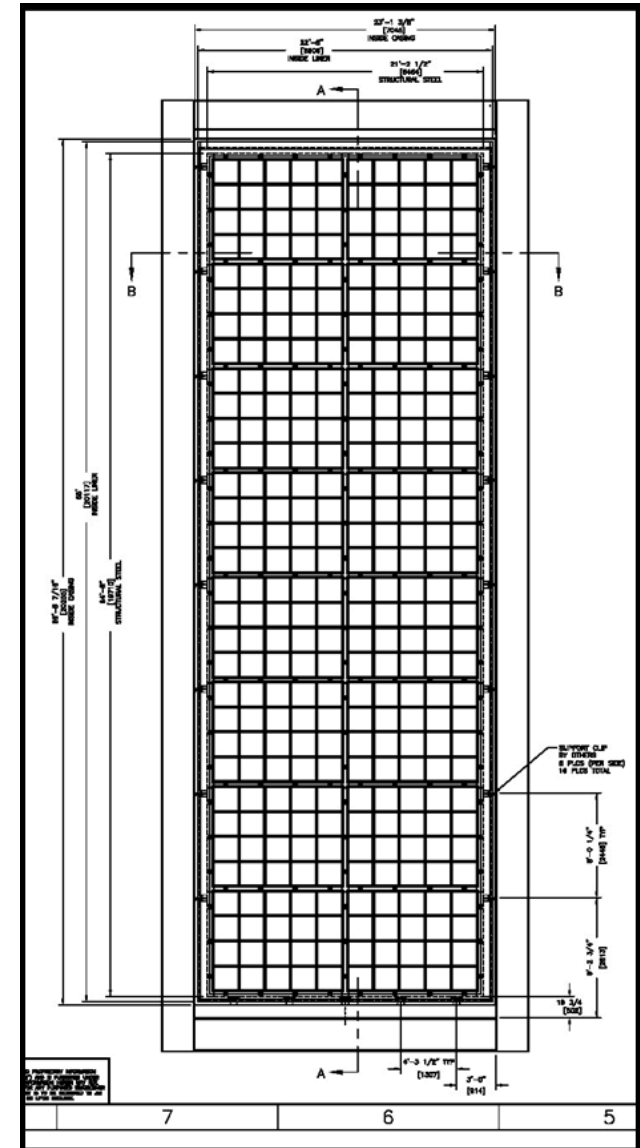
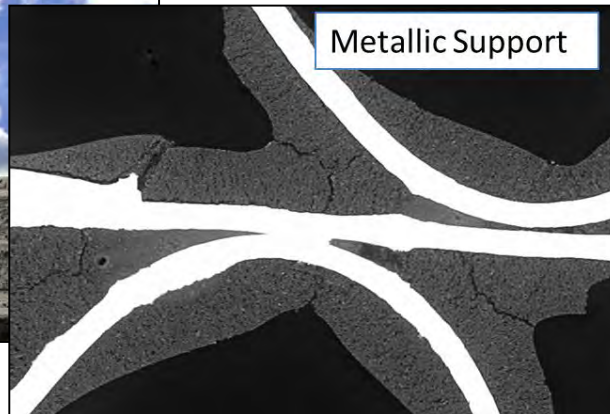
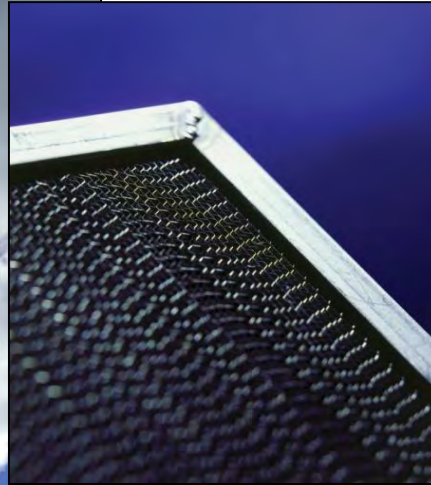
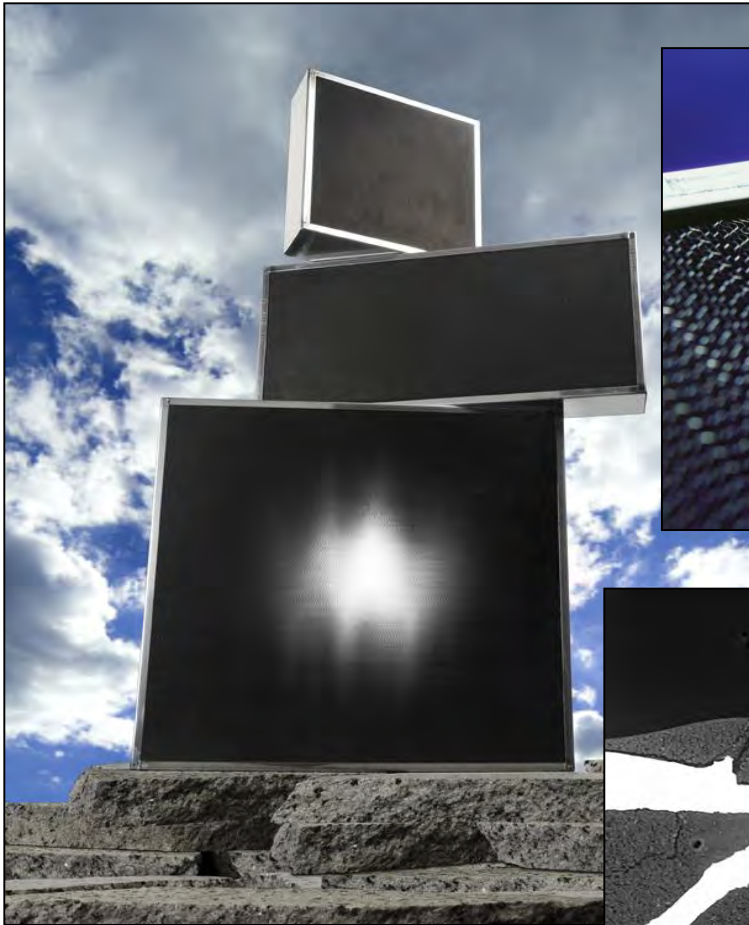


# CO / VOC Oxidation Catalyst



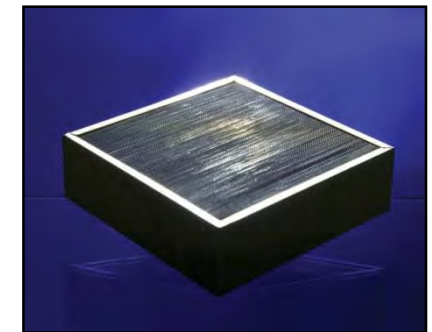
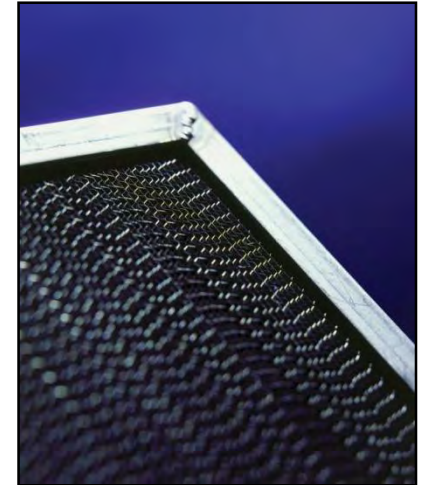
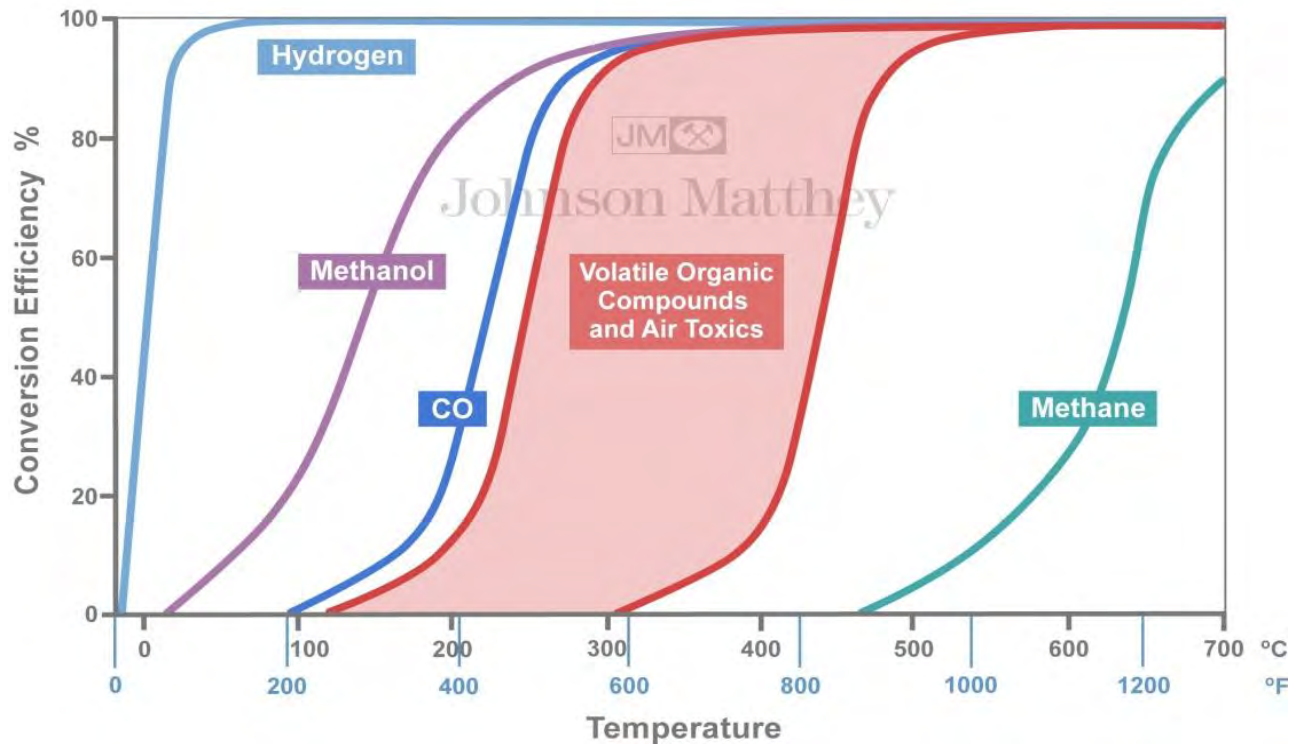
Coated Metal Honeycomb  
Typically 100 - 300 cells/in<sup>2</sup>

Catalyst blocks  
stacked in HRSG



# Oxidation Catalysts - Background

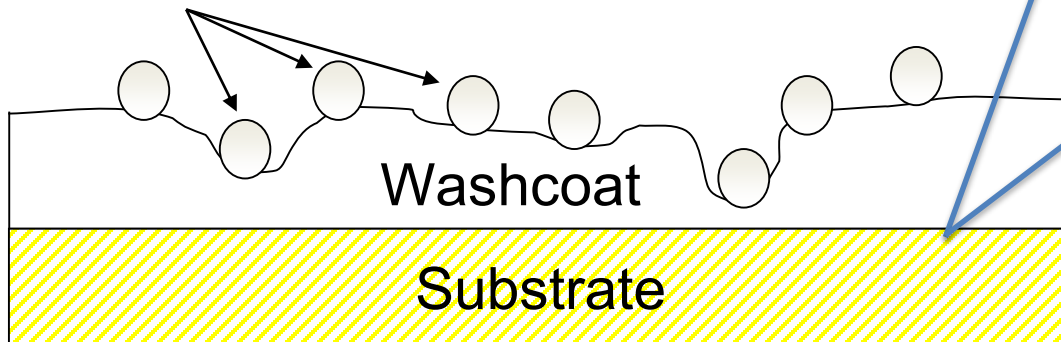
- Conversion requirements and temperatures will dictate required catalyst volumes
- Design specified with catalyst model developed from extensive database.



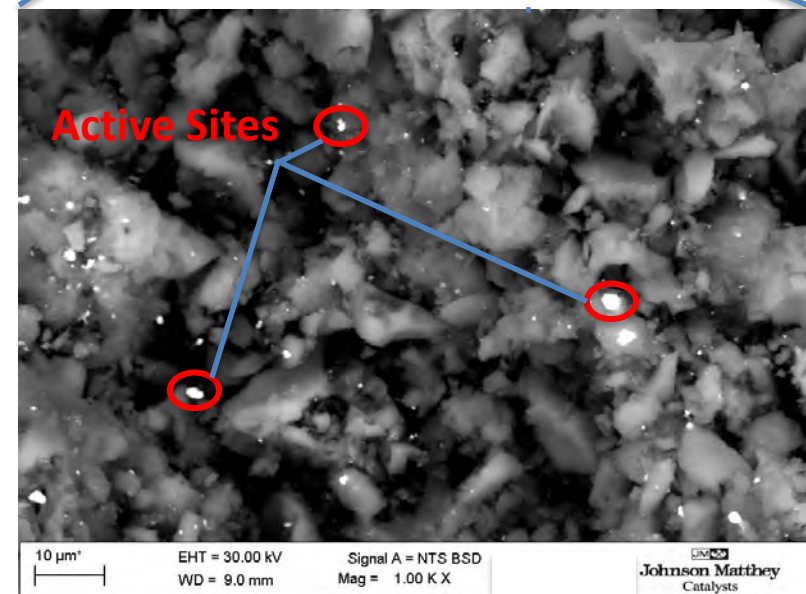
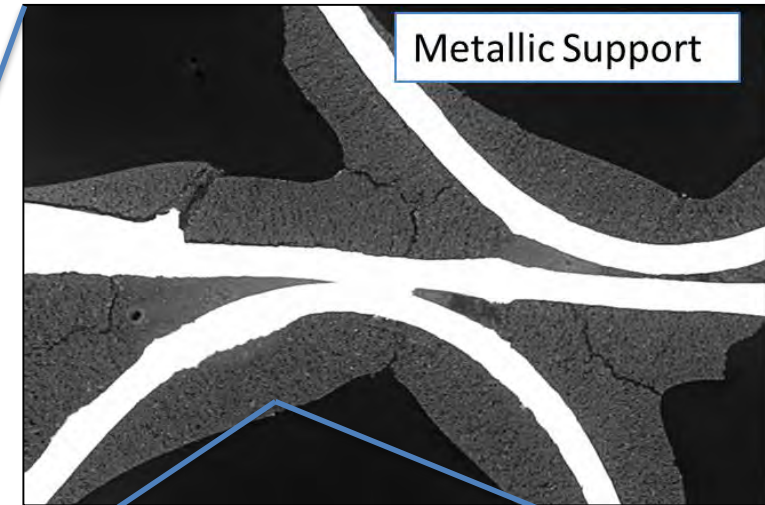
# Catalyst Conversion Efficiency

- Catalyst “conversion efficiency” is related to the catalyst durability, reactant residence time (gas hourly space velocity), temperature, and the active surface area of the catalyst

## Active Sites



- The number of “active sites” (active surface area) is maximized by dispersing the catalyst on substrate media coated with a high surface area washcoat



- **Thermal Deactivation:** *(typically irreversible)*
  - Failure of substrate material
  - Sintering of active catalytic species
  - Sintering of support
  - Reaction of catalyst materials
  - Catastrophic thermal event
  
- **Poisoning:** *(typically reversible)*
  - Chemical (selective) contamination of active sites
  - Physical (non-selective) contamination
    - ✓ *masking, fouling, plugging of cells/pores, washcoat attrition*

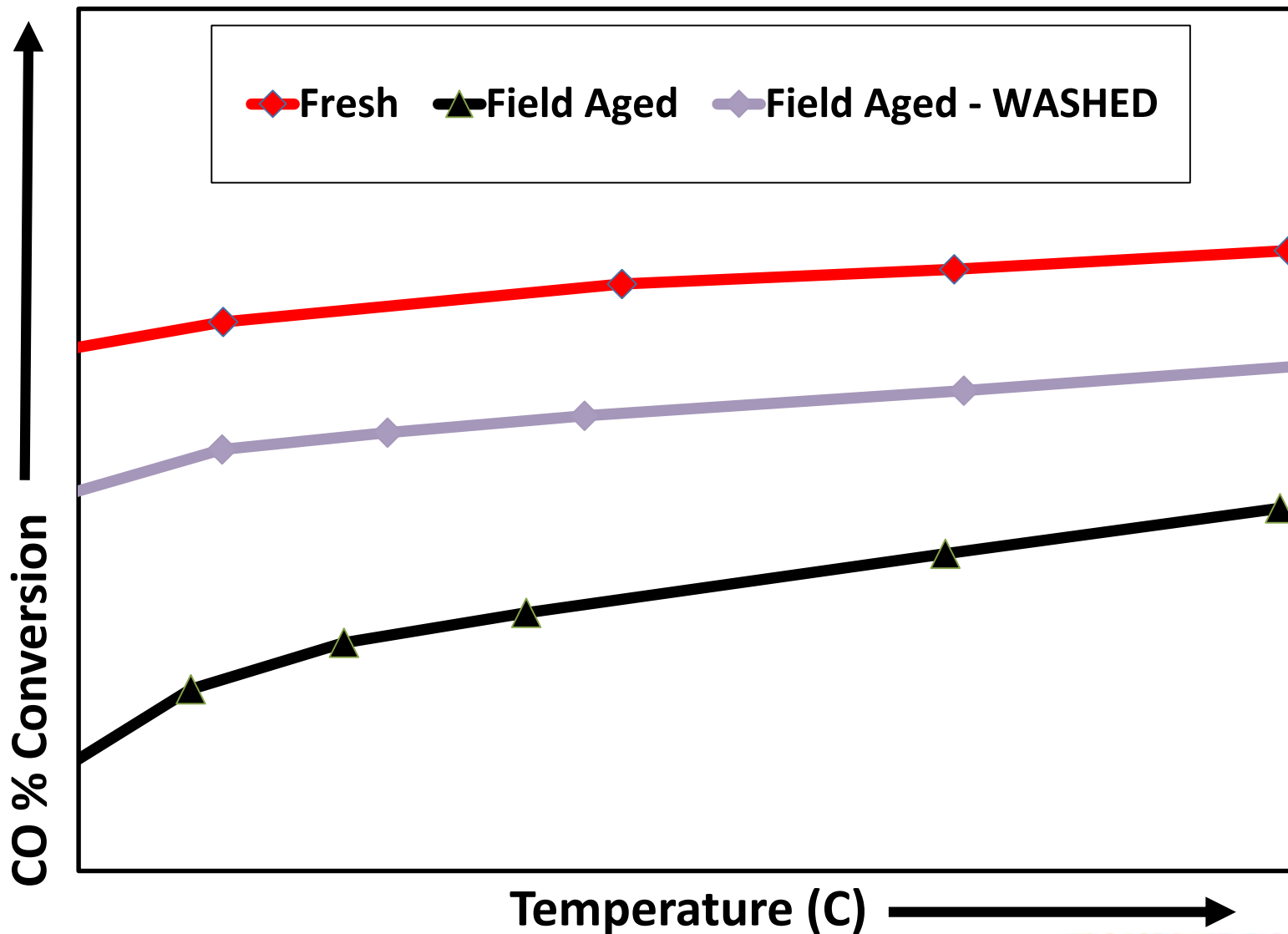


## Heavy and Base Metals

- *Lead (Pb)*
- *Arsenic (As)*
- *Zinc (Zn)*
- *Copper (Cu)*
- *Sulfur (S)*
- *Mercury (Hg)*
- *Tin (Sn)*
- *Iron (Fe)*
- *Chrome (Cr)*
- *Phosphorous (P)*
- *Silicon (Si)*
- *Nickel (Ni)*
- *Antimony (Sb)*

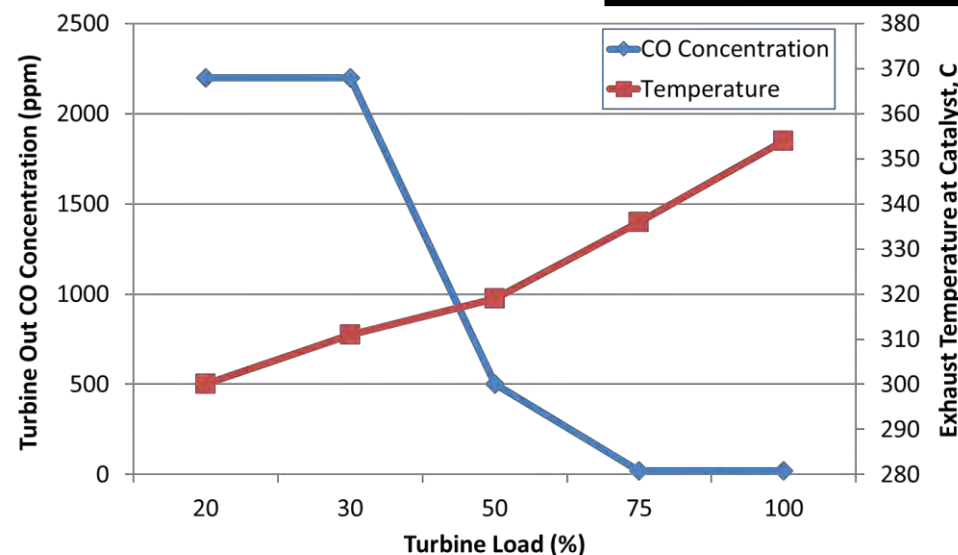
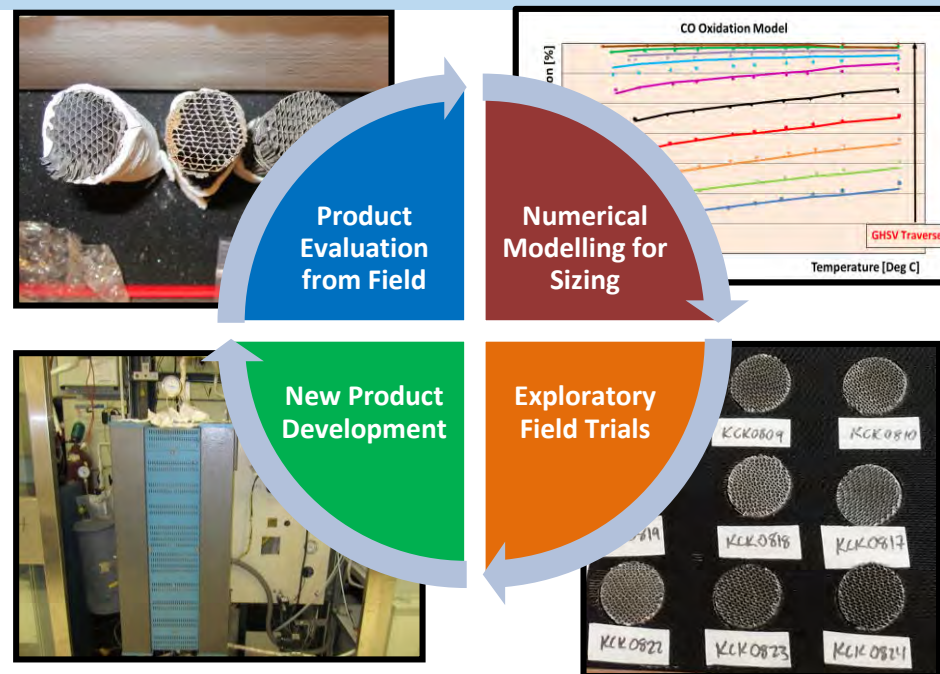


# Washing Allows Some Recovery of Catalyst Activity if Deactivation Mechanism is Through Poisoning

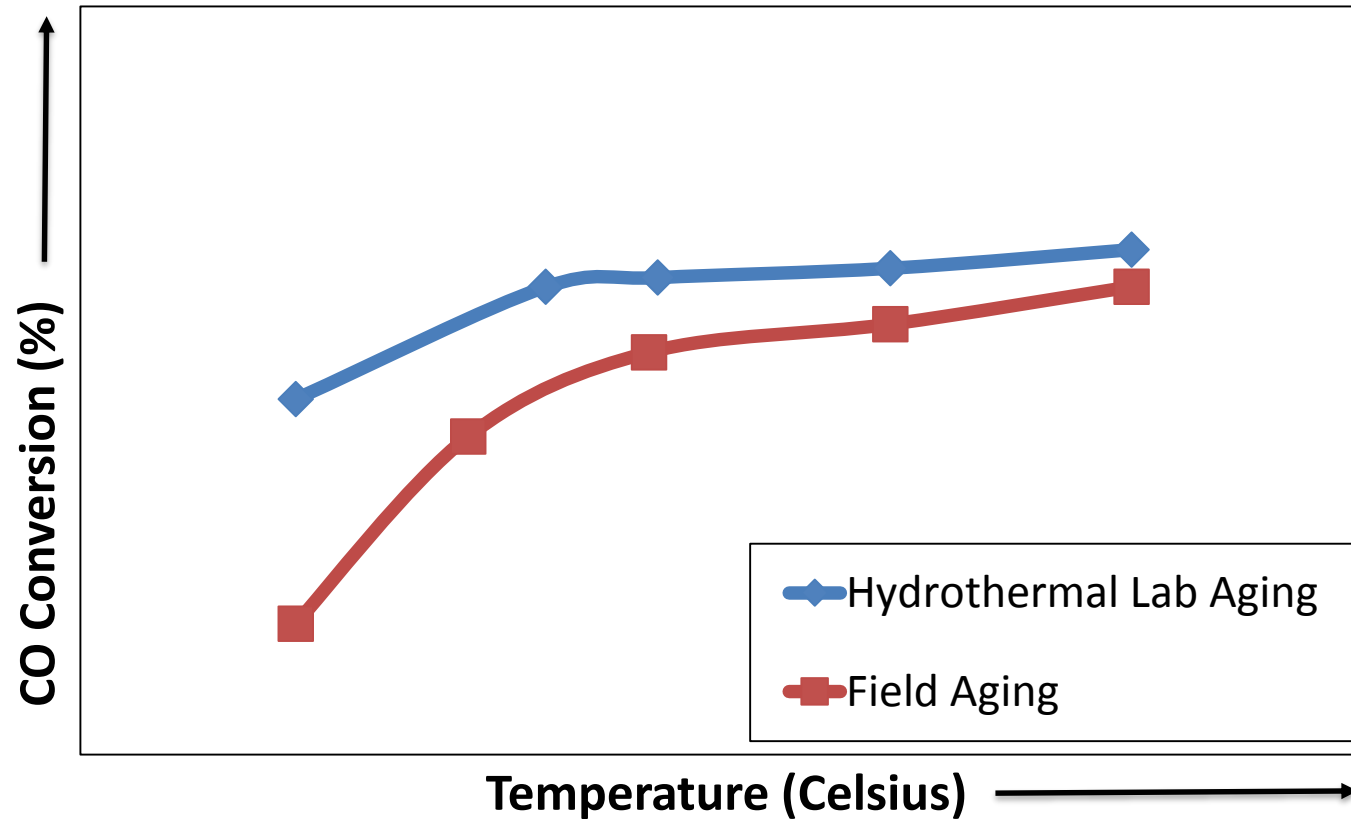


# Development of State-of-the-Art Technology

- Objective: Develop high activity catalyst technology durable to field conditions and lower temperatures
- GE Frame 7FA turbine running pipeline quality natural gas
  - Deactivation issues reported
  - Numerous washings of existing catalysts reported
- Temp. (base load) = 310°C - 354°C (590°F - 669°F)
- Temp. (partial load) = 288°F (550°C)



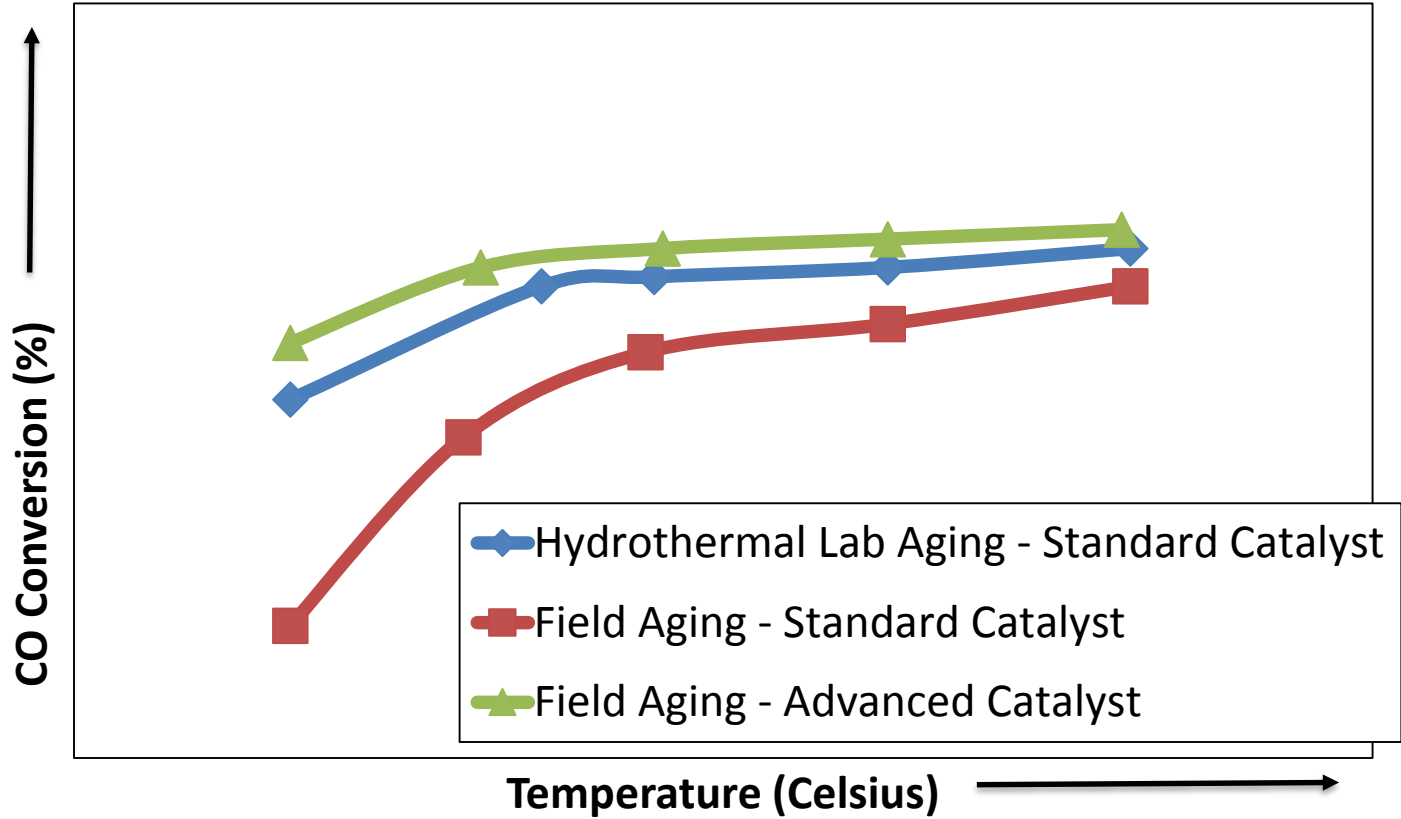
# Oxidation Catalysts – Lab vs. Field Aging



- Field aging introduces additional deactivation routes
- Field experience incorporated into catalyst designs



# Advanced Catalyst Shows Significantly Improved Field Durability



- Catalyst modifications made to reduce deactivation



# Development of Sulfur Resistant Catalyst

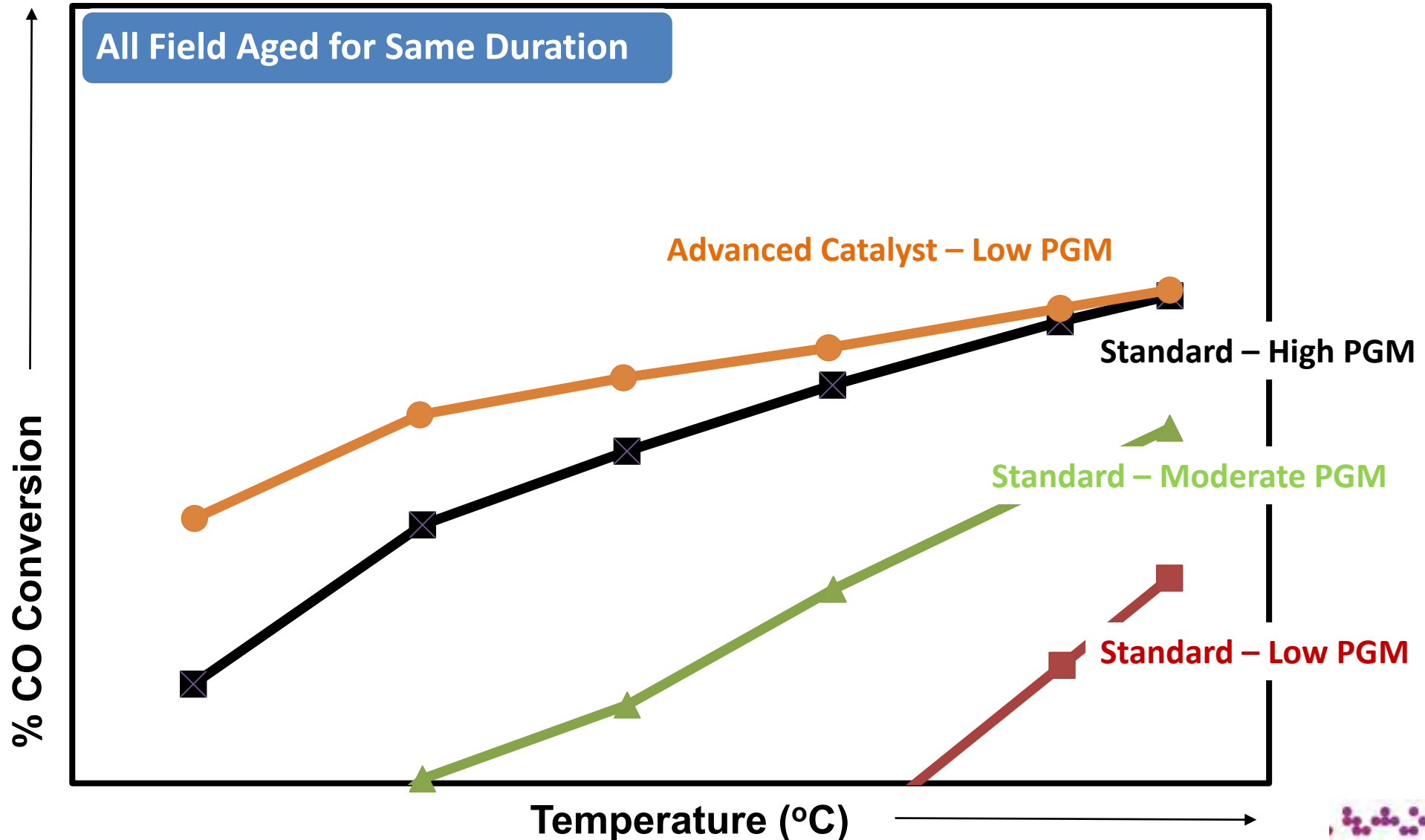
## Catalyst Sulfur Analysis (ICP Analysis, Relative Concentration)

<u>Catalyst</u>	<u>Hydrotherm. Lab Aged</u>	<u>Field Aged</u>	<u>Lab Sulfur Aged</u>
Standard	n.d.	1	2.35
Advanced	n.d.	0.69	0.67

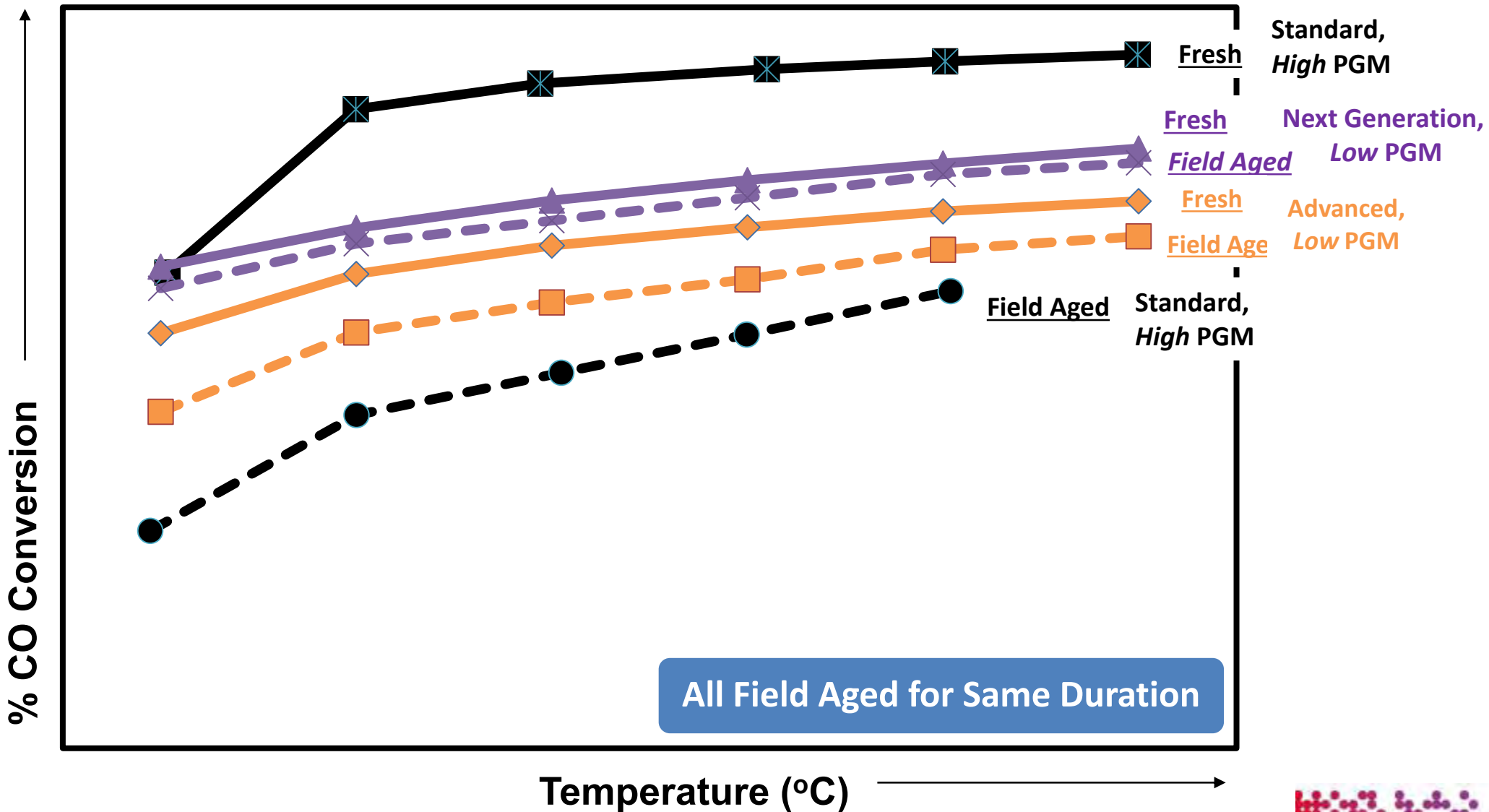
- Analysis of field aged catalyst shows presence of sulfur
- Advanced catalyst developed to reduce sulfur interaction with catalyst
- Lab sulfur aging developed to reproduce field mechanism (300°C, 5 ppm SO<sub>2</sub>)
- Continued field aging of advanced catalyst to understand durability



# Advanced Catalyst Technology More Active and Durable Than A Highly Loaded Standard Catalyst



# Next Generation Oxidation Technology in Development – Higher Activity, More Durable



- Site identified which shows high deactivation for Standard oxidation catalysts
  - Deactivation seen at all precious metal loads
- Laboratory aging developed to simulate field deactivation mechanism
- At this site, the Advanced low PGM catalyst shows durability superior to the Standard high PGM catalyst
- On-going development to identify Next Generation catalyst formulation with higher activity and durability



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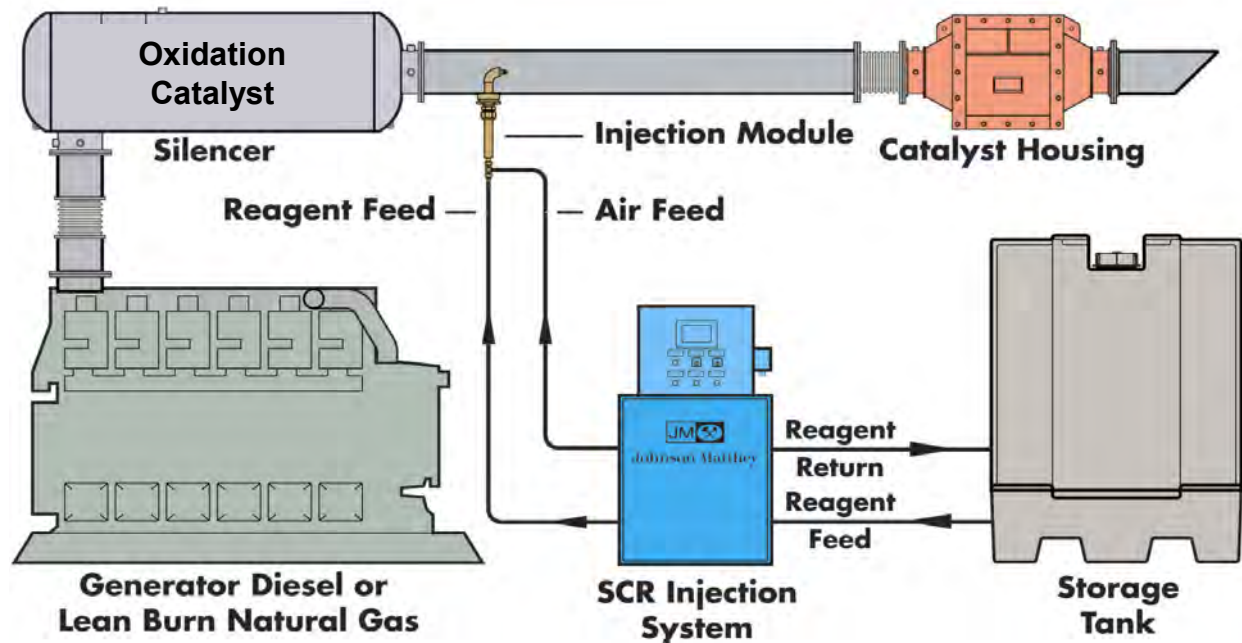
**Selective Catalytic Reduction (SCR)  
+  
Ammonia Slip Catalysts (ASC)**

**Simultaneous Elimination of  $\text{NH}_3$ ,  $\text{NO}_x$ , and CO**



# Over 30 Years Engine SCR Experience

- Over 30yrs Engine SCR Experience
- ~1 GW Installed SCR Systems since 2008 alone
  - Highly Utilized Application – Prime
- Fuel from HFO to ULSD to Natural Gas/Biogas
- Engine Sizes from 500kW to >18MW

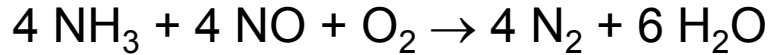


**Discussion Will Focus On Clean Fuels – ULSD/NG**

# SCR Uses NH<sub>3</sub> as the Reductant to Remove NO<sub>x</sub> From Lean Exhaust (Excess O<sub>2</sub>)



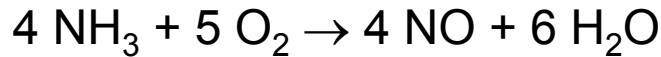
Relevant chemical reactions:



*standard SCR reaction (fast)*



*fast SCR (very fast)*



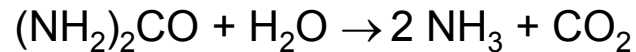
*undesired reaction (above 425°C)*

*note: there are other reaction pathways but the above reactions are dominant in lean exhaust*

**Reaction Stoichiometry: one molecule NH<sub>3</sub> reacts with one molecule of NO<sub>x</sub> (except slow NO<sub>2</sub> only SCR Reaction)**

Urea often used as NH<sub>3</sub> source because it is easier to handle/store than NH<sub>3</sub>

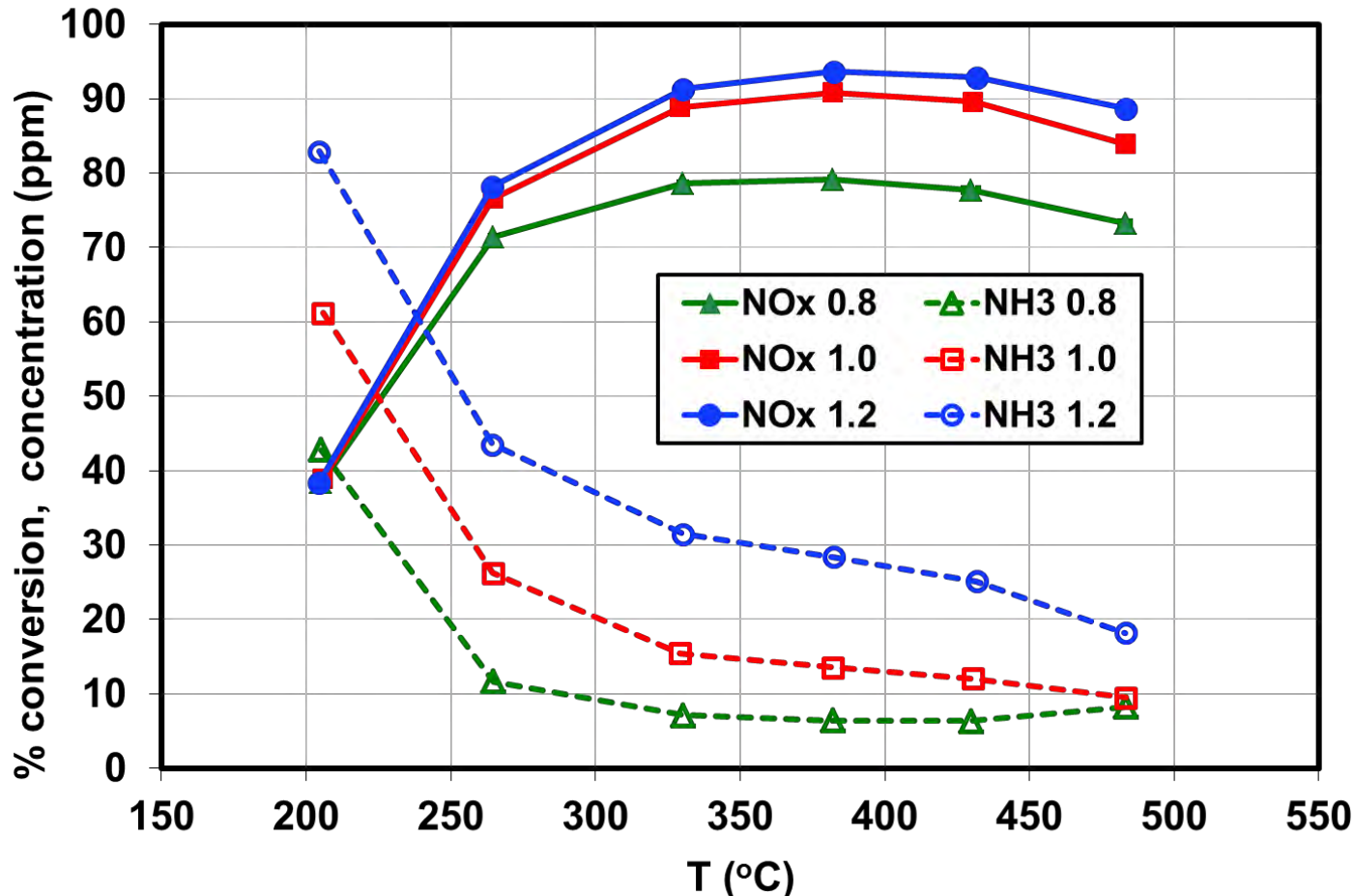
One molecule of urea decomposes into two moles of NH<sub>3</sub>:



# NO<sub>x</sub> Conversions and NH<sub>3</sub> Slip Values at Indicated ANRs Reflect 1:1 NH<sub>3</sub>:NO<sub>x</sub> Reaction Stoichiometry

Lab reactor data:

NO<sub>x</sub> conversion (solid) and corresponding NH<sub>3</sub> slip (dashed)



**At ANR 0.8** the max NO<sub>x</sub> conversion is 80% because there is insufficient NH<sub>3</sub> to fully react with the NO<sub>x</sub> although NH<sub>3</sub> slip is low

**At ANR 1.0** the max NO<sub>x</sub> conversion achieved is 90% with NH<sub>3</sub> slip ≈ 12 ppm

**At ANR 1.2** excess NH<sub>3</sub> enables slightly higher NO<sub>x</sub> conversion, but with much higher NH<sub>3</sub> slip

**Challenge:** High NO<sub>x</sub> conversion at low NH<sub>3</sub> slip with reasonable catalyst volume

## Challenge: High NO<sub>x</sub> Conversion at Low NH<sub>3</sub> Slip

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Non-uniform NH<sub>3</sub> distribution can result in localized ANRs:

- ANR < 1 results in incomplete NO<sub>x</sub> conversion
- ANR >1 results in NH<sub>3</sub> slip

Non-uniform NH<sub>3</sub> distribution can be a result of:

- Control system
- Gas flow characteristics
- Fluctuating load

Even the best SCR catalyst cannot achieve maximum NO<sub>x</sub> conversion with non-uniform NH<sub>3</sub> distribution

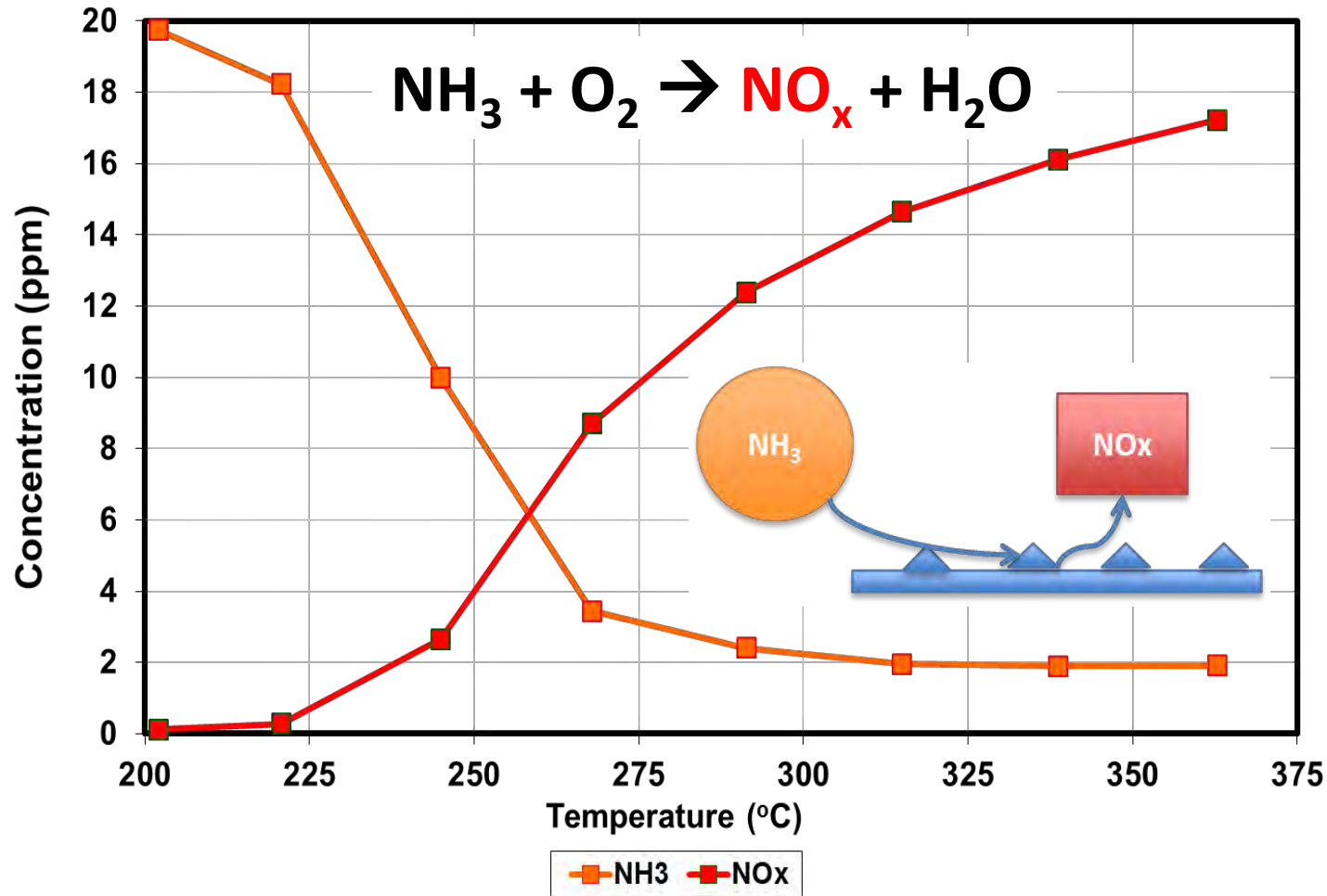
At high flow rates it is necessary to decrease ANR or increase catalyst volume in order to maintain low NH<sub>3</sub> slip

**Solution: Ammonia slip catalyst (ASC) to compensate for non-uniform NH<sub>3</sub> distribution and allow operation at higher ANR boosting NO<sub>x</sub> conversion while maintaining low NH<sub>3</sub> slip**

# Previous Generation ASC Exhibit Excellent Activity (High NH<sub>3</sub> Conversion) but Poor Selectivity (NO<sub>x</sub> Production)

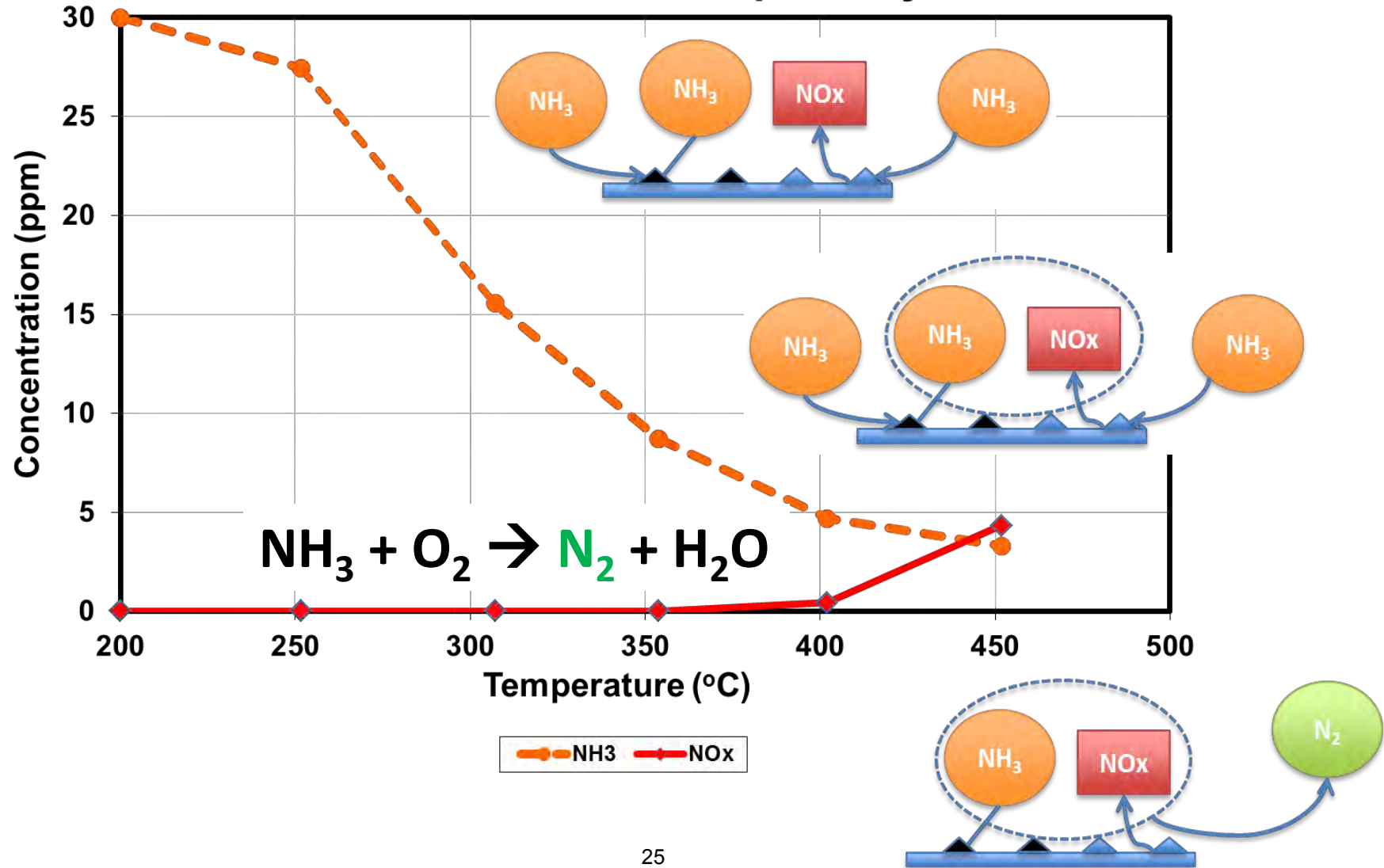


## Non-Selective Ammonia Slip Catalyst

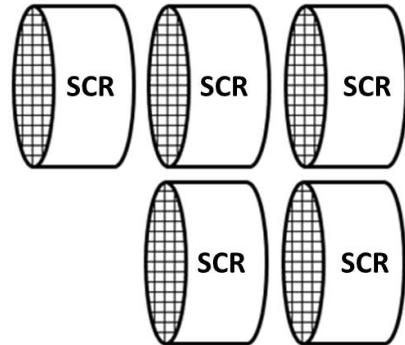


# Advanced ASC Performs Both Oxidation Function and SCR Function (Selective to N<sub>2</sub>) Simultaneously

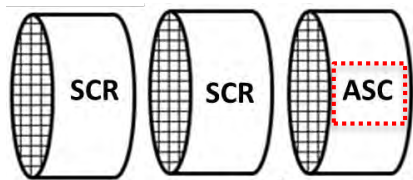
## Selective Ammonia Slip Catalyst



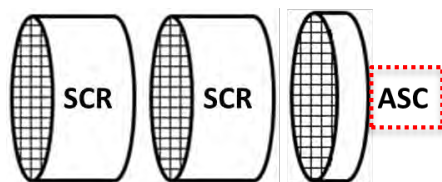
# Strategy Employed to Demonstrate Performance of Reduced Volume of SCR + ASC System



Establish baseline conversions with **baseline volume SCR** (3 pieces) and **reduced volume SCR** (2 pieces).



Replace 1/3 of the total SCR volume with ASC, maintaining total system volume (2 pieces SCR + 1 piece ASC). Evaluate performance of **constant volume SCR+ASC** system at each load.



Replace 1/3 of the total SCR volume with ASC volume equal to 1/6 the total, reducing the original system by about 20%. Evaluate performance of **reduced volume SCR+ASC** system at each load.



# Engine Testing Using Genset + Load Bank

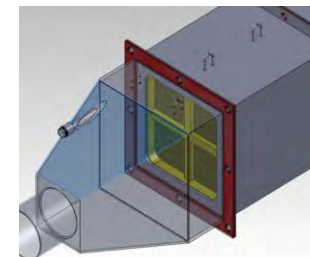
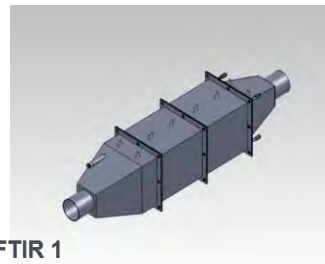
Testing performed on 11L, 1800 rpm, 270 kW Tier 2 genset + load bank

Load bank used to achieve 50kW, 100 kW, 150 kW, 200 kW, 250 kW

- single speed, limited operating temperatures and space velocities
- representative of actual engine application

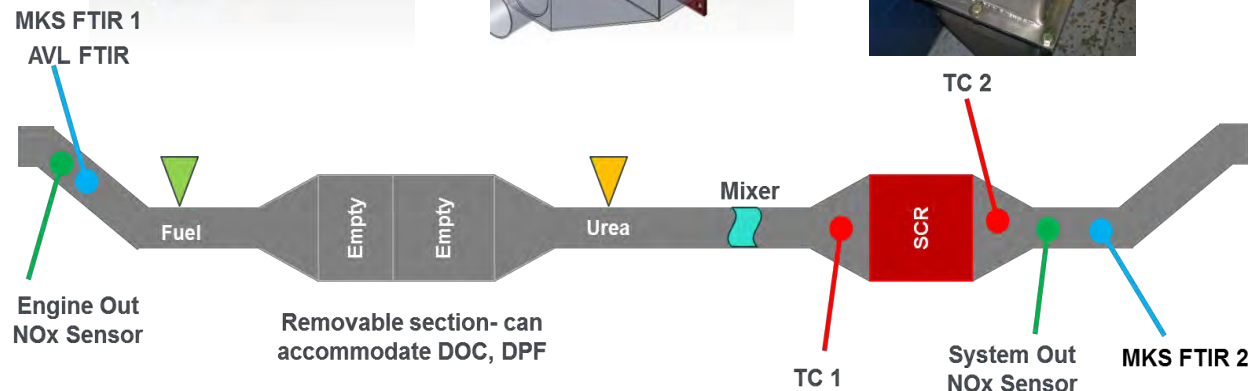
Typical engine performance targets:

- NO<sub>x</sub> 95% reduction
- NH<sub>3</sub> slip ≤ 10 ppm

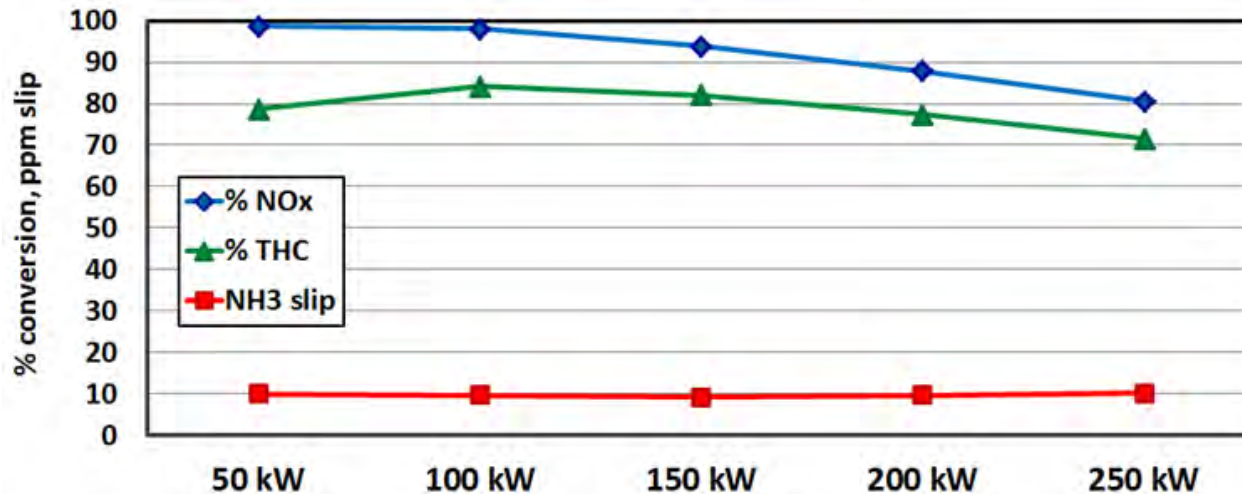


All tests were performed at constant 10 ppm NH<sub>3</sub> slip (9.0 to 10.5 ppm acceptable)

- Steady-state
- Adjust urea until max NO<sub>x</sub> conversion is achieved, without exceeding 10 ppm NH<sub>3</sub> slip

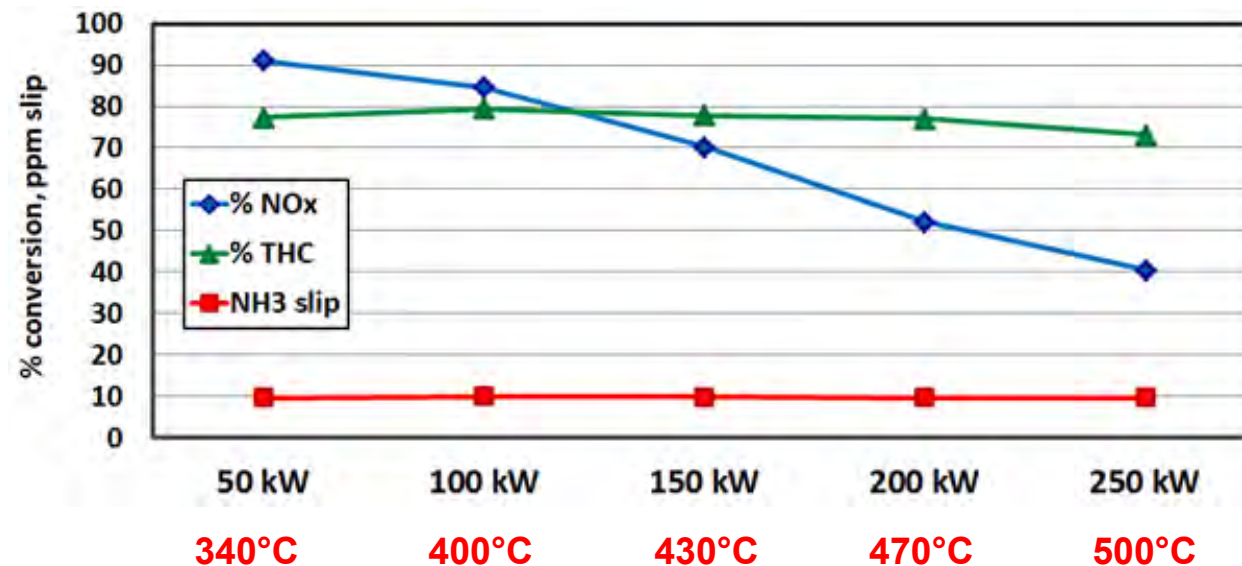
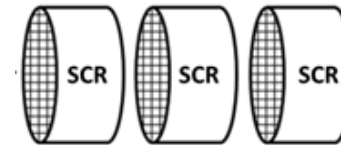


## Volume Reduction Cannot be Achieved by Simply Removing Catalyst



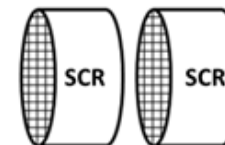
### Baseline volume SCR:

95% NOx conversion achieved at 50 kW – 150 kW load points



### Reduced volume SCR:

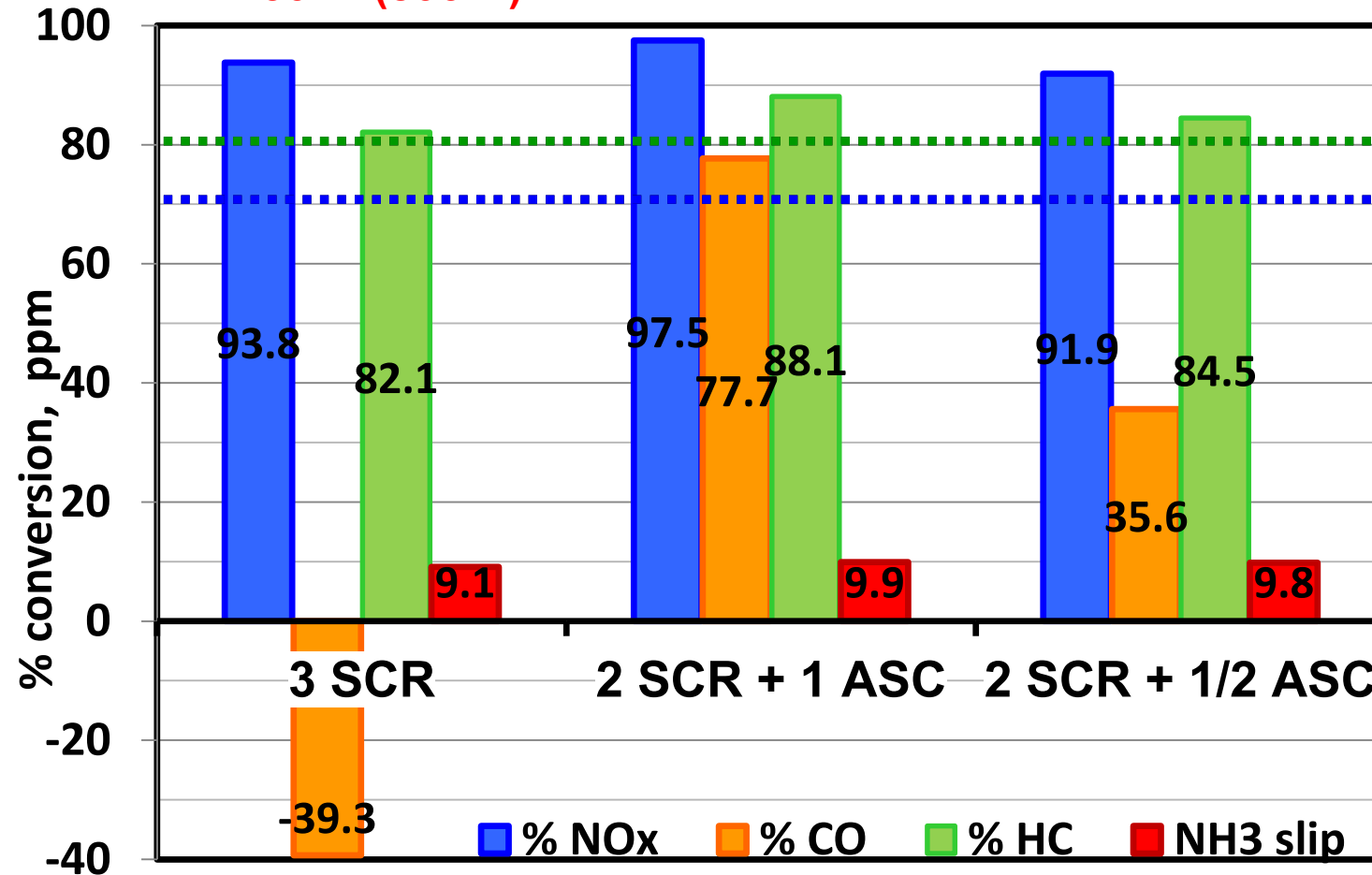
95% NOx conversion not achieved, even at 50 kW



# NOx, HC and CO Conversions Measured Over Baseline Volume, Constant Volume and Reduced Volume SCR and SCR+ASC Systems at 150 kW



**T = 430°C (806°F)**



% HC: 2 SCR only  
% NOx: 2 SCR only

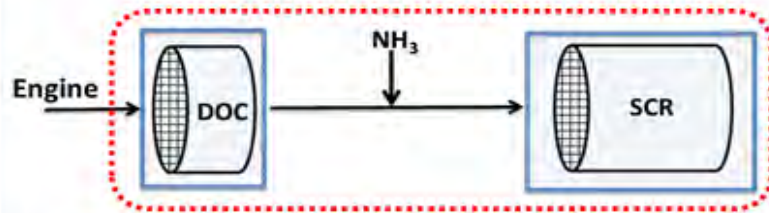
**Reduced volume SCR+ASC system delivers comparable NOx conversion, better HC conversion at  $\approx$  20% lower total catalyst volume**

**Added bonus of CO conversion**

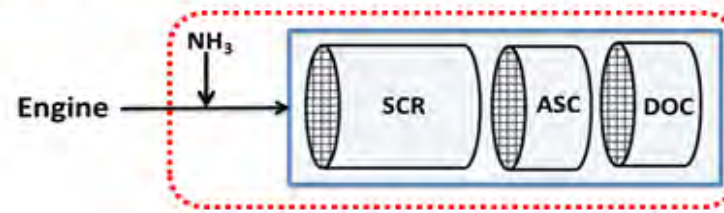


# Addition of Diesel Oxidation Catalyst (DOC) to Emission Control System May be Necessary When Very High VOC and CO Conversions are Required

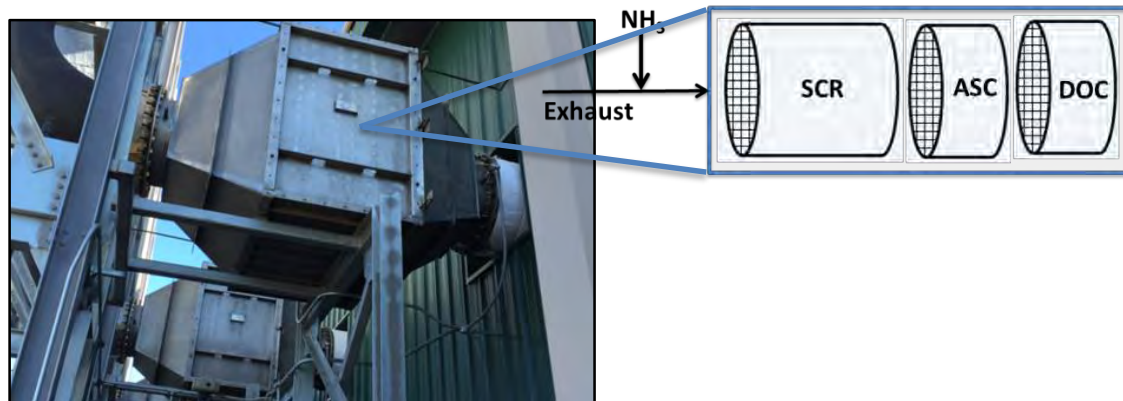
Utilization of ASC allows installation of DOC downstream of the SCR system:



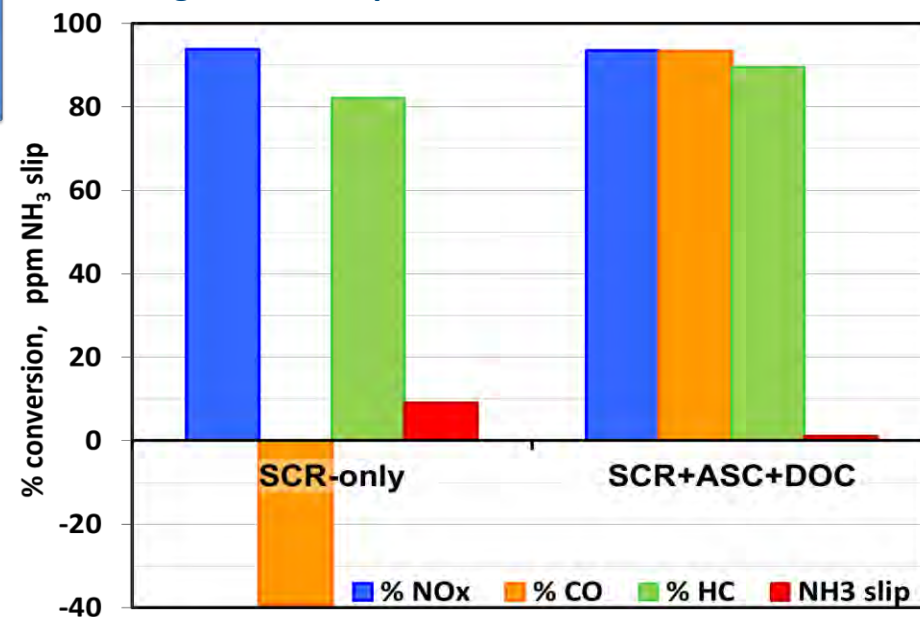
Without ASC: DOC oxidizes  $\text{NH}_3$  slip back to  $\text{NO}_x$ , must be upstream of  $\text{NH}_3$  injection



With ASC: Little  $\text{NH}_3$  slip; SCR+ASC+DOC can be put in smaller housing



Engine data: equal volume SCR and SCR+ASC+DOC



- More compact housing results in lower material costs
- High  $\text{NO}_x$ , HC and CO conversions achievable with SCR+ASC+DOC
- Low  $\text{NH}_3$  slip



## Demonstration Phase – Performance

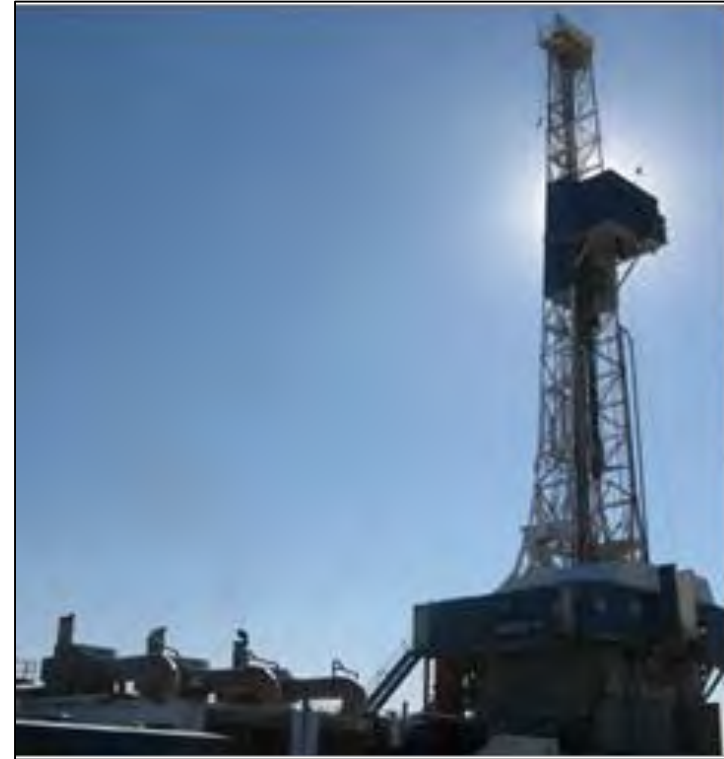
SCR operates only when the catalyst inlet temperature  $\geq 500^{\circ}\text{F}$  ( $260^{\circ}$ ), corresponds to  $\sim 20\%$  engine load

Engine-out NOx concentration range

- 400 ppm (20% load) to 1000 ppm (90% load)

Load bank was used to achieve engine loads of 20%-90%

After 6 months, NOx conversion and NH<sub>3</sub> slip measured at 10 loads in this range, results averaged:



**Gas drill rig powered by three 1476 hp diesel engines**

Species	Measured (at catalyst outlet)		
	Engine 1	Engine 2	Engine 3
% NOx conversion	98.2	98.3	98.1
ppm NH <sub>3</sub> slip	0.2	2.5	1.6



## Additional SCR+ASC Systems Installed

Project demonstrated that SCR+ASC could significantly reduce NOx at low NH<sub>3</sub> slip

State of Wyoming and BLM implemented emissions limits

- NOx: 90% conversion
- NH<sub>3</sub> slip ≤ 10 ppm

21 more SCR+ASC systems were added

Up to 24 SCR+ASC systems operate at one time

Systems installed 2008, still operating and achieving emissions targets

2016 NOx and NH<sub>3</sub> emissions measured, results are:



**Each diesel engine equipped with SCR+ASC system, above engine**

Species	Permit	Measured (at catalyst outlet)		
		Engine 1	Engine 2	Engine 3
% NOx conversion	90% conversion	96.6	94.9	96.5
ppm NH <sub>3</sub> slip	≤ 10 ppm slip	0.4	1.0	0.6



# Engine Ammonia Slip Catalysts (ASC) Summary

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- Active and Selective Ammonia Slip Catalysts (ASC) are in serial production at Johnson Matthey for many on and off road engine applications
- Robust performance demonstrated in the field despite rapid engine load swings
- Utilization of ASC allows continuous operation at higher ANRs which results in higher NO<sub>x</sub> conversion while maintaining low NH<sub>3</sub> slip
- ASC can also compensate for non-ideal NH<sub>3</sub> distribution
- The ASC can also allow system volume reductions under steady state and transient conditions
- Potential transfer of knowledge and experience to Gas Turbines applications



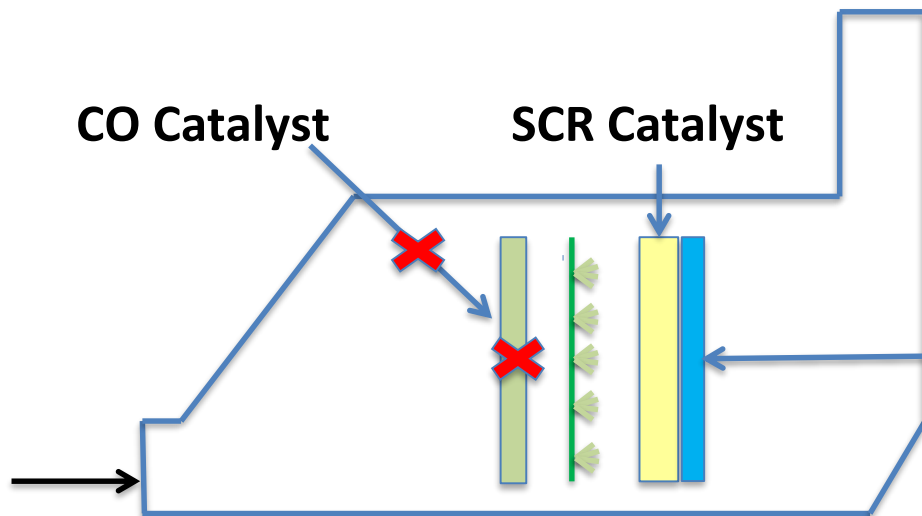
# Utilize Engine ASC Experience and Technology for Gas Turbine Emission Control



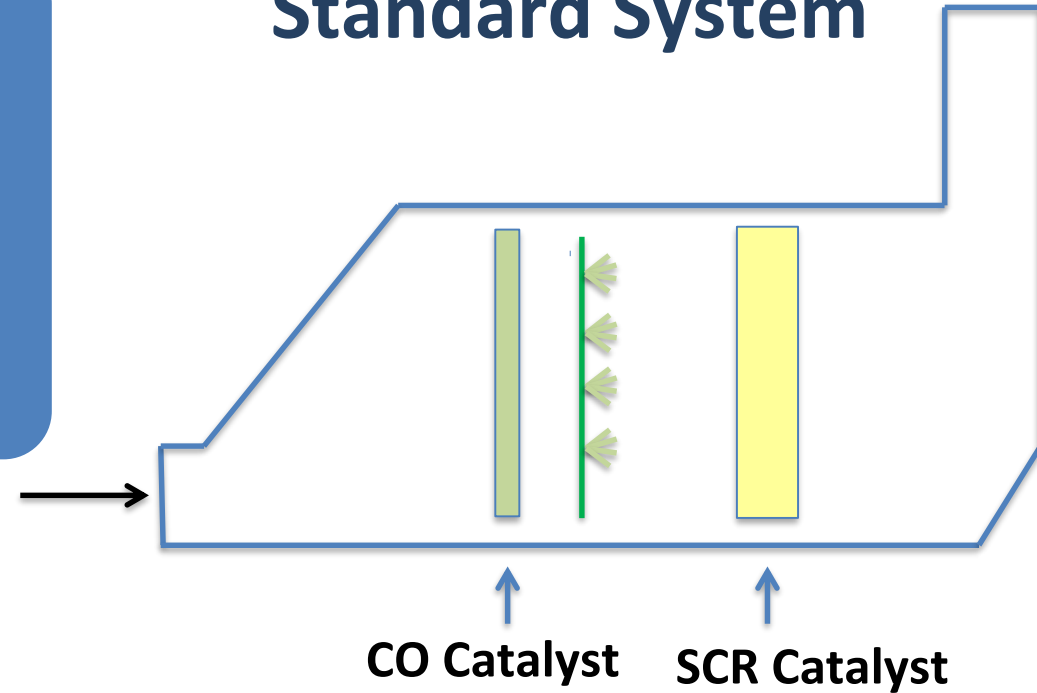
## SCR+ASC Advantages

- Reduced volume, delta P
- High NO<sub>x</sub> conversion, low NH<sub>3</sub> slip
- Reduced space and capital cost
- Reduced back-end deposits (NH<sub>3</sub> Salts)

## SCR+ASC System



## Standard System



Ammonia Slip Catalyst (ASC)

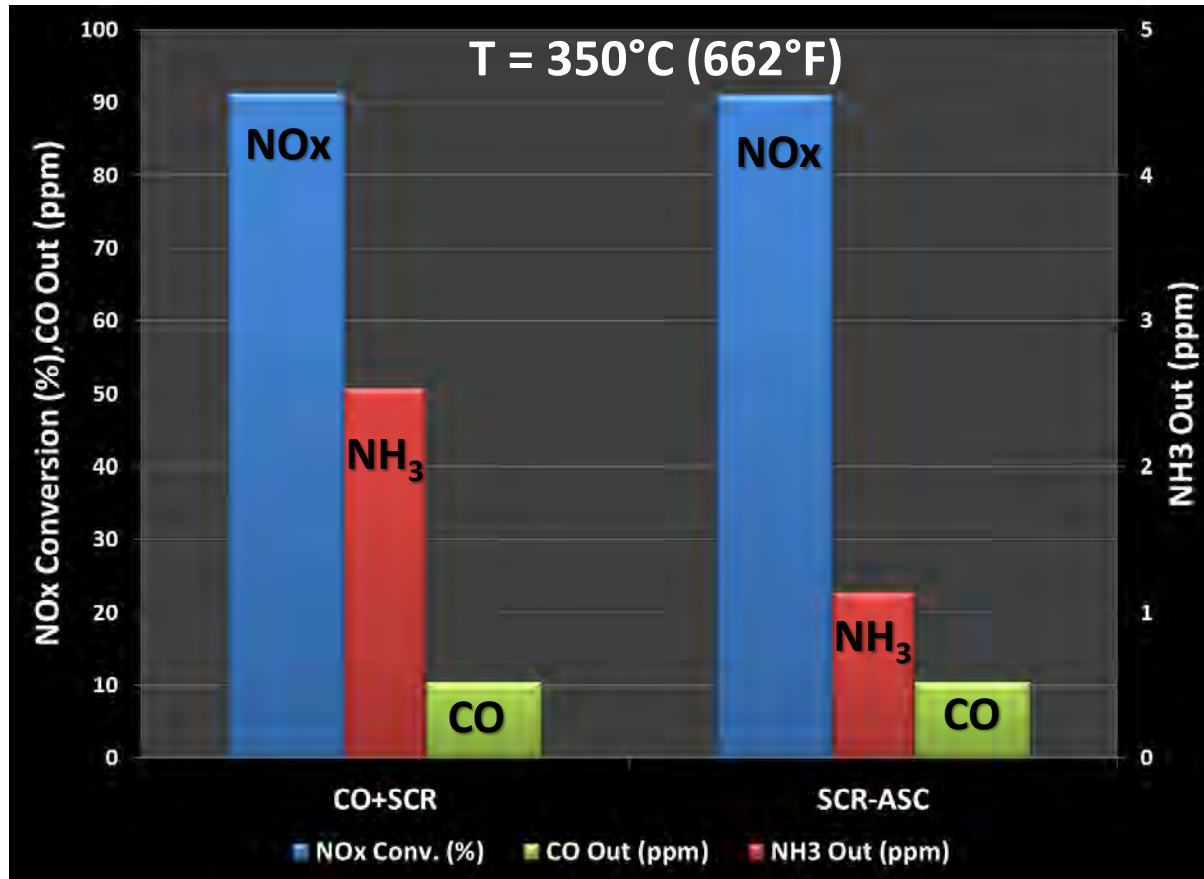


# SCR and ASC Catalysts Fitted in Power Plant to Investigate Durability in the Field – 1 year Duration



# Field Aged SCR – ASC System Requires Less Volume to Achieve NO<sub>x</sub> and CO Reduction of Standard CO-SCR System While Maintaining Lower NH<sub>3</sub> Slip

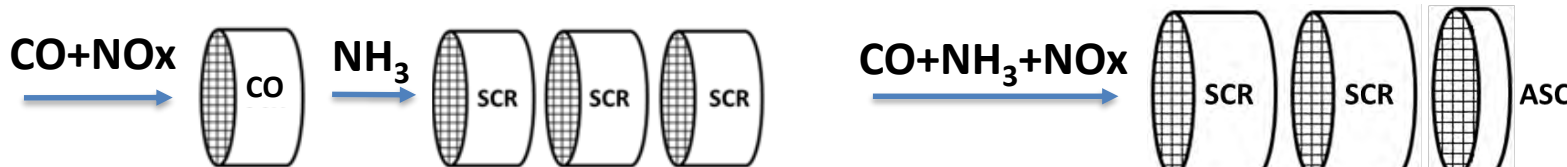
CO= 50ppm, NO<sub>x</sub>= 30ppm, ANR = 1, O<sub>2</sub>= 15%, H<sub>2</sub>O= 8%, CO<sub>2</sub> = 3%, Balanced by N<sub>2</sub>



SCR+ASC System Requires Less Total Volume

Lower NH<sub>3</sub> Slip With SCR+ASC System

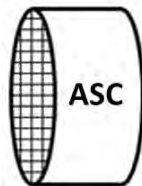
Equivalent NO<sub>x</sub> and CO Reduction Achieved in Both



# Selective Gas Turbine Aged ASC Shows High NH<sub>3</sub> Oxidation Activity and Low Selectivity to NO<sub>x</sub> Even With Over Injection

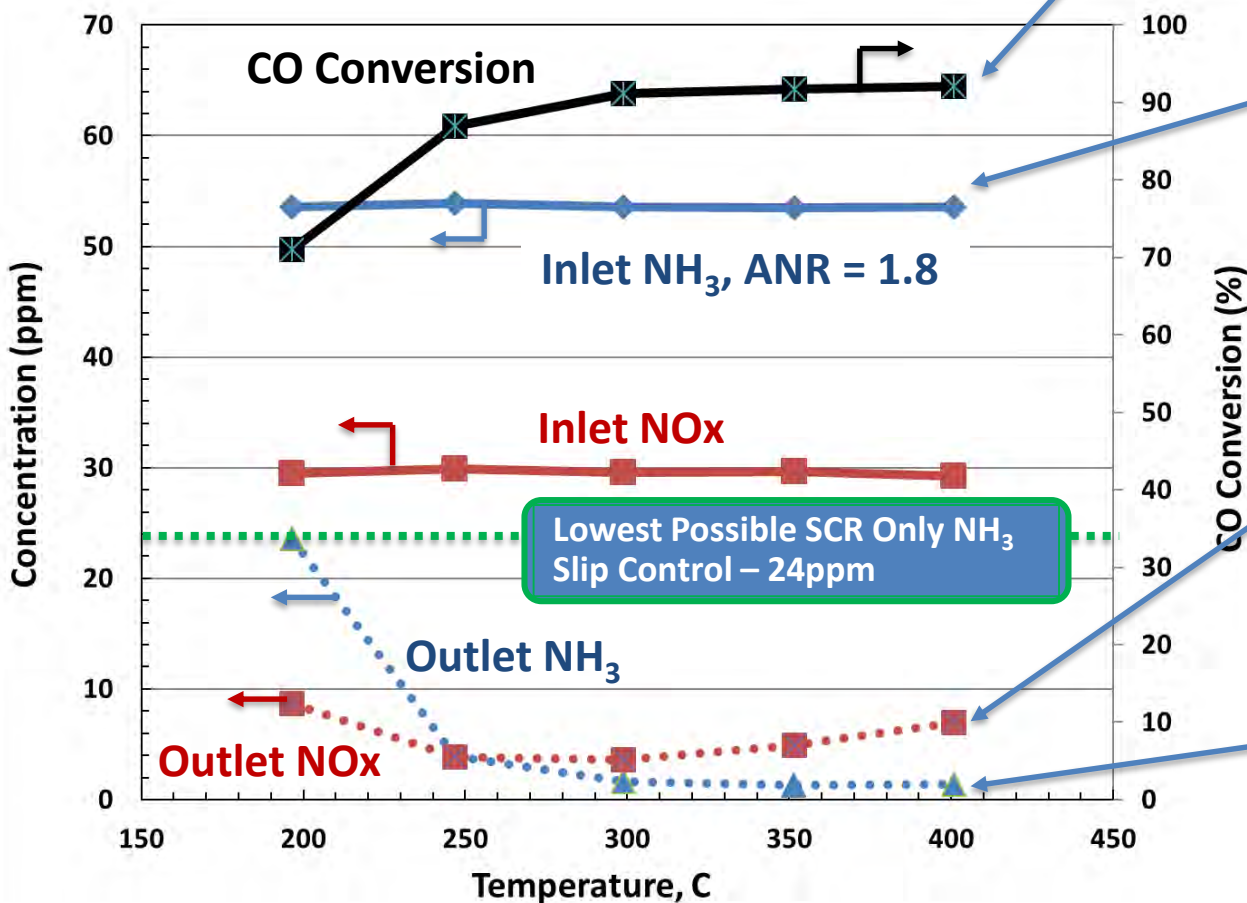


CO + NH<sub>3</sub> + NO<sub>x</sub> + O<sub>2</sub>



High CO Reduction

NH<sub>3</sub> Over Injection – 54ppm (ANR=1.8)



High NO<sub>x</sub> Conv. → Low NO<sub>x</sub> Outlet

Outlet NH<sub>3</sub> < 2ppm

CO= 50ppm, NO<sub>x</sub>= 30ppm, NH<sub>3</sub>=54ppm, O<sub>2</sub>= 15%, H<sub>2</sub>O= 8%, CO<sub>2</sub> = 3%, Balanced by N<sub>2</sub>

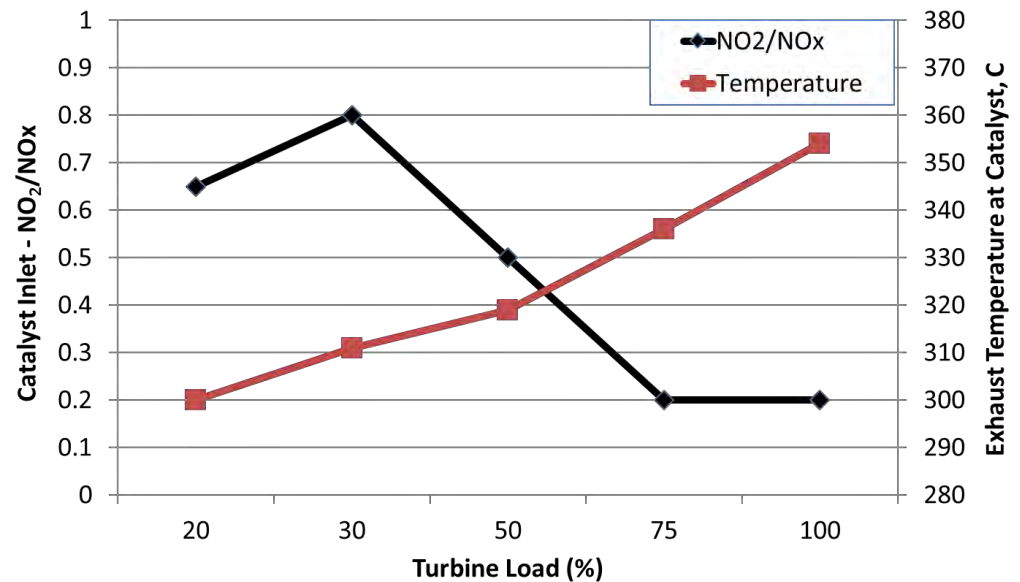
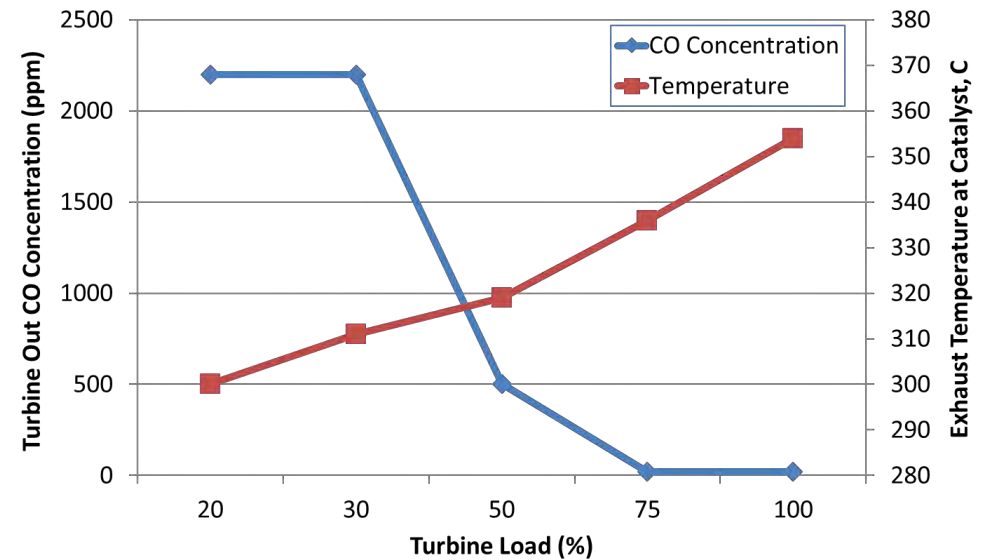


# Application Study – Emission Control at Low Loads

Desirable to have the capability to run gas turbine at low loads to provide flexibility in back up situations

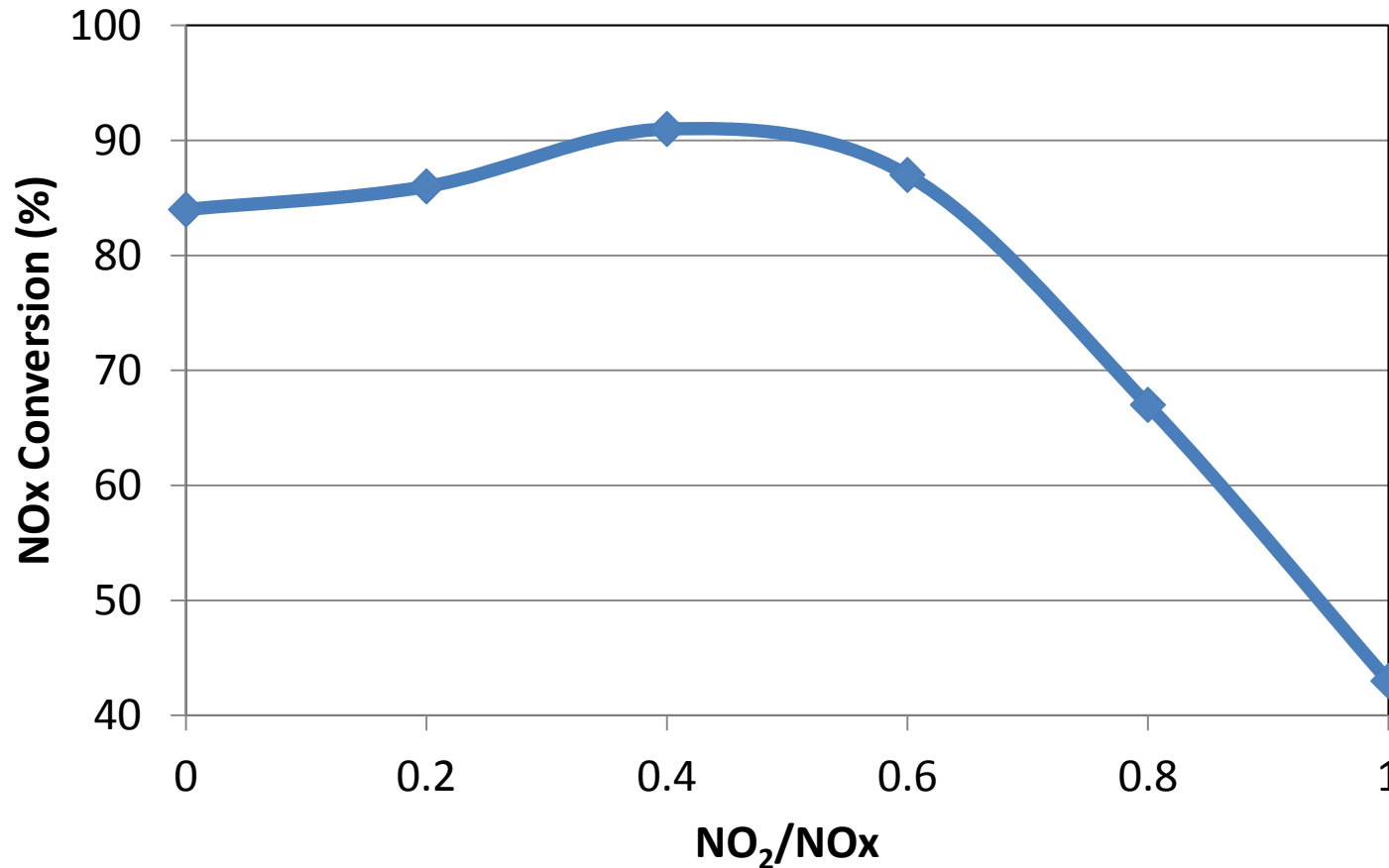
Turbine emissions can be very high under those conditions putting large demands on emission control system

Particular issues are high CO emissions and high NO<sub>2</sub> fraction



# NOx Conversion Drops Significantly at High NO<sub>2</sub> Levels

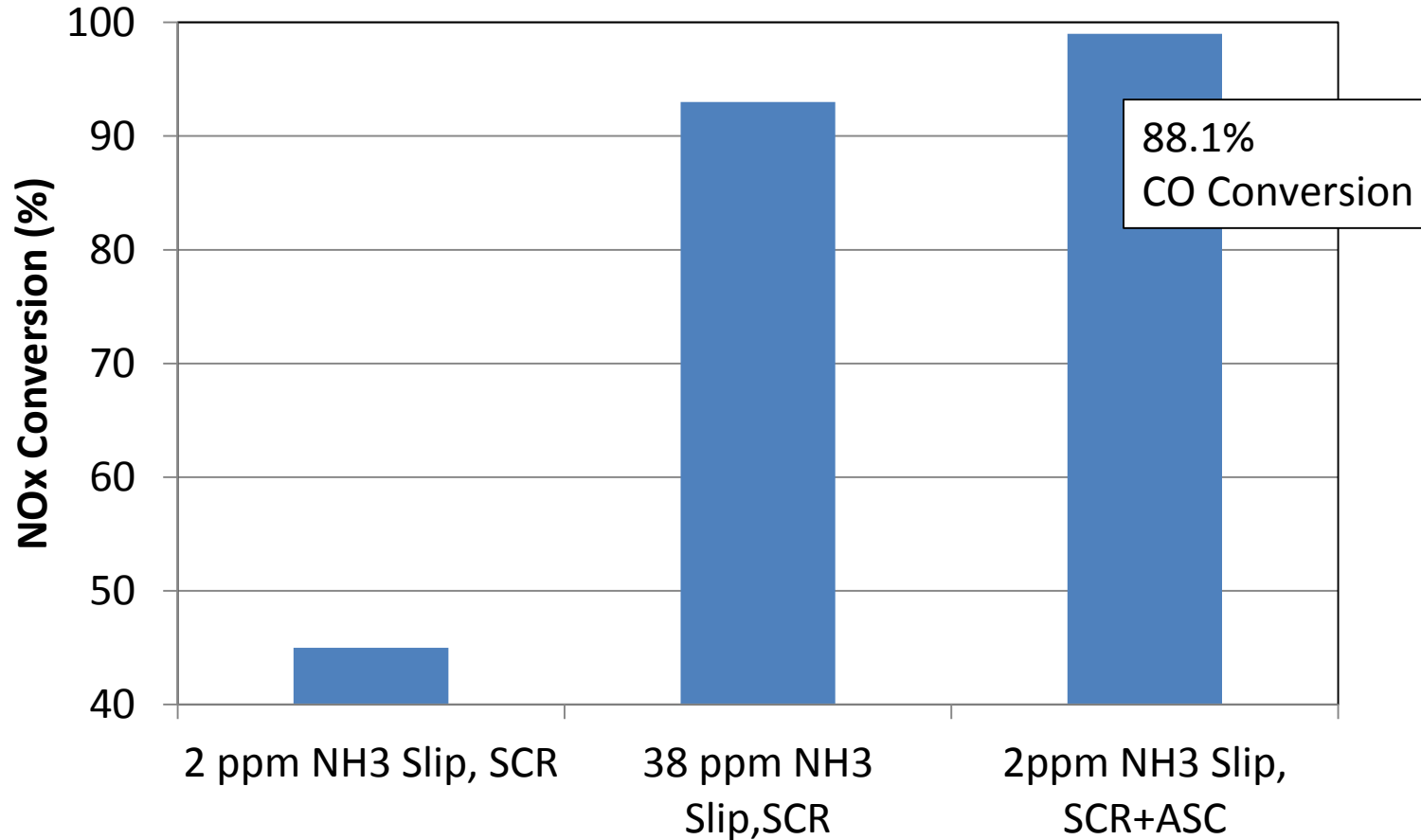
## NOx Conversion vs. NO<sub>2</sub> Content at 310°C (590°F)



# Increasing NH<sub>3</sub> Injection Increases NO<sub>x</sub> Conversion. ASC Addition Allows High NO<sub>x</sub> Conversion and Low NH<sub>3</sub> Slip



## NO<sub>x</sub> Conversion Under the 30% Load Condition



# New Products for Gas Turbine Emission Control

## Advanced Oxidation Catalyst

- Oxidation catalyst with improved activity
- Less susceptible to deactivation by poisons
- High conversion at low exhaust temperatures

## Ammonia Slip Catalyst (ASC)

- Active and selective catalyst allow low slip, reduced catalyst volumes, and low pressure drop
- Improve plant performance by reducing back-end deposits. Save O&M costs for removal. Meet permit slip limits, if applicable.
- Reduce space and capital cost requirements.
- Active for CO oxidation

## Application Study

- High performance SCR + ASC allows turbine operation down to 30% load

