

REINHOLD ENVIRONMENTAL Ltd.



**2014 APC Round Table  
& Expo Presentation**

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# Bromine Corrosion from The Operator's Perspective

Greg Betenson – Pacificorp, Jim Chaney - STEAG  
July 15, 2014



- 1. What s not being covered.**
- 2. Anecdotal Information.**
- 3. Why Bromine (Halogens) are being added.**
- 4. Bromine (Halogen) addition options.**
- 5. Variables**
- 6. Solutions and or directions.**
- 7. PAC Injection Case Study**
- 8. Utility Engineer's Perspective**

# What we are not talking about...



## Root Causes

### EPRI Study; Other Studies...

- Data Appears to be Inconclusive at this point
- Multiples Variables

### However there are:

## Potential Calcium Bromide Corrosion Mechanisms

- HBr formation from the addition of CaBr<sub>2</sub>
  - Direct Condensation
  - Gas Phase Oxidation
- Deliquescent Salts from un-reacted CaBr<sub>2</sub>
  - Road Salt
- Absorption of HBr into a condensed acid
  - H<sub>2</sub>SO<sub>4</sub>
- Cold End Average Air Heater Temperatures
  - Reduced load due to additional cycling
  - Dew points

## Patents

# Anecdotal Evidence



# Corrosion from Calcium Bromide Addition???



← “Refined Coal”



“BPAC Upstream of AH” →

Questions?



**No Direct Implication  
of Bromine Corrosion  
Determined to Date.**

**Questions?**

## Calcium Bromide (and other halogens) Enhances the Oxidation of Hg Improving the Potential to Collect in Downstream Devices

### MATS

- Hg Emission rate of 1.2 lbs/Tbtu
- State Specific Hr Emission Rates
  - Illinois
    - 0.0080 lb/GWHR
    - ~ < 1.0 lbs/Tbtu

## Direct Application of $\text{CaBr}_2$ onto the Coal Stream

### Refined Coal

- IRS Section 45 Tax Credits

### Injection of Brominated Activated Carbon

- Options are upstream or downstream of the air pre-heater

### Direction Injection of $\text{HBr}$ into the Flue Gas

- Enhanced Mercury Oxidation (EMO)
  - Shaw Group

# Liquid CaBr<sub>2</sub> Addition



Metering Pump

CaBr<sub>2</sub> Tote



Injection point to one feeder

## Definition of “Refined Coal” includes Additive Processes

.....

Section 3.01(a) of the Initial Guidance defined the term “refined coal” for purposes of the credit to include “a liquid, gaseous, or solid fuel produced from coal . . . .” The Revised Guidance adds after the word “fuel,” the following: “(including feedstock coal mixed with an additive or additives).” Thus, the Revised Guidance confirms that additive processes which mix certain chemicals or other additives with the coal in order to achieve emission reductions qualify for the refined coal tax credit.

## Why Install a Refined Coal Process?

- Can provide a source of needed halogen for Hg Oxidation
- Provides a financial return back to the utility.

**Before January 1, 2009, a reduction of at least 20 percent of the emissions of NO<sub>x</sub> and at least 20 percent of the emissions of either SO<sub>2</sub> or Hg**

**After December 31, 2008, a reduction of at least 20 percent of the emissions of NO<sub>x</sub> and at least 40 percent of the emissions of either SO<sub>2</sub> or mercury Hg**

## Chem-Mod (Arthur J. Gallagher & Co.)

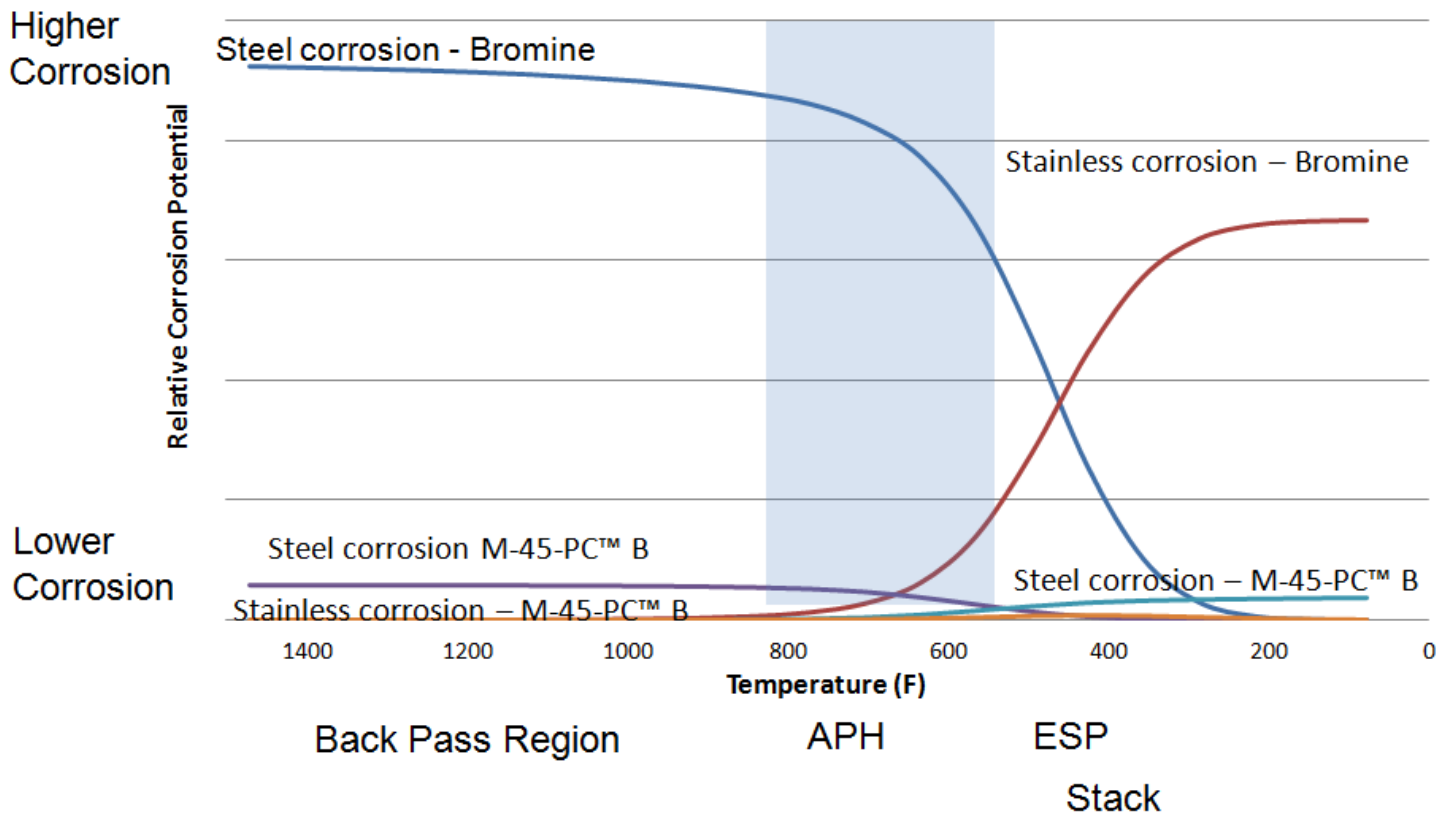
- Licensed to DTE, CERT
- Proprietary additives – S-Sorb for SO<sub>2</sub> Reduction and M-Sorb for Hg reduction.

## Clean Coal Solutions (ADA-ES, NexGen)

- CyClean™
- M-45™
- M-45-PC™
- Proprietary Hg reduction additive M-45-PC™ B.

# Relative Corrosion Potential

**M-45-PC™ B Mercury Control Chemical Significantly Reduces Active Corrosion Risks when Compared to 50ppm Bromine on Coal**



# PAC Injection



Courtesy ADA-ES

# Enhanced Mercury Oxidation (EMO)

## EMO Chemical Injection Process

SHAW

Shaw a world of Solutions™

5

## Halogen Addition Type

- CaBr<sub>2</sub>, HCL, others

## CaBr<sub>2</sub> Addition Rate

- Optimized for direct application
- Fixed for Refined Coal

## Air Heater Cold End Metal Temperature

## Moisture Content of the Flue Gas

## Types of Brominated PAC

- Gaseous (Br<sub>2</sub>), Sodium (NaBr), Potassium (KBr), Calcium (CaBr<sub>2</sub>)
- Potentially various release rates of bromine from BPAC

## Properties of Refined Coal Additives (Chlorides)

## Unit Cycling

- More operation time at lower loads

### **Enamel Coated APH Baskets**

- ~2X cost

### **PAC Injection Downstream of APH**

### **BPAC Selection**

### **APH Sootblowing Optimization**

### **APH Cold End Metal Temperature Control**

- Steam/Glycol pre-heaters

### **Corrosion Monitoring**

- Coupons
- On-line monitoring

### **Determination of HBr Dew point**

- Establish Minimum APH Metal Temperature

### **Speciated Hg Testing**

- Target minimum required halogen addition rate

### **Coal Handling with Refined Coal**

- Stop refined coal operation prior to a scheduled shut down to empty bunkers.

### **Plant Economics**

- Refined Coal income stream.
- PAC injection location. Upstream/downstream of APH.
- Sorbent Costs

Figure\_1\_201401\_2014\_PAC

## Model Domain

Economizer Outlet to ESP Inlets

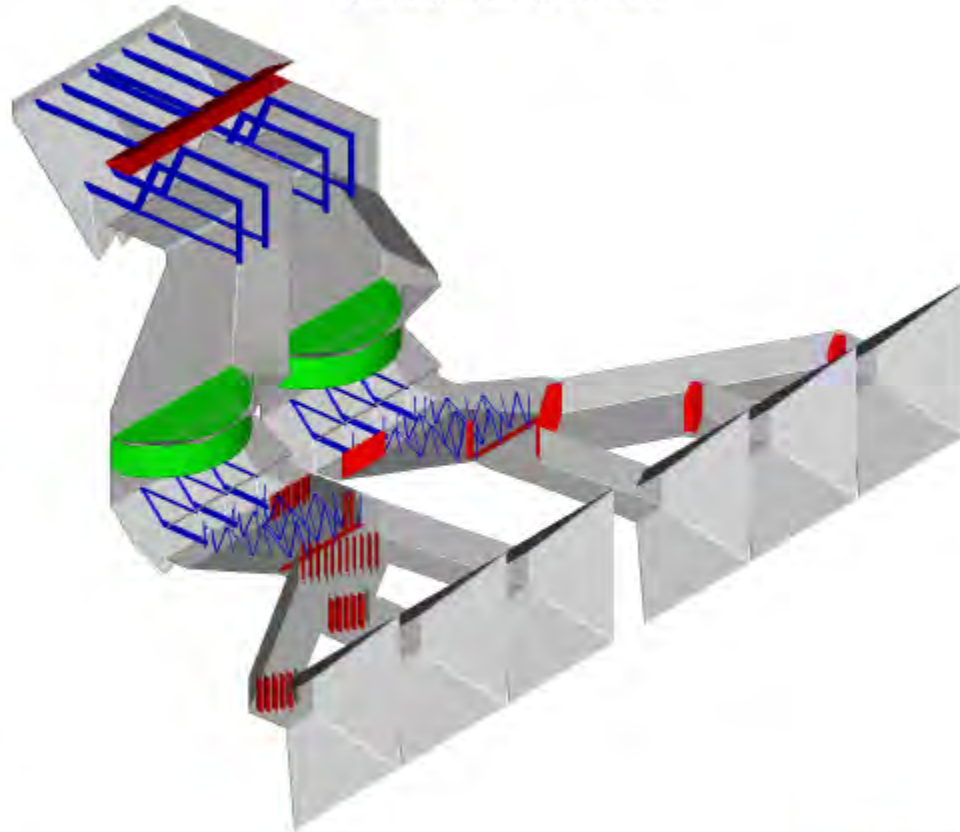


Figure 1



Airflow Sciences Corporation 

## Velocity Magnitude - Run 5 (Full Load) Cross-Sectional Planes - Economizer Outlet to AH Inlet

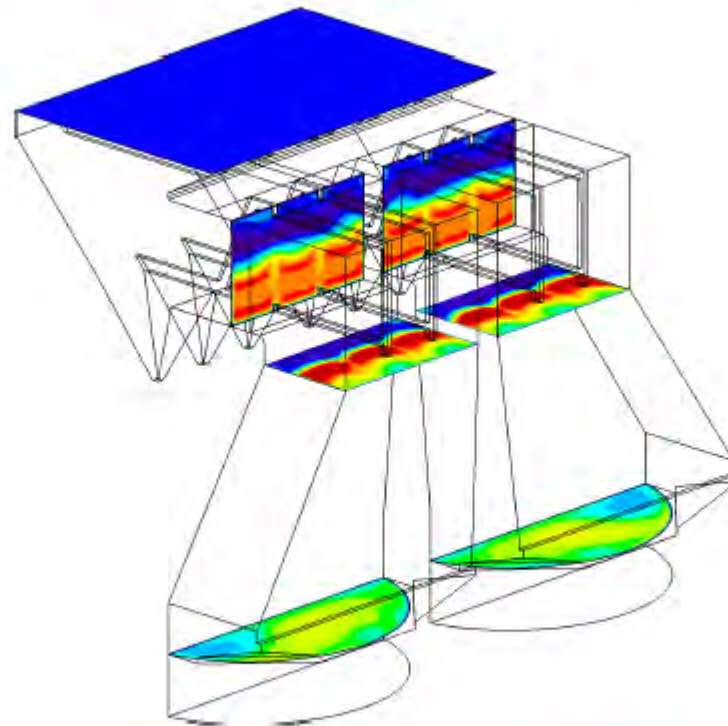
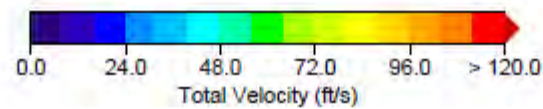


Figure 2



# Baseline Velocity Plot

## Velocity Magnitude - Run 5 (Full Load) Cross-Sectional Planes - North AH Outlet to ESP Inlets

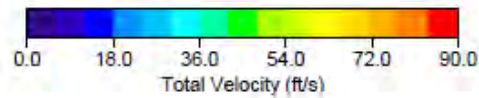
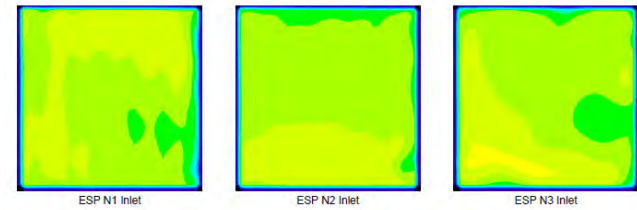
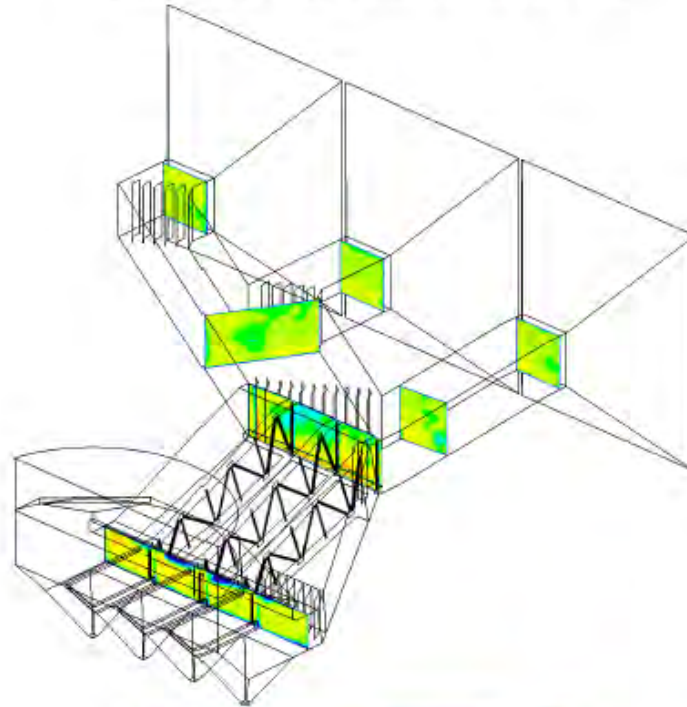
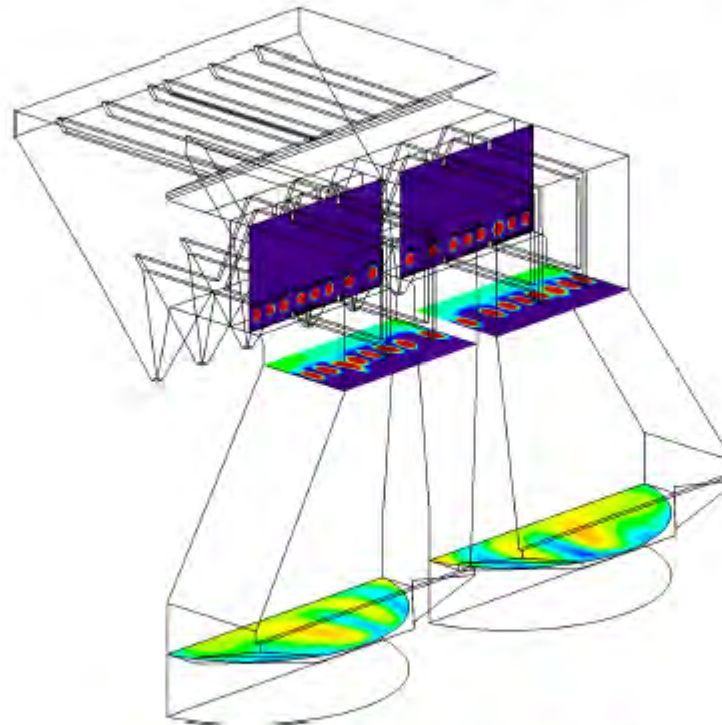


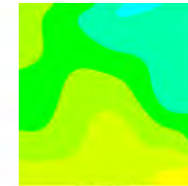
Figure 7

## Sorbent Mass Fraction - Run 5 (Full Load)

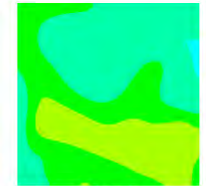
Injection Upstream of AH - Cross-Sectional Planes - Economizer Outlet to AH Inlet



ESP N1 Inlet  
Average Sorbent Mass Fraction =  $4.4 \times 10^{-5}$   
Sorbent Mass Fraction RMS = 3.6%



ESP N2 Inlet  
Average Sorbent Mass Fraction =  $4.3 \times 10^{-5}$   
Sorbent Mass Fraction RMS = 14.4%



ESP N3 Inlet  
Average Sorbent Mass Fraction =  $3.9 \times 10^{-5}$   
Sorbent Mass Fraction RMS = 10.6%

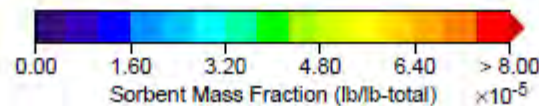
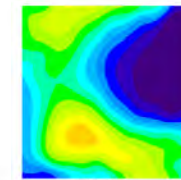
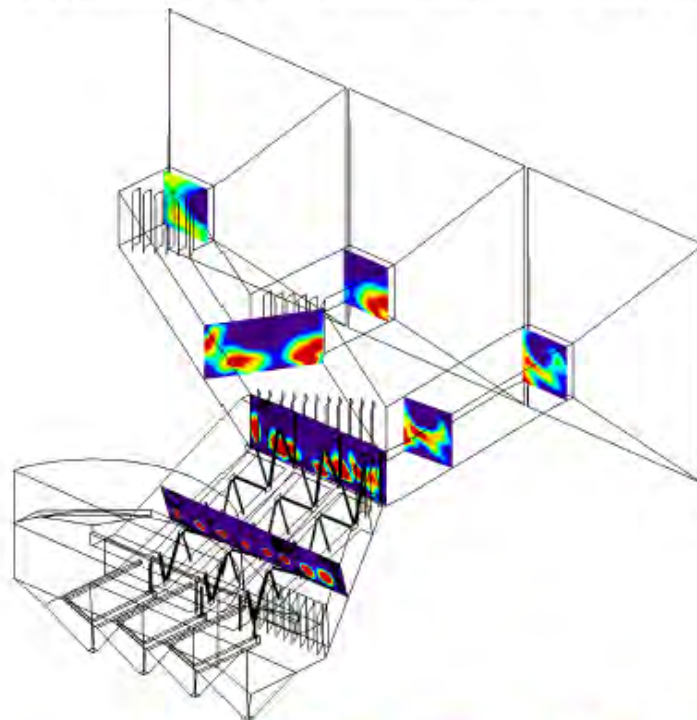


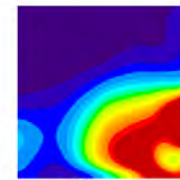
Figure 12



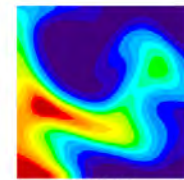
## Sorbent Mass Fraction - Run 5 (Full Load) Injection Downstream of AH - Cross-Sectional Planes - North AH Outlet to ESP Inlets



ESP N1 Inlet  
Average Sorbent Mass Fraction =  $4.5 \times 10^{-5}$   
Sorbent Mass Fraction RMS = 59.0%



ESP N2 Inlet  
Average Sorbent Mass Fraction =  $4.2 \times 10^{-5}$   
Sorbent Mass Fraction RMS = 109.4%



ESP N3 Inlet  
Average Sorbent Mass Fraction =  $3.9 \times 10^{-5}$   
Sorbent Mass Fraction RMS = 99.0%

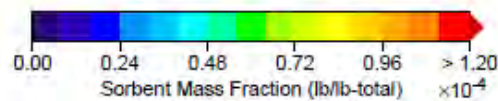
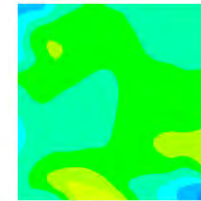
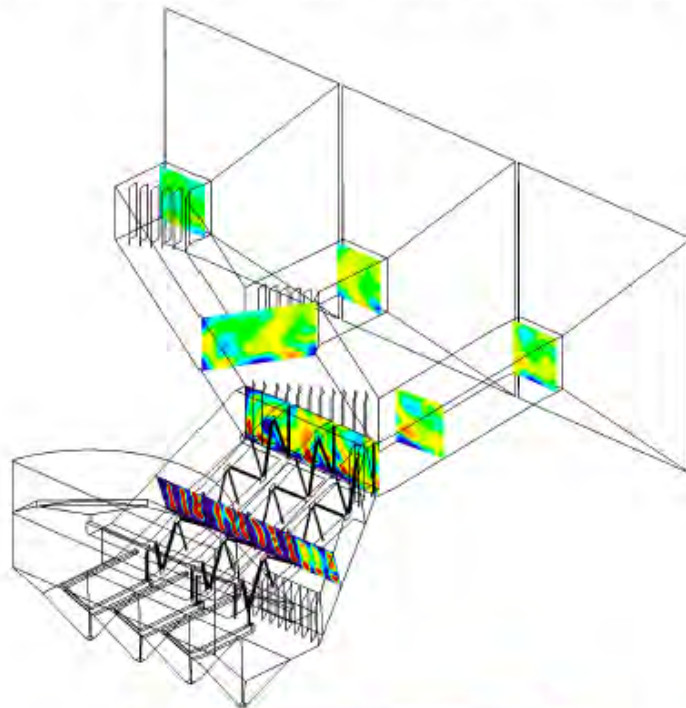


Figure 18

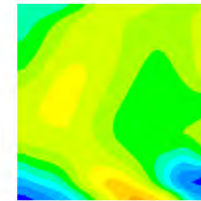
# Optimized PAC Downstream of APH

## PAC Mass Fraction - Run 24 (Full Load)

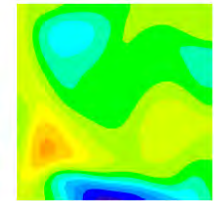
Cold-Side Injection - Cross-Sectional Planes - North AH Outlet to ESP Inlets



ESP N1 Inlet  
Average PAC Mass Fraction =  $3.8 \times 10^{-5}$   
PAC Mass Fraction RMS = 11.3%



ESP N2 Inlet  
Average PAC Mass Fraction =  $4.5 \times 10^{-5}$   
PAC Mass Fraction RMS = 19.3%



ESP N3 Inlet  
Average PAC Mass Fraction =  $4.3 \times 10^{-5}$   
PAC Mass Fraction RMS = 21.6%

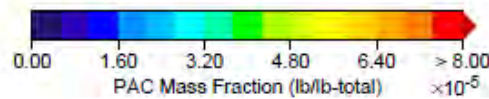
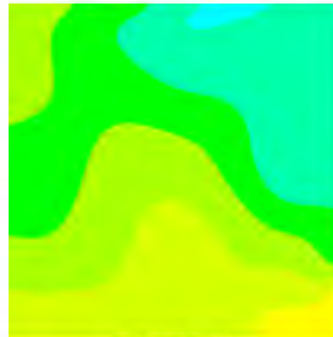


Figure 1

# Distribution Plots Upstream of APH and Optimized Downstream of APH



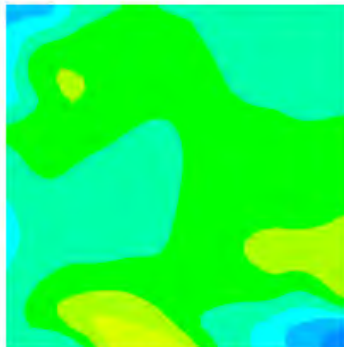
ESP N1 Inlet  
Average Sorbent Mass Fraction =  $4.4 \times 10^{-5}$   
Sorbent Mass Fraction RMS = 3.6%



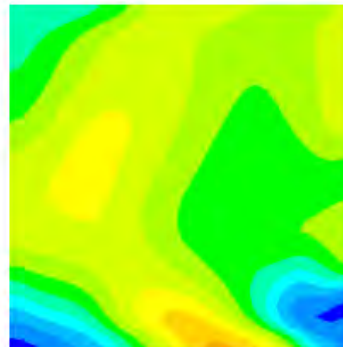
ESP N2 Inlet  
Average Sorbent Mass Fraction =  $4.3 \times 10^{-5}$   
Sorbent Mass Fraction RMS = 14.4%



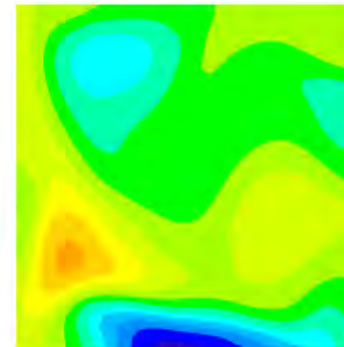
ESP N3 Inlet  
Average Sorbent Mass Fraction =  $3.9 \times 10^{-5}$   
Sorbent Mass Fraction RMS = 10.6%



ESP N1 Inlet  
Average PAC Mass Fraction =  $3.8 \times 10^{-5}$   
PAC Mass Fraction RMS = 11.3%



ESP N2 Inlet  
Average PAC Mass Fraction =  $4.5 \times 10^{-5}$   
PAC Mass Fraction RMS = 19.3%



ESP N3 Inlet  
Average PAC Mass Fraction =  $4.3 \times 10^{-5}$   
PAC Mass Fraction RMS = 21.6%

Questions?



# Questions?

# Br Corrosion

## A Western Utility Engineer's Perspective

Greg W. Betenson

Reinhold Round Table

Louisville, Kentucky

7.15.2014

# Western Utility Perspective

- PRB, Wyo Sub Bit & Utah Coal
  - Low Sulfur 0.5% and Low Halogen <50-100 ppm
  - Low Hg in Many Cases 2 lb/TBtu
  - Reactive Coal, Low UBC 0.5-3%
- ZLD Plants
- WFGD Operation Beginning in 1970's
- Evolution of APC Technology, ex: WFGD Improvements. Expect in Case of Hg Control.

# Background

- High Altitude Plants, 5k-7k Ft above sea level
- Wyoming Winters Common  $<-20$  °F Extended Periods
- Hg Field Testing 2010-11
- Hg Equipment Currently in Construction
- Fall 2014 Performance Testing

# Background

- Installing  $\text{CaBr}_2$ , PAC Injection and Hg Re-Emission Inhibitor at WFGD Units on all 12 Wyoming Units
- Spreadsheet Analysis: Preliminary Best Option Based on Performance Guarantee's
- Best Option Long Term Option TBD w/Operating Experience
- Br Corrosion at Co-Owned Plants and Sister Companies

# Plant Example – Green River Basin Coal

- 4x 550 MW T-Fired, CESP w/4-6 ppm SO<sub>3</sub> Injection, Sodium (Na<sub>2</sub>CO<sub>3</sub>) WFGD
- SCR Start Up: 2016, 2017, 2021, 2022
- Coal Hg Varies According to Source, 3-12 lb/TBTU. Typical 3-7 lb/TBtu
- CaBr<sub>2</sub>, PAC, B-PAC, C-PAC and 4 Different WFGD Additives Tested 2010-11

# CaBr<sub>2</sub> Considerations

- Max CaBr<sub>2</sub> Addition Rate WDEQ Permit Limit
- CaBr<sub>2</sub> Addition Rate w & w/o SCR in Service
- Hg<sup>0</sup> in Furnace Oxidation as f(x) CaBr<sub>2</sub> Injection Rate. 5-9 % WFGD By-Pass
- APH Outlet Temperatures, <-20 °F
- APH Cold End Basket Material of Construction Options, Plans and Budget Estimates
- 316L & 2205 Alloy FGD Vessels
- Measured & Predicted FGD Cl & Br ppm Concentration

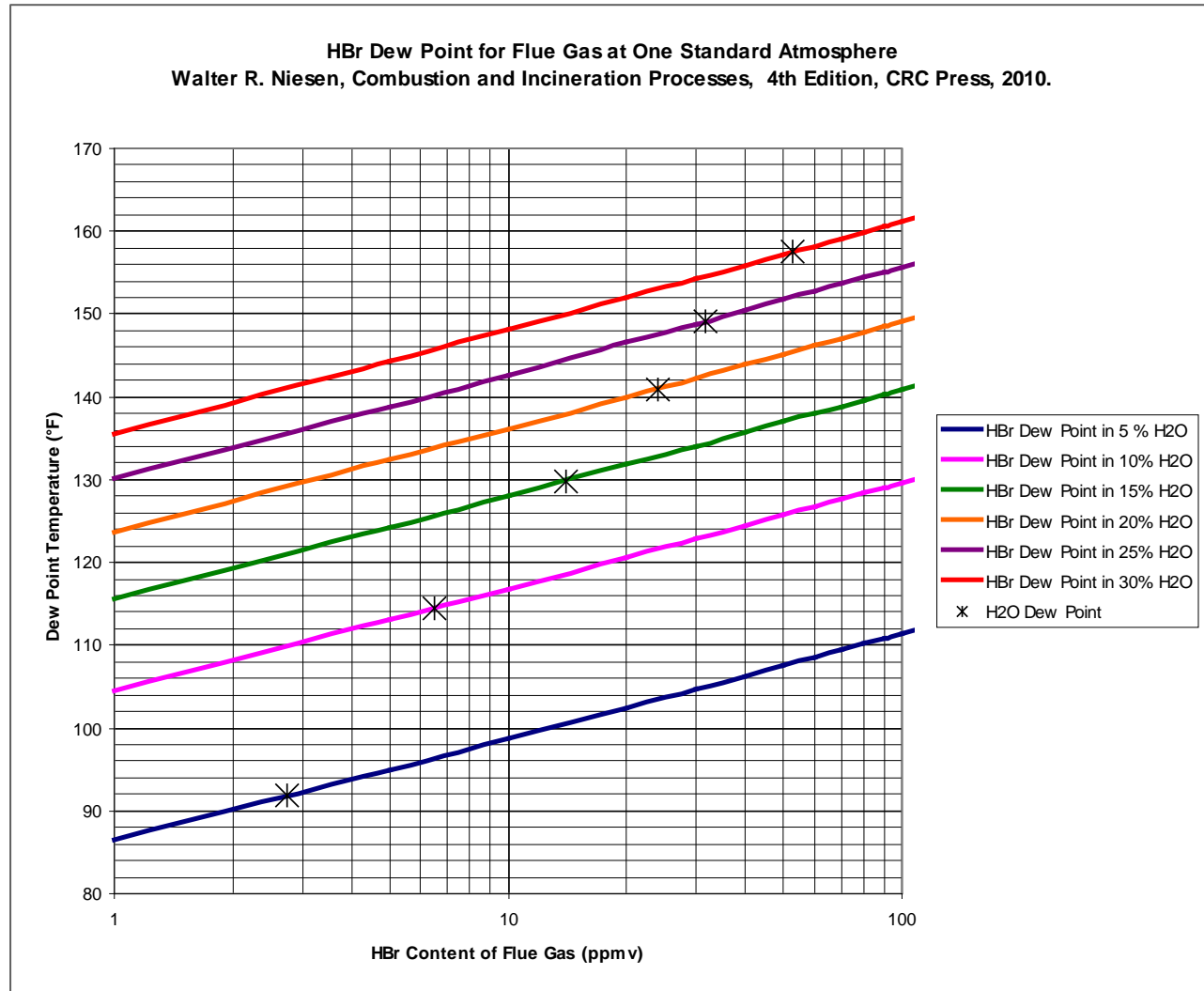
# WFGD Corrosion Studies

- Industry Testing Focused on Ca Based WFGD
- Attempt to Generalize Results to Na-WFGD
- On-Line Site WFGD Tests Planned with Nalco
- Details Under Development
- Several Alloys To Be Tested
- Need for and Economic Analysis of Coatings and/or Protective Corrosion vs PAC Options

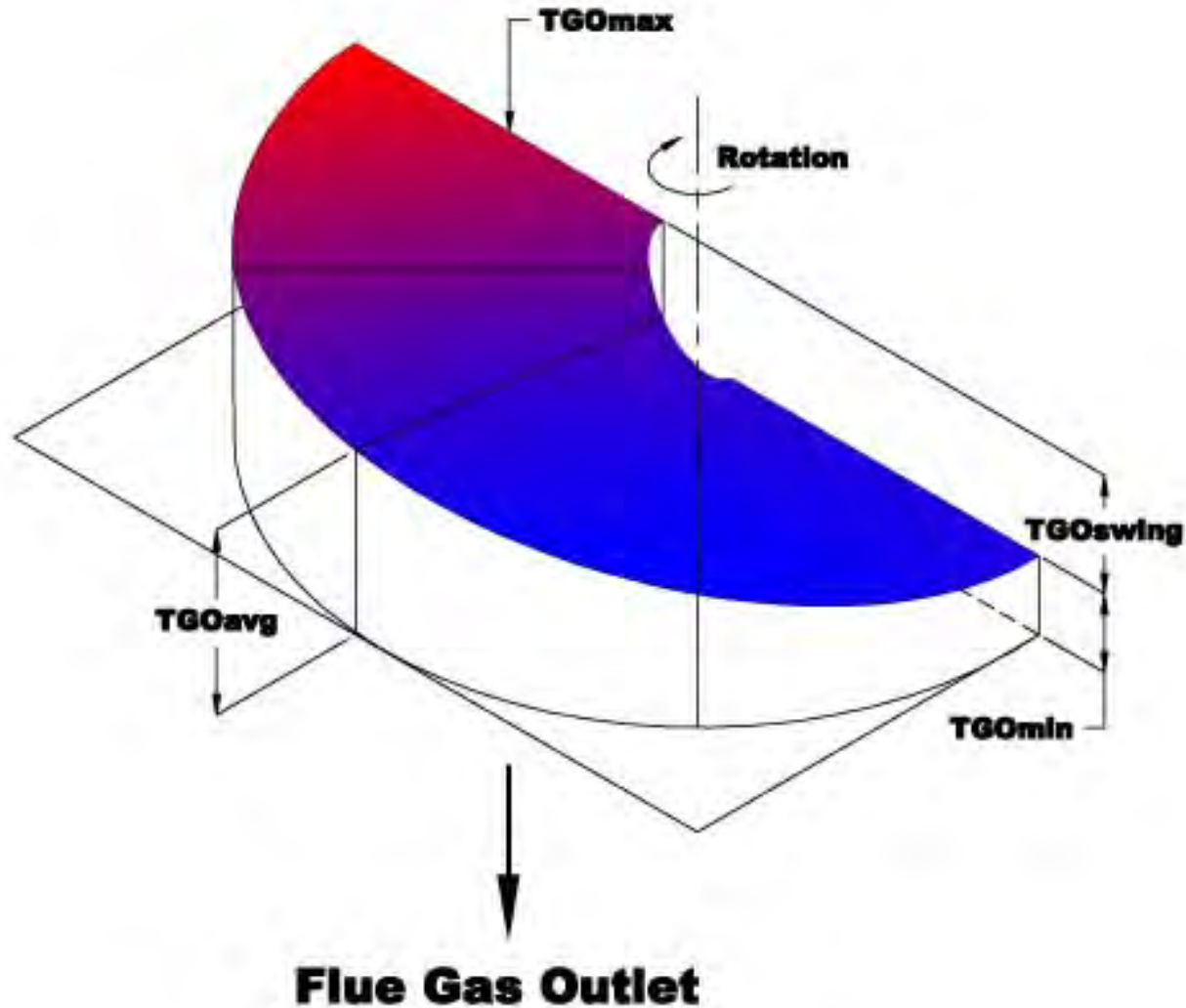
# APH Corrosion Analysis

- Study In Progress to Determine Need for Enamel Coated APH Baskets Due August 2014
- Alstom Model to Determine:
  - Winter APH Cold End Minimum Metal Temperature
  - ABS Formation in Cold End Baskets
  - Cold End HBr Dew Point Temperature
- Exact Corrosion Mechanism Unknown

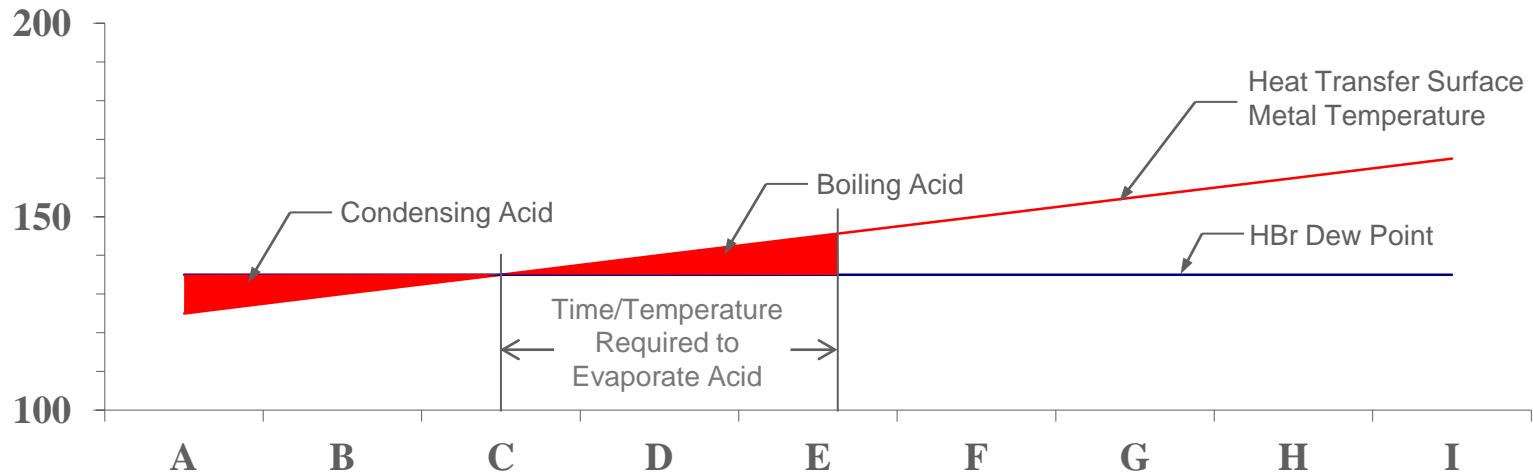
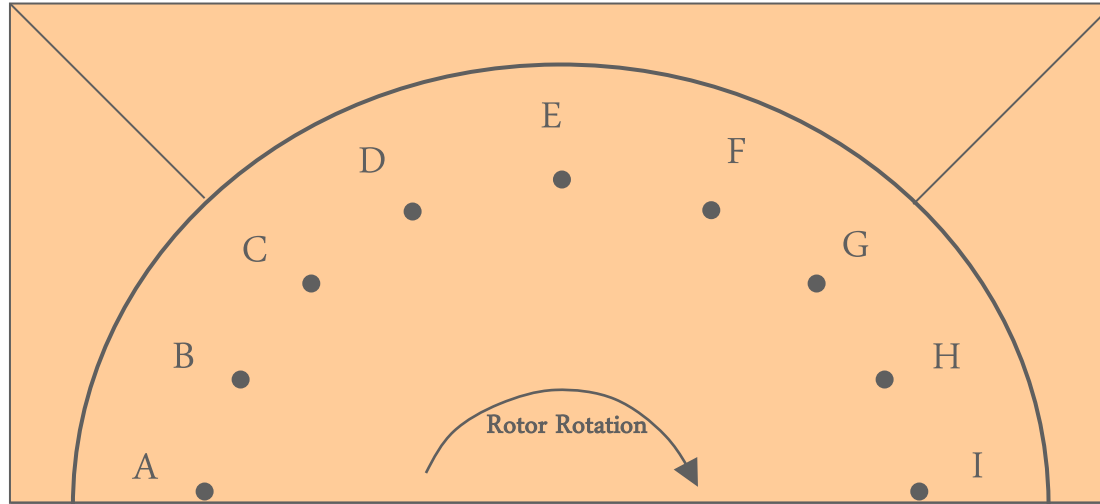
# HBr Dewpoint



# Flue Gas Temperature Profile Leaving the Air Preheater



# Acid Condensation/Evaporation Cycle As Heat Transfer Surface Passes Through Flue Gas Stream



# HBr Corrosion in 12" NF6 Cold End Element Layer



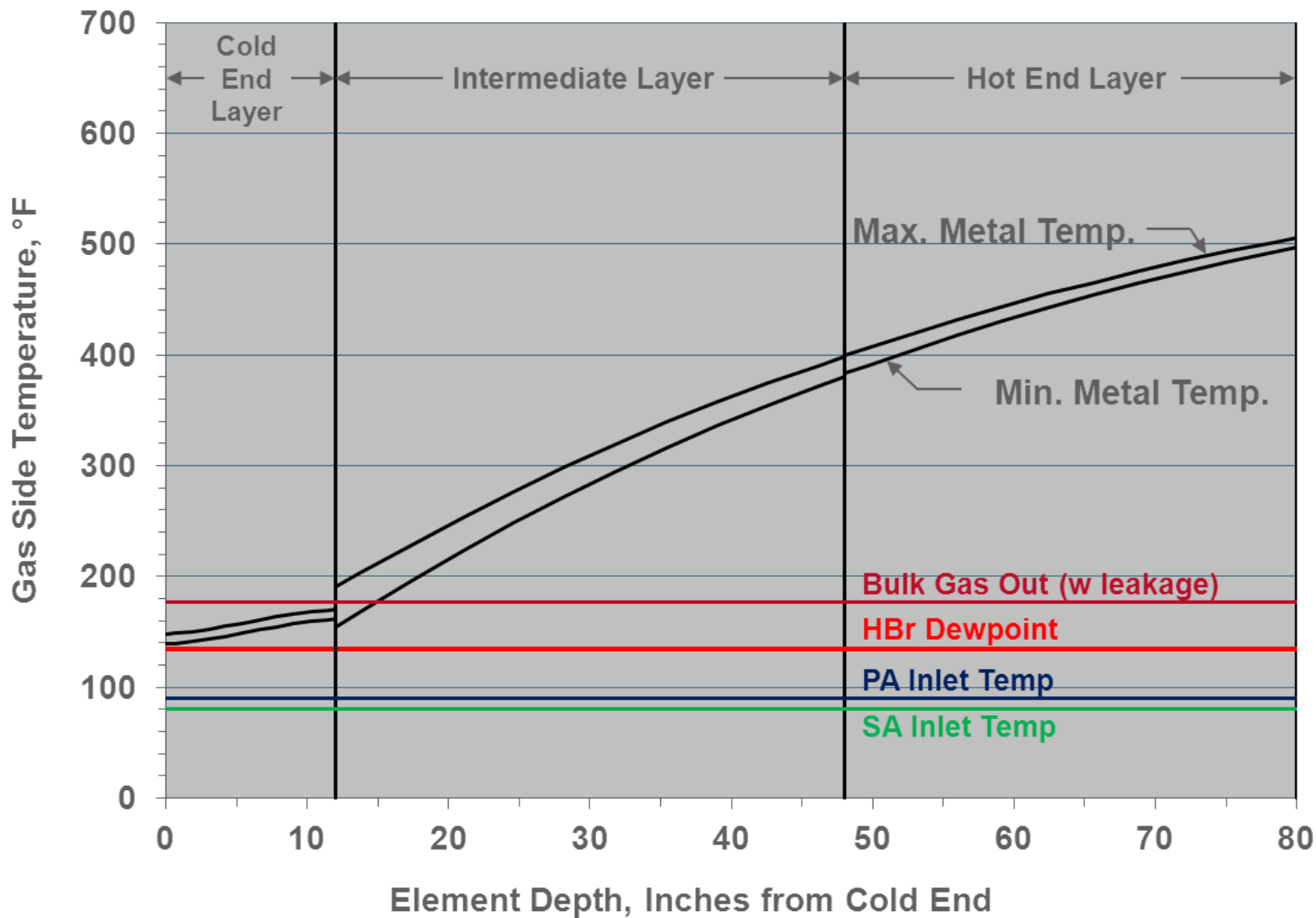
# HBr Corrosion

## Detail of Corrosion Effected Zone



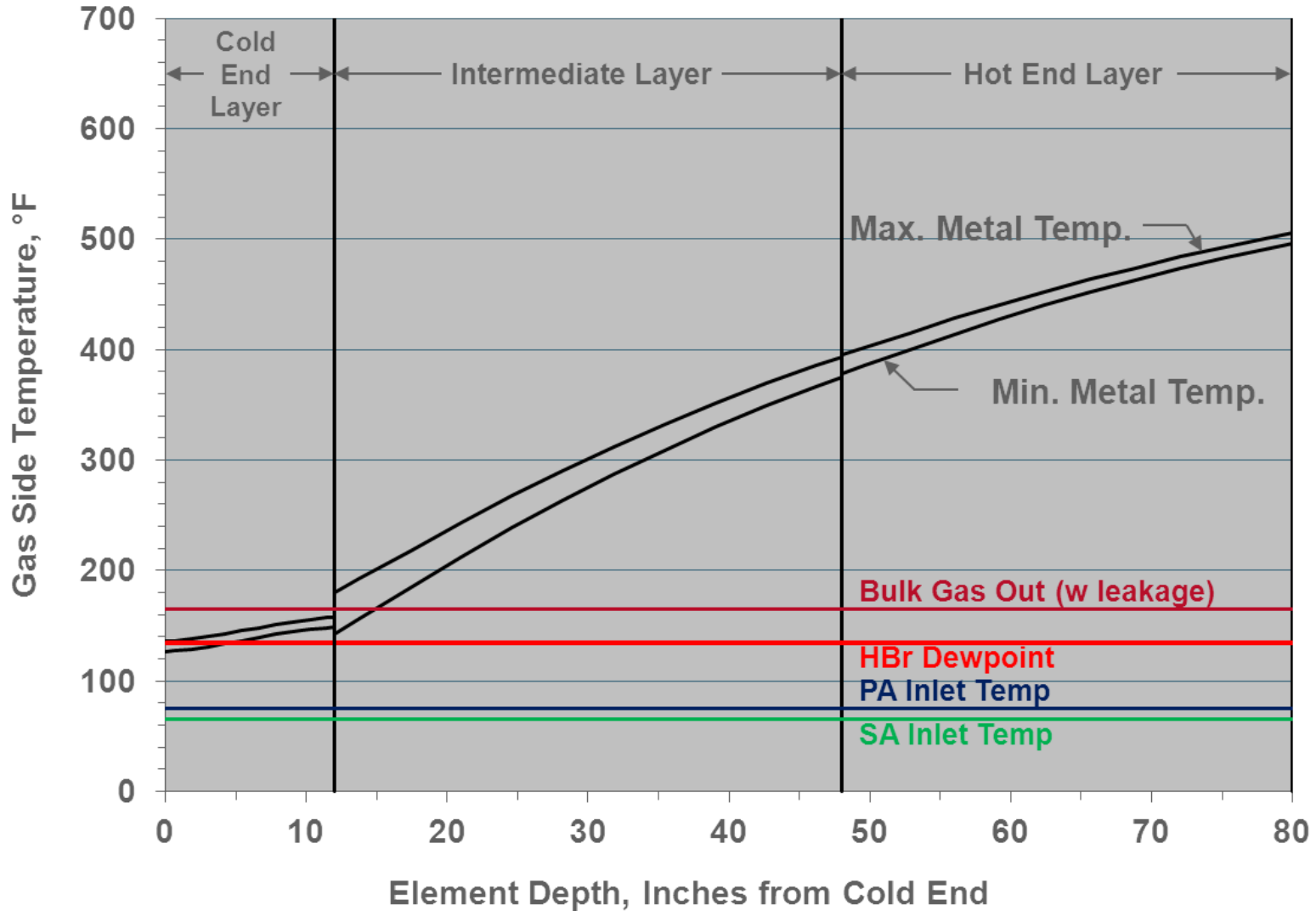
# Metal Temperature Profile

Sample Unit – Low Load / 75 DegF Ambient



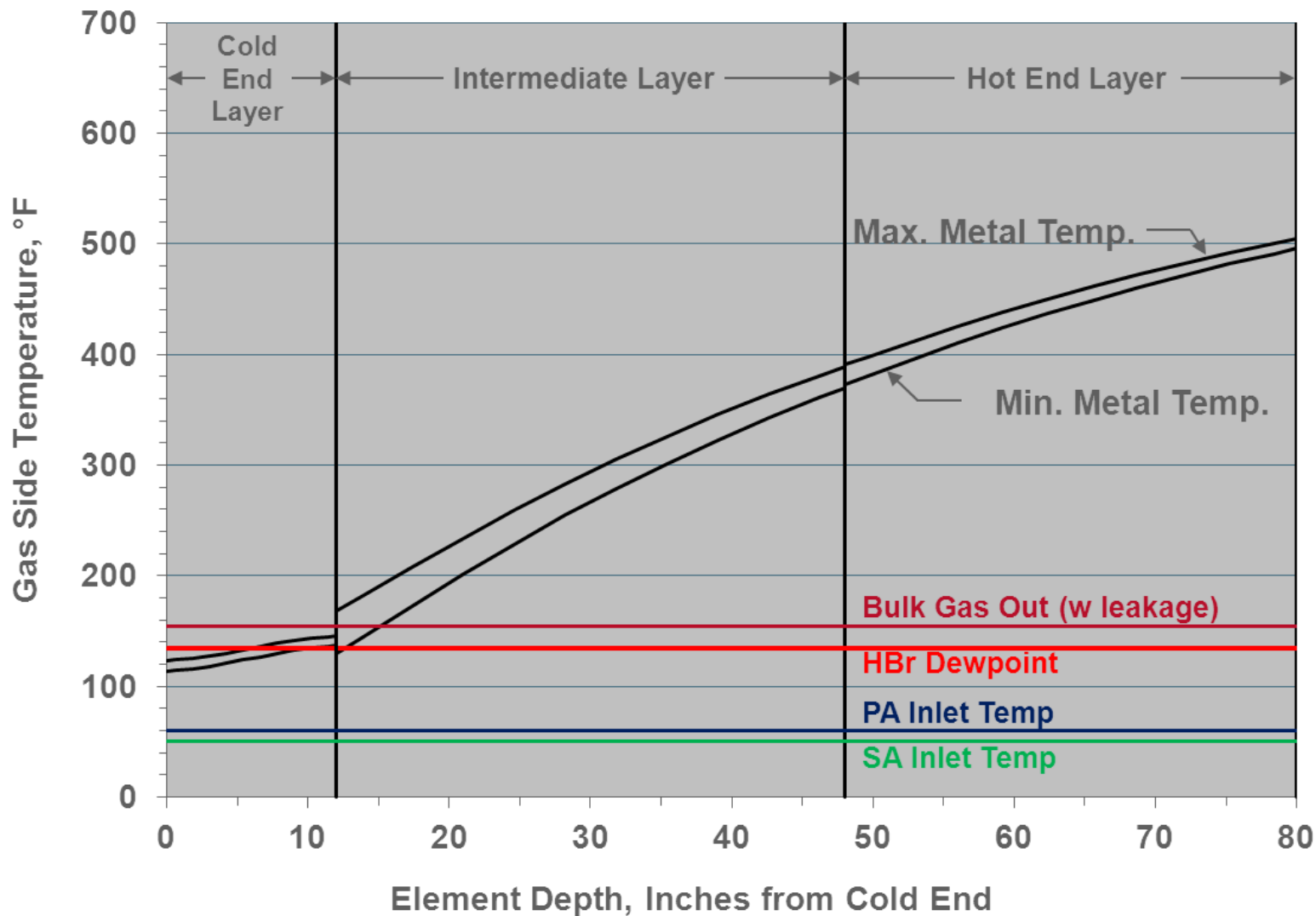
# Metal Temperature Profile

Sample Unit – Low Load / 60 DegF Ambient



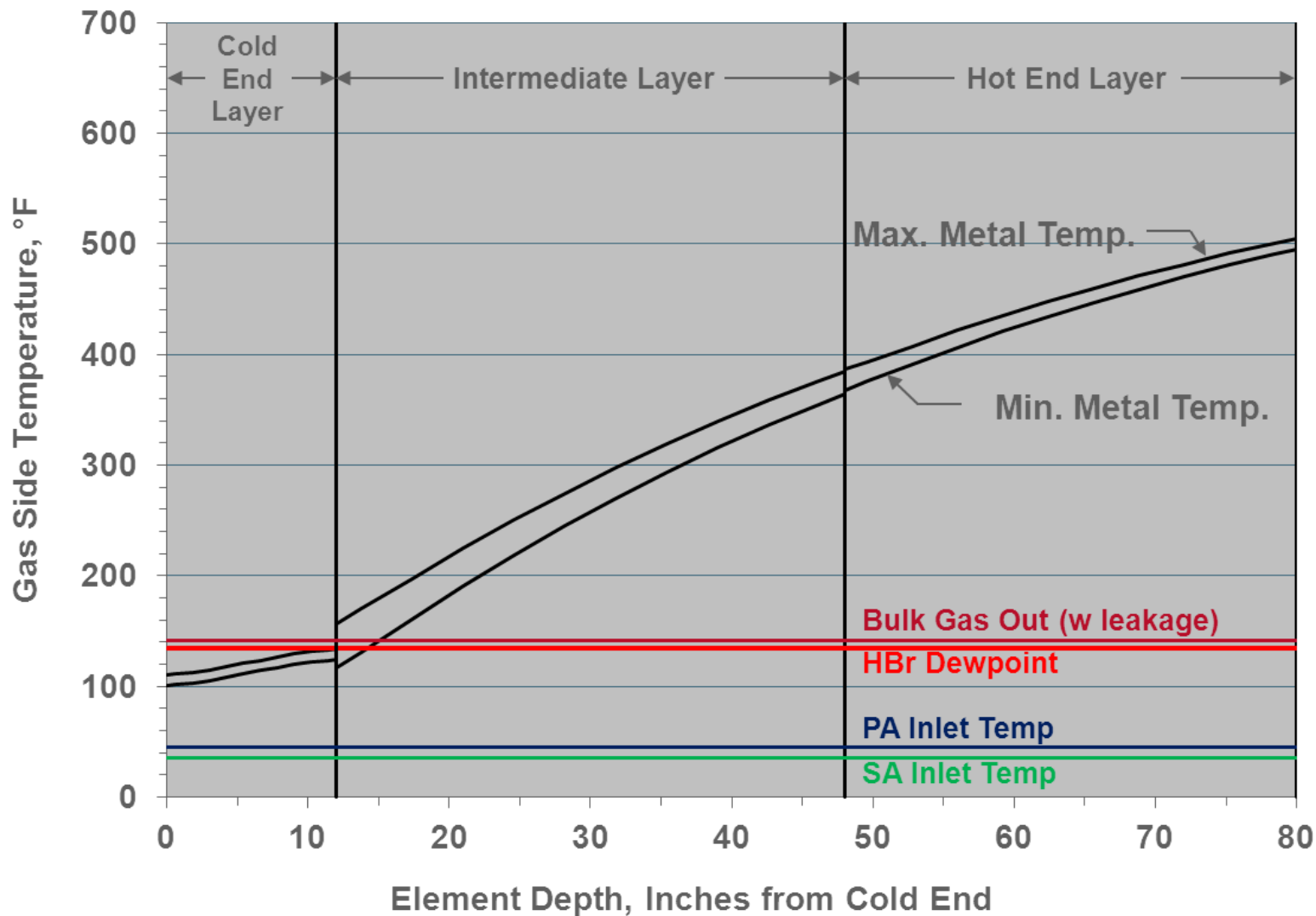
# Metal Temperature Profile

Sample Unit – Low Load / 45 DegF Ambient



# Metal Temperature Profile

Sample Unit – Low Load / 30 DegF Ambient



# On-Line APH Br Corrosion Testing

- REI/University of Utah/CM Ltd. U.K.
- Principal of Operation: Electro-Chemical Noise via Air-Cooled Corrosion Probe
- Previous Testing: U of U Pilot Combustor
- Planned Plant Testing Details TBD
- References:
  - *2013 Oxy Fuel Combustion Conf. 3, Ponferrada, Spain Sept. 9-13, 2013*
  - *Fry, A. Int. J Greenh Gas Conf. 2011, 55, S179-185*

# B-PAC Considerations at Plant

- “Concrete Friendly” B-PAC
- Large Fly Ash Sales to Cement Market
- Laboratory Tests w Plant Fly Ash & B-PAC with Ash Marketer and PAC Supplier
- Additional Lab Testing During Commercial Operation
- Concentration of B-PAC, Air Entrainment Addition Requirement and Concrete Tests

# B-PAC Considerations at Plant

- Decision to Inject PAC Downstream APH
  - Alstom Patent
  - PAC & Equipment Supplier Offerings
  - Increase in PAC Cost
  - ADA-ES Flue Gas Static Mixer Option
  - Other Trade Offs

# PacifiCorp Tentative Conclusions

- **CaBr<sub>2</sub> + WFGD Hg Additive** May Be Best Option for Low to Moderate Hg Coal, 3-7 lb/TBtu at Green River Coal Basin Plant & Kemmerer 2-3 lb/TBtu Coal. ***Both Plants: ESP w/SO<sub>3</sub> + Na WFGD***
- **C-PAC** May Be Best Option for ***Higher Hg Coal*** at First Plant
- ***Alternatively*** Other Wyoming PRB Coal Plants, ***ESP and SDA/FF, B-PAC*** May Be Best Option
- Therefore ***Enamel APH Baskets Likely not Req'd at PacifiCorp PRB Coal Plants*** since PAC inj. after APH
- Commercial Experience ***Will*** Clarify Best Option