REINHOLD ENVIRONMENTAL Ltd.

2013 NOx-Combustion Round Table & Expo Presentations

February 18 & 19, 2013, in Salt Lake City, UT / Hosted by PacifiCorp

CO Catalyst

William Hizny
BASF Corporation

Reinhold Environmental
2013 NO_X-Combustion Round Table & Expo
Hosted by PacifiCorp
Salt Lake City Marriott Downtown
Salt Lake City, UT
February 18-19, 2013

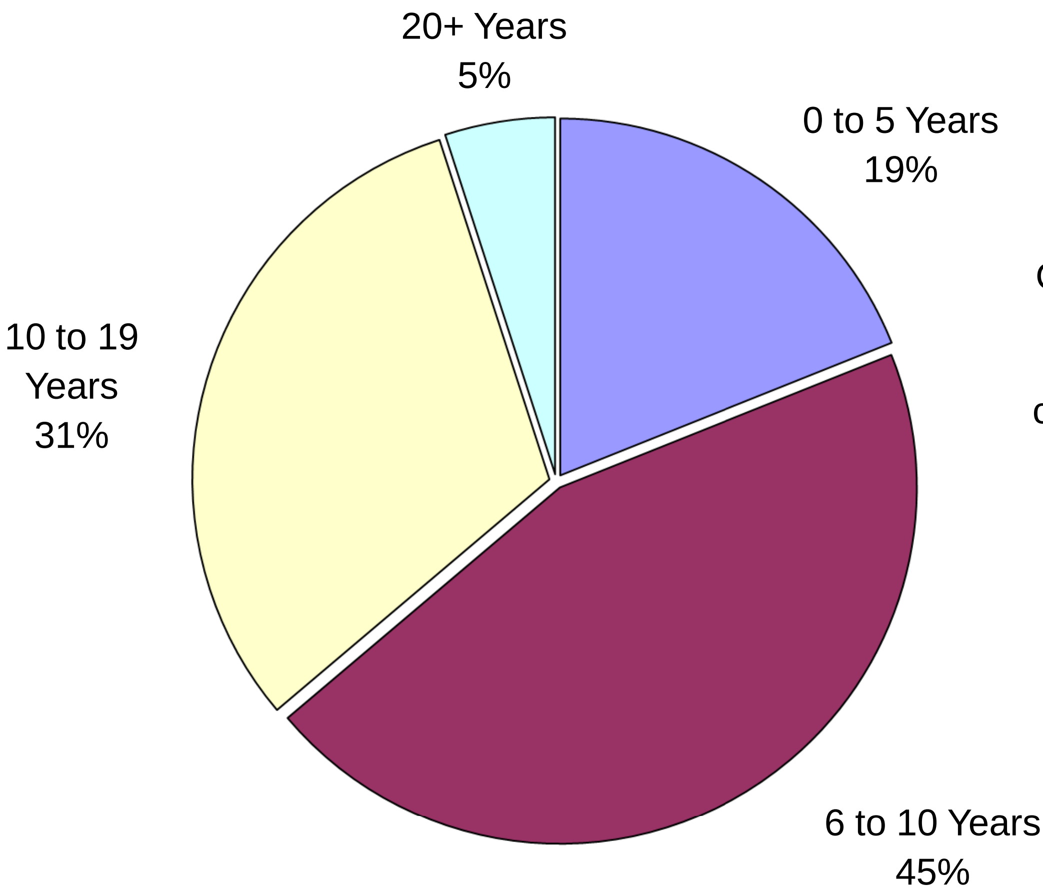
Description

- BASF reviews certain fundamentals of oxidation catalysts and discusses how they drive performance considerations for CO, VOC, and NO_X emissions abatement strategies, with specific examples focused on utility class boilers considering a coal-to-natural gas conversion or a gas turbine installation.

BASF
The Chemical Company

BASF is the leading oxidation catalyst supplier to the power generation industry

- BASF has been servicing the power generation industry for over 20 years.

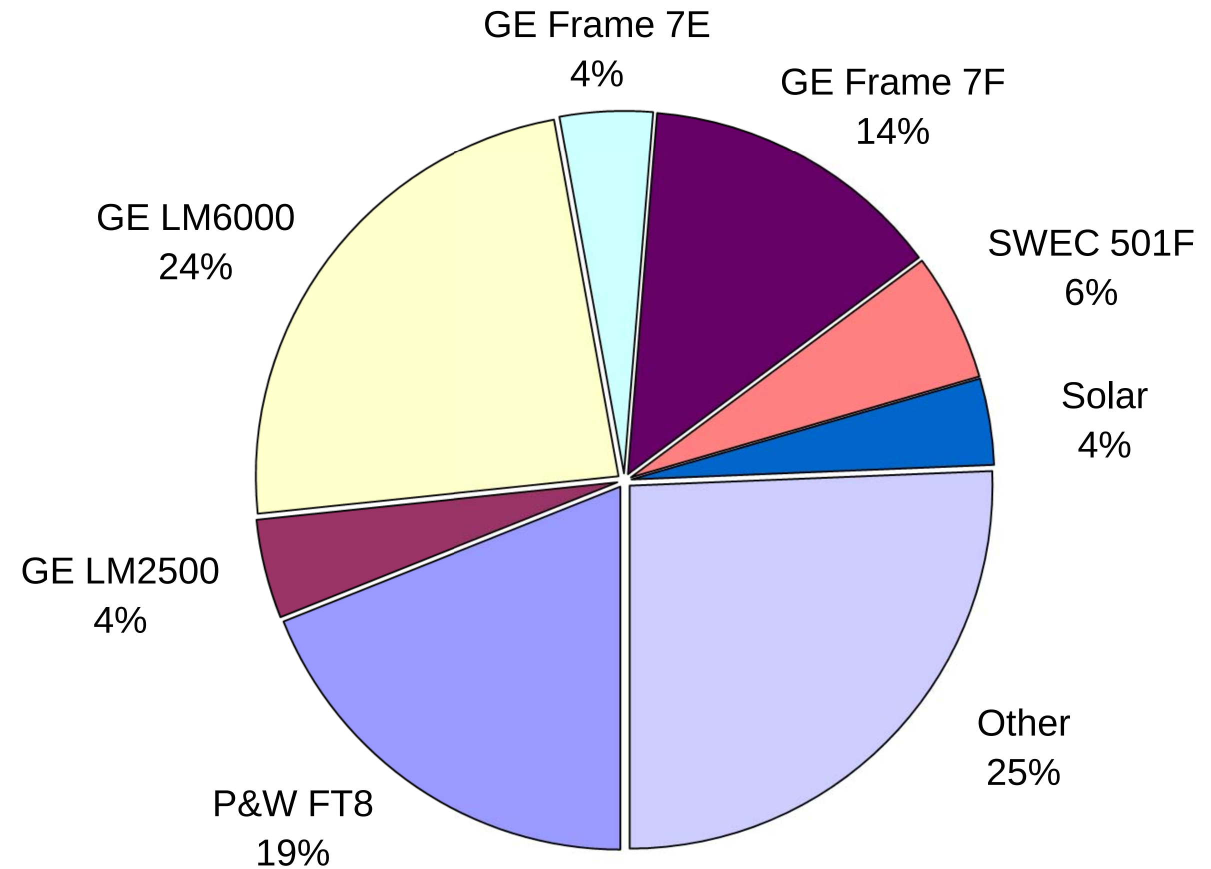


Operating life of installed oxidation catalyst base.

800+ units operating or under construction

BASF is the leading oxidation catalyst supplier to the power generation industry

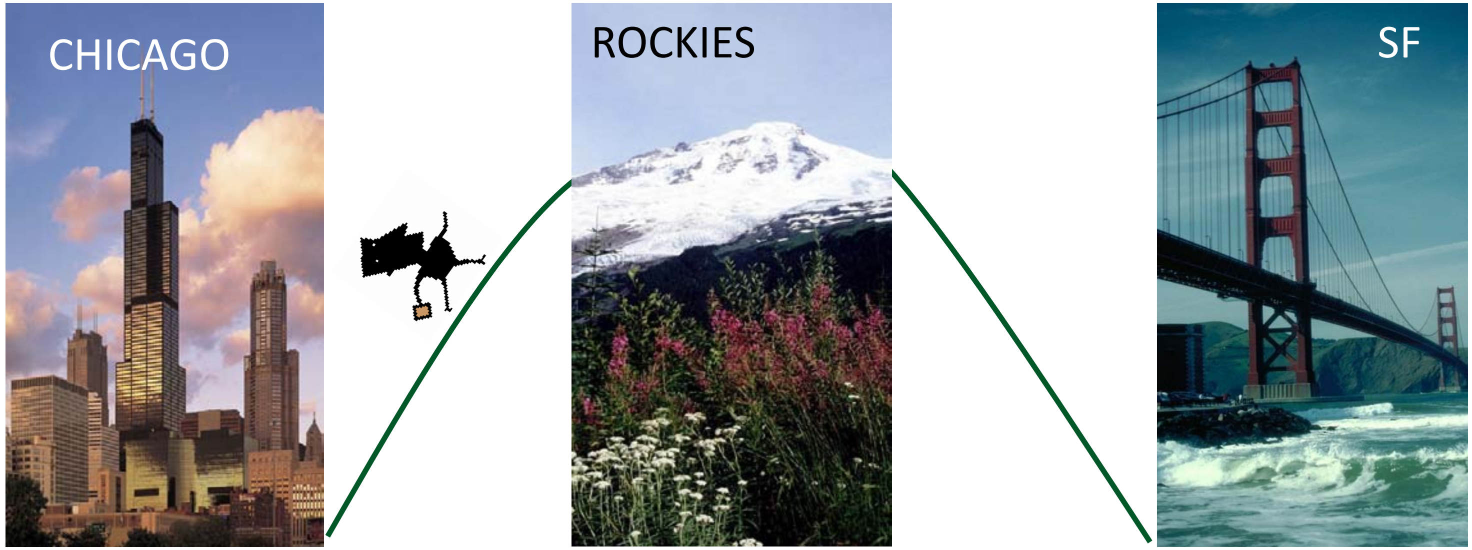
- Our breadth of experience encompasses virtually every make, model, and turbine configuration.



Overview – CO Catalysts

- CO catalyst fundamentals – crash course
- CO catalyst designs – risk management
  - Deactivation by contaminants
  - Application definition
    - – CO v. VOC v. HAP v. NMHC
    - – Coal to gas conversions & balance of plant effects
- Field maintenance
- Model cases for illustration
- Summary

BASF The Chemical Company



CO

HC

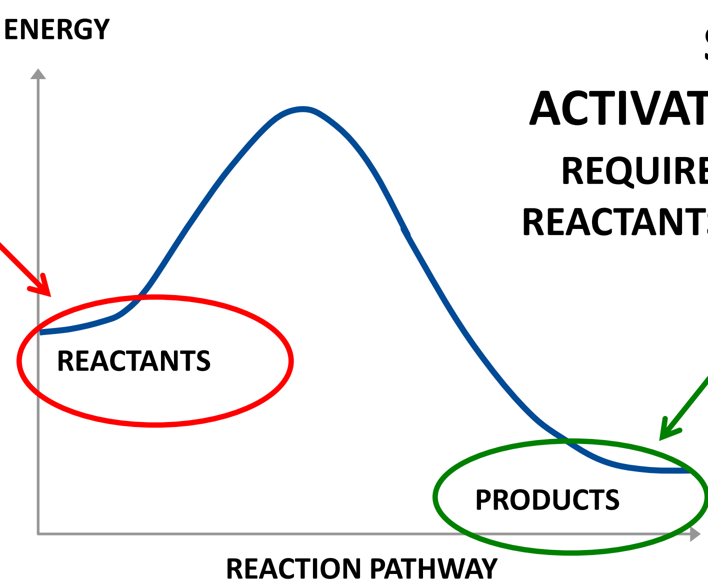
(e.g. propane)

VOC

(e.g. propylene)

HAP

(e.g. formaldehyde)



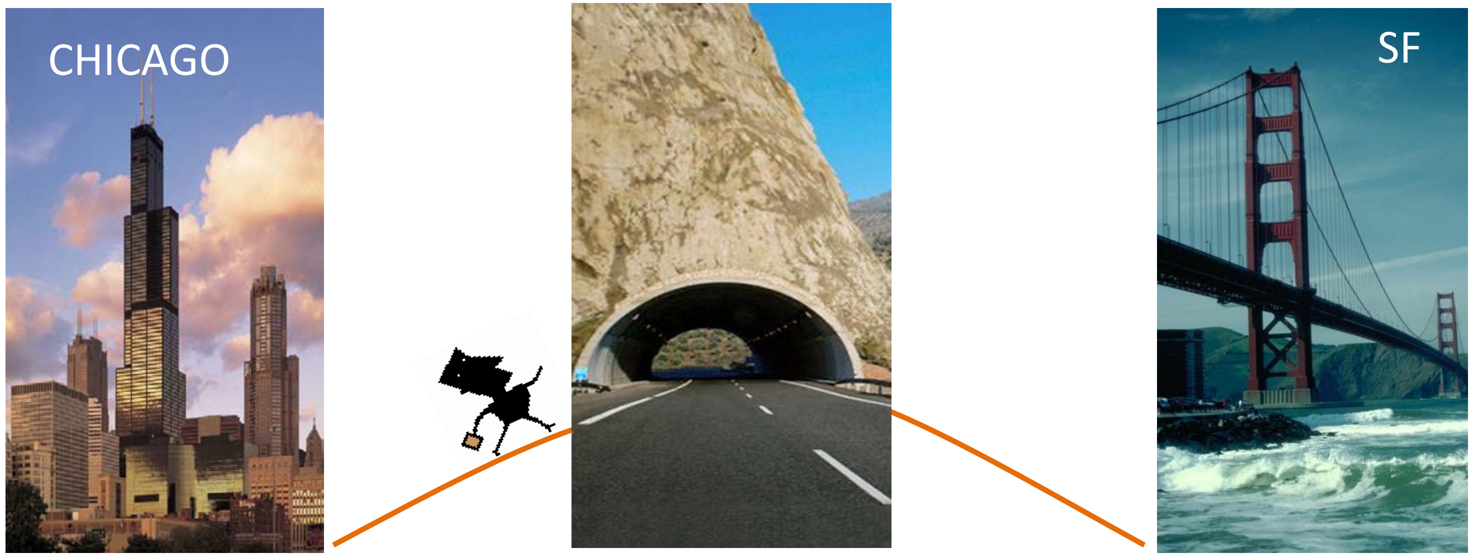
SIGNIFICANT ACTIVATION ENERGY

REQUIRED TO GO FROM REACTANTS TO PRODUCTS

CO_2

H_2O

BASF
The Chemical Company



CO

HC

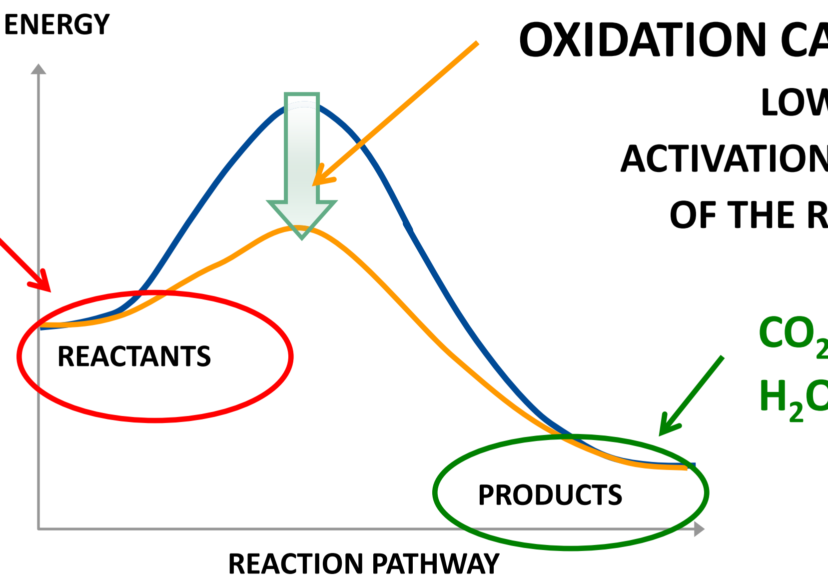
(e.g. propane)

VOC

(e.g. propylene)

HAP

(e.g. formaldehyde)



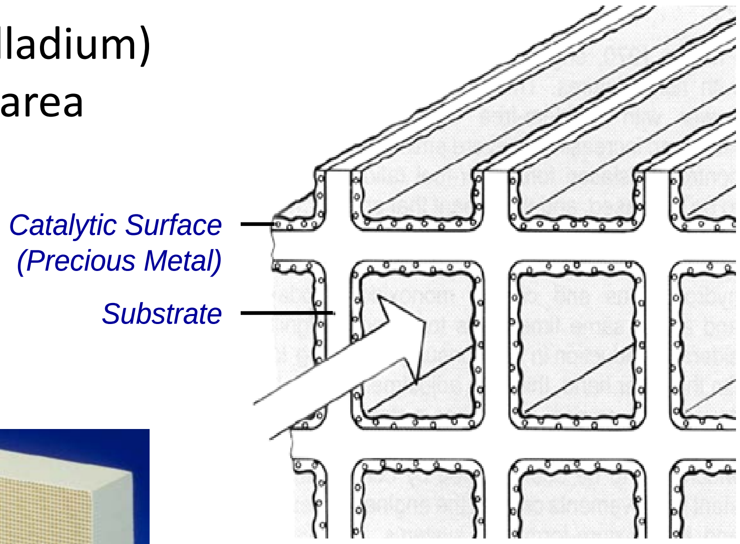
OXIDATION CATALYST

LOWERS THE ACTIVATION ENERGY OF THE REACTION

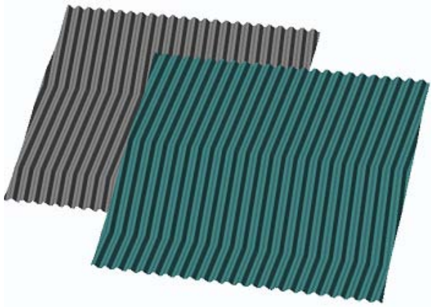
BASF The Chemical Company

CO Catalyst – What is it?

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



Schematic of honeycomb oxidation catalyst



Herringbone metal foil

Ceramic

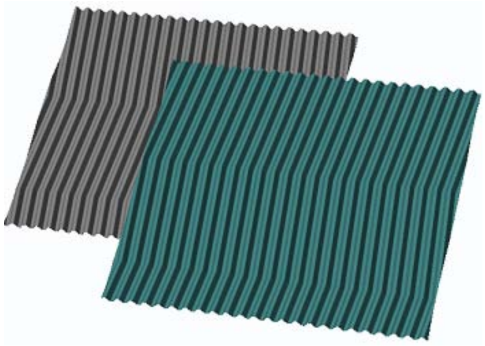
Oxidation catalyst is manufactured by surface coating – not an extrusion technology

BASF
The Chemical Company

Substrate preference driven by operating environment

- Low pressure drop, typically less than 2.0 in.w.c. for metal foil
- Customized to duct cross-section
- Ceramic well-suited for washing to extend useful life
- Ceramic resistant to acid gas environments
- No reagents needed
- Requires low/no sulfur
- Requires low/no dust in flue gas to avoid erosion and/or plugging issues

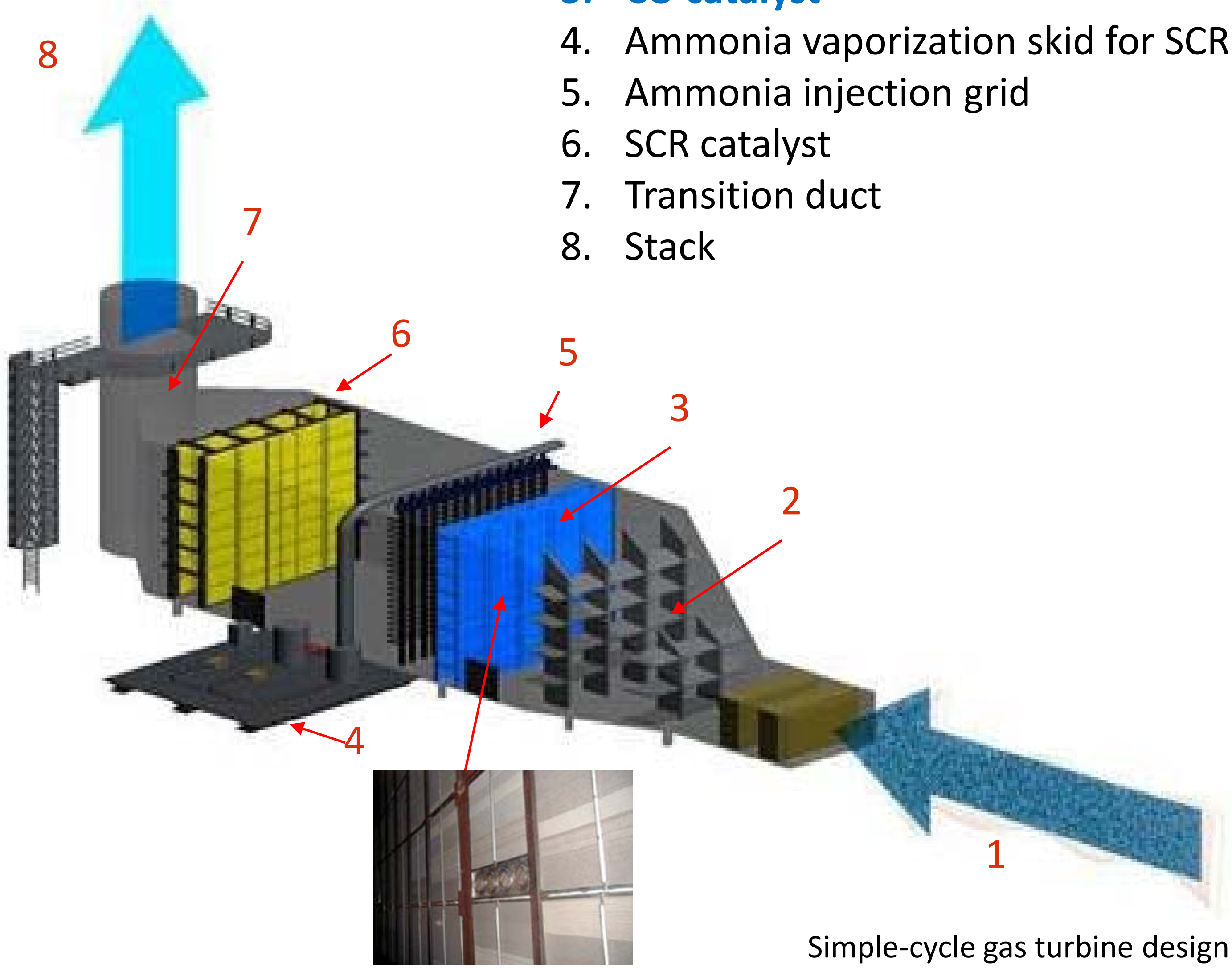
Ceramic



Herringbone metal foil

BASF The Chemical Company

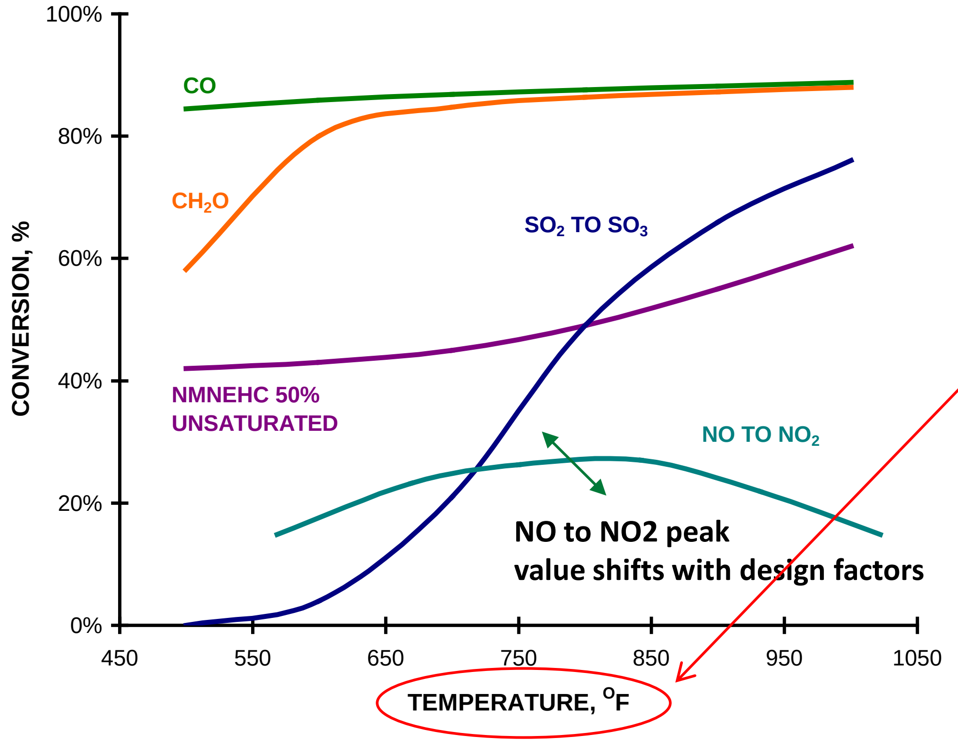
1. Exhaust from gas turbine
2. Guide vanes
3. **CO catalyst**
4. Ammonia vaporization skid for SCR
5. Ammonia injection grid
6. SCR catalyst
7. Transition duct
8. Stack

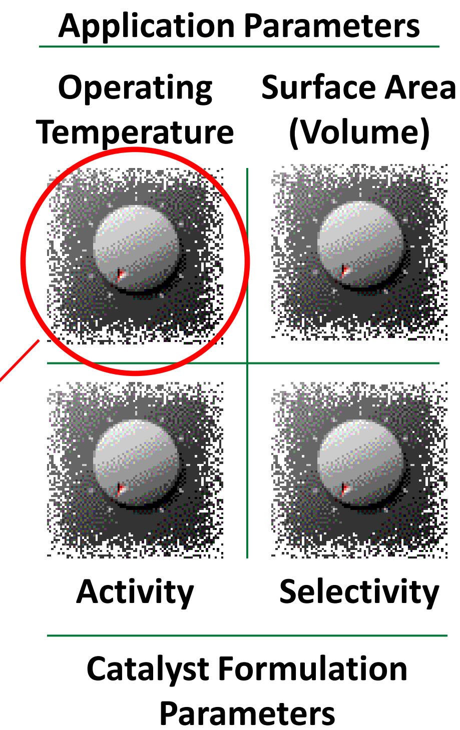


Simple-cycle gas turbine design

BASF
The Chemical Company

Catalyst performance set by initial design parameters – no active controls





Hypothetical stationary engine CO catalyst performance

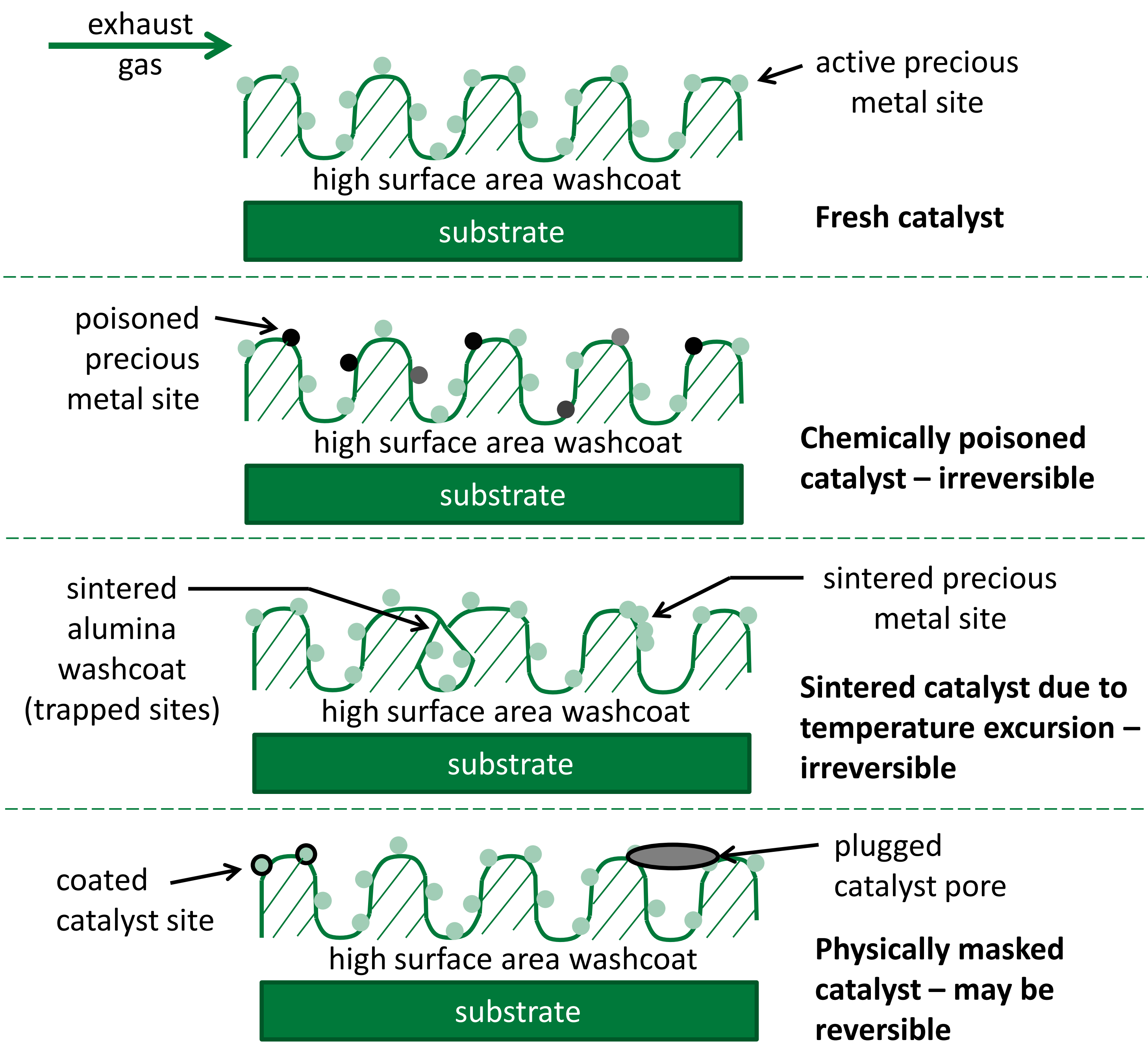
Oxidation catalyst is a "passive" technology providing "constant conversion" independent of inlet concentration

The Chemical Company

Overview – CO Catalysts

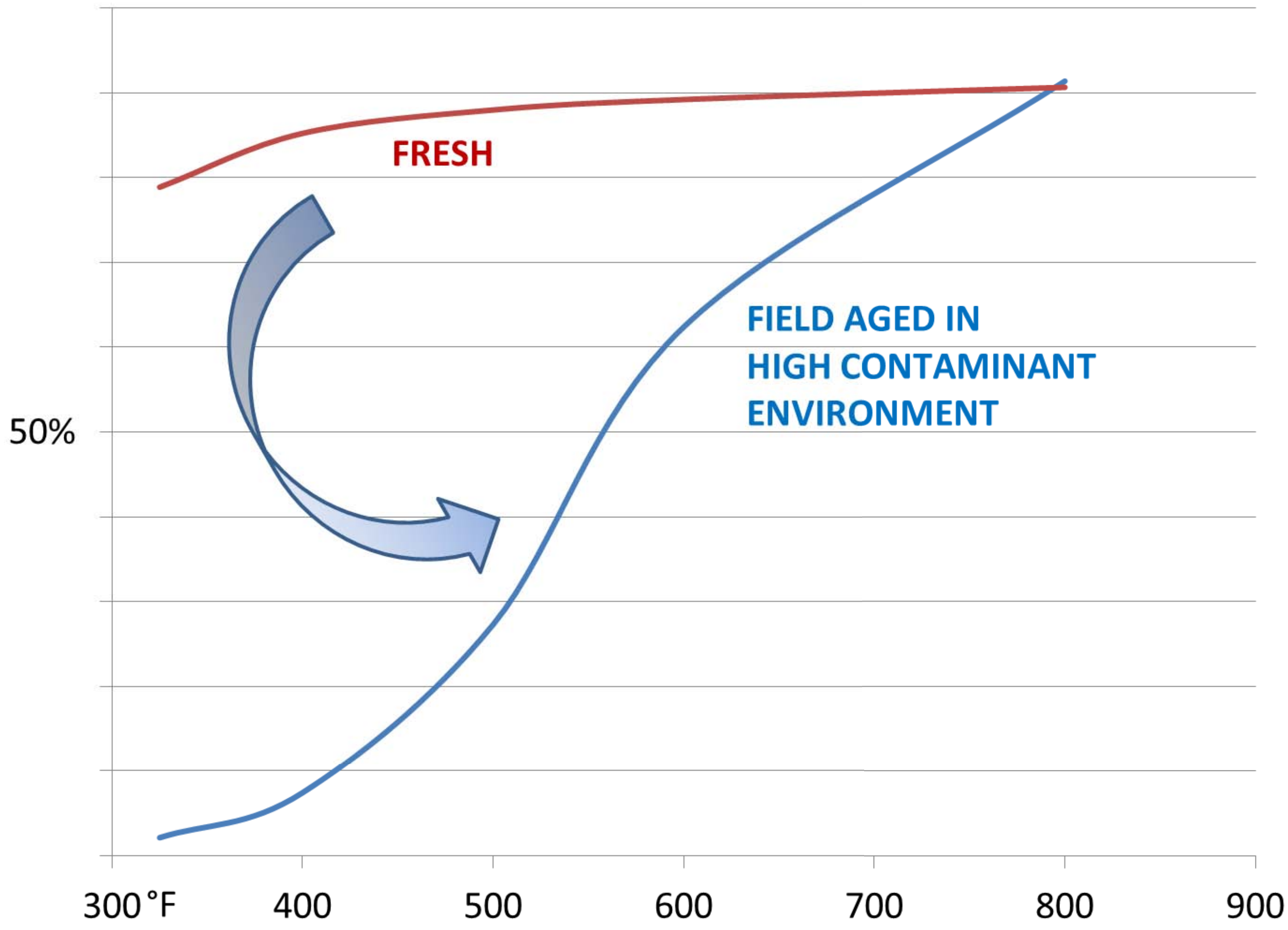
- CO catalyst fundamentals – crash course
- CO catalyst designs – risk management
  - Deactivation by contaminants
  - Application definition
    - – CO v. VOC v. HAP v. NMHC
    - – Coal to gas conversions & balance of plant effects
- Field maintenance
- Model cases for illustration
- Summary

BASF
The Chemical Company



BASF The Chemical Company

Contaminants – the loss of surface area – has greater relative impact at lower temperatures

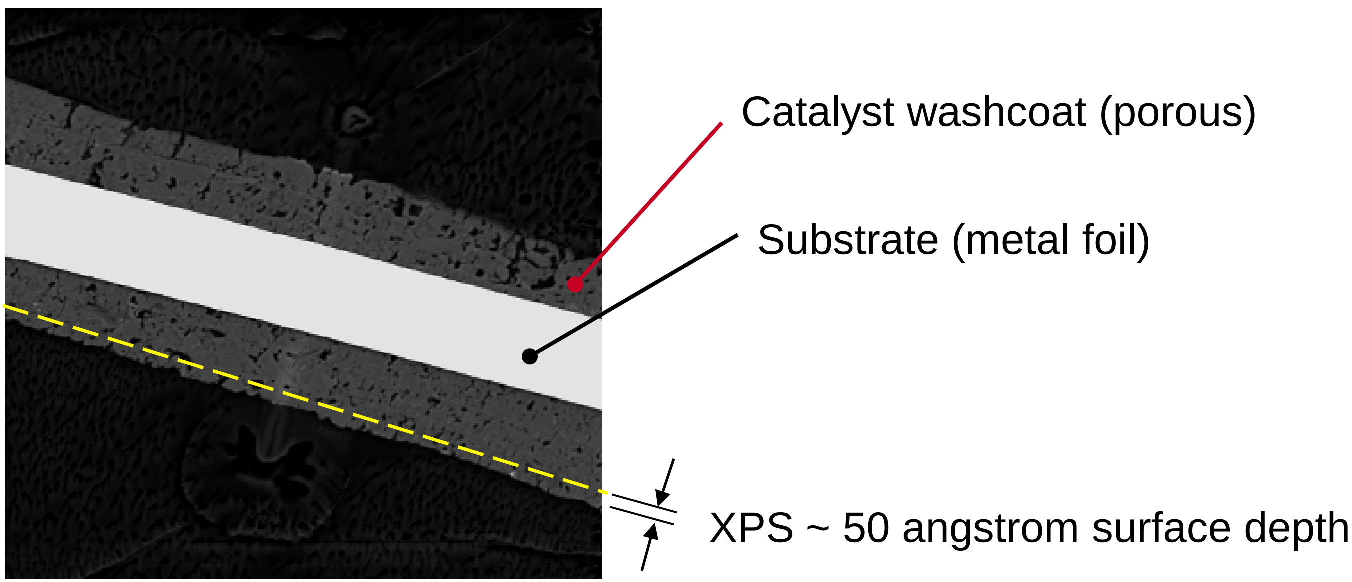


BASF assesses field contaminant risks through oxidation catalyst button evaluations

CO buttons submitted to BASF are routinely evaluated for intrinsic catalyst activity under standard lab conditions and compared to historical population, field data, and comments from the customer describing performance.

BASF
The Chemical Company

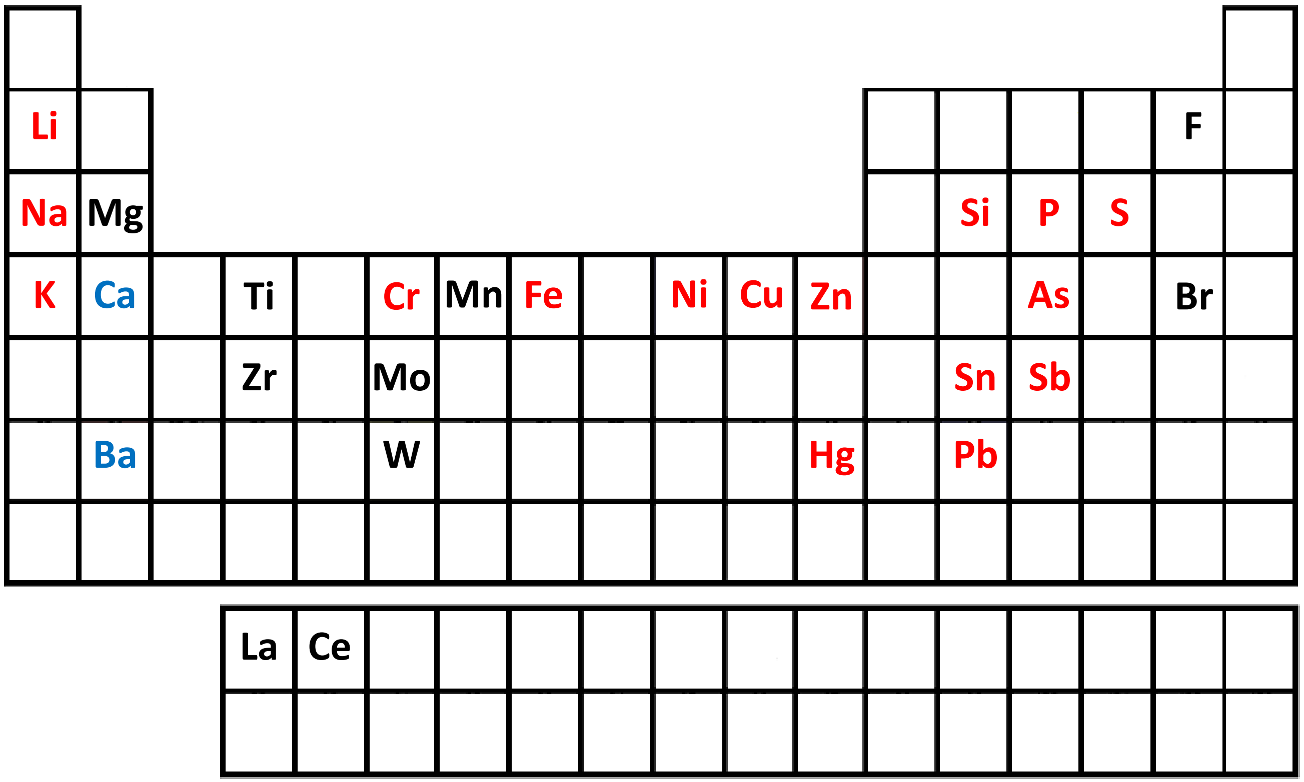
BASF routinely uses XPS to characterize the catalyst surface



XPS (X-ray Photon Spectroscopy) indicates the presence/absence of contaminants and their relative intensity within the first 50 angstroms of catalyst washcoat depth.

BASF
The Chemical Company

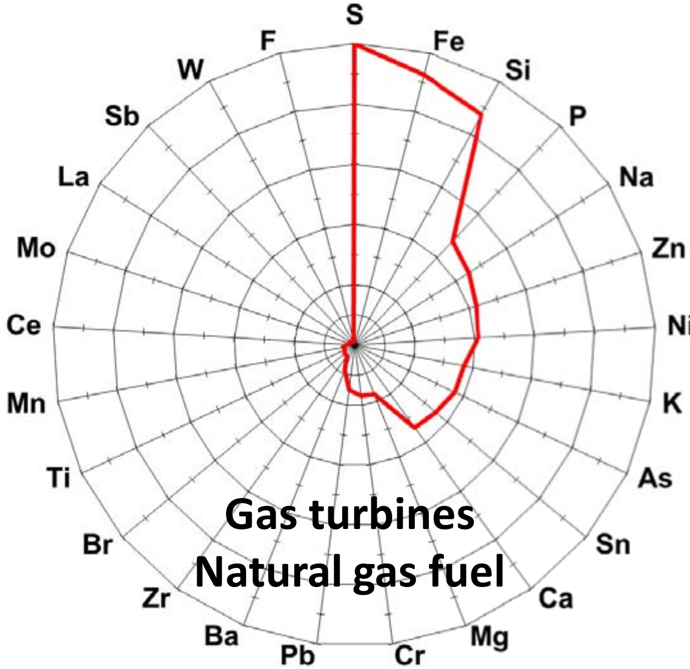
Known oxidation catalyst deactivators

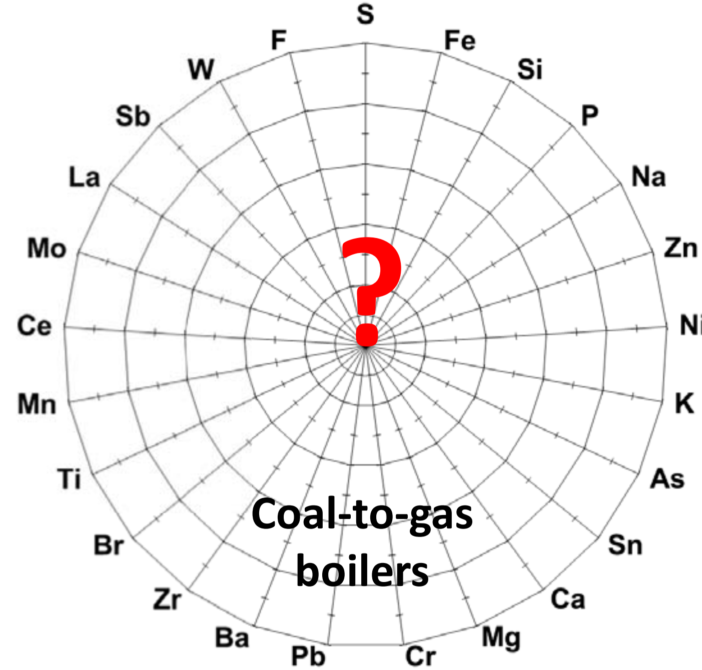


…also dust and particulate may mask catalyst surface

Oxidation catalyst loses performance when it loses surface area due to contaminants

Element deposition frequency on oxidation catalyst:





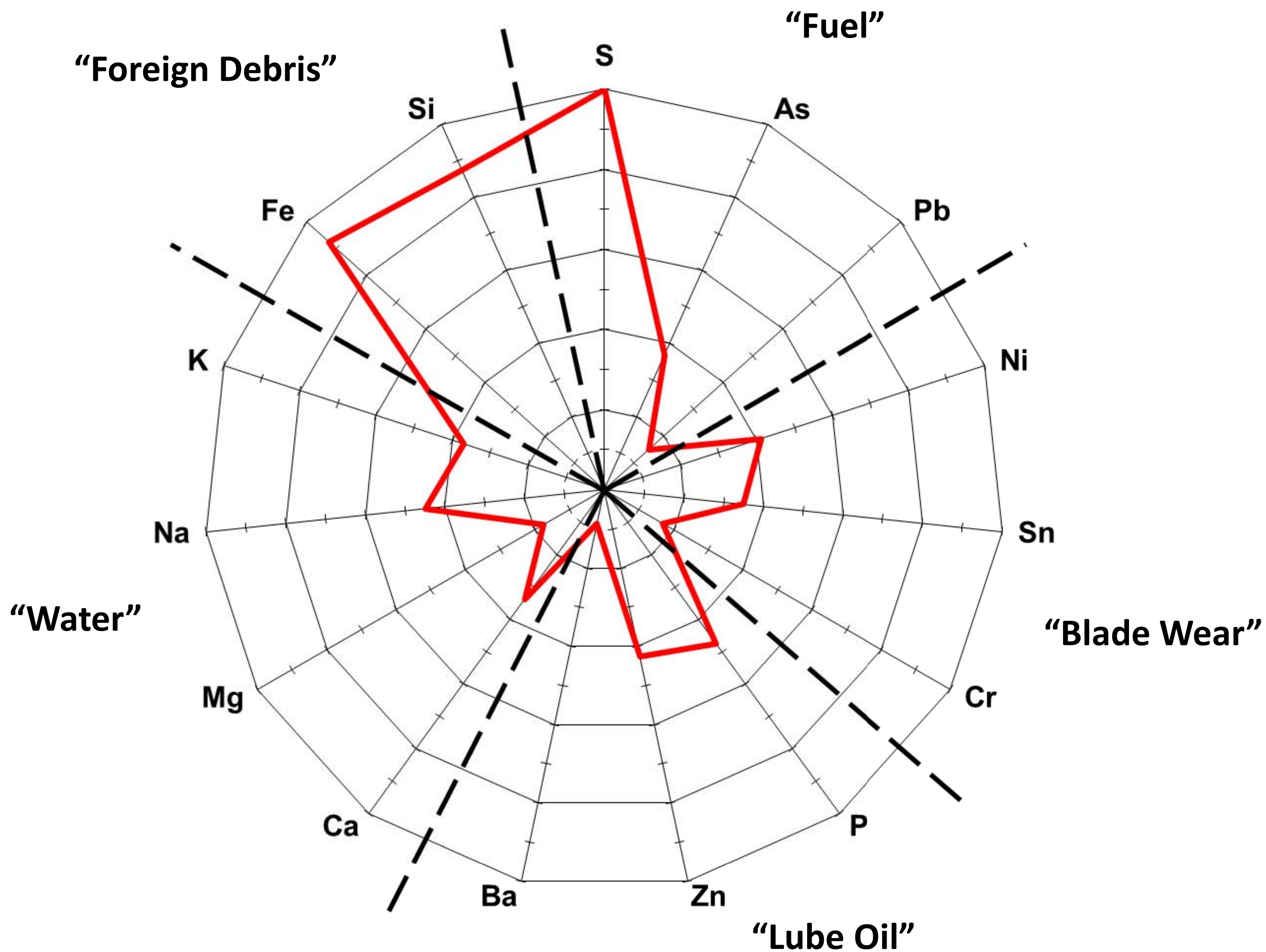
Low risk – well defined through extensive experience

High risk – not well defined; experience still developing

Oxidation catalyst is an expensive "air filter" – trace elements may deposit and poison or mask catalyst performance

BASF
The Chemical Company

Grouping the contaminants by possible source yields a characteristic occurrence “fingerprint”



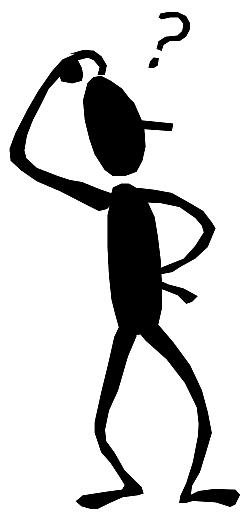
Catalyst supplier's perspective: "Whence these contaminants?"

Major Contaminants on Catalyst		Possible Sources of Contaminants for Gas Turbine				
		Lube Oil	Fuel (Natural Gas or Alternate Fuel)	Water	Blade Wear	Foreign Debris
S	Sulfur		X			
Fe	Iron	X				X
Si	Silicon	X				X
P	Phosphorous	X				
Na	Sodium	X		X		
Zn	Zinc	X				
Ni	Nickel	X	X		X	
K	Potassium	X		X		
As	Arsenic	X	X			
Sn	Tin		X		X	
Ca	Calcium	X		X		
Mg	Magnesium	X		X		
Cr	Chromium		X		X	
Pb	Lead	X	X		X	
Ba	Barium	X	X			

Table to promote thought and discussion; not intended to be definitive.

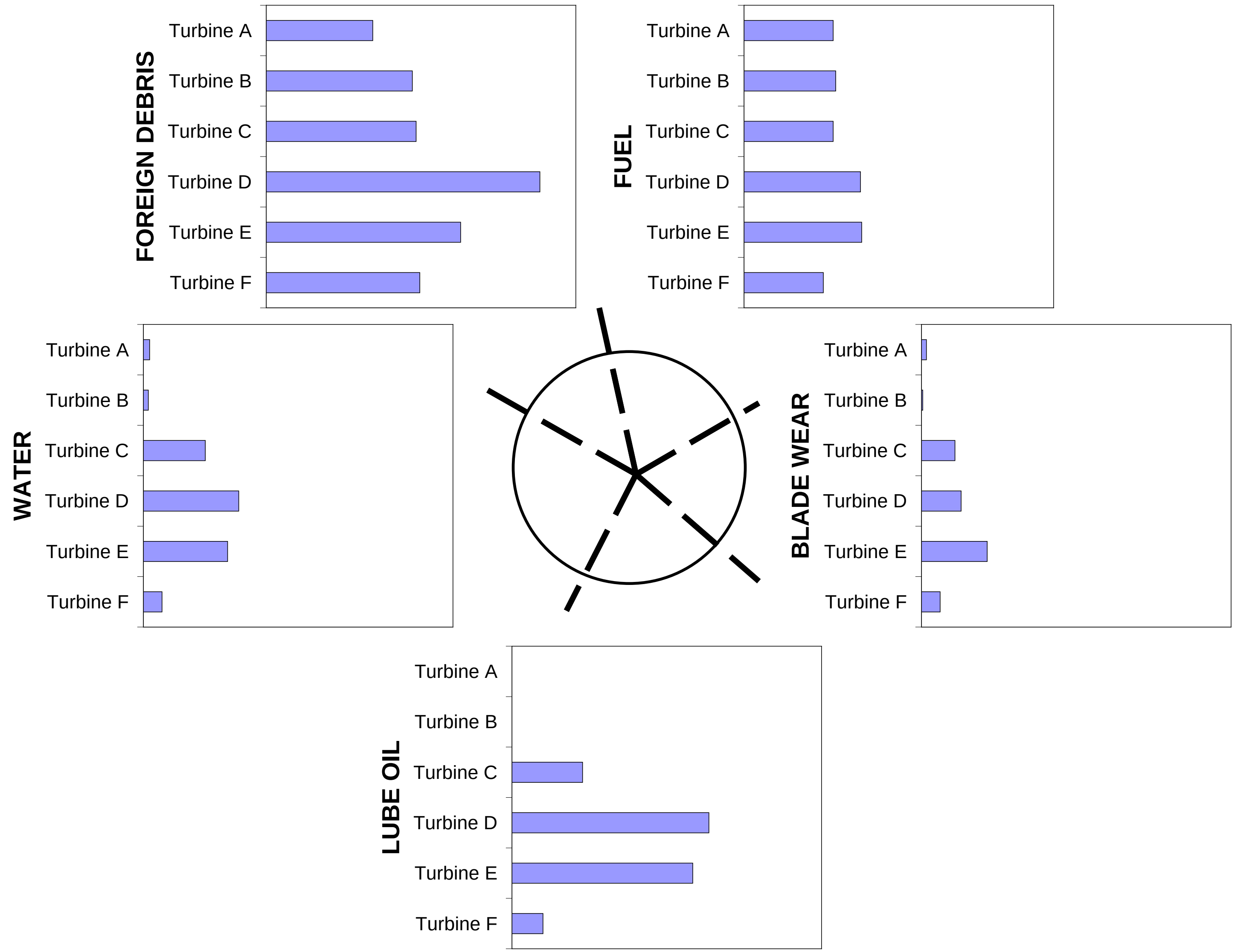
BASF The Chemical Company

So, we should expect **contaminant profiles** may **vary by turbine** or **by fuel?**



BASF
The Chemical Company

Turbines distinguish themselves by the relative occurrence of contaminant groups

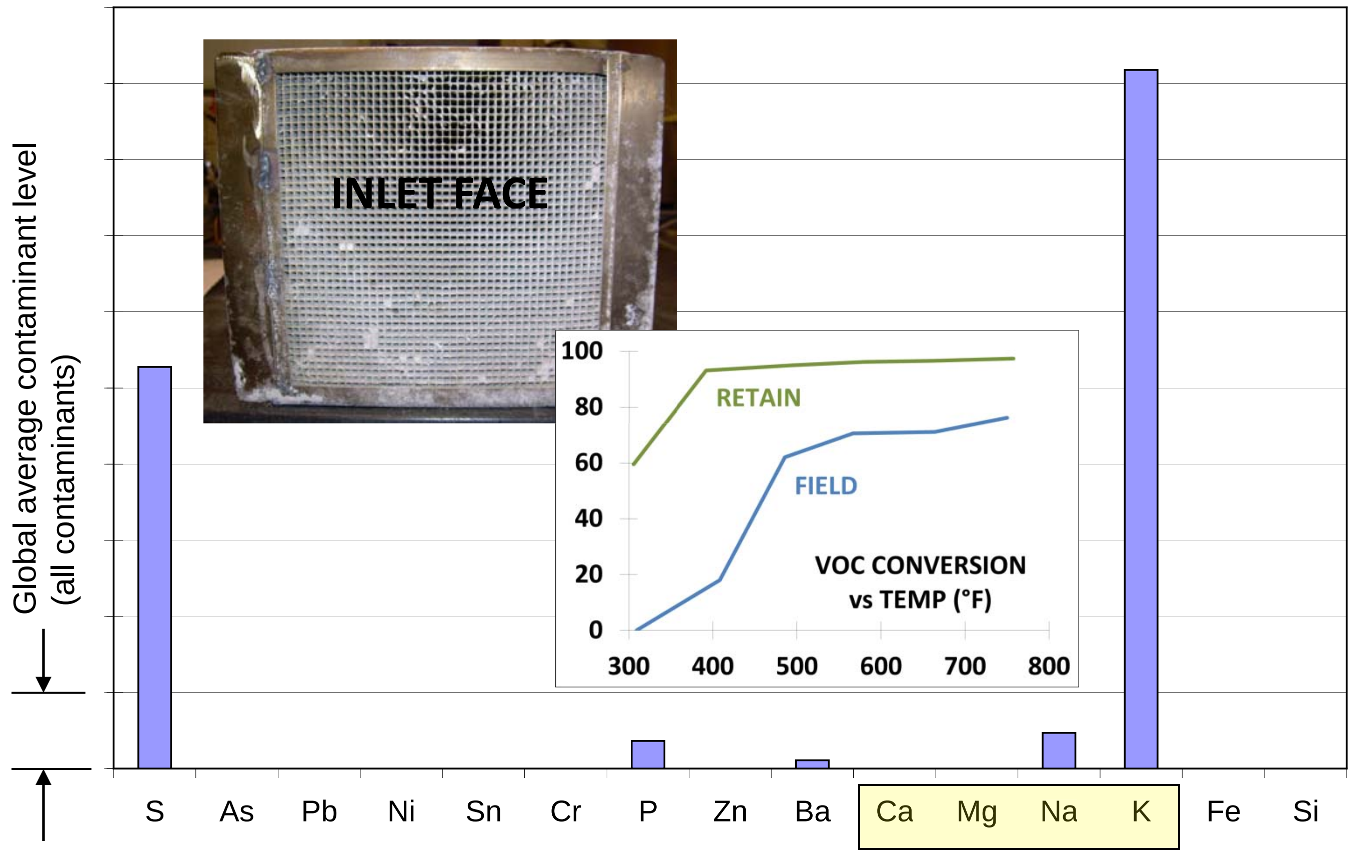


Unique challenges posed by bio-fuels / bio-blends to oxidation catalyst

- Biofuels/bio-blends may be
  - Effective solvents and/or corrosives, dissolving engine/component deposits or fuel system components
- "Trace" contaminants may be well in excess of typical natural gas
  - Processing catalysts residuals: Cu, Ni, Na, K
  - Alkali and alkaline earth metals: Mg, Ca, Na, K
- Siloxanes typical contaminant in landfill/digester gas
- For bio-blends, what is the real fuel "specification"?

BASF
The Chemical Company

Relative contaminant intensity may be characteristic of fuel: bio-fuel / bio-blend



Wikipedia: "Potassium sulfate (K_2SO_4) is a non-flammable white crystalline salt which is soluble in water. The chemical is commonly used in fertilizers, providing both potassium and sulfur." [http://en.wikipedia.org/wiki/Potassium_sulfate]

BASF
The Chemical Company

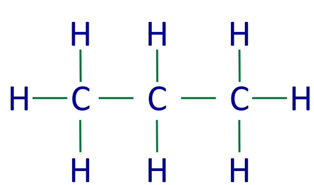
Overview – CO Catalysts

- CO catalyst fundamentals – crash course
- CO catalyst designs – risk management
  - Deactivation by contaminants
  - Application definition
    - – CO v. VOC v. HAP v. NMHC
    - – Coal to gas conversions & balance of plant effects
- Field maintenance
- Model cases for illustration
- Summary

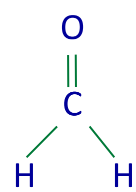
BASF
The Chemical Company

CO vs. VOC – Catalyst perspective

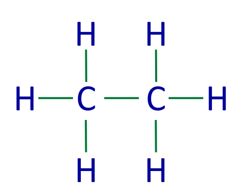
- **The term "VOC" represents a <u>class</u> of compounds**
  - EPA CFR 51.100(s) Definition – Volatile organic compounds (VOC): "…any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions."
  - EPA CFR 51.100(s)(1) "[VOC includes] …any such compound other than the following, which have been determined to have negligible photochemical reactivity: methane, ethane,…"
- **There is no one compound that may characterize the reaction of all VOCs across a given oxidation catalyst technology**



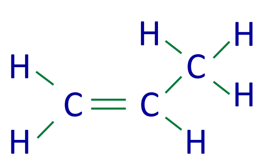
Propane
VOC & Saturated HC



Formaldehyde
VOC but not a HC



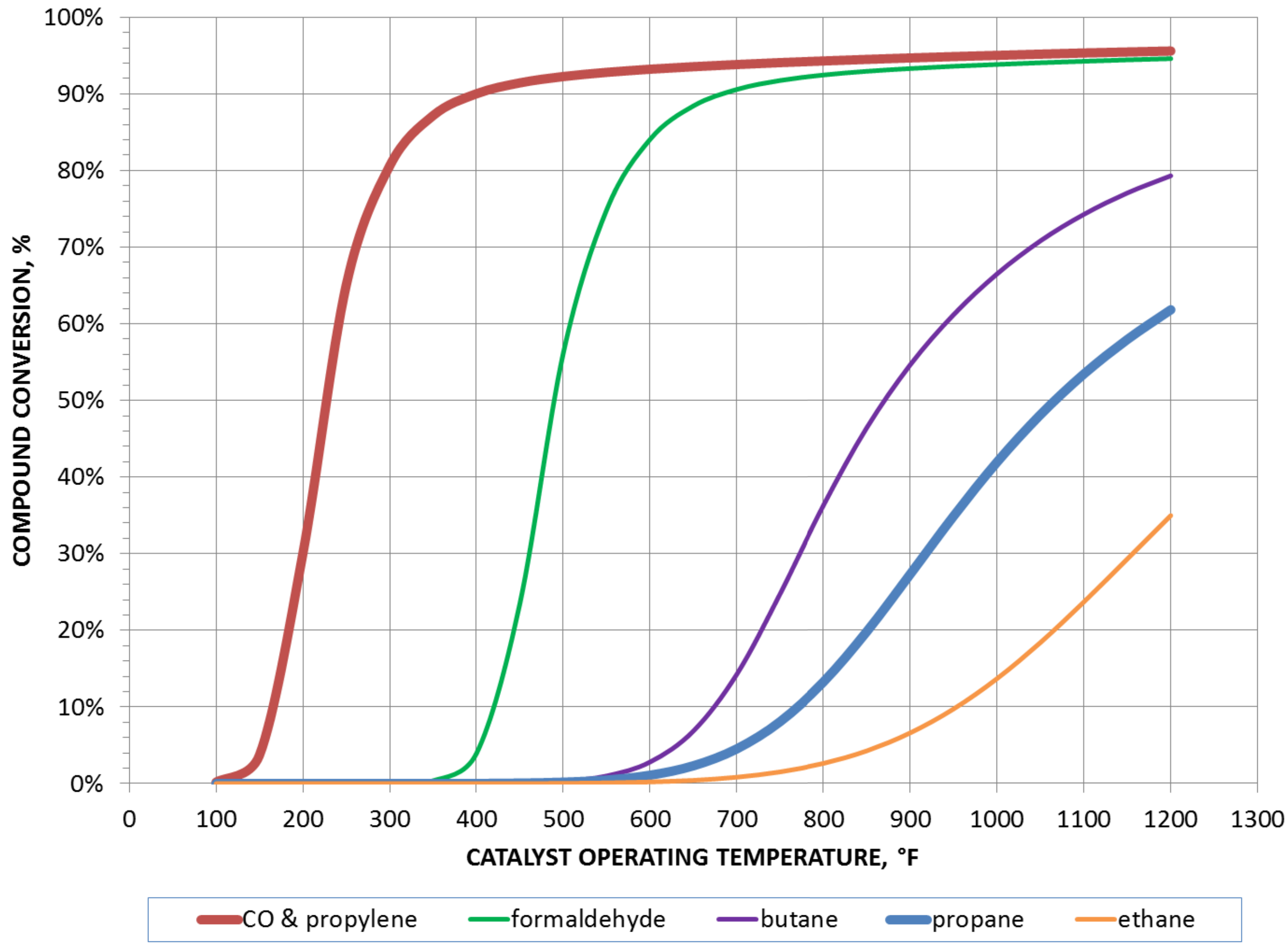
Ethane
HC but not a VOC



Propylene
VOC & Unsaturated HC

BASF
The Chemical Company

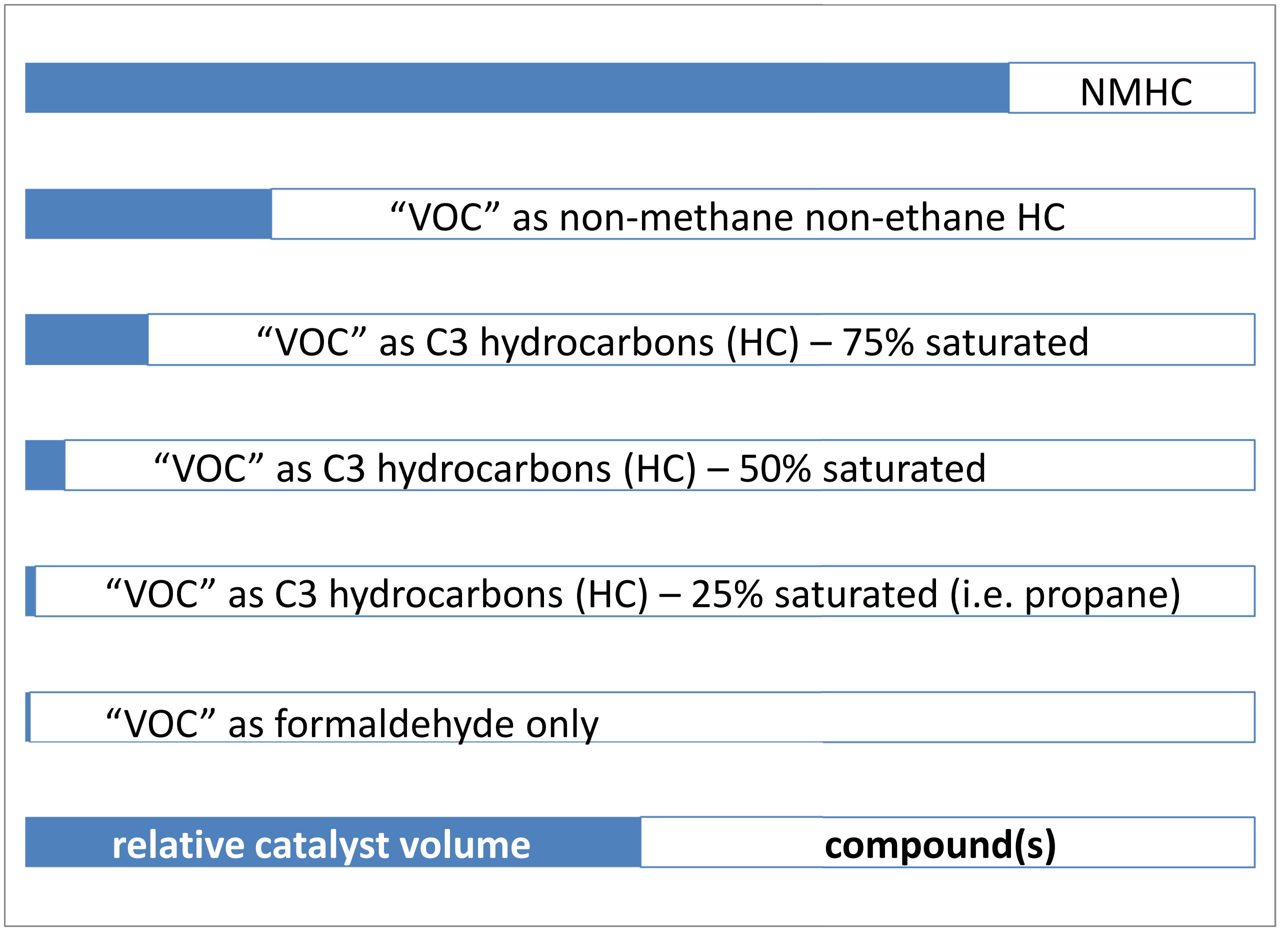
Each "VOC" compound has a unique, temperature-dependent conversion curve



BASF
The Chemical Company

“VOC” definition criticality

Oxidation catalyst design for
50% “VOC” (?) Conversion at fixed temperature



BASF
The Chemical Company

Practical definition of "VOC" for gas turbines

- The definition of "VOC" on gas turbines has evolved to jointly mesh the technology of catalysts with clarity needs of regulators
- "VOC" performance requirements on gas turbines typically set as "what comes along" with CO performance

BASF
The Chemical Company

Overview – CO Catalysts

- CO catalyst fundamentals – crash course
- CO catalyst designs – risk management
  - Deactivation by contaminants
  - Application definition
    - – CO v. VOC v. HAP v. NMHC
    - – Coal to gas conversions & balance of plant effects
- Field maintenance
- Model cases for illustration
- Summary

BASF
The Chemical Company

Risk management – Coal-to-gas conversion: Emissions definition

- New applications for oxidation catalyst, like coal-to-gas utility boiler conversions, highlight the need to be mitigate risk, and costs, by precisely defining the application
  - CO-VOC levels need to be defined at all loads and operating conditions (temperature, flow)
  - Natural gas boiler conversion may not yield the same CO-VOC profiles as natural gas turbine combustion
  - Current predictive modeling of catalyst performance lacks extensive database
    - CO control viable; but VOCs should be characterized without penalty until well understood

BASF
The Chemical Company

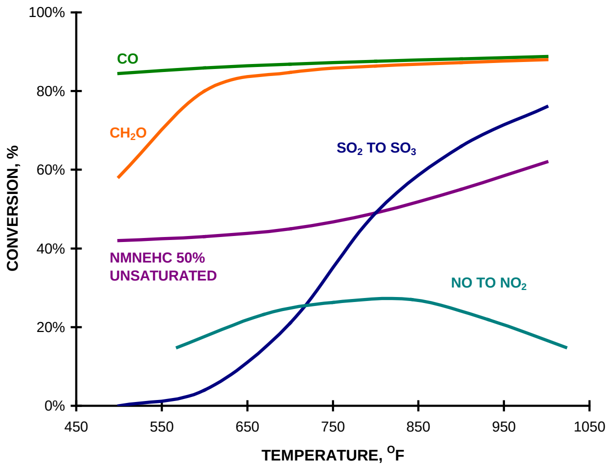
Risk management – Coal-to-gas conversion: Constraints in fuel switching

- Reverse fuel switching, from natural gas back to coal, would necessitate the physical removal of the oxidation catalyst before switch is made to avoid significant premature deactivation due to physical masking and chemical poisoning agents unique to coal (e.g. arsenic)
- Sulfur attacks CO catalyst and is oxidized from SO_2 to SO_3
- Ash would erode the catalytic coating
- Upstream ducting would need to be clean, even washed, before oxidation catalyst installation

BASF
The Chemical Company

Oxidation catalyst – balance of plant

- Oxidation catalyst will convert:
  - NO to NO_2
  - SO_2 to SO_3



- For coal-to-gas conversions, potential for brown (NO_2) plume generation in existing wide diameter stacks, as catalyst may shift NO/NO_2 ratio and raise the NO_X concentration at the stack.

BASF
The Chemical Company

Coal-to-gas conversion: Summary of options

	Natural Gas-Fired Only	Coal:Gas Switching
• Control CO	• Combustion tuning OR catalyst	• Bypass or Remove CO-VOC Catalyst when coal-firing
• Consider/Control VOC	• Must characterize or accept as co-benefit • Catalyst located >750F zone better	• Co-benefit, characterize when gas-firing
• Control NOx	• Trade-off in favor of CO control if possible • If CO catalyst needed, evaluate NO2, SO3 impact • Install SCR if NO2 must be mitigated or balanced against emission caps and optimal designs	• Run as permitted on coal • When gas-fired, minimize NO2 if CO-VOC catalyst is used • When gas-fired, tune for CO if no catalytic controls
• Operating constraints	• Need flue gas distribution balance with catalysts • If boiler/rust scale present, consider large catalyst open area and ceramic substrate • Evaluate stack impact for visibility (NO2 plume)	• Take offline and fully clean duct prior to switching fuels • Accept tonnage cap if catalyst solution not a fit

Source: Stephenson, N. *Catalytic Emission Control Coal-to-Gas Boiler Systems.* Reinhold Environmental 2012 Coal-to-Gas Round Table, Chattanooga, TN, Oct. 23-24, 2012.

BASF
The Chemical Company

Overview – CO Catalysts

- CO catalyst fundamentals – crash course
- CO catalyst designs – risk management
  - Deactivation by contaminants
  - Application definition
    - – CO v. VOC v. HAP v. NMHC
    - – Coal to gas conversions & balance of plant effects
- Field maintenance
- Model cases for illustration
- Summary

BASF
The Chemical Company

The oxidation catalyst bed
may be an expensive type of "fuse" or "filter"

- Increased pressure drop may mean oxidation catalyst plugging
  - Check for foreign debris (e.g. loose insulation impingement)
- A step change in stack emissions may imply an upset in operation
  - Usually a one-time event; usually not good
- A gradual change in stack emissions may still be noteworthy
  - Rate of change may imply a chronic rather than an acute condition
  - Catalyst activity assessment may help diagnose issue
  - The field retrieved catalyst sample may "see" the loss of activity under lab test conditions before the entire bed.

BASF
The Chemical Company

Catalyst activity assessment of field retrieved "button" sample

- Field retrieved catalyst sample tested under standard lab conditions that exaggerate deactivation relative to fresh catalyst
  - Lab results are translated back to expected performance under field operating conditions
  - Field data, data trends, and/or operating hours help in interpretation of lab results
- If lab assessment doesn't match field performance, further discussions may be needed
  - Button not representative / not-representative location
  - System issues (e.g. failed seals, gaskets) may obscure catalyst performance in the field

BASF
The Chemical Company

System maintenance maximizes the useful life of the installed oxidation catalyst

- When work identifies contaminants, it is prudent to quickly check to see if anything about the potential sources for these particular contaminants has changed
  - Fuel type/source (e.g. bio fuels)
  - Water injection system upset
  - Change in lube oil consumption rate
- Identifying and mitigating, or removing, the source of deposits will maximize the useful life of the installed oxidation catalyst.

BASF
The Chemical Company

Maintenance recommendations to those who've submitted a catalyst sample for analysis

- Catalyst bed maintenance recommendations:
  - 95% of the time, no active maintenance is required – catalyst is "aging" at or better than expected levels.
  - 5% of the time, catalyst cleaning is recommended per OEM manual procedures
    - Compressed air or DI water
    - Applied to catalyst surface from outlet face towards inlet face
    - Particularly applicable for recovery from one-time events
- System maintenance recommendation:
  - Identify sources of potential contaminants and mitigate or remove them from system
  - Without mitigation/removal of contaminants from the system, catalyst surface cleaning will result in only a temporary improvement in performance

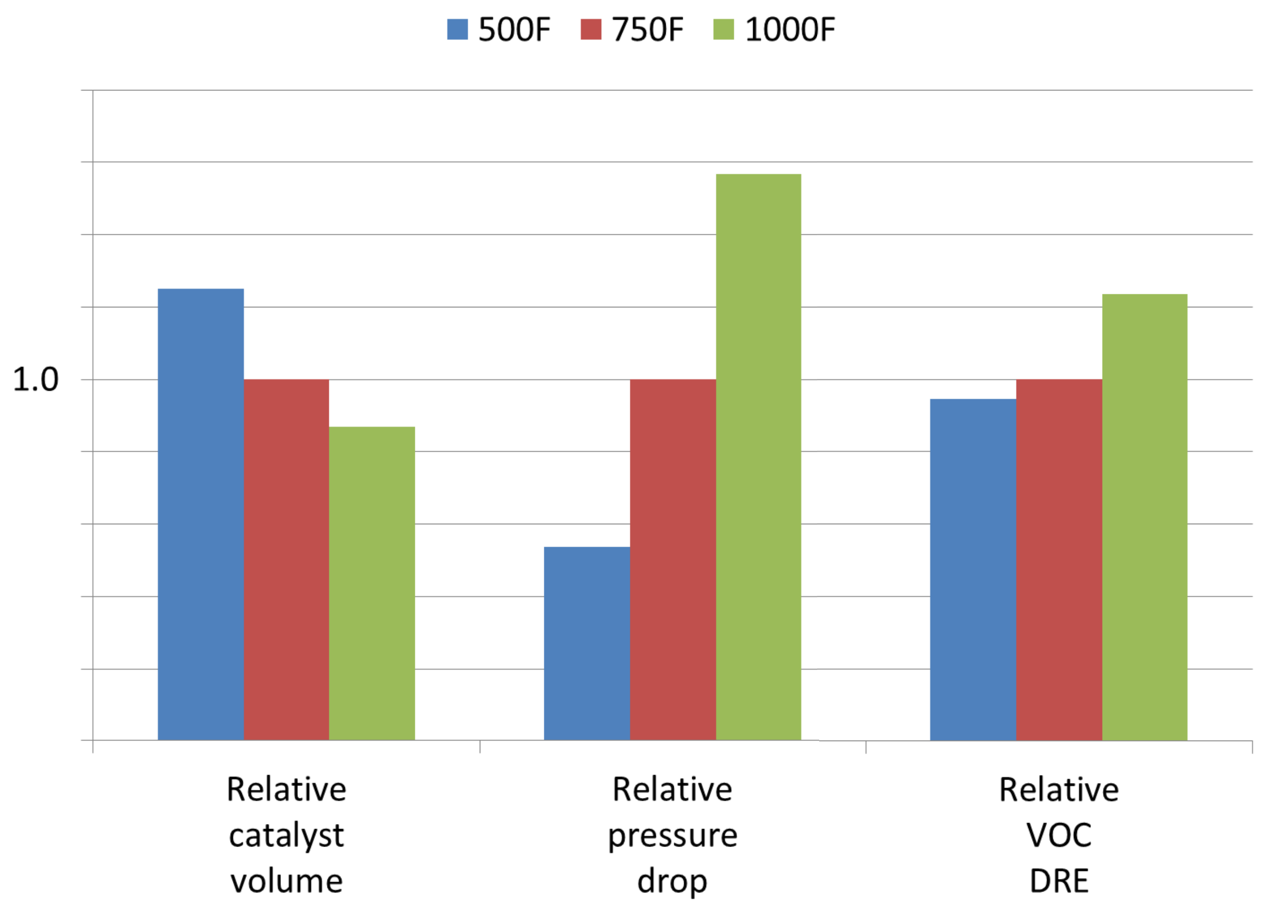
BASF
The Chemical Company

Overview – CO Catalysts

- CO catalyst fundamentals – crash course
- CO catalyst designs – risk management
  - Deactivation by contaminants
  - Application definition
    - CO v. VOC v. HAP v. NMHC
    - Coal to gas conversions & balance of plant effects
- Field maintenance
- Model cases for illustration
- Summary

BASF
The Chemical Company

Importance of catalyst location: Temperature impacts on a fixed catalyst bed



Example plant:
Natural gas-fired only

- 200 – 250 MW
- No catalytic controls in place now
- Targeted CO DRE – 90%
- VOC conversion – requested, but definition unspecified
- Base case + two alternate scenarios to highlight temperature issue

BASF
The Chemical Company

Model case:
Natural gas operation

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 fromprior coal combustion

Option #1
Oxidation Catalyst Option - Baseline
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 ft3 +/- 20% total catalyst volume
90% CO DRE
44% VOC DRE - C3 HC 50/50 Saturated
29% SO2 to SO3 conversion
12% NO to NO2 conversion
$275 per 1,000 lb/hour
0.9 in.w.c. dP
108 inlet NOx
Assume 20ppm NO2, 88ppm NO
Outlet 30.6 ppm NO2
Stack tolerance from 120 inches_max to 78 inches_max
Notes:
1. Metal foil substrate design, typical for gas turbine
2. Catalyst costs only; frame & installation extra
3. Ceramic substrate options yield higher up-front costs,
but may be better suited to the operating environment

BASF The Chemical Company

Model case: Relocate downstream, 550F

- ~ 15% increase in catalyst volume
- Significant increase in NO oxidation rate to NO_2
  - Equilibrium favors NO_2 formation at lower temperatures
  - May have stack diameter implications for plume generation

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 ft3 +/- 20% total catalyst volume
90% CO DRE
42% VOC DRE - C3 HC 50/50 Saturated
2% SO2 to SO3 conversion
46% NO to NO2 conversion
$325 per 1,000 lb/hour
0.7 in.w.c. dP
108 inlet NOx
Assume 20ppm NO2, 88ppm NO
Outlet 60.5 ppm NO2
Stack tolerance from 120 inches_max to 40 inches_max
Notes:
1. Metal foil substrate design, typical for gas turbine
2. Catalyst costs only; frame & installation extra
3. Ceramic substrate options yield higher up-front costs,
but may be better suited to the operating environment

BASF The Chemical Company

Model case:
Double catalyst volume @ 730F

- 200% increase in catalyst volume to evaluate VOC benefit
- Small benefit in VOC conversion
- Little contribution to VOC conversion from saturated C3 hydrocarbon
- Propane does not ignite across oxidation catalyst at 730°F

Option #3
Oxidation Catalyst Option @ 2x Catalyst Volume
20 ft x 48 ft duct cross-section
18 ft x 44.5 ft catalyst bed cross-section
6 inch catalyst depth
105 cells per square inch substrate
400 ft3 +/- 20% total catalyst volume
99% CO DRE
49% VOC DRE - C3 HC 50/50 Saturated
49% SO2 to SO3 conversion
14% NO to NO2 conversion
$550 per 1,000 lb/hour
1.8 in.w.c. dP
108 inlet NOx
Assume 20ppm NO2, 88ppm NO
Outlet 32.3 ppm NO2
Stack tolerance from 120 inches_max to 74 inches_max
Notes:
1. Metal foil substrate design, typical for gas turbine
2. Catalyst costs only; frame & installation extra
3. Ceramic substrate options yield higher up-front costs,
but may be better suited to the operating environment

BASF The Chemical Company

Overview – CO Catalysts

- CO catalyst fundamentals – crash course
- CO catalyst designs – risk management
  - Deactivation by contaminants
  - Application definition
    - – CO v. VOC v. HAP v. NMHC
    - – Coal to gas conversions & balance of plant effects
- Field maintenance
- Model cases for illustration
- Summary

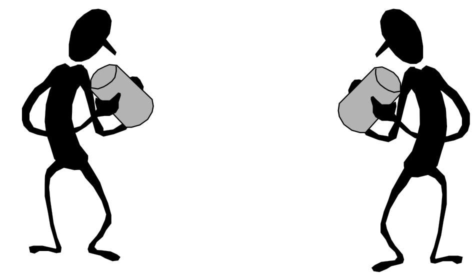
BASF The Chemical Company

A catalyst supplier's perspective on the use of oxidation catalyst on combustion turbines

- The use of oxidation catalyst to control emissions from gas-fired turbines is a robust technology with a history of proven success for over 20 years.
- New trends in the power generation industry (e.g. alternate fuels, tighter control standards on more emissions, etc…) have placed a premium on a deeper understanding of the in-situ performance of the catalyst, especially with regards to contaminants and aging.

BASF
The Chemical Company

Summary…

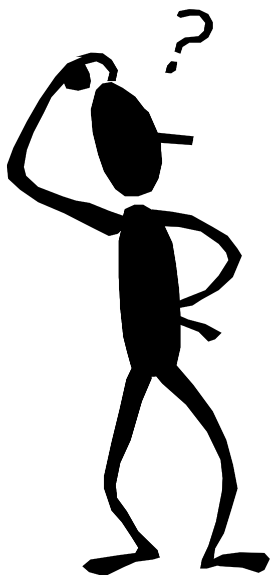


Customer asks about…	Catalyst supplier thinks about…
CO conversion	• Operating environment (including particulate and/or acid gases) • Emissions profile • Minimum required catalyst volume
VOC conversion	• Practical definition of “VOC”
Preferred catalyst bed location	• Impact of temperature on performance
Catalyst performance warranty	• Risk of catalyst poisoning and/or masking by contaminants
Balance of plant impacts	• Other reactants and products across catalyst bed

Discussions – early & often – on emissions control options with an oxidation catalyst supplier is recommended.

BASF
The Chemical Company

QUESTIONS



Sales Contact:

Bob Zeiss

Power Industry Sales Manager

Clean Air Business Unit

BASF Corporation

Phone: 732-205-6640

E-mail: **robert.zeiss@basf.com**

Technical Contact:

Mike Durilla

Product & Applications Development Manager

Clean Air Business Unit

BASF Corporation

Phone: 732-205-6644

E-mail: **mike.durilla@basf.com**

BASF thanks you for this opportunity to present at the Reinhold Environmental 2013 NO_x Combustion Round Table & Expo

BASF
The Chemical Company