

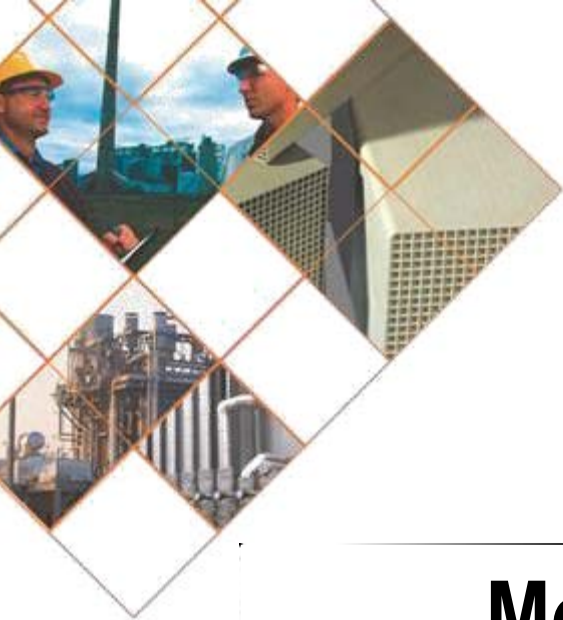
REINHOLD ENVIRONMENTAL Ltd.



**2013 NO_x-Combustion Round Table
& Expo Presentations**

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

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Mercury Oxidation Potential vs. Catalyst Condition

Scot Pritchard

Cormetech, Inc.

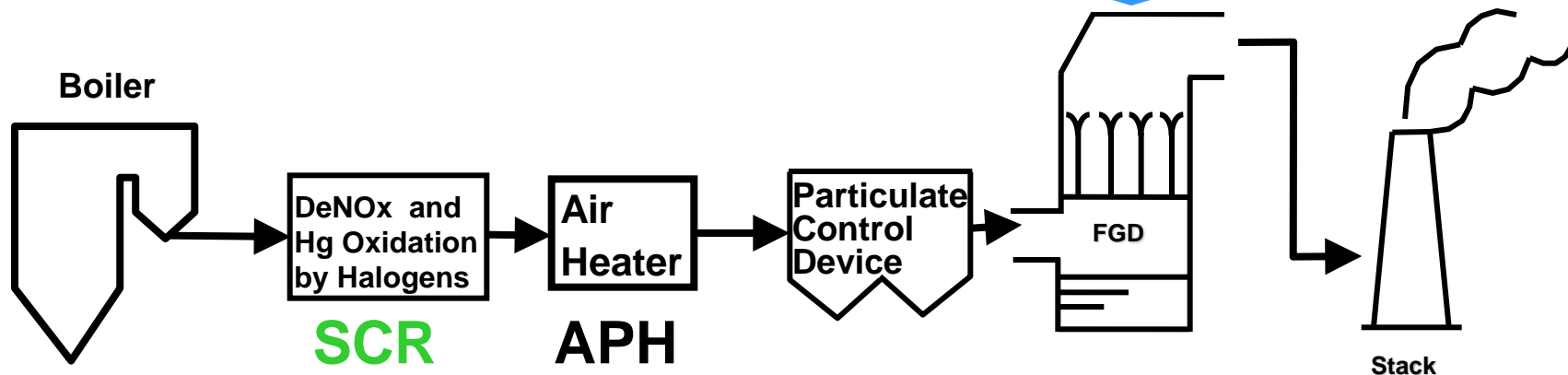
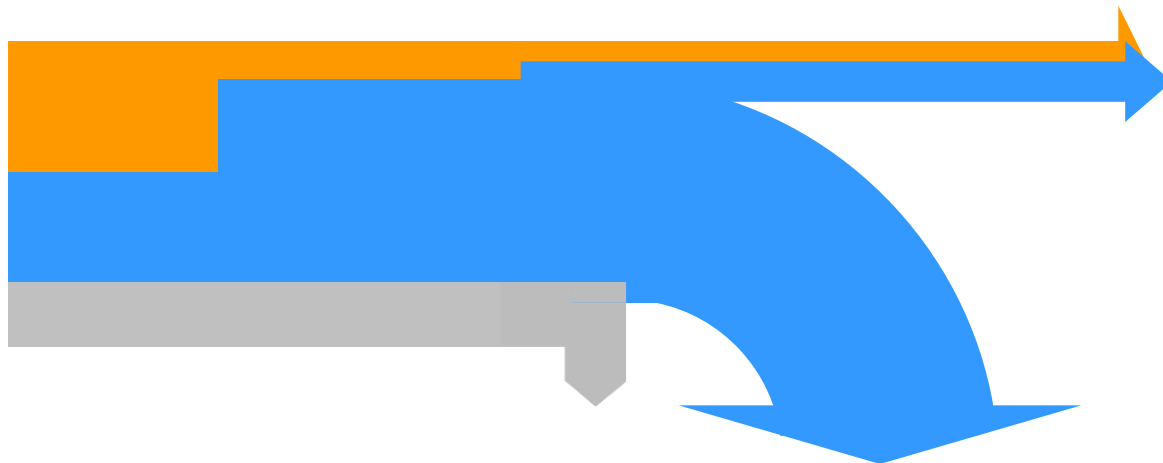
2013 Reinhold NOx-Combustion Round Table

- SCR Hg Oxidation Co-benefit
- DeNOx catalyst selection and management background
- Key Differences between DeNOx & Hg Oxidation
- Catalyst Characterization Process
- Catalyst Improvements
- Evaluation Inputs
- Case Study
- Summary

Background: SCR Co-Benefit



- ① Elemental
- ② Oxidized
- ③ Particle bound



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DeNOx Catalyst Potential, K/AV



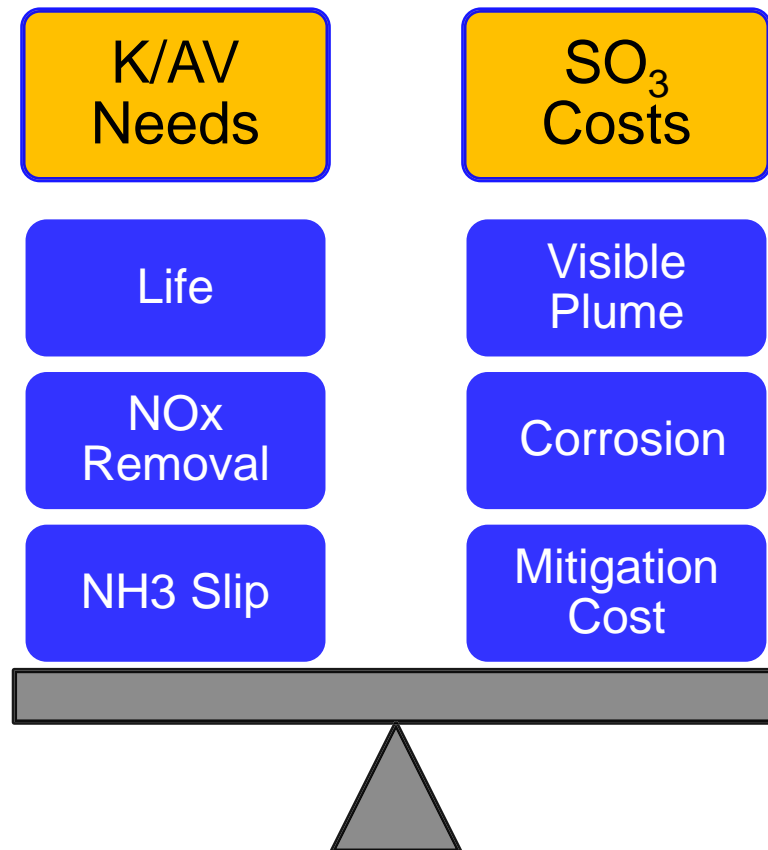
- K/AV defines:
 - capacity for X% DeNOx
 - with less than Y ppm NH3 slip
- Activity, K, depends on
 - Catalyst composition and age
 - Flue gas conditions
- AV = Area Velocity = (Gas Flow) / (Total GSA)
- Common equation for MR = 1 catalyst test:

$$\frac{K}{AV} = -\ln[1 - \% DeNOx]$$

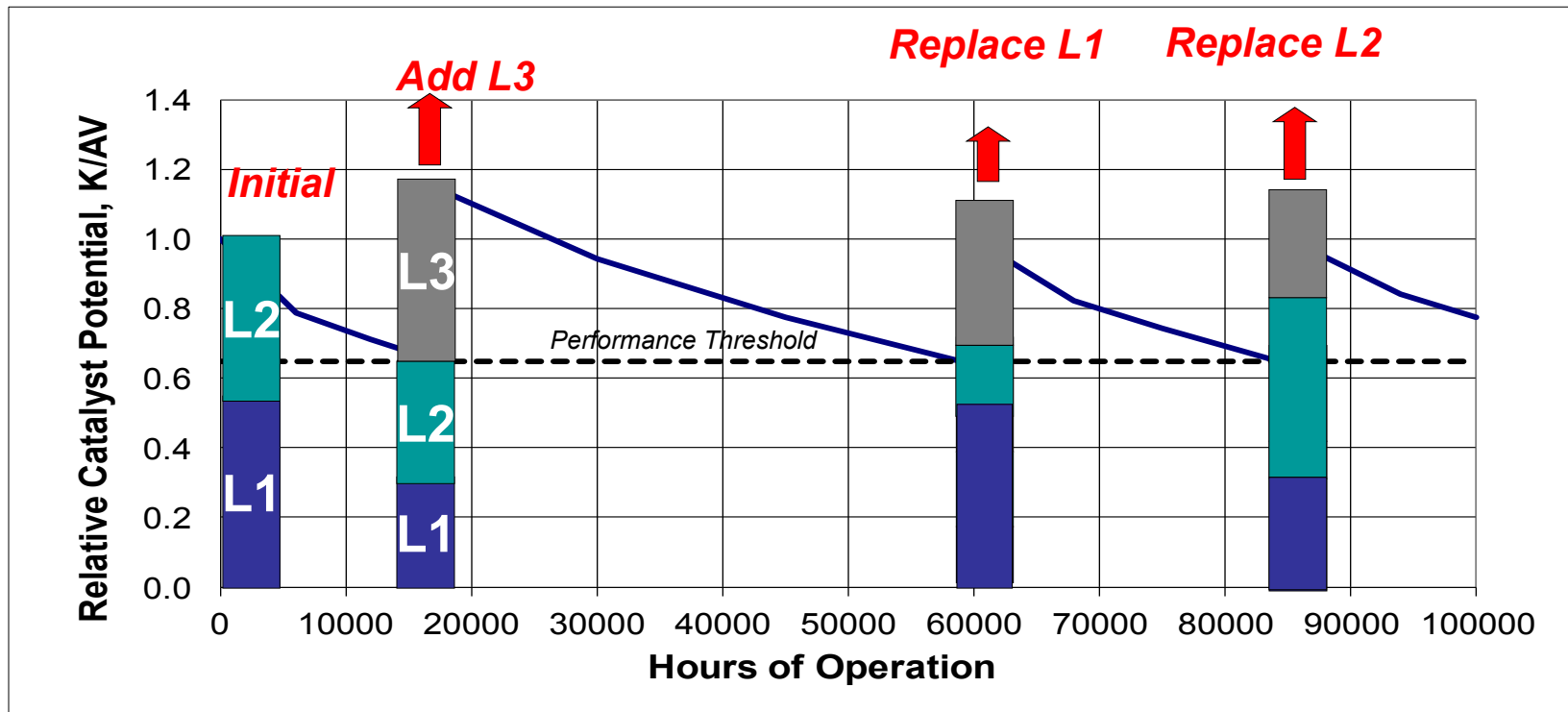
Catalyst Design Balance



Typically catalyst is formulated to achieve DeNO_x requirements while meeting given SO₂ oxidation constraints



DeNOx Catalyst Management Plan



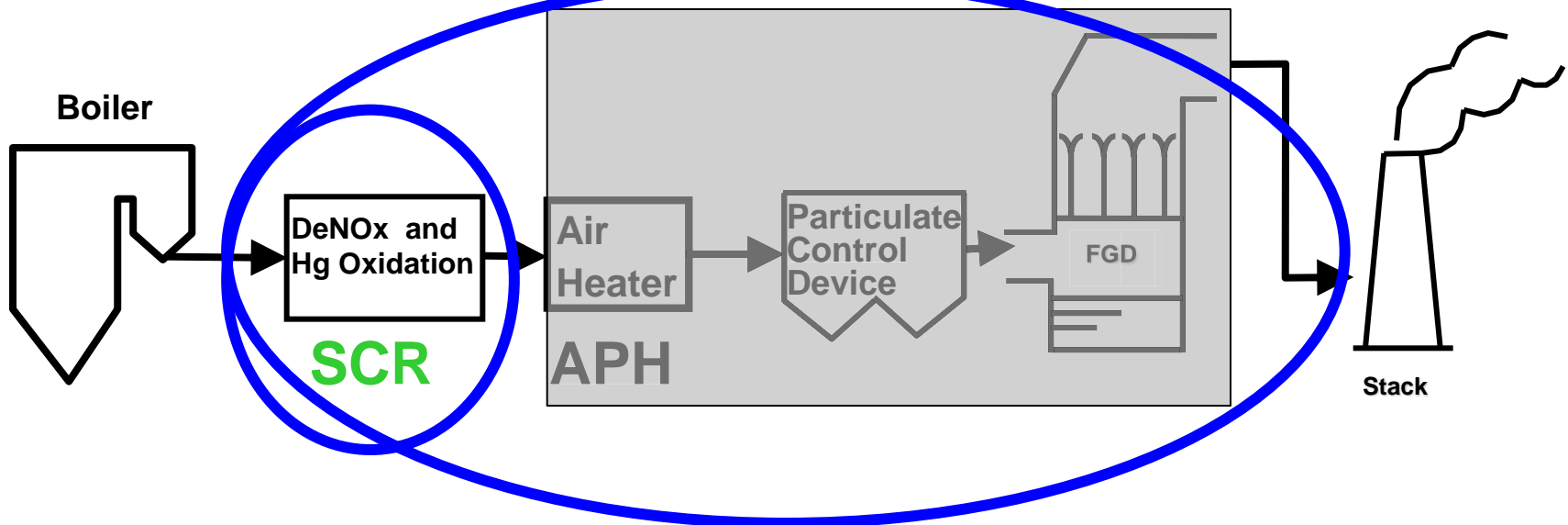
- Catalyst Layer Potentials tracked through periodic lab tests & inspections
- While there is a molar ratio impact the catalytic potential of each layer for the DeNOx reaction can still be reasonably characterized by MR=1 test and are essentially additive
- An analogous approach can be used for Hg oxidation

...but with some key differences which add to the complexity

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Key Differences for Hg vs. NOx

- DeNOx
 - Performance requirements typically well defined due to sole role of the SCR
- Hg
 - Performance requirements for the SCR typically not as well defined due to roles of downstream equipment in total compliance



Key Differences for Hg vs. NOx



DeNOx

– Key Parameters

- NOx inlet
 - Efficiency
 - Slip
- } **Performance Threshold**
- Temperature
 - SO₂ conversion (formulation)
 - Fuel → contaminants → K/Ko
 - Reactor condition
 - O₂, H₂O, SO₂ (lower impact)

Hg

– Key Parameters

- NOx inlet
 - Efficiency
 - Slip
- } **NH₃**
- Hg oxidation → Performance Threshold
 - Temperature
 - SO₂ conversion (formulation)
 - Fuel → contaminants → K/Ko
 - Reactor condition
 - Halogen (Fuel or additive)
 - Layer position (NH₃)
 - CO
 - O₂, H₂O, SO₂ (can be larger impact)

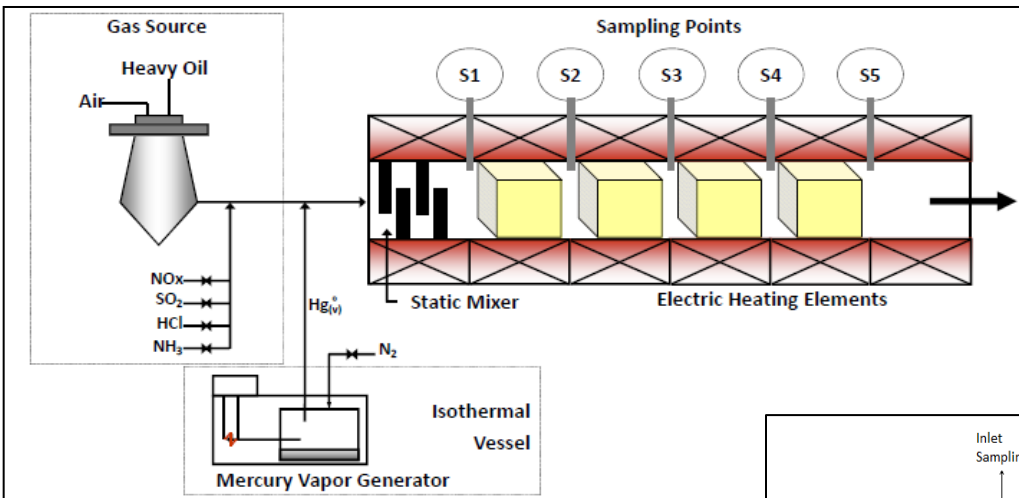
Catalyst Deactivation



- The deactivation trend for DeNox and Hg Oxidation from a catalytic potential under a defined test condition is similar however;
- Due to the additional parameters which influence the Hg oxidation reaction and the interdependency on the DeNox reaction, in terms of ammonia concentration throughout the catalyst layer(s), the trend alone does not provide enough information to form a management plan decision
- Therefore parametric tests and accurate modeling are necessary to assist with the management decision

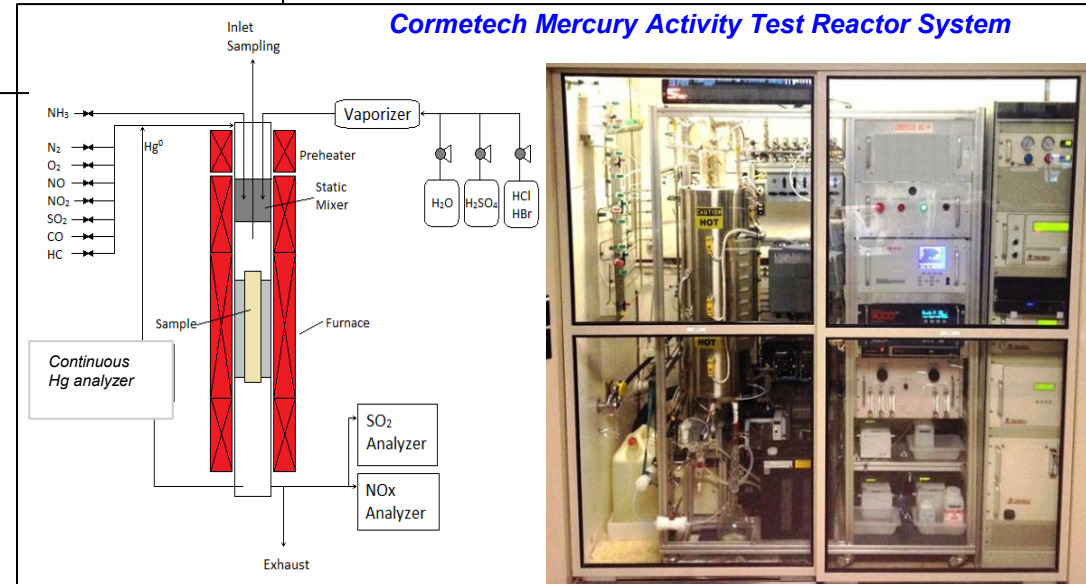
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Test Reactor Capabilities



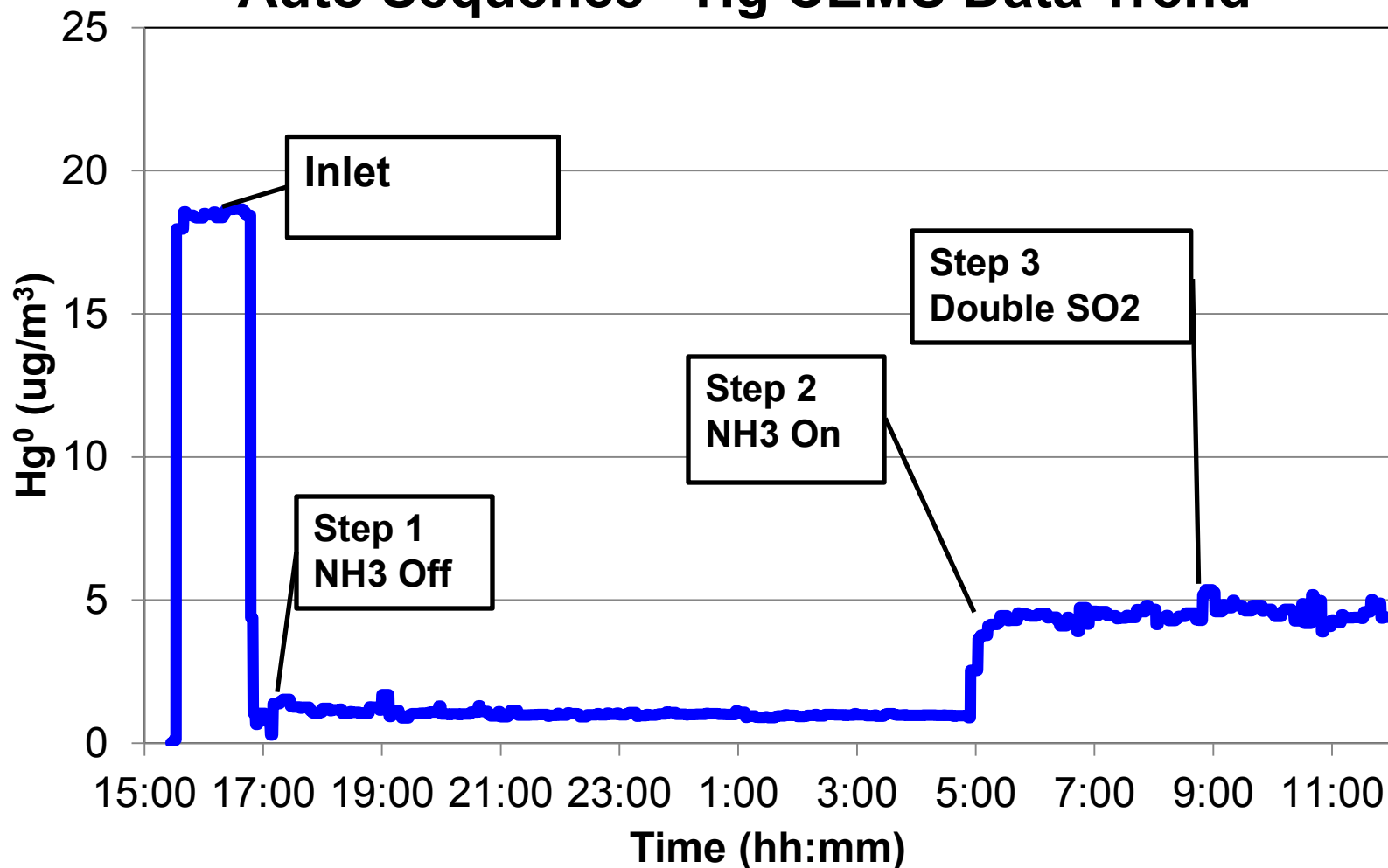
Courtesy of:  **MITSUBISHI HEAVY INDUSTRIES, LTD. TECHNICAL HEADQUARTERS**

- Collecting Hg oxidation data for development, designs, deactivation studies, and quality assurance since 2002.
- Allows necessary characterization of catalyst of any type/vintage



Automation allows us to understand the impact of many factors and interactions

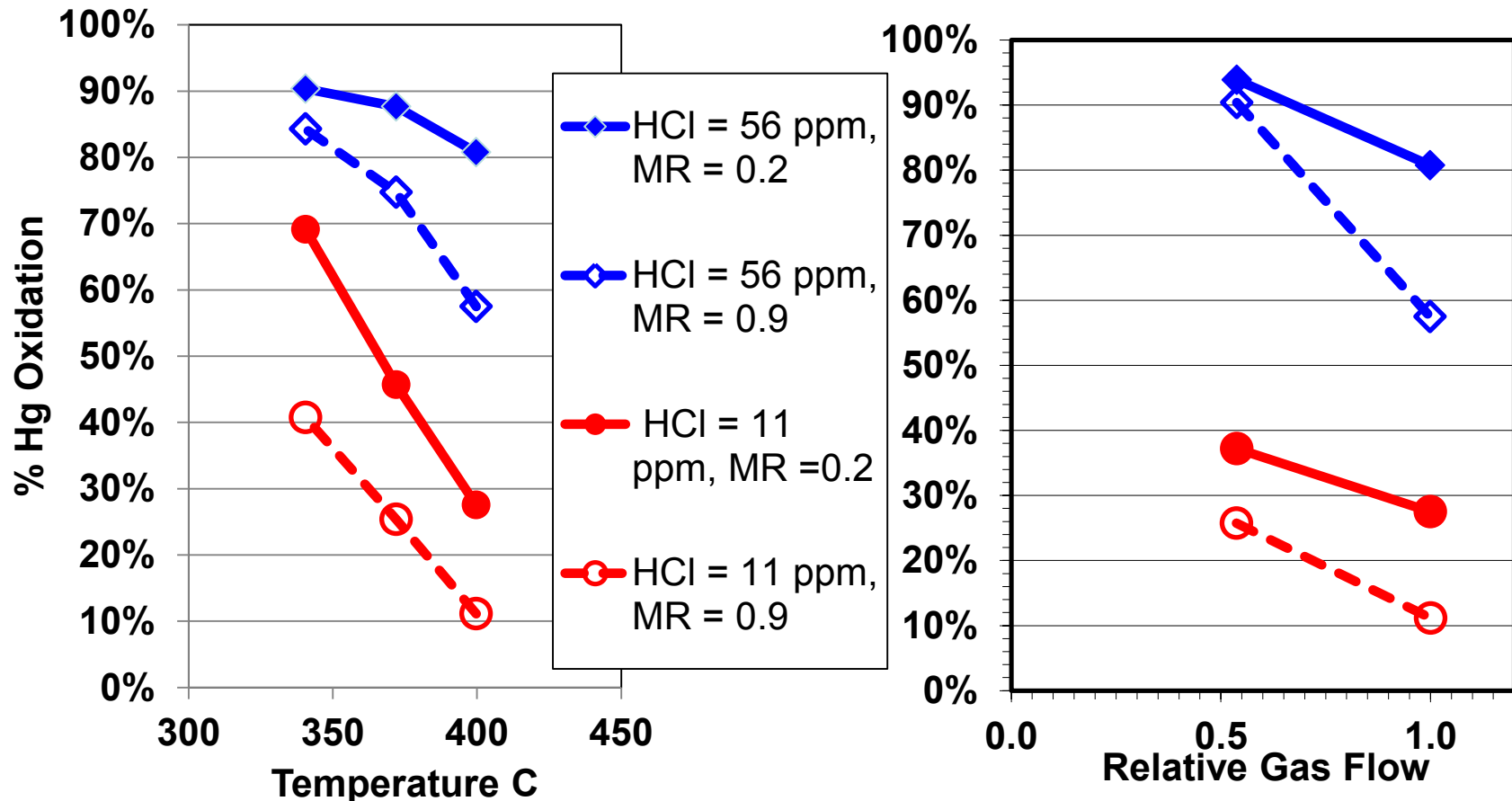
Auto Sequence - Hg CEMS Data Trend



Understanding Parameter Impacts



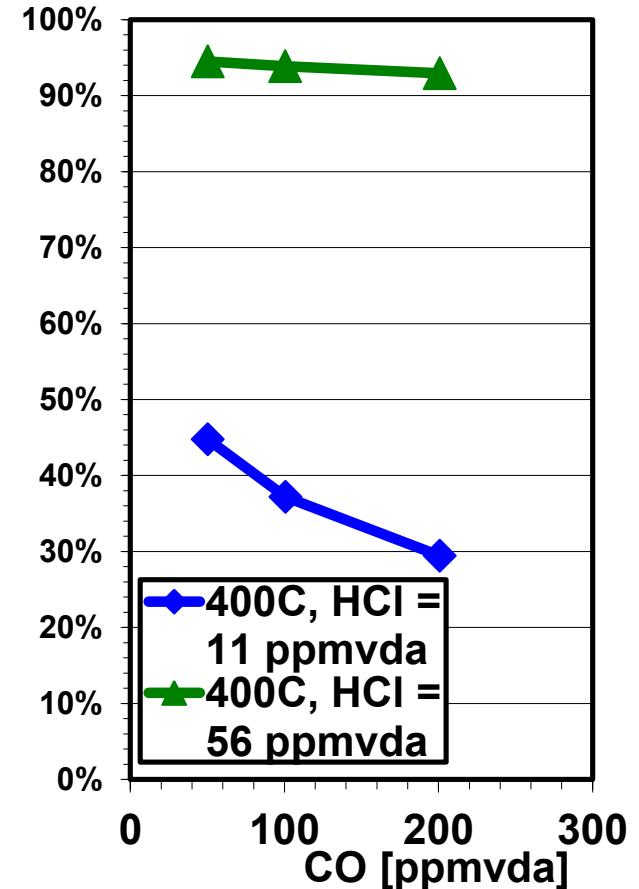
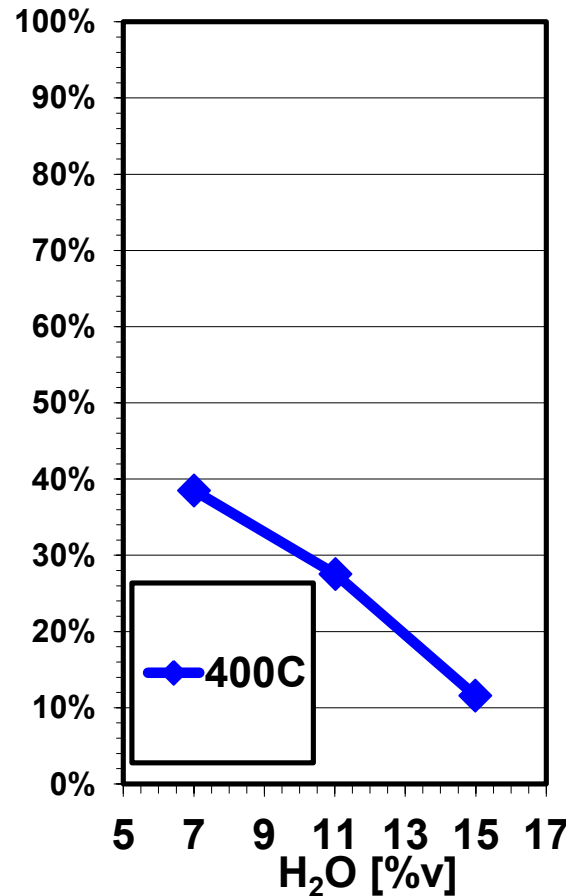
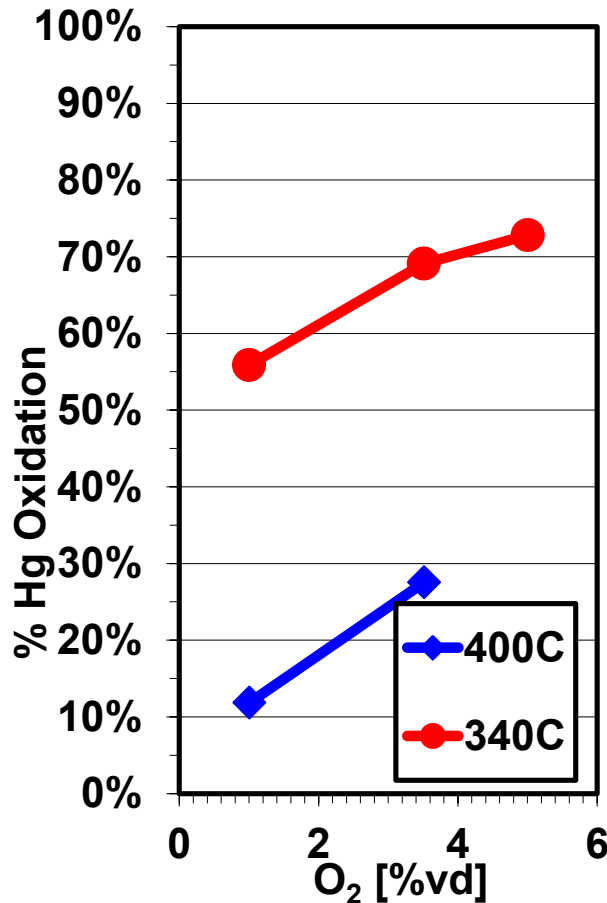
(Temperature, Flow, Halogens)



- Highest temperature with highest flow (i.e. Full load) typically design condition.
- Temperature impact more significant than for DeNOx and condition dependent
- Distribution of HCl content must be considered (May result in more than one design condition).

Understanding Parameter Impacts

(O₂, H₂O, CO)

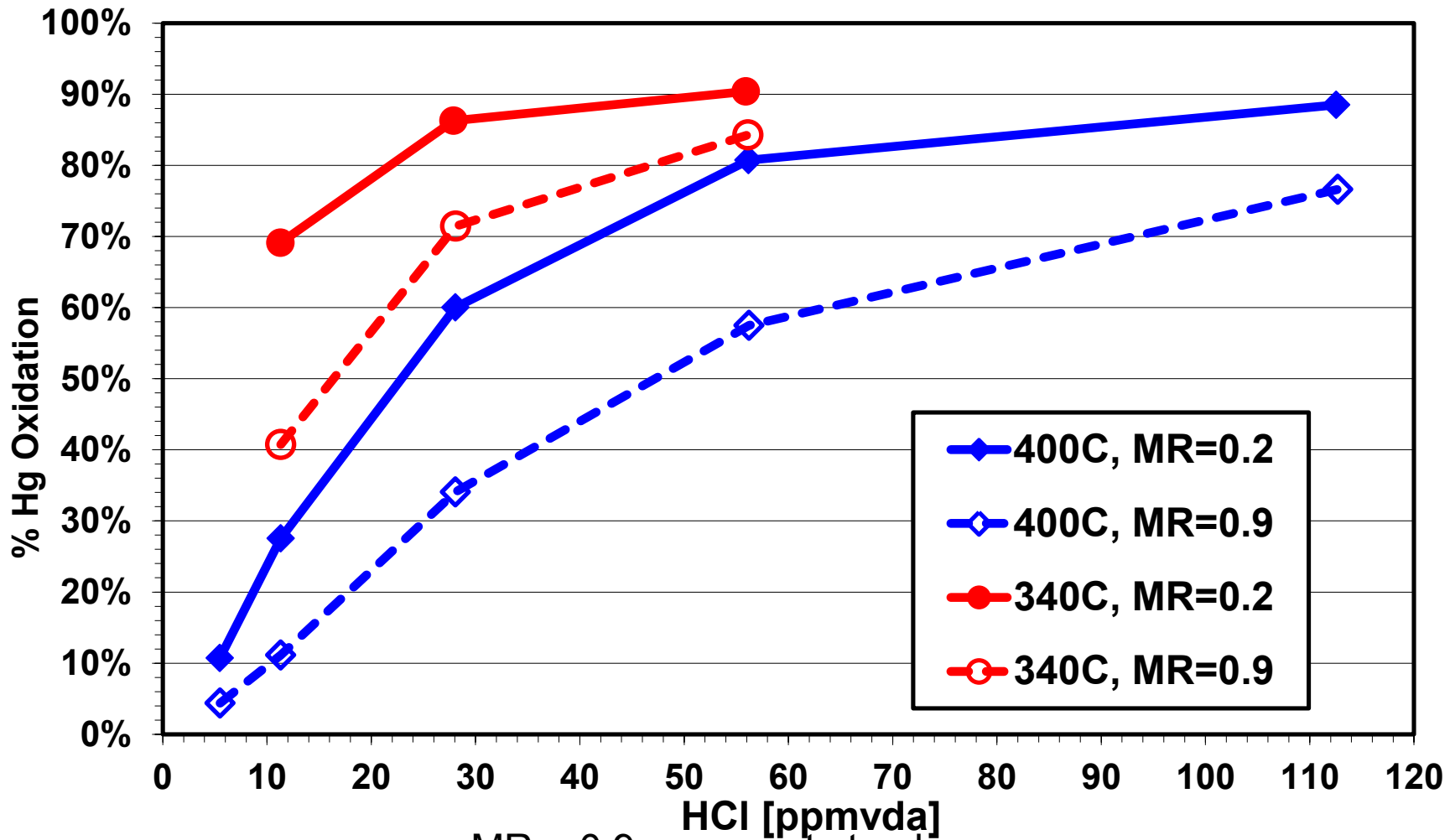


- O₂, H₂O and CO have significant impact (minimal impact on DeNO_x);
- Impact is condition dependent (CO for example)
- Distribution of these parameters should be considered in setting design conditions.

Understanding Parameter Impacts



Layer Dependency



MR = 0.9 represents top layer
MR = 0.2 represents a lower layer

Understanding Parameter Impacts



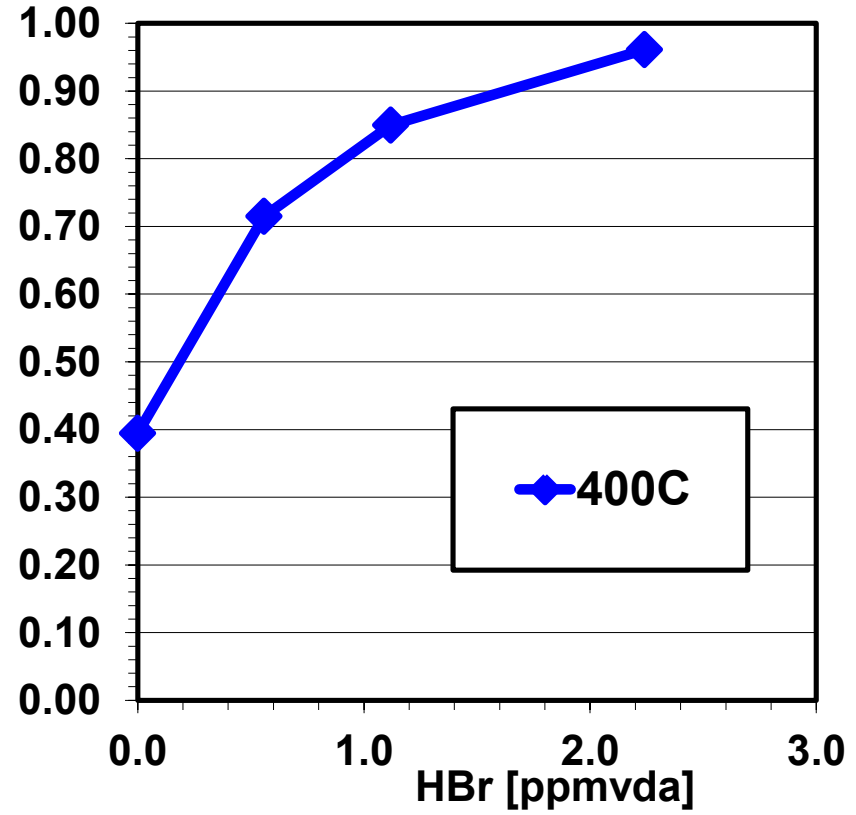
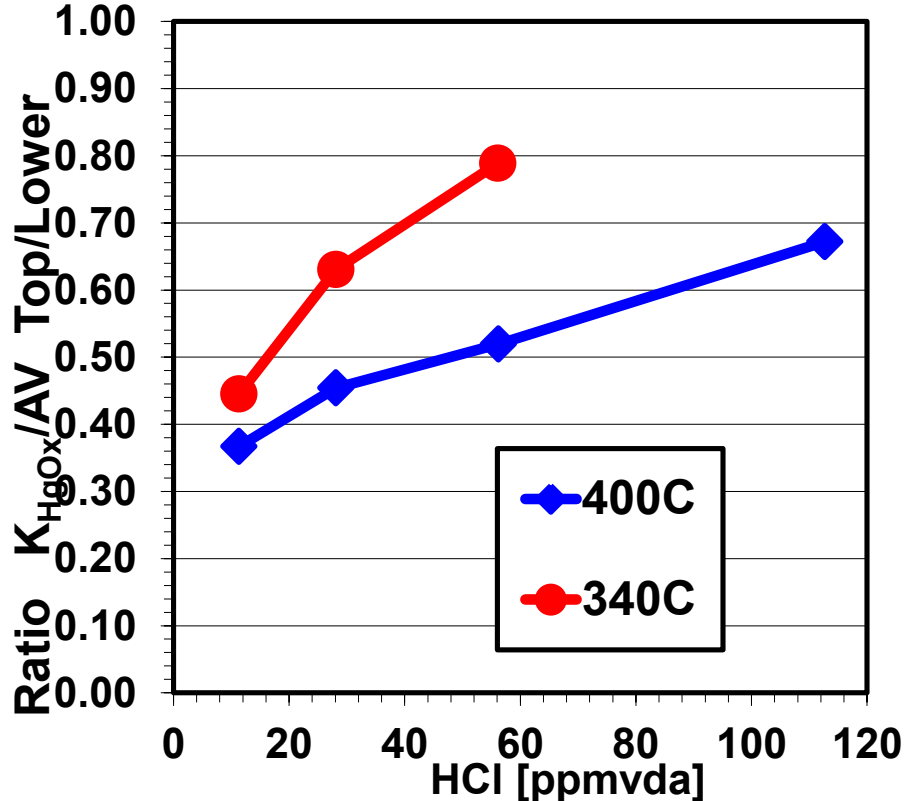
Layer Dependency

$$\frac{K}{AV} = -\ln[1 - \% DeNO_x] \quad \text{For Illustration} \quad \xrightarrow{\text{---}} \quad \frac{K_{HgOx}}{AV} = -\ln[1 - \% HgO_x]$$

@ MR=1

$$\frac{K_{HgOx}}{AV} = -\ln[1 - \% HgO_x]$$

f(variable MR)



- Due NH3 inhibition, Hg oxidation potential depends on layer position.
- The degree of dependency is dependent on temperature and halogen content

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Catalyst Improvements



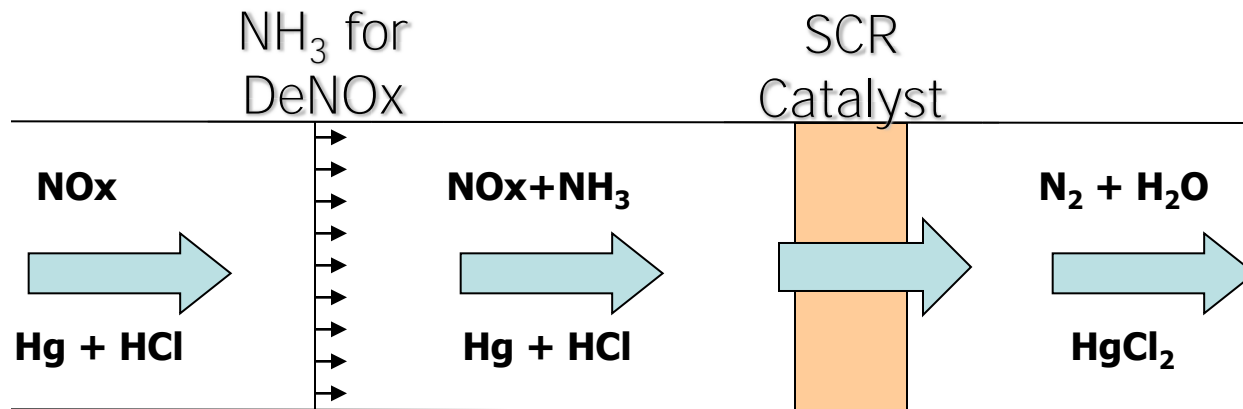
Desired Reactions:



(NO_x Reduction)



(Hg Oxidation)



Undesired Reactions:



(HgCl₂ Reduction by NH₃)



(HgCl₂ Reduction by SO₂)

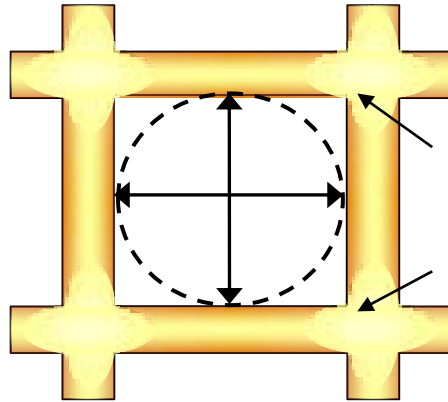


(SO₂ Oxidation)

Enhance Desired Reactions while reducing Undesired Reactions

Catalyst Improvements

- Catalyst Properties & Reaction Mechanisms

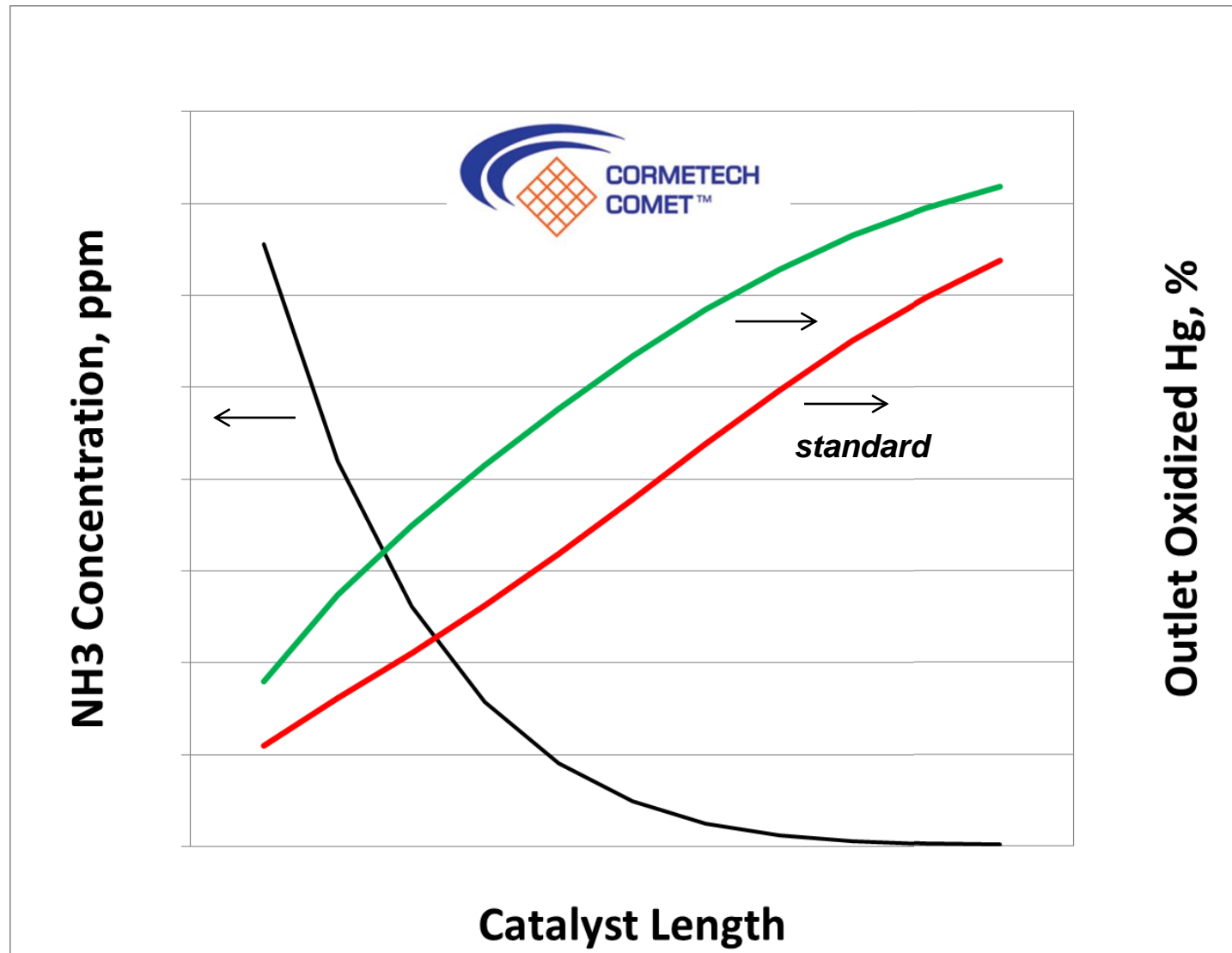


*Fast DeNO_x and Hg ox reactions limited by mass transport to wall (esp. corners).
Slow SO₂ oxidation reaction is not.*

Patented Gradient Technology allows optimized utilization of active components

- Catalyst Formulations
 - Enhanced formulations which allow greater utilization and/or enhanced capability to apply higher levels of active components through suppression of negative reactions

Ammonia & Hg Ox. vs. Length

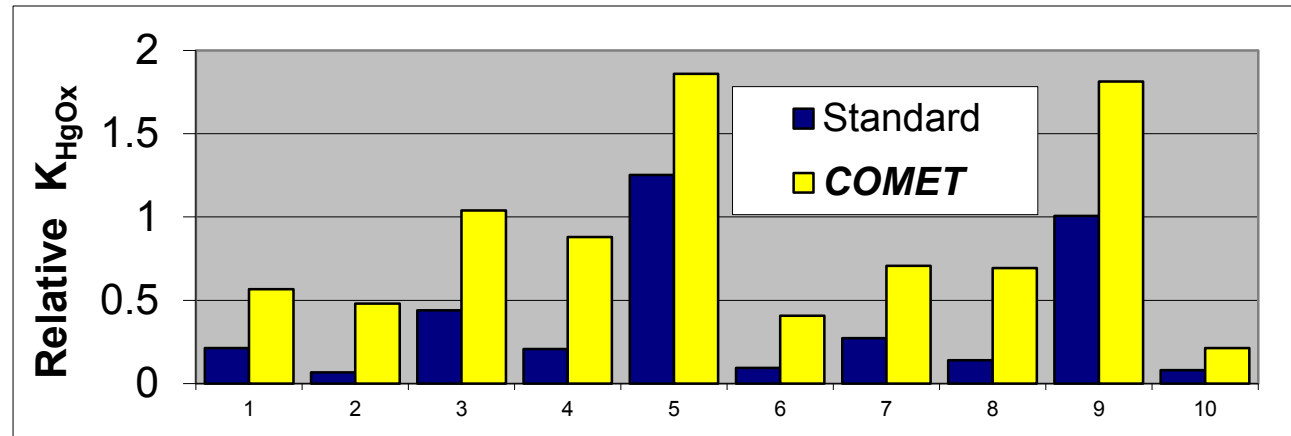


Catalyst Improvements



PRB Unit - Case Study: COMET™ –vs-Traditional

Constants	
Temp C	403
NOx ppm	107
O2 %	3.5
H2O %	14
SO2 ppm	345
HCl ppm	8



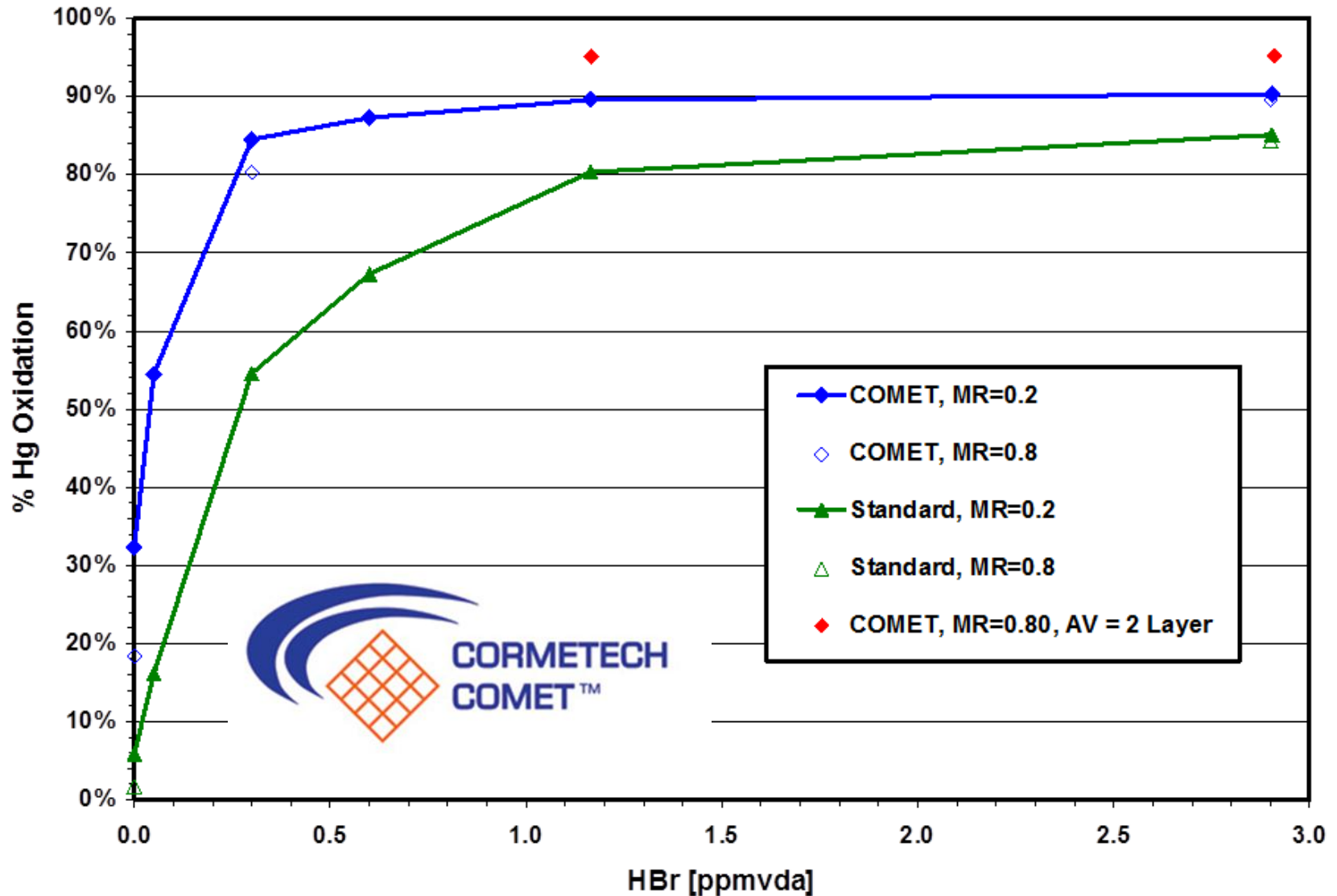
NH3	ppm	0	0	0	0	0	21	21	21	21	86
CO	ppm	0	100	0	100	0	0	0	100	0	0
HBr	ppm	0	0	0.1	0.1	1	0	0.1	0.1	1	0

**From 50% to 400% higher Hg ox Activity
With 10% higher DeNOx Activity**

SO₂ conversion maintained & lowered sensitivity to reducing species

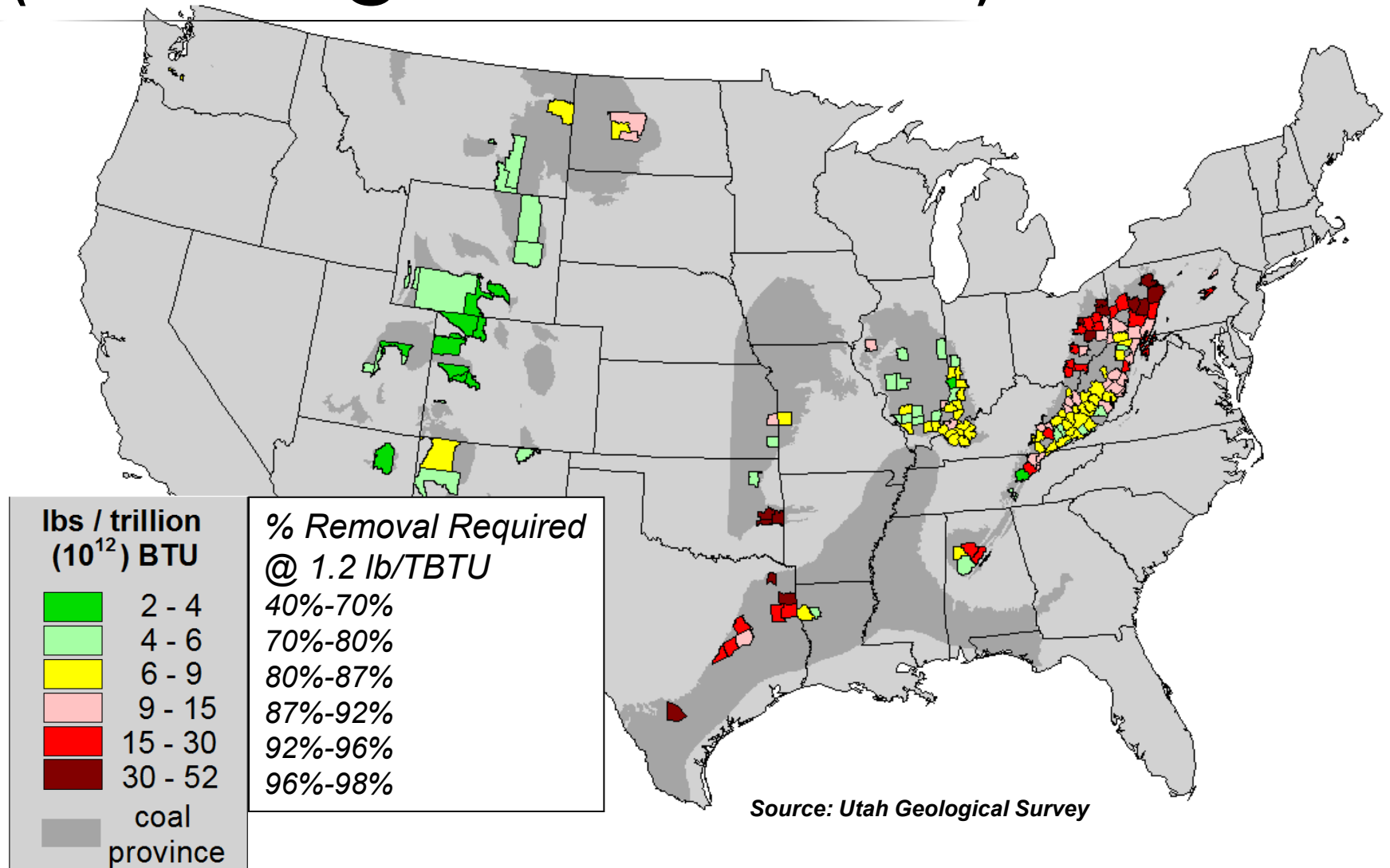
Levers can be custom balanced to reduce SO₂ conversion with same DeNox activity, etc.

Catalyst Improvements

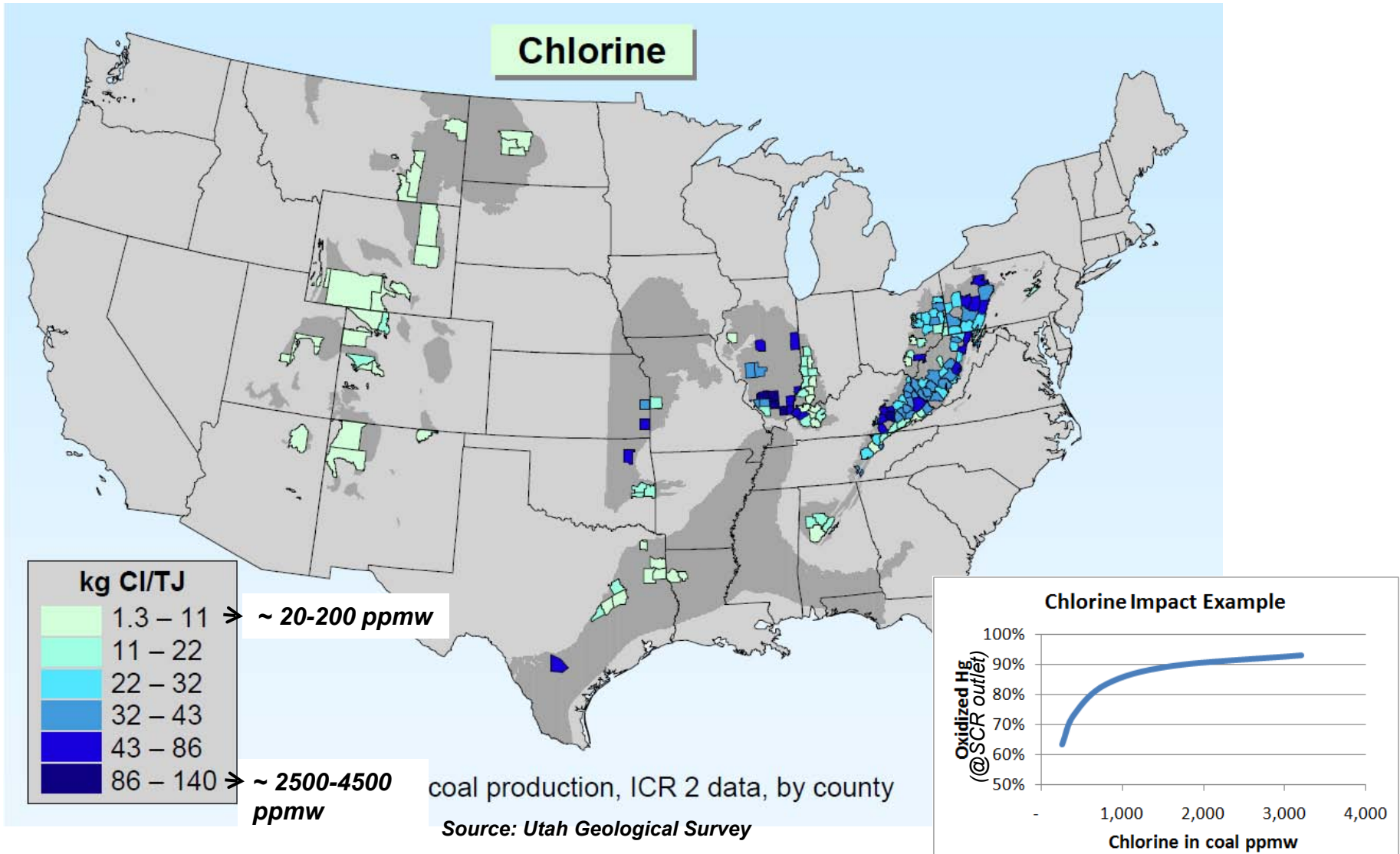


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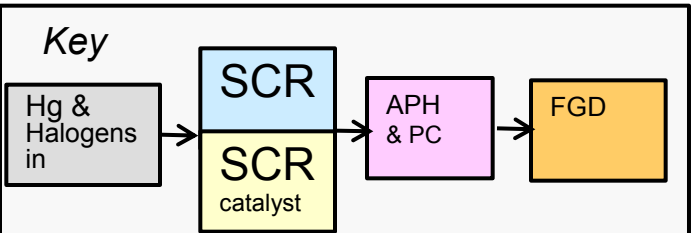
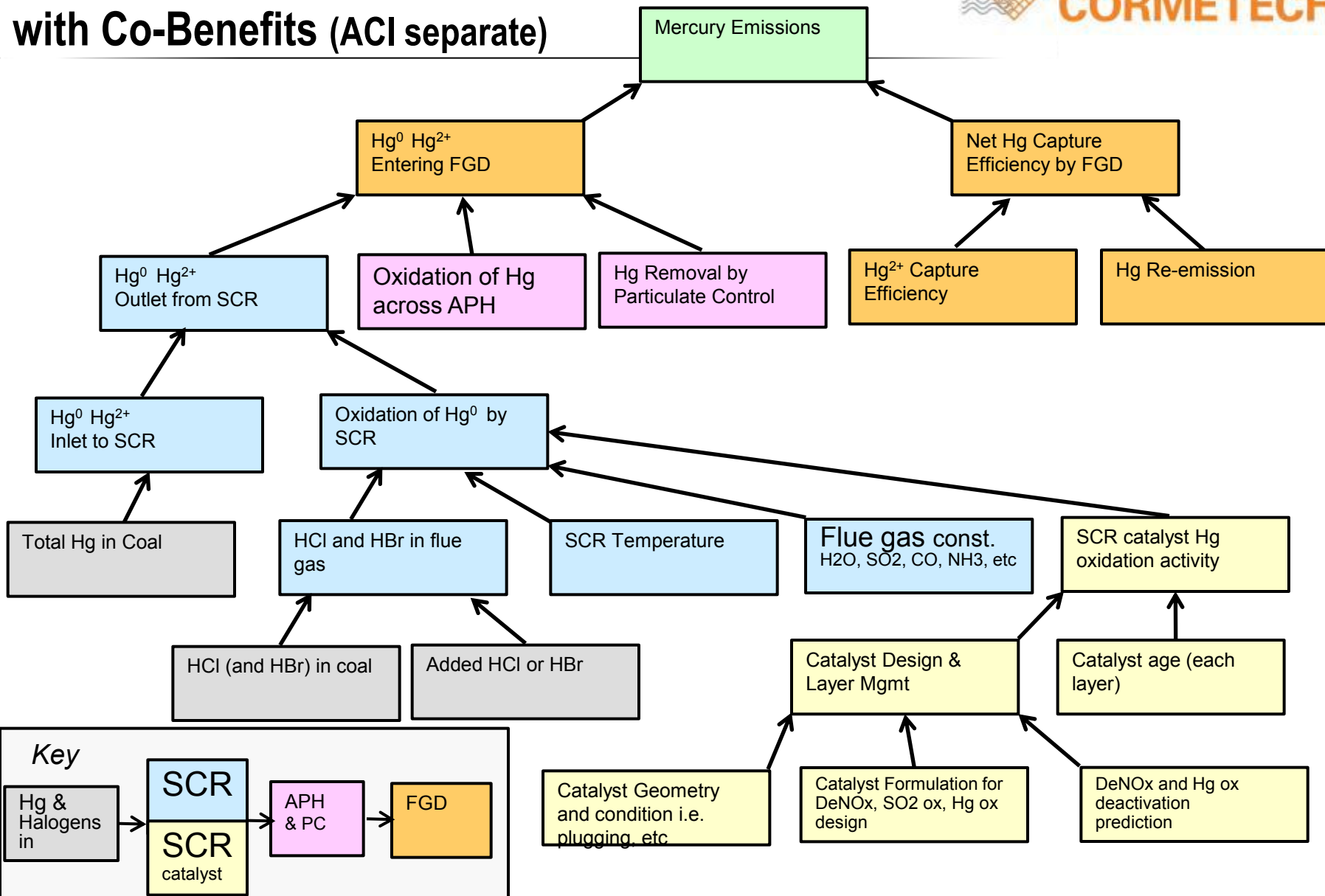
Key factors: Hg in Coal (% Removal @ 1.2 lb/TBTU emission)



Key factors: Chlorine in Coal



Background: Key Factors Impacting Hg Emissions with Co-Benefits (ACI separate)



Evaluation to set Catalyst Targets



No Halogen, ACI or DSI

Ib/Tbtu	Inlet	SCR	APH	PM/ACI	FGD	Net Reduction/Outlet	Notes
	10						
SCR							
Oxidation efficiency		84%					
Oxidized in device		8.37					
Elemental from device		1.63					
APH							
Oxidation efficiency			35%				
Oxidized in device			0.57				
Elemental from device			1.06				
Total oxidized			8.94				
ESP/Baghouse + optional ACI							
	no ACI						
Oxidation efficiency				10%			
Oxidized in device				0.11			
Elemental from device				0.95			
Total oxidized				9.05			
Particulate removal % elemental				10%			
Particulate removal % oxidized				10%			
Net elemental from device				0.86			
Net oxidized from device				8.14			
WFGD							
Collection efficiency					96%		
Oxidized available for collection					8.14		
Elemental					0.86		
						88.0%	
Outlet (No credit for PM bound)						1.2	Outlet Hg elemental + oxidized
						10.00	balance check

Note: No halogen injection in this case therefore no additional Hg Ox benefit taken for interaction

Evaluation to set Catalyst Targets



With DSI -- No Halogen, or ACI

Ib/Tbtu	Inlet	SCR	APH	PM/ACI	FGD	Net Reduction/Outlet	Notes
	10						
SCR							
Oxidation efficiency		81%					may also benefit SCR cat act.
Oxidized in device		8.05					
Elemental from device		1.95					
APH							
Oxidation efficiency	w/ DSI		50%				lower APH outlet temp
Oxidized in device			0.97				
Elemental from device			0.97				
Total oxidized			9.03				
ESP/Baghouse + optional ACI							
	w/o ACI						
Oxidation efficiency				10%			
Oxidized in device				0.10			
Elemental from device				0.88			
Total oxidized				9.12			
Particulate removal % elemental				10%			
Particulate removal % oxidized				10%			
Net elemental from device				0.79			
Net oxidized from device				8.21			
WFGD							
Collection efficiency					95%		
Oxidized available for collection					8.21		
Elemental					0.79		
Outlet (No credit for PM bound)						88.0%	
						1.2	Outlet Hg elemental + oxidized
						10.00	balance check

Note: No halogen injection in this case therefore no additional Hg Ox benefit taken for interaction

Evaluation to set Catalyst Targets



With ACI -- No Halogen, or DSI

Ib/Tbtu	Inlet	SCR	APH	PM/ACI	FGD	Net Reduction/Outlet	Notes
	10						
SCR							
Oxidation efficiency		78%					
Oxidized in device		7.75					
Elemental from device		2.25					
APH							
Oxidation efficiency			35%				
Oxidized in device			0.79				
Elemental from device			1.46				
Total oxidized			8.54				
ESP/Baghouse + optional ACI							
	w/ACI						
Oxidation efficiency				40%			low-med ACI usage/effect
Oxidized in device				0.58			
Elemental from device				0.88			
Total oxidized				9.12			
Particulate removal % elemental				10%			
Particulate removal % oxidized				10%			
Net elemental from device				0.79			
Net oxidized from device				8.21			
WFGD							
Collection efficiency					95%		
Oxidized available for collection					8.21		
Elemental					0.79		
Outlet (No credit for PM bound)						88.0%	
						1.2	Outlet Hg elemental + oxidized
						10.00	balance check

Note: No halogen injection in this case therefore no additional Hg Ox benefit taken for interaction

Evaluation to set Catalyst Targets



With ACI & DSI -- No Halogen

Ib/Tbtu	Inlet	SCR	APH	PM/ACI	FGD	Net Reduction/Outlet	Notes
	10						
SCR							
Oxidation efficiency		56%					may also benefit SCR cat act.
Oxidized in device		5.61					
Elemental from device		4.39					
APH							
Oxidation efficiency	w/ DSI		50%				lower APH outlet temp
Oxidized in device			2.19				
Elemental from device			2.19				
Total oxidized			7.81				
ESP/Baghouse + optional ACI							
Oxidation efficiency	w/ACI			60%			mod. ACI use/effect (lower SO3)
Oxidized in device				1.32			
Elemental from device				0.88			
Total oxidized				9.12			
Particulate removal % elemental				10%			
Particulate removal % oxidized				10%			
Net elemental from device				0.79			
Net oxidized from device				8.21			
WFGD							
Collection efficiency					95%		
Oxidized available for collection					8.21		
Elemental					0.79		
						88.0%	
Outlet (No credit for PM bound)						1.2	Outlet Hg elemental + oxidized
						10.00	balance check

Note: No halogen injection in this case therefore no additional Hg Ox benefit taken for interaction

Target Summary



Inlet Hg lb/Tbtu		10	10	10	10	20
	Outlet Hg lb/Tbtu					
SCR Requirement	1.2	84%	81%	78%	56%	91%
SCR Requirement	1.0	88%	86%	84%	68%	97%
DSI		✗	✓	✗	✓	✓
ACI		✗	✗	✓	✓	✓
APH		✓	✓	✓	✓	✓
PM		✓	✓	✓	✓	✓
FGD		✓	✓	✓	✓	✓

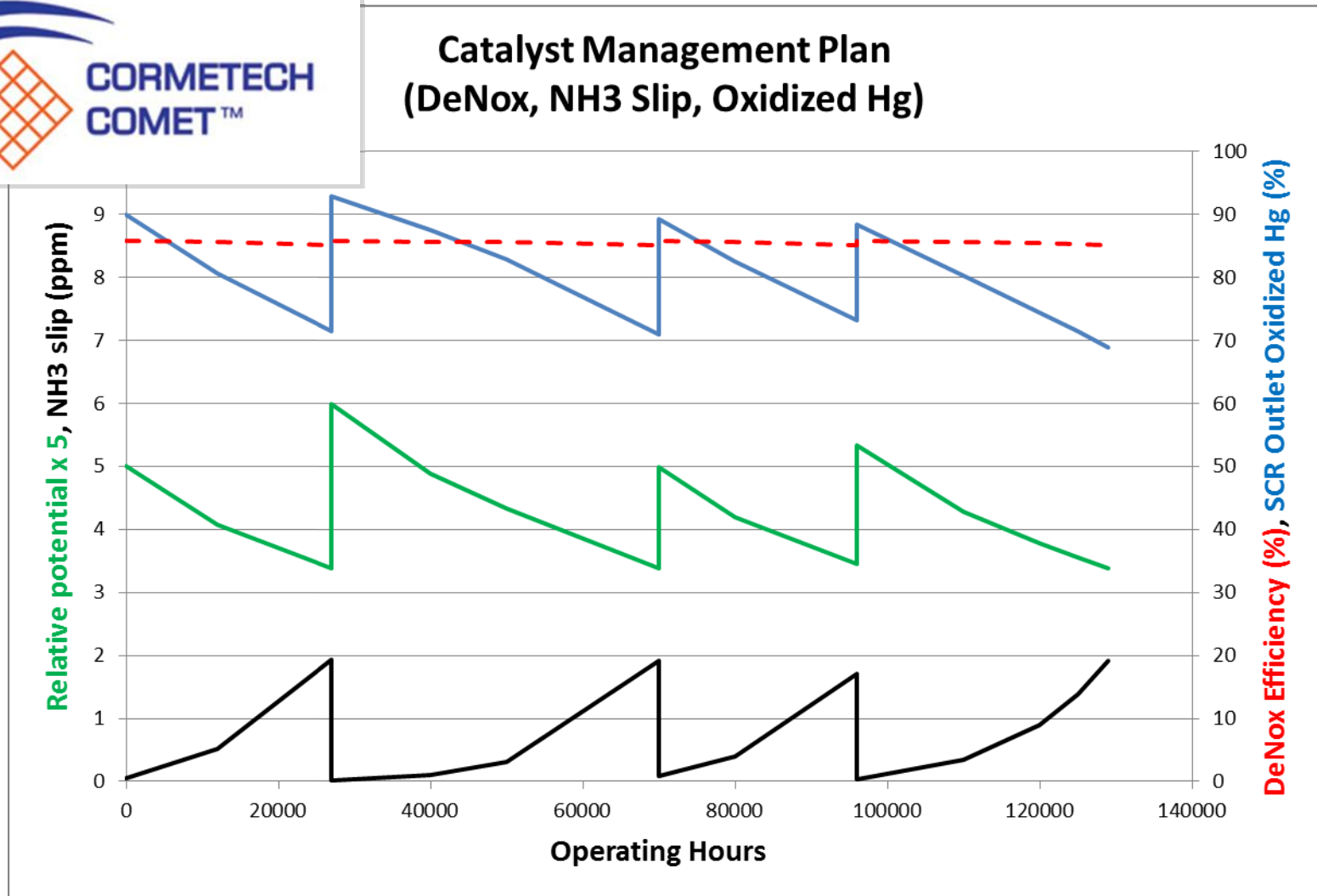
Note: No non-SCR halogen injection benefit or Hg PM slip assumed in scenarios shown

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Management Plan w/ DeNox Potential & Hg Oxidation



**Catalyst Management Plan
(DeNox, NH3 Slip, Oxidized Hg)**

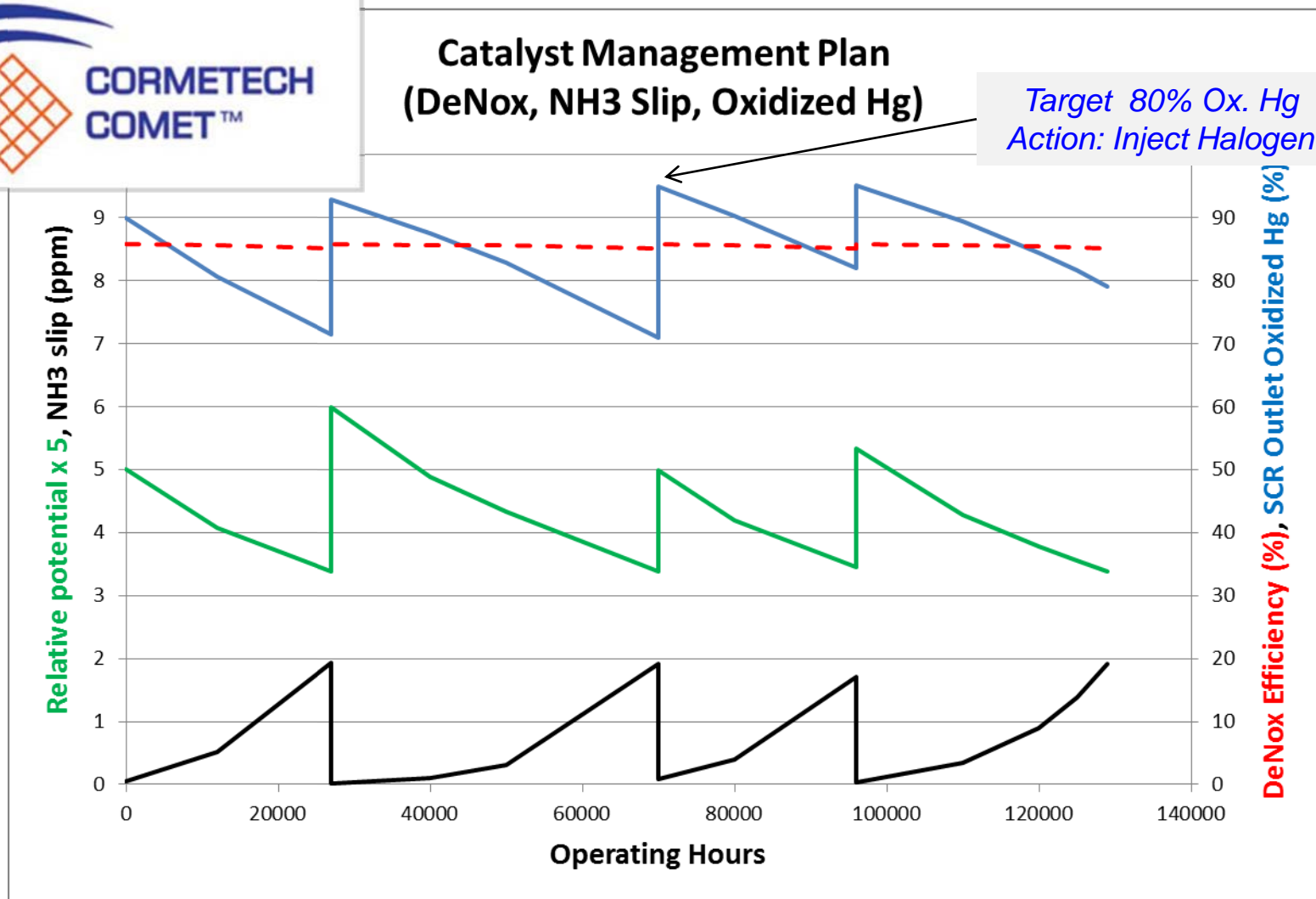


Management Plan w/ DeNox Potential & Hg Oxidation



Catalyst Management Plan (DeNox, NH3 Slip, Oxidized Hg)

Target 80% Ox. Hg
Action: Inject Halogen

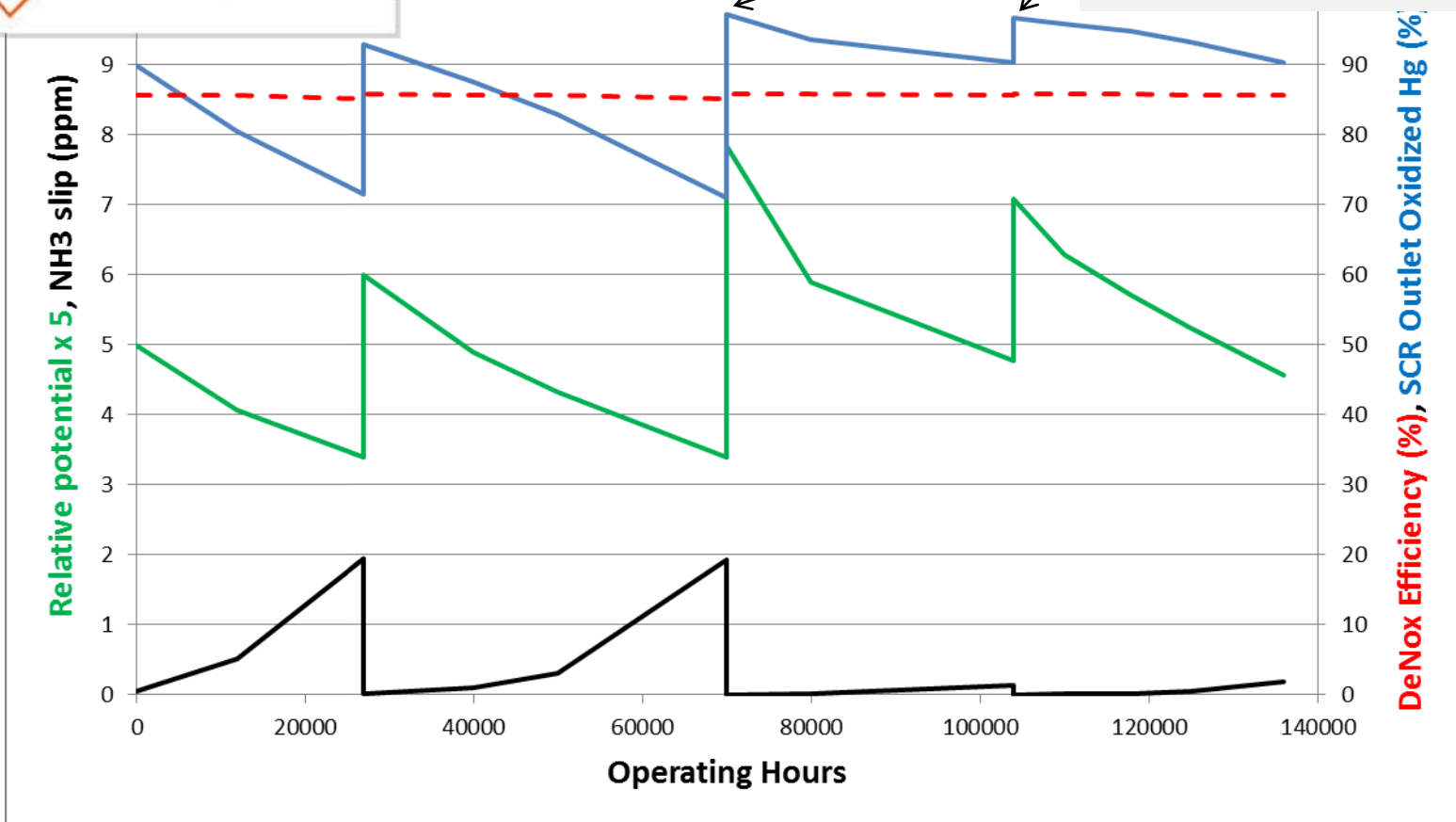


Management Plan w/ DeNox Potential & Hg Oxidation



**Catalyst Management Plan
(DeNox, NH3 Slip, Oxidized Hg)**

*Target: 90% Ox. Hg
Action: Initially change
2 layers to Max length
COMET™ and repeat
for layer 3*

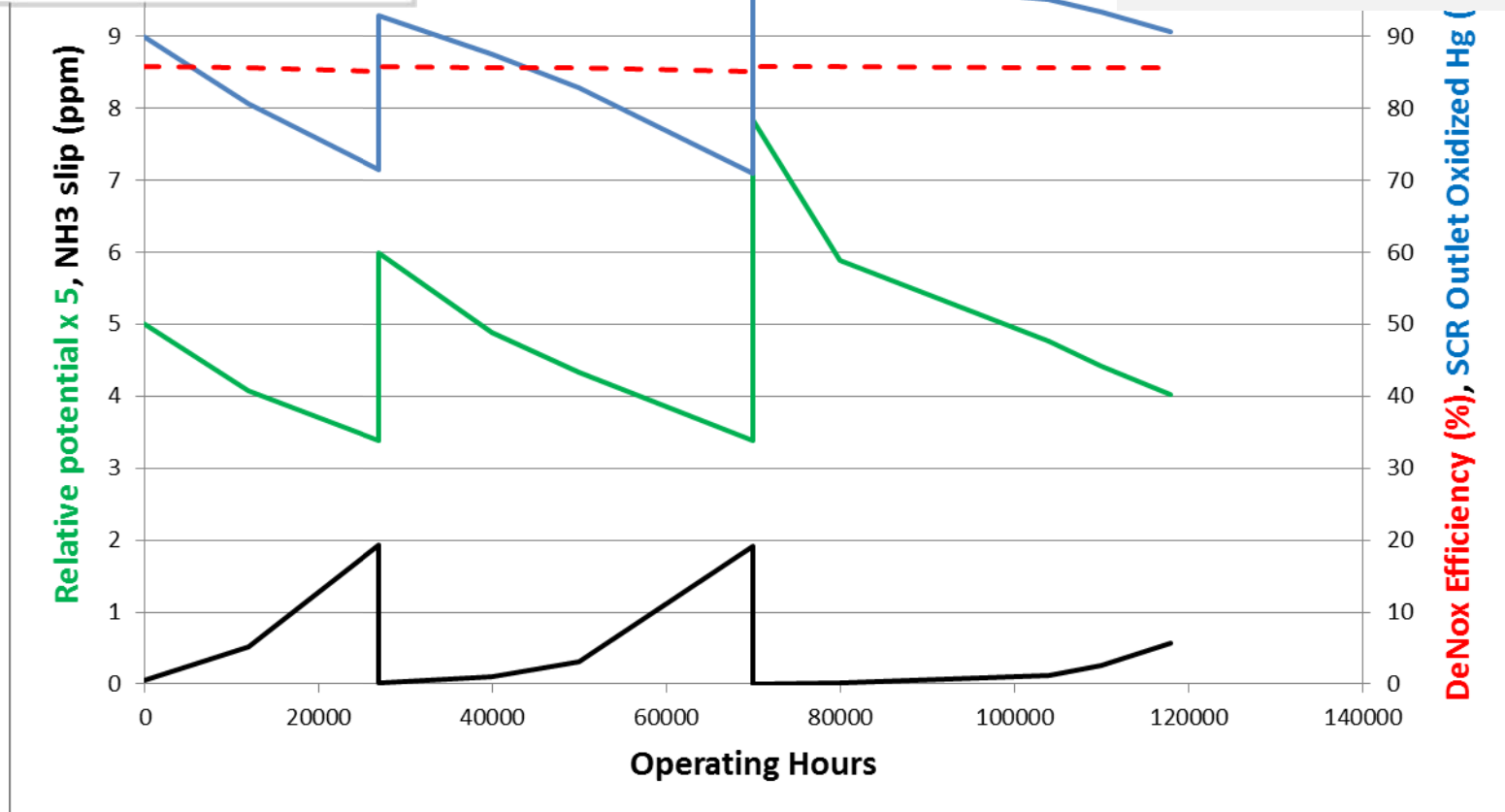


Management Plan w/ DeNox Potential & Hg Oxidation



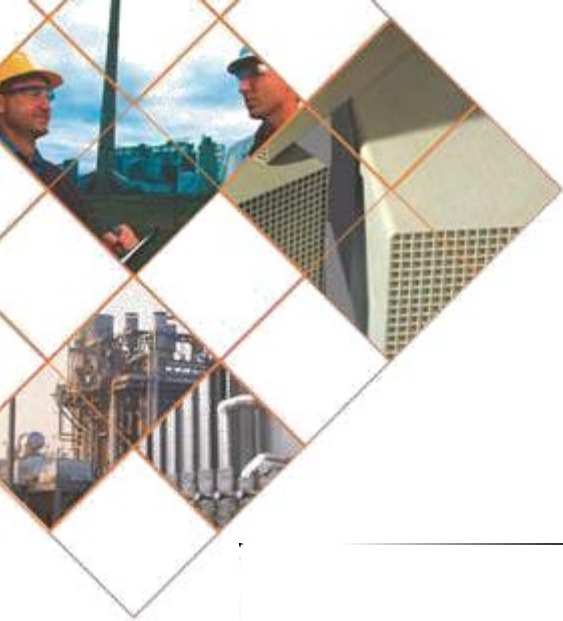
Catalyst Management Plan (DeNox, NH3 Slip, Oxidized Hg)

Target 90% Ox Hg
Action: Initially change 2 layers to Max length COMET™ and inject Halogen



Summary

- Catalyst additions and replacements can be managed to maintain Hg oxidation in a manner analogous to that for DeNOx, but with a few key differences:
 - Perf. Threshold (dependency on downstream equipment)
 - Layer dependency
 - Layer location and NH₃ inlet to each layer must be considered
 - More factors are needed in setting design conditions
 - HCl, HBr, CO; and more significant impacts of Temperature, O₂, and H₂O
- Understanding these dependencies, factors, requires thorough demonstrated testing capability, catalyst technology and application knowhow



CORMETECH



Thank You!

Questions/Discussion

Scot Pritchard

Cormetech, Inc.

2013 Reinhold NOx-Combustion Round Table
