Further Understanding of Furnace Wall Corrosion in Coal-Fired Boilers

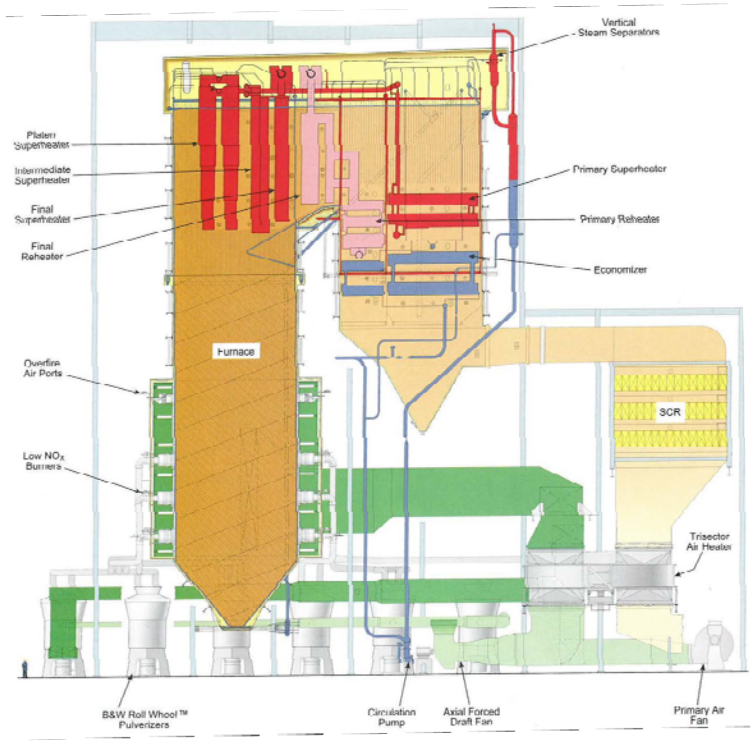
Steven C. Kung, Ph.D.

2014 NETL Crosscutting Research Review Meeting

May 21, 2014

Background

- Stage combustion to reduce NO_x emission results in widespread reducing conditions in lower furnace
- Sulfur in coal exists as SO_2 and H_2S at combustion gas temperatures
- Sulfur converts to H_2S at wall temperatures
- Corrosion attack dominated by oxidation/sulfidation on furnace walls
- Two corrosion models developed previously:
  - Model 1 – *Materials Performance, 36(12), p. 36, 1997*
  - Model 2 – *EPRI Report TR-111152, 1998*
- Prior work considered sulfur only
- Chlorine accelerates corrosion, but its role unclear



Approach

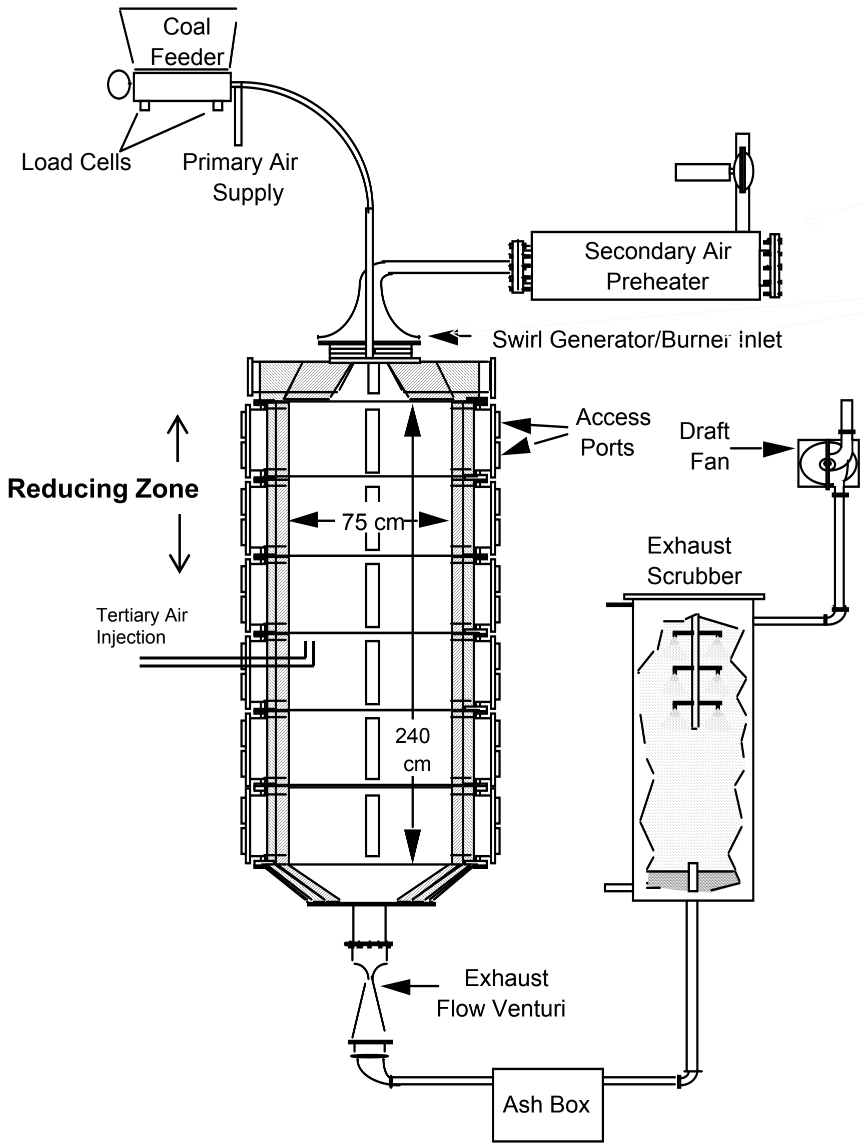
- Characterize corrosive environments in lower furnace of coal-fired boilers
  - Combustion of eight U.S. coals in a pilot-scale testing facility under staged air combustion
  - Online measurement of corrosive gaseous species
  - Collection and analysis of deposit samples
- Generate corrosion database
  - Perform laboratory corrosion tests under realistic low-NO_x conditions determined from pilot-scale study
- Develop models and predictive equations for furnace wall corrosion
  - Development of advanced corrosion model to account for both S and Cl

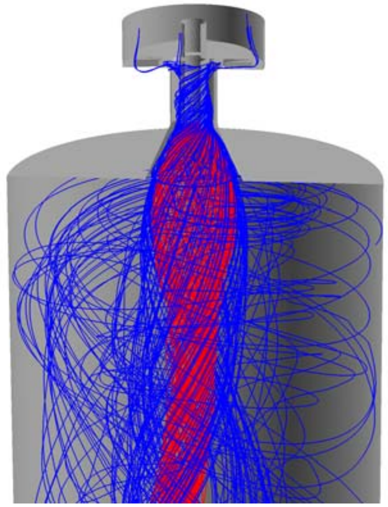
Eight U.S. Coals Studied

	ND B. Zap	WY PRB	IN #6 Gibson	OH Gatling	IL#6 Galatia	KY #11	OH Mahoning	Pitt. #8
RANK	**Lignite**	**Sub-Bit.**	**hvCb Bit**	**hvBb Bit**	**hvBb Bit**	**hvBb Bit**	**hvAb Bit**	**mvAb Bit**
PROXIMATE ANALYSIS (ASTM D-5142), As Received (weight %)								
Moisture	27.33	24.59	7.25	3.77	5.40	3.39	2.22	1.05
Ash	8.66	5.14	7.20	11.34	8.65	8.46	9.92	10.45
Volatile Matter	33.77	37.00	30.87	40.73	35.68	36.97	40.79	18.61
Fixed Carbon	30.24	33.27	54.68	44.16	50.27	51.18	47.07	69.89
ULTIMATE ANALYSIS (ASTM D-5142 / 5373), As Received (weight %)								
Moisture	27.33	24.59	7.25	3.77	5.40	3.39	2.22	1.05
Hydrogen	2.03	2.55	4.02	4.07	3.74	4.34	4.18	3.86
Carbon	46.56	54.75	69.48	67.11	70.16	70.89	74.67	77.37
Nitrogen	0.86	0.83	1.36	0.94	1.04	1.23	0.93	1.44
Sulfur	0.67	0.25	1.14	4.31	2.69	3.64	1.96	1.03
Oxygen	13.89	11.89	9.55	8.46	8.32	8.05	6.12	4.80
Ash	8.66	5.14	7.20	11.34	8.65	8.46	9.92	10.45
Chloride (wet basis)	0.001	0.001	0.212	0.039	0.389	0.206	0.199	0.0045
HEATING VALUE (ASTM D-5865), As Received (Btu/lb)								
Heating Value	7,792	9,156	12,400	12,191	12,575	12,905	13,404	13,715

Mine Locations of Eight U.S. Coals Studied

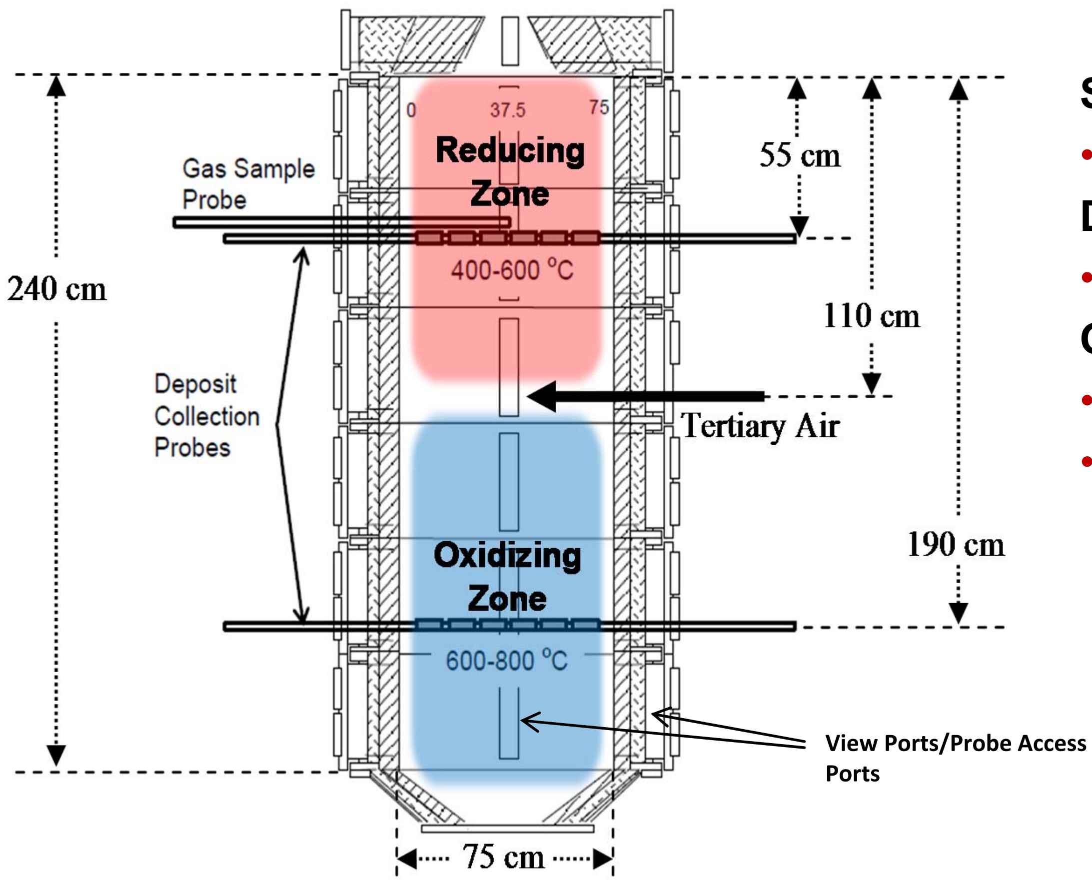
Pilot-Scale Combustion Testing Facility





- Down-fired combustor
- Variable swirl burner
- 160 KW_{th}
- Pulverized coal
- Swirl stabilized flame
- Staged air combustion

Gas and Deposit Sampling in Pilot-Scale Test Facility



Staged Air Combustion

- S.R. = 0.85 in burner zone

Deposit Sampling

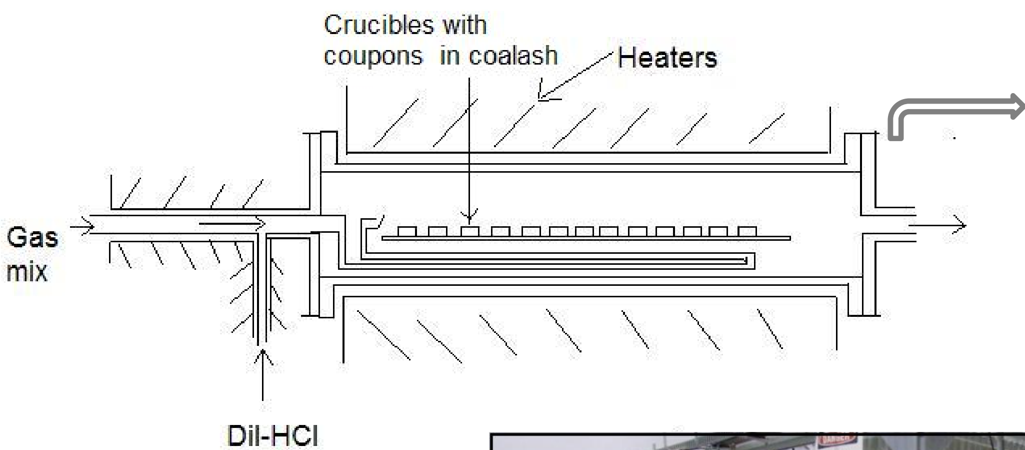
- Water-cooled deposition probe

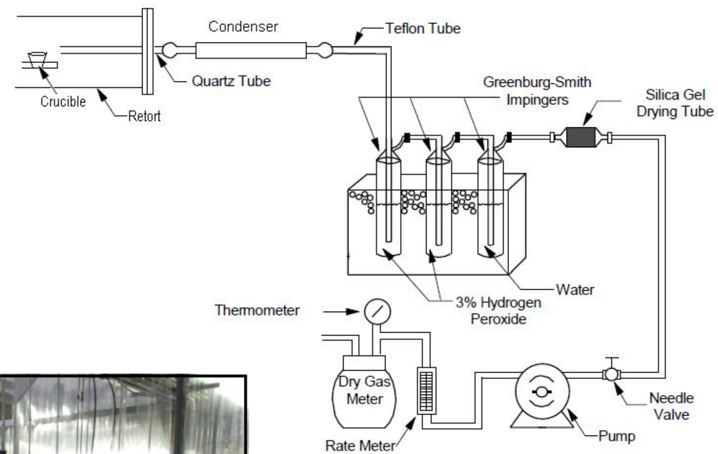
Online Gas Measurement

- FTIR + GC
- Heated sampling line (180°C) from furnace to analyzers

Laboratory Fireside Corrosion Testing

1000 hours/test

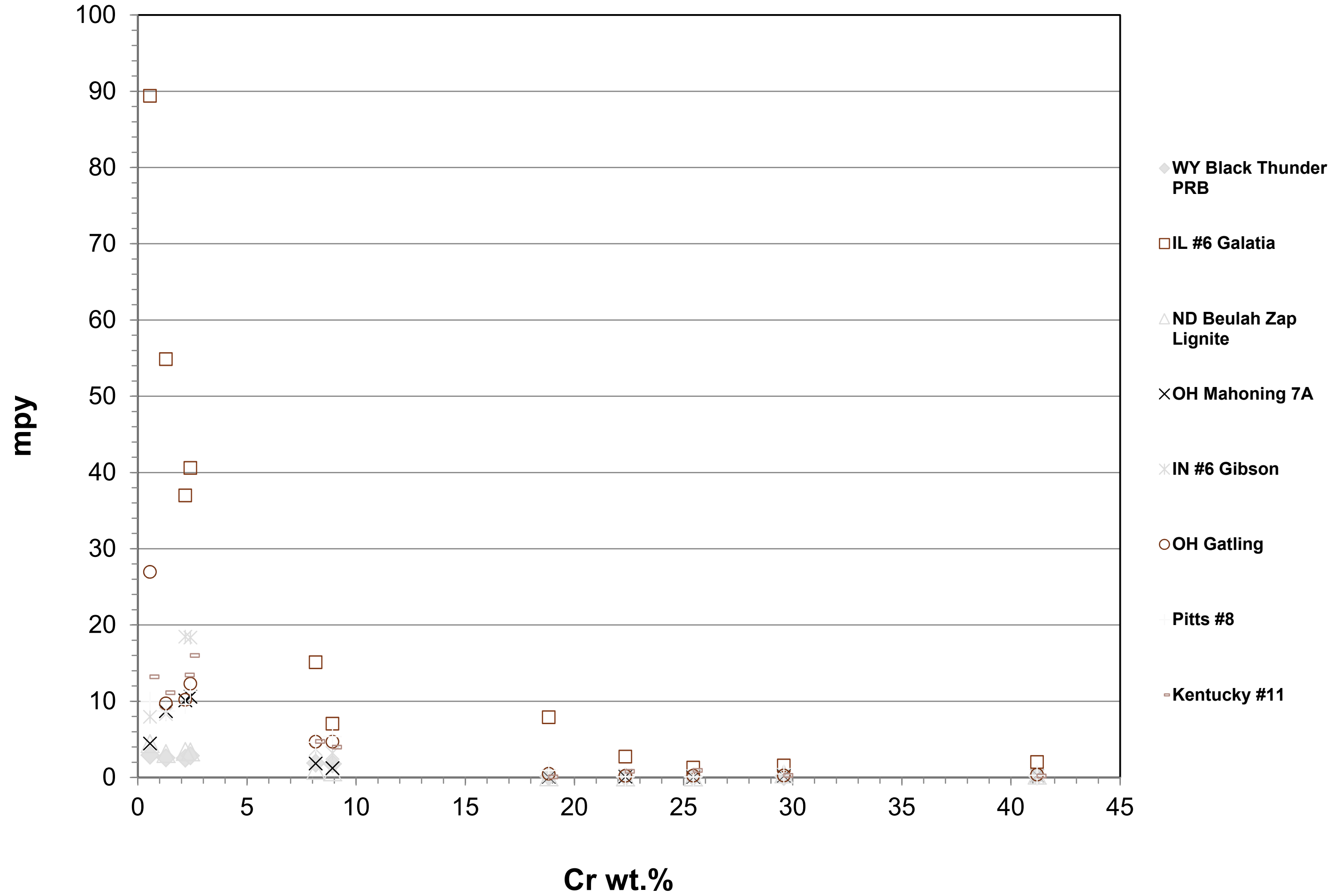




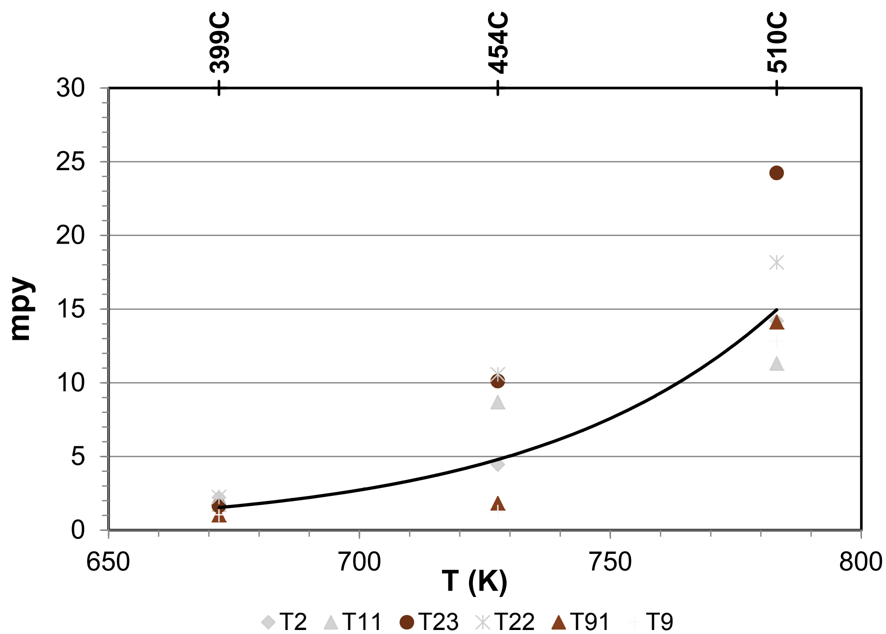
Materials Evaluated in Laboratory Corrosion Tests

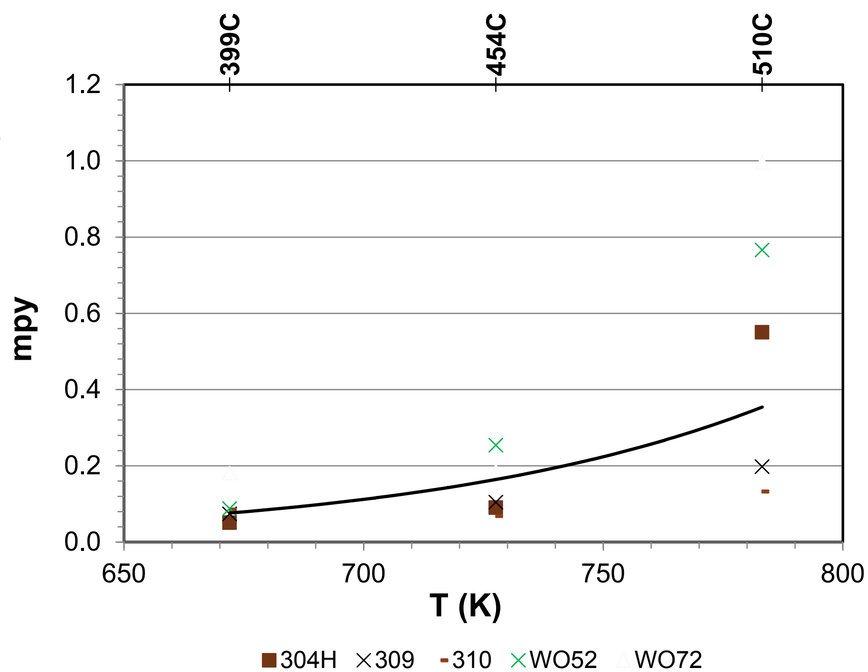
	T2	T11	T23	T22	Grade 91	Grade 9	304H	309H	310H	WO 52	WO 72
UNS#	K11547	K11597	K40714	K21590	K90901	K90941	S30409	S30909	S31009	N06052	N06072
Ni		0.04		0.13	0.14		11	12.48	19.37	56.3	47.2
Cr	0.56	1.29	2.18	2.41	8.15	8.92	18.83	22.34	25.45	29.6	>41.2
Fe		BAL	Bal	Bal	Bal	Bal	Bal	Bal	Bal	12.2	10.6
Mo	0.46	0.52	0.21	0.96	0.91	0.97		0.09	0.40	0.03	0.07
Co										0.003	0.02
C	0.12	0.07	0.084	0.15	0.11	0.110	0.05	0.05	0.04	0.029	0.023
N			0.0076		0.044	0.013					
B			0.001								
Mn	0.56	0.47	0.50	0.5	0.39	0.37	1.8	1.62	1.63	0.29	0.11
Si	0.20	0.59	0.25	0.23	0.27	0.73	0.45	0.31	0.63	0.2	0.16
Al		0.019	0.027	0.021	0.017	0.009				0.7	0.14
Ti				0.001	0.002					0.53	0.44
Nb			0.034		0.095						
Nb+Ta										0.02	0.02
V		0.001	0.25	0.013	0.21	0.03				0.02	0.02
W			1.46							ND	ND
Cu		0.06		0.19	0.25	0.19		0.40	0.17	0.02	0.03
P	0.011	0.018	0.009	0.008	0.014	0.016	0.01	0.023	0.021		
S	0.002	0.009	<0.001	0.013	0.004	0.006	0.013	0.003	0.0004		
Others		0.007 Sn			0.020 Sn	0.011 Sn				0.058	

Corrosion Rate vs. Cr wt.%

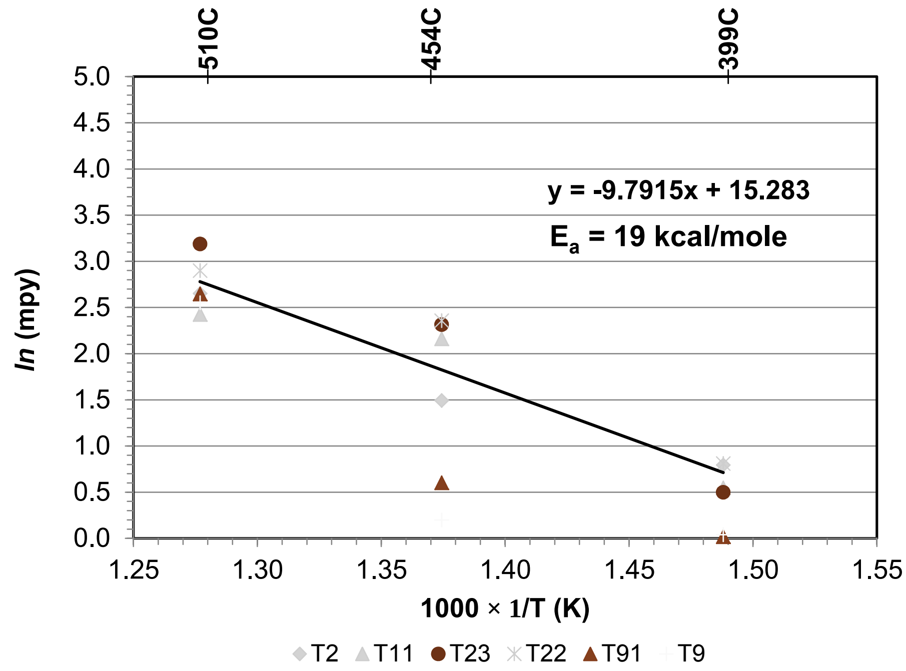


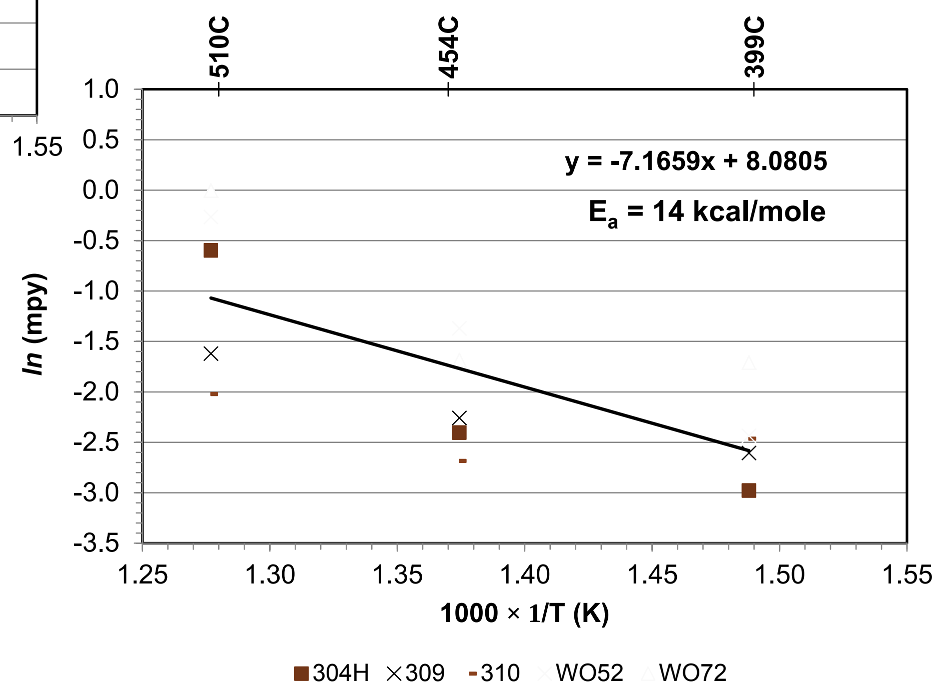
Corrosion Rate vs. Temperature



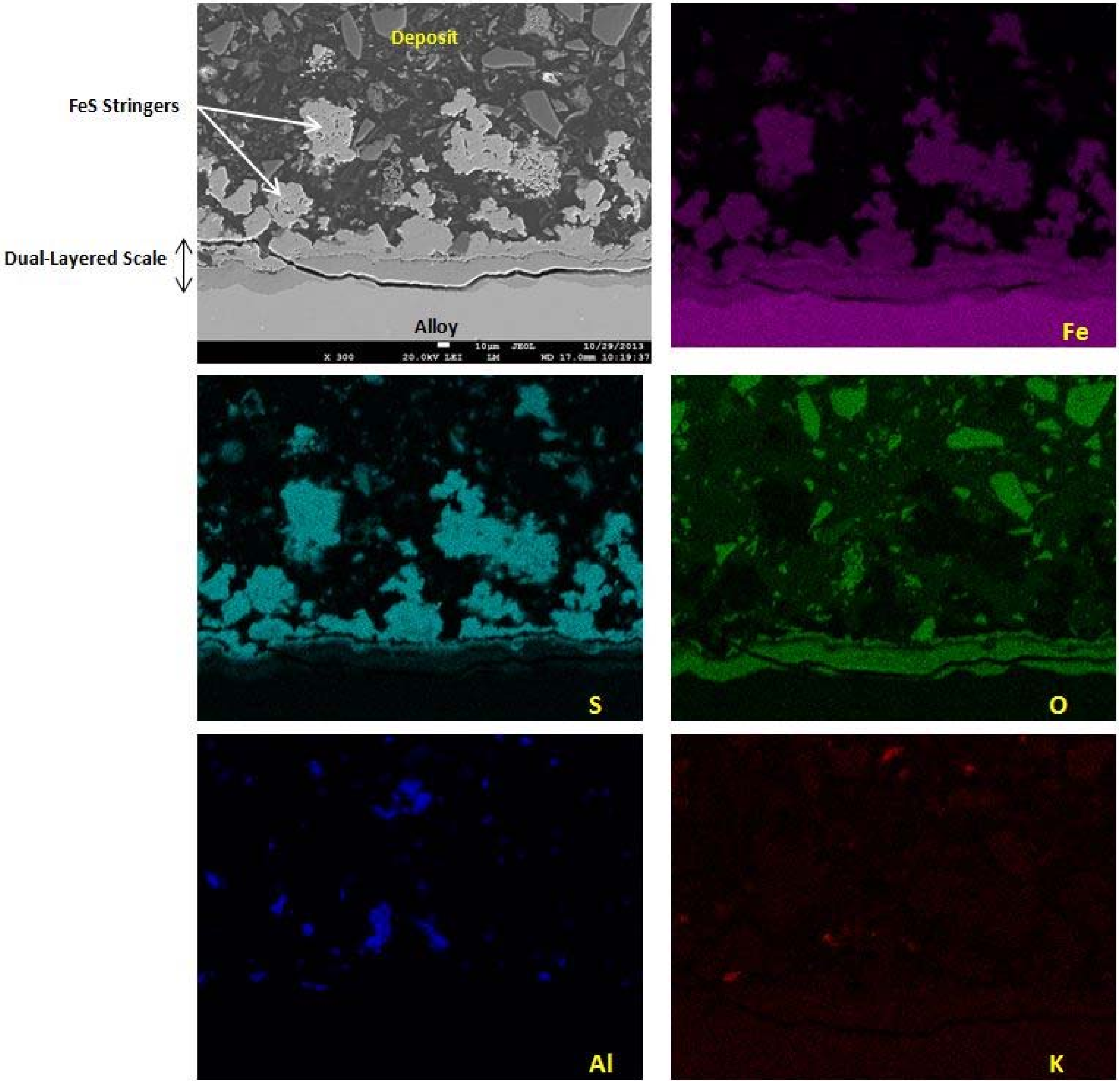


Corrosion Rate vs. 1/T

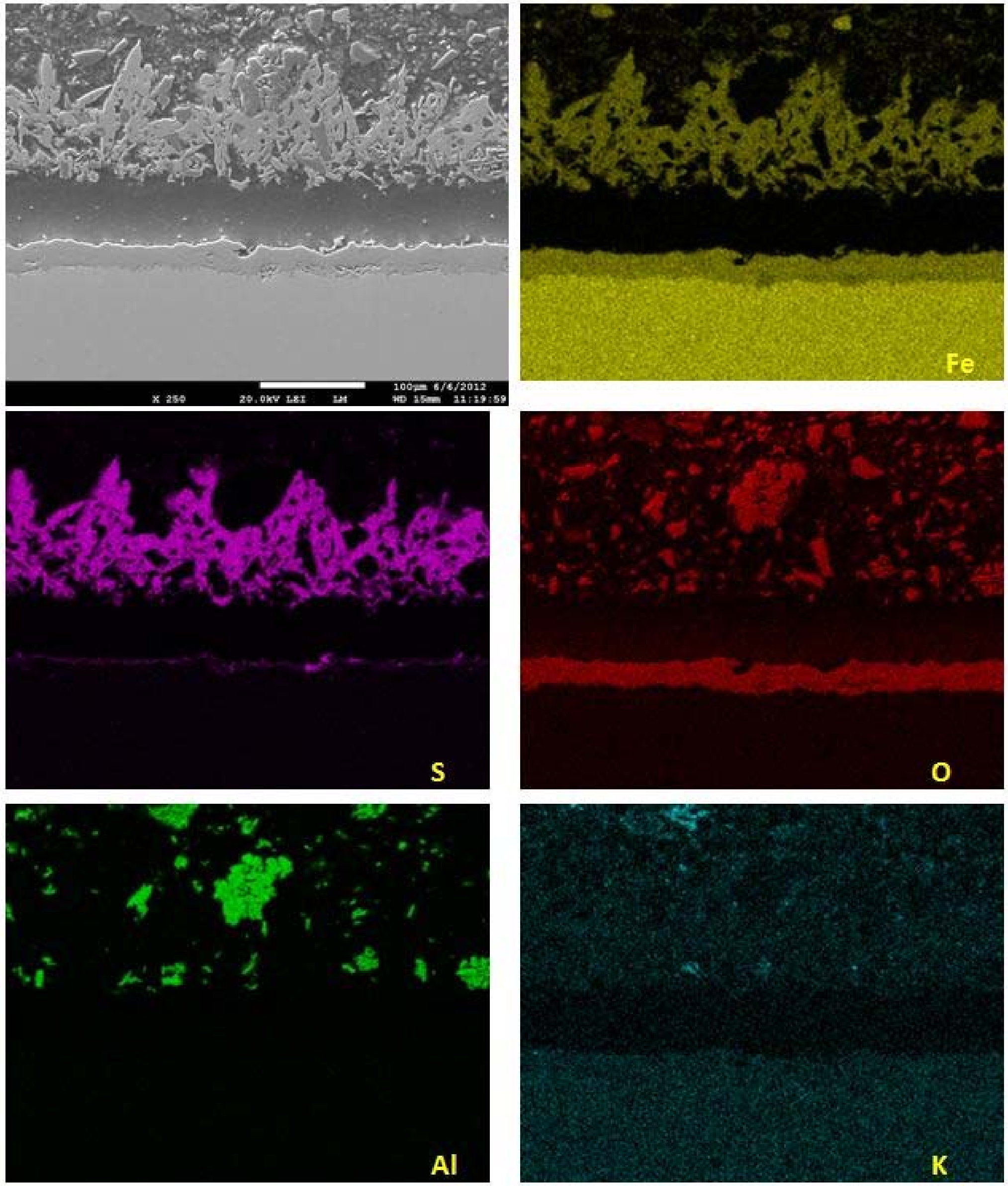




SEM/EDS Analysis of T11 after Exposure to OH Gatling at 454°C



SEM/EDS Analysis of T11 after Exposure to OH Mahoning at 454°C



Active Sulfidation Mechanism Proposed for Low-Alloy Ferritic Steels

- **At deposit/FeS interface** → high Fe activity

  $FeS\ (s) + 2\ HCl\ (g) = FeCl_2\ (g) + H_2S\ (g)$

  or

  $\underline{Fe} + 2\ HCl\ (g) = FeCl_2\ (g) + H_2\ (g)$

- **Away from base of deposit**→ low Fe activity

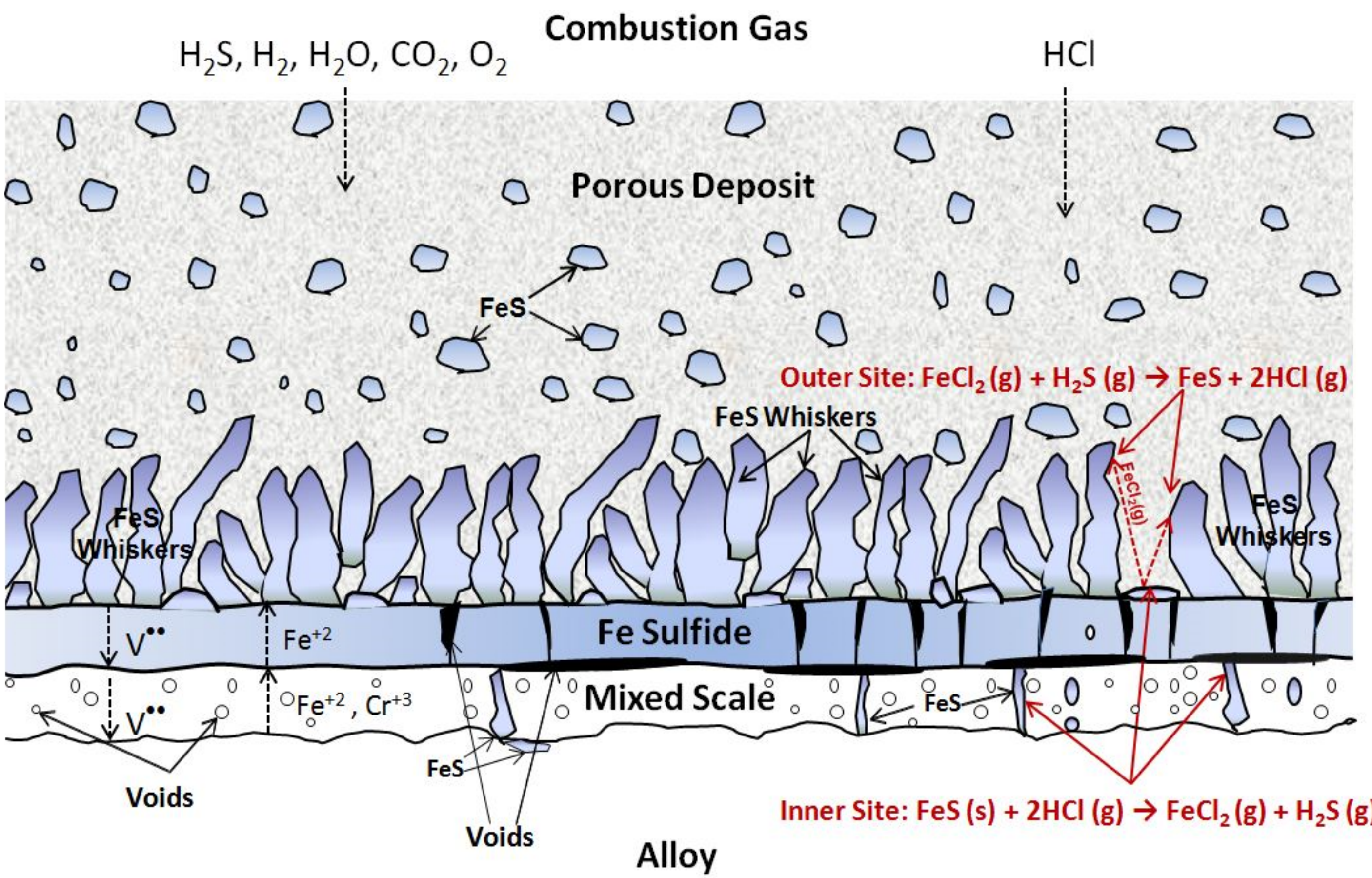
  $FeCl_2\ (g) + H_2S\ (g) = FeS\ (s) + 2\ HCl\ (g)$

  or

  $FeCl_2\ (g) + H_2\ (g) = \underline{Fe} + 2\ HCl\ (g)$

- **Cyclic reactions → Active Sulfidation**
  - Corrosion product of FeS in contact with HCl
  - Outward diffusion of $FeCl_2$ vapor into deposit
  - Porous FeS stringers formed in deposit
  - Condensed chloride not required

Active Sulfidation Mechanism



Maximum Rate of Active Sulfidation Mechanism

IL #6 Galatia Coal at 454°C

$FeS\ (s) + 2\ HCl\ (g) = FeCl_2\ (g) + H_2S\ (g)$

Thermodynamic data:

$$\log P_{FeCl2} = \log (P^2_{HCl}/P_{H2S}) + \log a_{Fe} - 1.456$$

Hertz-Knudsen equation:

$$P\ (torr) = 17.14 \times (T/M)^{1/2} \times G$$

G = evaporation rate

Apply test conditions:

$$G = 4.1 \times 10^{-6}\ gm/cm^2\text{-sec}$$

$$= 6{,}400\ mpy$$

- Corrosion mechanism governed by diffusion process (assisted by chlorine)

Conclusions

- Comprehensive study on furnace wall corrosion performed
- A new corrosion mechanism, Active Sulfidation, identified and proposed for low-alloy ferritic steels (less important for austenitic and nickel-base alloys)
- The role of chlorine in furnace wall corrosion revealed
- The presence of chlorine accelerates overall sulfidation via $FeCl_2$(g) cyclic reactions

Acknowledgement

- Work supported by U.S. Department of Energy with B&W cost share
- NETL Project Manager (DE-FC26-07NT43097): Vito Cedro
- Consultant: Professor Robert A. Rapp, Ohio State University