REINHOLD ENVIRONMENTAL Ltd.

2014 NOx-Combustion Round Table & Expo Presentations

February 10 & 11, 2014, in Charlotte, NC / Hosted by Duke Energy

Low and High Temperature Corrosion Associated with Pollutant Control Technologies

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For Energy and Environmental Solutions

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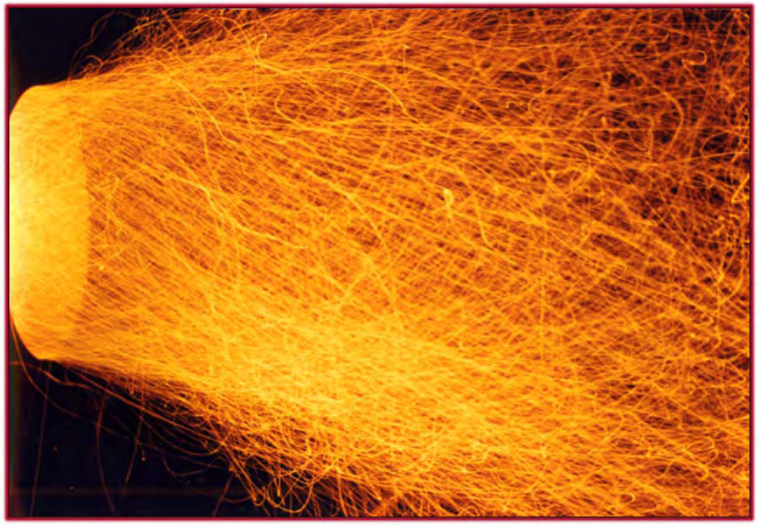
Reaction Engineering International

- 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 and testing

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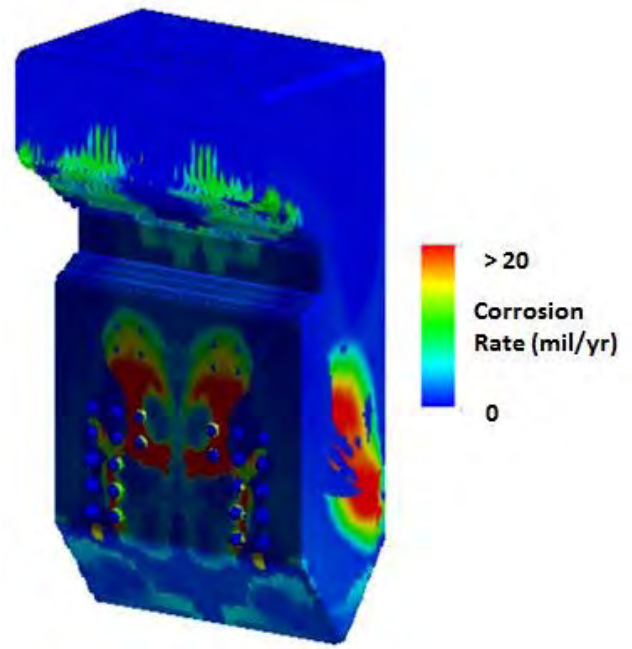
REI Coal-Fired Boiler Corrosion Experience

- **Efforts focused on impacts of firing system modifications, fuel changes, additive utilization, and operational optimization**
- **CFD-based modeling**
  - **Correlation-based approach resulting from collaborations with EPRI and KEPRI**
  - **Integrated with REI's CFD software (*GLACIER*)**
- **Real-time monitoring**
  - **Initially motivated by desire to validate modeling tools**
  - **Adaptation of an electrochemical approach in a collaborative effort with Corrosion Management (UK)**



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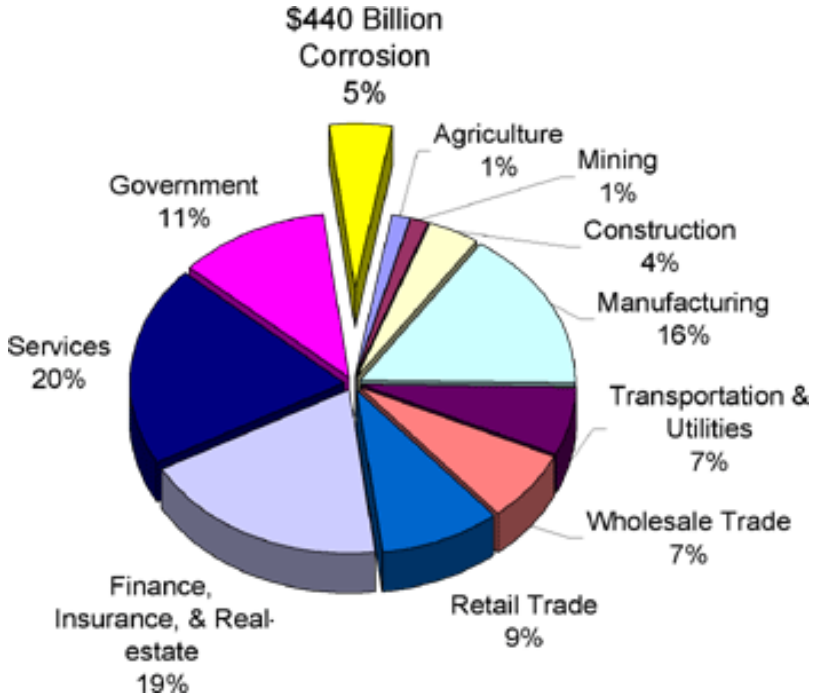
Impact of Corrosion

- **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**
  - **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

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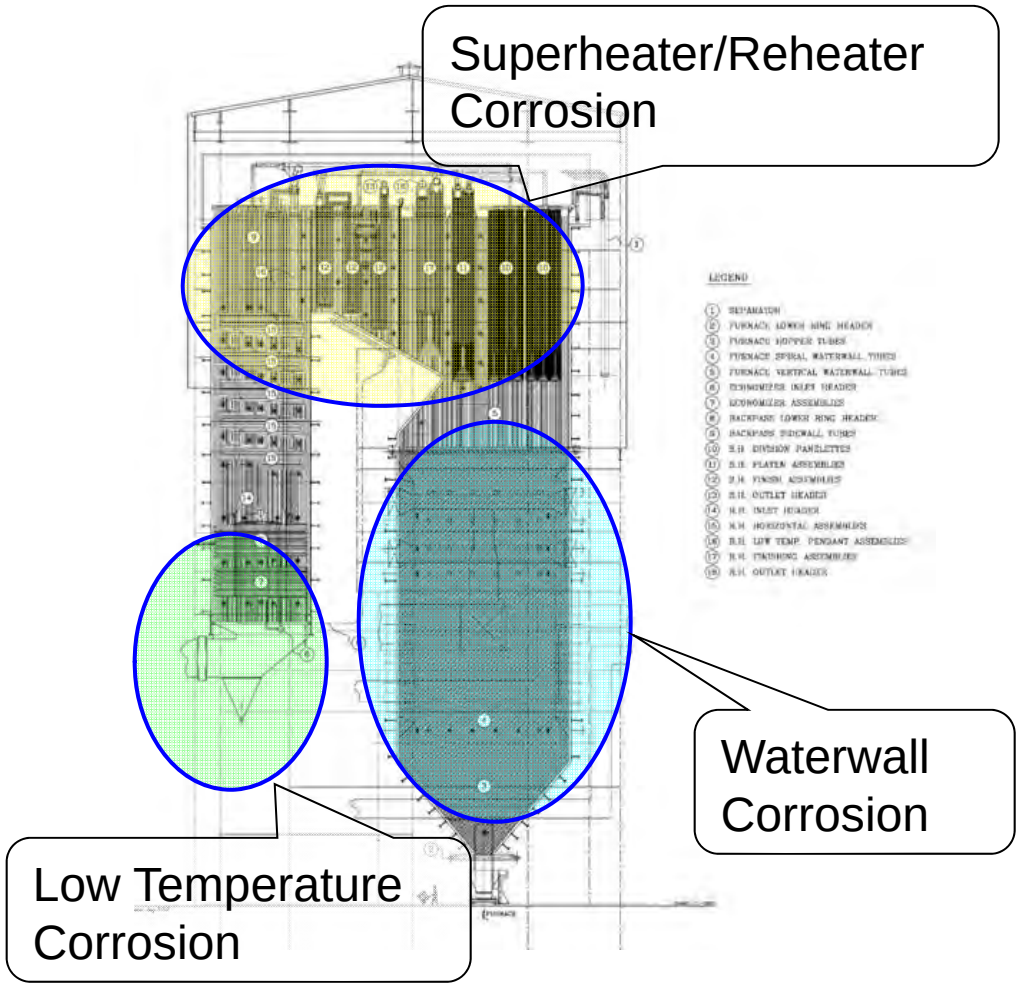
Fireside Corrosion



- **High temperature corrosion of waterwalls**
- **High temperature corrosion of superheater/reheater**
- **Low temperature corrosion of economizer**
- **Low temperature corrosion of air preheater**

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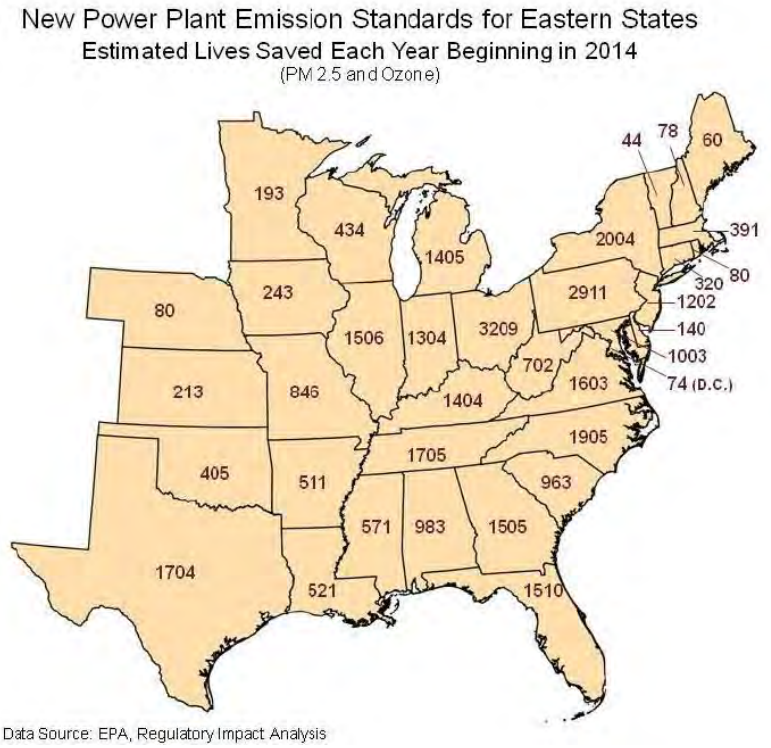
Waterwall Corrosion

NOx Regulations

- **Clean Air Act of 1970 and subsequent amendments (1990) required substantial reductions in NOx emissions from coal power plants**
- **Cross State Air Pollution Rule tightens limits on NOx in 28 eastern states**
- **CSAPR vacated Aug 2012, full court review denied Jan 2013, Clean Air Interstate Rule in effect until satisfactory replacement rule is developed by EPA**
- **Regional haze regions near 156 national parks/wilderness areas**



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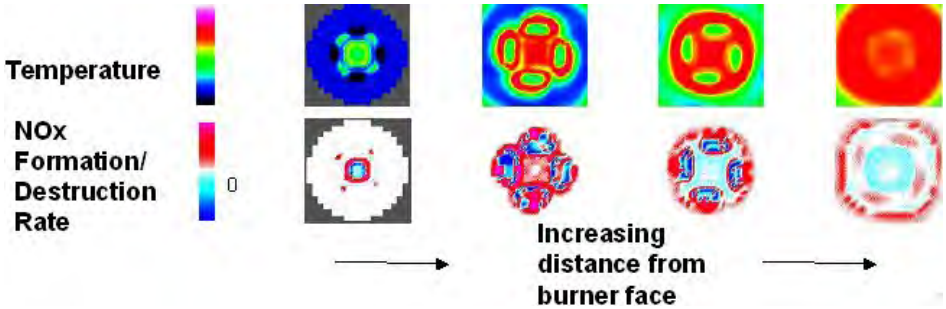
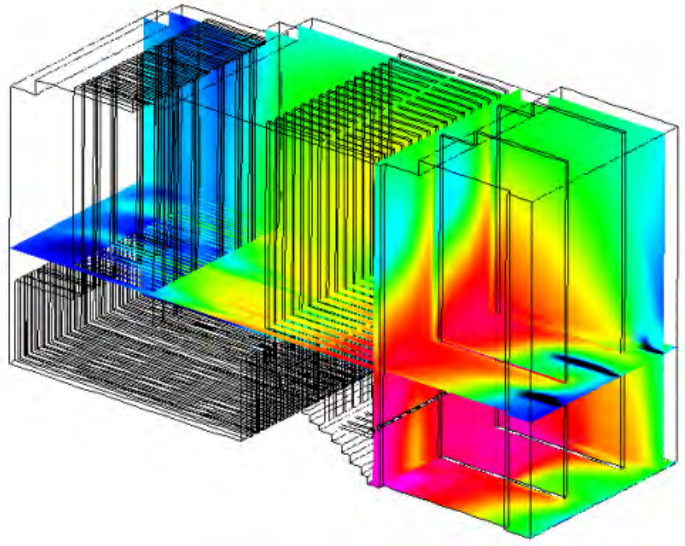
NOx Control Strategies

- **Technology experience**
  - Low NOx burners
  - Over-fire air
  - Fuel switching and blending/co-firing
  - Traditional Gas/coal and fuel-lean-gas reburning
  - Amine reagent injection (SNCR, advanced reburn, rich reagent injection)
  - SCR
- **Operational Impacts**
  - Carbon-in-ash
  - Waterwall wastage
  - Heat balance
  - CO emissions
  - Deposition and ash loading
  - Ammonia slip
  - Soot formation





Temperature Field for Ammonia Injection

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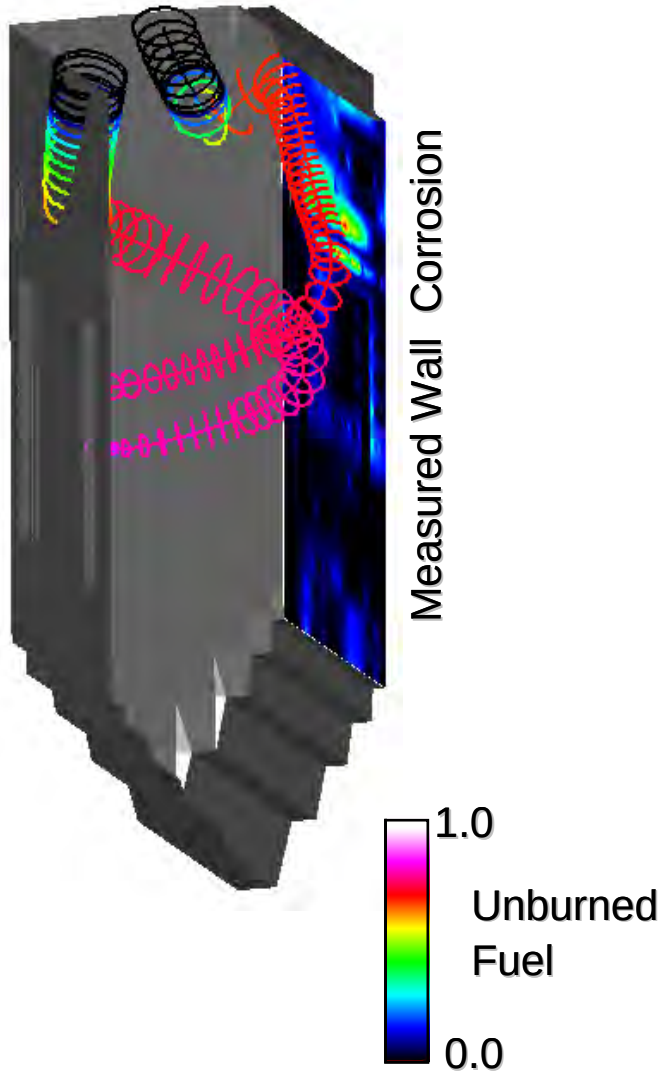
Corrosion and Coal-fired Boilers

- **Environmental and Economic Pressures vs. Corrosion**
  - **NOx emissions**
  - **Fuel cost and availability**
  - **Steam temperatures**
- **Sulfur Mechanism**
  - **Combustion modifications for NOx control**
  - **Supercritical steam cycle**
  - **High sulfur content fuel**
- **Chlorine Mechanism**
  - **Combustion modifications for NOx control**
  - **High heat flux to water-walls**
  - **High chlorine content fuel**



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Corrosion Mechanisms

- **Tube wall interaction with gaseous phase constituents**
  - **Under oxidizing conditions metal loss is very slow and a protective Fe_3O_4 scale forms**
  - **Under reducing conditions, reducing sulfur species or fuel chlorine may disrupt the protective scale and metal loss occurs**
- **Tube wall interaction with deposit**
  - **Pyrite (FeS_2) in coal is converted to FeS**
  - **Metal loss may occur in areas where unoxidized material, especially FeS, is deposited**
- **Highest wastage rates are due to tube wall interaction with chlorine and FeS deposits – up to 100 mil/yr or more**

Corrosion Modeling Approach

- **Development of advanced corrosion correlations (models) for three corrosion mechanisms**
  1. **Gas phase attack by reduced sulfur species such as H_2S**
  2. **Deposition of unreacted fuel and resulting sulfur-based attack**
  3. **Chlorine-based attack**
- **Incorporation of these correlations into two-phase, reacting CFD code**
- **Validation of the correlations through pilot-scale tests and CFD simulations**

Corrosion Due to Gaseous Sulfur Species

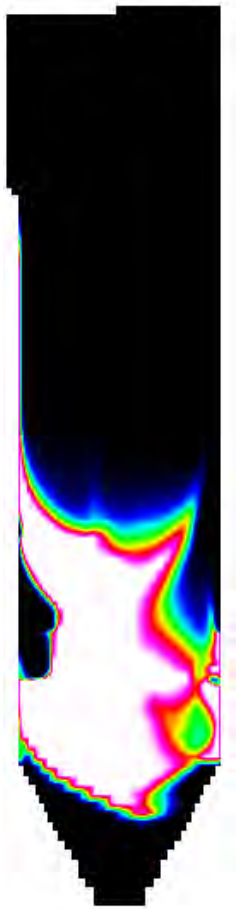
- **Sulfidation of metal primarily due to interaction with gaseous phase H_2S, also CS_2 & COS**
- **Corrosion rates are low**
- **Kung's correlation (Material Performance, (36)36-40 (1997)**
  - **For low alloy steels (*Cr*% < 10%):**

$$CR = 3.2\times10^{5}\exp\left(-\frac{15{,}818}{1.987T}\right)\times[H_2S]^{0.574}\times\frac{1}{(Cr\%+10.5)^{1.234}}\pm 2.2$$

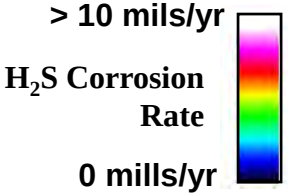
  - **For high chromium steels (10% < *Cr*% < 16%):**

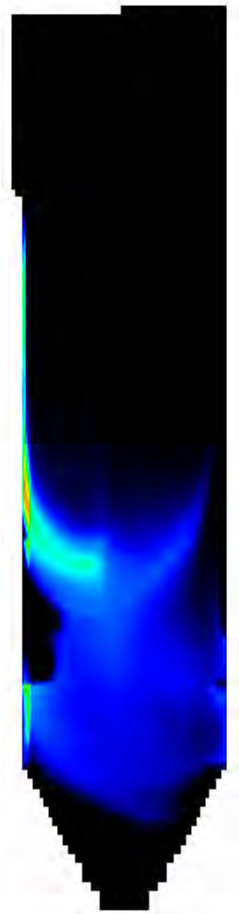
$$CR = 1.04\times10^{7}\exp\left(-\frac{19{,}230}{1.987T}\right)\times[H_2S]^{0.29}\times\frac{1}{(Cr\%+1.40)^{1.37}}\pm 1.2$$

Predicted H_2S Corrosion in a Wall-Fired Furnace

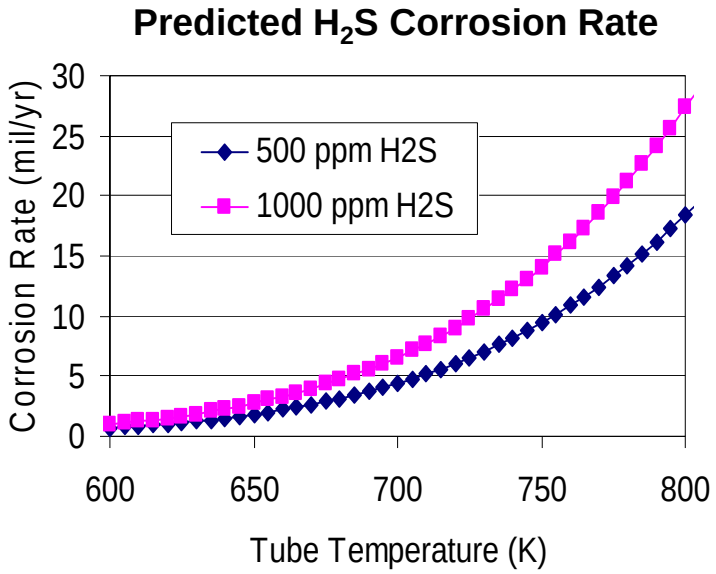


Predicted Side Wall H_2S Concentration





Predicted Side Wall H_2S Corrosion Rate



- H_2S corrosion alone cannot account for observed high corrosion rates (up to ~100 mil/yr), even at T_{tube} = 750 K

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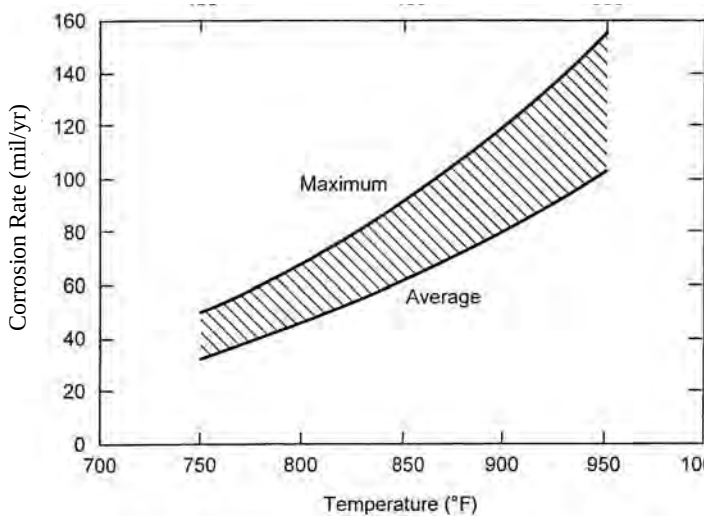
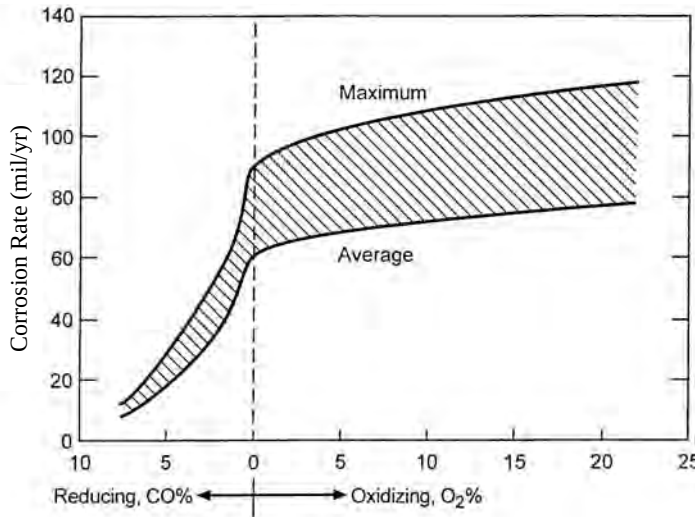
Corrosion Due to Deposition of FeS & Carbon

- **Corrosion may occur where unoxidized FeS and coal are deposited**
- **Deposit based corrosion is associated with a high fraction of unoxidized material in deposit, high tube temperatures, high heat flux**
- **Experimental evidence indicates that the highest corrosion rates occur when unoxidized deposits are exposed to oxidizing flue gas**

EPRI Experimental Work



Corrosion rate under FeS deposit as a function of temperature in a 1% O_2 environment.



Corrosion rate under FeS deposit as a function of gas O_2 and CO content at 450°C.

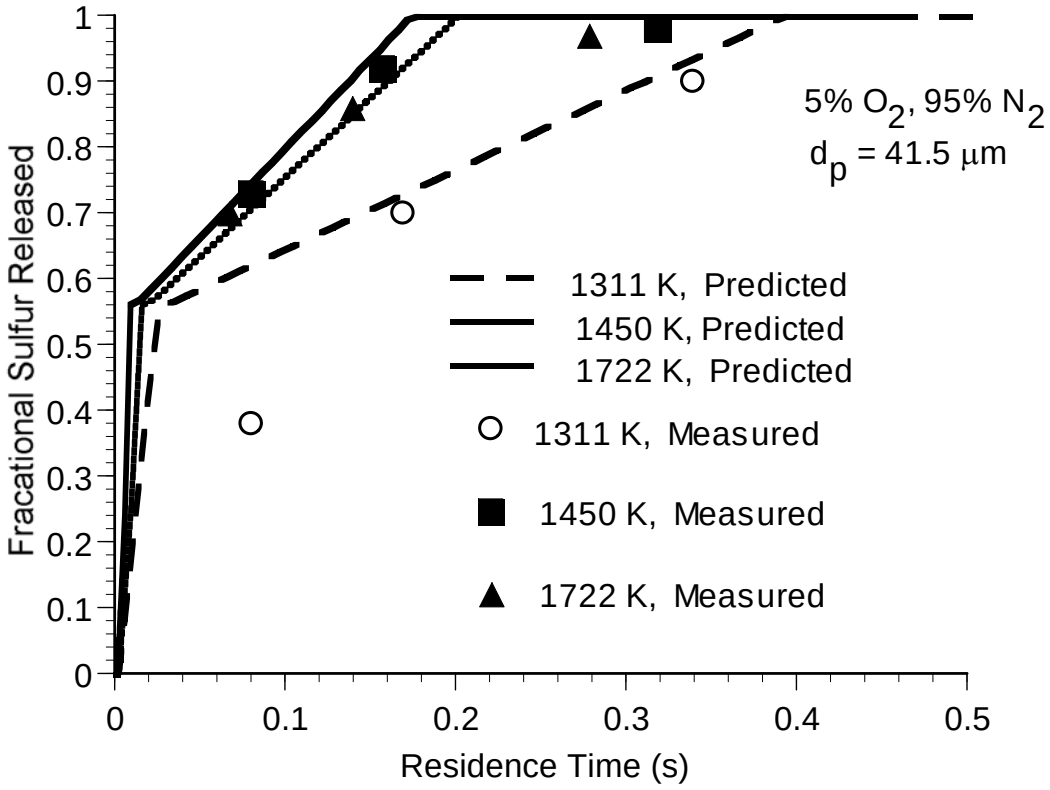
EPRI experimental work for metal under an FeS layer:

- **Very high corrosion rates may occur**
- **Corrosion rates increase with temperature**
- **Corrosion rates are highest under oxidizing or mildly reducing conditions**

Predicting Waterwall Deposition of Coal Sulfur

- **Included sulfur: pyrite (FeS_2) and organic sulfur bound within the coal particle matrix**
  - Tracked with the coal particles
  - Wall deposition predicted be particle wall impaction/deposition modeling
- **Excluded pyrite: pyrite particles**
  - Different density, particle size distribution, and kinetics than coal
  - Model of Srinivasachar and Boni model for pyrite kinetics (*Fuel*, 1989) has been included in *GLACIER*
    - Thermal decomposition of pyrite (FeS_2) to pyrrhotite ($Fe_{0.877}S$ or FeS) at 870 K (~1100 F) – occurs quickly
    - Oxidation of pyrrhotite ($Fe_{0.877}S$) to magnetite (Fe_3O_4) – occurs more slowly

Excluded Pyrite Kinetics: Model vs Measurement



Effect of Temperature

- Model shows the initial fast thermal decomposition from FeS_2 to $FeS_{0.877}$ followed by slower oxidation of $FeS_{0.877}$
- Sulfur evolution is faster at higher temperature
- Model predictions agree with measurements

Data from Levasseur et al., 1989

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Prediction of Corrosion Due to FeS Deposition

- Based on curve fit of published data

$$CR = A \times f(S) \times h(dep) \times g(SR) \times e^{-\left(\frac{Q_r}{RT}\right)}$$

CR = corrosion rate in mil/yr

f(*S*) is a linear function from 0 to 1 of the coal sulfur content *S*, reaching 1 for *S* = 1%

h(*dep*) is a linear function from 0 to 1 of the fraction of unoxidized material in the total material deposited *dep*, reaching 1 at *dep* = 0.2

Q_r = 10313 cal/mol

R = 1.987 cal/K/mol

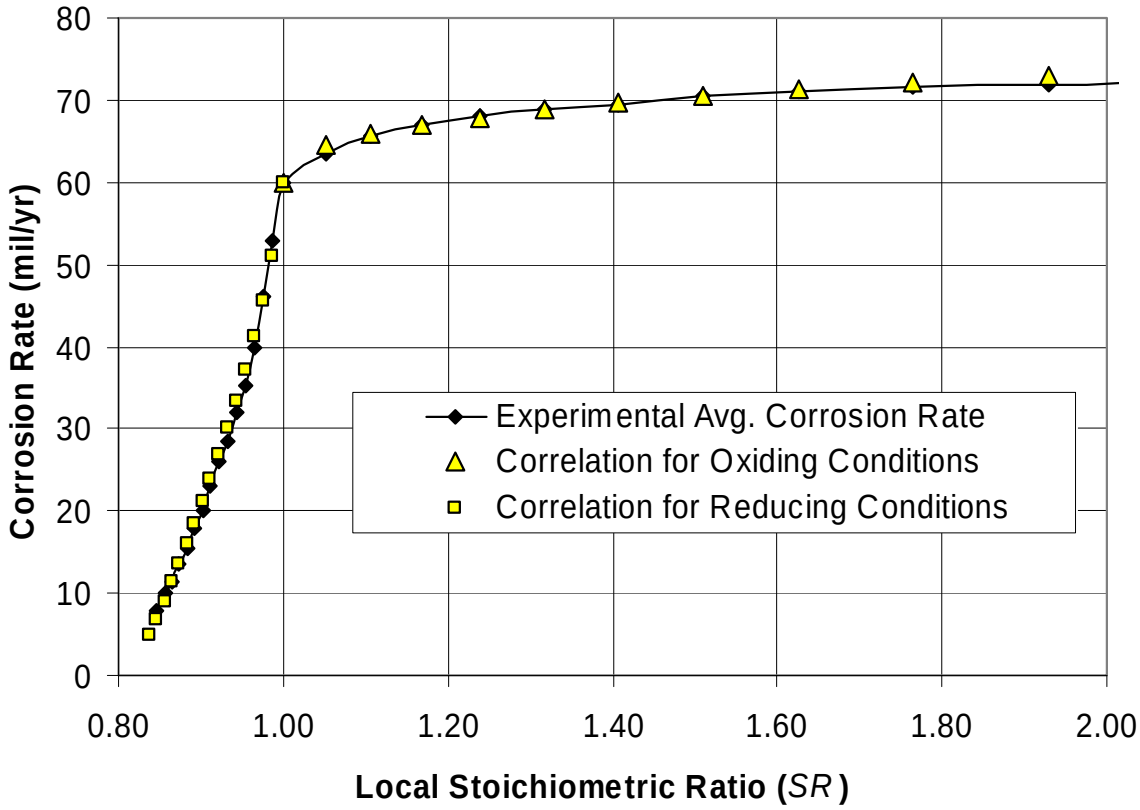
A = 1174

g(*SR*) = -197.6 x (1-*SR*)$^{0.7}$ + 60 for reducing conditions where *SR* ≤ 1

or

g(*SR*) = 13.4 x (*SR*-1)$^{0.37}$ + 60 for oxidizing conditions where *SR* ≥1

Predicted Corrosion Rates vs Measurements



Corrosion rate correlation vs. experimental data as a function of the local stoichiometric ratio (SR) for constant T = 450° C.

- Predicted corrosion rate as a function of stoichiometric ratio (SR) at 450° C. compares well with EPRI experimental data

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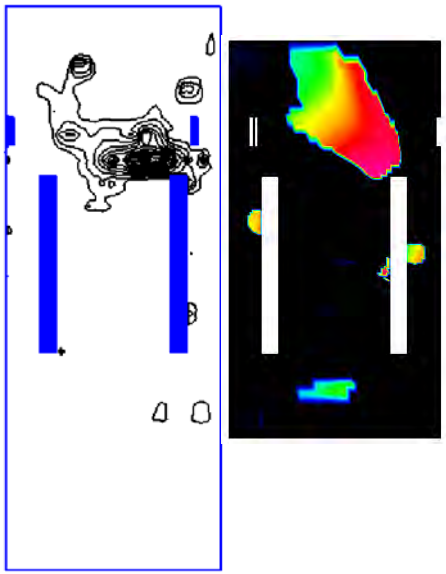
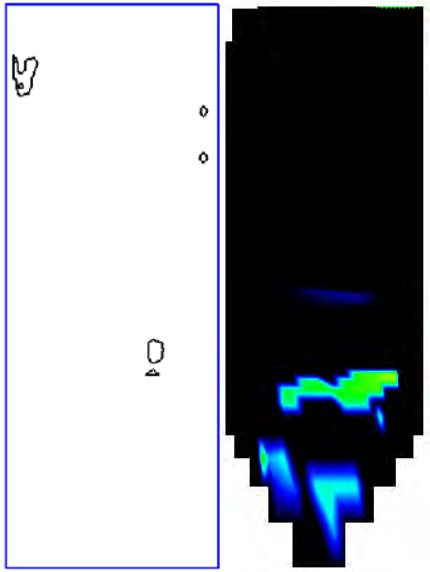
Validation Using Plant UT Data

Rear Wall



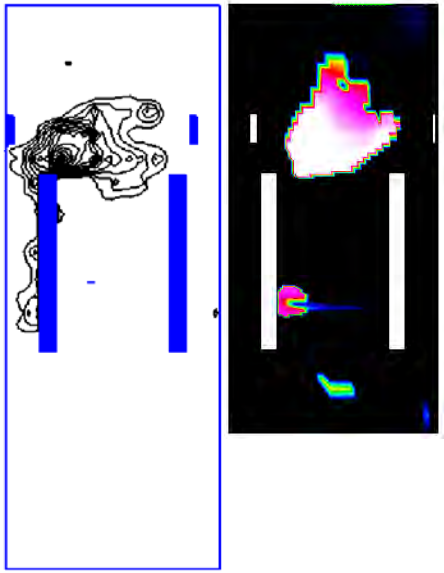
(max = 81 mil/yr)

Side Wall



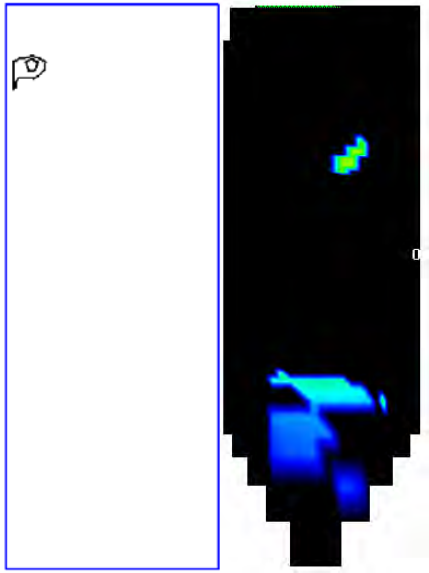
(max = 26 mil/yr)

Front Wall



(max = 94 mil/yr)

Center Wall



(max = 29 mil/yr)

(scale for simulations)

> 70

mils/yr

0

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Corrosion due to Chlorine

- **Well documented in the UK due to the relatively high chlorine content of UK coals**
- **Often associated with high fuel chlorine content (> 0.15%) and flame impingement**
- **Corrosion has not been consistently observed with high chlorine coal**
- **More recently observed in the U.S. in a few boilers using high chlorine coals**

Chlorine Corrosion Conditions and Mechanisms

- **Observed in presence of high heat flux, fuel-rich regions when fuel chlorine > 0.15%**
- **$FeCl_2$ forms at the metal surface, breaks up protective scale**
- **Complex interactive behavior in the presence of sulfur based on reducing and oxidizing conditions**
- **Davis et al. correlation (Material Science Forums, (369-372) 857-864 (2001)**

$$CR = \left(C \times \%Cl\right) \times \left(HF\right)^{m} \times \exp\left(-\frac{Q_{cl}}{RT}\right) - d$$

Chlorine Corrosion Correlation

- Based on curve fit of a published correlation

$$CR = (136.55 \times \%Cl) \times (HF)^{1.725} \times \exp\left(-\frac{12{,}590}{1.987T}\right) + 9.56$$

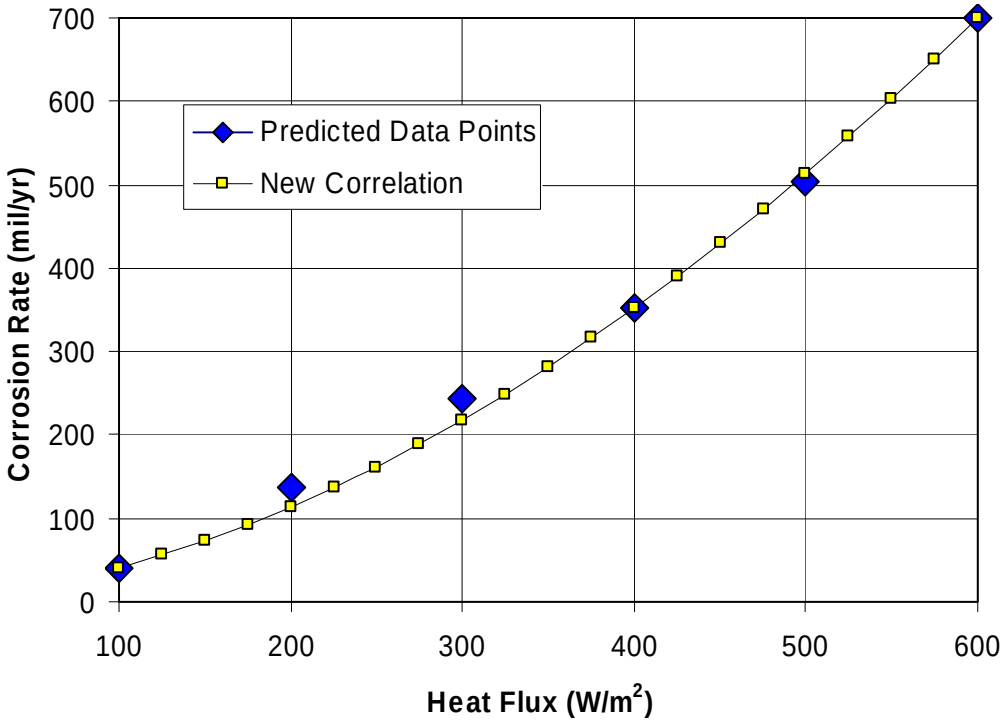
CR = chlorine corrosion rate in mil/yr

%Cl = weight % coal chlorine content

T = tube metal temperature in Kelvin

HF = wall heat flux in kW/m^2.

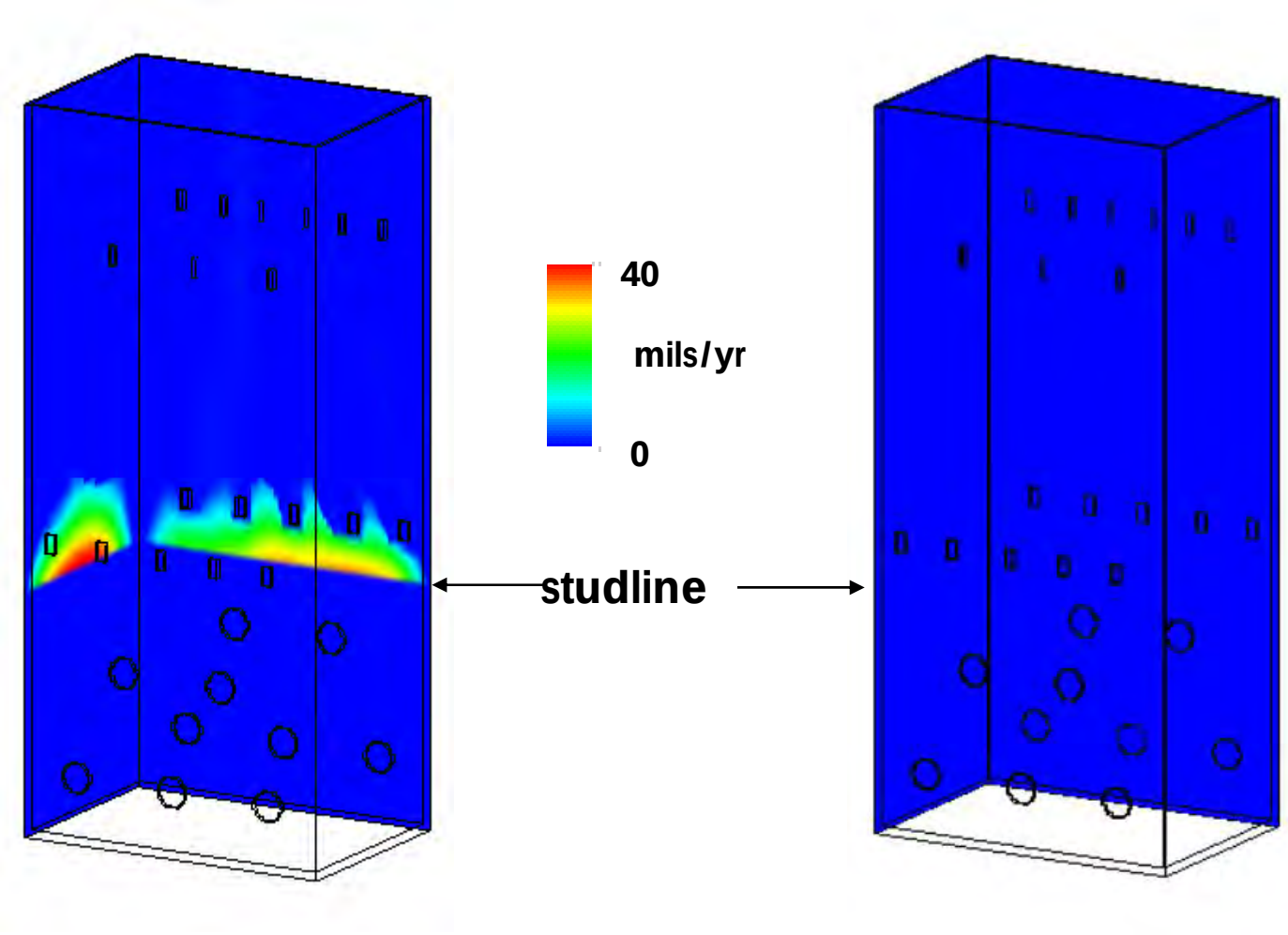
Chlorine Corrosion Correlation Tuning



Chlorine corrosion correlation vs. predicted data points of Davis et al (2000)

- **New correlation predicted chlorine corrosion rate is comparable to the experimentally verified predictions of Davis et al (2002)**

Cyclone-fired Boiler Chlorine Corrosion



40/60 Bit/PRB

10/90 Bit/PRB

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Waterwall Corrosion

- **Gas phase H_2S Corrosion**

$$CR_{H2S} = a \cdot f_1(T_m) \cdot f_2(Cr\%) \cdot f_3(H_2S) + b$$

- **Deposition of Unoxidized Material**

$$CR_{dep} = a \cdot f_1(dep) \cdot f_2(Stoichiometry) \cdot f_3(T_m) + b$$

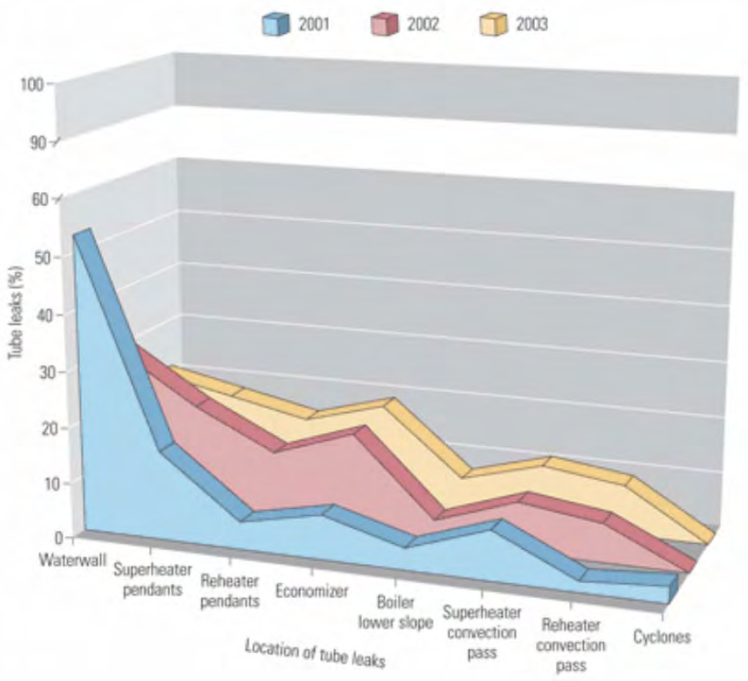
- **Chlorine-based Corrosion**

$$CR_{Cl} = a \cdot f_1(\%Cl) \cdot f_2(HeatFlux) \cdot f_3(T_m) + b$$

Superheater/Reheater Corrosion

Evolution of Boiler Corrosion

- **Corrosion problems have been identified but not solved, just avoided.**
- **2005 survey reports that more than half of the tube leakage is from corrosion.**
- **Corrosion can be enhanced by:**
  - **Formation of reducing environment through air staging**
  - **Deposition of unburned material**
  - **Enhanced steam conditions**



Patrick J, Oldani R, Behren DV, "Benchmarking boiler tube failures – Part 2," Power 149 (9), 55-59, November/December 2005

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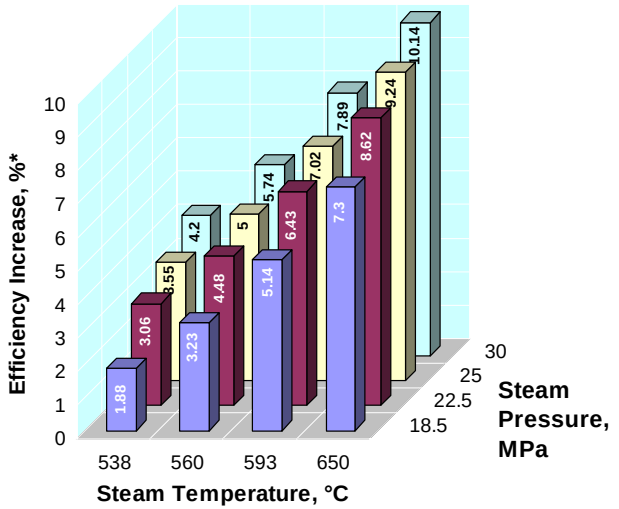
USC and Superheater Corrosion

- Ultra-supercritical plants increase thermal efficiency while reducing carbon consumption
- Enhanced steam pressure and temperature in ultra-supercritical (USC) unit
  - Current supercritical units: 540°C/16.5-24MPa
  - Plans for 650°C/34.5MPa
  - Currently 593°C/27MPa unit is operating
- Additional benefits include reduced emissions of SOx, NOx, and CO_2.
- Steam conditions present significant challenges to materials selection



* Based on 538°C/18.5MPa Single Reheat Case

adapted from Viswanathan R, Bakker WT, "Materials for Boilers in Ultra Supercritical Power Plants," Proceedings of 2000 International Joint Power Generation Conference, July 23-26, 2000.

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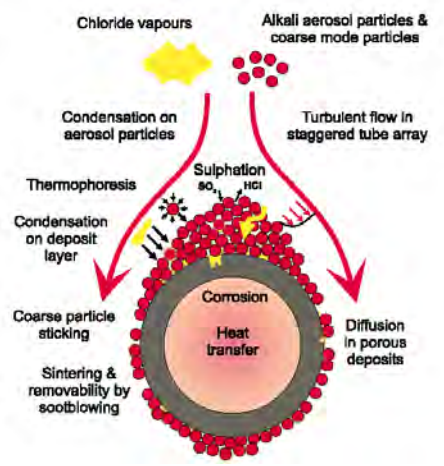
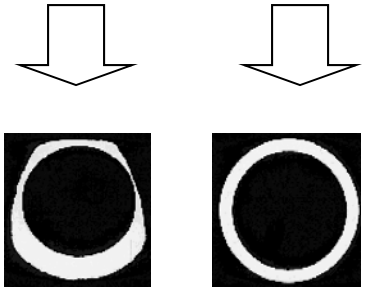
Major Corrosion Factors

- **Temperature**
  - Metal and Gas Temperature
  - Heat Flux
  - Temperature Gradient
  - Temperature Fluctuations
- **Fuel/Deposit Characteristics**
  - Sulfur, Chlorine, Alkali metal
- **Local Gas-Phase Stoichiometry**
- **Tube Metallurgy**
  - Cr, Ni, Al, etc.
- **Boiler Design**
  - tube spacing, tube location, etc.
- **Flue Gas Velocity**



Flue gas flow



worst best

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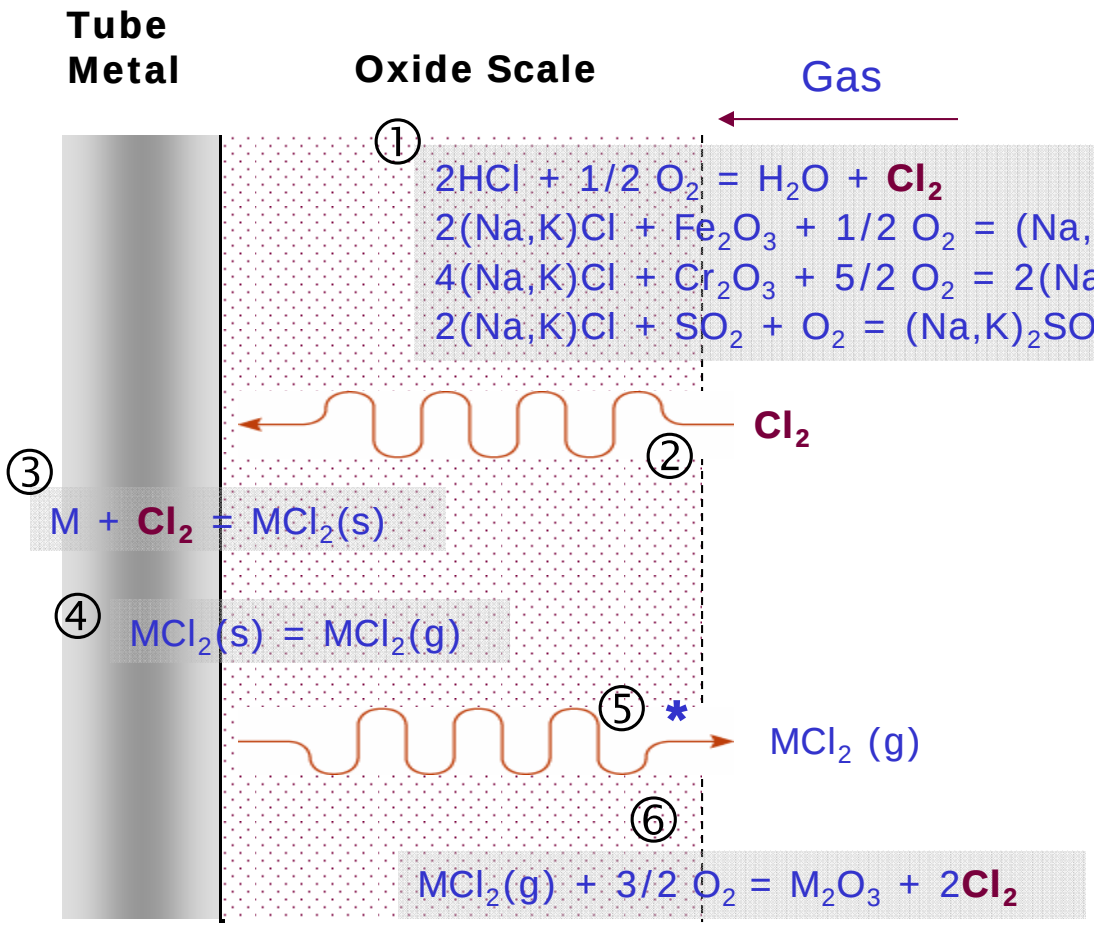
Active Oxidation



① Cl_2 formation at the scale surface
② Penetration of Cl_2
③ Formation of metal chlorides
④ Evaporation of metal chlorides
⑤ Diffusion of metal chlorides
⑥ Oxidation of metal chlorides

M = tube metal (Fe, Cr, Ni)

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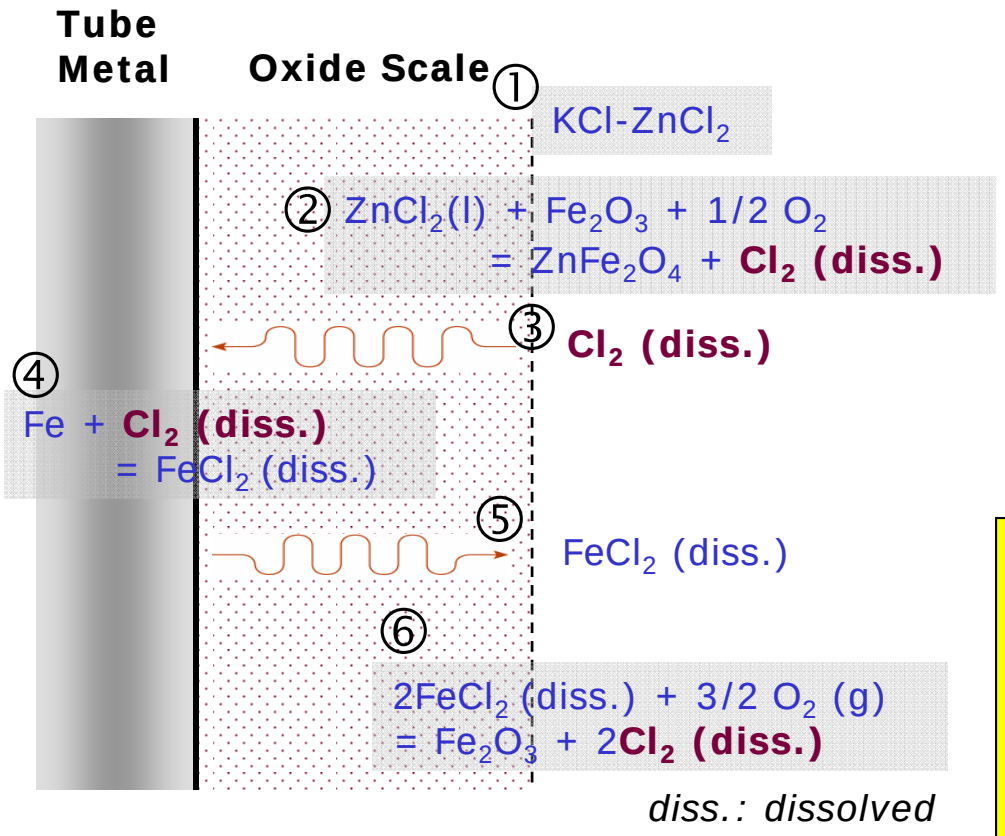
Molten Chlorides



- **Mixture of chlorides with low melting point (eutectic)**
  - **M_p of KCl: 772°C**
  - **With $ZnCl_2$ (47% KCl – 53% $ZnCl_2$): 355°C**

① Molten phase formation
② Cl_2 (dissolved) formation
③ Penetration of Cl_2
④ Metal chloride formation by dissolution
⑤ Migration of metal chlorides
⑥ Oxidation of metal chlorides

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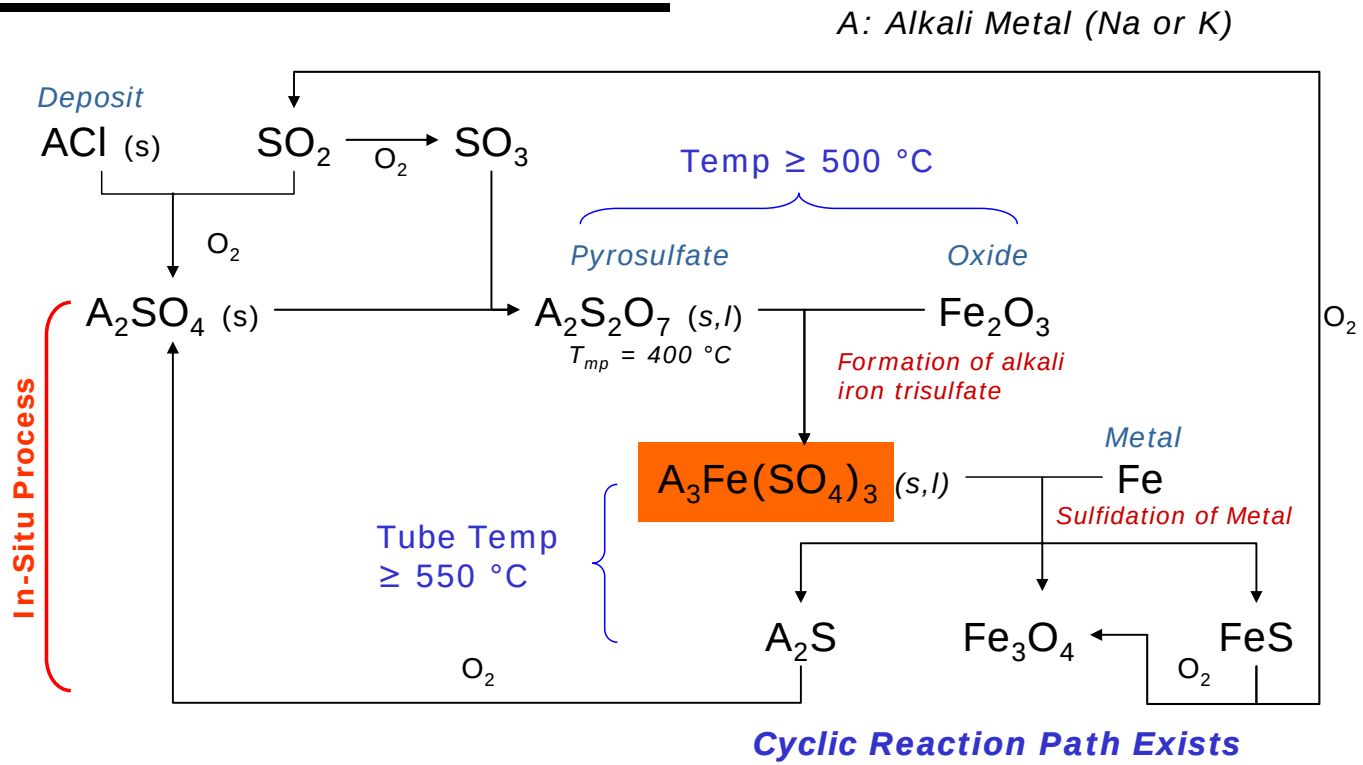
Coal-ash Corrosion
(Molten Sulfate)



- **Most commonly found superheater corrosion mechanism**
- **Corrosion rate shows classical bell-shape as a function of tube temperature based on formation and stability of alkali-metal-trisulfate**

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Superheater Corrosion

➔ **Active Oxidation**

$$CR_{AO} = f_1(T_m) \cdot f_2(Cr\%) \cdot f_3(T_g - T_m) \cdot f_4(Cl\%)$$

➔ **Molten Sulfate Corrosion**

$$CR_{MS} = a \cdot P \cdot HF \cdot f_1(T_m) \cdot f_2(Cr\%) \cdot f_3(\text{Fuel Corrosivity}) \cdot f_4(\text{dep}) + b$$

➔ **Sulfidation**

$$CR_{H2S} = a \cdot f_1(T_m) \cdot f_2(Cr\%) \cdot f_3(H_2S) + b$$

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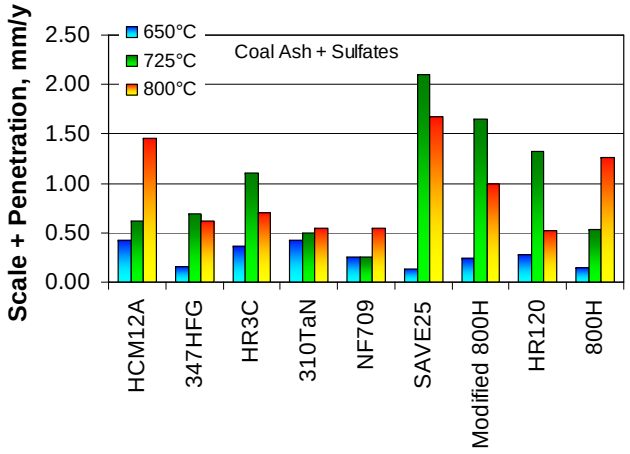
Candidate Materials for USC

Group	Steels	Specification		Composition, %															
		ASME	JIS	C	Cr	Ni	Co	Si	Al	W	Cu	Mo	Nb	Mn	V	B	N	Ti	Misc
1.25Cr	T11	T11		0.15	1.25			0.50				0.50		0.45					
	NFIH			0.12	1.25							1.00	0.07		0.20				
2Cr	T22	T22	STBA24	0.12	2.25			0.30				1.00		0.45					
	HCM2S	T23	STBA24J1	0.06	2.25			0.20		1.60		0.10	0.05	0.45	0.25	0.00			
	Tempaloy F-2W				2.00					1.00		0.60	0.05		0.25				
9Cr	T9	T9	STBA26	0.12	9.00			0.60				1.00		0.45					
	HCM9M		STBA27	0.07	9.00			0.30				2.00		0.45					
	T91	T91	STBA28	0.10	9.00	0.80		0.40				1.00	0.08	0.45	0.20		0.05		
	T92	T92		0.07	9.00			0.06		1.80		0.50	0.05	0.45	0.20	0.004	0.06		
	E911			0.12	9.00	0.25		0.20		0.90		0.94	0.06	0.51	0.20		0.06		
12Cr	HT91	(DIN x20CrMoV121)		0.20	12.00	0.50		0.40				1.00		0.60	0.25				
	HT9	(DIN x20CrMoWV121)		0.20	12.00	0.50		0.40		0.50		1.00		0.60	0.25				
	Tempaloy F-12M				12.00					0.70		0.70							
	HCM12		SUS410J2TB	0.10	12.00	0.30		0.30		1.00	0.90	1.00	0.05	0.55	0.25		0.03		
	TB12			0.08	12.00	0.10		0.05		1.80		0.50	0.05	0.50	0.20	0.30	0.05		
	HCM12A	T122	SUS410J3TB	0.10	12.00	0.30		0.30		2.00	0.90	0.40	0.05	0.50	0.20		0.05		
	NF12			0.08	11.00		2.50	0.20		2.60		0.20	0.07	0.50	0.20	0.004	0.05		
	SAVE12			0.10	11.00		3.00	0.30		3.00				0.20	0.20		0.04		0.07Ta 0.04Nd

Ferritic

Austenitic



Group	Specification		Composition, %																
	ASME	JIS	C	Cr	Ni	Co	Si	Al	W	Cu	Mo	Nb	Mn	V	B	N	Ti	Misc
18Cr-8Ni	TP304H	SUS304HTB	0.08	18.00	8.00		0.60						1.60					
	Super304H	SUS304J1HTB	0.10	18.00	9.00		0.20			3.00		0.40	0.80			0.10		
	TP321H	SUS321HTB	0.08	18.00	10.00		0.60						0.80				0.50	
	Tempaloy A-1	SUS321J1HTB	0.12	18.00	10.00		0.60					0.10	1.60				0.08	
	TP316H	SUS316HTB	0.08	16.00	12.00		0.60				2.50		1.60					
	TP347H	SUSTP347HTB	0.08	18.00	10.00		0.60					0.80	1.60					
	TP347HFG		0.08	18.00	10.00		0.60					0.80	1.60					
15Cr-15Ni	17-14CuMo		0.12	16.00	14.00		0.50			3.00	2.00	0.40	0.70		0.006		0.30	
	Esshete 1250		0.12	15.00	10.00		0.50		0.20		1.00		6.00	1.00			0.06	
	Tempaloy A-2		0.12	18.00	14.00		0.60				1.60	0.24	1.60				0.10	
20-25Cr	TP310	SUS310TB	0.08	25.00	20.00		0.60						1.60					0.045P 0.03S
	TP310NbN	SUS310J1TB	0.06	25.00	20.00		0.40					0.45	1.20			0.20		
	TP310HCbN (HR3C)		0.06	25.00	20.00		0.40					0.45	1.20			0.20		
	NF707*		0.08	21.00	35.00		0.50				1.50	0.20	1.00				0.10	
	Alloy 800H	NCF800HTB	0.08	21.00	32.00		0.50	0.40					1.20				0.50	
	Tempaloy A-3	SUS309J4HTB	0.05	22.00	15.00		0.40					0.70	1.50		0.002	0.15		
	NF709*	SUS310J2TB	0.15	20.00	25.00		0.50				1.50	0.20	1.00				0.10	
	SAVE25*		0.10	23.00	18.00		0.40		1.50	3.00		0.45	1.00			0.20		
HighCr-HighNi	CR30A*		0.06	30.00	50.00		0.30				2.00		0.20				0.20	
	HR6W*		0.08	23.00	43.00		0.40		6.00			0.18	1.20		0.00		0.08	
	Inconel 617			22.00	54.00	12.50	0.40	1.20			8.50		0.40					
	Inconel 671		0.05	48.00	51.50													

Argonne National Laboratory, 2002

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Candidate USC Material in Korea

➔ **Three ferrite and three austenite: T92, T91, T122, HR3C, S304H, and TP347HFG**

Candidate	Composition, %														Comments
	C	Fe	Cr	Ni	Si	Al	W	Cu	Mo	Nb	Mn	V	B	N	
T92	0.07	Bal	9	-	0.06	-	1.8		0.5	0.05	0.45	0.2	0.004	0.06	Ferrite
T122	0.1	Bal	11	-	0.1	-	2	1	0,4	0,05	0.6	0,20	0.003	0.06	Ferrite
HR3C	0.06	Bal	25	20	0.4	-	-		-	0.45	1.2	-	-	0.2	Austenite
T91		Bal	9						1						Ferrite
S304H	0.1	Bal	18.15	9.25	0.27			3		0.4	0.78			0.091	Austenite
TP347HFG	0.08	Bal	18	10	0.6					0.8	1.6				Austenite

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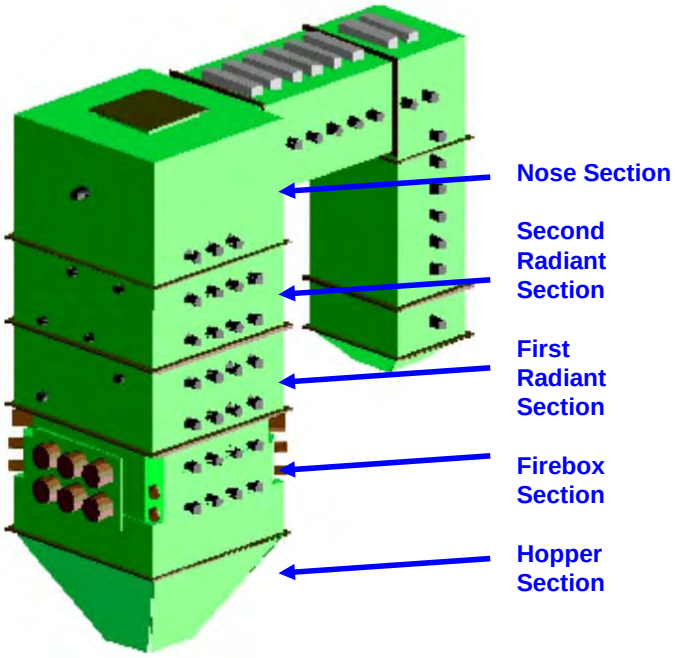
KEPRI Pilot-scale Test Furnace



- **5 MMBtu/hr on natural gas or coal**
- **Convertible firing methods: corner or wall-fired**
- **Furnace inside dimension: 1.6 x 1.9 x 7.1 meters (depth x width x height)**
- **Refractory casting**

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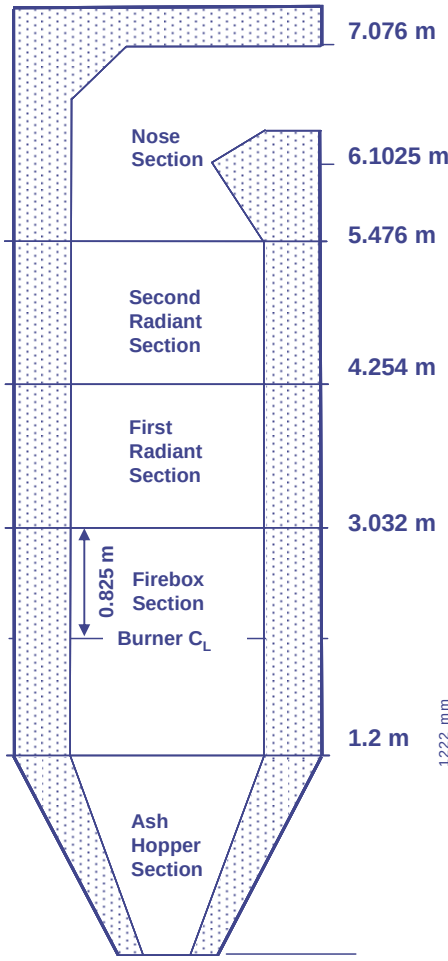
Refractory and Cooling Tubes

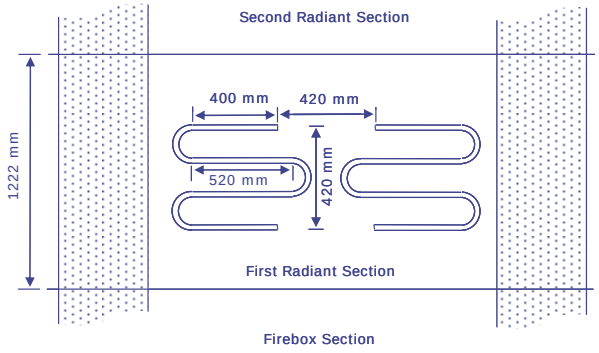


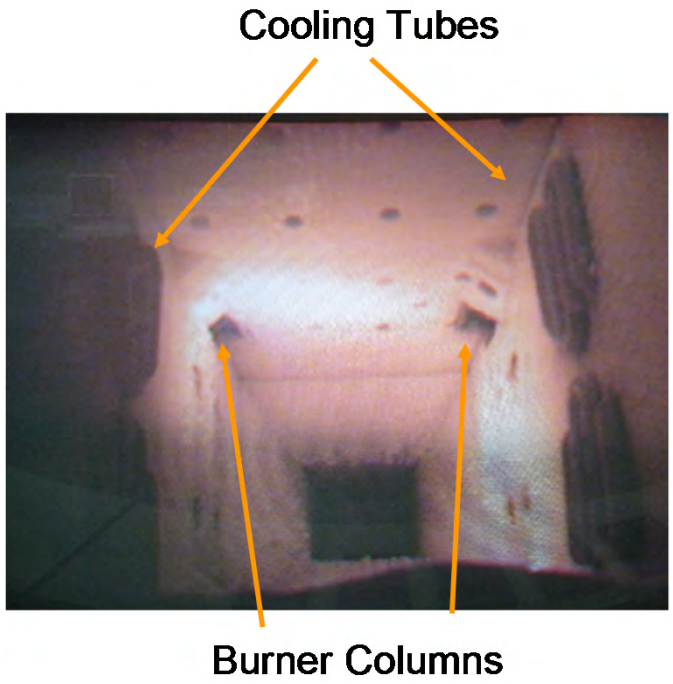
Nose Section Roof
- Castable: CT-155S, 10", k = 0.6978 W/m/°C
- Insulation: HTB, 2", k = 0.11 W/m/°C
- Carbon Steel, 0.38", k = 60 W/m/°C
- Total thermal resistance = 0.550 m^2 °C/W

Radiant Sections 1 & 2, Nose Section Walls
- Castable: CT-155S, 14", k = 0.6978 W/m/°C
- Insulation: HTB, 4", k = 0.11 W/m/°C
- Carbon Steel, 0.38", k = 60 W/m/°C
- Total thermal resistance = 1.448 m^2 °C/W

Ash Hopper & Burner Region
- Fire Brick: Al 85C, 4.5", k = 2.89 W/m/°C
- Castable: INCT-165S, 9.5", k = 0.5465 W/m/°C
- Insulation: Cerakwool, 4", k = 0.13 W/m/°C
- Carbon Steel, 0.38", k = 60 W/m/°C
- Total thermal resistance = 1.263 m^2 °C/W

Cooling Tubes





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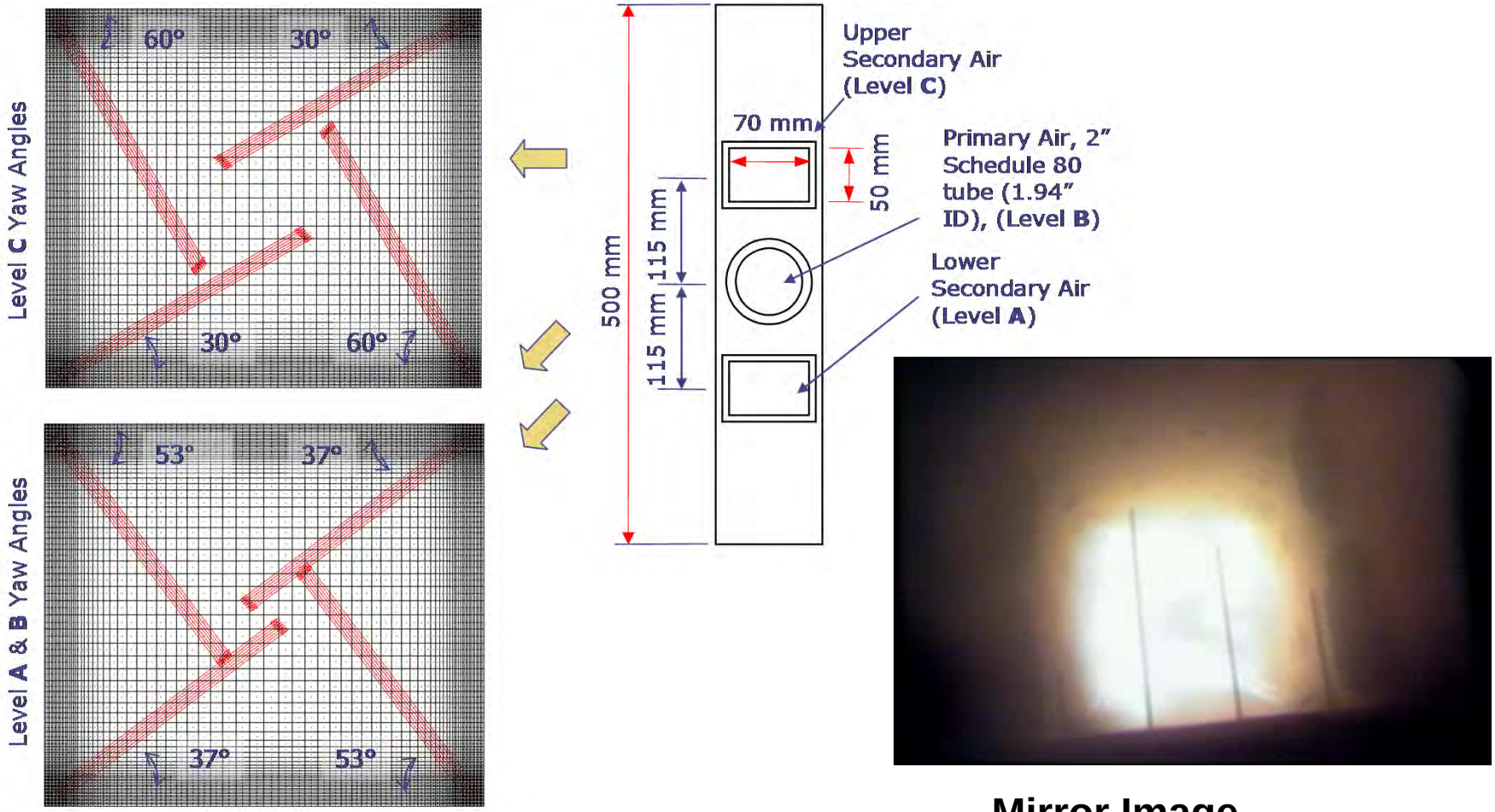
Burner Arrangement



Mirror Image

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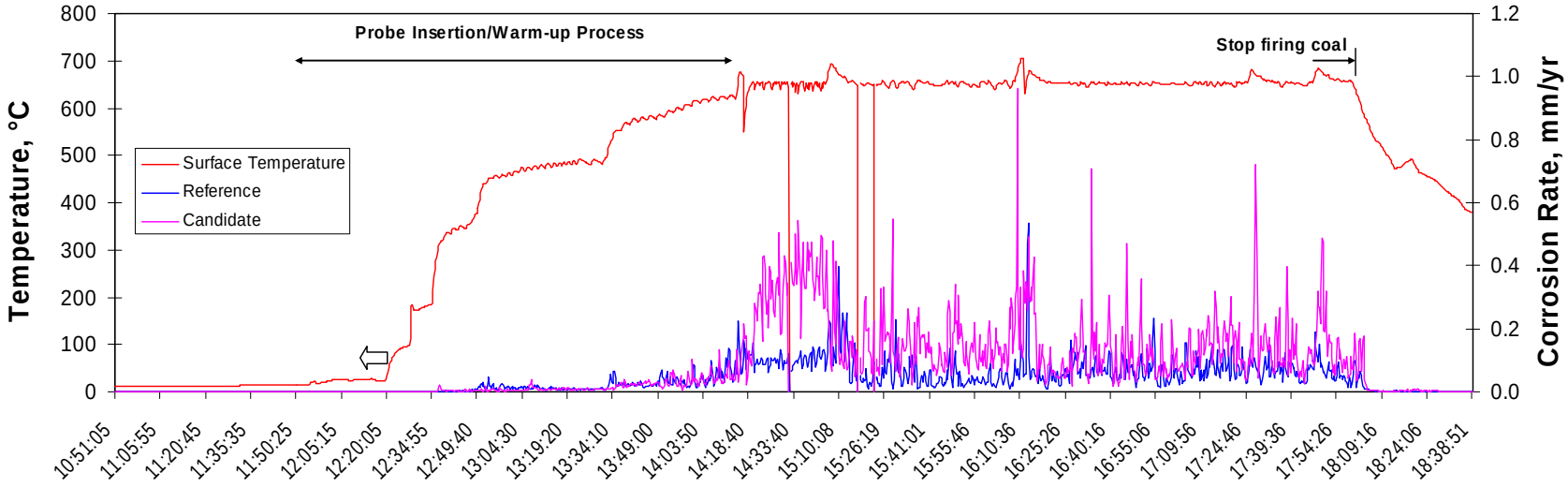
Corrosion Monitoring System



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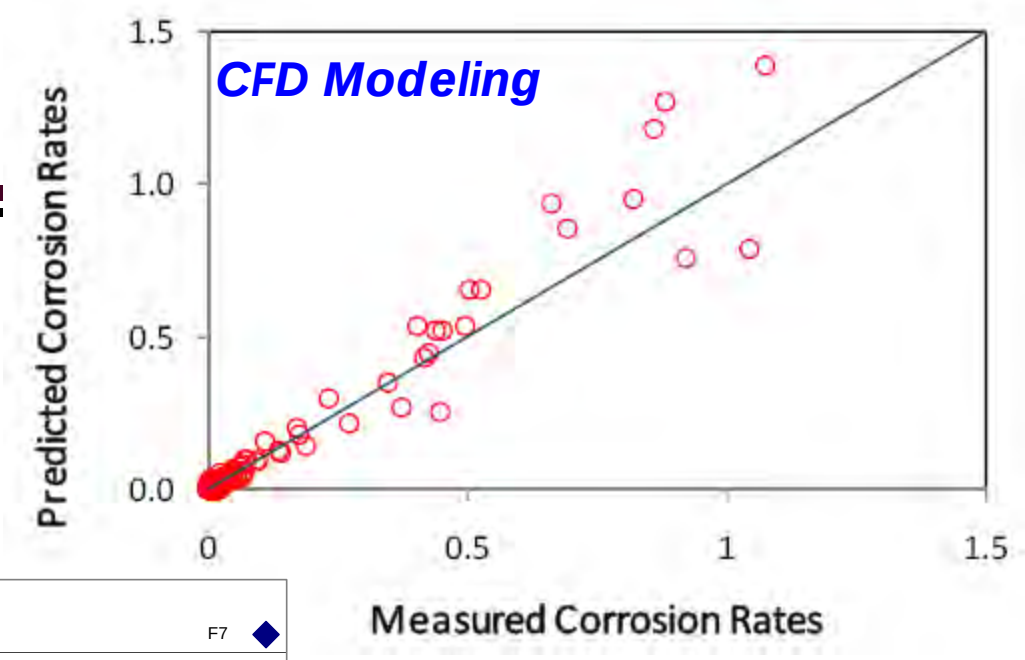
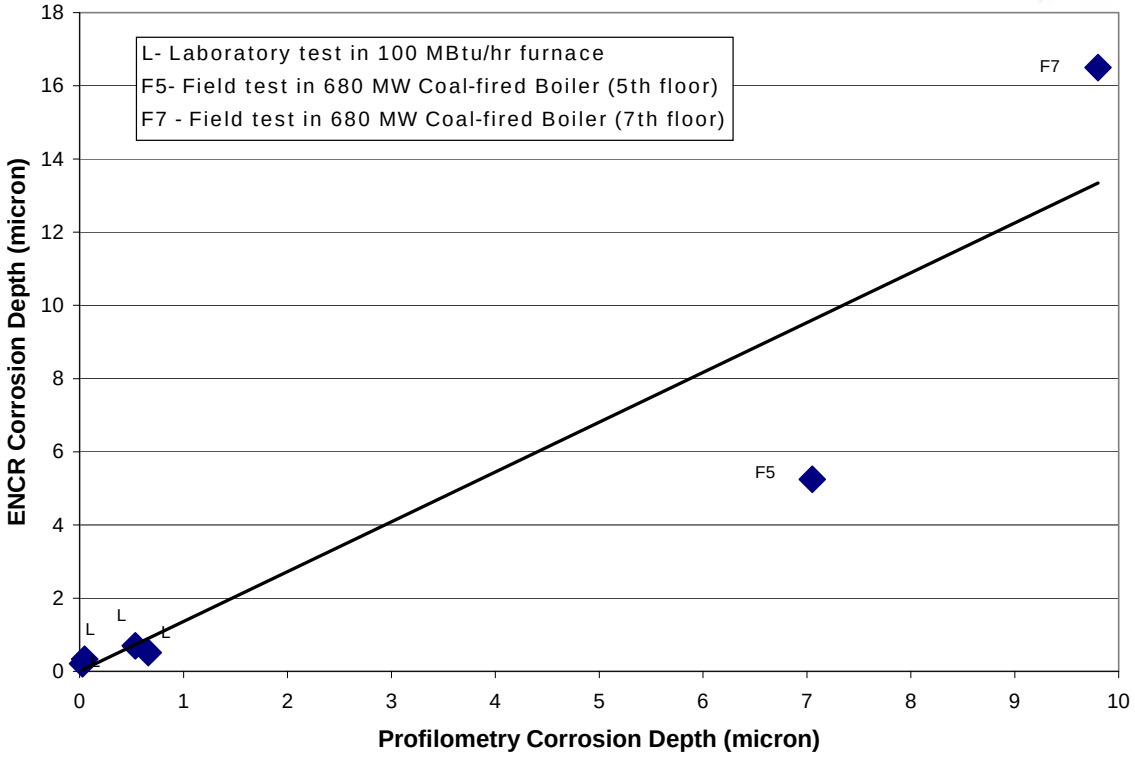
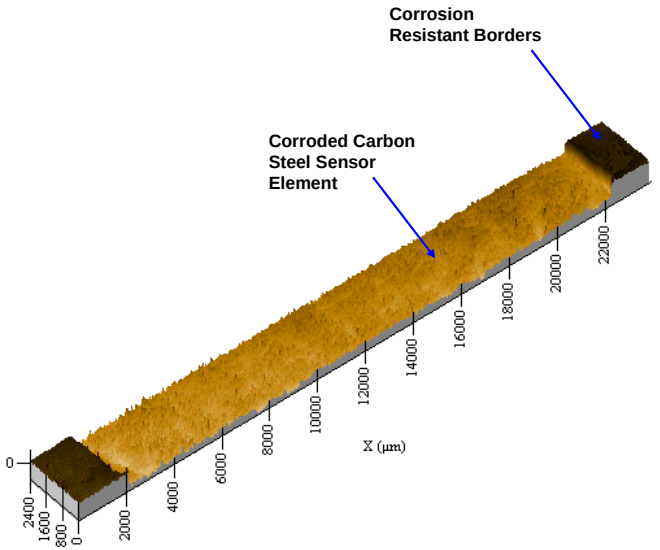
Quantitative Validation



Profilometry





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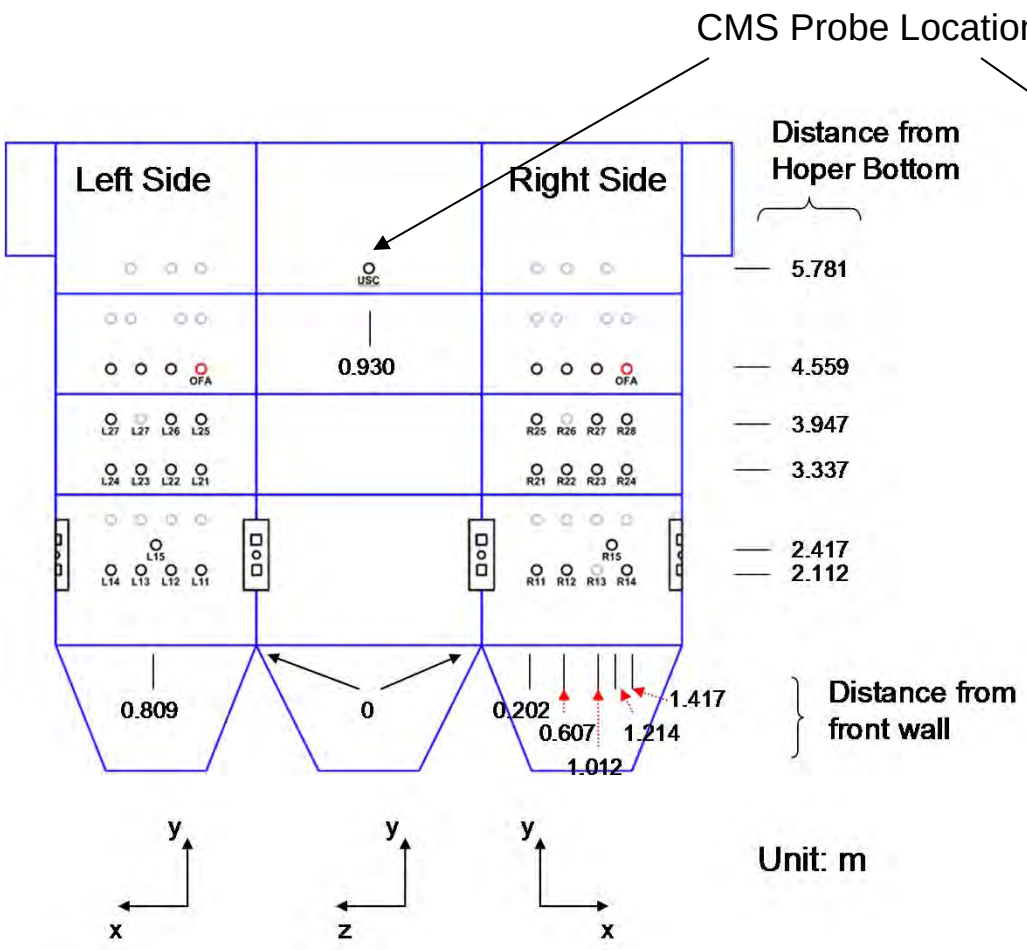
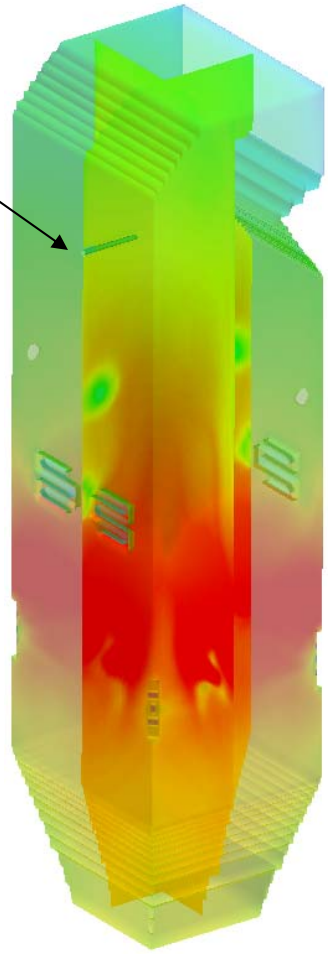
Probe Location





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Operating Conditions

	Unit	OP1
Coal		C&A
Coal Feeding Rate	kg/hr	180
Firing Rate	MW	1.45
Particle Size Distribution	% 200 mesh	70
Excess O_2	wet%	3.6
Burner Stoichiometry		0.9
Excess Air	%	20
Primary Air/Fuel		1.9
Combustion Air		
Primary	kg/s	0.095
Secondary	kg/s	0.472
Burner Secondary		0.330
Burner Sec A (bottom)	kg/s	0.165
Burner Sec C (top)	kg/s	0.165
Overfire Air	kg/s	0.142
Total Combustion Air	kg/s	0.567
Air Temperature		
Primary	°C	58
Secondary	°C	272

- **C&A coal is used.**
- **Excess air: 20%**
- **Burner Stoichiometry: 0.9**
- **Primary Air/Fuel : 1.9**
- **Firing Rate: 1.45MWth**
- **Corrosion rates were measured at the metal temperatures of 650, 675, and 700°C.**

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C&A Coal Properties

Ultimate Analysis	
Composition (wt%)	C&A
C	69.62
H	4.80
O	5.66
N	1.52
S	0.61
ash	13.44
H_2O	4.34
Total	100.00

Proximate Analysis	
	C&A
Fixed Carbon	53.00
Volatile	29.22
Ash	13.44
Moisture	4.34
Total	100.00

Heating Value	
	C&A
LHV, kcal/kg	6618
HHV, kcal/kg	6930

		C&A
ASH (wt%)	SiO_2	70.14
	Al_2O_3	19.25
	Fe_2O_3	3.6
	CaO	1.4
	MgO	0.8
	Na_2O	0.54
	K_2O	0.96
	TiO_2	0.84
	SO_3	0.8

- **Low sulfur (0.61 wt%) and chlorine (0.035 wt%)**
- **Fuel corrosivity ~ 0.11 based on Na, K, Ca, Mg, S contents**

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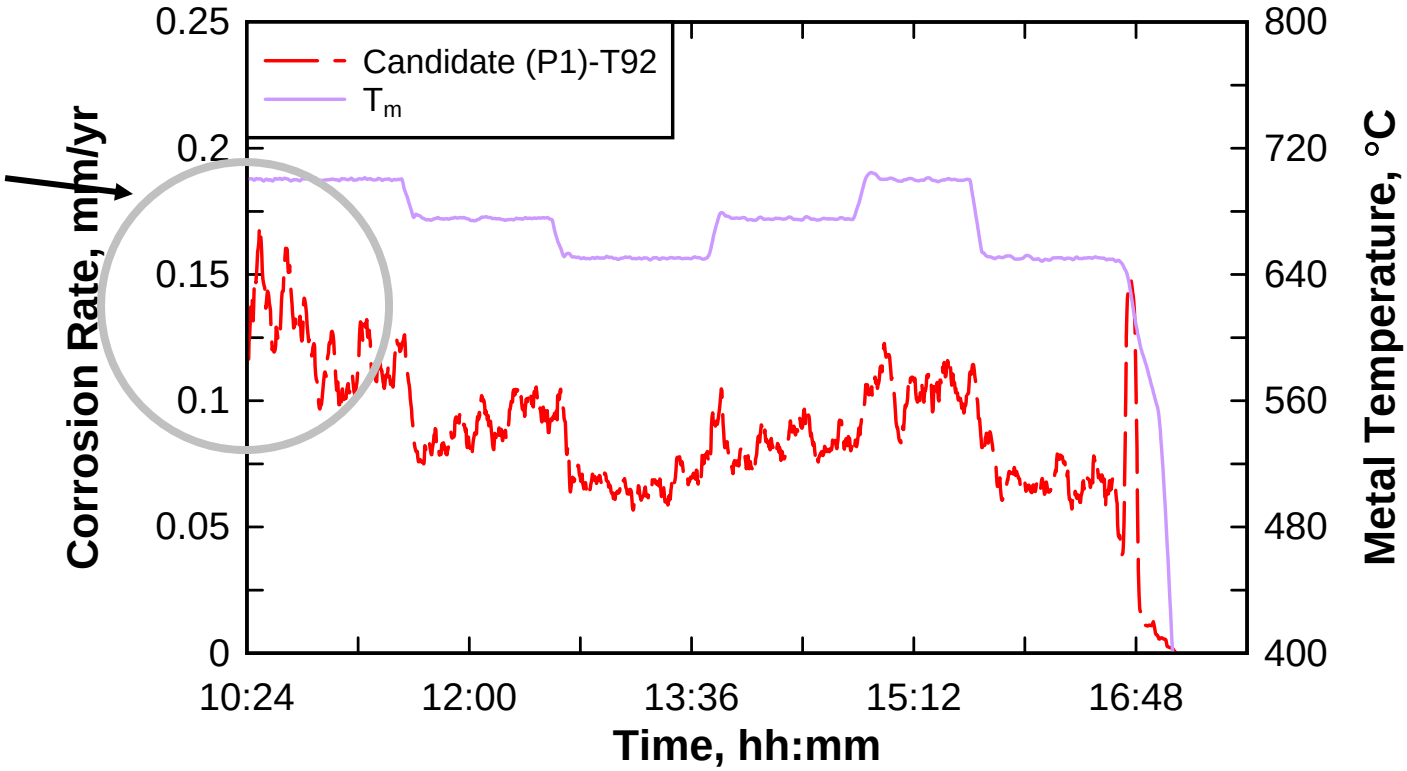
Corrosion Rate – T92

Initial conditioning of the metal



➔ **Corrosion rates varied according to the metal temperature change.**

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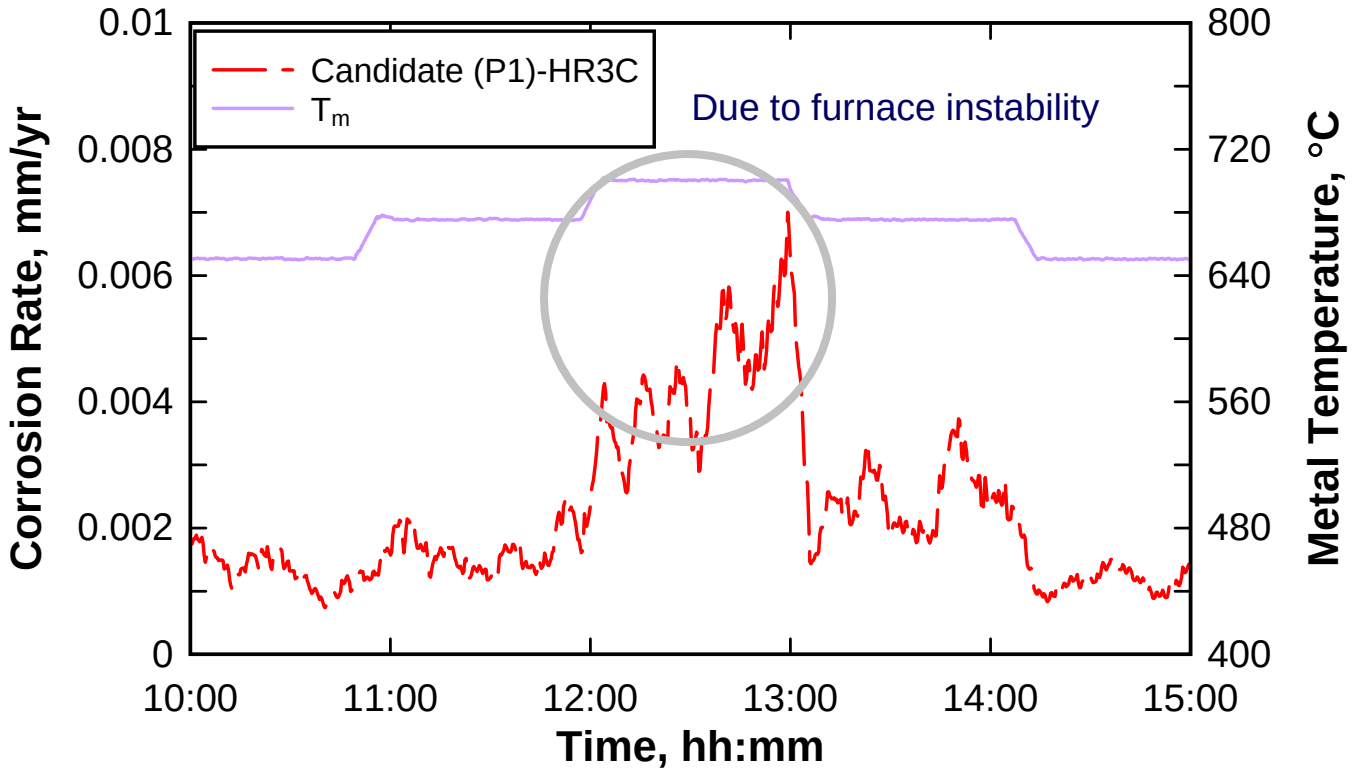
Corrosion Rates – HR3C



➔ **Low corrosion rates at all temperatures**

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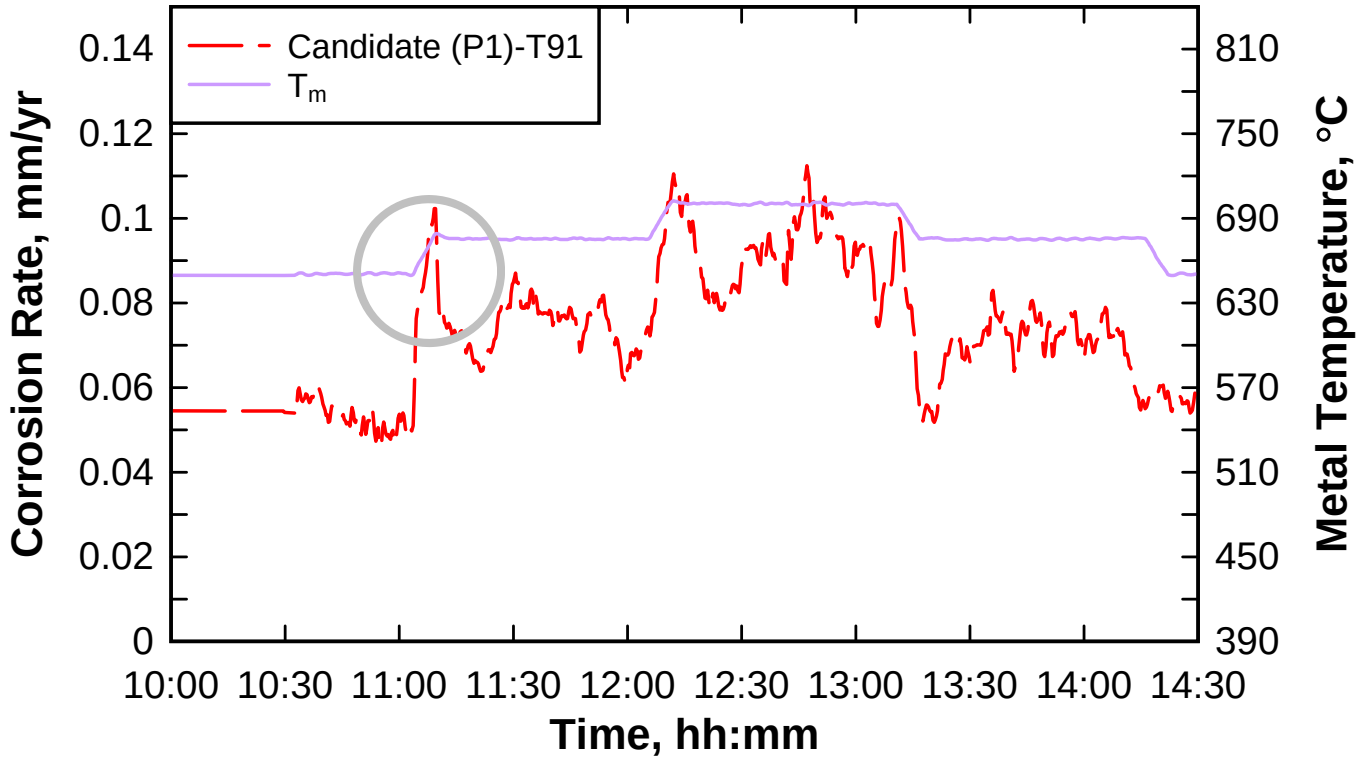
Corrosion Rates - T91



- **Corrosion rates varied according to the metal temperature change.**
- **Relatively high corrosion rates when the temperature changed.**
- **Similar corrosion rates to that of T92**

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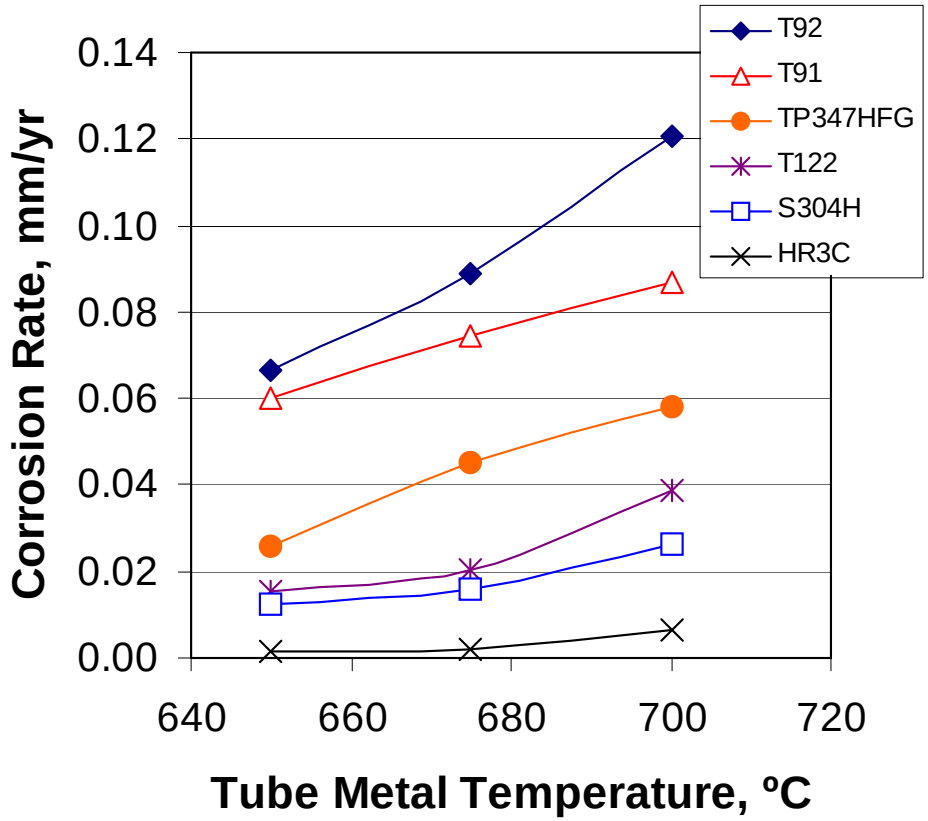
Material Comparison



➔ **Corrosion Rates:**

T92 > T91 > TP347HFG > T122 > S304H > HR3C

➔ **Corrosion rates increased with increasing metal temperature**

➔ **The difference between the materials becomes larger with increasing temperature in some cases.**

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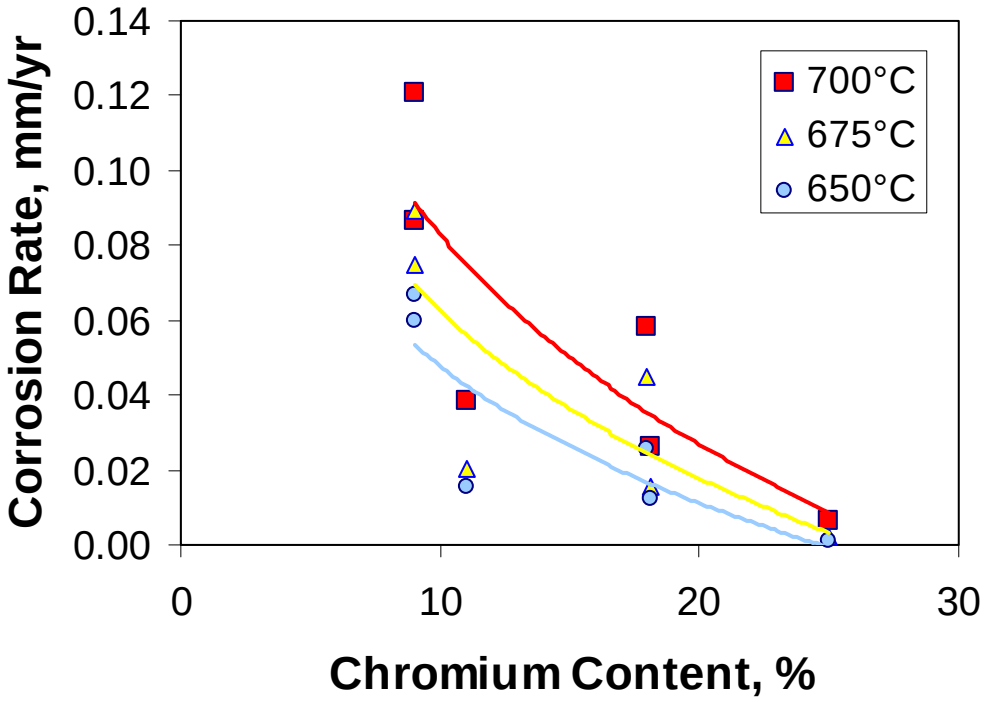
Corrosion Rates vs. Cr Contents



- **Corrosion rates increased with decreasing chromium contents.**
- **TP347HFG and T122 show exception.**

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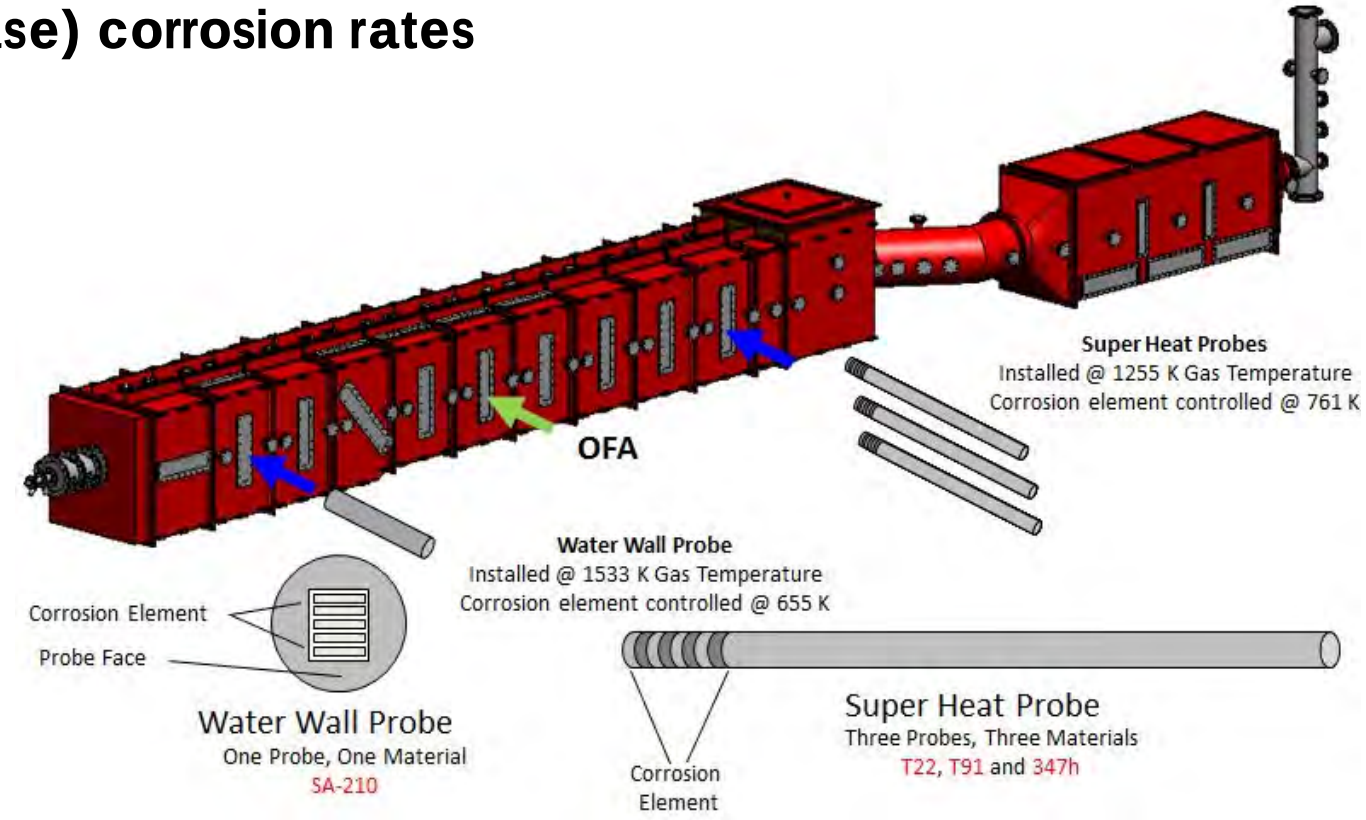
Corrosion under Oxy-coal Firing

Oxy-combustion under possible retrofit conditions affects both waterwall (slight decrease) and superheat (significant increase) corrosion rates



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Corrosion Element Material Analysis

Material	SA 210	T22	P91	347H
HT Surface	Waterwall	Superheat	Superheat	Superheat
C	0.07	0.11	0.10	0.048
Si	0.23	0.2	0.32	0.40
Mn	0.42	0.44	0.47	1.32
Ni	-	-	0.15	9.73
Cr	-	2.21	8.52	17.45
Mo	-	0.95	0.93	-
S	0.002	0.003	0.002	0.008
P	0.009	0.01	0.018	0.026
Cu	-	-	0.11	-
Al	-	-	0.01	0.005
Nb/Cb	-	-	0.07	0.63
V	-	-	0.22	0.078
N	-	-	0.044	-
Ta	-	-	-	0.02

* All values in mass %

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Normal Operating Conditions

Superheat corrosion probe (347h)

- **Probe Element Temperatures**
  - SA210 (655– 728 K)
  - T22 (761 – 839 K)
  - P91 (761 - 866 K)
  - 347h (761 – 978 K)
- **Gas Temperatures**
  - Water wall probe ~ 1533 K
  - Superheat probes ~ 1255 K
- **SO2 Concentrations**
  - Utah, Air ~ 500 ppmv
  - Utah, Oxy ~ 1,800 ppmv
  - PRB, Air ~ 100 ppmv
  - PRB, Oxy ~ 300 ppmv
  - Illinois, Air ~ 3,000 ppmv
  - Illinois, Oxy ~ 18,000 ppmv
- **Oxidizing / Reducing Conditions**
  - Water wall probe – Mostly reducing conditions (BSR = 0.9)
  - Superheat probes – Oxidizing conditions

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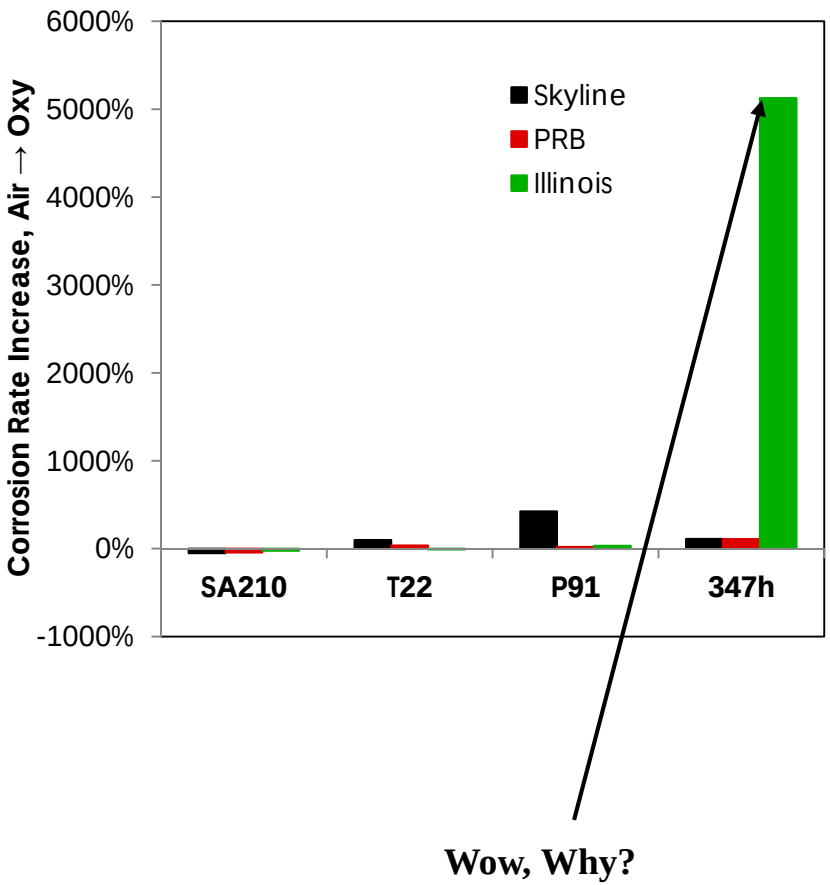
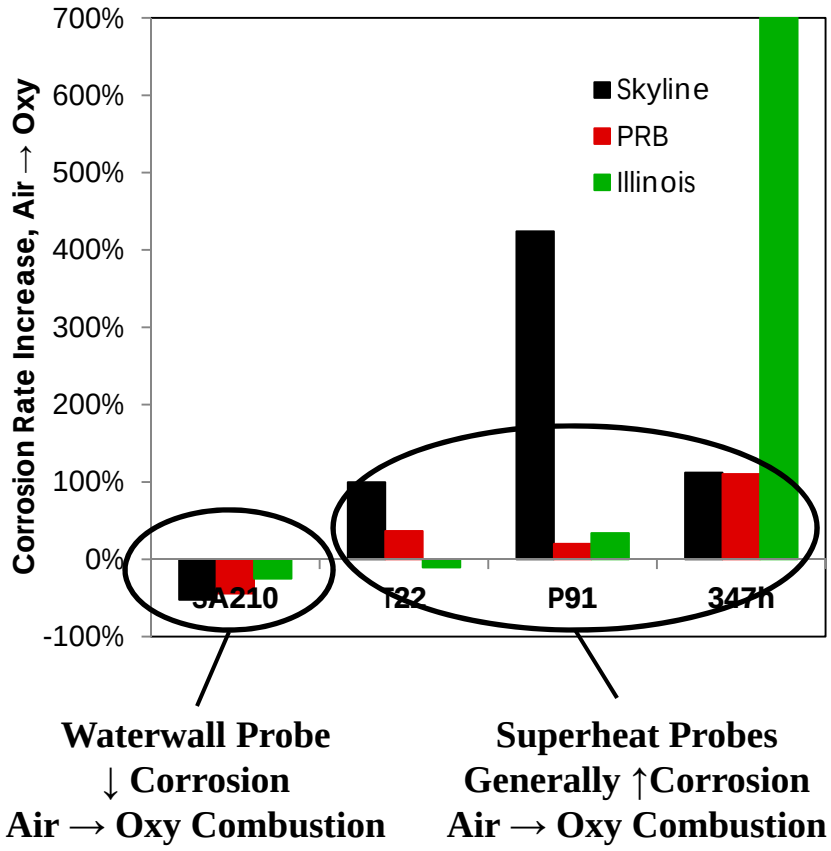
Increase in Corrosion Rate Air → Oxy

Baseline sensor element temperatures, probe locations and staging conditions





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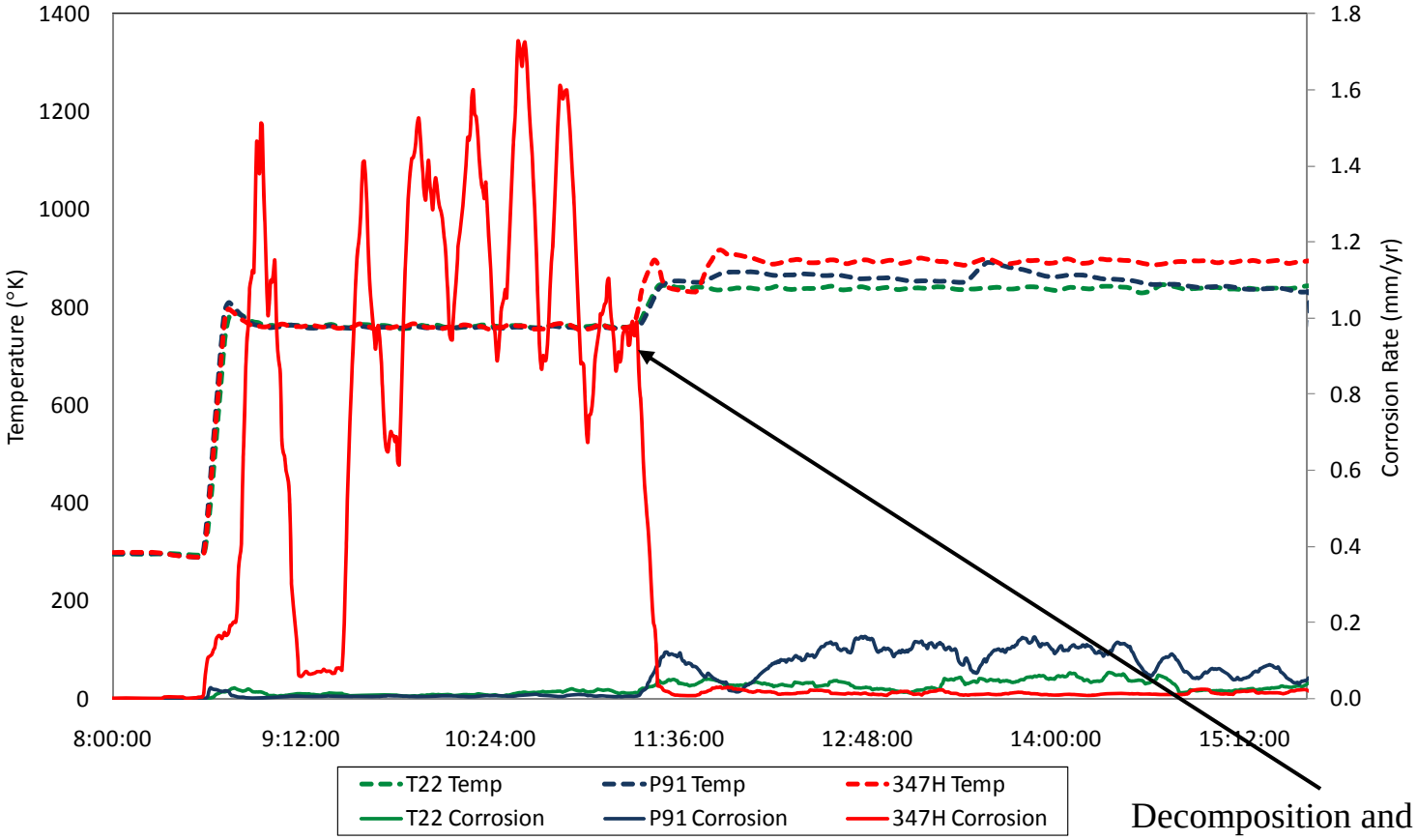
Temperature Effects on Corrosion



Decomposition and volatilization of the trisulphate species
(Viswanathan and Bakker, 2000)

Operation of 347H at subcritical temperatures in the presence of high SO_2 concentrations will produce extremely high corrosion rates.

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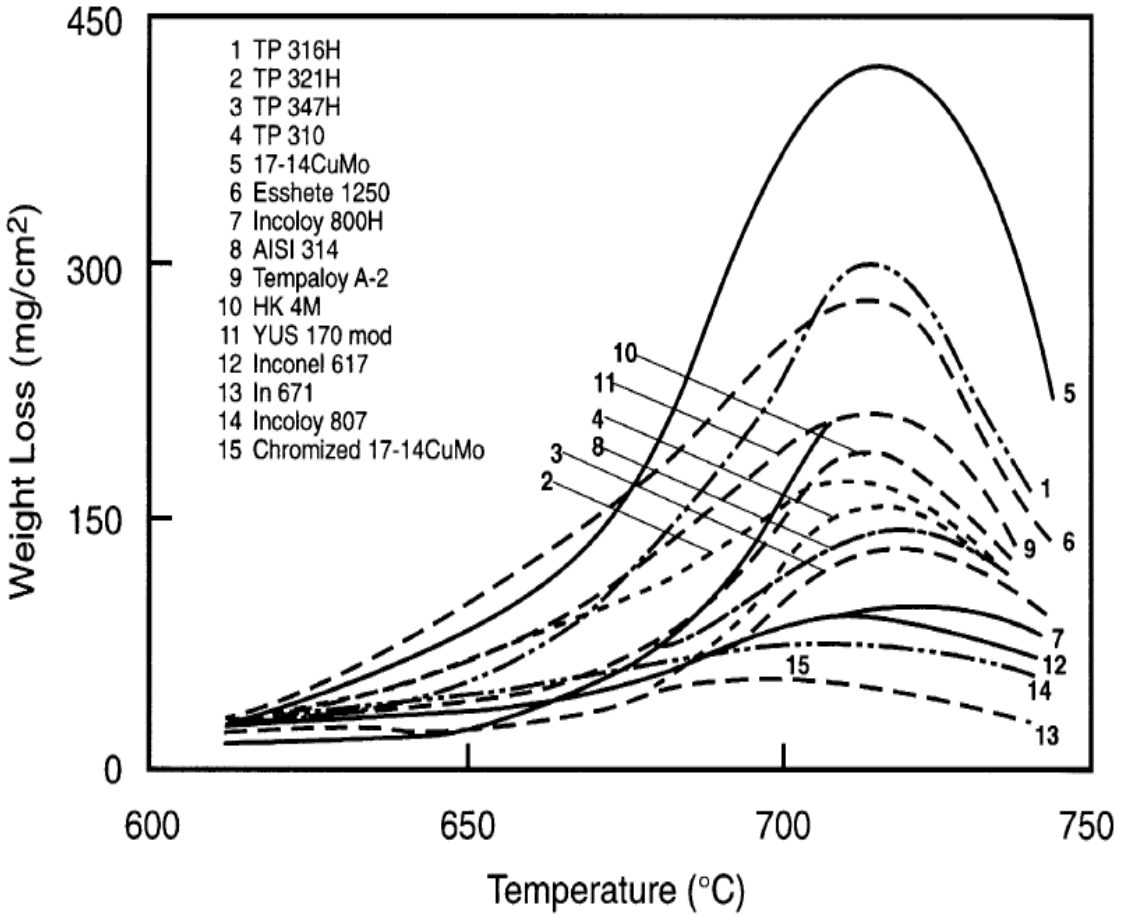
Alkali Iron Trisulfate Decomposition



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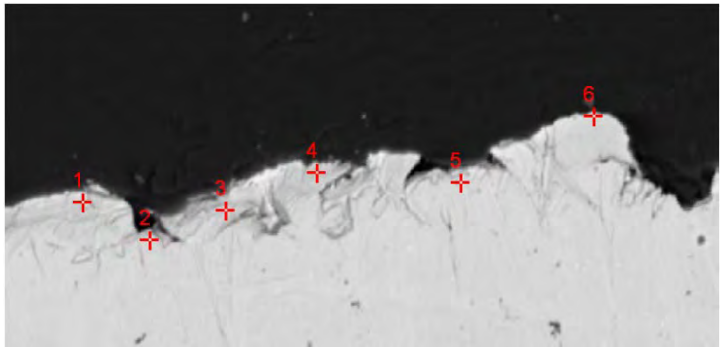
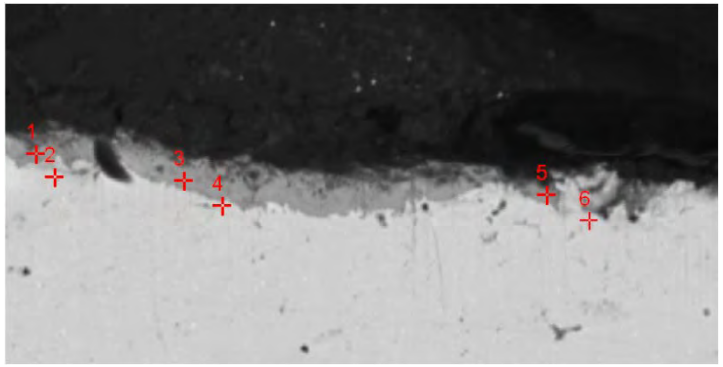
347H Metallographic Results

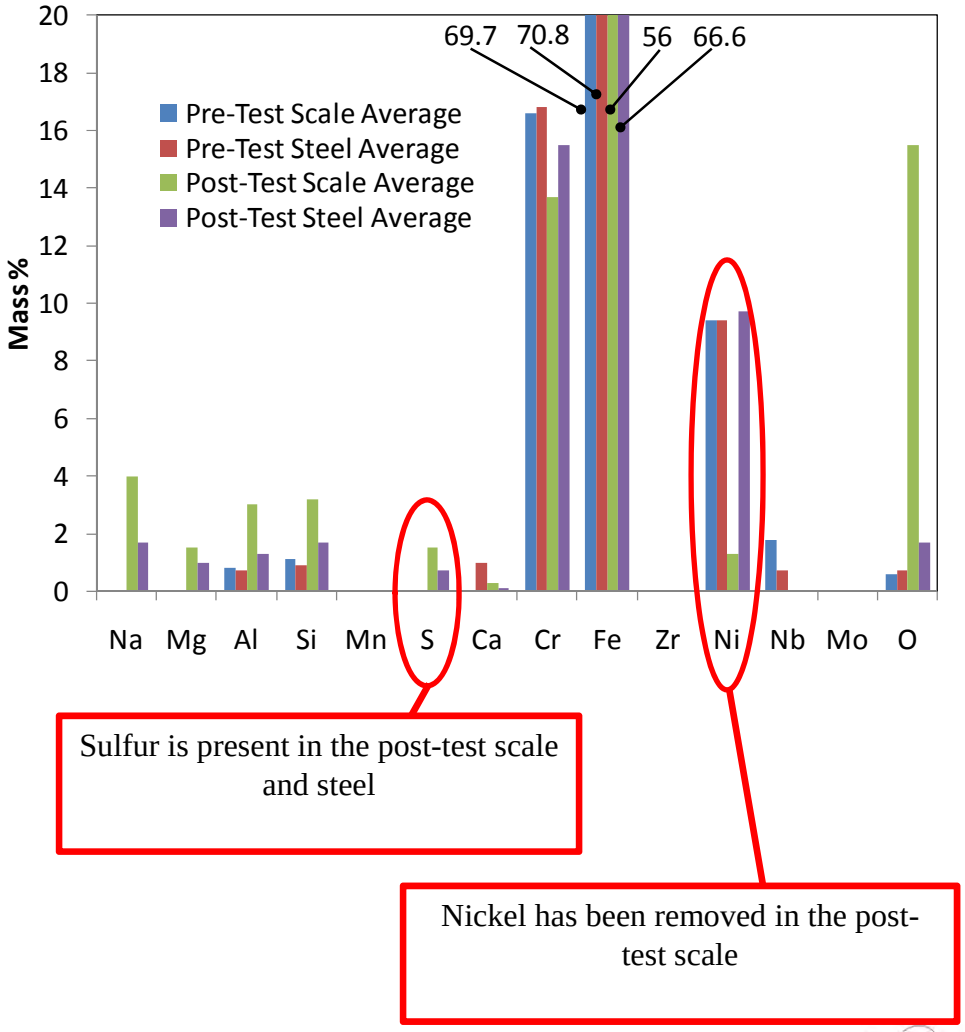
Backscattered Electron Images of the 347H Corrosion Element



Pre-Combustion Testing



Post-Combustion Testing



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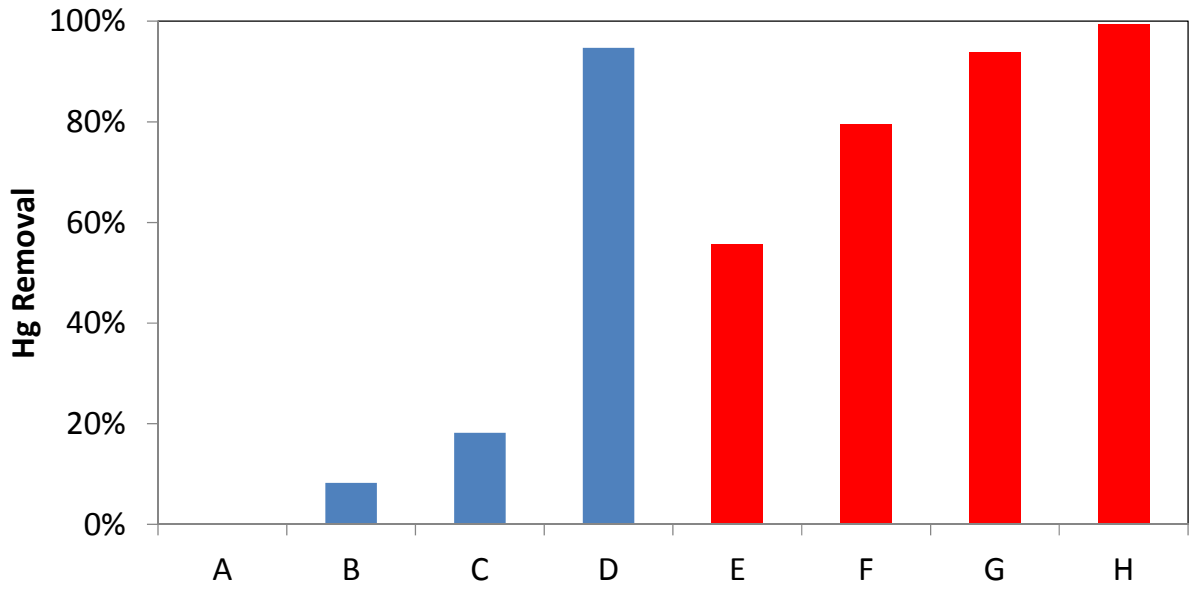
Air Heater Corrosion

Evaluation of Hg Control Options

MerSim™ total plant simulation



Case	Description	Plant Configuration	ACI	Boiler Additive	Hg removal
A	Baseline	Boiler + APH + ESP			0.0%
B	Co-benefit	Boiler + SCR + APH + ESP + wFGD			8.2%
C	Additive	Boiler + APH + ESP		3 gal/hr KNX	18.2%
D	Additive-Co-benefit	Boiler + SCR + APH + ESP + wFGD		3 gal/hr KNX	94.7%
E	ACI-ESP	Boiler + APH + ESP	2 lb/MMacf Darco Hg		55.6%
F	ACI-FF	Boiler + APH + FF	2 lb/MMacf Darco Hg		79.6%
G	BrACI-FF	Boiler + APH + FF	2 lb/MMacf Darco Hg-LH		93.9%
H	Additive-ACI-ESP	Boiler + APH + ESP	2 lb/MMacf Darco Hg	3 gal/hr KNX	99.3%

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Bromine and APH Corrosion

- **Brominated activated carbon injection (Br-ACI) can accelerate APH corrosion rates**
  - **Supplier-dependent impacts have been noted**
  - **Low temps in APH suspected to exacerbate problem**
- **EPRI/URS boiler bromide addition study [Dombrowski, 2013]**
  - **52 units with > 1yr operation had conducted inspections**
  - **24 of these units noted accelerated corrosion**
  - **Increased corrosion in PRB/lignite units has been particularly severe**

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Possible APH Corrosion Mechanisms

- **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 (higher Temp)**
- **Condensation appears likely in this study**
  - **Hydrobromic acid is one of the strongest mineral acids known**
  - **Simple calculations for relevant concentrations of bromine addition indicate dew points in the 90-130 °F range**
    - **90-150 °F for this study**
  - **Dew points for oxy-combustion as high as 150 °F**

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Pilot-scale Corrosion Measurements

Objective:

- **Measure changes in corrosion rates at temperatures representative of an air heater,**
- **In the presence of various mercury control additives (baseline, bromine, activated carbon),**
- **Under both air-fired and oxy-fired conditions**

Method:

- **Use air cooled corrosion probes positioned in the flue gas just upstream of the baghouse**
- **Vary probe cooling to control element surface temperature in a range considered representative of air heater temperatures, especially the colder extremes**

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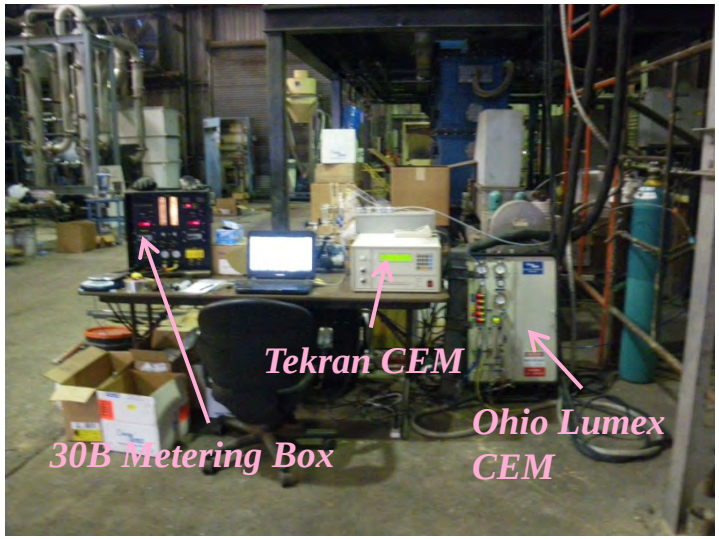
Complementary Pilot-Scale Measurements

- Objective - Measure impact of oxy-combustion on performance of mercury control technologies
- Approach
  - L1500 pilot-scale furnace
  - PRB and bituminous coals
  - Air and oxy-firing
  - Two Hg control technologies
    - Bromine boiler additive ($CaBr_2$)
    - Activated carbon injection
  - Hg measured before and after baghouse
  - Three different Hg measurement techniques
  - Testing in May and June 2013



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Operating Conditions

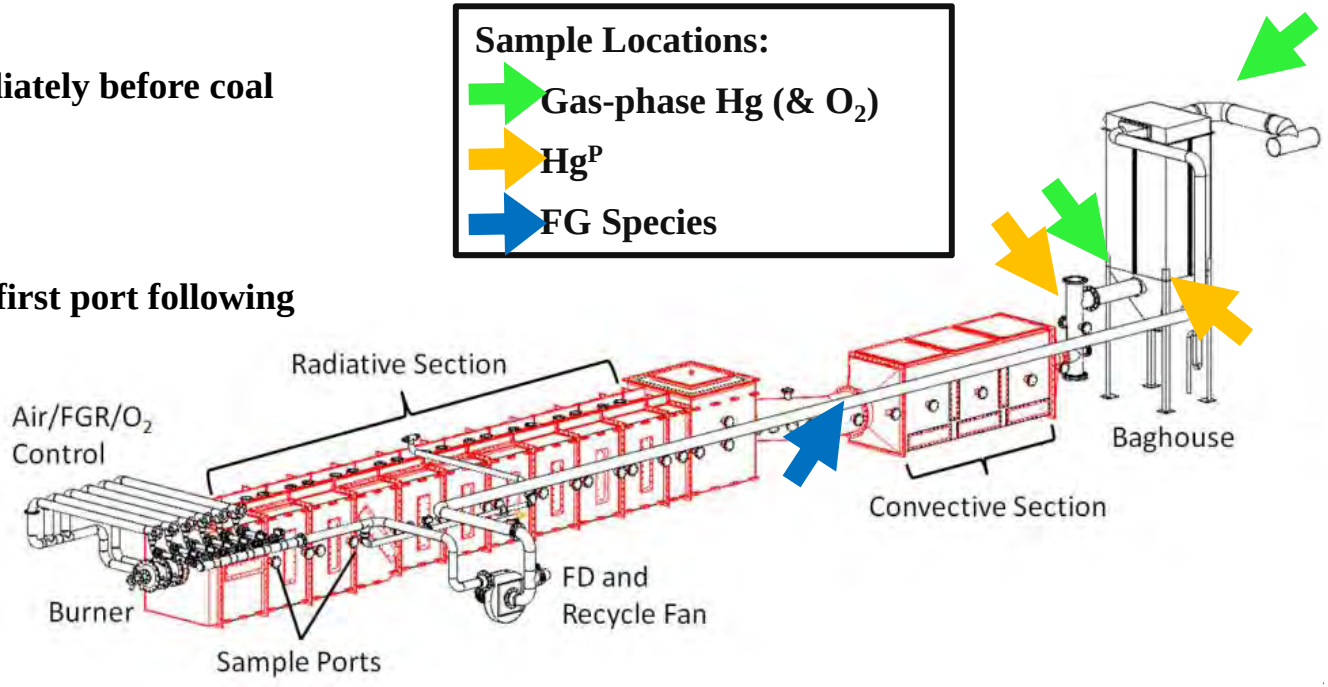
Coal	Condition	Firing Rate (kW)	O_2 (%, dry)	CO_2 (%, dry)	BH inlet (F)	BH outlet (F)
PRB	Air-Fired	780-860	4.0	14	380	250
PRB	Oxy-Fired	780	3.5	83	300	140
Bituminous	Air-Fired	775-1025	3.5	15	356	239
Bituminous	Oxy-Fired	775-880	3.4	87	341	146

Br addition:

Solid $CaBr_2$ injected immediately before coal entered burner
(~8-75 ppm Br wet on coal)

ACI:

Darco Hg injected through first port following convective section
(~0.5-10 lb/MMacf)



Coal Analysis

Black Thunder PRB			
Coal Analyses		Mineral Matter Analyses	
C	54.04	Al	14.19
H	3.74	Ca	16.13
N	0.82	Fe	5.99
S	0.38	Mg	3.33
O	13.69	Mn	0.04
Ash	5.66	P	0.71
Moisture	21.67	K	0.47
Volatile Matter	36.77	Si	36.76
Fixed Carbon	35.91	Na	0.93
HHV, Btu/lb	9320	S	10.11
Hg, μg/g	**0.047±0.004**	Ti	1.11

Pratt Bituminous			
Coal Analyses		Mineral Matter Analyses	
C	69.23	Al	25.91
H	4.82	Ca	3.41
N	1.69	Fe	13.20
S	2.22	Mg	1.18
O	6.54	Mn	0.04
Ash	13.14	P	0.83
Moisture	2.38	K	2.33
Volatile Matter	35.64	Si	44.78
Fixed Carbon	48.85	Na	0.47
HHV, Btu/lb	12659	S	3.72
Hg, μg/g	**0.21±0.01**	Ti	1.25

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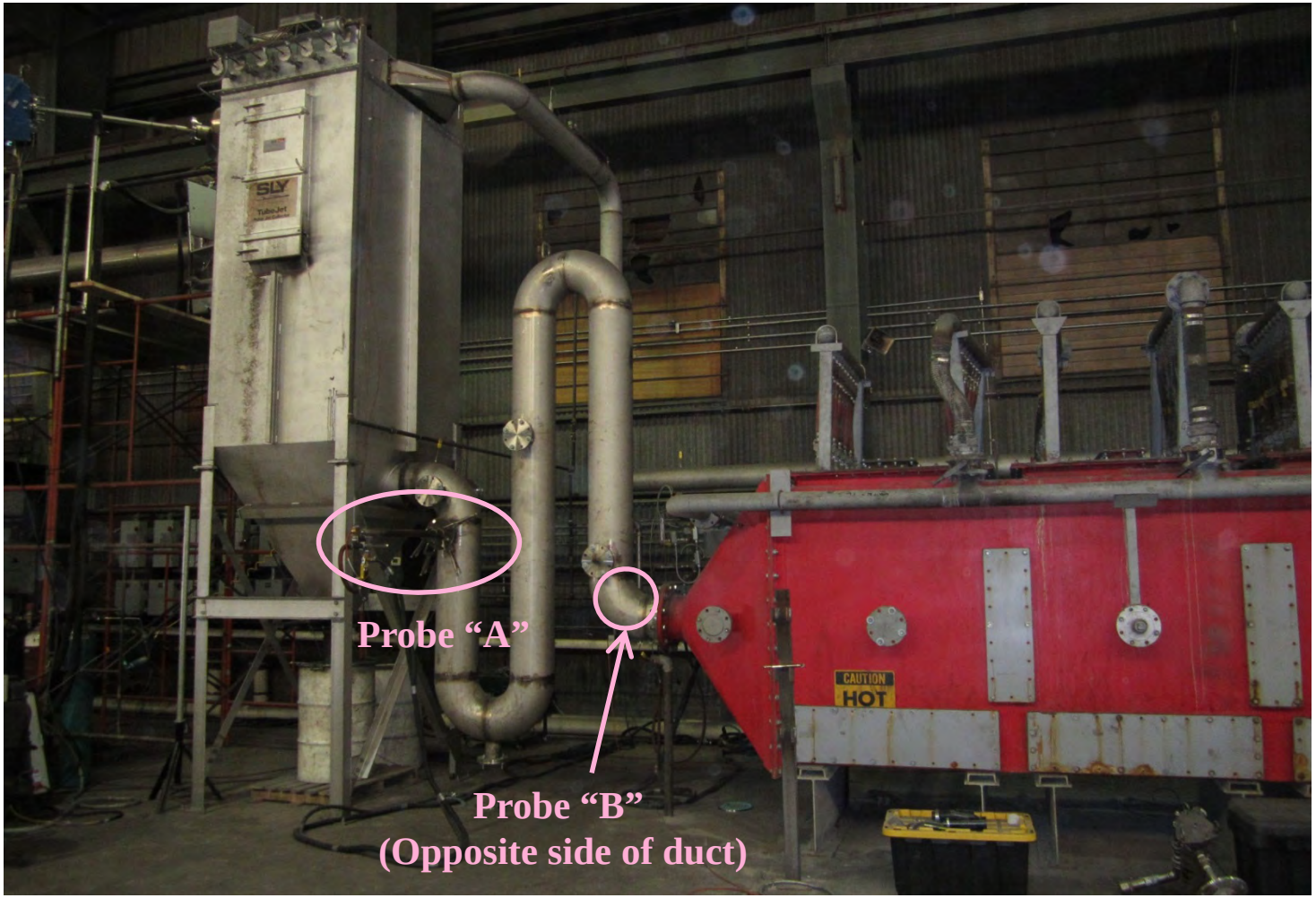
Corrosion Probe Placement



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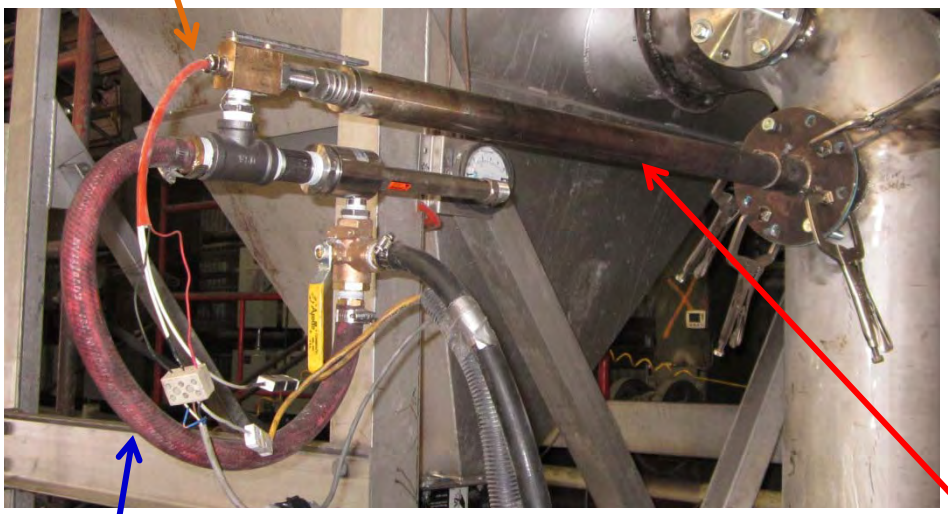
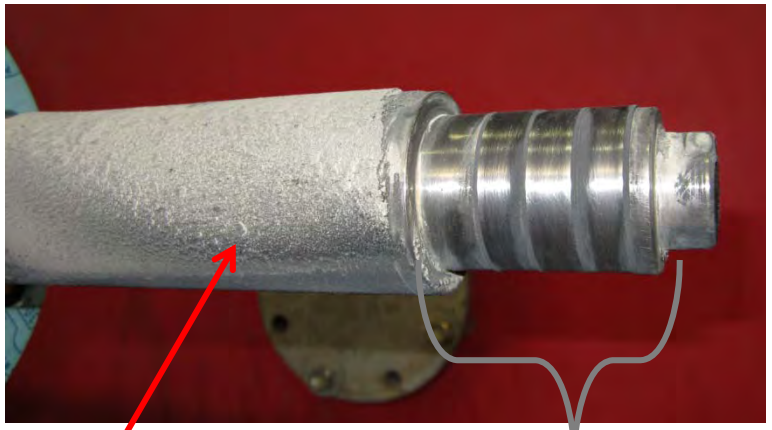
ECN Corrosion Probes

Signal wires and thermocouple leads





Cooling air into probe

Stainless Steal Probe Body

Carbon Steel Corrosion Sensor array (centered in flue gas duct)

Sensor surface temperatures were varied between ~350 °F and ~100 °F

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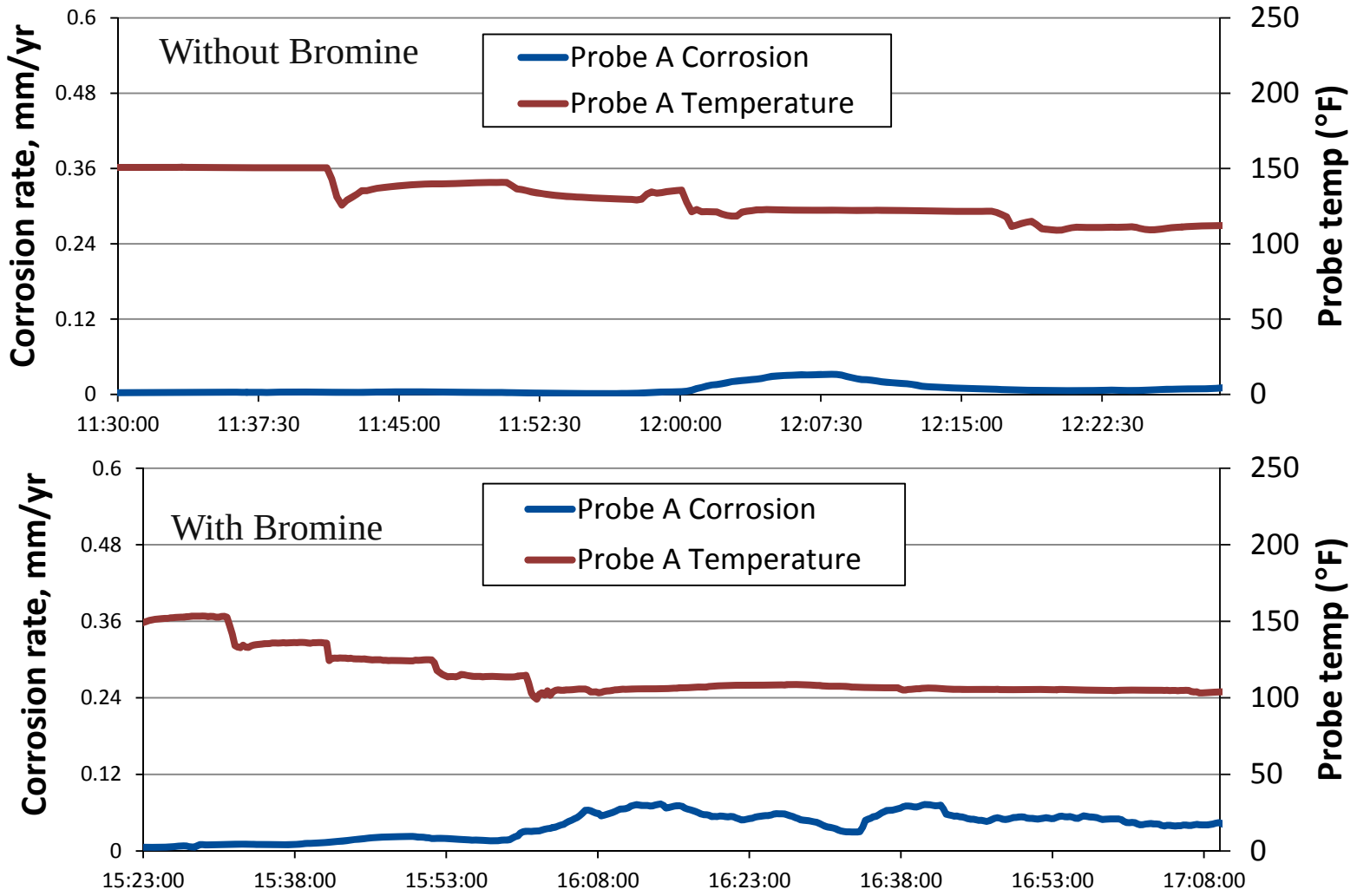
Corrosion Rates (air-fired)
(bituminous coal)



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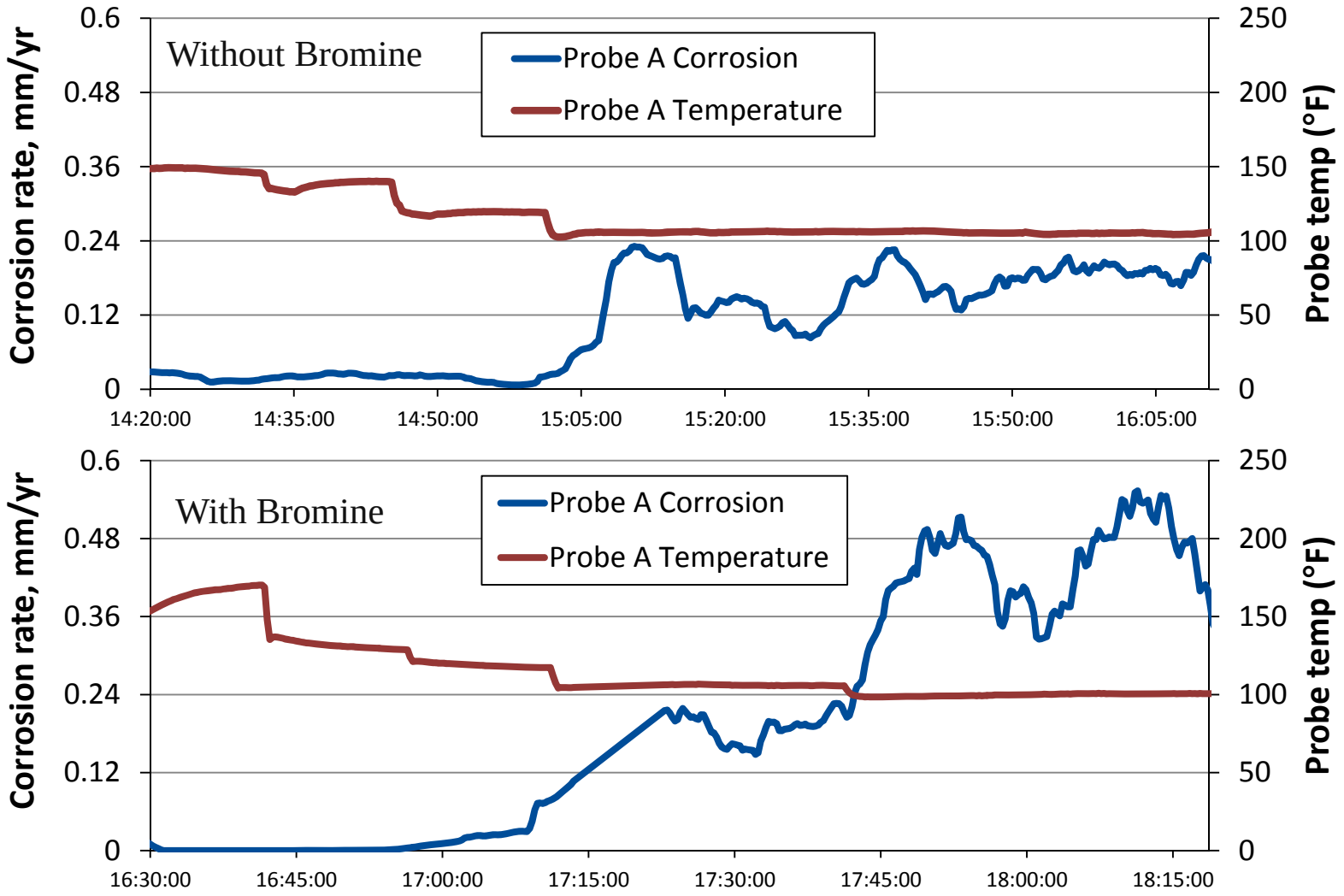
Corrosion Rates (oxy-fired)
(bituminous coal)



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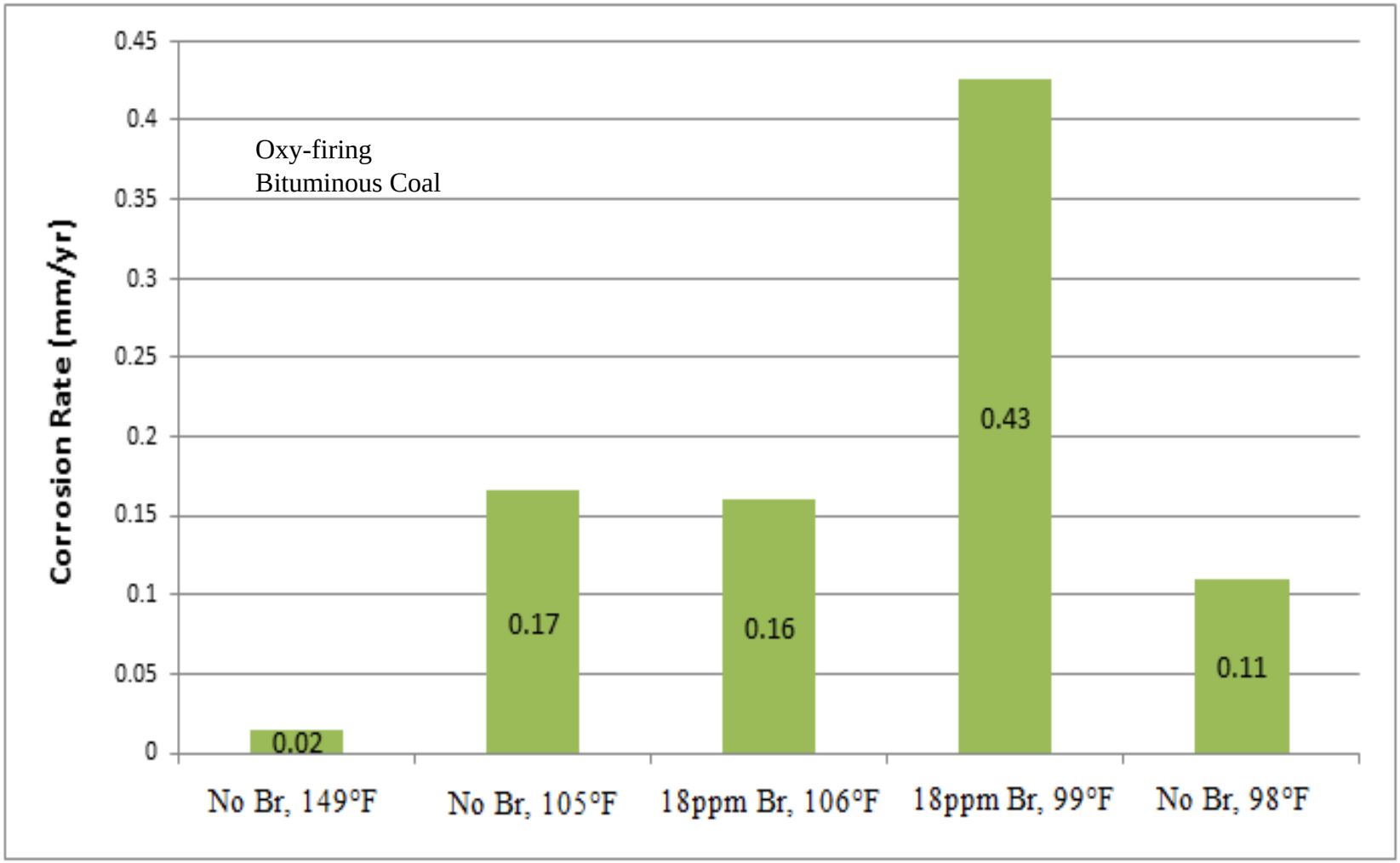
Dew Point Corrosion Considerations



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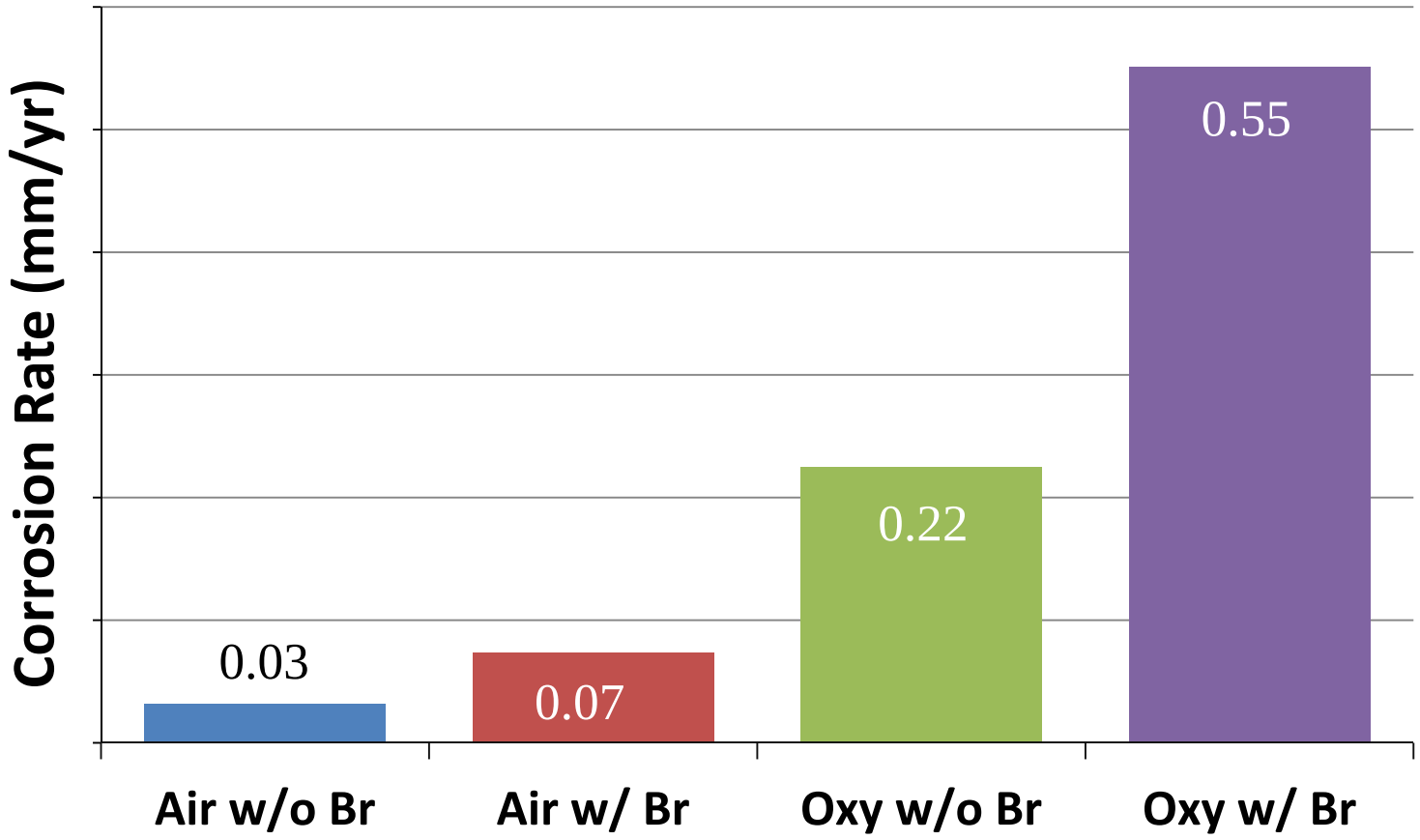
Peak Corrosion Rates, bit. coal



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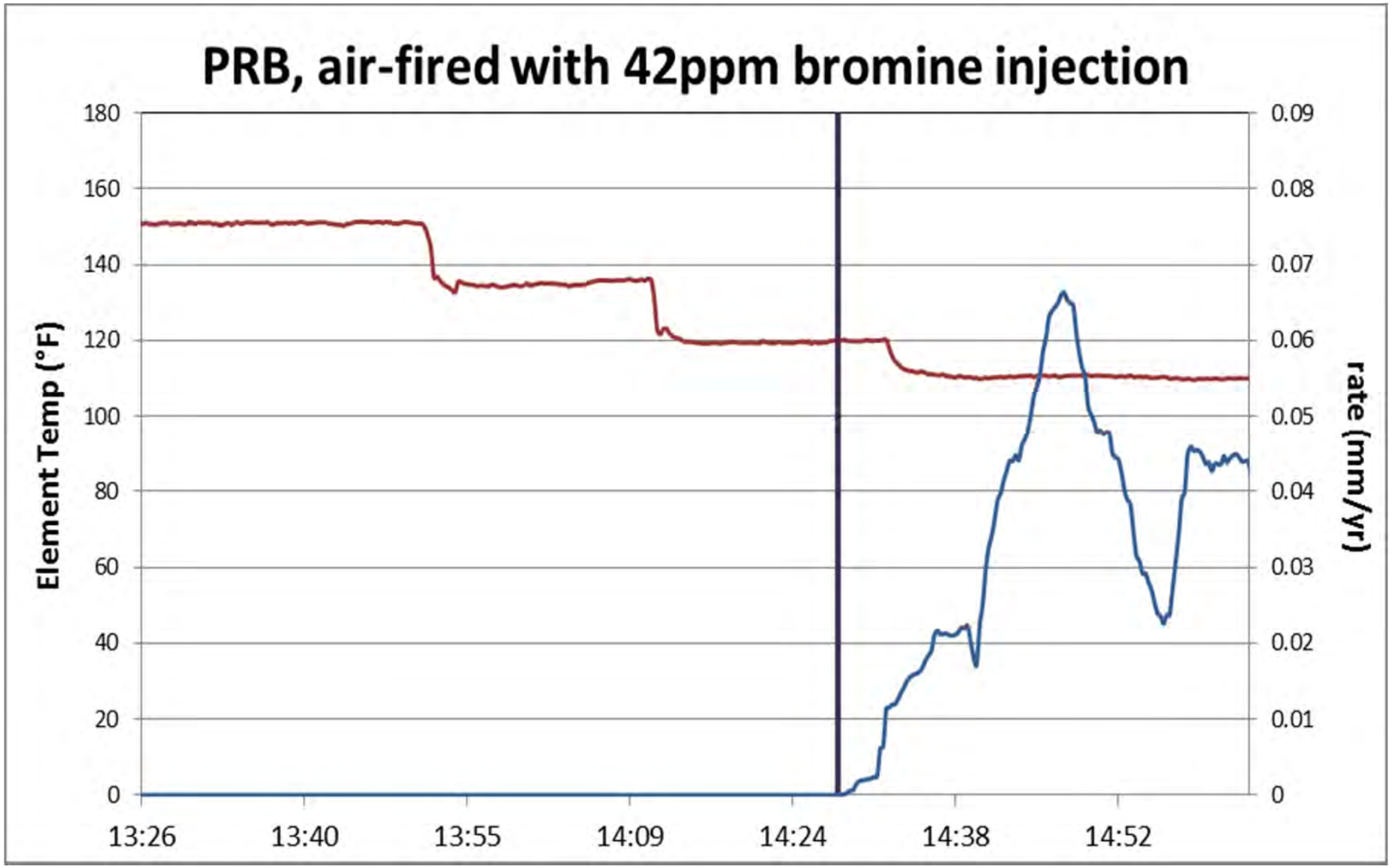
Dewpoint Corrosion with PRB



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Conclusions

- Corrosion rates at air heater temperatures can increase dramatically with bromine addition, if temperatures are sufficiently low
- Oxy-coal combustion has the potential to significantly increase air heater corrosion rates
- Dew point mechanisms are indicated and appear to involve sulfuric acid, HBr, HCl and water
  - Rates dependent on flue gas concentrations and moisture level (both higher with oxy-combustion)
- ACI appears to have a more complex impact on corrosion rates

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