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Mercury Seminar

October 30-31, 2012

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SCR and Hg Oxidation

Johnson Matthey Catalysts

WPCA Hg Co-benefits Seminar
Birmingham, AL
October 30-31, 2012

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ENVIRONMENTAL CATALYSTS AND TECHNOLOGIES

Agenda

- SCR Catalyst co-benefit
- Hg Oxidation Mechanism
- Effect of different constituents on Hg Oxidation
- Catalyst Management for Mercury Oxidation
- Mercury Oxidation Testing

Mercury Removal Requirement due to MATS rule

- Existing
  - 1.2 lb/TBTU (0.013 lb/GWh) for Bituminous Coal
  - 11 lb/TBTU (0.12 lb/GWh) for Subbituminous Coal Units
- New
  - 0.0002 lb/GWh for Bituminous Coal
  - 0.04 lb/GWh for Subbituminous Coal

- These limits to be met using a comprehensive AQCS Hg strategy

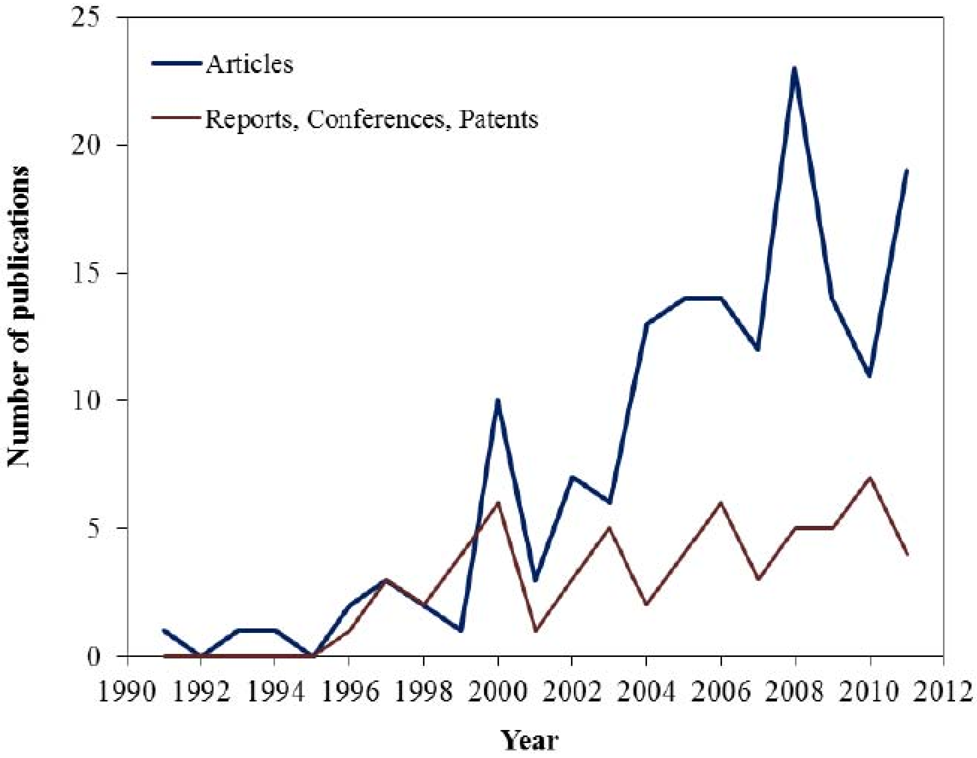
SCR and Mercury Oxidation

- Mercury emissions can exist in a variety of forms
  - Total – Hg^T includes Hg^0, Hg^{2+}, Hg^P
  - Hg^P – Particulate bound mercury
  - H^0 – elemental mercury
  - Hg^{2+} – oxidized mercury
- SCR catalyst has the ability to oxidize elemental mercury
  - Reaction is complex, and dependent on many parameters
- Oxidized mercury
  - Water soluble - able to be captured in wet-FGD
  - Easier to capture by activated carbon than elemental mercury
- Creating oxidized mercury does not guarantee capture

SCR and Mercury Oxidation

- SCR catalyst and Mercury Oxidation research increasing
  - Increase likely to continue due to MATS final rule and potential co-benefit of SCR
  - Can SCR-FGD configuration be relied on, or do alternate capture schemes need to be installed?

Number of Publications about Hg Oxidation



Source: Dranga et al. (2012)

Sponsored Oxidation Testing (not a complete list)

- DOE NETL Cooperative Agreement DE-FC26-02NT41589
  - Evaluation of Mercury Emissions from Coal-Fired Facilities with SCR and FGD systems (2006)
- EPA Cooperative Agreement R-829353-01
  - Effect of Selective Catalyst Reduction on Mercury (2004)
- US DOE NETL - Evaluation of the Effect of SCR NOx Control Technology on Mercury Speciation (2003)
- EPRI Report No. 1005400
  - Power Plant Evaluation of the Effect of Selective Catalytic Reduction in Mercury (2002)
- DOE Cooperative Agreement No: DE- FC26-03NT41728
  - Oxidation of Mercury Across SCR Catalyst in Coal Plants Burning Low Rank Coal (2004)
- **These and other studies demonstrate the SCR co-benefit; next step is refining plant operations to ensure consistent and predictable stack Hg emissions**

Mercury Capture

- Activated Carbon Injection (ACI)
  - Adsorbs both Hg^0 and Hg^{2+}, preferential towards Hg^{2+}
  - ACI then can be captured in particulate control device
- Novel Sorbent and Non-Carbon additive injection
  - Capture both Hg^0 and Hg^{2+}
  - Can be captured in particulate control device
- Wet-FGD
  - Captures mostly Hg^{2+}
  - Some issues in capture have been found, seem related to ORP
- Unburned carbon show some ability to capture mercury
- Oxidized mercury has potential to reduce back to elemental mercury downstream of SCR

Reactions of Hg

Desired Reactions – Hg oxidation

- $Hg + 2\ HCl + \frac{1}{2}\ O_2 \rightarrow HgCl_2 + H_2O$
- $Hg + SO_3 + \frac{1}{2}\ O_2 \rightarrow HgSO_4$
- $2\ HCl + \frac{1}{2}\ O_2 \rightarrow Cl_2 + H_2O$
- $Hg + Cl_2 \rightarrow HgCl_2$

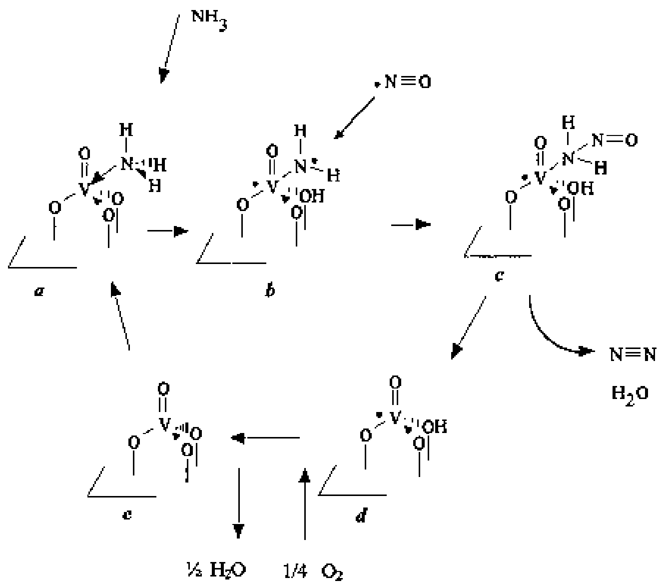
Other Reactions

- $Cl_2 + SO_2 + H_2O \rightarrow 2\ HCl + SO_3$
- $3\ HgCl_2 + 2\ NH_3 \rightarrow 3\ Hg + 6\ HCl + N_2$, reduction of Hg by NH_3
- $HgCl_2 + SO_2 + H_2O \rightarrow Hg + 2\ HCl + SO_3$, reduction of Hg by SO_2

Potential Mechanism

- There is an industry accepted mechanism of DeNOx – Eley Rideal

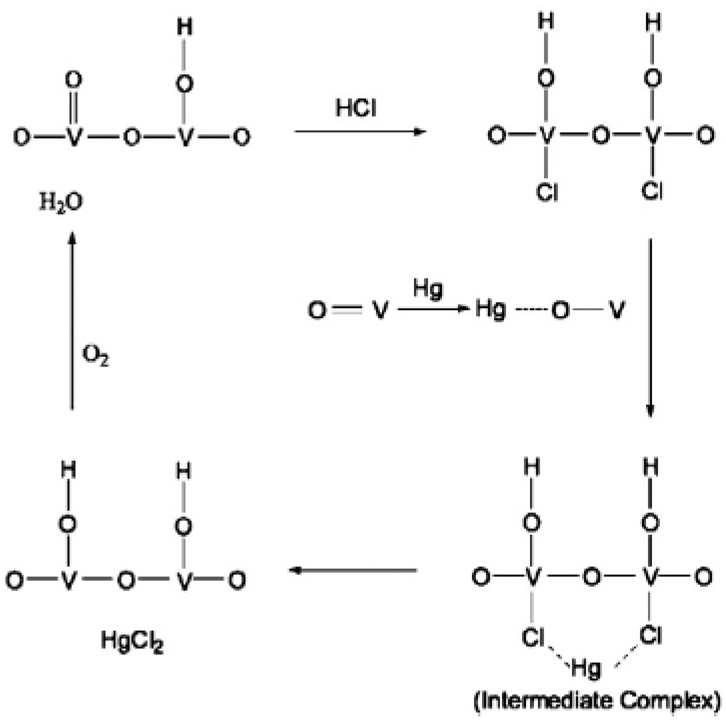
Source: Lietti et Al. (1998)



- Speculation on Mercury oxidation mechanism over SCR still exists, but:
  - Hg^0 seems to adsorb, then react
  - HCl reacts from either adsorbed state or gaseous state

Potential Hg Mechanism

Langmuir Hinshelwood:

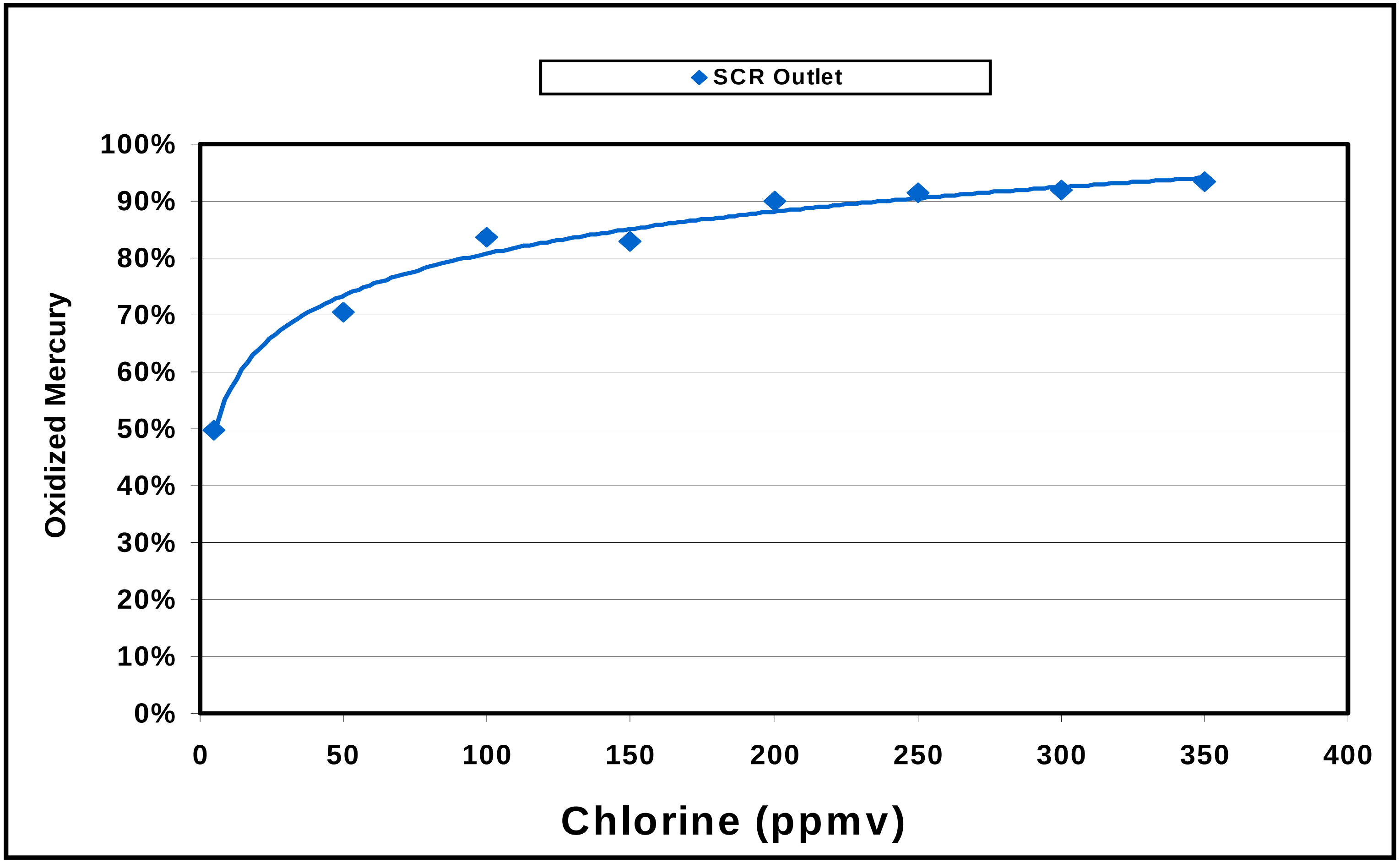


Source: He et al. (2009)

Eley Rideal, HCl does not adsorb:

- Hg adsorbs on vanadium oxide active site, creates a vanadium-mercury-oxide site
- HCl in the gas phase reacts with adsorbed Hg, creating oxidized mercury species
- Product diffuses off catalyst, active site is regenerated

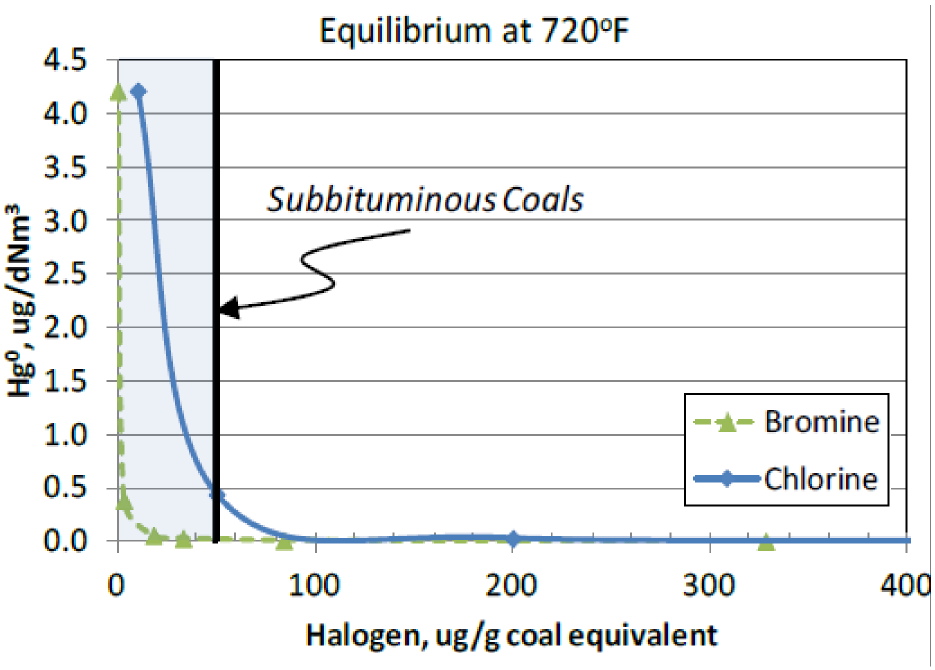
Hg Oxidation in Catalyst – General Effect of Cl



Reproduced by permission from *Effects of Chlorine and other Flue Gas Parameters on SCR Catalyst Mercury Oxidation and Capture,* EPRI, Palo Alto, CA 2009. 1020591

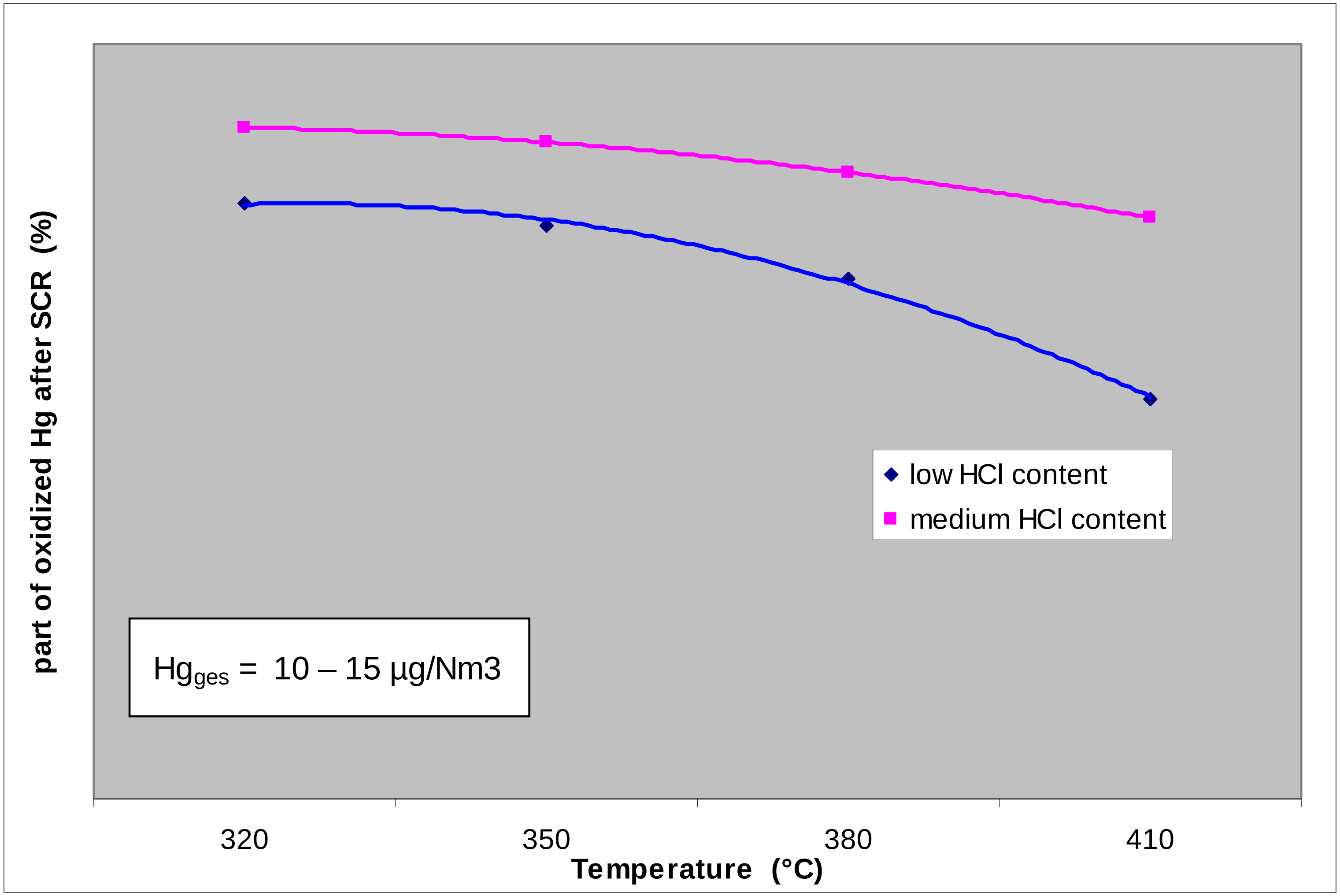
Key Characteristics of Mercury Oxidation

- Bromine is more effective than Chlorine at improving mercury oxidation
- Bromine has been shown to improve heterogeneous (over catalyst) and homogeneous (without catalyst) oxidation of mercury



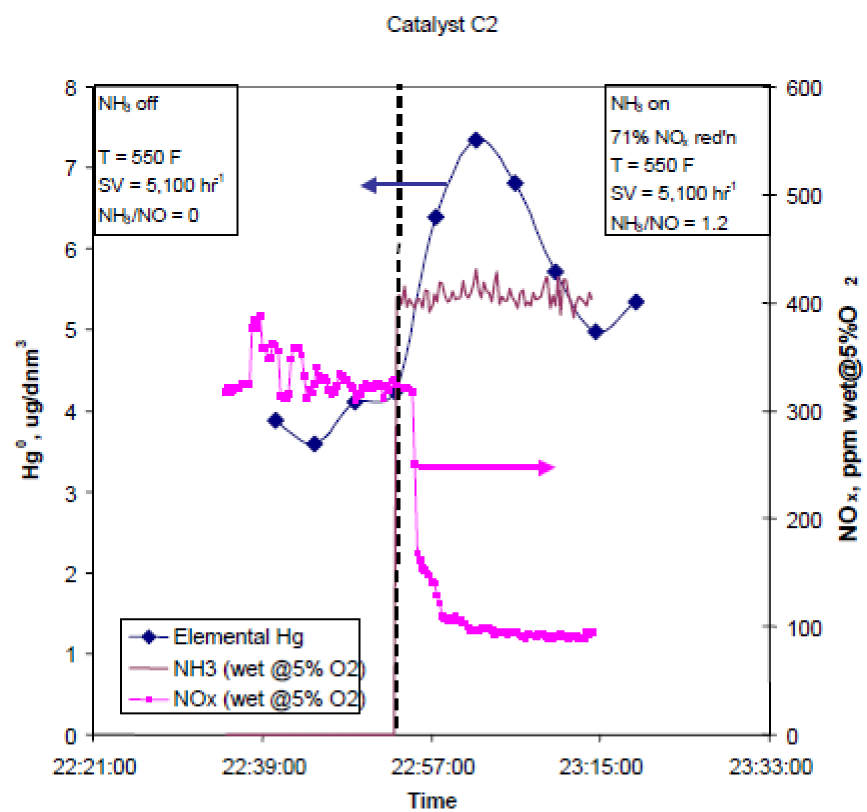
Source: Senior et al., Berry et al.

Hg Oxidation in Catalyst – Effects of Temperature and Cl



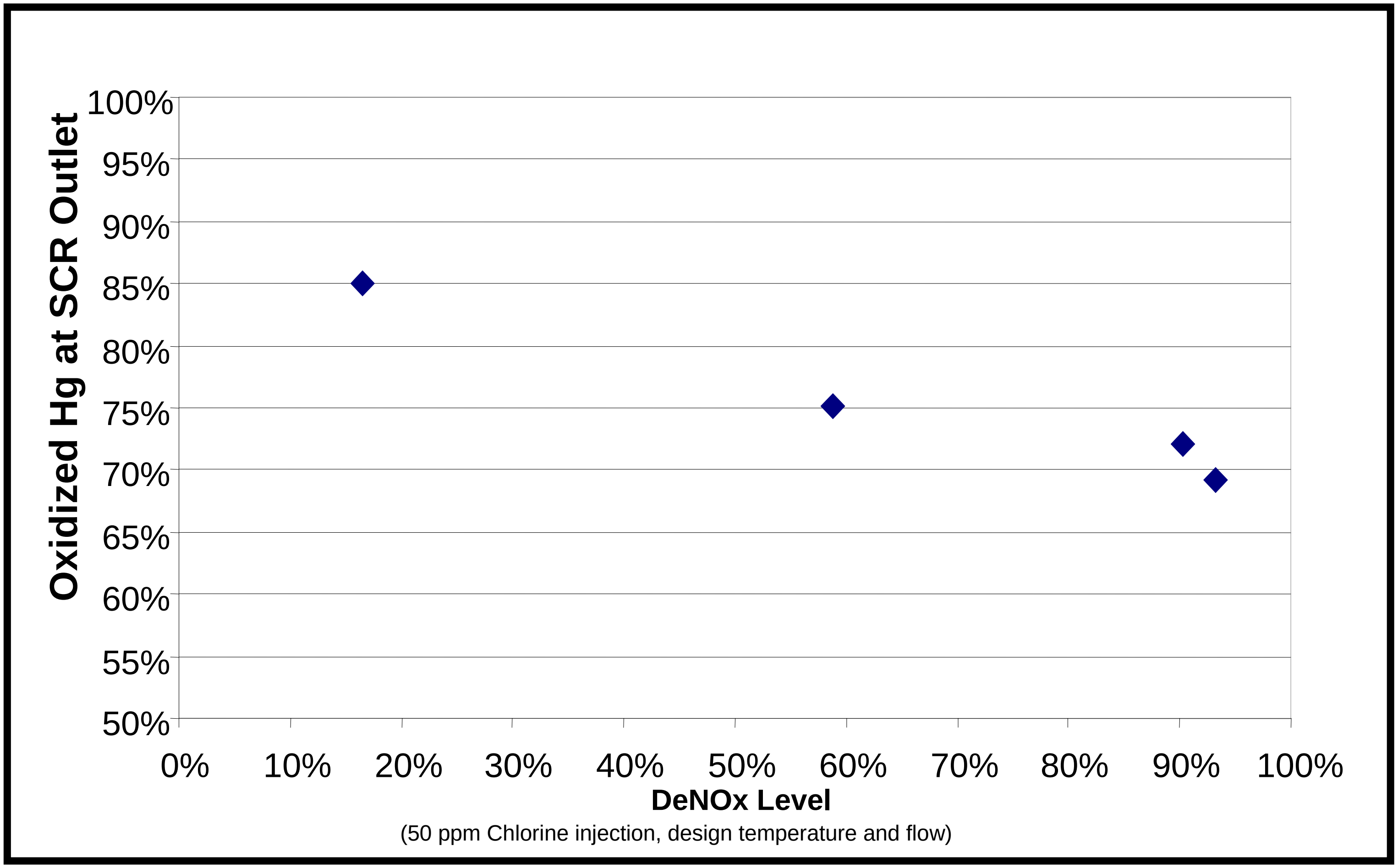
Key Characteristics of Mercury Oxidation

- Ammonia has ability to inhibit mercury adsorption on the catalyst
  - Decreases mercury oxidation when this occurs
  - Reaction not independent with respect to ammonia
  - Some data show that at very high halogen concentrations, mercury oxidation did not decrease to the extent predicted (Hinton 2012)



Source: Senior (2004)

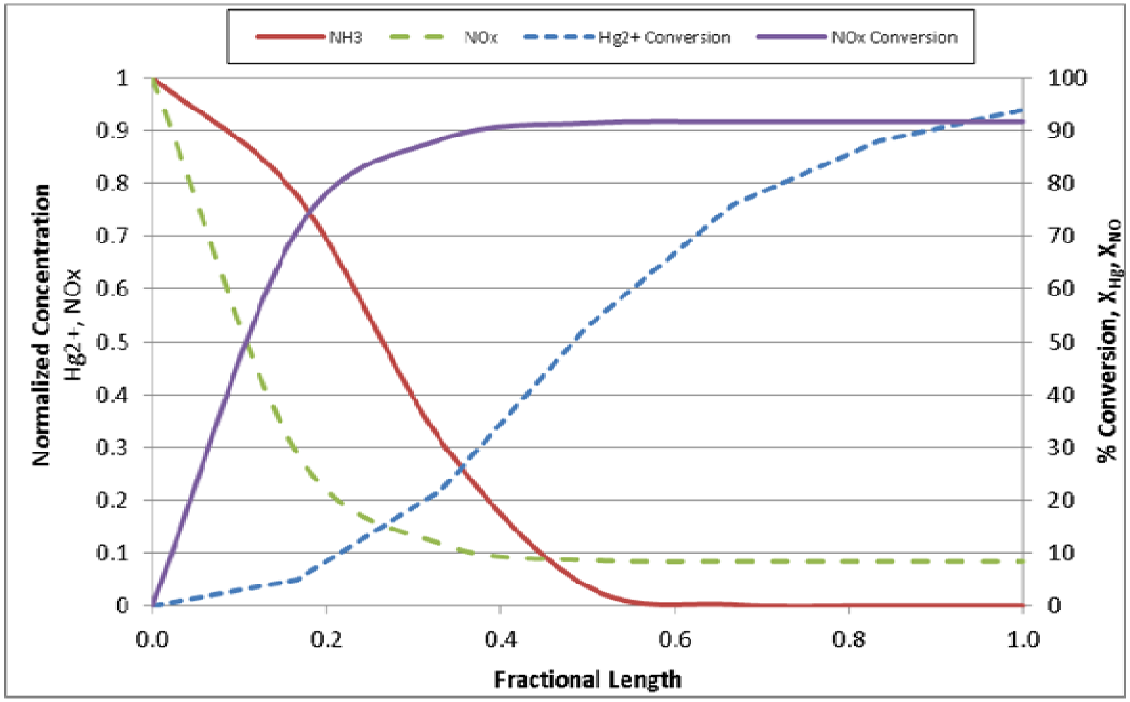
Hg Oxidation in Catalyst – General Effect of NH_3



Reproduced by permission from *Effects of Chlorine and other Flue Gas Parameters on SCR Catalyst Mercury Oxidation and Capture,* EPRI, Palo Alto, CA 2009. 1020591

Key Characteristics of Mercury Oxidation

- As ammonia is consumed within the SCR reactor, the oxidation of mercury increases



Key Characteristics of Mercury Oxidation

- Other parametric effects (all other parameters constant):
  - Increased Flowrate will decrease mercury oxidation (large impact)
  - Increased O_2 concentration will increase mercury oxidation (medium impact)
  - Increased SO_2 concentration will decrease mercury oxidation (small impact)
  - Increased SO_3 concentration will increase mercury oxidation
- Based on more limited data
  - Increased CO concentration will decrease mercury oxidation (medium impact)
  - Increased H_2O concentration (medium impact)

Catalyst Management and Mercury Oxidation

NOx reduction and Hg Oxidation compete

- NOx conversion can be maintained by increasing ammonia flow, allowing plant operators to maintain NOx outlet requirements
- Hg oxidation can be increased by decreasing NOx requirement

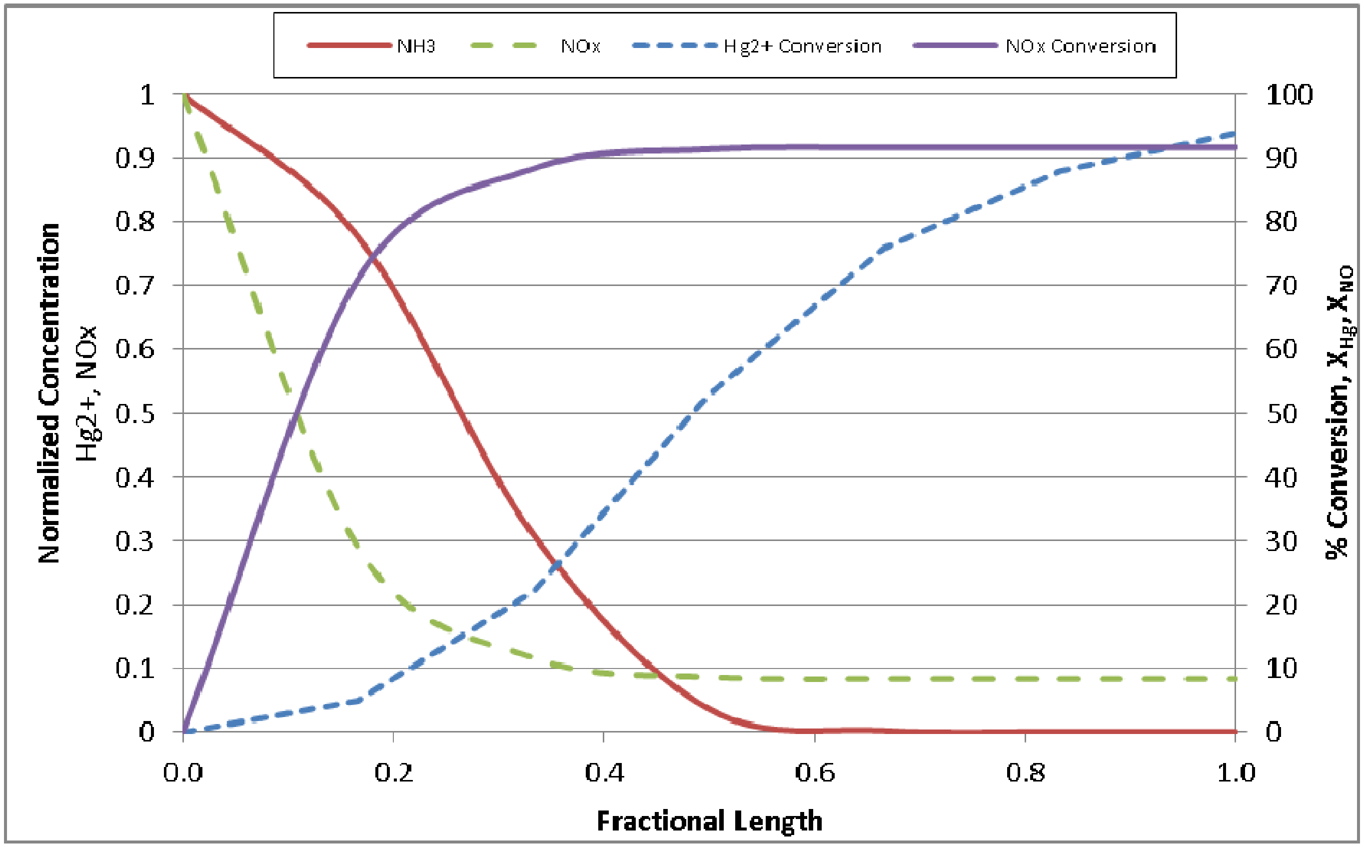
•Hg oxidation favored in lower catalyst layers as NH_3 is depleted

•Both can be increased by adding catalyst

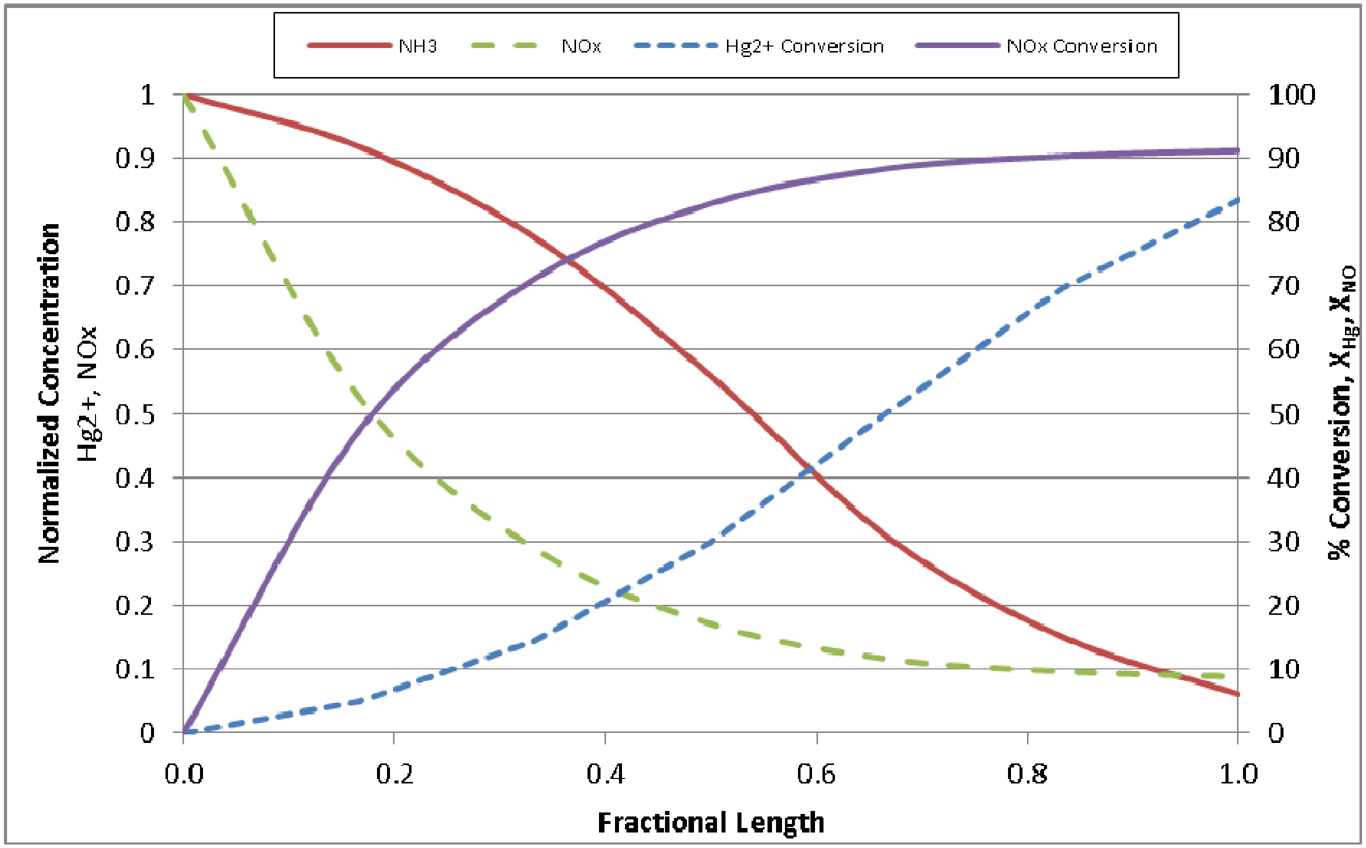
- Trade-offs – SO_2 conversion, pressure drop

•Many plants will start managing catalyst based on mercury oxidation potential

Effect of Catalyst Aging - New



Effect of Catalyst Aging - Exposed

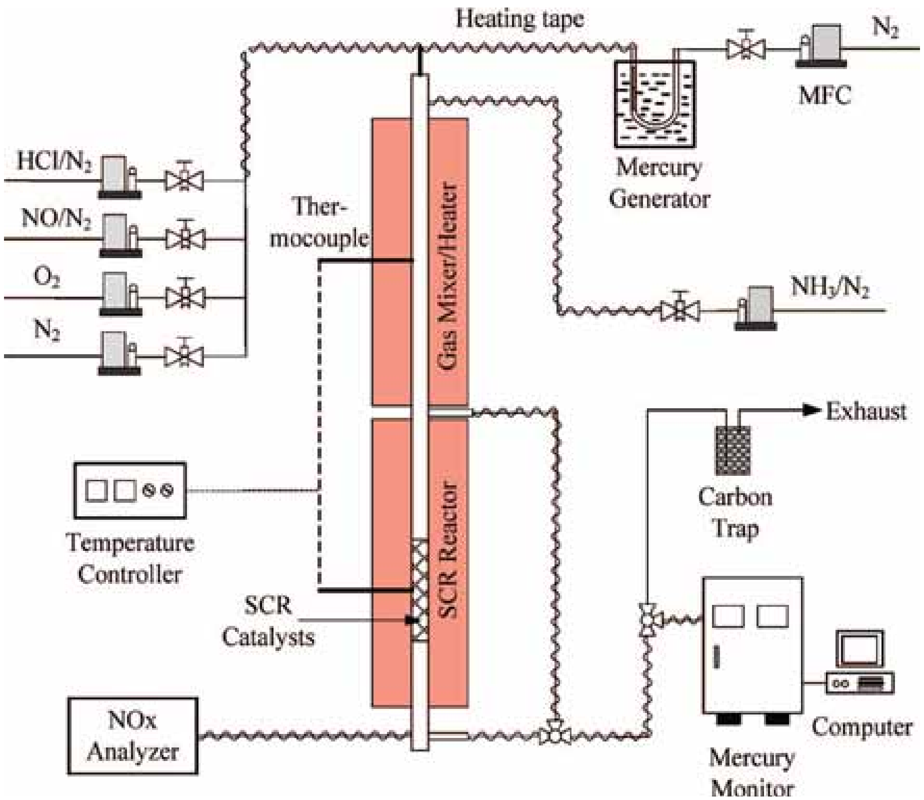


Lab Testing – Predicting Field Performance

- NOx reduction
  - Lab testing can be used to predict field performance
- SO_2 to SO_3 oxidation
  - Lab testing can not be used to predict field performance
    - Fly Ash adsorption of SO_3 in field
    - NH_3 reaction with SO_3 to form ABS
- Hg Oxidation
  - No industry standard lab testing protocol
  - Applicability to field performance still being determined

Hg Oxidation Lab Testing

- Often volume to area scaling issues
- Potential use
  - Parametric studies
  - Catalyst screening
  - Catalyst surveillance
  - Guarantee testing
- Matching ammonia profile along catalyst length is very important with regards to correlating to field results



Representative Lab schematic

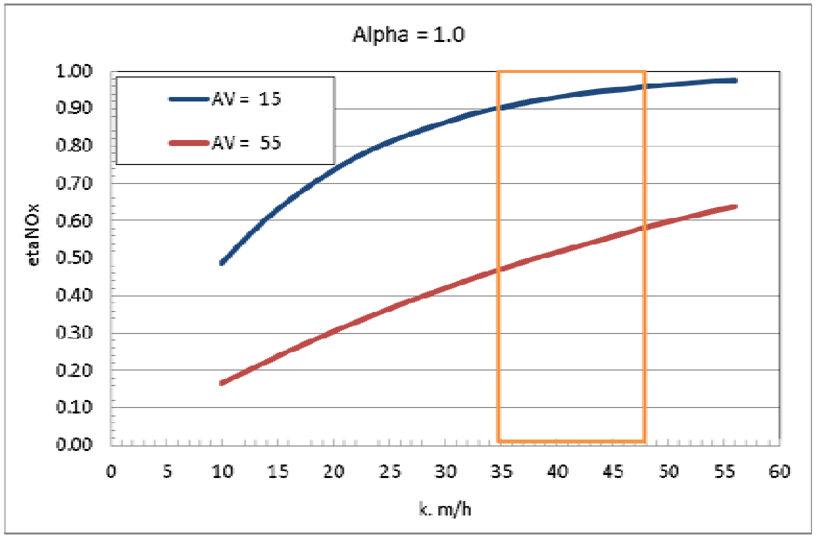
Source: He et al. (2009)

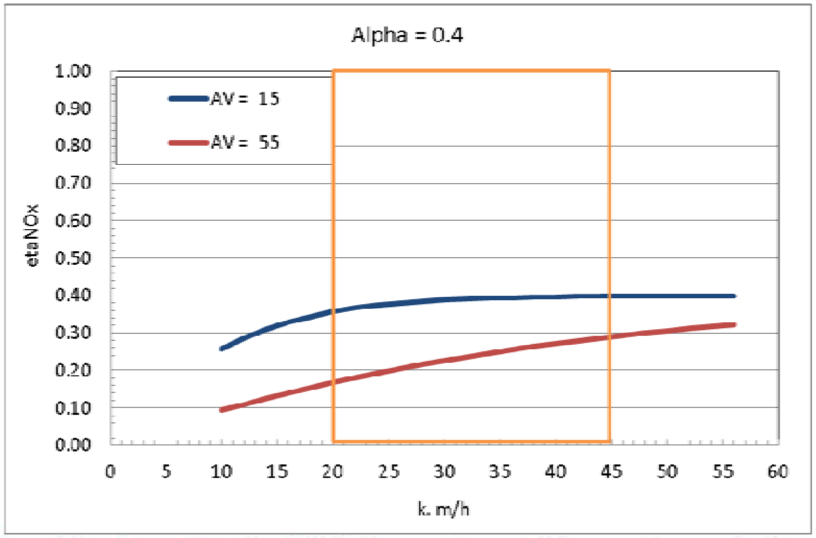
Relationship between AV, LV and Ammonia Profile

- Matching the ammonia profile in lab reactors can be difficult
  - Full layer area velocity (residence time) and linear velocity can not always be matched simultaneously
  - NOx activity dependent on linear velocity, not area velocity
  - Ammonia Profile dependent on area velocity
- Desired to have boundary conditions (inlet NH3 concentration and outlet NH3 concentration) as close to field as possible

Relationship between AV, LV and Ammonia Profile

- At lower AV, outlet NH3 is less dependent on NOx activity
- At lower NH3/NOx inlet, outlet concentration is approximately constant over expected activity range
- One potential method to approximating ammonia profile may be to match field AV and NH_3/NOx
  - Absolute ammonia and NOx concentration should be representative of what catalyst will be seeing





Field Testing

Variables exist in field testing that are not seen in lab testing

- Fuel variations
- Fly ash effects and plugging effects
- Ammonia injection transients
- Minute constituents (other halogens)

•Testing between layers is difficult or impossible (reloads)

•Scales of lab testing and field testing are different

•Large measurement errors

Takeaways

- Mercury Oxidation over the SCR based on many conditions
- Mercury Oxidation can be transient – not only over the SCR but through the entire system
  - Age effects
  - Boiler/Fuel effects
  - Flow, Temperature, Flue gas variations
- NOx reaction and Hg reaction compete
- Mercury oxidation over SCR for some plants will naturally be very good, other plants may have to enhance mercury oxidation or use alternate mercury capture methods
- Lab testing protocol and subsequent correlation to field performance are not currently available

Thank You!

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