# **CAAP Quarterly Report**

#### [06/29/2024]

**Project Name**: Multi-Compound Green Corrosion Inhibitor for Gas Pipeline: Synthesis, Optimization, and Evaluation

Contract Number: 693JK32350004CAAP

Prime University: Arizona State University

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*Reporting Period*: [4/2023 – 6/2024]

#### **Project Activities for Reporting Period:**

Task 1. Design and Synthesis of Multi-compound Green Inhibitors

During current reporting period, our team has made substantial progress in developing and assessing of green inhibitors. We have concentrated particularly on enhancing and analyzing the performance of pectin as a corrosion inhibitor. The primary activities are summarized as follows:

- 1.2: Synthesis and Characterization of Green Inhibitors from Renewable Feedstock
  - Developed innovative methods for the chemical modification of pectin, which could significantly enhance its anti-corrosion properties through a process of cross-linking. Furthermore, we refined adhesion techniques to reinforce its resilience and effectiveness in harsh conditions.
- 1.3: Corrosion Testing for Verification and Validation
  - Employed Tafel polarization, a sophisticated electrochemical testing method, to evaluate the effectiveness of pectin in mitigating corrosion and to gain insights into its electrochemical behavior.
  - Implemented Electrochemical Impedance Spectroscopy (EIS), an advanced electrochemical testing method, to assess the efficacy of pectin in reducing corrosion and to derive insights into its electrochemical behavior.
  - Conducted long-term weight loss experiments to evaluate the durability and protective properties of pectin, quantifying the material degradation and affirming its suitability for industrial applications.

#### Task 2. Simulation-Based Inhibitor Optimization in Gas Gathering and Transportation Pipelines

In current reporting period, we have achieved substantial advancements in Task 2, with a primary focus on developing a neural network framework to enhance the efficiency of flow regime predictions. The pivotal activities undertaken are summarized as follows:

- 2.1: Prediction of Wall Shear Stress with Uncertainty Quantification
  - Improved the Fourier neural operator model to predict the distribution of wall shear stress under different roughness profile.
  - Incorporated Bayesian method into the Fourier neural operator model for uncertainty quantification.
- 2.2: Multi-fidelity Approach
  - Constructed 2-D and 3-D pipe models for specific cases, enabling the collection and analysis of low-fidelity and high-fidelity results.
  - Implemented a convolutional neural network to discern the variations in Fluent parameters, thereby enabling the prediction of high-fidelity data based on provided low-fidelity information.

A comprehensive report detailing the aforementioned tasks is provided in the appendix. Additionally, the presentation file for the quarterly report, prepared for the Technical Advisory Panel (TAP) members and PHMSA program managers, is also enclosed in the appendix.

### **Project Financial Activities Incurred during the Reporting Period:**

For Task 1, we supported 1 RA at ASU For Task 2, we supported 2 RAs at ASU

### **Project Activities with Cost Share Partners:**

Engaged in discussions with members of the Technical Advisory Panel to solicit recommendations for our team's research activities.

#### **Project Activities with External Partners:**

Conducted regular discussions with the Technical Advisory Panel, in addition to several separate meetings and email communications with individual advisory members.

#### **Potential Project Risks:**

Nothing to report.

# **Future Project Work:**

### For Task 1:

- Implementing the chemical functionalization of pectin using an established method
- Creating a corrosive medium to enhance the simulation of pipeline corrosion
- Verifying A36 and API 5L steels exhibit similar corrosion performance
- Performing corrosion tests using API 5L steel to replicate real-world conditions
- Evaluating the efficacy of our developed bio-inhibitors in comparison to benchmark inhibitors commonly used in the industry
- Designing a setup to emulate pipeline flow and assess the impact of this flow on steel corrosion, thereby providing a more accurate representation of real-world conditions

# For Task 2:

- In the proposal, we proposed to use a Physics-Informed Neural Network (PINN) for the simulation of pipe flow and inhibitor injection behavior. During the research, we found that another physics-guided machine learning approach called Fourier Neural Operator (FNO) seems to give good simulation capability, and we invested in this method first. The method is mainly for flow simulation and wall shear stress estimation for corrosion loss prediction. In the future, we will apply a similar methodology for inhibitor injection simulation (e.g., multiphase flow).
- Continue the investigation of reduced order modeling to enhance the efficiency of pipe flow simulation
- Explore other multi-fidelity approaches for balanced prediction accuracy and computational complexity
- Include uncertainty quantification for multi-fidelity modeling and calculate the confidence bounds for model predictions
- Explore literature data for corrosion rate data to demonstrate and validate the proposed inhibitor degradation model
- Collaborate with task 1 group to develop new testing procedures to obtain in-house experimental data for model validation

Appendix 1 Technical Progress Description for Task 1

# Task 1. Design and Synthesis of Multi-compound Green Inhibitors

# Background:

In the initial phase of this project, we embarked on research and experimentation to develop ecofriendly corrosion inhibitors. Our focus was on utilizing citrus peels and shrimp shells as primary raw materials, with the objective of creating sustainable strategies to counter pipeline corrosion in industrial settings. Our overarching goal was to repurpose waste materials, thereby fostering environmental sustainability.

During the first quarter, our team undertook an exhaustive review of the literature to pinpoint potential eco-friendly inhibitors. This stage was pivotal in comprehending the potential and constraints of various natural resources. We also joined forces with industry frontrunners to ascertain that our methodology adhered to safety and compatibility norms. A notable accomplishment during this timeframe was the successful extraction of pectin from orange peels, a renewable resource recognized for its corrosion inhibiting potential. In the second quarter, we amplified our efforts to fine-tune the synthesis processes and enhance the functional attributes of our bio-based inhibitors. Our focus was on optimizing the extraction and functionalization of pectin to augment its interaction with metal surfaces, thereby improving its corrosion inhibition capabilities. In addition, we initiated the synthesis of chitosan from shrimp shells, thereby broadening our array of eco-friendly inhibitors. We also established stringent corrosion testing protocols, including weight loss measurement and electrochemical testing, to assess the effectiveness of these inhibitors with greater precision.

# **Quarter's Objectives**

Our primary objective for the past quarter was to enhance the long-term effectiveness of pectin as a corrosion inhibitor. Building upon promising initial results, we aimed to conduct a series of long-term corrosion inhibition tests using pectin. This included comprehensive evaluation through advanced electrochemical methods to ascertain the durability and effectiveness of pectin in varying corrosive environments.

Additionally, we planned to delve deeper into the electrochemical properties of pectin by employing sophisticated testing methods such as Tafel polarization and Electrochemical Impedance Spectroscopy (EIS). These tests were crucial for understanding the intricate mechanisms of electrochemical corrosion inhibition by pectin and provided valuable insights into the interaction between pectin and metal surfaces under corrosive conditions.

Furthermore, our team focused on improving the physical interaction between pectin and metal substrates. We explored chemical modification techniques aimed at enhancing the adhesion of pectin coatings to metal surfaces, thereby improving their protective efficacy against corrosion. This approach was expected to not only extend the lifespan of metal components but also optimize pectin's application as a sustainable corrosion inhibitive layer in industrial settings.

Task 1.2: Synthesis and Characterization of Green Inhibitors from Renewable Feedstock

Developed innovative methods for the chemical modification of pectin, which could significantly enhance its anti-corrosion properties through a process of cross-linking. Furthermore, we refined adhesion techniques to reinforce its resilience and effectiveness in harsh conditions.

For Task 1.2, we focused on establishing a method for enhancing pectin's corrosion efficiency performance through a series of chemical modifications. These modifications aimed to augment pectin's protective properties through cross-linking techniques and optimizing adhesion capabilities to improve performance in harsh environments.

Initially, a significant amount of pectin, precisely 10 grams, was dissolved in 300 mL of deionized water. To this solution, 50 mmol of EDC (1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide) and 16.7 mmol of NHS (N-Hydroxysuccinimide) were added. This mixture was then stirred magnetically for three hours in an ice bath. This step was crucial as it served to activate the carboxyl groups of pectin, making them more reactive for the subsequent modification process.

Following the activation, 50 mmol of an amino acid was dissolved in an additional 300 mL of deionized water. This amino acid solution was then combined with the activated pectin solution. The pH of the combined mixture was carefully adjusted to 5 using a 1 mol/L hydrochloric acid solution, setting the stage for the grafting reaction.

The grafting reaction was induced by stirring the mixture magnetically for 24 hours under the same ice bath conditions. This prolonged stirring was vital to ensure a complete reaction, leading to the formation of a modified pectin with enhanced adhesive properties and increased molecular stability.

After the reaction period, the mixture was treated with 600 mL of anhydrous ethanol to precipitate the modified pectin. The solution was then centrifuged to separate the precipitate, which was subsequently dialyzed against a 7000–14000 Dalton molecular weight cut-off membrane for 72 hours at room temperature. This step was necessary to remove residual reactants such as EDC, amino acids, and NHS, ensuring that the final product was pure and suitable for further testing.

The dialyzed product was finally freeze-dried to obtain a chemically modified pectin powder. This powder represents a refined version of the original biopolymer, now equipped with enhanced corrosion-inhibitive properties due to the introduction of new functional groups and a strengthened molecular structure.

The efficacy of this chemically modified pectin will be evaluated in subsequent corrosion tests in the next quarter.

- Task 1.3: Corrosion Testing for Verification and Validation
  - Employed Tafel polarization, a sophisticated electrochemical testing method, to evaluate the effectiveness of pectin in mitigating corrosion and to gain insights into its electrochemical behavior. Utilized Tafel polarization as an advanced electrochemical test to measure pectin's corrosion mitigation effectiveness and gather electrochemical behavior insights.
  - Implemented Electrochemical Impedance Spectroscopy (EIS), an advanced electrochemical testing method, to assess the efficacy of pectin in reducing corrosion and to derive insights into its electrochemical behavior. Utilized electrochemical impedance spectroscopy (EIS) as an advanced electrochemical test to measure pectin's corrosion mitigation effectiveness and gather electrochemical behavior insights.
  - Conducted long-term weight loss experiments to evaluate the durability and protective properties of pectin, quantifying the material degradation and affirming its suitability for industrial applications.

# 1.3.1 Tafel Polarization in Electrochemical Corrosion Testing

Tafel polarization, a cornerstone of electrochemical analysis, plays a critical role in assessing the durability and lifespan of metals under corrosive conditions. This technique, based on Tafel extrapolation, provides vital insights into the corrosion mechanisms of metals, making it indispensable in fields ranging from infrastructure engineering to the development of marine vessels.

The method derives its name from Julius Tafel, who, in the early 20<sup>th</sup> century, first described the relationship between the overpotential and the logarithm of the current density during electrochemical reactions. This foundational work laid the groundwork for using these relationships to probe the kinetics of electrochemical reactions, particularly corrosion processes.

Corrosion, an electrochemical phenomenon, involves the deterioration of materials due to interactions with their environment. In metals, this typically manifests as the oxidation of metal atoms, which lose electrons and form ions. The susceptibility of metals to corrosion depends on their environment and material properties, posing significant risks to their structural integrity and functionality.

# Relevance of Tafel Polarization in Modern Applications

In practical terms, Tafel polarization allows engineers and scientists to quantitatively measure the rate of corrosion using the corrosion current density derived from Tafel plots. These plots graph the potential versus the logarithm of the current density, revealing key information about the anodic and cathodic reactions that occur on the surface of the electrode.

The significance of Tafel polarization extends beyond simple measurement. The technique is critical for:

- Material Selection and Design: Helping select materials with better corrosion resistance for specific applications.
- **Corrosion Inhibitor Evaluation**: Testing the efficacy of various corrosion inhibitors to find the most effective compounds for protecting metals.
- **Predictive Maintenance and Life Prediction**: Providing data that aid in forecasting the need for maintenance or replacement of corroded components, thereby averting potential breakdowns.

#### Technical Overview of the Tafel Polarization Method

Technically, the Tafel polarization test involves several steps, starting with the measurement of the open circuit potential (OCP) to establish a baseline for the electrochemical system at equilibrium. The subsequent application of varying potentials helps mapping out the complete electrochemical behavior of the test material, capturing phenomena like passivation or activation that are critical to understanding its corrosion behavior.

During the test, both anodic (oxidation) and cathodic (reduction) reactions are explored. The anodic reaction involves the metal losing electrons, while the cathodic reaction involves the gain of electrons. The slopes of the lines in the Tafel plot, known as Tafel slopes, are indicative of the energy barriers for these reactions. Accurately determining these slopes is crucial for extrapolating the corrosion current density (i<sub>corr</sub>), which directly correlates to the metal's corrosion rate. Figure 1.1 shows the Tafel plot and measured corrosion parameters.





Figure 1.1. Graphical Representation of the Tafel Polarization Corrosion Test Results

A detailed analysis of the Tafel plot allows researchers to pinpoint the corrosion potential where the anodic and cathodic currents balance, a key metric in evaluating the stability of the metal in its operational environment. The intersection point of the extrapolated anodic and cathodic Tafel lines provides a precise measure of the corrosion rate, which is essential for assessing the protective qualities of corrosion inhibitors and the overall resilience of the metal.

Thus, Tafel polarization is more than just a testing method; it is a comprehensive approach that offers a deep understanding of corrosion processes. This knowledge is crucial for developing strategies to mitigate corrosion, enhance material performance, and ensure the longevity and safety of metal components across various industries.

# Methodology for Conducting the Tafel Polarization Test

### Equipment Setup and Preparation

For the Tafel polarization test, a controlled electrochemical setup was utilized, typically comprising a potentiostat, a three-electrode cell, and software for data acquisition and analysis. The three-electrode system consisted of a working electrode (the metal under test), a reference electrode, and a counter electrode.

### Stabilization of Open Circuit Potential (OCP)

The metal sample was immersed in the test solution, and the system was allowed to equilibrate to the open circuit potential (OCP). This step was crucial as it established a stable baseline condition for the electrochemical system. The OCP is the potential where the net current at the electrode

surface is zero, indicating that the rates of the anodic and cathodic reactions have reached equilibrium.

# Test Medium Preparation

To assess the impact of pectin as a corrosion inhibitor on A36 steel, a low-carbon steel used in the manufacturing of oil and gas pipelines, two distinct media were prepared:

- Medium 1 (Control): A pure 1M HCl solution served as the control to assess the corrosion impact on unprotected A36 steel in a highly corrosive environment.
- Medium 2 (Pectin Mixed): A 1M HCl solution containing 2g of pectin per liter of medium. This medium aimed to investigate the protective effects of pectin against steel corrosion in acidic conditions.

In this quarter (Q3), only A36 metal coupons were utilized in the corrosion tests. We are in the process of preparing metal coupons from a gas pipe material (API 5L). We aim to verify whether both A36 and API 5L exhibit similar corrosion performance. To better replicate real-world conditions, we plan to use API 5L in all future tests.

# Test Parameter Configuration

The configuration of the test parameters was performed through the software interface of the potentiostat. Key parameters entered included:

- Initial Potential (Einitial): Set 10 mV negative relative to the OCP. This was the starting point for the potential sweep.
- Final Potential (Efinal): Set 10 mV positive relative to the OCP. This defined the endpoint of the potential sweep.
- Scan Rate: Determined to be approximately 0.125 mV/s. The scan rate was crucial for ensuring that the system did not deviate significantly from equilibrium during the test.

# Execution of the Potentiodynamic Polarization Test

Once the parameters were set, the potentiodynamic polarization test was initiated. The software controlled the potentiostat to apply a linear sweep of potential from the initial to the final set values. During this sweep:

- The potential was incrementally increased from E<sub>initial</sub> to E<sub>final</sub>.
- The current response of the system was continuously measured as the potential was varied.

# Data Acquisition and Plotting

The current and potential data collected during the tests were automatically recorded by the software. This data was used to generate the Tafel plot, which graphed the potential (E) on the Y-

axis versus the logarithm of the current density (log I) on the X-axis. The Tafel plot was essential for analyzing the electrochemical behavior of the metal under the test conditions.

#### Identification of Linear Regions and Extrapolation

The Tafel plot typically exhibited linear regions corresponding to the anodic and cathodic branches. These regions were critical for the analysis as they reflected the kinetics of the oxidation and reduction reactions. Using the software:

- The linear portions of the anodic and cathodic curves were identified.
- These linear regions were extrapolated back to their intersection at the corrosion potential (E<sub>corr</sub>).

#### Calculation of Corrosion Current Density (icorr)

The intersection point of the extrapolated anodic and cathodic lines provided the value of the corrosion current density ( $i_{corr}$ ). This value was crucial as it directly related to the corrosion rate of the metal. The software facilitated the conversion of  $i_{corr}$  into the corrosion rate using pre-defined constants and material properties such as the equivalent weight of the metal and its density. Finally, the corrosion rate (CR) and efficiency of pectin on inhibition of corrosion (IE) were calculated using the following formulas.

$$CR = \frac{Icorr.K.EW}{\rho.A} \tag{1}$$

$$IE = \frac{CR_{pectin} - CR_{control}}{CR_{control}} \times 100$$
<sup>(2)</sup>

Where:

CR = Corrosion rate IE= inhibition efficiency k= Constant that depends on the units used for corrosion rate  $I_{corr} = Corrosion current density (A/cm<sup>2</sup>)$  EW = Equivalent weight of the corroding metal  $\rho = Density of the metal (g/cm<sup>3</sup>)$  A = Exposed surface area of the metal (cm<sup>2</sup>)

#### Result of the Tafel Polarization Tests

The Tafel polarization tests, carried out in two separate media, revealed unique corrosion properties for A36 steel, thereby highlighting the effectiveness of pectin as a corrosion inhibitor. The results of these tests produced Tafel plots, from which crucial parameters like corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), and corrosion rate were extracted. The raw data from the Tafel plots indicated the following outcomes for each medium:

Medium	dium E <sub>corr</sub>		CR (mmpy)	Inhibition Efficiency	
	(mV)				
1M HCl (Control medium)	-453.05	18.94	0.219	N/A	
1M HCl+2g/L pectin	-456.29	12.86	0.1487	32%	

Table 1.1 Raw data from the Tafel plots for each medium

The comparative analysis of the data from the two media reveals a clear decrease in both the corrosion current density and the corrosion rate in the presence of pectin. Specifically, the incorporation of pectin resulted in a reduction of  $i_{corr}$  by approximately 32%, indicating a significant decrease in the rate at which corrosion progressed.

The effectiveness of pectin as a corrosion inhibitor can be attributed to its ability to form a protective barrier on the metal surface. This barrier likely impedes the access of corrosive agents (HCl ions) to the steel surface, thereby reducing the electrochemical reactions that lead to corrosion. The slight shift in corrosion potential ( $E_{corr}$ ) in the presence of pectin (from -453.05 mV to -456.29 mV) supports the notion that pectin modifies the electrochemical environment at the steel surface.

The results underscore the potential of pectin as a viable, environmentally friendly corrosion inhibitor for A36 steel in acidic environments. The 32% inhibition efficiency indicates a substantial protective effect, which could translate into significantly increased lifespan and reduced maintenance costs for steel structures.

The Tafel polarization tests clearly demonstrated the efficacy of pectin as a corrosion inhibitor. The significant reduction in corrosion rate and the alteration in electrochemical behavior of the steel surface suggest that pectin or similar organic inhibitors could play an essential role in corrosion protection strategies, particularly in industries where steel is exposed to acidic conditions. Further research could explore the molecular interactions between pectin and metal surfaces to optimize the formulation and application methods for industrial use.

# **1.3.2 Electrochemical Impedance Spectroscopy in Electrochemical Corrosion Testing**

Electrochemical Impedance Spectroscopy (EIS) is a powerful and sensitive analytical technique widely used in the field of electrochemical corrosion testing. By measuring the impedance of a system over a range of frequencies, EIS provides detailed insights into the electrochemical processes occurring at the interface between a metal and its environment. This methodology has become indispensable for researchers and engineers involved in the development of corrosion-resistant materials and the assessment of protective coatings.

The theoretical foundation of EIS is rooted in the early 20th-century developments in electrochemistry and electrical engineering. However, it was not until the advent of modern electronics and computers in the latter half of the century that EIS evolved into the sophisticated tool it is today. Initially used for studying battery systems and fuel cells, the application of EIS in

corrosion science began to gain prominence as it provided a non-destructive means of analyzing corrosion mechanisms.

# Theoretical Principles of EIS

Electrochemical Impedance Spectroscopy operates on the principle of applying a small amplitude AC voltage to an electrochemical cell and measuring the resulting current. The response of the system is analyzed across a spectrum of frequencies to determine the impedance, a complex quantity comprising resistive and reactive (capacitive and inductive) elements. The impedance of a metal/environment interface is influenced by various factors, including the properties of the metal, the nature of the electrolyte, and the presence of any corrosion products or coatings.

# Components of an EIS System

An EIS setup typically includes:

- **Electrochemical Cell**: Contains the working electrode (material under test), a reference electrode, and a counter electrode.
- Frequency Response Analyzer: Generates the AC signal and measures the response.
- **Potentiostat**: Controls the potential of the working electrode against the reference electrode.

# Advantages of EIS in Corrosion Testing

EIS offers several advantages over traditional corrosion testing methods:

- **Non-Destructive**: EIS does not alter the sample during testing, allowing for real-time monitoring of corrosion processes.
- Sensitivity to Surface Changes: EIS can detect minute changes in the electrochemical properties of the interface, making it ideal for evaluating the effectiveness of corrosion inhibitors and coatings.
- Wide Range of Applications: From monitoring corrosion in reinforced concrete to assessing the integrity of coatings on aircraft, EIS's versatility makes it a valuable tool across diverse industries.

# EIS Data Interpretation

The interpretation of EIS data is typically facilitated through the use of Nyquist and Bode plots, which graphically represent the impedance characteristics of the system. These plots can reveal:

- Charge Transfer Resistance: Related to the ease with which electrons can move across the electrode/electrolyte interface.
- **Double Layer Capacitance**: Reflects the capacitive behavior at the interface, influenced by the thickness and properties of the electrochemical double layer.

• Warburg Impedance: Indicates diffusion-controlled processes, often seen in porous coatings or corrosion layers.

### Applications in Corrosion Science

In corrosion science, EIS is used to study:

- **Corrosion Kinetics**: Understanding how the corrosion rate changes with time under various environmental conditions.
- Evaluation of Corrosion Inhibitors: Assessing how different inhibitors affect the electrochemical behavior of the metal.
- **Coating Degradation**: Monitoring the degradation of protective coatings over time to predict failure and maintenance needs.

# Methodology for Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) tests were conducted to evaluate the efficacy of pectin as a corrosion inhibitor on A36 steel. These tests were performed in two different media:

- Medium 1 (Control): Pure 1M HCl solution.
- Medium 2 (Pectin Mixed): A 1M HCl solution containing 2g of pectin per liter of medium.

The EIS measurements utilized a standard three-electrode cell setup:

- Working Electrode: A36 steel specimen with polished surface using sand #80, #200, #400, #800, #1200. The sample surface was polished as per test protocol for higher accuracy of corrosion test results.
- **Reference Electrode**: Saturated Calomel Electrode (SCE).
- **Counter Electrode**: Platinum wire.

### Instrumentation and Measurement Parameters

The EIS was conducted using a frequency response analyzer coupled with a potentiostat, which maintained the electrode potential and measured the impedance response. The specific parameters used in the EIS tests are summarized in the table below:

Parameter	Value	Description
AC Signal Amplitude	10 mV	The amplitude of the alternating current
		signal.
Frequency Range	100 kHz to 10 mHz	The range over which impedance was
		measured.
Potentiostat Mode	Potentiostatic (constant	Maintains a constant electrode potential
	potential)	during measurements.

Table 1.2. Parameters used in the EIS tests

Equilibration Time	At least 3 hours	Allows the system to stabilize before
		measurements.

### Data Acquisition

EIS measurements were initiated after a stabilization period, during which the electrochemical system reached a steady state. Impedance data were acquired across the specified frequency range, capturing the complete electrochemical response.

# Data Analysis

The impedance data were analyzed by fitting them to an equivalent circuit model to extract key parameters such as solution resistance ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ), and constant phase element (CPE). These parameters were derived from Nyquist plots, which graph the imaginary part of impedance (Z'') against the real part (Z').

# Equivalent Circuit Model

The equivalent circuit used for analyzing the impedance plots consisted of:



Figure 1.2. Equivalent Circuit Diagram Derived from EIS Corrosion Test Results

- **R1**: Solution resistance (R<sub>s</sub>).
- **R2**: Charge transfer resistance (R<sub>ct</sub>).
- **CPE1**: Impedance of the constant phase element.

### Steps for Measuring Solution and Charge Transfer Resistance

- 1. **Perform EIS Measurement**: Conduct an EIS experiment over a broad frequency range.
- 2. Analyze Nyquist Plot: Plot the Nyquist diagram and identify the intercepts and features corresponding to R<sub>s</sub> and R<sub>ct</sub>.
- 3. Calculation of Parameters:
  - Solution Resistance  $(R_s)$ : High-frequency intercept on the real axis of a Nyquist plot.
  - Charge Transfer Resistance (R<sub>ct</sub>): Represents the electron transfer resistance at the electrode-electrolyte interface.



Figure 1.3. Nyquist diagram of electrochemical impedance spectroscopy test

The impedance characteristics, such as the diameters of the semicircles in Nyquist plots, indicate the corrosion resistance. An increased diameter implies higher corrosion resistance and is a direct measure of the inhibitory effects of pectin. The results were quantitatively assessed using the collected EIS parameters, specifically focusing on the changes in  $R_s$  and  $R_{ct}$ , to evaluate the performance of pectin as a corrosion inhibitor.

This systematic approach provided a comprehensive understanding of the corrosion behavior of A36 steel in the presence and absence of pectin, underlining the effectiveness of EIS in evaluating corrosion inhibitors in various media. The following formula was used to measure pectin's inhabitation efficiency (IE).

$$IE = \frac{R_{P Pectin} - R_{P Control}}{R_{P Control}}$$
(3)

#### Result of Electrochemical Impedance Spectroscopy Test

EIS tests were performed on A36 steel in both control and pectin-infused media, yielding important impedance data. These data were examined using Nyquist plots. The findings underscore substantial variations in the electrochemical behavior of the steel when the pectin inhibitor is present versus when it is absent.

### Interpretation of Nyquist Plots



Figure 1.4. Comparative Nyquist Plots for Both Media

Nyquist plots for both media displayed a single semi-circle, indicative of a charge-transfer controlled corrosion process. The key observations from the Nyquist plots include:

- Uninhibited Solution (Control):
  - Smaller semi-circle diameter, indicating lower impedance values.
- Inhibited Solution (Pectin Mixed):
  - Larger semi-circle diameter, suggesting increased impedance and thus enhanced resistance to corrosion.

These observations imply that the presence of pectin at the carbon steel-electrolyte interface increases the impedance, thereby reducing the corrosion rate.

### Quantitative Analysis

The EIS parameters extracted from the equivalent circuit model provided quantitative insights into the corrosion inhibition mechanism:

Parameter	Control	Pectin	Unit	Improvement with
		Mixed		Pectin
Solution Resistance (Rs)	2.1	1.9	Ω	Increased conductivity
			cm <sup>2</sup>	
Polarization Resistance (Rct)	1046	1616	Ω	Improved by 54.5%
			cm <sup>2</sup>	
Constant Phase Element	9.9×10 <sup>-5</sup>	7.2×10 <sup>-5</sup>	F/s	Reduced capacitance
(CPE)				
Inhibition Efficiency	-	54	%	Significant improvement

Table 1.3. EIS parameters extracted from the equivalent circuit model

Key Observations:

- Solution Resistance (Rs): A slight decrease in Rs in the pectin mixed solution indicates slightly better ionic conductivity.
- **Polarization Resistance (Rct)**: A significant increase in Rct from 1046  $\Omega$  cm<sup>2</sup> in the control to 1616  $\Omega$  cm<sup>2</sup> in the pectin mixed solution suggests a substantial improvement in corrosion resistance due to the inhibitory action of pectin.
- **Constant Phase Element (CPE)**: The decrease in CPE value reflects a reduction in the double-layer capacitance, possibly due to the formation of a more compact layer at the electrode surface.

The enhanced polarization resistance in the presence of pectin indicates that pectin molecules adsorb onto the steel surface, forming a protective barrier that impedes the charge transfer process associated with corrosion. This barrier effect not only increases the overall impedance but also modifies the electrochemical environment at the interface, making the corrosion process less favorable.

The slight imperfections in the semi-circle shape observed in the Nyquist plots, indicative of frequency dispersion, could be attributed to the roughness and heterogeneity of the metal surface. Such imperfections are typical in real-world scenarios and underscore the complexity of interpreting EIS data in practical corrosion systems.

So, the EIS test results convincingly demonstrate the effectiveness of pectin as a corrosion inhibitor in acidic environments. The quantitative data from the impedance analysis corroborate the visual and qualitative interpretations from the Nyquist plots, providing a comprehensive picture of the inhibitory mechanism. These findings not only validate the use of pectin as an eco-friendly corrosion inhibitor but also illustrate the utility of EIS as a diagnostic tool in the study of corrosion processes and inhibitor performance.

#### 1.3.3 Evaluating the Long-term Durability and Corrosion Inhibition Properties of Pectin

• Conducted long-term weight loss experiments to evaluate the durability and protective properties of pectin, quantifying the material degradation and affirming its suitability for industrial applications.

The corrosion tests employed A36 steel sheets, characterized by an unpolished (mill) finish, hot rolled, and conforming to ASTM A36 standards. The steel sheets, with a thickness of 0.06 inches, were cut using a CNC cutter into test coupons measuring 2.0 cm by 1.0 cm. A corrosive medium was prepared using 1M hydrochloric acid (HCl), formulated from 37 percent analytical reagent (AR) grade HCl. This solution aimed to simulate aggressive corrosion conditions. Two distinct mediums were prepared to evaluate the corrosion resistance of the steel coupons under varying conditions:

Medium 1 (Control): Pure 1M HCl solution, serving as the control to assess the effect of the corrosive medium on unprotected A36 steel.

Medium 2 (Pectin Mixed): A solution consisting of 0.2 g of pectin dissolved in 100 ml of water, mixed with pure 1M HCl. This medium aimed to investigate the influence of pectin presence in the corrosive media on steel corrosion.

The differences in weight loss across the two media were analyzed to assess the efficacy of pectin in mitigating corrosion on A36 steel.

### Test Procedure

For each test, the respective steel coupons were completely immersed in a 500 ml glass beaker containing one of the prepared test solutions. The experiments were conducted over several duration of 2 weeks, 4 weeks, and 6 weeks at a controlled temperature of 25 °C. To minimize the influence of oxygen and ensure consistent conditions, the beakers were placed in a fume hood. Before immersion, each steel coupon was accurately weighed to determine its initial mass. Following the exposure periods, the coupons were retrieved from their respective solutions. To remove any corrosion products formed during the test, each coupon was thoroughly scrubbed under running water using a bristle brush and cleaned with acetone. After cleaning, the coupons were dried in acetone to remove any residual moisture and reweighed to determine the final mass.

The primary evaluation metric for this experiment was the weight loss of the steel coupons, calculated by subtracting the final mass from the initial mass of each coupon. This measurement provided a quantitative assessment of the corrosion rate experienced by the steel in each medium, thus allowing for the comparison of the protective effects of pectin against corrosion when mixed

in the solution. Tables 1.4 to 1.6 show the average result of the weight loss test on each medium and the efficiency of pectin's corrosion inhabitation compared to the control samples.

	Condition	<b>W</b> <sub>1</sub> (g)	W2(g)	W3(g)	Average	Weight Loss(g)	Corrosio n (%)
2 week s in	Weight before corrosion	3.77704	3.7651 6	3.7932 6	3.778487	0.3348	8.862
1M HCl	Weight after corrosion	3.48571	3.3929	3.4523 6	3.443653		
2 week s in	Weight before corrosion	3.80058	3.8036 3	3.7935	3.799237		
HCl + Pecti n	Weight after corrosion	3.74578	3.6806	3.7181 5	3.714843	0.084	2.221
						Inhibitor Efficiency (%)	74.993

Table 1.4. Comparison of weight loss of metal coupons after 2 weeks



Figure 1.5. Visual Comparison of Metal Coupons Following Two Weeks of Corrosion Tests

	Condition	W1(g)	W2(g)	W3(g)	Average	Weight Loss(g)	Corrosio n (%)
4 week s in 1M HCl	Weight before corrosion	3.77715	3.7467 4	3.7753 1	3.76454	0.35407	9.405
	Weight after corrosion	3.3173	3.4360 3	3.4781 8	3.410503		
4 Weig week befo s in corros 1M HCl + Weight Pecti corros n	Weight before corrosion	3.79257	3.7804	3.8158	3.796257	0.17692	4.660
	Weight after corrosion	3.56769	3.6238 3	3.6664 9	3.619337		
				<u>.</u>	<u>.</u>	Inhibitor Efficiency (%)	50.451

Table 1.5. Comparison of weight loss of metal coupons after 4 weeks



Metal samples in HCL + Pectin



	Condition	<b>W</b> <sub>1</sub> ( <b>g</b> )	W <sub>2</sub> (g)	W3(g)	Average	Weight Loss(g)	Corrosio n (%)
6 wee	Weight before corrosion	3.7611	3.7851 5	3.7845 8	3.776943		
ks in 1M HC l	Weight after corrosion	3.2635	3.2902 5	3.3733 5	3.309033	0.46791	12.39
6 wee ks	Weight before corrosion	3.7308	3.7906	3.7784	3.7666		
in 1M HCl + Pec tin	Weight after corrosion	3.53846	3.5560 4	3.5792 5	3.557917	0.2086	5.54
						Inhibitor Efficiency (%)	55.28

Table 1.6. Comparison of weight loss of metal coupons after 6 weeks



Metal samples in HCL + Pectin

Figure 1.7. Visual Comparison of Metal Coupons Following Six Weeks of Corrosion Tests

Based on the data provided in Tables 1.4, 1.5, and 1.6 and the corresponding figures in this report, it is evident that pectin has shown significant potential as a green corrosion inhibitor. It effectively reduces metal corrosion in aggressive acidic environments during testing.

In the short-term test spanning two weeks, control samples immersed in 1M HCl exhibited an average corrosion percentage of 8.862% with a weight loss of 0.3348 grams. When pectin was introduced, the corrosion rate significantly dropped to 2.221%, with a weight loss of only 0.084 grams. This translates to an inhibitor efficiency of approximately 74.993%, highlighting pectin's remarkable effectiveness at curbing corrosion in a short period.

Extending the duration to four weeks, the corrosion in control samples slightly increased to a 9.405% corrosion rate and a weight loss of 0.35407 grams. However, samples treated with pectin showed a lower corrosion rate of 4.660% and a weight loss of 0.17692 grams, resulting in an inhibitor efficiency of about 50.445%. Although the effectiveness of pectin decreased compared to the two-week test, it still provided significant protection against corrosion.

For the long-term evaluation over six weeks, the untreated samples showed further increased corrosion, reaching 12.39% with a weight loss of 0.46791 grams. The pectin-treated samples maintained better resistance, showing a corrosion rate of 5.54% and a weight loss of 0.2086 grams, with an efficiency rate of 55.28%. Despite the longer exposure, pectin continued to offer considerable protection, albeit with a slight reduction in efficiency compared to the earlier intervals.

The visual evidence from Figures 1.5, 1.6, and 1.7 corroborates the quantitative data, showing that metal coupons treated with pectin exhibited considerably less surface corrosion than those left unprotected. This consistent trend across all test durations underscores pectin's capability to protect metal surfaces under varied conditions. However, despite the overall reduction in surface corrosion, some samples treated with pectin showed localized damage, such as piercing or the formation of ditches on the metal surfaces. This occurrence, while reducing the general corrosion rate, poses a significant risk if such a phenomenon were to occur in actual pipeline applications, where even minor structural failures can lead to severe consequences.

The occurrence of pitting corrosion is likely attributed to the presence of chloride in the testing medium. Typically, chloride can induce pitting corrosion when the metal surface undergoes passivation, as seen in this test that included an additional corrosion inhibitor. The chloride has the potential to integrate into the protective film formed by the inhibitor and compromise the metal surface at points where the film is weak <sup>[1]</sup>.

In summary, while pectin has demonstrated its effectiveness as a corrosion inhibitor, particularly in the initial exposure stages, its performance shows a slight decline over time but still provides substantial protection compared to unprotected samples. These findings suggest that pectin holds promise as a sustainable alternative to traditional corrosion inhibitors, especially in scenarios where minimizing environmental impact is crucial. The next phase of research should focus on addressing the observed localized damage to ensure the reliability and safety of pectin as a corrosion inhibitor in real-world applications.

The use of 1M HCl, a highly concentrated acid, was initially chosen to accelerate corrosion for rapid testing outcomes. However, following the recommendations of industry experts, the weight loss tests were also conducted using a diluted 0.25M HCl solution to more accurately simulate the milder corrosive environments typically found in pipelines. Following the established procedure, these tests involved immersing metal coupons in both types of acidic media for six weeks to assess and compare the effects of different acid concentrations on corrosion rates. Table 1.7 shows the average result of the weight loss test on each medium and the efficiency of pectin's corrosion inhabitation compared to the control sample.

	Condition	<b>W</b> <sub>1</sub> ( <b>g</b> )	W <sub>2</sub> (g)	W3(g)	Average	Weight Loss(g)	Corrosion (%)
6 wee	Weight before corrosion	3.78612	3.7786 5	3.7982 5	3.787673		
in 0.2 5M HC I	Weight after corrosion	2.29125	2.3887 6	2.1871 1	2.28904	1.498	39.566
6 wee ks in	Weight before corrosion	3.8106	3.7564	3.8113 8	3.792793	0.37686	9.936
0.2 5M HCl + Pec tin	Weight after corrosion	3.51761	3.3682	3.3619 9	3.41593		
	<u>.</u>	<u>.</u>			<u>.</u>	Inhibitor Efficiency (%)	74.887

Table 1.7. Comparison of weight loss of metal coupons after 6 weeks in diluted corrosive media



Figure 1.8. Visual Comparison of Metal Coupons Following Six Weeks of Corrosion Tests

The results from the diluted 0.25M HCl tests reveal a significant level of corrosion in the absence of pectin. Initially, the average weight of the metal coupons was approximately 3.787673 grams, which decreased sharply to 2.28904 grams after exposure, resulting in a high corrosion percentage of 39.566%. This level of corrosion underscores the aggressive nature of even diluted acidic environments and emphasizes the necessity for effective corrosion mitigation strategies. It was observed that an increased concentration of chloride accelerates the onset of pitting. However, the impact of chloride concentration on corrosion weight loss remains uncertain, given the various corrosion mechanisms involved <sup>[2]</sup>. Further investigations are needed to elucidate the corrosion mechanisms at various chloride concentrations.

Conversely, the addition of pectin to the diluted acid solution markedly improved the corrosion resistance of the metal coupons. With pectin, the initial average weight was slightly higher at 3.792793 grams, and the weight after the six weeks was reduced to only 3.41593 grams. This corresponds to a significantly lower corrosion percentage of 9.936%, demonstrating pectin's effectiveness in reducing material loss under corrosive conditions. The calculated inhibitor efficiency of 74.887% highlights the substantial protective capabilities of pectin against corrosion.

Figure 1.8 visually corroborates the quantitative data, showing that metal coupons treated with pectin exhibited considerably less surface damage compared to those immersed in the acid solution without any protective agent. The metal surfaces in the pectin-treated group showed fewer and less severe signs of surface corrosion, validating the effectiveness of pectin as a corrosion inhibitor. However, even in the diluted medium, occurrences of pierced and extensively corroded spots were observed on metals treated with pectin, which raises concerns about the potential detrimental effects of pectin, particularly its role in creating localized areas of significant damage.

In summary, while the tests in diluted corrosive media highlight the severe impact of even mild acidic conditions on metals, they also demonstrate the notable protective effects of pectin. These results support the potential of pectin as an effective and environmentally friendly corrosion inhibitor for industrial applications, particularly under conditions that mimic real-world corrosive environments. The overall consistency of pectin's protective performance across various conditions points to its appropriateness for broader industrial use. Nonetheless, the observed localized damage necessitates further investigation into pectin's long-term stability and mechanisms to prevent such detrimental effects, ensuring its reliability and safety in practical applications.

### <u>Task 2. Simulation-based Inhibitor Implementation Optimization in Gas Gathering and</u> <u>Transportation Pipelines</u>

#### Introduction

#### Background

In current protection approaches for pipeline systems, the application of corrosion inhibitors shows good efficiency and economics. Preventing the pipe wall from corrosive liquid or gas, corrosion inhibitors with reasonable implementation is able to largely expand the lifetime of the pipeline. However, the complicated near-wall flow regime leads to the difficulty of formulating the application scheme of inhibitors. Compared to static liquid, inhibitor particles suffer from more violent collision and erosion under the flow, which may accelerate the weakening and adhesion loss of the inhibitor protective film.

The degradation process of existing inhibitors with respect to different flow conditions is usually ambiguous, and many improved products of inhibitors have been gradually spread. At this point, only by increasing the safety factor (supplementing corrosion inhibitors more frequently) can the protective performance of the film be ensured to reduce irreversible damage to the pipe wall. But this will cause unnecessary resource waste. This research aims to investigate the mechanism of flow-induced inhibitor degradation.

Within the general pipeline of our project, the flow rate is always lower than 5 m/s that hardly leads to obvious near-wall turbulence. In the view of energy, the desorption of inhibitor particles from the wall can be assumed as the main reaction corresponding to inhibitor degradation, which is depicted in Figure 2.1. According to the Langmuir adsorption model, initially added inhibitors will reach the absorption-desorption balance, i.e., from (a) to (b) in Figure 2.1, in which only one layer of inhibitor film can strongly attach to the wall without a long time. This also conforms to the characteristics of inhibitor particles that cannot connect. The change from (a) to (b) will not largely impair protection performance. But as certain inhibitor particles gradually desorb from the pipe wall, i.e., from (b) to (c) in Figure 2.1, a part of the pipe wall surface will be exposed to the flow, leading to significant reduction of protection performance. The process from (b) to (c) is long-term and slow. Nevertheless, making clear the relationship between impact factors and inhibitor desorption can give the reference to the scheme of inhibitor application and thus improve its efficiency and economy.



Figure 2.1. The assumed desorption process of inhibitor particles from the wall.

In low-flow-rate pipeline, wall shear stress (WSS) serves as a key metric contributing to inhibitor desorption. Other factors, like the pipe size and flow rate, have proportional relation to WSS and can be totally considered by the latter. Therefore, the stability of the corrosion inhibitor film under fluid flow is evaluated using WSS as a pivotal reference, highlighting the critical relationship between flow dynamics and the integrity of corrosion protection.

To derive the WSS distribution within the pipeline, we need to run a large amount of refined computational fluid dynamics (CFD), for the pipe wall roughness surface profile is at least at the scale of 0.1 millimeters. The work in the last phase revealed the probability of applying deep learning for predicting WSS, which aimed to build a surrogate model that replaces CFD to produce WSS data more efficiently. Focus on numerical simulations, we specially developed Fourier neural operator (FNO). The well-trained FNO is expected to yield the target WSS data with given roughness shape information. However, the FNO framework established in the last phase failed to predict those with the roughness that never occurred in the training set, which would be improved in the research of this quarter.

As for the training of the applied neural network, another considerable issue is the acquisition of training data. In general, this data is derived by CFD in high fidelity that is helpful to increase the reliability of the surrogate model. However, concomitant much larger consumption of computational resource in the full high-fidelity flow field is not cost-effective, since only a small part of CFD results is needed, e.g., WSS in our research. To address this issue, we also aim to develop a multi-fidelity approach that learns the relationship between high-fidelity (HF) and low-fidelity (LF) data, so that we can predict the required HF results from LF information, achieving a balance between detail and efficiency.

The primary focus of task 2 is to improve the existing deep learning method to collect desired flow information, which serves to build a preliminary framework for specifying the relationship of protective film degradation and WSS under the use of different types of corrosion inhibitors.

The outcomes of this study are expected to contribute significantly to the development of more effective strategies for pipeline protection, enhancing the longevity and safety of these critical components in the energy infrastructure.

### Objectives

The main objective of this research is to improve the surrogate model to predict WSS with different roughness information. The resulting WSS is further used to study inhibitor degradation under a flow condition.

A key aim is to incorporate uncertainty quantification, including aleatoric uncertainty and epistemic uncertainty, into the surrogate model, providing reliability of predicted WSS.

The research also seeks to develop the multi-fidelity approach that can derive HF information of 3-D cases from given LF data of 2-D cases. The cross-fidelity prediction will balance the requirement on both detail and efficiency.

Additionally, the study aims to establish an experience model for describing inhibitor degradation for WSS, time and types of inhibitors. The supporting test will be preliminarily designed.

By achieving these objectives, the simulation project aspired not only to contribute to improving the longevity and safety of pipelines but also to demonstrate a scalable and efficient model for conducting simulations that traditionally require significant computational efforts from engineering design and analysis to research and development in fluid mechanics.

#### Methodology

#### WSS prediction

In establishing the surrogate model for a fast prediction of WSS, the training data is derived from CFD, in which A series of 2-D pipe segments is analyzed under different shapes of wall roughness. Then, the framework of FNO is applied to build the mapping between WSS and wall roughness. First, a brief overview of previous work on WSS prediction will be provided, followed by a detailed explanation of the surrogate FNO model's progress.

### **Brief review**

In the last phase, wall roughness is set at a 0.05m-length boundary of the 2-D pipe with the remaining part of being totally smooth for each computational case of CFD, as shown in Figure 2.2, which ensures the fully developed flow field in enough length. Specifically, each training or testing set contains the data at 200 continuous points, in which original values of x-coordinate and WSS are used, while the derivative of y over x ( $y'=\Delta y/\Delta x$ ) replaces y values to form the dataset. Here, x and y' are set as the input of FNO, and WSS is calculated by CFD as the output.



The comparison testing results with traditional fully-connected network demonstrated better adaptability of FNO in WSS prediction. However, we extracted training and testing data from the same roughness case in the previous work, and the existing FNO model was limited in prediction with the shape of wall roughness that never occurred in the training set. For this reason, we aim to improve the existing FNO model to predict WSS with different roughness information.

#### **Establishment of dataset**

Roughness profile is designed in trigonometric functions as  $y=a*\cos(f^*x)+a$ , where a and f denote the factors of amplitude and frequency, respectively. In the current research, a is considered in the series [0.12, 0.14, 0.16, 0.18] (millimeter), and f is in [0.05, 0.10, 0.15, 0.20, 0.25]. In total, twenty cases with different combinations of a and f are used. The roughness profile is integrated into the pipe segment shown in Figure 2.2 to run CFD in Ansys Fluent 2023, in which related settings about meshing and solution are similar to before.

CFD results provide the WSS data corresponding to each point of roughness profile that is still set as the only output of the FNO model. Different from the previous work, y-coordinate is incorporated as the input. As a result, three dimensions of data (x, y and  $y'=\Delta y/\Delta x$ ) are used to characterize location information. Figure 2.3 illustrates the data extraction approach that cuts out continuous points from a case and divides it into the "previous", "middle" and "next" segments. Location information of these three segments is totally set as the input, while only WSS with respect to the middle segment is used as the output. This implementation is under the consideration that WSS is affected by roughness profile. Besides, the figure also shows that data points in each case are extracted by moving slicing, and the moving step is usually less than the length of the full segments to increase the available data. In our cases, the lengths of the previous, middle and next segments are 200, 50 and 200 points, respectively; The moving step is set as 50 points.



Figure 2.3. Illustration of data extraction

### **FNO** setup

To illustrate the surrogate model more clearly, Figure 2.4 depicts the framework of the applied FNO model suitable to our cases. Considering one batch of data, the initial input is a matrix with three rows. It would be first expanded to a new one with more rows, which can be regarded as an encoder process incorporating more information. Then, a series of fast Fourier transform (FFT) and inverse fast Fourier transform (IFFT) are applied to the row space. Later, two row linear transfers are performed to condense the data to a row vector. Traditional FNO only got the output with the same size as the input. Therefore, we try two types of transfer to adjust the column number: The one is column linear reduction, and another is to directly cut down the redundant points of the "previous" and "next" segments. The comparison shows the latter one is better and is chosen as the final reduction approach. This is reasonable since FNO attaches importance to the location arrangement of each point. But the column transfer would hurt this arrangement. It can be also seen that in the previous layer transfer, FNO learned the data relationship only from row transfers.



Figure 2.4. Illustration of data flow in FNO

# **Prediction results of WSS**

The roughness case with a=0.1 and f=0.15 is used as the testing set, and the datasets corresponding to the remaining nineteen cases as training sets. Figure 2.5 shows the prediction results of WSS for three sets. From the figure, we can see that the predicted values follow the similar trend of change as a target. Taking into accounts the most unfavorable situations, we focused on the peak values, which cannot be always accurately predicted. The first peak in the third set of Figure 2.5, for example, got an obvious difference between target and predicted values. This may mainly due to the uncertainty of the WSS data, as reflected in Figure 2.6, which shows that the computational WSS from CFD has patent fluctuation. The complexity of the flow lead to this uncertainty even in a regular periodic roughness profile, let alone more chaotic boundary shapes in practice. The uncertainty appeared in WSS prediction should be quantified and will be further discussed later.



Figure 2.6. Illustration of the uncertainty appeared in WSS data

#### Contrastive study for WSS prediction

To investigate the in-depth research about the application of FNO on WSS prediction, two groups of contrastive studies are performed.

The first one is under a different data normalization approach. Figure 2.7 depicts the prediction results under four contrastive conditions: (a) all datasets conformed to the same mean values and variance, which are calculated from the integrity of the data in nineteen training cases, and this approach is applied by the FNO used in the last section; (b) data of each roughness case is

individually normalized; (c) data of each training and testing set, i.e., cut-out segment, is individually normalized; (d) no normalization is performed. There is certain difference among the first three conditions. But as mentioned before, this may be due to the uncertainty of computational WSS. In total, the first three normalization approaches are accessible to achieve acceptable prediction results. On the contrary, the result in Figure 2.7(d) shows that non-normalization cannot lead to a good prediction in our case.



Figure 2.7. WSS prediction results under different conditions of data normalization.

Another contrastive study is applied to the traditional fully-connected neural network (FCNN) with the model shown in Figure 2.8. Except that the FFT and IFFT layers are eliminated, other network setups of this model are the same as the FNO used in our research. The WSS results predicted by FCNN are shown in Figure 2.9, which are much worse than those in Figure 2.5 (results with FNO). This comparison emphasizes the superiority of FFT-related layers in the FNO framework.



Figure 2.8. Illustration of data flow in FCNN



Figure 2.9. Prediction results with FCNN.

#### Uncertainty quantification in FNO

For further improvement, we introduce the uncertainty qualification approach into FNO that considers both aleatoric uncertainty (AU) and epistemic uncertainty (EU). In a word, the former is about measurement noise and inadequate accuracy, and the latter is mainly about untouched points in training data. At the stage of implementation, the loss function of FNO containing AU has the following expression:

Loss = 
$$\frac{1}{N} \sum_{i=1}^{N} \frac{1}{2} \exp(-\sigma) \|y_i - f(x_i)\|^2 + \frac{1}{2}\sigma$$
 (4)

Where N denotes the number of datasets;  $y_i$  and  $f(x_i)$  are the target value and the prediction output of the *i*-th dataset, respectively; The variance  $\sigma$  is produced from the full layers, that is, from the input to output. Another network with the same framework but additional sets of parameters is trained for  $\sigma$ . EU can be quantified by adding the dropout into a layer, i.e., randomly dropping some neurons for data transfer. In this study, the EU-related dropout with the value of 0.5 is set at the row reduction layer in Figure 2.4.

The prediction results with uncertainty quantification are depicted in Figure 2.10, in which the blue areas show the 95% confidence interval of the prediction values. These results conform to the actual situation, that is, both AU and EU are larger when the actual prediction error is larger, such as those in the peak of WSS. But up to now, there is no specific method to determine to what extent the uncertainty qualification results can reflect the real uncertainty. It still needs more tests and clarity.



Figure 2.10: Uncertainty quantification results with FNO
#### 2.2 Multi-Fidelity Approach

The multi-fidelity approach is a powerful strategy used to enhance analysis and decision-making by integrating multiple data sets with varying levels of detail and accuracy. In obtaining precise fluent parameters, this approach has the following key benefits:

- **Cost Optimization**: By using LF models for initial analyses and HF models for detailed validation, the overall cost of simulations is reduced. This balance allows for the efficient allocation of resources.
- **Computational Efficiency**: LF models provide quick insights and preliminary results, reducing the need for extensive HF simulations in the early stages. This approach minimizes computational time and effort.
- Enhanced Decision-Making: The integration of both HF and LF data provides a comprehensive understanding of the system. LF models highlight general trends, while HF models confirm detailed interactions, leading to well-informed decisions.
- **Iterative Improvement**: Using LF models allows for rapid iterations and adjustments in the design process. HF models can then be applied selectively to verify critical aspects, ensuring a more robust and optimized design.
- **Risk Reduction**: By identifying potential issues early with LF models and validating solutions with HF models, the risk of errors and costly design flaws is significantly reduced.

This section will give detailed illustration for the application of the multi-fidelity approach in pipe cases.

#### 2.2.1 Data acquisition

Initially, we sought to use a 2-D coarse mesh as low-Fidelity and 2-D fine mesh as high-Fidelity, however, we noticed that there wasn't enough difference in results to consider them to be of different fidelity. For instance, in this scenario, a U-bend pipe is taken into consideration for a simple 2-D single phase, second-order turbulent flow CFD simulation. The K-epsilon model is used with a medium coarse mesh and a fine mesh. The two results produced highly similar results with a similar computational time, as shown in Figure 2.11, which is not ideal enough to be considered as cases with different fidelity.







Figure 2.11. Uncertainty quantification results with FNO.

Then, we switched things up to 2-D and 3-D, and the corresponding CFD results of the computational maximum static pressures are listed in Table 2.1. It is noticed that we collect sparse HF data, while LF data is relatively comprehensive since our target is to predict ungiven HF information with the existing data. The obvious difference between LF results (2-D) and HF (3-D) results indicates the availability of using these cases for study.

	1 1	J
Velocity	Maximum static pressure	
	LF (2-D)	HF (3-D)
1	2601.12	
1.25	2549.56	
1.5	2890.36	
1.75	3270.16	
2	3669.73	4302.568
2.25	4158.18	
2.5	4728.33	5435.338
2.75	5323.68	
3	5994.28	6672.125
3.25	6715.60	
3.5	7599.13	8469.341
3.75	8346.92	
4	9158.34	10355.25
4.5	11050.02	
4.75	12052.50	
5	13136.21	

Table 2.1. Comparison of maximum static pressure between fidelity

#### 2.2.2 Cross-fidelity prediction

The architecture of the applied neural network is as follows:

- Input Layer: Takes in multi-dimensional input that includes both LF and HF data points.
- **Convolutional Layer**: Extracts features from the input data using a convolutional neural network (CNN).

- Dense Layers: Comprises both a linear and non-linear path:
- Linear Path: Directly estimates the HF response.
- Non-linear Path: Captures the complex interactions between the LF and HF data.
- **Output Layer**: Combines the outputs of the linear and non-linear paths to predict the HF response.

The training of the neural network is accomplished in the Tensorflow module of Python, and Figure 2.12 shows the change of network loss over epochs. It can be seen that the training tends to converge after 100 epochs. As a result, Figure 2.13 depicts the curve for HF prediction (green line), which closely follows the trend of the high-fidelity actual values (red dots), indicating that the surrogate model effectively captures the detailed interactions and behaviors reflected in the HF data. The alignment of the model's predictions with the HF values demonstrates the success of integrating LF and HF data, leveraging the computational efficiency of LF data while maintaining the accuracy of HF data.



Figure 2.12. Loss over epochs in the training process.



Figure 2.13. Prediction results of high-fidelity data.

#### 2.3 Inhibitor desorption model

With given WSS, an inhibitor degradation model is preliminarily built, which is expressed by desorption rate k of the inhibitor in Arrhenius Equation as:

$$k = A(s,t,i_n) \exp\left(-\frac{E}{RT}\right)$$
(5)

Where A is the prefactor of desorption that is deemed to be related to s (WSS), t (time) and  $i_n$  (the *n*-th testing inhibitor); E denotes the reaction energy of desorption; R is the Molar gas constant; T denotes the temperature. To measure the desorption rate, the surface coverage rate  $\theta$  of the inhibitor should be first recorded in the experiment as:

$$\theta = \frac{CR_0 - CR_i}{CR_0}, \ \frac{d\theta}{dt} = k \tag{6}$$

Where  $CR_i$  and  $CR_0$  the corrosion rates with and without the inhibitor. With a series of points of  $\theta$ , the desorption rate is accessible as the derivative of  $\theta$  with respect to time. In general, the parameters *E*, *R* and *T* are accessible. Then, through measuring multiple values of *k* under different WSS, time and types of inhibitors, the relationship between inhibitor degradation and the three variables is expected to be clarified.

#### 3. Future research

As the main task, we focus on establishing a specific degradation model for different types of inhibitors. In the current work, we focused on the pectin-based inhibitor, and our TAP member suggests to compare with traditional inhibitors. We will try at least two types and extend to other types of inhibitors if necessary. Fig. 3.1 schematically illustrates the concept for three inhibitors (maybe less or more depending on future research findings). This relies on the flow experiment that is expected to be implemented in the next phase. The later designed experimental device will be in the similar form as that shown in Figure 3.1.  $s_1$  to  $s_4$  in the figure represent different WSS applied to testing pieces, and  $i_1$  to  $i_3$  are different types of inhibitors, which at least include a traditional one for comparison. The flow is driven by a pump to output fluid with a stable flow rate. To provide various WSS, we can choose to change the wall roughness or the pipe diameter at certain pipe segments. More details about the device design will be referred to existing mature cases of flow experiments.



Figure 3.1. Schematic diagram of the experimental flow device.

Given the multi-fidelity approach, our future work will focus on exploring and refining various types of Convolutional Neural Network (CNN) architectures to achieve more precise and accurate predictions, while using an even more complicated set of input points. Instead of using the CFD points now, we aim to enhance the network framework with the usage of functions of varying dimensions to optimize the model's prediction performance characterized by its generalizability power and computational efficiency.

To reduce uncertainty in our predictions, we also plan to explore Bayesian layers and active sampling in cross-fidelity prediction. Bayesian layers will be implemented to provide probabilistic predictions by treating network weights as distributions rather than fixed values, which allows for capturing the uncertainty in model parameters, resulting in predictions with confidence intervals.

Understanding the uncertainty associated with predictions is crucial for robust and reliable decision-making. Additionally, we will further improve active learning techniques to efficiently utilize computational resources. They have the potential to collect the most informative data points, iteratively refining the model by targeting areas where the model is most uncertain. This technique also reduces the amount of high-fidelity data required, optimizing the data collection process and ultimately lowering overall costs.

Besides, we are also trying to introduce some constraints into both the multi-fidelity approach and roughness prediction model based on the idea of the physics-guided neural network (PGNN) that is expected to optimize parameter relationships among the frameworks to produce more reliable and explainable results.

These advancements will push the boundaries of multi-fidelity modeling, leading to new levels of precision and reliability in our predictions, and opening new avenues for applications in complex system analysis and decision-making.

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Appendix 3 Presentation File for Quarterly TAP Meeting



# Multi-compound green corrosion inhibitor for gas pipeline: synthesis, optimization, and evaluation

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# Simulation-based Inhibitor Implementation Optimization in Gas Gathering and Transportation Pipelines

## **Progress made in Q3'2024**

- Build prediction model under different type of roughness shape
- Incorporate uncertainty qualification into estimated wall shear stress (WSS)
- Establish the basic framework of Multi-Fidelity prediction from 2D to 3D simulation
- Establish preliminary form of degradation model of inhibitor under flow



## **Overview of AI-enhanced simulation framework**



#### **Global/structural model for flow Simulation**



Reliability degradation with experiment calibration

Local WSS simulation with roughness  $\int_{0}^{2} k = A(s, t, i_1)e^{-\frac{E_{des}}{RT}} \circ i_{0}^{0} i_{0}^{0$ 

WSS-assisted inhibitor loss model



## Multi-Fidelity approach

Using 2D and 3D simulations in the context of low-fidelity (LF) and high-fidelity (HF) data acquisition provides a clear comparison in terms of computational time and resource requirements:

#### 2D Simulations (LF):

- Computational Time: Significantly faster to run compared to 3D simulations.
- Resource Requirements: Requires less memory and processing power, making it suitable for quick, iterative analyses.
- Data Acquisition: Provides basic flow patterns and general insights, useful for preliminary studies and identifying potential design issues early on.

#### **3D Simulations (HF):**

- Computational Time: Much longer run times due to the increased complexity and detail of the models.
- Resource Requirements: Requires substantial computational resources, including higher memory and processing power, often necessitating high-performance computing facilities.
- Data Acquisition: Delivers highly detailed and accurate flow characteristics, capturing complex interactions and behaviours that 2D simulations cannot, essential for final validation and detailed analysis.



## Multi-Fidelity approach

Multi-Fidelity is the integration of multiple data sets with varying levels of detail and accuracy to enhance overall analysis and decision-making.

- High-Fidelity (HF): Data or models that are highly accurate and detailed but often expensive and computationally intensive.
- Low-Fidelity (LF): Data or models that are less accurate and detailed but cheaper and faster to obtain.
- Purpose: Combines LF and HF data to optimize cost, accuracy, and computational efficiency in various applications.



Multi-fidelity Data Aggregation using Convolutional Neural Networks (MDA-CNN)



## **2D** multiphase model





Low-Fidelity case under different inlet flow rate



## **3D** multiphase model



Velocity (m/s)	Pressure (Pa)
2	4302.5682
3	6672.1253

#### High-Fidelity case under different inlet flow rate



## Multi-Fidelity approach



**Illustration of prediction results** 



## Background



#### **Research objects**

- Surrogate model for predicting near-wall stress using obtained flow conditions from global model.
- Effects of wall shear stress (WSS) on inhibitor degradation;





## Background



Shear stress = **shear rate** × viscosity

shear rate is proportionate to flow rate without turbulence

Schematic illustration of wall shear stress under different flow rate.



#### **Local roughness representation**

 $y=0.14*\cos(0.1*x)+0.14$  (mm)

 $y=0.14*\cos(0.15*x)+0.14$  (mm)

 $y=0.16*\cos(0.1*x)+0.16$  (mm)

y= 0.16 \*cos(0.15\*x)+0.16 (mm)

The roughness shapes are established in the form of y=a\*cos(f\*x)+a a=0.12, 0.14, 0.16, 0.18; f=0.05, 0.1, 0.15, 0.2, 0.25

Illustration of the form of roughness shapes.



## **Training and testing data separation**



**pre**: 200; **mid**: 50; **next**: 200; **step**: 50

Illustration of the form of the dataset.



## Neural Network model (FNO) setup



Illustration of FNO network for WSS prediction.



### **Prediction for unseen roughness profile**

a=0.12, 0.14, 0.16, 0.18

f=0.05, 0.1, 0.15, 0.2, 0.25

Eliminate  $y=0.16*\cos(0.15*x)+0.16$ 



 $y=0.16*\cos(0.15*x)+0.16$ 

Results of predicted WSS under the training data with combined amplitude and frequency values.



## **Importance of data normalization**



Comparison of results among different types of normalization.



**Comparison with benchmark machine learning model – off-the-shelf fully connected neural network model** 



The model of fully-connected neural network (FCNN) with similar number of parameters.



## Comparison







## **How confident are you about the simulation?** - Uncertainty Qualification (UQ)

- Aleatoric uncertainty (AU): measurement noise, inadequate accuracy and so on.
- Epistemic uncertainty (EU): untouched points in training data.





https://zhuanlan.zhihu.com/p/56986840



### uncertainty qualification method



Illustration of Bayesian FNO network.



### uncertainty qualification results



**Results under Bayesian FNO network.** 



## Flow-assisted inhibitor loss model – 1 (preliminary)

## Inhibitor desorption model

**Desorption rate expressed by Arrhenius Equation:** 

 $k = A(s, t, i_n)e^{-\frac{E}{RT}}$ 

- *A* —— Frequency prefactor of desorption: fitting in static regime.
- *s* —— Wall shear stress.
- *t* —— Time.
- $i_n$  The *n*-th inhibitor.
- *T* Temperature.
- *R*——Molar gas constant.
- *E* —— Reaction energy of desorption: molecules' property

[1] Corrosion inhibitors: physisorbed or chemisorbed?

[2] Inhibition of  $CO_2$  corrosion of mild steel – Study of mechanical effects of highly turbulent disturbed flow

Surface coverage rate:

$$\theta = \frac{C^0 - C^i}{C^0}, \ \frac{d\theta}{dt} = k$$

Required information:

- $C^i$  —— Corrosion rate with the inhibitor.
- $C^0$  —— Corrosion rate without the inhibitor.
- k—— desorption rate.

Evaluation of Natural Weed Extract on the Safety of Corrosion Inhibition of Stainless Steel-410 Pipelines in the De-scaling Process



## Flow-assisted inhibitor loss model – 2

### Inhibitor desorption model

**Desorption rate for one type of inhibitor:** 





## **Future work and plans**

- Establish a specific degradation equation of inhibitor film
- Establish Multi-Fidelity models suitable for flow field prediction in pipeline
- Design the experiment to study long-term inhibitor degradation





### Progress made in Q3'2024

- 1. Developed a comprehensive protocol for Electrochemical Impedance Spectroscopy (EIS), Tafel polarization, and weight loss methods. This protocol serves as a robust framework for evaluating the performance of various corrosion inhibitors.
- 2. Evaluated the effectiveness of pectin as a corrosion inhibitor using both electrochemical test methods and weight loss methods. This comparative analysis provided insights into the performance of pectin under different testing conditions.
- 3. Formulated a protocol for the chemical modification of pectin using EDC (1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide) and NHS (N-Hydroxysuccinimide). This protocol outlines the steps to enhance the properties of pectin, potentially improving its effectiveness as a corrosion inhibitor.
- 4. Conducted long-term weight loss methods to determine the efficiency of pectin in various media. These extended tests provided valuable data on the long-term performance of pectin as a corrosion inhibitor.
- 5. Established a baseline for evaluating corrosion inhibitors. This baseline provides a standard for comparison, helping to assess the performance of new or modified inhibitors.
- 6. Collected and analyzed data from existing literature on inhibitors. This comprehensive review of existing research helped to contextualize our findings and inform our future research.

## **Electrochemistry Corrosion Test**

A three-electrode cell will be used for the electrochemical studies via a potentiostat (VersaSTAT 4, ameteksi Instruments). In this setup, the carbon steel will act as the working electrode, while the reference electrode is Saturated Calomel Electrode (SCE). Graphite electrode will be used as a counter electrode.







## **Electrochemistry Corrosion Test**

Different electrochemical corrosion test will be done:

- Polarization Techniques
- Electrochemical impedance spectroscopy (EIS) under different corrosive media like: HCl,  $SO_2$ ,  $CO_2$  (Sweet corrosion), H<sub>2</sub>S (Sour corrosion), H<sub>2</sub>SO<sub>4</sub> at different inhibitor concentration and coated samples.



## **Polarization Techniques**

- Polarization techniques encompass several methods, including Tafel extrapolation, potentiodynamic measurements, cyclic polarization, and linear polarization resistance.
- Tafel extrapolation involves a destructive test. By examining extrapolation plots, any changes in the corrosion mechanism can be discerned through variations in the Tafel slope. Additionally, a direct measurement of the corrosion current is obtained.
- When a metallic electrode is immersed in a corrosive medium, anodic and cathodic reactions spontaneously occur on the electrode surface, triggering corrosion.



https://www.beyonddiscovery.org/corrosion-resistance-3/eq-1.html

## **Polarization Techniques**

### **Experimental Procedure:**

- 1. Measure Open Circuit Potential  $E_{CO}$  and allow to stabilize.
- 2. Apply initial E that is 10 mV negative of  $E_{OC}$ .

3. Scan at a slow scan rate (~0.125 mV/s) to a final E that is 10 mV positive of  $E_{OC}$ .

- 4. Measure current, plot E (Y-axis) versus I (X-axis).
- 5. Measure slope, which has units of resistance (E/i = R).
- 6. Convert Rp to  $i_{corr}$ .
- 7. Convert  $i_{corr}$  to Corrosion Rate.
- 8. This procedure works for every corrosion system



https://www.beyonddiscovery.org/corrosion-resistance-3/eq-1.html



Tafel polarization curve of carbon steel in 1M HCL


Tafel polarization curve of carbon steel in 1M HCL+ 2g/L Pectin



Sample	$E_{corr}$ (mV)	I <sub>corr</sub> (μA/cm <sup>2</sup> )	CR (mmpy)	Inhibition efficiency (%)				
Blank	-453.05	18.94	0.219					
Pectin	-456.29	12.86	0.1487	32%				
CD I <sub>corr</sub> . K. EW								

$$CR = \frac{I_{corr}.K.EW}{\rho.A}$$

where K is constant defines the units of *CR*, for *CR* in mm/year (mmpy), K = 3272 mm/(A cm year), *EW* (the equivalent weight) 27.92 g for carbon steel,  $\rho$  (density) = 7.9 g/cm<sup>3</sup> for copper, *A* (area) of the sample = 1 cm<sup>2</sup>.

$$IE = \frac{CR_0 - CRP}{CR_0} \qquad IE = \frac{I_{corr \_ 0} \_ I_{corr \_ P}}{I_{corr \_ 0}}$$



### **Electrochemical impedance spectroscopy**

Electrochemical Impedance Spectroscopy (EIS) is a nondestructive experimental technique that captures the response of a nonlinear electrochemical system as a function of applied potential. It provides valuable information about the metal/electrolyte interface.

Within short testing times, EIS measurements yield reliable data, enabling us to predict the long-term performance of inhibitors. The result of EIS is the impedance of the electrochemical system as a function of frequency.

We have the option to analyze EIS data using the common electrical equivalent circuit (EEC) approach, as well as with physics-based/mechanistic models.

Shahzad, Khuram, et al. "Electrochemical and thermodynamic study on the corrosion performance of API X120 steel in 3.5% NaCl solution." Scientific reports 10.1 (2020): 4314.





The Nyquist plots reveal a single semi-circle shape for both uninhibited and inhibited solutions, with the diameter increasing as the inhibitor concentration rises. This suggests that pectin molecules adsorb at the carbon steel-electrolyte interface without altering the corrosion mechanism, and the inhibition behavior is governed by the charge transfer process. However, the imperfections in the semi-circle shape indicate frequency dispersion, which is typically caused by the roughness and heterogeneity of the metal surface.



Nyquist plots for carbon steel in 1.0 mol HCl solution in the absence and presence of pectin



The electrical equivalent circuit employed to analyze the impedance plots. In this figure, R1 is the solution resistance at ' R2 is the charge transfer resistance (polarization resistance The impedance of the constant phase element is (CPE1).

<u>Element</u>	<u>Freedom</u>	<u>Value</u>	<u>Error</u>	Error %
R1	Free(±)	1.916	0.059769	3.1195
CPE1-T	Free(±)	7.2283E-05	3.7447E-06	5.1806
CPE1-P	Free(±)	0.88668	0.0075996	0.85708
R2	Free(±)	1616	39.3	2.4319

Chi-Squared: Weighted Sum of Squares:

Data File: Circuit Model File: Mode: Maximum Iterations: **Optimization Iterations:** Type of Fitting: Type of Weighting:

0.01287

1.7761

C:\New folder\EIS PECTIN 15May.z C:\New folder\Pectin circuit.mdl Run Fitting / Freq. Range (0.001 - 1000000) 100 0 Complex Calc-Modulus



The equivalent circuit used to fit the experimental data.







Z'



Sample	<i>Rs</i> (solution resistance) (Ω cm <sup>2</sup> )	$R_P$ (Polarization resistance) ( $\Omega$ cm <sup>2</sup> )	$\begin{array}{c c} R_P \ (Polarization \\ resistance) \\ (\Omega \ cm^2) \end{array} \qquad \begin{array}{c} CPE \ (constant \ phase \\ element) \ (F/s) \end{array}$		Inhibition efficiency (%)
Blank	2.1	1046	9.9 *10 <sup>-5</sup>	0.87	
Pectin	1.9	1616	7.2 * 10 <sup>-5</sup>	0.88	35%

	Parameters	Sample 1	Sample 2	Sample 3	
	Steel sample	Carbon steel	Carbon steel	Carbon steel	
	Weight before corrosion (g)	7.451	7.837	6.288	
)	Weight after corrosion (g)	7.363	7.804	6.238	
-	Pectin application	No	Pectin solution in HCl	Dip coating	
	Weight loss (g)	0.088	0.033	0.055	
	Corrosion percentage(%)	1.18%	0.423%	0.79%	
	Inhibitor efficiency	-	62.5% at 25°C	33% at 25 °C	

$$IE = \frac{R_P \_ P - RP \_ 0}{R_P \_ P}$$

Results from weight loss tests conducted for 24 hrs



Long Term Corrosion Weight Loss Tests

- 1M HCL Reference (2W, 4W, 6W)
- 1M HCL+ 2g/L PECTIN Solution (2W,4W,6W)
- 0.25 M HCL solution Reference
- 0.25 M HCl in 2g/L of Pectin solution

### **Duration:** Two Weeks

#### **1M HCL PURE SAMPLE**

CONDITION	W1(g)	W2(g)	W3(g)	AVARAGE	WEIGHT LOSS(g)	CORROSION (%)
Weight before corrosion	3.77704	3.76516	3.79326	3.778487		
Weight after corrosion	3.48571	3.3929	3.45236	3.443653	0.3348	<b>8.862</b> (%)

#### 1M HCL + 2g/L PECTIN INHIBITOR

CONDITION	W1(g)	W2(g)	W3(g)	AVARAGE	WEIGHT LOSS(g)	CORROSION (%)	INHIBITOR EFFICIENCY	
Weight before corrosion	3.80058	3.80363	3.7935	3.799237	0.004	2 221 (21)	74 002	
Weight after corrosion	3.74578	3.6806	3.71815	3.714843	0.084	<b>Z.ZZI</b> (%)	74.993	
$IE = \frac{CR_0 - CRP}{CR_0} \qquad \qquad \text{CORROSION\%} = \frac{Avg wt AC - Avg wt BC}{Avg wt BC}$								





**Metal samples in HCL + Pectin** 

### **Duration: Four Weeks**

#### **1M HCL PURE SAMPLE**

CONDITION	W1(g)	W2(g)	W3(g)	AVARAGE	WEIGHT LOSS(g)	<b>CORROSION</b> %
Weight before corrosion	3.77715	3.74674	3.77531	3.76454		
Weight after corrosion	3.3173	3.43603	3.47818	3.410503	0.35407	<b>9.405</b> %

#### 1M HCL + 2g/L PECTIN INHIBITOR

CONDITION t	W1(g)	W2(g)	W3(g)	AVARAGE	WEIGHT LOSS(g)	CORROSION	INHIBITOR EFFICIENCY
Weight before corrosion	3.79257	3.7804	3.8158	3.796257	7 0.17692		50.445%
Weight after corrosion	3.56769	3.62383	3.66649	3.619337	0.17692	4.660(%)	





**Metal samples in HCL + Pectin** 

### **Duration:** Six Weeks

#### **1M HCL PURE SAMPLE**

CONDITION	W1(g)	W2(g)	W3(g)	AVARAGE	WEIGHT LOSS(g)	<b>CORROSION %</b>
Weight before corrosion	3.7611	3.78515	3.78458	3.776943		
Weight after corrosion	3.2635	3.29025	3.37335	3.309033	0.46791	12.39%

#### 1M HCL + 2g/L PECTIN INHIBITOR

CONDITION	W1(g)	W2(g)	W3(g)	AVARAGE	WEIGHT LOSS(g)	CORROSION	INHIBITOR EFFICIENCY
Weight before corrosion	3.7308	3.7906	3.7784	3.7666	0.2086		
Weight after corrosion	3.53846	3.55604	3.57925	3.557917	0.2086	5.54(%)	55.28%





### 0.25 M Duration: Six Weeks

#### **0.25 M PURE SAMPLE**

CONDITION	W1(g)	W2(g)	W3(g)	AVARAGE	WEIGHT LOSS(g)	CORROSION %
Weight before corrosion	3.78612	3.77865	3.79825	3.787673		
Weight after corrosion	2.29125	2.38876	2.18711	2.28904	1.498	<b>39.566</b> %

#### 0.25 MHCL + 2g/L PECTIN INHIBITOR

CONDITION	W1(g)	W2(g)	W3(g)	AVARAGE	WEIGHT LOSS(g)	CORROSION	INHIBITOR EFFICIENCY
Weight before corrosion	3.8106	3.7564	3.81138	3.792793	3 0.37686		
Weight after corrosion	3.51761	3.3682	3.36199	3.41593	0.37686	9.936(%)	74.887%





Metal samples in 0.25M HCL + Pectin



### **Modification of Pectin**

- Dissolve 10 g of pectin, 50 mmol EDC, and 16.7 mmol NHS in 300 mL deionized water.
- Stir the solution magnetically for 3 hours in an ice bath to activate the carboxyl groups of pectin.
- Dissolve 50 mmol of amino acid in 300 mL deionized water
- Combine the activated pectin solution with the amino acid solution.
- Adjust the pH to 5 using 1 mol/L hydrochloric acid solution.
- Induce the grafting reaction by magnetically stirring the mixed solution for 24 hours under ice bath conditions.
- Add 600 mL anhydrous ethanol to the reaction mixture and mix evenly.
- Centrifuge the mixture and remove the supernatant. The precipitate was dialyzed with7000–14000 Dalton molecular weight cut-off membrane for 72 h at room temperature to remove residual EDC, amino acids, NHS.
- Remove water from the product by freeze-drying to obtain a dried powder.



### **Functionalization of Pectin**

- Add 50 ml of distilled water to a mixture of 2.00 g of commercial pectin and 5 ml of 95% ethanol. Stir until a homogeneous solution is obtained.
- Heat the solution to the desired temperature. Add 1 ml of the corresponding amino compound (e.g., 1.00 g of guanidine carbonate).
- Stir occasionally and maintain the temperature for the specified reaction time.
- Quench the reaction by adding 3 ml of acidified ethanol
- Stir the mixture for 30 minutes. Centrifuge the suspension for 30 minutes at 4000 rpm. Add 200 ml of 96% ethanol to the supernatant. Place the mixture in a refrigerator overnight.
- Centrifuge the coagulated mass for 30 minutes at 4000 rpm.
- Wash the coagulated mass three times with 100 ml portions of 70% acid ethanol Continue washing with 100 ml portions of 70% aqueous ethanol until the mass is free of chloride ions (Cl<sup>-</sup>).
- Dry the final product overnight at 40°C.

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This study confirms that pectin functionalization with amines and amino acids results in amination, saponification, decarboxylation, and depolymerization. These modifications activate carboxylic groups and alter the polysaccharide structure, enhancing pectin's reactivity and potential for diverse applications. Quantified degrees of esterification, amidation, and decarboxylation are discussed.



# **Design and Synthesis of Green Inhibitors** Key Observations

- In our experimental observations, we found that pectin demonstrated an efficiency ranging from 30 to 33 percent across all three tests conducted. These tests encompassed both electrochemical analyses and weight loss assessments.
- Interestingly, we noticed a significant increase in efficiency when the duration of the tests was extended. Specifically, efficiencies of 74%, 55%, and 50% were recorded for test durations of 2, 4, and 6 weeks respectively.
- While pectin serves as a protective agent against metal corrosion, it also exhibits a detrimental effect. It has been observed to create a perforation in the metal upon reaction with hydrochloric acid (HCl). This particular phenomenon was exclusively observed in the HCl media, indicating a unique interaction between pectin and HCl under these conditions.



# **Design and Synthesis of Green Inhibitors** Future work

- Establish a foundational performance metric using benchmark chemical inhibitors to gauge subsequent improvements.
- Investigate the intricate reaction mechanism between carbon steel and the combined HCl and pectin media to understand the corrosion process.
- Evaluate and refine test methods (pectin coating vs. pectin dispersion; static vs. flow medium), determining the suitability of HCl as a medium for these experiments.
- Explore alterations to the pectin structure to enhance its efficacy as a corrosion inhibitor.
- Continue weight loss and electrochemical tests under a variety of conditions to gather comprehensive data.
- Finalize the compilation of the inhibitor database, ensuring it is exhaustive and up-to-date.



We Need Your Guidance

- Benchmark Inhibitors
- Corrosion Test Media
- Corrosion Test Methods
- Additional Tests



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Please visit the below URL for more information: https://primis.phmsa.dot.gov/matrix/PrjHome.rdm?prj=506



### **Reason of case selection**

In this scenario, a U-bend pipe is taken into consideration for a simple 2D single phase, second-order turbulent flow CFD simulation. The K-epsilon model is used with a medium coarse mesh and a fine mesh. The two results produced highly similar results with a similar computational time, which *doesn't* seem ideal enough to be considered as different fidelity.





### WSS used in degradation model



Schematic illustration of predicting inhibitor degradation.



### **Pipe model for data collection**



Schematic diagram of the numerical pipe model



### Selection of data segment



Roughness segment of 0.02 < x < 0.04 is chosen as training or testing data

Illustration of selecting data segment with sinusoidal roughness



### **Comparison of different data transfers**



Comparison of iteration processes between different types of row transformation.



**Prediction model for wall shear stress** 



Illustration of data extraction from certain segment.

#### Difference analysis between FNO and FCNN

- FNO contains the process of Fast Fourier Transform (FFT) and inverse FFT to better identify curve characteristics.
- For random start points and end points from a same segment, FCNN may deem them as different roughness types and fail to learn the similarity among series, while FNO could consider the arrangement pattern of data.