REINHOLD ENVIRONMENTAL Ltd.

2017 NOx-Combustion-CCR Round Table Presentation

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Reducing the Cost of Mercury Control with Fuel Additives

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Reinhold NOx Roundtable ~ February 27, 2017

Disclaimer

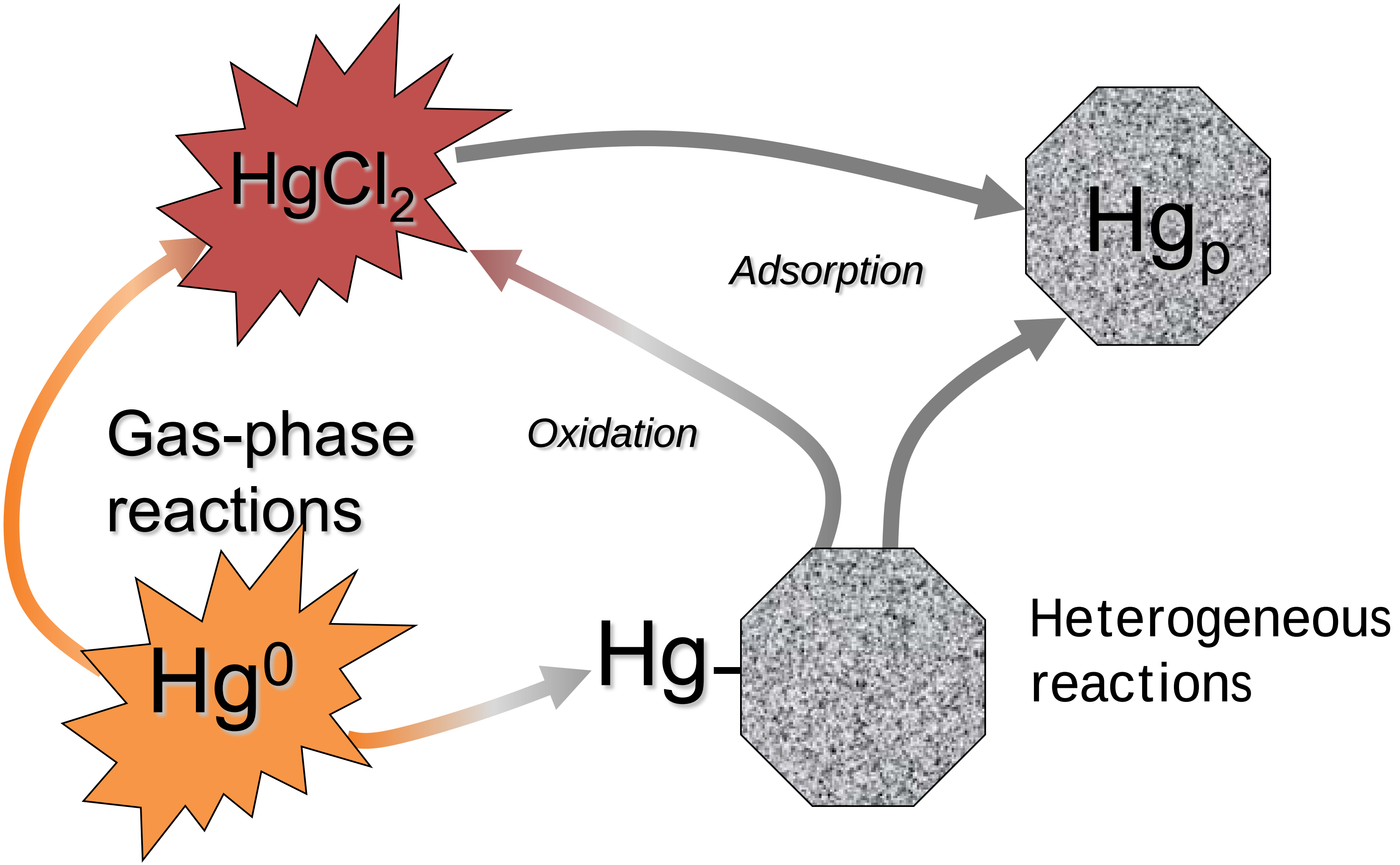
This presentation includes general information on coal and coal-fired boilers intended for education and illustration purposes only. All information is provided "AS-IS" and without warranty or liability of any kind.

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

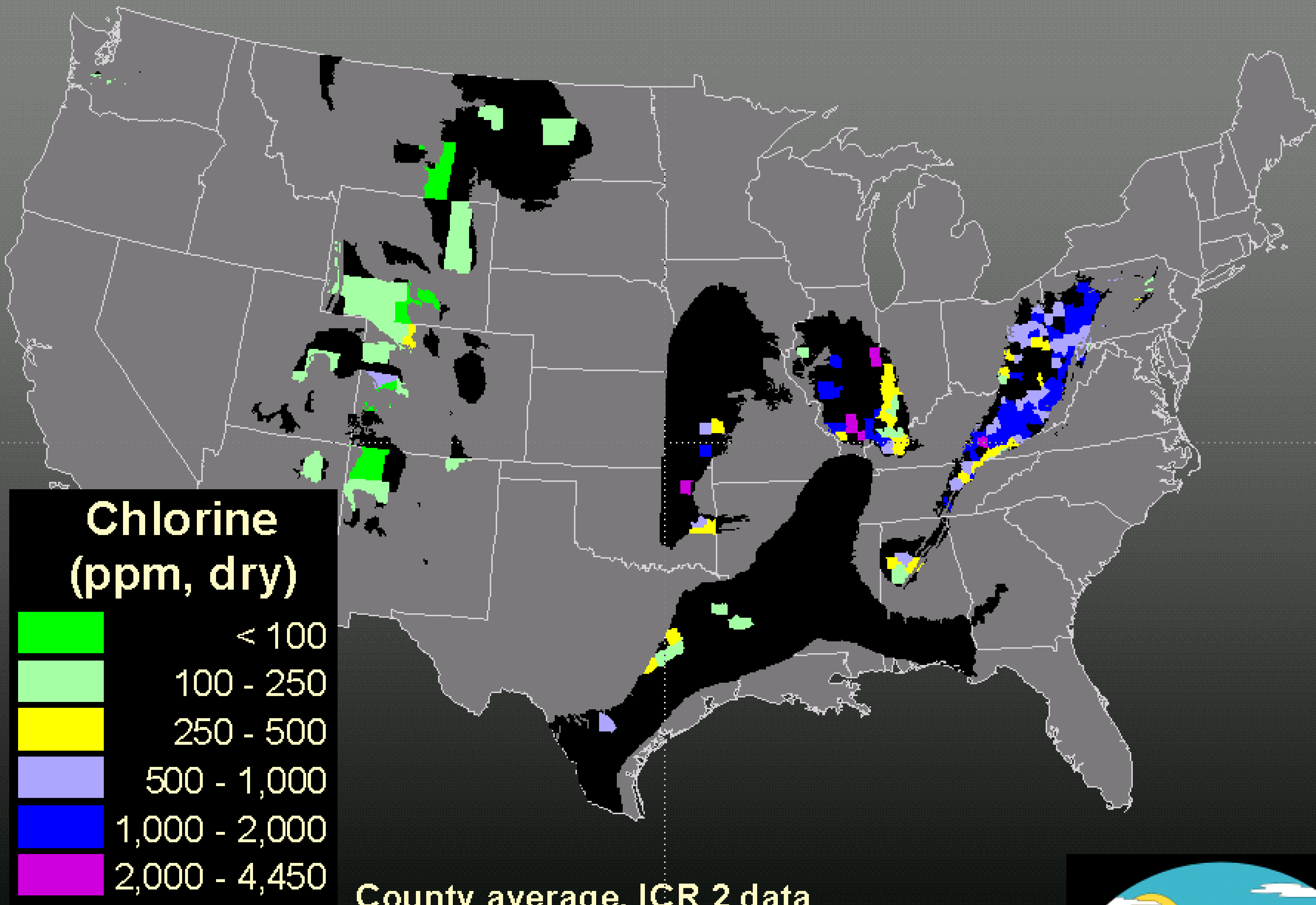
Chlorine

- 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%

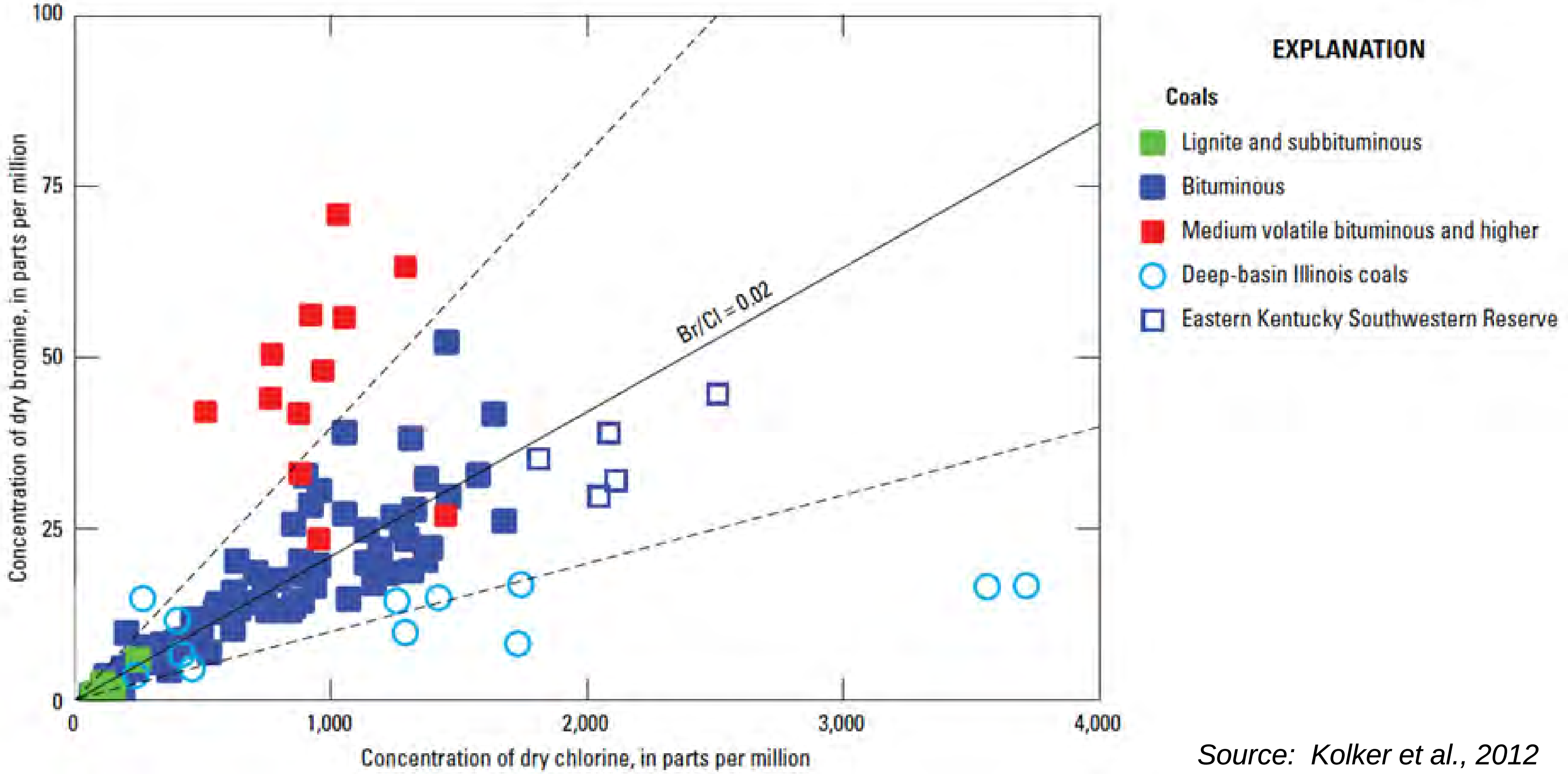
Chlorine in Coal



County average, ICR 2 data

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

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)

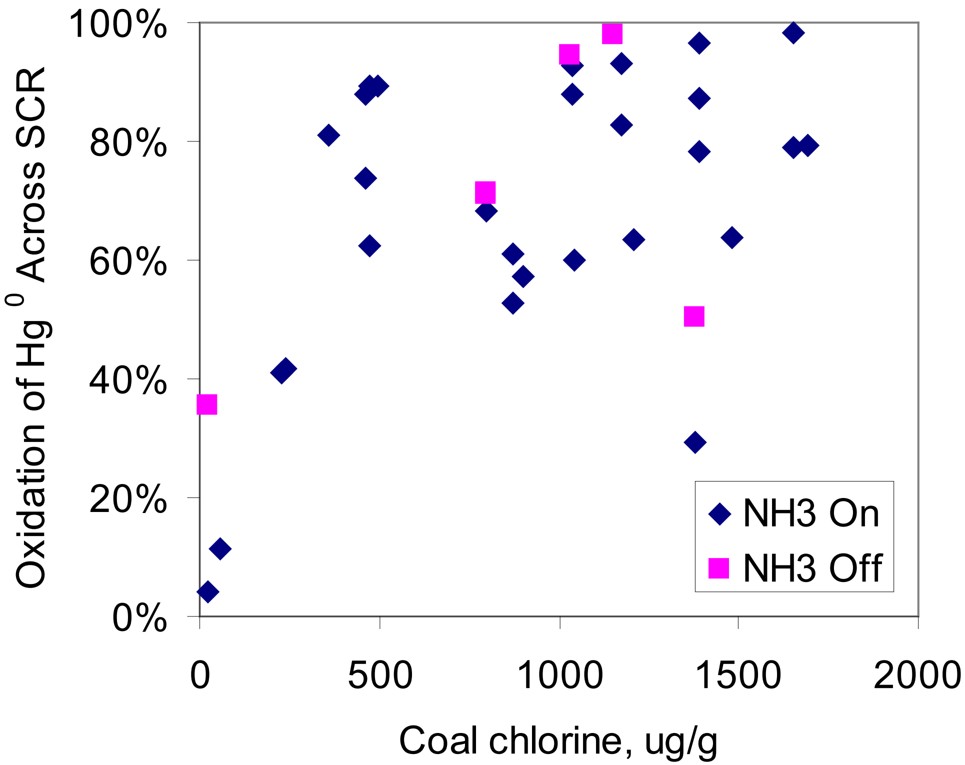
How Halogens Affect Hg In Coal-Fired Boilers & APCDs

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

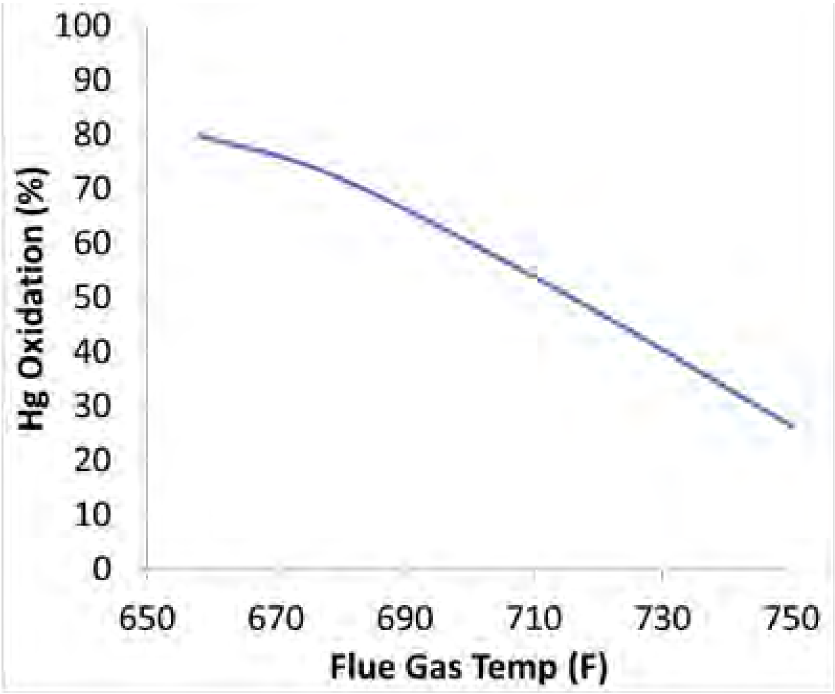
- Selective Catalytic Reduction (SCR)



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

Opportunities for Hg Oxidation

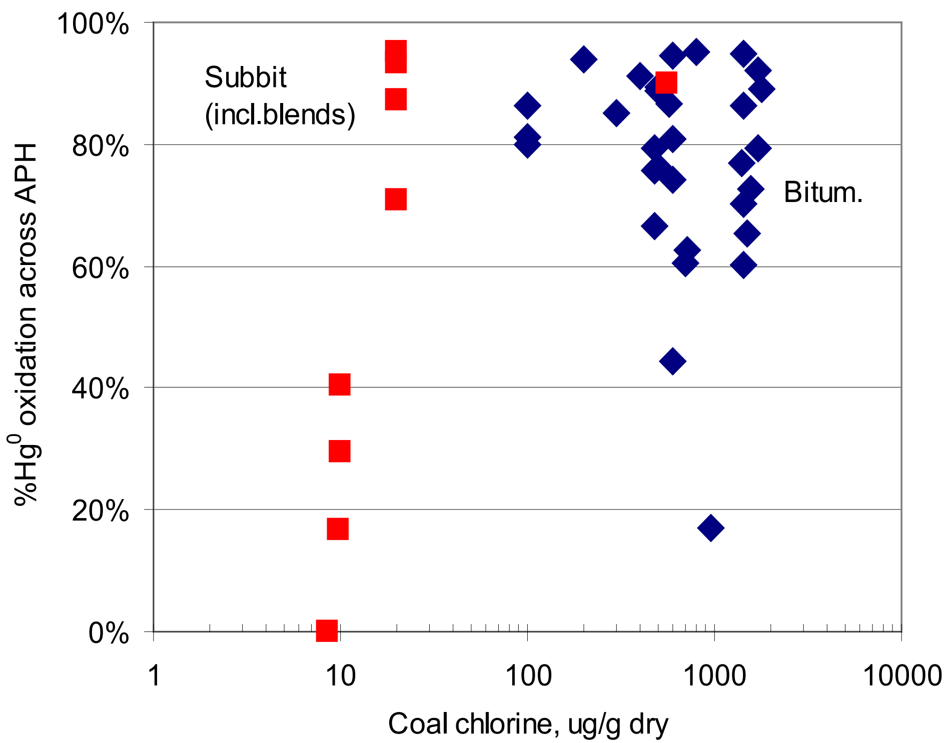
- Selective Catalytic Reduction (SCR)



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

Opportunities for Hg Oxidation

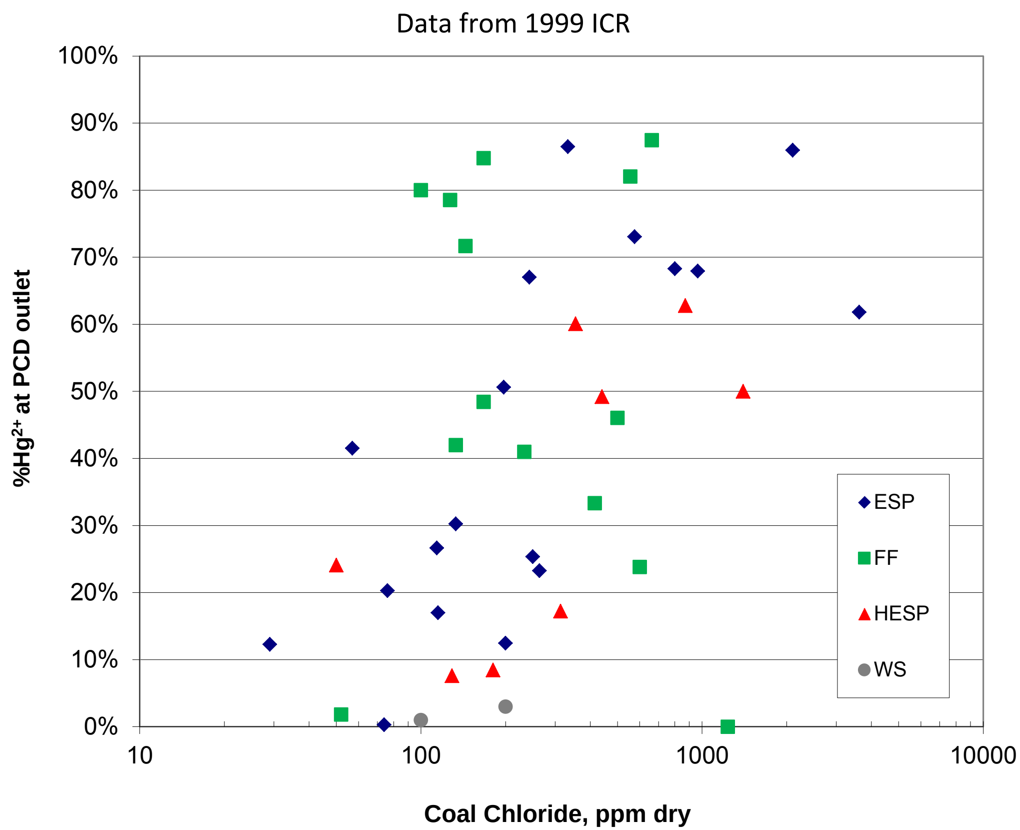
- Selective Catalytic Reduction (SCR)
- Air Preheater



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

Opportunities for Hg Oxidation

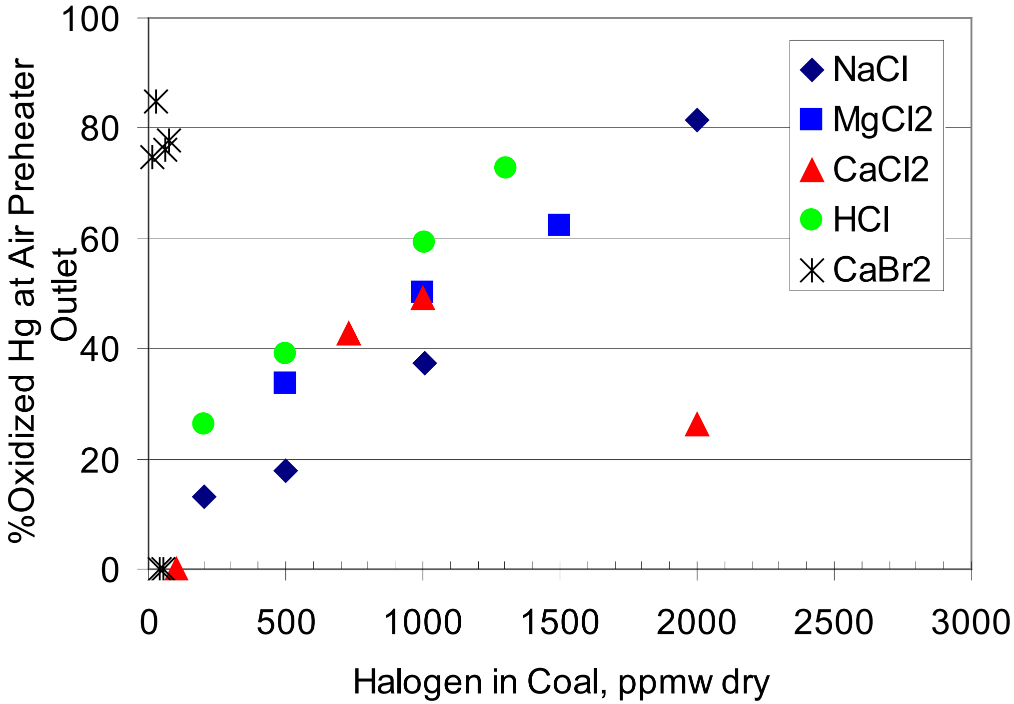
- Selective Catalytic Reduction (SCR)
- Air Preheater
- Particulate Control Devices



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

Opportunities for Hg Oxidation

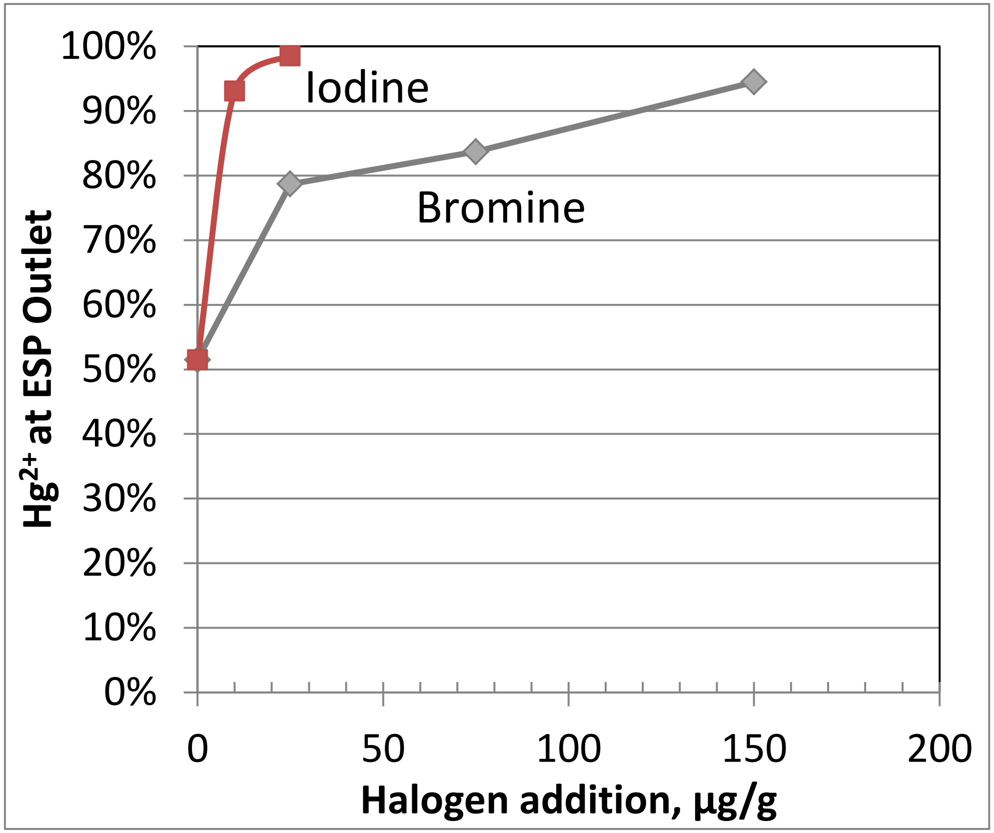
- Selective Catalytic Reduction (SCR)
- Air Preheater
- Particulate Control Devices
- How adding more halogens helps



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

Opportunities for Hg Oxidation

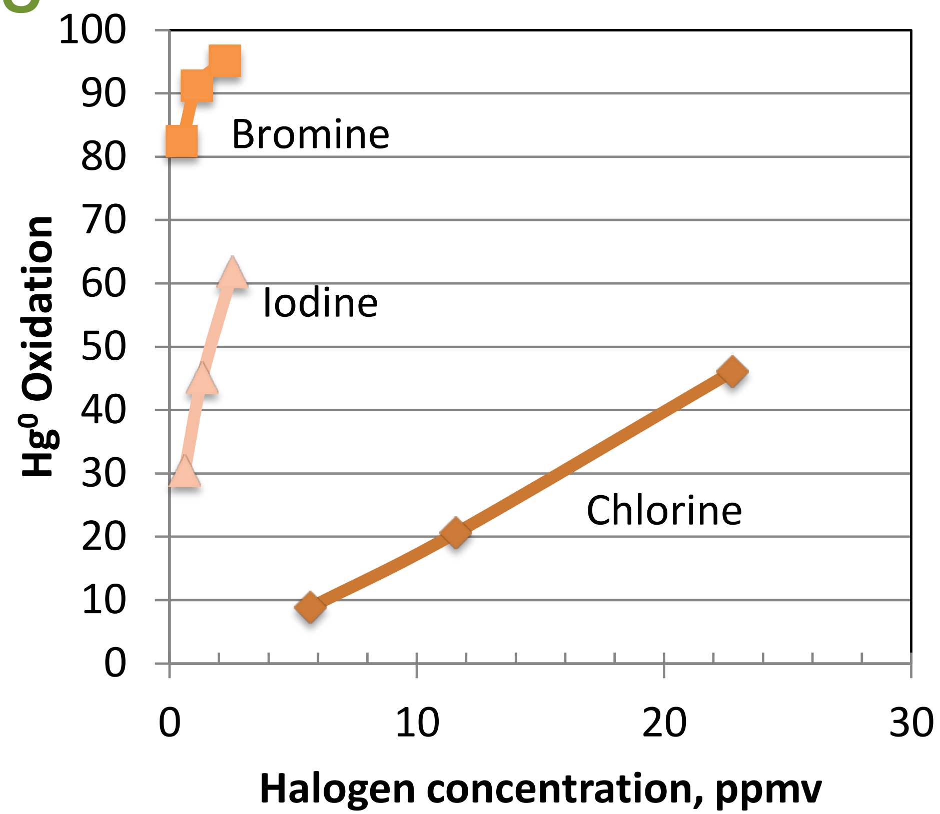
- Selective Catalytic Reduction (SCR)
- Air Preheater
- Particulate Control Devices
- How adding more halogens helps



- 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



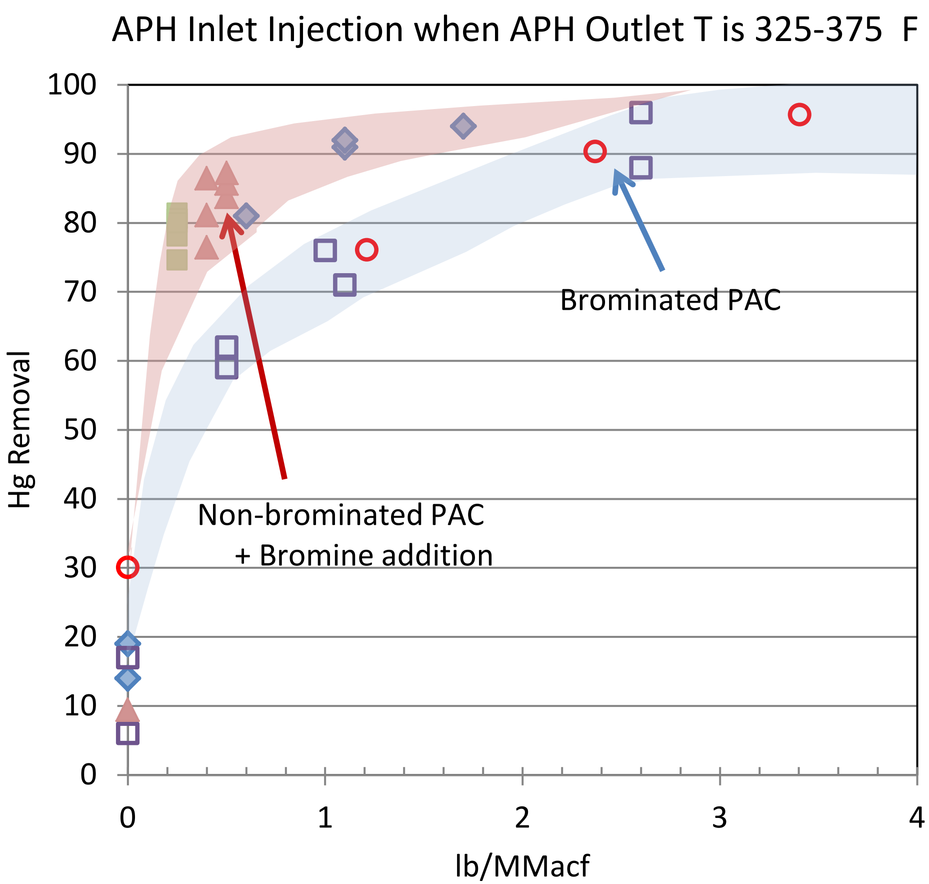
751°F, 350 ppmv NO, 0.9 MR, 3.5% O_2, 12% H_2O
1000 ppmv SO_2, 11 ppmv SO_3, 100 ppmv CO

Source: Bertole, NOx Roundtable 2015

- Having an SCR helps!

Using Halogens with PAC

- 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

Opportunities for Hg Absorption

- Wet or dry scrubbers

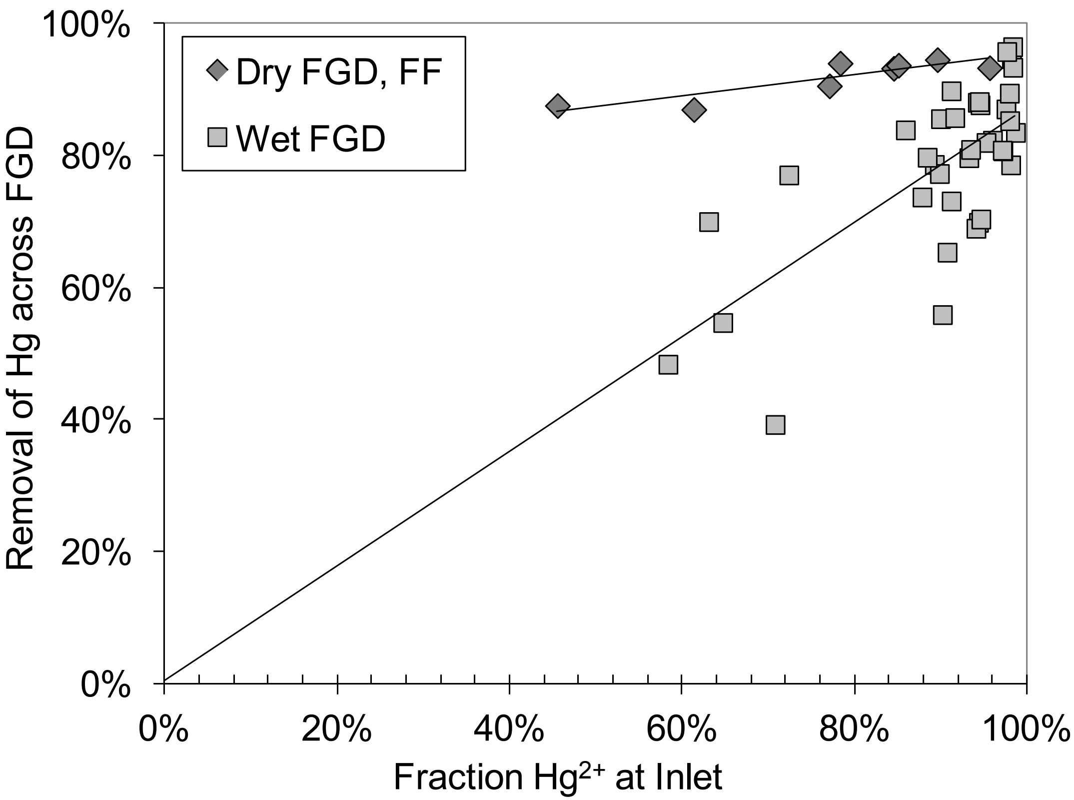
Species	Solubility at 50°C, mg/kg (ppmw)*
Hg^0	0.12
$HgCl_2$	1×10^5
$HgBr_2$	7×10^3

**As Hg*

- Different Hg species have different solubilities in water

Opportunities for Hg Absorption

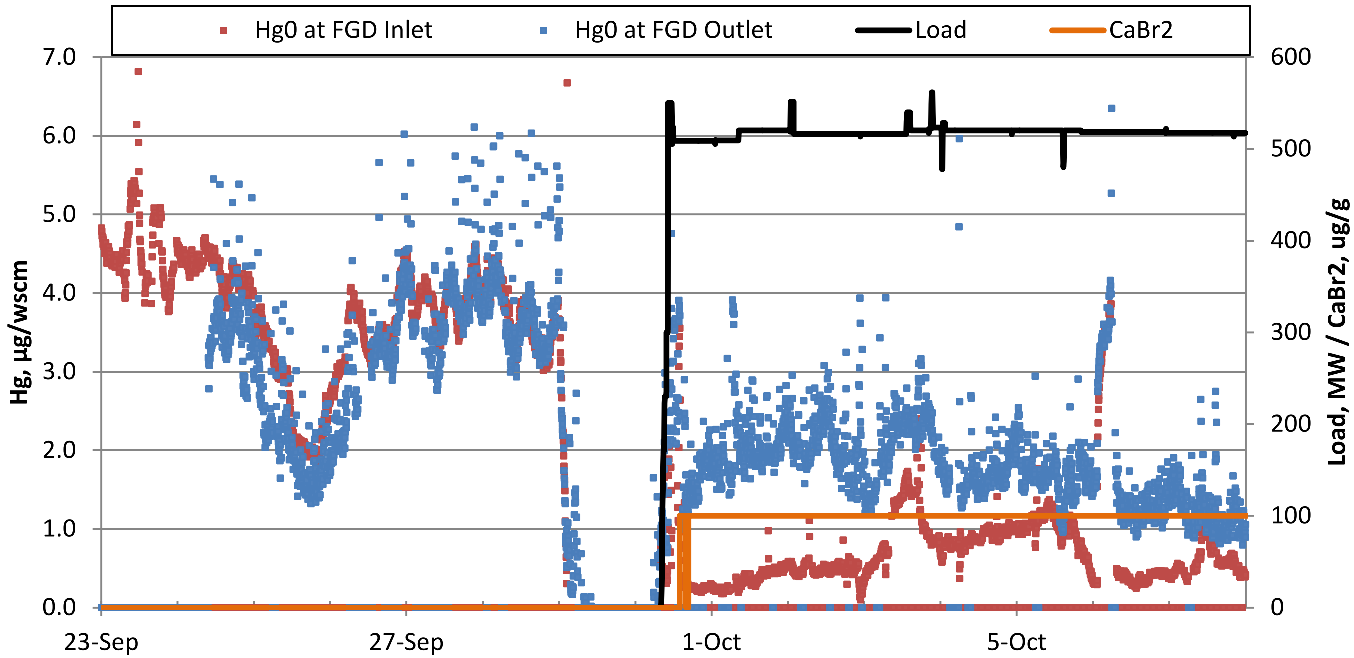
- Wet or dry scrubbers



- 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)

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



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

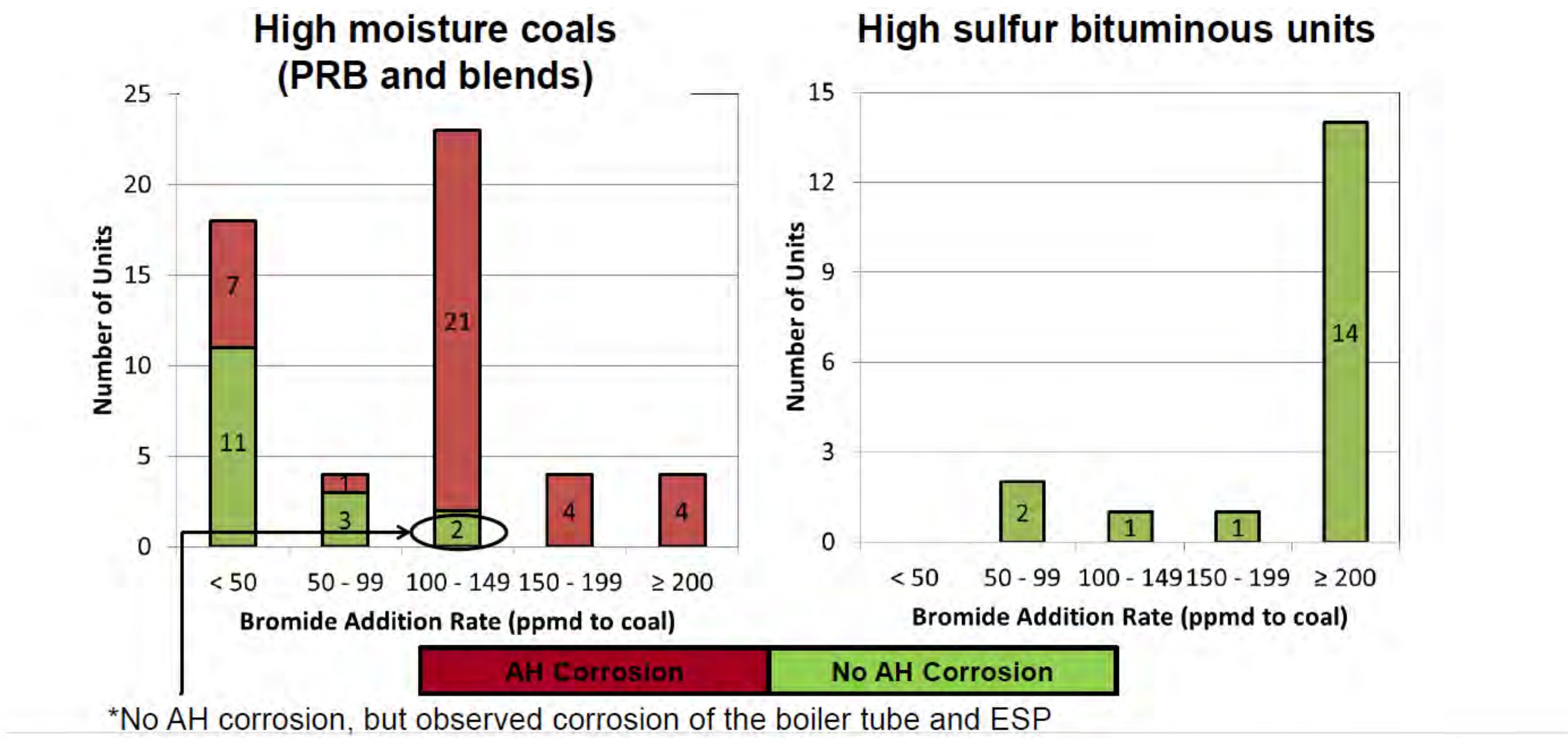
- Corrosion continually highlighted as significant problem for $CaBr_2$ and Br-PAC applications
  - EERC, EPRI/URS, Paragon Air Heater Technologies, Albermarle, Reaction Engineering International, Multiple Users
- Ongoing EPRI Bromine BOP Study (August 2016)
  - 46 units out of 72 surveyed reported corrosion

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

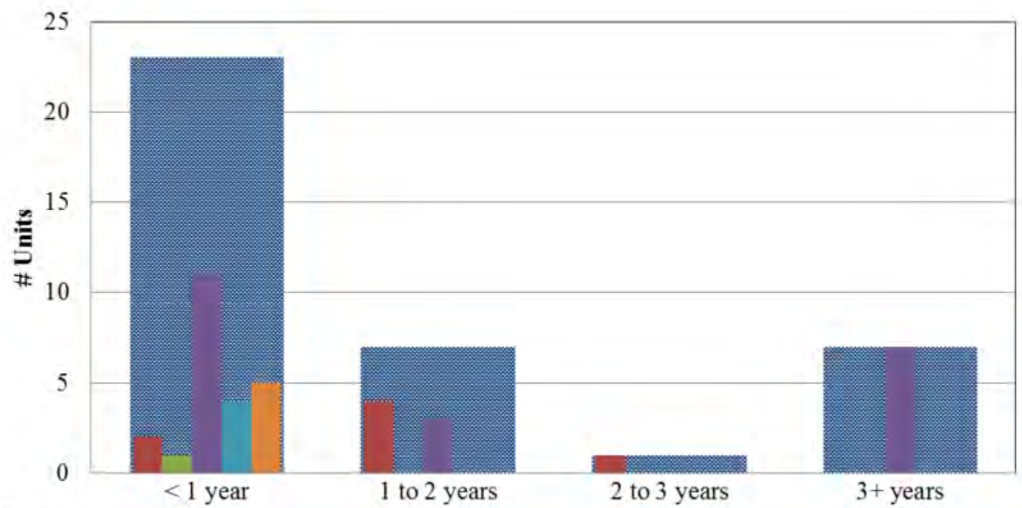
- EPRI surveyed plants using bromine fuel additives or brominated PAC
- PRB-fired boilers observed corrosion, primarily in air preheater (AH), but bituminous-fired boilers did not



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

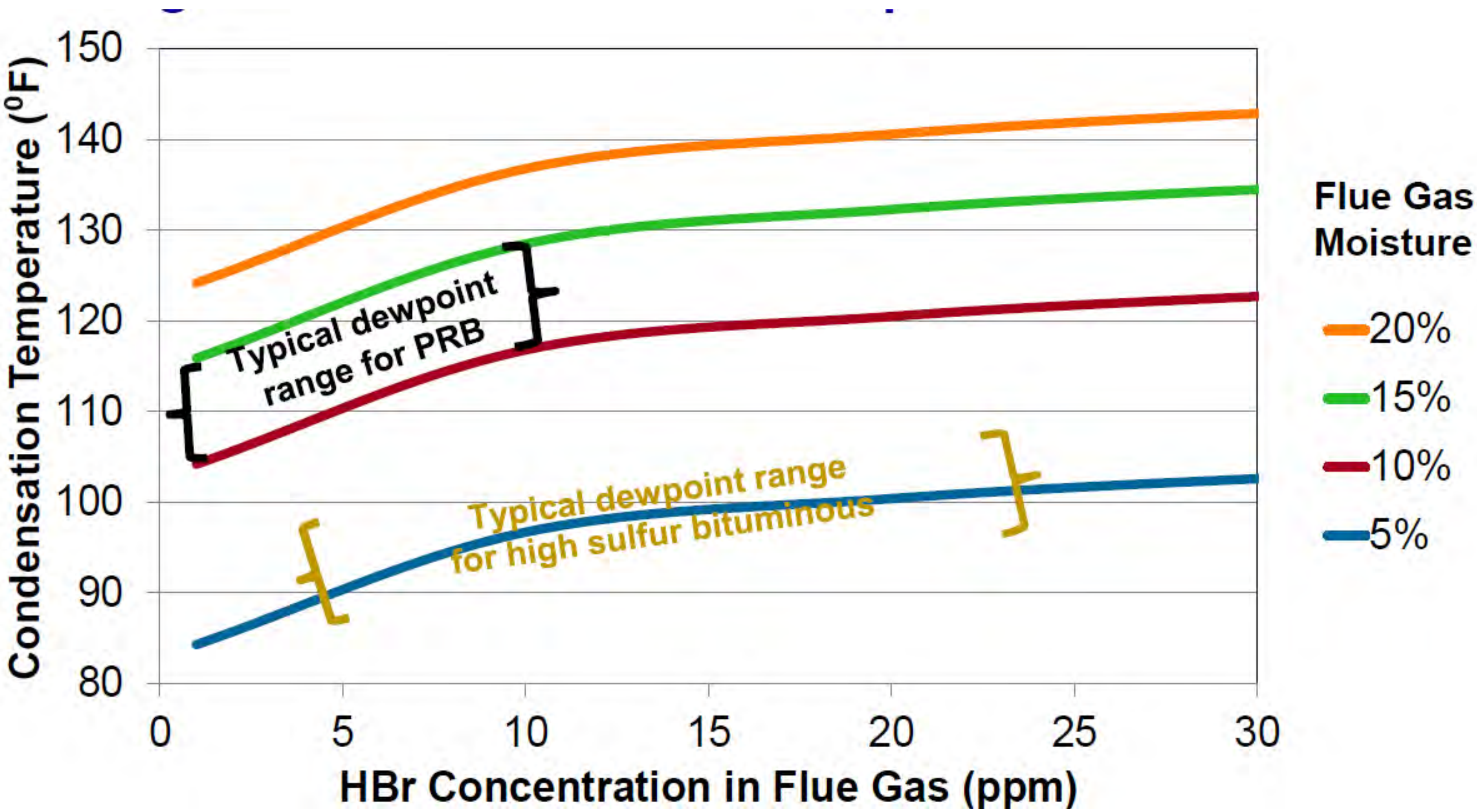


	< 1 year	1 to 2 years	2 to 3 years	3+ years
Total # Units	23	7	1	7
< 50 ppmd	2	4	1	0
50 - 99 ppmd	1	0	0	0
100 - 149 ppmd	11	3	0	7
150 - 199 ppmd	4	0	0	0
> 200 ppmd	5	0	0	0

Source: Arambasick et al., 2016 Mega Symposium

Dewpoint Corrosion

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



Source: Arambasick et al., 2016 Mega Symposium

Corrosion Rates for Different Halogens

- 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

How to Use Halogens to Improve Hg Control

Mercury Control Strategies

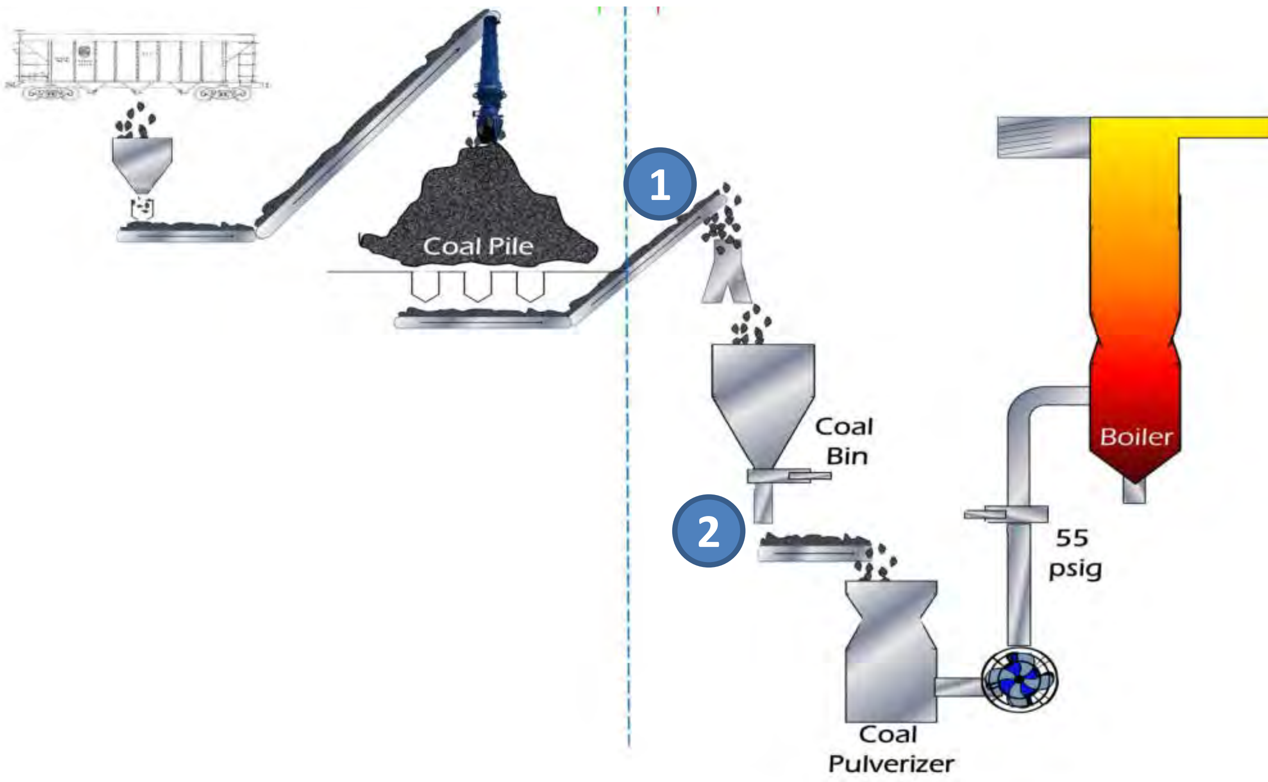
- Increase "native" Hg capture
  - Combustion modifications
  - Burn coal blends
  - Use additives or catalysts to increase oxidized Hg
  - Addition of scrubber to removed oxidized Hg
- Use of sorbents
  - Activated carbon
  - Oxidizing agents or additives plus sorbents

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

How Is Are Halogens Added?

- A liquid solution added to the coal either
  1. At the coal belt (before the bunker or day silo)
  2. At the coal feeders



How Is Are Halogens Added?

- A liquid solution added to the coal either
  1. At the coal belt (before the bunker or day silo)
  2. At the coal feeders
- Addition rate is often expressed in parts-per-million halogen by weight on the coal or gal/hr of solution
- Example: $CaBr_2$
  - Solution is 52 wt% $CaBr_2$ in water => 42 wt% bromine in solution
  - Density of solution is 14.2 lb/gal

How to calculate additive solution flow rate:

$$[\,Solution\ gal/hr] = \frac{[ppmw\ Br]10^{-6}\left[Coal\ {}^{lb}/_{hr}\right]}{0.42\ {}^{lb\ Br}/_{lb\ soln}\ 14.2\ {}^{lb\ soln}/_{gal}}$$

Case Study: 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 Testing at Labadie Unit 3

- Objective: Demonstrate MATS compliance levels of Hg emissions combining M-Prove additive and powdered activated carbon (PAC)
- Unit description:

Parameter Identification	Units	Unit 3
Boiler Manufacturer		Combustion Engineering
Furnace Type		Tangential Firing
Nominal Unit Rating	MWg	630
NO_x Control		LNCFS™ Level III, SOFA
SO_x Control		Low Sulfur Coal
Particulate Matter Control Device		Cold Side ESPs
ESP Manufacturer		"A" & "B" Research-Cottrell; "C" Flakt
Typical ESP Operating Temperature	°F	325-355
Typical APH Inlet Operating Temperature	°F	730
Flue Gas Flow Rate at Stack	MMacfm	2.2
Flue Gas Conditioning Agent		SO_3 or RESPond FGC
LOI	wt%	<0.5

M-Prove Testing at Labadie Unit 3

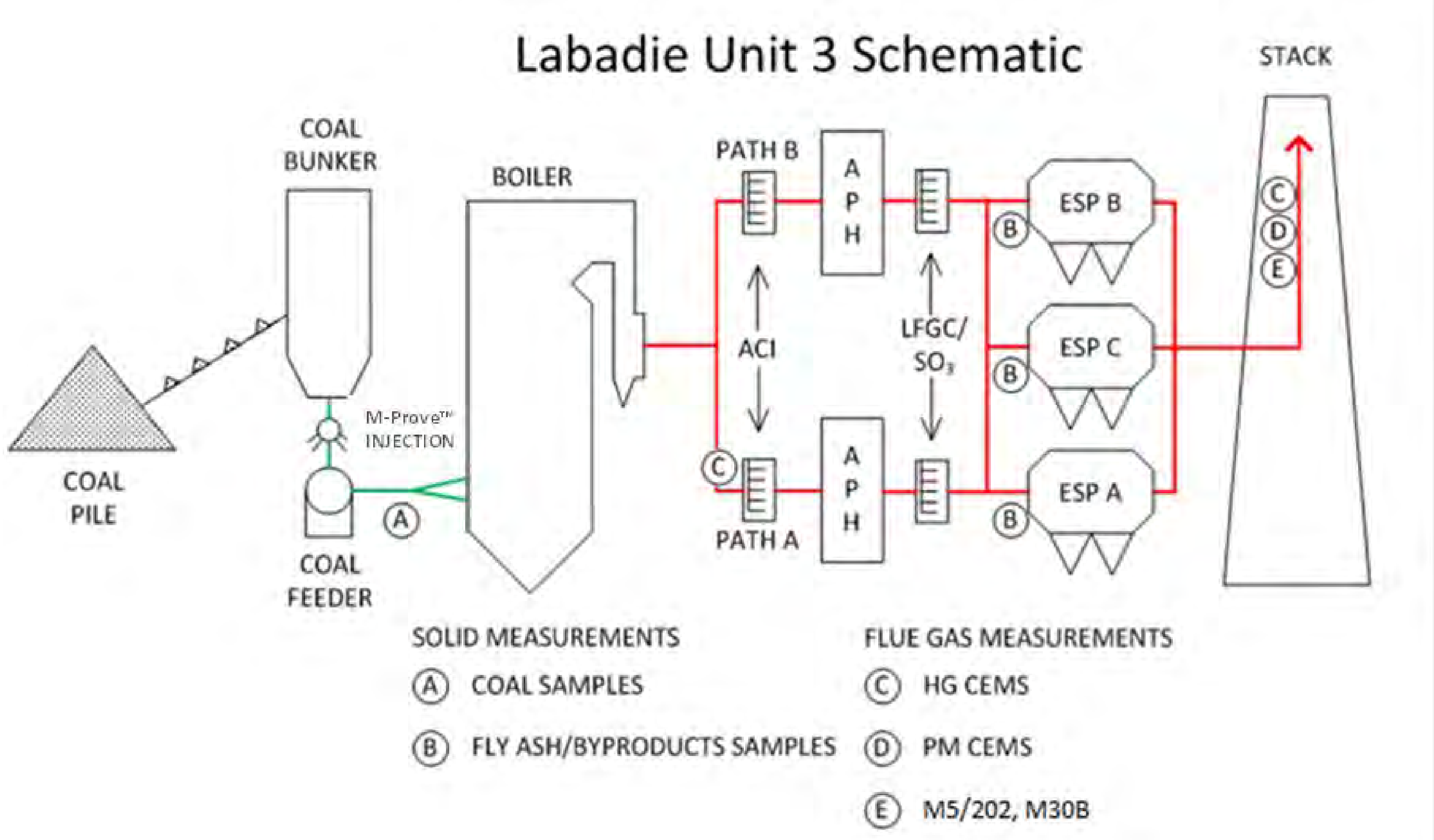
- Objective: Demonstrate MATS compliance levels of Hg emissions combining M-Prove additive and powdered activated carbon (PAC)
- Powder River Basin (PRB) coal:

Date	Ash, wt%	S, wt%	Btu/lb	Hg, lb/TBtu	Cl, µg/g
Day 1	4.80	0.30	8,858	5.70	< 15
Day 2	4.81	0.27	8,831	5.81	< 15
Day 3	4.36	0.23	8,806	4.88	< 15
Day 4	4.47	0.22	8,868	6.02	< 15
Day 5	4.53	0.24	8,791	4.64	< 15
Day 6	4.72	0.28	8,854	5.48	< 15
Day 7	4.67	0.32	8,836	5.88	< 15
Day 8	4.63	0.28	8,851	7.11	< 15

Corrected to 27% moisture

M-Prove Testing at Labadie Unit 3

- Sampling Locations:



Additive Injection

- ACI injection upstream of air preheaters
  - Twelve lances with six in each side of the split flue gas path
  - Lances staggered in length across width of the 9-foot deep duct
- Several different PACs were evaluated in the test program:
  - PAC A: standard lignite-based non-brominated PAC used for mercury capture
  - PAC B: enhanced non-brominated PAC used for mercury capture in short-residence times
  - PAC C: brominated lignite-based PAC
- M-Prove Additive injection using temporary pump skid
- Injected into one coal feeder

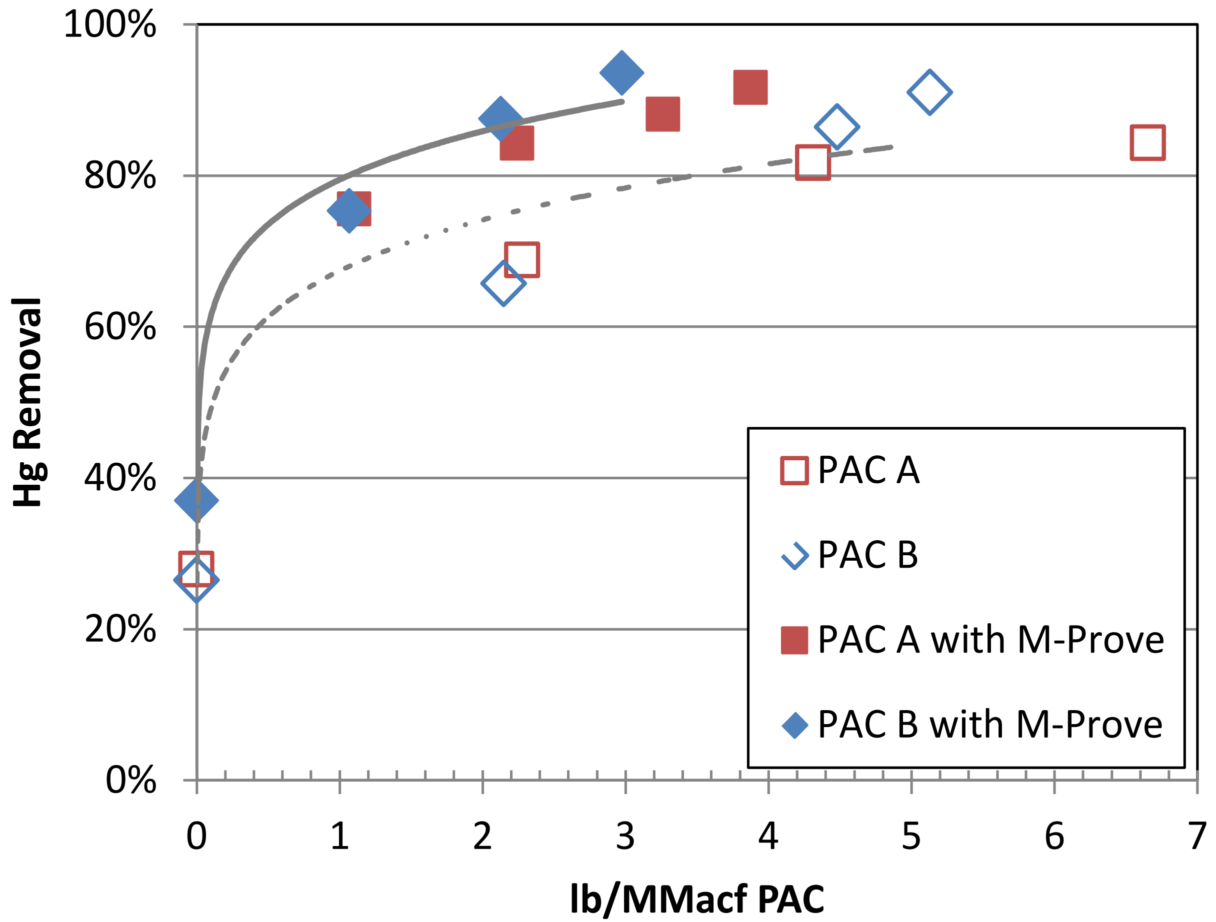
Baseline Hg Emissions

- "Native" Hg capture <25%

	Hg Emission Rate [lb/TBtu]		Hg Removal Based on CEMS [%]
	Econ.	Stack	Stack vs. Econ.
Day 1	8.8	6.6	25.0
Day 2	7.4	5.4	27.0
Day 3	9.1	9.9	-8.8

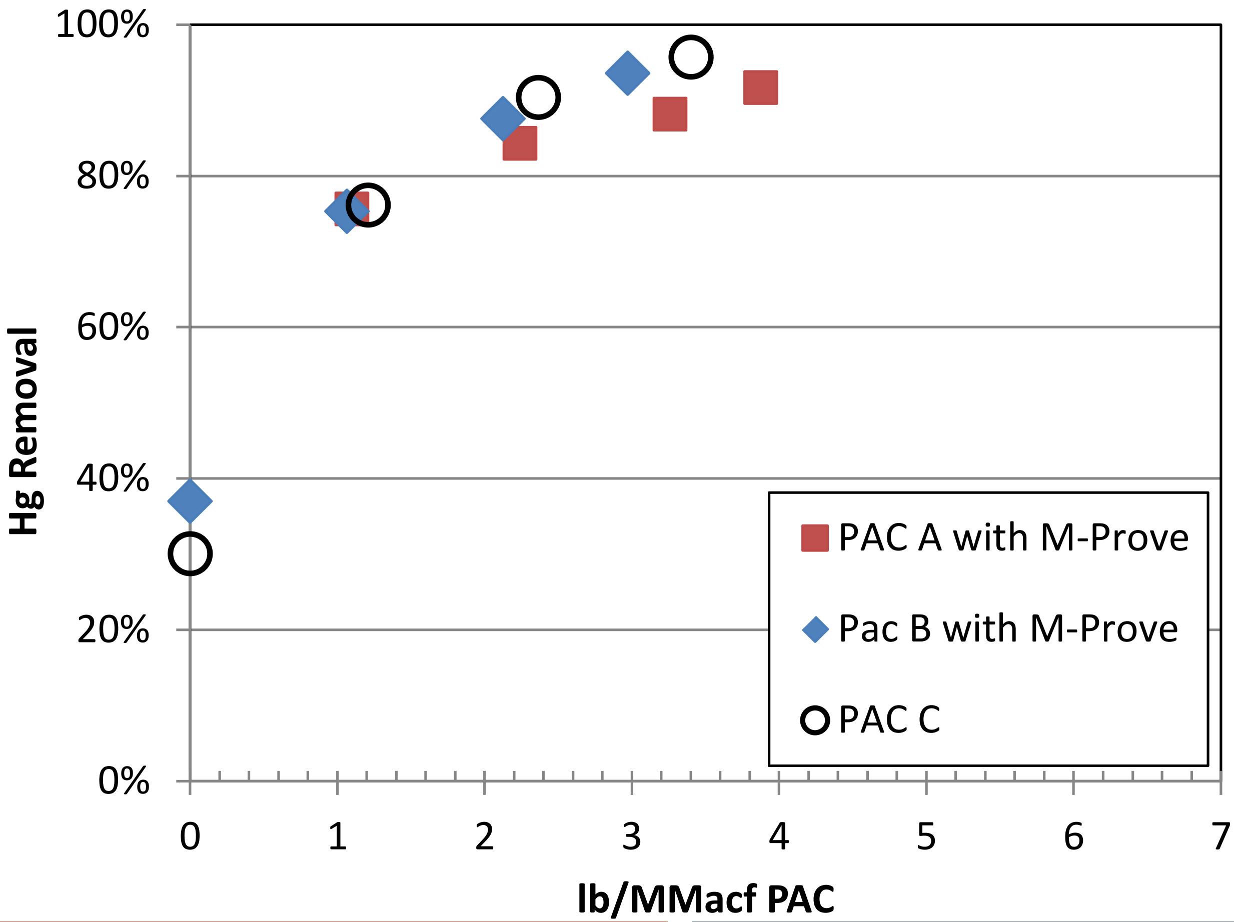
Hg Removal:
M-Prove Additive + Non-brominated PAC

- 5 ppmw M-Prove Additive
- Similar results for PAC A and PAC B



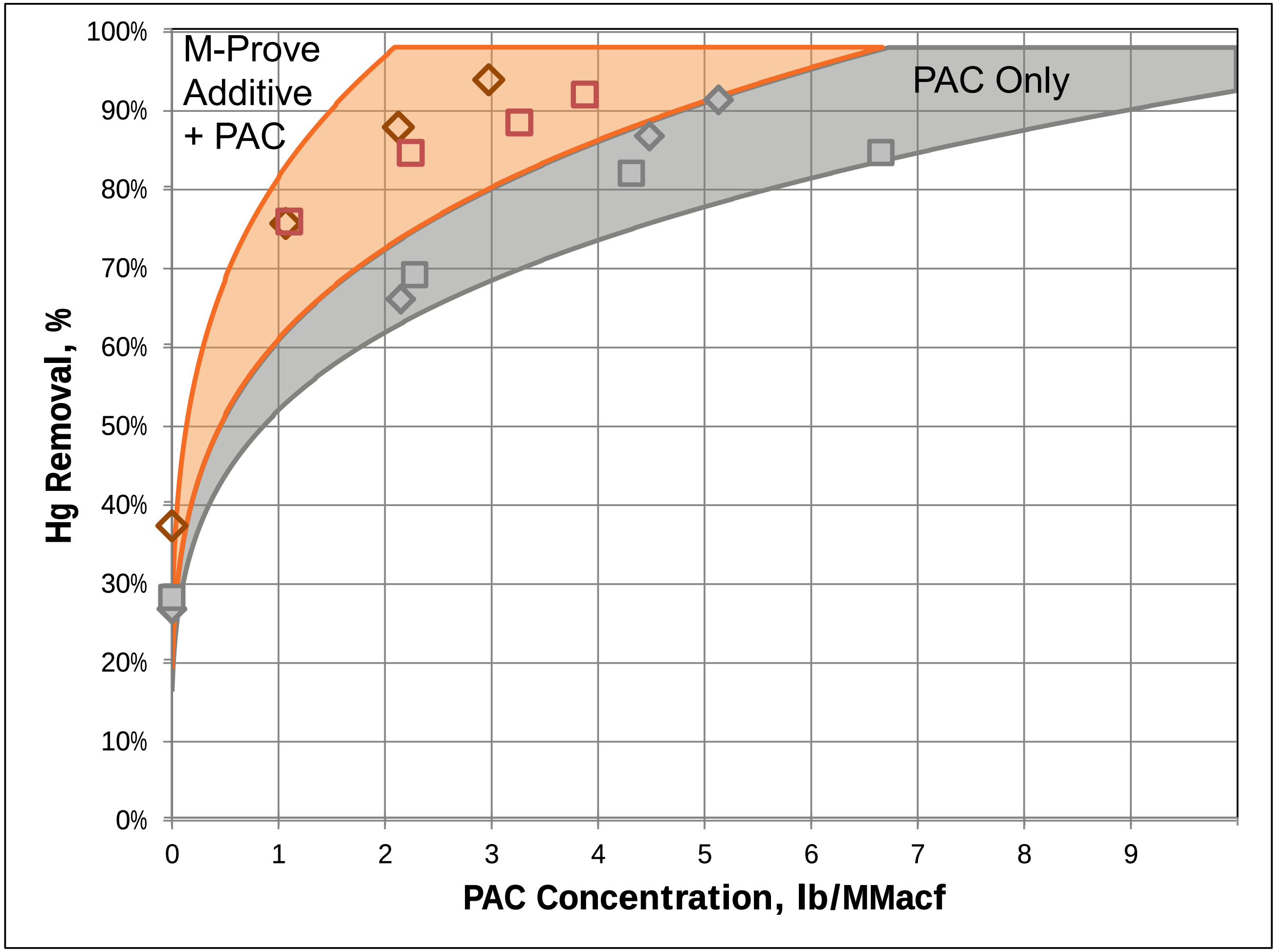
Hg Removal:
Comparison with Brominated PAC

- 5 ppmw M-Prove Additive plus non-brominated PAC performed similarly to brominated PAC (PAC C)



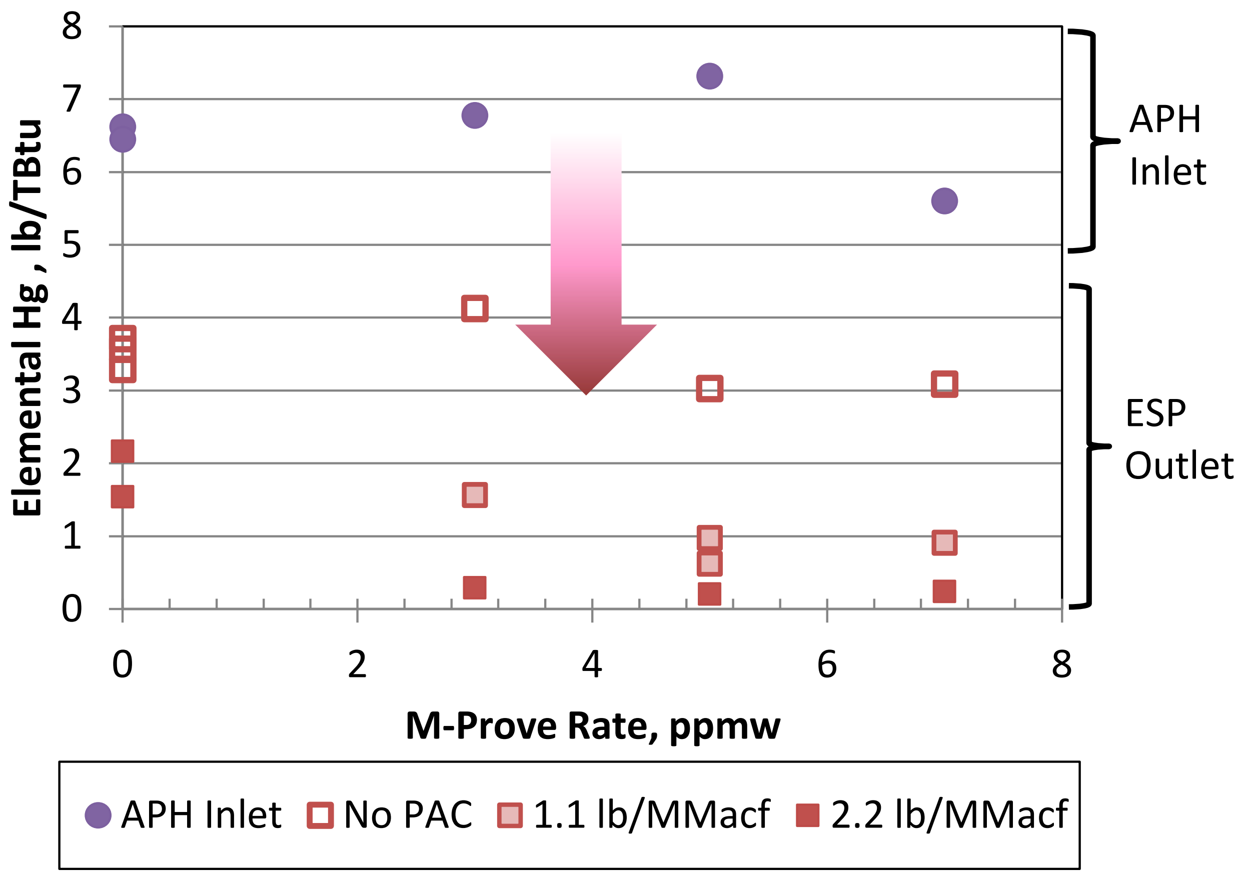
Hg Removal: Comparison with Other Plants

- M-Prove Additive has been tested at multiple plants with this configuration & coal type
- How do the Labadie results compare?



Hg Speciation

- M-Prove Additive reduces Hg^0 at ESP outlet => less than 1 lb/TBtu
- THAT IS, the fraction of oxidized Hg (Hg^{2+}) at ESP outlet increases
- PAC injection enhances oxidation of Hg at ESP outlet



Case Study Summary

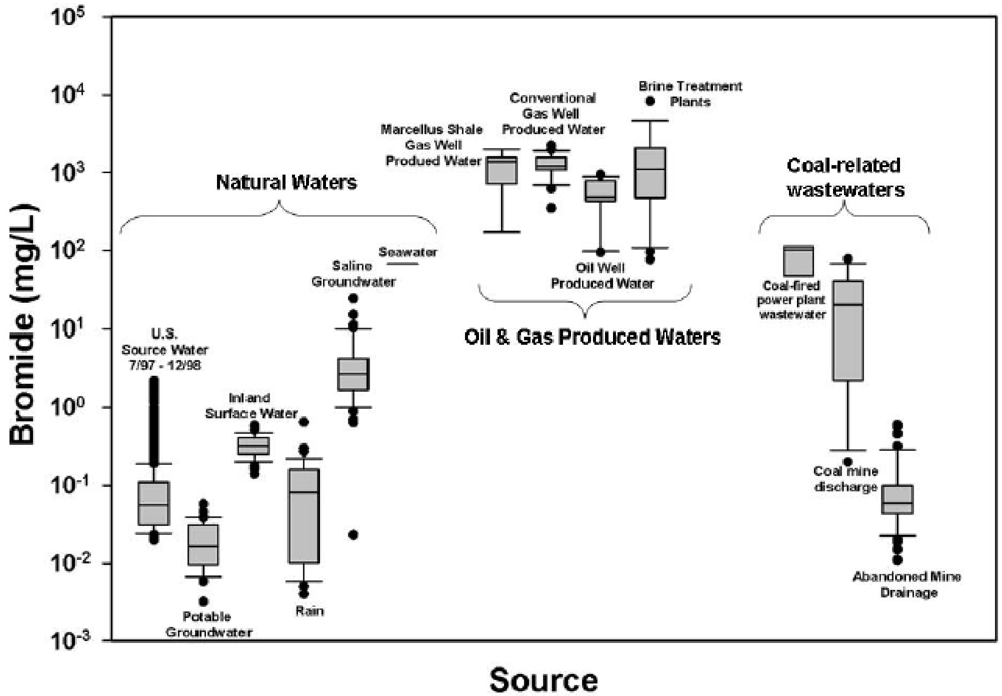
- M-Prove Technology enhanced the effectiveness of non-brominated PAC at Labadie Unit 3, cutting in half the amount of non-brominated PAC required for a given level of mercury removal
- M-Prove Technology plus non-brominated PAC was comparable to the performance of a brominated PAC.
- The combination of M-Prove Technology and PAC decreased the amount of elemental mercury at the ESP outlet dramatically
- Very low levels of M-Prove additive were needed
  - Such low levels reduce long-term corrosion risks to cut maintenance and repair costs and to enhance system reliability

Halogens in Power Plant Wastewater

Implications and Issues

Power Plant Wastewater

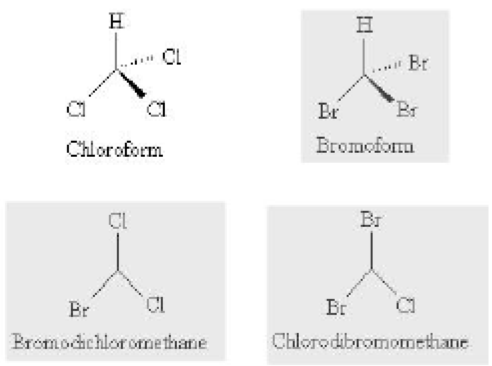
- Halogens in FGD wastewater discharge could increase concentration of halogens in rivers, etc.
- Bromine has been studied the most, because of an association with oil & gas extraction



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

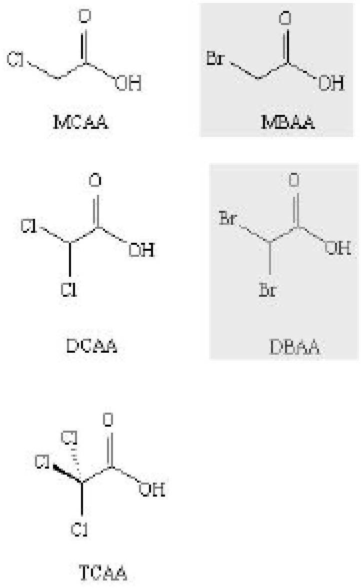
- Bromide in wastewater is probably not a great idea if the plant discharges upstream of a drinking water treatment facility
  - During disinfection, chlorine (typically applied as hypochlorous acid, HOCl) reacts with organics present in the source water (natural organic matter or NOM) to form chlorinated 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

- 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!

THANK YOU!

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