NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL Office of Research and Development Oxyfuel Combustion Research - Progress Update

Gordon R. Holcomb and E. David Huckaby

Materials Research Engineer and Mechanical Engineer

Carbon Constraint Possibilities with Oxyfuel Combustion

- **Materials Issues**
  - Gordon Holcomb will present ORD efforts
- **Design Issues**
  - David Huckaby will present ORD efforts

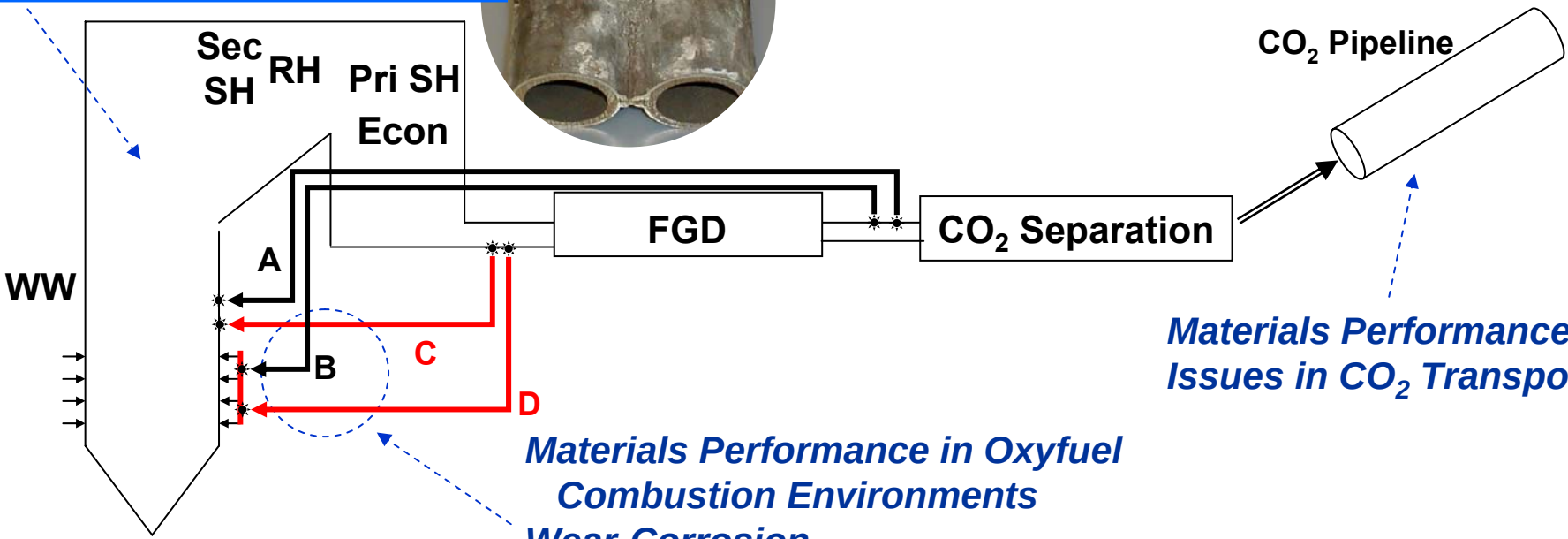
ORD Oxyfuel Materials Research

- **Refit Options and ORD Materials Research**
- **Project Spotlights**
  - Oxy-Combustion of Fossil Fuels with Carbon Capture
    Oxy-fuel Combustion Ash
  - Materials Performance in Oxyfuel Combustion Environments
    Fireside Corrosion

Refit Options and ORD Materials Research

Oxy-Combustion of Fossil Fuels with Carbon Capture
Oxy-Combustion Ash

Materials Performance in Oxyfuel Combustion Environments
Fireside Corrosion



Materials Performance Issues in CO_2 Transport

Materials Performance in Oxyfuel Combustion Environments
Wear-Corrosion

A Cold Recirculation with Cleanup and Reheat

B Cold Recirculation with Cleanup, Reheat and Coal Motivation

C Hot Recirculation

D Hot Recirculation with Coal Motivation

Increasing Efficiency
Increasing Corrosion Risk
Increasing Heat Changes

Oxy-Combustion of Fossil Fuels with Carbon Capture
Oxy-Combustion Ash

- **Background**
- **Initial Findings**
- **Challenges and Path Forward**

Oxy-Combustion Ash
Goals of NETL's studies

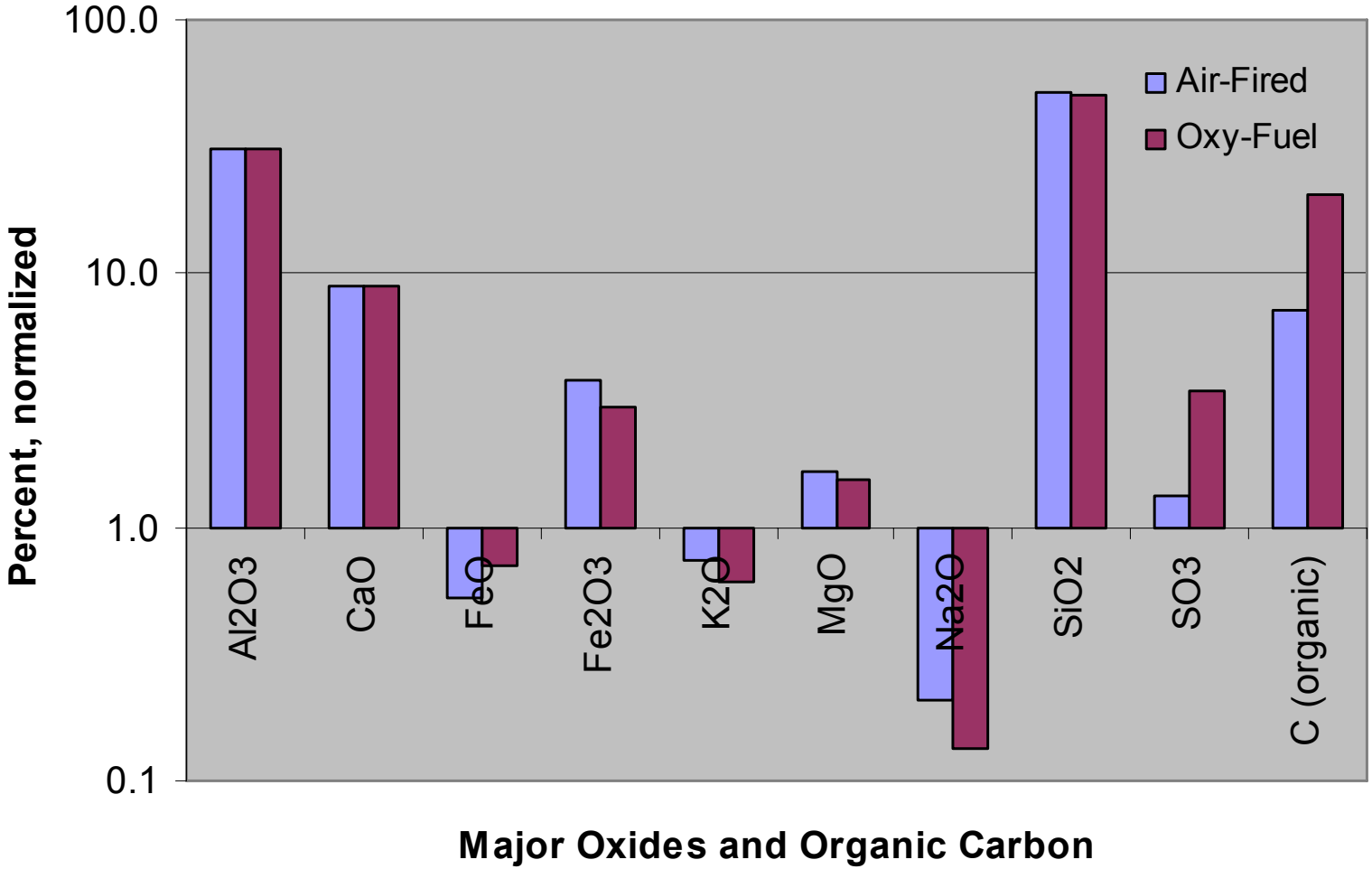
- **Predict power plant performance in oxy-combustion environment**
  - Materials performance
    - Corrosion and erosion implications
  - Slagging and fouling
    - Heat transfer and other deposition effects
- **Improve plant performance**
  - Identify limitations
  - Identify need for new materials
  - Identify need for operational changes

Oxy-Combustion Ash Sampling and data

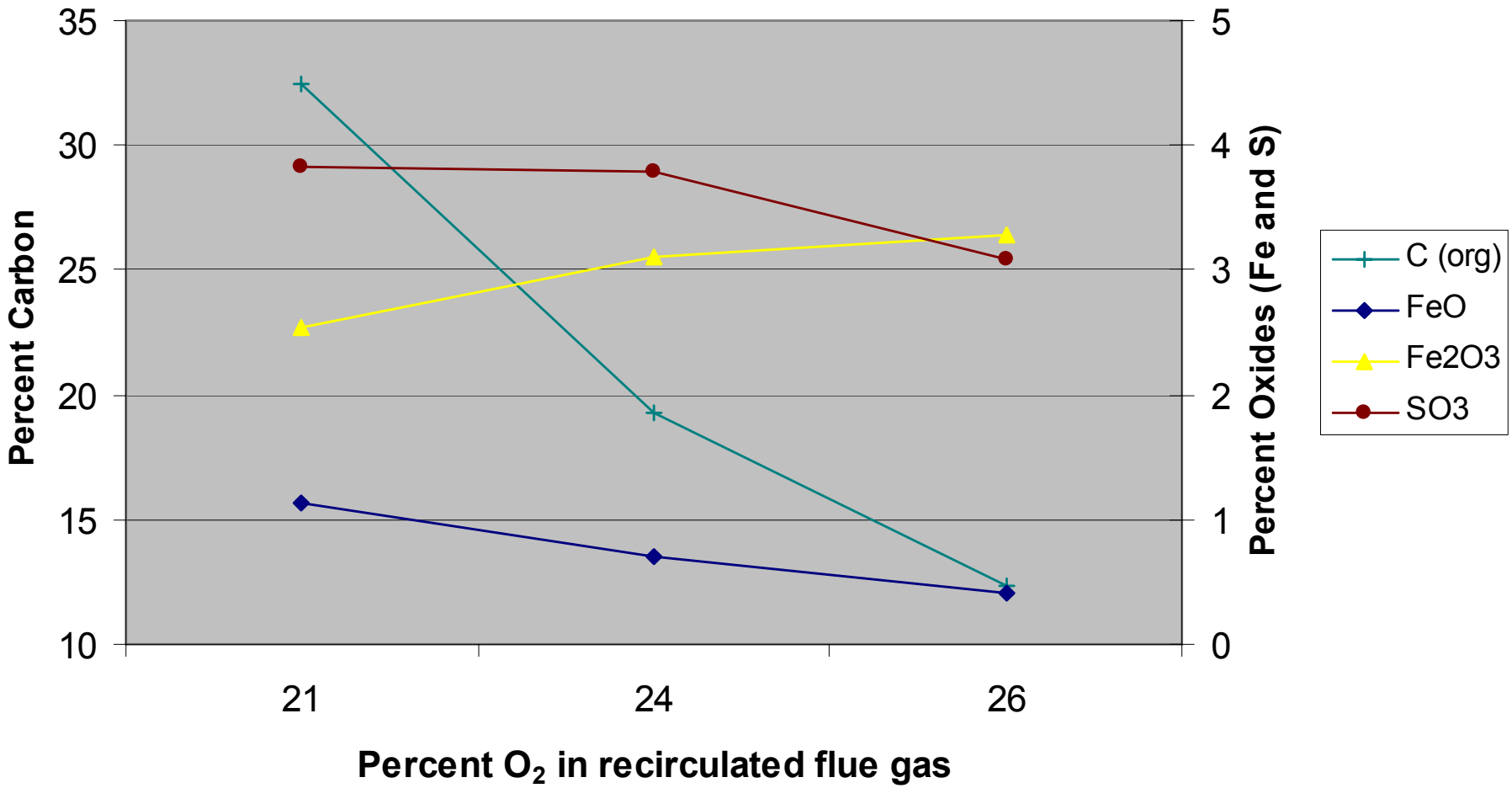
Bright Green Al & Si
Blue Ca
Red Ca & S

- **Characterization**
  - Changes from air-fired ash
    - Chemistry, size and surface area
- **Case #1 – Cyclone ash samples from air (2) and oxy (6) firing**
  - Oxy-firing tests varied % O_2 added to recycled flue gas
  - Low-sulfur coal (S. African Kleinjopke)
- **Case #2 – Boiler and cyclone ash analyses**
  - Oxy-firing conditions included FGR and no FGR but only one set of samples
  - Excess O_2 ~2.7% (average of 4 values)
  - Medium-sulfur coal (Illinois #6)

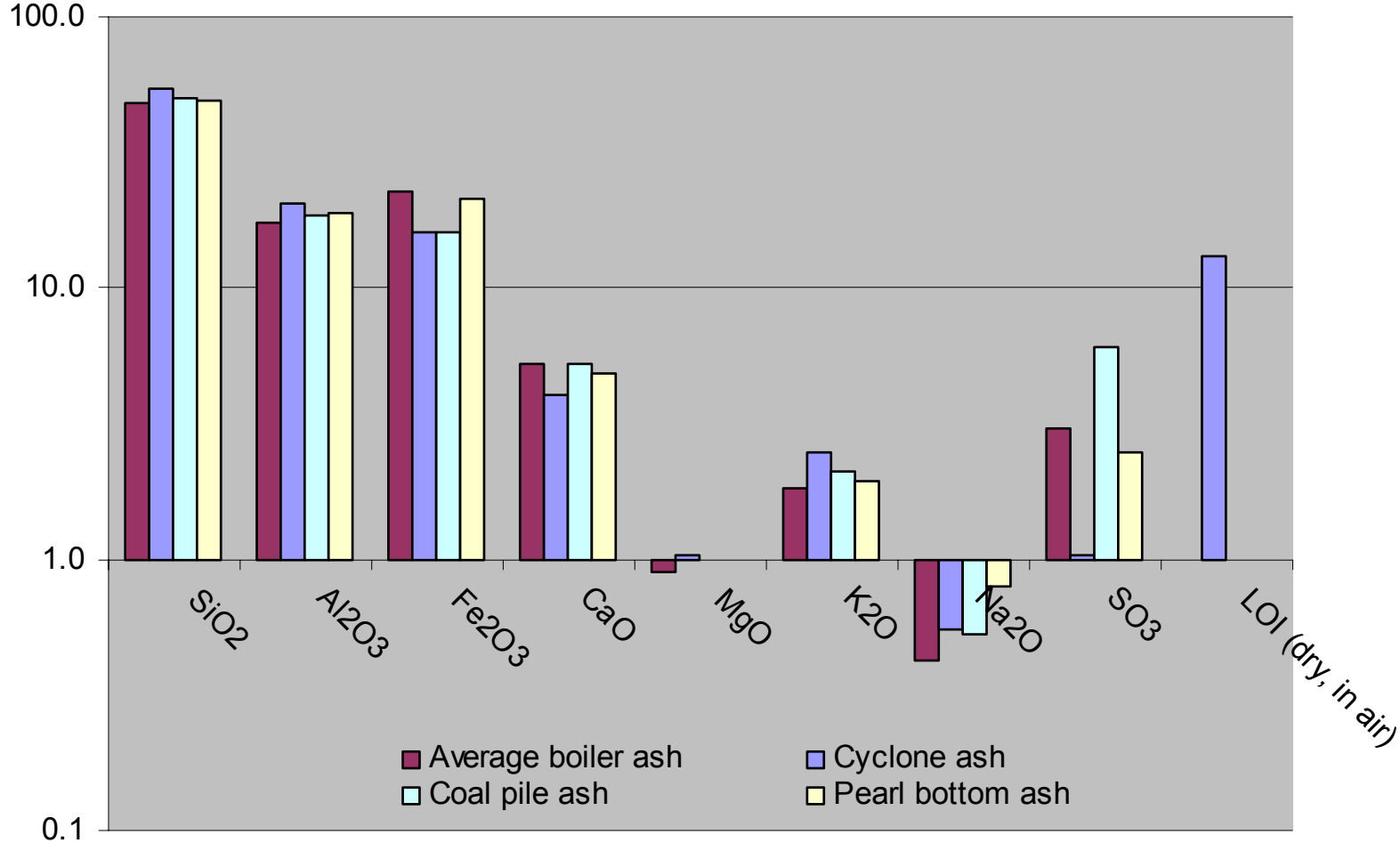
Case #1 – Cyclone ash samples
Oxy-firing tests varied % O_2 added to recycled flue gas
Low-sulfur coal (S. African Kleinjopke)



Case #1 – Cyclone ash samples
Oxy-firing tests varied % O_2 added to recycled flue gas
Low-sulfur coal (S. African Kleinjopke)



Case #2 – Boiler and cyclone ash analyses
Oxy-firing conditions included both FGR and no FGR
Excess O_2 ~2.7% (average of 4 values)
Medium-sulfur coal (Illinois #6)



LOI is Loss On Ignition

Oxy-Combustion Ash Conclusions

- **Oxy-firing affects sulfur content of ash**
  - Na_2SO_4 and K_2SO_4 tend to increase corrosion
  - Molten phases promote hot corrosion
- **Oxy-firing practices affect carbon content of ash**
  - Efficiency loss due to unburned fuel
- **Oxy-firing practices affect iron speciation of ash**
  - Unreduced FeS reported to be a corrosion concern

Oxy-Combustion Ash
So what?

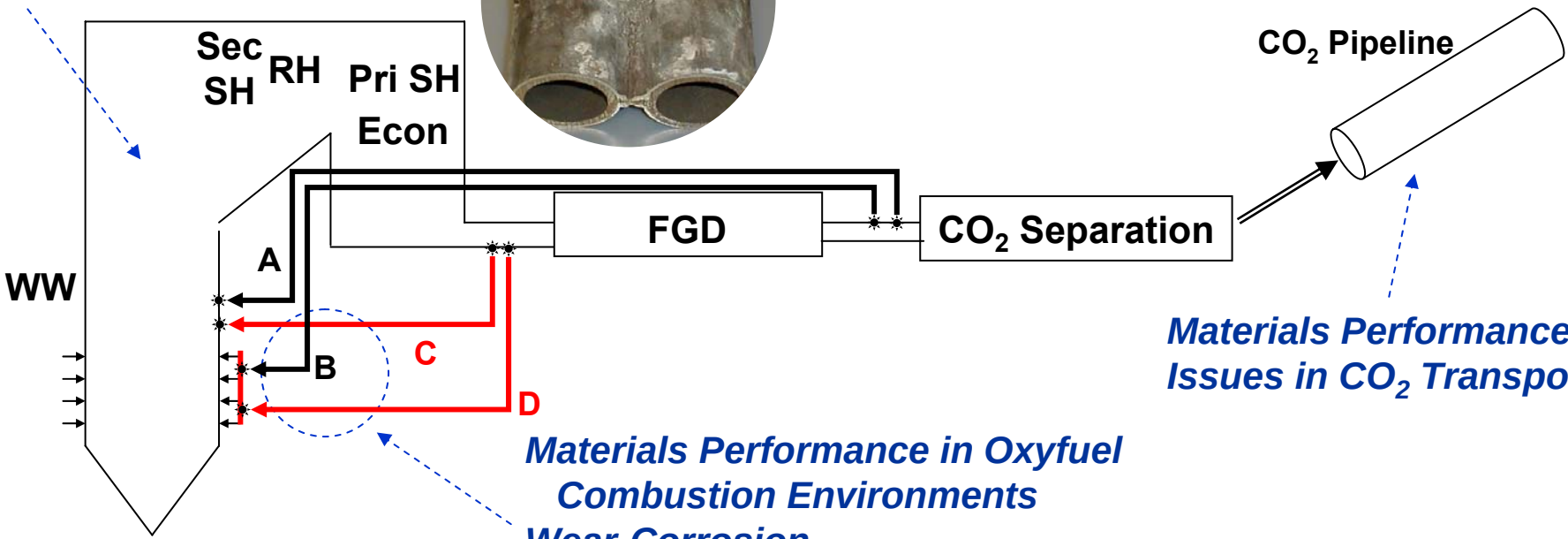
- **Predict materials performance**
  - Develop synthetic ash compositions for laboratory testing
- **Predict slagging and fouling**
  - Determine if calculated indices apply to oxy-combustion conditions
  - Lab and field testing
- **Predict utilization of ash by-products**
  - Carbon and SO_3 standards in cement industry

Refit Options and ORD Materials Research

Oxy-Combustion of Fossil Fuels with Carbon Capture

Oxy-Combustion Ash

Materials Performance in Oxyfuel Combustion Environments
Fireside Corrosion



Materials Performance Issues in CO_2 Transport

Materials Performance in Oxyfuel Combustion Environments
Wear-Corrosion

A Cold Recirculation with Cleanup and Reheat

B Cold Recirculation with Cleanup, Reheat and Coal Motivation

C Hot Recirculation

D Hot Recirculation with Coal Motivation

Increasing Efficiency
Increasing Corrosion Risk
Increasing Heat Changes

Materials Performance in Oxyfuel Combustion Environments
Fireside Corrosion

- **Background**
- **Initial Experiments and Findings**
- **Path Forward**
  - Long term exposure tests in “realistic” environments
  - Corrosion mechanism models & tests

Materials Performance in Oxyfuel Combustion Environments Fireside Corrosion

- **Goal: determine the effect of Oxyfuel environments on materials of construction for waterwalls and superheaters.**
  - Established Power Plants –will conversion to oxyfuel environments require new equipment with new materials?
  - New Power Plants –what are the best materials for equipment?
- **Oxyfuel combustion can change the boiler environment**
  - Gas composition
    - Non equilibrium, local “microclimates”
    - Can have elevated SO_2/SO_3 (depending on design)
  - Ash composition
    - Input from Oxy-fuel Combustion Ash project

Fireside Corrosion—Initial Experiments
Alloy Composition and Max Use Temperatures

Alloy	Composition, weight %							
	Fe	Cr	Ni	Mo	C	Mn	Other	Max Use T, °C
T22	95.8	2.07	0.19	0.91	0.102	0.49	-	601
T92	87.3	8.84	0.32	0.32	0.124	0.29	1.83 W	650
347	67.1	17.2	11.2	0.28	0.061	1.35	-	760
617	2.24	21.6	54.6	7.74	0.102	0.036	10.9 Co	760

Note: All alloys except 617 supplied as boiler tubes

Fireside Corrosion—Initial Experiments Gas Mixtures

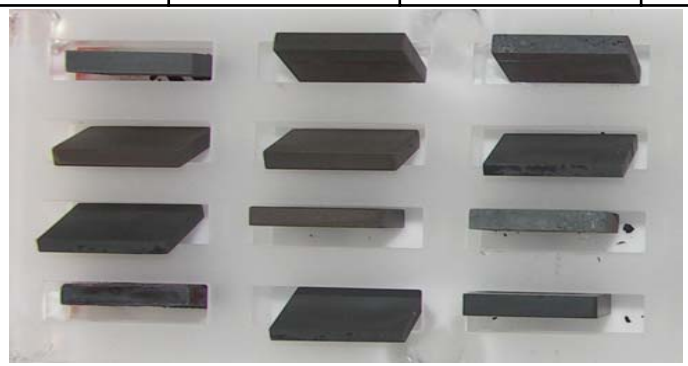
Environ.	Composition, volume %					*675 °C (1247 °F) Equilibrium*		
	N_2	O_2	CO_2	SO_2	H_2O	*O_2*	*SO_2*	*SO_3*
Air	74.1	6	14.6	0.3	5	*5.9*	*0.16*	*0.14*
Oxyfuel	0	2.5	60.1	0.9	32.6	*2.4*	*0.61*	*0.33*

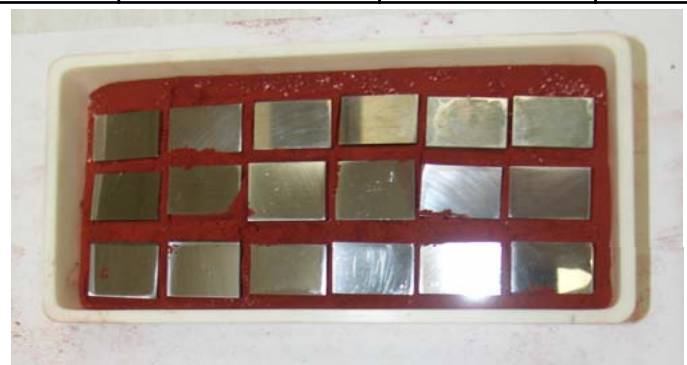
Fireside Corrosion—Initial Experiments

- Temperature = 675 °C (1247 °F), ~ Superheater Fireside
- Gas Linear Velocity = 6 cm/min (not meant to be representative of power plant gas velocities)
- Synthetic ash mixtures:

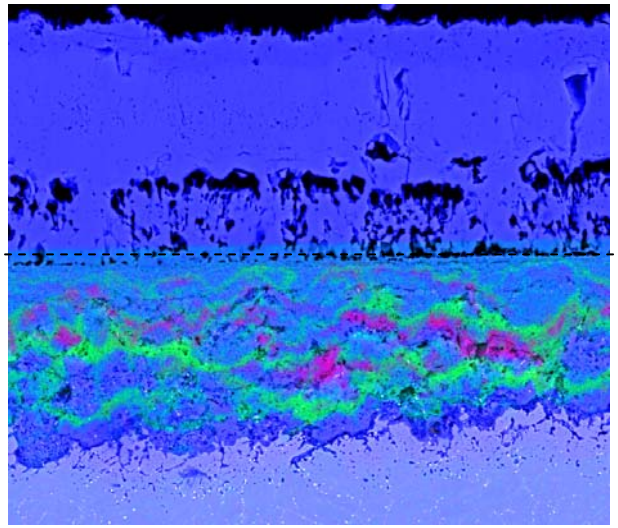
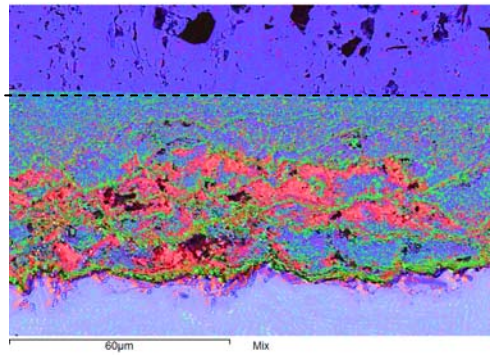
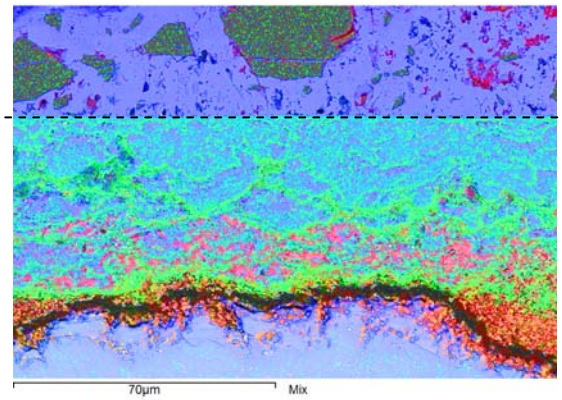
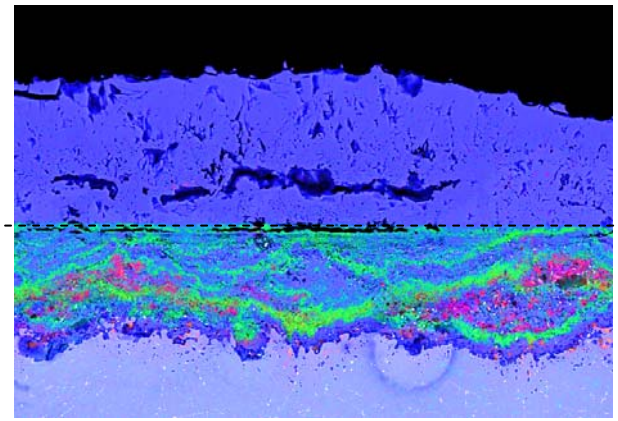
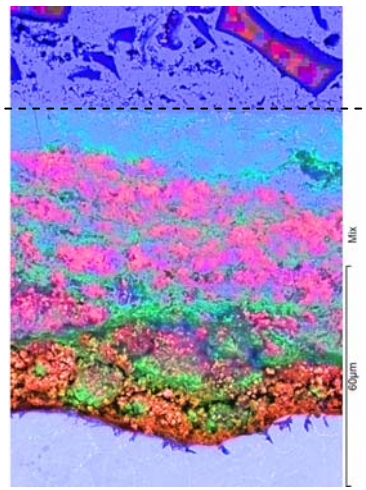
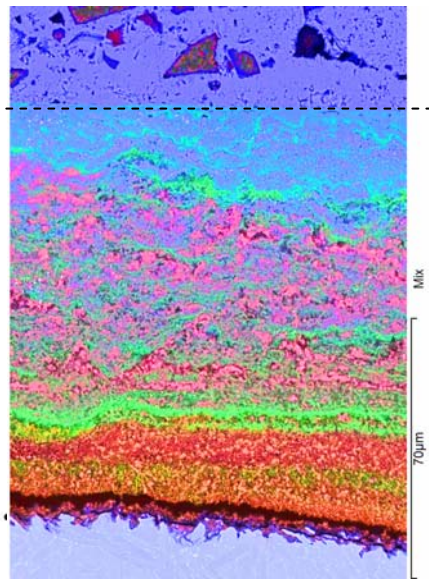
Ash Mixture	Composition, weight %					
	Fe_2O_3	Na_2SO_4	K_2SO_4	Al_2O_3	SiO_2	Calculated Base/Acid
A	31.67	2.5	2.5	31.67	31.67	0.52
B	30	5	5	30	30	0.54

No Ash





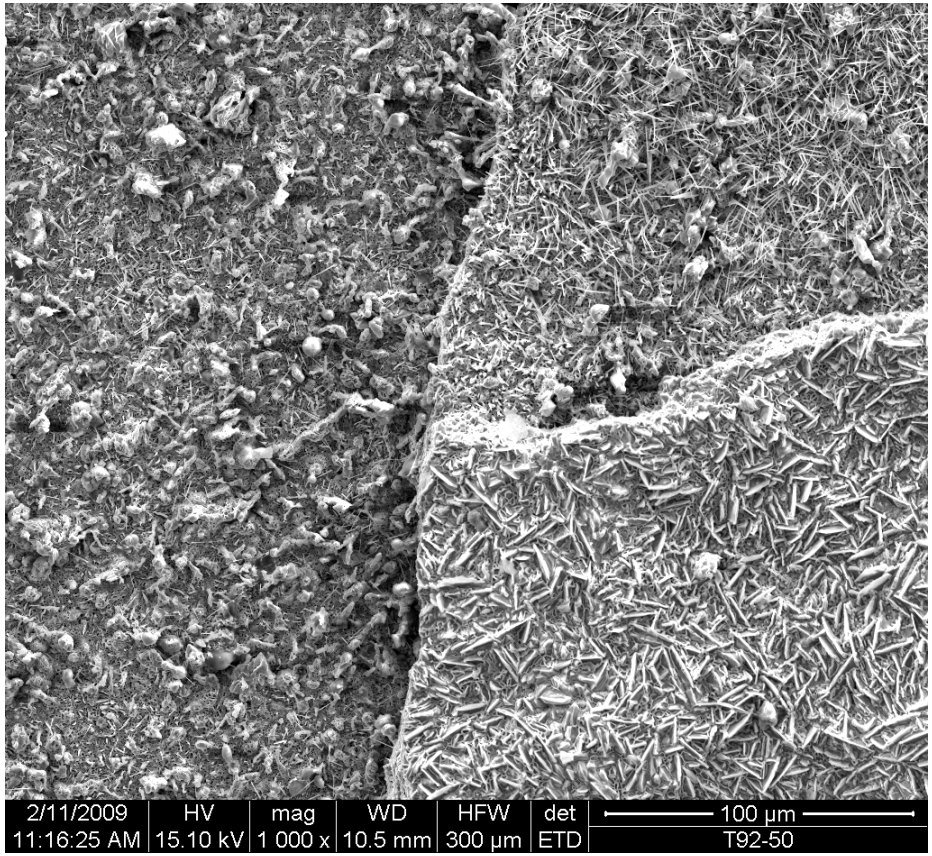
With Ash

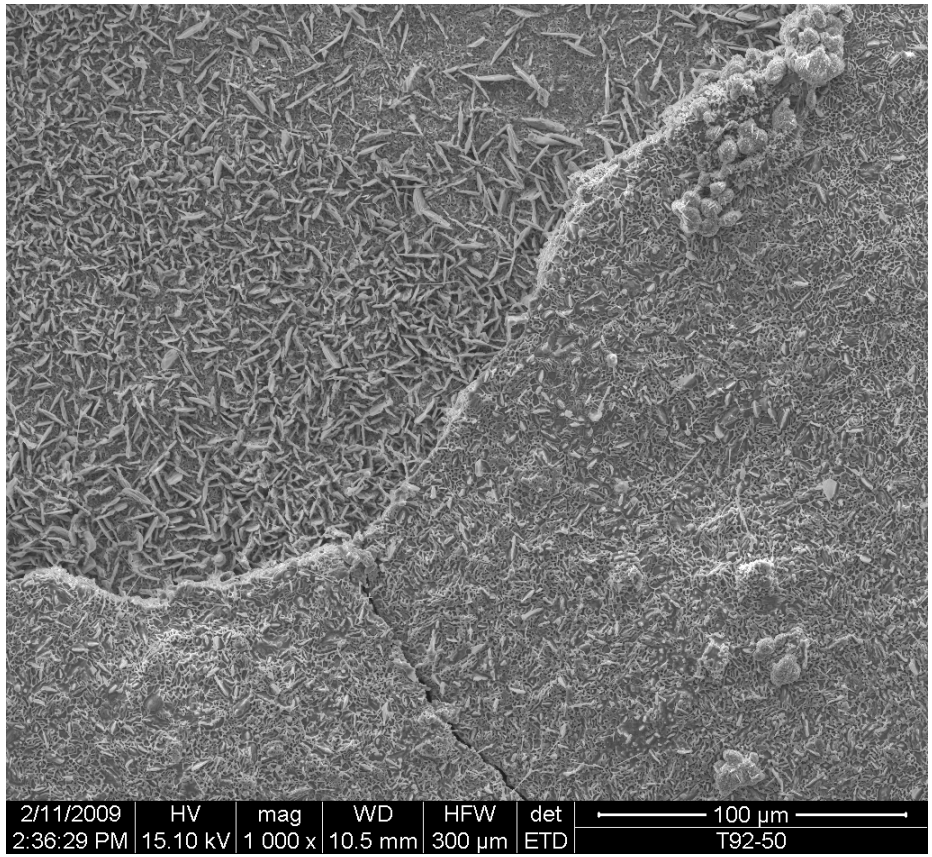
	No Ash	Ash A 2.5% Na_2SO_4 2.5% K_2SO_4	Ash B 5% Na_2SO_4 5% K_2SO_4
Oxy			
Air			

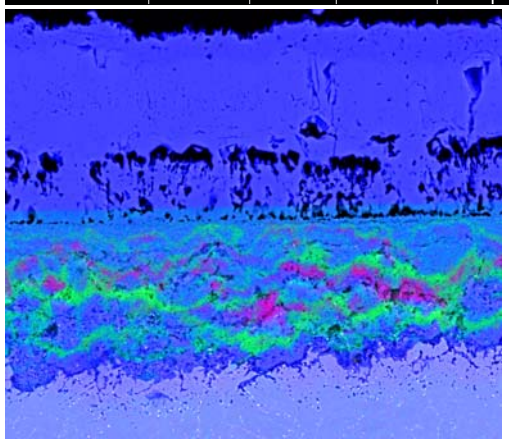
60 µm

T92 675 °C ~250 hr

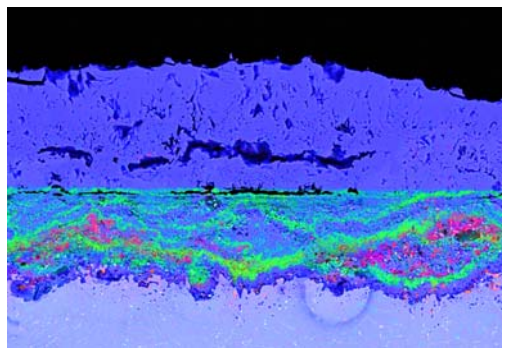
Fe = Blue Cr = Green S = Red







T92
No Ash
Oxy-fired
675 °C
260 hr



T92
No Ash
Air-fired
675 °C
260 hr

60 µm

Fe = Blue **Cr = Green** **S = Red**

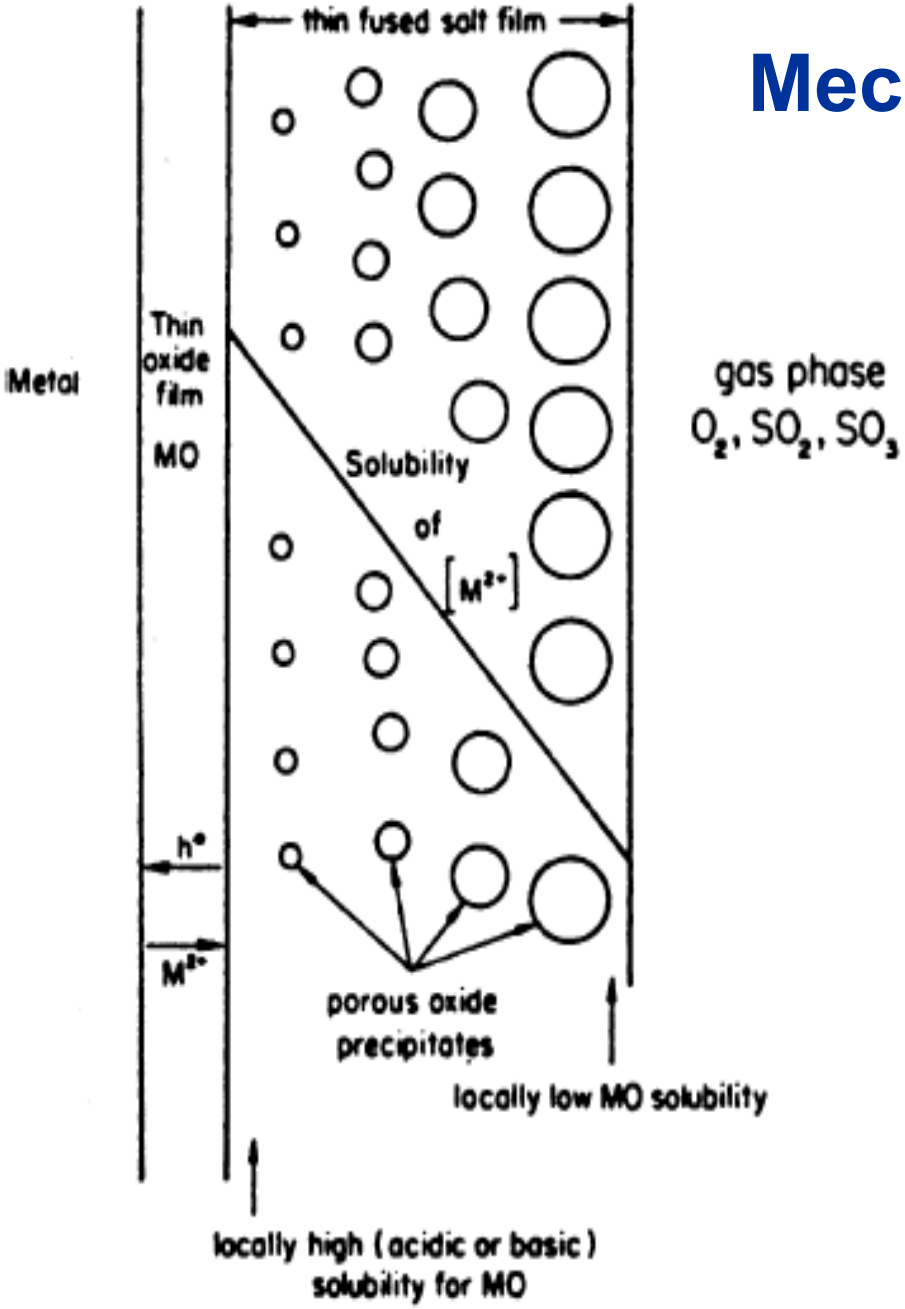
Fireside Corrosion—Initial Experiments Summary

- **Ash increases corrosion rates, but also appears to overwhelm the effect of combustion environment composition, making ash-covered corrosion rates in air and oxyfuel environments similar.**

Fireside Corrosion—Path Forward

- **Long term exposure tests in "realistic" environments**
  - Ash composition from Oxy-Combustion Ash project
  - Exposure tests on boiler tubes removed from service
- **Corrosion mechanism models & tests**
  - "Type 2" Hot Corrosion
    - Eutectic sulfates (with Fe from corrosion or ash) lower melting points of fused salts
    - Acidic & basic fluxing (dissolving) of protective oxides
    - Predicted influence of SO_3 on molten salt basicity and fluxing
  - Mechanistic Tests
    - Oxide solubility in the ash or molten salt as a function of SO_3

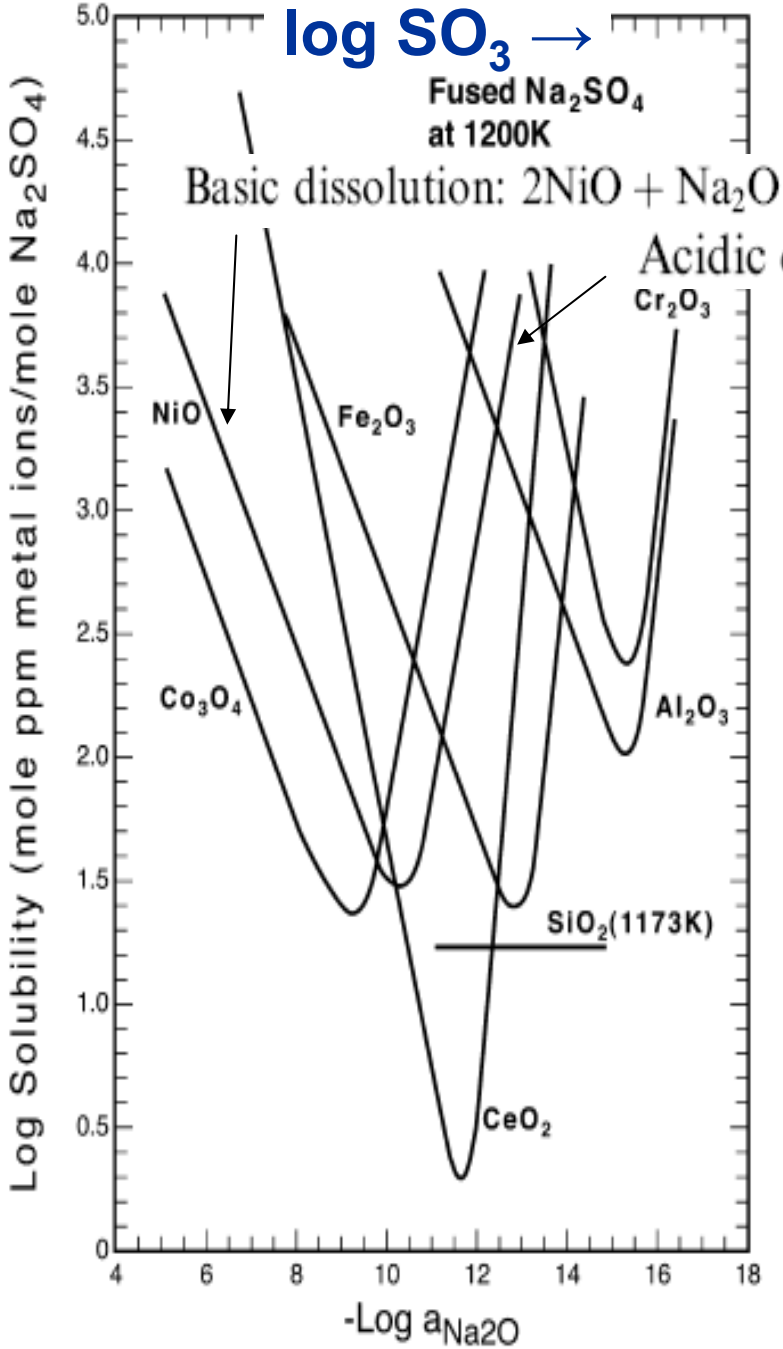
Mechanistic Approach (1)



- **Negative solubility gradient**
  - Non-protective oxide precipitation in the salt
  - favors continued rapid hot corrosion
- **Positive solubility gradient**
  - Somewhat protective oxide precipitation at the oxide
  - favors a reduction in hot corrosion

Rapp and Goto, 1981

Mechanistic Approach (2)



Rapp, 2002

- **Gas Phase**
  - SO_3 can change basicity
- **Ash Content**
  - Can change basicity
  - FeS → more basic
- **Effectiveness of Chromium**
  - Cr_2O_3 is very acidic
  - Positive solubility gradient even with basic dissolution
  - Deposits somewhat protective

Basicity: Salt-Oxide-Metal vs Gas Phase

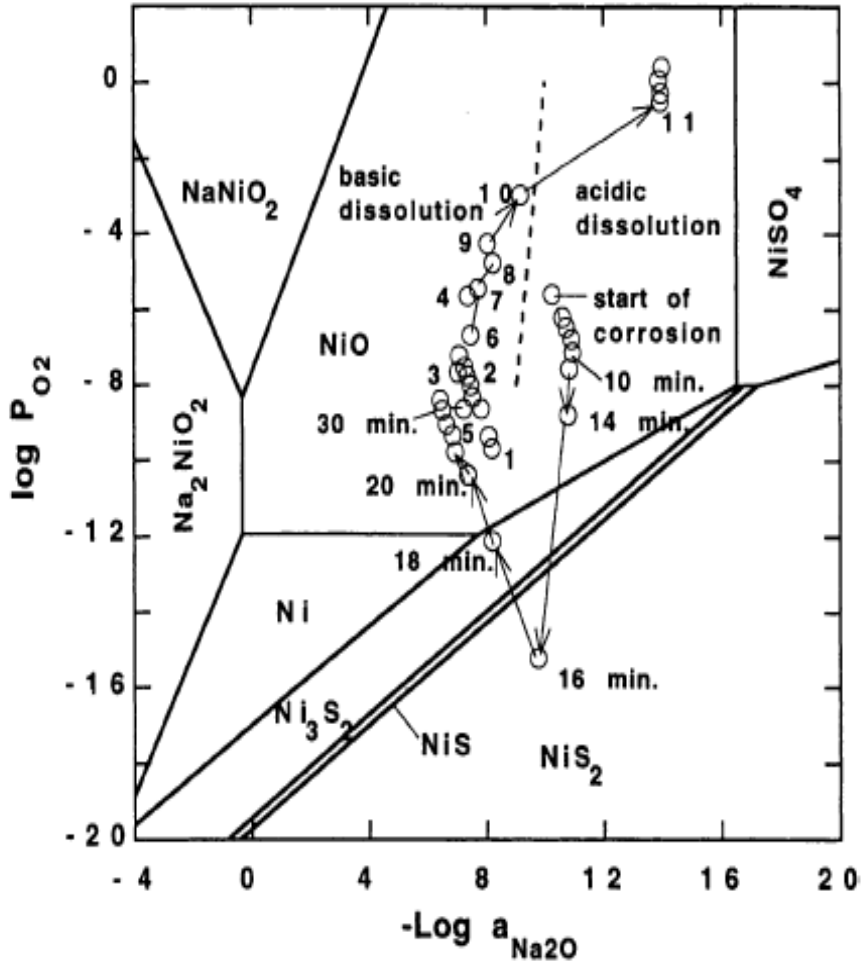


Fig. 4. Trace of basicity and oxygen activity measured on a preoxidized 99% Ni coupon with a Na_2SO_4 film at 1173 K in O_2–0.1% SO_2 gas. The central dashed line in the NiO stable field indicates the minimum in NiO solubility. Numbers in the figure designate the reaction time in hours, except indicated [26].

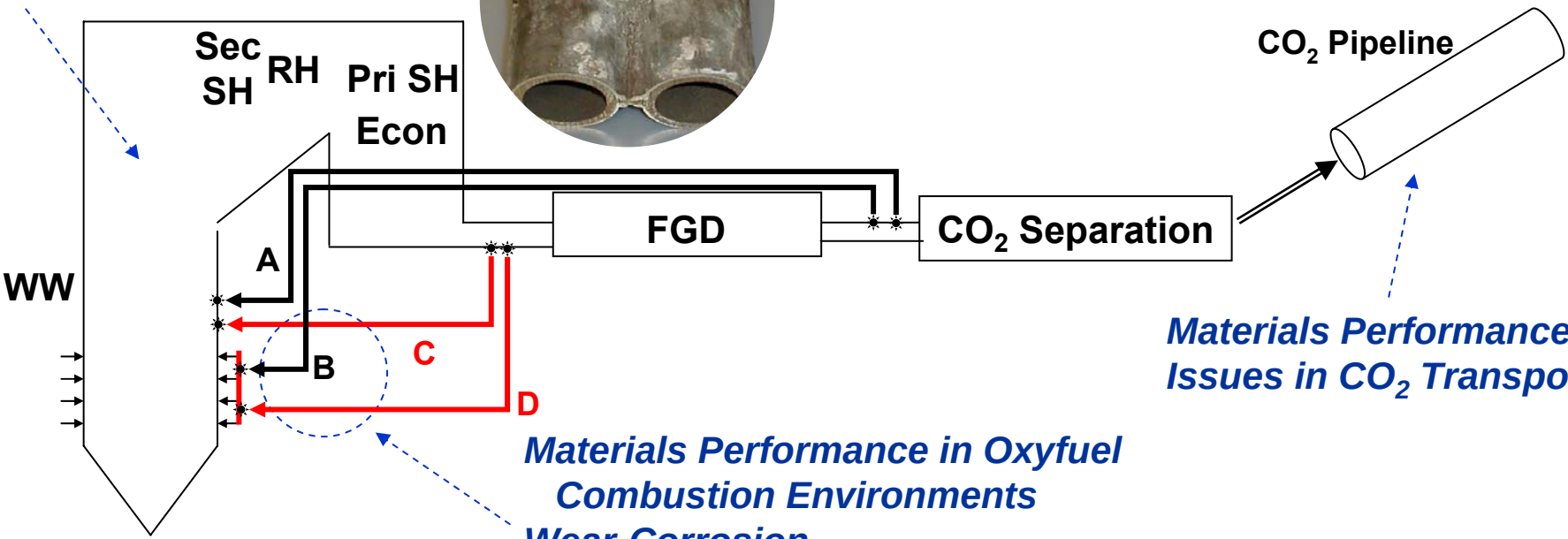
Rapp, 2002

Refit Options and ORD Materials Research

Oxy-Combustion of Fossil Fuels with Carbon Capture

Oxy-Combustion Ash

Materials Performance in Oxyfuel Combustion Environments
Fireside Corrosion



Materials Performance Issues in CO_2 Transport

Materials Performance in Oxyfuel Combustion Environments
Wear-Corrosion

A Cold Recirculation with Cleanup and Reheat

B Cold Recirculation with Cleanup, Reheat and Coal Motivation

C Hot Recirculation

D Hot Recirculation with Coal Motivation

Increasing Efficiency
Increasing Corrosion Risk
Increasing Heat Changes