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McIlvaine Hot Topic April 14th

NOx Catalyst Performance on Mercury and SO3

Mercury Oxidation Across SCR Catalysts in Coal-Fired Power Plants

2011 HOT TOPIC HOUR

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April 14, 2011

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

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

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

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

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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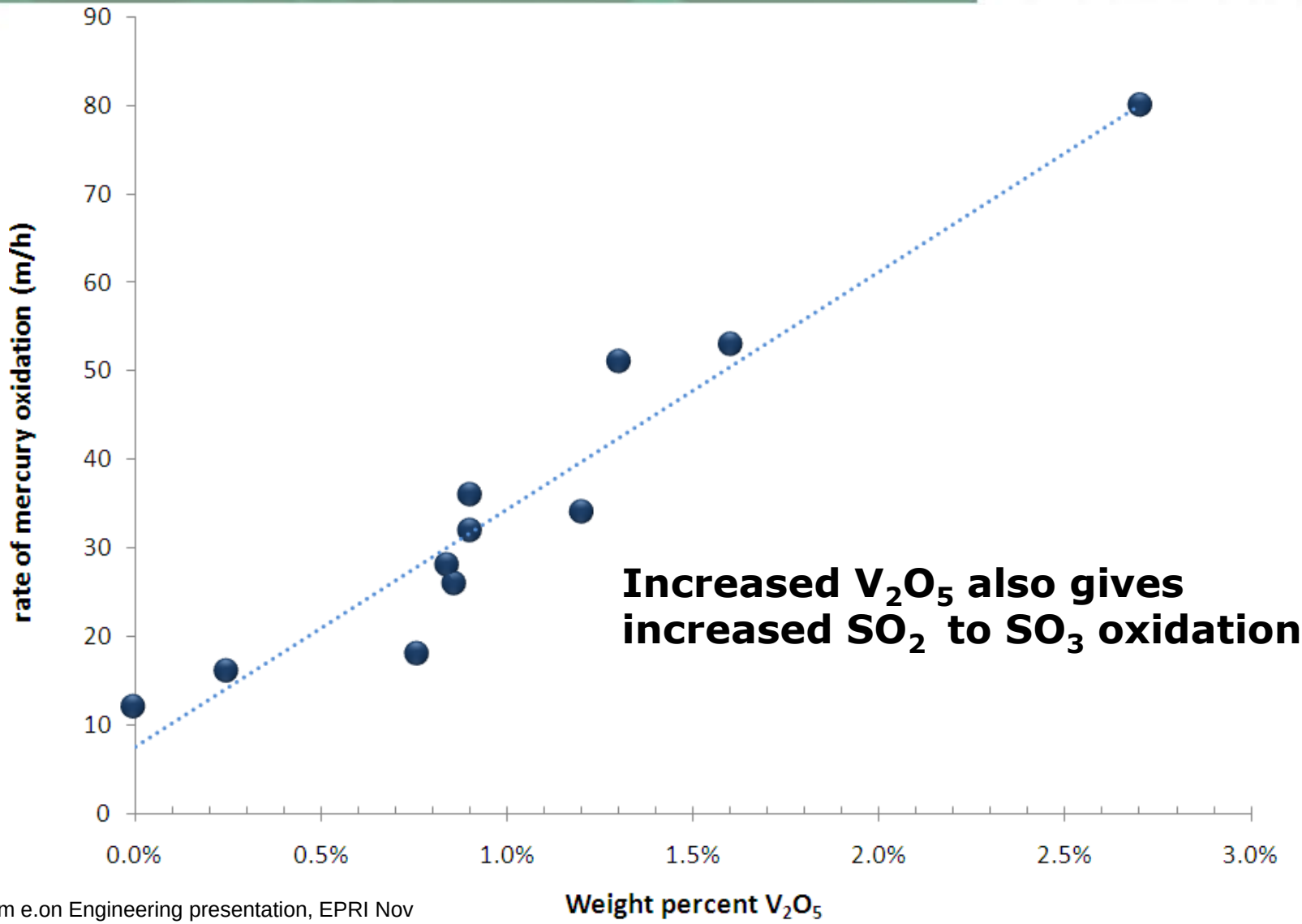

Increased V_2O_5 also gives increased SO_2 to SO_3 oxidation!

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

Effect of Temperature in SCR

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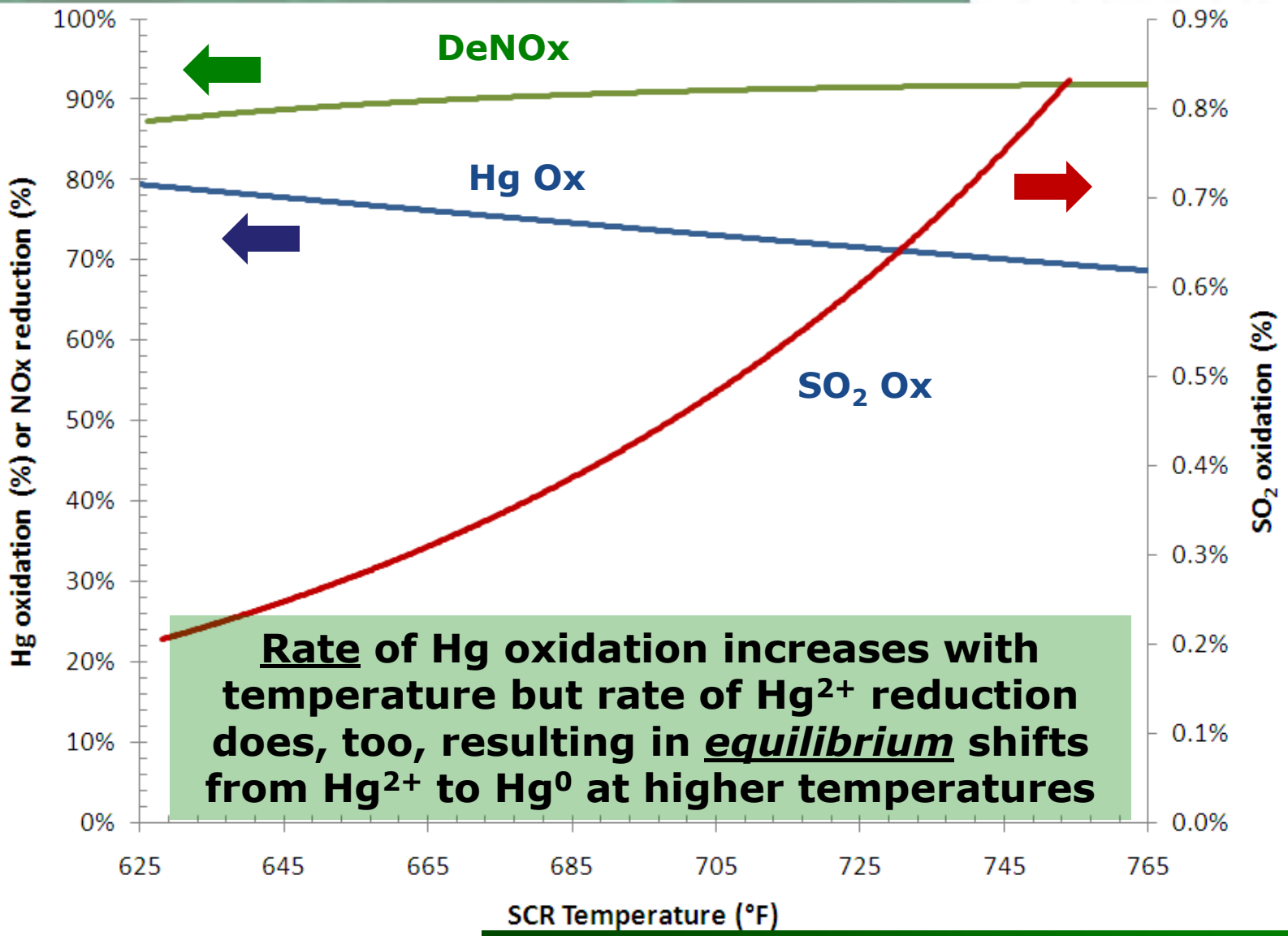

Rate of Hg oxidation increases with temperature but rate of Hg^{2+} reduction does, too, resulting in *equilibrium* shifts from Hg^{2+} to Hg^0 at higher temperatures

Coal Mercury Content

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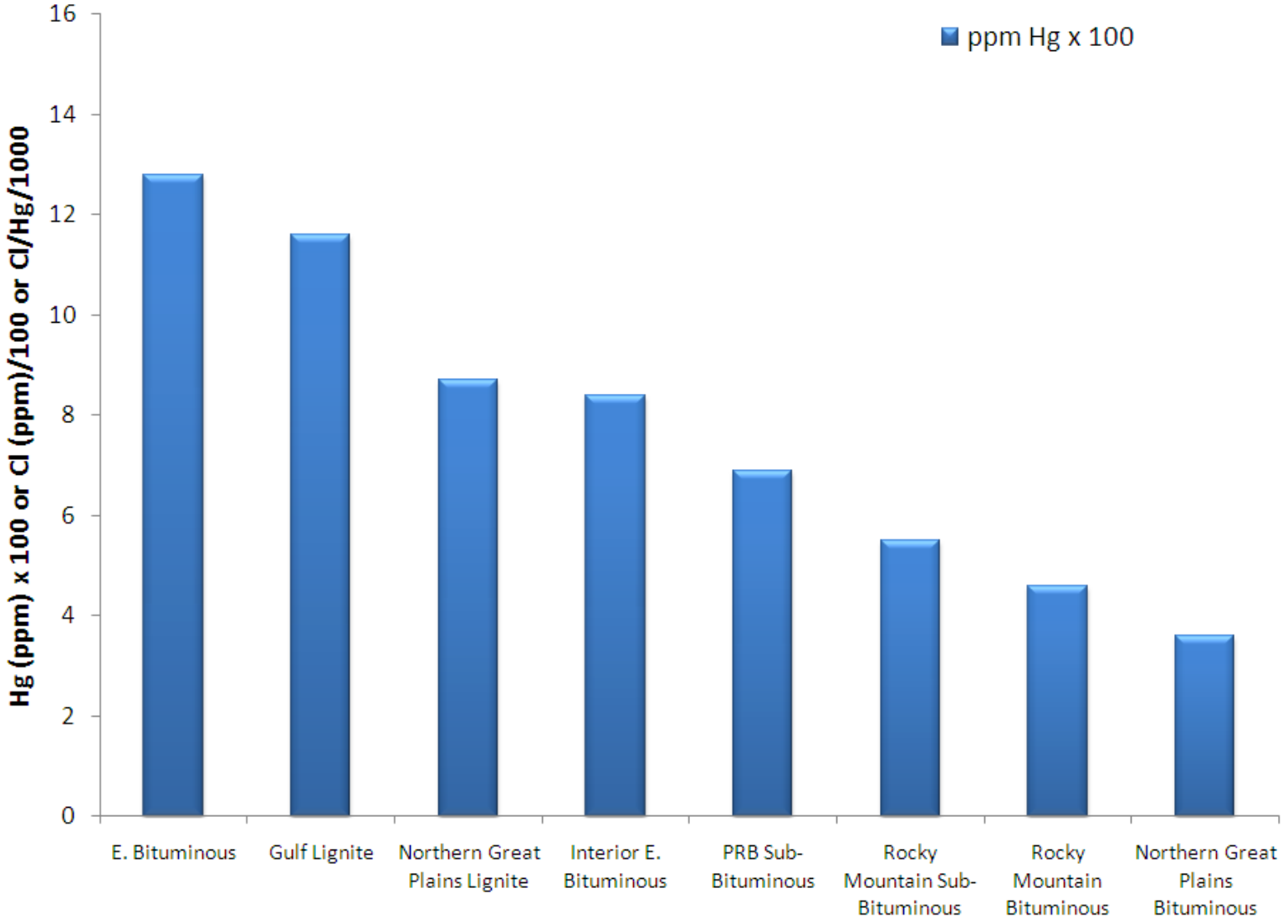

Coal Chlorine Content

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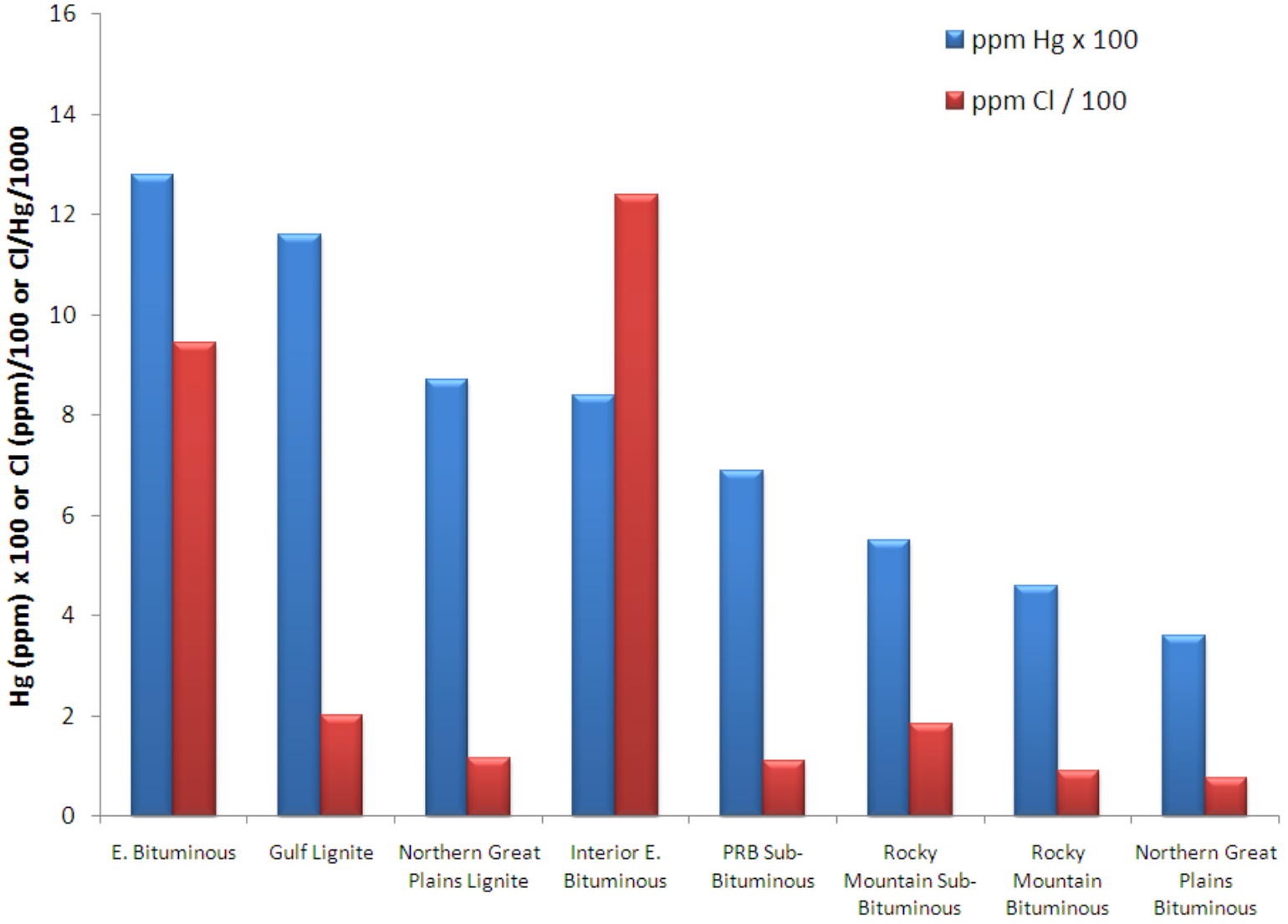

Chlorine:Mercury Ratio

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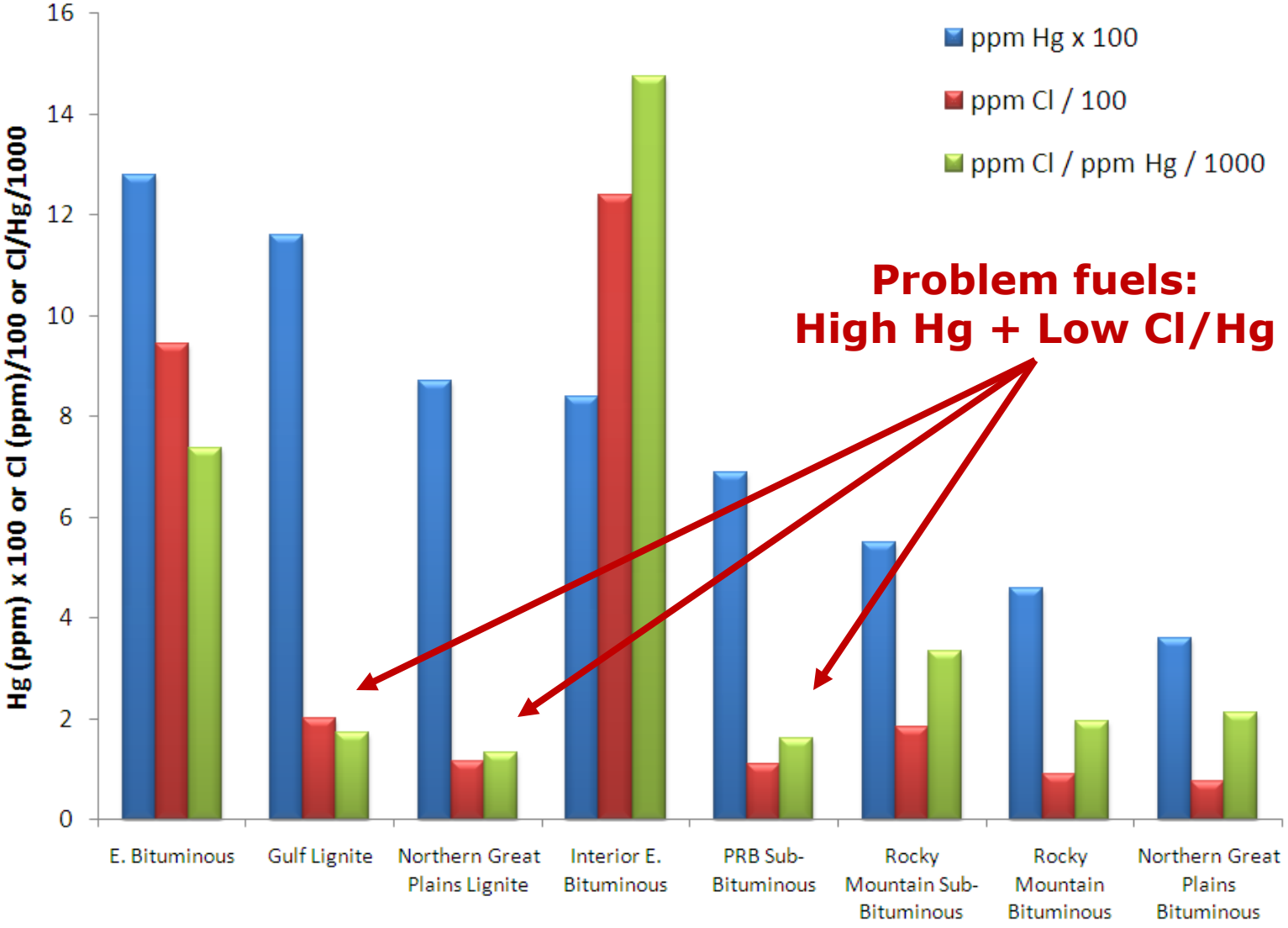

Effect of HCl & NH_3 in Flue Gas

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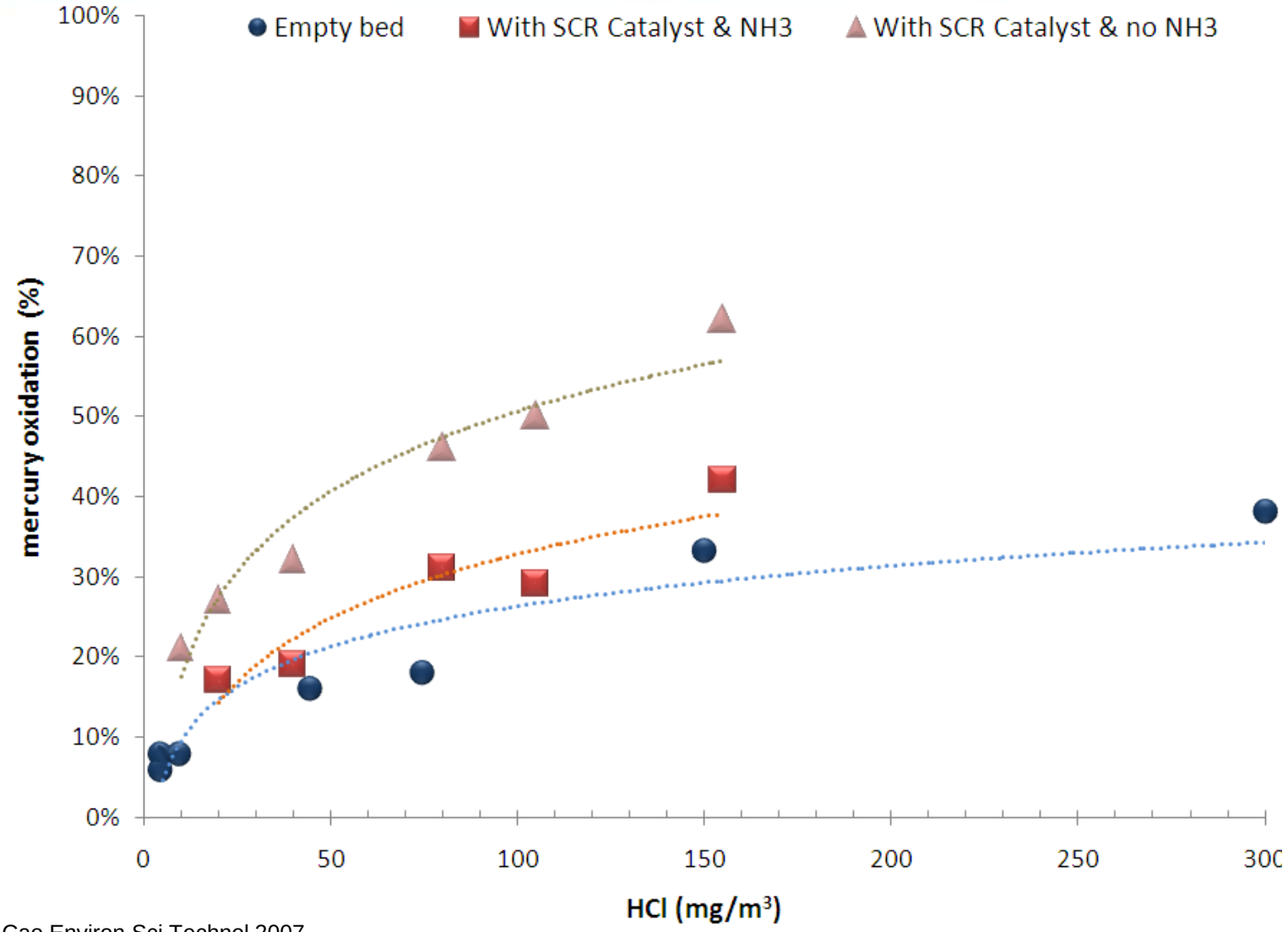

Data from Cao Environ Sci Technol 2007

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 Oxidation Within SCR

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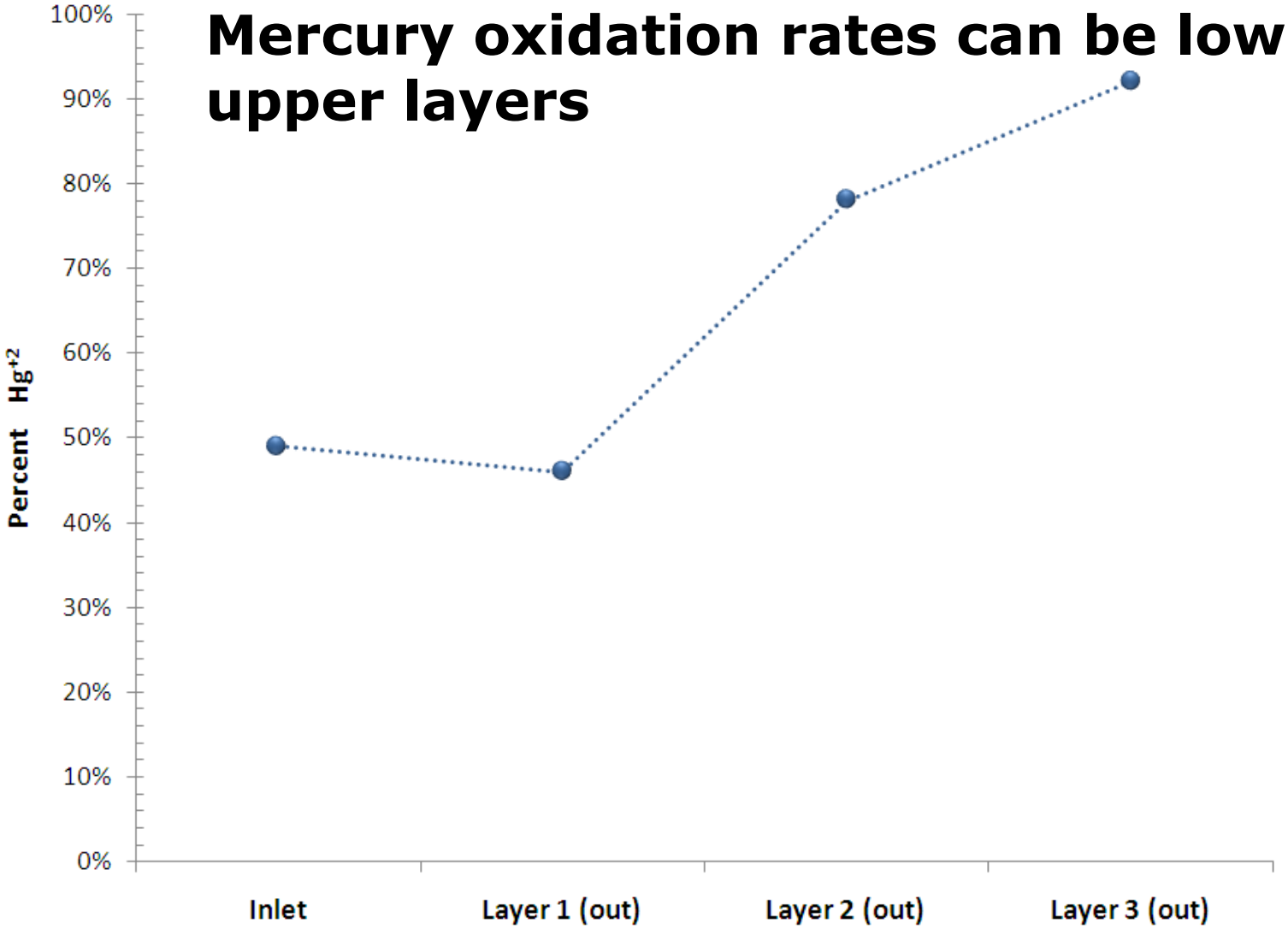
Mercury oxidation rates can be lower in upper layers



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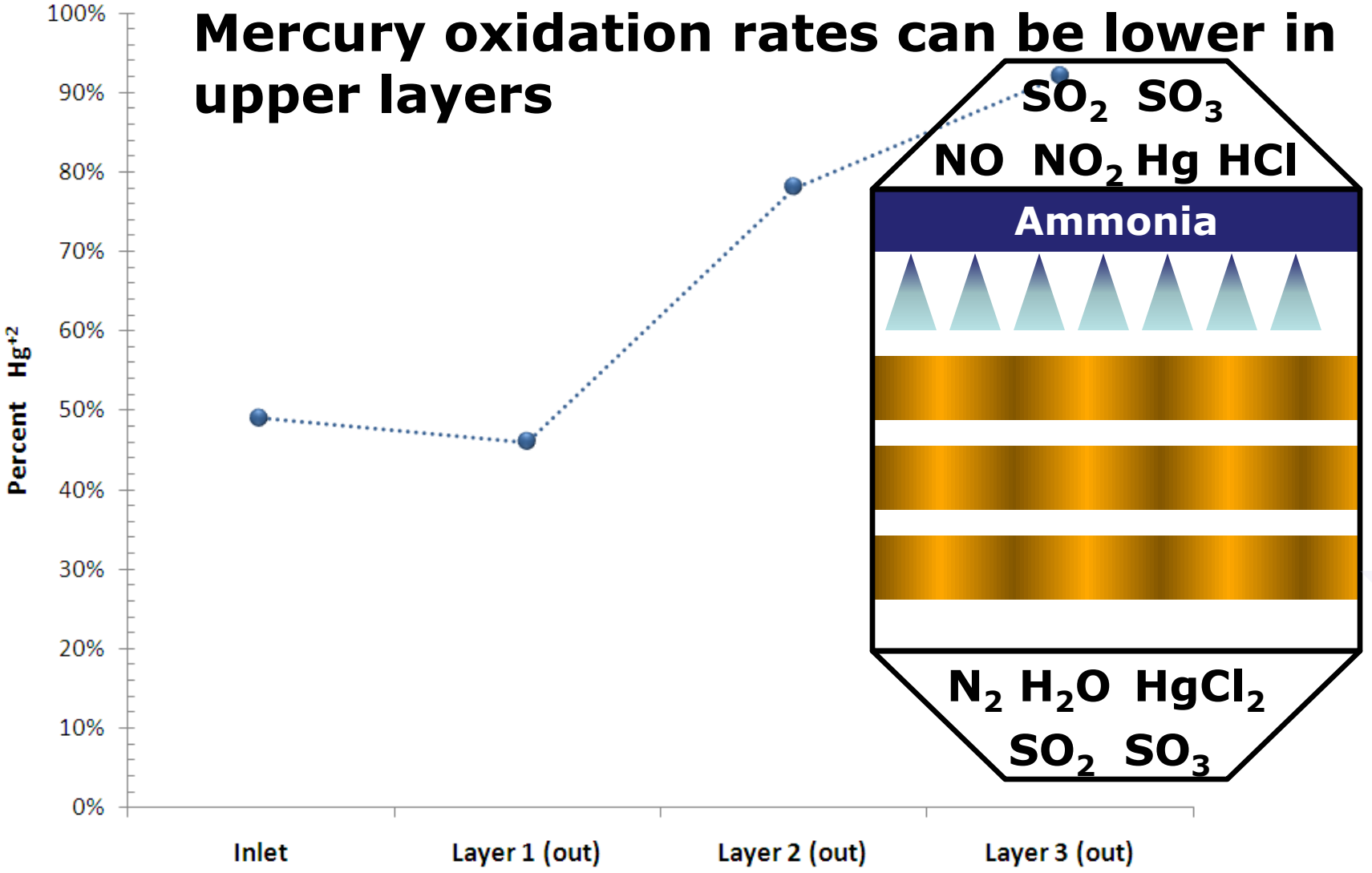

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Summary

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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