

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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Reinhold Environmental NOx Round Table February 19, 2013

Balancing NOx Reduction, Ammonia Slip and Mercury Oxidation

Presenters:

Megan Winter and John Cochran

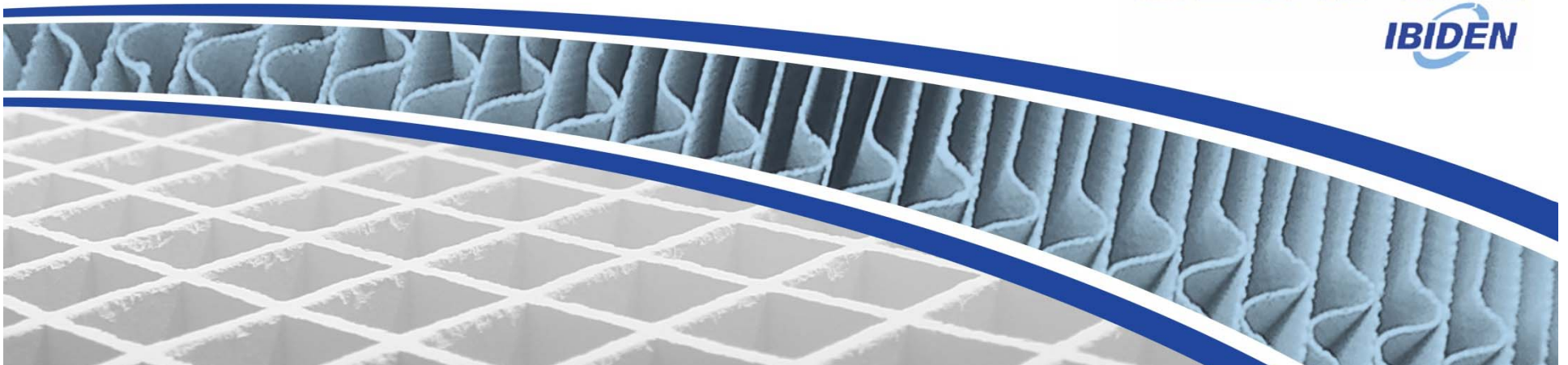
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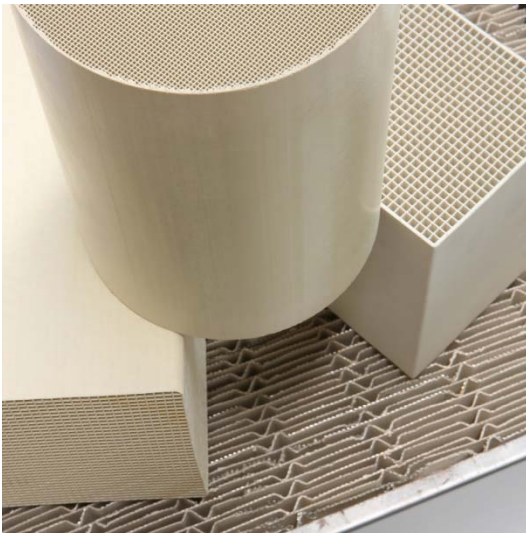


SCR System Catalyst Management Will Become More Complex With MATS

- To Date SCR Systems Have Been Managed to
 1. Achieve Targeted NO_x Emissions/Removal
 2. Limit Ammonia Slip Below Thresholds Protecting Operations and Byproduct Disposal/Reuse
 3. Limit SO₂ to SO₃ Conversion Avoiding Plume Visibility and Downstream Equipment Issues
- MATS Will Change the Game
 - Optimized Catalyst Management Strategies Needed to Support High Mercury Oxidation Rates
 - Strategies Will be Site Specific and Fuel Dependent
 - Additional Laboratory Testing of Plant Aged Catalyst Samples Will be Required to Support Planning
 - More Frequent Catalyst Changeouts Will Occur With MATS

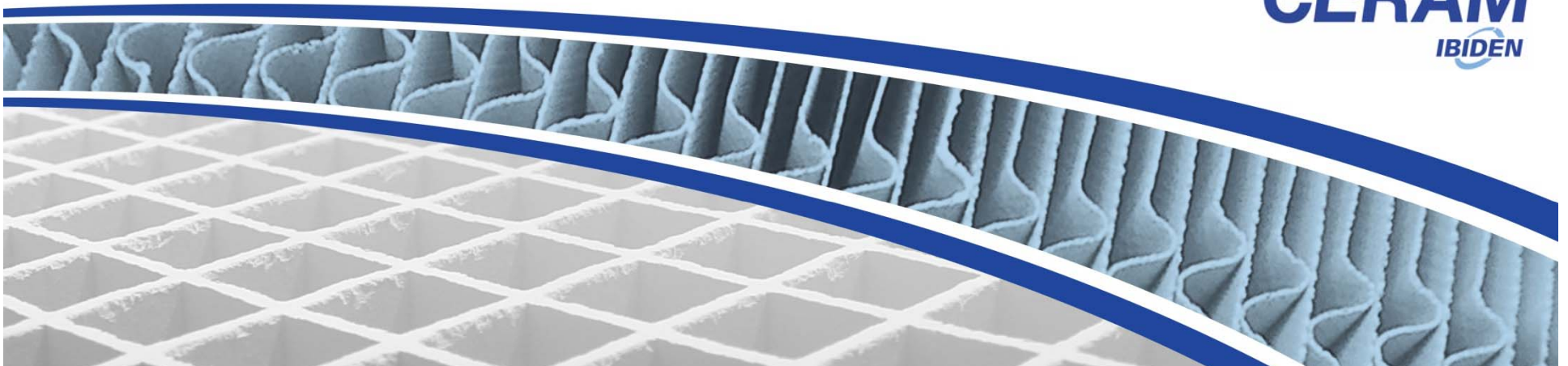
Presentation Road Map

- Presentation Objectives:
 - Illustrate the Complexity of Optimizing Mercury Oxidation
 - Provide Representative Catalyst Management Cost Impacts for Maintaining Mercury Oxidation
- Topics:
 - Mercury Oxidation Test Program Overview
 - Predominant Reactions on SCR Catalyst
 - Factors Affecting Mercury Oxidation
 - Mercury Oxidation Catalyst Testing
 - NO_x/Hg Targeted Catalyst Management Strategies
 - Representative NPV Economics for Combined NO_x/Hg Catalyst Management
 - Bituminous and Sub-Bituminous Fuels



Mercury Oxidation Characterization and Optimization Test Program Overview

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Mercury Oxidation Test Programs

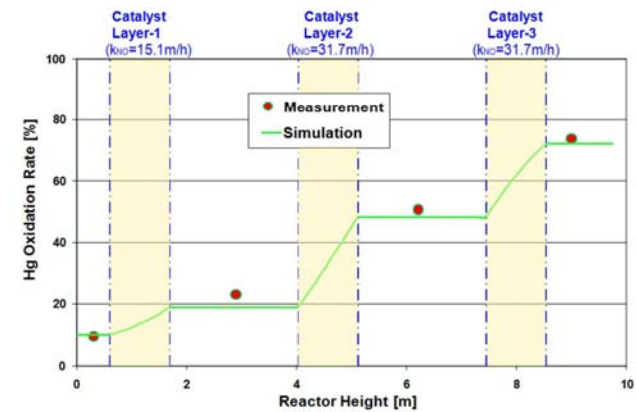
- CERAM is Working to Optimize Mercury Oxidation Potential in Extensive Pilot/Demonstration Programs
- First Program: DENOPT Program (completed June 2010)
- Second Program: DEVCAT Program (July 2010 – present)
- Participants: ENEL, E.ON, EnBW, CERAM, University of Stuttgart, and RECOM Services



Mercury Oxidation Test Programs

European Research Project [DENOPT](#)

- Research Fund for Coal and Steel RFCR-CT-2007-00008
- Project Objectives:
 - Development and evaluation of enhanced catalysts
 - Evaluation of mercury oxidation mechanism
 - Evaluation of deactivated and regenerated catalyst
 - Research on interaction between catalyst and FGD
 - Perform Laboratory (micro and bench), Slip-Stream and Full Scale Tests
 - Development of 3D-CFD catalyst model for HgOx Prediction



Mercury Oxidation Test Programs

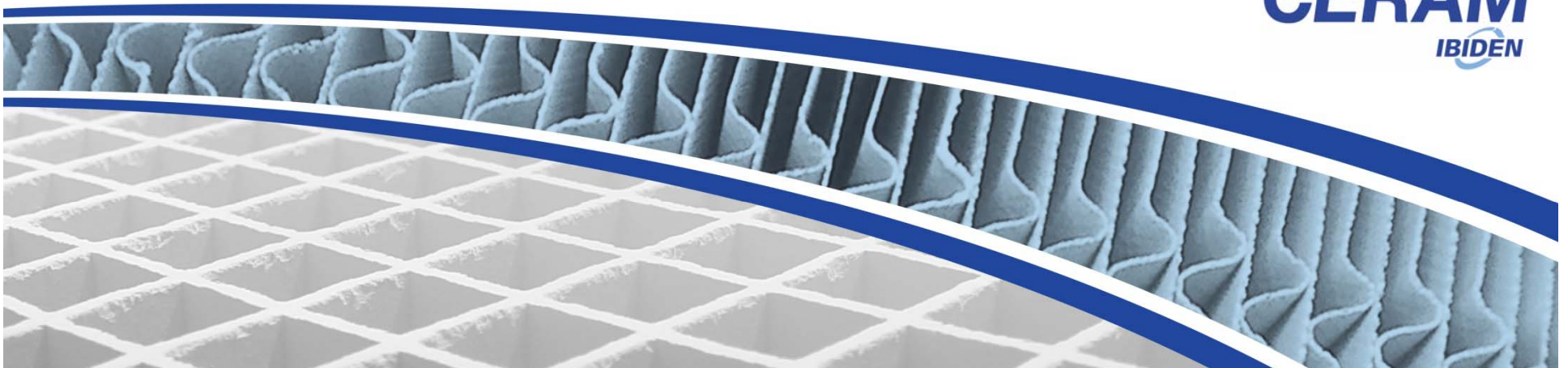
European Research Project [DEV](#)CAT

- Research Fund for Coal and Steel RFCR-CT-2007-00008
- Project Objectives:
 - Further evaluation of mercury oxidation mechanism
 - Development of enhanced and nano-material catalysts
 - Evaluation of different fuel affects on mercury oxidation
 - Research on interaction between catalyst and FGD
 - Standardization of SCR-DeNO_x-catalyst mercury oxidation testing
 - Further Development of 3D-CFD catalyst model for HgO_x Prediction



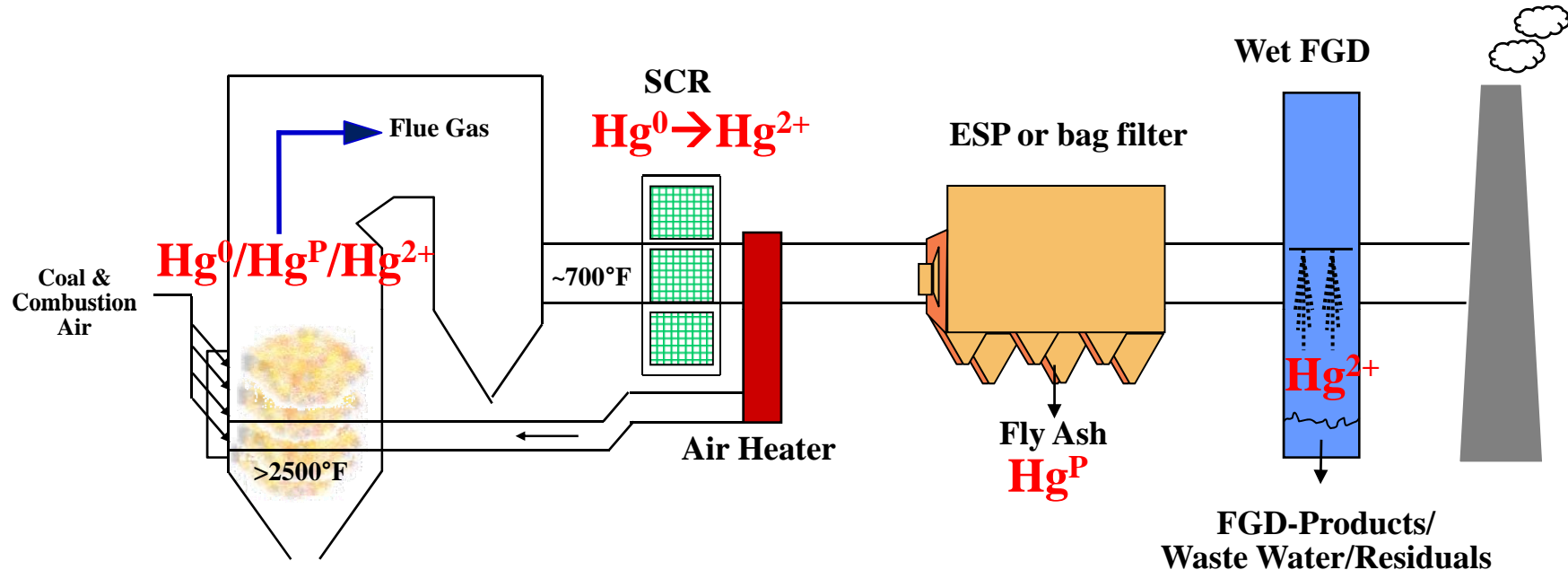
Predominant SCR Catalyst Reactions

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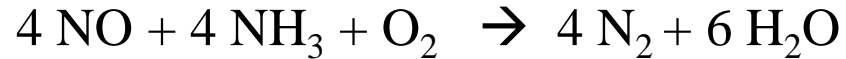
Mercury Speciation in Power Plants

Hg⁰, Hg²⁺, Hg^P – Species at boiler outlet important for Removal in Flue Gas Cleaning

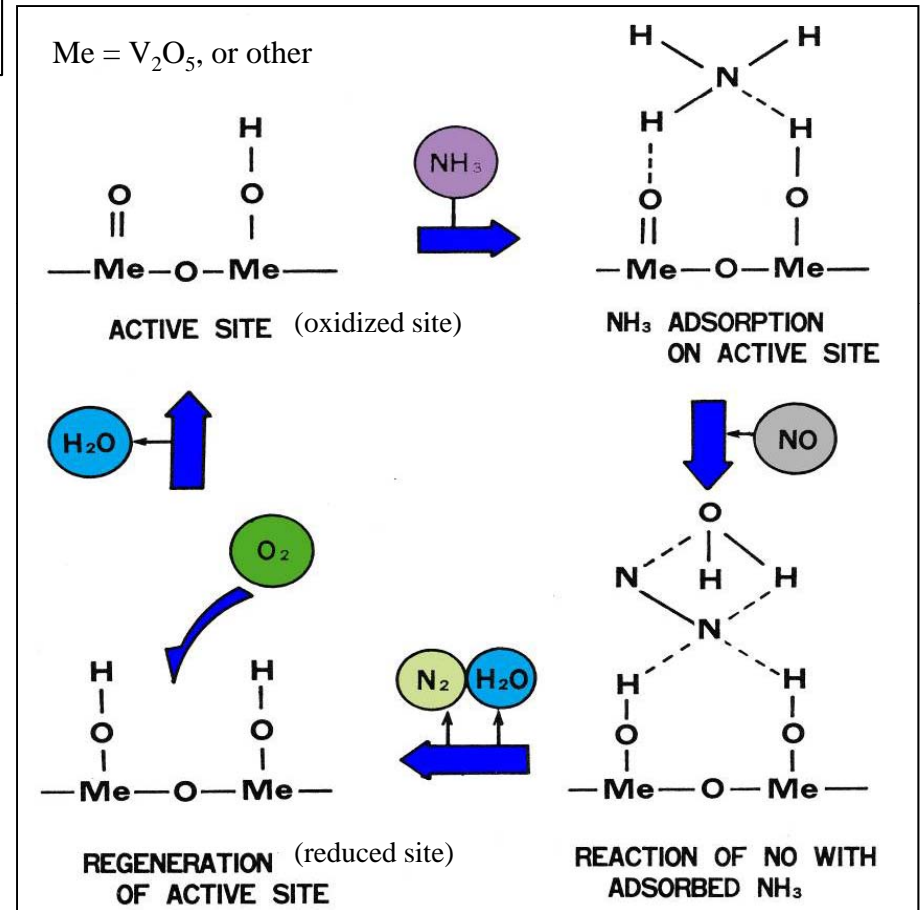


- Hg in Coal is Completely Released During Combustion Forming:
 - Elemental (Hg⁰), oxidized (Hg²⁺) and particulate (Hg^P) bound forms in flue gas exists
 - Hg²⁺ is Water Soluble and Efficiently Removed in Wet FGD
 - Hg^P Efficiently Removed by Particulate Control
- SCR Catalyst and Halogens Contained in Fuel Promote Hg-Oxidation

NO_x Reduction Reaction



- Catalyst Active Sites Constantly Being Regenerated in a Cycle
 - Active Site Available
 - Adsorb Ammonia
 - Reaction of NO_x with NH₃
 - Regenerate Site with O₂
- Active Sites Not Busy with NO_x Reduction (Ammonia) Available for Oxidation of SO₂, Hg⁰, UHC, VOC, Dioxins, etc.

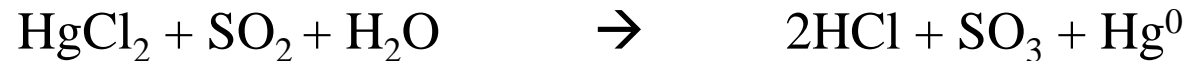


SCR Catalyst Reactions

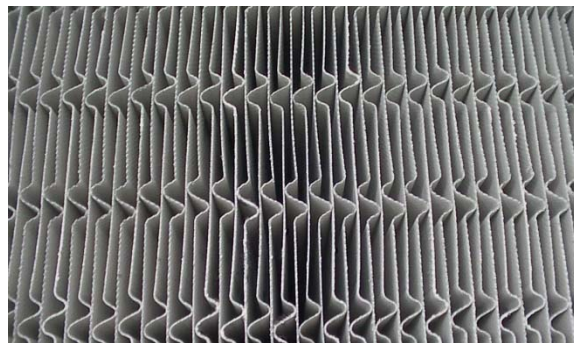
- NO_x Reduction



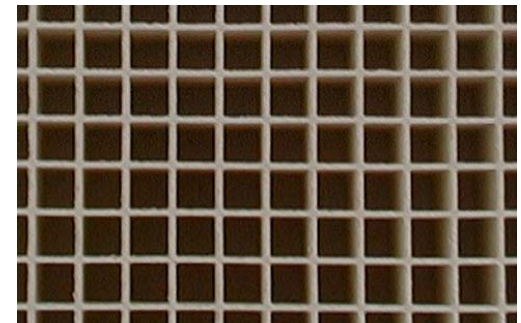
- Mercury Reactions



- SO₂/SO₃ Conversion

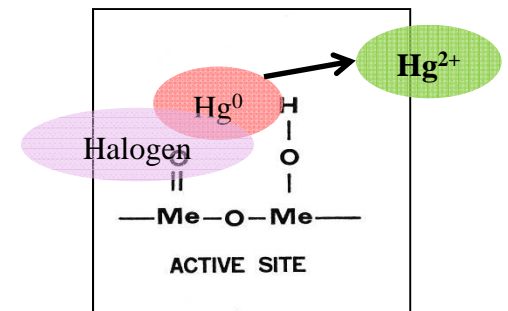
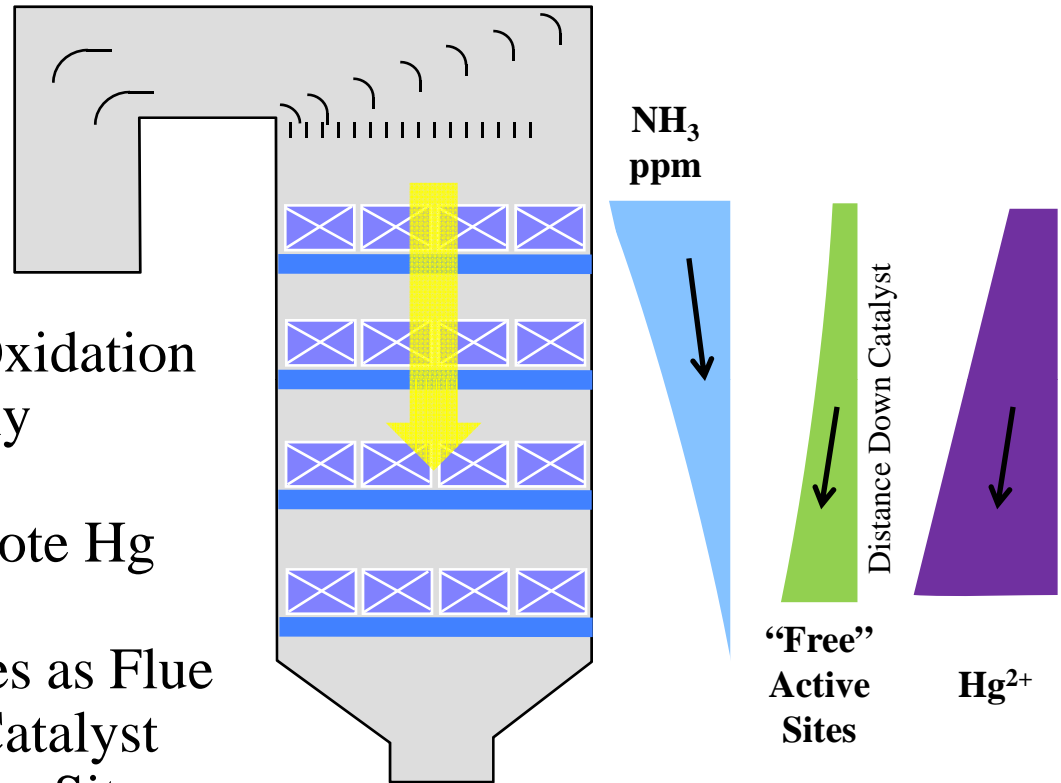


V₂O₅/TiO₂
Honeycomb or
Plate Catalysts



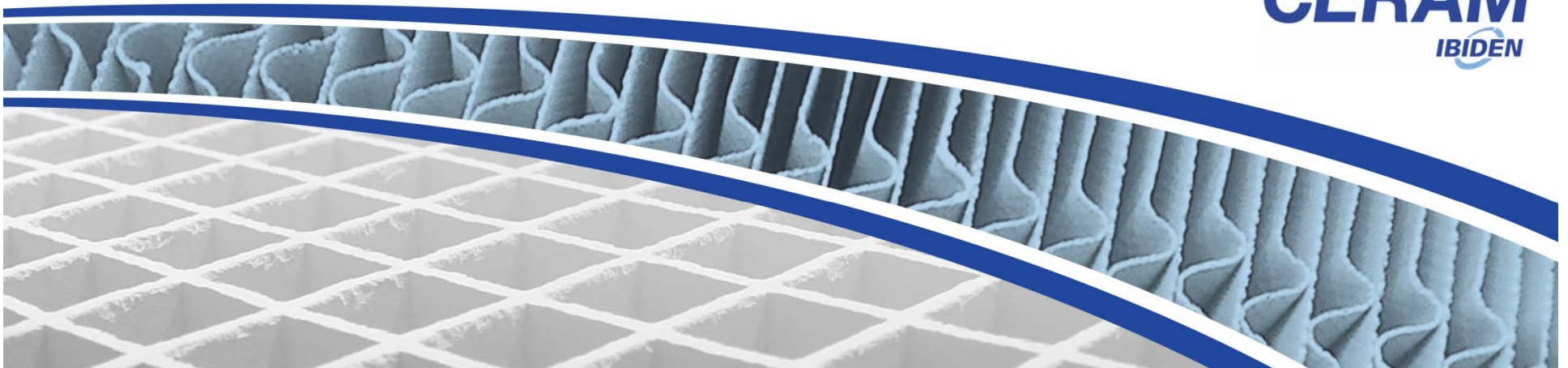
Hg-Oxidation Increases as Gas Flows Through Reactor

- Flue Gas NH₃ Inhibits Hg Oxidation
 - Active Sites Preferentially Occupied by NH₃
- Halogens (Cl, Br, I, F) Promote Hg Oxidation
- NH₃ Concentration Decreases as Flue Gas Flows Down Through Catalyst
 - Available or “Free” Active Sites Increase Down Through Reactor
- Active Sites Decrease With Catalyst Aging



Factors Affecting Mercury Oxidation

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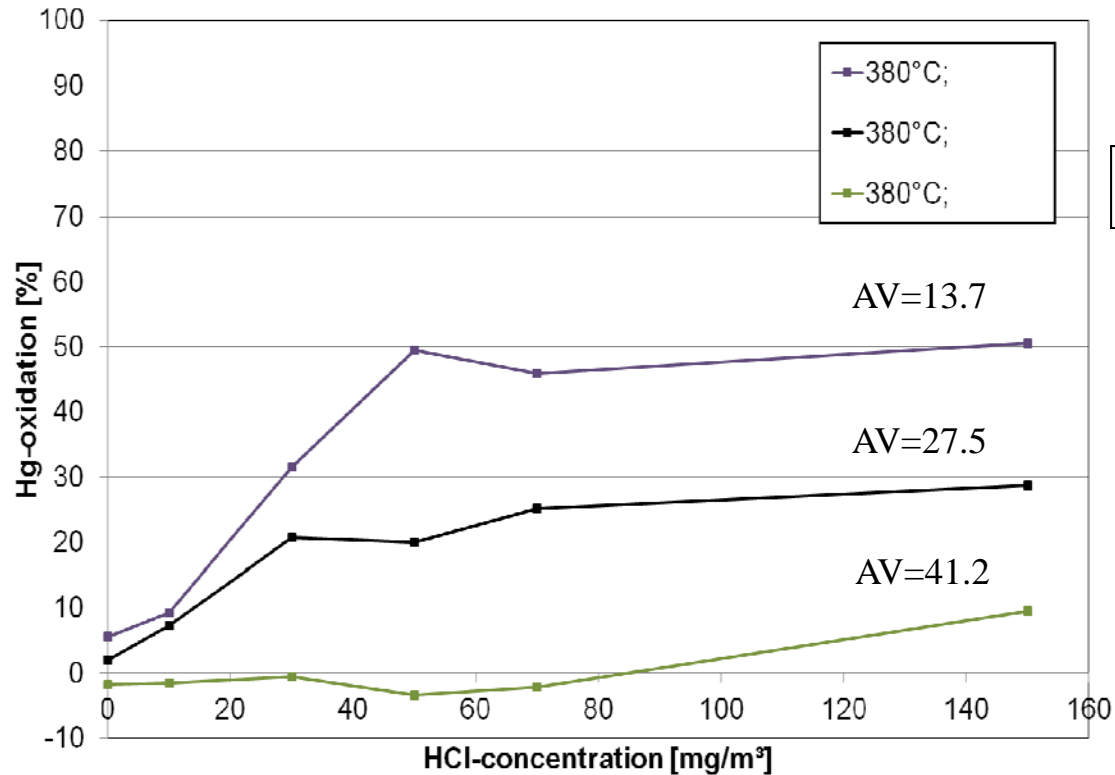


Factors Affecting Mercury Oxidation

Positive Influences	Negative Influences
Long Residence Time (Low Area Velocity, Space Velocity)	Ammonia (molar ratio)
High Halogen Content	Catalyst Deactivation
Lower Temperature (< 680°F)	Higher Temperature (> 750°F)
Catalyst Composition (V_2O_5 , other)	Increased SO_2 , CO, and H_2O Concentrations
Catalyst Geometry (smaller pitch)	

Influence of Area Velocity

Micro-Scale Reactor Tests



$$Av = Q_{fg} / A_{cat} = Q_{fg} / (V_{rcat} \times SSA)$$

Where:

Q_{fg} = flue gas flow rate, Nm³/h

A_{cat} = catalyst geometric surface area, m²

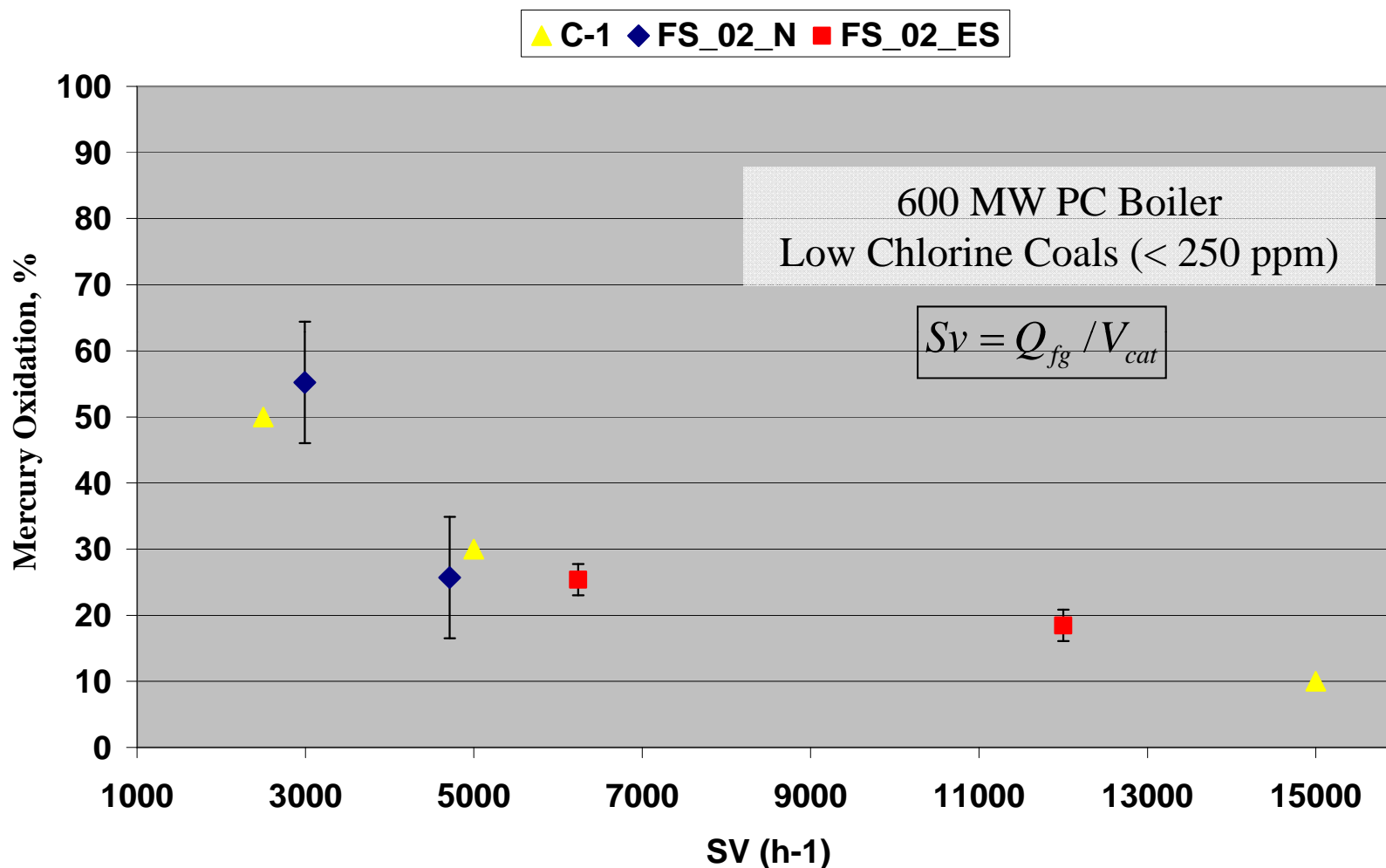
V_{rcat} = reactive catalyst volume available, m³

SSA = catalyst specific surface area, m²/m³

- Measured Under DeNOx Inactive Conditions (NH₃ Off)
- Hg-Oxidation Strongly Dependent on Area Velocity

Influence of Space Velocity (SV)

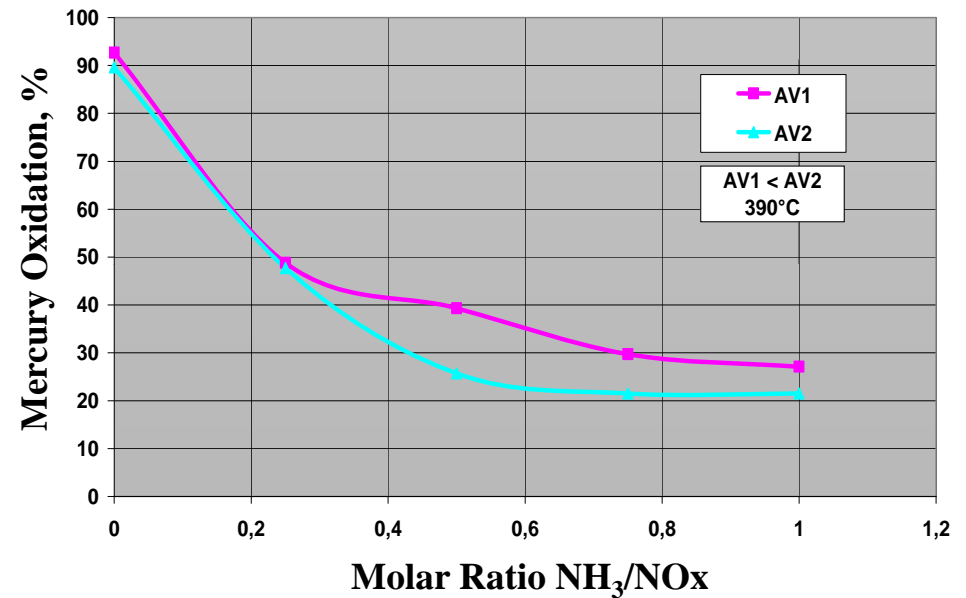
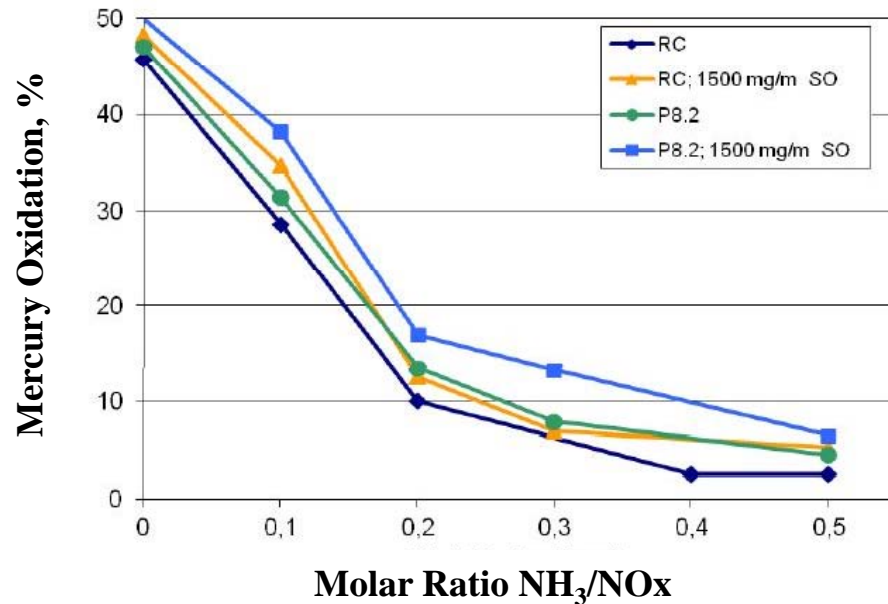
Slip Stream Reactor Tests



Lower Space Velocity = Higher Mercury Oxidation

Influence of Ammonia (NH_3/NO_x Molar Ratio)

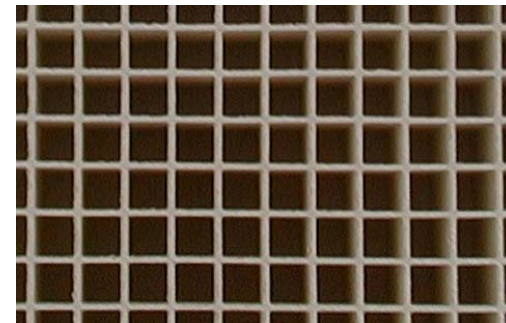
Micro-Scale Reactor Tests



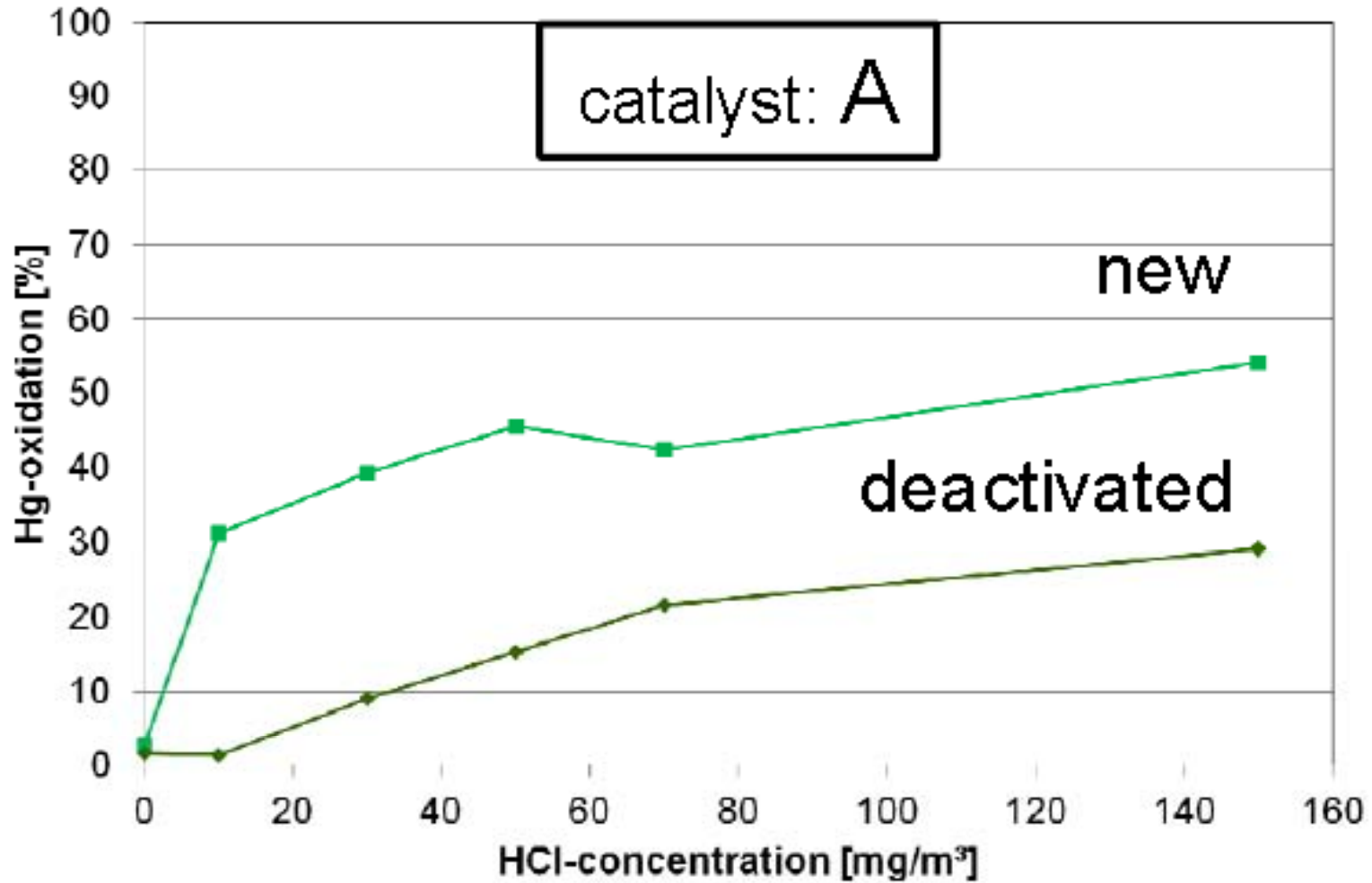
- Hg-Oxidation and NO_x -Reduction are Competing Reactions
- Hg-Oxidation Inhibited by De NO_x Reaction

Influence of Catalyst Geometry

- Wall Thickness
 - No influence expected similar to NO_x reduction
 - DENOPT program results inconclusive
- Pitch
 - Smaller pitch increases Hg oxidation significantly
 - Mass transfer is constraining



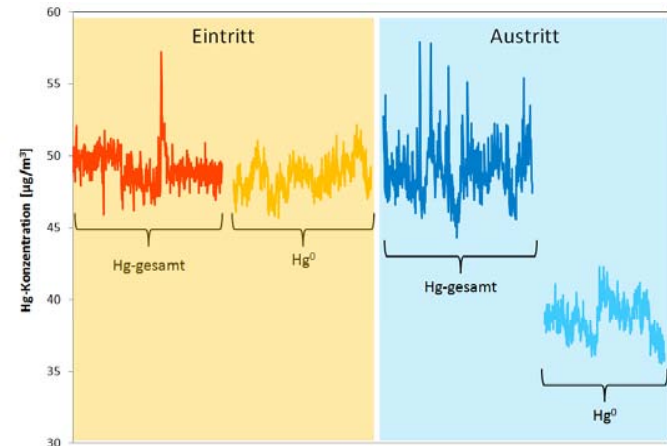
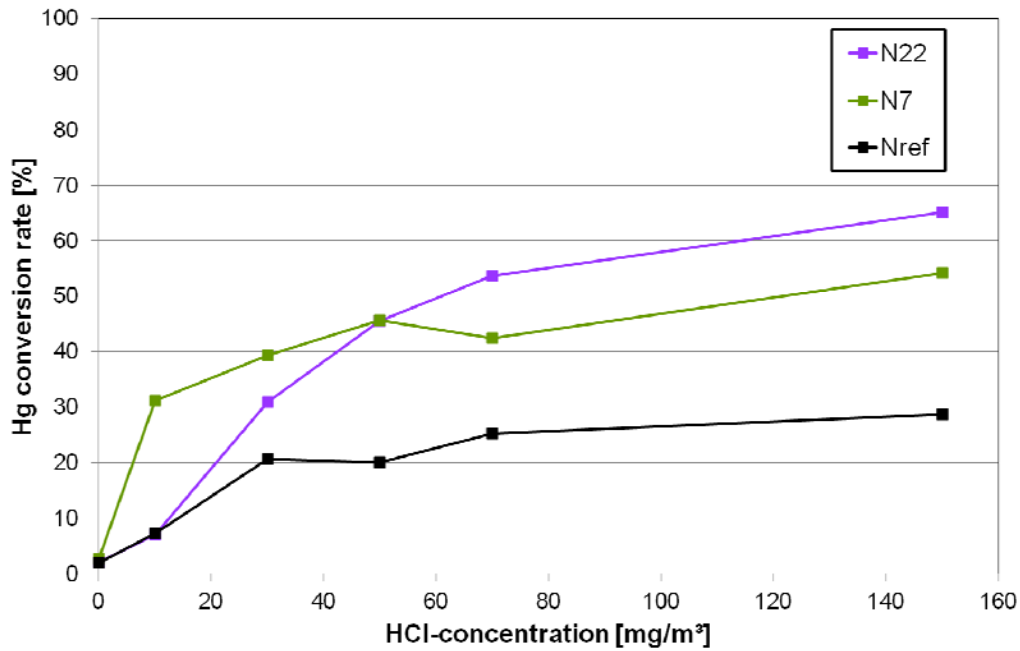
Influence of Catalyst Deactivation



Hg-Oxidation Decreases as Catalyst Deactivates

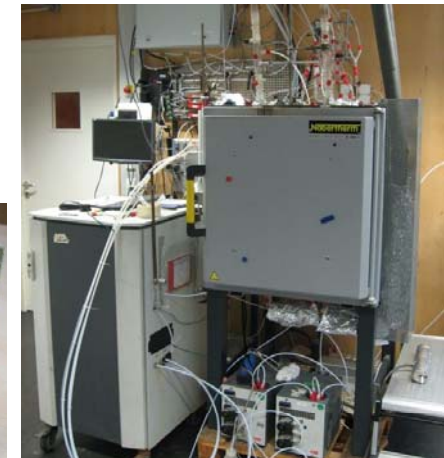
Influence of Halogens in Flue Gas (HCl)

Micro-Scale Reactor Tests



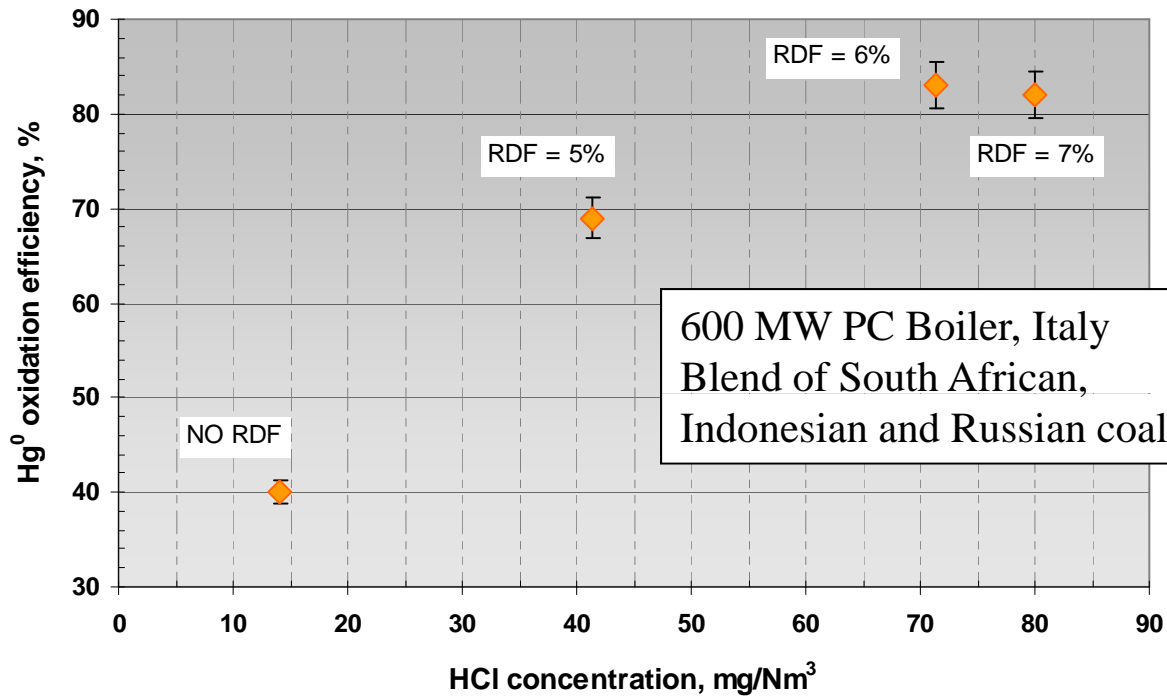
- Most important range: >0 – 50 mg/Nm³ HCl
- Very low HCl causes Hg adsorption in catalyst

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Influence of Halogens in Flue Gas

Full-Scale Tests

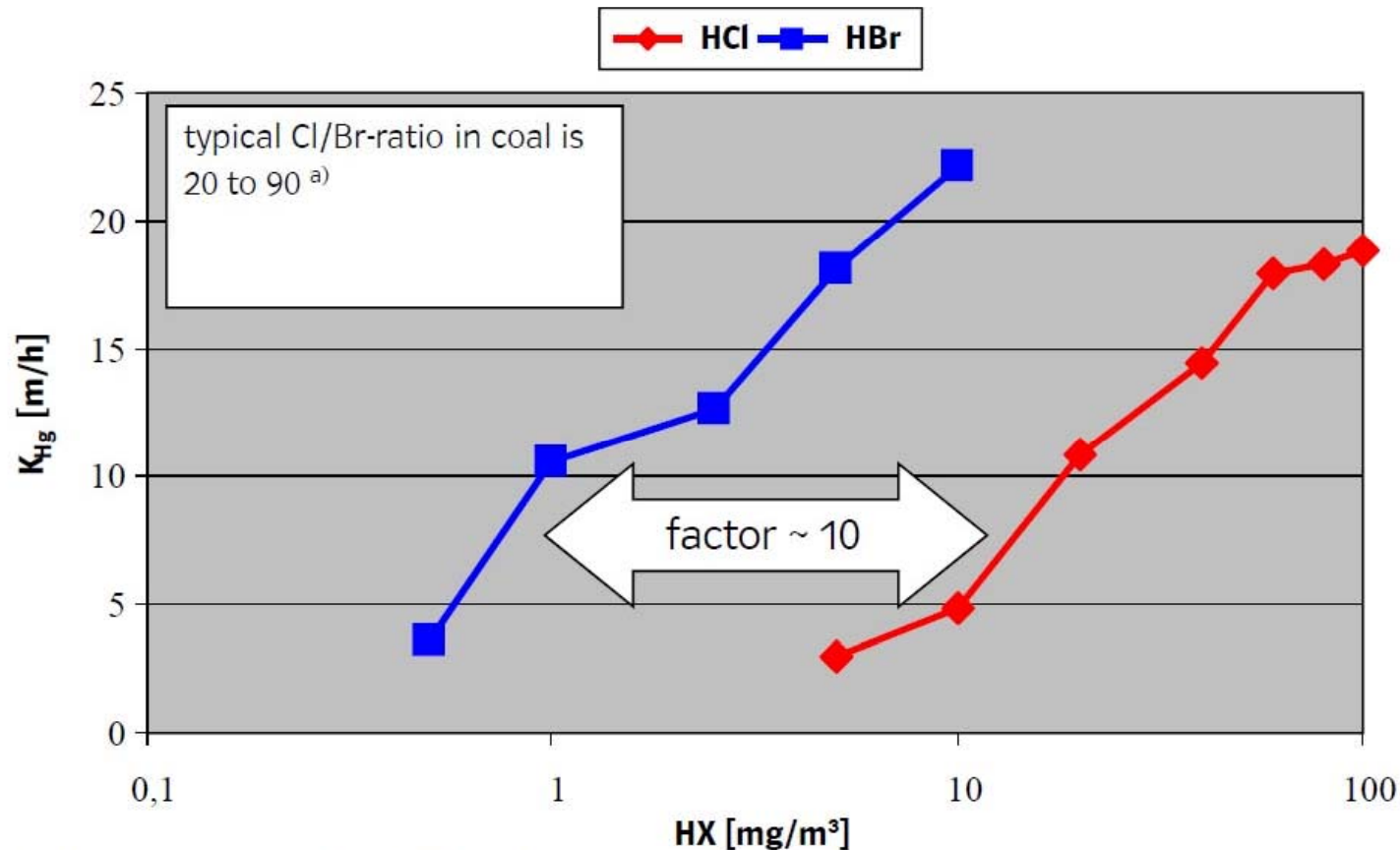


- **Co-Combustion of RDF** increases mercury oxidation in the SCR
- HCl concentration increases with increasing RDF



RDF %	HCl (flue gas) ppm	NOx Reduction %	Hg Oxidation %
0	8	54	40
5	25	49	69
6	44	49	83
7	49	54	82

Chlorine vs Bromine

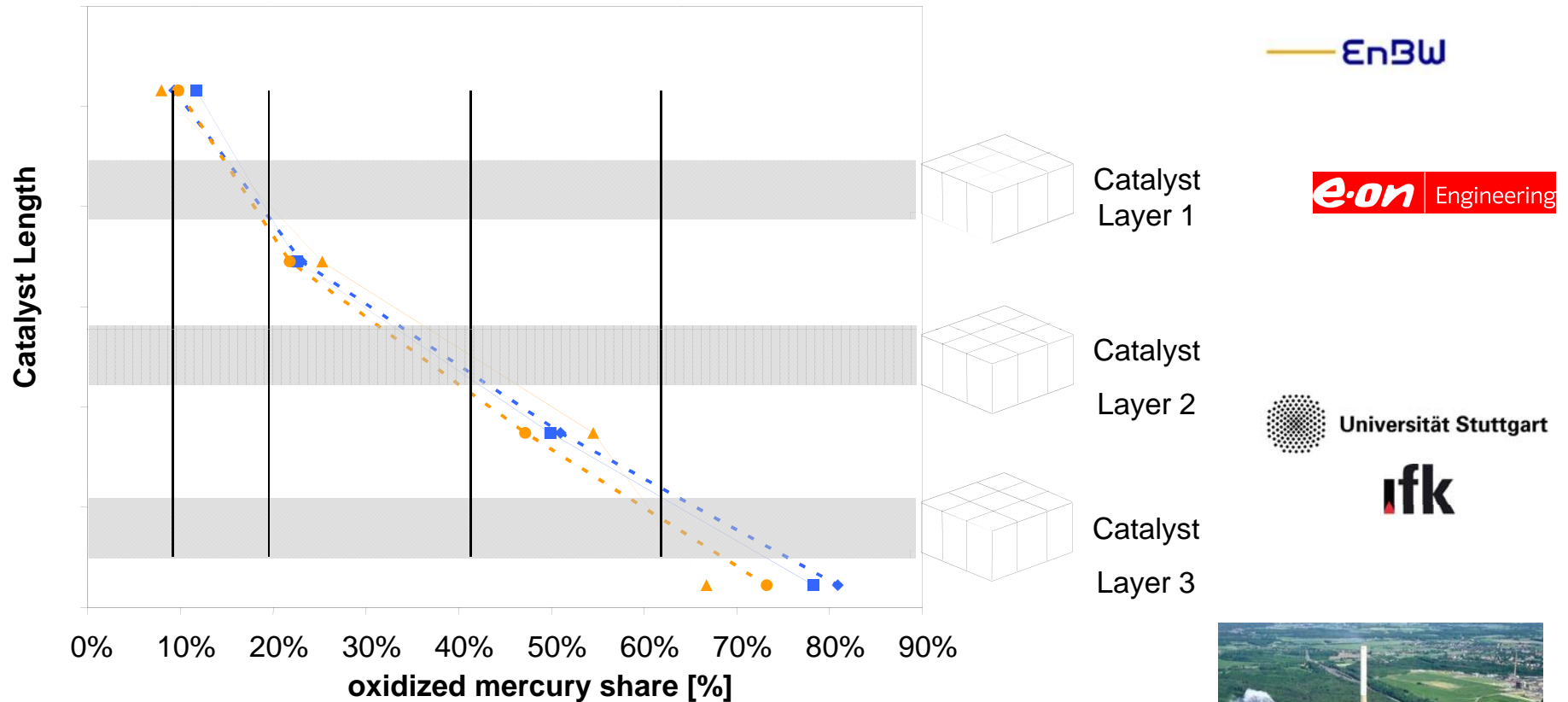


Source a: PC1 – Mercury Emissions and Control from Coal-Fired Power Plants, Electric Power Conference, Chicago, Illinois (2007)

- Bromine is effective with or without SCR, BUT much higher injection rates required (>200 ppm vs <30 to 50 ppm W/SCR)
- Iodine also is an effective Hg-oxidant

Oxidation Rates Increase Down the Reactor

Full-Scale Reactor Tests – 1st test

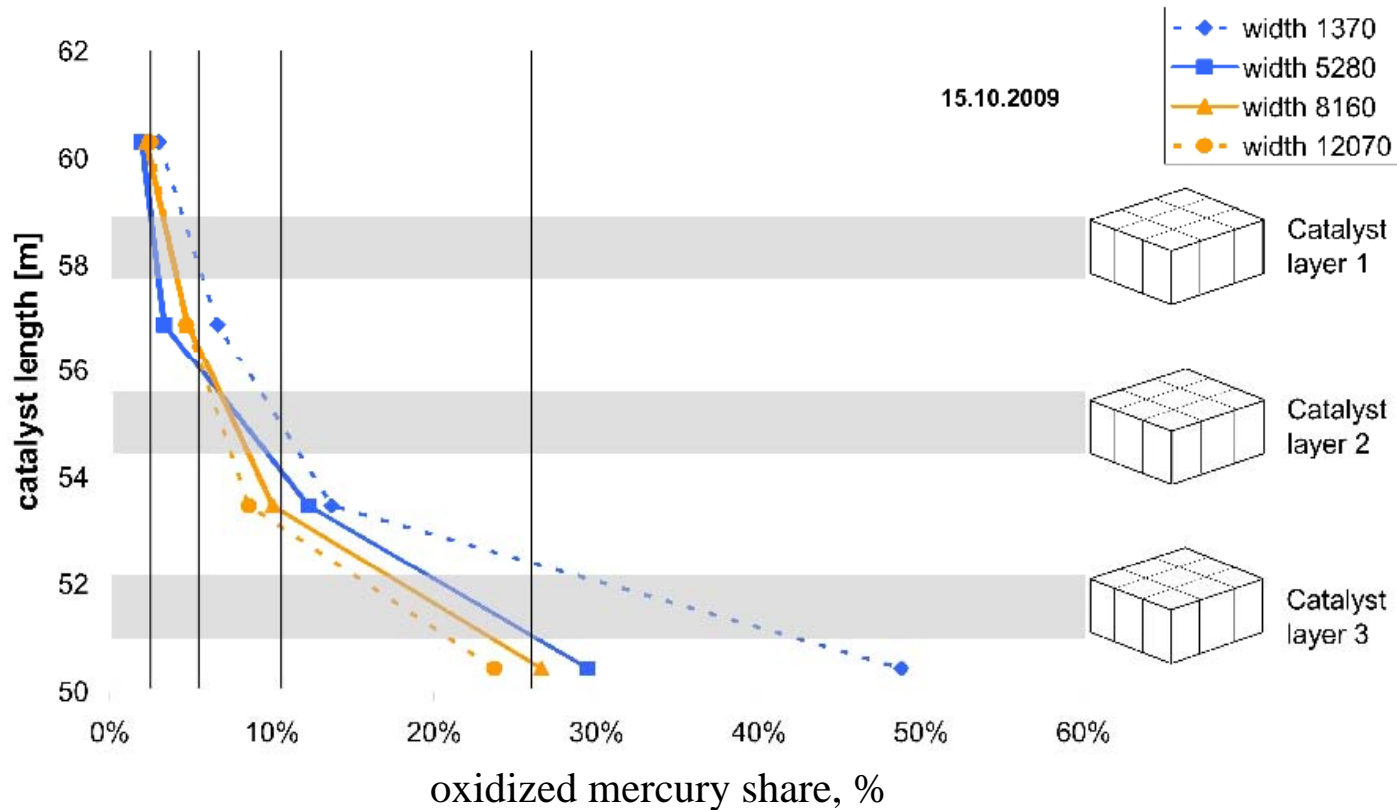


600 MW PC Boiler -High-Dust SCR
 3 Honeycomb Catalyst Layers
 US Coal - High Chlorides (~900 ppm in coal)



Oxidation Rates Increase Down the Reactor

Full-Scale Reactor Tests – 2nd test



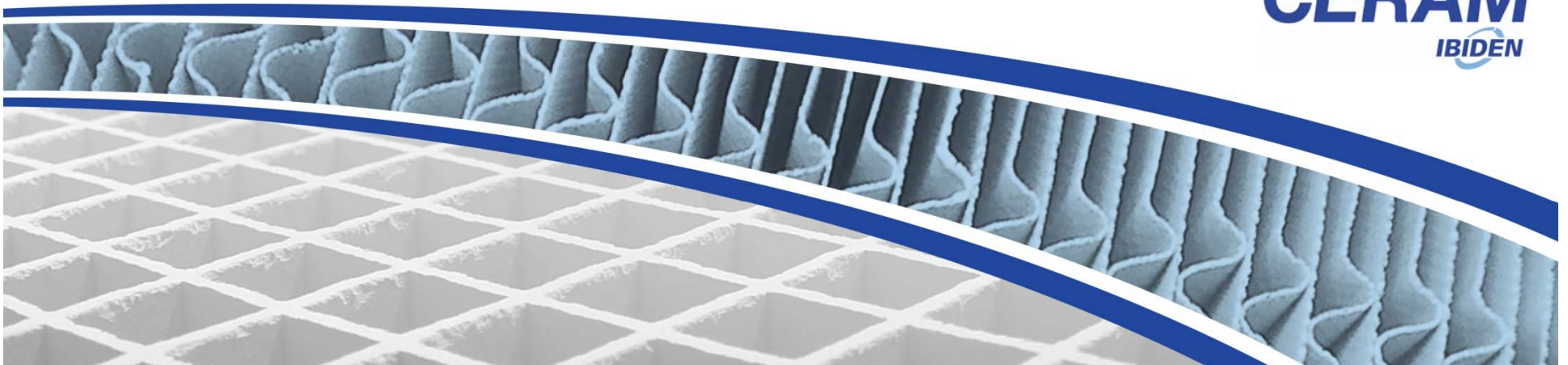
600 MW PC Boiler -High-Dust SCR
 3 Honeycomb Catalyst Layers
 Russian Coal - Low Chlorides (~62 ppm in coal)





Catalyst Testing of Hg Oxidation and Affects for NOx/Hg Management

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Catalyst Testing for Hg Oxidation

- NO_x Activity vs Mercury Oxidation Activity not Predictable
- Lab Tests Preferred Due to Cost of Field Tests
 - Lowest cost option is micro or semi bench vs bench
 - Reduced mercury required for testing in semi bench vs bench test
- Testing needed for individual catalyst composition and geometry
- Standard conditions vs actual operating conditions
- Test results used to calibrate model analysis accuracy

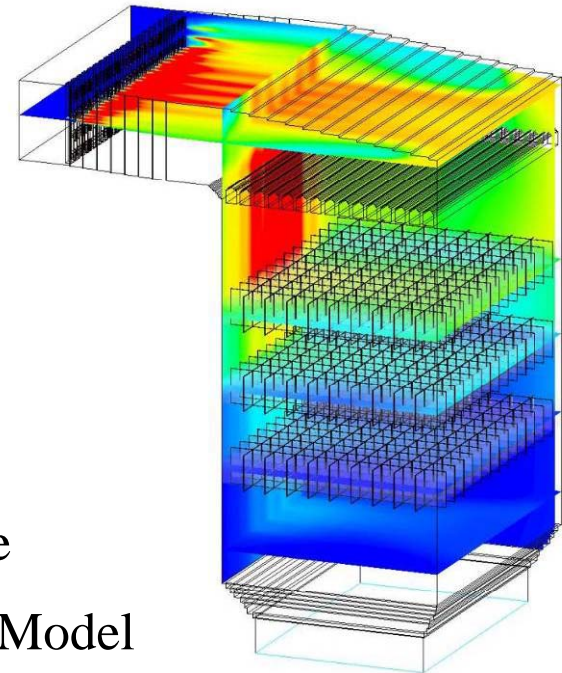
Recommended Laboratory Test Conditions to Assess Mercury Oxidation

- DeNOx Inactive Testing (NH₃ Off) Will Not be Representative of Operating Condition for Hg Oxidation
- Need Accurate Assessment of Operating Condition for New and Aged Catalyst
- Test Conditions Should Reflect Plant Operating Conditions
 - Area Velocity
 - Gas Temperature
 - Gas Composition (Hg⁰, NO_x, NH₃, HCl, HBr, SO₂, H₂O, O₂, etc.)
 - Gas Composition Determined by Fuel Quality and Operation Ranges Anticipated
- Annual Layer-by-Layer Testing Advised
- Characterization of Low to High Load Changes
- Test Results Used for Catalyst Management Planning

Mercury Oxidation 3-D Simulation Modeling

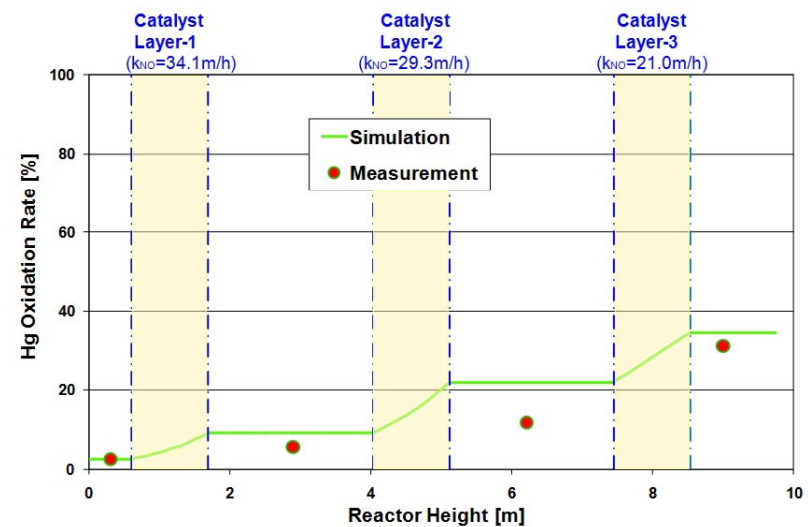
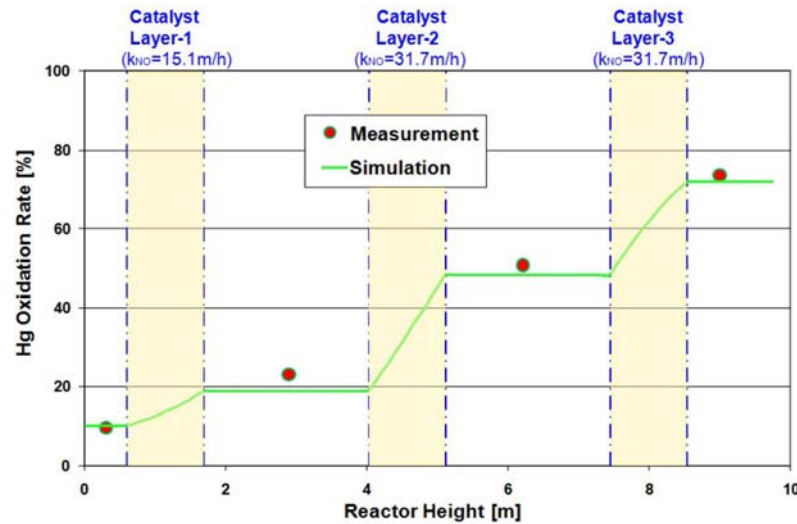
Program Objectives:

- Determine Integrated Mathematical Model for:
 - NO_x Reduction
 - Hg Oxidation
 - SO₂:SO₃ Conversion
 - Ash Accumulation/Reduced Catalyst Surface
- Implement Mathematical Models into 3-D CFD Model
- Model Validation Using Slip Stream and Full Scale Test Data



Assessment of Model Predictive Quality

Hg Oxidation along Reactor



- 3D-CFD model shows good correlation with plant measurements
- Change of one catalyst layer between measurement campaigns, but total DeNO_x potential almost same at time measurements
- Different chlorine content of the coals has strong impact
- Coal chlorine content is most important for high mercury oxidation

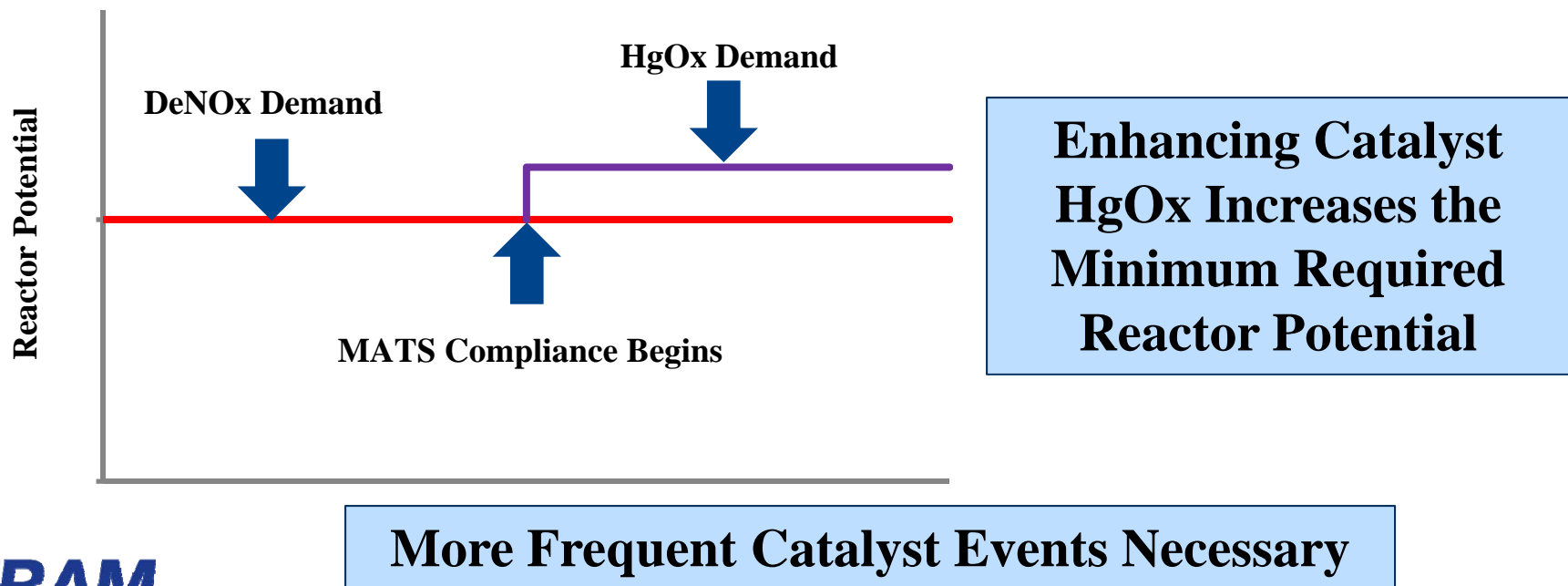
An aerial view of an industrial facility, likely a power plant or refinery, featuring a large white building with a blue steel structure on its roof. The facility is situated near a body of water. The CERAM and IBIDEN logos are overlaid on the image.

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Catalyst Management Effects for Optimizing Mercury Oxidation

Catalyst Management With MATS Compliance

- Optimizing Catalyst Hg Oxidation Performance Necessitates Increasing Reactor Potential Required for Catalyst Management
- DeNOx Demand (P_{req}) = Reactor Potential Required to Meet NOx Removal and NH₃ Slip Requirements
 - Calculated based on NOx removal requirements, NH₃ slip, and SCR reactor pluggage and distributions (velocity, NH₃/NOx, temperature)



Affect on Catalyst Management Planning

Current Practice: NO_x and NH₃ Slip Based Plans

- Consider Required NO_x/NH₃ Slip Performance
- Track K/Ko Trends
- Track/Assess Fuel Quality
- Track Operations Requirements
- Track Catalyst Pluggage

Future: NO_x, NH₃ Slip and HgO_x Based Plans

- + Consider HgO_x Targeted Performance
- + Track HgO_x K/Ko Trends
- + Track More Fuel Quality Data
- + Track More Operations Data
- + Consider Halogen Additions

Effective Planning Will Minimize Outage Schedule Impacts, Halogen Additions, and/or Activated Carbon Additions

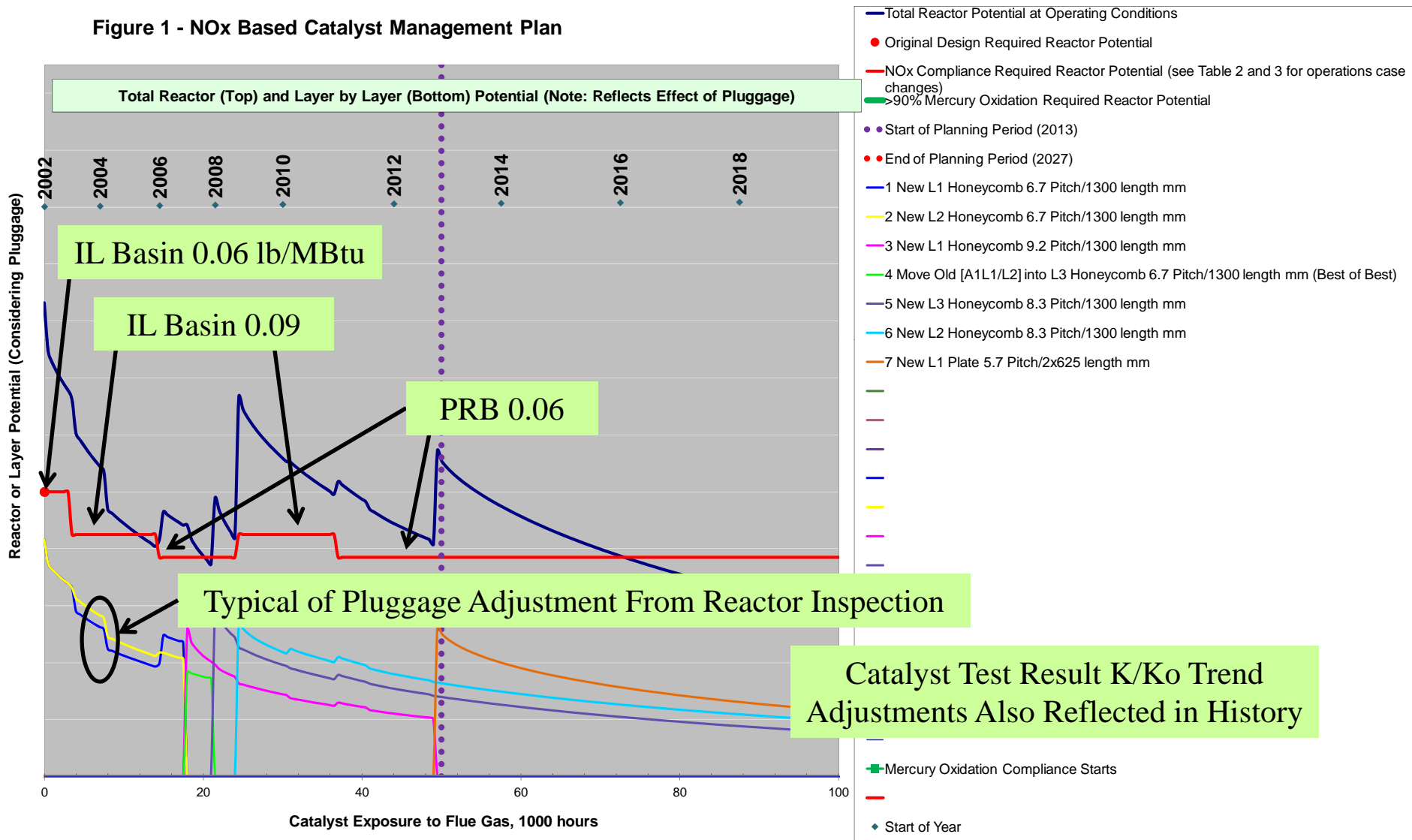
CERAM Has Adapted the Manage CATLife[®] Model for Combined NO_x and Hg Ox Catalyst Management Planning

Case Study: Catalyst Management Effects With MATS Compliance

- Case Study Intended to Illustrate Possible Catalyst Management Effects and Necessity to Optimize Integrated Approach
- Example Basis:
 - 600 MW Unit Currently Burning PRB (700 to 730 F), but is also Capable of Burning Illinois Basin Coal (650 to 655 F)
 - 3 Layer Reactor Design; NO_x In/Out 0.4/0.06 lb/MBtu PRB, 0.6/0.06 lb/MBtu Illinois Basin
 - Max SO₂ to SO₃ Conv: 3% at 730 F for PRB, 1.3% at 655 F for IL Basin
 - PRB Fuel Transition Led to Installation of Larger Pitch Catalyst
 - Mixture of Plate and Honeycomb Catalyst Currently Installed
 - Future Events a Mixture of Regenerated and New Catalyst
- Economic Analysis:
 - Catalyst (New and Regen) at Current Market Values
 - Includes In and Out Costs, ID Fan Energy Costs

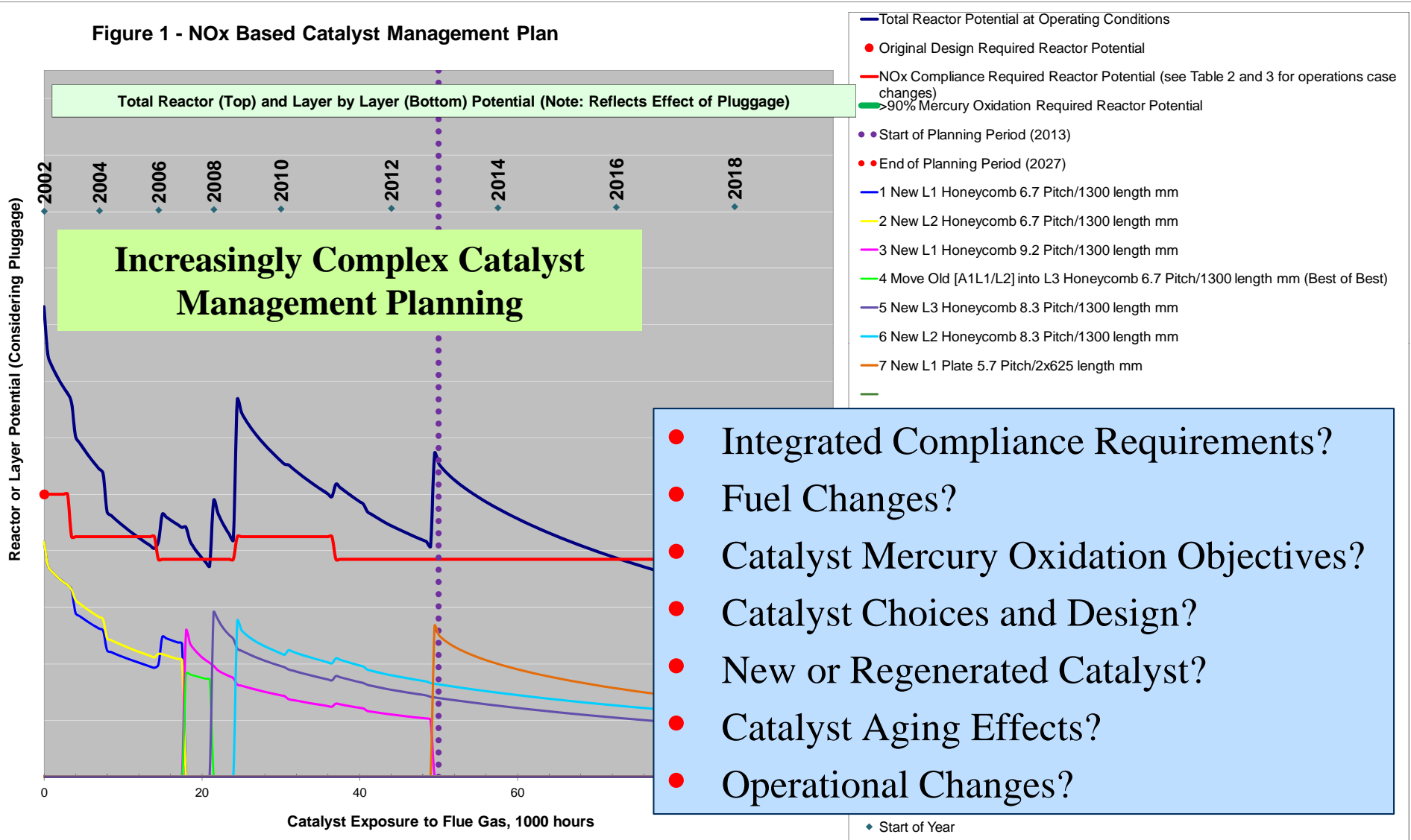
The History Up To Now – Fuel Switches, Reactor Inspection Results and K/Ko Results

Figure 1 - NOx Based Catalyst Management Plan



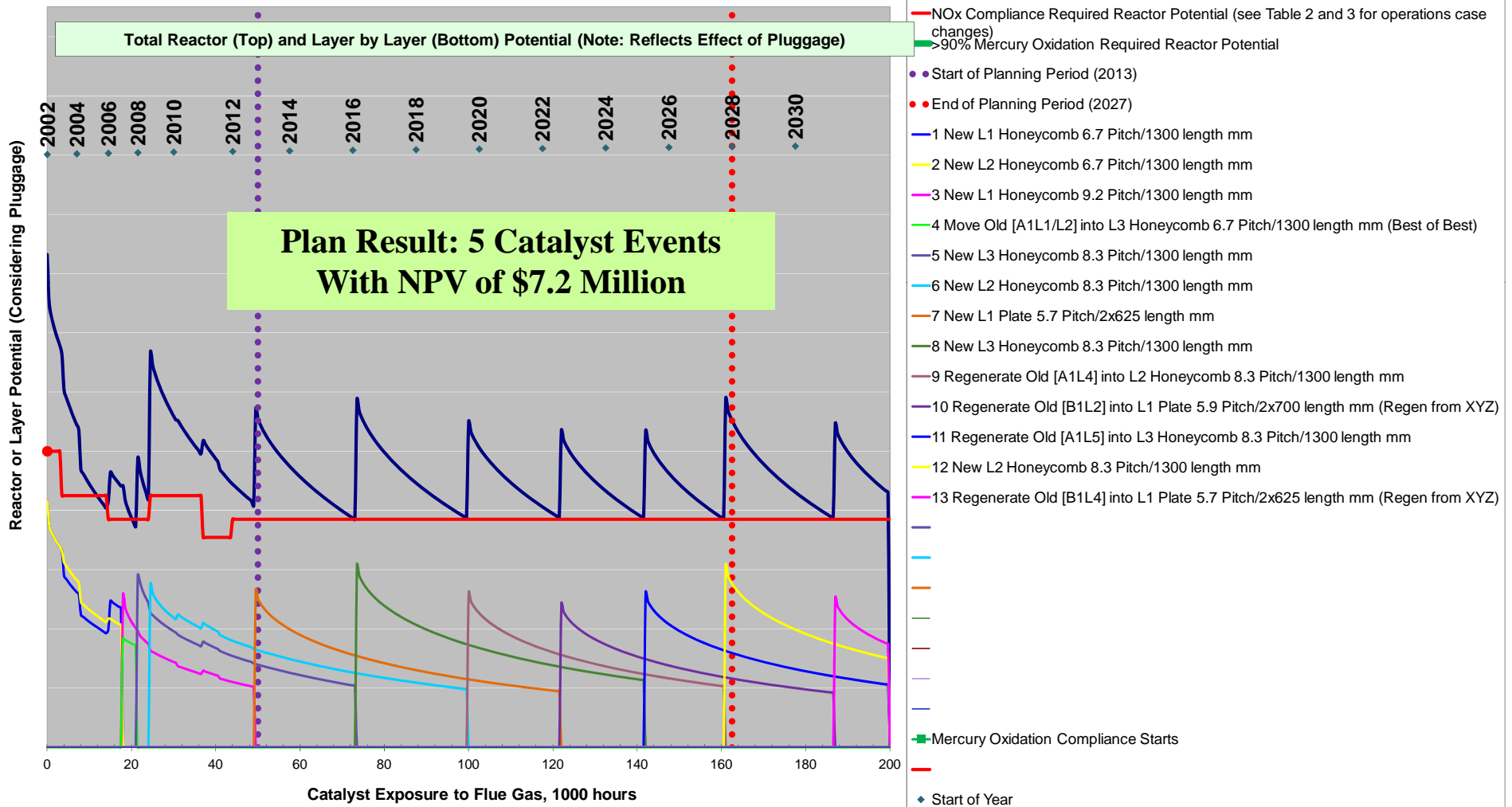
What's Next and When?

Figure 1 - NOx Based Catalyst Management Plan



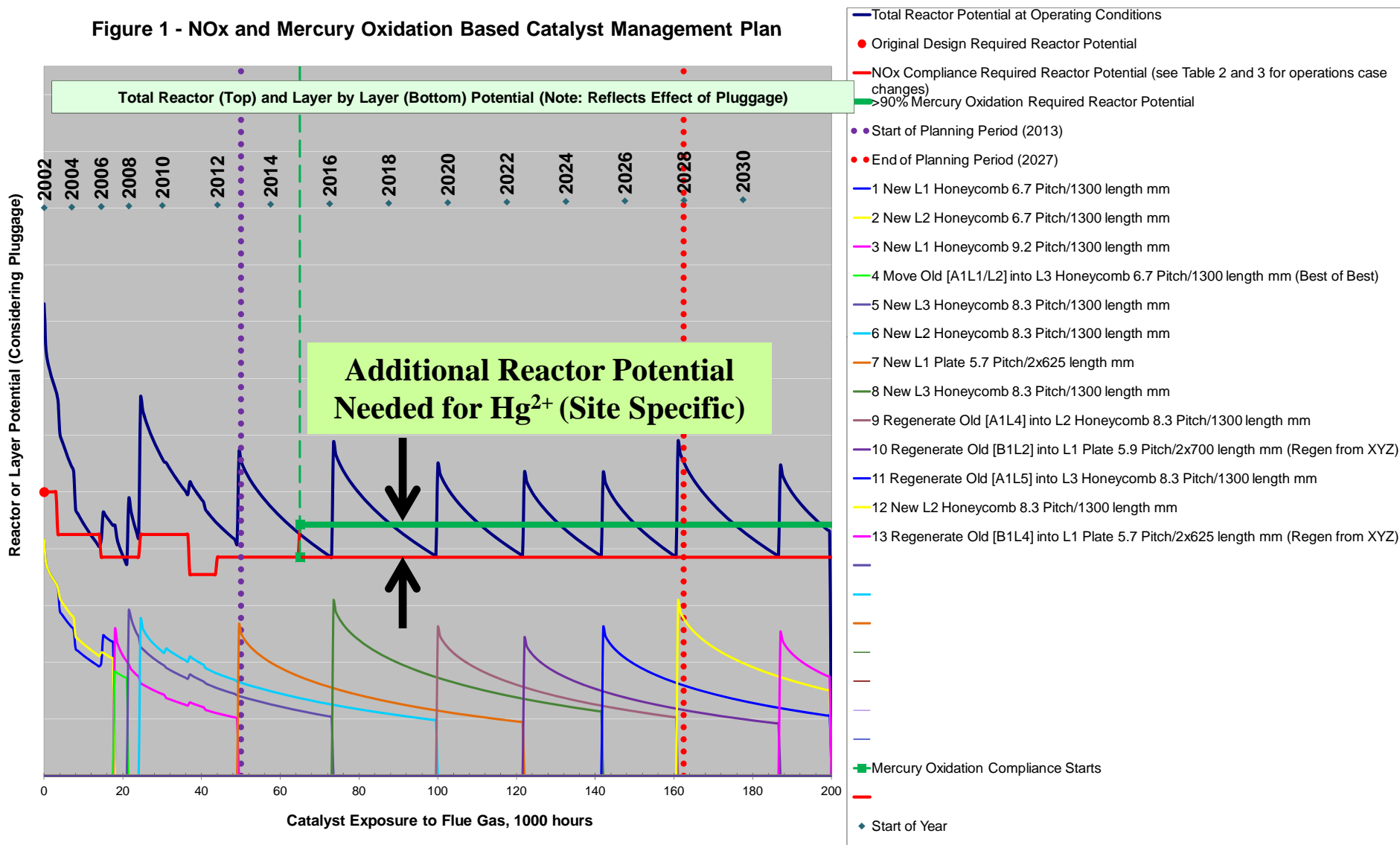
Catalyst Management Case Study Without MATS 600 MW Burning PRB Through Plan Period

Figure 1 - NOx Based Catalyst Management Plan



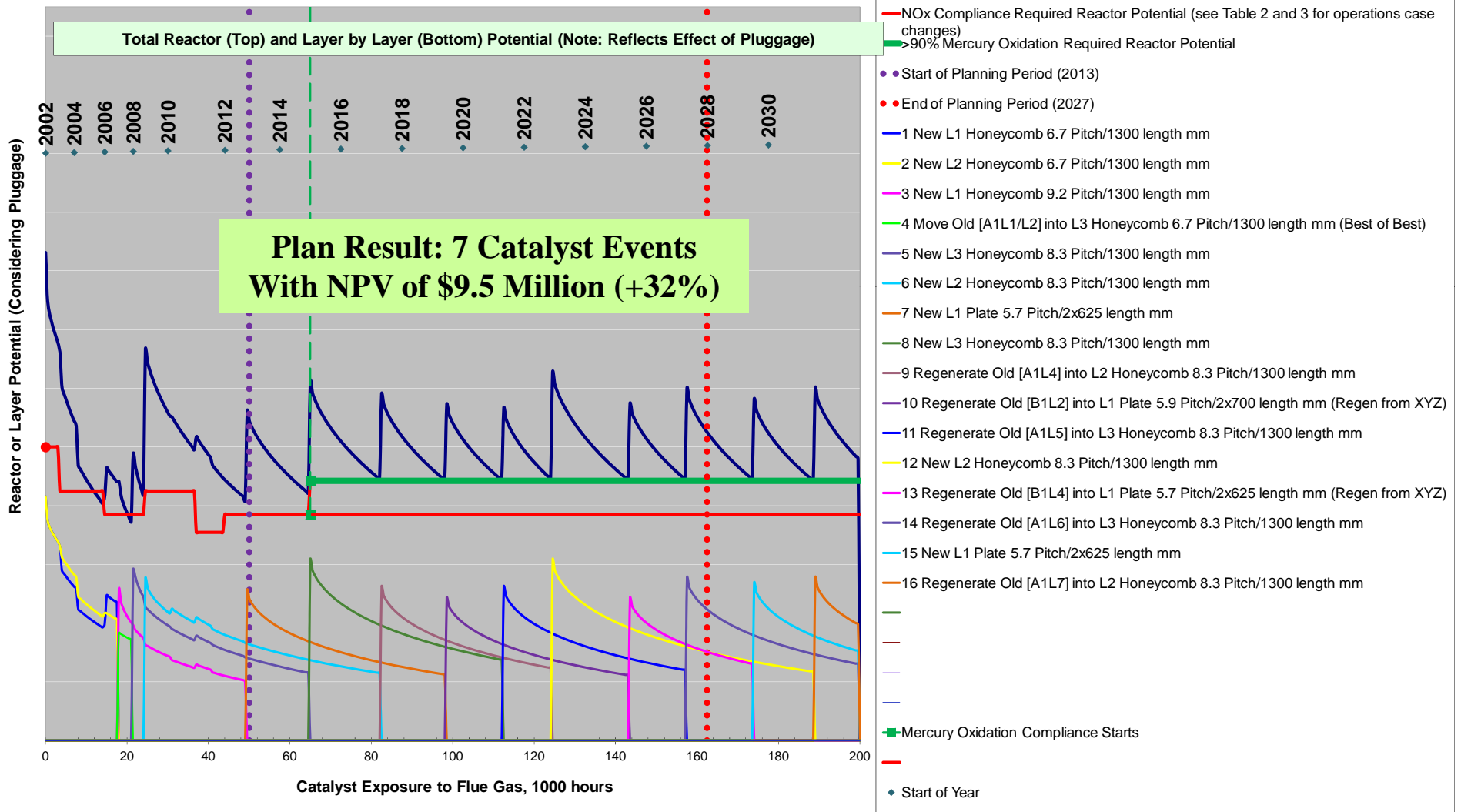
MATS Mercury Oxidation Will Change Required DeNOx Demand (especially for PRB)

Figure 1 - NOx and Mercury Oxidation Based Catalyst Management Plan



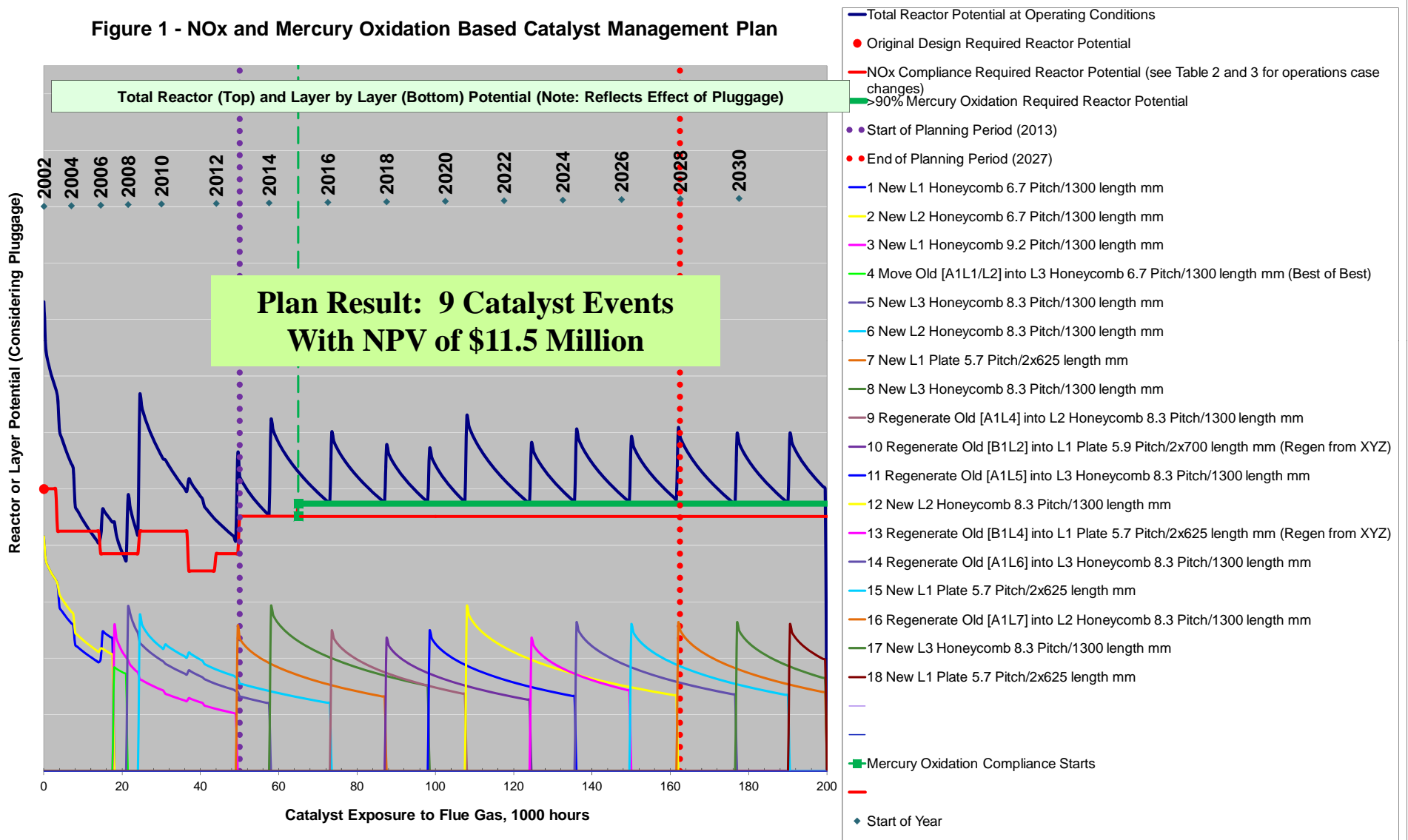
MATS Mercury Oxidation Will Increase # of Catalyst Events to Maintain Performance (600 MW PRB Example)

Figure 1 - NOx and Mercury Oxidation Based Catalyst Management Plan



The Impact of HgOx Will be Very Site Specific (600 MW Illinois Basin Coal Through Plan)

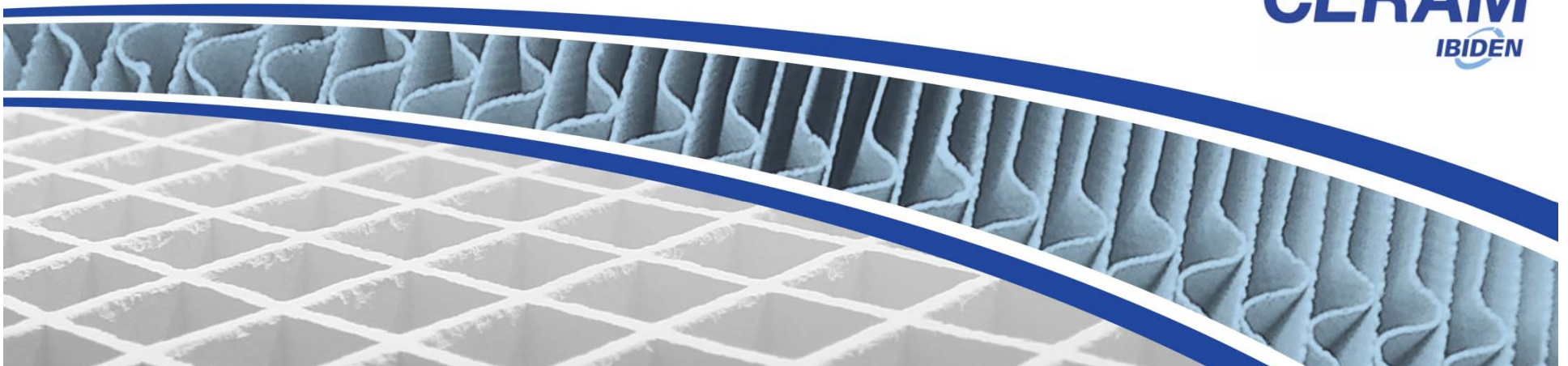
Figure 1 - NOx and Mercury Oxidation Based Catalyst Management Plan



Summary

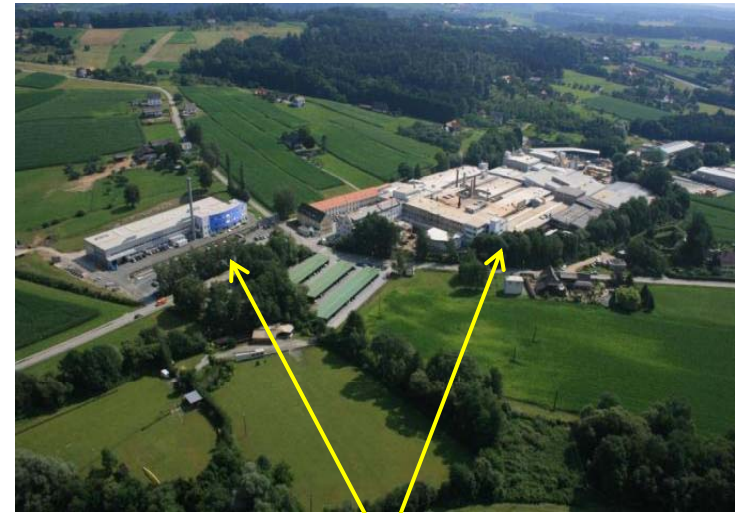
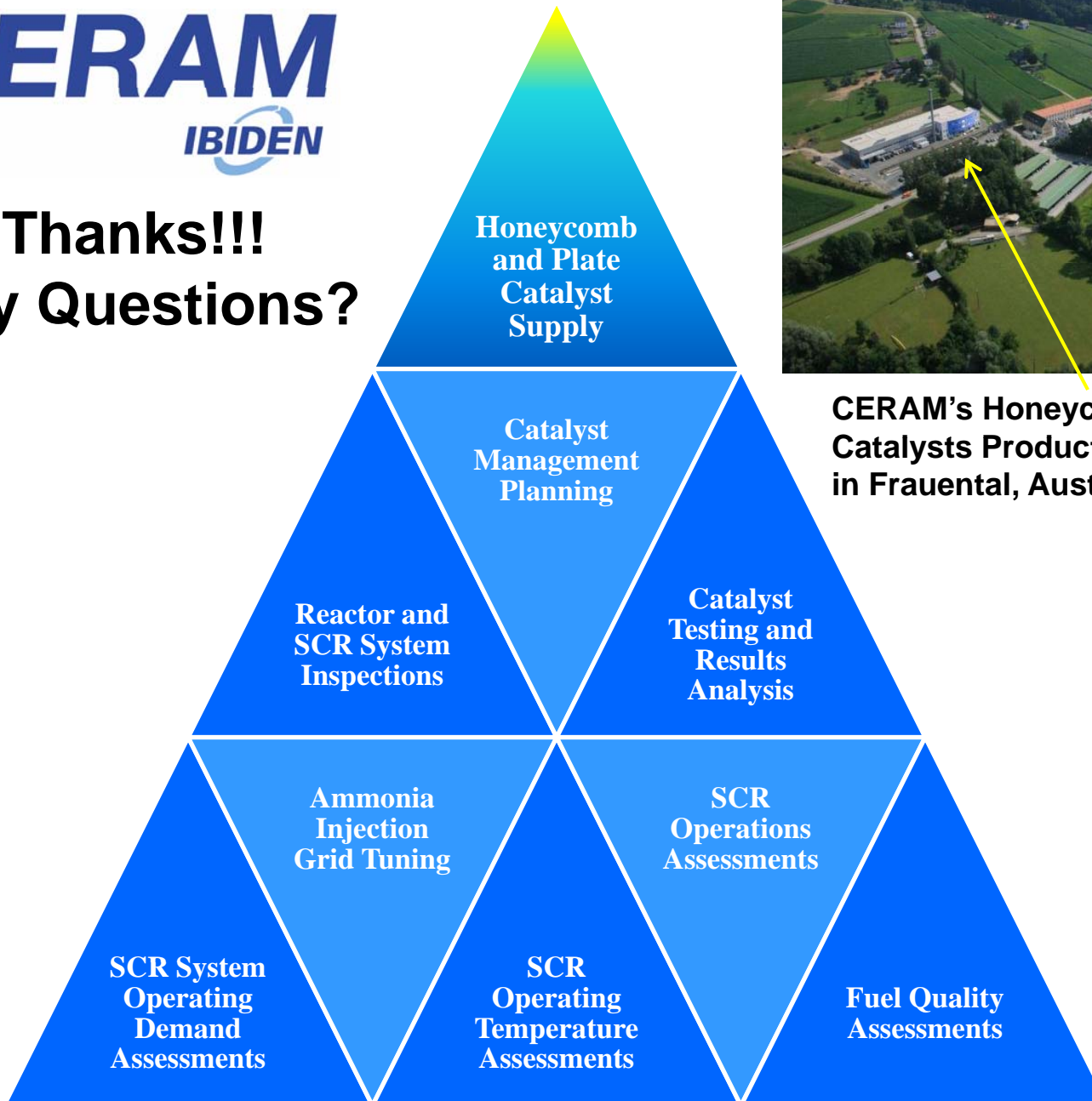
- Mercury Oxidation Technology and Related Parametric Influences are Rapidly Developing
- MATS Will Change the Approach to Catalyst Management
- Optimized Catalyst Management Strategies are Available to Support High Mercury Oxidation Rates
- Strategies Will be Site Specific and Fuel Dependent
- Additional Laboratory Testing of Plant Aged Catalyst Samples for HgOx Will be Required to Support Planning Work
- Comprehensive Planning Will Limit Cost Impacts

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**Thanks!!!
Any Questions?**



CERAM's Honeycomb and Plate Catalysts Production Plant Located in Frauental, Austria