

REINHOLD ENVIRONMENTAL Ltd.



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Mercury Mitigation – Update on Compliance Strategies and Technologies

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Disclaimer

This presentation includes general information on coal and coal-fired boilers intended for education and illustration purposes only. All information is provided “AS-IS” and without warranty or liability of any kind.

Training Road Map

- Fundamentals
- Review of operating plant configurations in US
- Key factors affecting mercury capture
- Overview of mercury control strategies in use
 - Technology basics
 - Review of strategies used for MATs compliance

Two Ways to Remove Mercury

▶ Adsorb Hg on particles

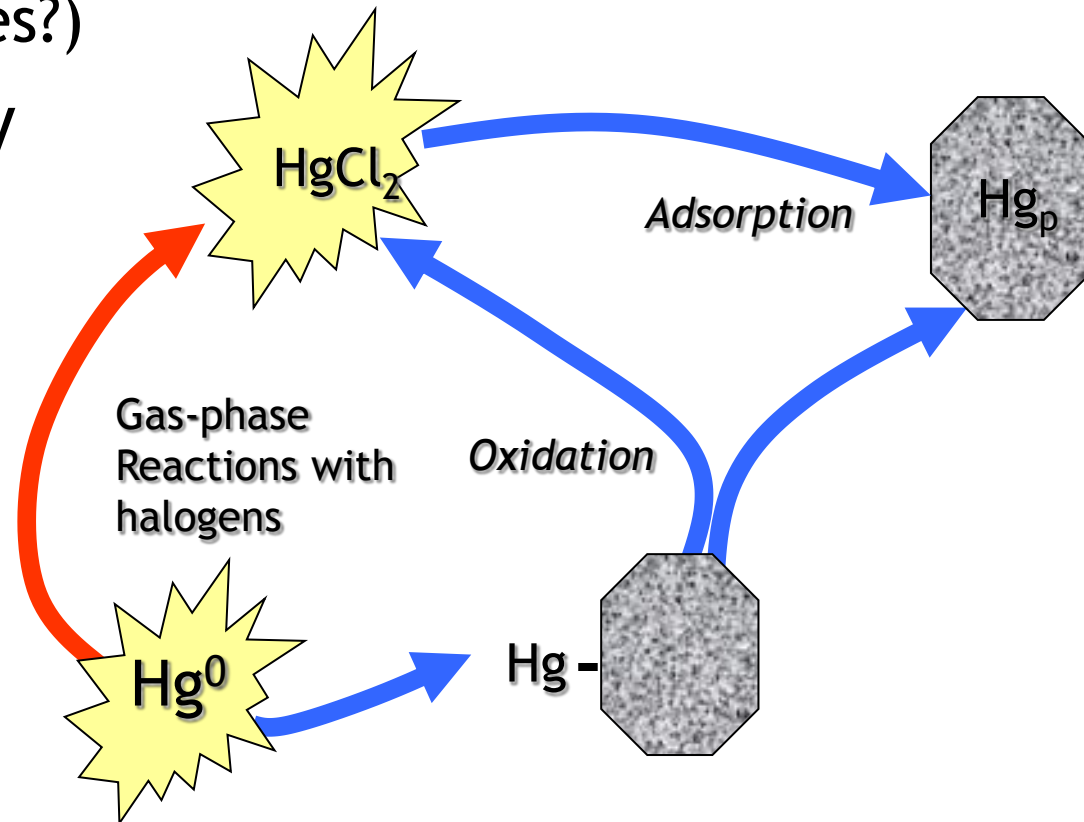
- ▶ Unburned carbon in fly ash
- ▶ Sorbent injection
- ▶ Fixed adsorption structures

▶ Absorb Hg (Primarily Hg^{2+})

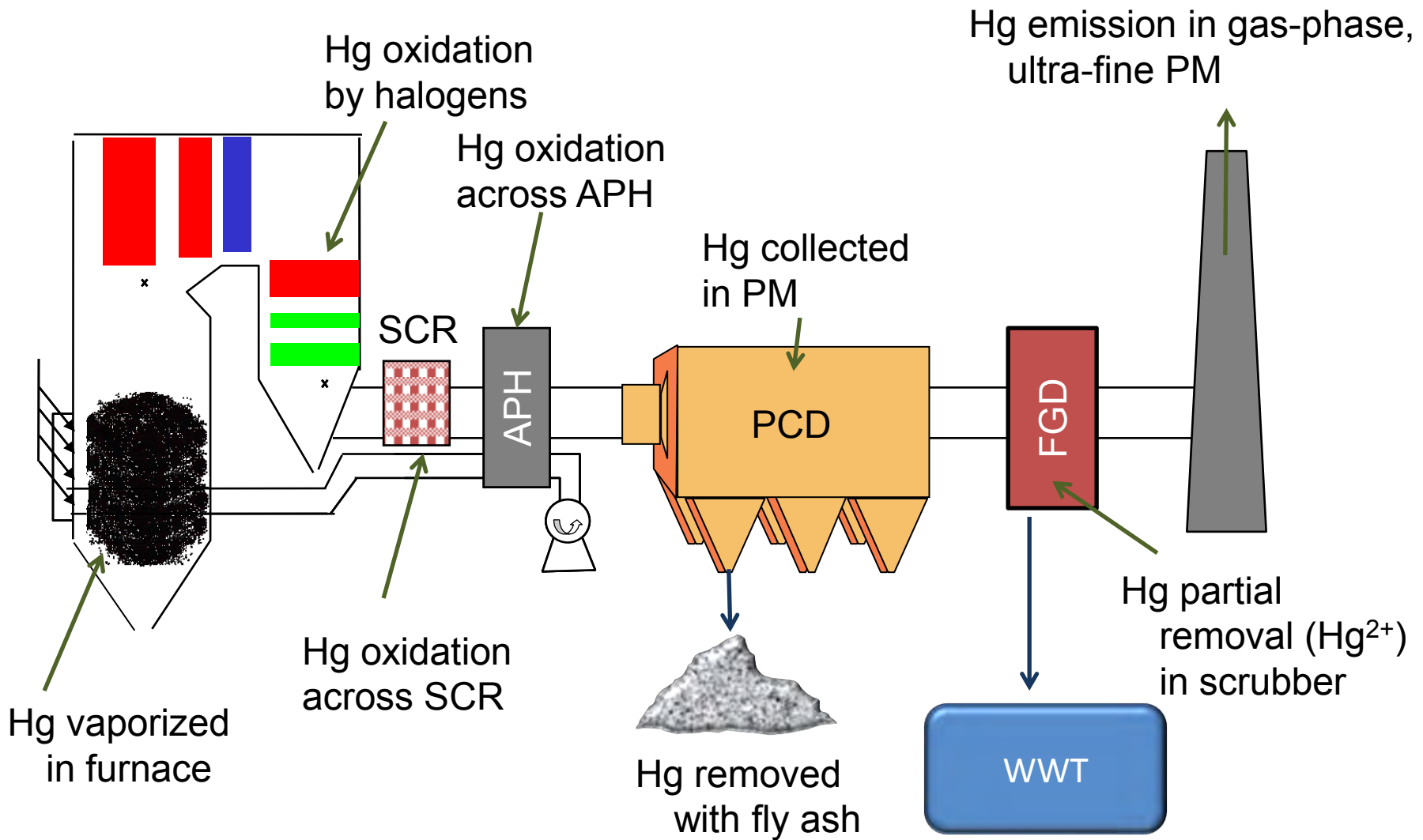
- ▶ Wet flue gas desulfurization (FGD) scrubbers
- ▶ Dry FGD scrubbers

What Do We Mean by Hg Speciation?

- ▶ Gas-phase mercury:
 - ▶ Elemental: Hg^0
 - ▶ Oxidized: Hg^{+2}
(HgCl_2 , other species?)
- ▶ Particulate mercury
 - ▶ Hg_p
 - ▶ Mercury (adsorbed on particles)



Fate of Hg in Coal-Fired Boilers



Primary Factors that Affect Mercury Emissions and Control Options

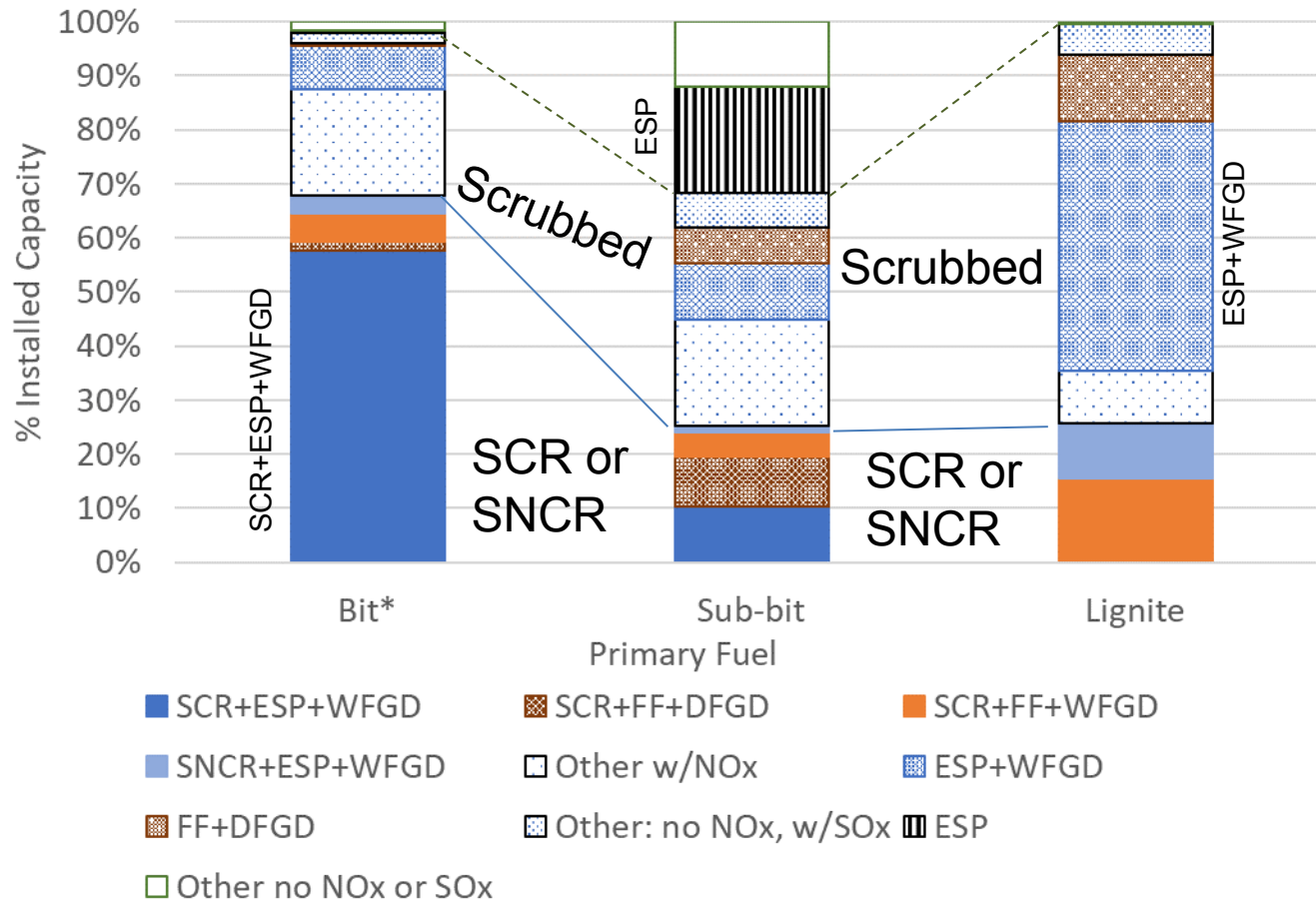
- Coal properties
 - Mercury, halogens, sulfur
- Air Pollution Controls
 - NO_x, SO_x, PM
- Other Considerations for Supplemental Controls
 - Economics
 - Balance-of-plant impacts
 - Environmental constraints (e.g. ancillary emissions or effluent discharges)

What Are Plants Doing?

- ▶ Now that MATS is in place, it's raining mercury data!
 - Plants in the US employ a variety of strategies to reduce mercury air emissions
 - We reviewed 11 months of US mercury emissions data for all coal-fired power plants reporting emissions
 - Information on the control technologies employed at specific plants can assess the efficacy of different control strategies



Comparison of Installed Controls By Generating Capacity

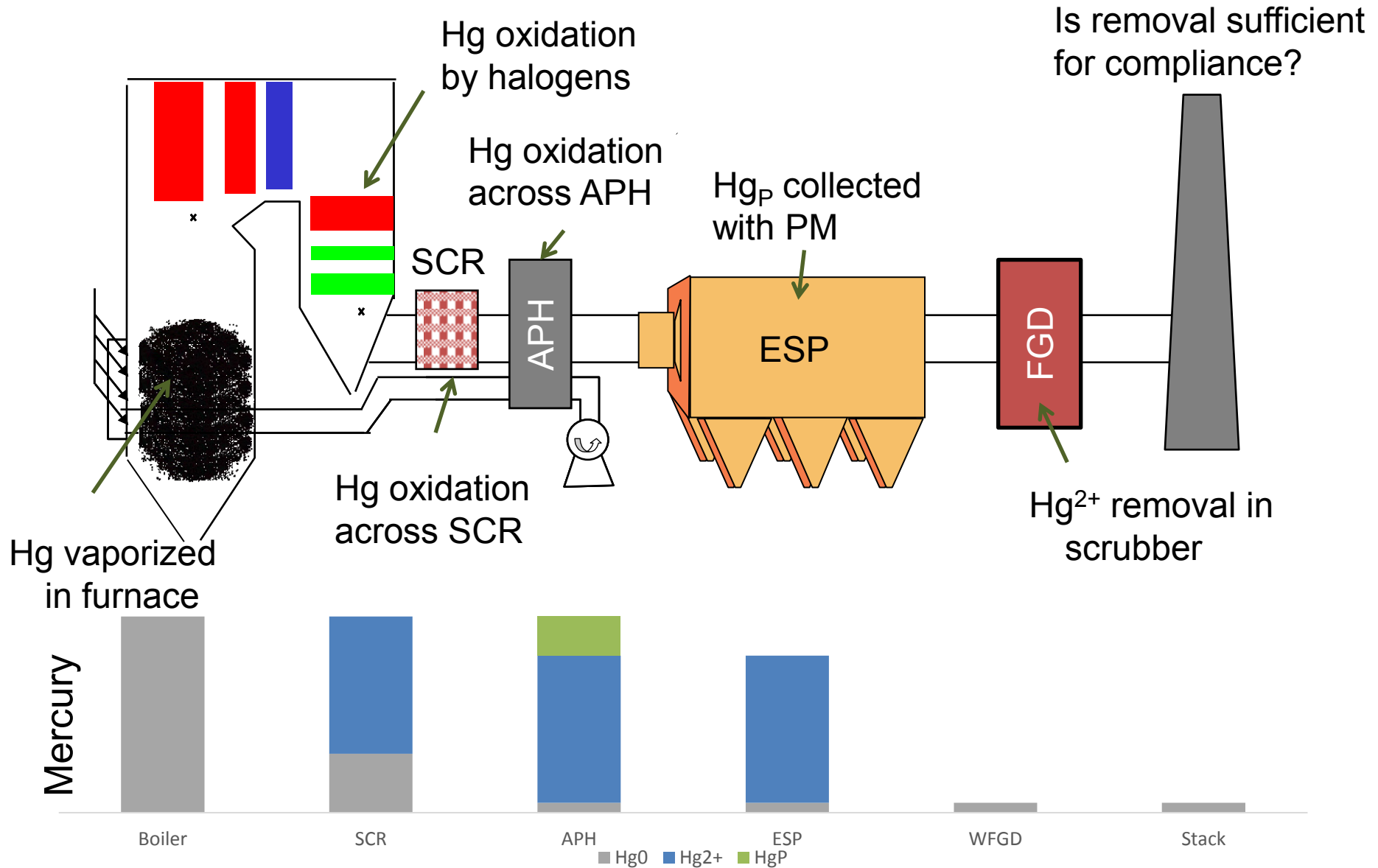


US: EPA Air Markets Program data

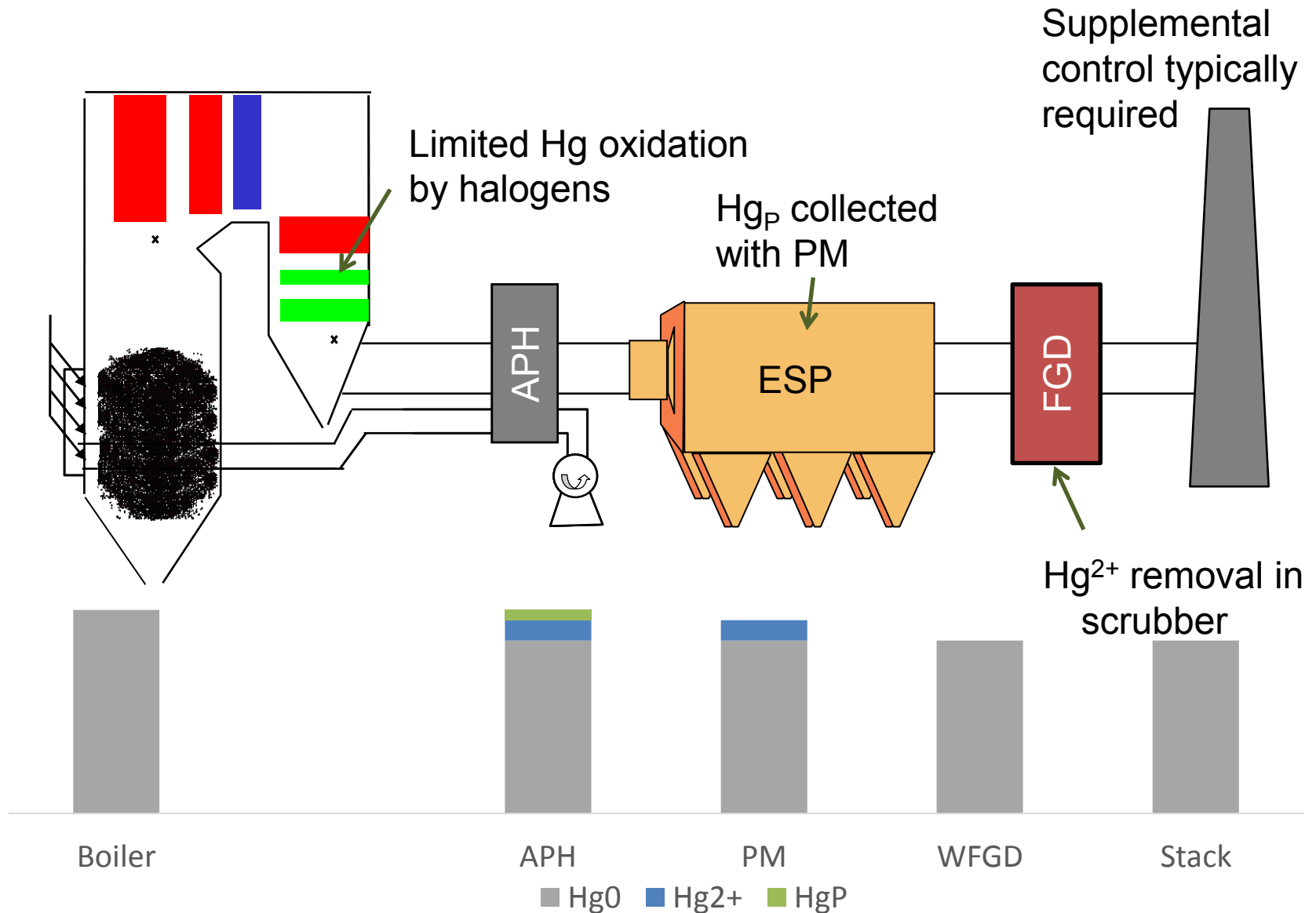
*Excludes western bit plants



Mercury Control: "Typical" Bituminous Plant

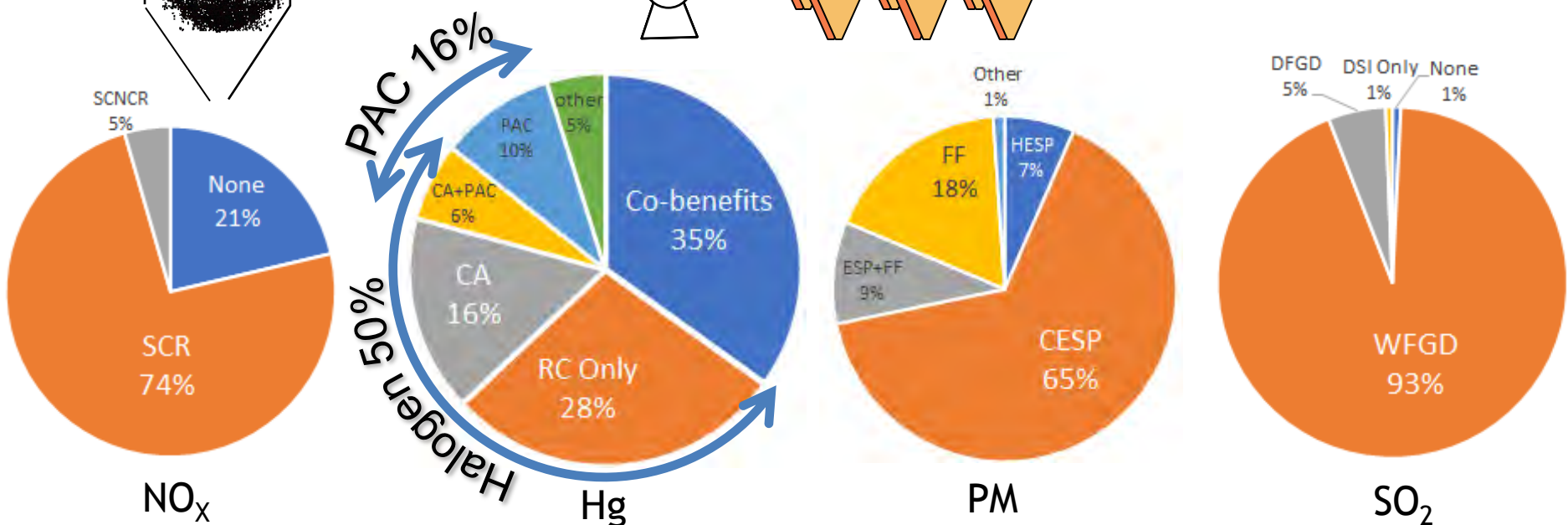
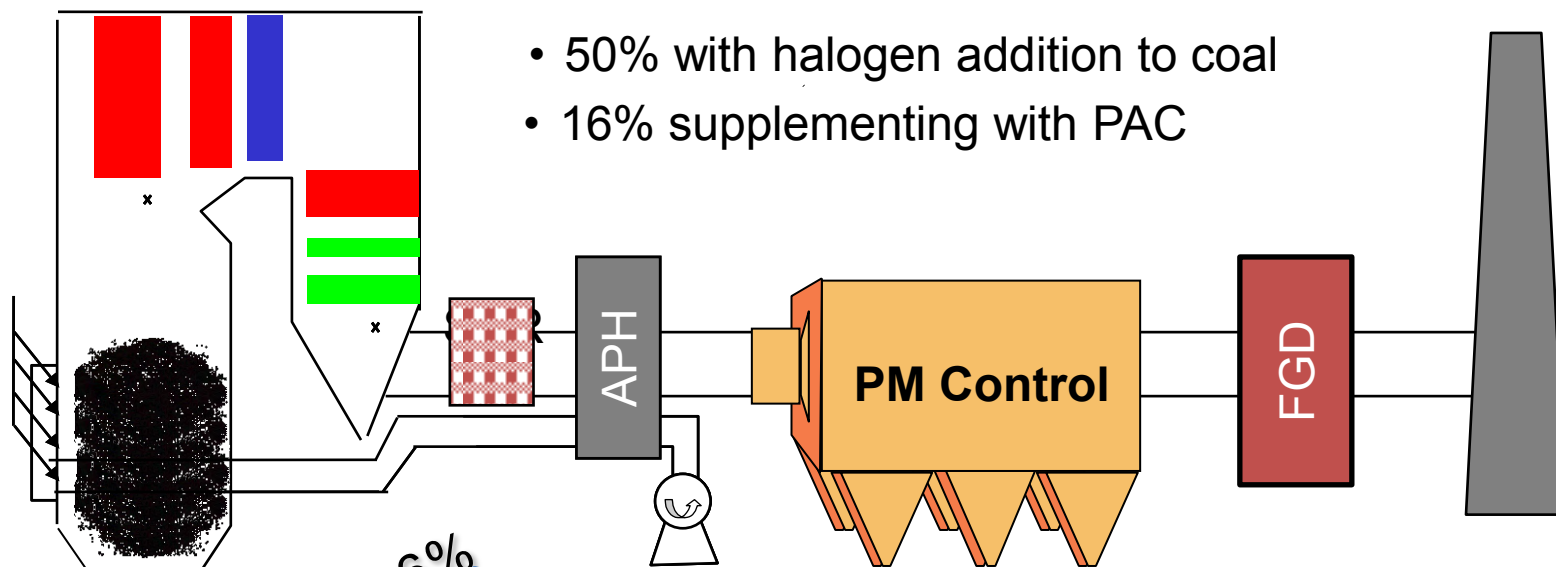


Subbituminous-Fired Plant with “Typical” APC

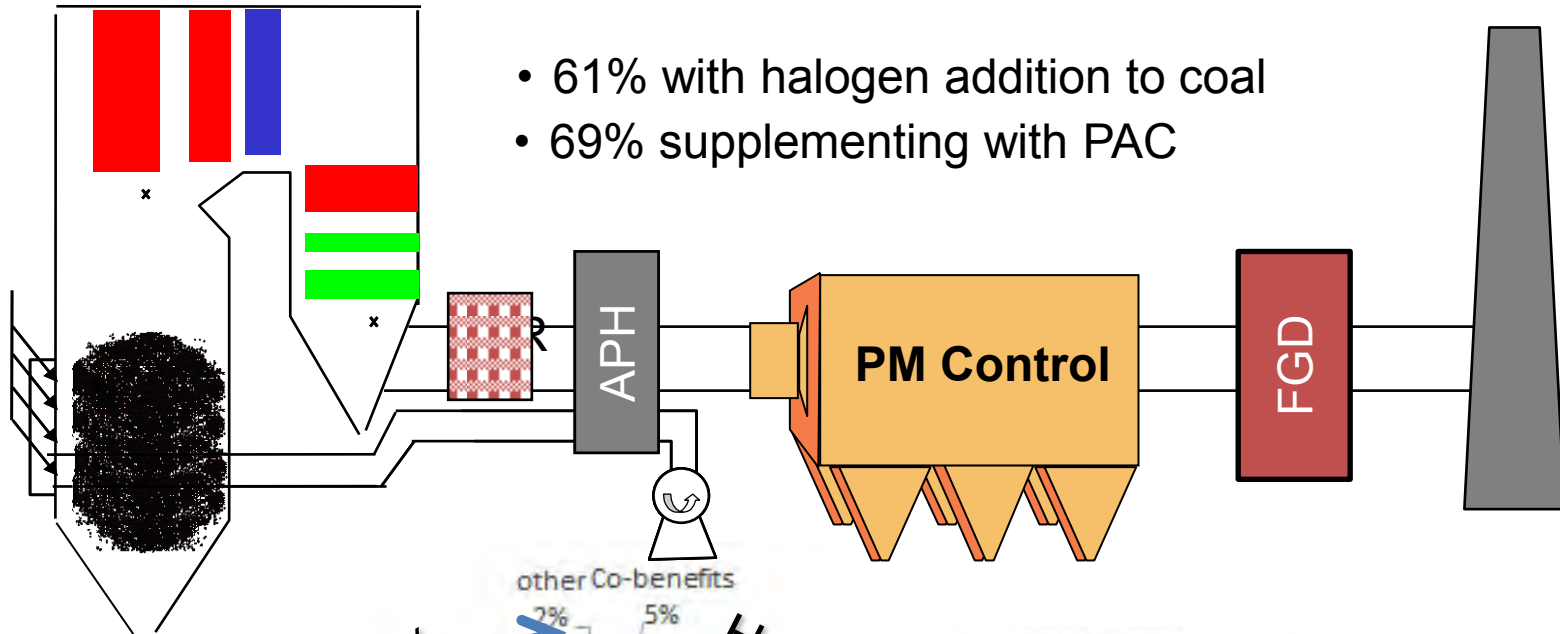


Mercury Controls Strategies: Bituminous Plants

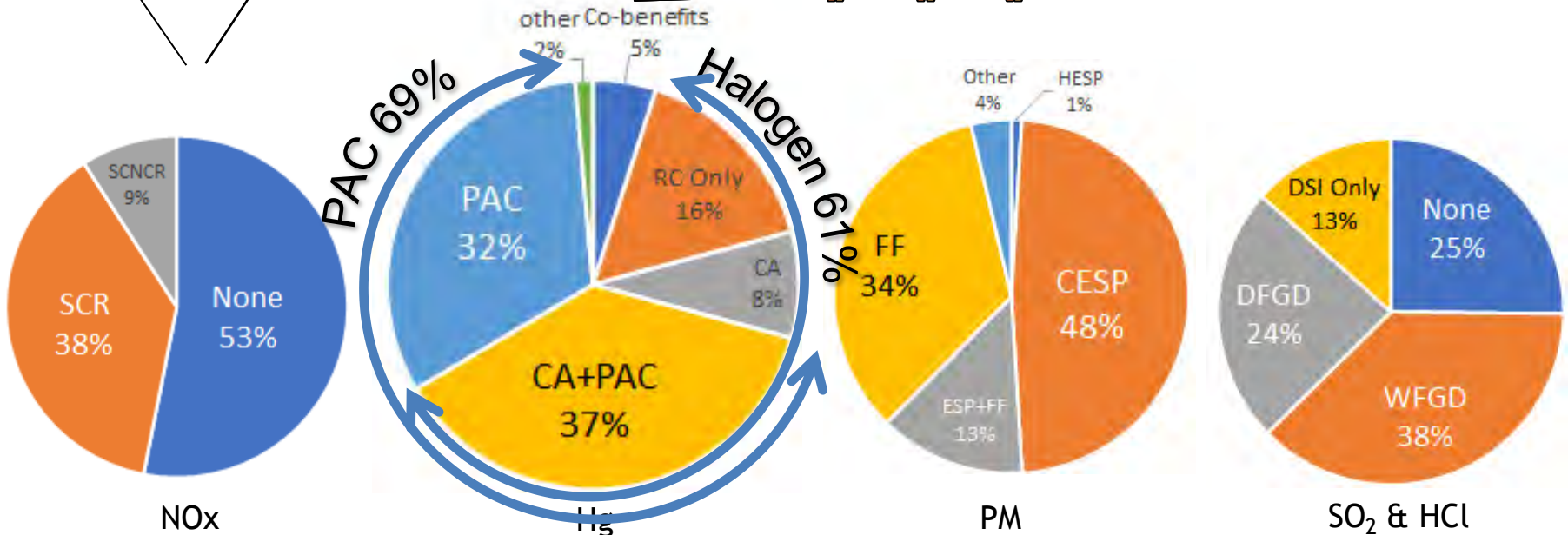
- 50% with halogen addition to coal
- 16% supplementing with PAC



APC Configurations: Subbituminous Plants



- 61% with halogen addition to coal
- 69% supplementing with PAC



Can Plants Rely on Co-Benefits Alone?

Success Factors

➤ Coal and combustion

- Mercury, halogen, sulfur, LOI

➤ SCR

- Lower = better: temperature, NH_3 , age, gas flow rate, CO , H_2O , SO_2
- Higher = better: halogen concentration, O_2
- Other: SCR type, SCR management scheme

➤ Particulate Controls

- Hg removed before WFGD: fraction of particulate-phase Hg (LOI, temperature, SO_3 , ESP SCA, FF cleaning)

➤ Scrubber

- Fraction of oxidized Hg at inlet, ORP, halogens, temperature, pH

YES:

35% of bituminous units and 5% of subbituminous units rely on co-benefits alone
All lignite plants report Hg controls

Mercury Control Strategies



➤ Use sorbents

- Powdered Activated Carbon (PAC)
- Brominated Activated Carbon (Br-PAC)
- Halogen or catalyst + PAC
- Use sulfur-tolerant PAC and/or DSI to mitigate SO_3 as needed
 - Caution: Don't lower SO_3 too far – it will affect ash resistivity and ESP performance
 - Caution: DSI will increase particulate load to ESP

➤ Increase “native” Hg capture

- Enhance Hg removal with unburned carbon through combustion modifications
- Blend fuels to enhance mercury control effectiveness
- Use oxidizing agents (e.g. coal additives) or catalysts to increase oxidized Hg

Halogens in US Coal

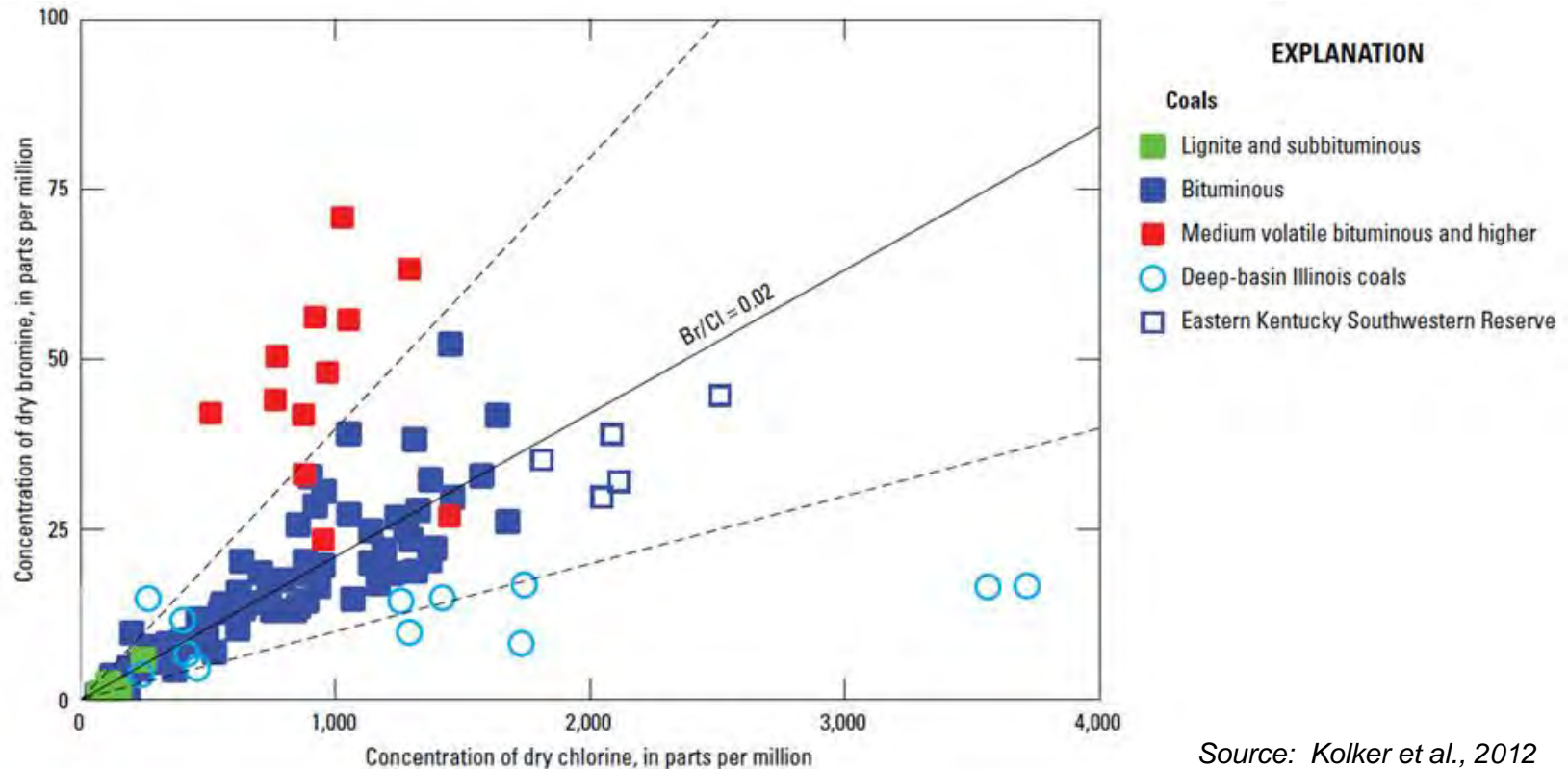
Chlorine

- Bituminous: 100-4,000 ppmw (dry)
- Subbituminous: <30 to 150 ppmw (dry)
- Lignite: 100-200 ppmw (dry)

Bromine

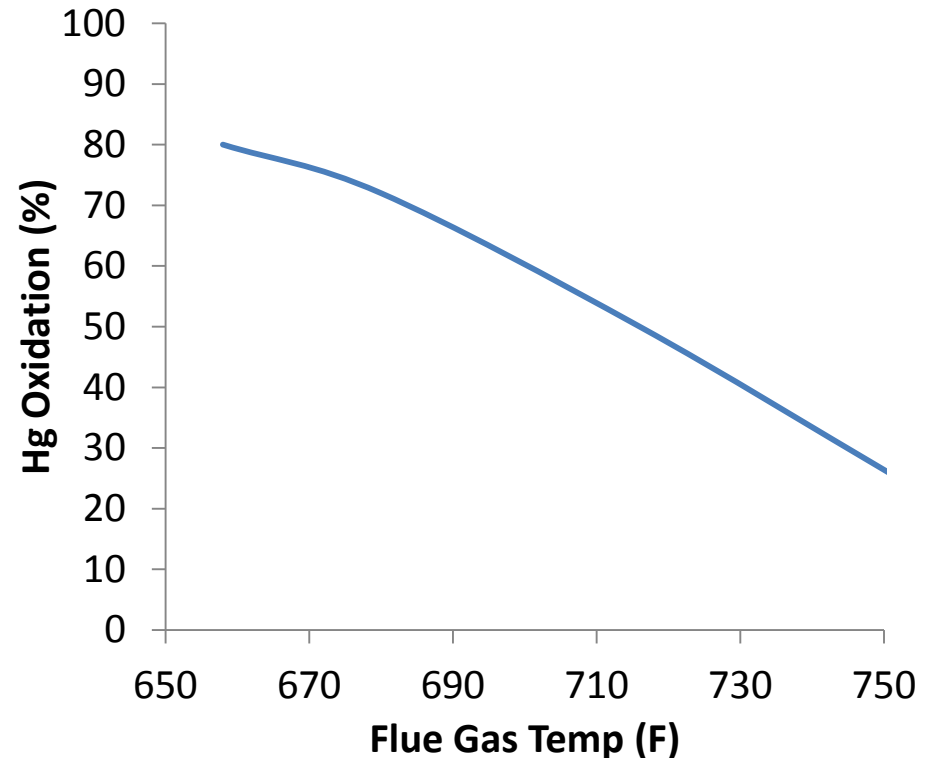
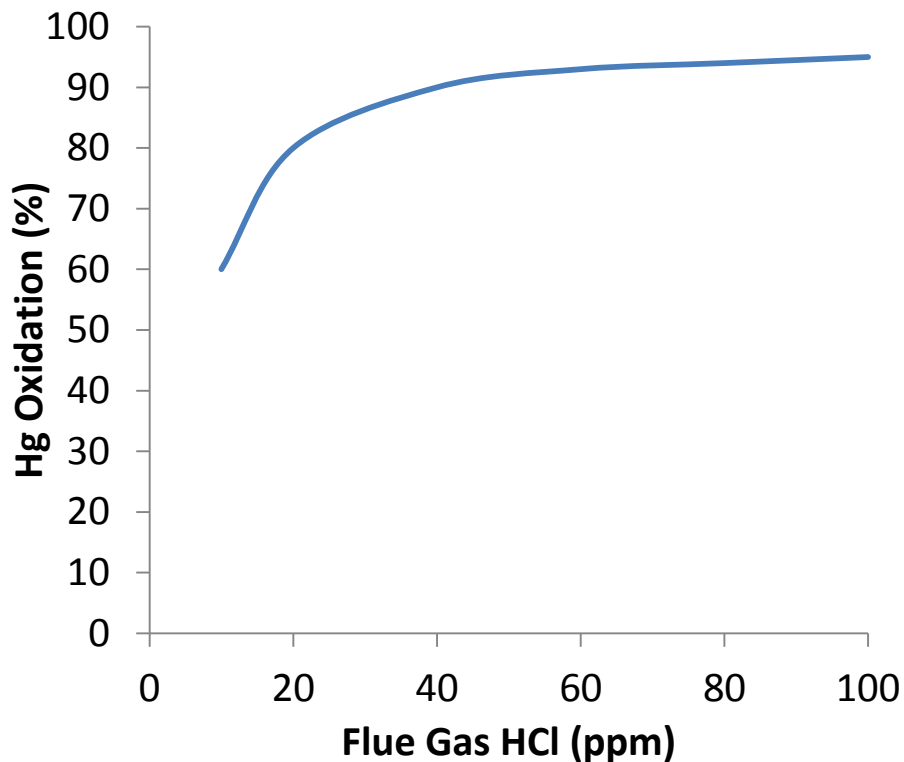
- Generally equal to 2% of chlorine content, with a range of 1-4%

Bromine in Coal



- Scatter-plot showing average chlorine (Cl) and bromine (Br) contents, in parts per million (ppm), for various ranks (grades) of coal produced in 110 US counties
- Contents of Br in coal are commonly about 2 percent of the Cl content ($Br/Cl = 0.02$), the ratio generally ranging from 1 to 4 percent (dashed lines indicate this range)

Factors Affecting Hg Oxidation Across SCRs



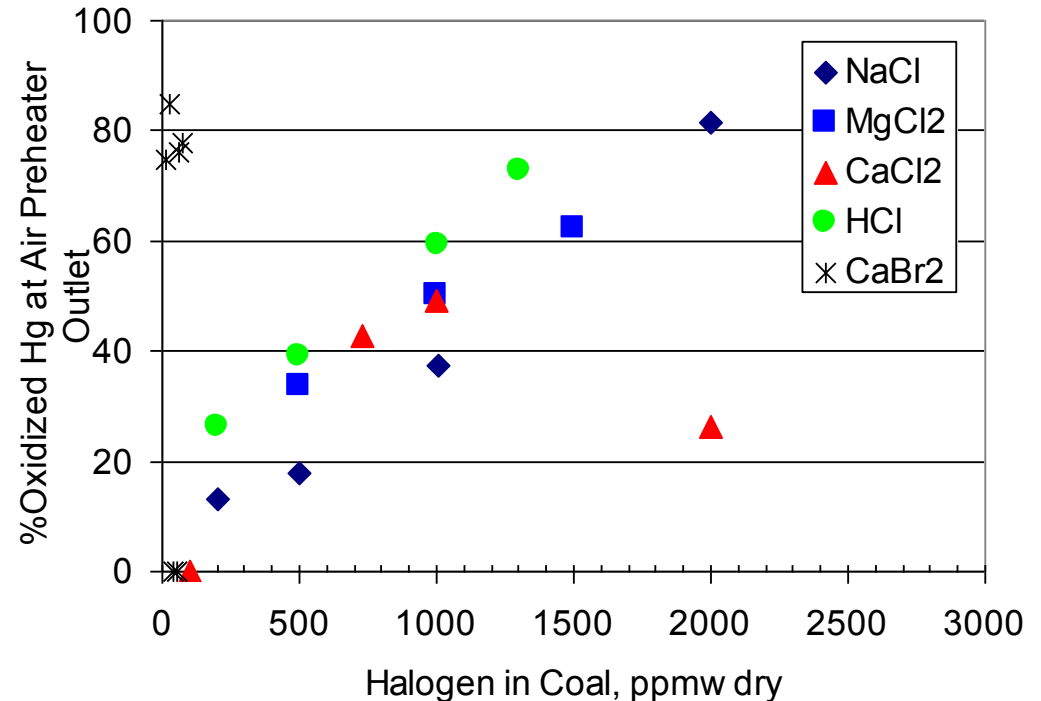
Higher temperature → Lower oxidation

Higher ammonia → Lower oxidation

Review of emissions data from several bituminous plants with SCR+WFGD do not show increased emissions during summer months

Opportunities for Hg Oxidation

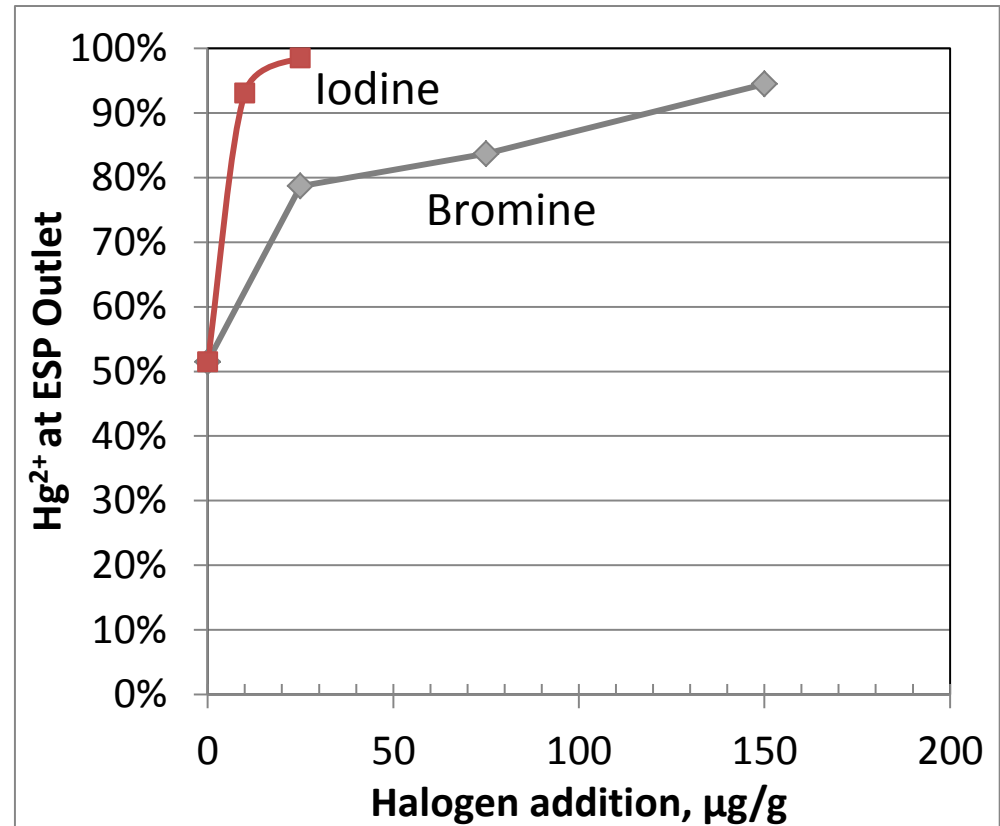
- Selective Catalytic Reduction (SCR)
- Particulate Control Devices
- How adding more halogens helps



- Bromine addition more effective than chlorine, lb per lb of coal
- Full-scale data from Dombrowski et al., 2006

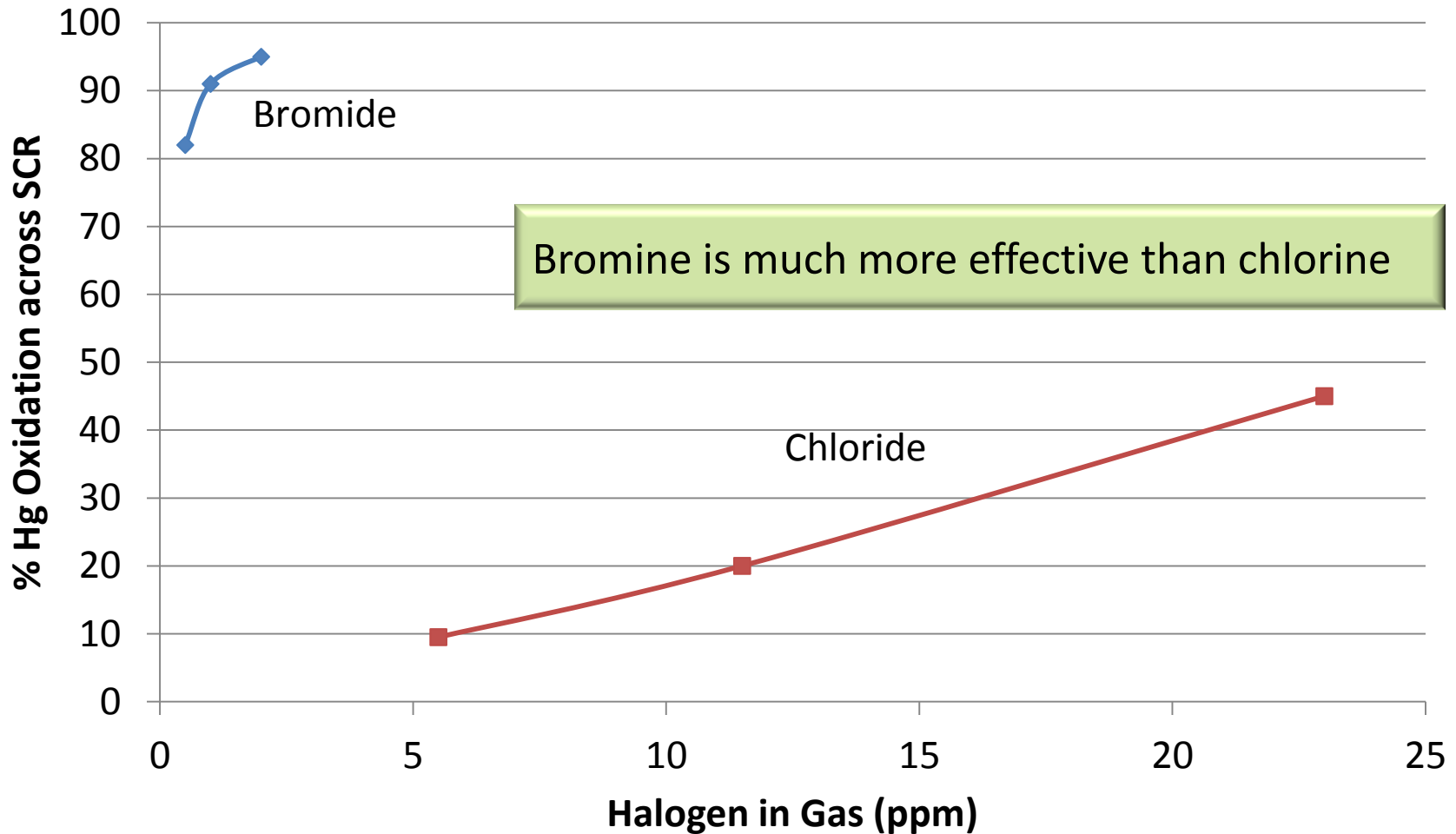
Opportunities for Hg Oxidation

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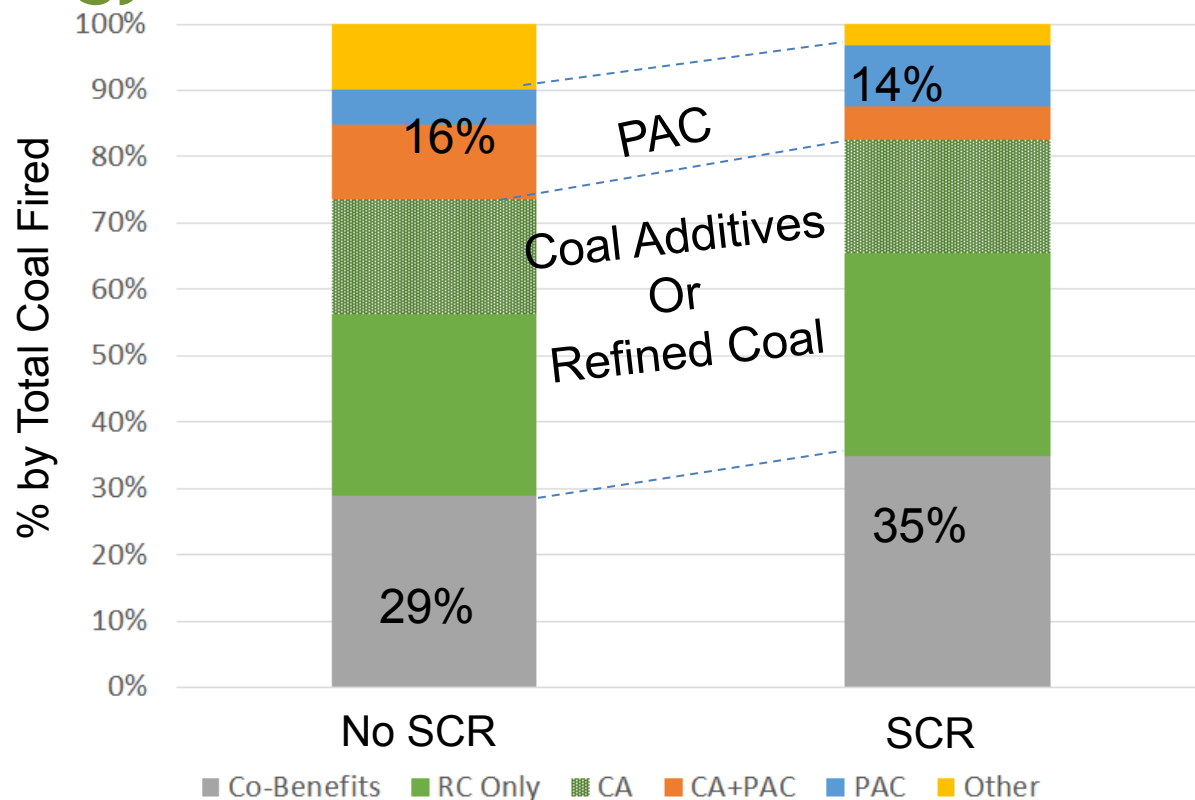
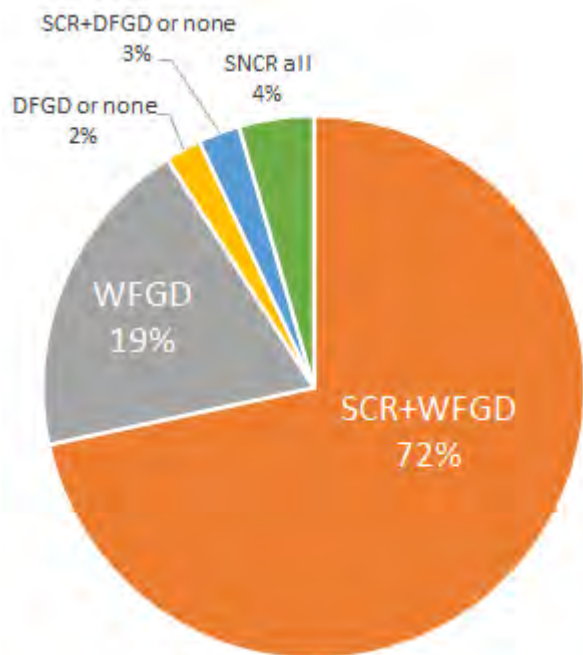
- Iodine addition more effective than bromine, lb per lb of coal
- Full-scale data from Gadgil, et al., 2015

Improving Hg Oxidation Across SCR with Halogens



Adapted from Cormetech,
2015 Reinhold NOx conference

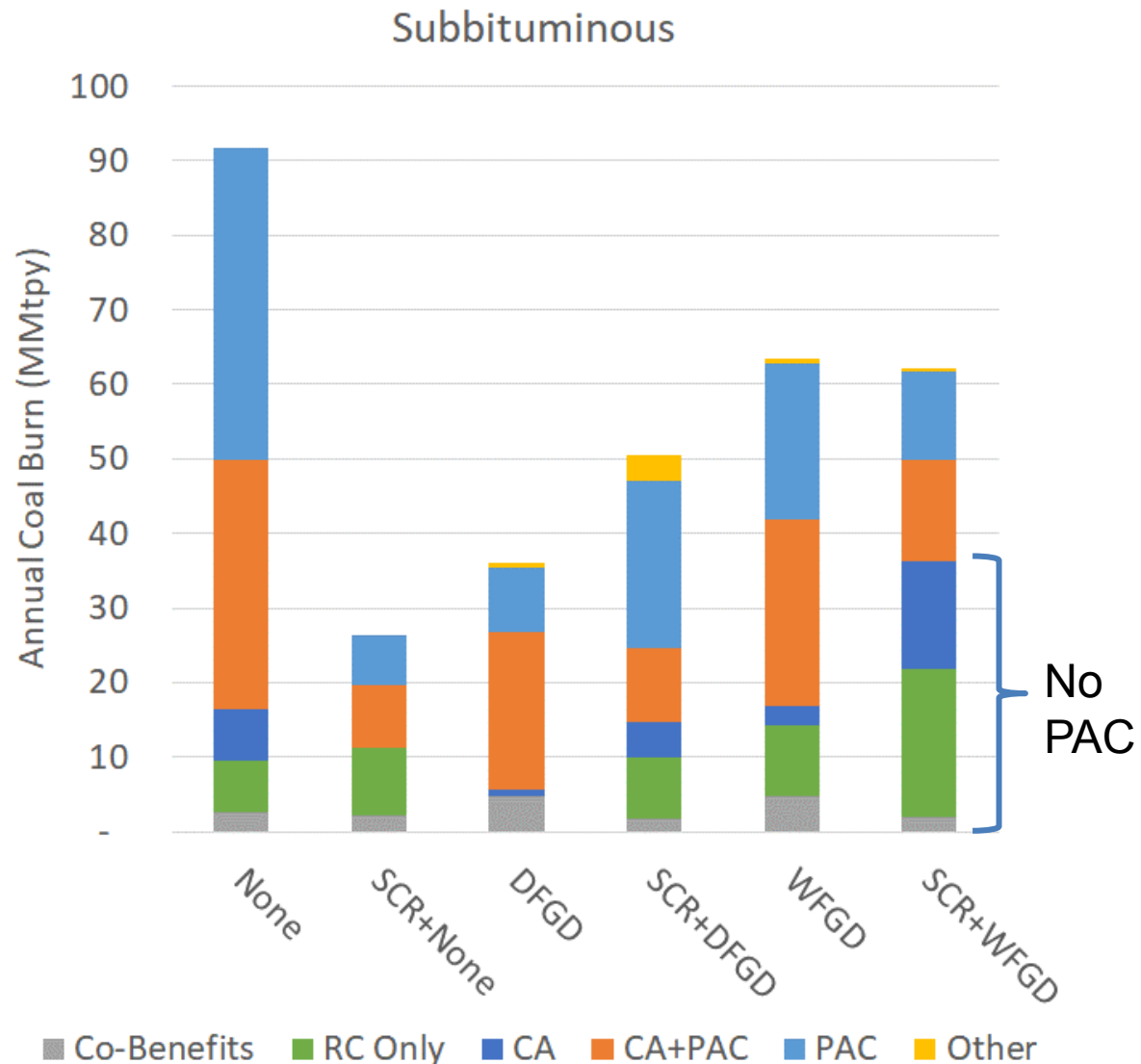
How Does an SCR Affect Choice of Hg Control Technology - Bituminous-Fired



- ▶ Larger fraction of units with SCRs relying on co-benefits alone compared to units without SCRs
- ▶ On average, an installed SCR has a minor impact on the fraction of bituminous units with SCRs reporting using PAC to supplement Hg compliance
 - ▶ Note that data on the amount of PAC or coal additives is not reported

Impact of SCR + SOx Controls on Mercury Controls - Subbituminous Plants

- Hg Control Strategies:
 - PAC: 69%
 - Coal Additives: 61%
 - Both: 37%
- Exception: 58% of subbit units with SCR + WFGD meet compliance without any PAC

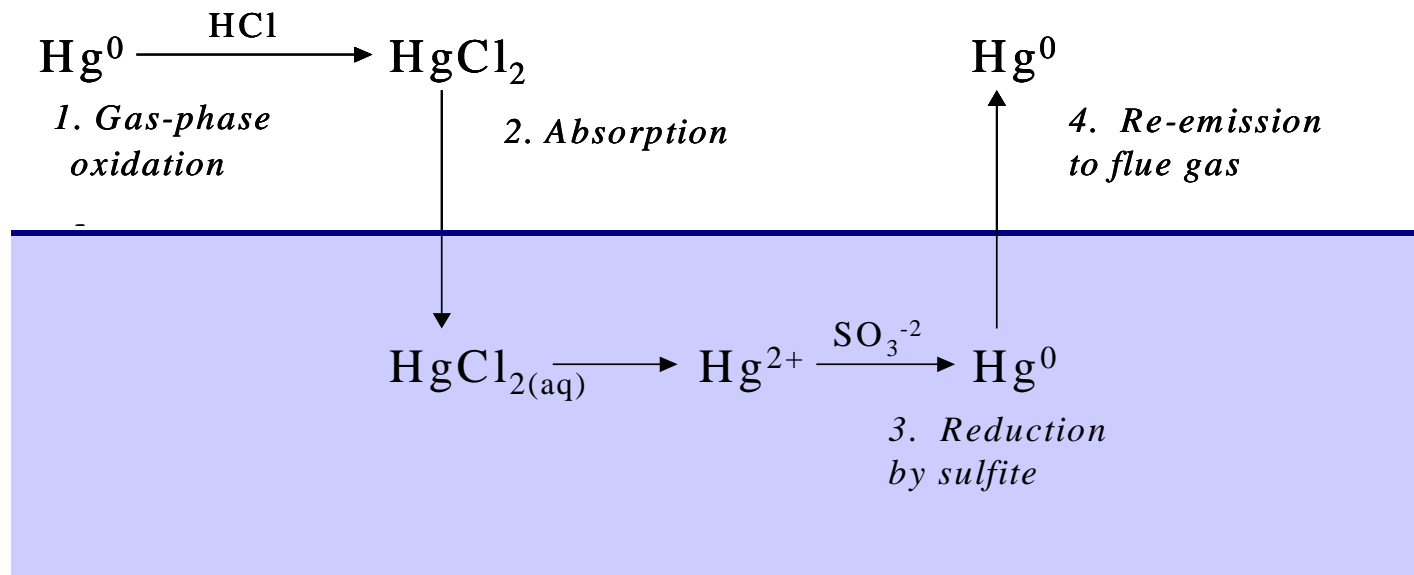


Factors Affecting Hg Control in Wet Scrubbers

- ▶ Inlet Hg speciation: how much gas-phase oxidized Hg
- ▶ Scrubber ORP... and all the things that affect ORP

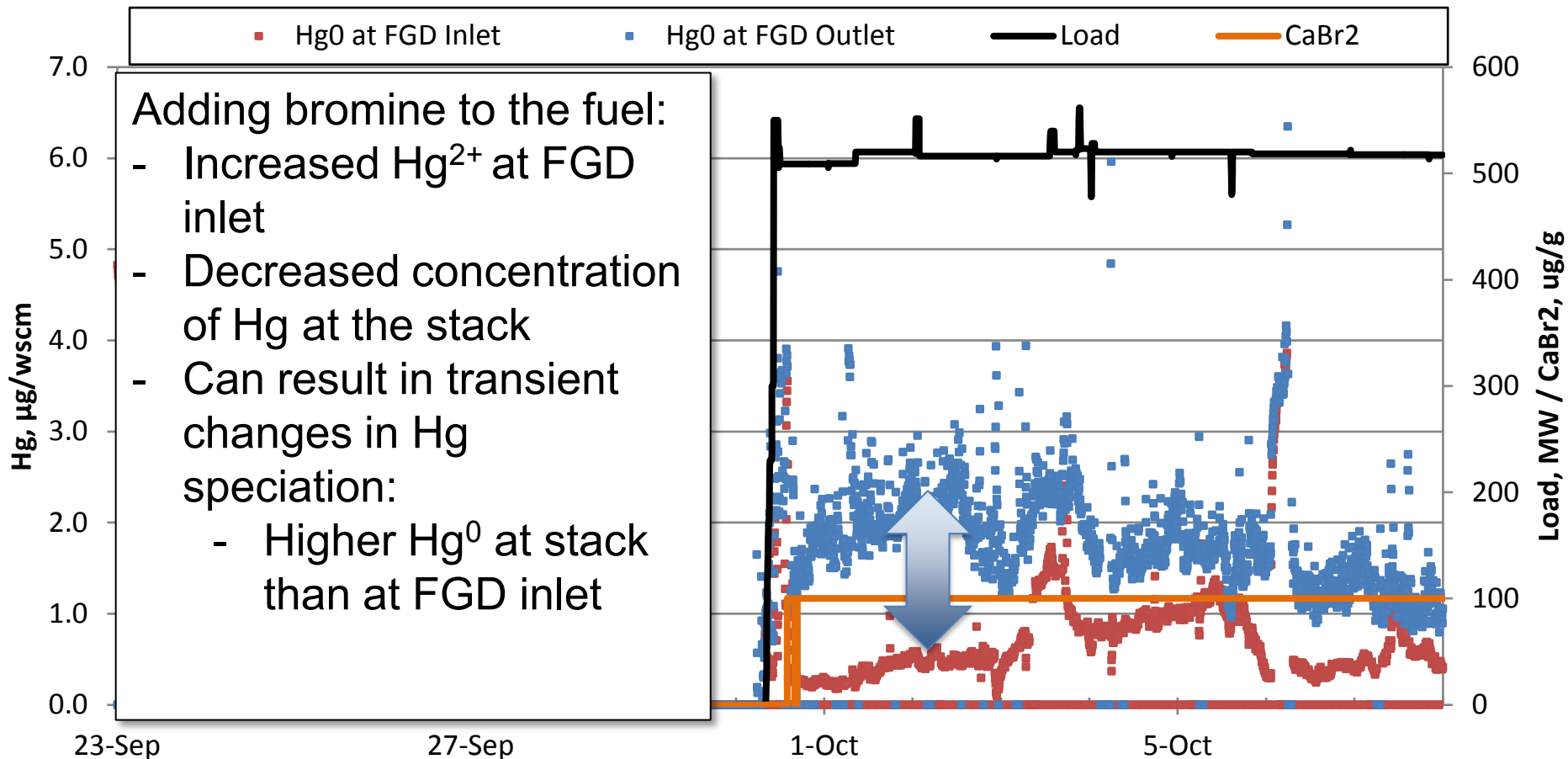
Mercury Re-Emission

- ▶ Ionic Hg (Hg^{2+}) can be reduced to Hg^0 in solution
- ▶ Limited solubility of Hg^0 can result in loss of Hg^0 back into flue gas
- ▶ Important factors: sulfite concentration, pH, halogens, transition metals



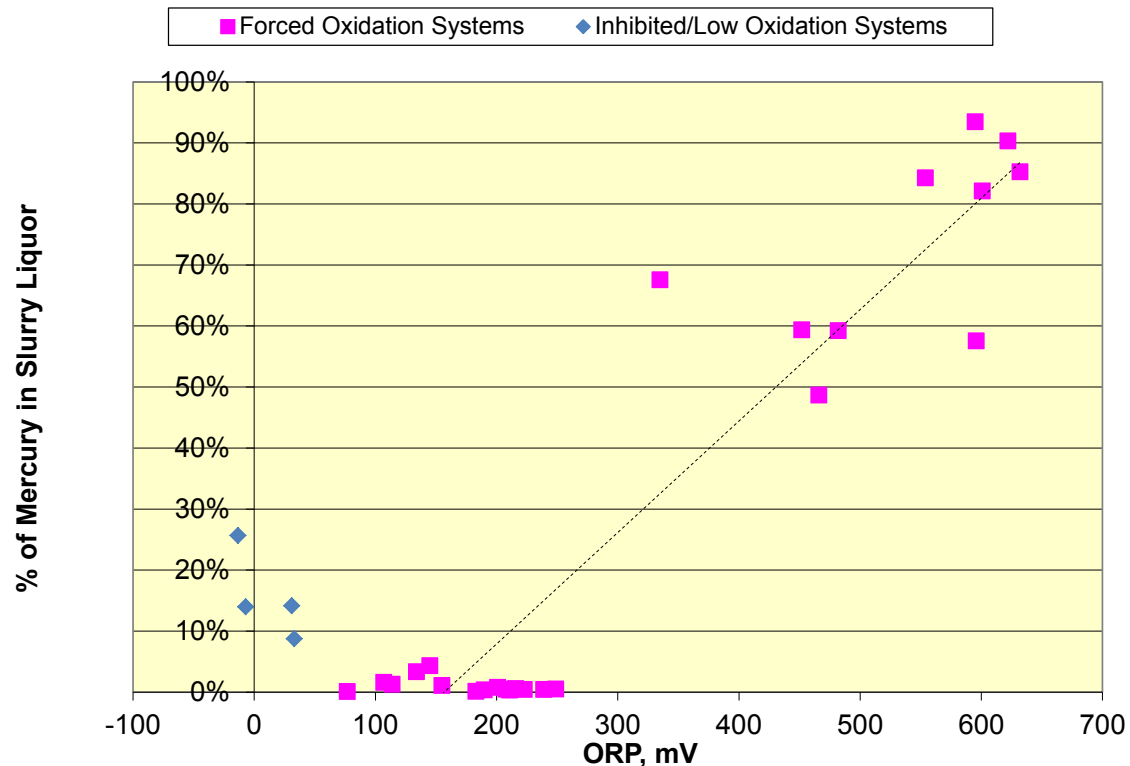
EXAMPLE: Re-Emission

- ▶ Bromine addition at subbituminous-fired plant with ESP and wet FGD



ORP Affects Dissolved Hg

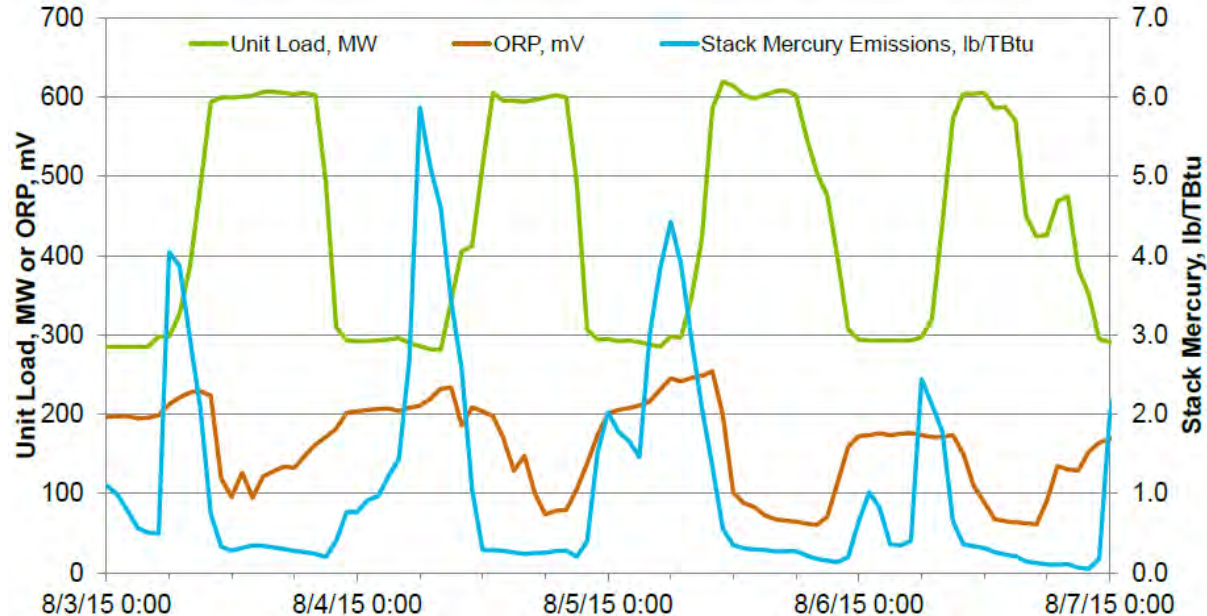
- ▶ Fraction of Hg in the liquid phase of scrubber slurry related to ORP
- ▶ LESS Hg in liquid phase means
 - ▶ Less potential for Hg re-emission during upsets
 - ▶ Less burden on WWT system



Source: Blythe et al., 2011

Impact of Load Cycling

- ▶ Cycling load affects ORP and Hg emissions
- ▶ Load affects L/G ratio, ratio of O₂ to SO₂ in flue gas and reaction tank



Source: Workshop 04, Effects of MATS Control and Variable Unit Load on ORP and Trace Metals in FGD Wastewater Reinhold APC Roundtable, 2016

Removal of Hg in Wet FGDs - Review

- Maximize gaseous oxidized Hg at scrubber inlet
- Stabilize Hg²⁺ in the liquid
 - Control redox potential (e.g., Mitsubishi Heavy Industries has a patent covering ORP control to optimize net mercury capture)
 - Halogens in the scrubbing solution can complex with Hg²⁺ and reduce Hg re-emission (sometimes)
- Increase amount of Hg removed in solid phase
 - Amount of suspended solids in the absorber slurry (impacts fines concentrations and surface area available for mercury adsorption)
 - Iron in fine particles (fines) in the scrubber (from limestone and/or fly ash) that react with Hg
 - Use an additive to the scrubbing solution to tie up Hg or precipitate to solid phase

Balancing Gypsum Quality and Mercury Re-Emissions

Optimum for Gypsum

- High oxidation air rates
↓ sulfite
- Low pH
- High blowdown to manage halogen levels

Optimum for Hg Control

- Reduce oxidation air
 - $< \sim 300 \text{ mV}^{1*}$
- Increased sulfite
- Increase pH
- High halogen



% Dissolved mercury, and risk of re-emission increases at ORP $> 300 \text{ mv}$

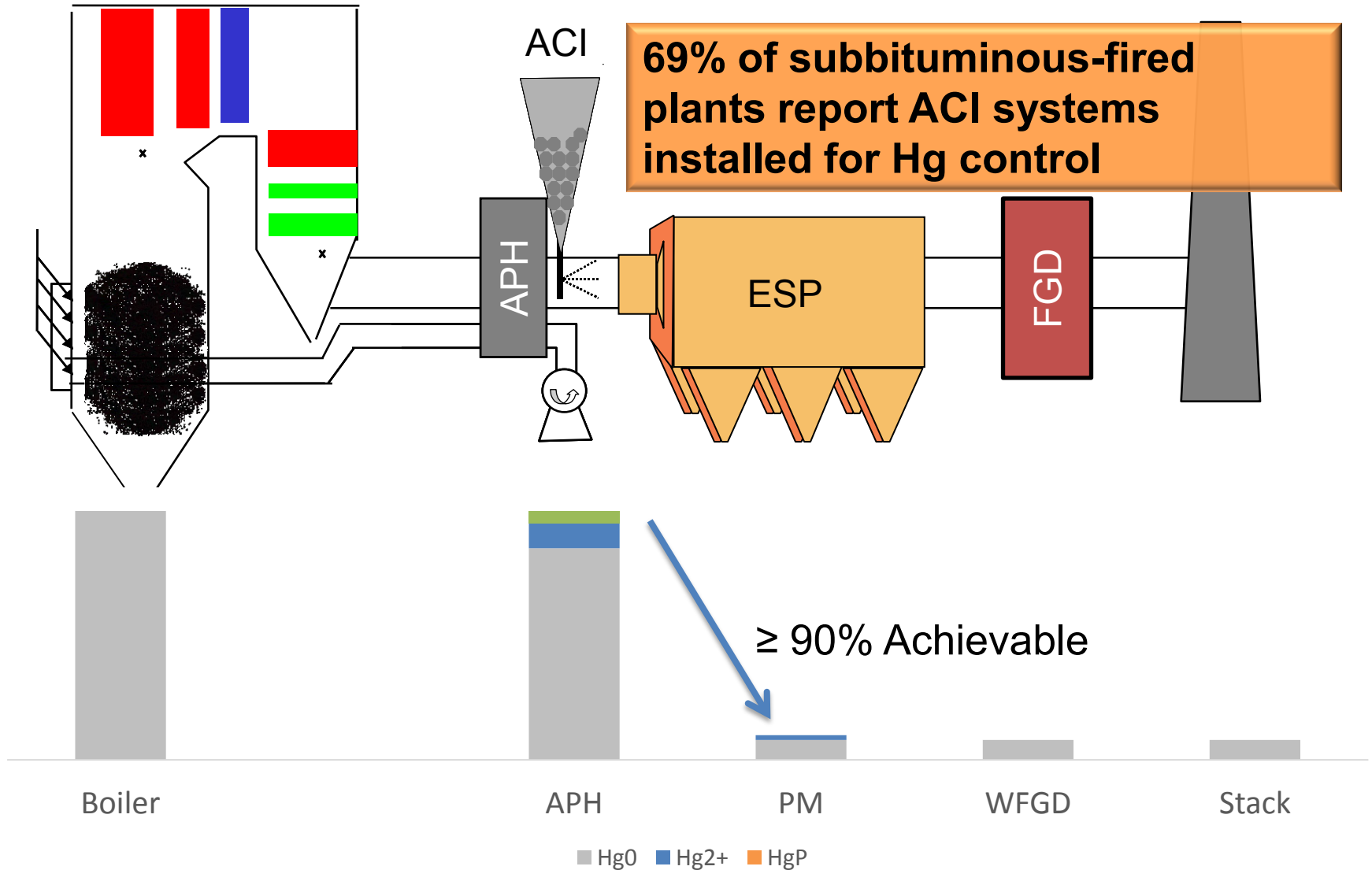
Mandi Richardson, AECOM

Increasing Native Capture with Halogen Addition

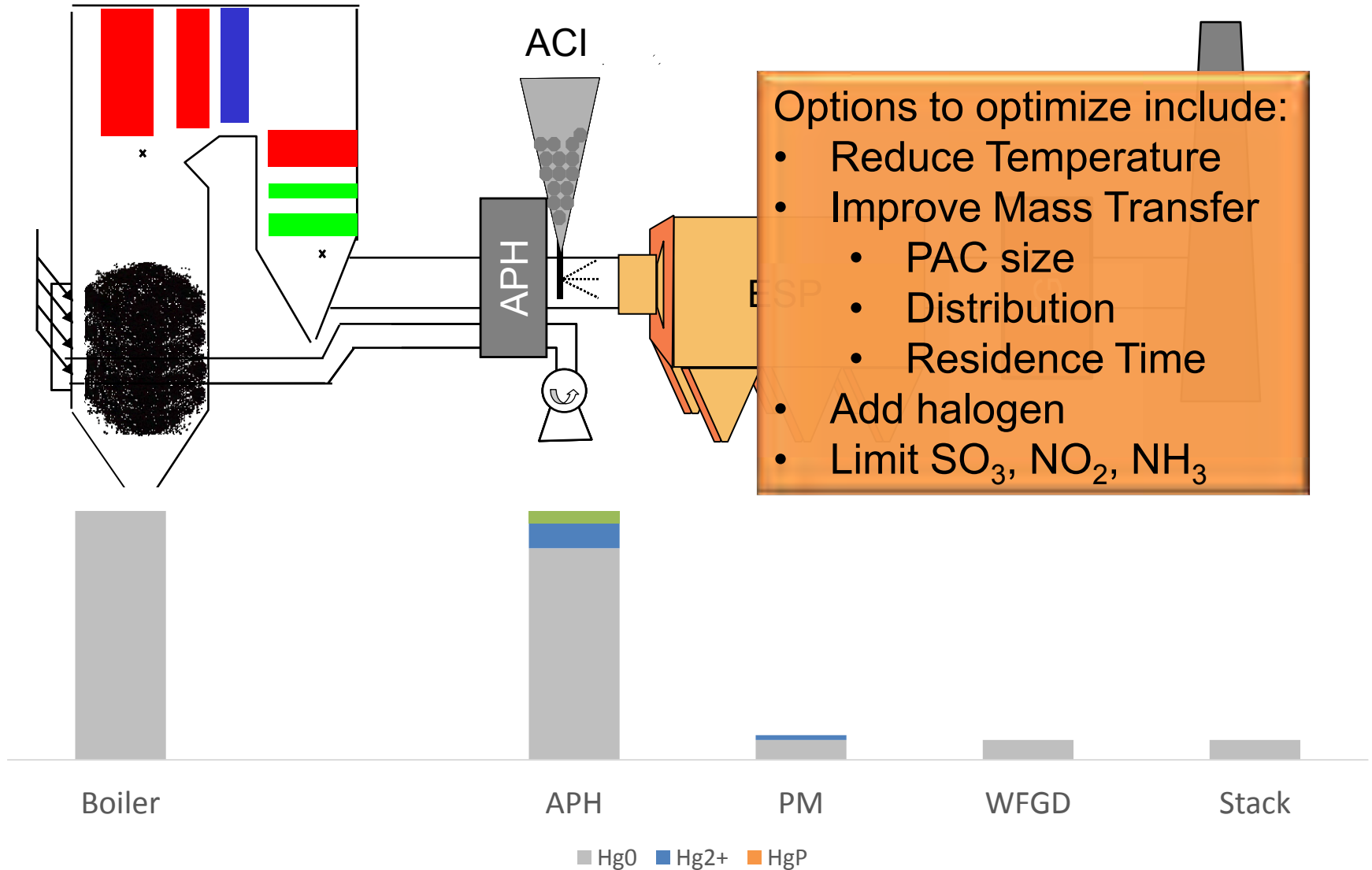
Summary and Cautions

- Adding halogens increases oxidized Hg:
 - Increase effectiveness of some kinds of activated carbon for Hg capture
 - Increase capture of Hg in SO₂ scrubber
- Potential balance-of-plant impacts:
 - Possible increased corrosion
 - Halogens build up in wet scrubber liquor
 - ▶ Average Cl removals for wet FGDs (2010 ICR): 81% for subbituminous, 97% for bituminous
 - ▶ Removal of Br at Plant Miller wet FGD: 94-96% (Dombrowski et al., 2008)
- Bromine treatment may contribute to formation of additional regulated disinfectant byproducts (DBPs) at drinking water treatment plants downstream of FGD wastewater discharge

Subbituminous-Fired with “Typical” APC Activated Carbon Injection (ACI)



Subbituminous-Fired with “Typical” APC Activated Carbon Injection (ACI)

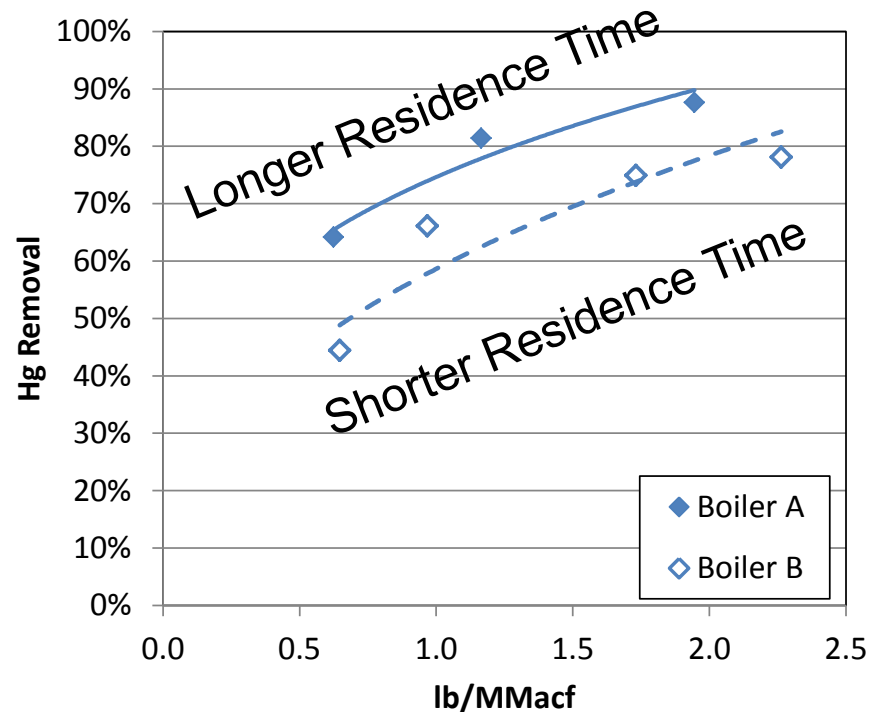


Mass Transfer Important for ESPs

Powdered Activated Carbon usage with an ESP can be reduced by improving mass transfer to the PAC

Option

- Place lances for longer residence time and optimal distribution
- Reduce PAC particle size



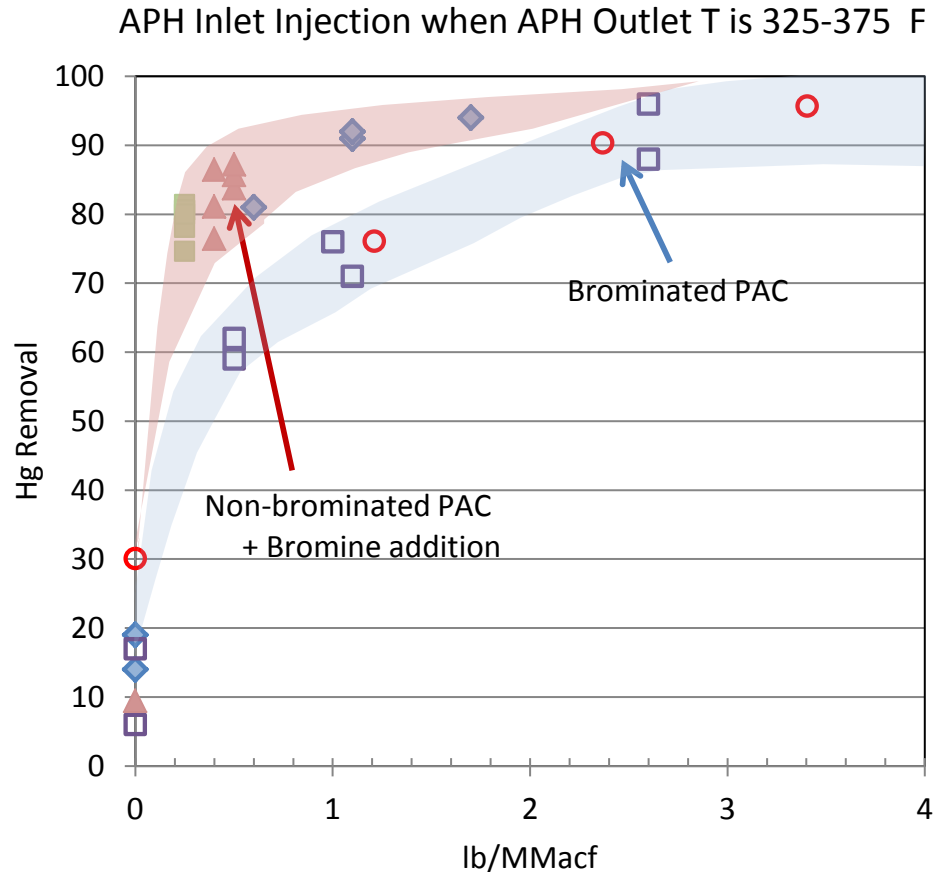
Example: Two boilers burning similar PRB coal
Testing of brominated PAC on both units at 315-320°F

Boiler B has short residence time between APH and ESP inlet AND Chevron-style inlets

Boiler A has longer duct residence time

Using Halogens with PAC

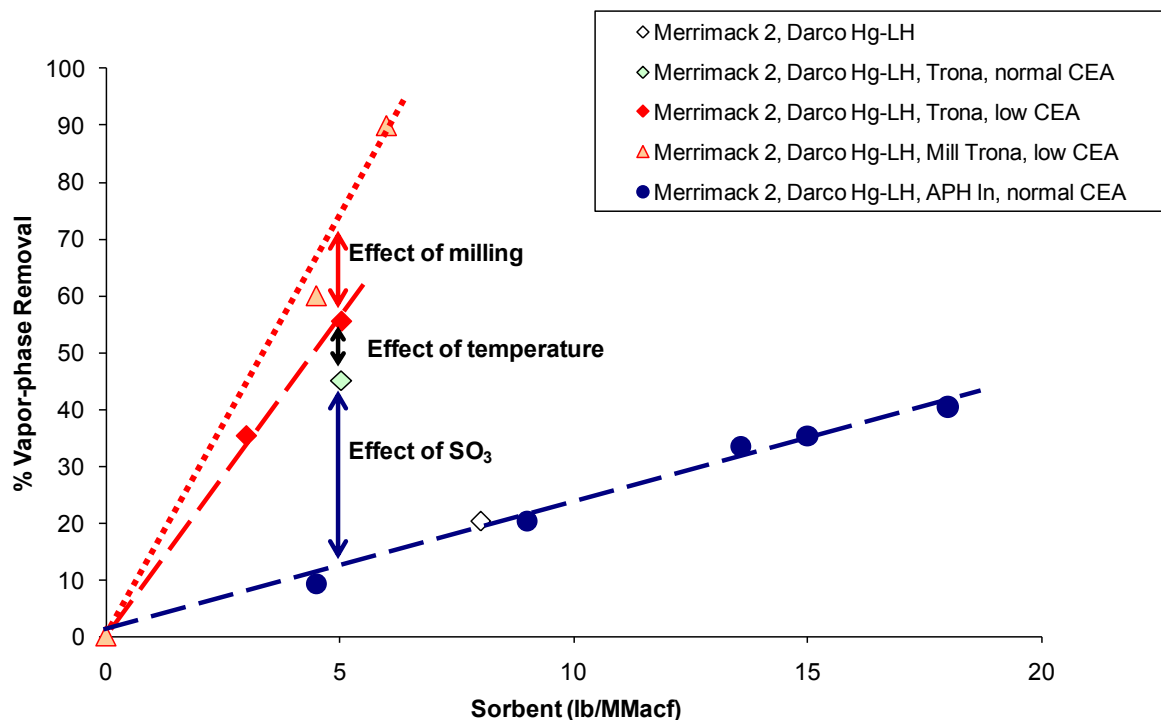
- Combining halogen addition with sorbent addition



- Full-scale plant data for PRB-fired units with cold-side ESP
- Comparison of bromine addition + PAC to use of brominated PAC

Activated Carbon Injection (ACI) with Bituminous Coal-Fired Plants

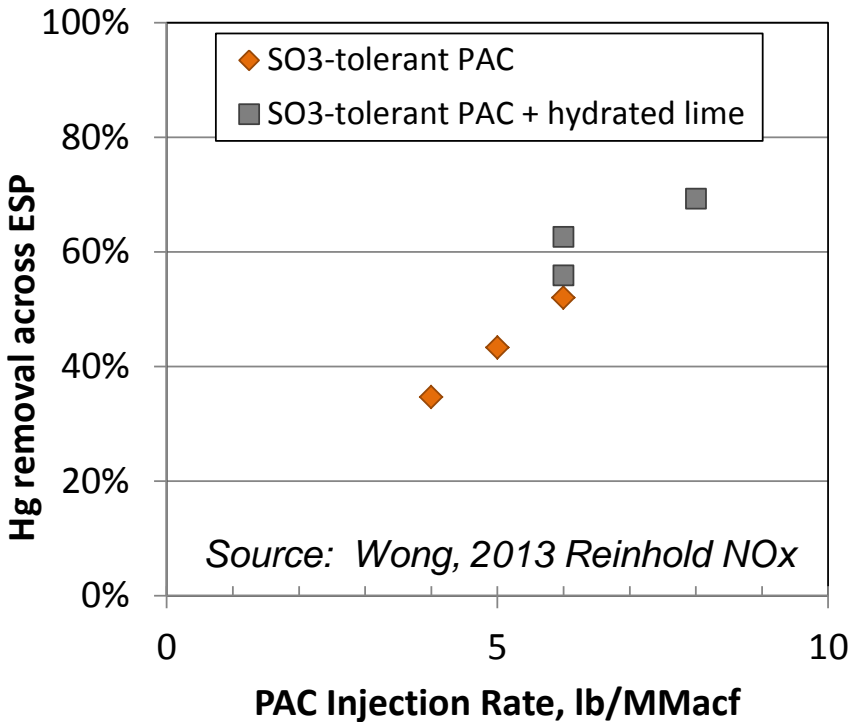
Plants with ESP and high SO_3 (i.e., high-sulfur coals or low-sulfur coals with an SCR/FGD) struggle to achieve high levels of removal



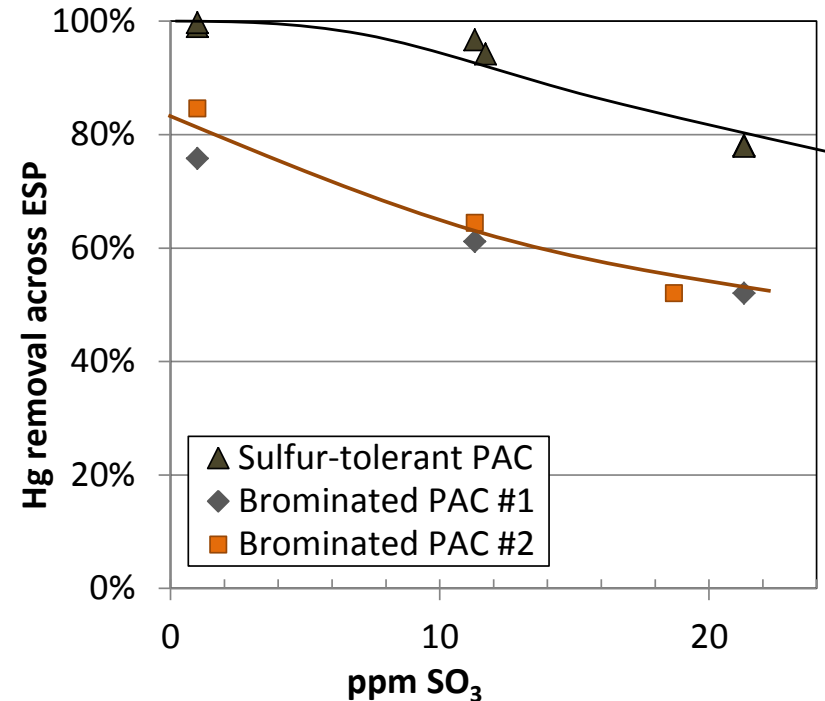
- High temperatures and high SO_3 concentrations in the flue gas downstream of the APH strongly affect sorbent performance
- Other factors, possibly important, including coal chlorine content and sorbent mixing in the flue gas duct

Sulfur-Tolerant Activated Carbon

Some plants use specialty carbon to achieve mercury control



High S coal, SCR-ESP-FGD,
> 15 ppmv SO₃

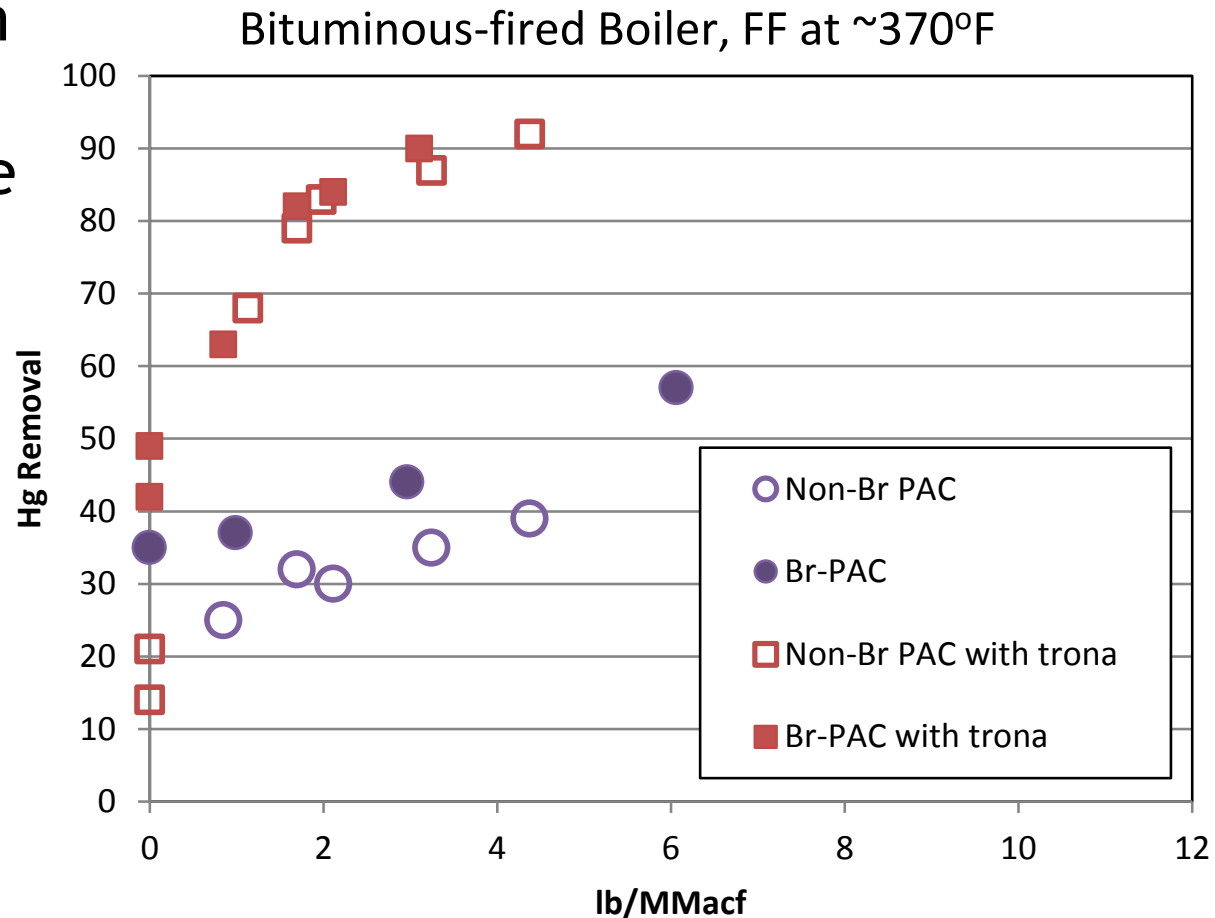


MRC Results: 10 lb/MMacf, injection
upstream of APH; APH outlet: 300 F

Source: Pollack, AQV

Variation: Trim with ACI, Use Alkaline Sorbents (DSI) to Lower SO_3

- Sodium or calcium DSI sorbents can be used to remove SO_3 and increase effectiveness of PAC
- Example:
Bituminous-fired boiler with FF, ~20 ppm SO_3 uncontrolled



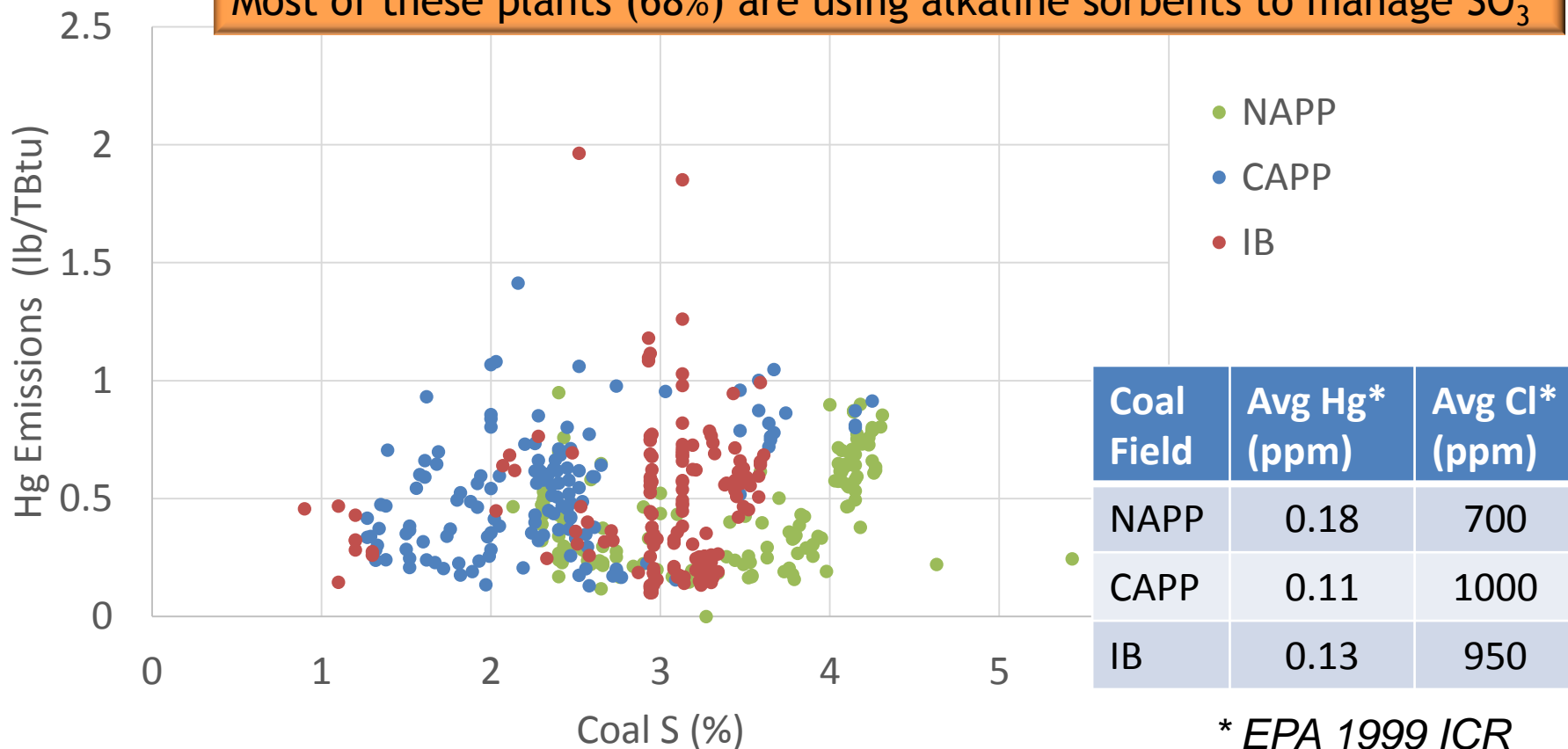
DSI-ACI Co-Treatment Considerations

- Potential for SO₃ reduction with DSI
 - **improved** Hg capture with PAC
- High-temperature injection of DSI sorbent could **reduce oxidation of Hg** in flue gas by removing halogens too soon
- Sodium sorbents can produce NO₂
 - can **reduce effectiveness of PAC** for Hg capture
 - Doesn't happen at every DSI installation: reaction kinetics, type of particulate control device (ESP vs. FF), and baseline NOx levels are important factors
- Particulate Control impacts
 - Loading increased – also impacts ash handling requirements
 - Resistivity impacted (↑Calcium, ↓ Sodium)
- Choose DSI sorbent and injection location carefully

Influence of Coal Sulfur on Mercury Emissions - Bituminous Plants, Co-Benefits

Why don't we see a correlation?

Most of these plants (68%) are using alkaline sorbents to manage SO_3



Bituminous plants, SCR, ESP, WFGD, no specific Hg controls
 Reported coal sulfur and Hg emissions 1 May 2017 - 31 April 2018, monthly averages

Mercury Emissions

Bituminous Coal, SCR+ESP+WFGD

	CA + PAC	CA	PAC	Co-Benefits	RC
Sample Size (Units)	6	20	10	53	35
Avg. Hg (lb/TBtu)	0.51	0.62	0.31	0.44	0.51
% time hourly Hg avg below 1.2 lb/TBtu	96%	92%	99%	98%	94%
% time hourly Hg avg >10% below 1.2 lb/TBtu	94%	89%	99%	97%	93%
% time hourly Hg avg >20% below 1.2 lb/TBtu	93%	84%	98%	96%	89%
Average Coal Sulfur (%)	2.5	2.4	2.7	2.9	2.6

1 lb/TBtu \approx 1 μ g/m³ at 7% O₂, dry

CA = Coal Halogen Additive

RC = Refined Coal (halogen addition)

PAC = Powdered Activated Carbon

Co-Benefits: No mercury-specific technology is reported

Based on reported emissions data
1 May 2017 – 31 April 2018

Primary Mercury Control Strategies - Review

- Co-Benefits: no mercury-specific controls
 - More common on scrubbed plants firing higher halogen coal
 - DSI co-injection may improve effectiveness on high-sulfur coal plants
- Coal Additives: Increase halogen content in coal
 - increase fraction of oxidized mercury
 - More common as a stand-alone option on scrubbed plants
- Activated carbon injection: increase concentration of particles that can adsorb mercury
 - Common on plants firing low-halogen fuel
 - DSI co-injection may improve effectiveness on high-sulfur coal plants

THANK YOU!

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