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Mercury Oxidation Across SCR Catalysts in Coal-Fired Power Plants

2011 NOx Combustion Round Table

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February 8, 2011

Mercury Emission Regulations for Electric Generating Units (EGUs)

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- 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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State	Compliance date	Percent reduction	Emission limit	Continuous emission monitoring req't	Comments
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;
	1/1/2018	90	0.0087 #/GWH	X	(2) plants must meet 80% reduction beginning 1/1/2012
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	*Legislatively prescribed schedule of specific APCs at specified times for each plant*				
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
-	12/31/2014	90	NA	X	date for DFGD and second date for WFGD.
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 SO2, Nox 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 NOx & SO2

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

$4\ NO + 4\ NH_3 + O_2 \rightarrow$
$4\ N_2 + 6\ H_2O$

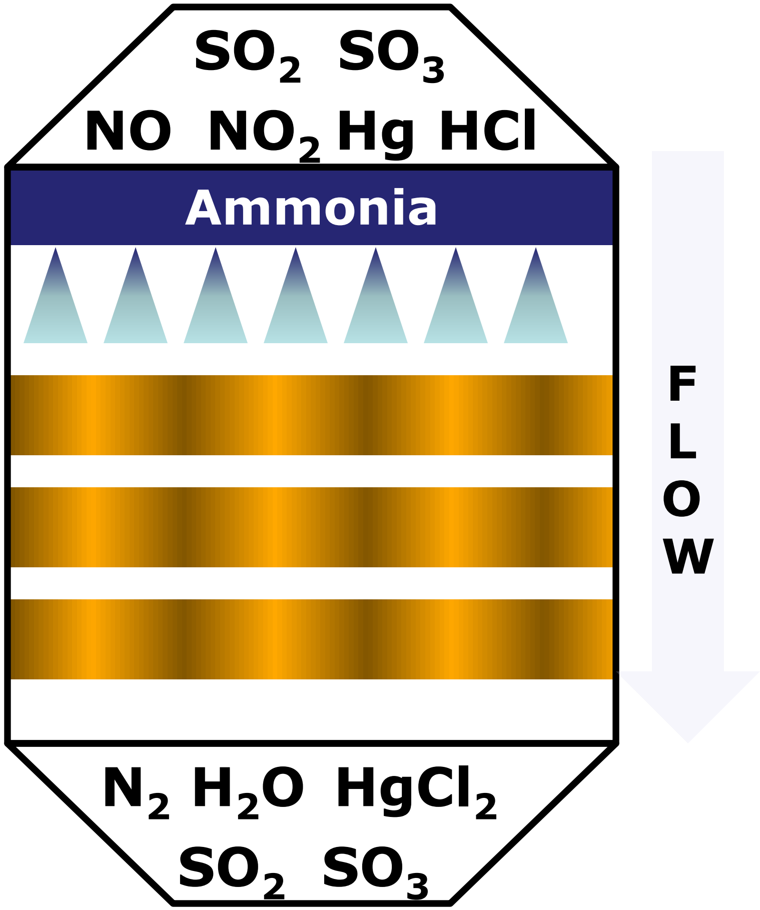
$2\ Hg + 4\ HCl + O_2 \rightarrow$
$2\ HgCl_2 + 2\ H_2O$

Detrimental Reactions

$2\ SO_2 + O_2 \rightarrow 2\ SO_3$

$4\ HgCl_2 + 4\ NH_3 + O_2 \rightarrow$
$4\ Hg + 8\ HCl + 2\ N_2 + 2\ H_2O$

$HgCl_2 + SO_2 + H_2O \rightarrow$
$Hg + 2\ HCl + SO_3$



SCR Catalyst Overview

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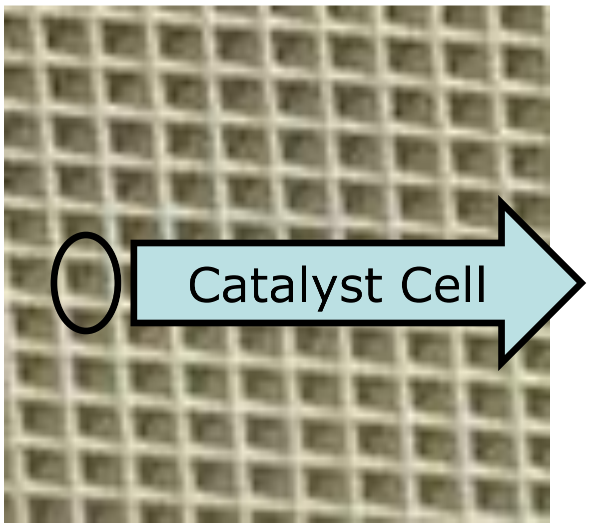
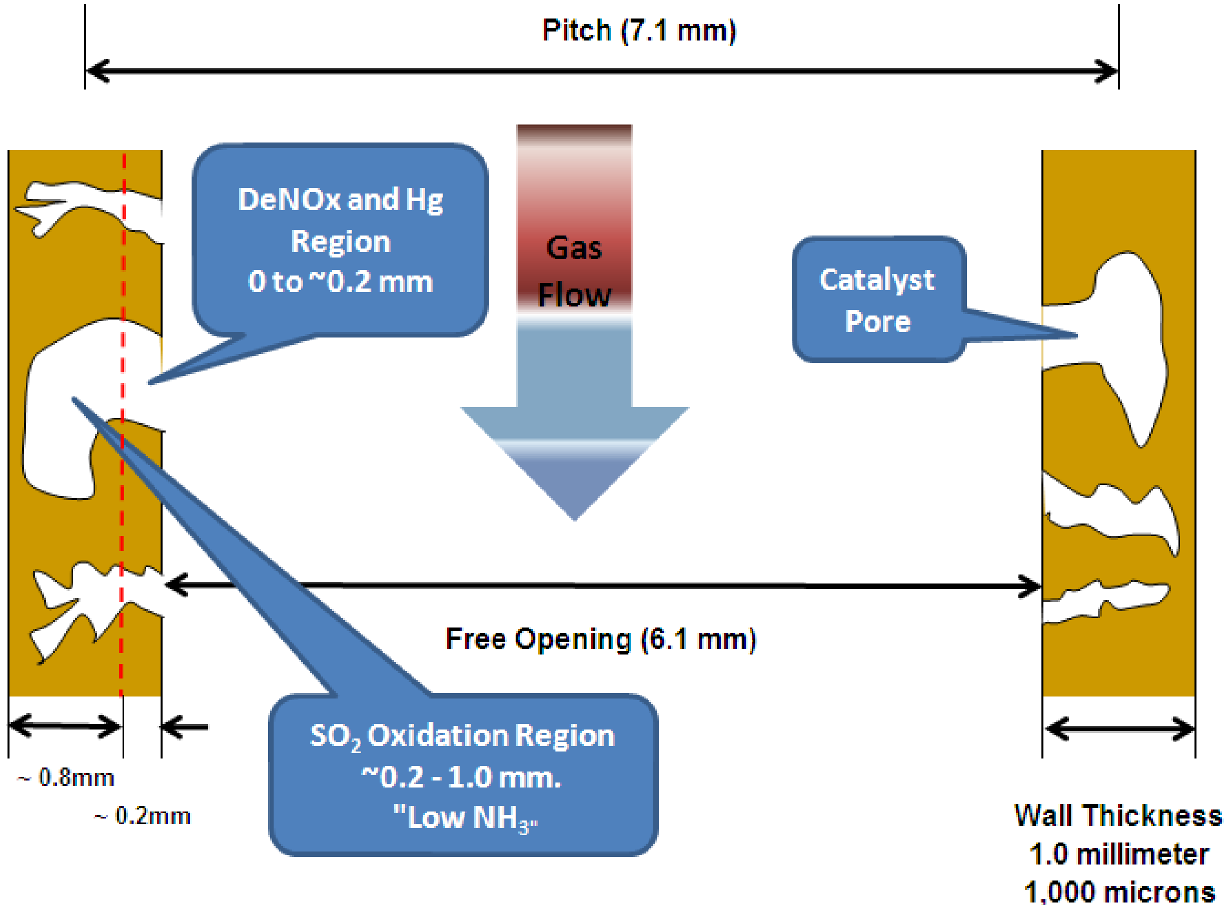


Honeycomb Element



- **Visible surface ~ 400 m^2/m^3**
- **Catalytic surface at 65 m^2/g**
- **30 million m^2/m^3**

Factors Affecting Mercury Oxidation

- **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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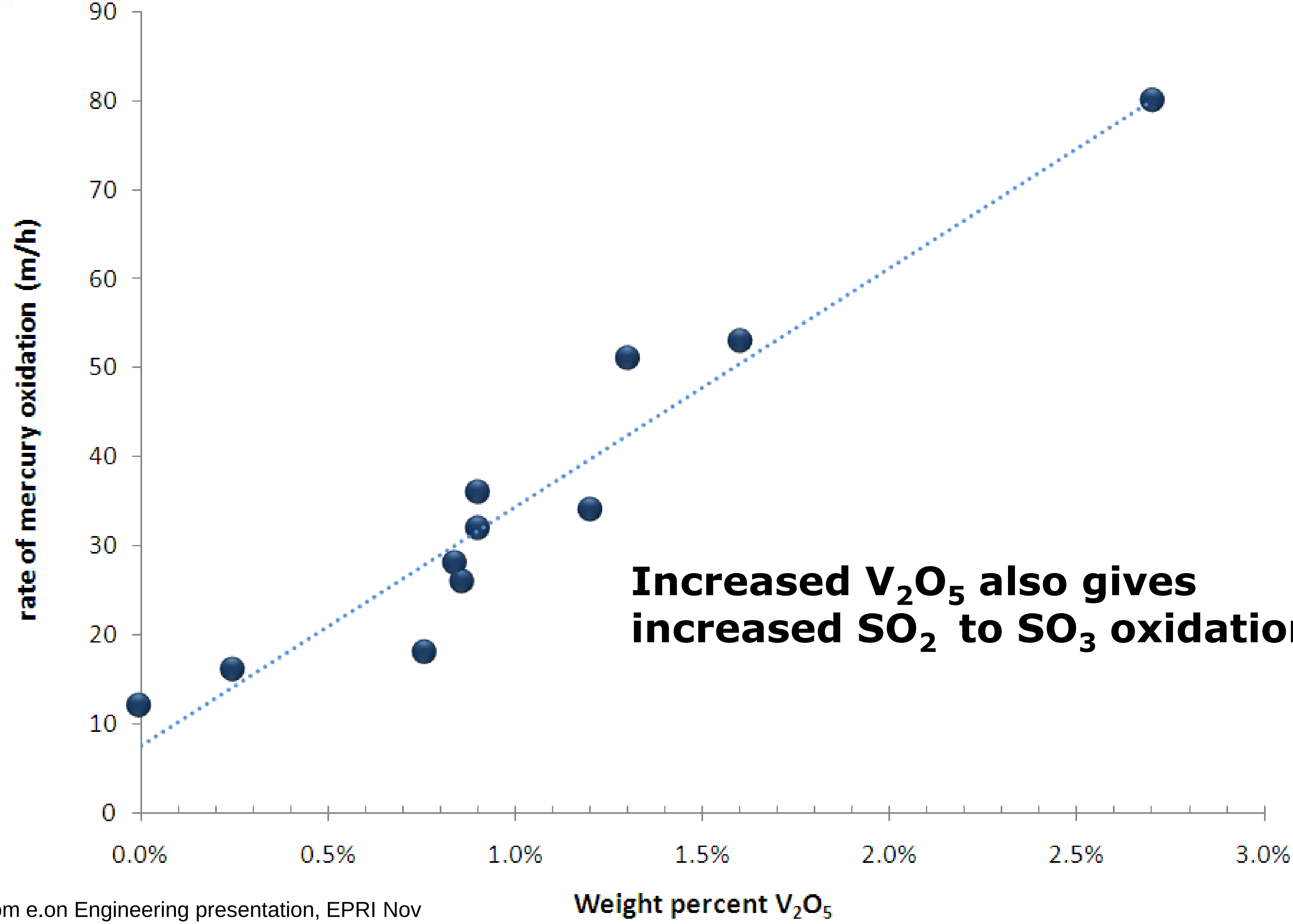

Increased V_2O_5 also gives increased SO_2 to SO_3 oxidation!

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

Effect of Temperature in SCR

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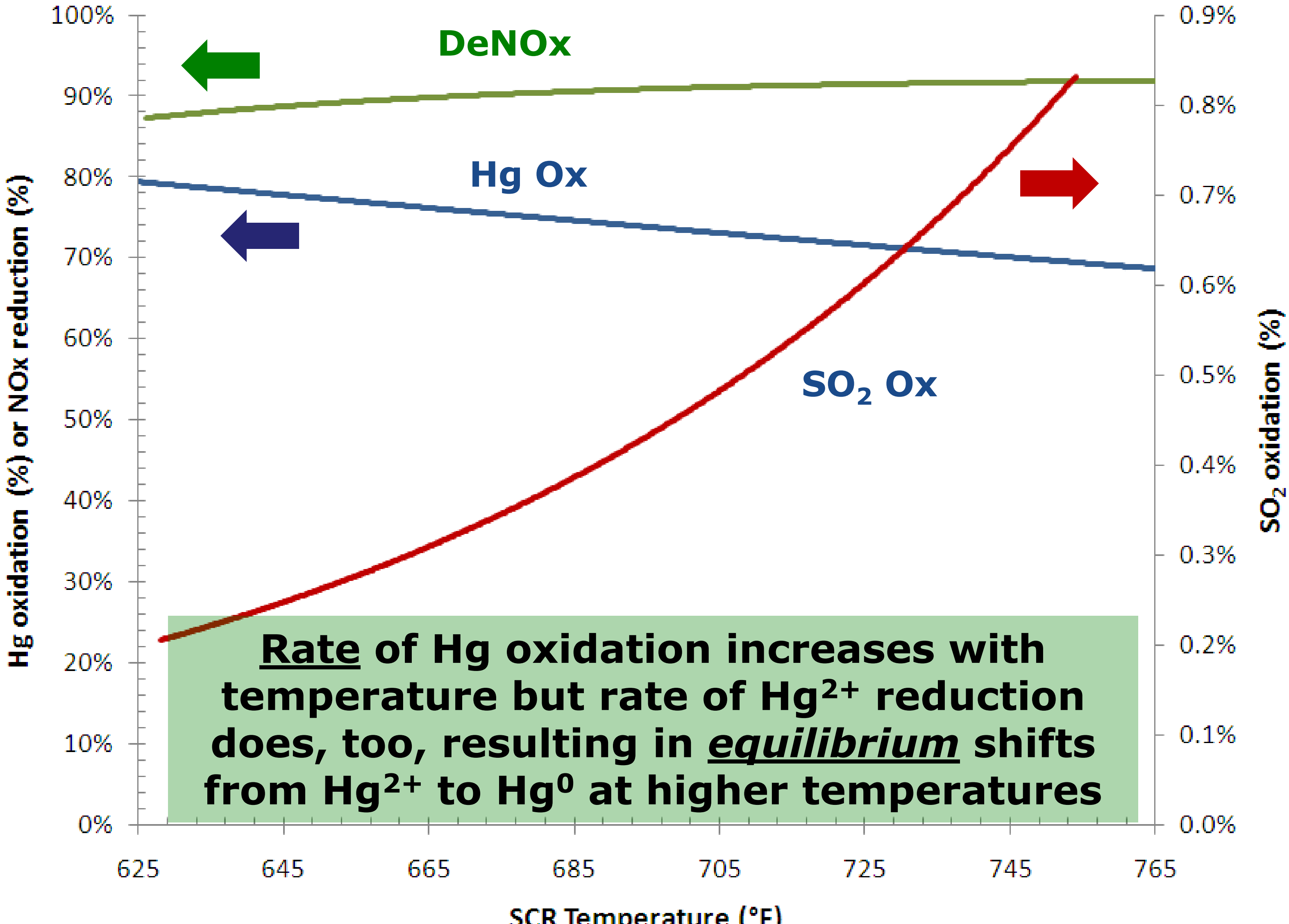

Rate of Hg oxidation increases with temperature but rate of Hg^{2+} reduction does, too, resulting in *equilibrium* shifts from Hg^{2+} to Hg^0 at higher temperatures

Coal Mercury Content

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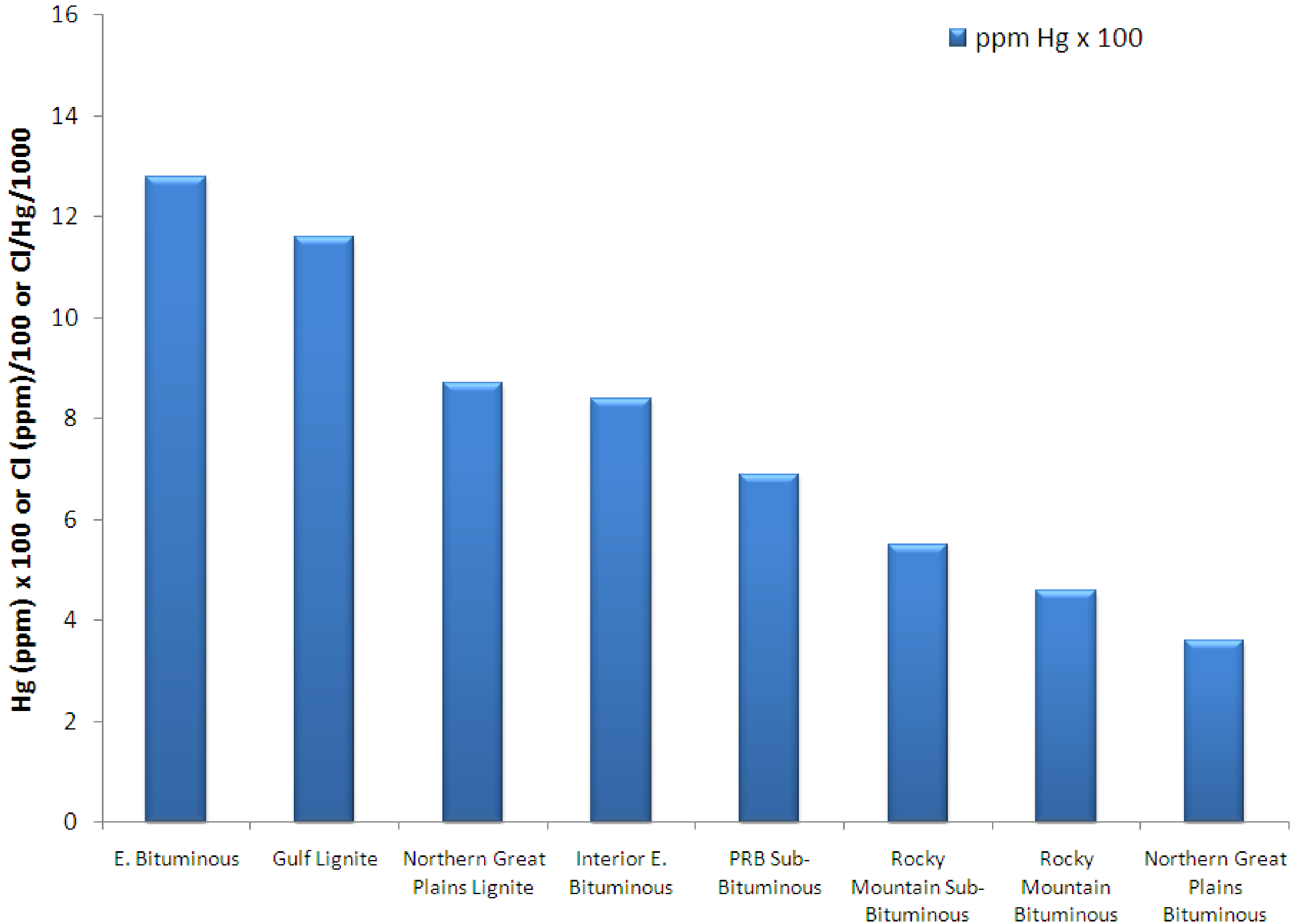

Coal Chlorine Content

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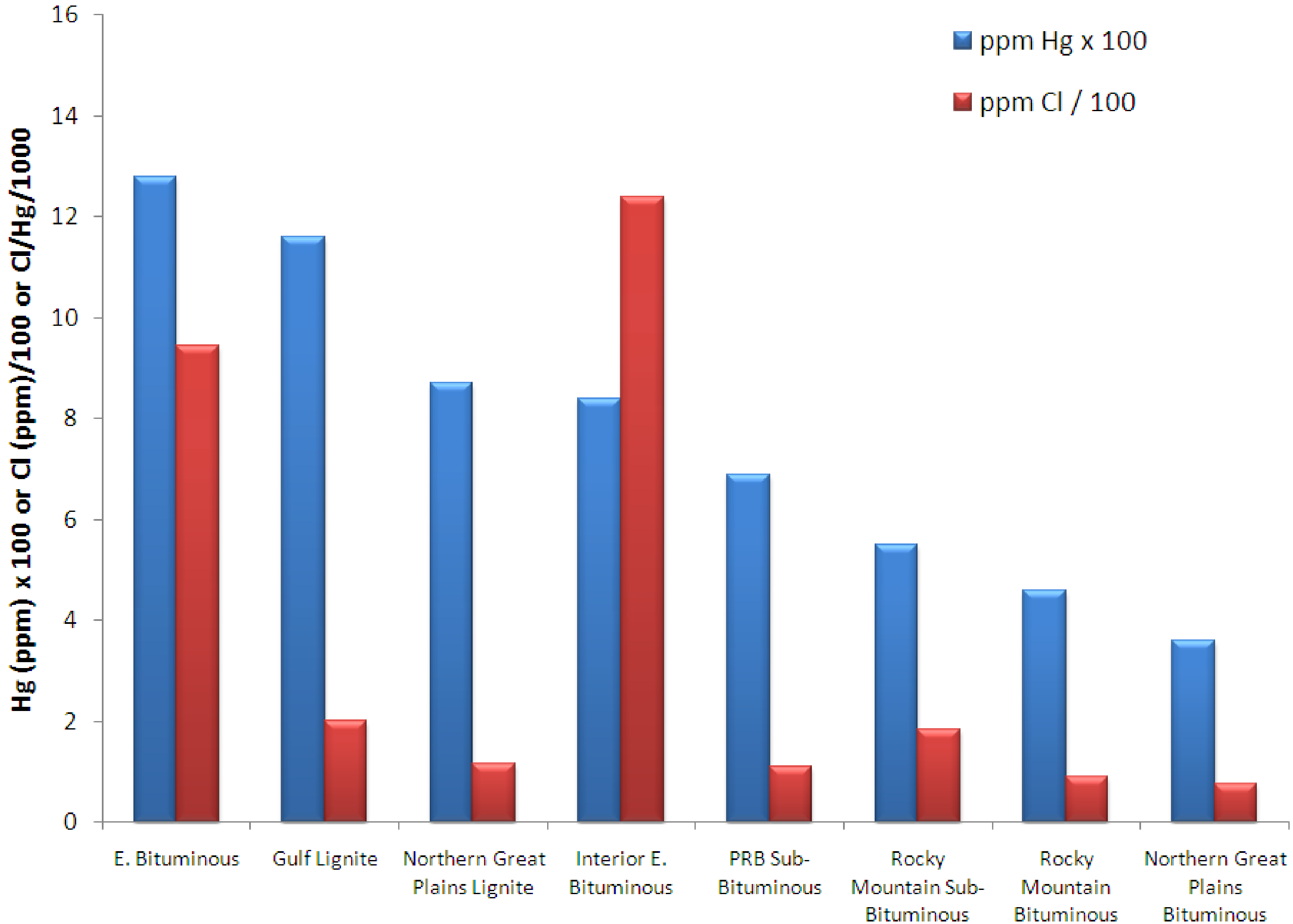

Chlorine:Mercury Ratio

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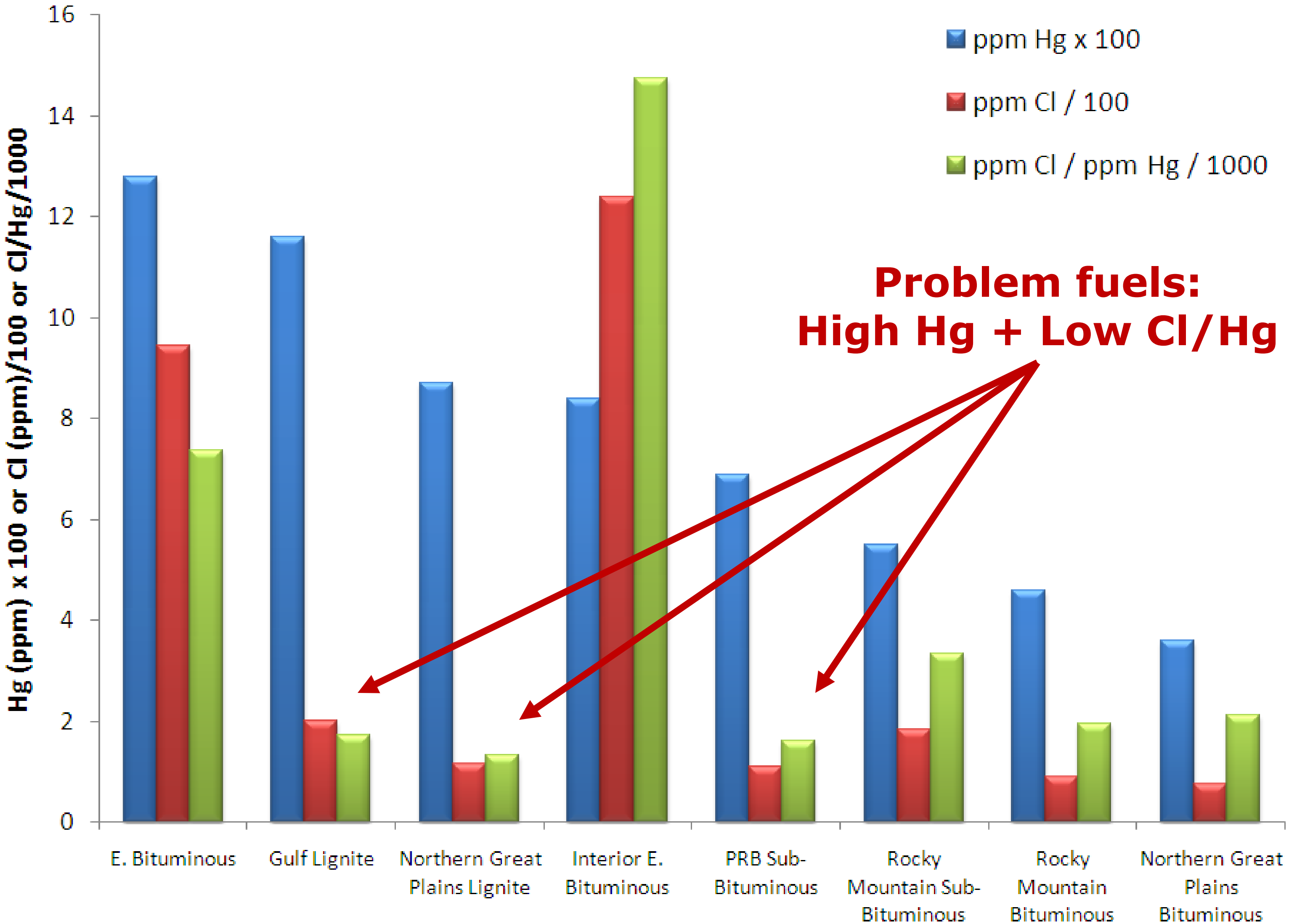

Effect of HCl & NH_3 in Flue Gas

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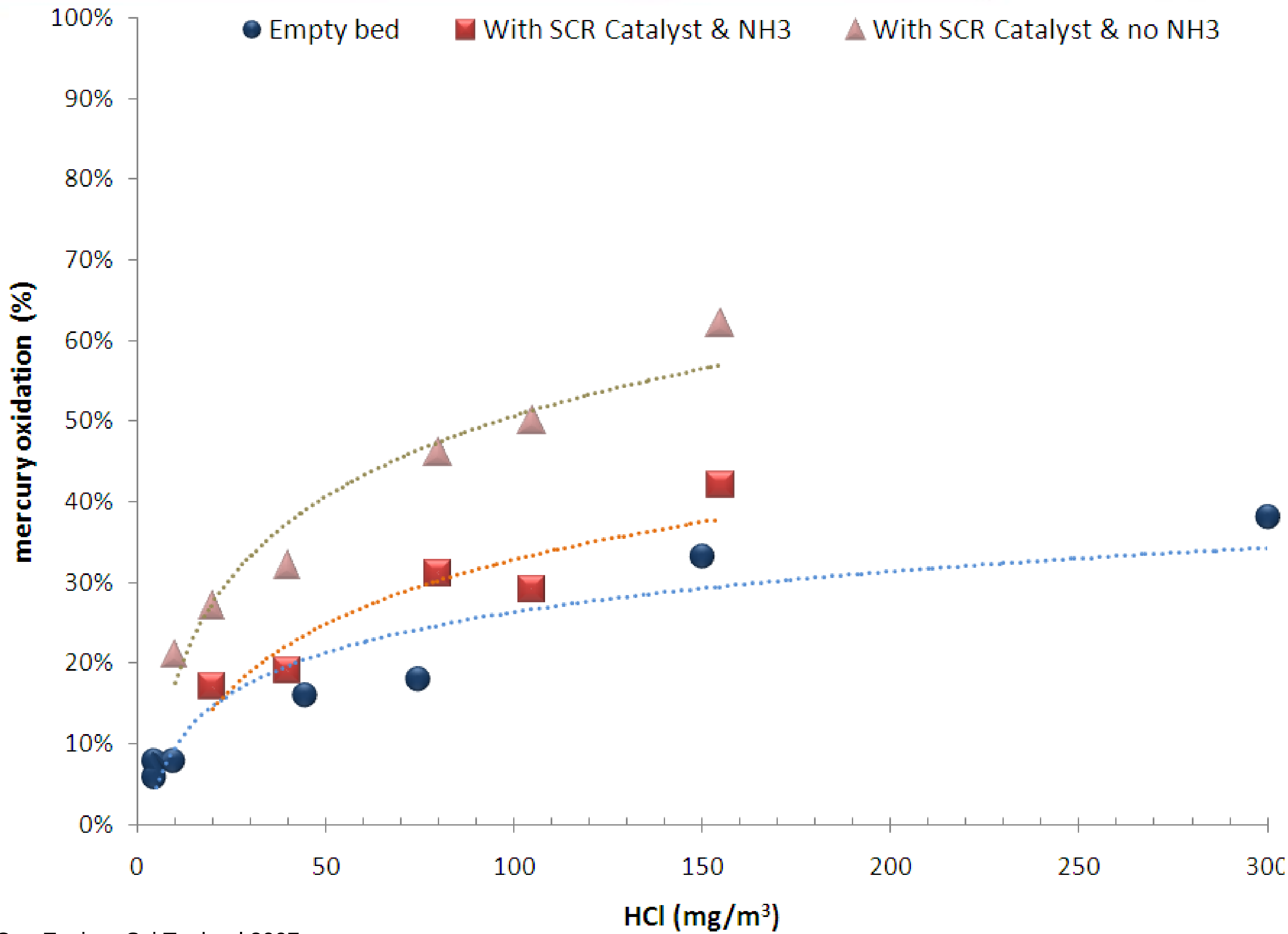

Data from Cao Environ Sci Technol 2007

Effect of Halogens

- 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 Hg^0 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 Partioning Around SCR

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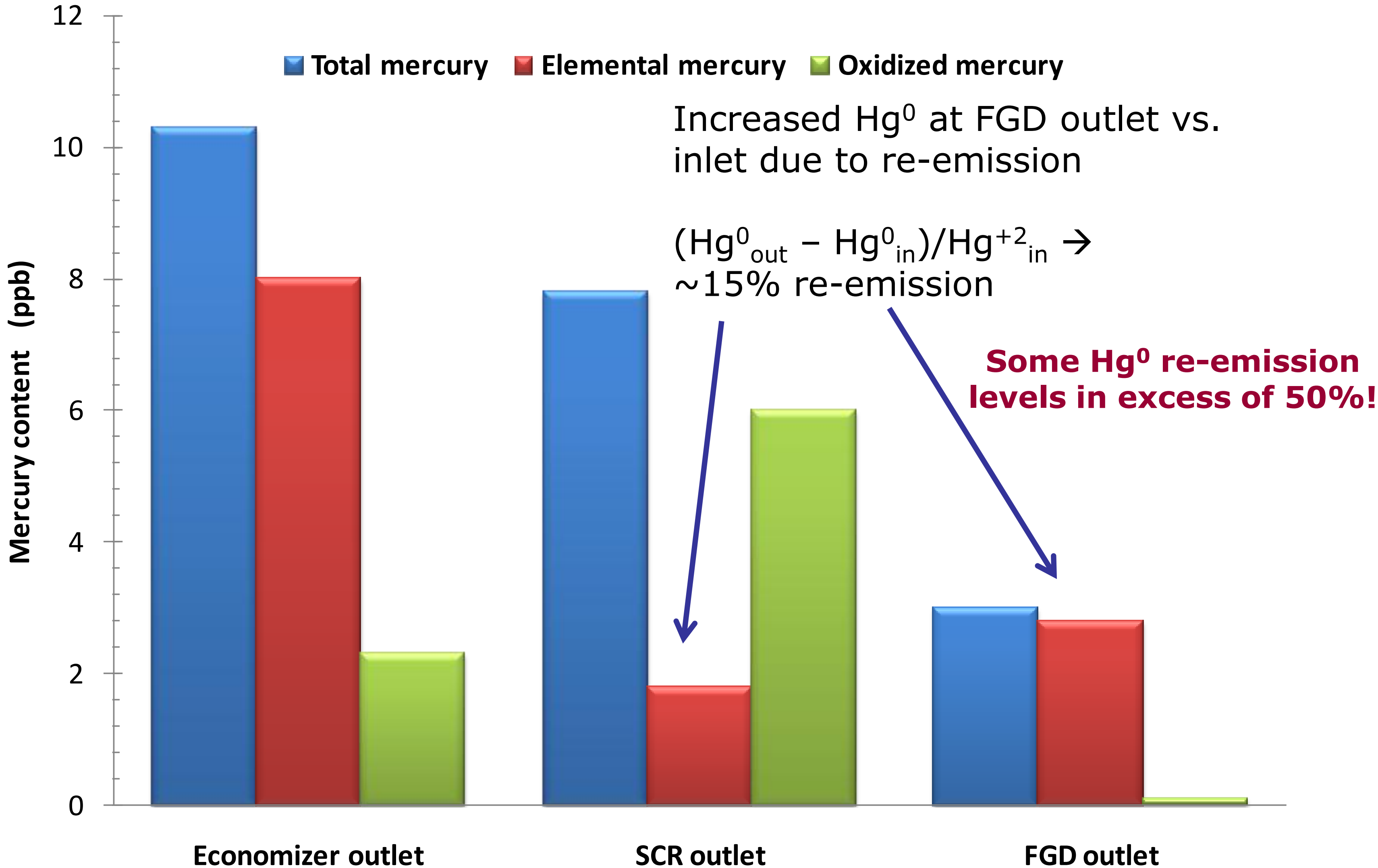
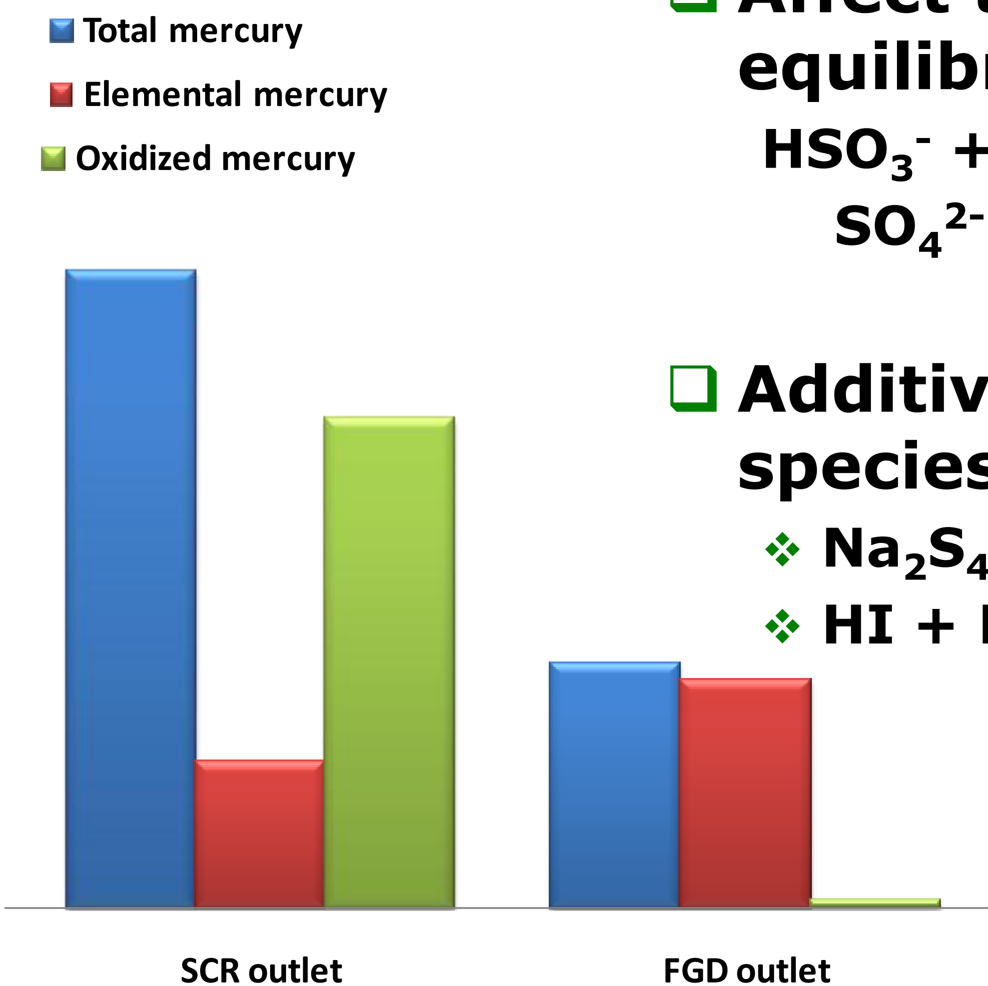


Mercury Re-Emission



- **Affect the Hg^{2+}/Hg^{0} equilibrium in FGD slurry**

  $$HSO_3^- + H_2O + Hg^{2+}_{(aq)} \longleftrightarrow SO_4^{2-} + 3H^+ + Hg^0$$

- **Additives to form insoluble species**
  - Na_2S_4 /NaHS + Hg^{2+} … → $HgS_{(s)}$
  - HI + Hg^{2+} → $HgI_{2(s)}$

Mercury Oxidation Within SCR

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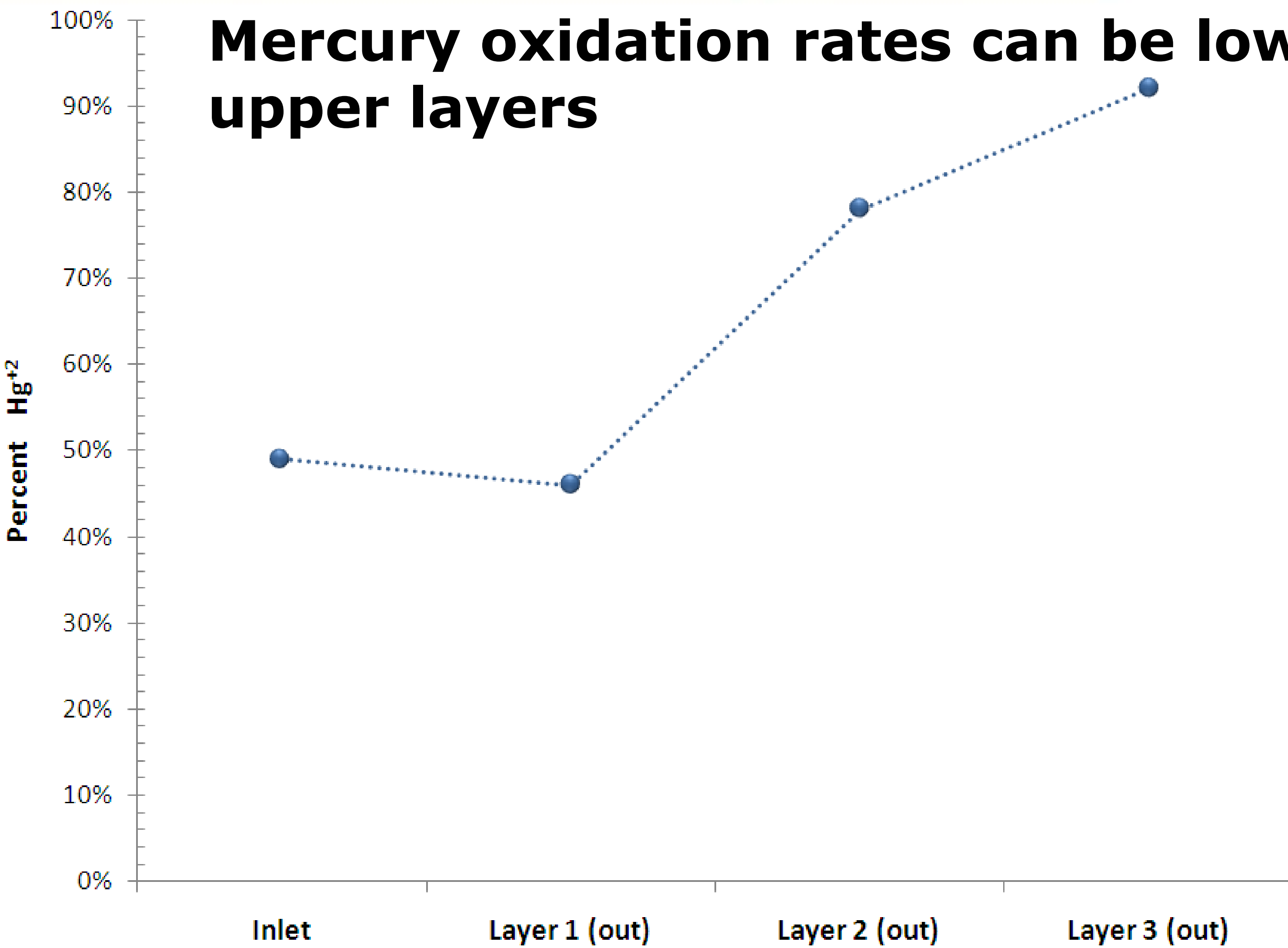

Data from e.on Engineering presentation, EPRI Nov 2008 Workshop, Charlotte, NC

Mercury Oxidation Within SCR

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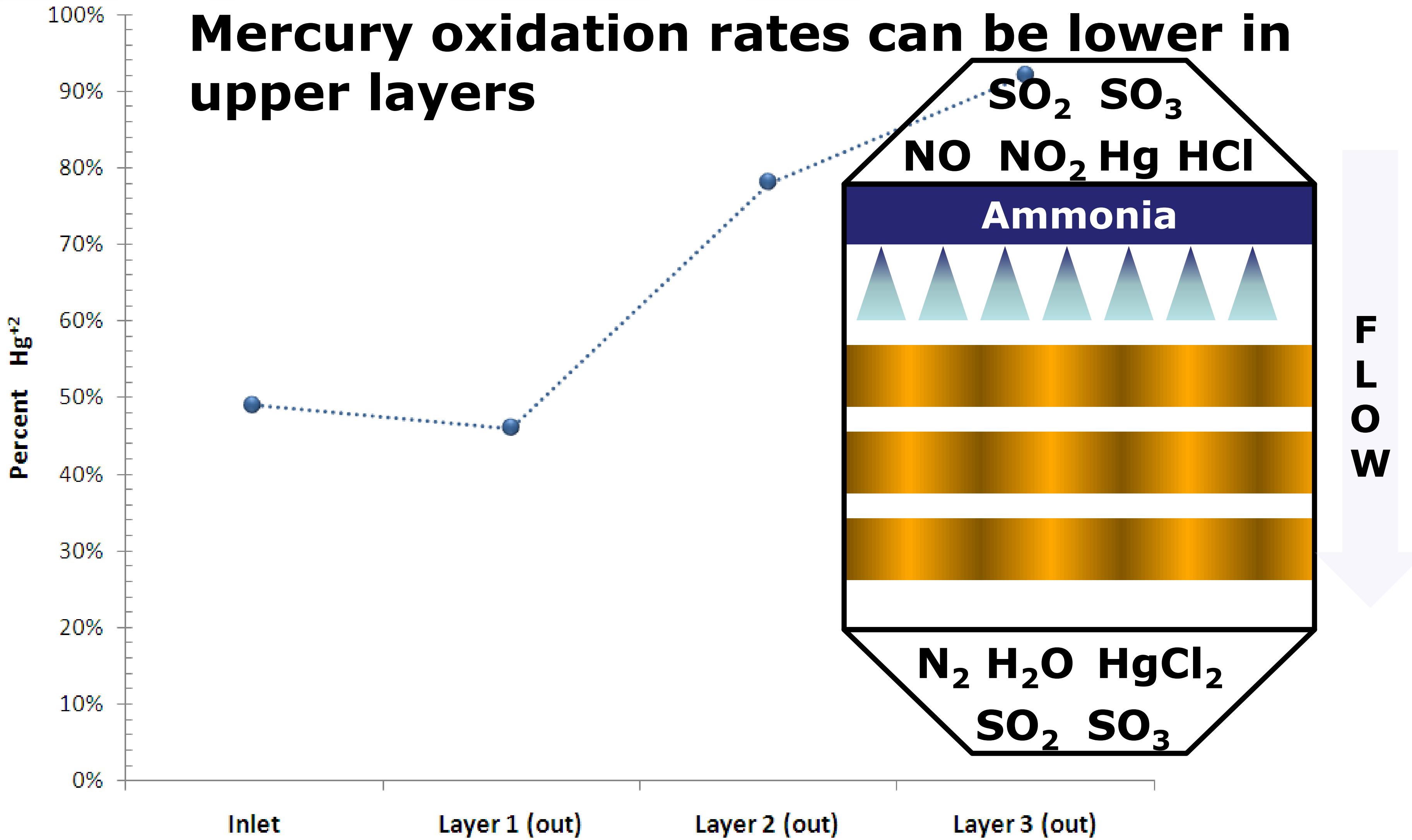
Mercury oxidation rates can be lower in upper layers



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Testing Challenges

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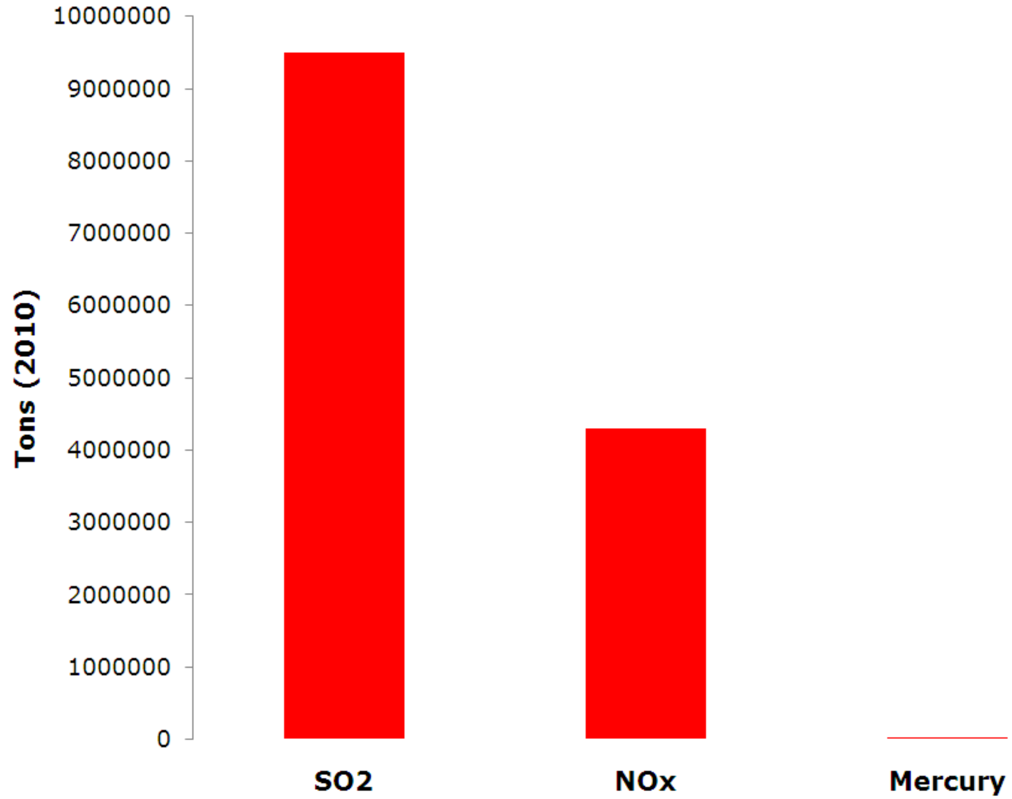

- **Measure a few parts per billion (~ 10 ppb total Hg) vs. a few parts per million (1-10 ppm SO_3) AND distinguish between Hg^0 and Hg^{2+}**

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

Testing Challenges - Lab

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- $SO_2 \rightarrow SO_3$ oxidation testing analogy:
  - Some test with added SO_3, some don't
  - Some people test at NH_3/NOx = 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 [H_2O], [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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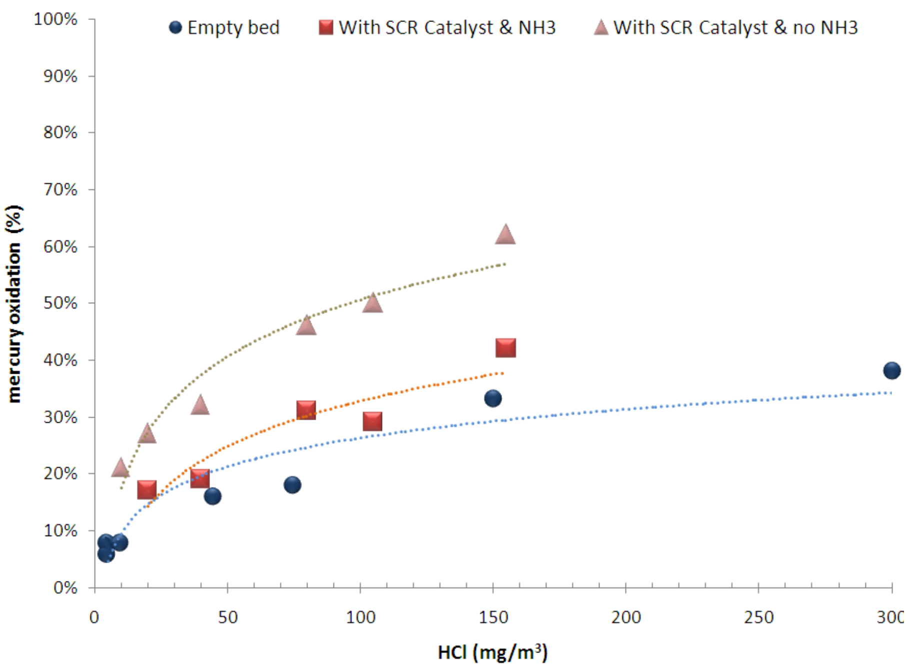

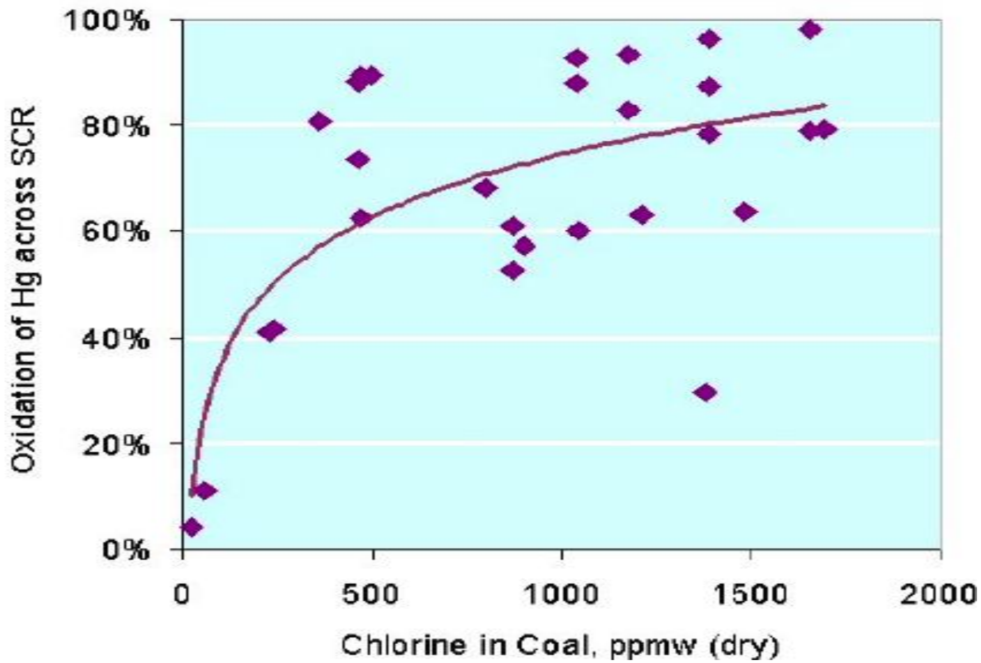

Data from Cao Environ Sci Technol 2007

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

SCR Catalyst Modifications

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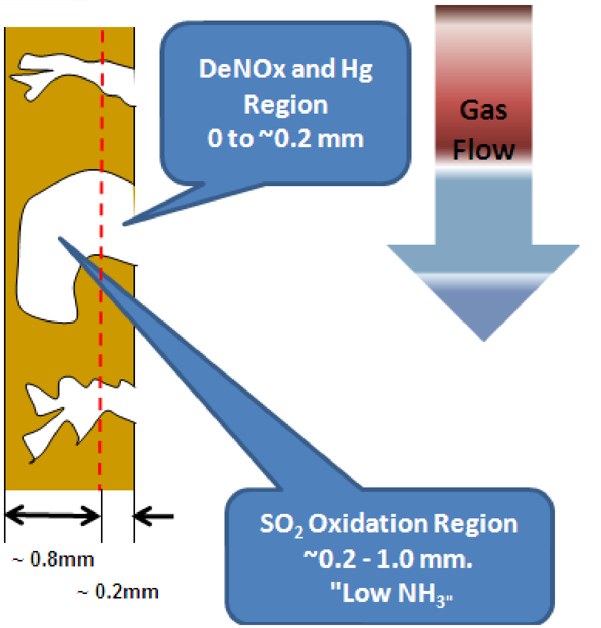
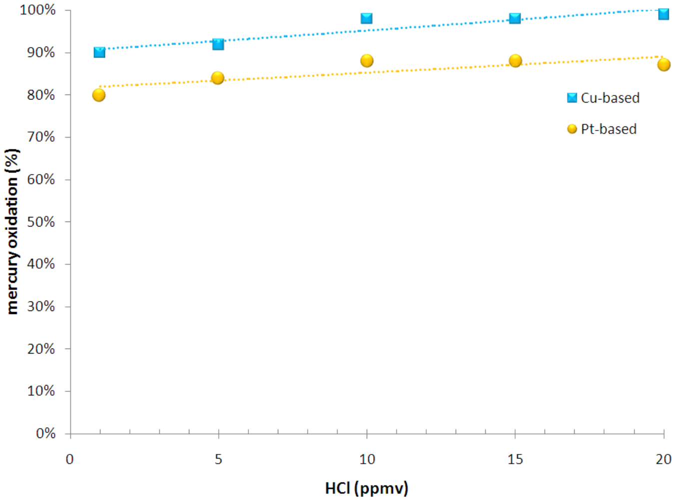
- Hg oxidation is mass transfer controlled (like deNOx), not kinetically controlled (like SO_2 oxidation)
  - Regenerate by placing vanadium-based catalyst at surface



- Add Hg functionality to SCR catalyst



Data from Lee Engineering & Technology 44 2008

Mercury Oxidation Over Regenerated Catalyst – Test

- **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

- Full-bench test on regenerated catalyst showed deNOx activity of 41 m/h, 0.3% SO_2 oxidation (comparable to new)
- Micro-reactor showed approximately 16% more mercury oxidation over regenerated catalyst than new catalyst

Sample	Inlet Hg^0 ($\mu g/m^3$)	Outlet Hg^0 ($\mu g/m^3$)	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%

Hg^0 and NOx Concentrations From Predictions From Micro-Reactor 1st Order Model

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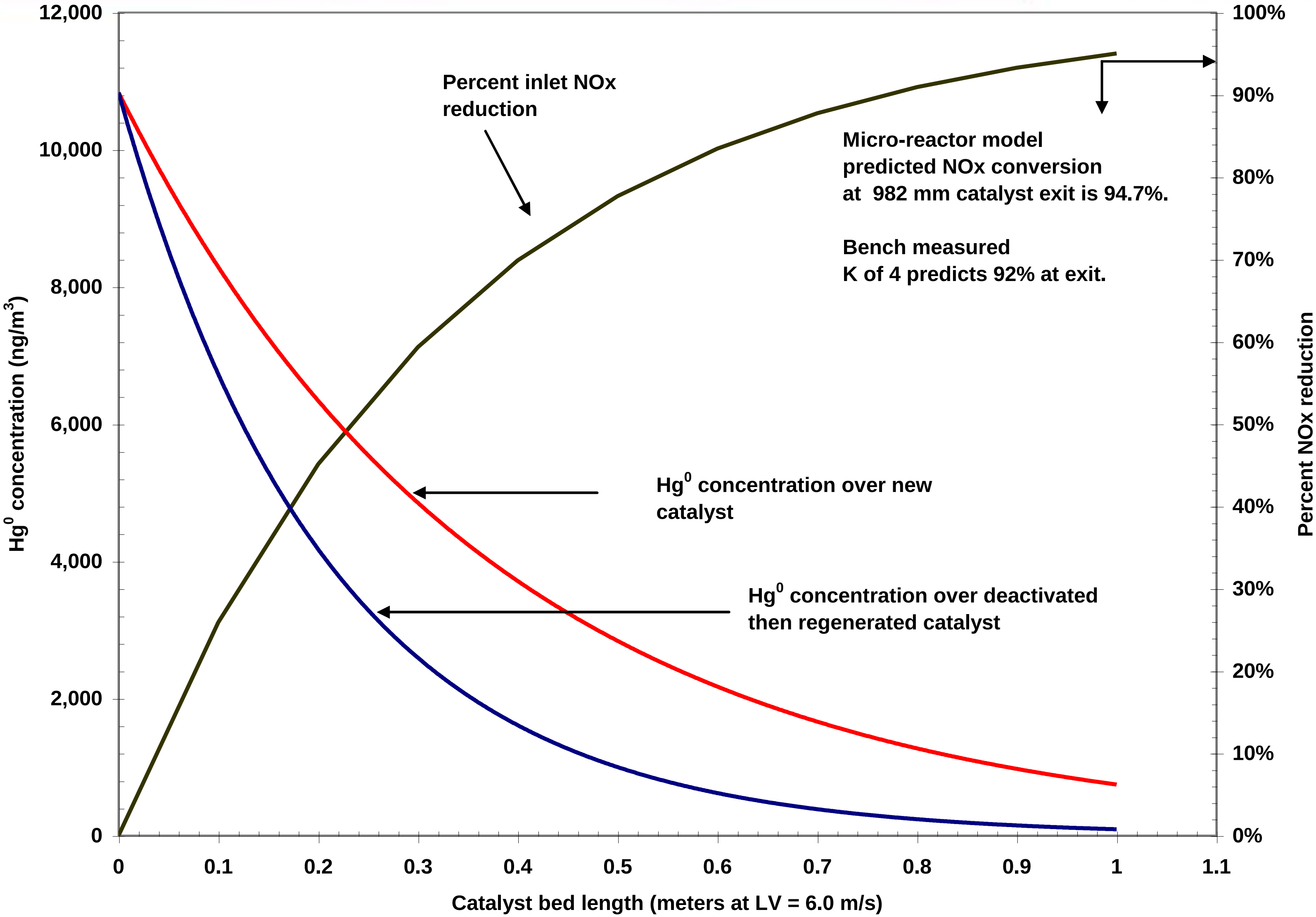

Summary

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- 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