REINHOLD ENVIRONMENTAL Ltd.

2016 APC-Wastewater Round Table & Expo Presentation

July 18 & 19, 2016 in Dearborn, MI / Hosted by DTE Energy

Holistic Operations

2016 APC-Wastewater Conference

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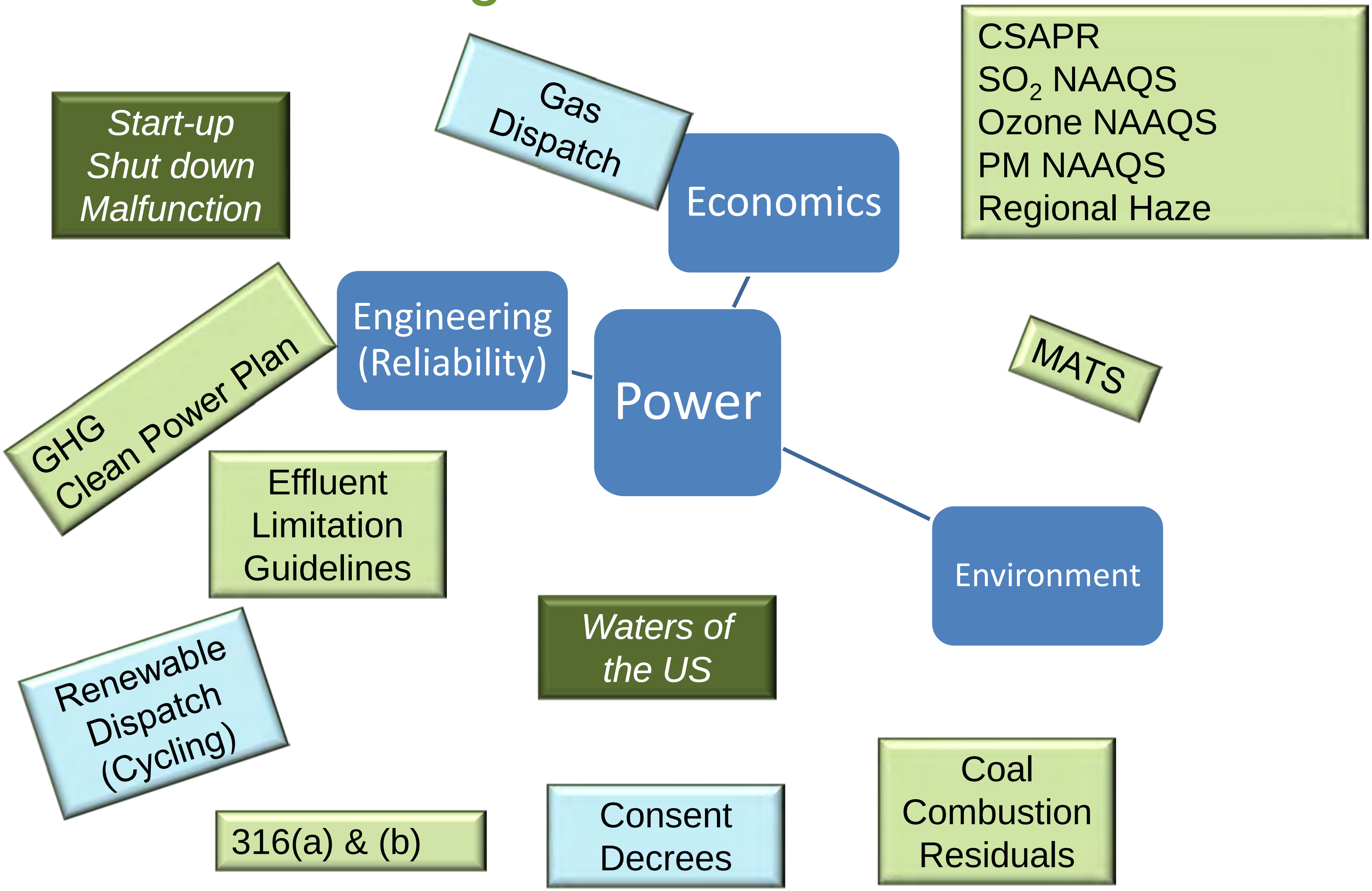
July 19, 2016

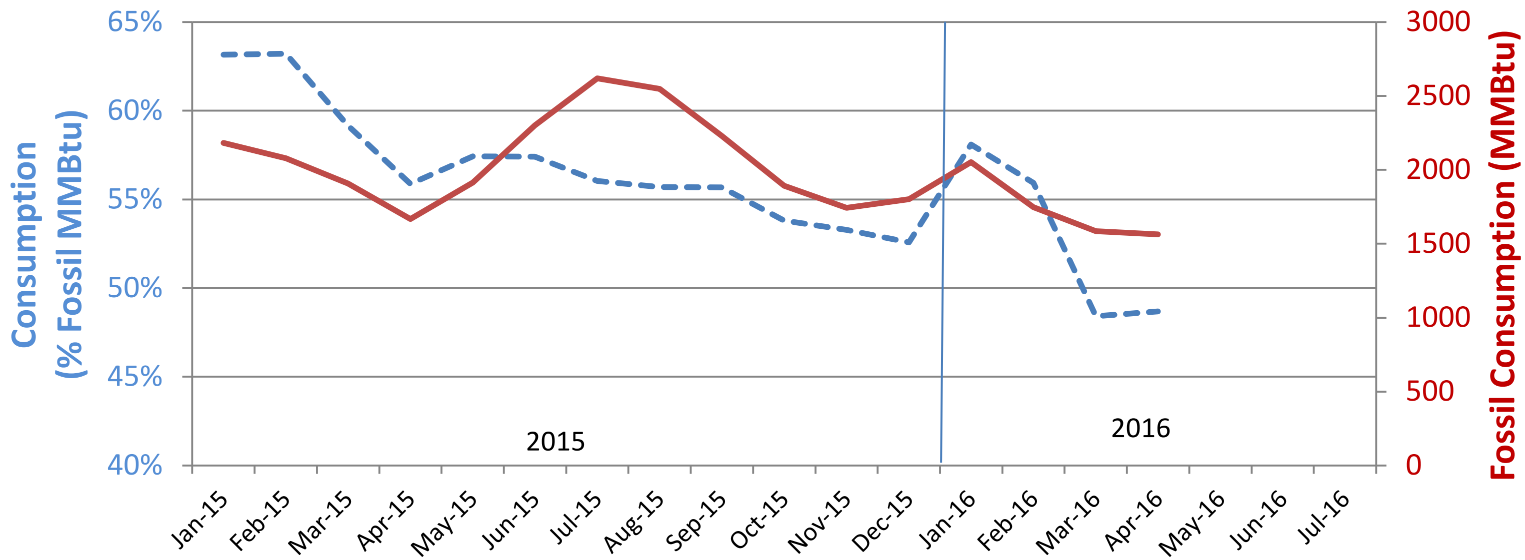
Disclaimer

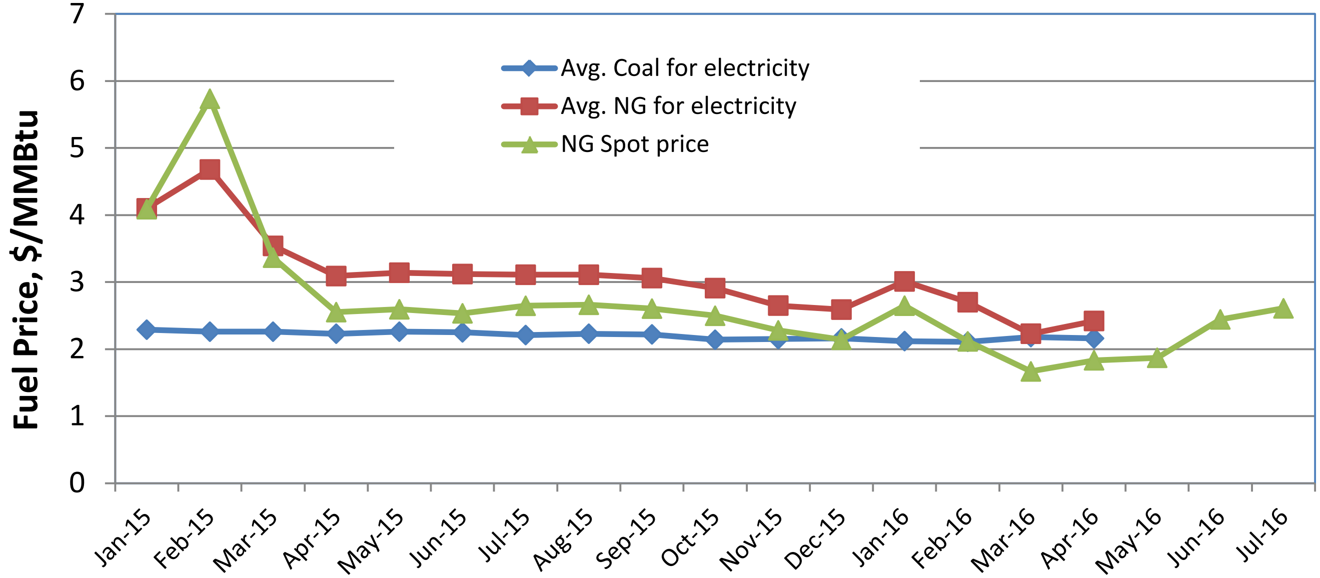
This presentation includes general information on coal and coal-fired boilers intended for education and illustration purposes only. All information is provided "AS-IS" and without warranty or liability of any kind.

Meeting the Demands



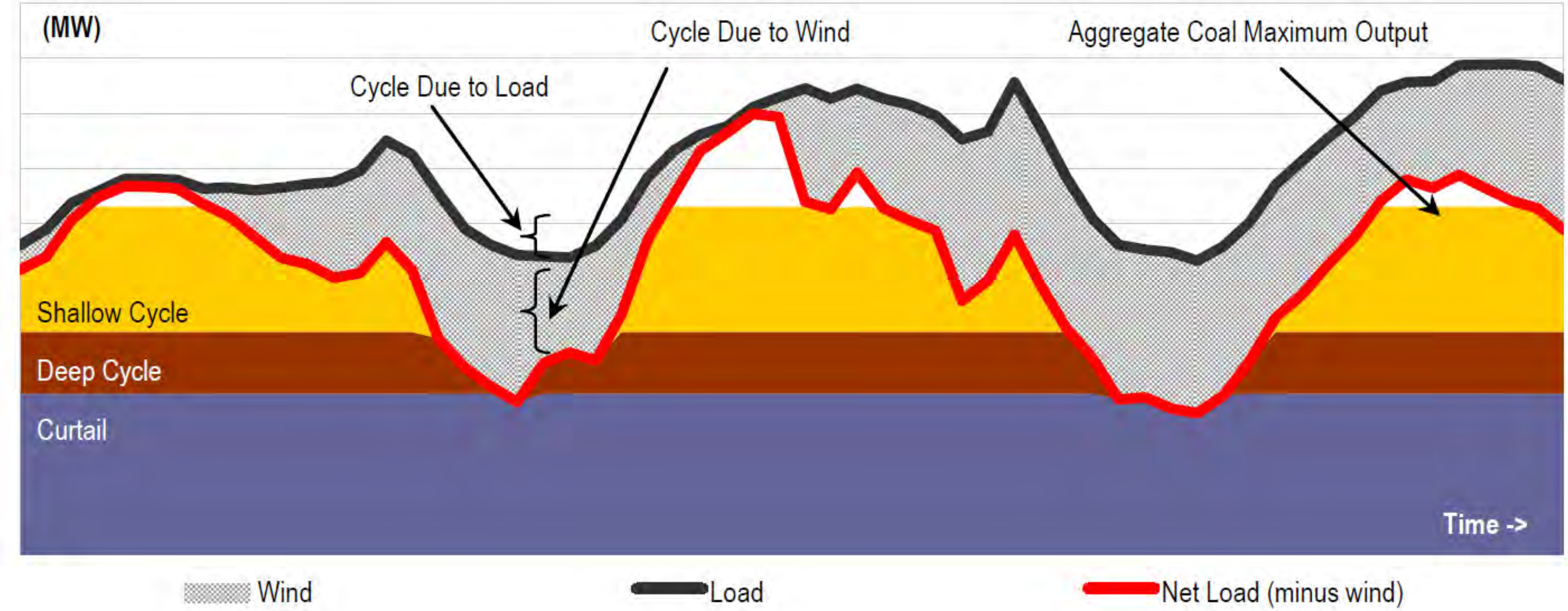
Average Generation Trends - Gas





EIA 2016

Generation Impacts from Wind



Plant, lower minimum and faster ramp rates	Annual cost impact due to cycling (2000 - 2013)	
Pawnee Unit 1, ~ 325 MW swing	5x	50% O&M, 10% Capex, 40% fuel
Harrington Unit 3, ~ 200 MW swing	3x	
Sherco Unit 2, ~ 425 MW swing	2x	

Wind Induced Coal Plant Cycling Costs, Connolly, PSCO Xcel 2011
Danneman, PSCO Xcel 2010

Finding the Right Balance

Boiler
- Slagging
- Fouling
- Corrosion

APH
- Plugging/Fouling
- Heat Rate
- Corrosion

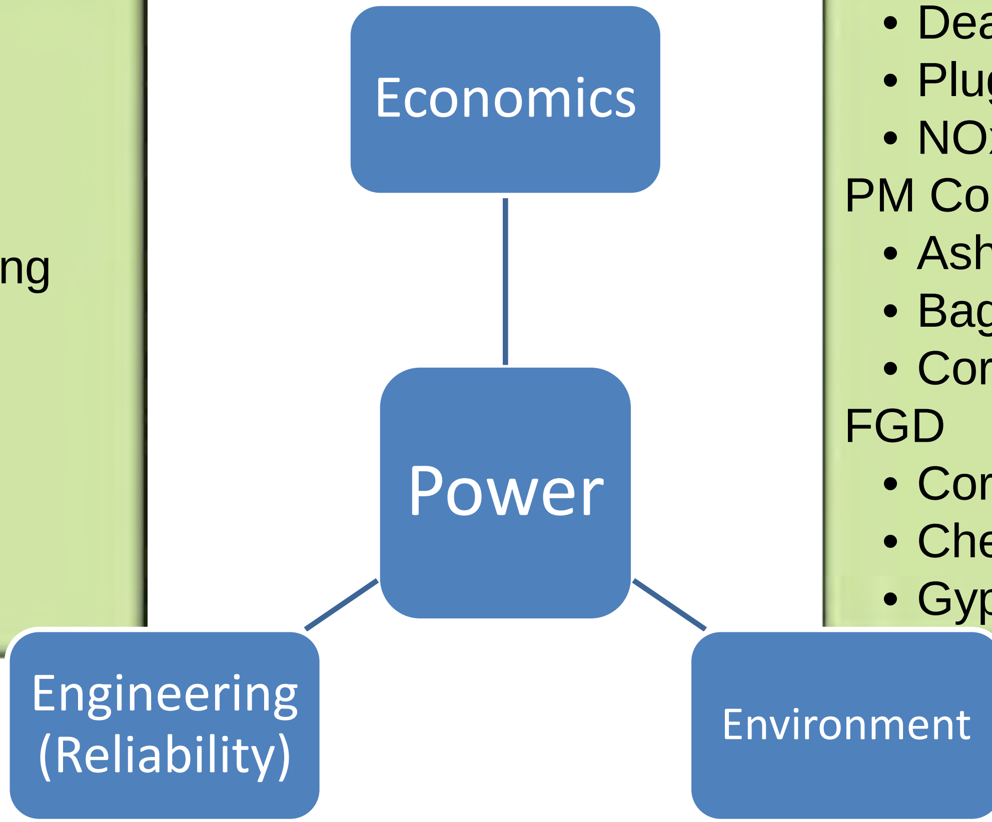
Fans/Ducts
- Corrosion
- Power

Cooling Tower

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

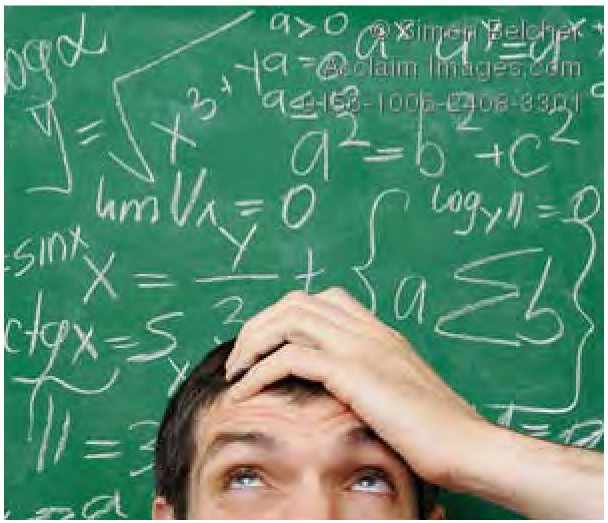
Water Balance

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

Groundwater Monitoring

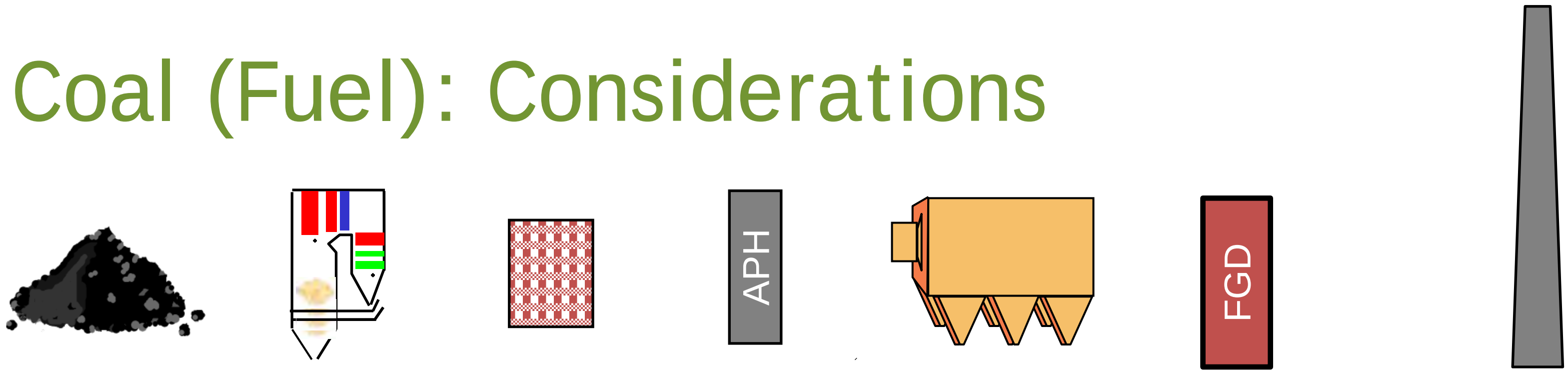
Stack Monitoring

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?

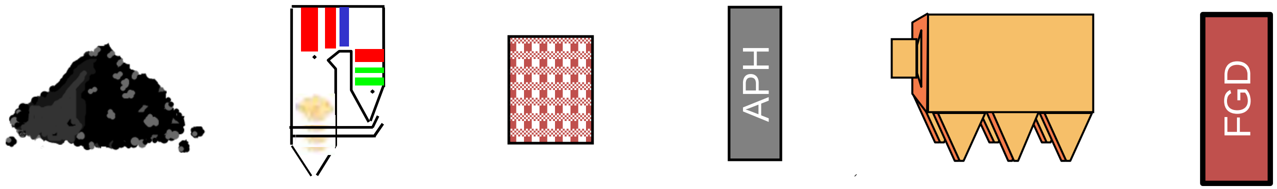
Coal (Fuel): Considerations



	Coal	Boiler	SCR	APH	PM	FGD	Stack	WWT
Sulfur					Resistivity ↓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)				↑Hg Ox'n, ↑Hg^P	↓Resistivity, Re-entrain.			
Halogen			Hg Ox'n			↓(Hg^{aq}→Hg^g)	HCl	TDS
Ca & Mg		Slag	SO_3 and Se rem.		PM rem.		PM	
Iron		Slag	Hg^{+2} (*catalyst*)		PM rem.	↑Hg solids		
Selenium								Se
Arsenic			Poison		PM rem.			As fines

Corrosion risk   Other risk

Chemicals Added for APC: Considerations

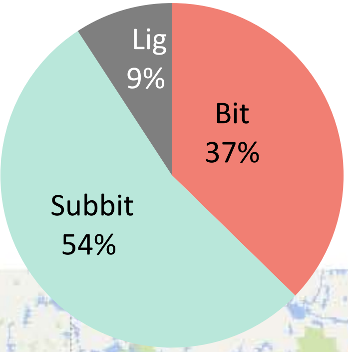


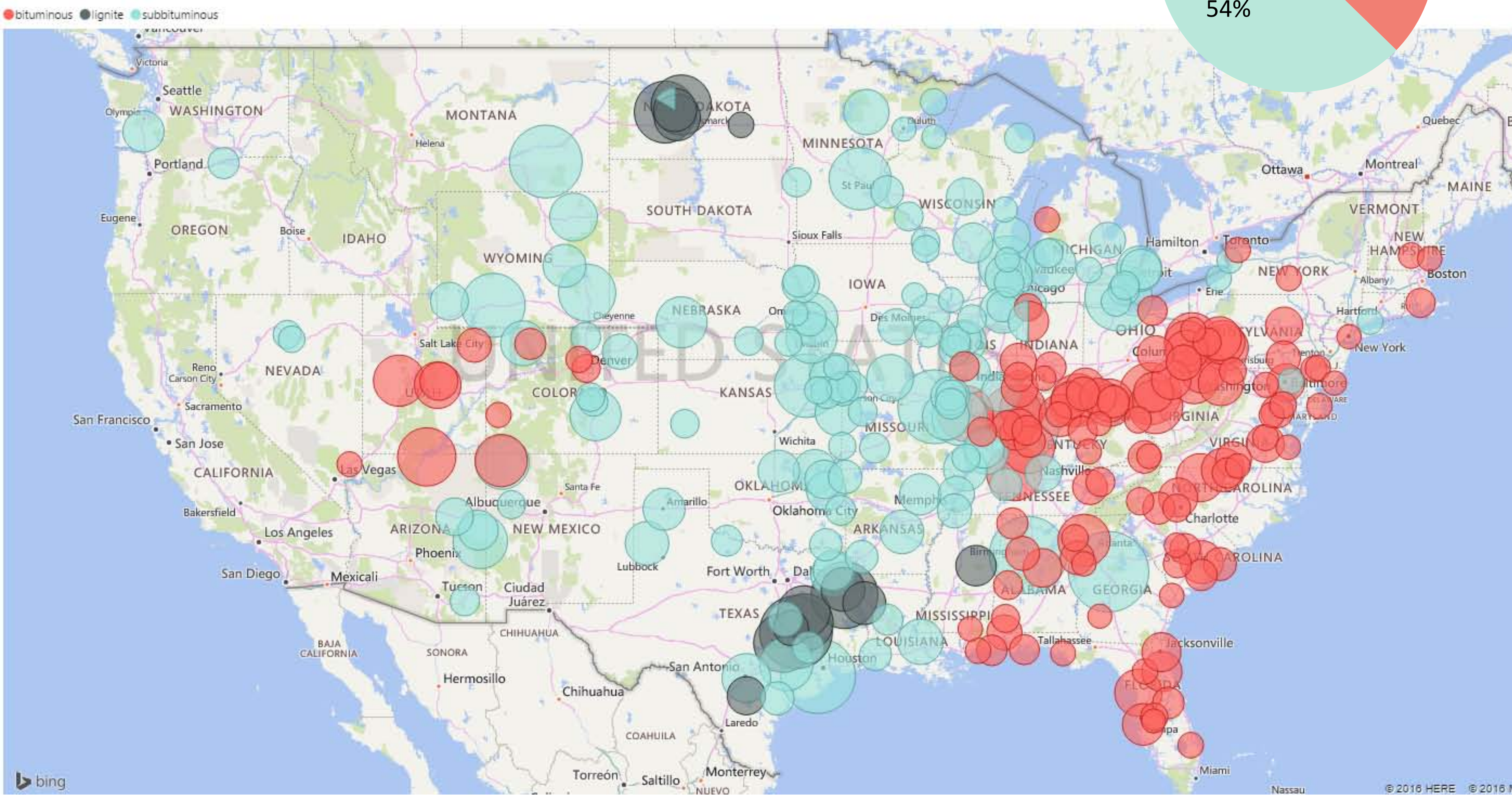
Chemical	Coal	Boiler	SCR	APH	PM	FGD	WWT
Limestone		↓As	SO_3 & Se			SO_2 rem	
Mg		Slag	SO_3 & Se				
Iron		Slag Se react.	↑Hg^{+2} (*catalyst*)				
Urea/NH_3		SNCR NOx	SCR NOx ↓Hg Ox'n				
Activated C					Hg^p rem.	Hg^{aq}→Hg^P	↓Hg^T
Halogen			Hg Ox'n	Hg Ox'n	↓Se in ash	Prevent Hg^{aq}→Hg^g	↑TDS ↑Se
SO_3					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

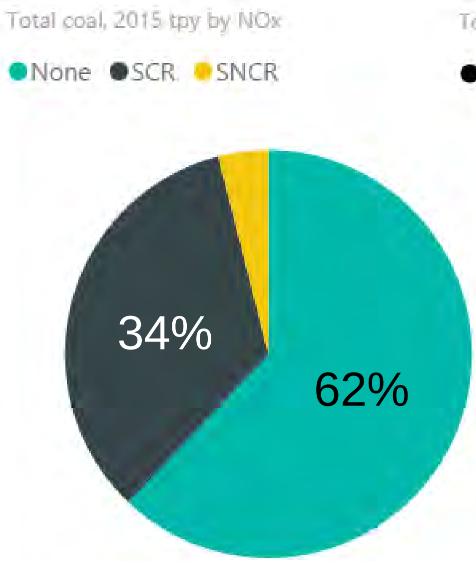
Primary Coal-Type Fired in 2015



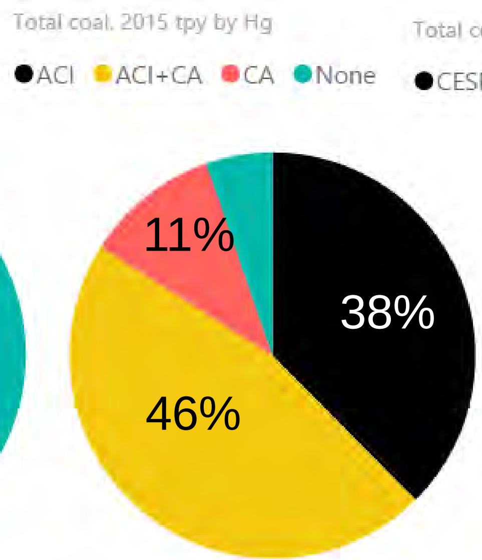


EIA Data

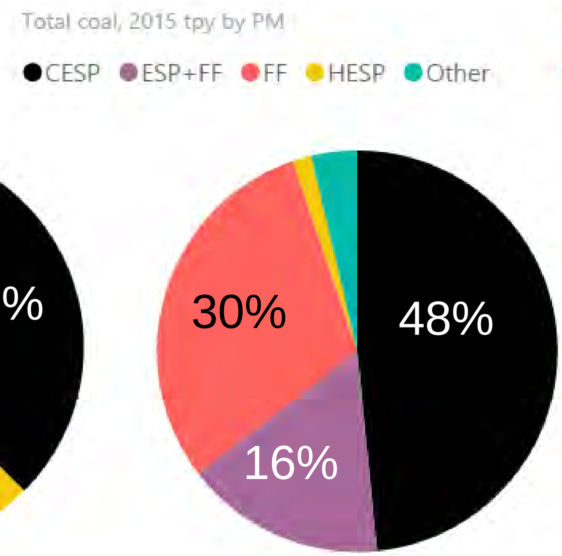
APC Configurations: Subbituminous Plants



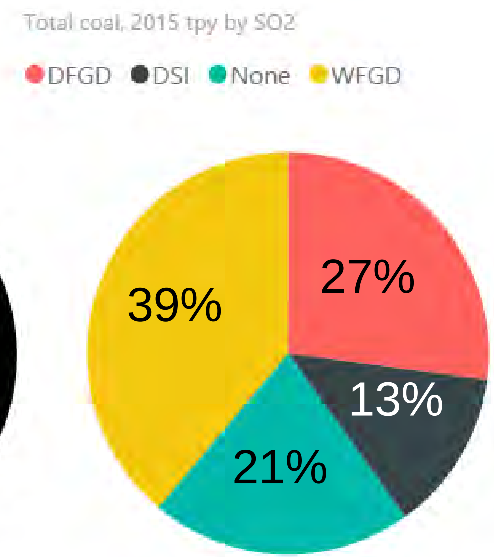
NOx



Hg



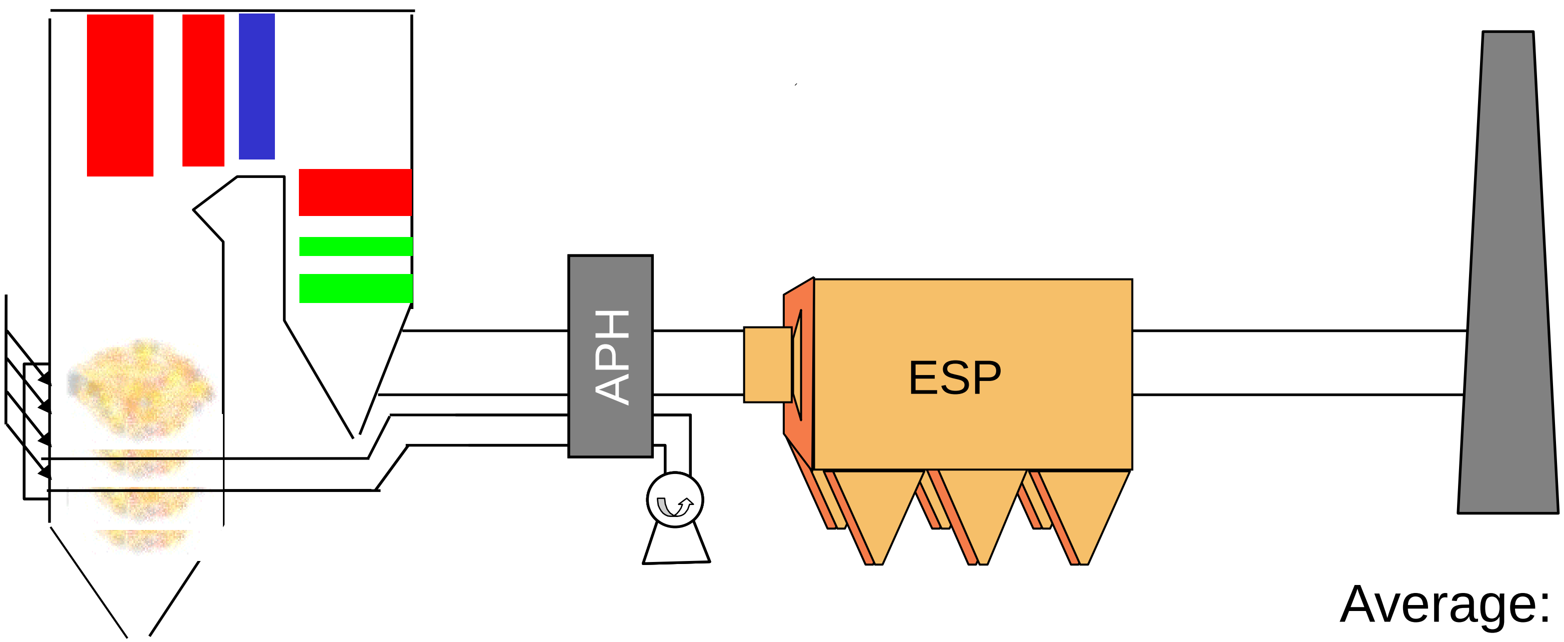
PM



SO_2 & HCl

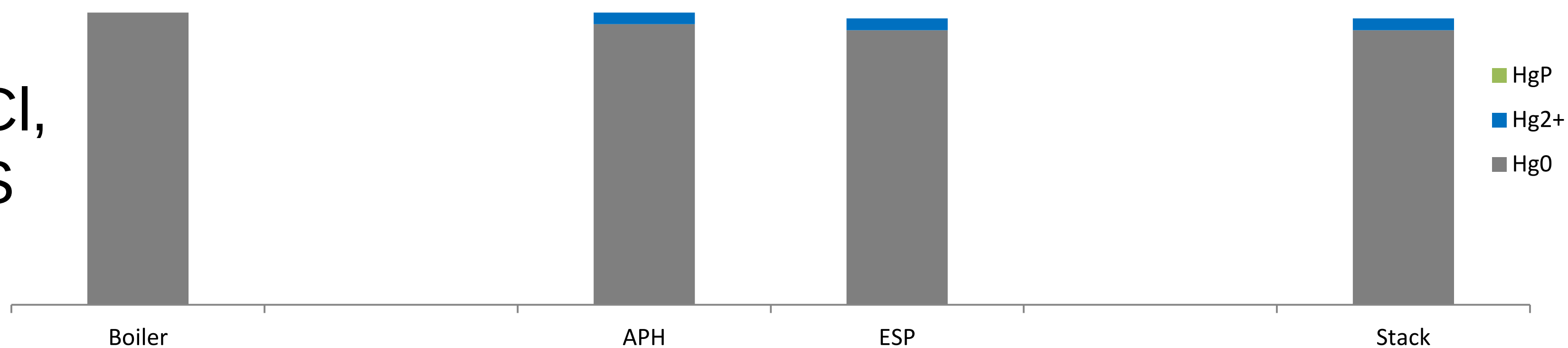
Based on Tons Coal Fired in 2015 (EIA data)

Workshop Focus: MATS- Subbituminous Coal



Average: 17%*

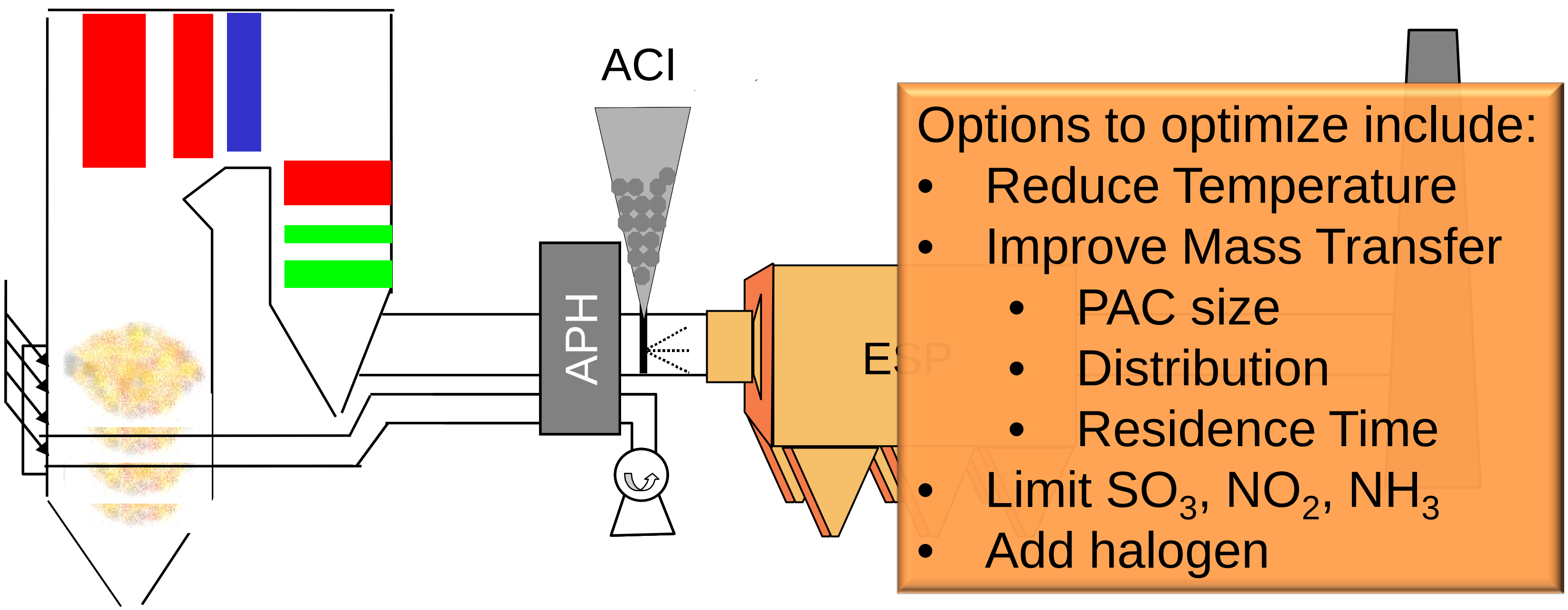
Low Cl,
Low S



Mercury Balance

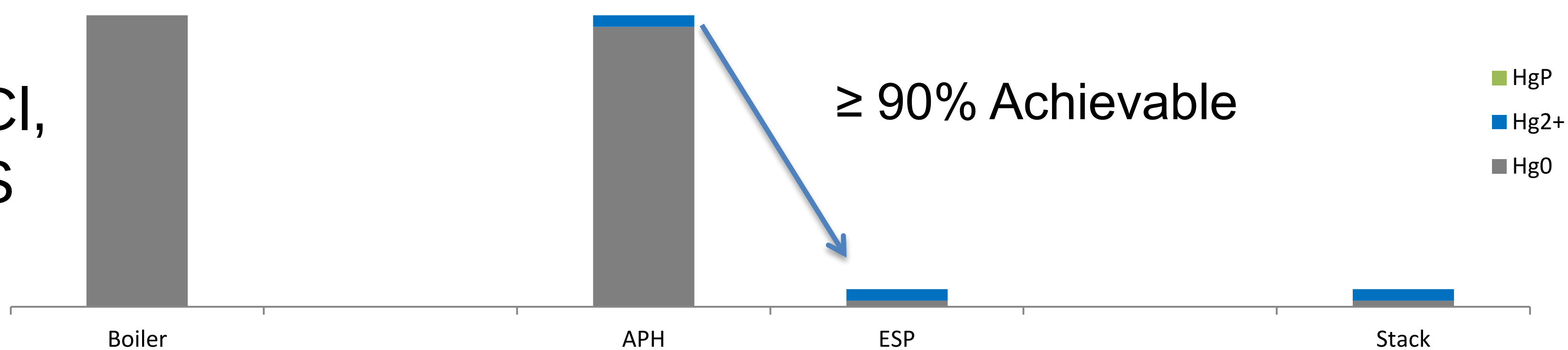
**Analysis of 1999 EPA ICR data*

Mercury Control - Subbituminous Coal

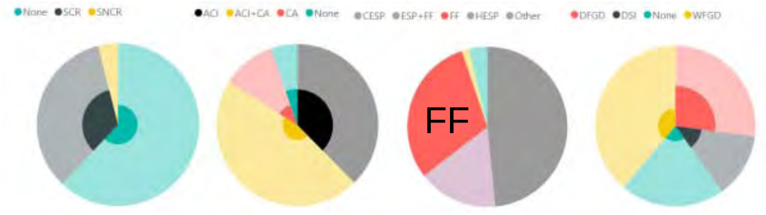


Options to optimize include:
- Reduce Temperature
- Improve Mass Transfer
  - PAC size
  - Distribution
  - Residence Time
- Limit SO_3, NO_2, NH_3
- Add halogen

Low Cl,
Low S

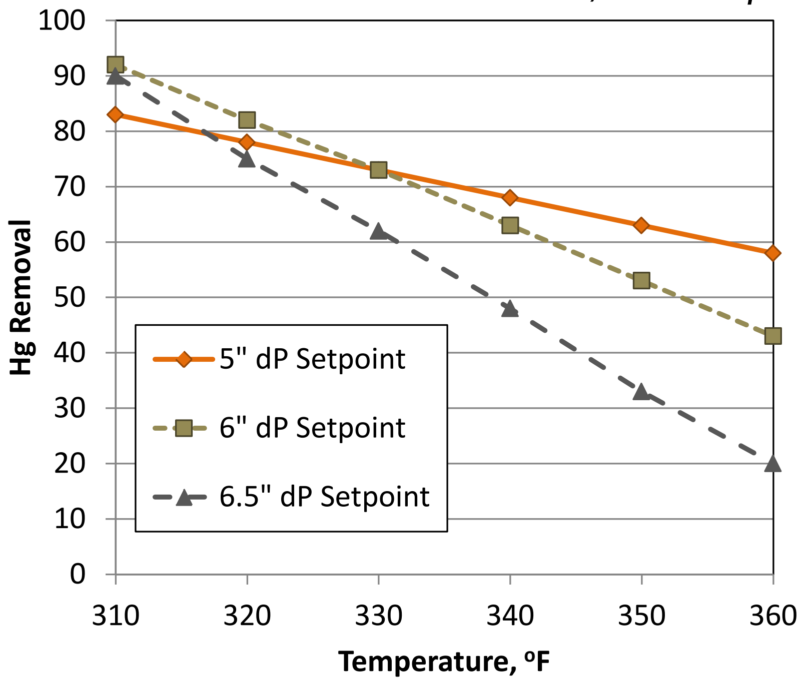


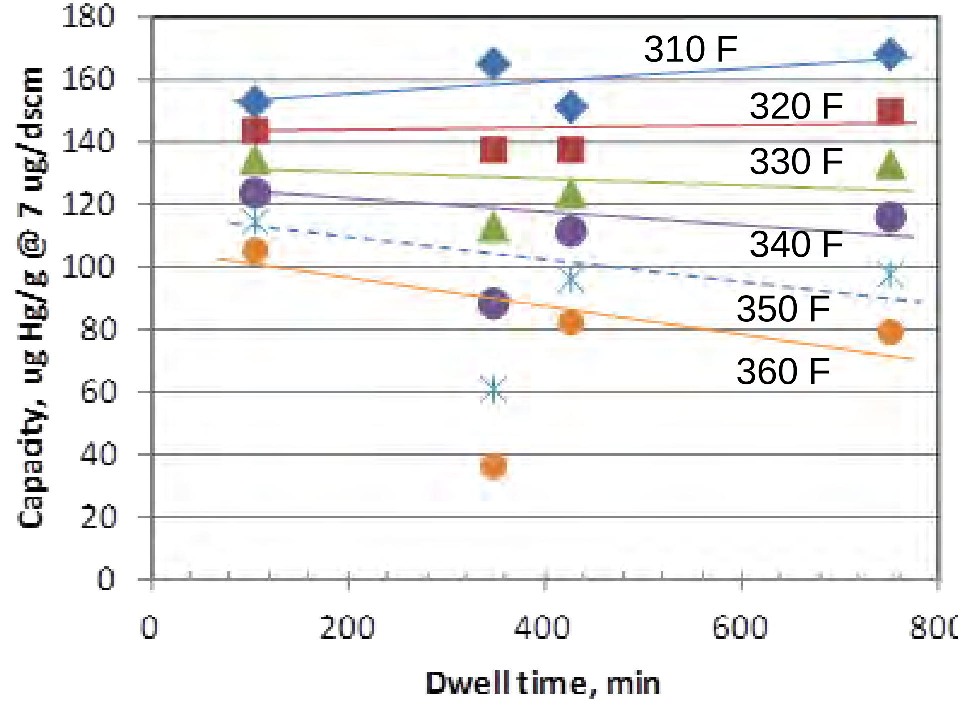
Getting the Most Out of ACI with Fabric Filters



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

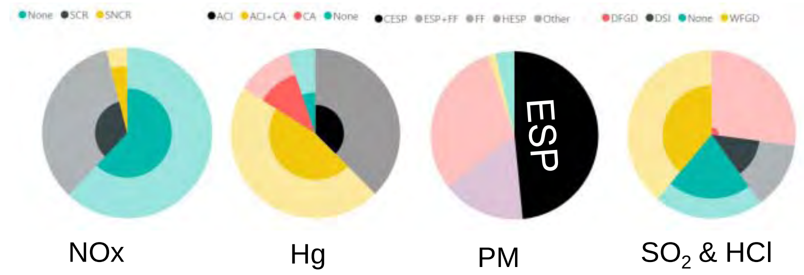
Source: Derenne and Stewart, Final Report





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

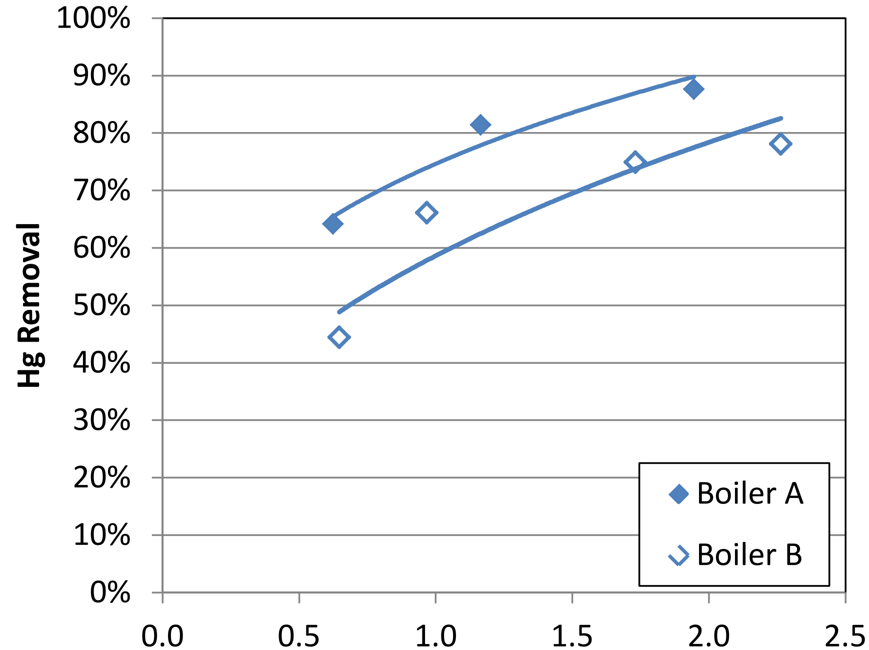
Mass Transfer Important for ESPs



- PAC usage with an ESP can be reduced by improving mass transfer to the PAC

Options

- Use a PAC with faster reaction kinetics
- Reduce PAC particle size
- Use mixing devices to improve distribution



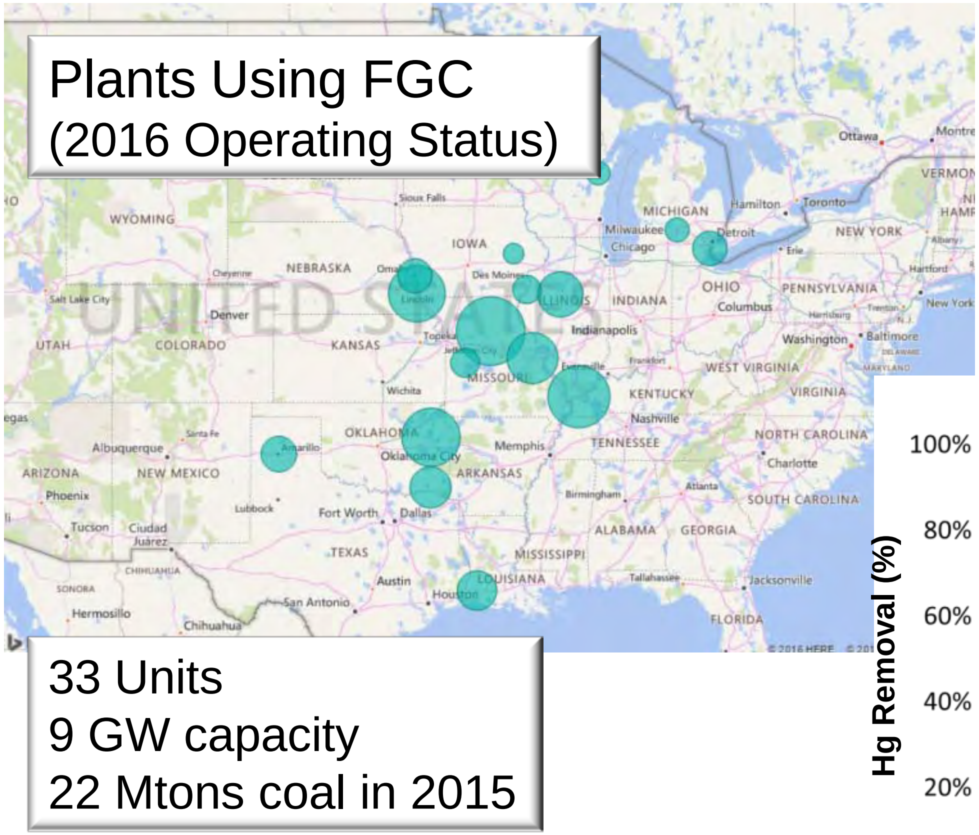
ADAir™ Mixer

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

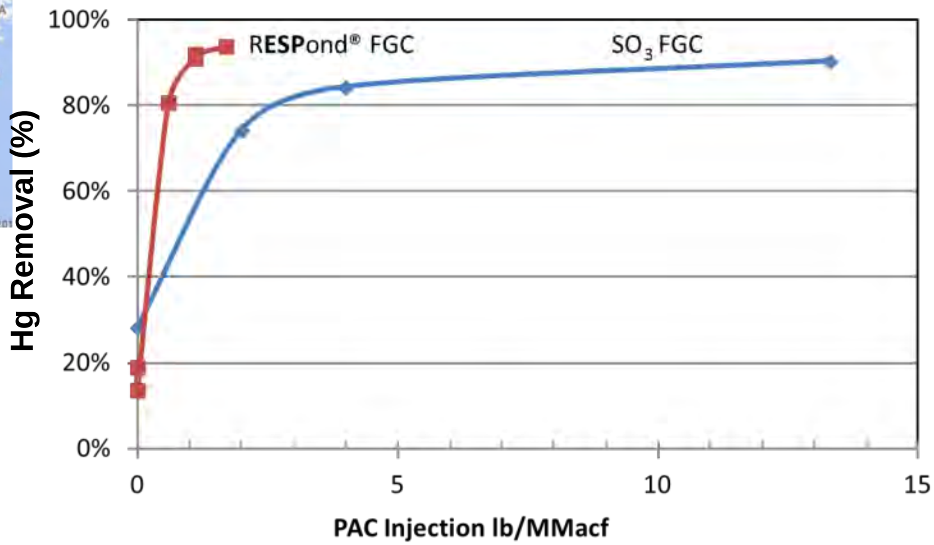
Boiler B has short residence time between APH and ESP inlet AND Chevron-style inlets

Boiler A has longer duct residence time

Impact of Flue Gas Conditioning

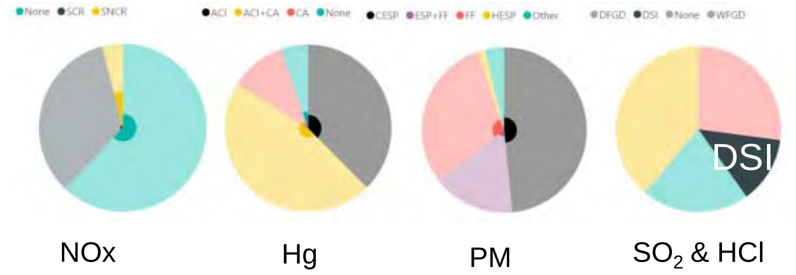


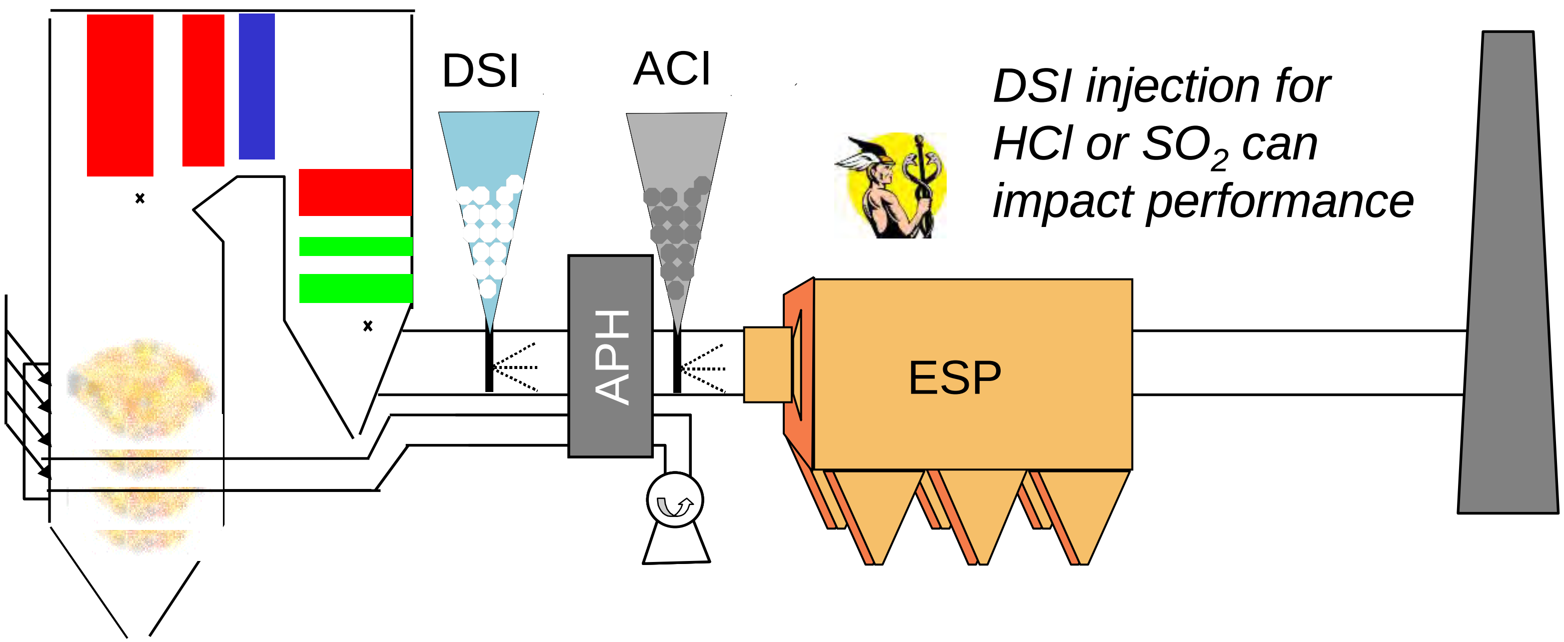
- Any SO_3 in gas phase appears to affect Hg capture
- Development continues on sulfur-tolerant PACs
- R**ESP**ond FGC does not contain SO_3
- FGC often only needed during full load operations



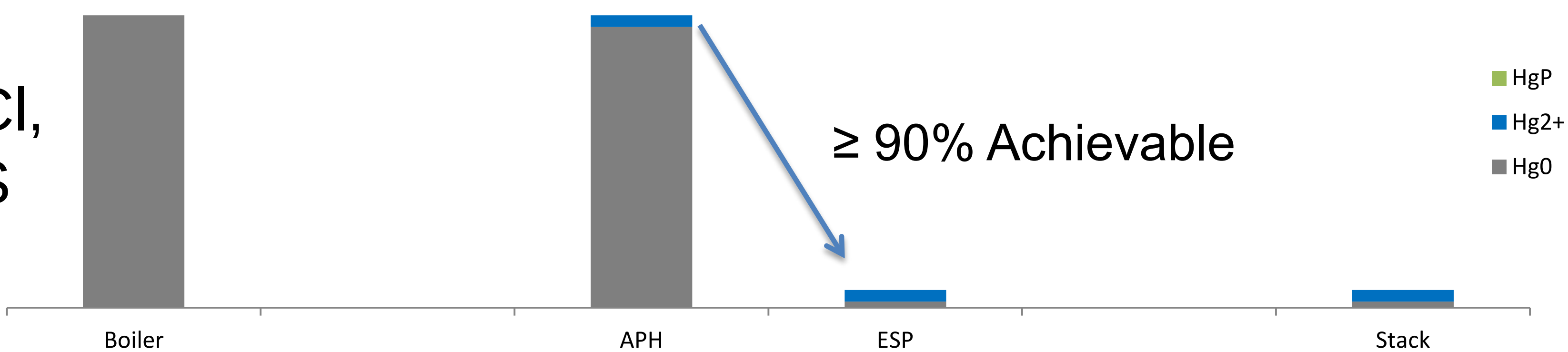
ACI upstream of APH (non-brominated PAC), 50µg/g Br on coal

Mercury and HCl Control
Subbituminous Coals





Low Cl,
Low S



DSI: What Sorbent Are Being Used

...Hydrated Lime when:

- Need to reduce SO_3 or HCl
- Opacity will not be a problem in the ESP (or there's a baghouse)
- Fly ash sales might be an issue or leachability in landfill a concern
- ACI will also be used (possible NO_2 interference using sodium sorbents)

...Sodium Sorbent when:

- Need to reduce SO_2
- Need to reduce SO_3 or HCl
- Opacity might be an issue in the ESP
- Fly ash not sold; no landfill issues

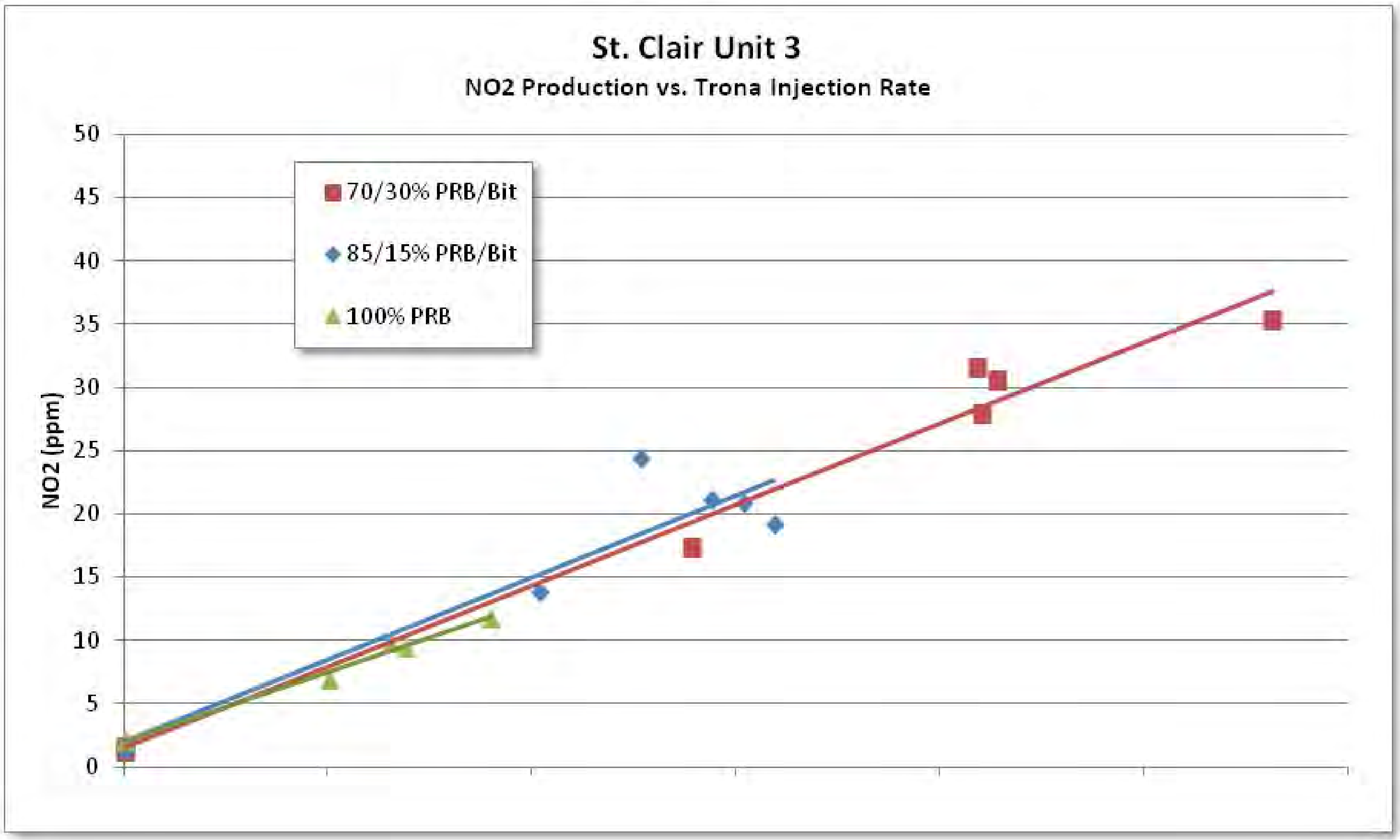
We estimate ~ 50|50 split between lime and sodium sorbents for subbituminous plants using DSI

DSI 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°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

More Challenges: NO_2 Production with Trona Injection

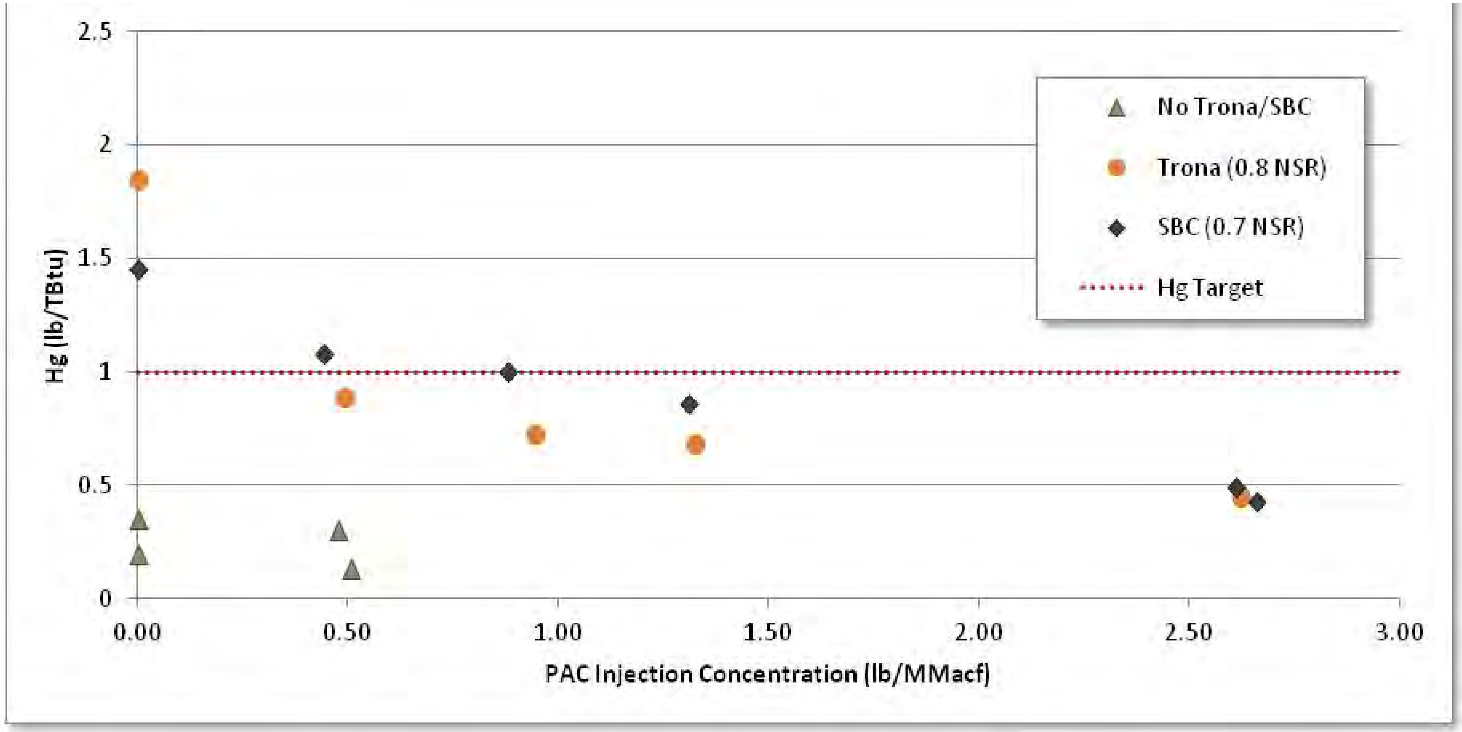
- Sodium-based DSI can increase flue gas NO_2
- Trona or SBC injection increased stack NO_2 to as much as 35 ppmv



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

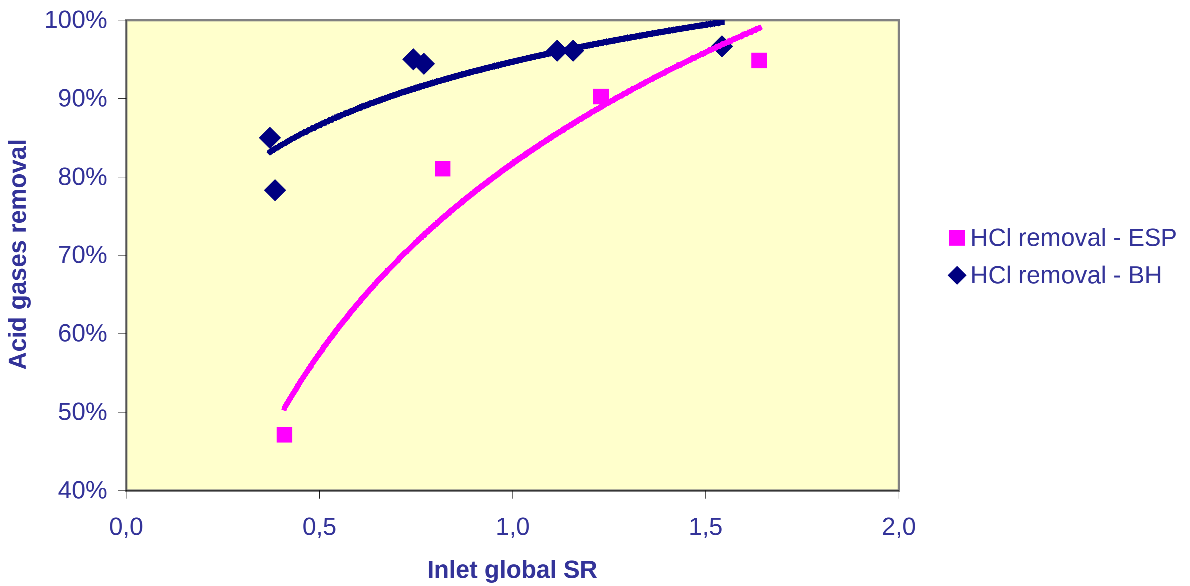
Results from Testing at DTE St. Clair Unit 3, W. Rogers, EUEC 2013

Effect of Mass Transfer

- Mass transfer affects removal
  - FF better than ESP
  - Particle distribution and particle size important
  - Using mixing devices can improve distribution

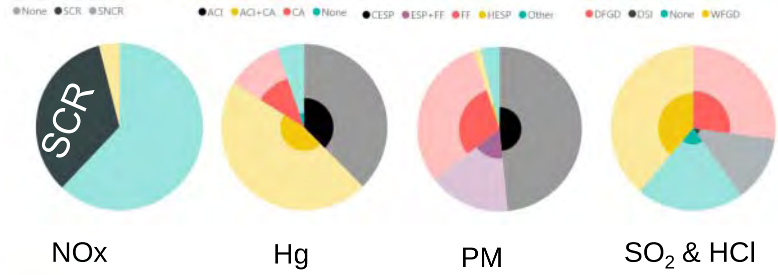
ADAir™ Mixer

Sorbacal®SPS - Influence of filtration at 350°F



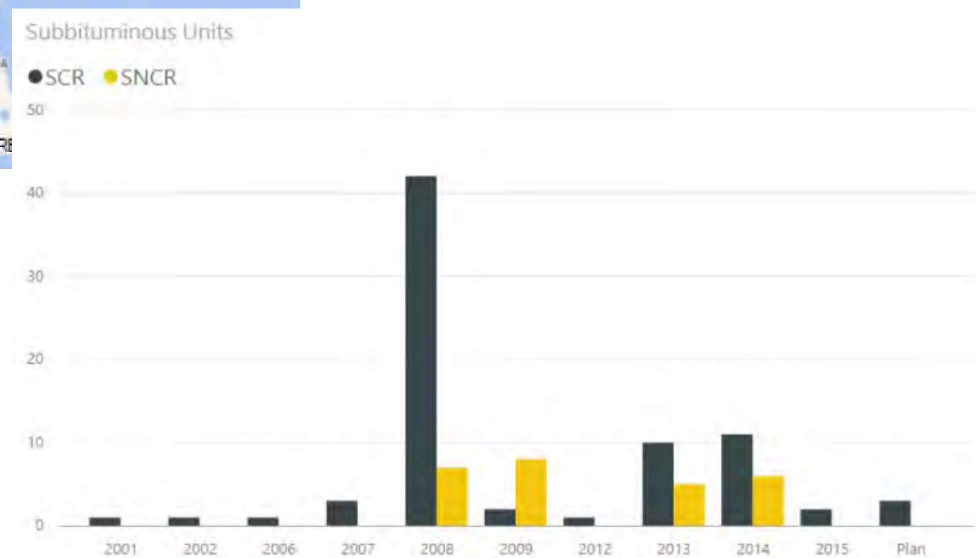
Source: L'Hoist, 2011

Emerging Issues: NH_3 Slip



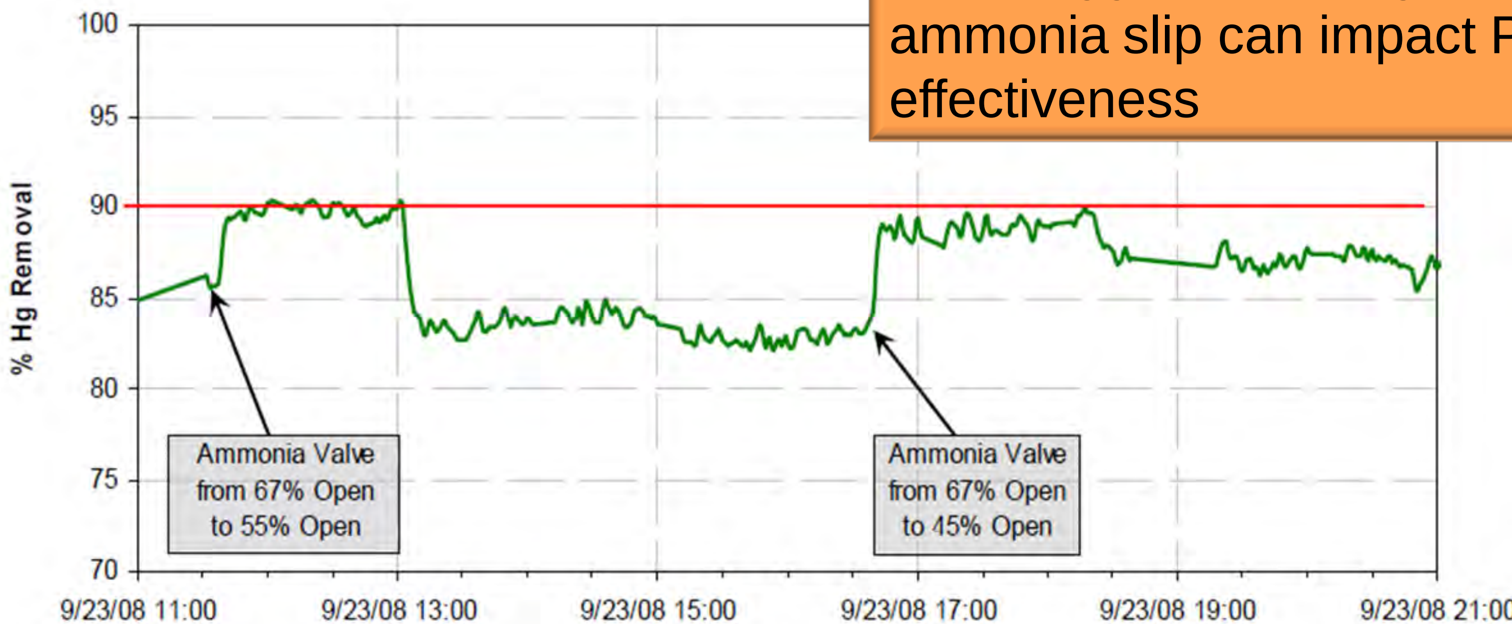
~ 38% of 2015 subbituminous coal generation on plants with SCR or SNCR

Increasing issues associated with NH_3 slip and PAC performance are emerging



Impacts of NH3 on PAC Performance
Clues from 2008 DOE Testing

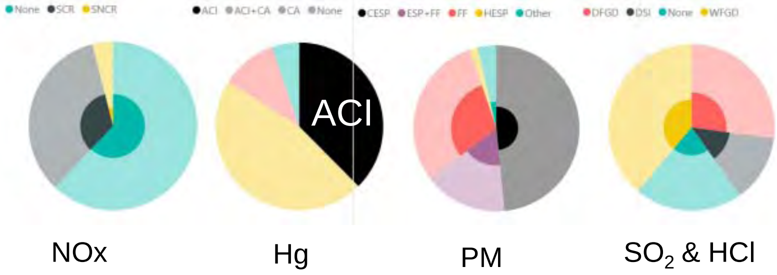
Data suggests that high ammonia slip can impact PAC effectiveness



Hardin Station: Spray Dryer + Fabric Filter, Subbituminous Coal

- Many plants use feedback control on NOX to control NH_3 injection
- Cycling operation can increase risk due to SCR degradation and reduced SCR efficiency
- Monitor NH_3 feed rate to manage risk

Option to Reduce PAC: Halogen Addition

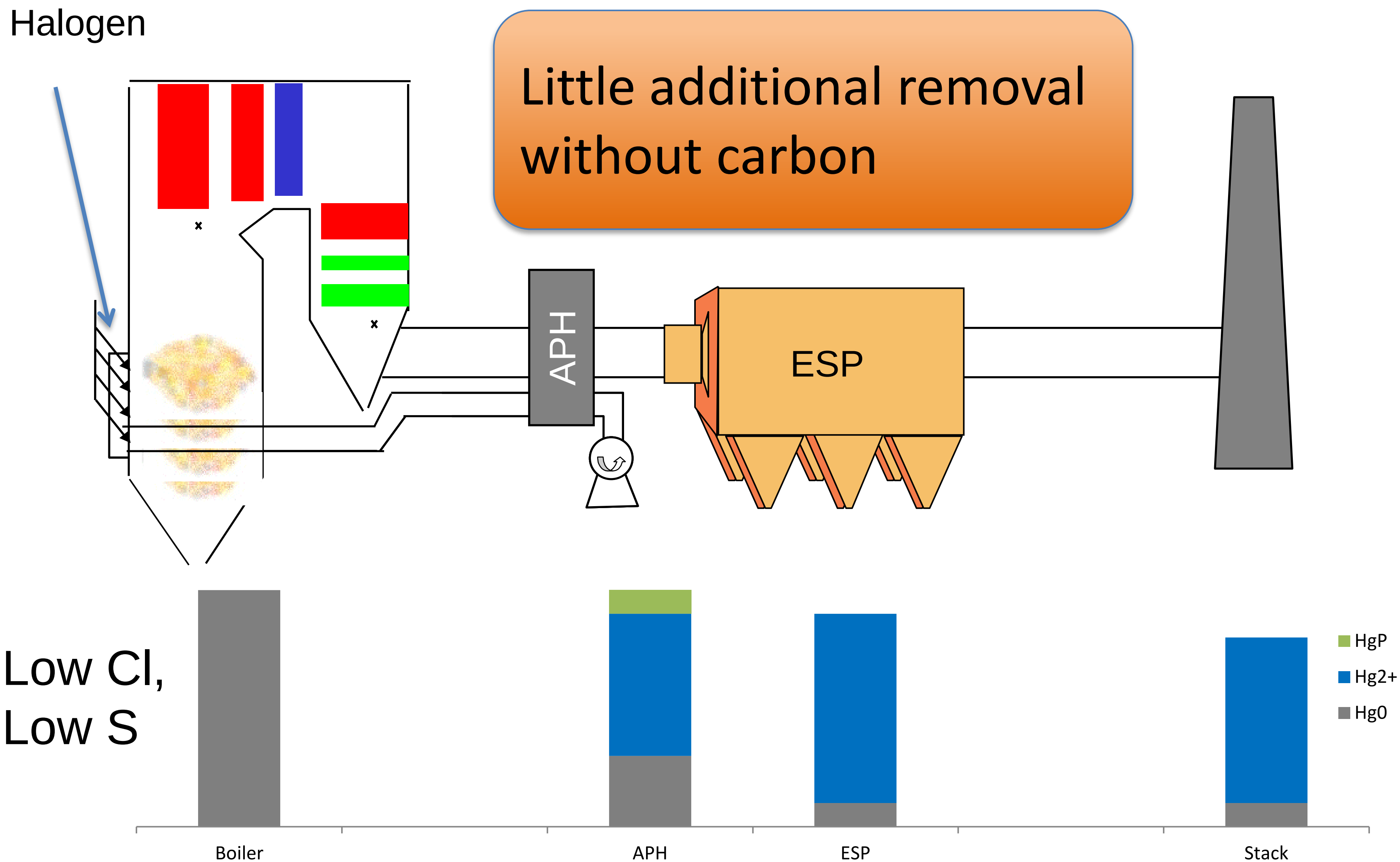


- Adding halogens increases oxidized Hg:
  - Increase effectiveness of some kinds of activated carbon for Hg capture
  - Increase capture of Hg in SO_2 scrubber
  - Adding some forms of iron can reduce halogen requirements*
- Potential balance-of-plant impacts:
  - Possible increased corrosion in flue gas
  - Halogens build up in wet scrubber liquor → Corrosion and potential permit issues

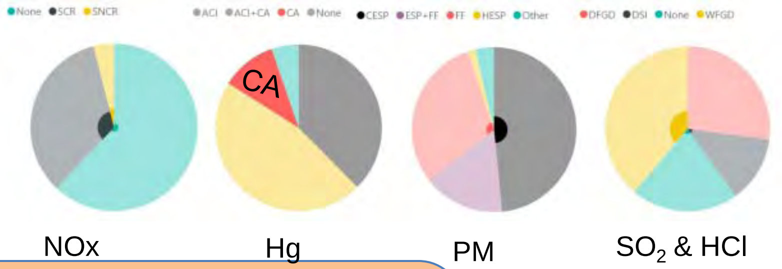
- Over 80% of units with ESPs have an additive system
- Less than 40% of units with FF's have an additive system

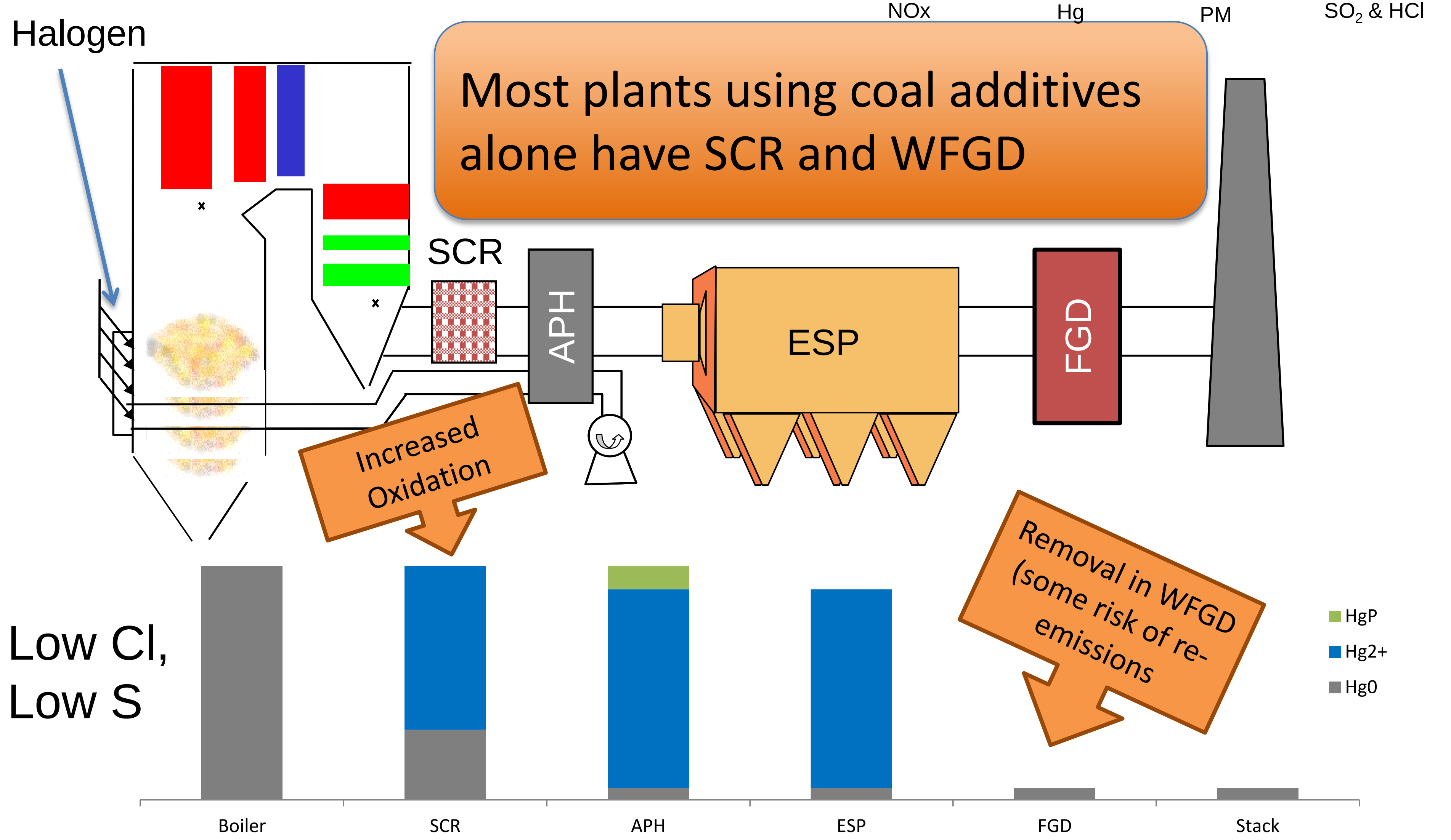
*ADA-ES, Inc. patented technology

Can Halogen Eliminate the Need for PAC?

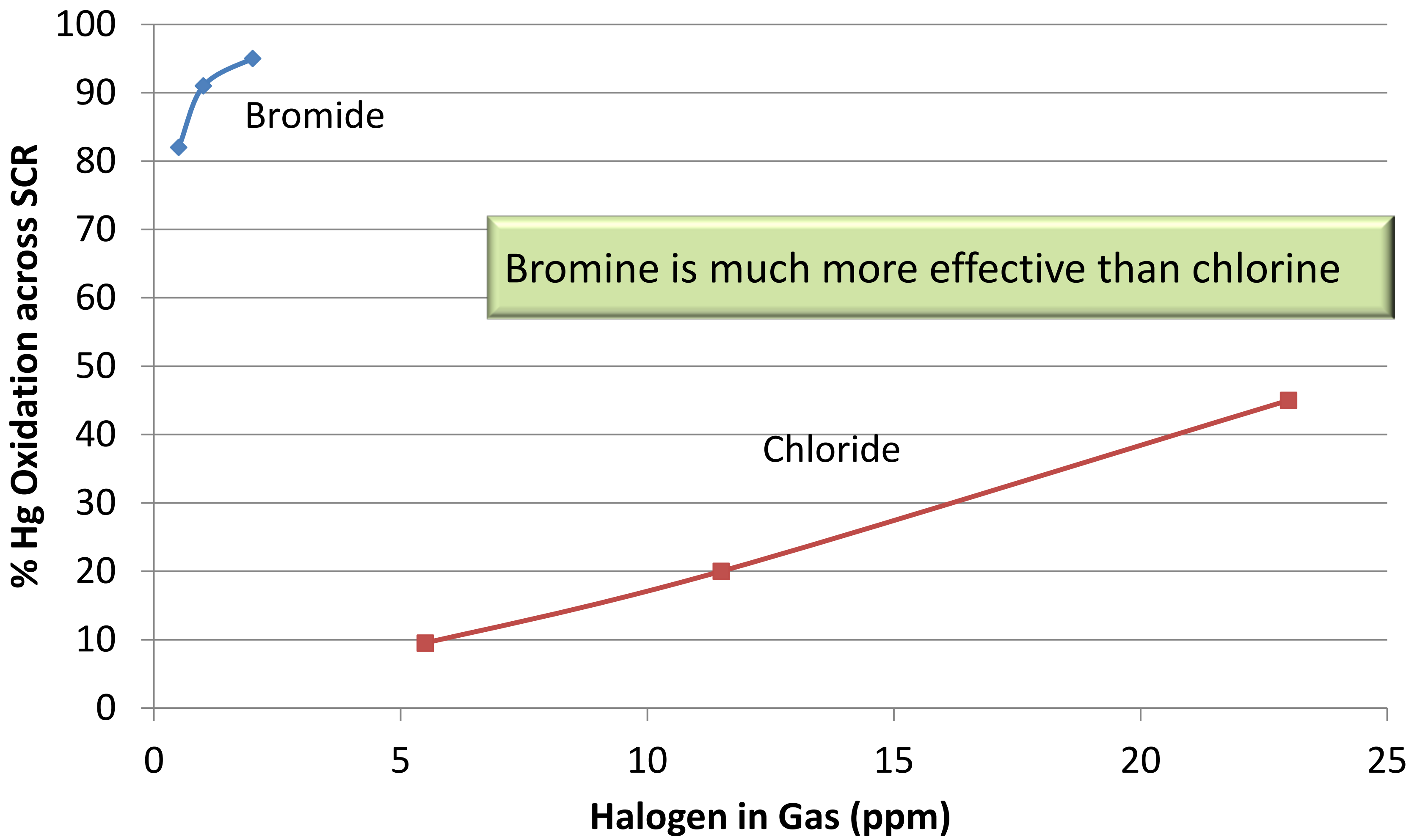


Subbituminous Coal with SCR and WFGD



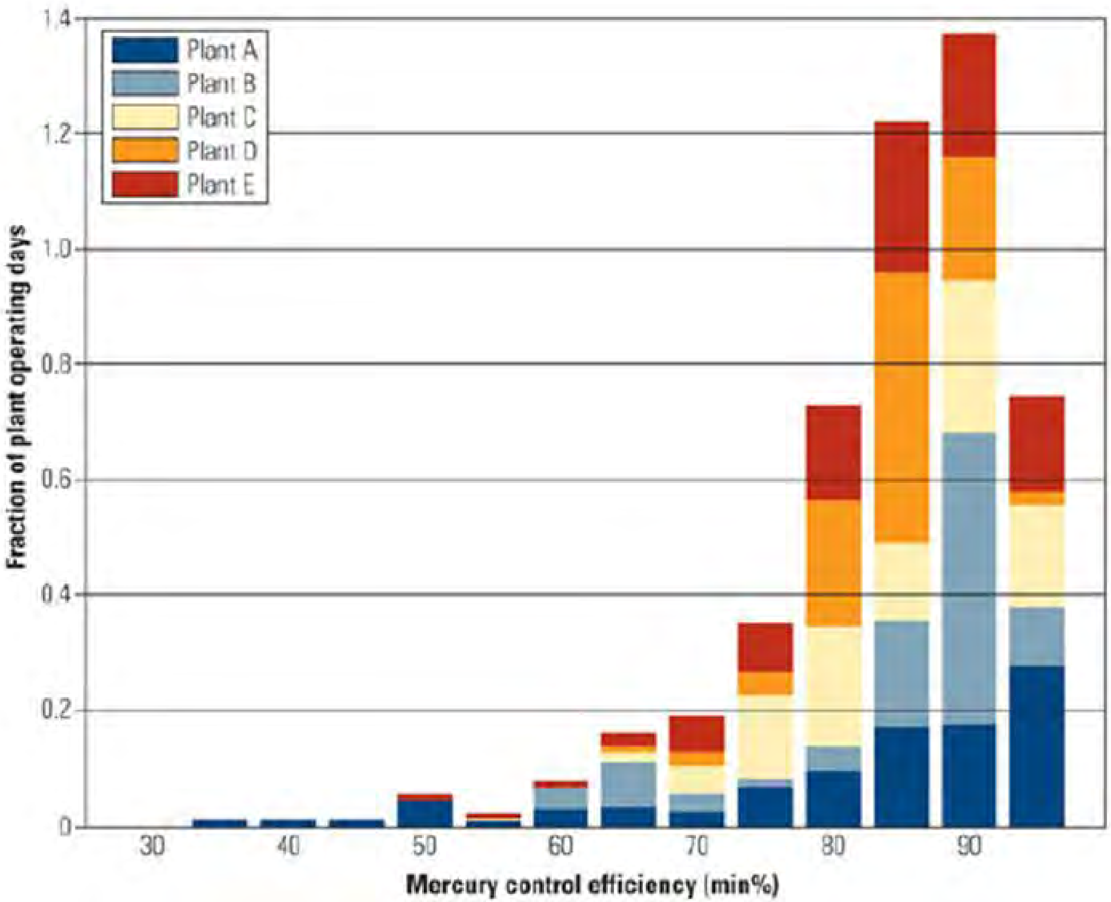


Improving Hg Oxidation Across SCR with Halogens



Adapted from Cormetech,
2015 Reinhold NOx conference

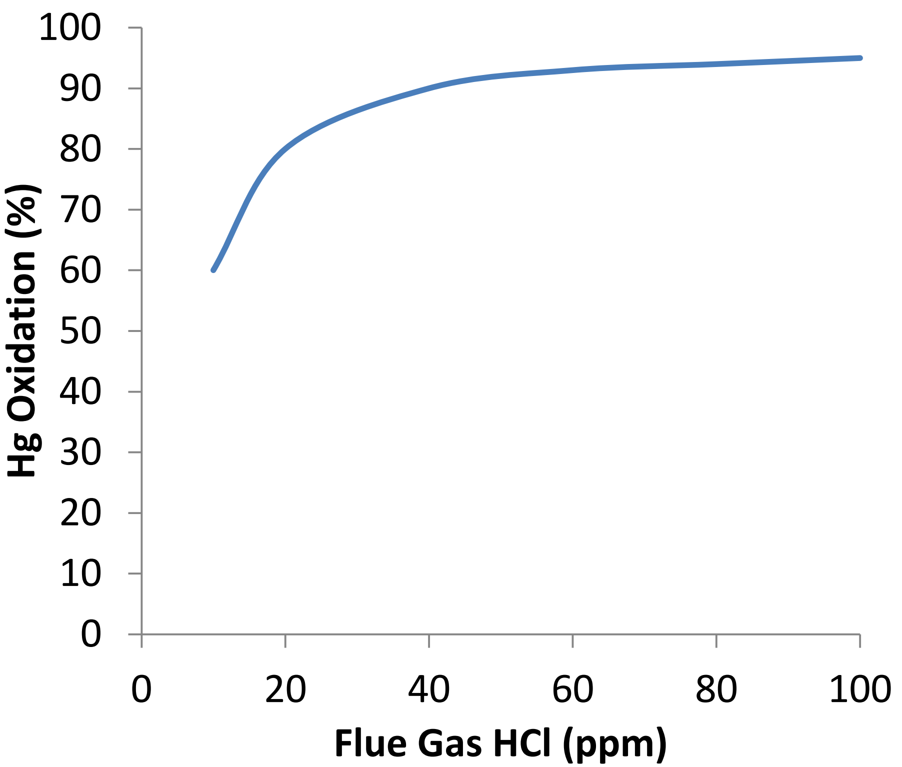
Can you Rely on Halogens and Co-Benefits?

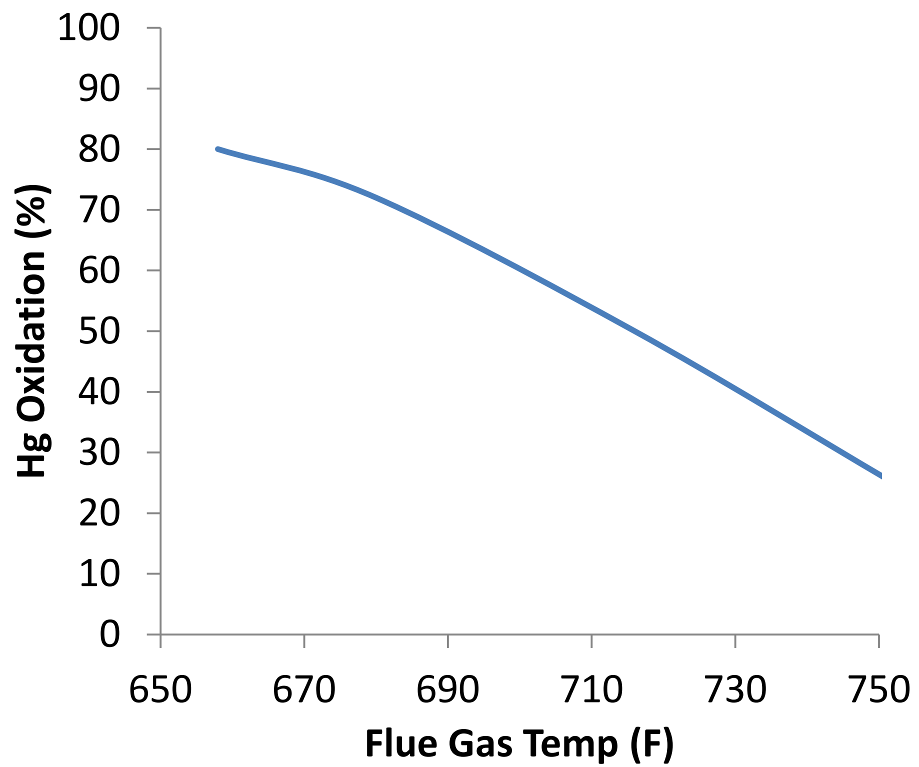


- Southern Company Plants with SCR, ESP, WFGD
- More than 40 months of WFGD operations
- Mercury control greater than 90% was achieved 47% of the time
- Important factors include SCR temperature, age, coal halogen

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

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

Potential Balance-of-Plant Impacts with Halogen Addition

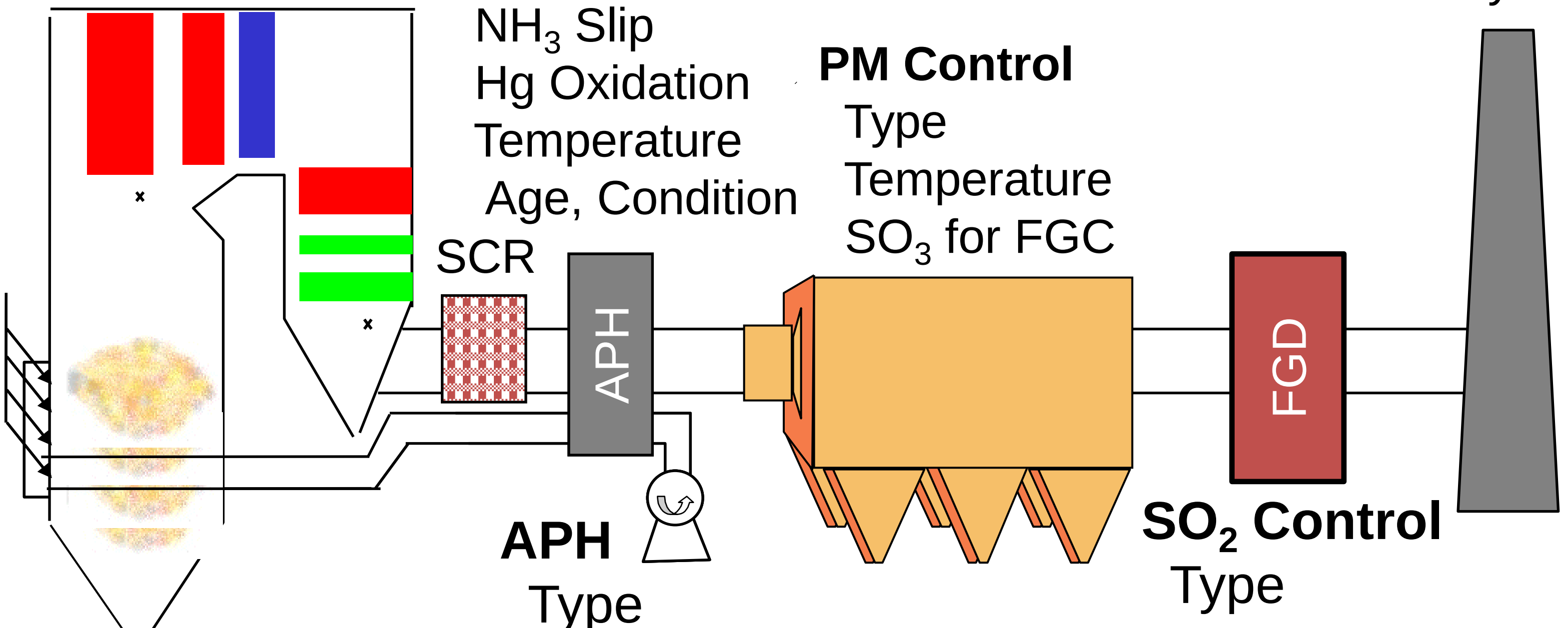
- APH cold-end corrosion
- Increased gas-phase Se at scrubber inlet
- Higher halogen levels in FGD (corrosion) and waste water (TDS and treatment)
- Formation of additional trihalomethanes (THM) in downstream water

Emissions Control – What's Important

SCR – NOx Control
- SO_2 to SO_3 conversion
- NH_3 Slip
- Hg Oxidation
- Temperature
- Age, Condition

Ancillary Emissions

PM Control
- Type
- Temperature
- SO_3 for FGC



APH
- Type
- Temperature

SO_2 Control
- Type
- Hg re-emissions
- Water management

Boiler Type

Coal
- Mercury
- Halogens
- Sulfur
- Ash: calcium, iron, etc.

Combustion (NOx, LOI)

→

- LOI
- Ash
- SO_2 and SO_3
- Halogens

→

- Carbon (LOI or PAC)
- Halogens
- SO_3
- Ash
- Oxidized Hg

→

- Halogens
- Oxidized Hg

Water Treatment
Ash Management

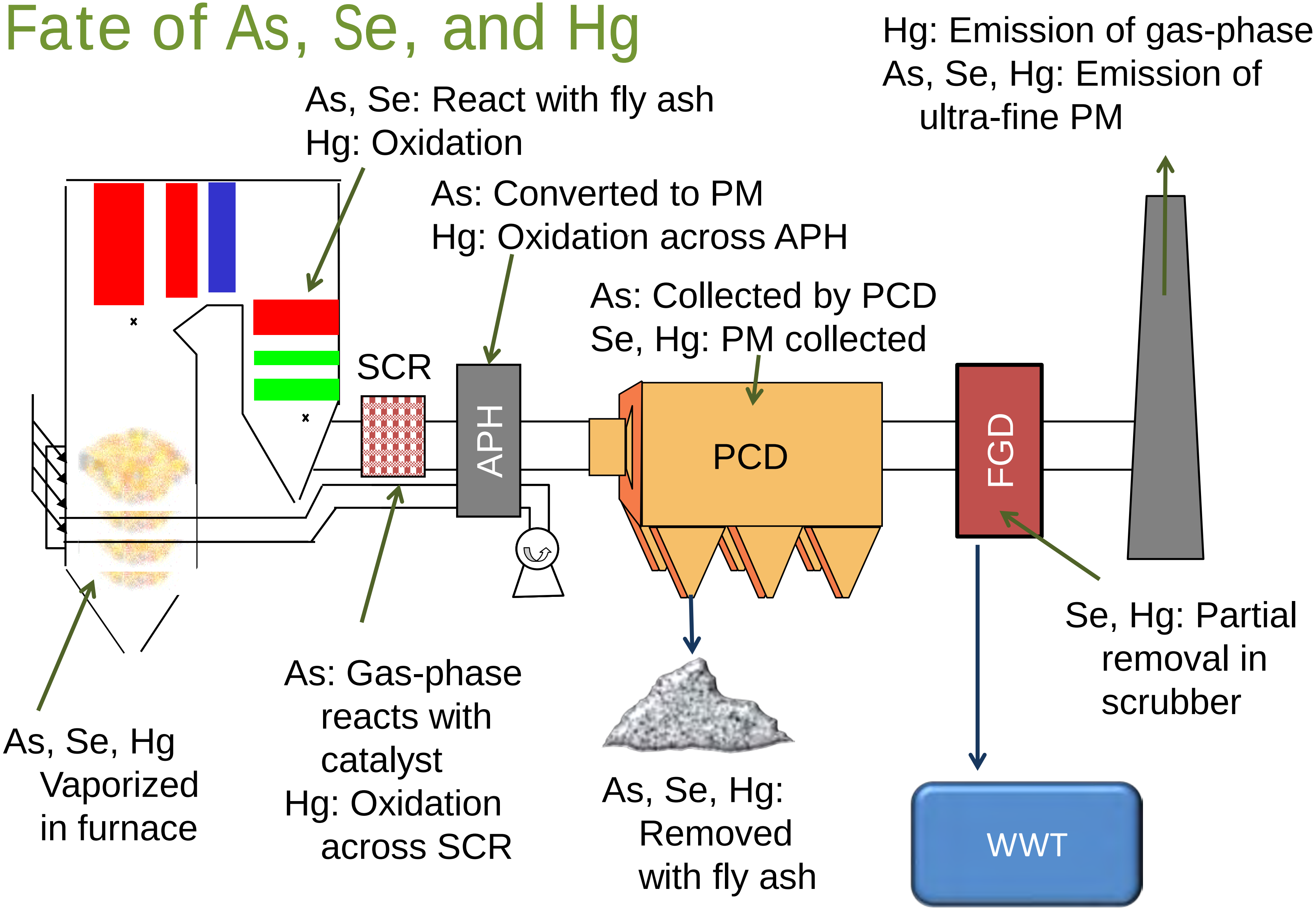
Key Factors Affecting Consistent and Reliable **MATS** Compliance

- 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
- HCl Controls
  - Minimize impact of DSI on PAC effectiveness and PM controls
- Particulate Controls
  - PM loading, changes to resistivity from sorbents, FGC impacts on PAC effectiveness

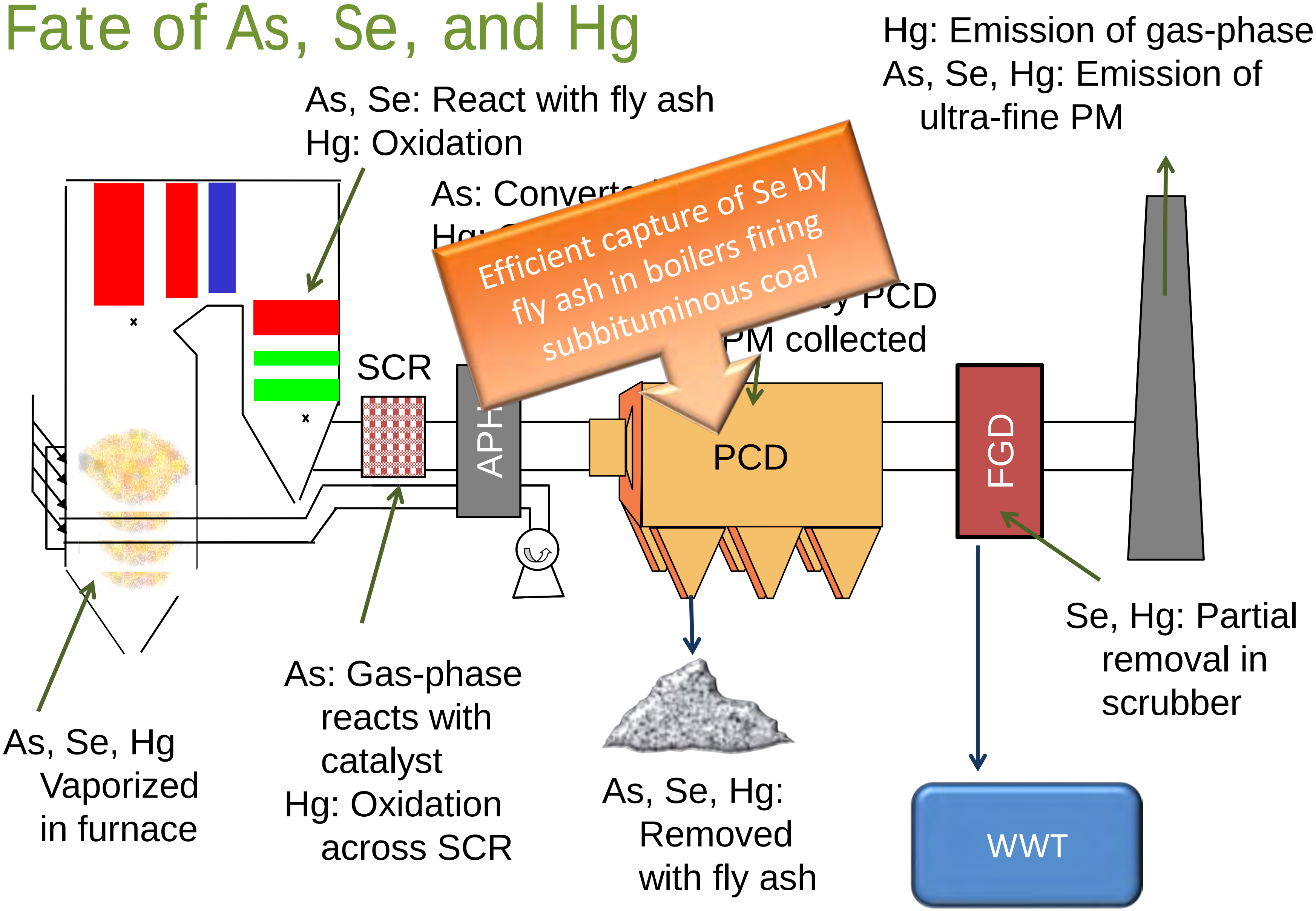
What Else is Important?

- 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
- Bromine addition to coal or in the FGD absorber has the potential to cause water quality problems and trigger the need for additional water quality-based effluent limitations in the NPDES permit

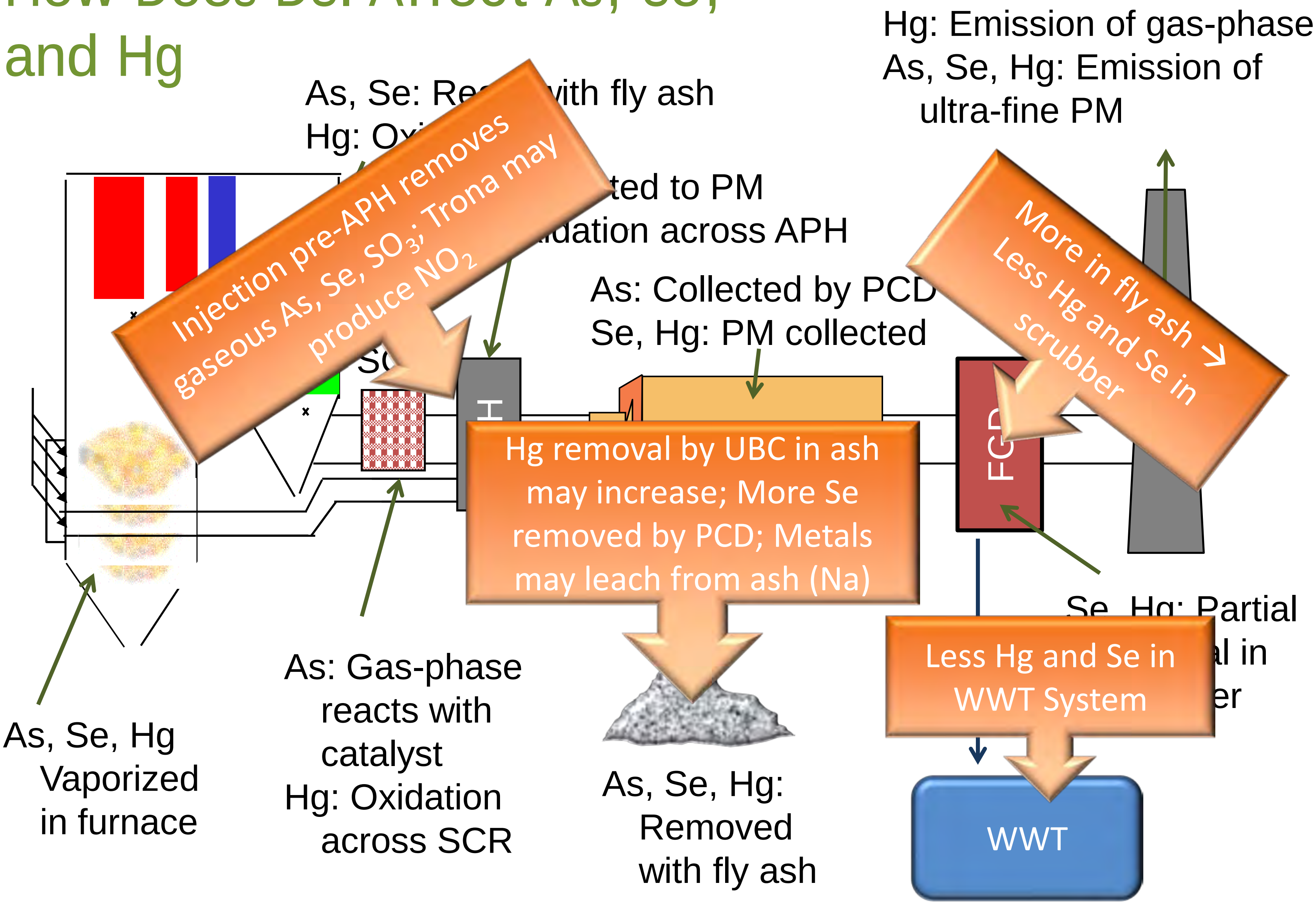
Fate of As, Se, and Hg



Fate of As, Se, and Hg



How Does DSI Affect As, Se, and Hg



Leaching from Ash-Sorbent Mixtures

Trona

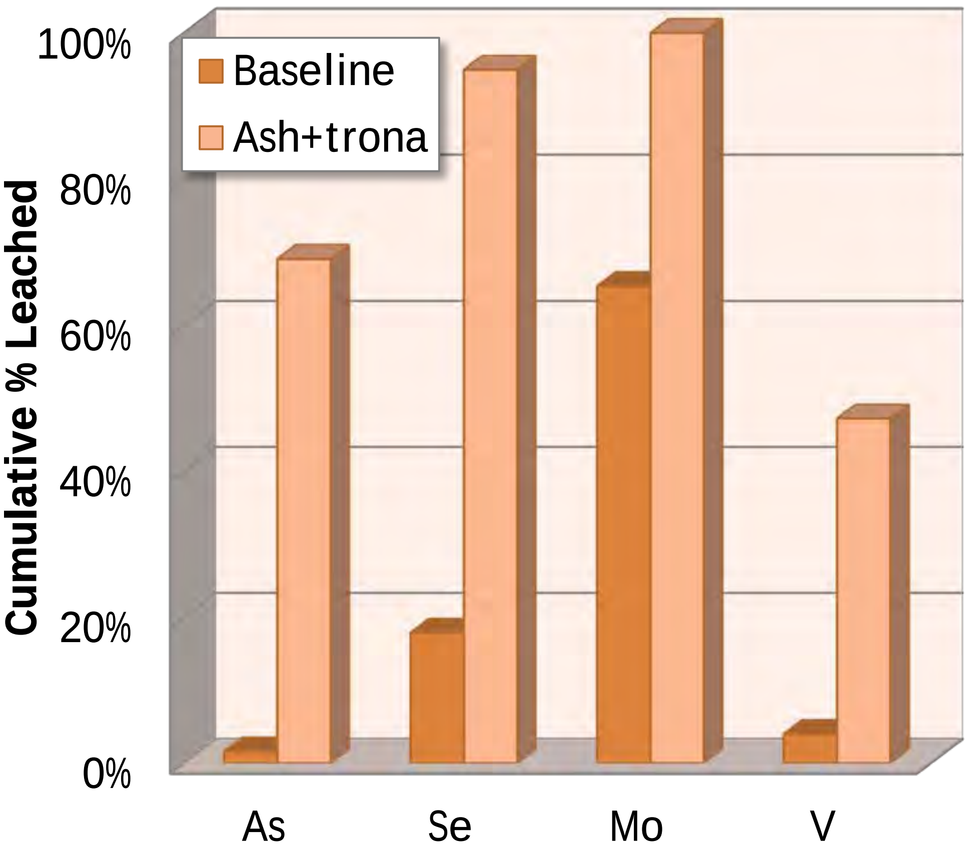
- Significantly enhanced leaching of major anions of concern, including Se, As, Cr, and V (but not Hg)
- With trona injection, distribution of these anions shifted to the soluble trona fraction of the ash
- pH of bituminous leachate increased from ~7.5 to ~11 with addition of trona

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

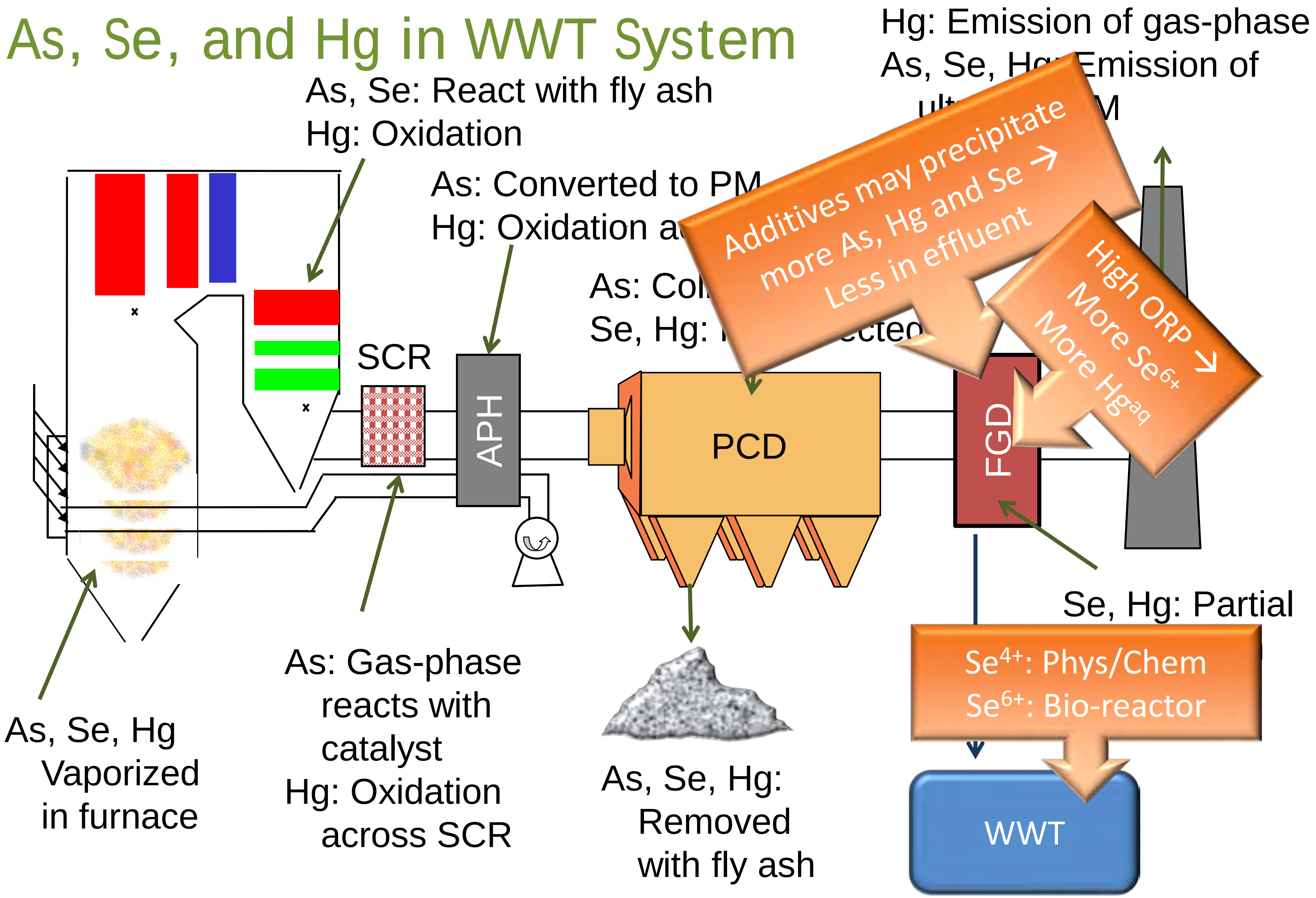
High ORP (> ~ 500 mv)

- 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)

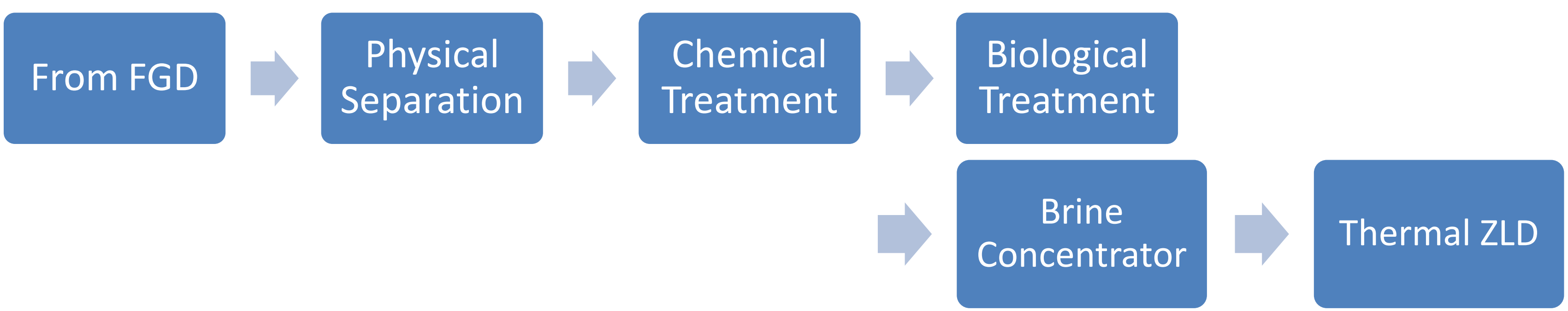
- Hg partitions to solid phase
- Se partitions to Selenite (Se^{4+}) and removed in Phys/Chem WWT
- Mn is soluble

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



EPA Recommended WW Treatment Technologies

- Chemical precipitation and filtration
  - Remove the heavy metals, particularly mercury and arsenic
- Chemical precipitation with **biological treatment**
  - Remove selenium, nitrates and sulfates
- 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)

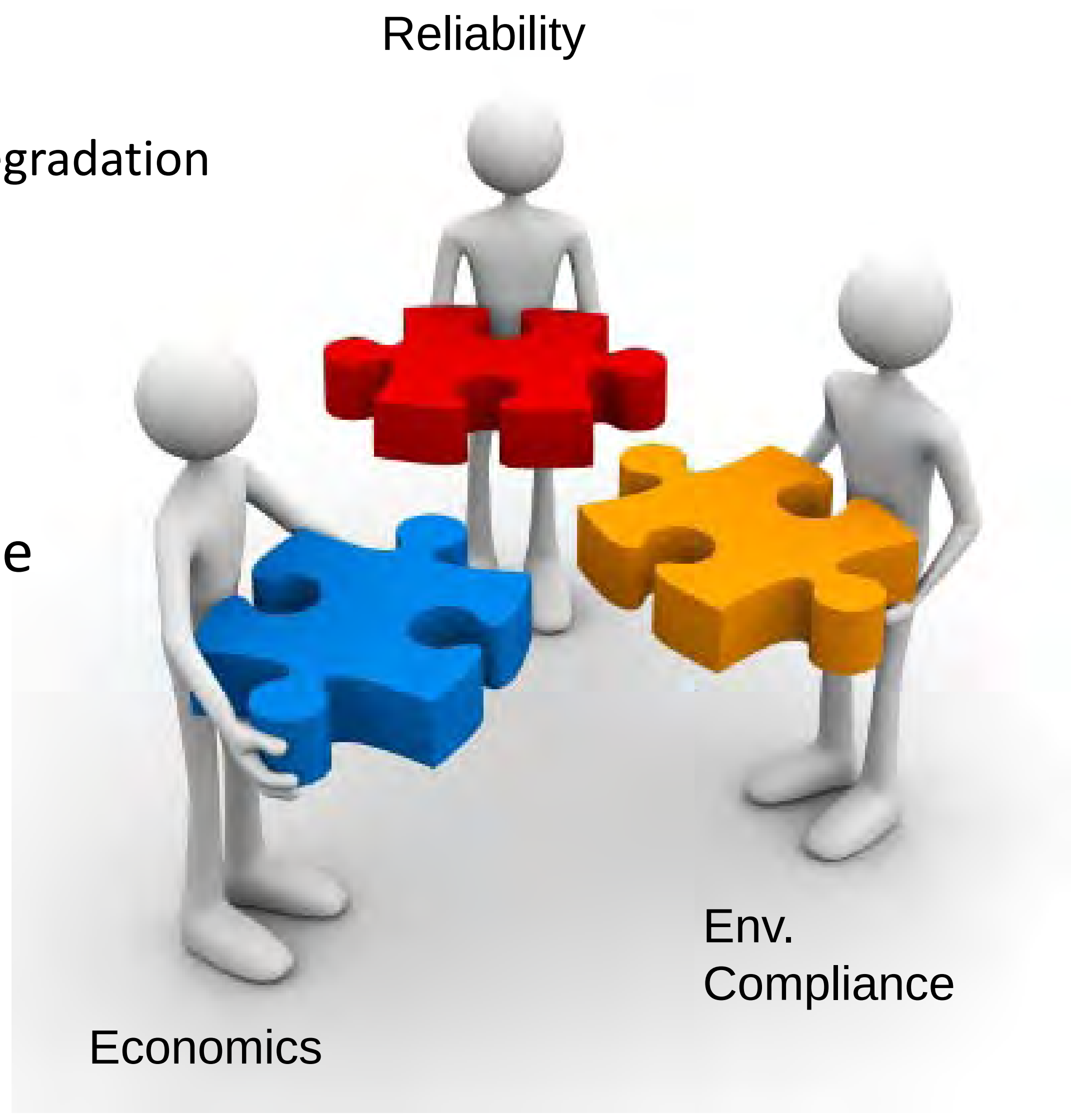


Operational Changes To Watch For

- 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
- Cycling operations that may result in temperature swings, SCR degradation, or other “non-equilibrium” conditions

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, NSR, CCR, ELG, NPDES, CPP, etc
- Economics
  - Asset management
  - Fuel
  - Maintenance, upgrades
  - Reagent use



Discussion and Questions