

REINHOLD ENVIRONMENTAL Ltd.



**2013 Coal to Gas Conversion Round Table
& Expo Presentation**

October 29, 2013, in Chattanooga, TN / Sponsored by Southern Company

All presentations posted on this website are copyrighted by Reinhold Environmental, Ltd (RE). Any unauthorized downloading, attempts to modify or to incorporate into other presentations, link to other websites, or obtain copies for any other uses than the training of attendees to RE's Conferences is expressly prohibited, unless approved in writing by RE or the original presenter. RE does not assume any liability for the accuracy or contents of any materials contained in this library which were presented and/or created by persons who were not employees of RE.

Practical Implications of NO to NO₂ Catalytic Conversion

William Hizny
BASF Corporation

Reinhold Environmental
Coal to Gas / PCUG Conference
Sponsored by Southern Co
October 29-30, 2013
Chattanooga, TN

Workshop description

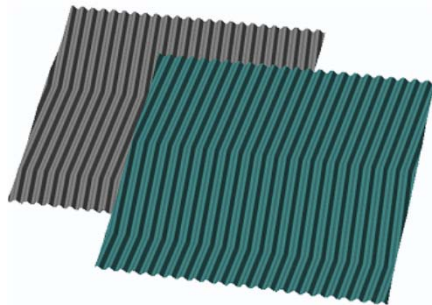
- “Learn what drives the conversion of NO to NO₂ through an oxidation catalyst and how it may impact coal-to-gas conversions and downstream SCR systems.”

Overview

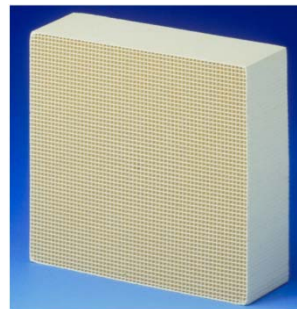
- Oxidation catalyst – big picture
- What drives the conversion of NO to NO₂ through an oxidation catalyst?
- How may it impact coal-to-gas conversions and downstream SCR systems?
- Example & case study

CO/NOx Catalyst – What is it?

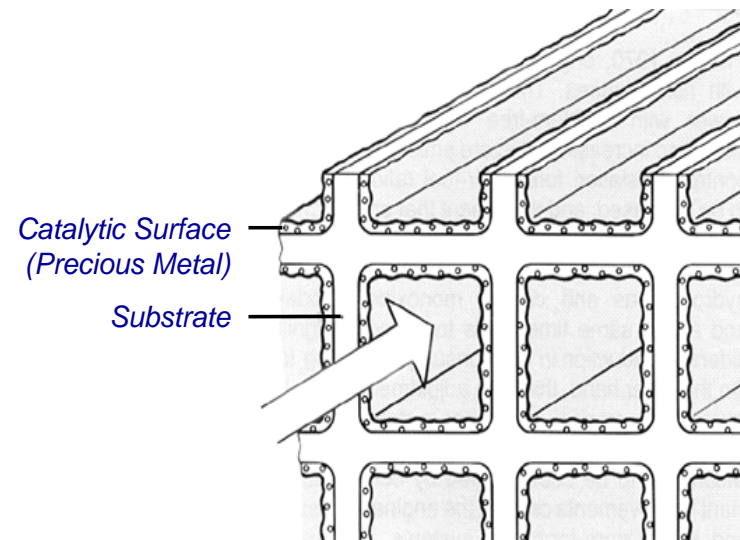
- Precious metal (PM) (e.g. platinum, palladium) dispersed through a high surface area coating on a substrate, such as ceramic block or corrugated metal foil



Herringbone metal foil



Ceramic



Schematic of honeycomb oxidation catalyst

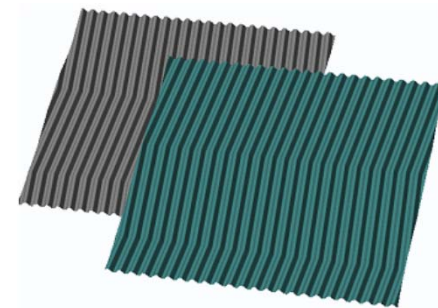
A surface coated technology

Physical characteristics

- Metal foil inherently lower pressure drop, typically 1.0 in.w.c.
- Customizable to the duct
- Ceramic can be washed to extend life
- Ceramic resistant to acid gas environments
- No reagents needed
- Requires low/no dust in flue gas to avoid plugging or erosion issues

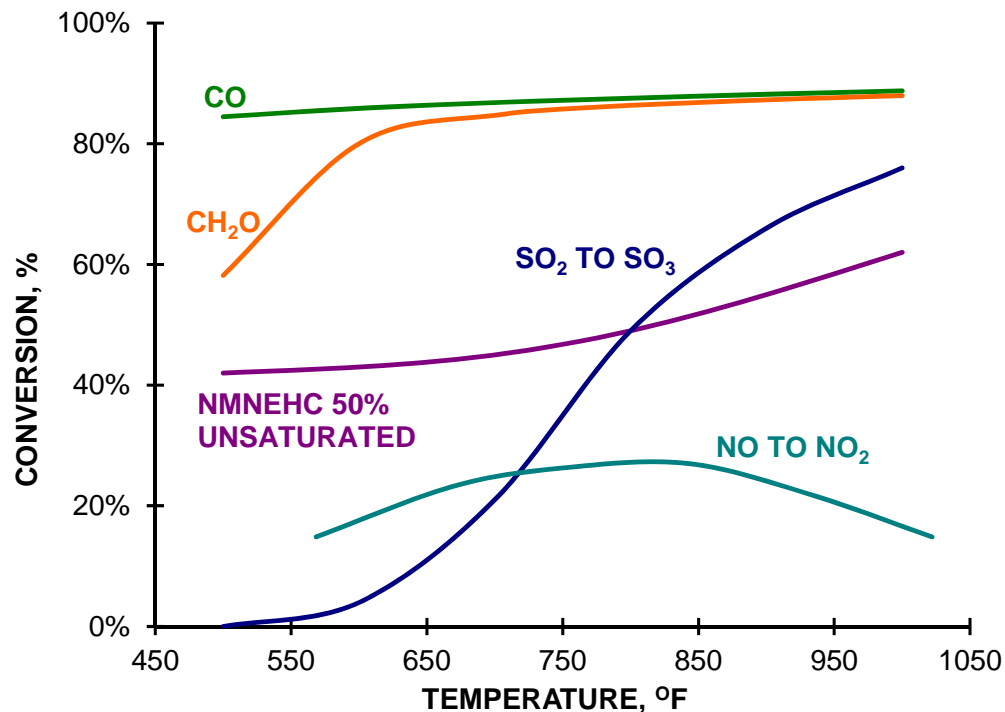


Ceramic



Herringbone metal foil

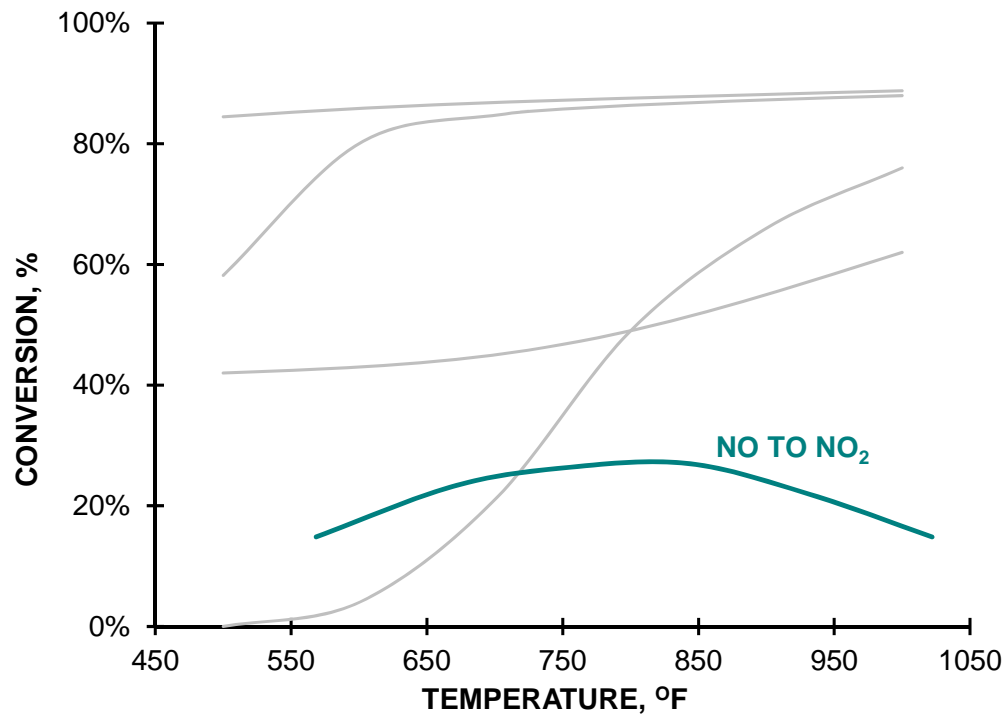
Oxidation catalyst impacts all compounds that pass through it



- Not all compounds are oxidized to the same degree (“activity”)
- Catalyst performance determined by catalyst surface area (i.e. residence time) and temperature
- May customize formulations to enhance or inhibit certain reactions (“selectivity”)

A “passive” technology – no reagents to control performance

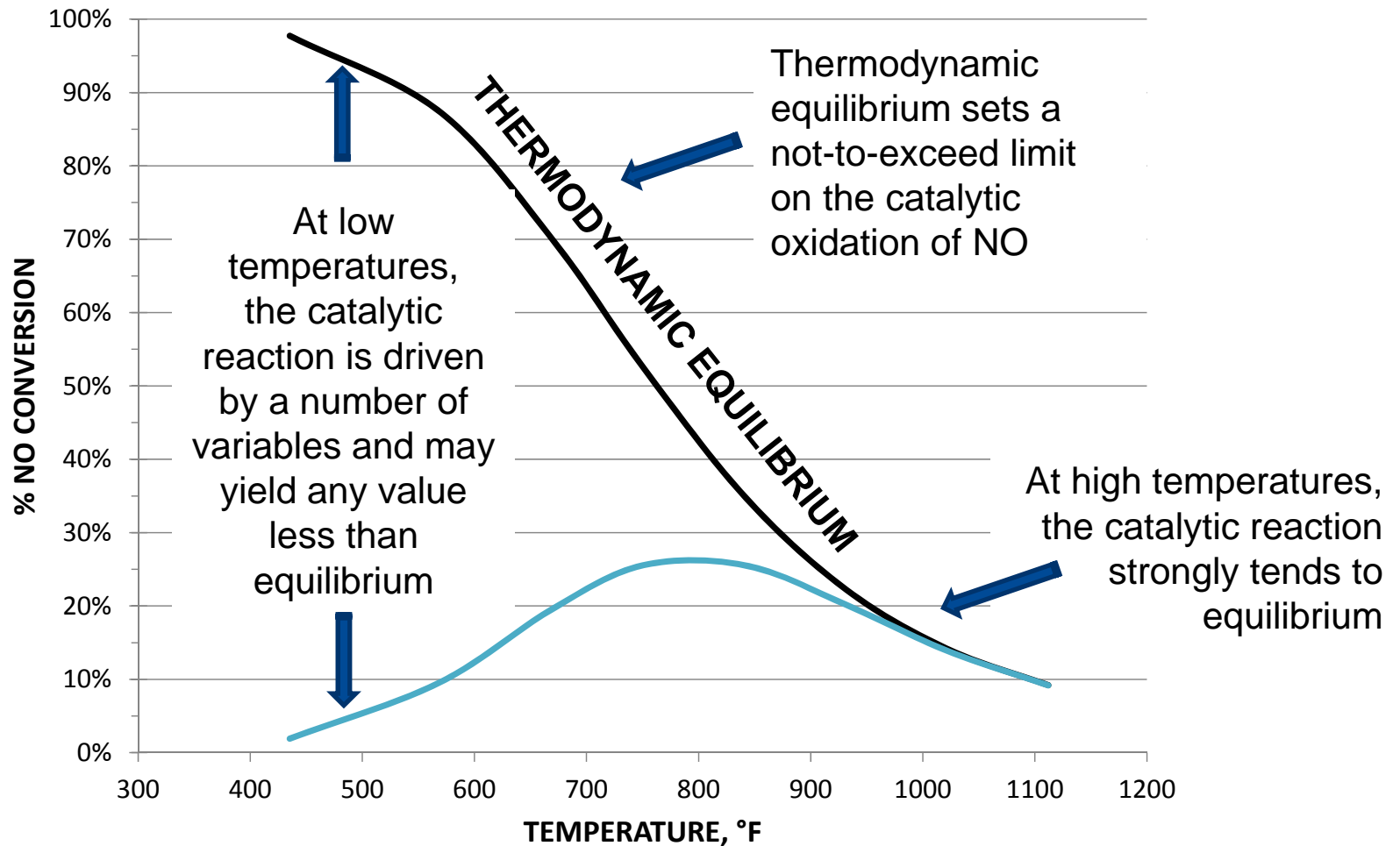
NO to NO₂ catalytic oxidation...



- Low conversion at both low and high temperatures
- Peak conversion somewhere in the middle
- Preferred operating condition may be difficult to identify
- A most perplexing curve?!

...what drives the shape of the curve ?

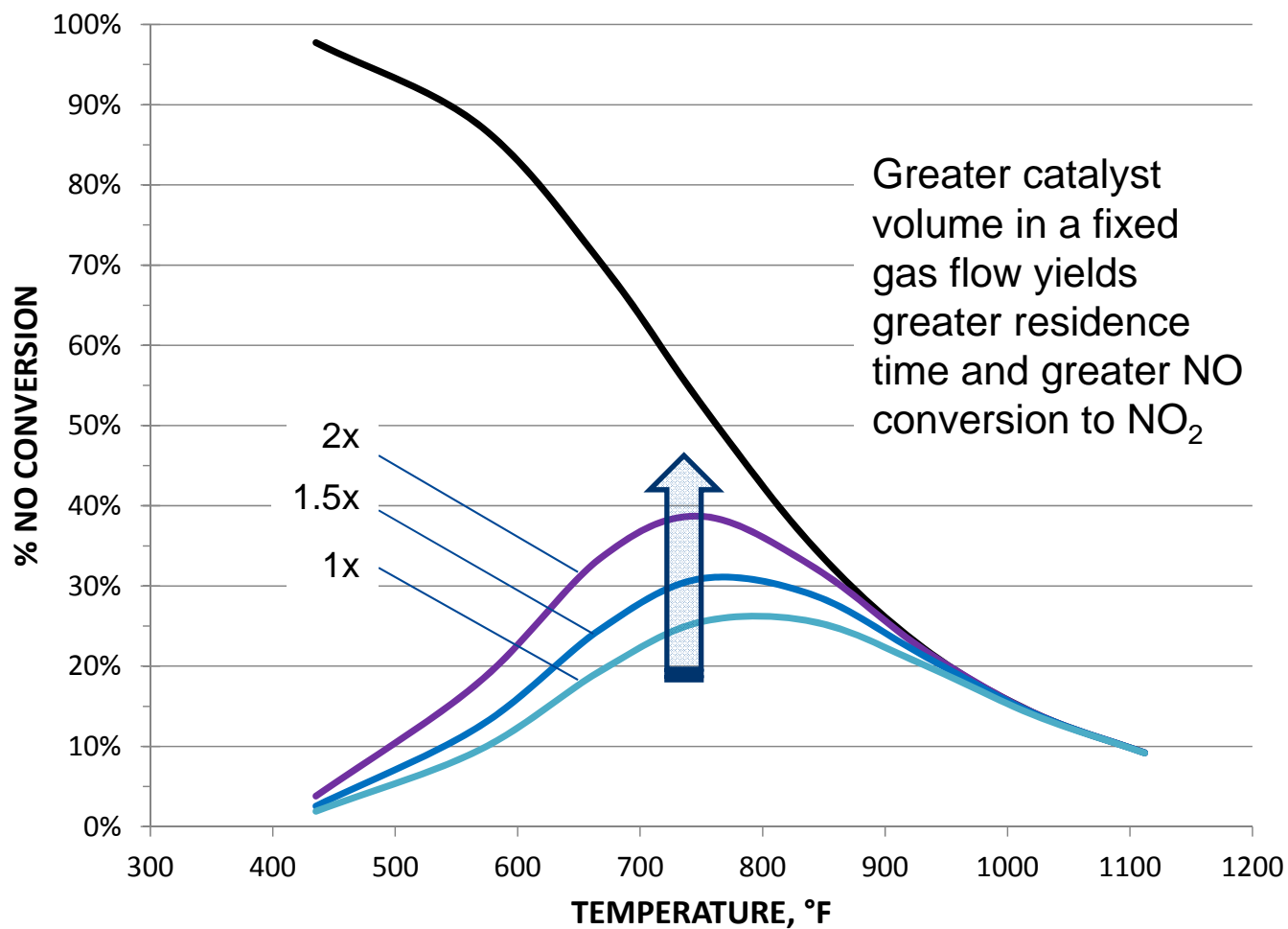
You can't violate the laws of thermodynamics



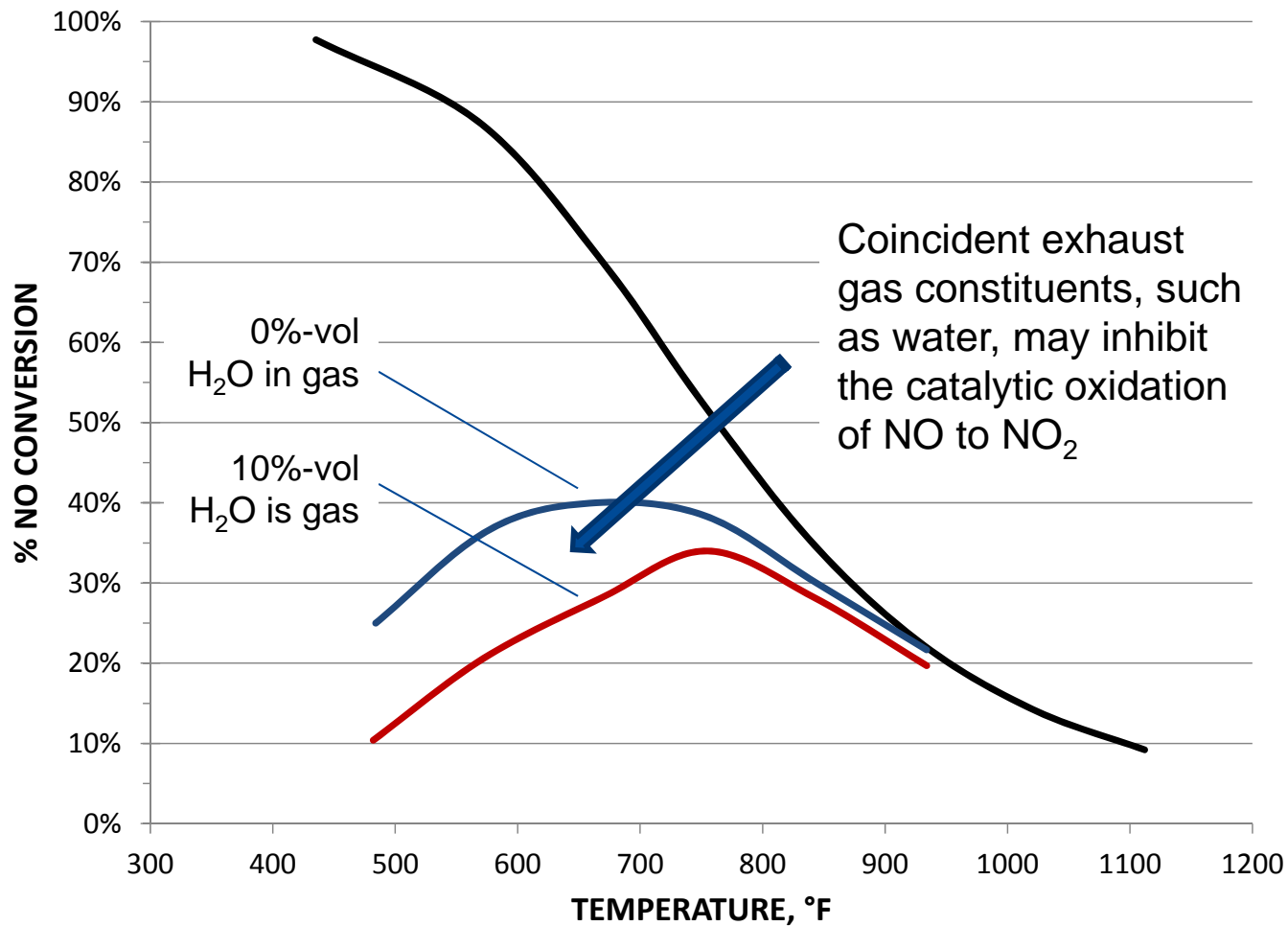
Catalyst properties that drive NO-to-NO₂ oxidation

- Reaction variables:
 - Example: catalyst volume (i.e. residence time)
- Application variables:
 - Example: coincident exhaust gas constituents
- Intrinsic variables:
 - Example: catalyst preparation
- Operational variables:
 - Example: operating hours

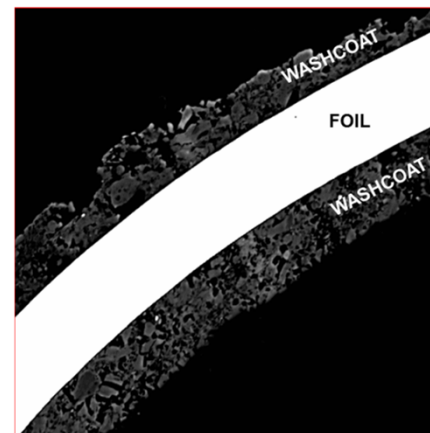
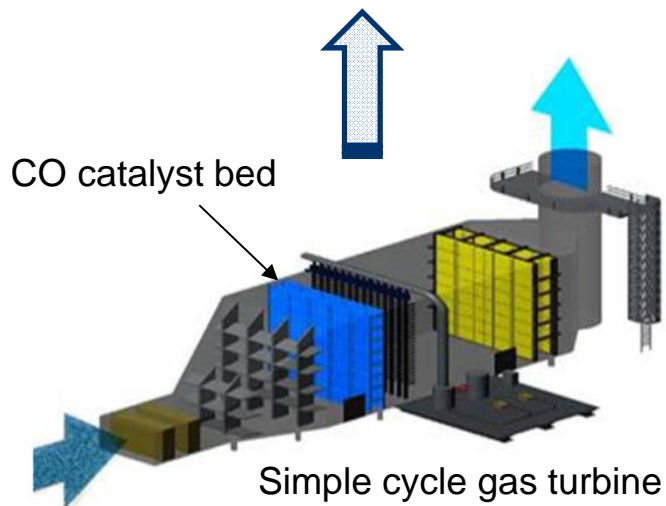
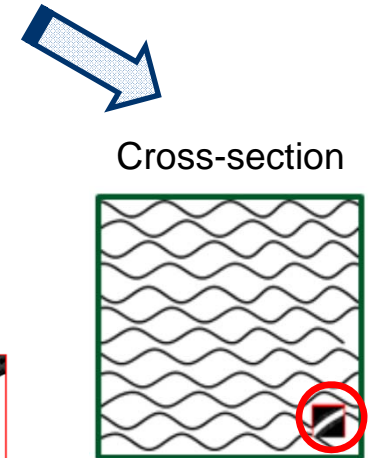
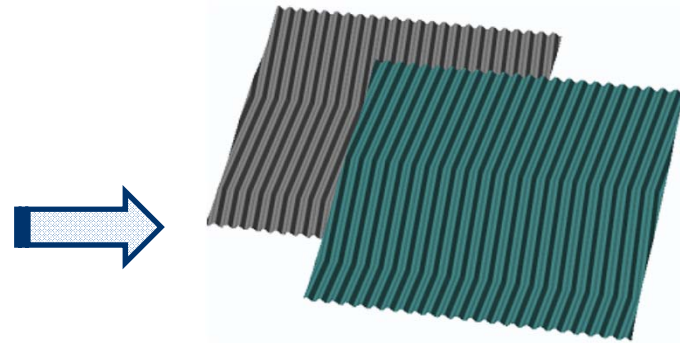
Reaction variable: Catalyst volume (i.e. residence time)



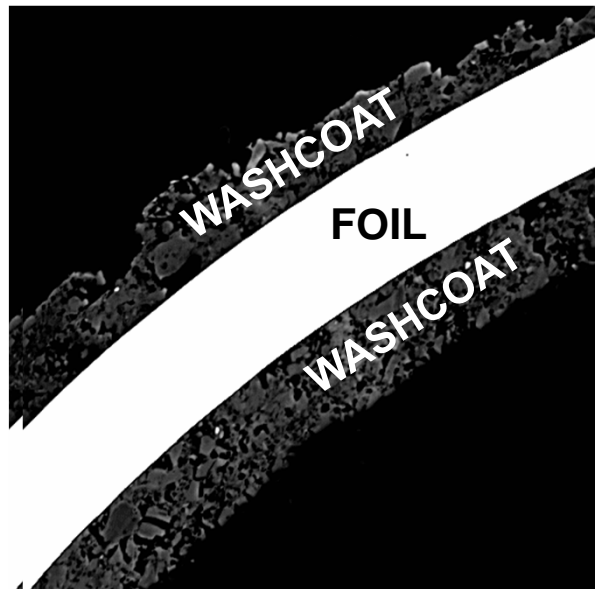
Application variable: Coincident exhaust gas constituents



To explore the last two examples, we have to rescale our understanding

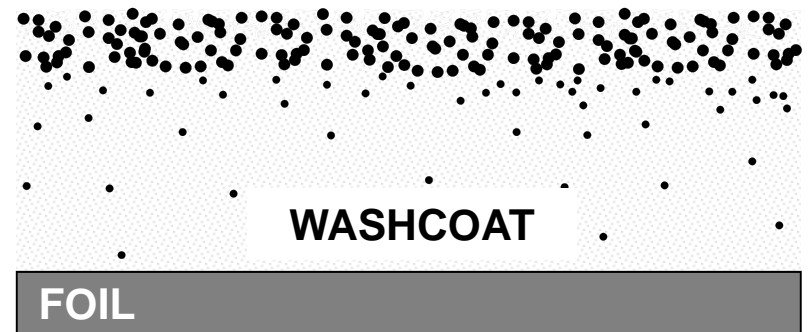
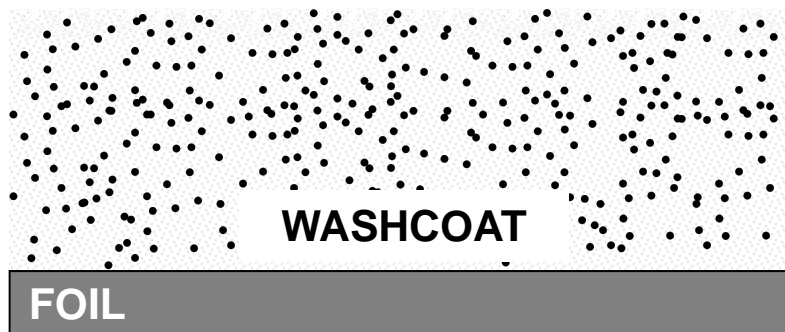


Intrinsic variable: Catalyst preparation – Where is the PM?

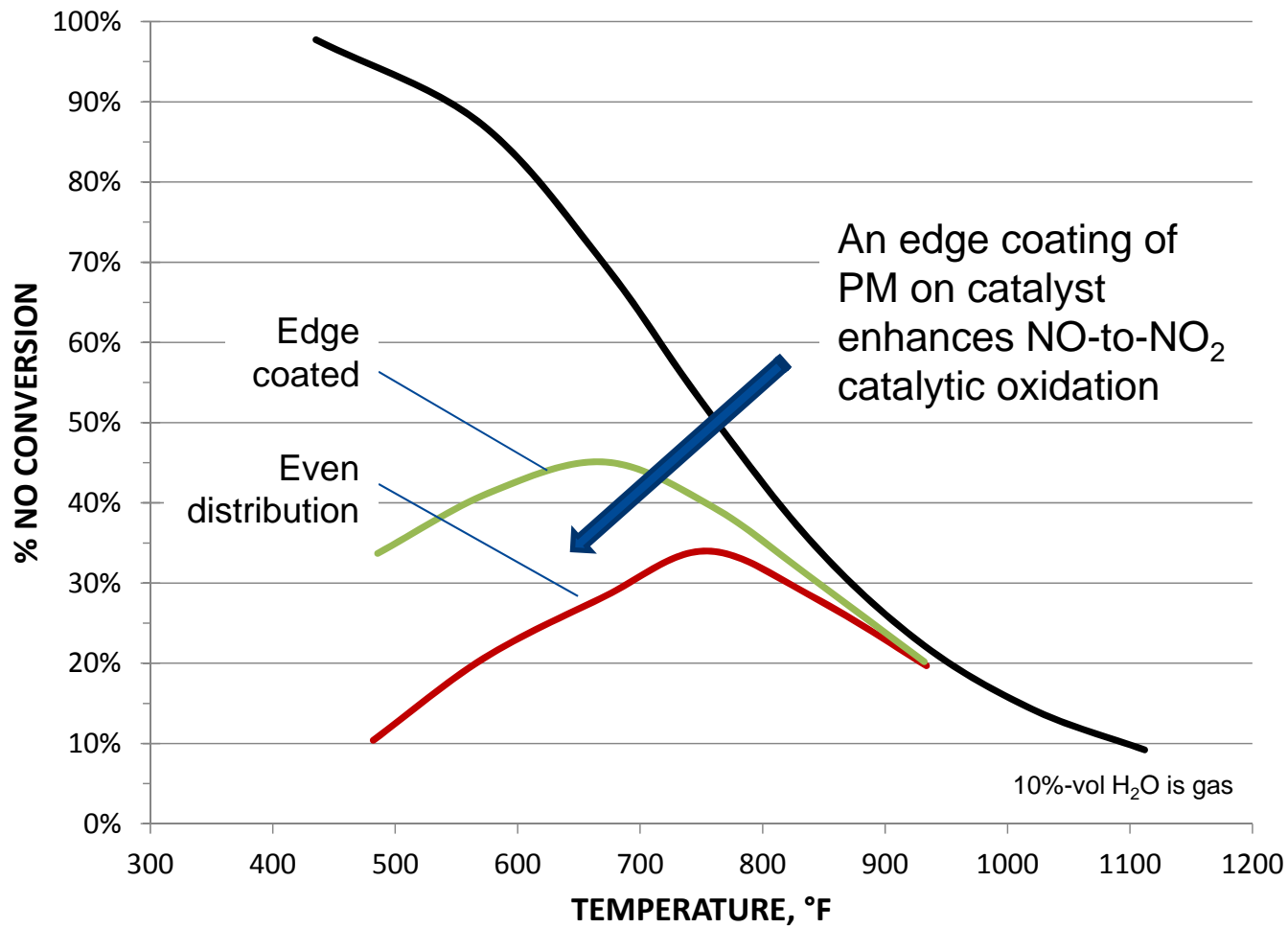


**EVEN
DISTRIBUTION of PM**

**EDGE
COATING of PM**

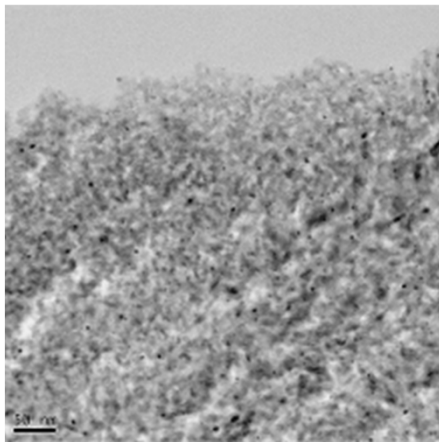


Intrinsic variable: Catalyst preparation

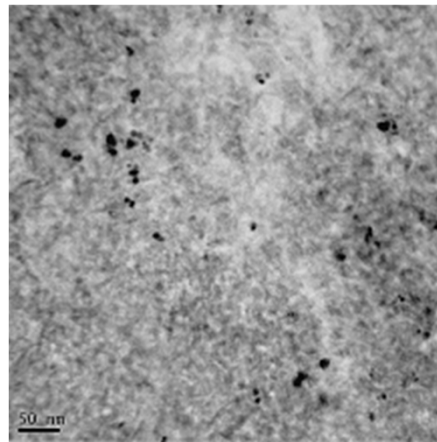


Operational variable: What does an “old” catalyst look like?

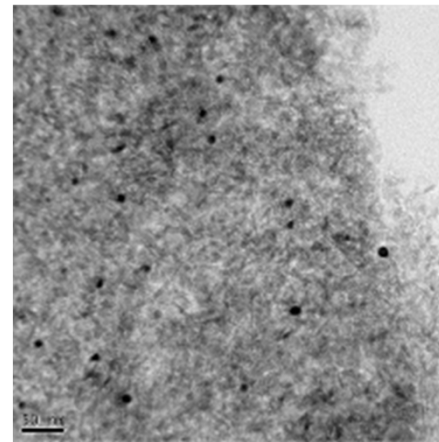
FRESH



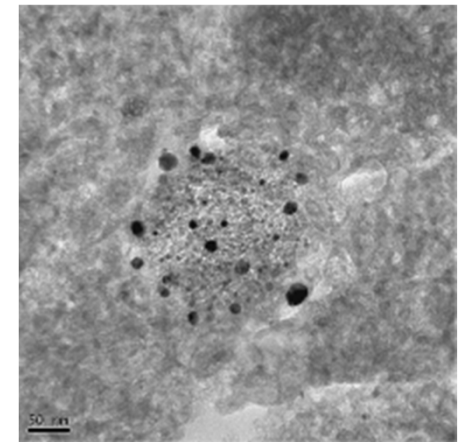
1 YEAR AGED



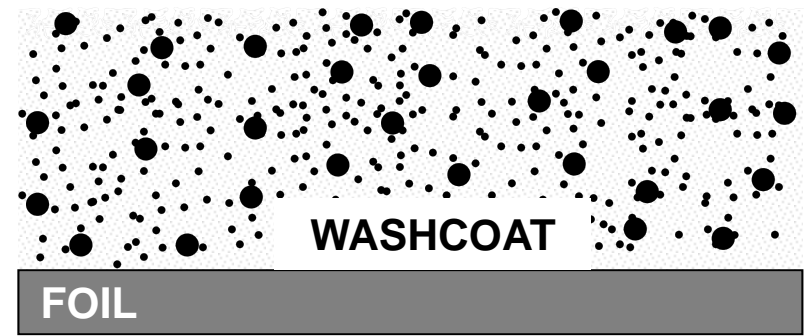
2 YEAR AGED



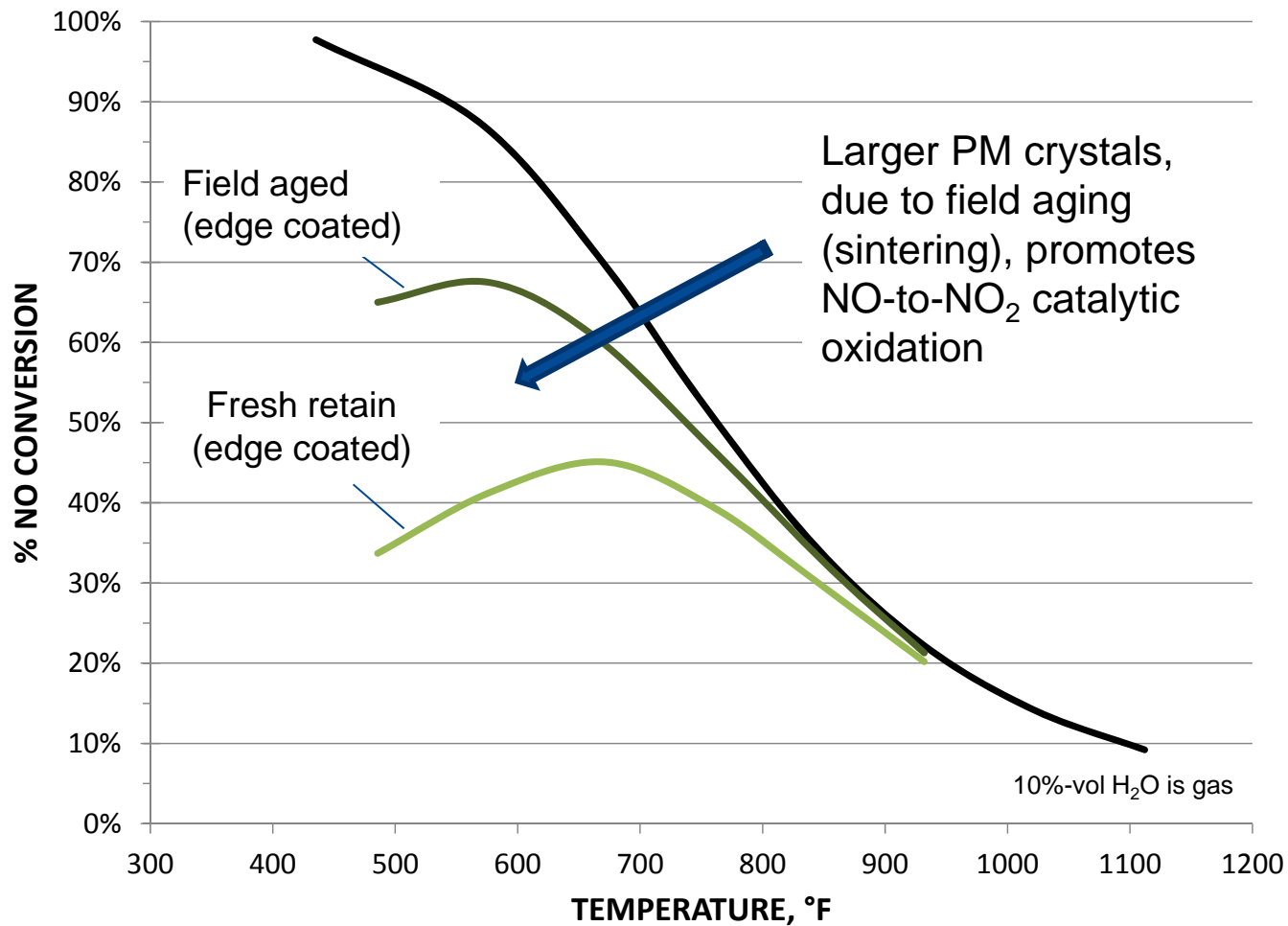
10 YEAR AGED



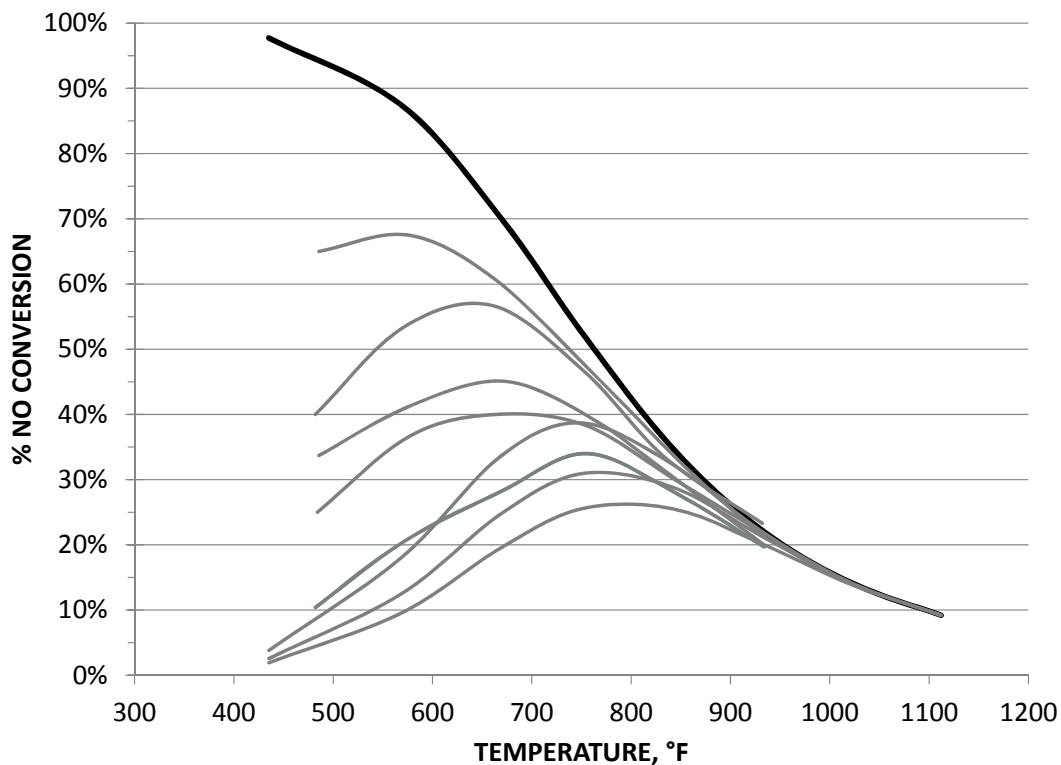
- Oxidation catalyst's precious metal sinters over time, even during operation at conventional temperatures (e.g. 572°F – 752°F)
- Sintering yields clumps of PM within the catalyst washcoat



Operational variable: Operating hours



So is there a “representative” curve for NO-to-NO₂ catalytic oxidation?



- Can't violate laws of thermodynamics – sets high temperature performance limit
- Catalyst volume (residence time), expected exhaust gas constituents, and aging may be factored into the design beforehand
- Consistent catalyst formulation required for consistent performance

...perhaps, if we constrain enough variables

Overview

- Oxidation catalyst – big picture
- What drives the conversion of NO to NO₂ through an oxidation catalyst?
- How may it impact coal-to-gas conversions and downstream SCR systems?
- Example & case study

NO-to-NO₂ catalytic oxidation

Impact on stack plume visibility

* The visible threshold concentration is related to the depth of the plume by:

$$C_o = \frac{2400}{d}$$

Where:

d = stack diameter, inches

C_o = NO₂ threshold concentration, ppm

4 inch (d) stack has a visible NO₂ concentration threshold of 600 ppm

40 inch (d) stack has a visible NO₂ concentration threshold of 60 ppm

400 inch (d) stack has a visible NO₂ concentration threshold of 6 ppm

* Hardison, L.C. "Techniques for Controlling the Oxides of Nitrogen", *Journal of the Air Pollution Control Association*, 20, 6, 377 (1970)

Potential for brown plume generation in existing wide diameter stacks due to higher NO₂ concentration

Example: Plant X*

Natural gas use only

- 200-250 MW
- No catalytic controls in place now
- CO conversion requested (90%)
- VOC conversion requested
- Question – importance of the catalyst bed location

Boiler Load	Full
Mwe	225
Fuel Type	NG
Gas Flow – Wet (lb/hr)	1,833,000
Flue Gas Composition:	
CO2 (vol. %, wet)	9.2
H2O (vol. %, wet)	18.9
N2 (vol. %, wet)	70.7
O2 (vol. %, wet)	1.2
SO2 (ppmvd @ actual O2)	negl.
SO3 (ppmvd @ actual O2)	negl.
Inlet NOx to SCR (ppmvd @ actual O2)	108
Nox, lbs/hr as NO2	268
Particulate Loading (gr/dscf)	negl.*
Flue Gas Temperature (F)	730
Velocity Distribution (%RMS)	15
Temperature distribution (± °F)	20
* Particulate does not include residual ash in duct from prior coal combustion	

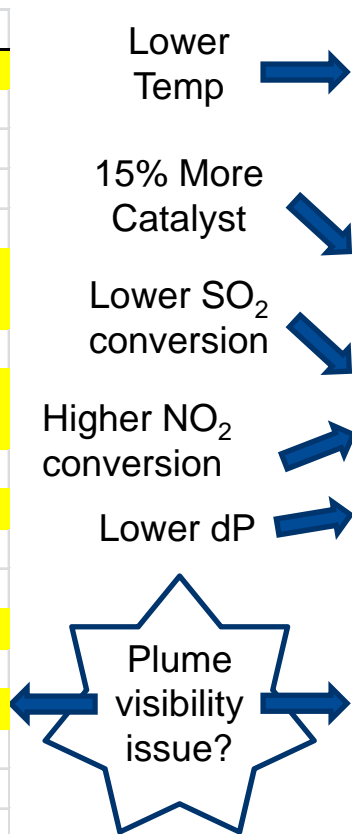
* Stephenson, N. (Cormetech). "Handling CO and VOC Concerns for Gas Fuel", Reinhold Environmental Coal-Gas Round Table & Expo. Chattanooga, TN October 23, 2012

Example: Plant X

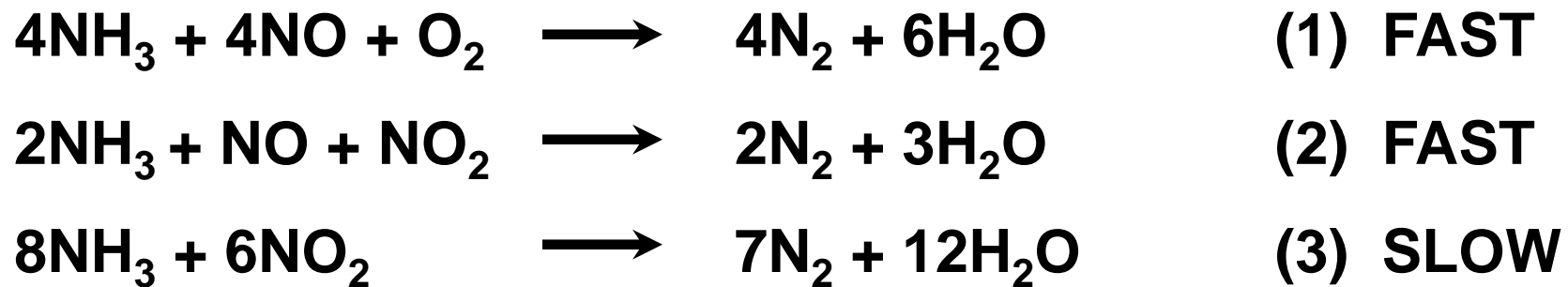
Lower temperature impacts on performance

Option #1
Oxidation Catalyst Option - Baseline 730F
20 ft x 48 ft duct cross-section
18 ft x 44.5 ft catalyst bed cross-section
3 inch catalyst depth
105 cells per square inch substrate
200 ft ³ +/- 20% total catalyst volume
90% CO DRE
44% VOC DRE - C3 HC 50/50 saturated
29% SO ₂ to SO ₃ conversion
12% NO to NO ₂ conversion
\$275 per 1,000 lb/hour
0.9 in.w.c. dP
108 inlet NO _x
Assume 20ppm NO ₂ , 88ppm NO
Outlet 30.6 ppm NO ₂
Stack tolerance from 120 inches_max to 78 inches_max
Notes:
1. Metal foil substrate design
2. Catalyst costs only; frame & installation extra
3. Ceramic substrate option yields higher costs, but are best suited to the operating environment

Option #2
Oxidation Catalyst Option @ 550F
20 ft x 48 ft duct cross-section
18 ft x 44.5 ft catalyst bed cross-section
3.5 inch catalyst depth
105 cells per square inch substrate
235 ft ³ +/- 20% total catalyst volume
90% CO DRE
42% VOC DRE - C3 HC 50/50 saturated
2% SO ₂ to SO ₃ conversion
46% NO to NO ₂ conversion
\$325 per 1,000 lb/hr
0.7 in.w.c. dP
108 inlet NO _x
Assume 20ppm NO ₂ , 88ppm NO
Outlet 60.5 ppm NO ₂
Stack tolerance from 120 inches_max to 40 inches_max
Notes:
1. Metal foil substrate design
2. Catalyst costs only; frame & installation extra
3. Ceramic substrate option yields higher costs, but are best suited to the operating environment



Downstream NO_x reduction: SCR reactions across V/Ti catalyst



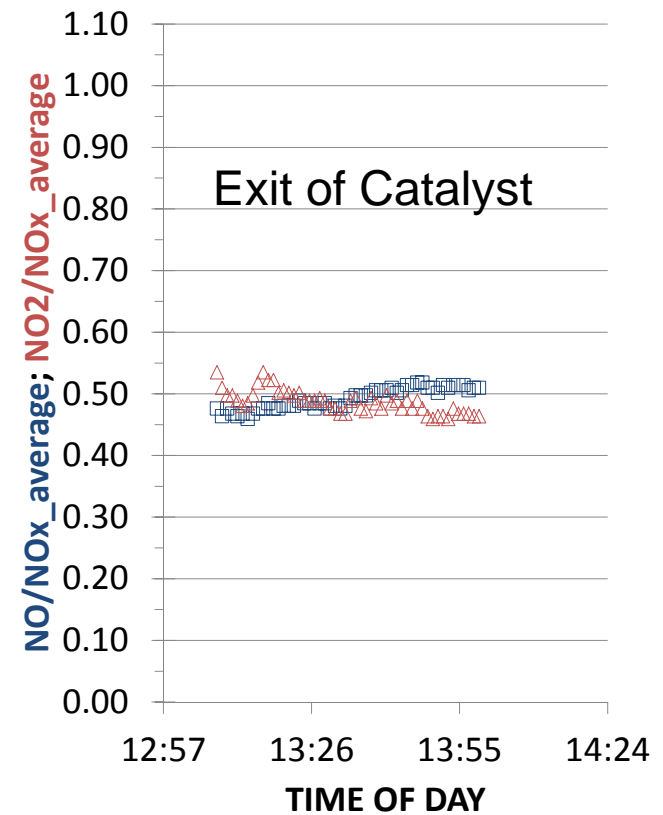
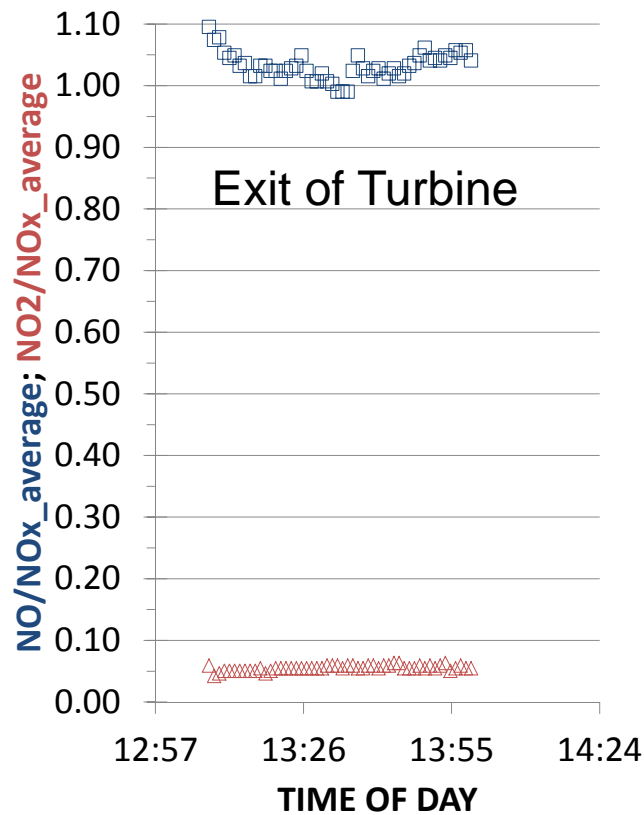
[NO₂]_{INLET} can affect overall SCR reaction rate

if NO₂/NO_x > 0.50

Case study: Natural gas turbine equipped with oxidation and SCR catalyst

- Combined cycle natural gas fired turbine equipped with an oxidation catalyst upstream of a SCR catalyst
- Field measurements of speciated NO_x emissions conducted upstream and downstream of the oxidation catalyst using two chemiluminescent analyzers
- What is the change in NO_x speciation across the oxidation catalyst?
- Will it impact the performance of the SCR catalyst?

Case study: Natural gas turbine NO_x emissions – set #1

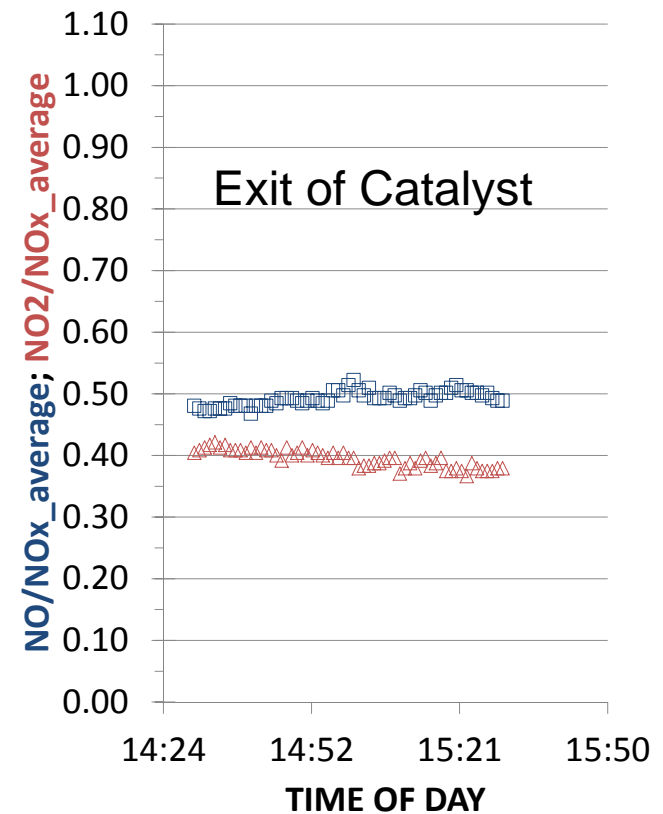
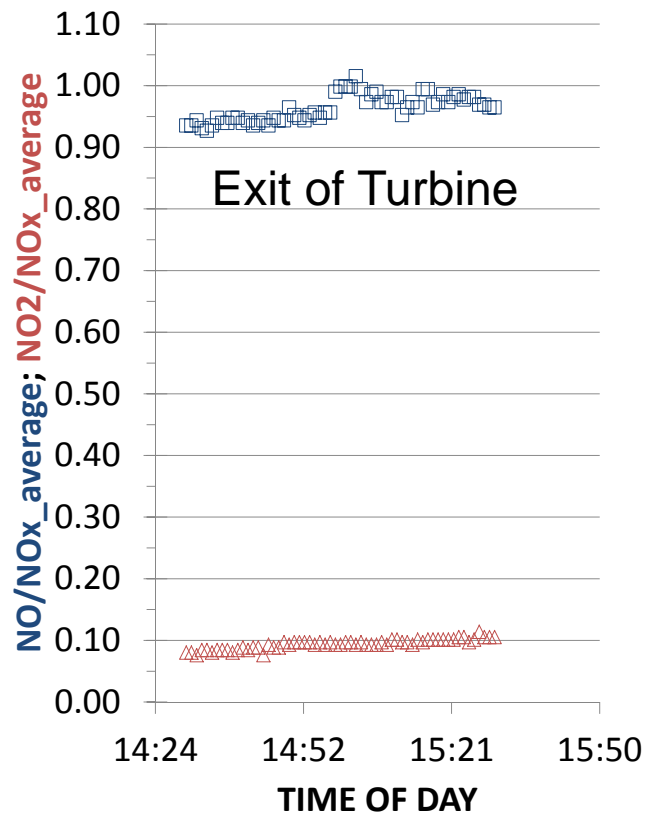


□ NO/NO_x_average △ NO₂/NO_x_average

Ox Catalyst

□ NO/NO_x_average △ NO₂/NO_x_average

Case study: Natural gas turbine NO_x emissions – set #2

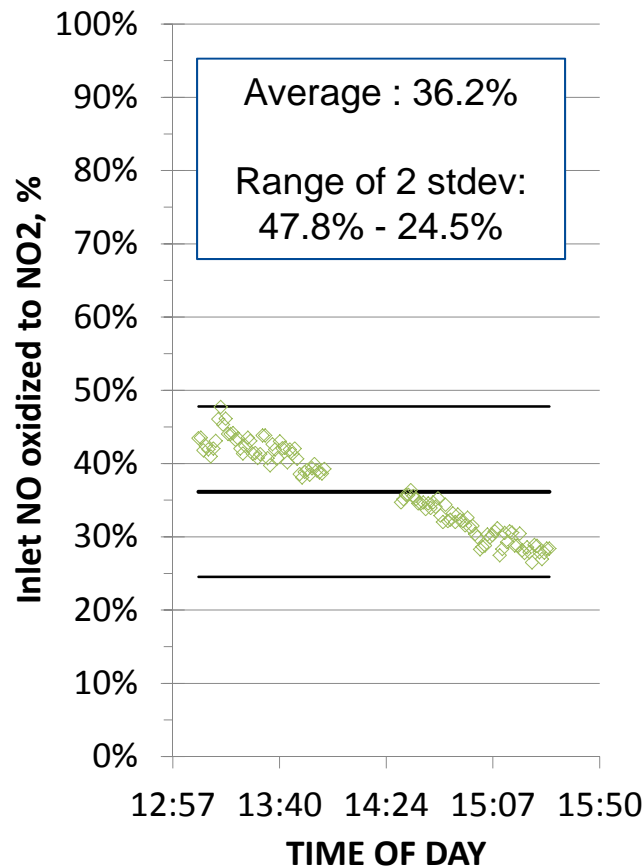


□ NO/NO_x_average △ NO₂/NO_x_average

Ox Catalyst

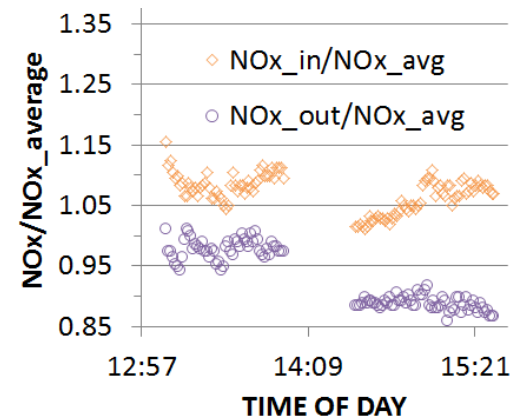
□ NO/NO_x_average △ NO₂/NO_x_average

Case study: Field measured NO-NO₂ oxidation



Variation to be explained (i.e. 47.8% - 24.5%)
~ 23.2 “basis points”

Propagation of NO_x measurement uncertainty
~ 16.5 basis points



Lab testing: 0 – 10% variation in H₂O vol-%
~ 12 basis points

Lab testing: 0 – 25 ppm variation in CO (ppm)
~ 7 basis points

Case study: Lessons drawn from field measurements

- In this case study, the field reported post-CO catalyst NO:NO₂ ratio (1.27 – 1.04) would not impact negatively the performance of the downstream SCR catalyst
- Difficult to characterize NO-to-NO₂ catalytic oxidation in the field
 - Challenging to capture speciated NO_x measurements across oxidation catalyst using two independent analyzers
 - Localized fluctuations in flow, temperature, and other gas constituents (e.g. CO, H₂O) may significantly impact catalyst performance
 - NO-to-NO₂ catalytic oxidation is more sensitive to subtle variations in operating conditions than mass transfer controlled oxidation (e.g. CO catalytic oxidation)

Summary

- NO to NO₂ catalytic oxidation is constrained by thermal equilibrium (can't violate the laws of thermodynamics)
- Several variables – reaction, application, intrinsic, operating – may compound and drive the NO to NO₂ catalytic oxidation rate
- NO₂ emissions will increase across an oxidation catalyst and may precipitate impacts on stack diameter (plume visibility) and/or SCR performance (ammonia consumption)
 - Due diligence is required
- NO to NO₂ catalytic oxidation remains an area of active catalyst research

*BASF thanks you for this opportunity
to discuss oxidation catalyst technology at the
Reinhold Environmental 2013 Coal-Gas Round Table*



QUESTIONS



Sales Contact:

Stan Mack

Business Manager

Clean Air Business Unit

BASF Corporation

Phone: 732-205-6174

E-mail: stan.mack@basf.com

Technical Contact:

William Hizny

Technical Projects Manager

Clean Air Business Unit

BASF Corporation

Phone: 732-205-6062

E-mail: william.hizny@basf.com