REINHOLD ENVIRONMENTAL Ltd.

2016 NOx-Combustion-CCR Round Table Presentation

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Corrosion Associated with Halide Fuel Additives for Hg Oxidation

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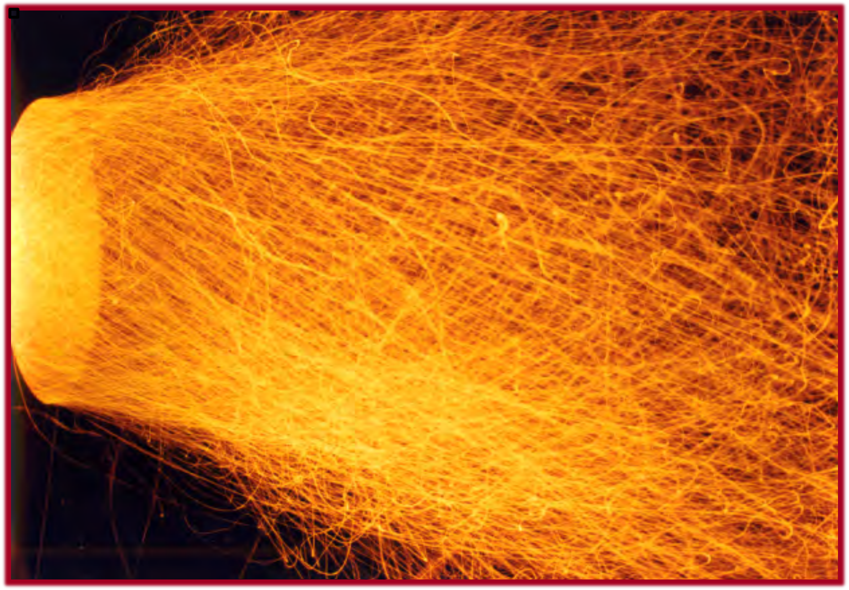
For Energy and Environmental Solutions
REACTION ENGINEERING INTERNATIONAL

Reinhold NOx – Combustion Roundtable
February 1-2, 2016
Orlando, FL

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

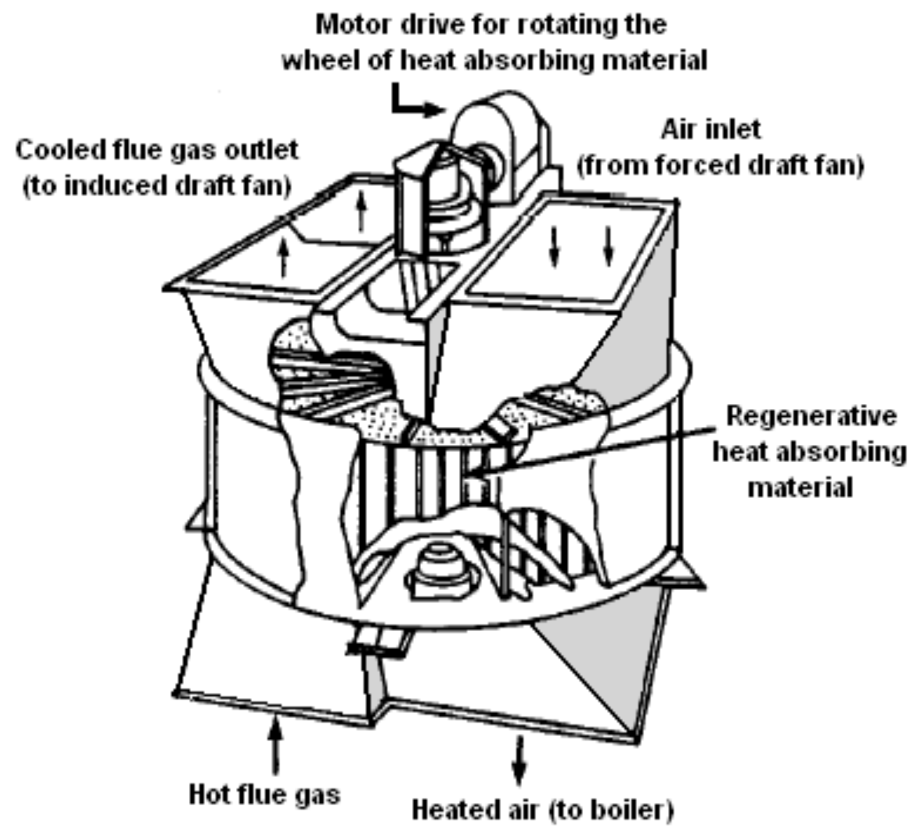


Mercury Emission Control

- Section 45 Refined Coal Tax Credit targeting >40% reduction
- MATS rule: Coal-fired EGUs must achieve stack Hg emissions of 1.2 lb/TBtu or less for Bituminous and Sub-Bituminous coals
- Mercury oxidation by halide addition to the coal feed and removal of the oxidized Hg is one of the more cost-effective methods for Hg emission control
- Balance-of-Plant effects must be considered

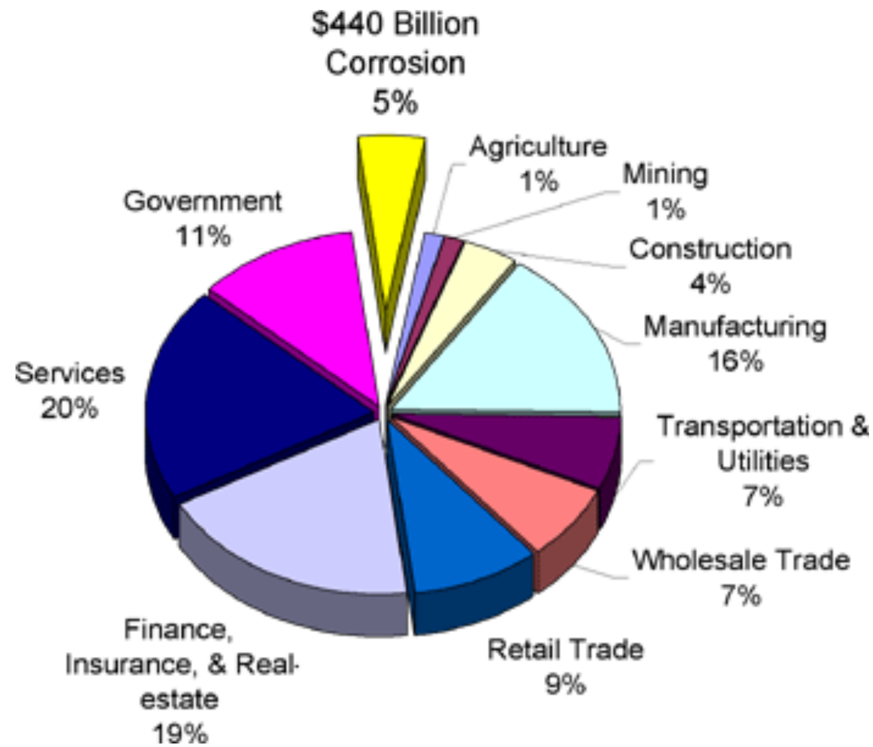
Halide-Induced Air Heater Corrosion

- 33 PRB units reported Air Heater (AH) cold-end basket corrosion, while 19 did not [EPRI, 2014]
- 14% of units using <100ppm bromine and 83% of units using 100-200ppm bromine experienced corrosion
- Lowest metal temperatures during contact with halogen are experienced as elements rotate into flue gas stream
- For PRB-fired units, AH operation and cold-end material selection decisions have not been particularly concerned with dewpoint corrosion
- It is hypothesized that the corrosion rate is directly related to the bromide addition rate



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

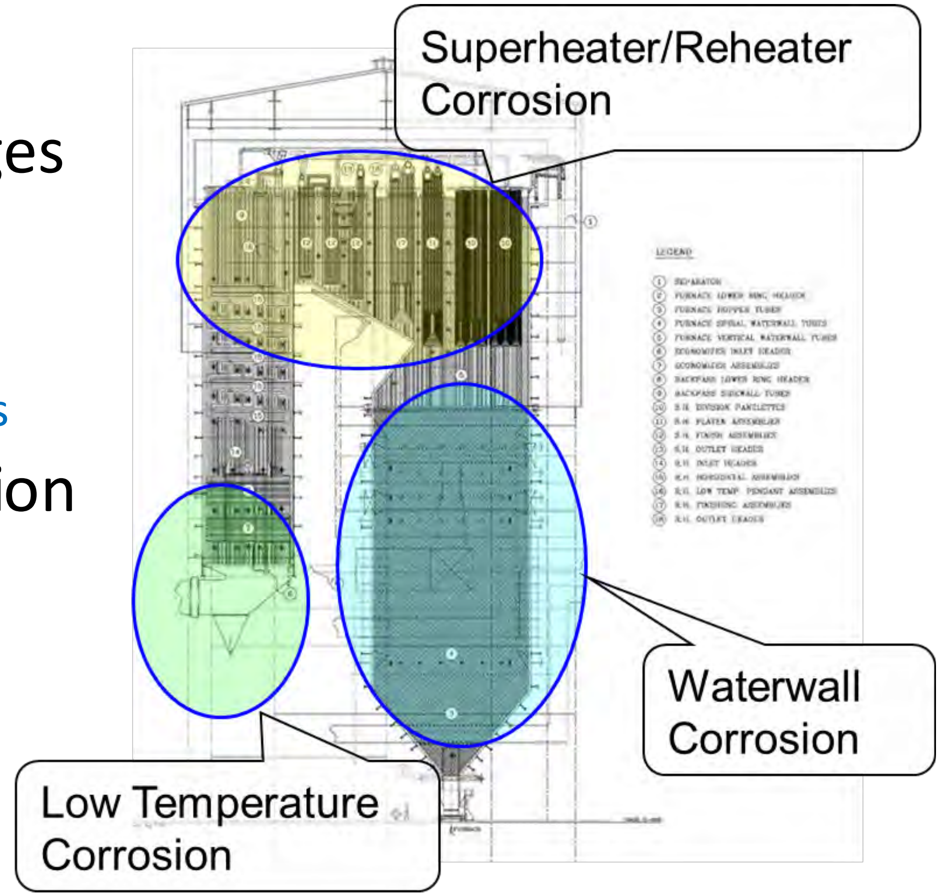


"… in 1998 the annual cost of corrosion in the U.S. electric power industry was $17.3 billion"

[EPRI, 2001]

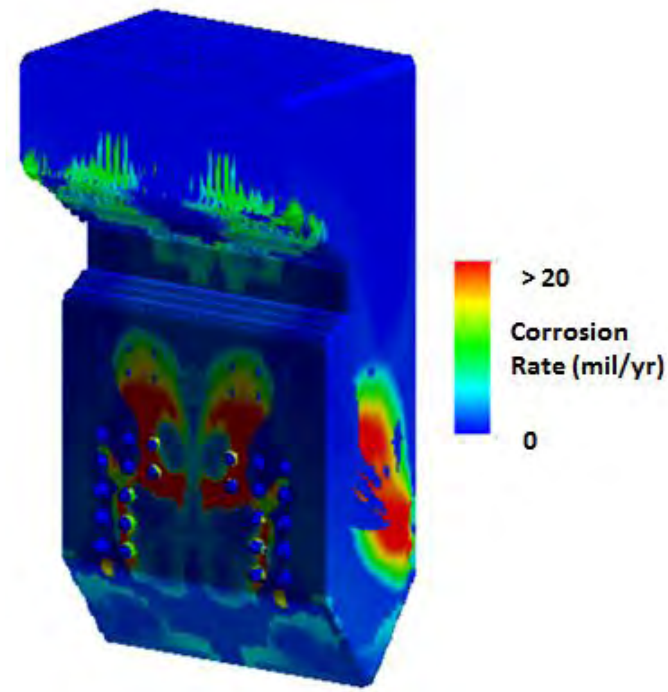
Benefits of Corrosion Management

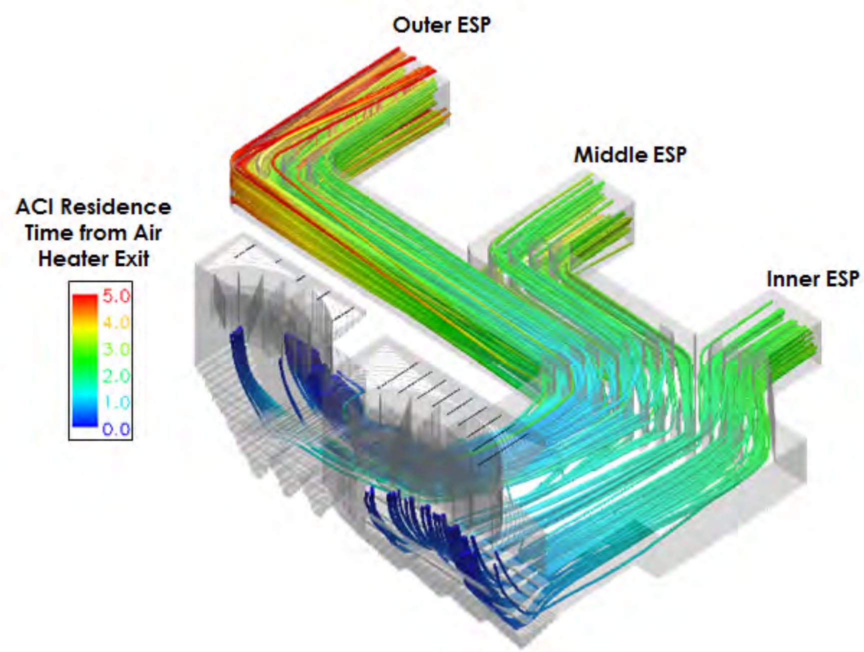
- Reduction in unscheduled outages
- Reduction in maintenance costs
  - Material life extension
  - Reduction in expensive overlay or coatings
- Improved operational optimization
- Quantitative guidance in fuel selection/blending/additive decisions
- Quantitative guidance in materials selection and life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



Tools

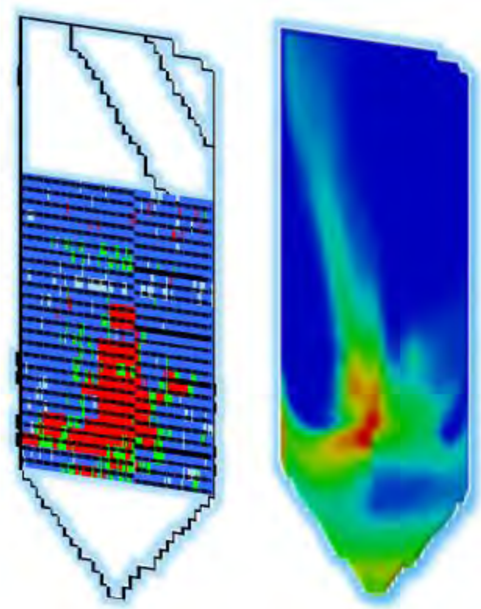
- CFD-based modeling
  - Validated correlation-based approach resulting from collaborations with EPRI and KEPRI for high temperature corrosion
  - Integrated with REI's CFD software (GLACIER)
- Process modeling (MerSim™)
  - Provides key information related to the evolution of mercury, sulfur, and halogen 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)





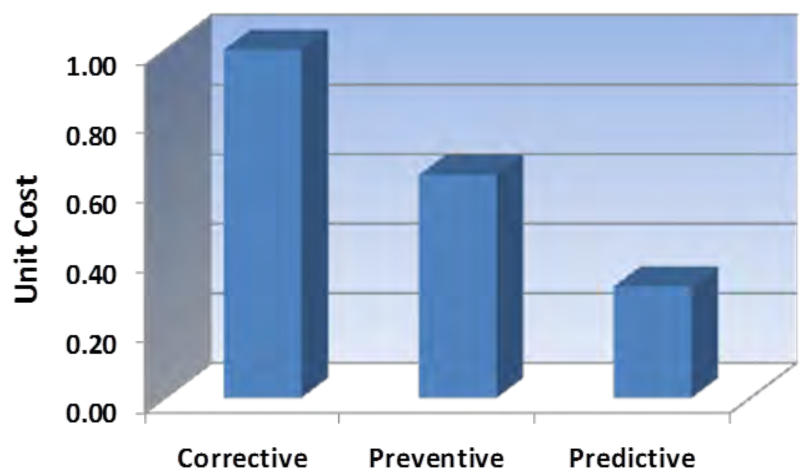
Solution Approach

- 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:

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

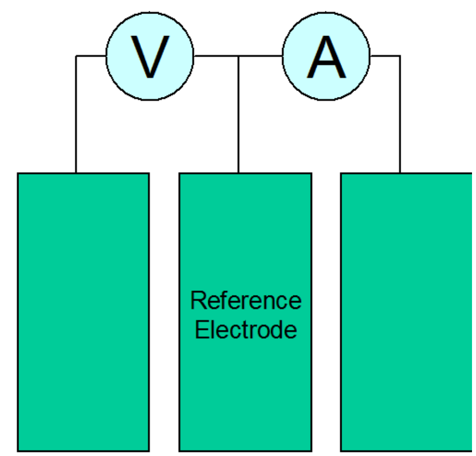
Cathodic reaction:

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

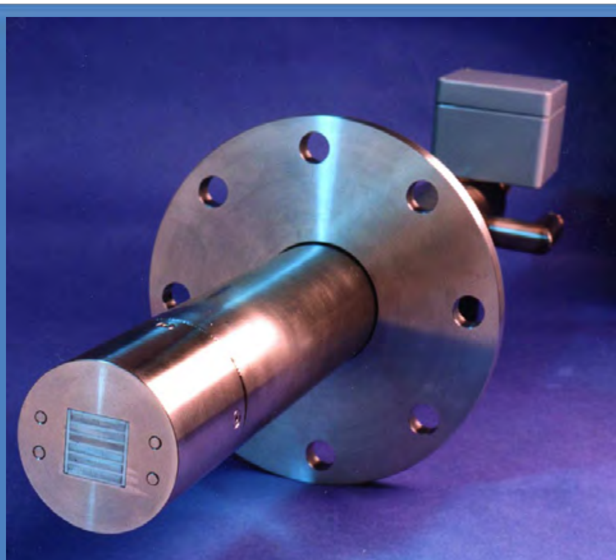
Combined:

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

Similarly, sulfur → sulfides
chlorine → chlorides

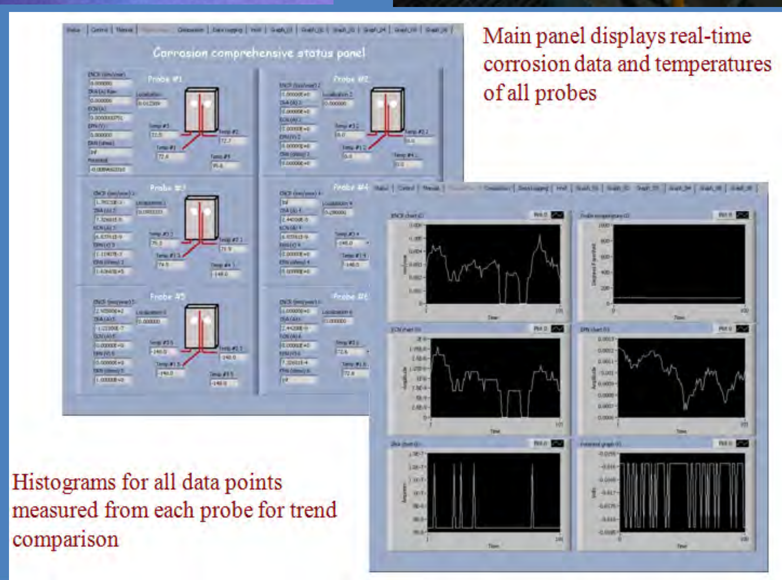


EN Probe for Corrosion Testing

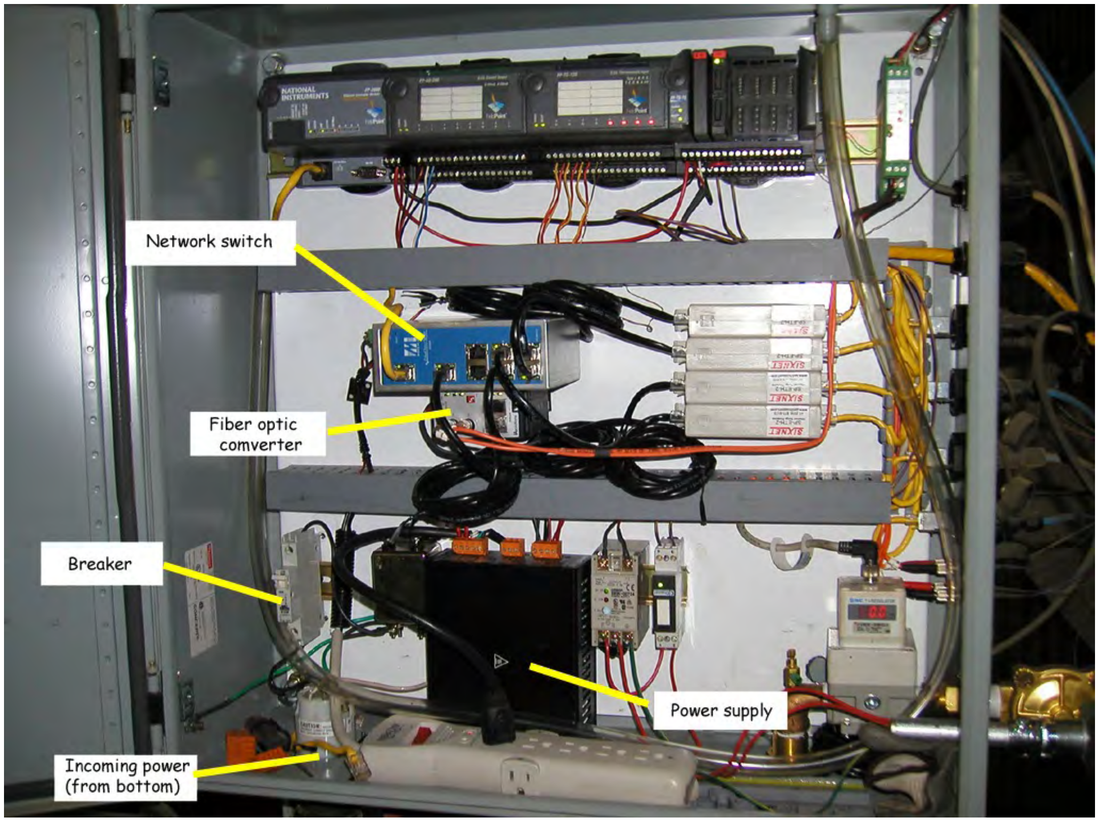


- High Sensitivity
- Instantaneous response
- Direct indication of corrosion
- Quantitative measurement
- Response related to corrosion mechanism

Data Acquisition

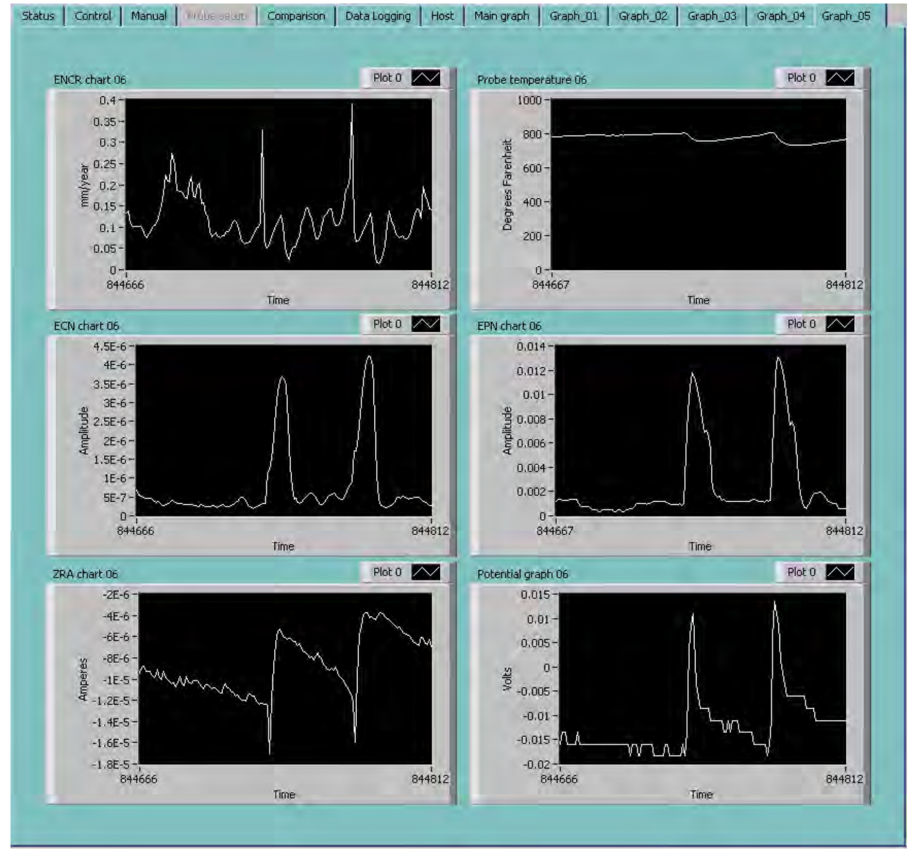


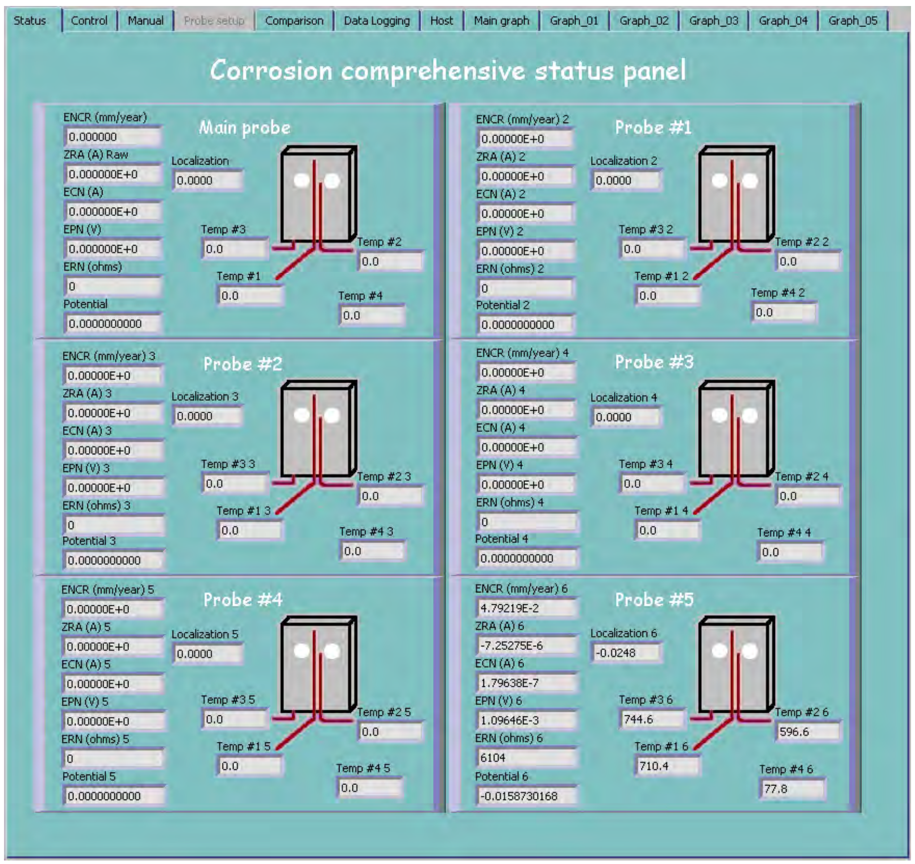
Electronics



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

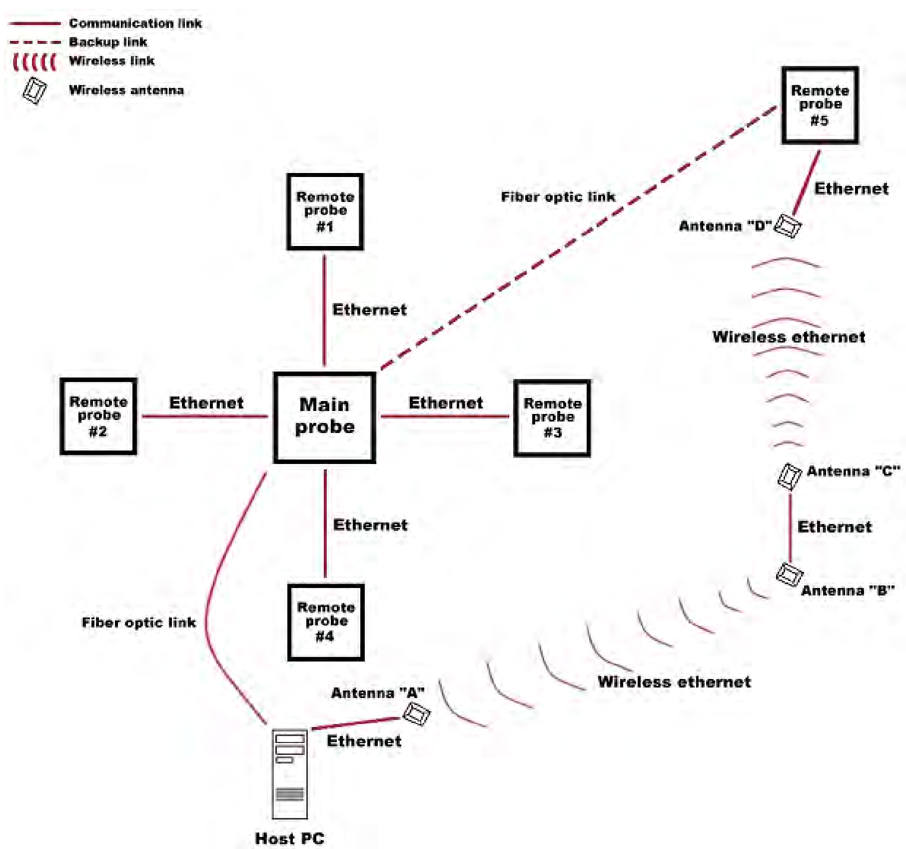
Software





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

Data Acquisition and Control

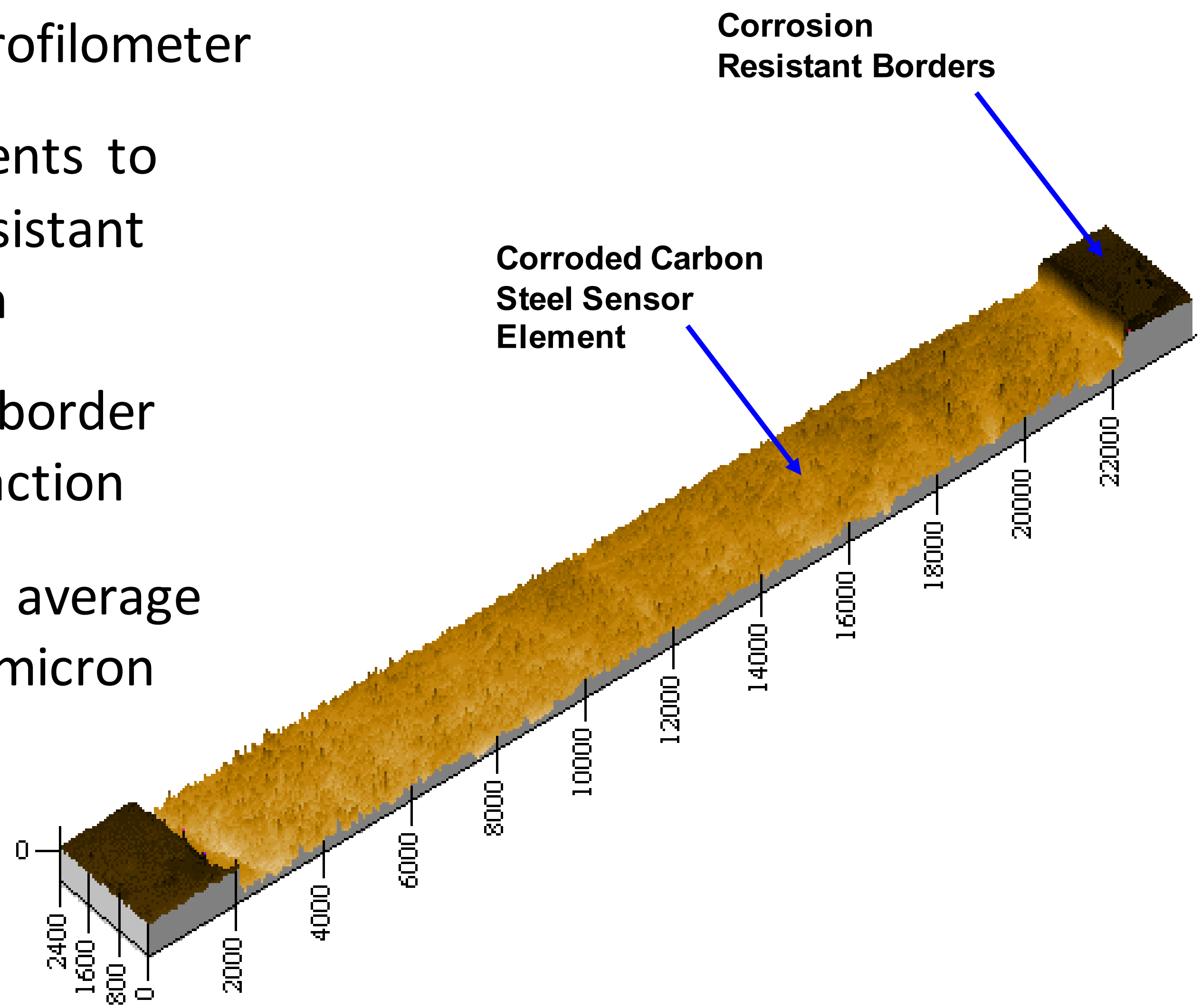


Control System Hardware

- 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

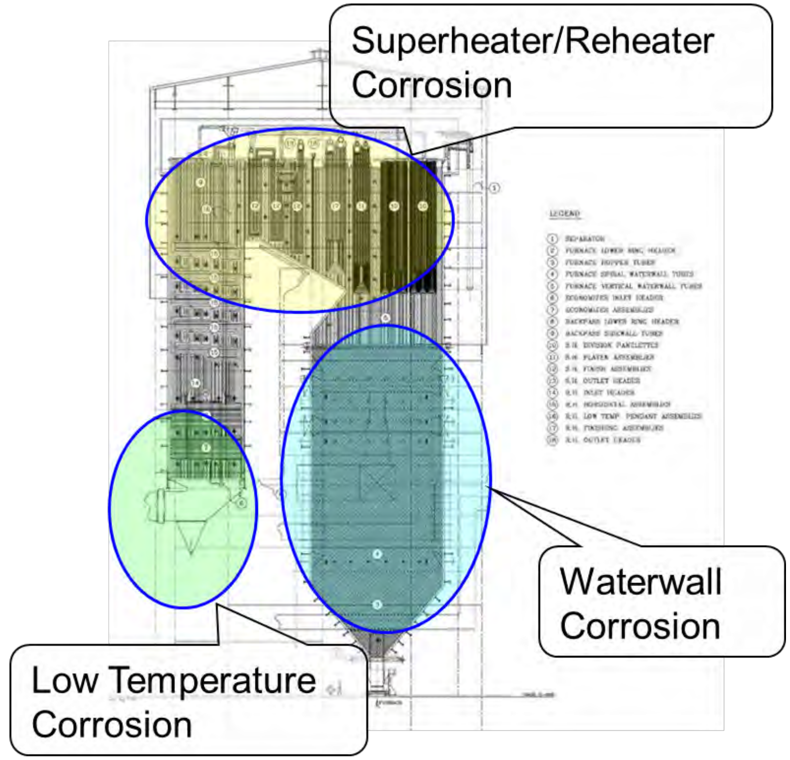
Rapid Turnaround Precision Metrology

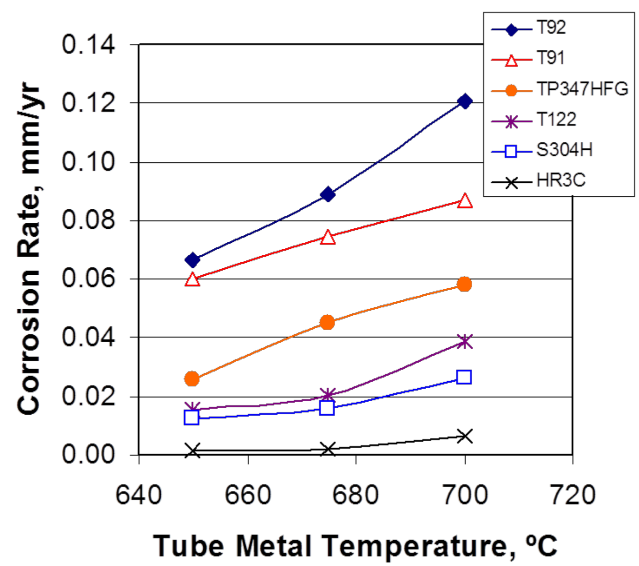
- Requires late model profilometer
- Modified sensor elements to provide a corrosion resistant surface for comparison
- In-house software for border recognition and subtraction
- Effective resolution on average corrosion depth < 0.1 micron



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



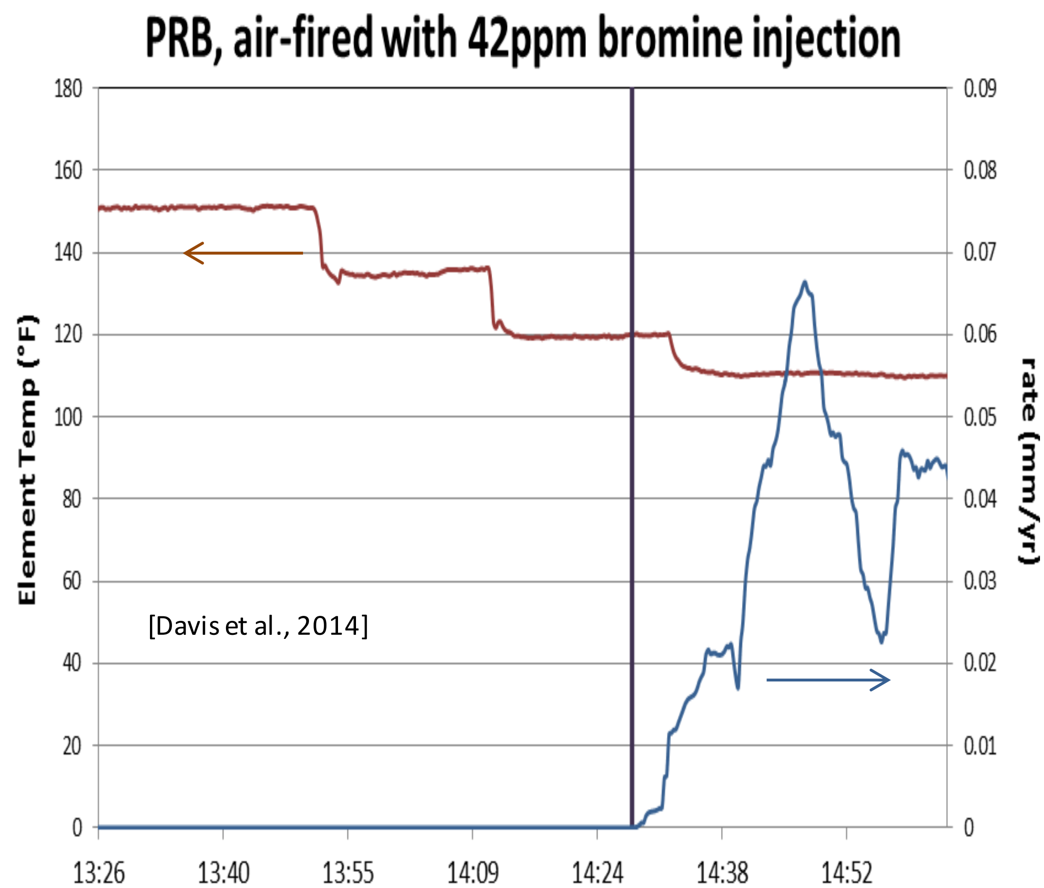


Sampling of Past Corrosion Studies

Facility	Project	Mechanism
UofU tube furnace	DOE PSA and OCDO	HCl gas-phase
UofU entrained flow 0.15 MBtu/hr	DE-AC22-95PC95103	Mid-furnace H2S
UofU 5 MBtu/hr	DE-AC22-95PC95103(PRDA2)	Mid-furnace H2S
UofU 5 MBtu/hr	Plasma Potassium Additive	Waterwall
UofU 5 MBtu/hr	DE-NT0005288 (Oxy-coal) phase I	Waterwall & SH sulfur
UofU 5 MBtu/hr	DE-NT0005288 (Oxy-coal) phase II	Bromine dewpoint
B&W Research Center	DOE	High temperature sulfur
Tangential pilot-scale USC	KEPRI	SH & WW sulfur corrosion
Conectiv BL England Station	DOE	Mid-furnace H2S
FirstEnergy Eastlake	DOE PSA and OCDO	Mid furnace sulfur deposit
AEP Gavin	DOE PSA and OCDO	Mid furnace sulfur deposit
Hsinwu Paper Mill CFB	ITRI	Molten salt&dewpoint
SCANA Canadys	Waste derived fuel	Waterwall/SH/econ/APH
80 and 240 MW Coal Boilers	Halide Additives	Bromine & Iodine APH corrosion
UofU Nanofab Lab	Refinery HFAU	Hydrofluoric acid corrosion

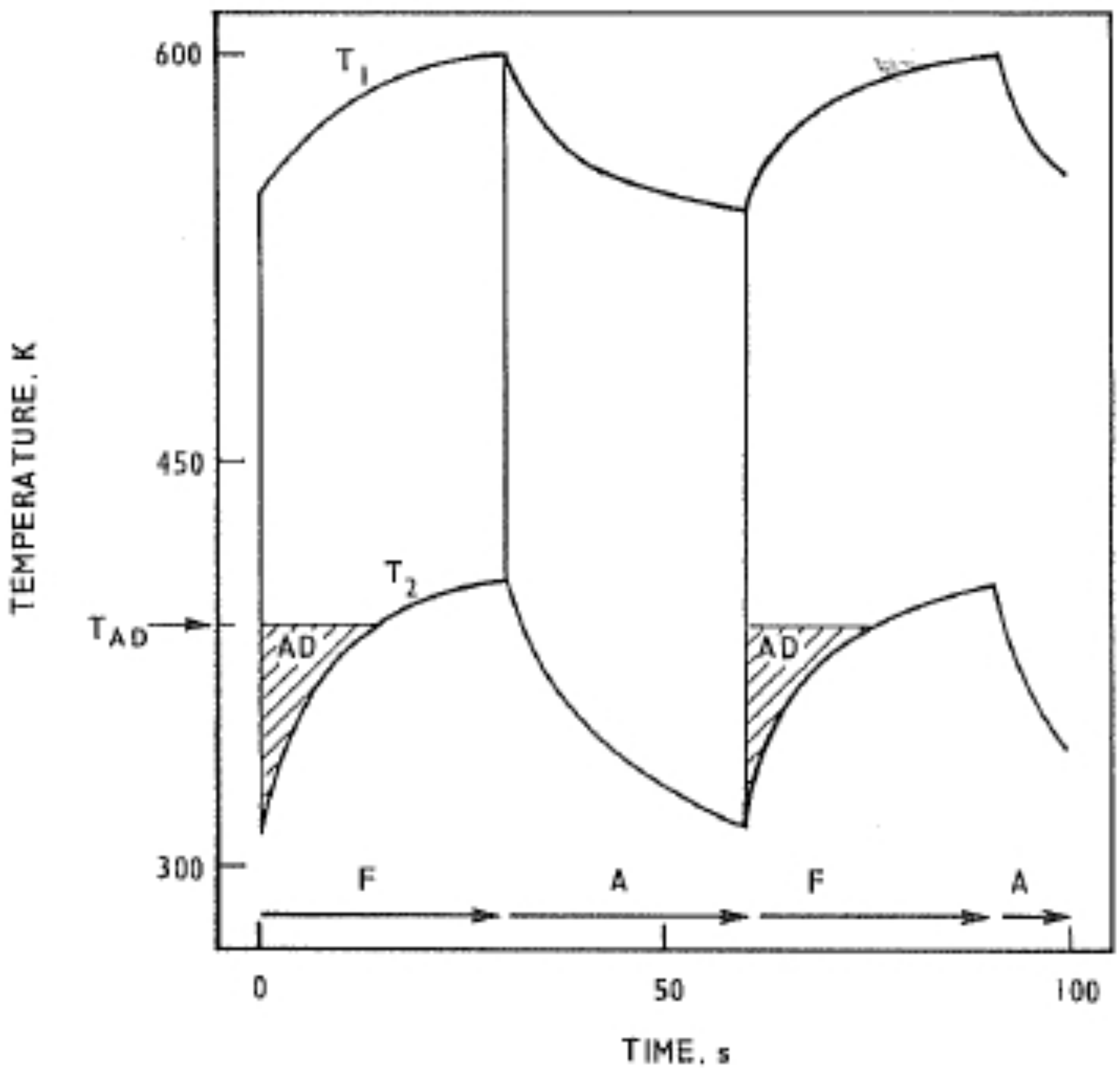
AH Corrosion Mechanism Involving Hydrohalides

- Recent results at both pilot- and full-scale suggest condensation mechanism
- Hydrohalide condensation
  - Hydrobromic and hydroiodic acid are two of the strongest mineral acids
  - Calculations for relevant concentrations of bromine addition indicate dew points are in the 110-125 °F range for high moisture PRB coal



APH Temperature Behavior

[Raask, 1985]



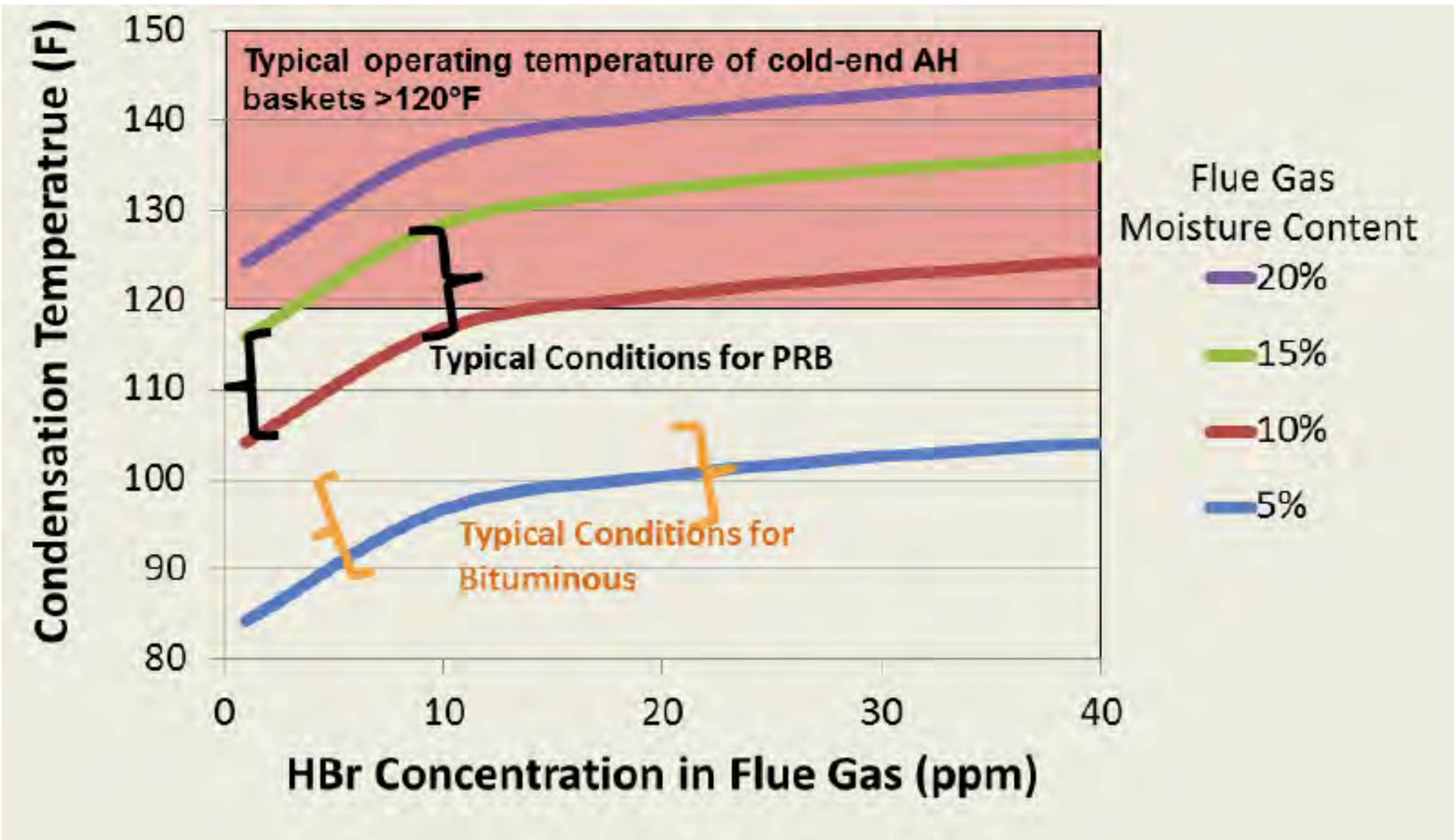
T1 – local AH surface temperature at flue gas inlet / air outlet

T2 – local AH surface temperature at air inlet / flue gas outlet

AD – acid deposition

HBr Dewpoint

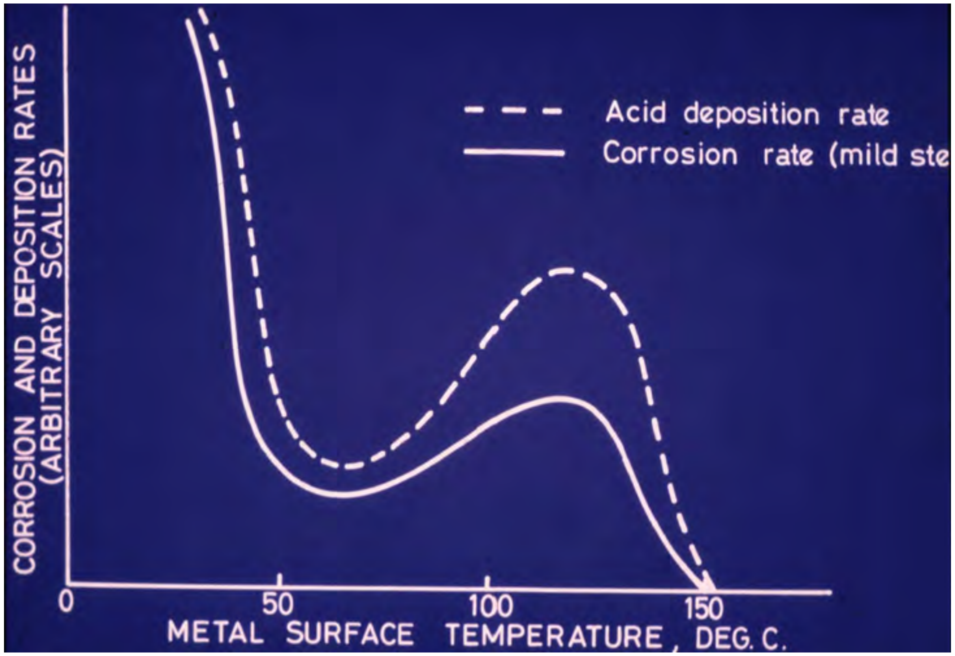
[Dombrowski et al., 2015]

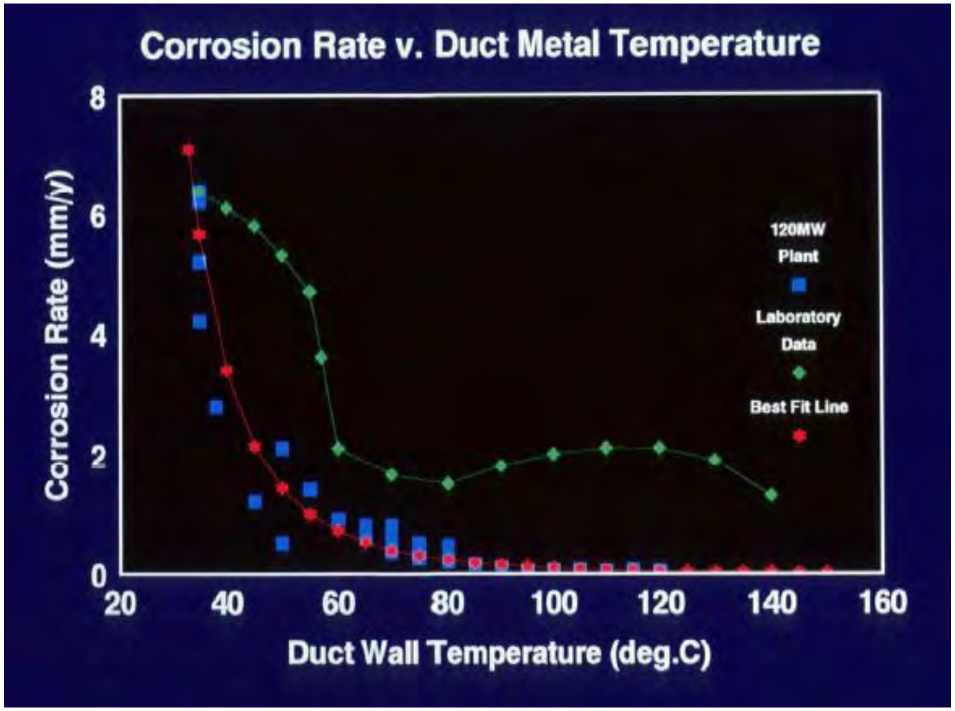


Dewpoint Considerations

[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

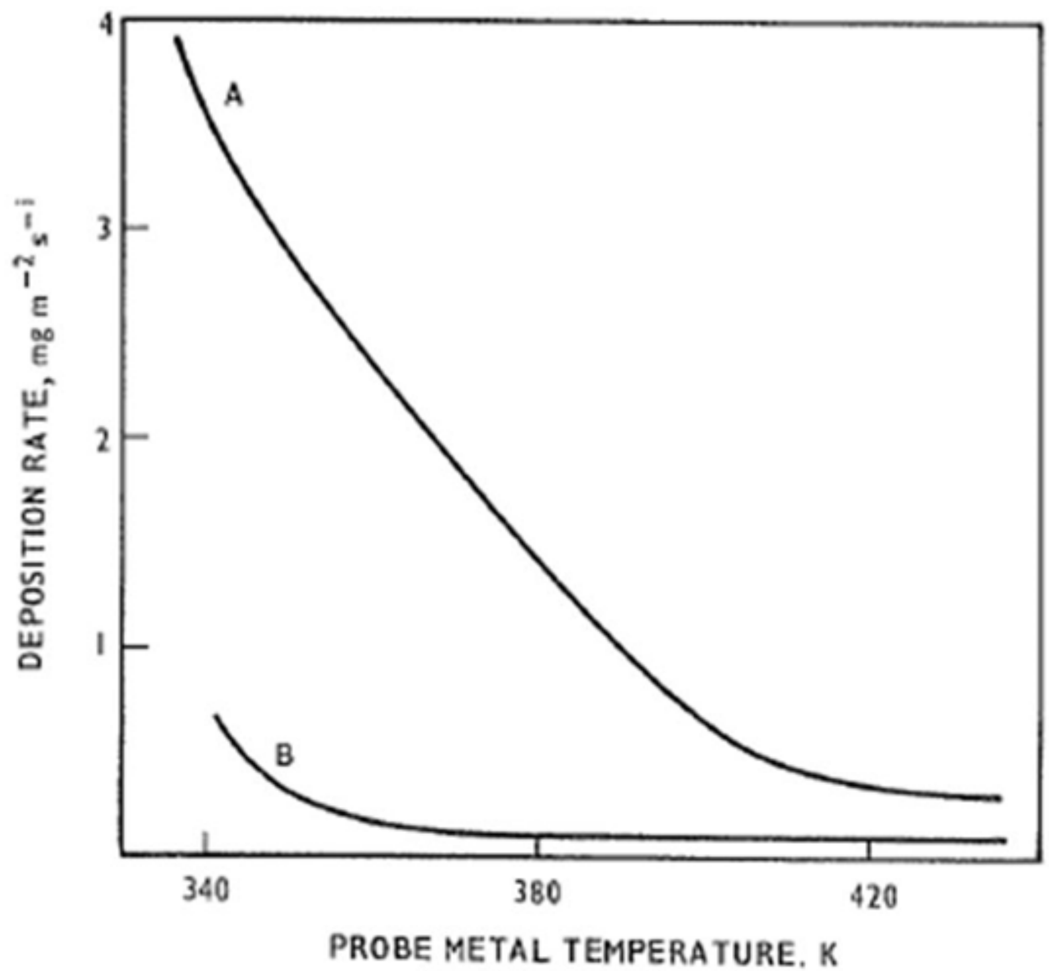




Impact of Ash on Acid Deposition

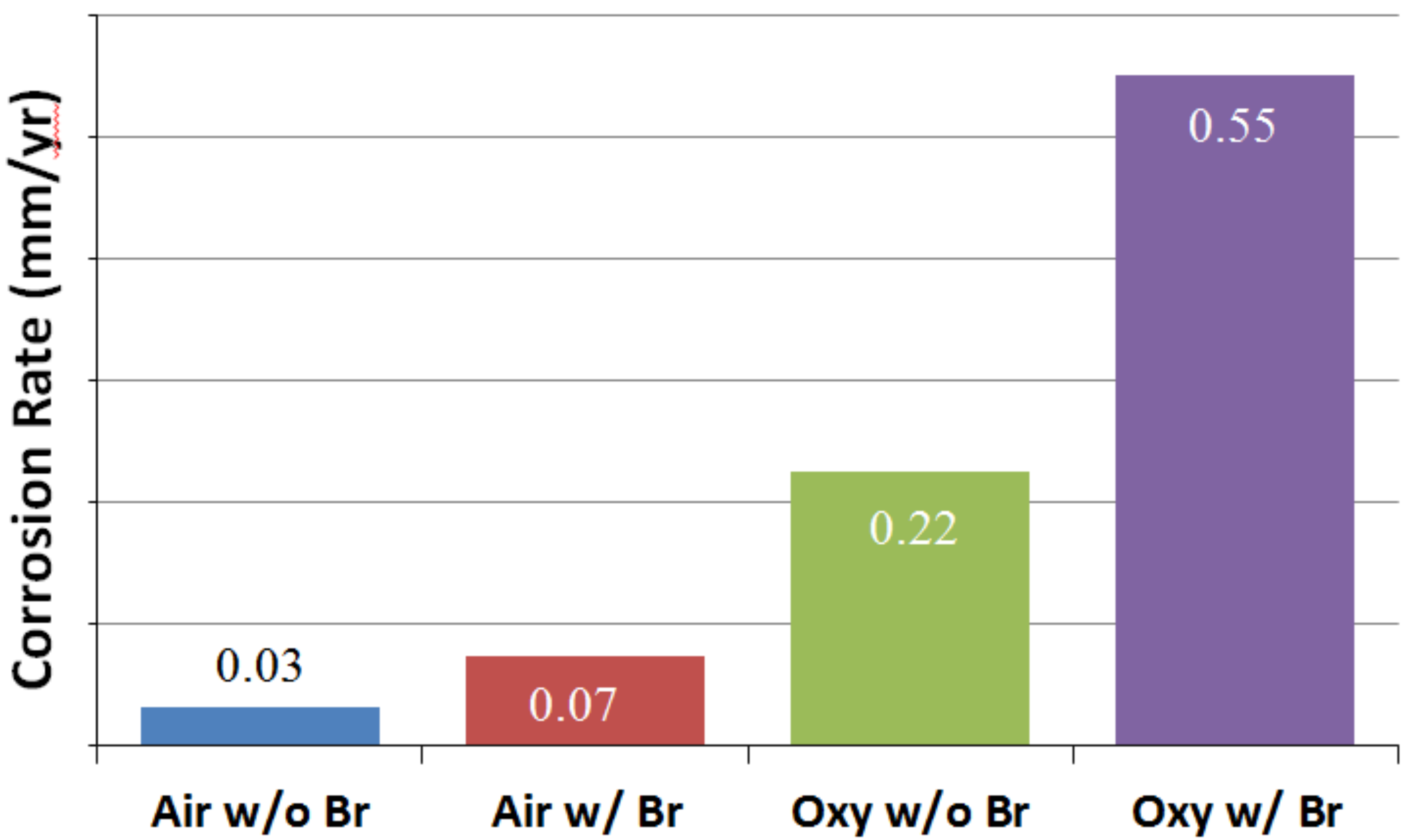
[Raask, 1985]

- 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



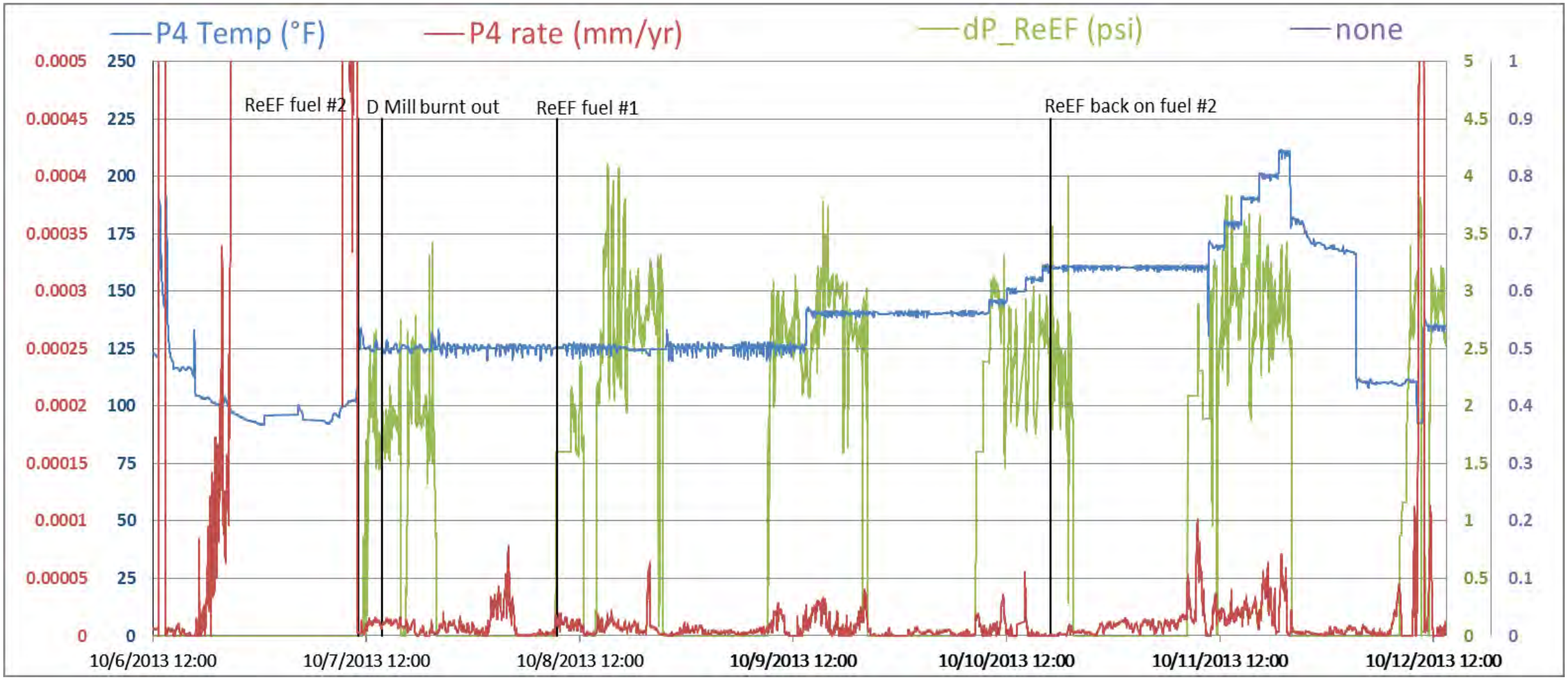
Peak Dewpoint Corrosion Rates during Pilot-scale Testing with Bituminous Coal

[Davis et al., 2014]



Accordant Coal Additive Impact on Air Heater

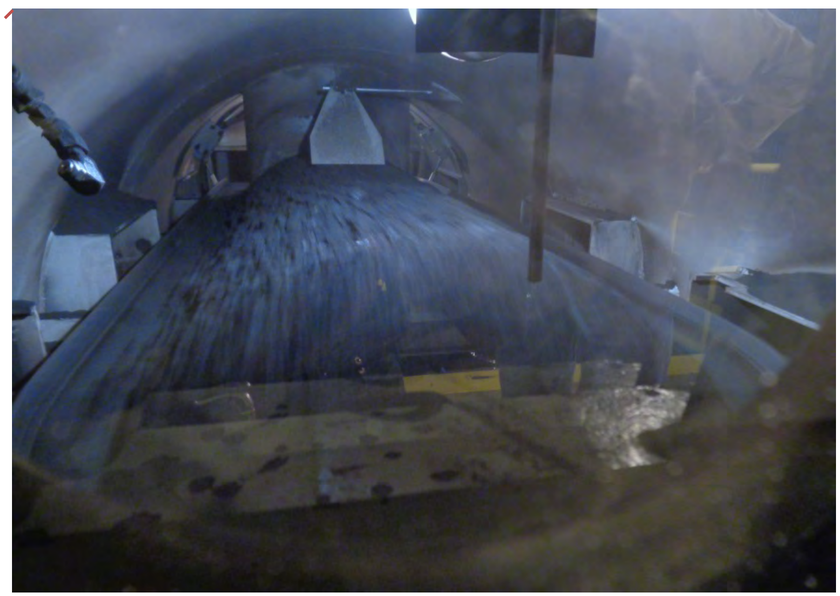
[Beutler et al., 2015]



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

Field Testing

- Two recent test campaigns investigating the impact of fuel halide addition in PRB-fired units have been completed:
  - 80 MW T-fired unit with ESP and FGD [Gadgil, 2015]
  - 240 MW wall fired unit with SCR and circulating dry scrubber
- 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 probe metallurgy: Carbon steel A192

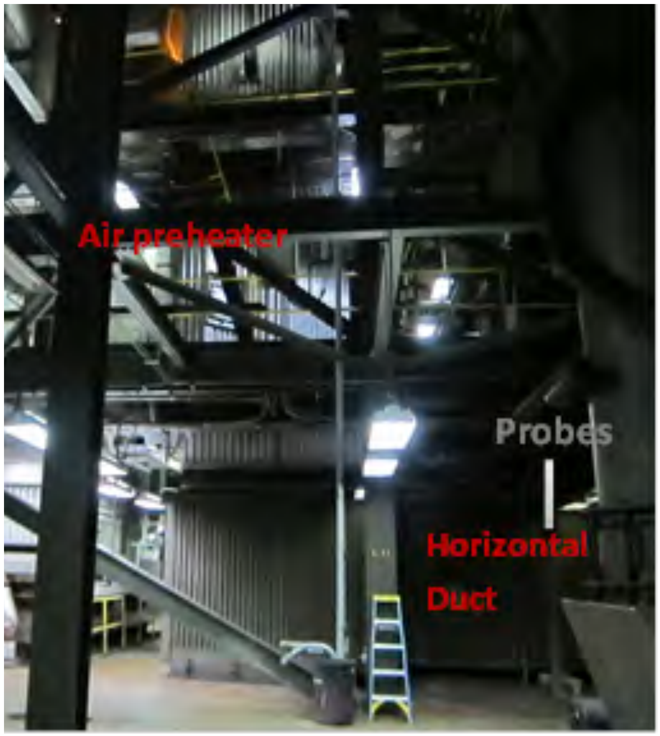


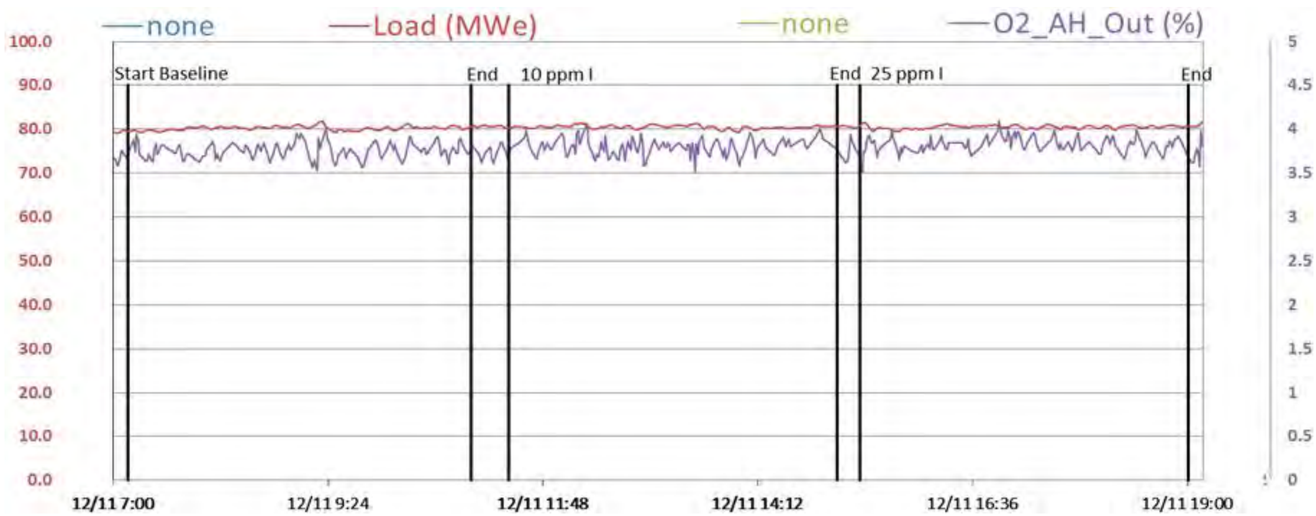
Halide Additive Injection

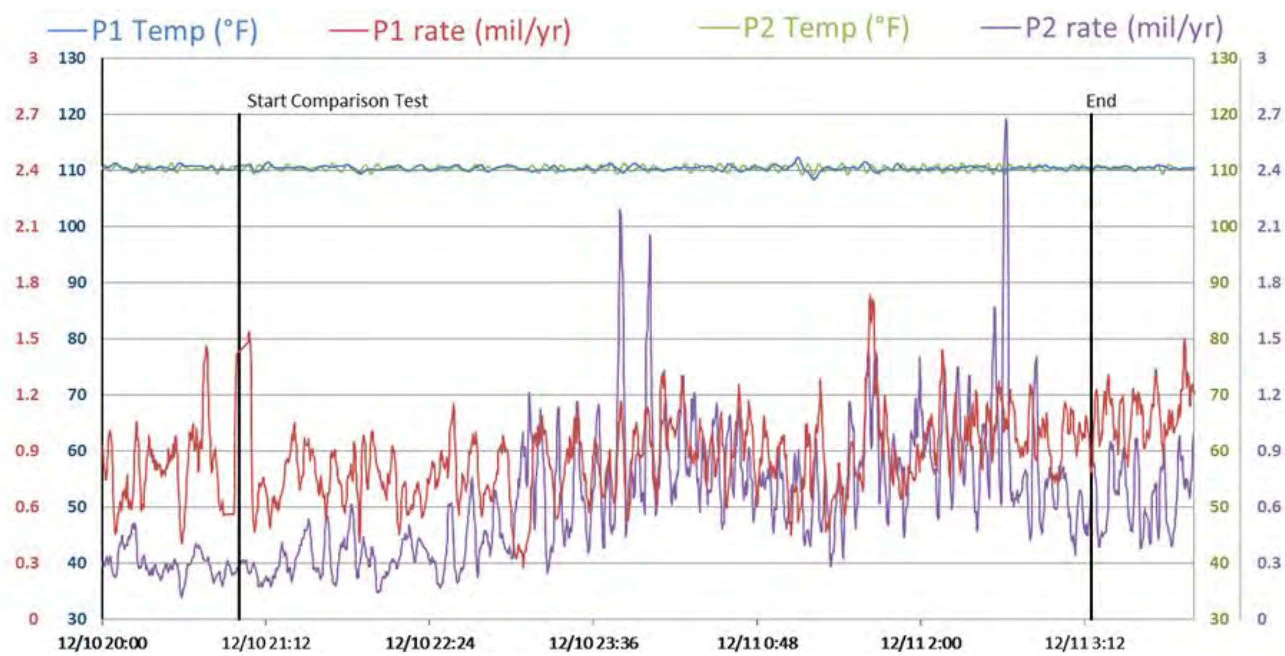
B&W
power generation group

Chem•Mod
Making Power Cleaner.

80 MW Testing







Corrosion Testing - EN Probe

Un-exposed probe

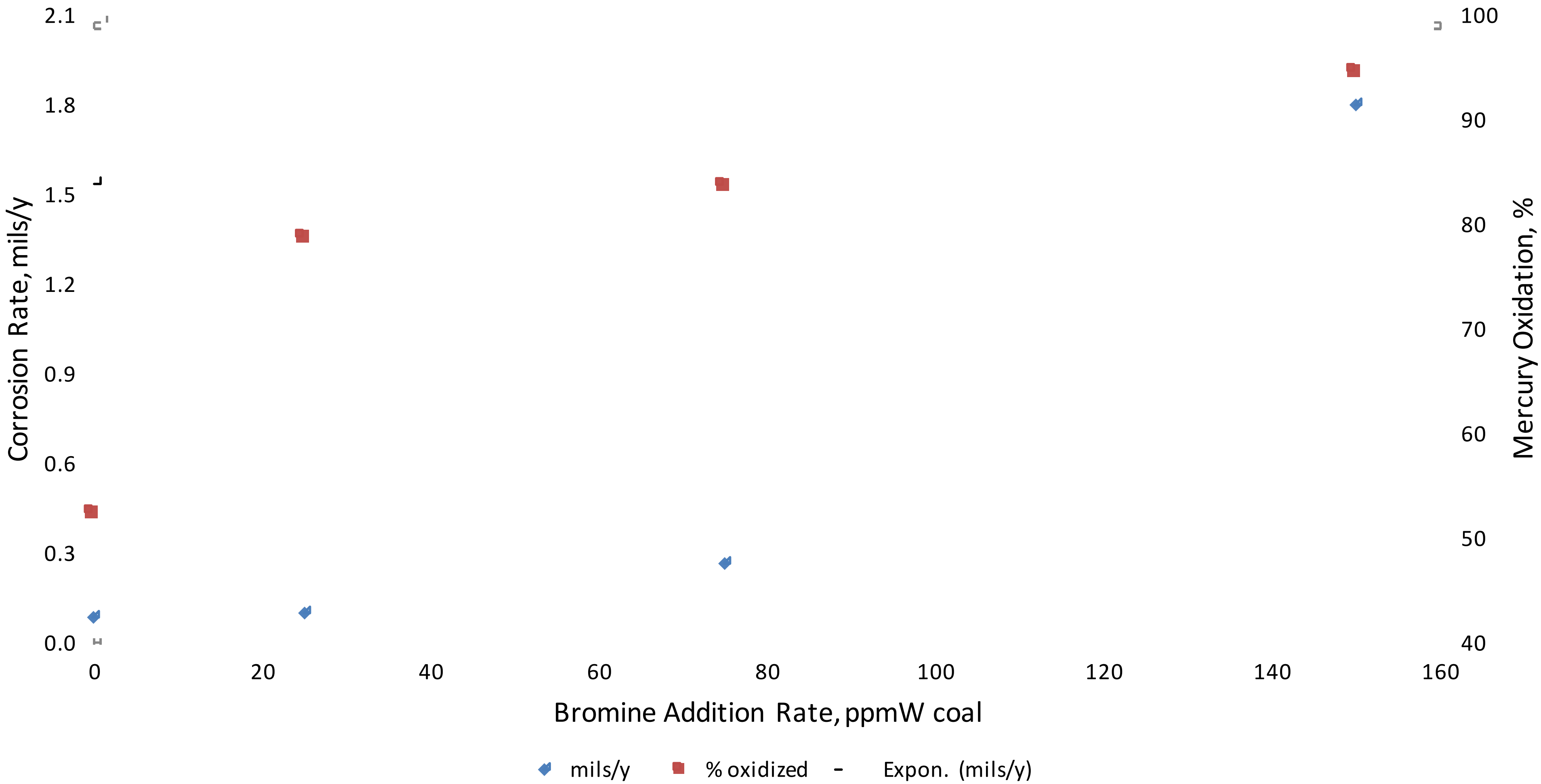
Deposit build-up following 4-hour period of 25ppm Iodine addition

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*	> 10x
12/11 AM 10 ppm Iodine	93.1	0.13	Similar
12/11 PM 25 ppm Iodine	98.5	0.28	2-3 X
12/12 AM 25 ppm Bromine	78.7	0.10	Similar
12/12 PM 75 ppm Bromine	83.7	0.27	2-3 X

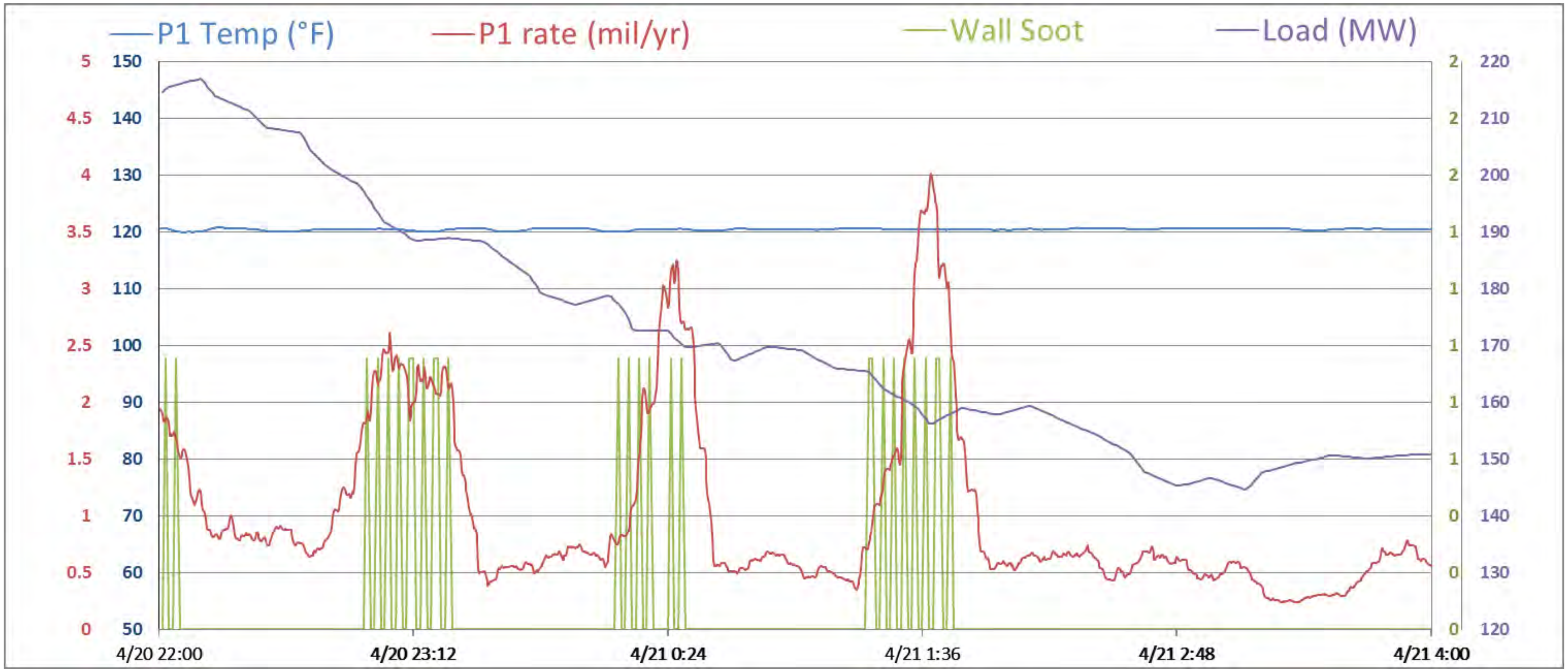
* Averaged over multiple test periods

Corrosion Rate & Hg Gas-Phase Oxidation vs Br Addition Rate



240 MW Testing

- Testing performed during large fluctuations in operating conditions
- Plant has had problems with AH leakage and distance between probe locations was much greater than 80 MW unit
- Soot blowing and load have significant impact on corrosion rate

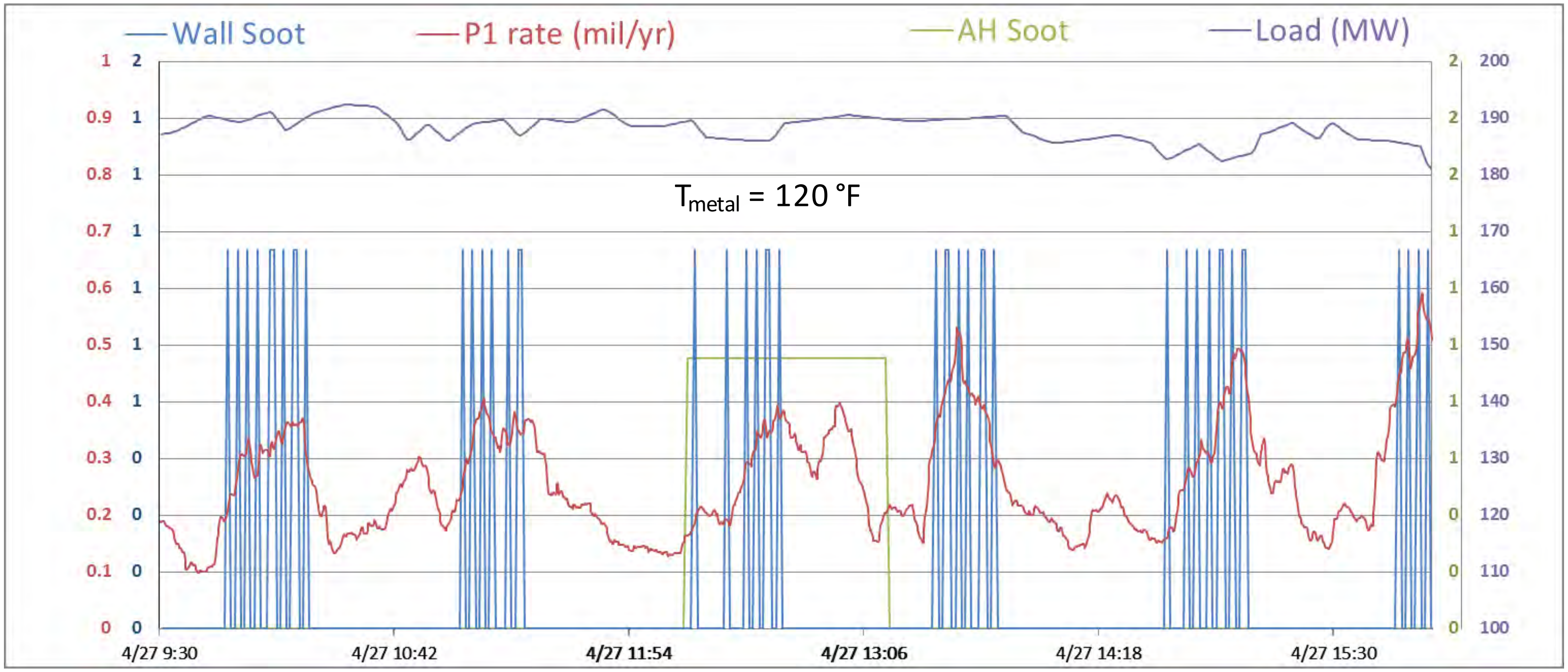


Impact of Iodine Addition Rate on Hg Removal

Stack Hg (µg/scm)				
Baseline*	Iodine Addition (ppm on dry coal)			
	4 ppm	10 ppm	30 ppm	50 ppm
0.64	0.19	0.20	0.20	0.16 0.21

- Baseline data with ACI in operation (plant references levels of 3-4 µg/scm without), ACI not in use during iodine injection
- < 4 ppm Iodine is required for MATS compliance at this particular unit
- Based on the low but consistent stack Hg during Iodine addition, it appears that
  - The unit's back-end (in particular the SCR and Circulating Dry Scrubber) provides an environment in which Iodine accumulation and extended Hg-I contact time results in nearly complete Hg oxidation at all Iodine addition rates
  - Capture of oxidized Hg is limited by ability of sorbent and flyash to adsorb oxidized gas-phase Hg

Impact of Soot Blowing on Corrosion Rate

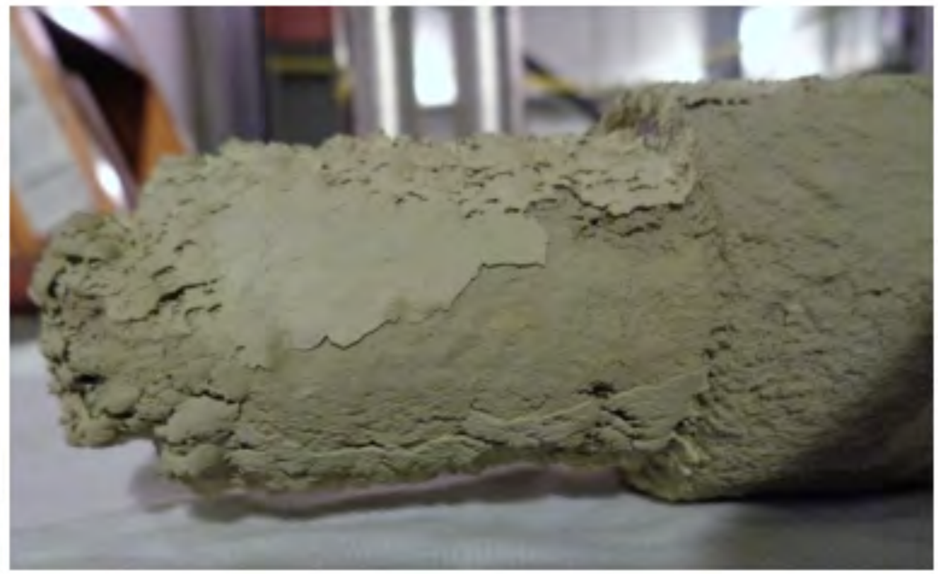


- Water cannons used on water walls and air heater cleaned with steam
- 2 fold increase in corrosion rate during soot blowing
- Soot blowing raises moisture content resulting in higher acid concentrations in flue and acid deposition rates on cold surfaces

Impact of Moisture Condensation on Ash Deposition

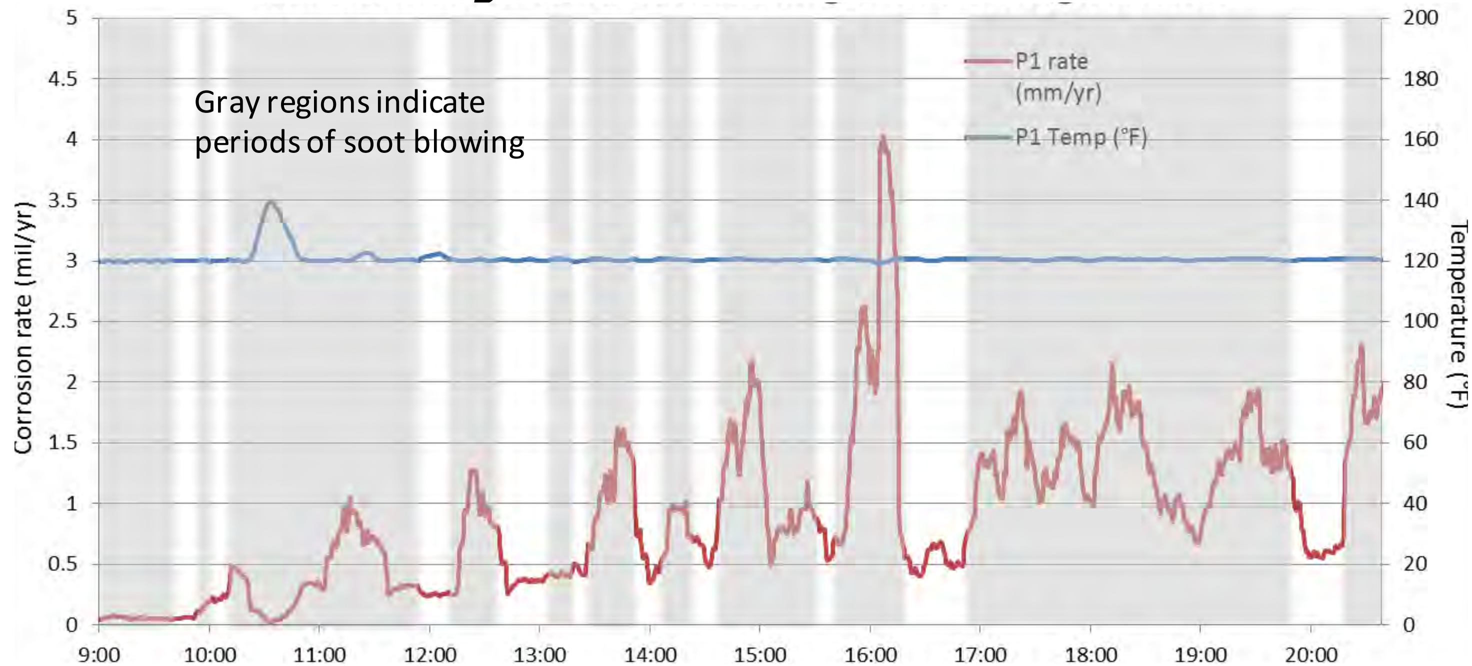
Above Water Dewpoint

Below Water Dewpoint

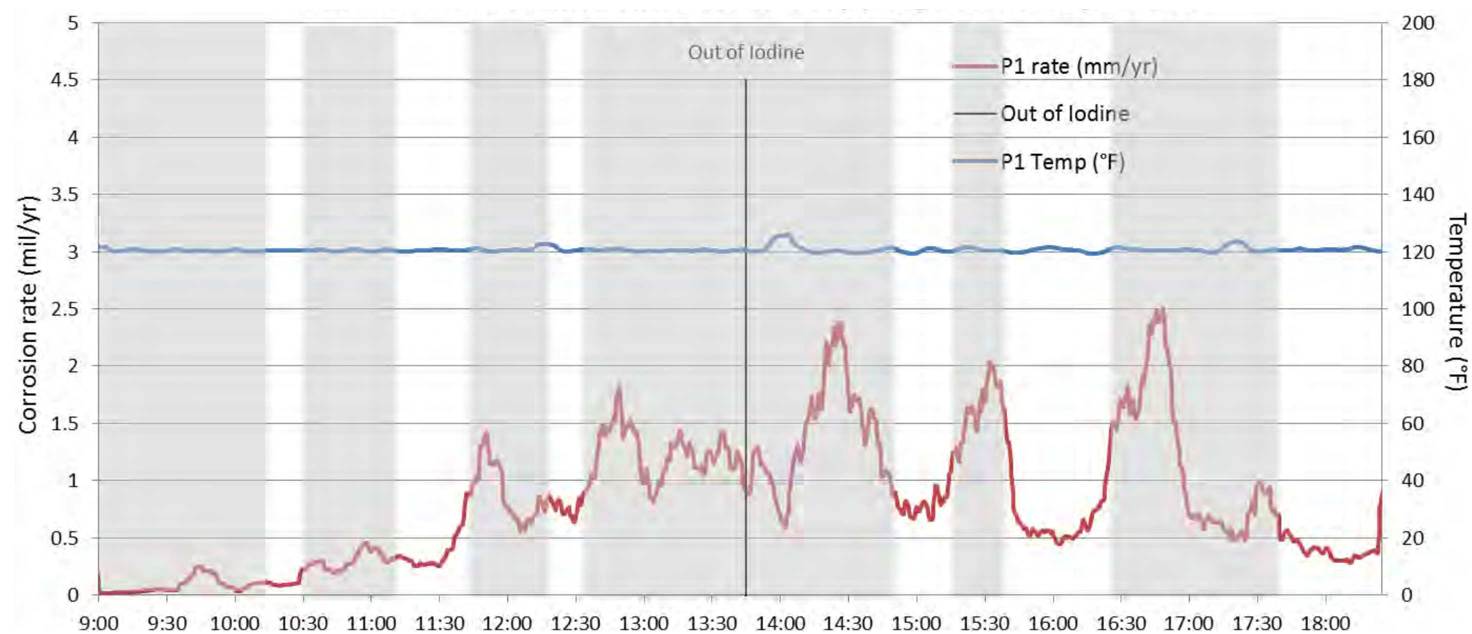


Impact of Iodine Injection on Corrosion Rate

Baseline



50 ppm Iodine



Observations

- To achieve 95% Hg oxidation, it was necessary to add 150 ppm Bromine to coal, and the rate of corrosion was <u>20 times higher</u> than baseline
- Addition of 25 ppm Bromine to coal results in no appreciable increase in the corrosion rate
- Injection of <10ppm of Iodine on coal has the potential to oxidize >90% of Hg in flue gas without a significant increase in corrosion
- Injection of increasing levels of Iodine do not appear to result in the rapid increase in corrosion observed with Bromine

Acknowledgements

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Questions?

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