Advancing Cleaner Energy

Mercury Control Technologies

Connie Senior
&
Sharon Sjostrom

WPCA, Kansas City, June 5-6, 2018

Disclaimer

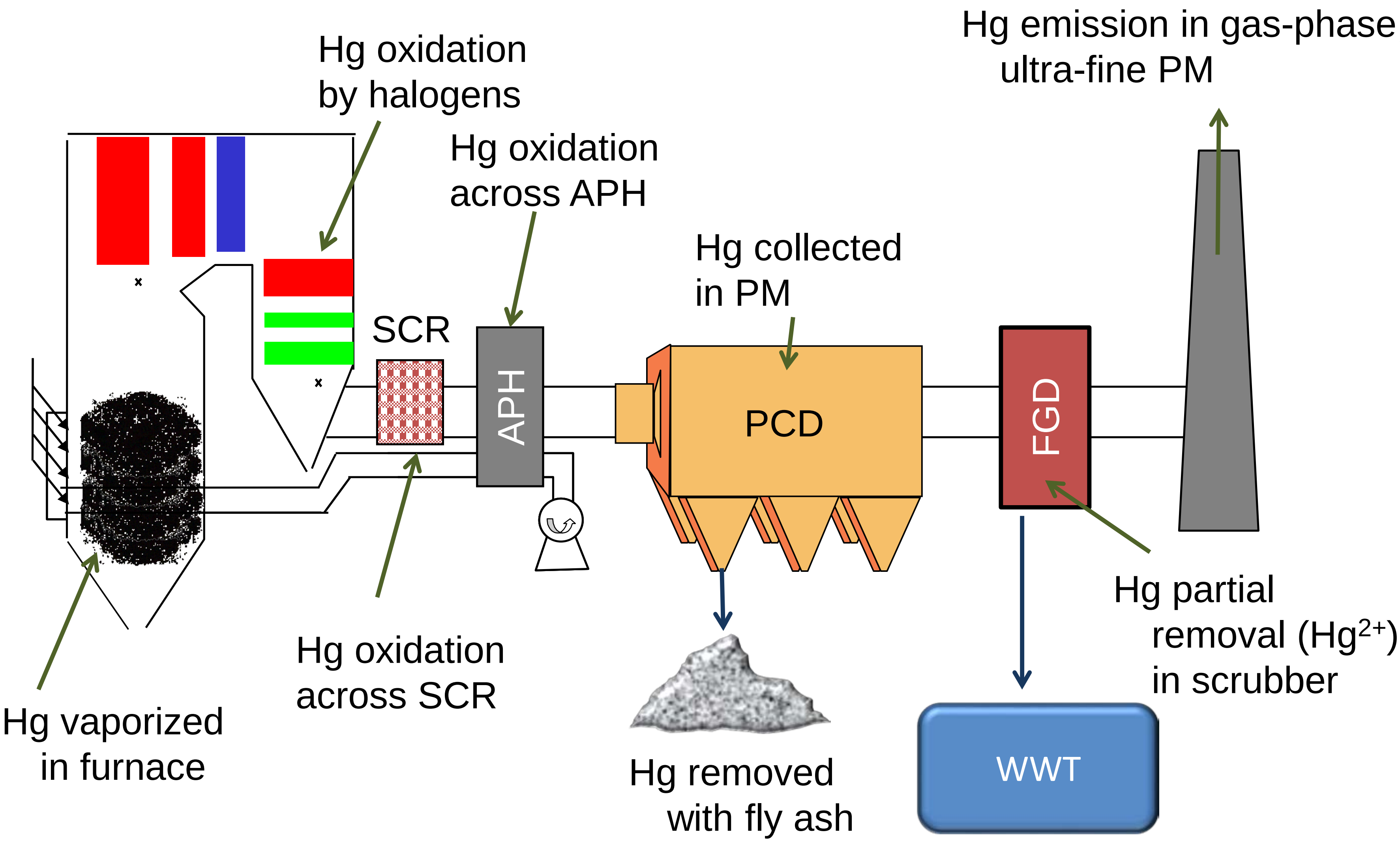
This presentation includes general information on coal and coal-fired boilers intended for education and illustration purposes only. All information is provided “AS-IS” and without warranty or liability of any kind.

Overview

- Factors affecting Hg control using
  - Baghouses
  - Wet FGD scrubbers
  - Dry FGD Scrubbers
  - ESPs

- We'll also look at balance-of-plant effects of Hg control, including corrosion from added halogens

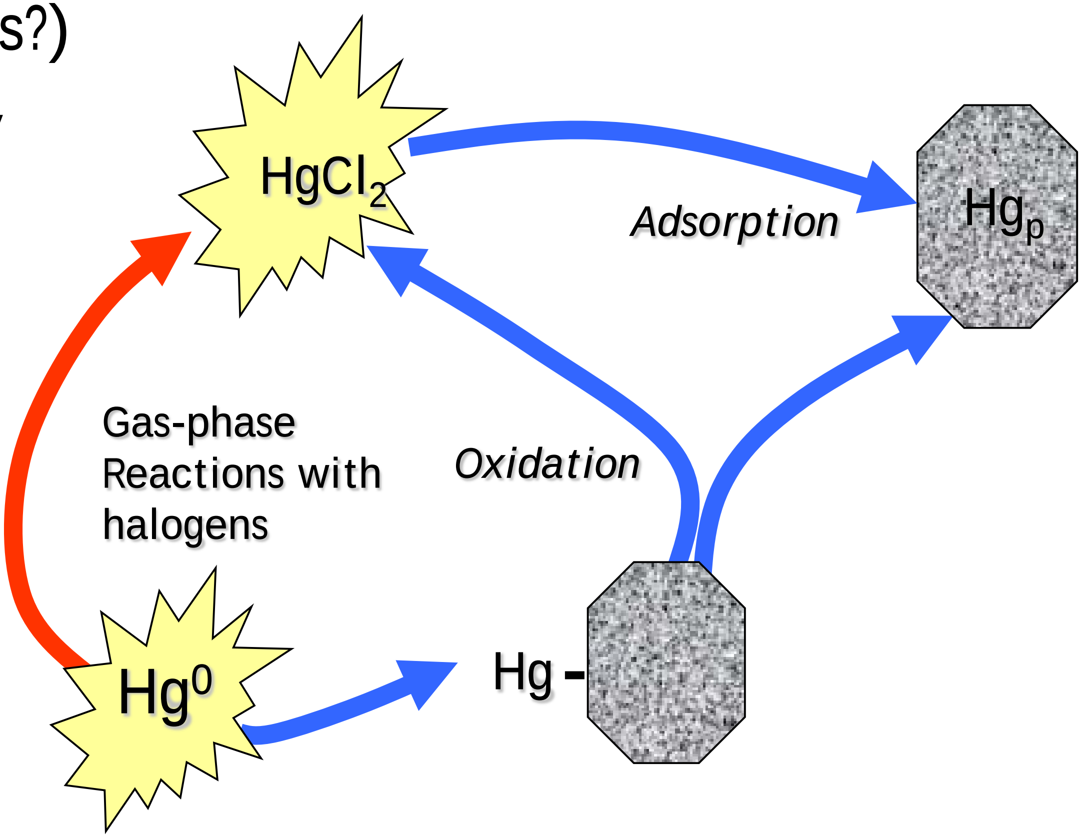
Fate of Hg in Coal-Fired Boilers



Mercury Emissions Control

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)



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

Mercury Control Technology Strategies

- Three main strategies for Hg air emissions control
  - Activated carbon injection (ACI)
  - Coal halogen injection (CHI)
  - Wet or dry FGDs
- These may be combined (e.g., ACI+CHI, CHI+FGD, ACI+FGD, etc.)
- Hg control can have an impact on halogens and selenium in flue gas, ash, and water

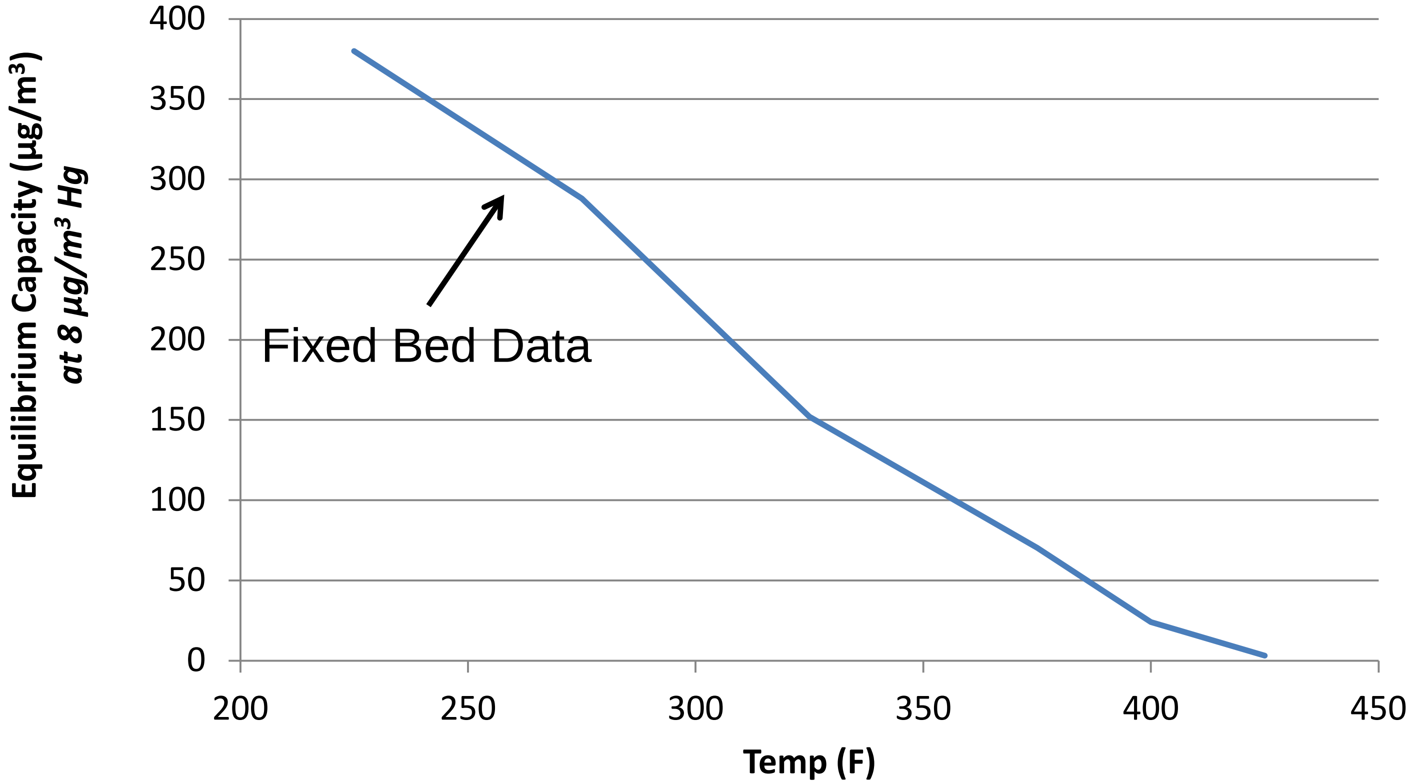
Mercury Control in Particulate Control Devices: Sorbents and Halogen Addition

Factors Affecting Hg Control in Particulate Control Devices

- Capacity of PAC/Fly ash
- Temperature
- SO_3
- Cleaning frequency (for baghouses)
- Residence time (for ESPs)

PAC Adsorption Capacity vs. Temperature

- The higher the temperature, the less Hg can be held on PAC
- This "equilibrium capacity" is also a function of the Hg concentration in the gas: Higher inlet Hg concentration => higher equilibrium capacity on PAC



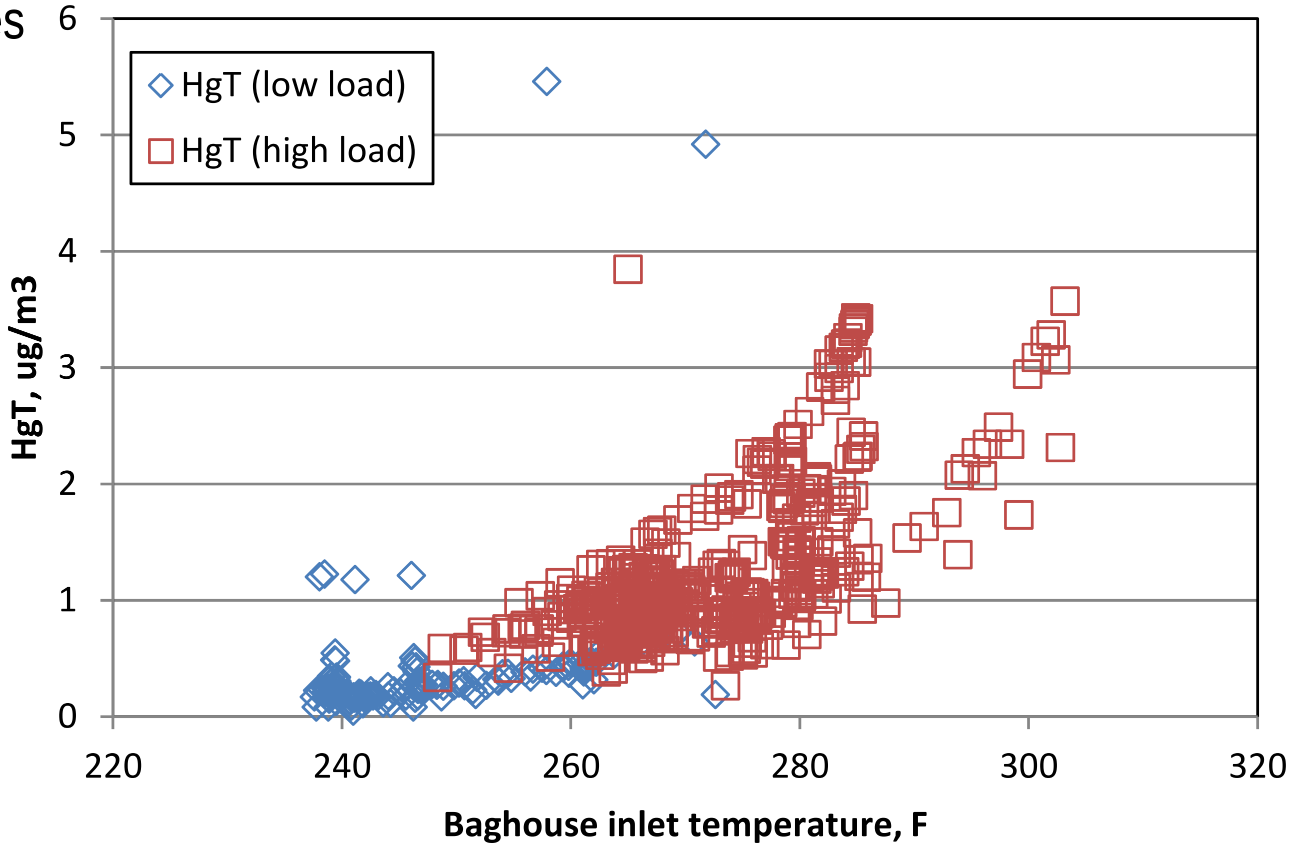
Lab data – simulated flue gas

Mercury “Breakthrough” and Baghouses

- In a baghouse, gas passes across a “fixed bed” of PAC on the filter cake
- If PAC is allowed to remain on the filter after becoming saturated with Hg, it will release mercury, especially if the temperature increases
- High oxidized Hg at the stack on a unit firing low halogen coal (e.g. PRB) suggests that the PAC is adsorbing and releasing Hg
- *<u>This looks a lot like re-emission</u>*

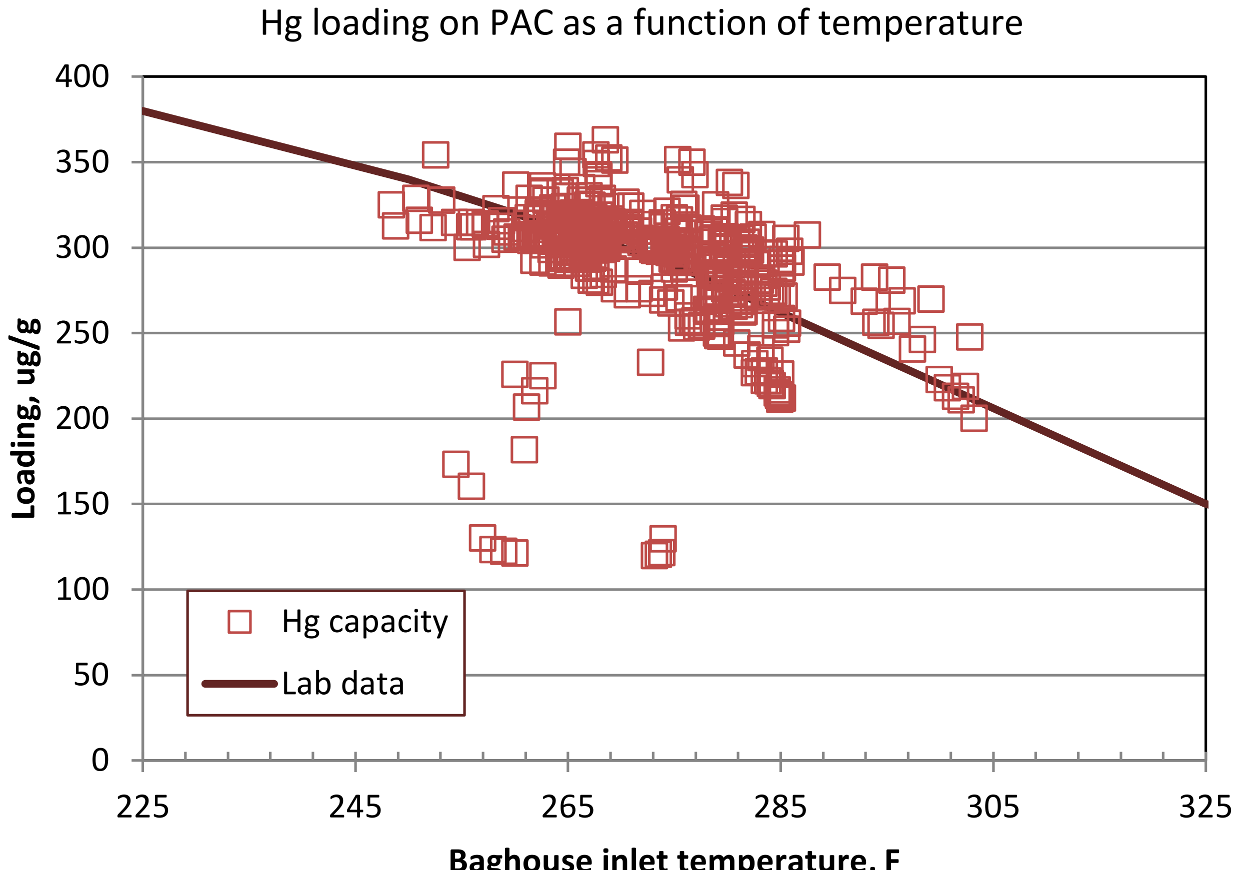
Example: BH Temperature and Hg Emissions

- PRB boiler with oversized BH using brominated PAC (fixed injection rate at high load; no injection at low load)
- Long times between cleaning mean that PAC approaches equilibrium capacity for Hg
- Hg typically increases at higher BH temperatures as maximum "capacity" decreases



Example: BH Temperature and Hg Emissions Estimated Hg loading on the PAC

- Long times between cleaning in this baghouse mean that PAC approaches "equilibrium capacity" for Hg => consistent with lab fixed bed data
- As temperature increases, the PAC holds less Hg on average
- Which means more PAC must be injected at higher temperatures to remove Hg



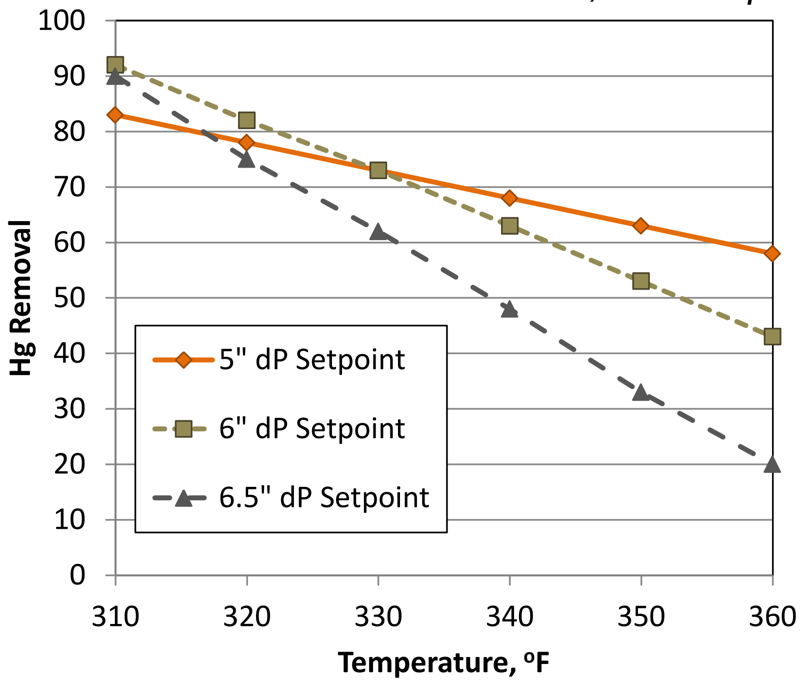
Suggestions for Managing Re-emissions from Baghouses

- **Increase the PAC injection rate at higher temperatures**
- Managing cleaning
  - Cleaning more frequently to remove PAC saturated with Hg (*does not overcome injection below required rates*)
  - Remove excess PAC before ramping load *(large increase in temp = potential to release previously collected Hg)*
- Improve the capacity of the PAC at higher temperatures (carbon selection)

Getting the Most out of ACI

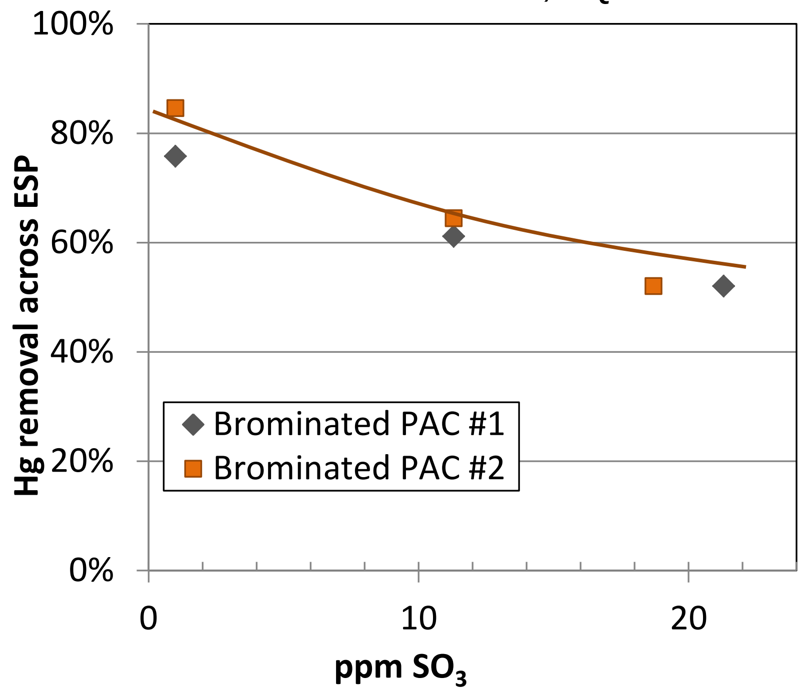
- Lower temperature at the particulate control device
- Lower SO_3 at the particulate control device

Source: Derenne and Stewart, Final Report



Presque Isle TOXECON fabric filter, 1 lb/MMacf Darco Hg sorbent

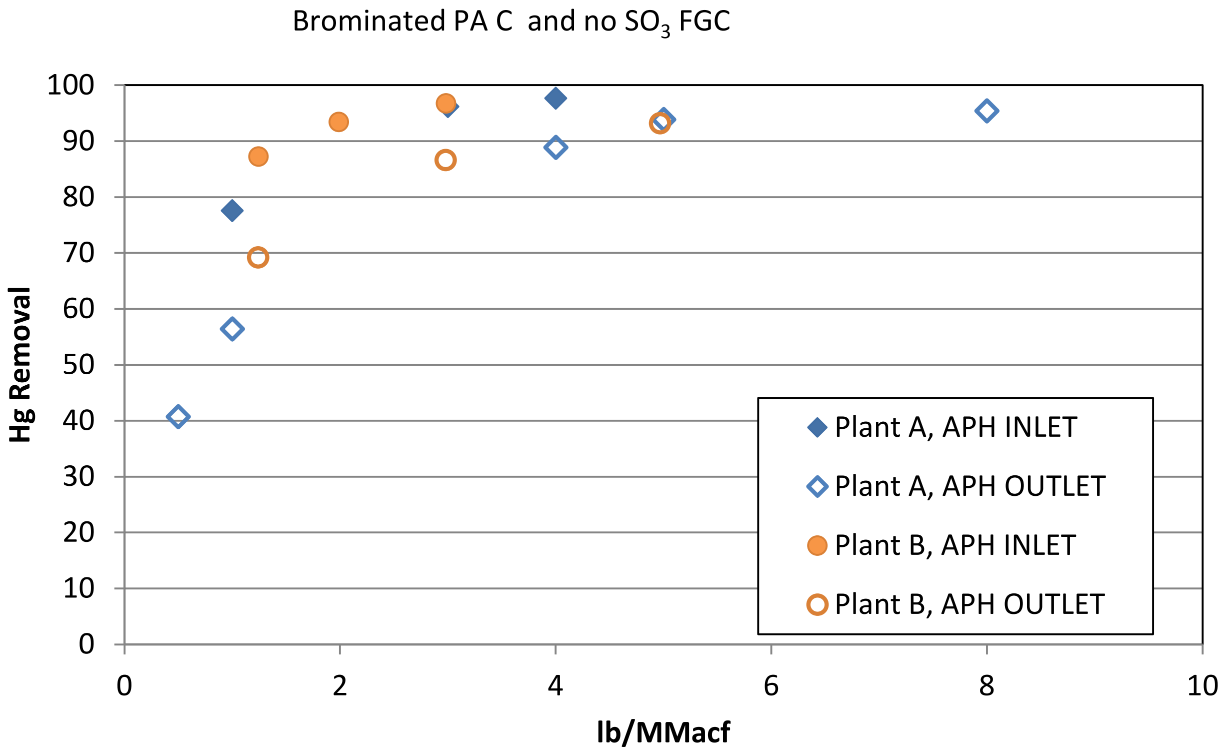
Source: Pollack, AQV



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

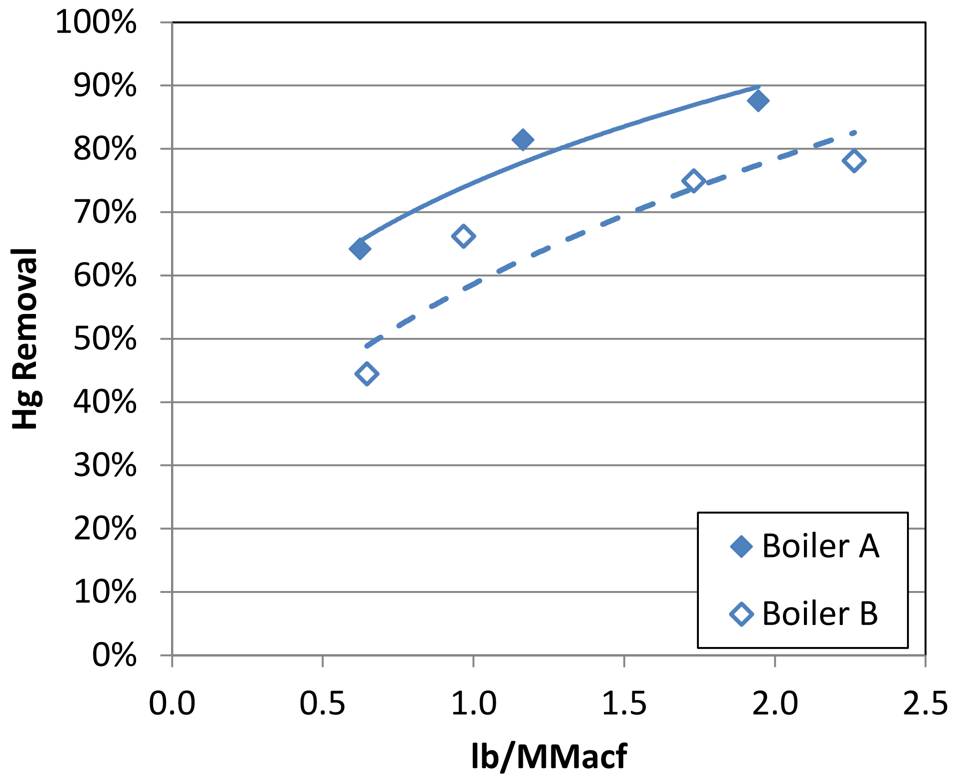
Residence time: Challenge for ESPs

- Short residence times on ESPs make it difficult to capture enough mercury, especially for injection downstream of APH
- Solution: inject upstream of APH



Residence time: Challenge for ESPs

- Two units burn similar PRB coals
- Boiler A has longer duct residence time
- Boiler B has short residence time between APH and ESP inlet AND Chevron-style inlets
- Testing of pre-APH brominated PAC injection on both units at 315-320 F



Summary: Sorbent Addition

- For ACI: lower temperature and lower SO_3 at the particulate control device is always better
- PAC usage with an ESP can be reduced by improving mass transfer to the PAC
  - Reducing particle size
  - Using mixing devices to improve distribution
  - Injecting upstream of APH
  - Using a PAC with faster reaction kinetics

Halogens in US Coal

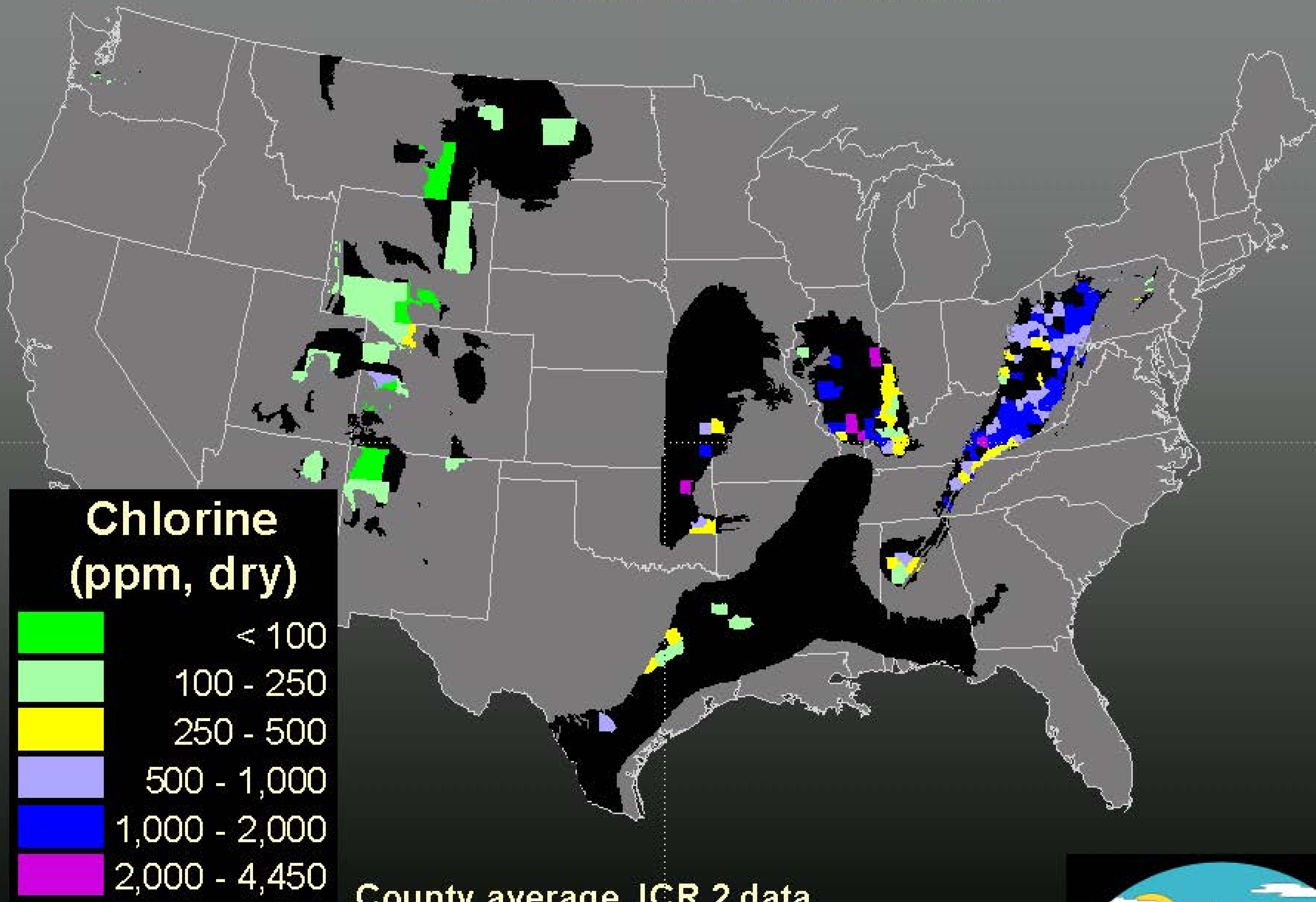
Chlorine

- 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%

Chlorine in Coal

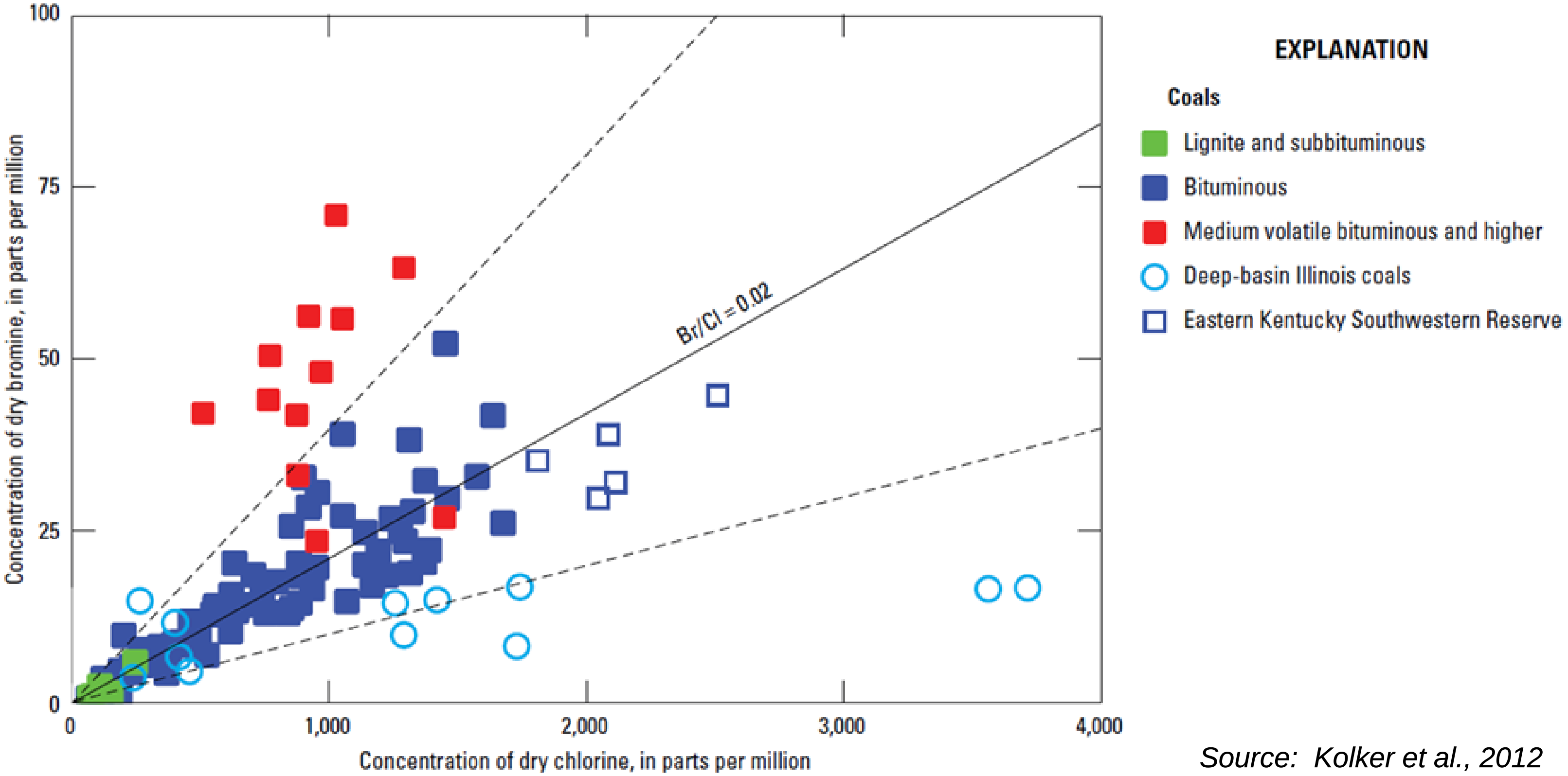


County average, ICR 2 data

http://ugs.utah.gov/emp/mercury/index.htm

UTAH GEOLOGICAL SURVEY

Bromine in Coal

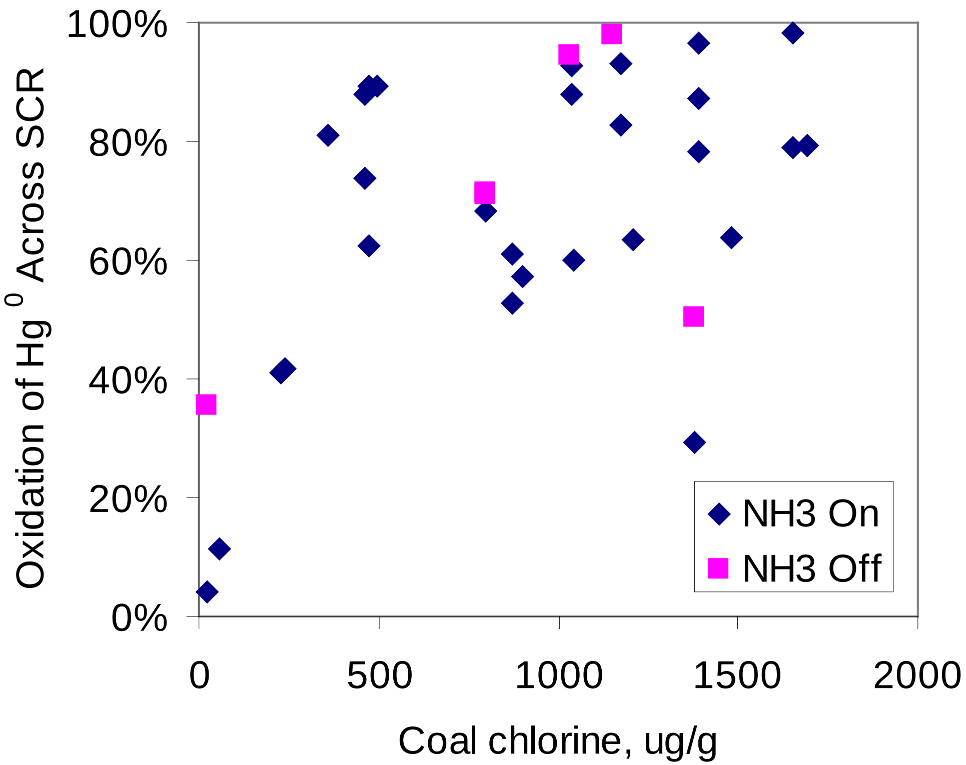


Source: Kolker et al., 2012

- 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)

Opportunities for Hg Oxidation

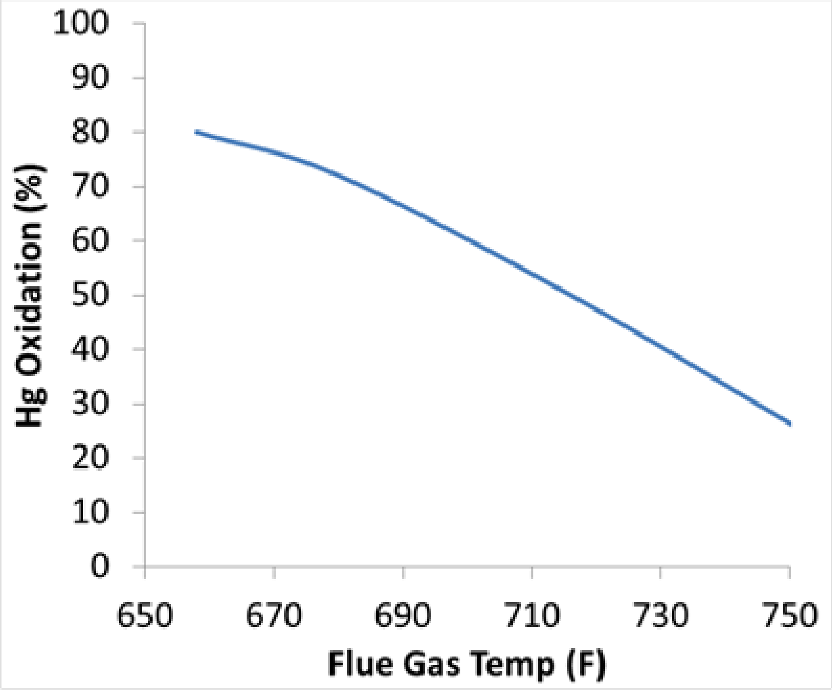
- Selective Catalytic Reduction (SCR)



- Full-scale plant data
- Effect of coal chlorine content

Opportunities for Hg Oxidation

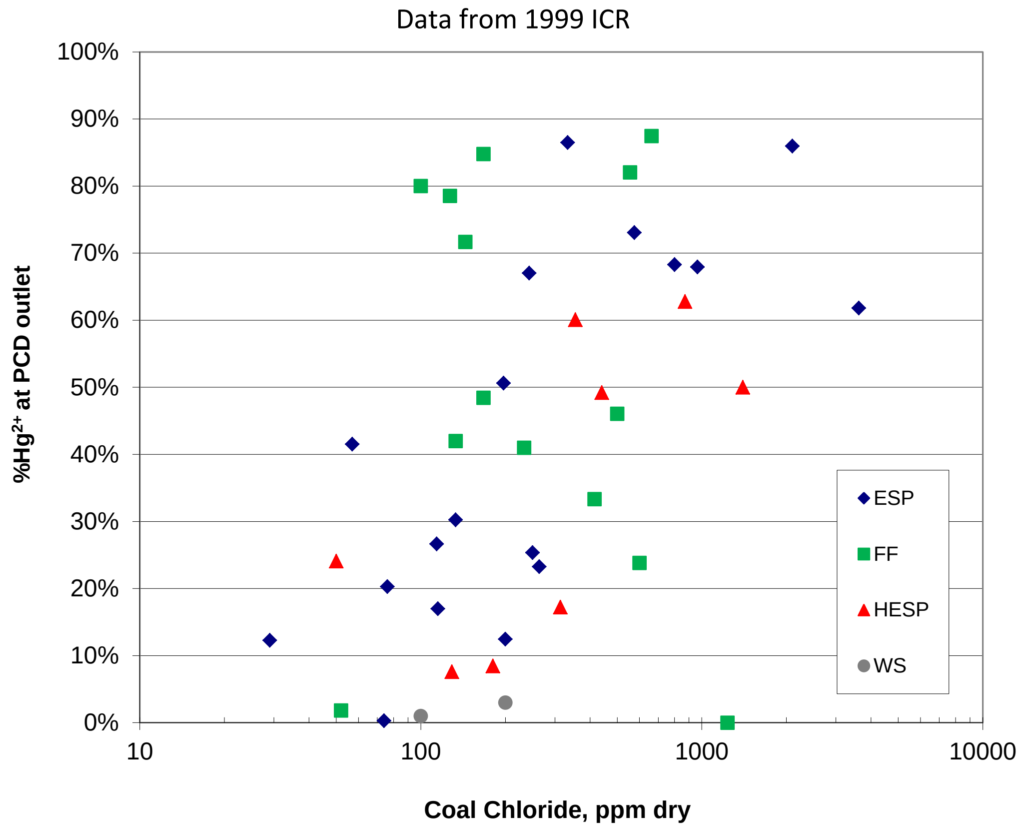
- Selective Catalytic Reduction (SCR)



- Temperature of SCR also affects oxidation
- Data from Honjo et al., 2012 at 10 ppm HCl in flue gas

Opportunities for Hg Oxidation

- Selective Catalytic Reduction (SCR)
- Particulate Control Devices

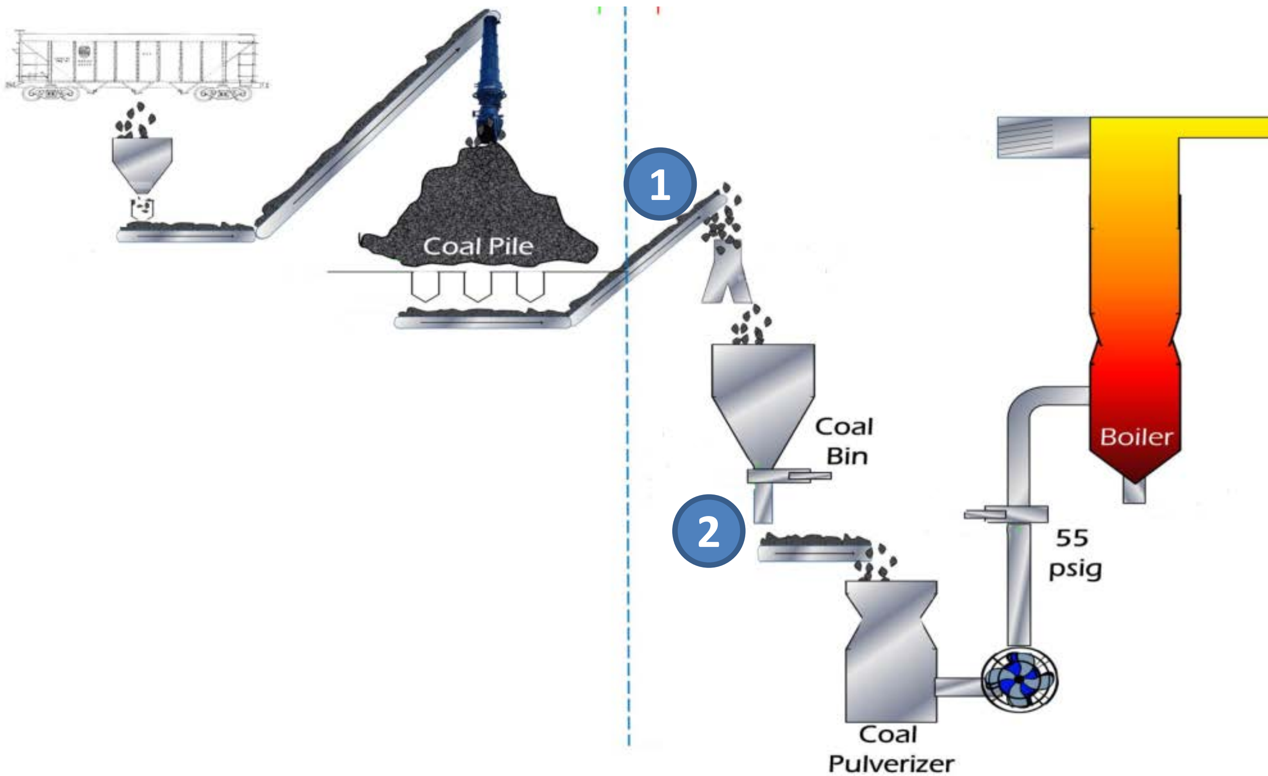


- Fabric filters show higher oxidized mercury at outlet than ESPs
- Full-scale plant data from 1999 ICR

How Are Coal Halogen Additives Injected?

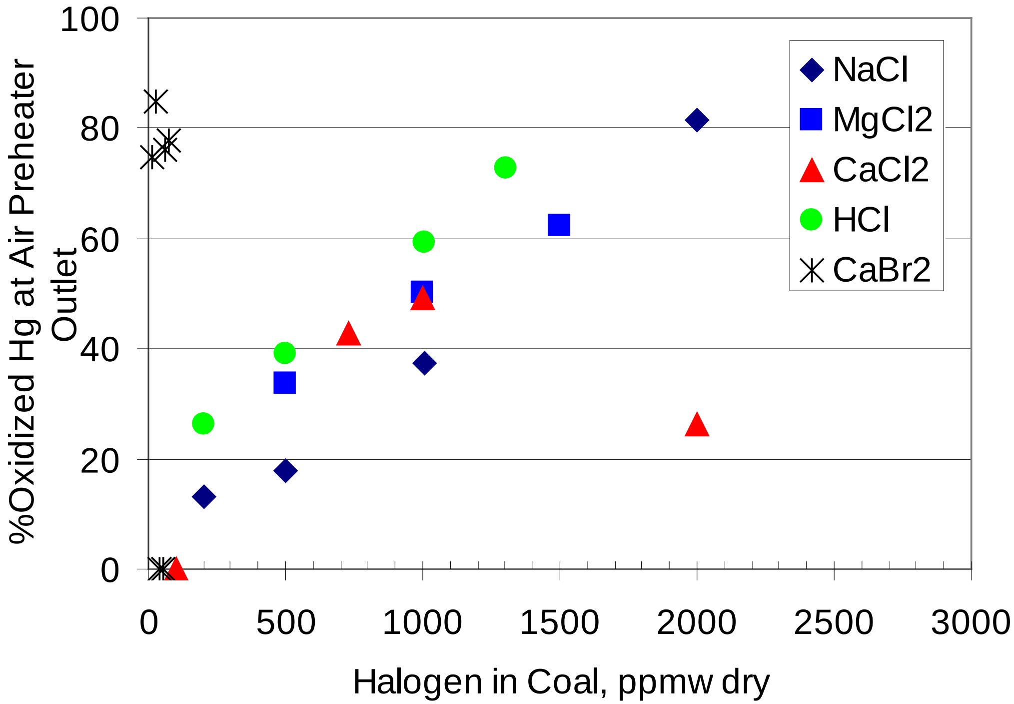
Liquid solution added to the coal either

1. At the coal belt (before the bunker or day silo)
2. At the coal feeders



Opportunities for Hg Oxidation

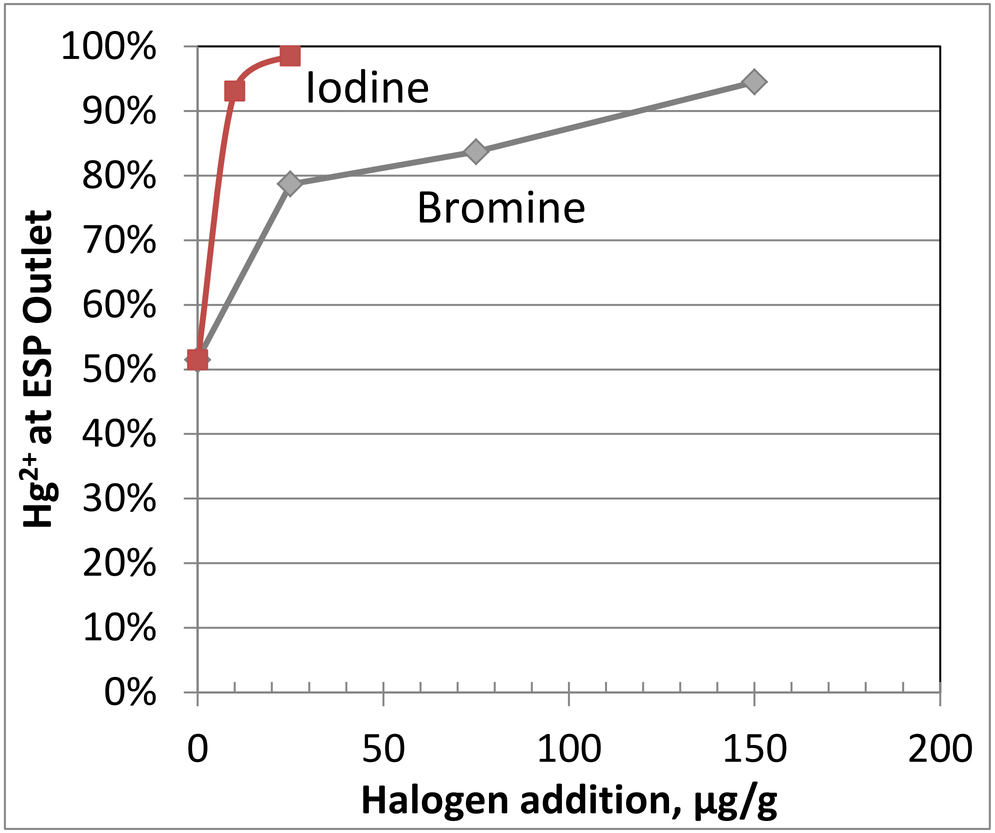
- Selective Catalytic Reduction (SCR)
- Particulate Control Devices
- How adding more halogens helps



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

Opportunities for Hg Oxidation

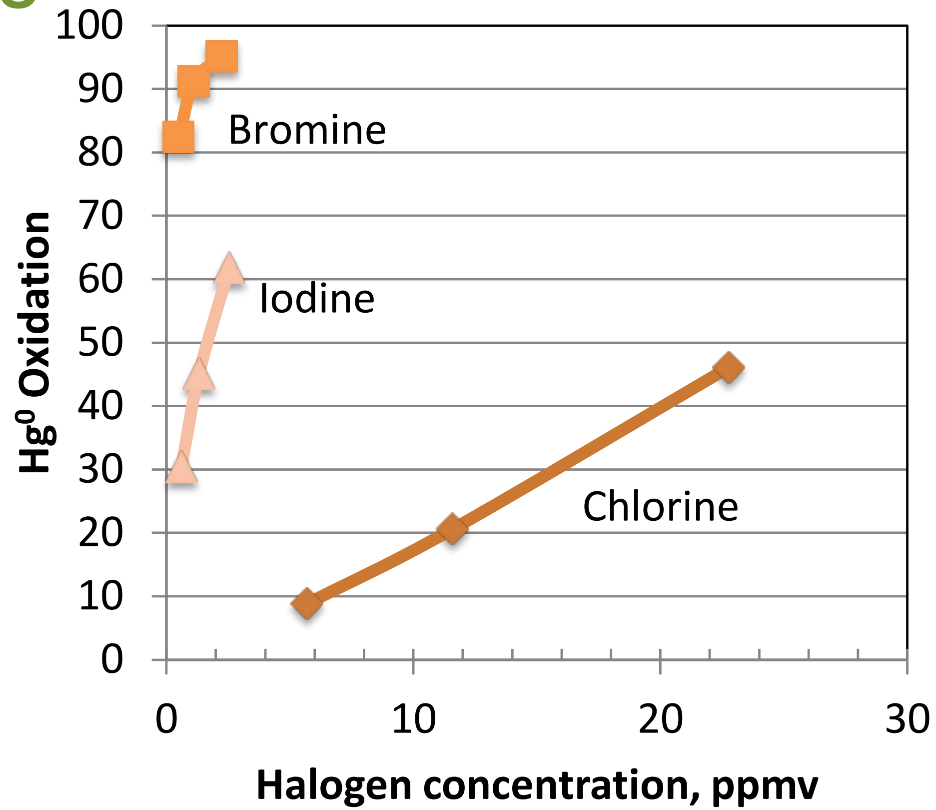
- Selective Catalytic Reduction (SCR)
- Particulate Control Devices
- How adding more halogens helps



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

Opportunities for Hg Oxidation

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



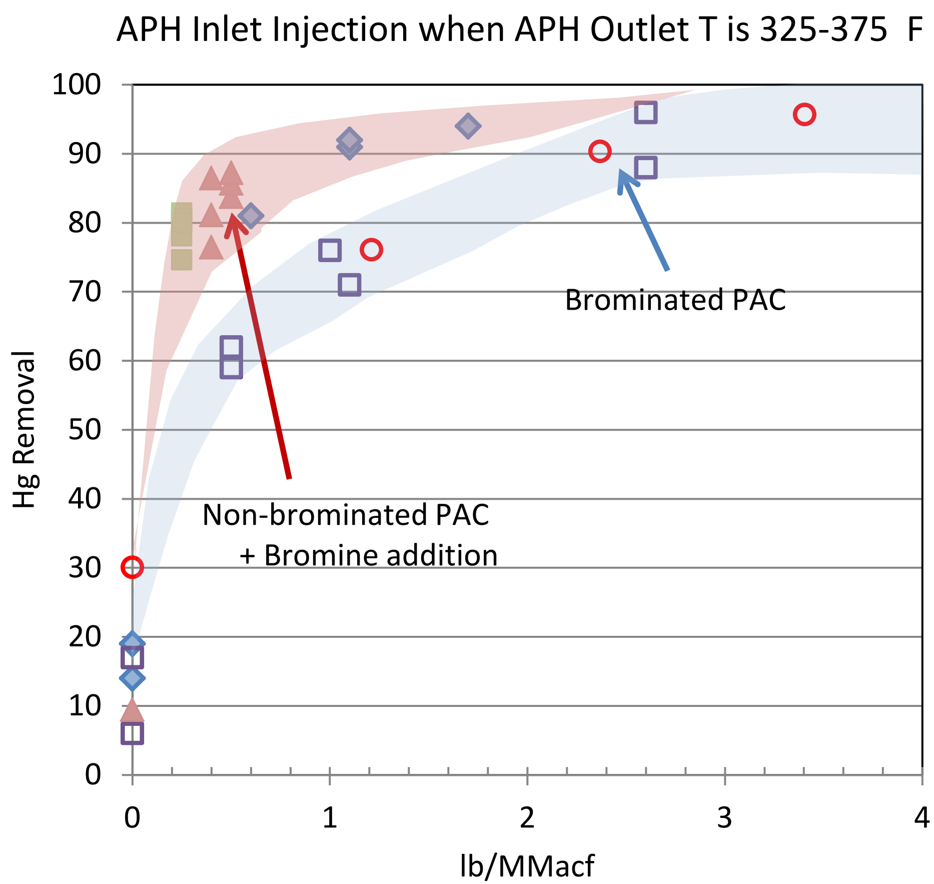
751°F, 350 ppmv NO, 0.9 MR, 3.5% O_2, 12% H_2O
1000 ppmv SO_2, 11 ppmv SO_3, 100 ppmv CO

Source: Bertole, NOx Roundtable 2015

- Having an SCR helps!

Using Halogens with PAC

- Combining halogen addition with sorbent addition
- Injecting PAC upstream of APH can reduce PAC usage when coal halogen additive is used

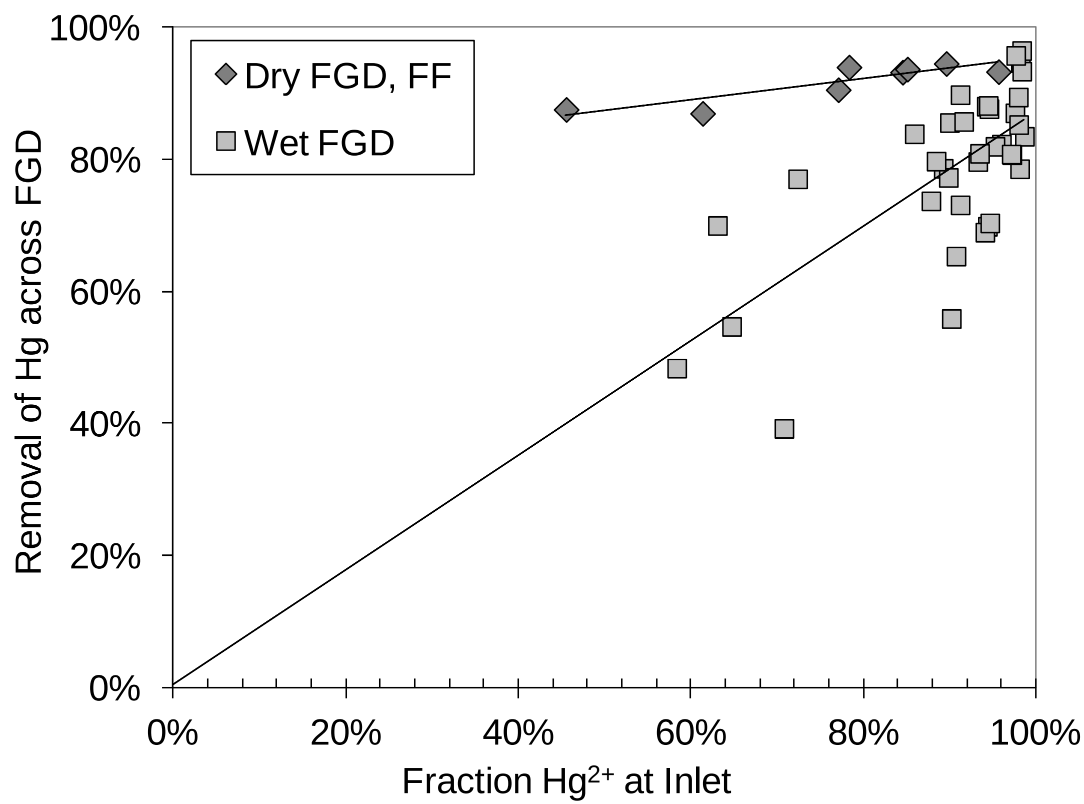


- Full-scale plant data for PRB-fired units with cold-side ESP
- Comparison of bromine addition + PAC to use of brominated PAC – injection upstream of APH

Mercury Control in Scrubbers: FGD Operation and Halogen Addition

Opportunities for Hg Absorption

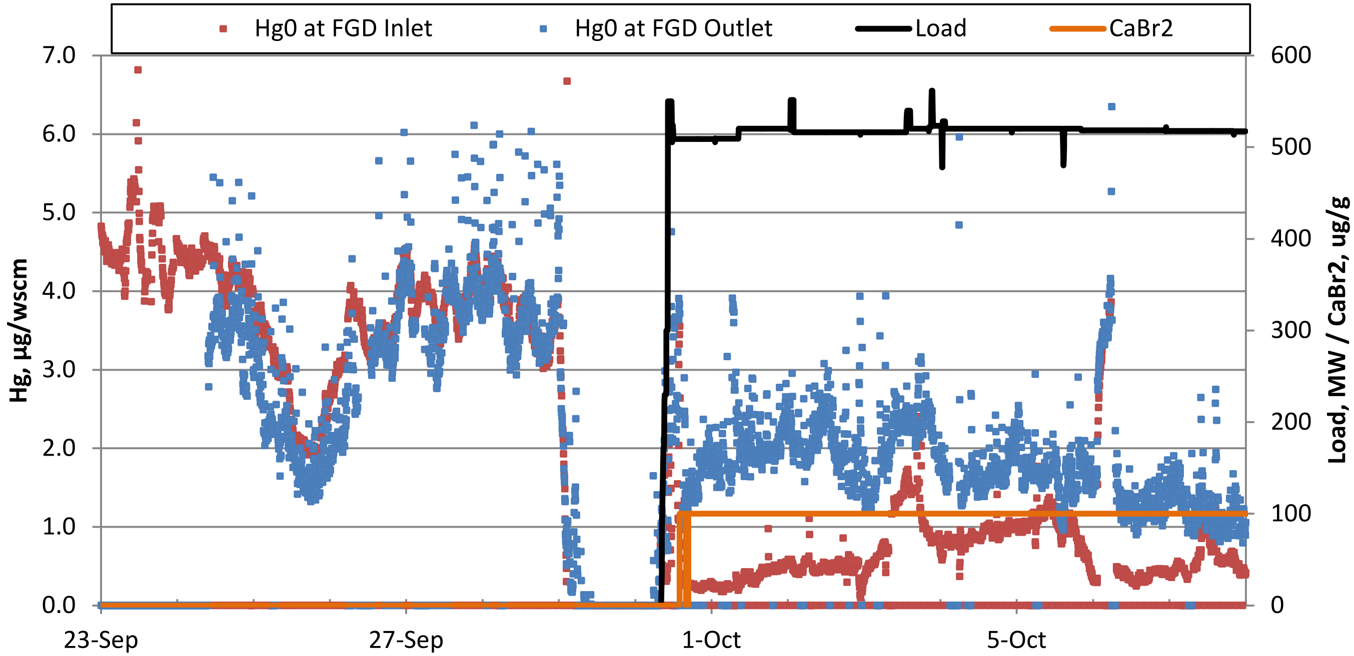
- Wet or dry scrubbers



- Full-scale plant data
- Scrubbers take advantage of native capture…if there's enough oxidized Hg (Hg^{2+})
- Note difference between dry and wet FGDs: effect of FF (dry) and re-emission of Hg^0 (wet)

Using Halogens with Wet Scrubbers

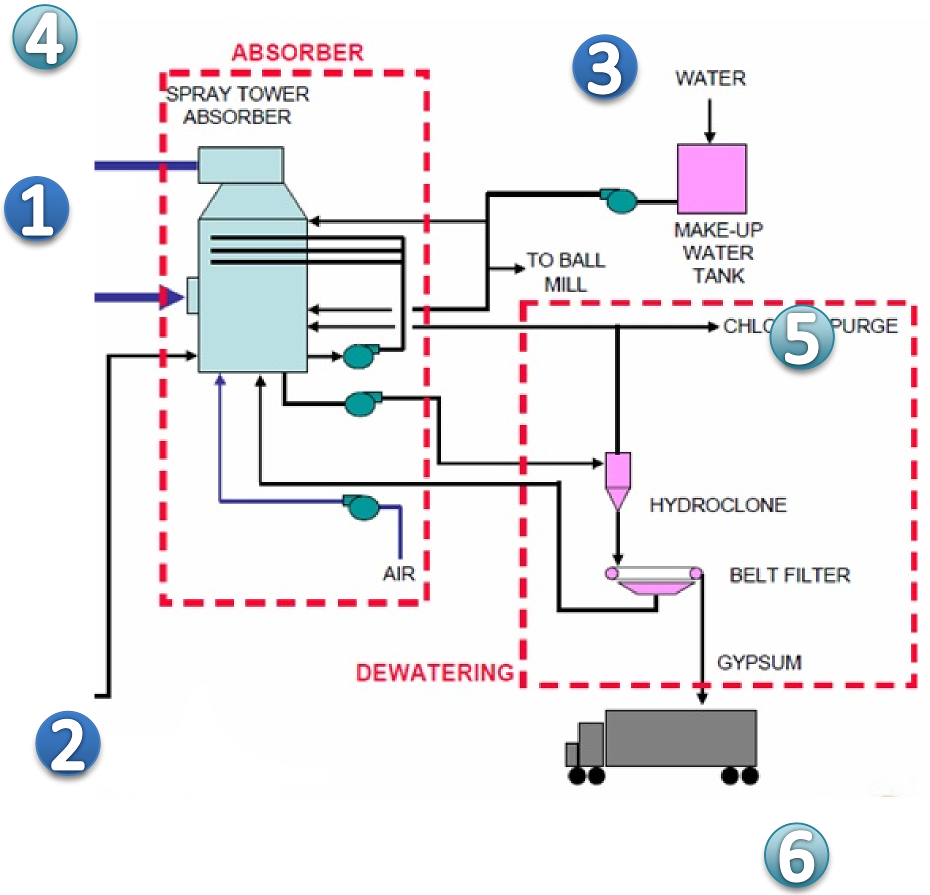
- Bromine addition at subbituminous-fired plant with ESP and wet FGD
- Adding bromine to the fuel:
  - Increased Hg^{2+} at FGD inlet
  - Decreased concentration of Hg at the stack
  - Can result in transient changes in Hg speciation:
    - Higher Hg^0 at stack than at FGD inlet



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 Flows



- Mercury In:
  1. Flue Gas
  2. Limestone
  3. Make-up Water
- Mercury Out:
  4. Flue Gas
  5. Chloride Purge (Blowdown)
  6. Gypsum (or Solid Byproduct)

Mercury Flows: IN

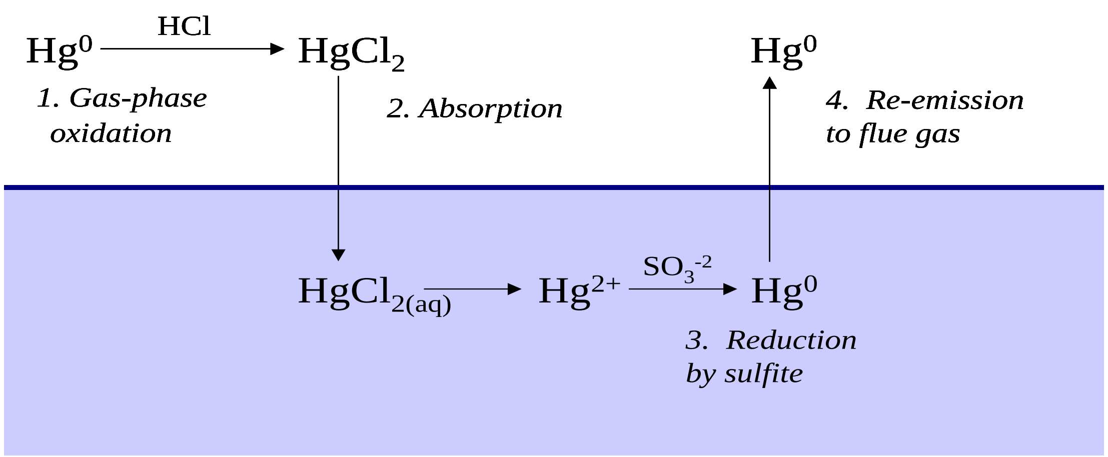
Species	Solubility at 50°C, mg/kg (ppmw)*
Hg^0	0.12
$HgCl_2$	1×10^5
$HgBr_2$	7×10^3

**as Hg elemental*

- Mercury In:
  1. Flue Gas
  2. Limestone
  3. Maker-up Water
- Most Hg enters FGD in flue gas
- Different Hg species have different solubilities

Mercury Flows: OUT

- 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

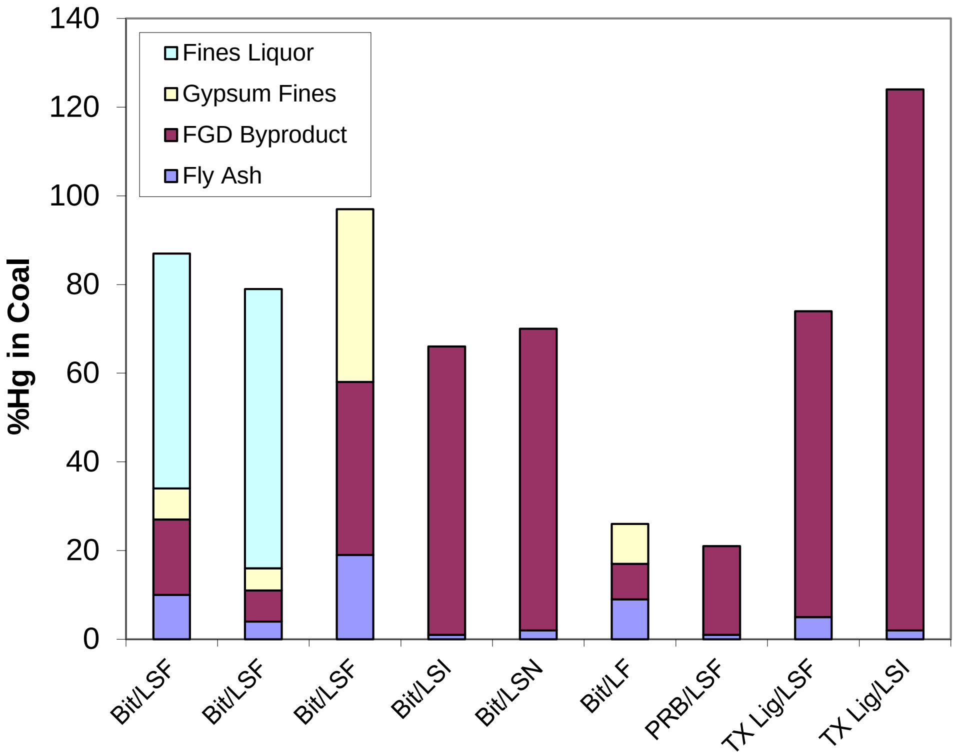


- Mercury In:
  1. Flue Gas
  2. Limestone
  3. Make-up Water

- Mercury Out:
  4. Flue Gas
  5. Chloride Purge (Blowdown)
  6. Gypsum (or Solid Byproduct)

Mercury Flows: OUT

- Distribution of Hg between FGD byproduct, gypsum fines, and fines liquor



LSF = Limestone Forced Oxidation
LS = Lime Forced Oxidation
LSI - Limestone Inhibited
LSN = Limestone Natural Oxidation

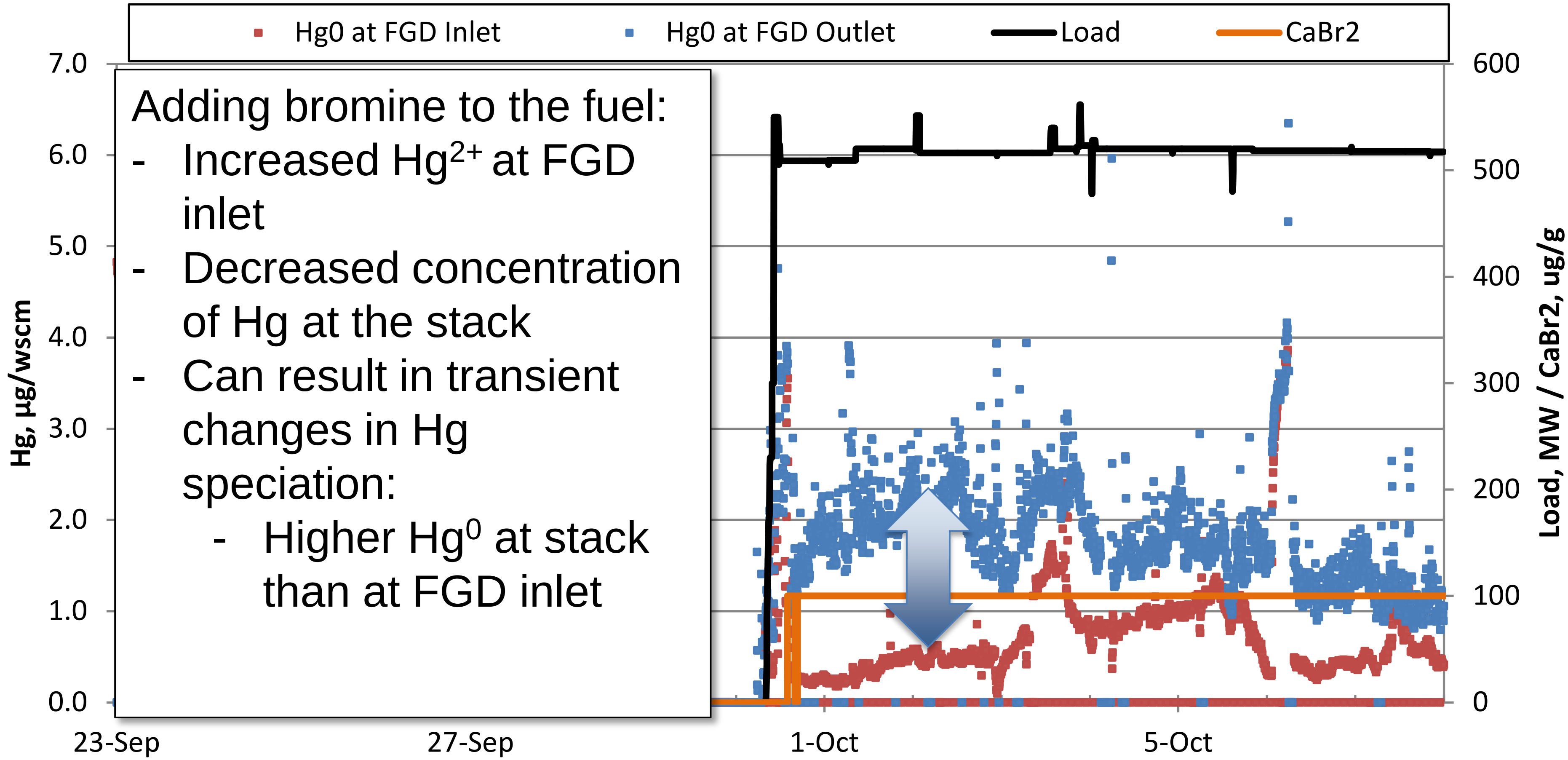
Source: Richardson et al., 2003

- Mercury In:
  1. Flue Gas
  2. Limestone
  3. Make-up Water

- Mercury Out:
  4. Flue Gas
  5. Chloride Purge (Blowdown)
  6. Gypsum (or Solid Byproduct)

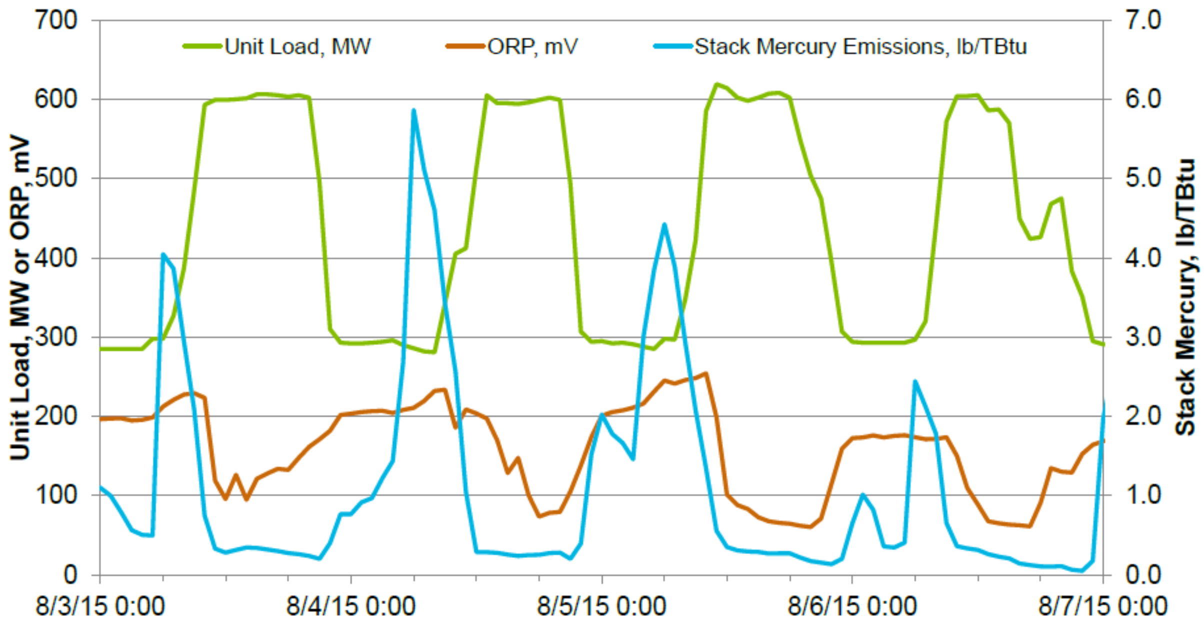
Example: Increasing Capture of Hg^{2+}

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



Impact of Load Cycling

- Cycling load affects ORP and Hg emissions
- Load affects L/G ratio, ratio of O_2 to SO_2 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

ORP Primer

- Oxidation-Reduction Potential (ORP) is a measurement that indicates the degree to which a solution is capable of oxidizing or reducing another substance
- ORP is measured in millivolts (mV) using an ORP meter
- The higher the ORP reading, the more oxidizing the solution

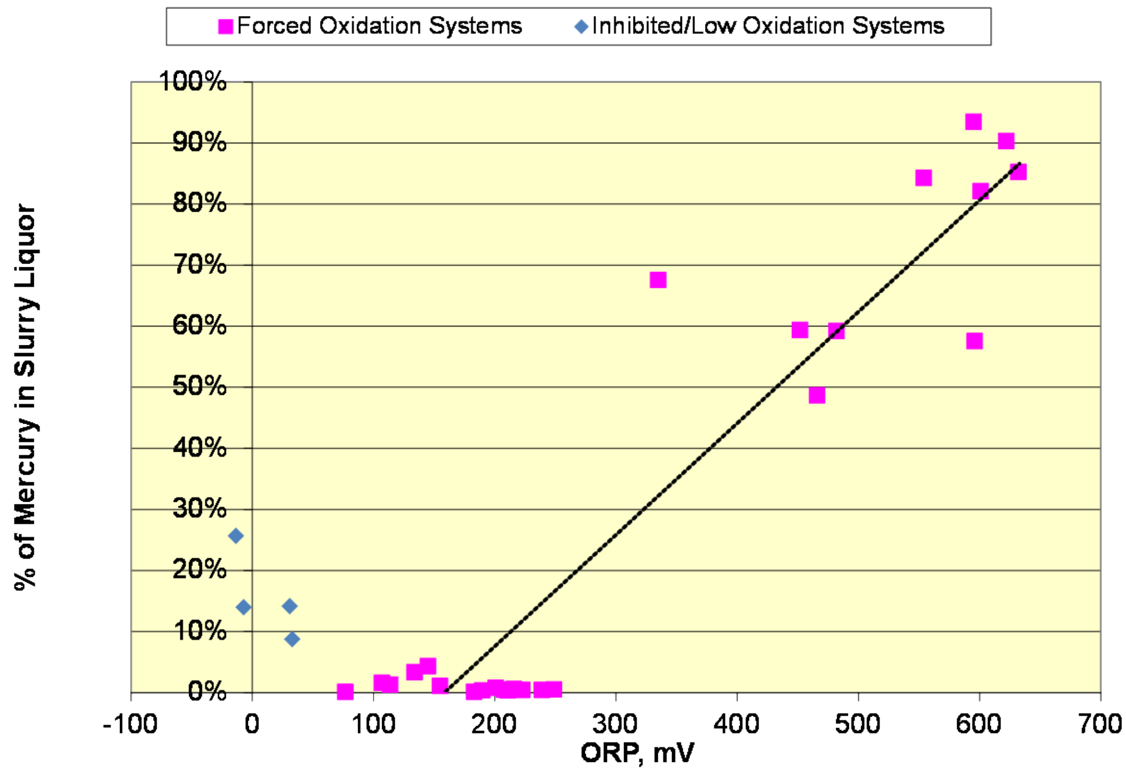
- Why is ORP important?
  - Measure of sulfite oxidation rate in scrubber slurry
  - Provides insight into trace metal behavior (Hg, Se, Mn, As)

ORP & Wet FGDs

- Why is it important to control ORP?
  - Reduce corrosion in FGD absorber
  - Maintain FGD product quality
  - Reduce trace metals (Hg, As, Se) in scrubber discharge
  - Reduce impact of load changes on Hg emissions
- What impacts ORP?
  - Mass rate of SO_2 scrubbed
  - Amount of O_2 absorbed by scrubber slurry
  - pH
  - Transition metal catalysts in scrubber slurry (Cu, Mn, Fe)
  - Reducing or oxidizing species added to scrubber (e.g., organic acid buffers, sulfur/thiosulfate, Hg re-emission additives)

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

Controlling ORP in Wet FGDs

- Forced oxidation scrubbers: lower oxidation air rate or turn off, if possible
- Raise pH set point
- Lower L/G ratio (fewer recycle pumps) at low load
- Increase SO_2/O_2 ratio in flue gas (lower excess air, higher sulfur coal)
- Increase TDS by tightening water balance
- Use reducing additives (e.g., organosulfides)
- Improve ESP performance to reduce transition metals from fly ash

Downstream Effects on WWT: FGD Design & Operation

- Design of the FGD and its operation affect speciation and concentration of Hg, Se, and As in the scrubber solution
  - Scrubber reagent
  - Design: Forced oxidation vs. natural or inhibited oxidation
  - Operation:
    - Load-following
    - ORP control

Balance of Plant Considerations

Halogen Corrosion Mechanisms in Flue Gas

- Dew Point Corrosion
  - Direct condensation when process temperature drops below respective dew point temperature
  - Sufficiently low temperatures possible at any air leak location
- Deliquescent Corrosion
  - Formation of halogen salts on cold surfaces -- reaction with flue gas moisture forms concentrated corrosive
- Active Corrosion
  - Gas-phase reactions with metals

Corrosion from The Operator's Perspective – PacifiCorp, Steag - Reinhold, 2014

Bromine Refined Coal Application

Brominated PAC - Upstream Injection

EPRI Study: Bromine Corrosion Potential

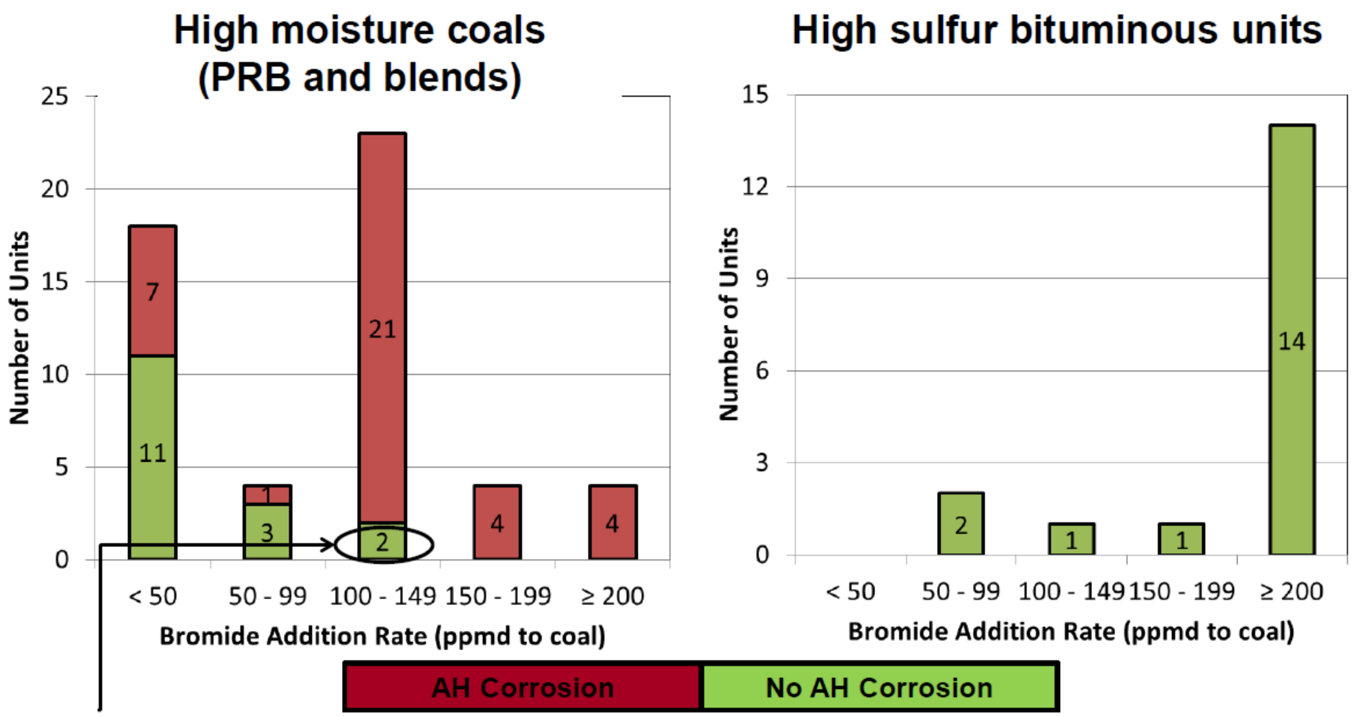
- Corrosion continually highlighted as significant problem for $CaBr_2$ and Br-PAC applications
  - EERC, EPRI/URS, Paragon Air Heater Technologies, Albermarle, Reaction Engineering International, Multiple Users
- Ongoing EPRI Bromine BOP Study (August 2016)
  - 46 units out of 72 surveyed reported corrosion

Location	Number of Units
Coal crusher	1
Coal pulverizer	5
Boiler tubes	1
Air preheater	38
Air preheater outlet duct	3
ESP	2
ESP outlet duct	4
ESP	4
ID fan	4
Venturi scrubber	4

Source: Arambasick et al., 2016 Mega Symposium

Corrosion from Bromine Fuel Additives Studied by EPRI

- EPRI surveyed plants using bromine fuel additives or brominated PAC
- PRB-fired boilers observed corrosion, primarily in air preheater (AH), but bituminous-fired boilers did not

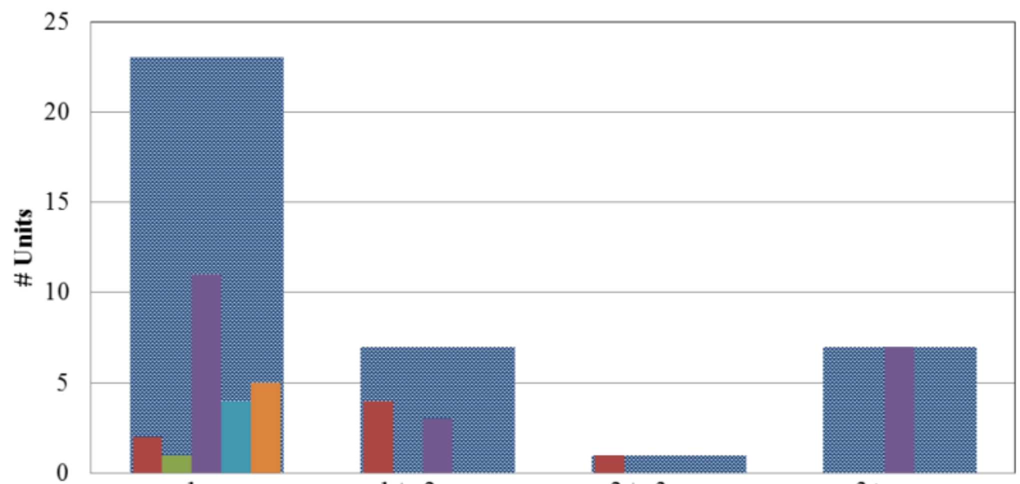


*No AH corrosion, but observed corrosion of the boiler tube and ESP

Source: Arambasick et al., 2016 Mega Symposium

Corrosion Reported in PRB-Fired Units using Bromine Additives

- Analysis of time elapsed from start of bromide addition until air preheater corrosion was first observed

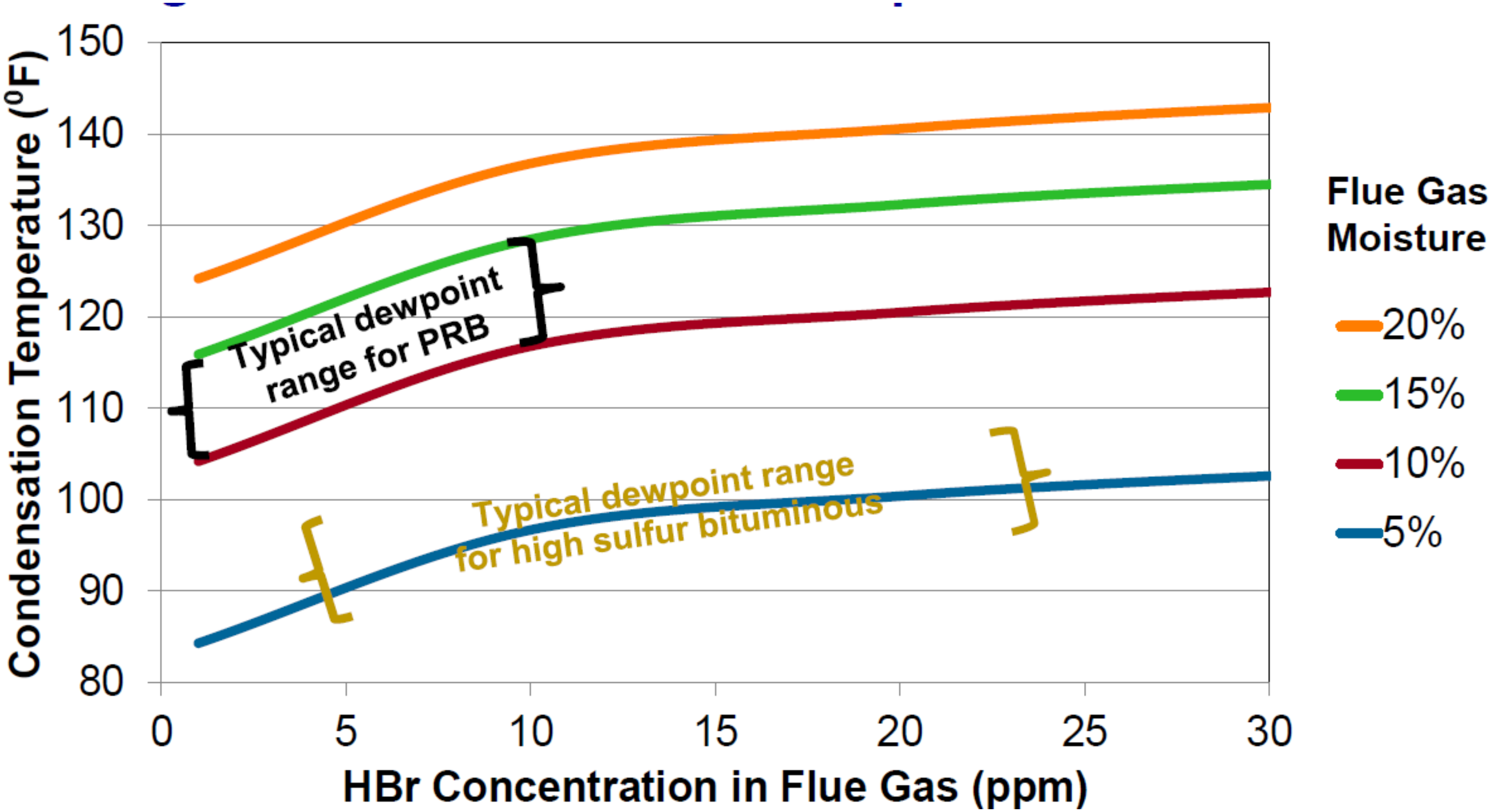


	< 1 year	1 to 2 years	2 to 3 years	3+ years
Total # Units	23	7	1	7
< 50 ppmd	2	4	1	0
50 - 99 ppmd	1	0	0	0
100 - 149 ppmd	11	3	0	7
150 - 199 ppmd	4	0	0	0
> 200 ppmd	5	0	0	0

Source: Arambasick et al., 2016 Mega Symposium

Dew Point Corrosion

- Bromine corrosion in PRB air preheaters appears to be because of lower dewpoint

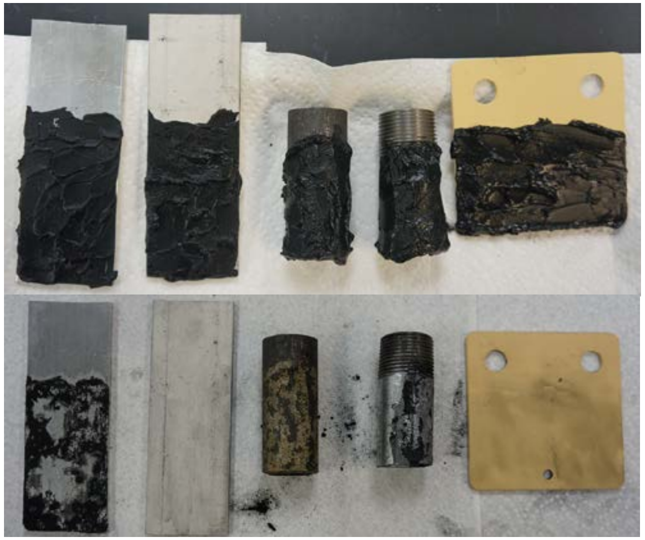


Source: Arambasick et al., 2016 Mega Symposium

Halogen Corrosion in ACI Systems

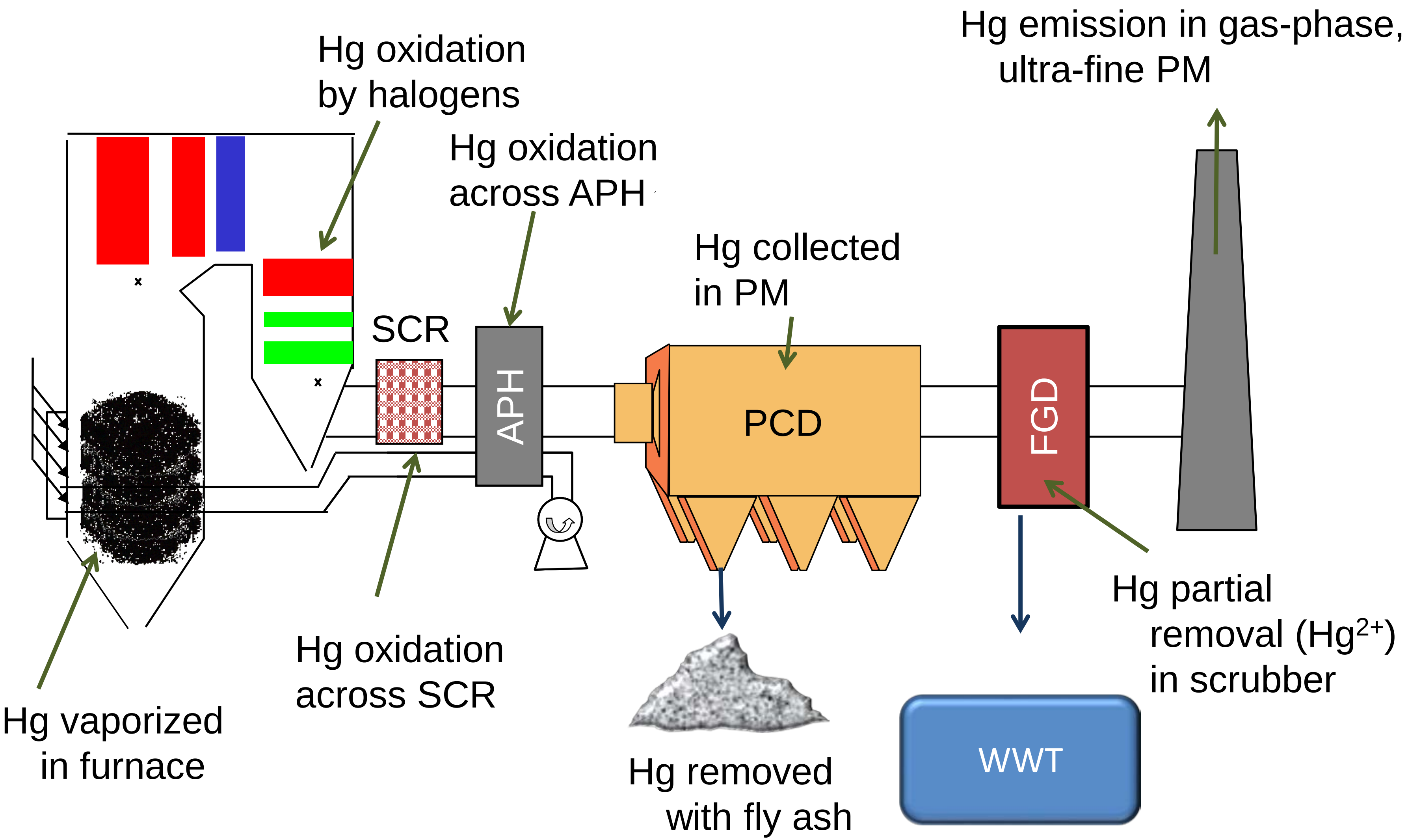
- Brominated PAC can cause corrosion in storage and conveying systems if moisture or water present
- Most silos installed for MATS compliance were coated on the inside, but older uncoated silos vulnerable to corrosion
- Components of metering and conveying system also vulnerable with excessive moisture
  - Lab testing of paste of Br-PAC plus water
  - One week exposure of various metals
  - Aluminum, schedule 40 steel pipe, and galvanized welded steel nipple all showed surface corrosion

Exterior corrosion on uncoated silo



Lab testing of various metals with Br-PAC

Fate of Hg in Coal-Fired Boilers



QUESTIONS?

connies@adaes.com