DOE Award DE-FE0031548

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

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

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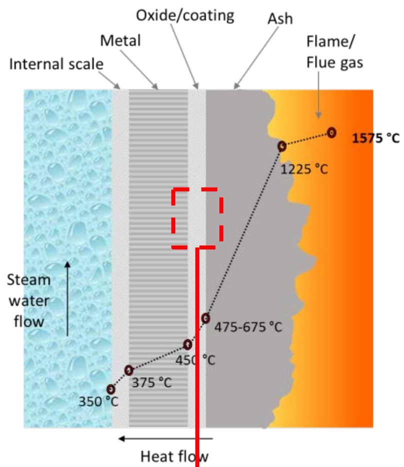
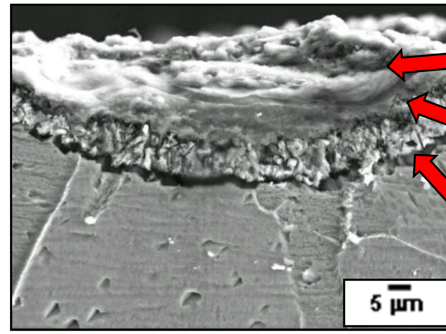
OUTLINE

- 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

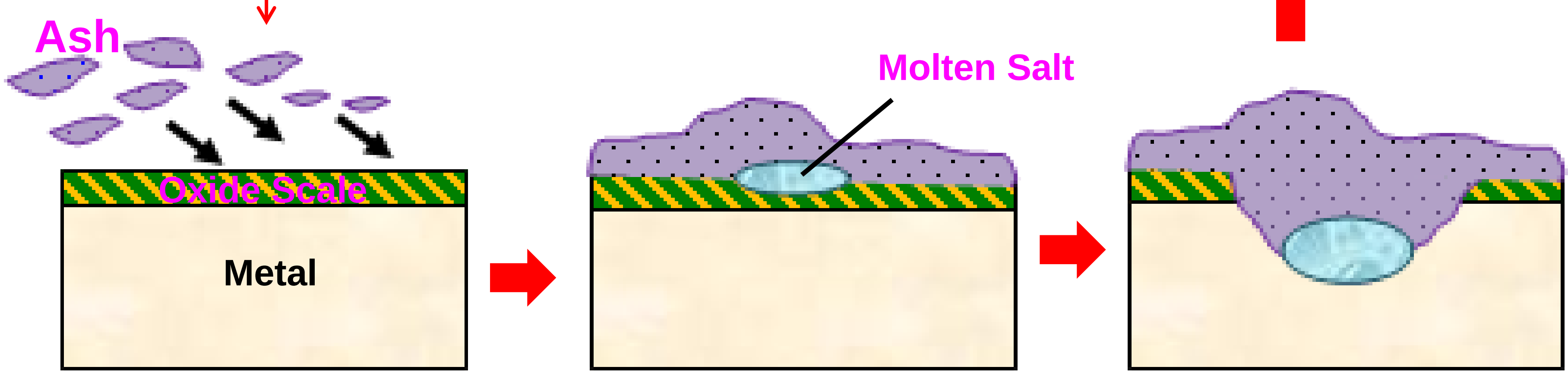




Oxidation in Cr,Ni-rich regions

External Sulfidation
in Cr,Ni-rich regions

Internal Sulfidation
in Ni,Cr-rich regions



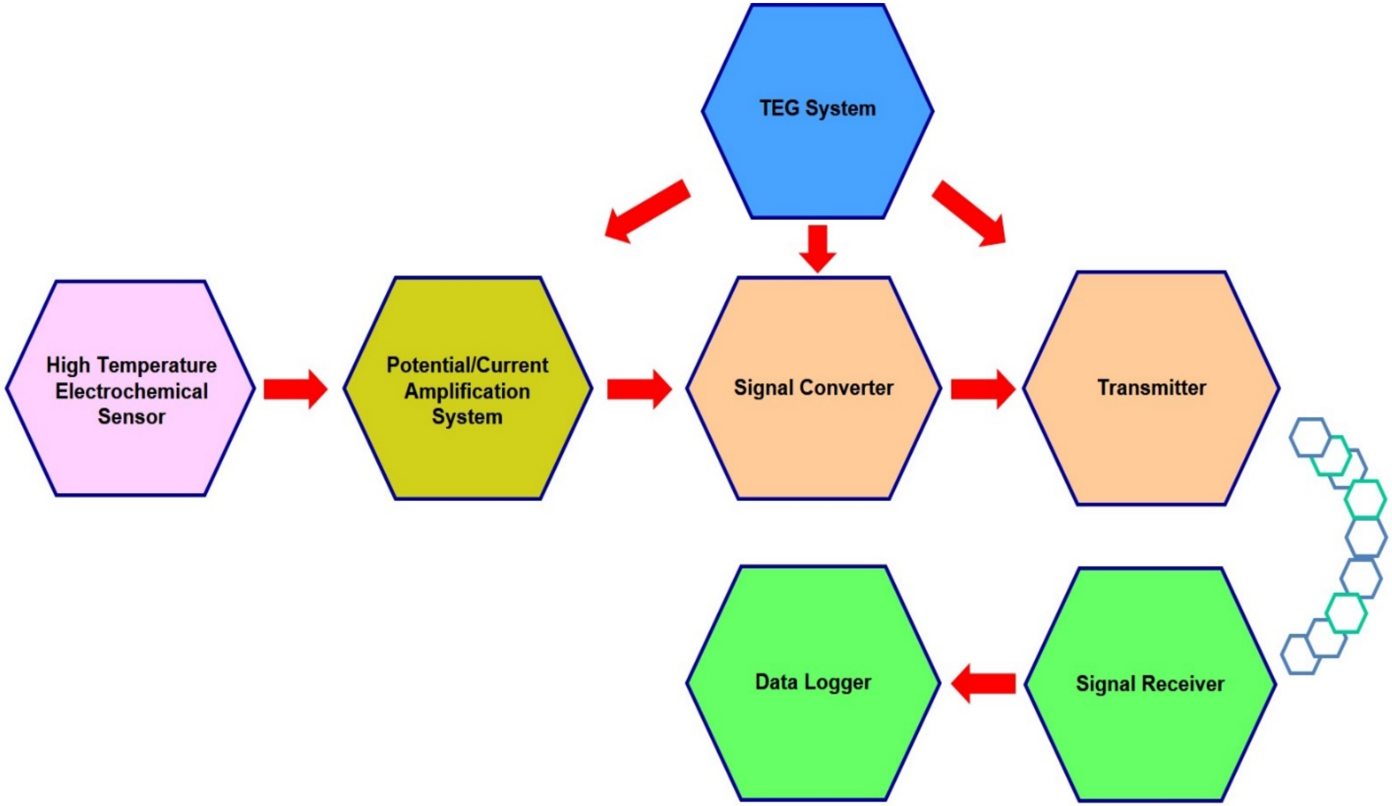
Ash deposition

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

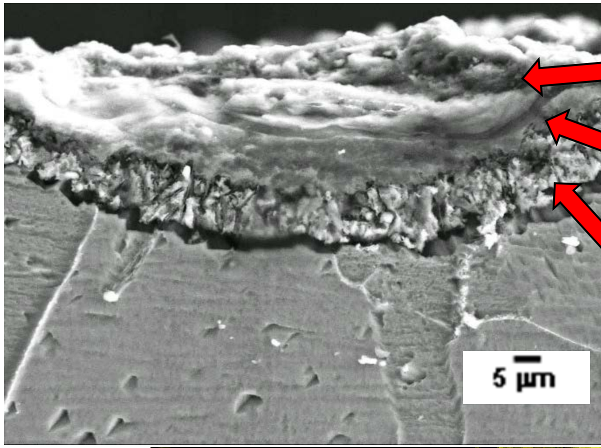
Direct reaction between bare metal and reduced sulphate species

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



Oxygen and Sulfur Diffusion During Oxidation & Sulfidation Stages



Oxidation in Cr,Ni-rich regions

External Sulfidation
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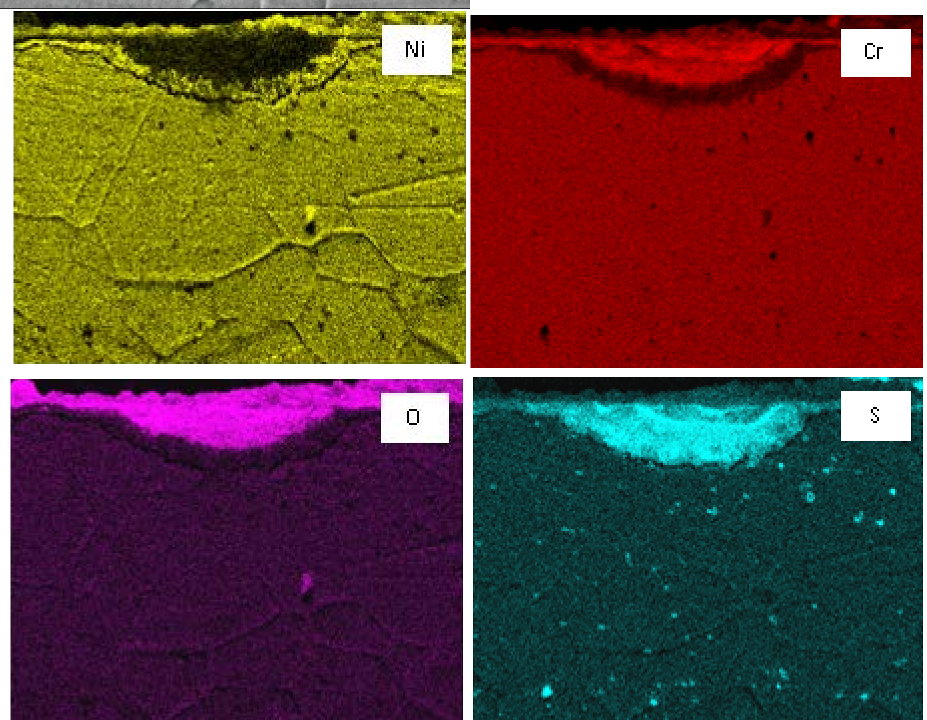
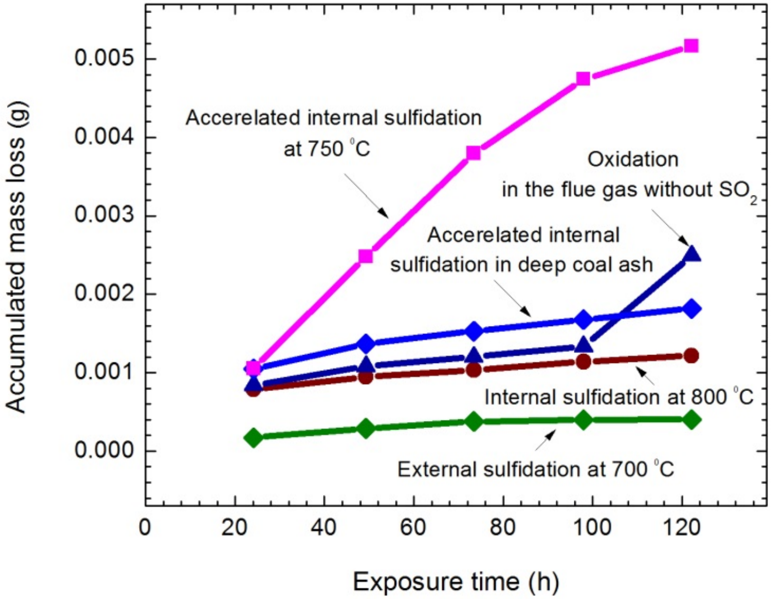
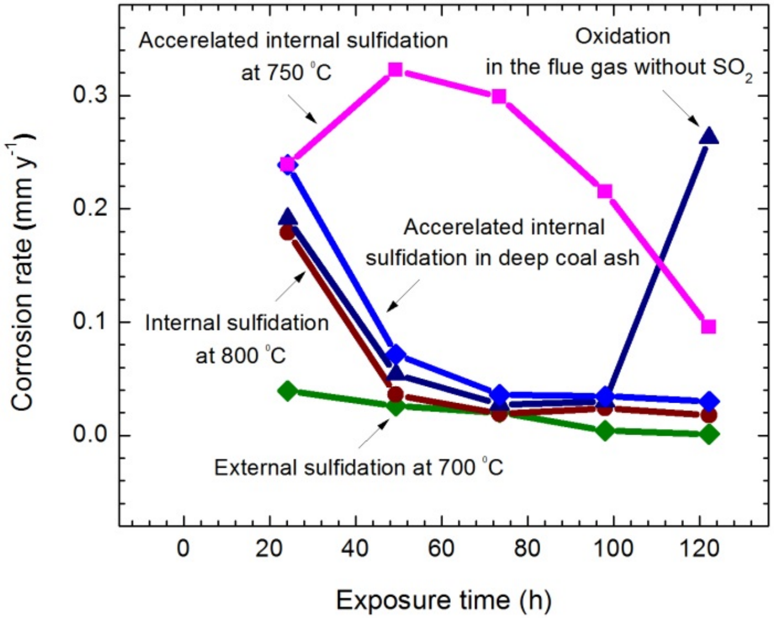
Internal Sulfidation
in Ni,Cr-rich regions



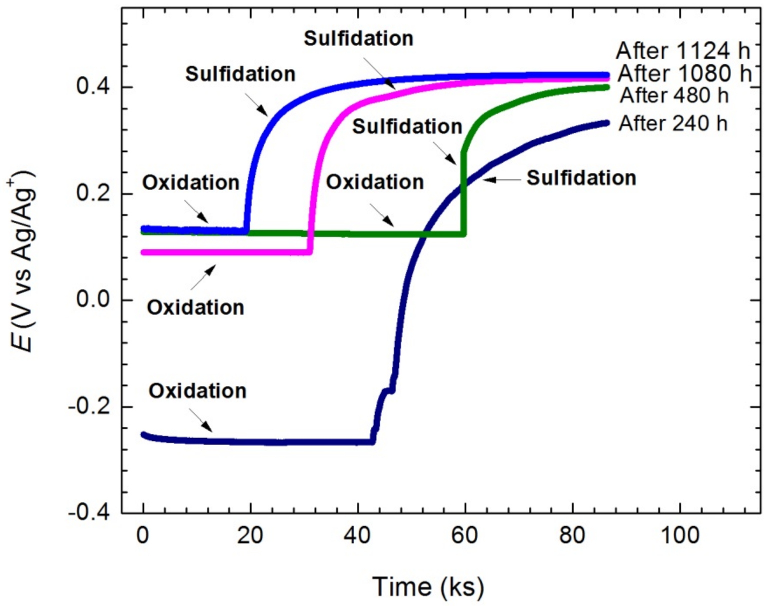
Evaluation of Corrosion Kinetics via EN Technique

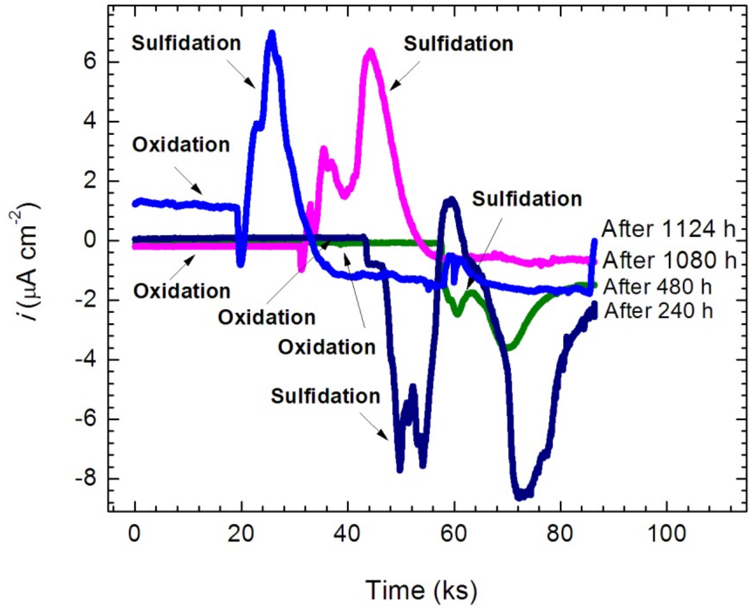




Reproducibility of Potential and Current Signals During Oxidation and Sulfidation

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





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

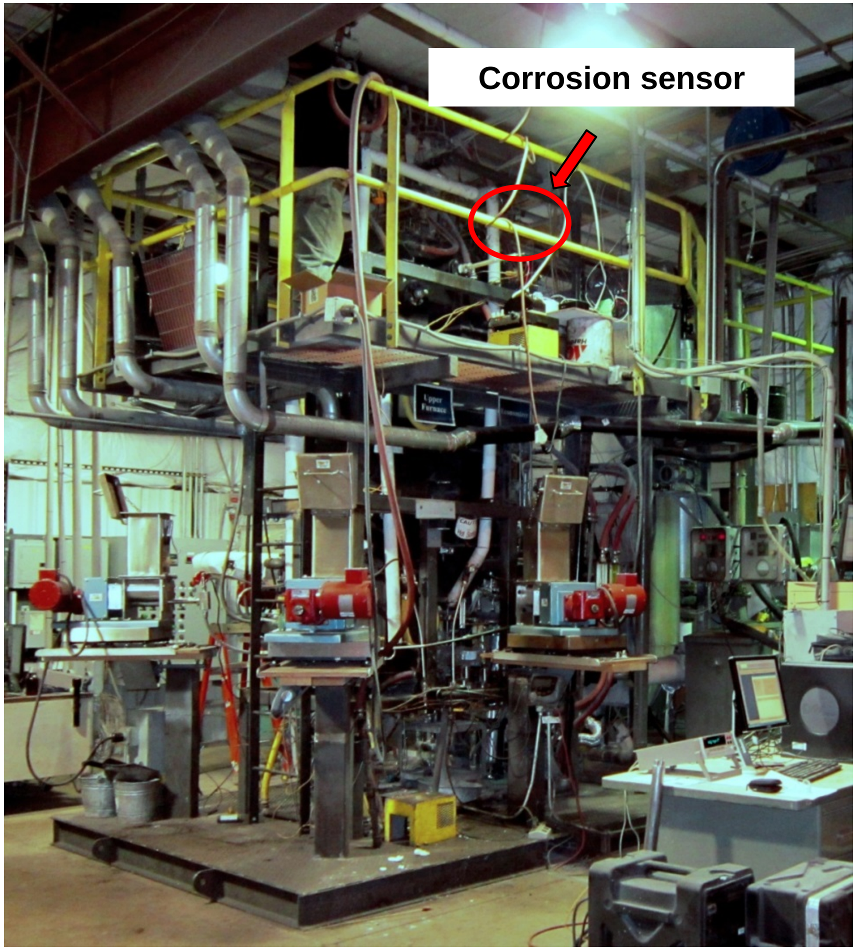
Electrochemical Potential Noise Signals

- 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

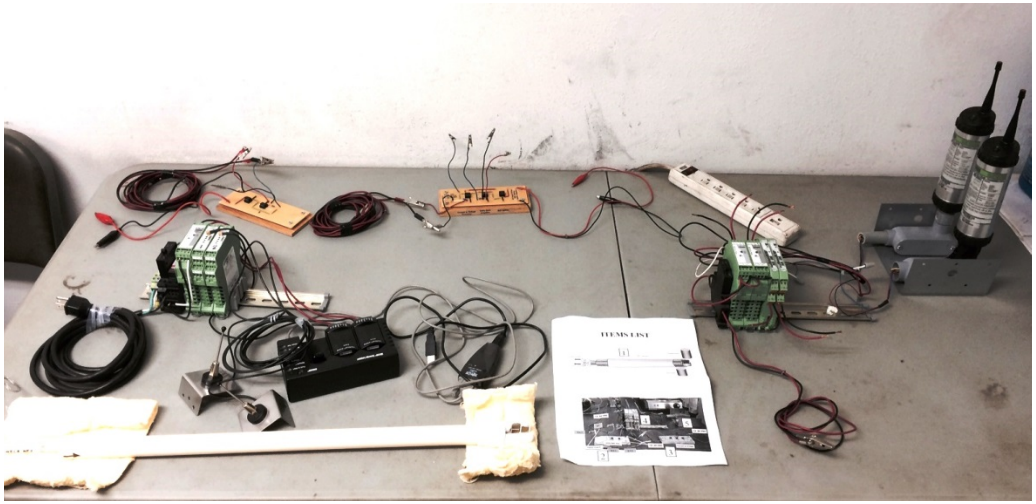
Electrochemical Current Noise Signals

- 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**)*.
- 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.

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

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						■	■			■	■	■

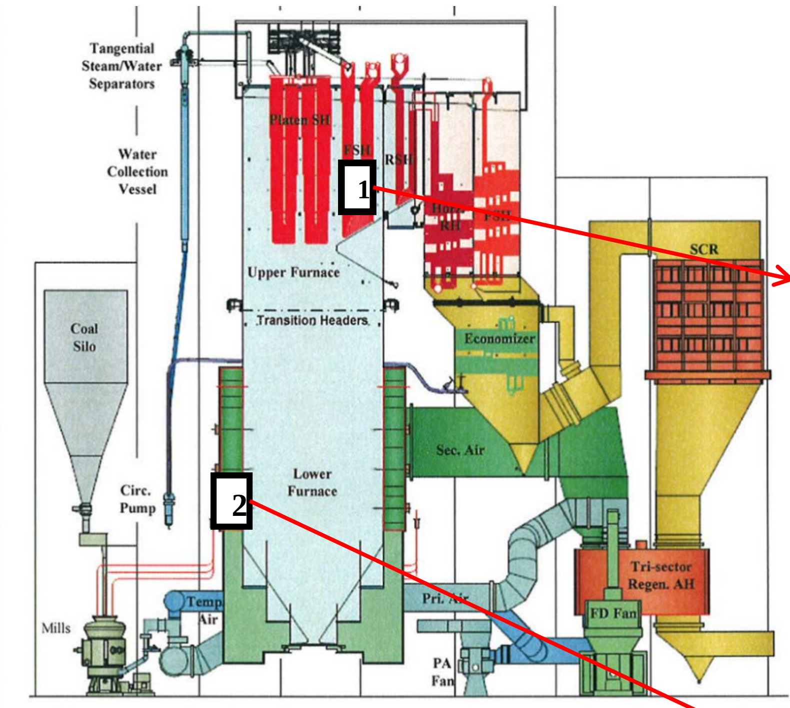
- Y1-Q1, finish updating PMP
- Y1-Q4, demonstrate the high temperature corrosion sensor can withstand the harsh environment in Longview's A-USC boiler.
- Y2-Q2, complete the NPV model and uncertainty analysis
- Y2-Q4, complete the electrochemical and corrosion database and model construction
- Y3-Q2,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

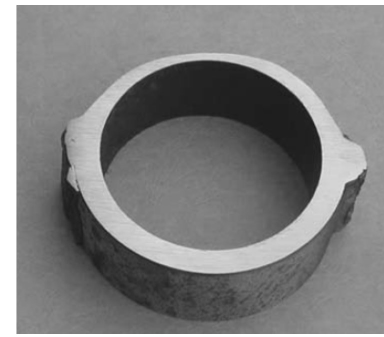
Sensor Testing @ Longview Power

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

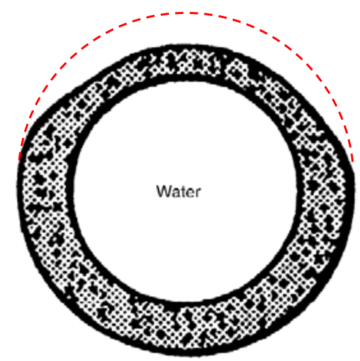
- Officially a "zero discharge" power plant in WV
- Includes a new air pollution control system that results in emissions that are Among the lowest in the nation for coal plants.
- Emits less CO_2 than most other coal plants because of its fuel efficiency

Sensor Testing Locations





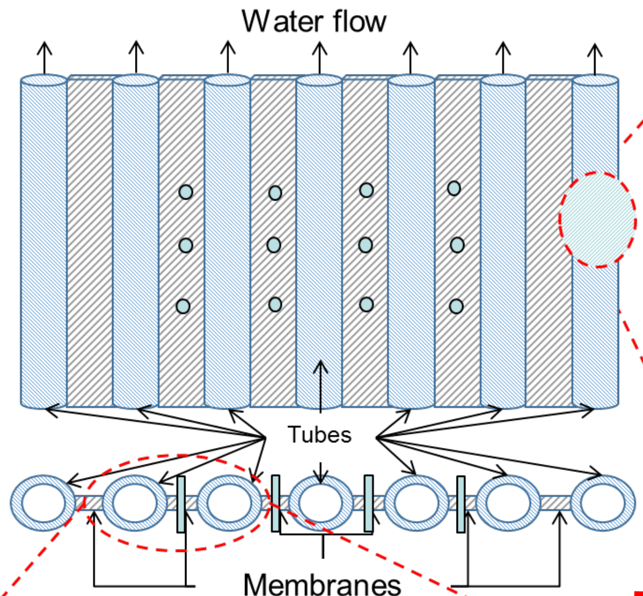
Fire side

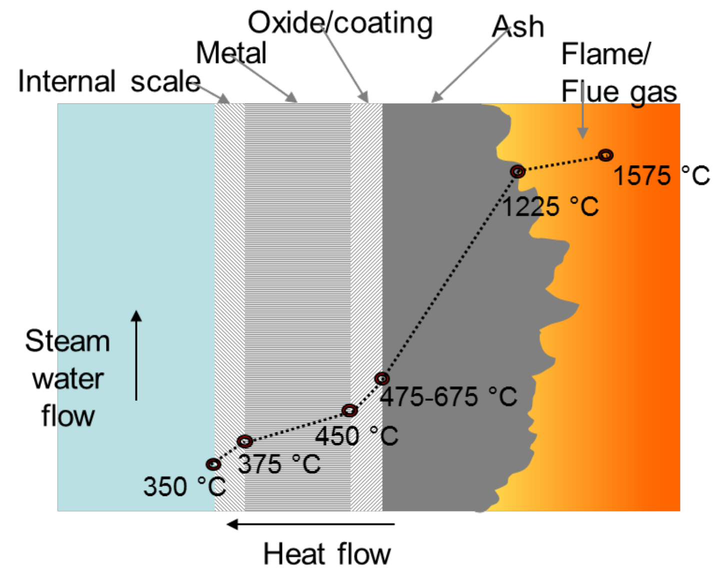


①Superheater/Reheater tubes:
High Temperature and Pressure,
Deposit-induced molten salt corrosion,
Made of nickel, inconel alloys or fire-resistant stainless steel.

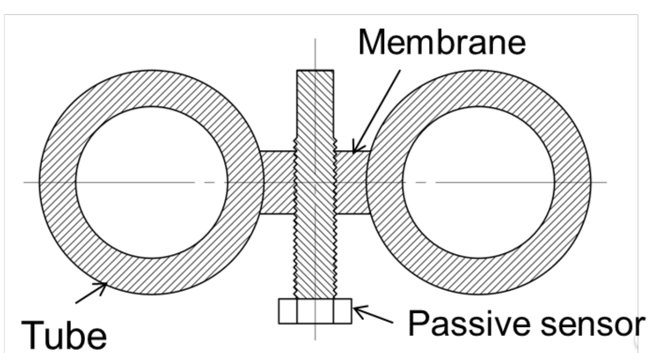
②Waterwall tubes:
Relatively low temperature,
Mainly made of carbon steel,
High corrosion rate but low maintenance cost;

Passive Sensor Design



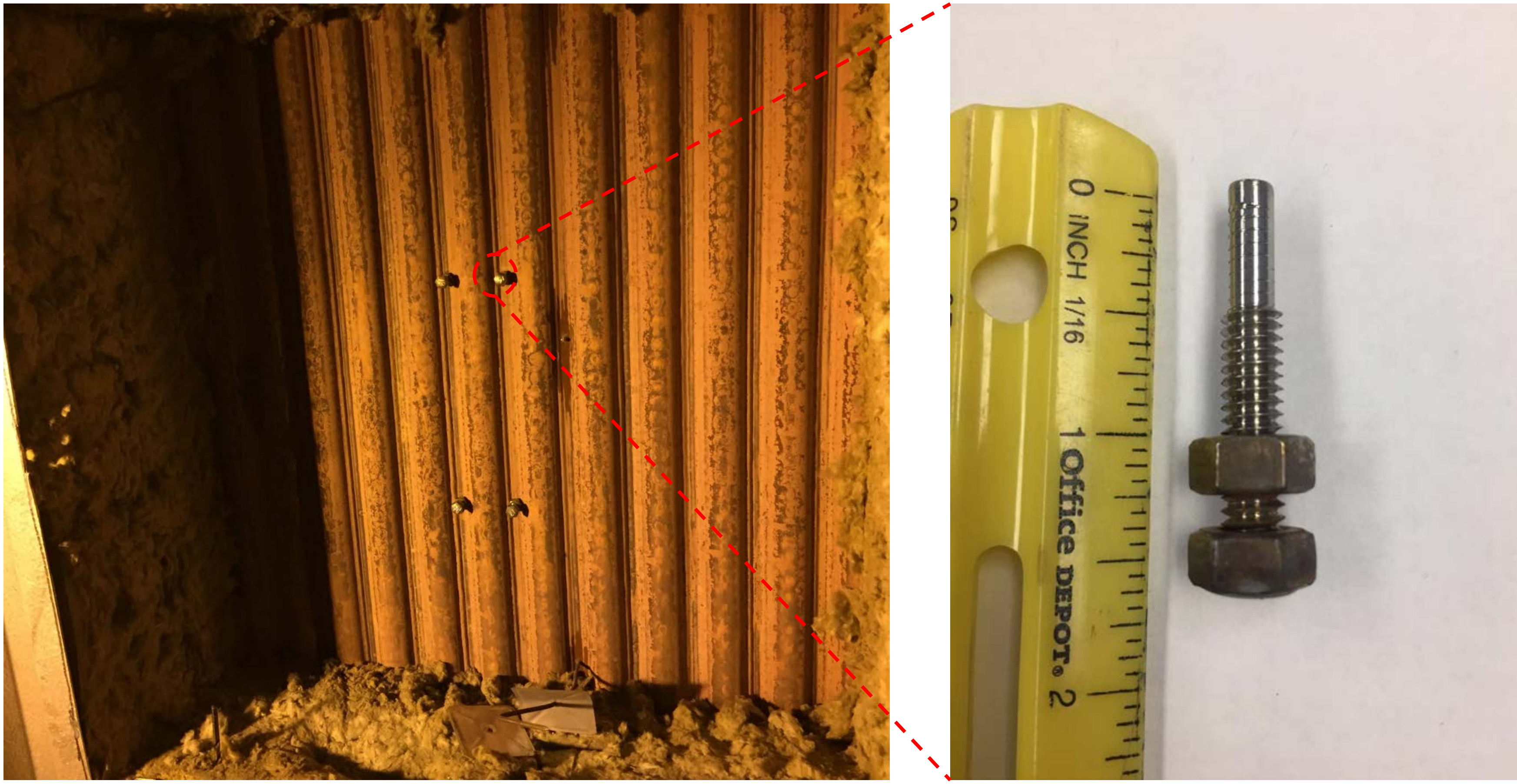


▲Temperature gradients through the waterwall tube[1]



▲Installation of passive sensor (weight loss)

Sensor Placing and Installation-Passive Sensor



▲ Bolt-like passive sensor installed on the membrane between tubes for both the waterwall and superheater.

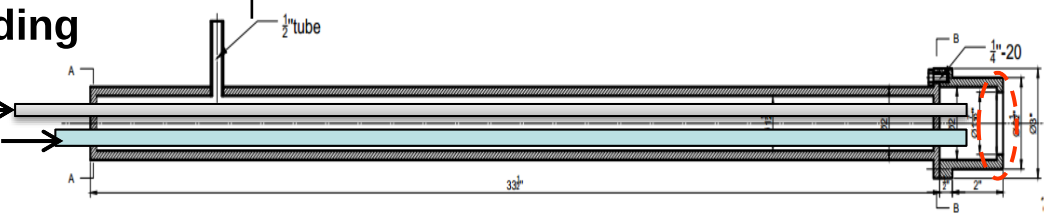
ECN Corrosion Sensor Design

WE1 + WE2 → **Current noise**

WE1 + RE → **Potential noise**

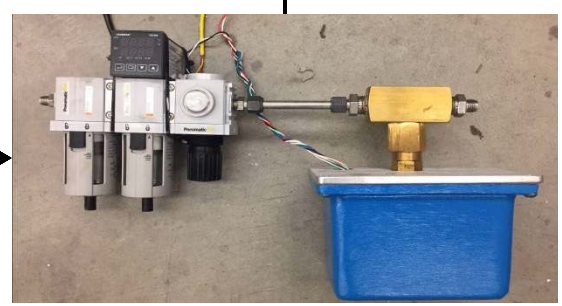
Signal recording

Air flow



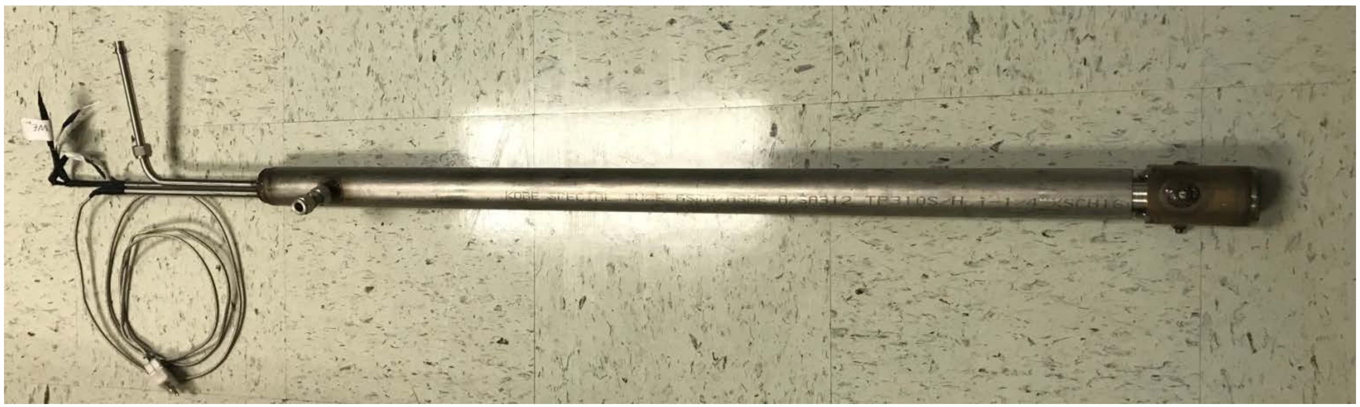
Air flow

Compressed air



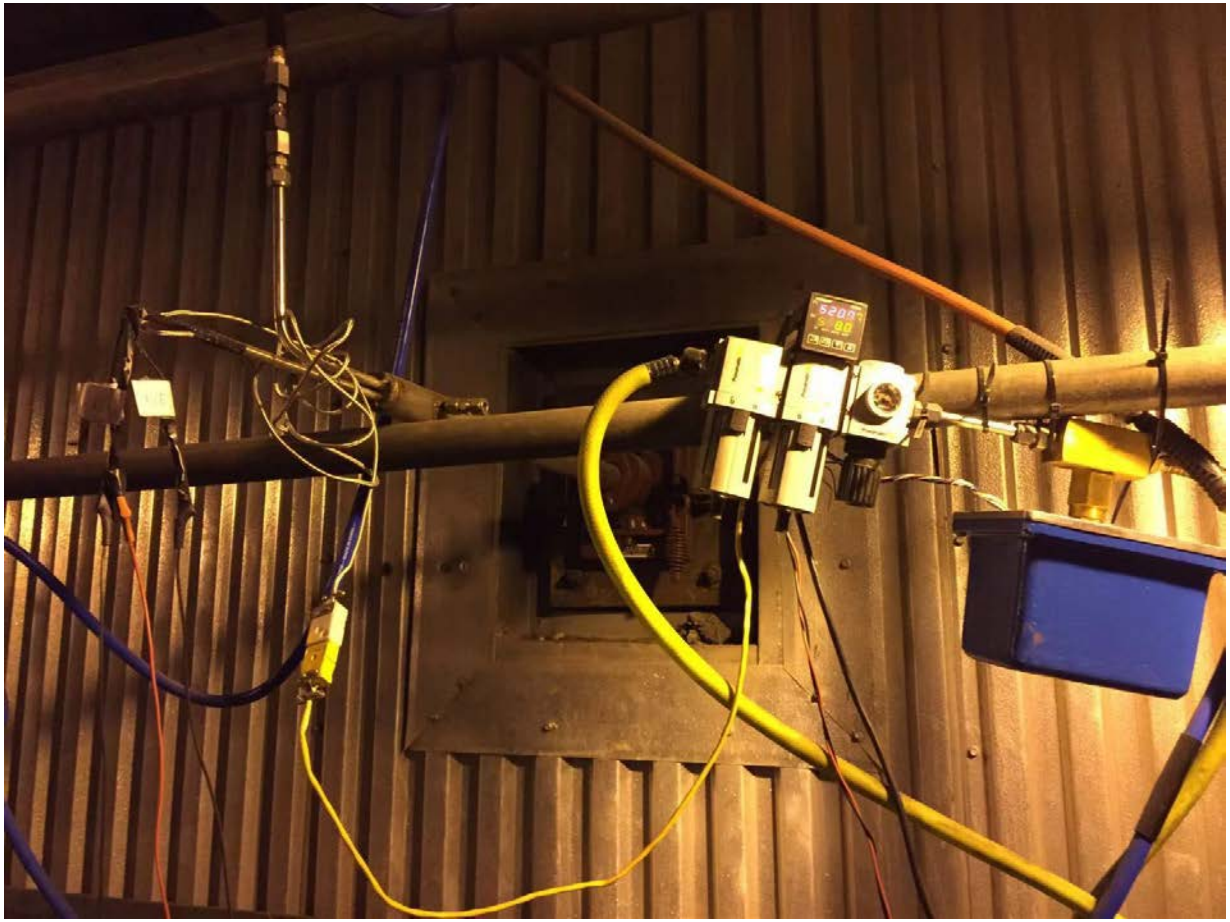
▲Air cooling system designed to control the sensor temperature

Sensor Packaging



▲Corrosion sensor installed at the superheater/reheater

Sensor Placing and Installation-ECN Sensor



▲ECN sensor system installed through the observation port near superheater (11th floor of the boiler). The temperature was controlled at around 548 ℃, which is the temperature of superheater fireside.

Predictive Model Development-Calculations of Corrosion Kinetics

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

Determined by Stern coefficient

$$V_{corr} = \frac{A}{R_p} \qquad R_n = \frac{\sigma_v}{\sigma_i} \quad \text{or} \quad R_{sn} = \lim_{f \to 0} \left| \frac{PSD_v}{PSD_i} \right|$$

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

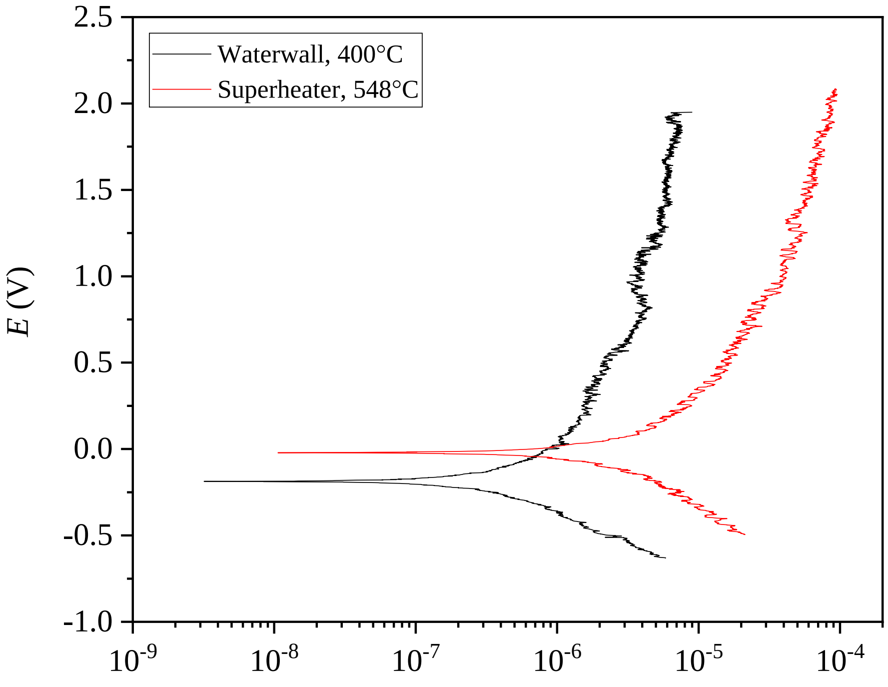
$$\Omega = f(t) \to V_{corr} = h(t)$$

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

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

④Surface analysis: SEM, EDX, 3D OM, et al. to verify the corrosion behavior and mechanism.

Field Measurement Results-PDP curves



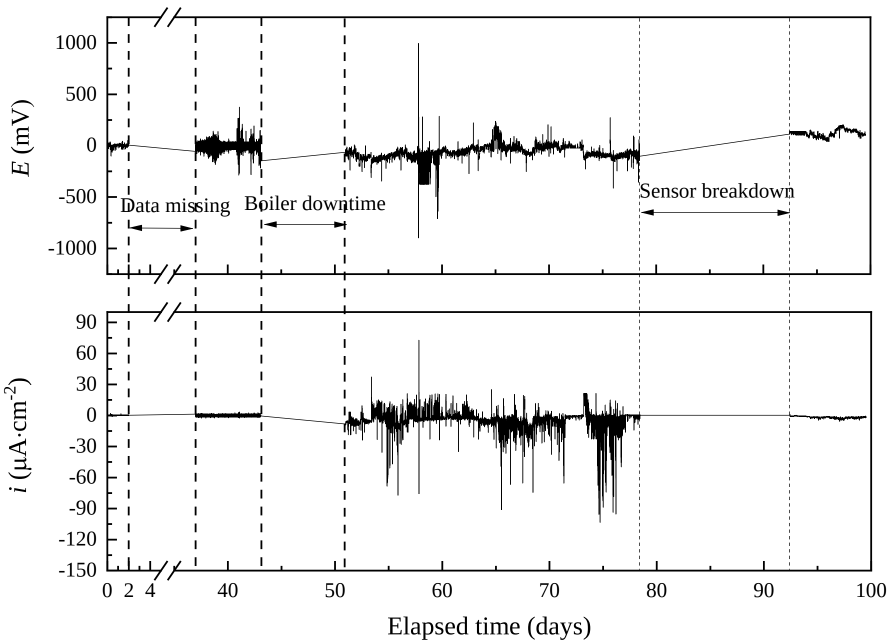
▲The potentiodynamic polarization curves measured at the waterwall place (400ºC) and the superheater place (548ºC).

Locations	Anodic tafel slope, α (mV/decade)	Cathodic tafel slope, β (mV/decade)	Stern-Geary coefficient, B (mV)
Waterwall	1034.40$\pm$224.51	145.30$\pm$3.25	127.40
Superheater	810.08$\pm$159.98	200.49$\pm$17.72	160.71

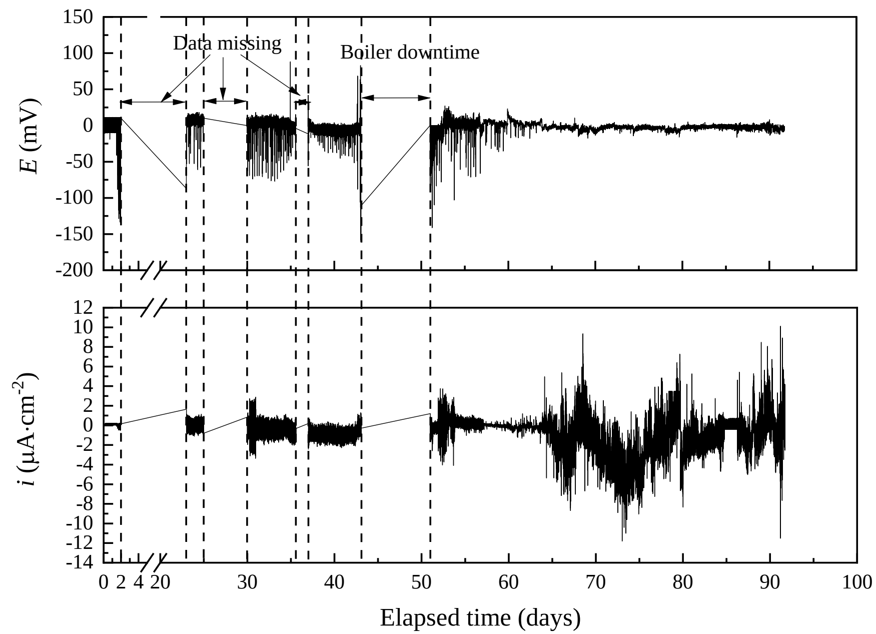
$$V_{corr} = \frac{A}{R_p} \approx \frac{A}{R_n} = \frac{3.27 \times B \times M}{n \times \rho \times R_n}, B = \frac{\alpha\beta}{\alpha + \beta}$$

For Fe→Fe^{3+}, n=3, ρ=7.8 g/cm^3, M=56 g/mol

Field Measurement Results-ECN Data



▲The electrochemical noises measured at the waterwall place (400ºC) since Nov. 19th 2018.



▲ The electrochemical noises measured at the superheater place (548ºC) since Nov. 19th 2018.

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

Field Measurement Results-Data Processing

编辑器 发布 视图

```matlab
tic;clear all; %clear all variables
[A]=xlsread('C:\Users\ustb_\Desktop\Matlab database\Potential noise.xlsx'); %read data
[B]=xlsread('C:\Users\ustb_\Desktop\Matlab database\Current noise.xlsx');%read data
i=1;j=1;
D=ones();
while (i<size(A,1)-2047)
    X=A(i+1023,1)-A(1,1); %choose time segment with size of 2048
    Yp=A(i:i+2047,2); %choose potential segment with size of 2048
    yp=detrend(Yp);%remove trend
    a=std(yp);%calculate standard deviation of potential noise
    Yc=B(i:i+2047,2);%choose current segment with size of 2048
    yc=detrend(Yc);%remove trend
    b=std(yc);%calculate the standard deviation of trend-removed current noise
    c=std(Yc);%calculate the standard deviation of current noise
    d=sqrt(sum(Yc.^2)./length(Yc));%calcualte the root mean square of trend-removed current noise
    Rn=a/b; %calculate noise resistance
    PI=c/d; %calculate localized corrosion index
    Vcorr=391/Rn;%calculate corrosion rate
    D(j,1)=X/3600/24;%output time value
    D(j,2)=Rn;%output noise resistance value
    D(j,3)=PI;%output localized corrosion index
    D(j,4)=Vcorr;%output corrosion rate
    j=j+1;
    i=i+2048;
end
format shortG
disp('time    noise resistance    localized index    corrosion rate')
D
figure();
subplot(311)
plot(D(:,1),D(:,2))
ylabel('Noise resistance, Rn (Ohm·cm^2)')
title('Calculation results');
subplot(312)
plot(D(:,1),D(:,3))
ylabel('Localized corrosion index, PI')
subplot(313);
```

命令行窗口

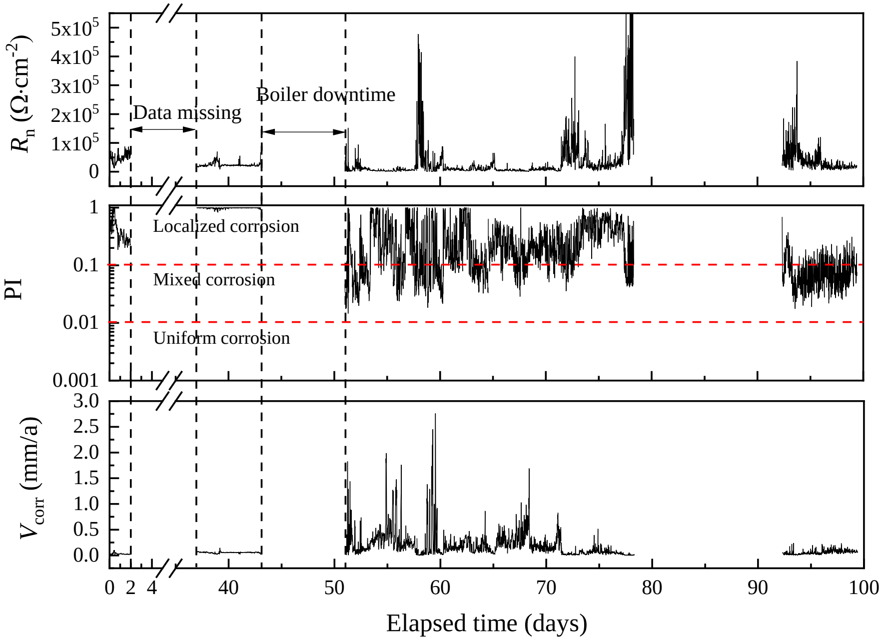
```
>> corrosionrate
  time  noise resistance  localized index  corrosion rate  Corrosion depth

D =
```

time	noise resistance	localized index	corrosion rate	Corrosion depth
0.0059276	36459	0.81556	0.034516	0
0.01778	45431	0.64483	0.027699	1.0101e-06
0.029632	47178	0.55084	0.026673	1.8929e-06
0.041484	37967	0.46094	0.033144	2.8641e-06
0.053336	50544	0.45316	0.024897	3.8064e-06
0.06519	44188	0.39482	0.028478	4.6731e-06
0.077042	54998	0.38671	0.022881	5.5069e-06
0.088894	48630	0.45421	0.025877	6.2986e-06
0.10075	46679	0.55351	0.026959	7.1564e-06
0.1126	52221	0.57653	0.024097	7.9853e-06
0.12445	46632	0.51438	0.026986	8.8146e-06
0.1363	53908	0.4957	0.023343	9.6317e-06
0.14815	72062	0.50212	0.017463	1.0294e-05
0.16001	44301	0.44027	0.028405	1.1039e-05
0.17186	51677	0.34678	0.024351	1.1896e-05
0.18371	52617	0.38985	0.023916	1.2679e-05
0.19556	44109	0.71204	0.028529	1.3531e-05
0.20741	37880	0.70445	0.03322	1.4533e-05
0.21927	42552	0.53573	0.029573	1.5553e-05
0.23112	40057	0.54975	0.031415	1.6543e-05
0.24298	39075	0.60997	0.032205	1.7576e-05
0.25483	30700	0.66034	0.040989	1.8765e-05
0.26669	68701	0.90297	0.018317	1.9728e-05
0.27854	26554	0.58166	0.047391	2.0795e-05
0.2904	26524	0.46738	0.047444	2.2335e-05
0.30225	33638	0.36418	0.03741	2.3713e-05
0.31411	24868	0.44786	0.050603	2.5143e-05
0.32596	51286	0.965	0.024537	2.6363e-05
0.33782	33188	0.72816	0.037917	2.7377e-05

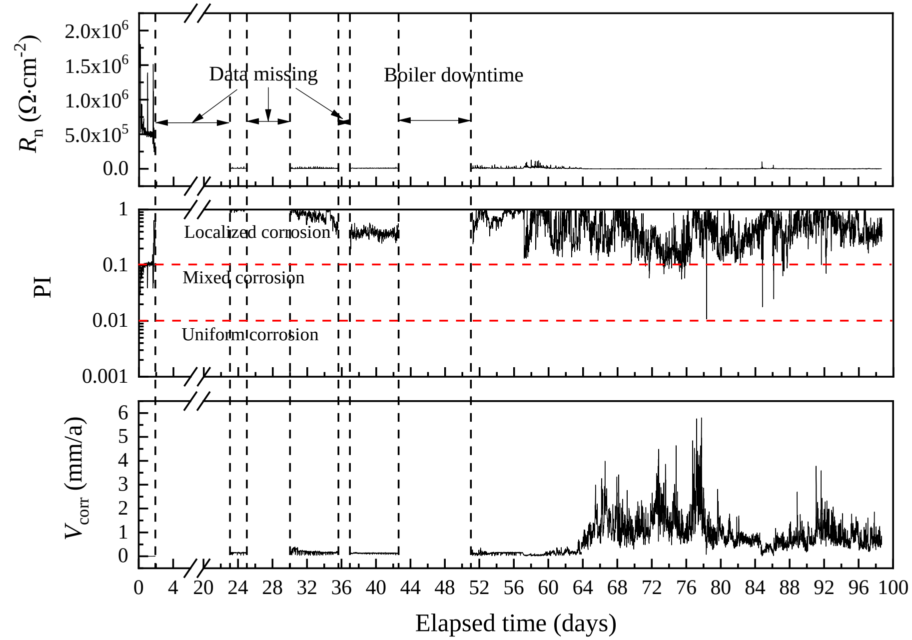
关闭

- ✓ 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.

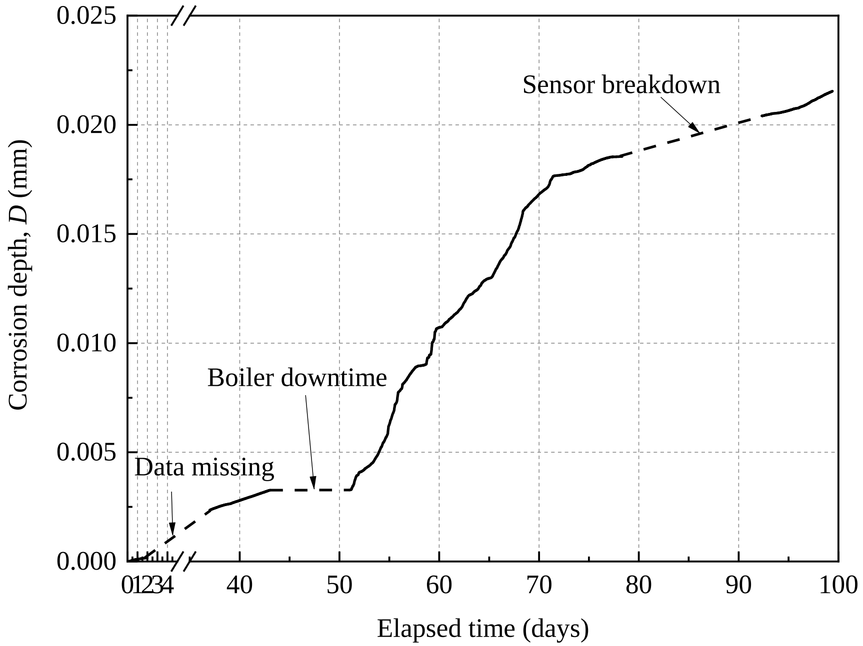


▲Corrosion indexes calculated from the electrochemical noises measured at the superheater place.

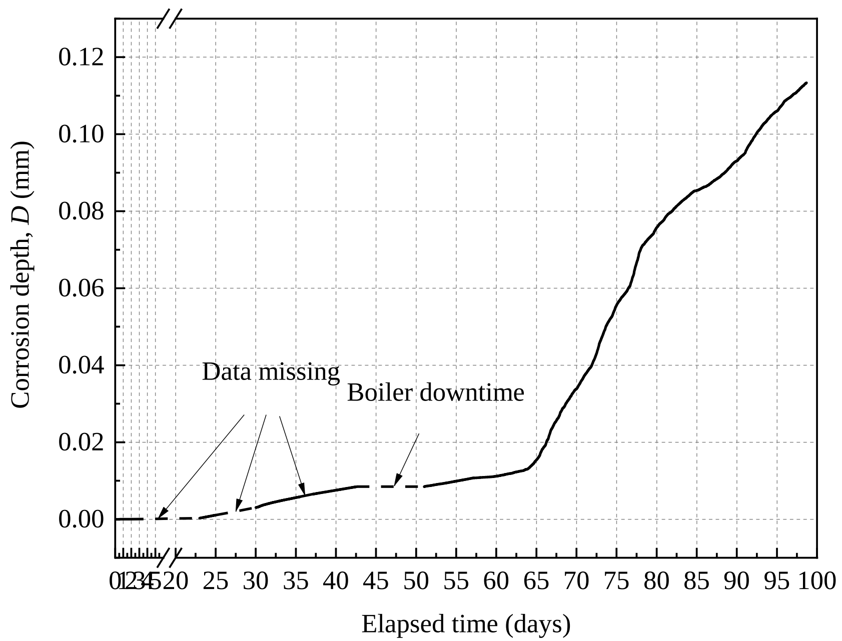
(R_n represents the corrosion resistance, PI represents the localized corrosion tendency, V_{corr} represents the corrosion rate.)

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

Field Measurement Results – Corrosion Rates



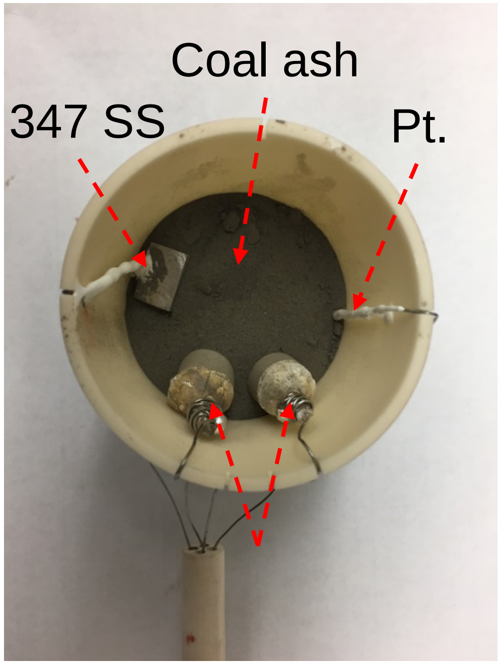
▲Time dependence of the accumulated corrosion depth calculated from the electrochemical noises measured at the waterwall.

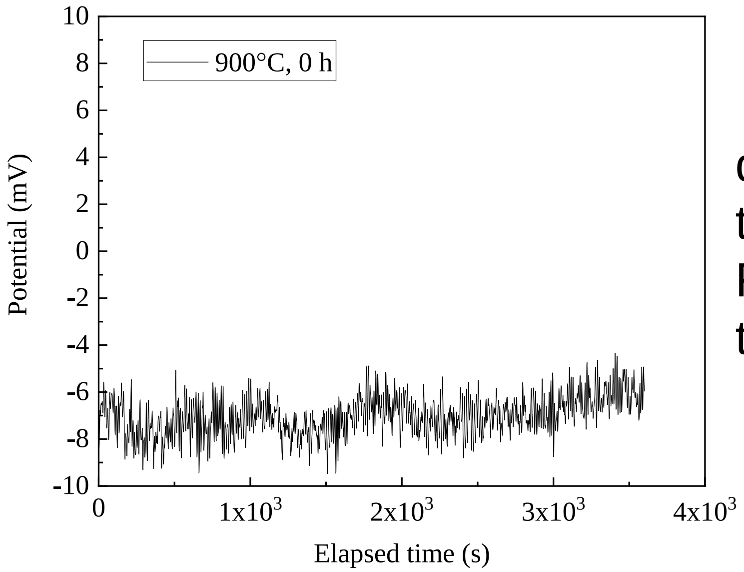


▲Time dependence of the accumulated corrosion depth calculated from the electrochemical noises measured at the superheater place.

Lab-Scale Sensor Optimization

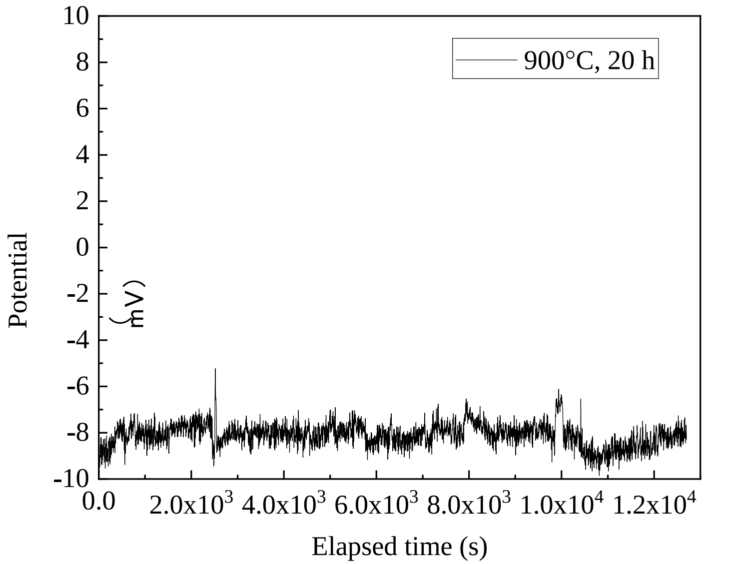
Modified RE





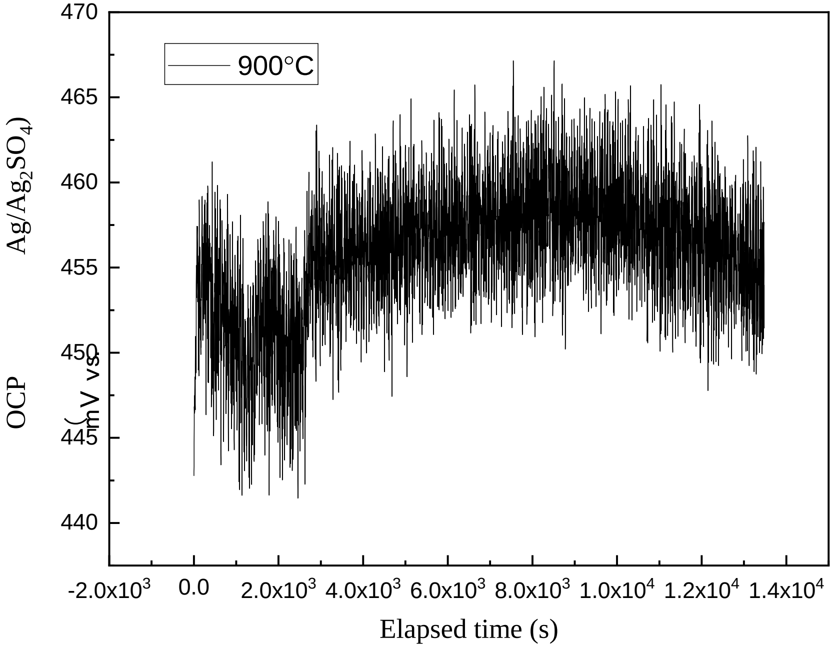
◀ The potential difference between the two identical REs measured at the initial time

ΔE<10 mV

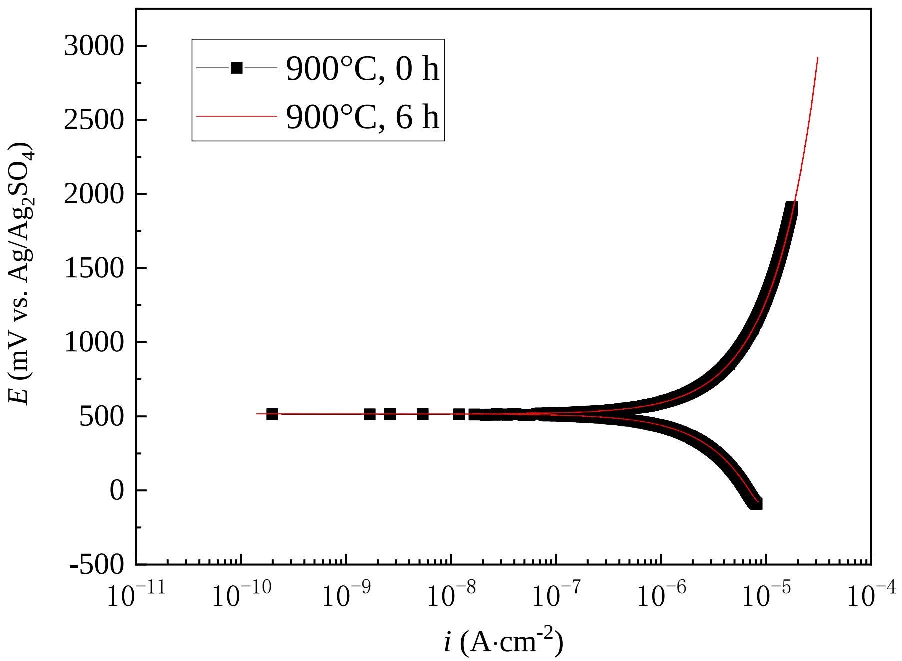


◀ The potential difference between the two identical REs measured after 20 hours.

Lab-Scale Sensor Optimization



▲The OCP of 347 stainless steel measured with modified RE in coal ash

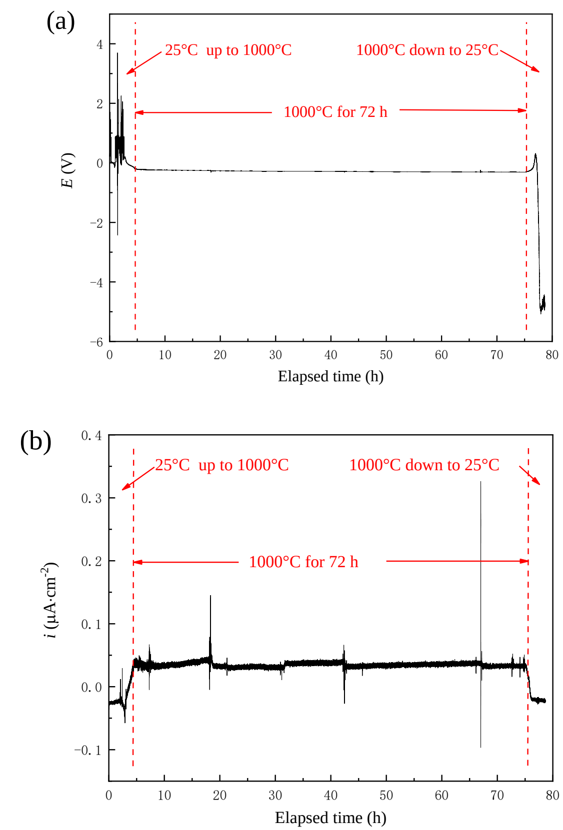


▲The PDP curves of 347 stainless steel measured with modified RE in coal ash

✓ Tests verified that the custom-designed RE can be reliable.

Lab-Scale Sensor Optimization

After running for **72 h** under 1000 ℃ with samples cooled down to 500 ℃

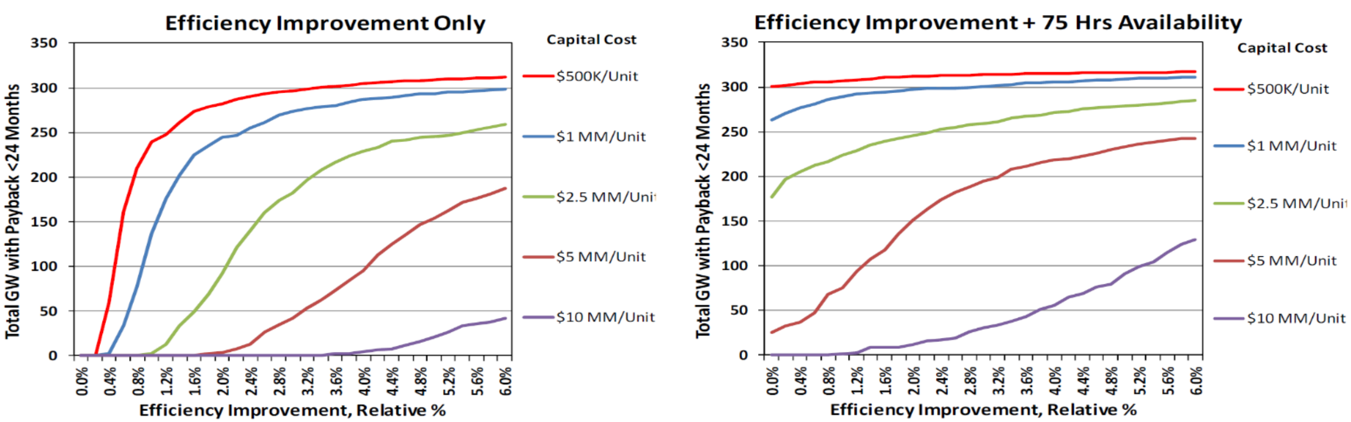


- ✓ The new-made sensor using the modified RE and the ceramic casting powder works well during 72 hours at 1000 ºC. The durability still needs to be verified on site in the boiler.

Techno-Economic Analysis - Motivation

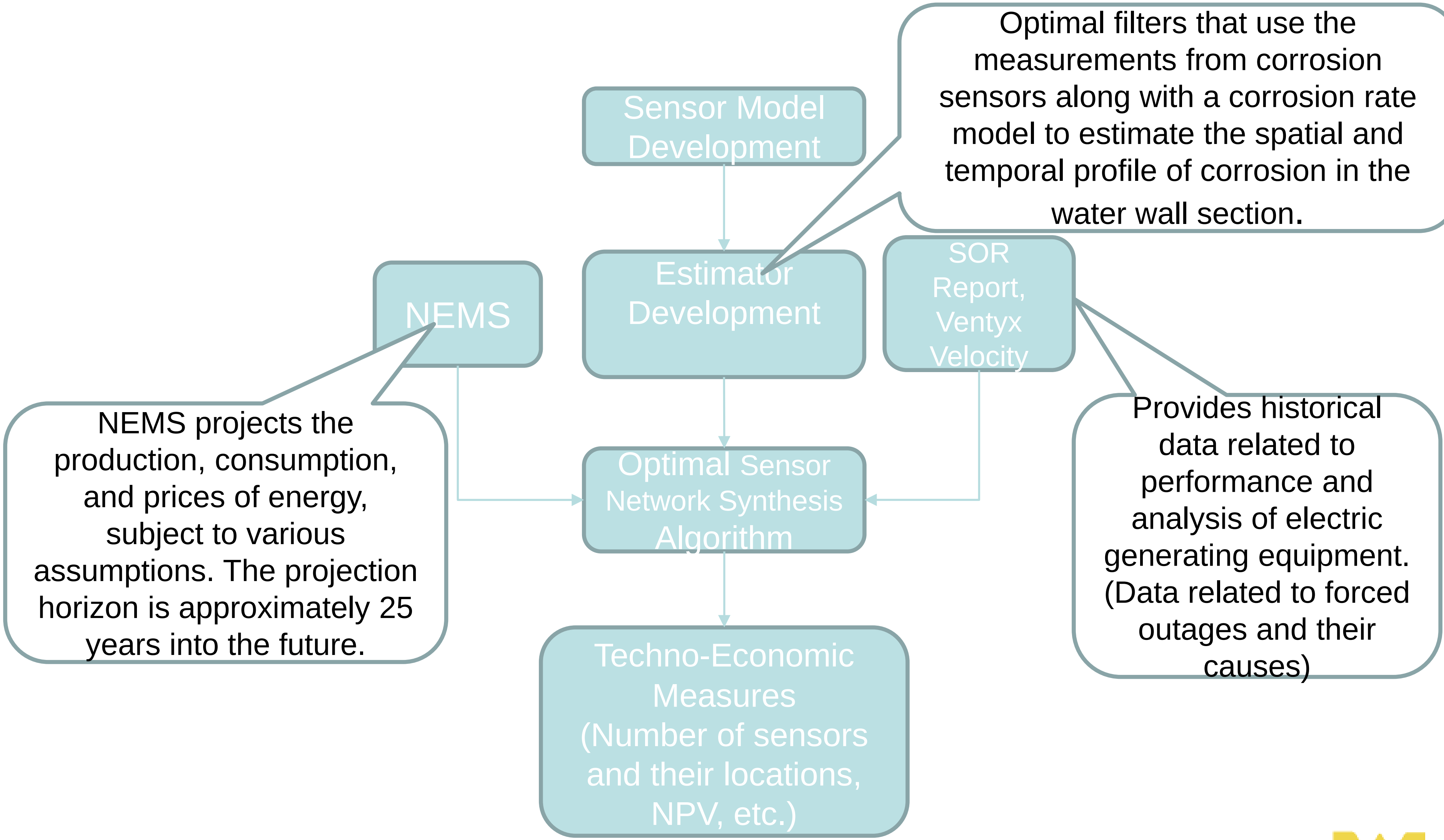
- As per State of Reliability (SOR) report by North American Electric Reliability Council (NERC), waterwall failure accounts for about 6-7% of the production lost due to forced outages over past several years.

- 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.



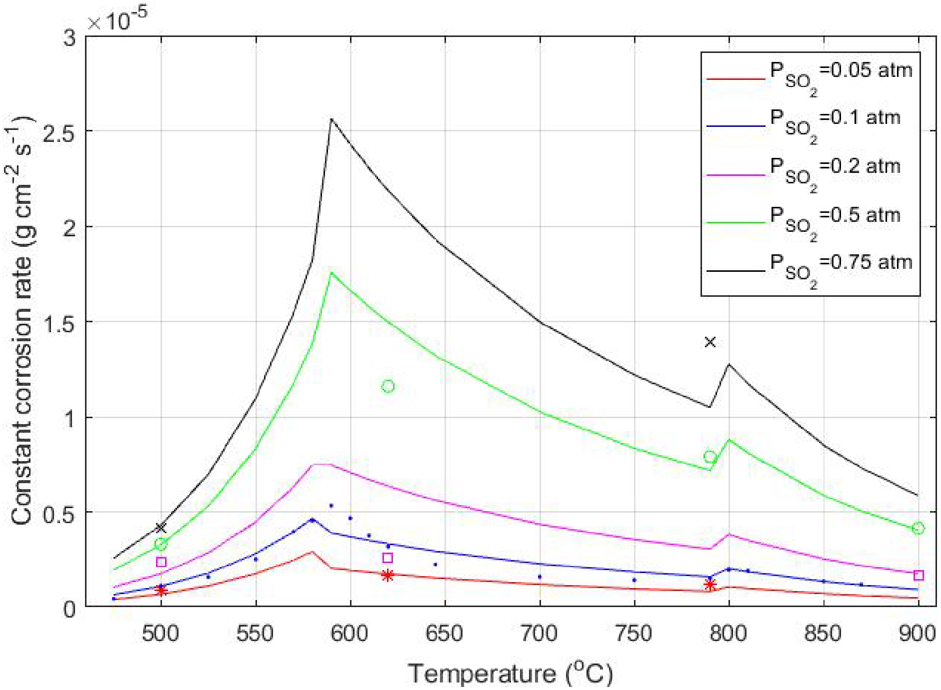
Impacts of efficiency, availability and capital cost (Krulla et al. NETL Report, DOE/NETL-342/03082013, 2013)

TEA - Approach



TEA – Sensor Model Development

- Model developed using the experimental corrosion data for nickel in argon-sulphur dioxide atmosphere*



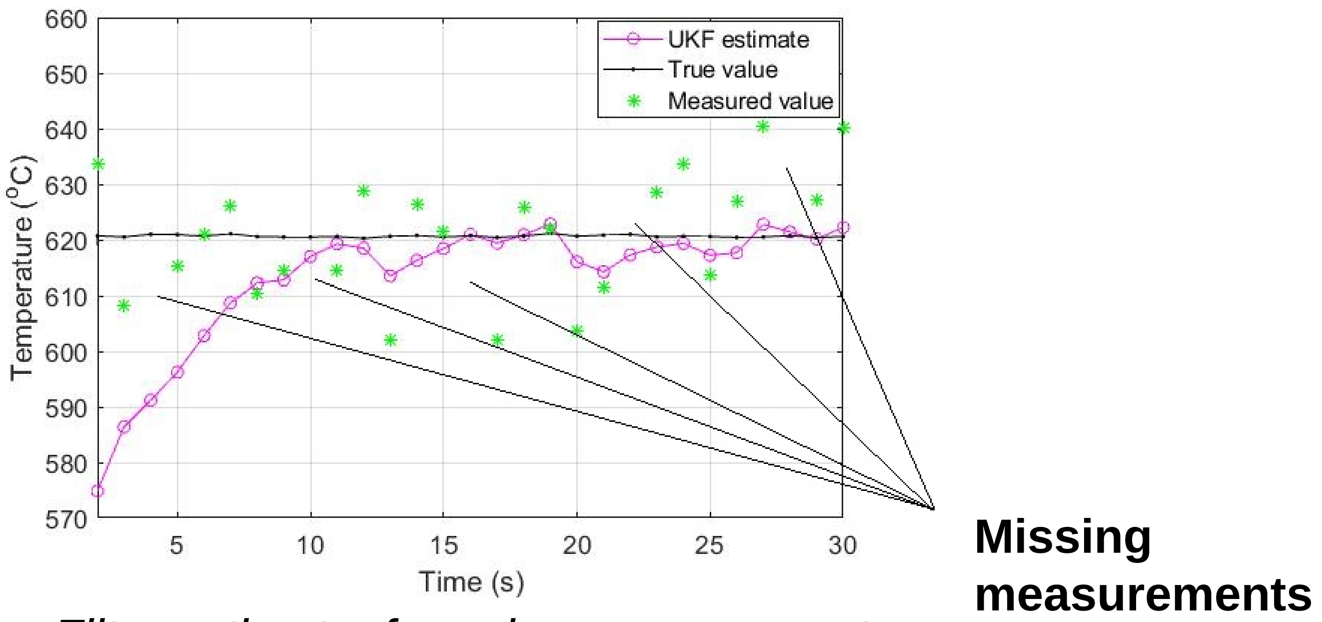
Region I	Region II	Region III
475 – 580 °C	590 – 790 °C	800 – 900 °C
The reaction of Ni metal with SO_2 increases with the temperature, up to a maximum value. NiO, $NiSO_4$ & Ni_3S_2 are corrosion products	Ni_3S_2 and Ni form a eutectic mixture. The presence of protective NiO and eutectic mixture slow down sulphidation. Hence, there is a drop in the corrosion rate.	Ni_3S_2 is no longer stable and melts. Cr present in metal is transported to surface. Cr oxidizes to form protective scale Cr_2O_3, hence no significant hot corrosion occurs.

Comparison of experimental vs model corrosion rates at different temperatures and partial pressures of SO_2

**Wootton, M. R. and Birks, N., "The Oxidation of Nickel in Atmospheres Containing Sulphur Dioxide ", Corrosion Science, 12, 829, (1972).*

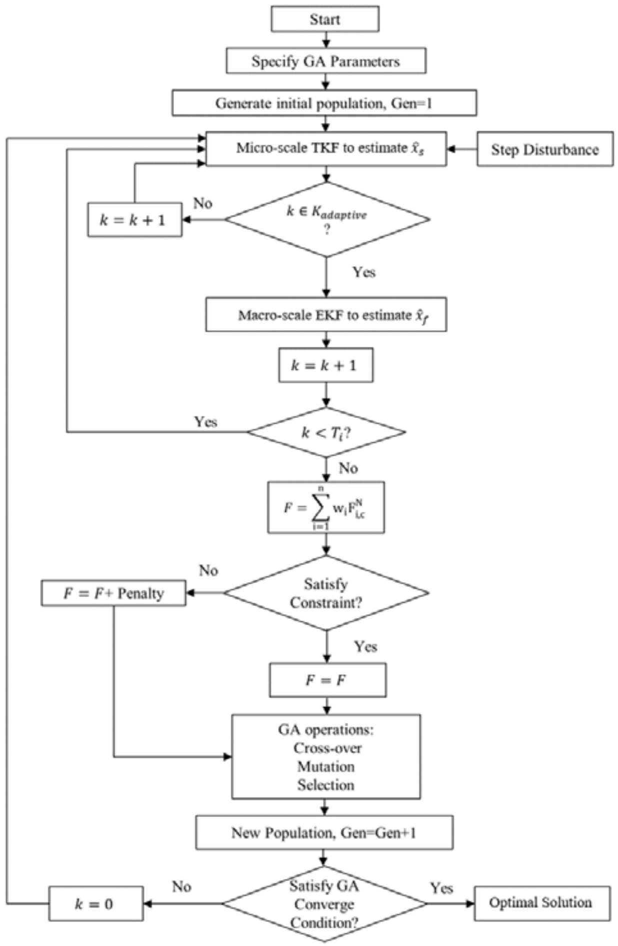
TEA - Estimator Development

- 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).



Filter estimate for noisy measurement data and missing measurements.

TEA - Cost-Optimal Sensor Network Synthesis Algorithm



- 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.

TEA - Future work

- 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.

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