# *Measurement of Corrosion Rate Associated with Halogen for Hg Oxidation*

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# *Presentation Agenda*

- **Halogens for Mercury Oxidation**
- **Balance of Plant Effects of Halogen Injection**
- **Corrosion Testing by ECN Technique**
- **Test Observations**
- **Mitagent Benefits**



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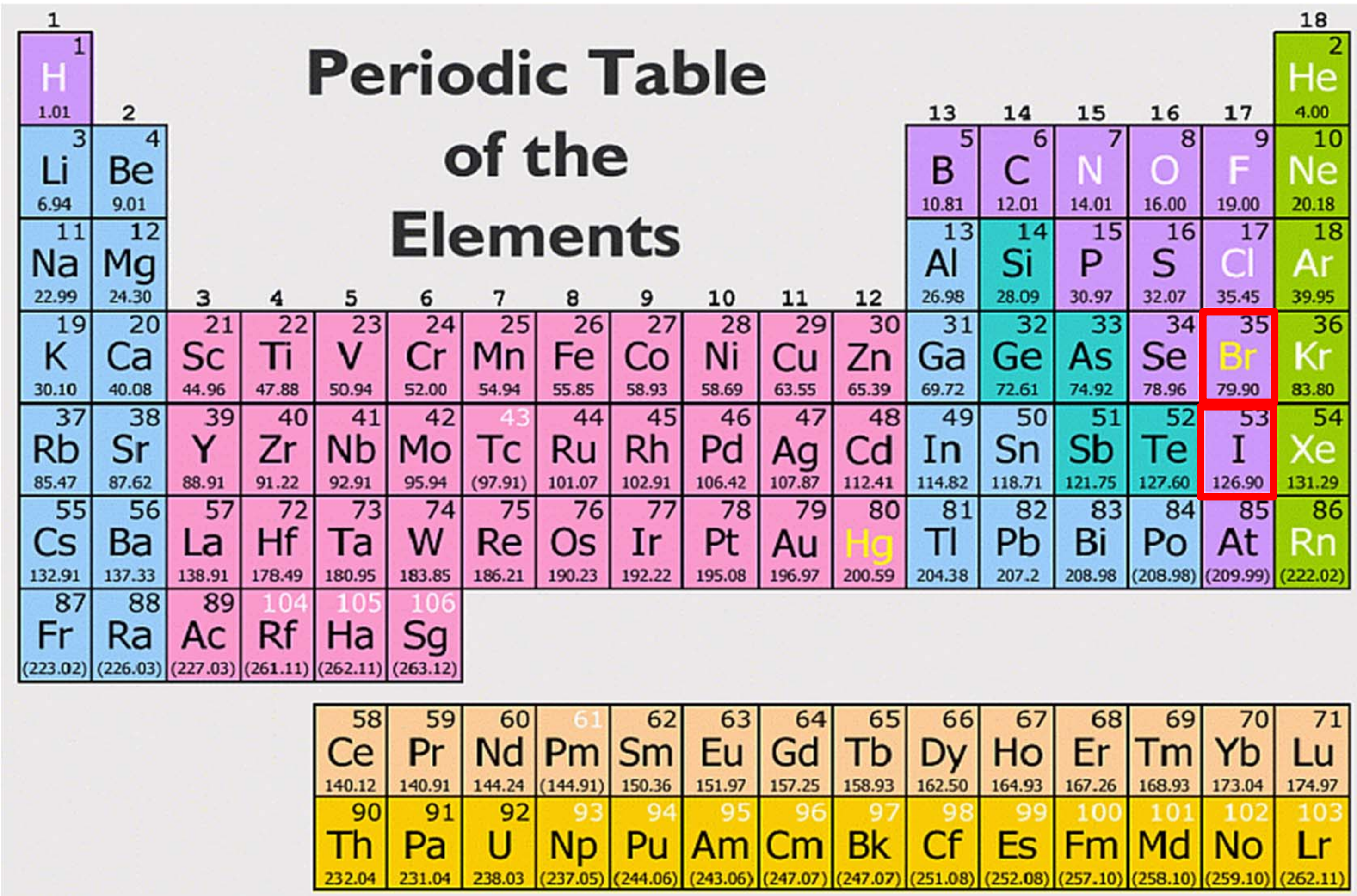
# *Periodic Table of the Elements*





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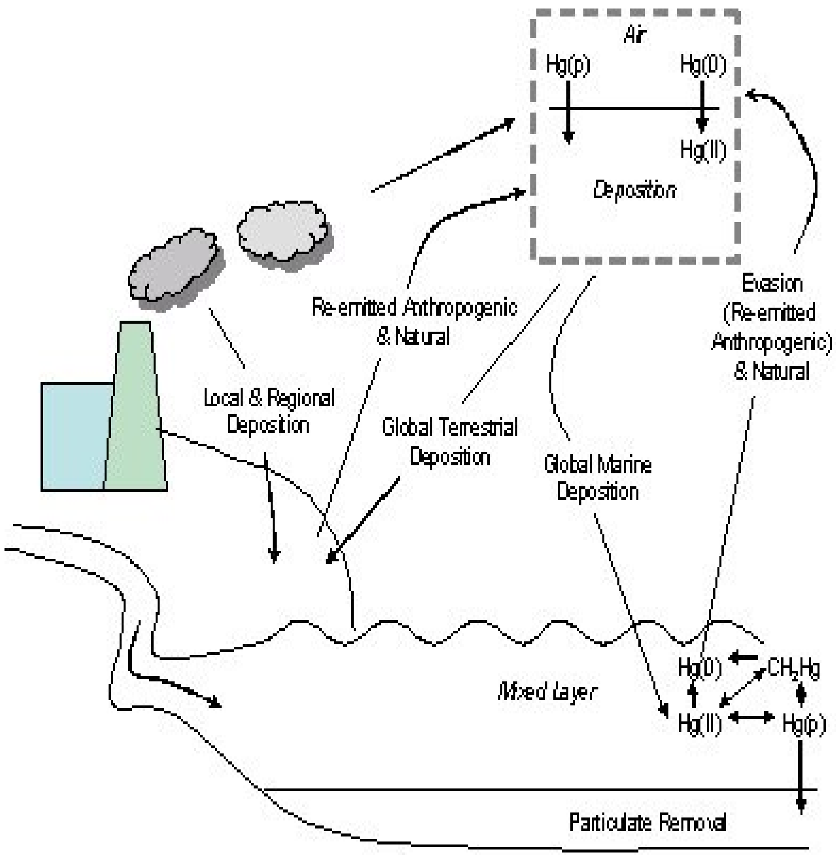
# Mercury Emission Control

- MATS rule: Coal-fired EGUs must achieve stack Hg emissions of 1.2 lb/TBtu or less for Bit. and Sub-Bit. coals
- Mercury oxidation by halogen injection and removal of the oxidized Hg either by FGD's or by sorbents is one of the most cost-effective methods for Hg emission control
- Halogen injection is very simple, and reliable method for Hg oxidation
- Necessary to consider Balance-of-Plant effects with the long-term use of halogens

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# *Halogens for Hg Oxidation*

- Chlorine, Bromine, and Iodine are main halogens used for Hg oxidation
- Bromine most widely used (low-cost and effective)
- In furnace, Bromine additives first form $HBr_{(g)}$
- Deacon Reaction: $4HBr + O_2 \rightarrow H_2O + 2Br_2$
- $Hg + Br_2 \rightarrow HgBr_2$ (oxidized Hg)
- Catalytic sites important factor in conversion of HBr to $Br_2$
- Unconverted hydrogen halide main cause of BoP issues with any halogen (not just Bromine)

**Dead Sea**





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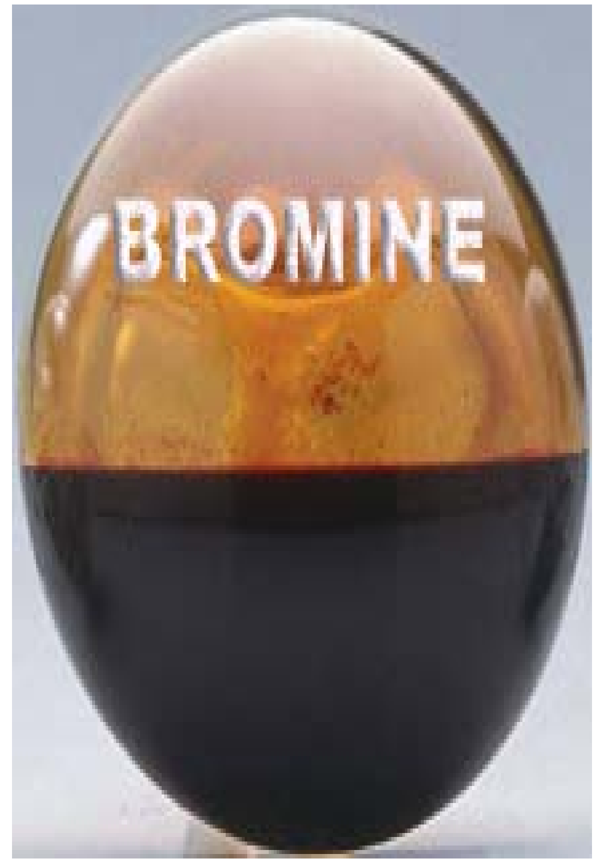
# *BoP Issues with Halogen for Oxidation*

- Higher Bromine (Br) levels in WFGD liquor and waste water is only BoP issue for Eastern Bituminous coals
- Br in water may lead to formation of additional Trihalomethanes (THMs) in downstream water systems
- Air Heater cold-end basket corrosion is most common BoP issue for low-rank coals (PRB, W Bit and Lignite)
- Halogen injection affects Selenium (Se) speciation, resulting in increased gas-phase Se at WFGD inlet, which may increase Se levels in WFGD liquor and waste water

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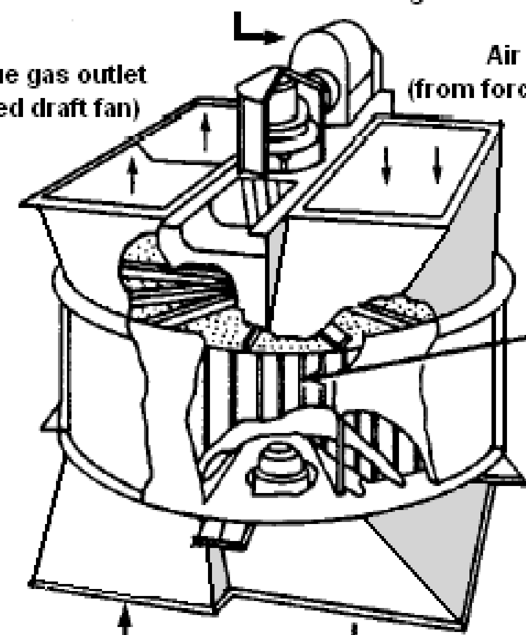
# Air Heater Corrosion

- 33 PRB units reported Air Heater (AH) cold- end basket corrosion, while 19 did not (Update on EPRI's Balance of Plant Effects Study of Bromine-Based Mercury Controls, 2014)
- Key difference is Bromine application rate, >100 ppm vs. <100 ppm
- HBr dew-point temperature is ~125°F
- Lowest metal temperatures are experienced during basket rotation back into flue gas stream
- Cold-end AH baskets on PRB-fired units not typically constructed of corrosion-resistant materials or enameled
- It is hypothesized that the corrosion ***rate*** is dependent on the Bromine application rate





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# *Corrosion Testing*

- Testing was performed on a 80 MW PRB coal fired unit with ESP as AQCS
- Test Objectives: To investigate effects of halogen type, and halogen injection rate on Hg oxidation and Air Heater corrosion rates
- Data Collection and Analysis: ElectroChemical Noise (ECN) probe, Stack CEMS, and EPA M5 and M30B
- Air Heater metallurgy: Carbon Steel A192, selected because it has lowest corrosion resistance

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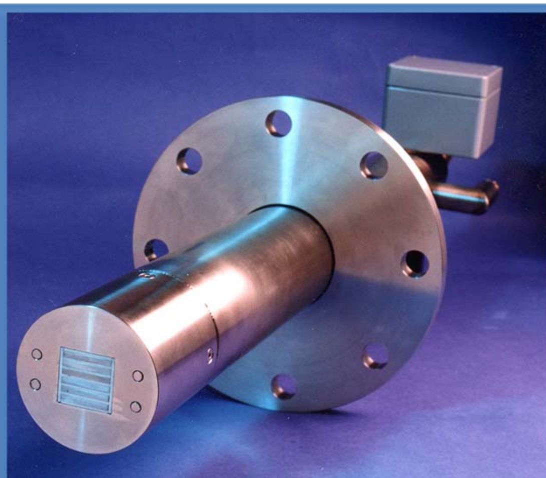
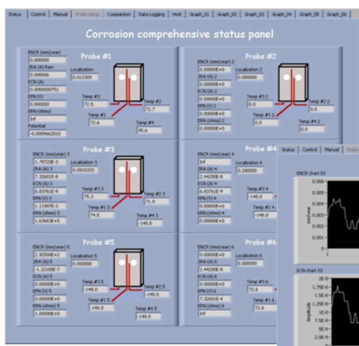
# *ECN Probe for Corrosion Testing*

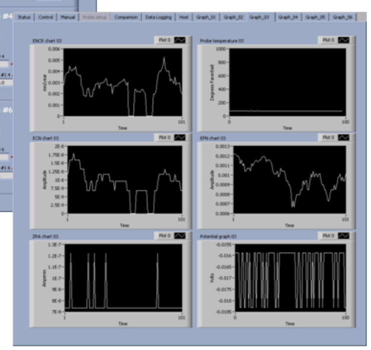


- High Sensitivity
- Instantaneous response
- Direct indication of corrosion
- Quantitative measurement
- Response related to corrosion mechanism

Data Acquisition




Main panel displays real-time corrosion data and temperatures of all probes



Histograms for all data points measured from each probe for trend comparison

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# Corrosion Testing - ECN Probe

Un-exposed probe

Deposit build-up following 4-hour period of 25ppm Iodine addition



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# Test Results

| 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 | Same |
| 12/11 PM 25 ppm Iodine | 98.5 | 0.28 | 2-3 X |
| 12/12 AM 25 ppm Bromine | 78.7 | 0.10 | Same |
| 12/12 PM 75 ppm Bromine | 83.7 | 0.27 | 2-3 X |

* Averaged over multiple test periods


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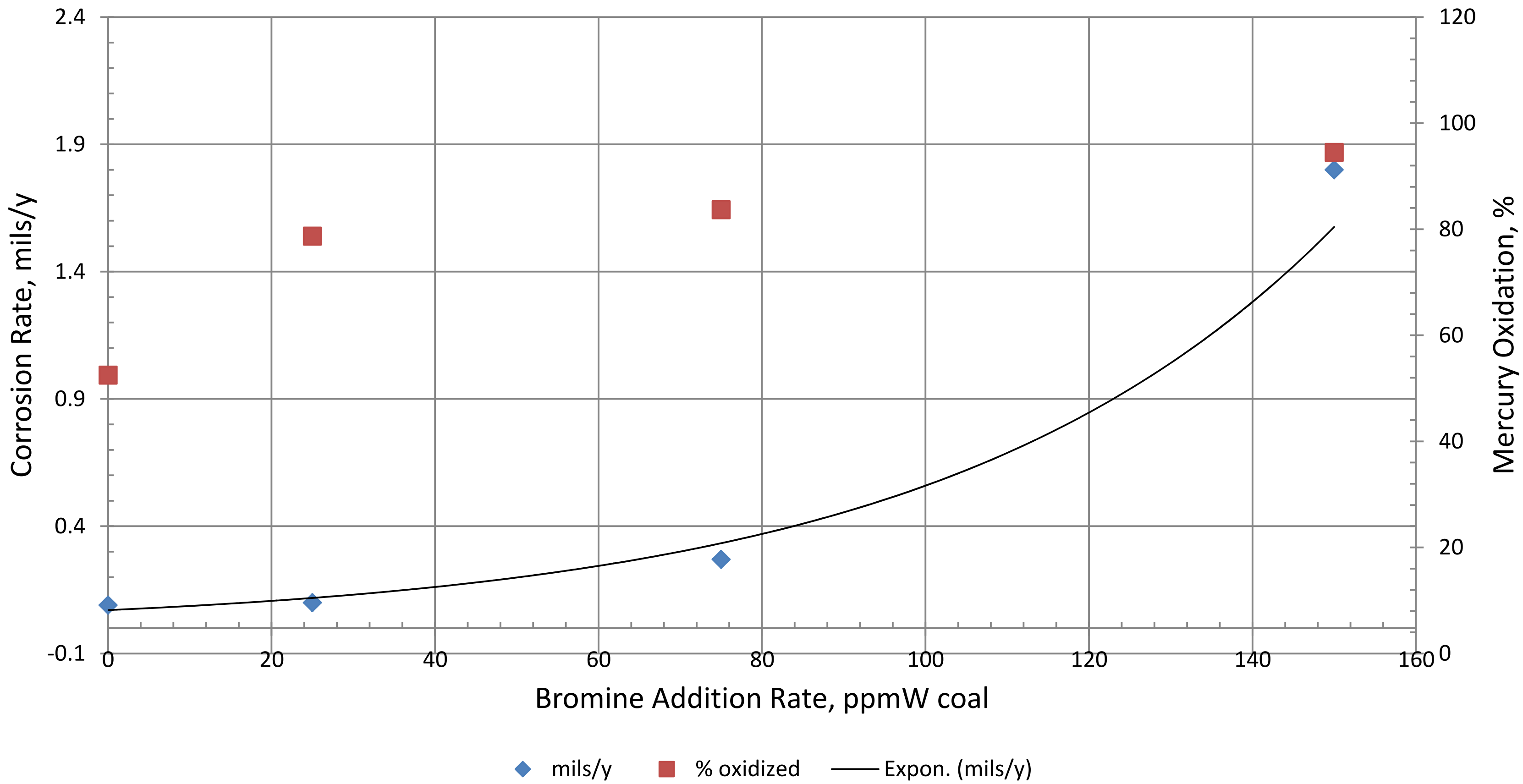
# Corrosion & Hg Oxidation Vs Br Addition Rate





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# *Observations*

- 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 <u>20 times higher</u> than baseline
- Data did show that rate of corrosion is function of rate of halogen application to coal
- Mitagent additive can make a significant difference

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# *Mitagent Benefits*

- Mitagent is patented coal additive developed by B&W PGG
- Among other benefits, Mitagent can reduce the rate of SCR catalyst deactivation by phosphorous poisoning on staged combustion PRB units
- Mitagent also facilitates efficient use of halogen containing additives for Hg oxidation by catalyzing the Deacon reaction w/o SCR
- This can lead to either reduced halogen injection rate to coal  to get similar Hg oxidation or improvement in Hg oxidation with similar halogen injection rate
- Full-scale and pilot-scale test data has demonstrated efficient halogen utilization with Mitagent addition

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# Bromine Reduction by Mitagent

## PRB Unit : Dec 2013

| Bromine added to coal (ppm, dry basis) | Mitagent added to coal (lb/hr) | % Oxidized Hg @ Stack (Method 30b) |
|---|---|---|
| 0 | 0 | 38.0 |
| 70 | 0 | 46.5 |
| 100 | 0 | 62.5 |
| 40 | 11.4 | 56.0 |

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# *Expected Performance Improvement with Mitagent*

| Condition | % Hg Oxidation | Corrosion Rate @ 120°F, mils/year |
|---|---|---|
| 25 ppm Bromine | 78.7 | 0.26 |
| Expected Rate<br>25 ppm Br with Mitagent | 90 | 0.26 |
| 10 ppm Iodine | 93.1 | 0.16 |
| Expected Rate<br>7 ppm I with Mitagent | 90 | 0.15 |

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# *Mitagent Benefits*

- Mitagent reduces injection cost for Iodine by 30-50% while providing same 90+% Hg oxidation levels
- Mitagent further improves Hg oxidation by 20-30% for low Bromine application rates (25 ppm or less)
- Mitagent reduces application rates by 30-50% for high Bromine addition rates (>100 ppm), and therefore associated corrosion risks
- Mitagent use results in significant operating cost reduction by reducing halogen usage
- On going long-term testing indicates no negative effect on boiler or AQCS performance


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# Questions?


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