REINHOLD ENVIRONMENTAL Ltd.

2013 NOx-Combustion Round Table & Expo Presentations

February 18 & 19, 2013, in Salt Lake City, UT / Hosted by PacifiCorp

Bromine Balance of Plant Study

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Reinhold NO_X Combustion Roundtable
February 19, 2013

ELECTRIC POWER RESEARCH INSTITUTE

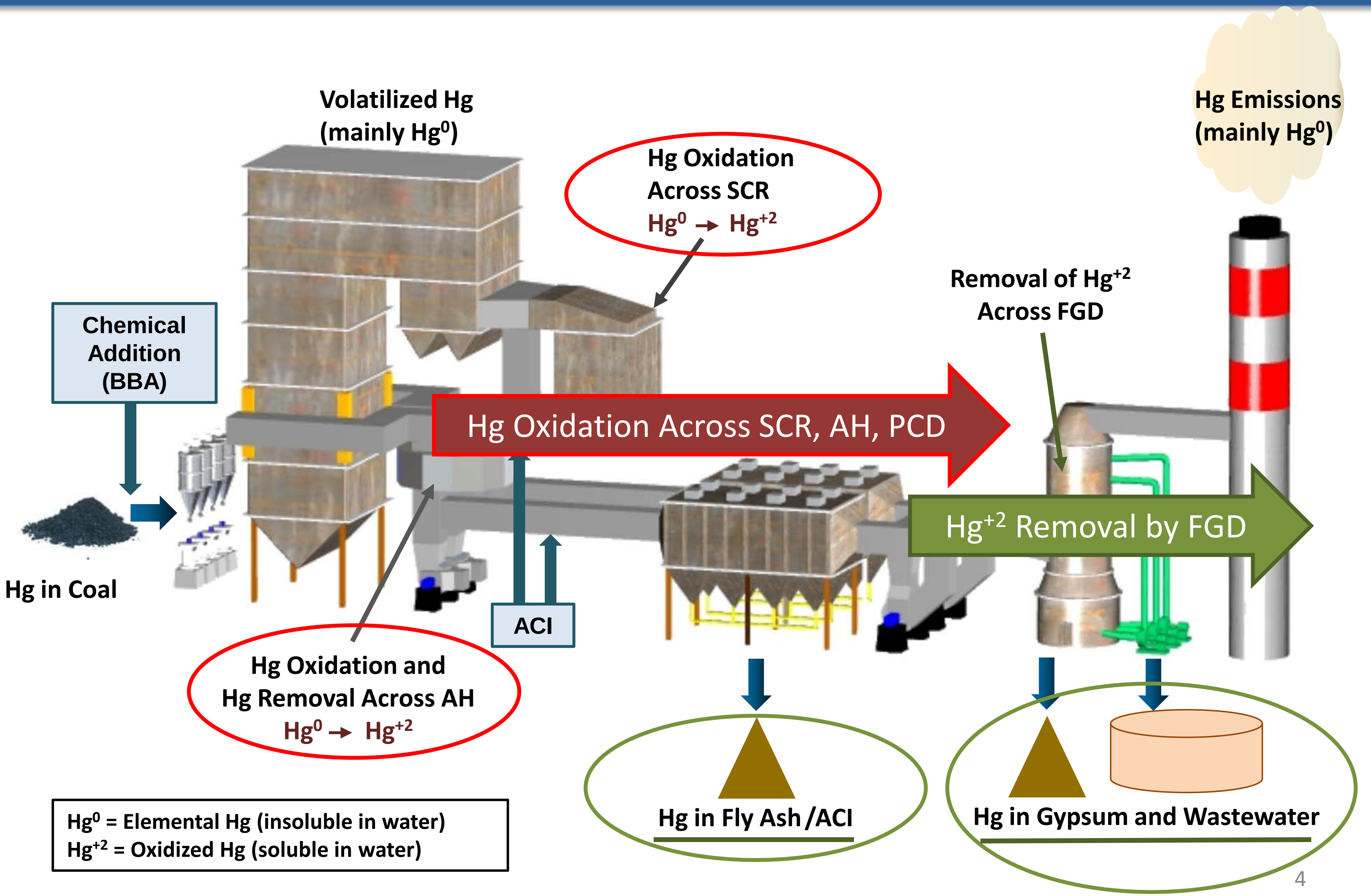
Outline

- **Bromine based Hg control technologies**
- **EPRI Br BOP survey**
- **Fate of Br in power plant**
- **Br and Corrosion**
  - Coal handling
  - Boiler
  - Air heater
  - Duct internals
  - FGD

Bromine Based Hg Control Technologies

- **Brominated Activated Carbon Injection (Br-ACI)**
  - Removal of Hg in particulate control device
- **Boiler Bromide Addition (BBA)**
  - Enhance oxidation of Hg for removal in scrubber
  - Enhance performance of ACI

Fate of Mercury Across Flue Gas Path



Hg^0 = Elemental Hg (insoluble in water)
Hg^{+2} = Oxidized Hg (soluble in water)

Unit Configurations Surveyed

Coal Type	# of Units in Survey	PCD	# of Units in Survey	NO_X control	# of Units in Survey	FGD	# of Units in Survey
E.Bit	11	CSESP	35	SCR	15	W. FGD	14
W.Bit	3	HSESP	3	SNCR	4		
PRB/ PRB blend	35	FF	9				
ND Lignite	1	Venturi scrub.	4				

EPRI seeking SD/FF units using $CaBr_2$ to participate in survey

Hg Emissions Limits

- **Section 45:** **40% Hg reduction**
- **State regulations:** **vary by state**
- **MATS (Non-Lignite Coal):** **1.2 lb/Tbtu**
- **MATS (Lignite):** **4.0 lb/Tbtu**

For MATS compliance:

Halogen Addition must be coupled with FGD, ACI and/or high LOI ash

Balance of Plant Effects: Bromide Addition

EPRI Bromine BOP Study **54 units participated**

- **Fly ash sales - no effects observed**
- **Opacity - increase at one plant with SCR/FF/FGD**
- **SNCR – negative synergy of BBA and SNCR**
- **FGD effluent - potential areas of concern**
  - Increase in Hg
  - Increase in selenium
  - Increase in bromide
  - Increase in brominated organics

FGD discharge method has not been affected at any plants

Balance of Plant Effects: Corrosion

EPRI Bromine BOP Study

- **Corrosion – potential areas of concern**
  - Coal handling
  - Air Heater
  - Duct Internals
  - FGD
  - Low load operation
- **At the time of the survey**
  - 27 BBA units with > 1 yr operating time
  - 18 of these units had conducted inspections
  - 7 of these units observed corrosion

Observations of AH corrosion for brominated ACI units with low AH exit temps

Expressing Br Addition Rate

Min Reported Addition Rate	Max Reported Addition Rate	Units (all ppm values are by weight in coal)
<65	740	ppm 52 wt% $CaBr_2$ solution to as-received coal
< 40	440	ppm Br to the dry coal **PRB coal ≈ 25 ppm Cl, dry**
3.5	40	gph 52 wt% $CaBr_2$ solution for 600 MW unit

Fate of Br in Power Plant System

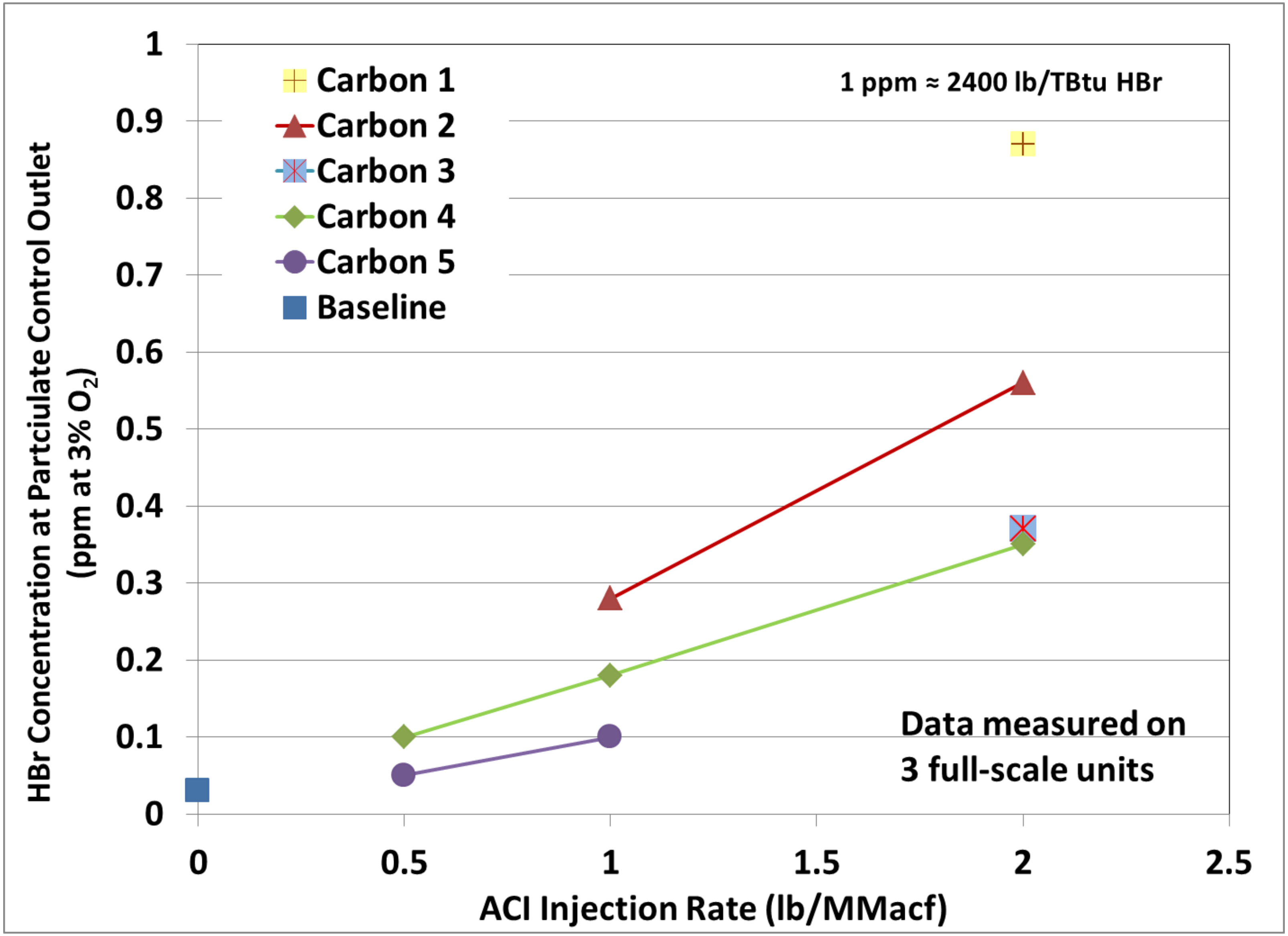
Flue gas HBr/Br_2 concentrations increase

- **$CaBr_2$ Addition**

  10 ppm Br in coal, dry ≈ 0.3 ppm HBr in flue gas

- **Br-ACI**
  – Br volatilizes from carbon
  – EPRI fixed bed laboratory study to measure Br volatility from various commercial carbons
    - Effect of impregnation technique
    - Effect of halogen loading
    - Effect of temperature
    - Results available to EPRI Program 75 members this spring

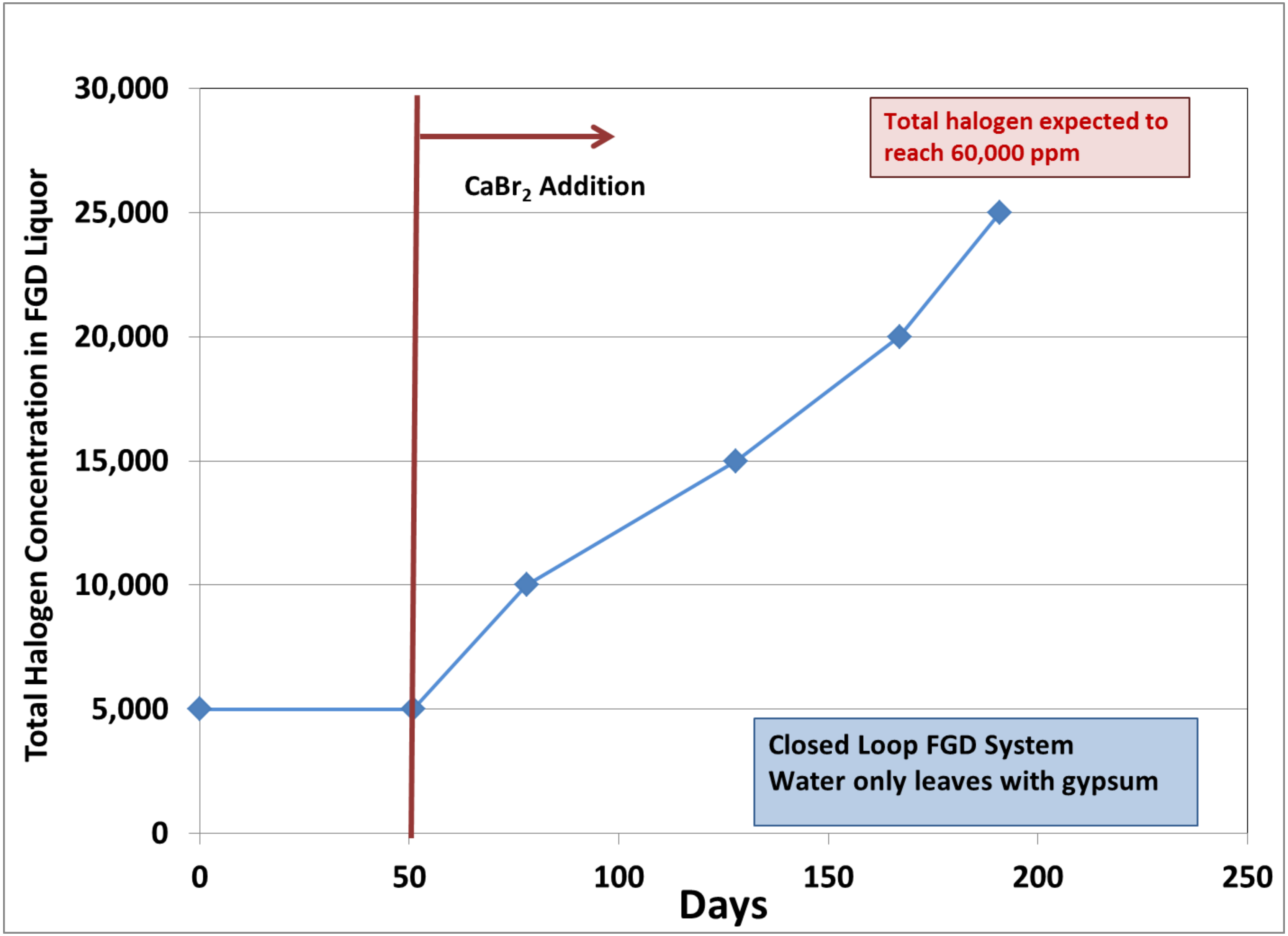
Br Volatility from Br-ACI



Fate of Br in Power Plant System

- **Br concentrations in fly ash**
  - Low LOI fly ash: 1% Br reports to fly ash
- **Br concentrations in FGD scrubber**
  - Br scrubbed efficiently by FGD
  - [Br] in FGD depends on
    - Br addition rate to flue gas
    - Coal sulfur
    - Water balance
  - Closed loop systems may take months to reach steady-state [Br]

Increase in Br in FGD Liquor: Measurements from Full-scale FGD



Cases of Reported Br Corrosion

Location	Number of Reports of Corrosion	Comments
Coal Handling	1	Pulverizer pressure frame
Boiler	0	EPRI lab tests and ICL-IP diesel-fueled boiler tests indicated low potential for corrosion
Air Heater	11	6 $CaBr_2$ units • 2 units had low AH outlet gas T • 2 units had old baskets 5 Br-ACI units • 4 units injected same carbon • 4 units had low AH outlet gas T
Duct Internals	1	ESP corrosion on SD-ESP unit with $CaBr_2$ addition
FGD	1	$CaBr_2$ not directly implicated; absorber constructed of 2205

Boiler Corrosion

- **EPRI laboratory tests and modeling**
  - Low potential for Br corrosion in boiler at Br addition rates needed for Hg control
- **EPRI survey**
  - No reports of boiler tube corrosion due to $CaBr_2$ addition to coal
- **ICL-IP coupon test in diesel fuel steam boiler**
  - Corrosion rate negligible (< 1mpy) up to 1000 ppm Br
- **Corrosion rate in coal-fired boiler**
  - Coupon tests
  - Electrochemical noise probe?

Air Heater Corrosion

- **6 BBA units reported air heater corrosion**
  - One unit: BBA + ACI; low AH outlet gas temperatures
  - One unit: operated BBA for 3 years without AH corrosion; lower operating loads in the past year
  - Two units: old air heater baskets
  - Two units: refined coal plants
- **5 Br-ACI units reported AH corrosion**
  - 4 units operated at low AH outlet temperatures
    - Units did not experience severe corrosion previous to the implementation of ACI
    - Units all used the same carbon
  - 1 unit operated with a different carbon
    - Cold-end sootblowers slowed corrosion rate

Example AH Corrosion

Cold-end baskets, 2 years old

BBA + ACI, 1 year operation

Source: davidnfrench.com

Possible AH Corrosion Mechanisms

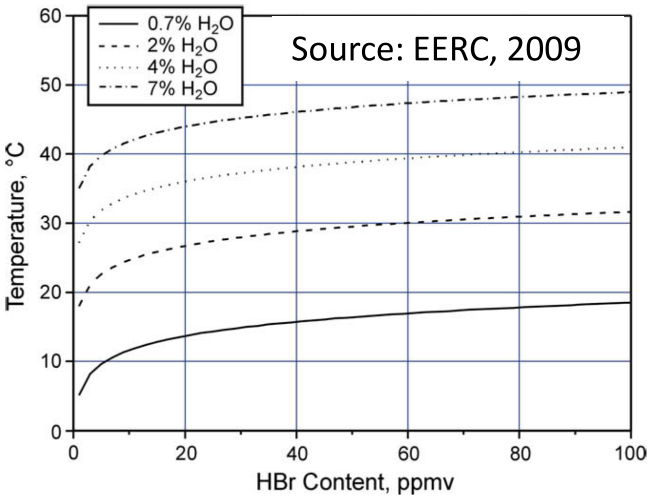
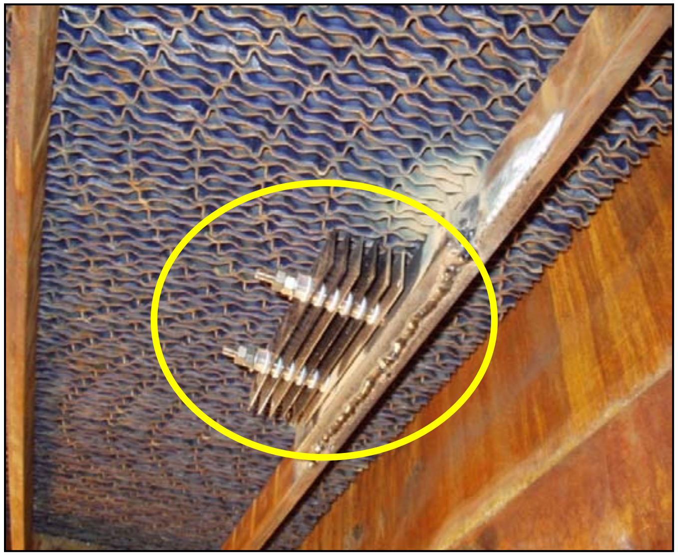


Fig. 1. Dew point behavior of HBr at various water contents of the gas, calculated from the formula of Kiang [19].

- **Direct condensation of HBr on the metal**
  - Dewpoint of HBr is low
- **Absorption of HBr into condensed acid**
  - SO_3 has a higher dew point than HBr
  - More aggressive corrosion agent?
- **Adsorption of HBr onto fly ash**
- **Gas phase oxidation by HBr**
  - EERC lab tests at 51 ppm HBr in gas (vs. 1-10 ppm HBr typical)
  - Active oxidation of carbon-steel by HBr observed at 300°F and 150°F
  - Condensation corrosion observed at 150°F and 80°F
- **Attack by other constituents in the PAC**
  - e.g., formation of SO_3 on PAC that has deposited on air heater

On-going Corrosion Tests: AH

- **Site A (High-S EBit) and Site B (PRB/CAPP/EBit Blend)**
  - Br source: Refined coal use (120 ppm Br, dry)
  - Coupon location: AH rotor - basket bars
  - AH config: Horizontal and vertical shaft
  - Coupon types: (Total 5)
    - Enamel Coated LACR (element)
    - A606 (basket/element)
    - A588 (diaphragm plate)
- **Test Duration: Next outage**



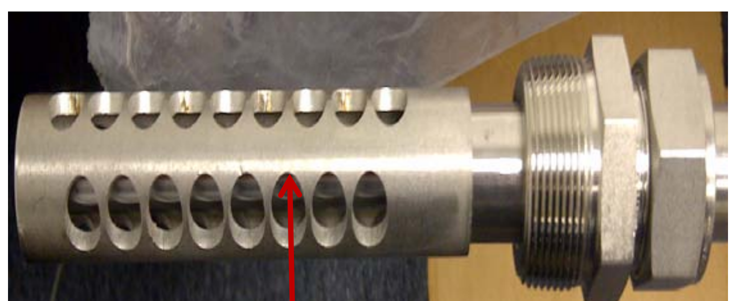
On-going Corrosion Tests: Duct

Electrical Resistance (ER) Probe

- Linearized signal α to metal loss of the exposed element
- Yearly Corrosion Rate estimated with change in corrosion film and the time between measurements
- Data logged hourly

- **Site C: TxL/PRB coal**
  - Br source: Refined coal (120 ppm)
  - Coupon location: AH_{in} /AH_{out} /ESP_{out}
  - Coupon types: Basket/Duct/SCR screen
  - Probes: Electric Resistance (ER) at ESP_{out}
- **Test Duration: 1 month & ?**

Weight loss Coupons



ER probe

FGD Corrosion

Can we replace with Br^- or (Cl^-+Br^-)?

Wet FGD Alloy Selection Guide

		Mild	Moderate		Severe		Very Severe		
	Chlorides:	500	1,000	5,000	10,000	30,000	50,000	100,000	200,000
Mild	pH - 6.5	Type 316L SS or Duplex 2304 or Duplex 2003						Nickel Alloy 625 etc.	
Moderate	pH - 4.5	316L or Duplex 2003	Type 317LMN or 22% Cr Duplex SS				6% Moly Superaust. SS		
Severe	pH - 2.0	Type 317LM SS		22% Cr Duplex SS	25% Cr Super Duplex SS			Nickel Alloy C276 etc.	
Very Severe	pH - 1.0	Type 317LMN SS	6% Moly Superaustenitic SS			Nickel Alloy 625 etc.			

Developed by the Nickel Institute (http://www.nickelinstitute.org/) using the PREN, lab and field coupon tests, user surveys, industrial experience, etc.

FGD Corrosion

- **Goal: Develop equivalence function**
  - $[Cl]_{eq} = f([Br])$
  - $[Cl]_{total} = [Cl] + [Cl]_{eq}$
  - Keep $[Cl]_{total} < [Cl]_{limit}$
- **Preliminary attempt: lab electrochemical tests**
  - Tested under ideal test conditions
    - Smooth alloy
    - Synthetic FGD liquor
  - Corrosivity of Br vs. Cl is alloy dependent
    - 2205: Br more corrosive than Cl
    - 316L: Cl more corrosive than Br

FGD Corrosion – Lab Results

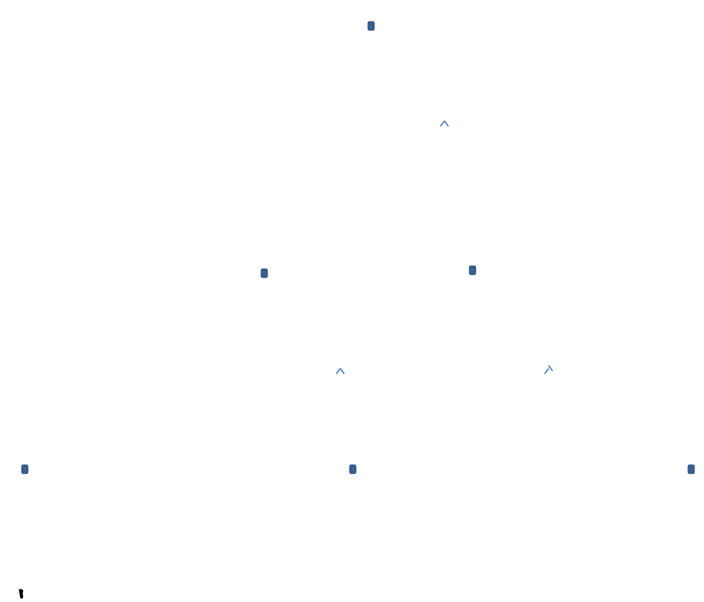
- Critical bromide concentration to induce pitting for fixed chloride conditions
- Developed under ideal conditions

Alloy	PRB Simulation	
	Cl^- Concentration in FGD (ppm)	Critical Br^- Concentration Range in FGD (ppm)
C276	6,400	>31,000
AL 6XN	6,400	>31,000
2205	6,400	$8,000 < Br^- < 31,000$
317LM	5,000	$6,300 < Br^- < 24,200$
316L	700	$900 < Br^- < 3,400$
304L	300	>1,500

Scaling from Lab to Field Tests to Real-world Operation

Determine if lab tests provide predictive relationships for [Br] that translate to the field

- More realistic laboratory tests (ongoing)
- Field tests with slipstream liquor (planned)

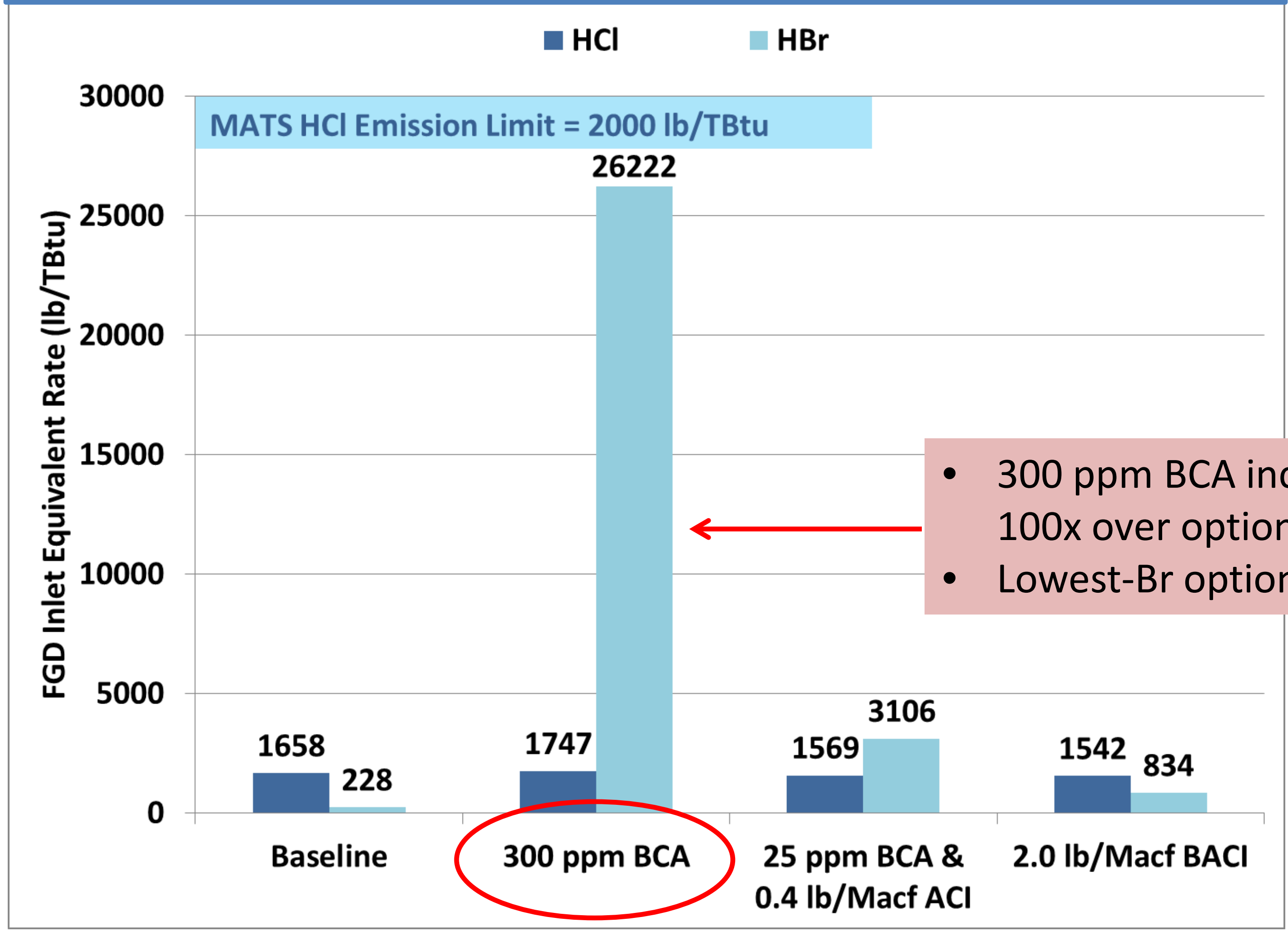


Reducing Risk of Br-Corrosion

- **Select technology that provides the required mercury removal performance with the smallest release of bromine**
- **Design $CaBr_2$ and ACI delivery systems to be flexible**
- **Minimize sorbent usage**
  - Ensure good sorbent distribution via lance design and placement (CFD modeling)
  - On-site grinding to de-agglomerate particles
- **Adjust air heater operation**
  - Use air pre-heat
  - Employ cold-end sootblowers
  - Increase outlet gas temperature
- **If possible, blow down FGD system at higher rate to reduce [Br] in the FGD system**

Limiting HBr Exposure with Technology Choice

Halogens at FGD Inlet



GRE Coal Creek Station
NDLignite/ESP/FGDw

- 300 ppm BCA increases flue gas HBr 100x over options using ACI
- Lowest-Br option will be unit-specific

Options for MATS Hg Compliance: 4 lb/TBtu

Reducing Risk of Br-Corrosion

Selection of $CaBr_2$ Addition Location

$CaBr_2$ Addition Location	Advantages	Disadvantages
Upstream of day silos	• Keeps storage and truck deliveries away from unit • Compatible with Section 45 coal refining process	• Entire coal handling path is exposed to $CaBr_2$ • Requires larger pumps
Upstream of pulverizers	• Fewer parts of coal handling train exposed to $CaBr_2$ • Option exists to not treat all coal feeders • Better process control	• Direct exposure of weigh belt and pulverizers to $CaBr_2$

Reducing Risk of Br-Corrosion

Selection of Br-ACI Injection Location

Br-ACI Injection Location	Advantages	Disadvantages
Upstream of air heater	• Possibly lower ACI rate needed due to increased residence time	• Higher Br volatility • AH exposed to carbon and Br
Downstream of air heater	• Lower Br volatility • AH not exposed to carbon or Br	• Possibly higher ACI rate needed

EPRI Bromine BOP Activities for 2013

Flue Gas Corrosion

- Analysis of field coupons from Sites A, B, C
- Supplemental EPRI Programs at other sites

FGD Corrosion (Br vs. Cl)

- Electrochemical test with FGD slipstream; spike with $CaBr_2$
- Parallel lab study with same slurries to validate

Lab tests

- Investigate effect of HBr in dilute H_2SO_4 with coupons
- More Br-ACI volatility tests (other carbon types)

Site Survey

- SD-FF and CDS units adding $CaBr_2$
- Updates from original survey participants