REINHOLD ENVIRONMENTAL Ltd.

2017 NOx-Combustion-CCR Round Table Presentation

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

CO Control in Gas Turbine

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Reinhold Environmental
2017 NO_X-Combustion-CCR Round Table
Hosted by FirstEnergy
Renaissance Cleveland Hotel
Cleveland, OH
February 27 – March 2, 2017

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Workshop description

fundamentals

performance

The workshop reviews certain fundamentals of oxidation catalysts and discusses how they drive CO/VOC emissions control performance in gas turbines. In particular, the complicating, and often times dramatic, effects of fuel quality on CO/VOC catalyst performance are described along with strategies to mitigate the impacts.

fuel quality

mitigate

BASF / Catalysts Division / Clean Air Business

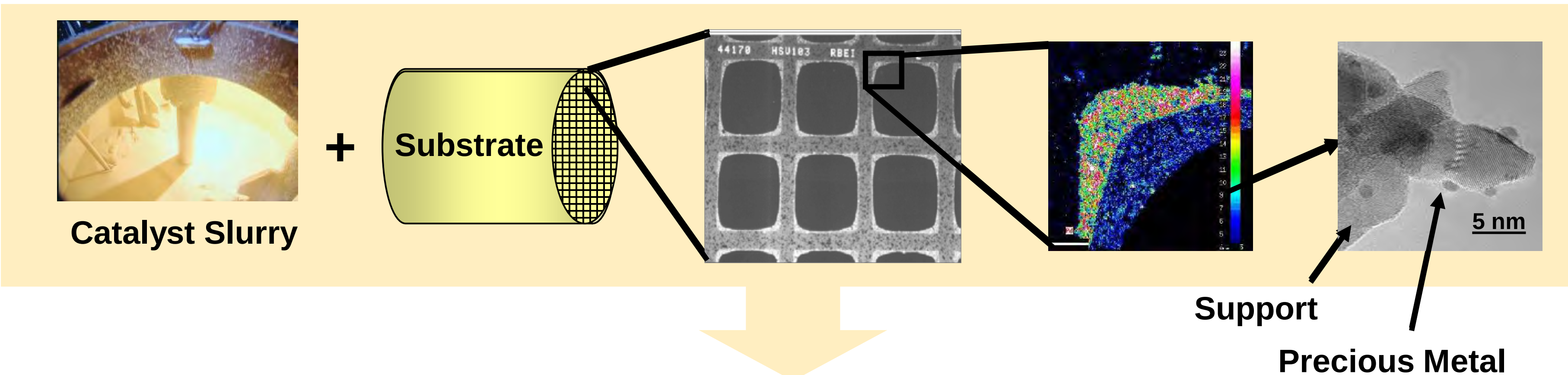
Who We Are and What We Do

BASF We create chemistry

- BASF's Clean Air Business has been serving the power generation industry for more than 30 years with over 850 units operating or under construction. BASF customers value our experience and technical expertise as the premier supplier of oxidation catalyst solutions to the power generation industry.
- Our breadth of experience encompasses virtually every make, model, and turbine configuration. Our R&D, application, and project engineering expertise ensures maximum performance for both new source applications and replacement catalyst for existing applications.

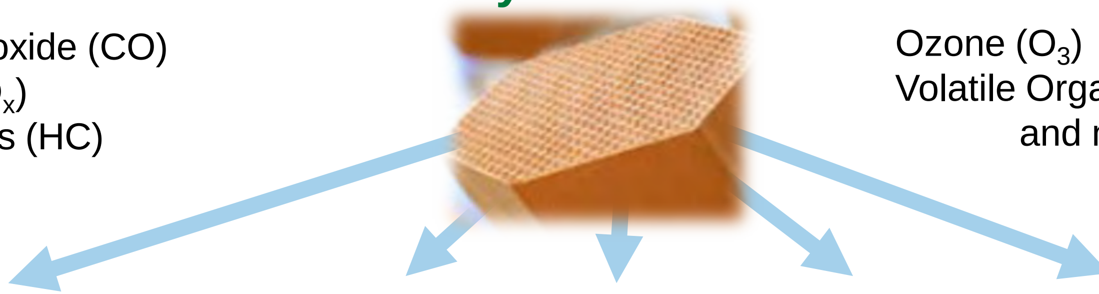
Clean Air Solutions

Broad Range of Innovative Technologies for Emissions Control

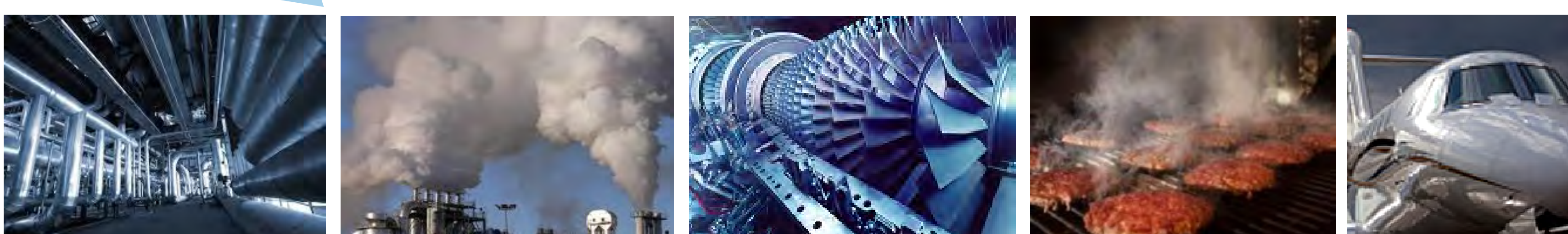


"Catalytic Converter"

Carbon Monoxide (CO)
Nitrogen (NO_x)
Hydrocarbons (HC)



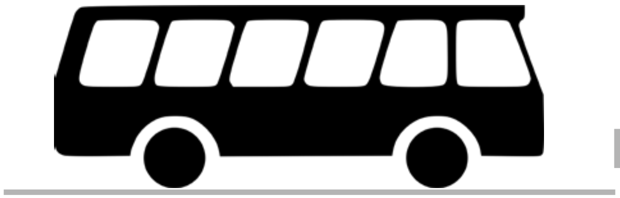
Ozone (O_3)
Volatile Organic Compounds (VOC)
and more.....



Workshop road map

CO Control in Gas Turbine

fundamentals



performance

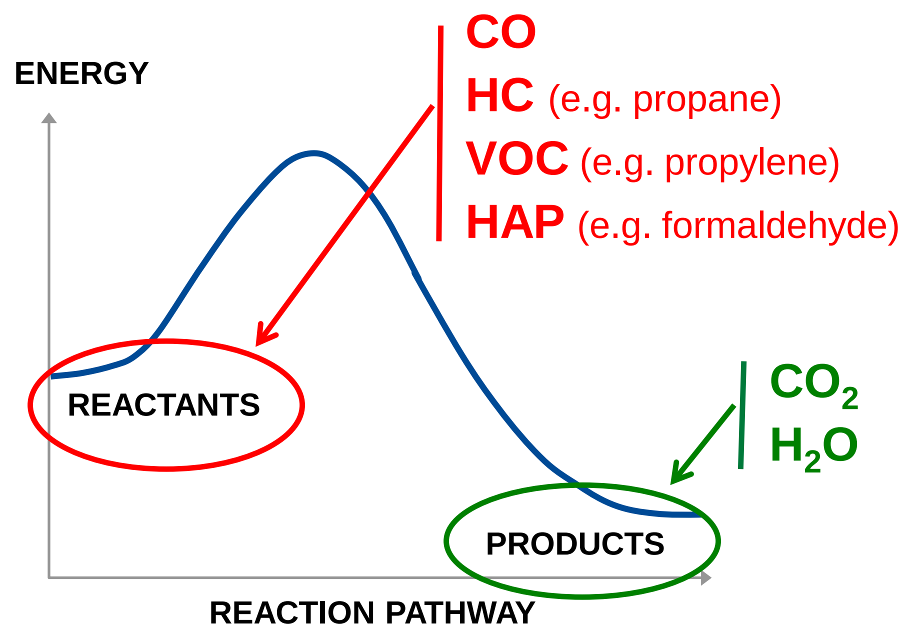
fuel quality

mitigate

Significant activation energy is required to cross mountains or create chemistry

SIGNIFICANT ACTIVATION ENERGY

REQUIRED TO GO FROM REACTANTS TO PRODUCTS



Like a tunnel through a mountain, oxidation catalyst provides an alternate, low energy path

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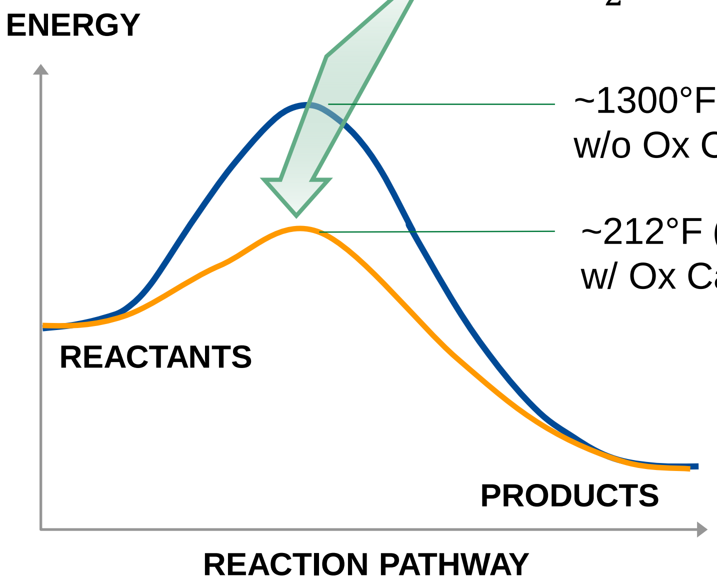
OXIDATION CATALYST

LOWERS THE ACTIVATION ENERGY OF THE REACTION

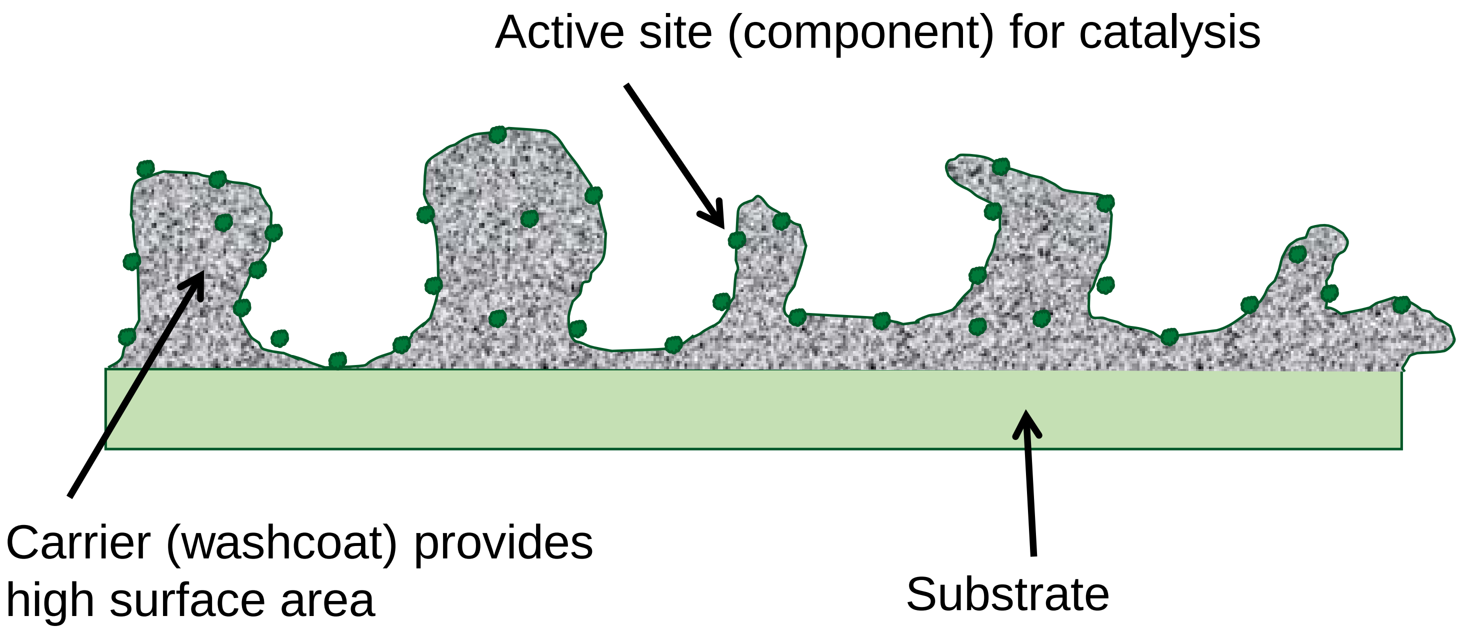
$$CO + \frac{1}{2} O_2 = CO_2$$



What is a catalyst?

Active component + Carrier + Substrate

Active component (e.g. precious or base metal) dispersed through a high surface area carrier (washcoat) on a substrate, such as a ceramic honeycomb block or a corrugated metal foil.



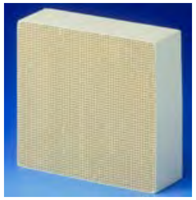
Active component

- For most power generation applications, the common active component(s) are precious metals, including platinum, palladium, and rhodium
- The active component(s) need to be well dispersed within the carrier – and fixed properly – to assure high performance and long operating life
- The interaction of active component(s) with the carrier is critical, as it is relatively simple to produce a catalyst that can operate well when fresh, but achieving long-term, stable performance requires expertise

Carrier

- A carrier is a very high surface area material ("washcoat") with a complex pore structure to permit high mass transfer of gas to active component materials dispersed throughout the carrier
- Carrier design is critical as it significantly impacts performance and aging
- Carriers are designed to maintain
  - Activity – catalyst performance
  - Selectivity – minimizing unwanted side reactions
  - Durability – resistance to catalyst contaminants and their impacts

Substrates – Metal foil v. Ceramic



Herringbone Metal Foil

- Lower pressure drop
- Higher surface area
- Custom cell density (cpsi)
- Greater design flexibility
- Greater substrate flexibility:
  - Skew
  - Herringbone

Ceramic Substrate

- Broader history of washing
- Resistant to acid-gas environments
- Often used for stationary engine applications in conjunction with SCR catalyst
- Broader use of washcoats for high sulfur or halogen applications

CO control in gas turbine

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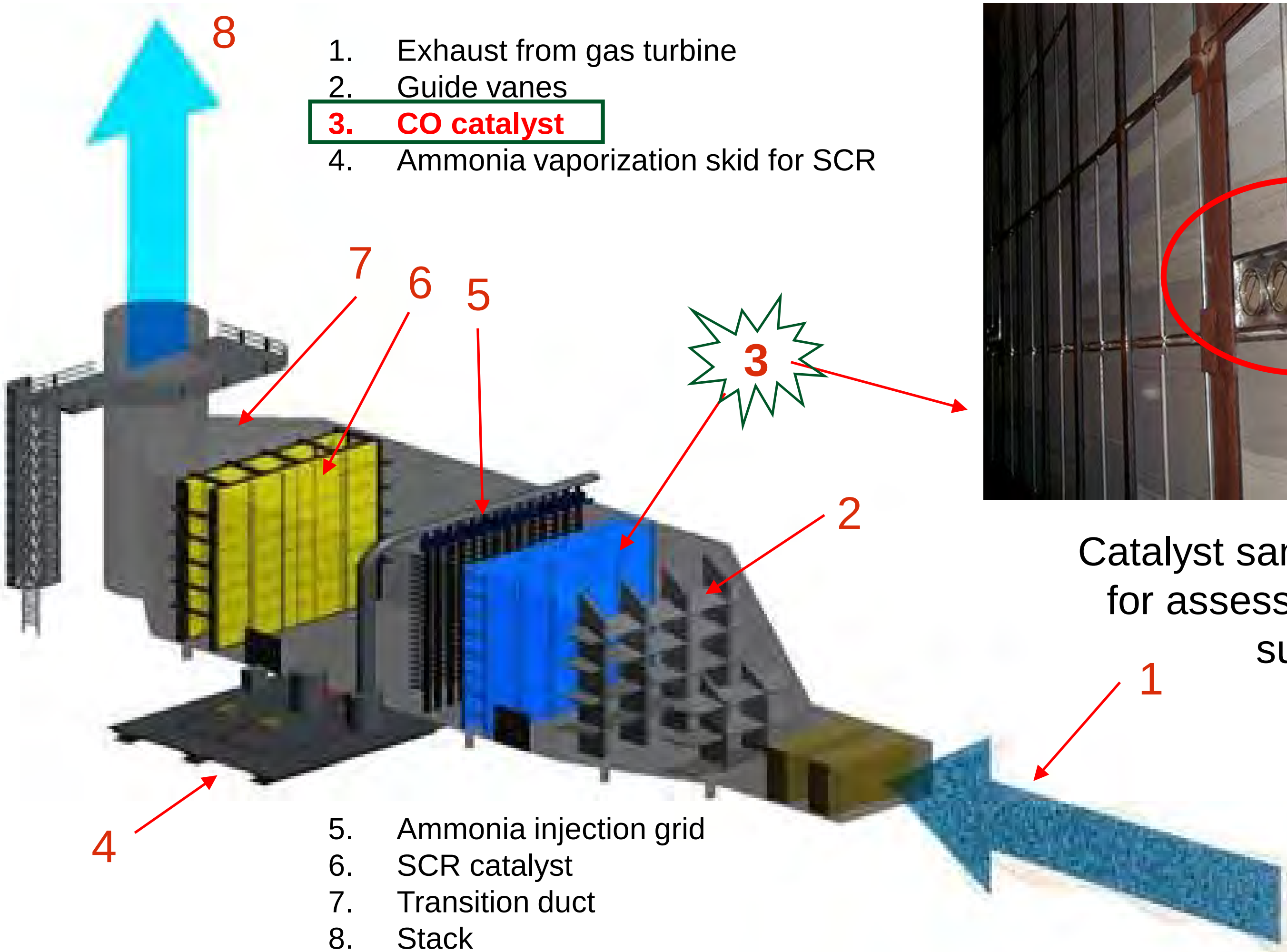

1. Exhaust from gas turbine
2. Guide vanes
3. **CO catalyst**
4. Ammonia vaporization skid for SCR

Catalyst sample “buttons” allow for assessment of activity and surface contaminants

5. Ammonia injection grid
6. SCR catalyst
7. Transition duct
8. Stack

Simple-cycle gas turbine design

Overview

fundamentals

- Catalyst as tunnel
- Each catalyst component is critical
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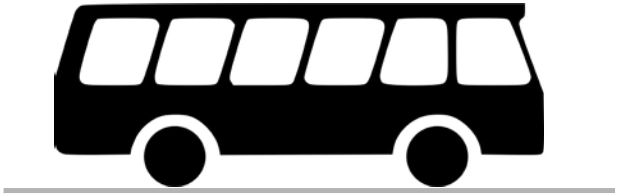
performance



fuel quality

mitigate

CO oxidation catalyst bed design requires experienced insights into many variables

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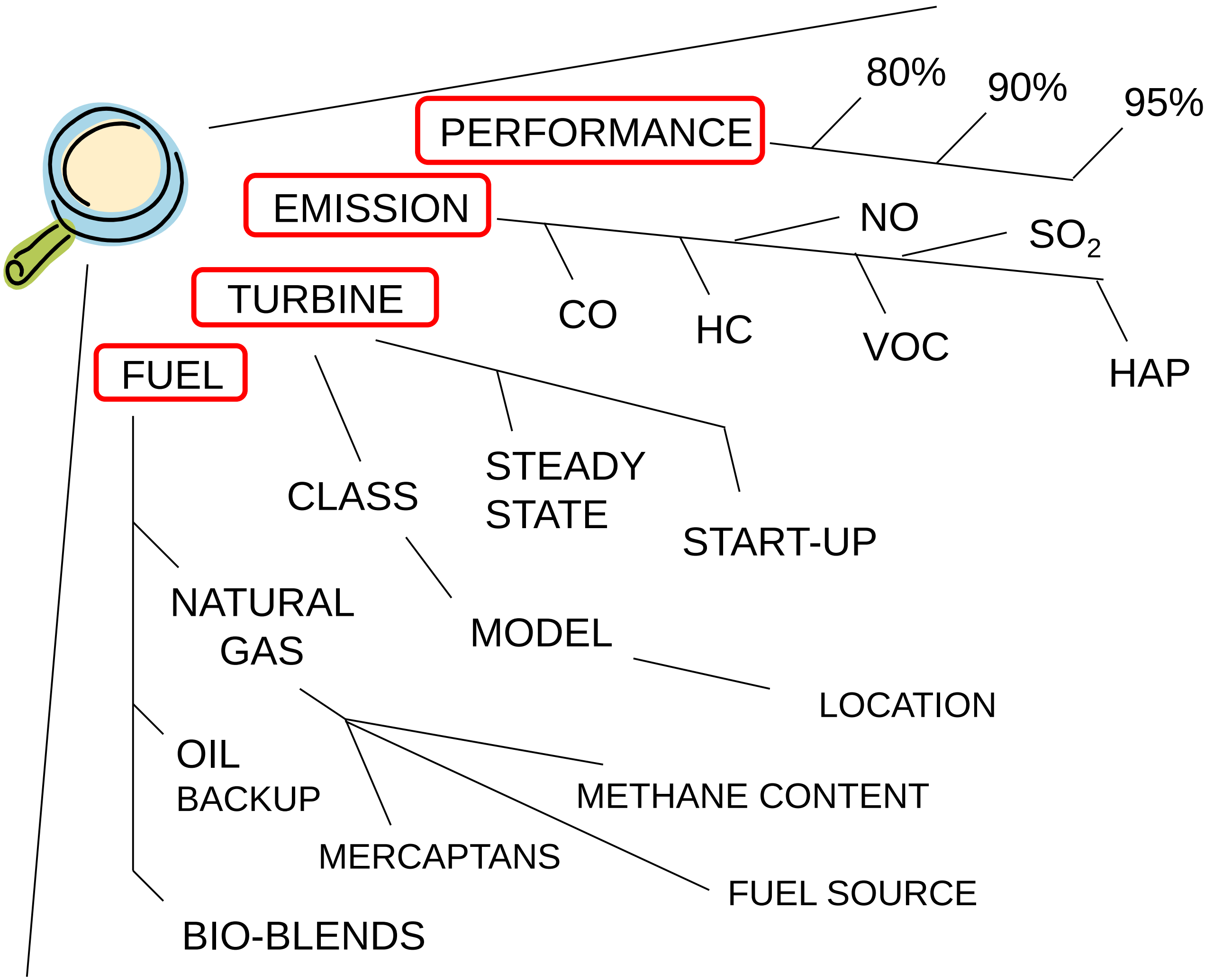
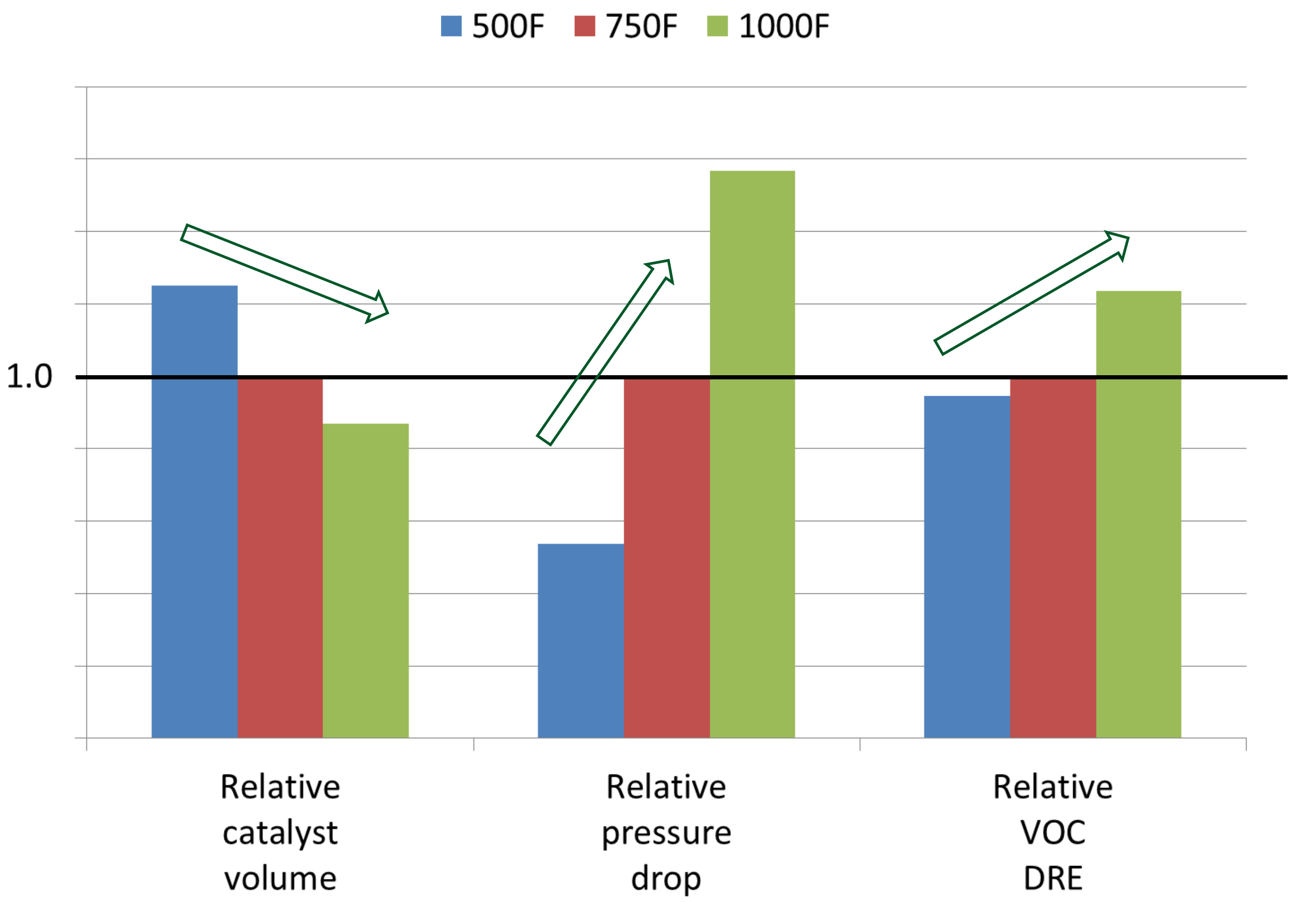
What does a catalyst design focus upon to manage risk



CO catalyst design perspective

Catalyst location and operating temperature

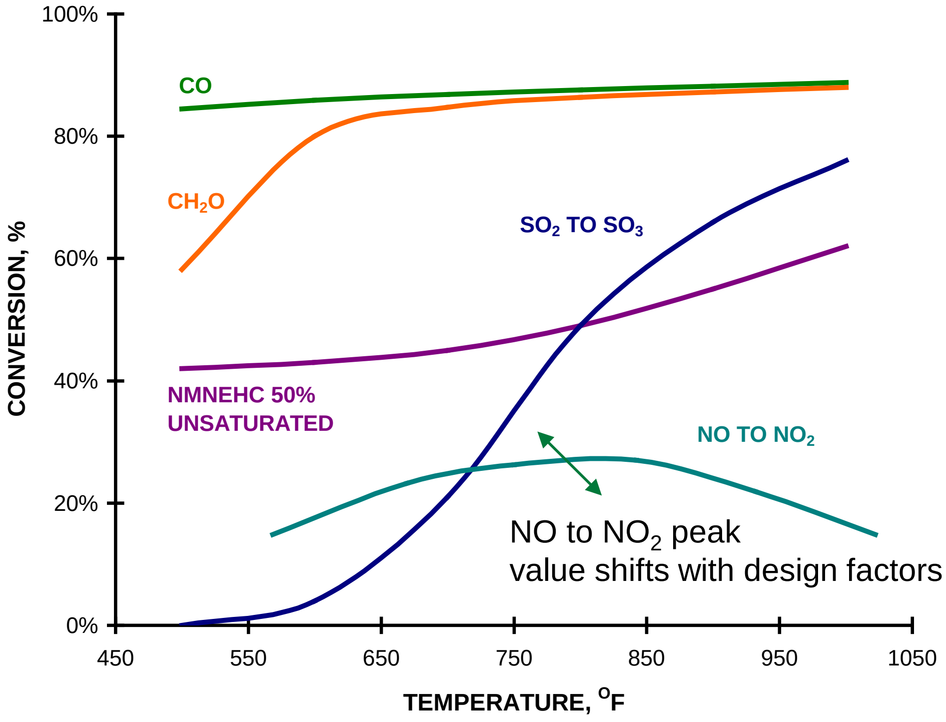


A conventional CO catalyst design is a multi-variable optimization problem – trading off catalyst volume with performance, including VOC conversion, and pressure drop

PERFORMANCE

CO catalyst design perspective

Oxidation catalyst impacts more than just CO emissions



Hypothetical stationary engine CO catalyst performance

Oxidation catalyst is a "passive" technology providing "constant conversion" of all compounds, to varying degrees, independent of inlet concentration

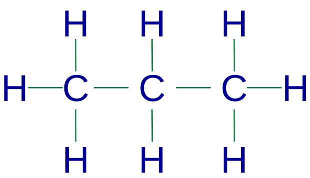
All compounds need to be considered in the CO catalyst design

EMISSIONS

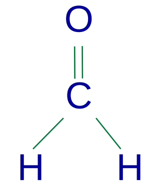
CO catalyst design perspective

CO v. VOC

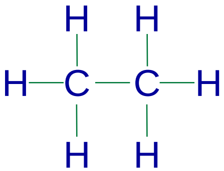
- The term “VOC” represents a class of compounds
- There is no single compound that may characterize the reaction of all VOCs across a given oxidation catalyst technology
- The practical definition of “VOC” on gas turbines has evolved to jointly mesh the technology of catalysts with the clarity needs of regulators
- “VOC” performance requirements on gas turbines are typically set as “what comes along” [co-benefit] with CO performance



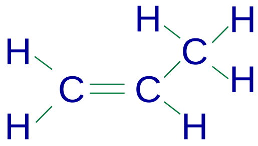
Propane
VOC &
Saturated HC



Formaldehyde
VOC but not a HC



Ethane
HC
but not a
VOC



Propylene
VOC &
Unsaturated HC

EMISSIONS

Hydrocarbon saturation level drives expected VOC conversion co-benefit

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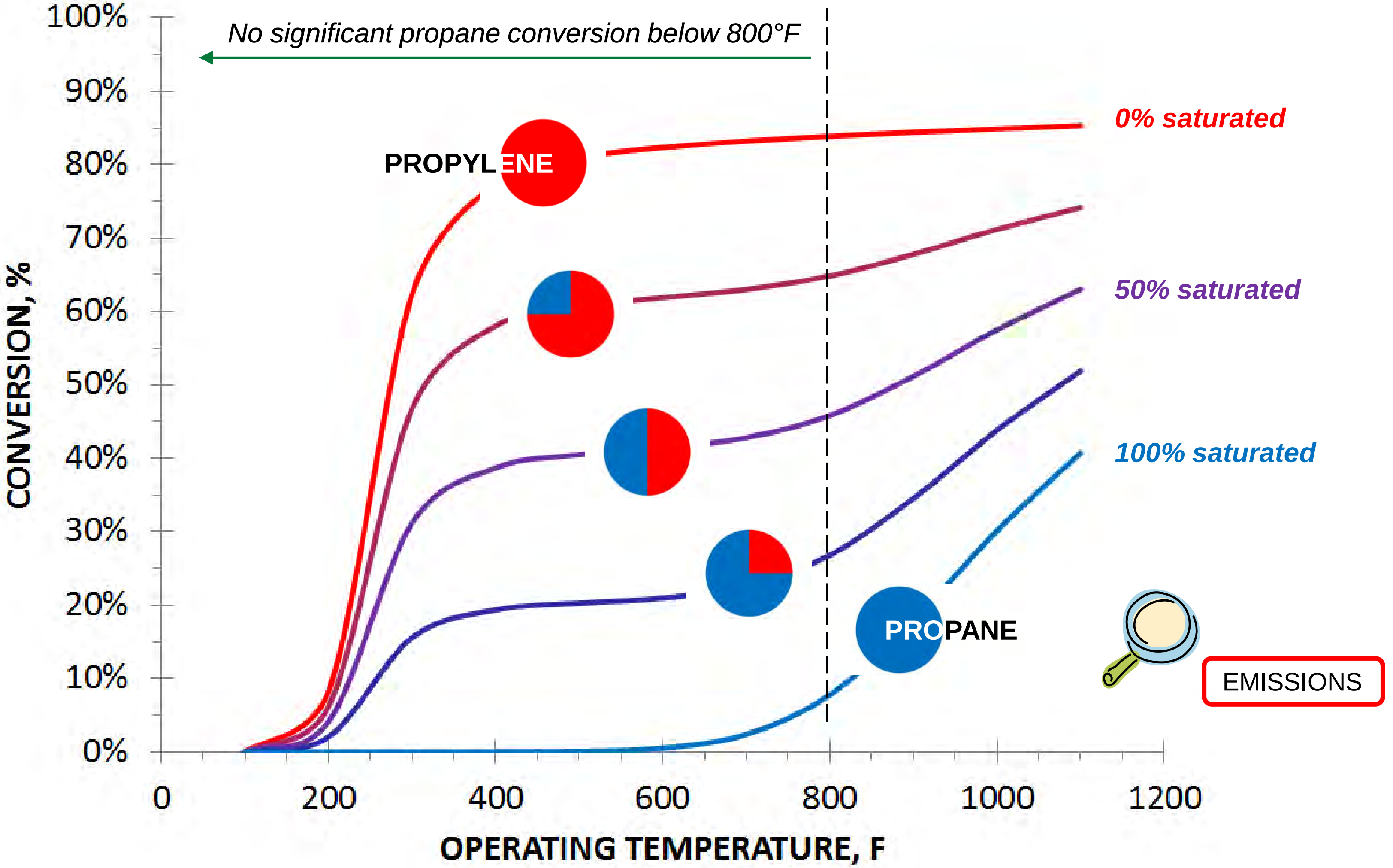
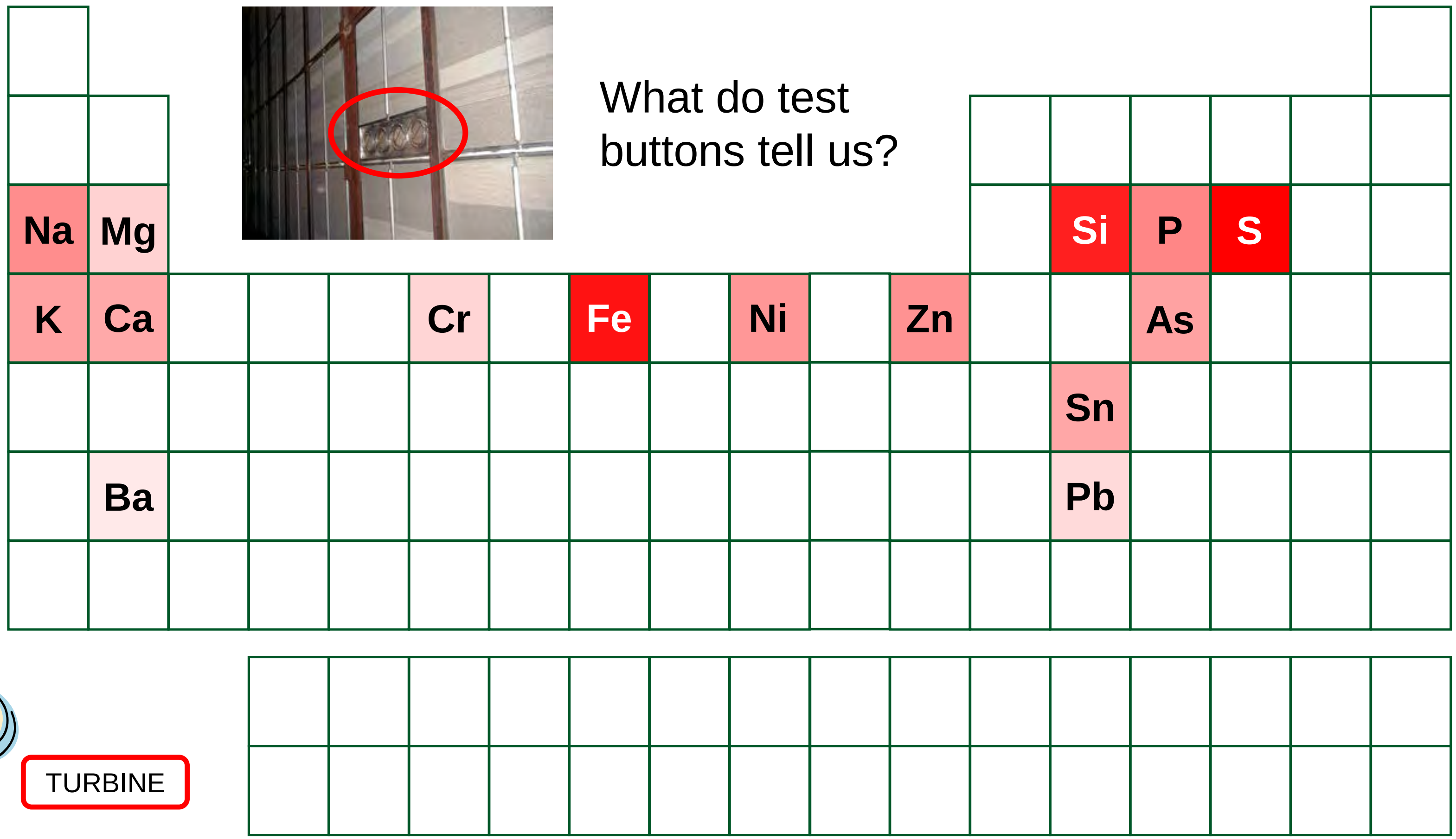


CO catalyst contaminants found in test button evaluations from gas turbine applications



TURBINE

Shading indicates relative rate of occurrence in sampled test button population from gas turbine applications

CO catalyst design perspective

Possible origins of contaminants

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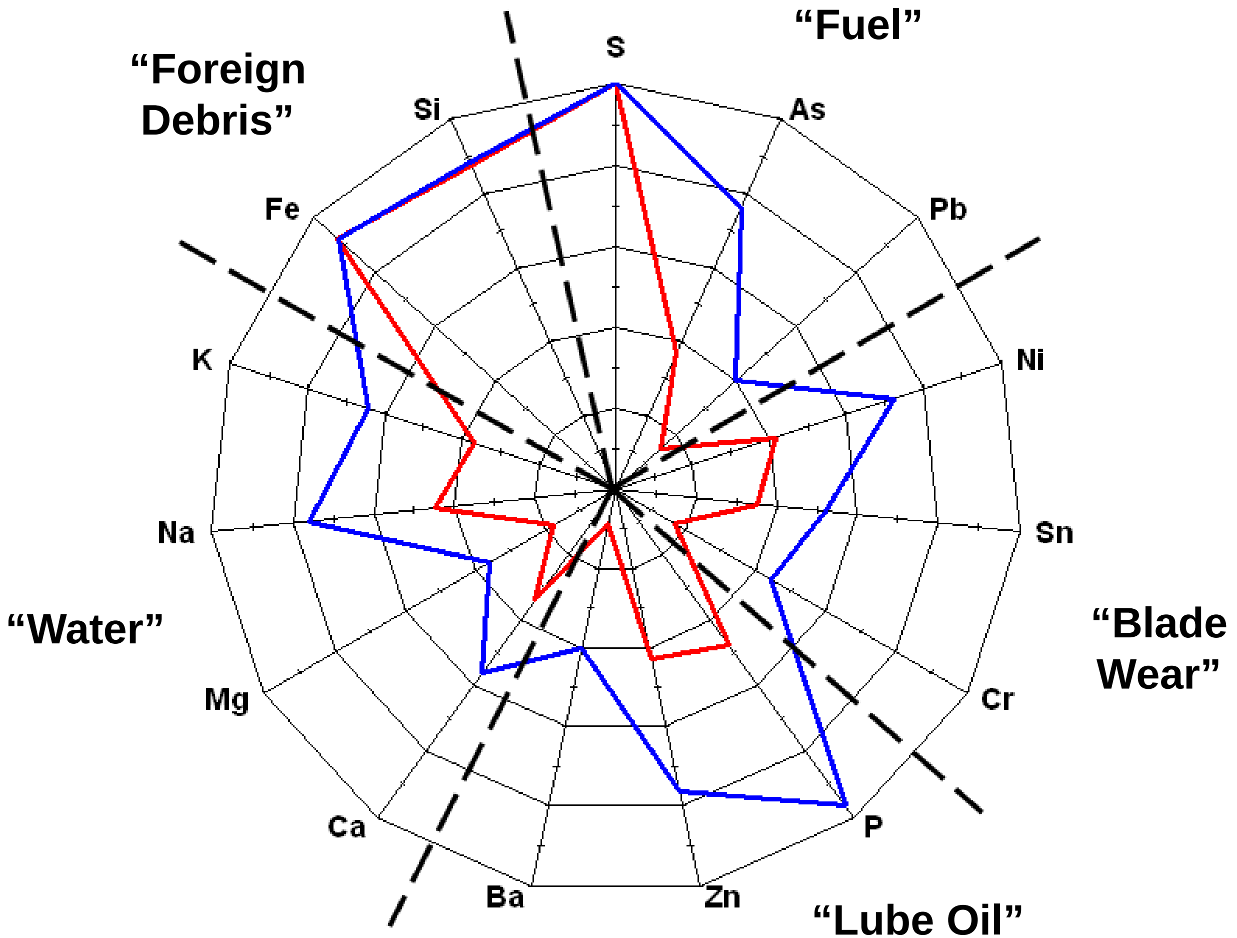
Major Contaminants on Catalyst		Possible Sources of Contaminants for Gas Turbine				
		Lube Oil	Fuel (Natural Gas or Alternate Fuel)	Water	Blade Wear	Foreign Debris
S	Sulfur		X			
Fe	Iron	X				X
Si	Silicon	X				X
P	Phosphorous	X				
Na	Sodium	X		X		
Zn	Zinc	X				
Ni	Nickel	X	X		X	
K	Potassium	X		X		
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			

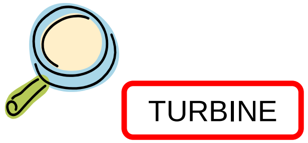
TURBINE

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

Turbines distinguish themselves by the relative occurrence of catalyst contaminants



The blue turbine shows a distinctively higher occurrence of most catalyst contaminants than the red turbine, thus posing a more challenging operating environment for the CO oxidation catalyst



Overview

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fundamentals

- Catalyst as tunnel
- Each catalyst component is critical
  - Active component
  - Carrier
  - Substrate

performance

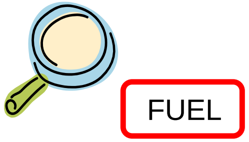
- Catalyst operating conditions
- VOC definition
- Expected catalyst contaminant profile from application
  - Gas turbine type

fuel quality

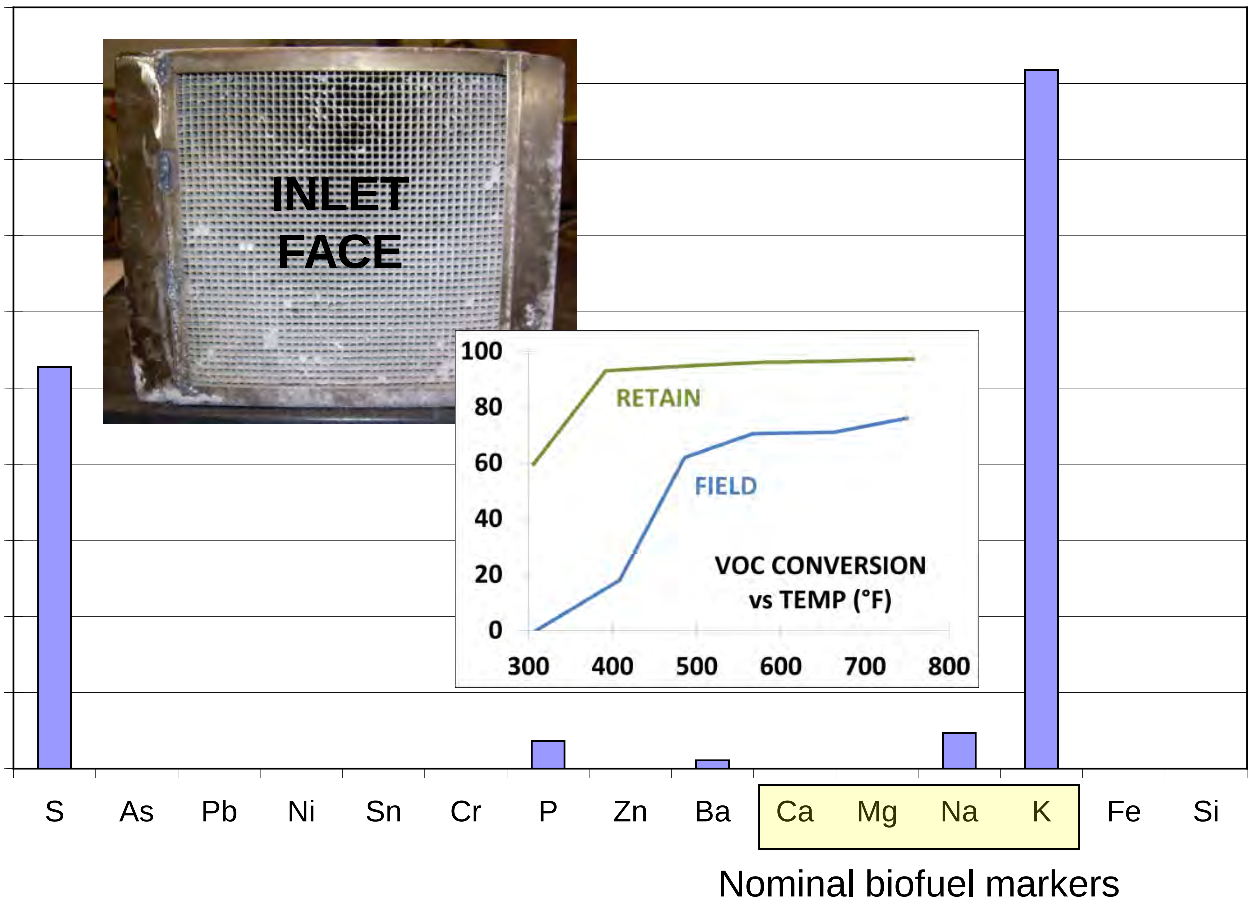
mitigate

Biofuels and bio-blends are a good example of how a fuel may impact oxidation catalyst

- Biofuels/bio-blends may act as effective solvents and/or corrosives, dissolving engine/component deposits or fuel system components
- “Trace” contaminants may be well in excess of typical natural gas
  - Residuals of processing catalysts: Cu, Ni, Na, K
  - Residuals from fuel precursors: Mg, Ca, Na, K
- Siloxanes typical contaminant in landfill/digester gas
  - Siloxane oxidation leaves silica behind contaminating the active site
- Biofuel/bio-blend specification – accurate and complete – is critical to assess the risk to catalyst before implementation



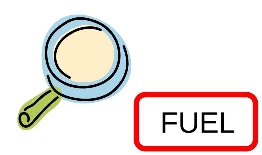
Example of biofuel application
Oxidation catalyst on stationary engine



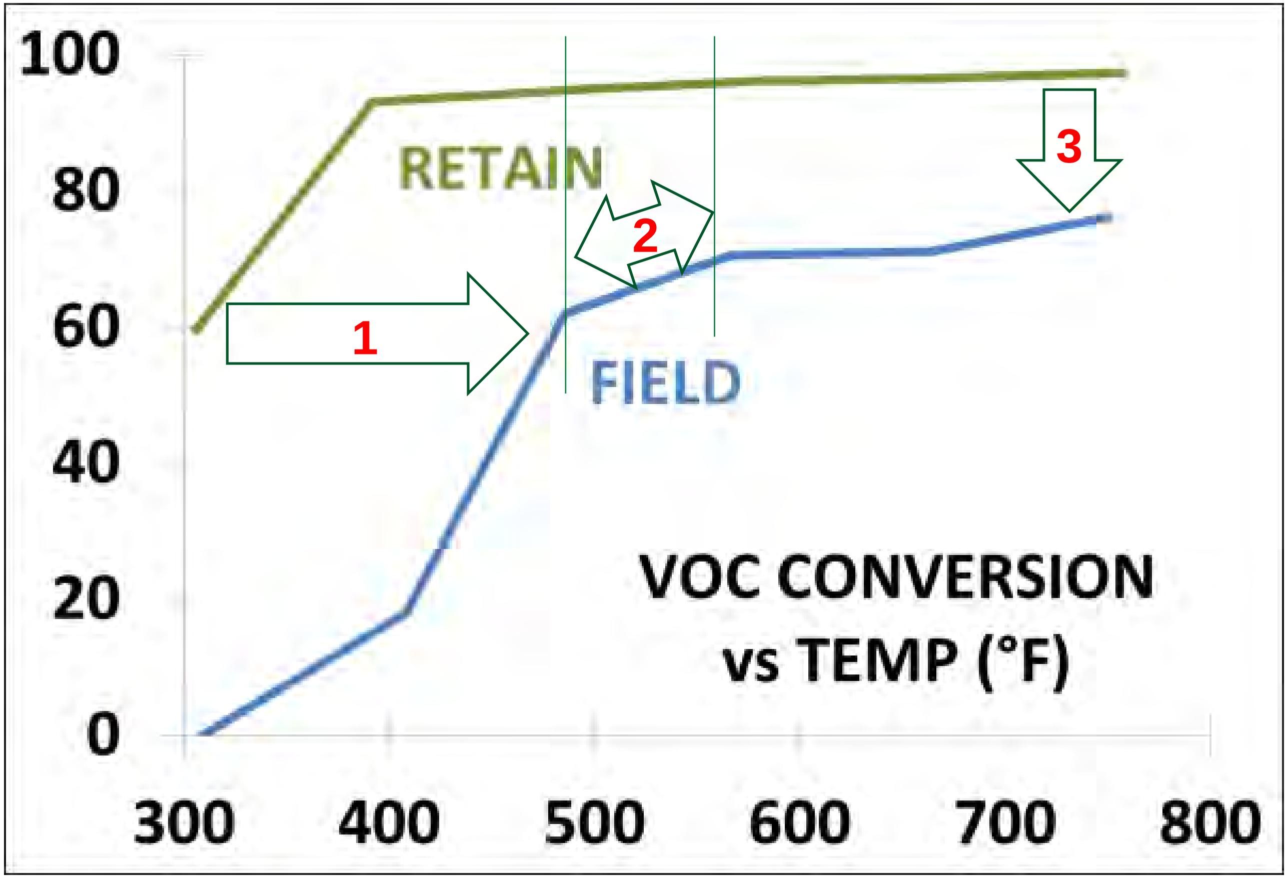
Wikipedia:

"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]



The shape of the performance curve reveals insights into the state of the catalyst

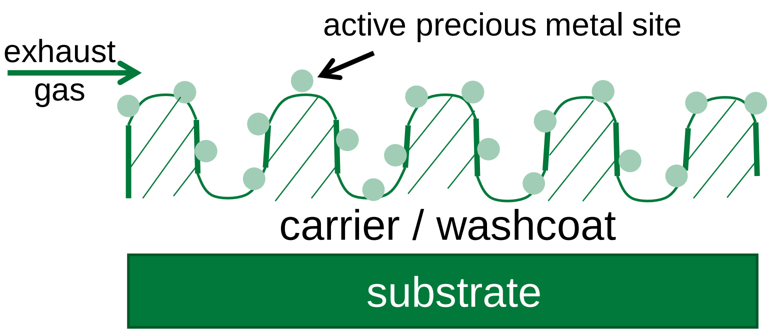


1 – Loss of active sites shifts curve to right

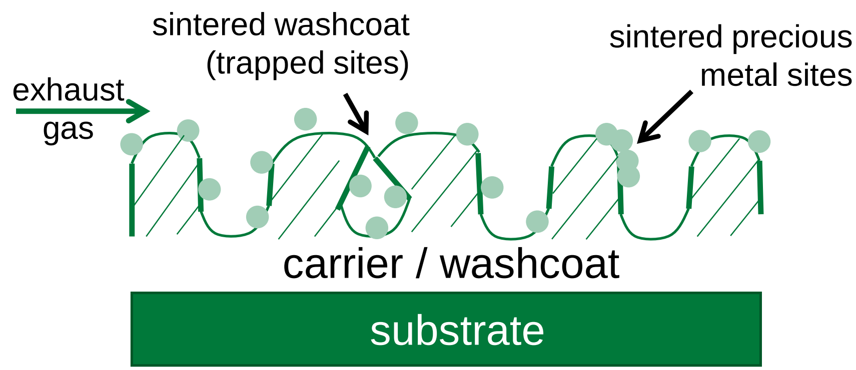
2 – Obstructed carrier pore structure limits diffusion and changes slope of curve

3 – Masked catalytic surface area no longer participates and shifts curve downward

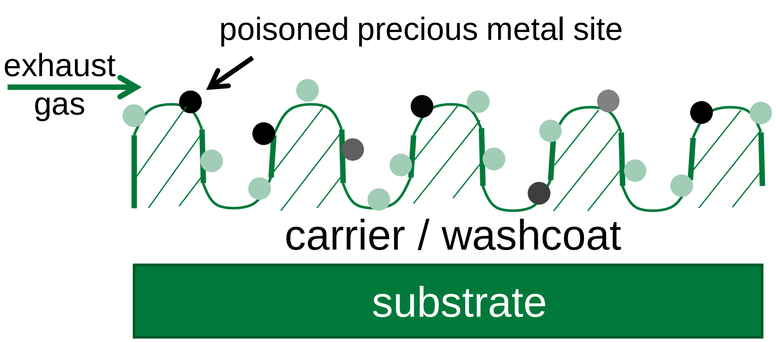
Oxidation catalyst deactivation mechanisms



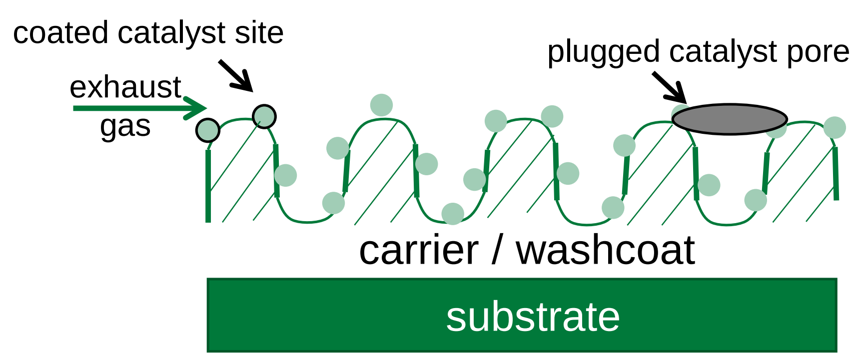
Fresh catalyst



Sintered catalyst due to temperature excursion [irreversible]



Chemically poisoned catalyst [irreversible]



Physically masked catalyst [may be reversible]

CO catalyst contaminants found in test button evaluations from gas turbine applications

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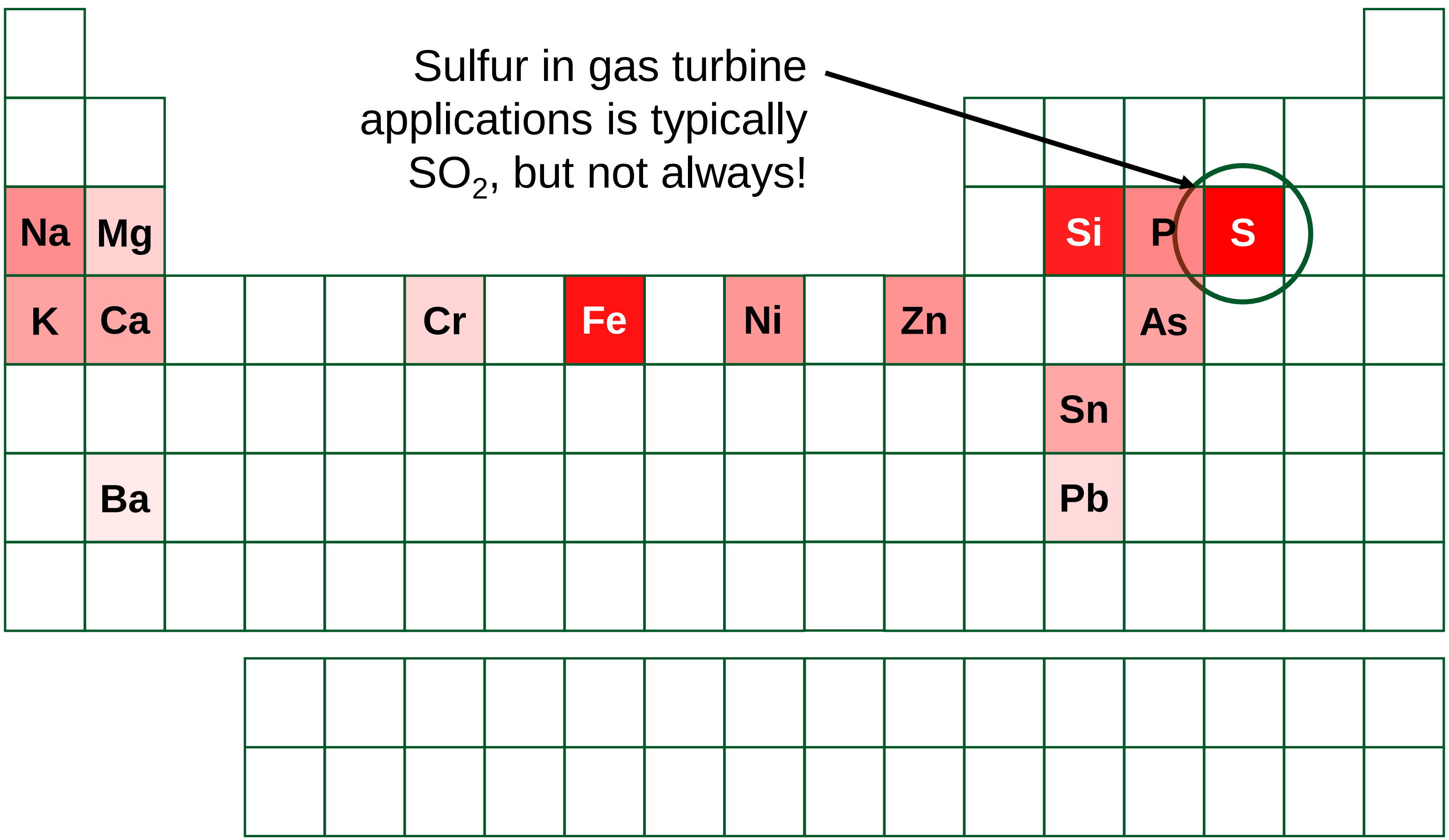

Shading indicates relative rate of occurrence in sampled test button population from gas turbine applications

Sulfur impact – Inhibition

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- The sulfur “sits on” the active component (precious metal) but there is no chemical interaction
  - The sulfur “sitting” on the active component blocks access and results in lower observed activity
- If you remove the source of the sulfur, the sulfur “sitting” on the surface will come off. Similarly, if the temperature is raised, the sulfur might be driven off
  - As the sulfur comes off the surface, the observed activity will improve
- Example – turbine applications, where oil is used as a backup fuel to natural gas, the amount of sulfur inhibition may be estimated and accounted for in the design

Sulfur impact – Sulfation

- Sulfur chemically reacts with the carrier and its impact is much harder to reverse
- Sulfation of the carrier results in “clogged up” pore structure and lost surface area, which results in lower performance
- In turbine applications, the sulfur is assumed to reach the catalyst as SO_2
- If the sulfur comes in another form, the effects can be more dramatic than what would occur from simply elevated SO_2 levels

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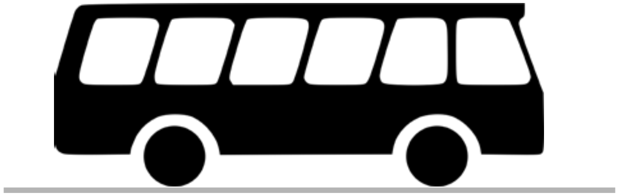
- Expected catalyst contaminant profile from application
  - Gas turbine type

fuel quality

- Biofuels may introduce unintended catalyst contaminants
- Relatively high, or fluctuating, sulfur content from unconventional natural gas sources

mitigate



Power generation market challenge: Sulfur tolerant CO oxidation catalyst

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- Sources and quality of natural gas are changing due to the emergence of fracking/shale gas
- Many natural gas fired power plants using fracking gas are also experiencing high levels of sulfur contamination
- The power generation market needs a CO oxidation catalyst that is more tolerant to sulfur contamination
  - Provides greater fuel sourcing flexibility
  - Mitigates against unforeseen fuel quality upset conditions

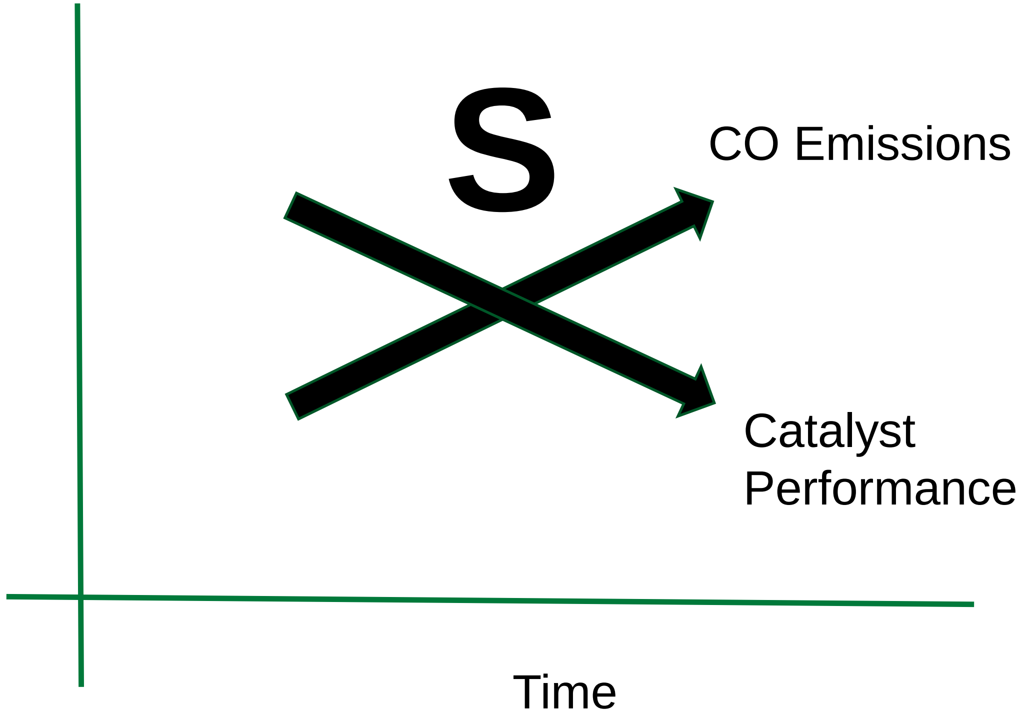
Case Study – BASF Camet™ ST™

- A major US natural gas utility utilized a conventional CO oxidation catalyst for converting carbon monoxide (CO) emissions from two GE 7EA turbines.

Case Study – BASF Camet™ ST™

Call to action

- Upon start-up, the CO catalyst did not meet the performance guarantee.
- The utility “discovered” their issue with a high inlet sulfur content.



Case Study – BASF Camet™ ST™

Action and Result

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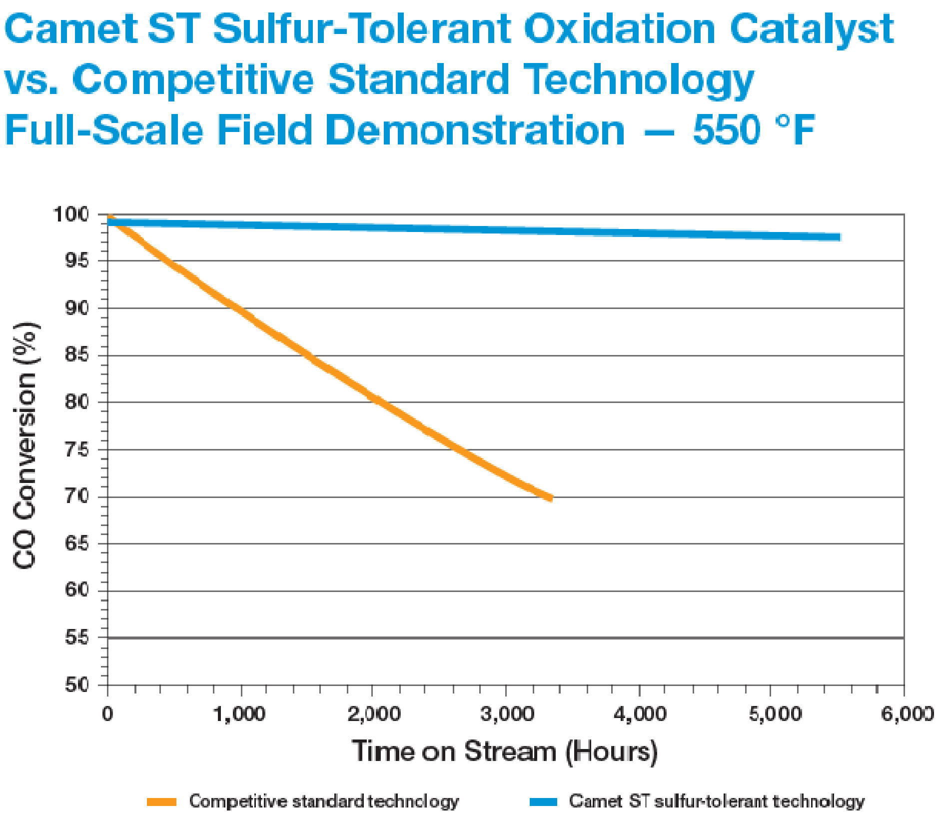
- Action – A detailed, competitive on-site catalyst evaluation was conducted by a third party catalyst consulting and testing firm.
- Result – The catalyst consultant reviewed all the competitive results and recommended installation of BASF Camet ST Sulfur Tolerant CO oxidation catalyst.
- The CO conversion activity has remained stable for a year as demonstrated by the evaluation of test buttons removed from the unit.



BASF Camet™ ST™

An example of sulfur tolerant CO catalyst

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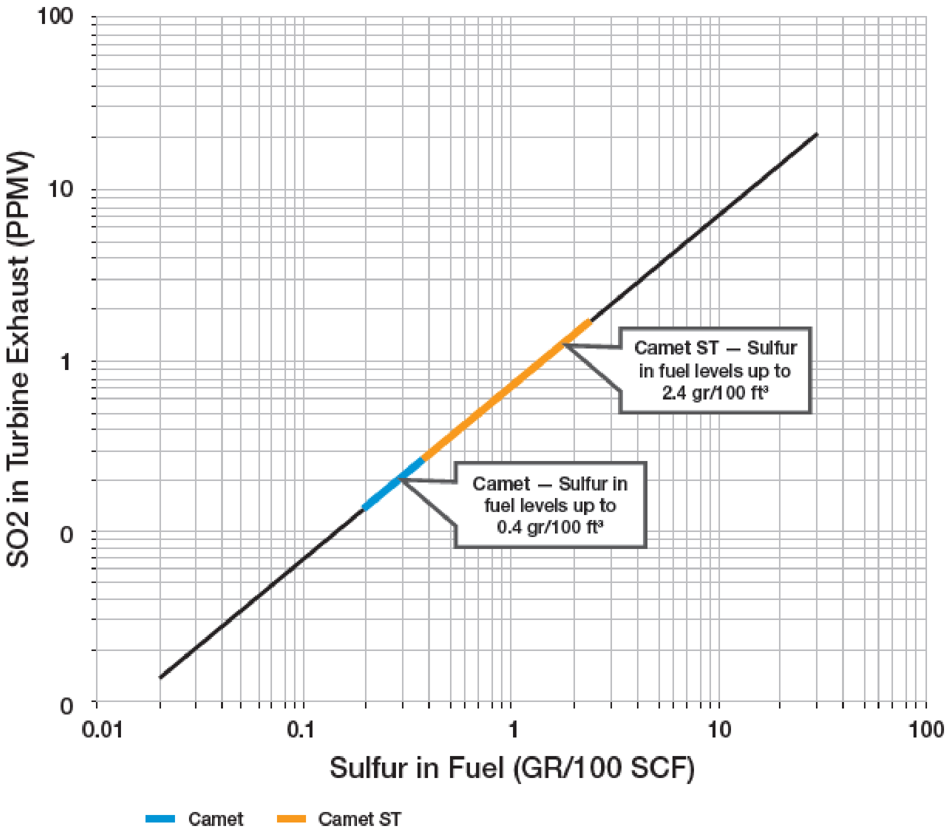
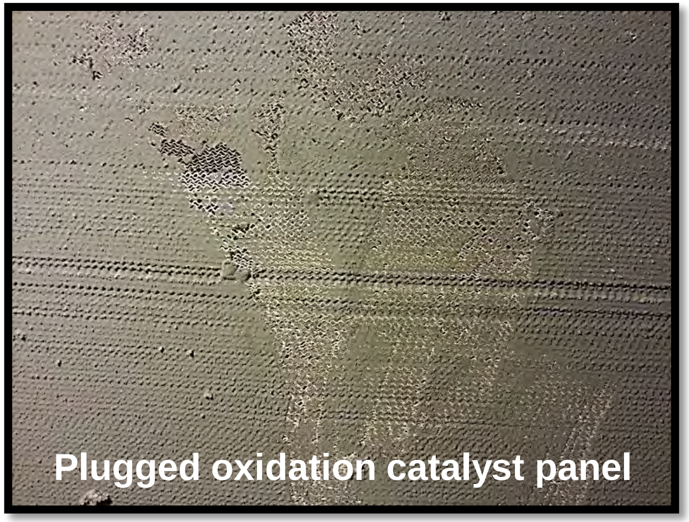
Camet ST Sulfur-Tolerant Oxidation Catalyst



Facts	
Product Use	Sulfur-tolerant CO oxidation for power generation
Substrate	Metal foil
Typical CPSI	105–300
Typical pressure drop (WC)	0.5–3.0
Typical CO design conversion (%)	90–98
Washable	Yes
Maximum use temperature (°F)	1,200
Typical operating temperature (°F)	600–900
Maximum sulfur tolerance (gr/100 ft³)	2.4

A regular catalyst field sampling program may mitigate performance issues

- 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


Plugged oxidation catalyst panel

Catalyst field retrieved “button” sample is assessed for activity and contaminants

- 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
  - The field retrieved catalyst sample may “see” the loss of activity under aggressive lab test conditions before the entire bed in the field.
- Catalyst surface analysis can identify contaminants and their relative magnitudes, providing insight into system operation

Mitigation by system maintenance to maximize the useful life of the installed oxidation catalyst

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- The CO catalyst bed may serve as an expensive “fuse” or “filter” for the turbine’s exhaust treatment system
- 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.

Summary

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- VOC definition
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fuel quality

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mitigate

- Regular catalyst bed assessment
- Sulfur tolerant CO oxidation catalyst formulations
  - Camet ST

BASF thanks you for your attention and welcomes any questions you may have

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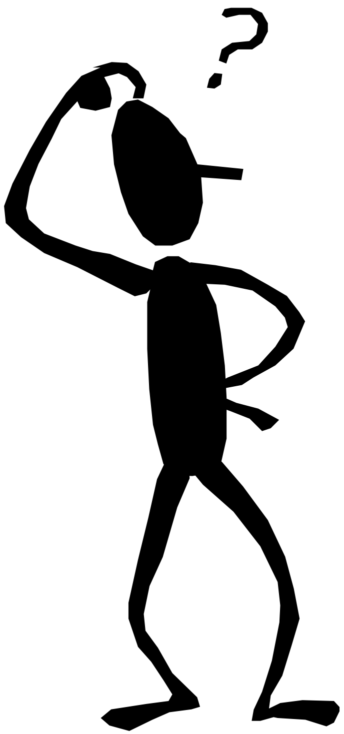
ANY QUESTIONS ?



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