REINHOLD ENVIRONMENTAL Ltd.

2016 NOx-Combustion-CCR Round Table Presentation

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

Managing Mercury Oxidation for Optimizing Mercury Control Costs

Connie Senior
ADA-ES, Inc.

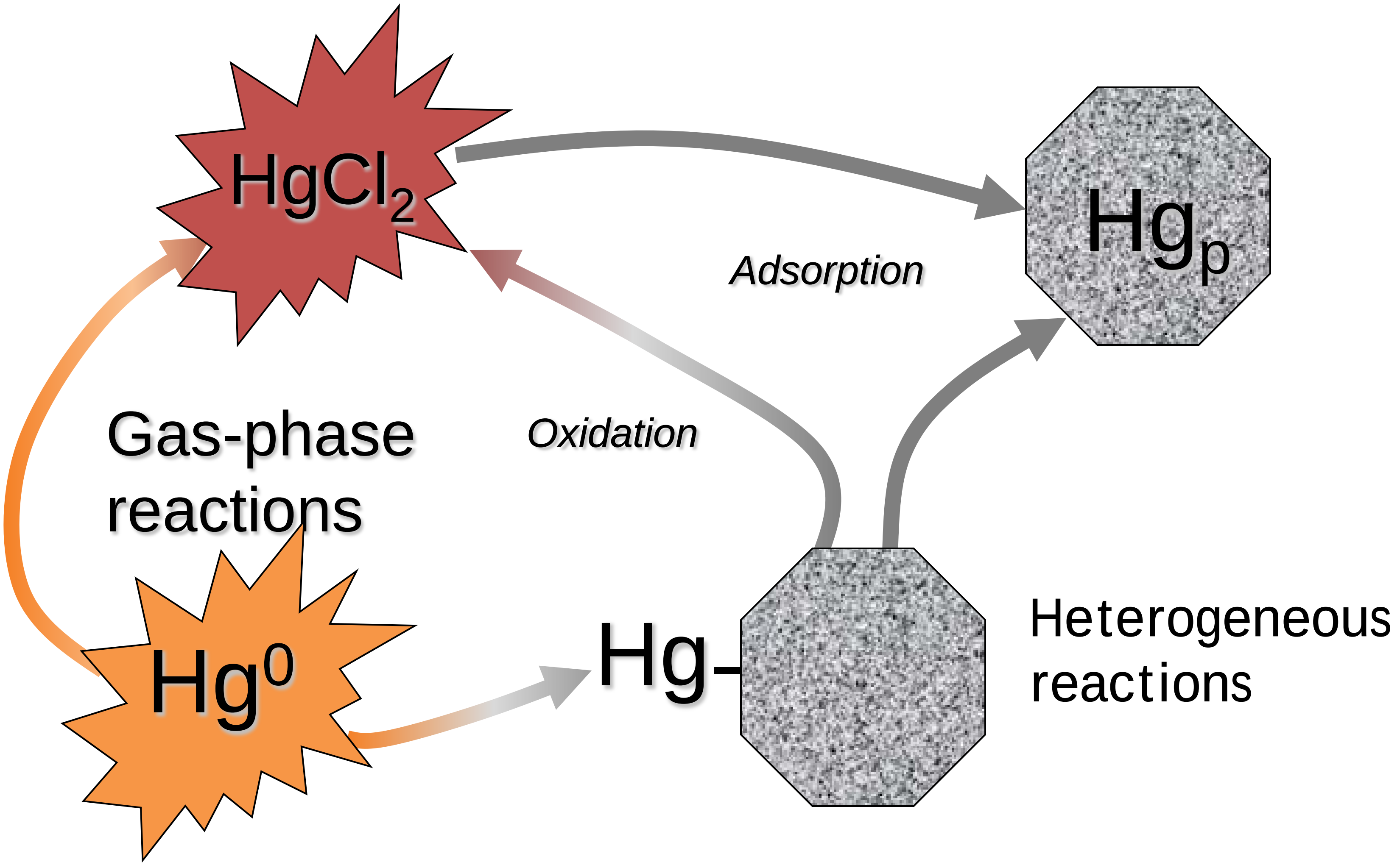
Reinhold NOx Roundtable ~ February 1, 2016

Agenda

- Hg Chemistry in Flue Gas
- How Halogens Affect Hg in Coal-Fired Boilers and Air Pollution Control Devices
- How to Use Halogens to Improve Hg Control
- Balance of Plant
- Summary

Hg Chemistry in Flue Gas

Mercury Chemistry in Flue Gas



Halogens in US Coal

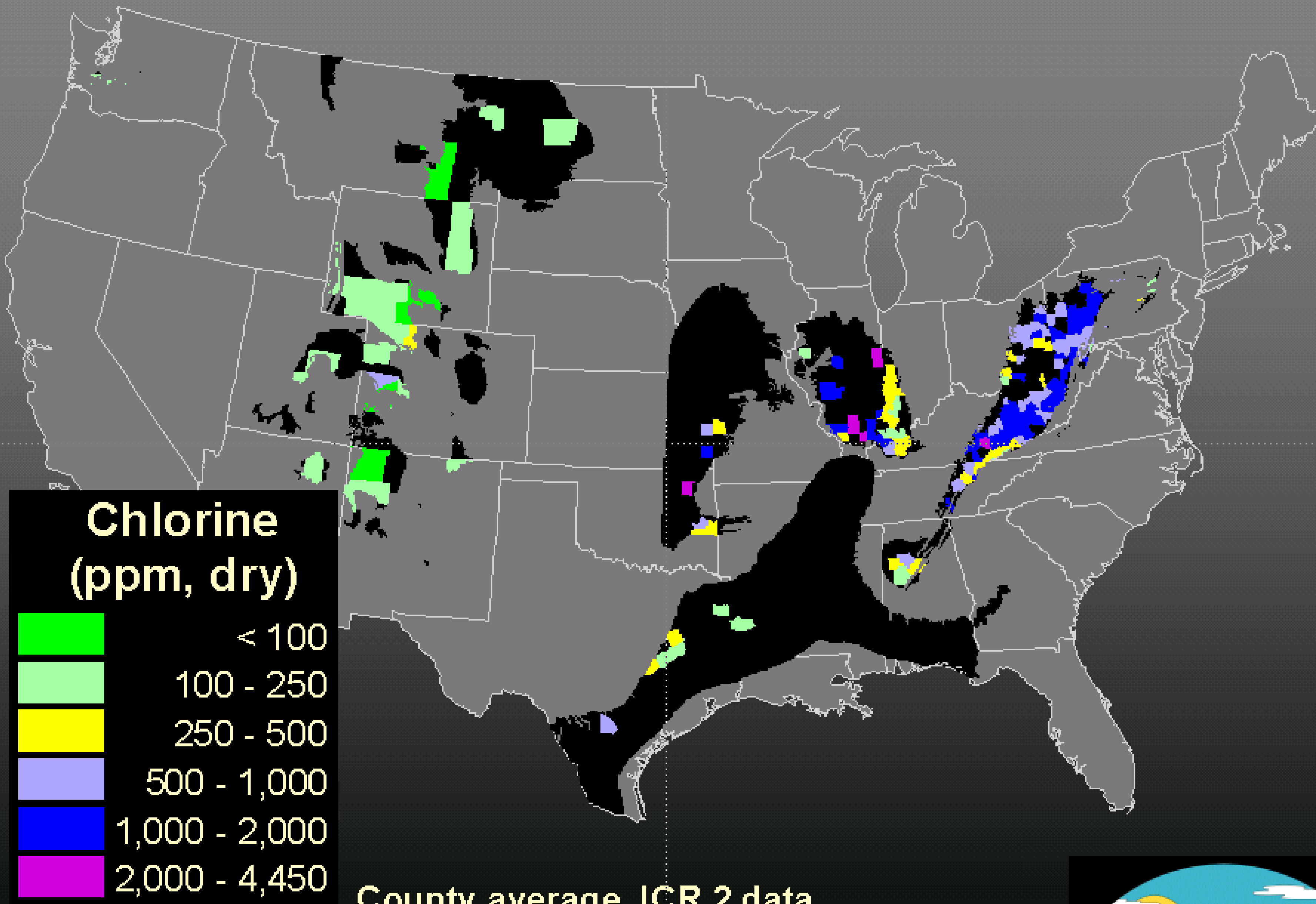
Chlorine

- 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

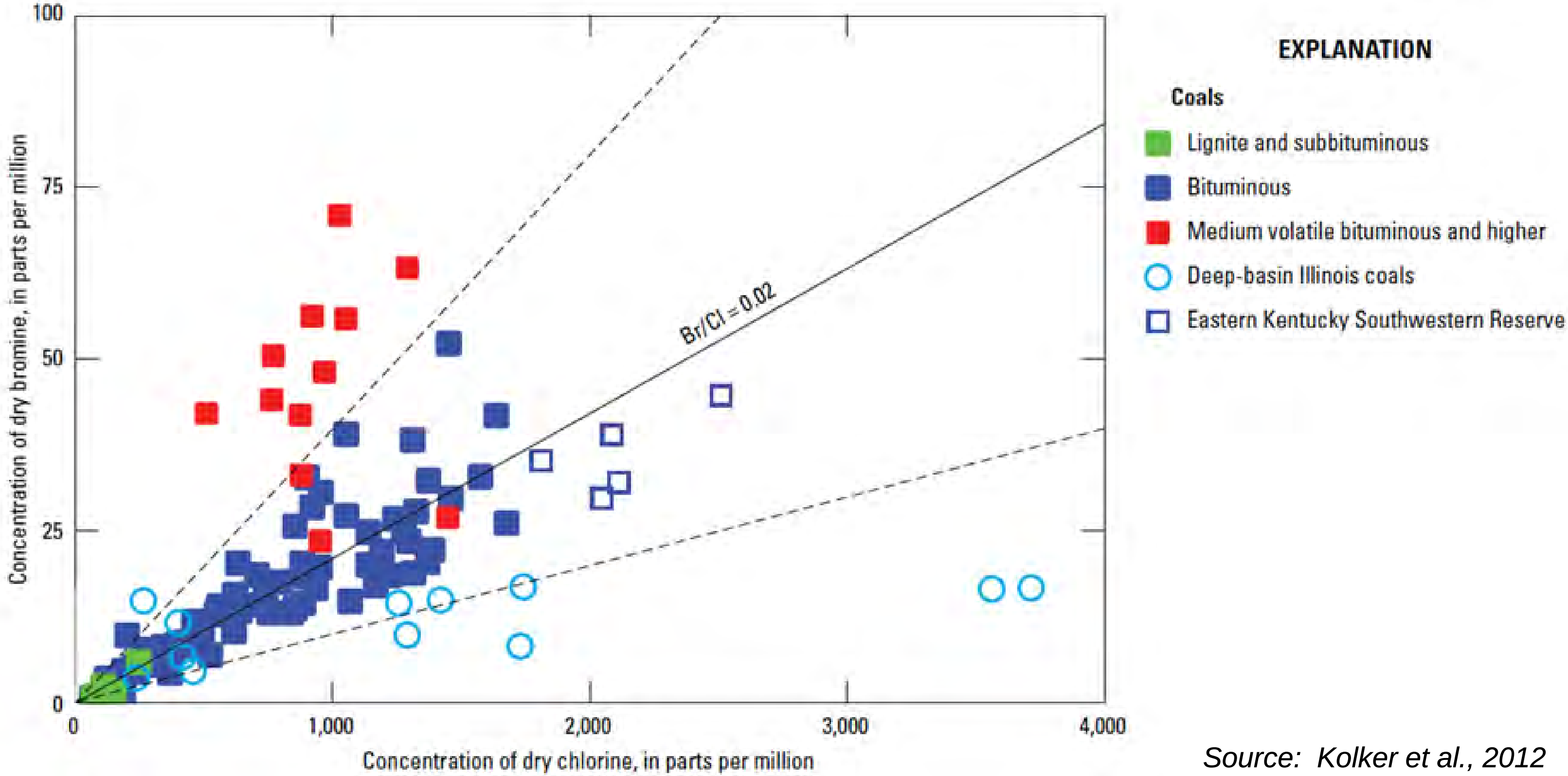


County average, ICR 2 data

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 U.S. 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)

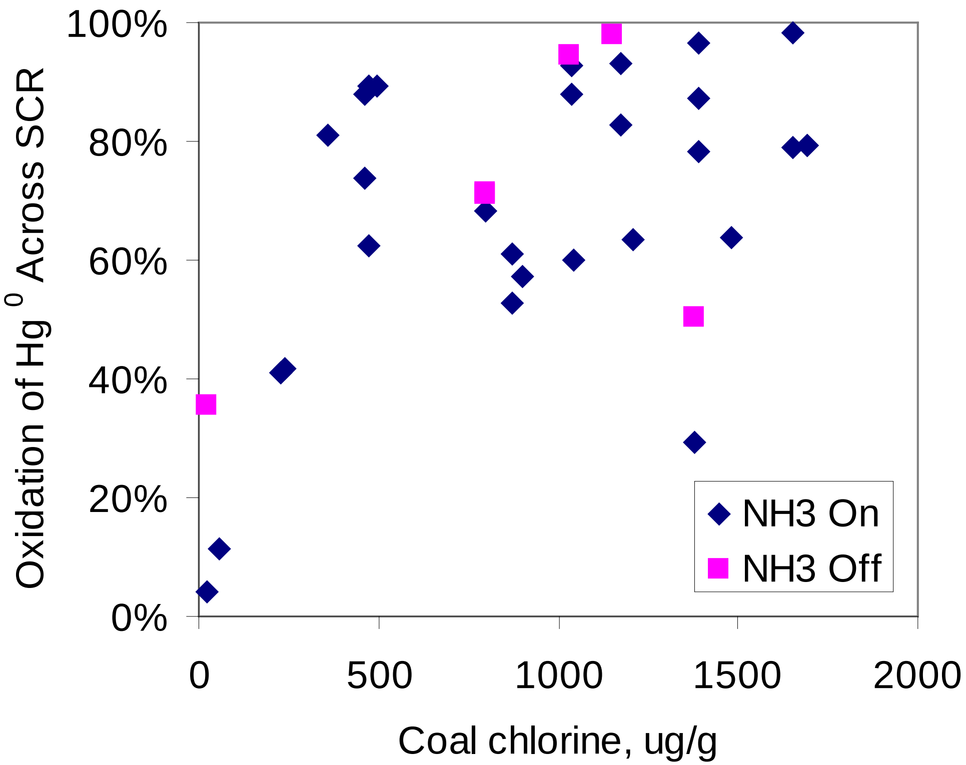
How Halogens Affect Hg In Coal-Fired Boilers & APCDs

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

Opportunities for Hg Oxidation

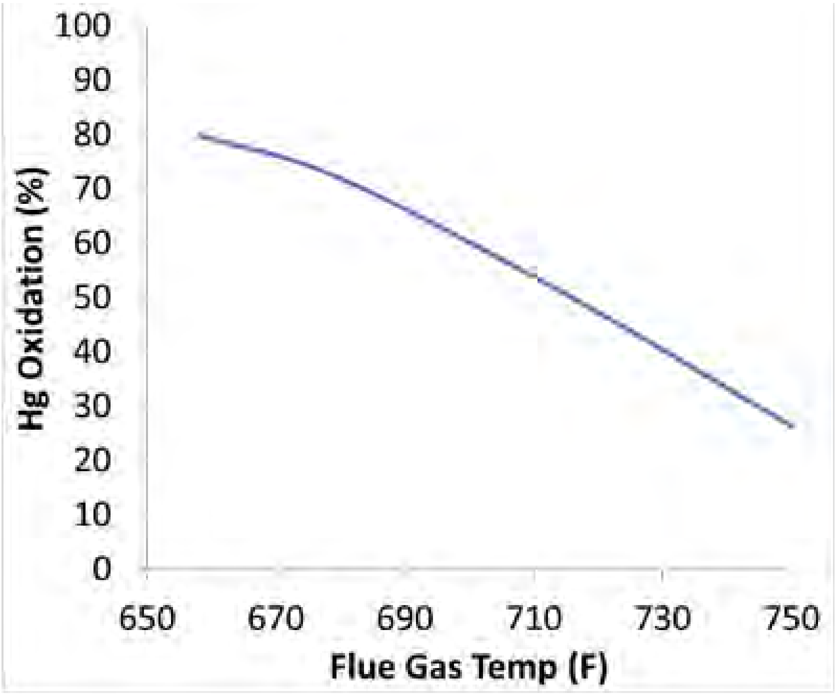
- Selective Catalytic Reduction (SCR)



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

Opportunities for Hg Oxidation

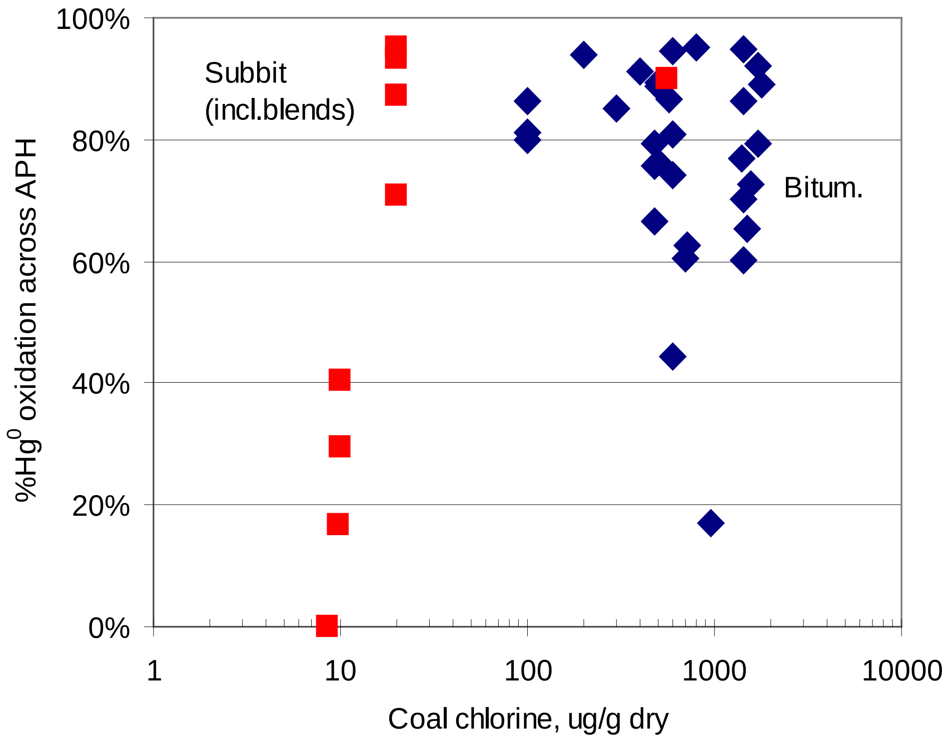
- Selective Catalytic Reduction (SCR)



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

Opportunities for Hg Oxidation

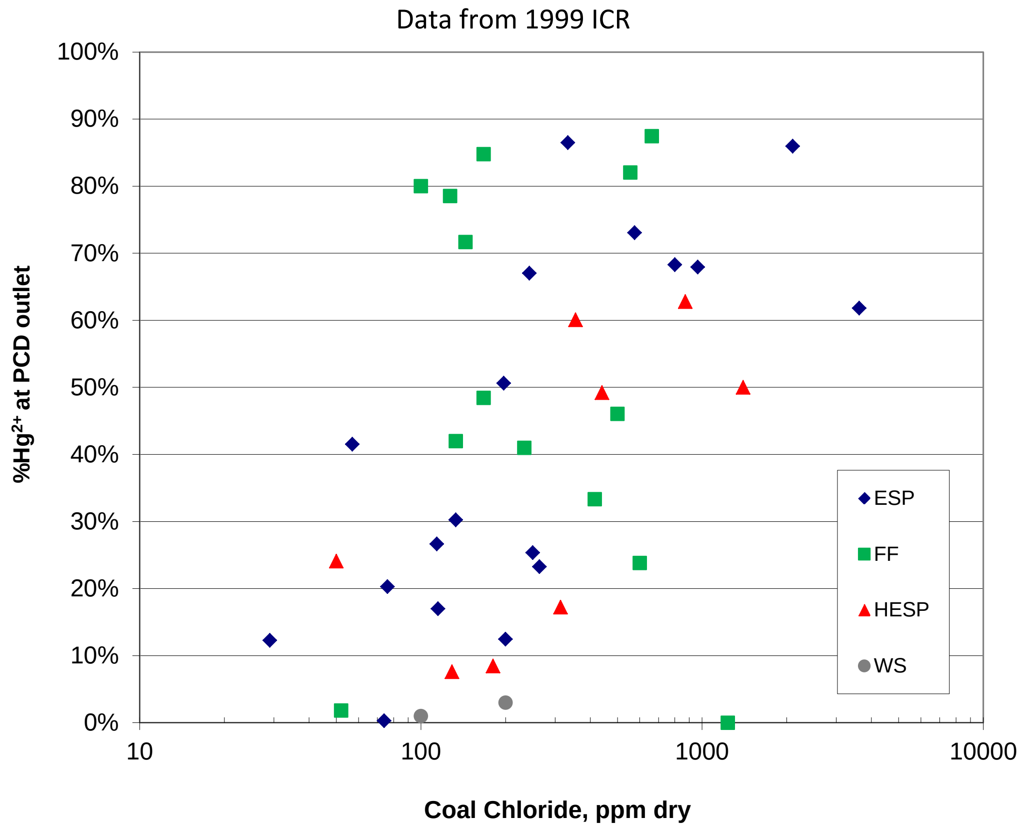
- Selective Catalytic Reduction (SCR)
- Air Preheater



- Full-scale Hg speciation measurements
- Significant oxidation across Air Preheater:
  - APH exit temperature
  - Chlorine
  - SO_2/SO_3
  - LOI

Opportunities for Hg Oxidation

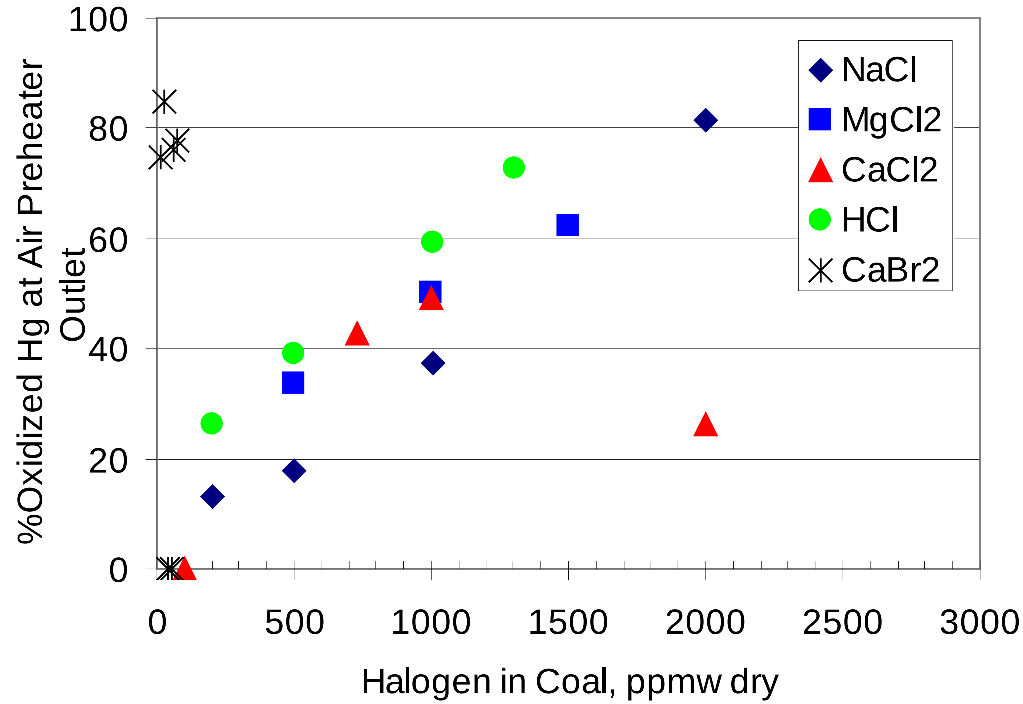
- Selective Catalytic Reduction (SCR)
- Air Preheater
- Particulate Control Devices



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

Opportunities for Hg Oxidation

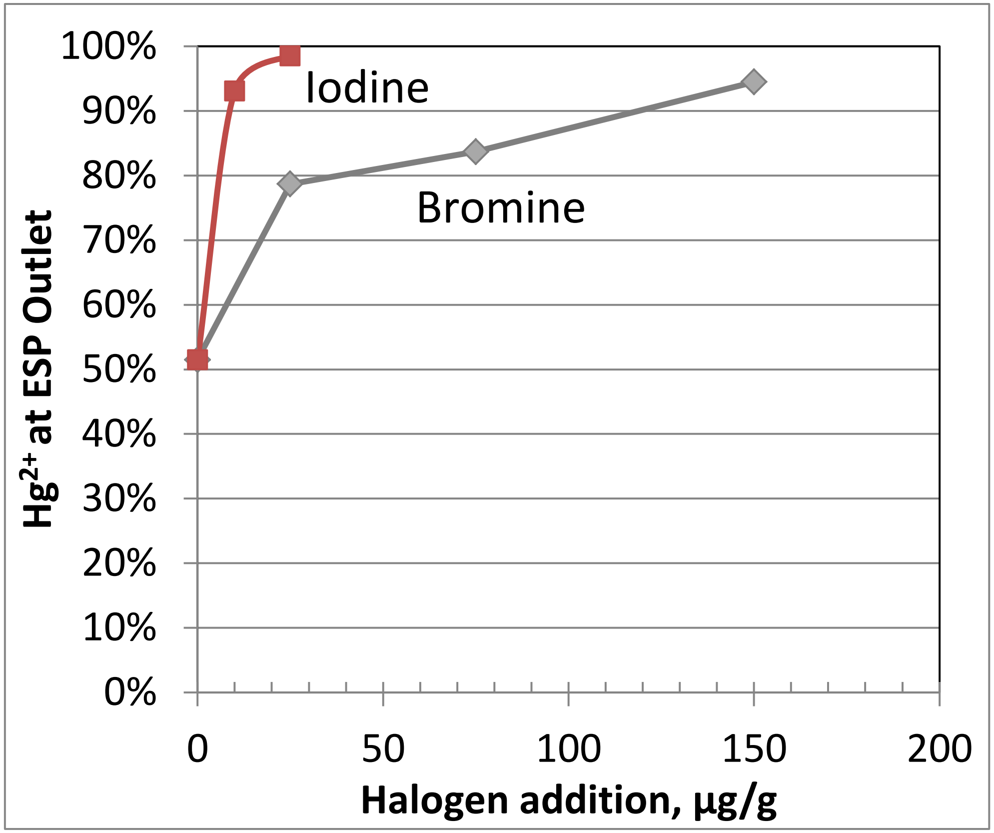
- Selective Catalytic Reduction (SCR)
- Air Preheater
- Particulate Control Devices
- How adding more halogens helps



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

Opportunities for Hg Oxidation

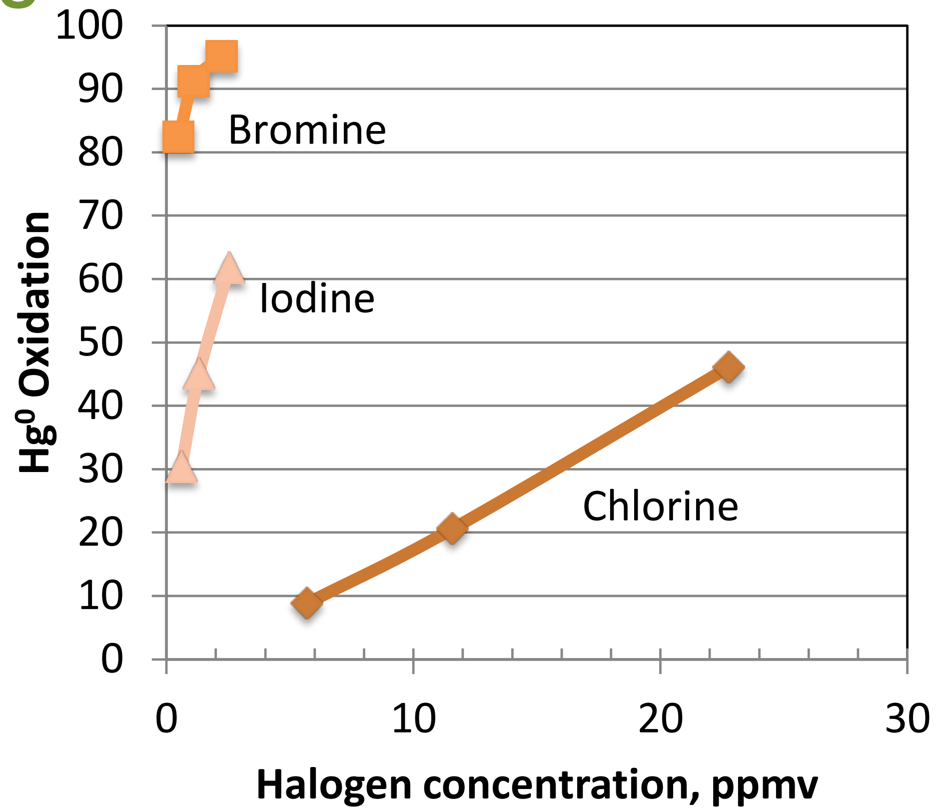
- Selective Catalytic Reduction (SCR)
- Air Preheater
- Particulate Control Devices
- How adding more halogens helps



- 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)
- Air Preheater
- 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!

Opportunities for Hg Absorption

- Wet or dry scrubbers

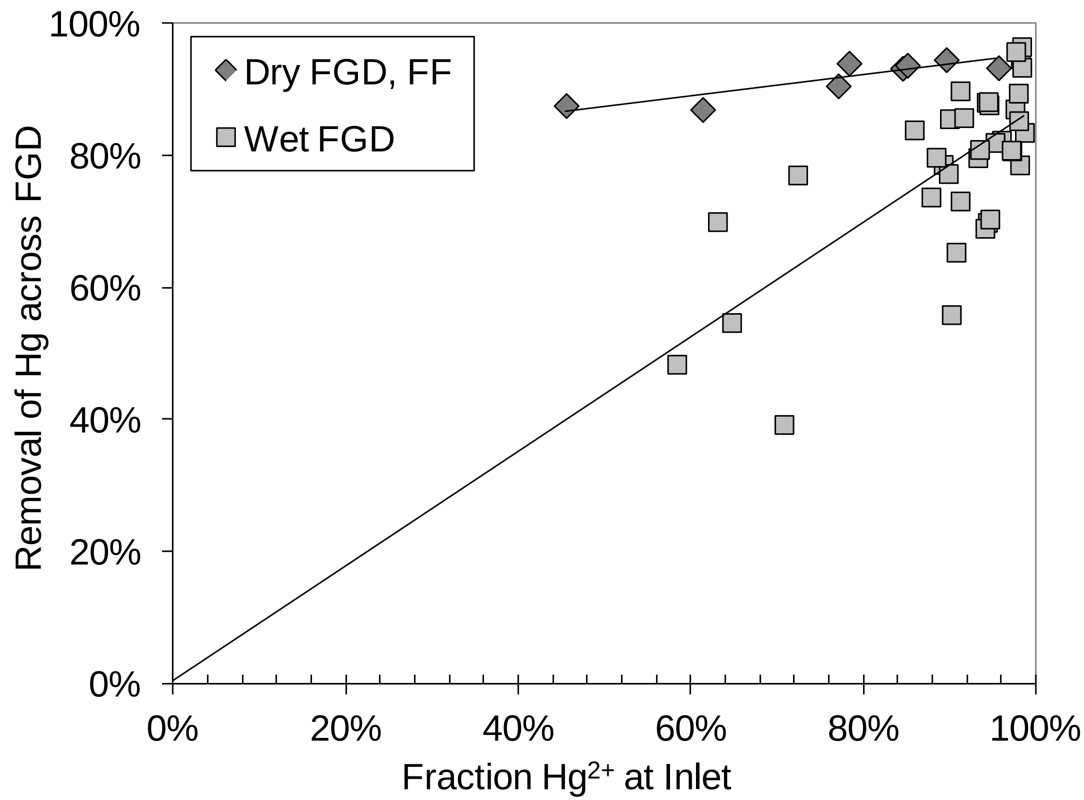
Species	Solubility at 50°C, mg/kg (ppmw)*
Hg^0	0.12
$HgCl_2$	1×10^5
$HgBr_2$	7×10^3

**As Hg*

- Different Hg species have different solubilities in water

Opportunities for Hg Absorption

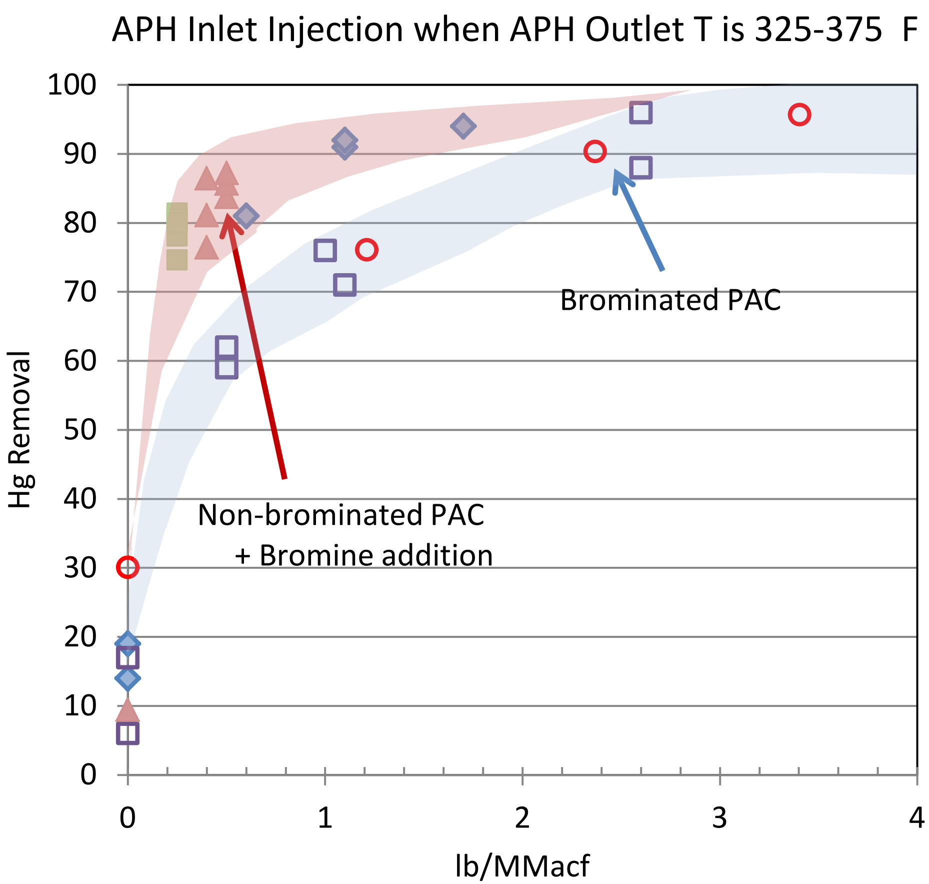
- Wet or dry scrubbers



- 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)

Opportunities for Hg Adsorption

- Wet or dry scrubbers
- 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

How to Use Halogens to Improve Hg Control

Mercury Control Strategies

- Increase “native” Hg capture
  - Combustion modifications
  - Burn coal blends
  - Use additives or catalysts to increase oxidized Hg
  - Addition of scrubber to removed oxidized Hg
- Use of sorbents
  - Activated carbon
  - Oxidizing agents or additives plus sorbents

How Halogens Fit into Hg Control Strategies

- Low "native" halogen in coal
  - Predominantly lignite and subbituminous coals
  - Some bituminous can have low (~ 300 ppmw) chlorine (e.g., some IL Bit)
- Wet or dry scrubbers
- Use less expensive, non-brominated PAC

ADA M-Prove™ Technology

- Proprietary[1] liquid coal additive product for enhanced mercury oxidation and removal in coal-fired boilers
- Applied at various stages of the coal feed process
- Application rates 8 – 10 times less than typical bromine treatment rates to achieve equal Hg oxidation
- Mitigates balance-of-plant impacts associated with other halogen-based additives

[1]Patents: *US 8,372,362, US 8,496,874, US 8,524,179*

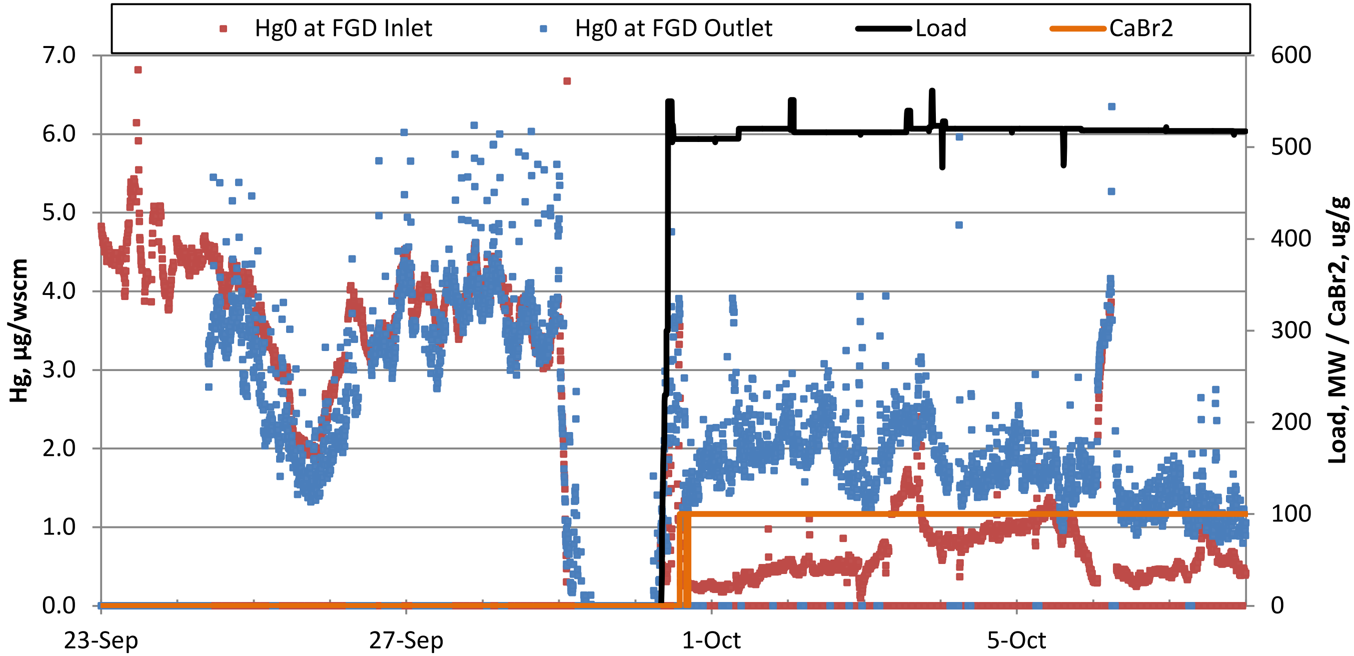
M-Prove™ Technical Development - Testing

- 57 full-scale tests of M-Prove™ process, majority of testing on C-ESP configured plants
- 41 tests w/ PRB coal, 8 tests w/ blended coal (85% PRB)
- 23 separate test locations; configurations included variations with SCR, SNCR, C-ESP, H-ESP, DSI, ACI, WFGD and FF
- 55 - 75% average Hg reduction on majority of testing at significantly low treatment rates

Feed Stock	Plant Configuration
PRB / PRB Blend (>85%)	SCR / CSE
PRB / PRB Blend (>85%)	CSE
PRB / PRB Blend (>85%)	SCR or SNCR / CSE / WFGD
100% PRB	HSE
100% Lignite	SNCR / CSE / WFGD
Lignite Blend (> 90%)	CSE / WFGD
100% Lignite	FF
Bituminous	SCR / DSI / CSE / WFGD

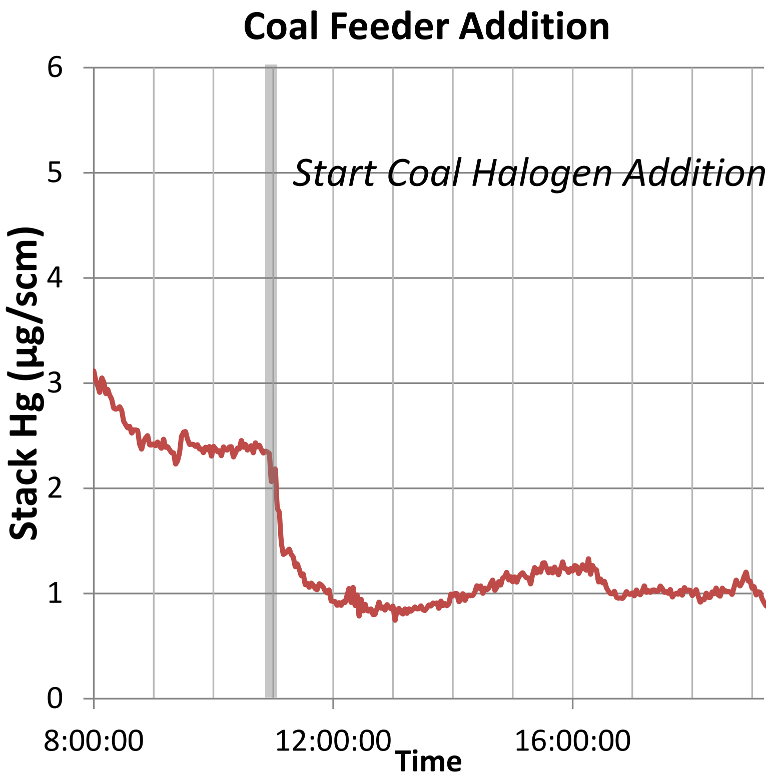
Using Halogens with Wet Scrubbers

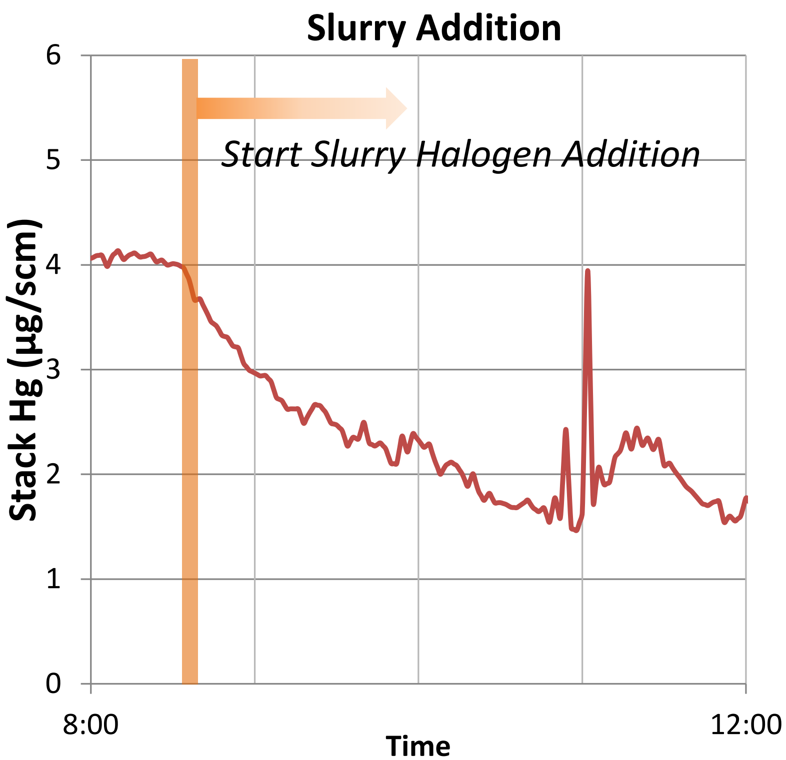
- Bromine addition at subbituminous-fired plant with ESP and wet FGD
- Adding bromine to the fuel:
  - Increased Hg^{2+} at FGD inlet
  - Decreased concentration of Hg at the stack
  - Can result in transient changes in Hg speciation:
    - Higher Hg^0 at stack than at FGD inlet



Using Halogens with Dry Scrubbers

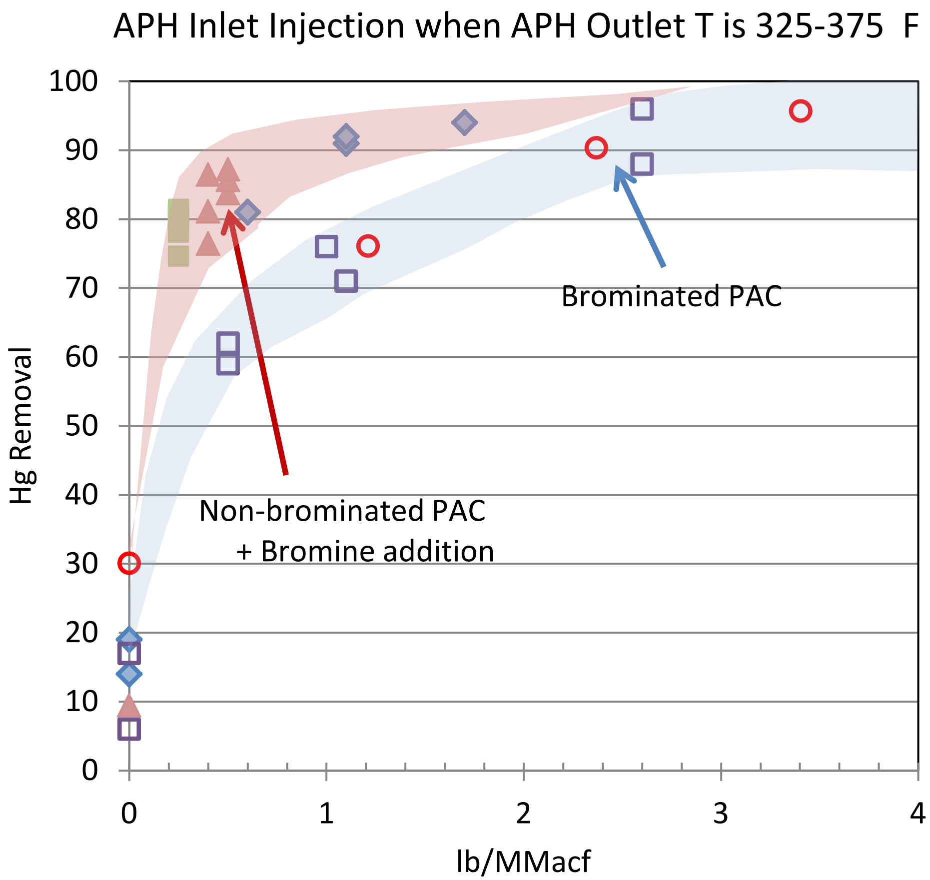
- M-Prove Addition (BL+1 Level) to PRB-fired plant with dry FGD-FF
- Addition at either Coal Feeder or SDA Slurry





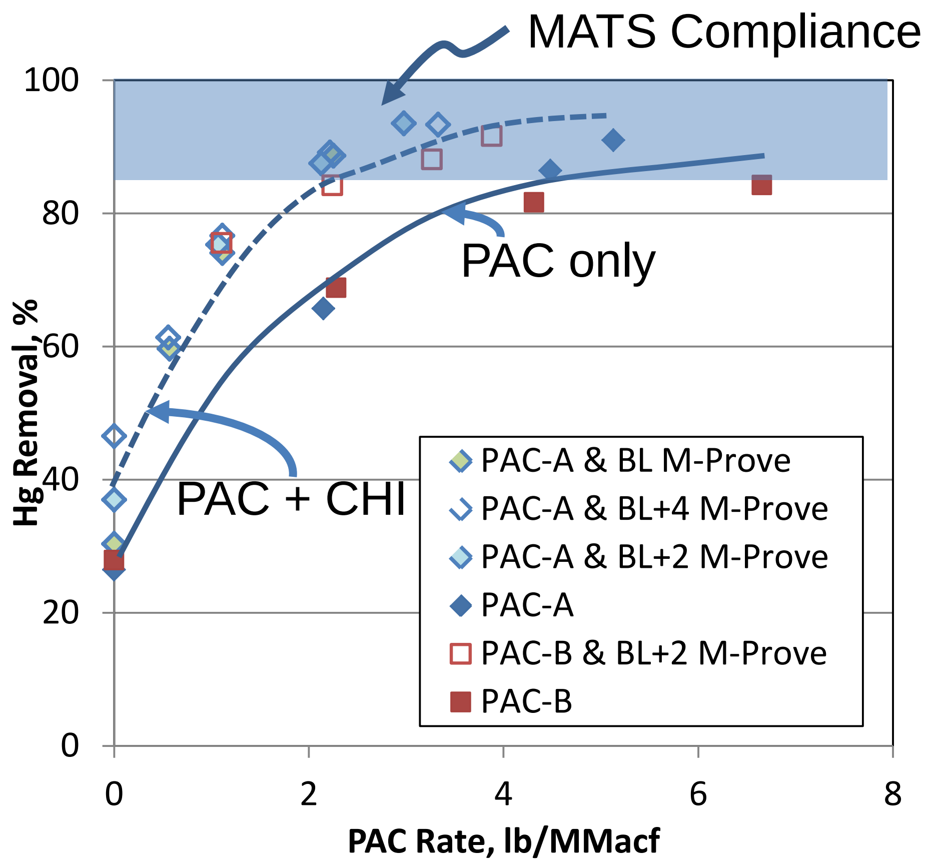
Using Halogens with Activated Carbon

- Combining halogens and PAC can improve performance
- Using halogen addition when PAC is injected upstream of APH improved non-brominated PAC performance, relative to brominated PAC



Using Halogens with Activated Carbon

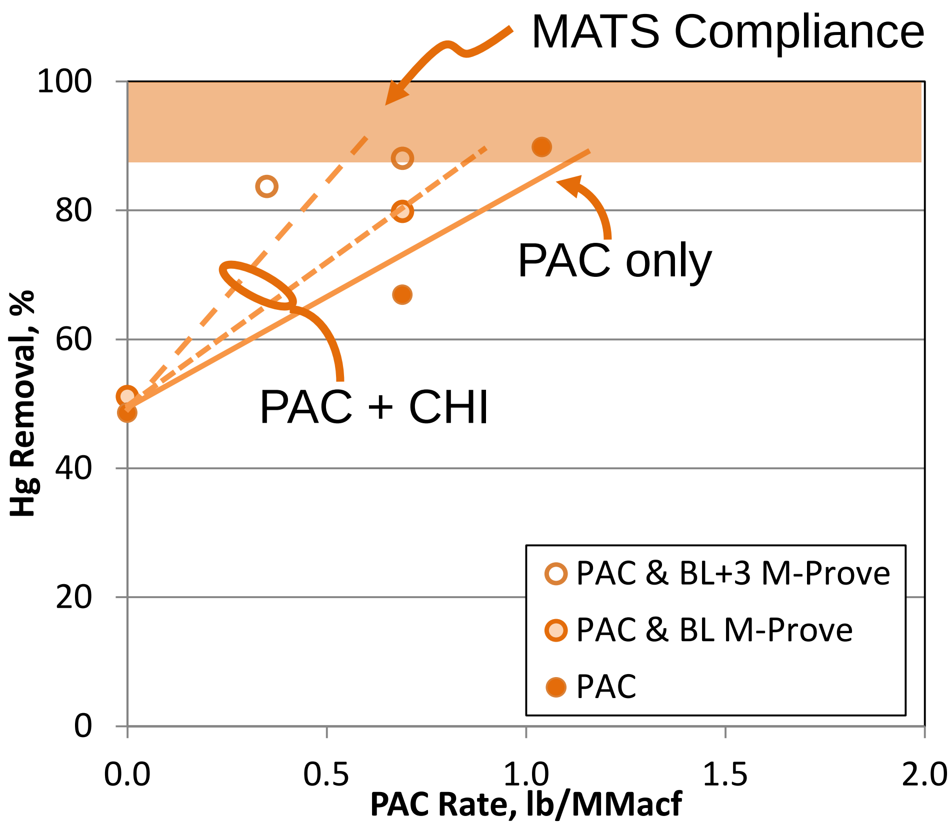
- M-Prove™ addition to coal plus non-brominated PAC injection
- Combining halogens and PAC can improve performance



- Full-scale plant data for PRB-fired unit with cold-side ESP
- Injection of non-brominated PACs upstream of APH

Using Halogens with Activated Carbon

- M-Prove™ addition to coal plus non-brominated PAC injection
- Combining halogens and PAC can improve performance



- Full-scale plant data for lignite-fired unit with fabric filter
- Injection of non-brominated PACs downstream of APH

Balance of Plant Considerations

Halogen Corrosion Mechanisms

- 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

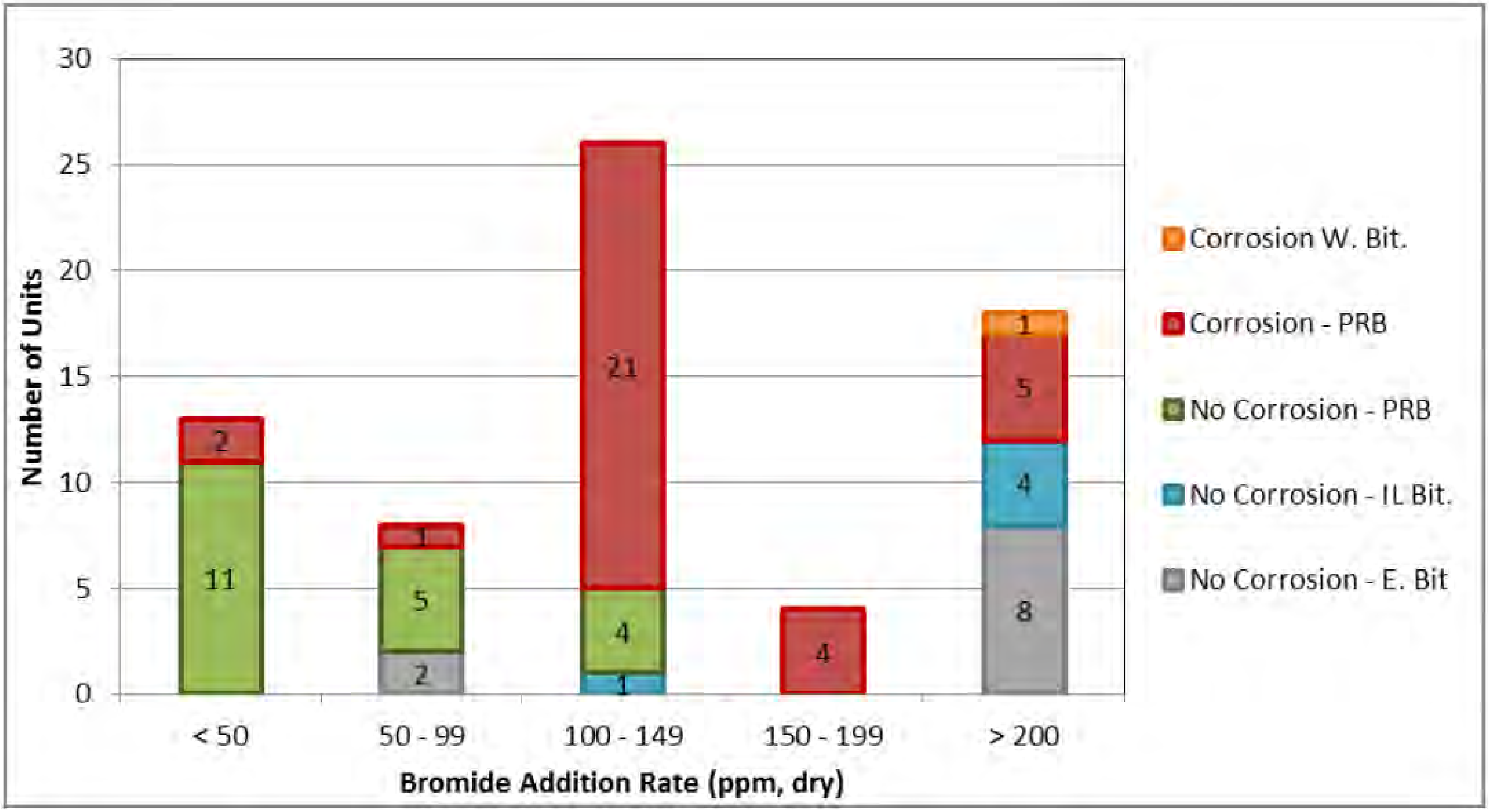
Bromine Corrosion Potential

- Corrosion continually highlighted as significant problem for CaBr2 and Br-PAC applications
  - EERC, EPRI/URS, Paragon Air Heater Technologies, Albermarle, Reaction Engineering International, Multiple Users
- Ongoing EPRI Bromine BOP Study (May 2012)
  - 41 PRB Units with > 1 year operation w/ bromine addition
  - 33 PRB units with > 10 ppm treatment rate
  - 20 units with reported corrosion (61%)

Location	Number of Units
Pulverizer	3
Boiler tubes	2
Air preheater	33
Air preheater outlet duct	7
ESP	2
FGD	2
ID Fan	4

Source: Arambasick et al., 2014 Mega Symposium

Corrosion Reported in PRB-Fired Units using Bromine Additives



Source: Arambasick et al., 2014 Mega Symposium

- With addition of 10 ppm of Iodine, oxidized Hg was 93% with no change in corrosion rate as compared to baseline
- With addition of 25 ppm Bromine to coal, there was no appreciable increase in the corrosion rate
- On 25 ppm to coal basis, Iodine exhibited higher Hg oxidation and higher corrosion rate compared to Bromine
- To achieve 95% Hg oxidation, it was necessary to add 150 ppm Bromine to coal, and rate of corrosion was 20 times higher than baseline
- Data did show that rate of corrosion is function of rate of halogen application to coal

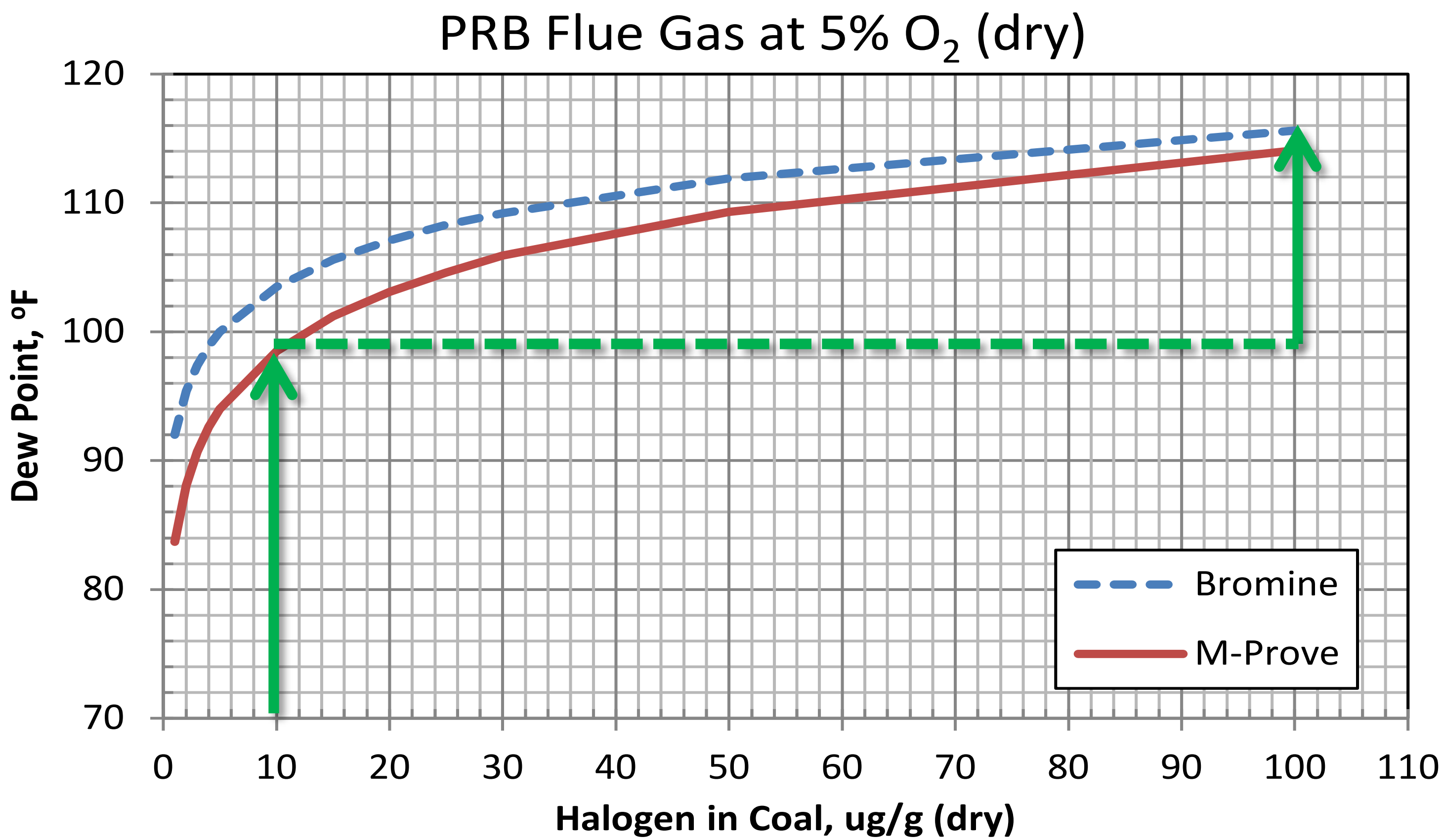
Test ID	% Oxidation	Rate of Corrosion, mils/year	Comparison to Baseline
12/9 Baseline	51.5	0.09*	N/A
12/10 150 ppm Bromine	94.5	1.8*	20 X
12/11 AM 10 ppm Iodine	93.1	0.13	Similar
12/11 PM 25 ppm Iodine	98.5	0.28	3 X
12/12 AM 25 ppm Bromine	78.7	0.10	Similar
12/12 PM 75 ppm Bromine	83.7	0.27	3 X

Reinhold NOx – Combustion Roundtable
February 23-24, 2015
Richmond, VA

Lower Risk of Corrosion w/ M-Prove™

Dew Point Corrosion

- Application rates typically 8-10 times less than bromine
- M-Prove dew point temperature 10 – 20 degrees less than HBr



Bromine Ancillary Emissions

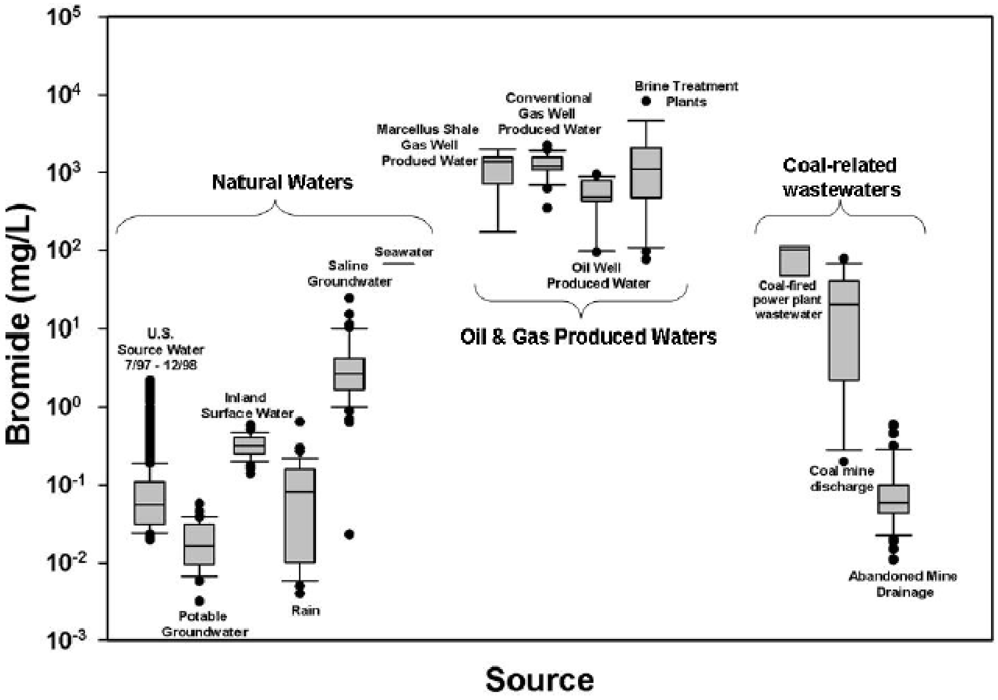
- Bromine additive or Br-PAC results in increased Br in fly ash
  - 50% of Br on fly ash leached in SPLP test
  - 50 - 100% of fuel added halogen emitted at stack - ESP units
- Br in water may cause additional Trihalomethanes (THMs) in downstream water systems
- Increased Se speciation and subsequent concentration in WFGD liquor or waste water
- Potential impacts for disposal / storage of facility waste streams

Halogens in Power Plant Wastewater

Implications and Issues

Power Plant Wastewater

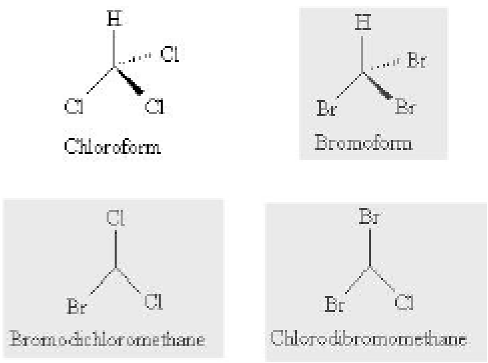
- Halogens in FGD wastewater discharge could increase concentration of halogens in rivers, etc.
- Bromine has been studied the most, because of an association with oil & gas extraction



Bromide concentrations (mg/L on log scale) in natural waters, oil and gas produced waters, and coal-related wastewaters. All oil and gas produced waters and coal-related wastewater data from Southwestern Pennsylvania [Source: VanBriesen, 2014]

Power Plant Wastewater

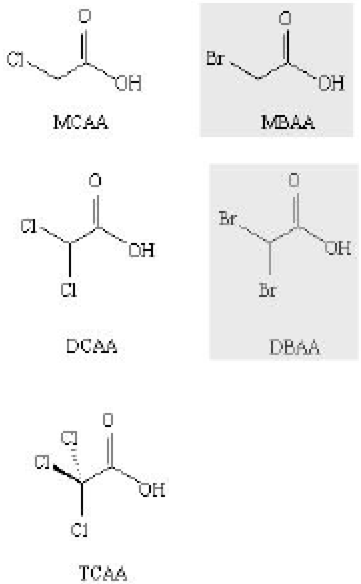
- Everyone seems to agree that bromide in wastewater is probably not a great idea if the plant discharges upstream of a drinking water treatment facility
  - During disinfection, chlorine (typically applied as hypochlorous acid, HOCl) reacts with organics present in the source water (natural organic matter or NOM) to form chlorinated disinfection by-products (DBPs)
  - If bromide is present, the free chlorine reacts with it and organic matter to form brominated and mixed chlorinated-brominated disinfection byproducts (DBPs)
  - While specifics for each chemical remain largely unknown, in general, brominated (and iodated) DBPs present higher risks than do chlorinated DBPs



Some trihalomethanes (TTHMs)

Power Plant Wastewater

- Everyone seems to agree that bromide in wastewater is probably not a great idea if the plant discharges upstream of a drinking water treatment facility
- EPA has set Maximum Contaminant Levels (MCLs) for DBPs:
  - 0.010 mg/L for bromated due to increased cancer risk from long-term exposure
  - 0.060 for haloacetic acids (HAAs) due to increased cancer risk from long-term exposure
  - 0.080 mg/L for total trihalomethanes (TTHMs) due to increased cancer risk and liver, kidney or central nervous system problems from long-term exposure



Some haloacetic acids (HAAs)

Summary

Reducing Costs of Compliance using Coal Halogen Addition

- Coal halogen injection (CHI) can, in *some* cases, be used instead of activated carbon injection (ACI) – for example, in wet or dry scrubbers – reducing capital and operating costs
- In *other* cases, CHI can be combined with ACI to reduce operating costs by
  - Lowering powdered activated carbon (PAC) usage, leading to better operation of particulate control devices and continued ability to sell fly ash
  - Possibly lowering PAC costs, by switching from brominated to non-brominated PAC, for example
- RESULT: Lower total cost of compliance

DISCLAIMER: Economic estimates specific to individual plants – difficult to generalize!

- Two ways to remove Hg from flue gas: absorption (scrubbers) and adsorption (particulate matter/sorbents)
- Coal halogen content has a big effect on both Hg oxidation and adsorption on particles
  - Main halogen in coal is chlorine, which can vary by ***three orders of magnitude*** in US coals
  - Bromine in US coals is about 2% of chlorine content; iodine content is even lower
- Adding halogens to the fuel or boiler increases mercury removal using scrubbers or activated carbon
- In some plants, levels of bromine addition > ~125 ppmw have shown corrosion, mostly in air preheaters
- When halogens are added to a boiler with a wet scrubber, there can be transfer of halogens to FGD wastewaters
  - No regulation on halogen in wastewater discharge
  - But if the plant discharges upstream of a drinking water treatment facility, there might be concerns in the future about formation of disinfection byproducts (DBPs)

Advancing Cleaner Energy

THANK YOU!

Connie Senior
connies@adaes.com