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

Xingbo Liu, Debangsu Bhattacharyya, Shanshan Hu, Tianliang Zhao, Liang Ma
West Virginia University
Brandon Rumberg
Aspinity
Jared Custer, Chad Hufnagel
Longview Power
OUTLINE

- Technical Background
- Project Objectives
- Field Test Results
- Reference Electrode Development
- Corrosion Database Development
- Techno-Economical Analysis Progress
- Summary and Future Work
- Acknowledgement
Hot corrosion: the degradation of an alloy at elevated temperature induced by a thin molten salt layer under an oxidizing atmosphere.

<table>
<thead>
<tr>
<th>Sulfate salt</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td>884</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>1069</td>
</tr>
<tr>
<td>Na$_2$SO$_4$-CoSO$_4$</td>
<td>575</td>
</tr>
<tr>
<td>K$_2$SO$_4$-CoSO$_4$</td>
<td>535</td>
</tr>
<tr>
<td>K$_2$Fe(SO$_4$)$_3$</td>
<td>624</td>
</tr>
<tr>
<td>Na$_3$Fe(SO$_4$)$_3$</td>
<td>618</td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_7$</td>
<td>400.9</td>
</tr>
<tr>
<td>K$_2$S$_2$O$_7$</td>
<td>325</td>
</tr>
</tbody>
</table>

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

Conceptual design of the self-powered HT corrosion sensor system

Two stages of hot corrosion were revealed by SEM: oxidation and sulfidation (external sulfidation and internal sulfidation).

Morphology and element distribution of cross-sectional morphology of corroded sample

Reproducibility of Potential and Current Signals During Oxidation and Sulfidation

Both potential and current noise are effective and efficient signals to reveal the stages of corrosion process (oxidation and sulfidation) in the simulated coal-fired power plant environment.

Fig. 6 (a) potential and (b) current noise signals obtained for Inconel 740 alloy beneath a thin layer of coal ash at 850 °C.

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.

Publications in Peer-Reviewed Journals

Effect of SO₂ in flue gas on coal ash high-temperature electrochemical corrosion

Nan-Ning Aung, Xingbo Liu

Department of Power Engineering, University of Minnesota, Minneapolis, MN 55455, USA

Abstract

The effect of SO₂ in flue gas on the electrochemical corrosion of coal ash was investigated. The experiments were conducted using a high-temperature microelectrochemical corrosion cell. The results showed that SO₂ significantly increased the corrosion rate of coal ash. The corrosion rate was found to be dependent on the concentration of SO₂ in the flue gas. The mechanism of SO₂-induced corrosion was also discussed.

Keywords: electrochemical corrosion, coal ash, SO₂, high-temperature corrosion.
Sensor Testing @ Prototype Boiler

Fig. 3 Corrosion and Wireless Sensor Location at WRI’s Combustion Test Facility

Photographs of WVU high temperature corrosion sensor: (a) new sensor; (b) sensor 45 days post-exposure in boiler at WRI’s Combustion Testing Facility
Project Objectives

➢ To validate the effectiveness of our 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></td>
<td></td>
<td>Q1</td>
<td>Q2</td>
<td>Q3</td>
</tr>
<tr>
<td>1</td>
<td>Project management</td>
<td></td>
<td></td>
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<tr>
<td>2</td>
<td>Sensor development &amp; optimization</td>
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<tr>
<td>2.1</td>
<td>Design &amp; construct sensors</td>
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<td>2.2</td>
<td>Sensor packaging</td>
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<tr>
<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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<tr>
<td>5.2</td>
<td>Electrochemical and corrosion monitoring validation</td>
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<tr>
<td>5.3</td>
<td>Post-mortem analysis</td>
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<tr>
<td>5.4</td>
<td>Database and predictive model development</td>
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<tr>
<td>5.5</td>
<td>Software development</td>
<td></td>
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<tr>
<td>6</td>
<td>Tech-transfer &amp; commercialization</td>
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<tr>
<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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<tr>
<td>6.3</td>
<td>Commercialization pathway development</td>
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</table>

- 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
Location | Monongalia County 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 is among the lowest in the nation for coal plants.
- Emits less CO₂ than most other coal-fired power plants because of its high fuel efficiency.
Sensor Testing Locations

Superheater/reheater tubes working conditions: high temperature and pressure (550-750°C, 30MPa), high salt concentration (\(\text{Na}_2\text{SO}_4, \text{K}_2\text{SO}_4\)), corrosive flu gas (\(\text{O}_2, \text{SO}_2\), and \(\text{SO}_3\)).

Component: Nickel-based alloys (e.g., 282, 740) or fire-resistant stainless steel (e.g., 347H).
ECN Corrosion Sensor Design

Data Acquisition System

- Voltmeter
- Ammeter
- Resistance meter
- Thermometer

Stainless steel tube

Alumina tube

Temperature controller

Air compressor

Air flow

B-B

A-A

B

Ceramic casting

TC
Sensor Packaging-Data Acquisition System

- This data acquisition system has a reliable accuracy.
- The latest version also enables remote data collection (developed in Feb 2020).

[Left] PIECES hardware. (a) Top view of the fully-assembled device. (b) Bottom view of the Front Panel. (c) Top view of the Measurement Board. [Right] Verification of each measurement type.

Envisioned data pipeline for the corrosion sensor.
Sensor Packaging - Data Acquisition

✓ Easy access to real-time data stored in the Cloud
Sensor Placing and Installation-ECN Sensor

✓ An updated electrochemical sensor was successfully installed on Aug 30th, 2019

ECN sensor system installed through the observation port near superheater (11th floor of the boiler).
Field Measurement Results - PDP curves

- PDP curve was successfully obtained after 1d, demonstrating the formation of molten salt layer on 347H SS.
- Stern-Geary coefficient was calculated from PDP curve as 69.78.

The potentiodynamic polarization (PDP) curve of 347H SS measured at superheater place (550ºC)

Parameters obtained from the PDP

<table>
<thead>
<tr>
<th>Materials and location</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>347 SS, Superheater</td>
<td>810.08±159.98</td>
<td>200.49±17.72</td>
<td>69.78</td>
</tr>
</tbody>
</table>

Anodic reaction: $\text{Fe} - 3e^- \rightarrow \text{Fe}^{3+}$

$n=3$, $\rho=7.8$ g/cm$^3$, $M=56$ g/mol
Predictive Model Development - Calculations of Corrosion Rate

✓ Corrosion depth can be calculated by EN data through eq. (6).

Measure PDP Reference Curve using an Electrochemical Workstation

Calculate the Tafel Slope from the PDP Reference Curve using Eq. 1

Calculate the Corrosion Current using Eq. 2

Calculate the Corrosion Rate using Eq. 3

Measure Potential Noise and Current Noise by Voltmeter and Ammeter

Calculate the Noise Resistance from the Potential Noise and Current Noise using Eq. 4

Replace Polarization resistance ($R_p$) by Noise Resistance ($R_n$)

Calculate the Corrosion Rate using Eq. 5

Introduce constants $M = 56, n = 3, \rho = 7.874, B = 69.78$

Calculate Corrosion Rate using Eq. 6

Processes to calculate the corrosion depth by electrochemical noise data

\[
B = \frac{\alpha \beta}{\alpha + \beta} \quad (1)
\]

\[
I_{corr} = \frac{B}{R_p} \quad (2)
\]

\[
V_{corr} = \frac{3.27 \times B \times M}{n \times \rho \times R_p} \quad (3)
\]

\[
R_n = \frac{\sigma_v}{\sigma_i} \quad (4)
\]

\[
V_{corr} = \frac{3.27 \times B \times M}{n \times \rho \times R_n} \quad (5)
\]

\[
V_{corr} = \frac{540.9}{R_n} \quad (6)
\]
The latest electrochemical sensor works well in the last seven months.

EN data was successfully collected unless the boiler is down.

Electrochemical noises measured at the superheater (548°C) since Aug 30th, 2019.
EN data were readily converted into corrosion rate by using MATLAB.
Field Measurement Results – Corrosion Rates

✓ The corrosion depth calculated by EN data is about ___ mm in last six months.
Two kinds of coal ashes have different crystal structures.
The main elements in both sets of coal ash are O, Al, Si, Fe, Ca, Na, K.
Some alkaline sulfate (Na$_2$O, K$_2$O and SO$_3$) was confirmed in both kinds of coal ashes.

Some metal oxides are found in both coal ashes.

Analysis result is similar to others reported in the literature.

Various oxides in two kinds of coal ashes from Longview:

<table>
<thead>
<tr>
<th></th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>MnO</th>
<th>P$_2$O$_5$</th>
<th>K$_2$O</th>
<th>SiO$_2$</th>
<th>Na$_2$O</th>
<th>SO$_3$</th>
<th>TiO$_2$</th>
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<tbody>
<tr>
<td>120</td>
<td>20.88</td>
<td>5.18</td>
<td>11.82</td>
<td>1.15</td>
<td>0.05</td>
<td>0.23</td>
<td>2.26</td>
<td>49.17</td>
<td>0.64</td>
<td>0.92</td>
<td>0.99</td>
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<tr>
<td>122</td>
<td>61.46</td>
<td>2.33</td>
<td>0.62</td>
<td>0.08</td>
<td>0.01</td>
<td>0.20</td>
<td>0.10</td>
<td>27.81</td>
<td>0.21</td>
<td>0.08</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Representative chemical compositions of the coal ash in Literature:

<table>
<thead>
<tr>
<th></th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>Na$_2$SO$_4$</th>
<th>K$_2$SO$_4$</th>
<th>NaCl</th>
<th>CaSO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>29.25</td>
<td>29.25</td>
<td>29.25</td>
<td>29.25</td>
<td>5.625</td>
<td>5.625</td>
<td>5.625</td>
<td>1</td>
</tr>
<tr>
<td>22</td>
<td>6</td>
<td>39</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>29</td>
</tr>
</tbody>
</table>
 Experiment conditions (gas composition and coal ash composition) were decided based on the analysis result and reported data in literature.

347H, component of the superheater, was obtained from Longview Power Plant.

Representative chemical composition of the flue gas in literature

<table>
<thead>
<tr>
<th></th>
<th>N₂</th>
<th>CO₂</th>
<th>SO₂</th>
<th>O₂</th>
<th>H₂O</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>81.25</td>
<td>15</td>
<td>0.25</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>15</td>
<td>1</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bal.</td>
<td>13.4</td>
<td>1300 vpm</td>
<td>4</td>
<td>8.6</td>
<td>400 vpm</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>10</td>
<td>1.5</td>
<td>3.5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>82.9</td>
<td>14</td>
<td>0.1</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Element composition of the 347H obtained from Longview Power Plant

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Nb</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight ratio (%)</td>
<td>0.041</td>
<td>1.75</td>
<td>0.02</td>
<td>0.003</td>
<td>0.32</td>
<td>17.52</td>
<td>9.22</td>
<td>0.26</td>
<td>0.71</td>
<td>Bal</td>
</tr>
</tbody>
</table>
Corrosion Database Development - Effect of Temperature

✓ OCP increases by time because of the growth of passive film
✓ This reference electrode can provide a stable potential at this working environment.

(a) OCP of 347H in the first 1h and (b) potentiodynamic polarization curve (PDP) at various temperature
Corrosion Database Development - Effect of Temperature

- Potential noise reveals two stages of the corrosion process: **oxidation** from 1 to 49h, **sulfidation** after 49h.

- Current noise needs to be verified again.

Time sequences of (a) potential and (b) current noise at 550 °C in a 7d exposure period.
✓ Corrosion resistance varies by time at 550 °C.
✓ $R_n$ and $R_{sn}$ show the same trend.

Variation of (a)$R_n$ and (b)$R_{sn}$ at different exposure time at 550 °C
Localized corrosion occurs at 550 ºC

(a) Localization index at various exposure time and (b) PDP curve after 7d exposure at 550 ºC
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)
NEMS projects the production, consumption, and prices of energy, subject to various assumptions. The projection horizon is approximately 25 years into the future.

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)

Sensor Model Development

Estimator Development

SOR Report, Ventyx Velocity

Optimal Sensor Network Synthesis Algorithm

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

- TIMES model generator is used to explore possible energy futures based on scenarios.
- A scenario is created by increasing availability of the coal fired power plants due to the use of the corrosion sensors by about 5% compared to current value.
- The electricity produced by coal fired power plants in the U.S. is computed by the EPAUS9rT model with and without scenario. The results are compared with that from AEO 2019 report.

Comparison of amount of electricity generated from coal (billion kWh) from that of the AEO 2019 report, and EPAUS9rT model with and without scenario

Comparison of amount of electricity generated from solar energy (billion kWh) from that of the AEO 2019 report, and EPAUS9rT model with scenario
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.
SUMMARY & FUTURE WORK

Progress-to-date

➢ Last sensors has been running @ Longview for seven month with good performance
➢ Remote data collection has been enabled and data obtained seems to be stable & reasonable
➢ Real time corrosion monitoring has been realized
➢ A predictive model has been developed to calculate the corrosion rate by EN data
➢ Lab-scale RE with good stability and reproducibility has been developed.
➢ Corrosion database development and techno-economical analysis (TEA) are ongoing in schedule.

Future work

➢ Incorporate the new RE in the sensor @ Longview.
➢ Design an anti-dust data acquisition system.
➢ Continue corrosion database development.
➢ Continue techno-economical analysis (TEA)
  ➢ using the optimal sensor network
  ➢ Work is also being continued on extracting the projected cost of electricity produced as well from TIMES.
AKNOWLEDGEMENT

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• Special Metals - Jack deBarbadillo, Brian Baker, Gaylord Smith
• ILZRO - Frank Goodwin
• NETL-Albany - Paul Jablonski, Jeff Hawk, Gordon Holcomb, Dave Alman etc.
• Longview Power – Jared Custer, Chad Hufnage, Jeffrey Westfall
• Aspinity - Brandon Rumberg, Don Boucher