

REINHOLD ENVIRONMENTAL Ltd.




2011 NO_x-Combustion Round Table & Expo Presentation

February 7-8, 2011, in Birmingham, AL / Hosted by Southern Company

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Mercury Oxidation Across SCR Catalysts in Coal-Fired Power Plants

2011 NOx Combustion Round Table
Brian Adair, Ph.D., CoaLogix / SCR-Tech, LLC
February 8, 2011

A solid green horizontal bar is located at the bottom of the slide, centered horizontally.

Mercury Emission Regulations for Electric Generating Units (EGUs)



Meeting the World Energy Challenge.

- ❑ States currently awaiting promulgation of new federal utility MACT
 - ❖ Maximum Achievable Control Technology

- ❑ Many states have 70% to 90% Hg emission reduction plans in place (or soon to be in place)

- ❑ New federal utility MACT
 - ❖ Initial proposal expected March 2011
 - ❖ Comments period
 - ❖ Final ruling expected November 2011

Mercury Regulations from States



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<u>State</u>	<u>Compliance date</u>	<u>Percent reduction</u>	<u>Emission limit</u>	<u>Continuous emission monitoring req't</u>	<u>Comments</u>
AZ	12/31/2013	90	0.0087 #/GWH	X	Alt stnds may be applied under certain circumstances
CO	7/1/2014	80	0.0174 #/GWH	X	Alt stnds may be applied under certain circumstances; (2) plants must meet 80% reduction beginning 1/1/2012
	1/1/2018	90	0.0087 #/GWH	X	
CT	7/1/2008	90	0.60 #/TBTU		Alt stnds may be applied under certain circumstances
DE	1/1/2009	80	1.0 #/TBTU	X	Applies to large plants
	1/1/2013	90	0.60 #/TBTU	X	Mass emission caps began in 2009; more stringent 2013
GA	<i>Legislatively prescribed schedule of specific APCs at specified times for each plant</i>				
IL	7/1/2009	90	0.0080 #/GWH	X	Alt stnds may be applied under certain circumstances
MD	1/1/2010	80	NA	X	
	1/1/2013	90	NA	X	
MA	1/1/2008	85	0.0075 #/GWH	X	
	10/1/2012	95	0.0025 #/GWH	X	
MN	12/31/2010	90	NA	X	Alt stnds may be applied under certain circumstances; first date for DFGD and second date for WFGD.
	12/31/2014	90	NA	X	
MT	1/1/2010	NA	0.90 #/TBTU	X	Alt stnds may be applied under certain circumstances Specific lignite standard = 1.5 #/GWH
NH	7/1/2013	80	NA	X	Alt stnds may be applied under certain circumstances
NM	1/1/2010	NA		X	
	1/1/2018	NA		X	
NJ	12/15/2007	90	3 mg/MWH		
NY	1/1/2010	NA	0.60 #/TBTU	X	(13) plants specific limits 2010-2015; all plants by 2015.
NC	12/31/2013	NA	NA	X	Requires technology for SO ₂ , NO _x and mercury
OR	7/1/2012	90	0.60 #/TBTU	X	Alt stnds may be applied under certain circumstances
UT	12/31/2012	90	0.65 #/TBTU	X	Alt stnds may be applied under certain circumstances
WI	1/1/2010	40	NA	X	Applies to (4) major Utility Cos.
	1/1/2015	90	0.0080 #/GWH	X	Applies to large coal-fired plants; flexibility for NO _x & SO ₂

Source: GAO Report 10-47 Dated October 2009 Appendix III

Mercury in Power Generation



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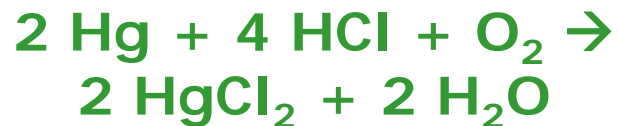
- ❑ Mercury in coal as sulfide compounds – generally pyrites
- ❑ Mercury in coal-fired flue gas: elemental (Hg^0), oxidized (Hg^{2+}), plus particulate-bound (Hg_p)
- ❑ Hg^{2+} species (e.g. HgBr_2 , HgCl_2) soluble and removed from flue gas in wet FGDs ; Hg_p removed in ESPs
- ❑ Hg^0 tough to remove
 - ❖ High vapor pressure and insolubility in FGD slurry liquid allow it to pass into the atmosphere at the stack
 - ❖ Elemental mercury converts to toxic methyl mercury
 - ❖ One strategy: Oxidize elemental mercury to Hg^{2+} in SCR
- ❑ A combination of unit ops (SCR, FGD, ESP) used in mercury mitigation

SCR Reaction Network

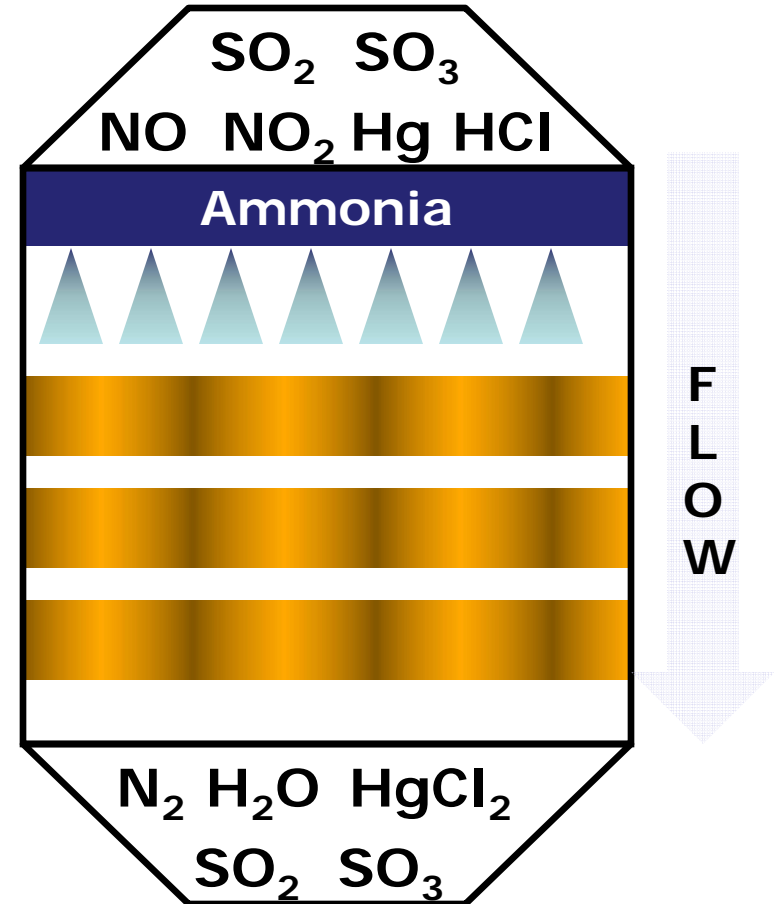
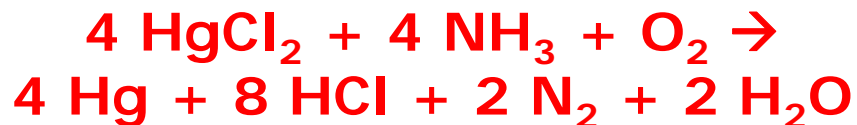
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Beneficial Reactions

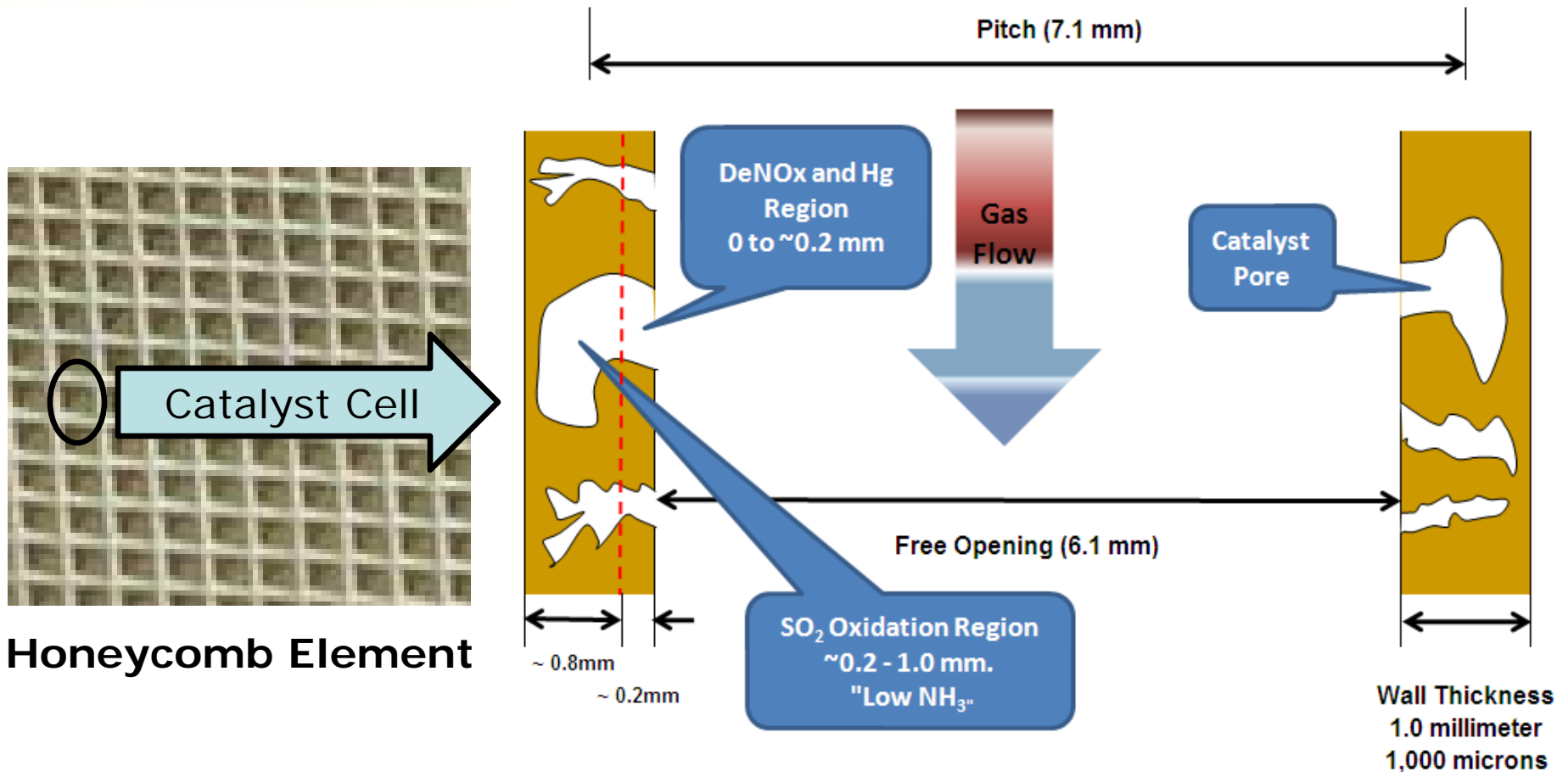


Detrimental Reactions



SCR Catalyst Overview

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- Visible surface $\sim 400 \text{ m}^2/\text{m}^3$
- Catalytic surface at $65 \text{ m}^2/\text{g}$
- 30 million m^2/m^3

Factors Affecting Mercury Oxidation

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□ Promoters

- ❖ SCR catalyst!
- ❖ Lower temperatures
- ❖ Halogens
- ❖ V_2O_5
- ❖ NOx

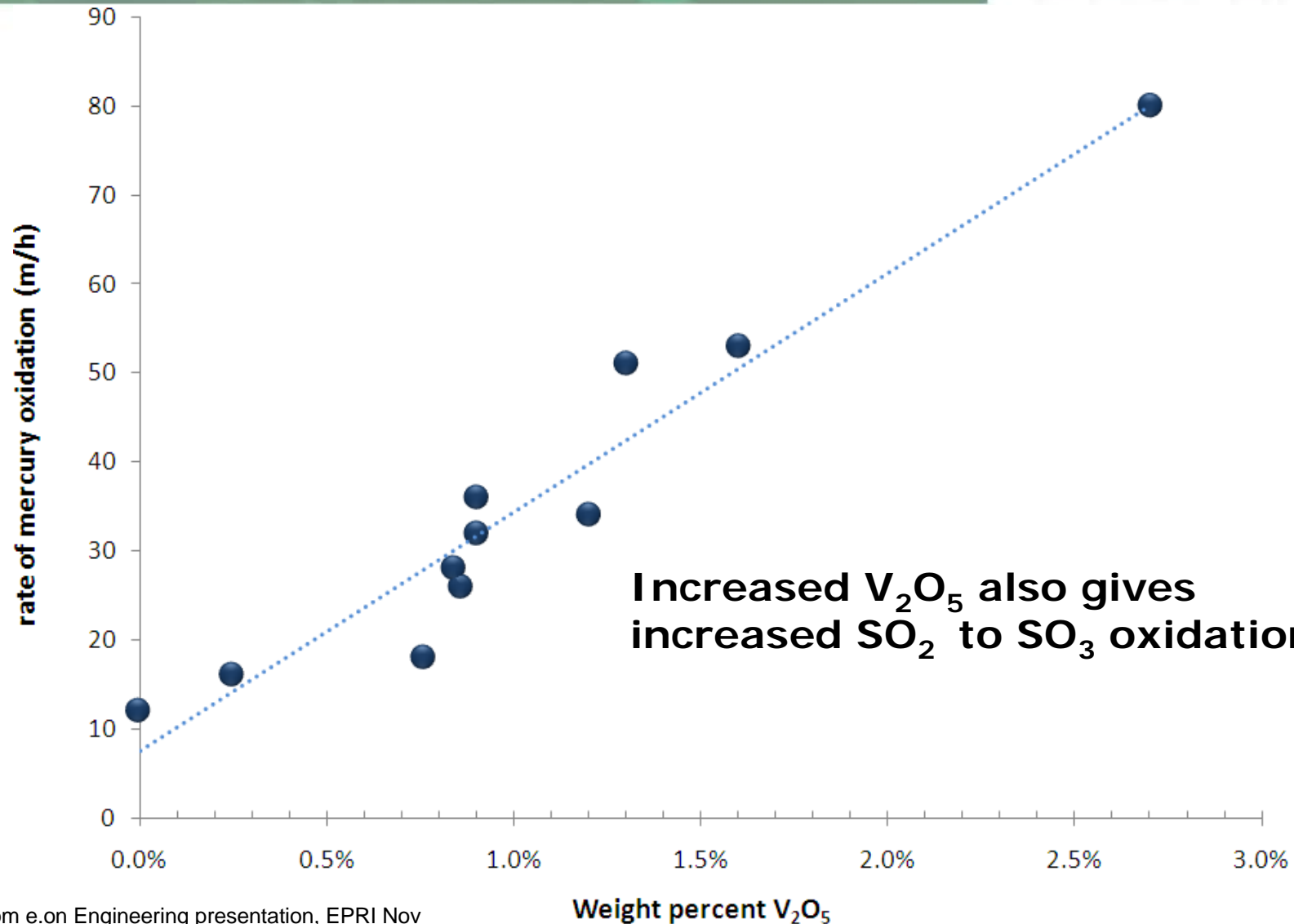
□ Inhibitors

- ❖ NH_3
- ❖ H_2O
- ❖ SO_2

Effect of V_2O_5 Concentration in SCR Catalyst



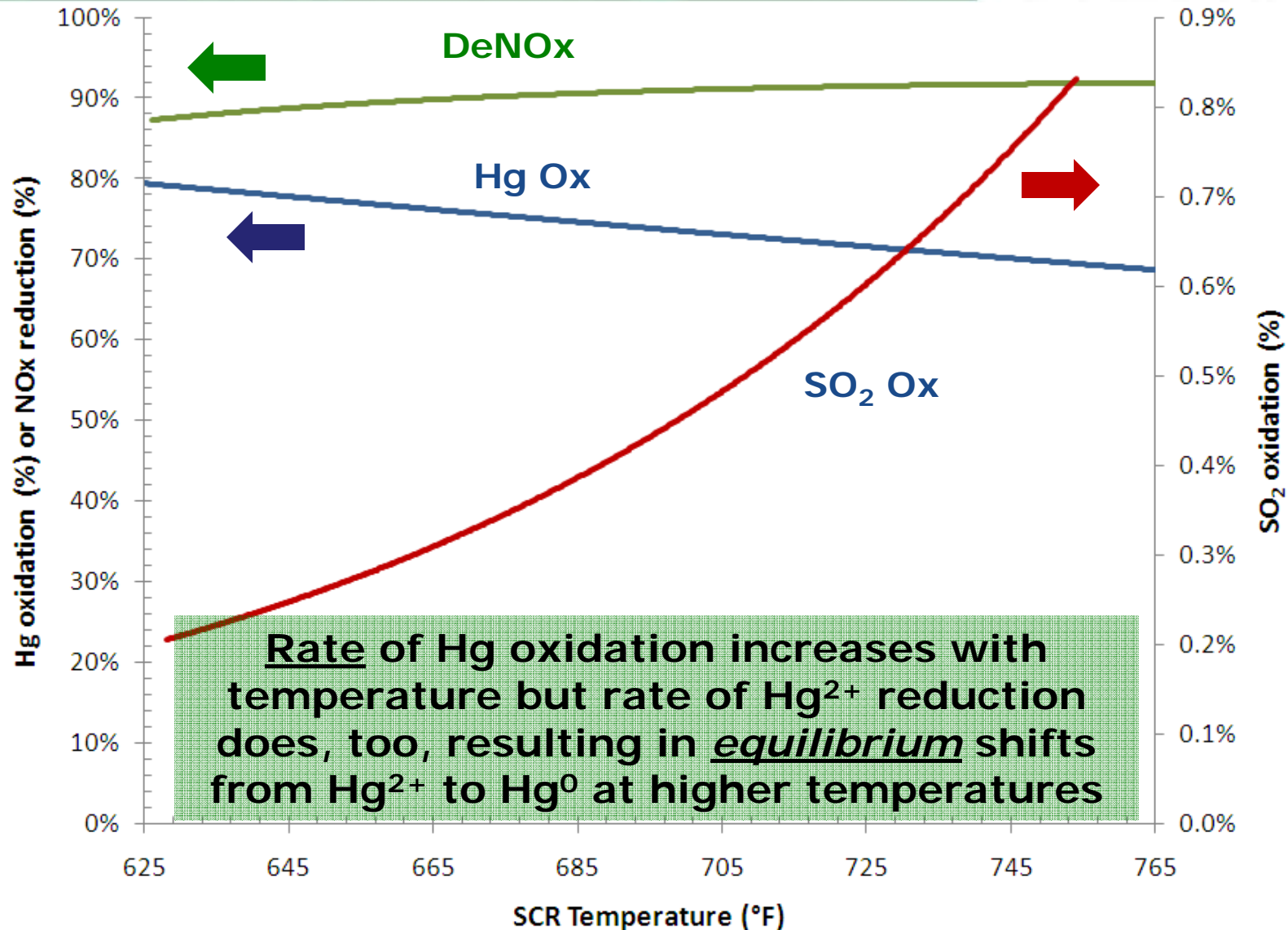
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Data from e.on Engineering presentation, EPRI Nov 2008 Workshop, Charlotte, NC

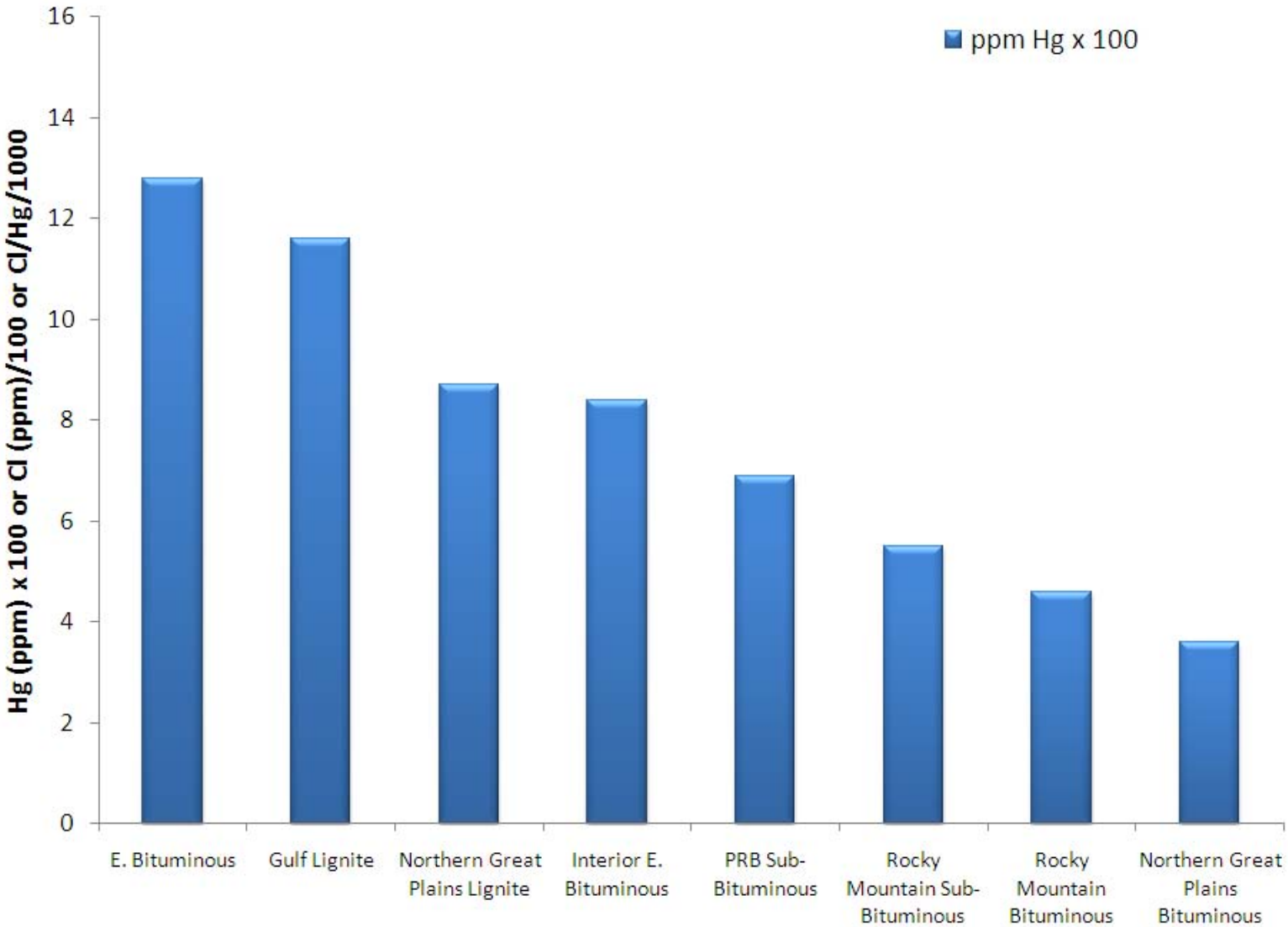
Effect of Temperature in SCR

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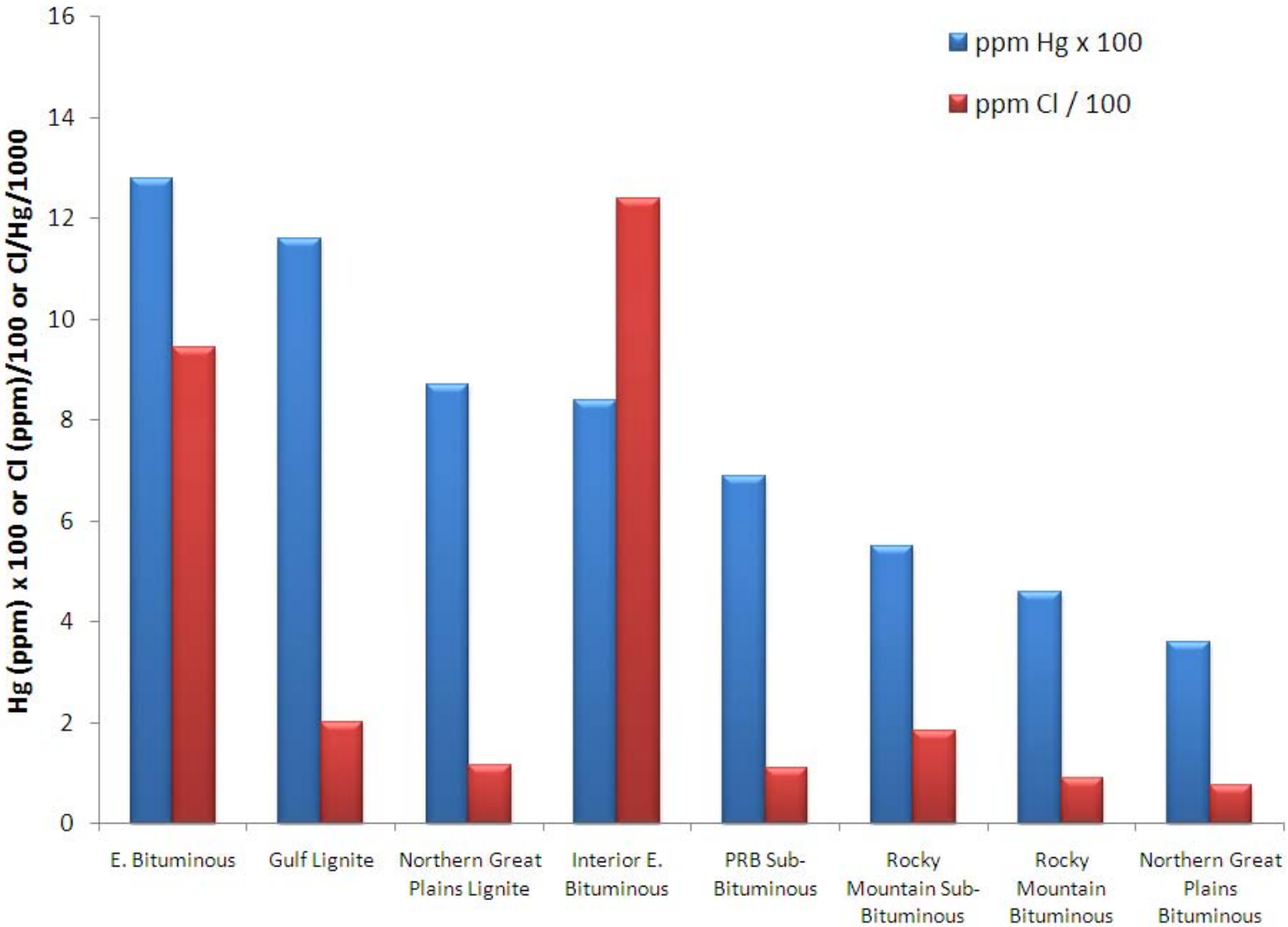
Coal Mercury Content

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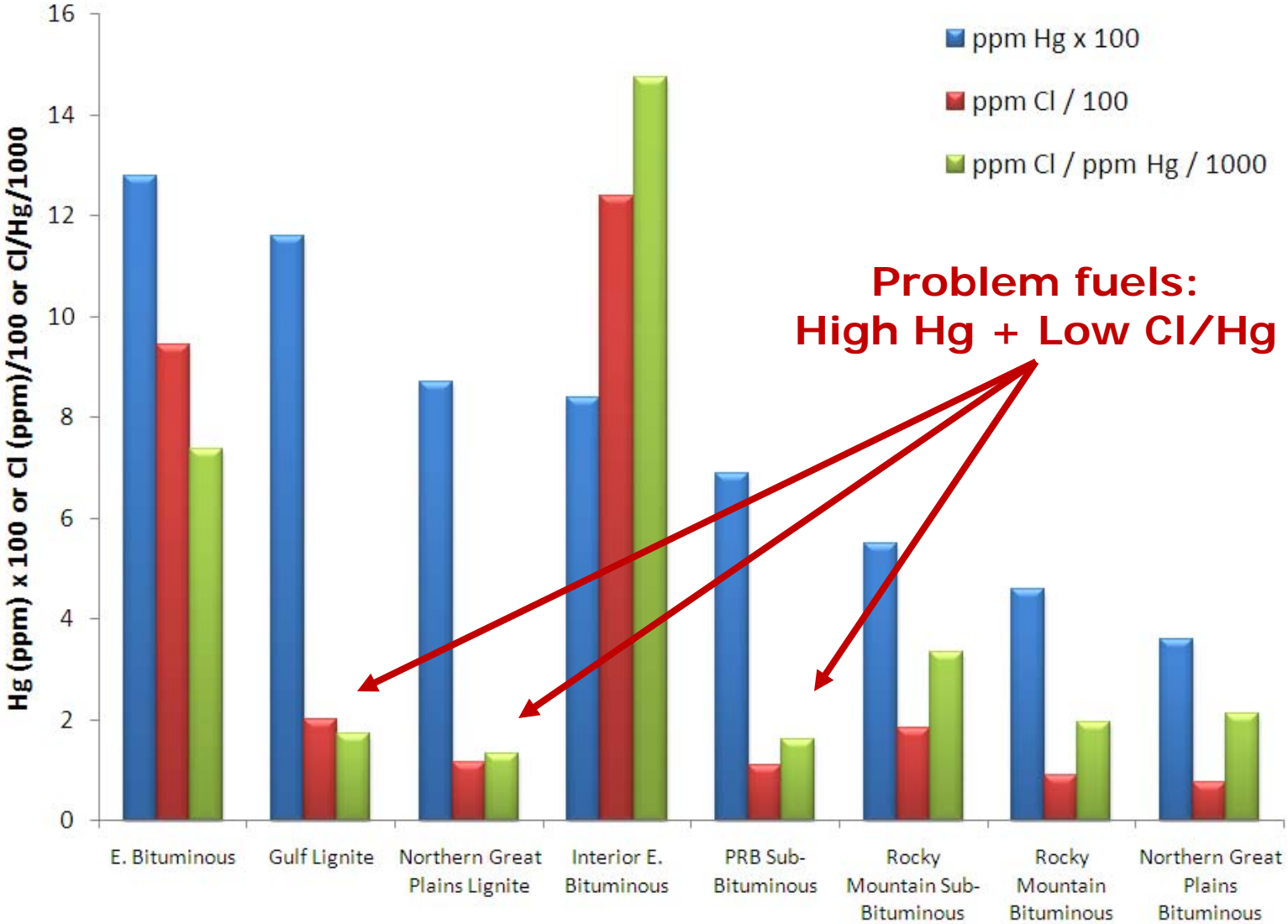
Coal Chlorine Content

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Chlorine:Mercury Ratio

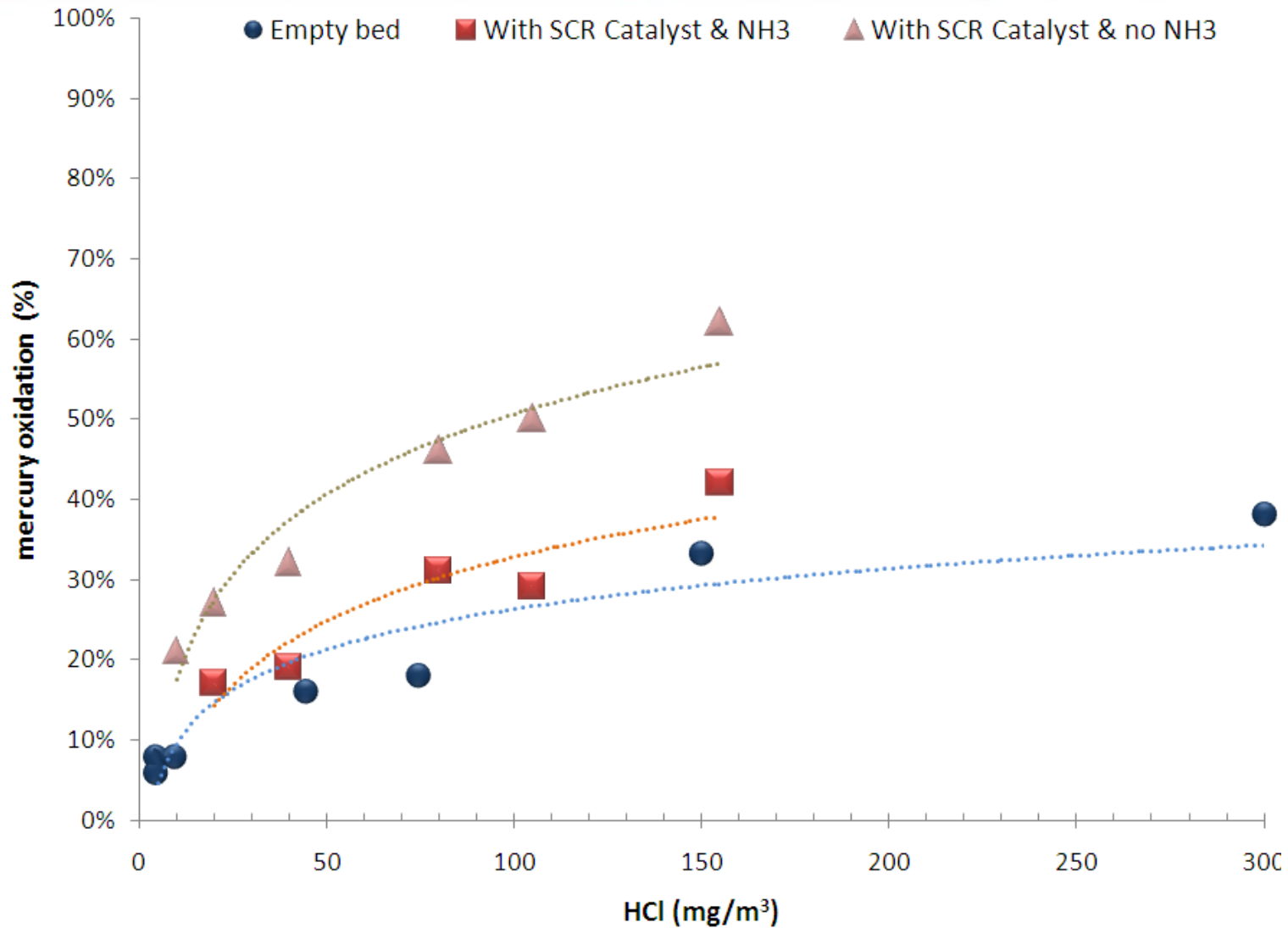
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**Problem fuels:
High Hg + Low Cl/Hg**

Effect of HCl & NH₃ in Flue Gas

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Data from Cao Environ Sci Technol 2007

Effect of Halogens

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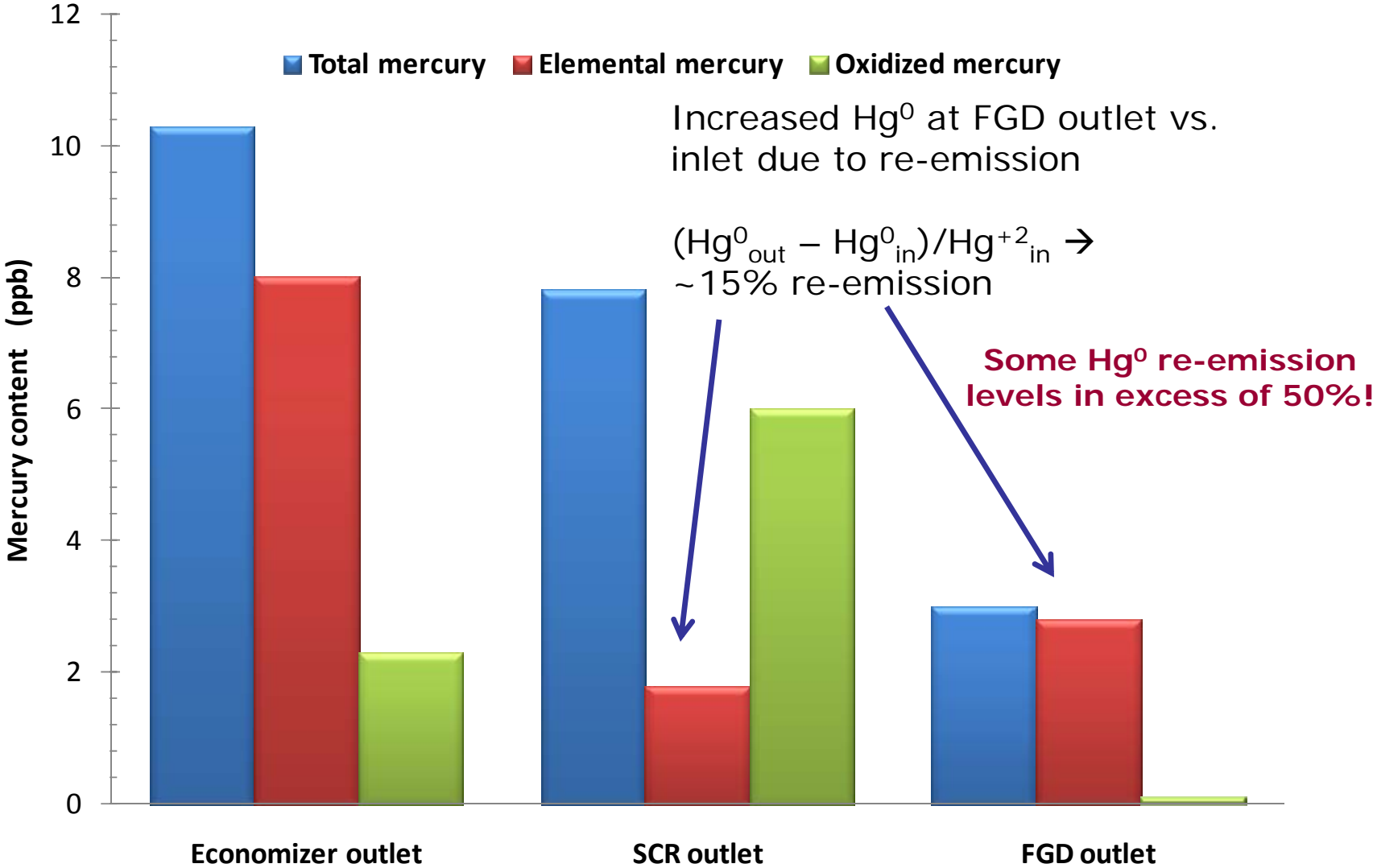
- ❑ HF, HCl, HBr, and HI all affect Hg oxidation
- ❑ Chlorine and fluorine species often 100-1000x the level of bromine and iodine species in coal
- ❑ However, bromine and iodine species play important roles in Hg⁰ oxidation
 - ❖ HBr > HI >> HCl ~ HF

Species	Flue gas (ppmv)	Hg ⁰ oxidation
HF	10	30%
HCl	10	25%
HCl	150	70%
HBr	6	70%
HI	10	70%

Data from Cao Environ Sci Technol 2007

Mercury Partitioning Around SCR

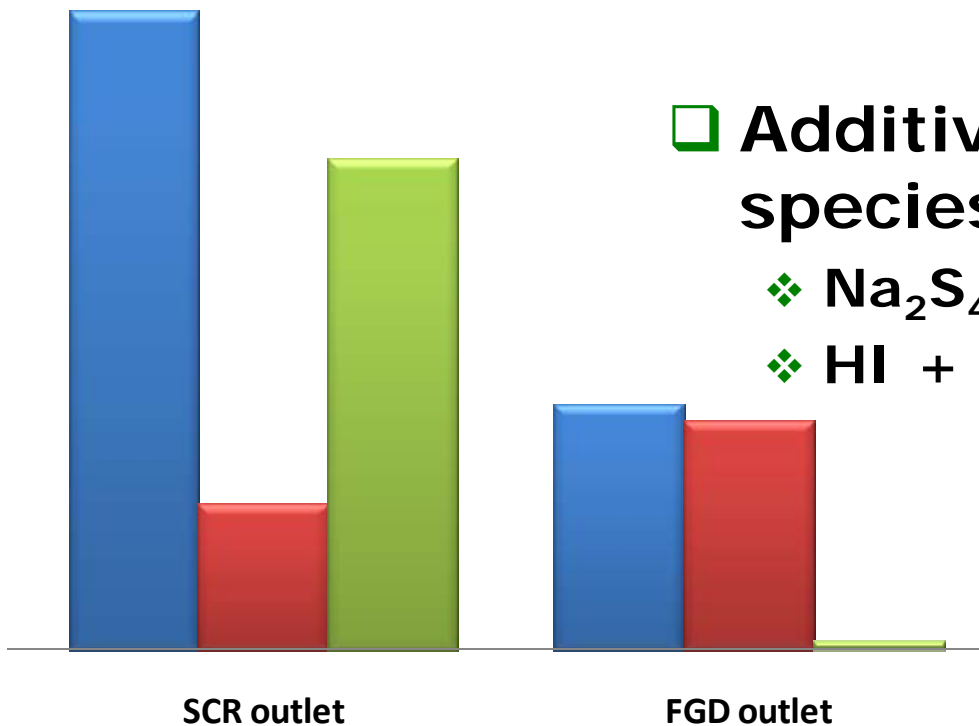
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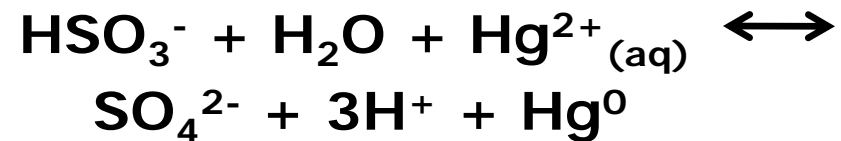
Mercury Re-Emission

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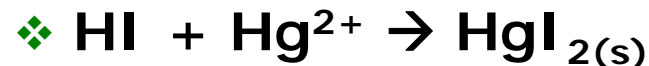
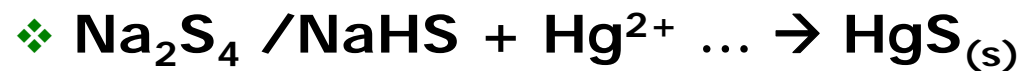
- Total mercury
- Elemental mercury
- Oxidized mercury



- Affect the $\text{Hg}^{2+}/\text{Hg}^0$ equilibrium in FGD slurry

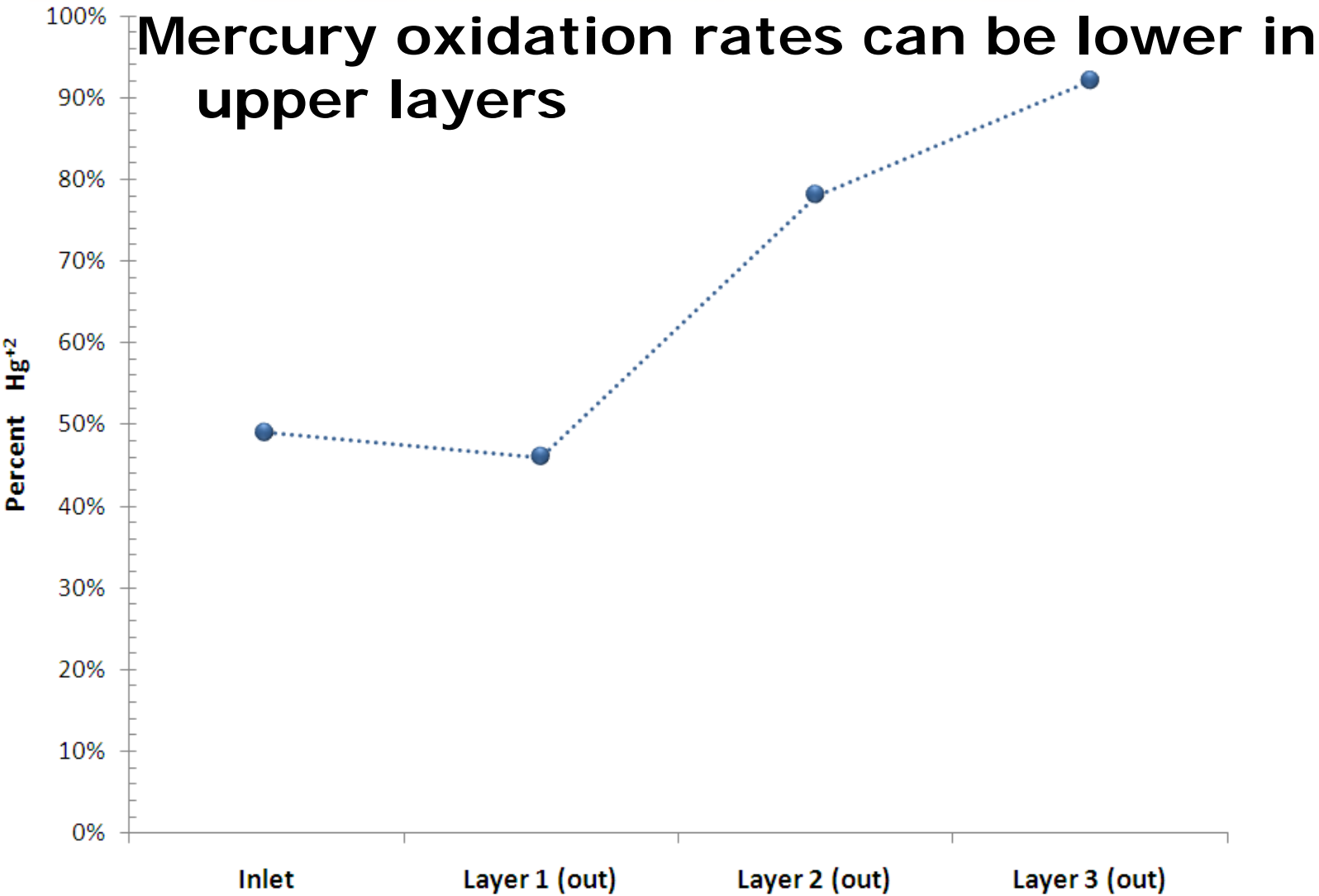


- Additives to form insoluble species



Mercury Oxidation Within SCR

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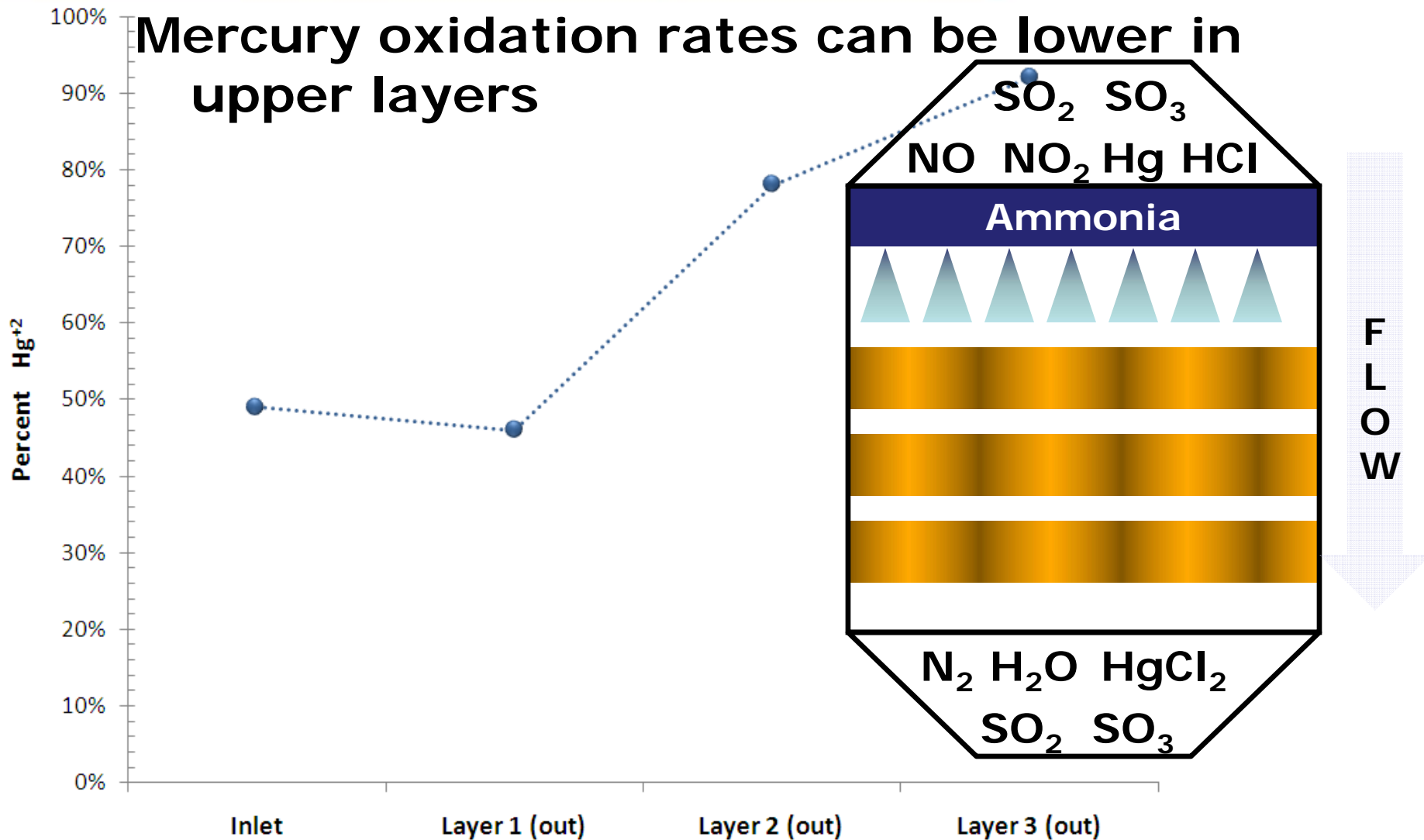


Data from e.on Engineering presentation, EPRI Nov 2008 Workshop, Charlotte, NC

Mercury Oxidation Within SCR

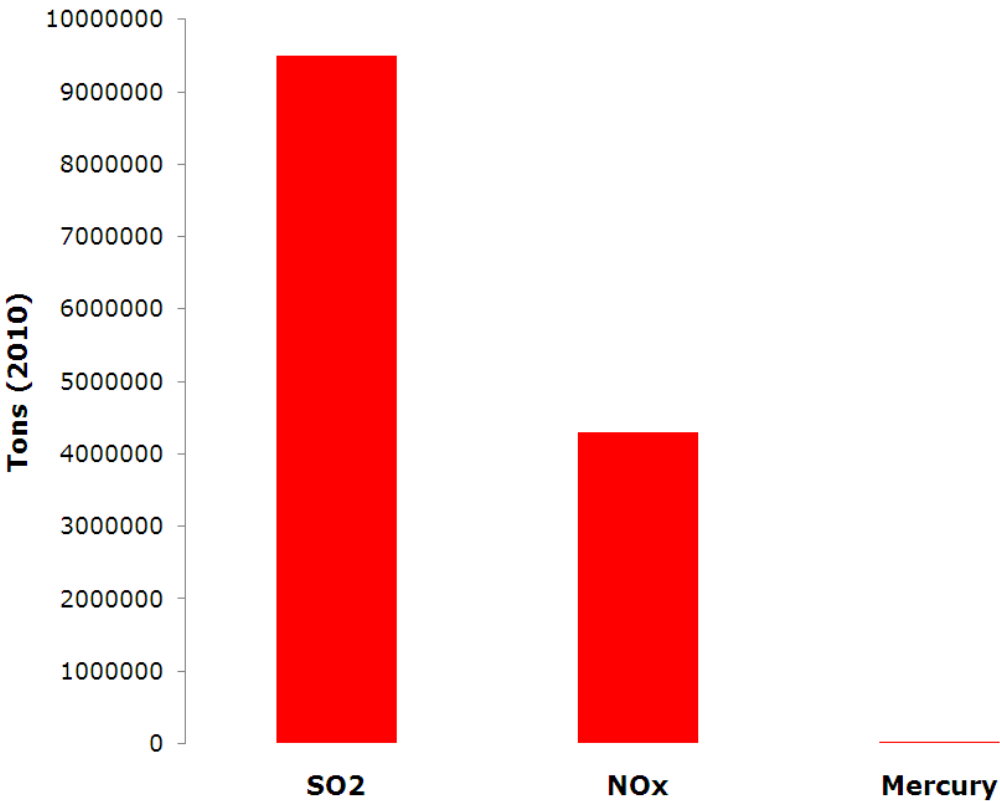


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Testing Challenges

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❑ Measure a few parts per billion (~ 10 ppb total Hg) vs. a few parts per million (1-10 ppm SO₃) AND distinguish between Hg⁰ and Hg²⁺

Data from U.S. Energy Information Administration, DOE, 2010 levels

Testing Challenges - Lab



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□ $\text{SO}_2 \rightarrow \text{SO}_3$ oxidation testing analogy:

- ❖ Some test with added SO_3 , some don't
- ❖ Some people test at $\text{NH}_3/\text{NO}_x = 0$, some at 0.9-1.0
- ❖ Conditioning critical ... > 3 days to test new catalysts for SO_3 adsorbing a few ppm SO_3
- ❖ Good correlations now between SO_2 oxidation and $[\text{H}_2\text{O}]$, $[\text{SO}_2]$, etc.

□ Inputs - significant cost in matching plant conditions for some of these inputs

- ❖ Elemental & Oxidized Mercury
- ❖ HCl , HBr , ...
- ❖ Fly-ash

Testing Challenges – Plant

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- ❑ E.g. tranverses across duct work

- ❑ Regulations based on stack but ...
 - ❖ Economizer, air heaters, SCR, FGD, all affect Hg so we'd really like to do measurements in all these places to understand how the system behaves

- ❑ Problems in sample extraction and delivery
 - ❖ Temperature control
 - Cold spots can bias low due to Hg plating
 - Hot spots can cause unintended oxidation
 - ❖ Particulate impact
 - Removal or oxidation across particulate filters
 - Filter contamination by other elements

Measurement Options

- ❑ **Continuous Emission Monitors (CEMs)**
 - ❖ Real-time direct measurement, but may have detection limitations
 - ❖ Pre-concentration/absorption based (gold amalgamation)

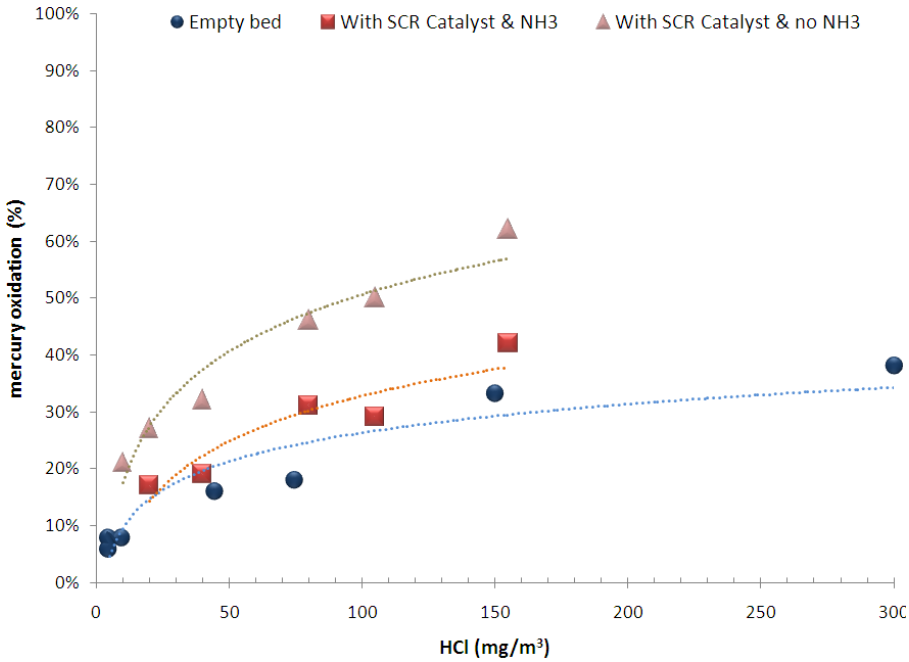
- ❑ **Species selective sorbent traps**

- ❑ **Wet chemical manual methods**
 - ❖ Ontario Hydro, Modified Ontario Hydro, ...

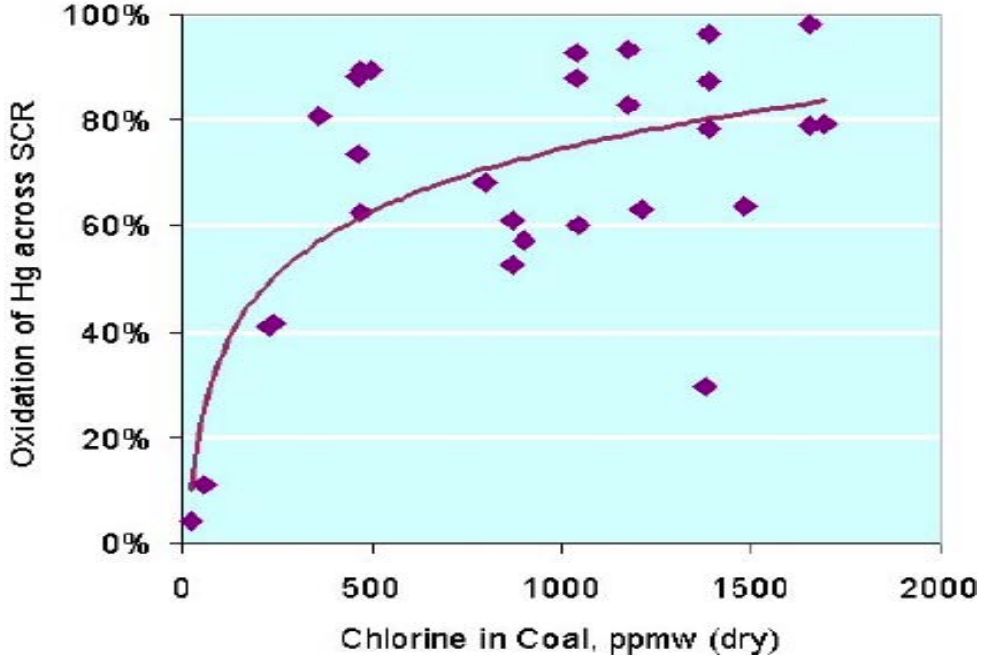
- ❑ **Bias between measurement methods can make oxidation comparisons difficult**

Testing Challenges

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Data from Cao Environ Sci Technol 2007



Data from C. Senior, Reaction Engineering International, Mercury Control Technology R&D Program Review, Pittsburgh 2005

SCR Catalyst Modifications

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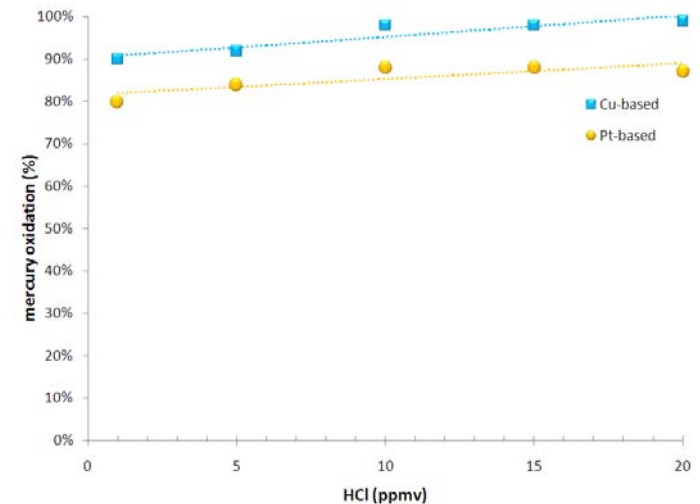
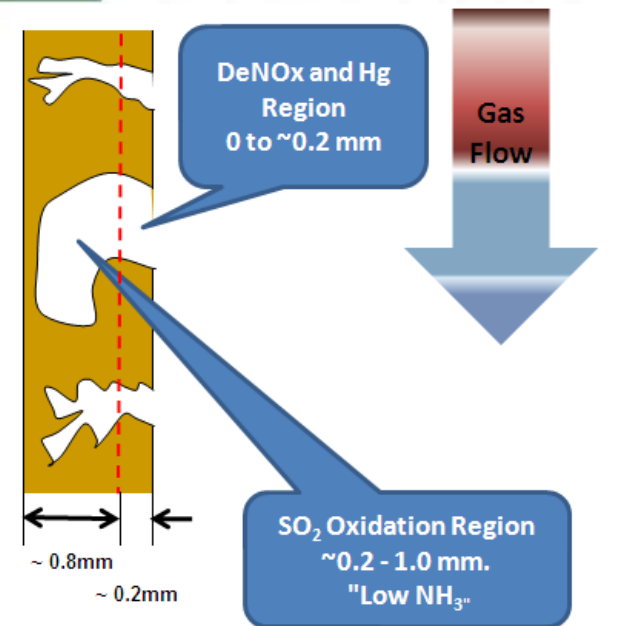
- Hg oxidation is mass transfer controlled (like deNO_x), not kinetically controlled (like SO₂ oxidation)

- ❖ Regenerate by placing vanadium-based catalyst at surface

- Add Hg functionality to SCR catalyst

Data from Lee Engineering & Technology 44 2008

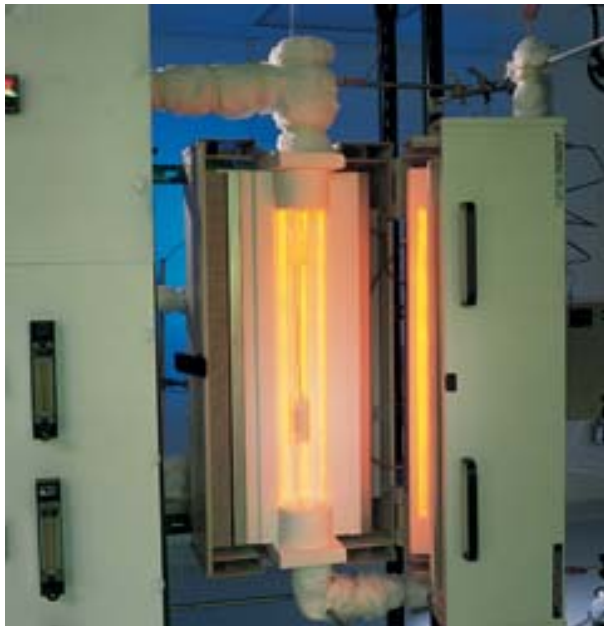
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Mercury Oxidation Over Regenerated Catalyst – Test

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- ❑ Conducted at Southern Research Institute's Catalyst Test Facility using a gas-phase micro-reactor
- ❑ Samples of fresh vs. regenerated honeycomb: 7.1mm pitch, 0.66mm wall, 4 channels, ~ 305mm length
- ❑ Synthetic flue gas (NO , H_2O , NH_3 and SO_2) to mimic plant SCR (LV 3.4 m/s)
- ❑ Inlet Hg^0 ~ 10 ppb; inlet halogen 50 ppmv as HCl
- ❑ Both total and elemental Hg concentrations measured with Tekran model 2537A mercury vapor analyzer

Mercury Oxidation Over Regenerated Catalyst – Results



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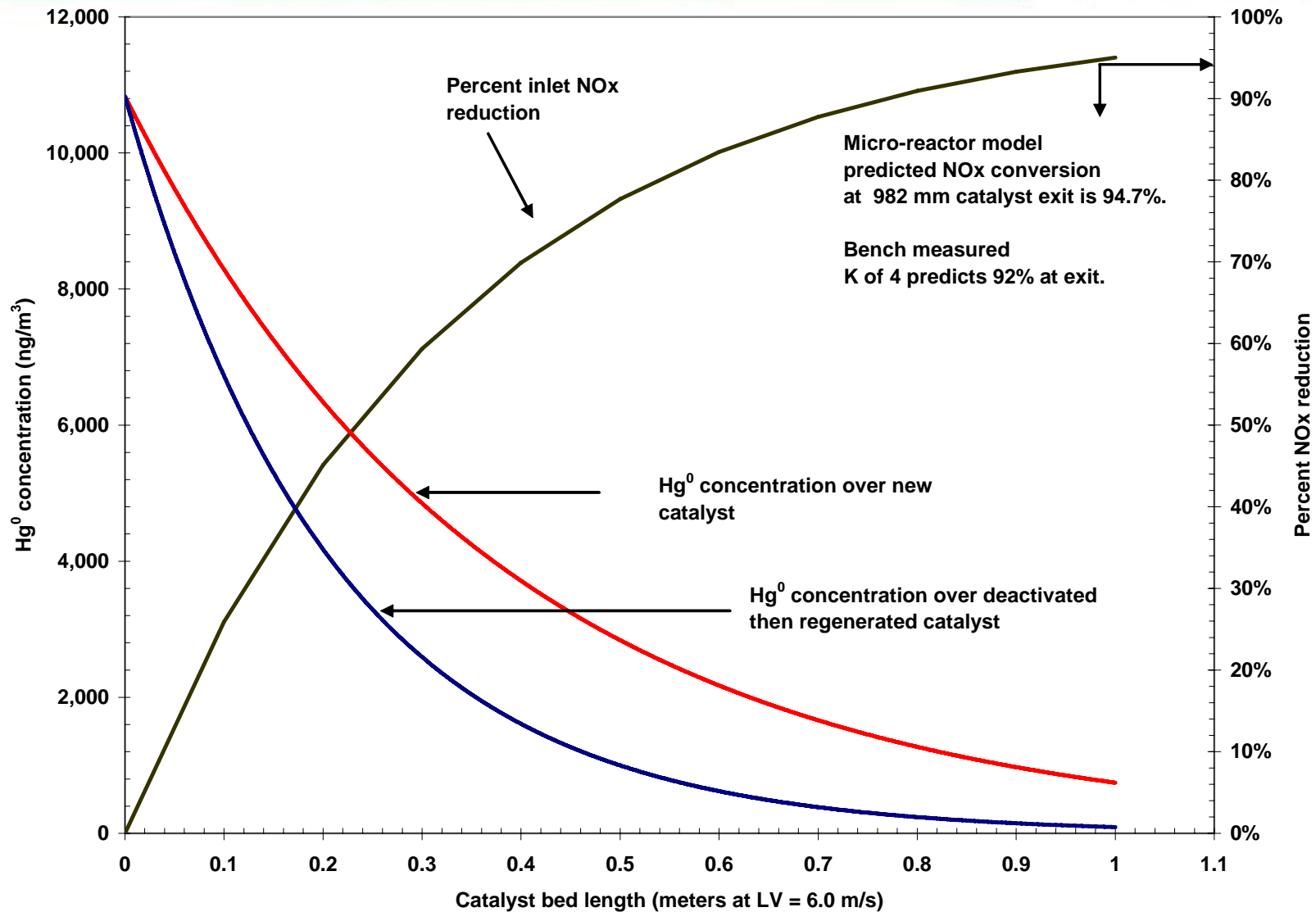
- ❑ Full-bench test on regenerated catalyst showed deNOx activity of 41 m/h, 0.3% SO₂ oxidation (comparable to new)
- ❑ Micro-reactor showed approximately 16% more mercury oxidation over regenerated catalyst than new catalyst

Sample	Inlet Hg ⁰ (µg/m ³)	Outlet Hg ⁰ (µg/m ³)	Δ Hg ⁰ %	Inlet NOx (ppm)	Outlet NOx (ppm)	Δ%
New	10.83	2.51	-77%	424.8	55.1	- 87%
Regenerated	10.10	0.73	-93%	427.4	61.7	- 86%

Hg⁰ and NOx Concentrations From Predictions From Micro-Reactor 1st Order Model



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Summary

- ❑ SCR reactor plays key part in an overall mercury mitigation strategy
- ❑ Mercury regulations still unclear, but we're planning for the need to have increased Hg oxidation functionality in regenerated SCR catalysts
- ❑ Fuel halogen:mercury ratio key factor
 - ❖ Sensitive to small amounts of HBr, HI
- ❑ Testing challenges still exist in the lab and in the field
 - ❖ No VGB-type Hg testing standards developed
- ❑ Catalyst regeneration results show beneficial impact on Hg oxidation