

CORMETECH



The SCR Toolbox for Mercury Emission Management

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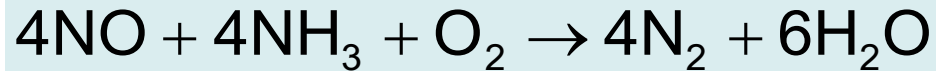
2015 Reinhold NOx-Combustion Round Table

- **Background**
 - The SCR's role in Hg control
 - Quantifying and testing SCR catalyst potential
- **Review the factors that affect the SCR catalyst potential for Hg oxidation**
 - Flue gas conditions
 - Hg^0 , Hg^{2+} , O_2 , H_2O , NO , Molar Ratio, Temperature, CO , SO_2
 - Halogens
 - HCl , HBr , HI
 - Catalyst
 - Traditional
 - Advanced

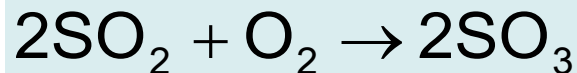
SCR Catalyst Functionality



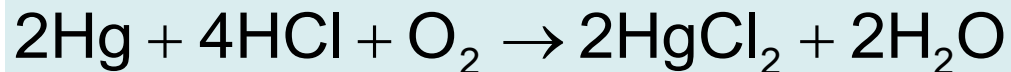
□ Reduce NOx



□ Minimize undesirable side reaction



□ Oxidize elemental Hg



SCR Hg Mass Balance



- At the SCR inlet, Hg is present in three forms:

$$\text{Hg}_{\text{in}}^{\text{total}} = \text{Hg}_{\text{in}}^0 + \text{Hg}_{\text{in}}^{2+} + \text{Hg}_{\text{in}}^{\text{particulate}}$$

Particulate Hg is not affected by the SCR

- Hg mass balance across SCR (at steady state):

$$\text{Hg}_{\text{in}}^0 + \text{Hg}_{\text{in}}^{2+} = \text{Hg}_{\text{out}}^0 + \text{Hg}_{\text{out}}^{2+} \quad 2\text{Hg} + 4\text{HCl} + \text{O}_2 \rightarrow 2\text{HgCl}_2 + 2\text{H}_2\text{O}$$

- Quantify Hg oxidation by the SCR:

$$\eta_{\text{HgOx}} = \frac{\text{Hg}_{\text{in}}^0 - \text{Hg}_{\text{out}}^0}{\text{Hg}_{\text{in}}^0}$$

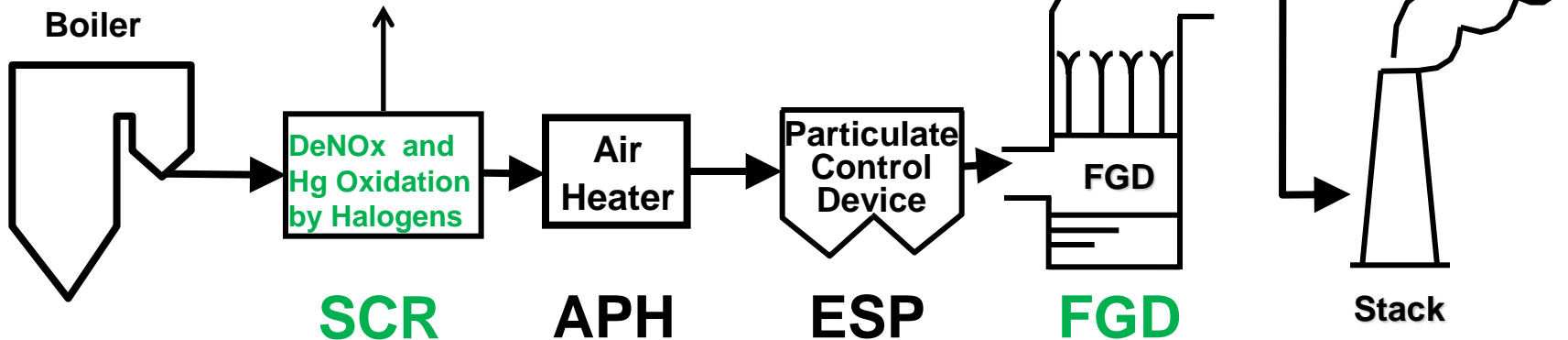
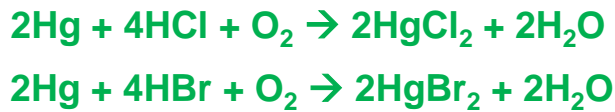
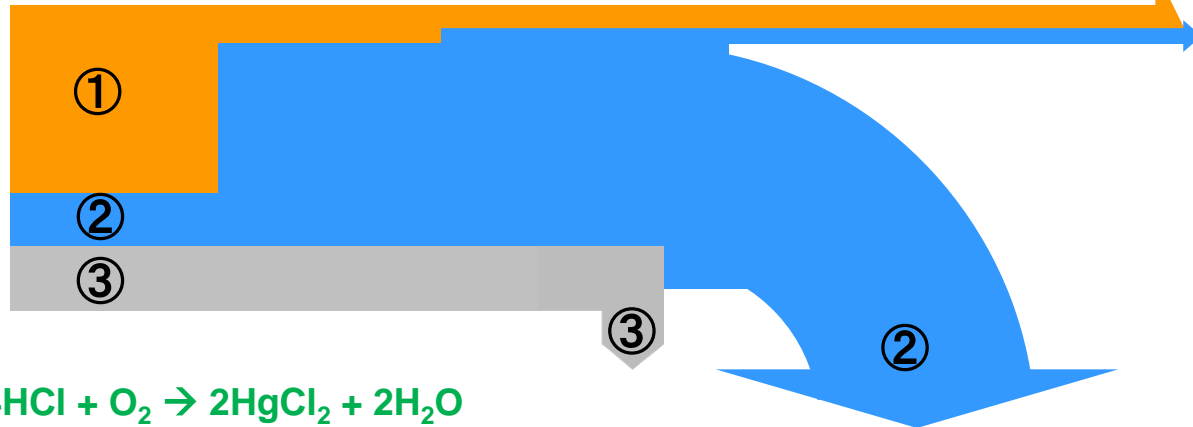
$$\% \text{ Oxidized} = \frac{\text{Hg}_{\text{out}}^{2+}}{\text{Hg}_{\text{out}}^0 + \text{Hg}_{\text{out}}^{2+}}$$

The SCR's Role in Hg Removal



Oxidize Hg for Downstream Capture!

- ① Elemental
- ② Oxidized
- ③ Particulate



Water solubility values (g/l) at ~20°C:
 Hg = 5.6×10^{-5} , HgO = 5.3×10^{-2} , HgCl₂ = 74

HgCl₂ removal

Plant Hg Removal Strategy

Site Specific. Includes All or Some Components.



Coal Type and Combustion

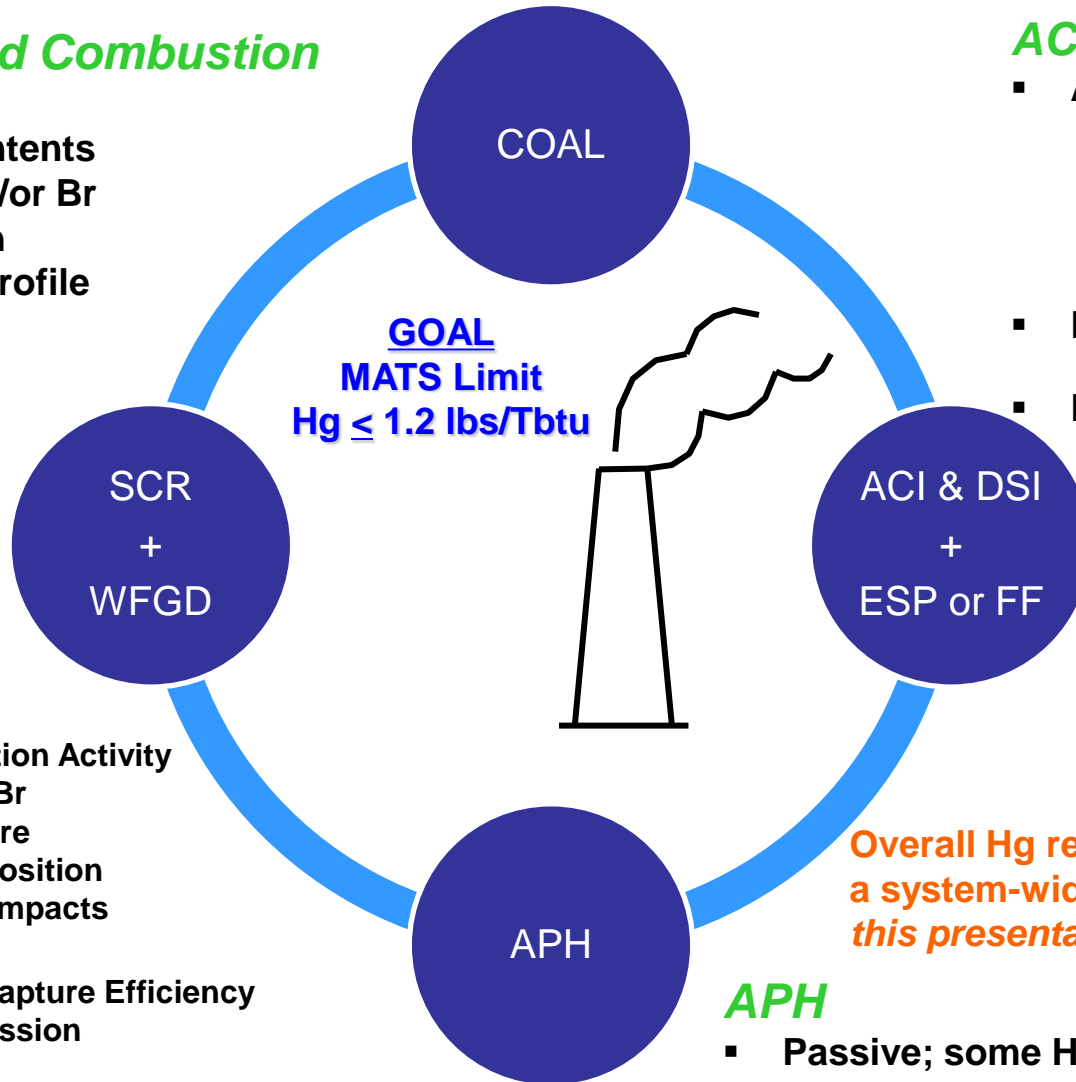
- Hg Content
- Cl and Br Contents
- Added Cl and/or Br
- LOI in Fly Ash
- Boiler Load Profile

ACI & DSI + ESP or FF

- ACI:
 - Hg Capacity
 - Temperature
 - SO₃ Concentration
 - HCl and HBr
 - Sorbent Injection Rate
- DSI:
 - SO₃ Mitigation
- ESP or FF:
 - ACI, DSI Capture
 - Ash Capture (Hg on LOI)

SCR + WFGD

- SCR:
 - Hg⁰ Oxidation Activity
 - HCl and HBr
 - Temperature
 - Gas Composition
 - Seasonal Impacts
- WFGD:
 - Hg²⁺ Net Capture Efficiency
 - Hg⁰ Reemission



Overall Hg removal strategy requires a system-wide perspective. Focus of this presentation is on the SCR.

APH

- Passive; some Hg Oxidation

SCR Catalyst Potential



$$\frac{K}{AV} = \text{Catalyst Potential}$$

$$AV = \frac{\text{Gas Flow}}{\text{Total GSA}}$$

$$\frac{K}{AV} = \text{Catalyst Potential for } X\% \text{ DeNO}_x$$

$$\frac{K_{\text{HgO}_x}}{AV} = \text{Catalyst Potential for } Y\% \text{ Hg Oxidation}$$

$$\frac{K_{\text{SO}_2\text{O}_x}}{AV} = \text{Catalyst Potential for } Z\% \text{ SO}_2 \text{ Oxidation}$$

SCR Catalyst Potential



$$\frac{K}{AV} = -\ln(1 - \eta_{\text{NO}_x})$$

Activity, K , depends on:

- Catalyst composition and age
- Flue gas conditions
 - Temperature
 - MR (NH_3), O_2 , H_2O , SO_2 , SO_3

$$\frac{K_{\text{HgO}_x}}{AV} = -\ln(1 - \eta_{\text{HgO}_x})$$

Activity, K_{HgO_x} , depends on:

- Catalyst composition and age
- Flue gas conditions
 - Temperature
 - MR (NH_3), O_2 , H_2O , SO_2 , SO_3
 - +HCl, HBr, HI, CO, HC

K_{HgO_x} is strongly condition dependent, but it's still a useful parameter!

$$\frac{K_{\text{SO}_2\text{O}_x}}{AV} = -\ln(1 - \eta_{\text{SO}_2\text{O}_x})$$

Activity, $K_{\text{SO}_2\text{O}_x}$, depends on:

- Catalyst composition, ρ_{bulk} and age
- Flue gas conditions
 - Temperature
 - MR (NH_3), SO_2 , SO_3

Measuring SCR Hg Oxidation

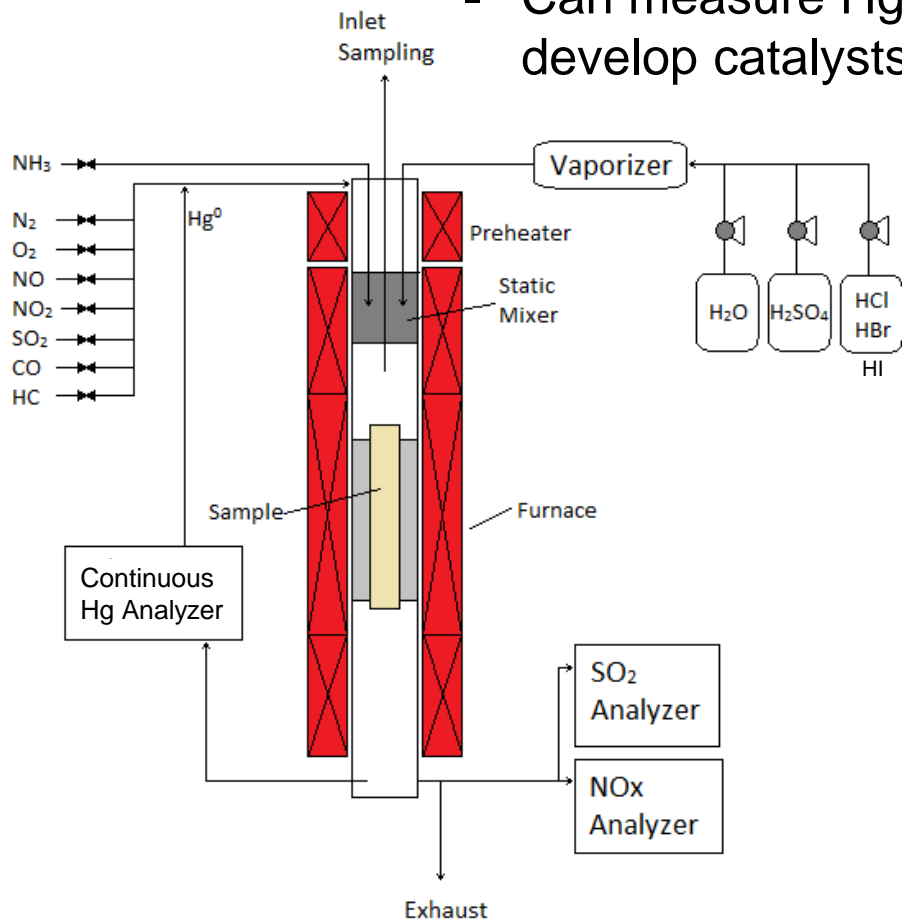


- **Measure Hg⁰ and Hg²⁺**
 - CEMS
 - Sorbent traps
- **Lab-scale catalytic reactors**
 - Micro reactor
 - Bench reactor
- **Field (full scale reactor)**
 - SCR inlet and outlet measurements
 - Particulate challenge (high dust difficult to measure)
 - Stack measurements
 - Final system performance
 - SCR contribution combined

- *Each reactor type can be used to generate quality data.*
- *Each reactor type has it's own advantages and limitations.*
- **Micro is well-suited for parametric studies**
 - Automation can help rapidly test a large set of conditions
- **Bench is well-suited for field audit testing**
 - **Full size element**
 - Catalyst poisons not evenly distributed throughout log.
 - Micro may require multiple samples to fully characterize log.
 - **Multi-layer system test**
 - System and individual layer performance in a single test
 - Micro may need multiple step-wise tests using results of upper layers to set conditions for lower layers.
 - Aging times are similar to micro scale

Micro Reactor

- Example shown is fully-automated for efficient data collection.
- Can measure Hg oxidation under a full range of conditions to develop catalysts and assist with management strategies.

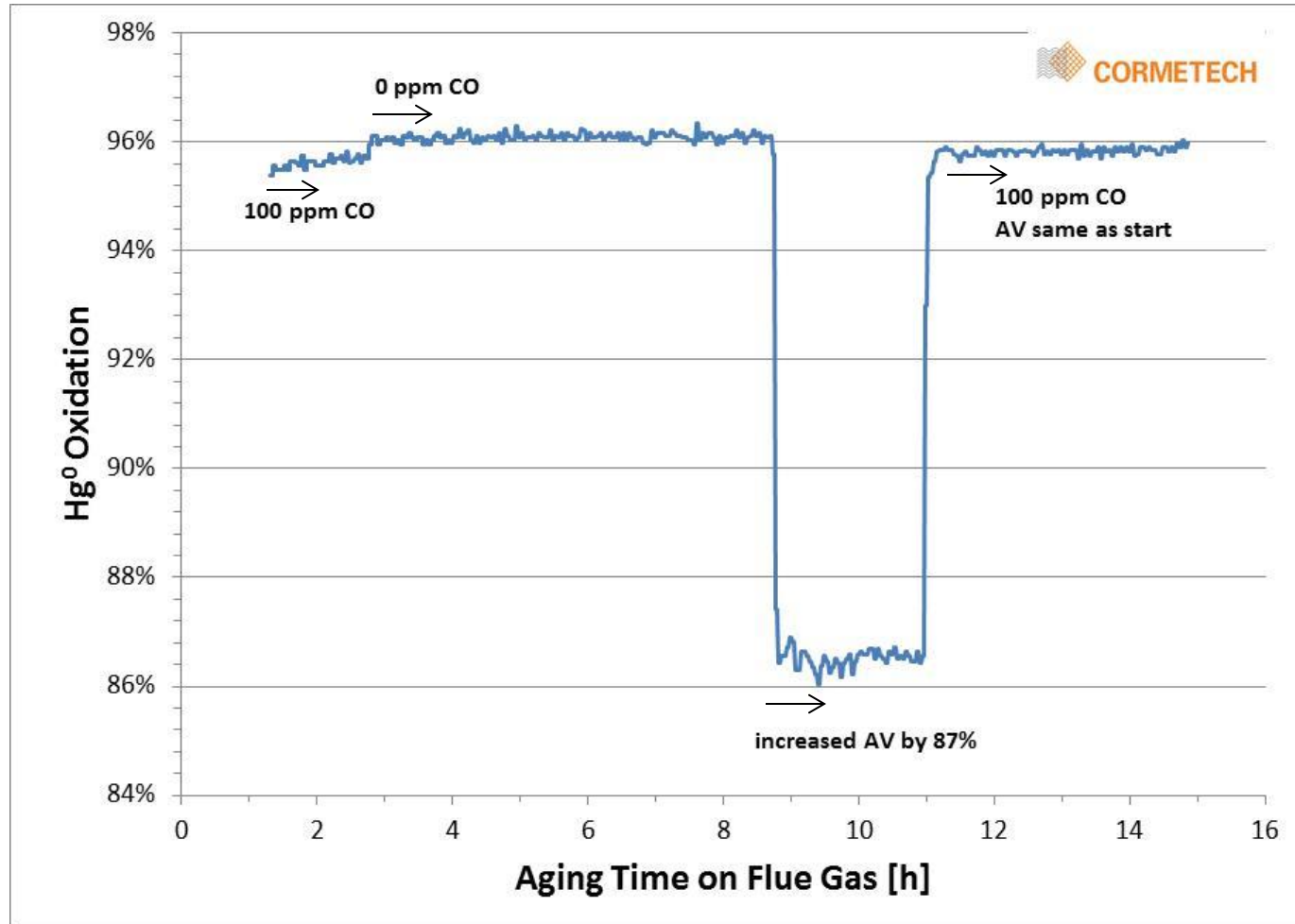


Micro Reactor: Aging Times

Fresh Catalyst



Transients are typically short. Steady state for this test is achieved is < 1 hour.



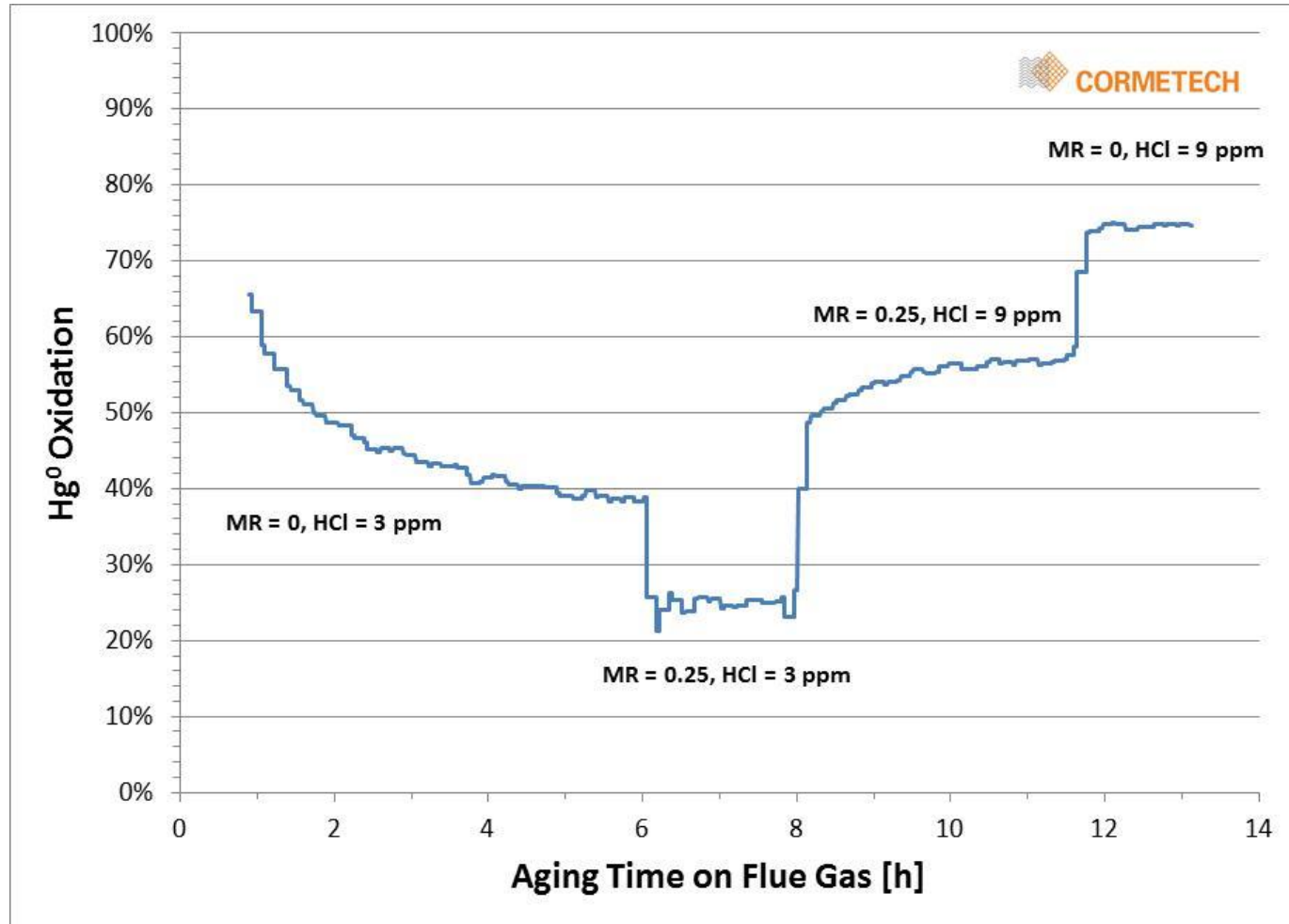
357°C, 5.4% O₂, 9.7% H₂O, 46 ppm HCl, 1450 ppm SO₂, 15 ppm SO₃, 0 or 100 ppm CO, 275 ppm NO, MR = 0

Micro Reactor: Aging Times

Fresh Catalyst



Transients can be longer when HCl is < 10 ppm. Steady state for this series is achieved in < 5 hours.



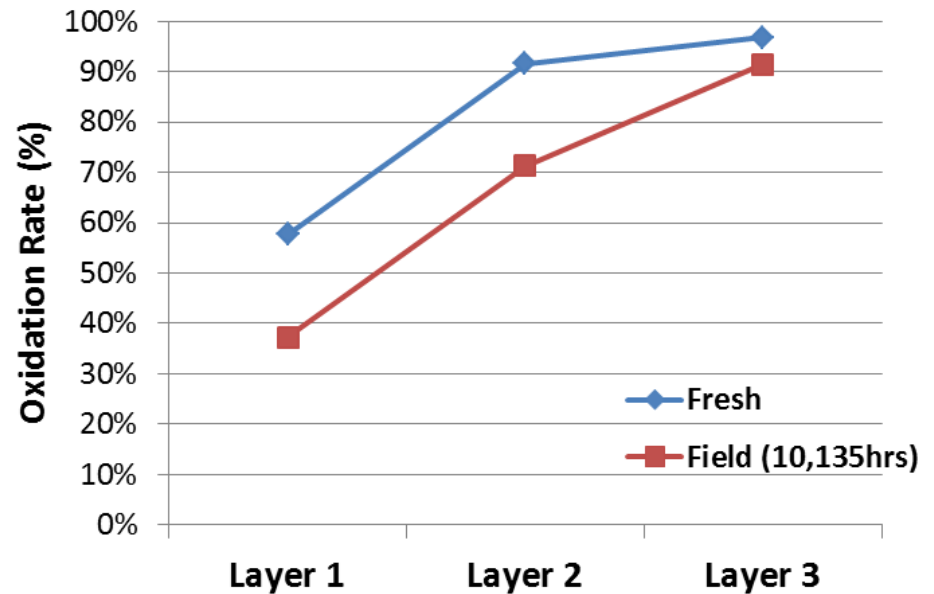
400°C, 3.3% O₂, 11% H₂O, 3 or 9 ppm HCl, 490 ppm SO₂, 5 ppm SO₃, 50 ppm CO, 375 ppm NO, MR = 0 or 0.25

Bench Reactor

- Bench scale allows full-size element testing (single or multi-layer).
- Test fresh or deactivated catalyst.
- Inject HCl/HBr, O₂, H₂O, SO₂, SO₃, NO_x, CO, HC.
- Full H₂O concentration control

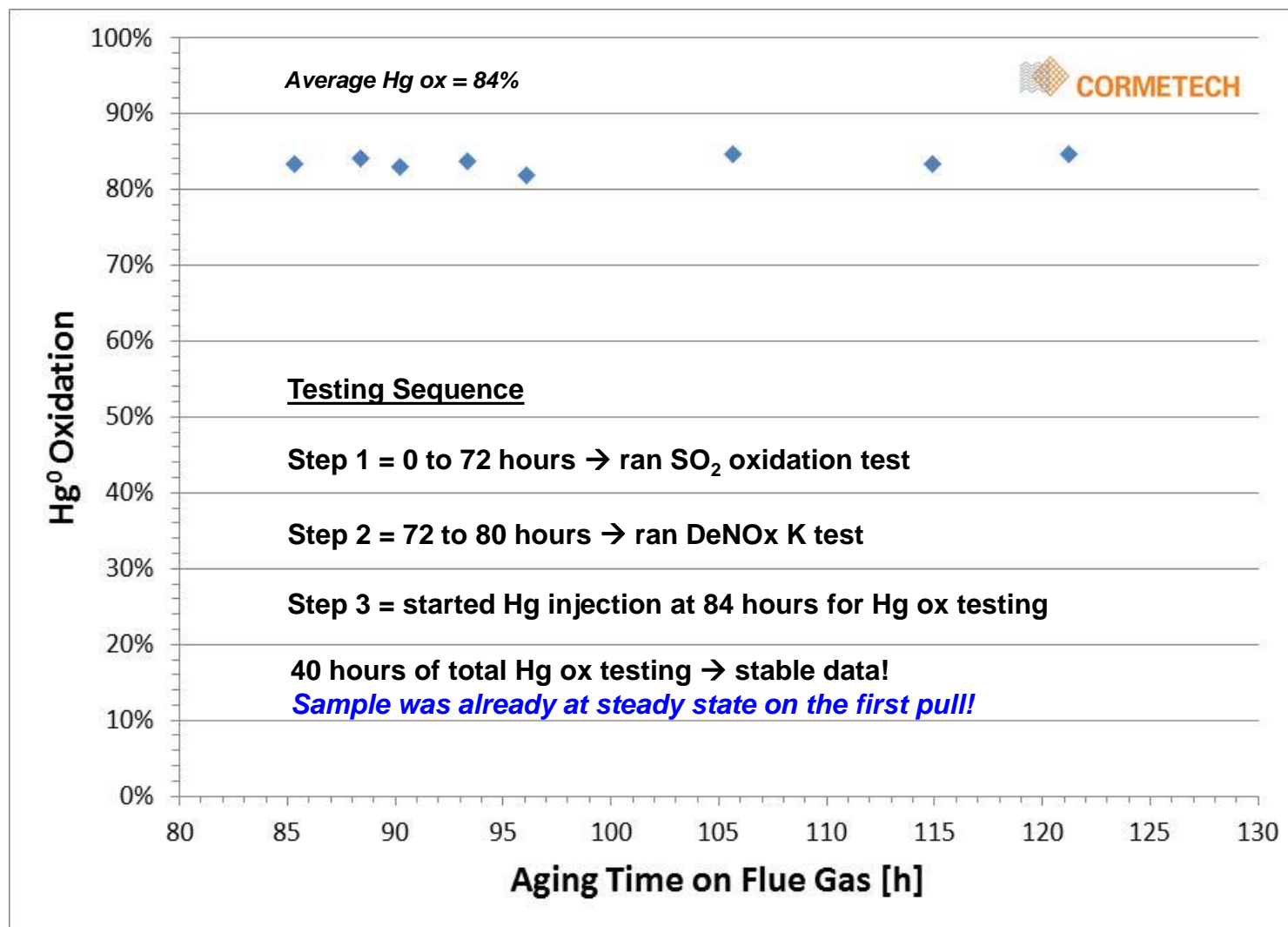


Hg oxidation performance measured on bench reactor



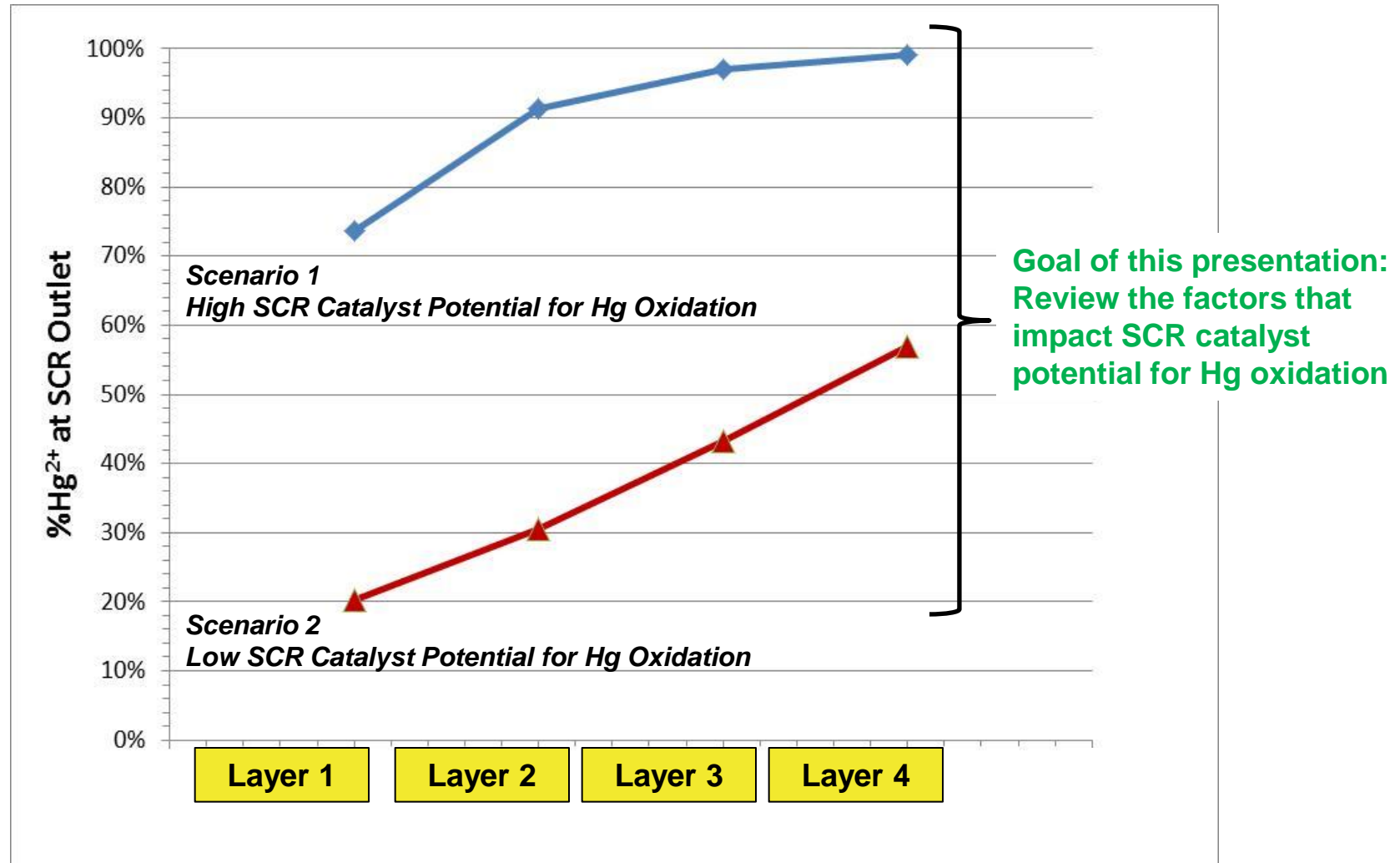
Bench Reactor Data

New Catalyst



371°C, 4.3% O₂, 8.5% H₂O, 58 ppm HCl, 850 ppm SO₂, 9 ppm SO₃, 100 ppm CO, 300 ppm NO, 11 ppm NH₃

Main Presentation Focus...



Summary of Factor Impacts

Positive Correlations













Factor	Hg Oxidation Correlation with Increasing Factor Value	Note
HCl	↑	Strong interdependence with T and concentration
HBr	↑	Strong interdependence with T and concentration
HI	↑	Strong interdependence with T and concentration
O ₂	↑	
Catalyst surface area	↑	Determined by layer length and Ap/pitch selection
Catalyst V ₂ O ₅	↑	
Advanced catalysts	↑	Improve Hg ox at constant DeNO _x and SO ₂ ox
Hg ⁰	○	No impact: kinetics are first order in Hg ⁰

Summary of Factor Impacts

Negative Correlations



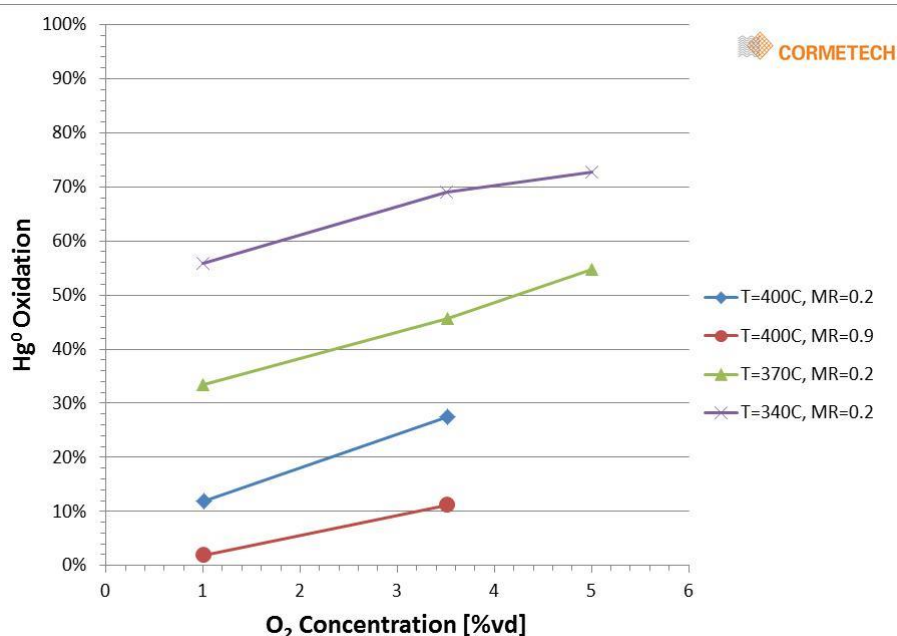
Factor	Hg Oxidation Correlation with Increasing Factor Value	Note
Hg ²⁺		Impact depends on re-reduction activity
Temperature		Strong interdependence with HCl, HBr, NH ₃ , catalyst
NH ₃		Strong interdependence with T, HCl, HBr, catalyst
NO		Impact is cross-correlated through NH ₃
H ₂ O		
SO ₂		
SO ₃		
CO		Strong interdependence with T, HCl, HBr, catalyst
Hydrocarbons		
Catalyst Age		Strong interdependence with catalyst type

Impact of O₂ and H₂O

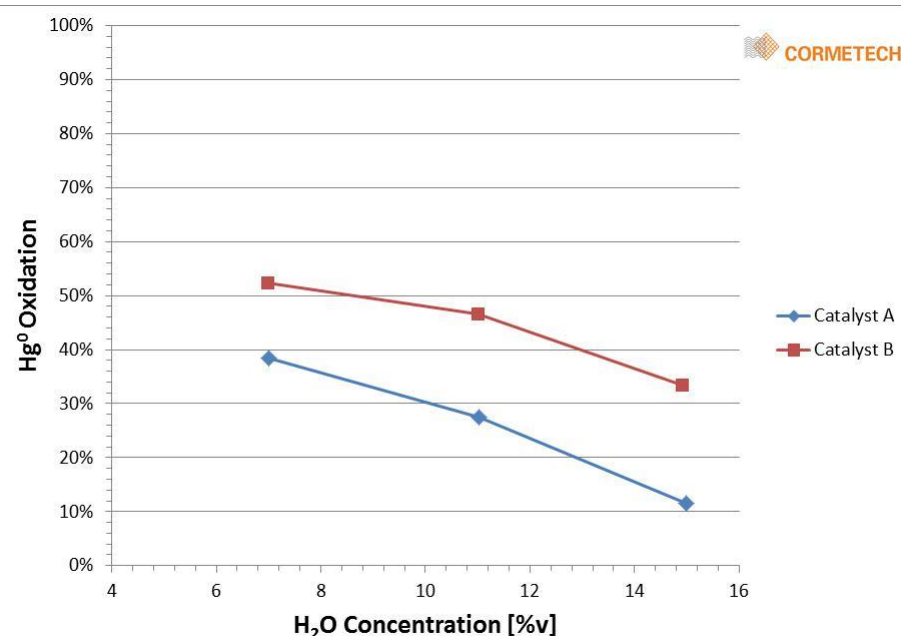
Hg Oxidation Activity



O₂ and H₂O both have a significant impact on Hg oxidation activity. In comparison, these parameters have a much smaller impact on DeNO_x or SO₂ oxidation rates.



11% H₂O, 350 ppm NO, 0.2 Molar Ratio, 1000 ppm SO₂,
10 ppm SO₃, 100 ppm CO, 11 ppm HCl



400°C, 3.5% O₂, 350 ppm NO, 0.2 Molar Ratio, 1000 ppm SO₂,
10 ppm SO₃, 100 ppm CO, 11 ppm HCl

Impact of Hg⁰

Hg Oxidation Activity



Steady state data reveal that the Hg oxidation reaction is 1st order in Hg⁰ → Hg oxidation is constant with varied inlet Hg⁰ concentration.

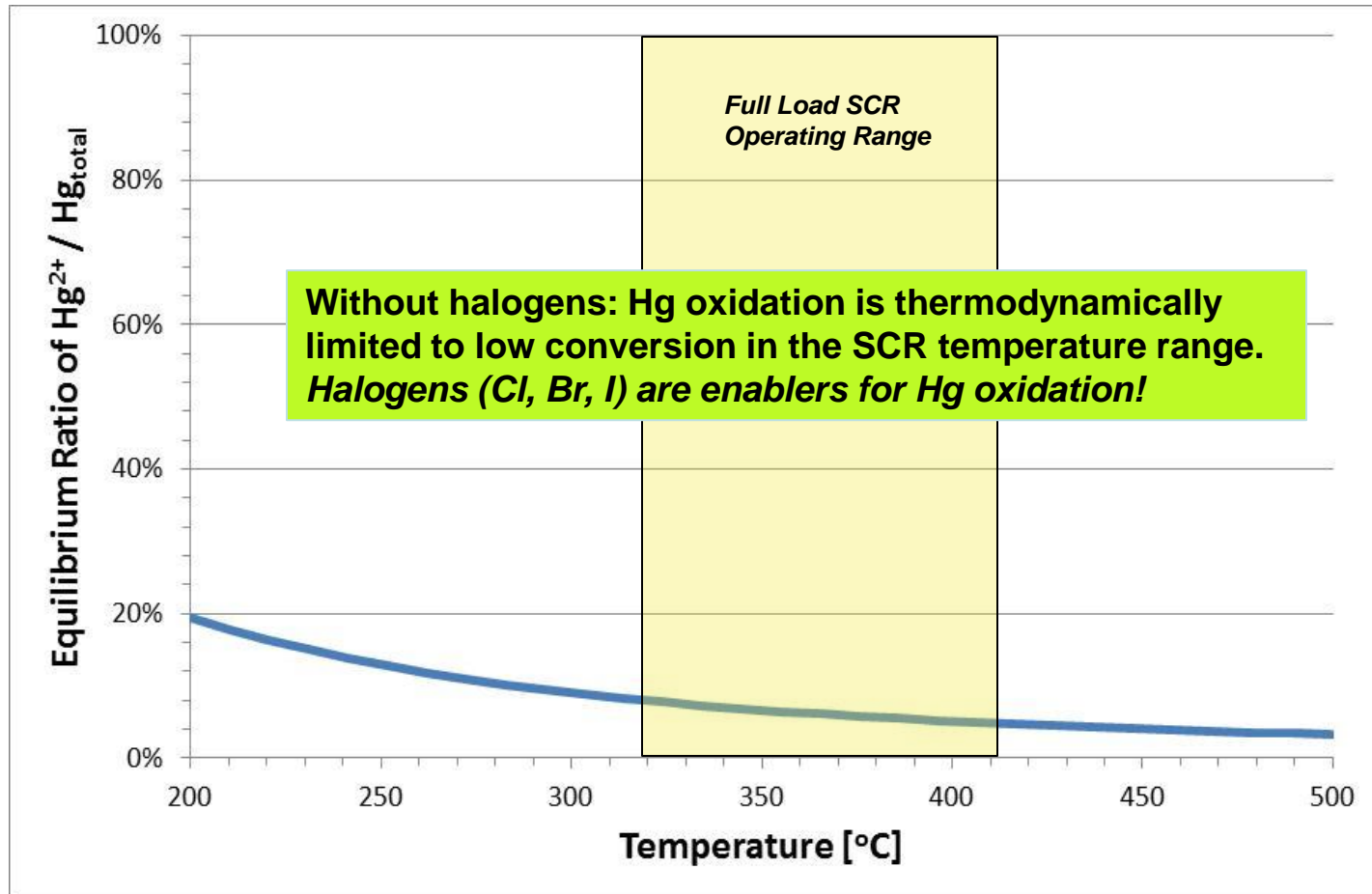
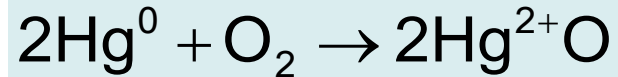
Inlet NH ₃ /NO _x	HCl [ppmvd]	Hg Oxidation with inlet Hg 21 µg/Nm ³	Hg Oxidation with inlet Hg 11 µg/Nm ³
0.2	11	28%	27%
0.9	11	11%	14%
0.2	56	81%	81%
0.9	56	58%	61%

400°C, 3.5% O₂, 11% H₂O, 350 ppm NO, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO

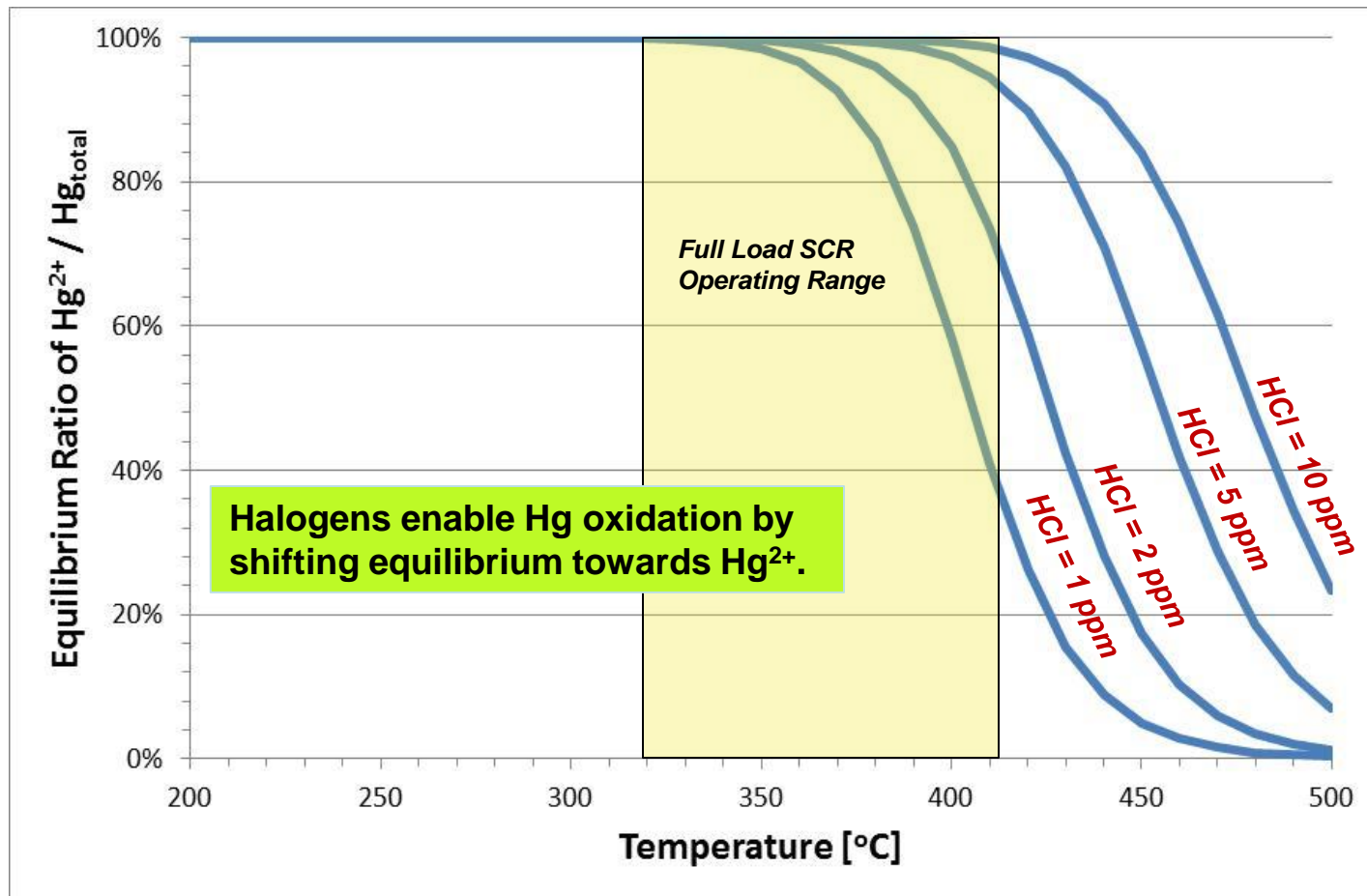
The overall kinetic rate law, however, is more complex, and includes the kinetic effects of HCl and O₂, and inhibition effects of H₂O, NH₃, CO and SO₂.

Why are Halogens Needed?

(No halogens included).



Why are Halogens Needed?

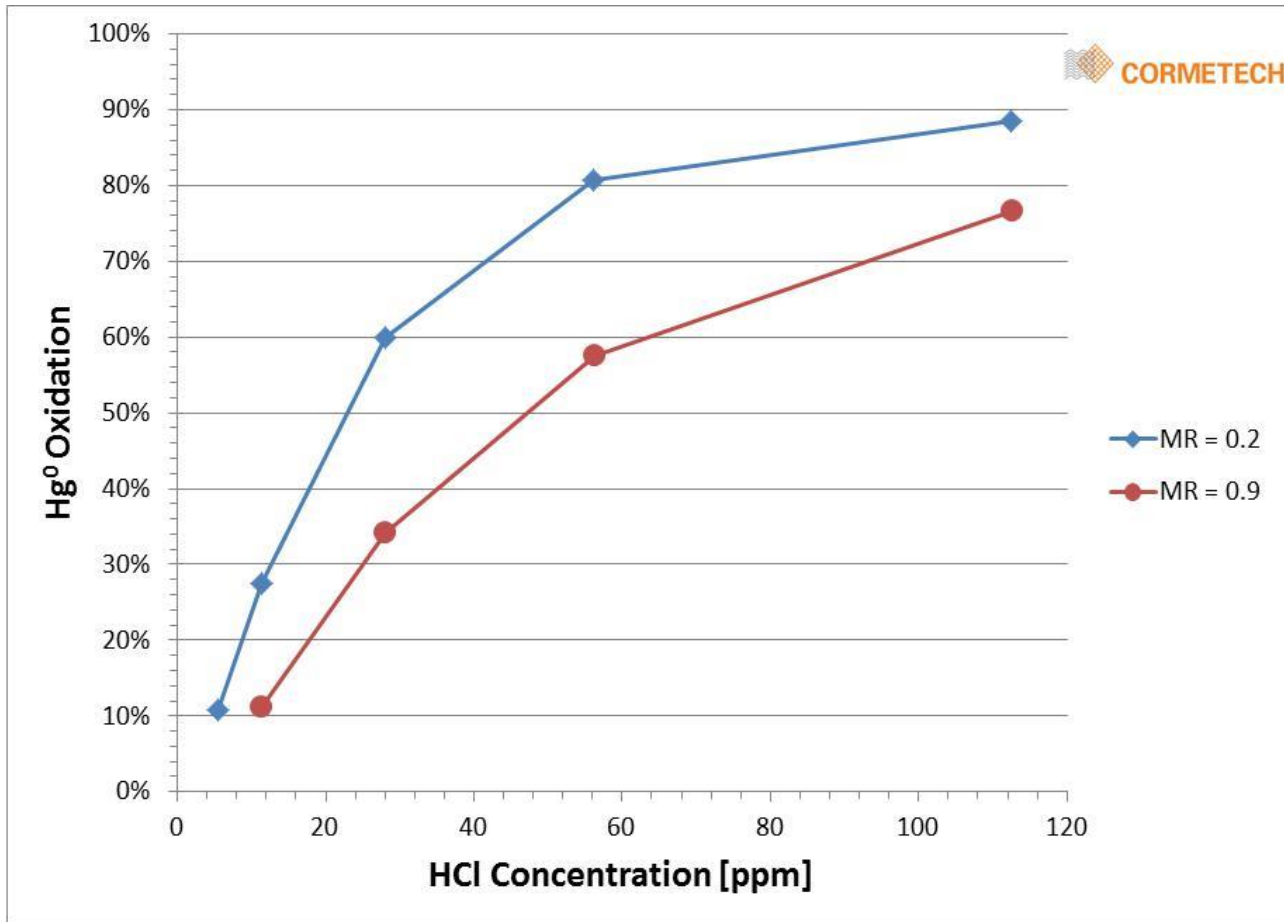


Impact of HCl

Hg Oxidation Activity



The kinetic data are consistent with a mechanism where HCl adsorbs on the catalyst. NH_3 can significantly inhibit Hg oxidation activity.

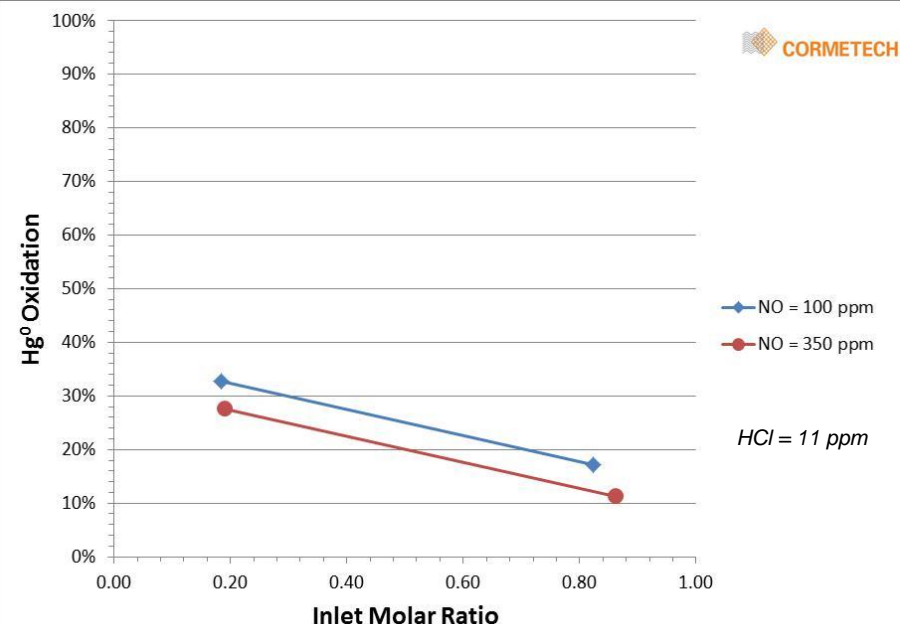
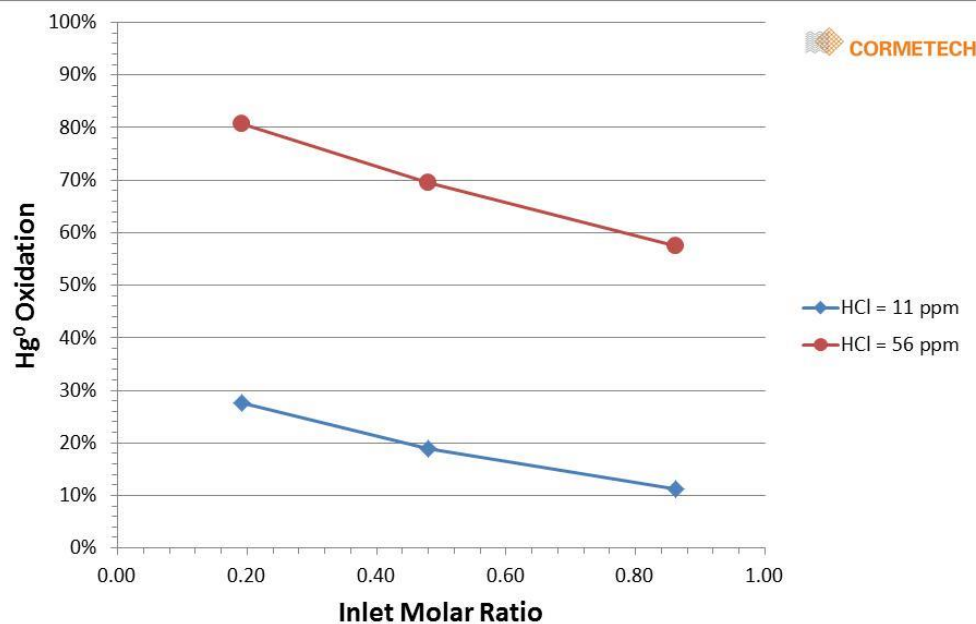


400°C, 3.5% O_2 , 11% H_2O , 350 ppm NO , 1000 ppm SO_2 , 10 ppm SO_3 , 100 ppm CO ; MR = Inlet Molar Ratio

Impact of NH₃ and NO_x Hg⁰ Oxidation Activity



NH₃ can significantly inhibit Hg⁰ oxidation activity. Negative impact of higher inlet NO_x is caused by higher inlet NH₃ (we tested at fixed molar ratio values).



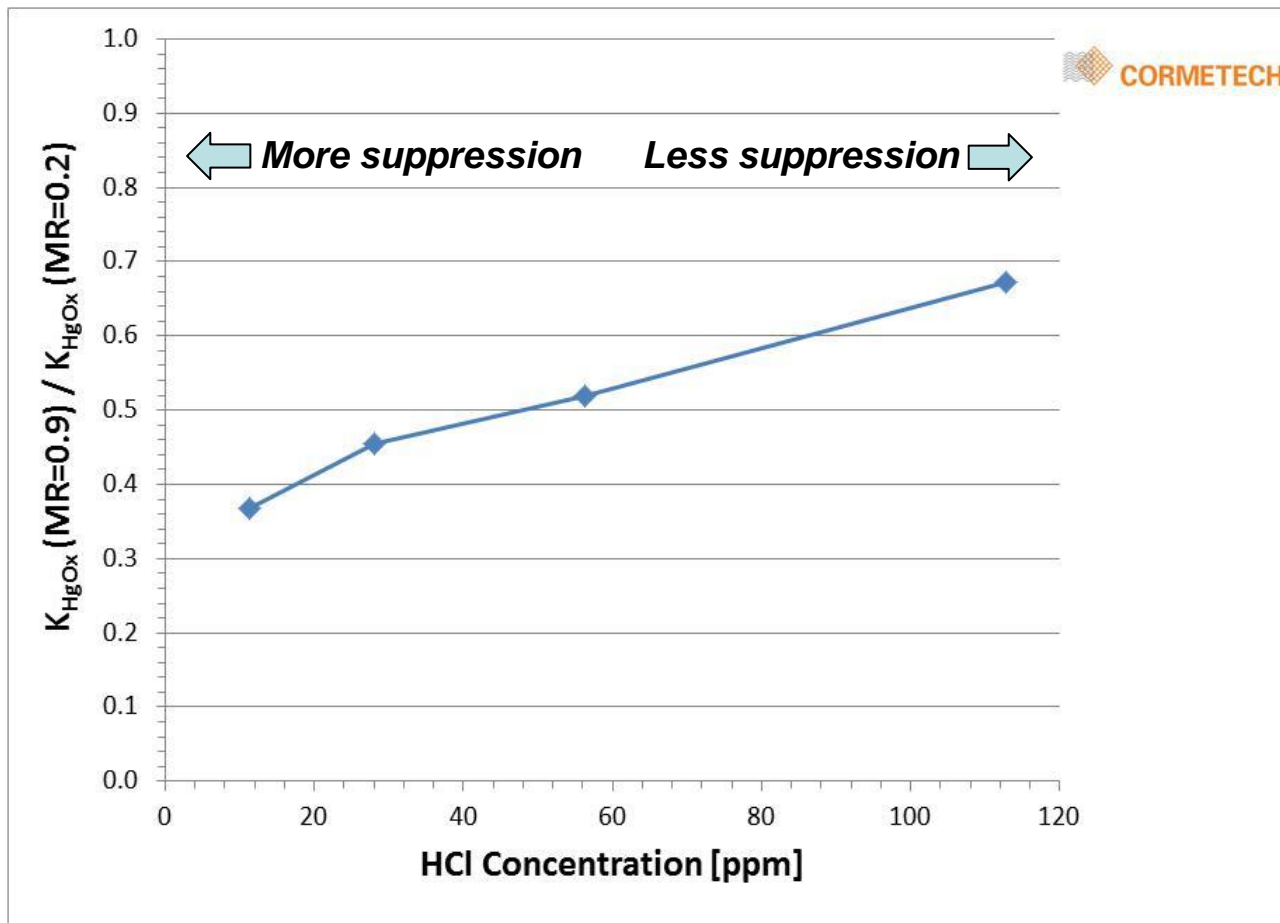
400°C, 3.5% O₂, 11% H₂O, 350 ppm NO, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO

Impact of HCl on NH₃ Inhibition

Hg Oxidation Activity



There is a strong Interdependence between the HCl concentration and the degree of NH₃ suppression of the Hg oxidation rate.



400°C, 3.5% O₂, 11% H₂O, 350 ppm NO, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO; MR = Inlet Molar Ratio

Impact of HCl on NH₃ Inhibition

First Layer vs. Lower Layer Performance



Strong interdependence between the HCl content and the degree of NH₃ suppression of the Hg oxidation rate → one implication is that layer 1 catalyst can contribute more to overall Hg oxidation under higher HCl conditions!

Single Layer Performance Example					
Position	Case	MR	HCl [ppm]	Layer Hg Ox	Hg Ox Delta Layer 1 vs. Lower Layer
Layer 1	Low HCl	0.9	28	36%	-27%
Lower Layer	Low HCl	0.2	28	63%	
Layer 1	High HCl	0.9	113	79%	-11%
Lower Layer	High HCl	0.2	113	90%	

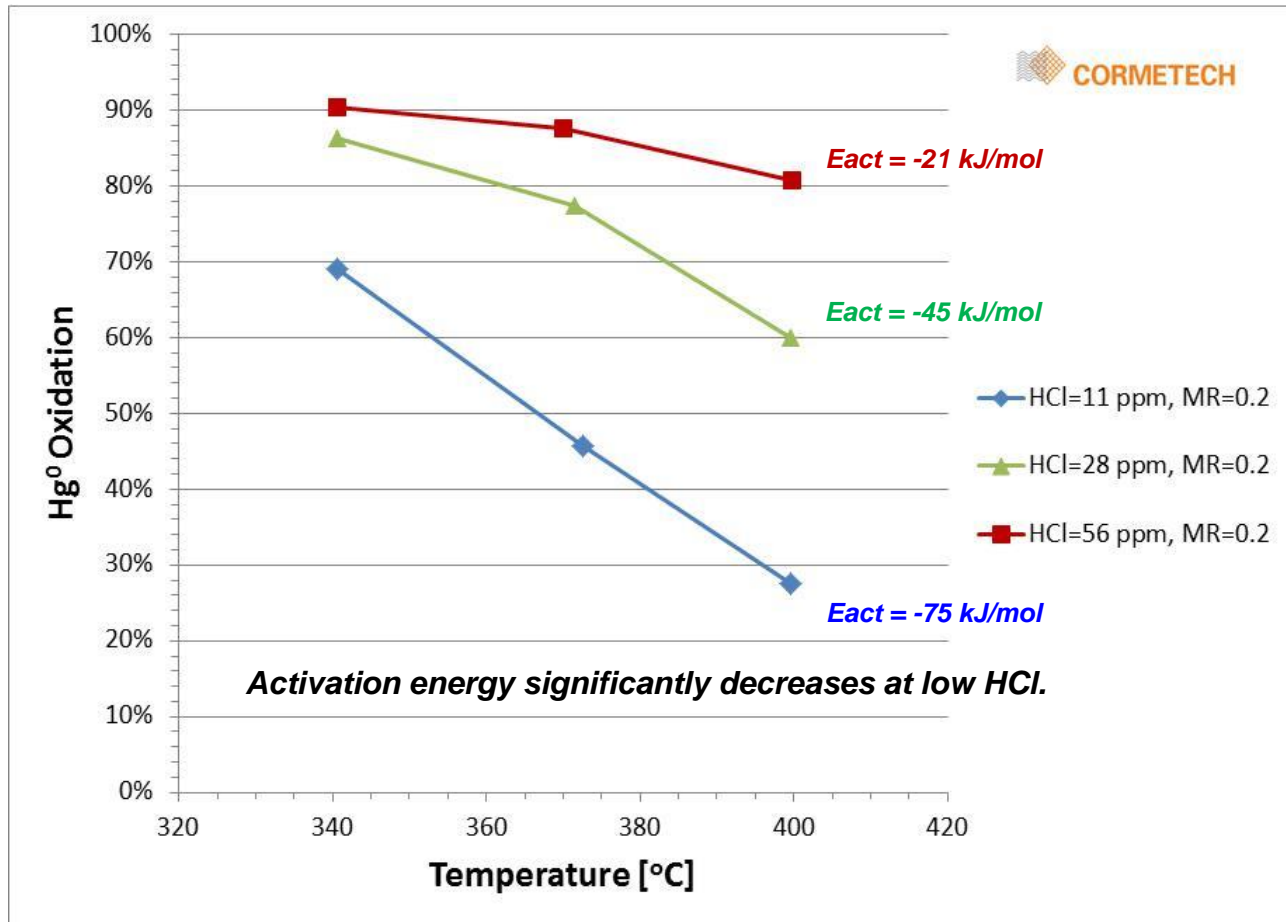
400°C, 3.5% O₂, 11% H₂O, 350 ppm NO, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO; MR = Inlet Molar Ratio

Impact of Temperature (MR=0.2)



Hg⁰ Oxidation Activity

Listed activation energy values are for the overall Hg oxidation reaction. Values are negative because the rate decreases as temperature increases.



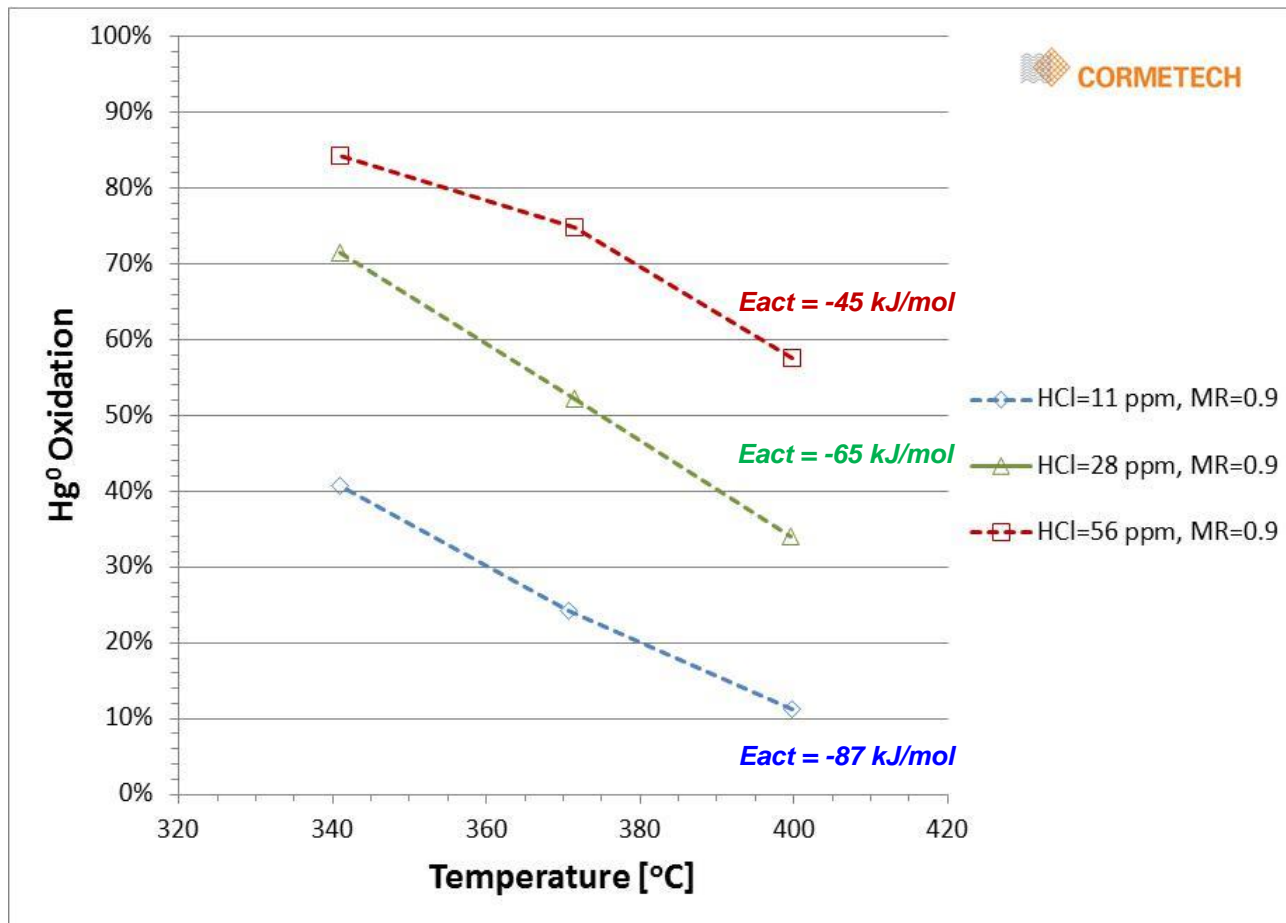
3.5% O₂, 11% H₂O, 350 ppm NO, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO; MR = Inlet Molar Ratio

Impact of Temperature (MR=0.9)



Hg⁰ Oxidation Activity

With high inlet NH₃, the activation energy decreases for constant HCl, which indicates that NH₃ inhibition can become more pronounced at high temperature.



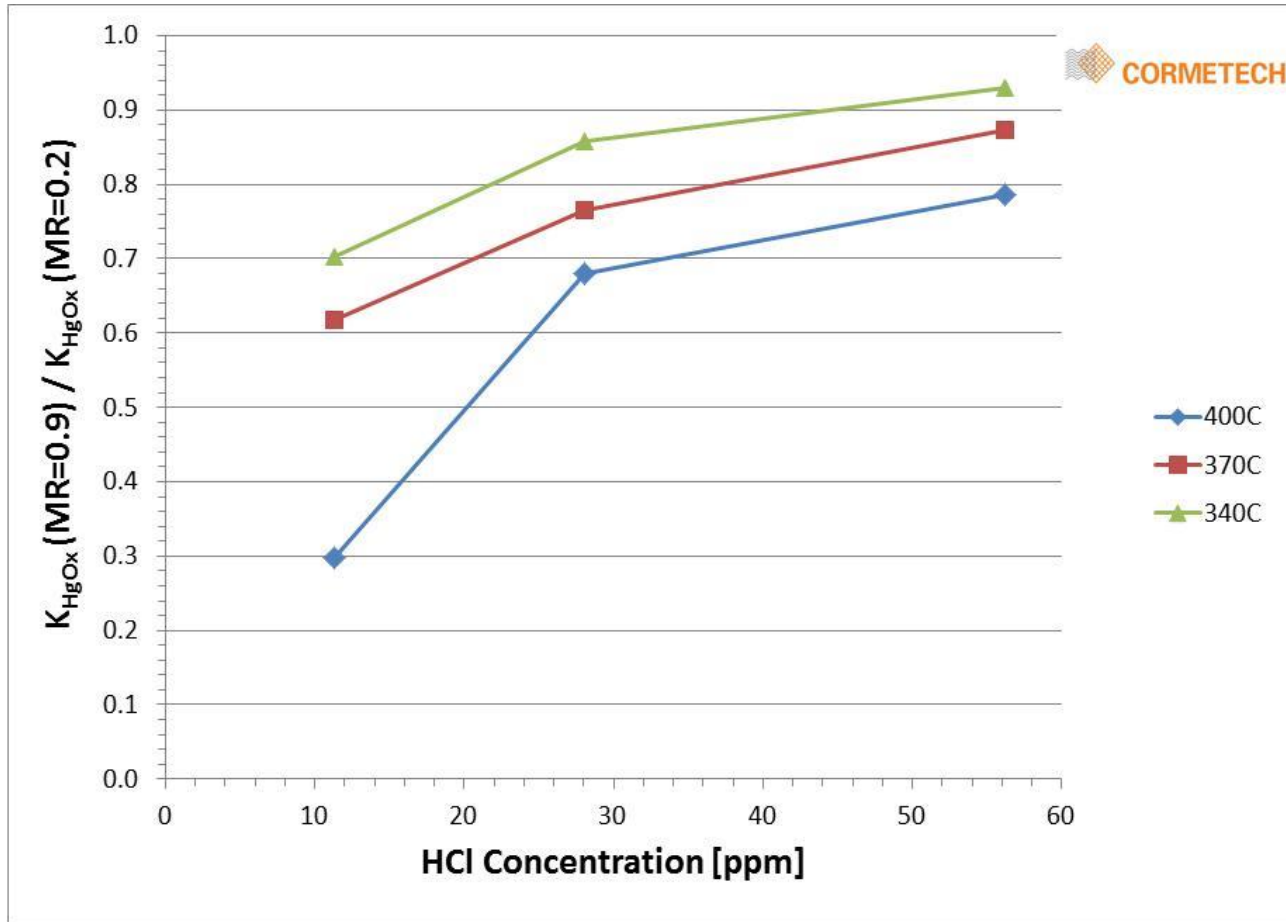
3.5% O₂, 11% H₂O, 350 ppm NO, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO; MR = Inlet Molar Ratio

Impact of Temperature

Hg Oxidation Activity



Increasing HCl can reduce the amount of NH₃ suppression across the temperature range.



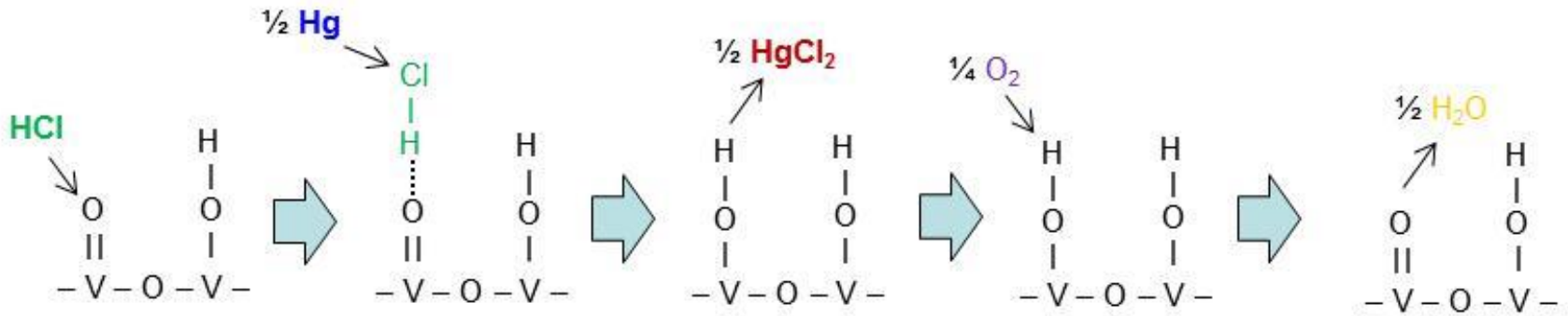
3.5% O₂, 11% H₂O, 350 ppm NO, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO; MR = Inlet Molar Ratio

Reaction Mechanism

Several Hypotheses in the Literature



One example: Eley – Rideal (HCl adsorbs, Hg reacts from gas phase)



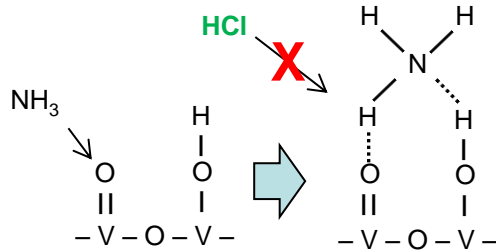
Two other examples (both include Hg adsorption steps):

Langmuir – Hinshelwood (both HCl and Hg adsorb before reaction occurs)

Mars – van Krevelen (reaction of adsorbed Hg with lattice chloride)

How NH₃ Inhibits Hg Oxidation

1. Competitive adsorption of HCl and NH₃: (more significant at lower temperature)

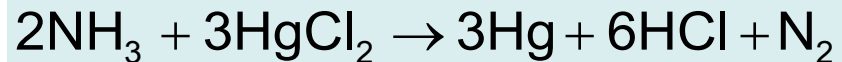


We verified that HgCl₂ reduction by NH₃ occurs by running experiments with 100% Hg²⁺ injection and measuring the Hg⁰ that formed.

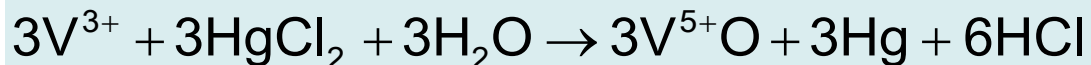
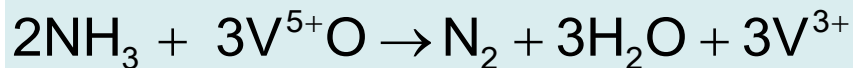
2. Re-reduction of HgCl₂ by NH₃: (more significant at higher temperature)

	MR	Hg0 in	Hg2+ in	Hg0 out	Hg2+ out	Delta Hg0	Delta Hg2+	Hg Ox
with Hg2+ injection	0.0	0.0	19.7	1.7	18.0	1.7	-1.7	-9%
with Hg2+ injection	0.9	0.0	19.7	3.8	15.9	3.8	-3.8	-19%

400°C, 4% O₂, 11% H₂O, 350 ppm NO, 1000 ppm SO₂, 10 ppm SO₃



What will happen on a more detailed level (simplified):



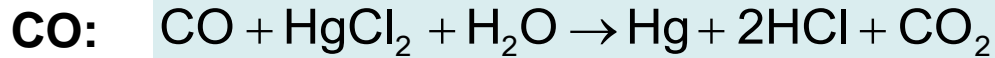
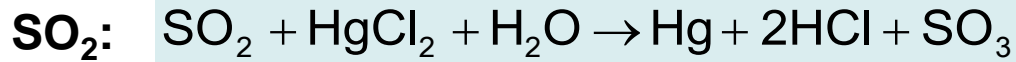
Coal-type SCR has a low activity for NH₃ oxidation.

Impact of Reducing Agents

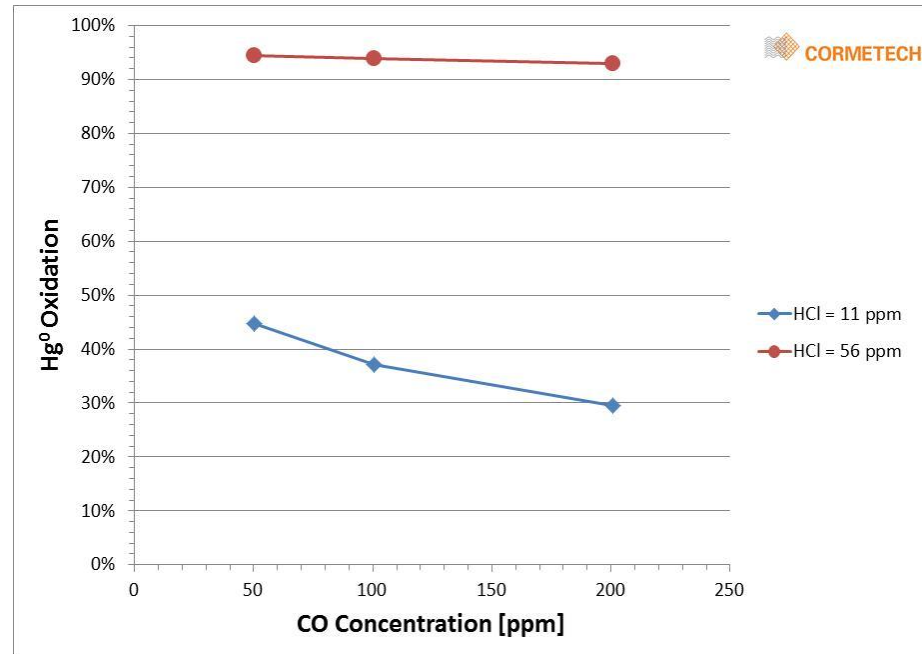
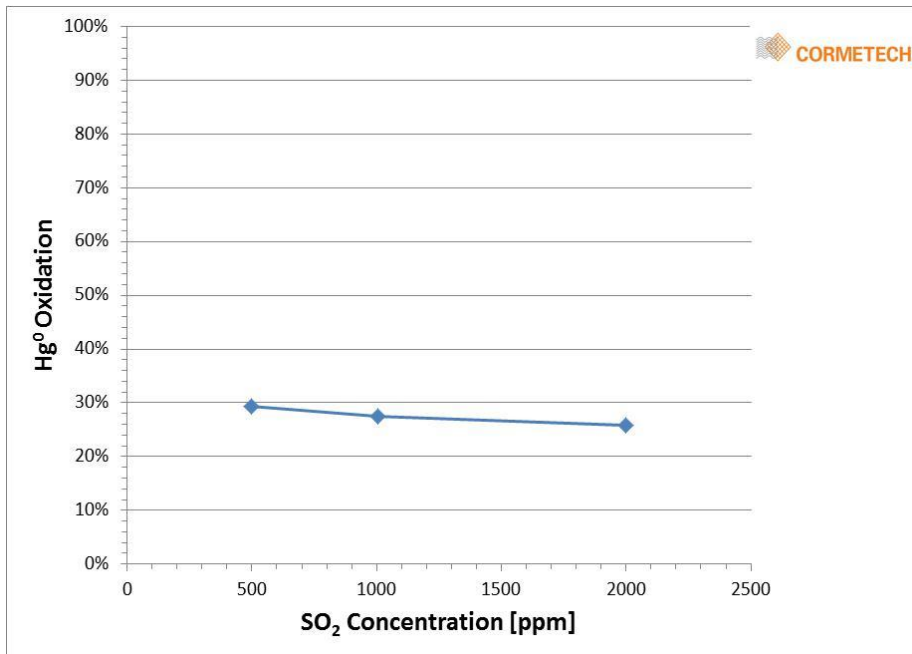
Hg Oxidation Activity



In addition to NH₃, there are additional flue gas species that can act as catalyst reducing agents and inhibit Hg oxidation by reduction of HgCl₂.



Hydrocarbons can oxidize over SCR catalyst and partially reduce V⁵⁺ sites, but the hydrocarbon concentration in coal flue gas tends to be fairly low.



400°C, 3.5% O₂, 11% H₂O, HCl = 11 ppm or as specified, 350 ppm NO, 0.2 MR, SO₂ = 1000 ppm or as specified, SO₃ = 1% of SO₂, CO = 100 ppm or as specified

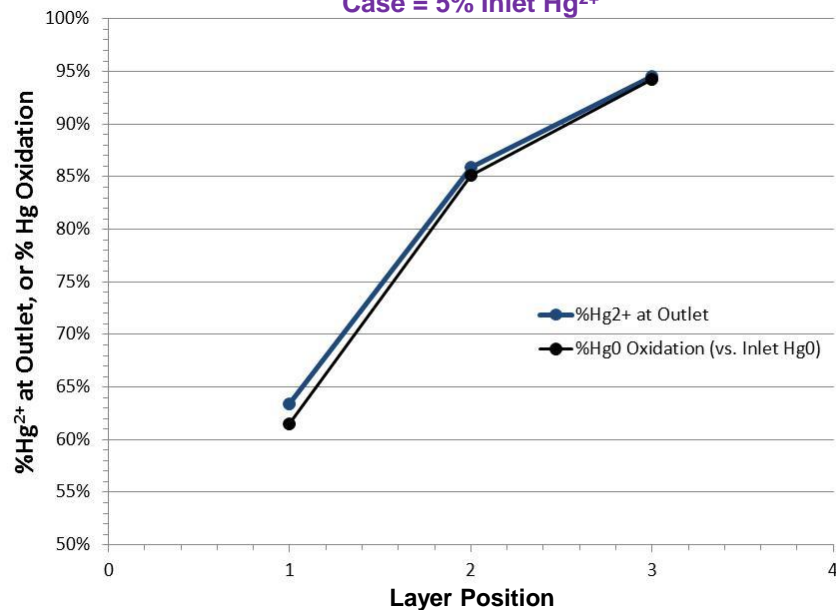
Impact of Inlet Hg Speciation

Model Simulation

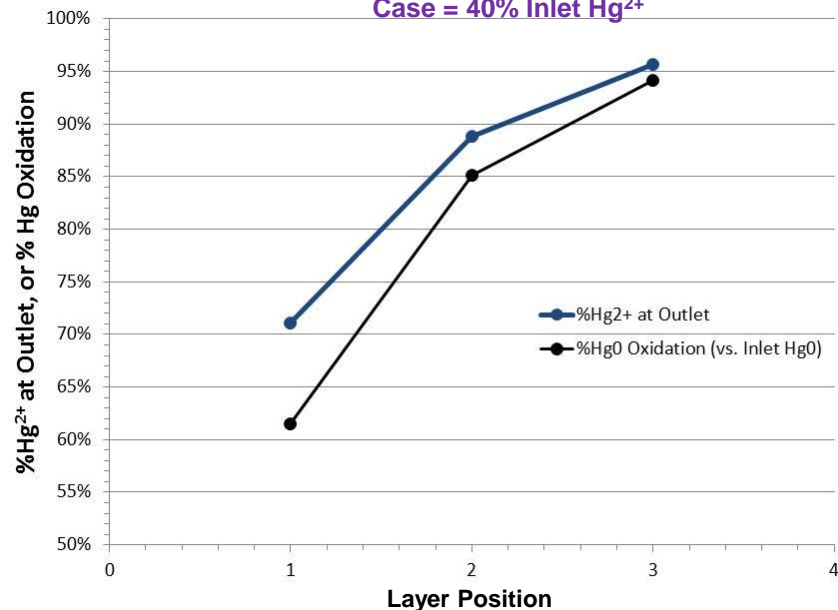


Hg oxidation reactivity held constant. Hg^{2+} reduction activity by NH_3 set at 0 (inactive).

Case = 5% Inlet Hg^{2+}



Case = 40% Inlet Hg^{2+}



In the limit where Hg^{2+} reverse reactions are inactive \rightarrow Hg oxidation is independent of inlet Hg^{2+} speciation, and the outlet % oxidized Hg^{2+} is effectively additive (= inlet Hg^{2+} + amount of Hg^0 oxidized in the SCR)

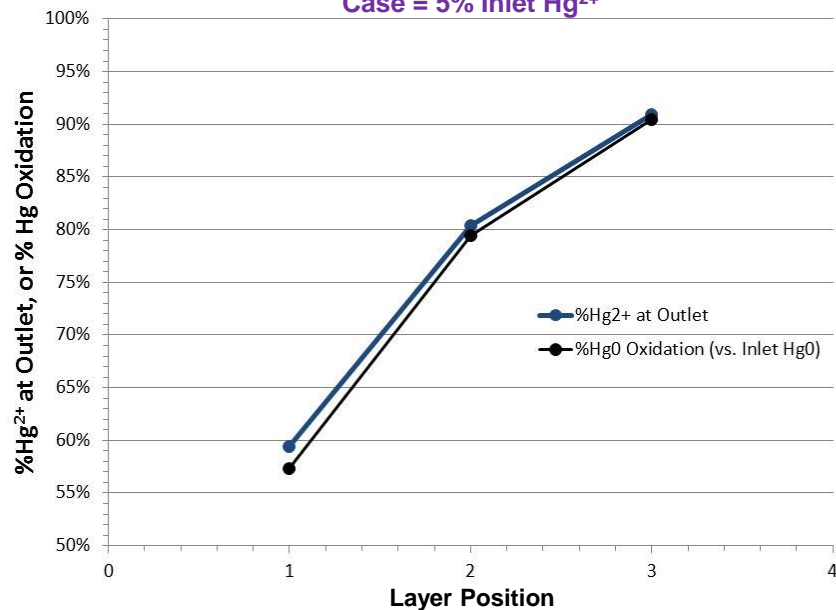
Impact of Inlet Hg Speciation

Model Simulation

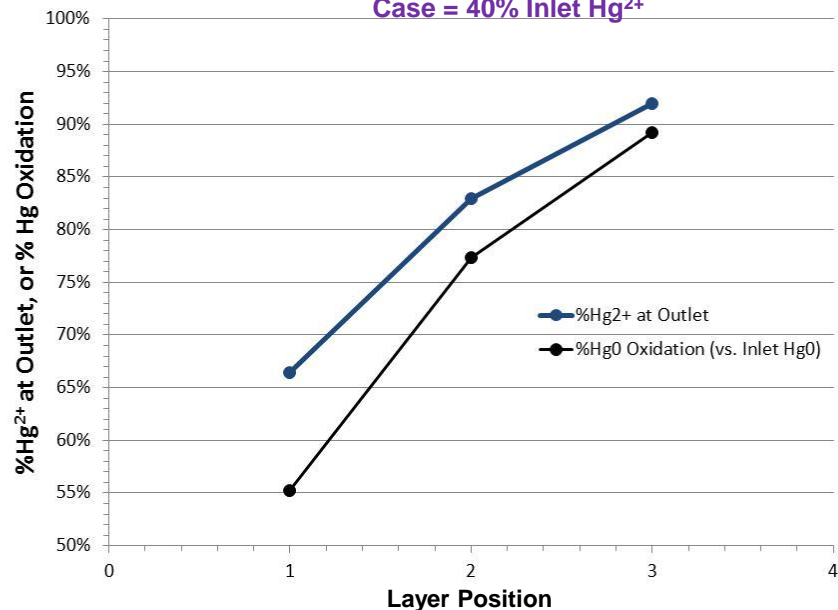


Hg oxidation reactivity held constant. Hg^{2+} reduction activity by NH_3 set at a low value.

Case = 5% Inlet Hg^{2+}



Case = 40% Inlet Hg^{2+}



Higher inlet Hg^{2+} decreases the effective Hg oxidation due to reverse reactions. Note that the outlet Hg^{2+} for the 40% inlet oxidized case is higher than the 5% inlet oxidized case.

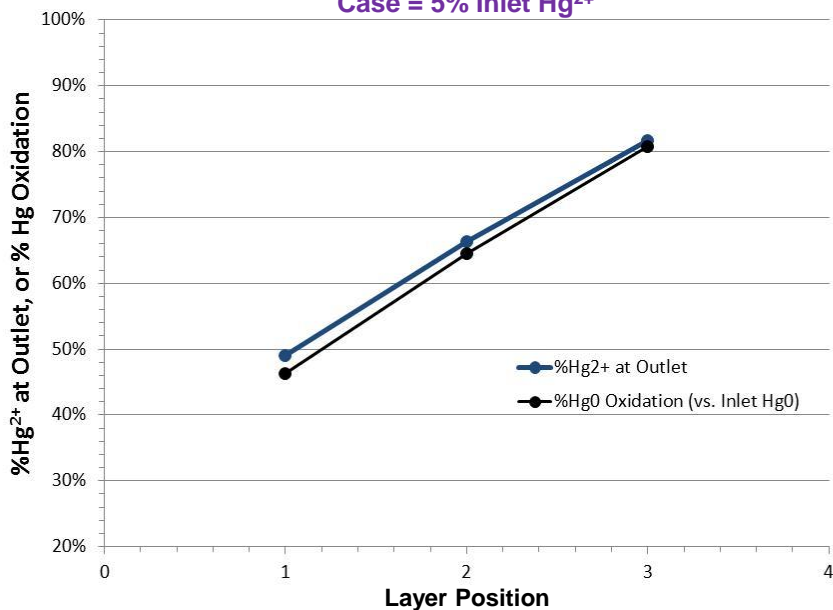
Impact of Inlet Hg Speciation

Model Simulation

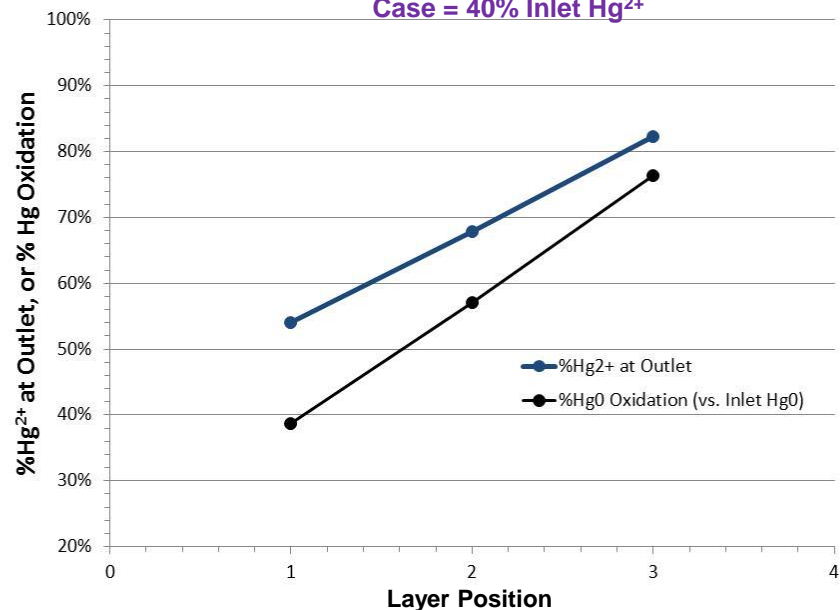


Hg oxidation reactivity held constant. Hg^{2+} reduction activity by NH_3 further increased.

Case = 5% Inlet Hg^{2+}



Case = 40% Inlet Hg^{2+}



Higher inlet Hg^{2+} decreases the effective Hg oxidation due to reverse reactions. Note that the outlet Hg^{2+} for the 40% inlet oxidized case is still higher than the 5% inlet oxidized case (but the difference is becoming smaller).

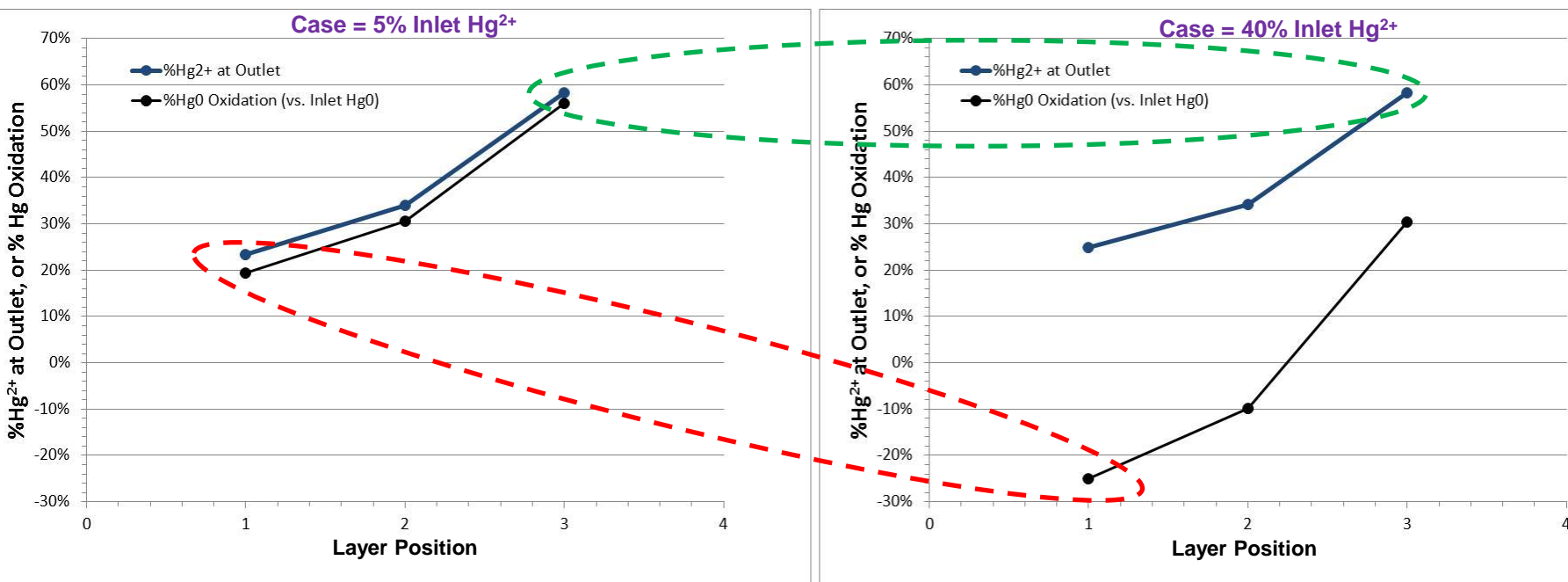
Impact of Inlet Hg Speciation

Model Simulation



Hg oxidation reactivity held constant. Hg^{2+} reduction activity by NH_3 increased again.

In the limit where reverse reactions are dominant, the %outlet Hg^{2+} achieved is independent of the %inlet Hg^{2+} .



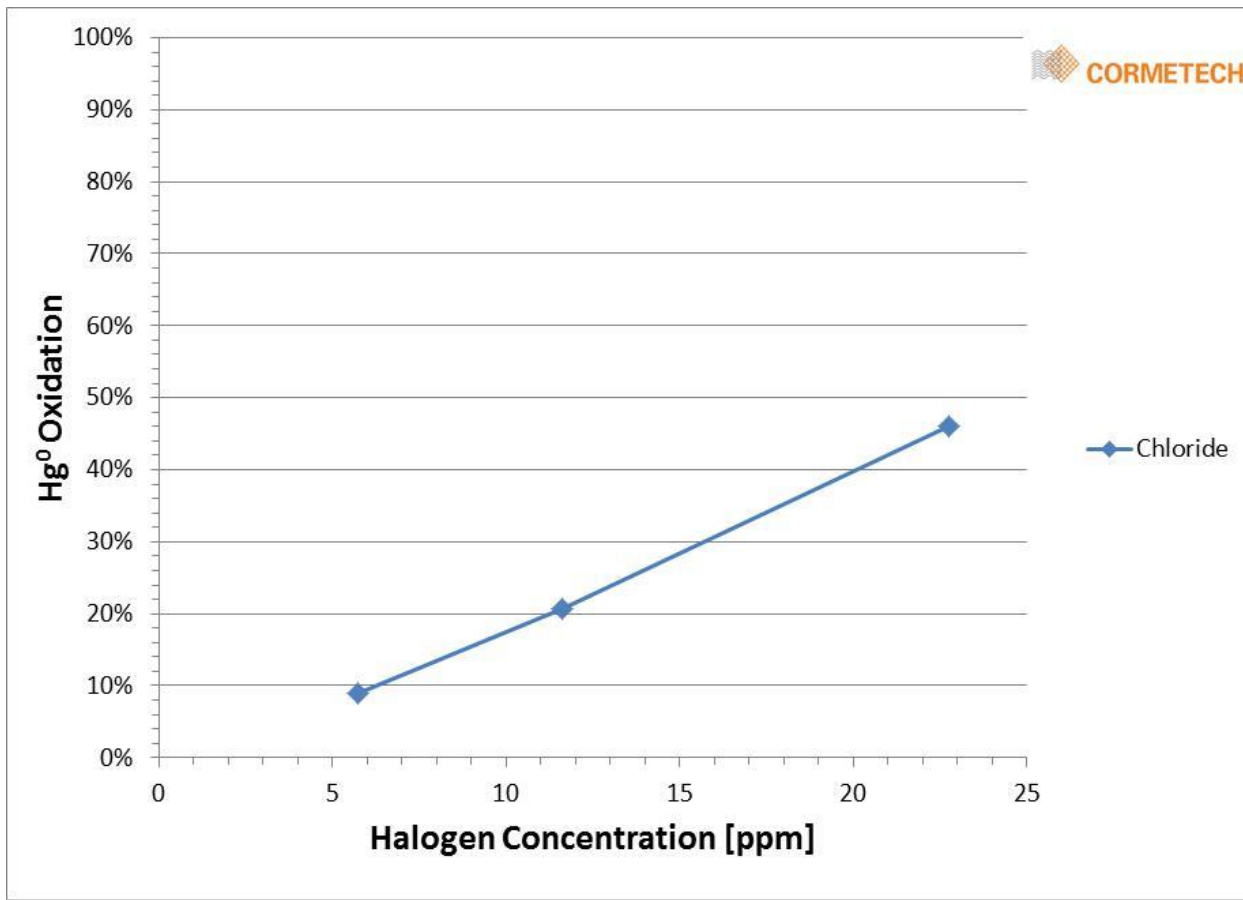
In the limit where reverse reactions are dominant, Hg oxidation of top layers can become negative for high %inlet Hg^{2+} .

Halogens: Cl vs. Br vs. I

Hg⁰ Oxidation Activity



Baseline with chloride only. Challenging Hg oxidation condition.



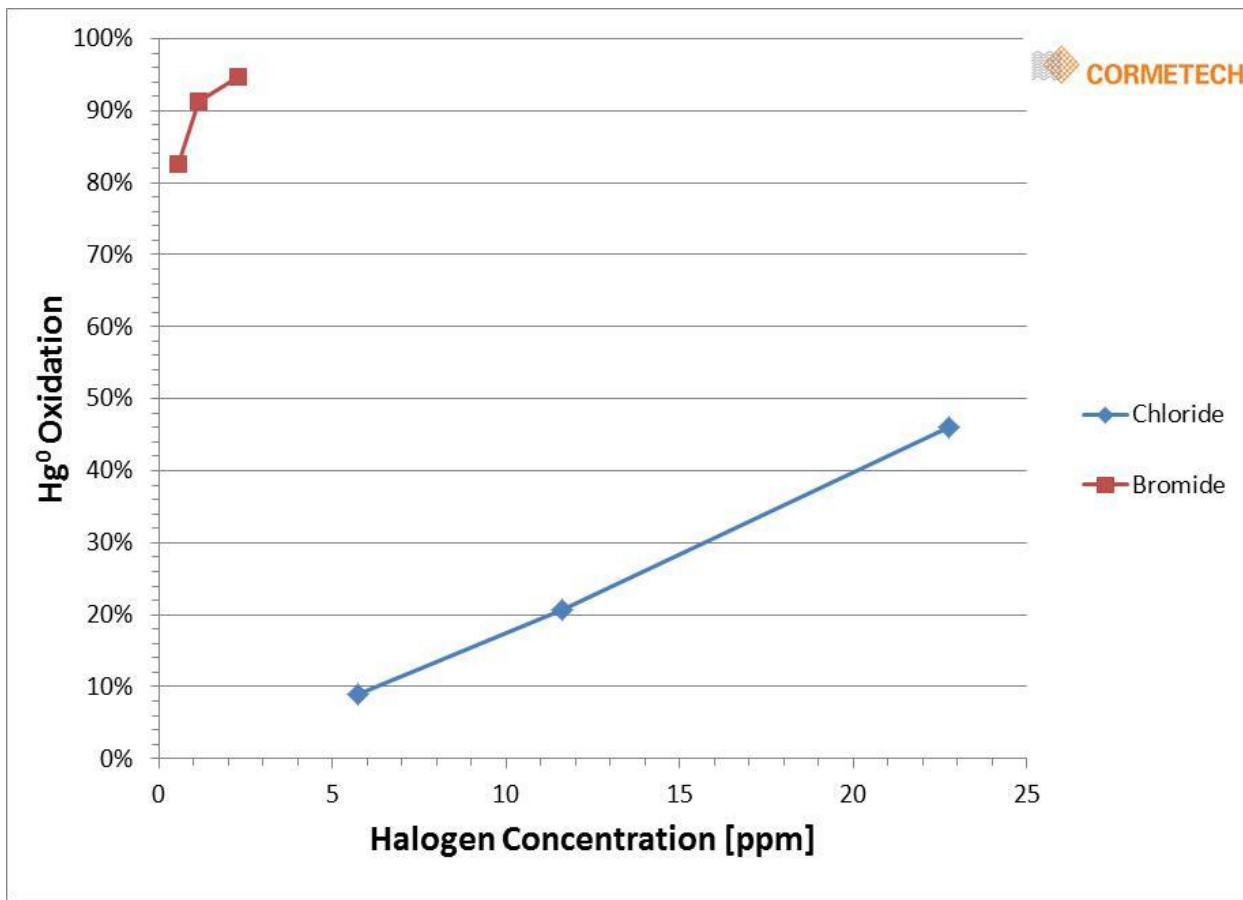
400°C, 350 ppm NO, 0.9 MR, 3.5% O₂, 12% H₂O, 1000 ppm SO₂, 11 ppm SO₃, 100 ppm CO.

Halogens: Cl vs. Br vs. I

Hg⁰ Oxidation Activity



Bromide is much more effective than chloride for Hg oxidation.



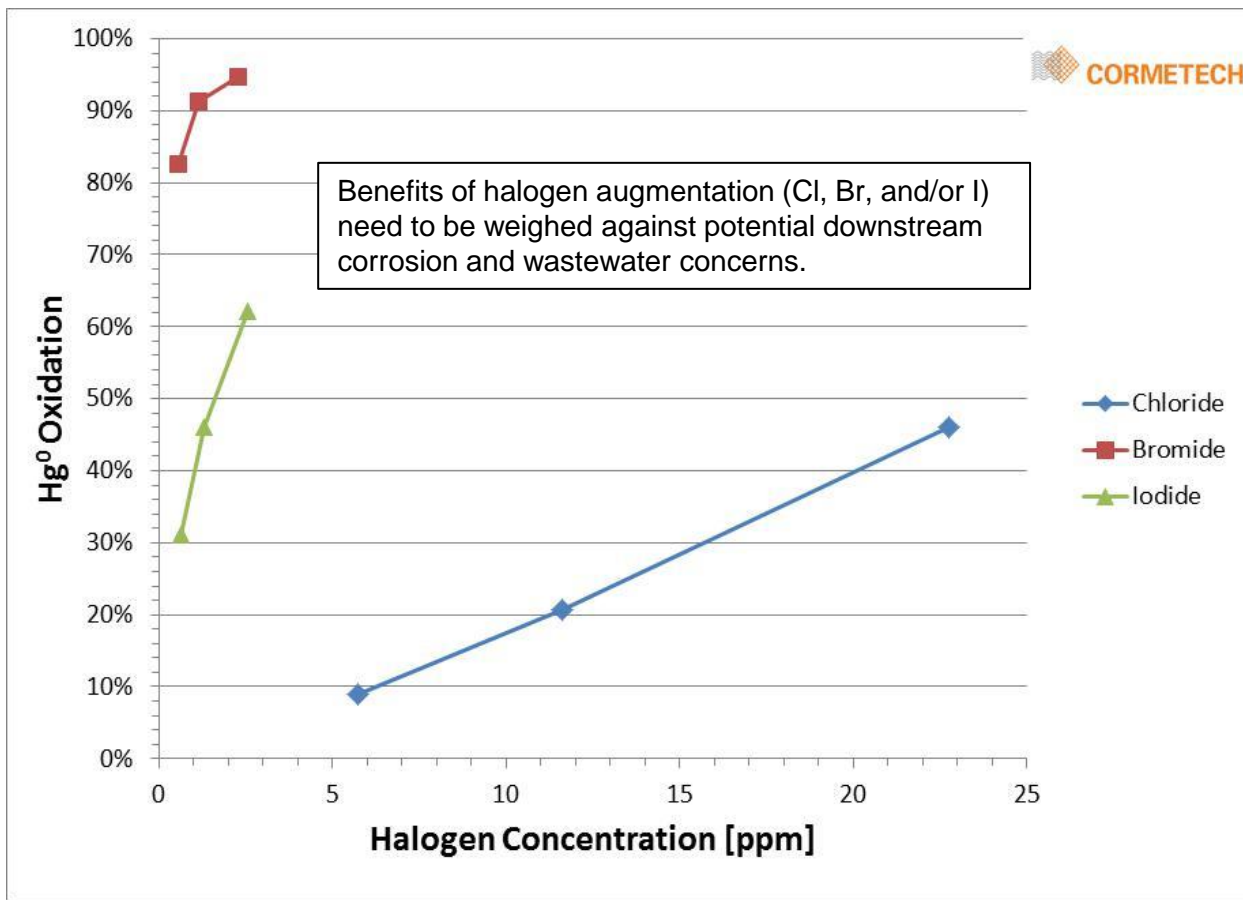
400°C, 350 ppm NO, 0.9 MR, 3.5% O₂, 12% H₂O, 1000 ppm SO₂, 11 ppm SO₃, 100 ppm CO.

Halogens: Cl vs. Br vs. I

Hg⁰ Oxidation Activity



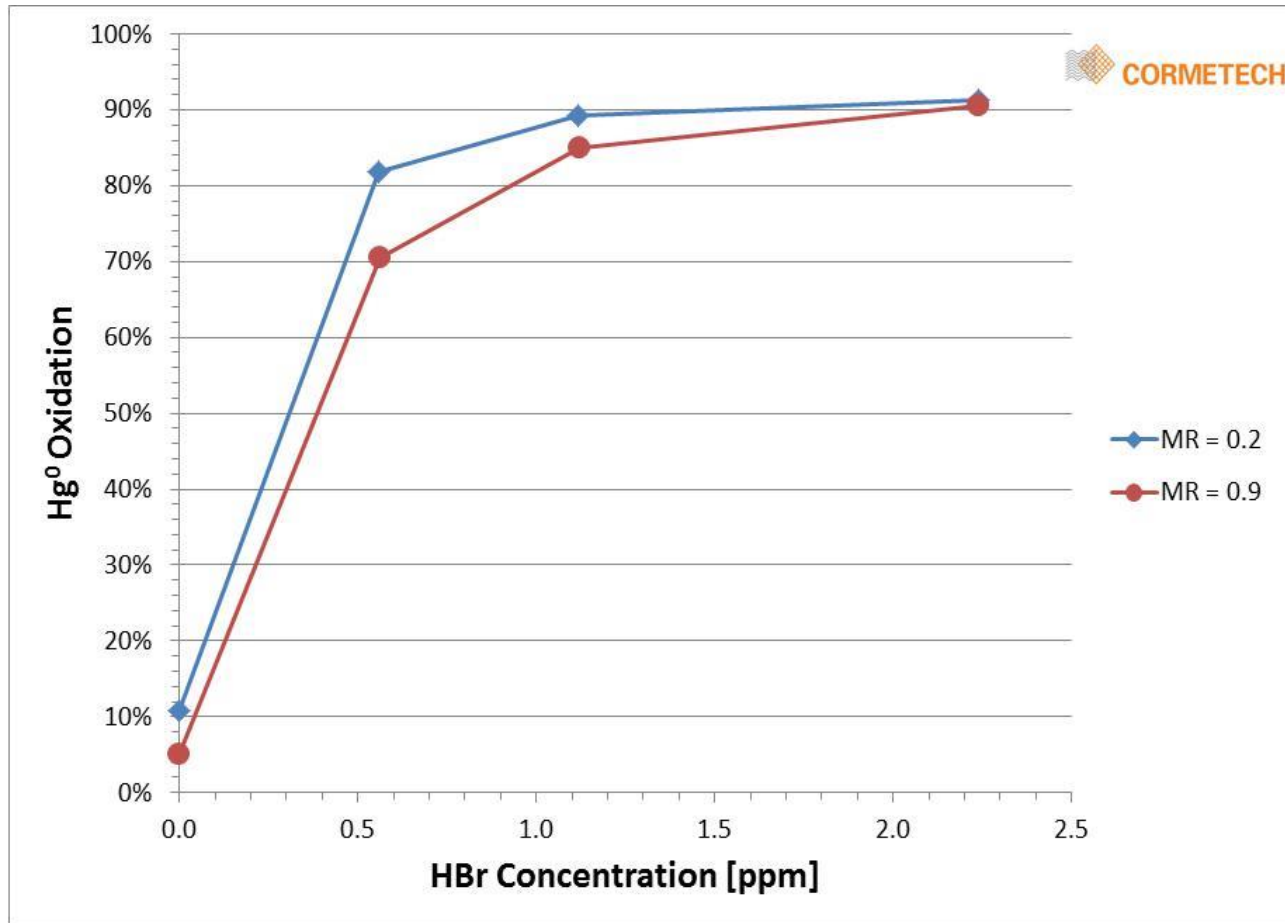
Rank of halogen effectiveness for Hg oxidation: Br > I > Cl.



400°C, 350 ppm NO, 0.9 MR, 3.5% O₂, 12% H₂O, 1000 ppm SO₂, 11 ppm SO₃, 100 ppm CO.

HBr Impact on NH₃ Inhibition

Testing data set at MR = 0.2 and MR = 0.9.

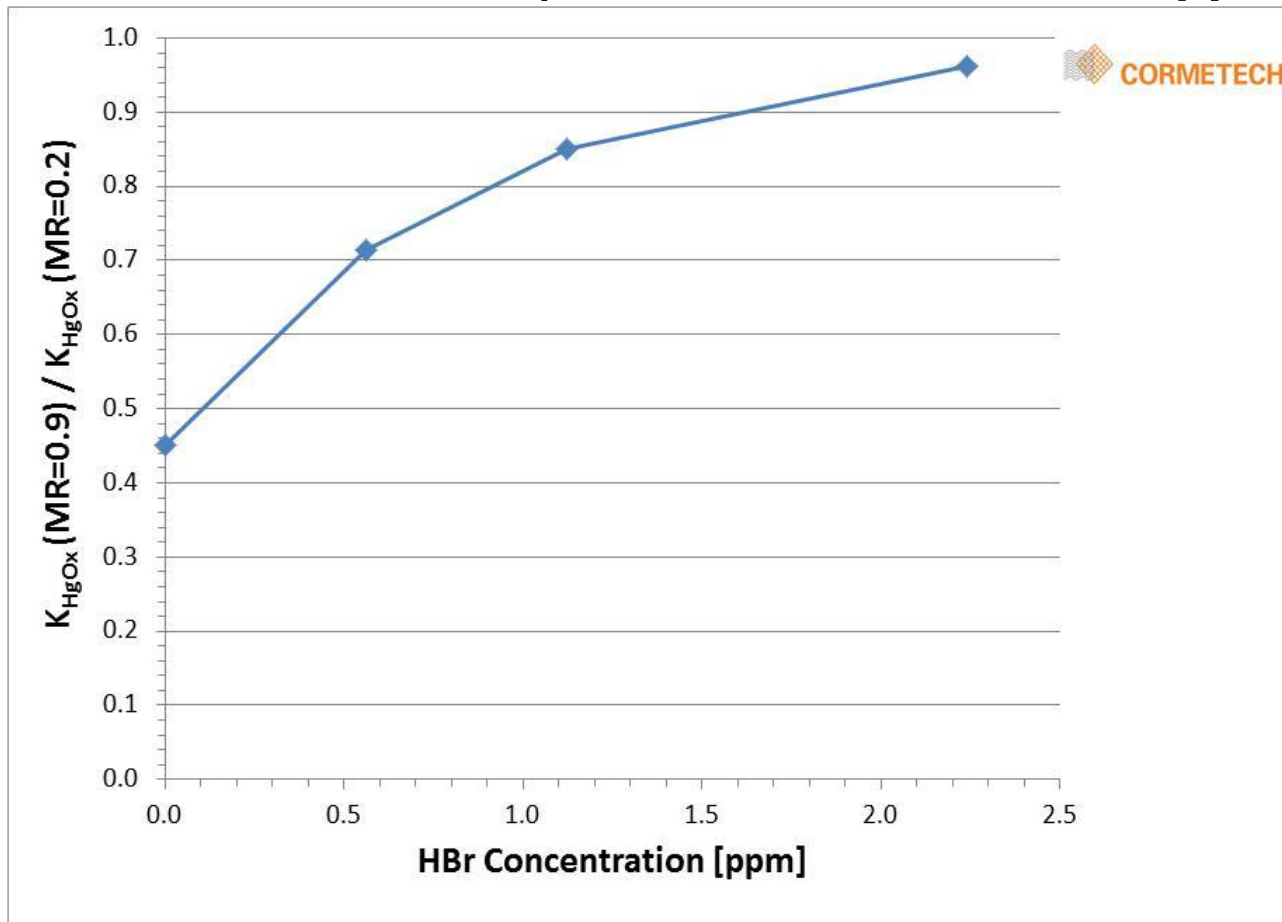


400°C, 3.5% O₂, 11% H₂O, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO, HCl = 5 ppm; MR = Inlet Molar Ratio

HBr Impact on NH₃ Inhibition



The catalyst's Hg oxidation activity is much less sensitive to NH₃ at high HBr concentration (almost no inhibition at 2 ppm HBr).



400°C, 3.5% O₂, 11% H₂O, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO, HCl = 5 ppm; MR = Inlet Molar Ratio

Impact of HBr on NH₃ Inhibition

First Layer vs. Lower Layer Performance



Strong interdependence between the HBr content and the degree of NH₃ suppression of Hg ox rate → as with higher HCl, the layer 1 catalyst will contribute more to overall Hg oxidation with HBr injection!

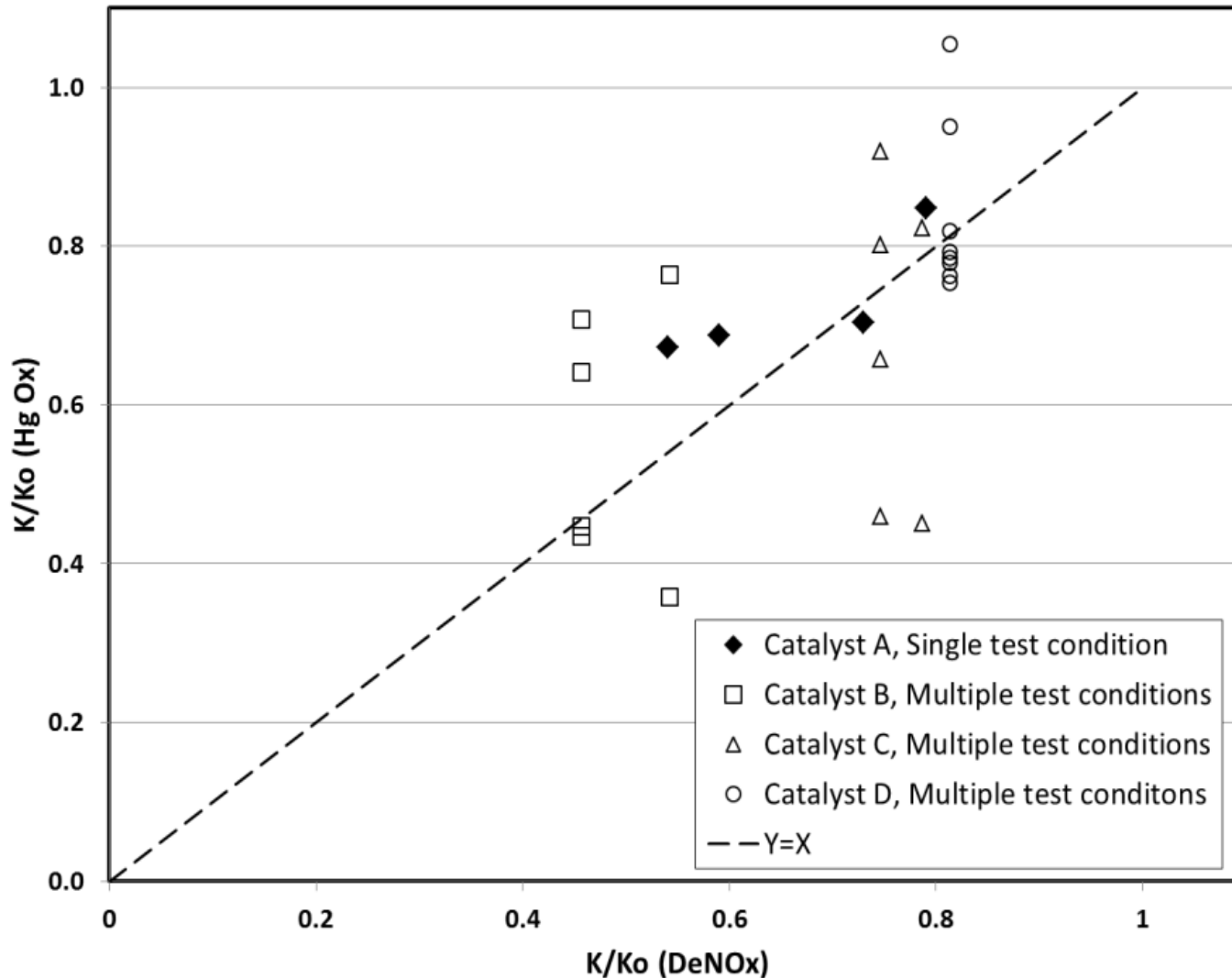
Single Layer Performance Example						
Position	Case	MR	HCl [ppm]	HBr [ppm]	Layer Hg Ox	Hg Ox Delta Layer 1 vs. Lower Layer
Layer 1	no HBr	0.9	6	0	5%	-6%
Lower Layer	no HBr	0.2	6	0	12%	
Layer 1	HBr = 1	0.9	6	1	87%	-4%
Lower Layer	HBr = 1	0.2	6	1	91%	
Layer 1	HBr = 2	0.9	6	2	92%	-1%
Lower Layer	HBr = 2	0.2	6	2	93%	

400°C, 3.5% O₂, 11% H₂O, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO, HCl = 5 ppm; MR = Inlet Molar Ratio

- **Including Hg is analogous to DeNOx...**
 - *With the caveats for K_{HgOx} previously outlined*
- **DeNOx or Hg oxidation establishes the design minimum volume**
 - *Depends on the relative catalyst potential and performance requirements for each reaction*
- **Considerations**
 - Layer auditing (lab reactor testing)
 - Catalyst action selection (traditional, regen, advanced)
 - Halogen augmentation potential

Catalyst Deactivation

Correlation with DeNOx Deactivation



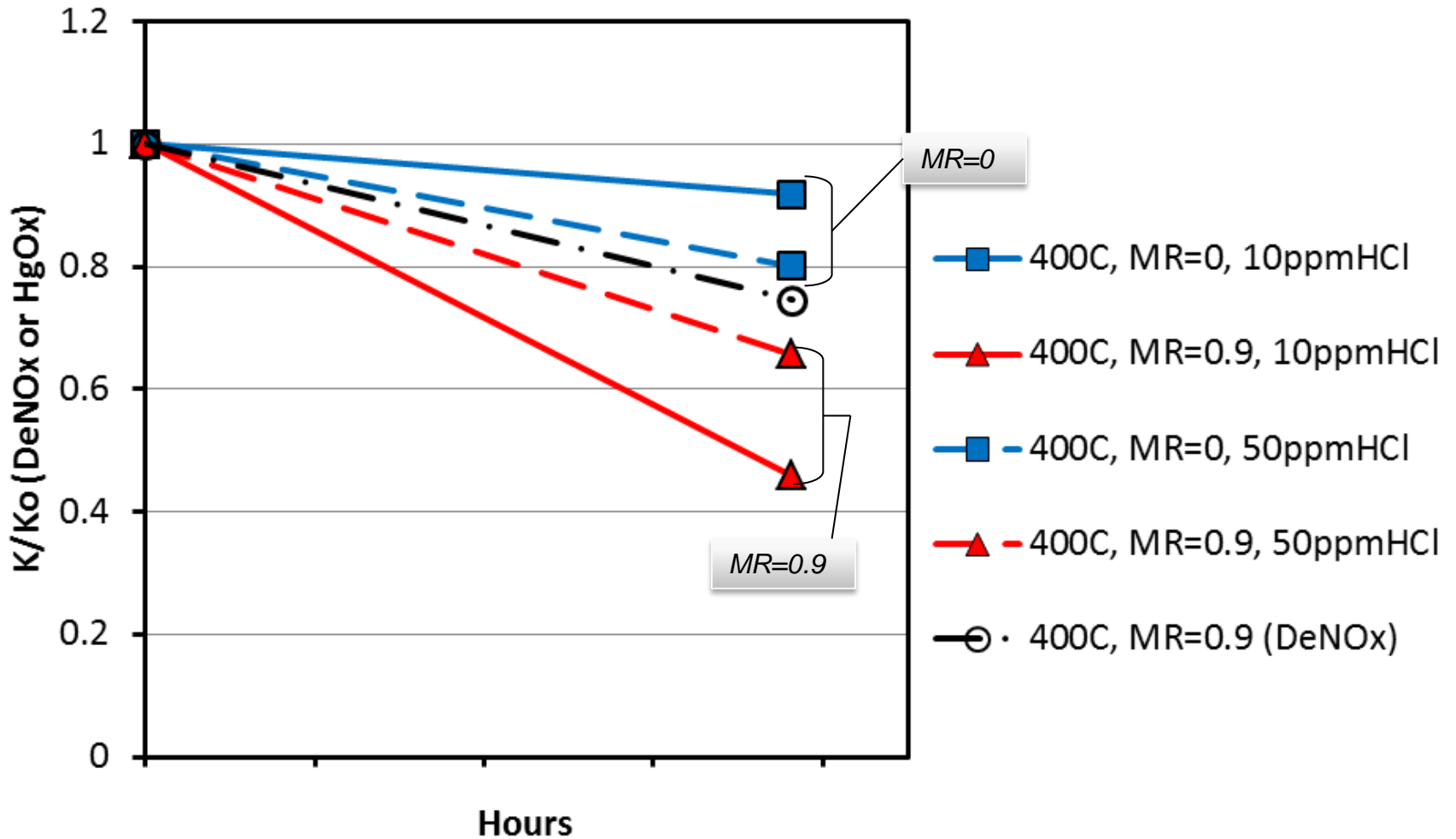
Hg oxidation deactivation generally correlates with DeNOx deactivation.

The extent of deactivation for the two reactions may not be equivalent:

K/Ko (Hg Ox) is sensitive to operating conditions (especially NH₃, HCl, temperature, and catalyst type).

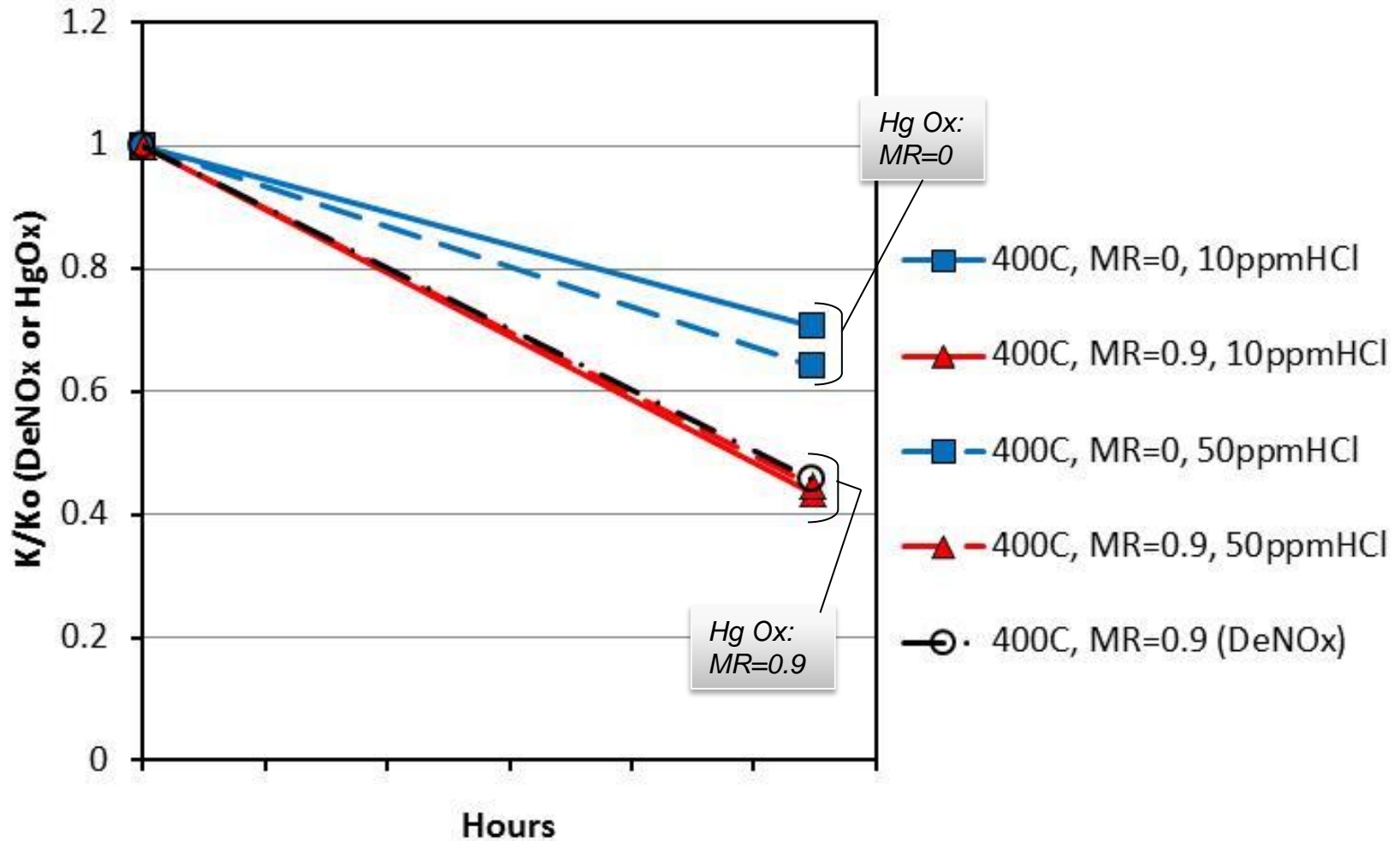
Catalyst Deactivation

PRB-Firing Unit Example (Ca, P)



Catalyst Deactivation

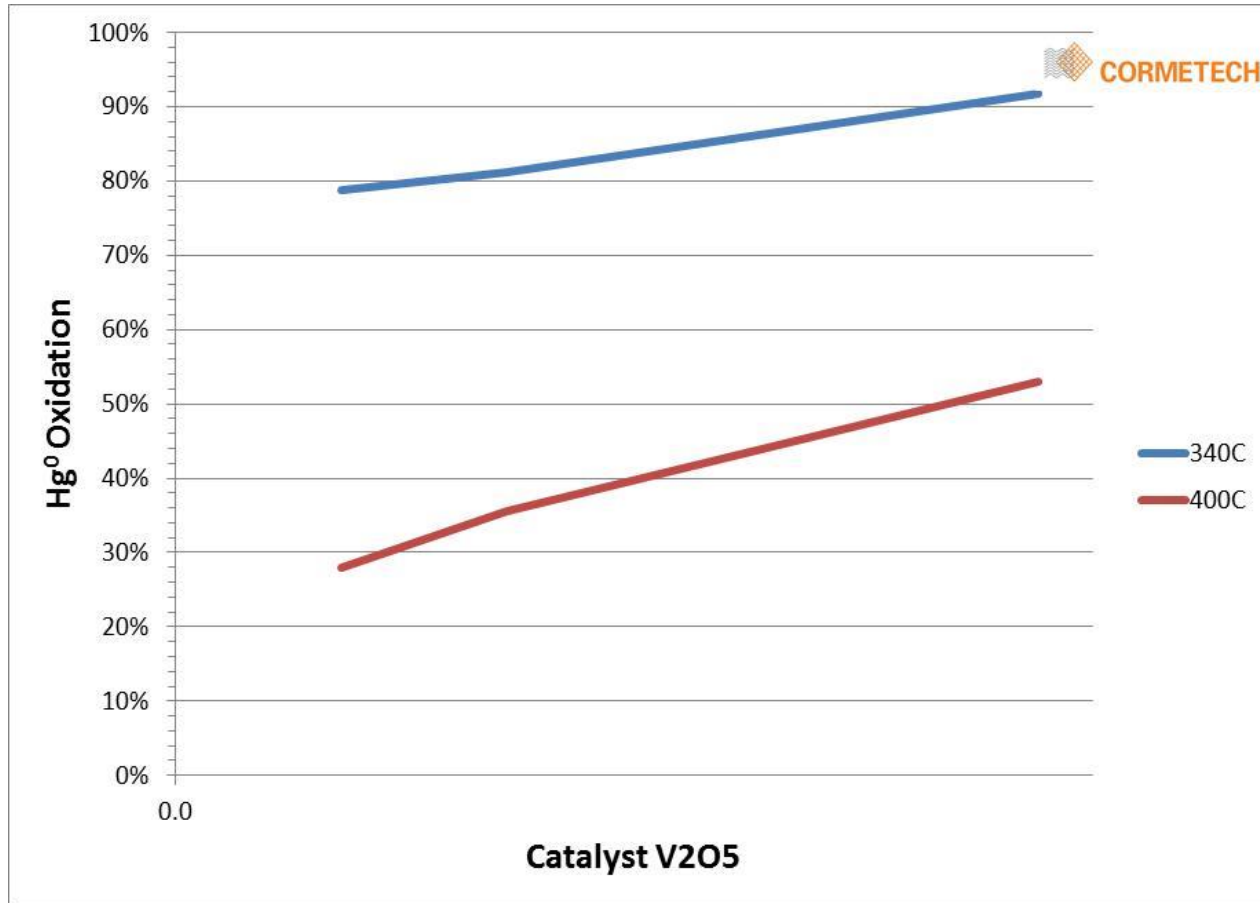
Bituminous-Firing Unit Example (As)



Impact of Catalyst V_2O_5 Content



Higher V_2O_5 improves Hg oxidation and DeNO_x, but it must be balanced relative to SO₂ oxidation constraints (e.g., PRB vs. bituminous, SO₃ mitigation).

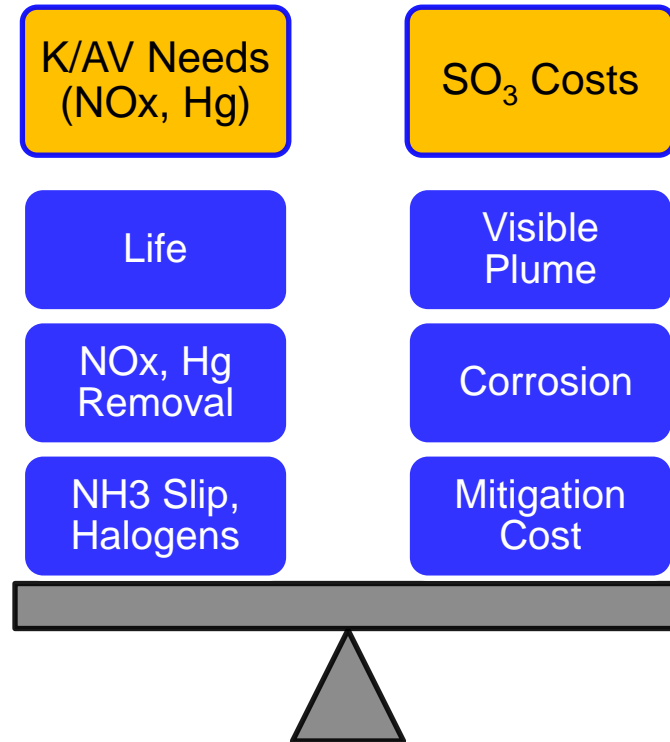


400°C, 3.5% O₂, 11% H₂O, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO, HCl = 11 ppm; MR = 0

SCR Catalyst: Design Approach

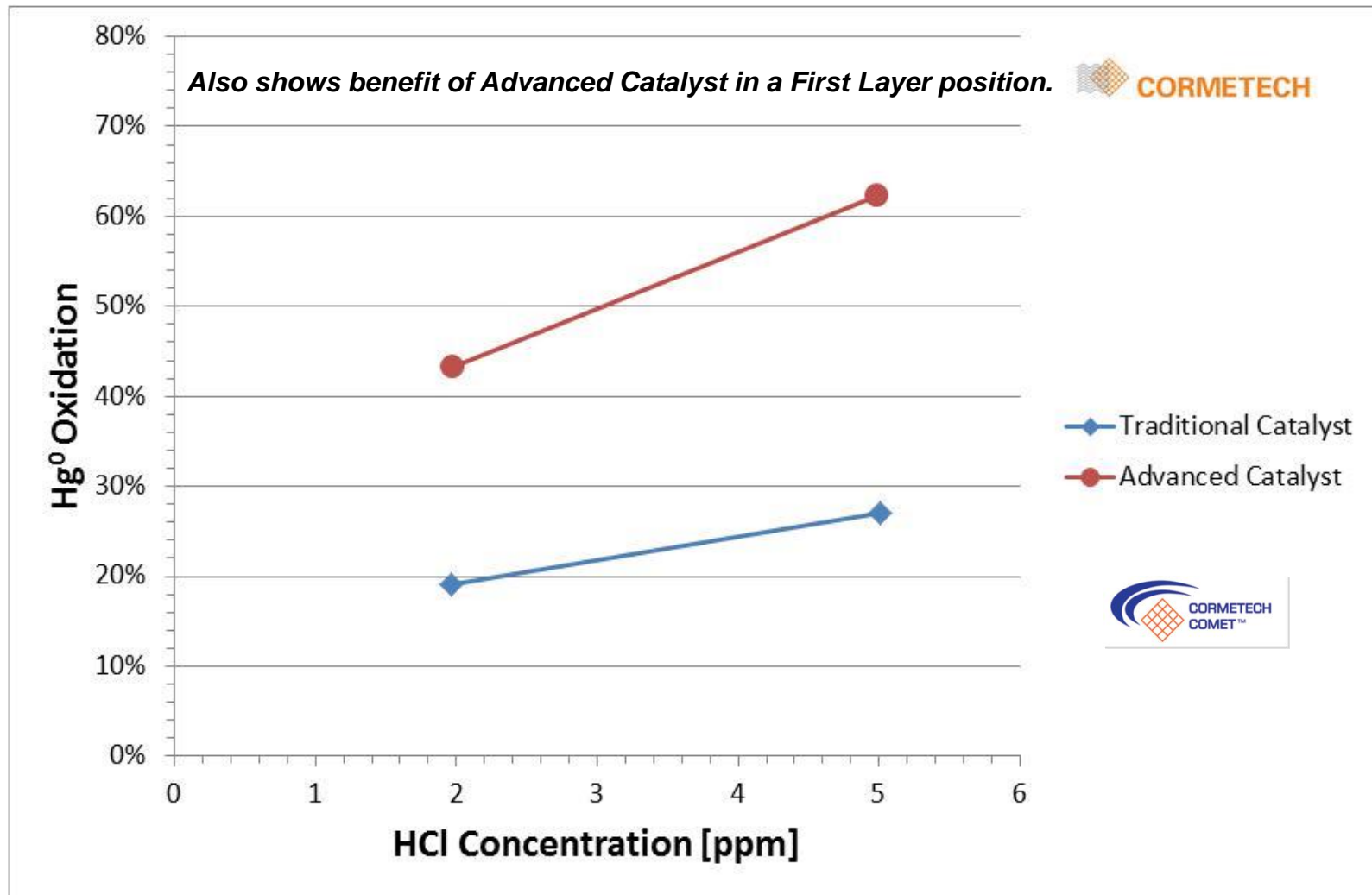


SCR catalyst is formulated to achieve DeNO_x and Hg oxidation requirements, while meeting SO₂ oxidation constraints. Either DeNO_x or Hg oxidation will be controlling for catalyst volume; the other will have excess potential.



- **For challenging conditions, such as...**
 - Lower HCl, and/or
 - Higher temperature, and/or
 - Higher concentration of reducing agents (NH₃, CO, SO₂)
- **...we can modify catalyst formulation and processing to improve Hg oxidation relative to DeNOx and SO₂ oxidation**

Advanced Catalyst: Low HCl



370°C, 250 ppm NO, 0.9 MR, 4% O₂, 14% H₂O, 400 ppm SO₂, 4 ppm SO₃, 100 ppm CO

Advanced Catalyst: NH₃ Impact

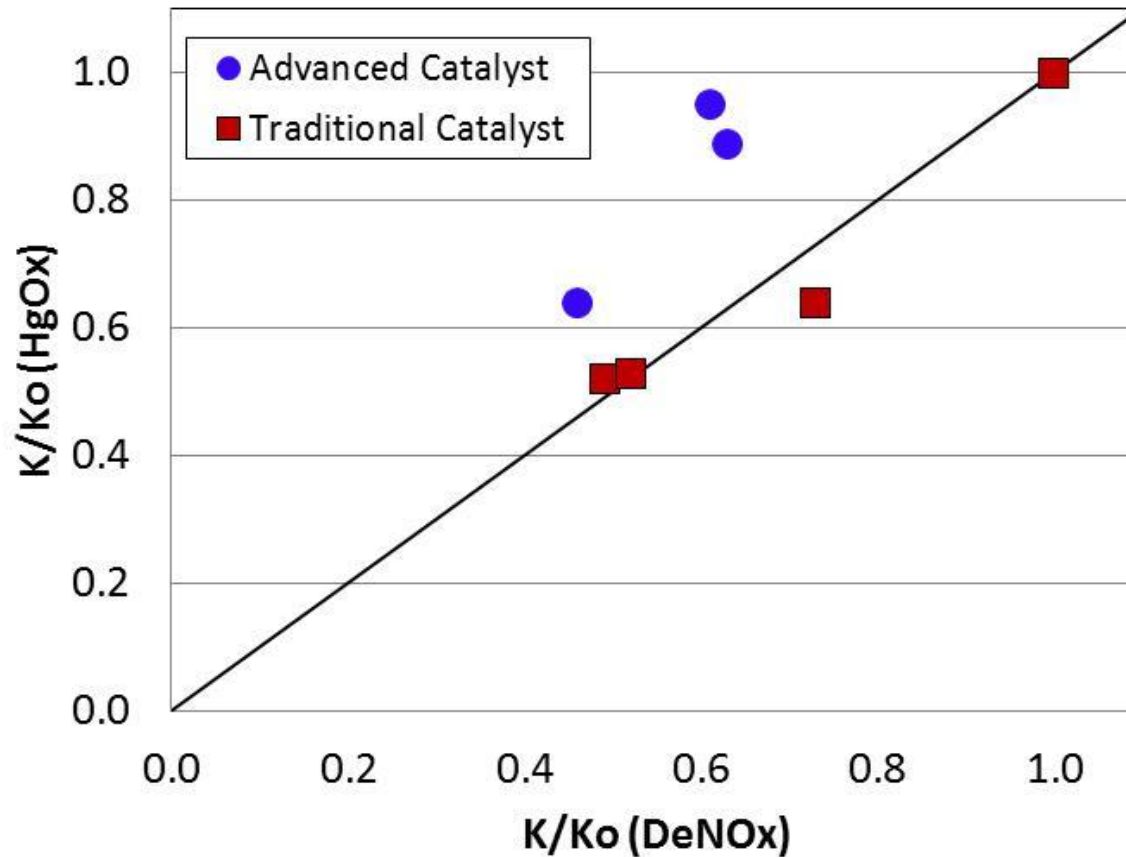


Advanced Catalyst also has a performance benefit in the First Layer position for higher HCl cases.

Single Layer Performance Example					
Position	Case	MR	HCl [ppm]	Layer Hg Ox	Hg Ox Delta Advanced vs. Traditional
Layer 1	Traditional Catalyst	1.0	58	53%	
Layer 1	Advanced Catalyst	1.0	58	72%	18%

371°C, 305 ppm NO, 1.0 MR, 4.3% O₂, 8.5% H₂O, 850 ppm SO₂, 8 ppm SO₃, 100 ppm CO.

Advanced Catalyst: K/Ko



400°C, 350 ppm NO, 0.9 MR, 3.5% O₂, 12% H₂O, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO, 56 ppm HCl

- **SCR Hg oxidation is influenced by multiple factors**
 - Layer dependency
 - More factors in setting design conditions
 - Interdependencies between factors
 - Impacts of catalyst type & formulation

Understand these factors and incorporate them into the design process to optimize the SCR for Hg oxidation, maintain NO_x reduction and manage SO₂ oxidation.



CORMETECH



Thank You!

Questions?

Christopher Bertole

Cormetech, Inc.

2015 Reinhold NOx-Combustion Round Table
