Multimedia Impacts of Halogen Injection for Mercury Control in Coal-Fired Boilers

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Motivation for This Presentation

• Adding halogens increases Hg oxidation, native capture, and removal efficiency of ACI
• You’ll hear a lot about halogens at EUEC…

...sometimes perspective is useful
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

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?

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  - 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

Source: Dombrowski et al., 2006
Why Add Halogens?

- Adding halogens to fuel or flue gas:
  - Halogen content of US coals varies widely
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  - Many plants’ APCDs can take advantage of native capture

Source: 1999 ICR
Why Add Halogens?

- Adding halogens to activated carbon increases the ability to capture elemental Hg in low-halogen flue gas (subbituminous or lignite)
Summary: Why Add Halogens?

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  – Halogen content of US coals varies widely
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• 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
- Increased Hg removal across scrubbers

Source: DOE/EPRI sampling campaigns
How Effective Are Halogens?

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- Increased Hg removal across scrubbers

Monticello: PRB/lignite, ESP, wet FGD

![Graph showing the relationship between total Hg removal and halogen in coal]

- Chlorine addition
- Bromine injection

Total Hg Removal (coal-to-stack) vs. Halogen in coal, ug/g
How Effective Are Halogens?

- Halogens increase oxidized mercury: Br more effective than Cl
- 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 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)
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

Dombrowski et al., 2008
Chlorine Emission from APCDs

Source: 2010 ICR
Bromine Emission from APCDs

All boilers are pulverized coal, burning subbituminous coal

Percent of added halogen emitted in stack
Chlorine Emission from APCDs

Source: 2010 ICR
Halogens in Wet Scrubbers

- Adding halogens (Cl or Br) increases oxidized Hg, which increase 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
Halogen injection at Monticello (EERC, URS data)

Halogen injection at Monticello (EERC, URS data)

- Halogens build up in wet scrubber liquor... slowly, depending on scrubber design.
Halogens and Wet Scrubbers

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

<table>
<thead>
<tr>
<th></th>
<th>Se in fly ash, µg/g</th>
<th>% Se capture by fly ash</th>
<th>Se in FGD liquor, µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>24</td>
<td>70%</td>
<td>300</td>
</tr>
<tr>
<td>Br addition</td>
<td>10</td>
<td>20%</td>
<td>4900</td>
</tr>
</tbody>
</table>

(Dombrowski et al., 2011)

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

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