DoE Award No. DE-FE31548

# High Temperature Electrochemical Sensors for In-situ Corrosion Monitoring In Coal-Based Power Generation Boilers

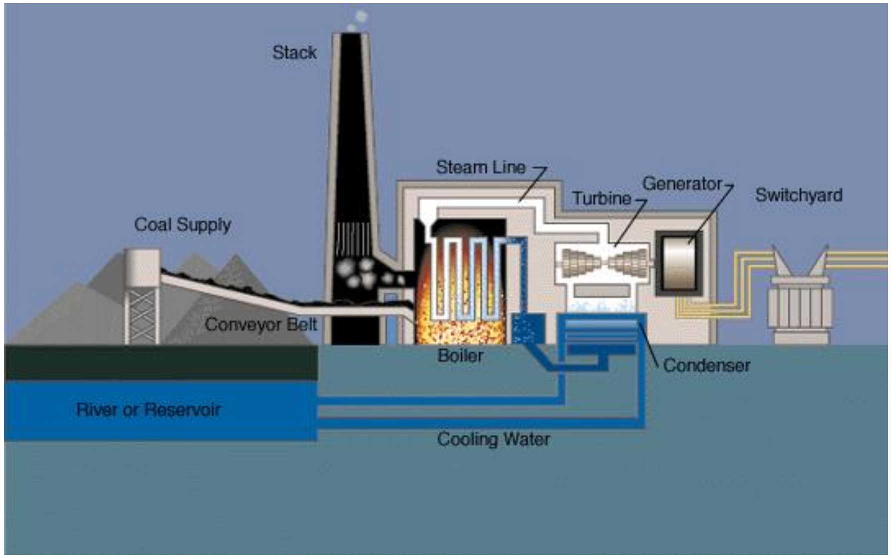
Xingbo Liu[1], Debangsu Bhattacharyya[1], Brandon Rumberg[2], Chad Hufnagel[3]

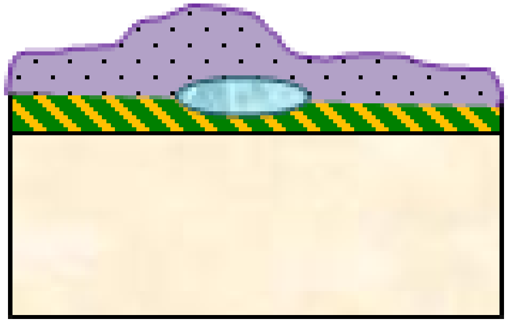
1. West Virginia University; 2 Aspinity, 3, Longview Power

February 6, 2018

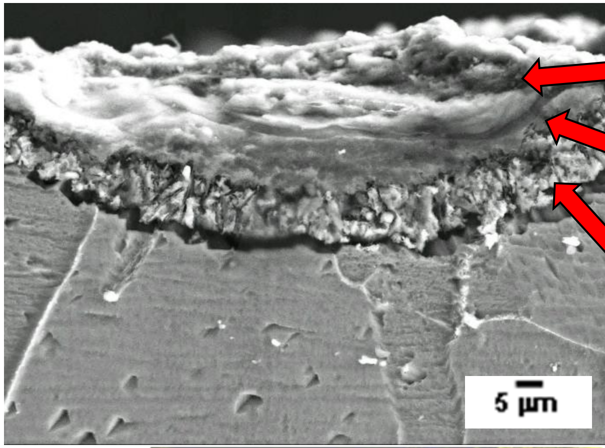
# OUTLINE

- Background & Preliminary Results
- Project Objectives
- Project Team
- Planed Tasks & Milestones



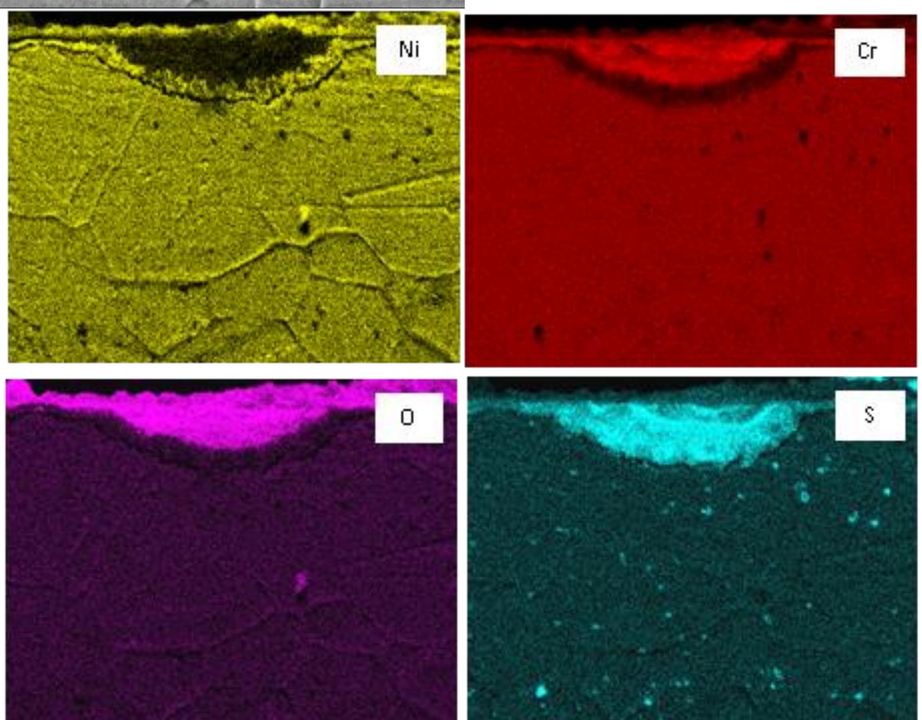
# Serious Coal Ash Hot Corrosion Issues




**Oxidation** in Cr,Ni-rich regions

**External Sulfidation**
in Cr,Ni-rich regions

**Internal Sulfidation**
in Ni,Cr-rich regions




# 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

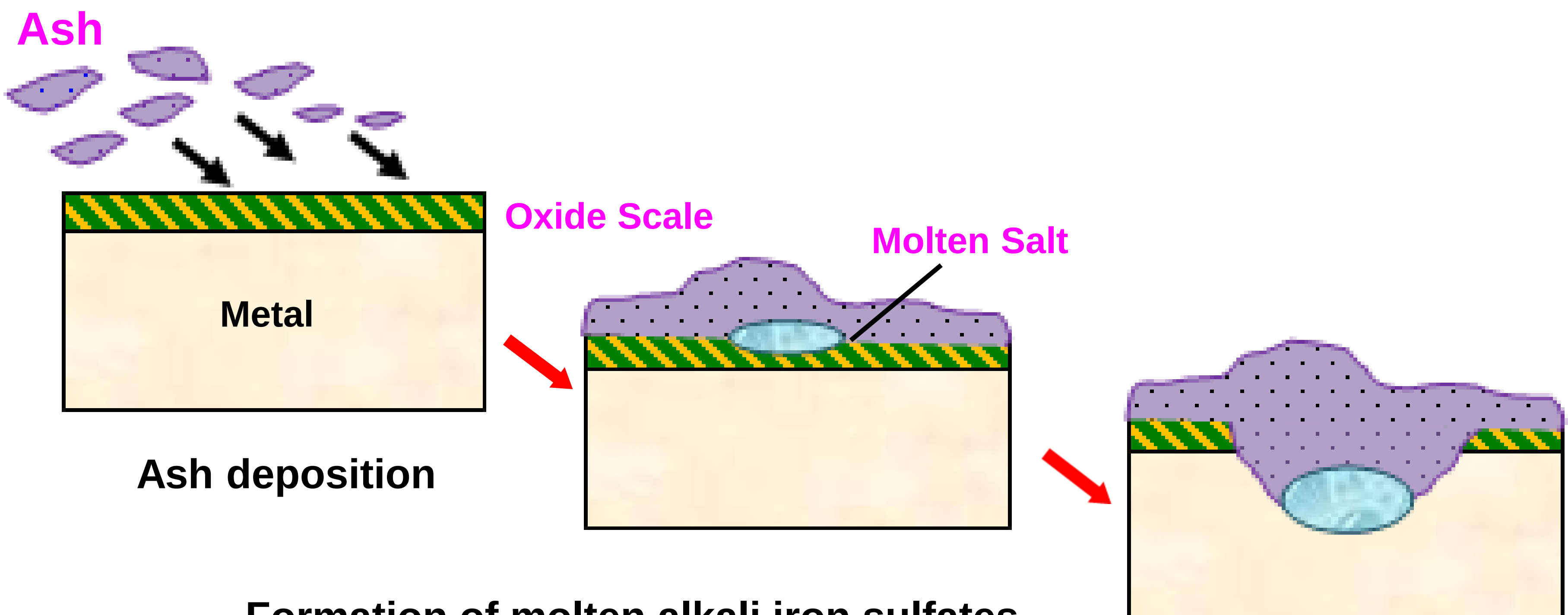
## In the Lower Furnace

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



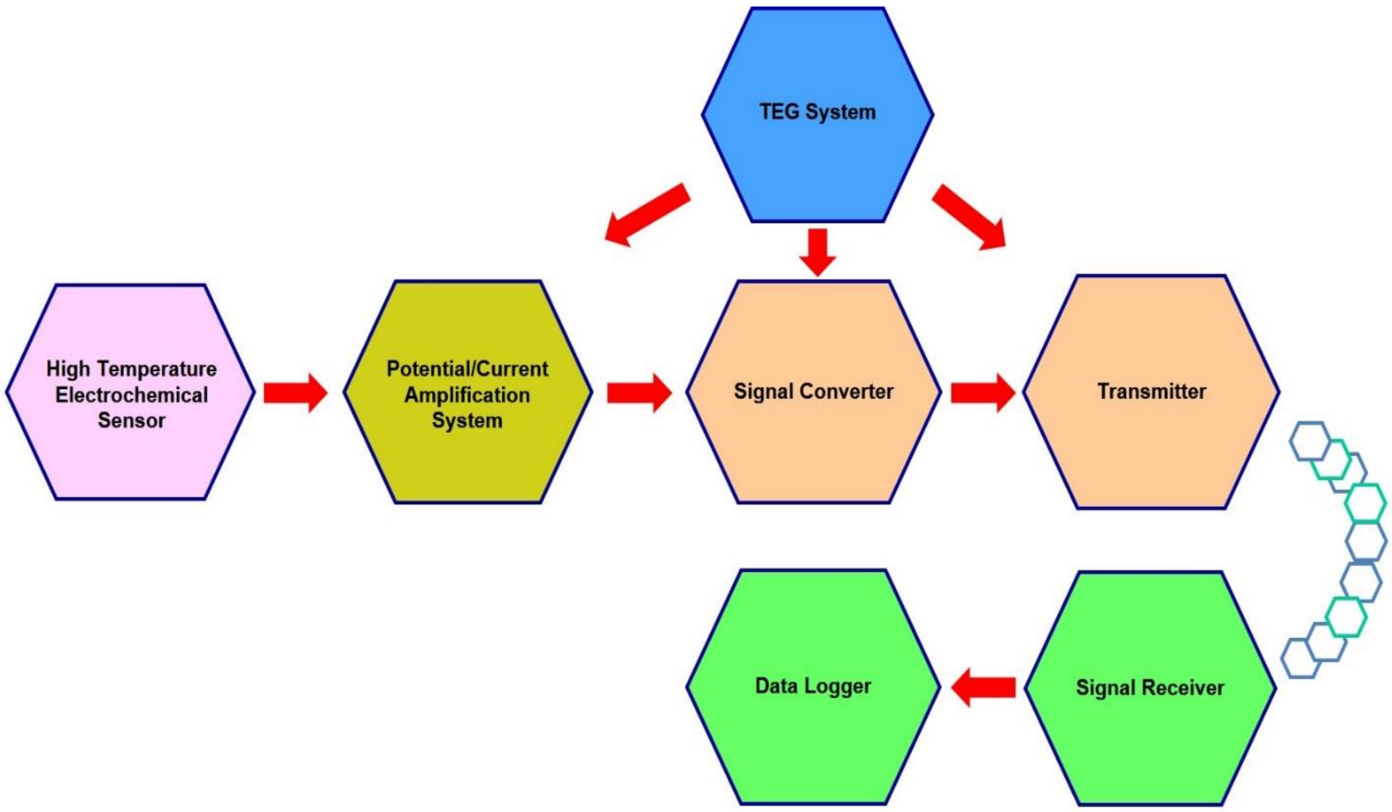

**Ash deposition**

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

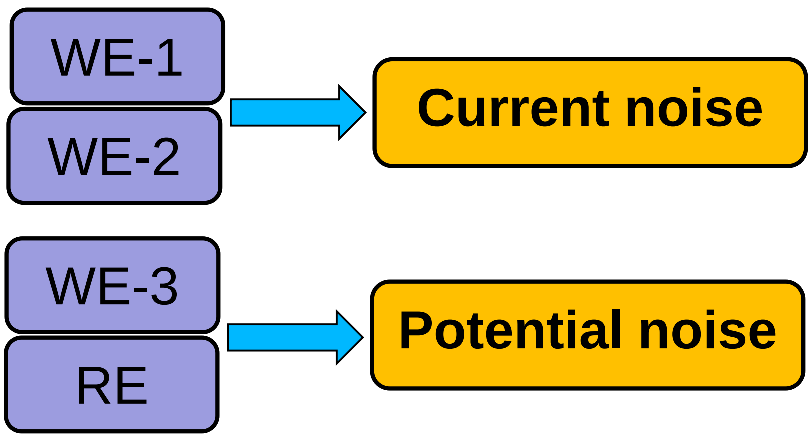
**Direct reaction between bare metal and reduced sulphate species**

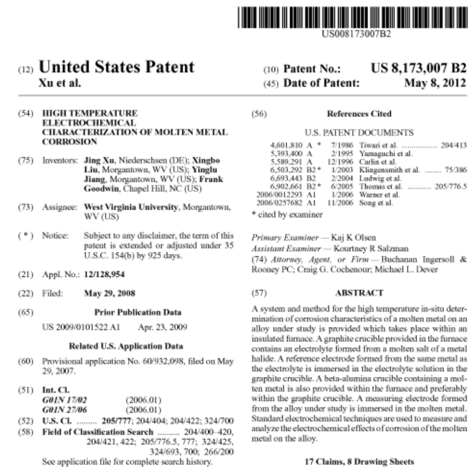
# Self-Powered Wireless-Ready Electrochemical Sensor For In-Situ Corrosion Monitoring of Coal-Fired A-USC Boiler Tubes

- DoE Award No. DE- FE0005717
- Funded by NETL – Coal Utilization Science Program (2010-2015)
- Team: WVU, Special Metals, International Zinc Association, Western Research Institute



# High Temperature Corrosion Sensor Design for Concurrent Potential & Current Signals Measurement

US008173007B2

(12) **United States Patent**
**Xu et al.**

(10) **Patent No.:** **US 8,173,007 B2**
(45) **Date of Patent:** **May 8, 2012**

(54) **HIGH TEMPERATURE ELECTROCHEMICAL CHARACTERIZATION OF MOLTEN METAL CORROSION**

(75) Inventors: **Jing Xu**, Niederschsen (DE); **Xingbo Liu**, Morgantown, WV (US); **Yinglu Jiang**, Morgantown, WV (US); **Frank Goodwin**, Chapel Hill, NC (US)

(73) Assignee: **West Virginia University**, Morgantown, WV (US)

( * ) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 925 days.

(21) Appl. No.: **12/128,954**

(22) Filed: **May 29, 2008**

(65) **Prior Publication Data**

US 2009/0101522 A1 Apr. 23, 2009

**Related U.S. Application Data**

(60) Provisional application No. 60/932,098, filed on May 29, 2007.

(51) **Int. Cl.**
*G01N 17/02* (2006.01)
*G01N 27/06* (2006.01)

(52) **U.S. Cl.** ......... **205/777**; 204/404; 204/422; 324/700

(58) **Field of Classification Search** .......... 204/400–420, 204/421, 422; 205/776.5, 777; 324/425, 324/693, 700; 266/200
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

| | | | | |
|---|---|---|---|---|
| 4,601,810 A * | 7/1986 | Tiwari et al. | ................ | 204/413 |
| 5,393,400 A | 2/1995 | Yamaguchi et al. | | |
| 5,589,291 A | 12/1996 | Carlin et al. | | |
| 6,503,292 B2 * | 1/2003 | Klingensmith et al. | ........ | 75/386 |
| 6,693,443 B2 | 2/2004 | Ludwig et al. | | |
| 6,902,661 B2 * | 6/2005 | Thomas et al. | ........... | 205/776.5 |
| 2006/0012293 A1 | 1/2006 | Warner et al. | | |
| 2006/0257682 A1 | 11/2006 | Song et al. | | |

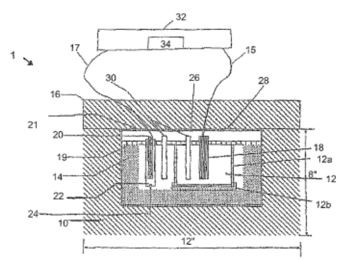
* cited by examiner

*Primary Examiner* — Kaj K Olsen
*Assistant Examiner* — Kourtney R Salzman
(74) *Attorney, Agent, or Firm* — Buchanan Ingersoll & Rooney PC; Craig G. Cochenour; Michael L. Dever

(57) **ABSTRACT**

A system and method for the high temperature in-situ determination of corrosion characteristics of a molten metal on an alloy under study is provided which takes place within an insulated furnace. A graphite crucible provided in the furnace contains an electrolyte formed from a molten salt of a metal halide. A reference electrode formed from the same metal as the electrolyte is immersed in the electrolyte solution in the graphite crucible. A beta-alumina crucible containing a molten metal is also provided within the furnace and preferably within the graphite crucible. A measuring electrode formed from the alloy under study is immersed in the molten metal. Standard electrochemical techniques are used to measure and analyze the electrochemical effects of corrosion of the molten metal on the alloy.

**17 Claims, 8 Drawing Sheets**



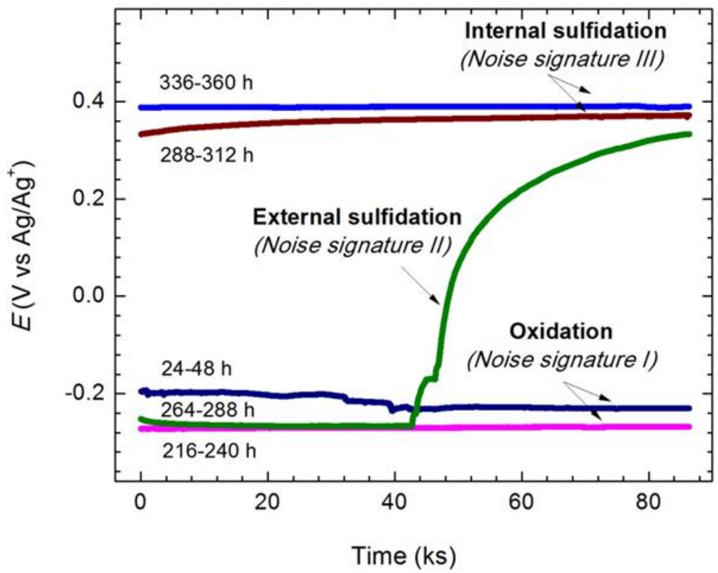
Jing Xu, Frank Goodwin, Yinglu Jiang, **Xingbo Liu***: High Temperature Electrochemical Characterization of Molten Metal Corrosion, (2012) US 8,173,007

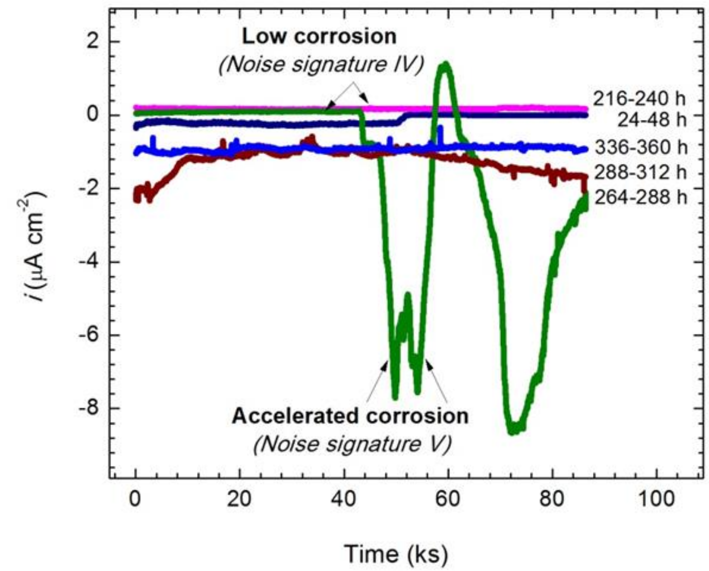
"Multifunctional Metallic and Refractory Materials for Energy Efficient Handling of Molten Metals (DE-FC36-04GO14038)" funded by EERE-AMO (2004-2009)

# Experimental Conditions

| Corrosion condition | |
|---|---|
| Materials | INCONEL 740 |
| Temperature | 650-850°C |
| The Flue Gas Composition | With/without $SO_2$<br>15 $CO_2$ + 4 $O_2$ + 80 $N_2$ + 1 $SO_2$ |
| Coal ash thickness | Uniform /Localized Thin film<br>89 % Ash +10% Alkali +1% NaCl |
| Exposure time | Up to 30 days |

# THREE Different Stages of Coal Ash Hot Corrosion Process



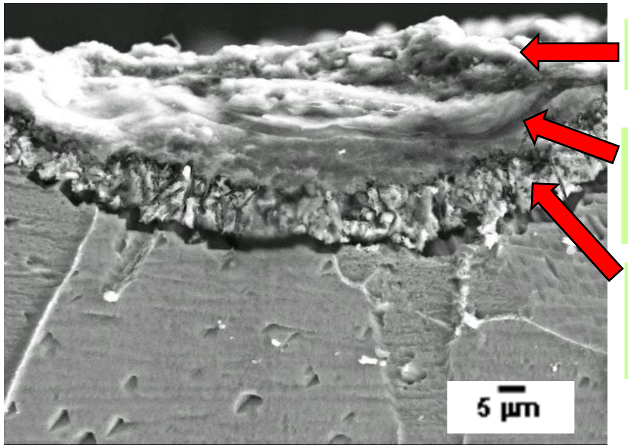




**Coal Ash Hot Corrosion Process**

**Oxidation Stage**

**Sulfidation Stage**

- **External**
- **Internal**

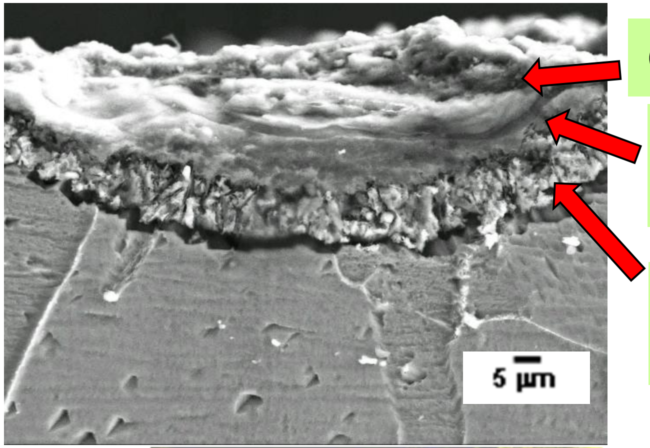



**Oxidation** in Cr,Ni-rich regions

**External Sulfidation** in Cr,Ni-rich regions

**Internal Sulfidation** in Ni,Cr-rich regions

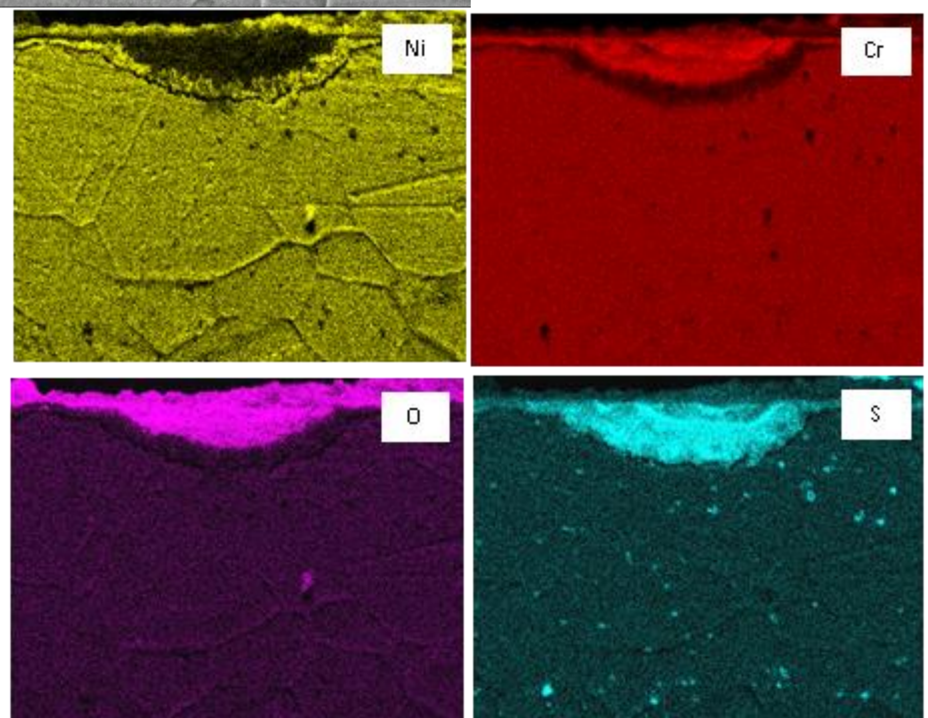
# Oxygen and Sulfur Diffusion During Oxidation & Sulfidation Stages




**Oxidation** in Cr,Ni-rich regions

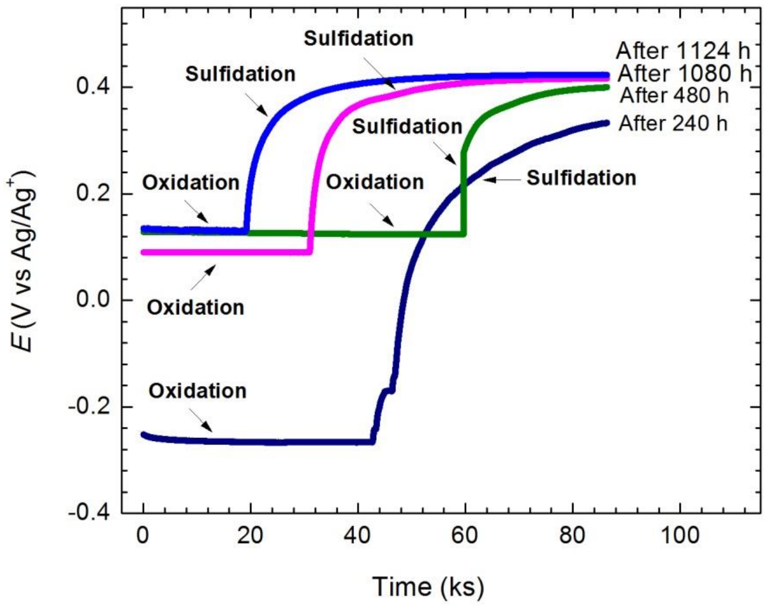
**External Sulfidation**
in Cr,Ni-rich regions

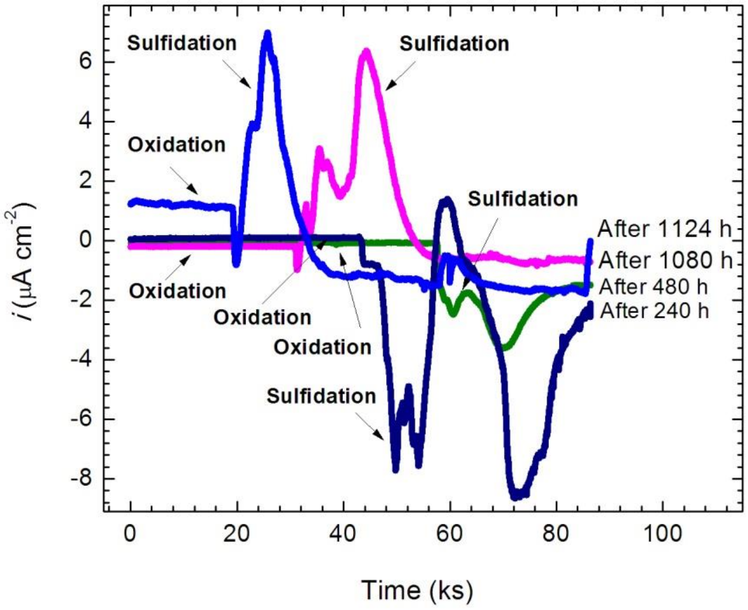
**Internal Sulfidation**
in Ni,Cr-rich regions



# Reproducibility of Potential and Current Signals During Oxidation and Sulfidation

**INCONEL 740 alloy + 850 °C + Thin coal ash + without /with $SO_2$**



# New Version of Faraday's Law Expression for Calculation of Corrosion Kinetics

$$\text{Corrosion Rate, } R = \frac{KM}{n\rho}\, i_{max}$$

K = Constant for converting units

M = Atomic mass

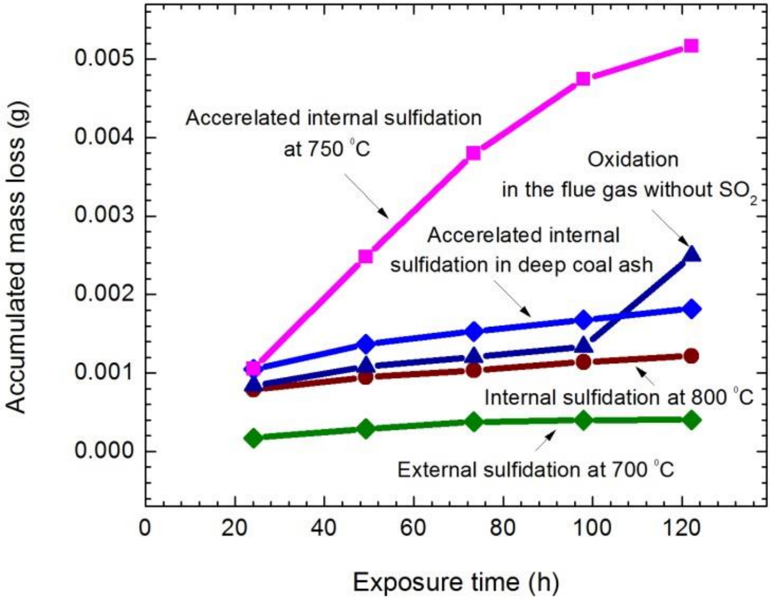
n = Number of electrons freed by the corrosion reaction

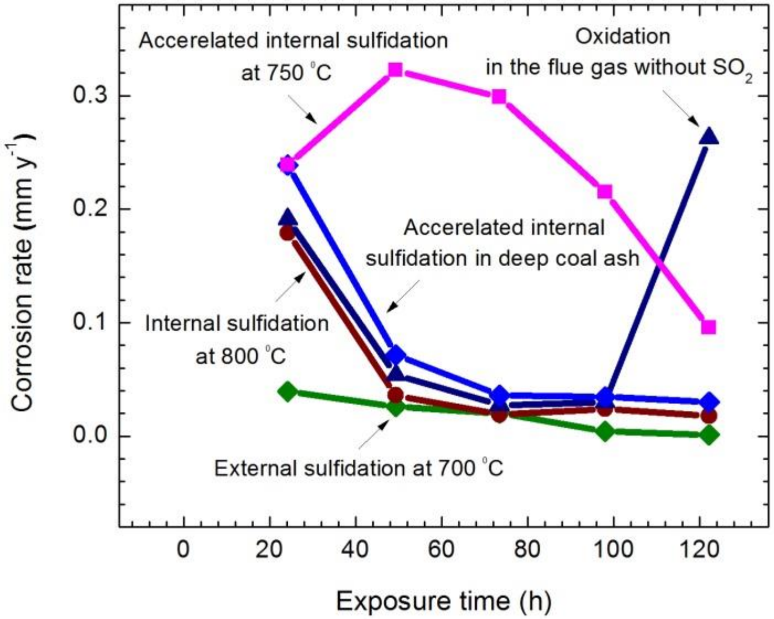
$\rho$ = Density

$$\text{Corrosion Depth, } D = K \times R \times \text{period}$$

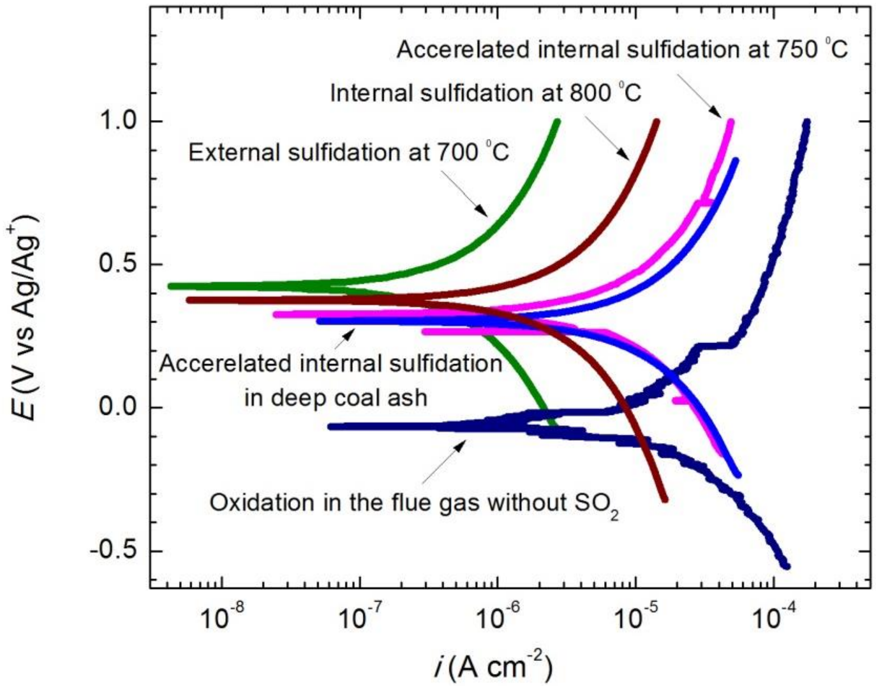
where the period is normally 24 h and the corrosion rate is assumed to be constant

# Evaluation of Corrosion Kinetics via EN Technique



# Evaluation of Corrosion Potentials and Rates Via Potentiodynamic Polarization




| Corrosion condition | Predominant corrosion mechanism | $E_{corr}$ (mV vs. Ag/Ag$^+$) | $i_{corr}$ (μA cm$^{-2}$) | Corrosion rate (mm y$^{-1}$) |
|---|---|---|---|---|
| The flue gas without $SO_2$ | Oxidation | –68 | 5.19 | 0.06 |
| 700 °C | External sulfidation | 424 | 0.58 | 0.01 |
| 800 °C | Internal sulfidation | 377 | 2.46 | 0.03 |
| 750 °C | Accelerated internal sulfidation | 327 | 9.25 | 0.11 |
| Deep coal ash | Accelerated internal sulfidation | 303 | 9.97 | 0.12 |

Naing Naing Aung, **Xingbo Liu***: Effect of Temperature on Coal Ash Hot Corrosion Resistance of Inconel 740 Superalloy, *Corrosion Science 82 (2014)227-238*

# FIVE Typical Noise Signals Measured in the Coal Ash Hot Corrosion Process

## Electrochemical Potential Noise Signals

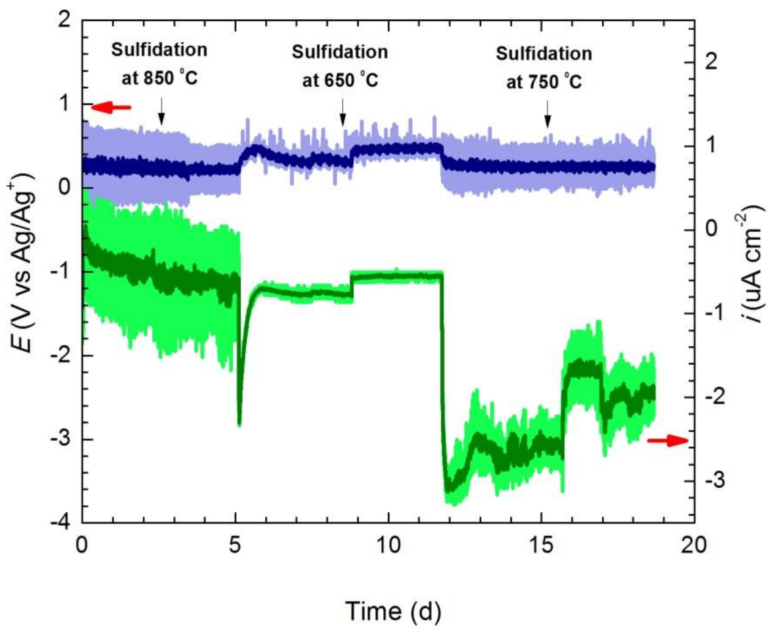
- The noise signature of a gradual potential continuously changing in the negative region ***(Noise Signature I)*** corresponded with the Oxidation Stage
- The noise signature of quick potential continuously approaching more positive values ***(Noise Signature II)*** correlated to the External Sulfidation Stage.
- The noise signature of positive potential fluctuating randomly in a narrow range ***(Noise Signature III)*** corresponded with the Internal Sulfidation Stage

## Electrochemical Current Noise Signals

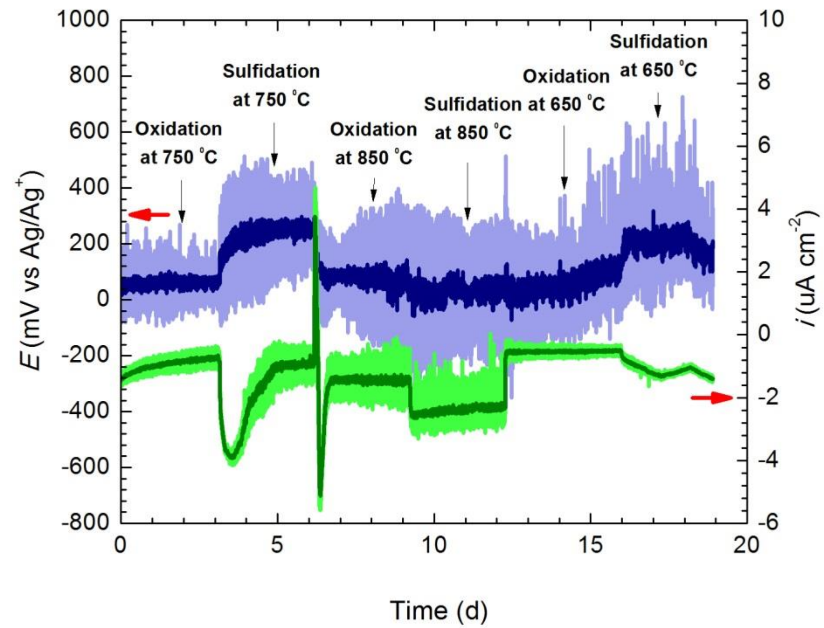
- The noise pattern of the noise signature of current fluctuating with no sudden spike correlated to the Low Extent of Oxidation/Sulfidation ***(Noise Signature IV)***.
- The noise pattern of sudden change in current values followed by slow or no recovery corresponded with the Accelerated Oxidation/Sulfidation ***(Noise Signature V)***. These signatures can be seen clearly at 750 °C, in the flue gas without $SO_2$ as well as deep coal ash.

# Concurrent Transmission of Corrosion Potential and Current Signals

**Under Uniform Thin Coal Ash Film**

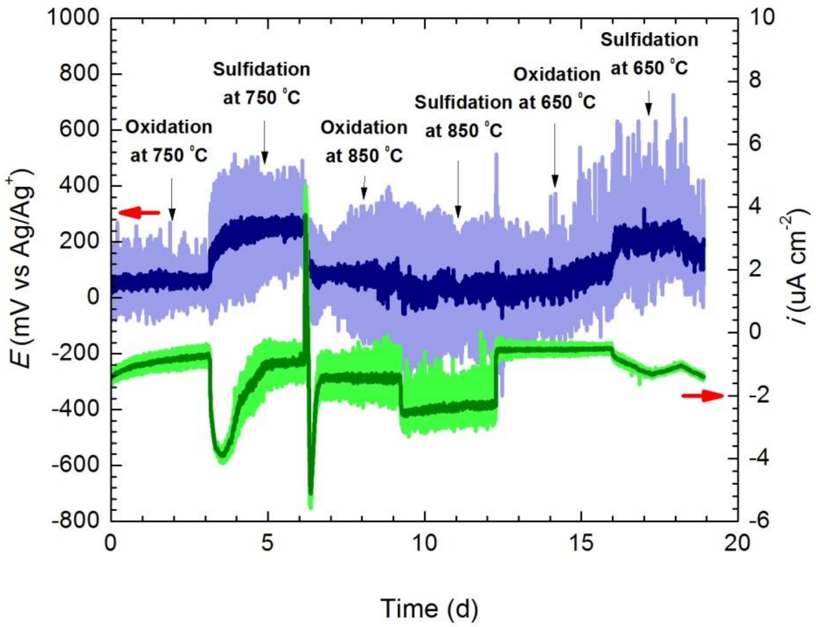



**Under Localized Thin Coal Ash Film**

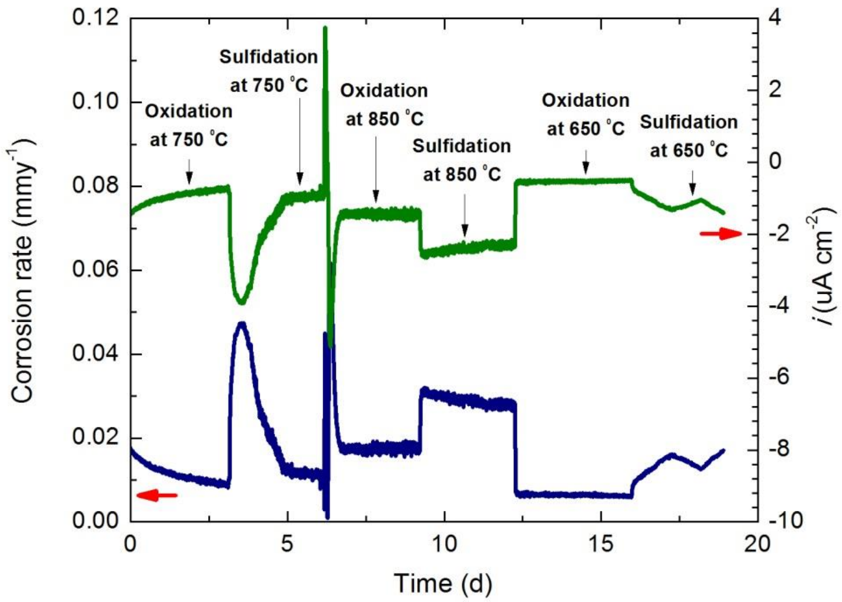


# Calculation of Corrosion Rate from Current Noise Signals

**Corrosion Potential and Current**



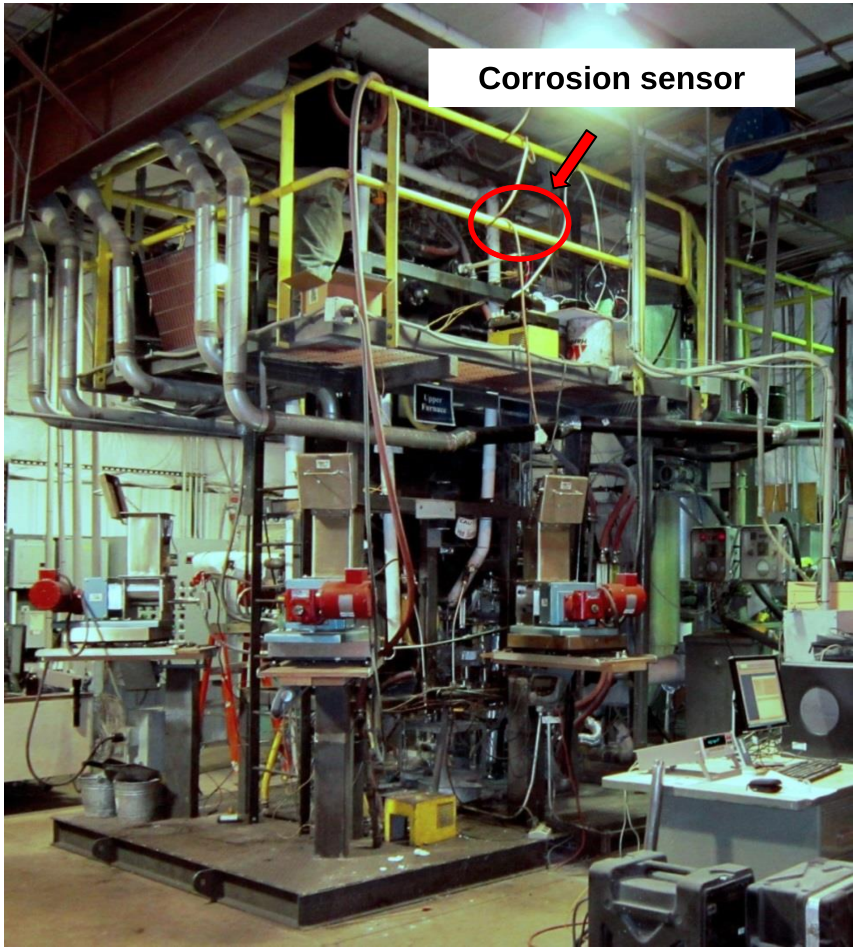

**Corrosion Current and Corrosion Rate**



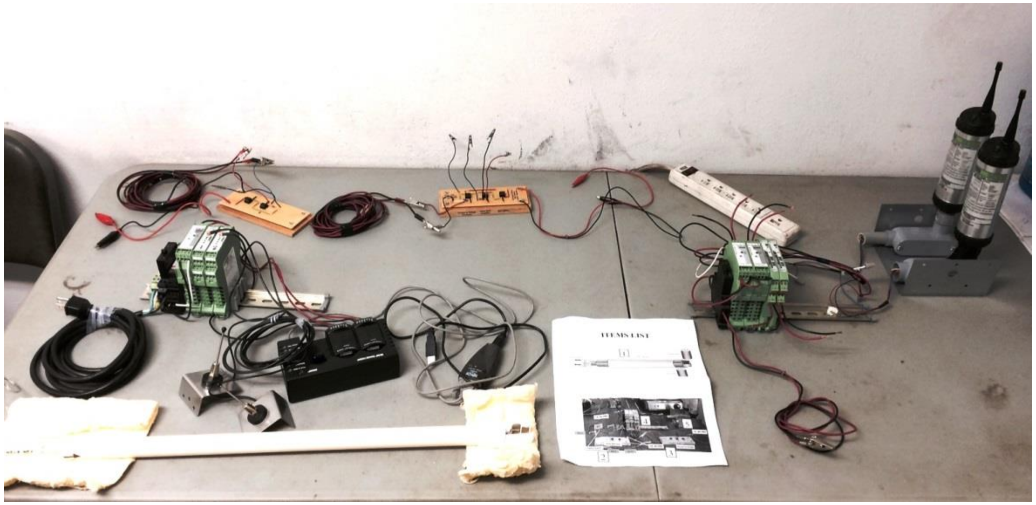
# Testing Sensor in Industrial USC Boiler Setting (Western Research Institute, Laramie WY)

# Sensor Setting
# Inside and Outside USC Boiler System

## 22 April 2015




**Wireless Sensing System**
**for Concurrent Potential and Current Signals Measurement**



# Conclusions

- A self-powered wireless sensing system has been successfully developed for concurrent transmission of potential and current signals from coal ash hot corrosion.
- Characteristic patterns in the wireless concurrent potential and current noise signals can clearly identify the oxidation and sulfidation stages of coal ash hot corrosion process after data smoothing.
- Localized under- coal ash deposit corrosion behaviour of Inconel 740 superalloy was studied using the sensor. The predominant stages during the LUDC process can be identified with three typical potential noise patterns and their extents of the corrosion can be evaluated with two characteristic current noise patterns.
- Analysis of electrochemical noise signals by power spectral density (PSD) was applied to coal ash hot corrosion study. PSD plots using coefficient 1000 of MEM show more reasonable information for mechanism of the oxidation and sulfidation processes.

# Publications & Tech Transfer Activities

## Peer-Reviewed Journal Publications

- Naing Naing Aung, Xingbo. Liu, High temperature electrochemical sensor for in situ monitoring of hot corrosion, Corros. Sci. 65 (2012) 1-4.
- Naing Naing Aung, Xingbo Liu, Effect of $SO_2$ in flue gas on coal ash hot corrosion of Inconel 740 alloy - a high temperature electrochemical sensor study, Corros. Sci. 76 (2013) 390-402.
- Naing Naing Aung, Xingbo Liu, Effect of temperature on coal ash hot corrosion resistance of Inconel 740 superalloy, Corros. Sci. 82 (2014) 227-238.
- Naing Naing Aung, Edward Crowe, Xingbo Liu, Development of Self-Powered Wireless-Ready High Temperature Electrochemical Sensor for In Situ Corrosion Monitoring in Coal-Fired Power Plant, ISA Trans. 55 (2015) 188-194.

# NEW PROJECT OBJECTIVES

- To validate the effectiveness of the Recipient's previous electrochemical sensor for high temperature (HT) corrosion in coal-based power generation boilers;
- To optimize the Recipient's HT sensor (currently at technology readiness level TRL-6) to reach TRL-8;
- To develop a pathway toward commercialization of such technology.

# Project Team Member – Longview Power

| | |
|---|---|
| Location | Monongalia County,<br>near Maidsville, WV |
| Status | Operational |
| Commission date | 2011 |
| Owner(s) | Longview Power |
| Thermal power station | |
| Primary fuel | Coal and natural gas |
| Type | Steam turbine |
| Power generation | |
| Nameplate capacity | 700 MW |

- Officially a "zero discharge" power plant in WV
- Includes a new air pollution control system that results in emissions that are Among the lowest in the nation for coal plants.
- Emits less $CO_2$ than most other coal plants because of its fuel efficiency

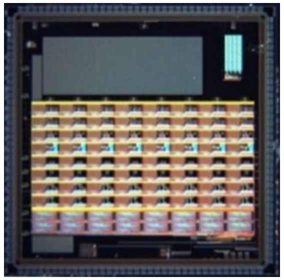
# Project Team Member – Aspinity

ASPINITY

- Provide solutions to the "power vs. performance" challenges that confront energy-constrained sensing systems
  - Key product is low-power analog processor
- History
  - Spun out of WVU research
  - Collaborating with MEMS and consumer companies on low-power speech solutions
  - 2016 – Raised first investment
  - 2017 – ARL subcontract, Alexa Accelerator, …

## Capabilities

*Chip design*



*Circuit board design*


*Software*

- Signal processing
  - Audio, vibration, etc.
- Embedded microcontrollers
- Wireless networks



techstars

*Techstars Company*

Alexa Fund
Portfolio Company
amazon alexa


*EE Times Silicon 60: Startups to Watch*


*EE News Analog, MEMS and Sensor Startups to Follow*

# PLANNED TASKS & DELIVERABLES

| ID | Task | Year 1 | | | | Year 2 | | | | Year 3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Q1 | Q2 | Q3 | Q4 | Q1 | Q2 | Q3 | Q4 | Q1 | Q2 | Q3 | Q4 |
| 1 | Project management | ■◆ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| 2 | Sensor development & optimization | | | | | | | | | | | | |
| 2.1 | Design & construct sensors | ■ | ■ | | | ■ | ■ | | | ■ | ■ | | |
| 2.2 | Sensor packaging | | ■ | ■ | | | ■ | ■ | | | ■ | ■ | |
| 3 | Signal processing & communication instruments | | ■ | ■ | | | ■ | ■ | | | ■ | ■ | |
| 4 | Corrosion sensor testing @ Longview Power's boiler | | | | | | | | | | | | |
| 4.1 | Sensor placement and installation | | | ■ | | | | ■ | | | | ■ | |
| 4.2 | Sensor testing | | | ■ | ■◆ | | | ■ | ■ | | | ■ | ■ |
| 4.3 | Post-mortem analyses | | | | ■ | ■ | | | ■ | ■ | | | ■ |
| 5 | Corrosion monitoring software & database development | | | | | | | | | | | | |
| 5.1 | Lab-scale sensor optimization | ■ | ■ | | | ■ | ■ | | | ■ | ■ | | |
| 5.2 | Electrochemical and corrosion monitoring validation | | ■ | ■ | | | ■ | ■ | | | ■ | ■ | |
| 5.3 | Post-mortem analysis | | | ■ | ■ | | | ■ | ■ | | | | ■ |
| 5.4 | Database and predictive model development | | | ■ | ■ | | | ■ | ■ | | | ■ | ■ |
| 5.5 | Software development | | | ■ | ■ | | | ■ | ■◆ | | | ■ | ■ |
| 6 | Tech-transfer & commercialization | | | | | | | | | | | | |
| 6.1 | NPV model & uncertainty analysis | ■ | ■ | ■ | ■ | ■ | ■◆ | ■ | ■ | | | ■ | ■ |
| 6.2 | NEMS model and economic analysis | | | | | | | ■ | ■ | ■ | ■ | ■◆ | ■ |
| 6.3 | Commercialization pathway development | | | | | | ■ | ■ | | | ■ | ■ | ■ |

- Y1-Q1, finish updating PMP
- Y1-Q4, demonstrate the high temperature corrosion sensor can withstand the harsh environment in Longview's A-USC boiler.
- Y2-Q2, complete the NPV model and uncertainty analysis
- Y2-Q4, complete the electrochemical and corrosion database and model construction
- Y3-Q2, complete the NEMS model and economic analysis

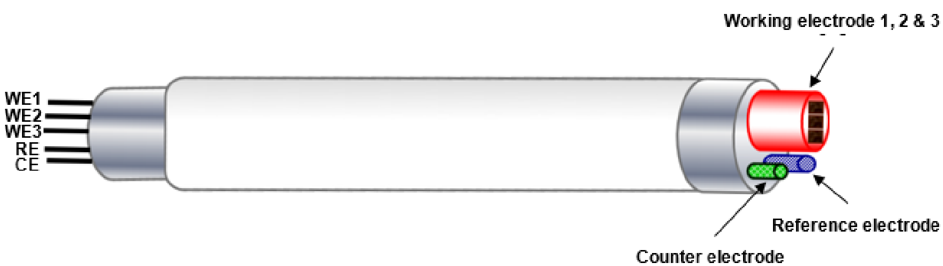
# Tasks 1 & 2

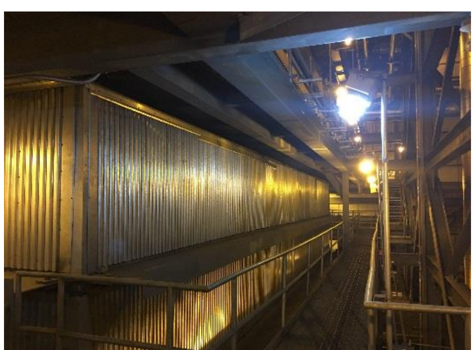
**Task 1.0: Project Management and Planning**

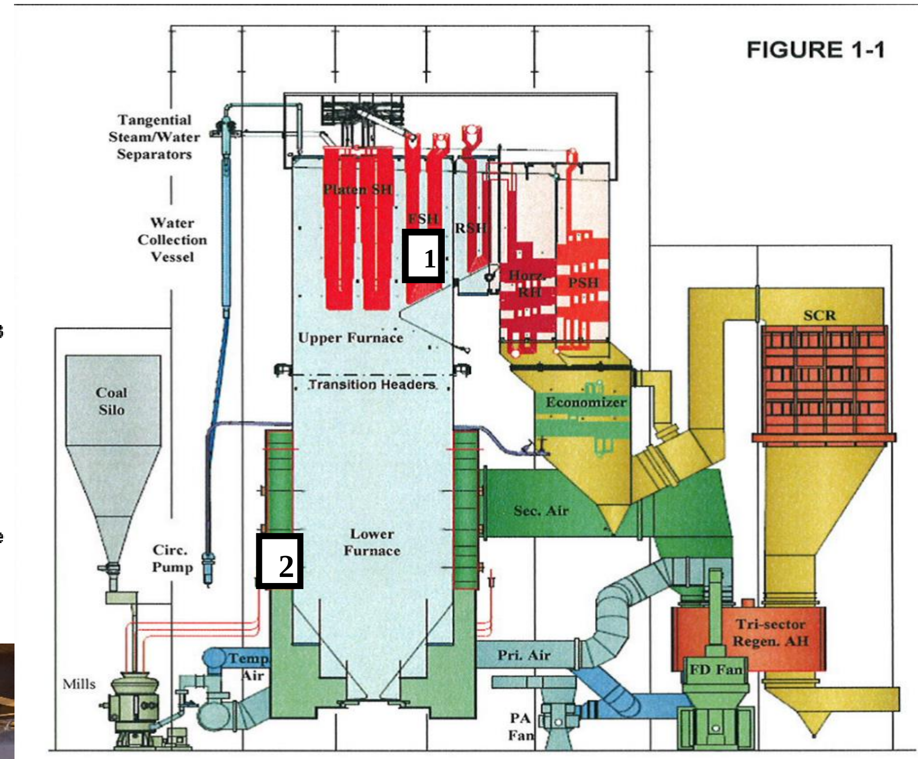
**Task 2.0: Design and Construction of Corrosion Sensor for Utility Boiler**

***Subtask 2.1*** *Design & Construct Sensors*

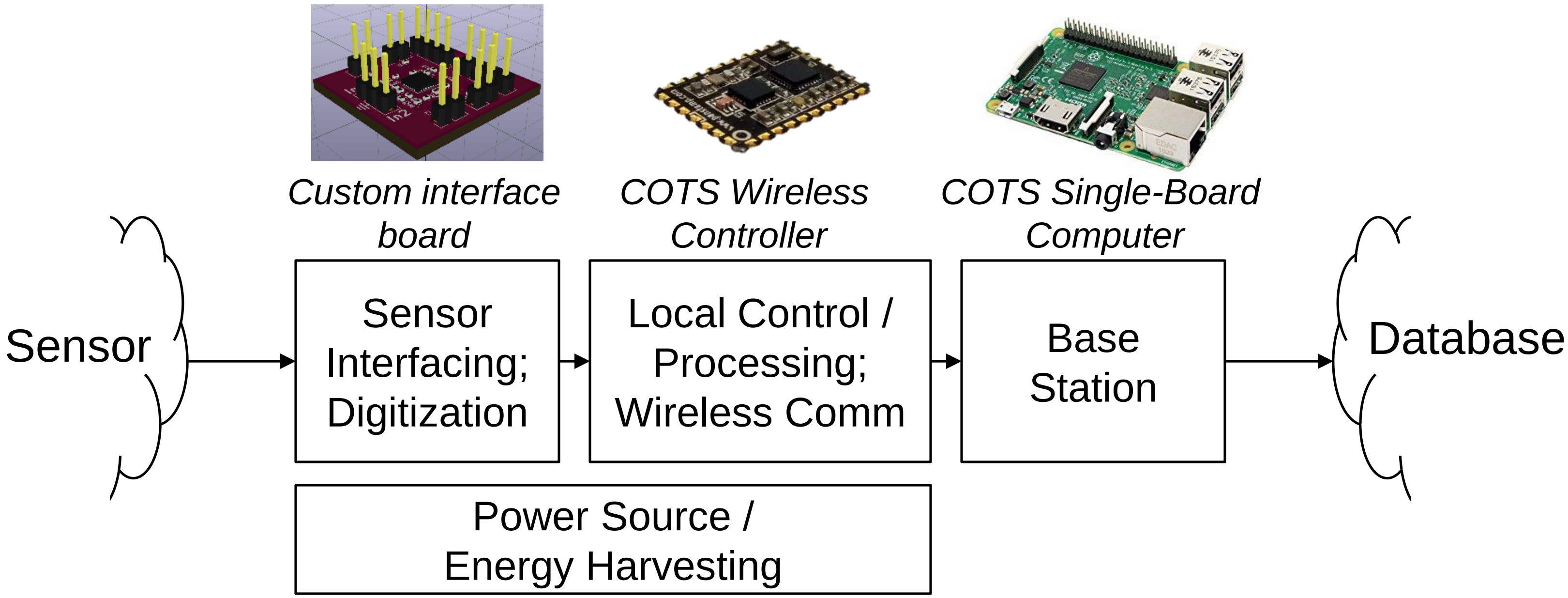
***Subtask 2.2*** *Sensor Packaging*





# Task 3 - Signal Processing and Wireless Communication systems




- Provide the pipe between the transducer and the backend user
  - Precise measurement of the transducer and communication of required data to the backend
  - Previous project proved the concept…
  - … Aspinity will redesign the electronics for
    - Measurement performance
    - SWaP (Size, Weight, and Power) and cost
    - Ease of installation/interfacing

# Task 3 - Signal Processing and Wireless Communication systems

## Interfacing/Digitization

- Purpose: Obtain precise and stable readings of transducer
- Build a custom interface board w/ amplifiers, references, and ADC
- Prototype interface will be modular to plug into different controllers (Raspberry Pi, Panstamp, …)

## Local Control/Wireless Comm

- Purpose: Control measurement (timing, mode, …), log and process data, hand data off to basestation or cloud
- Initial prototype will use Raspberry Pi
  - Run Python or Octave locally for easy data analysis & visualization
  - Wifi connection to pull software updates (git) and push data (Google Drive?)
- Later prototype use Panstamp or similar device with ISM-band radio to connect to base station

## Power Source/Energy Harvesting

- Purpose: Simplify installation and maintenance of device
- Low data rate (0.5 samples/s) enables power optimization of above tasks on later prototypes
- Interface to commercially-available TEG harvester

## Base Station

- Purpose: Gather data from wirelessly-deployed sensors
- Study industry standards to enhance compatibility for easy installation
- Initially use a Raspberry Pi with an ISM-band radio

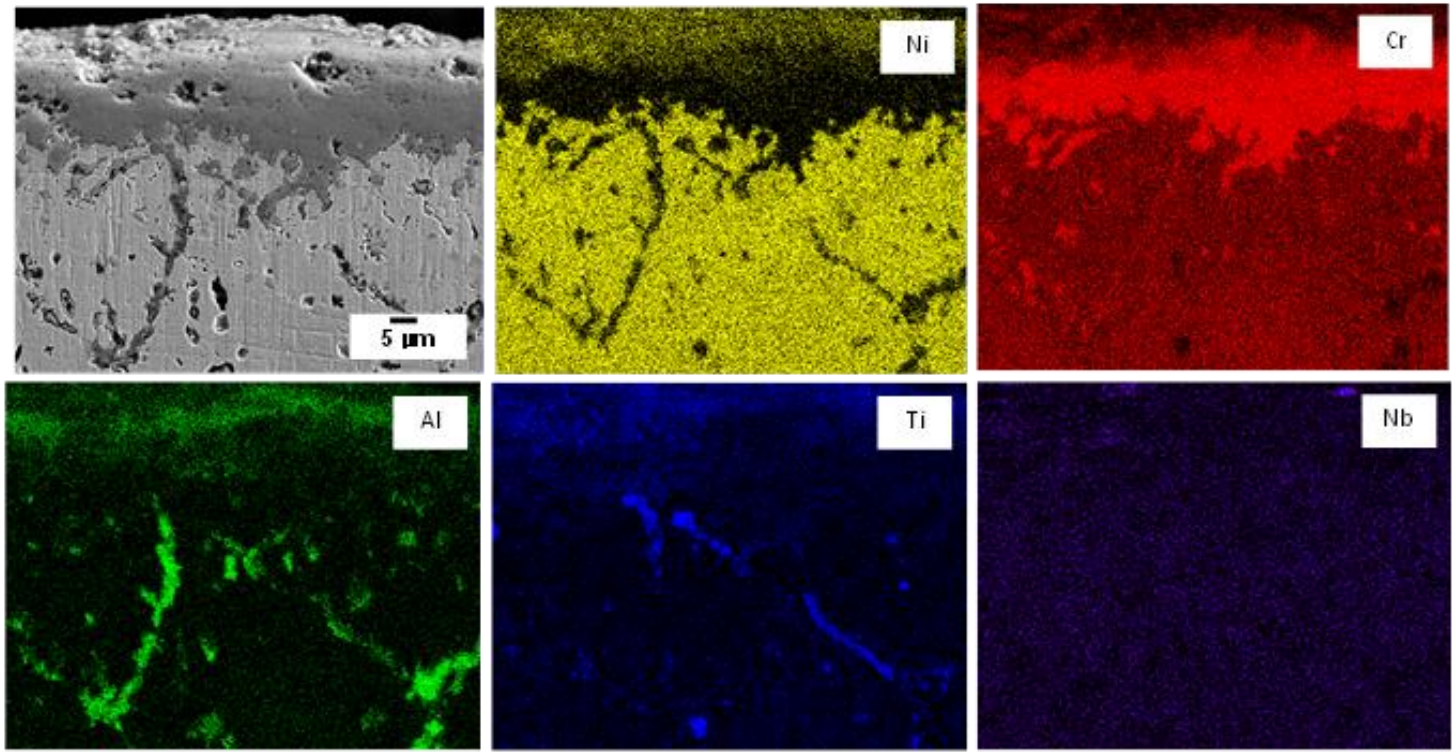
# Task 4 - In-situ Corrosion Monitoring Testing in Utility Boilers


***Subtask 4.1** Sensor Placement and Installation*

***Subtask 4.2** Sensor Testing*

***Subtask 4.3** Post Mortem Analyses*

***Subtask 4.4** Prepare and Submit Media-Ready Documentation of the Test Results*



# Task 5 - Corrosion Database Development

***Subtask 5.1*** *Lab-scale Sensor Optimization*

***Subtask 5.2*** *Electrochemical and Corrosion Monitoring Validation*

***Subtask 5.3:*** *Post-mortem Analysis*

***Subtask 5.4:*** *Electrochemical and Corrosion Database and Predictive Model Development*

***Subtask 5.5:*** *Corrosion Monitoring Software Development*

# Task 6 - Tech-Transfer & Commercialization

- Historical generation data will be obtained from Ventyx Velocity Suite and Generating Availability Data System (GADS) from North American Electric Reliability Council (NERC)
- Duration and cause of forced outage information will be obtained from NERC GADS.
- Analysis of more than 1500 fossil-fired units in 2015 shows that the boiler tube failure (mainly water tube, reheater, and superheater) remains the leading cause for forced outage causing loss of 600 TWh of power (NERC GADS, 2016)
- Revenue loss due to forced outages in larger power plants is significantly higher than the smaller ones. For example, the loss in revenue in 2015 in a 1000 MW power plants was about 5 times that of a 300 MW plant (NERC GADS, 2016). Thus large power plants such as Longview is an ideal candidate.

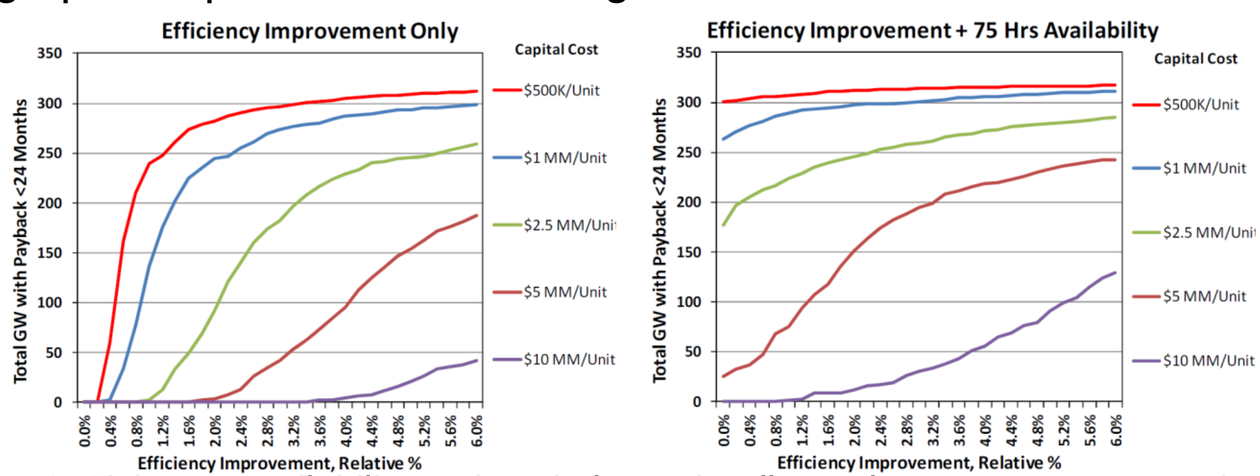



Figure: Impacts of efficiency, availability and capital cost (Krulla et al. NETL Report, DOE/NETL-342/03082013)

# Task 6 - Tech-Transfer & Commercialization

- Assessment of the potential economic and environmental benefits of the proposed corrosion sensor will be obtained using the National Energy Modeling System (NEMS) software from Energy Information Administration (EIA).

- NEMS projects the production, imports, conversion, consumption, and prices of energy, subject to various assumptions, providing an integrated projection.

- In contrast to the NPV analysis which provides information about economic feasibility at a single time point, the NEMS software can provide information about the change in the cost of electricity because of the higher availability of the power plant.

- With a detailed evaluation of the entire energy economy, the NEMS software will also provide information about the environmental impact such as change in the $CO_2$ and $SO_2$ emission due to the increased availability.

- Results from the TEA can be leveraged for securing potential investments.

# Task 6 - Tech-Transfer & Commercialization

- Sensor deployment cost will be calculated assuming ‘N$^{th}$ of a kind’ deployment.
- Monte Carlo analysis in the TEA will be undertaken for uncertain variables such as the extent of market penetration and true reduction in forced outage.
- Uncertainty analysis would yield information such as the 95% confidence interval for achieving the payback within a desired period and the uncertainty bound on the NPV at the end of the project period.
- Due to the confounding effects of various operating variables, especially under load-following operation, it is very difficult to identify the real cause(s) of a corrosion failure simply through post-mortem analysis. The sensor can be helpful in understanding the effect of various operating conditions on the corrosion rate and thus can be helpful in identifying the root cause(s).
- Eventually, the sensor can also be helpful to develop active feedback control strategies as part of the plant coordinated control strategy, thereby resulting in an increased boiler life.

# ACKNOWLEDGEMENT

**DoE Award No. DE-FE5717**

- DoE-NETL Coal Utilization Sciences Program
- Bob Romanosky, Susan Maley, Chuck Miller etc.
- WVU Team: Ed Crowe, Naing Naing Aung, Meng Yao, Greg Collins, Kathleen Cullen etc.
- Industrial Partners: WRI (Don Collins, Vijay ), Special Metals (Jack deBarbadillo, Brian Baker, Gaylord Smith), ILZRO (Frank Goodwin)

**DoE Award No. DE-FE31548**

- Cross-cutting Program: Briggs White, Sidni CJessica Mullen
- Current Team: WVU (Debangsu Bhattacharyya, Trina Wafle), Aspinity (Brandon Rumberg), Longview (Chad Hufnagel)


Thanks