WestVirginiaUniversity
College of Engineering and Mineral Resources

DoE Award No. DE- FE0005717

Development of Self-Powered Wireless-Ready High Temperature Electrochemical Sensors for In-Situ Corrosion Monitoring of Boiler Tubes

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Project Objectives

- To develop in-situ corrosion monitoring sensors for corrosion of USC boiler tubes in next generation coal-based power systems

- To develop thermal-electric based energy harvesting and telecommunication devices for the self-powered wireless ready sensor system

Current Milestones

July to September 2011

- Initiate preliminary high-temperature electrochemical corrosion rate (ECR) probe design

October to December 2011

- To complete the design and construction of (ECR) probe for lab scale corrosion experiments and to complete laboratory test configuration

January to March 2012

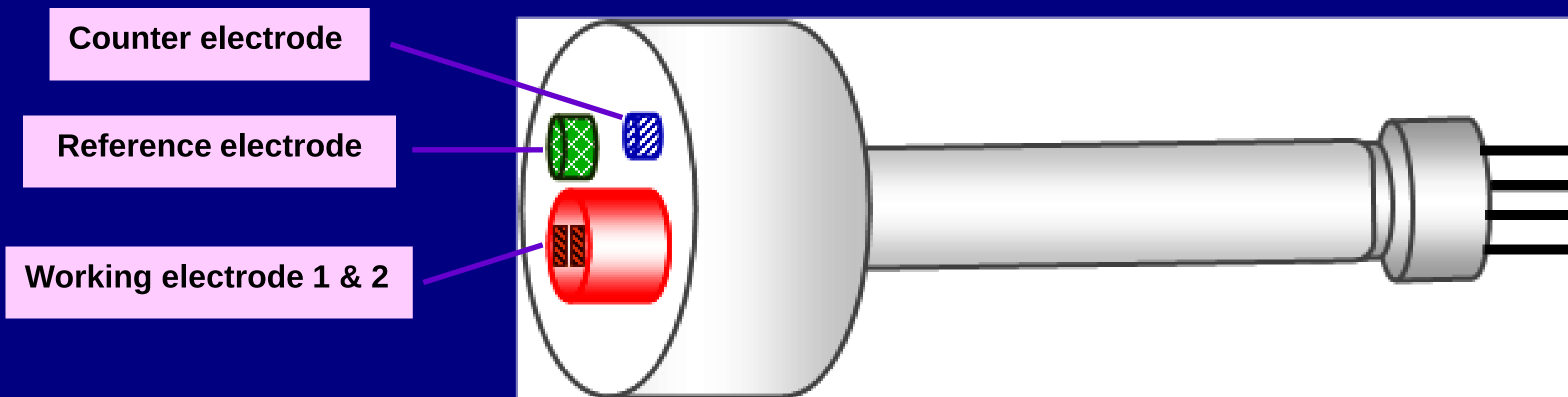
- To demonstrate the results of the corrosion tests as a function of exposure time, temperature and various simulated boiler exposure environments in lab-scale setting

Project Milestone Status

July to September 2011

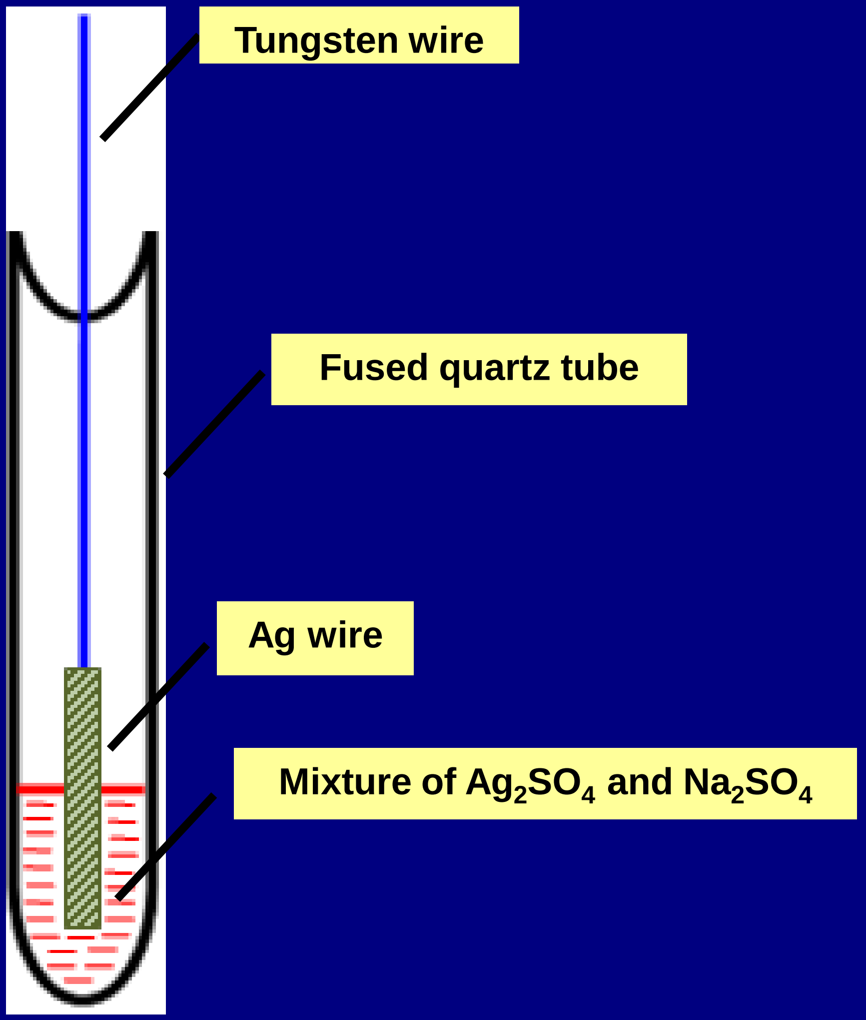
- High temperature electrochemical corrosion rate (ECR) probe for lab scale corrosion experiments has been designed and constructed.

Developed High Temperature Corrosion Sensor

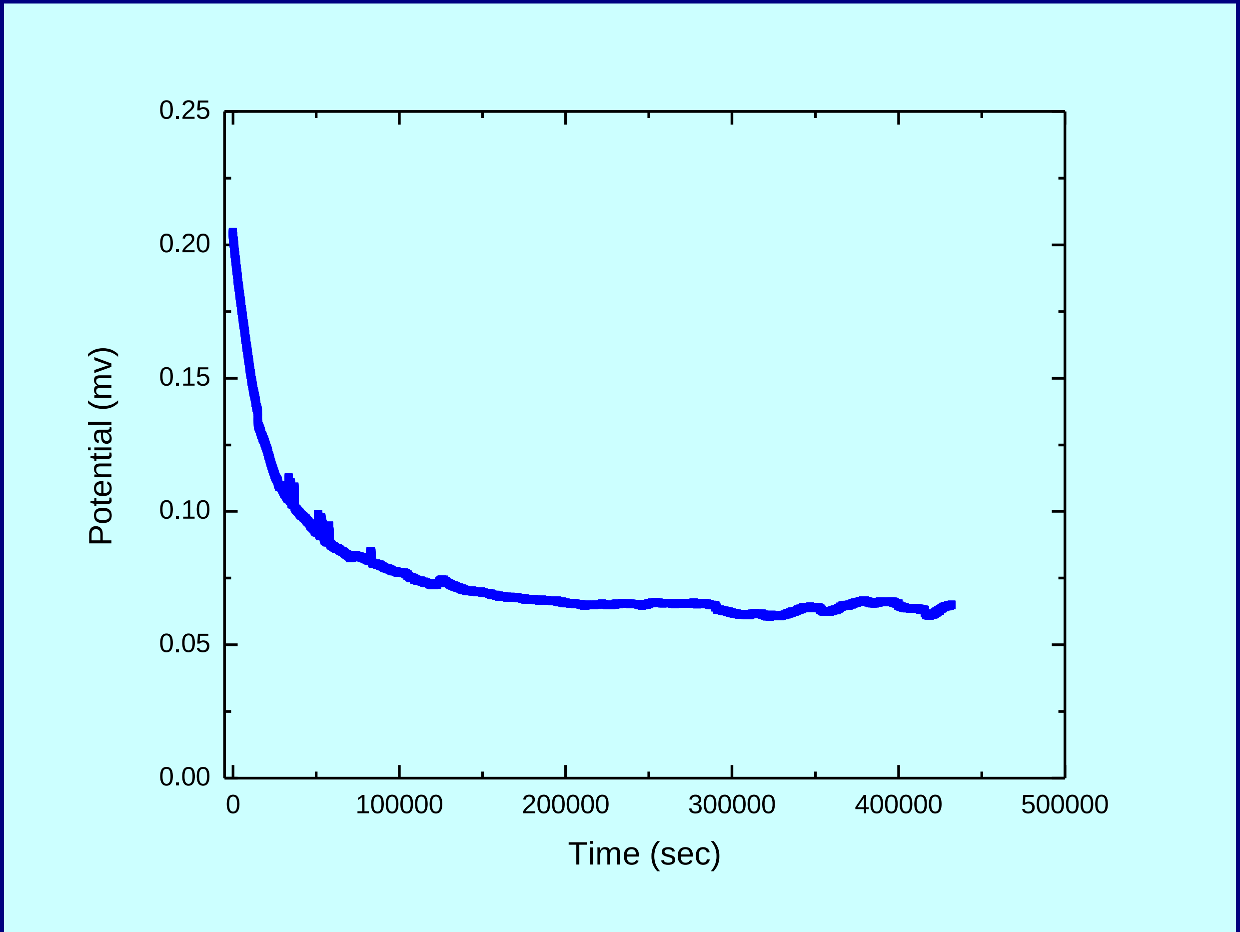


Ag/Ag^+/Fused-Quartz Reference Electrode

Stability
Reproducibility
Reusability



Time Dependency of the Potential of Ag/Ag^+/fused-quartz Reference Electrode in Synthesis Coal Ash Mixture at 800 °C



Project Milestone Status

October to December 2011

- Construction of custom-designed coal ash exposure unit for lab-scale corrosion experiments has been completed in WVU.

Laboratory Test Configuration

Project Milestone Status

January to March 2012

- Coal ash corrosion behaviour of nickel- based Superalloy IN740-1 in synthetic coal ash mixture at 800 °C as a function of exposure time

Corrosion in Coal-Fired Boilers

In the Upper Furnace

Higher Steam Temperature and Pressure
Deposit-induced Liquid Phase Corrosion

↓

Coal Ash Corrosion in Superheater/Reheater alloys

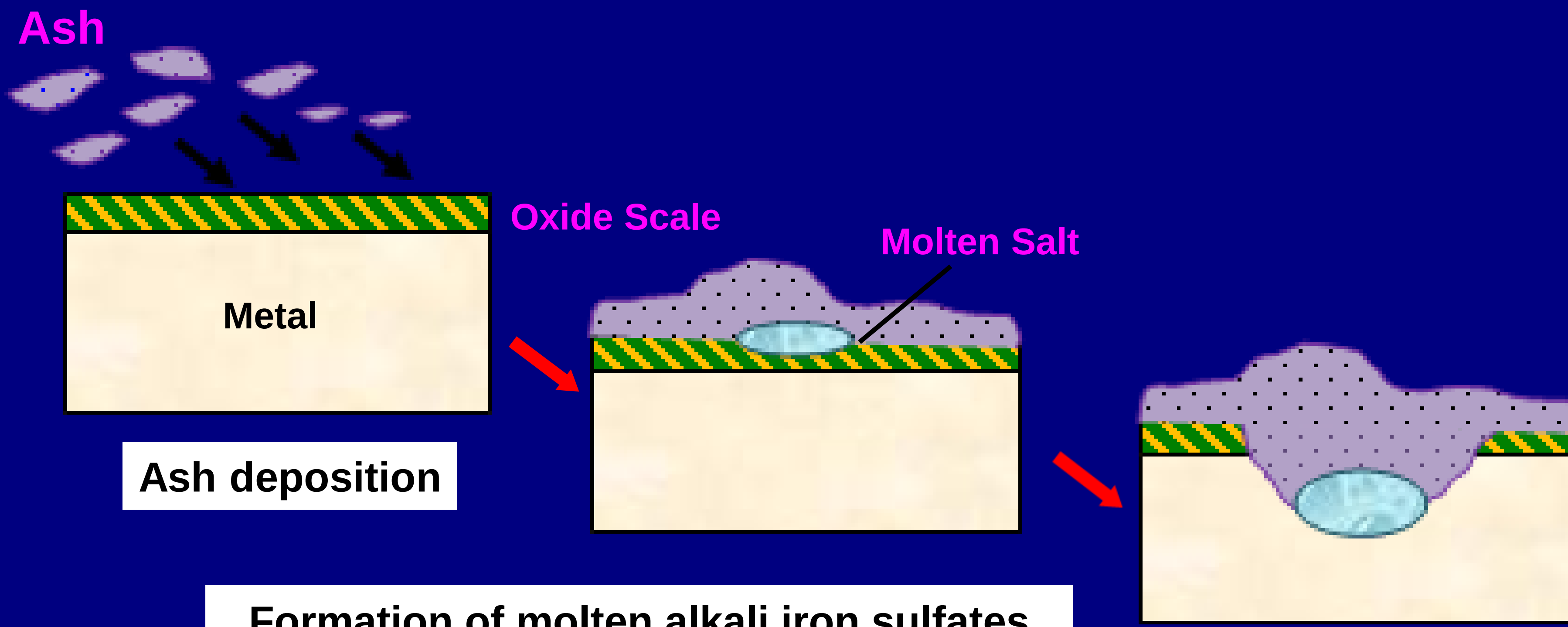
In the Lower Furnace

Low-NO_X combustion produces H_2S in the flue gas and FeS in the deposit due to incomplete combustion of the sulfur-bearing species in coal

↓

Furnace Wall Corrosion on Waterwalls of the Boiler Tubes

Coal Ash Corrosion Mechanism



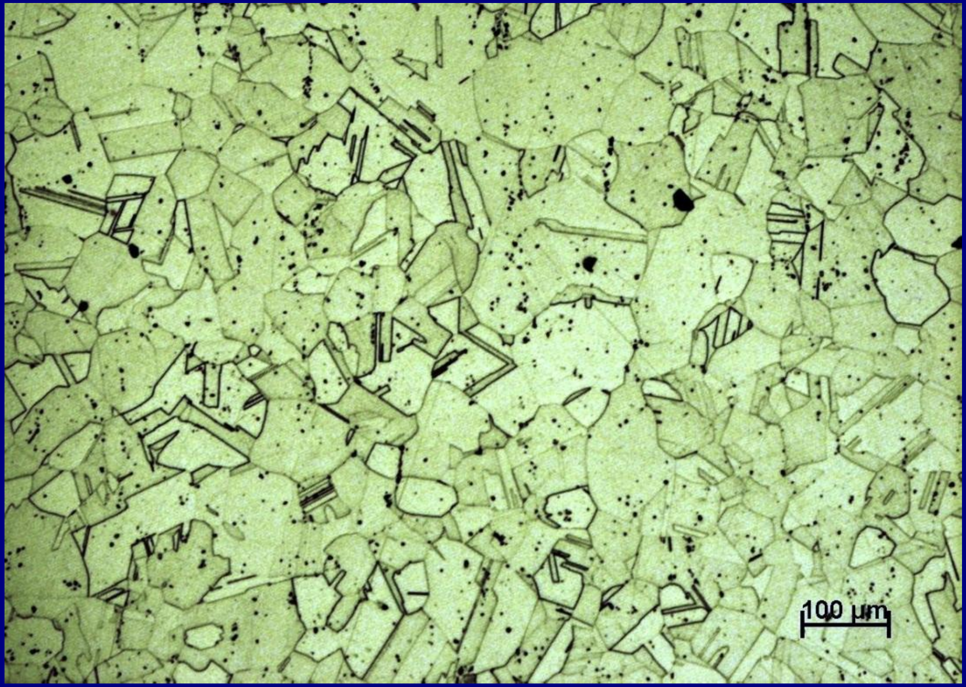
Ash deposition

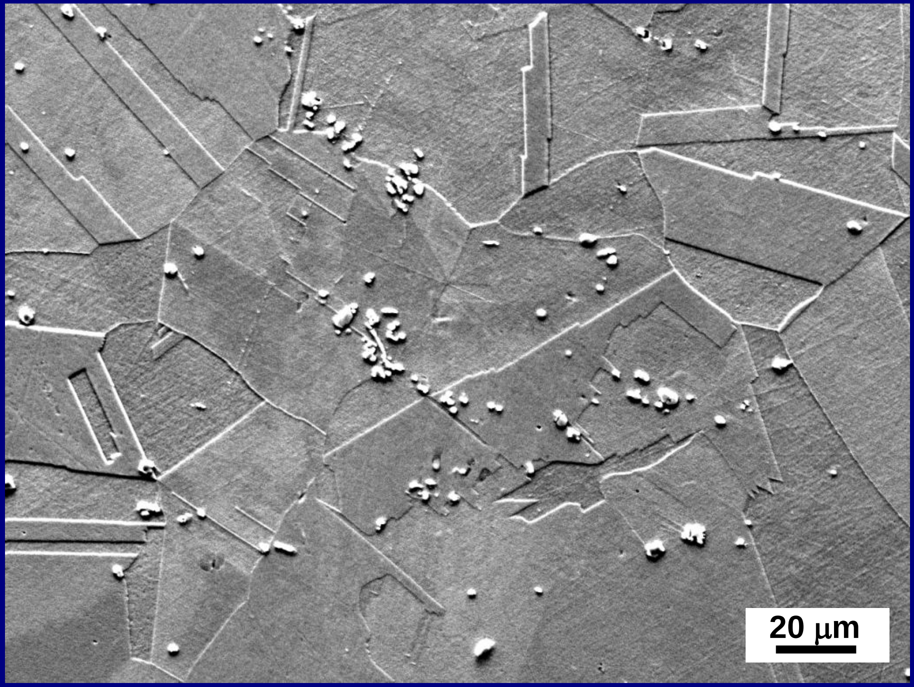
Formation of molten alkali iron sulfates
$(Na, K)_3Fe(SO_4)_3$
and fluxing away of protective oxide film

Direct reaction between bare metal and reduced sulphate species

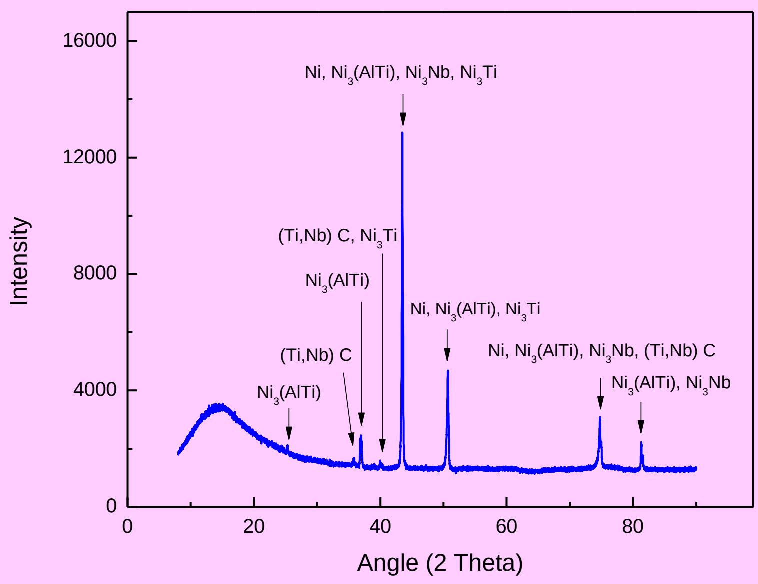
IN 740-1 Ni-Base Superalloy

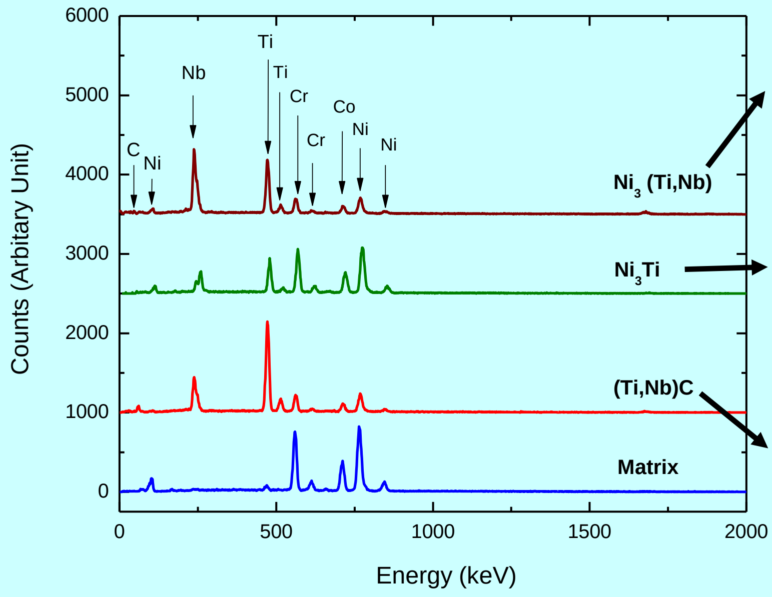
Ni	Cr	Fe	Cu	Co	Mo	Nb	Al	Mn	Ta	Ti	W	Si	C	Sn
35–80	5–25	<42	<35	<30	<17	<6	<5	<5	<5	<5	<5	<1	0	0

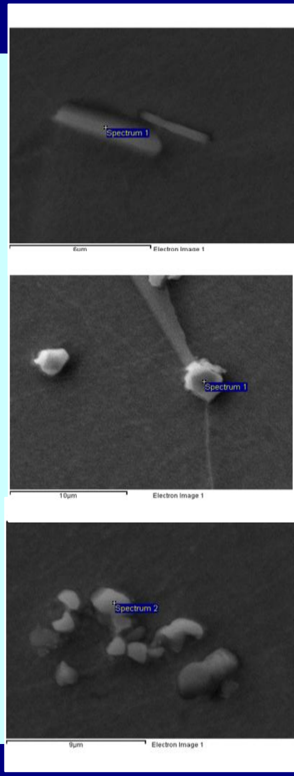




Intermetallic Phases in IN 740-1 Ni-Base Superalloy







Corrosive Media
For Coal Ash Corrosion

Synthetic Flue Gas

$15\ CO_2 + 4\ O_2 + 1SO_2 + 80\ N_2$

Coal Ash Mixture

Ash+10% Alkali Sulfates+1% NaCl

mp=800 °C

Ash - SiO_2, Al_2O_3, and Fe_2O_3 in the ratio of 1:1:1 by weight

mp=1600 °C mp=2027 °C mp=1566 °C

Alkali sulfate mixture - Na_2SO_4 and K_2SO_4 in the ratio of 1:1 by weight

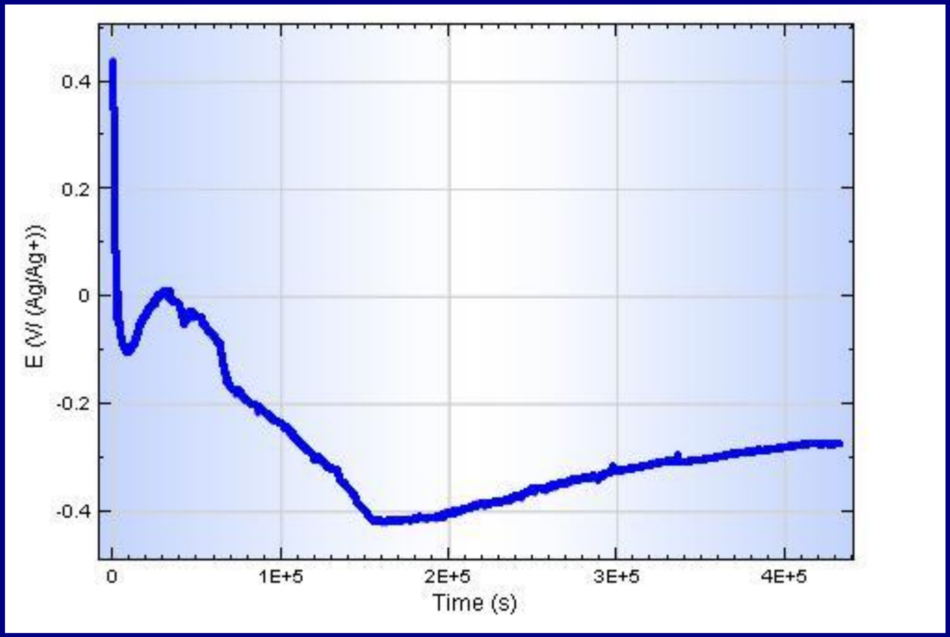
mp= 880 °C mp= 1067 °C

Electrochemical Techniques Used to Study Corrosion

- Open Circuit Potential (OCP) Measurement
- Linear Polarization Resistance (LPR)
- Electrochemical Impedance Spectroscopy (EIS)
- Electrochemical Noise Analysis (ENA)

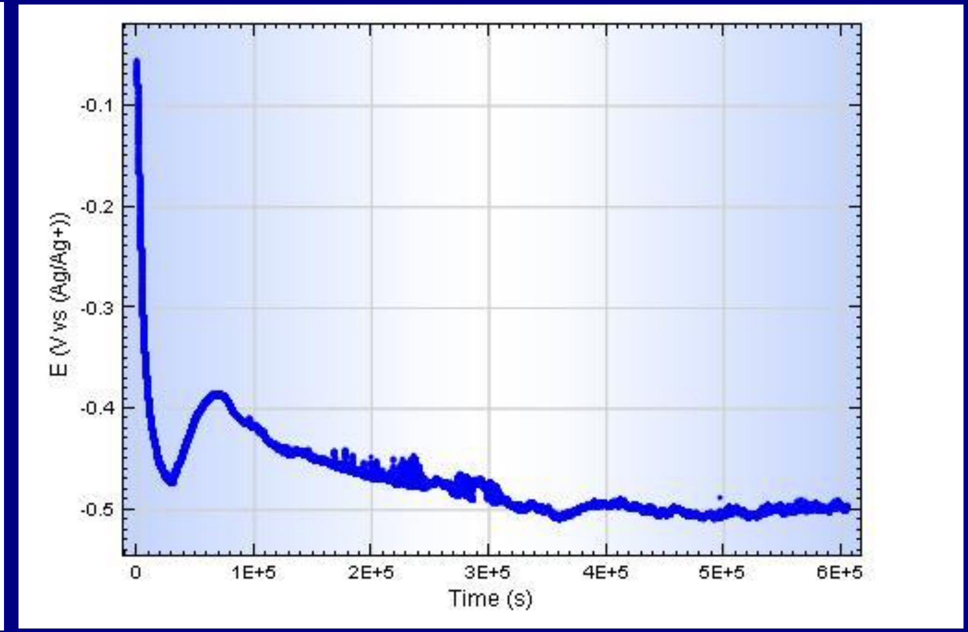
OCP for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

Without Synthetic Flue Gas



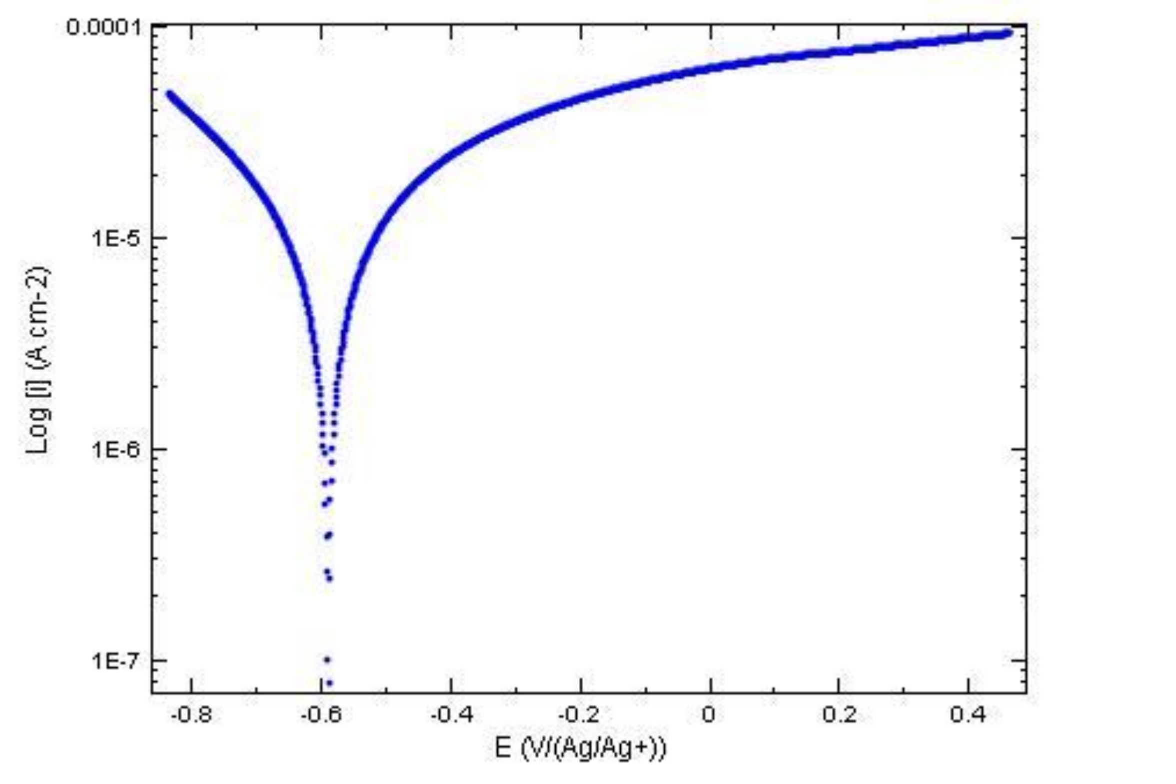
OCP = - 274 mV vs. Ag/Ag^+

With Synthetic Flue Gas



OCP = -497 mV vs. Ag/Ag^+

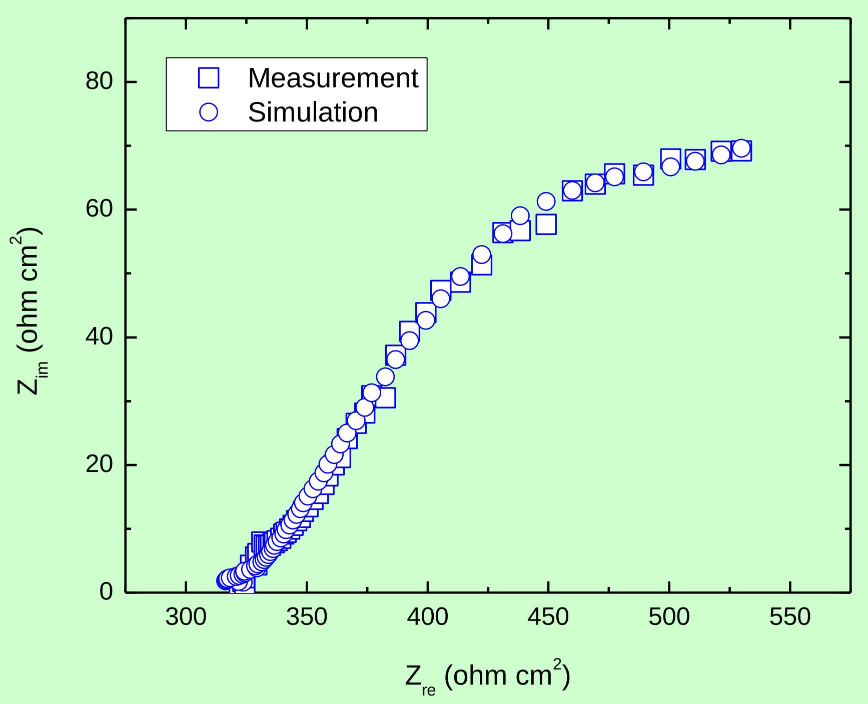
E_{corr} and I_{corr} Values for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

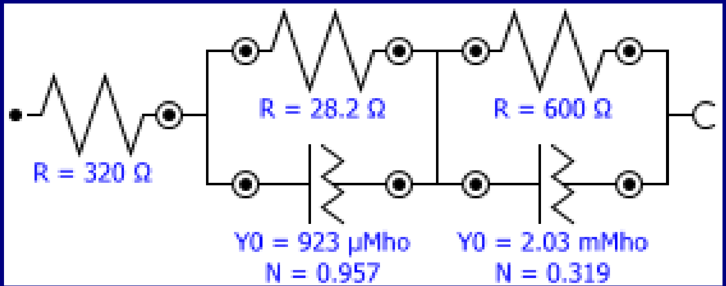


OCP (mV vs. Ag/Ag^+)	E_{corr} (mV vs. Ag/Ag^+)	i_{corr} ($\mu A\ cm^{-2}$)	β_a $mV\ dec^{-1}$	β_c $mV\ dec^{-1}$	Corrosion rate ($mm\ y^{-1}$)
-538	-592	4.71	198	217	0.11

Electrochemical Impedance for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

After 2 h

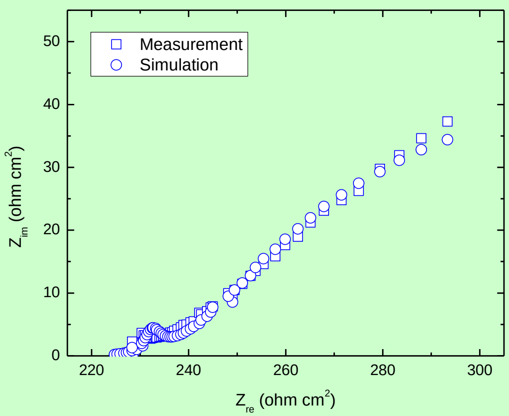


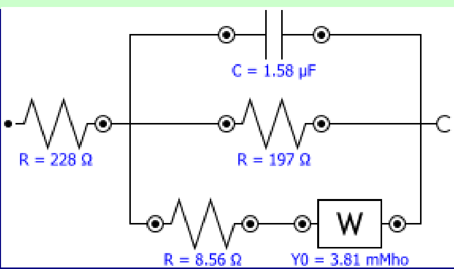


The transport of the oxygen to the alloy surface and the formation of a oxide scale

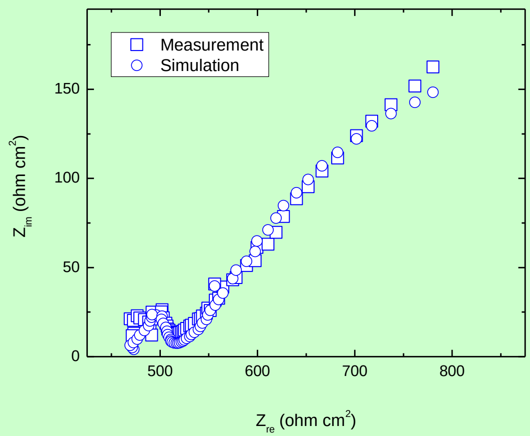
Electrochemical Impedance for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

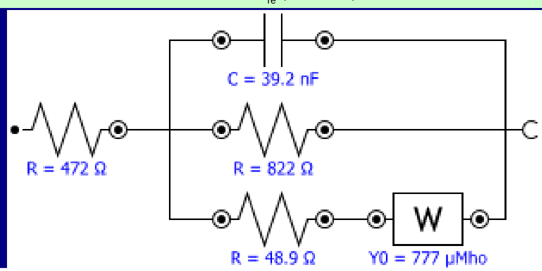
After 24 h



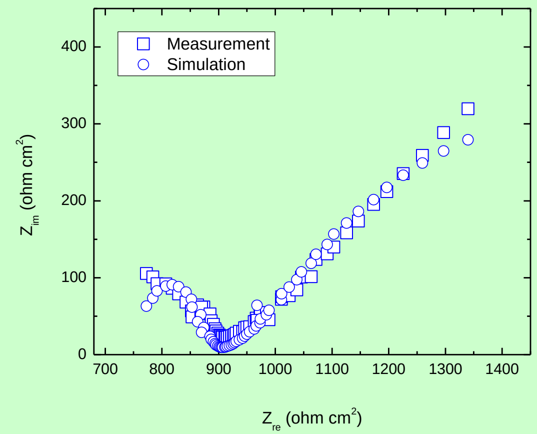


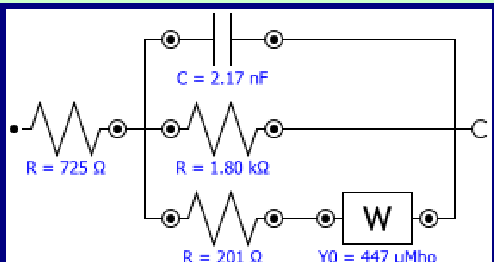
After 48 h





After 72 h





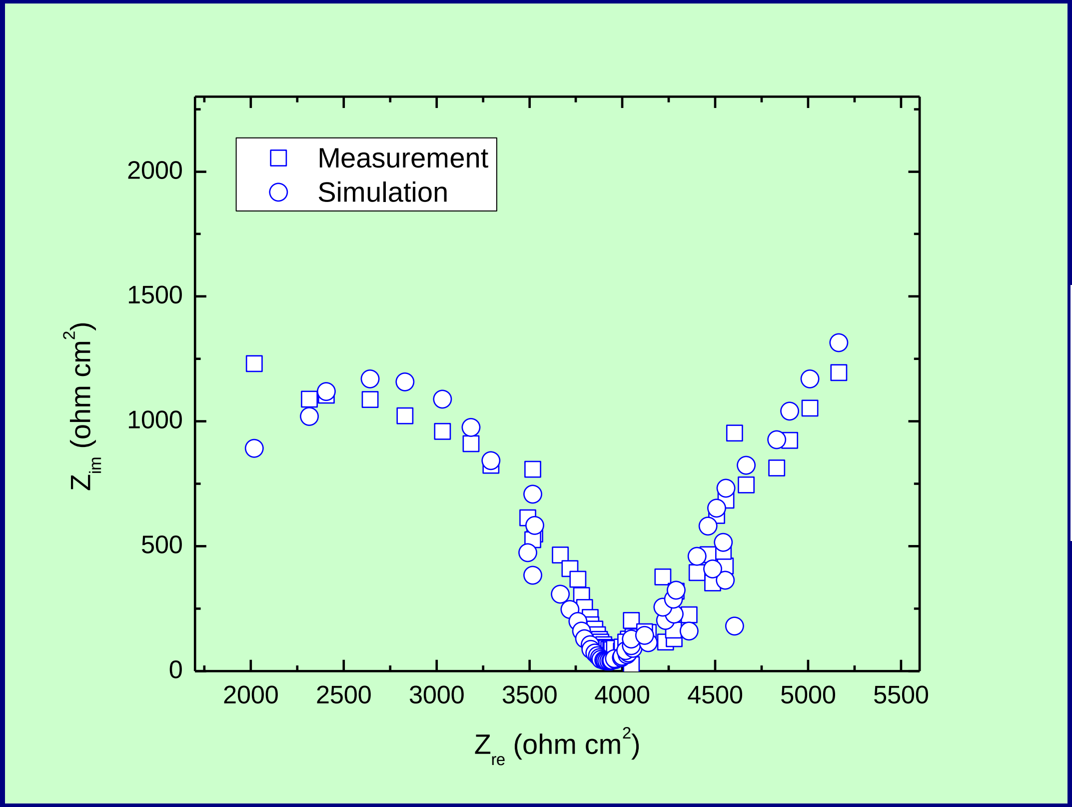
$$\vec{Z}(\omega) = \left\{\frac{1}{Y_0\sqrt{j\omega}}\right\} \tanh\left[B\sqrt{j\omega}\right] \qquad \vec{Y}(\omega) = \left\{Y_0\sqrt{j\omega}\right\} \coth\left[B\sqrt{j\omega}\right]$$

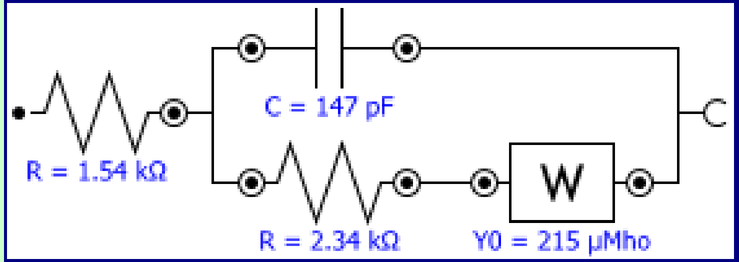
$$Z = A(i\omega)^{-\alpha}$$

Forming a porous scale in molten salts and the corrosion of the alloy is controlled by diffusion of the oxidant in the melt

Electrochemical Impedance for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

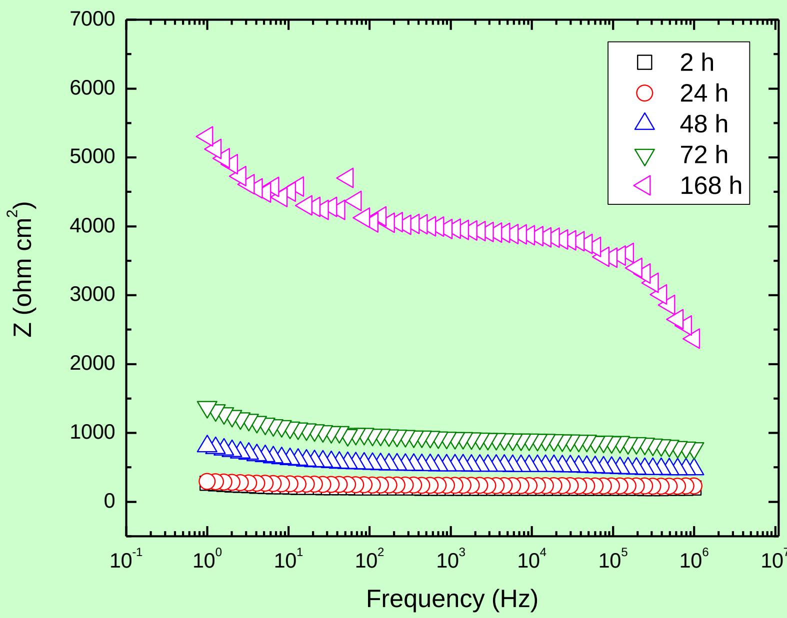
After 168 h

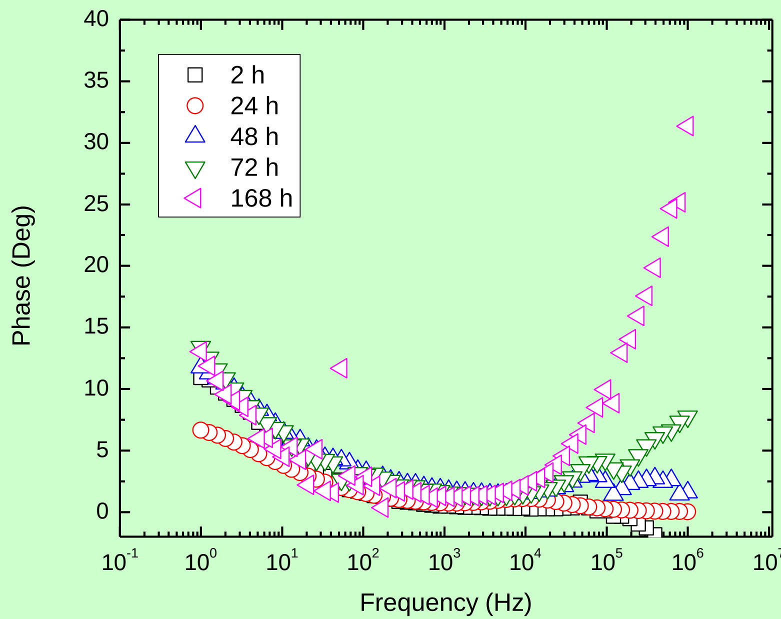




The corrosion of the alloy is controlled by diffusion of the ions through the scale after forming a compact scale

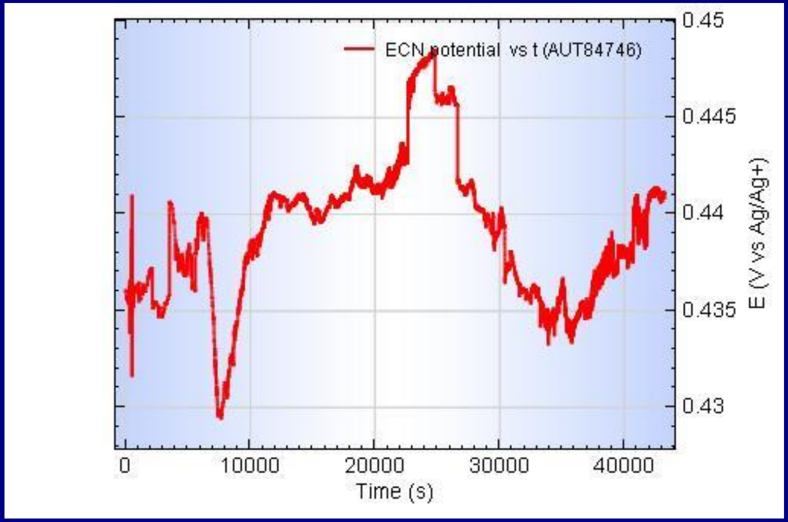
Bode Plots for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C



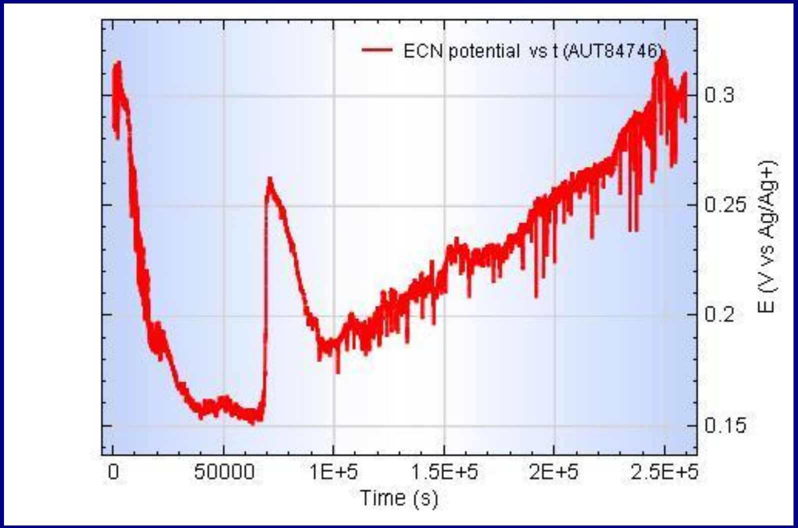


Typical Potential Noise Signatures from Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

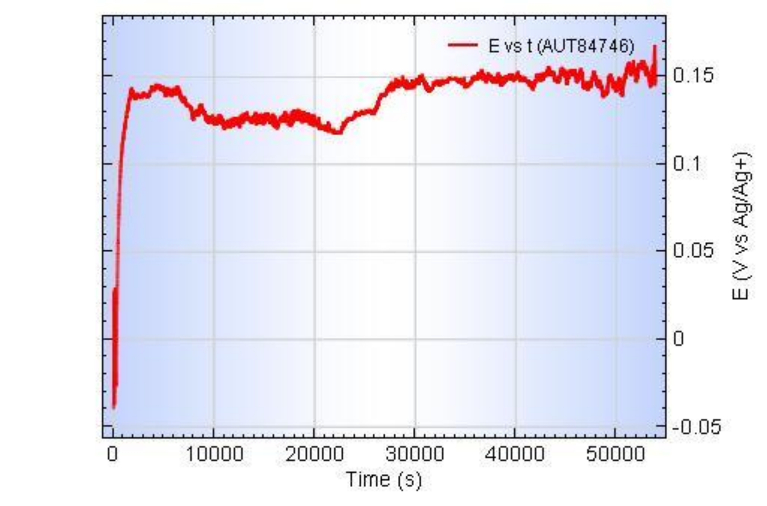
After 24 h



After 72 h

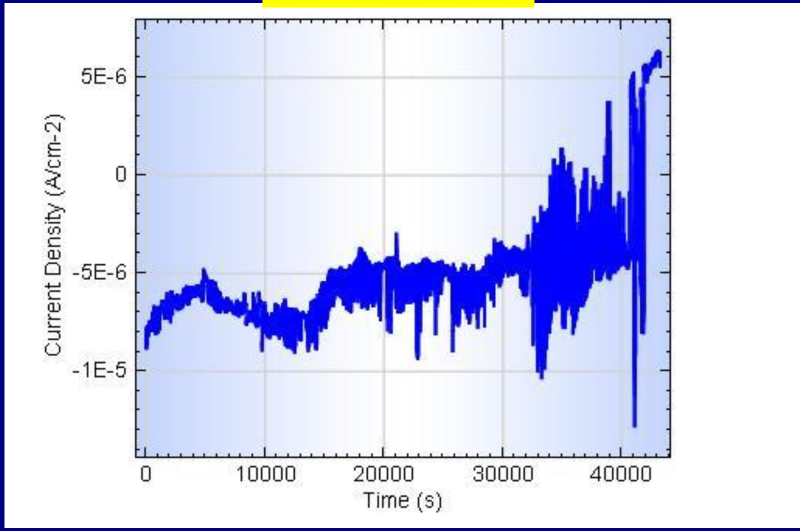


After 168 h

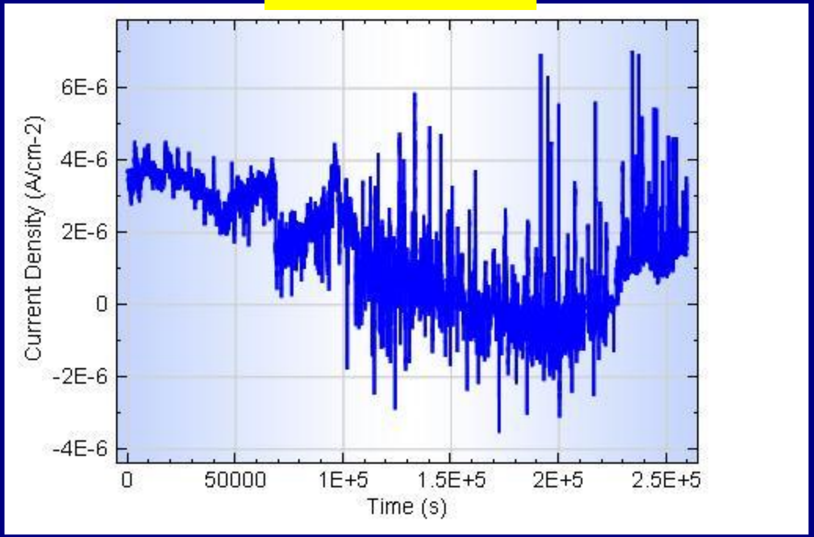


Typical Current Noise Signatures from Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

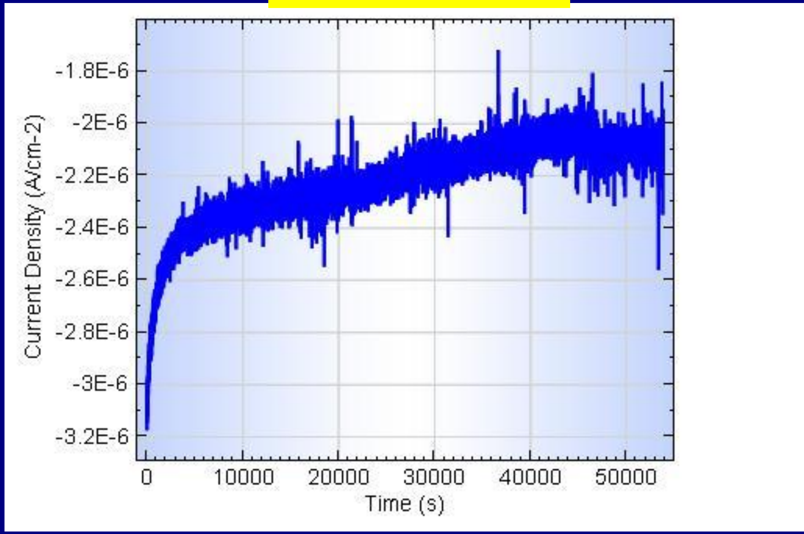
After 24 h



After 72 h

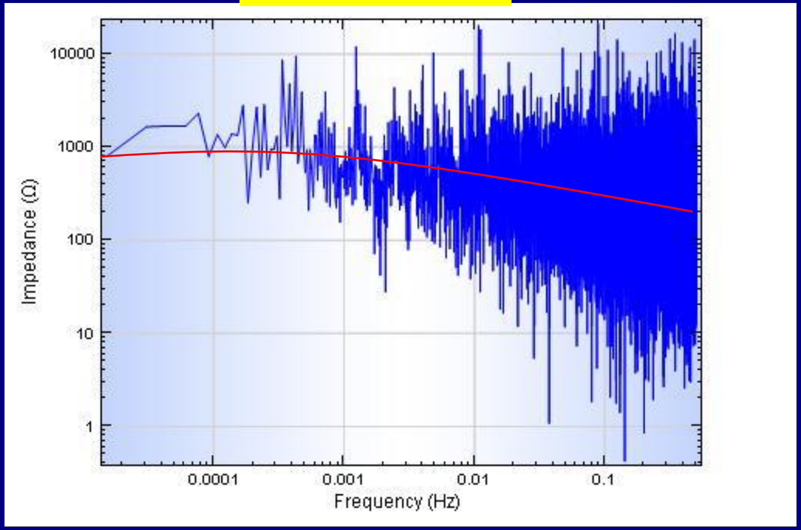


After 168 h

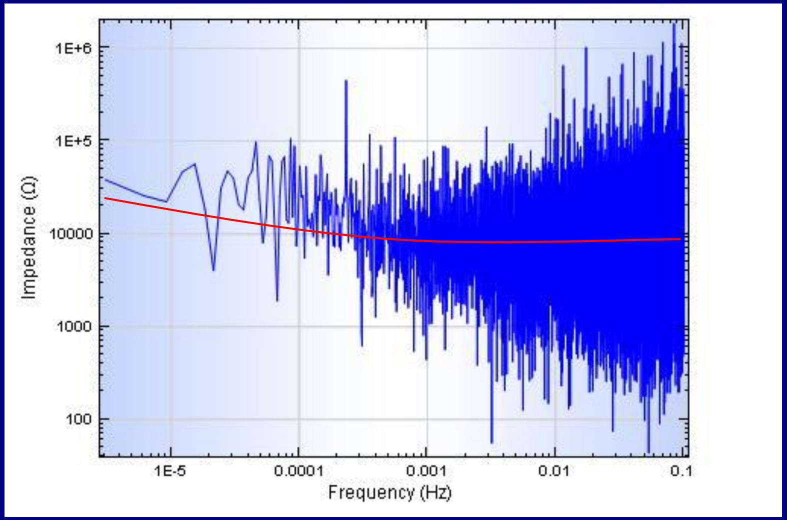


Typical Noise Impedance from Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

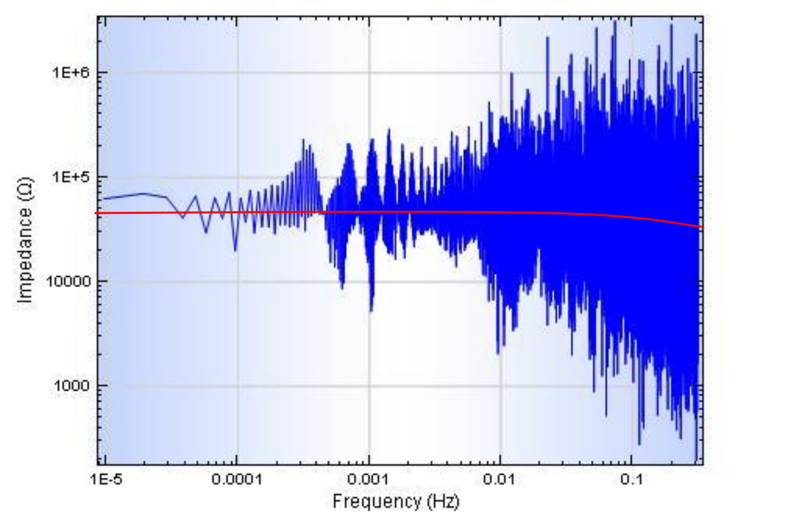
After 24 h



After 72 h



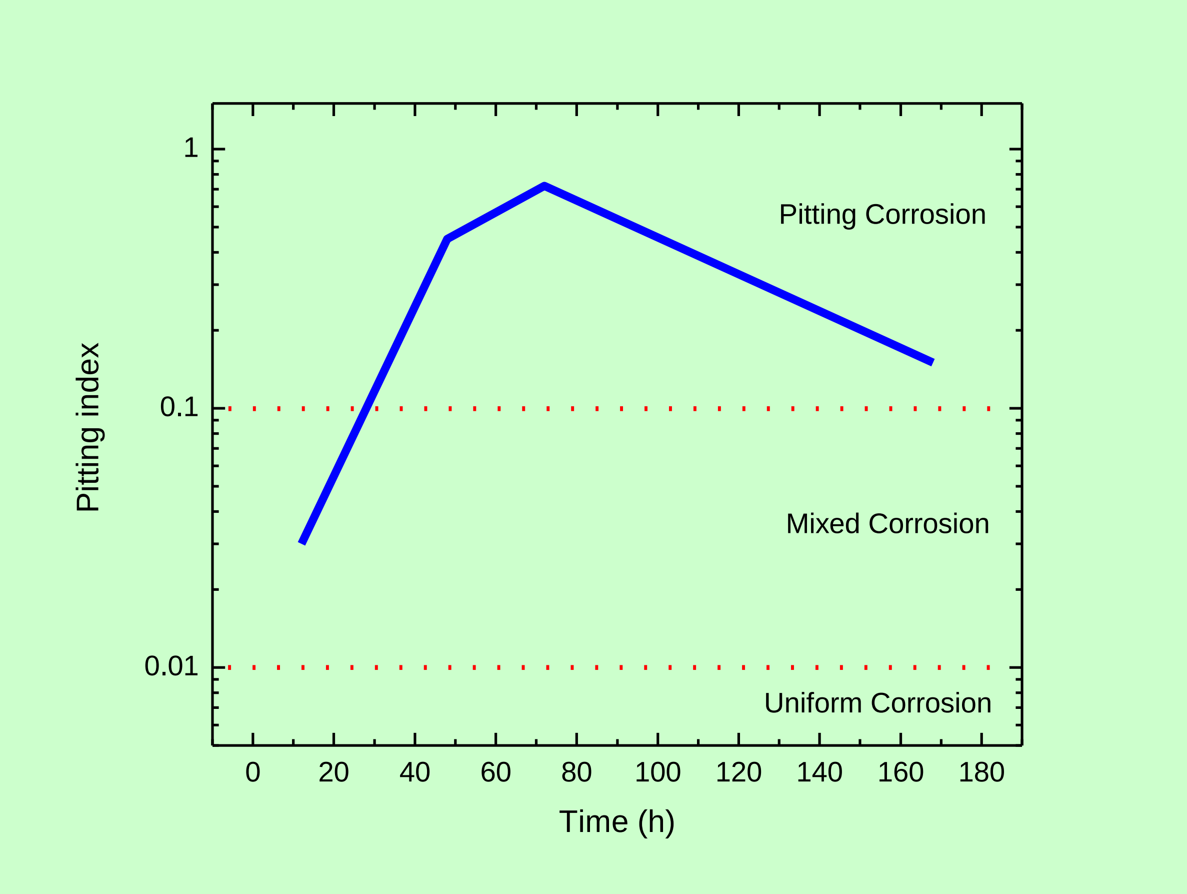
After 168 h



Noise Resistance for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

	Exposure Time (h)	Noise Resistance (R_n) (kΩ)
Pit initiation	24	1.46
Pit propagation	72	30.13
Stable pit formation	168	112.183

Pitting Index for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C



PI = 0 , the individual current x_i show only small deviations from the mean value of current

PI = 1 , x_i >> than the mean value of current

Stern-Geary Linear Approximation

$$R_p = R_n = \frac{\Delta E}{\Delta I_{app}} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c) I_{corr}} = \frac{B}{I_{corr}}$$

Rp = Resistance obtained from the LPR and EIS techniques

Rn = Resistance obtained from the EN

B = Stern-Geary constant

βa = Anodic Tafel constant

βc = Cathodic Tafel constant

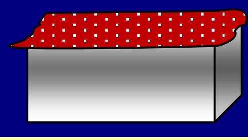
Icorr = Corrosion current density

$$\text{Corrosion rate (mm y}^{-1}\text{)} = \frac{3.28M}{n\rho} i_{corr}$$

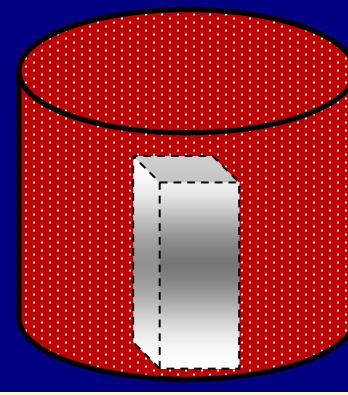
n = Number of electrons freed by the corrosion reaction

M = Atomic mass

Weight Loss Measurement



For thin coal ash film corrosion



For deep molten coal ash corrosion

$$\text{Corrosion rate (mm y}^{-1}\text{)} = \frac{1}{0.274 \times \rho}\left[\frac{(W_b - W_a - B) \times 10}{At}\right]$$

W_b = Weight of test sample before test, g

W_a = Weight of test sample after test, g

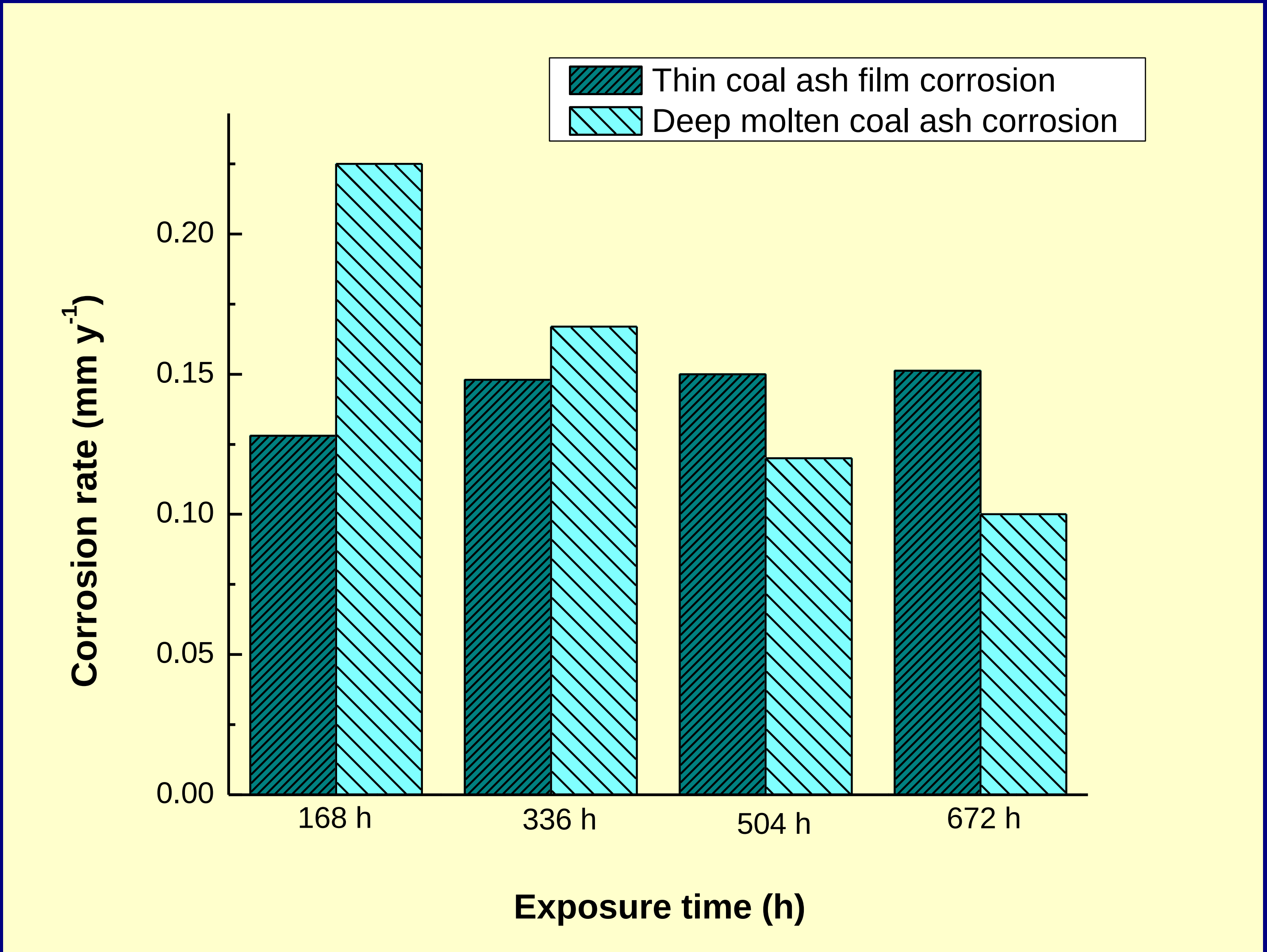
B = Weight loss of blank, g (the average weight loss from 3 unused and clean sample was used as the blank correction)

A = Surface area of sample, cm^2

t = Exposure time, day

ρ = Density of alloy

Weight Loss Rates for Deep Molten Coal Ash Corrosion and Thin Coal Ash film Corrosion of IN740-1 Alloy at 800 °C



Corroded Surfaces for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

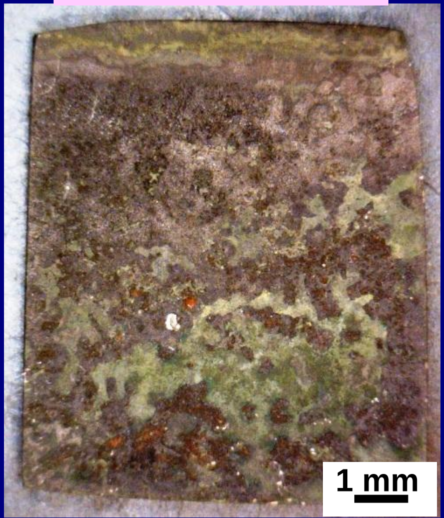
Before Corrosion

Without Synthetic Flue Gas

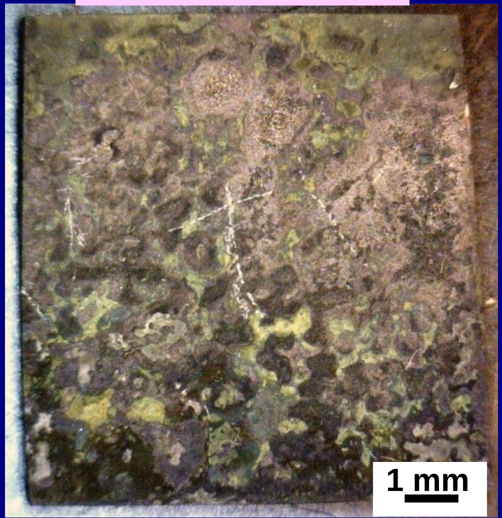
After 1 weeks

After 2 weeks

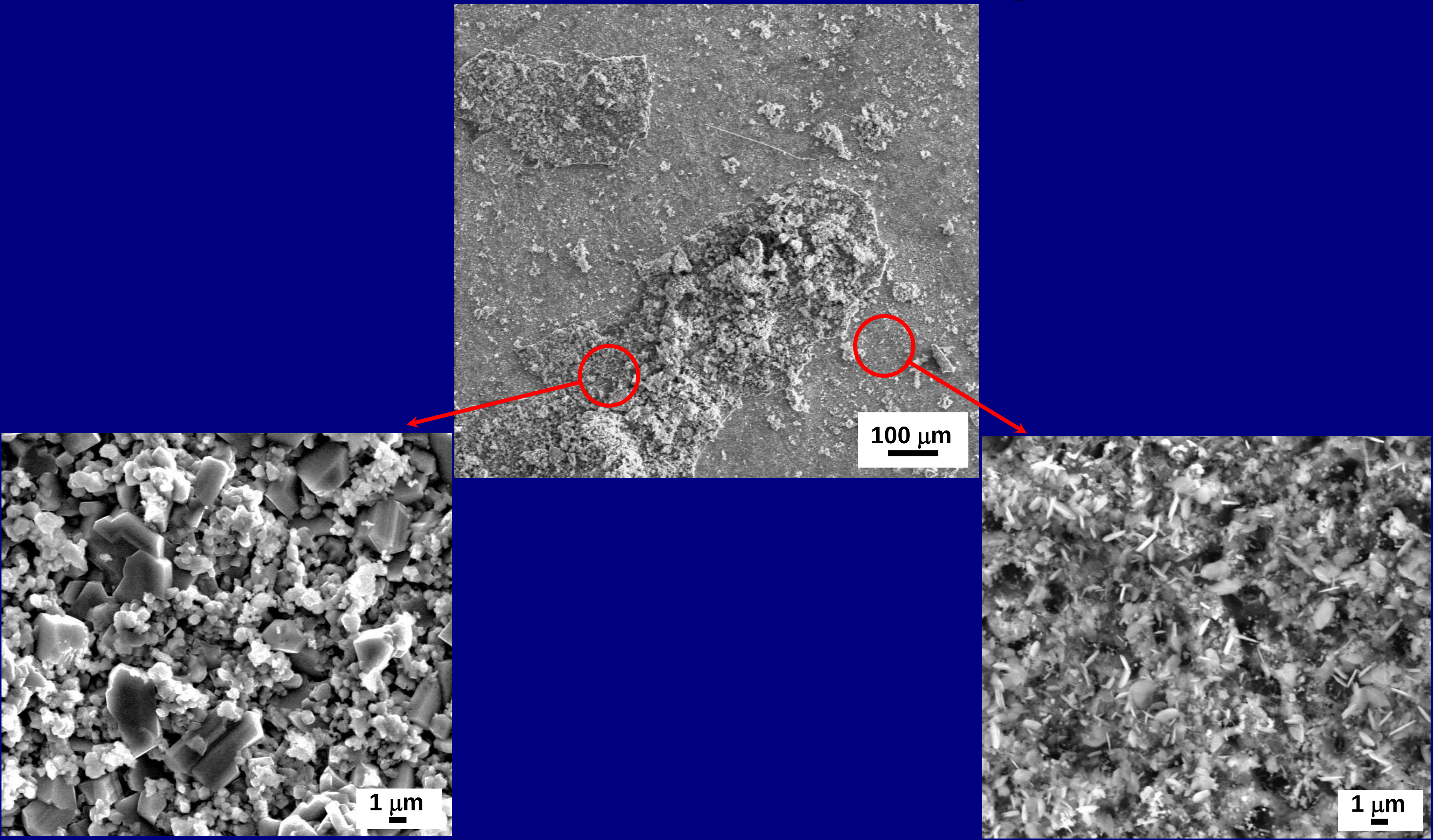
After 3 weeks



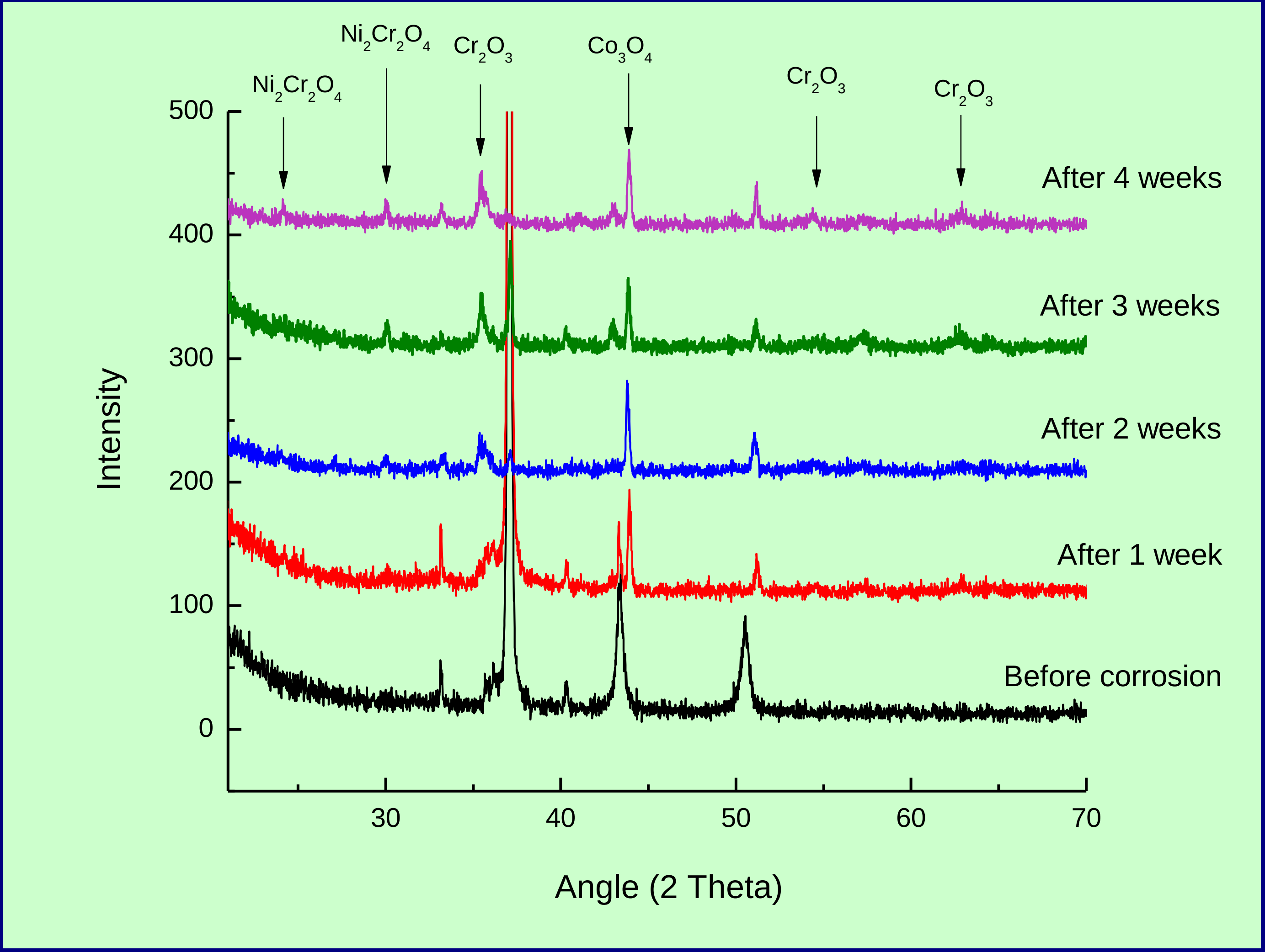
After 4 weeks



Oxide Layer Formation on Corroded Surfaces for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C



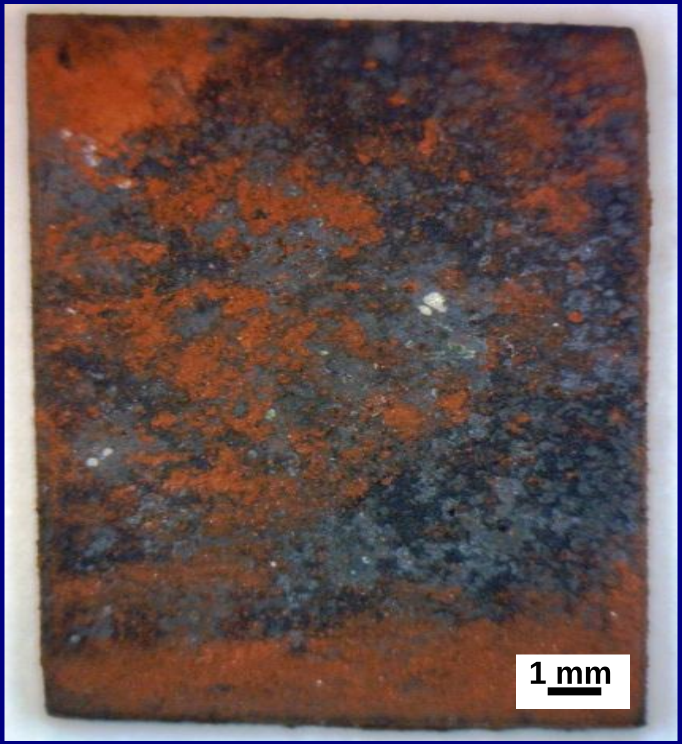
Oxides Formation on Corroded Surfaces for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C



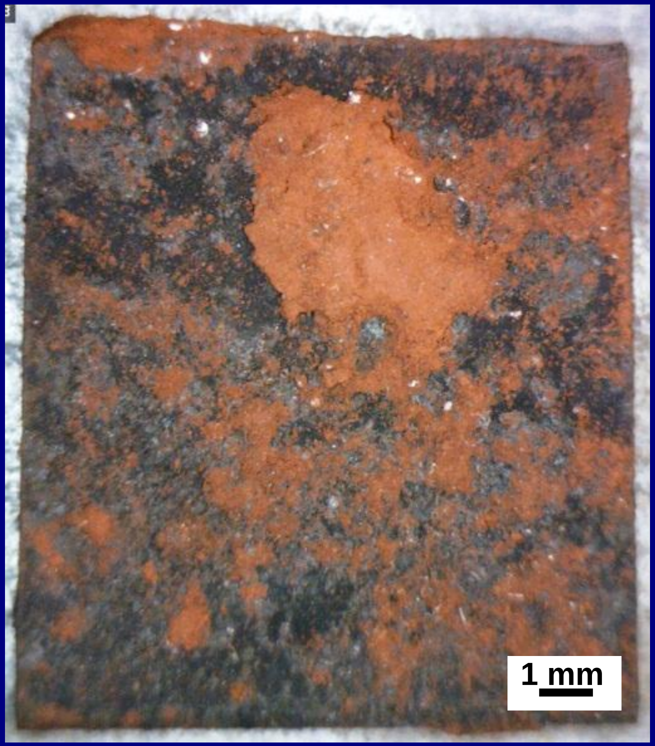
Corroded Surfaces for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

With Synthetic Flue Gas

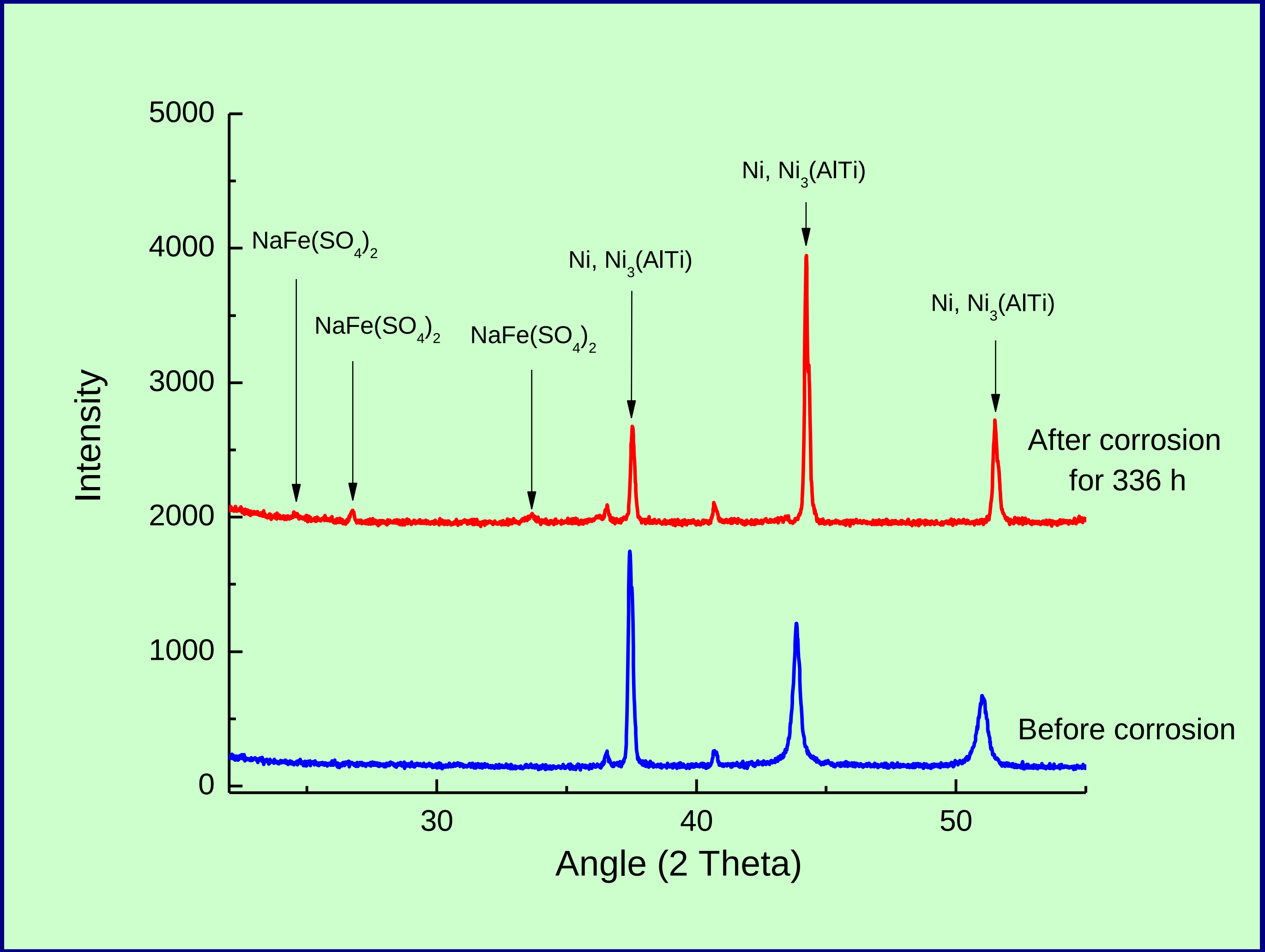
After 1 weeks



After 2 weeks



Molten Alkali Iron Sulfate Formation During Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

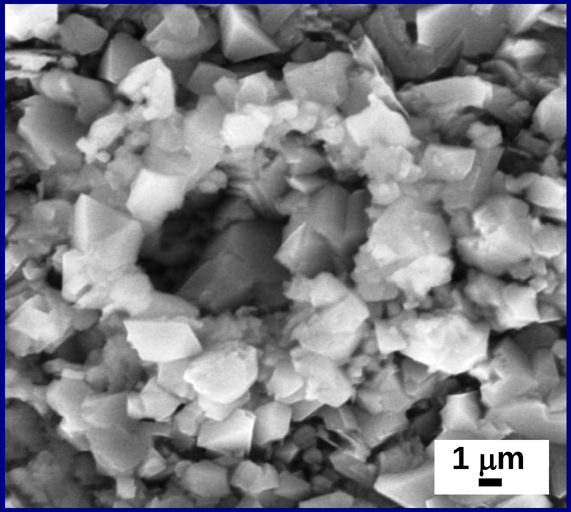


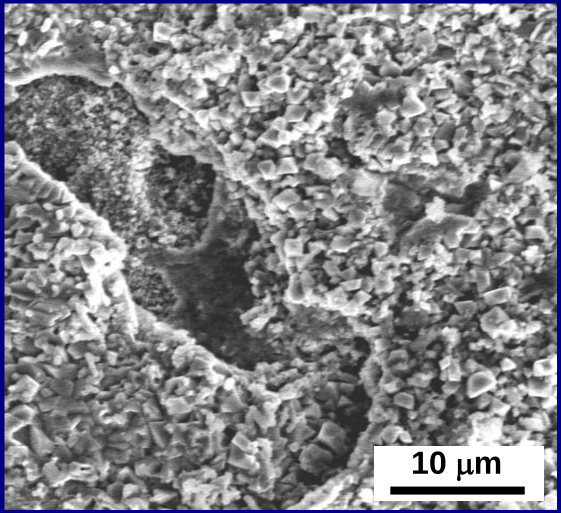
Pits Formation on Corroded Surfaces for Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C

After 1 week

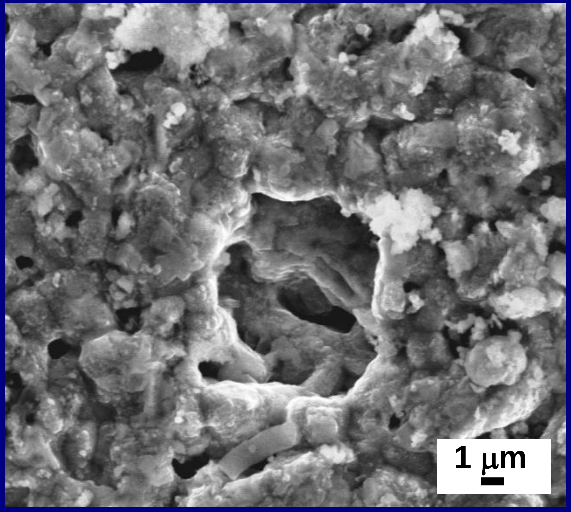
After 2 weeks

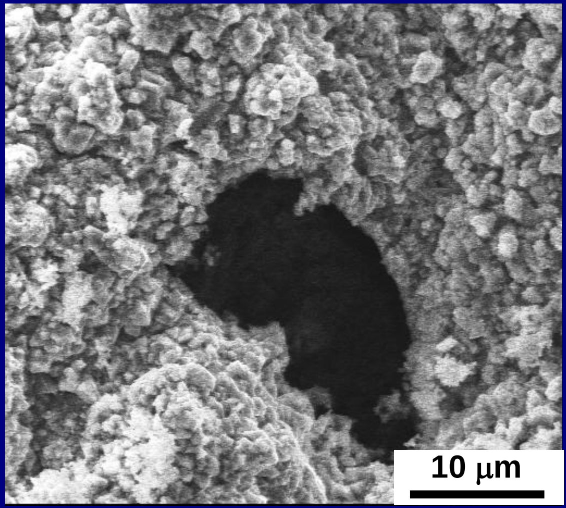
Without Synthetic Flue Gas



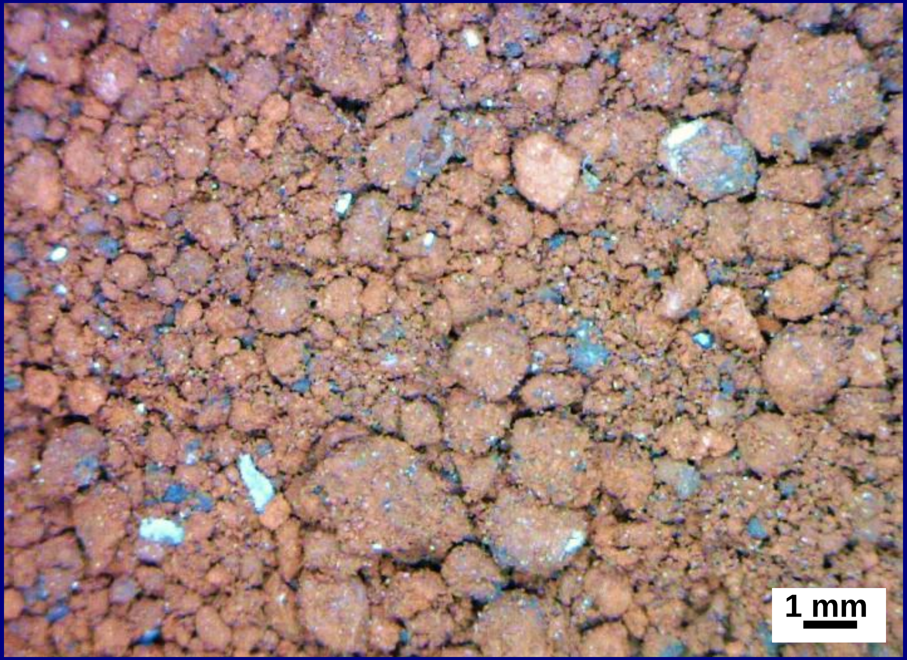


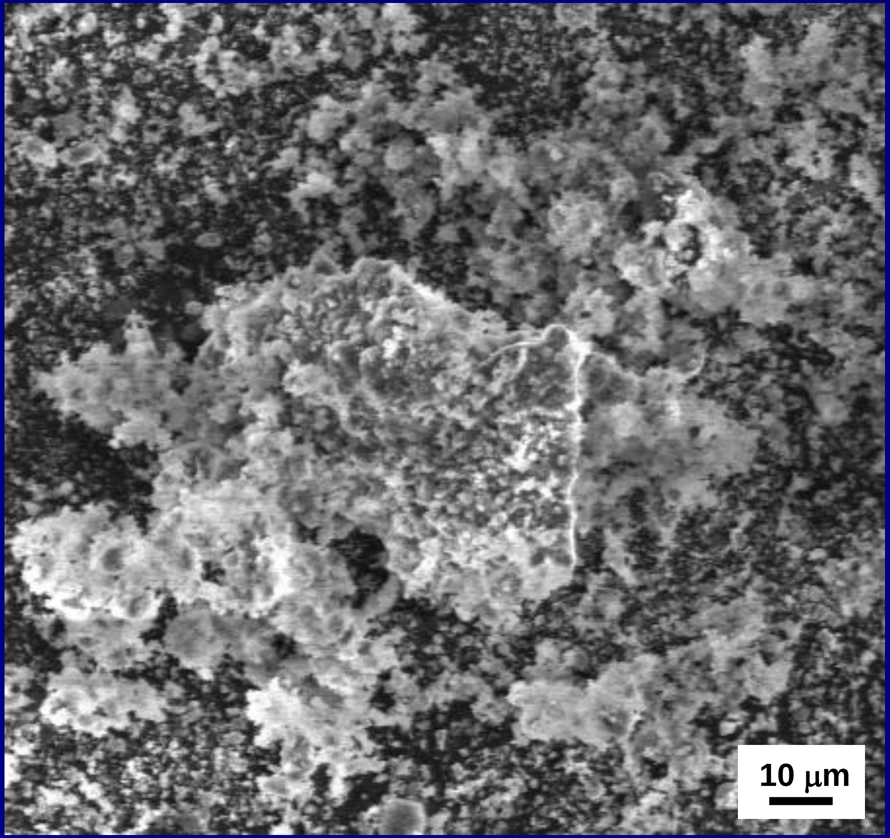
With Synthetic Flue Gas





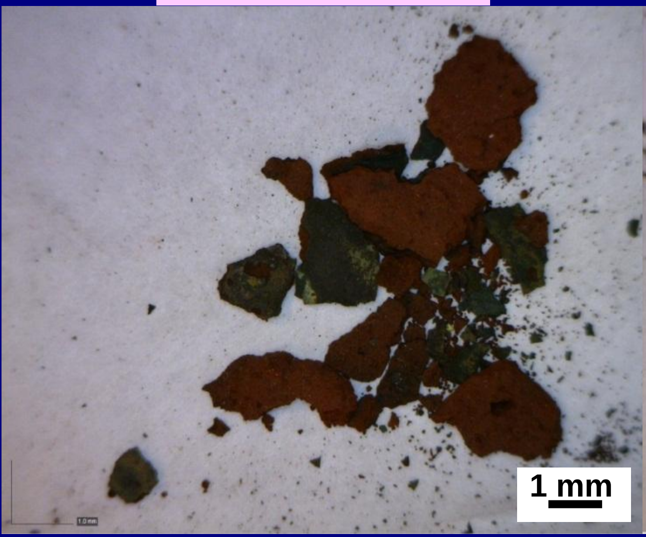
Corrosion Products in Coal Ash from Deep Molten Coal Ash Corrosion of IN740-1 Alloy at 800 °C



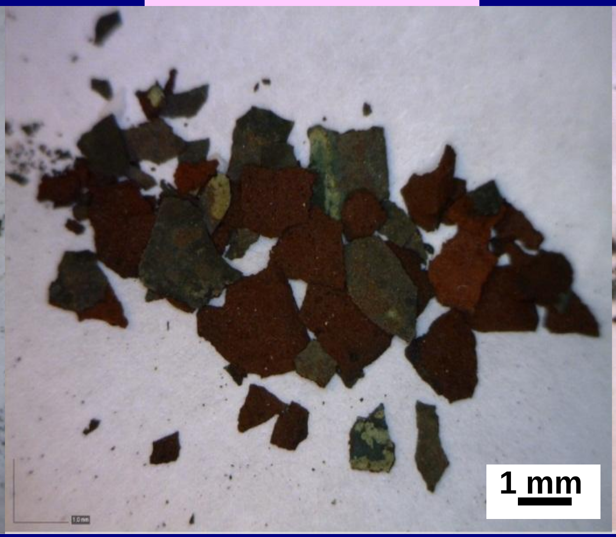


Corrosion Products in Coal Ash from Thin Coal Ash Film Corrosion of IN740-1 Alloy at 800 °C

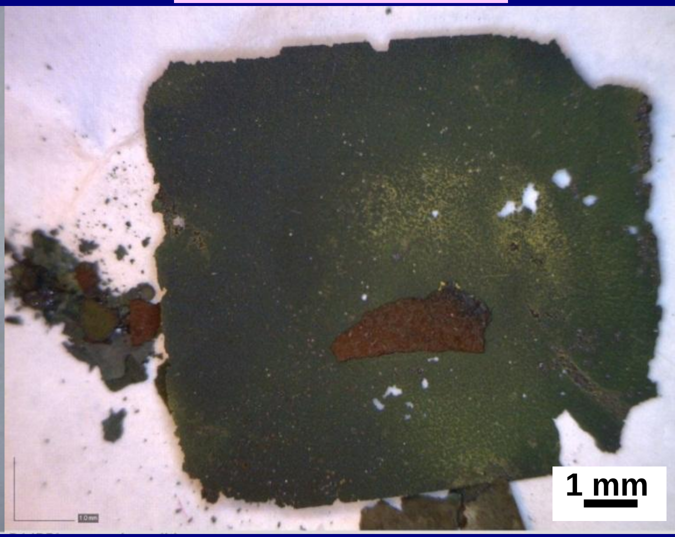
After 2 weeks

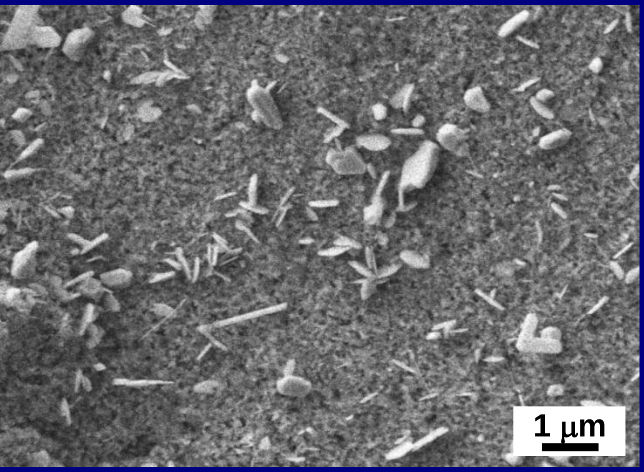


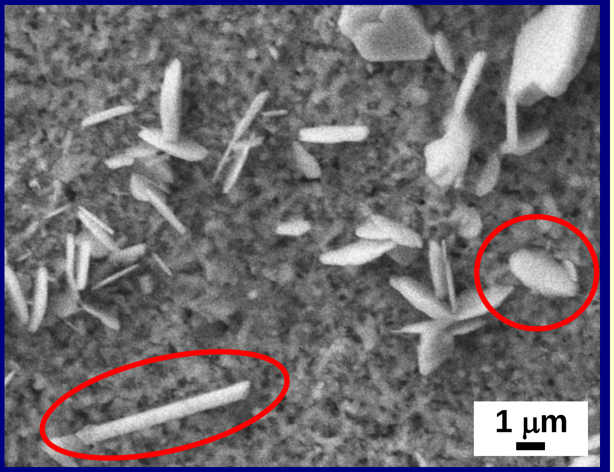
After 3 weeks

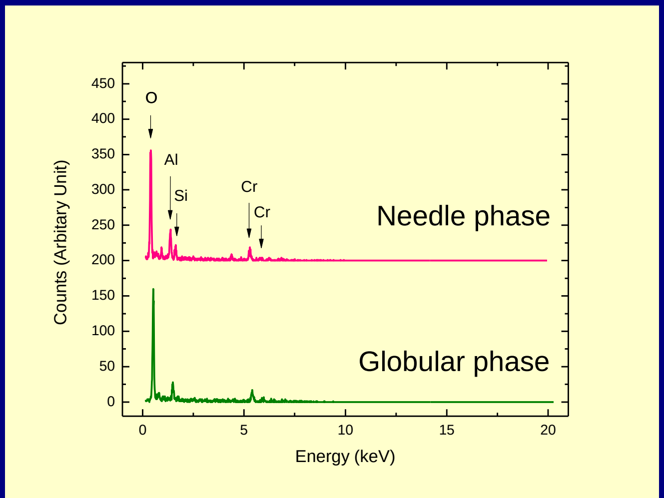


After 4 weeks









Coal Ash Corrosion Mechanism

Initiation Stage

The transport of the oxygen to the alloy surface and the formation of an oxide scale

↓

Propagation Stage

Formation of porous scale in molten salts and corrosion is controlled by soluble diffusion of the oxidant in the melt

↓

Stabilization Stage

Corrosion is controlled by diffusion of the ions through the scale after forming a compact scale

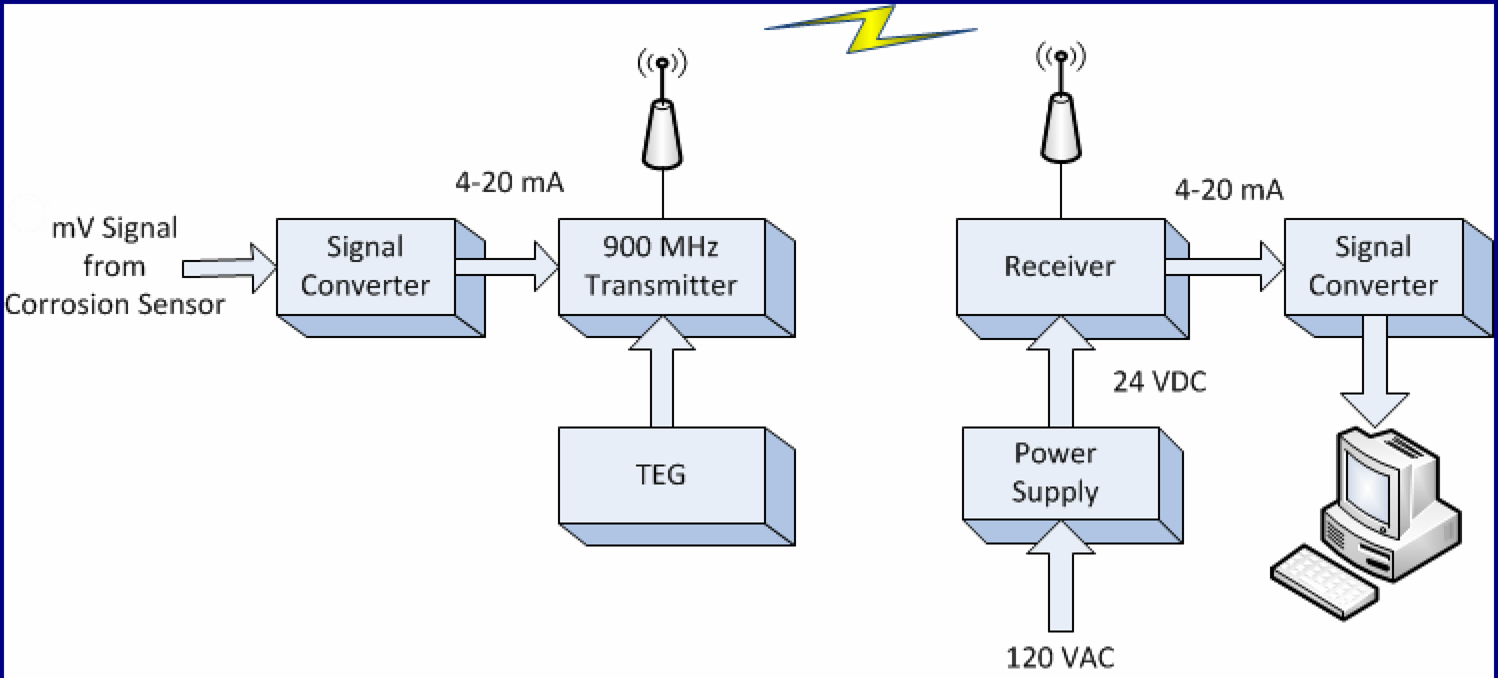
Conclusions

- The preliminary results suggest that the developed high temperature corrosion sensor allows accurate analysis of the sample material via several electrochemical techniques.

- Electrochemical and weight loss measurements show that corrosion of IN740-1 alloy in synthesis coal ash mixture at 800 °C was due to localized or pitting corrosion behavior.

- Three different stages of deep molten coal ash corrosion of IN740-1 alloy in synthesis coal ash mixture at 800 °C have been proposed.

Self-Powered Wireless Communication



Commercially available hardware

- 1 Watt transmitter - frequency-hopping, spread spectrum technology in the 902-928 MHz ISM band
- Preliminary testing of the thermoelectric generator (TEG) shows a 5 Watt output potential when contacting a surface temperature in the 300° C to 350° C range

Completed:

- Purchased off-the-shelf TEG and wireless transmitter & receiver
- Demonstrated bench scale feasibility of TEG

Next Steps:

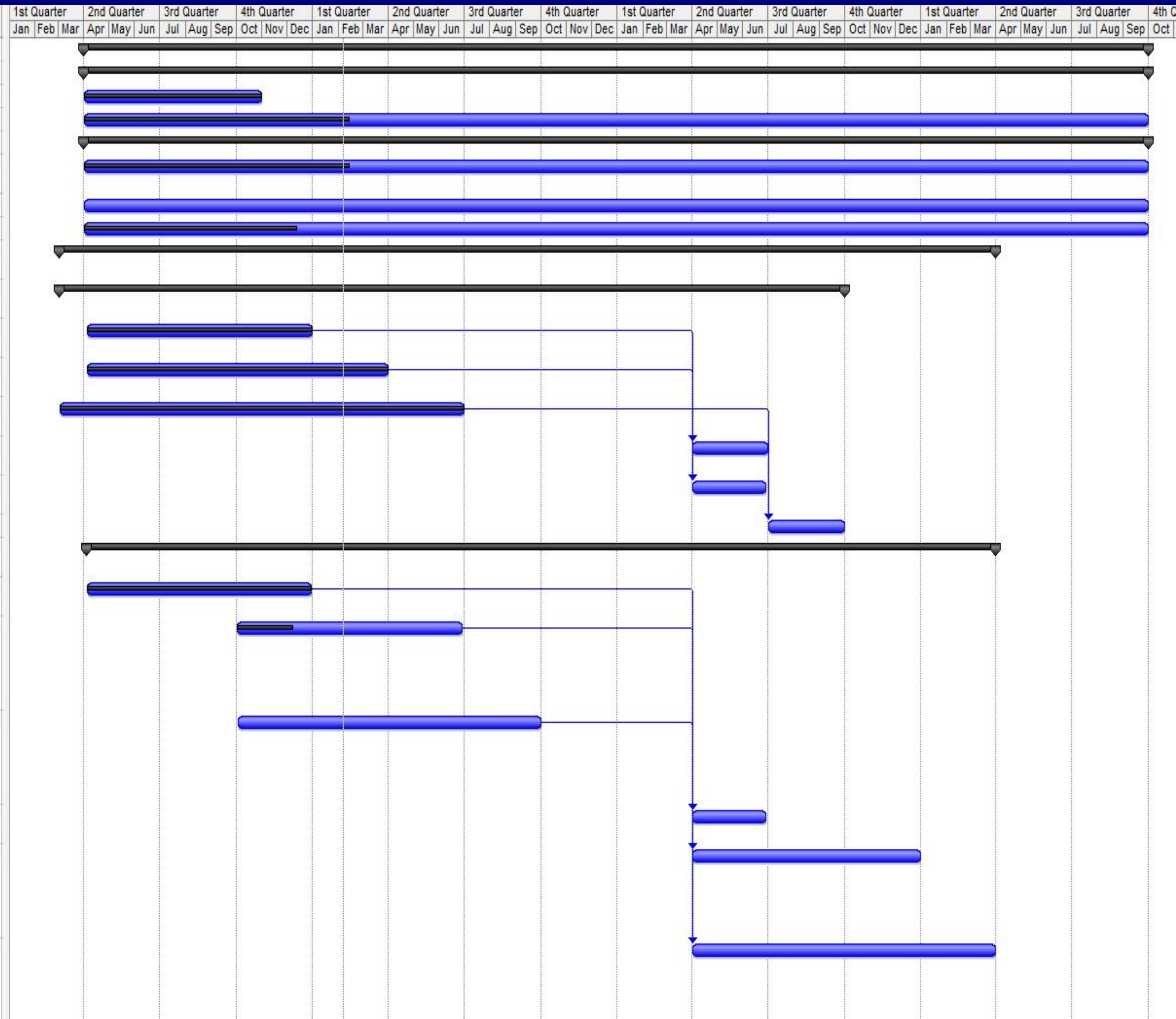
- Profile TEG power vs. temperature range
- Demonstrate wireless transmission capability with simulated signal
- Finalize specifications of signal converter for corrosion sensor input
- Complete lab scale demonstration

Future Work

- Validate results with real-time USC boiler systems
- Extend test results to develop corrosion model for USC boiler systems
- Make alterations to sensor design to include power source and transmitter
- Test sensor reliability and sensitivity for in situ applications

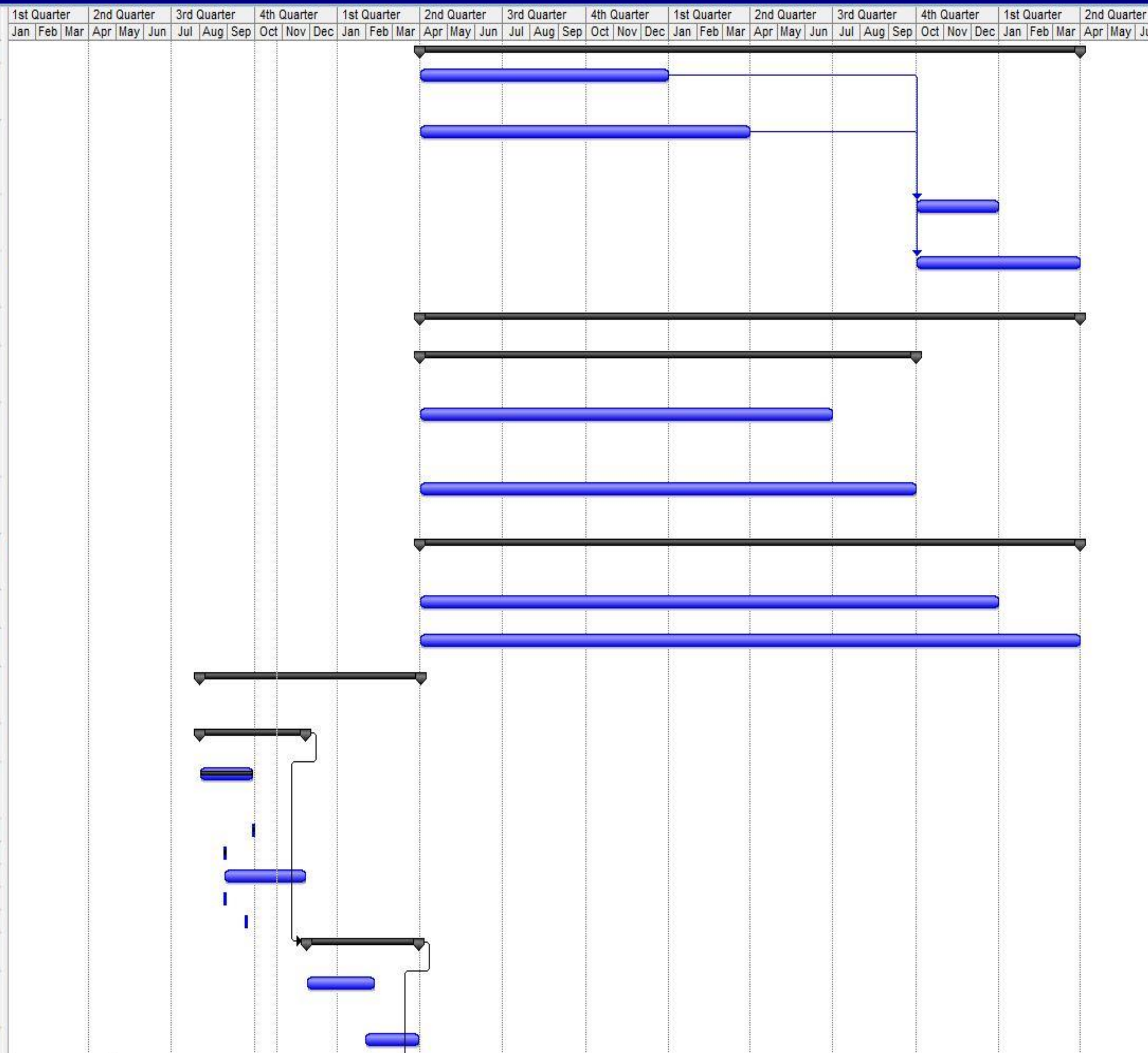
Milestone Status Report

	Task Name	Duration	Start	Finish
1	**1.0 Project Management**	**915 days?**	**Fri 4/1/11**	**Tue 9/30/14**
2	**1.1 Project Management Plan**	**915 days?**	**Fri 4/1/11**	**Tue 9/30/14**
3	Finalize Project Management Plan	153 days?	Fri 4/1/11	Mon 10/31/11
4	Manage project	915 days?	Fri 4/1/11	Tue 9/30/14
5	**1.2 Project Communication**	**915 days?**	**Fri 4/1/11**	**Tue 9/30/14**
6	Preparation and publication of reports	915 days?	Fri 4/1/11	Tue 9/30/14
7	Project Meetings	915 days?	Fri 4/1/11	Tue 9/30/14
8	Tracking milestones	915 days?	Fri 4/1/11	Tue 9/30/14
9	**2.0 Development of High Temperature Corrosion Sensor**	**805 days?**	**Thu 3/3/11**	**Mon 3/31/14**
10	**2.1 Design and Construction of Corrosion Sensor**	**675 days?**	**Thu 3/3/11**	**Mon 9/30/13**
11	Complete preliminary ECR probe design	196 days?	Mon 4/4/11	Sat 12/31/11
12	Complete design ECR probes for lab-scale corrosion experiments	261 days?	Mon 4/4/11	Sat 3/31/12
13	Complete construction of ECR probes	349 days?	Thu 3/3/11	Sat 6/30/12
14	Make any changes and finalize ECR probe design	65 days?	Mon 4/1/13	Sun 6/30/13
15	Make any changes and finalize ECR probes for lab-scale corrosion	65 days?	Mon 4/1/13	Fri 6/28/13
16	Finalize construction of ECR probes	66 days?	Mon 7/1/13	Mon 9/30/13
17	**2.2 In-Situe Corrosion Monitoring Validation**	**783 days?**	**Mon 4/4/11**	**Mon 3/31/14**
18	Complete laboratory test configuration	196 days?	Mon 4/4/11	Fri 12/30/11
19	Demonstrated resultes of the corrosion tests as a function of exposure temperature, time, and various simulated boiler exposure environments in lab-scale setting	196 days?	Sat 10/1/11	Thu 6/28/12
20	Demonstrated results of the high temperature corrosion tests as a function of exposure temperature, time, and various simulated boiler exposure environments	261 days?	Mon 10/3/11	Sun 9/30/12
21	Make final changes and finalize laboratory test configuration	65 days?	Mon 4/1/13	Fri 6/28/13
22	Final results of the corrosion tests as a function of exposure temperature, time, and various simulated boiler exposure environments in lab-scale setting	197 days?	Mon 4/1/13	Tue 12/31/13
23	Final results of the high temperature corrosion tests as a function of exposure temperature, time, and variou simulated boiler exposure environments	261 days?	Mon 4/1/13	Mon 3/31/14



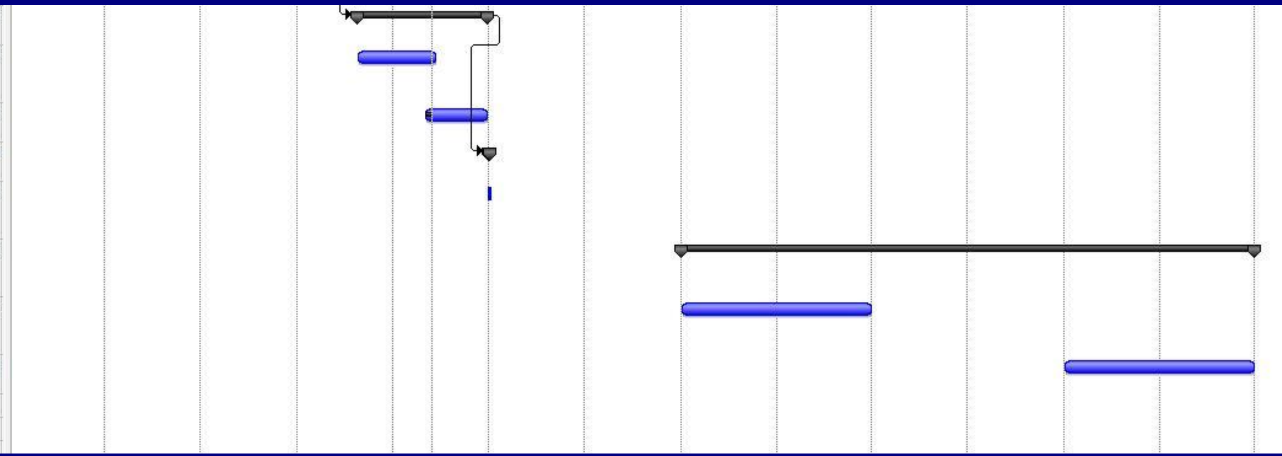
Milestone Status Report

	Task Name	Duration	Start	Finish
24	**2.3 Post Mortem Analysis**	**522 days?**	**Sun 4/1/12**	**Mon 3/31/14**
25	Quantify results of corrosion tests and the rate of corrosion development in lab-scale tests	197 days?	Sun 4/1/12	Mon 12/31/12
26	Quantify results of high temperature corrosion tests and the rate of corrosion in lab-scale tests	261 days?	Sun 4/1/12	Sun 3/31/13
27	Final results of corrosion tests and the rate of corrosion development in lab-scale tests	66 days?	Tue 10/1/13	Tue 12/31/13
28	Final results of high temperature corrosion tests and the rate of corrosion in lab-scale tests	130 days?	Tue 10/1/13	Mon 3/31/14
29	**3.0 Electrochemical Modeling and Predictive Model Development**	**522 days?**	**Sun 4/1/12**	**Mon 3/31/14**
30	**3.1 Develop Electrochemical Model to Characterize the General Corrosion of Boiler Tube**	**392 days?**	**Sun 4/1/12**	**Mon 9/30/13**
31	Predictive model to characterize the performance and life expectation of materials under lab-scale simulated USC operating conditions	326 days?	Sun 4/1/12	Sun 6/30/13
32	Validate model with data obtained under industrial USC operating conditions	392 days?	Sun 4/1/12	Mon 9/30/13
33	**3.2 Develop Predictive System for Localized Corrosion in the Boiler Tubes**	**522 days?**	**Sun 4/1/12**	**Mon 3/31/14**
34	Develop method to detect localized corrosion via EN and EIS	458 days?	Sun 4/1/12	Tue 12/31/13
35	Confirm method to identify nature of corrosion products	522 days?	Sun 4/1/12	Mon 3/31/14
36	**4.0 Development of Self-Powered Hardware Selection and Modeling of TEG Array**	**177 days?**	**Mon 8/1/11**	**Sun 4/1/12**
37	**4.1 Hardware selection and design of TEG array**	**86 days?**	**Mon 8/1/11**	**Fri 11/25/11**
38	Identify and purchase commercial hardware for wireless transmission of sensor data	43 days?	Mon 8/1/11	Wed 9/28/11
39	Hardware ordered	1 day?	Thu 9/29/11	Thu 9/29/11
40	Hardware received	1 day?	Mon 8/29/11	Mon 8/29/11
41	Identify, purchase and evaluate TE(	66 days?	Mon 8/29/11	Fri 11/25/11
42	Hardware ordered	1 day?	Mon 8/29/11	Mon 8/29/11
43	Hardware received	1 day?	Wed 9/21/11	Wed 9/21/11
44	**4.2 Demonstrate TEG and wireless communication system**	**90 days?**	**Mon 11/28/11**	**Fri 3/30/12**
45	Demonstrate the wireless communication system functionality in lab-scale tests	55 days?	Mon 11/28/11	Fri 2/10/12
46	Demonstrate the TEG functionality via lab-scale tests	44 days?	Tue 1/31/12	Fri 3/30/12



Milestone Status Report

44	**4.2 Demonstrate TEG and wireless communication system**	**90 days?**	**Mon 11/28/11**	**Fri 3/30/12**
45	Demonstrate the wireless communication system functionality in lab-scale tests	55 days?	Mon 11/28/11	Fri 2/10/12
46	Demonstrate the TEG functionality via lab-scale tests	44 days?	Tue 1/31/12	Fri 3/30/12
47	**4.3 Demonstrate TEG and wireless communication system**	**1 day?**	**Sun 4/1/12**	**Sun 4/1/12**
48	Demonstrate wireless/TEG functionality under USC operating conditions	1 day?	Sun 4/1/12	Sun 4/1/12
49	**5.0 In-Situ Corrosion Monitoring Testing in Industrial USC Boiler Setting**	**391 days?**	**Mon 10/1/12**	**Mon 3/31/14**
50	Determine reliability and precision of corrosion sensors operating in industrial USC boiler conditions	130 days?	Mon 10/1/12	Sun 3/31/13
51	Optimize sensor construction and corrosion model development	130 days?	Tue 10/1/13	Mon 3/31/14



Thank You