

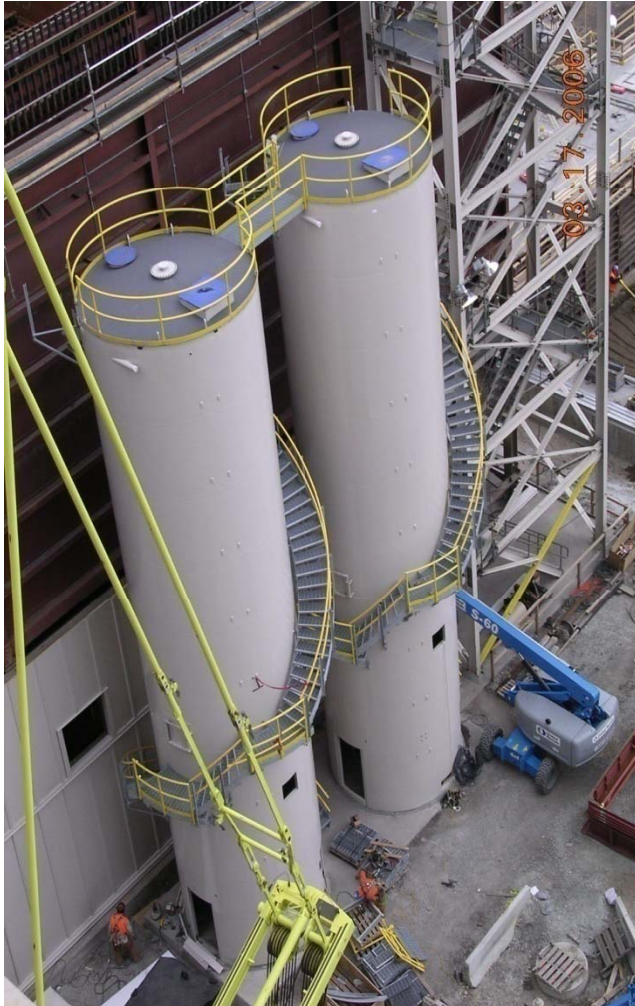
REINHOLD ENVIRONMENTAL Ltd.



2012 NO_x-Combustion Round Table & Expo Presentation

February 13-14, 2012, in Columbus, OH / Hosted by AEP

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Mercury Control in the Boiler

Connie Senior

*Reinhold NOx Roundtable
Columbus, Ohio
February 13-14, 2012*

ADA: Innovate, Develop, Commercialize

Motivation for This Presentation

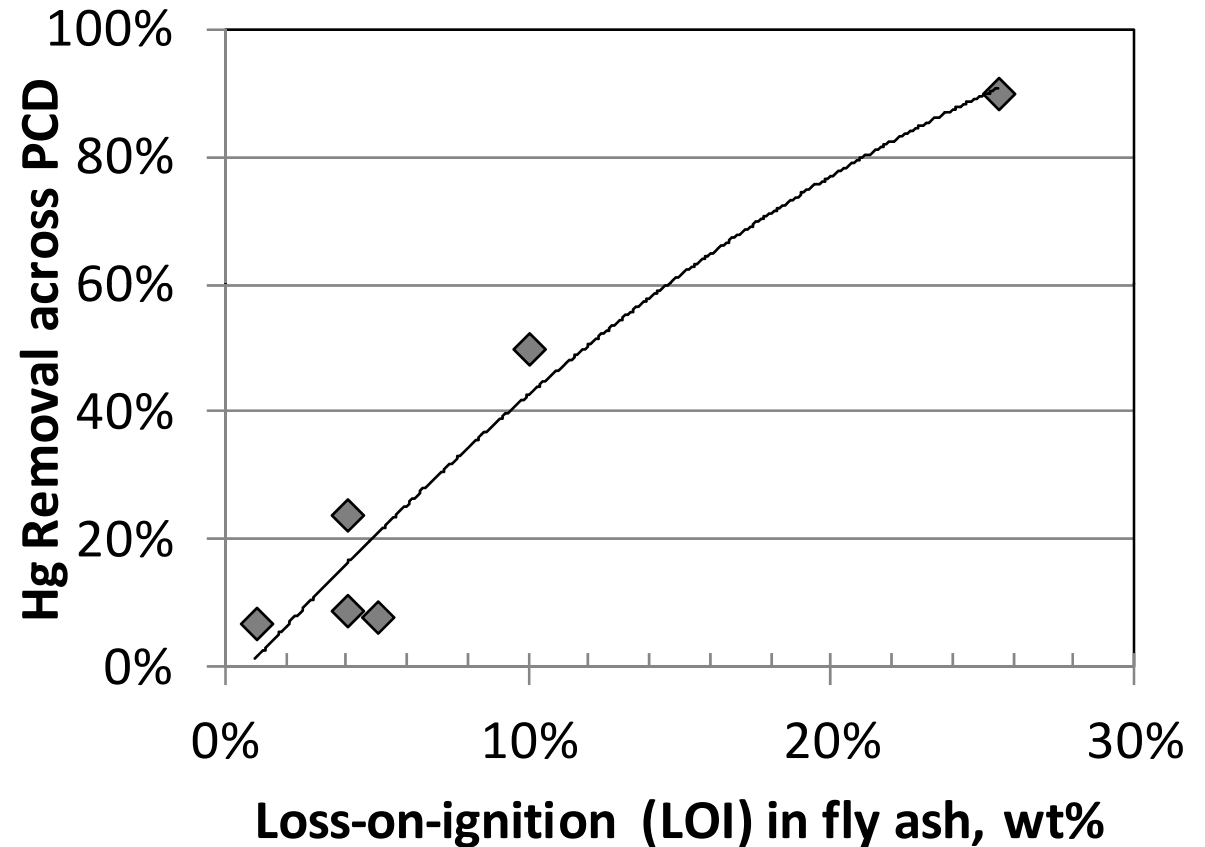
- There's more than activated carbon, when it comes to mercury control in coal-fired boilers
- Chemistry of mercury in the boiler and the interaction of mercury with other control processes, like SCR, affect the performance of downstream mercury control from activated carbon injection or scrubbers
- Topics to be discussed: control of unburned carbon, halogen injection, impact of SCRs

Hg Removal in the Boiler

- Hg isn't removed in the boiler
- But, some things that happen in the boiler affect how much mercury can be removed downstream
- How is Hg removed?
- Adsorption on particles (fly ash, sorbents) and removal in the particulate control device
- Absorption of oxidized mercury in scrubbers

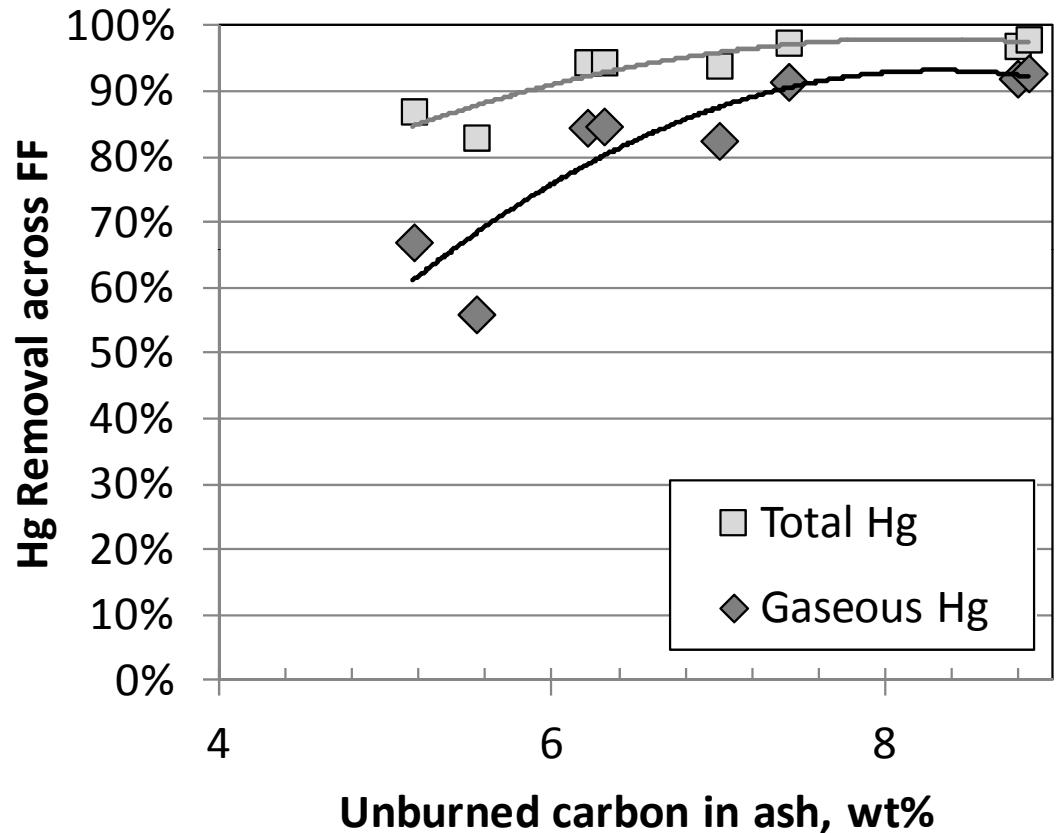
Unburned Carbon & ESPs

- Data from bituminous coals in pc-fired boilers



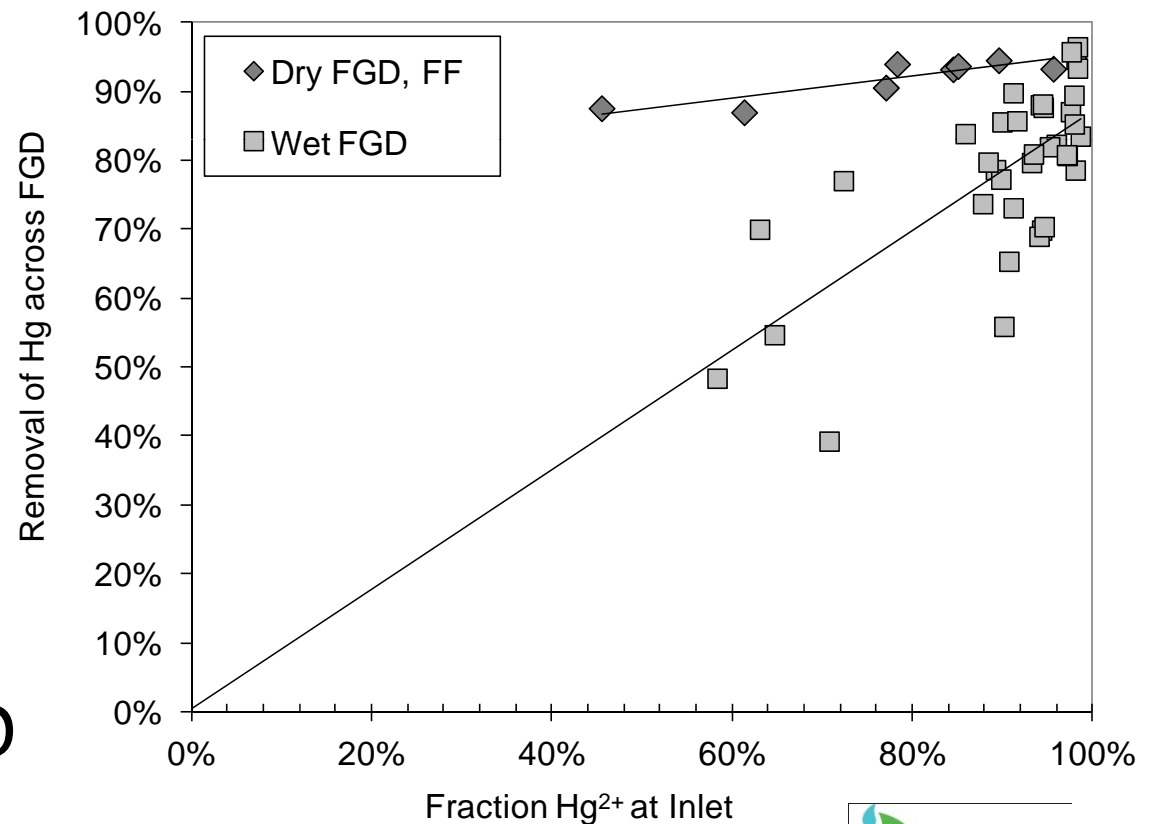
Unburned Carbon & Fabric Filter

- T-fired boiler with low-NO_x combustion system, low-sulfur fuel
- Unburned carbon changed by changing combustion parameters



Absorption

- How do we get more Hg into the scrubber?
- Higher fraction of oxidized Hg at scrubber inlet => higher Hg removal
- Factors:
 - Halogen in fuel
 - Re-emission of Hg^0 in wet FGD



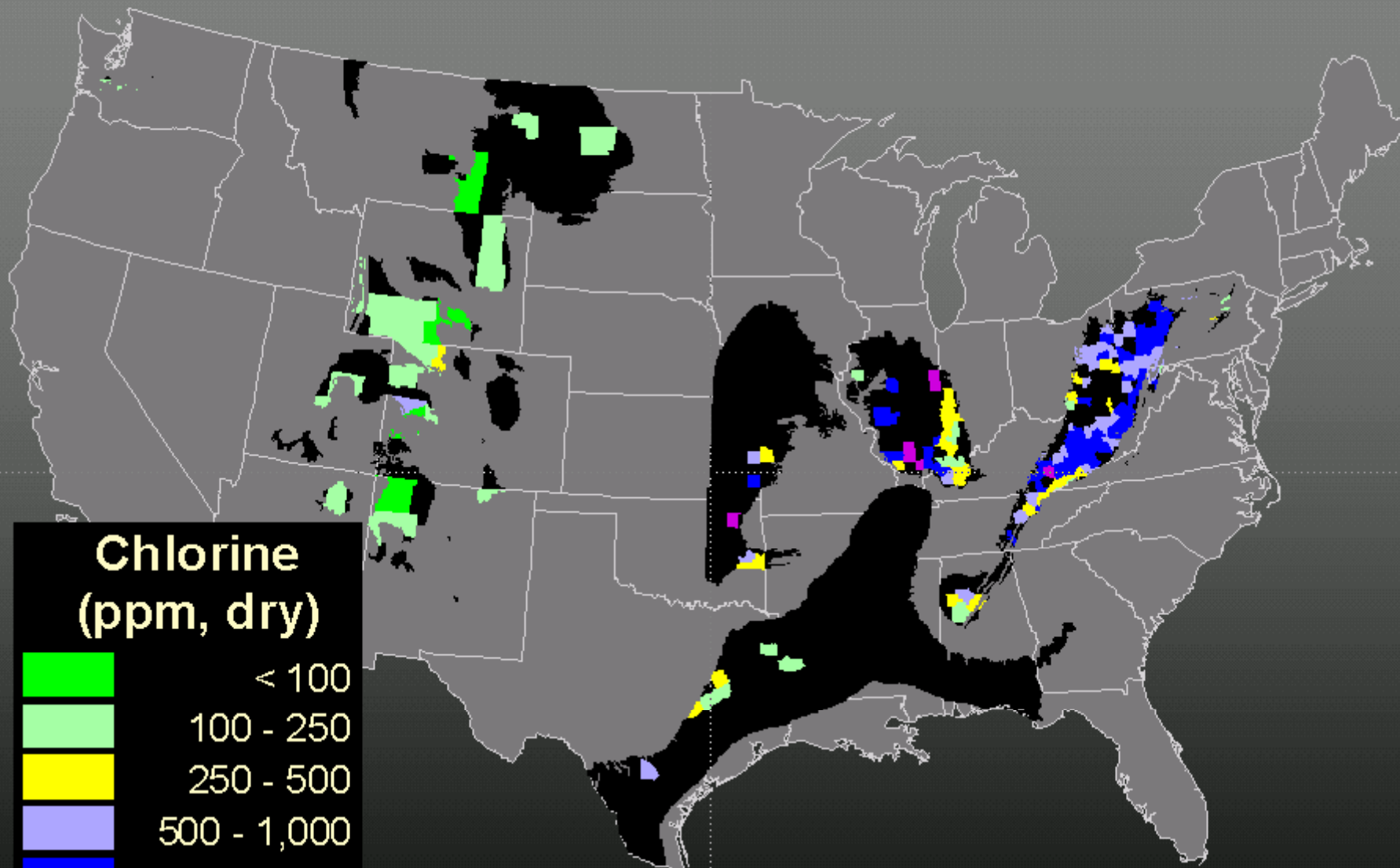
Source: NETL, EPRI demos



Why Add Halogens?

- Adding halogens to fuel or flue gas:
 - Halogen content of US coals varies widely

Chlorine in Coal



**Chlorine
(ppm, dry)**

< 100

100 - 250

250 - 500

500 - 1,000

1,000 - 2,000

2,000 - 4,450

County average, ICR 2 data

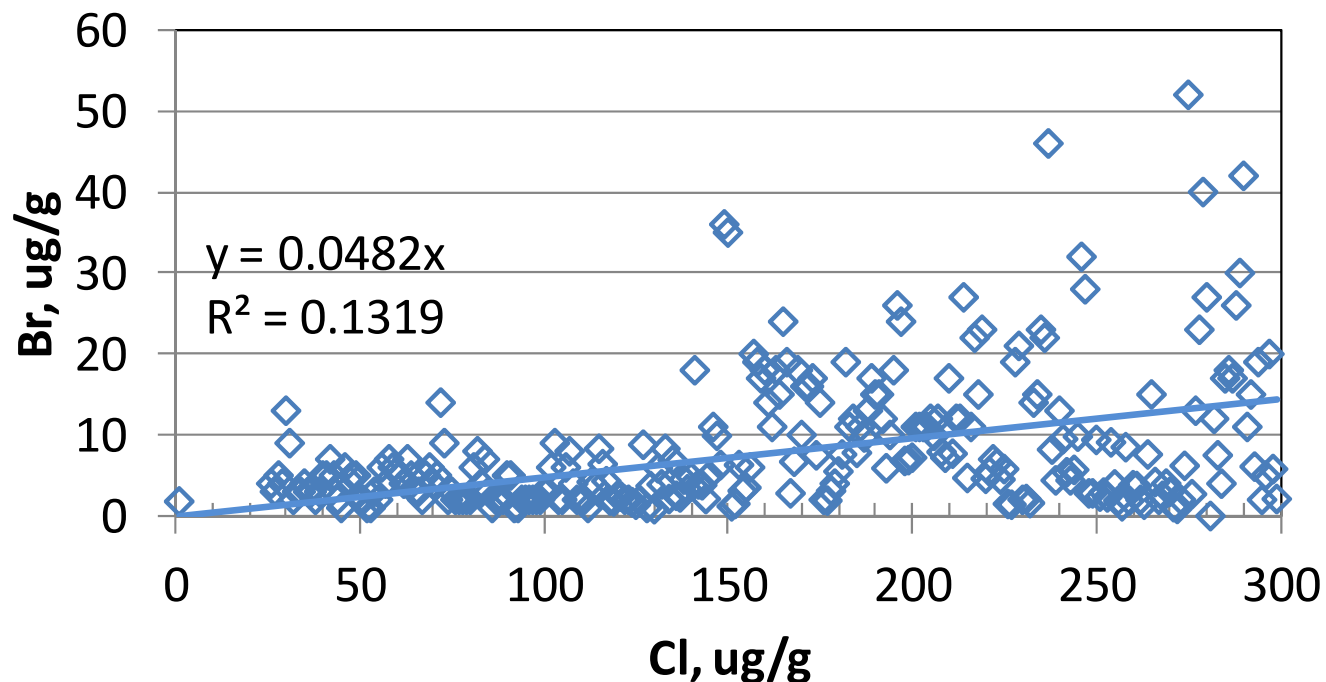
<http://ugs.utah.gov/emp/mercury/index.htm>



Why Add Halogens?

- Adding halogens to fuel or flue gas:
 - Halogen content of US coals varies widely
 - Bromine content typically 1% to 4% of chlorine content

Eastern Interior (Illinois Basin)

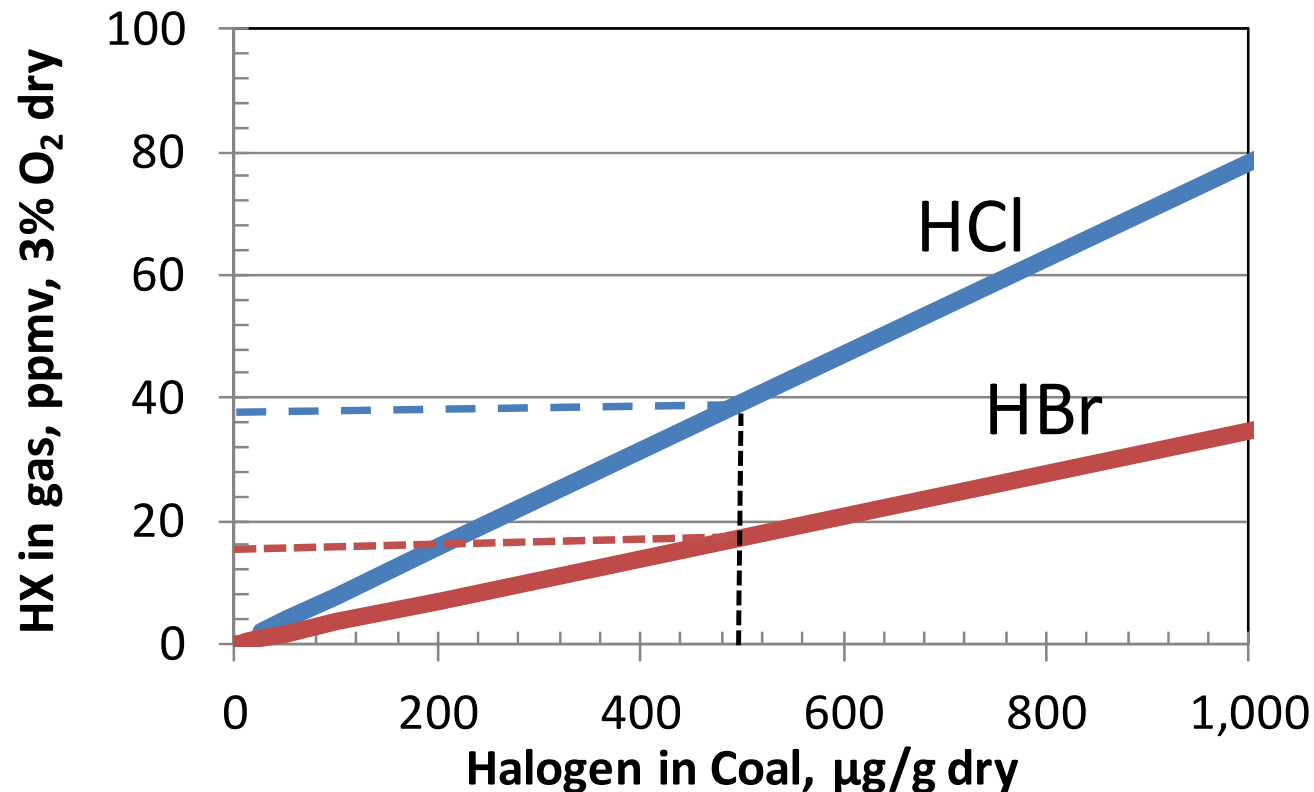


Source: USGS COALQUAL database



Why Add Halogens?

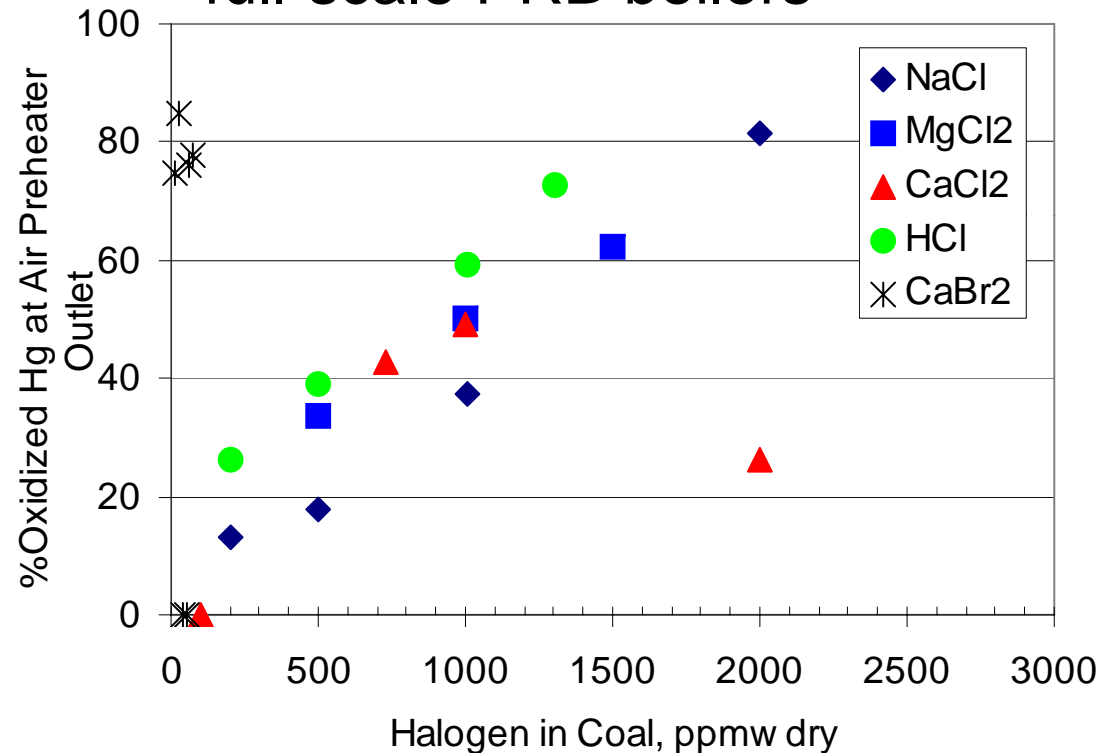
- Adding halogens to fuel or flue gas:
 - 500 $\mu\text{g/g}$ Cl in coal = ~40 ppmv HCl in flue gas
 - 500 $\mu\text{g/g}$ Br in coal = ~17 ppmv HBr in flue gas



Why Add Halogens?

- Adding halogens to fuel or flue gas:
 - Halogen content of US coals varies widely
 - Oxidation of Hg and capture of Hg on fly ash enhanced with additions of halogens, like Cl and Br

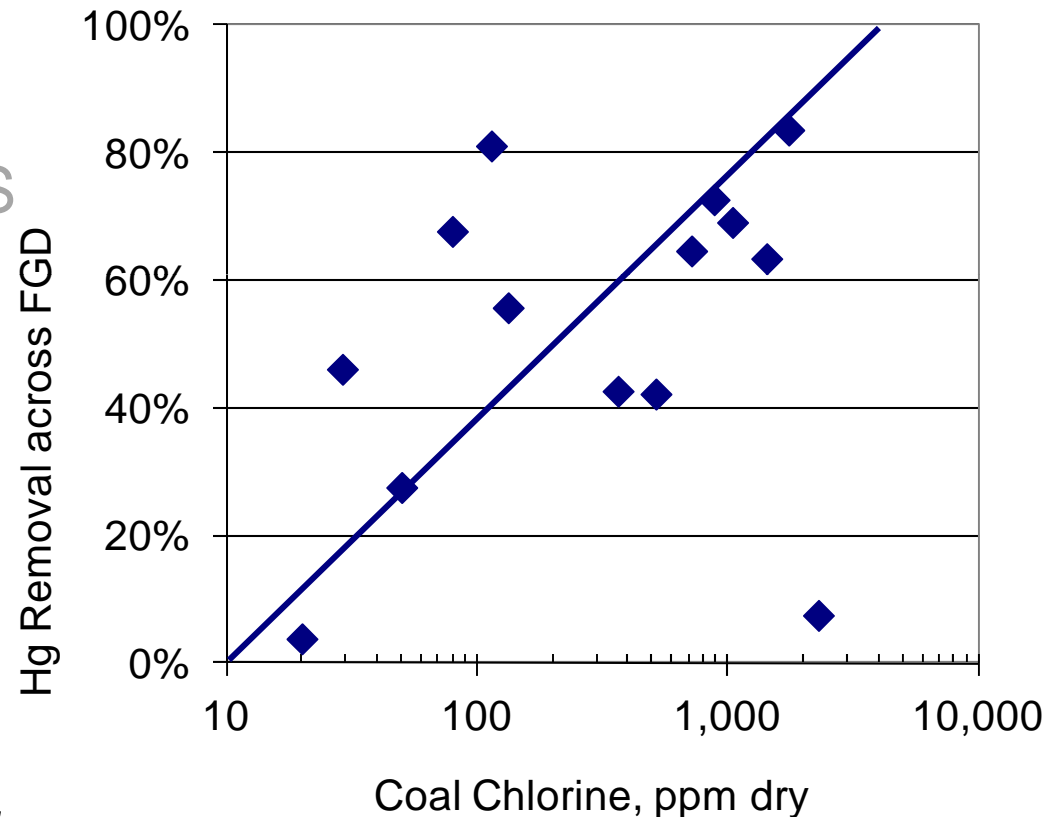
Halogen addition at various full-scale PRB boilers



Source: Dombrowski et al., 2006

Why Add Halogens?

- Adding halogens to fuel or flue gas:
 - Halogen content of US coals varies widely
 - Oxidation of Hg and capture of Hg on fly ash enhanced with additions of halogens, like Cl and Br
 - Many plants' APCDs can take advantage of native capture



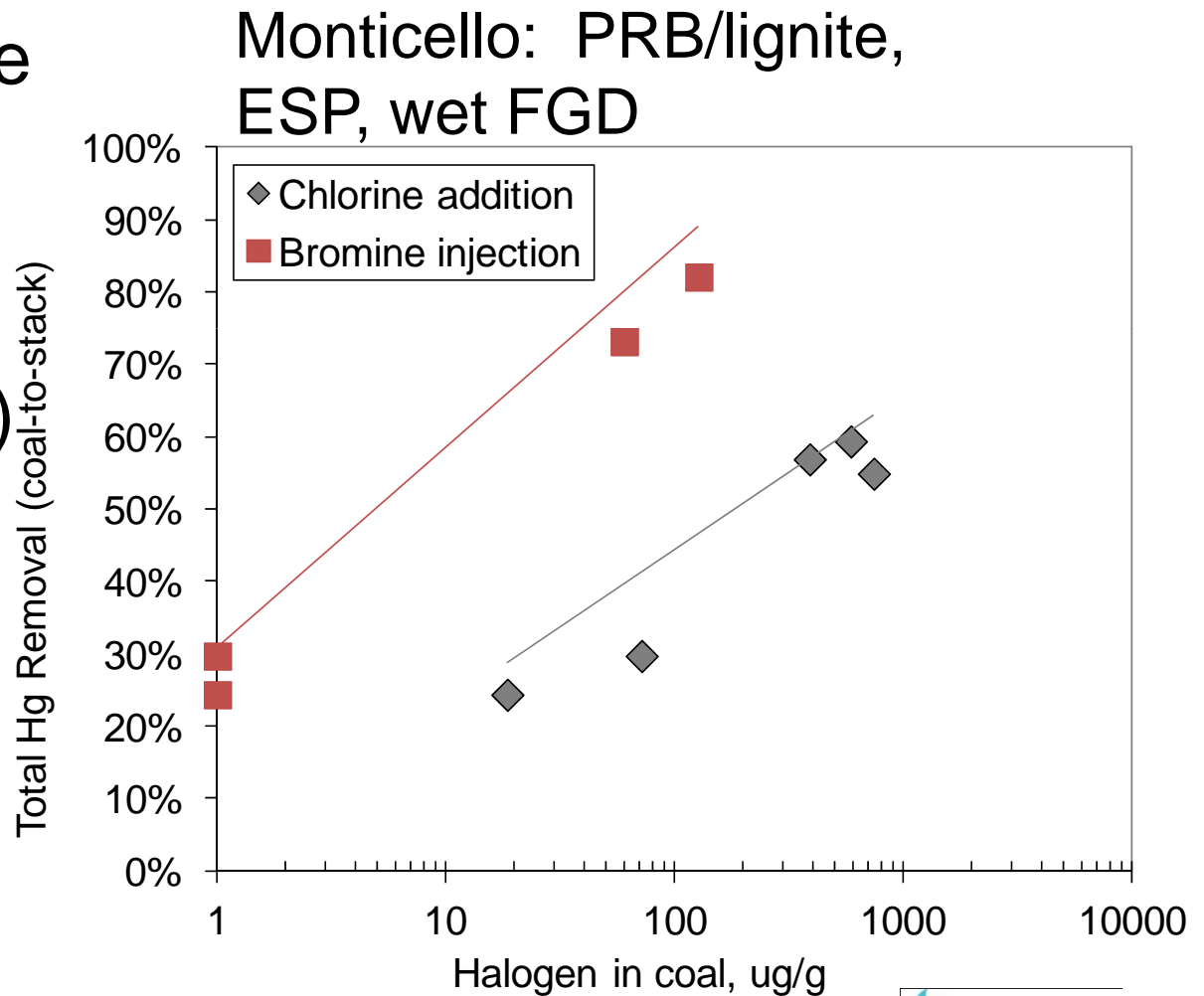
Source: 1999 ICR

Summary: Why Add Halogens?

- Adding halogens to fuel or flue gas:
 - Halogen content of US coals varies widely
 - Oxidation of Hg and capture of Hg on fly ash enhanced with additions of halogens, like Cl and Br
 - Many plants' APCDs can take advantage of native capture
- Adding halogens to activated carbon increases the ability to capture elemental Hg in low-halogen flue gas

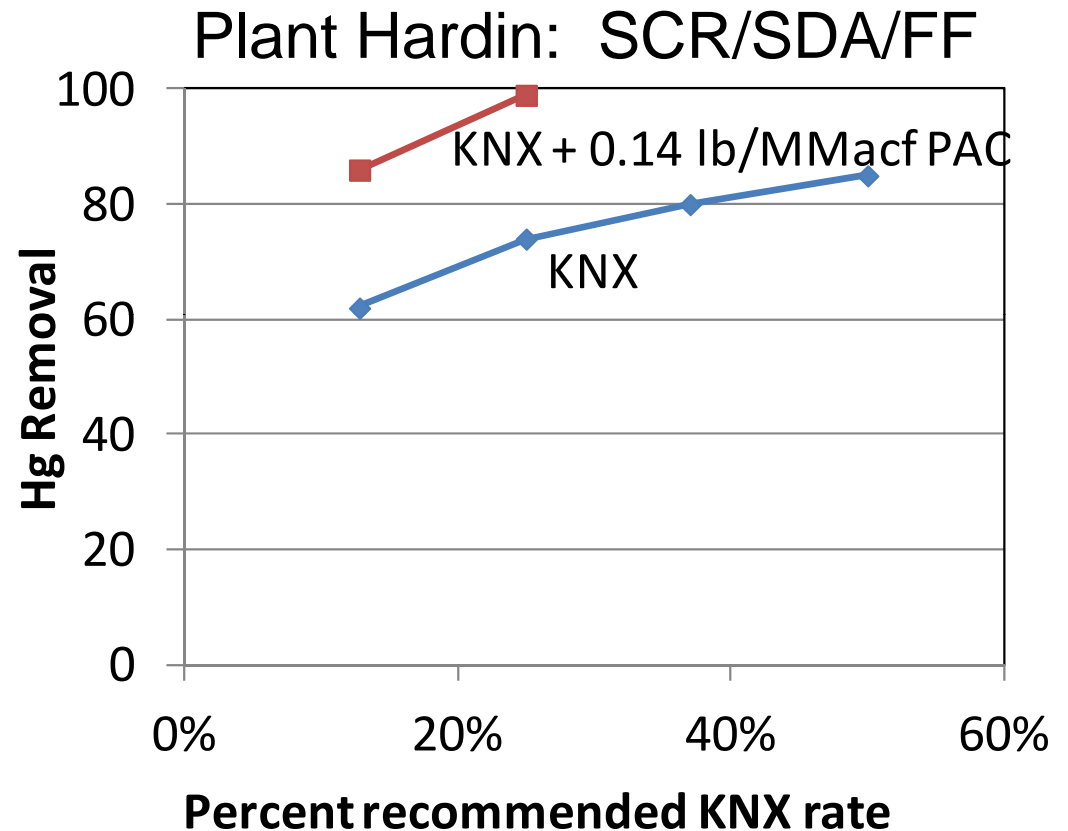
How Effective Are Halogens?

- Halogens increase oxidized mercury: Br more effective than Cl (on an equal mass basis)
- Increased Hg removal across scrubbers



How Effective Are Halogens?

- Halogens increase oxidized mercury: Br more effective than Cl (on an equal mass basis)
- Increased Hg removal across scrubbers
- Halogens increase effectiveness of PAC

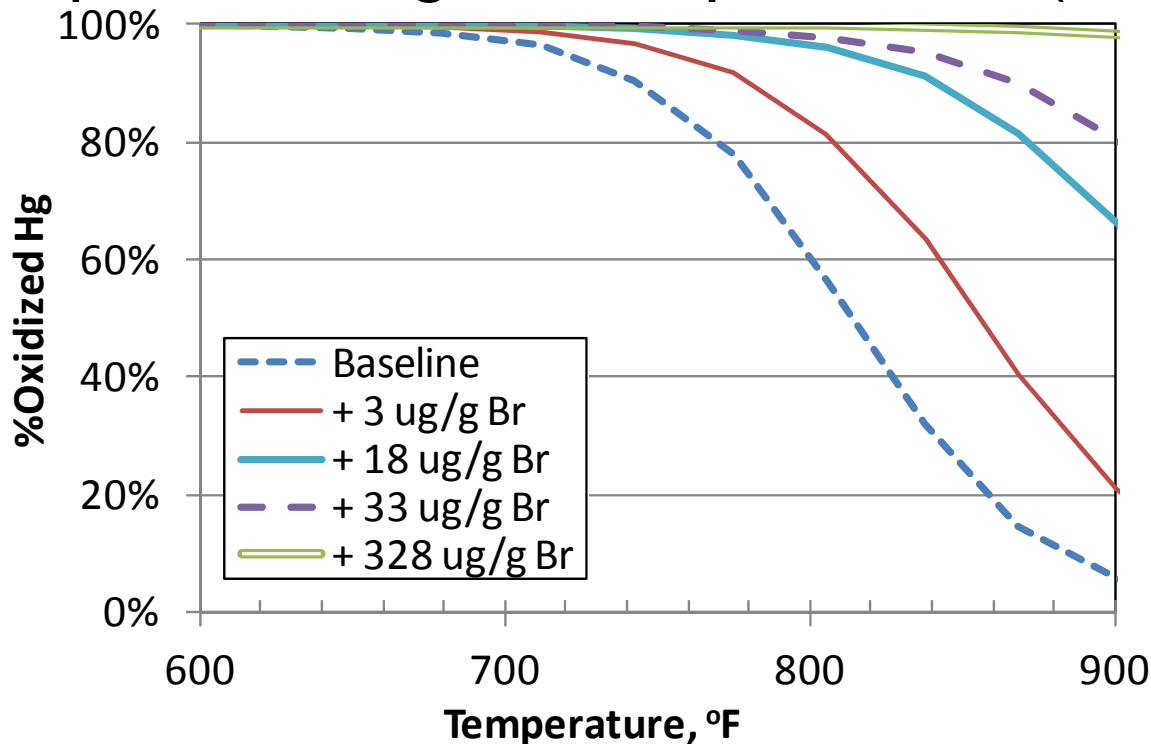


Source: DOE/EPRI sampling campaigns



Effect of SCRs on Added Halogens

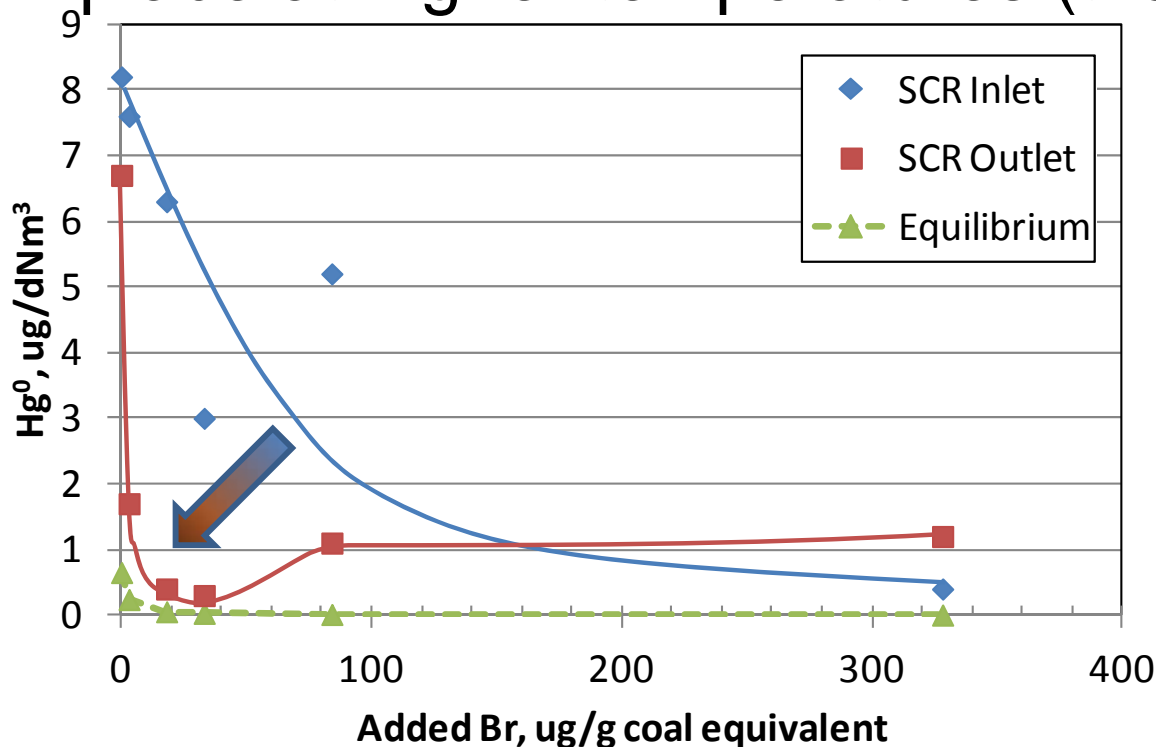
- Catalysts drive reactions toward equilibrium
 - Results will be catalyst-specific
- Adding Br to the fuel makes the shift to Hg^{2+} take place at higher temperatures (than Cl)



Equilibrium modeling of Plant Miller data of Berry *et al.*

Effect of SCRs on Added Halogens

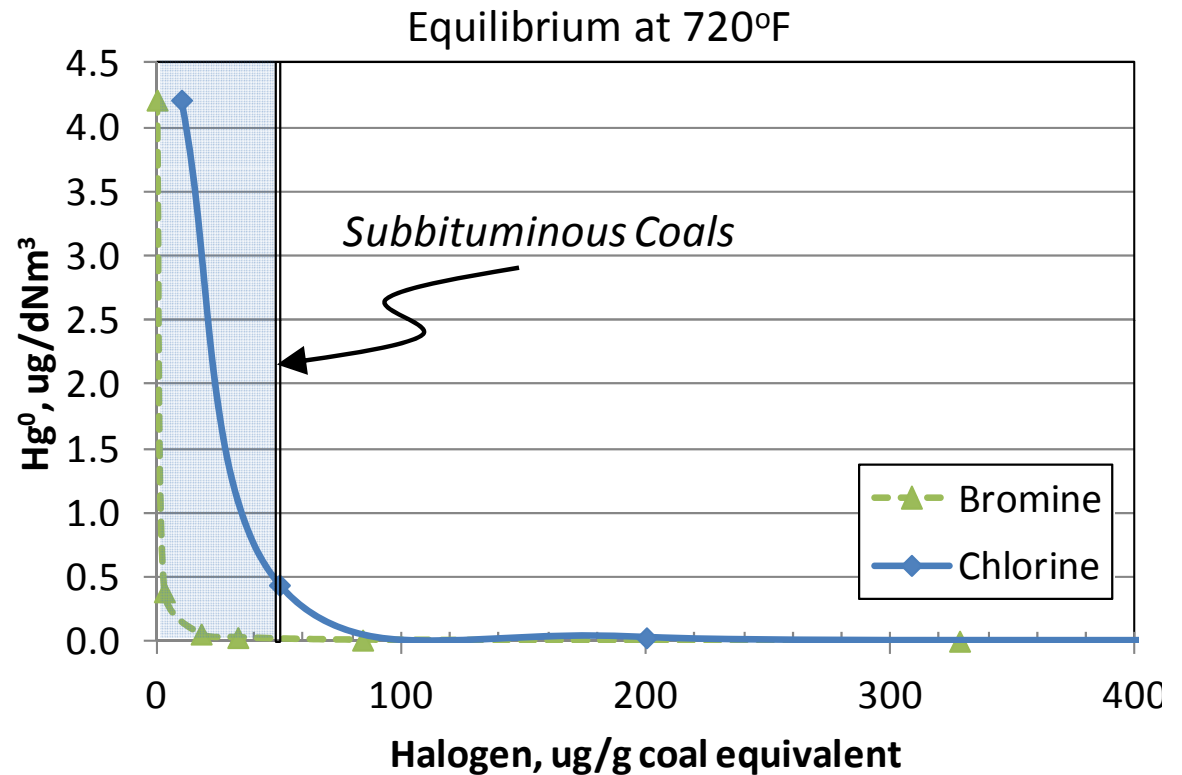
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Comparison of Plant Miller data of Berry *et al.* with calculated equilibrium

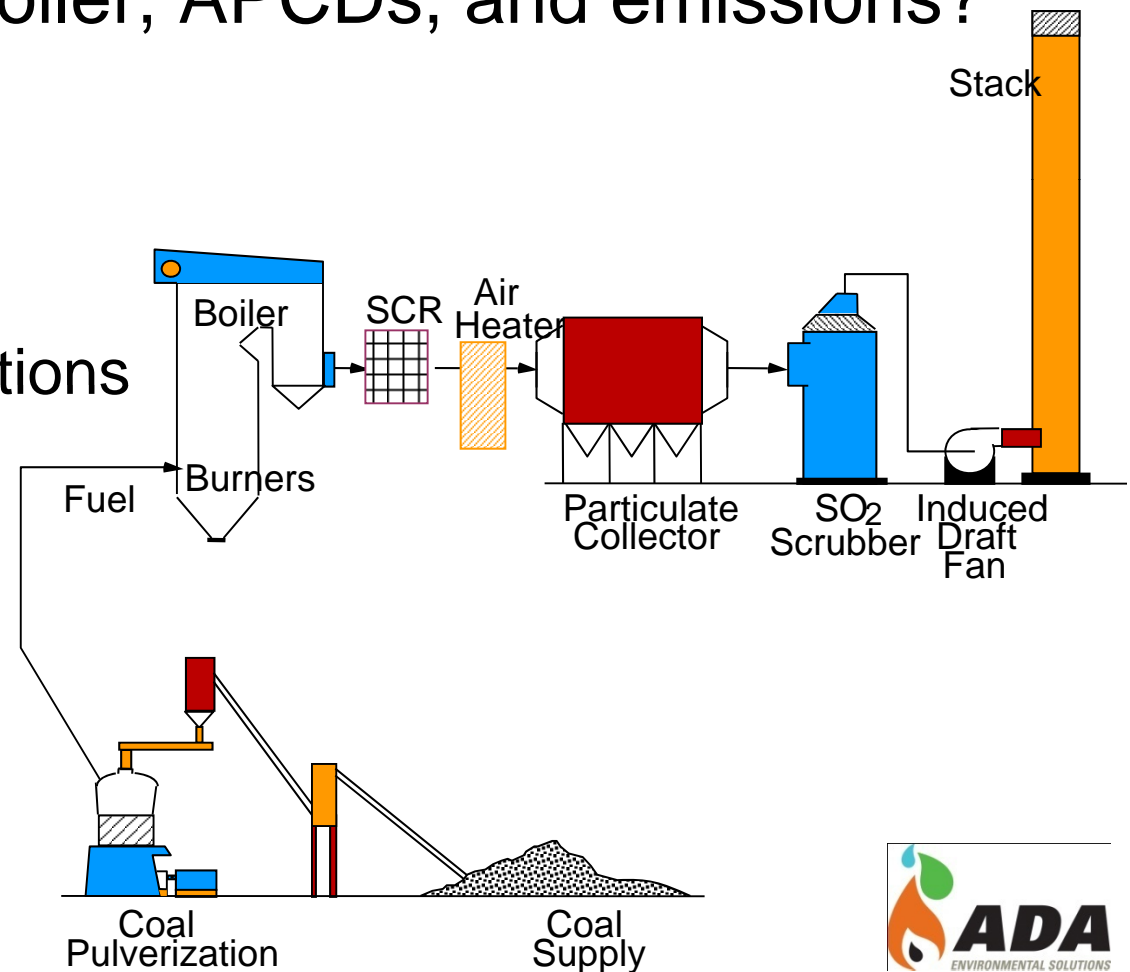
Effect of SCRs on Added Halogens

- Bromine is more efficient (equal mass basis) than chlorine at oxidizing Hg across SCRs
 - Results will be catalyst-specific
 - Subbituminous (low-chlorine) coals only



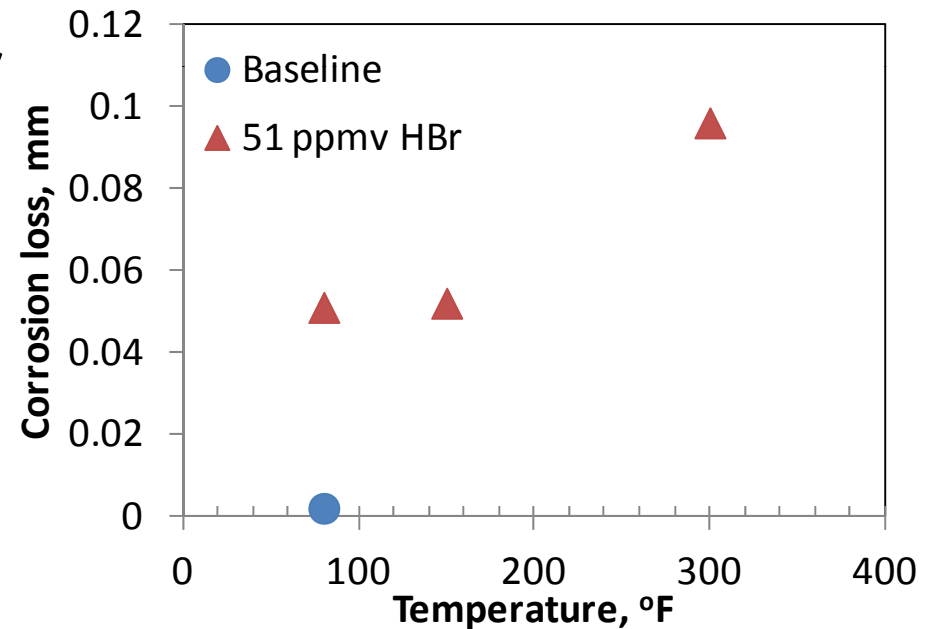
Fate and Impacts of Halogens

- What are the potential impacts of halogen addition on the boiler, APCDs, and emissions?
 - Corrosion
 - Fly ash
 - Stack emissions
 - Scrubber interactions



Corrosion in Flue Gas

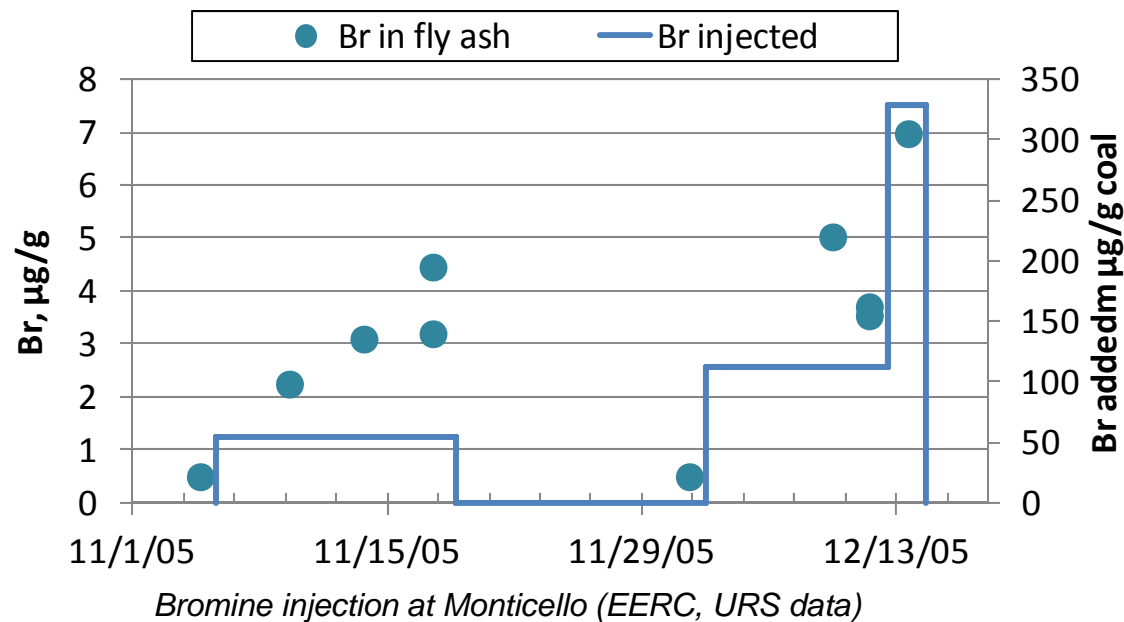
- Chlorine corrosion in furnaces can occur for very high levels of chlorine in coal ($> 2000 \mu\text{g/g}$)
 - Bromine addition at much lower concentrations
- Indirect evidence that HBr might be more corrosive than HCl at flue gas temperature
- No direct comparison, but HBr corrosion higher than baseline (no HBr) in simulated flue gas (6-month study)



Zhuang et al., 2009

Bromine Addition: Fly Ash Impacts

- Bromine additive or brominated PAC results in increase in Br in fly ash
- Example: Br injection at Monticello (C-ESP)

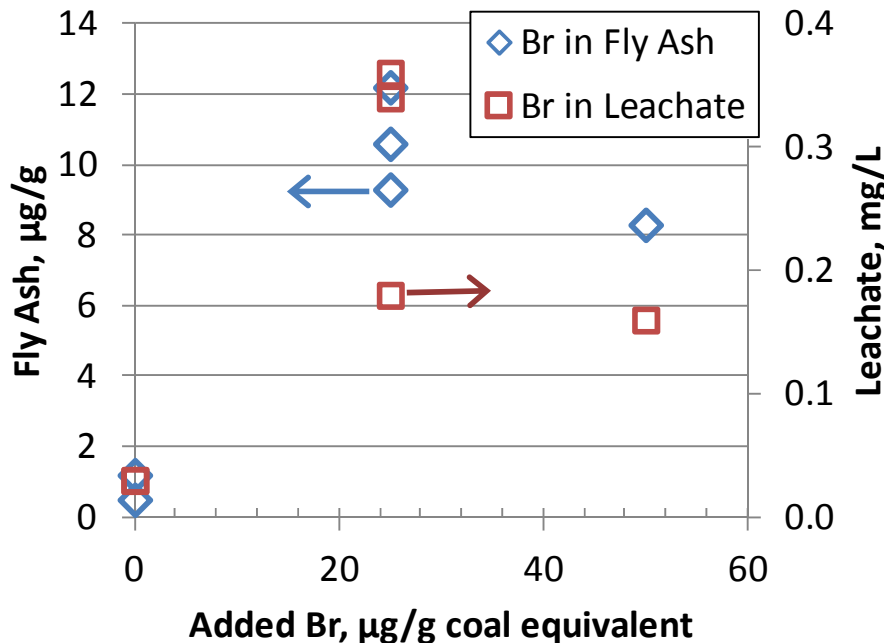


Bromine Addition: Fly Ash Impacts

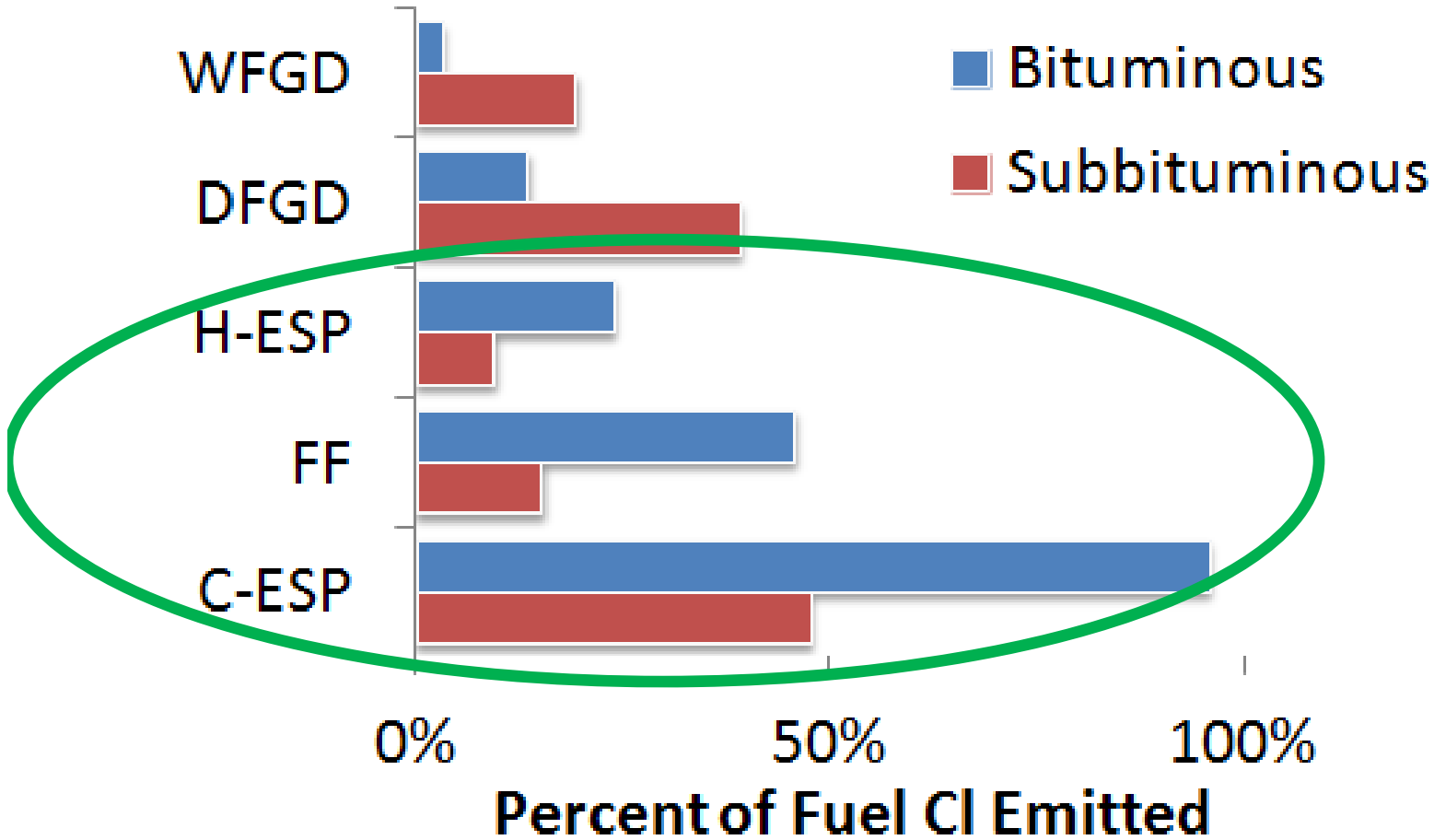
- Bromine additive or brominated PAC results in increase in Br in fly ash
- Example: Br injection at Plant Miller (PRB, C-ESP)

- According to the authors:

- Hg concentration in fly ash didn't increase with Br injection
- 1% of Br captured by fly ash
- 50% of Br on fly ash leached in SPLP test

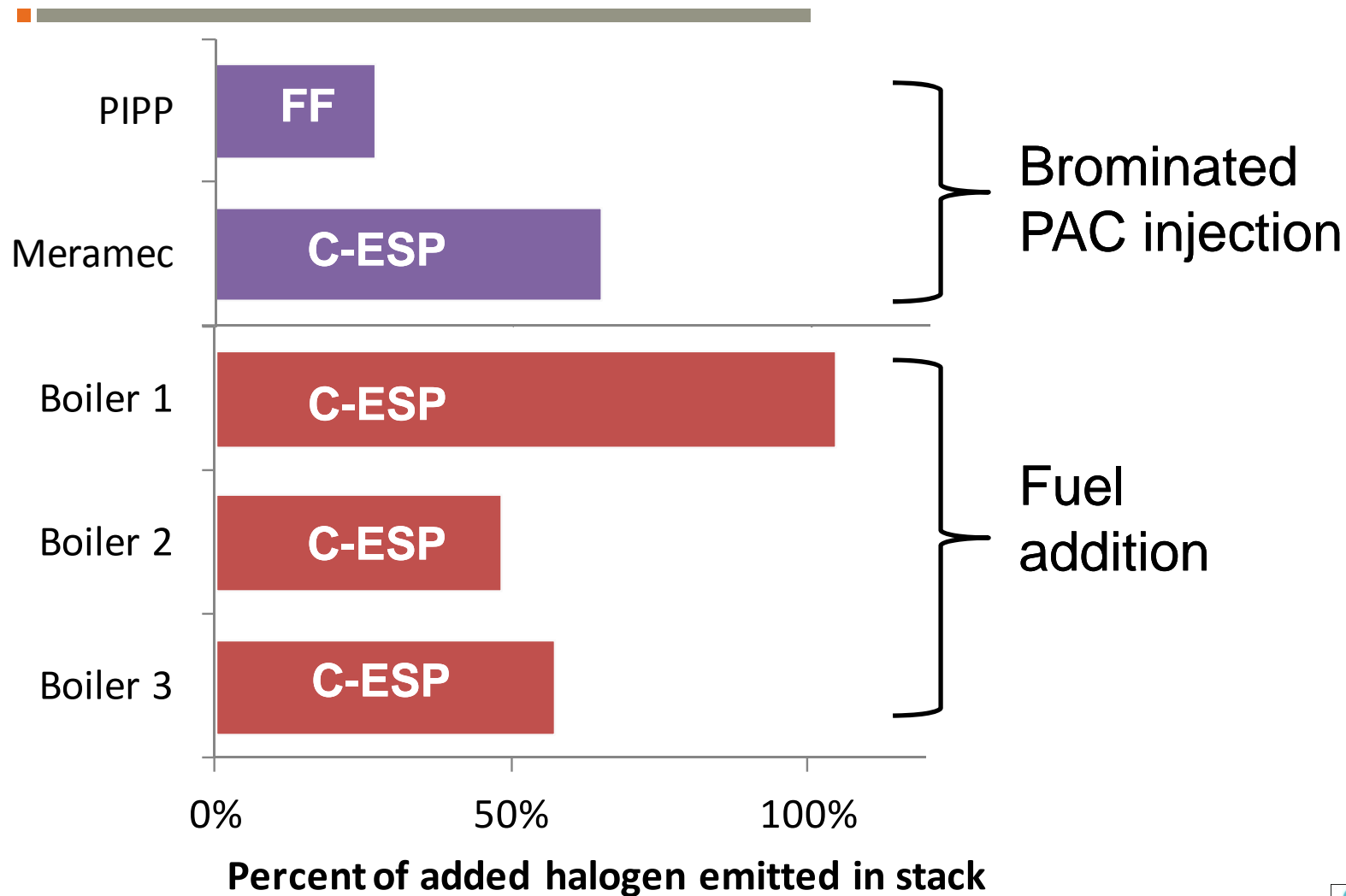


Chlorine Emission from APCDs



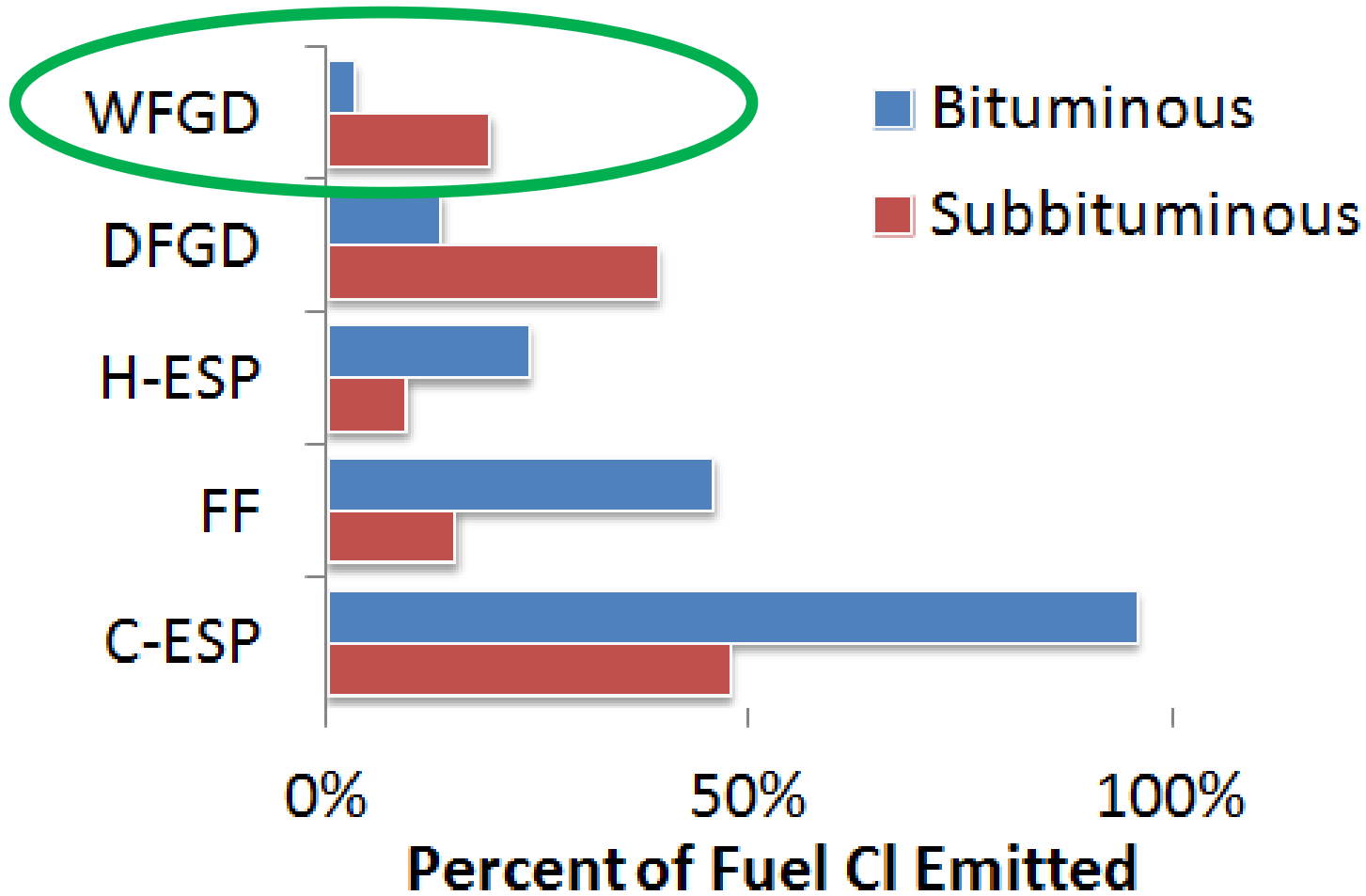
Source: 2010 ICR

Bromine Emission from APCDs



All boilers are pulverized coal, burning subbituminous coal

Chlorine Emission from APCDs



Source: 2010 ICR

Halogens in Wet Scrubbers

- Adding halogens (Cl or Br) increases oxidized Hg, which increases capture of Hg in scrubber
- Wet FGD scrubbers remove halogens efficiently
 - Average Cl removals for wet FGDs (2010 ICR): 81% for subbituminous, 97% for bituminous
 - Removal of Br at Plant Miller wet FGD: 94-96% (Dombrowski et al., 2008)
- Halogens build up in wet scrubber liquor

Halogens and Wet Scrubbers

- Increased Cl, Br concentration in scrubber liquor can decrease Hg re-emission

Halogens and Wet Scrubbers

- Recent observations (Air Quality VIII) that Br addition to the fuel increases Se in scrubber liquor

Data from bituminous site with C-ESP, wet FGD

	Se in fly ash, $\mu\text{g/g}$	% Se capture by fly ash	Se in FGD liquor, $\mu\text{g/L}$
Baseline	24	70%	300
Br addition	10	20%	4900

(Dombrowski et al., 2011)

- Less uptake of Se by fly ash means more Se enters FGD

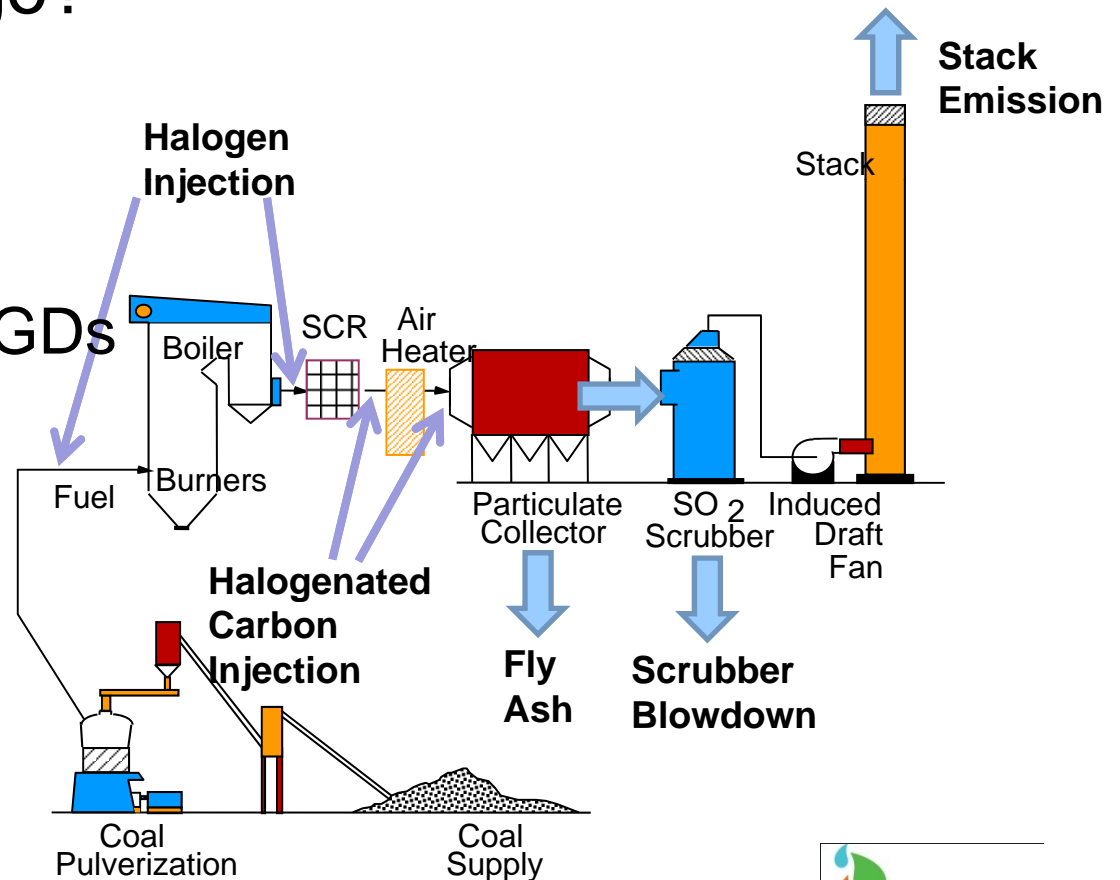
Halogens Summary

- Halogen fuel/flue gas additives OR halogenated PAC
- Where do halogens go?

- Some removal in particulate control devices
- Efficient removal in FGDs

- Br is “new kid on the block” – information needed:

- Corrosion
- Multi-media fate
- Trace metal interactions



Hg Removal in the Boiler

- How is Hg removed?
- Adsorption on particles (fly ash, sorbents) and removal in the particulate control device
- Absorption of oxidized mercury in scrubbers
- How can we improve removal by what happens in the boiler?
 - Increase unburned carbon – if you can
 - Consider adding more halogens if
 - There's enough LOI, but halogens are low
 - There's a scrubber
 - Keep SO₃ low post-APH

Questions?

ADA: Innovate, Develop, Commercialize



ADA Environmental Solutions creates and delivers cutting edge technical and chemical solutions to reduce emissions from coal-fired power plants, Portland cement kilns and industrial boilers, helping customers meet environmental goals while balancing their business needs.

NASDAQ: ADES

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