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Role of Coal Ash in the Corrosion Performance of Structural Alloys in Simulated Oxy-Fuel Environments

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26th Annual Conference on Fossil Energy Materials, Pittsburgh, PA, April 17-19, 2012

Work supported by DOE/Office of Fossil Energy, Advanced Research Materials Program

What and Why Oxy-Fuel Combustion

- *Global climate change - One of the causes identified is CO_2 increase in atmosphere - one of the source for CO_2 is exhaust from fossil fuel combustion plants*

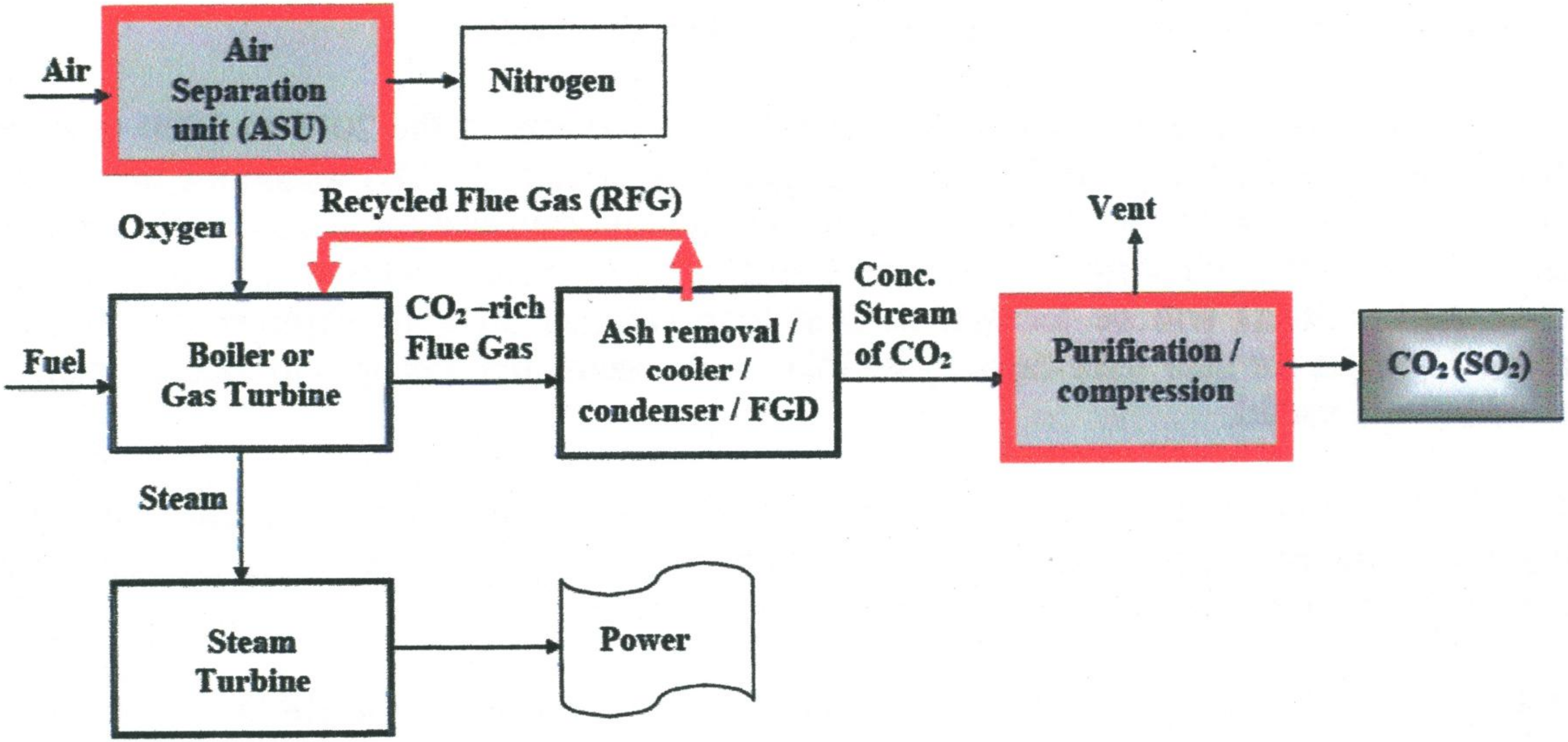
- *Energy production (in particular, electricity) is expected to increase due to population increase and per capita increase in energy consumption*

- *To meet the energy needs, fossil fuels (coal, gas, oil, etc.) will play a major part in production even with a projected increase from alternate sources*

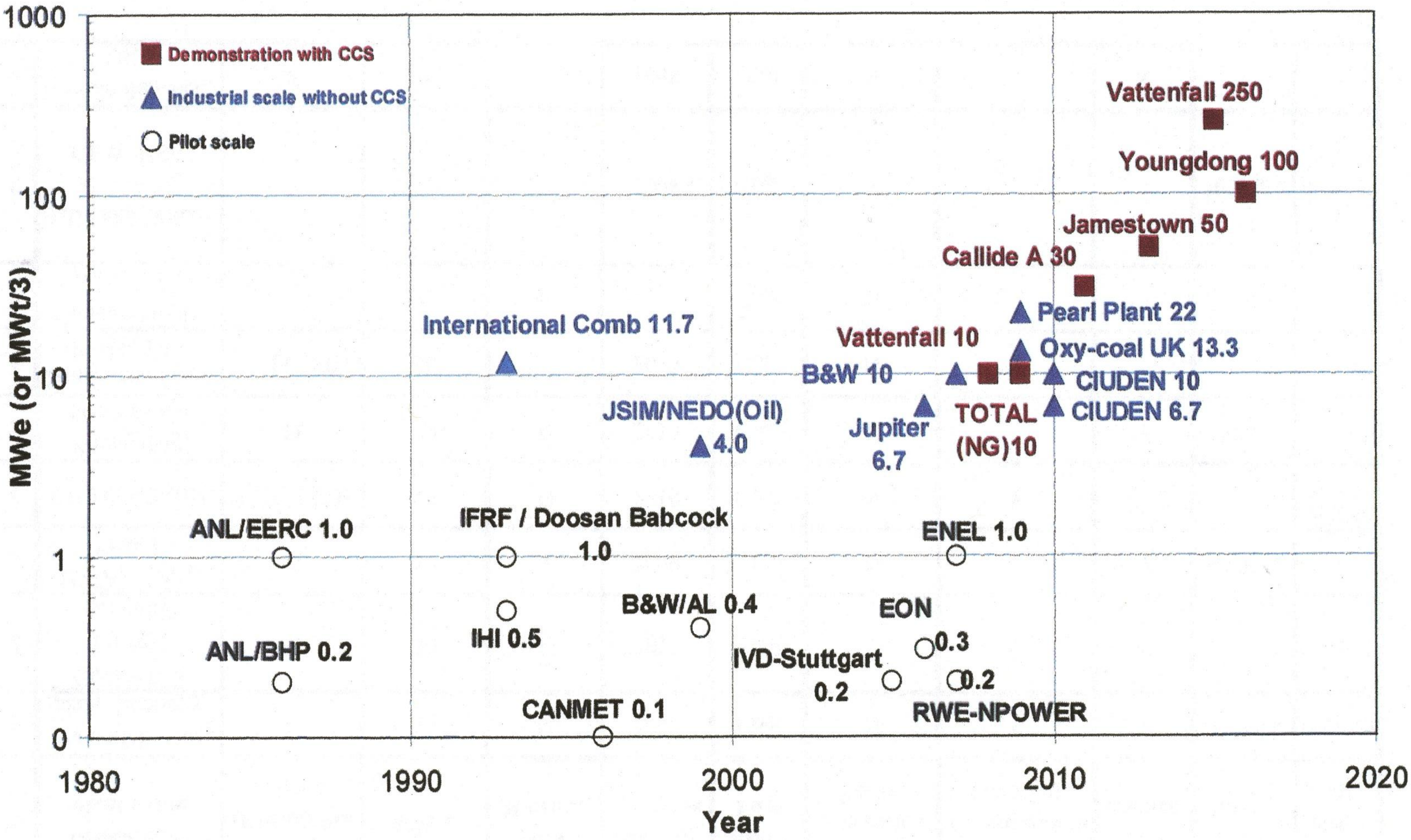
- *To minimize CO_2 emission - current systems emphasize capture from power plants and sequestration*

- *Oxy-fuel combustion systems – enable retrofit of PC boilers, recycle CO_2 in the combustion process, use novel gas turbines, and emphasize reuse*

Oxy-Fuel Combustion System



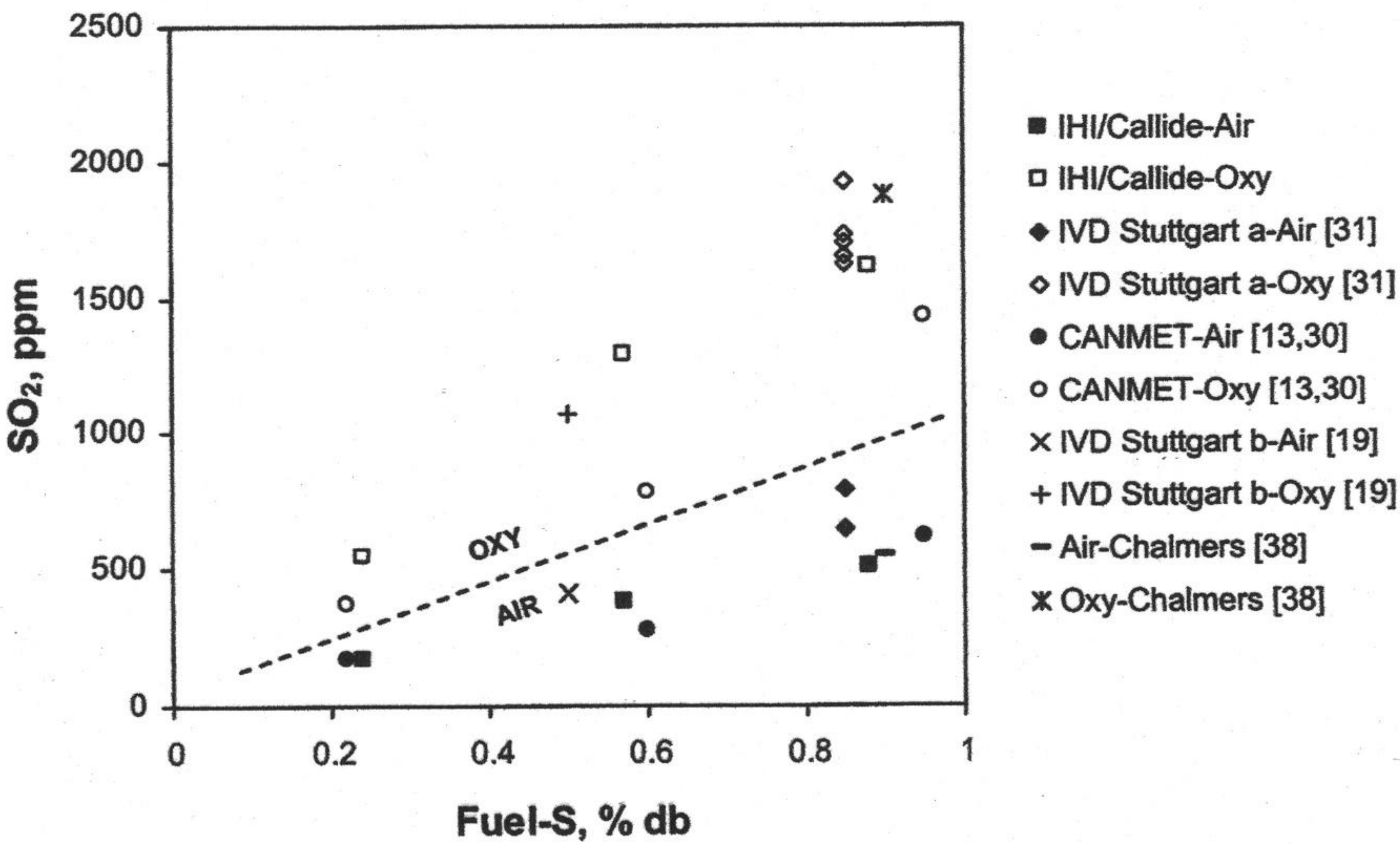
Historical Development of Oxy-Fuel Systems



List of Large Demonstration Oxy-Combustion Plants

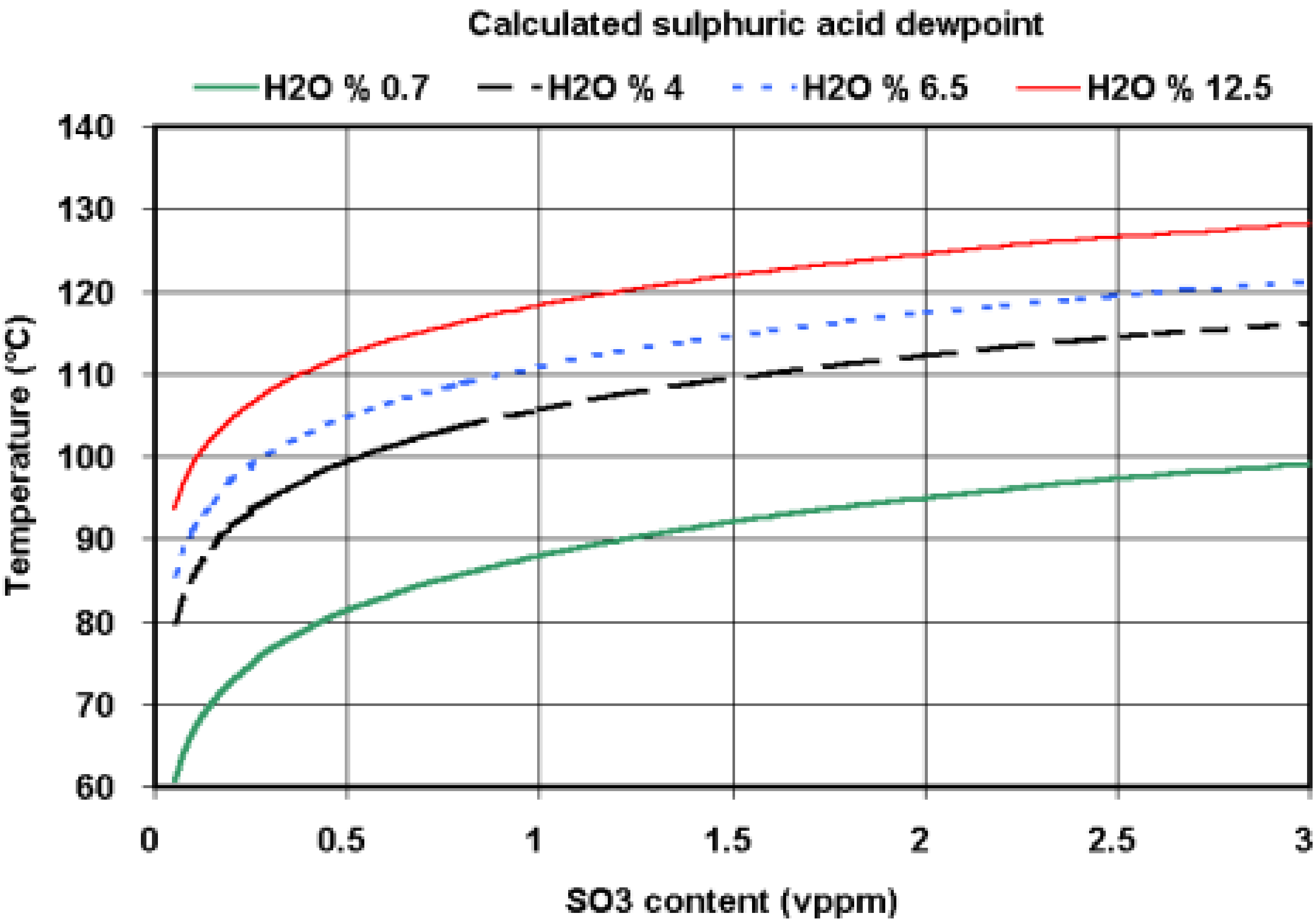
No	Demo/pilot-plant name	Scale (Demo/Pilot plant)	MW e	New Retrofit	Startup/ Duration	Main Fuel	Electricity generation Yes/No	CO2 Compression (Yes/No)	CO2 use/Seq	CO2 purity	Gas clean up
1	Vattenfall pilot plant, Germany	P	10	N	2008	Coal	N	Y	Y	99.90%	FGD ESP
2	Callide (CS Energy, Australia)	D	30	R	2011	Coal	Y	Y	Y		FF
3	TOTAL, Lecq, France	D	10	R	2009	NG	N	Y	Y	99.90%	
4	CIUDEN, Spain	P (PC/CFB)	17	N	2010	Coal	N	Y	Y		SCR FF FGD
5	Youngdong, South Korea	D	100	R	2016	Coal	Y		Y	98%	SNCR FF
6	Jamestown/Praxair Plant, USA	D(CFB)	50	N	2013	Coal	N	Y			
7	Jupiter Pearl plant, USA	D	22	R	2009	Coal	N	N			
8	Babcock&Wilcox pilot plant, B&W, USA	P	10	R	2008	Coal	N		N	70% dry	FGD ESP
9	Doosan Babcock, UK	P	30	N/A	2008	Coal	N		N		

SO_2 concentration in air-fired and oxy-fuel combustion



Stranger and Wall, 2011

Effect of SO_3 and Water Vapor on Acid Dewpoint



ANL Program Objectives

- Evaluate the effect of coal ash with additions of alkali, sulfur, and chlorine compounds on the corrosion performance
- Perform long-term experiments to enable corrosion rate and life prediction for structural alloys in simulated oxy-fuel environments
- Establish the kinetics of scaling and internal penetration, if any, and develop correlations for long term performance of metallic materials
- Identify viable alloys for structural and gas turbine applications
- Over the long term, evaluate the influence of exposure environment on the mechanical properties (especially creep, fatigue, and creep-fatigue) of the candidate alloys

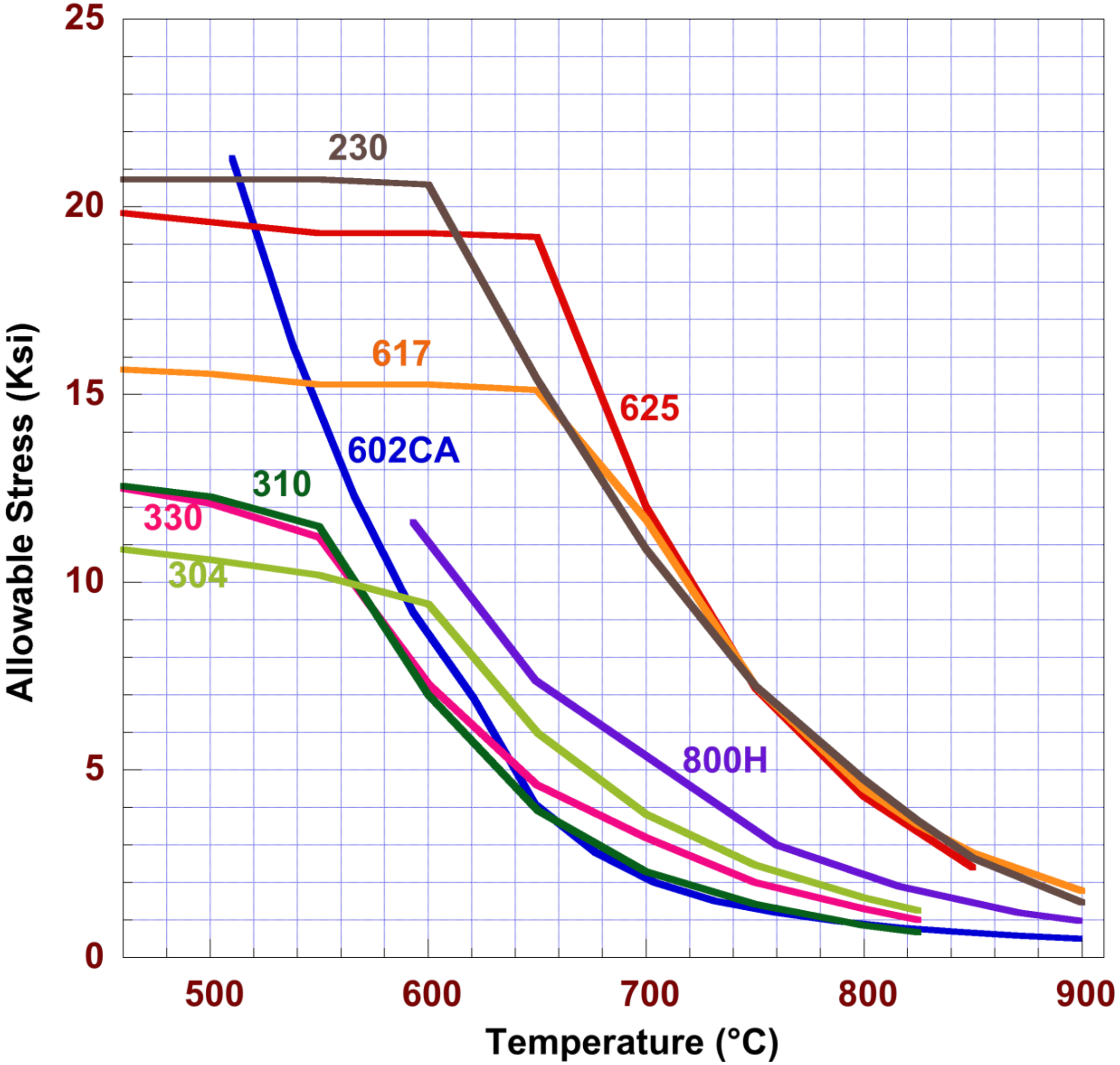
Outline

- *Background*
- *Objectives*
- *Materials and experimental procedure*
- *Alloys for evaluation*
- *Role of ash environment on corrosion*
- *Corrosion performance of alloys*
- *Project Summary*

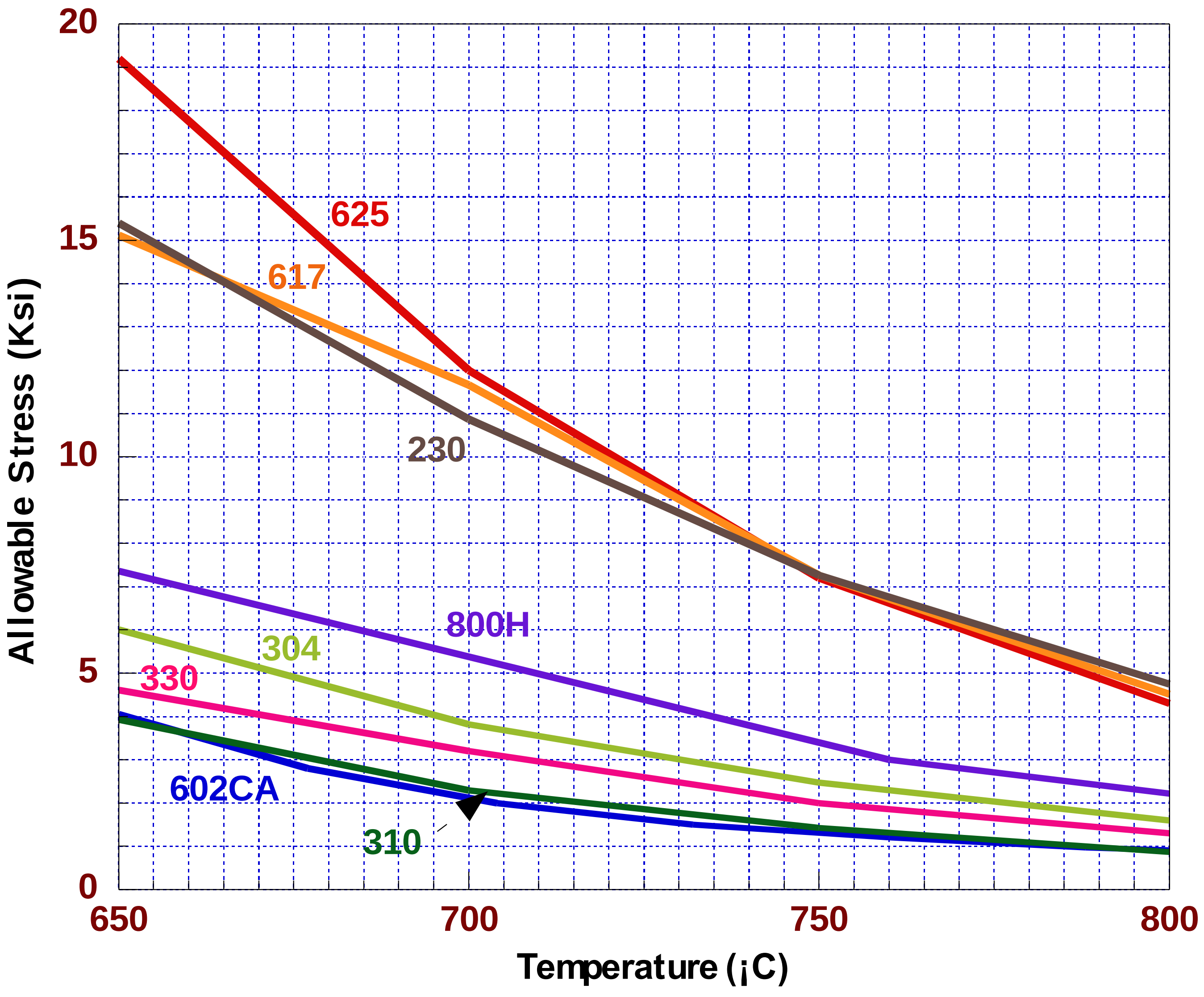
Current List of Alloys in the Study

Material	C	Cr	Ni	Mn	Si	Mo	Fe	Other
153MA	0.05	18.4	9.5	0.6	1.4	0.2	Bal	N 0.05, Nb 0.07, V 0.2
800H	0.08	20.1	31.7	1.0	0.2	0.3	Bal	Al 0.4, Ti 0.3
330	0.05	10.0	35.0	1.5	1.25	-	Bal	-
333	0.05	25.0	45.0	-	1.0	3.0	18.0	Co 3.0, W 3.0
617	0.08	21.6	53.6	0.1	0.1	9.5	0.9	Co 12.5, Al 1.2, Ti 0.3
625	0.05	21.5	Bal	0.3	0.3	9.0	2.5	Nb 3.7, Al 0.2, Ti 0.2
602CA	0.19	25.1	62.6	0.1	0.1	-	9.3	Al 2.3, Ti 0.13, Zr 0.19, Y 0.09
230	0.11	21.7	60.4	0.5	0.4	1.4	1.2	W 14, Al 0.3, La 0.015
693	0.02	28.8	Bal	0.2	0.04	0.13	5.8	Al 3.3, Nb 0.67, Ti 0.4, Zr 0.03
740	0.07	25.0	Bal	0.3	0.5	0.5	1.0	Co 20.0, Ti 2.0, Al 0.8, Nb+Ta 2.0
718	-	19.0	52.0	-	-	3.0	19.0	Nb 5.0, Al 0.5, Ti 0.9, B 0.002
MA956	-	20.0	-	-	-	-	Bal	Al 4.5, Ti 0.5, Y_2O_3 0.6
WASP	0.07	20.0	Bal	0.1	0.1	5	-	Al 1.4, Ti 3, Co 13.5
ANL-5	0.2	25.0	Bal	-	-	-	-	Al 3.3, Ti 0.3, Zr 0.2, Y 0.1

ASME Code Allowable Stress Values



ASME Code Allowable Stress Values at 650-800℃



Laboratory Test Details

Key variables: Temperature, time, alloy composition

Materials: Fe- and Ni-base alloys, coatings

Environments: $95\%CO_2$-$0.99\%SO_2$-$3.97\%O_2$

$68.1\%CO_2$-$26.9\%H_2O$-$0.99\%SO_2$-$3.97\%O_2$

Ash mixture: 90% (SiO_2 :Al_2O_3:Fe_2O_3 = 1:1:1) and 10%(Na_2SO_4:K_2SO_4 = 1:1)

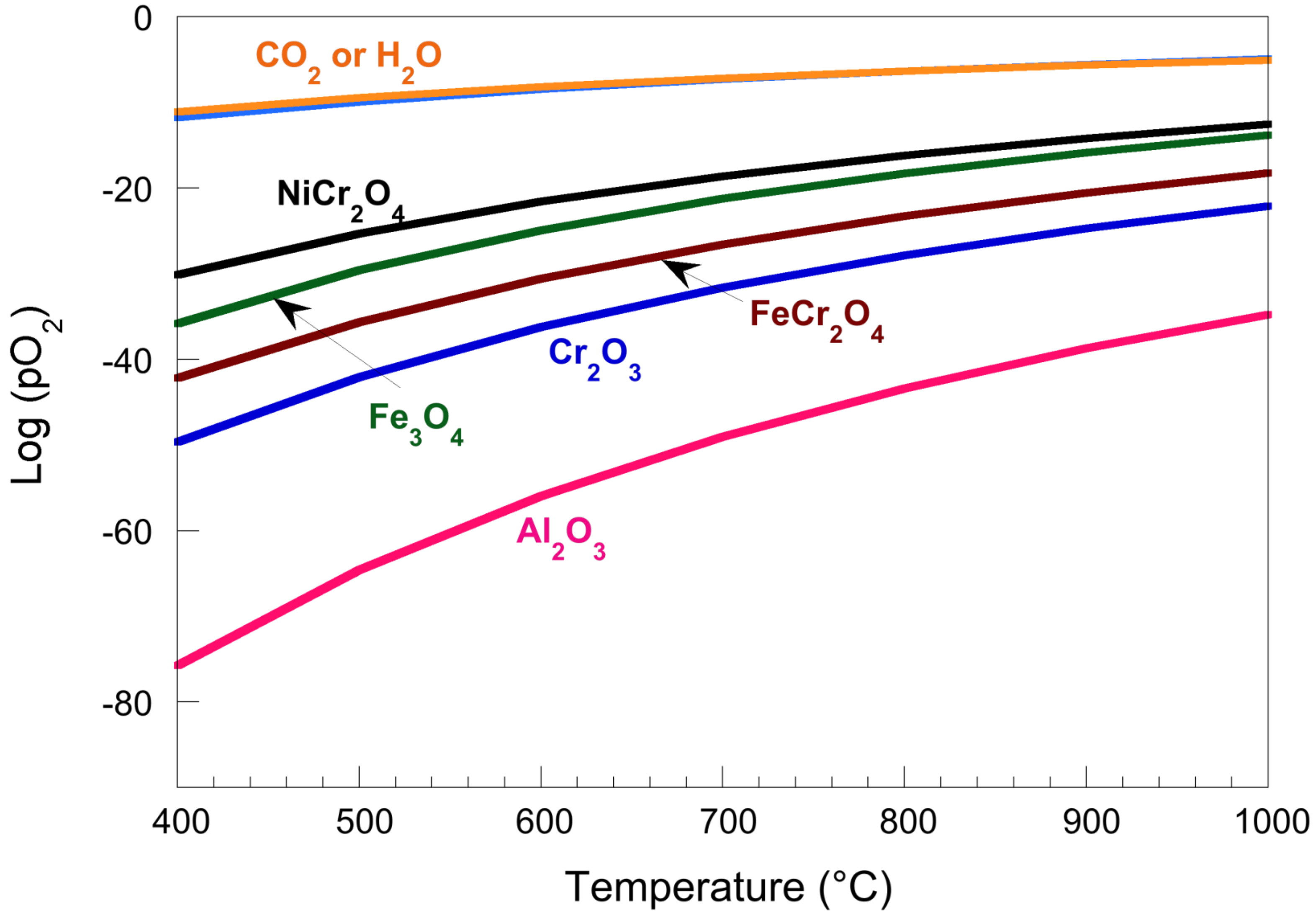
$36\%SiO_2$-$16\%Al_2O_3$-$9\%Fe_2O_3$-29%CaO and 10%(Na_2SO_4:K_2SO_4 = 1:1)

Test temperature range: 650-1000°C

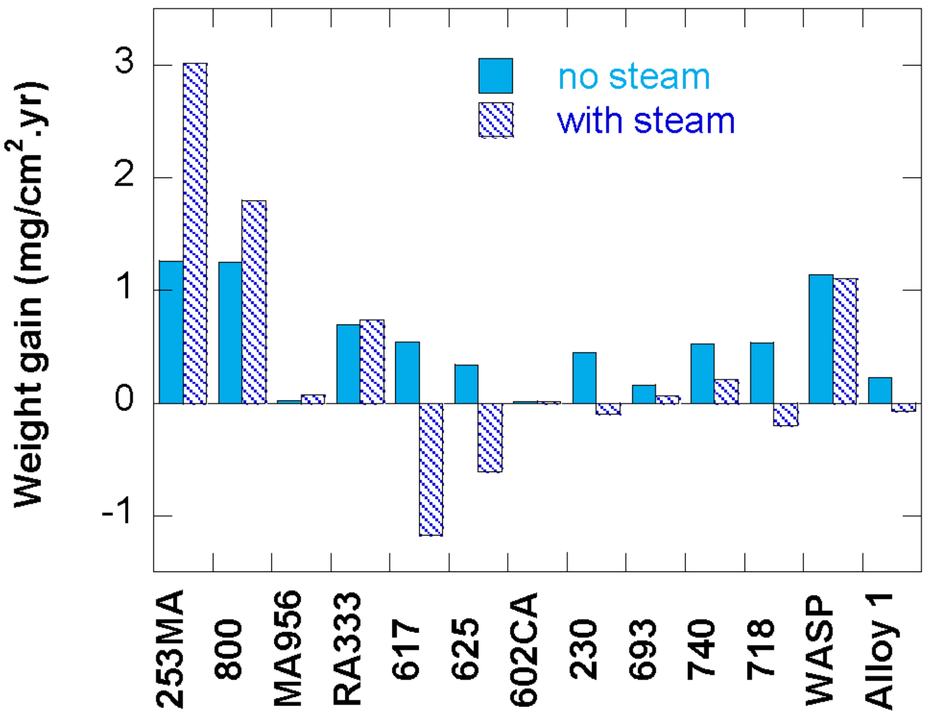
Test times: up to 5,000 h

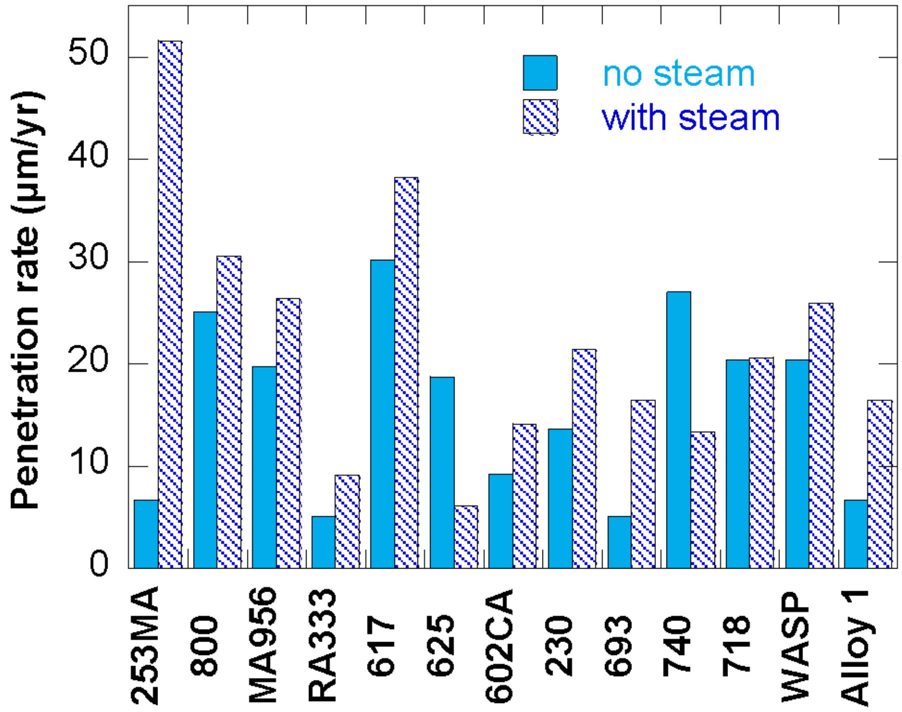
Specimen evaluation:
- weight change
- scanning electron microscopy
- energy dispersive X-ray analysis
- X-ray diffraction
- synchrotron nanobeam analysis

Thermodynamic Stability of Oxide Phases in the Scale



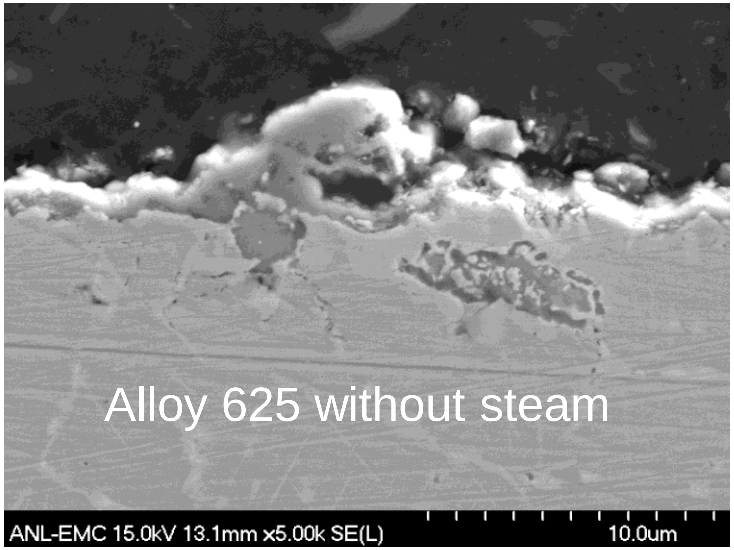
Alloy Penetration Rates in CO_2 - H_2O - O_2 at 750ºC (no ash)

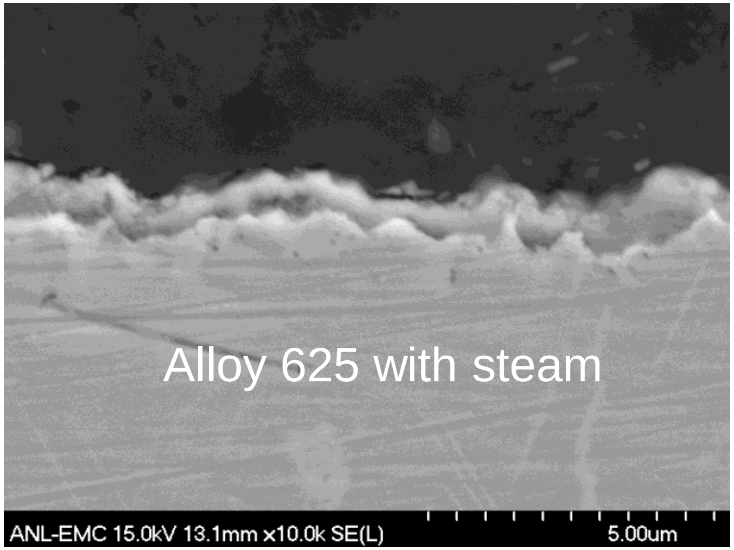


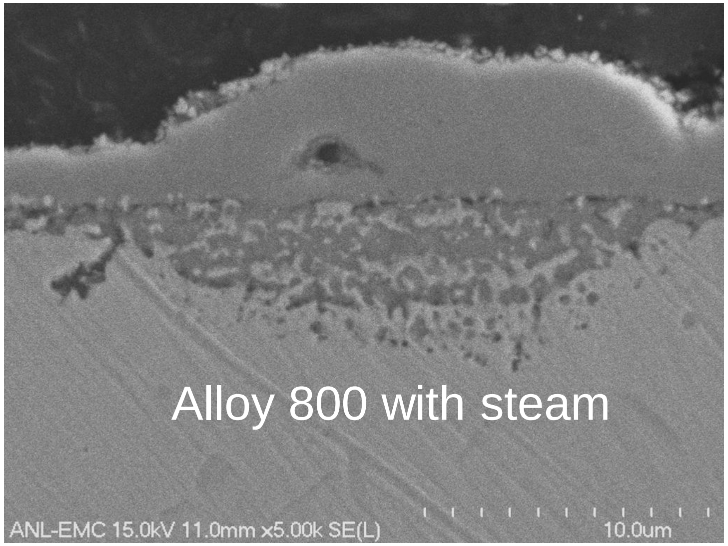


No steam: CO_2 - 3.97% O_2
With steam: CO_2 – 27.4% H_2O - 3.97% O_2
High Cr, Al beneficial; Nb detrimental

Ni-base alloys performed better than Fe-base alloys

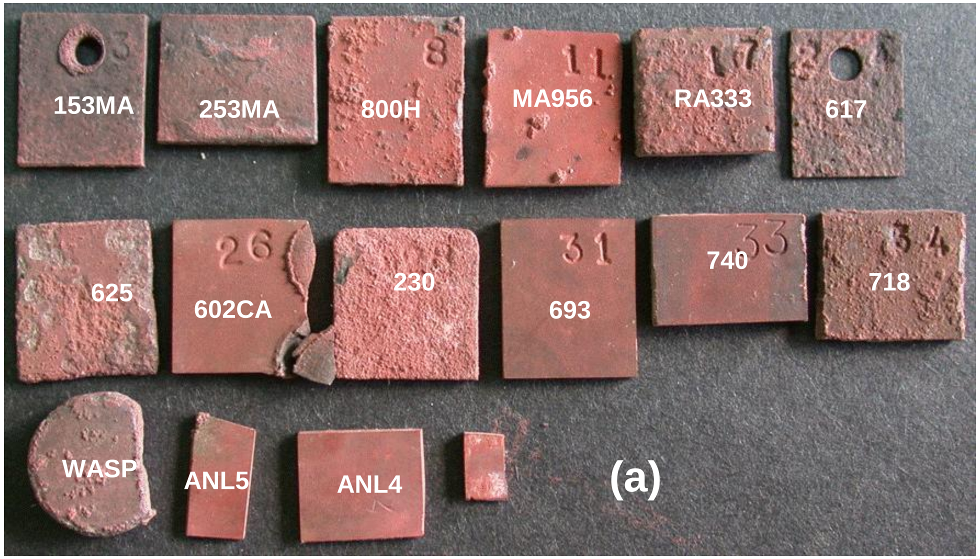






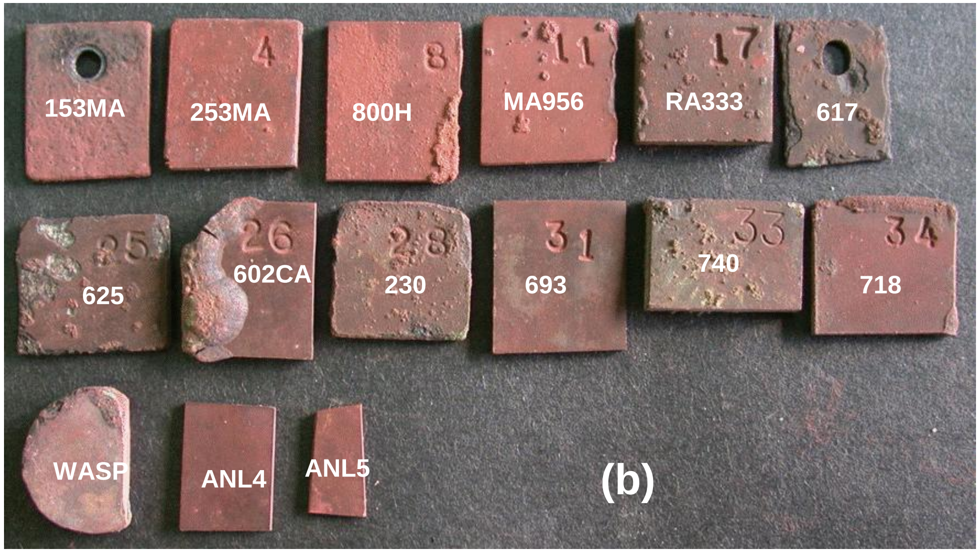
Ni-base alloy exhibit less localized corrosion

Photograph of Specimens Exposed to Ash (US Eastern Coal)



1200 h at 750ºC in ash
and Gas with steam

Uniform corroded: 153MA, 253A, 617
Localized corroded: 800H, MA956, RA333, 625, 602CA, 230, 718, WASP, ANL5
No corroded: 693, 740, ANL4



1200 h at 750ºC in ash
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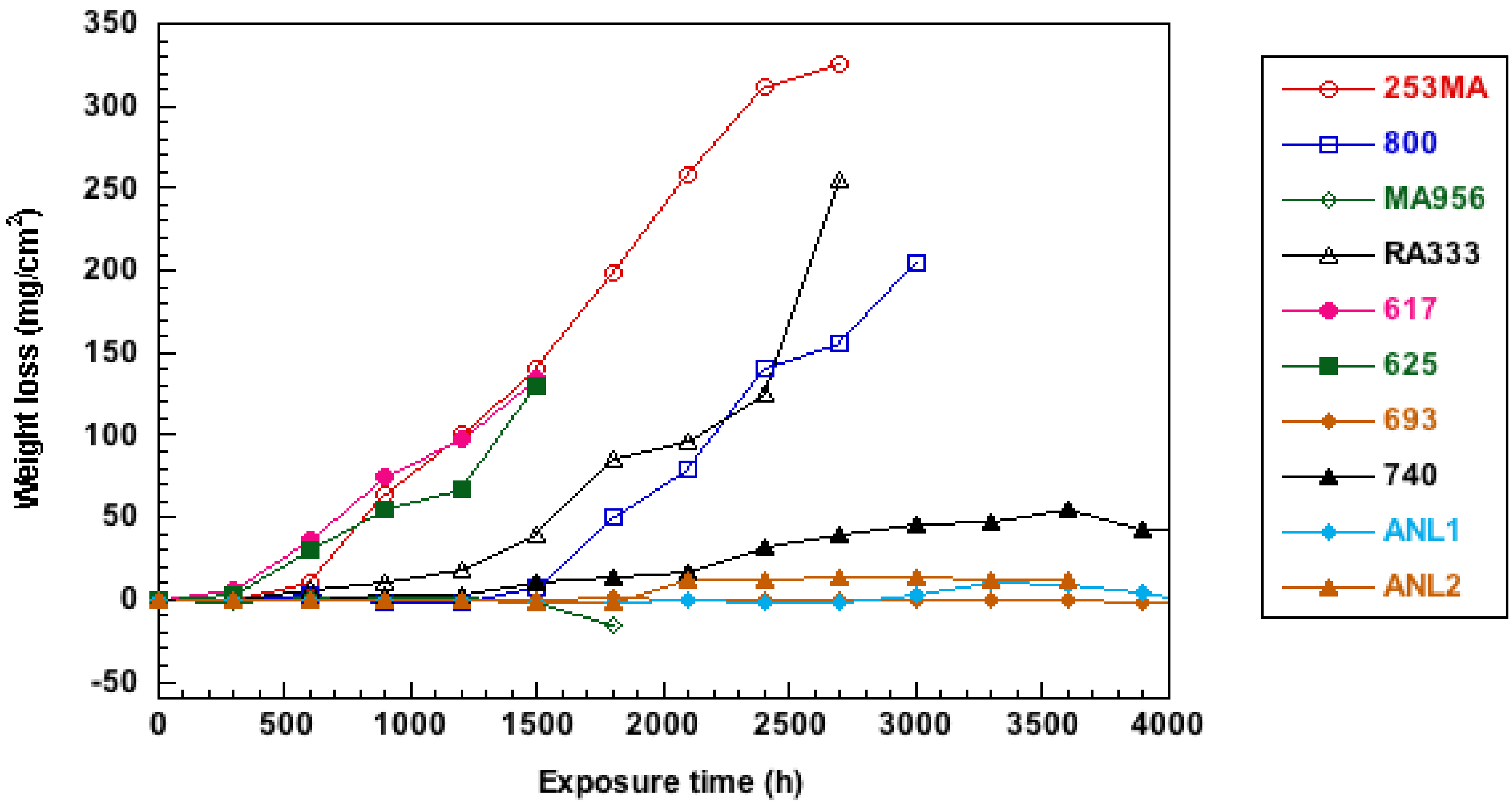
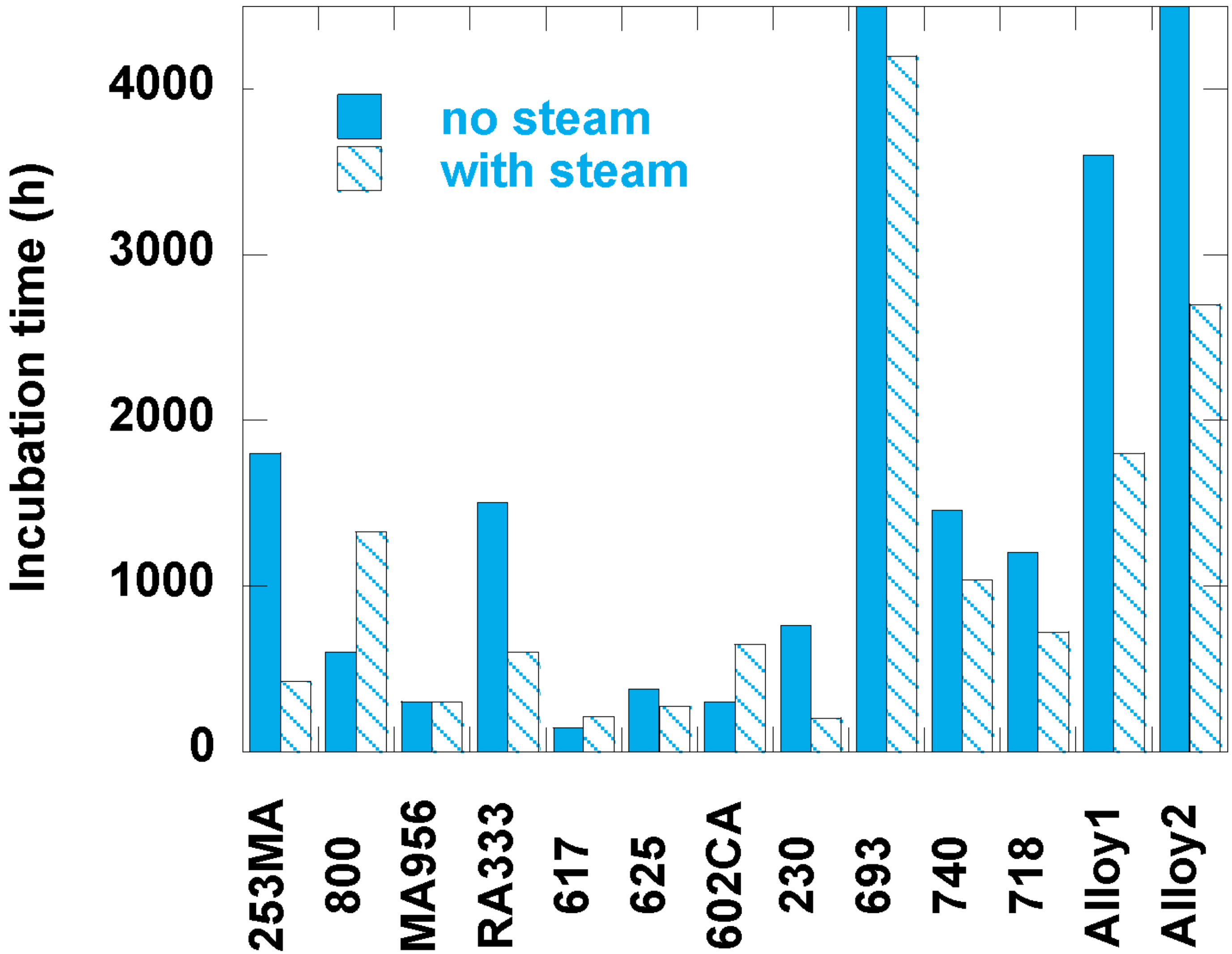
Uniform corroded: 153MA,
Localized corroded: 800H, MA956, RA333, 617, 625, 602CA, 230, 718, WASP, 740
No corroded: 253MA, 693, ANL4, ANL5

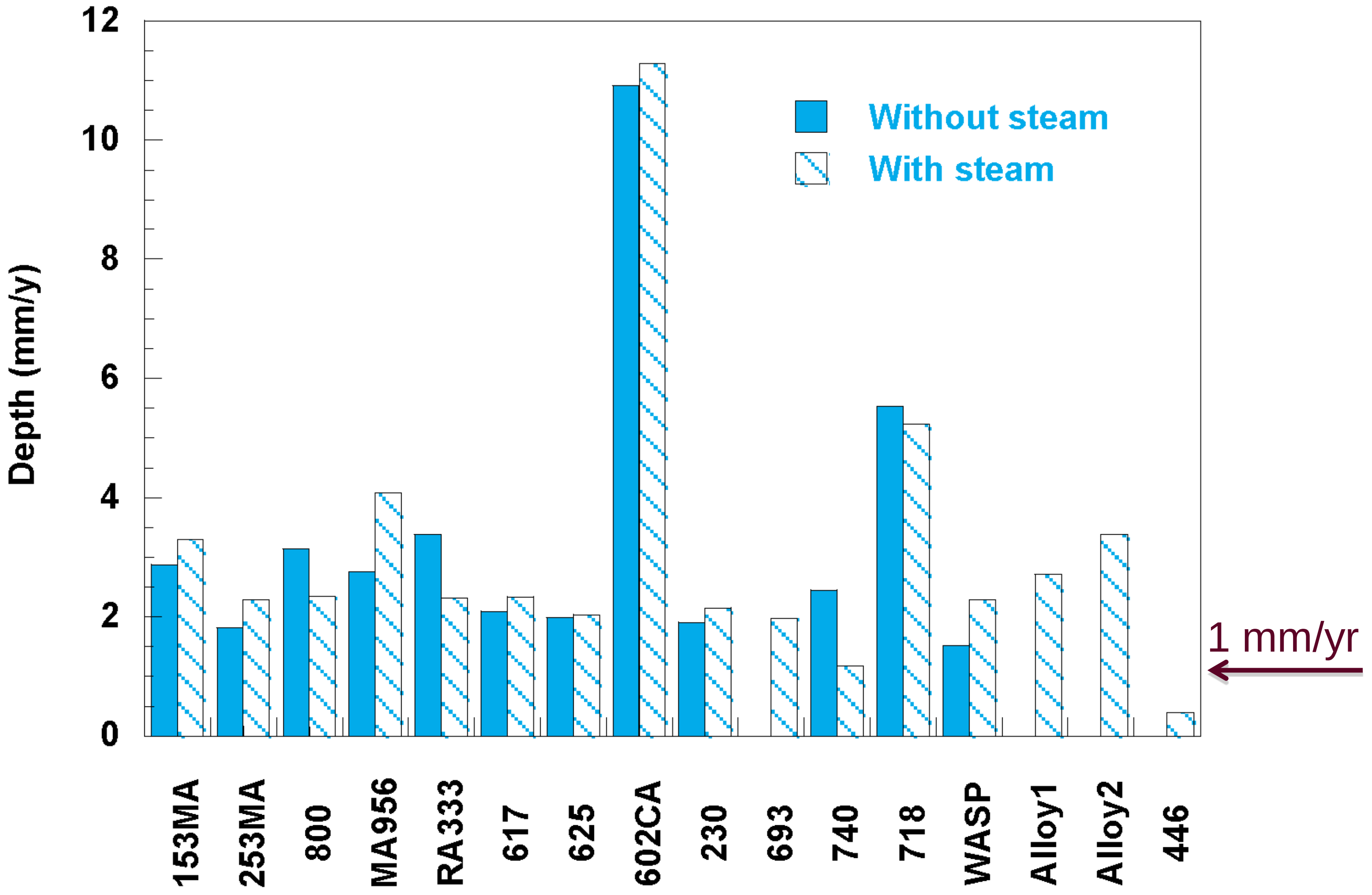
Weight Loss Data at 750 ℃ to Oxy-fuel Environment containing Eastern Coal Ash and Steam



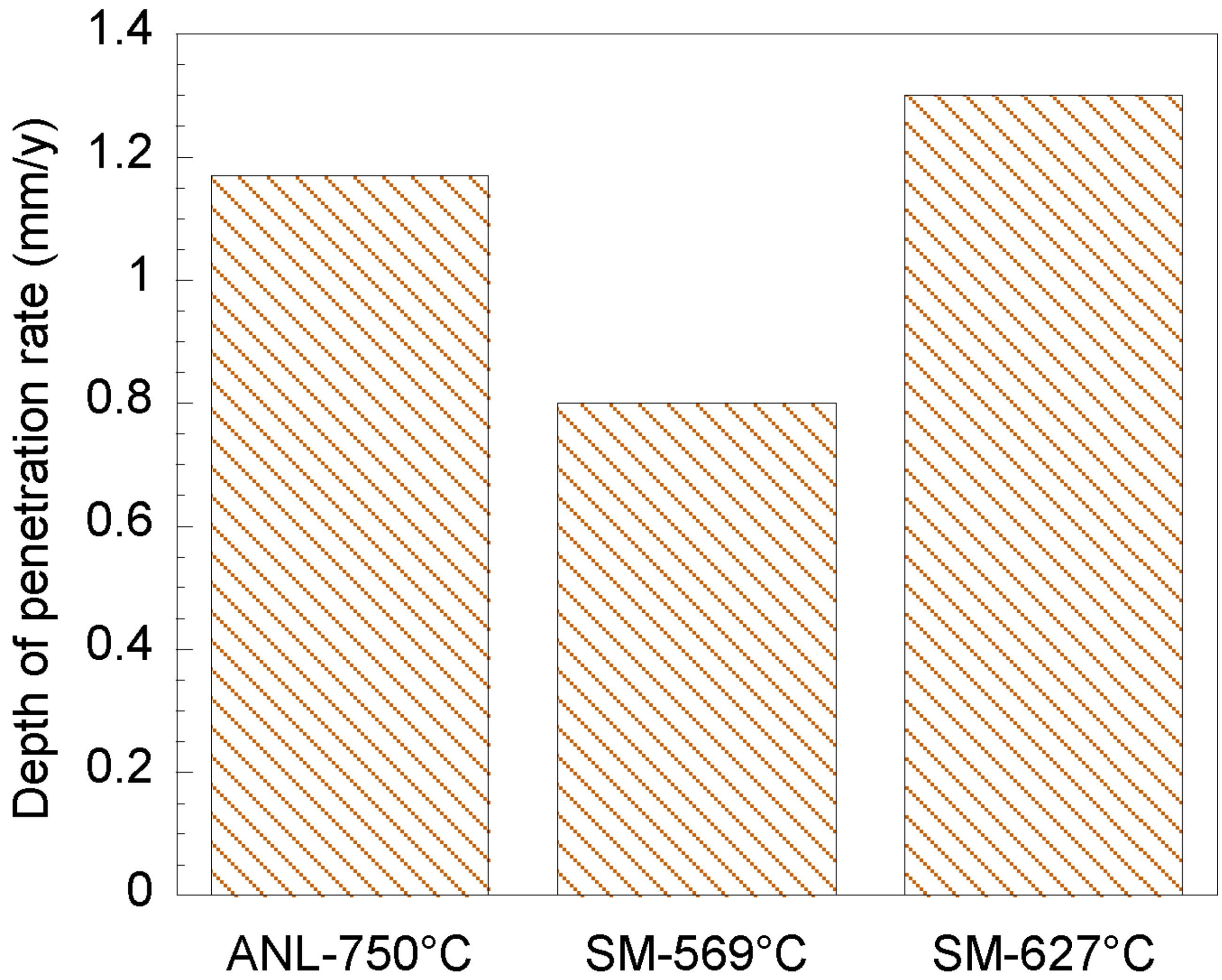
Incubation time

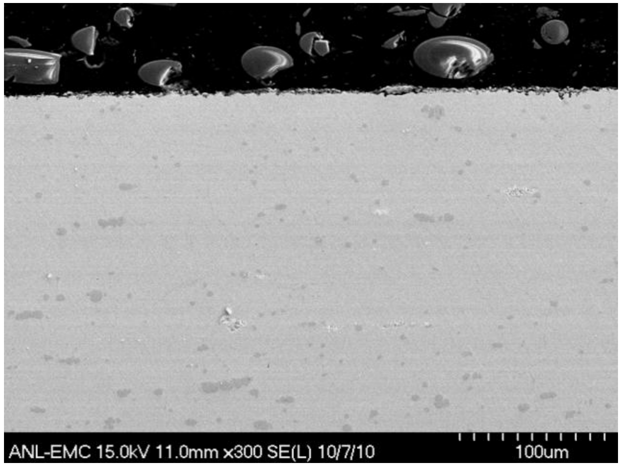


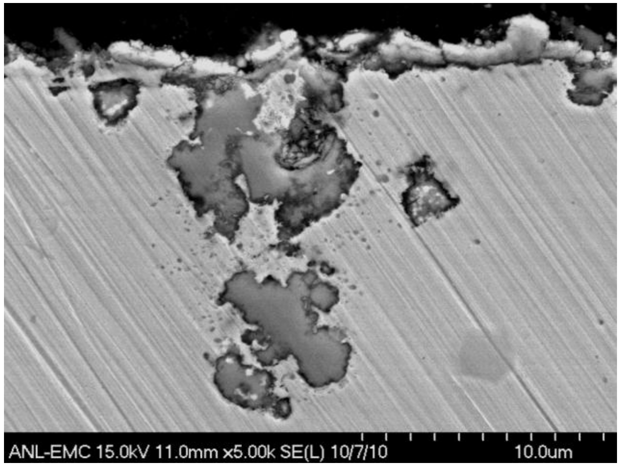
Corrosion depth rate (subsequent to incubation) upon exposure at 750℃ in oxy-fuel environment containing Eastern coal ash



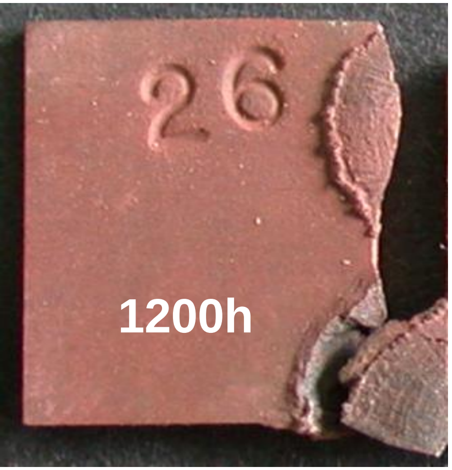
Comparison of Corrosion Depth Data for Alloy 740

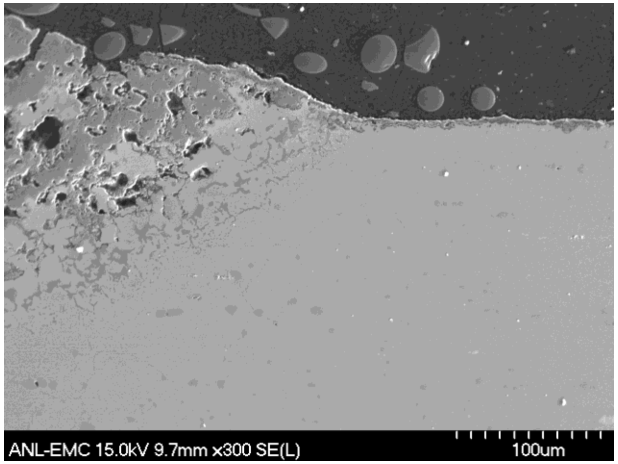


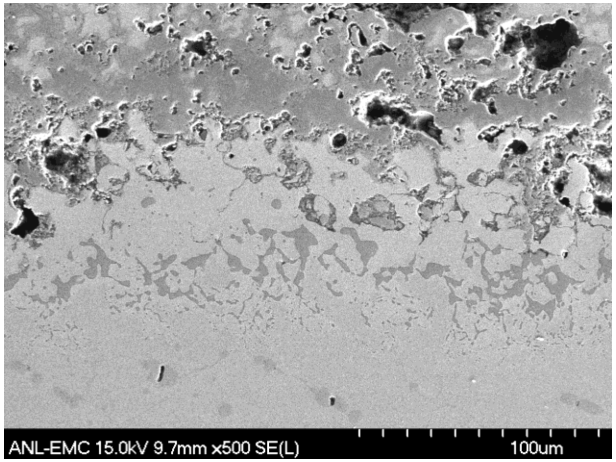




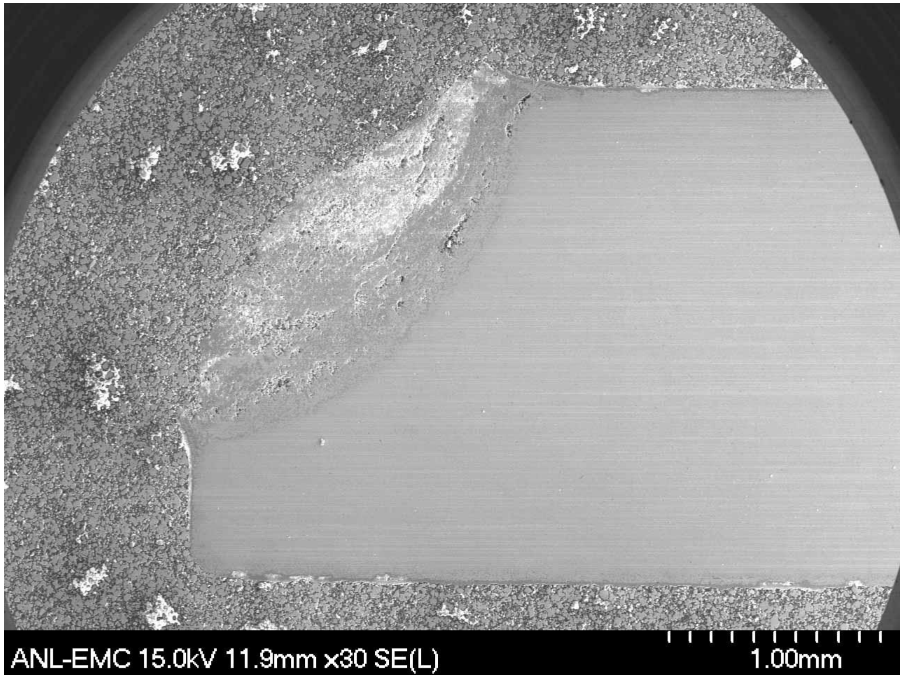
Alloy 602CA before incubation time in the gas with steam

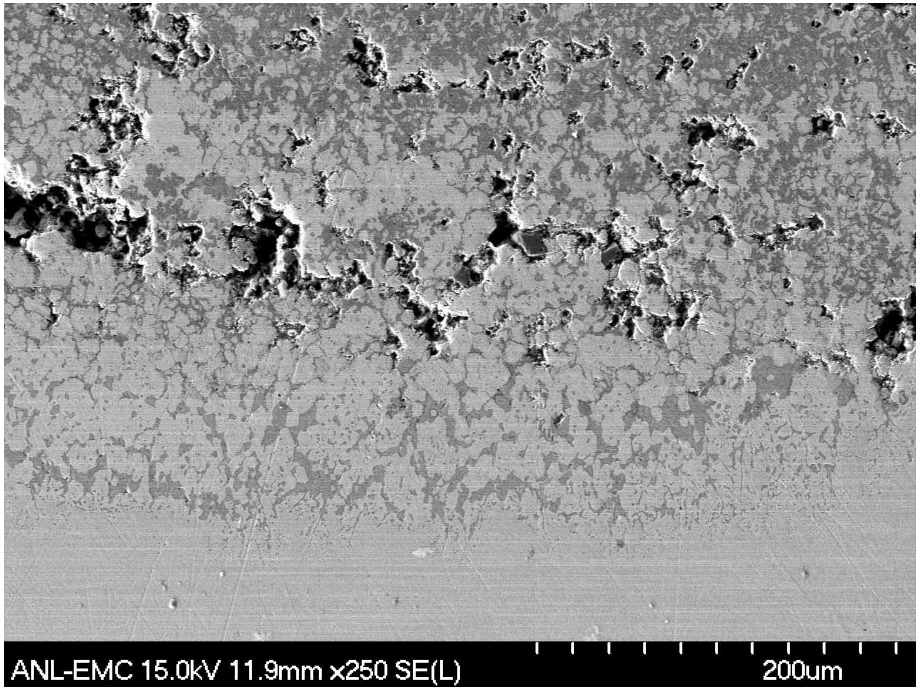






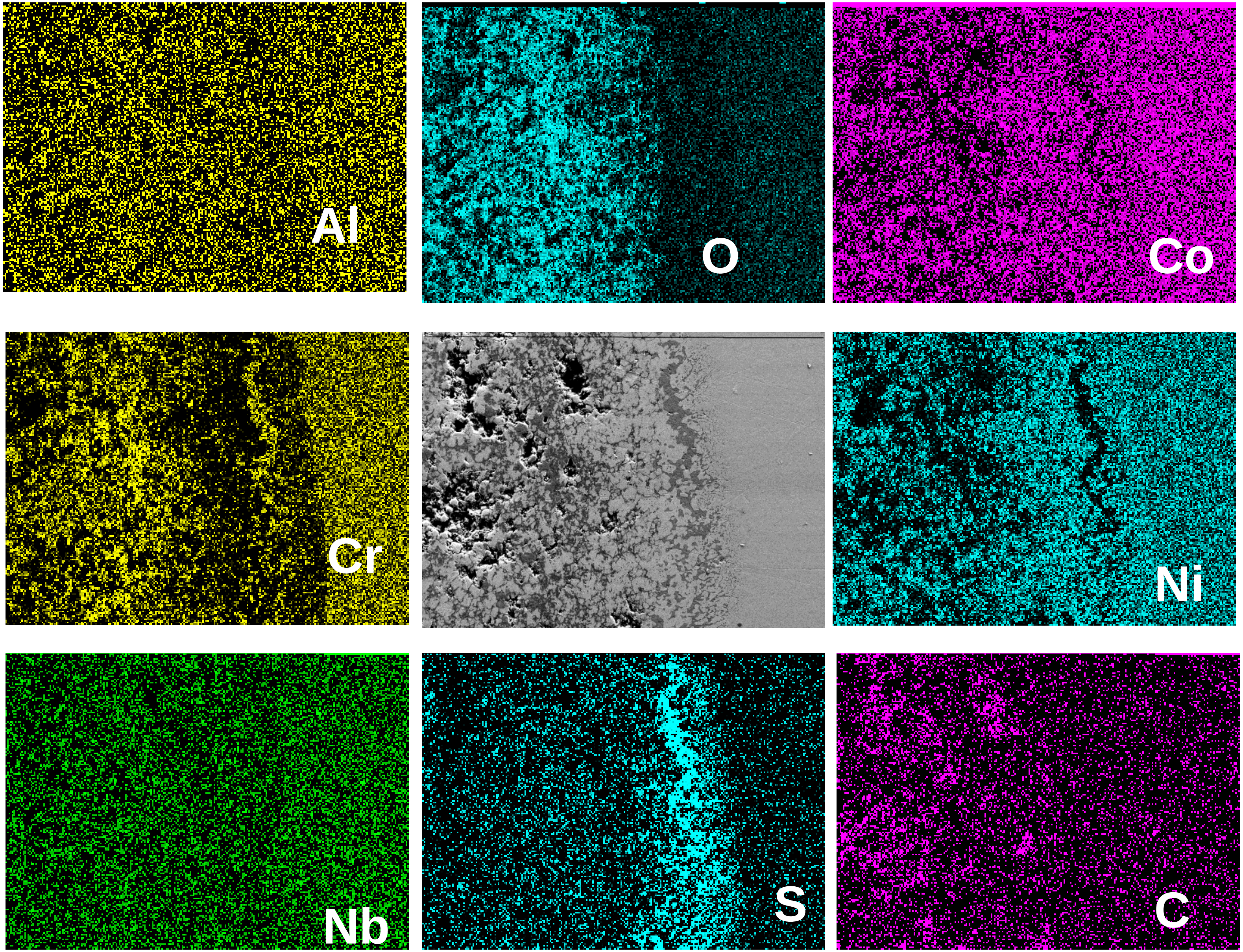
Alloy 602CA after incubation time



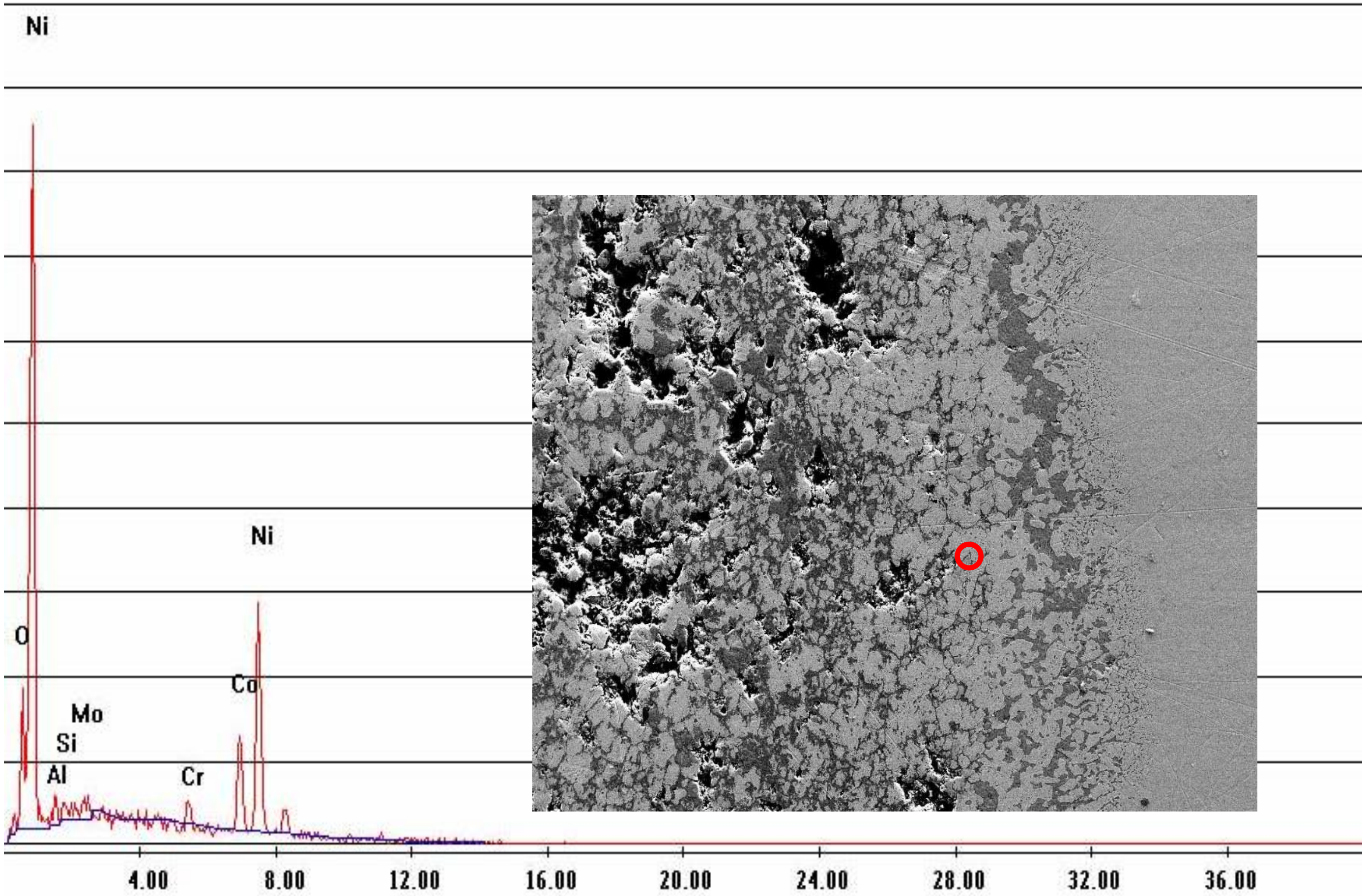


Alloy 740, Exposure time >4,000h

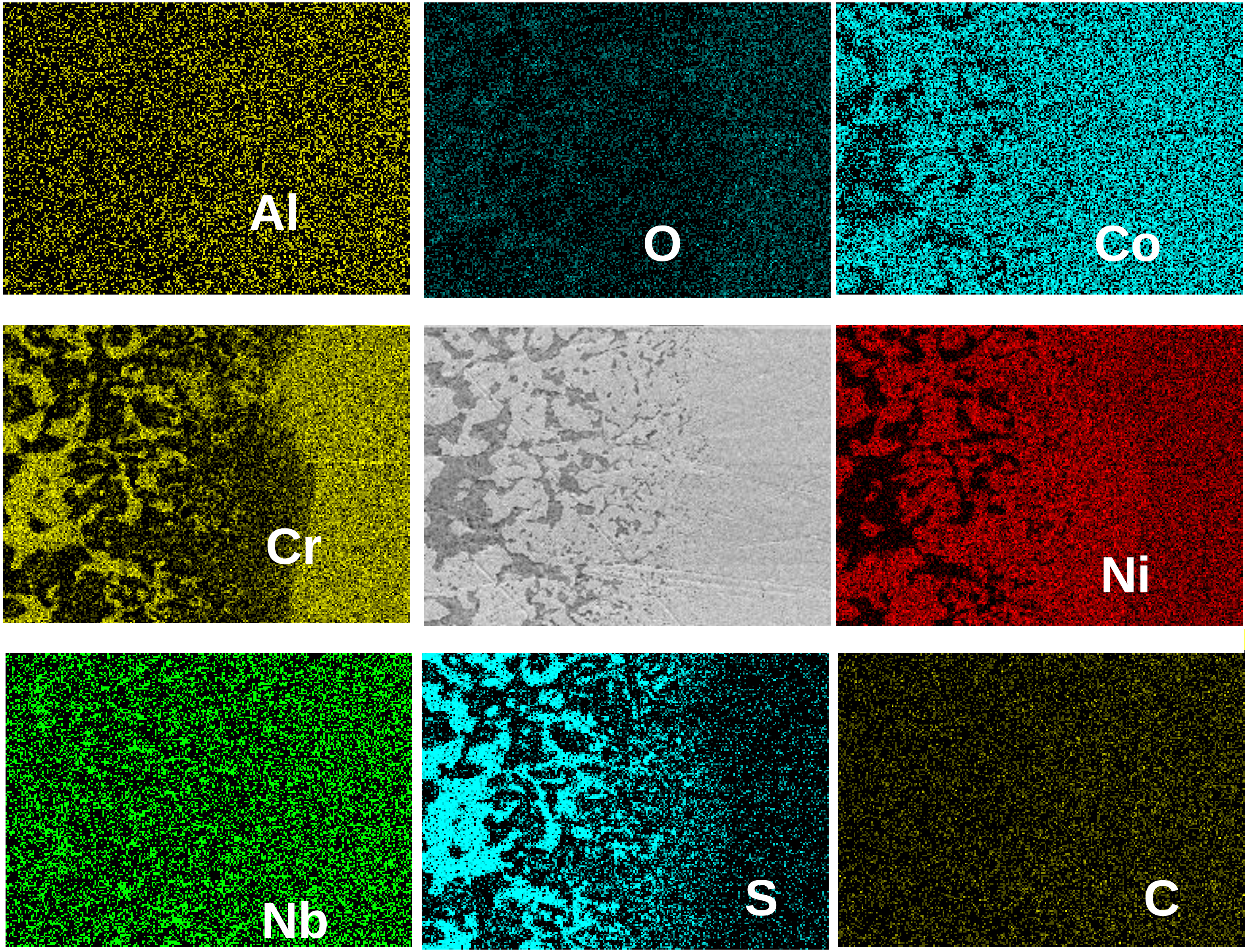
Alloy 740, EDX at corroded region



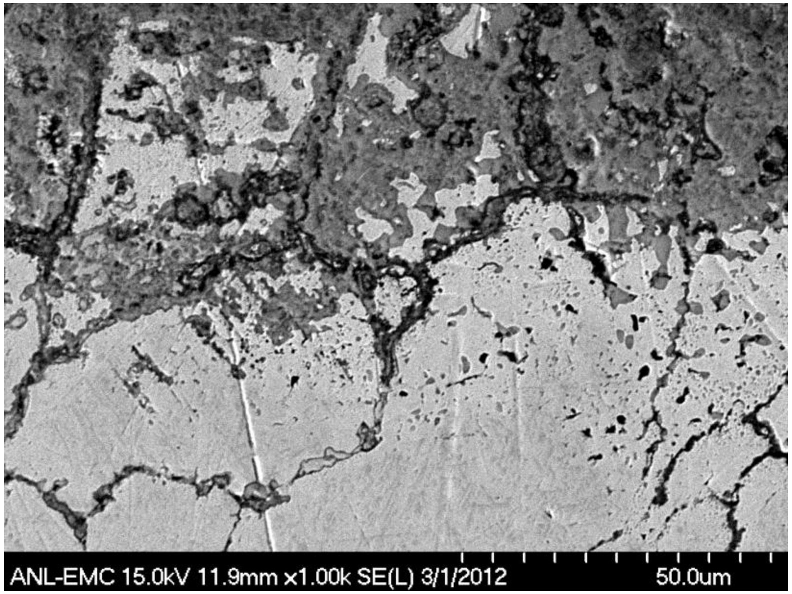
EDX of the interior region of corroded Alloy 740



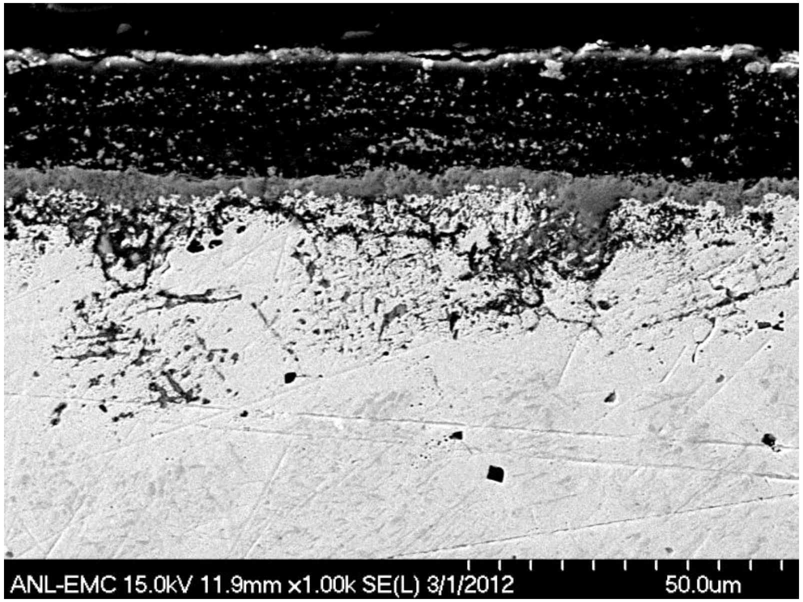
Alloy 740, EDX at scale/alloy interface region



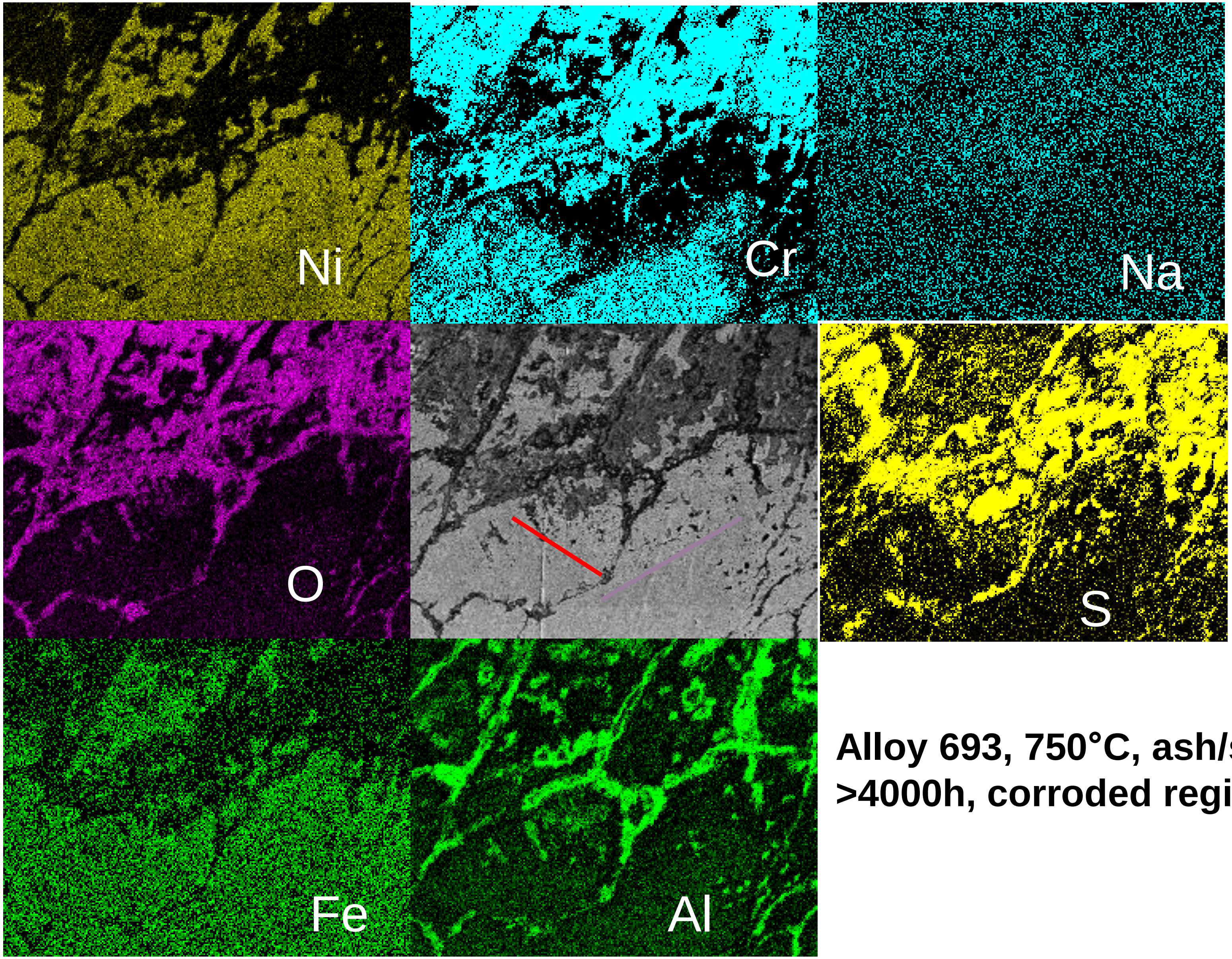
Alloy 693, 750°C, ash and steam, >4000h



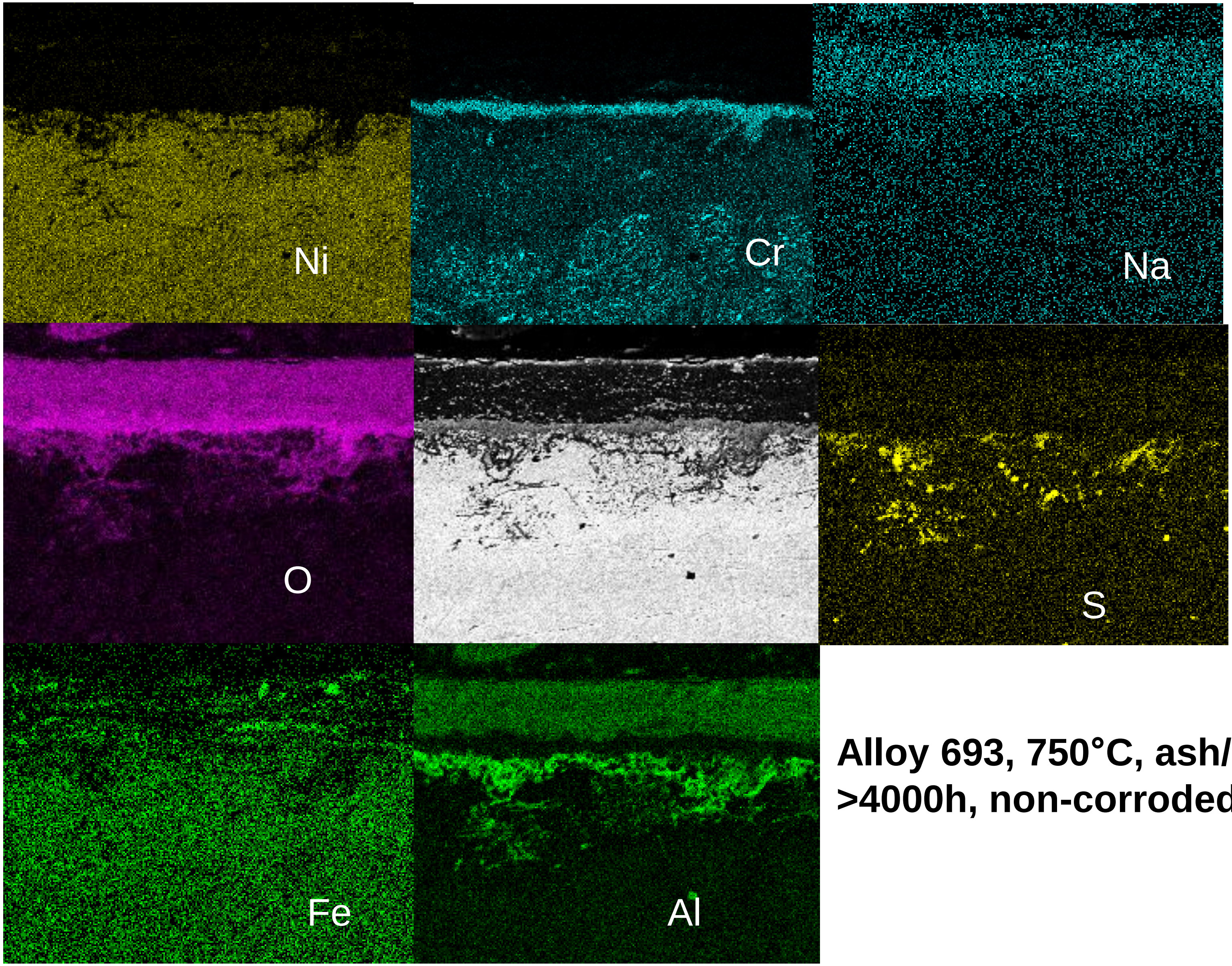
Corroded region



Non-corroded region



Alloy 693, 750°C, ash/steam >4000h, corroded region



Alloy 693, 750°C, ash/steam >4000h, non-corroded region

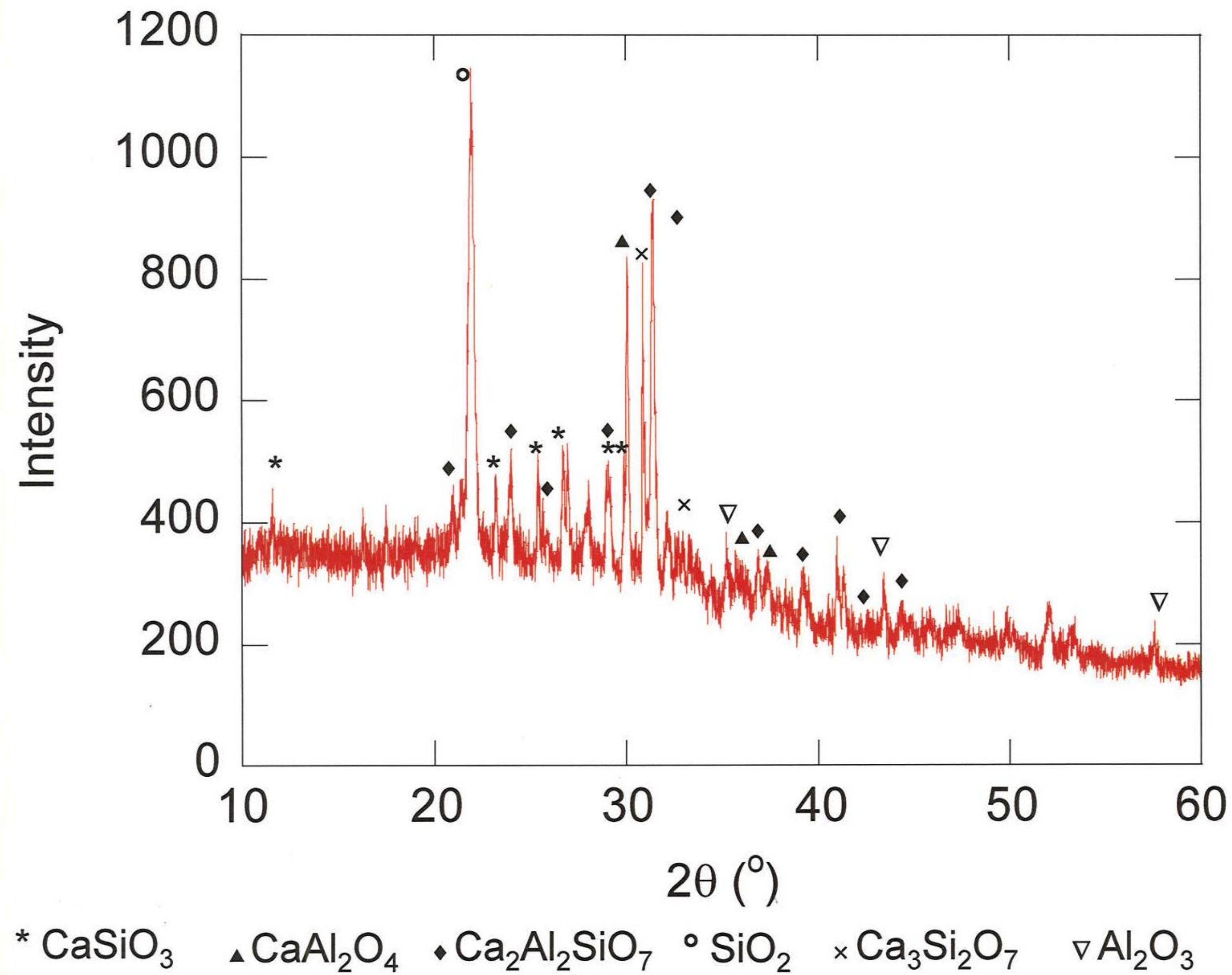
Without CaO in ash, 600h

With CaO, without pre-sintering (without steam) 300h at 750°C

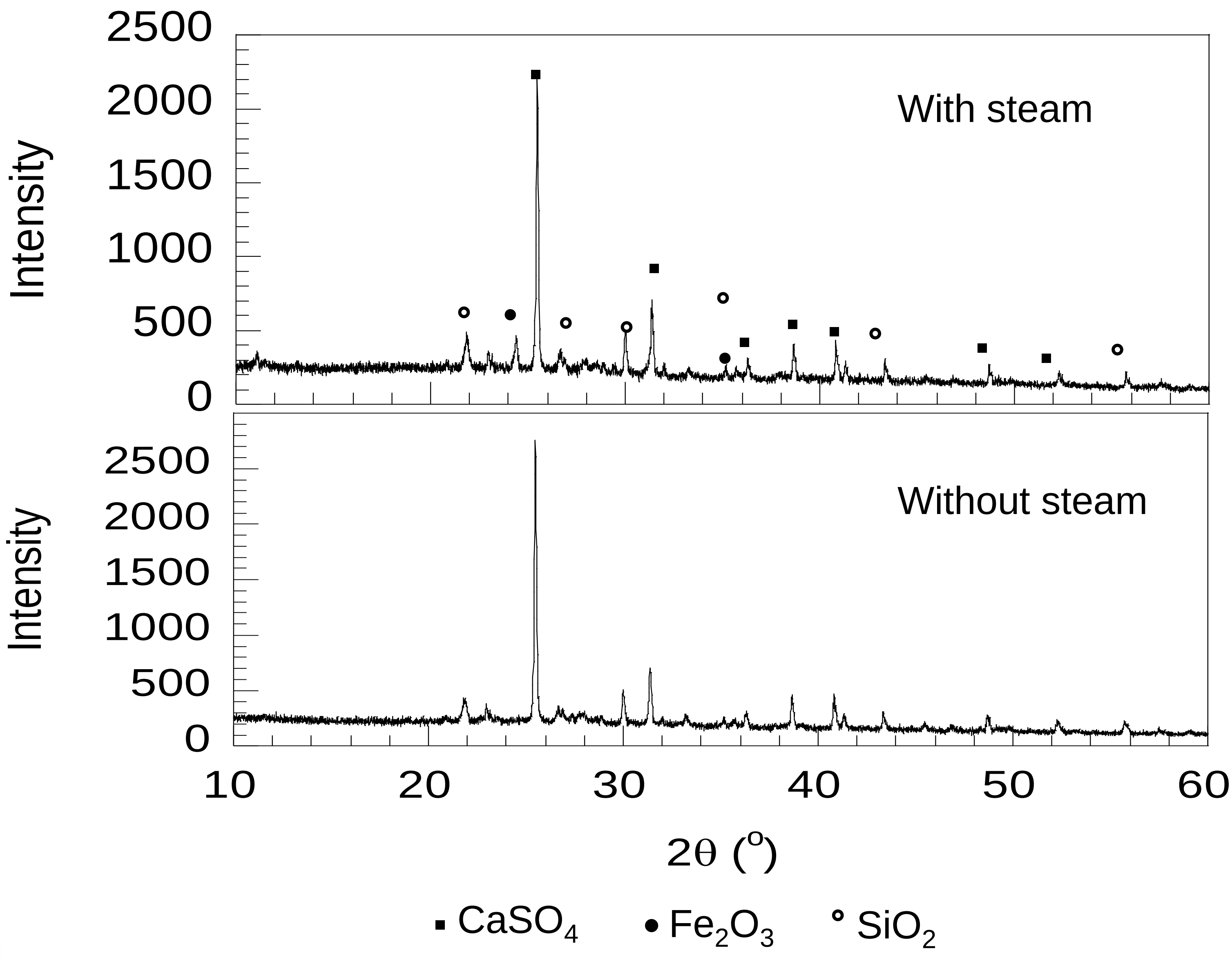
CaO sintered with SiO_2 + Al_2O_3+ Fe_2O_3 at 1100°C (without steam)

With steam and Ca-containing ash, 300h at 750°C

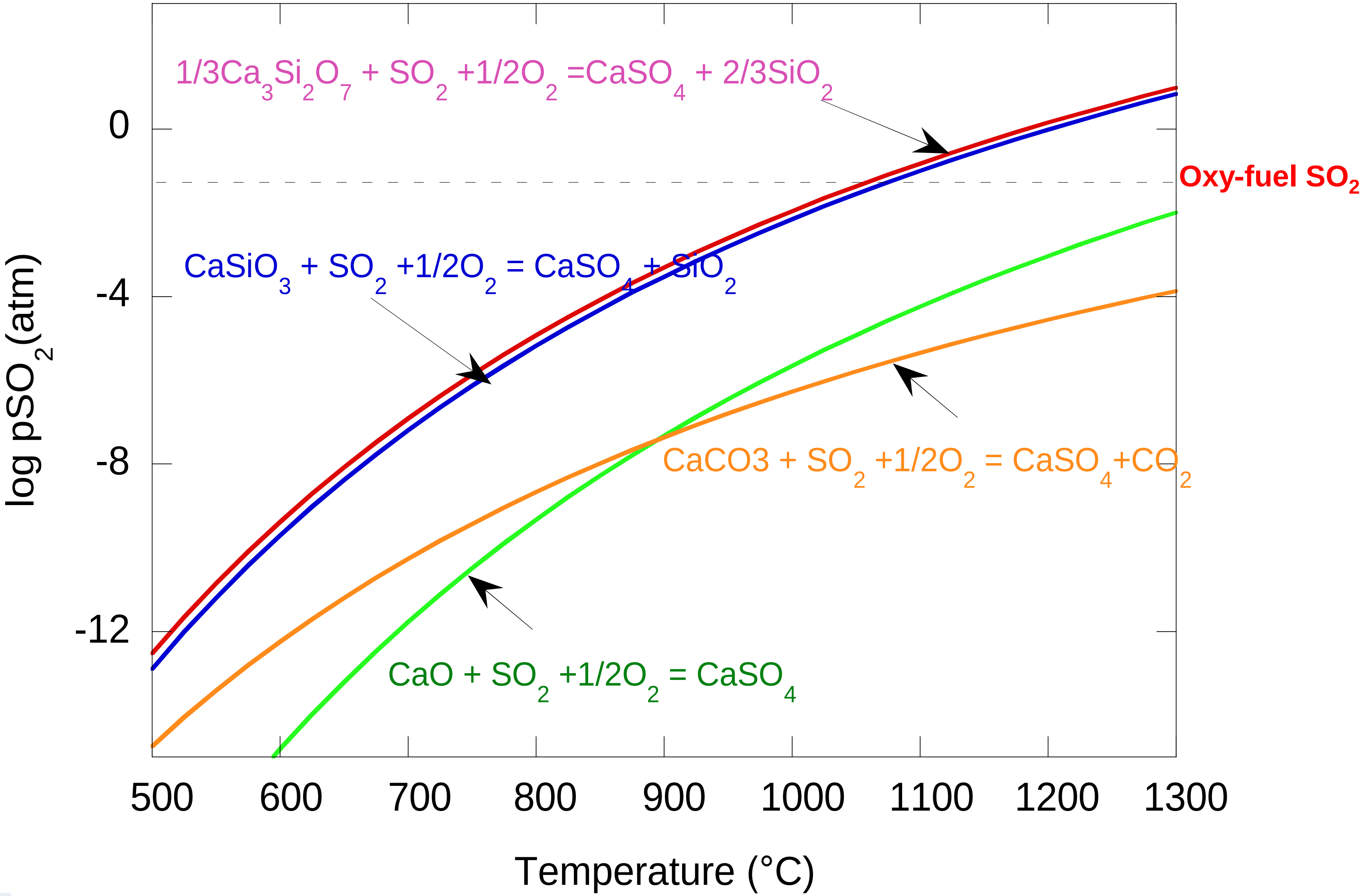
XRD of Ca-containing Ash After Sintering at 1100℃



XRD of Ca-containing Ash After 300-h exposure in corrosion test



Thermodynamic Stability of Ca compounds in Oxy-Fuel Environment



Project Summary

- We have conducted a study to evaluate the oxidation performance of structural alloys in simulated coal ash environments at 750°C. We believe the corrosion rates in these environments (in the absence of sulfur) are acceptable for service. However, the effect on mechanical properties is not established
- Results indicate that the oxide scales that develop on the alloys are not that protective and internal carburization of the substrate may occur
- The presence of Eastern coal ash (with alkali sulfates) coupled with steam in the gas environment accelerates corrosion of all structural alloys
- We have examined the role of steam and the effect of pO_2 on the corrosion scaling and internal penetration
- Ash/alkali sulfate effect initiates as localized corrosion in most of the alloys

Summary continued

- The corrosion process generally follows parabolic kinetics in most of the alloys, when tested in gas phase environments (with or without steam) in the absence of ash
- In the presence of ash, the alloys exhibit an incubation period during which the corrosion rates are low. Upon exceeding the incubation period, the corrosion accelerates and the process follows a linear kinetics. This is based on the microstructural examination of the tested specimens for internal oxidation/sulfidation/penetration of the substrate alloys
- In typical oxy-fuel combustion environments used in this study, most of the alloys exhibit corrosion rates ≥ 2 mm/year, based on linear kinetics
- Preliminary experiments in Ca-containing ash (typical of US Western coals) indicate potential for sulfur capture and possibly reduced corrosion of structural alloys

Future Plans for the ANL research project

- Complete corrosion evaluation of structural alloys in oxy-fuel environments containing different ashes, alkali sulfates, and alkali chlorides. This includes a range of coal ash chemistry and gas environments at temperatures up to 750°C.
- Experimentation to mitigate corrosion of structural alloys in both advanced steam-cycle and oxy-fuel combustion systems
  - Conventional coatings
  - Ash additives
  - Alloy surface modification using nano-structures