EmeraChem™

THE POWER OF CATALYSIS

"Integrating HRSG & Catalyst Design For High Performance & Low Cost"

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2013 ABMA Annual Meeting
Environmental Session

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Range of Applications

EmeraChem is an OEM developer and manufacturer of catalytic products to control air pollution from

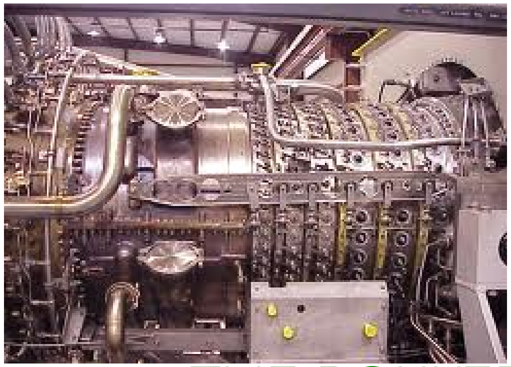
large gas turbines

large reciprocating engines

Industrial boilers

…in the power generation and natural gas markets

>240 Combustion Turbines
Oxidation Catalyst & Support Structure



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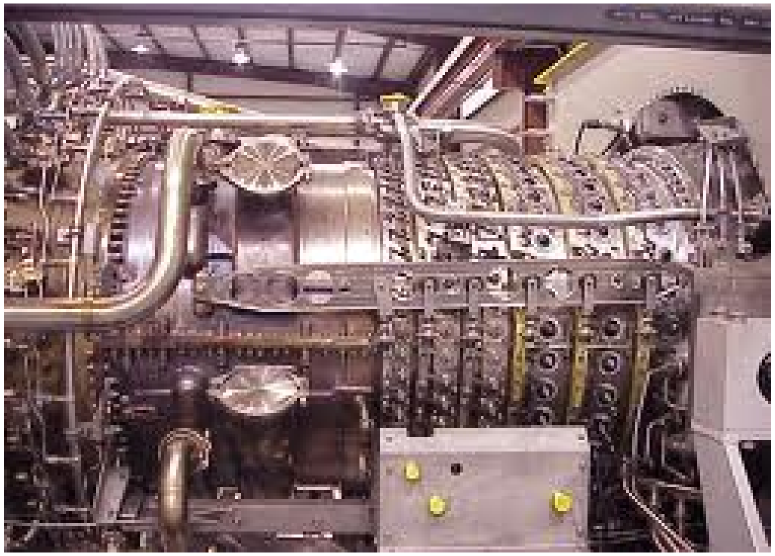
>240 Catalyst Systems for GTs

GE 7H	2
GE 7FA	33
GE 7EA	3
GE FRAME 6 F	5
GE FRAME 6 B	1
GE LM6000	64
GE LM 5000	1
GE LM 2500	6
Mitsubishi 501D	2
Mitsubishi 501F	20
Mitsubishi 501G	6
Siemens SGT 5000	5
Siemens SGT 800	2
Siemens SGT 400	5
Pratt & Whitney FT-8	25
Alstom GTX 100	6
Solar TITAN 130	4
Solar TAURUS 70	7
Solar TAURUS 60	8
Solar CENTAUR 40	2
Solar SATURN 20	3
Rolls Royce TRENT 60	2
Westinghouse W251B	1
AVON MK 1533	1
VS-7	1
Unspecified GTs	33

Individual projects ranging from
24 to 2400 catalyst elements



>40,000 MW
controlled by
EmeraChem catalyst

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Starting Point: Application Design
(system variables that affect emissions)

- **Information input**
  - engine name and model
  - fuel type(s) and sulfur content
  - water injected or evap cooling? (water quality)
  - HRSG or simple cycle (no. starts/stops/yr.)
  - Duct firing? Fuel type.
  - exhaust mass flow rate, catalyst operating temp,
  - % flow and temperature variation
  - Inlet emissions, (CO, VOC, NO/NO_2, SO_2)
  - performance requirements
    - (% reduction CO, VOC, NO-NO_2, SO_2-SO_3)
    - Start-up & shutdown performance included?
  - desired warranty period and service life
  - installation information;
    - NEW or REPLACEMENT
    - Gas Path Size
    - allowable pressure drop

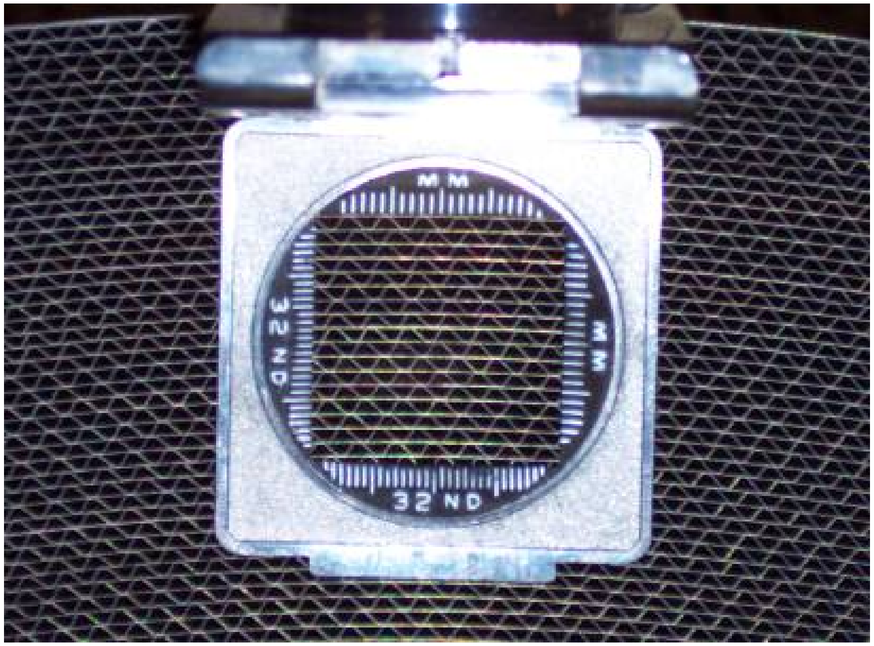
It's possible to "over specify":
- low temperature
- very high performance
- very low pressure drop
- small gas path
- lot's of starts & stops
- long warranty period
- "cheap"

Catalyst Design
(catalyst variables that affect emissions)

- substrate cell geometry and geometric surface area
- wash coat formulation & loading
- precious metal formulation
- precious metal loading
- method of applying precious metals
- gas hourly space velocity

Substrate Design Variables

- Cell structure geometry and surface area
- Cell density
- Pressure drop
- Diffusion bonded (10-yr mechanical warranty)



"discrete cell"

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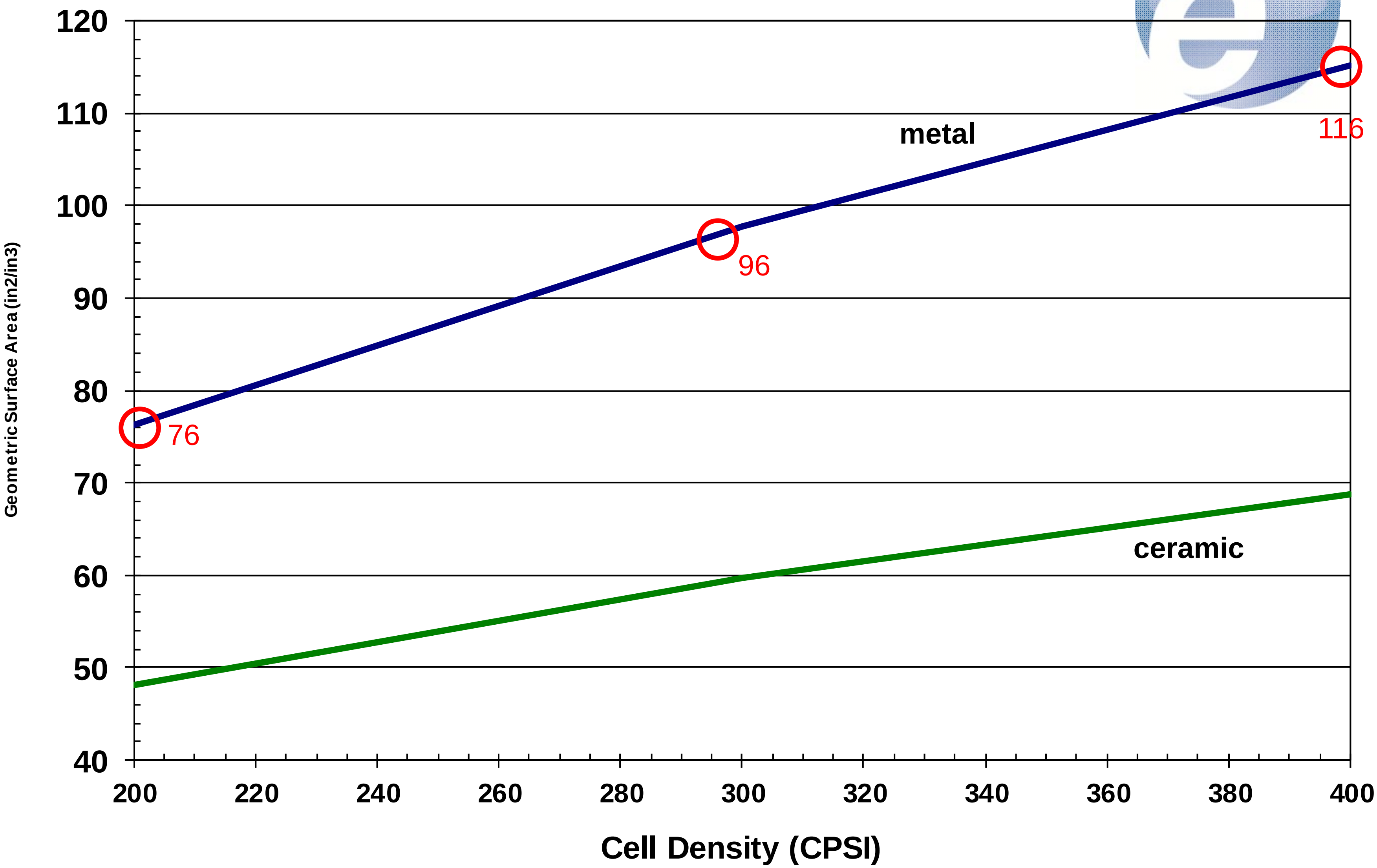
Geometric Surface Area as a Function of Cell Density



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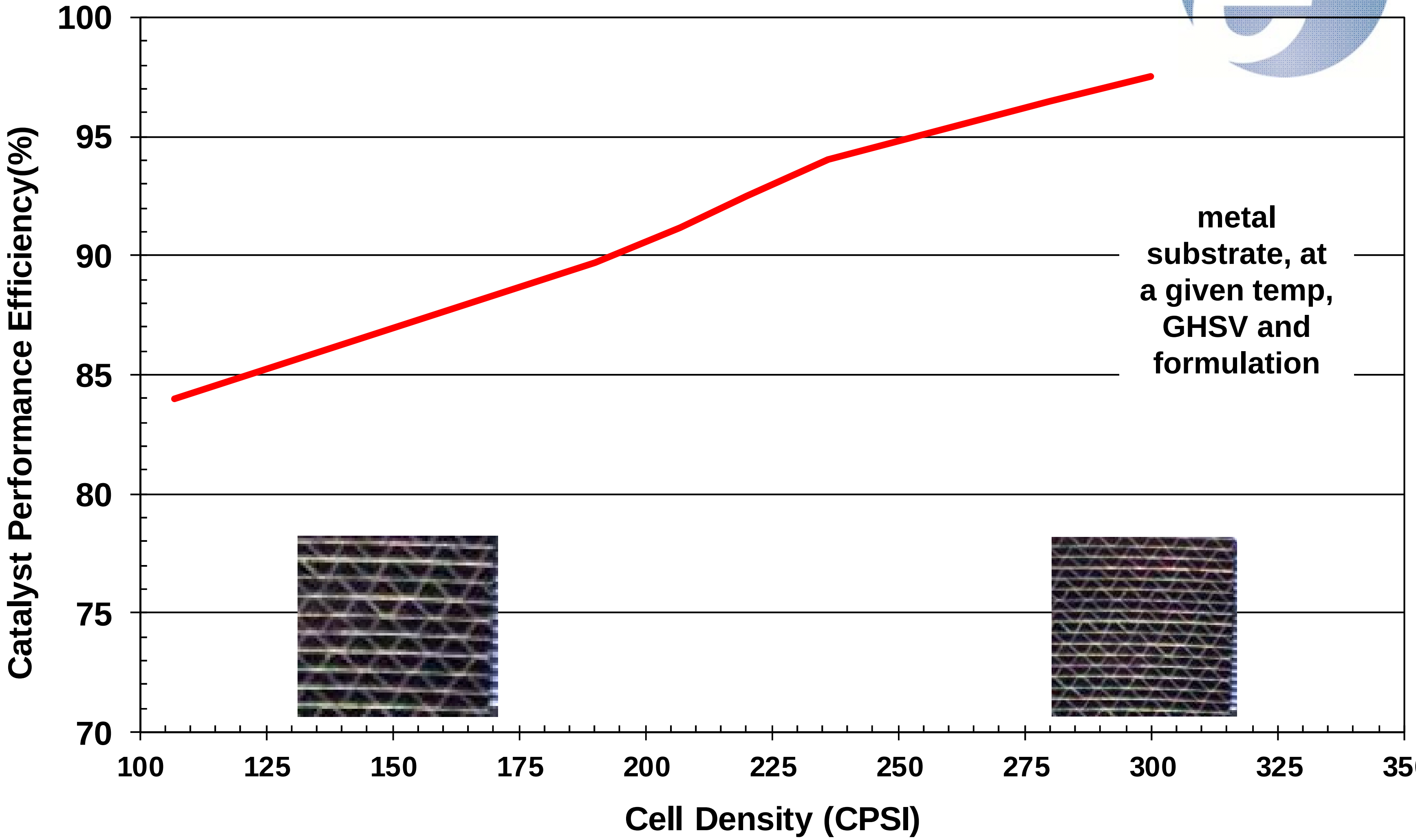
Performance as a Function of Cell Density



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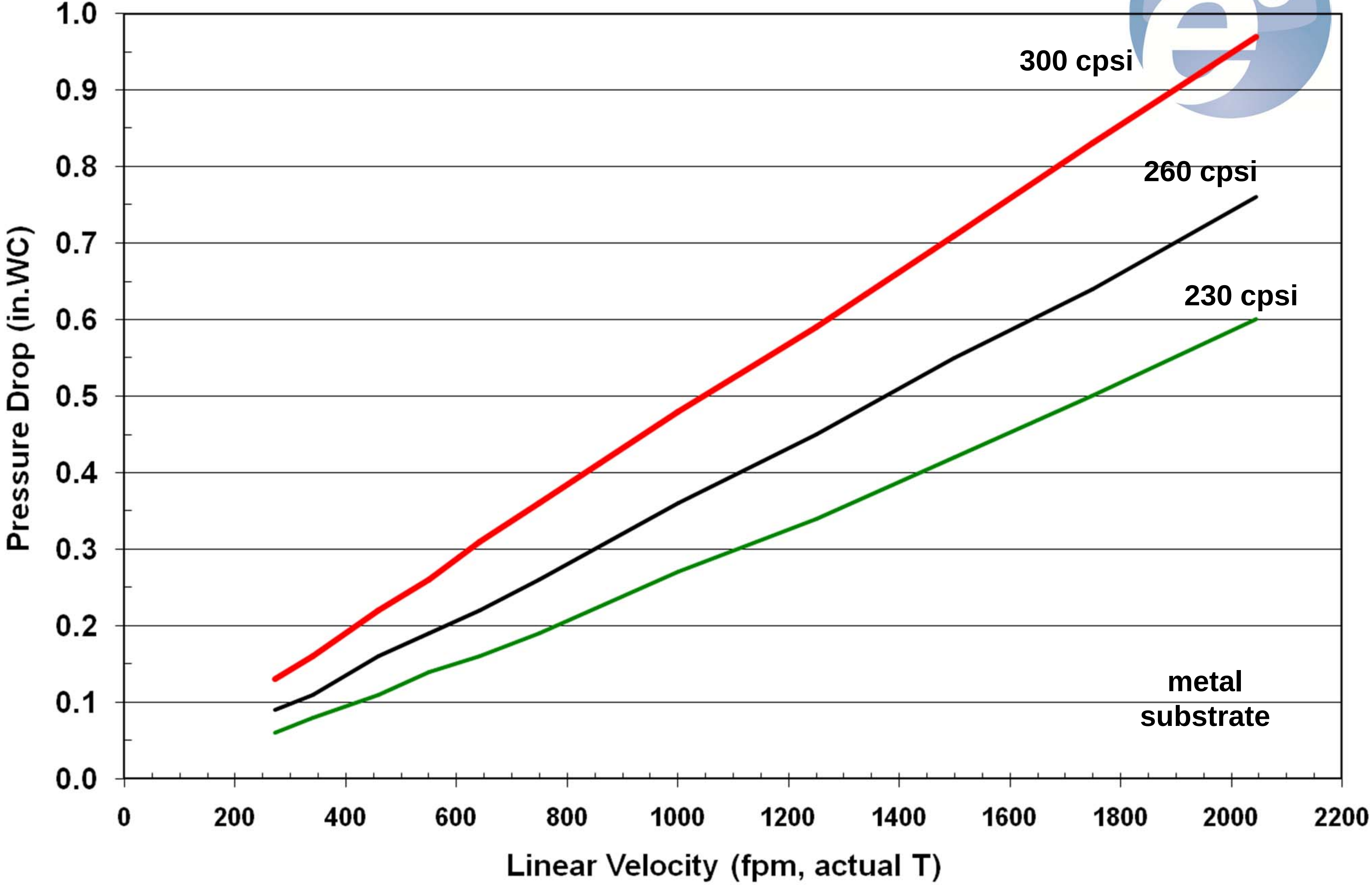
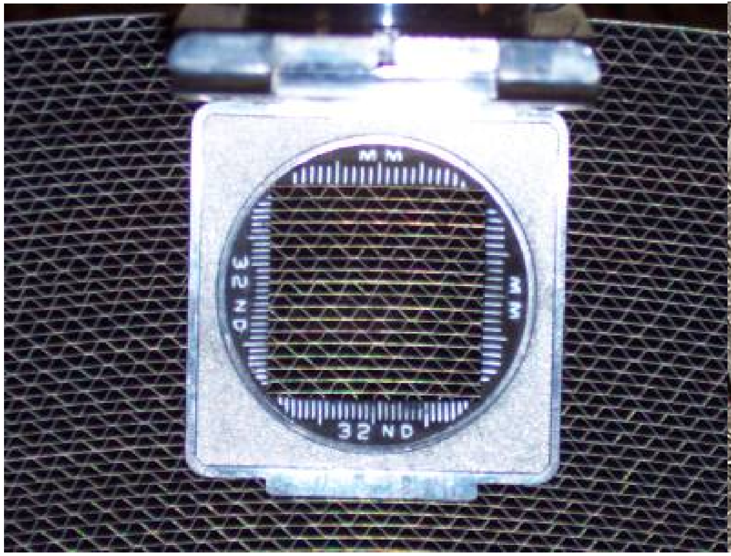
Pressure Drop as a Function of Cell Density



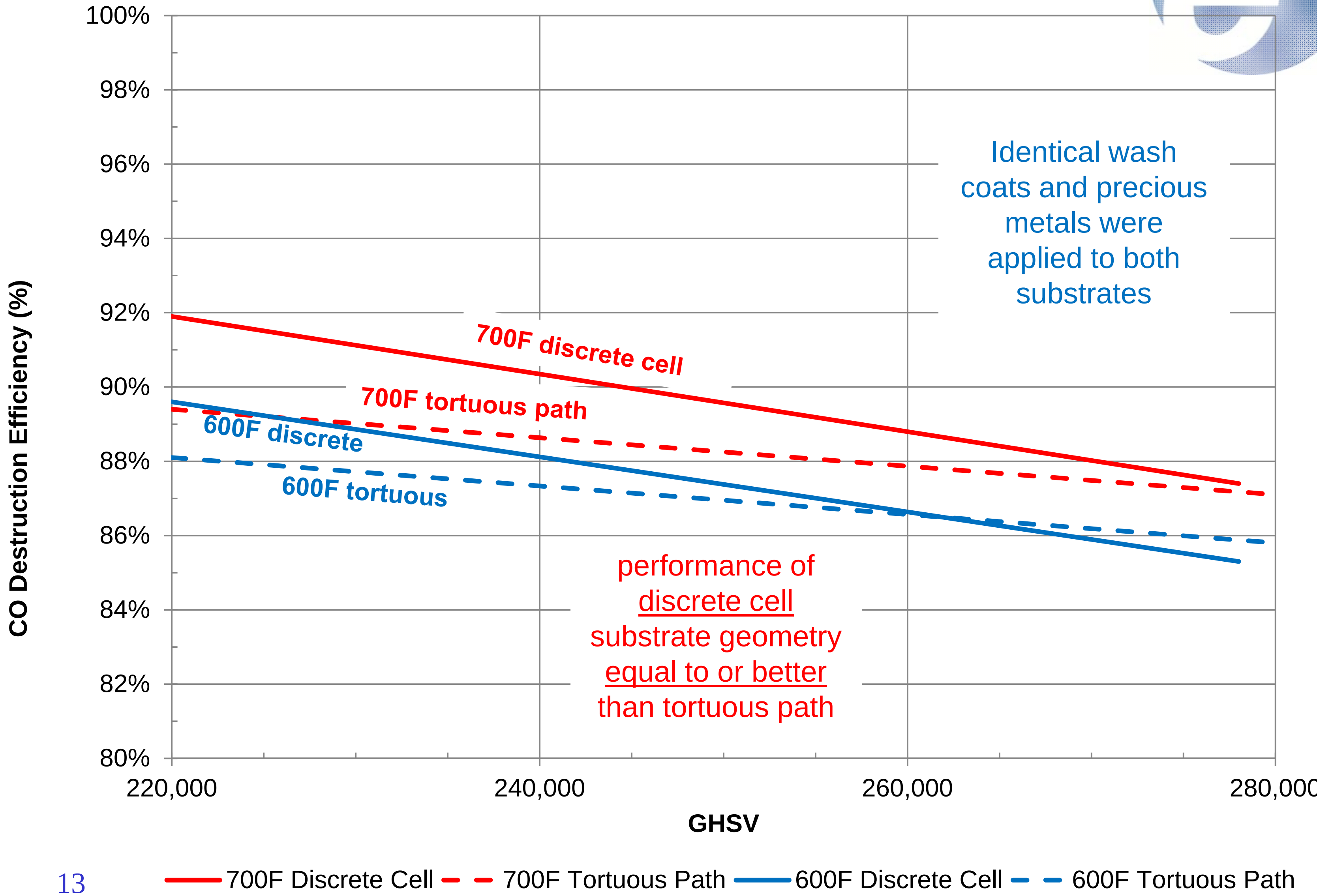
Variations in Cell Structure & Geometry

- "discrete cell"
  - diffusion bonded; 10-yr warranty
- "tortuous path"
  - loosely layered "herringbone"



"discrete cell"

Oxidation Catalyst Performance Discrete Cell vs. Tortuous Path



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What is a VOC?

U.S. EPA Definition of VOC

40 CFR Ch. 1, Subpart F - Procedural Requirements, Section 51.100 – Definitions, Paragraph (S) - VOCs, Subparagraph (1)

(s) **Volatile organic compounds (VOC)** means any compound of carbon, ***excluding*** carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.

> **(1)** This includes any such organic compound ***other than the following***, which have been determined to have negligible photochemical reactivity: ***methane; ethane***; methylene chloride (dichloromethane); 1,1,1-trichloroethane (methyl chloroform); etc.

origin of "NMNEHC"

Similarity Between Fuel Gas and Exhaust Gas THC Composition

THC Constituent	Fuel Composition	Exhaust Composition
Methane	82.0%	79%
Ethane	12.4%	11%
Ethylene		3.0%
Propane	4.42%	3.9%
Propylene		0.5%
Butane	0.98%	0.9%
Formaldehyde		2.0%
Acetaldehyde		0.0%

products of incomplete combustion

Estimating Catalytic Performance on VOCs

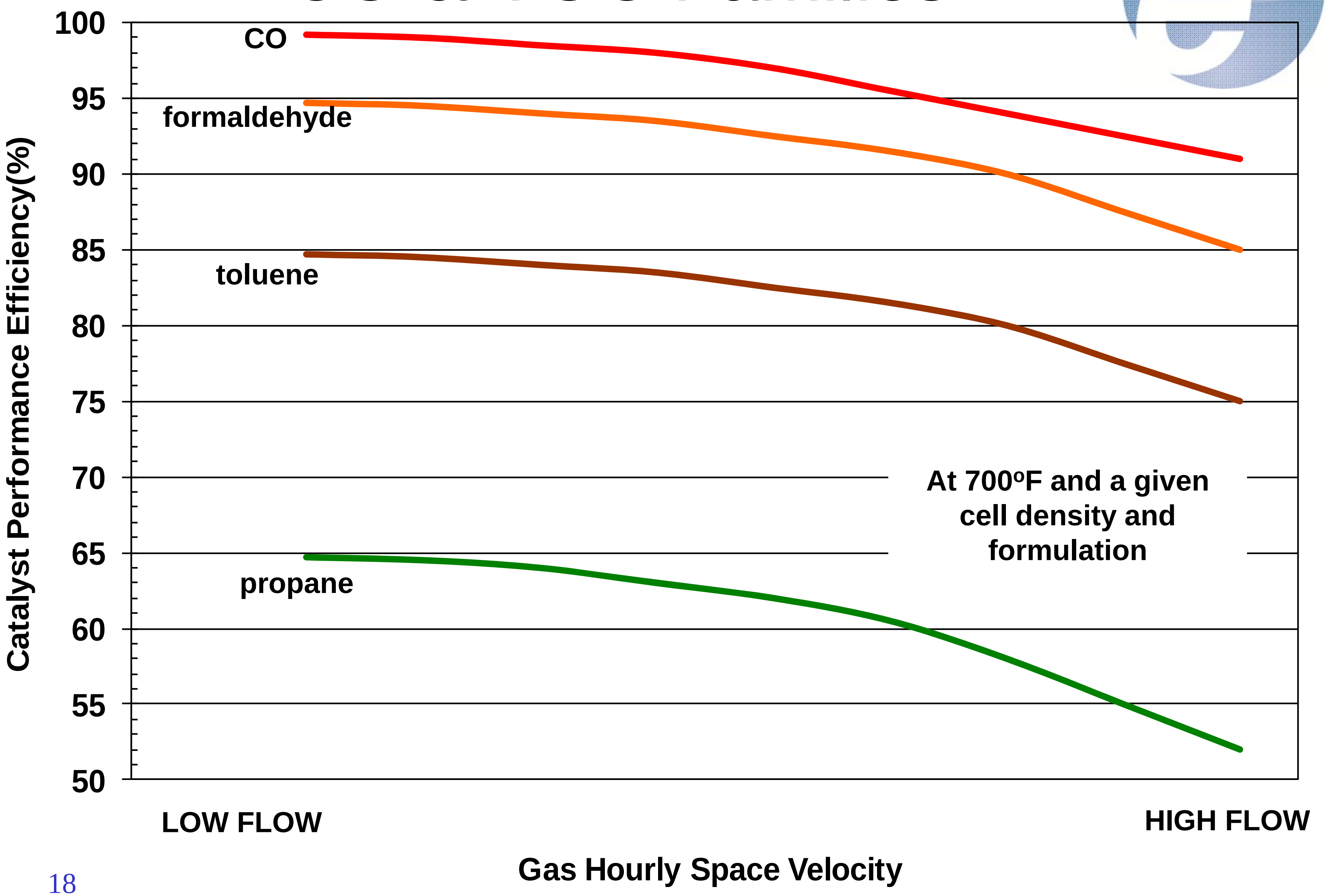
THC Constituent	Exhaust Composition
Methane	79%
Ethane	11%
Ethylene	3.0%
Propane	3.9%
Propylene	0.5%
Butane	0.9%
Formaldehyde	2.0%
Acetaldehyde	0.0%

Not included in measurement of VOCs

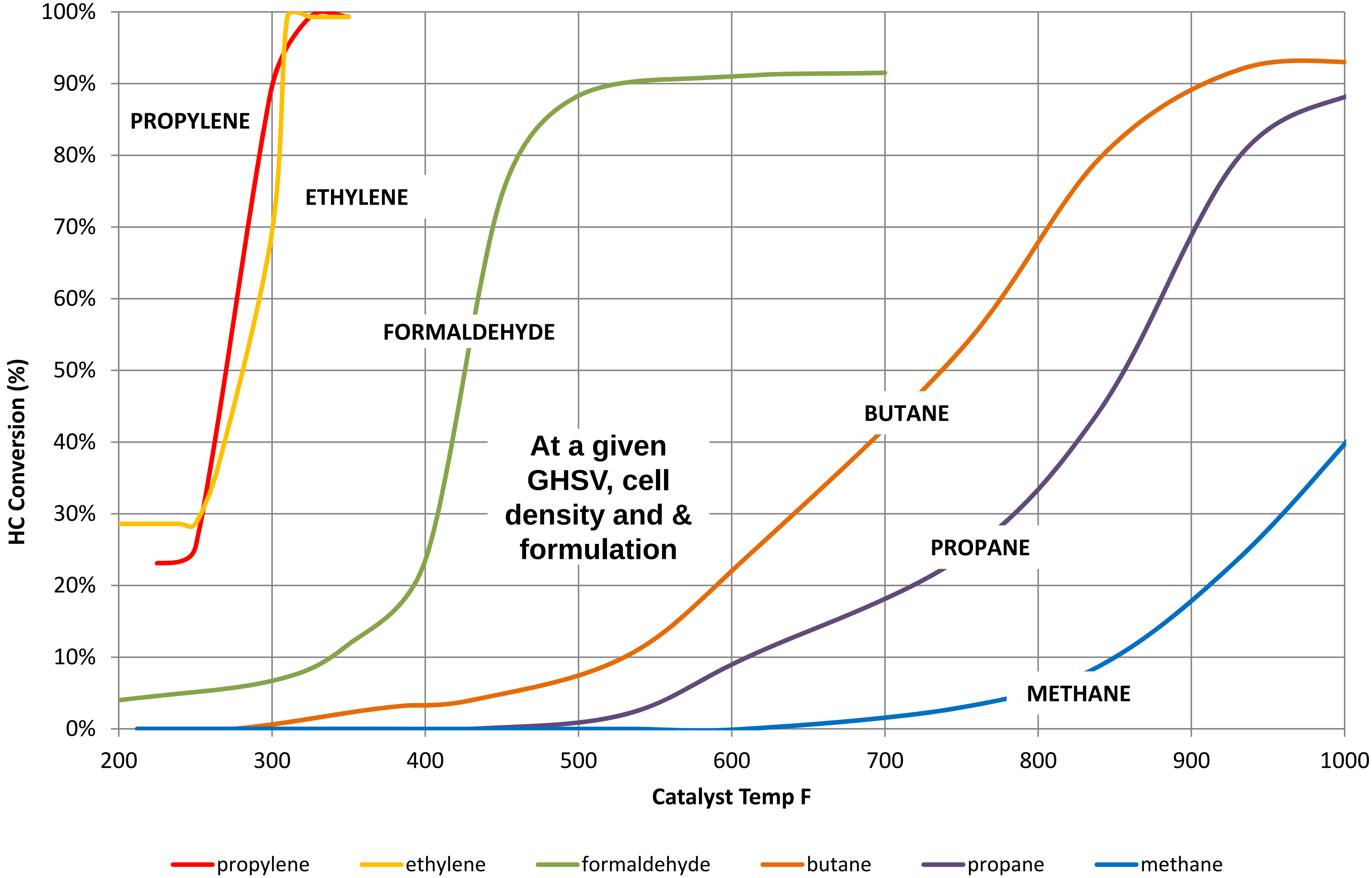
Catalytic performance is different for every compound.

Overall performance is a weighted-average.

Oxidation Performance for CO & VOC Families



Hydrocarbon Conversion over Pt Oxidation Catalyst



Estimating Catalytic Performance on VOCs

THC Constituent	Exhaust Composition
Ethylene	3.0%
Propylene	0.5%
Formaldehyde	2.0%
Butane	0.9%
Propane	3.9%

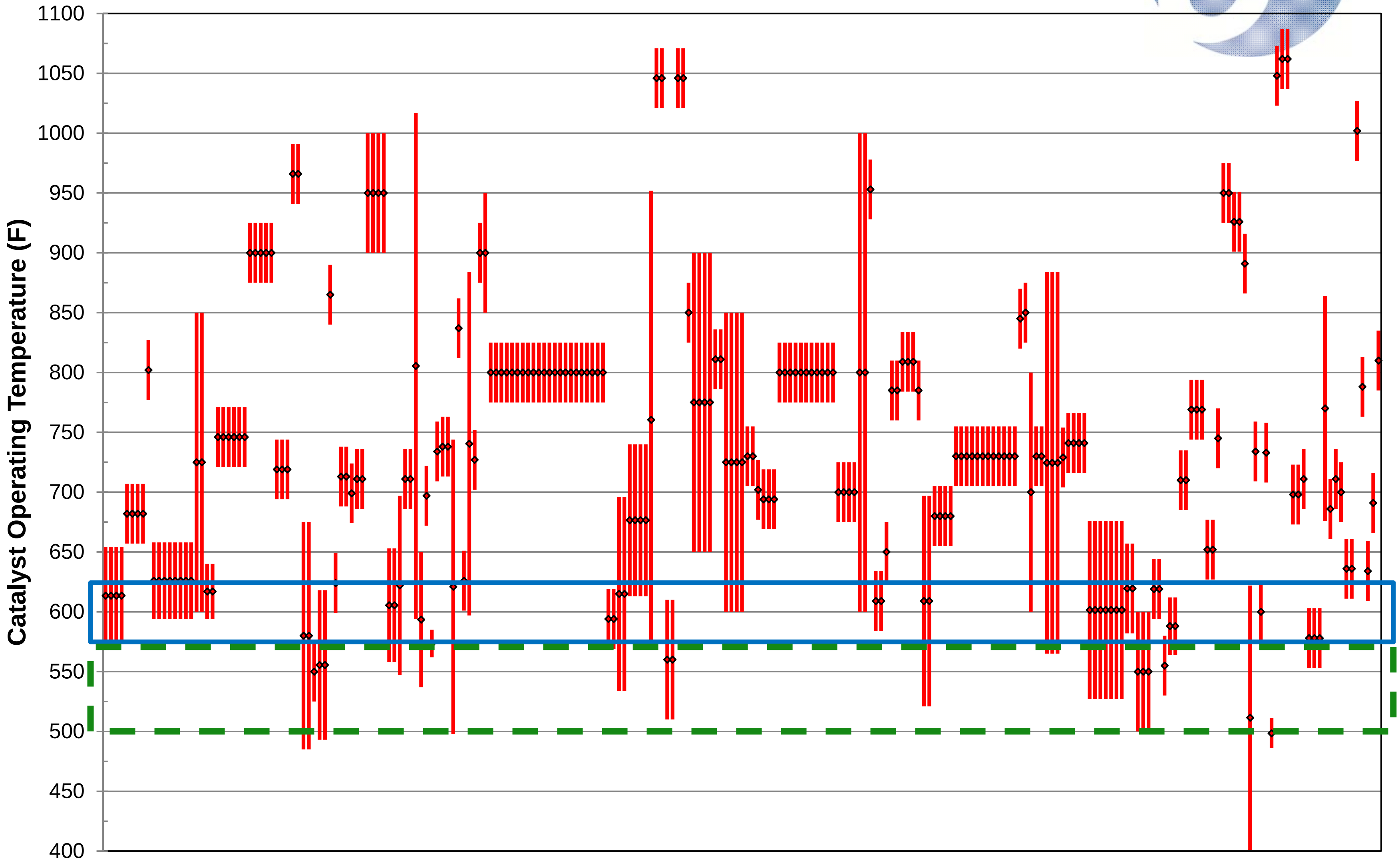
High oxidation efficiency

More difficult to oxidize

Most stable and most difficult to oxidize

Overall performance is a weighted-average

Field Experience >240 GTs



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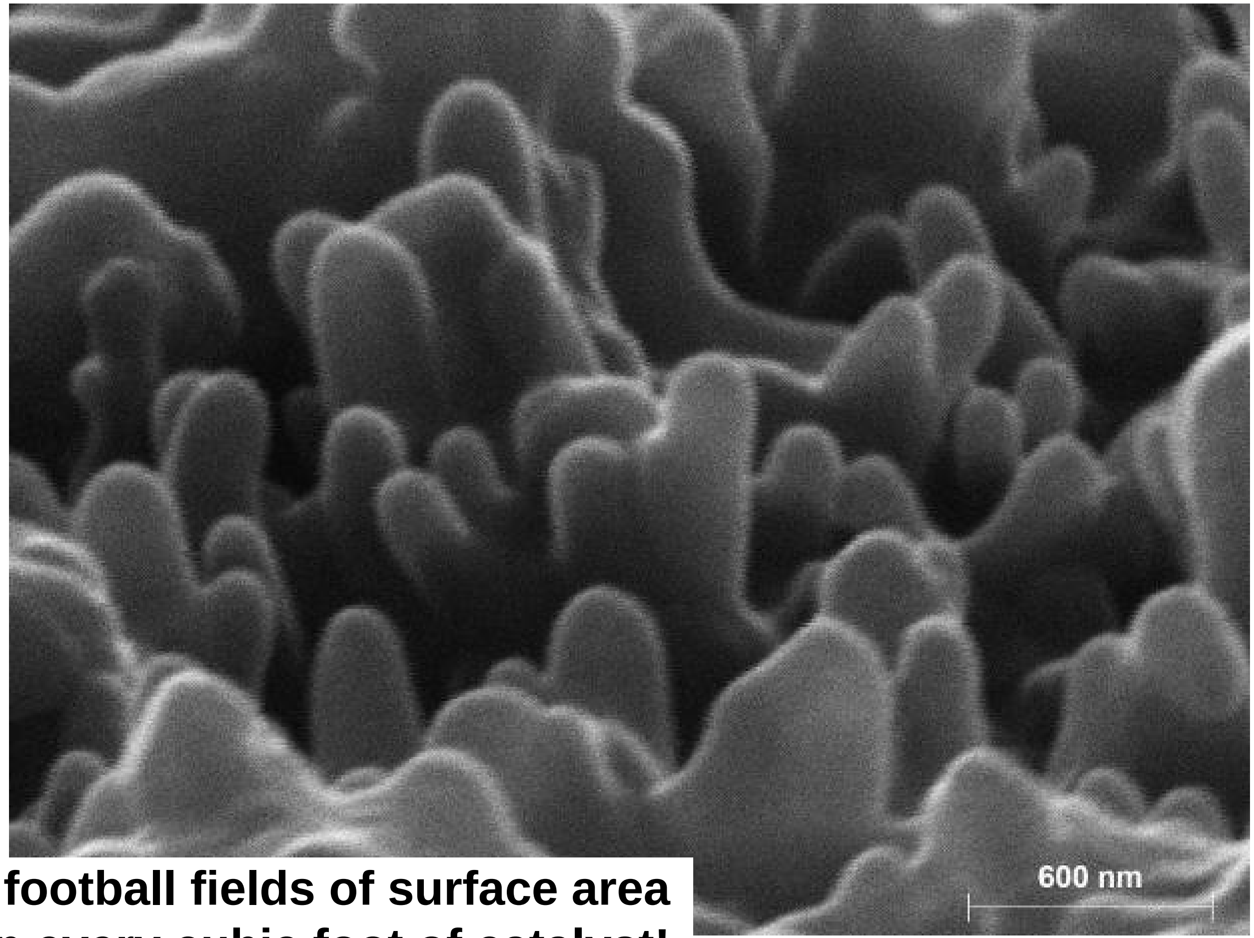
Low Catalyst Temps Impose Other Risks to Owner

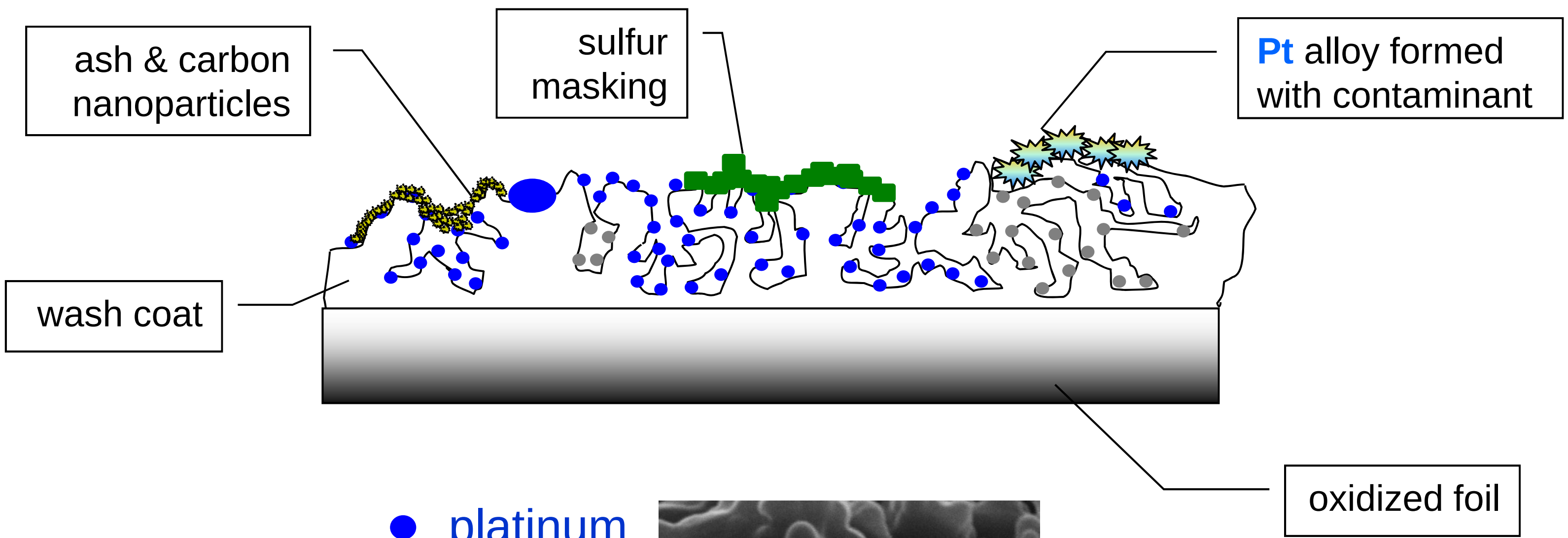
- BEWARE: Below 600ºF a number of contaminants are prone to accumulation
  - Even common masking agents (sulfur) could be problematic
  - If mixed with high temp cases, desorption is possible
- Of >240 installations the few that experienced high levels of contamination
  - All below 600ºF
  - All accumulated enormous amounts of sulfur and phosphorous

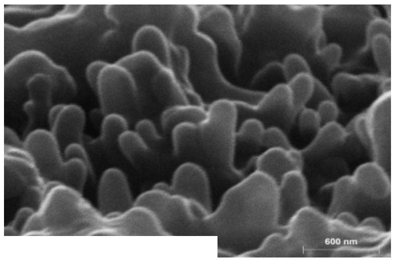
High Surface Area Coatings



55 football fields of surface area in every cubic foot of catalyst!

Examples of Chemical Contamination





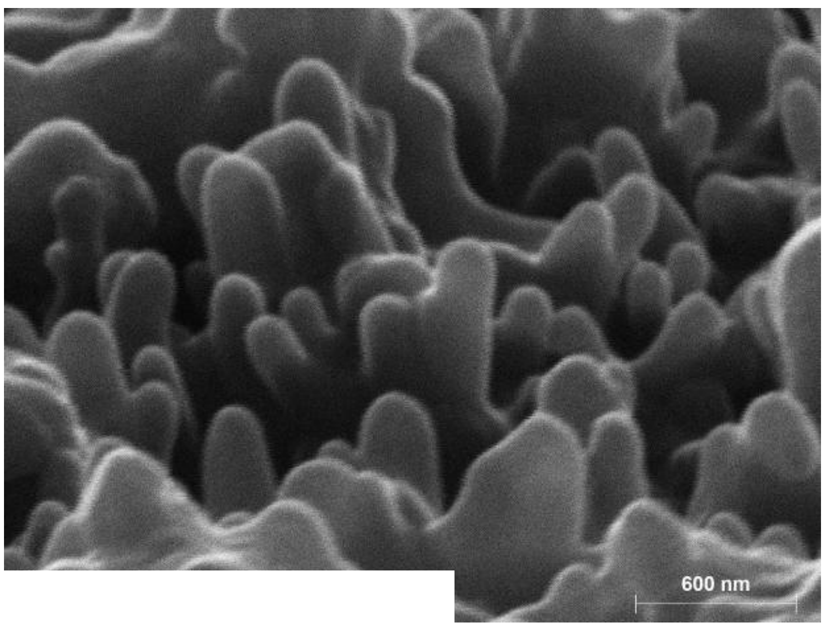
Case Study #1: Sulfur Accumulation at Low Temperature

Turbine Make & Model	GE 7EA
Catalyst Operating Temperature	505 (unfired) - 615F (fired)
Catalyst GHSV	106,000 - 163,000

Sulfur Accumulation	14,613 mg S/ft3 after 250 hours (10 days) (exacerbated by carbon buildup)

- Operation typically <600F
- Pipeline quality natural gas
- H2S in evap water

14,613 mg
sulfur
accumulated on
every ft3 of catalyst
in 250 hours (10 days)!!



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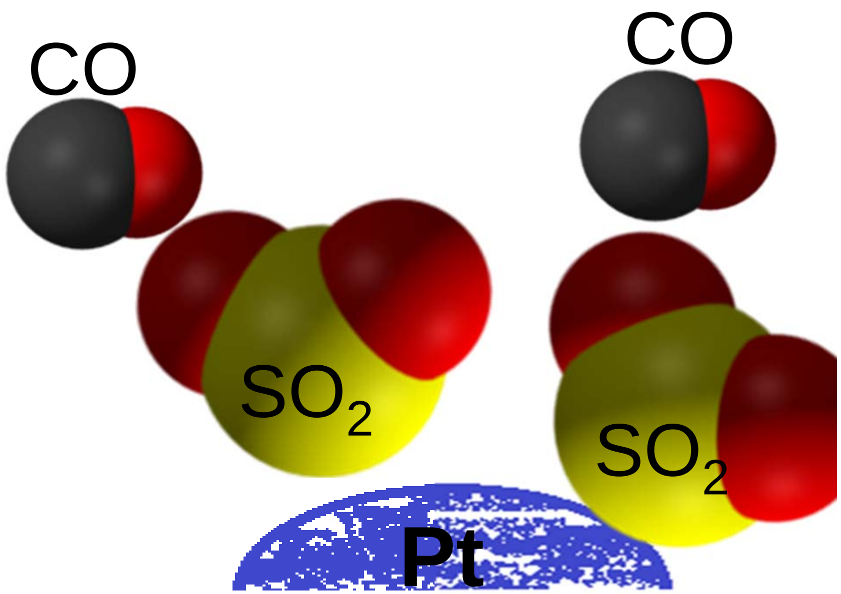
Effects of Sulfur on Catalyst

- Effect on precious metal: <570ºF SO_2 chemisorbs on Pt sites & reduces sites for CO

  "steric hindrance" –large sulfate group adsorbed on the surface physically interferes with CO molecules reaching a platinum crystal



- Effect on substrate: SO_2 converted to SO_3 and reacts with Al_2O_3 in the wash coat forming $Al_2(SO_4)_3$ which damages structure

Effects of Sulfur on Precious Metals

- Physically blocks access
- Reduces catalytic activity
- Platinum (Pt) has durability and <u>poison resistance</u>
  - regenerable with chemical washing
- Palladium (Pd) vulnerable to permanent <u>deactivation</u>
  - weak & unpredectable response to chemical washing

Case Study #2: Sulfur Accumulation at Low Temperature

Turbine Make & Model	Alstom GT-26
Catalyst Operating Temperature	500 - 640F (mostly <600F)
Catalyst GHSV	65,000 design (130,000 max)

Sulfur Accumulation	13,624 mg S/ft3 after 238 hours (10 days)

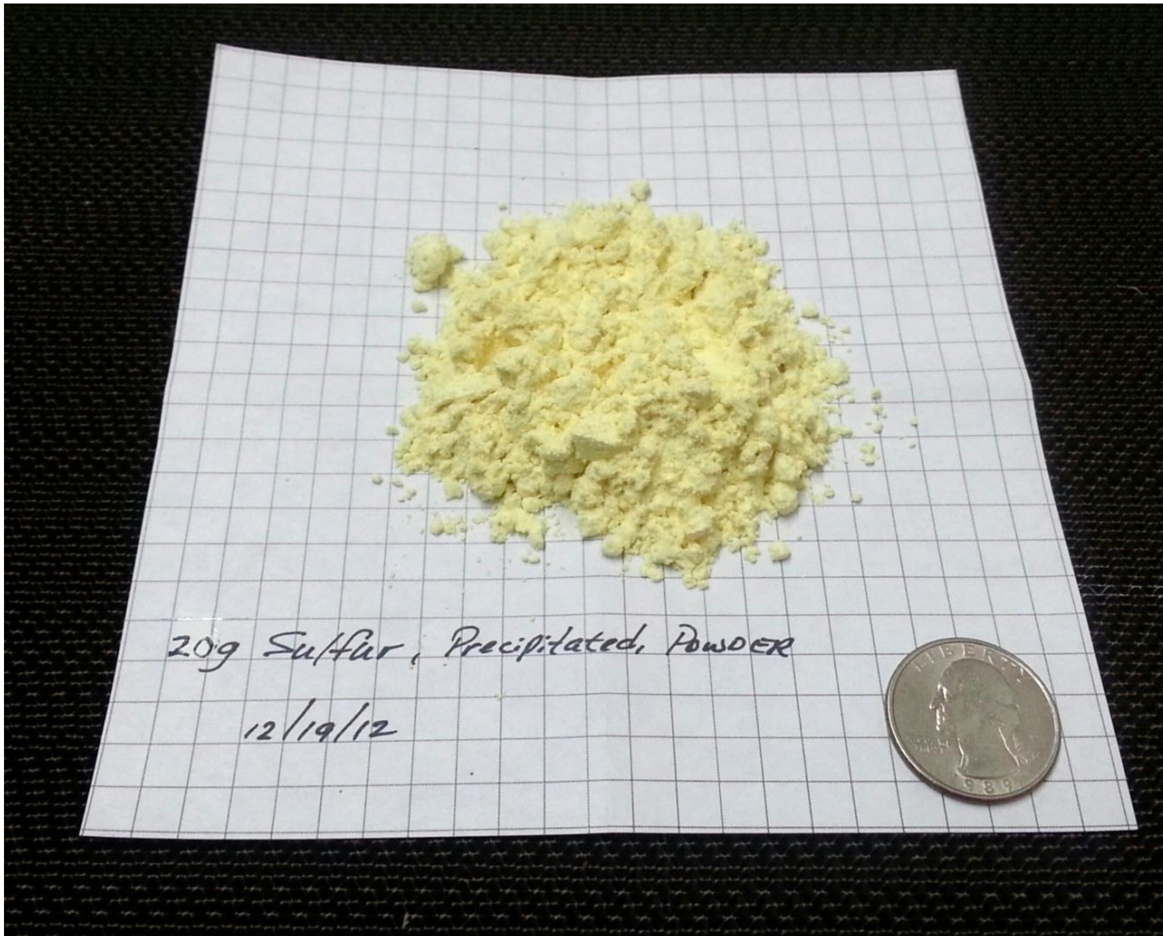
- Operation typically <600F
- Sulfur higher than pipeline quality natural gas

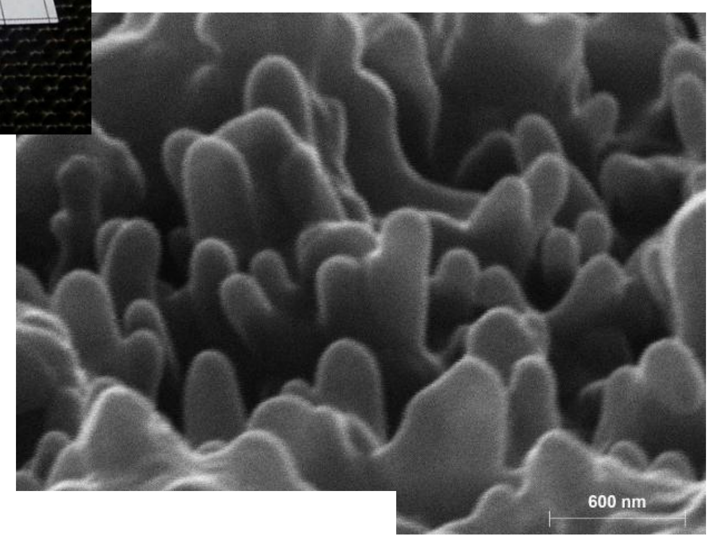
Case Study #3: Sulfur Accumulation At Low Temperature

Turbine Make & Model	GE 7FA
Catalyst Operating Temperature	504 (unfired) - 647F (fired)
Catalyst GHSV	118,000 - 197,000

Sulfur Accumulation	19,036 - 20,943 mg S/ft3 after 22 days

- Operation typically <600F
- pipeline quality natural gas





20,000 mg sulfur
accumulated on every cubic foot
of catalyst in 22 days!!

Platinum Catalyst Responds to Chemical Washing

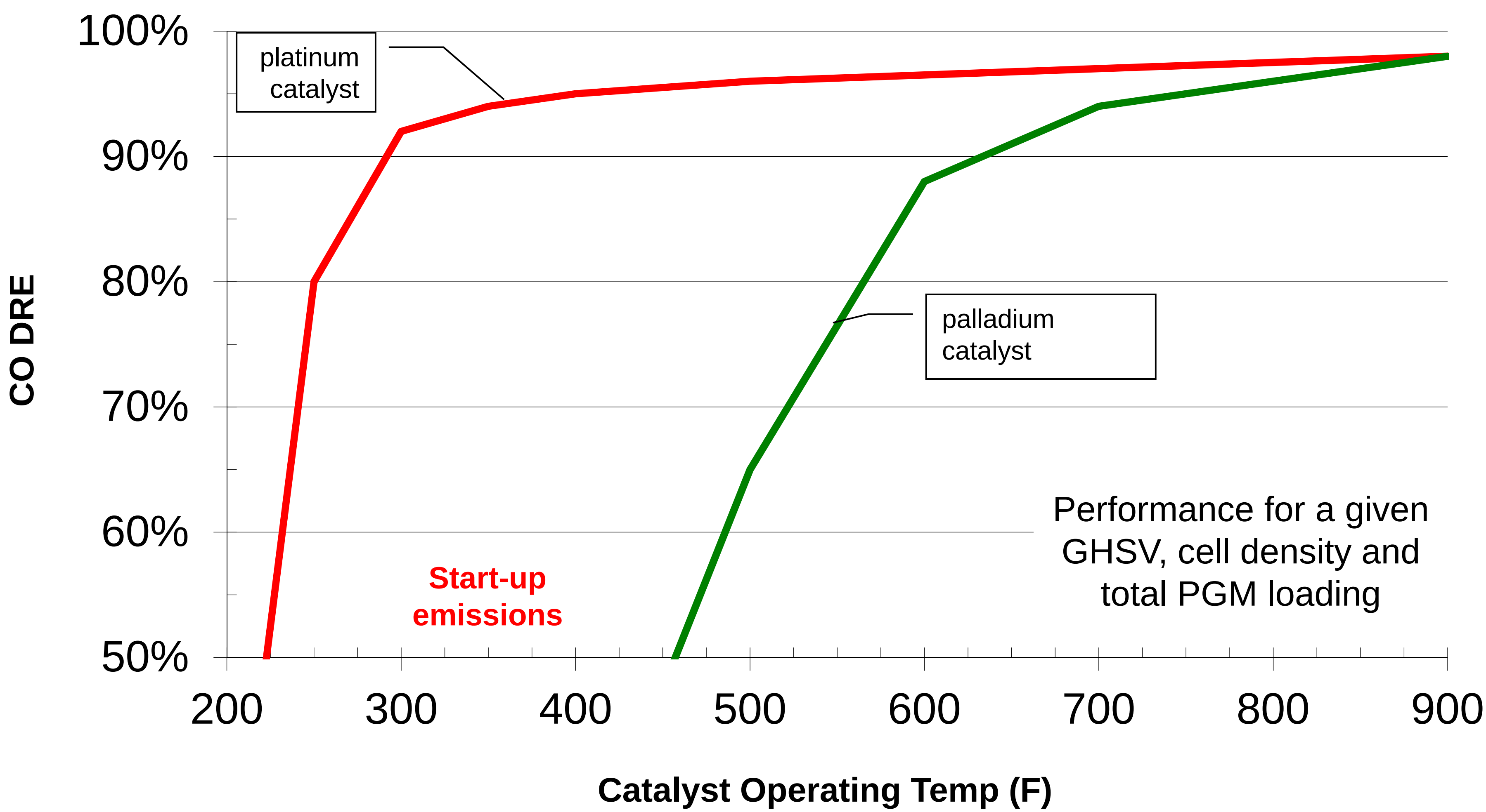
Catalyst Type: Platinum Oxidation
Condition: Temp = 525 F

	GHSV	Pre-Wash CO Performance	Post-Wash CO Performance
(HI-flow)	357,000	6.4%	**62.5%**
	200,000	12.7%	**85.8%**
(LO-flow)	150,000	15.7%	**93.8%**
	Catalyst Manufacturer: EmeraChem, LLC		
	Date of Manufacture: June 2000		

Selecting Precious Metals for Oxidation Catalyst

	Platinum	**Palladium**
CO	Best	Good when new
VOCs	Best	Good when new
Light-off temp	250-400ºF	400-650ºF
Catalytic activity	High	Moderate
Thermal stability	Good to 1200ºF	Good to 1200ºF
Poison resistance	High	Low
Response to chemical washing	Good	Poor
Durability	High	Low to moderate
Price per troy oz.	$1560	$690

Oxidation Performance Platinum vs. Palladium



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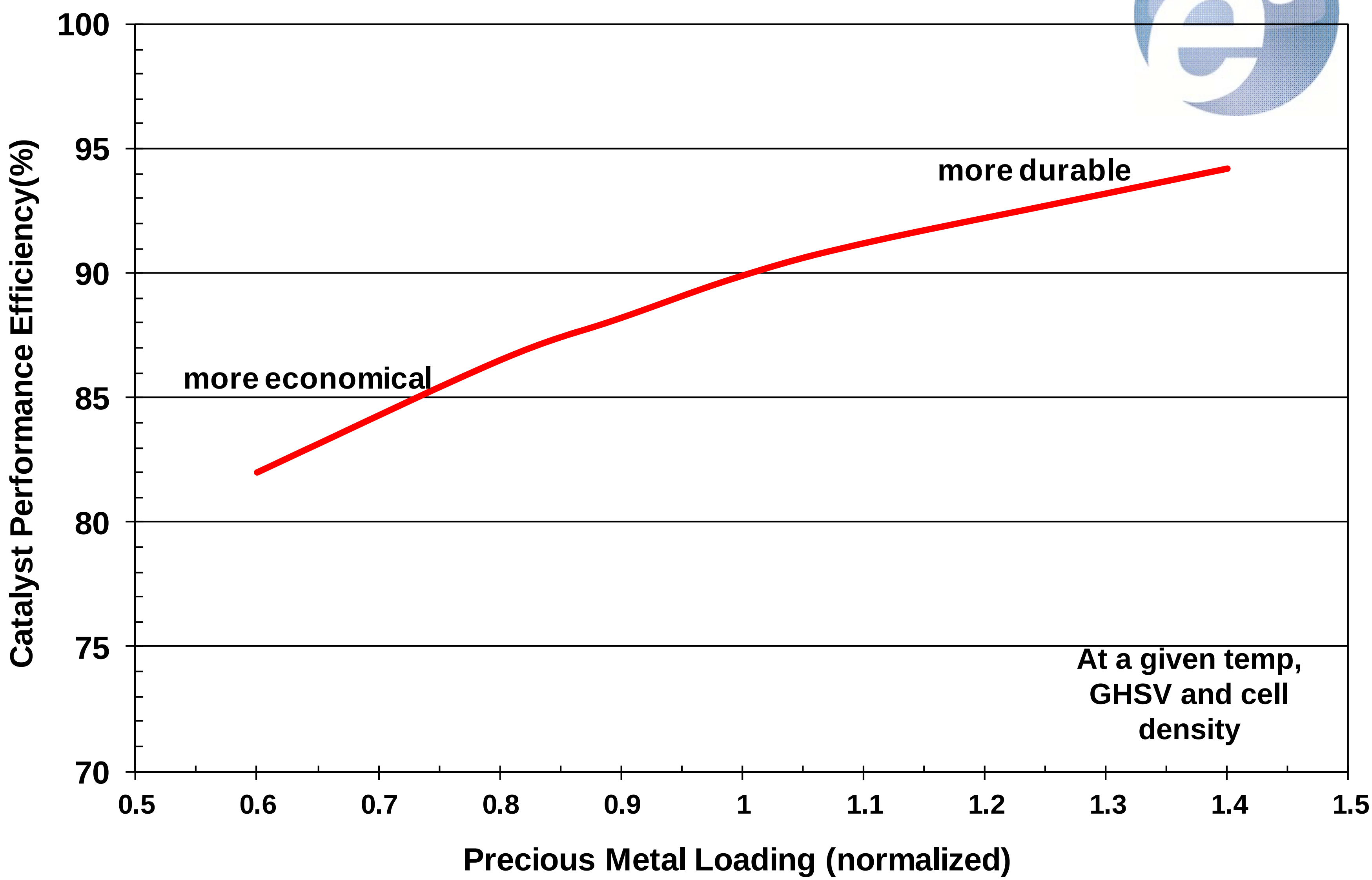
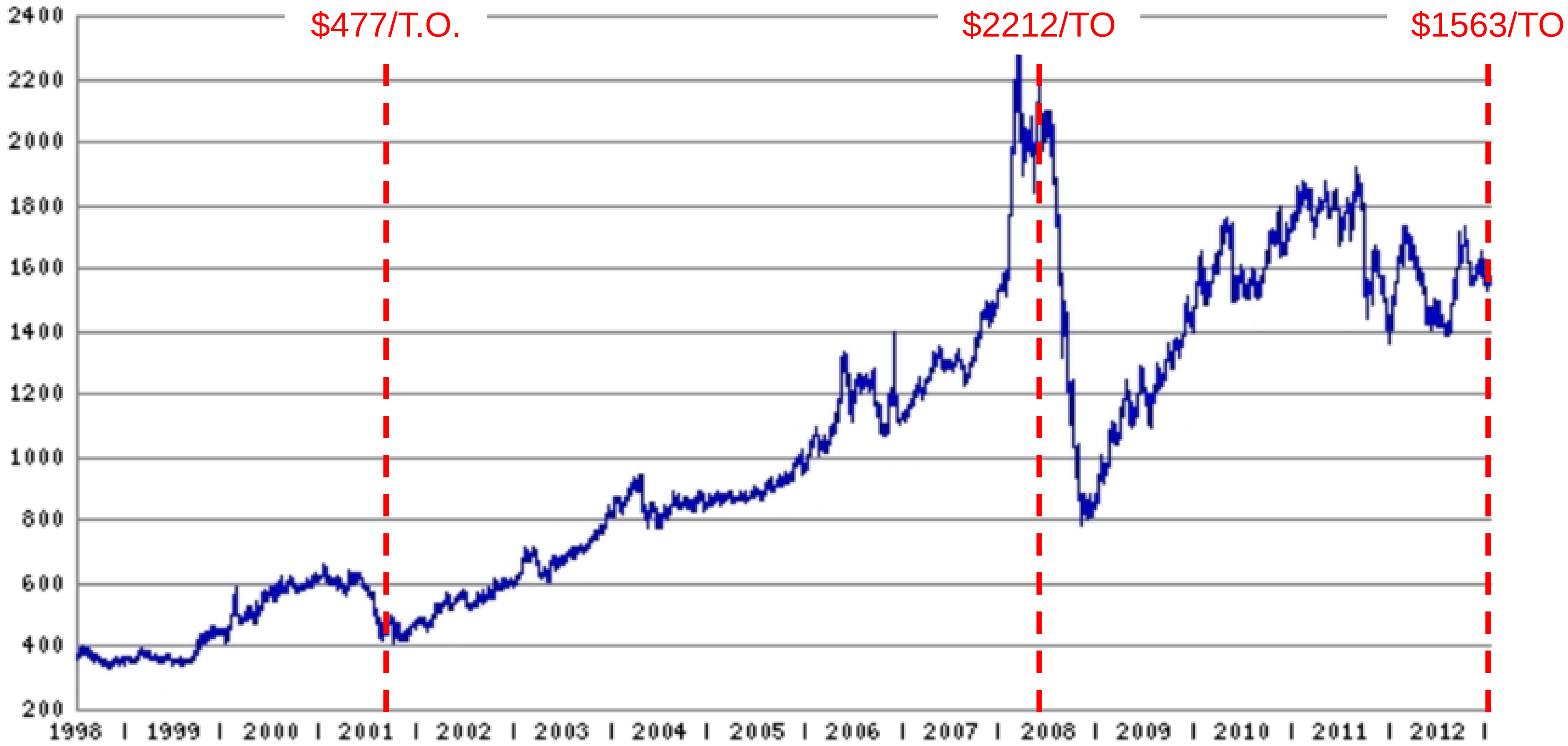
Performance as a Function of Precious Metal Loading



What effect has platinum escalation had on catalyst design and price?

Escalation of Platinum



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Example: GE7FA gas turbine

- Exhaust
  - 3,603,880 lb/hr exhaust
  - 20 ppmv CO at GT exhaust
  - 2.0 ppmv CO at stack
  - 90% CO removal efficiency
- Catalyst
  - GHSV ~200,000
  - 247 cuft catalyst

Effect of Pt Price on Catalyst Design and Price

- August 2001
  - Platinum was similar in cost to the foil substrate
  - Catalyst companies used more platinum rather than more substrate volume
  - Platinum loading of 28 to 42 g/ft3 was common
  - Extremely durable
    - High-performance
    - Low-temperature light-off
    - Sulfur tolerant & regenerable
    - Tolerant of many start/stop cycles
    - 10-year life
  - Pt cost for the GE 7FA was ~**$136,000** for 36 g/ft3

Effect of Pt Price on Catalyst Design and Price

- August 2001
  - Pt loading 36g/ft3 costs **$136,000**
- May 2008
  - Same Pt loading would have cost ~**$633,000**
  - Outcry from end users! ***"No way!"***
  - Holding cost to $136,000 would buy <8 g/ft3
    - Too risky; vulnerable to low-T and sulfur; low durability
  - Some catalyst companies switched to **palladium**
    - $459/TO vs. $2,212 for platinum
    - Light-off temp higher than Pt (poor for startup emissions)
    - Poisoned by sulfur; not responsive to washing
    - Low durability

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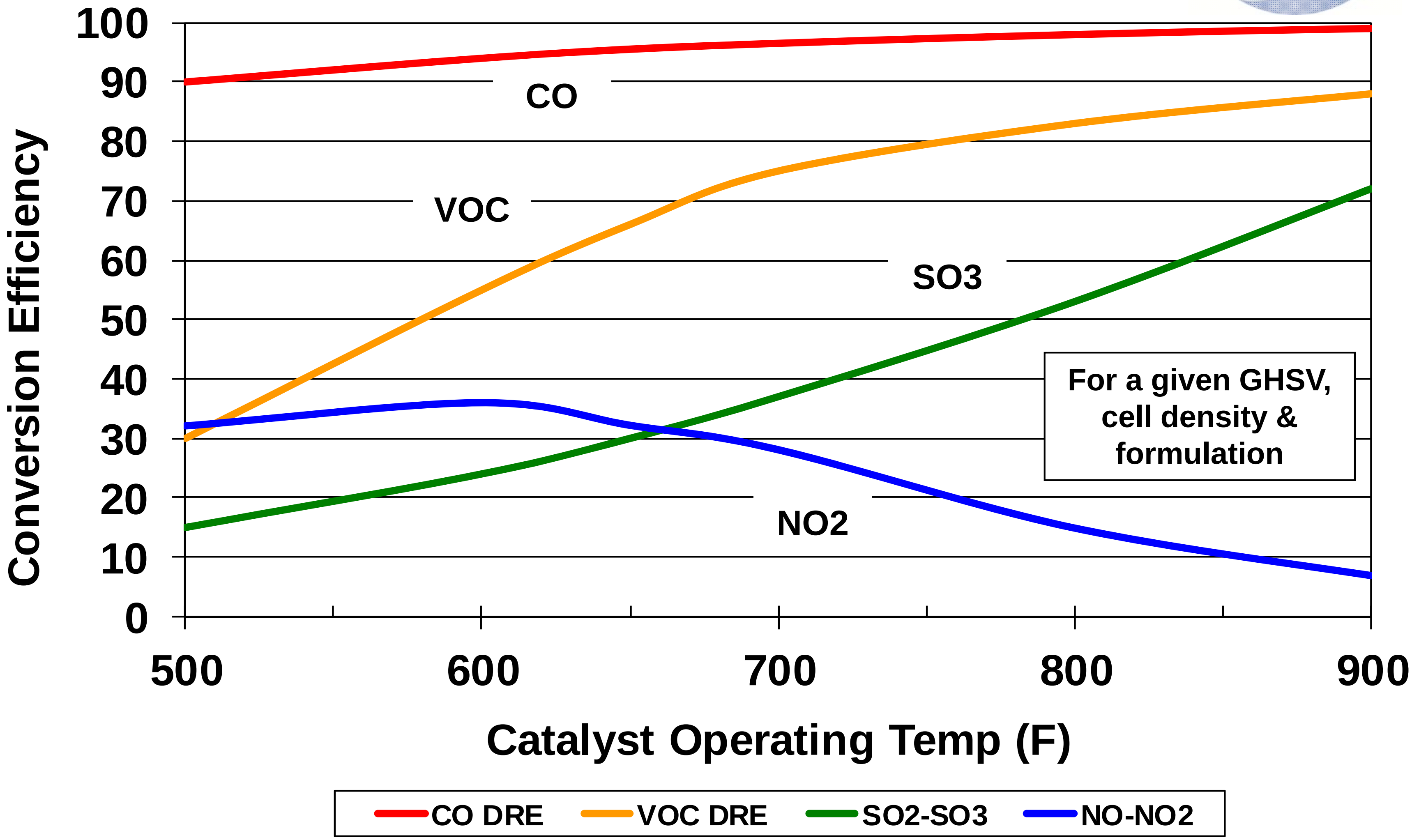
Effect of Pt Price on Catalyst Design and Price

- August 2001
  - 36 g/ft3 loading for **$136,000**
- May 2008
  - 36 g/ft3 for **$633,000**; <8 g/ft3 for $136,000
- Today, January 2013
  - Pt loading of 36 g/ft3 would cost ~**$447,000** (*too costly*)
  - Spending $136,000 would buy 11 g/ft3 (*too low*)
  - Improved substrate & wash coat
  - Improved Pt application techniques (Pt size,distribution)
  - Restrictions on low-temp, sulfur, no. starts/stops
  - 10-yr expected life reduced to 3+ years

Simultaneous Collateral Reactions

- NO-NO_2 Oxidation
  - Favors NO_2 at low temps; NO at high temps
  - Effects SCR reactions, NH_3 consumption
  - Destroys sulfur bound carbon nanoparticles
- SO_2-SO_3 Oxidation
  - Increases with temperature
  - Precursor to particulate matter
  - Ammonia slip reacts to form bi-sulfate particulate after SCR
- Catalyst formulations can suppress these

Overall Effect of Operating Temp on Catalyst Reactions



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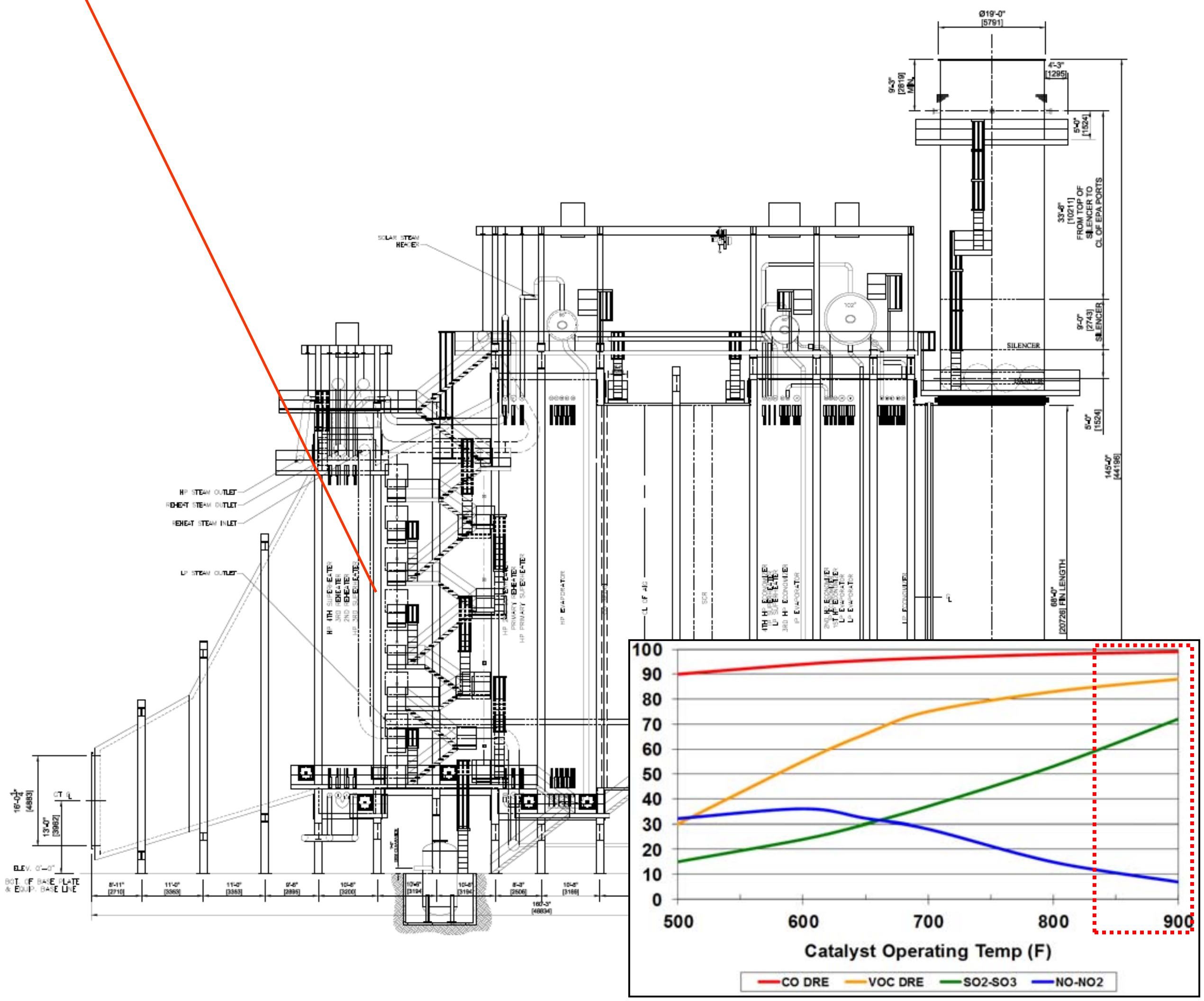
Putting it all together…

How does HRSG temperature effect catalyst design and price?

Effect of HRSG Temperature Zone on Oxidation Catalyst Performance

~1000ºF

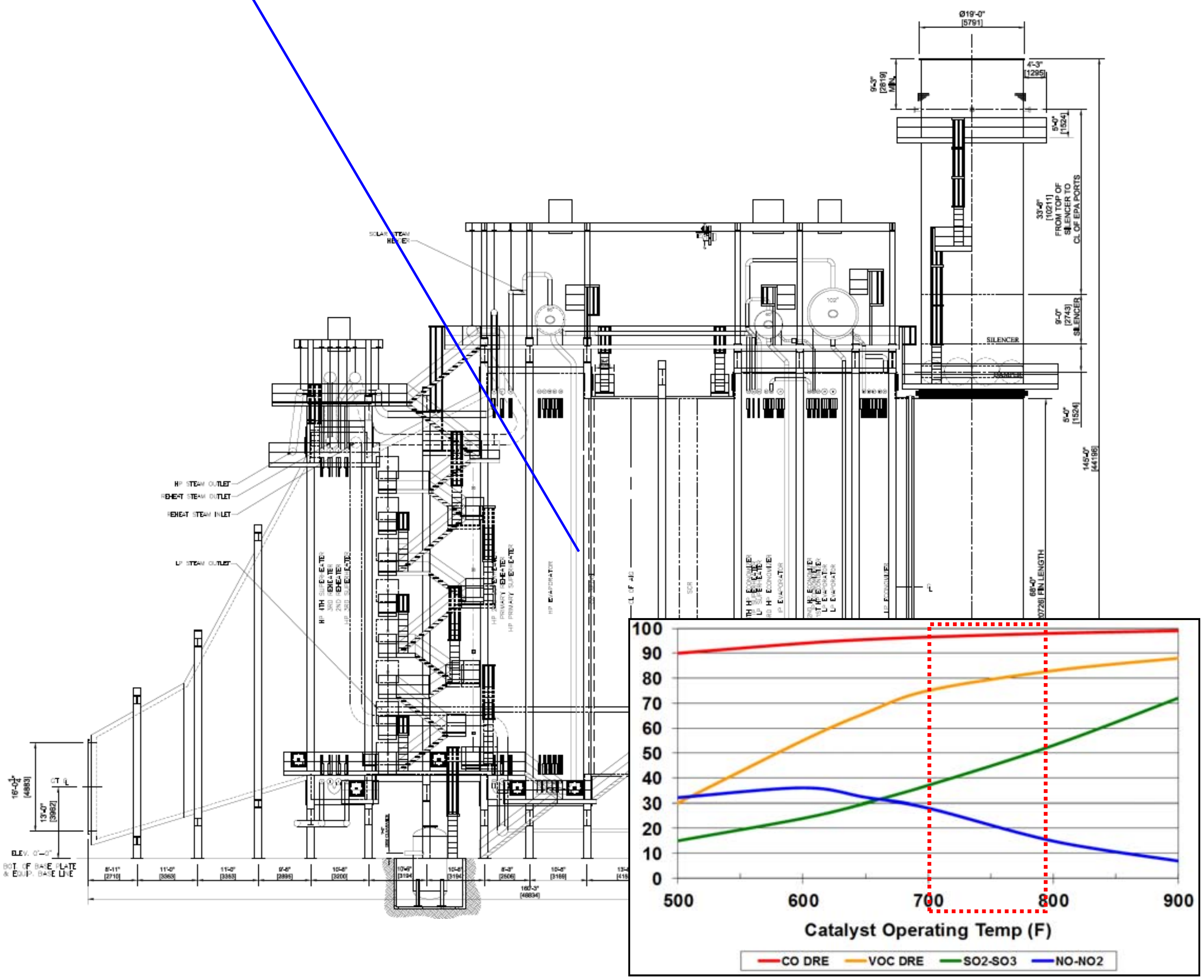
- **Hi CO performance**
- **Hi VOC performance**
- **Lowest catalyst volume**
- **Lo NO to NO_2 conversion**
- **Hi SO_2 to SO_3 conversion**
- **Lower Pt**
- **Lowest cost catalyst**



Effect of HRSG Temperature Zone on Oxidation Catalyst Performance

~750ºF

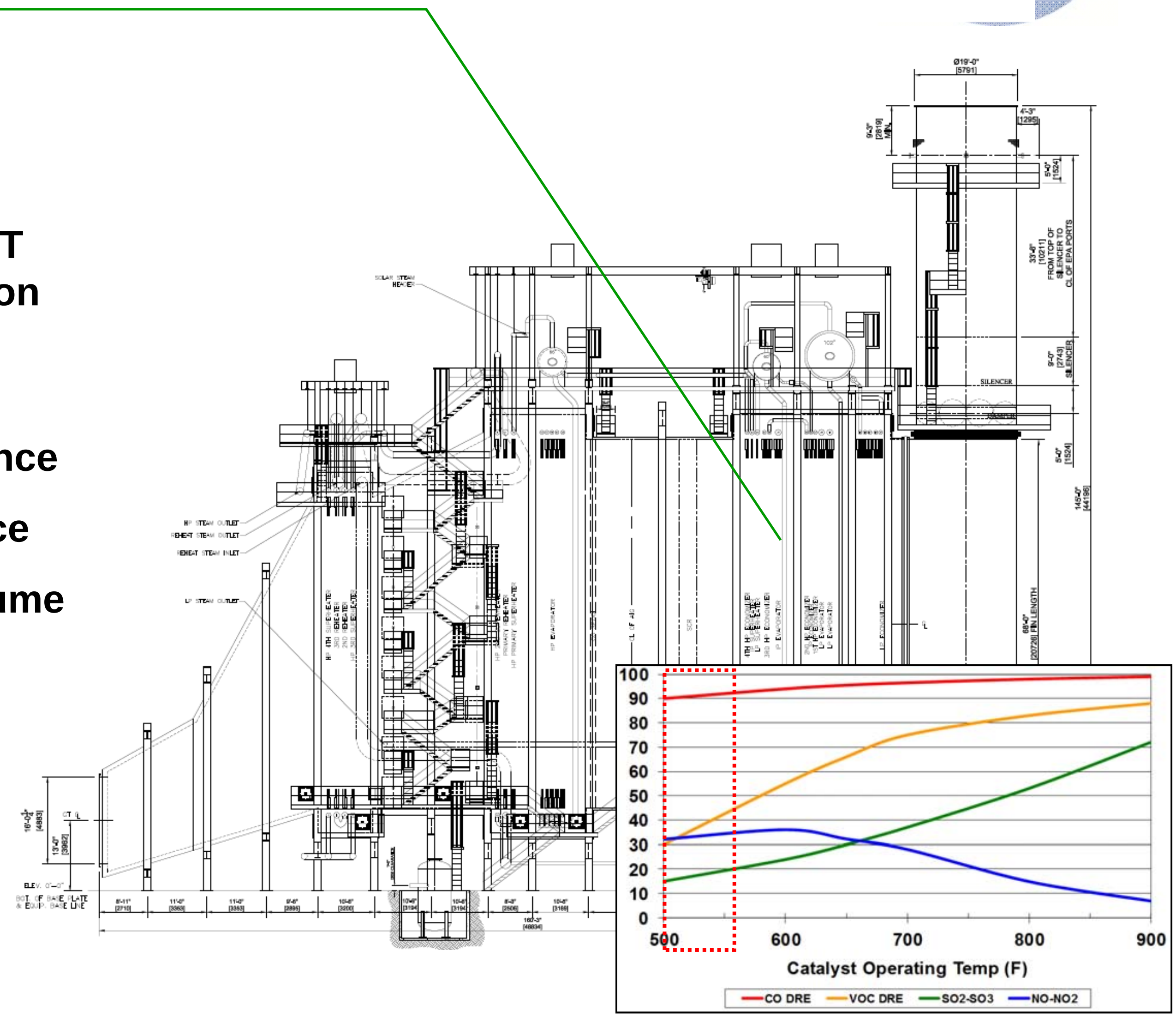
- **Hi CO performance**
- **Good VOC performance**
- **Moderate catalyst volume**
- **Moderate NO to NO_2 conversion**
- **Moderate SO_2 to SO_3 conversion**
- **Economical Pt-loading**



Effect of HRSG Temperature Zone on Oxidation Catalyst Performance

500-550^oF

- **Risk of sulfur accumulation with decreased life**
- **Increase Pt for low-T lightoff and protection from masking & poisoning**
- **Good CO performance**
- **Lo VOC performance**
- **Larger catalyst volume**
- **High NO to NO_2 conversion**
- **Low SO_2 to SO_3 conversion**
- **Highest catalyst $$**



Effect of HRSG Temperature Zone on Catalyst System Price

- Examine EmeraChem catalyst in >70 large GTs
  - GE 7H, 501G
  - 7FA, 501F
  - 7EA, 501D5A
- Three temperature ranges
  - 500-650^{o}F
  - 700-825^{o}F
  - 850-1000^{o}F
- Example of a GE7FA.05 at 3 temperatures

Effect of HRSG Temperature Zone on Catalyst System Price

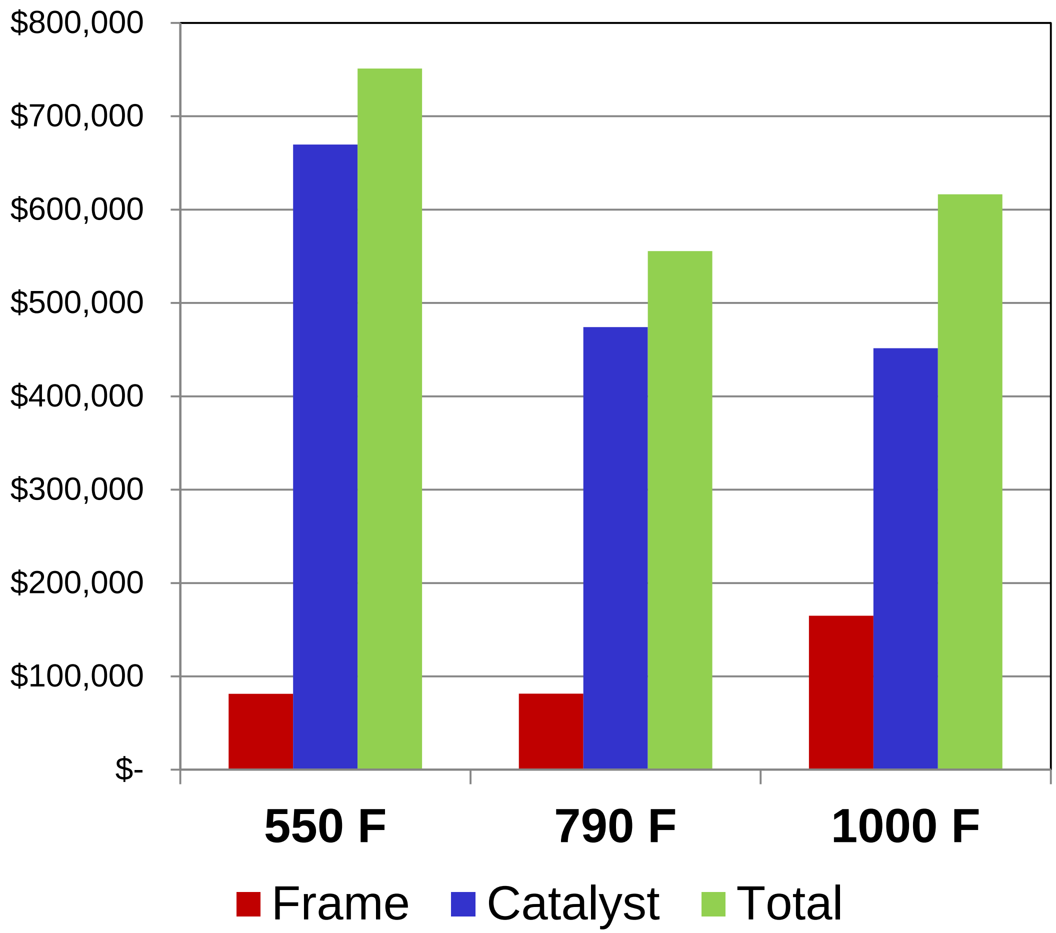
- Flow rate: 4,024,000 lb/hr
- 90% CO reduction (10 to 1 ppm)
- 67% VOC reduction (3 to 1 ppm)
- Gas path: 72'x27'
- Consider three temperature options:
  - 550^{o}F
  - 790^{o}F
  - 1000^{o}F

Effect of HRSG Temperature Zone on Catalyst System Price

	550 F	790 F	1000 F
Catalyst GHSV*	175,000	200,000	215,000
Catalyst Volume	310 ft3 most catalyst due to lower activity	270 ft3	250 ft3 least catalyst due to high activity
Platinum Loading	~1.5X more Pt due to likely accumulation of contaminants	X	X
Frame Material	carbon steel	carbon steel	stainless steel

** Catalyst GHSV is approximate for illustration only, based upon a given cell density and formulation.*

Effect of HRSG Temperature Zone on Catalyst System Price



Catalyst and frame prices are approximate for illustration only, based upon a given exhaust characteristic, catalyst design, gas path and Pt price.

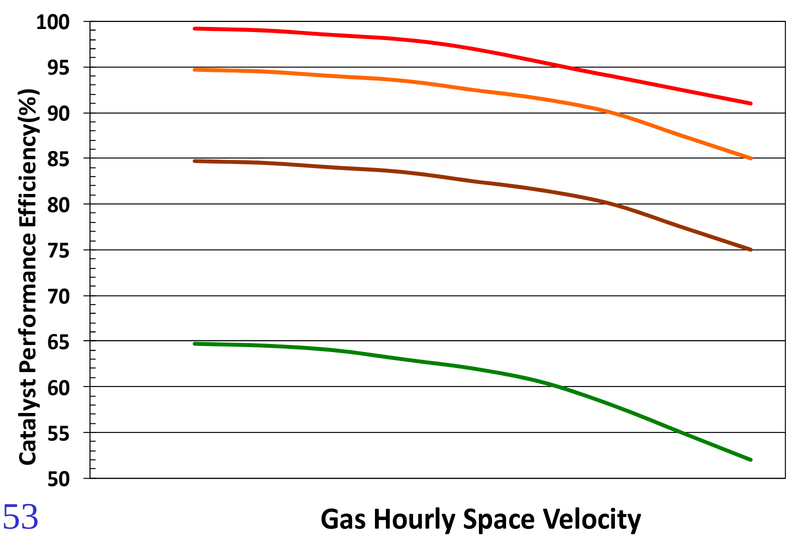
Evaluate all operating cases
(temp, flow, performance)

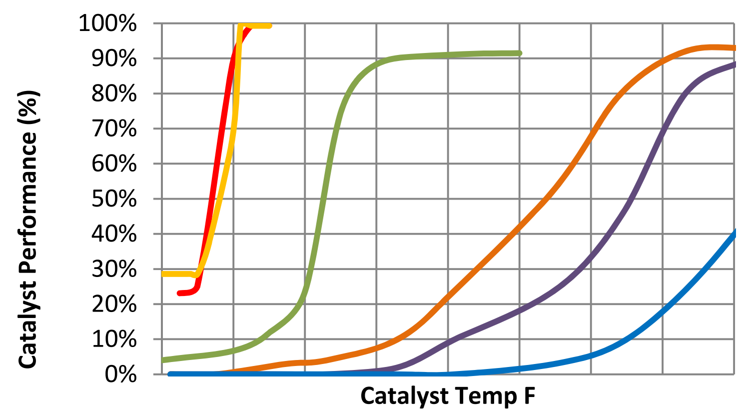
PARAMETER	Units	DESIGN BASIS	100	102	111	112	126	129
CASE DESCRIPTION								
GENERAL INFORMATION								
GT Load		0.50035542	100%	50%	50%	100%	50%	50%
GT Fuel Type		Natural Gas	Natural Gas	Natural Gas	Natural Gas	Natural Gas	Natural Gas	Natural Gas
Ambient Temp	ºF	20	60	60	100	0	80	100
Temp at Catalyst	ºF	832	835	824	955	845	958	977
EXHAUST CHARACTERISTICS FROM GT								
GT Flow with Tempering Air	lb/hr	647,792	866,129	629,703	522,225	874,486	517,015	492,086
Gas Composition	% vol							
O2		14.55	13.75	14.79	13.47	14.06	13.81	13.66
H2O		5.94	8.76	6.72	9.85	6.26	8.42	9.19
N2		75.65	73.54	74.87	72.70	75.58	73.81	73.20
CO2		2.95	3.07	2.72	3.09	3.19	3.07	3.07
Ar		0.91	0.89	0.90	0.87	0.90	0.88	0.88
Total		100.00	100.00	100.00	99.99	99.99	99.99	99.99
MW	lb/lb-mole	28.57	28.27	28.46	28.15	28.55	28.31	28.22
Flow Rate (wet)	scfh	8,593,971	11,610,925	8,384,926	7,030,717	11,607,285	6,922,442	6,608,366
Flow Rate (dry)	scfh	8,083,203	10,594,153	7,821,332	6,337,931	10,880,855	6,339,469	6,001,203
O2 Concentration Dry	%	15.47	15.07	15.85	14.95	15.00	15.08	15.04
CO AT CATALYST INLET								
CO as ppmvd at 15% O2		70.10	25.02	70.20	69.99	24.99	69.99	69.99
CO Flow	lb/hr	38.6	19.4	34.7	33.1	20.1	32.3	30.8
CO AT CATALYST OUTLET								
CO as ppmvd at 15% O2		5.5	5.5	5.5	5.5	5.5	5.5	5.5
CO Destruction Required	%	92.2	78.0	92.2	92.1	78.0	92.1	92.1
VOC AT CATALYST INLET								
VOC as ppmvd at 15% O2		8.41	3.00	8.42	8.40	3.00	8.40	8.40
VOC AT CATALYST OUTLET								
VOC as ppmvd at 15% O2		2.00	2.00	2.00	2.00	2.00	2.00	2.00
VOC Destruction Required	%	76.2	33.4	76.3	76.2	33.3	76.2	76.2
ADDITIONAL DATA								
Required Pressure Drop	"H_2O	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Expected Pressure Drop	"H_2O	0.7	1.0	0.7	0.7	1.0	0.7	0.7

DETERMINE "GHSV" FOR EACH FLOW RATE AND TEMPERATURE TO ACHIEVE REQUIRED CO & VOC PERFORMANCE

Determine “GHSV” for each flow rate & temp to achieve CO & VOC performance

PARAMETER	Units	DESIGN BASIS	100	102	111	112	126	129
CASE DESCRIPTION								
GENERAL INFORMATION								
GT Load		0.50035542	100%	50%	50%	100%	50%	50%
GT Fuel Type		Natural Gas	Natural Gas	Natural Gas	Natural Gas	Natural Gas	Natural Gas	Natural Gas
Ambient Temp	°F	20	60	60	100	0	80	100
Temp at Catalyst	°F	832	835	824	955	845	958	977
EXHAUST CHARACTERISTICS FROM GT								
GT Flow with Tempering Air	lb/hr	647,792	866,129	629,703	522,225	874,486	517,015	492,086
Gas Composition	% vol							
O_2		14.55	13.75	14.79	13.47	14.06	13.81	13.66
H_2O		5.94	8.76	6.72	9.85	6.26	8.42	9.19
N_2		75.65	73.54	74.87	72.70	75.58	73.81	73.20
CO_2		2.95	3.07	2.72	3.09	3.19	3.07	3.07
Ar		0.91	0.89	0.90	0.87	0.90	0.88	0.88
Total		100.00	100.00	100.00	99.99	99.99	99.99	99.99
MW	lb/lb-mole	28.57	28.27	28.46	28.15	28.55	28.31	28.22
Flow Rate (wet)	scfh	8,593,971	11,610,925	8,384,926	7,030,717	11,607,285	6,922,442	6,608,366
Flow Rate (dry)	scfh	8,083,203	10,594,153	7,821,332	6,337,931	10,880,855	6,339,469	6,001,203
O_2 Concentration Dry	%	15.47	15.07	15.85	14.95	15.00	15.08	15.04
CO AT CATALYST INLET								
CO as ppmvd at 15% O_2		70.10	25.02	70.20	69.99	24.99	69.99	69.99
CO AT CATALYST OUTLET								
CO as ppmvd at 15% O_2		5.5	5.5	5.5	5.5	5.5	5.5	5.5
CO Destruction Required	%	92.2	78.0	92.2	92.1	78.0	92.1	92.1
VOC AT CATALYST INLET								
VOC as ppmvd at 15% O_2		8.41	3.00	8.42	8.40	3.00	8.40	8.40
VOC AT CATALYST OUTLET								
VOC as ppmvd at 15% O_2		2.00	2.00	2.00	2.00	2.00	2.00	2.00
VOC Destruction Required	%	76.2	33.4	76.3	76.2	33.3	76.2	76.2
ADDITIONAL DATA								
Required Pressure Drop	"H_2O	2.0	2.0	2.0	2.0	2.0	2.0	2.0





Convert GHSV into catalyst volume

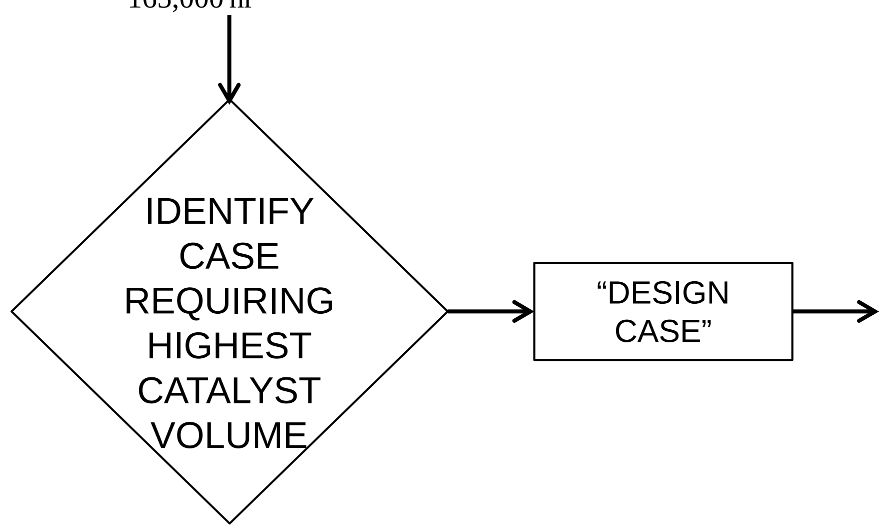
- GHSV varies by
  - performance level
  - compound
  - temperature
  - formulation and loading of precious metals
  - formulation of wash coating
- catalyst volume (*cubic feet)* calculated by dividing volumetric gas flow rate *(s-ft^3/hr)* by GHSV *(1/hr)*

$$\frac{8{,}593{,}971\ \text{scfh}}{165{,}000\ \text{hr}^{-1}} = 52.1\ \text{ft}^3$$

Calculate the required catalyst volume for each case

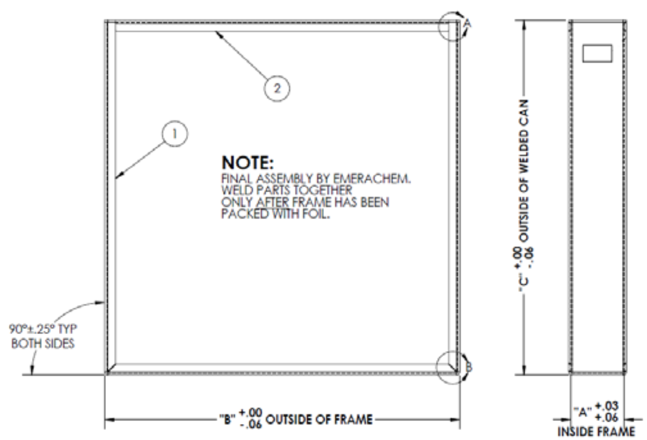
PARAMETER	Units	DESIGN BASIS	100	102	111	112	126	129
CASE DESCRIPTION		117	With Dilution/Tempering Air Injection			Without Dilution/Tempering		
GENERAL INFORMATION								
GT Load		0.50035542	100%	50%	50%	100%	50%	50%
GT Fuel Type		Natural Gas	Natural Gas	Natural Gas	Natural Gas	Natural Gas	Natural Gas	Natural Gas
Ambient Temp	ºF	20	60	60	100	0	80	100
Temp at Catalyst	ºF	832	835	824	900	840	908	877
EXHAUST CHARACTERISTICS FROM GT								
GT Flow with Tempering Air	lb/hr	647,792	866,129	629,703	522,225	874,486	517,015	492,086
Gas Composition	% vol							
O2		14.55	13.75	14.79	13.47	14.06	13.81	13.66
H2O		5.94	8.76	6.72	9.85	6.26	8.42	9.19
N2		75.65	73.54	74.87	72.70	75.58	73.81	73.20
CO2		2.95	3.07	2.72	3.09	3.19	3.07	3.07
Ar		0.91	0.89	0.90	0.87	0.90	0.88	0.88
Total		100.00	100.00	100.00	99.99	99.99	99.99	99.99
MW	lb/lb-mole	28.57	28.27	28.46	28.15	28.55	28.31	28.22
Flow Rate (wet)	scfh	8,593,971	11,610,926	8,384,920	7,030,717	11,607,285	6,922,442	6,608,366
Flow Rate (dry)	scfh	8,083,203	10,594,153	7,821,332	6,337,931	10,880,855	6,339,469	6,001,203
O2 Concentration Dry	%	15.47	15.07	15.85	14.95	15.00	15.08	15.04
CO AT CATALYST INLET								
CO as ppmvd at 15% O2		70.10	25.02	70.20	69.99	24.99	69.99	69.99
CO Flow	lb/hr	38.6	19.4	34.7	33.1	20.1	32.3	30.8
CO AT CATALYST OUTLET								
CO as ppmvd at 15% O2		5.5	5.5	5.5	5.5	5.5	5.5	5.5
CO Destruction Required	%	92.2	78.0	92.2	92.1	78.0	92.1	92.1
VOC AT CATALYST INLET								
VOC as ppmvd at 15% O2		8.41	3.00	8.42	8.40	3.00	8.40	8.40
VOC AT CATALYST OUTLET								
VOC as ppmvd at 15% O2		2.00	2.00	2.00	2.00	2.00	2.00	2.00
VOC Destruction Required	%	76.2	33.4	76.3	76.2	33.3	76.2	76.2
ADDITIONAL DATA								
Required Pressure Drop	"H_2O	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Expected Pressure Drop	"H_2O	0.7	1.0	0.7	0.7	1.0	0.7	0.7

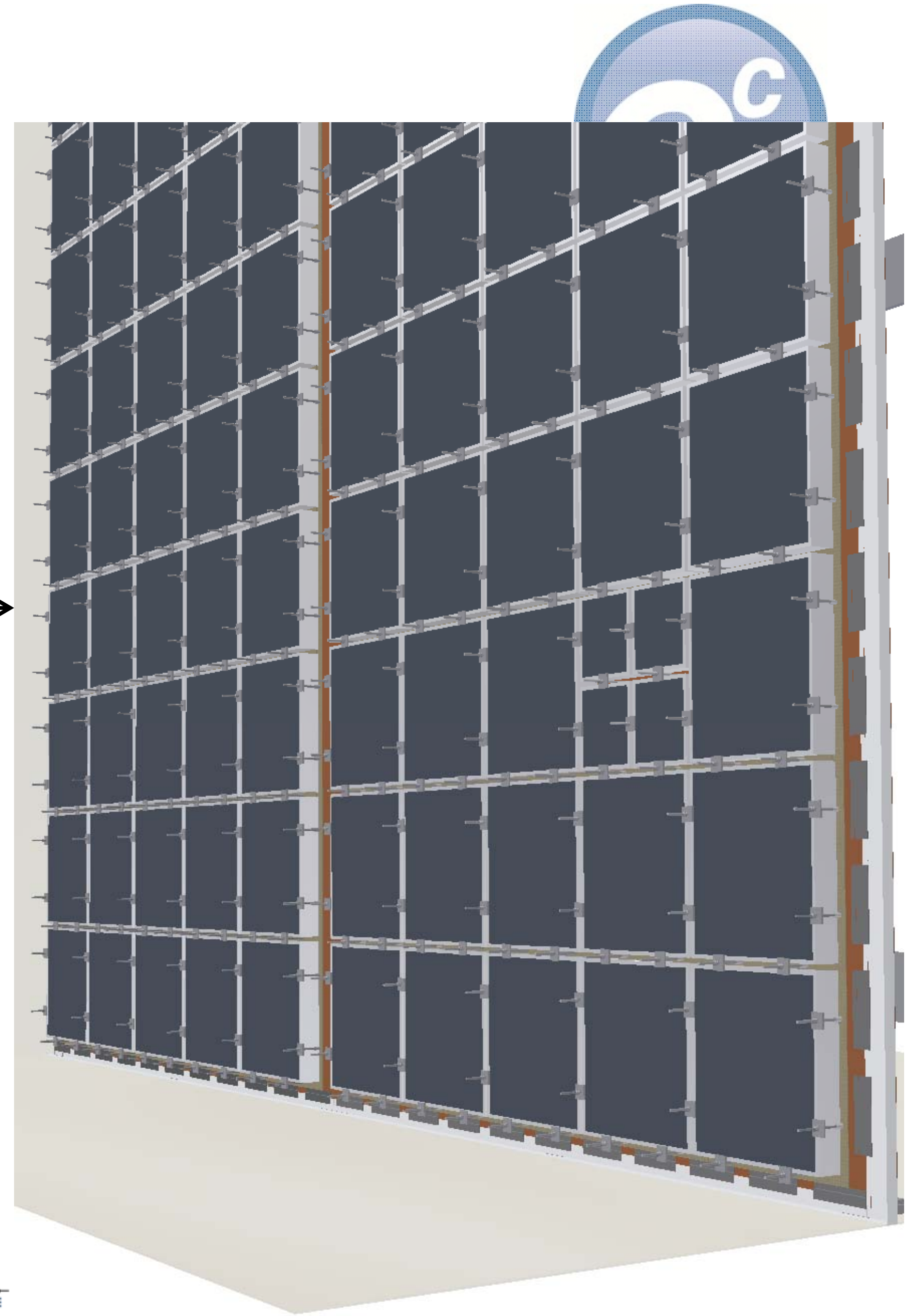
$$\frac{8{,}593{,}971\,\text{scfh}}{165{,}000\,\text{hr}^{-1}} = 52.1\,\text{ft}^3$$



Calculate catalyst depth

IDENTIFY CASE REQUIRING HIGHEST CATALYST VOLUME → CALCULATE CATALYST DEPTH →

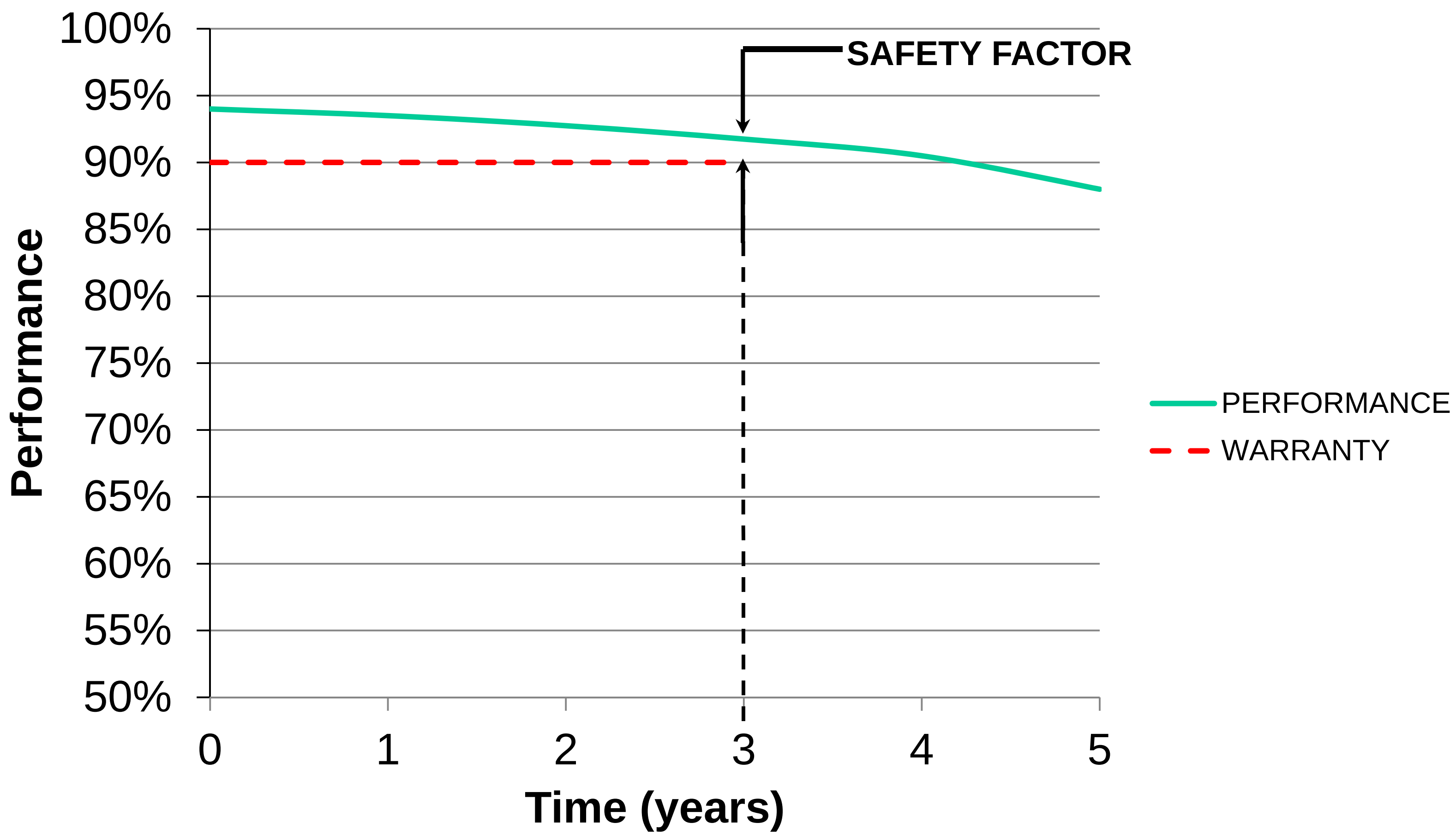




Remember…

- Catalyst performance dictates catalyst volume
  - (for a given cell density, Pt loading, wash coat, etc)
- Once catalyst volume is determined
  - Changing duct size results in thicker or thinner catalyst (to maintain volume)
  - Large frontal area and thin vs. small area and thick
- However, 100 ft^3 of catalyst in 100 modules costs less than 100 ft^3 in 120 modules
- There is a practical *minimum* thickness

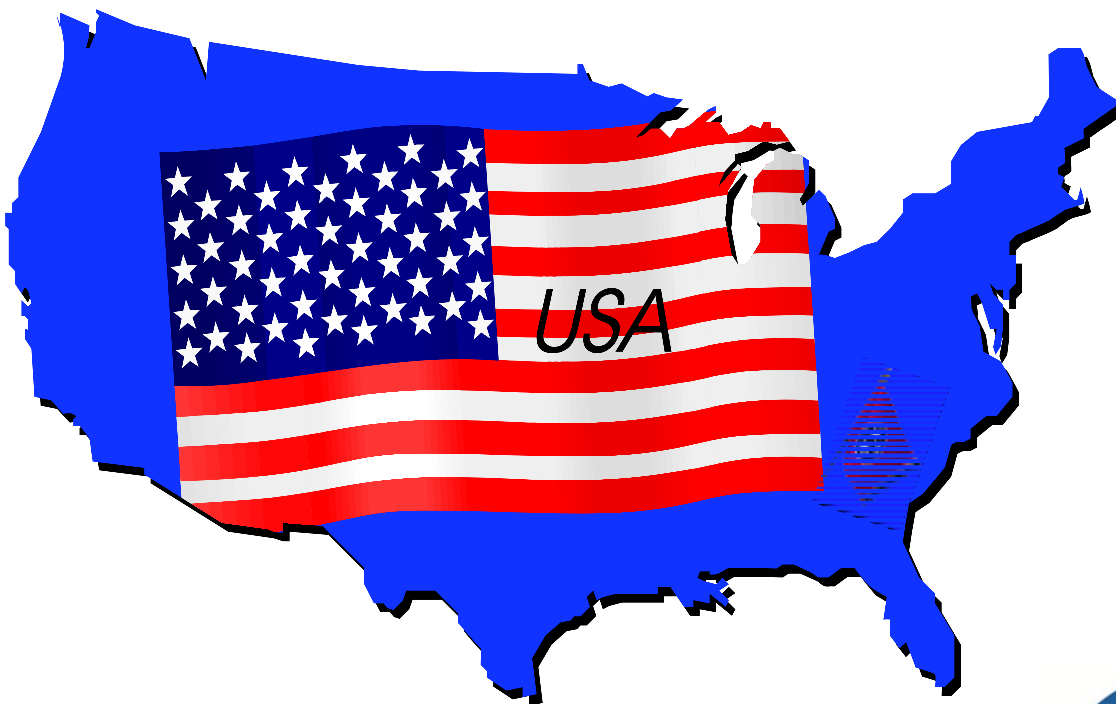
Performance Over Time



Origin of "Safety Factor"

- Emission performance over time is a function of system variables
  - type of combustion turbine
  - start-up profiles (no. starts/stops/yr.)
  - water injection & evap cooling
  - exhaust gas temperature
  - engine fuel composition – particularly **Sulfur**
  - seals, leakage and bypass
  - contaminants present in engine exhaust
  - effect of engine lube oil on catalyst
- Owners don't report data over time for every combination

Thank you from EmeraChem



THE POWER OF CATALYSIS