REINHOLD ENVIRONMENTAL Ltd.

2018 NOx-Combustion Round Table & Expo Presentation

February 19-20, 2018, in St. Louis, MO / Hosted by Dynegy

Mercury Mitigation – Update on Compliance Strategies and Technologies

Sharon Sjostrom
Connie Senior

Reinhold Round Table, Feb 20, 2018

Training Road Map

- Coal basics
- Mercury from Coal to Stack
- Overview Mercury Control Strategies
  - Technology basics
  - Review of strategies used for MATs compliance

Federal Mercury and Air Toxics Standards (MATS)

- What’s regulated?
  - Mercury (Hg), acid gases (HCl) and particulate matter (PM)
- Who’s affected?
  - All coal-fired electricity generating units (EGUs) greater then 25 MW electricity
- When?
  - Almost all compliance by April 16, 2016

Update on MATS

- In April 2017, a review by the U.S. Court of Appeals for the D.C. Circuit of a “supplemental finding” associated with the cost benefit analysis of the MATS rule conducted by EPA was stayed at the request of the Trump Administration. The court case continues to be stayed indefinitely, but the MATS Rule is still in force until the issue is resolved. The EPA has not issued any further official proceedings regarding MATS rulemaking

Primary Factors that Affect Mercury Emissions and Control Strategies

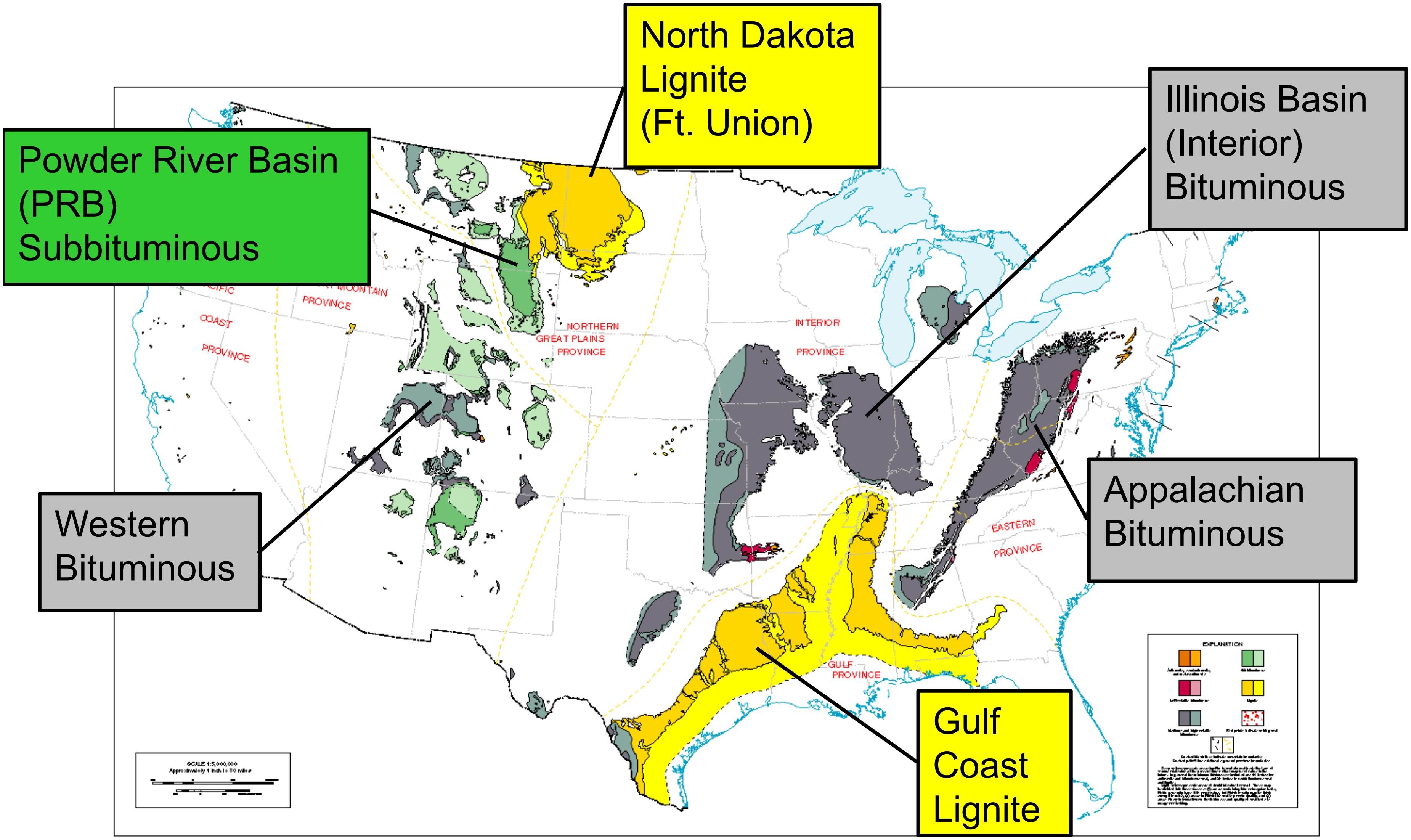
- Coal properties
  - Mercury, halogens, sulfur
- Air Pollution Controls
  - NOx, SOx, PM
- Other Considerations for Supplemental Controls
  - Economics
  - Balance-of-plant impacts
  - Environmental constraints (e.g. ancillary emissions or effluent discharges)

What Does It All Mean?

- Many plants have relatively new processes for controlling one or more of these air emissions:
  - Hg, HCl, SO_2, SO_3
- Plus all the previous air pollution control!
- We can learn what combinations of pollution control work by coal type by reviewing what the industry is using to meet compliance

Coal Properties

Major Coal Fields in the US



Typical Coal Properties

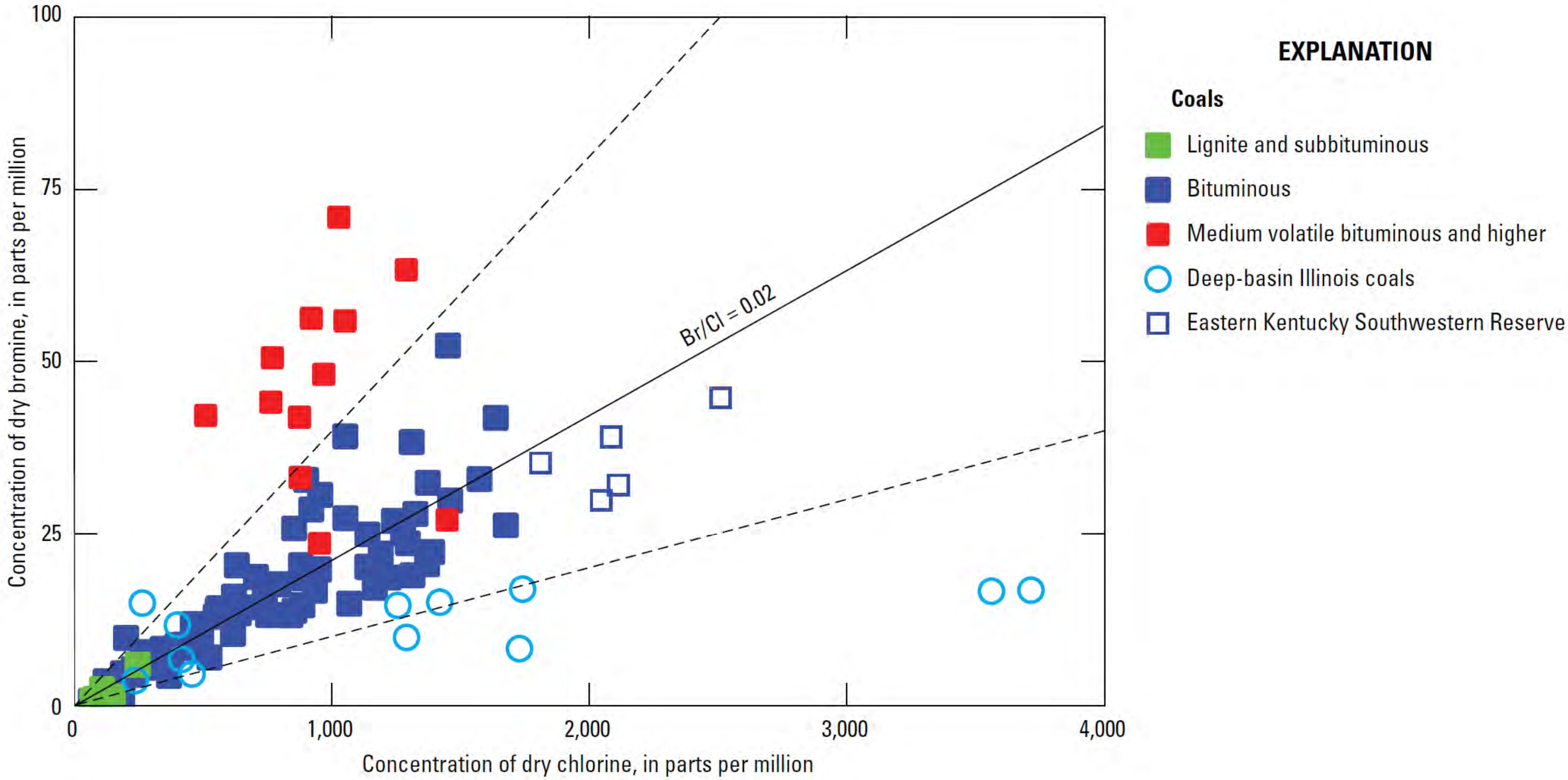
Low Rank | High Rank

Rank	Lignite	Subbituminous	Bituminous	Anthracite
Age (million yrs)	~60	~100	~300	~350
Heating Value	~ 7,000	~ 10,000	12,000-15,000	~ 15,000
% Carbon	65-72	72-76	76-90	90-95
% Moisture	30-70	10-30	5-10	~5
%Sulfur*	0.4-1	<2	1-4	0.6-0.8
Chlorine* (ppm)	50-150	<100	100-2000+	
Mercury* (lb/TBtu)	Gulf: 20-40 Ft. Union: 10-30	PRB: 5-15	NAPP: 15-20 CAPP: 5-15 East Int: 5-10	PA: 5-10

* Key contributors to Hg emissions

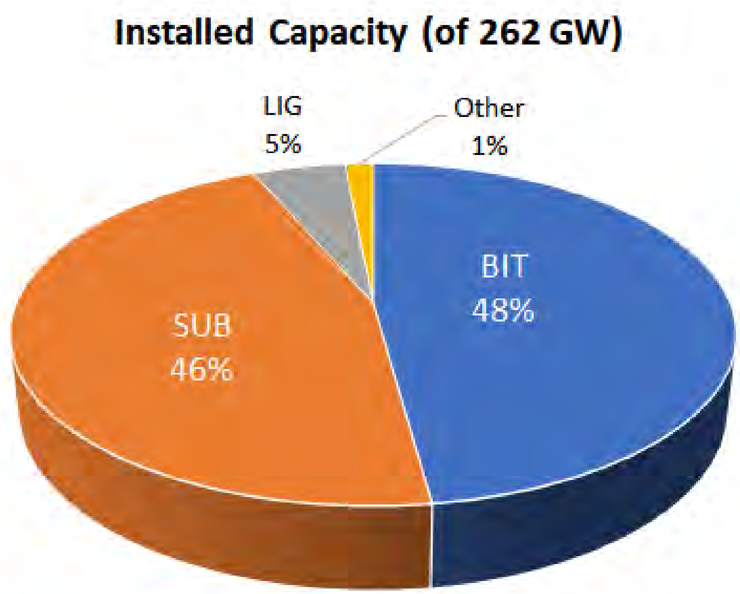
Mercury from USGS: https://pubs.usgs.gov/fs/fs095-01/fs095-01.html
Chlorine from USGS:

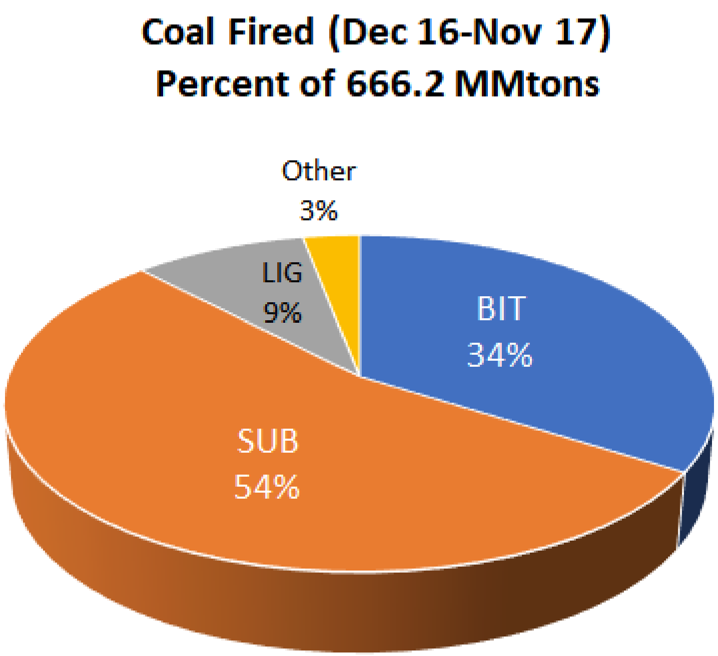
Coal Halogen: Chlorine and Bromine



Primary Coal-Type Fired in 2017

Coal	MW	Coal (MMtpy)	Avg CF (%)	EGUs
BIT	125,481	226.5	43%	294
SUB	119,888	358.5	55%	294
LIG	12,928	61.3	69%	29
Other	3,944	19.9	71%	26



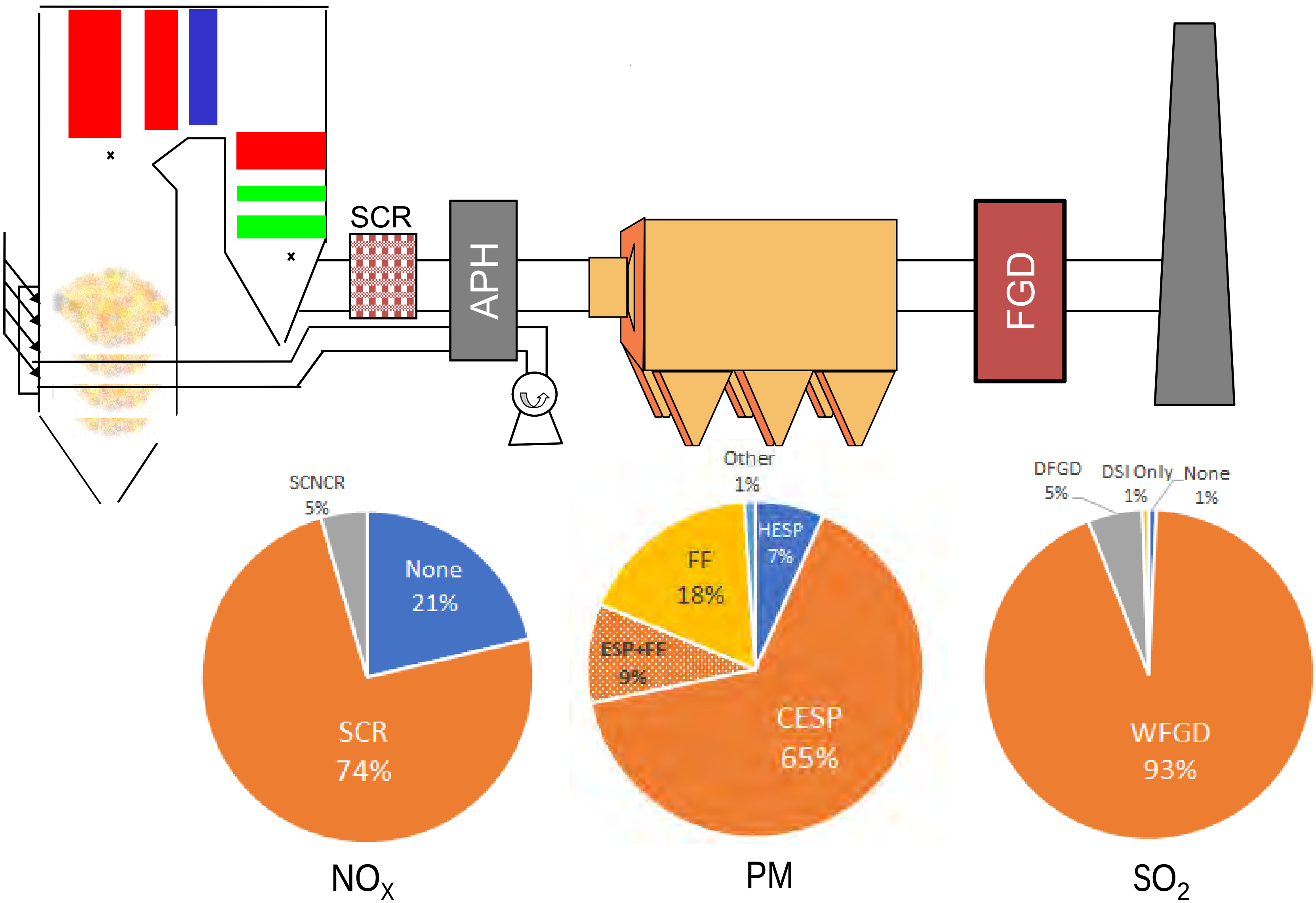


- The fraction of installed capacity firing primarily bituminous and subbituminous is similar
- 54% of coal fired for generation is subbituminous
  - Higher capacify factor (CF) for subbituminous-fired units

EIA Data, 2017

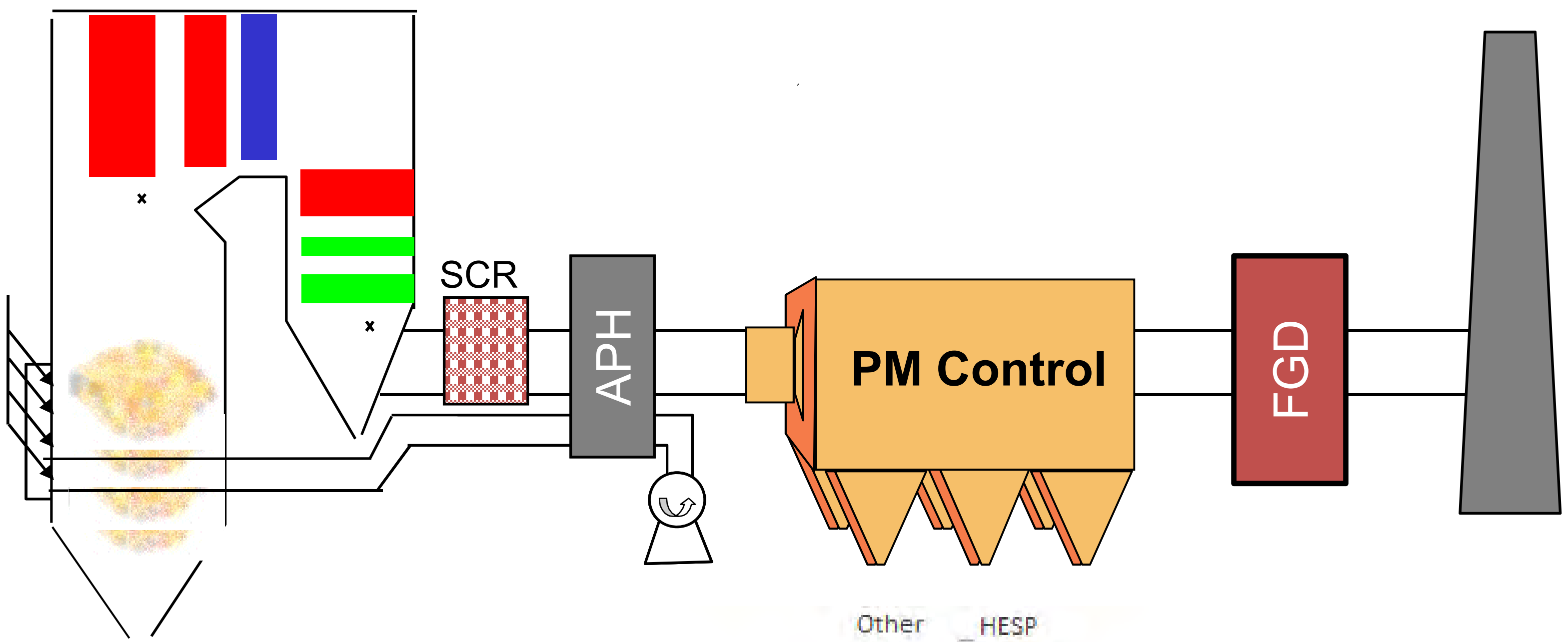
Air Pollution Controls

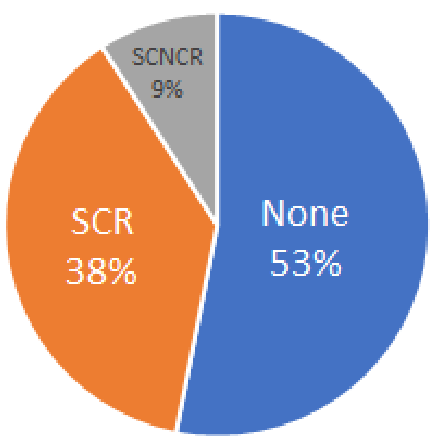
APC Configurations: Bituminous Plants



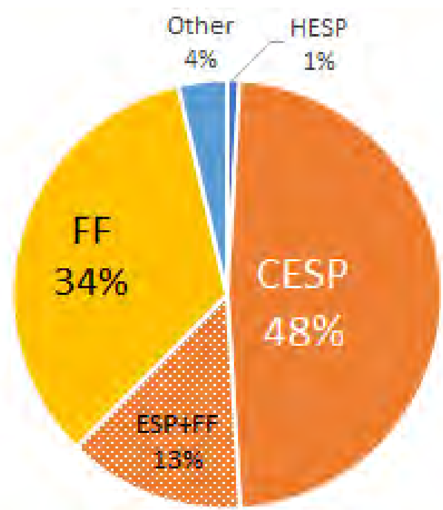
Based on 2017 EIA and CAMD data

APC Configurations: Subbituminous Plants

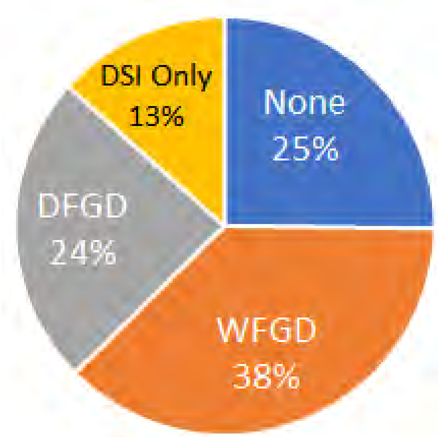




NOx



PM



SO_2 & HCl

Based on 2017 EIA and CAMD data

Mercury in Coal Plants

- Fundamental Chemistry
- Control Strategies

Mercury: What Do We Mean by Speciation?

- Gas-phase mercury:
  - Elemental: Hg^0
  - Oxidized: Hg^{+2} ($HgCl_2$, $HgBr_2$ other species?)

Oxidized mercury is **VERY** soluble in water (120°F)

$HgCl_2$: **13.2g/100g water**

$HgBr_2$: **1.3g/100g water**

Hg^0: **$< 1 \times 10^{-5}$/100g water**

- Particulate mercury:
  - Hg_P
  - Mercury (adsorbed on particles)

Two Ways to Remove Mercury

Remove with PM

Adsorb Hg on particles

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

Remove in scrubber

Absorb Hg (Primarily Hg^{2+})

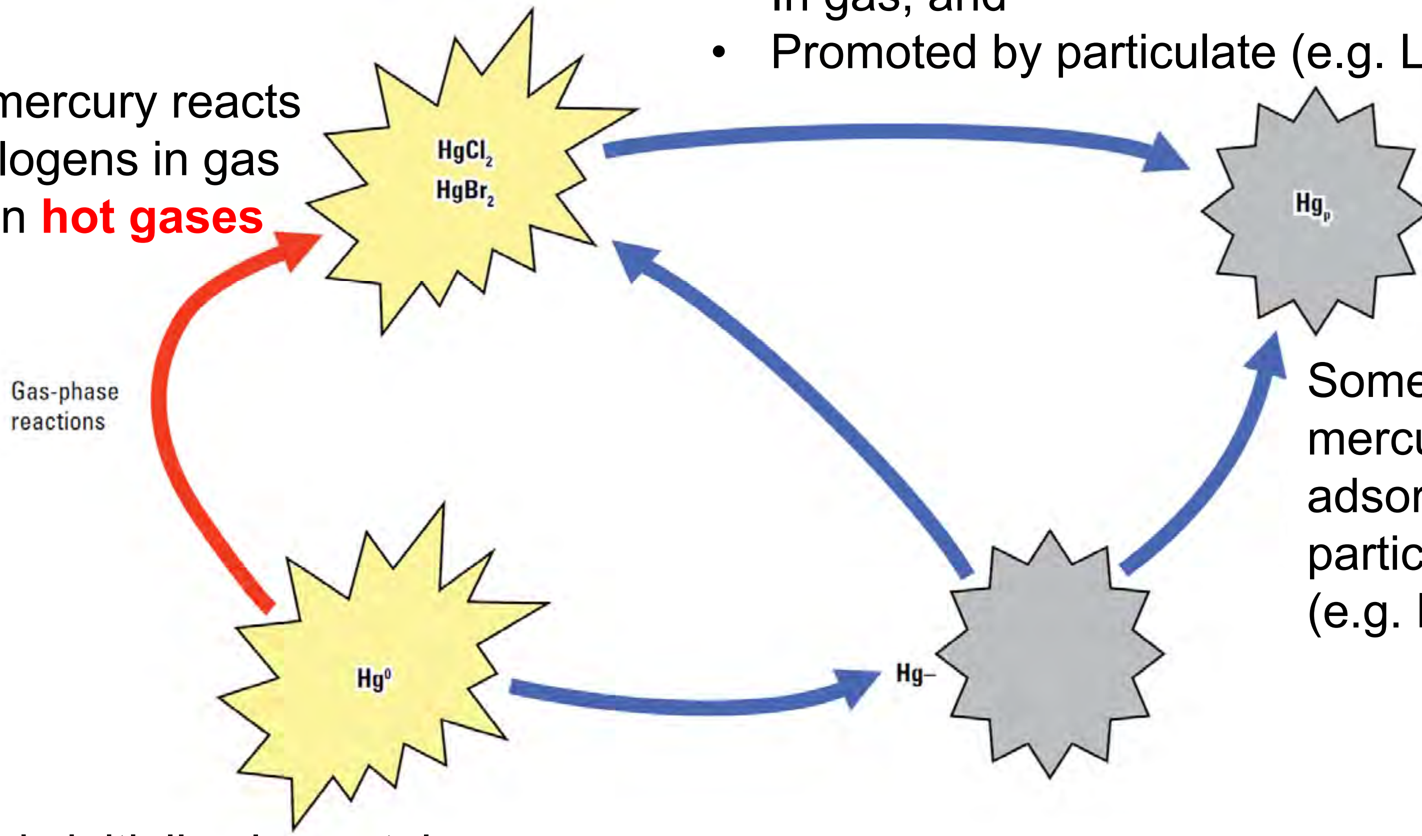
- Wet flue gas desulfurization (FGD) scrubbers
- Dry FGD scrubbers

Mercury: Reaction Pathways During Combustion and Cooling

Additional reactions with halogens can occur during **cooling**

- In gas, and
- Promoted by particulate (e.g. LOI)

Some mercury reacts with halogens in gas phase in **hot gases**



Some mercury adsorbed by particulate (e.g. LOI)

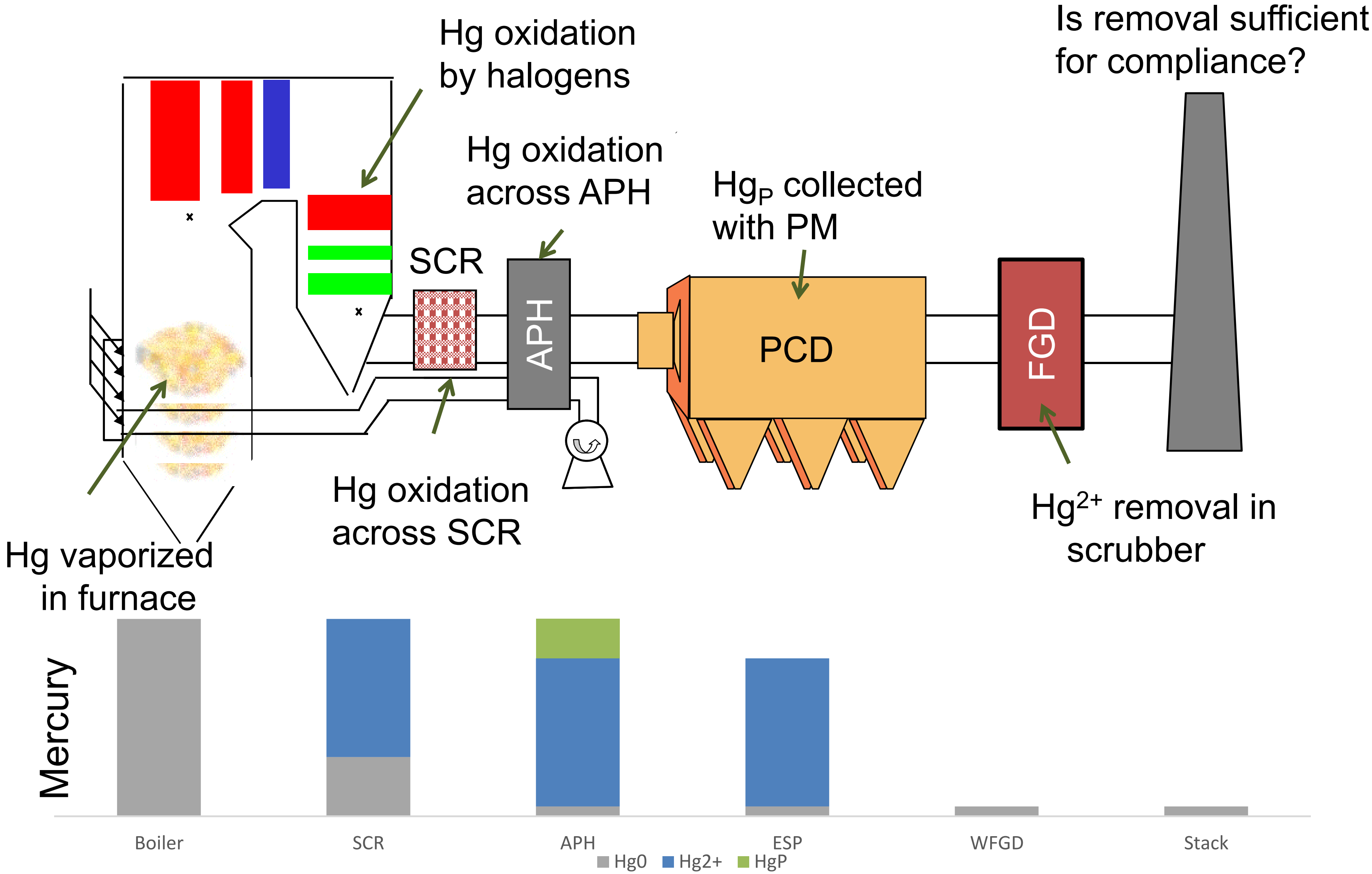
All Hg is initially elemental mercury (Hg^0) after combustion

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 or catalysts to increase oxidized Hg

Mercury Control: "Typical" Bituminous Plant



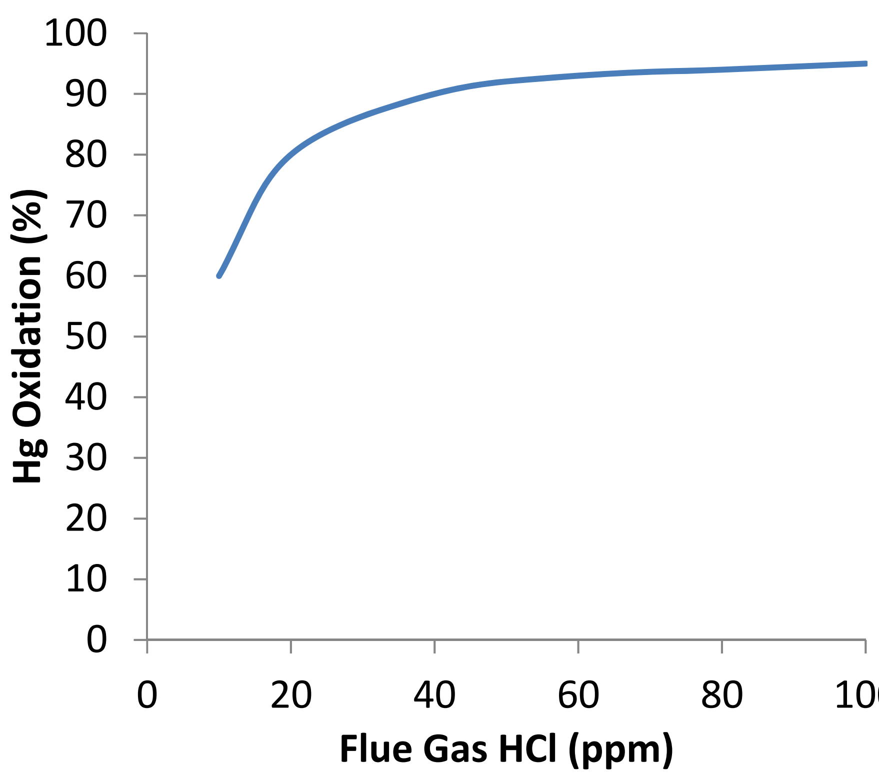
Can Plants Rely on Co-Benefits Alone?

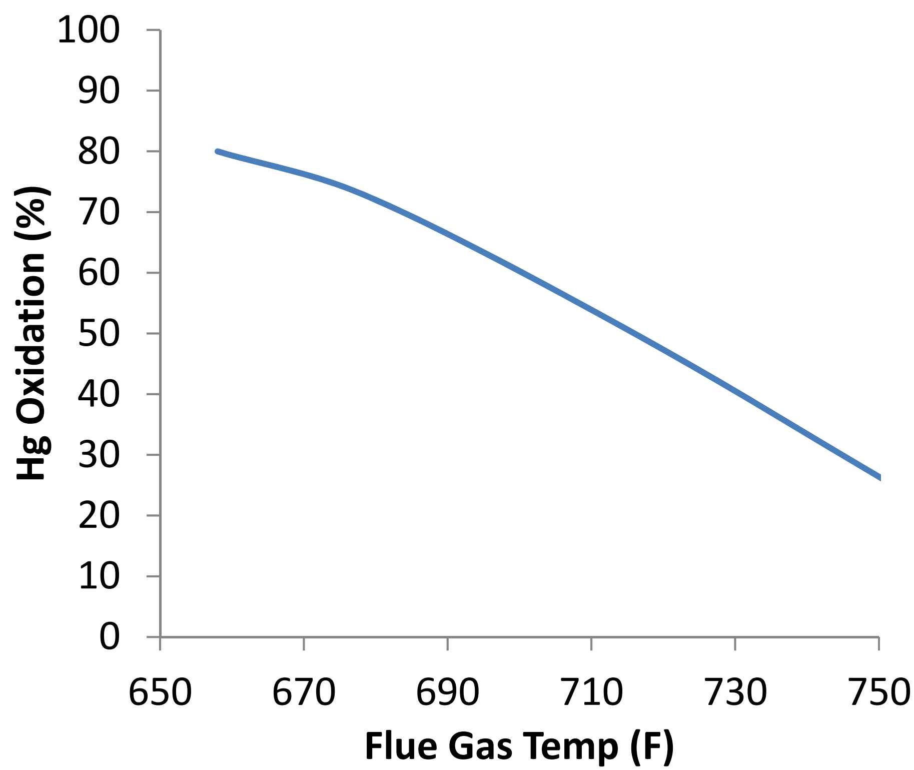
YES:
35% of bituminous units and
5% of subbituminous units
rely on co-benefits alone

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

Factors Affecting Hg Oxidation Across SCRs





Higher temperature → Lower oxidation

Higher ammonia → Lower oxidation

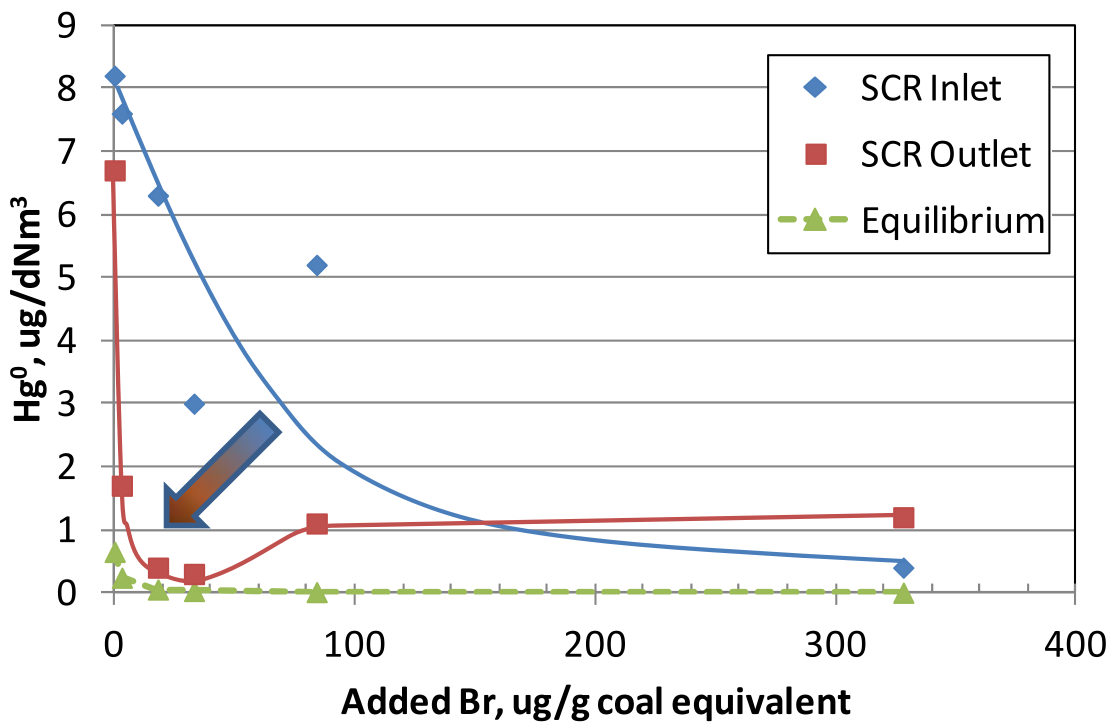
Review of emissions data from several bituminous plants with SCR+WFGD do not show increased emissions during summer months

Shintaro Honjo, Mitsubishi Heavy Industries America, Mega Symposium 2012

Co-Benefit Trim

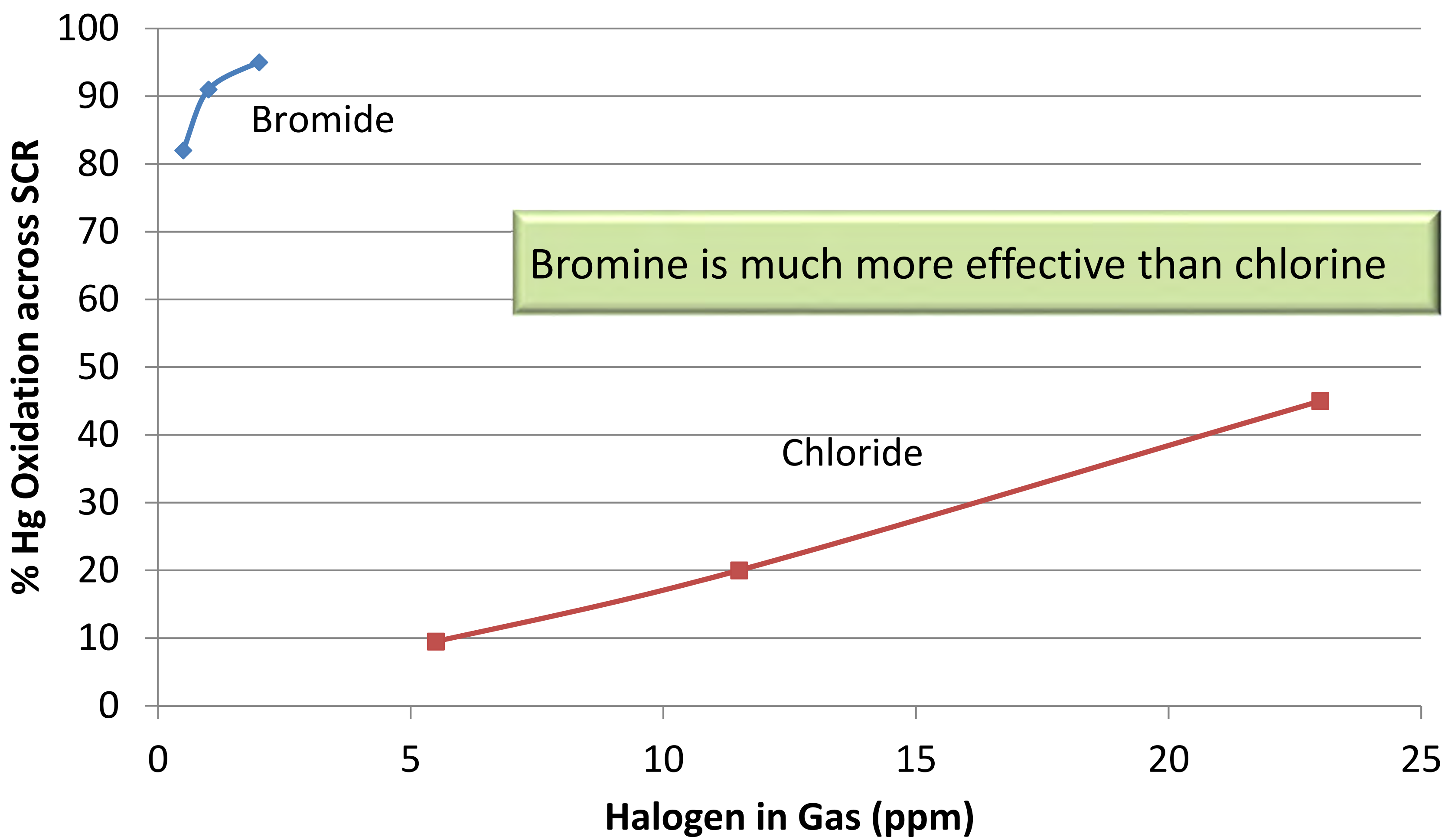
Effect of Added Halogens on Mercury

- Halogens (Cl, Br, etc.) promote oxidation of Hg in the boiler and SCRs improve this oxidation
- Adding Br to the fuel makes the shift to Hg^{2+} take place at higher temperatures (than Cl)



Comparison of Plant Miller data of Berry *et al.* with calculated equilibrium

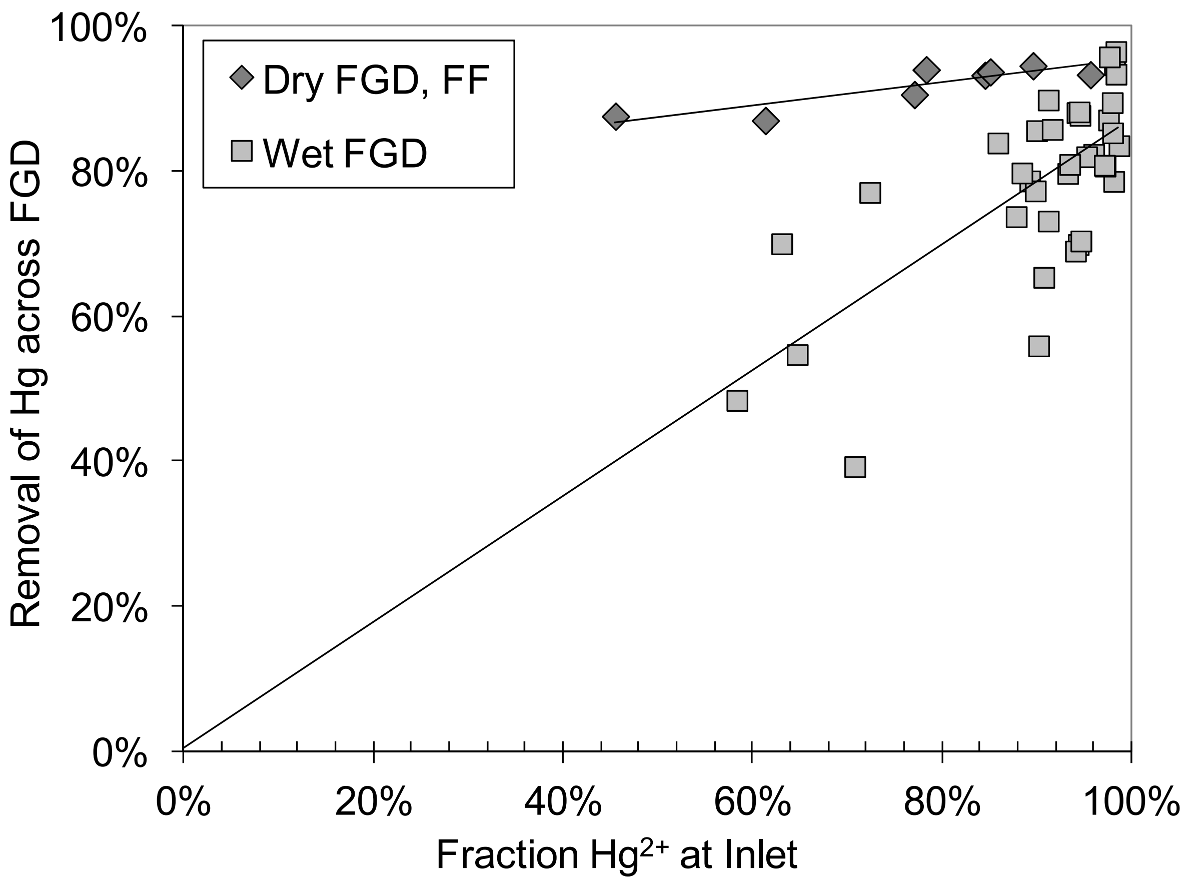
Improving Hg Oxidation Across SCR with Halogens



Adapted from Cormetech,
2015 Reinhold NOx conference

Benefits of Oxidized Mercury

Many scrubbed plants effectively remove oxidized Hg (Hg^{2+})



Removal of Hg in Wet FGDs

- Maximize gaseous oxidized Hg at scrubber inlet
- Stabilize Hg^{2+} 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 Hg^{2+} 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

Scrubber Mercury Re-emission Additives

- Chemical additives that have successfully improved wet FGD mercury reduction through control of mercury re-emission and can be grouped into five categories:
  - Inorganic sulfides
  - Organic sulfides
  - Organic compounds containing nitrogen and sulfur
  - Organic compounds containing oxygen and sulfur
  - Low molecular weight sulfur-containing polymers
- Some plants add activated carbon directly into the scrubber liquor to remove mercury

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

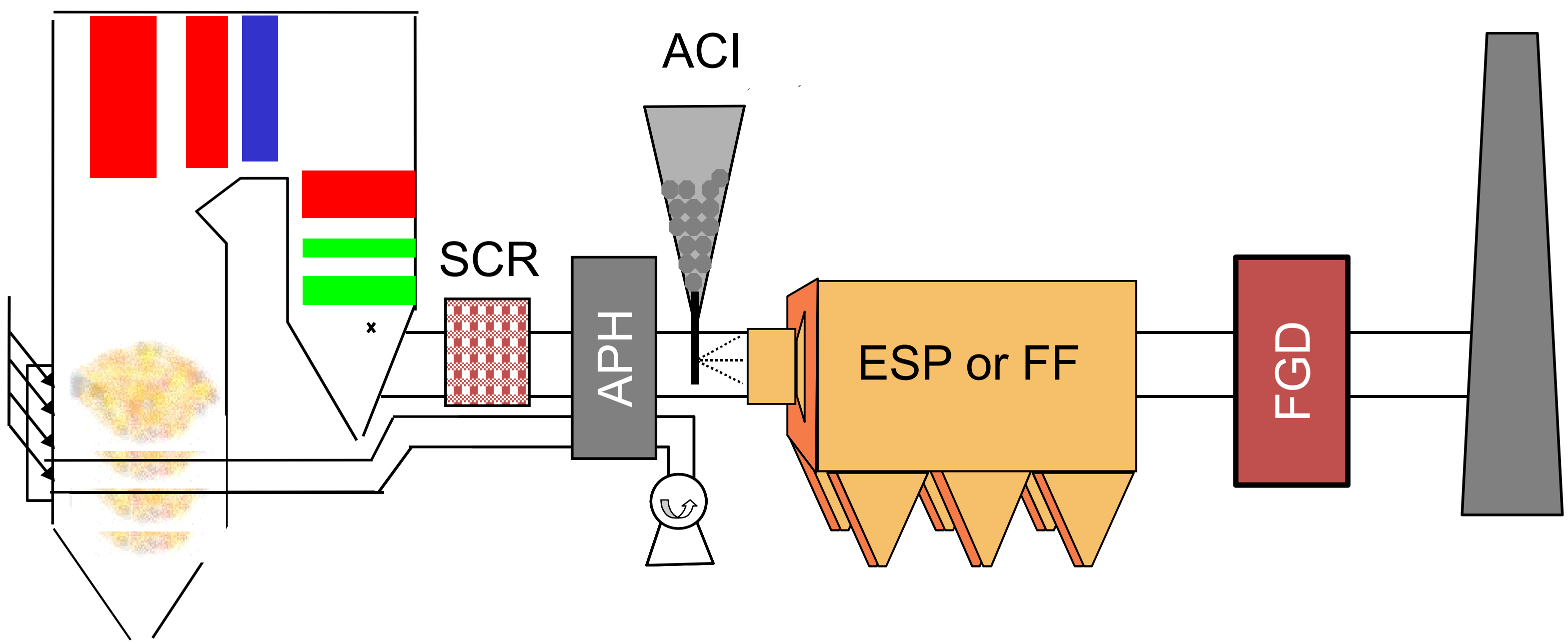
- Reduce oxidation air
  - < ~ 300 mV[1*]
- Increased sulfite
- Increase pH
- High halogen

[1] % Dissolved mercury, and risk of re-emission increases at ORP > 300 mv

Mandi Richardson, AECOM

Supplemental Control: Activated Carbon

Challenges for Hg Removal

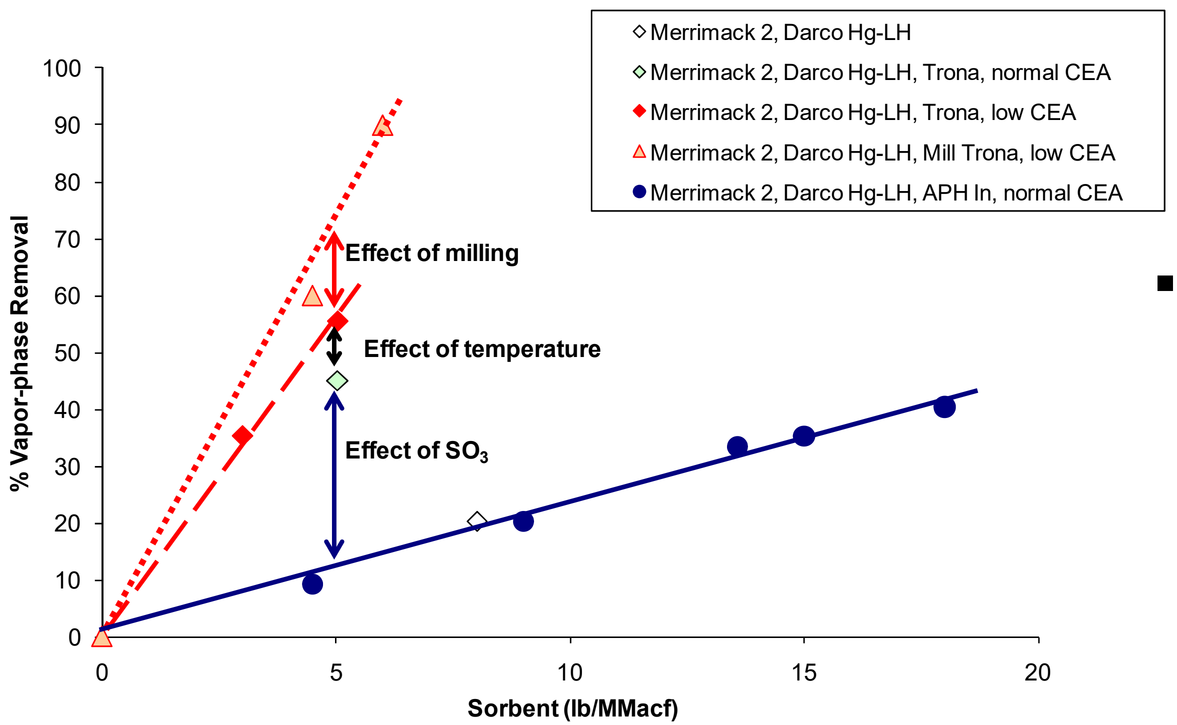


Temperature
SO_3
Halogens
Oxidized Hg

SO_3 and temperature have compounding negative impact on performance of activated carbon

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

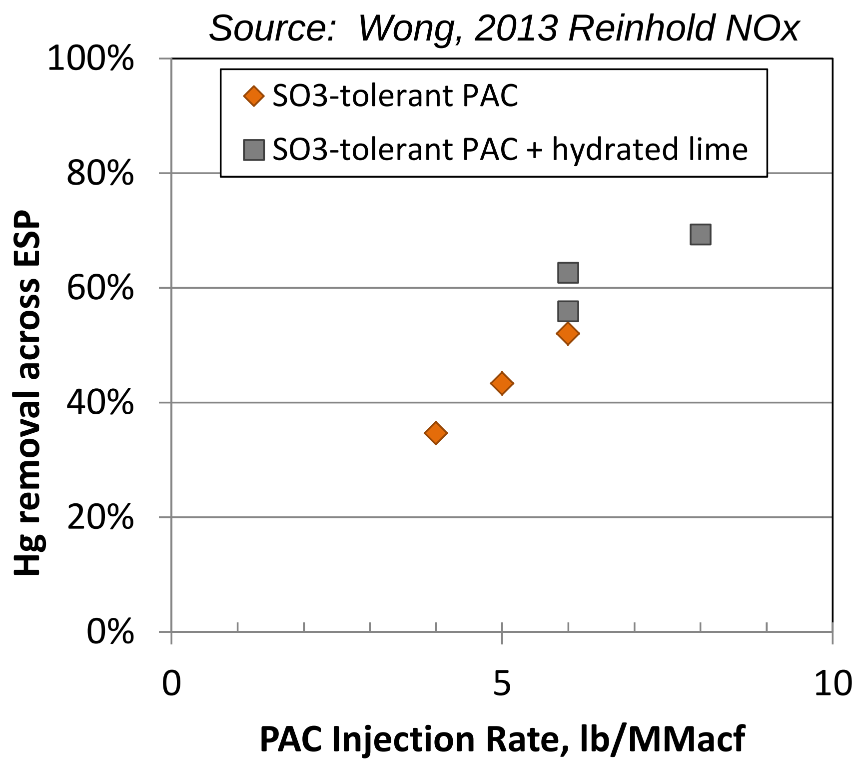


- High temperatures and high SO_3 concentrations in the flue gas downstream of the APH strongly affect sorbent performance
- Other factors, possibly important, including coal chlorine content and sorbent mixing in the flue gas duct

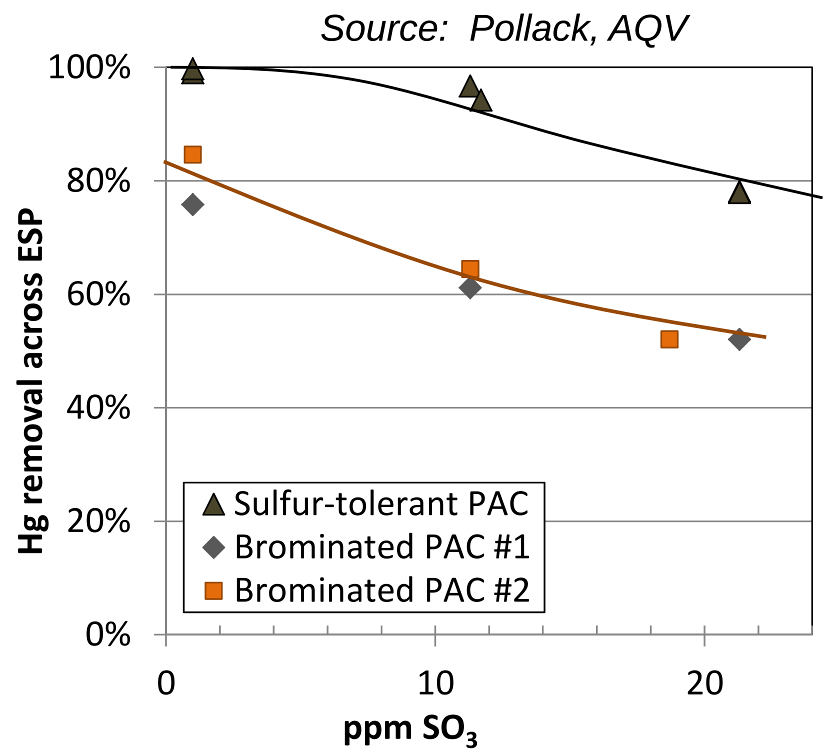
Co-Benefit Trim

Sulfur-Tolerant Activated Carbon

Some plants use specialty carbon to achieve mercury control



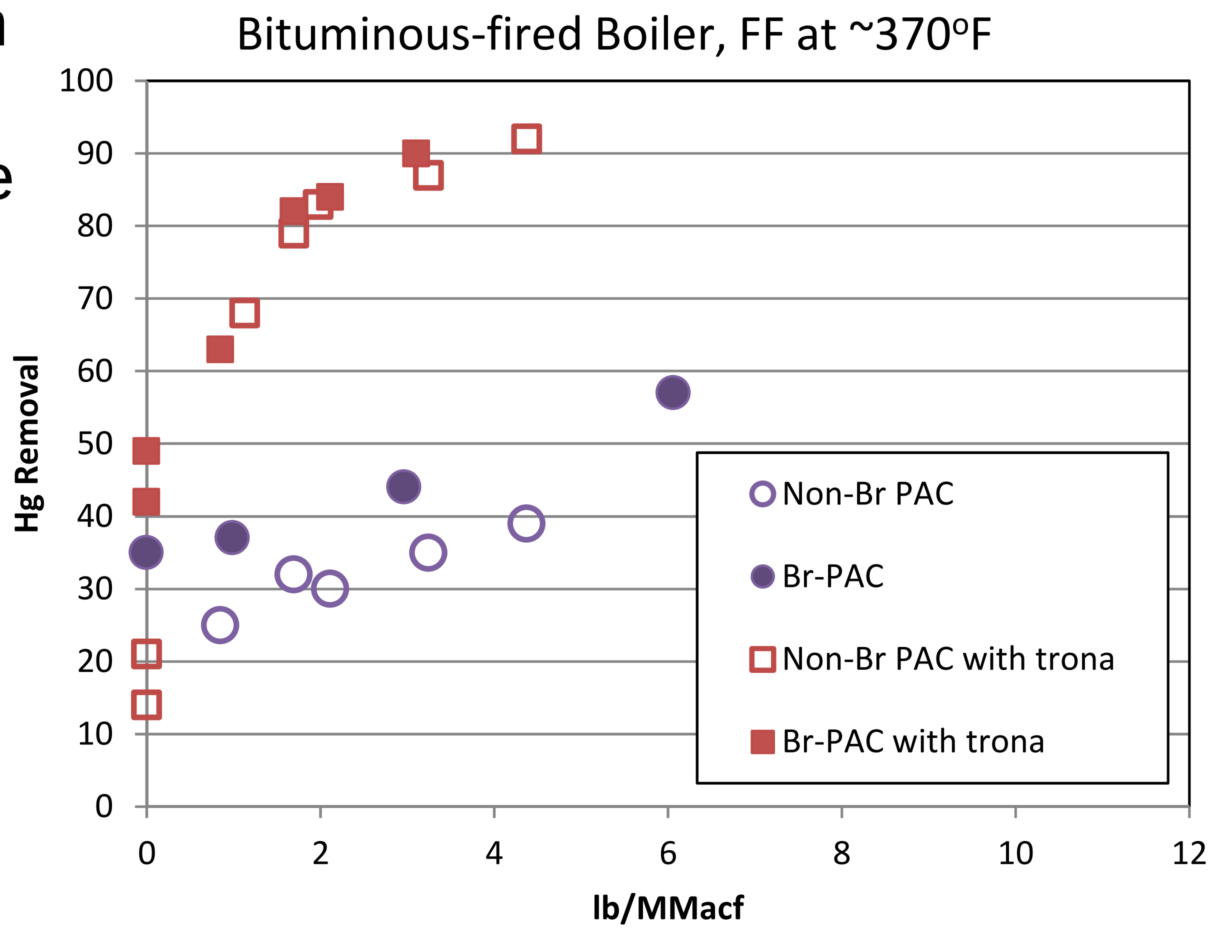
High S coal, SCR-ESP-FGD,
> 15 ppmv SO_3



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

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
- <u>Example:</u> Bituminous-fired boiler with FF, ~20 ppm SO_3 uncontrolled

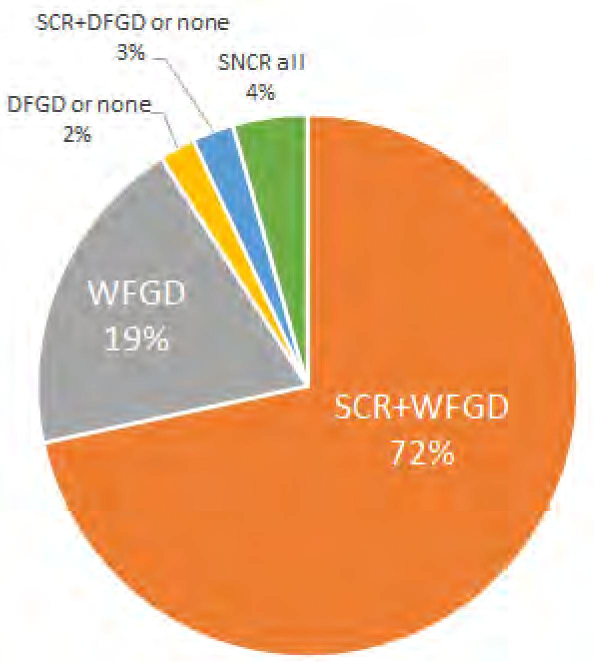


Co-Benefit Trim

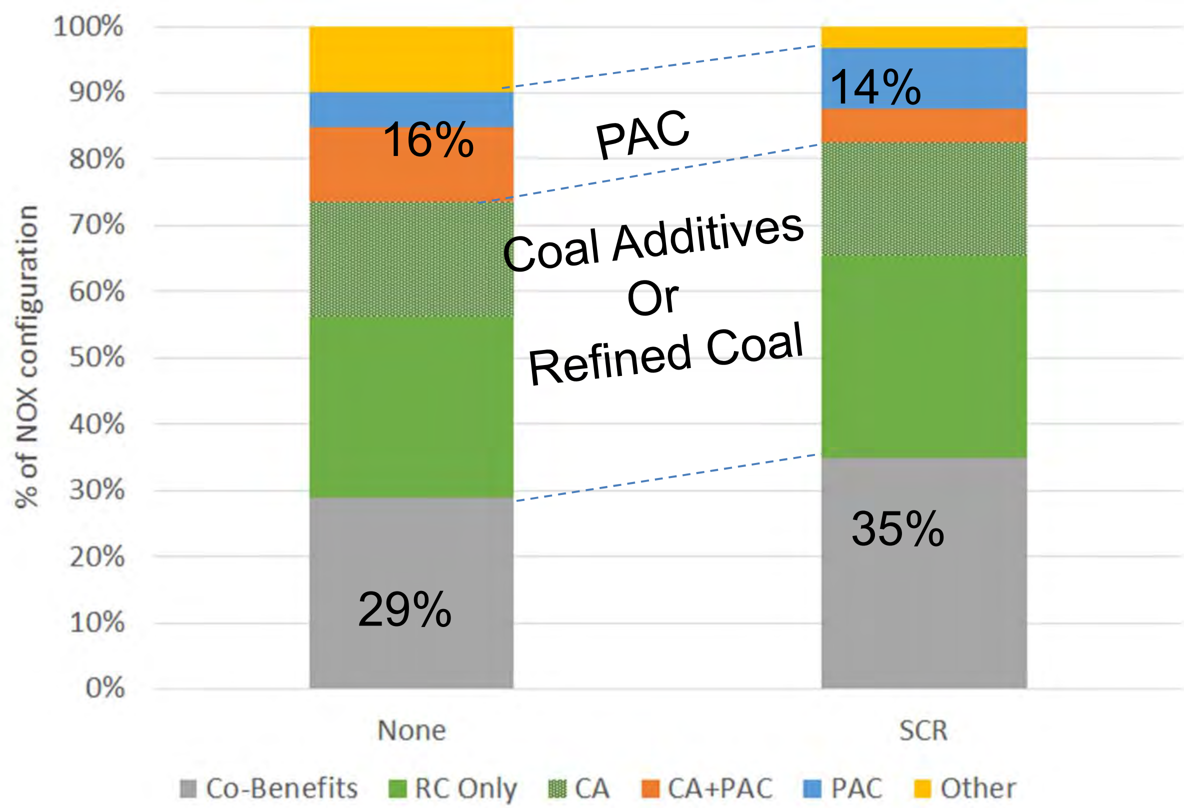
DSI-ACI Co-Treatment Considerations

- Potential for SO_3 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 NO_2
  → 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

SOx and NOx Controls: Influence on Mercury Controls: Bituminous-Fired Units



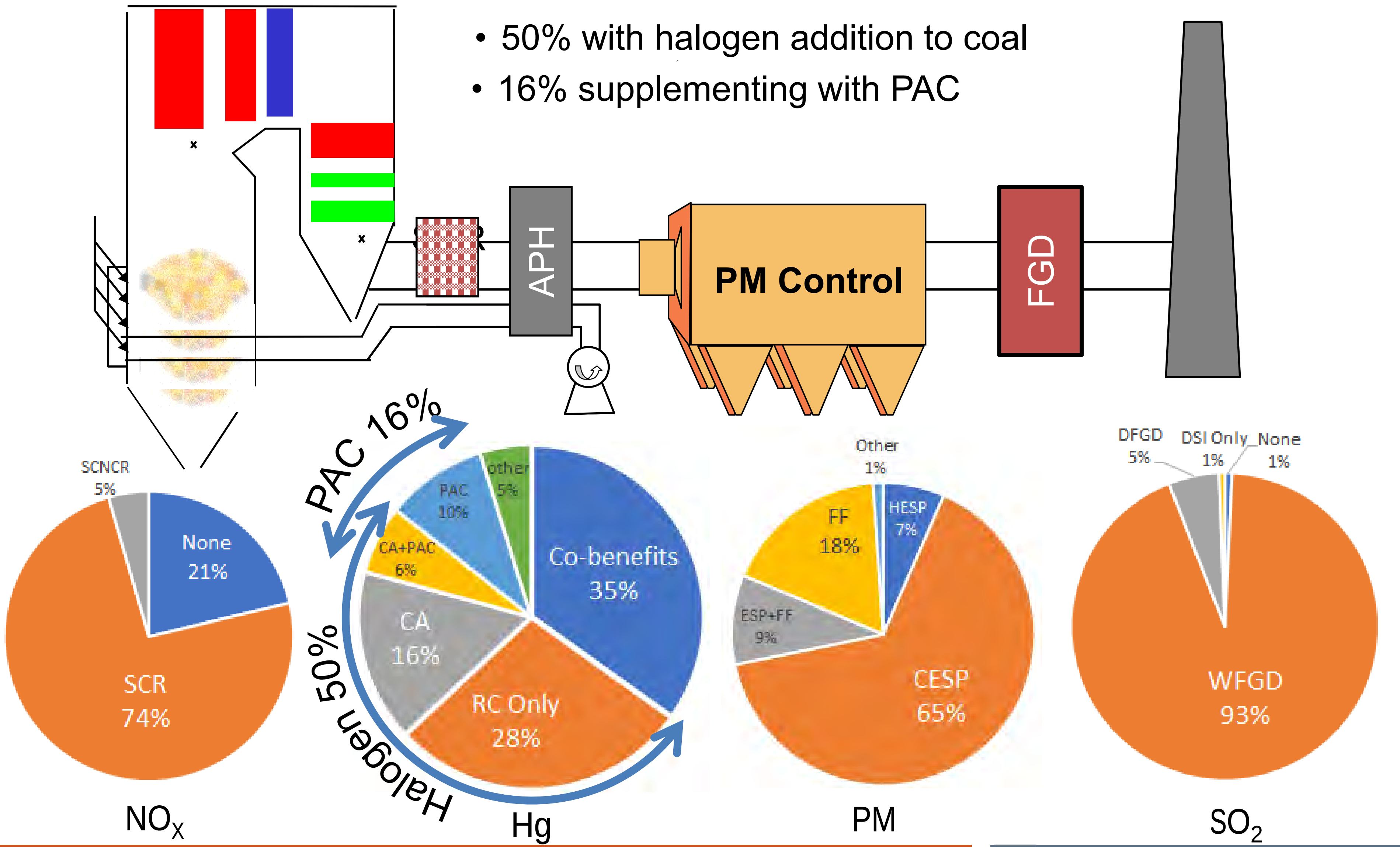
Bituminous-Fired Units



- On average, an installed SCR has a minor impact on the fraction of bituminous units with SCRs reporting using PAC to supplement Hg compliance
  - Data on the amount of PAC or coal additives is not reported
- Larger fraction of SCR + WFGD units relying on co-benefits alone compared to WFGD alone

Mercury Controls Strategies: Bituminous Plants

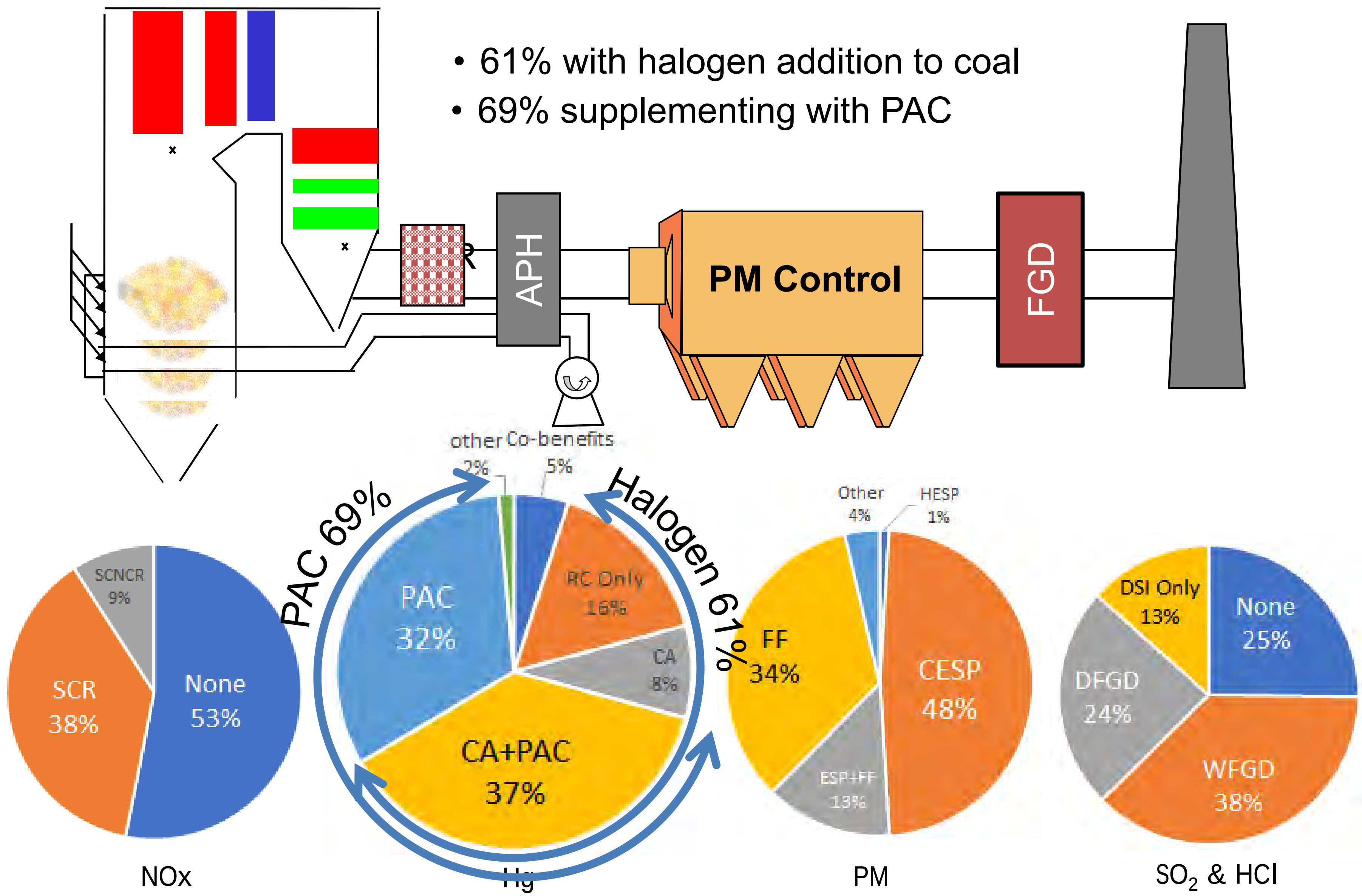
- 50% with halogen addition to coal
- 16% supplementing with PAC



Based on 2017 EIA and CAMD data

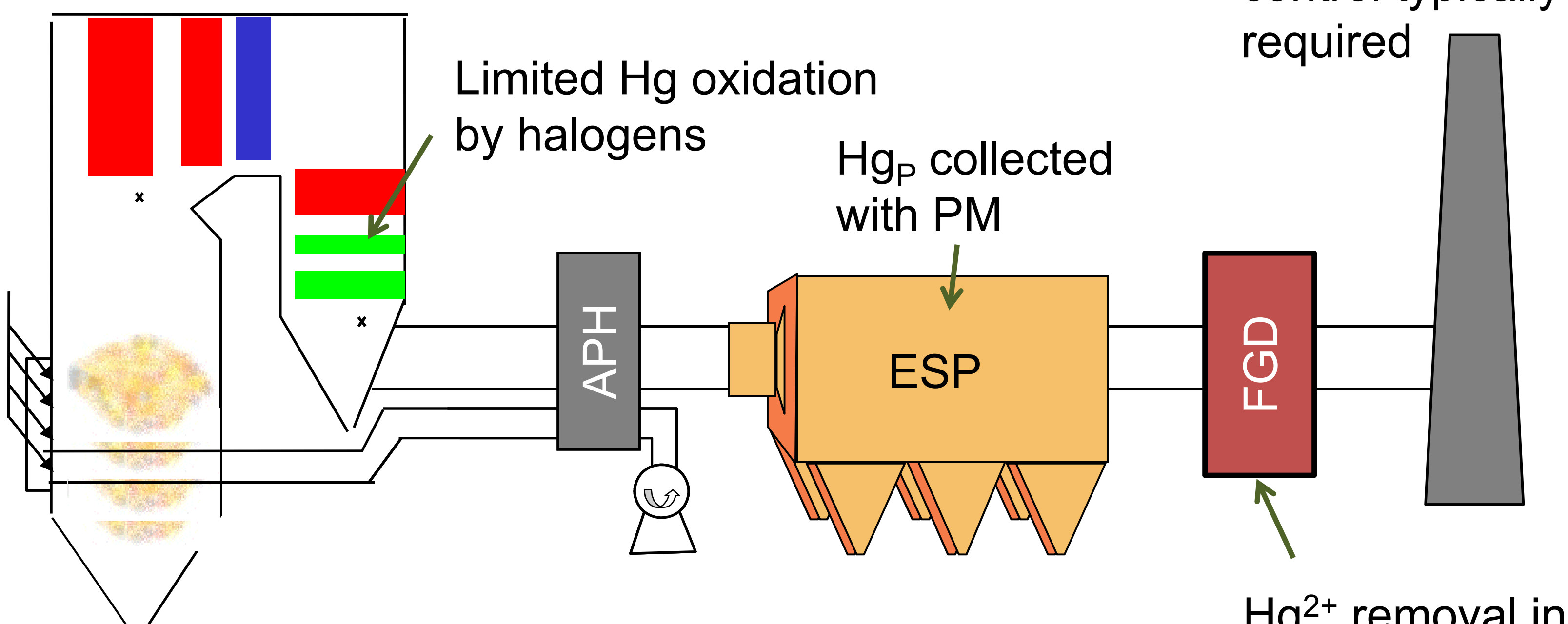
APC Configurations: Subbituminous Plants

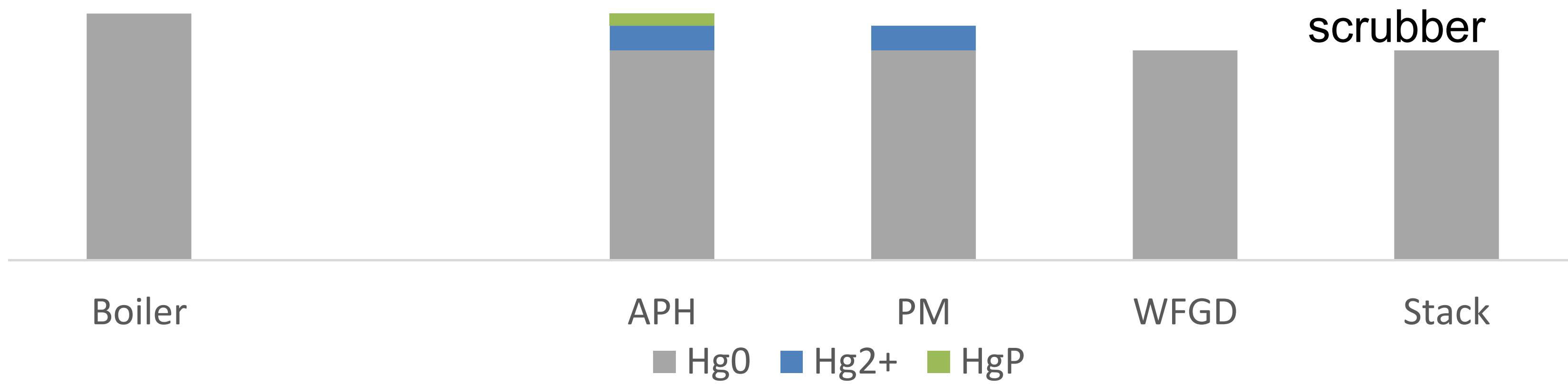
- 61% with halogen addition to coal
- 69% supplementing with PAC



Based on 2017 EIA and CAMD data

Subbituminous-Fired Plant with “Typical” APC

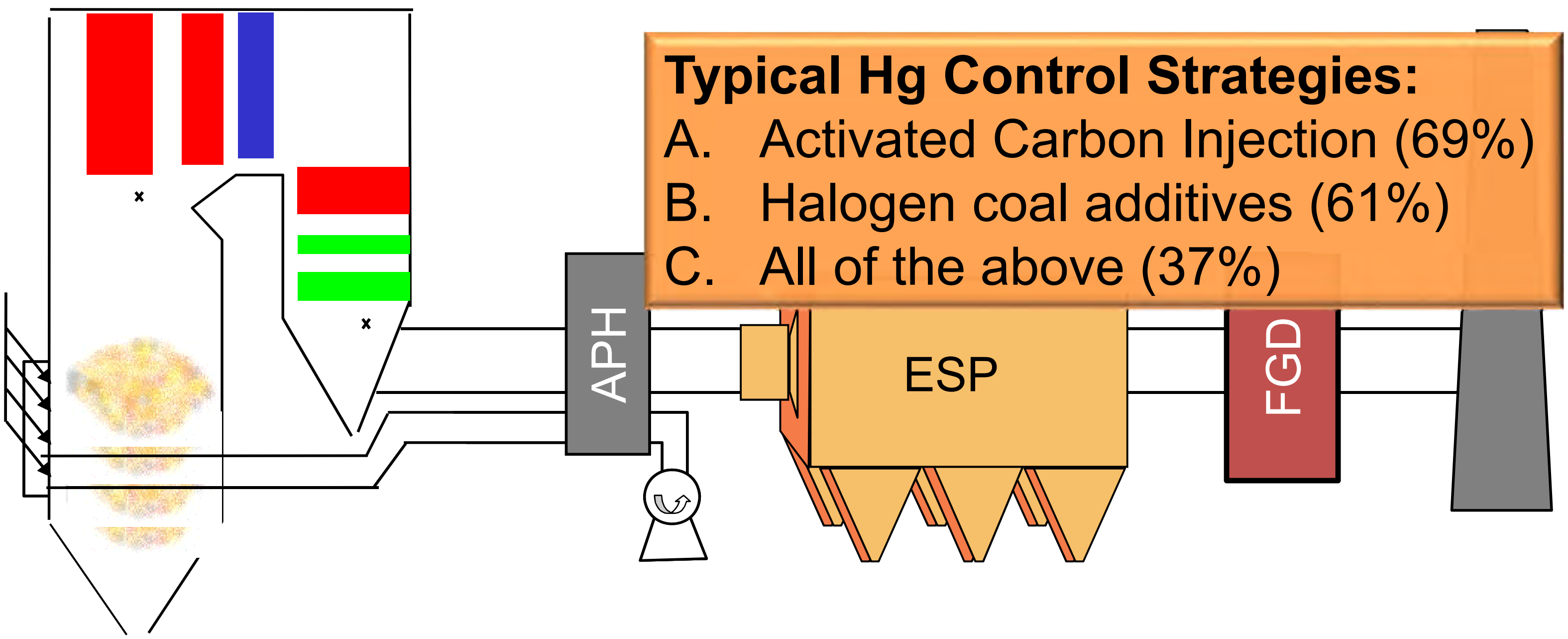


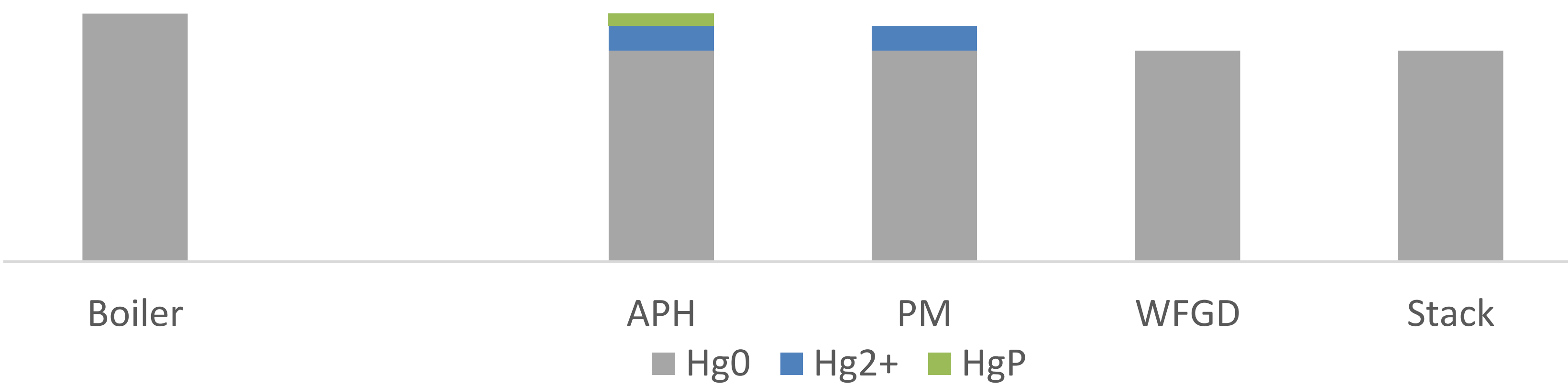


Subbituminous-Fired Plant with “Typical” APC

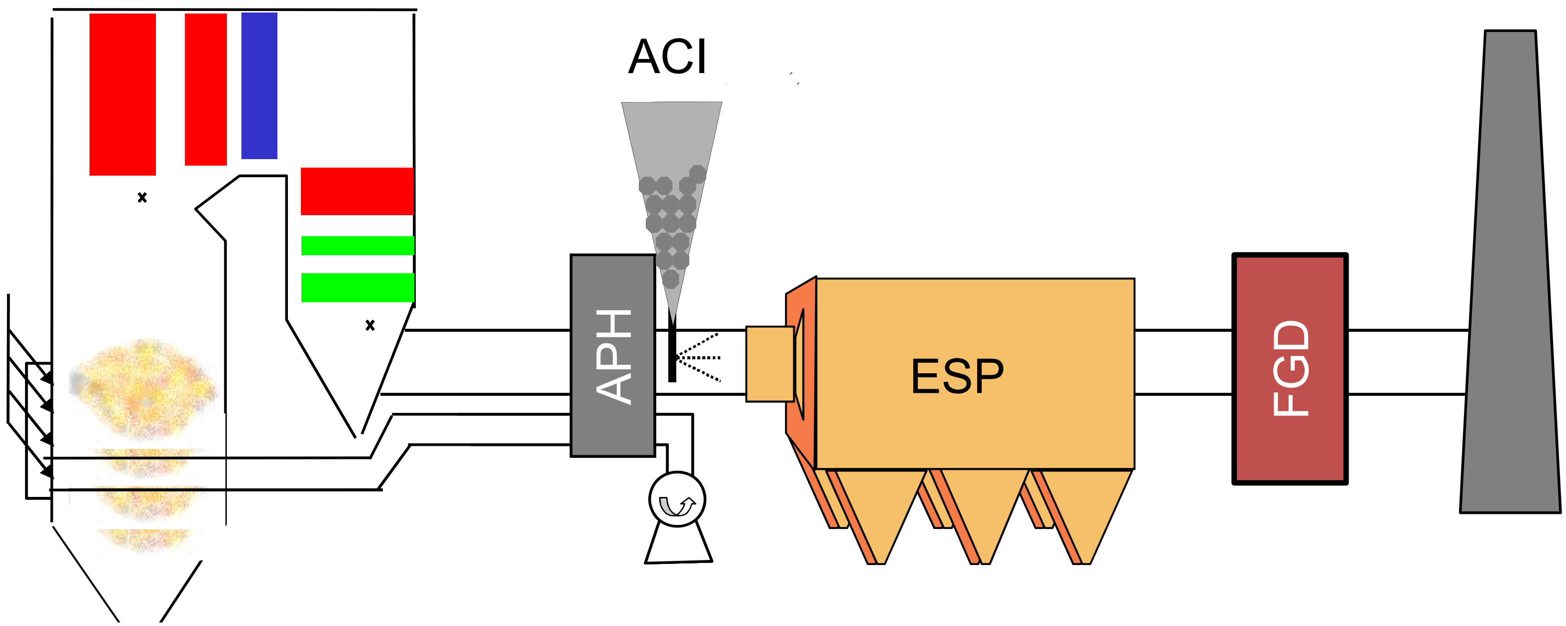
Typical Hg Control Strategies:

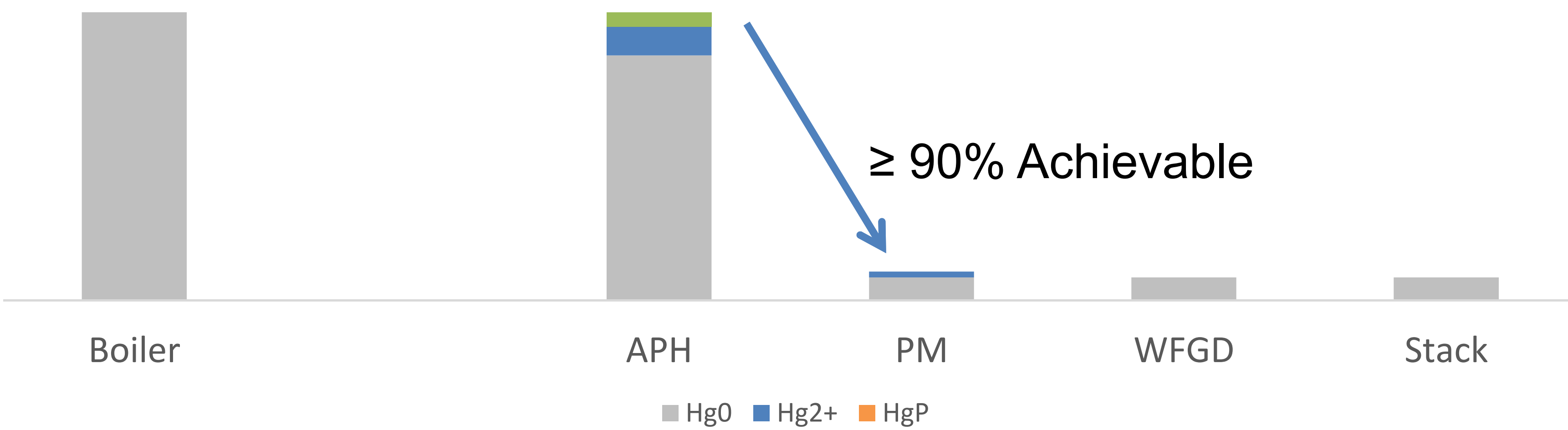
A. Activated Carbon Injection (69%)
B. Halogen coal additives (61%)
C. All of the above (37%)



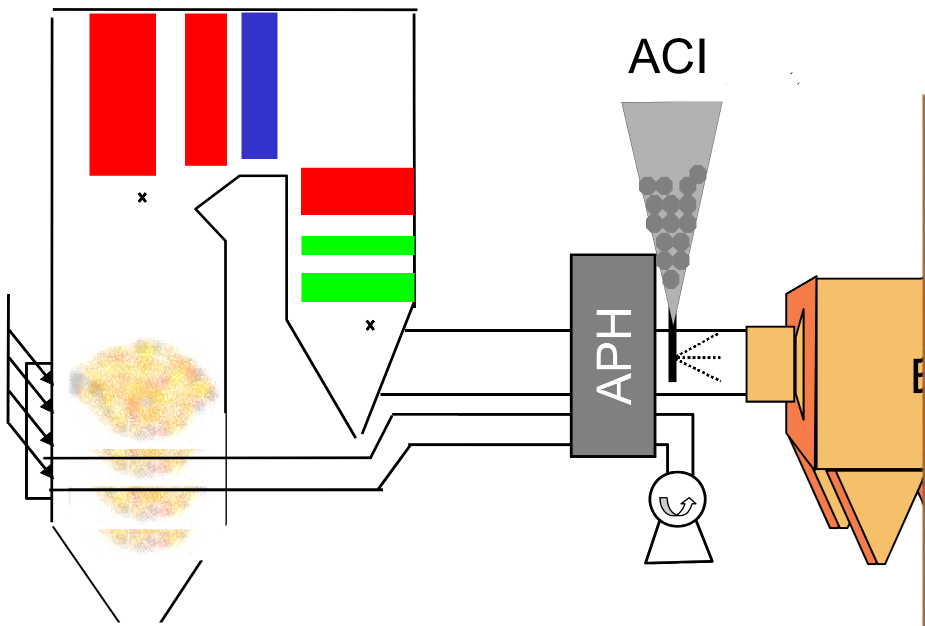


Subbituminous-Fired with "Typical" APC
Activated Carbon Injection (ACI)



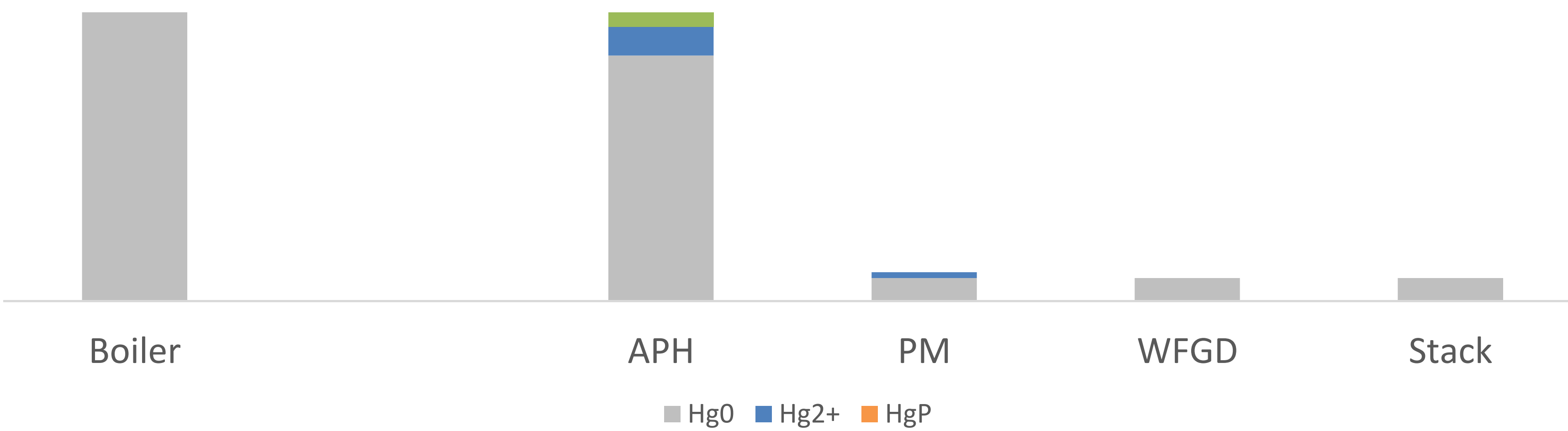


Subbituminous-Fired with "Typical" APC Activated Carbon Injection (ACI)



Options to optimize include:

- Reduce Temperature
- Improve Mass Transfer
  - PAC size
  - Distribution
  - Residence Time
- Limit SO_3, NO_2, NH_3
- Add halogen

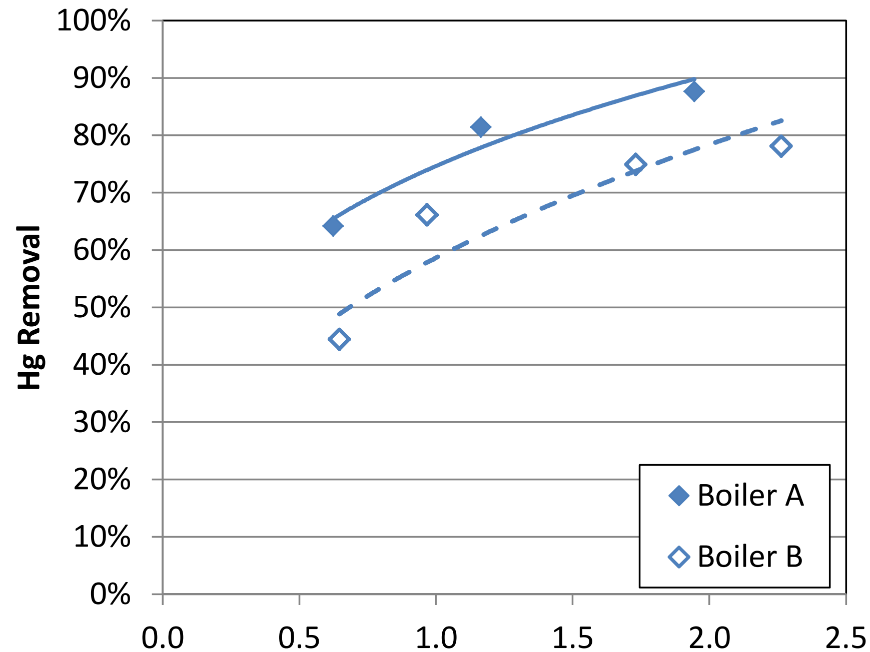


Mass Transfer Important for ESPs

Powdered Activated Carbon (PAC) 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

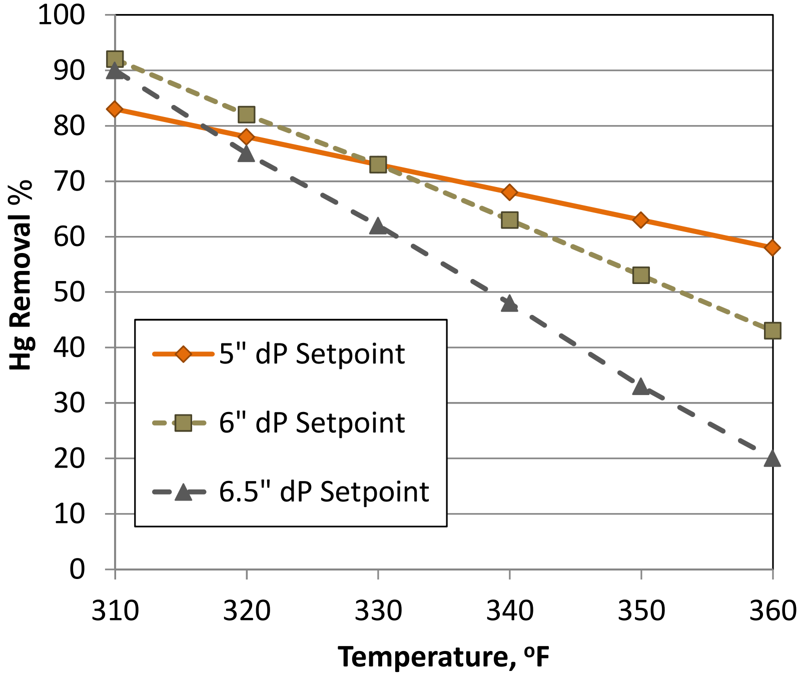
Boiler B has short residence time between APH and ESP inlet AND Chevron-style inlets

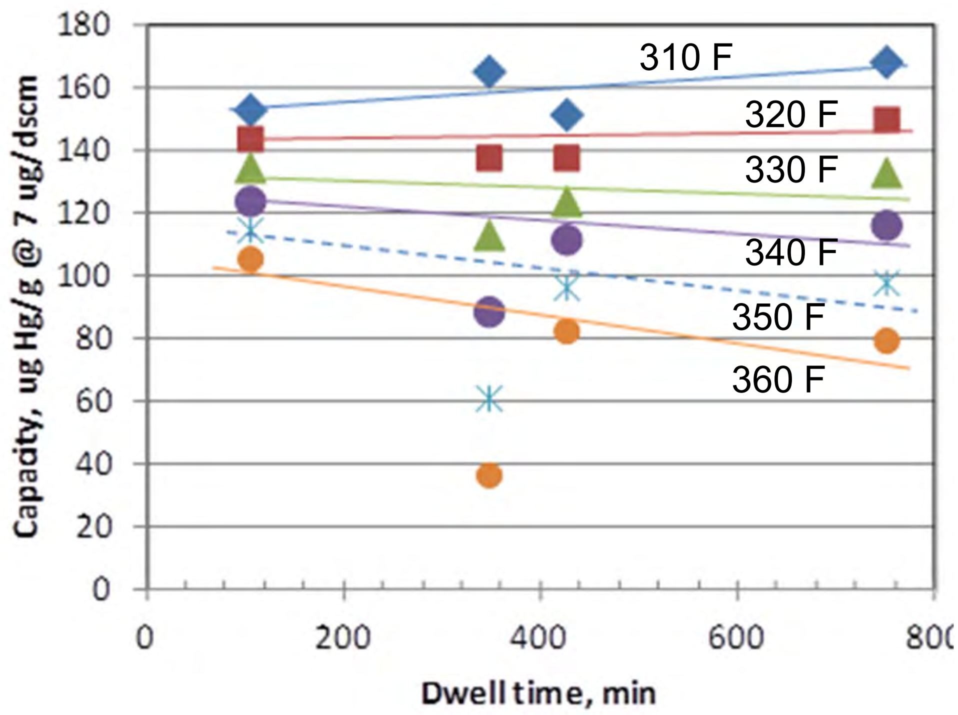
Boiler A has longer duct residence time

Getting the Most Out of ACI with Fabric Filters

- Lower temperature at the particulate control device
- Provide sufficient contact time
- Clean bags before increasing temperature

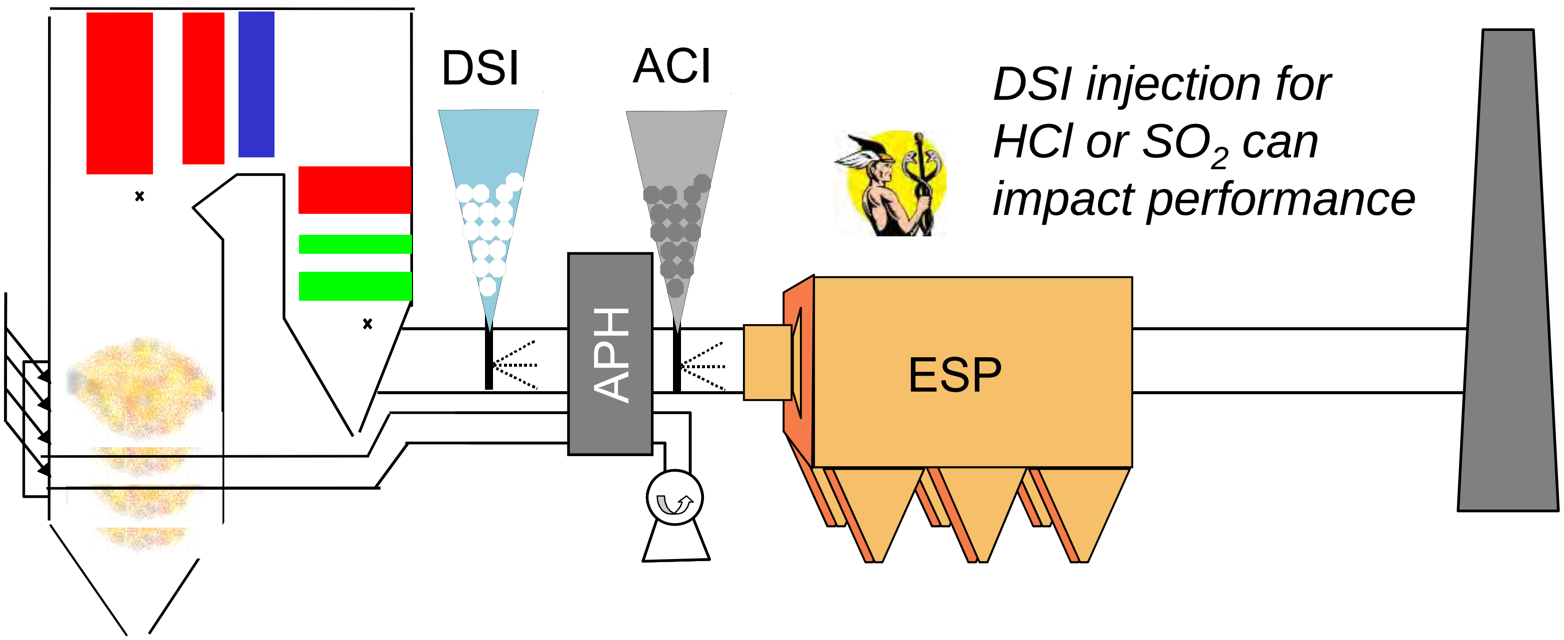
Source: Derenne and Stewart, Final Report



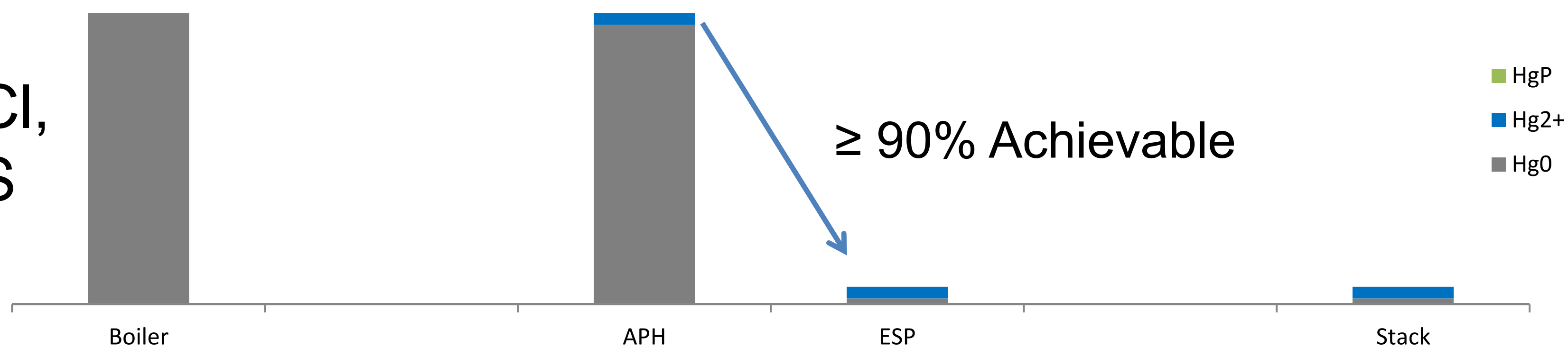


Presque Isle TOXECON fabric filter, 1 lb/MMacf non-brominated PAC

Mercury and HCl Control Subbituminous Coals

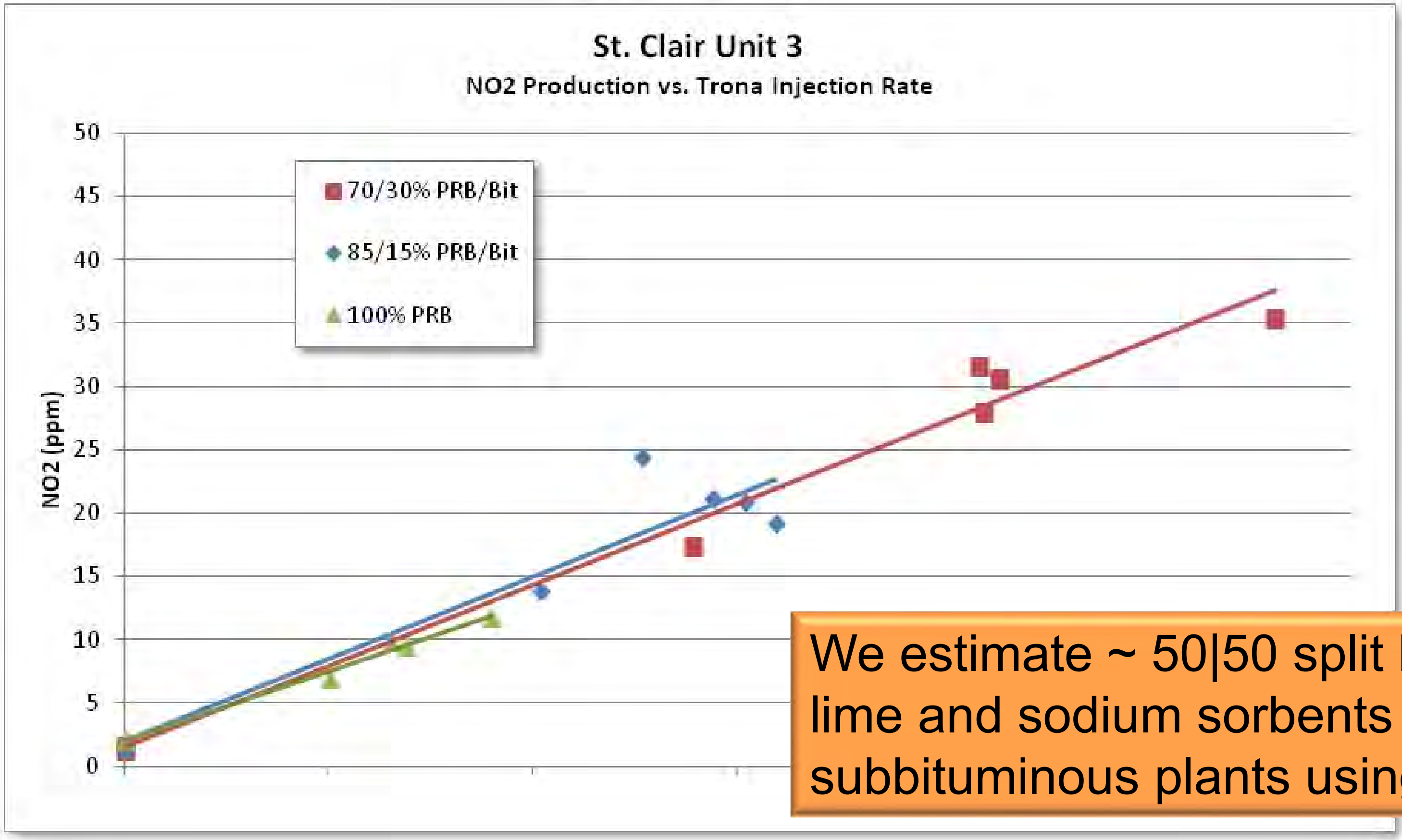


Low Cl,
Low S



Potential DSI Challenges:
NO_2 Production with Trona Injection

- Sodium-based DSI can increase flue gas NO_2
- Trona or SBC injection increased stack NO_2 to as much as 35 ppmv

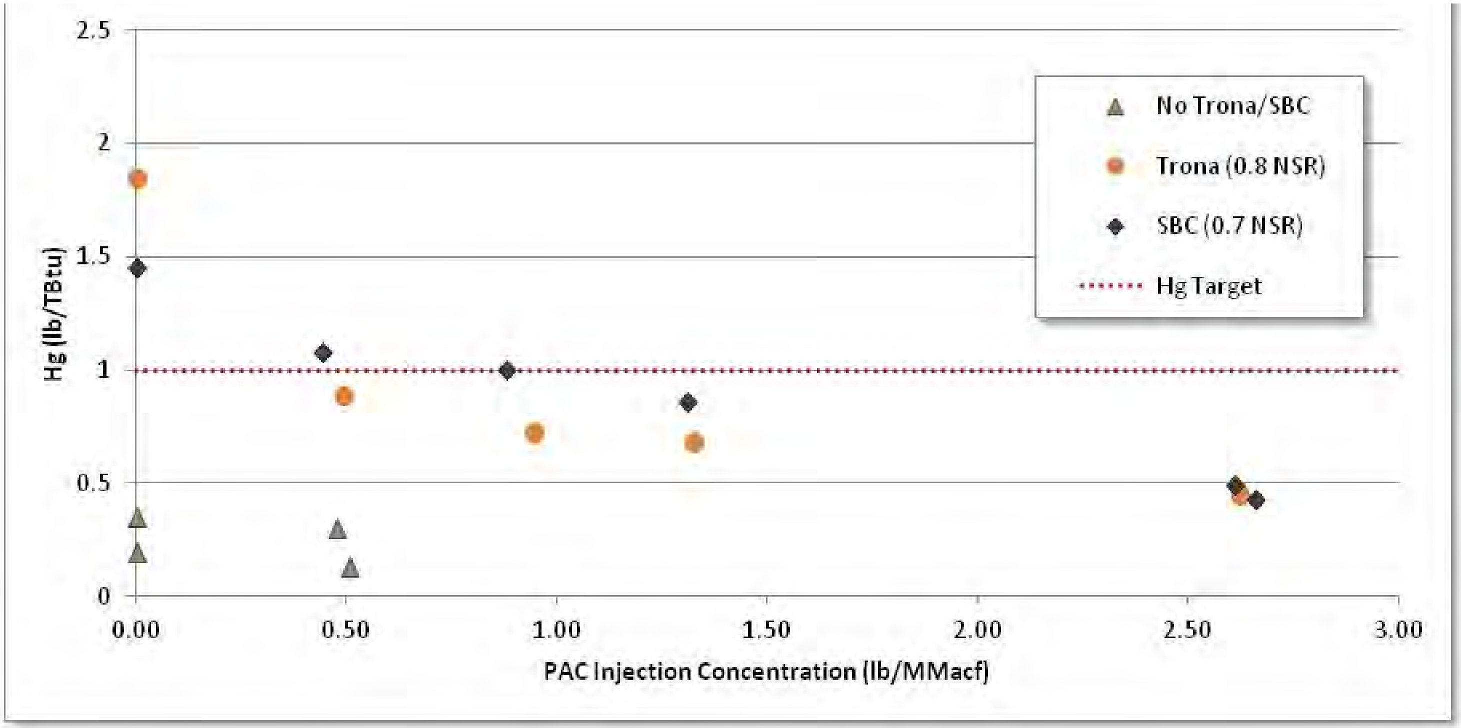


We estimate ~ 50|50 split between lime and sodium sorbents for subbituminous plants using DSI

Results from Testing at DTE St. Clair Unit 3, W. Rogers, EUEC 2013

Impacts of NO_2 on PAC

- NO_2 will interfere with Hg removal by PAC



Non-brominated PAC injected downstream of air preheater and trona or sodium bicarbonate injected upstream of air preheater for HCl control

Results from Testing at DTE St. Clair Unit 3, W. Rogers, EUEC 2013

Increase Native Capture: Halogen Addition

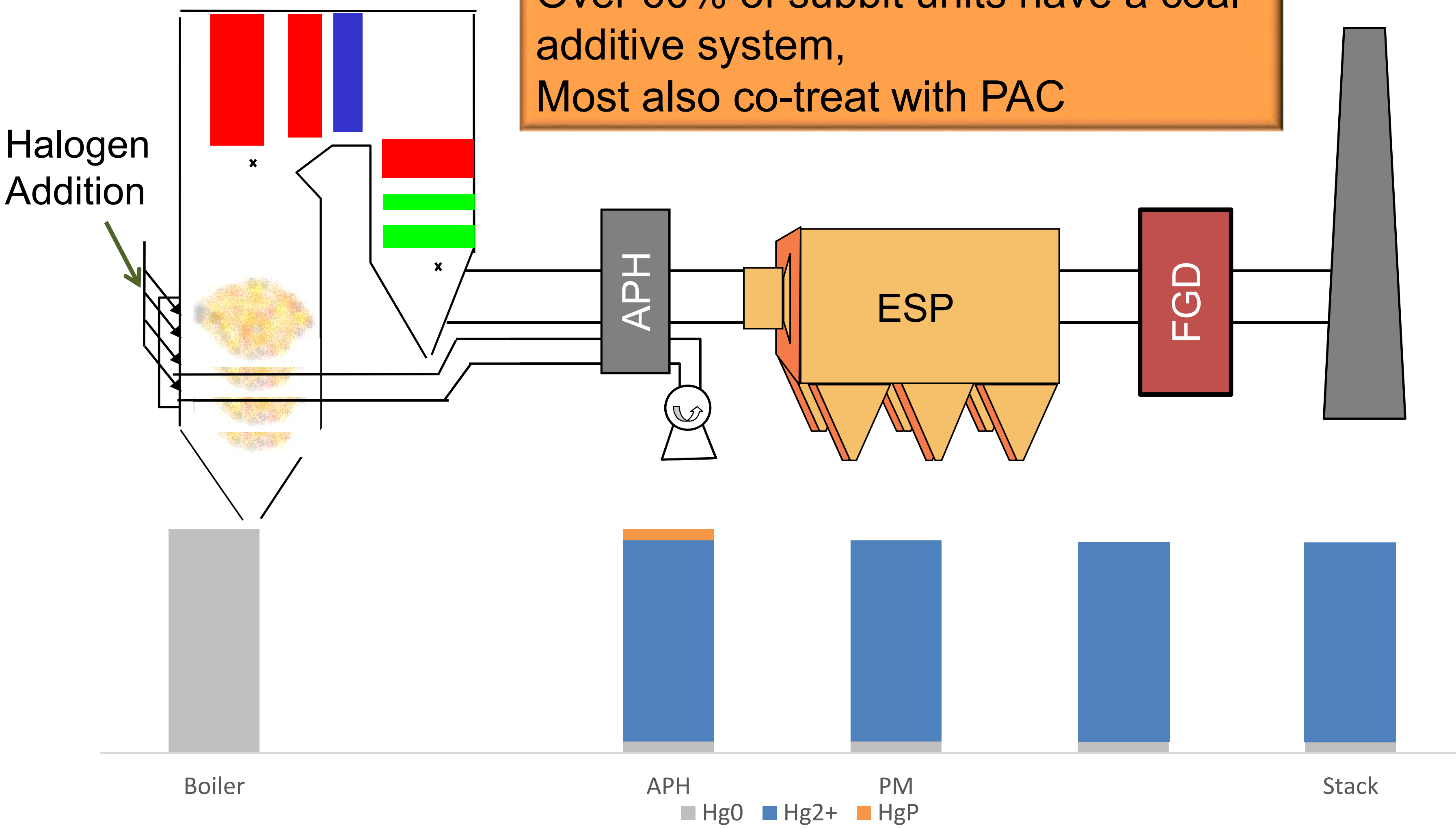
- Adding halogens increases oxidized Hg:
  - Increase effectiveness of some kinds of activated carbon for Hg capture
  - Increase capture of Hg in SO_2 scrubber
- Potential balance-of-plant impacts:
  - Possible increased corrosion
  - Halogens build up in wet scrubber liquor
    - Average Cl removals 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

Emerging Issue: Bromine in Scrubber Effluent

- The US EPA has established limits for eleven DBPs in drinking water after determining that some DBPs are associated with increased cancer rates. These include four trihalomethanes (THMs), five trihalomethanes (HAAs), bromate, and chlorite.
- Increased use of bromine for mercury control has heightened awareness of potential risk associated with bromine-containing effluent discharged into waterways
  - Example: There are > 6,000 public water systems in North Carolina alone

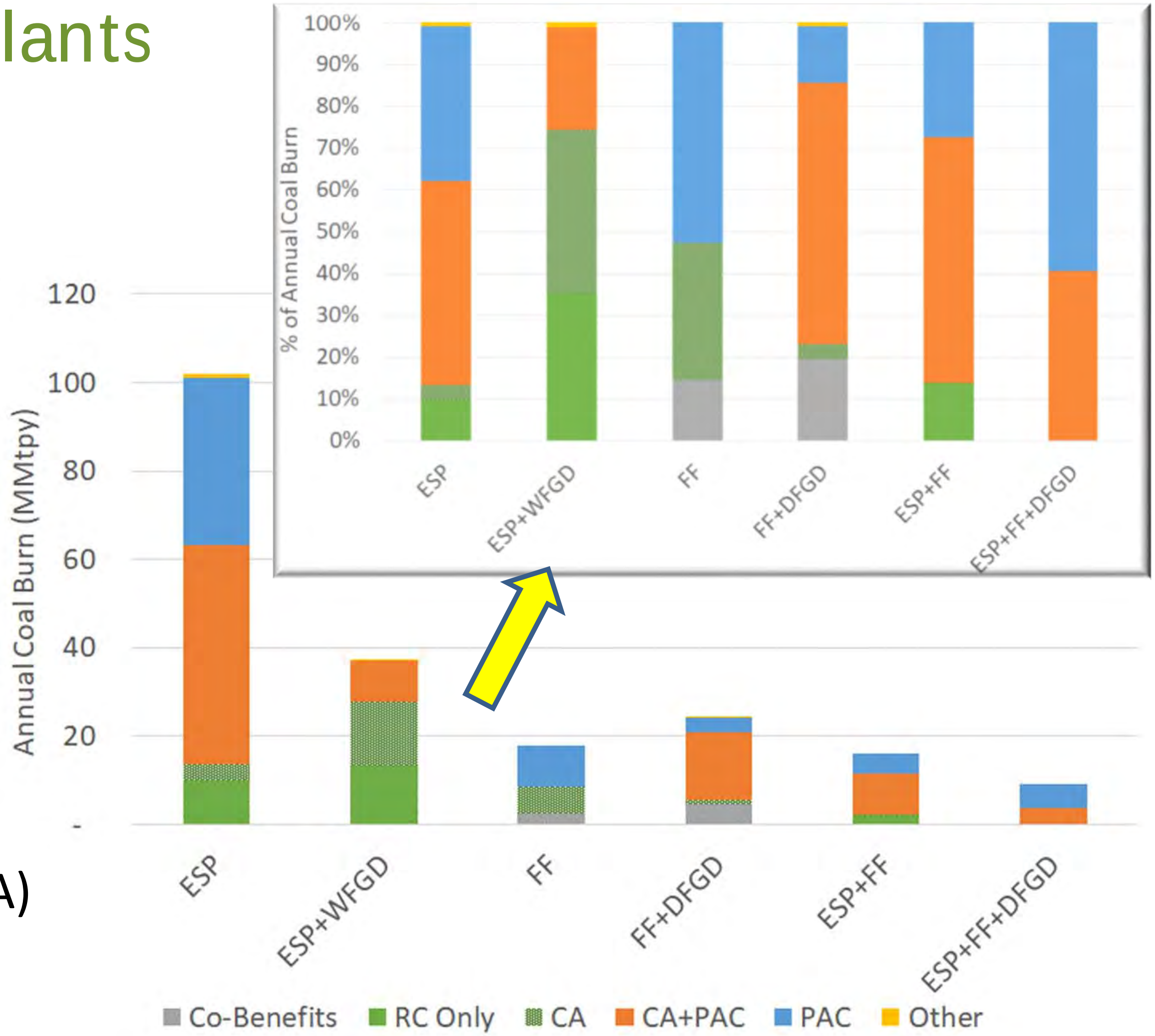
Subbituminous-Fired Plant, “Typical” APC & Coal Additives (Halogen Injection)

Over 60% of subbit units have a coal additive system,
Most also co-treat with PAC



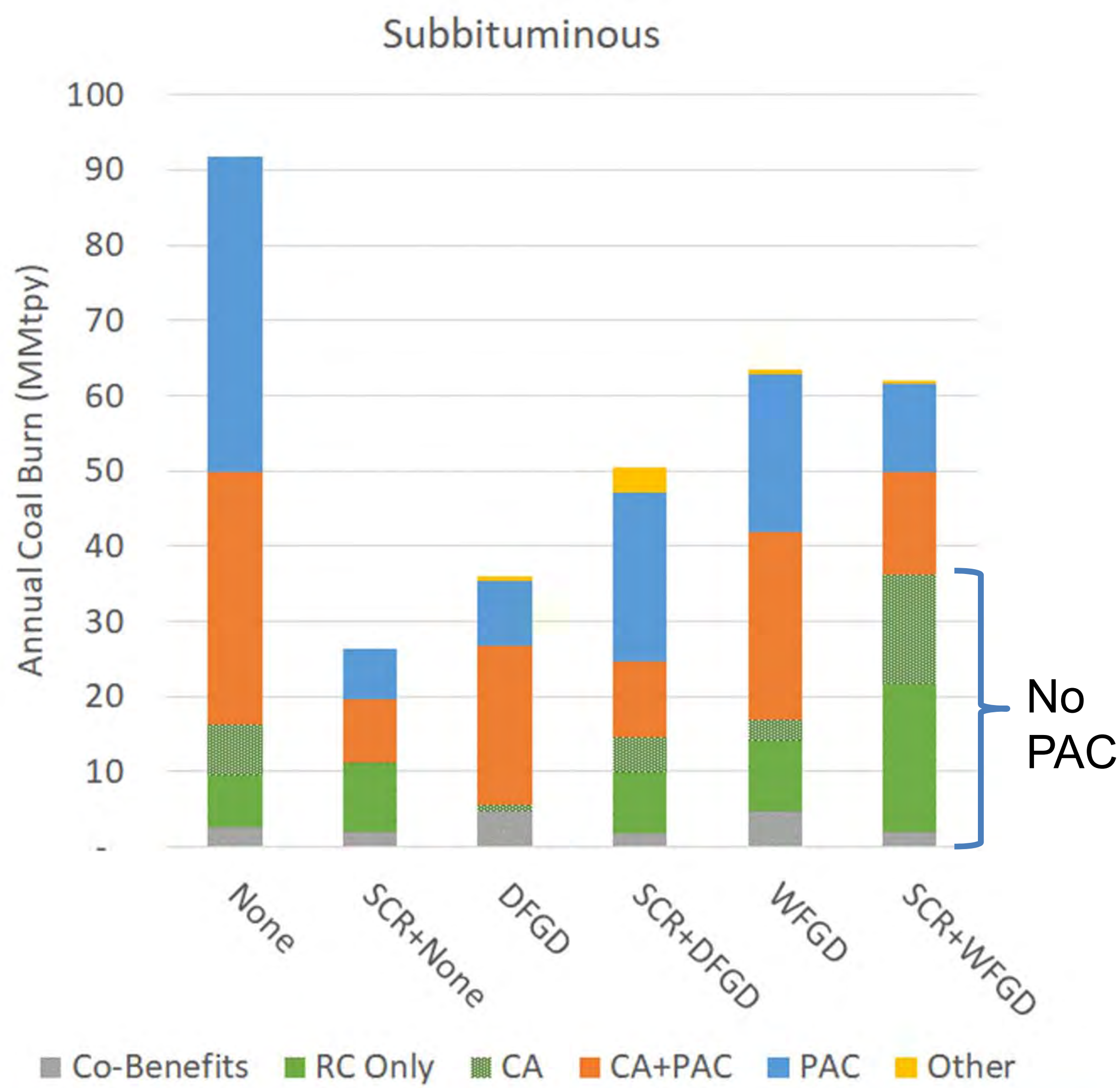
Impact of Particulate and SOx Controls on Mercury Controls (No SCR or SNCR): Subbituminous Plants

- Only ~ 20% can meet compliance with coal additives alone
- Most units (typ > 80%) require some PAC to meet compliance
  - Many use a combination of PAC and coal additives (CA)

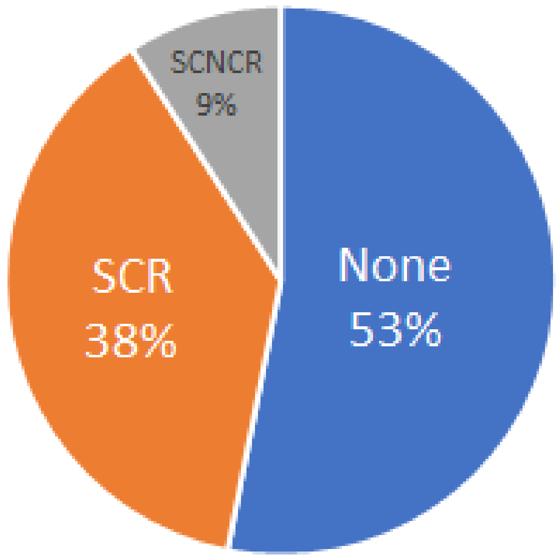


Impact of SCR + SOx Controls on Mercury Controls

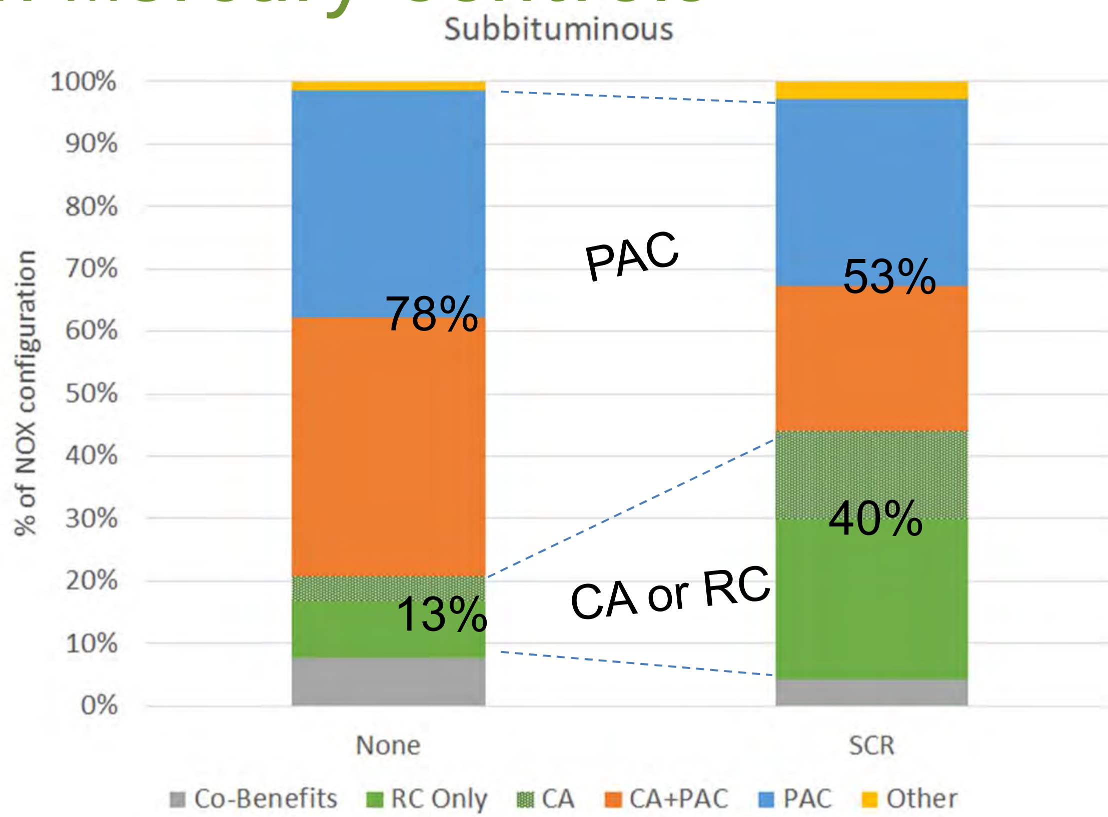
- On average, subbit plants rely on PAC to meet compliance
- Exception: 58% of subbit units with SCR + WFGD meet compliance without any PAC



Impact of SCR on Mercury Controls

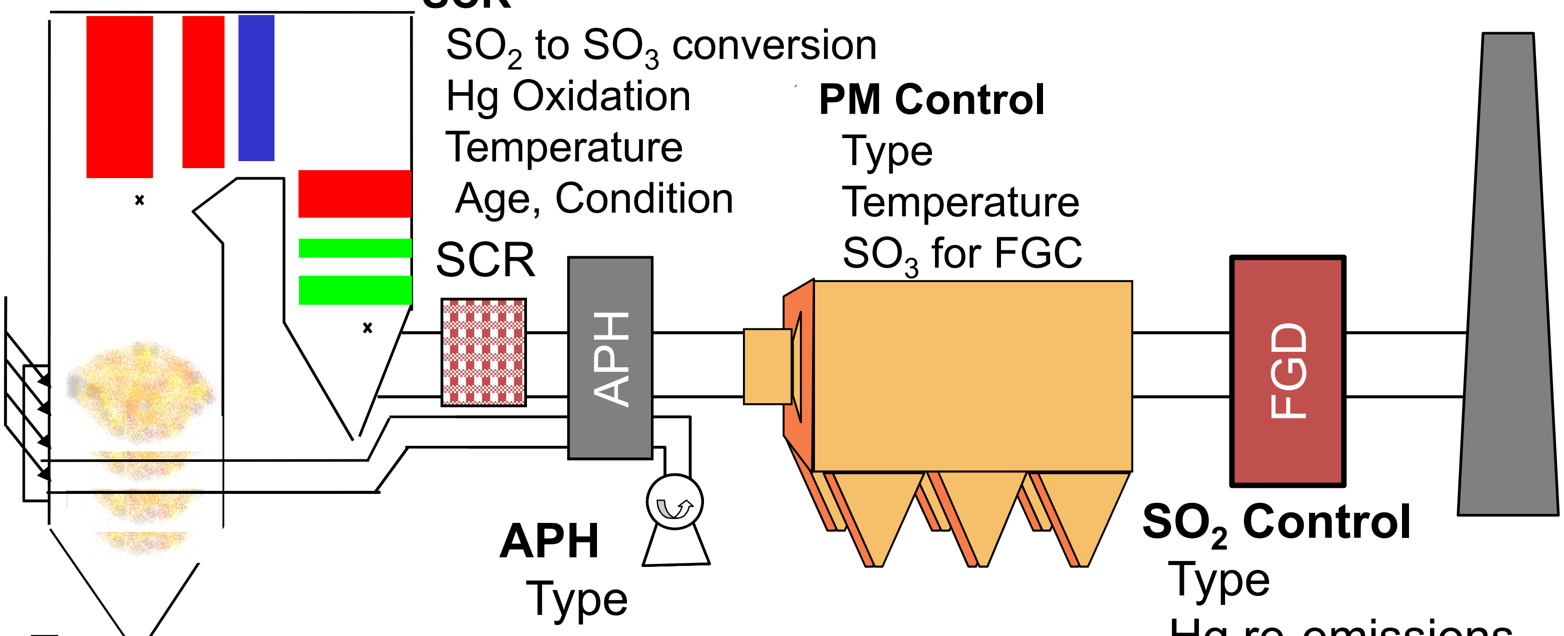


Subbituminous Coal



- Units with installed SCRs are **three times** more likely to report using coal additives alone (no PAC) for Hg oxidation than those without SCRs
  - Data on the amount of PAC or coal additives is not reported

Review:
What's Important for Mercury Control



SCR
SO_2 to SO_3 conversion
Hg Oxidation
Temperature
Age, Condition

PM Control
Type
Temperature
SO_3 for FGC

APH
Type
Temperature

SO_2 Control
Type
Hg re-emissions
Water management

Boiler Type
Combustion Efficiency (LOI)
Coal
Mercury
Halogens
Sulfur
Ash: calcium, iron, etc.

→

LOI
Ash
SO_2 and SO_3
Halogens

→

LOI
Halogens
SO_3
Ash
Oxidized Hg

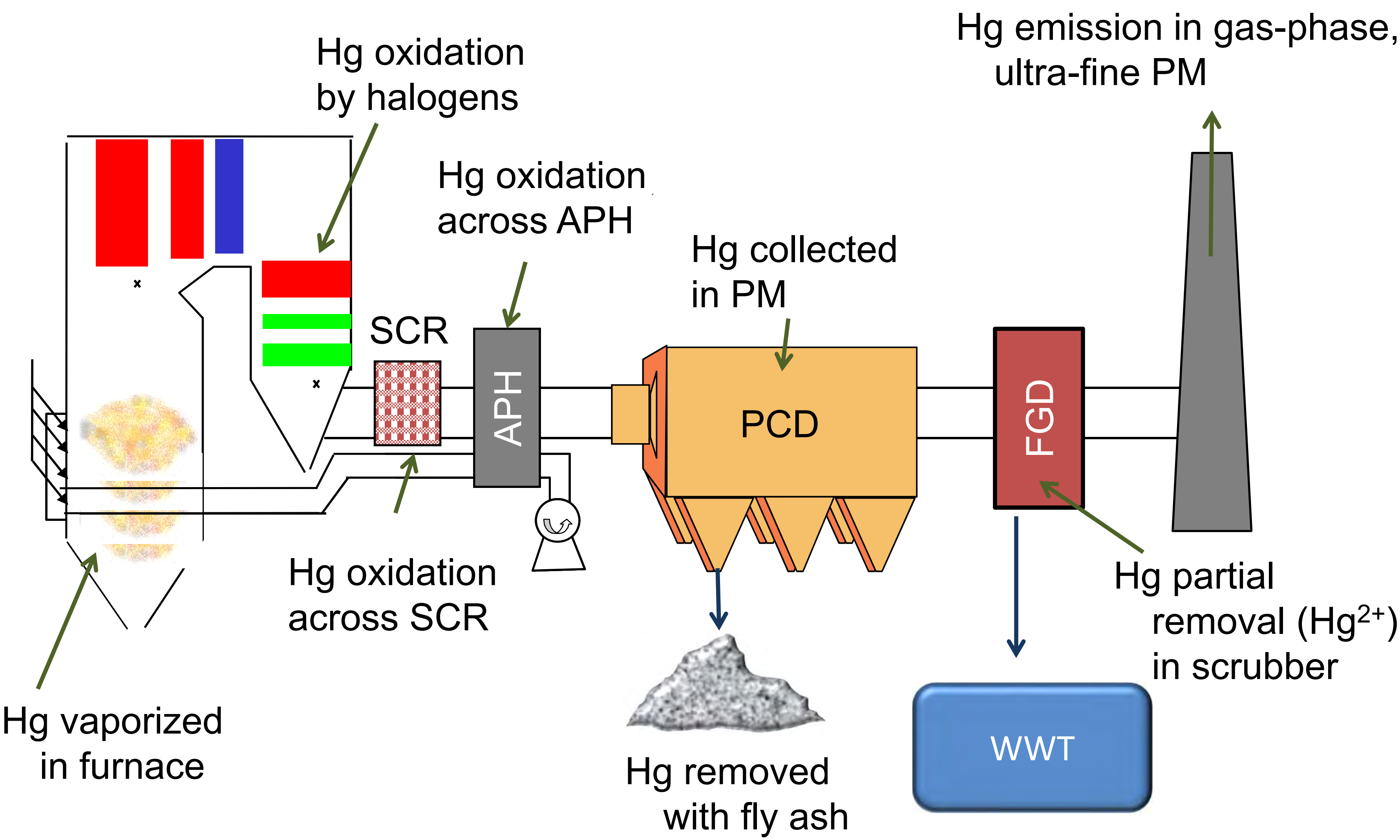
→

Halogens
Oxidized Hg

Primary Mercury Control Strategies

- Co-Benefits: no mercury-specific controls
  - More common on scrubbed plants firing higher halogen coal
- 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

Fate of Hg in Coal-Fired Boilers



Compliance Strategies for Mercury

- 80 to >90% control at the stack to meet MATS emission limits required for most units
- MATS limits achievable with ACI or ACI + coal additives on most subbituminous units if SO_3 flue gas conditioning (FGC) is eliminated
- For units with SCR/FGD:
  - Provide sufficient halogens to oxidize the Hg
  - Minimize re-emission of Hg^0 from wet FGD
  - Use ACI as needed for trim
- MATS limits may be challenging on units with higher sulfur coals. Year round compliance may require SO_3 mitigation and careful WFGD re-emissions management

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THANK YOU!

Contacts:
Sharon Sjostrom
sharons@adaes.com

Connie Senior
Connies@adaes.com