

REINHOLD ENVIRONMENTAL Ltd.



2015 NO_x-Combustion Round Table & Expo Presentations

February 23 & 24, 2015, in Richmond, VA / Hosted by Dominion

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2015 NO_x-Combustion Round Table

Mercury Treatment Options For MATS Compliance: A Review

**Behrooz Ghorishi
Nick Pollack**



February 23, 2015

Evolution of Mercury Control For Coal Fired Power Plants

Early 2000



R&D/Competition



Today



- Non Brominated Carbon
- Injection Rates > 5#/MMACF

- Treatment Cost Greatly Reduced
- Injection rates reduced 3-5 X
- Far more options to achieve compliance



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Evolution of Mercury Control For Coal Fired Power Plants

Early 2000



R&D/Competition



Today



Plant Configurations	Coal Types	Oxidants	Re Emission Chemicals	Sorbents	Locations
Wet Scrubber	Bituminous	Calcium Bromide	5 different Sulfide Forms	Non Bromnated	Upstream APH
Dry Scrubber	Lignite	Calcium Chloride		Brominated	Down Stream APH
ESP	PRB	Hbr		Sulfur Tolerant	Upstream Scrubber
Baghouse				Concrete Friendly	
				Other Enhanced	



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The Basics – How is Mercury Removed?

Oxidation



Adsorption/Absorption



Oxidant must be present (Cl_2/Br_2)
- HCl/HBr from Coal or added

Requires an active catalyst surface
- SCR Catalyst
- Fly Ash constituent surfaces
- Sorbent surface

Favored at Lower Temperature
Reducing agents can inhibit oxidation
- NH_3 , CO, H_2O

Fly Ash LOI
Sorbents
Scrubber Solution
Lime in Dry Scrubbers

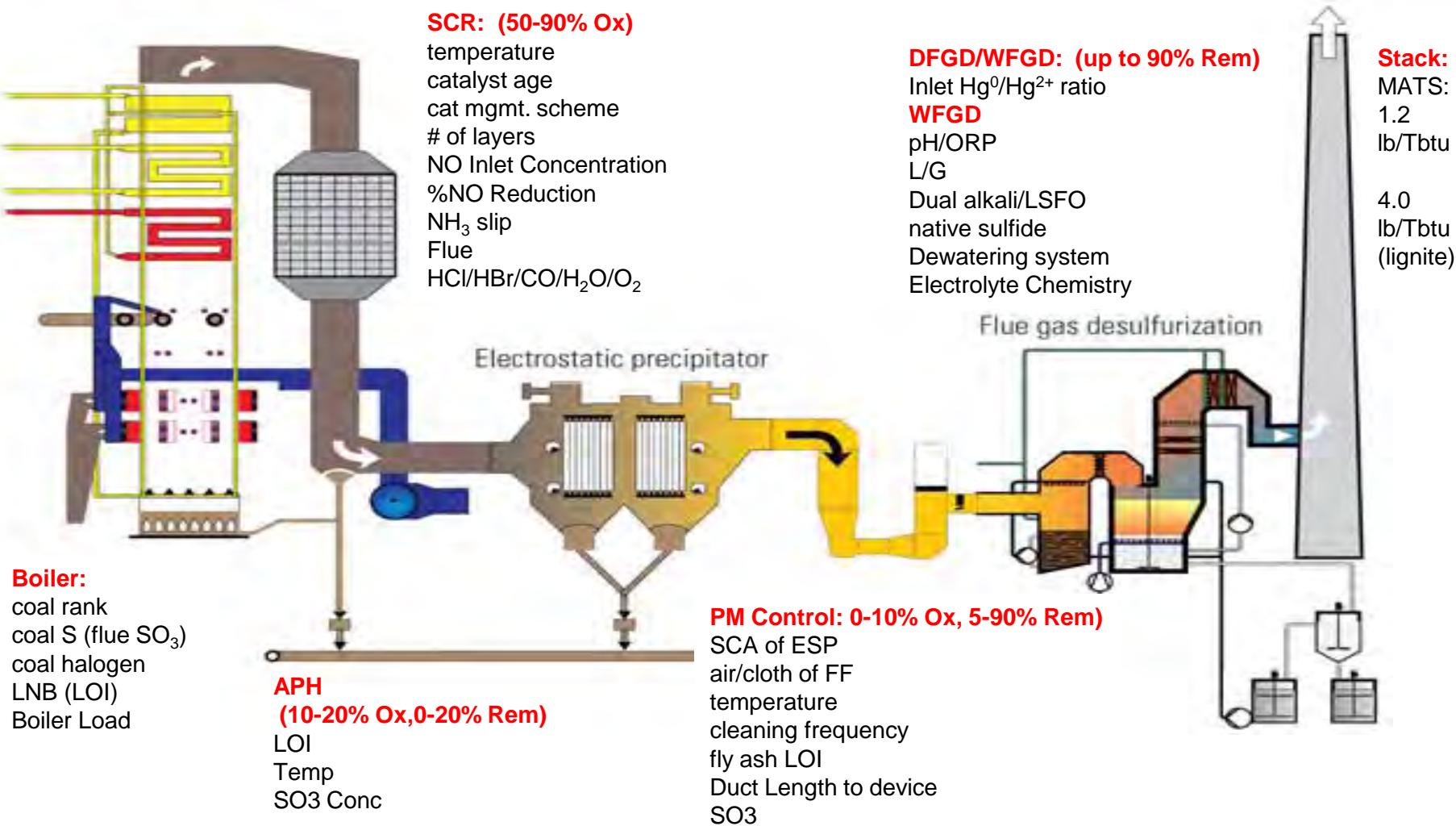


Solution Selection Matrix

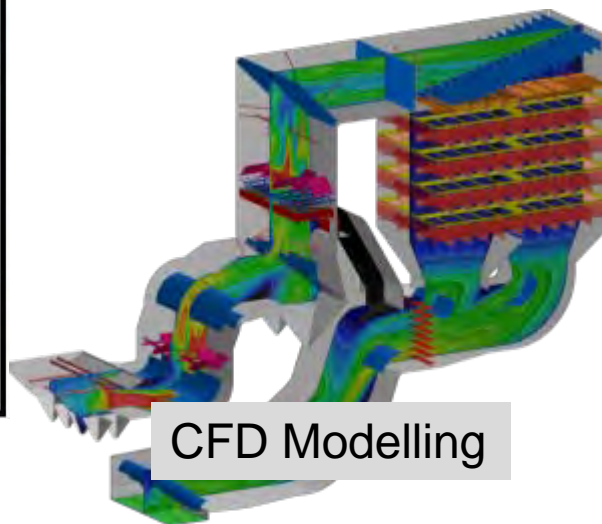
NO Control	SO2 Control	Particulate Control	Coal Type	Mercury Solution	Number of Units	Average Unit Size (MW)	% of Total	Name Plate Capacity (MW)
SCR	Dry Scrubber	Baghouse/ESP	Sub	Co Benefit-Oxidation	16	447	1.6	7146
SCR	Dry Scrubber	Baghouse/ESP	Bit	Co Benefit-Oxidation	19	414	1.9	7860
SCR	Wet Scrubber	ESP/Baghouse	Bit	Co Benefit-Oxidation- Re Emission	134	588	13.5	78737
SCR	Wet Scrubber	ESP/Baghouse	Sub	Co Benefit-Oxidation- Re Emission	22	354	2.2	15619
Total					328		33.0	
No SCR	Wet Scrubber	ESP/Baghouse	Sub	Oxidation-ReEmission-Enhanced Non Brominated	61	295	6.1	30546
No SCR	Dry Scrubber	Baghouse/ESP	Sub	Oxidation-Enhanced Non Brominated	27	439	2.7	11854
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No SCR	None	ESP	Bit	Sulfur Tolerent/DSI Brominated	252	140	25.4	35212
No SCR	Wet Scrubber	ESP/Baghouse	Bit	Co Benefit - Re Emission - Sulfur Tolerent	122	295	12.3	35949
No SCR	Dry Scrubber	Baghouse/ESP	Bit	Co Benefit - Sulfur Tolerent	15	289	1.5	4339



Factors affecting co-benefit effectiveness



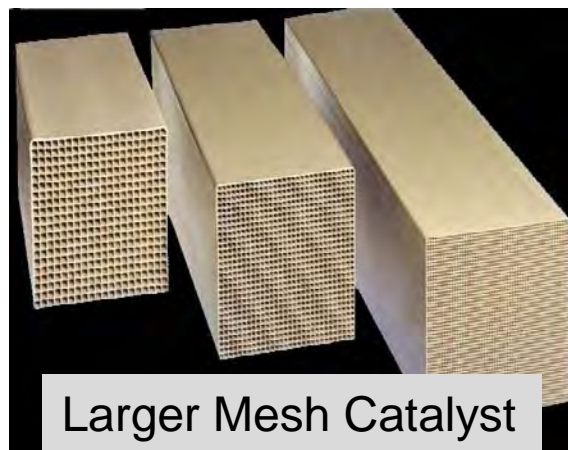
Maximizing SCR CO BENEFITS: MAINTAIN THE REACTOR



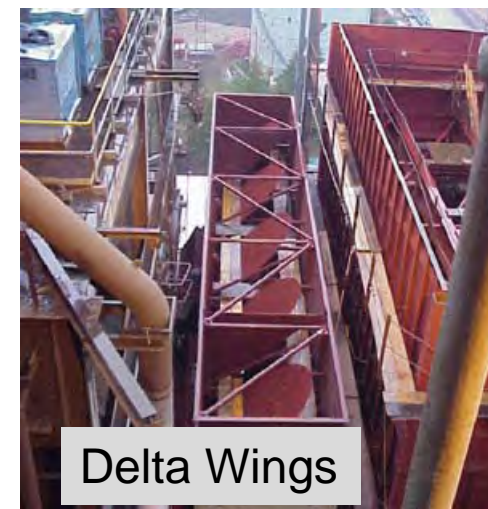
Ash Sweepers



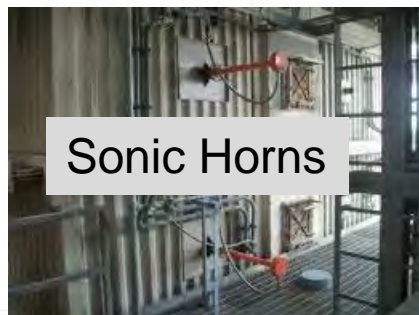
LPA Screens



Larger Mesh Catalyst



Delta Wings

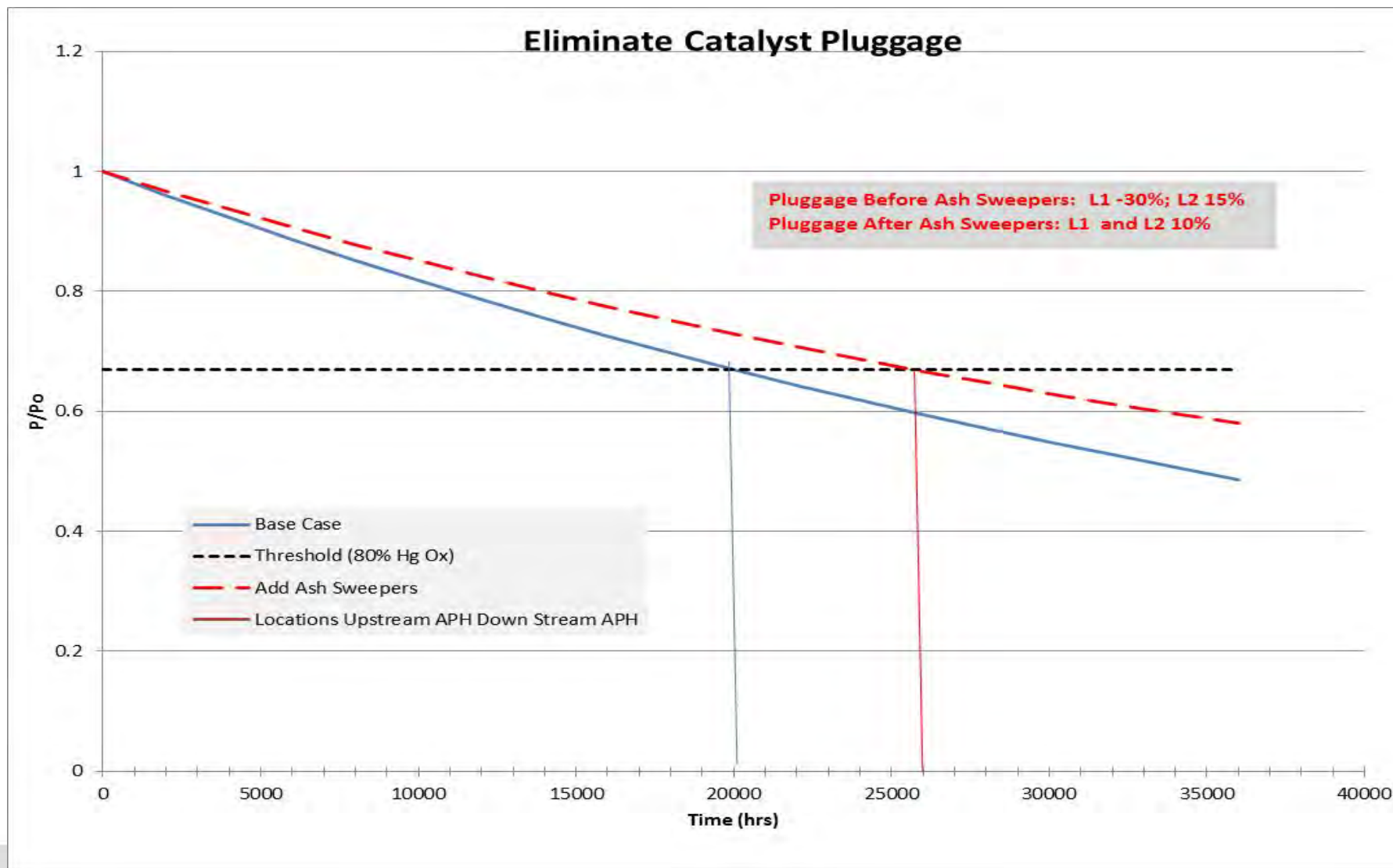


Sonic Horns

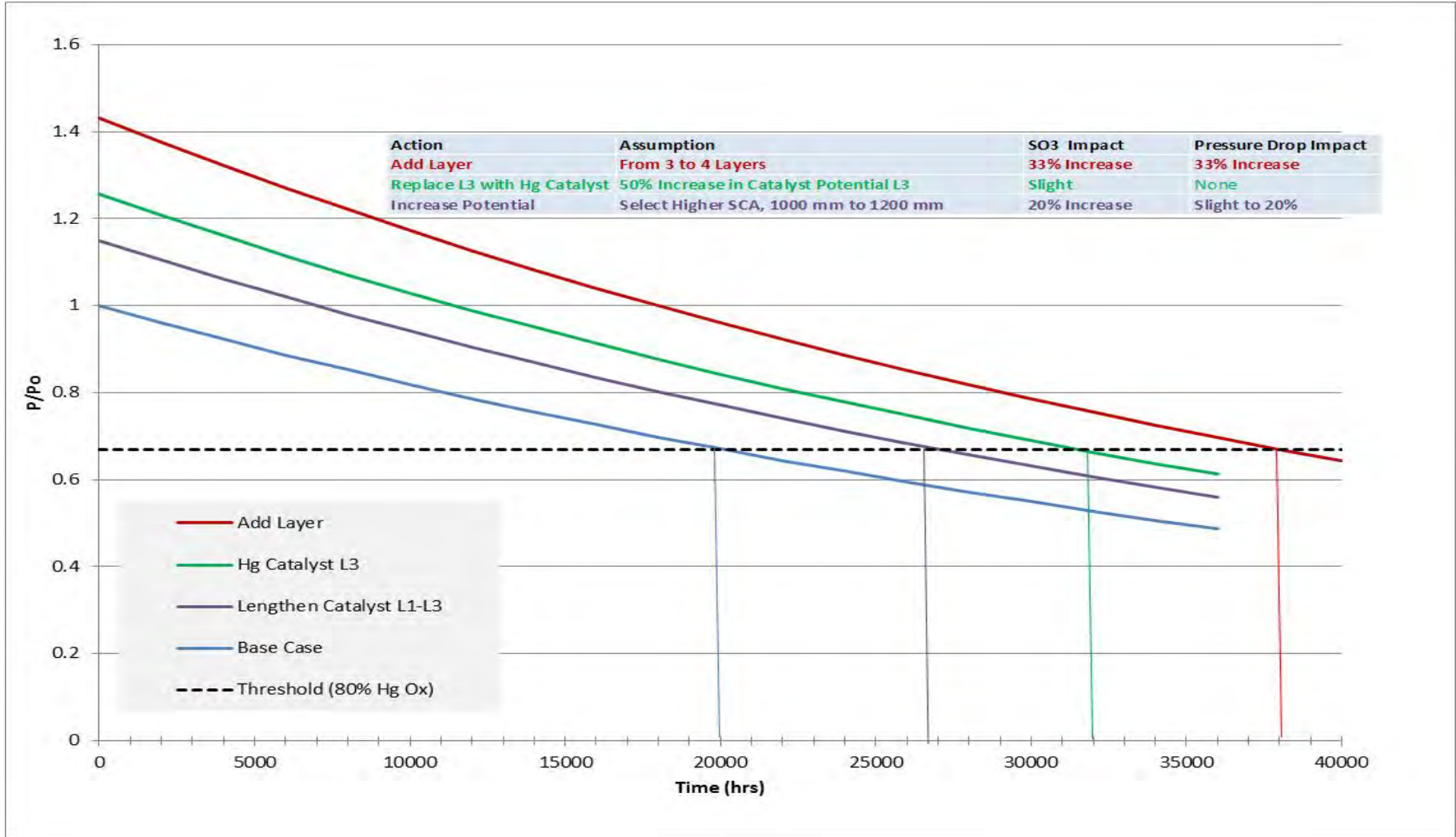
Soot Blowers



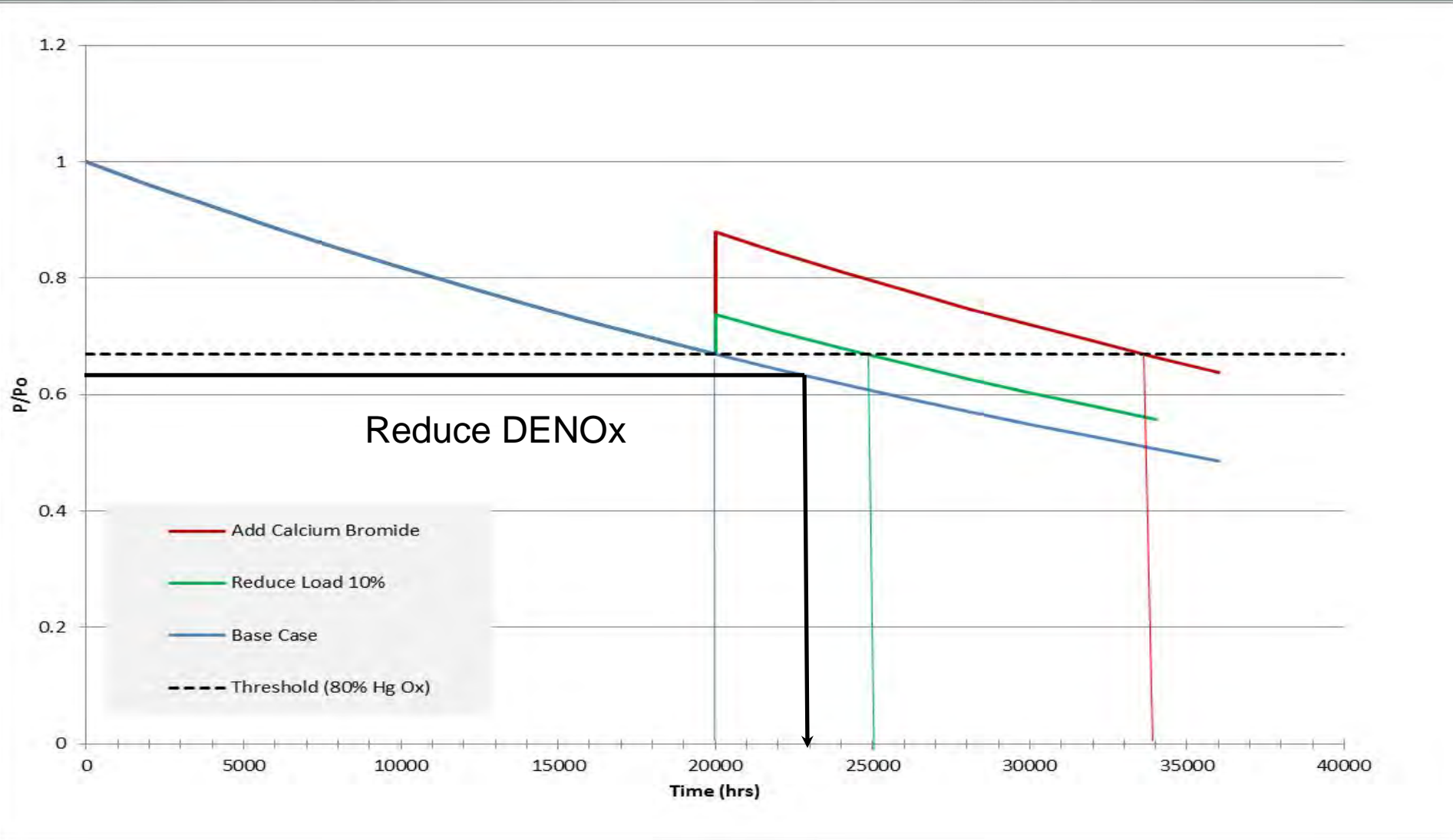
Maximizing SCR CO BENEFITS: MAINTAIN THE REACTOR



Maximizing SCR Co Benefits : Add Potential



Extending SCR Oxidation Performance In Between Outages



Oxidants



NO Control	SO2 Control	Particulate Control	Coal Type	Mercury Solution	Number of Units	Average Unit Size (MW)	% of Total	Name Plate Capacity (MW)
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Oxidants; how they work and options

- Convert Elemental Hg to Oxidize Hg in boiler and/or across SCR.
 - Requires Hg capture mechanism (i.e. Sorbent, LOI, Scrubber)
 - Generally not effective for bituminous coals unless SCR is present

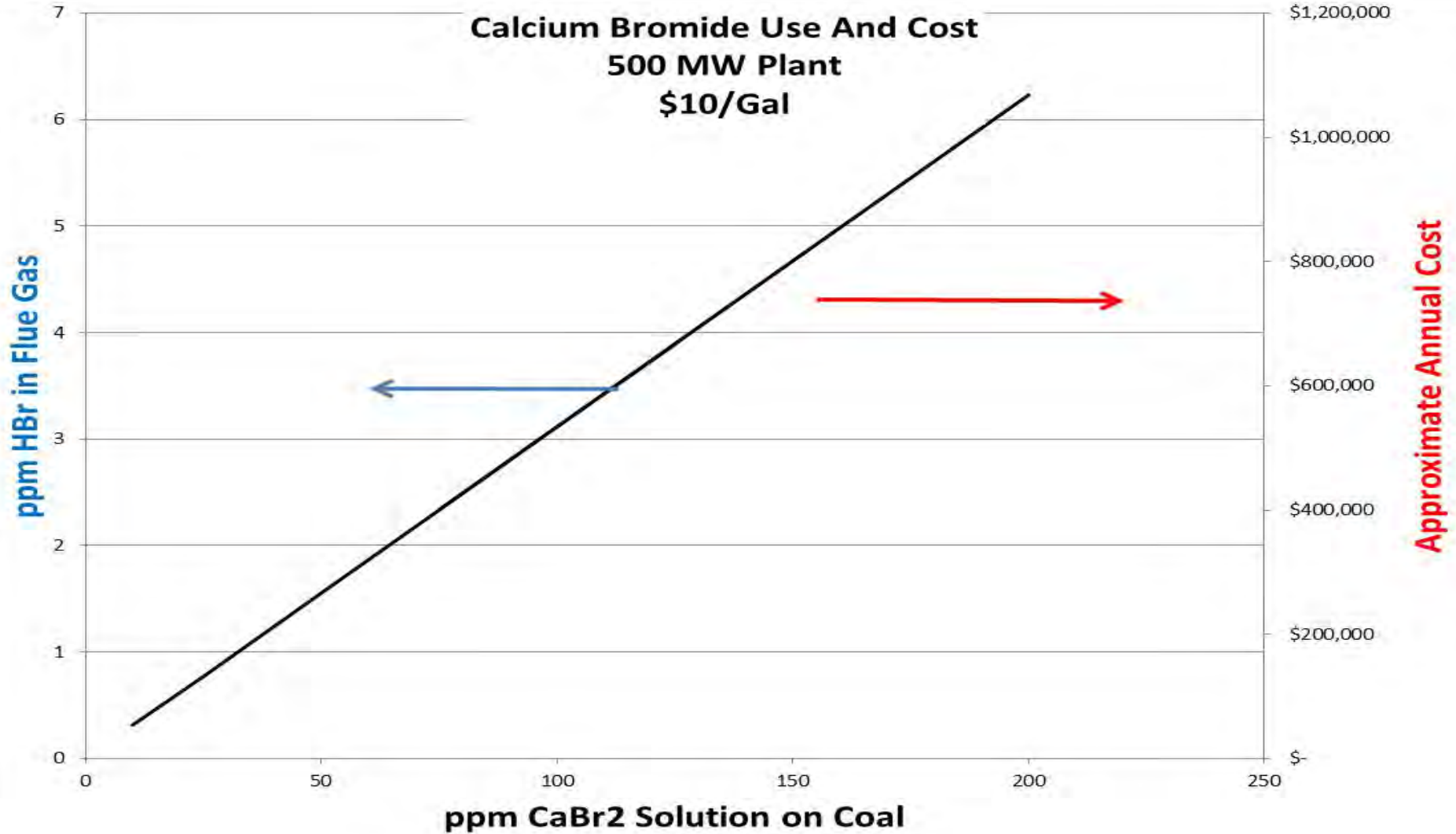
- Halide Salts decompose to form Halide Acid (HCl, HBr)
 - Added to coal in salt form
 - Added to Flue gas upstream of SCR in Halide Acid form.

- HBr is more active than HCl (1-5 ppm vs 30-50 ppm in Flue Gas)
 - 500-900 ppm CaCl₂ Soln on Coal (CaCl₂: \$.3-\$.6/gal)
 - 20-150 ppm CaBr₂ Soln on Coal (CaBr₂: \$ 8- \$13/gal)

- Air Preheater Basket Corrosion has been observed.
 - Depending on concentration, HBr dew point usually ~110 °F
 - Likely is reached due to air leakage.
 - Many Section 45 (tax credit) Users have upgraded to coated baskets
 - Recent studies show corrosion rate increases rapidly above 50 ppm Soln.



Oxidants – Low Operating Cost



Scrubber Re-Emission Additives

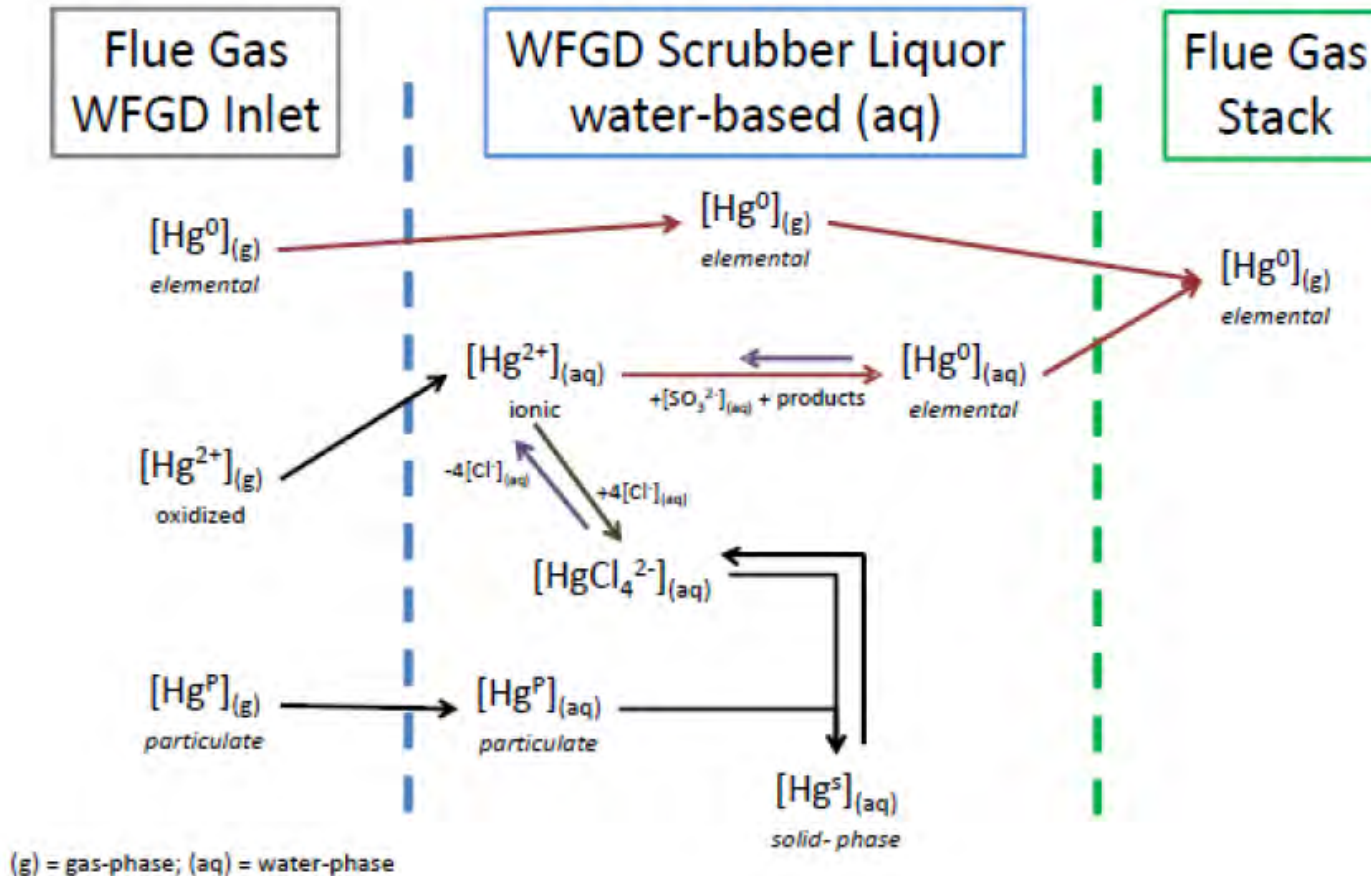


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WFGD Hg re-emission mechanism

- **Mechanism** (more information at: Institute of Clean Air Companies (ICAC) white paper "Improving Capture of Mercury Efficiency of WFGDs by Reducing Mercury Reemissions" June 2014);
http://c.ymcdn.com/sites/www.icac.com/resource/resmgr/Standards_WhitePapers/ICAC_Reemission_Paper_v23_Fi.pdf



WFGD Hg re-emission additives for its control

- Sulfide Additives: based on precipitation of $\text{Hg}^{2+}_{\text{aq}}$ as HgS (one of most insoluble compounds)
 - Inorganic sulfide
 - Organic sulfide
 - Organic compounds containing nitrogen and sulfur
 - Organic compound containing oxygen and sulfur
 - Low molecular weight sulfur-containing polymers
- Activated Carbon: based on surface adsorption of $\text{Hg}^{2+}_{\text{aq}}$
 - Usually added to the recirculation line (can be added to the flue at the inlet)
 - Dewatering system is also modified for separation



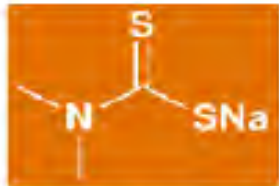
Examples of sulfide-bearing scrubber additives



Inorganic Sulfides
Sodium bisulfide



Organic Sulfides
polythiocarbonate, disodium salt



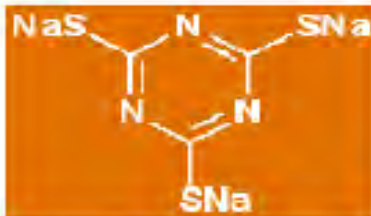
Organic with nitrogen and sulfur
Dimethyl dithiocarbamate



Organic with oxygen and sulfur
2,3-dimercaptopropanol



Organic with oxygen and sulfur
mercaptoacetic acid



Organic with nitrogen and sulfur
trimercaptotriazine



Low molecular weight polymers with sulfur
polydithiocarbamate polymers



WFGD additives: dosage, cost and balance of scrubber

- Dosage is scrubber and compound specific and requires field testing
- Each scrubber behaves differently and dosage can vary greatly
- Treatment costs range from \$200,000 to \$1,000,000/year for a 500 MW Plant
- For inorganic sulfide (e.g. NaHS) rule of thumb is about 50-80 lb of active compound/hour for a 500 MW scrubber
- Other sulfides (organic) cost are proprietary and needs to be provided by their vendors
- Balance of WFGD refers to how the precipitated Hg is separated in the dewatering system and the effect on oxidation of scrubber
 - Crystalline size of precipitated solid Hg is very important
 - Usually precipitated Hg is in fine solids
 - The over flow of the secondary hydroclone can be filtered to separate solid Hg
 - Design of dewatering system can be optimized
 - For forced oxidation system, sulfite to sulfate oxidation needs to be monitored closely



Sorbents



No SCR	Wet Scrubber	ESP/Baghouse	Sub	Oxidation-ReEmission-Enhanced Non Brominated	61	295	6.1	30546
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				Total	348		35.0	

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Sorbents

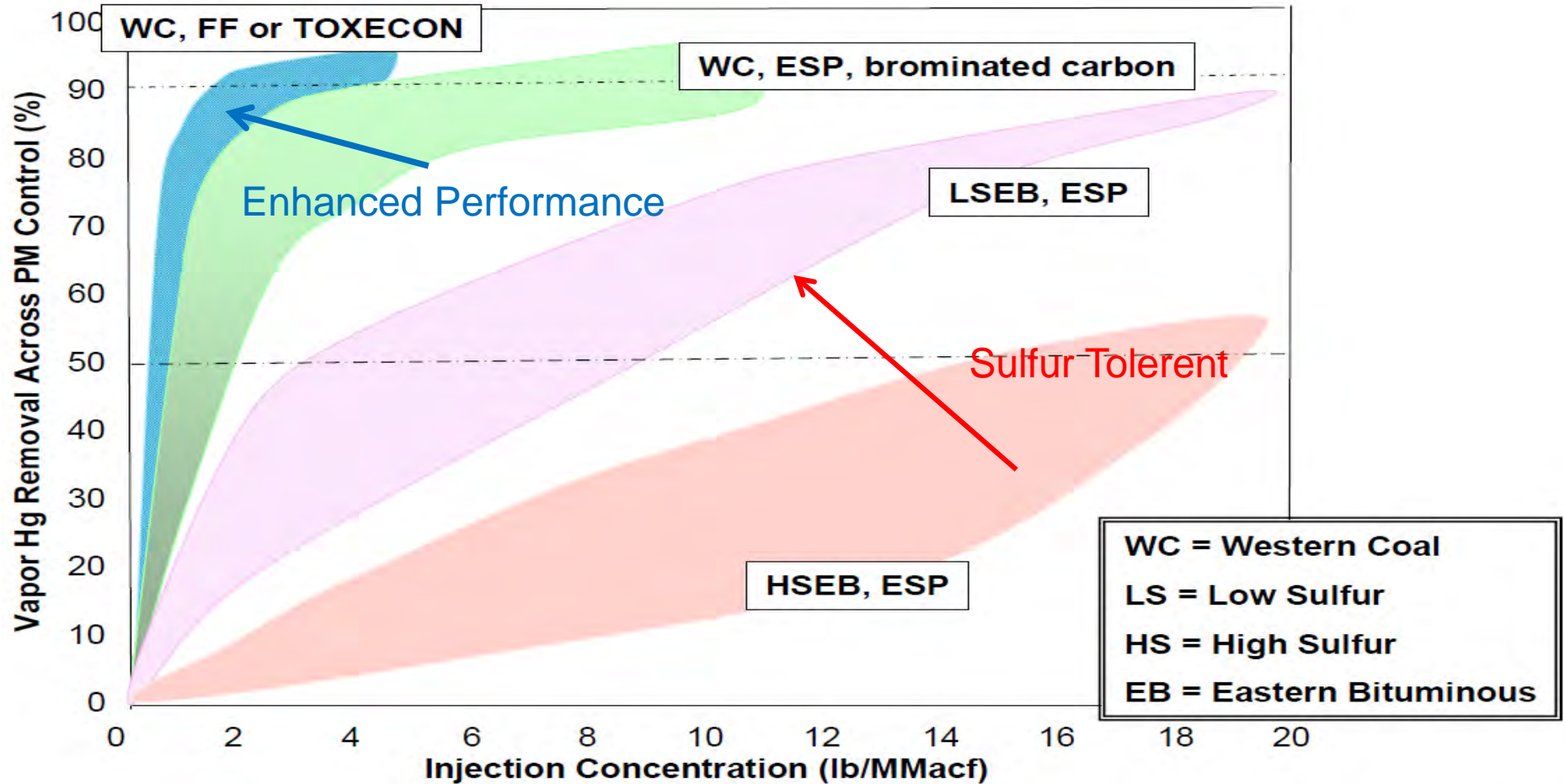
- Required to remove oxidized Hg.
- Non Brominated Carbon
 - Require Oxidant (Calcium Bromide) to be effective
 - Used almost exclusively with PRB Coals
- Brominated Carbons
 - Bi Functional – Oxidize and Remove Hg
 - Two basic types – Gas Phase and Bromine Salt.
 - Generally used for Bituminous coals where oxidants are not effective
- Cost is approximately \$1MM/Year at \$1/lb for a 500 MW Plant Injecting 1#/MMACF.



Specialty Advanced Sorbents

Formulation Changes from base non brominated and brominated

Typically particle size and base material but may include additives



Specialty or Enhanced Sorbents; Cont'd

- Concrete Compatible activated carbon
 - Allow for sale of fly ash (freeze/thaw capability of concrete)
 - Finer pore structure to prevent adsorption of concrete Air-Entraining Admixtures (AEA; added to created bubbles).
 - Most carbon sorbents can be manufactured as concrete compatible

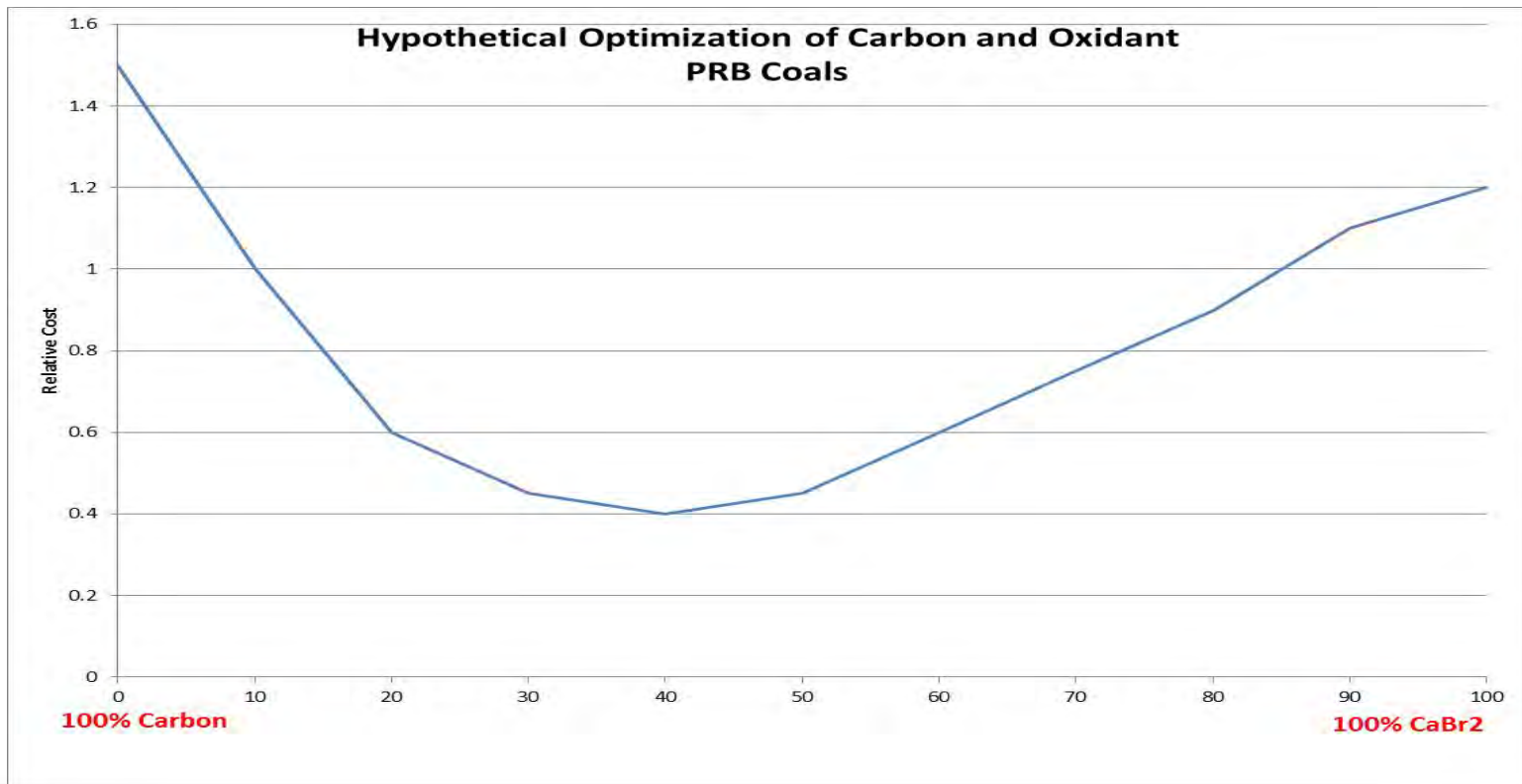
- Non Carbon Sorbents (e.g. Amended Silicates™)
 - Inherently concrete compatible (do not adsorb AEA)
 - Appears to work effectively in Dry Scrubbers.
 - More data as to its effectiveness for ESP and Baghouse applications needed

- Enhanced Sorbent Economics
 - Feed system can be sized ½ to ¼ smaller
 - Lower Trans cost (fewer deliveries)
 - Impact on Fly ash is greatly reduced



Oxidation-Enhanced Non Brominated

- Optimize both Oxidant and Carbon Sorbent
 - Targeting high oxidation rates with oxidant first can lead to over dosing
 - Oxidant and Sorbent work Synergistically (Carbon serves as catalytic Site)
 - Inject sorbent upstream of APH.



Oxidation-Enhanced Non Brominated

- DSI for SO₂ Control can dramatically increase use rates.
 - Consider Injecting DSI Down Stream of APH.

- ESP Conditioning can also increase injection rates.
 - May require Sulfur Tolerant Product.

- Capital Cost for Injection System \$1-\$2MM

- Cost for Baghouse and Scrubbers
 - Typical injection rates (< 50 ppm Oxidant and <.25 MMACF Carbon)
 - Total solution for a 500 MW plant <\$500,000/year.

- ESP Costs
 - Injection Rate 1-2 lb/MMacf
 - Total Solution for 500 MW Plant (\$1.3-\$2.4 MM/year)



Sulfur Tolerant/DSI-Brominated

- SO_3 Level will Influence Economics between DSI-Brominated and Sulfur Tolerant
 - Up to 20 ppm SO_3 Sulfur Tolerant (3-17#/MMACF)
 - Rates above 10 #/MMACF may overload ESP/Baghouse.
 - DSI is only solution above 20 ppm SO_3
- May consider injecting After APH
 - Lower SO_3 Levels



Final Thoughts: Navigating MATs Compliance

- Maximize Co-Benefits
 - Prevent catalyst plugging and tune AIG.
 - Maximize potential.
- No substitution for field trials
 - Every Plant is like a Snow Flake – No Two Plants are equal.
 - Testing cost is typically < 10% of annual treatment cost
 - Identify limiting mechanism (Oxidation, Re Emission, Ad/Absorption)
 - Evaluate 2-3 Products and obtain product/solution economics .
 - Select based on track record on similar Units.
 - Select experienced program manager and testing company,
- Retain samples from field trial for product Characterization.
 - Sorbents
 - Particle size (micron size spec)
 - Active additive amount and form (e.g. Bromination method)
 - Base material, i.e coal type for activated carbon
 - moisture content, ash content
 - Surrogate for Surface area/pore volume Iodine/butane #)
 - Scrubber additive
 - Dosage rate to eliminate re-emission (do not over dose)
 - Hg mass balance (where Hg ended up)
 - How easy to separate the Hg fraction





Questions?

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