REINHOLD ENVIRONMENTAL Ltd.

2016 NOx-Combustion-CCR Round Table Presentation

February 1 & 2, 2016, in Orlando, FL / Hosted by OUC

Advancing Cleaner Energy

Holistic Operations

2016 NOx – Combustion Roundtable

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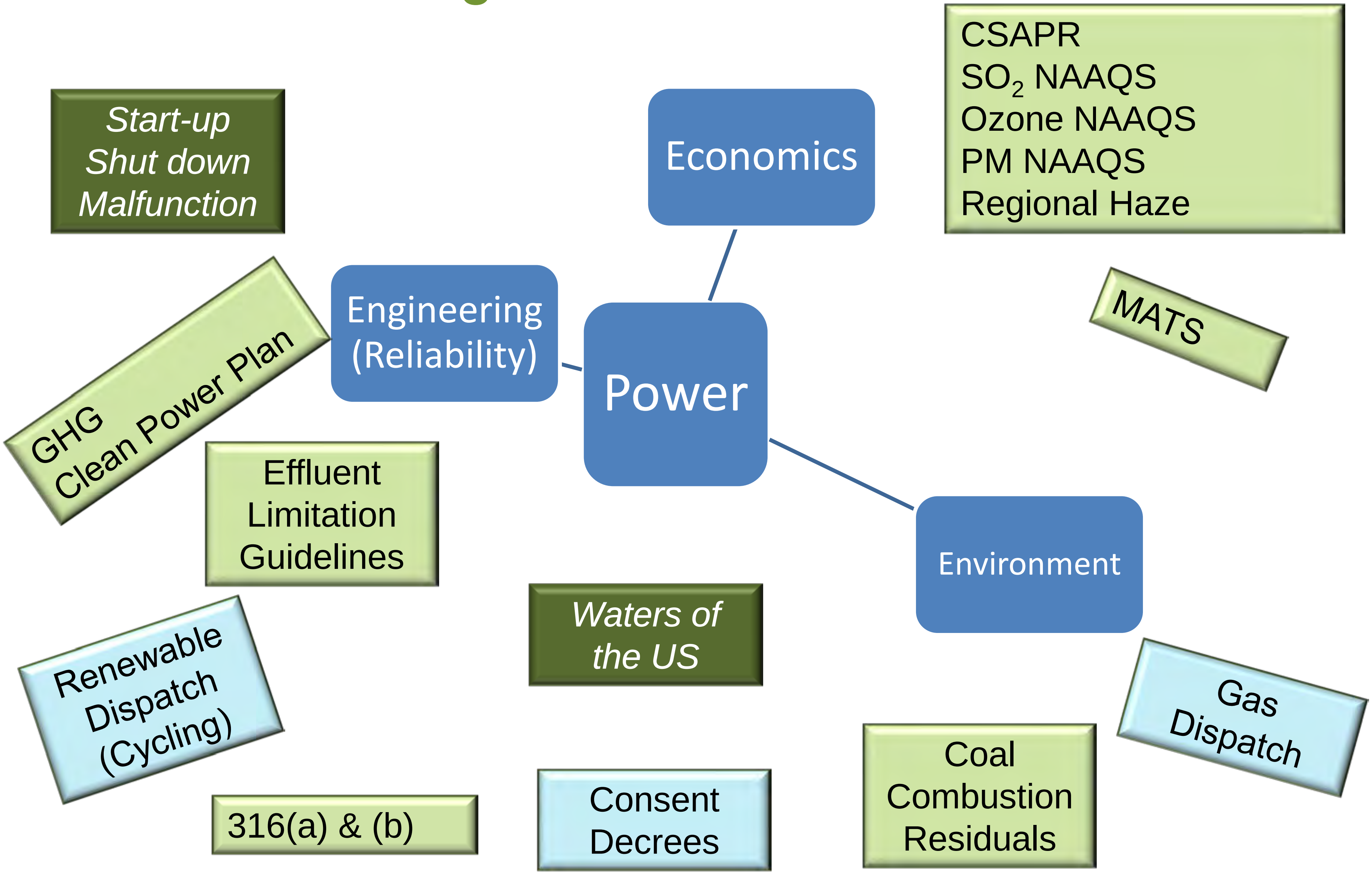
February 1, 2016

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.

Meeting the Demands



Finding the Right Balance

Boiler
- Slagging
- Fouling
- Corrosion

APH
- Plugging/Fouling
- Heat Rate
- Corrosion

Fans/Ducts
- Corrosion
- Power

Cooling Tower

Economics

Power

Engineering (Reliability)

Environment

SCR
- Deactivation
- Plugging
- NOx, SOx, Hg

PM Control
- Ash Resistivity
- Bag Blinding/Failure
- Corrosion

FGD
- Corrosion
- Chemistry (SO_2, Hg)
- Gypsum Quality

Fuel Reagents

Additives Sorbents

Waste Water
- As, Se, Hg
- Bug mortality
- Instability

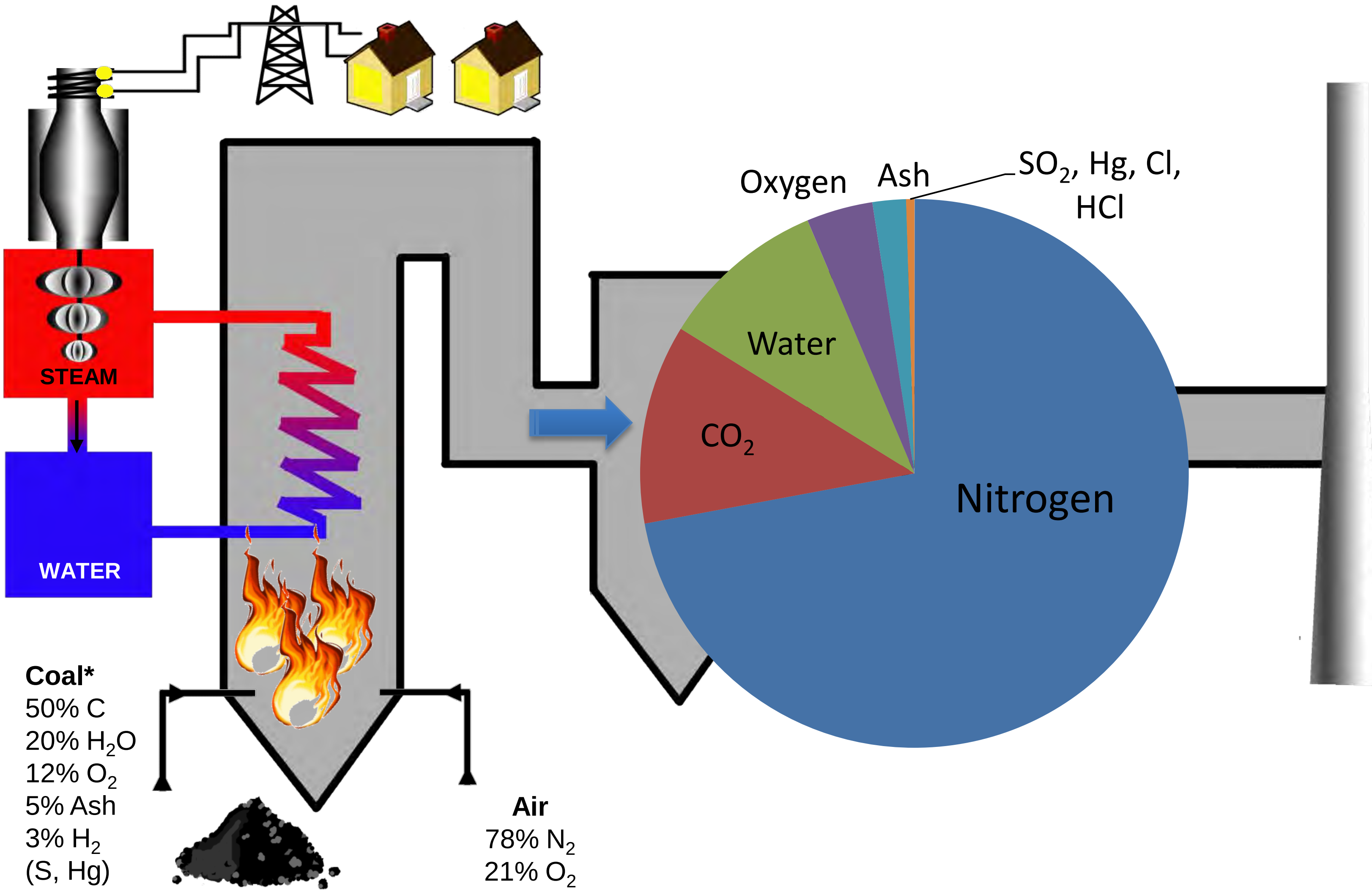
Water Balance

Ash/solids
- Closing ponds
- Leaching
- Stabilization
- Landfills

Groundwater Monitoring

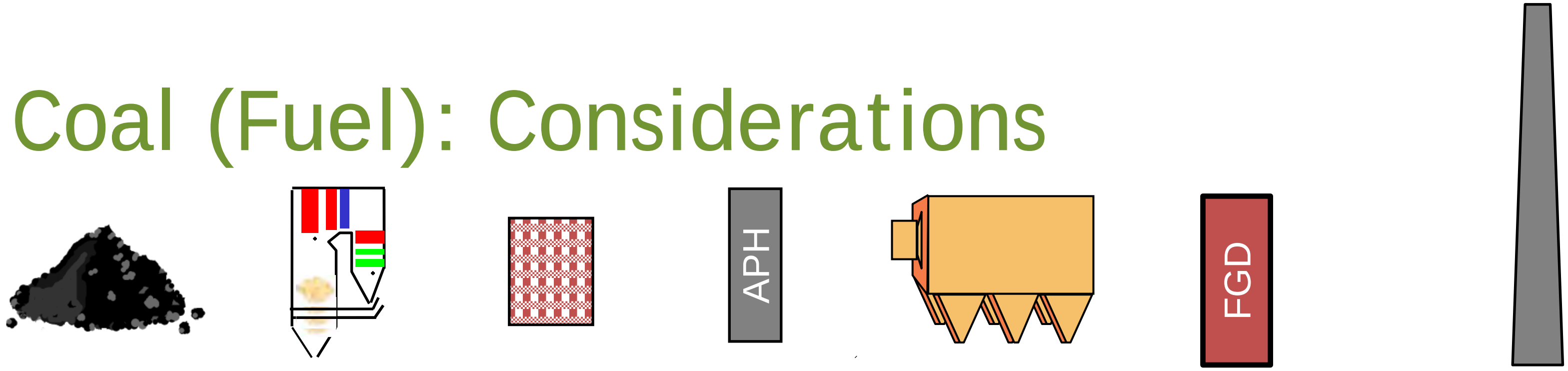
Stack Monitoring

Coal-Fired Power Generation and Emissions Control



*Coal composition varies greatly with grade and source.

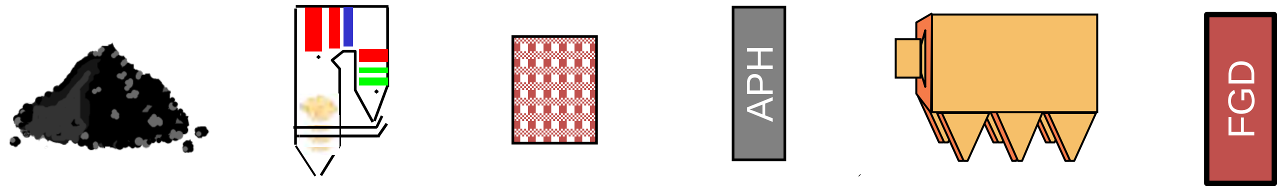
Coal (Fuel): Considerations



Coal	Boiler	SCR	APH	PM	FGD	Stack	WWT
Sulfur				Resistivity $\downarrow Hg^P$	Reagent Gypsum qual	SO_2, SO_3	
Mercury	Hg^0	$Hg^{0,+2}$	$Hg^{0,+2,P}$	Hg^p rem.	Hg^{+2} rem	Hg^T	$Hg^{aq,P}$
Carbon (UBC)			$\uparrow$Hg Ox'n, $\uparrow Hg^P$	$\downarrow$Resistivity, Re-entrain.			
Halogen		Hg Ox'n			$\downarrow(Hg^{aq} \rightarrow Hg^g)$	HCl	TDS
Ca & Mg	Slag	SO_3 and Se rem.		PM rem.		PM	
Iron	Slag	Hg^{+2} (*catalyst*)		PM rem.	$\uparrow$Hg solids		
Selenium							Se
Arsenic		Poison		PM rem.			As fines

Corrosion risk (yellow) Other risk (pink)

Chemicals Added for APC: Considerations

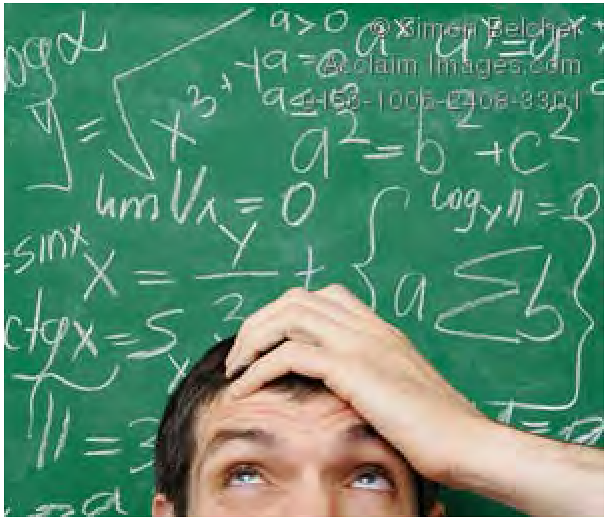


Chemical	Coal	Boiler	SCR	APH	PM	FGD	WWT
Limestone		↓As	SO_3 & Se			SO_2 rem	
Mg		Slag	SO_3 & Se				
Iron		Slag Se react.	↑Hg^{+2} *(catalyst)*				
Urea/NH_3		SNCR NOx	SCR NOx ↓Hg Ox'n				
Activated C					Hg^p rem.	$Hg^{aq} \rightarrow Hg^P$	↓Hg^T
Halogen			Hg Ox'n	Hg Ox'n	↓Se in ash	Prevent $Hg^{aq} \rightarrow Hg^g$	↑TDS ↑Se
SO_3					PM rem ↓Hg^P rem		
DSI: Lime/Trona*			SO_3 and Se rem	SO_2 and HCl rem.	S^P, Cl^P, Se^P Resistivity		↓Se

*Also affects metal solubility

Treatment Location Option

How Are You Going to Comply, Maintain Reliable Operation, and Make Money?

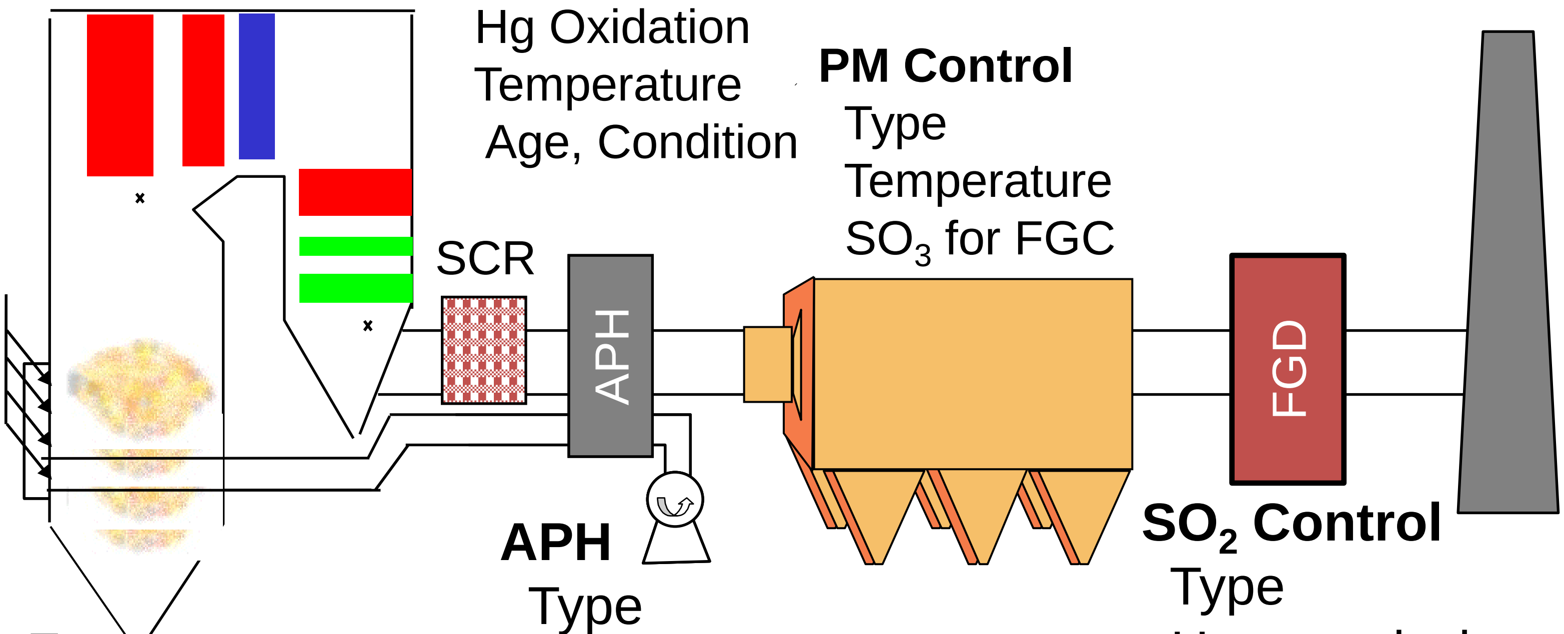


- How does fuel choice impact operations and environmental compliance
- Air – solids – liquids
  - How can you optimize controls?
  - MATS & ELG: Reduce Hg in stack emissions, and in water discharge. What about selenium?
- How best to integrate fuel choice and all APCDs to achieve your emission-reduction goals?

Co-Benefit Mercury Control – What's Important

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

→

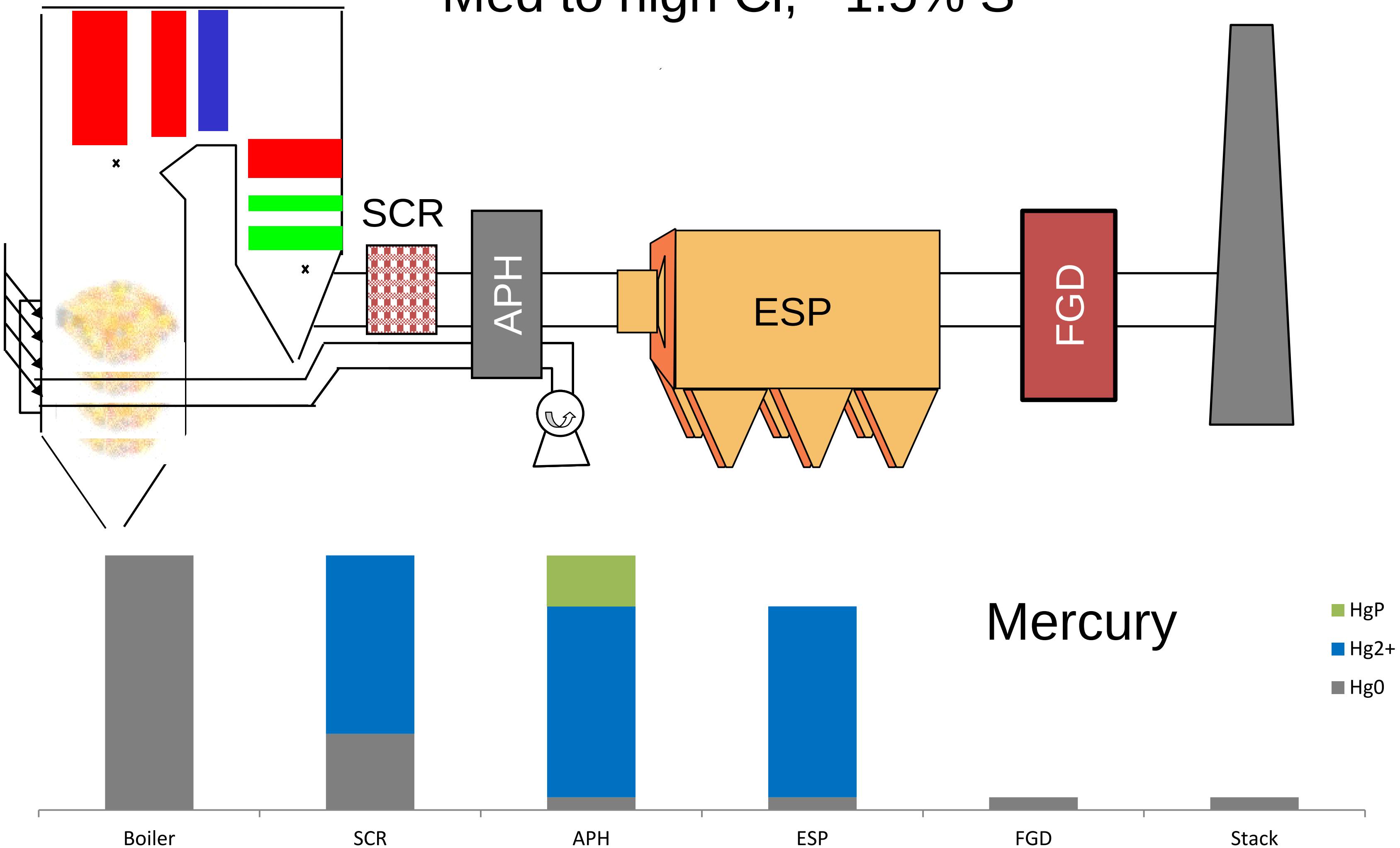
Halogens
Oxidized Hg

Key Factors Affecting Success with Co-Benefit Approach for Mercury Control

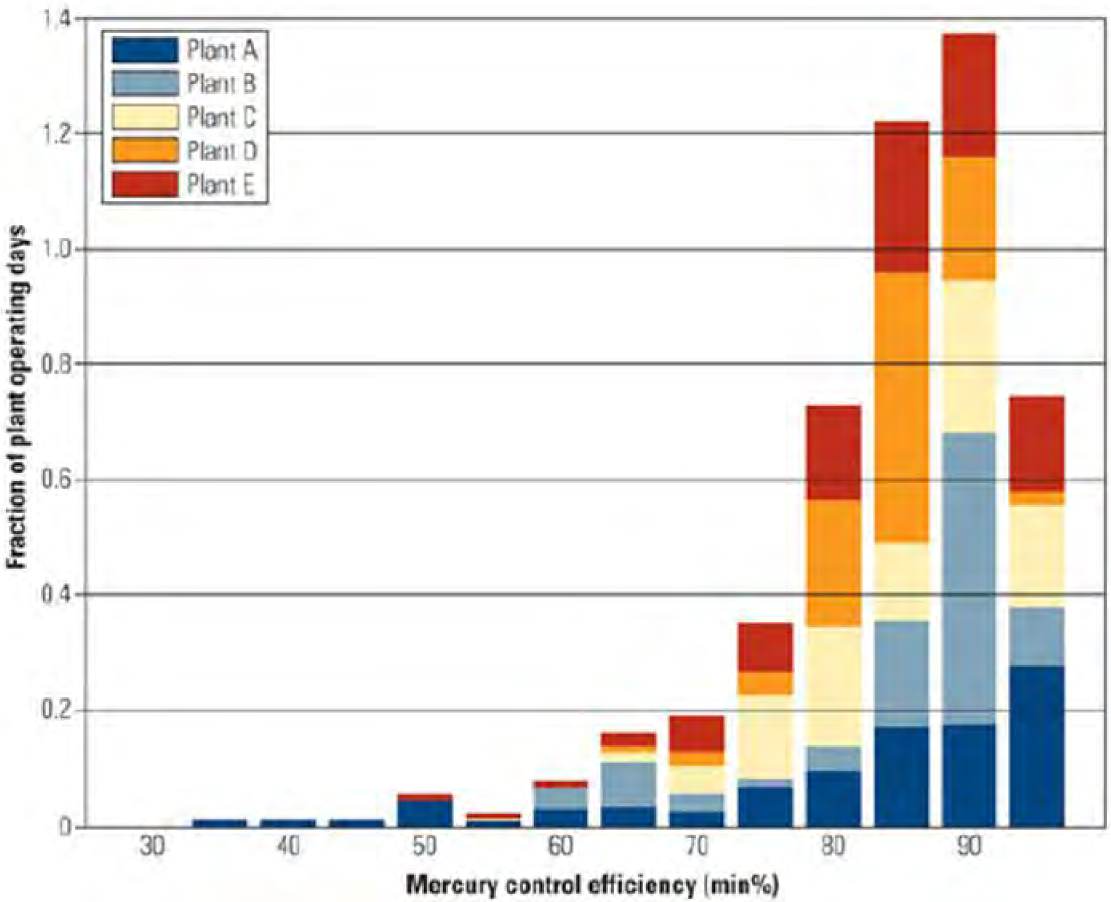
- Coal
  - Sulfur, mercury, halogen, LOI
- SCR
  - Lower = better: temperature, NH_3, age, gas flow rate, CO, H_2O, SO_2
  - Higher = better: halogen concentration, O_2
  - Other: SCR management scheme
- Particulate Controls
  - Hg removed before WFGD: fraction of particulate-phase Hg (LOI, temperature, SO_3, ESP SCA, FF cleaning)
- Scrubber
  - Fraction of oxidized Hg at inlet, ORP, halogens, temperature, pH

Example: CAPP Coal, Co-Benefit Hg Control

Med to high Cl, ~1.5% S



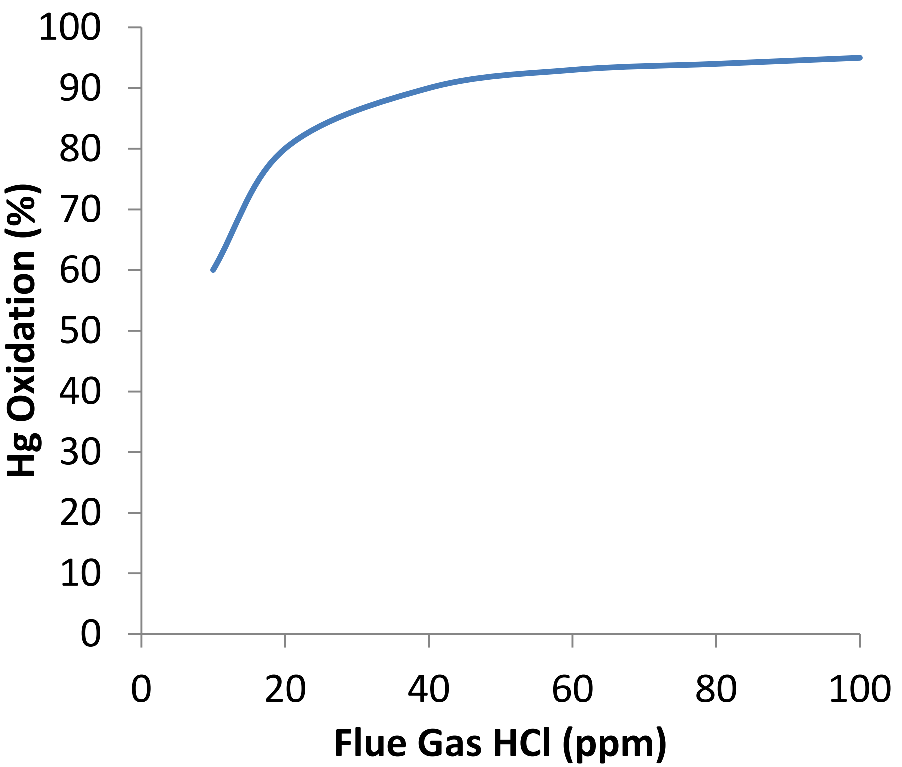
Can you Rely on Co-Benefits?

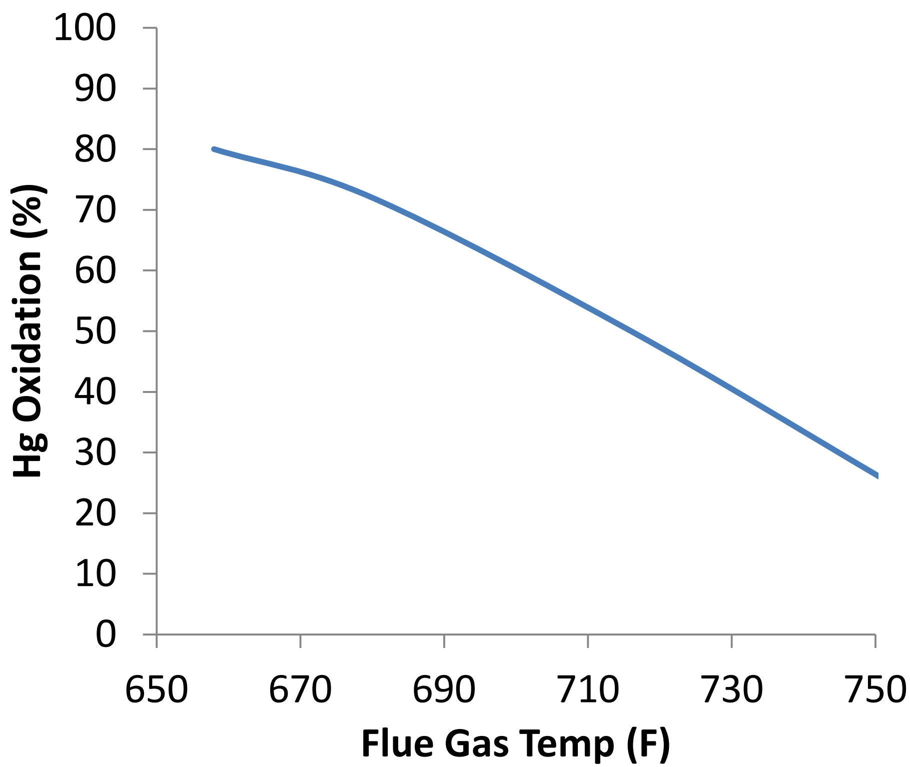


- Southern Company Plants with SCR, ESP, WFGD
- More than 40 months of WFGD operations
- Mercury control greater than 90% was achieved 47% of the time
- Important factors include SCR temperature, age, coal halogen

Corey A. Tyree, Southern Company, 2010

Factors Affecting Hg Oxidation Across SCRs





- Higher temperature → Lower oxidation
- Higher ammonia → Lower oxidation

Some plants may achieve good oxidation EXCEPT during summer months

Shintaro Honjo, Mitsubishi Heavy Industries America, Mega Symposium 2012

Summary of Options to Improve Hg Removal

Medium Sulfur Coal

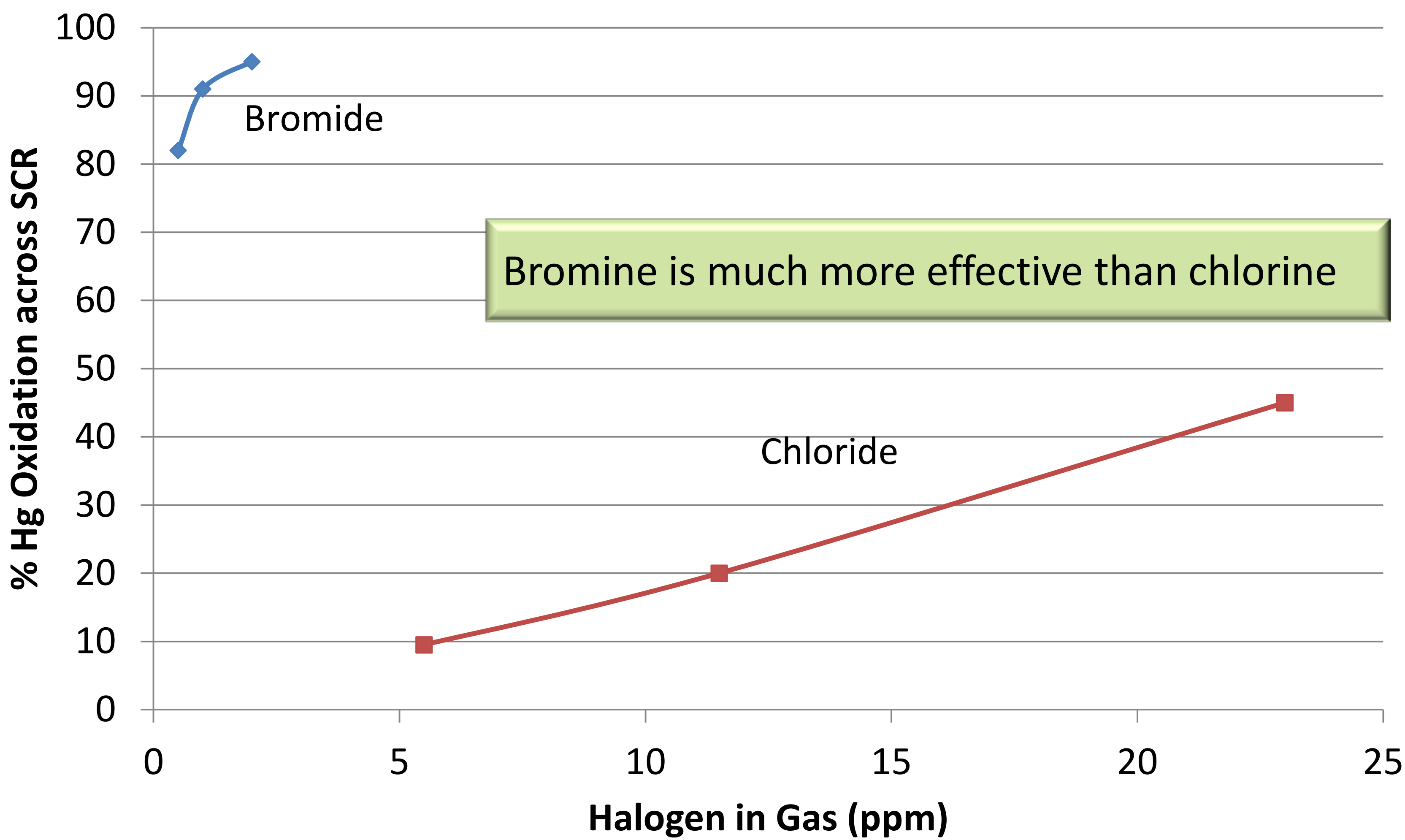
- Add halogen to coal: Bromine is more effective than chlorine and may supplement native chlorine
  - Caution: Increased halogen can affect corrosion, Se partitioning, TDS, leaching, etc.
- Use ACI trim, as needed

Medium to High Sulfur Coal

- Use 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
- Add halogen to coal
  - Caution: Many higher sulfur coals are also higher in chlorine
    Excess halogen may not help
- Use ACI trim, as needed

Improving Hg Oxidation Across SCR with Halogens

Co-Benefit Trim



Adapted from Cormetech, 2015 Reinhold NOx conference

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

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
- Increased sulfite
- Increase pH
- High halogen

Co-Benefit Trim

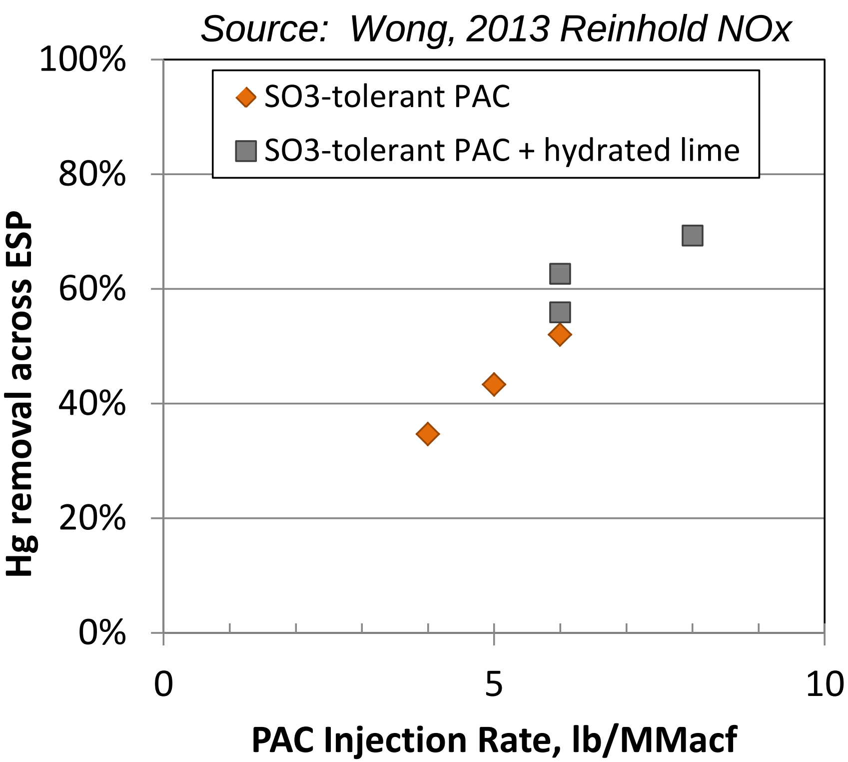
Potential Balance-of-Plant Impacts with Halogen Addition

- APH cold-end corrosion
- Increased gas-phase Se at scrubber inlet
- Higher halogen levels in FGD (corrosion) and waste water (TDS and treatment)
- Formation of additional trihalomethanes (THM) in downstream water

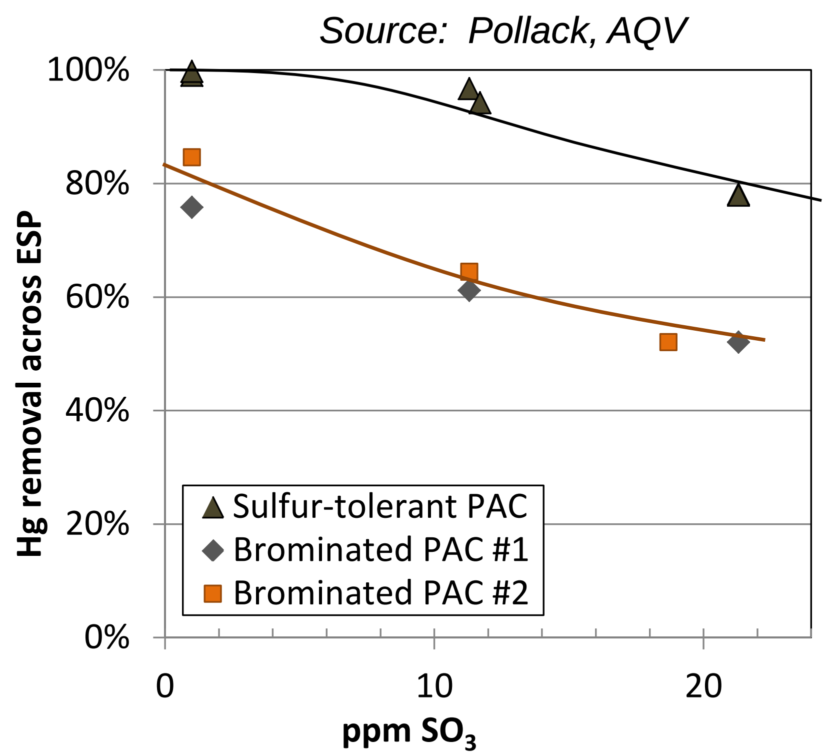
Co-Benefit Trim

Alternate Option for Hg Control: Trim with Sulfur-Tolerant Carbon

PAC development to improve SO_3 tolerance continues



Recent full-scale results: High S coal, SCR-ESP-FGD, > 15 ppmv SO_3

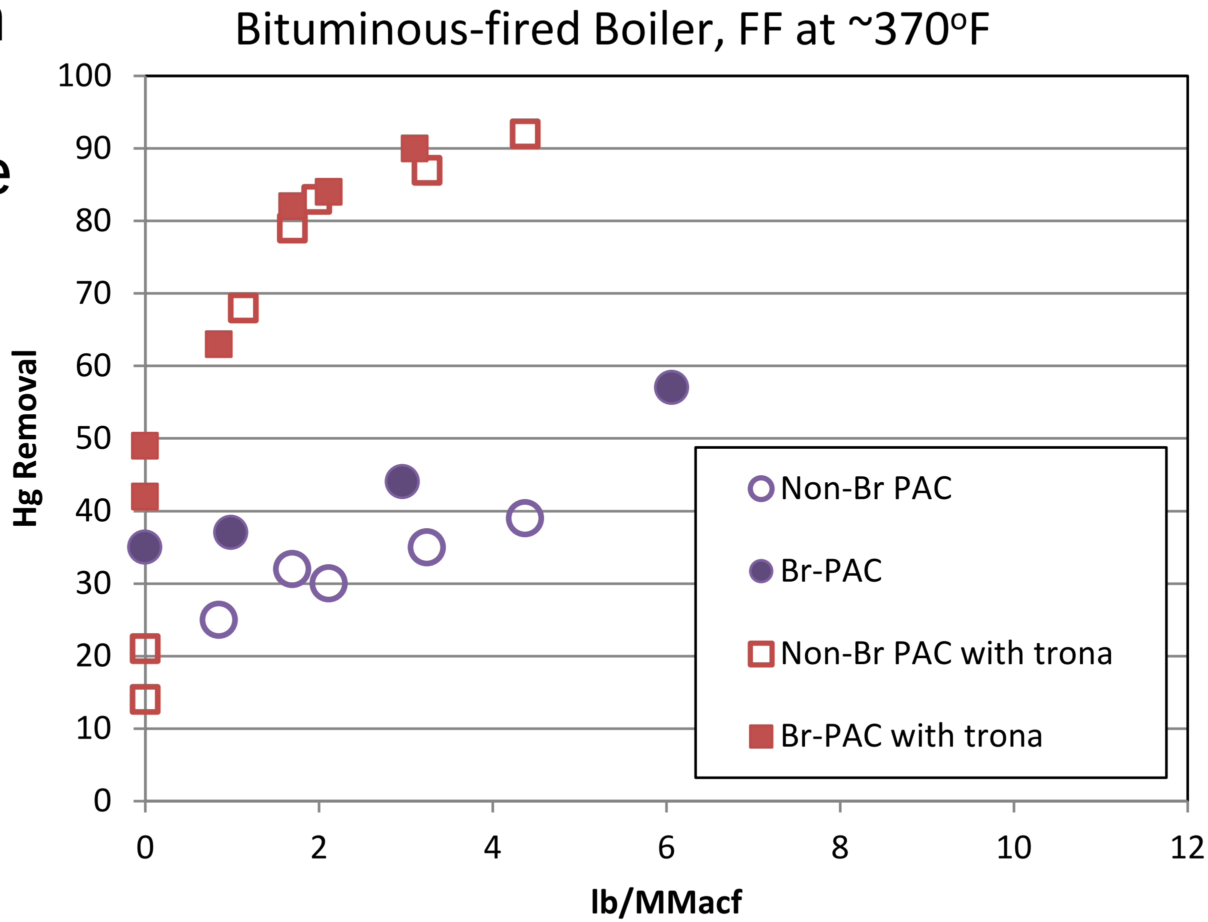


MRC Results: 10 lb/MMacf, injection upstream of APH; APH outlet: 300 F

Co-Benefit Trim

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

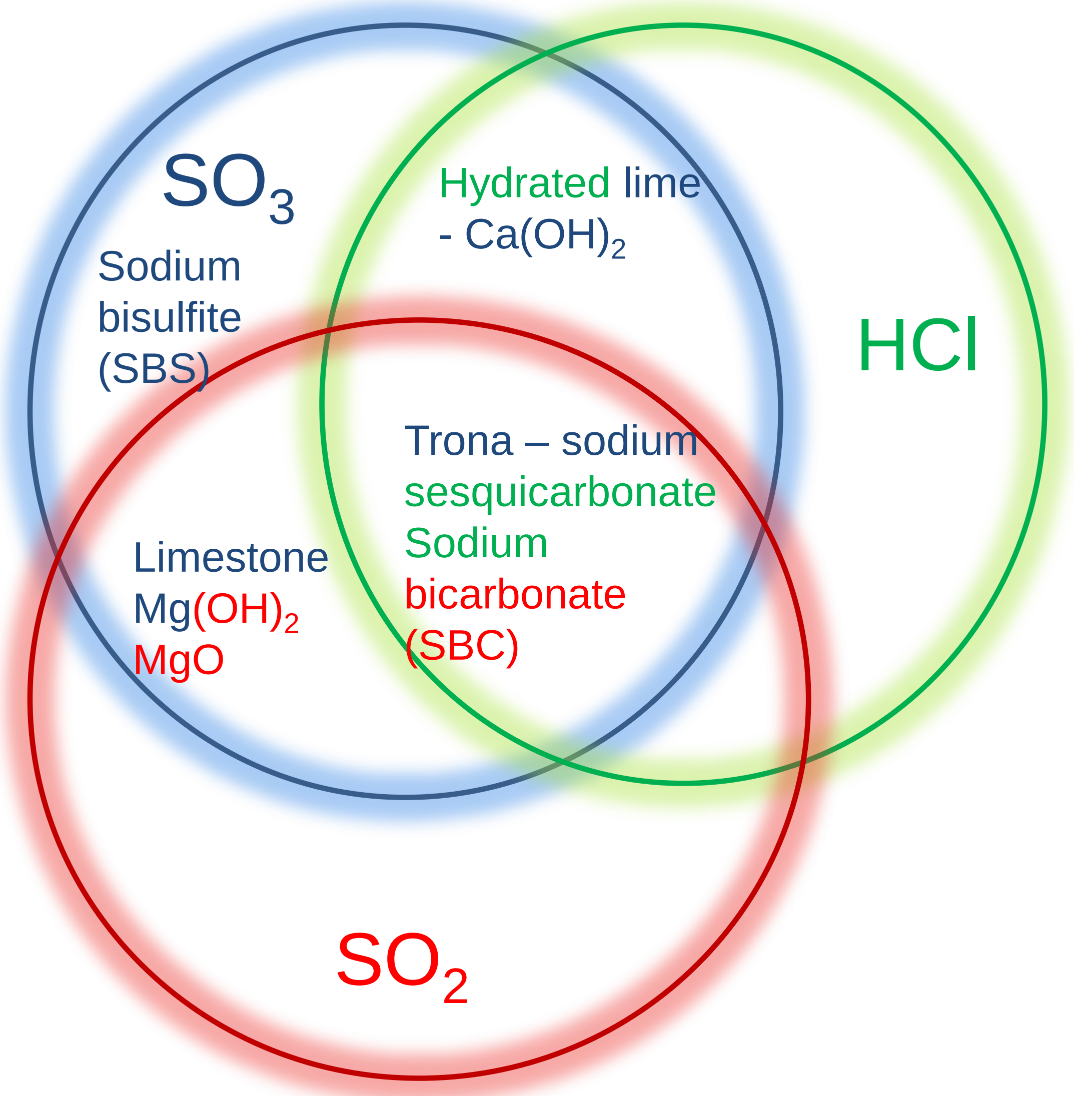


Co-Benefit Trim

DSI-ACI Challenges

- 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

DSI: More than Just SO_3 Control



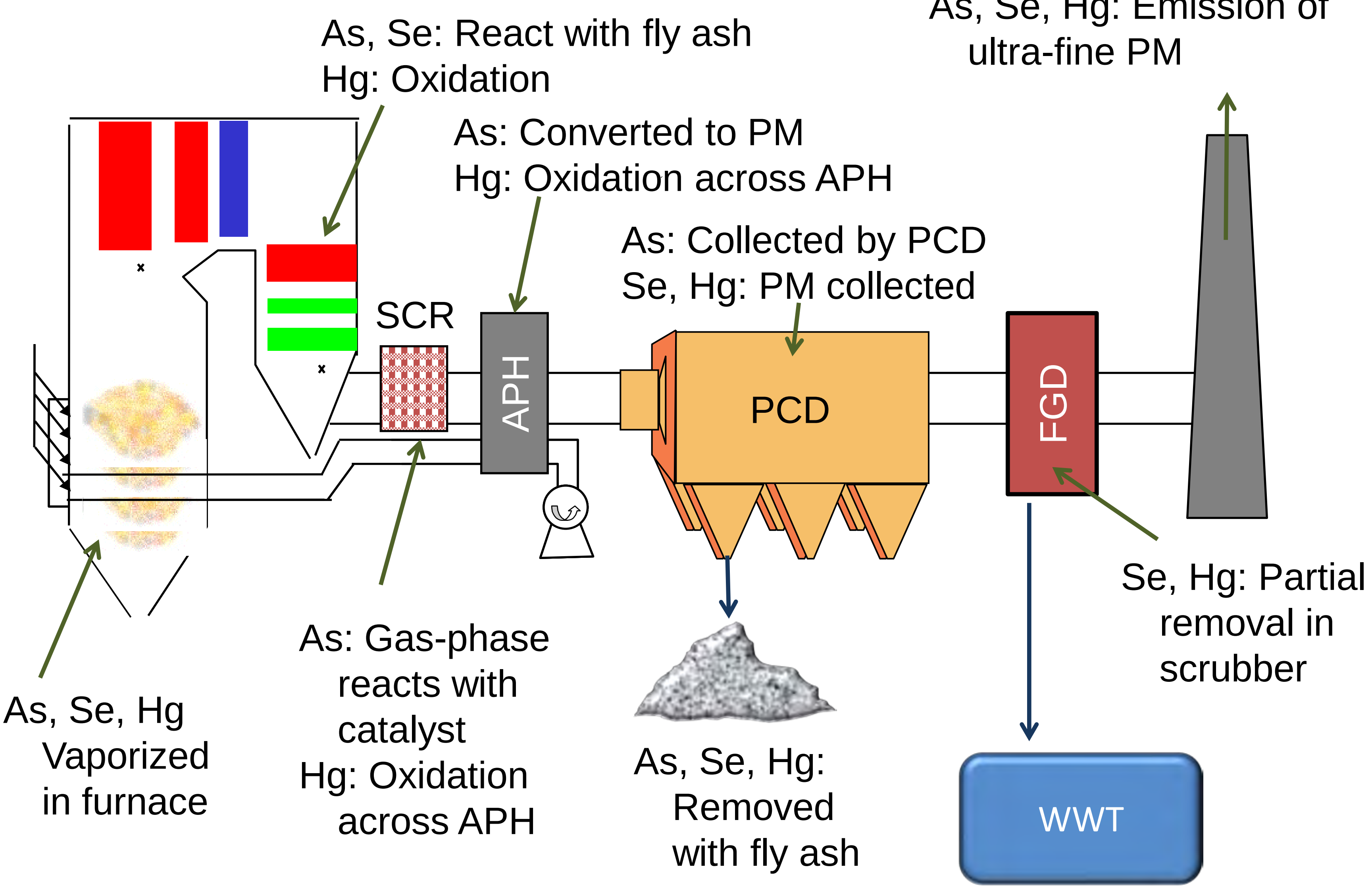
DSI Potential Balance of Plant Impacts

	Hydrated Lime	Sodium Sorbents
Air Preheater	Potential solid deposition (calcium carbonate)	Potential solid deposition (sodium bisulfate)
Ductwork	No significant issues observed	Formation of molten sodium bisulfate deposits: T>350^{o}F, SO_3 removal application
ESP	Increases PM loading to ESP Increases resistivity of fly ash, which might increase opacity	Increases PM loading to ESP But can condition ash & offset increase in resistivity associated with removal of SO_3
FF	No significant issues observed	No significant issues observed
FGD	No significant issues observed	No significant issues observed
Fly Ash	No significant issues observed	High sodium might not be suitable for selling ash Increased leachability of As, Se in fly ash
ACI	Reduction in SO_3 increases Hg capture	Reduction in SO_3 increases Hg capture NO_2 produced by sorbent inhibits performance of PAC

What Else is Important?

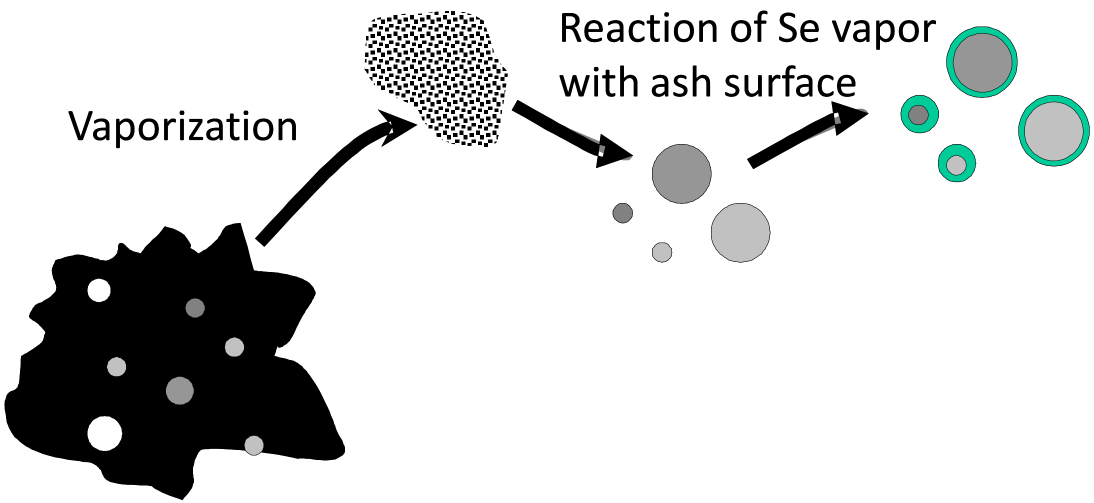
- Discharge levels of As, Se, Hg, Nitrates regulated in Effluent Limitation Guidelines (ELG)
- Changes in water balance, sodium or calcium levels in ash, or TDS in water may alter ash pond pH and affect partitioning of metals

Fate of As, Se, and Hg



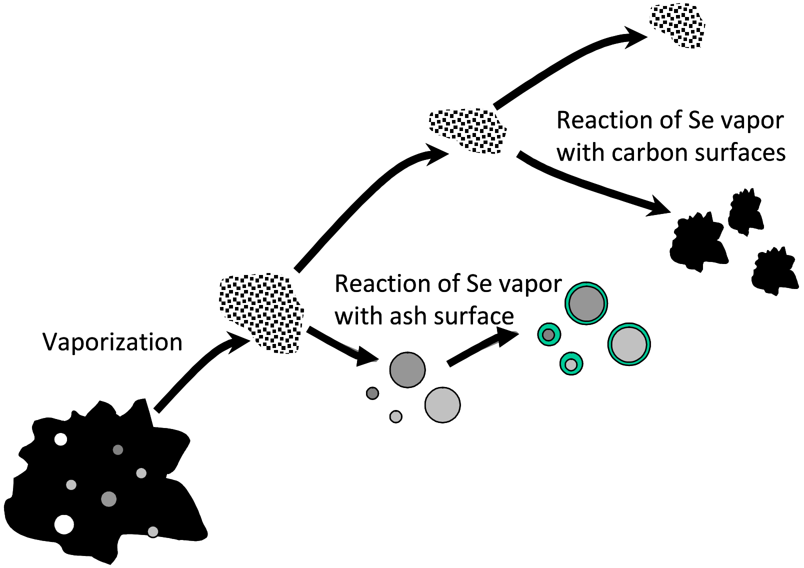
Behavior of Se in Coal-Fired Boilers

- Post-combustion reactions:
  - Iron reacts with selenium at temperatures above 1200°C/2200°F (possibly reaction with Fe-Si-Al glasses at sufficiently low viscosity of the ash)
  - Calcium reacts with selenium at temperatures less than 800°C/1470°F
  - SO_2 reacts with calcium and iron, but more strongly with calcium



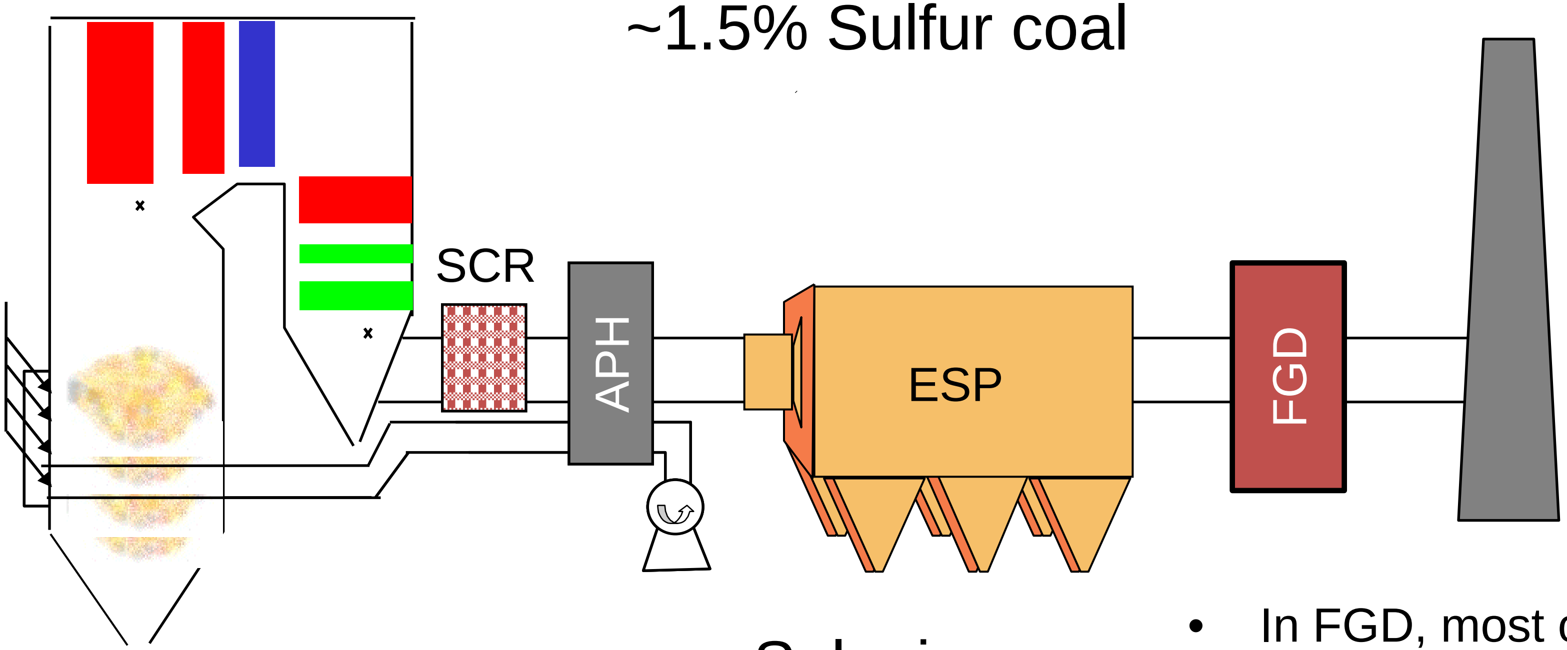
Implications for emissions and control

- **Poor capture of Se by fly ash in boilers firing high-sulfur bituminous**
- Efficient capture of Se by fly ash in boilers firing subbituminous and lignites

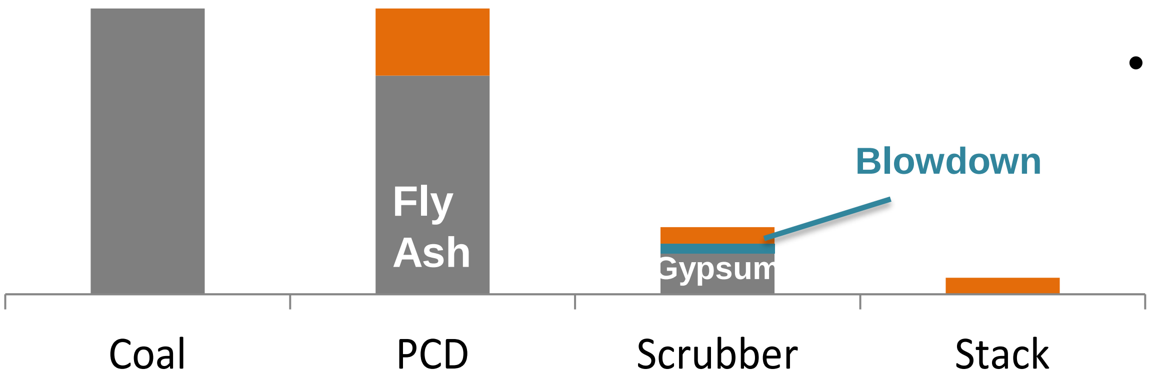


Example: CAPP Coal

~1.5% Sulfur coal



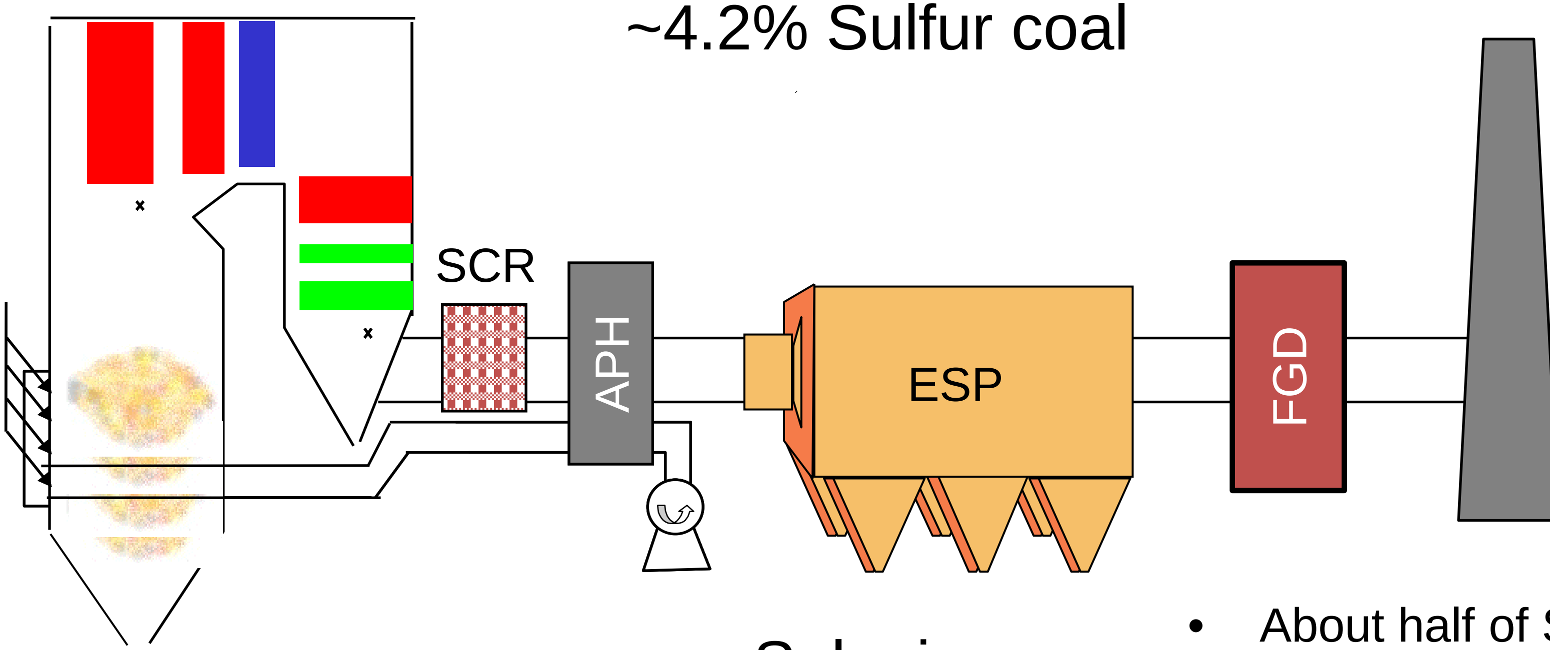
Selenium

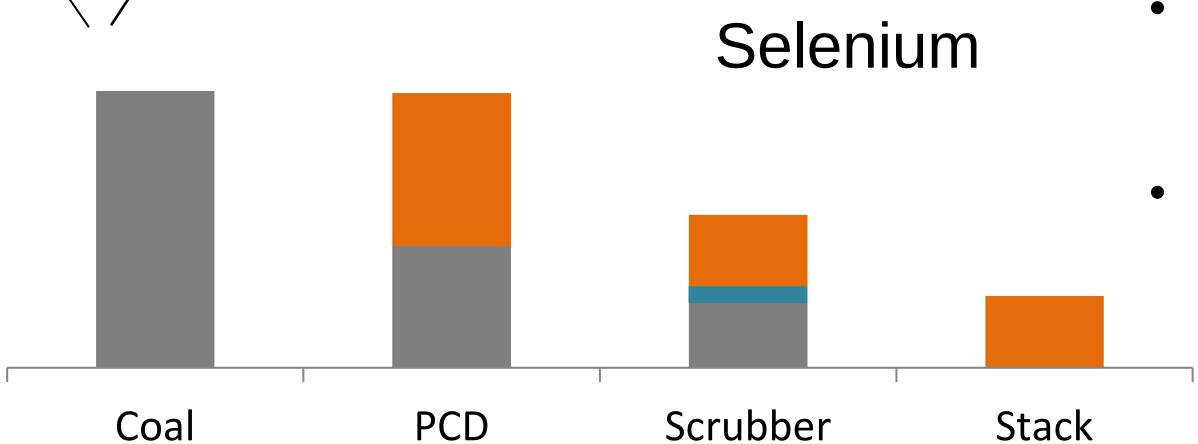


- In FGD, most of Se removed with gypsum
- *Example based on measured data*

Example: IB Bituminous Coal

~4.2% Sulfur coal





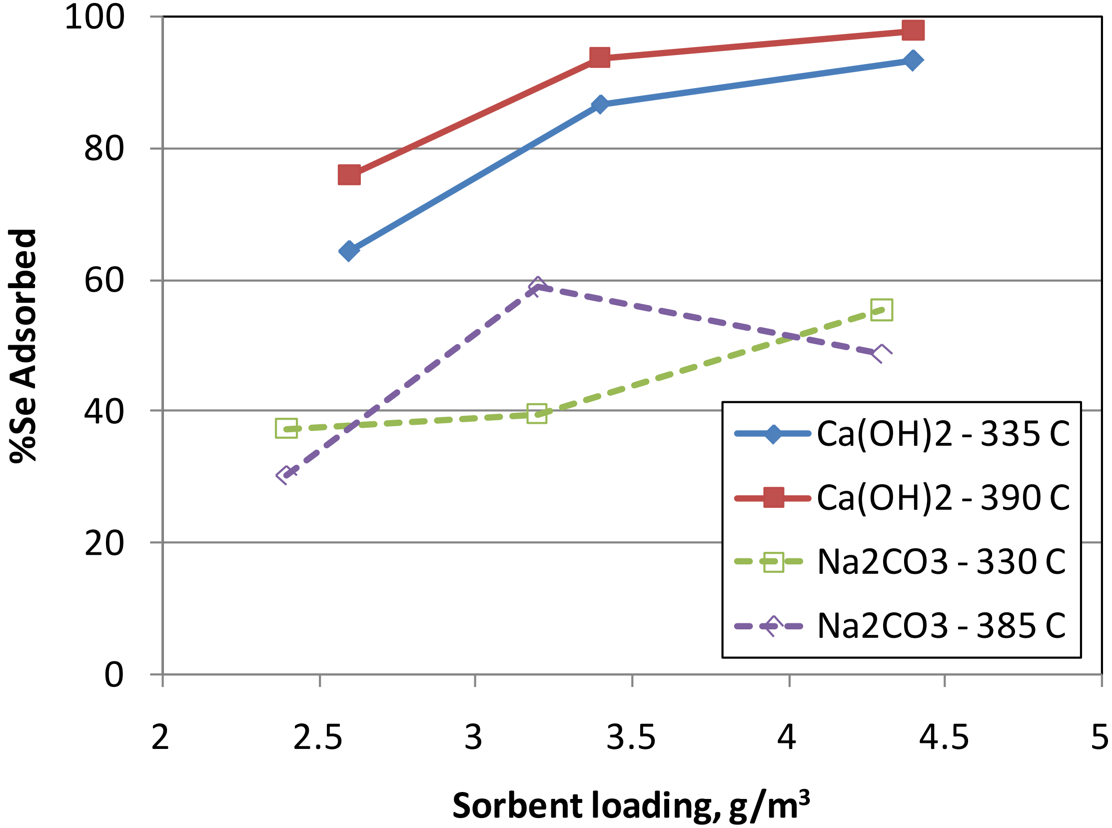
- About half of Se removed in scrubber (mostly to gypsum)
- *Example based on measured data*

Se in APCDs: Implications for Emissions and Control

- Significant portion of Se can enter FGD in gas-phase
- Removal of SeO_2 across wet FGDs less than removal of SO_2 (60%-90%)
- Selenium in scrubbers can report to gypsum (LSFO) or purge stream
- Selenium removed across wet FGDs could become an issue in wastewater discharge

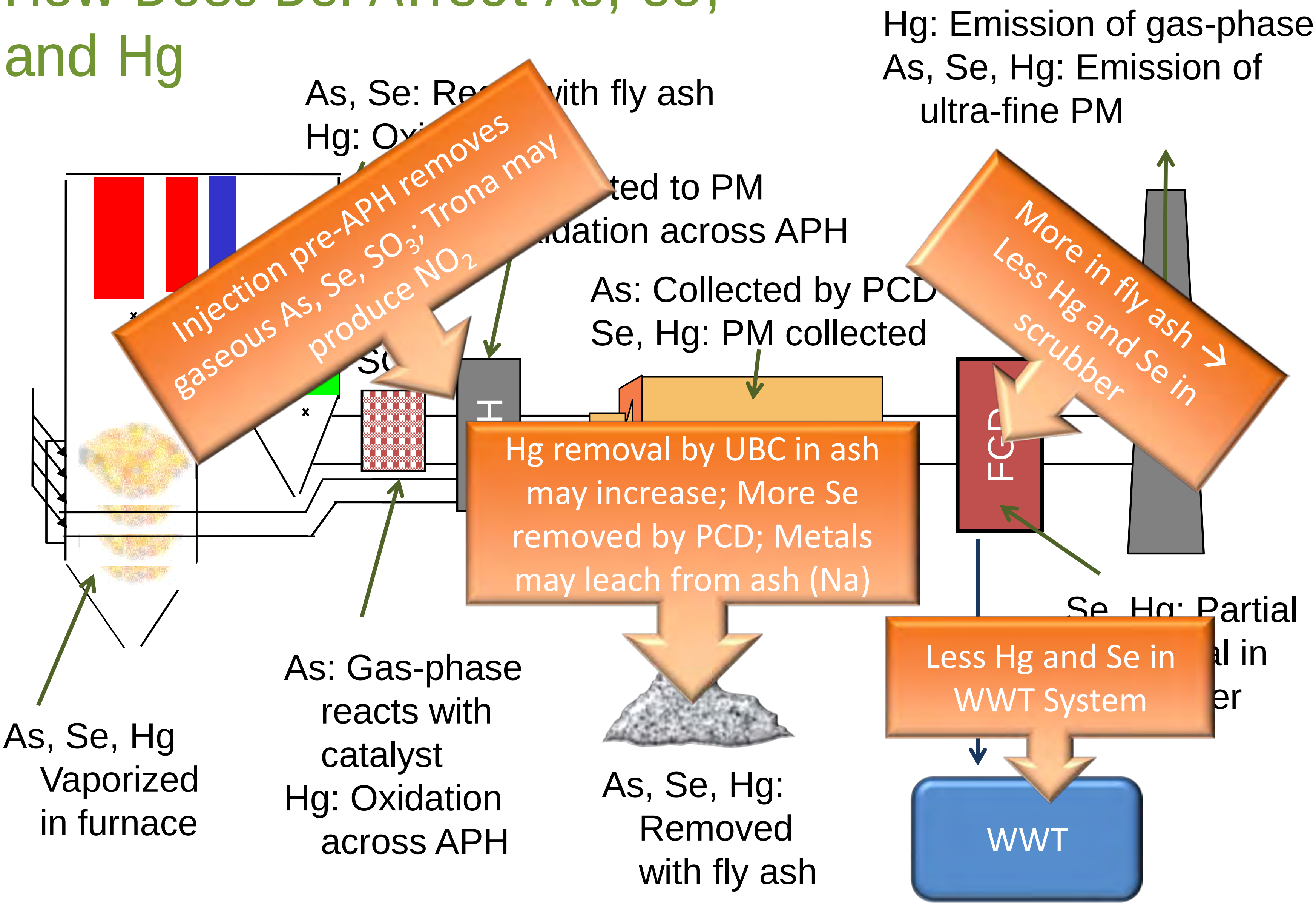
Sorbent Injection for Selenium Control

- When sodium or calcium sorbents are injected into coal flue gas, they can react with Se
- Selenium adsorption as a function of sorbent loading for injection of calcium hydroxide or sodium carbonate in the exhaust of glass furnaces



Kircher, U. "Waste Gas Treatment of Soda Lime Silica Glass Furnaces – Investigations with Different Absorption Agents." Ceramic Trans. ***1998****, 82, 75-80.*

How Does DSI Affect As, Se, and Hg



Leaching from Ash-Sorbent Mixtures

Trona

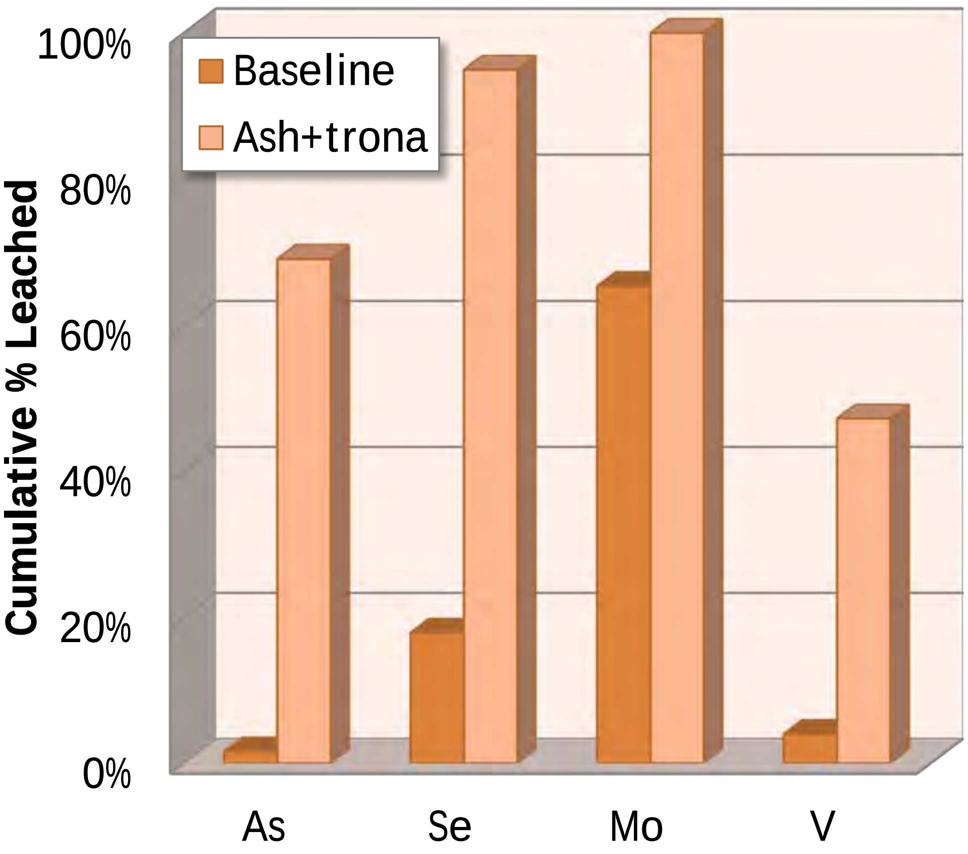
- Significantly enhanced leaching of major anions of concern, including Se, As, Cr, and V (but not Hg)
- With trona injection, distribution of these anions shifted to the soluble trona fraction of the ash
- pH of bituminous leachate increased from ~7.5 to ~11 with addition of trona

Hydrated Lime

- Limited data available
- Some increase in Se leaching (no other metals of concern), but small enhancement compared to trona

Leaching from Fly Ash-Trona Mixtures: Subbituminous Ash

- Set of paired fly ash samples collected from C-ESP at a full-scale power plant that burned subbituminous coal: control ash collected before trona injection and a trona ash collected during trona injection test
- Batch leaching experiments (24 hours) conducted using DI water under unadjusted pH conditions at L/S ratio of 10:1



Dan, Y.; Zimmerman, C.; Liu, K.; Shi, H.; Wang, J. Increased Leaching of As, Se, Mo, and V from High Calcium Coal Ash Containing Trona Reaction Products. *Energy Fuels*, **2013**, *doi/10.1021/ef3020469*.

The Importance of Scrubber ORP

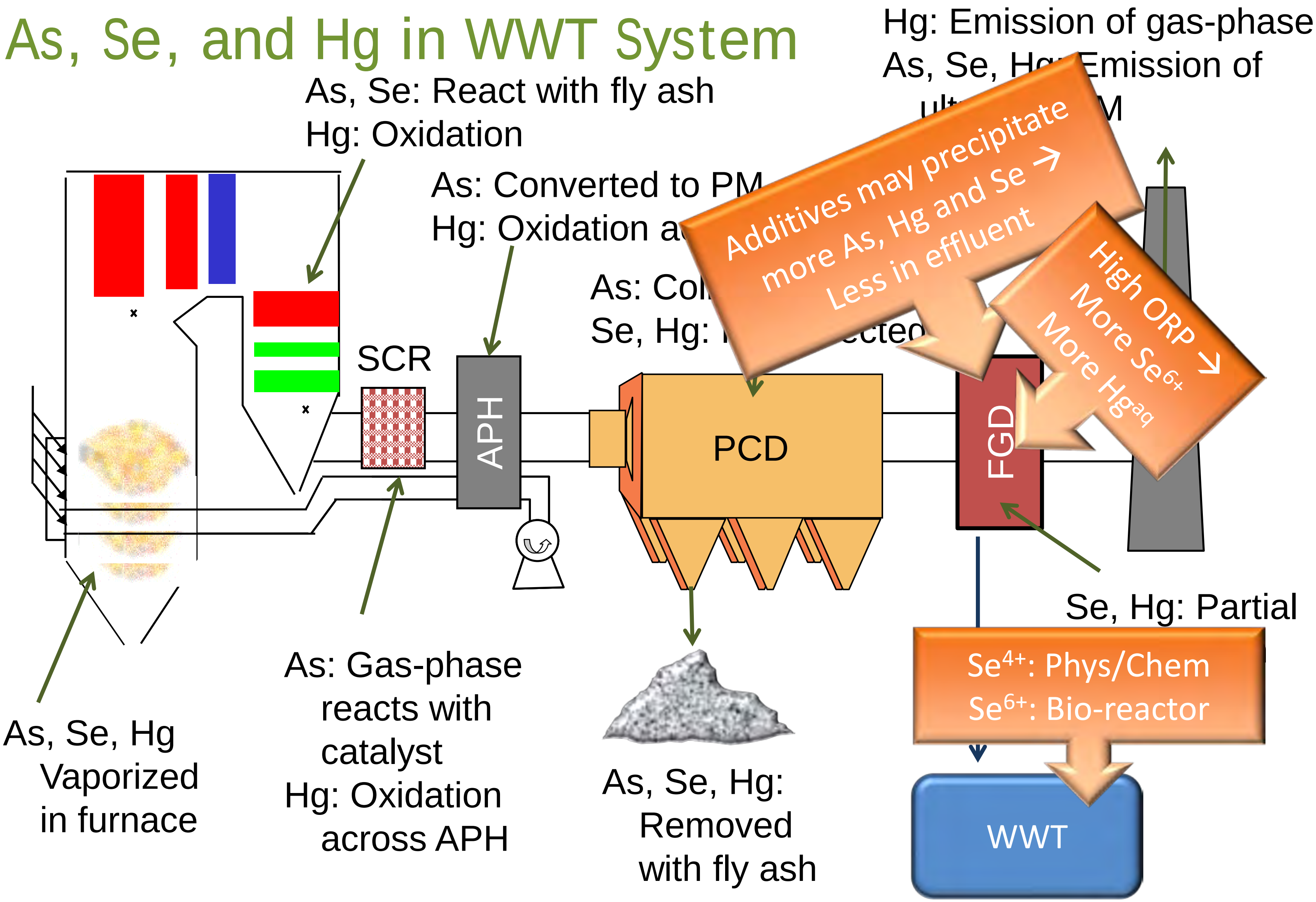
High ORP (> ~ 500 mv)

- Hg partitions to liquid phase
- Se partitions to Selenate (Se^{6+}), difficult to treat, often requires biological WWT
- Often causes MnO_2 to precipitate, leading to potential for severe and accelerated corrosion

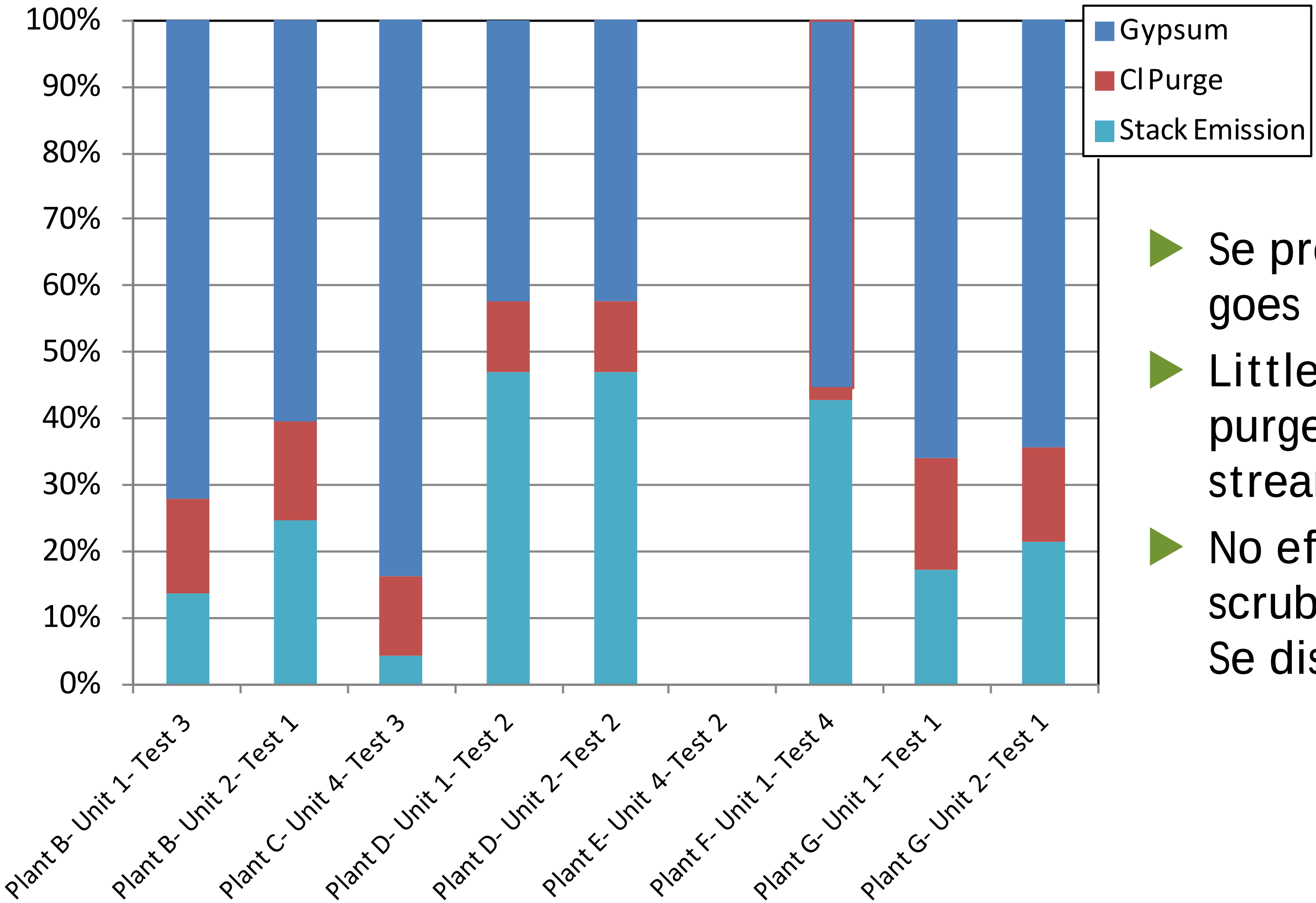
Low ORP (< ~ 300 mv)

- Hg partitions to solid phase
- Se partitions to Selenite (Se^{4+}) and removed in Phys/Chem WWT
- Mn is soluble

How Does Scrubber Affect As, Se, and Hg in WWT System



Output of Se from Scrubbers: 2010 EPRI Study



- Se predominantly goes into gypsum
- Little Se into Cl purge (blowdown) stream
- No effect of scrubber type on Se distribution

Normalized to 100% of output

Selenium

- Selenium speciation is important
  - Selenite (Se[IV], Se^{+4}) more toxic
  - Selenate (Se[VI], Se^{+6}) more difficult to remove
- Se^{+4} can be removed through iron co-precipitation, Se^{+6} needs some bugs .. or more
- Forced oxidation WFGD may increase fraction of Se^{+6}
- Upstream controls (DSI) may reduce Se load to WFGD

EPA Recommended WW Treatment Technologies

- Chemical precipitation and filtration
  - Remove the heavy metals, particularly mercury and arsenic
  - $15 million for a 500 to 600 MW plant (EPRI: $25 to $50M)
- Chemical precipitation with **biological treatment**
  - Remove selenium, nitrates and sulfates
  - $24 million for a 500 to 600 MW plant
- Chemical precipitation followed by "**vapor-compression evaporation**"
  - Evaporation in brine concentrator
  - Crystallized salts and dispose in a landfill
  - Recycle or evaporate all liquid (zero discharge)
  - $50 million for a 500 to 600 MW plant (EPRI: > $100M)

ZLD Options

- Brine concentrator + crystallizer → landfill salts
  - Risk: salts are very soluble (leachable) and hydroscopic
  - High energy required to dry
- Stabilize Brines/Salts
  - Difficult due to mobility of metals
  - Mixing with other materials can increase mobility (including lime)
  - Options: Geopolymers with low leachability

Co-Benefits MATS & ELG Approach - Summary

- Maximize Hg oxidation across SCR
  - Manage SCR cleaning and replacement
  - Minimize NH_3 slip
  - Reduce inlet SO_3 and flue gas temperature
- Additional Hg trim may be required during some operating conditions
  - High temperature, high NH_3, high gas flow
  - Trim with halogens, ACI, or ACI/DSI
    - Halogens may increase corrosion throughout system
    - DSI may be required to mitigate SO_3 for ACI effectiveness

Co-Benefits MATS & ELG Approach - Summary

- ELG and CCR
  - Halogens will likely increase selenium reporting to scrubber
  - Trona can affect leaching of metals
  - Halogens, DSI, and changes in water management to prepare for pond closures can impact fraction of metals associated with solids and liquids in ponds

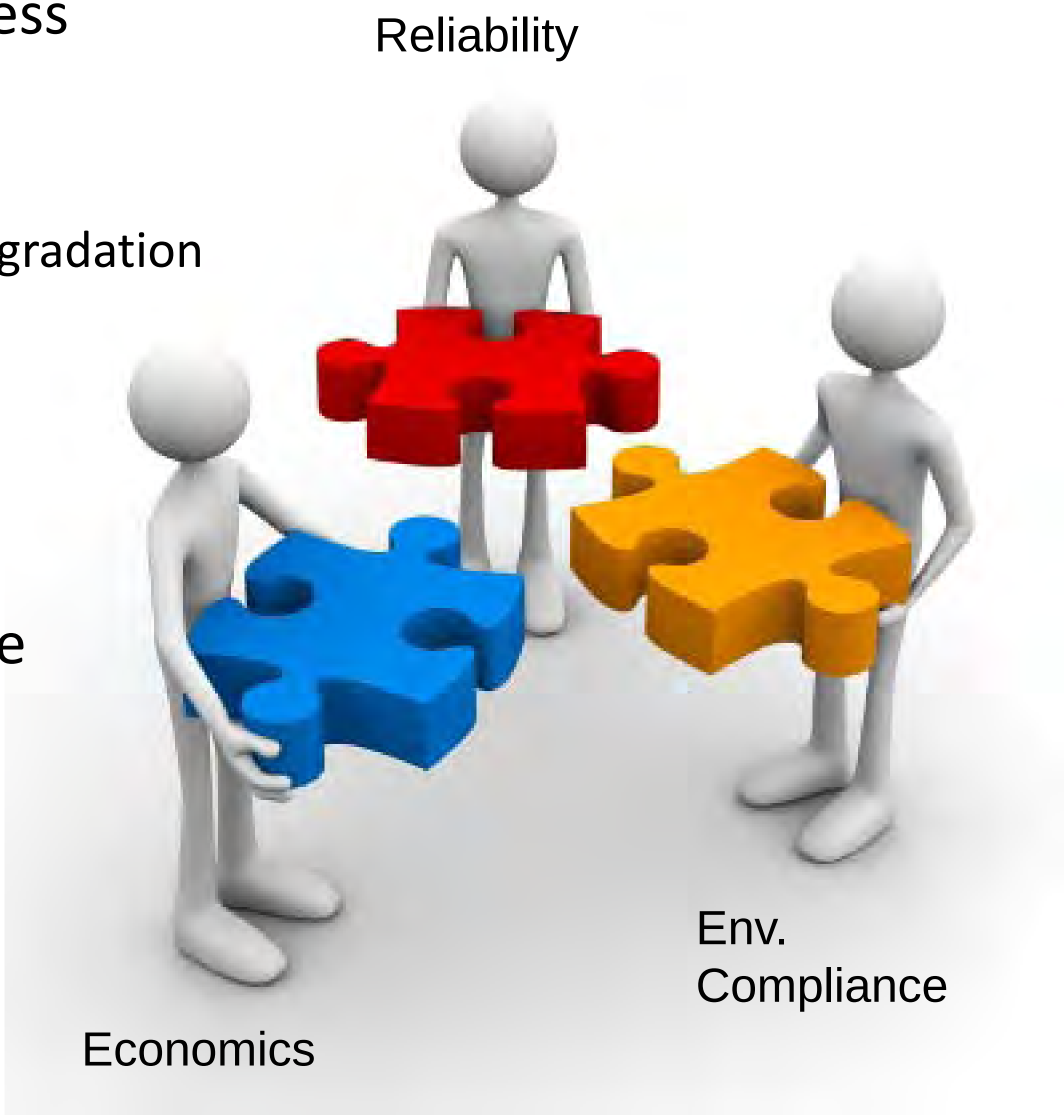
- Other
  - Iron can reduce halogen requirements, but may impact slag

Other "Tweaks" To Watch For

- Repairing leaks
  - Can increase flue gas temperature and decrease Hg removal
- Combustion Tuning
  - Can reduce LOI and native Hg capture
- Staging for Lower NOx
  - Lower load on SCR (Potential positive impact on Hg oxidation)
  - High CO (potential negative impact on Hg oxidation)
  - High LOI (potentially higher particulate Hg and Hg oxidation)
- Routine Cleaning

Holistic Operations

- Consider impacts on process equipment
  - Boiler slagging and fouling
  - SCR poisoning, plugging, degradation
  - Corrosion
  - ESP and FF operation
  - Scrubber operation
  - WWT operations
- Environmental Compliance
  - Air rules, CCR, ELG, etc
- Economics
  - Fuel
  - Maintenance
  - Reagent use



Discussion and Questions