REINHOLD ENVIRONMENTAL Ltd.

2015 NOx-Combustion Round Table & Expo Presentations

February 23 & 24, 2015, in Richmond, VA / Hosted by Dominion

Corrosion Rate Measurements when Adding Iodine and Bromine for Hg Oxidation

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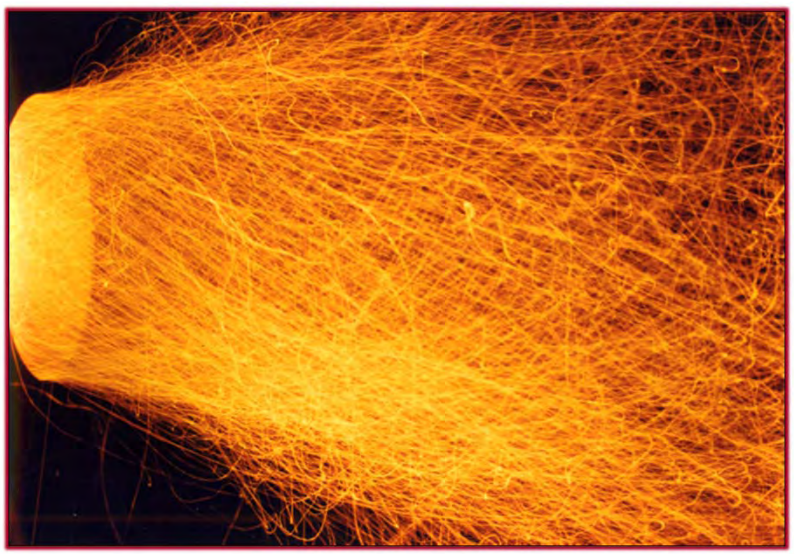
Reinhold NOx – Combustion Roundtable
February 23-24, 2015
Richmond, VA

Presentation Agenda

- Fireside Corrosion in Coal Boilers
- Corrosion Management Tools
- Real-time Corrosion Monitoring by EN
- Acid Dewpoint Corrosion
- Halogens for Mercury Oxidation
- Balance of Plant Effects of Halide Injection
- Field Test Results
- Mitagent Benefits

Reaction Engineering International

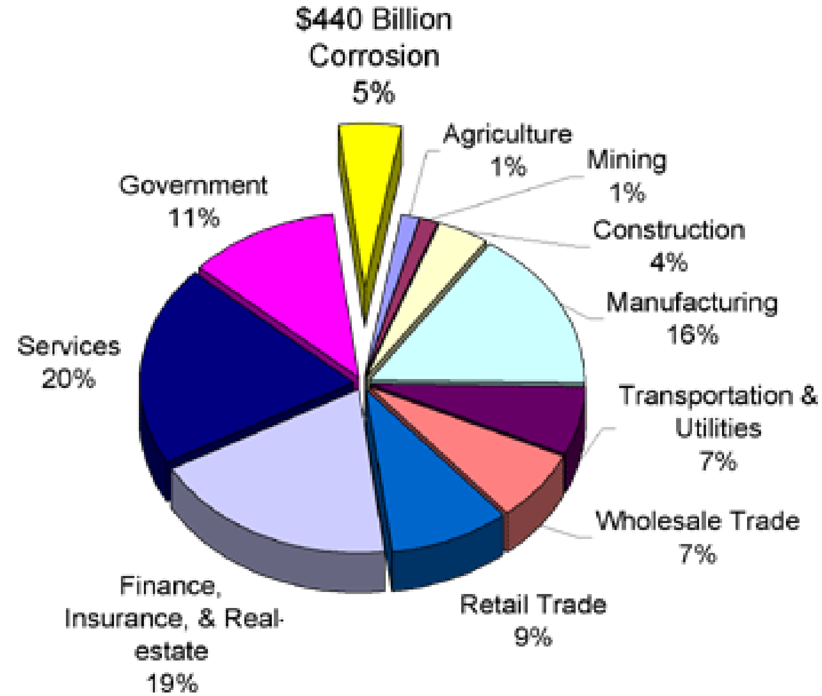
Privately held consulting firm recognized for independent analysis and evaluations involving a range of industrial combustion applications



- Technical focus on multi-phase, chemically reacting flows
- Serving the utility industry since 1990
- Affiliates in Asia and Europe
- Established capabilities include advanced modeling, process evaluation and testing

Impact of Corrosion

- Overall US Economic Impact: $440 billion/yr or 5% of GDP (Federal Highway Administration)
- Large impact on the US Electric Power Industry
- Economic and environmental pressures are increasing corrosion challenges:
  - NOx / Hg emissions
  - Fuel cost and availability
  - Generation efficiency
  - Increased turndown and load cycling
  - Opportunity fuels
  - CO2 separation

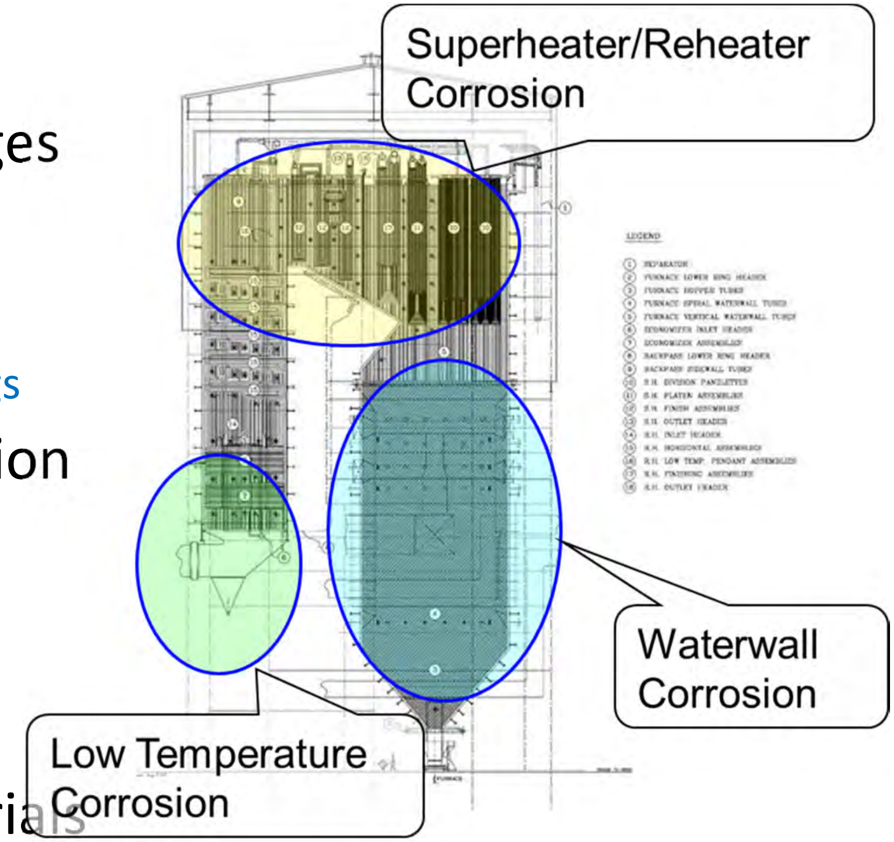


"Corrosion costs the U.S. electric power industry up to $10 billion per year and is the cause of roughly half of the forced outages in steam generating plants."

EPRI, 1998

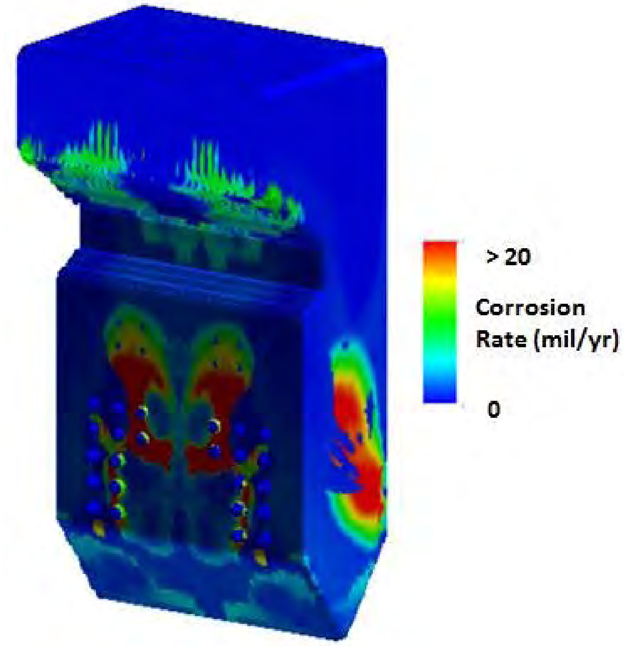
Benefits of Corrosion Management

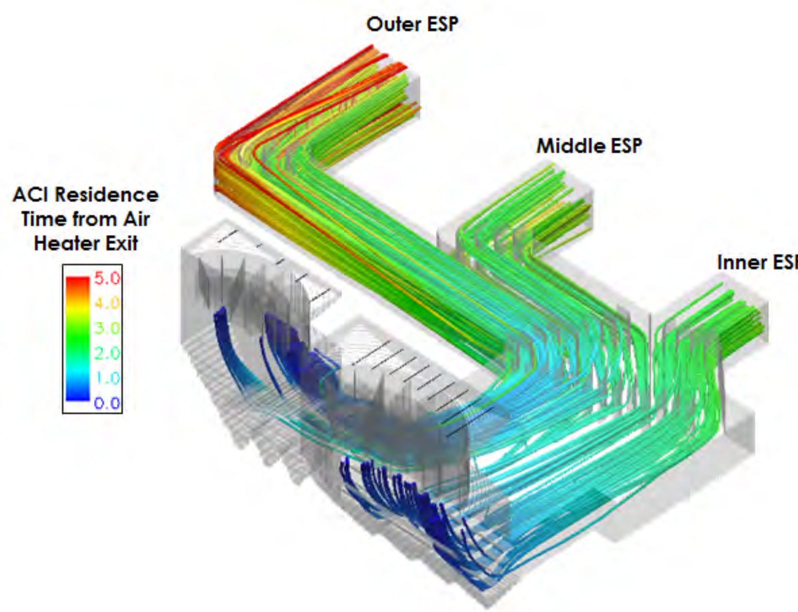
- Reduction in unscheduled outages
- Reduction in maintenance costs
  - Material life extension
  - Reduction in expensive overlay or coatings
- Improved operational optimization
- Quantitative assistance in fuel selection/blending/additive decisions
- Quantitative assistance in materials selection and life cycle certainty



Tools

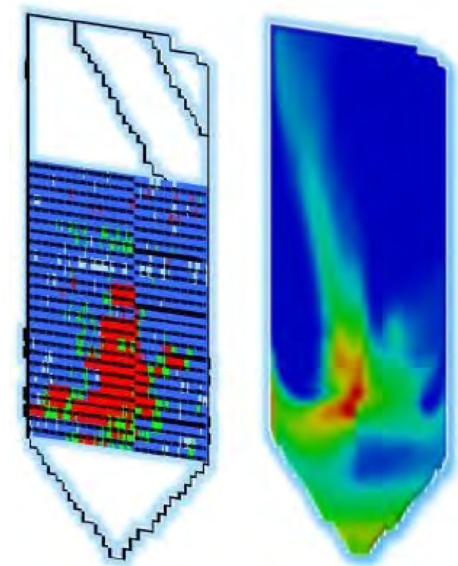
- CFD-based modeling
  - Validated correlation-based approach resulting from collaborations with EPRI and KEPRI
  - Integrated with REI's CFD software (GLACIER)
- Process modeling (MerSim^{TM})
  - Provides key information related to the evolution of mercury, sulfur, and halogen species
  - Developed using 144 data sets from 28 plants where operating conditions and mercury measurements were coupled
- Real-time monitoring
  - Critical to relating this highly non-linear phenomena to operating conditions, fuel properties and additive utilization
  - REI has a unique tool for this purpose involving adaptation of an electrochemical approach resulting from a collaborative effort with Corrosion Management (UK)



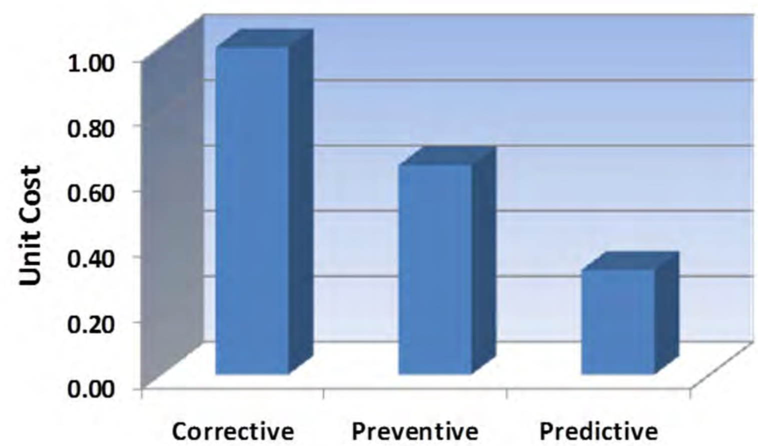


Solution Approach

- Evaluation of potential corrosion mechanisms
  - Gas-phase sulfur species
  - Gas-phase chlorine species
  - Deposition of unreacted material
  - Acid gas dewpoint
- Identification of high risk locations
  - Application of CFD/process modeling
  - Wastage measurements and/or observations of material failures
- Installation of real-time monitoring system
- Data reduction including comparisons with concurrent historical plant data
- identification and validation of corrosion management strategies



Ultrasonic tube thickness measurements | CFD−based corrosion predictions



“Power Plant Diagnostics Go On-Line”
Mechanical Engineering, Dec 1989

Corrosion Monitoring

- Visual Inspection
- Ultrasonic tube wall thickness testing
- Weight Loss Coupons
- Precision Metrology
- Electrical Resistance
- Linear Polarisation Resistance
- Electrochemical Impedance Measurement
- Thin Layer Activation
- Electrochemical Noise

T11 KEMCOP, Bakker 2003

Electrochemical Noise (EN) Technique

- DC technique that evaluates only spontaneous transients generated by corrosion process itself
- From Ohms Law: V=IR or R=V/I
- $R_{polarization} = \Delta V/\Delta I$
- Similarly $R_{noise} = V_{noise} / I_{noise}$
- From Stearn Geary Equation $I_{corr} = 1/ R_{noise}$
- The corrosion currents estimated using these techniques can be converted into penetration rates using Faraday's law

Anodic reaction:

$$\text{Metal} \rightarrow Me^{2+} + 2e^-$$

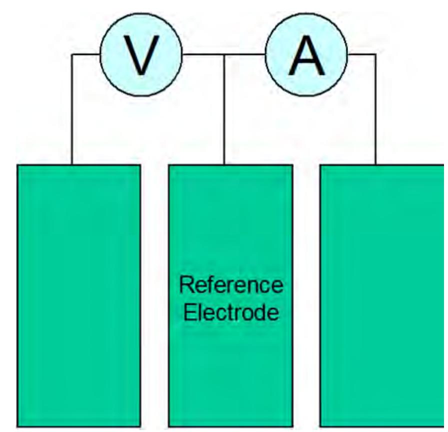
Cathodic reaction:

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

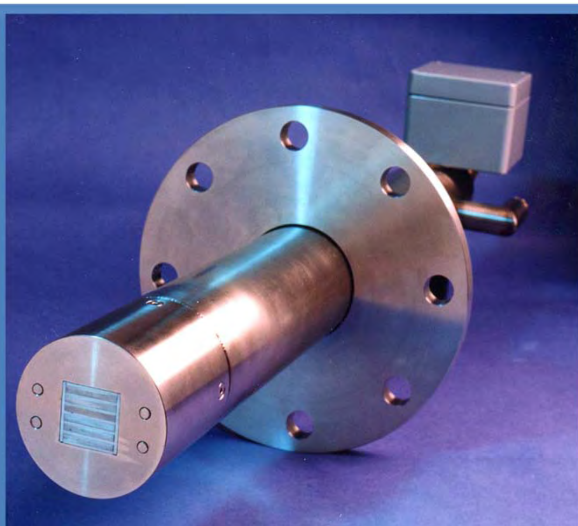
Combined:

$$2Me^{2+} + 2O^{2-} \rightarrow 2MeO_{(dep)}$$

Similarly, sulfur → sulfides
chlorine → chlorides

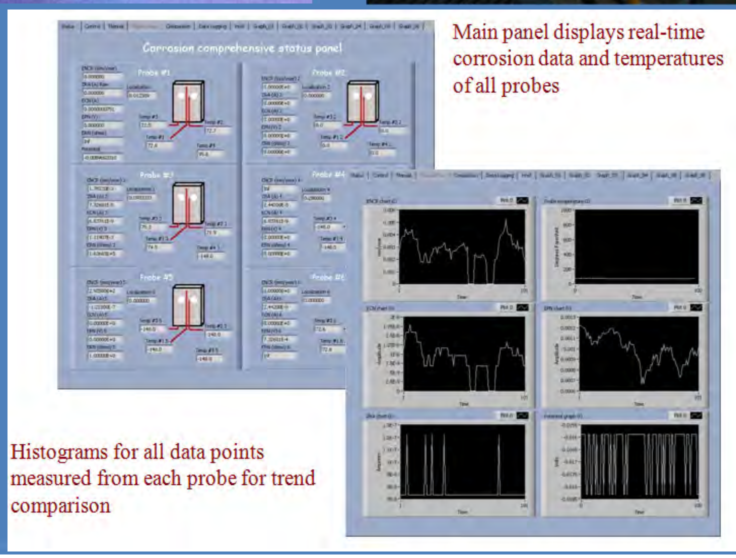


EN Probe for Corrosion Testing

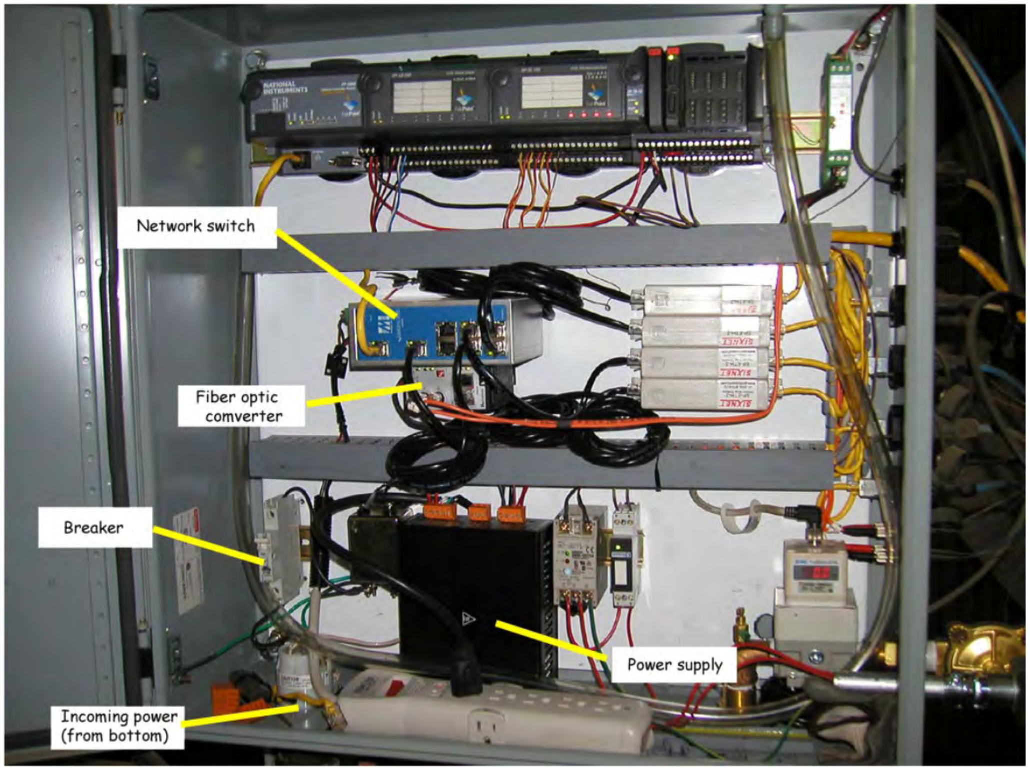


- High Sensitivity
- Instantaneous response
- Direct indication of corrosion
- Quantitative measurement
- Response related to corrosion mechanism

Data Acquisition

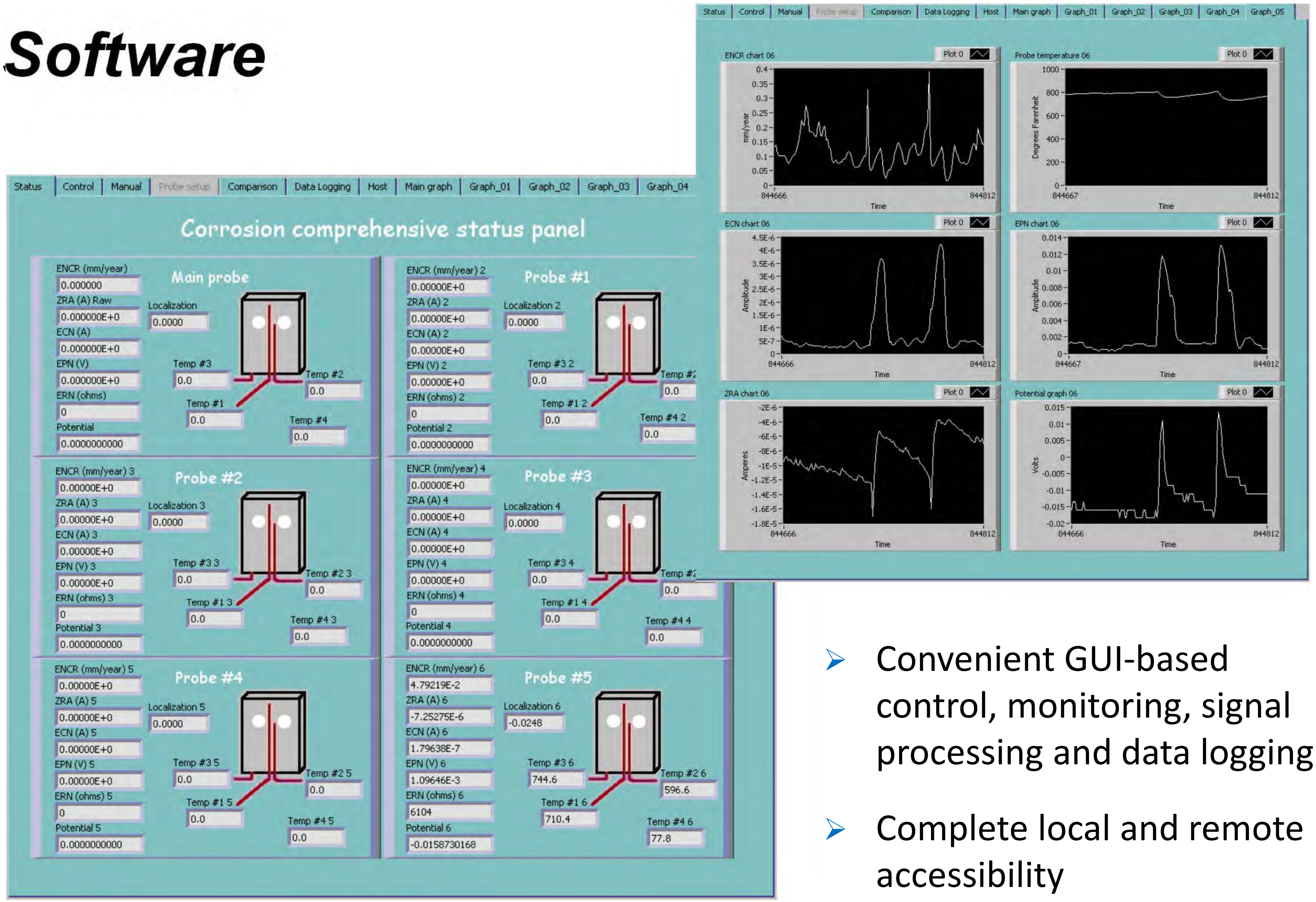


Electronics



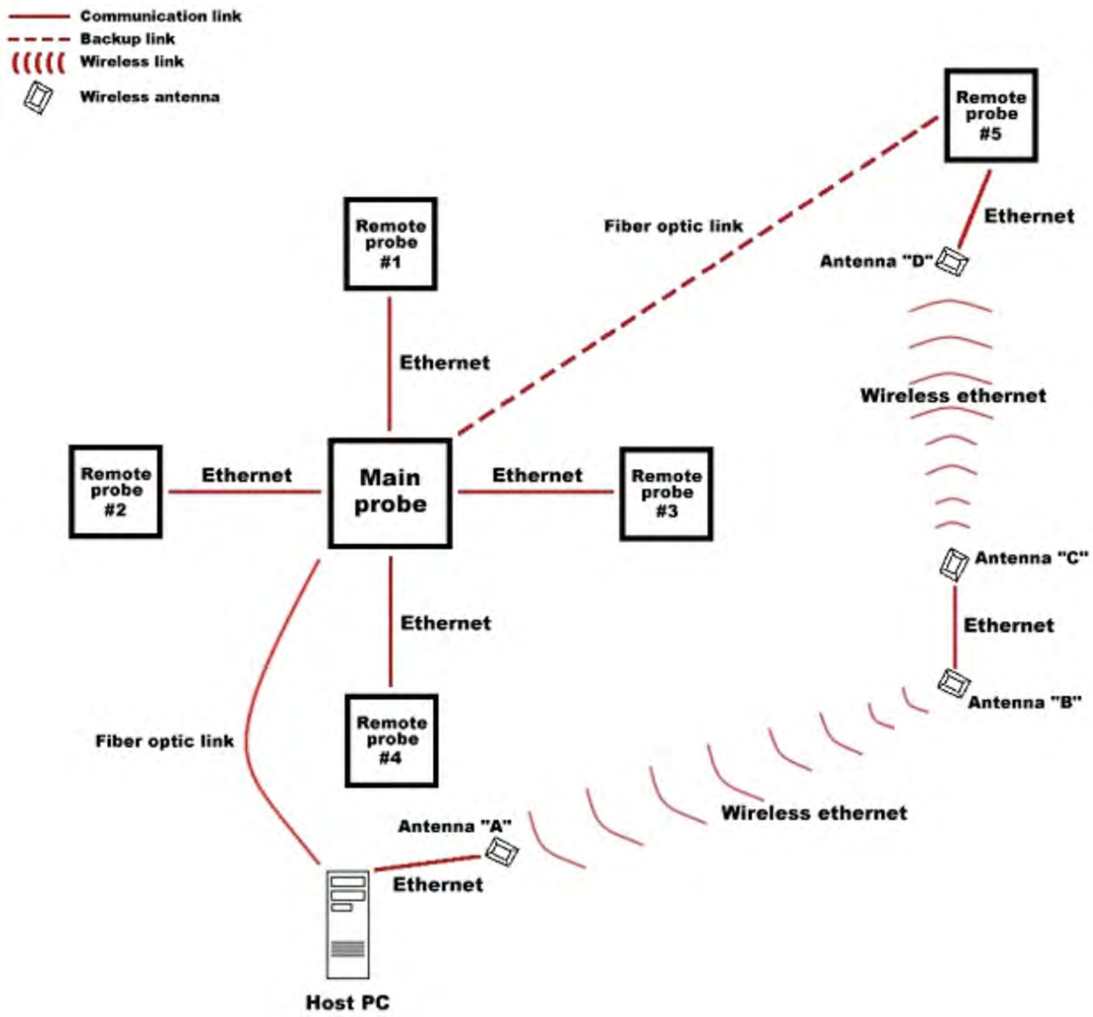
- Primarily off-the-shelf components
- Unique proprietary module for processing current and voltage signals
- Limited instrument air requirement for cooling

Software



- Convenient GUI-based control, monitoring, signal processing and data logging
- Complete local and remote accessibility

Data Acquisition and Control

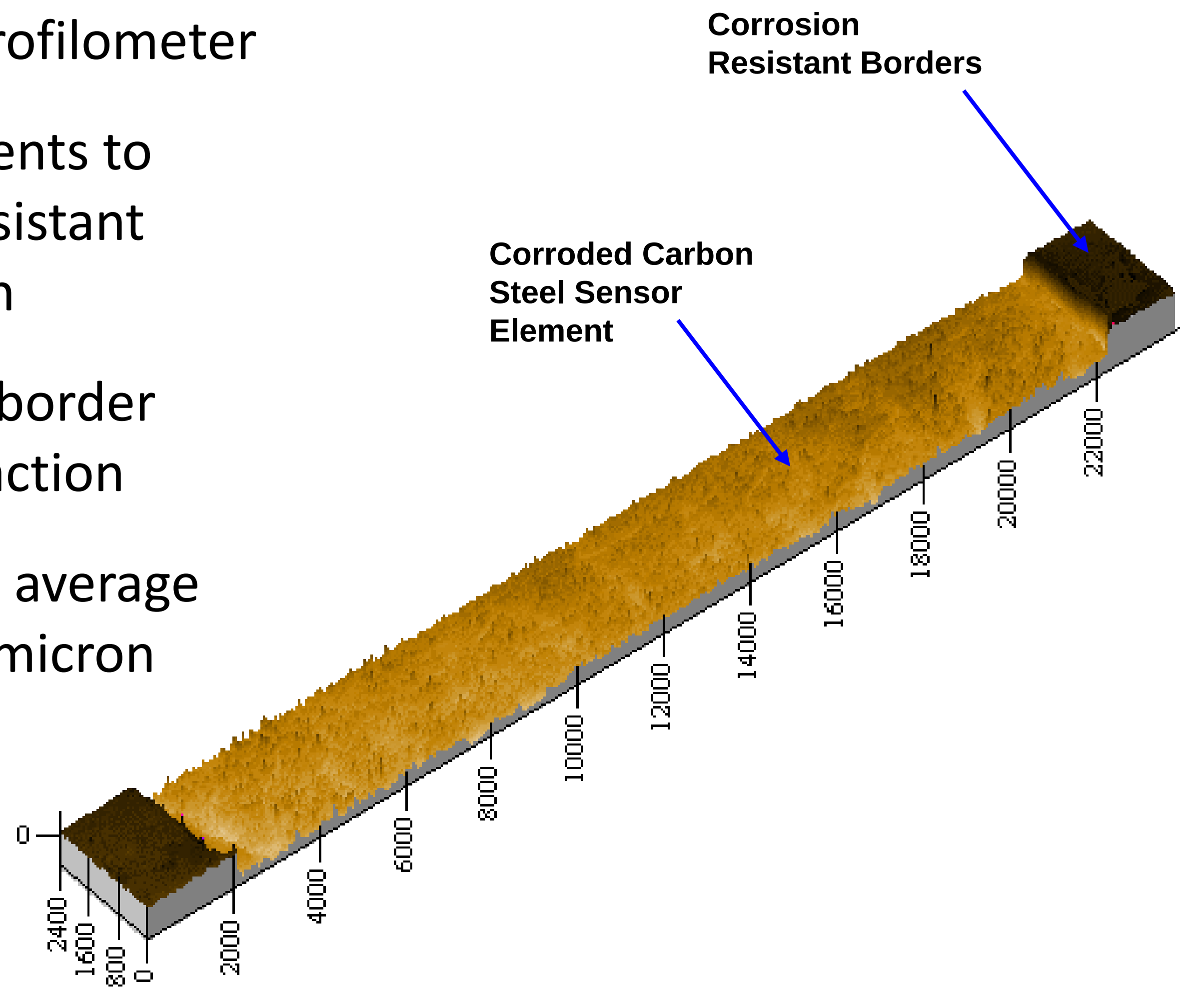


Control System Hardware

- Proprietary signal conditioning
- Embedded controller
- Runs deterministic OS
- Ethernet link for logging and communication
- Accessible using ftp, telnet, http, etc
- Core hardware – National Instruments Fieldpoint

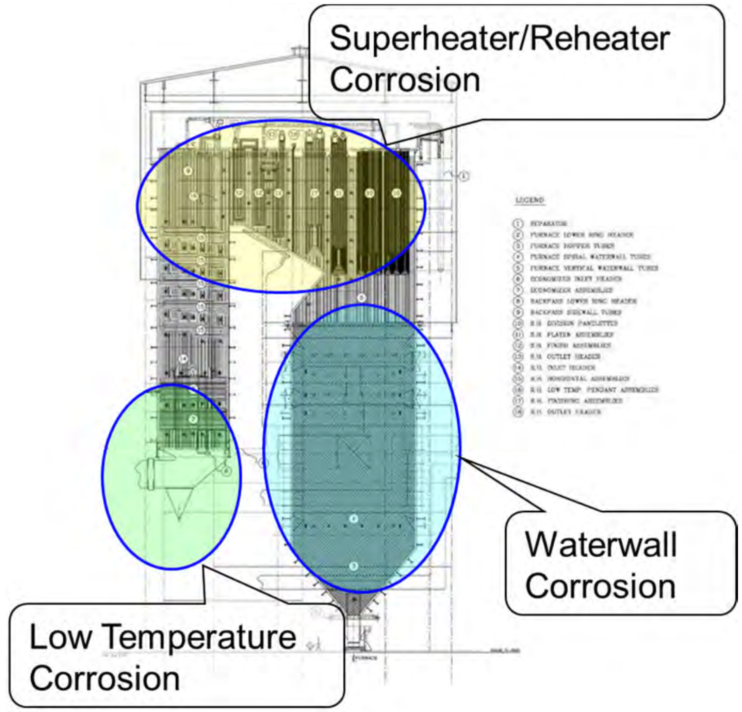
Rapid Turnaround Precision Metrology

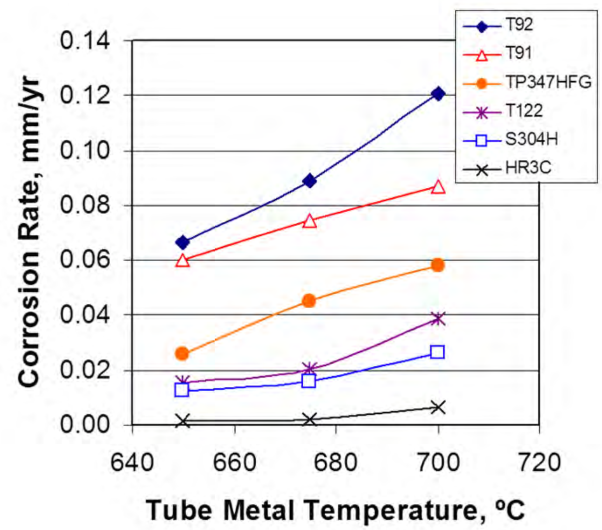
- Requires late model profilometer
- Modified sensor elements to provide a corrosion resistant surface for comparison
- In-house software for border recognition and subtraction
- Effective resolution on average corrosion depth < 0.1 micron



Real-time Corrosion Monitoring Experience

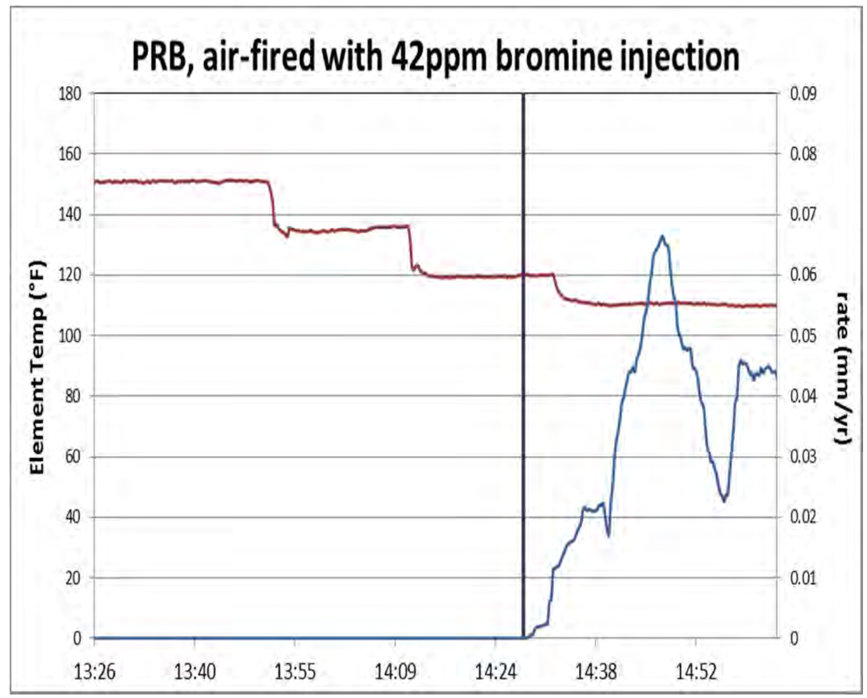
- Over 15 years of application at lab-, pilot- & full-scale
  - Wall-fired
  - Tangentially fired
  - Cyclone-fired
  - CFB
- Mechanisms involving sulfur, chlorine, and bromine, iodine
- Waterwall, superheater, economizer, air heater
- Materials from inexpensive carbon steels to expensive alloys
- Up to six simultaneous probes





Possible APH Corrosion Mechanisms Involving Hydrohalides

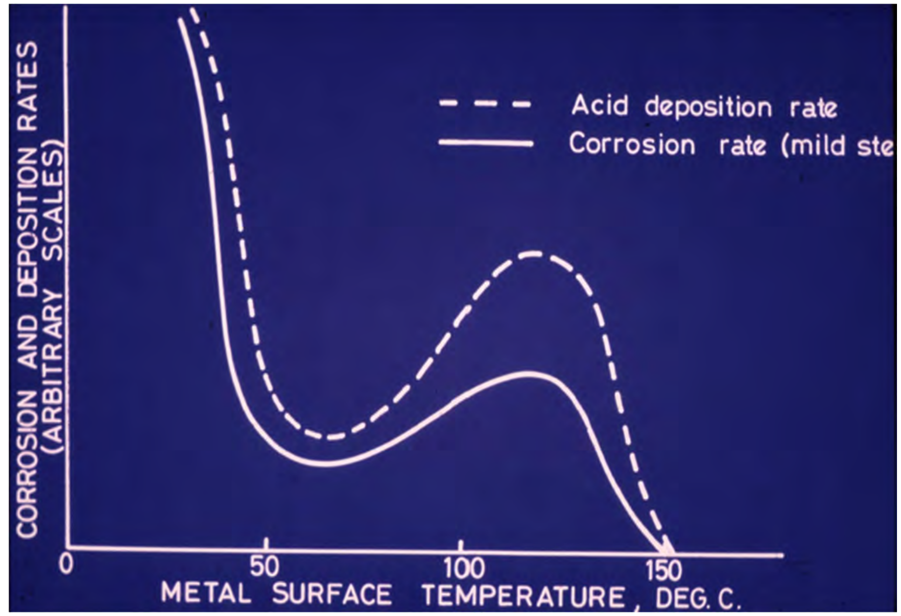
- Possible mechanisms:
  - Direct condensation of HBr
  - Absorption of HBr by condensed SO_3
  - Formation of Brominated salts on fly ash
  - Gas-phase attack by HBr
- Recent results at both pilot- and full-scale suggest condensation mechanism
- Hydrohalide condensation
  - Hydrobromic and hydroiodic acid are two of the strongest known mineral acids
  - Calculations for relevant concentrations of bromine addition indicate dew points in the 90-130 °F range

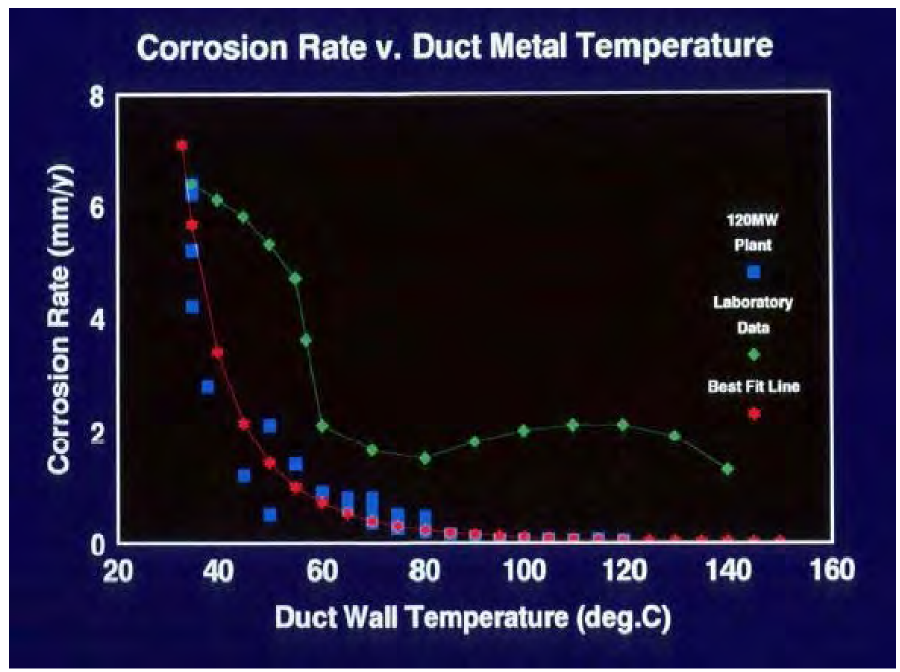


Dewpoint Considerations

[Cox and Meadowcroft, 1985]

- Ash-free acid deposition rates can be estimated and confirmed in the lab
- Comparison with field data complicated by ash interactions

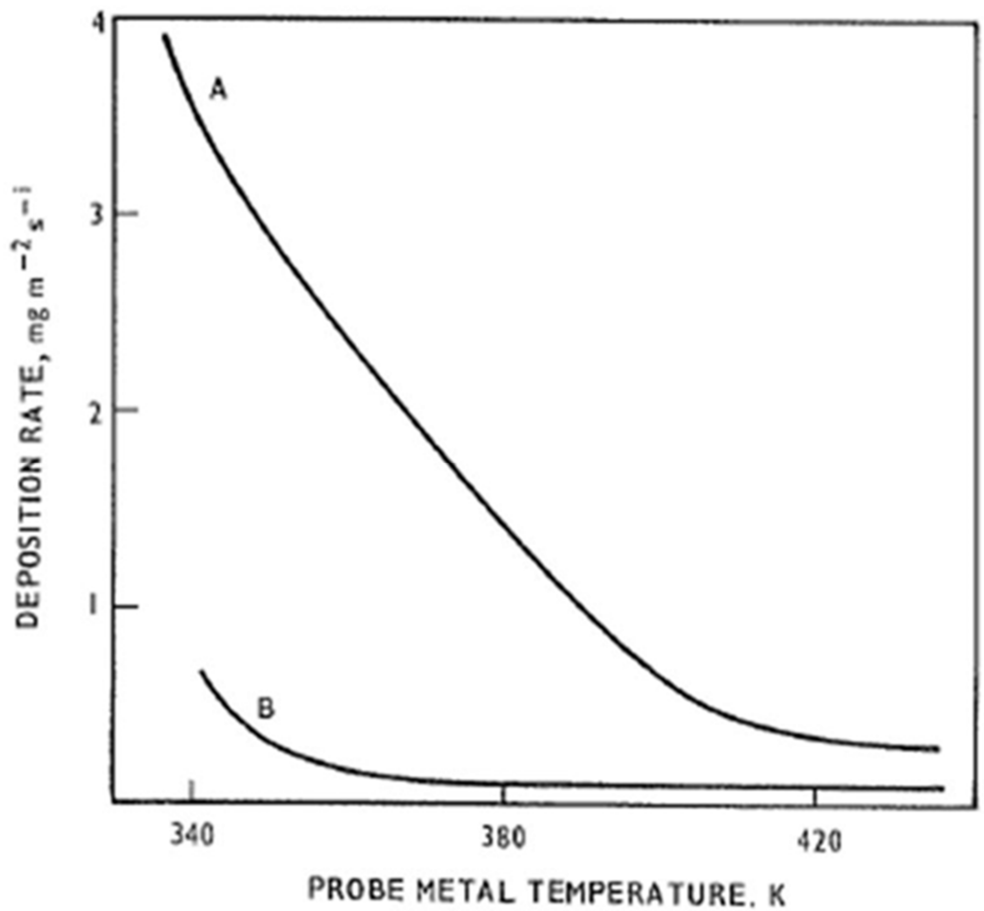




Impact of Ash on Acid Deposition

[Raask, 1985]

- Air-cooled probe inserted in the APH duct
- Boiler A with 0.9% sulfur coal with low calcium ash
- Boiler B with 1.5% sulfur coal with high calcium ash



APH Temperature Behavior

[Raask, 1985]

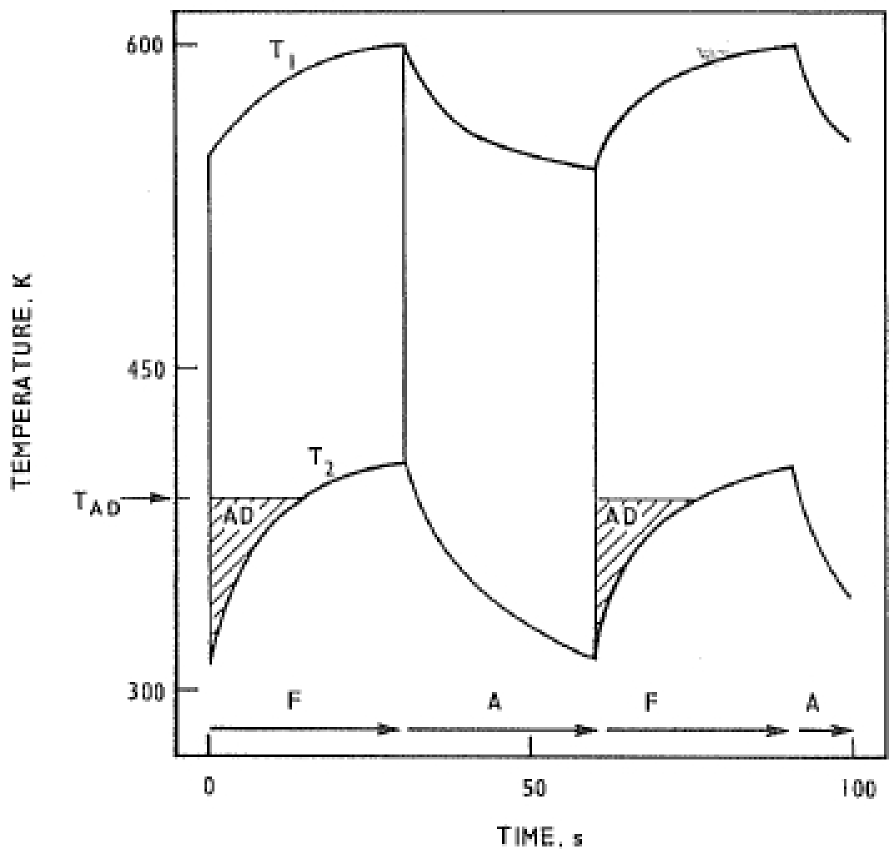
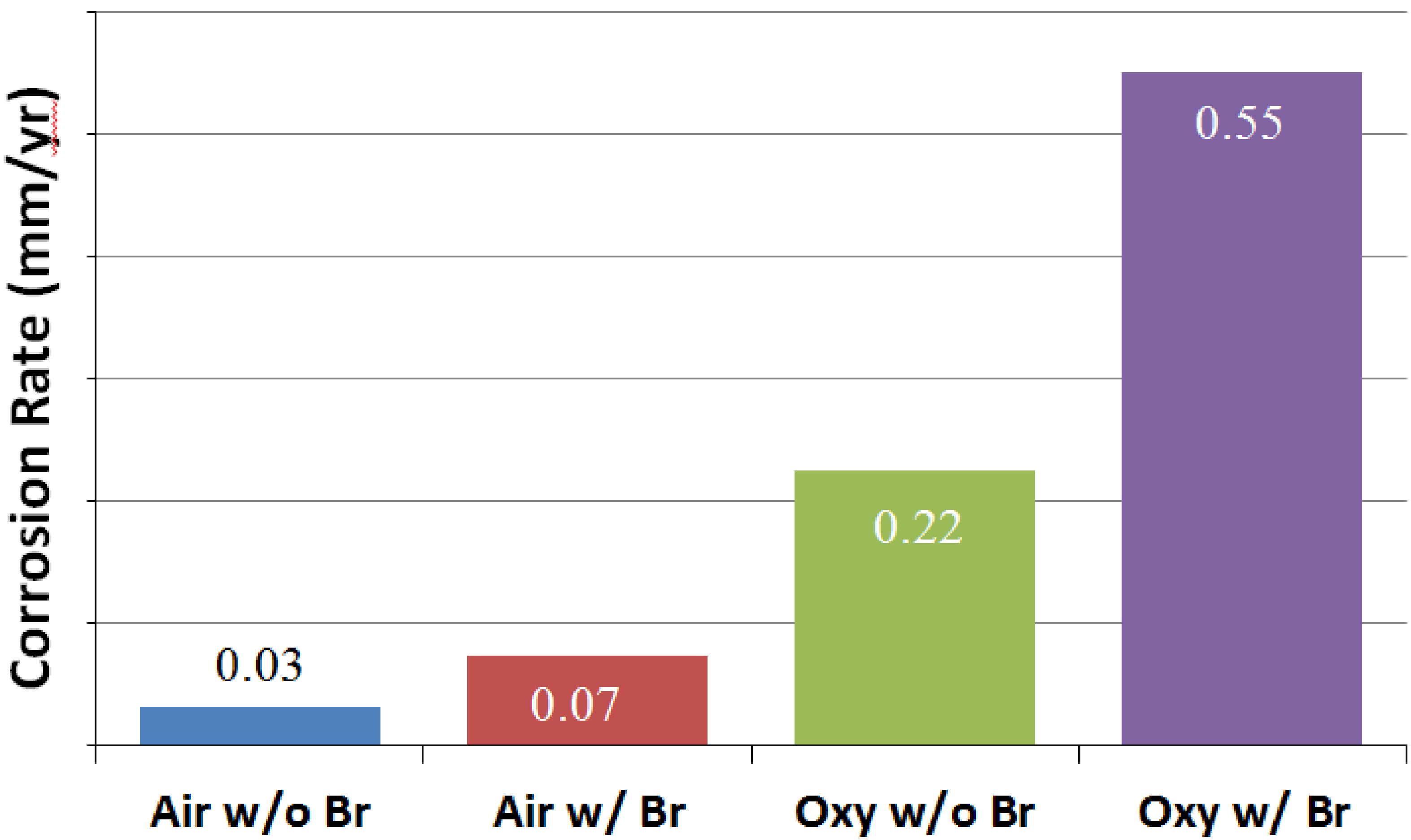


Figure 19.3 Changing metal temperatures and acid dewpoint in rotating regenerative air heater: T_1, air-heater inlet tempeature; T_2, air-heater outlet temperature; F, heating in flue gas; A, cooling in air; T_{AD}, acid dewpoint tempeature; AD, acid deposition.

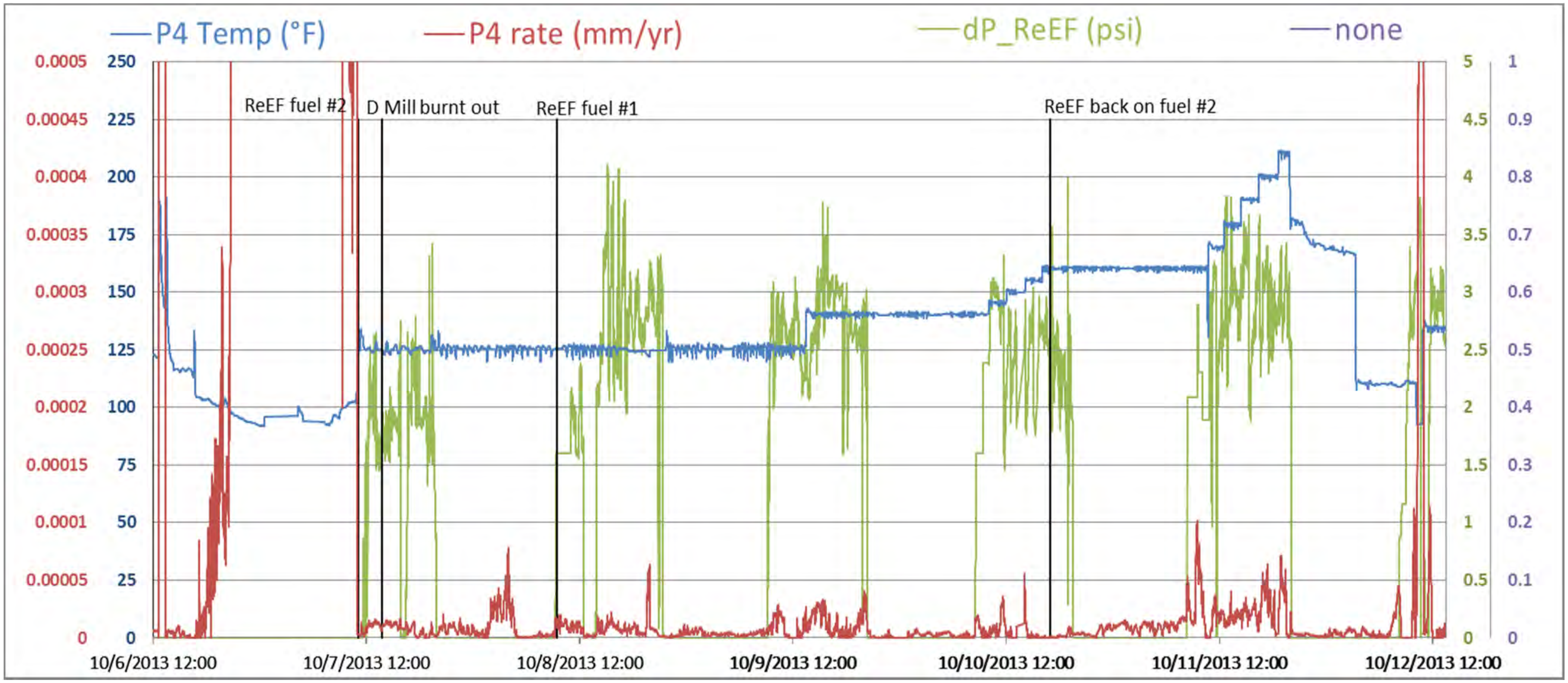
Peak Dewpoint Corrosion Rates during Pilot-scale Testing with Bituminous Coal

[Davis et al., 2014]



Accordant Coal Additive Impact on Air Heater

[Beutler et al., 2015]



- Clear impact of moisture condensation
- Noticeably higher rates while co-firing additive, although corrosion rates remain very small
- Sensitivity of EN illustrated

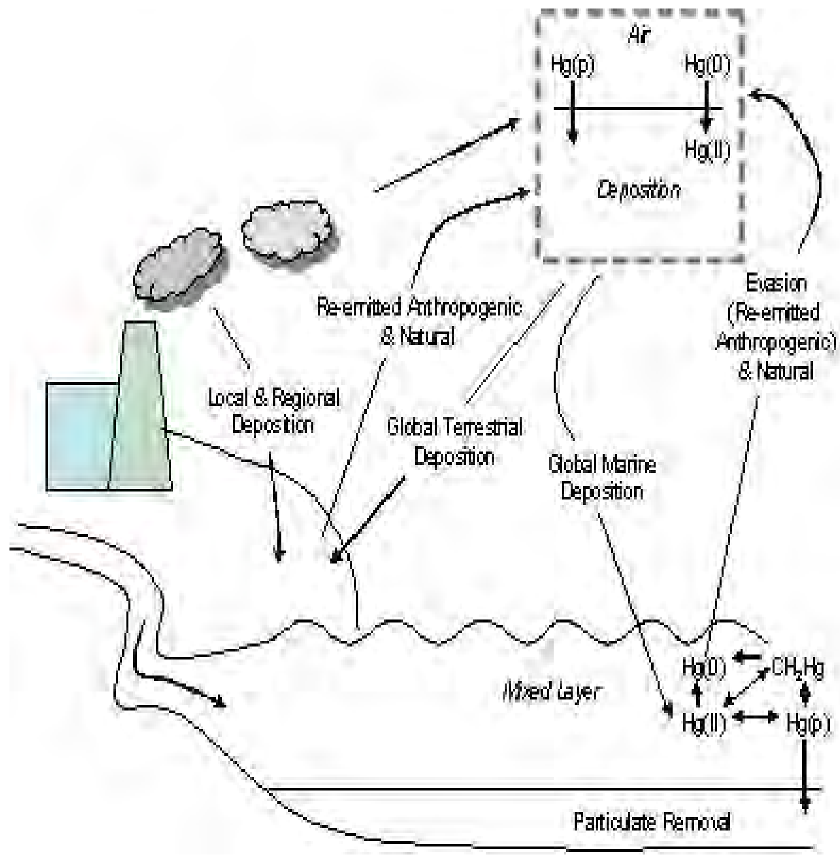
Periodic Table of the Elements

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 30.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (97.91)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (208.98)	85 At (209.99)	86 Rn (222.02)
87 Fr (223.02)	88 Ra (226.03)	89 Ac (227.03)	104 Rf (261.11)	105 Ha (262.11)	106 Sg (263.12)												
				58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (144.91)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
				90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237.05)	94 Pu (244.06)	95 Am (243.06)	96 Cm (247.07)	97 Bk (247.07)	98 Cf (251.08)	99 Es (252.08)	100 Fm (257.10)	101 Md (258.10)	102 No (259.10)	103 Lr (262.11)

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



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)

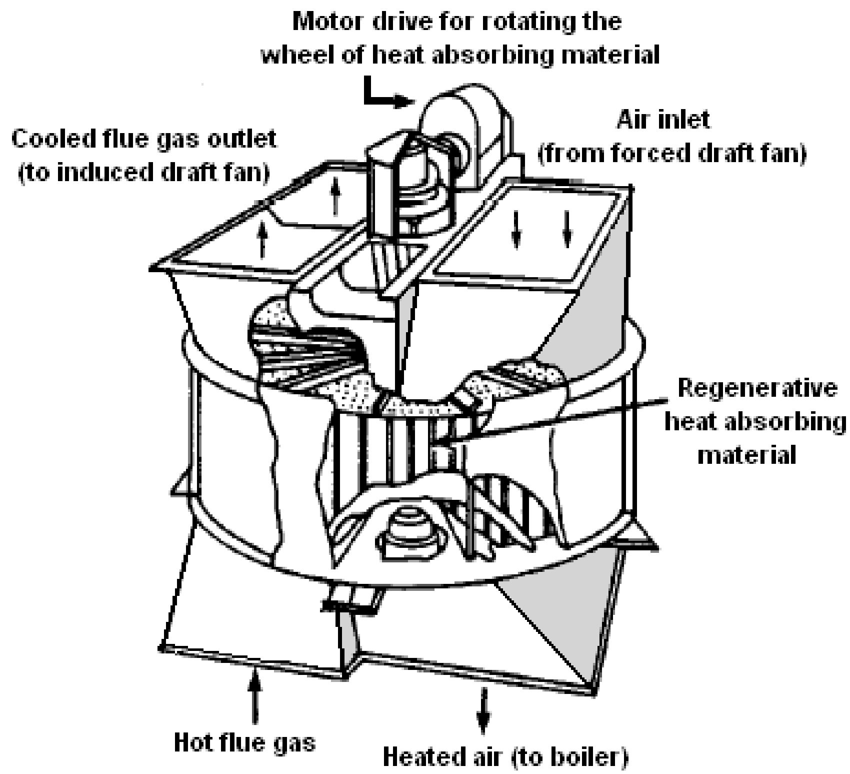
Dead Sea

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

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



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 (EN) probe, Stack CEMS, and EPA M5 and M30B
- Air Heater metallurgy: Carbon Steel A192

Halide Additive Injection

Corrosion Testing - EN Probe

Un-exposed probe

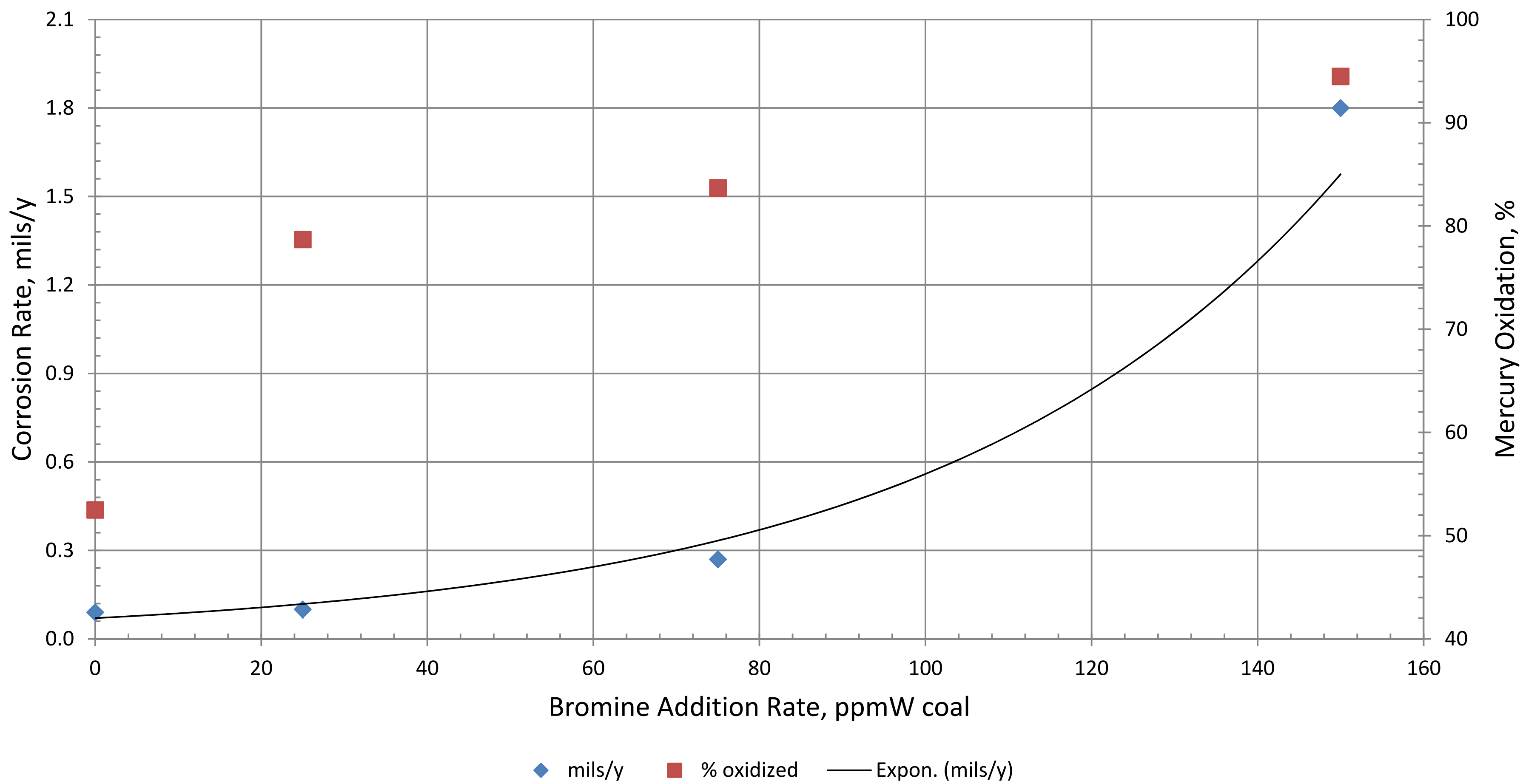
Deposit build-up following 4-hour period of 25ppm Iodine addition

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	Similar
12/11 PM 25 ppm Iodine	98.5	0.28	3 X
12/12 AM 25 ppm Bromine	78.7	0.10	Similar
12/12 PM 75 ppm Bromine	83.7	0.27	3 X

* Averaged over multiple test periods

Corrosion Rate & Hg Oxidation vs Br Addition Rate



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

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

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

B&W power generation group

Chem•Mod Making Power Cleaner.

Expected Performance Improvement with Mitagent

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

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

Questions?

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