A Course project Report on

Modeling Corrosion Kinetics from QCM-D Data using Machine Learning and Weibull Models (Corrosion Analysis with AI)

undergone for the course

MT400- Corrosion Engineering

Submitted to

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ABSTRACT

This work investigates corrosion behavior using Quartz Crystal Microbalance with Dissipation (QCM-D) data and applies machine-learning-based modeling to predict mass-loss trends. Five corrosion conditions were analyzed to understand uniform and localized corrosion behavior through real-time mass change. The data was preprocessed using Savitzky–Golay smoothing, and analyzed with Linear Regression, Polynomial Regression, Random Forest, Generalized Additive Model (GAM), and Weibull kinetic modeling. Performance was evaluated using RMSE, time-series R^2, and Chatterjee's ξ to ensure monotonic physical behavior. Results show that corrosion behavior varies between conditions, exhibiting phases of activation, passivation, and breakdown. GAM provided the most consistent and physically meaningful predictions, while Weibull effectively modeled single-phase behavior. This combined approach integrates corrosion science with data-driven prediction, providing a framework for real-time corrosion monitoring and forecasting.

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1. INTRODUCTION

Corrosion is a naturally occurring degradation process that results in progressive metal loss. Understanding the kinetics and mechanism of corrosion is important for predicting service life and designing protection strategies. QCM-D enables nanogram-level mass-loss monitoring, making it highly suitable for studying early-stage corrosion and protective film breakdown.

1.1. Challenges:

- Corrosion signals are nonlinear and time-dependent
- Film formation and breakdown introduce multi-stage behaviour
- Traditional linear models fail to capture real-world kinetics
- QCM-D data contains high-frequency noise requiring careful smoothing

1.2. Motivation for the work:

Modern corrosion studies require real-time monitoring and predictive intelligence. By combining QCM-D sensing with machine learning and kinetic modeling, this work aims to build a reliable corrosion prediction framework that supports early detection of failure mechanisms.

2. LITERATURE SURVEY

2.1. *Introduction to Literature Survey:*

Corrosion monitoring and prediction are essential for assessing material durability and ensuring structural reliability in engineering applications. Traditional corrosion evaluation methods rely heavily on electrochemical techniques and post-exposure mass-loss measurements, which provide only limited real-time insight. With the emergence of high-resolution sensing tools such as Quartz Crystal Microbalance with Dissipation (QCM-D) and recent advances in data analytics, there is increasing interest in combining experimental sensing with modern computational models to understand and forecast corrosion behaviour.

This section reviews the existing literature on corrosion monitoring, QCM-D-based mass-tracking, data-driven degradation modelling, and statistical/ML methods relevant to this work.

2.2. *Related Work:*

2.2.1. Corrosion Behavior and Modeling

Foundational corrosion concepts including uniform corrosion, passivation, and localized breakdown mechanisms are well-established in classical texts such as Fontana's *Corrosion Engineering*. These works highlight that metals may exhibit multi-stage dissolution behaviour due to film formation, stabilization, and breakdown processes—behaviours directly observed in QCM-D corrosion curves.

Studies in *Corrosion Science* and *Electrochimica Acta* further demonstrate that passive films form transiently and rupture under aggressive environments, producing nonlinear dissolution trends.

2.2.2. QCM-D Studies in Corrosion

QCM-D has been used to quantify film formation, coating degradation, and under-film corrosion onset with nanogram-level mass-loss precision. Literature reports the technique's sensitivity for tracking early corrosion stages and dissolution kinetics, especially for polymers, steel passivation films, and inhibitor studies. These findings align with the observed plateau-then-drop behaviour in the present work.

2.2.3. Machine Learning for Corrosion

Recent reviews highlight the rising role of machine learning for corrosion prediction, especially in oil & gas and material degradation systems. Khalaf et al. (2024) reviewed emerging AI technologies for corrosion monitoring, emphasizing the need for robust, data-driven models that capture non-linear patterns in corrosion progress — a gap addressed in this study with GAM and Random Forest models.

2.2.4. Statistical & Nonlinear Modeling Approaches

The Weibull distribution has been widely used to describe material failure and degradation kinetics, making it suitable for corrosion rate evolution modelling. Generalized Additive Models (GAM), introduced by Wood (2017), provide powerful non-linear trend fitting capabilities without imposing a strict functional form, making them ideal for complex corrosion curves with passivation and breakdown phases.

Chatterjee et al. (2021) introduced a monotonic dependence measure (ξ-coefficient) that validates directional trend alignment between predicted and observed data — particularly relevant since corrosion mass loss must be monotonic.

2.3. Outcome of Literature Review:

The literature demonstrates:

- Corrosion frequently follows multi-phase kinetics: activation → passivation → breakdown.
- QCM-D provides high-resolution insight into surface dissolution and film behaviour.
- Classical linear models cannot capture non-linear corrosion transitions.
- Non-linear kinetic functions (e.g., Weibull) and flexible machine-learning models (e.g., GAM) are necessary for capturing real corrosion behaviour.
- Ensuring monotonicity in predicted signals is critical in corrosion research.

Thus, integrating QCM-D with modern ML and kinetic modelling addresses a recognized research need.

2.4. Problem Statement:

To analyze QCM-D corrosion mass-loss data and develop machine-learning–based and mechanistic models that can accurately predict and interpret corrosion progression, including phases of passivation and breakdown.

2.5. Research Objectives:

- Perform noise-preserving smoothing for QCM-D data
- Analyse corrosion signatures across five environmental conditions
- Fit linear, polynomial, GAM, Random Forest, and Weibull models
- Evaluate model accuracy through RMSE and time-series R^2
- Validate corrosion monotonicity using Chatterjee's ξ-statistic
- Forecast corrosion behaviour beyond observed duration

3. METHODOLOGY AND FRAMEWORK

3.1. *Block diagram / flowchart:*

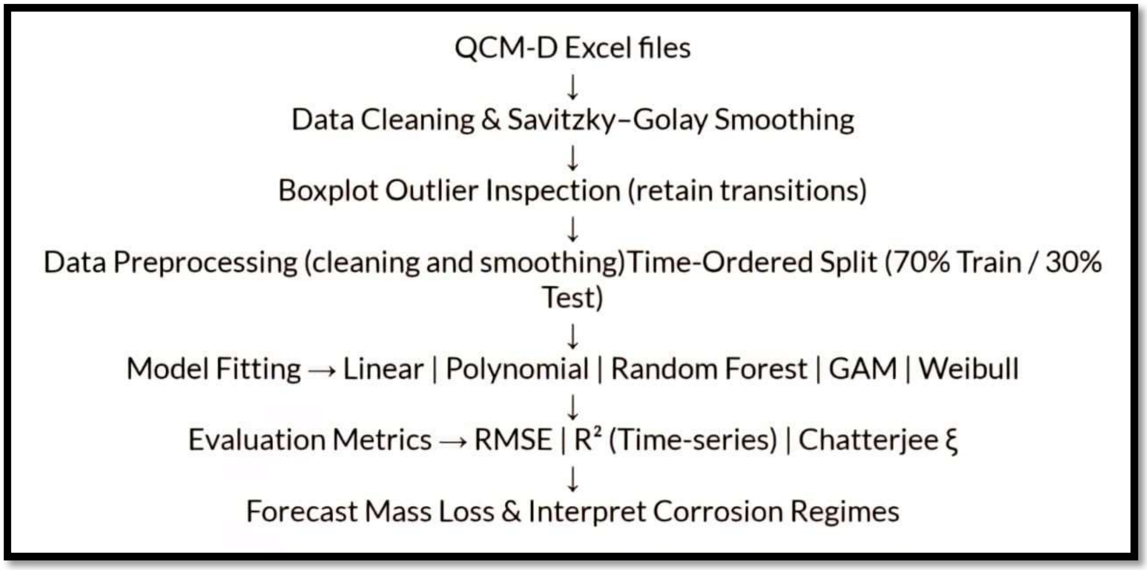


Figure 3.1: Methodology Workflow (Data-to-Model Pipeline)

3.2. *Algorithms and Techniques:*

- Savitzky–Golay smoothing to remove noise while preserving trends
- GAM splines for non-linear corrosion curve modelling
- Weibull for degradation kinetics
- Time-ordered testing to mimic real-world forecasting
- Chatterjee ξ for monotonic physical behaviour check

3.3. *Detailed Methodologies:*

This section explains the complete workflow followed in this study — from data preprocessing to corrosion modeling and interpretation.

3.3.1. Data Acquisition

Corrosion mass-loss data was obtained from a Quartz Crystal Microbalance with Dissipation (QCM-D) instrument under five different exposure conditions (CondA–CondE). The QCM-D measures nanogram-level mass changes on the metal surface over time using frequency shifts, following the Sauerbrey relationship.

Each dataset contained:

- Time (min)
- Frequency shift & dissipation
- Computed mass change (Δm)
- Smoothed mass change (Δm_smooth)

These signals represent real-time corrosion processes including dissolution, oxide formation, and film breakdown.

3.3.2. Pre-processing and Data Cleaning

Raw QCM-D output contains minor fluctuations due to:

- Instrument sensitivity
- Temperature/viscosity fluctuations
- Initial electrolyte contact effects

To ensure clean and physically meaningful corrosion trends, the following steps were applied:

Table 3.1: Data Pre-processing in R

Step	Operation	Purpose
1	Remove unused columns	Prevent noise from irrelevant variables
2	Check for missing values	Ensure numerical integrity
3	Preserve time order	Maintain true time-series behavior
4	Apply Savitzky–Golay filter	Smooth noise while preserving slope & kinetics
5	Visual outlier check via boxplots	Confirm spikes represent real corrosion events

Savitzky–Golay smoothing was chosen instead of moving average because it maintains the original curve shape and derivatives, essential for detecting passivation and breakdown behaviour.

Important note: Detected "outliers" were not removed because they represented corrosion transitions, not noise.

3.3.3. Trend Analysis & Region Identification

For each condition, the mass-loss curve was visually and statistically analysed to identify:

- Initial activation region (oxide removal)
- Passivation / plateau period
- Breakdown / accelerated dissolution
- Stabilized long-term corrosion slope

This step allowed linking machine-learning behaviour to real corrosion mechanisms.

3.3.4. Train–Test Split

Corrosion is time-dependent and cannot be randomized.

Table 3.2: Train-Test Splitting: Time-Ordered

Parameter	Approach
Training data	Early portion of time series (~70%)
Testing data	Future region (~30%)
Rationale	Mimics real-time prediction of corrosion progression

Random shuffle was not used to avoid breaking chronological structure.

3.3.5. Modeling Techniques

Multiple models were applied to capture different corrosion characteristics:

Table 3.3: Modelling Techniques

Model	Purpose
Linear Regression	Baseline constant-rate corrosion
3rd-Order Polynomial	Captures simple curvature, benchmark for overfitting

Random Forest	ML pattern learner, tests non-parametric approach
GAM (Generalized Additive Model)	Smooth, flexible, handles complex multi-stage corrosion
Weibull Kinetic Fit	Physics-based degradation model

This combination ensured both data-driven and mechanistic perspectives.

3.3.6. Model Evaluation

Models were evaluated using:

Table 3.4: Model Evaluation- Performance Metrics

Metric	Meaning
RMSE	Absolute prediction error
Time-series R^2	Trend accuracy for time-ordered data
Chatterjee ξ	Monotonicity check — ensures corrosion does not reverse

Chatterjee's ξ was specifically chosen to validate physical realism, since corrosion should be monotonic (mass should not increase).

3.3.7. Interpretation and Corrosion Mechanism Mapping

For each condition, predictions were compared with actual trends to map corrosion mechanisms:

- Uniform corrosion → linear downward slope
- Passivation → plateau or reduced slope
- Film breakdown / pitting onset → sudden acceleration
- Multi-phase behaviour → transitions in trend

GAM successfully captured complex patterns. Weibull explained uniform or single-phase kinetics. Final predictions were extrapolated beyond test window to estimate future mass-loss behaviour.

3.3.8. Documentation & Validation

- Plots generated for raw vs smoothed, predicted vs actual
- Behaviour cross-checked with corrosion theory

- Code packaged in reproducible R script with auto-package install
- Literature support cited for each method

Condition	pH	Dissolved Inorganic Carbon (mg C/L)	Sulfate (mg/L)	Chloride (mg/L)	Free Chlorine (mg Cl_2/L)	Orthophosphate (mg PO_4/L)	Duration (hr)
A pH 6.5 water	6.5	10	120	60	3	0	6
B pH 9.0 water	9	10	120	60	3	0	6
C pH 6.5+PO_4 water	6.5	10	120	60	3	6	6
D pH 9.0+PO_4 water	9	10	120	60	3	6	6
E	6.5	10	120	60	3	0	3
pH 6.5 pH 6.5+PO_4 water	6.5	10	120	60	3	6	3

Sauerbrey equation

$$\Delta f = -\frac{f}{t_q \rho_q}\Delta m = -n\frac{2{f_0}^2}{\upsilon_q \omega_q} = -n\frac{\Delta m}{C}$$

Figure 3.2: About the Dataset- 5 Conditions

4. <u>WORK DONE</u>

4.1. Implementation:

4.1.1. Data Description & Pre-processing

- Dataset: *Corrosion of new copper surfaces in drinking water* (Kaggle)
- Measurement tool: QCM-D, providing mass-loss (Δm) over time
- Imported raw CSV for five exposure conditions (A–E)
- Removed non-required columns & handled missing values
- Applied Savitzky–Golay filter to smooth Δm signal

  Reason: Reduces noise while preserving physical corrosion trend

4.1.2. Feature Preparation

- Primary input: Time (min)
- Output variable: Mass loss Δm (ng/cm^2)
- Verified monotonic decrease (expected for corrosion)
- Normalized time scale where needed (model stability)

4.1.3. Model Categories & Rationale

Table 4.1: Model Comparison

Category	Model Used	Purpose
Baseline	Linear Regression	Simple corrosion trend benchmark
Nonlinear Classical	Polynomial (3rd-order)	Captures curvature in kinetics
Machine Learning	Random Forest, GAM	Non-parametric modeling of complex decay
Kinetic (Mechanistic)	Weibull Decay	Physics-guided corrosion kinetics

GAM (Generalized Additive Model) was chosen as primary model due to its smooth-trend ability and strong physical interpretability for corrosion curves.
Weibull added to benchmark mechanistic corrosion behaviour.

4.1.4. Model Execution

- Split data into train (70%) and test (30%) – Time-Ordered
- Fit each model & generate forecasts 50–100 min ahead
- Plotted actual vs predicted trends for each condition
- Evaluated using:
  - RMSE (fit error)
  - R^2_ts (trend match)
  - Chatterjee's ξ (monotonic dependence check)

4.1.5. Monotonicity Check

- Computed Chatterjee ξ for all conditions
- Ensured corrosion trend remained monotonic despite smoothing
- GAM and Weibull showed high $\xi \rightarrow$ physically consistent decay

4.1.6. Visualization & Interpretation

- Plotted:
  - Raw & smoothed Δm curves
  - Model comparison charts (Linear / Poly / RF / GAM / Weibull)
  - Future trend forecasts

- Analysed curve shape to identify corrosion regime transitions:
  Initial rapid loss → diffusion-controlled plateau → accelerated breakdown

4.1.7. Tools & Environment

- Language: R
- Key Packages: mgcv, minpack.lm, ggplot2, signal
- Platform: R / RStudio

4.2. Results and Analysis:

Table 4.2: Suitability of models

Method	Findings
Linear	Oversimplified, poor forecasting
Poly	Good fit in-range, unstable outside (overfitting)
Random Forest	Flat predictions, cannot extrapolate
GAM	Best performance, preserves physical curve
Weibull	Good for smooth uniform decay, limited in multi-phase

4.2.1. Corrosion Interpretation

- Some conditions showed uniform corrosion
- Others showed passivation → breakdown behaviour, similar to pitting initiation
- SG filter preserved transitions
- GAM curve matched physical corrosion phases, polymeric (cubic) model overfit and explode, RF flattens

- $\xi \approx 0.97$ confirmed monotonic corrosion trend modelling

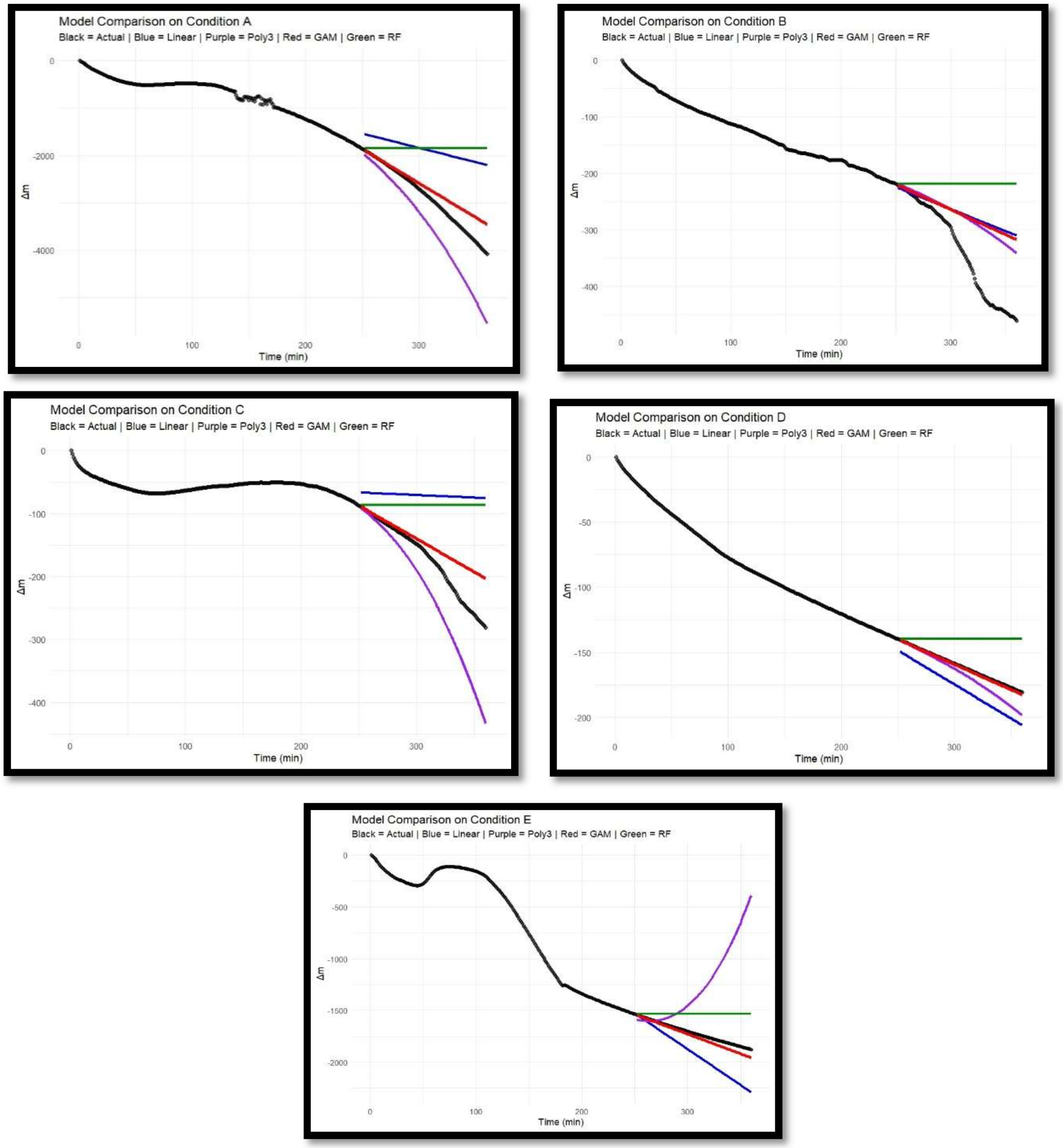
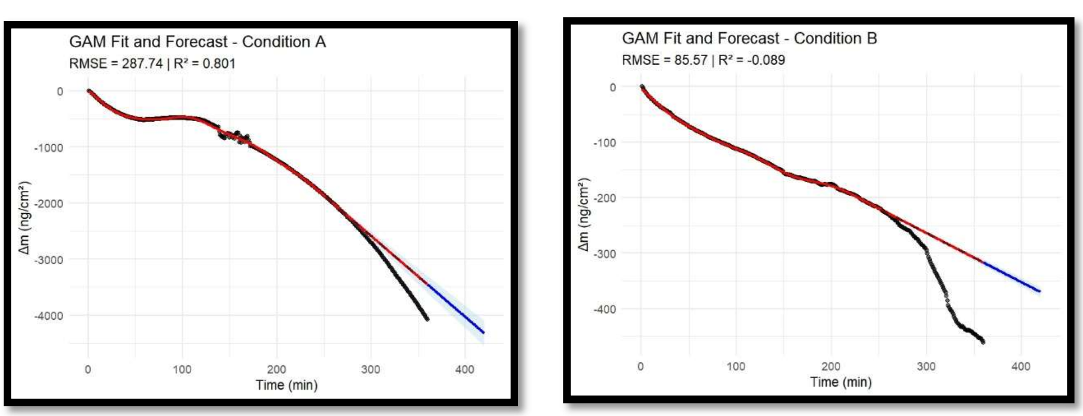


Figure 4.1 (A-E): Model Comparison of Condition A to E



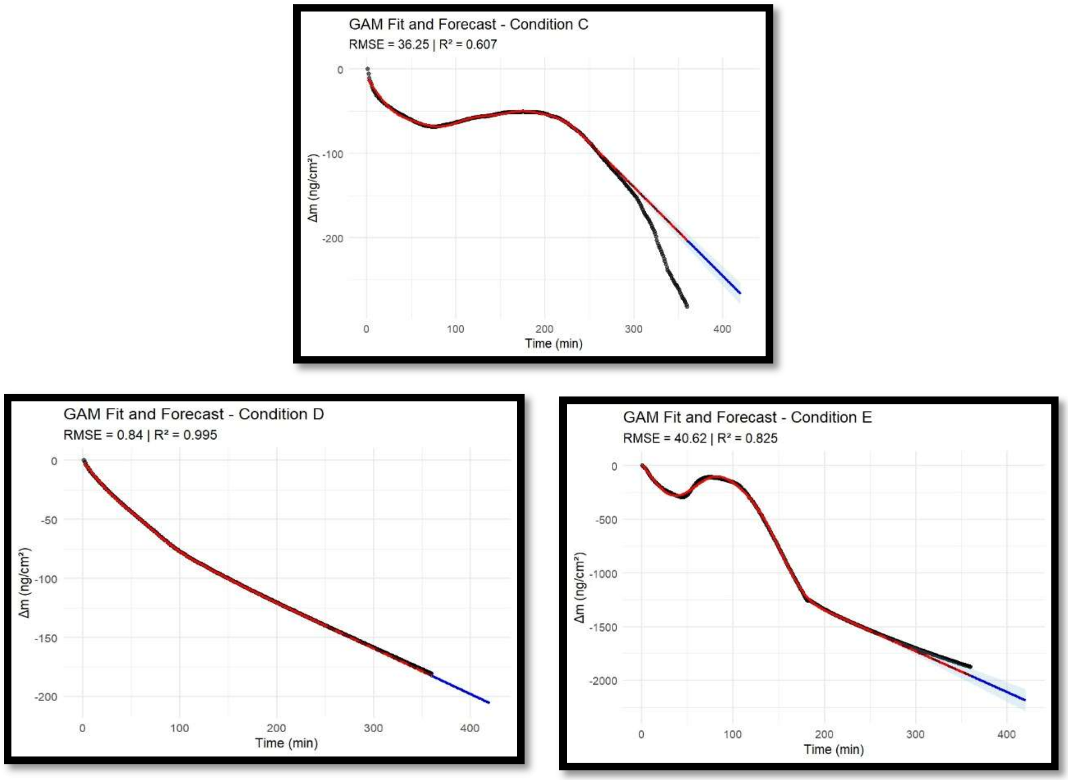
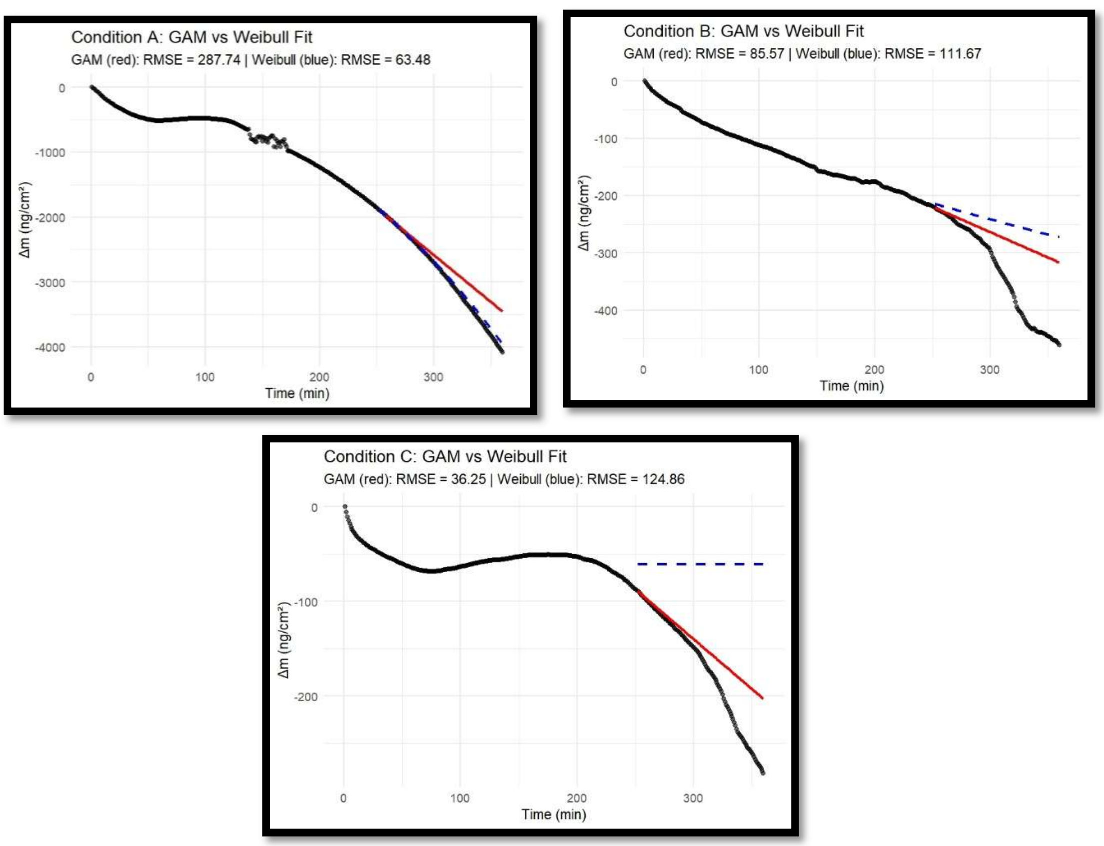


Figure 4.2 (A-E): GAM Fit and Forecast of Condition A to E



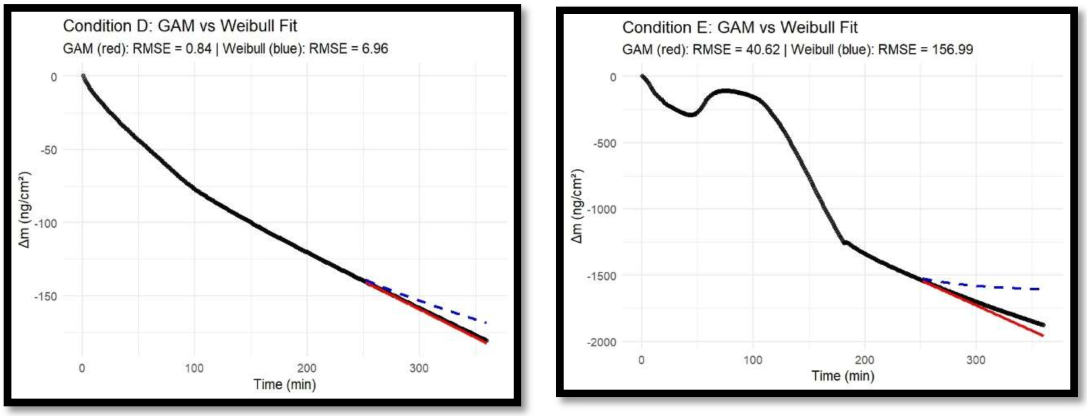


Figure 4.3 (A-E): GAM vs Weibull fit of Condition A to E

Table 4.3 (A-E): Performance metrics of GAM and Weibull of Condition A to E

Condition	GAM RMSE	GAM R^2_ts	Weibull RMSE	Weibull R^2_ts	ξ(Time vs Δm)	ξ(GAM vs Actual)
A	287.74	0.801	63.48	0.9903	0.9825	0.9727
B	85.57	-0.0887	111.67	-0.8540	0.9903	0.9707
C	36.24	0.607	124.86	-3.6609	0.9813	0.9727
D	0.84	0.995	6.96	0.6481	0.9813	0.9727
E	40.62	0.825	156.99	-1.6127	0.9866	0.9727

5. CONCLUSION AND FUTURE WORK

This work analyzed QCM-D corrosion data using statistical, machine-learning, and kinetic models to predict mass-loss behavior across five conditions. The results showed multi-phase corrosion patterns including activation, temporary passivation, and breakdown. Among all models, the Generalized Additive Model (GAM) provided the most consistent and physically realistic predictions, accurately capturing non-linear and multi-stage corrosion behavior. Linear and polynomial models failed to generalize, Random Forest could not extrapolate time-series trends, and Weibull performed well only for single-phase uniform corrosion. Overall, the GAM-based approach proved most suitable for corrosion forecasting and mechanism interpretation, demonstrating strong potential for smart corrosion monitoring applications.

The future scope is as follows-

• Extend models to corrosion inhibitor and coating datasets

• Combine QCM-D with EIS for multi-modal corrosion analysis

• Develop a Shiny-based web tool for real-time corrosion forecasting

• Incorporate Gompertz and Bi-Weibull models for complex kinetics

• Enable continuous real-time corrosion monitoring and prediction

• Validate models on long-term industrial exposure datasets (using piecewise regression)

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APPENDIX

(includes acronyms, paper selected if research paper implementation etc.)

Acronym	Description
QCM-D	Quartz Crystal Microbalance with Dissipation
Δm	Change in Mass
Δf	Change in Frequency
ΔD	Change in Dissipation
ML	Machine Learning
GAM	Generalized Additive Model
RF	Random Forest
RMSE	Root Mean Square Error
R^2	Coefficient of Determination
ξ (Xi)	Chatterjee Monotonic Dependence Coefficient
SG	Savitzky–Golay (Filter)
LM	Linear Model
Poly-3	Third-Order Polynomial Model
Nls	Non-Linear Least Squares
CSV	Comma-Separated Values
EIS	Electrochemical Impedance Spectroscopy
GUI	Graphical User Interface
AI	Artificial Intelligence
SNR	Signal-to-Noise Ratio
SD	Standard Deviation

```
Chatterjee ξ Values:
>       cat("Time vs Δm:", round(xi_time, 4), "\n")
Time vs Δm: 0.9866
>       cat("Linear:", round(xi_lin, 4), "\n")
Linear: NA
>       cat("Poly3:", round(xi_poly, 4), "\n")
Poly3: 0.9727
>       cat("Random Forest:", round(xi_rf, 4), "\n")
Random Forest: 1
>       cat("GAM:", round(xi_gam, 4), "\n")
GAM: 0.9727
```

```
>        print(results)
           Model      RMSE      R2_ts
1         Linear 1107.4296 -1.9514851
2  Polynomial(3)  740.6878 -0.3203186
3            GAM  287.7416  0.8007429
4  Random Forest 1218.7090 -2.5744430
```

```
> print(results)
          Model      RMSE       R2_ts
1        Linear  88.73882 -0.17080379
2 Polynomial(3)  78.04956  0.09427215
3           GAM  85.57126 -0.08871116
4 Random Forest 142.44304 -2.01674961
```

```
Chatterjee ξ Values:
> cat("Time vs Δm:", round(xi_time, 4), "\n")
Time vs Δm: 0.9866
> cat("Linear:", round(xi_lin, 4), "\n")
Linear: NA
> cat("Poly3:", round(xi_poly, 4), "\n")
Poly3: 0.9707
> cat("Random Forest:", round(xi_rf, 4), "\n")
Random Forest: 1
> cat("GAM:", round(xi_gam, 4), "\n")
GAM: 0.9707
```

```
Chatterjee ξ Values:
> cat("Time vs Δm:", round(xi_time, 4), "\n")
Time vs Δm: 0.9903
> cat("Linear:", round(xi_lin, 4), "\n")
Linear: NA
> cat("Poly3:", round(xi_poly, 4), "\n")
Poly3: 0.9727
> cat("Random Forest:", round(xi_rf, 4), "\n")
Random Forest: 1
> cat("GAM:", round(xi_gam, 4), "\n")
GAM: 0.9727
```

```
> print(results)
          Model      RMSE      R2_ts
1        Linear 114.54372 -2.9224484
2 Polynomial(3)  69.00119 -0.4234028
3           GAM  36.24538  0.6072466
4 Random Forest 102.98833 -2.1709590
```

```
> print(results)
          Model       RMSE      R2_ts
1        Linear 17.4638517 -1.2183245
2 Polynomial(3)  7.8823212  0.5480886
3           GAM  0.8423468  0.9948391
4 Random Forest 24.2419922 -3.2744635
```

```
Chatterjee ξ Values:
> cat("Time vs Δm:", round(xi_time, 4), "\n")
Time vs Δm: 0.9813
> cat("Linear:", round(xi_lin, 4), "\n")
Linear: NA
> cat("Poly3:", round(xi_poly, 4), "\n")
Poly3: 0.9727
> cat("Random Forest:", round(xi_rf, 4), "\n")
Random Forest: 1
> cat("GAM:", round(xi_gam, 4), "\n")
GAM: 0.9727
```

```
Chatterjee ξ Values:
> cat("Time vs Δm:", round(xi_time, 4), "\n")
Time vs Δm: 0.9917
> cat("Linear:", round(xi_lin, 4), "\n")
Linear: NA
> cat("Poly3:", round(xi_poly, 4), "\n")
Poly3: 0.9672
> cat("Random Forest:", round(xi_rf, 4), "\n")
Random Forest: 1
> cat("GAM:", round(xi_gam, 4), "\n")
GAM: 0.9727
```

```
> print(results)
          Model      RMSE      R2_ts
1        Linear 231.75598  -4.693800
2 Polynomial(3) 644.02076 -42.968335
3           GAM  40.62358   0.825057
4 Random Forest 208.11228  -3.591300
```

R Codes which computed Chatterjee correlation, RMSE, R^2_ts for conditions A, B, C, D, and E respectively

CORROSION ASPECT OF THIS PROJECT

Condition	Water Chemistry	Key Plot Shape Features	Corrosion Interpretation	GAM vs Weibull
A — pH 6.5, No Inhibitor	Chlorine present, no orthophosphate	• Rapid mass loss initially • Short plateau (10–120 min) • Then accelerating mass loss	Active uniform corrosion of fresh copper surface → high dissolution because pH < 7 and free chlorine promotes Cu oxidation	✓ GAM captures early slope change indicating oxide formation ✓ Weibull fits acceleration phase well → corrosion rate increases over time
B — pH 9.0, No Inhibitor	Alkaline water, chlorine present	• Slower early corrosion • Sudden breakdown after ~250 min → sharp downward curve	Evidence of protective cupric oxide film at pH 9 Later film breakdown → localized pitting onset	✓ GAM clearly shows film stability then failure ✗ Weibull less accurate → corrosion not uniform
C — pH 6.5 + Orthophosphate	Low pH but passivating phosphate	• Early corrosion but quickly forms plateau • Late acceleration but less severe than A	Phosphate film delays corrosion → improved passivity at acidic pH	✓ GAM captures initial stabilization zone ✗ Weibull overpredicts — film protection violates Weibull decay assumptions
D — pH 9.0 + Orthophosphate	Most protective chemistry	• Smooth, nearly linear small mass loss • No sharp film breakdown	Very low uniform corrosion Strong, stable $Cu_3(PO_4)_2$ + CuO layer → ideal condition	✓ GAM fits almost perfectly ($R^2 \approx 0.995$) ✓ Weibull (RMSE very low) confirms minimal degradation kinetics
E — pH 6.5 → 6.5 + Phosphate shift	Acidic start then inhibitor added halfway	• Early active corrosion • Distinct “elbow” at ~200 min → slope reduces	Initially aggressive corrosion, phosphate addition restores passivity mid-experiment	✓ GAM highlights protection onset timing ✗ Weibull incorrect shape → rapid kinetic change not monotonic