Worldwide Pollution Control Association

WPCA-

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Mercury Seminar

October 30-31, 2012

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Mercury Control and Combustion

Connie Senior

WPCA Mercury Seminar
Birmingham, Alabama
October 30, 2012

Motivation for This Presentation

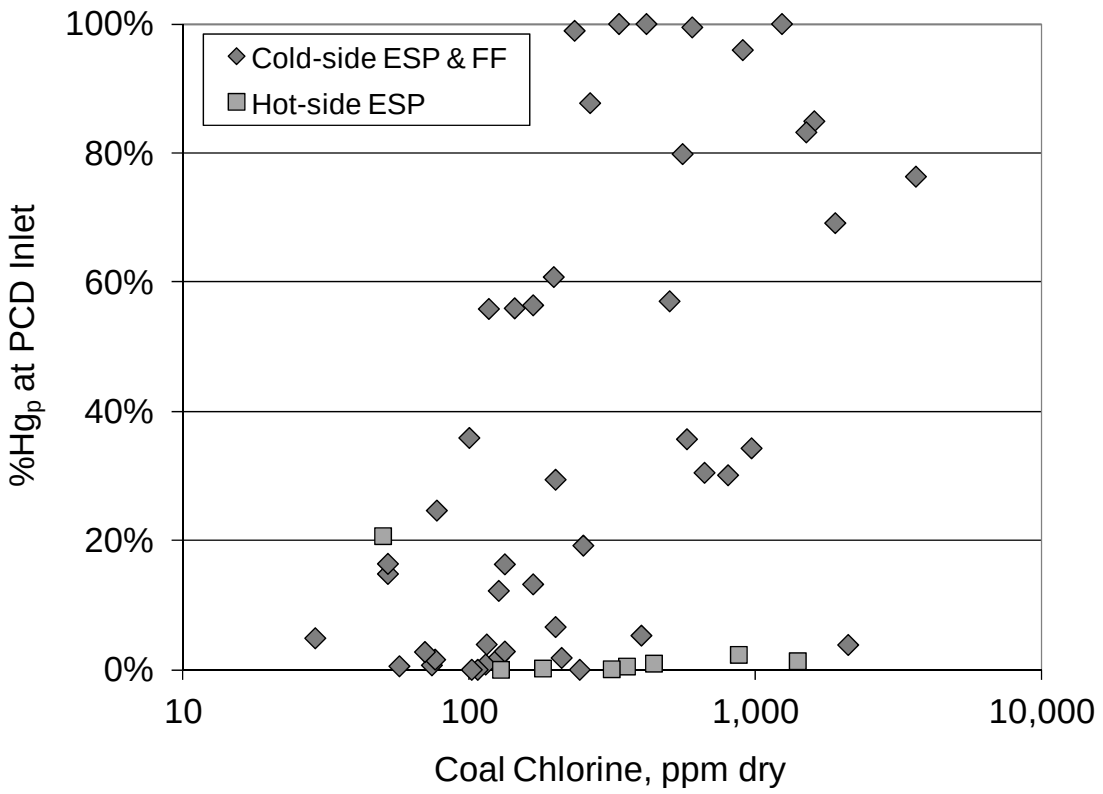
- There's more than activated carbon, when it comes to mercury control in coal-fired boilers
- Chemistry of mercury in the boiler and the interaction of mercury with other control processes, like SCR, affect the performance of downstream mercury control from activated carbon injection or scrubbers
- Topics to be discussed: mercury chemistry in boilers, halogen injection, impact of SCRs and SO_3 on mercury control

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

Adsorption

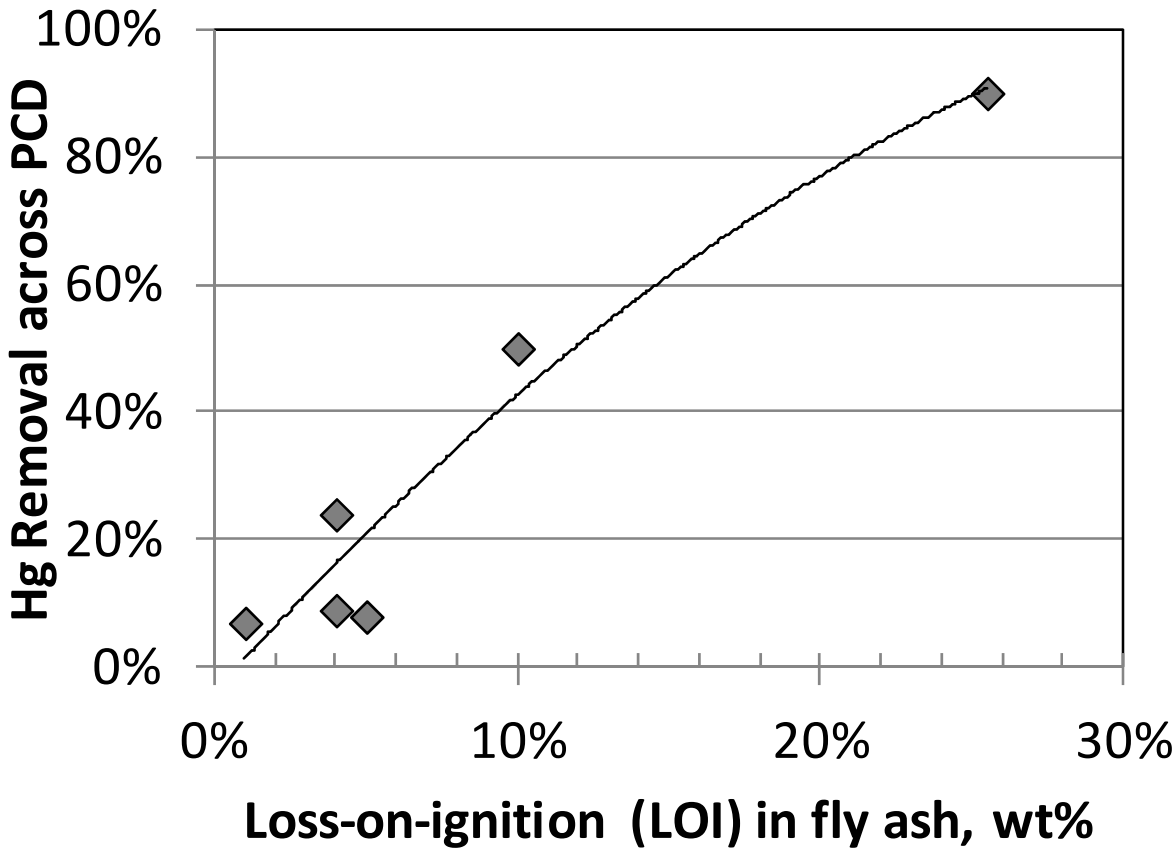
- How do we get more mercury onto particles?
- More halogens generally mean more particulate Hg
- Other factors:
  - Type of PCD
  - SO_3
  - Unburned carbon in ash



Source: 1999 ICR Data

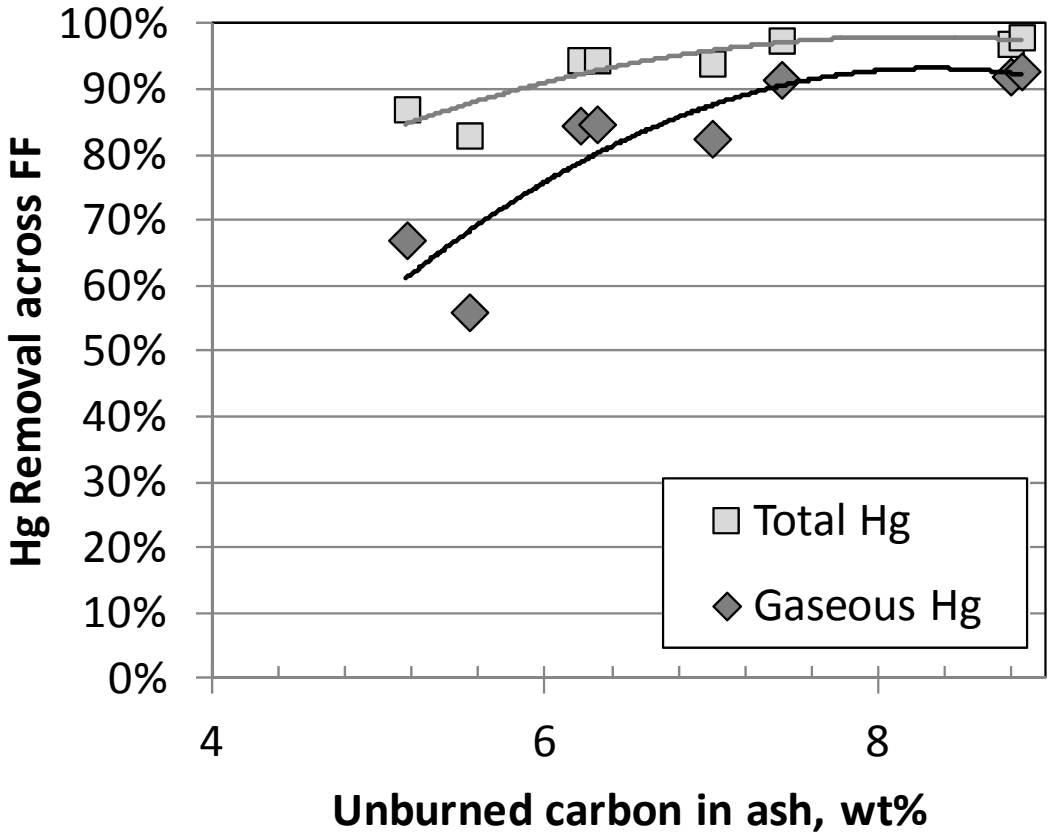
Unburned Carbon & ESPs

- Data from bituminous coals in pc-fired boilers



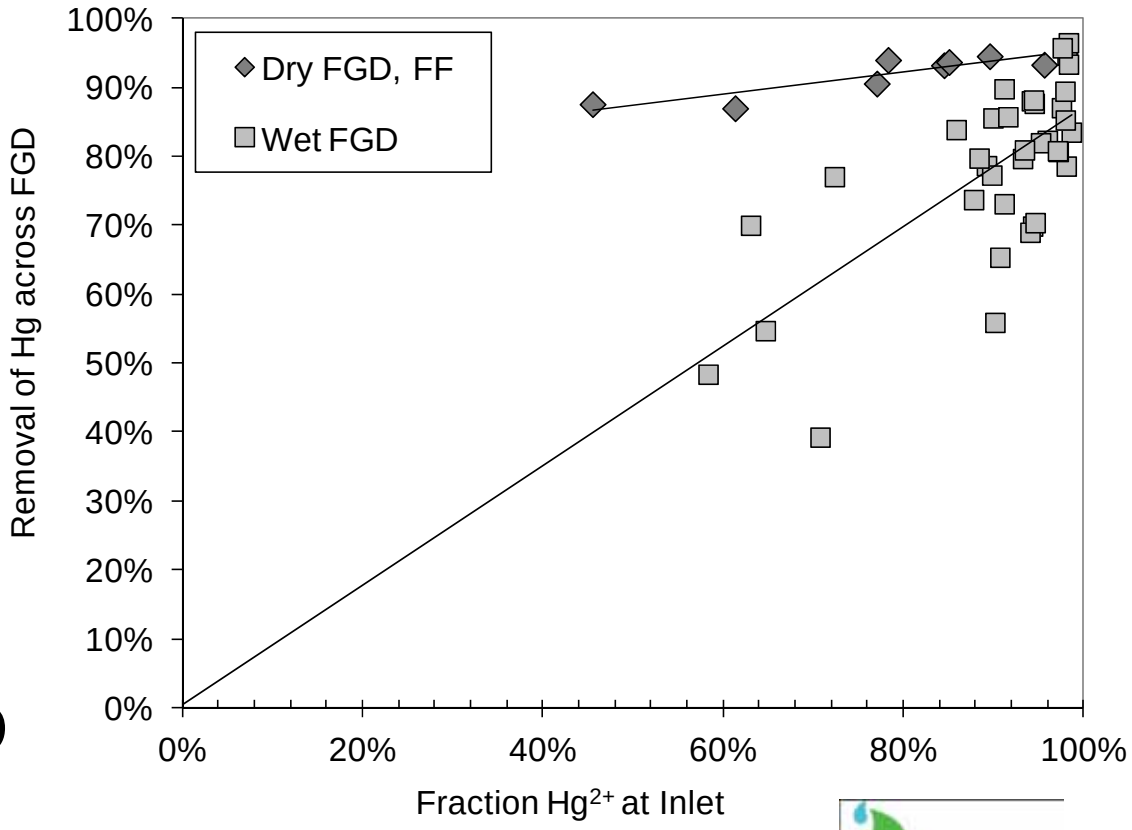
Unburned Carbon & Fabric Filter

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



Absorption

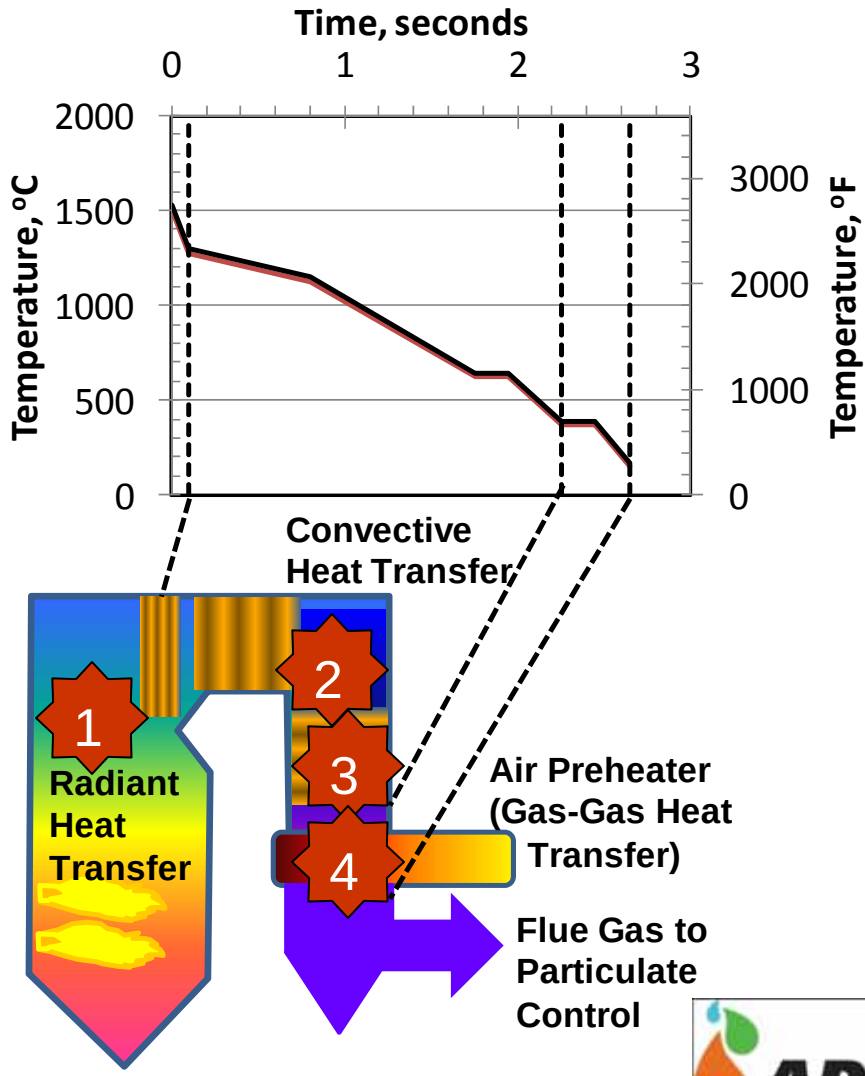
- How do we get more Hg into the scrubber?
- Higher fraction of oxidized Hg at scrubber inlet => higher Hg removal
- Factors:
  - Halogen in fuel
  - Re-emission of Hg^0 in wet FGD



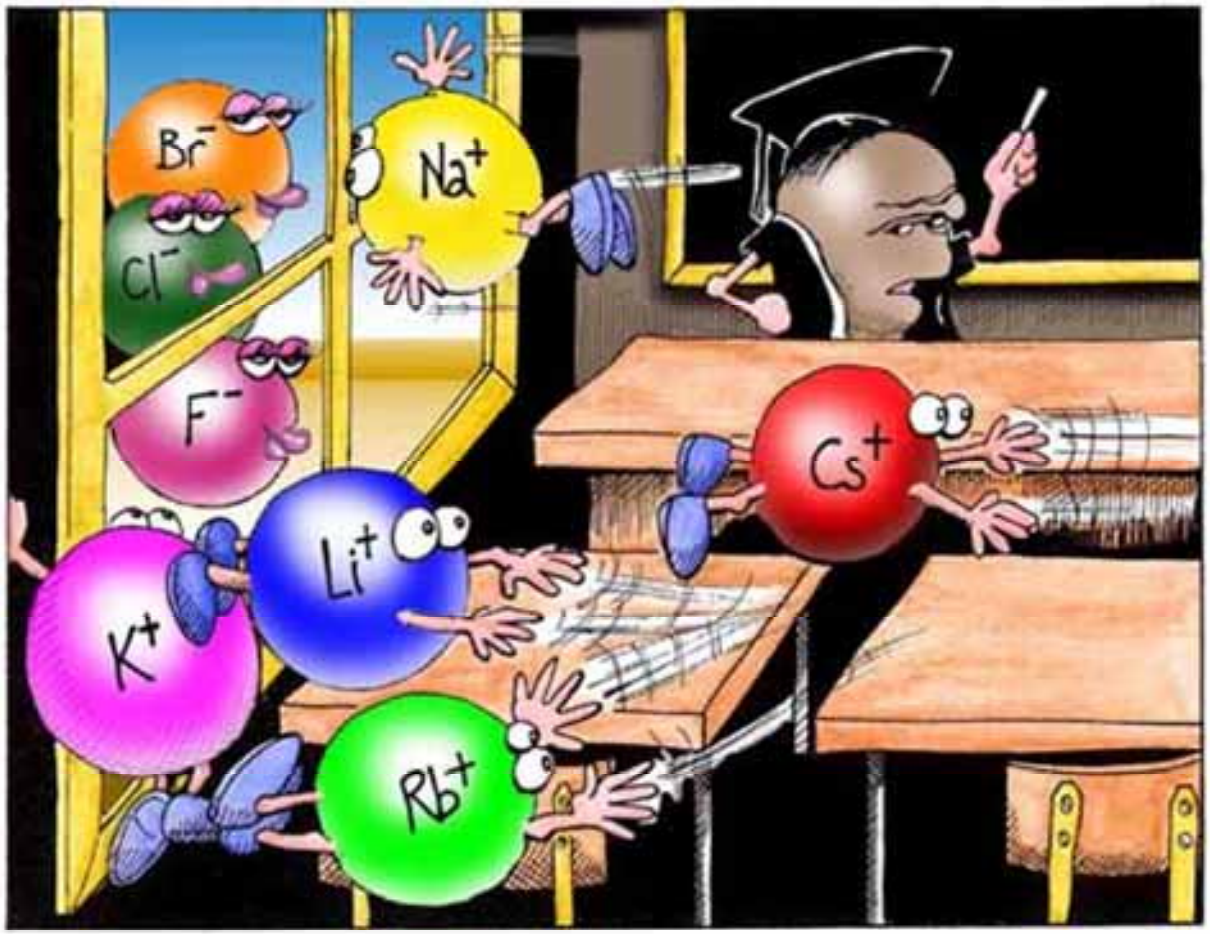
Source: NETL, EPRI demos

What Happens in the Boiler?

1. Hg is released from fuel, while UBC and SO_3 develop in the flame zone
2. After the convective pass, halogens can begin to oxidize Hg in the flue gas
3. If SCR present, oxidation of Hg^0 and production of SO_3
4. Oxidation of Hg^0 across APH and removal of some SO_3

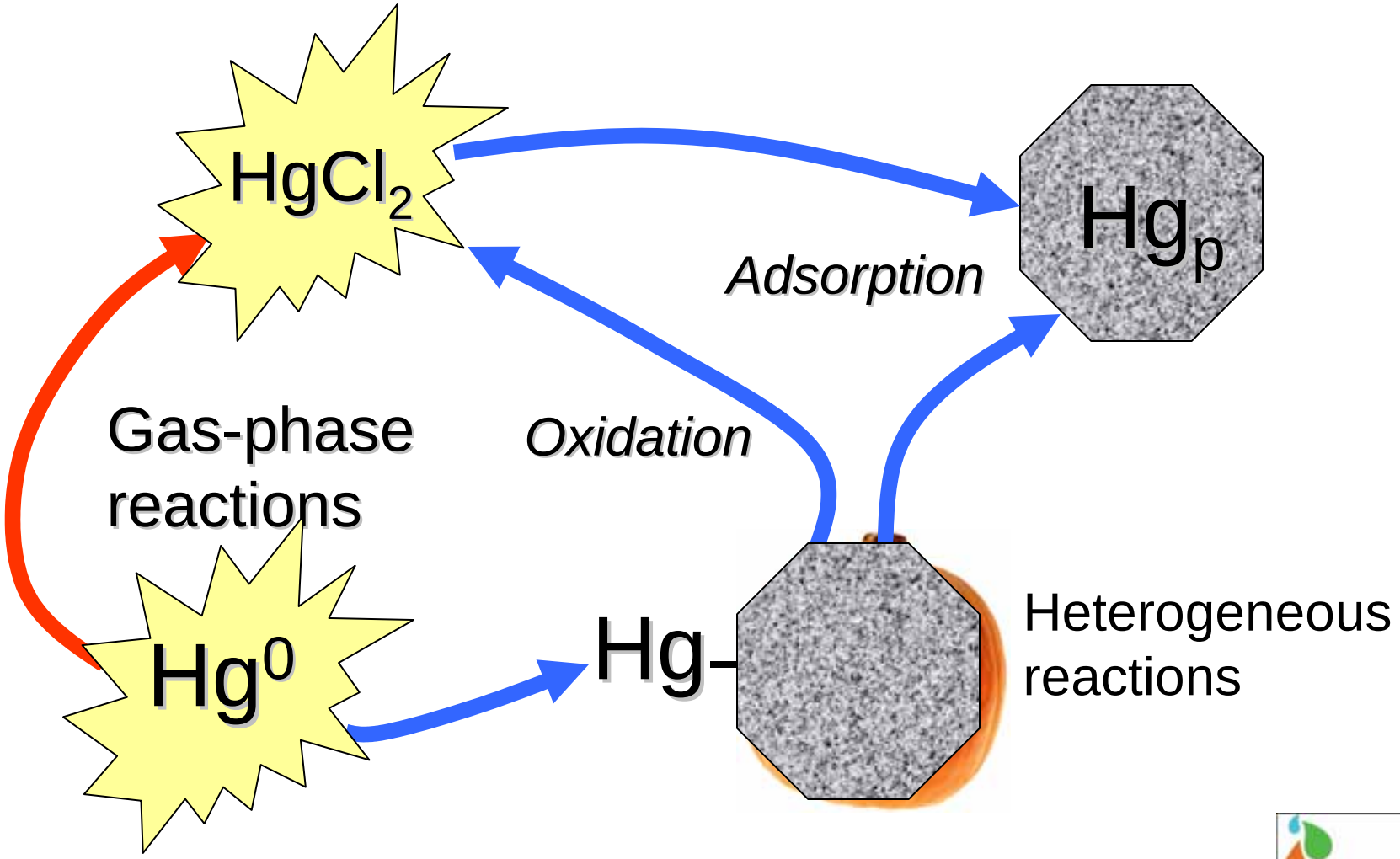


Mercury Chemistry in Flue Gas



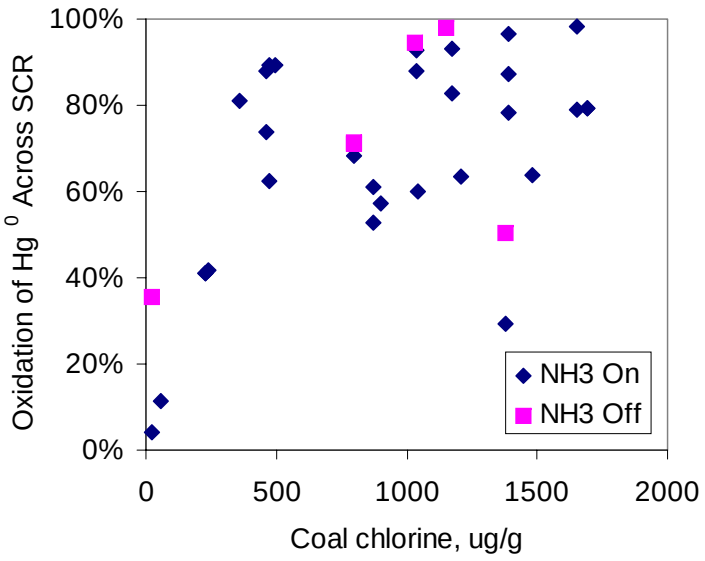
"Perhaps one of you gentlemen would mind telling me just what it is outside the window that you find so attractive...?"

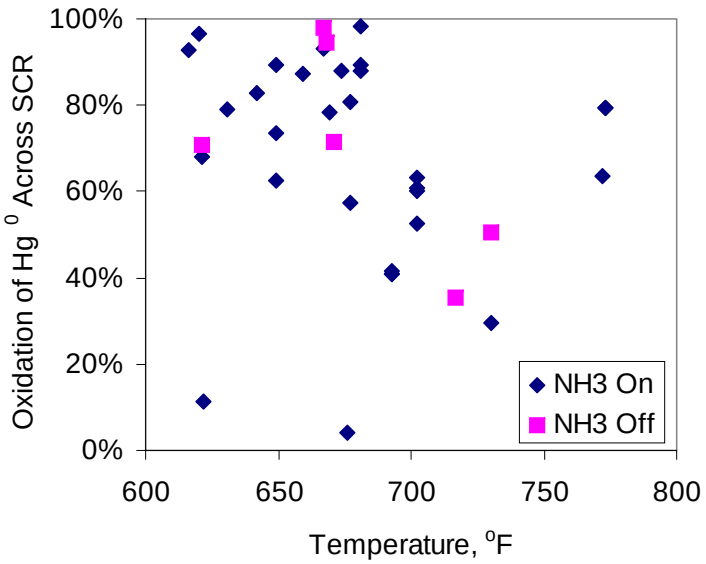
Mercury Chemistry in Flue Gas



Oxidation Across Full-Scale SCRs

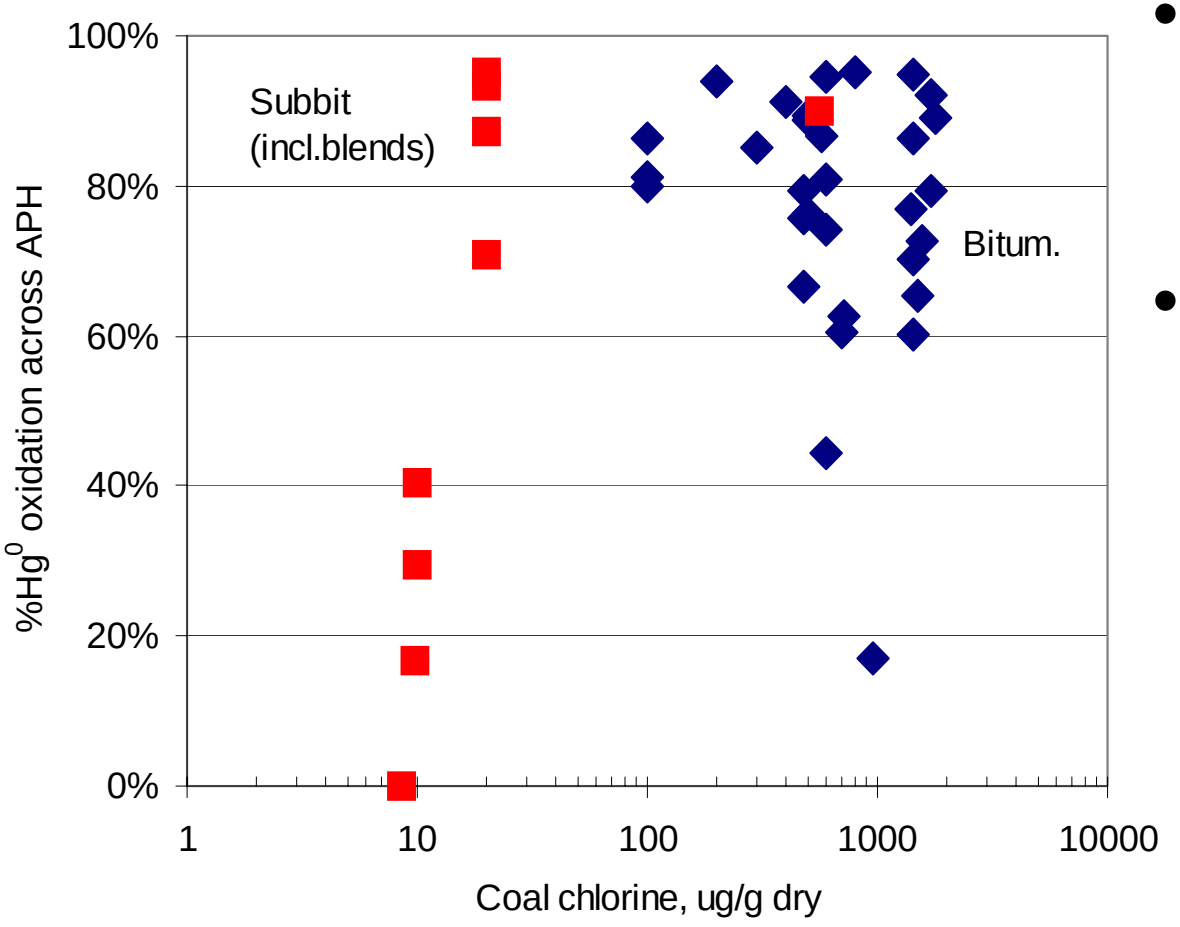
- Full-scale data
- Large variation in observed oxidation





- Effect of Cl:
  - Low oxidation with PRB (low chlorine coal)
- Effect of T:
  - Lower oxidation at higher temperatures

Oxidation of Hg Across APHs

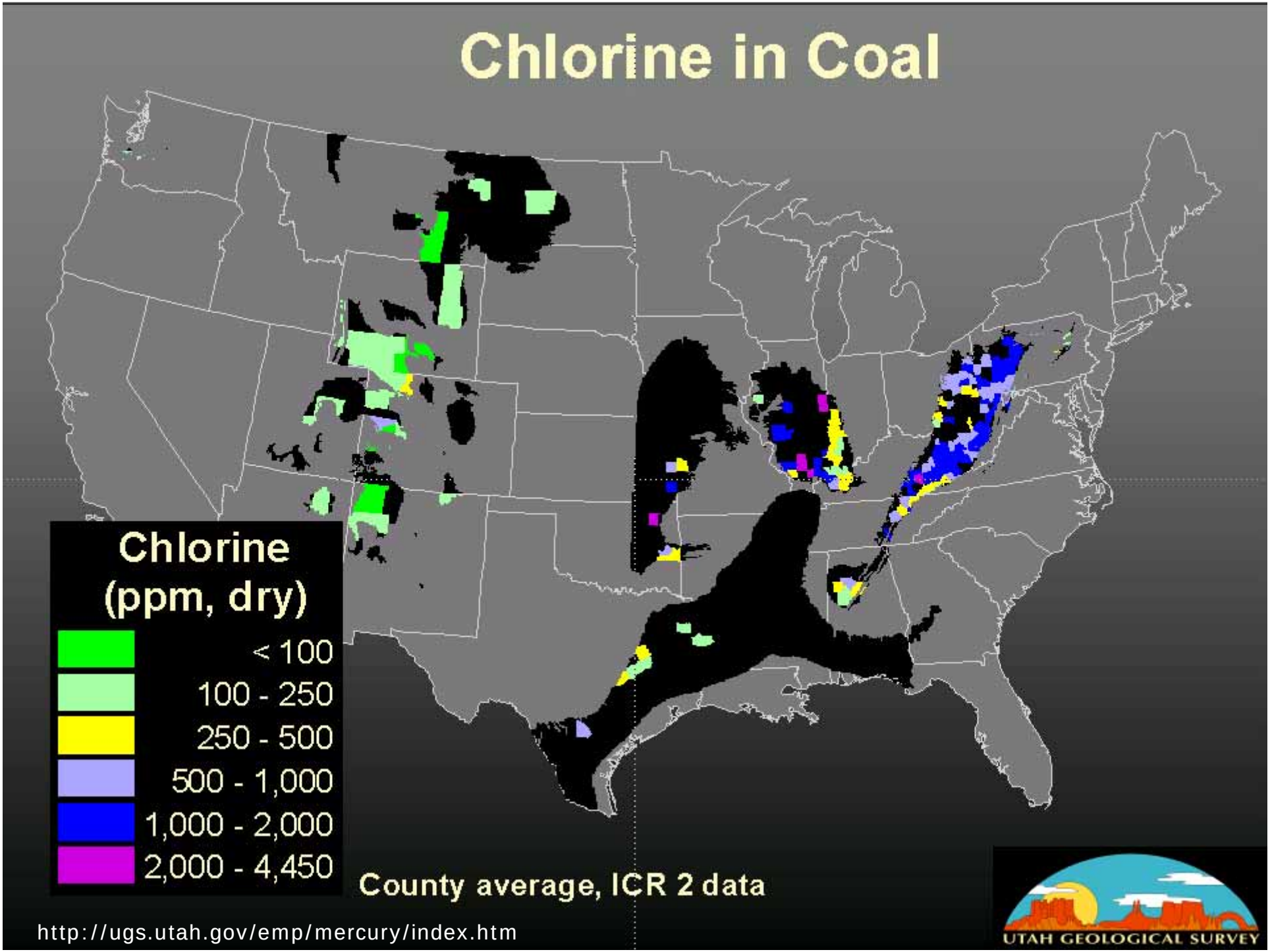


- Full-scale Hg speciation measurements
- Significant oxidation across Air Preheater:
  - —APH exit temperature
  - —Chlorine
  - —SO_2/SO_3
  - —LOI

Why Add Halogens?

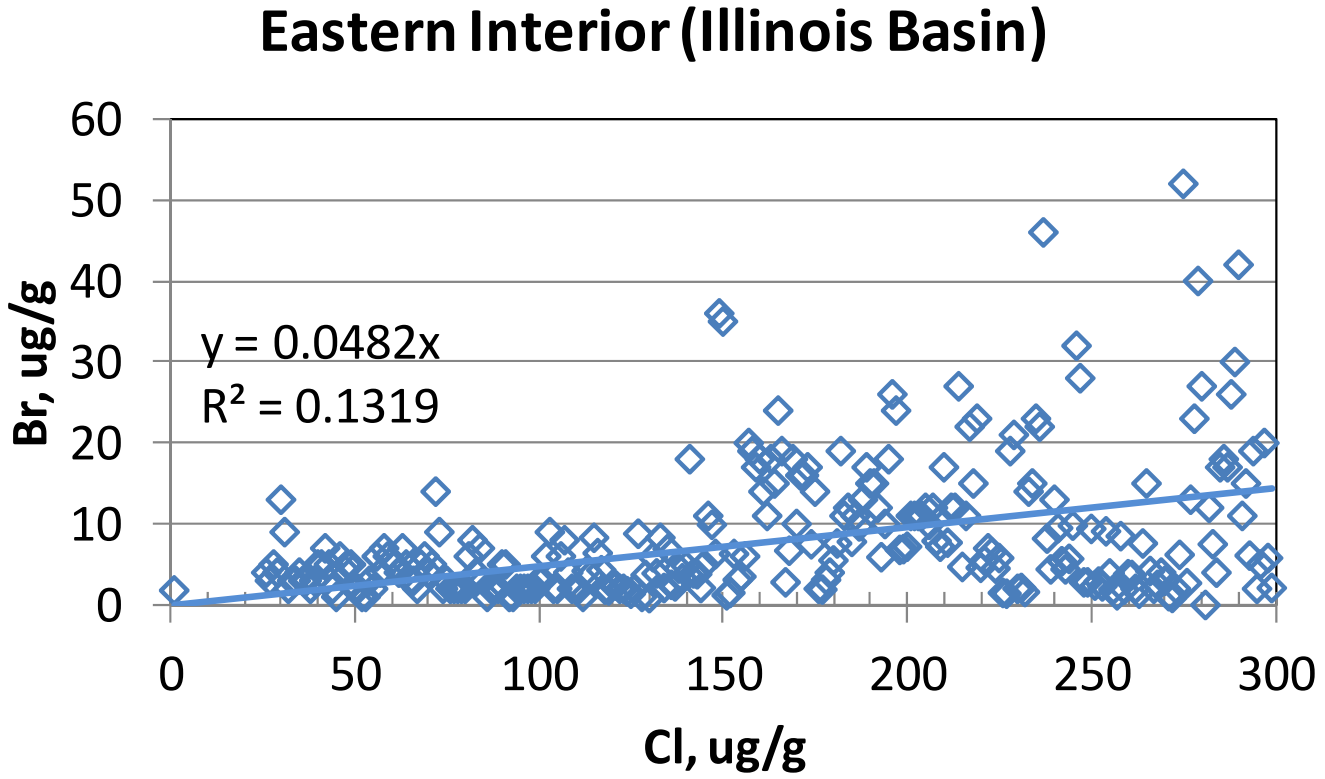
- Adding halogens to fuel or flue gas:
  - Halogen content of US coals varies widely

Chlorine in Coal



Why Add Halogens?

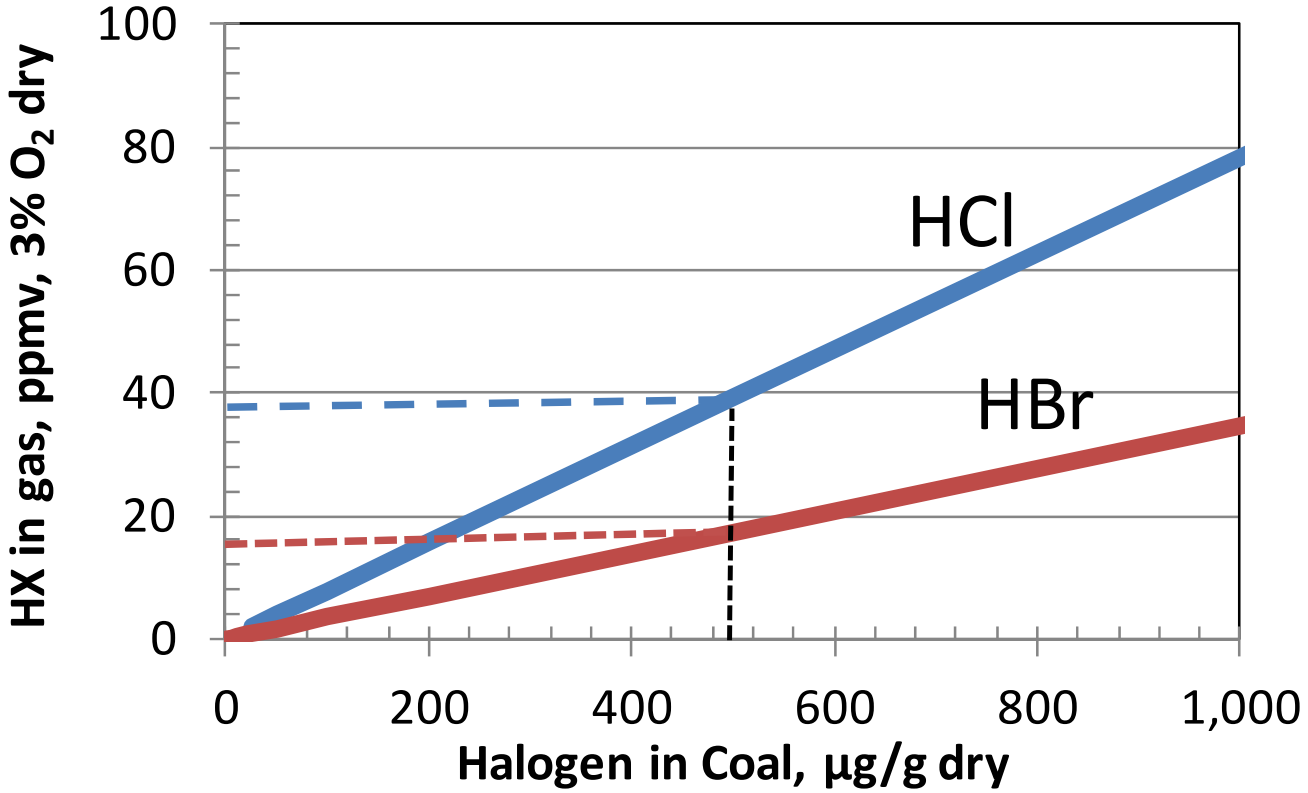
- Adding halogens to fuel or flue gas:
  - Halogen content of US coals varies widely
    - Bromine content typically 1% to 4% of chlorine content



Source: USGS COALQUAL database

Why Add Halogens?

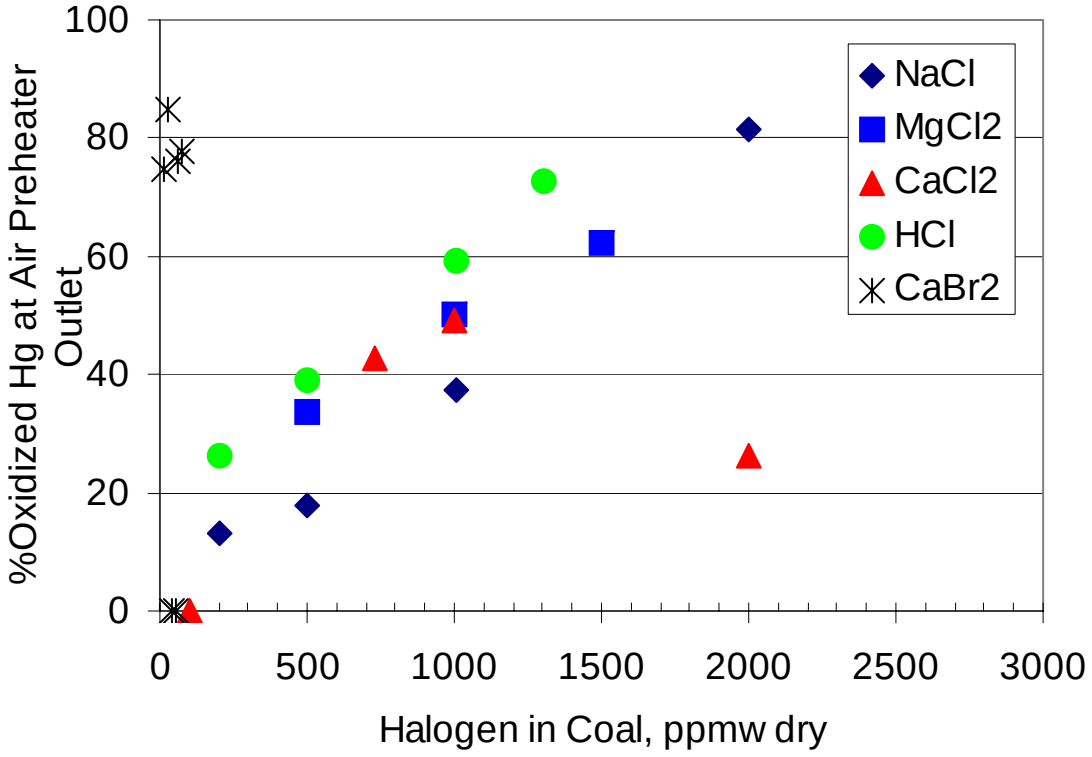
- Adding halogens to fuel or flue gas:
  - 500 ug/g Cl in coal = ~40 ppmv HCl in flue gas
  - 500 ug/g Br in coal = ~17 ppmv HBr in flue gas



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

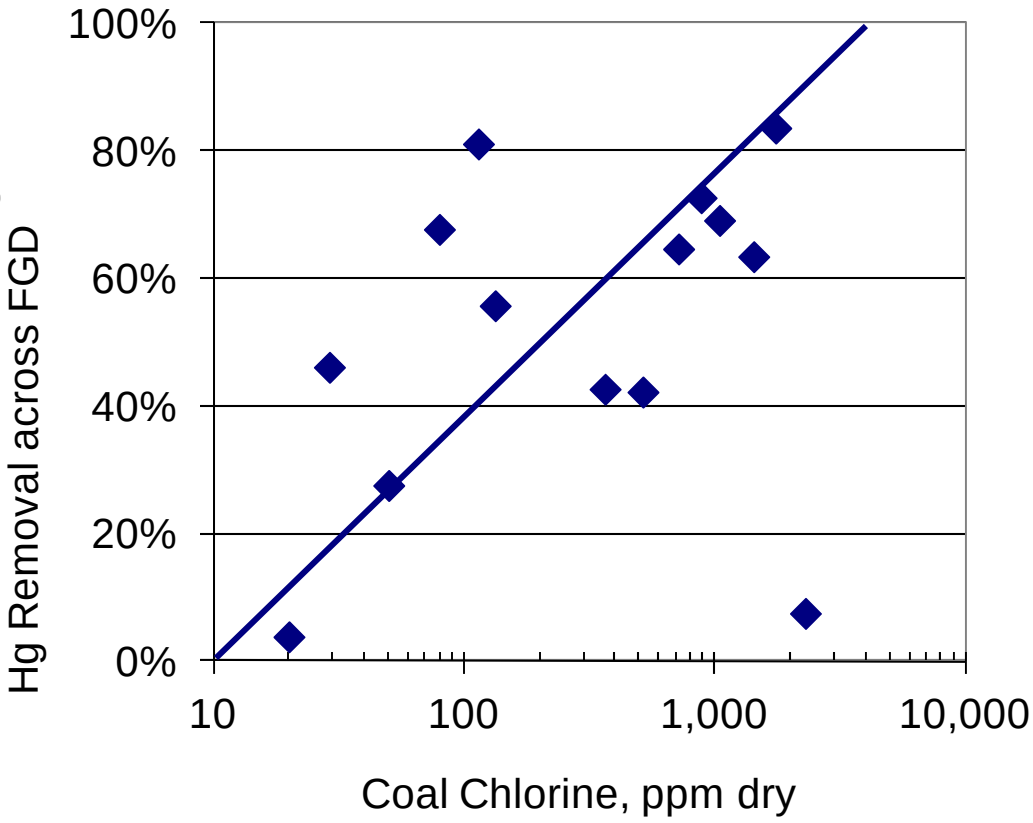
Halogen addition at various full-scale PRB boilers



Source: Dombrowski et al., 2006

Why Add Halogens?

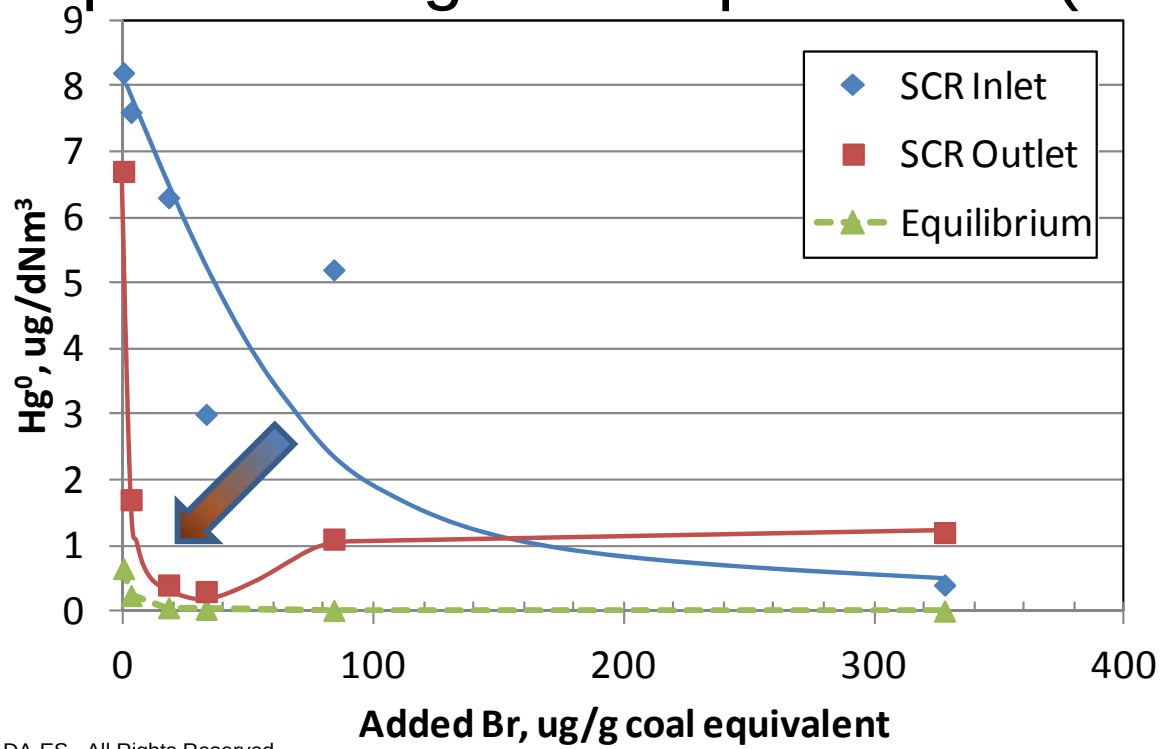
- Adding halogens to fuel or flue gas:
  - Halogen content of US coals varies widely
  - Oxidation of Hg and capture of Hg on fly ash enhanced with additions of halogens, like Cl and Br
  - Many plants' APCDs can take advantage of native capture



Source: 1999 ICR

Effect of SCRs on Added Halogens

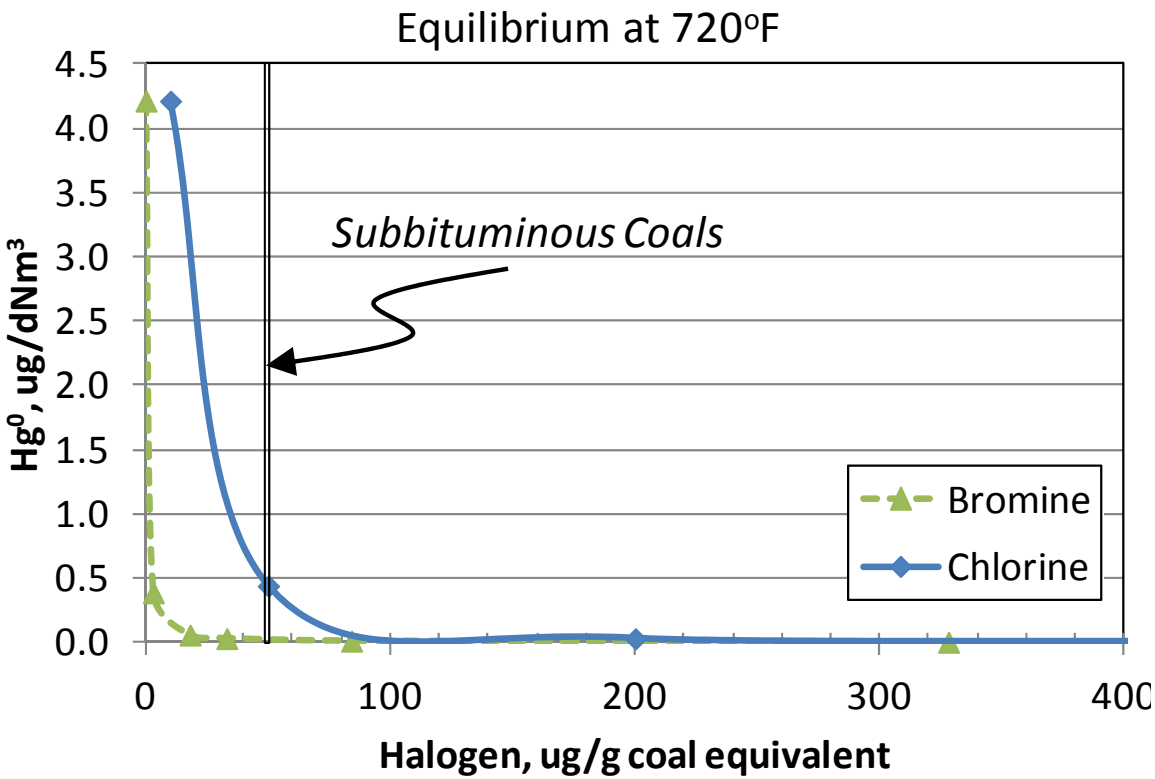
- Catalysts drive reactions toward equilibrium
  - Results will be catalyst-specific
- Adding Br to the fuel makes the shift to Hg^{2+} take place at higher temperatures (than Cl)



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

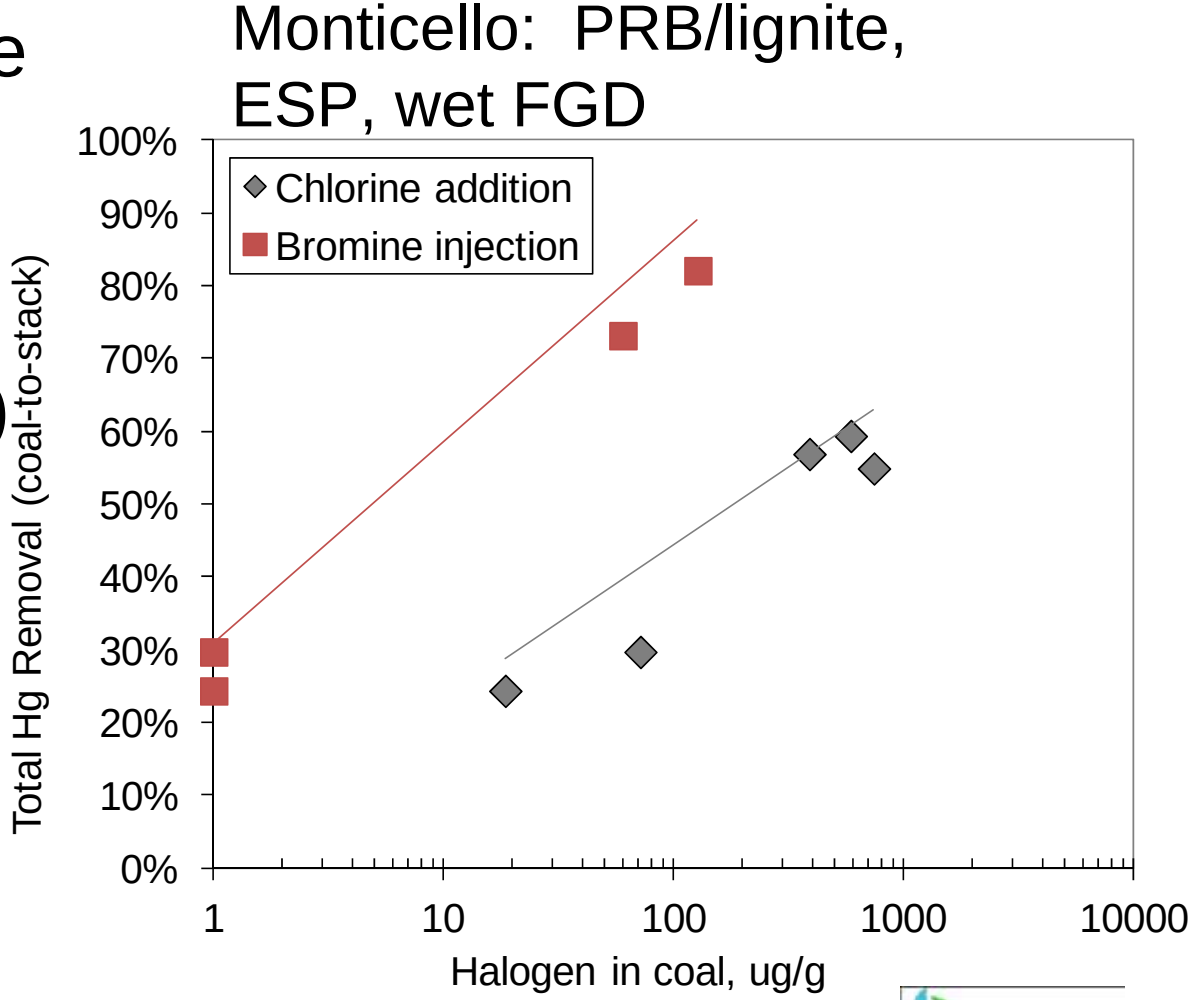


Summary: Why Add Halogens?

- Adding halogens to fuel or flue gas:
  - Halogen content of US coals varies widely
  - Oxidation of Hg (especially in SCRs) 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

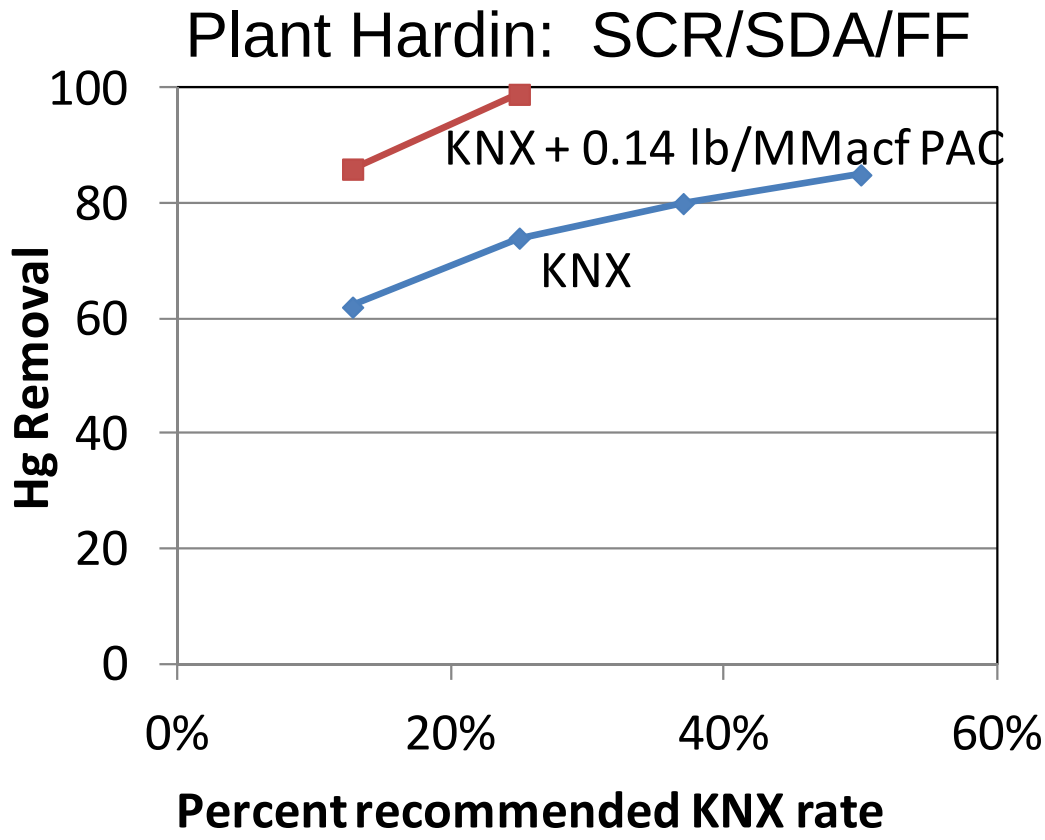
How Effective Are Halogens?

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



How Effective Are Halogens?

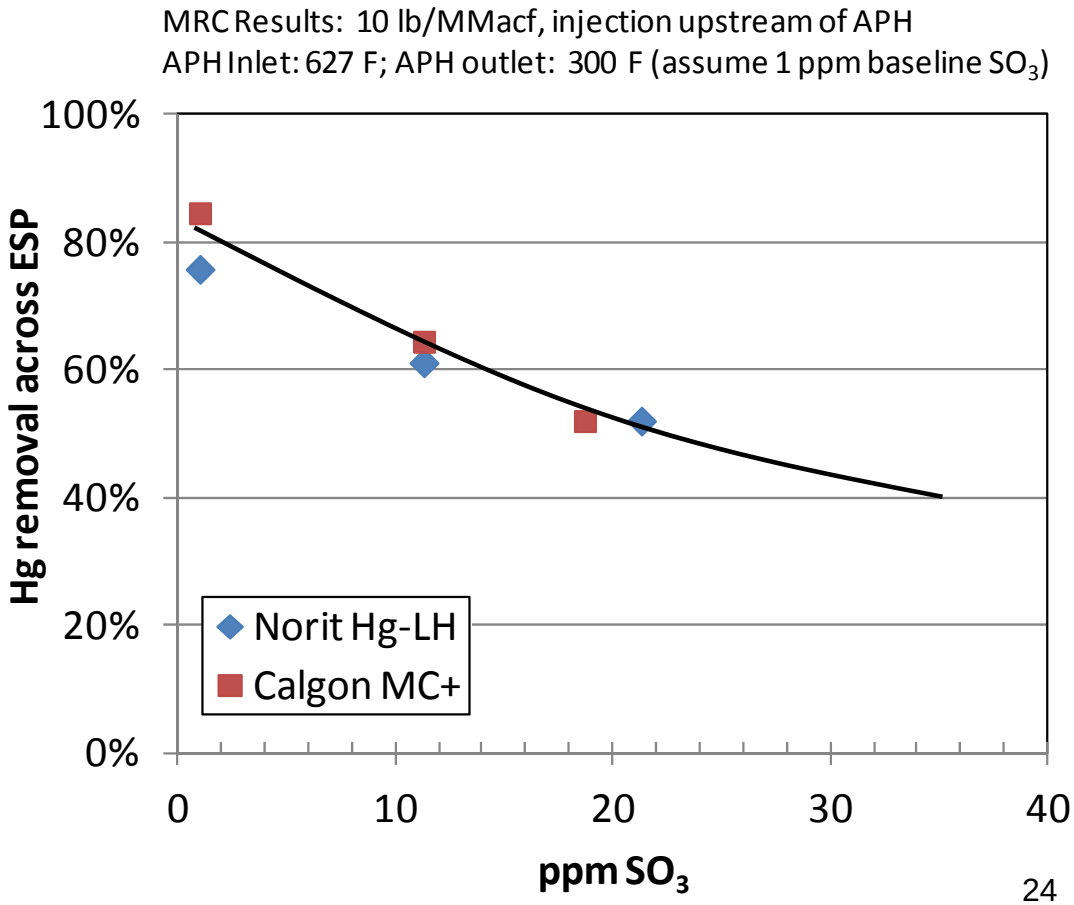
- Halogens increase oxidized mercury: Br more effective than Cl (on an equal mass basis)
- Increased Hg removal across scrubbers
- Halogens increase effectiveness of PAC



Source: DOE/EPRI sampling campaigns

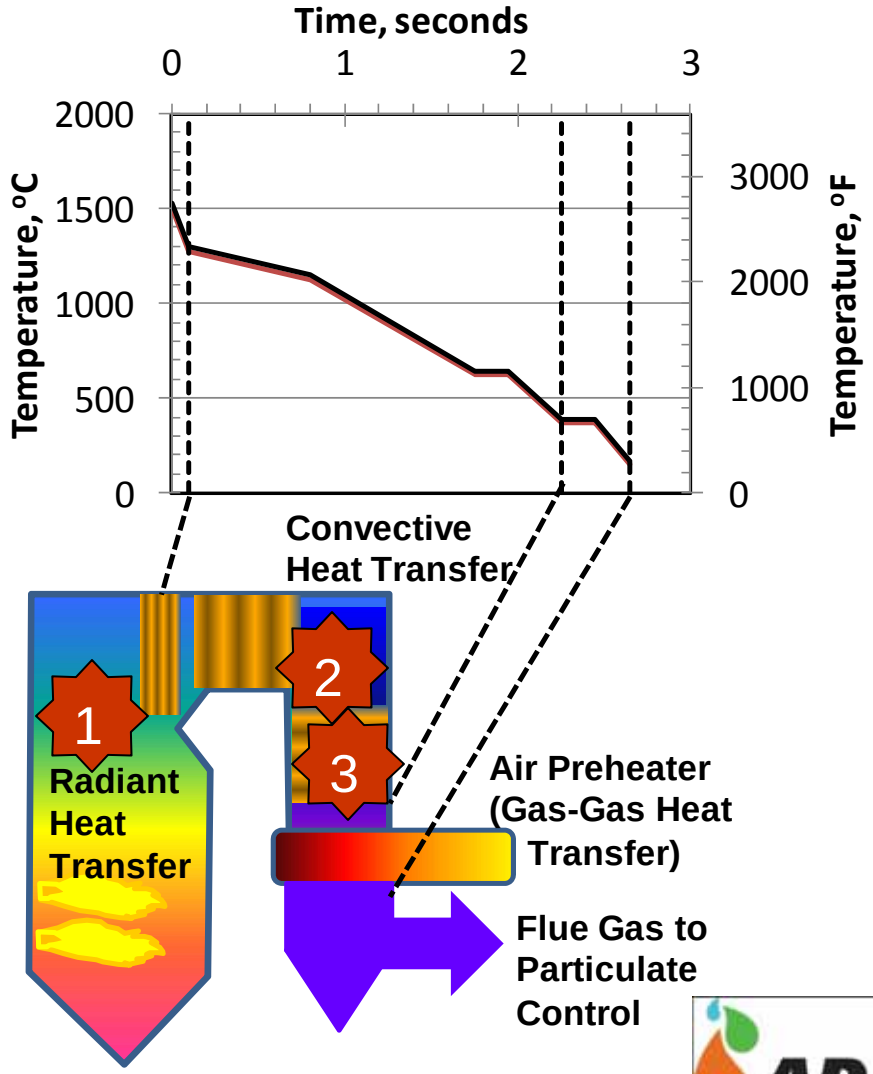
SO_3 Affects Hg Control

- SO_3 affects Hg control with activated carbon
- Any SO_3 in gas phase appears to affect Hg capture with PAC
  - SO_3 is used to condition fly ash for better capture in ESPs
  - SO_3 higher in bituminous flue gas, especially after SCR



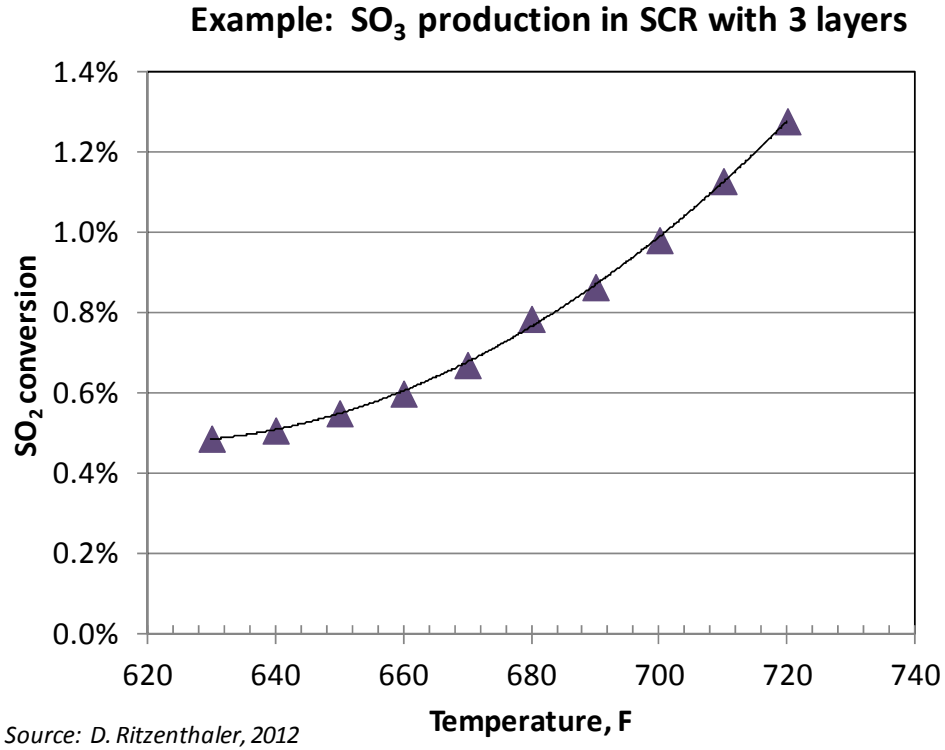
The SO_3 Story

1. SO_3 is produced in the flame zone by oxidation of SO_2
2. In the convective pass, high-iron fly ash can act as a catalyst and produce more SO_3
3. OR high-calcium fly ash can reduce SO_3 by adsorption

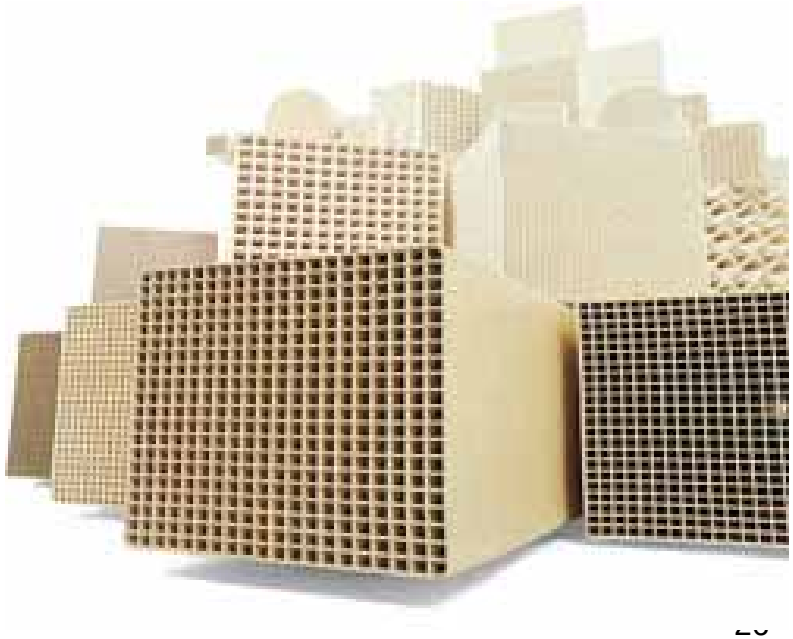


SO_3 Production in SCRs

- Selective Catalytic Reduction (SCR) process uses a catalyst to destroy NOx
- But SCR creates SO_3 by oxidation of SO_2

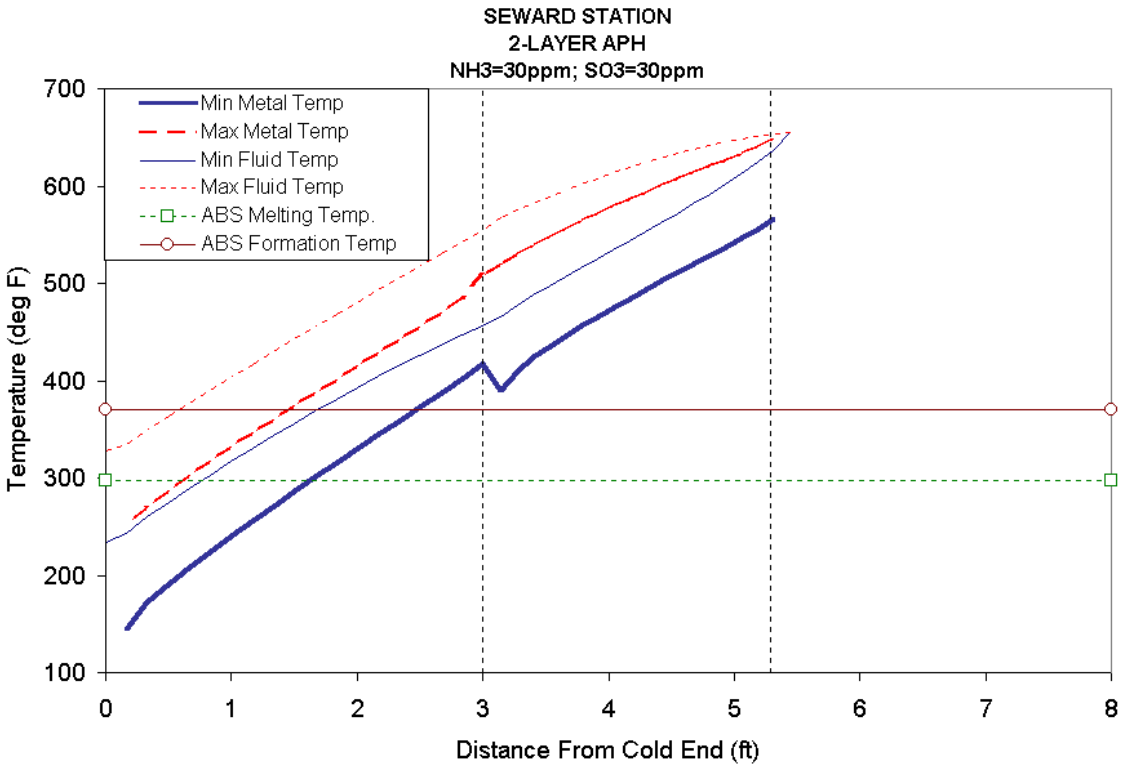


Source: D. Ritzenthaler, 2012



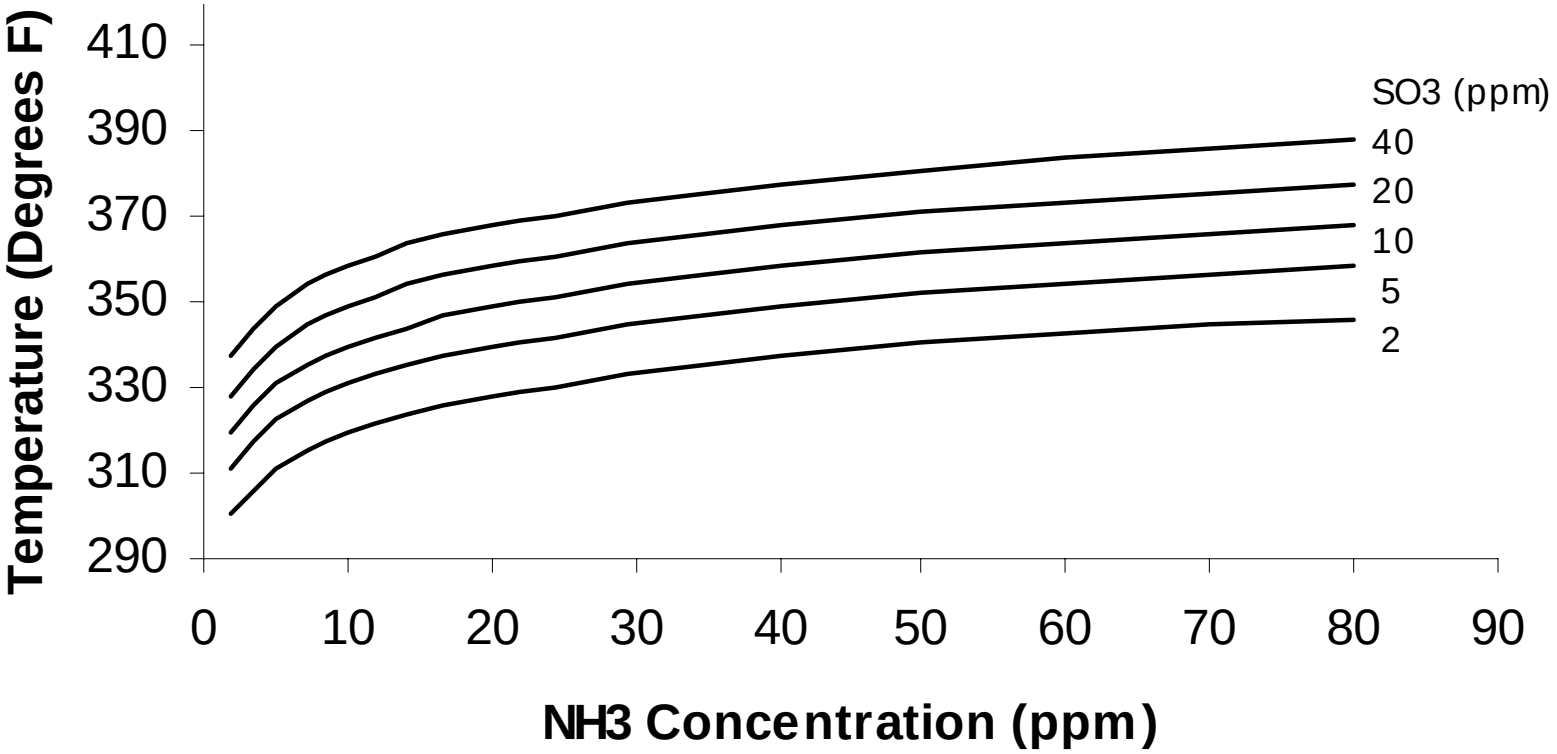
Removal of SO_3 in Air Preheaters

- Two mechanisms for removal of SO_3 across APHs:
  - Condensation on surfaces below dew point temperature
  - Formation of ammonium bisulfate (ABS) solid (reaction between ammonia and SO_3)



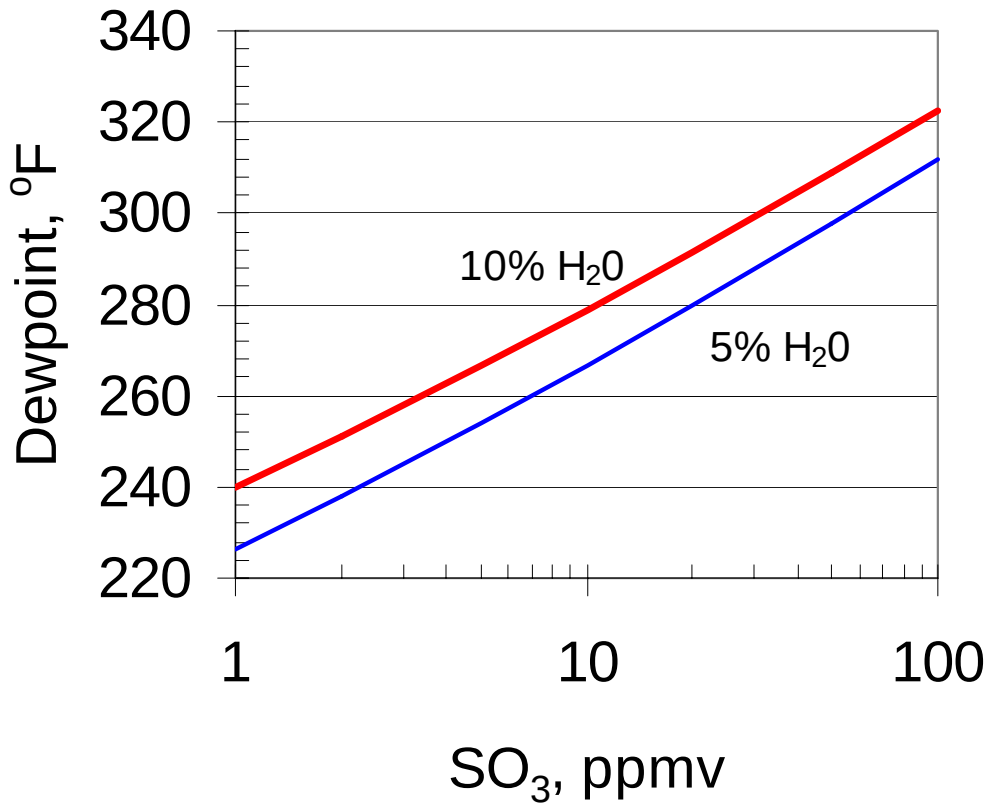
Source: Biggs et al., 2001

Formation of Ammonium Bisulfate



Source: Marshall et al., 2001

Dew Point of SO_3 in Flue Gas



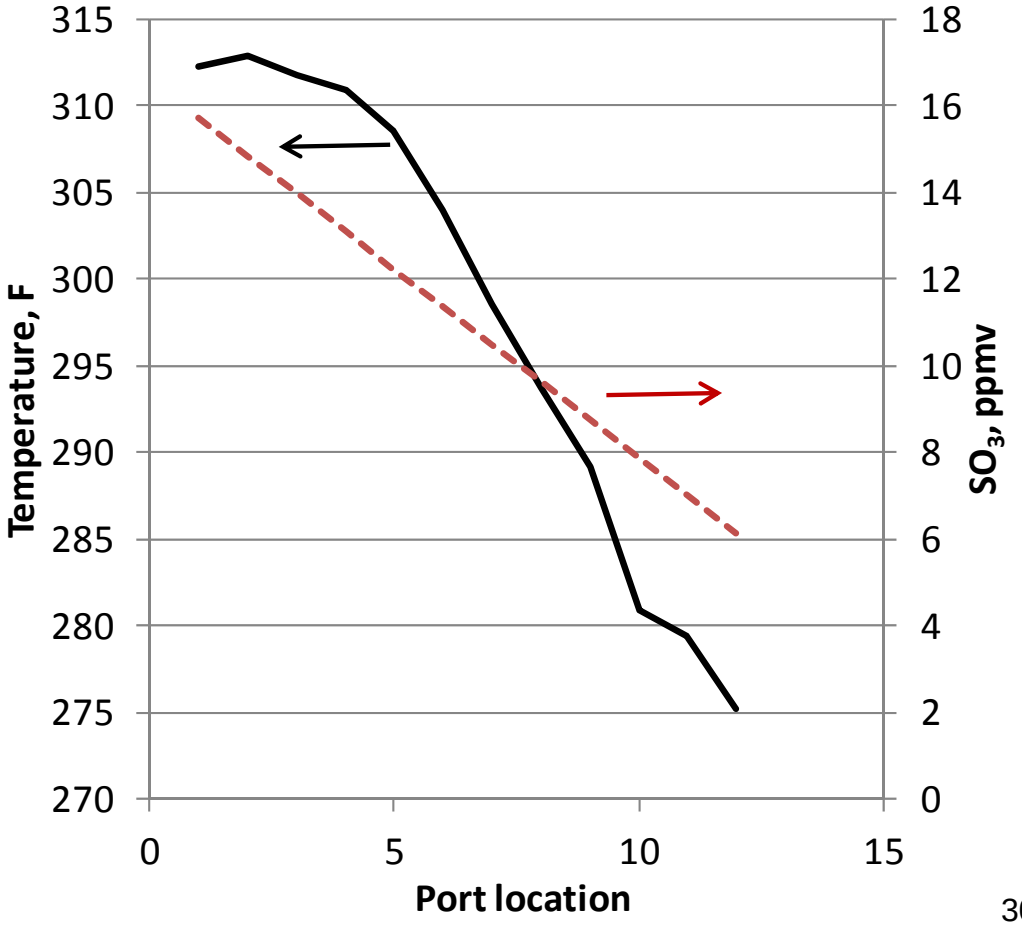
- SO_3 dew point depends on flue gas temperature and water content

$$\frac{1}{T_{Dewpoint}} = 2.276x10^{-3} - 2.943x10^{-5}\ln\left(P_{H_2O}\right) - 8.58x10^{-5}\ln\left(P_{H_2SO_4}\right) + 6.20x10^{-6}\ln\left(P_{H_2O}\right)\ln\left(P_{H_2SO_4}\right)$$

- $T_{Dewpoint}$ in Kelvin
- Partial pressures in mm Hg

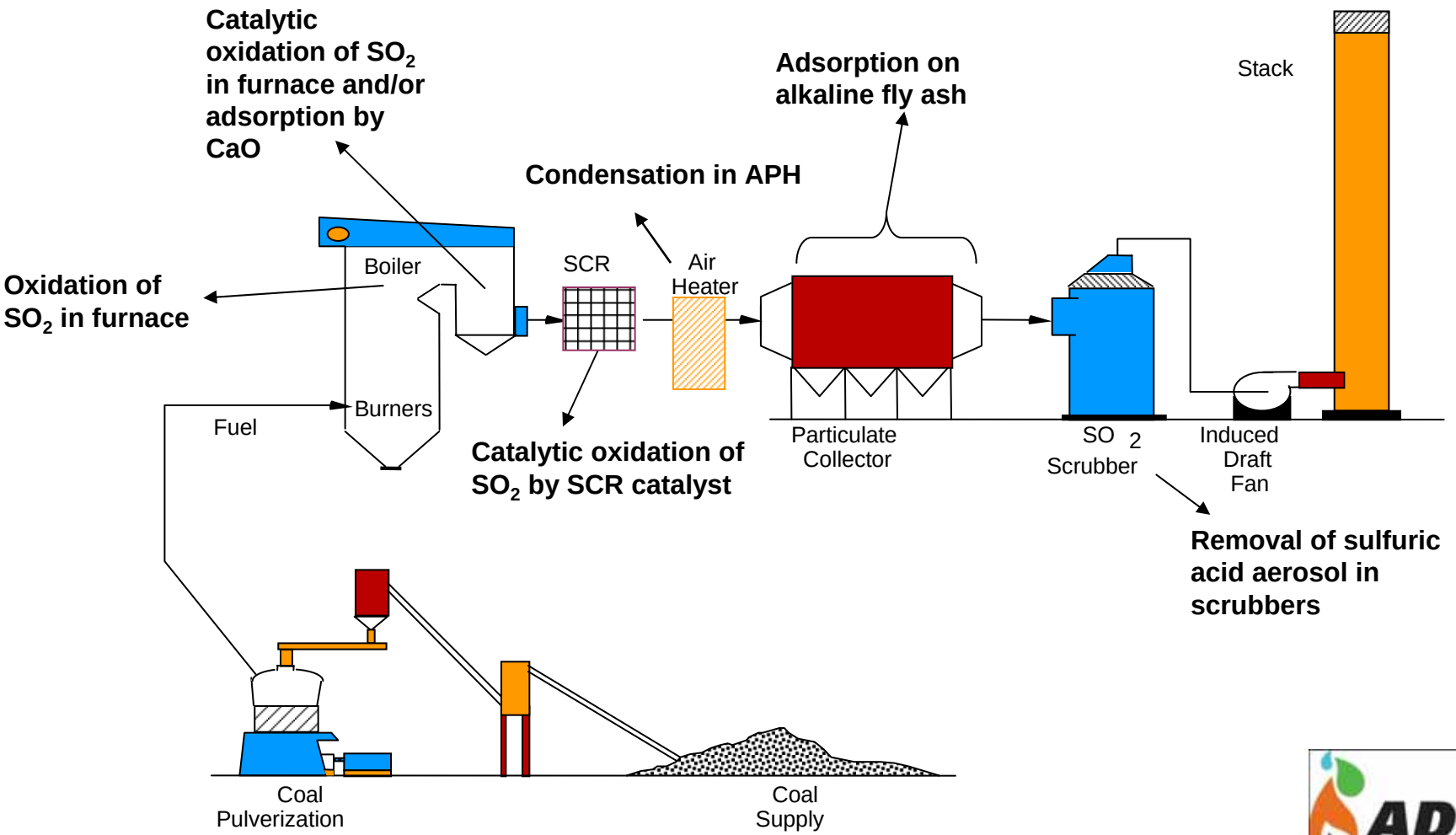
Condensation of SO_3 in APH: Example

- SO_3 measured across duct downstream of regenerative APH
- Correlation between APH exit temperature and SO_3 concentration



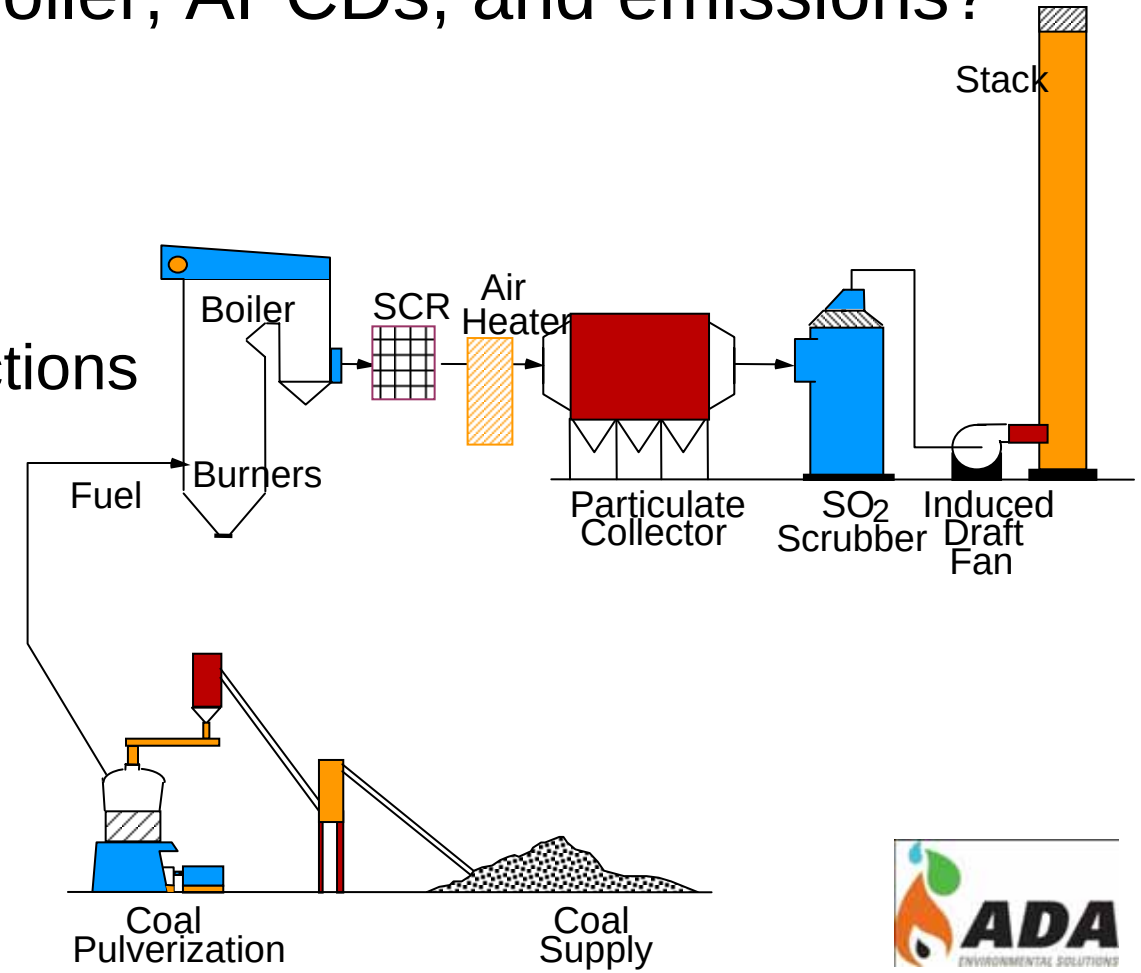
Source: DeVito, 1999

Summary: SO_3 Sources/Sinks



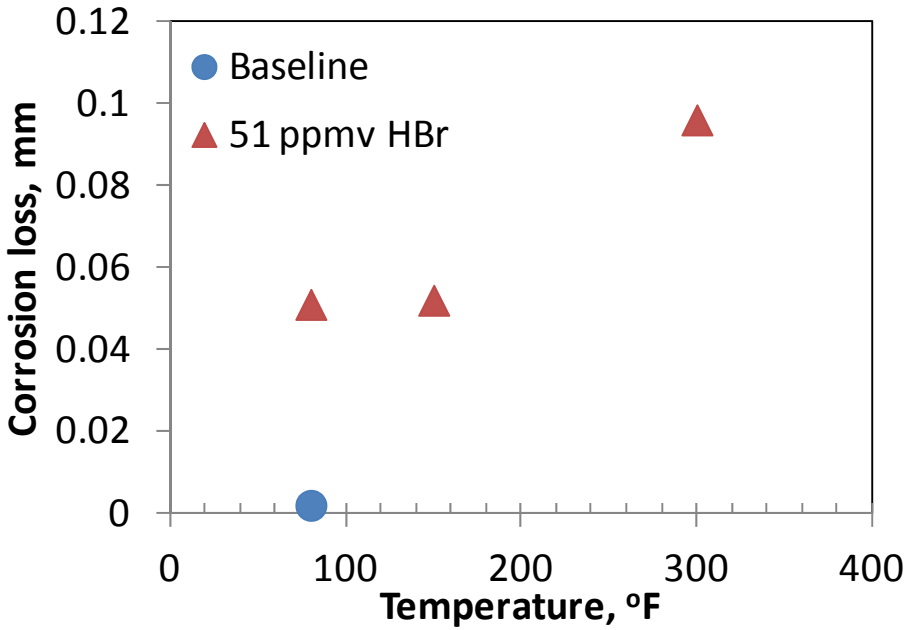
Fate and Impacts of Halogens

- 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

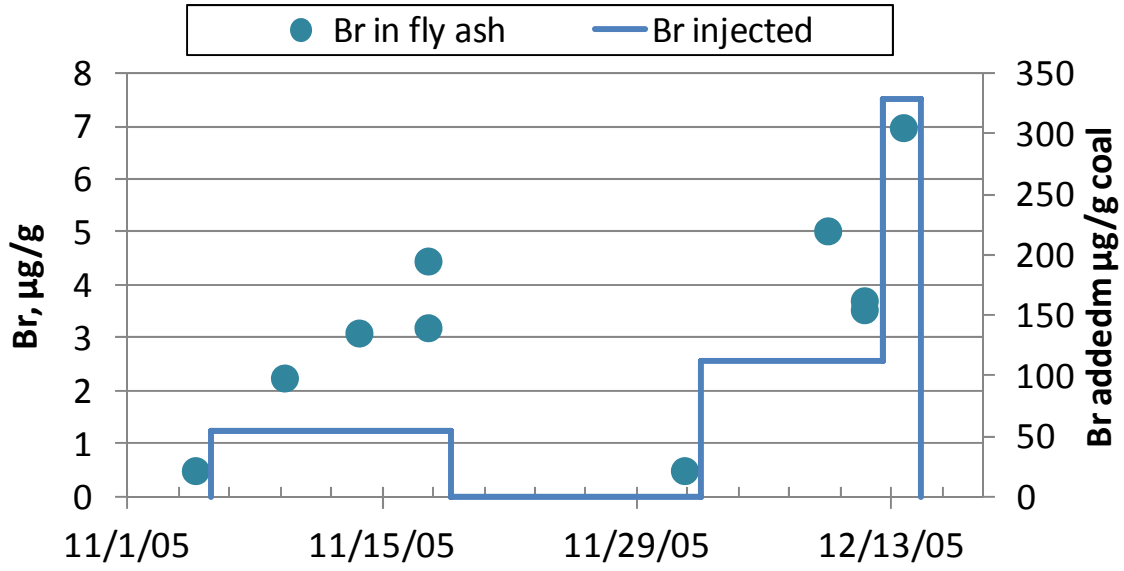
- Chlorine corrosion in furnaces can occur for very high levels of chlorine in coal (> 2000 µg/g)
  - Bromine addition at much lower concentrations
- Indirect evidence that HBr might be more corrosive than HCl at flue gas temperature
- No direct comparison, but HBr corrosion higher than baseline (no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



Zhuang et al., 2009

Bromine Addition: Fly Ash Impacts

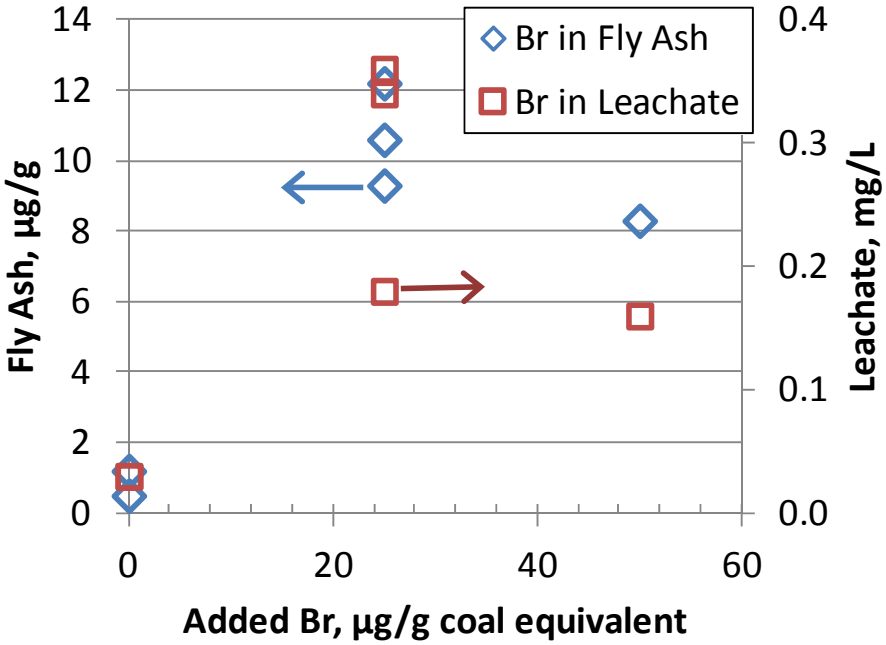
- Bromine additive or brominated PAC results in increase in Br in fly ash
- Example: Br injection at Monticello (C-ESP)



Bromine injection at Monticello (EERC, URS data)

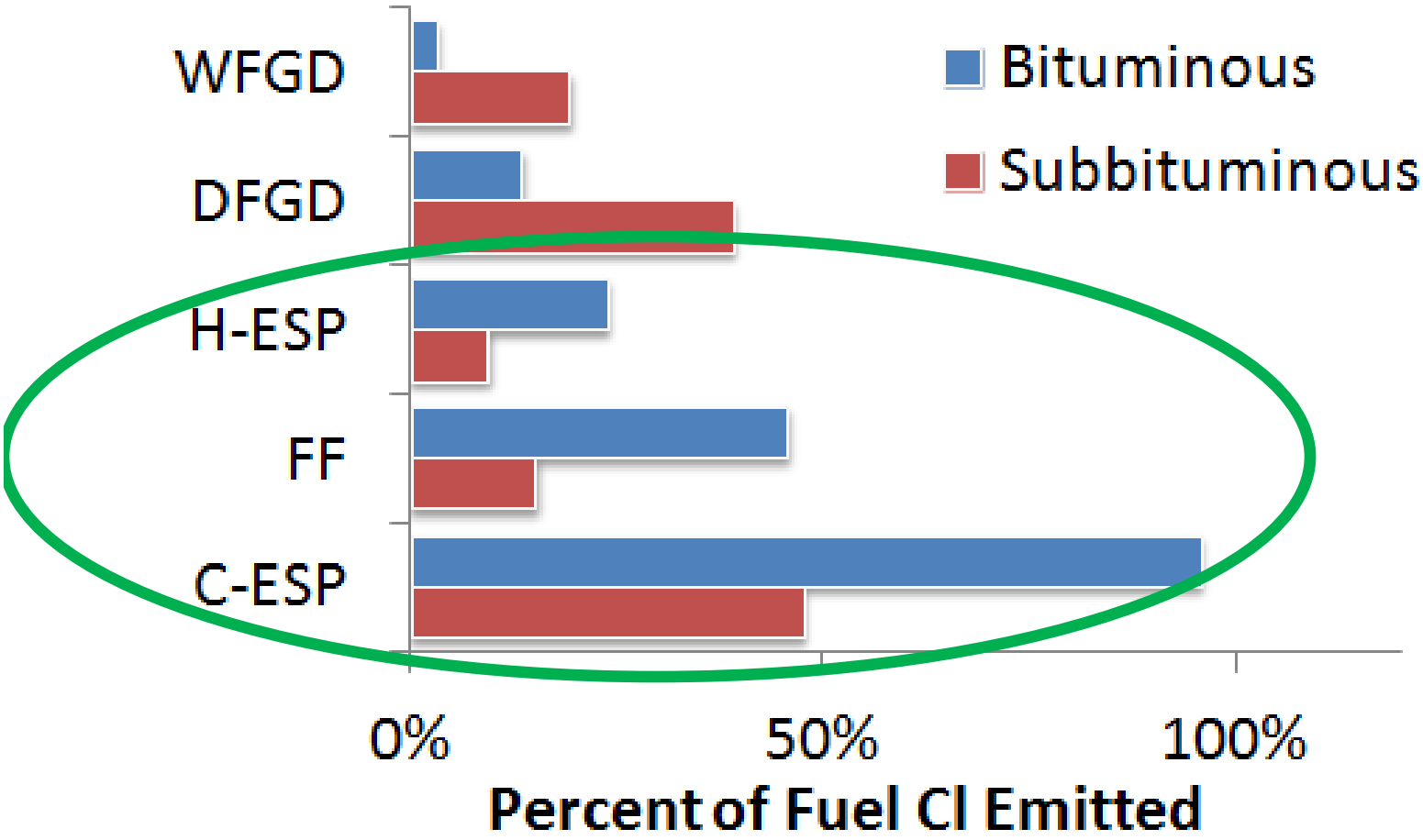
Bromine Addition: Fly Ash Impacts

- 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



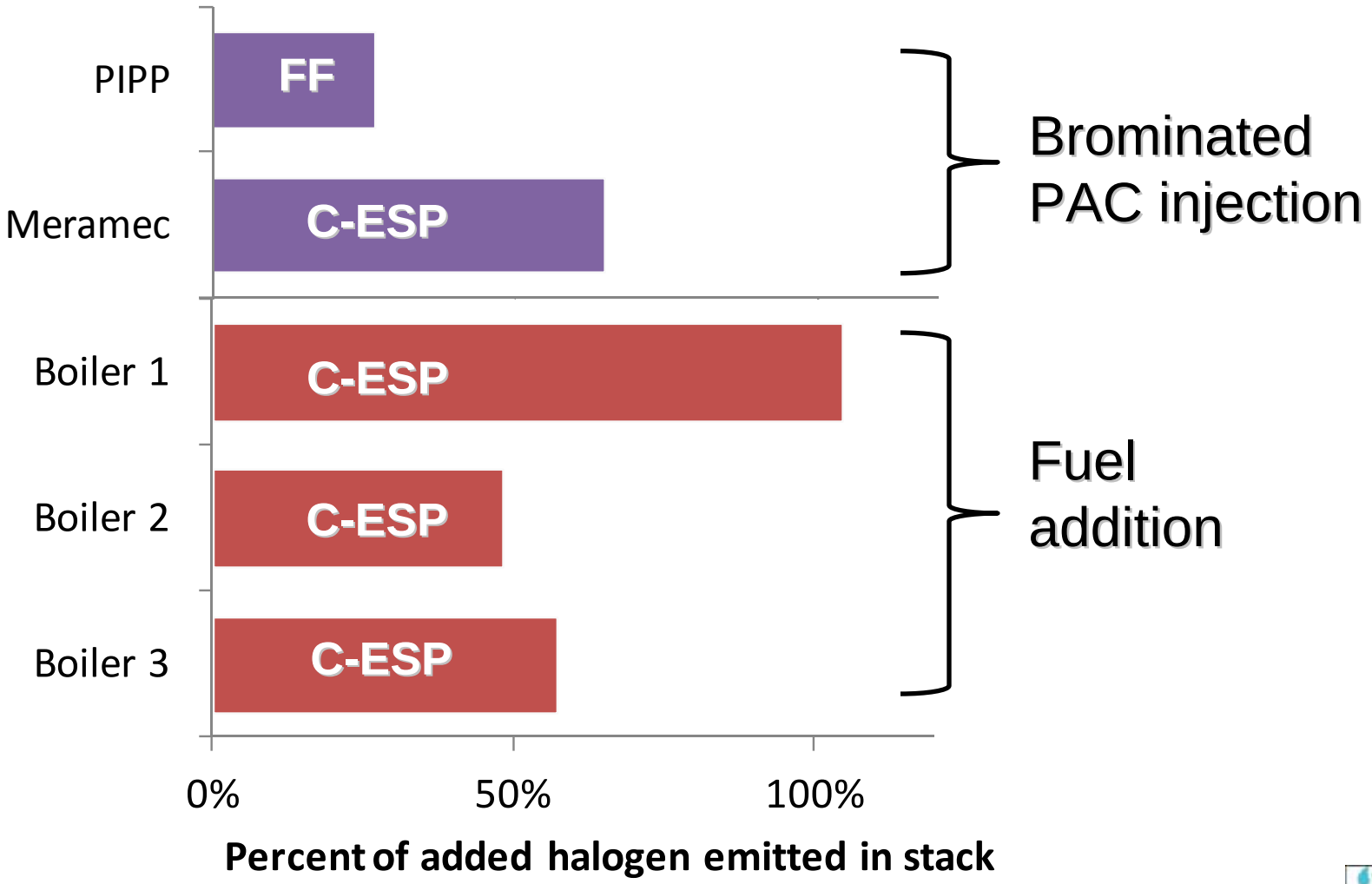
Dombrowski et al., 2008

Chlorine Emission from APCDs



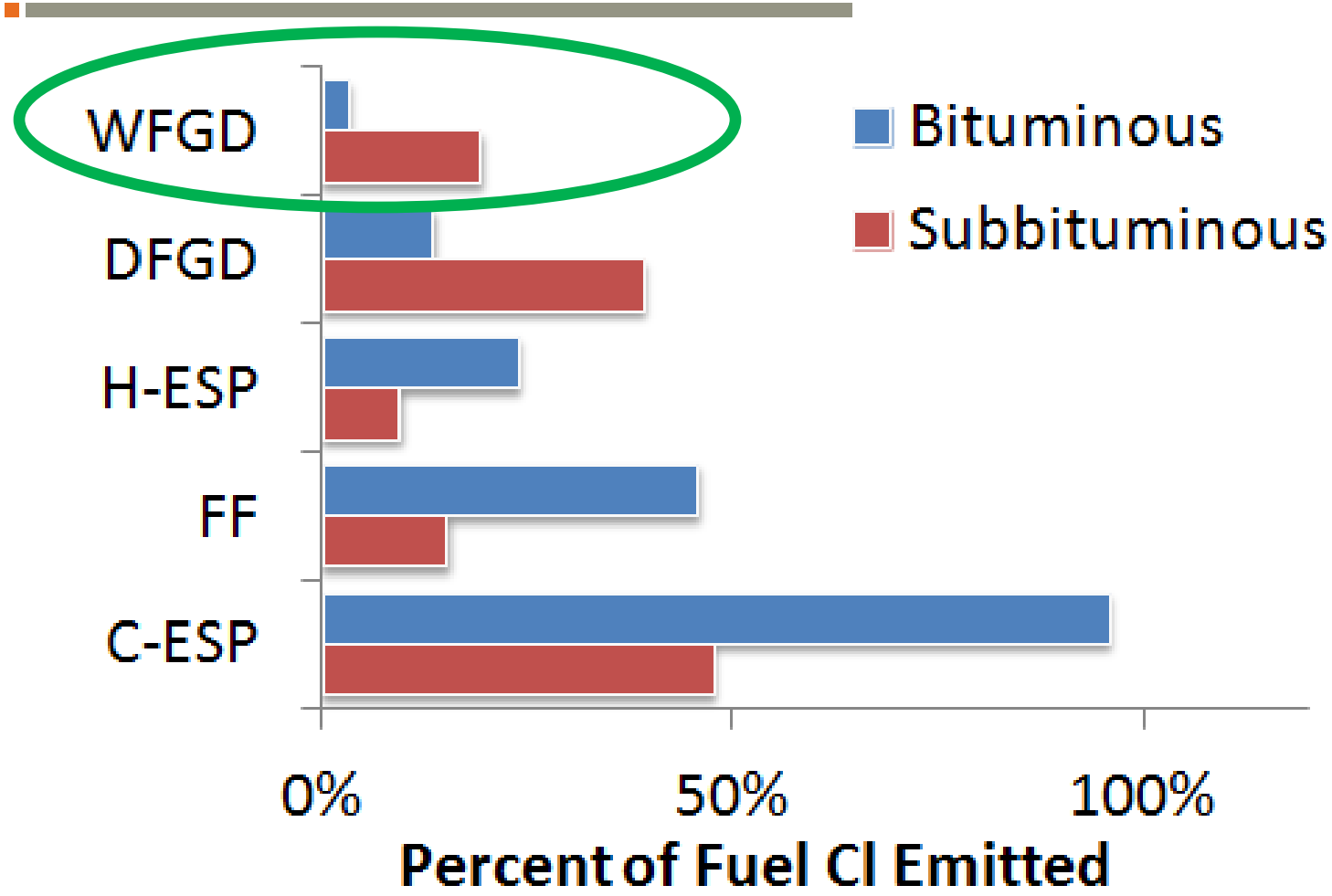
Source: 2010 ICR

Bromine Emission from APCDs



All boilers are pulverized coal, burning subbituminous coal

Chlorine Emission from APCDs



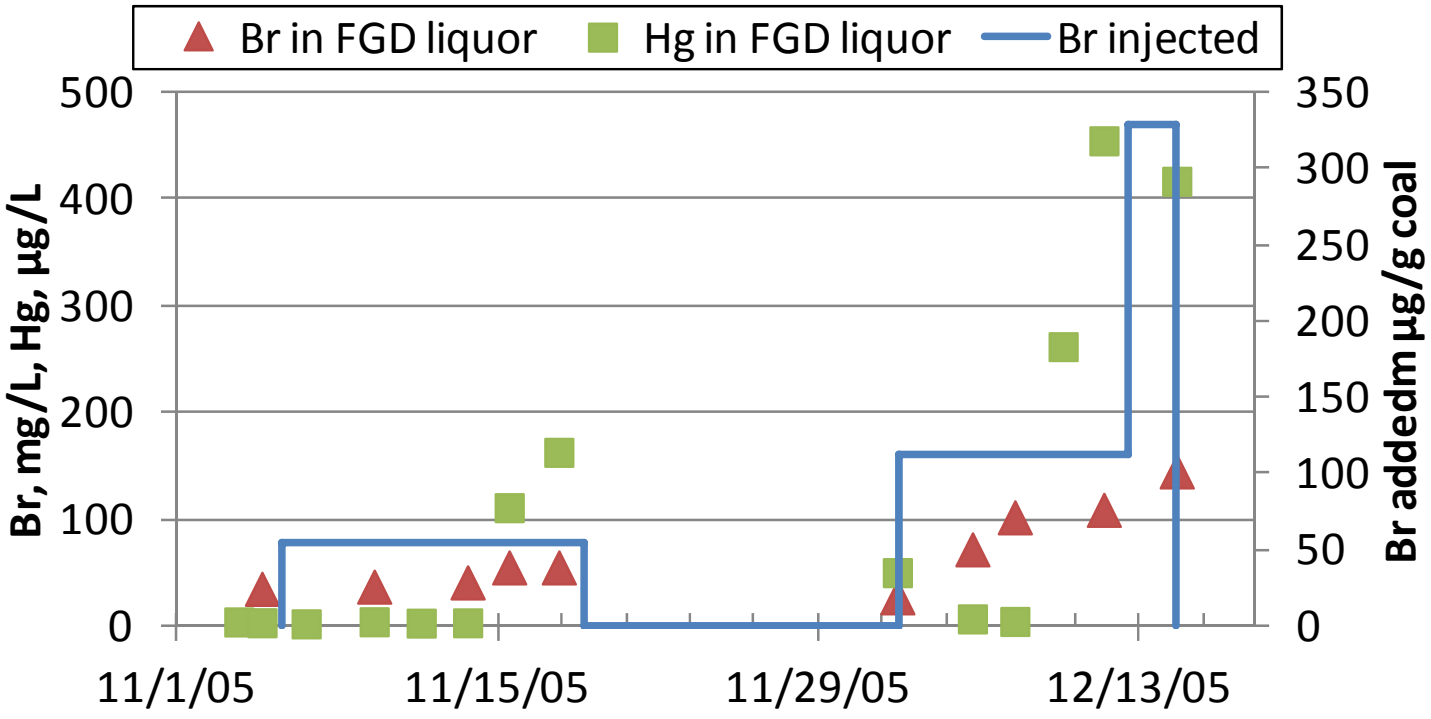
Source: 2010 ICR

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 in Wet Scrubbers

- Halogens and Hg build up in wet scrubber liquor… slowly, depending on scrubber design



Bromine injection at Monticello (EERC, URS data)

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

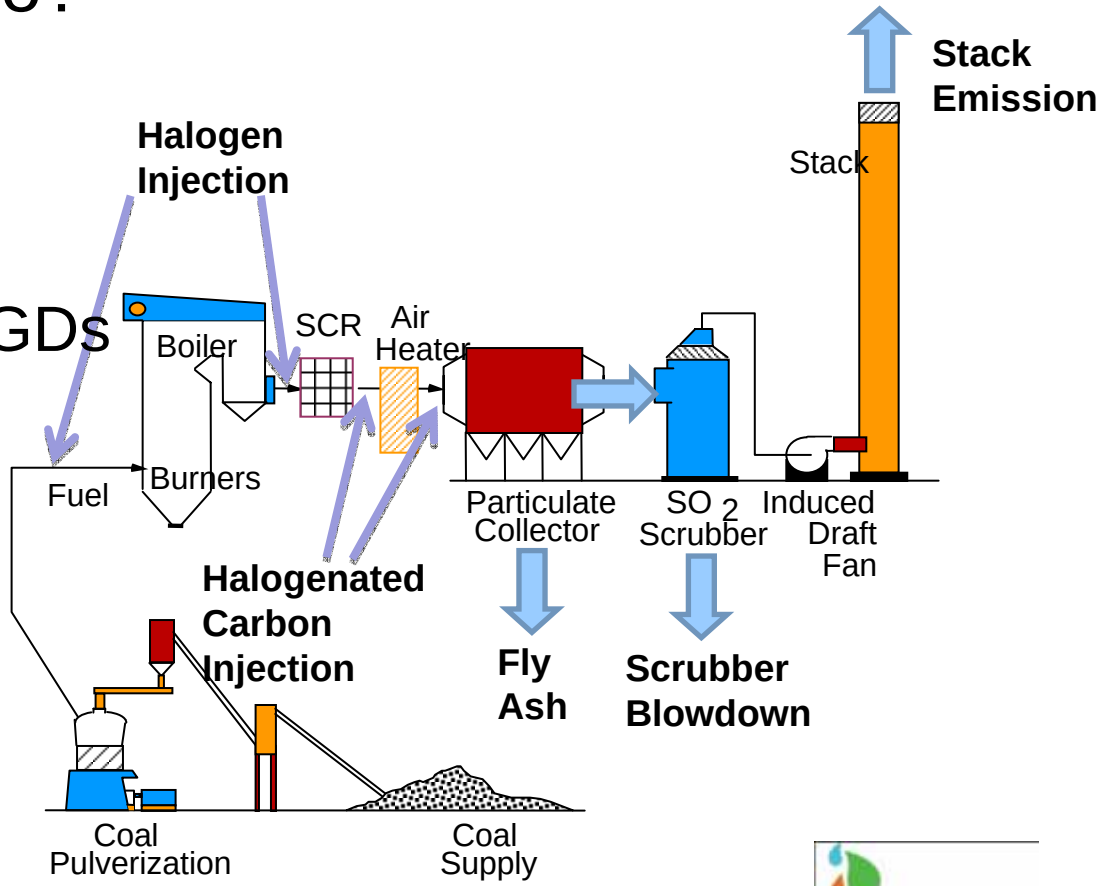
	Se in fly ash, µg/g	% Se capture by fly ash	Se in FGD liquor, µg/L
Baseline	24	70%	300
Br addition	10	20%	4900

(Dombrowski et al., 2011)

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

Halogens Summary

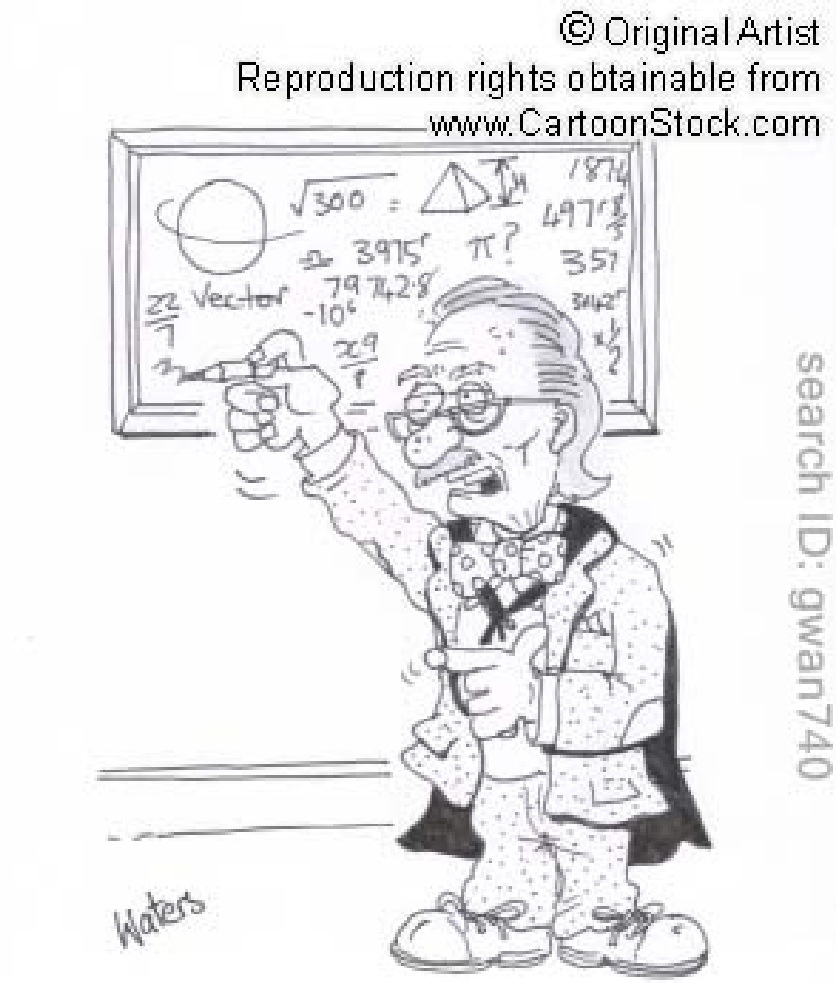
- Halogen fuel/flue gas additives OR halogenated PAC
- Where do halogens go?
  - Some removal in particulate control devices
  - Efficient removal in FGDs
- Br is “new kid on the block” – information needed:
  - Corrosion
  - Multi-media fate
  - Trace metal interactions



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 SO_3 low post-APH

Questions?



"If you're not confused then you really don't know what's going on...!"