


REINHOLD ENVIRONMENTAL Ltd.



2017 NO_x-Combustion-CCR Round Table Presentation

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

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*Ian Saratovsky, PhD, Fuel Tech
Gary Meyer, Redox Solutions
Reinhold NOx Conference 2017*

SCR Operations and FGD Additives for Hg Control



Agenda

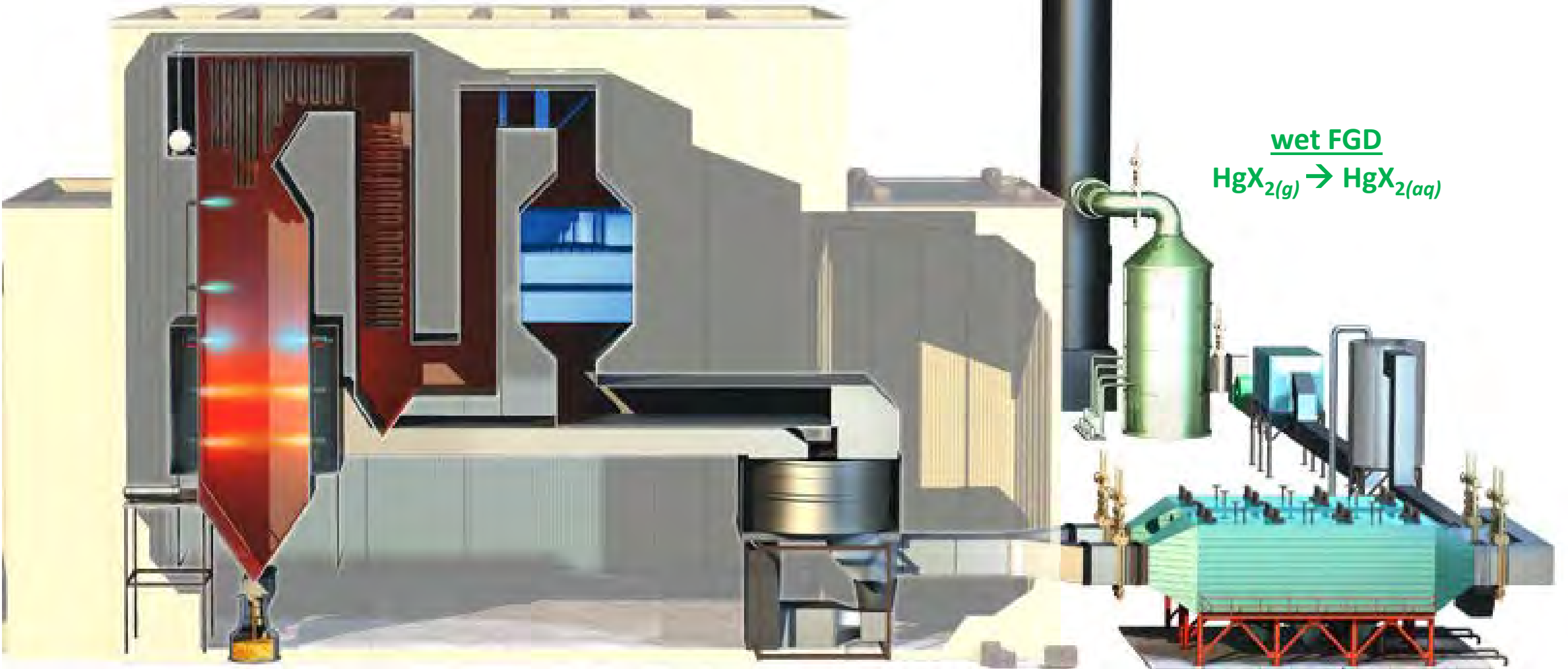
- Impacts of SCR operations on mercury
- SCR and catalyst management
 - $\text{NO}_x / \text{NH}_3$
 - Pluggage and poisons
- Retrofitting SCR for improved operation
- Managing Hg as catalysts degrade
- Redox-Hg FGD additives
- Conclusions

SCR

Primary: $\text{NO}_{(g)} \rightarrow \text{N}_{2(g)}$
Secondary: $\text{Hg}^0 \rightarrow \text{HgX}_2$ (X = Cl, Br, I)

wet FGD

$\text{HgX}_{2(g)} \rightarrow \text{HgX}_{2(aq)}$



SCR Operation Parameters and Influences on Hg

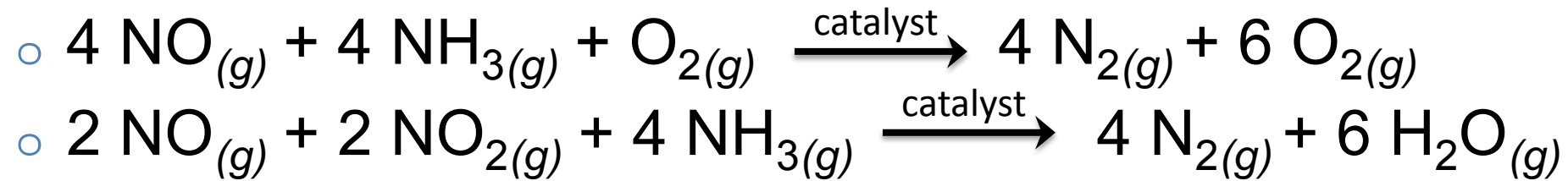
- Load profile
 - Baseload vs. load cycling
- Ash loading/particle size distribution
- Flow stratification
- % transition metals in catalyst (e.g. V, W, Mo)
 - Can also increase SO₂ to SO₃ conversion rate
- Catalyst poisons
 - Particulate, CaSO₄, As, Se, Na, K

SCR Operations : Major O&M Cost Factors

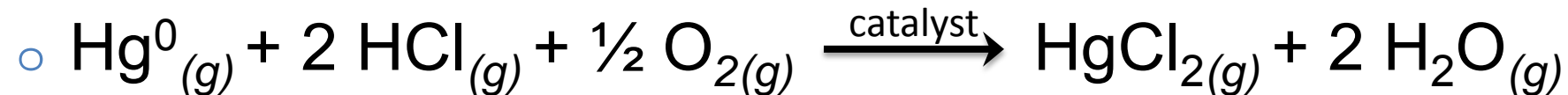
- Catalyst changes/regeneration/rejuvenation
 - Driven by performance degradation
 - NO_x reduction
 - Hg^0 oxidation
 - Catalyst pluggage/poisoning
 - Catalyst washes
- SO_2 to SO_3 conversion rates
 - Increased SO_3 emissions may require sorbent injection
- Minimum operation temperature (MOT)
 - Driven by ABS formation and performance
 - Decrease SO_3 through sorbent injection upstream of SCR
 - TIFI $\text{Mg}(\text{OH})_2$, limestone, hydrated lime, sodium sorbents

SCR Catalyst Design

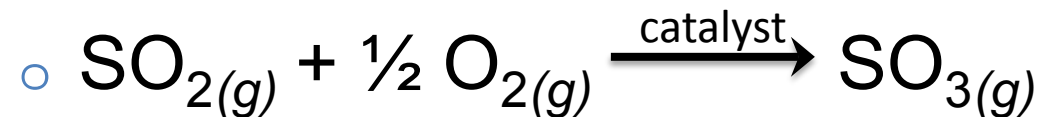
1) NO_x reduction



2) Hg⁰ oxidation



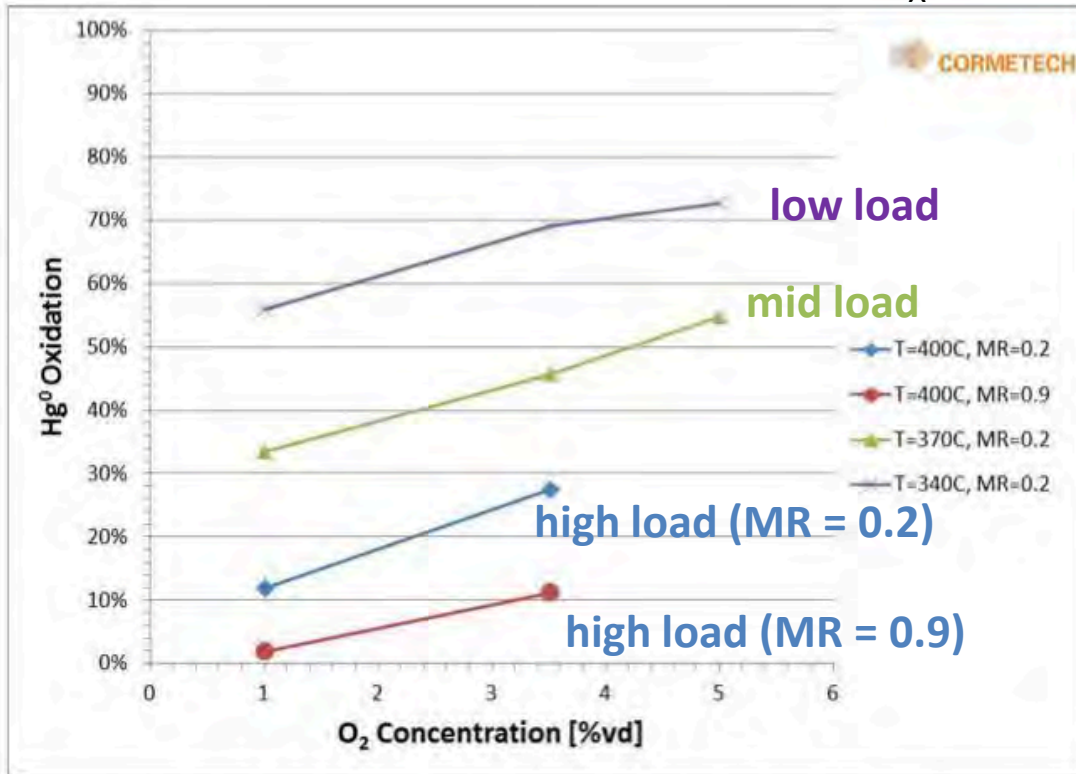
3) SO₂ oxidation



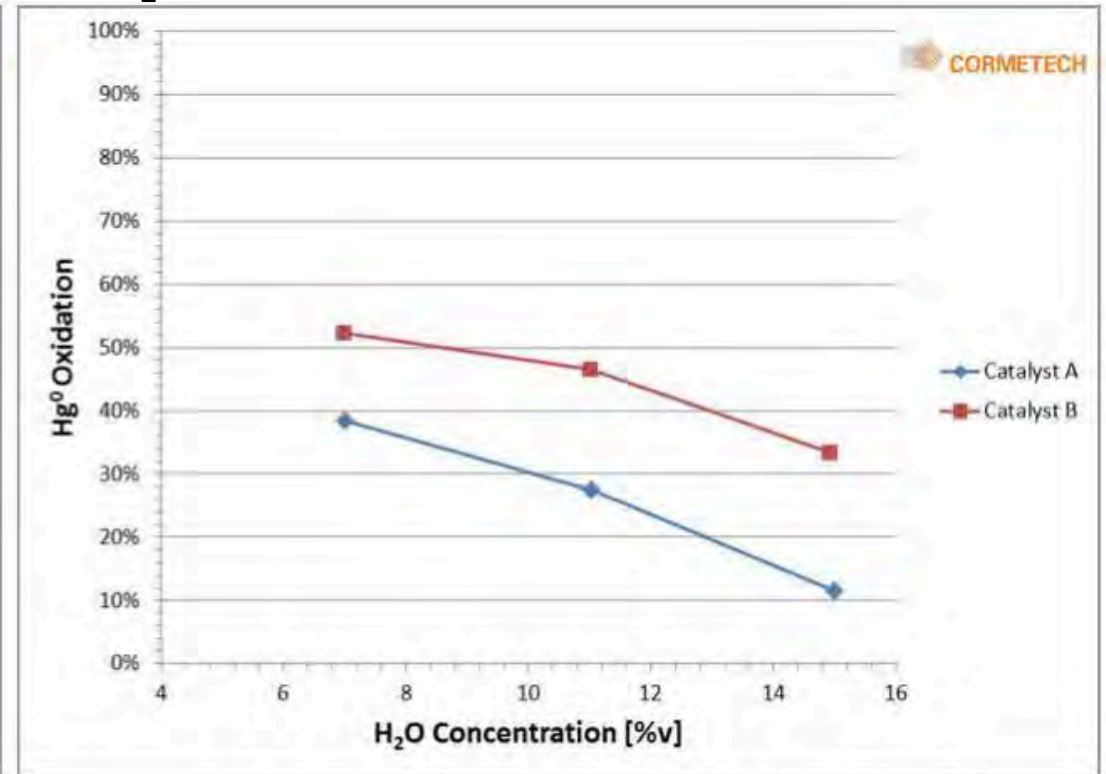
Goal: Maximize reaction (1) and (2), minimize reaction (3)

Hg⁰ Oxidation Impact Factors : NH₃, H₂O, O₂

- O₂ and H₂O significantly impact Hg oxidation activity
 - These have minimal impacts on NO_x reduction/SO₂ oxidation



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

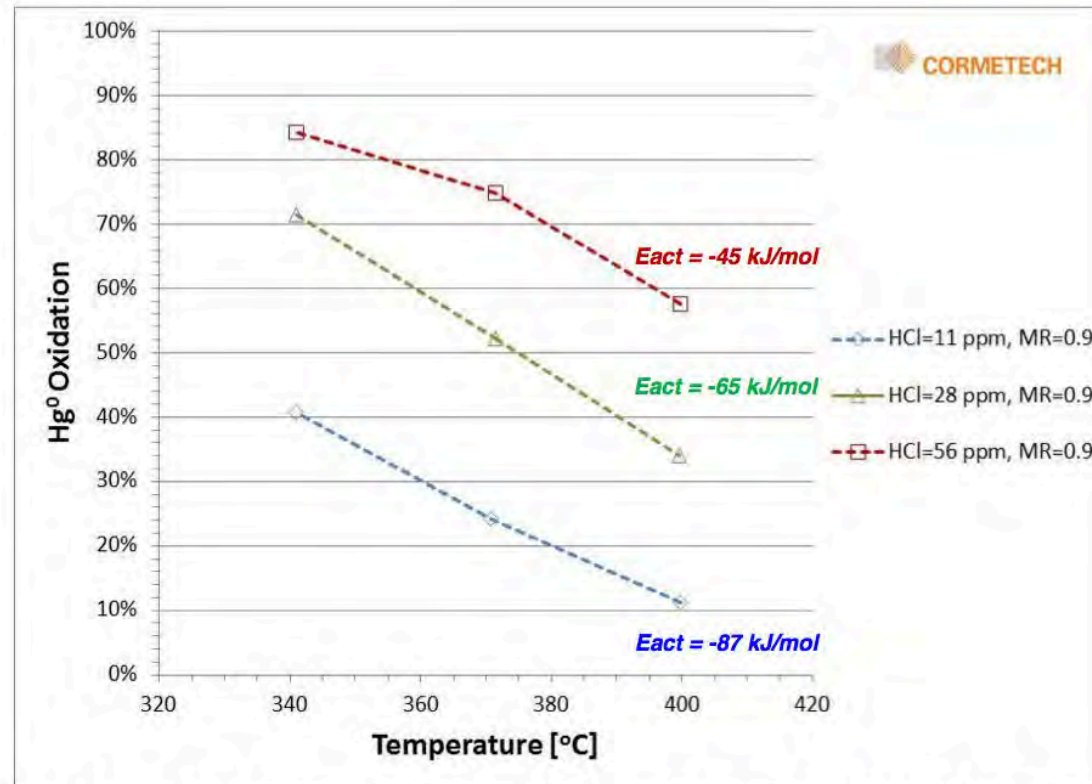


400°C, 3.5% O₂, 350 ppm NO, 0.2 Molar Ratio, 1000 ppm SO₂,
10 ppm SO₃, 100 ppm CO, 11 ppm HCl

Reference: Bertole, C.; Reinhold 2015 NO_x-Combustion Round Table; Richmond, Va.

Hg⁰ Oxidation Impact Factors : HCl

- Hg⁰ oxidation activity decreases with increasing temperature and increasing NH₃ concentrations
- NH₃ and HCl compete for active sites on catalyst

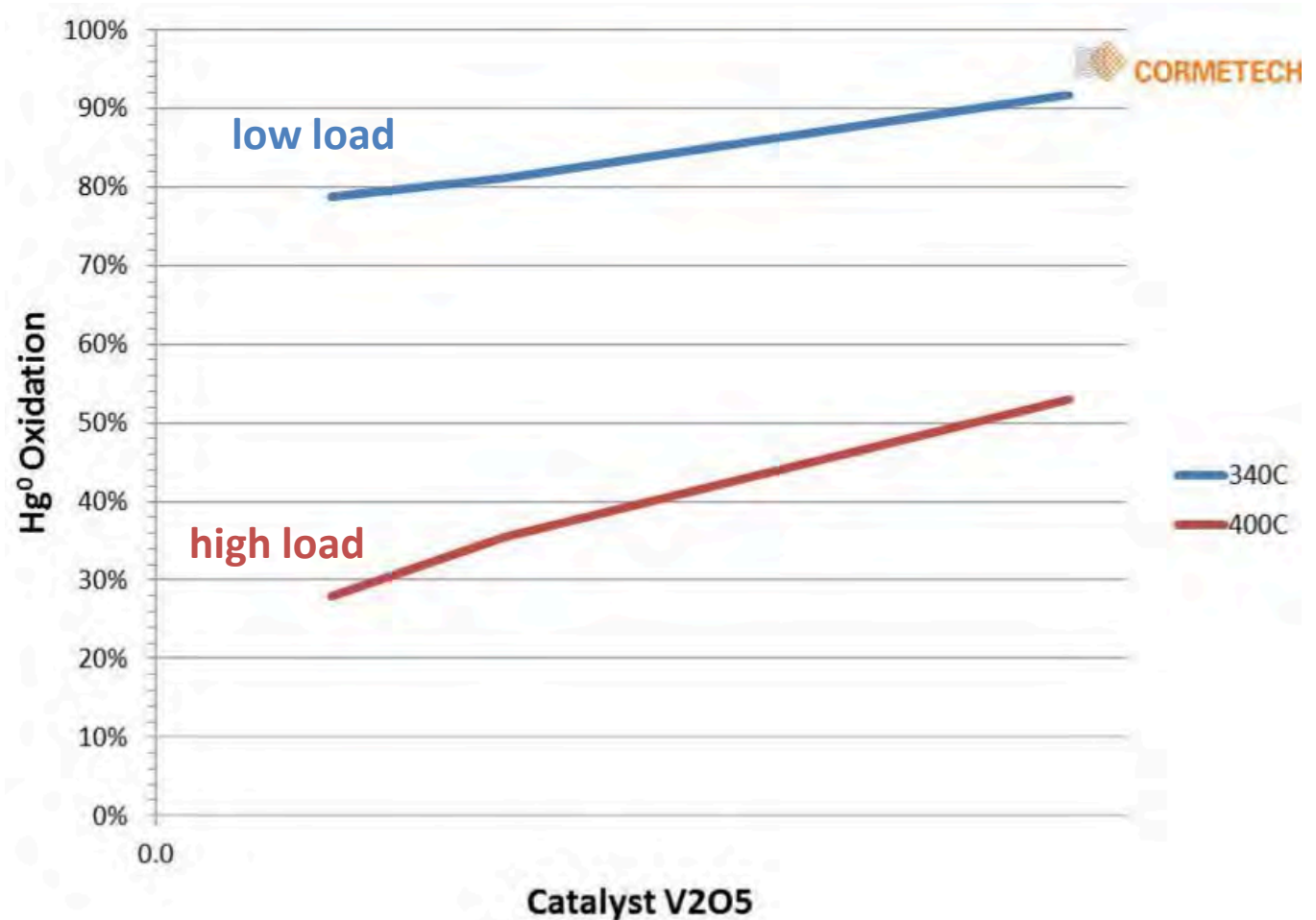


3.5% O₂, 11% H₂O, 350 ppm NO, 1000 ppm SO₂, 10 ppm SO₃, 100 ppm CO; MR = Inlet Molar Ratio

Reference: Bertole, C.; Reinhold 2015 NO_x-Combustion Round Table; Richmond, Va.

Hg⁰ Oxidation Impact Factors : V₂O₅ Content and Temperature

- Load cycling significantly impacts Hg⁰ oxidation
- Higher V₂O₅ improves Hg⁰ oxidation and NO_x reduction
 - Must be balanced with SO₂ oxidation



Reference: Bertole, C.; Reinhold 2015 NO_x-Combustion Round Table; Richmond, Va.

Hg⁰ Oxidation Impact Factors

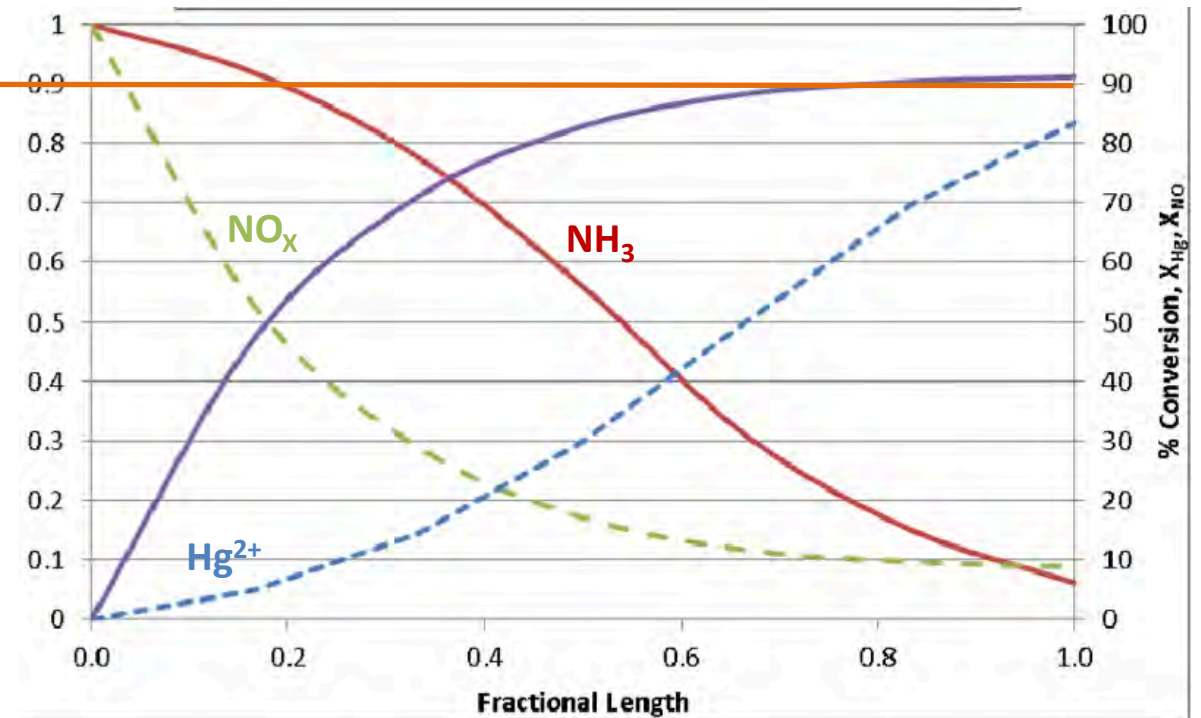
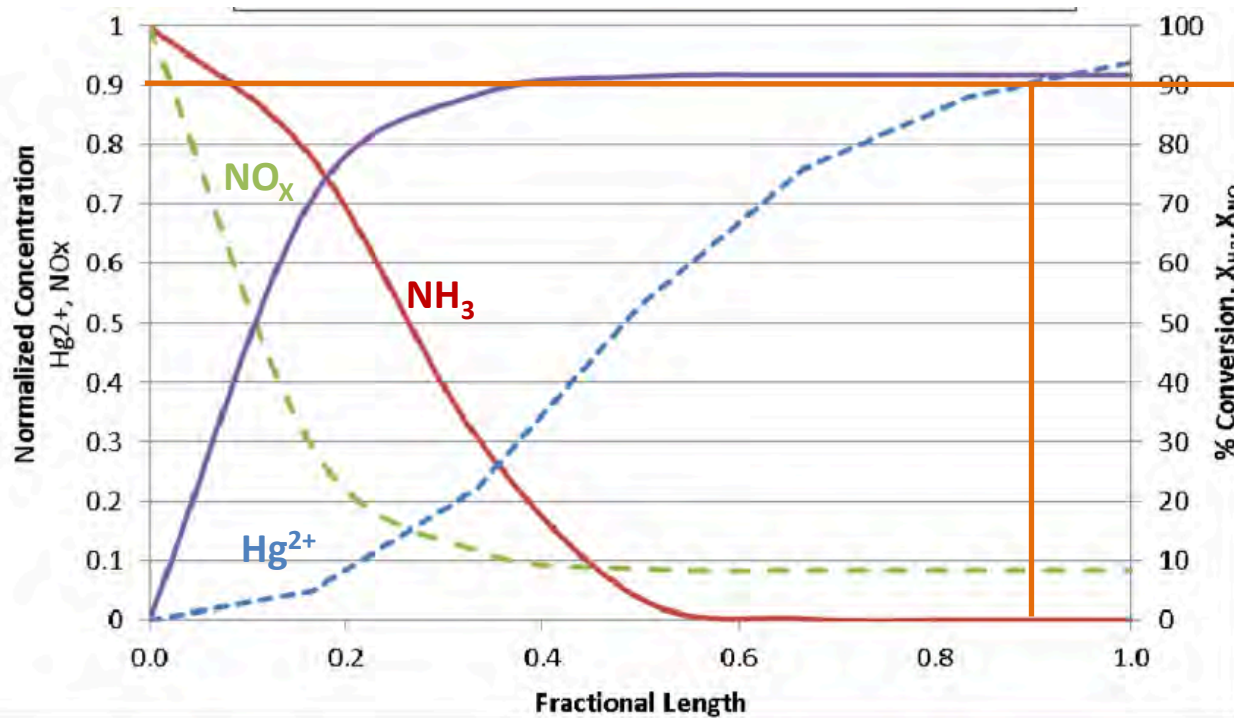
- Halogens are critical to high Hg⁰ oxidation across SCR
 - Catalysts alone do not significantly oxidize Hg⁰
- NH₃ can significantly inhibit Hg⁰ oxidation activity
 - Proper flow distribution is critical to minimize local high NH₃ concentrations

Reference: Bertole, C.; Reinhold 2015 NO_x-Combustion Round Table; Richmond, Va.

Impact of Catalyst Aging

New Catalyst

Aged Catalyst



Mercury oxidation over SCR is based on many conditions and is transient

Reference: Repp, D.; WPCA Mercury Seminar, October 2012, Birmingham, AL

Hg⁰ Oxidation Impact Factors

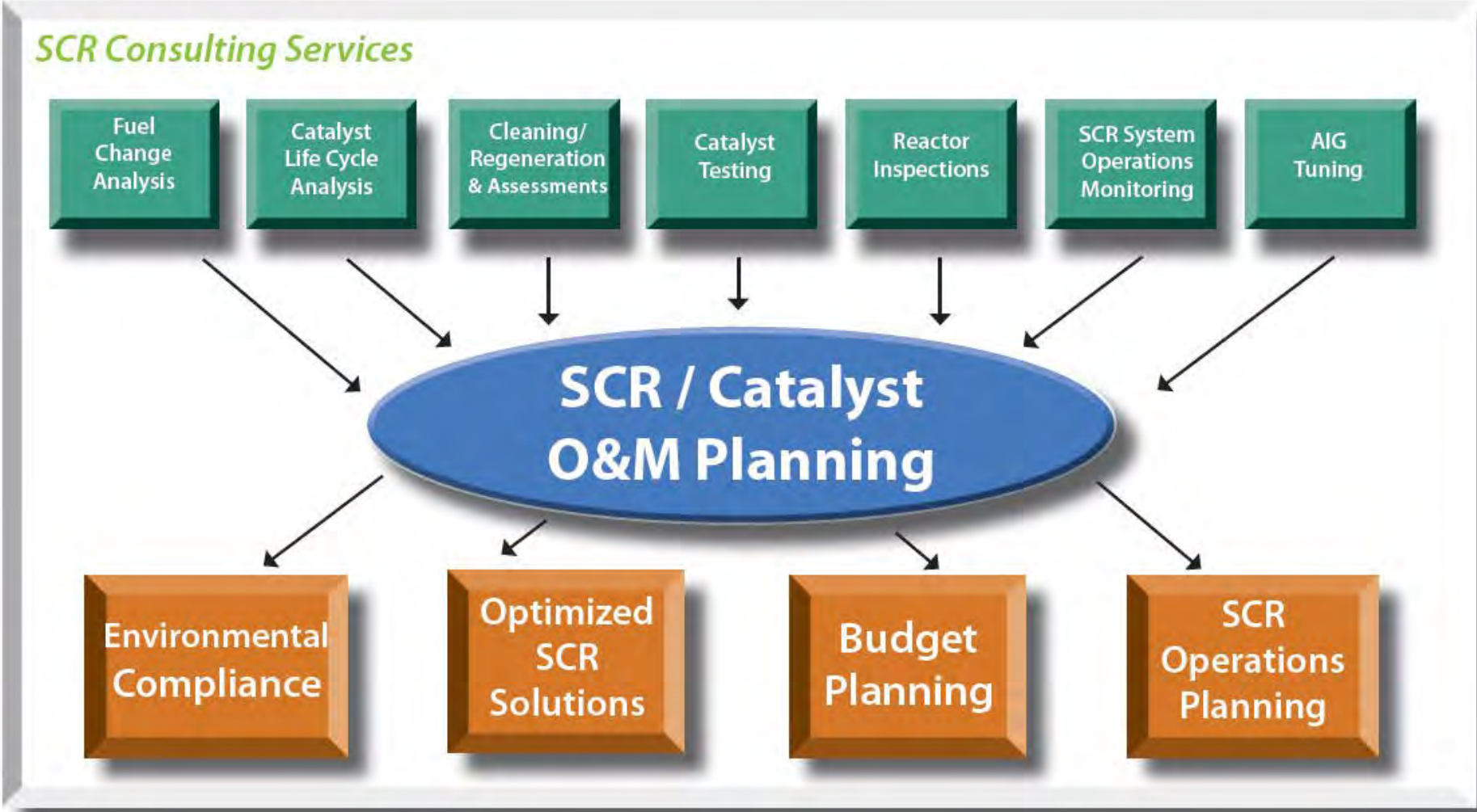
- Hg⁰ oxidation performance degrades with:
 - Usage/life (linear decline)
 - Load cycling (variable, temperature, flow rate)
 - NH₃ concentration (linear)
 - H₂O and O₂ (variable)
- Catalyst management dampens variability
- Wet scrubber additive can be used to dampen variability
 - Capture Hg⁰ and Hg²⁺
 - Cost effective and can be done on-demand



Fuel Tech - SCR Catalyst Management



SCR Consulting Services



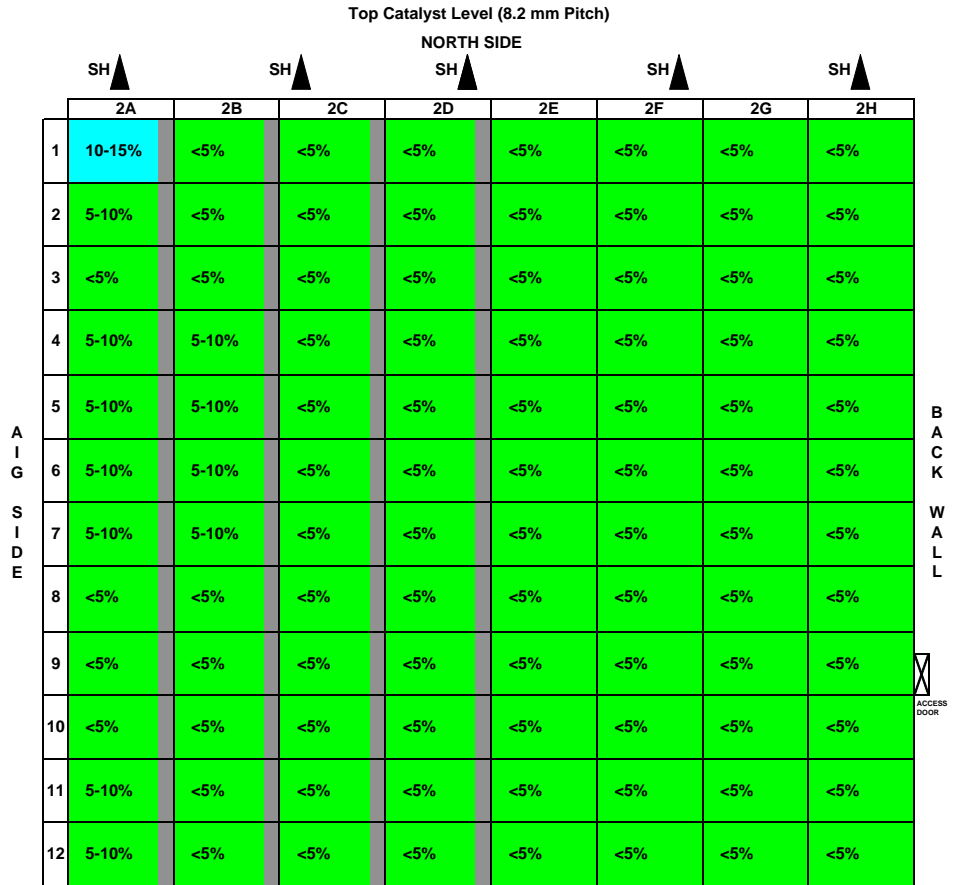
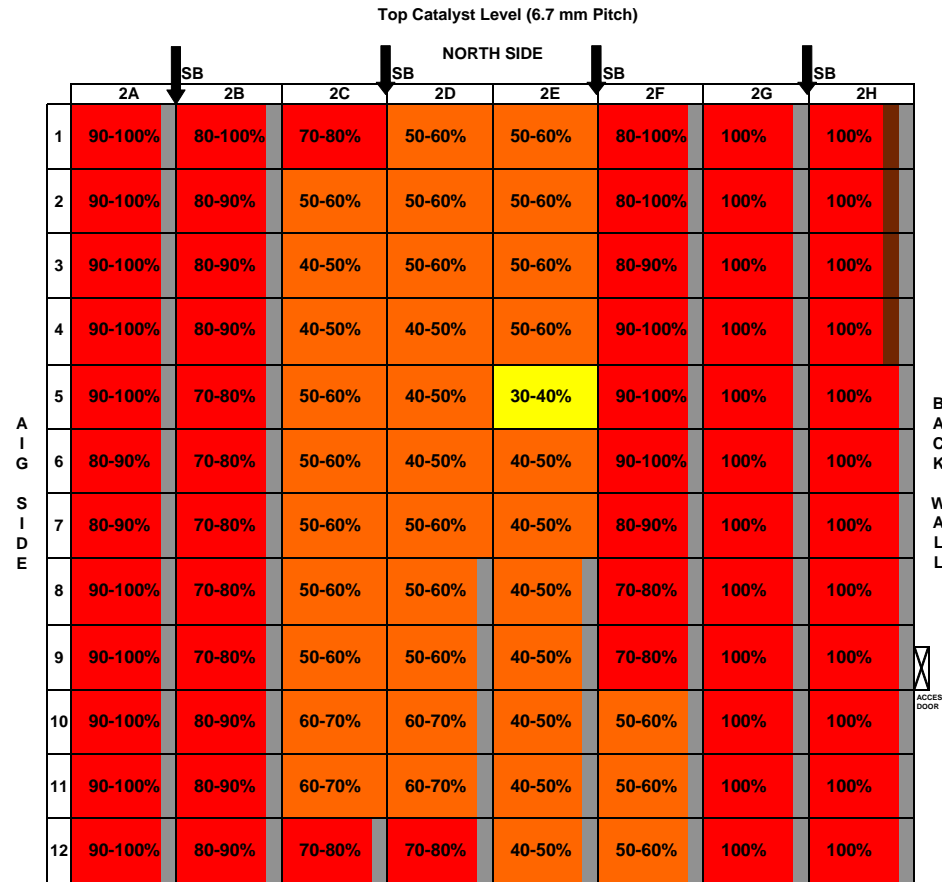
Program Attributes

- FTEK does NOT:
 - Produce or manufacture catalyst
 - Regenerate catalyst
 - Rejuvenate catalyst
- FTEK does:
 - Optimize SCR Operation
 - Investigates ways to prolong life of existing catalyst
 - Helps client with planning and budgeting
- 28 years and more than 80,000 MW of Experience
- All SCR performance related know-how is in house

SCR and Reactor Inspections



Reactor Inspections – Ash Pluggage



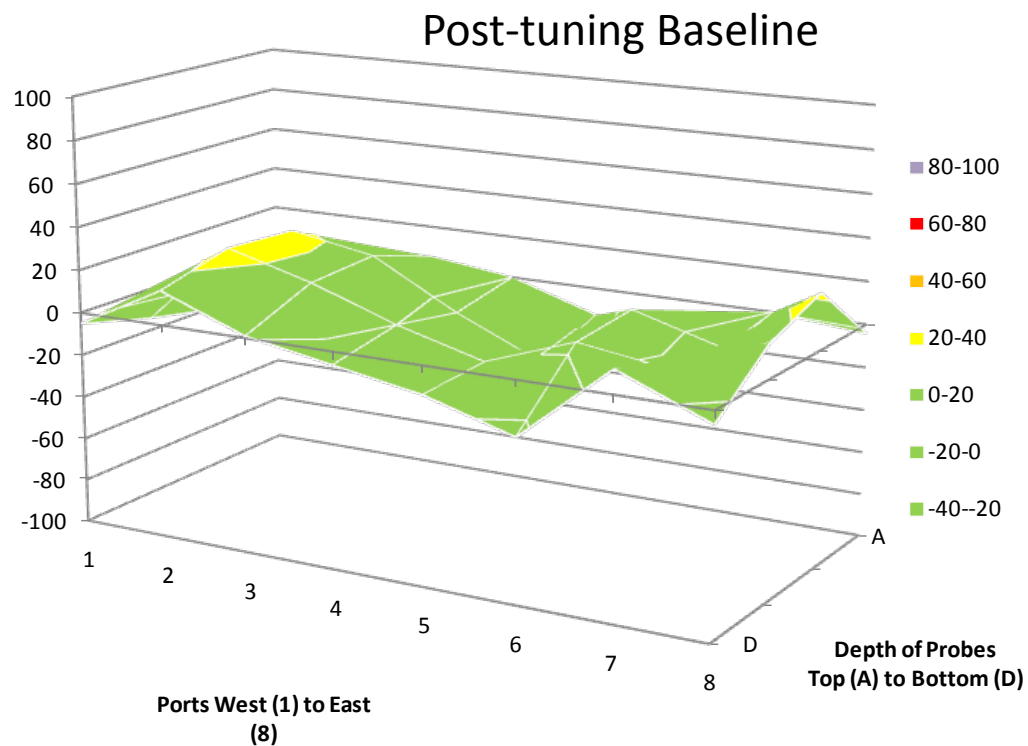
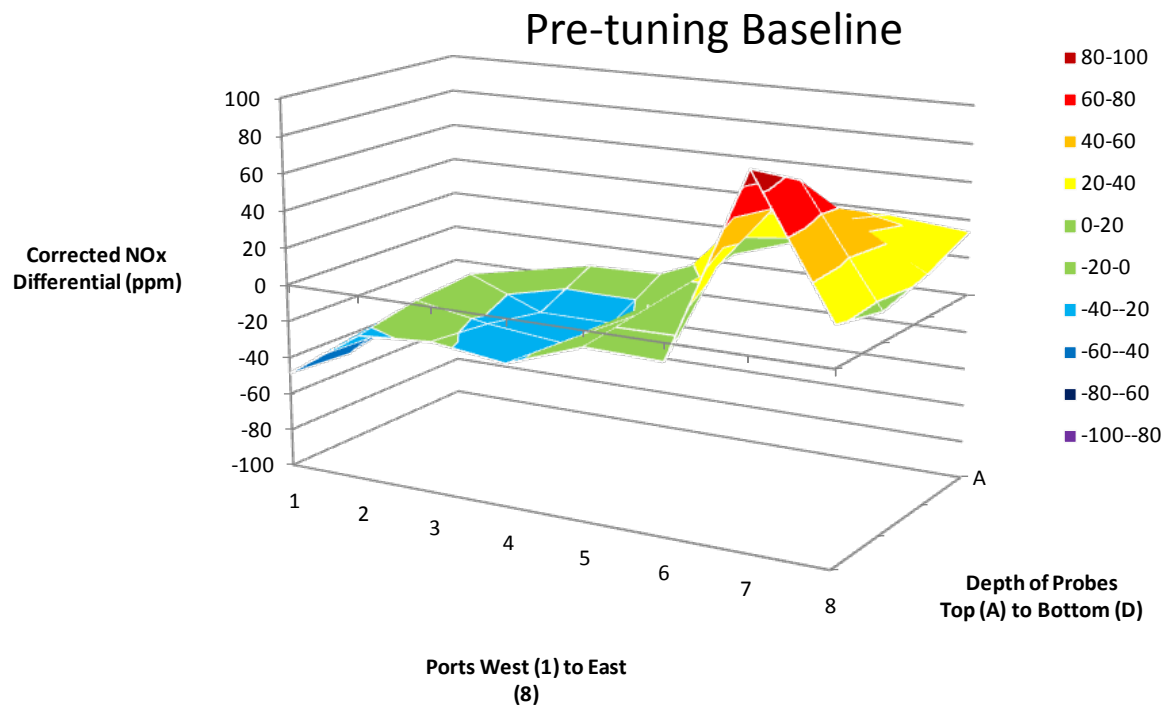
Ammonia Injection Grid Tuning

- Utilizing fixed measurement grid for NO_x measurements and DCS data regarding SCR system operations results
- Tuning objective = ± 15 to 25 ppm outlet NO_x dependent on AIG and gas path configuration
- Providing comprehensive tuning report
- AIG tuning services since 1999
 - 100+ AIGs tuned
 - 10+ (> 20,000 MW) of catalyst management programs



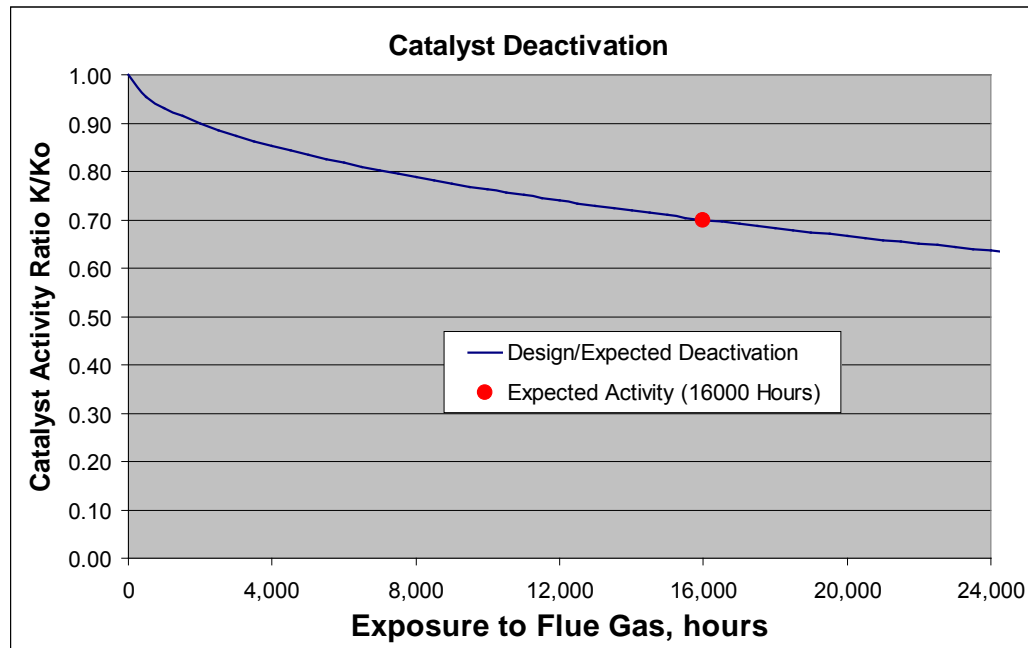
Reporting and Analysis

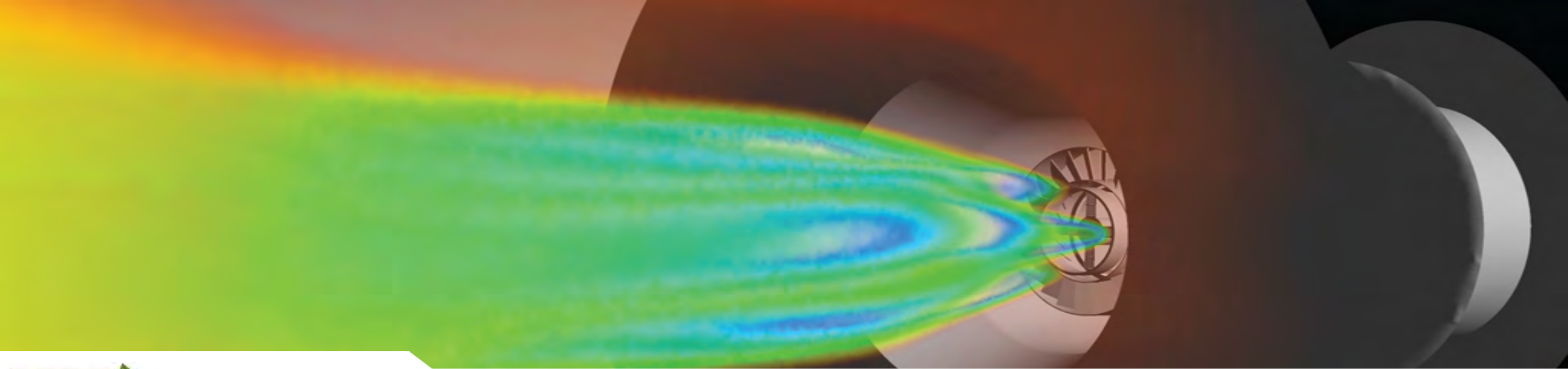
AIG Tuning and Balancing - Representative AIG Tuning Result



Catalyst Testing

- Independent review
- Use 3rd Party Lab for Testing
- Review, analyze, and interpret testing results
- Use results to identify a Catalyst Management Strategy



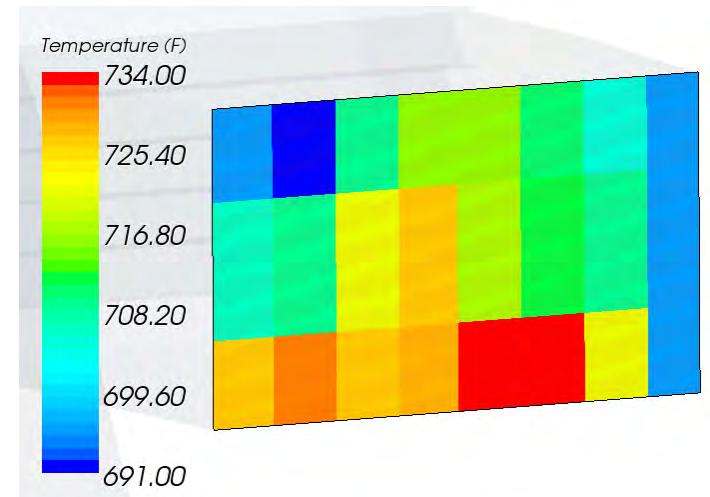
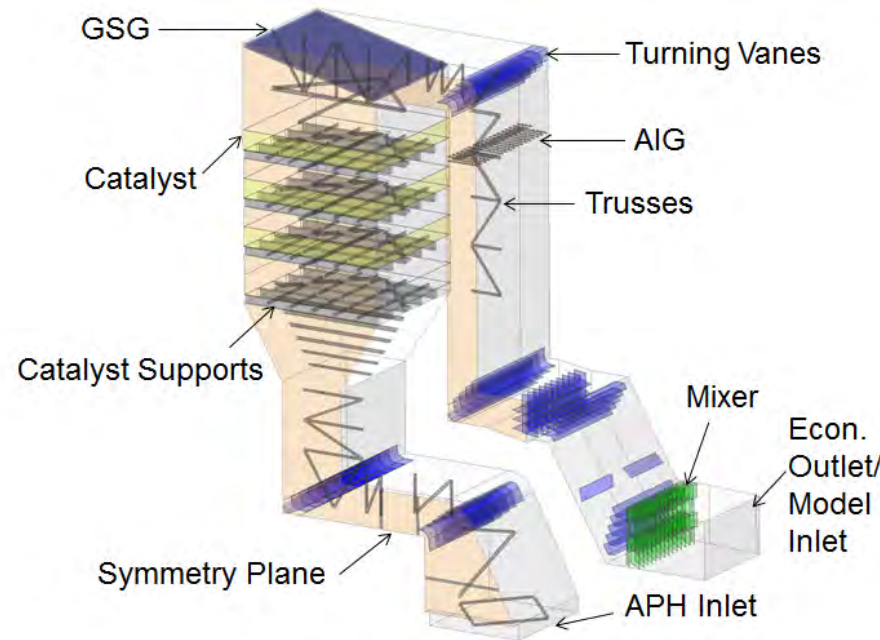


Common Challenges



Temperature and Flow (Mal)Distribution

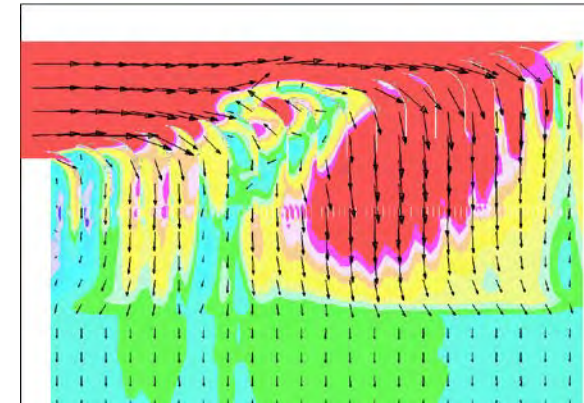
- The economizer outlet temperature on PRB units can exceed 800 °F (427 °C) when the boiler becomes dirty
- Imperative to minimize the temperature distribution before the AIG with modeling



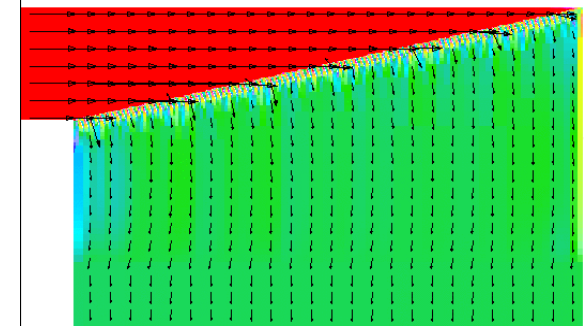
GSG™ Graduated Straightening Grid



- Improves flue gas velocity distribution without increasing cost, complexity, or compromise on performance
- Minimizes angle at which ash particles enter catalyst, near perfectly vertical flow into catalyst
- Innovative design allows for
 - Higher flue gas velocity, improved operating and financial performance via longer catalyst life and reduce downtime
 - Reduction in time required to tune ammonia injection grid
 - Higher flue gas velocity translates into smaller cross-section and less pressure drop, lower capital



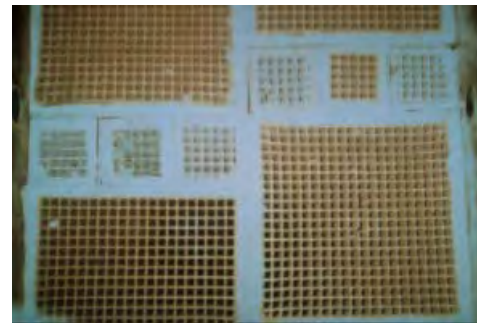
Typical Arrangement



GSG Arrangement

Minimum Operating Temperature (MOT)

- Desire to decrease load below MOT, driven by financial savings
 - Temperature below which catalyst reactivity declines below guarantee level
- ABS (NH_4HSO_3) forms at $T < \sim 650$ °F and can condense on catalyst layers
 - $T_{\text{formation}}$ depends on NH_3 and SO_3 concentrations
 - MOTs typically range from 600 °F to 625 °F
- Flow and temperature can be stratified across catalyst;
- Sorbents can be injected ahead of SCR to capture SO_3 , and limit ABS-related pluggage
 - $\text{CaO} + \text{SO}_3 \rightarrow \text{CaSO}_4$ (insoluble particulate)
 - $\text{MgO} + \text{SO}_3 \rightarrow \text{MgSO}_4$ (water soluble particle)



Clean Catalyst

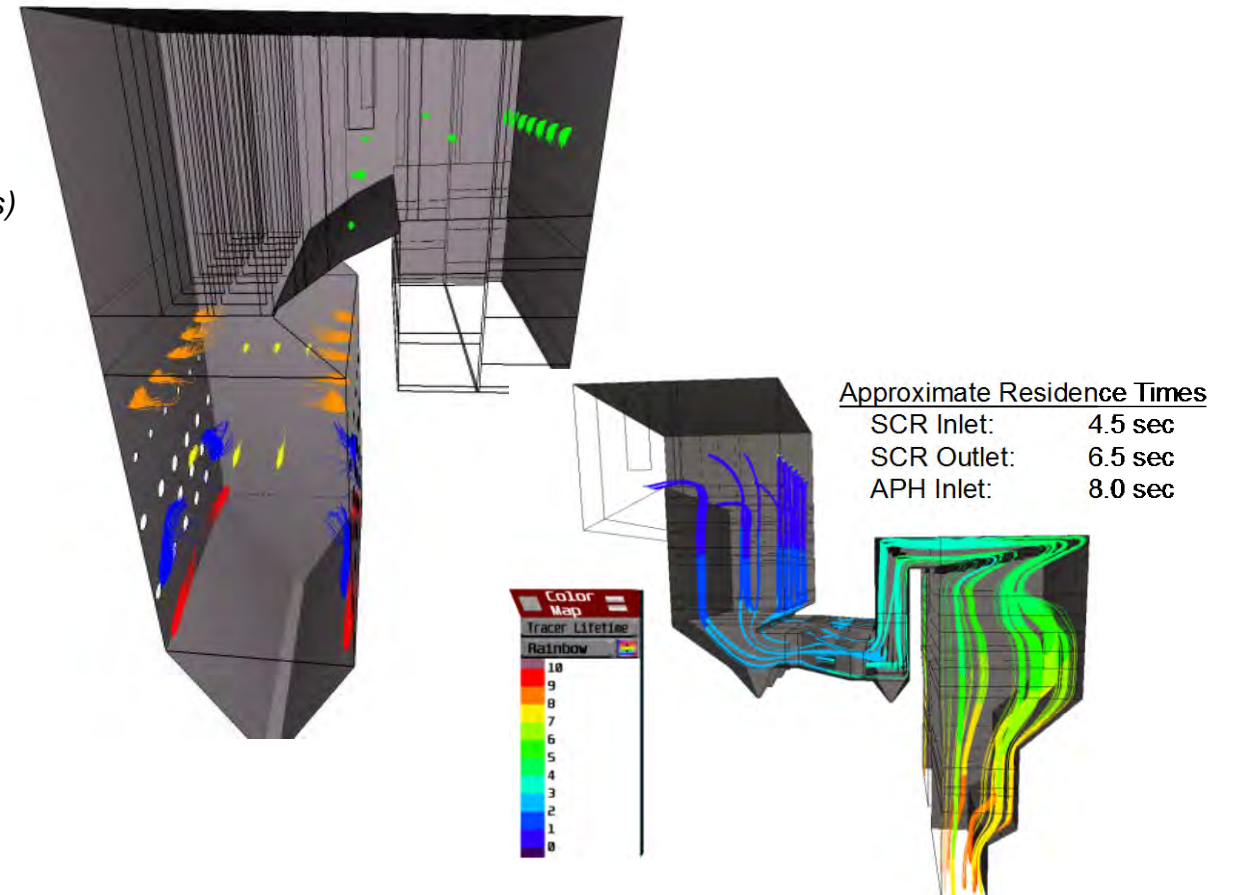


ABS-Fouled Catalyst

Reducing MOT with TIFI Mg

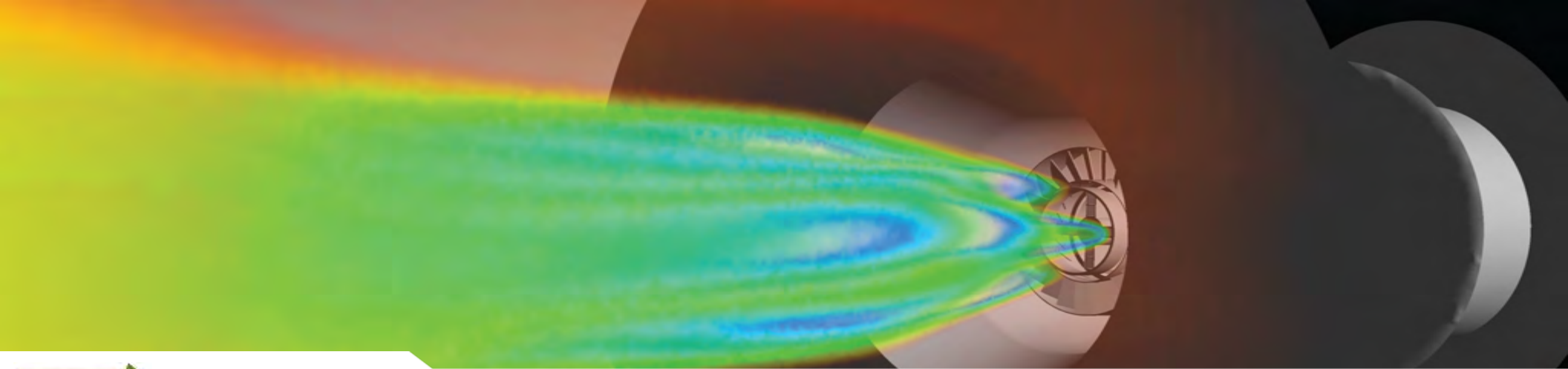
- $\text{Mg}(\text{OH})_2$ reagent fed into furnace just prior to primary superheater
 - Slag/fouling control
 - $\text{Mg}(\text{OH})_{2(\text{slurry})} \rightarrow \text{MgO}_{(s)} + \text{H}_2\text{O}_{(g)} + \text{SO}_{3(g)} \rightarrow \text{MgSO}_{4(s)}$
- Captures furnace- and SCR-generated SO_3
- Efficient reaction = low NSRs = cost-effective

Targeted In-Furnace Injection™ TIFI® Mg Injection



Reducing MOT Through SO₃ Capture: O&M Impact

Off-peak power price	\$13.24/MW
Unit generation variable cost	\$17.00/MW
Design minimum load	320 MW
New minimum load	260 MW } 60 MW decrease
Off-peak period (hrs/day)	7.5 hours
Off-peak days (days/week)	7 days
<i>Savings from minimum load decrease (350 days/yr)</i>	<i>\$3,158,400</i>
Fuel Tech TIFI™ Mg(OH) ₂ Program	(\$750,000)
<i>Net Annual Savings</i>	<i>\$2,408,000</i>



Case Study



La Cygne U1

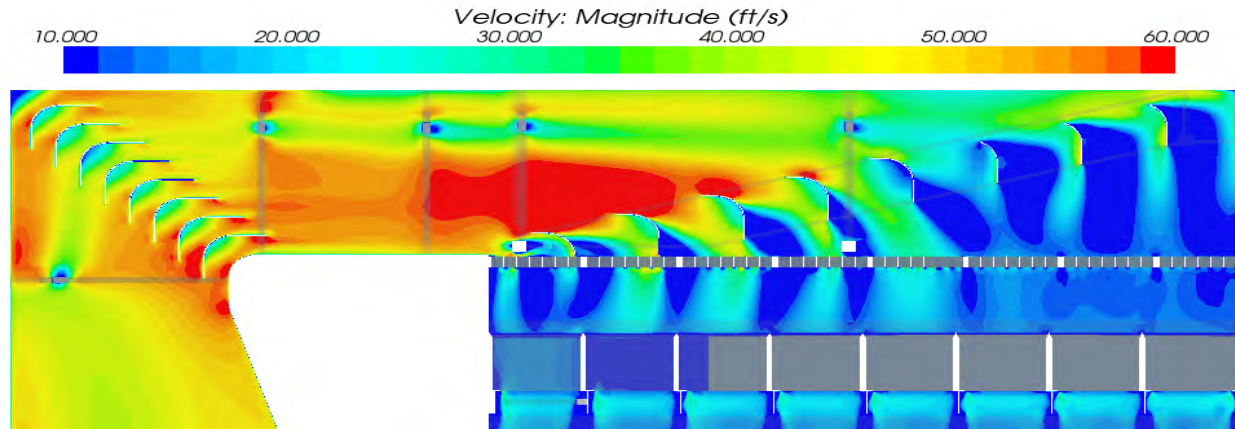
SCR Retrofit Project Summary

- Fuel Tech provided KCP&L Computational Fluid Dynamics (CFD) modeling and design services for the La Cygne Unit 1 SCR
 - 815 MW B&W cyclone boiler with OFA and SCR
 - Second oldest WFGD installation in the country
- Installed in 2007 with a “3+1” catalyst layer configuration
 - Plagued with excess fly ash accumulations
 - Original design allowed for extensive ash buildup/plugging in back of reactor which increased velocities elsewhere causing catalyst erosion
- Project Goals:
 - Improve flow and velocity distribution
 - Eliminate recirculation areas in the reactor hood

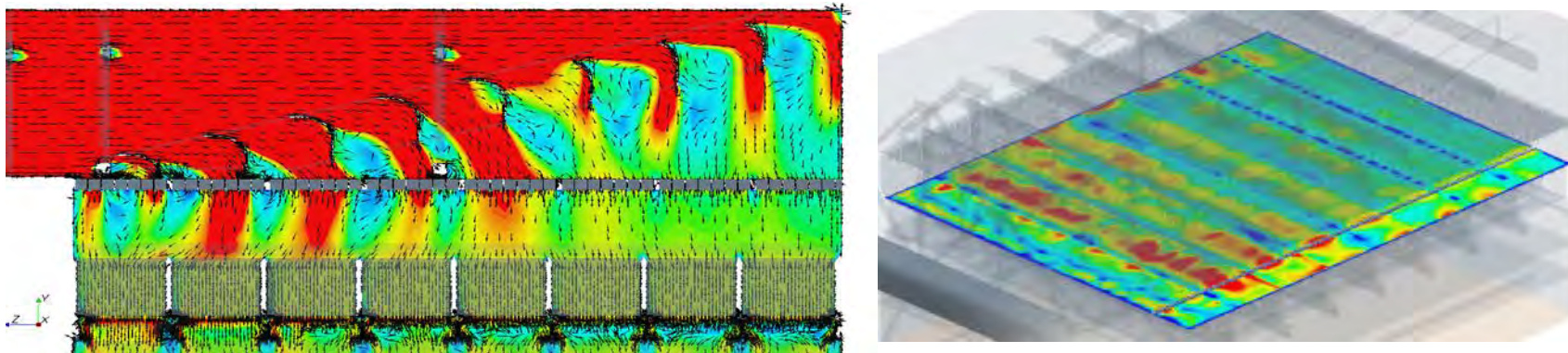
Before – Ash Pluggage



Baseline Results – Velocity Profile

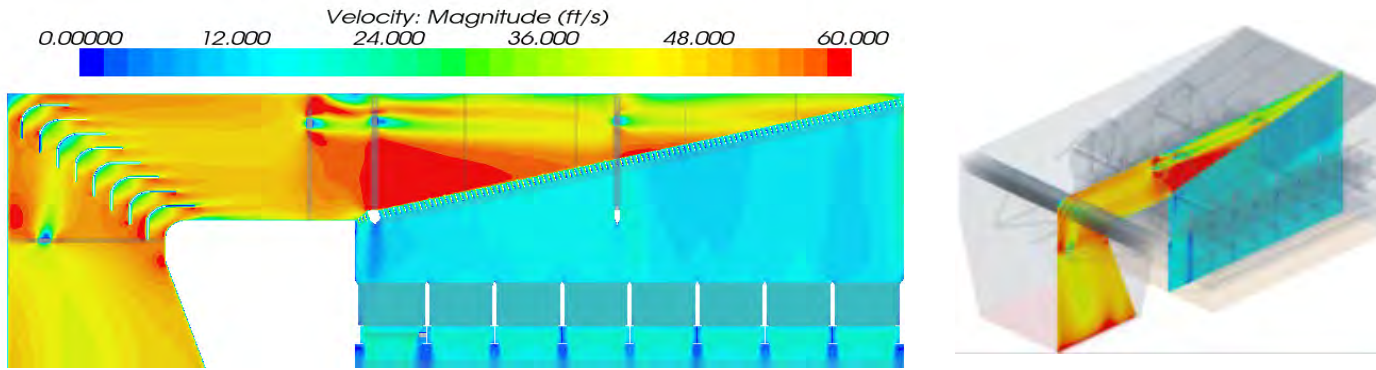


High and low spots from the turning vanes are helped by the straightening grid and perforated plate but still **yield a poor distribution into the 1st catalyst layer.**

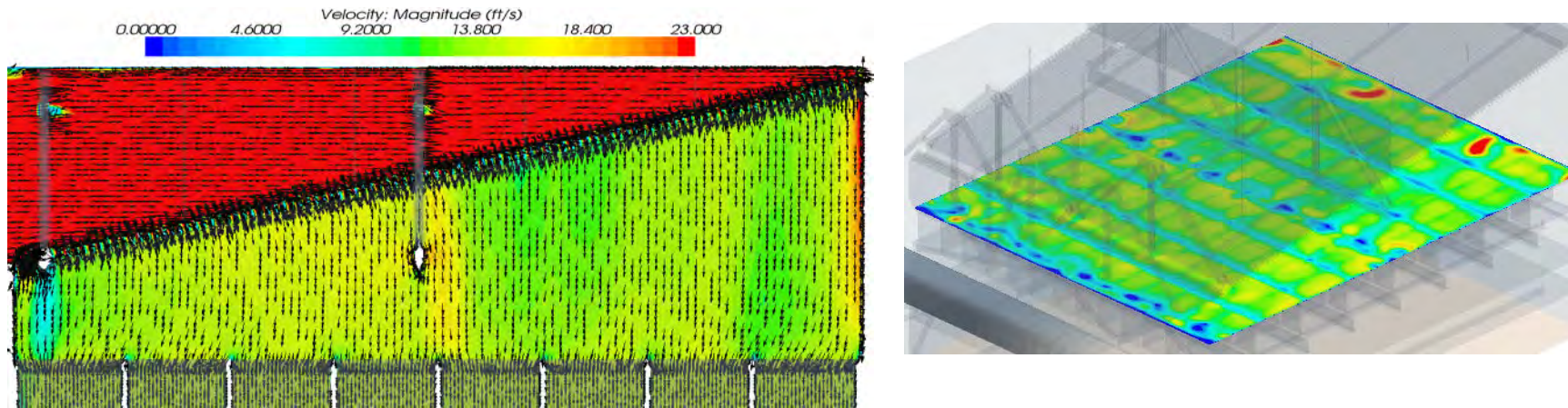


Vectors near vanes show recirculation areas where potential ash fallout can occur

Final Results – Velocity Profile



Flow shadows from large truss reduced with new design



Uniform flow vectors; no recirculation

Finished Product



No ash buildup after months of operation

La Cygne Statistics

- **Baseline catalyst inlet velocity profile – 17.5% RMS**
 - % within +/- 15% of average = 57.9%
 - % within +/- 30% of average = 88.6%
- **Final Catalyst Inlet Velocity Profile – 9.4% RMS**
 - % within +/- 15% of average = 90.8%
 - % within +/- 30% of average = 98.8%
- **Unit in Operation since November 2012**
 - Lower rise in dP and reduced fan power
 - Short outage inspections show clean reactor
 - Reduced ash pluggage aids reactor potential and decreases deactivation
 - Lengthened catalyst life and reduced costs
 - Reduced vacuuming and rejuvenation
 - Lower ammonia use and slip (reduced FGD foaming)

FTEK SCR Experience – Partial List

Owner	Plant	Size, MW	Firing Method	Sub-Contract/Support To	Year of Service	Types of SCR Services Provided
AECI	New Madrid 1 & 2	600	Cyclone	B&V	1999-2001	A, B, C, D, E, F, G
NIPSCO	Michigan City 12	540	Cyclone	B&V	2003	A, B, C, D, E, F, G
NIPSCO	Schahfer #14	520	Cyclone	B&V	2004	A, B, C, D, E, F, G
KCPL	Sibley Unit 3	420	Cyclone	KCPL	2008-2009	A, B, C, D, E, F, G
City Utilities of Springfield	Southwest 1	195	Cyclone	Babcock and Wilcox	2006-2008	A, E
AECI	Thomas Hill 1, 2, & 3	175, 295, 725	Cyclone	Burns & McDonnell	2005-2010	A, B, C, D, E, F, G
LG&E	Trimble County	600	PC - Wall	Doosan Babcock	2006	A, F
WE Energies	South Oak Creek	600	Low Dust SCR	URS Washington Group	2007-2008	A, B, D
Georgia Power	Scherer 1 - 4	820	PC	SCS	2007	D
KCPL	Iatan 1 & 2	700	PC	Schiff Hardin	2008	G
Westar	Jeffrey Energy Center 1	775	T-Fired	Westar	2011/12	A, B, E
KCPL	La Cygne 1	800	Cyclone	KCPL	2012	C, F
OPPD	Nebraska City 2	682	PC Wall	OPPD	2012	C, F

Types of SCR Services Provided:

- | | | |
|--|---|---|
| A) SCR Consultation | B) SCR Process Design | C) SCR Arrangement and Component Design |
| D) SCR Catalyst Design | E) SCR Specification Preparation and Review | F) SCR Physical Flow and CFD Model Design |
| G) SCR Startup, Troubleshooting, Tuning and Optimization | H) SCR Catalyst Management | I) Other: AIG Tuning, reactor inspection, catalyst specification review, etc. |

SCR Operation and Mercury Oxidation

Changes in SCR operating conditions can adversely affect the expected co-benefit on mercury (Hg) oxidation.

Unexpected increases in elemental mercury (Hg^0) entering the wet FGD system will immediately increase the total stack mercury (Hg), thus jeopardizing the MATS 30-day rolling average for mercury compliance.

SCR Condition	Effect on Mercury Oxidation
NH_3 (ammonia) Slip	- Excess NH_3 inhibits Hg^0 oxidation across catalyst
Increasing SCR exit gas temps	- Reverts portion of Hg^{2+} back to Hg^0
Increased SO_2 to SO_3 conversion	- Degrades Hg capture by PAC - ABS fouling
Ash plugging or ash path issues	- Blinds catalyst active sites = degraded Hg^0 oxidation
Catalyst Aging	- Hg^0 oxidation decreases as catalyst reaction sites are consumed. Potential of Hg^0 to stack increases.

What options do you have?



Redox-Hg in wFGD



Redox-Hg Technology Overview

Redox Technology Group, LLC, (d/b/a Redox Solutions) is an Indiana-based chemical manufacturer specializing in the development and synthesis of highly reactive, insoluble inorganic sulfide solutions marketed under the brand names Redox-Hg and FerroBlack®.

These reagents are ideal for the treatment of aqueous, gaseous, or solid media contaminated with heavy metals such as:

- ✓ Oxidized Mercury (Hg^{2+})
- ✓ Elemental Mercury (Hg^0)
- ✓ Selenite (Se^{4+})
- ✓ Arsenic (As)
- ✓ Hexavalent chromium (Cr^{6+})
- ✓ Copper (Cu)
- ✓ Nickel (Ni)

Product Advantages

Colloidal suspension:

- Ferrous sulfide particles sometimes referred to as “mackinawite or “amorphous ferrous sulfide”
- pH range from 10.0 to 13.0 and ORP from -600 to -1,200 mV.

Multiple pollutant removal mechanisms:

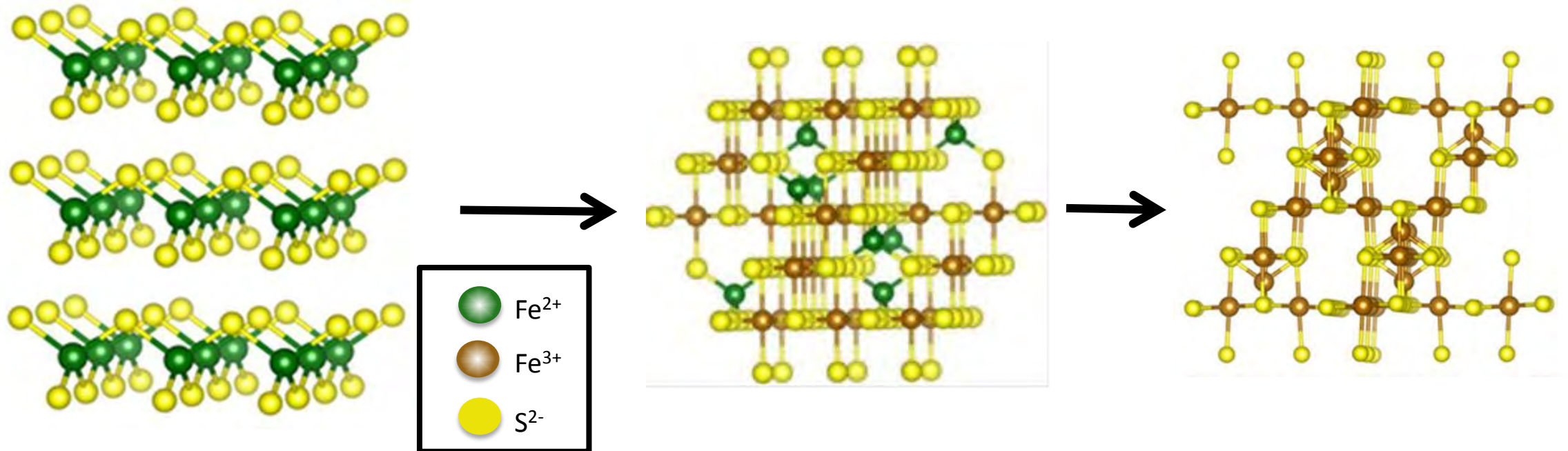
- Dissolution / precipitation
- Occlusion / mixed crystal formation / physical entrapment
- Surface adsorption
- Electron transfer / Electron “hopping”

Redox-Hg continues to operate when other additives are ineffective

How Does Redox-Hg Work?

- Minimum solubility
 - $\text{FeS} \leftrightarrow \text{Fe}^{2+} + \text{S}^{2-}$ or $\text{FeS} + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{HS}^-$
 - $\text{Hg}^{2+} + \text{S}^{2-} \leftrightarrow \text{HgS} \downarrow$
- Adsorb and holds metals at the particle surface
 - $\equiv\text{FeS} + \text{Hg}^{2+} \leftrightarrow \equiv\text{FeS}-\text{Hg}^{2+}$ (surface adsorption)
 - $2[\equiv\text{Al}(\text{OH})_3] + \text{Hg}^{2+} \leftrightarrow 2[\equiv\text{Al}(\text{OH})_3]-\text{Hg}^{2+}$ (surface adsorption)
- Electron transfer and hopping
 - Ability to oxidize Hg^0 on the particle surface ($\text{Hg}^0 + 2 \text{Fe}^{3+} \leftrightarrow \text{Hg}^{2+} + 2 \text{Fe}^{2+}$)
- Stable to oxidation vs. competition
 - Minimally soluble particles release reactive sulfides over time
 - Other soluble sulfides (e.g. NaHS, polymers, etc.) are prone to oxidation of reactive sulfides to inert SO_3^{2-} and SO_4^{2-}
 - Diminished reactivity over time = more chemical required

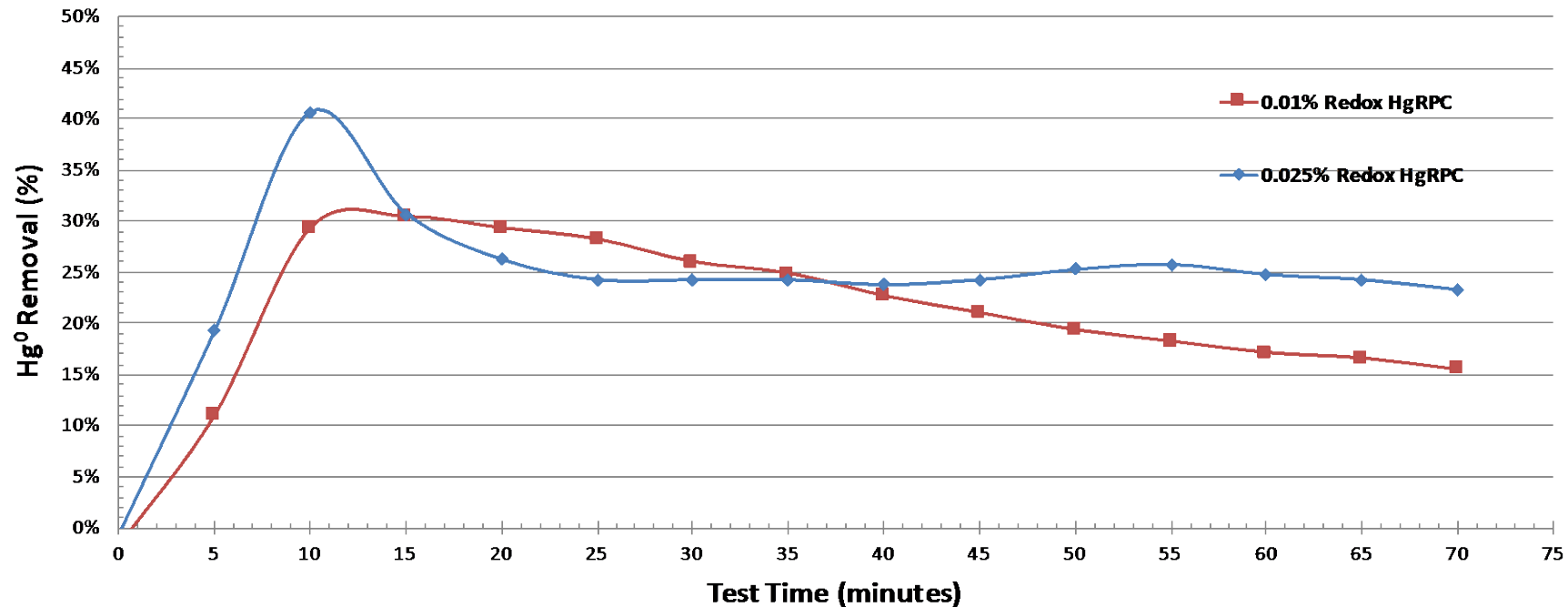
Reaction Mechanisms : Redox Activity of $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$



- In wFGD, Fe^{2+} oxidizes to Fe^{3+} , cation vacancies develop to maintain overall charge balance
- Cation vacancies (negatively-charged holes) promote positively-charged metals adsorption

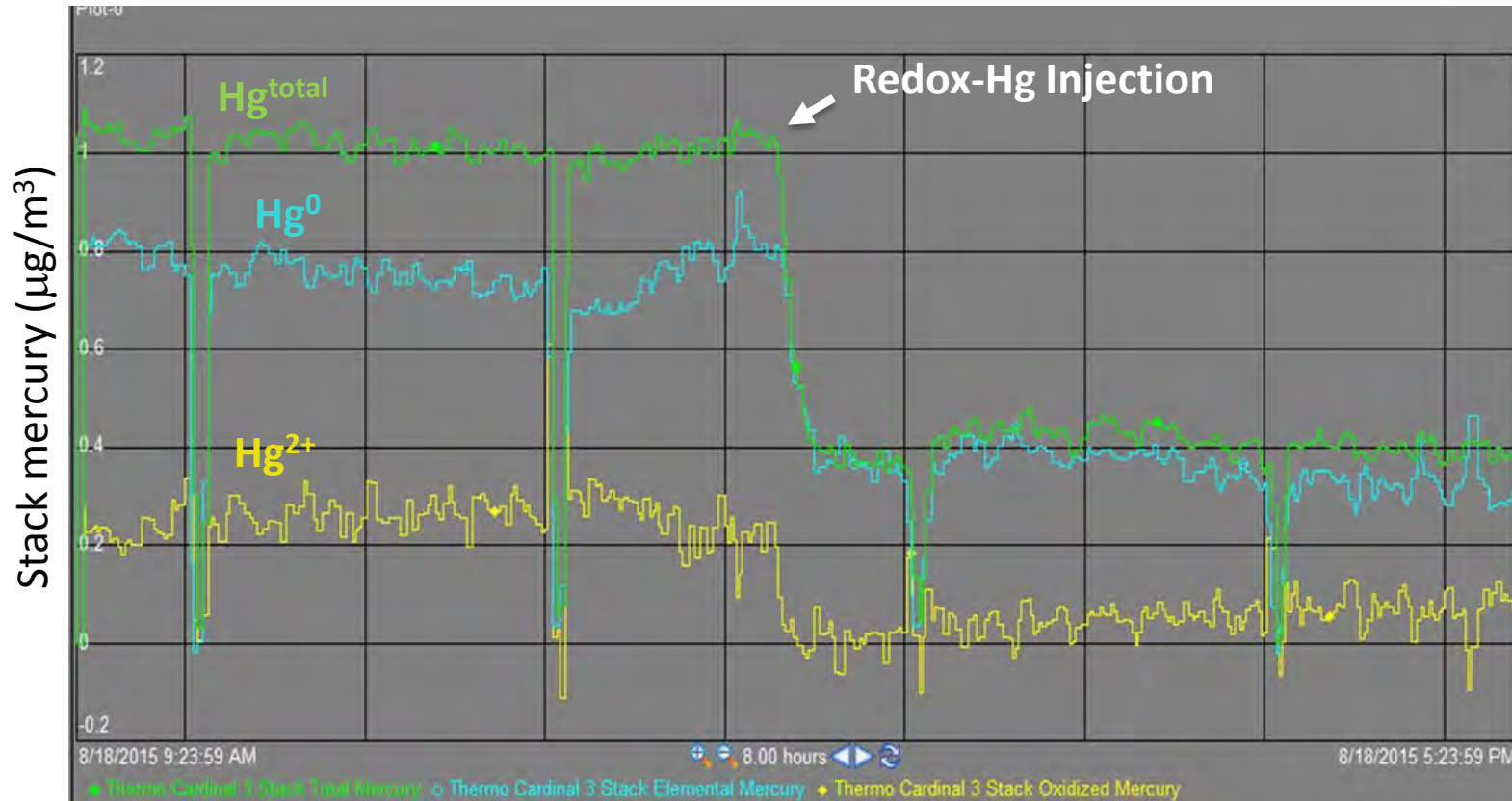
Direct Removal of Elemental Hg (Hg^0): Simulated wFGD

Redox-Hg Removal of Hg^0 in Simulated Wet Scrubber Module



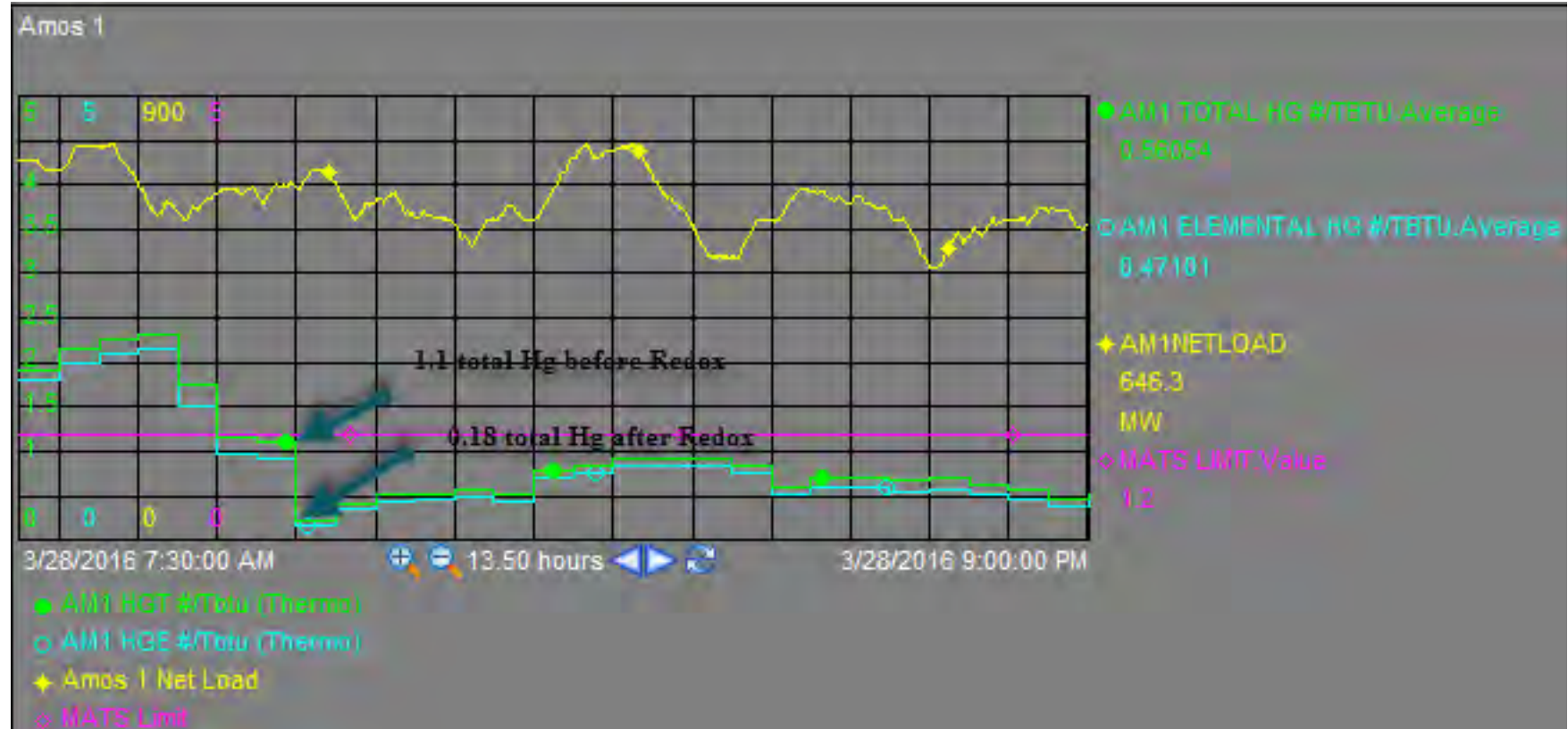
- Bench-scale tests specifically targeted Hg^0
- Batch reactor with continuous Hg^0 gas feed was treated with single dose of Redox-Hg
- Results were consistent with initial field trials
- Reagent added as % of total scrubber liquor volume

Direct Removal of Hg⁰ in wFGD



- On-demand Redox-Hg injection into wFGD captures Hg^0 going into the scrubber during “upset” conditions.
- Redox-Hg controls Hg re-emission that may contribute to total stack mercury until “normal” SCR operations are restored

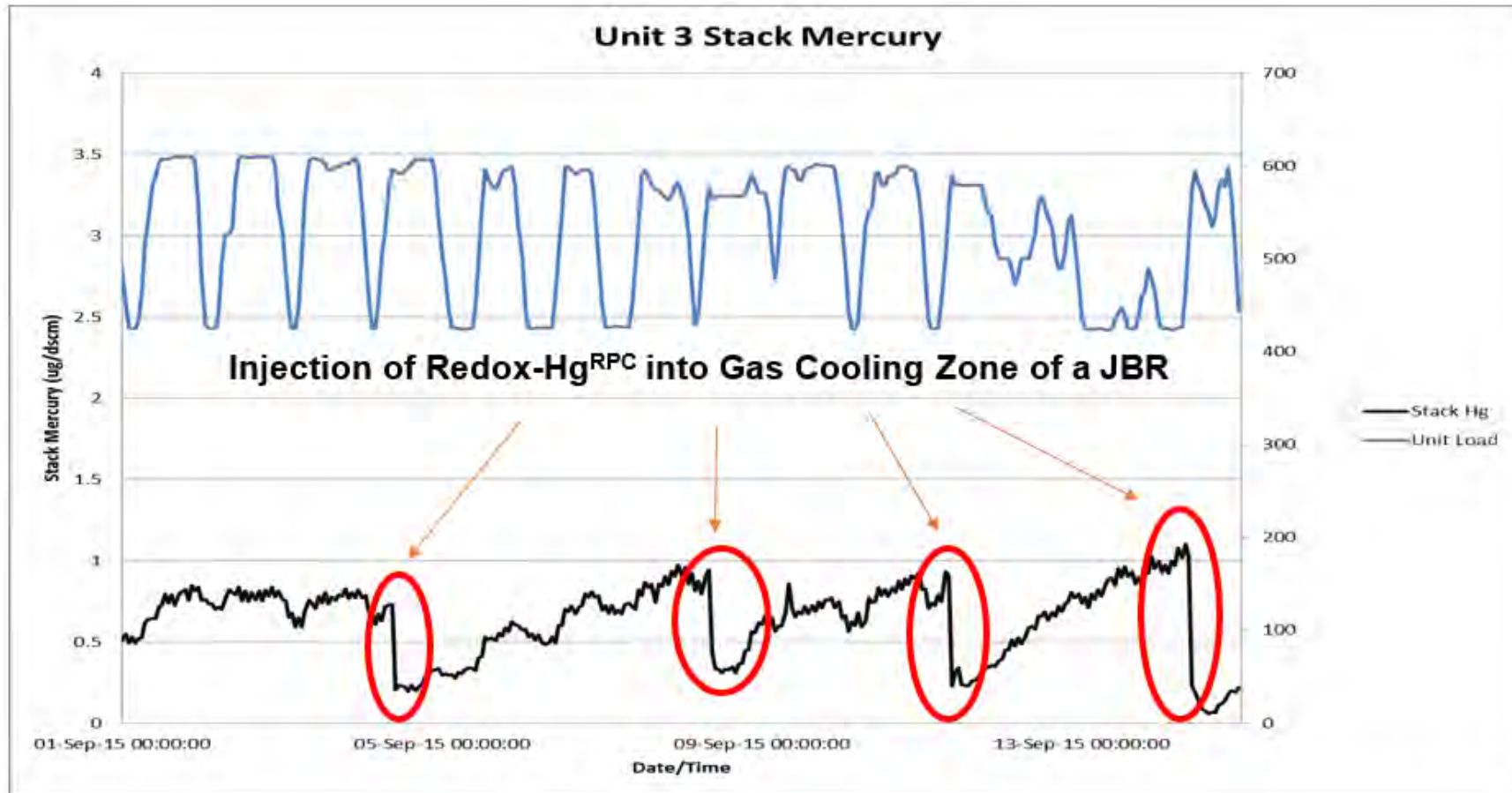
Rapid Response to Stack Hg Emissions



- Recent emergency response to Hg emission concern
- Total injection of 1 tote (300 gallons)
- B&W Spray Tower, single 1 MM gallon absorber

Redox-Hg: Rapid Response to Stack Hg

300 gallon tote injected into wFGD (0.027% v/v) over 30 to 45 minute span
AEP Cardinal Station: 650MW BIT SCR CESP WFGD (JBR type scrubber)

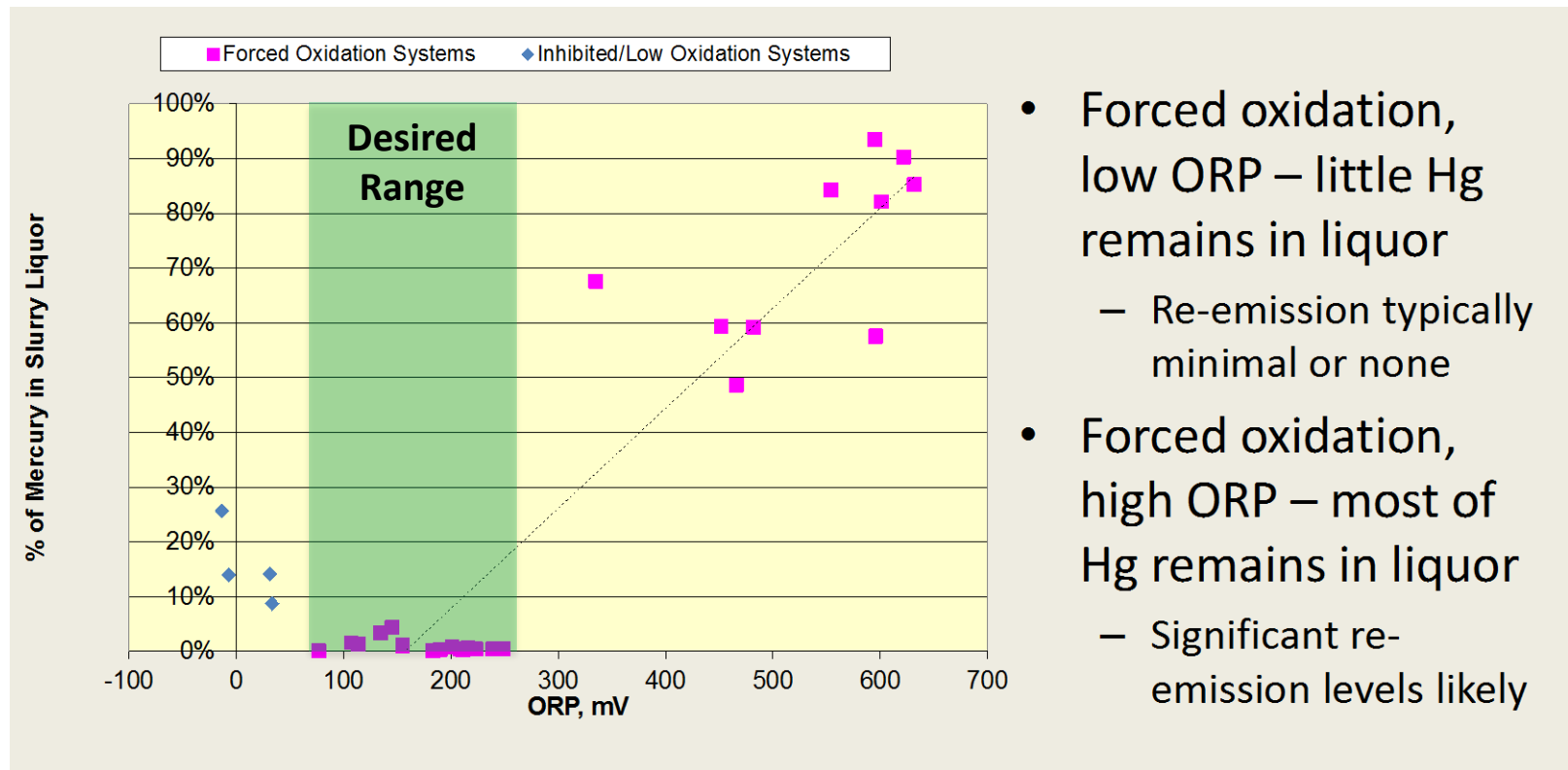


Feed Modes

- Rapid response allow Redox-Hg to be used in several modes:
 - *Batch mode*
 - 0.03% – 0.1% (v/v) to reduce scrubber Hg content
 - *Continuous feed mode*
 - 1-10 gph to maintain ORP and scrubber Hg content to prevent stack emissions

Impact of ORP on Mercury Emissions

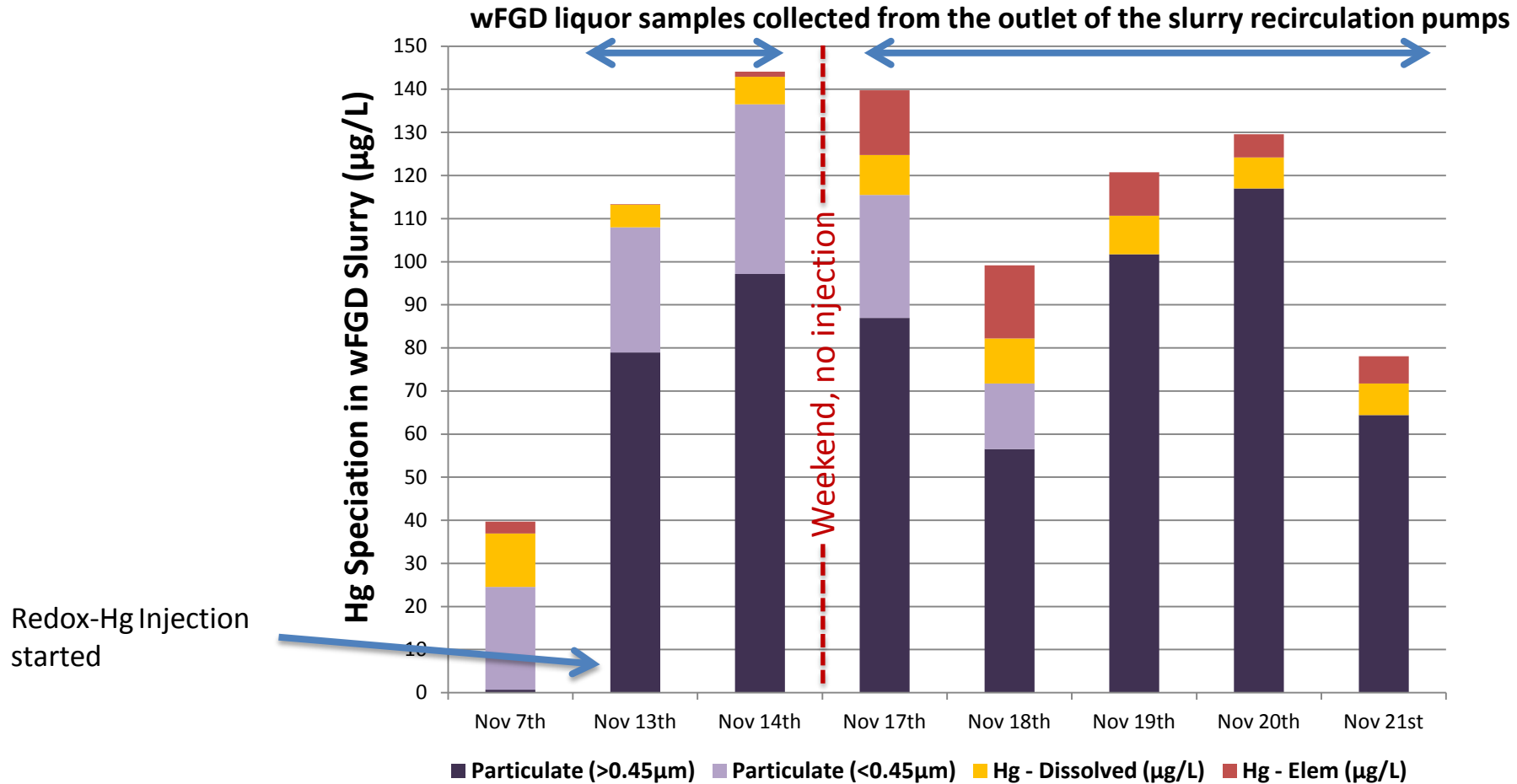
- At low ORP (< 100 mV) and high ORP (> 300 mV)
 - Emissions at stack increase



- Forced oxidation, low ORP – little Hg remains in liquor
 - Re-emission typically minimal or none
- Forced oxidation, high ORP – most of Hg remains in liquor
 - Significant re-emission levels likely

Reference: Blythe, G. et al, <http://www.tppa.com/wp-content/uploads/TPPA-2015-by-AECOM-FINAL.pdf>

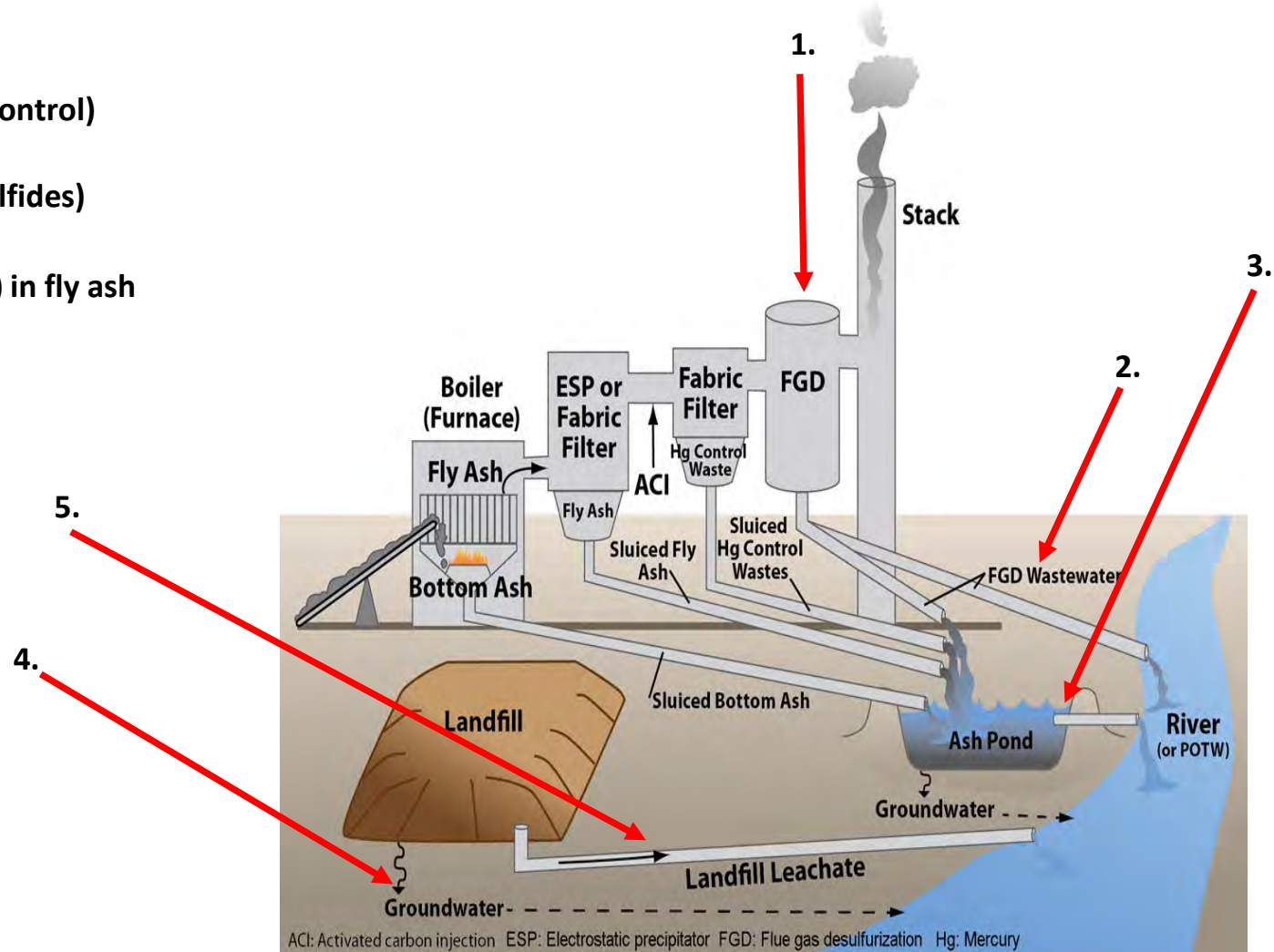
Mercury Adsorption – Speciation in wFGD



Shift dissolved Hg into particulate form for removal with scrubber solids

Total Metals Management: Injection Locations

1. Wet Scrubber Additive (Hg^0 , Hg^{+2} , As, Se^{+4} , ORP Control)
2. Waste water treatment (alternative to organo-sulfides)
3. Immobilization of mobile metals (TCLP and Total) in fly ash
4. In-situ control of metals in landfill seeps
5. Landfill leachate treatment



Advantages of Redox Reagents

- Fast-acting mercury control option
 - Start-up, SCR bypass, ORP excursions, or other events that higher Hg stack emissions
- Lowers Hg⁰ across the scrubber and total stack mercury emissions by greater than 95%
 - Doesn't impact quality of fly ash or gypsum
- Effective over a wider pH (4.5 to 7.0) and ORP (-200 to +600mV) ranges than traditional soluble sulfides and works within existing scrubber conditions
- Eliminates the potential of leachable heavy metals in solids and ash
- Additional co-benefits:
 - Lower chemical consumption in WWTPs for heavy metals removal
 - Inhibits selenium oxidation in wFGD slurry (e.g. selenite (Se⁺⁴) to selenate (Se⁺⁶))
 - Removal of selenite (Se⁺⁴) from the scrubber liquor and waste water
 - Reducing total dissolved mercury (Hg), arsenic (As) and selenium (Se) in ash pond water

“Section 5... Give Me The Limit”

And time marches on into
the late afternoon.