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Monitoring Corrosion Under Insulation Utilising Electrochemical Testing

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What is Corrosion Under Insulation?

- Corrosion Under Insulation (CUI) refers to the corrosion process that occurs beneath insulation materials on industrial equipment and pipelines.
- CUI is a significant concern in many industries, including oil and gas, chemical, and power generation.
- It is caused by the presence of moisture, oxygen, and corrosive substances trapped between the insulation and the metal surface.
- CUI can lead to extensive damage, including metal loss, pitting, and structural failures, posing safety risks and increasing maintenance costs.



[1] – figure 1 – Corrosion Under Insulation Pipe Leak







Stage 1 - Initial Moisture Entry





Stage 2 - Breakdown of Protective Layers





Stage 3 - Corrosion Initiation and Continual Worsening





Stage 4 - Component Failure





Closer look at Corrosion Process



- The chemical reaction formula below represents the ion transfer between the cathode and anode of a ferric metal. At the anode, an oxidation reaction occurs (top). At the cathode, a reduction reaction occurs (bottom).
 Fe(s) → Fe²⁺(aq) + 2e⁻ (Anode)
 O₂(g) + 4H⁺(aq) + 4e⁻ → 2H₂O(l) (Cathode)
 - $2Fe^{2+} + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$ (Iron Hydroxide) $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$ (Iron (III) Hydroxide)
- The corrosion process was found in the analysis of the project's experimental samples. The analysis was conducted using SEM and EDS methods, this analysis was backed up further by relevant literature. The corrosion was furthered forming ferric compounds magnetite (Fe₃O₄) and iron (III) oxide (Fe₃O₄) dependent on conditions.



What is Electrochemical Testing?

- Electrochemical monitoring obtains in-situ information about a chemical reaction via its electrical presence.
- The method of electrochemical monitoring used was EIS, which characterizes a chemical system's time response using an applied lowamp AC current over a range of frequencies.
- EIS data is quantified in Nyquist [3] and Bode [2] plots; various electrochemical system characteristics can be identified from these.





Theory of Equivalent Circuit Modelling

- In matching EIS data to an equivalent circuit model, the data of the circuit can be physically represented, and trends or behavior's can be established.
- Each circuit element represents a behaviour in the physical electrochemistry of the system; for example, the resistor in an equivalent circuit model can represent the cell's solution resistance.
- Most electrochemical cells can't be represented using just one element, to attain the most accurate representation, multiple elements must be arranged specifically to represent their electrochemical property.

Component	Physical Model	Current vs Voltage	Impedance
Resistor		E= IR	Z = R
Inductor		E = L di/dt	Z = jωL
Capacitor		I = C dE/dt	$Z = 1/j\omega C$

Figure 4 – Electrical components and their relationships



Methodology

- To determine if a stainless-steel woven wire mesh could be used as the working electrode, acting as a sensor for the system.
- A series of prior experiments were completed to understand system variables and data processing.
- A three-electrode system consisting of a saturated calomel reference electrode (SCE), a graphite counter electrode, and the sample connected as the working electrode. The electrodes were connected to the Ivium vertex unit, which served as the central controlling unit for the system. The experiment was conducted with Ivium Soft as a post-processing and analysis tool.









Results – Bode Plots

The Bode plots of each of the sample assessed during the experiment is shown below, a Bode plot displays an electrochemical cells impedance relevant to its frequency.



Day 1 Day 3 Day 6 Day 8 Day 10 Figure 7 – Bode Plot Results



Results – Nyquist Plots

The Nyquist plots of each of the sample assessed during the experiment is shown below, a Nyquist plot displays an electrochemical cells imaginary impedance relevant to its real frequency.



Figure 8 – Nyquist Plot Results



Initial Analysis of Raw Results

- The analysis of the Bode and Nyquist plots presented a large differential in magnitude. Therefore, a corrective scale factor was used to estimate values of actual impedance or charge transfer resistance. However, using the mesh in conjunction with the Bode and Nyquist plots gave a good indication of the condition of the interface by showing characteristics such as coating degradation and passive layer breakdown.
- An interesting observation is that within the mesh samples there is a daily decrease in impedance indicating the saturation/degradation of the insulation over time agreeing with the trend in the non-mesh sample.



Figure 9 – Experimental Sample Raw Results



Equivalent Circuit Modelling

- To more accurately investigate the electrochemical processes occurring at the interface and remove the need for graph interpretation equivalent circuit modelling was utilised. Figure 10 demonstrates each of the applied equivalent circuits utilised within this study.
- For each of the four different test sample arrangements, a different circuit was constructed. Each circuit was used to measure unique parameters that the sample experienced, for example, scale was only visible on the bare steel sample therefore the measurement of scale capacitance and resistance were unique to that circuit.



Figure 10 – Mesh Equivalent Circuit Models



Analysis of Resistances

- The equivalent circuits in figure 10 were then used to find the charge transfer resistance.
- Using this gave an excellent insight into the condition of the interface and the potential for corrosion within the cell. These are shown in figure 11.
- Scales are corrosion products that form on the surface of a corroded material, and they can indicate the severity of the corrosion process.
- The resistance of these scales was measured with and without the mesh and calculated theoretically. These are shown in figure 12.



Figure 11 – Charge Transfer Resistance Measured by Mesh





Analysis of Capacitances Figure 13 – (A) Insulation Capacitance

- To investigate the condition of the mesh and coating through the mesh interface, the capacitance of the different layers was investigated.
- Insulation capacitance was derived using circuits C and D in figure 10. Figure 13 shows these results.
- Coating capacitance was found using circuits B and D in figure 10. Figure 14 displays these results.
- As expected, all the measured values were less than the theoretical total cell capacitance in both the insulation and coating capacitances.
- These results highlight the potential usefulness of the mesh for measuring cell capacitances.







Total Resistance and Capacitance Analysis

- The system's total resistance and total capacitance are measured between the working and reference electrodes.
- Resistance and capacitance of the system are the inverses of each other.
- The relationship is as expected and is • backed up by relevant literature.
- It shows that this method has good potential use in an industrial application using the steel wire mesh as a corrosion sensor at the interface.

Figure 15 - (A) - No Mesh Total Resistance 1.00E+04 (Ohms) (Ohms) 1.00E+08 1.00E+03 1.00E+06 1.00E+06 1.00E+04 1.00E+02 1.00E+02 **Fotal Resistance** 1.00E+02 1.00E+01 1.00E+00 10 0 10 Duration (Days) Duration (Days)





Figure 16 - (B) - Mesh Total Resistance



Conclusions

- The mesh interface can measure similar trends when studying Bode and Nyquist plots, just at a reduced value.
- Using equivalent circuit modelling the mesh interface can unveil the condition of the material through the values of charge transfer resistance, scale resistance and coating capacitance.
- Using the mesh to calculate total cell resistance, an accurate interface condition was determined, this would allow for practical industrial implementation.



Recommendations and Next Steps

Further progression of this project is necessary before the novel sensor method can be applied to industrial applications. A list of improvements and recommendations can be seen below to remediate any issues and improve the proposed new technique.

- Insert a deliberate defect in the coating experiments to learn its behaviour.
- Study the corrosive activity of the mesh independently.
- Use a conductive non-corrosive mesh to improve the lifespan of the sensor and remove measurement interference.
- Conduct further experiments using temperature cycles and wet/dry cycles as the corrosion behaviour will alter and provide further information about how the cui interface behaves in a more practical environment.



References

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- [2] [3] GAMRY, 2022. *Basics of EIS: Electrochemical Research-Impedance*. [online]. www.gamry.com. Available from: <u>https://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/</u>.