Oxy-Combustion Boiler Material Development

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2011 NETL CO_2 Capture Technology Meeting
Pittsburgh, PA
August 22-26, 2011

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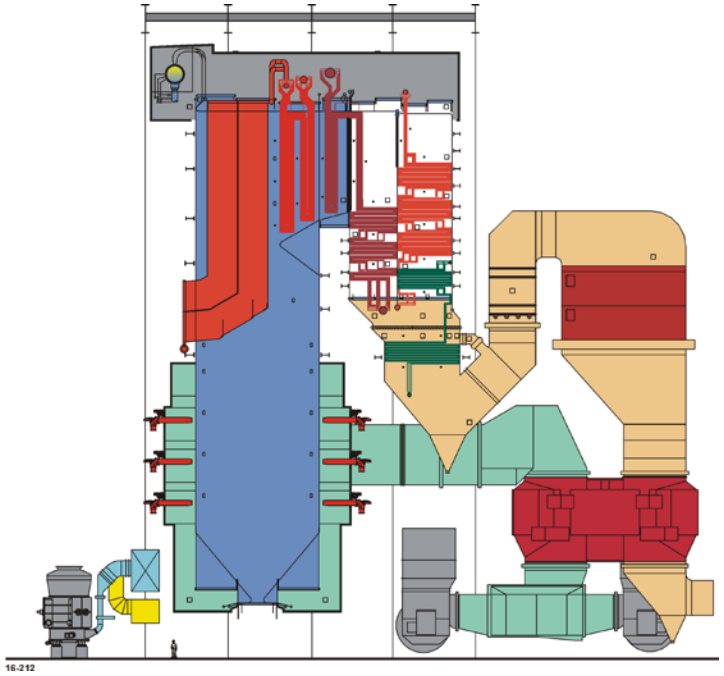
US DOE Cooperative Agreement DE-NT0005262
Project Objectives



Typical Pulverized Coal-Fired (PC)Boiler

Facilitate Retrofit of PC Boilers with Oxy-Combustion for Carbon Capture and Sequestration

- Assess Corrosiveness of Oxy Flue Gas
- Identify Oxy Corrosion Mechanisms
- Determine Oxy Effects on Boiler Materials
- Recommend Materials for Oxy Boilers

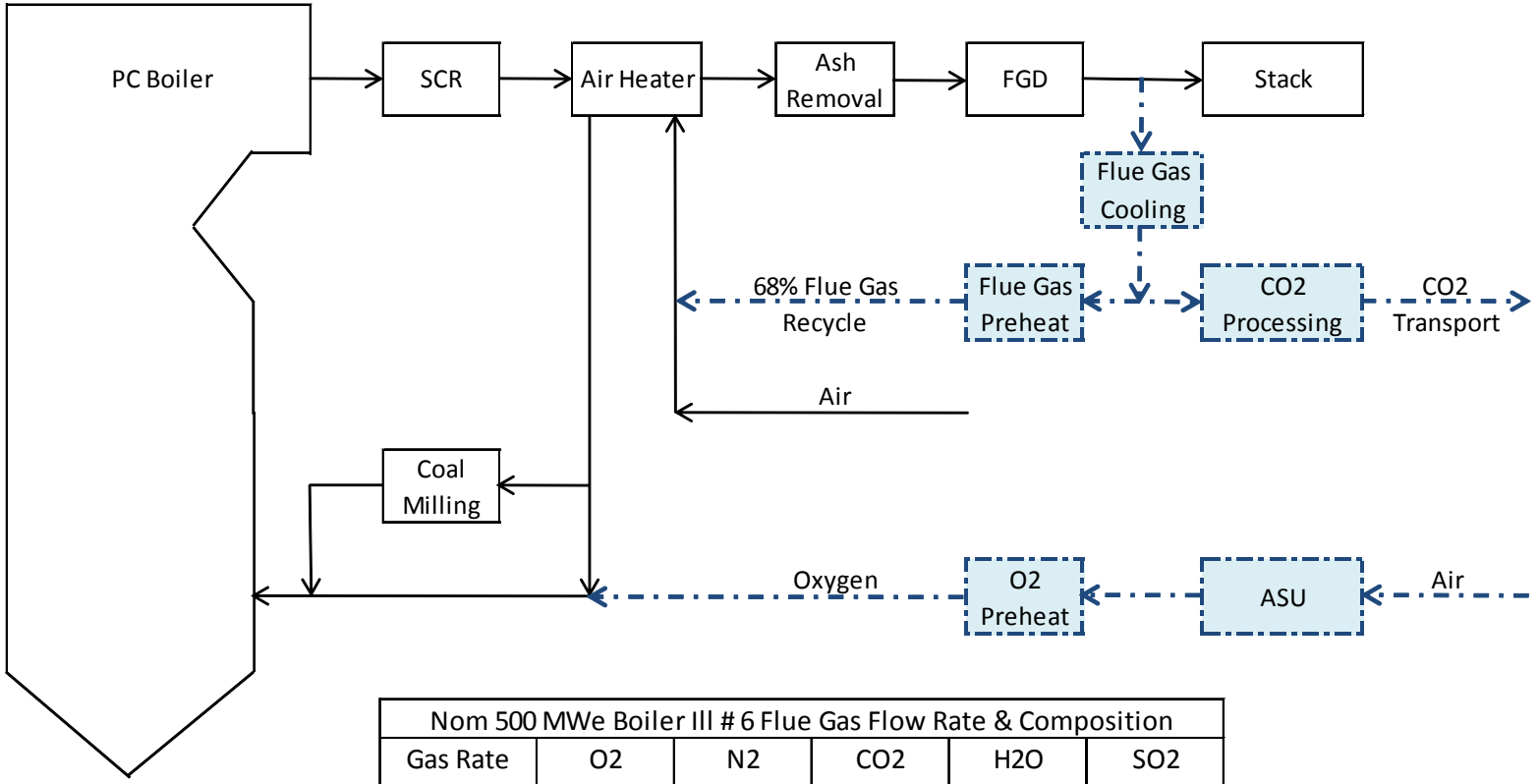
Boiler Fireside Corrosion

- **Corrosion Rates Influenced by Composition and Temperature of:**
  - Tube Materials
  - Deposits
  - Bulk Flue Gas and Wall Micro Climates
- **Corrosion Mechanisms Vary with Boiler Locations**
  - Furnace Walls From Reducing Gases and Incompletely Burned Coal
  - Superheater / Reheaters From Condensing Vapors and Deposits

Oxy-Combustion Boiler Retrofits will Utilize Flue Gas Recycle

- **Replaces Air N_2 and Enables Operation w/o Boiler De-rating**
  - Set to Maintain Air-Fired Boiler Heat Absorption
  - Limits Combustion Temperature and “Saves” the Boiler
- **Results in Dramatically Different Flue Gas (High CO_2 + H_2O)**
- **Increases Flue Gas Levels of Corrosive Contaminants**
  - 3 to 5 Fold Increase if Flue Gas is Not “Cleaned” Before Recycle
- **To Minimize Risks Extract Recycle Downstream of FGD**

Simplified Schematic of Oxy-Fired Boiler Retrofit



Nom 500 MWe Boiler Ill # 6 Flue Gas Flow Rate & Composition						
	Gas Rate 10^6lb/hr	O2 Vol%	N2 Vol%	CO2 Vol%	H2O Vol%	SO2 ppmv wet
Air-Firing	3.6	3.0	73.4	13.8	9.1	2030
Oxy-Firing	3.1	2.7	8.2	67.2	20.6	3170*

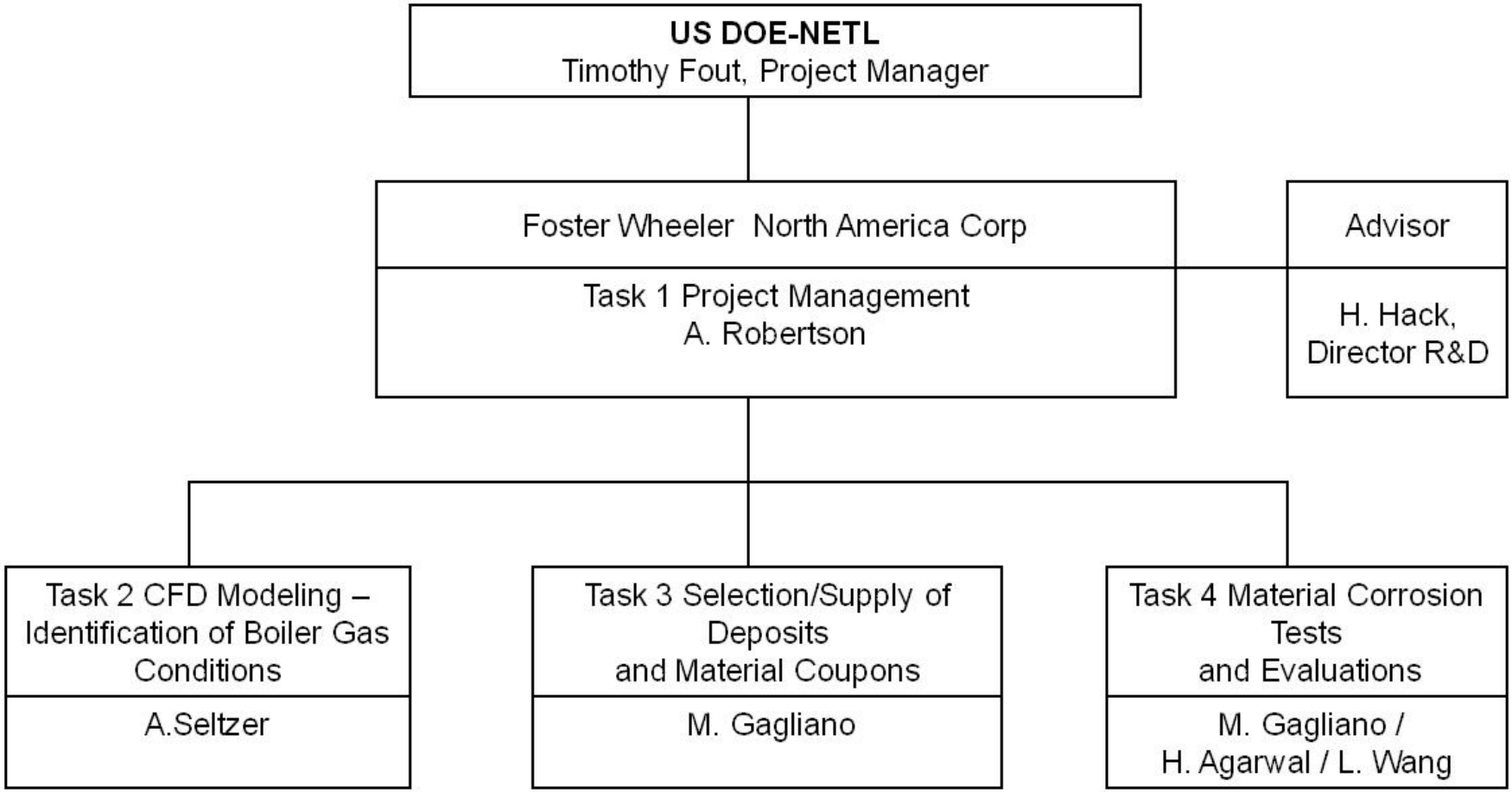
Retrofit Changes

*FGD at 86% Efficiency for Worst Case Boiler SO2 Levels

Project Approach

- **Conduct Fire-Side CFD Analyses of PC Boilers to Determine:**
  - Oxy Flue Gas Recycle to Maintain Air-Fired Heat Absorption
  - Composition of Bulk Flue Gas and Wall Micro-Climates
- **Subject Materials to CFD Predicted Worst Case Gas Compositions**
  - Conduct Tests in Electric Tube Furnaces
  - Measure Material Wastage Rates
- **Recommend Materials for Oxy Retrofit and New Applications**

Project Organization and Tasks



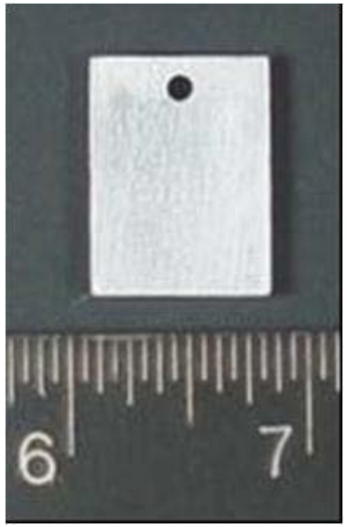
Project Costs

Budget Period	Calendar Year	Total Costs	DOE Portion at 80%	FW Portion at 20%
1	2009	$798,107	$638,486	$159,621
2	2010	$666,025	$532,820	$133,205
3	2011	$527,662	$422,130	$105,532
Totals		$1,991,794	$1,593,435	$398,359

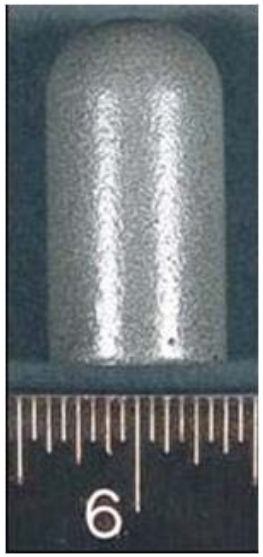
Electric Furnace Corrosion Testing at Foster Wheeler

- **Used to Screen Materials and Study Corrosion Mechanisms**
  - Materials Coated with Deposits
  - Exposed to Gases at Elevated Temperature in Sealed Furnaces
- **Gases Synthesized from Pressurized Cylinders**
- **Deposits Produced from Reagent Grade Powders**
- **Tests Involve Up to 1000 Hrs of Exposure Time**
  - Materials Inspected & Recoated with Deposits Every 100 Hours

Typical Material Test Coupons

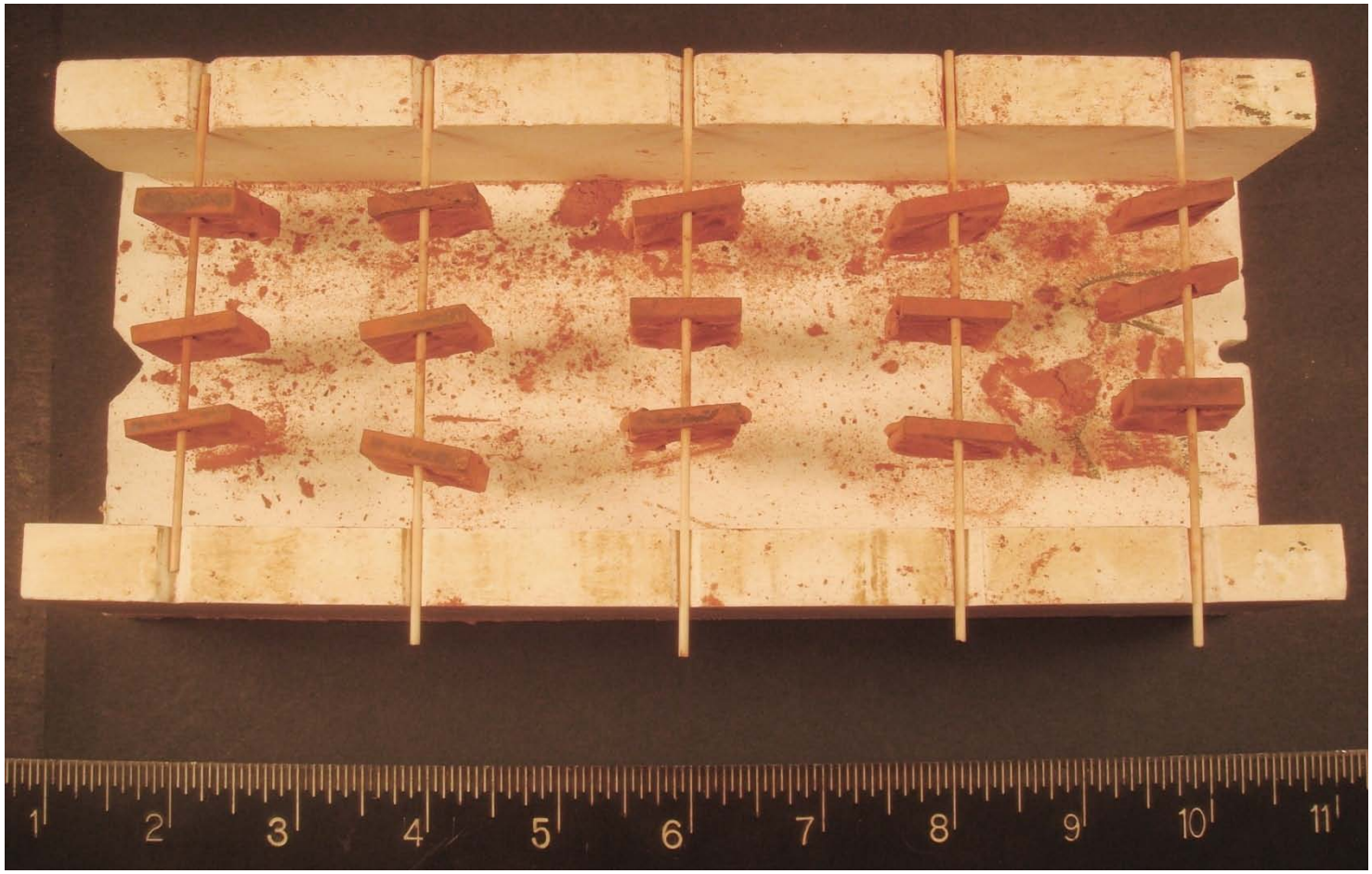


Rectangular Shaped
1/8” T x ¾” W x 1” H

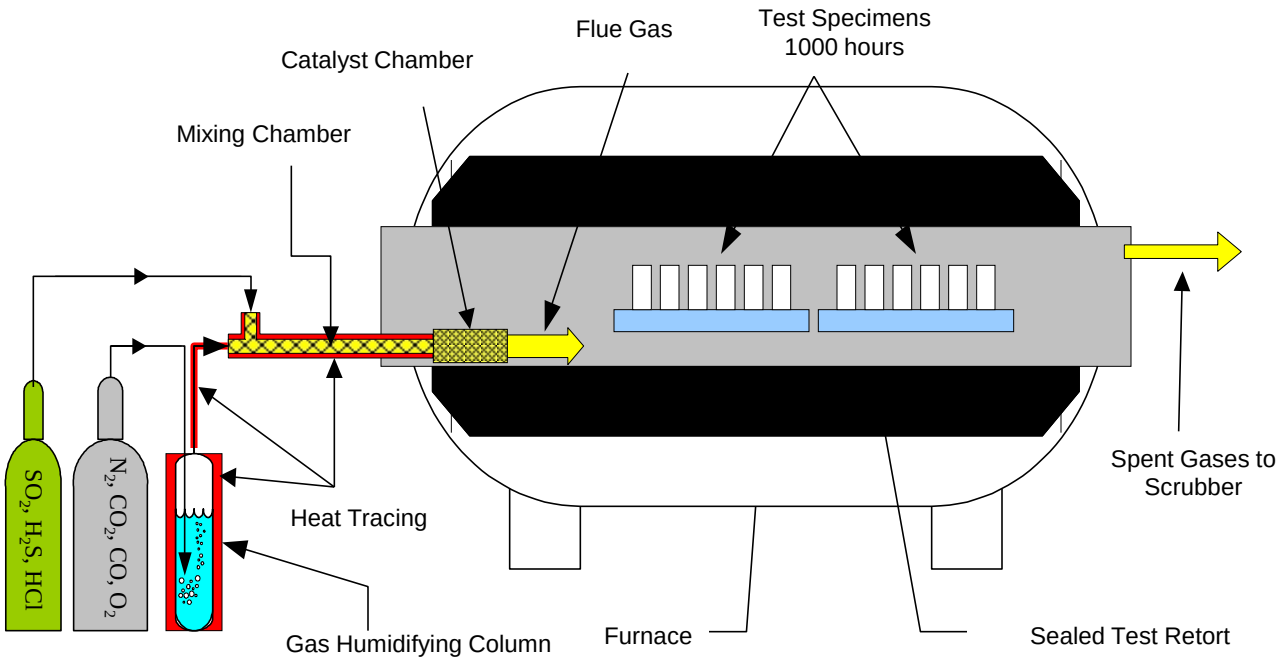


Bullet Shaped
¾” Dia x 1-1/2” H
(Used for Coatings)

Typical Test Rack Coupon Arrangement



Simplified Electric Furnace Test Schematic



Selection of Test Gas Compositions

- **Two Nominal 500 MWe Air-Fired Boilers Studied**
  - One Wall-Fired - the Other Tangential-Fired
  - Air-Fired Performance Determined with Three Coals
    - 2.5% Sulfur Illinois # 6 with FGD
    - 0.7% Sulfur Coal for 1.2 lbs/10^6 BTU Stack (no FGD)
    - 0.3% Sulfur Eagle Butte Coal with FGD
  - Boiler Performance Re-Determined Under Oxy-Firing
    - Flue Gas Recycle Set to Maintain Air-Fired Boiler Heat Absorption
  - Investigated Effect of Alternate Flue Gas Recycle Extraction Points

Effect of Recycle Flue Gas on Boiler SO_2 Levels

Coal Sulfur Wt %	Firing Mode	Flue Gas Recycle		Boiler SO2 (ppmv wet)	
		Quantity	Sulfur Removal	Air-Fired	Oxy-Fired
0.3	Air	0	NA	300	
0.3	Oxy	70%	0%		1200
0.3	Oxy	70%	70%*		500
0.7	Oxy	71%	0%		2500
2.5	Air	0%	NA	2000	
2.5	Oxy	71%	0%		9100
2.5	Oxy	71%	98%		2700
2.5	Oxy	71%	86%*		2900
2.5	Oxy	68%	86%*		3200

*NSPS Minimum Plant Requirement

- **9100 ppmv wet SO_2 Condition Unacceptable for Boiler Retrofits**
  - Excessive Shtr/Rhtr Corrosion will Require Major / Expensive Upgrades
  - 3200 ppmv wet SO_2 Should be an Upper Limit for Retrofits
- **3200 ppmv wet SO_2 Conditions Selected for Corrosion Testing**

Ill #6 Wall-Fired Boiler Gas Conditions Selected for Testing

- **Wall-Fired Boiler Had Strongest Furnace Wall Reducing Zones**
  - 68% Flue Gas Recycle Matched Air-Fired Boiler Heat Absorption
  - Flue Gas Mixed with O_2 Yielded 28% O_2 by Volume to Boiler
  - Maximum Furnace Wall Heat Flux ~5% Lower than Air-Fired
  - Bulk Gas SO_2 Levels (ppmv wet): 3200 Oxy-Firing vs 2000 for Air-Firing
  - Strongest Furnace Wall Reducing Zones at:

	CO	H_2S	CO_2	H_2O
Air-Fired	9%	0.14%	11%	8%
Oxy-Fired	20%	0.26%	48%	18%

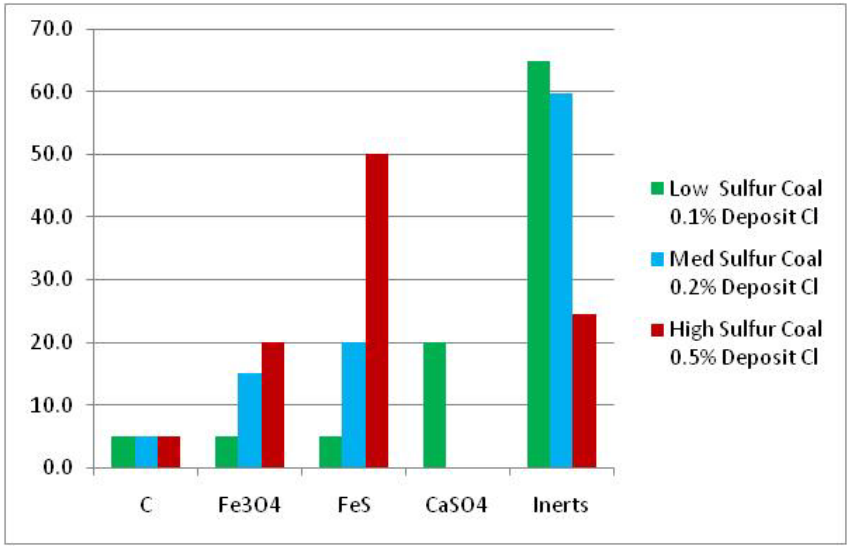
Corrosion Test Gas Compositions (Vol%)

Gas	Waterwall: Oxy-Combustion			
	20% CO	5% CO	2% CO	1% O_2
CO_2	55%	67%	69%	70%
H_2O	18%	20%	20%	21%
N_2	7%	8%	8%	8%
H_2S	0.26%	0.07%	0.03%	0.00%
SO_2	0.17%	0.29%	0.30%	0.32%
HCl	0.02%	0.02%	0.02%	0.02%
Total	100%	100%	100%	100%

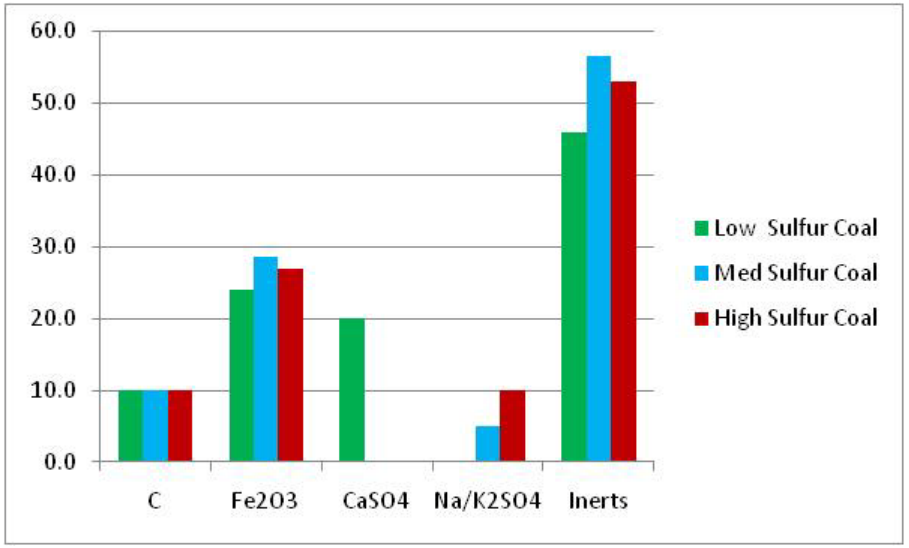
Gas	Waterwall: Air-Fired		
	5% CO	2% CO	1% O_2
CO_2	13%	14%	14%
H_2O	9%	9%	9%
N_2	73%	74%	76%
H_2S	0.08%	0.03%	0.00%
SO_2	0.19%	0.21%	0.20%
HCl	0.02%	0.02%	0.02%
Total	100%	100%	100%

Gas	Superheater/Reheater	
	Oxy: 2% O_2	Air: 3% O_2
CO_2	69%	14%
H_2O	21%	9%
N_2	8%	74%
H_2S	0.00%	0.00%
SO_2	0.32%	0.20%
HCl	0.02%	0.02%
Total	100%	100%

Corrosion Test Deposit Compositions (Wt%)



Waterwalls



Superheater/Reheater

Boiler Materials Selected for Corrosion Tests

- **10 Waterwall and 10 Superheater/Reheater Materials Selected**
  - Waterwalls Tested at 750ºF, 875ºF and 1000ºF
  - Superheater / Reheater Tested at 1000ºF, 1100ºF, & 1200ºF
- **Each Material Coated with 3 Different Deposits**
  - Deposits Representative of High, Medium, & Low Sulfur Coals
    - 3 Furnace Deposits and 3 Superheater / Reheater Deposits
- **Tests Utilized 6 Furnaces and Involved:**
  - 4 Oxy-Fired and 3 Air-Fired Furnace Wall Gas Micro-Climates
  - 1 Oxy-Fired and 1 Air-Fired Superheater / Reheater Bulk Gas Climate

Waterwall Materials Selected for Testing

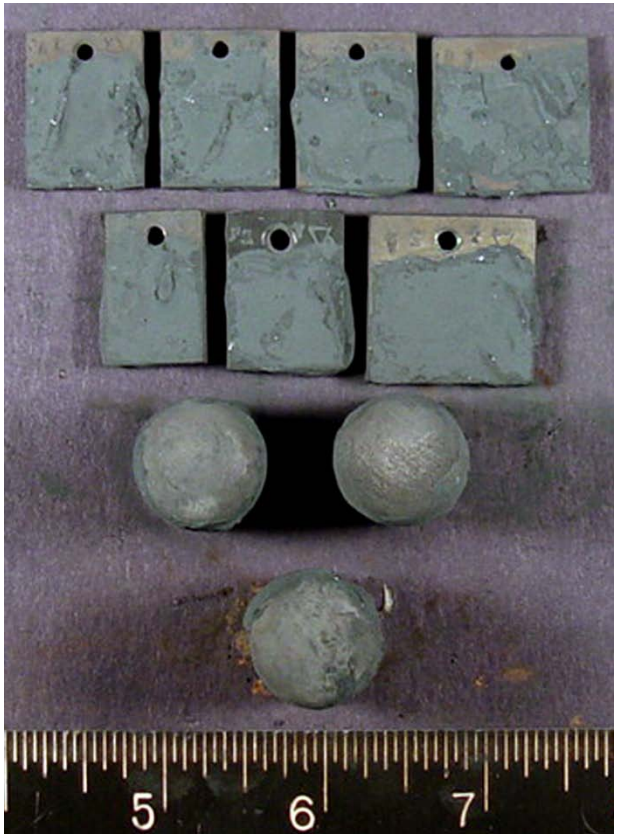
Coupon	Material	Description	Boiler Use	Composition
1	Tube	SA210-A1	Conventional	0.27%Carbon
2	Tube	SA213-T2	Conventional	1/2 Cr-1/2Mo
3	Tube	SA213-T11	Conventional	1-1/4Cr-1/2Mo
4	Weld	T11 to T11	Conventional	1-1/4Cr-1/2Mo
5	Weld Overlay	309L StnStl	Conventional	24Cr-13Ni
6	Weld Overlay	Inconel 622	Conventional	21Cr-58Ni
7	Weld Overlay	VDM Alloy 33	Conventional	33Cr-31Ni
8	Thermal Spray	IGS UTEx 5-500	Relatively New	15Cr-80Fe
9	Thermal Spray	IGS UTEx 5-480	Relatively New	25Cr-60Ni
10	Thermal Spray	IGS UTEx 5-450	Relatively New	40Cr-55Ni

Superheater/Reheater Materials Selected for Testing

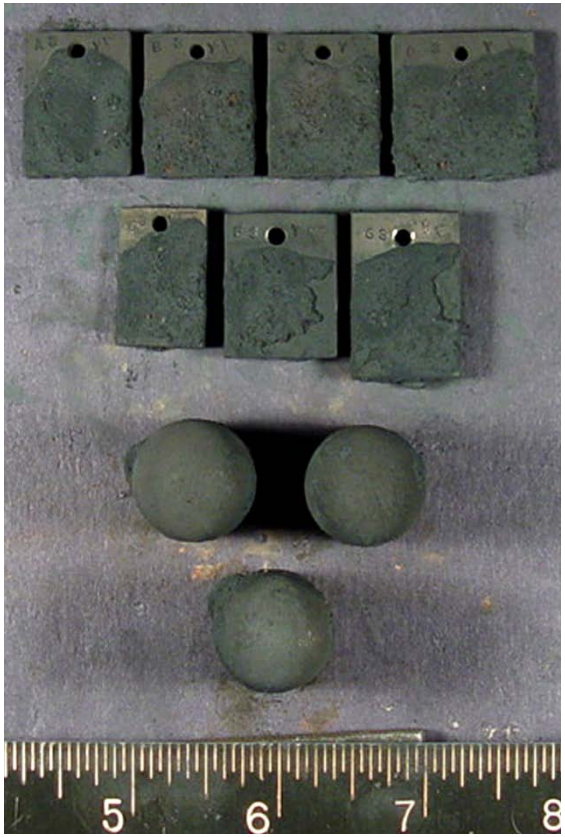
Coupon	Material	Description	Boiler Use	Composition
1	Tube	SA213-T22	Conventional	2-1/4Cr-1Mo
2	Tube	SA213-304H	Conventional	18Cr-8Ni
3	Tube	SA213-347H	Conventional	18Cr-9Ni
4	Weld	T22 to 304H	Conventional	1-1/4 Cr to 18 Cr
5	Tube	SA213-T91	Newer Boilers	9Cr
6	Tube	NF709	Newer Boilers	20Cr-25Ni
7	Tube	HR3C	Newer Boilers	25Cr-20Ni
8	Weld Overlay	Inconel 622	Conventional	21Cr-55Ni
9	Weld Overlay	VDM Alloy 33	Conventional	33Cr-31Ni
10	Weld Overlay	Inconel 72	Conventional	44Cr-55Ni

Waterwall Coupons After 1000 Hr 2% CO Oxy Micro-Climate Test

Low Sulfur Deposit

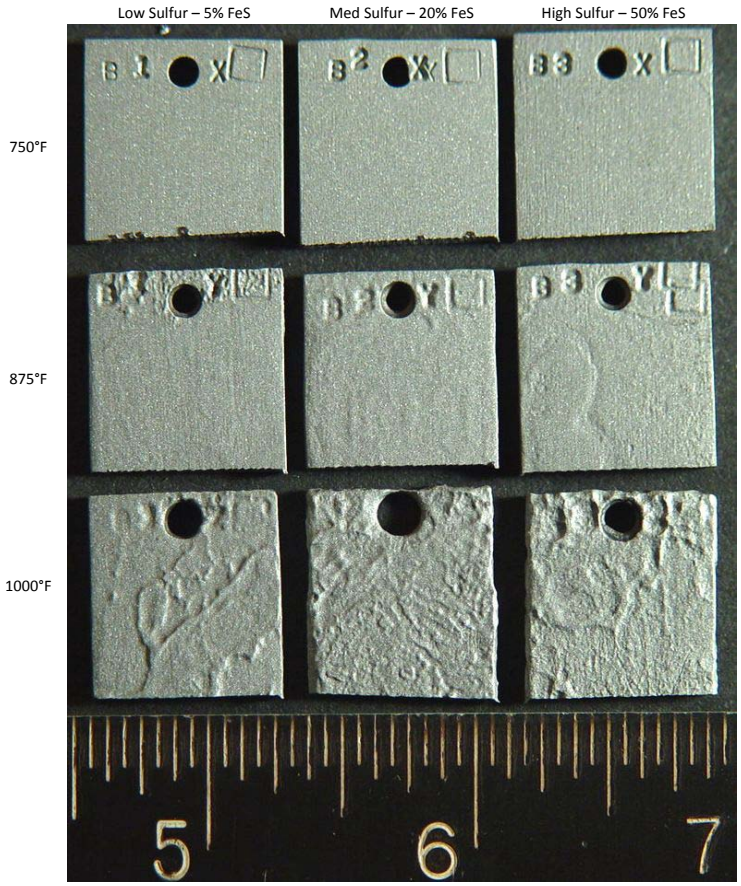


High Sulfur Deposit

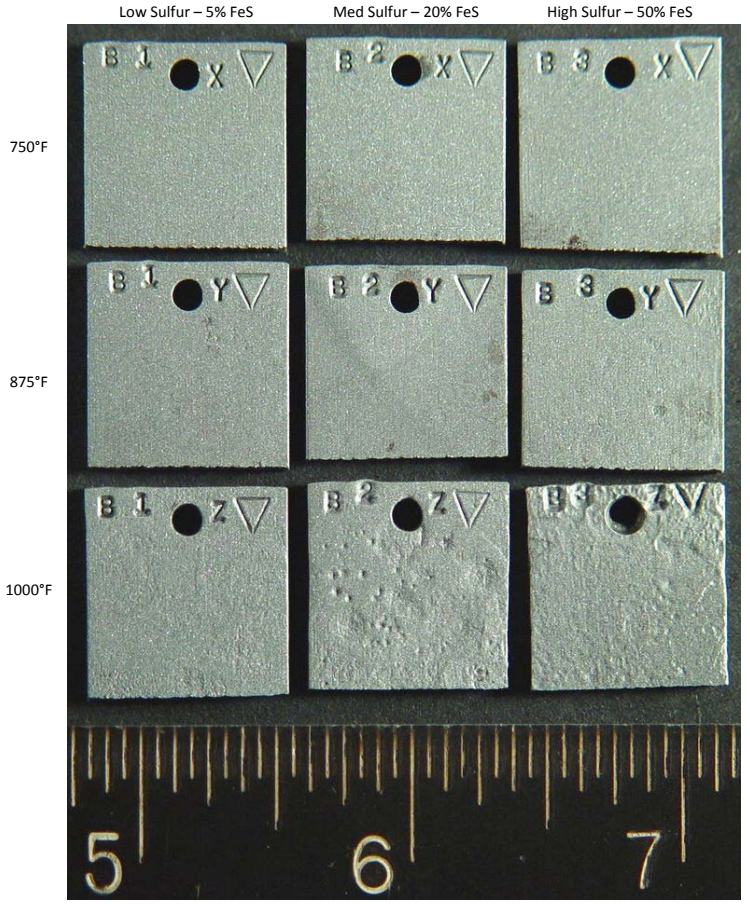


Cleaned Waterwall T2 Coupons After 1000 Hr 2% CO Micro-ClimateTest

Air-Fired

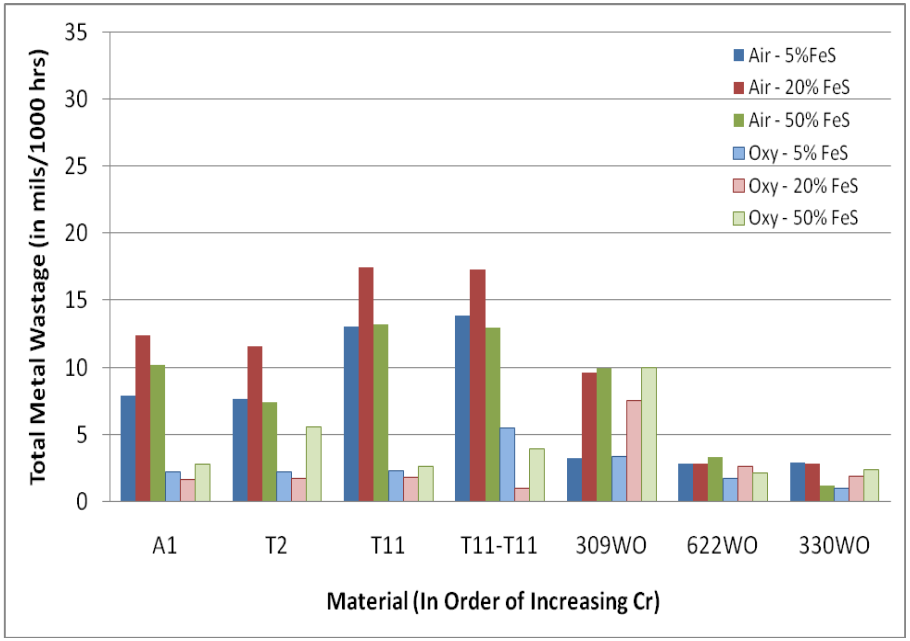


Oxy-Fired

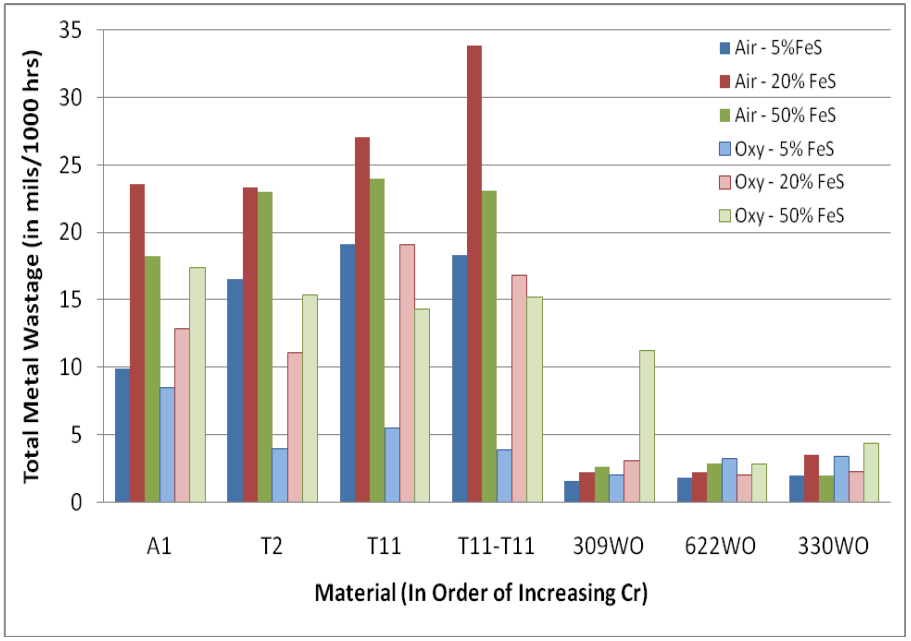


Preliminary Waterwall Material Wastage (2% CO Air and Oxy Micro-Climates)

875°F Test Temperature

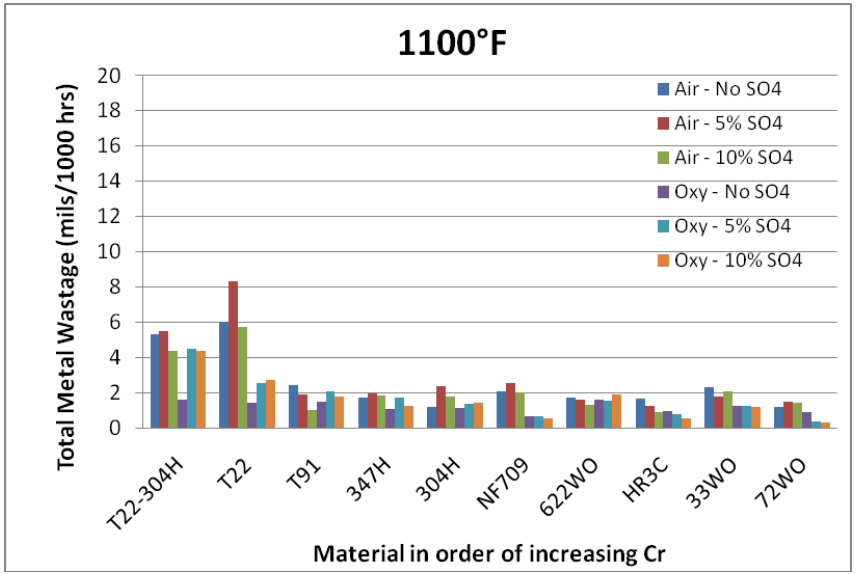


1000°F Test Temperature

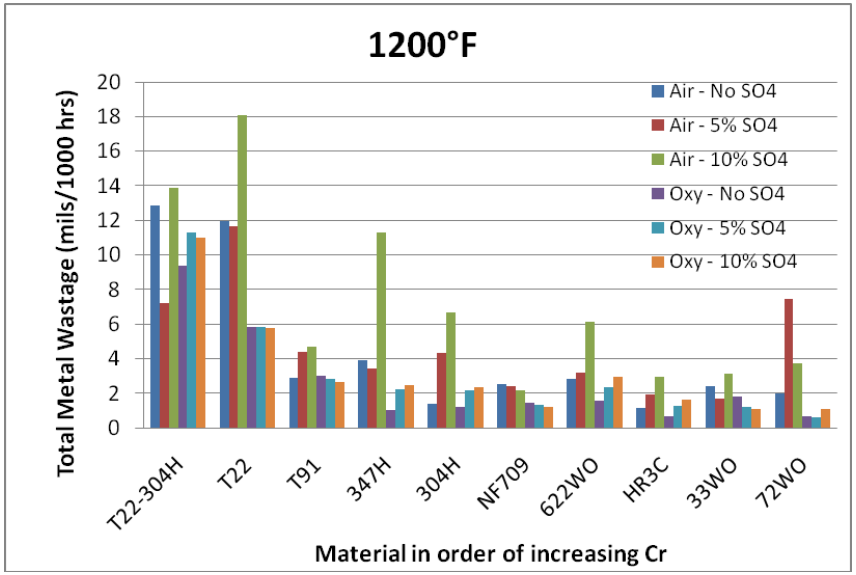


Preliminary Shtr/Rhtr Material Wastage (Test Gas SO_2 ppmv wet : Air @ 2000 Oxy @ 3200)

1100°F Test Temperature



1200°F Test Temperature

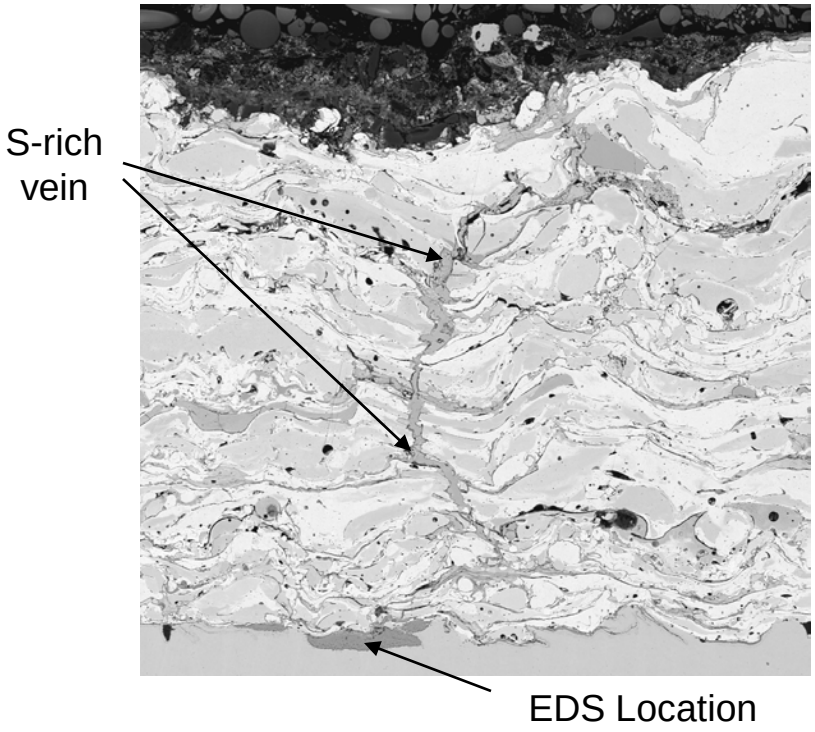


Thermal Spay Coating Performance

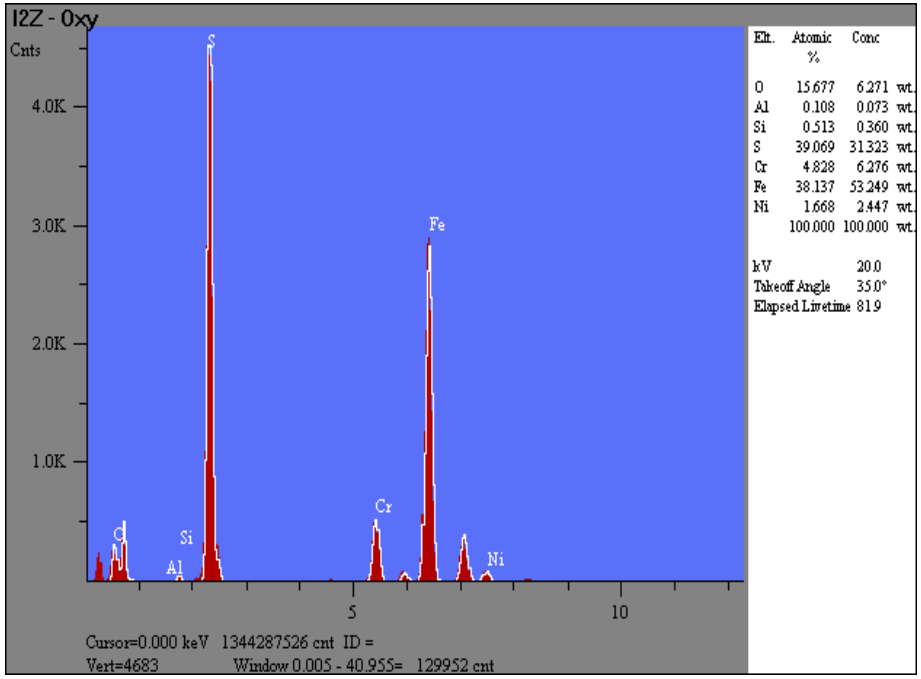
- **3 Different Coatings for Furnace Wall Applications Tested**
  - Low Cost 15 Chrome - 80 Iron to High Cost 40 Chrome - 55 Nickel
  - As Received Coating Thicknesses Ranged from 9 to 16 mils
- **Each Coating Subjected to 63 Different Test Conditions**
  - 4 Oxy and 3 Air-Fired Micro-Climates , 3 Temperatures, and 3 Deposits,
  - Total of 189 Coated Coupons Tested
- **Upon Completion of Testing Each Coupon:**
  - Visually Inspected for Cracking, Fissures, and Spalling
  - Sectioned & SEM/EDS for Penetration of Oxygen and or Sulfur Species

Nominal 25Cr-60Ni UTEx 5-480 Coating After 1000 Hr 2% CO Test @ 1000°F with 20% FeS Deposit

Back Scatter SEM Image Through Coating Thickness



EDS Spectrum of Coating at Substrate Interface



Thermal Spray Coating Performance (Continued)

- **After 1000 Hrs of Exposure All 189 Coatings Remained Intact**
- **Wastage, Cracking, and Fissures Varied with Test Conditions**
  - Most Aggressive Conditions Resulted in Some Bulk Wastage
  - No Coating was Completely Consumed by Corrosion
- **Coatings Allowed Gaseous Diffusion and Penetration**
  - 186 of 189 Evidenced Oxides and or Sulfur at Substrate Interface
  - 3 Remaining Coupons Evidenced 6 to 11 mils of Penetration into Coating
- **Penetration into Substrate was Generally Less than 2 to 4 mils**
- **All Three Coatings May Provide Some Protection but Short Term**

Project Preliminary Findings and Schedule

- **Lab Testing for 3200 ppmv wet Oxy Bulk SO_2 Completed**
- **Oxy Corrosion Varied with Material, Deposit, and Temperature**
- **Lab Tests Suggest Oxy Corrosion Should Not Be a Retrofit Problem**
  - Oxy Corrosion Rates Typically No Worse / Often Less Than Air-Fired
  - Conventional Weld Overlays Can Protect Against Oxy Atmospheres
  - Metallographic Analyses of Coupons Revealed No Carburization
- **Lab Results May Be Consistent with Coal-Fired Pilot Plant Data**
  - Vattenfall Schwartze Pumpe 30 MWt and Univ of Utah 1 MWt Tests
- **Final Report to be Issued End of December 2011**

Acknowledgement and Disclaimer

- **Project Funded by Co-operative Agreement DE-NT0005262**