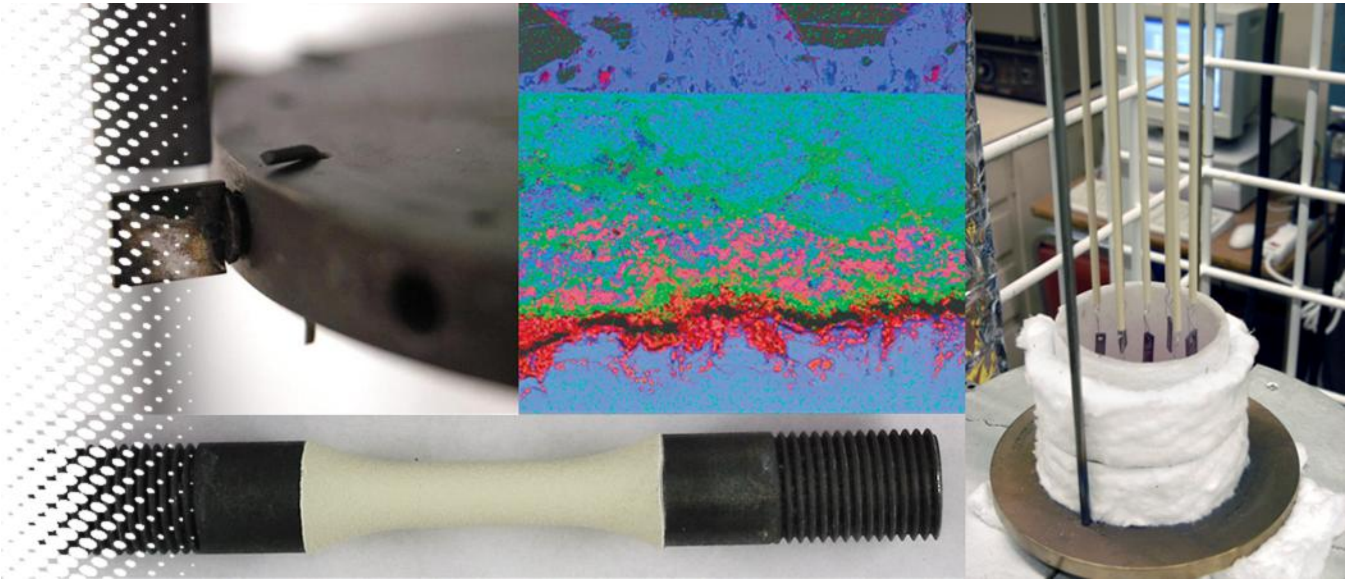
NATIONAL ENERGY TECHNOLOGY LABORATORY



Oxy-Combustion Environment Characterization: Fire- and Steam-Side Corrosion in Advanced Combustion

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NETL-RUA Regional University Alliance

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Outline

Introduction

- Goals
- Project Background

Research Progress

- Long-term oxy-combustion fireside corrosion tests
- Effects of pressure—update on A-USC steam autoclave

Summary

Goals

DOE Office of Clean Coal goal for pulverized coal boilers

- Achieve 90% CO_2 capture at no more than a 35% increase in levelized cost of electricity of post-combustion capture for new and existing conventional coal-fired power plants

Project goals

- Provide high-temperature corrosion information to aid in materials development and selection for oxy-fuel combustion (fireside corrosion) and A-USC steam conditions (steam oxidation)
- Identify corrosion mechanism and behavior differences between air- and oxy-firing

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Project Background

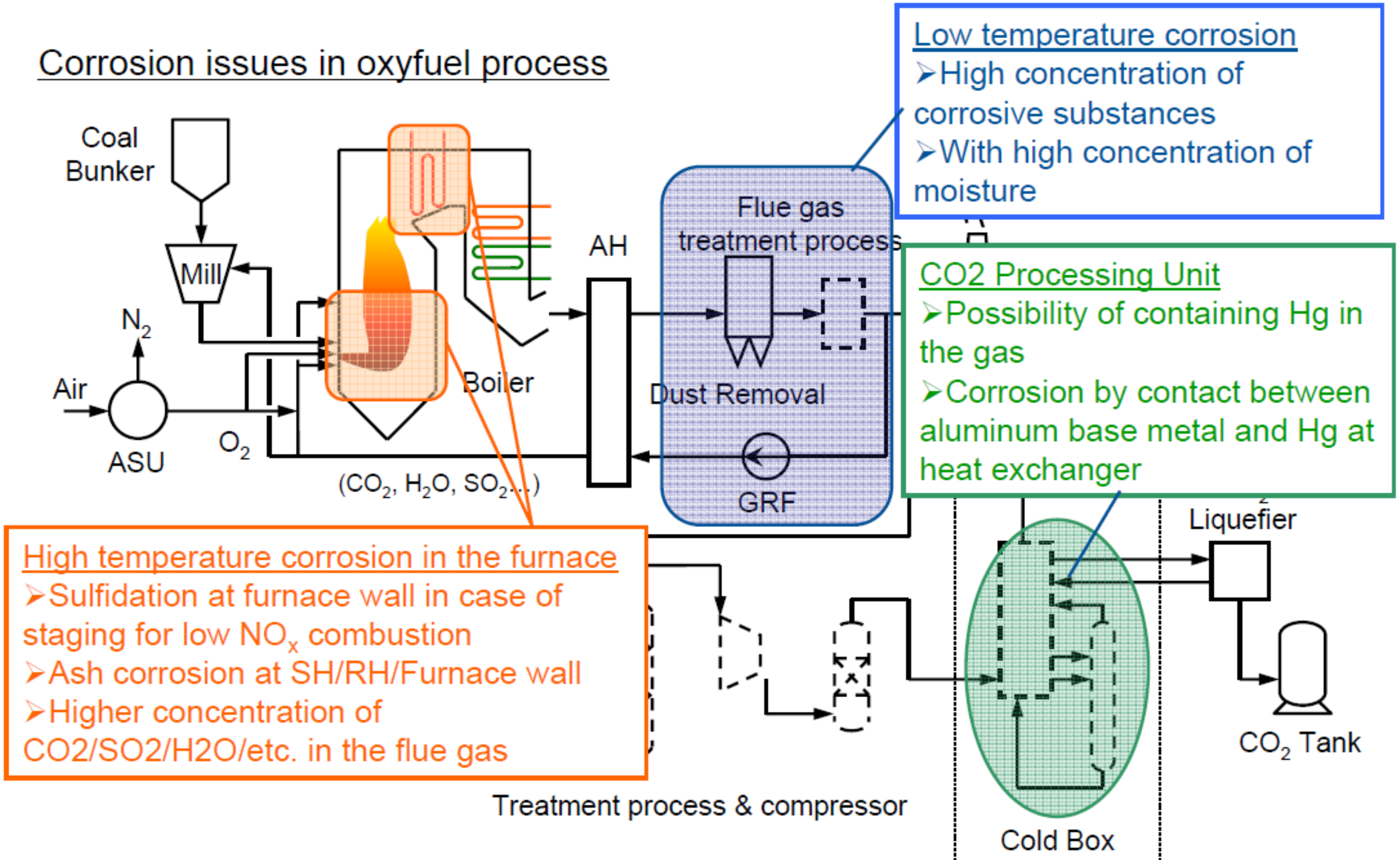
Fireside Corrosion

- **Long-term oxy-combustion fireside corrosion tests**
- Short-term oxy-combustion fireside corrosion tests
  - Jerry Meier's presentation
- Field exposures in collaboration with JCOAL and IHI
- Post economizer flue gas corrosion (oxy-firing leading to lower dew points)—Laboratory and field tests
- Use of TBCs for protection in oxy-combustion environments

Steam Side Oxidation

- **Effects of pressure—update on A-USC autoclave**
- Chromia evaporation in steam
- Round robin study on T92 in atmospheric pressure steam (US-UK collaboration)
- Examination of oxide spallation comparing flat and whole tube section samples
- Hydrogen transport as a by-product of steam oxidation
  - Jerry Meier's presentation

Fireside Corrosion Associated with Oxy-Combustion



- **Main corrosion areas in changing from air- to oxy-firing. In the boiler this project considers**
  - **Waterwall (WW) corrosion—reducing conditions**
  - **Waterwall (WW) corrosion—oxidative conditions**
  - **Superheater/Reheater (SH/RH) corrosion—oxidative conditions**
  - **3 different flue gas recycle choices**

Takashi Kiga, IHI Corporation, IEAGHG Special Workshop on Oxyfuel Combustion, 2011

Fireside Corrosion Associated with Oxy-Combustion

Oxy-combustion is quite complex to simulate. Challenge is to combine different tests to understand the ramifications of oxy-firing.

- Long term tests with step differences in gas phases approximating air- and 3 oxy-firing cases
- Short term tests to examine other variables without the time and equipment availability issues of the long term tests
- Field exposures in an oxy-firing test facility
  - Exposure samples would see all the different combustion trials, thus correlation with environment is difficult
  - Electrochemical sensors offer instantaneous corrosion measurements, but with not exact correlation with section loss

Laboratory Test Issues

Ash Phase

- Wigley and Goh (2009)—oxy ash particles similar in size, more rounded, more sintering
- Brzozowska et al (2011)—more sulfur in oxy ash
- Hjörnhede et al (2010)—increased oxy ash deposition
- Ash phase complications differences between air- and oxy-firing not considered in long-term tests. Could be addressed in short-term tests

Heat Flux and Temperature Gradients

- Refit boilers use flue gas recirculation to match heat rate, so not much of an issue
- New boiler designs like will have higher heat rates and so this could be a concern
- Heat flux complications between air- and oxy-firing not considered

Laboratory Test Issues

Gas Phase

- Not constant even in air-firing
- Long-term tests bin the gas phase into 3 locations in the boiler and representing 1 air-firing case and 3 oxy-firing cases
- Short-term tests examine more varieties of gases
- Use Pt catalyst to form SO_3(g)

Alloys

- There is an extensive variety of candidate alloys. We narrowed the focus to a few types of alloys
- Commercial alloys (T22, T91, T92, TP347H, IN617)
- Model alloys (Fe-Cr, Fe-Cr-Ni, Ni-Cr)

Alloys and Deposits

Model Alloys (wt%)

- Fe-10Cr, Fe-13.5Cr, Fe-22Cr (ferritic/martensitic)
- Fe-12Ni-18Cr, Ni-22Cr (austenitic)

Commercial Alloys (wt%)

Alloy	Fe	Cr	Ni	Co	Mo	C	Si	Al	Mn	W	Nb	V	Cu	N	Other
T22	Bal	2.07	0.19		0.91	0.10			0.50						
T91	Bal	8.48	0.16		0.99	0.10	0.35		0.41			0.20	0.18	0.04	
T92	Bal	8.84	0.32		0.32	0.12	0.28		0.29	1.83				0.14	
P92	Bal	8.90	0.23		0.38	0.07	0.30		0.43	1.20					
TP347	Bal	17.55	11.04	0.10	0.39	0.08	0.57		1.57	0.04	0.93	0.07	0.35		0.02 Ta
IN617	0.39	21.87	Bal	11.46	9.65	0.10	0.01	0.98	0.04		0.03		0.01		0.47 Ti

Ash and deposits (all wt% except for SCM)

- *Deposit A: 50SiO_2-25Al_2O_3-12.5Fe_2O_3-12.5CaO (baseline)*
- *Deposit B: 49SiO_2-25Al_2O_3-12.5Fe_2O_3-12.5CaO-1K_2SO_4 (some variations with more K_2SO_4)*
- *Deposit C: 67% deposit A + 33% graphite*
- *Deposit D: 30SiO_2-30Al_2O_3-30Fe_2O_3-5Na_2SO_4-5K_2SO_4* **[deposit used in long term tests]**
- *SCM: K_2SO_4, Na_2SO_4 , Fe_2O_3 - 1.5:1.5:1.0 molar ratio*

Long Term Fireside Tests in SECERF

Severe Environment Corrosion Erosion Research Facility

Modular laboratory for safely examining hot-corrosion and wear of materials at temperatures to 1600^{o}C in a mixture of any of the following gases: O_2, N_2, CO, CO_2, CH_4, H_2, H_2S, SO_2, HCl, He, Ar, dry air, and water vapor.

Environments (1 air- and 3 oxy-firing cases)

Conditions		Oxidative				Reducing			
	SH/RH	700 °C (T91, TP347, IN617)							
	WW	450 °C (T22, T91, IN617)				450 °C (T22, T91, IN617)			
		Air	Oxy			Air	Oxy		
			FGD <H_2O	FGD	wo FGD		FGD <H_2O	FGD	wo FGD
Gas	N_2	Bal	8	8	8	Bal	8	8	8
	CO_2	14	Bal	Bal	Bal	14	Bal	Bal	Bal
	CO					5	5	5	5
	H_2S					0.1	0.1	0.1	0.3
	H_2O	9	9	20	20	9	9	20	20
	O_2	2.5	2.5	2.5	2.5				
	SO_2	0.3	0.3	0.3	0.9	0.2	0.2	0.2	0.6

Long Term Fireside Corrosion Tests

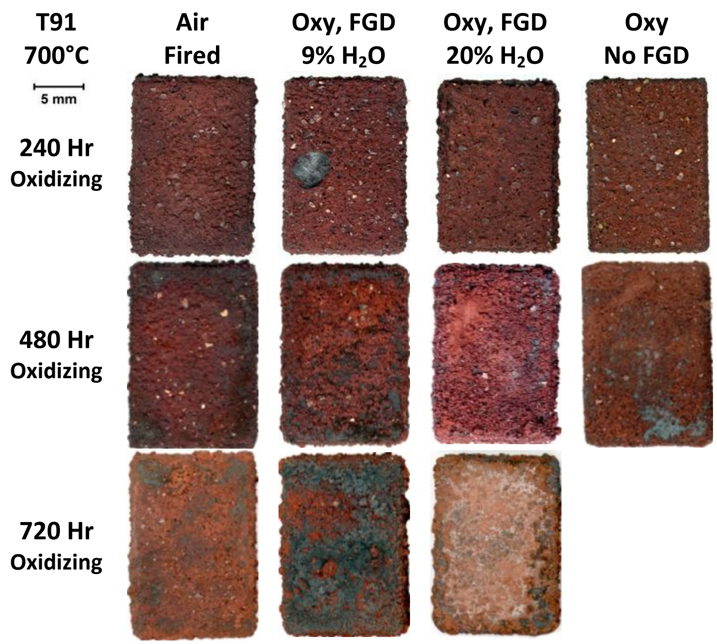
Plan is to run experiments for 1440 hours, in nominally 240 hr increments, then decide if further exposures are warranted

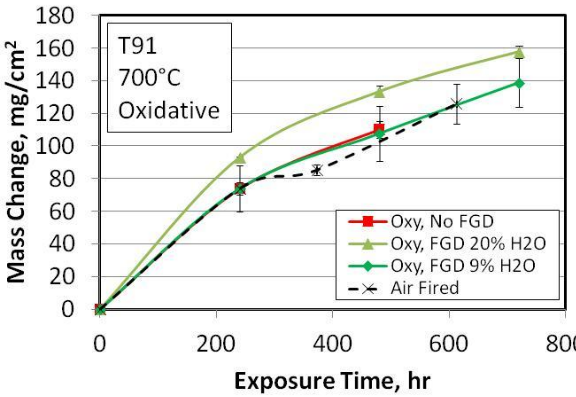
Section off part of one of the triplicate samples for each alloy after 240, 720, and 1440 hr for cross-section examination

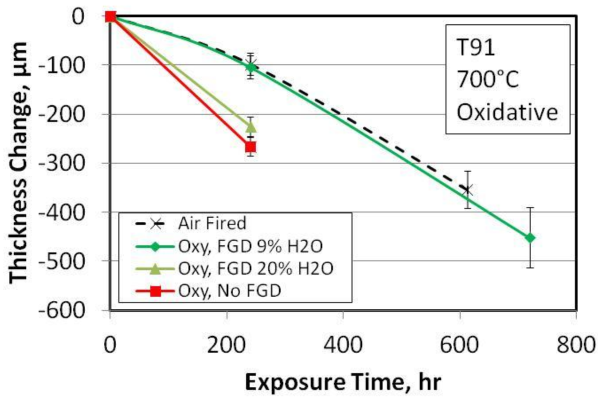
Test progress as of 3/31/2012:

Condition	Oxidative, 700°C	Oxidative, 450°C	Reducing, 450°C
Air-fired	60%	42%	17%
Oxy, FGD 9% H_2O	50%	50%	17%
Oxy, FGD 20% H_2O	50%	50%	17%
Oxy, No FGD	33%	50%	17%

T91 at 700°C, Oxidative Conditions

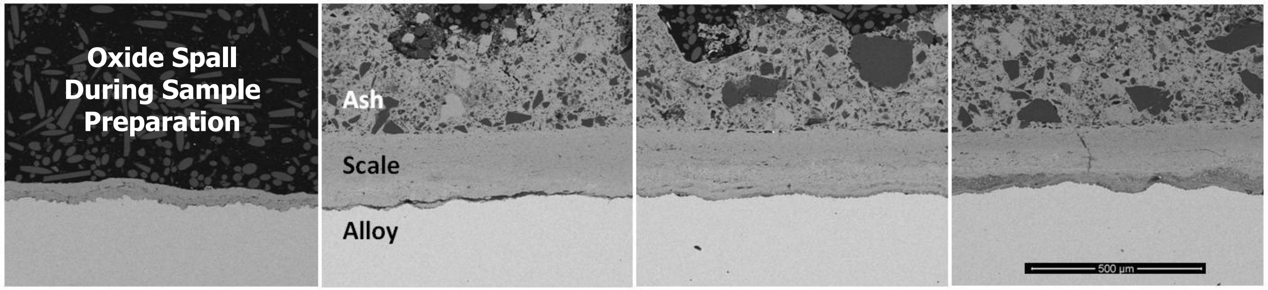




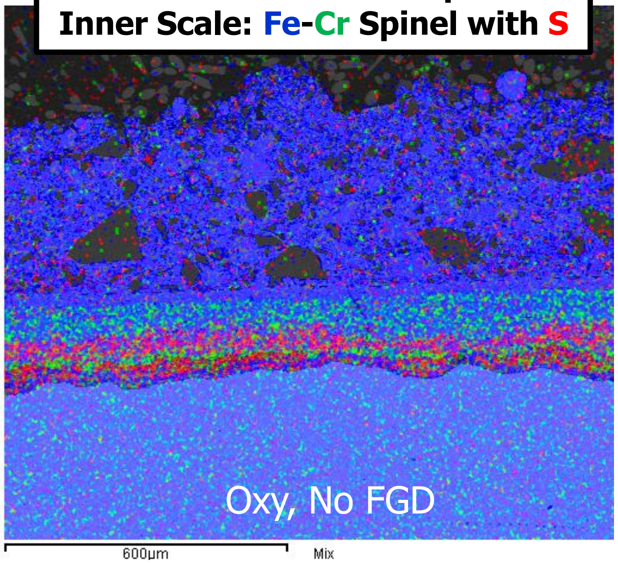


Outer Scale: Fe Oxide
Middle Scale: Fe-Cr Spinel
Inner Scale: Fe-Cr Spinel with S

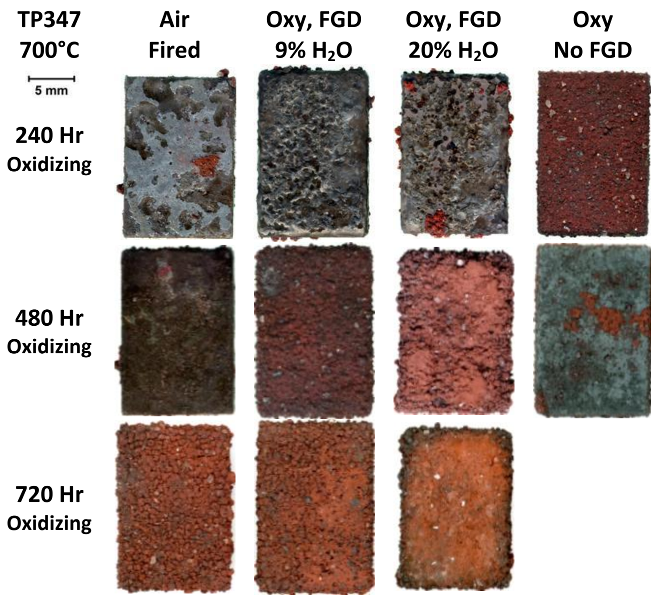
Fe = Blue
Cr = Green
S = Red

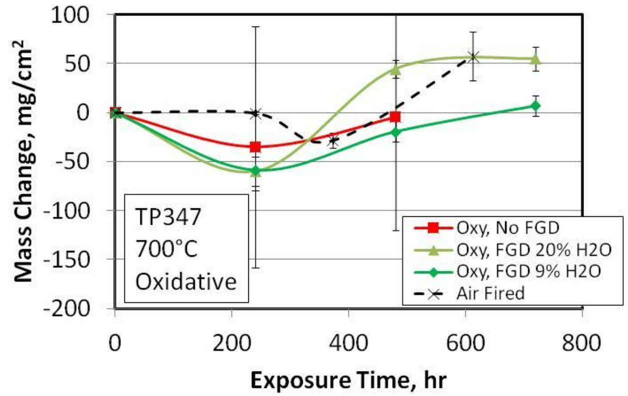


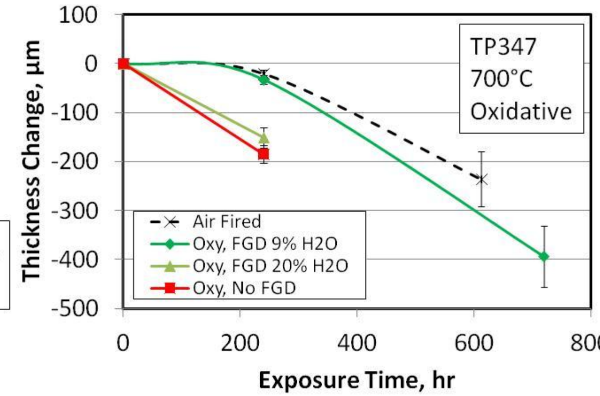
Air-Fired | Oxy, FGD 9%H_2O | Oxy, FGD 20%H_2O | Oxy, No FGD

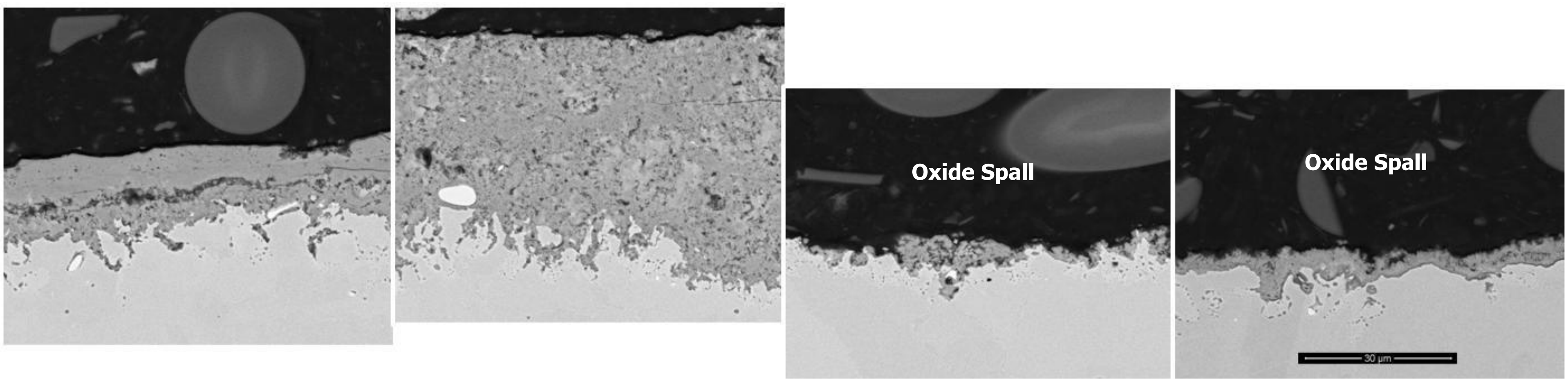


TP347H at 700°C, Oxidative Conditions









Air-Fired　　Oxy, FGD 9%H_2O　　Oxy, FGD 20%H_2O　　Oxy, No FGD

617 at 700°C, Oxidative Conditions

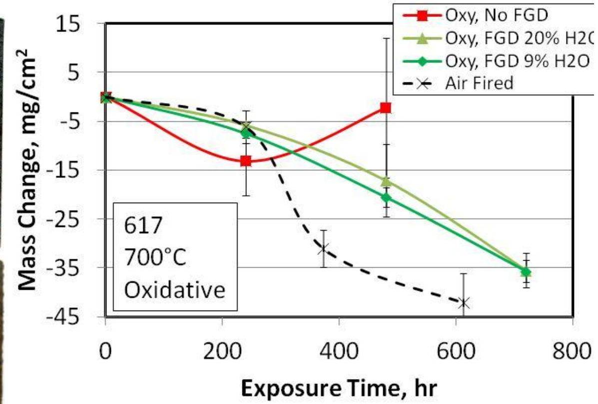
617 700°C	Air Fired	Oxy, FGD 9% H_2O	Oxy, FGD 20% H_2O	Oxy No FGD

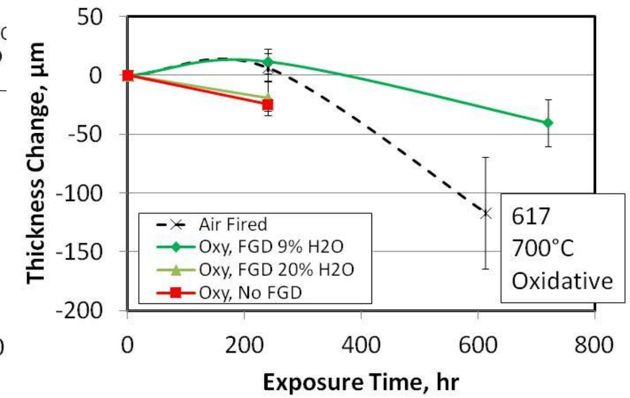
5 mm

240 Hr Oxidizing

480 Hr Oxidizing

720 Hr Oxidizing

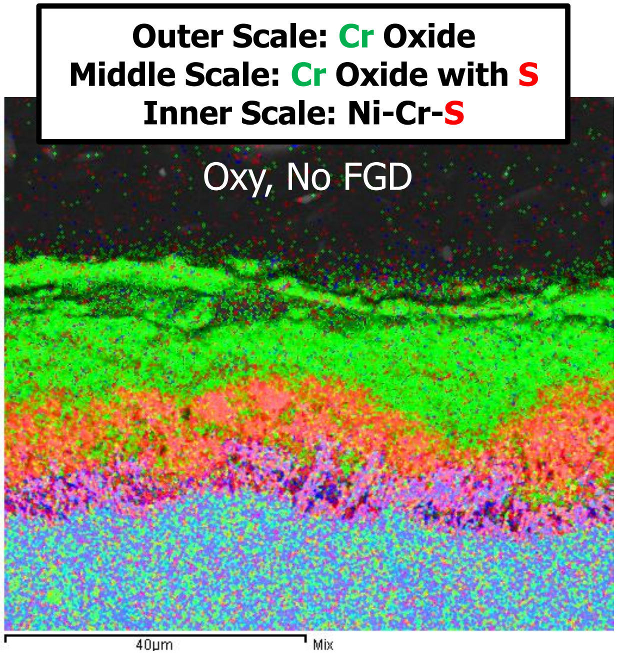


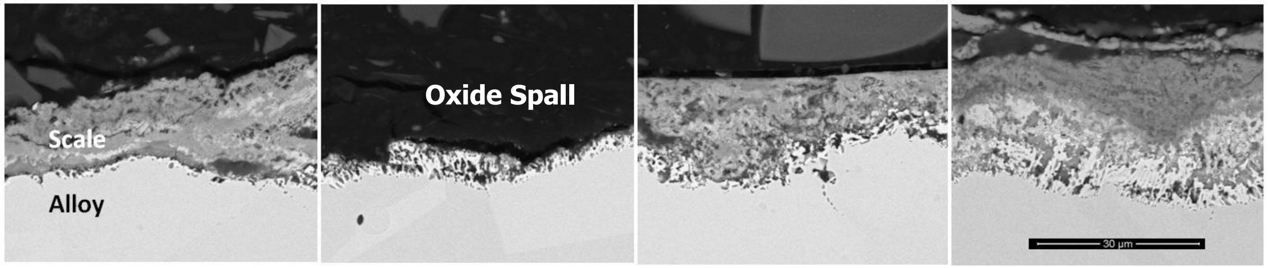


Ni = Blue

Cr = Green

S = Red





Air-Fired | Oxy, FGD 9%H_2O | Oxy, FGD 20%H_2O | Oxy, No FGD

T22, 450°C, Oxidative Conditions

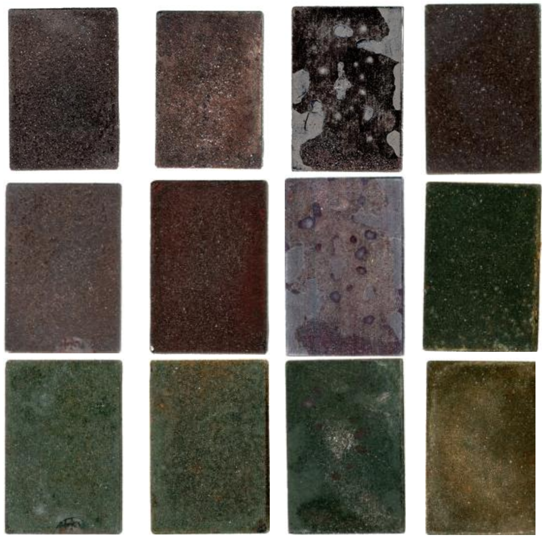
T22 450°C | Air Fired | Oxy, FGD 9% H_2O | Oxy, FGD 20% H_2O | Oxy No FGD

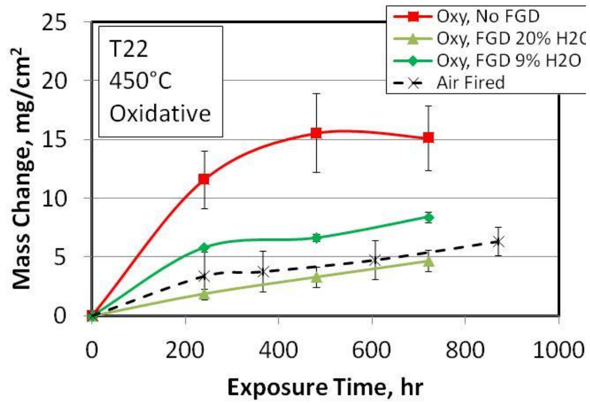
5 mm

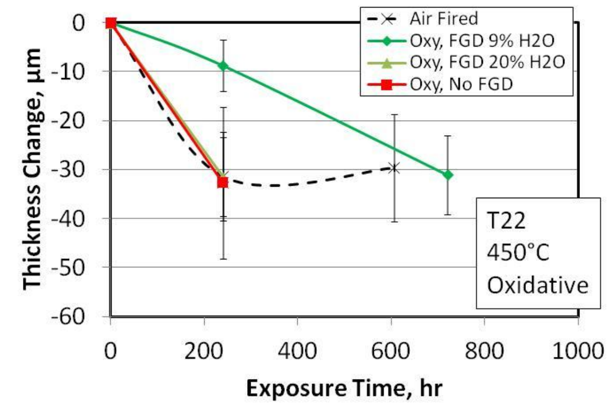
240 Hr Oxidizing

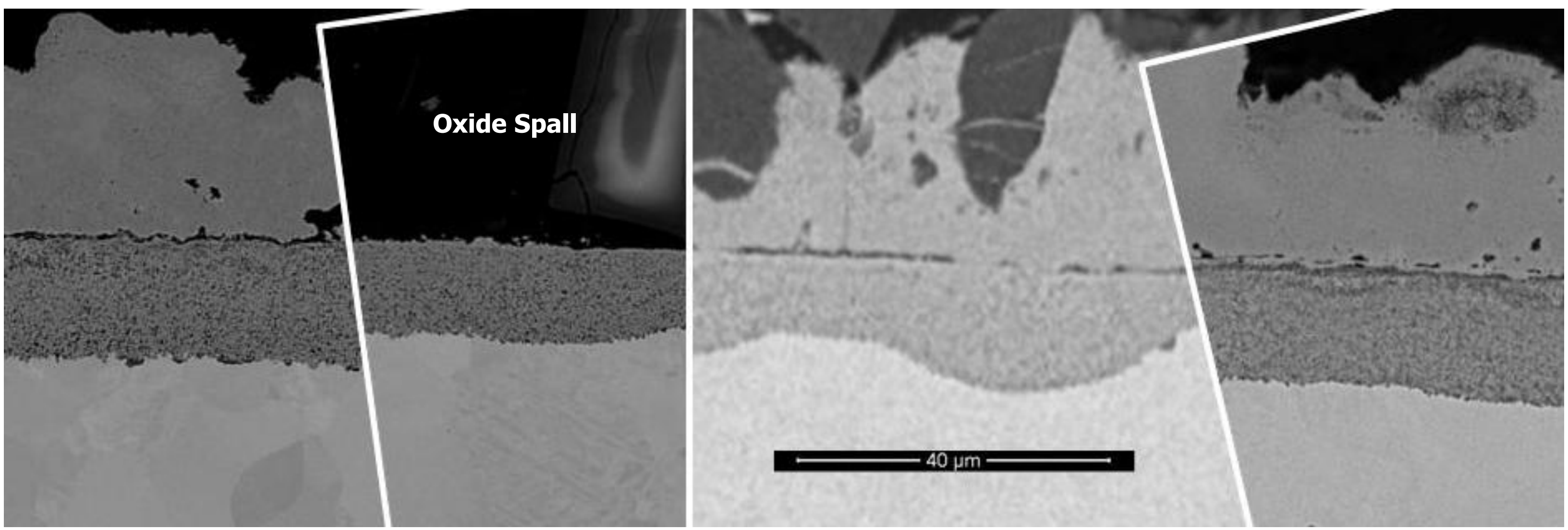
480 Hr Oxidizing

720 Hr Oxidizing









Air-Fired Oxy, FGD 9%H_2O Oxy, FGD 20%H_2O Oxy, No FGD

T91, 450°C, Oxidative Conditions

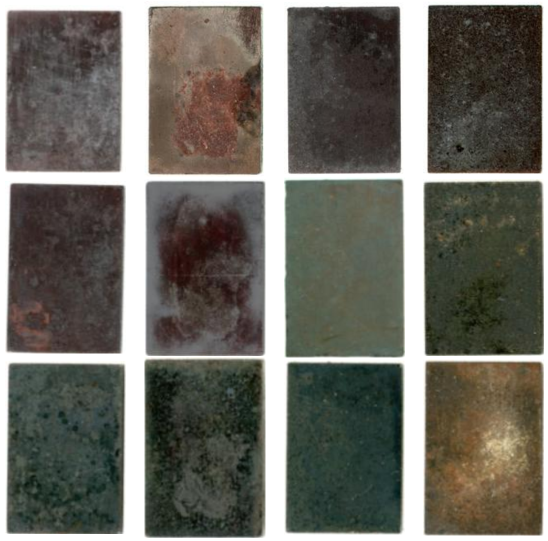
T91 450°C	Air Fired	Oxy, FGD 9% H_2O	Oxy, FGD 20% H_2O	Oxy No FGD

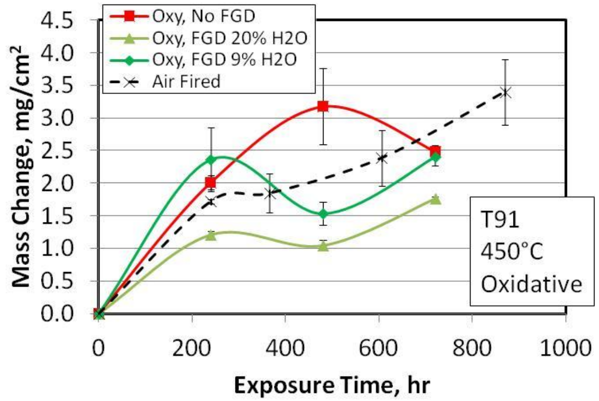
5 mm

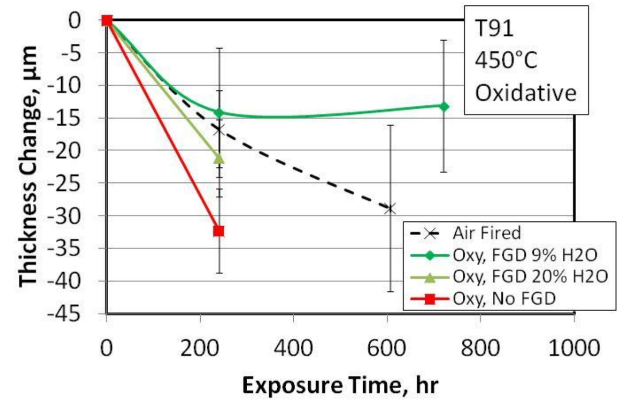
240 Hr Oxidizing

480 Hr Oxidizing

720 Hr Oxidizing

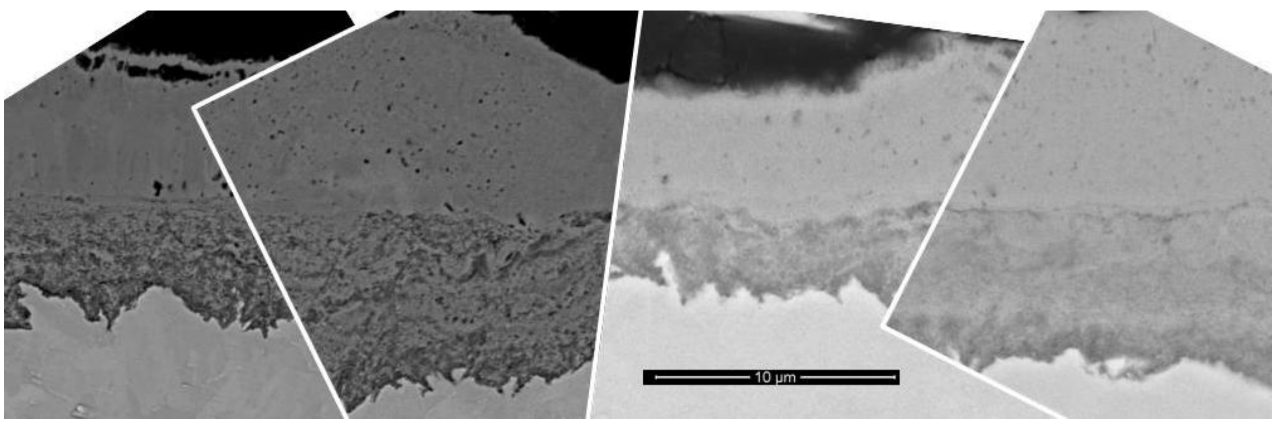


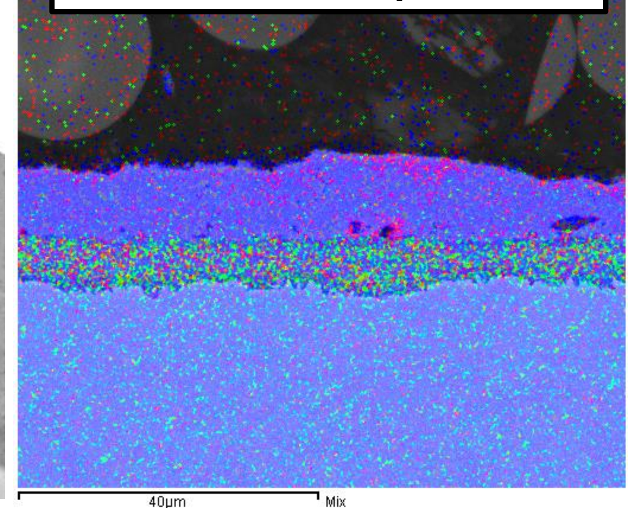




Fe = Blue
Cr = Green
S = Red

Outer Scale: Fe Oxide with S
Inner Scale: Fe-Cr Spinel with S





Air-Fired | Oxy, FGD 9%H_2O | Oxy, FGD 20%H_2O | Oxy, No FGD | Oxy, FGD 20%H_2O

617, 450°C, Oxidative Conditions

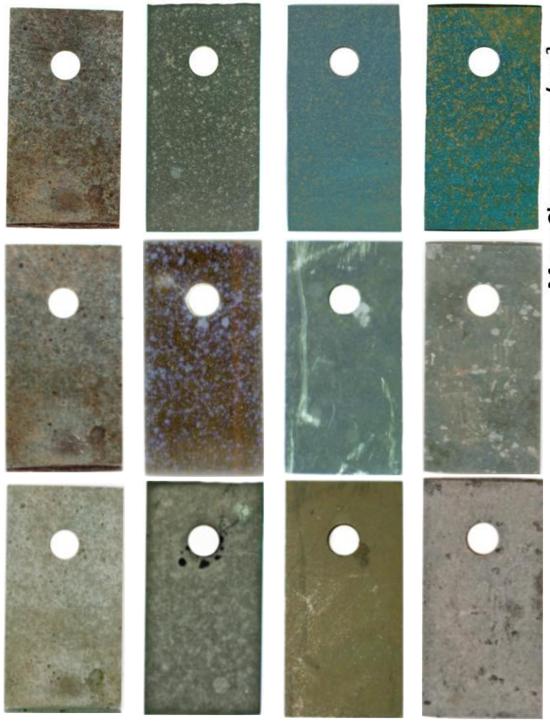
617 450°C	Air Fired	Oxy, FGD 9% H_2O	Oxy, FGD 20% H_2O	Oxy No FGD

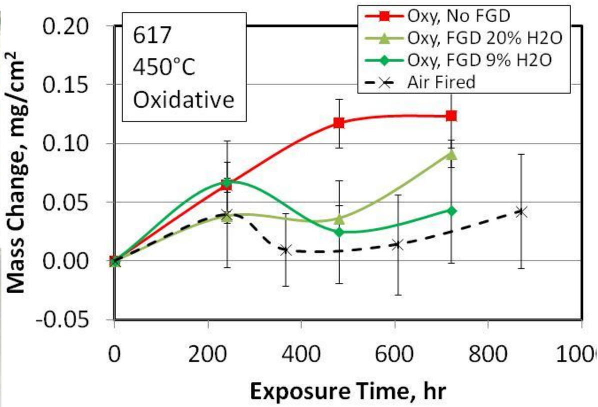
5 mm

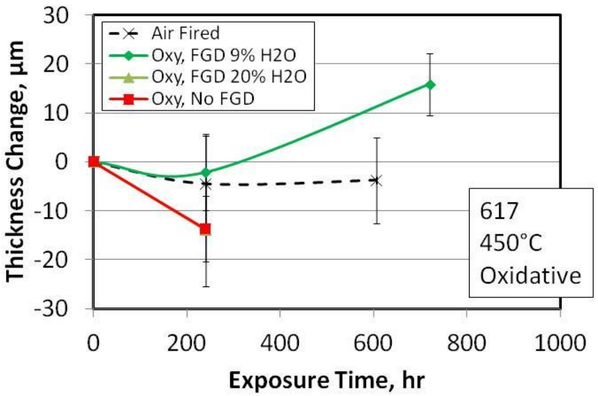
240 Hr Oxidizing

480 Hr Oxidizing

720 Hr Oxidizing



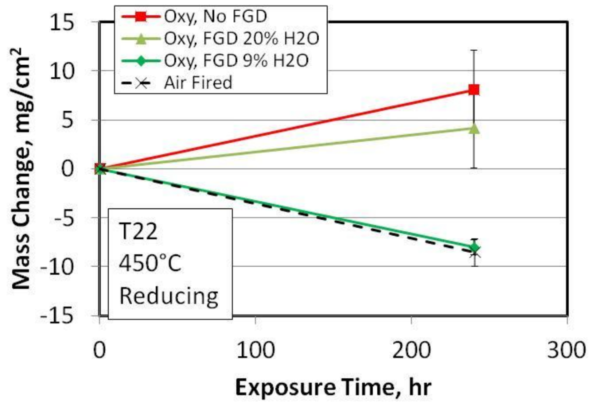




450°C, Reducing Conditions

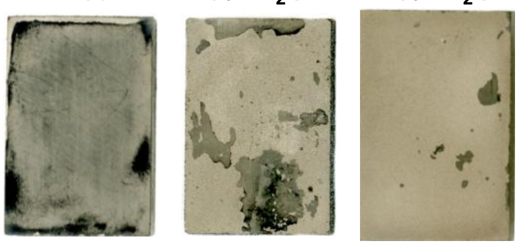
T22
450°C
5 mm
240 Hr
Reducing

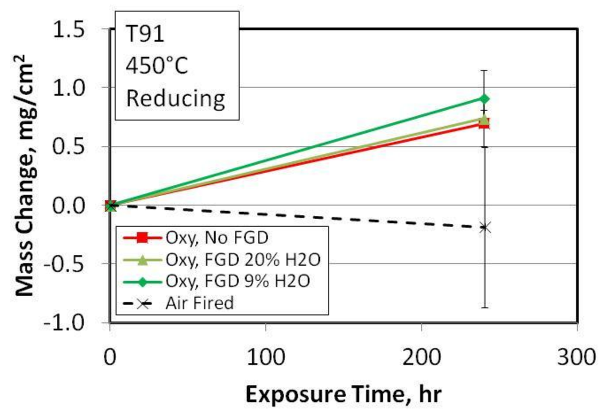
Air Fired	**Oxy, FGD 9% H_2O**	**Oxy, FGD 20% H_2O**



T91
450°C
5 mm
240 Hr
Reducing

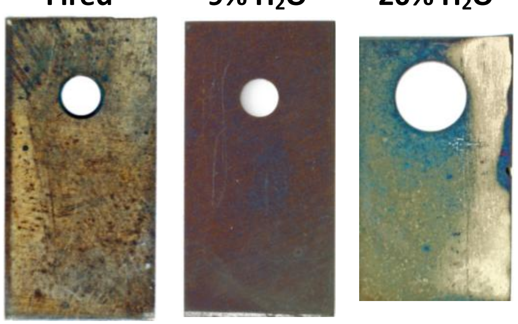
Air Fired	**Oxy, FGD 9% H_2O**	**Oxy, FGD 20% H_2O**

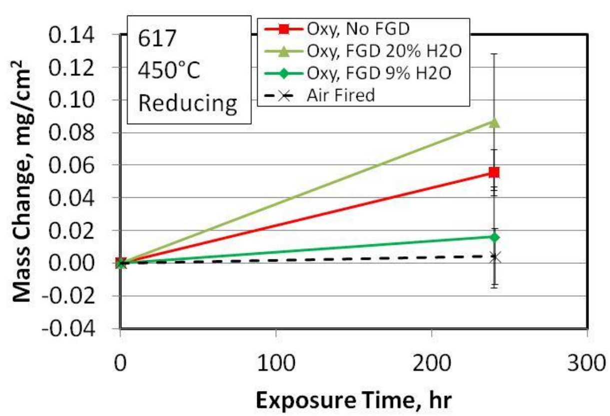




617
450°C
5 mm
240 Hr
Reducing

Air Fired	**Oxy, FGD 9% H_2O**	**Oxy, FGD 20% H_2O**





Observation—Long Term Tests

Initial Section Loss Results

- At 700°C T91 had more section loss in the high water FGD with 20% H_2O and without FGD cases
- At 700°C TP347 had more section loss in the high water FGD with 20% H_2O and without FGD cases
- At 450°C (both oxidative and reducing) 617 is essentially free of corrosion in all cases
- No clear differentiation yet for other alloys and conditions

Corrosion Mechanism Possibilities

SH/RH Conditions (650-700°C, Oxidative Conditions)

SO_3 threshold (shown below in terms of SO_2)

- Between 100 & 1000 ppm SO_2 with SCM ash (Jerry Meier's talk)
- Between 100 & 3000 ppm SO_2 with 30-30-30-5-5 ash (deposit D)
- Could mean a large oxy-corrosion difference for some range of S in coals, and small difference in others

Fluxing mechanism for T91

- Fe oxide dissolving into ash
- Ash attachment as Fe deposits within ash
- Very thin Fe-oxide portion of scale
- Usually requires a molten phase
  - Na_2SO_4 and K_2SO_4 have too high of melting points
  - FeNaK tri-sufates have lower melting points (SCM composition)
  - Tri-sulfates require SO_3 in gas phase for stability—threshold tie-in?

Steam Side Oxidation
Effects of pressure—update on A-USC autoclave

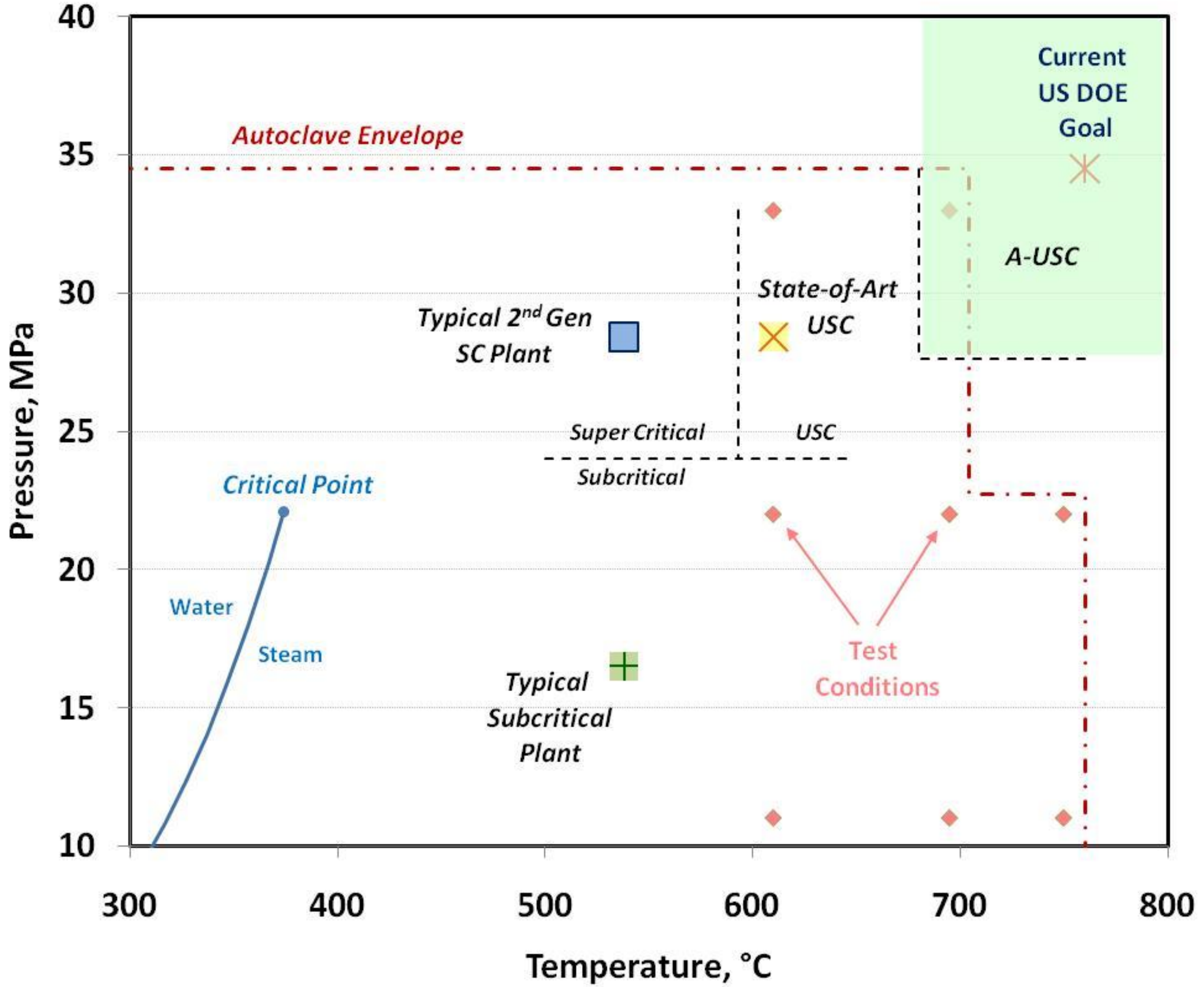
Overview of System and Plans

Shakedown Progress and Current Status

Coal-fired power plant nomenclature, conditions, and typical efficiency

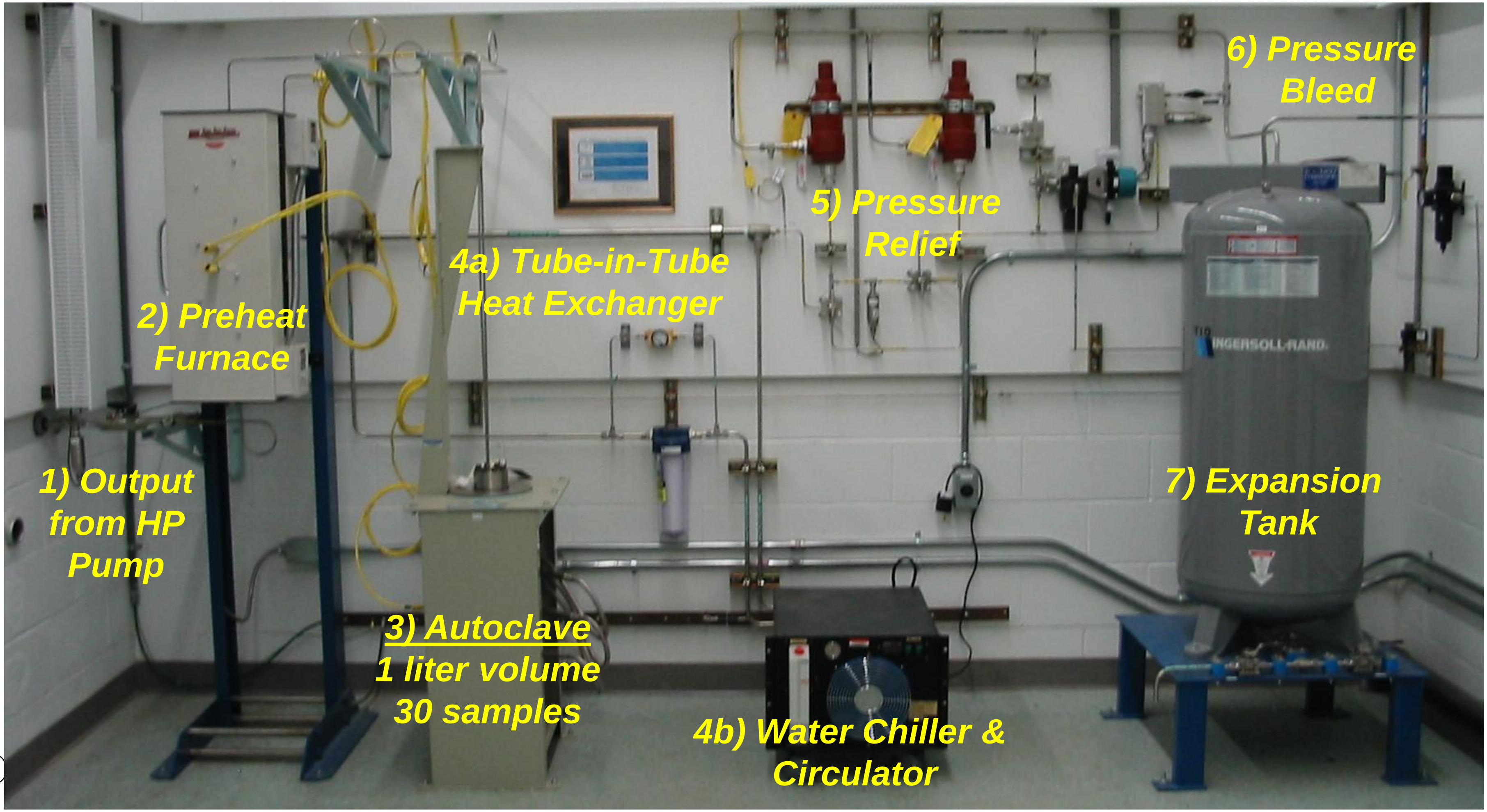
Nomenclature	Conditions	Net Plant Efficiency (%, HHV)
Subcritical	16.5 MPa (2400 psi) 566°C /566°C (1050°F/1050°F)	35
Supercritical (SC)	>24.8 MPa (3600 psi) 566°C /579°C (1050°F/1075°F)	38
Ultra-supercritical (USC)	>24.8 MPa (3600 psi) 593°C /621°C (1100°F/1150°F)	>42
Advanced Ultra-Supercritical (A-USC)	27.6-34.5MPa (4000-5000 psi) 704-760°C (1300-1400°F) main steam	>45

Steam Oxidation at Pressure Test Conditions



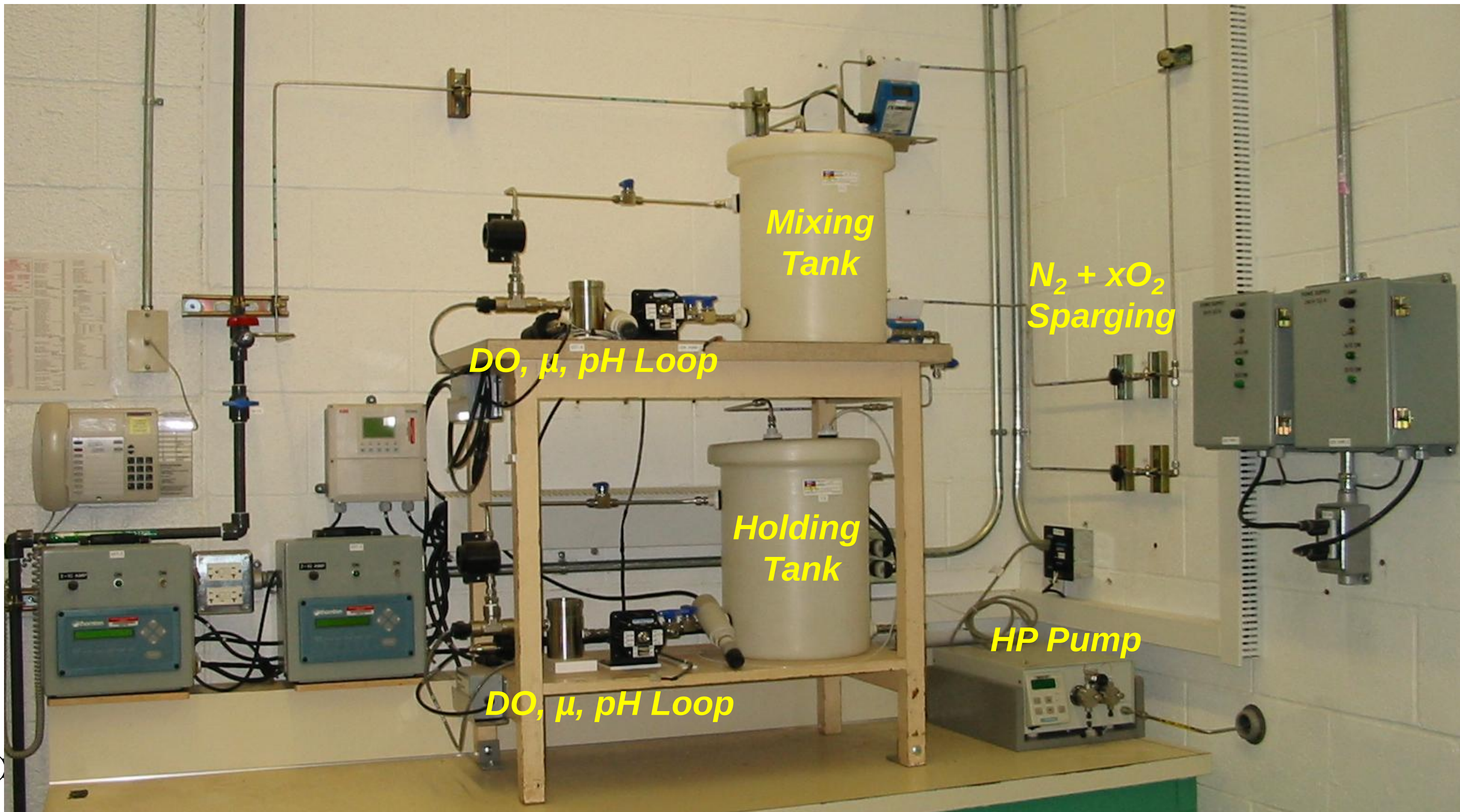
Dual Rated Flowing Steam A-USC Autoclave

- *5000 psig (34.5 MPa) at up to 704°C*
- *3300 psig (22.7 MPa) at up to 760°C*
- *Haynes 230 used for autoclave and high T/P line material*



A-USC Steam Autoclave Water Treatment

- Two tank system
- Dissolved oxygen, pH, and conductivity



Pressure Test Alloys

Alloy Group A—All pressures and temperatures

- H230, H263, H282, IN740u

Alloy Group B—All pressures, 695 and 750°C

- IN617, IN625, IN740, HR6W, U720Li, IN718

Alloy Group C—All pressures, 610 °C

- TP304H, TP347u
- T91, T92

Alloys with the "u" designation are alloys from the US-UK Phase I round robin tests

Pressures are 11, 22, and 33 MPa

Current Status of Shakedown Activates

USC conditions achieved

Good control of pressure

- ±10 psi at 3100 psig

In the process of improving temperature control

Water chiller currently not working

- awaiting repairs

Summary

Long-term oxy-combustion fireside corrosion tests

- Oxidative tests ~50% complete
- At 700°C T91 had more section loss in the high water FGD with 20% H_2O and without FGD cases
- At 700°C TP347 had more section loss in the high water FGD with 20% H_2O and without FGD cases
- At 450°C (both oxidative and reducing) 617 is essentially free of corrosion in all cases
- No clear differentiation yet for other alloys and conditions
- Probable SO_3 gas threshold at 650-700°C
- Evidence of fluxing mechanism for T91 at 700°C

Effects of pressure—update on A-USC autoclave

- USC steam conditions achieved
- Currently finishing shakedown tests