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

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OUTLINE

- Technical Background
- Project Objectives
- Field Test Results
- Lab-Scale Sensor Optimization
- Corrosion Database Development
- Techno-Economical Analysis Progress
- Summary and Future Work
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

- Oxidation in Cr,Ni-rich regions
- External Sulfidation in Cr,Ni-rich regions
- Internal Sulfidation in Ni,Cr-rich regions

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
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
Evaluation of Corrosion Kinetics via EN Technique

![Graph showing corrosion rate vs. exposure time](image)

- Accelerated internal sulfidation at 750 °C
- Oxidation in the flue gas without SO₂
- Internal sulfidation at 800 °C
- External sulfidation at 700 °C

![Graph showing accumulated mass loss vs. exposure time](image)

- Accelerated internal sulfidation in deep coal ash
- Oxidation in the flue gas without SO₂
Reproducibility of Potential and Current Signals During Oxidation and Sulfidation

INCONEL 740 alloy + 850 °C + Thin coal ash + without /with SO$_2$
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*). These signatures can be seen clearly at 750°C, in the flue gas without SO$_2$ as well as deep coal ash.
- The noise pattern of sudden change in current values followed by slow or no recovery corresponded with the Accelerated Oxidation/Sulfidation (*Noise Signature V*).
Sensor Testing @ Prototype Boiler

Wireless Sensing System for Concurrent Potential and Current Signals Measurement

Technology Readiness Level - 5
Project Objectives

- To validate the effectiveness of the Recipient’s lab-scale 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-5) to reach TRL-6;

- To develop a pathway toward commercialization of such technology.
## Planned Tasks & Deliverables

<table>
<thead>
<tr>
<th>ID</th>
<th>Task</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Project management</td>
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<tr>
<td>2</td>
<td>Sensor development &amp; optimization</td>
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<td>2.1</td>
<td>Design &amp; construct sensors</td>
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<td>Sensor packaging</td>
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<td>3</td>
<td>Signal processing &amp; communication instruments</td>
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<td>4</td>
<td>Corrosion sensor testing @ Longview Power’s boiler</td>
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<tr>
<td>4.1</td>
<td>Sensor placement and installation</td>
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<td>4.2</td>
<td>Sensor testing</td>
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<td>4.3</td>
<td>Post-mortem analyses</td>
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<td>5</td>
<td>Corrosion monitoring software &amp; database development</td>
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<td>5.1</td>
<td>Lab-scale sensor optimization</td>
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<td>5.2</td>
<td>Electrochemical and corrosion monitoring validation</td>
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<td>Post-mortem analysis</td>
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<td>Database and predictive model development</td>
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<td>Software development</td>
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<td>6</td>
<td>Tech-transfer &amp; commercialization</td>
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<td>6.1</td>
<td>NPV model &amp; uncertainty analysis</td>
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<td>6.2</td>
<td>NEMS model and economic analysis</td>
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<td>6.3</td>
<td>Commercialization pathway development</td>
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- 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
## Sensor Testing @ Longview Power

<table>
<thead>
<tr>
<th></th>
<th>Monongalia County near Maidsville, WV</th>
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<tbody>
<tr>
<td><strong>Status</strong></td>
<td>Operational</td>
</tr>
<tr>
<td><strong>Commission date</strong></td>
<td>2011</td>
</tr>
<tr>
<td><strong>Owner(s)</strong></td>
<td>Longview Power</td>
</tr>
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</table>

### Thermal power station

<table>
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<tr>
<th><strong>Primary fuel</strong></th>
<th>Coal and natural gas</th>
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<tbody>
<tr>
<td><strong>Type</strong></td>
<td>Steam turbine</td>
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### Power generation

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<tr>
<th><strong>Nameplate capacity</strong></th>
<th>700 MW</th>
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- 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 CO2 than most other coal plants because of its [fuel efficiency](#).
Sensor Testing Locations

① Superheater/Reheater tubes:
High Temperature and Pressure,
Deposit-induced molten salt corrosion,
Made of nickel, inconel alloys or fire-resistant stainless steel.

② Waterwall tubes:
Relatively low temperature,
Mainly made of carbon steel,
High corrosion rate but low maintenance cost;
Passive Sensor Design

Installation of passive sensor (weight loss)

Temperature gradients through the waterwall tube[1]
Bolt-like passive sensor installed on the membrane between tubes for both the waterwall and superheater.
ECN Corrosion Sensor Design

Air flow

Signal recording

Compressed air

▲ Air cooling system designed to control the sensor temperature

Potential noise

Current noise

WE1
WE2
WE3
RE
Corrosion sensor installed at the superheater/reheater
ECN sensor system installed through the observation port near superheater (11th floor of the boiler). The temperature was controlled at around 548 °C, which is the temperature of superheater fireside.
Predictive Model Development - Calculations of Corrosion Kinetics

① Electrochemical Noise: as the main method to monitor the corrosion rate.

\[ V_{corr} = \frac{A}{R_p} \quad R_n = \frac{\sigma_v}{\sigma_i} \quad \text{or} \quad R_{sn} = \lim_{f \to 0} \frac{PSD_v}{PSD_i} \]

Determined by Stern coefficient

② Electric Resistance (ER): as the method to verify the results of ECN.

\[ \Omega = f(t) \rightarrow V_{corr} = h(t) \]

③ Passive Sensor (Weight Loss): as the method to calibrate the results of ECN.

\[ H_{corr} = \int_0^T V_{corr} \, dt \]

④ Surface analysis: SEM, EDX, 3D OM, et al. to verify the corrosion behavior and mechanism.
The potentiodynamic polarization curves measured at the waterwall place (400°C) and the superheater place (548°C).

\[
V_{corr} = \frac{A}{R_p} \approx \frac{A}{R_n} = \frac{3.27 \times B \times M}{n \times \rho \times R_n}, \quad B = \frac{\alpha \beta}{\alpha + \beta}
\]

For Fe→Fe³⁺, \(n=3\), \(\rho=7.8\) g/cm³, \(M=56\) g/mol

<table>
<thead>
<tr>
<th>Locations</th>
<th>Anodic tafel slope, (\alpha) (mV/decade)</th>
<th>Cathodic tafel slope, (\beta) (mV/decade)</th>
<th>Stern-Geary coefficient, (B) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waterwall</td>
<td>1034.40 ± 224.51</td>
<td>145.30 ± 3.25</td>
<td>127.40</td>
</tr>
<tr>
<td>Superheater</td>
<td>810.08 ± 159.98</td>
<td>200.49 ± 17.72</td>
<td>160.71</td>
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</tbody>
</table>
The electrochemical noises measured at the waterwall place (400ºC) since Nov. 19th 2018.

- Typical sharp transient peaks indicate the quick occurrence and recovery of pitting corrosion.

The electrochemical noises measured at the superheater place (548ºC) since Nov. 19th 2018.
The ECN data were converted into corrosion indexes and corrosion rate by using Matlab. We hope that the data could be converted and displayed in real time.
Field Measurement Results

▲ Corrosion indexes calculated from the electrochemical noises measured at the waterwall place.

(\( R_n \) represents the corrosion resistance, PI represents the localized corrosion tendency, \( V_{corr} \) represents the corrosion rate.)

✓ Some corrosion details can be seen from these corrosion indexes.

▲ Corrosion indexes calculated from the electrochemical noises measured at the superheater place.
\[\text{▲ Time dependence of the accumulated corrosion depth calculated from the electrochemical noises measured at the waterwall.}\]

\[\text{▲ Time dependence of the accumulated corrosion depth calculated from the electrochemical noises measured at the superheater place.}\]
Lab-Scale Sensor Optimization

The potential difference between the two identical REs measured at the initial time is $\Delta E < 10 \text{ mV}$. The potential difference between the two identical REs measured after 20 hours is also shown on the graph.
The OCP of 347 stainless steel measured with modified RE in coal ash

The PDP curves of 347 stainless steel measured with modified RE in coal ash

Tests verified that the custom-designed RE can be reliable.
✓ The new-made sensor using the modified RE and the ceramic casting powder works well during 72 hours at 1000 ºC. The durability still needs to be verified on site in the boiler.
Techno-Economic Analysis - Motivation

- As per State of Reliability (SOR) report by North American Electric Reliability Council (NERC), waterwall failure accounts for about 6-7% of the production lost due to forced outages over past several years.

- Revenue lost 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 than that of a 300 MW plant (NERC GADS, 2016). Thus large power plants such as Longview is an ideal candidate.

Impacts of efficiency, availability and capital cost (Krulla et al. NETL Report, DOE/NETL-342/03082013, 2013)
TEA - Approach

NEMS projects the production, consumption, and prices of energy, subject to various assumptions. The projection horizon is approximately 25 years into the future.

Sensor Model Development

Estimator Development

Optimal Sensor Network Synthesis Algorithm

Techno-Economic Measures (Number of sensors and their locations, NPV, etc.)

SOR Report, Ventyx Velocity

Optimal filters that use the measurements from corrosion sensors along with a corrosion rate model to estimate the spatial and temporal profile of corrosion in the water wall section.

Provides historical data related to performance and analysis of electric generating equipment. (Data related to forced outages and their causes)
Comparison of experimental vs model corrosion rates at different temperatures and partial pressures of SO₂

• Various optimal linear and nonlinear filtering algorithms have been developed for estimation in the face of missing and/or noisy measurements.

• Example results using a nonlinear estimator for a heat exchanger (representing a superheater) shows that even though there is high measurement noise, the estimation is were not available at certain time instants (5 of them).
A cost-Optimal sensor network synthesis algorithm is being developed.

The objective function takes into account the capital cost of sensors including installation while considering the improvement in plant profitability due to the increased availability because of the installation of the corrosion sensors.

The integer programming problem is solved by using a genetic algorithm.
• Corrosion model will be validated with the recently obtained in-house experimental data.

• The estimator framework will be completed for corrosion for the water wall section.

• Optimal sensor network will be synthesized. To this end, information from the NEMS software will be extracted to obtain the cost of improved availability.

• Techno-economic analysis will be conducted for the optimal sensor network.
SUMMARY & FUTURE WORK

Progress-to-date
- 1st generation sensors has been installed @ Longview
- Data obtained seems to be stable & reasonable
- Software to directly convert electrochemical signal to corrosion rates has been developed. Real time corrosion monitoring realized
- Lab-scale RE development and corrosion database development are ongoing

Future work
- Continue optimizing the design and materials.
- Incorporate the new RE in the sensor.
- Install the sensor on the sites where corrosion occurs most severely.
- Design and fabricate a wireless communication set for the interface unit.
- Continuing database development.
DoE-NETL:
- DE-FE5717: Bob Romanosky, Susan Maley, Chuck Miller, etc.
- DE-FE 31548: Briggs White, Sydni Credle, Jessica Mullen, etc.

Collaborators and Partners:
- WRI - Don Collins, Vijay Sethi
- Special Metals - Jack deBarbadillo, Brian Baker, Gaylord Smith
- ILZRO - Frank Goodwin
- NETL-Albany - Paul Jablonski, Jeff Hawk, Gordon Holcomb, Dave Alman etc.