Corrosion Performance of Structural Alloys and Weldments in Simulated Oxy-fuel Environments

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For Presentation at the Meeting on "2014 NETL Crosscutting Research Review Meeting" Pittsburgh, PA, May19-23, 2014

1. Corrosion of base alloys
2. Mechanistic understanding of corrosion
3. Performance of weldment specimens

Corrosion of Base Alloys

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
253MA	0.09	20.9	10.9	0.6	1.6	0.3	Bal	N 0.19, Ce 0.04
800H	0.08	20.1	31.7	1.0	0.2	0.3	Bal	Al 0.4, Ti 0.3
MA956	-	20.0	-	-	-	-	Bal	Al 4.5, Ti 0.5, Y_2O_3 0.6
446	0.17	26.7	0.3	0.7	0.5	-	Bal	N 0.19
WASP	0.02	20	Bal	0.5	0.75	4.3	2.0	Co 12-15, Ti 2.6-3.25, Al 1.0-1.5, Zr 0.1
617	0.08	21.6	53.6	0.1	0.1	9.5	0.9	Co 12.5, Al 1.2, Ti 0.3
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
333	0.05	25.0	45.0	-	1.0	3.0	18.0	Co 3.0, W 3.0
718	-	19.0	52.0	-	-	3.0	19.0	Nb 5.0, Al 0.5, Ti 0.9, B 0.002
625	0.05	21.5	Bal	0.3	0.3	9.0	2.5	Nb 3.7, Al 0.2, Ti 0.2
230	0.11	21.7	60.4	0.5	0.4	1.4	1.2	W 14, Al 0.3, La 0.015
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
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
214	0.04	15.9	Bal	0.2	0.1	0.5	2.5	Al 3.7, Zr 0.01, Y 0.006
263	0.06	20	52	0.6	0.4	6	0.7	Al 0.6, Ti 2.4, Cu 0.2
282	0.06	20	57	0.3	0.15	8.5	1.5	Al 1.5, Ti 2.1, Co 10, B 0.005
R41	0.09	19	58	0.1	0.5	10	5	Al 1.5, Ti 3.1, Co11, B 0.006

Fe-

Ni-

weldments

Laboratory Test Details

Key variables: Temperature, time, alloy composition

Materials: Fe- and Ni-base alloys

Environments: Gas A: 68.1%CO_2-26.9%H_2O-0.99%SO_2-3.97%O_2

Gas B: 95%CO_2-0.99%SO_2-3.97%O_2

Ash mixture

Eastern ash: 90% (SiO_2 :Al_2O_3:Fe_2O_3 = 1:1:1) and 10%(Na_2SO_4:K_2SO_4 = 1:1)

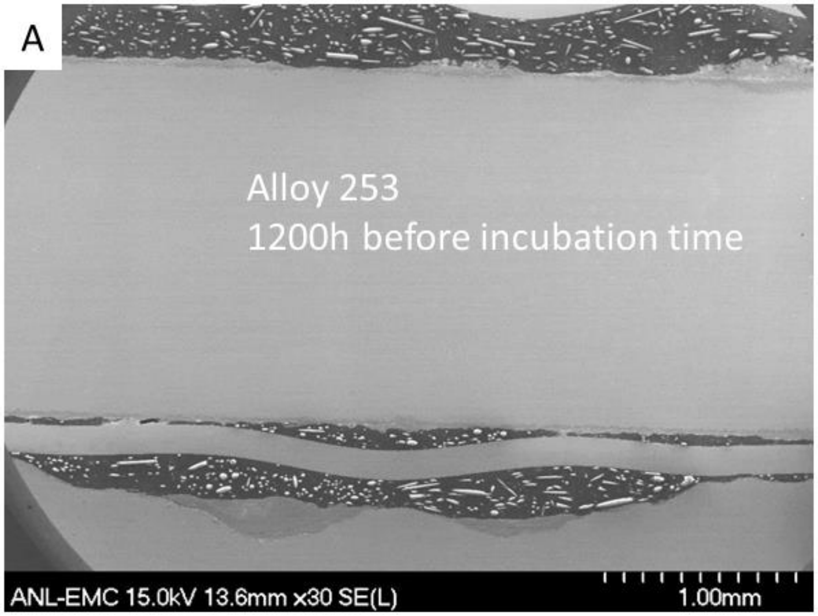
Western ash: 36%SiO_2-16%Al_2O_3-9%Fe_2O_3-29%CaO and 10%(Na_2SO_4:K_2SO_4 = 1:1)

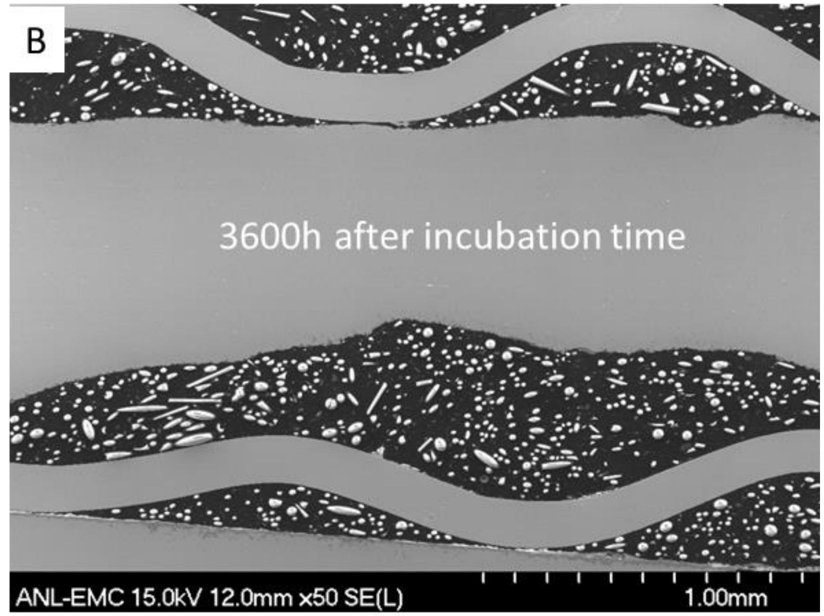
Test temperature range: 750 °C

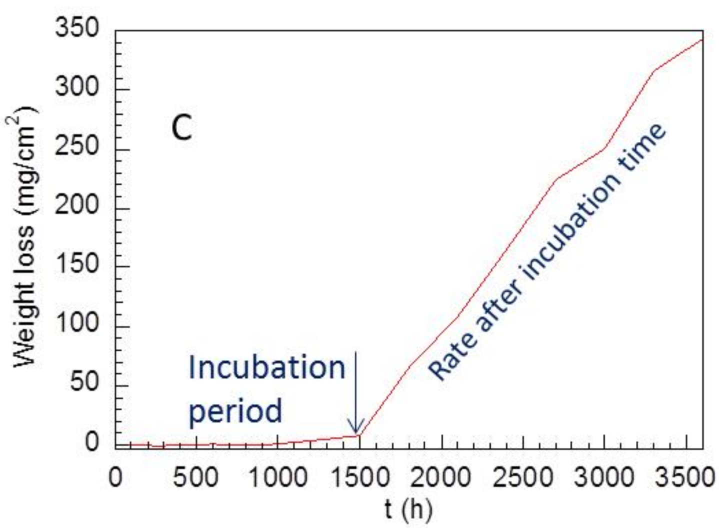
Test times: up to 6,300 h

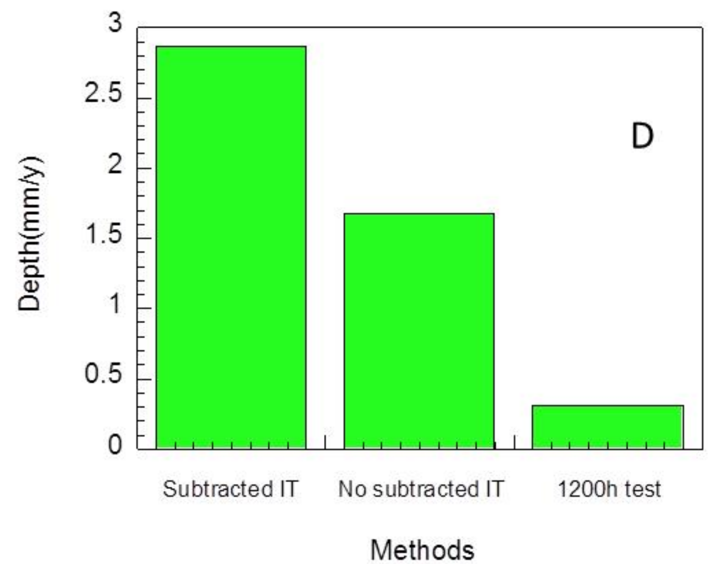
Specimen evaluation:
- **weight change**
- **scanning electron microscopy**
- **energy dispersive X-ray analysis**
- **X-ray diffraction**
- **synchrotron nanobeam analysis**

Incubation period for ash corrosion



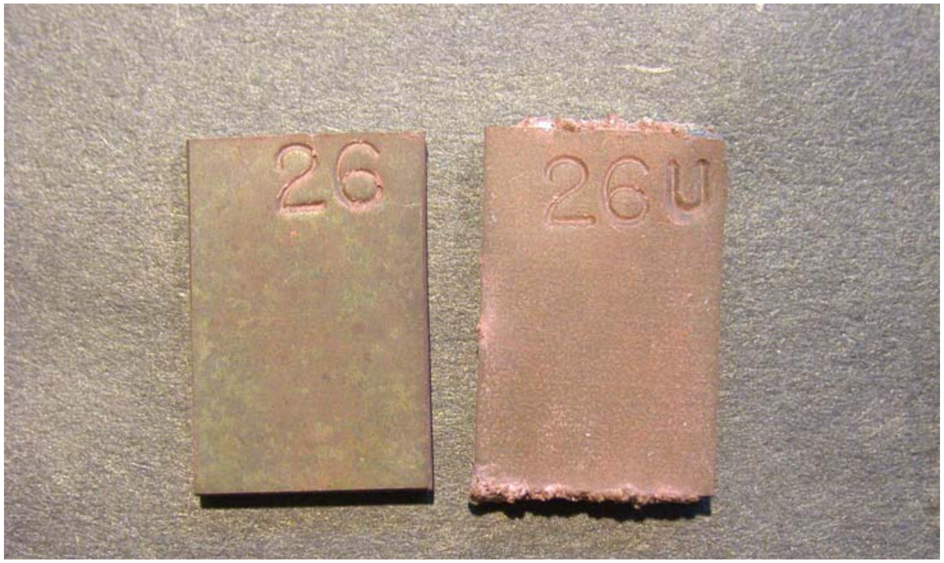






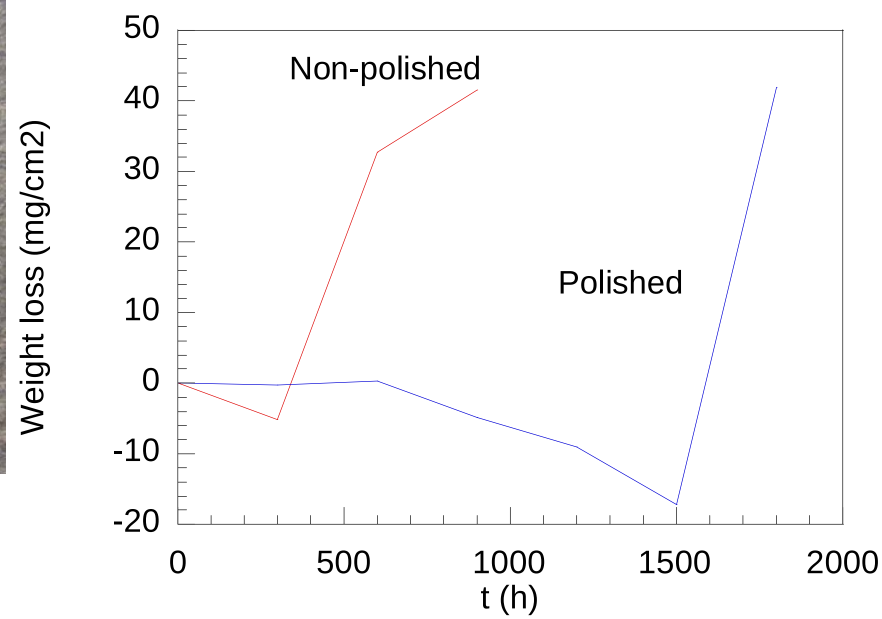
$$\text{Corrosion rate} = \frac{\text{Depth}}{\text{Total exposure time} - \text{incubation time}}$$

Effect of surface condition on incubation time



Polished Non-polished

602CA, 300h



Eastern ash, Gas A: 68.1%CO_2-26.9%H_2O-0.99%SO_2-3.97%O_2 ,750°C

General character of localized corrosion

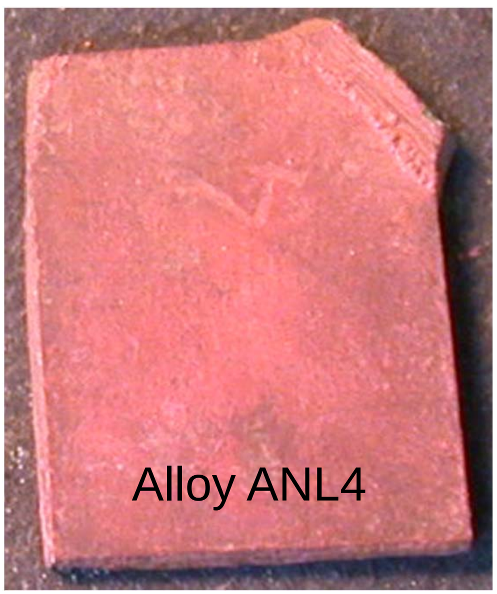
Incubation time: Strongly affected by surface condition

Short term test results not reliable due to the effect of incubation time.

How to determine incubation time?

3300 h

6300 h



Eastern ash, Gas A: 68.1%CO_2-26.9%H_2O-0.99%SO_2-3.97%O_2 ,750°C

Cut sample to obtain scale thickness

vs

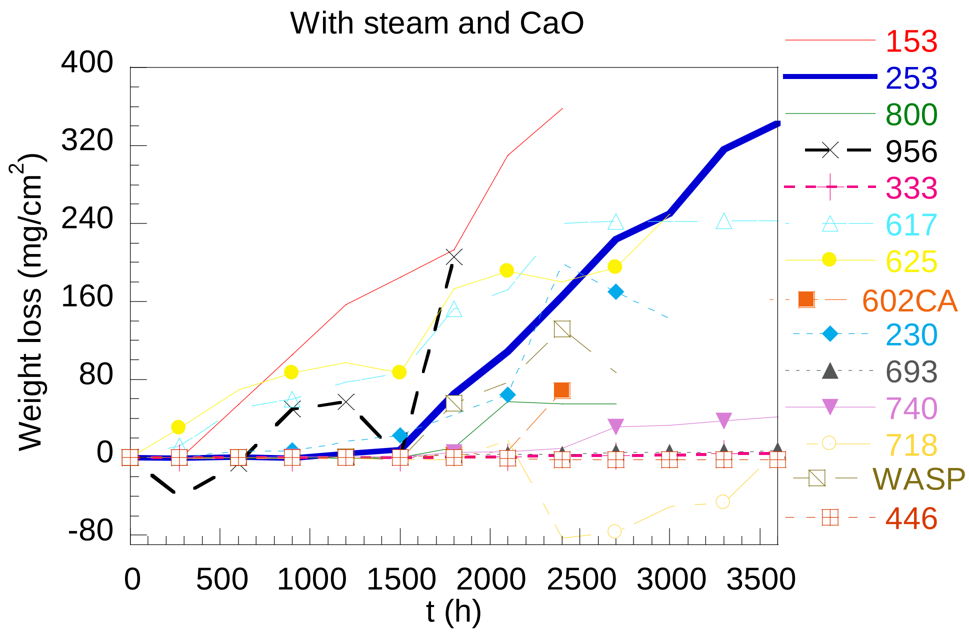
Significant weight change

Realistic method+ not change surface condition

Weight Change data after exposure

Western ash:

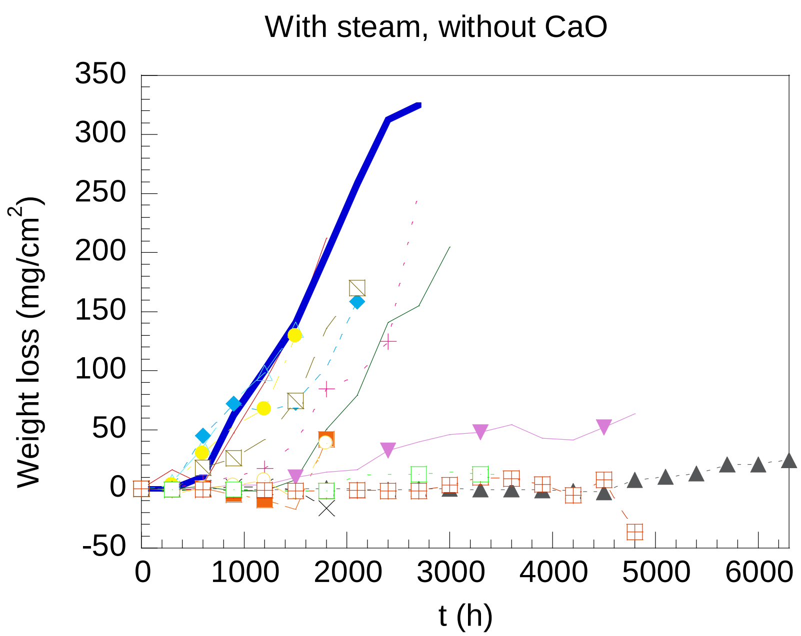
16%Al_2O_3, 36%SiO_2, 9%Fe_2O_3, 29%CaO, 5%K_2SO_4, 5%Na_2SO_4



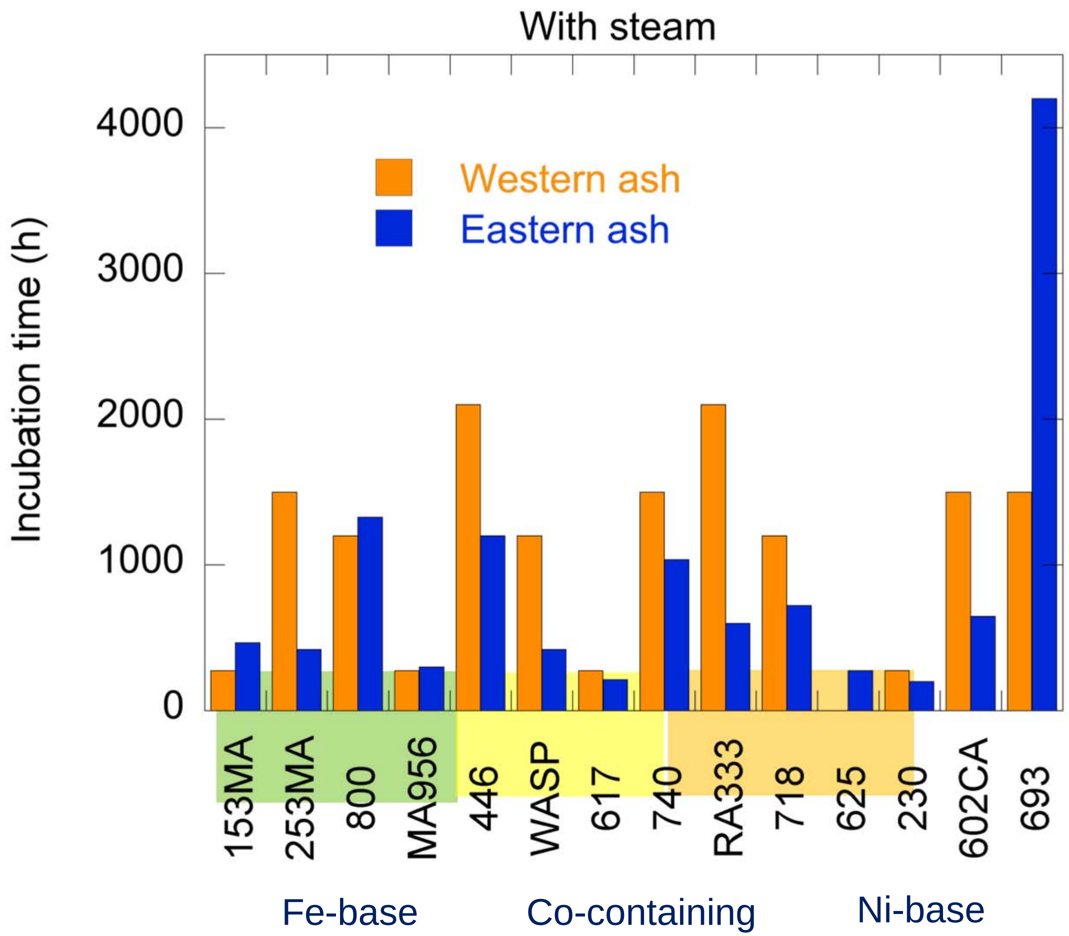
Gas: 68.1%CO_2-26.9%H_2O-0.99%SO_2-3.97%O_2

Eastern ash:

30%Al_2O_3, 30%SiO_2, 30%Fe_2O_3, 5%K_2SO_4, 5%Na_2SO_4



Effect of ash chemistry on incubation time

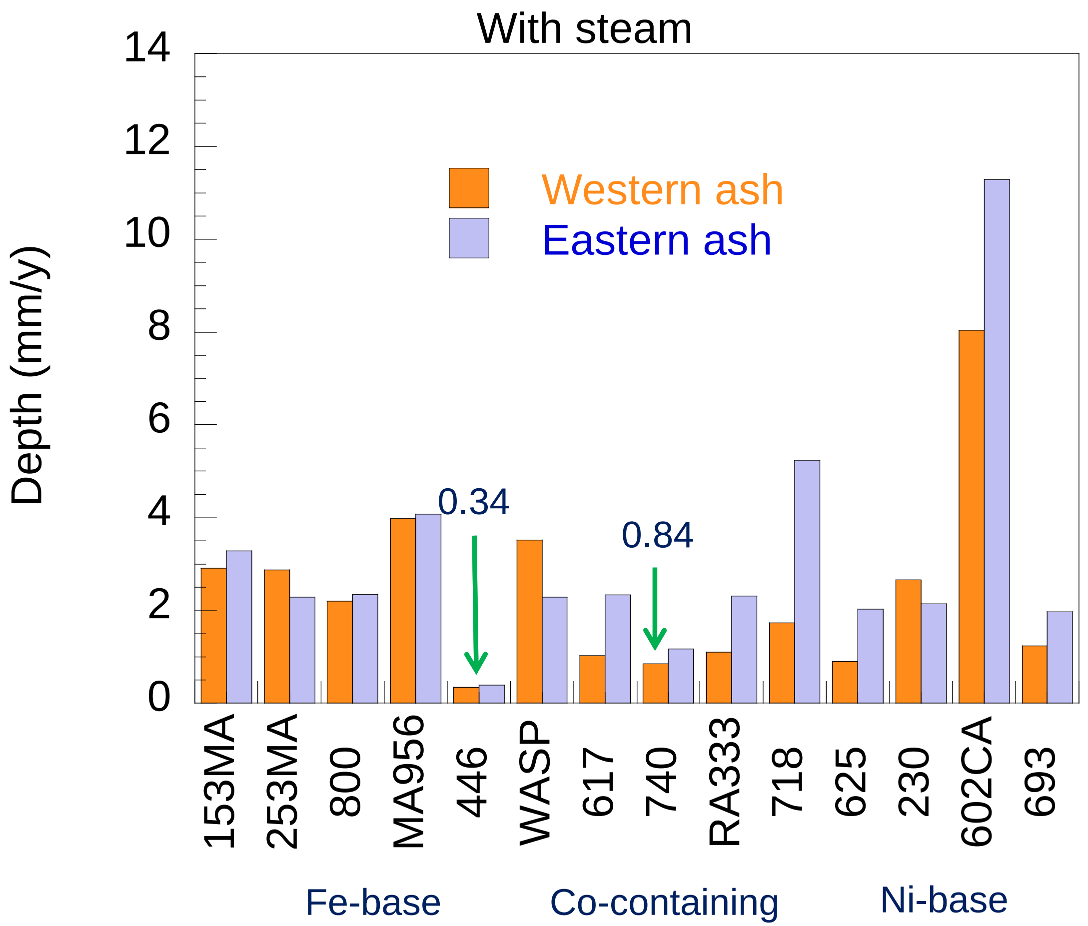


Western ash: 16%Al_2O_3, 36%SiO_2, 9%Fe_2O_3, 29%CaO, 5%K_2SO_4, 5%Na_2SO_4

Eastern ash: 30%Al_2O_3, 30%SiO_2, 30%Fe_2O_3, 5%K_2SO_4, 5%Na_2SO_4

Gas: 68.14%CO_2-26.9%H_2O-0.99%SO_2-3.97%O_2

Effect of ash chemistry on corrosion rate



Western ash: 16% Al_2O_3, 36% SiO_2, 9% Fe_2O_3, 29% CaO, 5% K_2SO_4, 5% Na_2SO_4

Eastern ash: 30% Al_2O_3, 30% SiO_2, 30% Fe_2O_3, 5% K_2SO_4, 5% Na_2SO_4

Gas: 68.14% CO_2-26.9% H_2O-0.99% SO_2-3.97% O_2

CaO addition reduces corrosion rates of most Co-containing and Ni-base alloys

Mechanistic Understanding of Corrosion Processes

Ash corrosion mechanism

Chemical	Melting temperature (°C)
$K_3Al(SO_4)_3$	690
$Na_3Al(SO_4)_3$	646
$K_3Fe(SO_4)_2$	618
$Na_3Fe(SO_4)_3$	624
$KFe(SO_4)_2$	694
$NaFe(SO_4)_2$	690

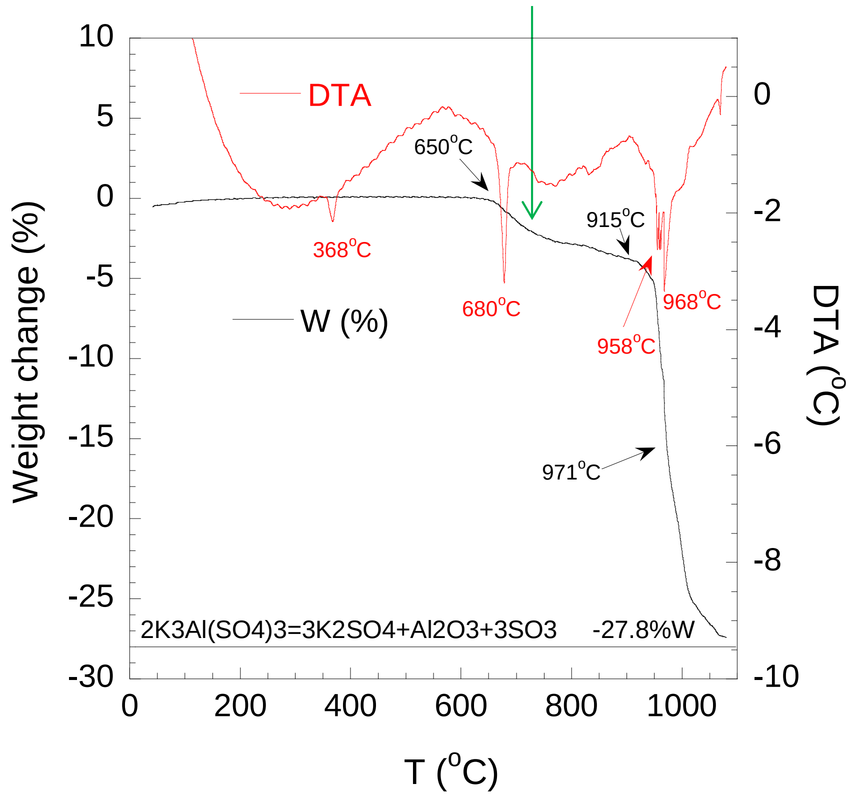
Do all sulfates decompose?

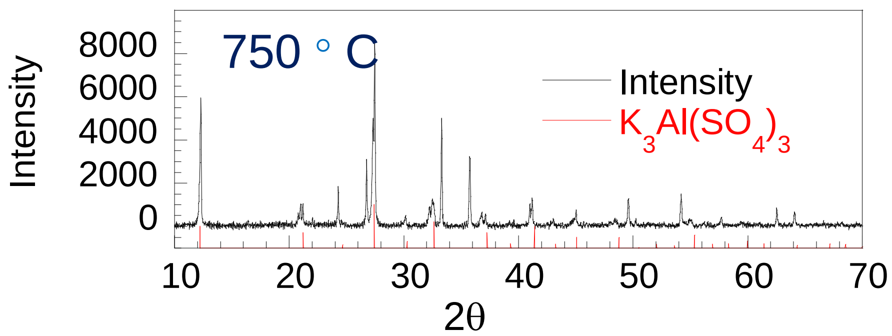
	Western	Eastern
SiO_2	36.04	40.35
Fe_2O_3	5.86	28.33
Al_2O_3	16.84	22.56
CaO	21.61	2.62
MgO	5.06	0.69
SrO	0.35	0.09
BaO	0.62	0.11
Na_2O	1.69	0.41
K_2O	0.5	1.28
TiO_2	1.32	1.04
MnO_2	0.02	0.05
P_2O_5	1	0.22
SO_3	9.09	2.25

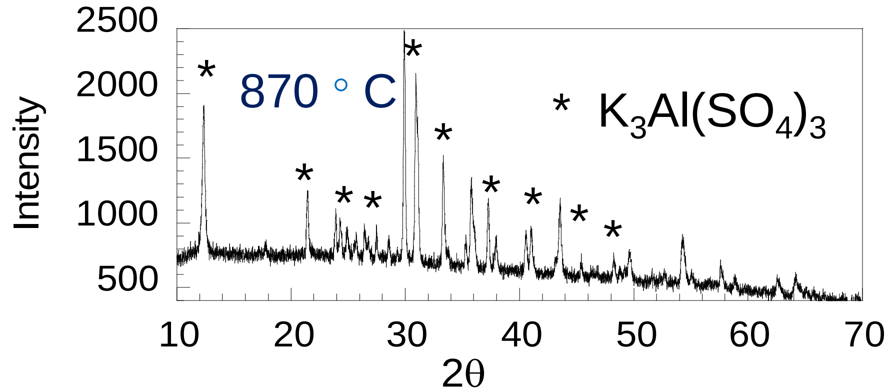
Decomposition of sulfates

$K_3Al(SO_4)_3 = KAl(SO_4)_2 + K_2SO_4$

$4KAl(SO_4)_2 = 2K_2SO_4 + 2Al_2O_3 + 6SO_2 + 3O_2$







$K_2SO_4 + Al_2O_3 + Fe_2O_3 + SiO_2$

Gas: 68.14%CO_2-26.9%H_2O-0.99%SO_2-3.97%O_2

Change of the kinetics of decomposition of sulfates

$4KAl(SO_4)_2=2K_2SO_4+2Al_2O_3+6SO_2+3O_2$

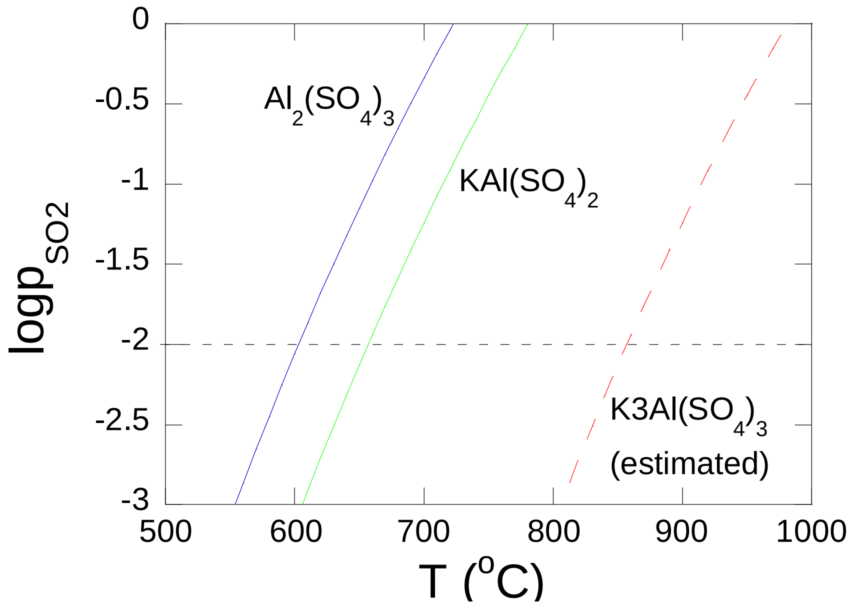
$$K = \frac{1}{p_{SO2}^6 * p_{O2}^3}$$ without solvent

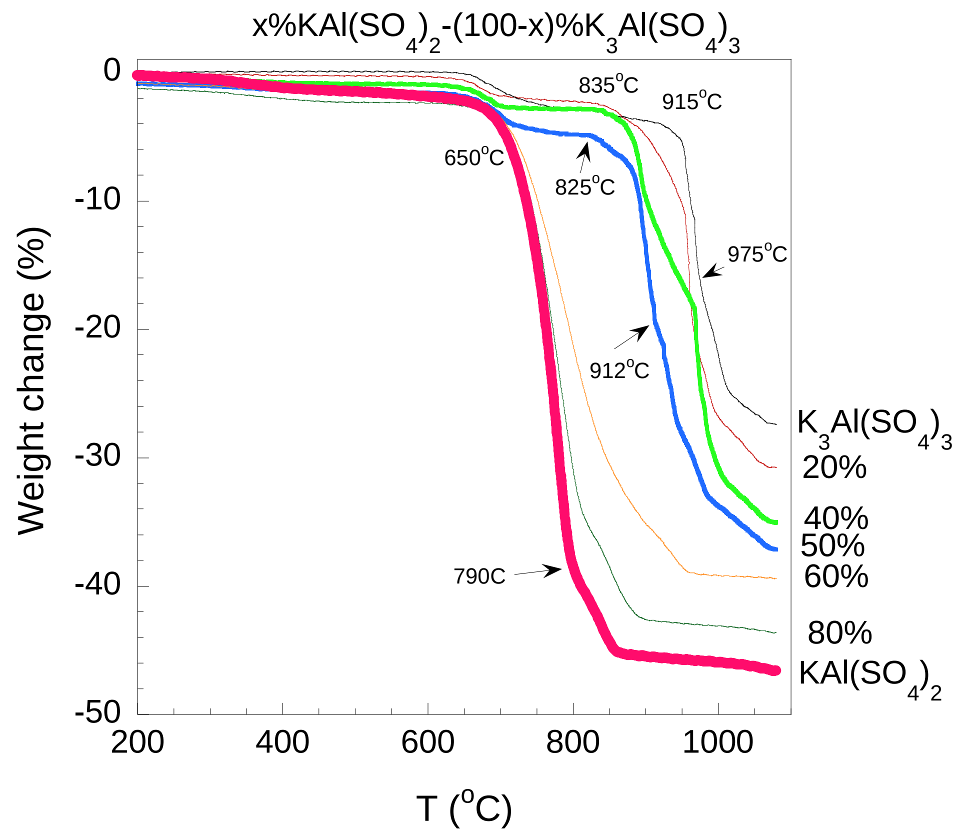
$$K = \frac{C_{KAl(SO4)2}}{p_{SO2}^6 * p_{O2}^3}$$ in $K_3Al(SO_4)_3$ solution

If a stable $K_3Al(SO_4)_3$ exists at 750°C, low stability sulfates such as $KAl(SO_4)_2$, $Na_3Al(SO_4)_3$, and $K_3Fe(SO_4)_3$ would not simply decompose at ~650°C

Peak at 700°C ?

p_{O2} = 0.04 atm





Why corrosion rate with high CaO ash is lower?

$2Al_2O_3 + 6K_2SO_4 + 6SO_2 + 3O_2 = 4K_3Al(SO_4)_3$ melting T 690 °C

$CoO + SO_2 + 1/2O_2 = CoSO_4$ melting T 735 ° C

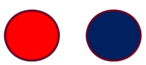
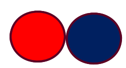
$NiO + SO_2 + 1/2O_2 = NiSO_4$ $NiSO_4$-Na_2SO_4 melting T 671 ° C

$3CaO + 2K_3Al(SO_4)_3 = 3CaSO_4 + 3K_2SO_4 + Al_2O_3$

melting T 1460° C 1069 ° C

$3CaSiO_3 + 2K_3Al(SO_4)_3 = 3CaSO_4 + 3K_2SO_4 + 3SiO_2 + Al_2O_3$

$3CaCO_3 + 2K_3Al(SO_4)_3 = 3CaSO_4 + 3K_2SO_4 + 3CO_2 + Al_2O_3$

 Solid state reaction 

$CoSO_4 + CaCO_3 = CaSO_4 + CoO + CO_2$

$NiSO_4 + CaCO_3 = CaSO_4 + NiO + CO_2$

$CoSO_4 + CaSiO_3 = CaSO_4 + CoO + SiO_2$

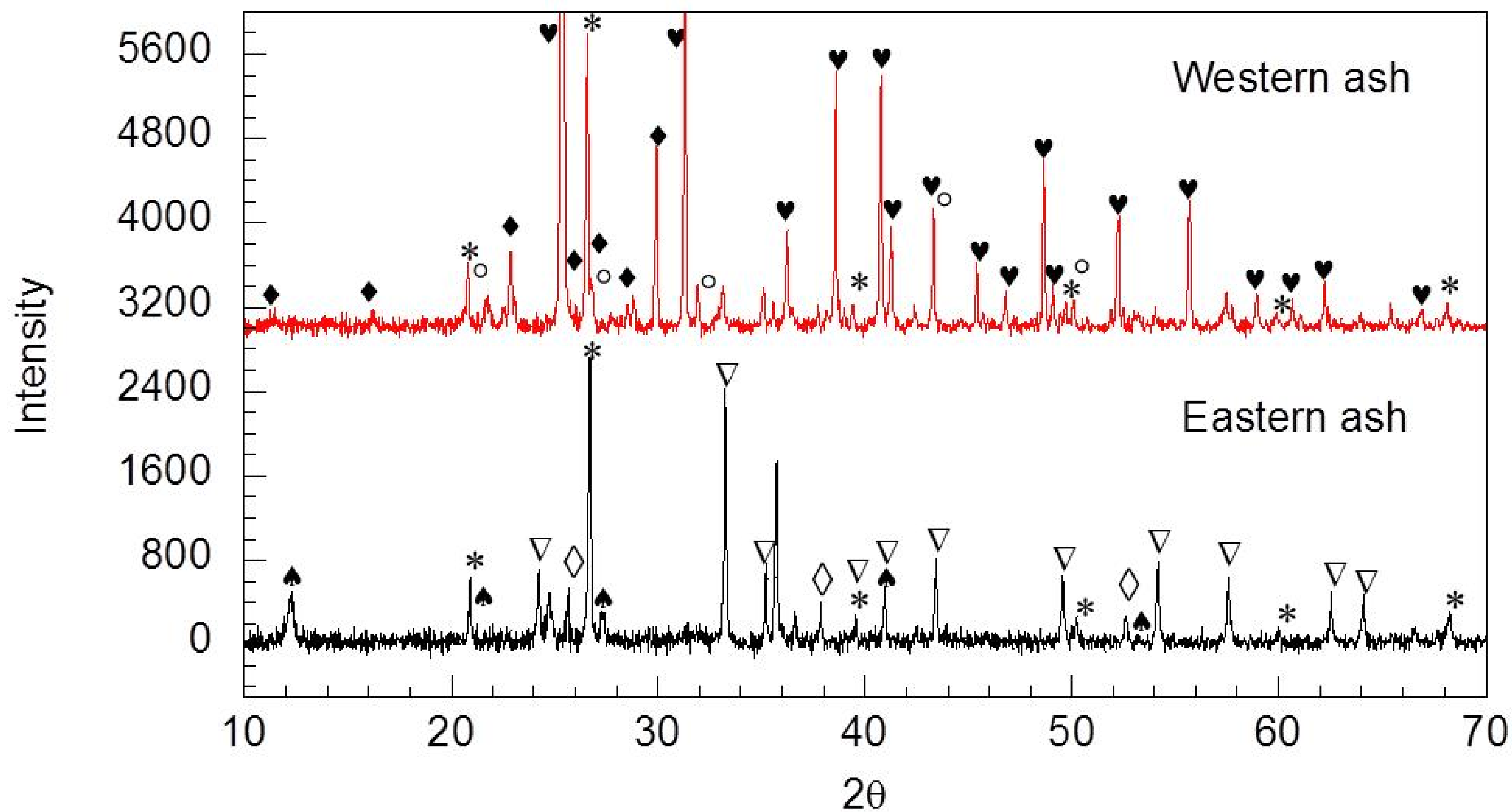
$NiSO_4 + CaCO_3 = CaSO_4 + NiO + CO_2$

Is there an inhibitor for ash corrosion?

Method to terminate ash corrosion:
convert low-melting-temperature sulfates to high melting temperature sulfates

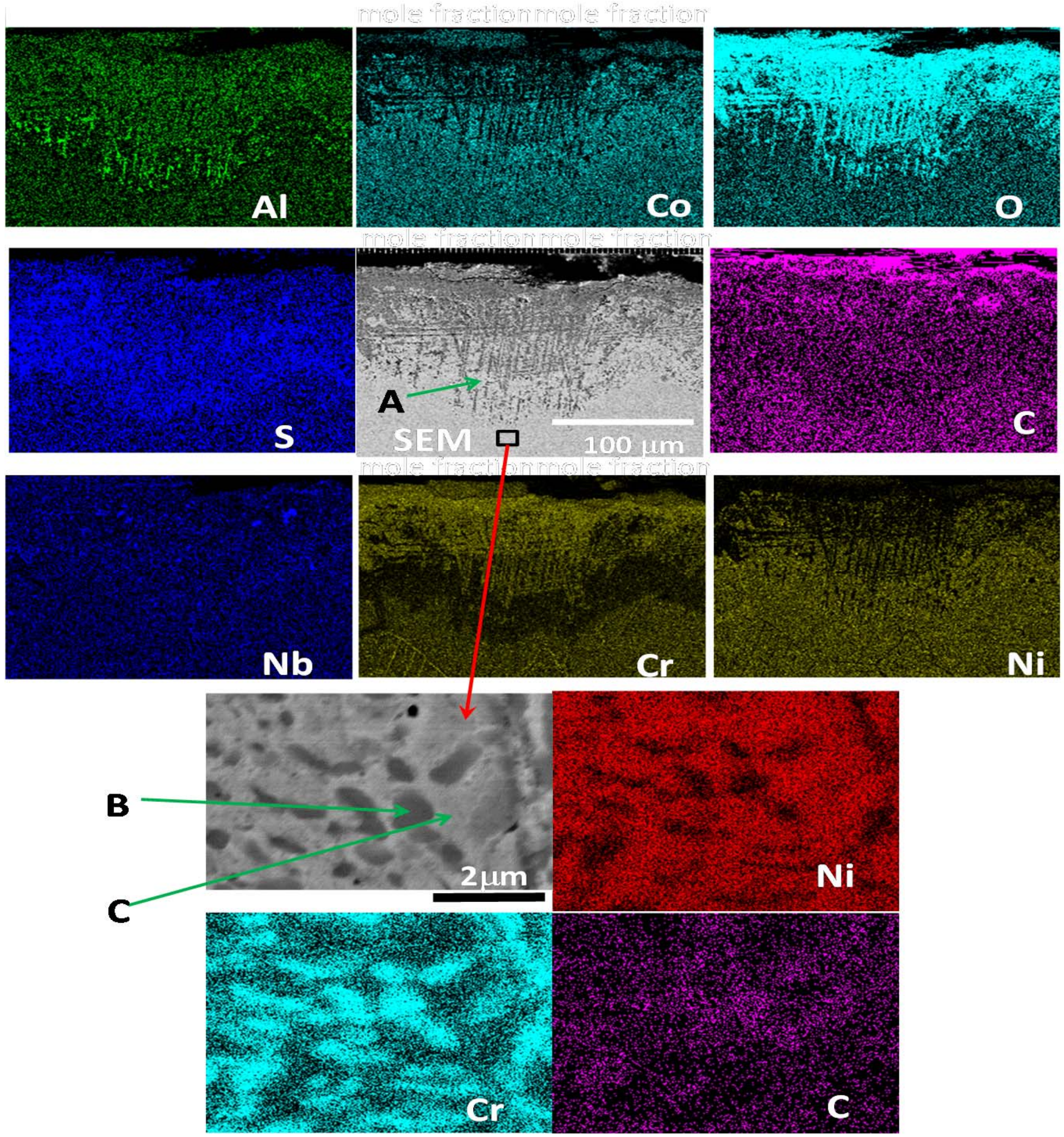
	$K_3Al(SO_4)_3$	$CaSO_4$	K_2SO_4	$K_2SO_4 – K_2Ca_2(SO_4)_3$
melting T:	690°C	1460°C	1069°C	875°C

X-ray diffraction of ash



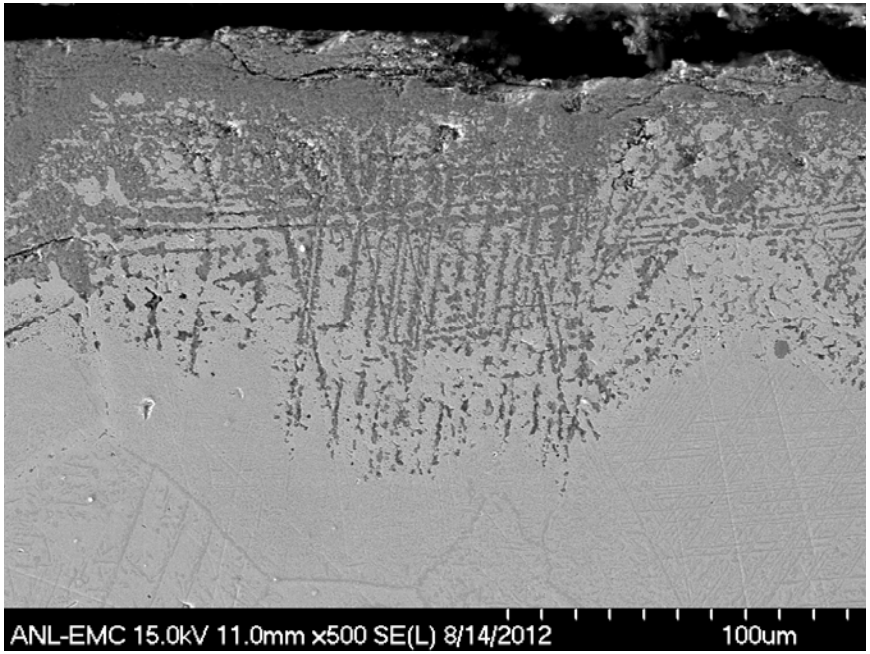
X-ray diffraction of simulated Eastern and Western ashes after exposure to Gas A at 750°C for 300h
♥: $CaSO_4$; ♠: $K_3Al(SO_4)_3$; ∗: SiO_2; °: $K_2Ca_2(SO_4)_3$; ∇: Fe_2O_3; ◊: Al_2O_3; ♦: $CaSiO_3$

Carburization after incubation time



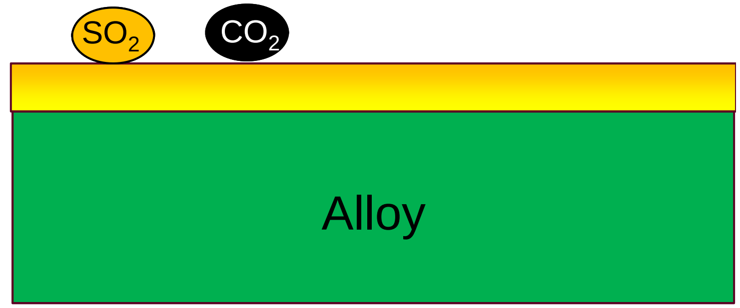
EDX mapping of the cross section of Alloy 740 after exposure to Gas B at 750°C for 3600h.

What does it incubate for?



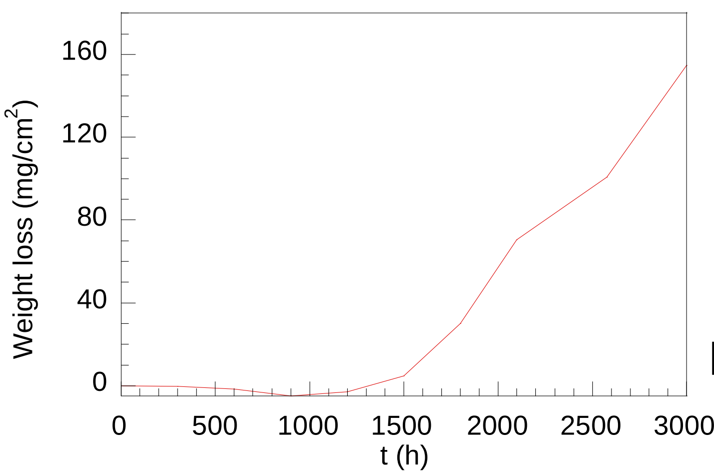
Parabolic rate law

Combination of sulfidation, oxidation and carburization



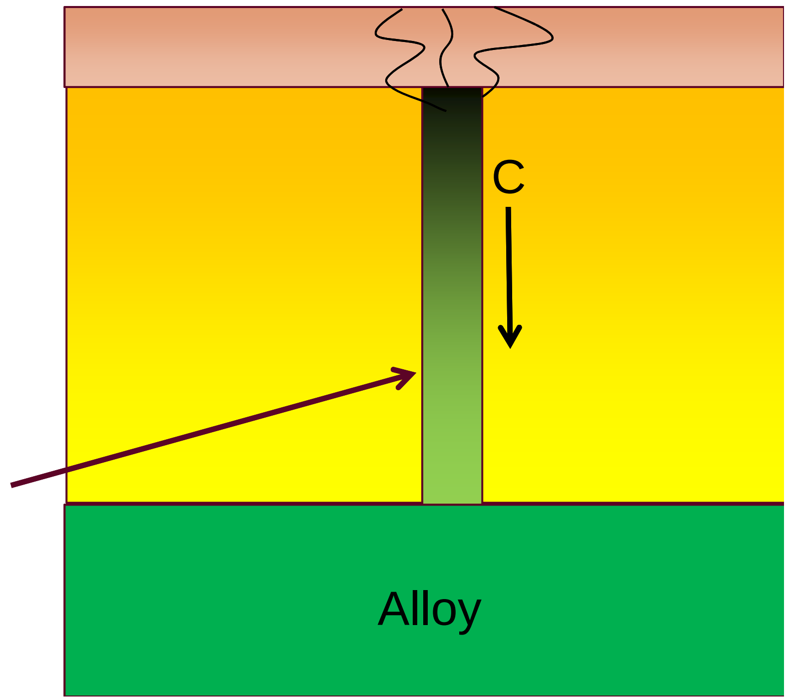
Effects of gas contents

Crack defects

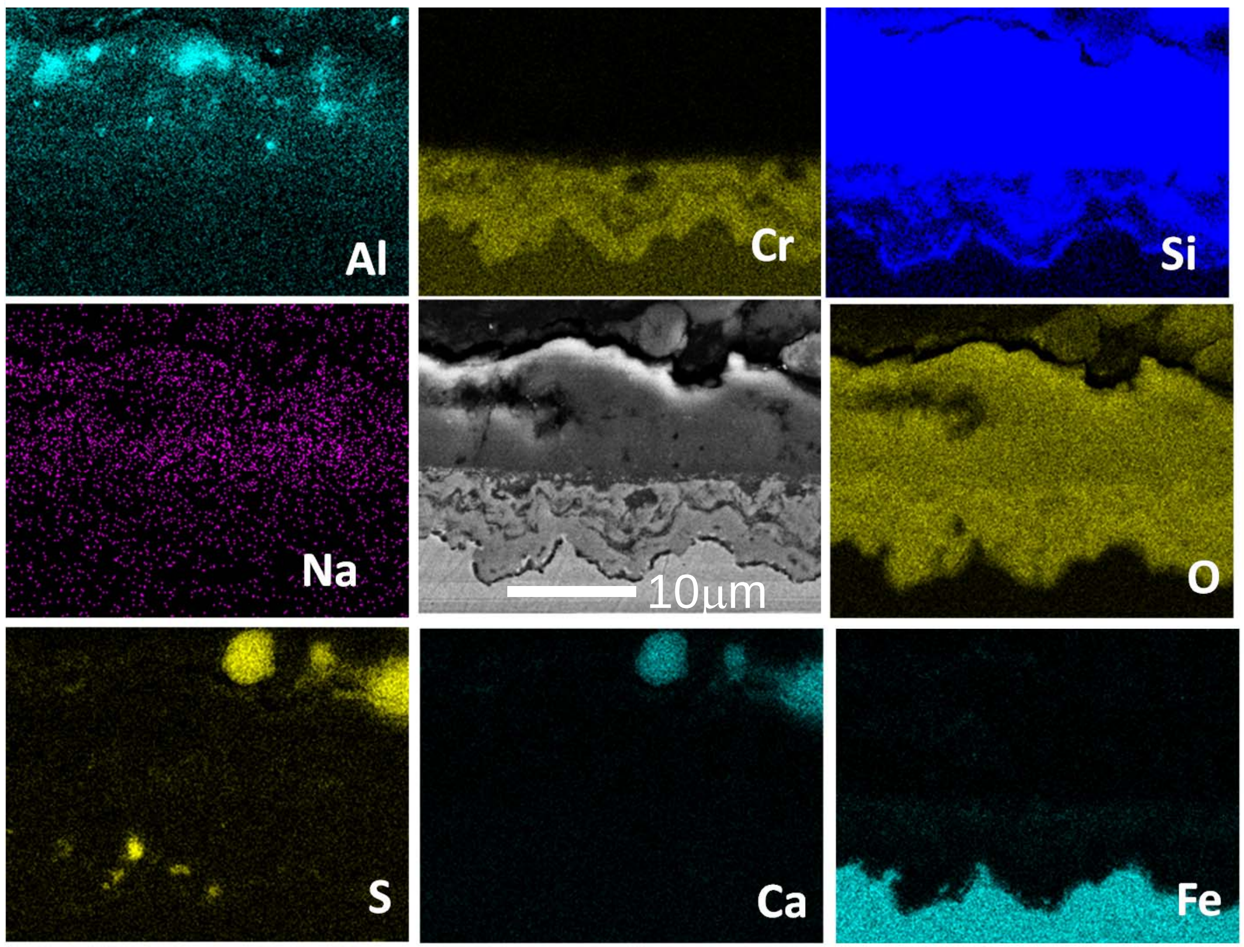


Linear rate law

Metallic networks

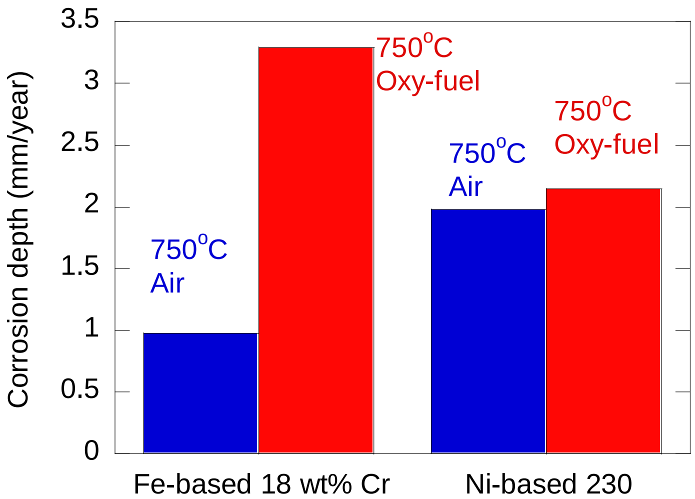


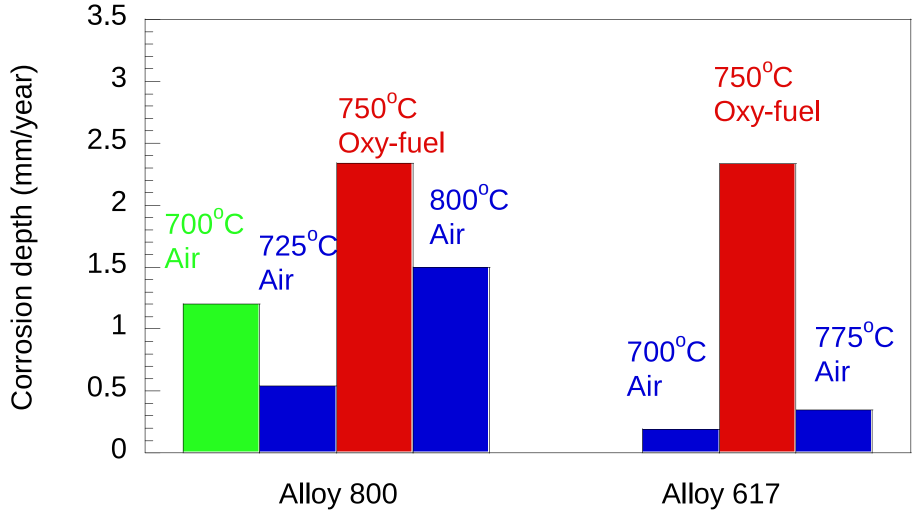
Self-assembled silicon oxide layer on alloy surface to resist ash corrosion



EDX of the cross section of Alloy 446 after exposure to the ash with a high calcium content (simulating US Western coal) plus alkali sulfates in Gas A (with steam) at 750°C for 3600 h.

Alloy corrosion rates under oxy-fuel and air combustion





Penetration rates of alloys after subtracting incubation period of alloys after exposure to coal ash and gas environments of oxy-fuel and air-combustion.
A: Fe-based alloys with Cr contents ~ 18 wt% and Ni-based Alloy 230 at 750°C.
B: Alloy 800 at 725°C in air combustion, 750°C in oxy-fuel, and 800°C in air combustion .
The rate at 700°C is taken from Castello. The corrosion rates of Alloy 617 exposed to a simulated air combustion environment are taken from Baker.

Alloy corrosion rates after incubation time under oxy-fuel combustion are generally higher than in air combustion.

Controversy results on complicate localized corrosion?

Test time: test results obtained below incubation time are not reliable and not realistic for long term application.

Temperature: ANL data at 750°C, other literature data at lower temperature, most from short time test without deleting incubation time.

Project Summary

- It is necessary to obtain corrosion rate after incubation time for long term application.
- The observed corrosion rates are similar to those reported from the UK research results under Task 2 in US/UK collaboration
- Alloy corrosion rates after incubation time under oxy-fuel combustion condition are generally higher than in air combustion due to higher SO_2 and CO_2 concentrations under oxy-fuel combustion conditions.
- It is possible to reduce the long term alloy corrosion rate by increasing the calcium concentration in ash.
- It is possible to reduce the long term alloy corrosion rate by selecting alloys with adequate chemical composition as cladding or coating

Corrosion Behavior of Weldments

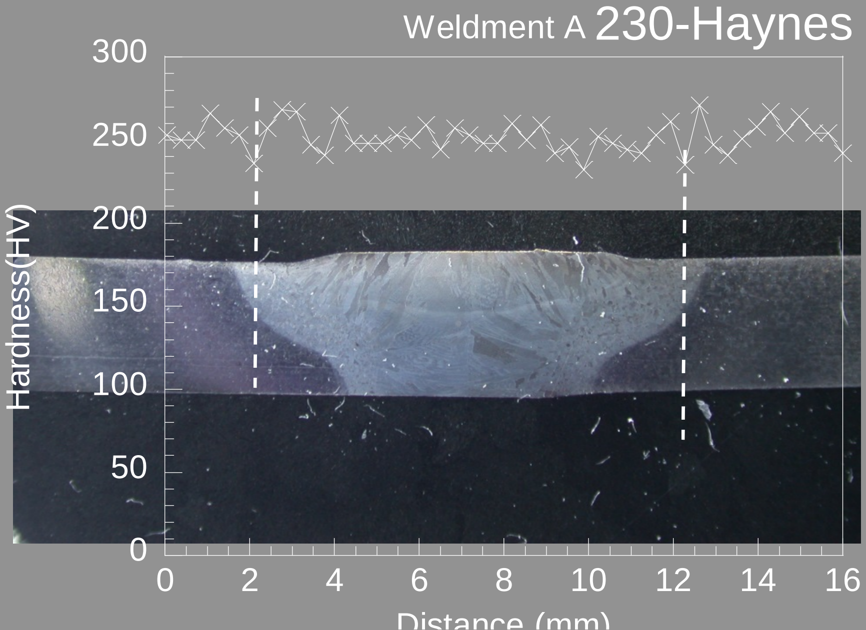
3. Performance of weldment specimens

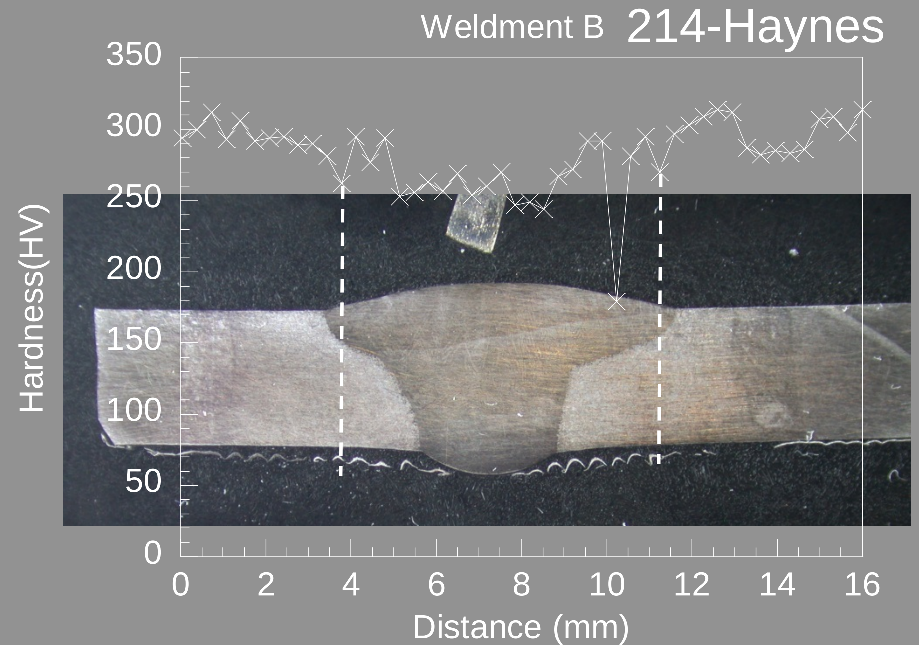
Weldment specimens

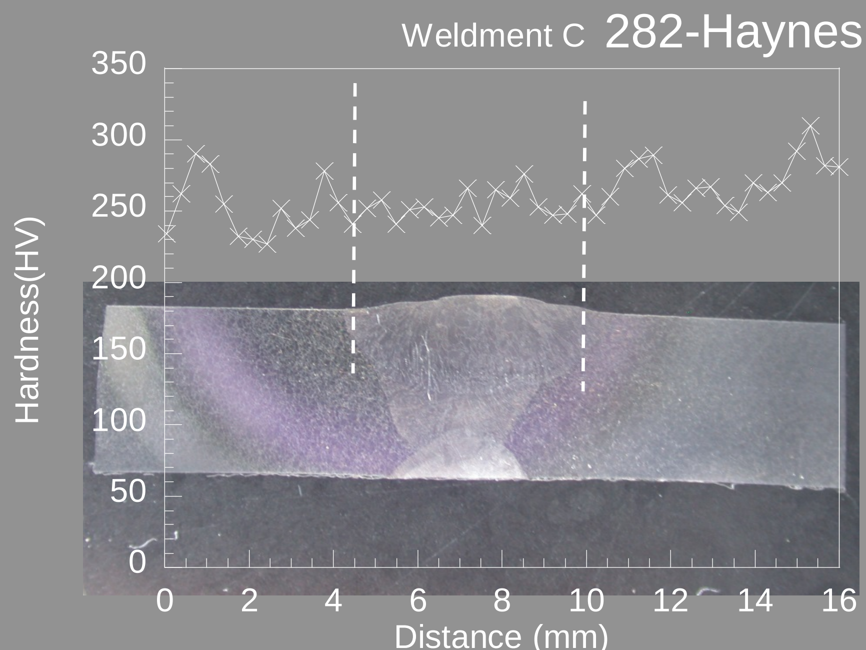
Weldment	Alloys	Filler	ID
A	230	230-H	7-7814
B	214	214-H	6-7434
C	282	282-H	4-8352
D	263	263-SM	HT5371PKII
E	617	617-SM	XX2312UK
F	740	740-SM	HT31305X
G	R41	R41-H	9-8317
H	WASP	WASP-H	9-6506
I	617	617-H	5-8806
J	263	263-H	1-9434

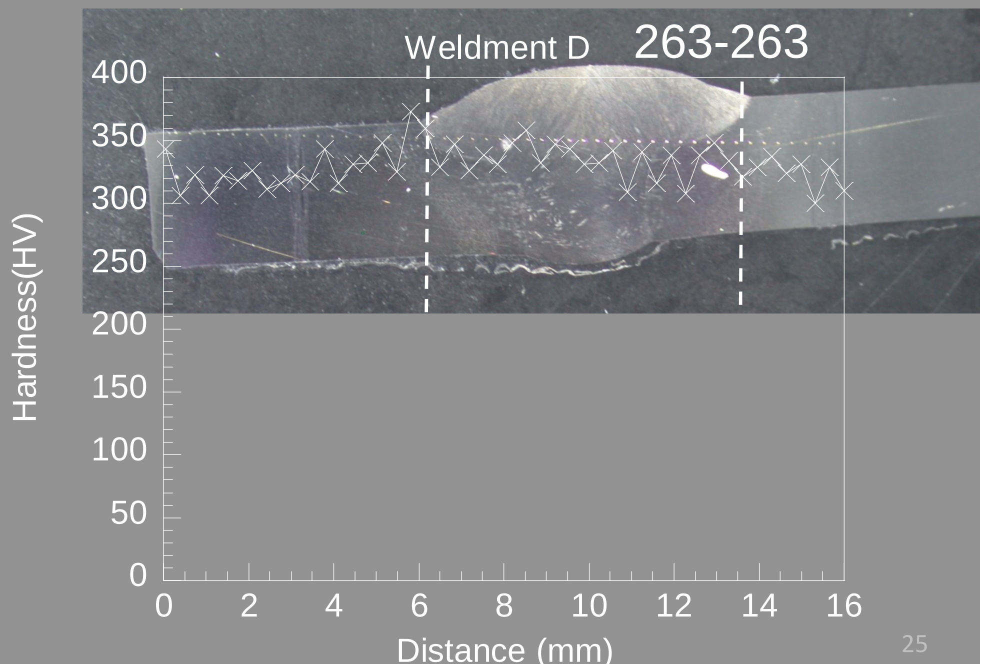
Alloys 214, 282, 263, R41, 740 are testing together with weldments
*H – Haynes International
**SM – Special Metals

Hardness of Weldments before exposure

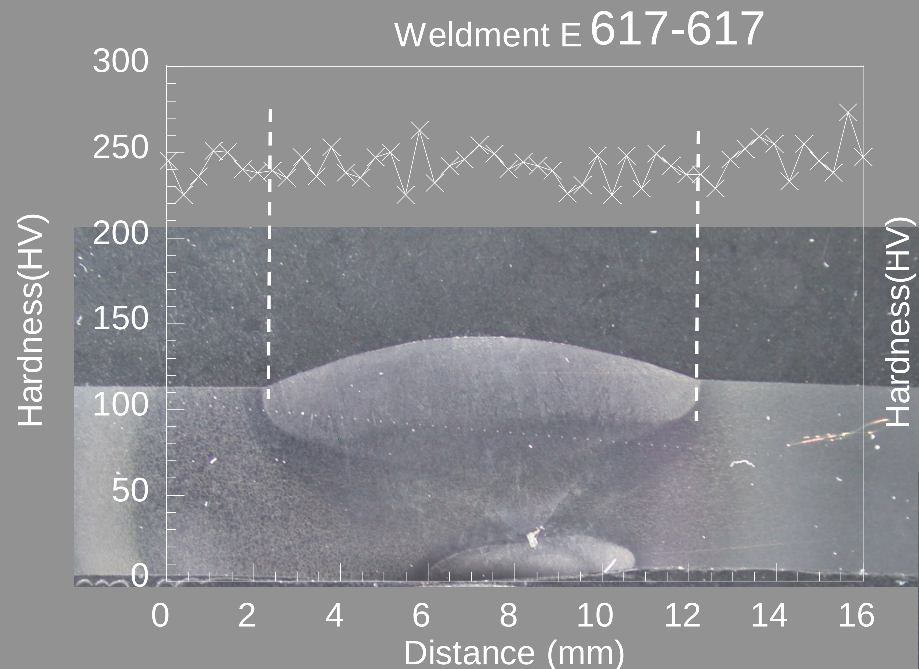


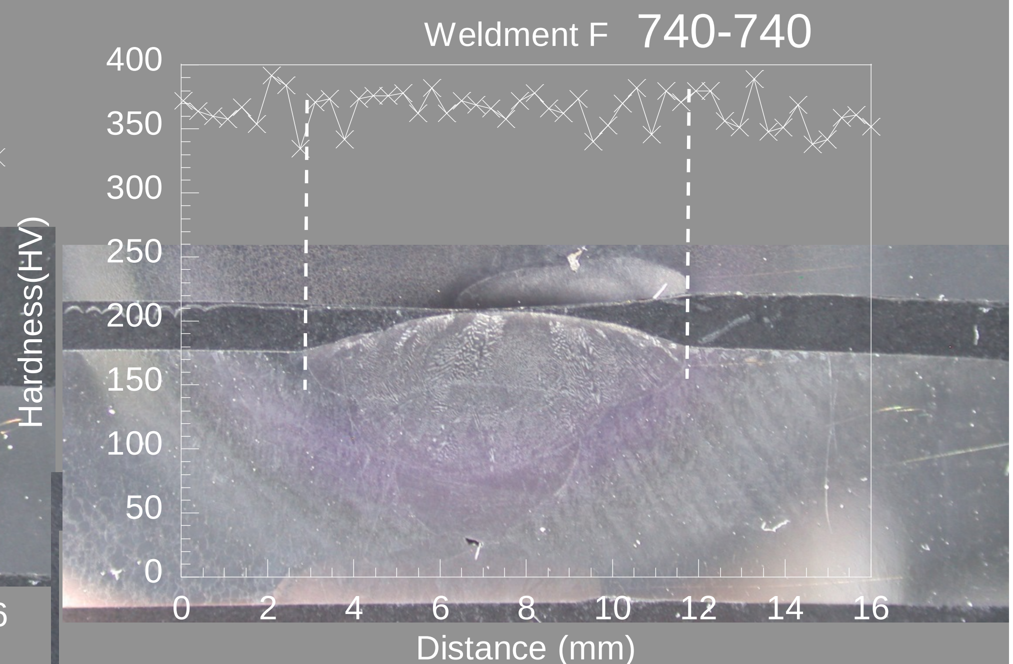


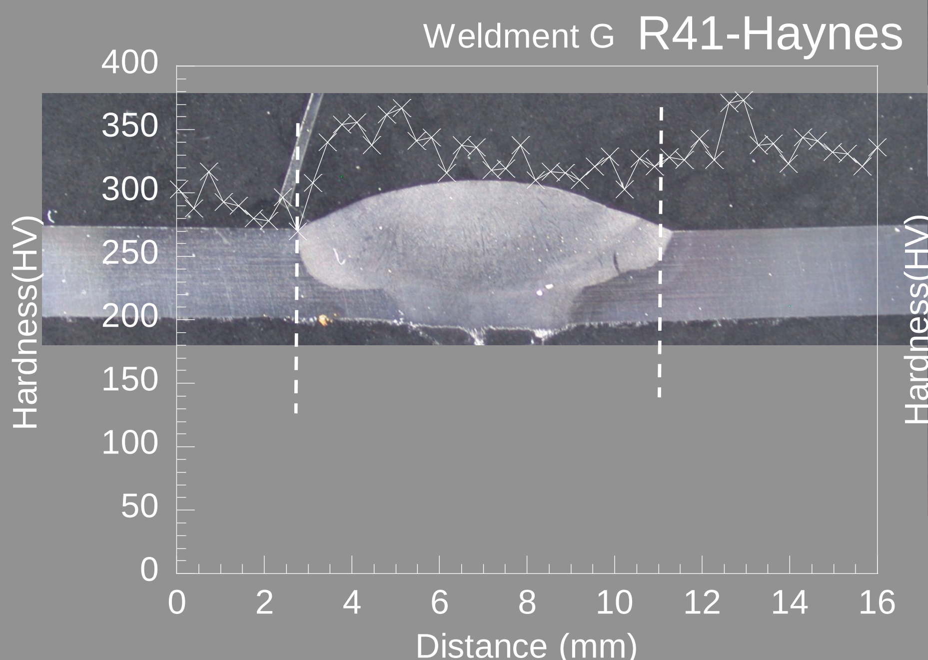


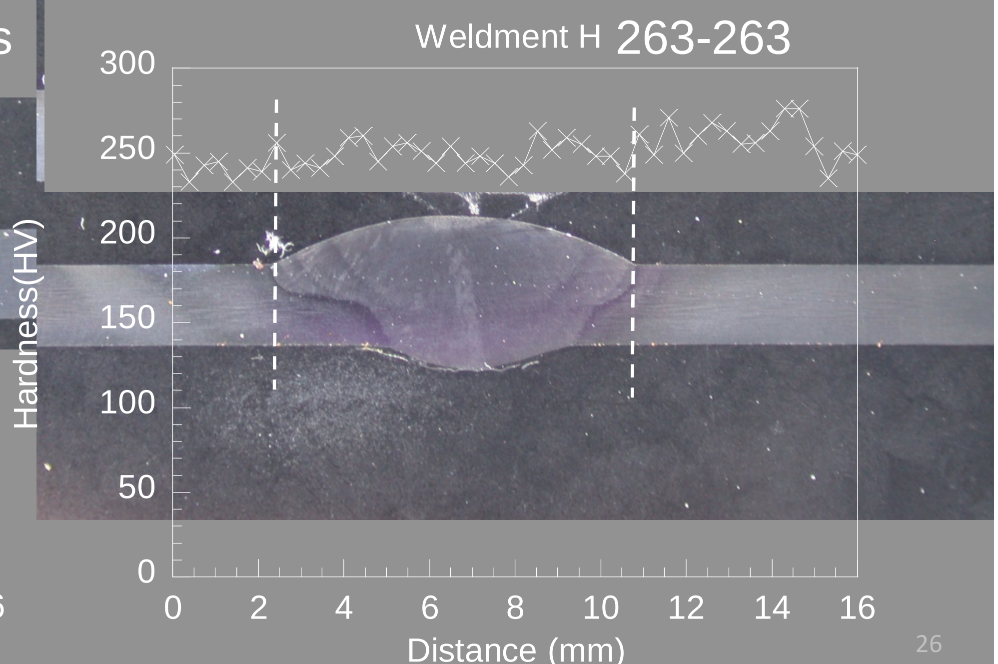


Hardness of Weldments before exposure

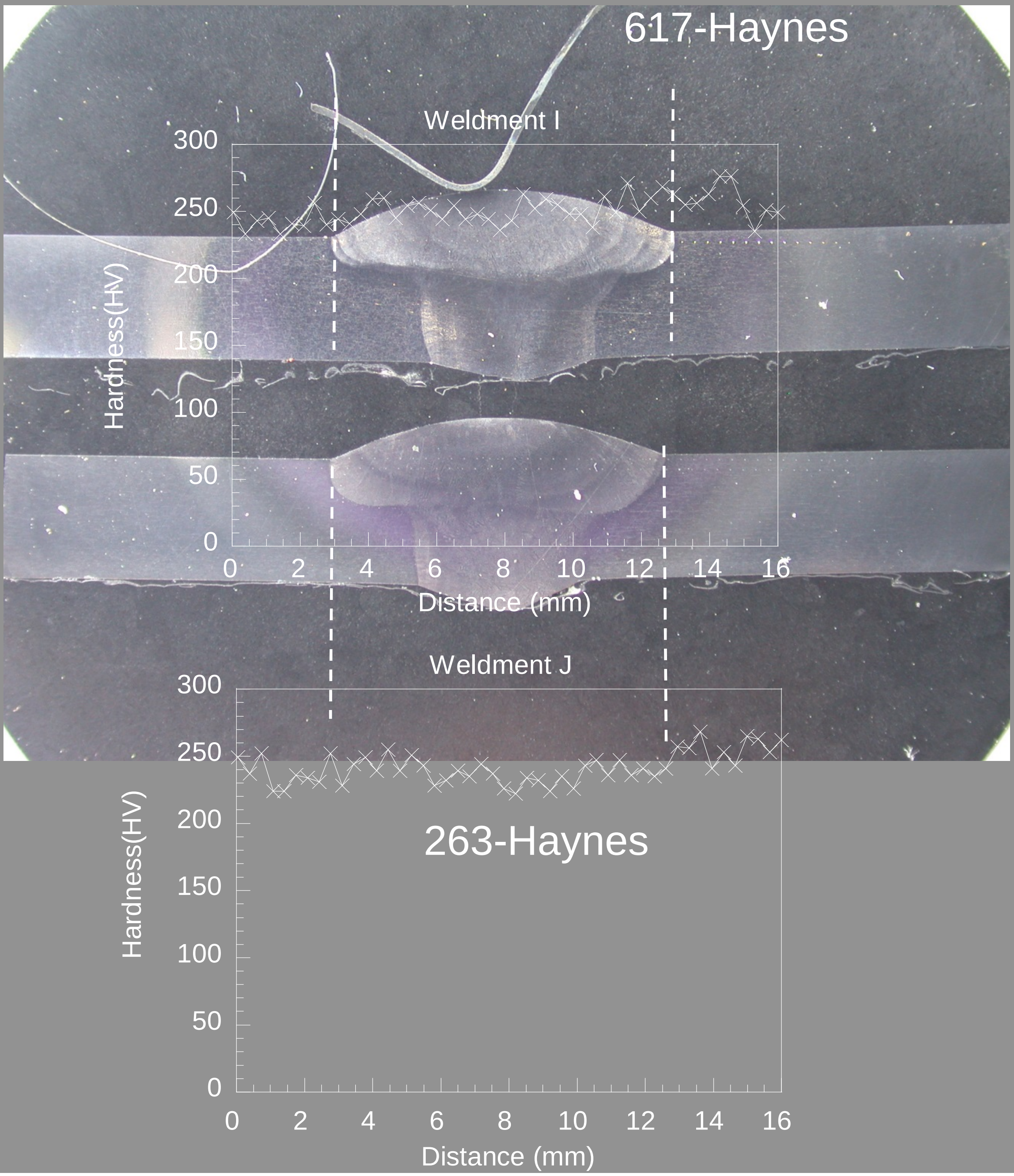








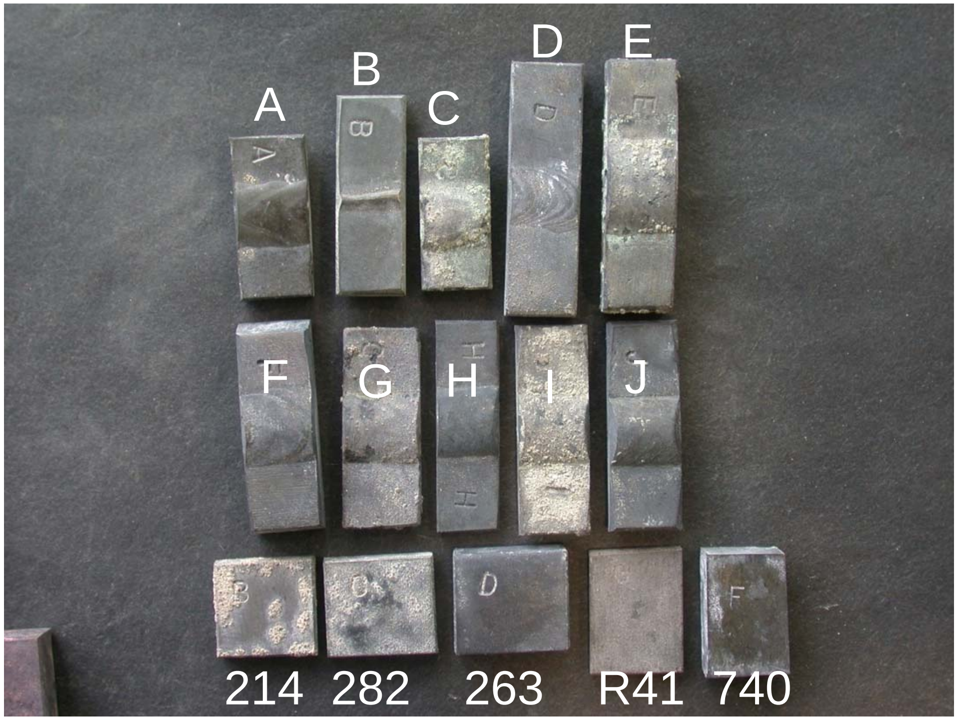
Hardness of Weldments before exposure



Photos of weldments after 300h exposure to 750°C

Gas composition: 68.14%CO_2-26.9%H_2O-0.99%SO_2-3.97%O_2

Western ash:16%Al_2O_3,36%SiO_2, 9%Fe_2O_3, 29%CaO, 5%K_2SO_4, 5%Na_2SO_4



Eastern ash:30%Al_2O_3,30%SiO_2, 30%Fe_2O_3, 5%K_2SO_4, 5%Na_2SO_4

Eastern ash sticks to sample surface

$2Fe_2O_3 + 6K_2SO_4 + 6SO_2 + 3O_2 = 4K_3Fe(SO_4)_3$ melting T 694 ° C

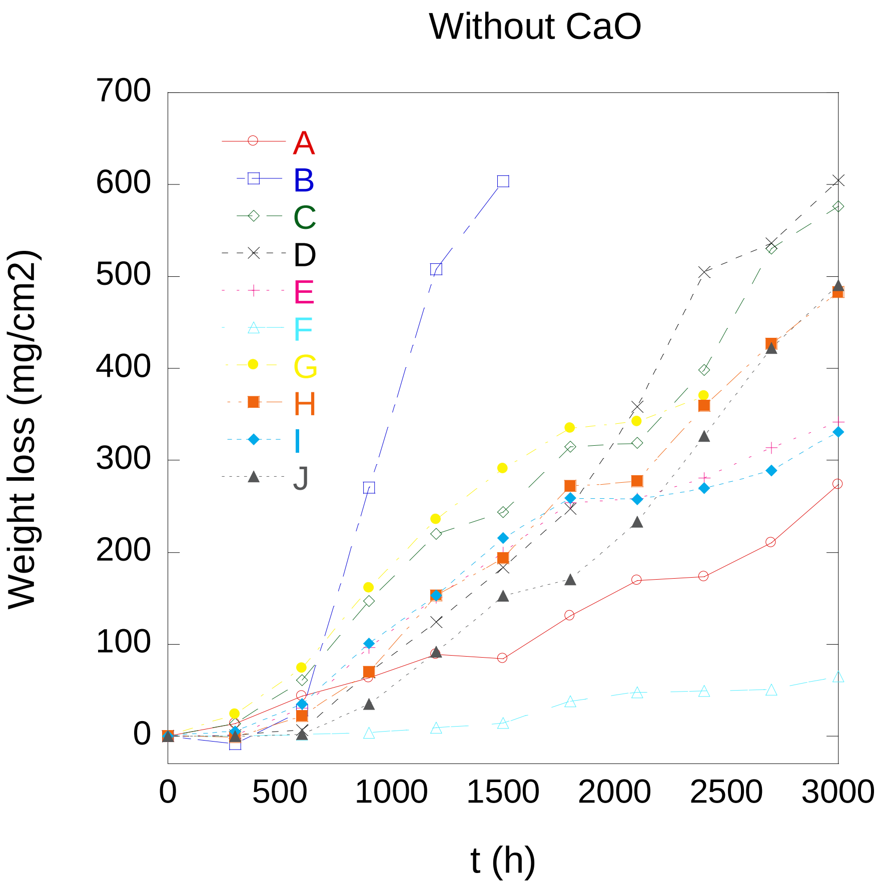
$2Al_2O_3 + 6Na_2SO_4 + 6SO_2 + 3O_2 = 4K_3Al(SO_4)_3$ melting T 654 ° C

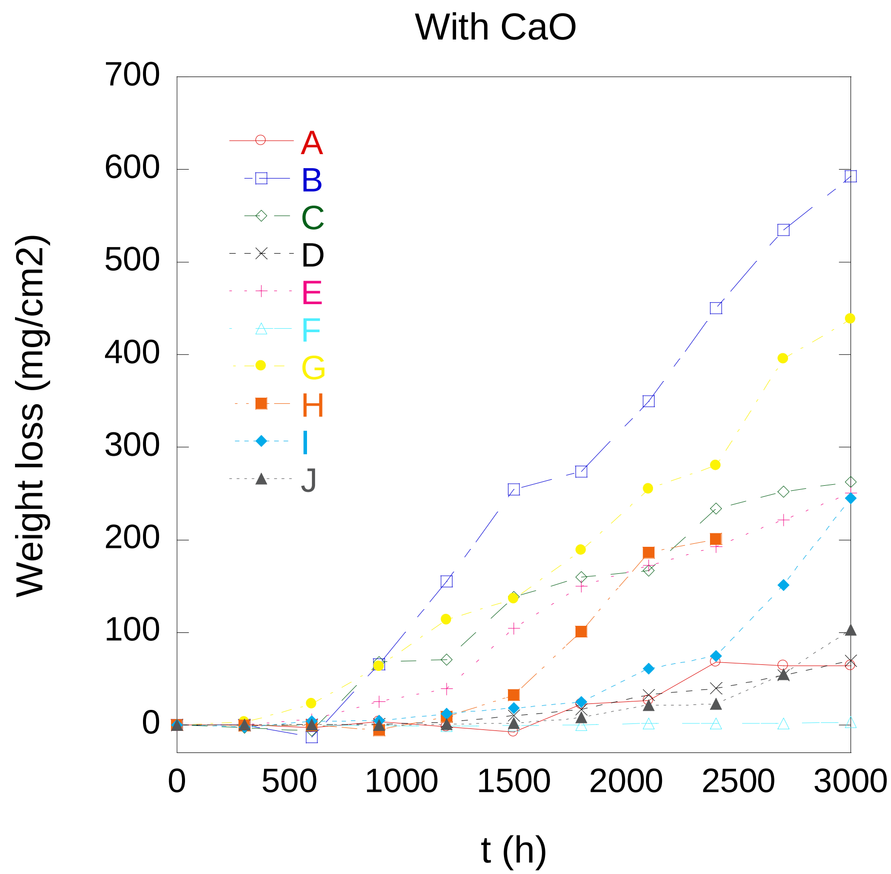
$3CaCO_3 + 2K_3Fe(SO_4)_3 = 3CaSO_4 + 3K_2SO_4 + 3CO_2 + Fe_2O_3$

$3CaCO_3 + 2K_3Al(SO_4)_3 = 3CaSO_4 + 3K_2SO_4 + 3CO_2 + Al_2O_3$

melting T 1460 ° C 1069 ° C

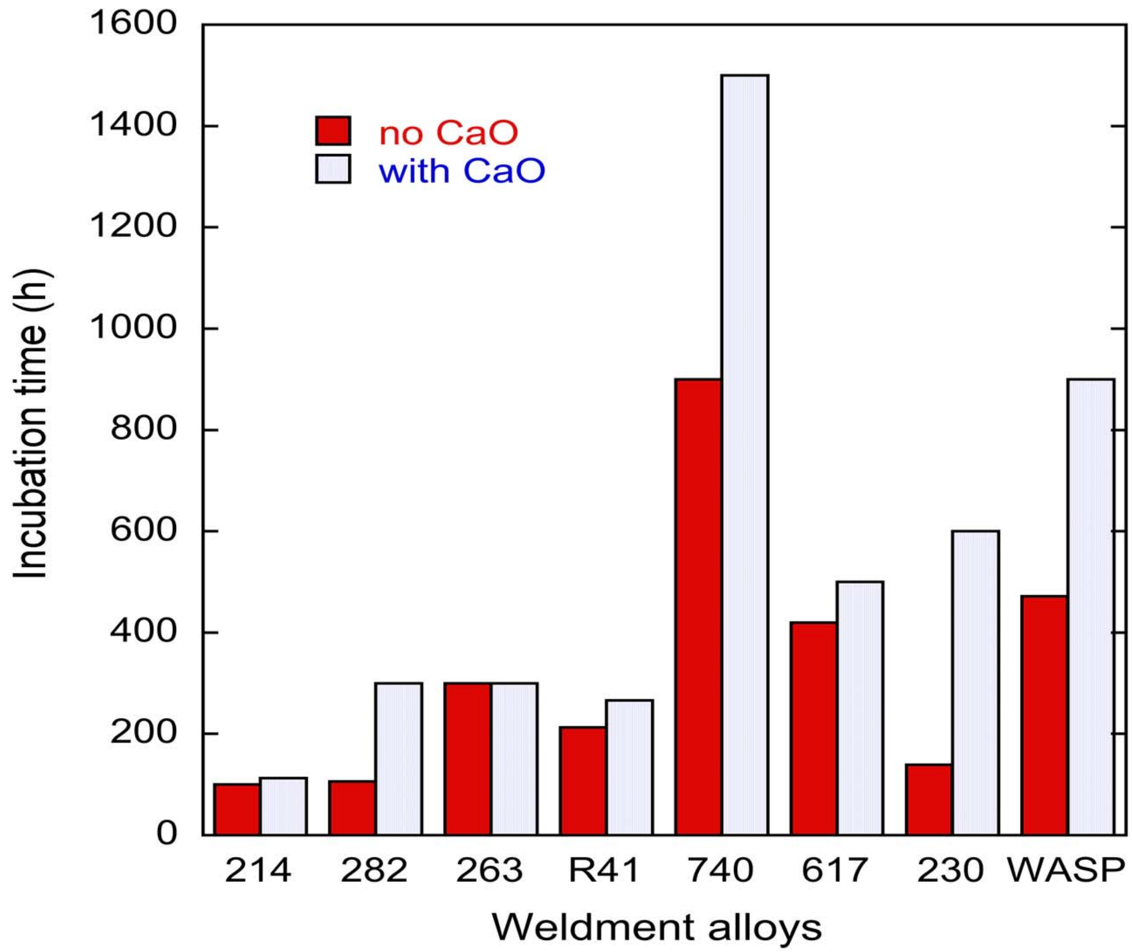
Weight Change data after exposure



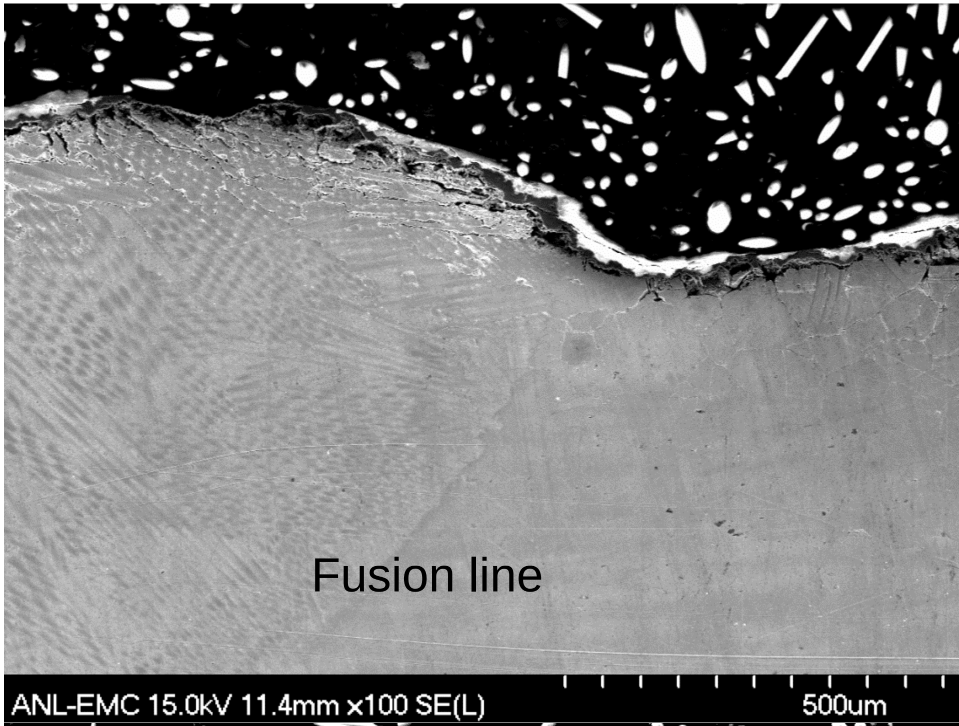


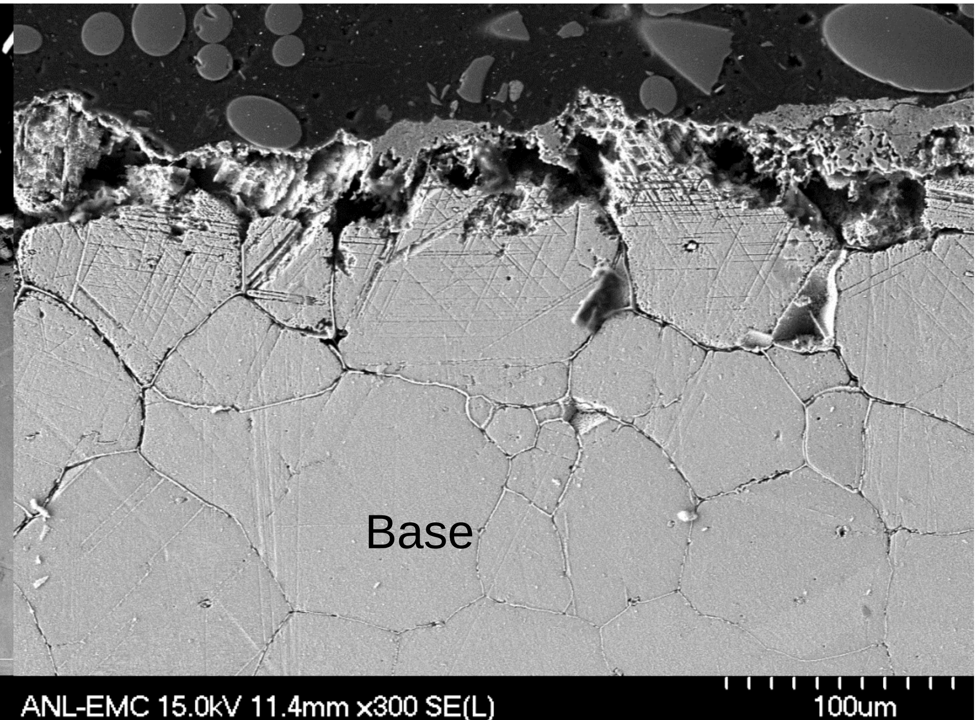
A	B	C	D	E	F	G	H	I	J
230	214	282	263	617	740	R41	WASP	617	263

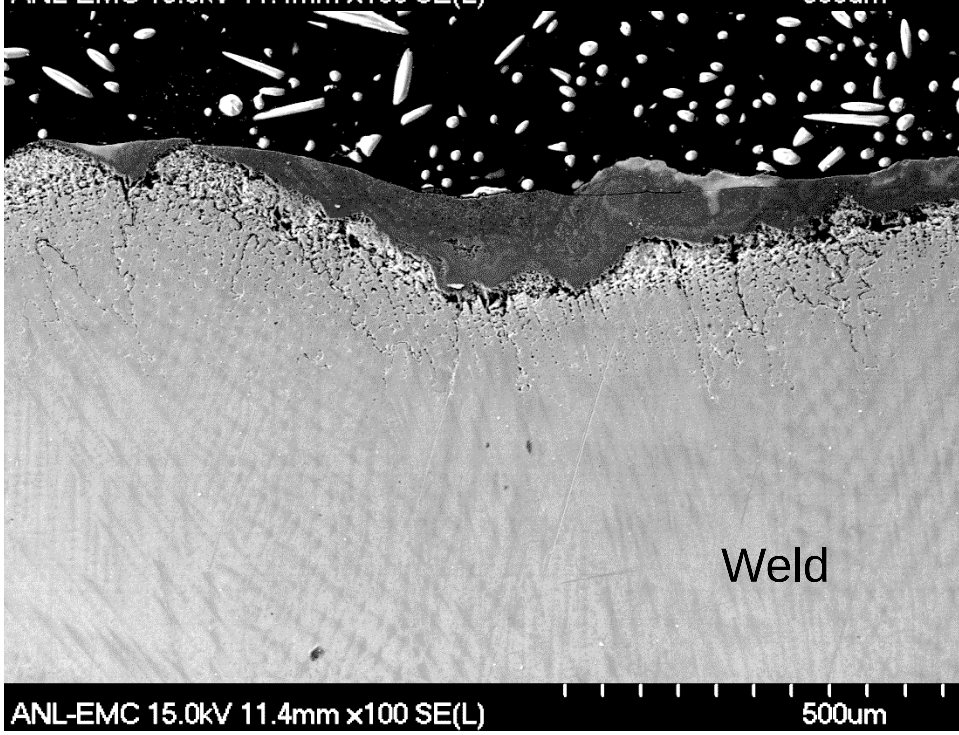
Incubation time for weldments



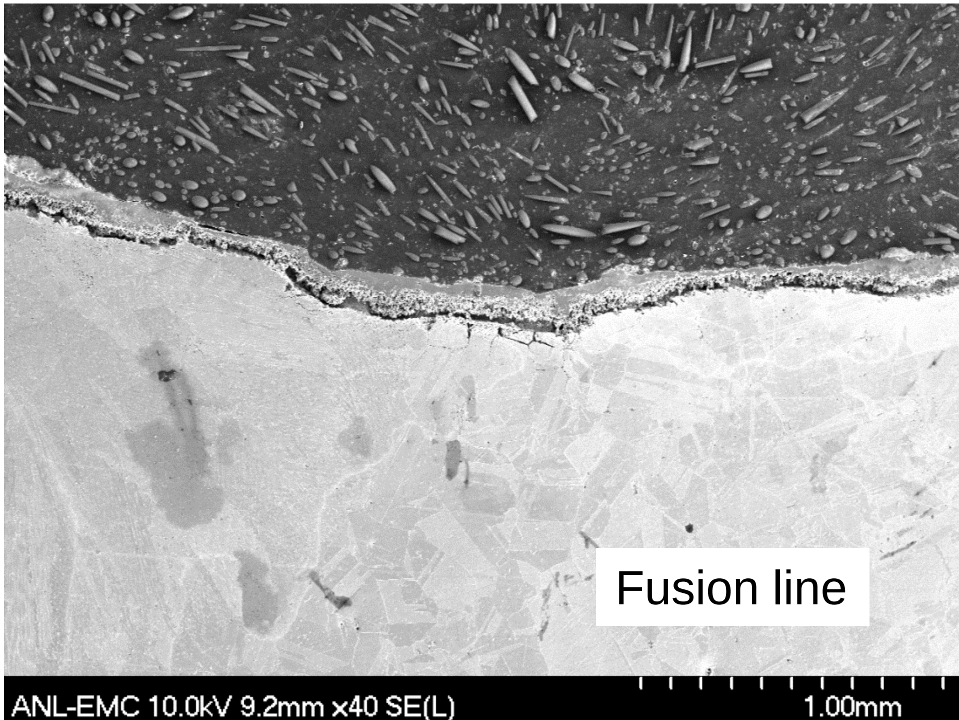
A	B	C	D	E	F	G	H	I	J
230	214	282	263	617	740	R41	WASP	617	263

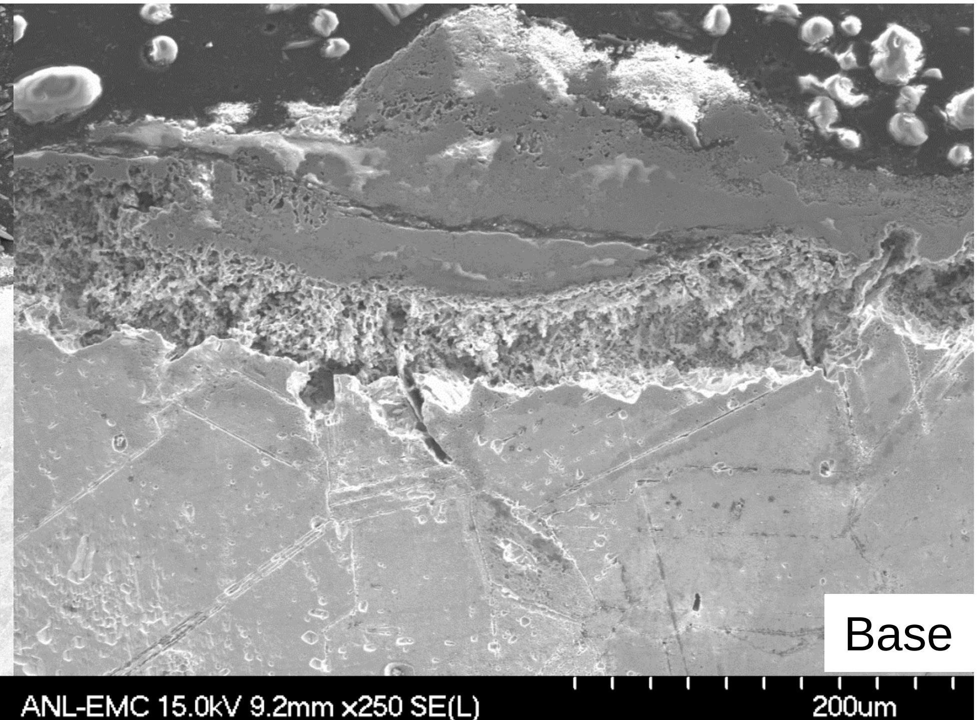


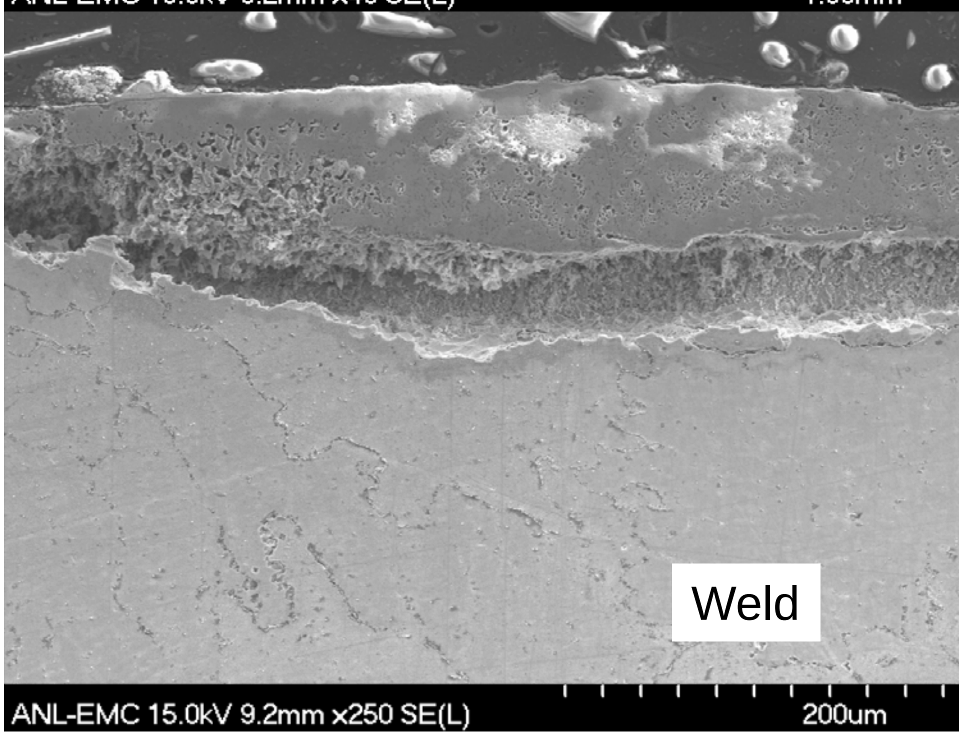




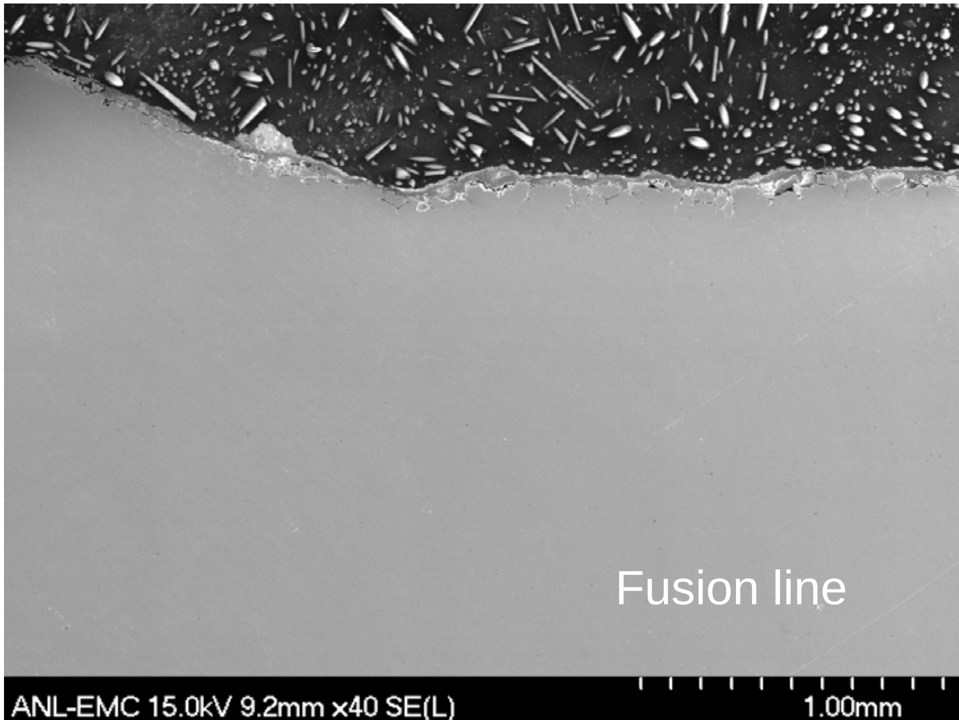
Weldment D (263) without CaO

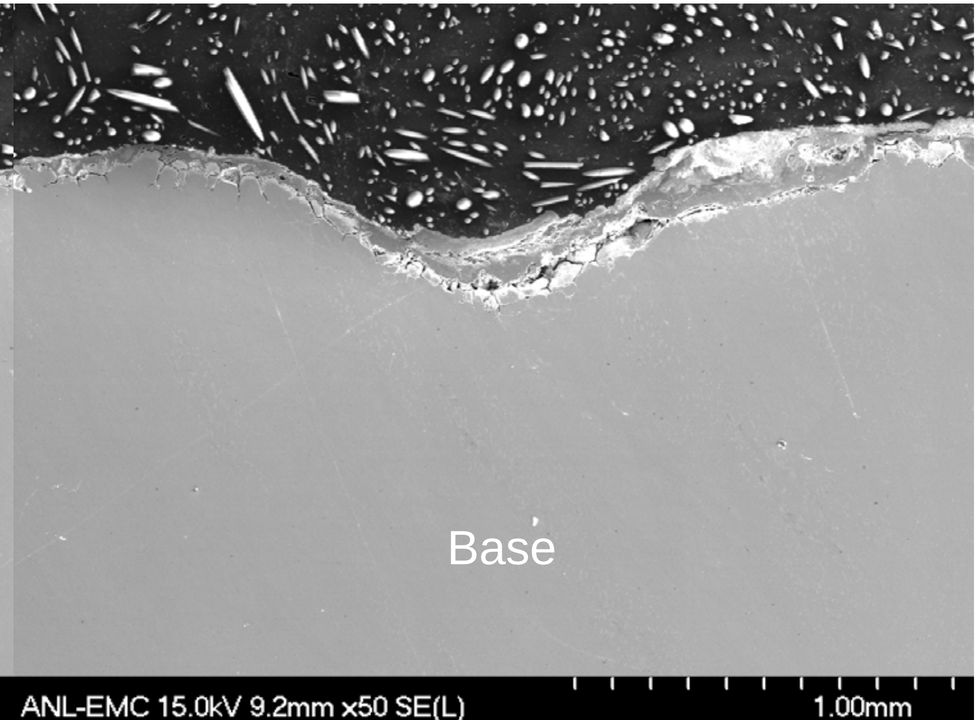


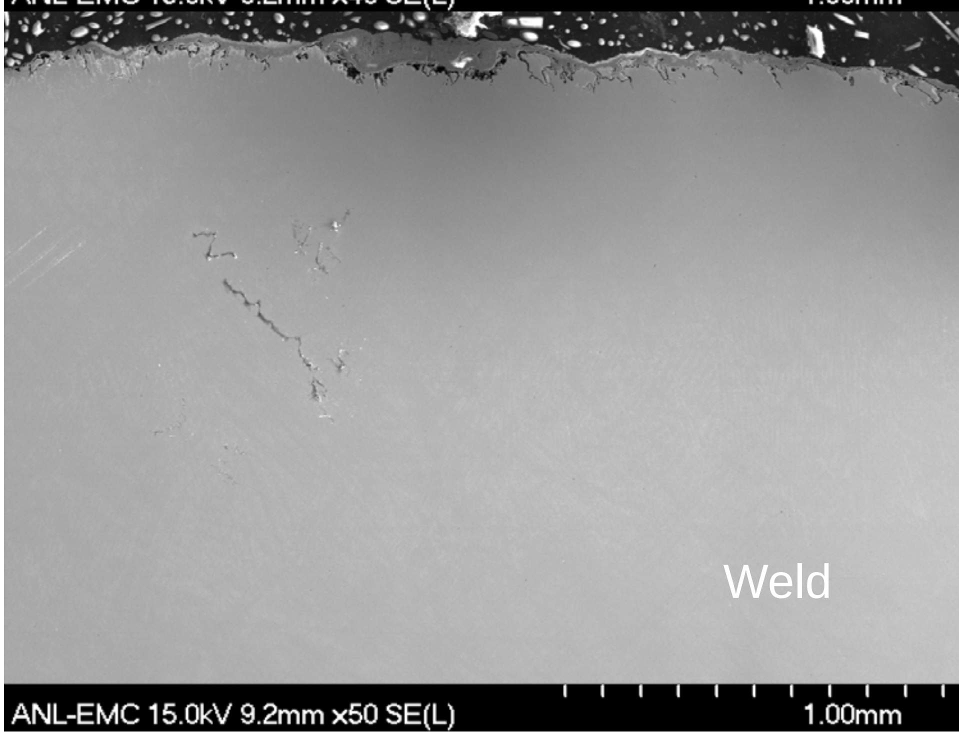




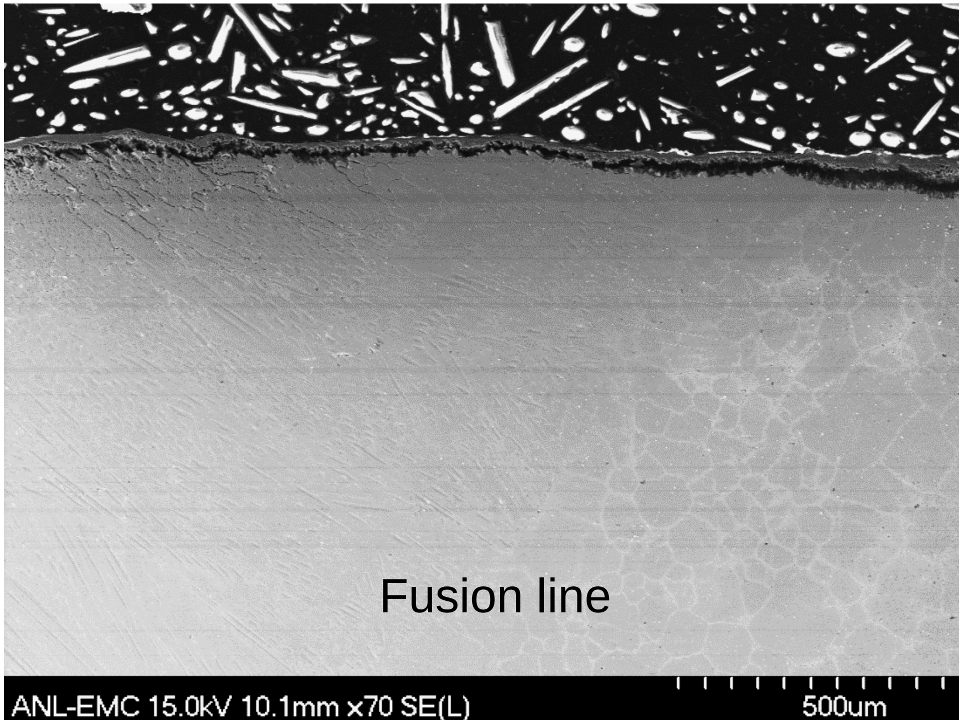
Weldment F (740) without CaO

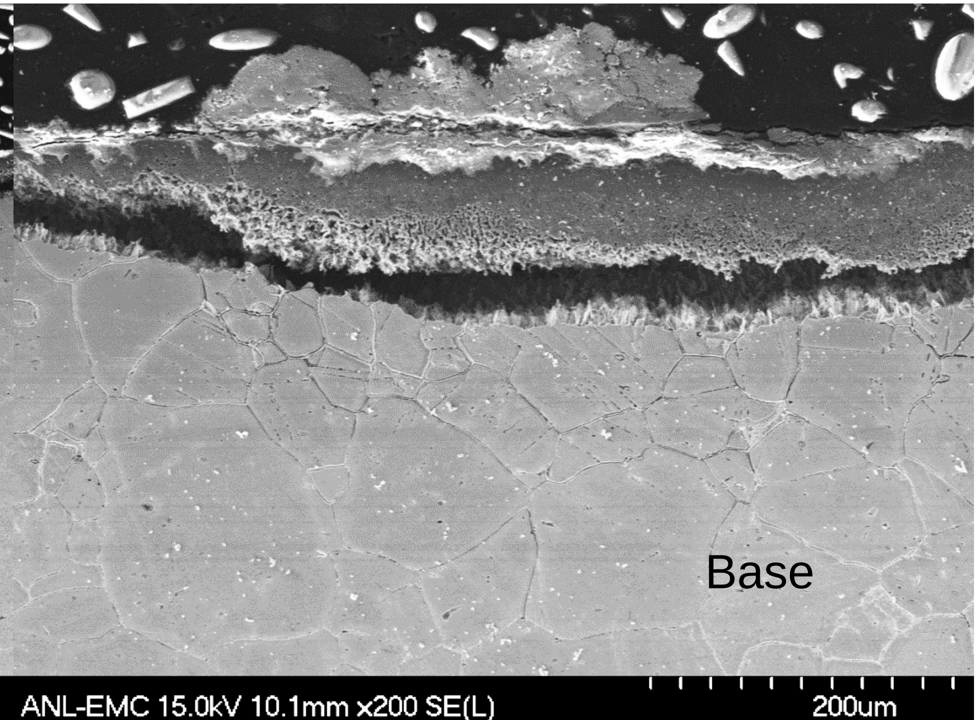


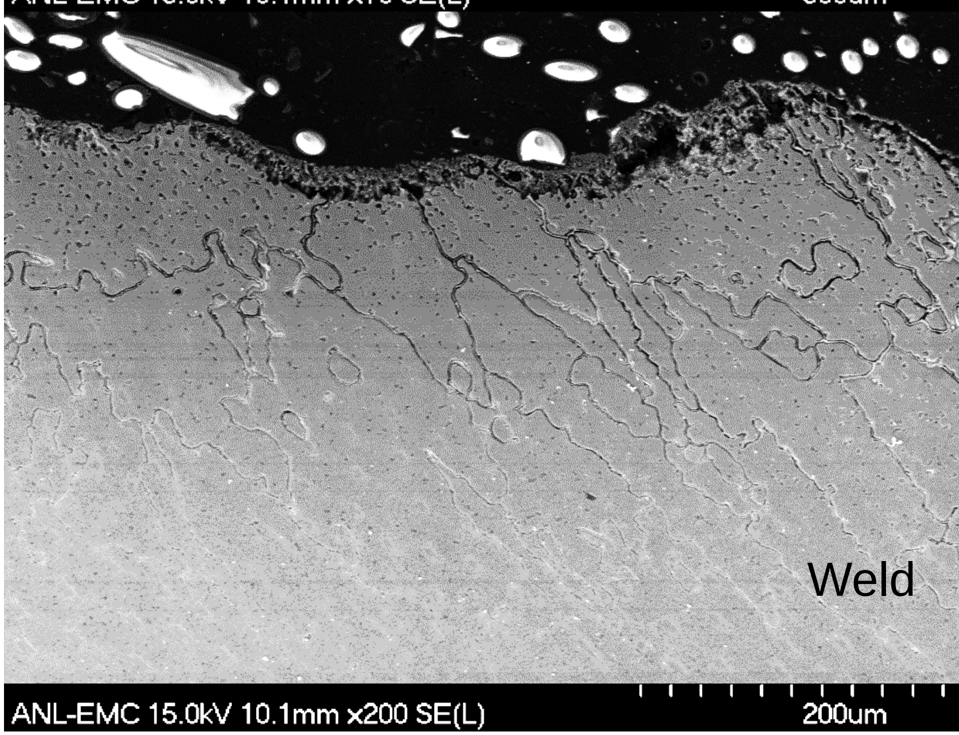




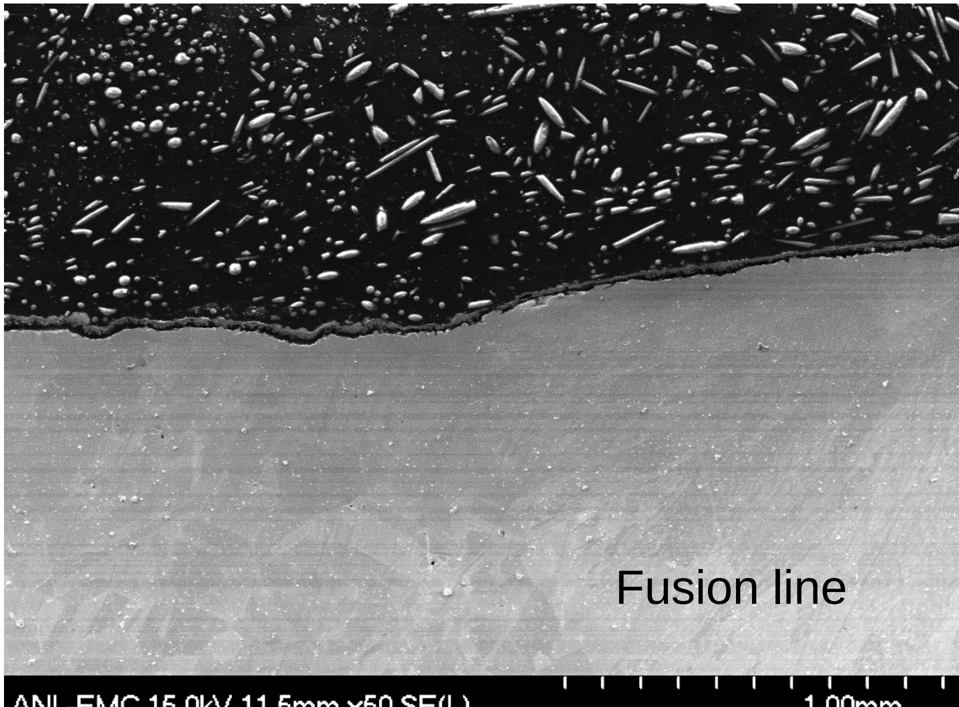
Weldment I (617H) without CaO

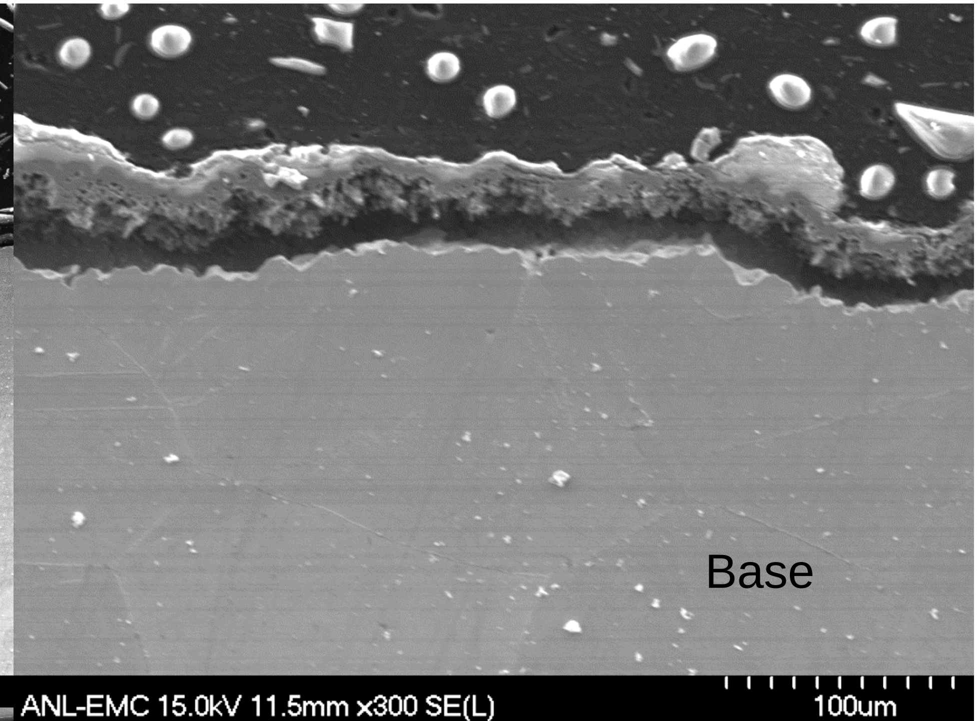


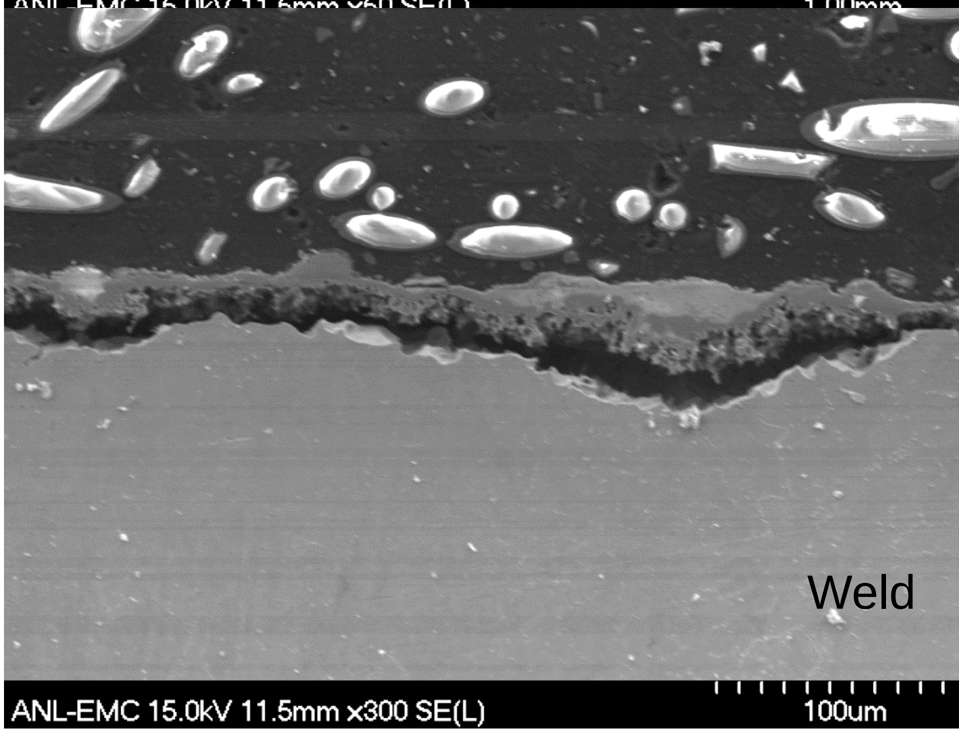




Weldment D (263) with CaO

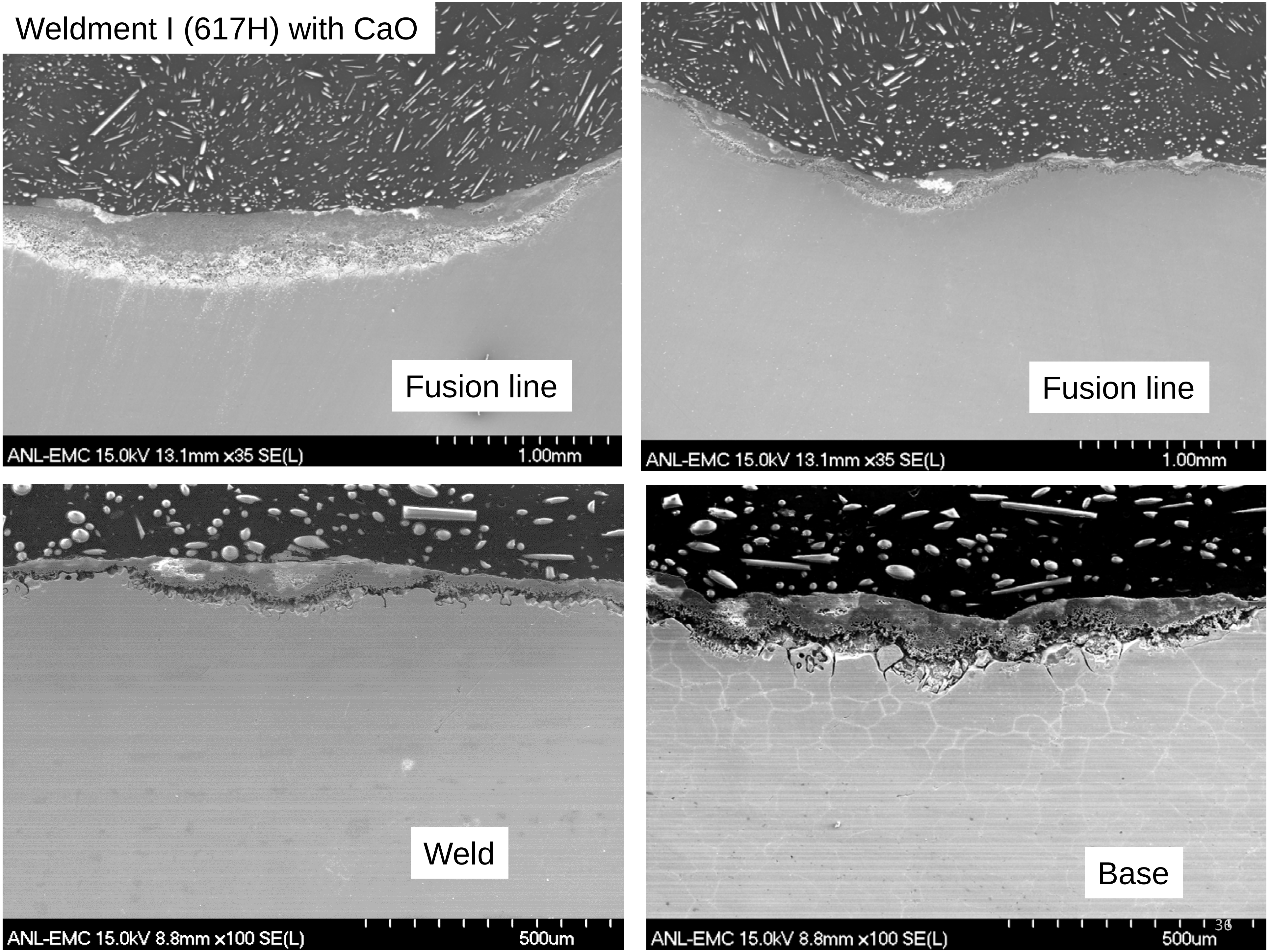




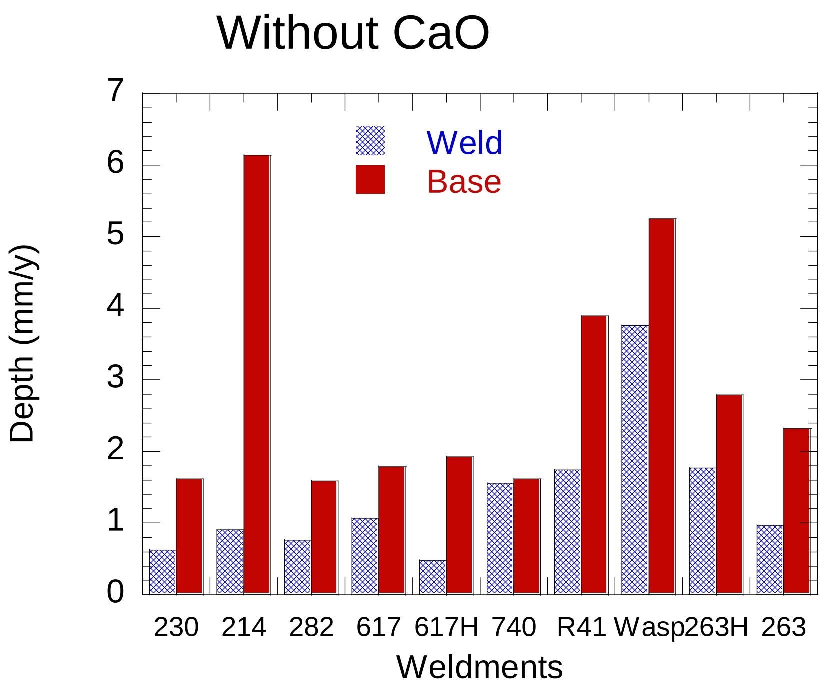


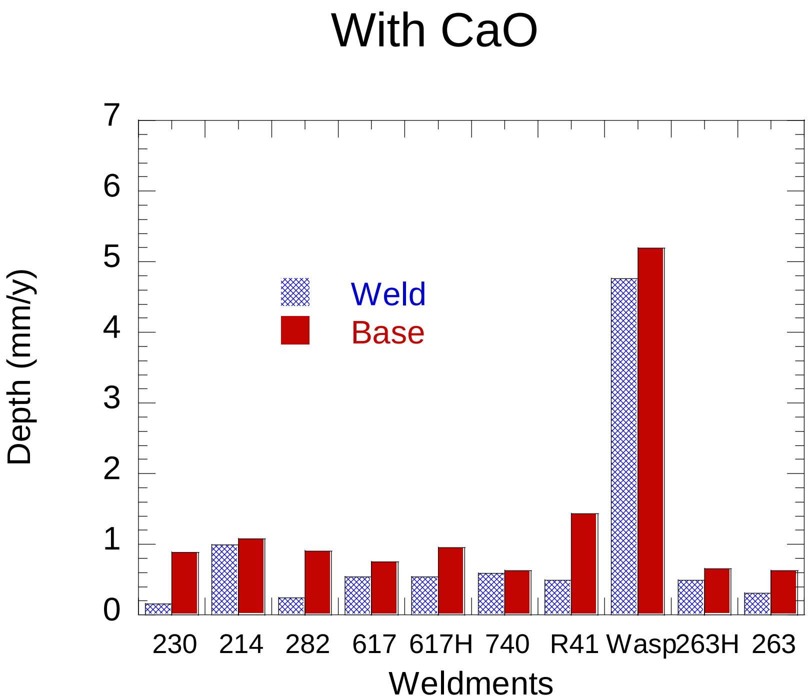
Weldment F(740) with CaO

Weldment I (617H) with CaO



Corrosion rate of weldments

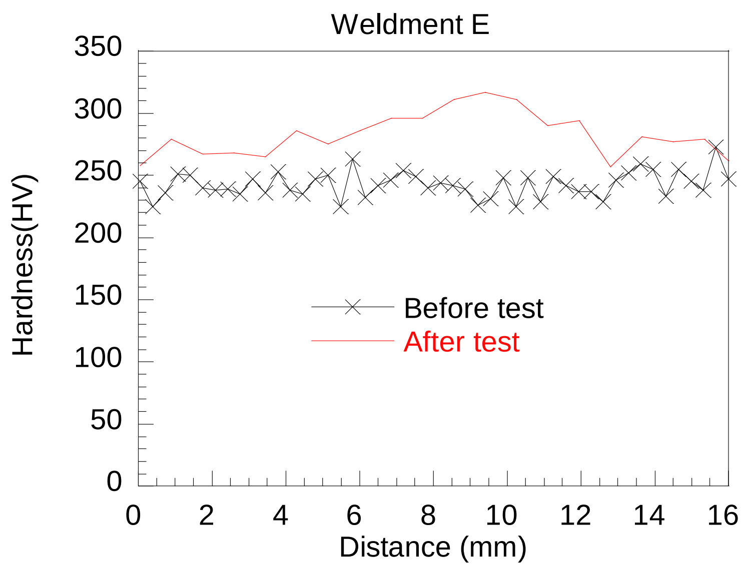


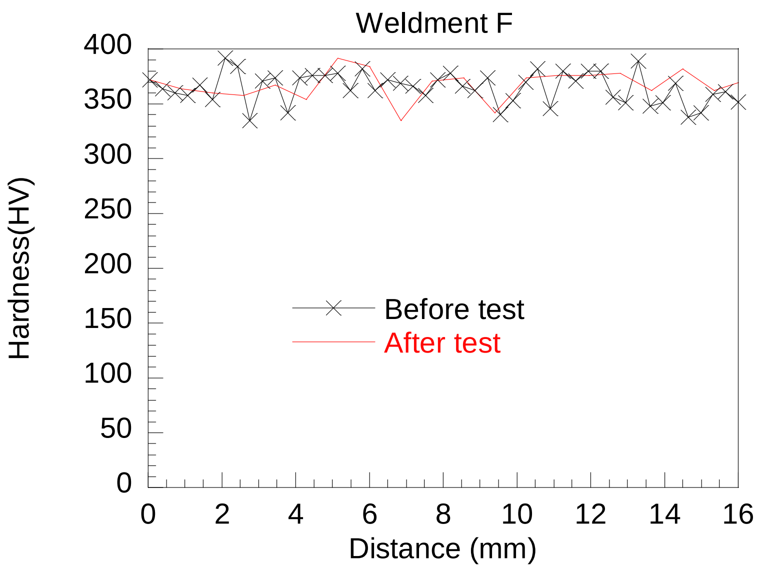


- It is possible to reduce the long term corrosion rate by using alloys with smaller grain size.

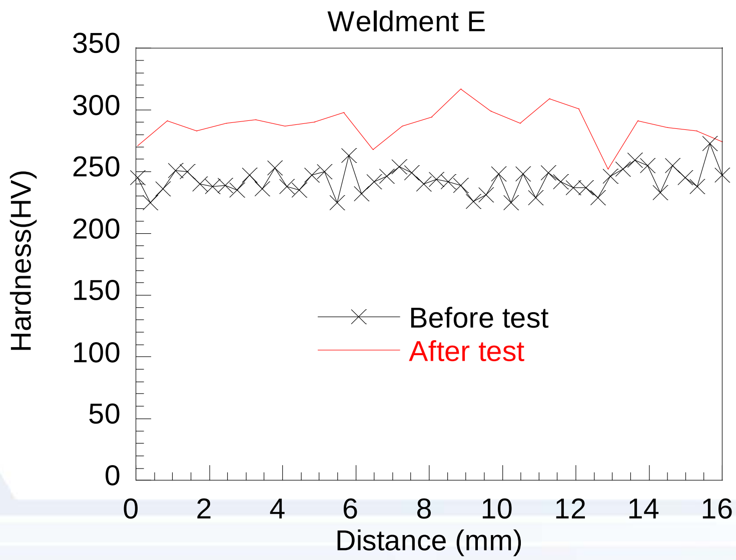
Hardness data after exposure for 2400h

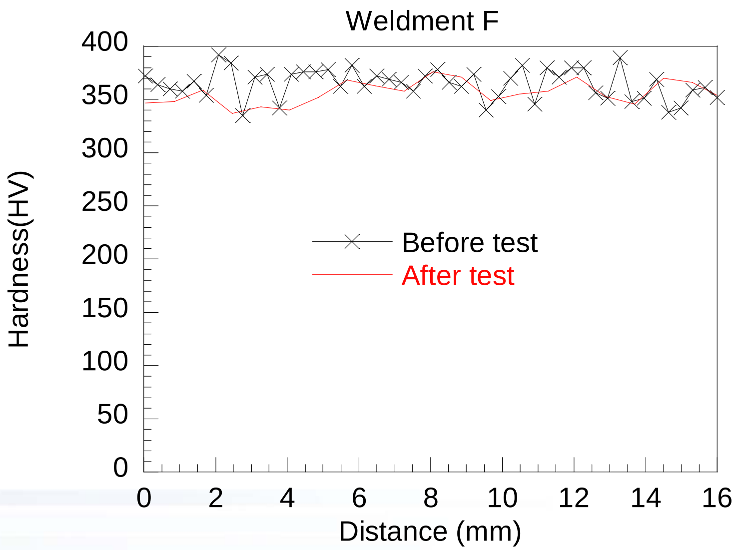
With CaO





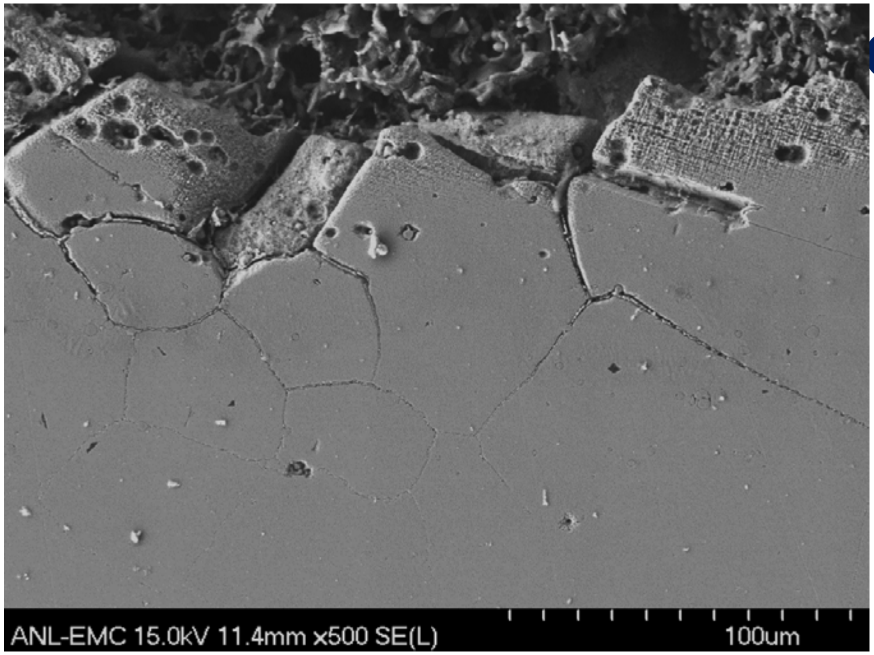
Without CaO

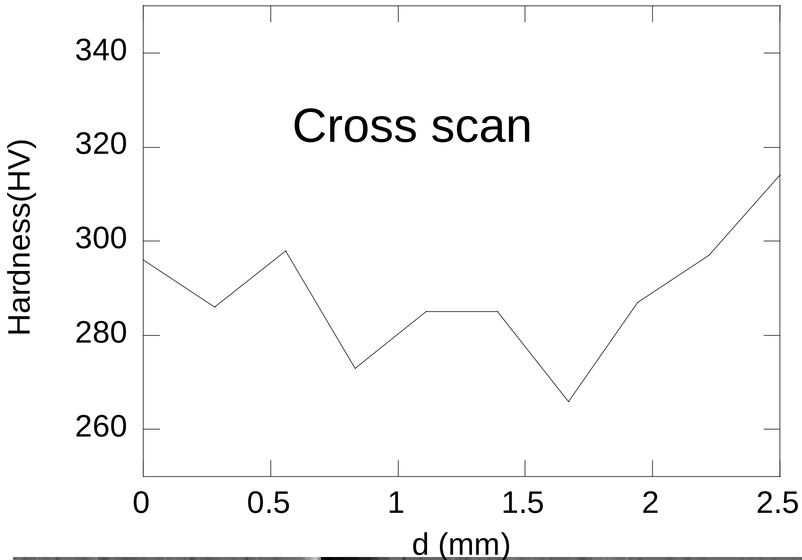


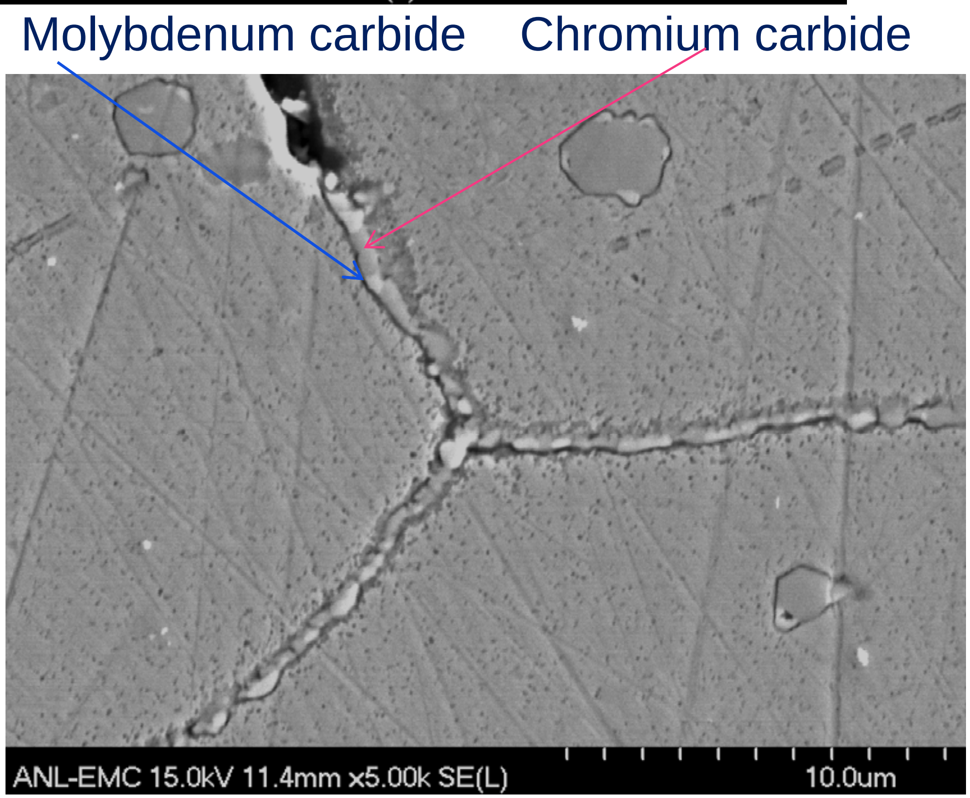


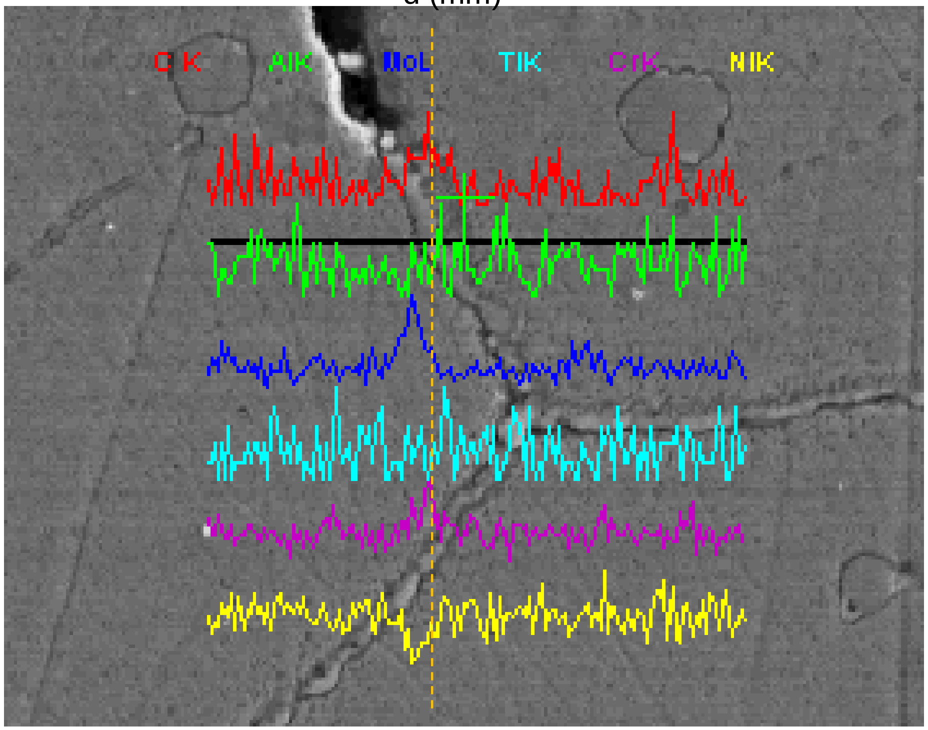
Carburization after incubation time

Weldment E(617) without CaO

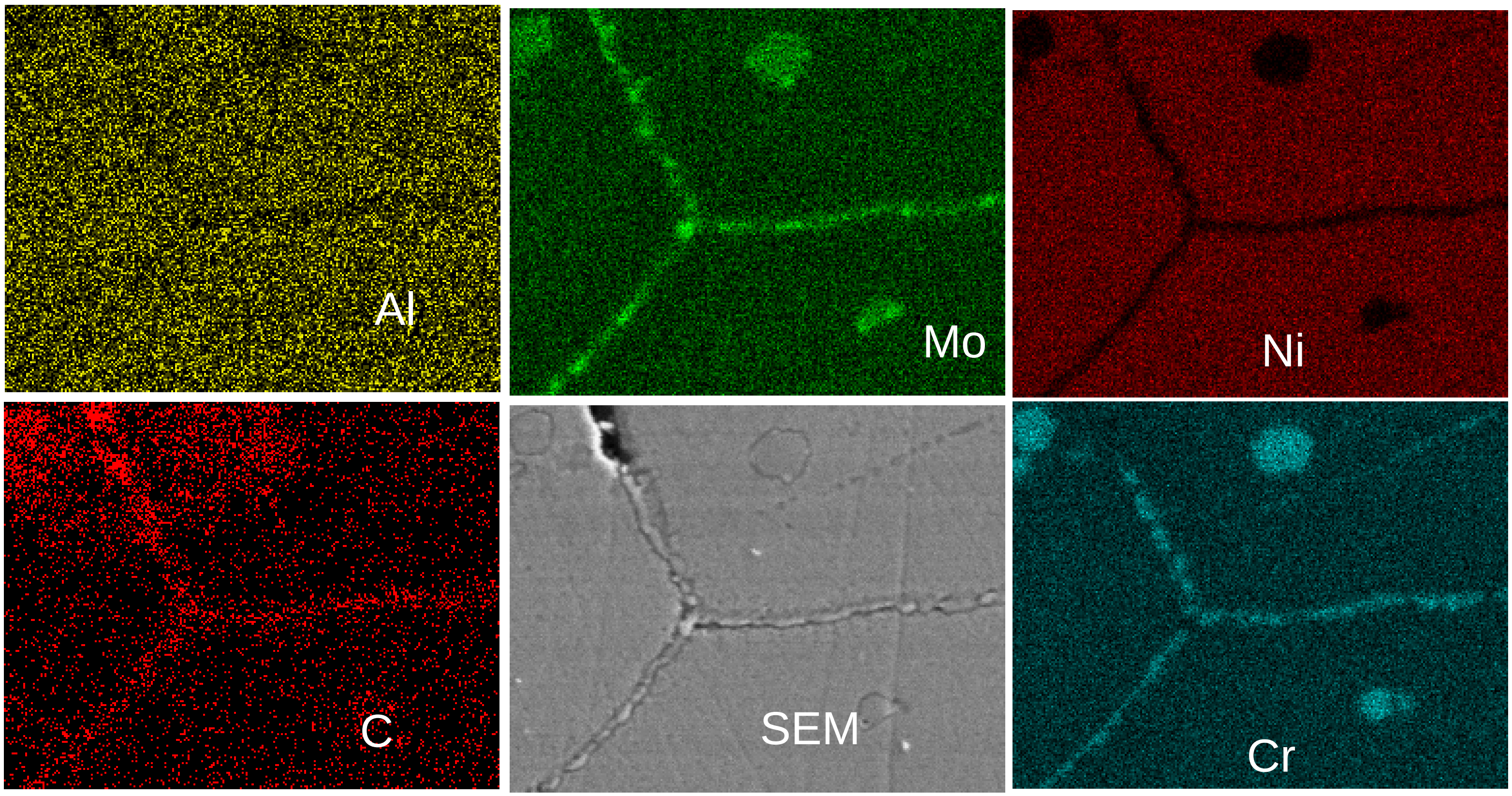








Carburization after incubation time



EDX map of Weldment E(617) without CaO

Summary continued

- **The ash corrosion rates at fusion zone of weldments are generally less than at base alloys.**
- **Carburization after incubation time can increase the hardness.**
- **The performance of Alloy 740 weldment is the best among the weldments tested.**
- **It is possible to reduce the long term corrosion rate of weldment by increasing the calcium concentration in ash.**
- **It is possible to reduce the long term alloy corrosion rate by using alloys with smaller grain size or by using alloy compositions as cladding or coating.**

Future Plans for the ANL research project

- **Complete corrosion evaluation of structural alloys in oxy-fuel environments containing different ashes, alkali sulfates, and chlorides. This includes a range of coal ash chemistry and gas environments at temperatures up to 750 °C. Test has been performed in oxy-fuel gas environment with 200ppm HCl at 750°C for 300h. Long term exposures are being continued.**
- **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**
  - **Study alloys with nano-grain size**

Thank you

This work was supported by the DOE/Office of Fossil Energy, Advanced Research Materials Program. Patricia Rawls is the Program Manager. We thank Richard Dunst and Vito Cedro of NETL for their support. We would like to acknowledge Jack deBarbadillo of Special Metals and Krishna Srivastava of Haynes International for supplying the welded plates of various alloys.