McIlvaine "Hot Topic Hour"
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Mercury Oxidation Test Program Results

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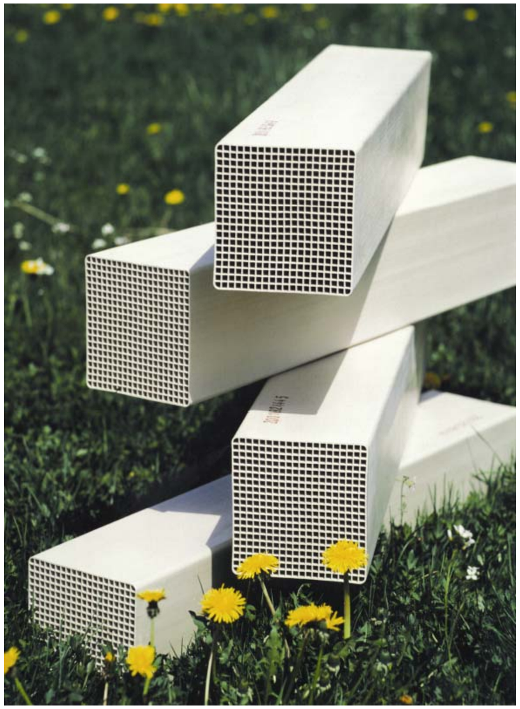
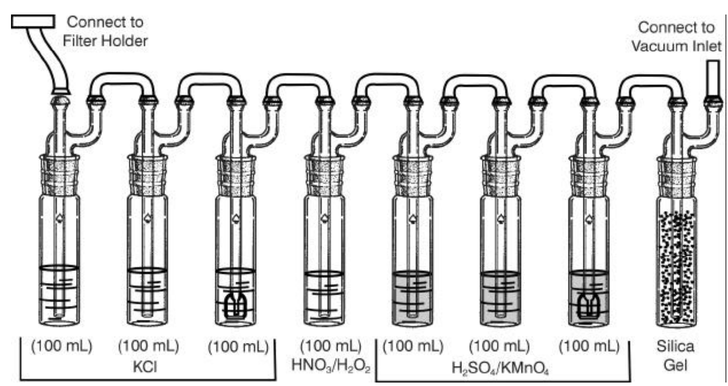
Presentation Topics



- Main Reactions on SCR Catalyst
- Mercury Oxidation Characterization and Optimization Test Program
  - Test Plan and Objectives
  - Pilot, Bench, Full Scale Results
  - Simulation Modeling Results
- Representative Full Scale Results
- Low Temperature Mercury Oxidation



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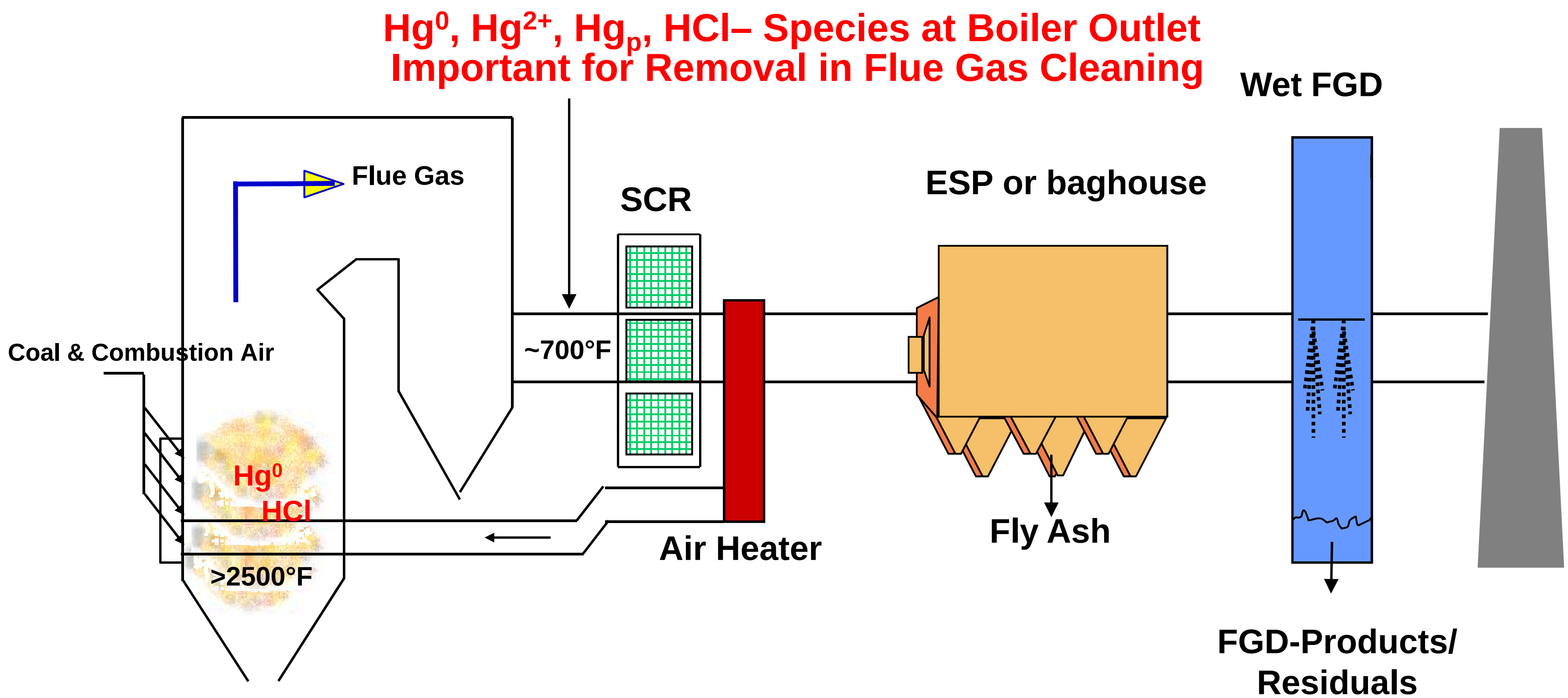
Example of Flue Gas Cleaning System in Power Plants



- Use Existing Flue Gas Cleaning Systems for Mercury Removal
  - Hg Oxidation on SCR Catalyst
  - Removal of Particulate Hg (ESP, baghouse)
  - Separation and Removal of Oxidized Hg in FGD
- Clean Air Mercury Rule (CAMR) – Reduce Hg Emissions (≈48 tons/yr Uncontrolled in U.S.)
- Combination of high-dust SCR/ESP/FGD may result in Hg removal up to 95%

Important Step: Hg^0-Oxidation on SCR Catalyst

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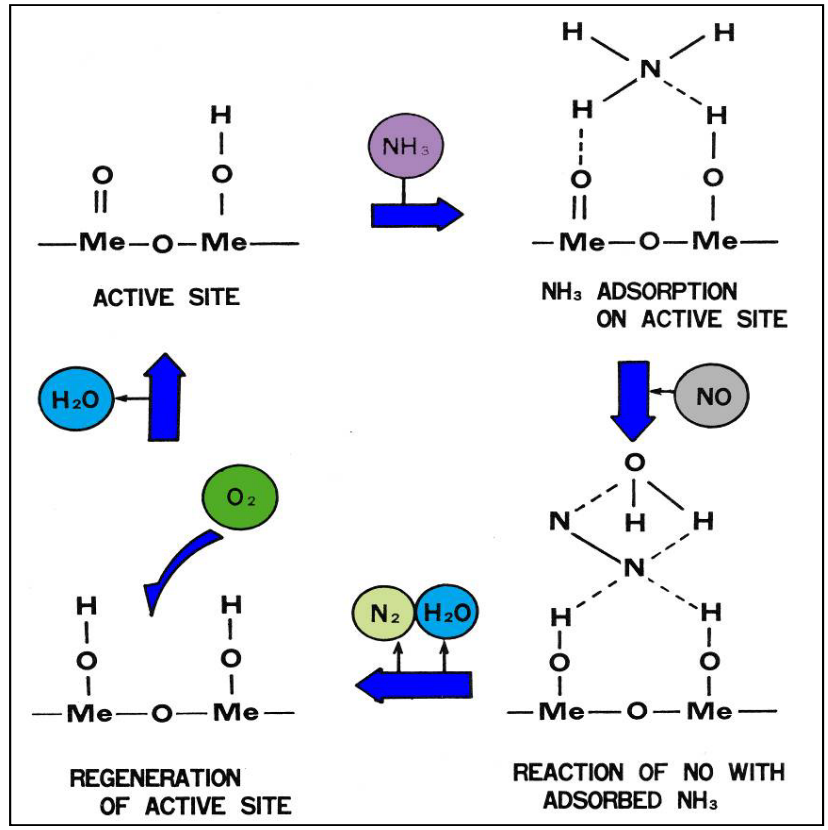
SCR DeNOx Reaction – Process Basics

- Catalyst Active Sites Constantly Being Regenerated in a Cycle
  1. Active Site Available
  2. Adsorb Ammonia
  3. Reaction of NOx With NH_3
  4. Regenerate Site With O_2

- Active Sites **Not Busy** With NOx Reduction (Ammonia) **Available** For Oxidation of SO_2, Hg^0, Unburned Hydrocarbons, VOC, Dioxins, etc.



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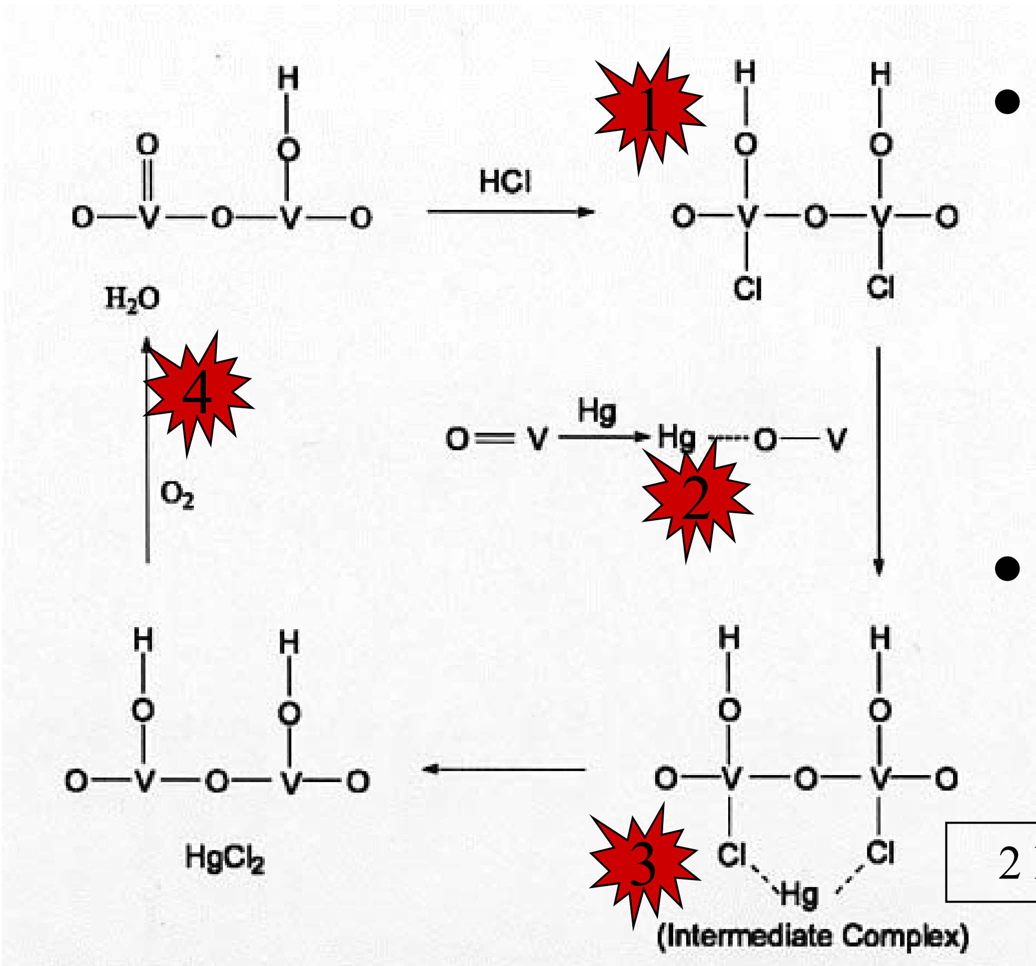
Hg Oxidation With Titanium/Vanadium SCR-Catalysts



Source: Energy & Fuels, 2009, Zhou et al..

- **Langmuir-Hinshelwood-Mechanism at adjacent active sites**
  1. HCl adsorb onto V sites
  2. Reactive Cl generated
  3. Weakly adsorbed Hg^0
  4. O_2 re-oxidizes active sites
- **Deacon Reaction**
  1. V_2O_5 and HCl React to Produce Cl_2 Which Reacts With Hg^0

$$2\ Hg + 4\ HCl + O_2 \rightarrow 2\ HgCl_2 + 2\ H_2O$$

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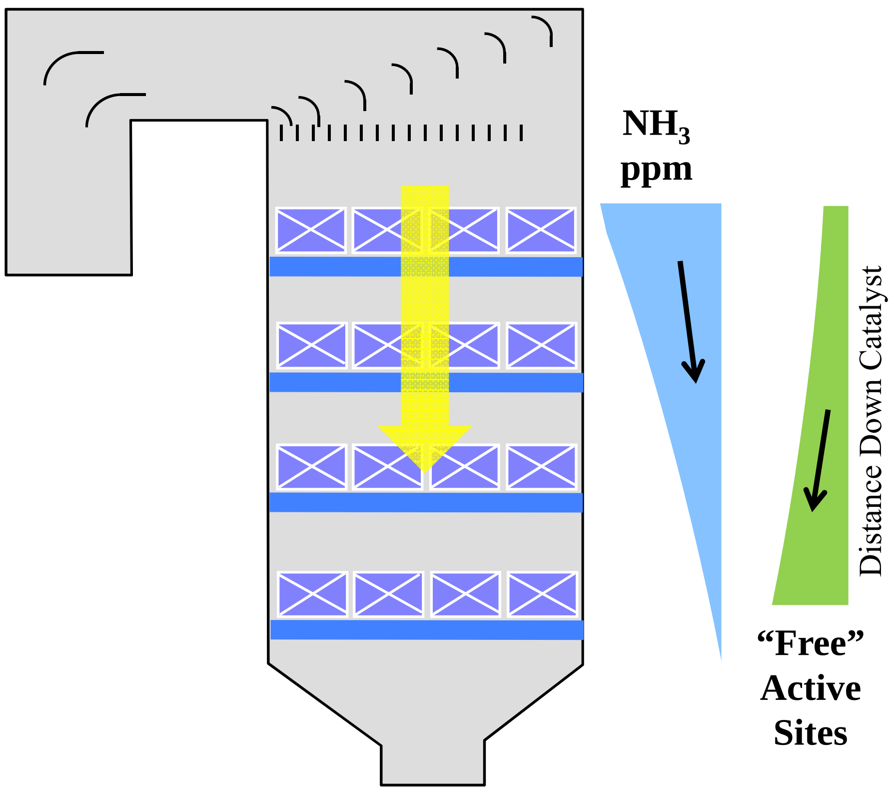
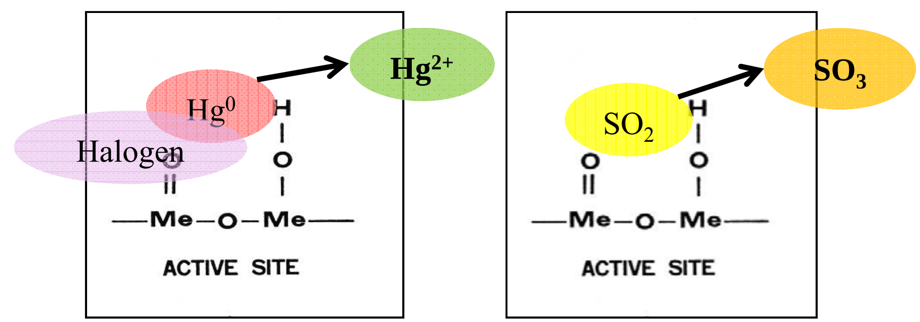
Oxidation Rates Vary Based on Location in the Reactor



- Ammonia Concentration Decreases as Flue Gas Flows Down Through Catalyst Layers
  - Surplus or "Free" Active Sites Increase Down Through Reactor
- Surplus Active Sites Result in Increasing Rate of…
  - SO_2 to SO_3 Oxidation
  - Mercury Oxidation
  - Dependent on Catalyst Aging



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CERAM Participating in Comprehensive Mercury Oxidation Test Programs

- CERAM Working to Optimize Mercury Oxidation Potential in Extensive Pilot/Demonstration Programs
- European Research Project DENOPT

  Research Fund for Coal and Steel RFCR-CT-2007-00008
- Participants - ENEL, E.ON, EnBW, CERAM, Reaction Engineering, University of Stuttgart, and RECOM Service
- Test Approach:
  - Evaluating Different Catalyst Compositions
  - Evaluating New, Deactivated, and Regenerated Catalyst
  - Bench and Pilot Scale Tests
  - Full Scale Tests (600 MW PC) When Firing Coal and Co-Firing Coal and Biomass
  - CERAM is the Only Catalyst Supplier Participating

Research Fund for Coal & Steel

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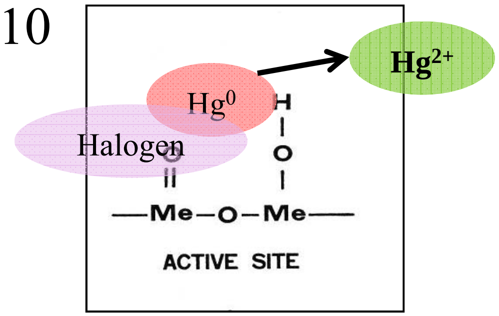
CERAM Participating in Comprehensive Mercury Oxidation Test Programs

- Program Objectives:
  - Fully Characterize Oxidation Reactions – Develop Mathematical Model
  - Evaluate Commercial and Innovative Low and High Temperature Catalyst Compositions Directed at Promoting Mercury Oxidation
  - Assess Catalyst Effects on Mercury Speciation for Different Coals
  - Investigate Effects of Operating Conditions (Area Velocity, Catalyst Age, and Deactivation Levels) on Oxidation Rate
  - Optimization of SCR Catalyst Performance Related to Mercury Oxidation and Limiting Deactivation
- Program DENOPT completed June 2010
  - Research has Expanded CERAM's Knowledge Base Regarding Hg Oxidation Reaction Mechanisms and Kinetics
- Second Program DEVCAT (**DEV**elopment of High Performance SCR **CAT**alyst Related to Different Fuel Types) started July 2010 (ongoing for three years)



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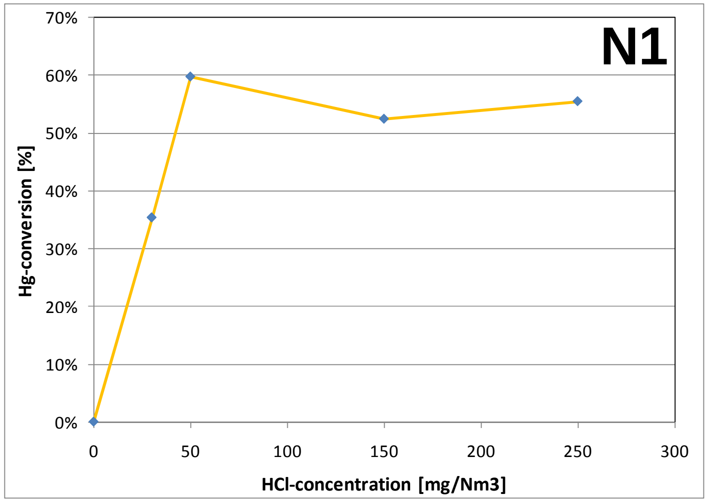
Micro-scale Reactor Tests on Different Catalysts

Influence of HCl-concentration



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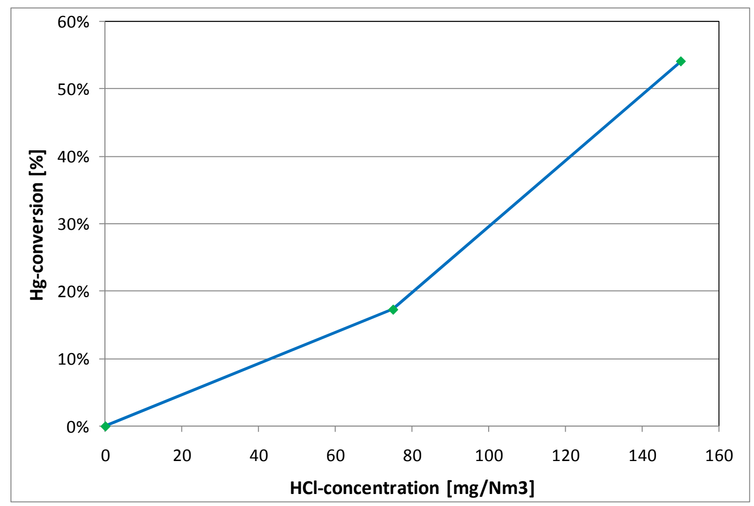

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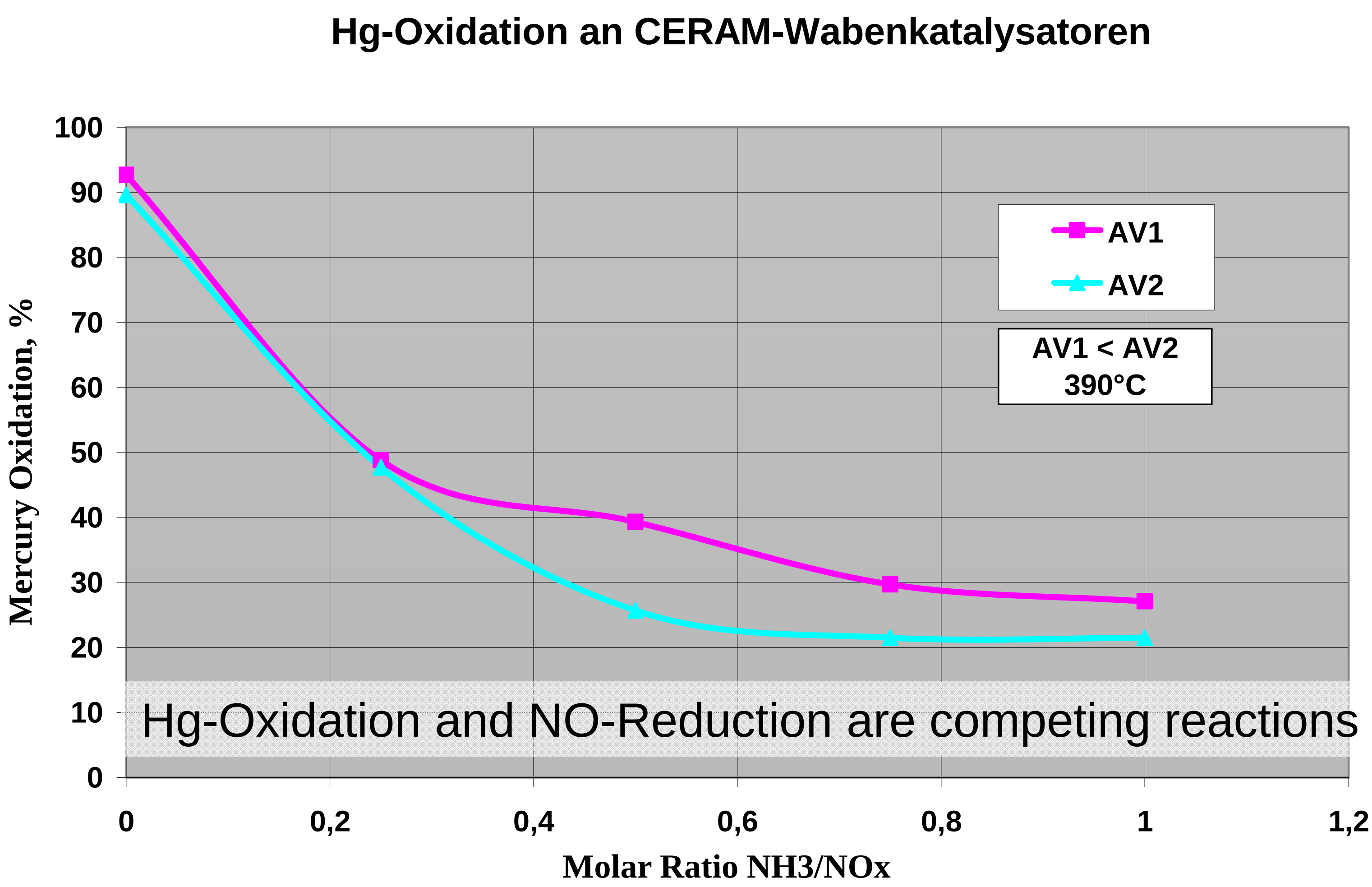
Influence of Molar Ratio NH_3/NOx



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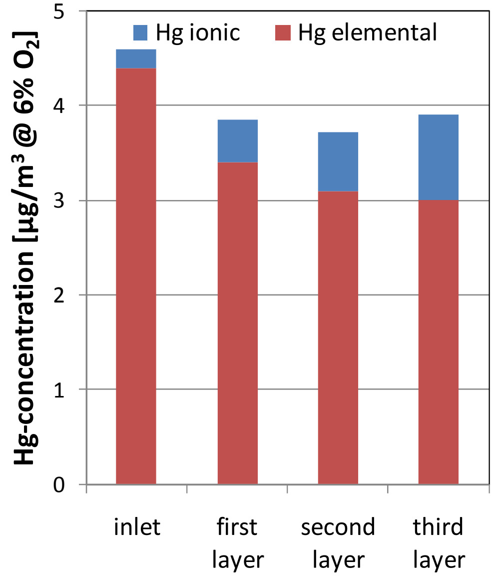
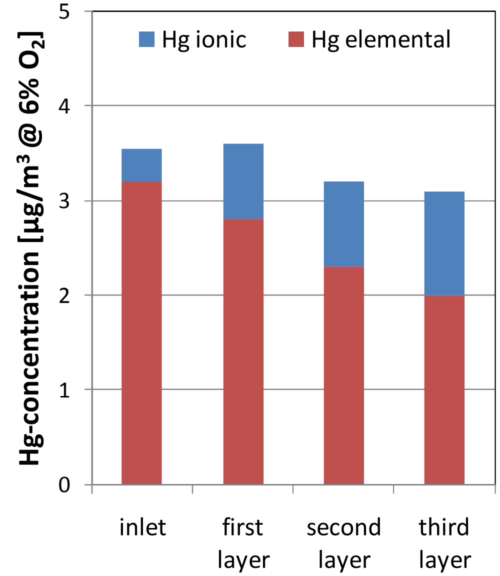
Tests Results for 500kW Test Rig

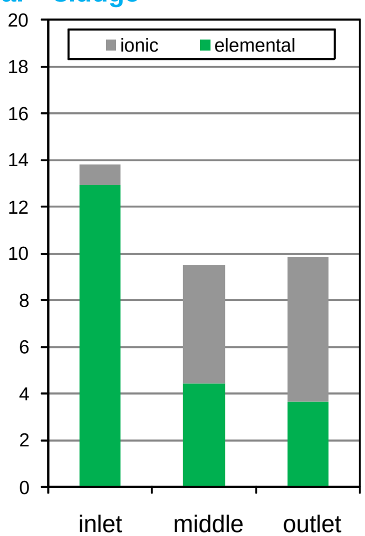
Coal – Catalyst 1



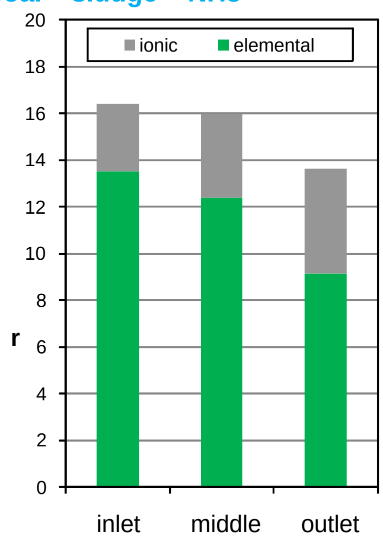
Coal – Catalyst 2



coal + sludge



coal + sludge + NH3



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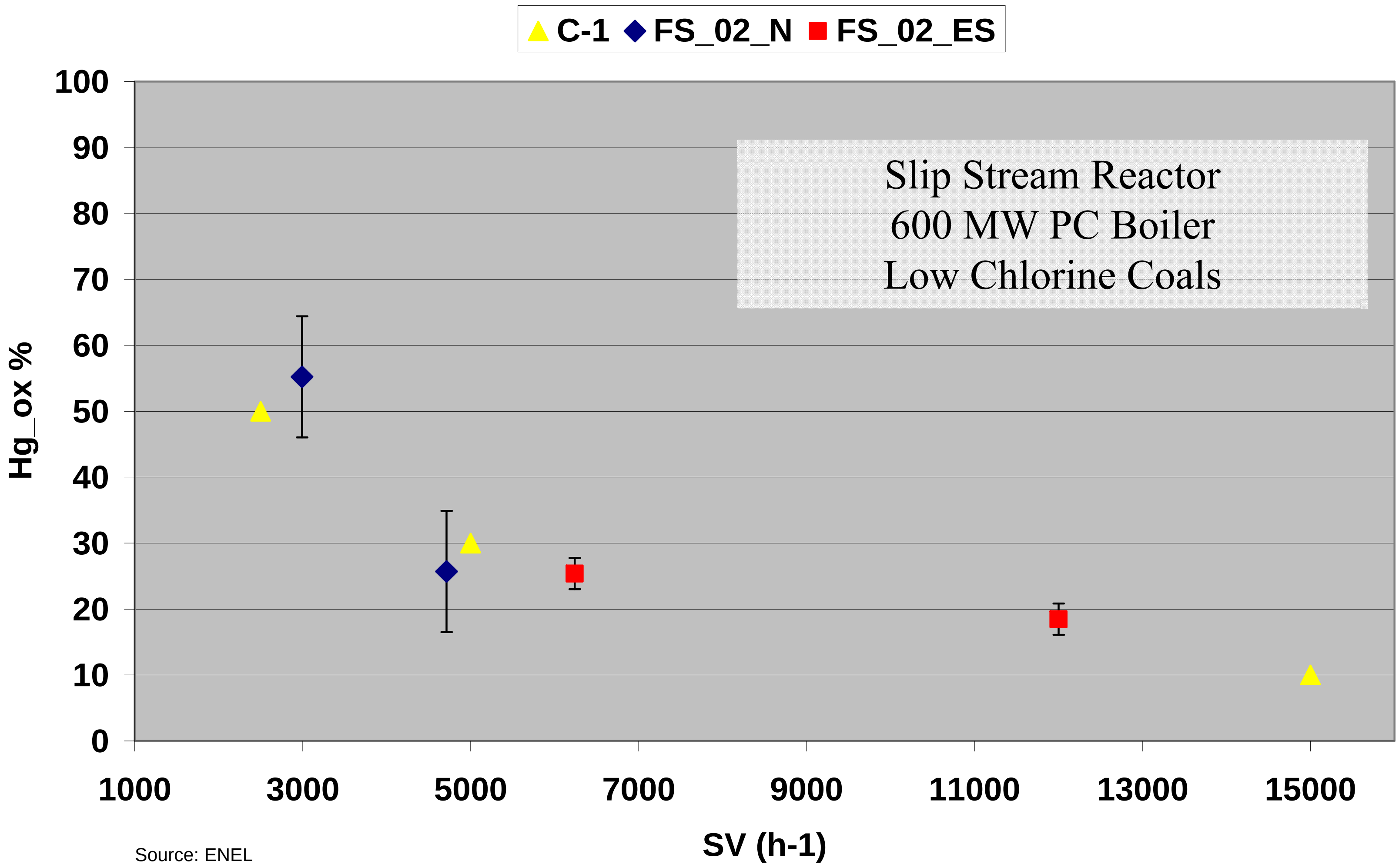
Note: Test Results for High Area Velocity Not Typical for Full Scale

Influence of Space Velocity (SV)



Power Plant Measurements

600 MW PC Boiler

High-Dust SCR

3 Honeycomb Catalyst Layers

High Chlorides (~900 ppm in coal)

EnBW

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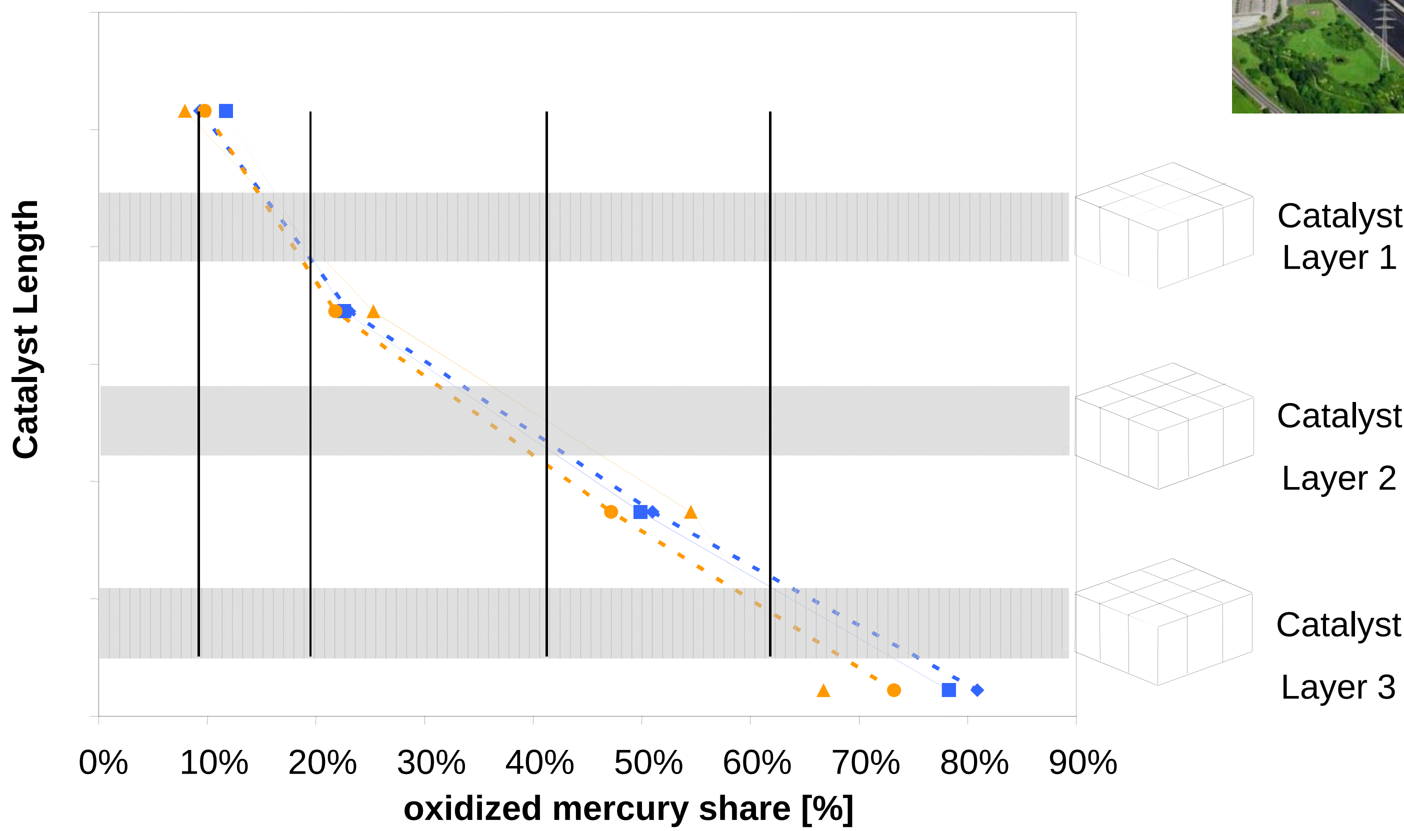

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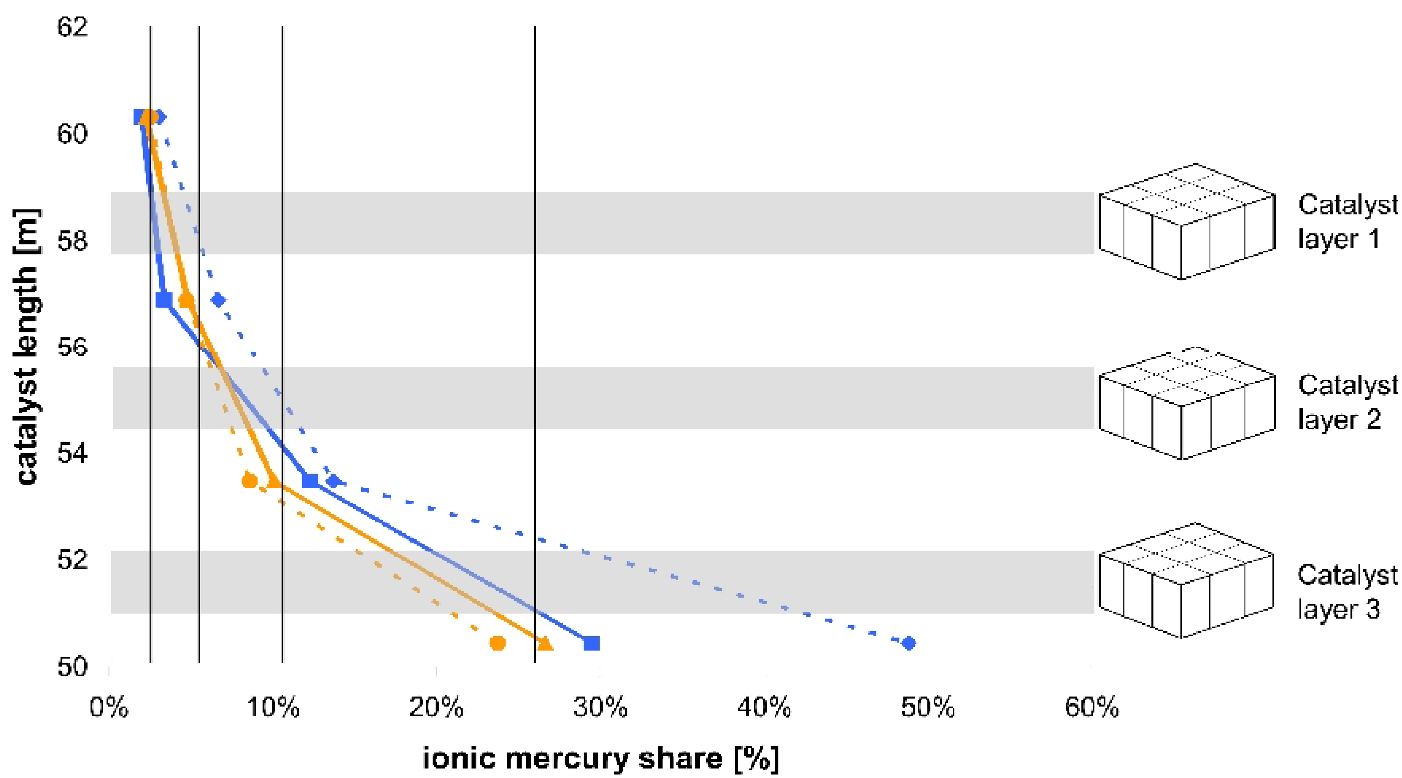
Power Plant Measurements

2nd Measuring Campaign

Coal Chlorine 62 ppm

Sulfur 0.43%



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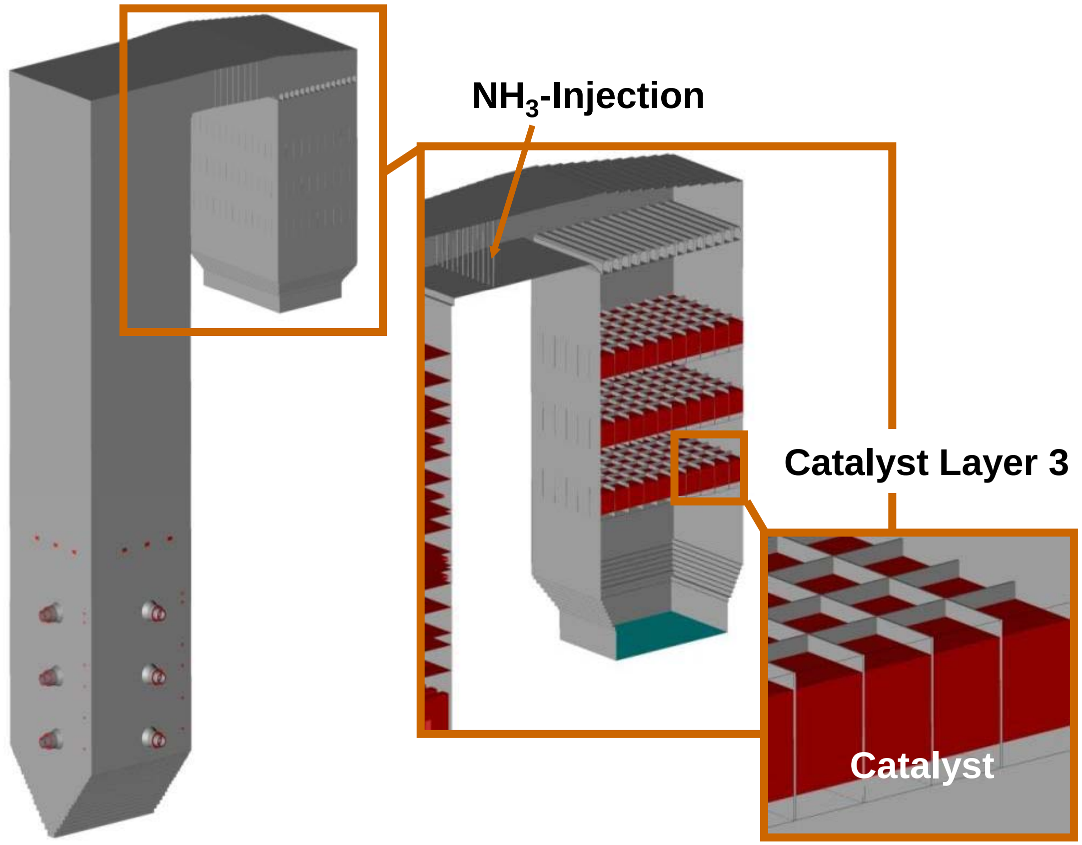
Implementation into Simulation Model

- Use Existing 3D-CFD Simulation Model for Boiler
- Developing and Applying New Model for SCR system
- Implementation of Catalyst Chemistry (NOx, Hg, SO_2/SO_3 conversion)
- Input Data from Full-scale and Lab Measurements for Model Validation



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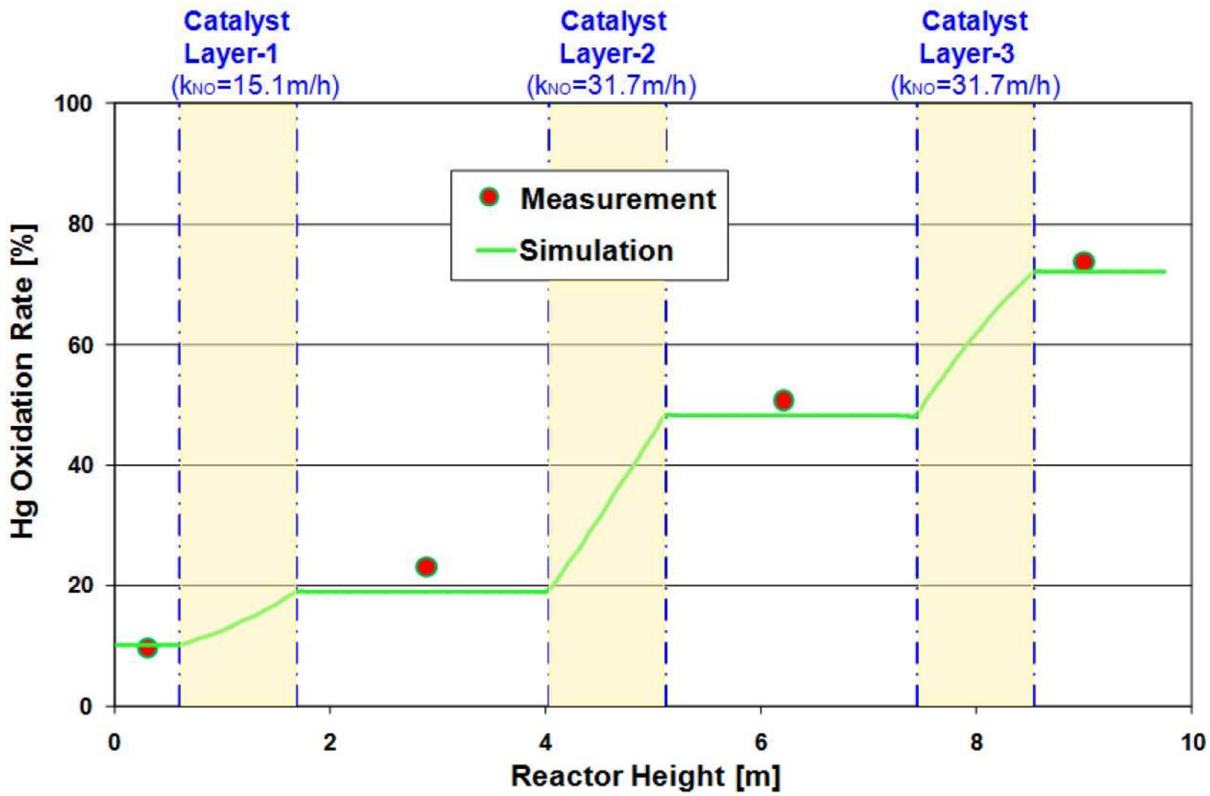
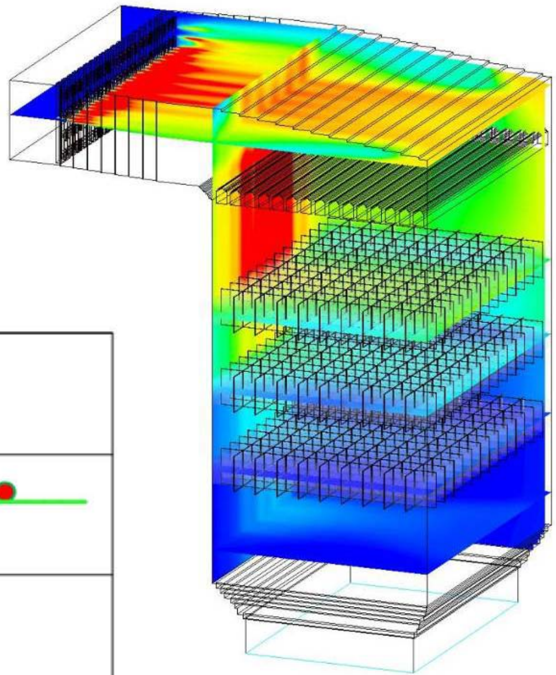
Assessment of Model Predictive Quality

Hg Oxidation Rate along Reactor





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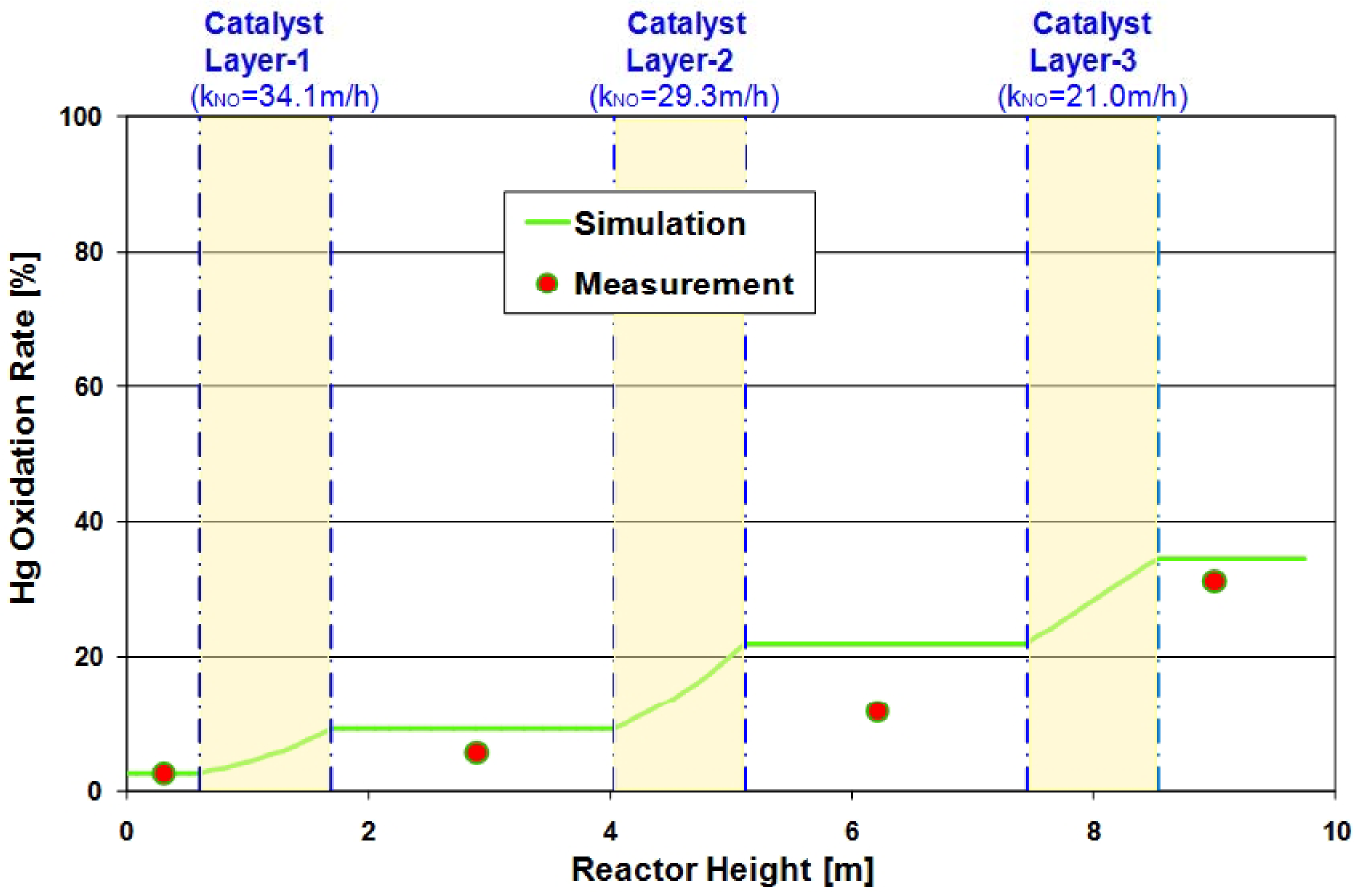
Assessment of Model Predictive Quality (2)

Hg Oxidation Rate along Reactor



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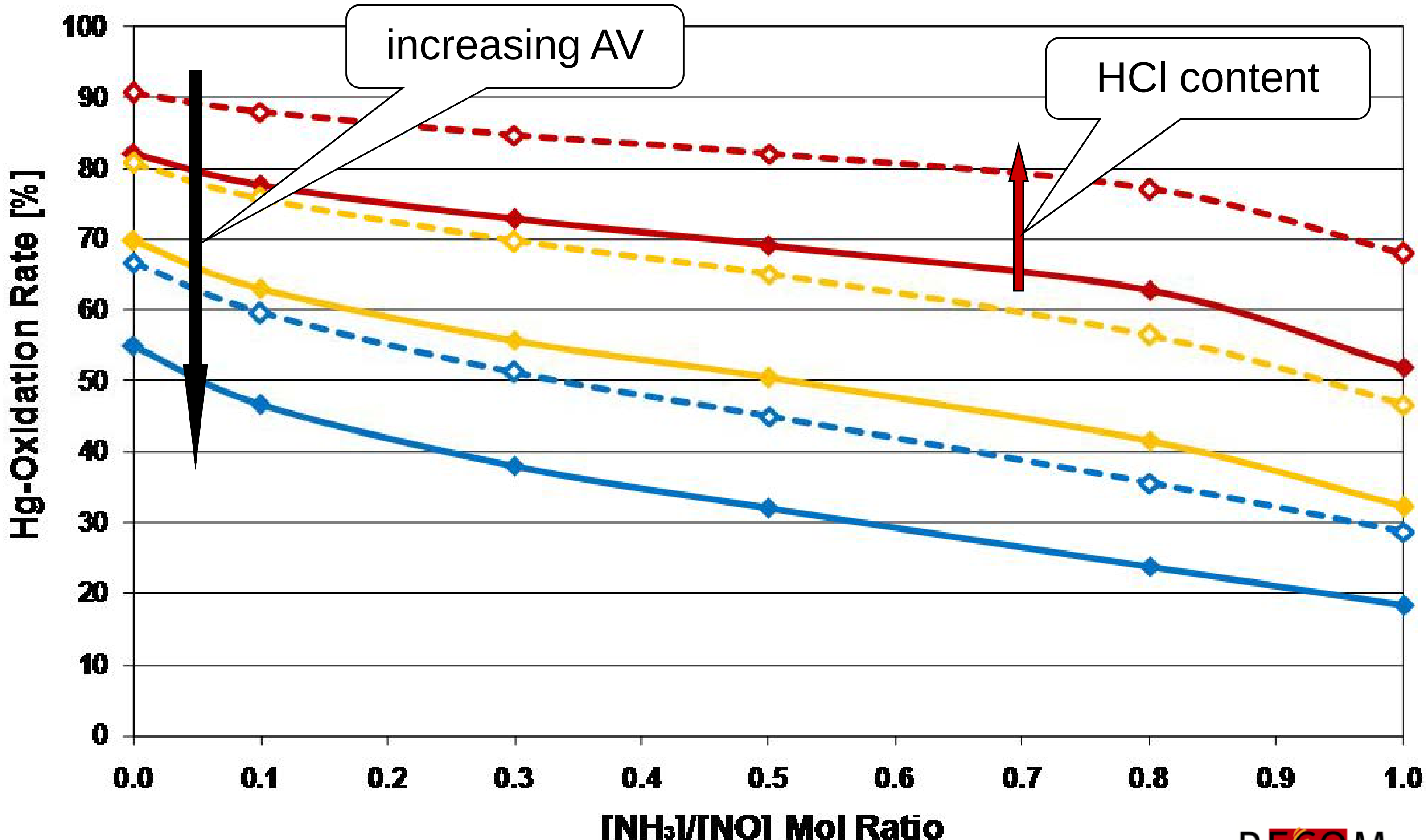
Mercury Oxidation Kinetic Model



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Representative U.S. Results for CERAM Catalyst

	Plant 1	Plant 2	Plant 3
NOx Removal	>91%	>90%	>92%
Coal Sulfur	>3%	>3.5%	>3.5%
Coal Chlorine	0.13%	0.15%	>0.1%
Operating Temperature	700 F	720 F	770 F
SO_2 to SO_3 Conversion Rate Across Reactor	<0.5%	<0.5%	<0.5%
Catalyst Layer Design	3+1	3+1	2+2
Catalyst Age	4,000 hr (3)	4,000 hr (1) 21,000 hr (3)	21,000 hr (2)
Mercury Removal	>95%	>80%	>85%

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Summary

- CERAM Participating in Comprehensive Long Term Mercury Oxidation Characterization and Optimization Test Program
  - DENOPT Program Complete
  - DEVCAT Program Ongoing Through 2013
- Mercury Oxidation Reactions are Complex and Vary as a Function of…
  - Flue Gas Composition (HCl, Other Halogens, SO_2, etc.)
  - Reactor Operating Conditions (NH_3/NOx, Area or Space Velocity, Temperature, etc.)
  - Catalyst Composition
  - Surplus Reactor Potential Present
  - Exposure to Flue Gas (Catalyst Aging)
  - Mercury Oxidation Possible with Low SO_2/SO_3 Oxidation Catalyst
- Simulation Model Developed to Better Predict Performance
- Low Temperature Mercury Oxidation Process is Developmental but Promising

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