

Document Version

Final published version

Licence

CC BY-NC-ND

Citation (APA)

Zhang, K. (2026). *Data-Driven Study of Atmospheric Corrosion Under Multi-Droplet Conditions: An End-To-End Experimental-Computational Multi-Modal Framework For Electrolyte-Resolved Corrosion Kinetics Investigation*. [Dissertation (TU Delft), Mechanical Engineering]. <https://doi.org/10.4233/uuid:81d952ef-695d-4938-b32b-44bc80db56ce>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

In case the licence states "Dutch Copyright Act (Article 25fa)", this publication was made available Green Open Access via the TU Delft Institutional Repository pursuant to Dutch Copyright Act (Article 25fa, the Taverne amendment). This provision does not affect copyright ownership.
Unless copyright is transferred by contract or statute, it remains with the copyright holder.

Sharing and reuse

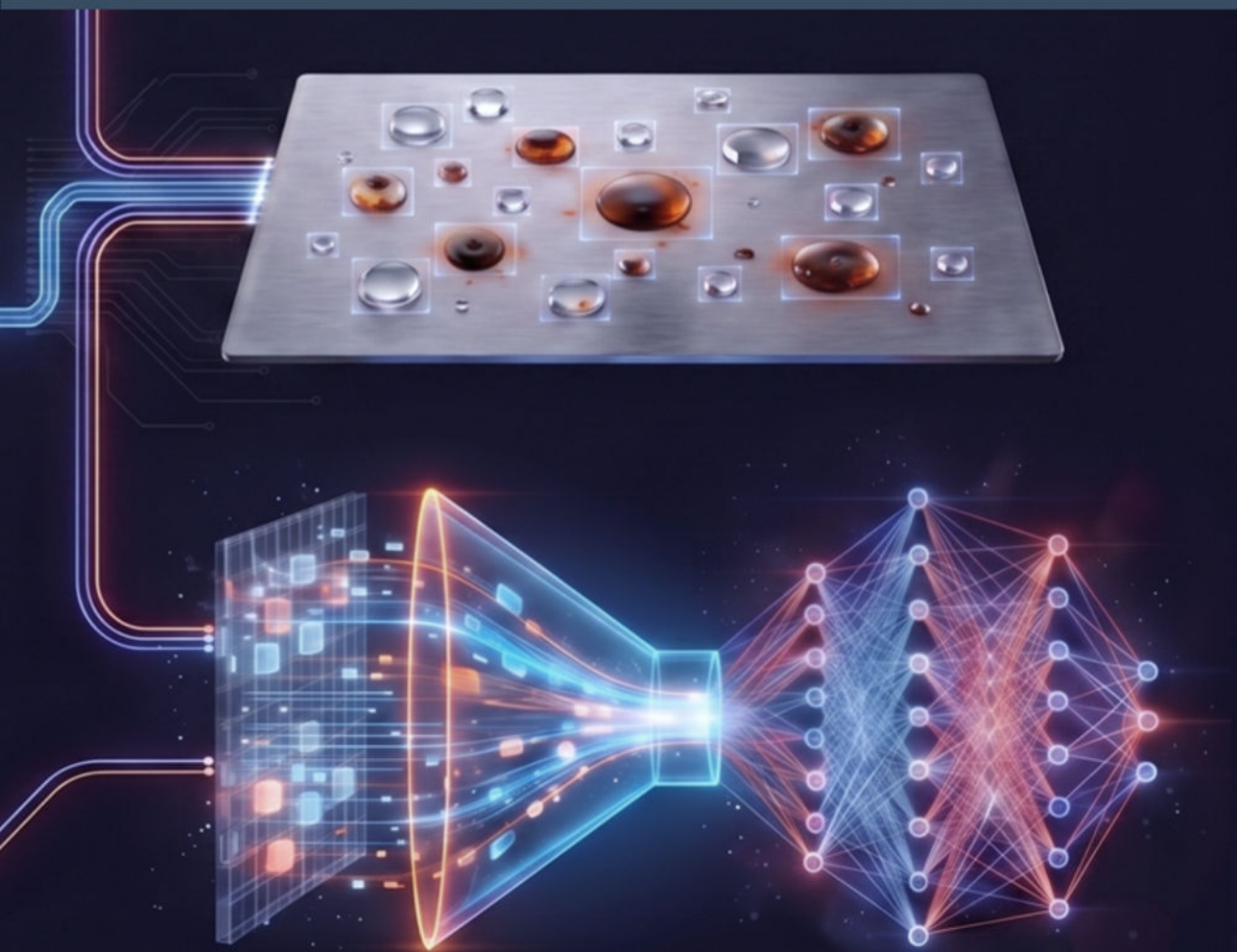
Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

DATA-DRIVEN STUDY OF ATMOSPHERIC CORROSION UNDER MULTI-DROPLET CONDITIONS

AN END-TO-END EXPERIMENTAL-COMPUTATIONAL
MULTI-MODAL FRAMEWORK FOR ELECTROLYTE-RESOLVED
CORROSION KINETICS INVESTIGATION



Keer ZHANG

DATA-DRIVEN STUDY OF ATMOSPHERIC CORROSION UNDER MULTI-DROPLET CONDITIONS

**AN END-TO-END EXPERIMENTAL-COMPUTATIONAL
MULTI-MODAL FRAMEWORK FOR ELECTROLYTE-RESOLVED
CORROSION KINETICS INVESTIGATION**

DATA-DRIVEN STUDY OF ATMOSPHERIC CORROSION UNDER MULTI-DROPLET CONDITIONS

**AN END-TO-END EXPERIMENTAL-COMPUTATIONAL
MULTI-MODAL FRAMEWORK FOR ELECTROLYTE-RESOLVED
CORROSION KINETICS INVESTIGATION**

Dissertation

for the purpose of obtaining the degree of doctor
at Delft University of Technology
by the authority of the Rector Magnificus Prof. dr. ir. H. Bijl,
chair of the Board for Doctorates,
to be defended publicly on
Monday 14 September 2026 at 10:00

by

Keer ZHANG

This dissertation has been approved by the promotor.

Composition of the doctoral committee:

Rector Magnificus,	chairperson
Prof. dr. ir. J.M.C. Mol,	Delft University of Technology, promotor
Dr. Y. Gonzalez-Garcia,	Delft University of Technology, copromotor

Independent members:

Prof. dr. J. Dik,	Delft University of Technology
Dr. T. Prošek,	University of Chemistry and Technology Prague, Czech Republic
Prof. dr. ir. H.A. Terry,	Vrije Universiteit Brussel, Belgium
	Delft University of Technology
Prof. dr. D. Zhang,	University of Science and Technology Beijing, China
Prof. dr. M. Zheludkevich,	University of Kiel, Germany
	Helmholtz-Zentrum Hereon, Germany

Reserve member:

Prof. dr. V.A. Popovich,	Delft University of Technology
--------------------------	--------------------------------

This research was carried out under Project no. T18016 in the framework of the Research Program of the Materials Innovation Institute (M2i) supported by the Dutch Government, within the Faculty of Mechanical Engineering, Delft University of Technology.



Keywords: Atmospheric corrosion; Carbon steel; Multi-droplet electrolyte; Corrosion kinetics; Electrical resistance monitoring; Computer vision; Weakly supervised learning; Data-driven modelling

Printed by: Ridderprint

Front & Back: Generated by Keer Zhang using Google Gemini and Imagen

Copyright © 2026 by Keer Zhang

ISBN: 978-94-6518-427-2

An electronic version of this dissertation is available at

<http://repository.tudelft.nl/>.

*Do not go gentle into that good night,
Old age should burn and rave at close of day;
Rage, rage against the dying of the light.
Though wise men at their end know dark is right,
Because their words had forked no lightning they
Do not go gentle into that good night.*

— Dylan Thomas

CONTENTS

Summary	xi
Samenvatting	xiii
摘要	xv
Preface	xvii
1 Introduction	1
1.1 Social importance of atmospheric corrosion management	2
1.2 From international Standards to machine learning	2
1.3 The experimental bottleneck: field vs. industry vs. laboratory	3
1.4 Theoretical framework	5
1.5 Research objectives and thesis outline	9
2 Developing An Experimental Framework for Monitoring Atmospheric Corrosion Kinetics under Multi-droplet Conditions	21
2.1 Introduction	23
2.2 Materials and methods	25
2.2.1 The climate chamber	25
2.2.2 The Electrical Resistance (ER) method	25
2.2.3 Variable correlation analysis	26
2.2.4 Materials and roughness quantification	27
2.2.5 Droplet evolution monitoring	27
2.2.6 Droplet image analysis method	27
2.3 Results and discussion	29
2.3.1 Design of the experimental setup	29
2.3.2 Surface roughness measurement	30
2.3.3 ER signal acquisition and analysis	31
2.3.4 Droplet monitoring and image analysis	34
2.3.5 Validation experiments: corrosion of carbon steel in exposure to 1 M NaCl solution	35
2.4 Conclusions.	41
2.S Supplementary Information	43
2.S.1 ER signal filtering method	43
2.S.2 ER signal filtering results and discussion	44
2.S.3 Droplet image analysis method	46
2.S.4 Weight loss - ER cross validation	46
2.S.5 Droplet electrolyte concentration estimation	49
2.S.6 Ratio of sensor track to reference track.	50

3	Developing A Data-driven Framework for Analyzing Atmospheric Corrosion	57
	Optical Recording	
3.1	Introduction	59
3.2	Experimental methodology	60
3.2.1	Sample Preparation and Corrosion Monitoring	60
3.2.2	Time-lapse Imaging	60
3.3	Results and discussion	61
3.3.1	Development of a Data-Driven Framework	61
3.3.1.1	Droplets Segmentation and ROI Definition	61
3.3.1.2	Feature Extraction and Clustering.	61
3.3.1.3	Continuous probability-based mapping of corrosion evolution	64
3.3.2	Application of the Framework	66
3.3.2.1	Representative Corrosion Behaviors.	66
3.3.2.2	Comparative Temporal Analysis of Corrosion Progression in Inner and Outer ROIs	68
3.3.2.3	Influence of Droplet Size on Corrosion Probability	72
3.3.2.4	Influence of Droplet Size on Corrosion Characteristics Over Time	74
3.4	Conclusions.	75
3.S	Supplementary Information	77
3.S.1	Outer ROI region definition	77
3.S.2	Post-mortem SEM-EDS analysis	77
3.S.3	Convolutional neural-network-based autoencoder for feature extraction	78
3.S.4	The multi-stage optimization process	80
3.S.5	Misclassification on per-droplet temporal corroding status using binary classification	81
3.S.6	Consistency check validating the use of end-frame cluster centers.	81
3.S.7	Sensitivity analysis of the corrosion status classification criteria	84
3.S.8	Effect of droplet spatially clustering behavior on corrosion product development in outer ROIs.	86
4	A Weakly Supervised Framework for Droplet-Level Corrosion Inference from Global Measurements	93
4.1	Introduction	95
4.2	Experimental Platform and Dataset Preparation	96
4.3	Methodology	98
4.3.1	Image processing and feature extraction	99
4.3.2	Dataset preparation and sampling strategy	100
4.3.3	Model architecture.	101
4.3.4	Training and ensemble strategy	101
4.3.5	Model evaluation	104
4.3.6	Model Interpretability	104
4.3.7	Droplet-level behavior validation	105

4.4	Results and discussion	105
4.4.1	Data statistics	106
4.4.2	Global performance comparison.	106
4.4.3	Global interpretability analysis.	109
4.4.4	Per-droplet behavior validation	109
4.5	Conclusions.	113
4.S	Supplementary Information	115
4.S.1	Outer ROI region definition	115
4.S.2	Sensitivity analysis of the material loss volume threshold	115
4.S.3	Spatiotemporal evolution of additional droplets	116
5	Surface Roughness and Atmospheric Corrosion: Droplet-Scale and Global Kinetics	125
5.1	Introduction	127
5.2	Methodology	129
5.2.1	Experimental conditions and data acquisition	129
5.2.2	Construction of droplet-level feature space and probability-based indicators	131
5.3	Results and discussion	133
5.3.1	Initial droplet geometry across surface finishes	133
5.3.2	Global corrosion kinetics from ER measurements	135
5.3.3	Droplet-level final spatial distribution and extent of corrosion product accumulation from probability-based indicators.	136
5.3.4	Droplet-level corrosion evolution from probability-based indicators	140
5.3.5	Relationship between probability-based descriptors and ER-based corrosion kinetics	143
5.4	Conclusion	144
5.S	Supplementary Information	146
5.S.1	Lognormal fitting of initial droplet size distribution	146
5.S.2	Determination of the Savitzky-Golay filter window length for a representative run	146
6	Conclusions and Outlook	153
6.1	Conclusions.	154
6.2	Outlook	156
	Epilogue	159
	Acknowledgements	161
	Curriculum Vitæ	165
	List of Publications	167

SUMMARY

Atmospheric corrosion is the most economically significant form of material degradation, costing an estimated \$2.5 trillion annually and affecting infrastructure across every industrial sector. Carbon steel, perhaps the world's most widely used structural material, is particularly vulnerable. Despite decades of research, accurately predicting atmospheric corrosion rates under realistic and dynamic conditions remains an open challenge.

The current state of the art relies on two classes of models. Empirical standards, such as ISO 9223 dose-response functions, correlate macroscopic environmental parameters directly with material mass loss. More recently, machine learning models have improved predictive accuracy by capturing non-linear dependencies in high-dimensional environmental datasets. Nevertheless, both approaches share a deeper limitation: neither monitors nor models the electrolyte layer that physically mediates every corrosion reaction. In empirical testing, samples are exposed and mass loss is measured, but the instantaneous electrolyte conditions (i.e. droplet geometry, concentration, spatial distribution) during the test usually go unrecorded. In data-driven models, environmental inputs are mapped statistically to corrosion outputs with no mechanistic representation of the intervening electrochemical reality. The result is that outcomes cannot be interpreted, failures cannot be diagnosed, and results cannot be transferred across test paradigms. Because the electrolyte is the universal physical mediator of electrochemical corrosion, whether exposure occurs under field conditions, accelerated salt spray, or controlled laboratory simulation, a framework grounded in electrolyte dynamics would offer a principled basis for bridging all three. Accelerated and laboratory conditions are additionally well-documented and temporally inexpensive to generate, making them practical entry points for validating such a framework.

This thesis directly addresses that gap. Under realistic atmospheric conditions, surface moisture does not form a uniform film; it exists as a stochastic population of interacting droplets with distinct geometry, chemistry, and temporal evolution. Yet experimental studies have historically restricted themselves to either idealized single droplets or continuous thin films, neither of which captures this multi-droplet reality. The central contribution of this work is an end-to-end experimental and computational framework that, for the first time, quantitatively links the spatiotemporal dynamics of a realistic multi-droplet electrolyte population to global macroscopic corrosion kinetics.

The framework relies on three integrated components. First, a custom climate chamber and electrical resistance (ER) sensor system was designed and validated to continuously monitor corrosion kinetics under discontinuous, droplet-based electrolyte conditions, under which conventional electrochemical methods fail. Second, a fully auto-

mated computer vision pipeline was developed, combining large vision models for zero-shot droplet segmentation with probability-based color metrics to track corrosion product formation continuously across thousands of individual droplets simultaneously. The approach reveals that droplet size is a key governing parameter: larger droplets exhibit earlier onset and faster accumulation of corrosion products, and two distinct spatial patterns of attack: an Evans-like inner-footprint mode and an outer-periphery mode, are identified and quantified. Third, a weakly supervised machine learning framework was developed to solve the kinetic inverse problem: by framing per-droplet kinetic inference as a multiple-instance regression, the global ER signal is disaggregated into individual droplet contributions without requiring any droplet-level ground truth labels.

The framework's mechanistic sensitivity is demonstrated by applying it to study surface roughness. Rougher surfaces produce larger, more elongated droplets through enhanced pinning and coalescence, leading to measurably higher and earlier-developing corrosion rates. The results are fully traceable through the optical and global kinetic data streams.

Taken together, this work establishes a new experimental paradigm for atmospheric corrosion research: one that opens the black box by making the electrolyte population visible, measurable, and linkable to damage. The resulting coupled datasets provide the experimental foundation needed to validate and inform the next generation of physically interpretable, transferable corrosion prediction models.

SAMENVATTING

Atmosferische corrosie is de economisch meest ingrijpende vorm van materiaalveroudering, met een geschatte jaarlijkse kostprijs van 2,5 biljoen dollar en gevolgen voor infrastructuur in alle industriële sectoren. Koolstofstaal, verreweg het meest gebruikte constructiemateriaal ter wereld, is bijzonder kwetsbaar. Ondanks decennia van onderzoek blijft het nauwkeurig voorspellen van atmosferische corrosiesnelheden onder realistische en dynamische omstandigheden een open vraagstuk.

De huidige stand van de techniek steunt op twee klassen van modellen. Empirische standaarden, zoals de dosis-responsfuncties van ISO 9223, correleren macroscopische omgevingsparameters direct met materiaalverlies. De afgelopen jaren hebben machine learning-modellen de voorspellende nauwkeurigheid verbeterd door niet-lineaire afhankelijkheden in hoogdimensionale omgevingsdatasets te capteren. Beide benaderingen delen echter een diepere beperking: geen van beide bewaakt of modelleert de elektrolytlaag die elke corrosiereactie fysisch medieert. Bij empirisch testen worden monsters blootgesteld en wordt massaverlies gemeten, maar de instantane elektrolytomstandigheden (druppelgeometrie, concentratie, ruimtelijke verdeling) tijdens de test worden doorgaans niet geregistreerd. In datagestuurde modellen worden omgevingsinputs statistisch gekoppeld aan corrosie-uitkomsten, zonder mechanistische representatie van de tussenliggende elektrochemische werkelijkheid. Het gevolg is dat uitkomsten niet geïnterpreteerd kunnen worden, fouten niet gediagnosticeerd kunnen worden en resultaten niet overdraagbaar zijn tussen testparadigma's. Omdat het elektrolyt de universele fysische mediator is van elektrochemische corrosie, of de blootstelling nu plaatsvindt onder veldcondities, versnelde zoutnevelproeven of gecontroleerde laboratoriumsimulaties, biedt een kader dat gebaseerd is op elektrolytdynamica een principiële basis om alle drie te overbruggen. Versnelde en laboratoriumomstandigheden zijn bovendien goed gedocumenteerd en tijdsgoedkoop te genereren, waardoor ze praktische uitgangspunten vormen voor de validatie van een dergelijk kader.

Dit proefschrift pakt die lacune direct aan. Onder realistische atmosferische omstandigheden vormt oppervlaktevocht geen uniform film, maar bestaat het als een stochastische populatie van wisselwerkende druppels met een eigen geometrie, samenstelling en temporele evolutie. Toch hebben experimentele studies zich historisch gezien beperkt tot geïdealiseerde enkele druppels of continue dunne films, die geen van beide deze meervoudige-druppelrealiteit weergeven. De centrale bijdrage van dit werk is een end-to-end experimenteel en rekenkundig kader dat voor het eerst de ruimtelijk-temporele dynamiek van een realistische meervoudige-druppel elektrolyt populatie kwantitatief koppelt aan globale macroscopische corrosiekinetiek.

Het kader steunt op drie geïntegreerde componenten. Ten eerste werd een klimaatka-

mer op maat en een elektrisch weerstandssensorsysteem (ER) ontworpen en gevalideerd om corrosiekinetiek continu te bewaken onder discontinue, druppelgebaseerde elektrolytomstandigheden, waarbij conventionele elektrochemische methoden tekortschieten. Ten tweede werd een volledig geautomatiseerde computer vision-pijplijn ontwikkeld, die grootschalige visiemodellen voor zero-shot druppelsegmentatie combineert met op waarschijnlijkheid gebaseerde kleurmetrieën om de vorming van corrosieproducten continu te volgen over duizenden individuele druppels tegelijkertijd. De aanpak toont aan dat druppelgrootte een bepalende parameter is: grotere druppels vertonen een eerder begin en snellere ophoping van corrosieproducten, en twee ruimtelijk onderscheiden aanvalspatronen worden geïdentificeerd en gekwantificeerd: een Evans-achtig binnenvoetafdrukpatroon en een buitenperifeerpatroon. Ten derde werd een zwak gesuperviseerd machine learning-kader ontwikkeld om het kinetische inverseprobleem op te lossen: door de per-druppel kinetische inferentie te formuleren als een meervoudige-instantie regressie wordt het globale ER-sigitaal opgesplitst in individuele druppelbijdragen, zonder dat per-druppel grondwaarheidslabels vereist zijn.

De mechanistische gevoeligheid van het kader wordt gedemonstreerd door het toe te passen op de studie van oppervlakteruwheid. Ruwere oppervlakken produceren grotere, meer langwerpige druppels door verbeterde vastzetting en coalescentie, wat leidt tot meetbaar hogere en eerder optredende corrosiesnelheden. De resultaten zijn volledig traceerbaar via de optische en globale kinetische datastromen.

Samenvattend vestigt dit werk een nieuw experimenteel paradigma voor atmosferisch corrosieonderzoek: een paradigma dat de zwarte doos opent door de elektrolytpopulatie zichtbaar, meetbaar en koppelbaar aan schade te maken. De resulterende gekoppelde datasets bieden de experimentele basis die nodig is om de volgende generatie fysisch interpreteerbare en overdraagbare corrosievoorspellingsmodellen te valideren en te informeren.

摘要

大气腐蚀是经济影响最为深远的材料退化形式，其每年造成的经济损失估计高达2.5万亿美元，各行各业的基础设施均受其影响。碳钢作为世界上应用最广泛的结构材料，尤为容易受到大气腐蚀的侵害。尽管经过多年的研究，在真实动态条件下准确预测大气腐蚀速率仍是一个悬而未决的难题。

目前，该领域主要依赖两类方法。以ISO 9223剂量响应函数为代表的经验性标准，直接将宏观环境参数与材料质量损失相关联。近年来，机器学习模型通过捕捉高维环境数据集中的非线性依赖关系，进一步提升了预测精度。然而，这两类方法存在共同的深层局限：两者均未对每一个腐蚀反应的物理媒介，即电解质层，进行监测或建模。在经验性测试中，通常经过暴露后测量样品质量损失以确定腐蚀速率，但测试过程中的瞬时电解质状态（即液滴几何形态、浓度、空间分布）通常未被记录。在数据驱动模型中，环境输入通过统计方式映射到腐蚀结果，而对其间的电化学生理现实缺乏机理性描述。由此带来的后果是：结果无法被解释，错误无法被诊断，结论也无法在不同测试体系之间迁移。由于电解质是电化学腐蚀的普适物理媒介，即无论暴露发生在野外环境、加速盐雾试验还是受控实验室模拟中，以电解质动力学为核心构建的预测框架，从原理上为衔接三类测试体系提供了可能。此外，加速试验和实验室条件具有文献记录完善、数据获取成本低的优势，是验证上述框架的理想切入点。

本论文直接针对这一空白展开研究。在真实大气条件下，表面水分并非形成均匀液膜，而是以具有各自独特几何形态、化学组成和时间演化特征的随机液滴群形式存在。然而，既往实验研究在历史上大多局限于理想化的单液滴或连续薄液膜体系，两者均无法反映多液滴共存的真实情形。本研究的核心贡献在于，构建了一套端到端的实验与计算框架，首次将真实多液滴电解质群的时空动力学与宏观整体腐蚀动力学进行了定量关联。

该框架由三个相互整合的组成部分构成。其一，设计并验证了一套定制气候腔体与电阻（ER）传感器系统，能够在非连续液滴电解质条件下持续监测腐蚀动力学，而传统电化学方法在此类条件下往往失效。其二，开发了一套全自动计算机视觉处理流程，融合大型视觉模型实现液滴的零样本分割，并结合基于概率的颜色特征，同时连续追踪数千个单液滴的腐蚀产物形成过程。该方法揭示了液滴尺寸是腐蚀行为的关键调控参数：较大液滴表现出更早的腐蚀起始时间和更快的腐蚀产物累积速率；同时，两种空间上截然不同的腐蚀形貌被识别并量化：类Evans液滴内部腐蚀模式与外周边缘模式。其三，开发了一套弱监督机器学习框架以求解动力学反问题：通过将单液滴动力学推断建模为多实例回归问题，在无需液滴级标注数据的前提下，将全局ER信号分解为各液滴的独立贡献。

通过将该框架应用于表面粗糙度的研究，验证了其对于机理性参数的敏感性。较粗糙的表面因液滴钉扎效应增强和碰撞聚并，产生更大、更扁长的液滴，导致可测

量的更高且发展更早的腐蚀速率。上述结果可通过光学成像与整体动力学数据流完整追溯。

综上所述，本研究为大气腐蚀领域确立了一种新的实验范式：通过使电解质液滴群可视化、可量化、并与材料损伤建立关联，从而打开机器学习“黑箱”。所形成的多模态耦合数据集，为验证和推动下一代具有物理可解释性与跨场景迁移能力的腐蚀预测模型奠定了实验基础。

PREFACE

There is a lot of science in this film, but it's there for the people who are interested in it and want to dig a little deeper.

— Christopher Nolan, on *Interstellar*, 2014

When Christopher Nolan set out to depict a black hole on screen for the first time, he did not ask audiences to simply trust that it looked right. He brought in theoretical physicist Kip Thorne, who derived the actual equations governing how a black hole bends light, and handed them to the visual effects team. The result was imagery that had never existed before: not as an artistic impression, but as a genuine scientific rendering made visible for the first time. Audiences did not need to understand the mathematics to feel its truth. But the mathematics was there for those who wanted it, and its presence made everything more honest.

I find that story instructive for a field like atmospheric corrosion. For decades, corrosion in application has operated with a version of the just-trust-it problem. Engineers have learned which surface treatments work and which do not. Standards have accumulated vast empirical databases. Machine learning models have found statistical patterns in environmental data that predict damage with reasonable accuracy. All of this works, in the same way that a film, can be emotionally effective without showing you the real physics of a black hole. But none of it shows you what is actually happening. The electrolyte layer that mediates every corrosion reaction – the thin, stochastic population of droplets that forms on a steel surface, evolves, interacts, and drives damage, has remained invisible.

This thesis is an attempt to make that invisible process visible. What follows is a framework: experimental, computational, and data-driven, that tracks thousands of individual droplets in real time, watches corrosion products form and spread beneath each one, and connects what it sees to quantitative measurements of material loss. It does not ask scientists to accept correlations they cannot interpret, nor does it ask engineers to trust a black box they cannot inspect. The mechanisms are there for those who want them. The outcomes are traceable for those who need them.

Nolan has said he hopes *Interstellar* will make people think about humanity's place in the universe. This thesis has more modest ambitions. But I do hope that anyone who has ever stood in front of a corroding infrastructure and wondered precisely what is happening at that surface, and why, will find something useful in these pages.

Keer Zhang
Delft, March 2026

1

INTRODUCTION

This research focuses on three primary topics: (1) the development of a "White Box" experimental framework that couples dynamic electrolyte monitoring with global kinetic measurements; (2) the formulation of dynamic probability descriptors to characterize visual corrosion propagation, and the implementation of weakly supervised learning to infer material loss evolution for each droplet from droplet visual features and global corrosion kinetics; and (3) the statistics investigation of how surface roughness modulates corrosion mechanism via altering electrolyte population. This chapter provides an overview of the research background and its associated challenges, followed by a discussion of the existing knowledge gaps and an outline of the thesis structure.

1.1. SOCIAL IMPORTANCE OF ATMOSPHERIC CORROSION MANAGEMENT

Atmospheric corrosion is the most prevalent form of material degradation, affecting infrastructure, transportation, and energy sectors globally. Unlike specific degradation mechanisms that require continuous immersion, atmospheric corrosion is a widespread phenomenon driven by the interaction between materials and dynamic environmental conditions, particularly fluctuating humidity, wet-dry cycles, and the presence of surface electrolytes or pollutants[1]. The economic burden is substantial; according to the NACE International IMPACT study, the global cost of corrosion is estimated at \$2.5 trillion annually, equivalent to roughly 3.4% of global Gross Domestic Product (GDP)[2]. A significant fraction of this cost arises from atmospheric corrosion of carbon steel[2]. Carbon steel is a primary construction material widely utilized across civil infrastructure, marine, offshore, and transportation applications. It serves as the central focus of this thesis. Consequently, the ability to accurately predict its corrosion rates and service life under complex atmospheric conditions has become a critical requirement for predictive maintenance and management.

1.2. FROM INTERNATIONAL STANDARDS TO MACHINE LEARNING

To address this predictive challenge, the corrosion community has traditionally relied on empirical modeling. The current state-of-the-art, as described in standards such as ISO 9223 [3], utilizes Dose-Response Functions (DRFs) to estimate corrosion rates. These functions operate as statistical regressions that correlate environmental parameters, such as relative humidity (RH), temperature (T), and pollutant concentrations (e.g., SO₂, Cl⁻), directly with material mass loss. While effective for broad corrosivity categorization, these linear models struggle to capture the complex and non-linear interactions in dynamic weather systems.

In recent years, the field has moved toward data-driven approaches by employing Machine Learning (ML) algorithms, such as Artificial Neural Networks (ANNs) and Random Forests, to analyze high-dimensional environmental datasets[4–8]. These models significantly outperform traditional DRFs by capturing non-linear dependencies and integrating a wider array of variables. Furthermore, techniques such as transfer learning have been introduced to adapt models trained in data-rich regions to new locations with sparse data[9].

Despite these advances, a fundamental limitation persists that both traditional DRFs and modern ML models operate as “Black Boxes”. They map environmental inputs directly to corrosion outputs via bypassing the physicochemical reality of the process. Consequently, they suffer from two critical weaknesses:

- First, the data dependency. Their accuracy is intrinsically bound to the quality and granularity of the training data. Most models rely on historical environmental monitoring that is often coarse (hourly or daily averages), which smooths out the

rapid fluctuations in wetting and drying that drive corrosion initiation.

- Second, lack of mechanistic insights: A model trained on data from one climate learns the statistical correlations specific to that region. When applied to a different climate, purely statistical transfer learning struggles because it does not “understand” how changes in environmental parameters fundamentally alter the electrolyte phase, which usually appears as a thin, dynamic liquid film that serves as the direct medium for interfacial electrochemical reactions.

In short, the model optimizes correlation but ignores causation. To achieve true transferability, which predicts corrosion in a new environment without historical data, we must open the black box and explicitly model the electrolyte layer as the governing transfer function.

1.3. THE EXPERIMENTAL BOTTLENECK: FIELD VS. INDUSTRY VS. LABORATORY

To move beyond statistical correlation and validate mechanistic models[10], researchers require high-resolution coupled data, specifically, data with sufficient spatiotemporal resolution to synchronize dynamic physical changes with transient electrochemical responses. This data should link a broad input space, including environmental conditions, material properties, and the dynamic electrolyte configurations, which is the primary focus of this thesis to the corrosion kinetics.

Historically, continuous corrosion monitoring sensors, such as Electrical Resistance (ER) [11–15], galvanic Atmospheric Corrosion Monitor (ACM)[6, 16–19], and gravimetric [20, 21] sensors have been widely employed to bridge this gap. While these sensors are excellent in providing time-resolved kinetic data in atmospheric research, correlating their outputs directly with the complex, instantaneous physical state of the surface remains a challenge. Consequently, current experimental methodologies lack the ability to provide the fully coupled data necessary for mechanistic validation.

Field exposure test (FET)

FET in application sites (e.g., test centers in coastal or industrial zones) serves as the “ground truth” of atmospheric corrosion. However, from a modeling perspective, the field functions as a black box. While FET yields valuable quantitative outcomes, such as integrated mass loss, localized attack metrics, corrosion morphology, and time-resolved macroscopic environmental information, the instantaneous evolution of direct corrosion mediums (i.e. the formation, growth, and evaporation of electrolyte droplets) is stochastic and barely recorded. While knowing the material is actively corroding, the specific wetting events or droplet configurations that cause the damage remain unknown. This lack of temporal resolution makes it impossible to validate dynamic mechanistic models.

Accelerated corrosion tests (ACT)

To overcome the time constraints and uncontrollability of field exposure, the industry

relies on ACT, ranging from continuous salt spray (e.g. ASTM B117[22]) to more complex cyclic tests (e.g., ISO 14993[23]). ACTs are commonly designed for qualitatively evaluating the corrosion resistance of materials under specific protocols. While cyclic tests attempt to mimic atmospheric transitions by alternating between wet and dry phases, direct monitoring of the electrolyte conditions encountered during the tests is often absent[24], making it hard to establish quantitative transferability to how the material would corrode in field applications.

Fundamental lab-scale tests

To uncover the fundamental physicochemical mechanisms driving atmospheric corrosion, academic research has produced an extensive body of work combining surface-sensitive techniques and localized electrochemical testing. Techniques such as the Scanning Kelvin Probe (SKP)[25–31], Electrochemical Impedance Spectroscopy (EIS) [32–42], potentiodynamic polarization [32, 39, 40, 43–46], Electrochemical Noise (EN) [32, 47–52], and Wire Beam Electrodes (WBE) [53–57] have been widely deployed to measure transient corrosion kinetics and local potential fields.

However, previous in-situ investigations into atmospheric corrosion rarely focus directly on the geometry of the thin electrolyte layer. Instead, they typically examine the direct influence of macroscopic environmental parameters, such as relative humidity[34, 40, 42, 45], ambient temperature[34, 40, 43, 50] and atmosphere composition[35, 41] on the metal's corrosion behavior. When the electrolyte configuration is explicitly considered to achieve mechanistic clarity, studies typically restrict their focus to highly idealized geometries. Research thus falls into two physically distinct scenarios: continuous thin electrolyte films[26, 28, 33, 58–60] which provide relatively homogeneous boundary condition or isolated single droplets[29–32, 53, 55, 56] which allow for precise analysis of localized electrochemical gradients. This necessary idealization ignores a critical physical reality: due to surface tension, wetting properties, and dynamic environmental transitions, atmospheric moisture most often exists as a complex, discontinuous, and interacting multi-droplet population.

The gap in mechanistic modeling

The discrepancy between idealized lab-scale experiments and real-world multi-droplet environments highlights a major bottleneck in current predictive modeling. As discussed previously, while empirical standards and data-driven models are excellent at finding statistical correlations, they operate as black boxes which lack causal interpretability. To achieve true mechanistic prediction by looking for causation rather than just correlation, the field mostly relies on physics-based numerical modeling, such as Finite Element Models (FEM). FEM approaches attempt to explicitly simulate the underlying physical reality by calculating ion transport, oxygen diffusion, and local potential distributions based on interfacial electrochemical kinetics.

However, because these mechanistic models require explicitly defined spatial boundaries, they are heavily constrained by the same idealized geometries used in lab experiments. Current FEM simulations are highly effective at modeling a static single droplet[61–

63] or a continuous thin film[24, 64–67]. More recently, significant efforts have been made to extend FEM into multi-droplet realities. For instance, Van den Steen et al[68] developed a framework that computes corrosion current densities for individual droplet geometries and applies them to imposed droplet-size distributions. However, because experimental data coupling multi-droplet population distributions with actual corrosion rates is largely missing, such models must rely on synthetic size distributions rather than measured inputs for comparison. Consequently, these mechanistic frameworks remain fundamentally bottlenecked by a lack of direct experimental validation linking realistic multi-droplet configurations to corrosion kinetics.

1.4. THEORETICAL FRAMEWORK

To bridge the gap between laboratory models, the accelerated corrosion tests, and realistic field behavior via exploring the role of electrolyte configurations, this thesis integrates concepts from four scientific domains: interfacial electrochemistry, electrical resistance monitoring, computer vision, and weakly supervised machine learning. As illustrated in Fig. 1.1, this thesis positions the droplet electrolyte as the governing transfer function linking all three scales of corrosion research.

This section outlines the fundamental operating principles of these domains necessary to understand the proposed multi-modal framework.

The interfacial electrochemistry: from Evans droplet to dynamic multi-droplet systems

Central to the mechanistic understanding of atmospheric corrosion is the behavior of the discrete electrolyte droplets. Unlike immersion under a bulk or continuous thin film electrolyte, where material access with electrolyte is uniform, a sessile droplet on a metal surface creates a condition of differential aeration. This phenomenon, first elucidated by U.R. Evans[69], serves as the foundational conceptual reference for localized atmospheric corrosion.

As illustrated in the classical Evans model (Fig. 1.2), oxygen from the surrounding atmosphere first dissolves into the electrolyte and must then diffuse through the liquid phase to reach the metal surface. Because the electrolyte is thinnest at the droplet's periphery (the three-phase boundary), the dissolved oxygen diffusion path is shortest there, enabling rapid replenishment and establishing an oxygen-rich region that facilitates the cathodic reduction reaction:



Conversely, the thicker electrolyte near the droplet center sustains a longer diffusion path, leading to dissolved oxygen depletion and establishing an anodic region where active metal dissolution occurs:



As Fe^{2+} ions migrate outward and OH^- ions migrate inward, they meet in an intermediate zone where they interact to form insoluble iron hydroxides and oxides, and precipitate

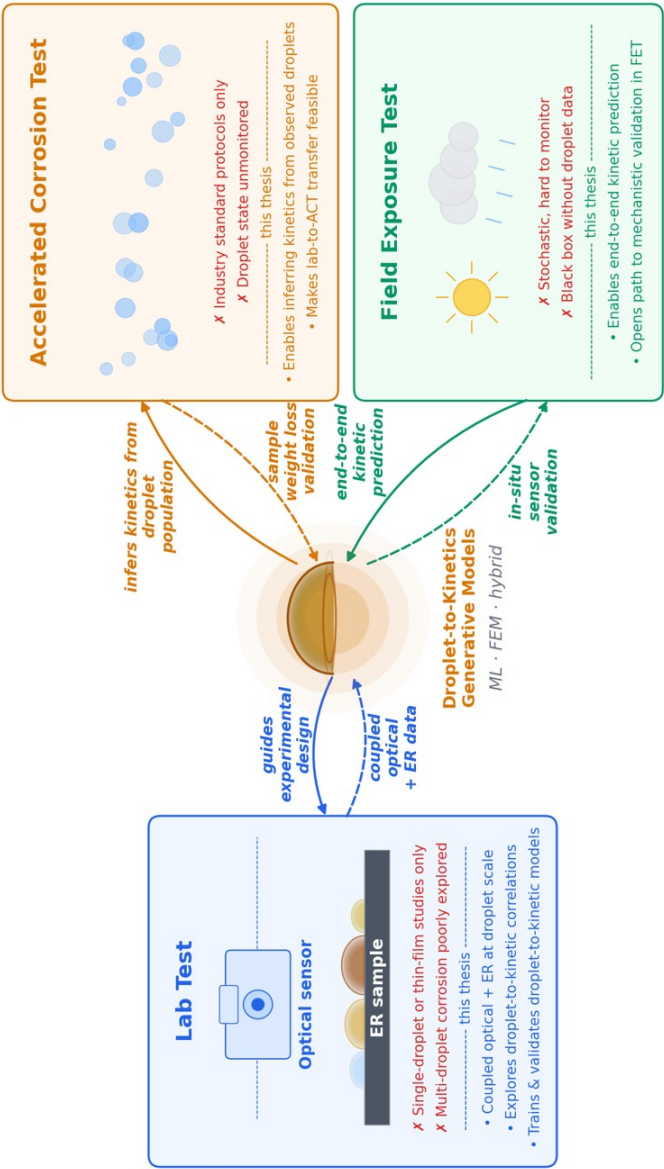


Figure 1.1: The droplet electrolyte as a governing transfer function bridging three scales of atmospheric corrosion research. Current limitations in each domain and the contributions enabled by this thesis are indicated.

tate as a distinct membranous mantle or "rust ring".

While Evans accurately captured the dynamic precipitation and physical movement of corrosion products within these spatially separated zones, his foundational work pri-

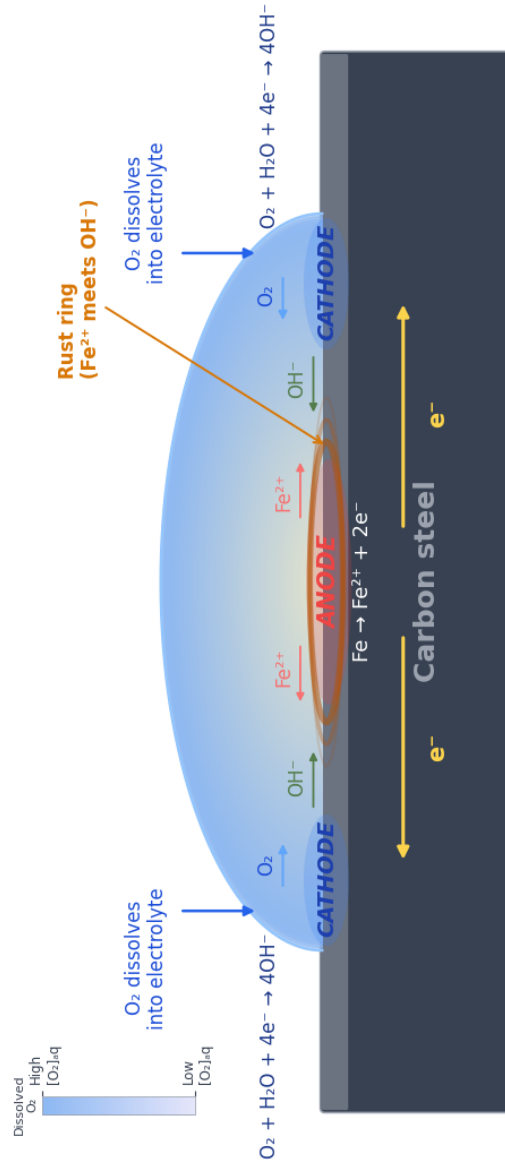


Figure 1.2: Schematic illustration of Evans droplet corrosion model

marily examined macroscopically isolated and stable droplets. Real atmospheric corrosion, however, introduces two additional layers of complexity: first, as discussed in the last section, multiple droplets can co-exist and interact through several mechanisms, including merging via wet area expansion, electrochemical coupling when their electrolyte zones overlap, and ion redistribution driven by evaporation-induced flows; and

second, the properties of an individual droplet can be highly transient. As stochastic multi-droplet populations evaporate, merge, and interact, local concentration gradients emerge due to enhanced vapor flux at the edges. This induces internal capillary and Marangoni flows that redistribute ions and further complicate the localized kinetics[70–72]. Furthermore, depending on droplet size and electrolyte composition, sample surface condition and environmental conditions, corrosion is not strictly confined to the initial footprint. For instance, expansion of the wet area surrounding the original primary droplet is observed[73], and sometimes corrosion is also found to propagate outward from the area covered by the primary droplet[74, 75], which further enables inter-droplet interactions.

Translating electrochemistry to visual signatures

This dynamic electrochemical heterogeneity directly translates into observable optical features. Whether confined to the original droplet footprint or spreading to the surrounding regions, the localized anodic and cathodic activities result in the spatial distribution of corrosion products. Because the precipitation of iron oxides involves distinct color shifts (e.g., from a clear electrolyte to highly opaque yellowish, brownish, or black rust), these insoluble products act as a direct, physical proxy for underlying corrosion propagation[76]. By applying automated data pipelines to analyze the spatiotemporal evolution of these visual signatures, it becomes possible to optically quantify the corrosion progression of thousands of droplets simultaneously without interrupting the physical electrochemical process.

The kinetic monitoring: the electrical resistance (ER) method

To quantify the corrosion kinetics generated by these droplets without interrupting the reaction process, this work utilizes the Electrical Resistance (ER) technique. Electrochemical methods such as EIS, EN and galvanic method often struggle under realistic atmospheric conditions because they typically require a continuous bulk electrolyte to maintain ionic conductivity between electrodes. In contrast, the ER method is exceptionally well-suited for atmospheric corrosion research particularly under multi-droplet conditions. It is non-invasive and focuses on the macroscopic physical properties of the corroding material itself, making it capable of measuring integrated mass loss even under highly discontinuous or purely droplet-based electrolyte conditions.

The method functions by directly linking mass loss to changes in electrical properties. It relies on the inverse relationship between the electrical resistance (R) of a metallic element and its cross-sectional area (A), governed by Ohm's law:

$$R = \rho \frac{L}{A} \quad (1.3)$$

where ρ is the resistivity and L is the length. As corrosion reduces the metal thickness, the cross-sectional area decreases, leading to a measurable increase in resistance (R). Because ER can change with temperature, a moisture-blocked reference sample is introduced to compensate for thermal effects. In the context of this thesis, the ER signal serves as the “global ground truth”. While it is important to acknowledge that the ER method has inherent limitations in spatial resolution since it assumes thickness loss is

uniform across the sensor track and thus cannot capture the exact depth or geometry of localized pitting attacks, it provides a precise, robust and time-resolved measurement of the total integrated material loss across the entire surface. This global kinetic data serves as the most reliable quantitative validation target for the data-driven predictive models developed in this work.

The computational logic: from vision to weakly supervised learning

A primary challenge in correlating visual droplet dynamics with corrosion rates is the “corrosion status quantification”. A single experiment generates hundreds of images containing tens of thousands of droplets, making manual annotations infeasible. To resolve this, this thesis establishes a multi-stage computational pipeline that progresses from robust segmentation to kinetic inference.

- **Semantic segmentation via Large Vision Models (LVM)** Traditional thresholding algorithms (e.g., Otsu’s method[77]) struggle to distinguish between transparent droplets, corrosion products, and background artifacts. To overcome this, this work utilizes state-of-the-art Large Vision Models (e.g., SAM[78]) to perform robust, zero-shot segmentation of the droplet areas followed by post-processing, which provides the geometrical basis for all subsequent analysis.
- **Corrosion feature construction** Once segmented, the pipeline extracts high-dimensional features for each droplet at each time step. Probability-based corrosion indicators are then constructed for inferring the likelihood of corrosion initiation based on the evolution of segment color, which serves as the quantitative proxy for corrosion status evolution.
- **Kinetic disaggregation via weakly supervised learning** Meanwhile, to link these local optical corrosion features with physical mass loss, the framework employs weakly supervised learning to solve an “inverse problem”. The algorithm takes the time-resolved visual features from all droplet segments and correlates them with the single global corrosion kinetic signal measured by the ER sensor. By learning temporal weights that best map the collective visual features to the measured increase in resistance, the model effectively disaggregates the global signal to infer the specific kinetic contribution of each individual droplet without requiring per-droplet ground truth labels. It must be noted that this data-driven disaggregation does not replace mechanistic understanding; rather, it complements it. By providing localized kinetic estimations that are experimentally impossible to measure directly, this framework serves as a bridge between macroscopic sensor data and microscopic droplet electrochemistry.

1.5. RESEARCH OBJECTIVES AND THESIS OUTLINE

The primary objective of this thesis is to investigate atmospheric corrosion under a collection of droplets coexisting on the same surface, which serves as a simplified model for discontinuous electrolyte configurations. By computationally analyzing the spatiotemporal optical evolution of the localized electrolyte, this work aims to establish a quantitative framework that links macroscopic corrosion rates with microscopic multi-droplet

dynamics. This data-driven approach directly bridges the gap between the idealized single-droplet geometry in fundamental lab-scale models with the stochastic, large-scale droplet population observed in field and accelerated corrosion tests. To achieve this, the research strategy is structured as a comprehensive experimental-computational pipeline progressing from experimental platform designing, multi-modal data acquisition and signal processing to automated feature extraction, kinetic inference, and finally, mechanistic application. The outline of the full thesis is presented in [Fig. 1.3](#). The first major

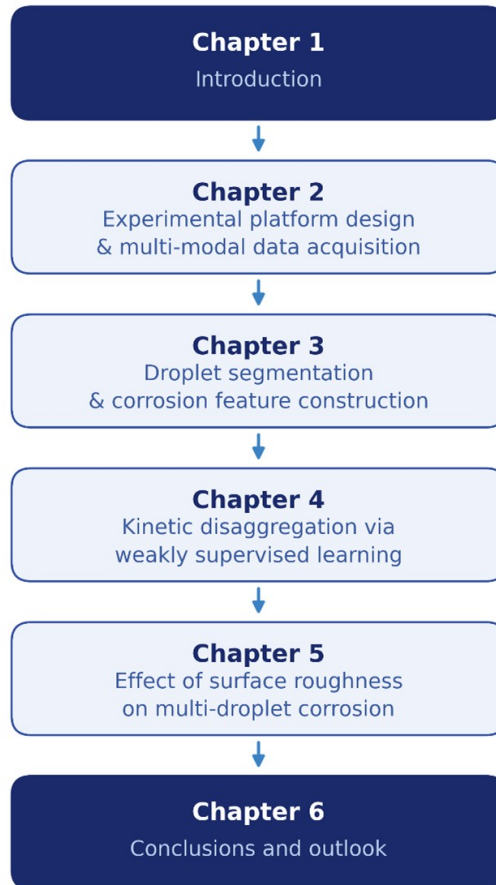


Figure 1.3: Thesis outline

objective of this thesis is to design and validate an experimental framework that integrates real-time optical monitoring with precise corrosion kinetic measurements. Accordingly, [Chapter 2](#) establishes the data-generation and signal-processing foundations of the thesis. It details the design and validation of a novel pipeline that synchronizes the continuous signal acquisition of droplets' optical evolution with ER-based corrosion kinetics.

Once these high-resolution data streams are established, the next objective is to computationally extract quantitative features from the complex visual environment of a corroding surface. Traditional segmentation fails due to transparent droplets, textured metals, and visually confusing corrosion products. [Chapter 3](#) utilizes state-of-the-art large vision models to achieve robust, zero-shot segmentation of transparent droplets against these noisy backgrounds. It then addresses the oversimplification of binary corrosion classification by developing continuous, probability-based indicators from raw visual features to quantitatively track the gradual progression of corrosion.

With local optical features computationally extracted and global kinetic data recorded, the research confronts an "inverse problem". While mechanistic corrosion operates at the local droplet level, the electrical resistance sensors capture an integrated, macroscopic effect across the entire surface. [Chapter 4](#) aims to link global kinetic signals to local visual features using weakly supervised machine learning. This approach effectively infers the specific kinetic contribution of each individual droplet without requiring per-droplet ground-truth labels.

[Chapter 5](#) applies this fully developed data-driven framework to investigate a fundamental governing parameter of atmospheric corrosion: surface roughness. The objective is to determine how surface topography acts as a governing parameter to alter droplet population dynamics, and consequently, to quantify its effect on the underlying corrosion mechanisms.

Finally, [Chapter 6](#) concludes the dissertation by summarizing the main findings, demonstrating that the core research objectives have been met, and outlining potential directions for future data-driven research in atmospheric corrosion.

BIBLIOGRAPHY

- [1] C. Leygraf, I. O. Wallinder, and J. Tidblad. "Atmospheric Corrosion". In: John Wiley & Sons, Ltd, 2016. Chap. 1, pp. 1–6.
- [2] G. H. Koch et al. *International Measures of Prevention, Application, and Economics of Corrosion Technologies Study*. Tech. rep. Koch. NACE, 2016.
- [3] ISO-9223. *Corrosion of metals and alloys — Corrosivity of atmospheres — Classification, determination and estimation*. 2012.
- [4] L. Yang et al. "Corrosion resistance optimization of Sn-additional low-alloy high strength steel by data-driven identification and field exposure verification". In: *Journal of Materials Research and Technology-Jmr&T* 25 (2023), pp. 3624–3641. ISSN: 2238-7854. DOI: [10.1016/j.jmrt.2023.06.159](https://doi.org/10.1016/j.jmrt.2023.06.159). URL: [%3CGo%20to%20ISI%3E://WOS:001091643100001](https://www.scopus.com/search/result?query=%3CGo%20to%20ISI%3E://WOS:001091643100001).
- [5] Y. N. Shi et al. "Data mining to online galvanic current of zinc/copper Internet atmospheric corrosion monitor". In: *Corrosion Science* 133 (2018), pp. 443–450. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2018.02.005](https://doi.org/10.1016/j.corsci.2018.02.005). URL: [%3CGo%20to%20ISI%3E://WOS:000429764100041](https://www.scopus.com/search/result?query=%3CGo%20to%20ISI%3E://WOS:000429764100041).
- [6] Z. B. Pei et al. "Towards understanding and prediction of atmospheric corrosion of an Fe/Cu corrosion sensor via machine learning". In: *Corrosion Science* 170 (2020). ISSN: 0010-938x. DOI: [ARTN10869710.1016/j.corsci.2020.108697](https://doi.org/10.1016/j.corsci.2020.108697). URL: [%3CGo%20to%20ISI%3E://WOS:000533523500048](https://www.scopus.com/search/result?query=%3CGo%20to%20ISI%3E://WOS:000533523500048).
- [7] Q. Li et al. "Long-term corrosion monitoring of carbon steels and environmental correlation analysis via the random forest method". In: *Npj Materials Degradation* 6.1 (2022). DOI: [ARTN110.1038/s41529-021-00211-3](https://doi.org/10.1038/s41529-021-00211-3). URL: [%3CGo%20to%20ISI%3E://WOS:000741373100001](https://www.scopus.com/search/result?query=%3CGo%20to%20ISI%3E://WOS:000741373100001).
- [8] L. B. Coelho et al. "Reviewing machine learning of corrosion prediction in a data-oriented perspective". In: *Npj Materials Degradation* 6.1 (2022). DOI: [ARTN810.1038/s41529-022-00218-4](https://doi.org/10.1038/s41529-022-00218-4). URL: [%3CGo%20to%20ISI%3E://WOS:000747144900001](https://www.scopus.com/search/result?query=%3CGo%20to%20ISI%3E://WOS:000747144900001).
- [9] V. Vangrunderbeek et al. "Exploring the potential of transfer learning in extrapolating accelerated corrosion test data for long-term atmospheric corrosion forecasting". In: *Corrosion Science* 225 (2023). ISSN: 0010-938x. DOI: [ARTN11161910.1016/j.corsci.2023.111619](https://doi.org/10.1016/j.corsci.2023.111619). URL: [%3CGo%20to%20ISI%3E://WOS:001107012300001](https://www.scopus.com/search/result?query=%3CGo%20to%20ISI%3E://WOS:001107012300001).
- [10] B. G. Koushik et al. "Review on modelling of corrosion under droplet electrolyte for predicting atmospheric corrosion rate". In: *Journal of Materials Science & Technology* 62 (2021), pp. 254–267. ISSN: 1005-0302. DOI: [10.1016/j.jmst.2020.04.061](https://doi.org/10.1016/j.jmst.2020.04.061). URL: [%3CGo%20to%20ISI%3E://WOS:000601221700025](https://www.scopus.com/search/result?query=%3CGo%20to%20ISI%3E://WOS:000601221700025).

- [11] M. Takeyama. “High-Temporal-Resolution Corrosion Monitoring in Fluctuating-Temperature Environments with an Improved Electrical Resistance Sensor”. In: *Sensors* 25.1 (2025). DOI: [ARTN26810.3390/s25010268](#). URL: [%3CGo%20to%20ISI%3E://WOS:001393814600001](#).
- [12] Z. L. Li et al. “Application of An Electrical Resistance Sensor-Based Automated Corrosion Monitor in the Study of Atmospheric Corrosion”. In: *Materials* 12.7 (2019). ISSN: 1996-1944. DOI: [ARTN106510.3390/ma12071065](#). URL: [%3CGo%20to%20ISI%3E://WOS:000465500700064](#).
- [13] M. Kouril et al. “Corrosion monitoring in archives by the electrical resistance technique”. In: *Journal of Cultural Heritage* 15.2 (2014), pp. 99–103. ISSN: 1296-2074. DOI: [10.1016/j.culher.2013.04.002](#). URL: [%3CGo%20to%20ISI%3E://WOS:000333348800001](#).
- [14] F. Martinelli-Orlando and U. Angst. “Monitoring corrosion rates with ER-probes - a critical assessment based on experiments and numerical modelling”. In: *Corrosion Engineering Science and Technology* 57.3 (2022), pp. 254–268. ISSN: 1478-422x. DOI: [10.1080/1478422x.2022.2053036](#). URL: [%3CGo%20to%20ISI%3E://WOS:000773192900001](#).
- [15] K. Popova, M. F. Montemor, and T. Prosek. “Application of Resistometric Sensors for Real-Time Corrosion Monitoring of Coated Materials”. In: *Corrosion and Materials Degradation* 5.4 (2024), pp. 573–592. DOI: [10.3390/cmd5040026](#). URL: [%3CGo%20to%20ISI%3E://WOS:001383777400001](#).
- [16] V. Vangrunderbeek et al. “Corrosion and environmental sensor response delays during monitored multi-droplet wetting: Unraveling time lags in atmospheric corrosion”. In: *Corrosion Science* 255 (2025). ISSN: 0010-938x. DOI: [ARTN11315410.1016/j.corsci.2025.113154](#). URL: [%3CGo%20to%20ISI%3E://WOS:001524798700002](#).
- [17] D. M. Yang, H. W. Mei, and L. M. Wang. “Corrosion Measurement of the Atmospheric Environment Using Galvanic Cell Sensors”. In: *Sensors* 19.2 (2019). ISSN: 1424-8220. DOI: [ARTN33110.3390/s19020331](#). URL: [%3CGo%20to%20ISI%3E://WOS:000458569300114](#).
- [18] F. Mansfeld and J. V. Kenkel. “Electrochemical Monitoring of Atmospheric Corrosion Phenomena”. In: *Journal of the Electrochemical Society* 123.8 (1976), pp. C246–C246. ISSN: 0013-4651. URL: [%3CGo%20to%20ISI%3E://WOS:A1976BZ76700130](#).
- [19] D. To, T. Shinohara, and O. Umezawa. “Experimental Investigation on the Corrosivity of Atmosphere through the Atmospheric Corrosion Monitoring (ACM) Sensors”. In: *Atmospheric -and- Marine Corrosion* 75.29 (2017), pp. 1–10. ISSN: 1938-5862. DOI: [10.1149/07529.0001ecst](#). URL: [%3CGo%20to%20ISI%3E://WOS:000469281300001](#).
- [20] M. Strebl and S. Virtanen. “Real-Time Monitoring of Atmospheric Magnesium Alloy Corrosion”. In: *Journal of the Electrochemical Society* 166.11 (2018), pp. C3001–C3009. ISSN: 0013-4651. DOI: [10.1149/2.0011911jes](#). URL: [%3CGo%20to%20ISI%3E://WOS:000452951500001](#).

- [21] V. A. Kotenev et al. "Gravimetry, resistometry, and Fourier-transform infrared spectroscopy for monitoring the corrosivity of the atmosphere with the use of an iron-oxide nanocomposite sensor layer". In: *Protection of Metals and Physical Chemistry of Surfaces* 49.5 (2013), pp. 597–603. ISSN: 2070-2051. DOI: [10.1134/S2070205113050055](https://doi.org/10.1134/S2070205113050055). URL: [3CGo%20to%20ISI%3E://WOS:000324396700015](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000324396700015).
- [22] ASTM-B117. *Standard Practice for Operating Salt Spray (Fog) Apparatus*. 2019.
- [23] ISO-14993. *Corrosion of metals and alloys — Accelerated testing involving cyclic exposure to salt mist, dry and wet conditions*. 2018.
- [24] N. Van den Steen et al. "An integrated modeling approach for atmospheric corrosion in presence of a varying electrolyte film". In: *Electrochimica Acta* 187 (2016), pp. 714–723. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2015.11.010](https://doi.org/10.1016/j.electacta.2015.11.010). URL: [3CGo%20to%20ISI%3E://WOS:000367235600083](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000367235600083).
- [25] A. Nazarov, F. Vucko, and D. Thierry. "Scanning Kelvin Probe for detection of the hydrogen induced by atmospheric corrosion of ultra-high strength steel". In: *Electrochimica Acta* 216 (2016), pp. 130–139. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2016.08.122](https://doi.org/10.1016/j.electacta.2016.08.122). URL: [3CGo%20to%20ISI%3E://WOS:000385495000016](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000385495000016).
- [26] M. Stratmann and H. Streckel. "The Investigation of the Corrosion of Metal-Surfaces, Covered with Thin Electrolyte Layers - a New Experimental-Technique". In: *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics* 92.11 (1988), pp. 1244–1250. ISSN: 0005-9021. DOI: [DOI10.1002/bbpc.198800305](https://doi.org/10.1002/bbpc.198800305). URL: [3CGo%20to%20ISI%3E://WOS:A1988R362500011](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:A1988R362500011).
- [27] D. de la Fuente, B. Chico, and M. Morcillo. "A SEM/XPS/SKP study on the distribution of chlorides in contaminated rusty steel". In: *Corrosion Science* 48.8 (2006), pp. 2304–2316. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2005.07.009](https://doi.org/10.1016/j.corsci.2005.07.009). URL: [3CGo%20to%20ISI%3E://WOS:000240055200029](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000240055200029).
- [28] A. Nazarov, M. G. Olivier, and D. Thierry. "SKP and FT-IR microscopy study of the paint corrosion de-adhesion from the surface of galvanized steel". In: *Progress in Organic Coatings* 74.2 (2012), pp. 356–364. ISSN: 0300-9440. DOI: [10.1016/j.porgcoat.2011.10.009](https://doi.org/10.1016/j.porgcoat.2011.10.009). URL: [3CGo%20to%20ISI%3E://WOS:000303307000011](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000303307000011).
- [29] J. S. Wang et al. "Observation and micro-electrochemical characterisation for micro-droplets in initial marine atmospheric corrosion". In: *Corrosion Engineering Science and Technology* 51.4 (2016), pp. 308–312. ISSN: 1478-422x. DOI: [10.1080/1478422x.2015.1110373](https://doi.org/10.1080/1478422x.2015.1110373). URL: [3CGo%20to%20ISI%3E://WOS:000379540100011](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000379540100011).
- [30] S. Qian and Y. F. Cheng. "Corrosion of steel in a CO₂-containing solution droplet generated in wet gas pipelines studied by scanning Kelvin probe". In: *Journal of Pipeline Science and Engineering* 2.1 (2022), pp. 71–77. DOI: [10.1016/j.jpse.2021.12.003](https://doi.org/10.1016/j.jpse.2021.12.003). URL: [3CGo%20to%20ISI%3E://WOS:001059324700001](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:001059324700001).
- [31] S. Ootsuka et al. "Quantification of subsurface hydrogen in corroding mild steel using Scanning Kelvin Probe calibrated by electrochemical permeation technique". In: *Corrosion Science* 221 (2023). ISSN: 0010-938x. DOI: [ARTN11136210.1016/j.corsci.2023.111362](https://doi.org/10.1016/j.corsci.2023.111362). URL: [3CGo%20to%20ISI%3E://WOS:001054543100001](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:001054543100001).

- [32] E. Rahimi et al. "Atmospheric corrosion of iron under a single droplet: A new systematic multi-electrochemical approach". In: *Corrosion Science* 235 (2024). ISSN: 0010-938x. DOI: [ARTN11217110 . 1016 / j . corsci . 2024 . 112171](https://doi.org/10.1016/j.corsci.2024.112171). URL: [%3CGo%20to%20ISI%3E://WOS:001256286000001](https://www.wos.org/doi/abs/10.1016/j.corsci.2024.112171).
- [33] A. Nishikata, Y. Ichihara, and T. Tsuru. "Electrochemical impedance spectroscopy of metals covered with a thin electrolyte layer". In: *Electrochimica Acta* 41.7-8 (1996), pp. 1057–1062. ISSN: 0013-4686. DOI: [Doi10 . 1016 / 0013 - 4686 \(95 \) 00438 - 6](https://doi.org/10.1016/0013-4686(95)00438-6). URL: [%3CGo%20to%20ISI%3E://WOS:A1996UK66700014](https://www.wos.org/doi/abs/10.1016/0013-4686(95)00438-6).
- [34] L. F. Shen et al. "Understanding the corrosion evolution of galvanic steel under simulated marine atmospheric environment using real-time EIS measurement". In: *Anti-Corrosion Methods and Materials* 72.3 (2025), pp. 331–342. ISSN: 0003-5599. DOI: [10.1108/Acmm-07-2024-3056](https://doi.org/10.1108/Acmm-07-2024-3056). URL: [%3CGo%20to%20ISI%3E://WOS:001431270900001](https://www.wos.org/doi/abs/10.1108/Acmm-07-2024-3056).
- [35] X. Z. Ma et al. "Investigation on the initial atmospheric corrosion of mild steel in a simulated environment of industrial coastland by thin electrical resistance and electrochemical sensors". In: *Corrosion Science* 204 (2022). ISSN: 0010-938x. DOI: [ARTN11038910 . 1016 / j . corsci . 2022 . 110389](https://doi.org/10.1016/j.corsci.2022.110389). URL: [%3CGo%20to%20ISI%3E://WOS:000808009000003](https://www.wos.org/doi/abs/10.1016/j.corsci.2022.110389).
- [36] Z. Liu et al. "EIS measurement on atmospheric exposure induced degradation of a pre-engineered passive coating on tinplate surface". In: *Measurement* 231 (2024). ISSN: 0263-2241. DOI: [ARTN11464610 . 1016 / j . measurement . 2024 . 114646](https://doi.org/10.1016/j.measurement.2024.114646). URL: [%3CGo%20to%20ISI%3E://WOS:001226224400001](https://www.wos.org/doi/abs/10.1016/j.measurement.2024.114646).
- [37] Y. Seechurn, J. A. Wharton, and B. Y. R. Surnam. "Mechanistic modelling of atmospheric corrosion of carbon steel in Port-Louis by electrochemical characterisation of rust layers". In: *Materials Chemistry and Physics* 291 (2022). ISSN: 0254-0584. DOI: [ARTN12669410 . 1016 / j . matchemphys . 2022 . 126694](https://doi.org/10.1016/j.matchemphys.2022.126694). URL: [%3CGo%20to%20ISI%3E://WOS:000861689200001](https://www.wos.org/doi/abs/10.1016/j.matchemphys.2022.126694).
- [38] H. Y. Tian et al. "Atmospheric corrosion and mechanical property degradation of 2524-T3 aluminum alloy in marine environments". In: *Corrosion Science* 239 (2024). ISSN: 0010-938x. DOI: [ARTN11239810 . 1016 / j . corsci . 2024 . 112398](https://doi.org/10.1016/j.corsci.2024.112398). URL: [%3CGo%20to%20ISI%3E://WOS:001306992200001](https://www.wos.org/doi/abs/10.1016/j.corsci.2024.112398).
- [39] T. Z. Gu et al. "Initial atmospheric corrosion of zinc-aluminum-magnesium coated steel and galvanized steel in regions of extremely cold and industrial climate". In: *Materials Chemistry and Physics* 291 (2022). ISSN: 0254-0584. DOI: [ARTN12668610 . 1016 / j . matchemphys . 2022 . 126686](https://doi.org/10.1016/j.matchemphys.2022.126686). URL: [%3CGo%20to%20ISI%3E://WOS:000855545800002](https://www.wos.org/doi/abs/10.1016/j.matchemphys.2022.126686).
- [40] Y. W. Liu et al. "Effect of temperature and ultraviolet radiation on corrosion behavior of carbon steel in high humidity tropical marine atmosphere". In: *Materials Chemistry and Physics* 277 (2022). ISSN: 0254-0584. DOI: [ARTN12496210 . 1016 / j . matchemphys . 2021 . 124962](https://doi.org/10.1016/j.matchemphys.2021.124962). URL: [%3CGo%20to%20ISI%3E://WOS:000732830200002](https://www.wos.org/doi/abs/10.1016/j.matchemphys.2021.124962).

- [41] L. Y. Xiao et al. "Study on corrosion mechanism of Al-Zn coatings in the simulated polluted marine atmosphere". In: *Journal of Materials Research and Technology-Jmr&T* 25 (2023), pp. 6446–6458. ISSN: 2238-7854. DOI: [10.1016/j.jmrt.2023.07.091](https://doi.org/10.1016/j.jmrt.2023.07.091). URL: [10.1016/j.jmrt.2023.07.091](https://www.wos.org/doi/abs/10.1016/j.jmrt.2023.07.091).
- [42] C. L. Li et al. "EIS monitoring study of atmospheric corrosion under variable relative humidity". In: *Corrosion Science* 52.11 (2010), pp. 3677–3686. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2010.07.018](https://doi.org/10.1016/j.corsci.2010.07.018). URL: [10.1016/j.corsci.2010.07.018](https://www.wos.org/doi/abs/10.1016/j.corsci.2010.07.018).
- [43] H. C. Yao et al. "Experimental study on the dew point corrosion behavior in atmospheric tower system". In: *Materials Today Communications* 36 (2023). DOI: [10.1016/j.mtcomm.2023.106829](https://doi.org/10.1016/j.mtcomm.2023.106829). URL: [10.1016/j.mtcomm.2023.106829](https://www.wos.org/doi/abs/10.1016/j.mtcomm.2023.106829).
- [44] R. Yuan et al. "Research on corrosion mechanism of microstructure on low alloy steel in humid atmosphere". In: *Materials Today Communications* 31 (2022). DOI: [10.1016/j.mtcomm.2022.103715](https://doi.org/10.1016/j.mtcomm.2022.103715). URL: [10.1016/j.mtcomm.2022.103715](https://www.wos.org/doi/abs/10.1016/j.mtcomm.2022.103715).
- [45] T. Montoya et al. "Influence of Realistic, Cyclic Atmospheric Cycles on the Pitting Corrosion of Austenitic Stainless Steels". In: *Journal of the Electrochemical Society* 170.4 (2023). ISSN: 0013-4651. DOI: [10.1149/1945-7111/acc42e](https://doi.org/10.1149/1945-7111/acc42e). URL: [10.1149/1945-7111/acc42e](https://www.wos.org/doi/abs/10.1149/1945-7111/acc42e).
- [46] Y. Wang et al. "Research on Dynamic Marine Atmospheric Corrosion Behavior of AZ31 Magnesium Alloy". In: *Metals* 12.11 (2022). DOI: [10.3390/met12111886](https://doi.org/10.3390/met12111886). URL: [10.3390/met12111886](https://www.wos.org/doi/abs/10.3390/met12111886).
- [47] H. Q. Fan et al. "Mechanistic study of the atmospheric corrosion of BC550 weathering steel in simulated marine environments by in-situ electrochemical noise". In: *Anti-Corrosion Methods and Materials* 73.2 (2026), pp. 202–213. ISSN: 0003-5599. DOI: [10.1108/Acmm-05-2025-3249](https://doi.org/10.1108/Acmm-05-2025-3249). URL: [10.1108/Acmm-05-2025-3249](https://www.wos.org/doi/abs/10.1108/Acmm-05-2025-3249).
- [48] J. Z. Hu et al. "Corrosion monitoring method of 304 stainless steel in a simulated marine-industrial atmospheric environment: electrochemical noise method". In: *Anti-Corrosion Methods and Materials* 69.6 (2022), pp. 629–635. ISSN: 0003-5599. DOI: [10.1108/Acmm-08-2021-2529](https://doi.org/10.1108/Acmm-08-2021-2529). URL: [10.1108/Acmm-08-2021-2529](https://www.wos.org/doi/abs/10.1108/Acmm-08-2021-2529).
- [49] P. C. Deng et al. "Corrosion Behavior of E690 Steel in Tropical Marine Atmospheres Based on Electrochemical Noise Technique". In: *Electrochemistry* 93.2 (2025). ISSN: 1344-3542. DOI: [10.5796/electrochemistry.24-00098](https://doi.org/10.5796/electrochemistry.24-00098). URL: [10.5796/electrochemistry.24-00098](https://www.wos.org/doi/abs/10.5796/electrochemistry.24-00098).
- [50] Y. Y. Zhang et al. "Electrochemical noise analysis of the hot corrosion of TP347H stainless steel: Effect of temperature and coal ash thickness". In: *Electrochimica Acta* 525 (2025). ISSN: 0013-4686. DOI: [10.1016/j.electacta.2025.146105](https://doi.org/10.1016/j.electacta.2025.146105). URL: [10.1016/j.electacta.2025.146105](https://www.wos.org/doi/abs/10.1016/j.electacta.2025.146105).

- [51] L. F. Xie et al. "Understanding the galvanic corrosion behavior of the titanium TB5/CFRP couple in salt fog environment using electrochemical noise". In: *Electrochimica Acta* 555 (2026). ISSN: 0013-4686. DOI: [ARTN14818910.1016/j.electacta.2026.148189](https://doi.org/10.1016/j.electacta.2026.148189). URL: [%3CGo%20to%20ISI%3E://WOS:001688698500001](https://www.wos.org/doi/abs/10.1016/j.electacta.2026.148189).
- [52] C. S. Somayajula et al. "Hot Corrosion Monitoring in Boilers Using a Nonlinear Estimator and Electrochemical Noise-Based Corrosion Sensors". In: *Industrial & Engineering Chemistry Research* 63.1 (2023), pp. 394–409. ISSN: 0888-5885. DOI: [10.1021/acs.iecr.3c03542](https://doi.org/10.1021/acs.iecr.3c03542). URL: [%3CGo%20to%20ISI%3E://WOS:001140885300001](https://www.wos.org/doi/abs/10.1021/acs.iecr.3c03542).
- [53] Y. J. Tan. "Wire beam electrode: A new tool for studying localised corrosion and other heterogeneous electrochemical processes". In: *Corrosion Science* 41.2 (1999), pp. 229–247. ISSN: 0010-938x. URL: [%3CGo%20to%20ISI%3E://WOS:000078779000002](https://www.wos.org/doi/abs/10.1016/j.corsci.2013.11.012).
- [54] Z. J. Liu et al. "Study of corrosion behavior of carbon steel under seawater film using the wire beam electrode method". In: *Corrosion Science* 80 (2014), pp. 523–527. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2013.11.012](https://doi.org/10.1016/j.corsci.2013.11.012). URL: [%3CGo%20to%20ISI%3E://WOS:000330605200062](https://www.wos.org/doi/abs/10.1016/j.corsci.2013.11.012).
- [55] M. Y. Wang et al. "Visualizing and understanding corrosion evolution beneath a condensed droplet using the multi-electrode array". In: *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 684 (2024). ISSN: 0927-7757. DOI: [ARTN13325210.1016/j.colsurfa.2024.133252](https://doi.org/10.1016/j.colsurfa.2024.133252). URL: [%3CGo%20to%20ISI%3E://WOS:001166707000001](https://www.wos.org/doi/abs/10.1016/j.colsurfa.2024.133252).
- [56] M. Y. Wang et al. "Probing top-of-the-line corrosion using coupled multi-electrode array in conjunction with local electrochemical measurement". In: *Npj Materials Degradation* 7.1 (2023). DOI: [ARTN1610.1038/s41529-023-00332-x](https://doi.org/10.1038/s41529-023-00332-x). URL: [%3CGo%20to%20ISI%3E://WOS:000945396100001](https://www.wos.org/doi/abs/10.1038/s41529-023-00332-x).
- [57] X. Z. Ma et al. "Atmospheric corrosion of mild steel under thin oil film: Emulsification, dispersion, and simulation of saline microdroplets in the oil phase". In: *Corrosion Science* 252 (2025). ISSN: 0010-938x. DOI: [ARTN11294210.1016/j.corsci.2025.112942](https://doi.org/10.1016/j.corsci.2025.112942). URL: [%3CGo%20to%20ISI%3E://WOS:001476207300001](https://www.wos.org/doi/abs/10.1016/j.corsci.2025.112942).
- [58] C. S. Zhao et al. "Effect of UV Illumination on the Corrosion Behavior of Under a Thin NaCl Electrolyte Layer". In: *International Journal of Electrochemical Science* 17.11 (2022). ISSN: 1452-3981. DOI: [Artn22116410.20964/2022.11.80](https://doi.org/10.1016/j.ijechem.2022.11.80). URL: [%3CGo%20to%20ISI%3E://WOS:000968974300034](https://www.wos.org/doi/abs/10.1016/j.ijechem.2022.11.80).
- [59] C. Thee et al. "Atmospheric corrosion monitoring of a weathering steel under an electrolyte film in cyclic wet-dry condition". In: *Corrosion Science* 78 (2014), pp. 130–137. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2013.09.008](https://doi.org/10.1016/j.corsci.2013.09.008). URL: [%3CGo%20to%20ISI%3E://WOS:000329420900015](https://www.wos.org/doi/abs/10.1016/j.corsci.2013.09.008).
- [60] Y. Z. Shi, E. Tada, and A. Nishikata. "A Method for Determining the Corrosion Rate of a Metal under a Thin Electrolyte Film". In: *Journal of the Electrochemical Society* 162.4 (2015), pp. C135–C139. ISSN: 0013-4651. DOI: [10.1149/2.0101504jes](https://doi.org/10.1149/2.0101504jes). URL: [%3CGo%20to%20ISI%3E://WOS:000349827200050](https://www.wos.org/doi/abs/10.1149/2.0101504jes).

- [61] S. Y. Du et al. “High-throughput investigation and finite element modelling of atmospheric corrosion on carbon steel under varying droplets”. In: *Npj Materials Degradation* 9.1 (2025). DOI: [ARTN14510.1038/s41529-025-00695-3](#). URL: [%3CGo%20to%20ISI%3E://WOS:001618630300001](#).
- [62] L. Guerra-Camacho et al. “Influence of convection during droplet evaporation on corrosion product distribution in CFRP-AA2024 galvanic couple: Modeling and experimental approaches”. In: *Corrosion Science* 240 (2024). ISSN: 0010-938x. DOI: [ARTN11246210.1016/j.corsci.2024.112462](#). URL: [%3CGo%20to%20ISI%3E://WOS:001321801000001](#).
- [63] W. C. Li et al. “Numerical simulation and experimental verification on the kinetics of droplet corrosion of carbon steel”. In: *Electrochimica Acta* 514 (2025). ISSN: 0013-4686. DOI: [ARTN14560710.1016/j.electacta.2024.145607](#). URL: [%3CGo%20to%20ISI%3E://WOS:001399227500001](#).
- [64] W. C. Li et al. “Numerical simulation of carbon steel atmospheric corrosion under varying electrolyte-film thickness and corrosion product porosity”. In: *Npj Materials Degradation* 7.1 (2023). DOI: [ARTN310.1038/s41529-022-00316-3](#). URL: [%3CGo%20to%20ISI%3E://WOS:000912389800001](#).
- [65] F. Thébault et al. “Modeling bimetallic corrosion under thin electrolyte films”. In: *Corrosion Science* 53.1 (2011), pp. 201–207. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2010.09.010](#). URL: [%3CGo%20to%20ISI%3E://WOS:000284861700025](#).
- [66] H. Simillion et al. “Geometry influence on corrosion in dynamic thin film electrolytes”. In: *Electrochimica Acta* 209 (2016), pp. 149–158. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2016.04.072](#). URL: [%3CGo%20to%20ISI%3E://WOS:000379504600017](#).
- [67] M. S. Venkatraman, I. S. Cole, and B. Emmanuel. “Model for corrosion of metals covered with thin electrolyte layers: Pseudo-steady state diffusion of oxygen”. In: *Electrochimica Acta* 56.20 (2011), pp. 7171–7179. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2011.05.009](#). URL: [%3CGo%20to%20ISI%3E://WOS:000294881400041](#).
- [68] N. Van den Steen et al. “Predicting the effect of droplet geometry and size distribution on atmospheric corrosion”. In: *Corrosion Science* 202 (2022). ISSN: 0010-938x. DOI: [ARTN11030810.1016/j.corsci.2022.110308](#). URL: [%3CGo%20to%20ISI%3E://WOS:000793828200001](#).
- [69] U. R. Evans. “Oxygen distribution as a factor in the corrosion of metals”. In: *Industrial and Engineering Chemistry* 17 (1925), pp. 363–372. ISSN: 0019-7866. DOI: [DOI10.1021/ie50184a012](#). URL: [%3CGo%20to%20ISI%3E://WOS:000188442900132](#).
- [70] V. Soulié et al. “Salt-induced iron corrosion under evaporating sessile droplets of aqueous sodium chloride solutions”. In: *Materials and Corrosion-Werkstoffe Und Korrosion* 68.9 (2017), pp. 927–934. ISSN: 0947-5117. DOI: [10.1002/maco.201609319](#). URL: [%3CGo%20to%20ISI%3E://WOS:000408983300001](#).

- [71] V. Soulié et al. “The evaporation behavior of sessile droplets from aqueous saline solutions”. In: *Physical Chemistry Chemical Physics* 17.34 (2015), pp. 22296–22303. ISSN: 1463-9076. DOI: [10.1039/c5cp02444g](https://doi.org/10.1039/c5cp02444g). URL: [%3CGo%20to%20ISI%3E://WOS:000359971300060](https://www.wos.org/wos/000359971300060).
- [72] F. Lequien et al. “Corrosion influence on the evaporation of sessile droplet”. In: *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 546 (2018), pp. 59–66. ISSN: 0927-7757. DOI: [10.1016/j.colsurfa.2018.02.047](https://doi.org/10.1016/j.colsurfa.2018.02.047). URL: [%3CGo%20to%20ISI%3E://WOS:000429302300007](https://www.wos.org/wos/000429302300007).
- [73] T. Tsuru, K. I. Tamiya, and A. Nishikata. “Formation and growth of micro-droplets during the initial stage of atmospheric corrosion”. In: *Electrochimica Acta* 49.17-18 (2004), pp. 2709–2715. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2004.01.032](https://doi.org/10.1016/j.electacta.2004.01.032). URL: [%3CGo%20to%20ISI%3E://WOS:000221779900002](https://www.wos.org/wos/000221779900002).
- [74] J. Weissenrieder and C. Leygraf. “studies of filiform corrosion of iron”. In: *Journal of the Electrochemical Society* 151.3 (2004), B165–B171. ISSN: 0013-4651. DOI: [10.1149/1.1645263](https://doi.org/10.1149/1.1645263). URL: [%3CGo%20to%20ISI%3E://WOS:000188943800029](https://www.wos.org/wos/000188943800029).
- [75] B. E. Risteen, E. Schindelholz, and R. G. Kelly. “Marine Aerosol Drop Size Effects on the Corrosion Behavior of Low Carbon Steel and High Purity Iron”. In: *Journal of the Electrochemical Society* 161.14 (2014), pp. C580–C586. ISSN: 0013-4651. DOI: [10.1149/2.1171412jes](https://doi.org/10.1149/2.1171412jes). URL: [%3CGo%20to%20ISI%3E://WOS:000345975500055](https://www.wos.org/wos/000345975500055).
- [76] A. C. Scheinost and U. Schwertmann. “Color identification of iron oxides and hydroxysulfates: Use and limitations”. In: *Soil Science Society of America Journal* 63.5 (1999), pp. 1463–1471. ISSN: 0361-5995. URL: [%3CGo%20to%20ISI%3E://WOS:000083839800051](https://www.wos.org/wos/000083839800051).
- [77] N. Otsu. “Threshold Selection Method from Gray-Level Histograms”. In: *Ieee Transactions on Systems Man and Cybernetics* 9.1 (1979), pp. 62–66. ISSN: 0018-9472. DOI: [Doi10.1109/Tsmc.1979.4310076](https://doi.org/10.1109/Tsmc.1979.4310076). URL: [%3CGo%20to%20ISI%3E://WOS:A1979GE96000010](https://www.wos.org/wos/A1979GE96000010).
- [78] A. Kirillov et al. “Segment Anything”. In: *2023 Ieee/Cvf International Conference on Computer Vision, Iccv* (2023), pp. 3992–4003. ISSN: 1550-5499. DOI: [10.1109/Iccv51070.2023.00371](https://doi.org/10.1109/Iccv51070.2023.00371). URL: [%3CGo%20to%20ISI%3E://WOS:001159644304024](https://www.wos.org/wos/001159644304024).

2

DEVELOPING AN EXPERIMENTAL FRAMEWORK FOR MONITORING ATMOSPHERIC CORROSION KINETICS UNDER MULTI-DROPLET CONDITIONS

This chapter has been published as:

Zhang, K.; Rahimi, E.; van den Steen, N.; Terryn, H.; Mol, A.; Gonzalez-Garcia, Y. Monitoring atmospheric corrosion under multi-droplet conditions by electrical resistance sensor measurement. *Corros Sci* 2024, 236. DOI: ARTN 112271 10.1016/j.corsci.2024.112271.

Abstract

This paper presents a novel approach to investigate atmospheric corrosion kinetics of carbon steel under multi-droplet conditions. A homemade climate chamber has been developed to accurately control and monitor environmental conditions, including temperature (T) and relative humidity (RH), during exposure. Carbon steel corrosion kinetics are monitored with a custom-designed Electrical Resistance (ER) sensor pair. Savitzky-Golay (S-G) based filtering technique has been used for the corrosion signal processing. In parallel, top-view droplet temporal evolution has been recorded by microscopic imaging and analyzed for both droplet size distribution and the solid-liquid contact angle. The droplet size distribution can typically be described with a power-law form curve. The curve shows a decrease in height and a concurrent expansion in width with progressive drying. The introduction of NaCl into the electrolyte and surface roughness variations have also been identified to substantially influence the carbon steel corrosion rate. A strong correlation between the corrosion rate derived from the ER monitoring method and the RH can be observed. Additionally, this correlation can be further expanded to droplet-based electrolyte conditions. This study offers valuable insights into the development of mechanistic and kinetic prediction models for atmospheric corrosion.

2.1. INTRODUCTION

Atmospheric corrosion usually initiates and proceeds under a thin, continuous, or discontinuous electrolyte layer. In either scenario, the thin electrolyte film exhibits a low thickness at a scale of several tens of micrometers, facilitating the oxygen diffusion through the layer and enabling the occurrence of redox reactions at the metal-electrolyte interface[1]. This characteristic differs significantly from bulk-electrolyte corrosion, where the rate of oxygen diffusion primarily governs the kinetics of corrosion[2].

Under natural conditions, the formation of the thin electrolyte layer typically results from several processes. These include the deliquescence of pre-deposited salt, physical condensation initiated by the local temperature gradient between the sample surface and the surrounding environment, or direct deposition from environmental sources such as rain, snow, and fog. Conversely, in accelerated exposure conditions like salt spray tests, the thin electrolyte layer usually forms through direct deposition. In both cases, the thin electrolyte layer can appear to be quite discontinuous due to variations in relative humidity, temperature and wind speed[3].

The geometry, thickness and chemical nature of the thin electrolyte layer are essential in determining oxygen accessibility at the solid-liquid interface. When the thin electrolyte layer is discontinuous, or in extreme scenarios where the layer resembles a group of droplets, each droplet can be considered as an individual electrochemical cell, commonly referred to as an Evans droplet[4]. In the context of an Evans droplet, the metal located at the center of the droplet usually functions as an anode due to a higher local thickness in the thin electrolyte layer, resulting in lower oxygen availability at the solid-liquid interface. On the other hand, the metal situated under the peripheral part of the droplet usually functions as a cathode. The dynamic change in droplet geometry during the drying process could also induce internal flows, such as Marangoni flow and capillary flow. These flows can lead to a dispersion in salt concentration within the droplet when salt is introduced[5]. Furthermore, complex changes in droplet geometry, such as merging between adjacent droplets, could also occur in scenarios involving multiple dynamic droplets, leading to a change in droplet size distribution.

Previous in-situ investigations into atmospheric corrosion have rarely directly focused on the geometry of the thin electrolyte layer. These investigations typically involve a direct examination into the influence of various environmental parameters, such as relative humidity, temperature, rainfall precipitation, corrosive gases, and particulate contaminants, on the corrosion behavior of metals, such as corrosion rate and corrosion product formation. Electrochemical techniques such as electrochemical impedance spectroscopy (EIS)[3, 6, 7], galvanic couple sensors or atmospheric corrosion monitors (ACM)[8–13] and electrochemical noise (EN)[14], or non-electrochemical techniques such as electrical resistance (ER)[15–23] and quartz crystal microbalance (QCM)[24], have been utilized to study metal corrosion behavior in a controlled or monitored environment. Some other studies focusing on the thin electrolyte layer geometry usually assume a simplified condition, where the thin electrolyte layer is modelled as either a thin film that is homogeneous in thickness and composition[25–27], or as a single droplet[28–33]. By adopting

this assumption, metal corrosion behavior can be assessed with electrochemical methods such as EIS[26, 28, 29], potentiodynamic polarization[27, 29, 30], and open circuit potential measurements[25, 31–33]. However, as discussed previously, this thin electrolyte layer can also appear relatively discrete and would be more accurately described as a group of droplets. Besides, some investigations[34–36] have also stated that when relative humidity exceeds the threshold for NaCl to deliquesce, several monolayers of absorbed moisture could also exist where droplets are not visible. These monolayers will then introduce continuity among (part of) the droplets, acting as bridges to transfer ions between them. Some studies have also investigated the electrolyte geometry condition through modeling approaches[29, 37]. Jiang et al.[29] have assessed the effect of droplet size distribution under multiple-droplet conditions, analyzing it from the perspective of the total three-phase boundary (TPB) area. They argued that corrosion tends to be less significant under a single large droplet than ten smaller droplets when the total solid-liquid contact area is equivalent, at 1 cm² for both scenarios. Van den Steen et al.[37] have proposed a steady-state iron corrosion model for single droplet condition, and subsequently extended the analysis to include multi-droplet conditions, incorporating the distribution of droplets. Both works have revealed a considerable dependence of corrosion rate on droplet distribution, which consequently affects the corrosion process.

This calls for a method where both corrosion kinetics and droplet distribution can be studied simultaneously in an in-situ configuration. In situations where multiple droplets are involved, non-electrochemical methods are often preferred since they can capture corrosion information even when the thin electrolyte layer is (partially) discontinuous. For QCM, a calibration into deposited mass of salt, relative humidity with QCM response is always necessary to differentiate corrosion-induced mass gain from other factors, such as that resulting from moisture absorption. ER-based corrosion rate assessment is another widely employed method since its introduction in the 1950s[38]. Prosek et al.[20] have utilized this method to study the corrosion kinetics of both carbon steel and zinc during atmospheric corrosion tests, and later applied the same technique to assess the corrosion rate of bronze in an atmosphere where formic or acetic acid is also present[21]. Diler et al. have employed this method to investigate the degradation of both metallic and organic coatings on carbon steel during atmospheric corrosion tests[15]. Subsequently, they have examined the deviation between ER-based corrosion depth from the mean localized corrosion depth and emphasized that such deviation is directly related to the distribution and size of pits[16]. Regarding the electrical conductivity of the thin electrolyte layer itself, Rafehi[22] has studied the possible short circuit effect by this layer during electrical resistance measurements, and confirmed that such an effect is negligible even when dealing with a fluid possessing electrical conductivity equivalent to that of seawater. Nevertheless, there is still a research gap concerning the impact of the precise geometry of the thin electrolyte layer on corrosion, which calls for further investigations. Additionally, effective signal filtering techniques are also essential for accurately retrieving real-time corrosion depth and corrosion rate from the acquired electrical resistance signals. With these parameters determined, it is possible to further analyze the relationship between corrosion rate and various factors, such as droplet geometry and environmental parameters. This work proposes a setup where corrosive multi-droplet-

based electrolyte condition is created, and the corrosion rate is actively monitored using the electrical resistance method. The sample surface is simultaneously monitored with an optical microscope, from which both droplet distribution evolution and corrosion product formation can be visualized. Special attention has been paid to lowering the effect of thermal noises while keeping droplet boundaries recognizable under the optical microscope. A detailed discussion into corrosion signal and image processing has also been addressed.

2.2. MATERIALS AND METHODS

2.2.1. THE CLIMATE CHAMBER

While this work focuses on corrosion under multi-droplet-based electrolyte condition, ideally, after the initial formation of droplets on the metal surface, the droplets should be maintained as long as possible. This is crucial because corrosion takes time to initiate, progress and become optically observable under the microscope. This is achieved with a homemade climate chamber, the details of which will be provided in the result section. An environmental probe (HygroSmart HS3 probe, Michell Instruments, United Kingdom) is included for environmental conditions monitoring. To accurately record the initial conditions, all monitoring channels are started prior to introducing the corrosive environment. These include the monitoring of environmental conditions with the environmental probe, as discussed above, corrosion kinetics monitoring using the electrical resistance track pair, and droplet evolution monitoring with a camera and lens, which will be discussed subsequently.

2.2.2. THE ELECTRICAL RESISTANCE (ER) METHOD

The ER method monitors corrosion kinetics by actively measuring metal sample electrical resistance. As corrosion progresses, metal will gradually transform into oxides, which possess significantly lower electrical conductivity compared to the uncorroded metal. Consequently, the resistance of the sample will increase. In the case of atmospheric corrosion, localized corrosion usually first appears at discrete sites and gradually spreads over the sample. These local corrosion products can also deviate in size, shape, and depth. Considering the specific configuration of localized corrosion products, the electrical resistance (R) of a corroding sample can be described with Eq. 2.1, using the electrical resistivity of iron (ρ) without accounting for temperature variations.

$$R = \rho \int_0^L \frac{1}{A(l)} dl = \rho \int_0^L \frac{1}{\int_0^W h(l, w) dw} dl \quad (2.1)$$

Here, L (or l for specific location), W (or w), and H (or h) represent length, width, and height (or thickness) of the sample, respectively. The electrical currents flow in the length direction of the sample. L and W are constant throughout the test, while H decreases because of corrosion. Due to the complexity in Eq. 2.1, sample electrical resistance is simplified to Eq. 2.2 by assuming thickness loss is the same over the whole L - W plane.

$$R = \rho \frac{L}{H \cdot W} \quad (2.2)$$

Sample electrical resistance is continuously monitored with an EL3692 EtherCAT terminal, coupled with an EK1100 EtherCAT coupler for power supply (provided by Beckhoff Automation GmbH & Co. KG, Germany). Four-wire measurements are performed to eliminate contact resistance. To account for the effect of temperature, a reference track (R_{ref}), composed of the same material as the sensor track (R_{sens}) which is actively corroding, is also included and placed in the same environment as the sensor track. Additionally, it is covered with a moisture-blocking layer to prevent its exposure to the corrosive environment.

By continuously monitoring R_{ref} and R_{sens} , corrosion depth ($\Delta H(t)$) can be obtained with Eq. 2.3, where t_0 and t represents the initial state and the state at the time of measurement, and h_0 represents the initial thickness of the substrate.

$$\Delta H(t) = h_0 \left(1 - \frac{R_{ref}(t)}{R_{sens}(t)} / \frac{R_{ref}(t_0)}{R_{sens}(t_0)} \right) \quad (2.3)$$

As reported in the standards ASTM-G96 and ISO 11844-2[39, 40], insufficient temperature compensation remains a challenge for the electrical resistance method, even with the implementation of a reference track. Efforts have been made throughout previous studies to tackle this issue, mainly through two approaches: precise temperature control by keeping fluctuations within a narrow range[3, 21], or restricting corrosion analysis to period where both temperature and relative humidity are stable[20].

Track geometry also plays a crucial role in minimizing thermal noises. In general, a larger L , and smaller W and H is preferred to enhance the detection of corrosion effects by amplifying the change in R for the same corrosion depth. Such geometry can, however, potentially result in a delay in heat transfer between the track and the environment when there is a sudden change in environment conditions, due to an increased track heat capacity. Furthermore, the presence of moisture-blocking material on the reference track may further contribute to this delay in its thermal responses to environmental changes. To address this issue, efforts have been made to enhance the heat exchange between the reference track and the environment, with further details to be discussed in the result section.

Additionally, a proper filtering technique is applied on electrical resistance signals to extract the underlying trend. The details about electrical resistance signal filtering method are described in the Supplementary Information, under Section 2.S.1.

2.2.3. VARIABLE CORRELATION ANALYSIS

The Pearson correlation (Eq. 2.4), a widely accepted criterion for evaluating the linearity between two variables, is employed in this study to assess the linear correlation between the electrical resistance of reference and sensor track with the ambient temperature. Later, this criterion is also applied to assess the relationship between relative

humidity and corrosion rate.

$$r_{x,y} = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2} \sqrt{\sum_{i=1}^n (y_i - \bar{y})^2}} \quad (2.4)$$

Here, $r_{x,y}$ denotes Pearson correlation coefficient, x and y represent variables. Specifically, $\bar{x}$ and $\bar{y}$ represent the mean value of x and y .

2.2.4. MATERIALS AND ROUGHNESS QUANTIFICATION

The electrical resistance samples are prepared by cold-cutting from EN 10139 DC01-C590 carbon steel sheet measuring 25 μm thickness (Georg Martin GmbH, Germany). The elemental composition is as follows: 0.12 wt % C, 0.6 wt % Mn, 0.05 wt % P, 0.045 wt % S, with the remainder being Fe. Two different surface finishes have been applied to the electrical resistance track pairs to facilitate various aspects of the study. Initially, one group of the samples is finished with 3 μm colloidal silica polishing suspension. This finish is chosen to minimize background distortion and enhance the clarity of droplet distribution, aiding droplet image analysis. The second group is finished with 2000 grit silicon carbide (SiC) grinding paper. This choice is based on an analysis into the results obtained from the 3 μm samples, details of which will be addressed later in the result section. After surface preparation, all samples are rinsed with deionized water (18.2 M Ω cm) followed by isopropanol, and then dried with compressed air. All samples are stored in a drying box for 1 day before the exposure test. Sample surface roughness is analyzed with atomic force microscopy (AFM) and quantified by the roughness average (Ra) according to ISO 4287[41].

2.2.5. DROPLET EVOLUTION MONITORING

Droplets are pre-deposited onto the sample surface by spraying to avoid a fast evolution in droplet distribution configuration, which can add extra complexity to droplet image analysis. Following the initial deposition of droplets, moisture composed of the same electrolyte as the droplet is generated by a humidifier (Spring light wood diffuser, Asakuki, Japan) and then introduced to the chamber to increase the relative humidity. The droplet geometry is continuously monitored with a camera (Manta G319-B camera provided by Allied Vision Technologies GmbH, Germany, with sensor pixel size being 3.45 $\mu\text{m} \times 3.45 \mu\text{m}$) and lens (10X telecentric objective lens and 3X compact objective lens, both provided by Mitutoyo Corporation, Japan) system. The metal surface is illuminated with a ring light to enhance the visualization of the droplet boundaries[42]. To avoid any potential damage caused by moisture, both camera and lens are positioned outside the climate chamber.

2.2.6. DROPLET IMAGE ANALYSIS METHOD

A Python program has been developed for auto-recognition of droplets. As an illustration, Fig. 2.1a shows a snapshot of the image acquired with the camera and 10X lens on a sample finalized with 3 μm polishing suspension. As presented in the figure, each droplet is identifiable through a distinct bright contour (indicated with blue arrows) projected from the ring light for illumination. This study uses the bright contour for droplet

size analysis due to its proximity to the droplet perimeter.

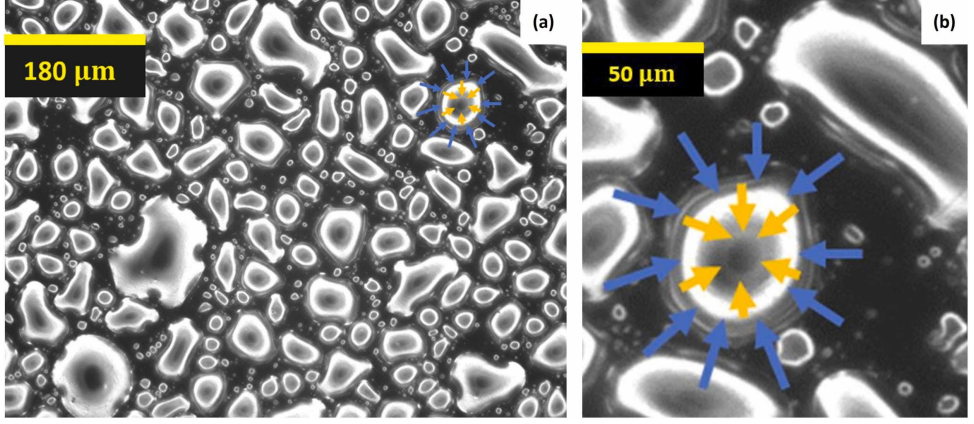


Figure 2.1: (a) An image illustrating the distribution of droplets on the sensor track surface of an electrical resistance track pair. The droplets were formed using deionized water deposited by spraying, and tracks' surface was finished using 3 μm polishing suspension. The image was acquired using a 10X lens. A specific droplet is highlighted with blue arrows indicating the contour formed with refraction, and yellow arrows indicating the contour formed by reflection, to facilitate further analysis into droplet's solid-liquid contact angle. (b) A high-resolution microscopic top-view image of the marked droplet.

As discussed in the introduction, droplet contact angle can have a great impact on corrosion kinetic by affecting oxygen concentration at the metal-liquid interface. The conventional methodology for droplet contact angle measurement typically involves observing a sessile droplet from side-view with a goniometer[43]. This approach is, however, less applicable when dealing with multiple dynamic droplets that are coexisting and undergoing drying on the same surface. Overlapping or obscuring of droplets in a side-view can occur, making geometrical analysis difficult. This study analyzes the contact angle directly from the top-view droplet distribution image (Fig. 2.1a), using a method proposed by Campbell and Christenson[43]. As illustrated in Fig. 2.1b, in addition to the bright contour highlighted with blue arrows, a smaller second contour with lower brightness, indicated by yellow arrows, can also be observed. Campbell and Christenson[43] suggested that the inner contour (yellow arrows in Fig. 2.1b) is formed with reflection from the droplet surface, while the outer contour (blue arrows in Fig. 2.1b) originates from refraction by the metal surface. Based on either contour, an estimation into contact angle is possible by ignoring the effect of gravity and assuming each droplet behaves like a lens. Contact angle approximations from reflection and refraction contours are achieved with Eq. 2.5 and Eq. 2.6, respectively. In this analysis, the droplet perimeter is distinguished from the bright contour to align with these two equations.

$$\theta \approx \frac{\Phi}{2n_m} \left(\frac{NA}{d^l} - \frac{1}{2Z_0} \right) \quad (2.5)$$

$$\theta \approx \frac{\Phi}{2n_m} \left(\frac{n}{n_m} - 1 \right)^{-1} \left(\frac{NA}{d^r} + \frac{1}{2Z_0} \right) \quad (2.6)$$

Here Φ represents droplet diameter, n_m stands for air refractive index ($n_m=1.00$ for air), n stands for the droplet refractive index ($n=1.31$ for water and $n=1.34$ for 1 M NaCl solution), NA for numerical aperture (10X lens: NA=0.21, 3X lens: NA=0.07), d_l for reflection contour diameter, d_r for refraction contour diameter, Z_0 (10X lens: 32.2 mm, 3X lens: 20.1 mm) for a measurable lens property in a unit of length that can be measured with experiments. When salt, such as NaCl, is introduced, the chloride concentration can experience a substantial increase with droplets drying. By combining the information on both droplet diameter and contact angle, it becomes possible to estimate the real-time salt concentration without the need for direct measurement (details can be found in Supplementary Information under [Section 2.S.5](#)) as such measurement could potentially distort droplet geometry.

2.3. RESULTS AND DISCUSSION

2.3.1. DESIGN OF THE EXPERIMENTAL SETUP

The experiments are carried out in a homemade climate chamber ([Fig. 2.2](#)) with a transparent cover made of acrylic plastic. [Fig. 2.3](#) illustrates a schematic drawing of the geometrical configuration and dimension of electrical resistance track pairs (the relative positions of both tracks are presented in [Fig. 2.3a](#)), with special emphasis being placed on reducing thermal noises in the system.

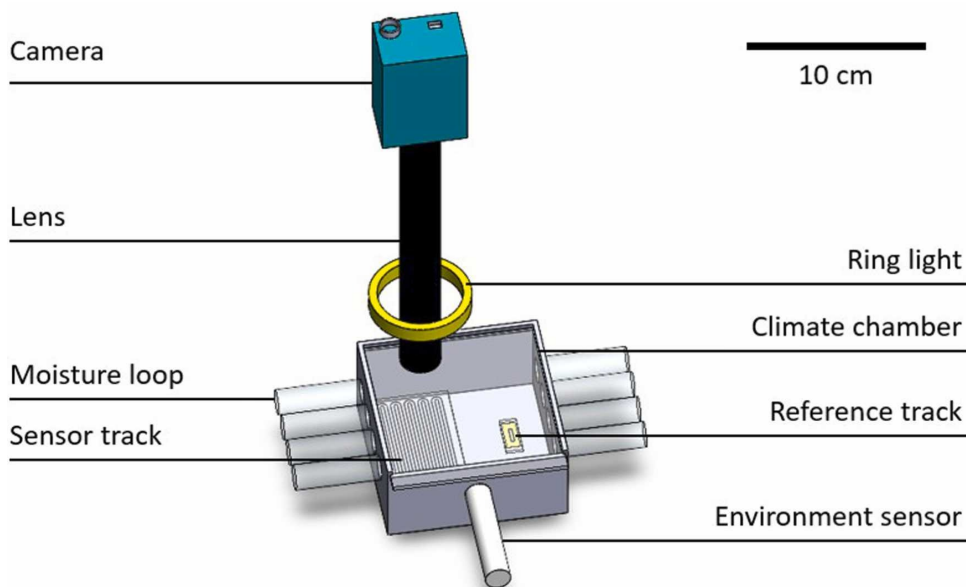


Figure 2.2: A schematic drawing of the experimental setup.

The sensor track, which is actively corroding, has a snake-like configuration to amplify the electrical resistance increase caused by the corrosion process. The track has a sig-

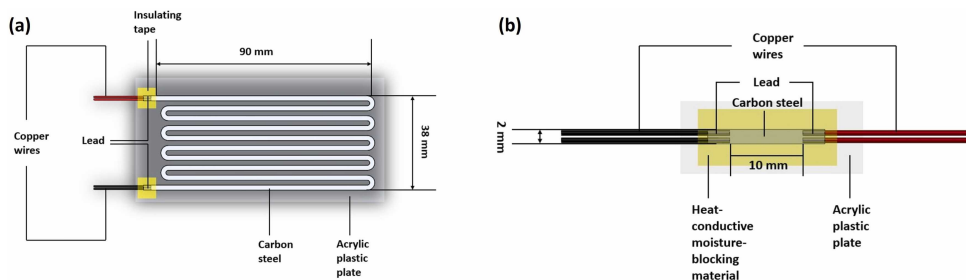


Figure 2.3: A schematic drawing showing the geometry and dimension of the electrical resistance track pair, including (a) sensor track, and (b) reference track.

nificantly large length (900 mm in total) compared to its width (approx. 2 mm) and out-of-box thickness ($25 \mu\text{m}$). It is attached to an acrylic plastic plate ($50 \text{ mm} \times 100 \text{ mm} \times 2 \text{ mm}$) as mechanical base support. After cutting and surface preparation, the sensor track has an initial resistance between 2.5Ω to 4.0Ω at room temperature. The variation mainly originates from the difference in width between samples during cutting and the initial thickness after surface preparation. Width and initial thickness are always fixed along the length of each sample. Furthermore, initial thickness is calibrated by knowing the initial sensor track electrical resistance and sensor track width, where the former is obtained from electrical resistance monitoring and the latter is directly available via droplet image monitoring. The calibration is later confirmed with scanning electron microscope (SEM). Eq. 2.7 experimentally correlates these three terms together by examining 10 samples, where $R_{sens,0}$, W and h_0 denote sensor track initial electrical resistance, sensor track width and sensor track initial thickness after surface preparation.

$$h_0[\mu\text{m}] = \frac{87}{R_{sens,0}[\Omega] \cdot W[\text{mm}]} \quad (2.7)$$

This work employs pyrolytic graphite sheet (Panasonic Holdings Corporation, Japan. Heat conductivity: $1600 \text{ W/m}\cdot\text{K}$) as moisture-blocking material applied on the reference track. Theoretically, temperature compensation is valid as long as the reference track is composed of the same material as the sensor track. This work utilizes a reference track that is significantly smaller than the sensor track, aiming to reduce its heat capacity for a faster response to temperature changes, as well as to minimize temperature variations across the track. In this way, the delay in heat transfer on reference track introduced by the moisture-blocking layer can be partially compensated.

2.3.2. SURFACE ROUGHNESS MEASUREMENT

Figs. 2.4a and 2.4b show representative AFM topography maps and height distribution plots of the sample after different surface preparation. The R_a values are obtained from the analysis of the AFM images. For the case of mirror-like finishing ($3 \mu\text{m}$ polishing suspension), surface has an R_a value of $5.04 \pm 0.51 \text{ nm}$. For 2000 grit SiC paper, the surface has an R_a value of $47.32 \pm 3.22 \text{ nm}$.

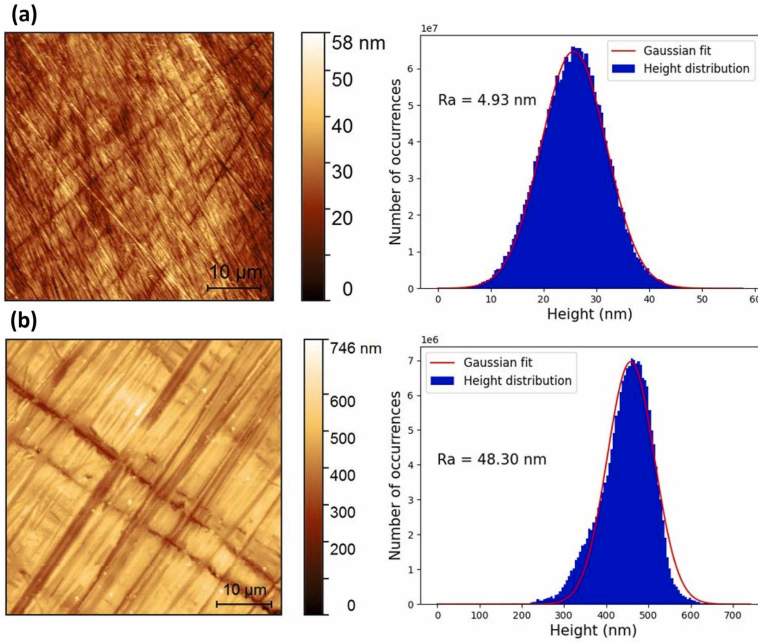


Figure 2.4: AFM topography maps and height distribution analysis of the sensor track surface after preparation with (a) 3 μm polishing suspension and, (b) 2000 grit SiC grinding paper.

2.3.3. ER SIGNAL ACQUISITION AND ANALYSIS

To facilitate droplet image analysis by minimizing background distortion and enhancing the clarity of droplet distribution, measurements are performed on the mirror-like sample (after 3 μm polishing) using deionized water as the electrolyte to constitute the droplets. Fig. 2.5 summarizes the parameters monitored during the experiments: temperature, relative humidity, electrical resistance of both reference and sensor tracks, and corresponding corrosion depth. From Fig. 2.5a, it is observed that relative humidity mostly remains above 70 % within the chamber except at the very beginning of the test, while fluctuation in temperature is kept within $\pm 2^\circ\text{C}$.

Despite the implementation of the reference track and the efforts made to constrain temperature fluctuations within the climate chamber, the adequacy of temperature compensation remains to be validated. Eq. 2.8 shows the relationship between the electrical resistance and temperature of a metal sample[44], ignoring any change caused by corrosion.

$$R(T) = R(T_0) \cdot (1 + \alpha(T - T_0)) = R(T_0) \cdot \alpha T + (1 - \alpha T) \cdot R(T_0) \quad (2.8)$$

Here T and T_0 denote the measured and reference temperatures, α represents the temperature coefficient of electrical resistance and R refers to sample electrical resistance at a specific temperature. In case where temperature variations are small, α can be treated as a constant. Consequently, sample electrical resistance theoretically exhibits a linear correlation with sample temperature in the absence of corrosion. If temperature compensation is effective, R_{ref} and ambient temperature should be almost linearly

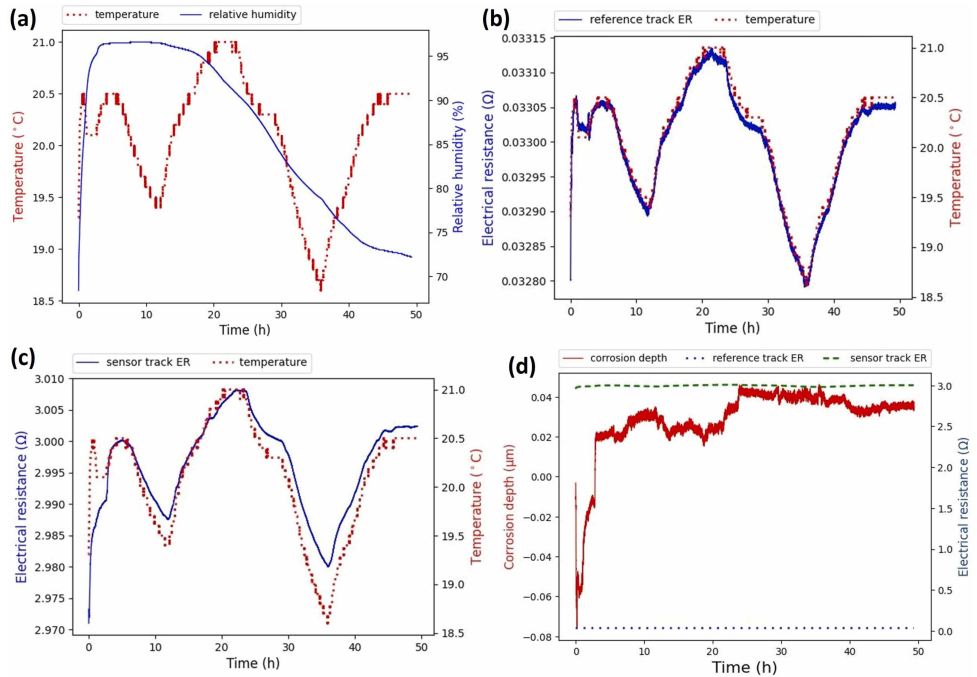


Figure 2.5: Environment parameters and electrical resistance signal monitoring were conducted during the exposure of an electrical resistance track pair to droplets of deionized water deposited on the surface. The tracks' surface was finished with 3 μm polishing suspension. The details are as follows: (a) ambient temperature and relative humidity within the chamber (b) ambient temperature and reference track electrical resistance (R_{ref}) (c) ambient temperature and sensor track electrical resistance (R_{sens}) (d) electrical resistance of both reference and sensor track, along with the corrosion depth calculated from electrical resistance.

correlated. Fig. 2.5b visually shows that R_{ref} and ambient temperature have a very high level of correlation. The Pearson correlation analysis conducted on R_{ref} and temperature reveals a coefficient of approximately 0.995. This high coefficient indicates a very strong linear correlation between R_{ref} with ambient temperature, suggesting the reference track can effectively represent the temperature change in the surrounding environment.

The effect of temperature on sensor track electrical resistance is assessed by analyzing R_{sens} and ambient temperature. Fig. 2.5c shows a comparison between these two variables. The two curves share a very similar trend over time, and the Pearson correlation analysis yields a coefficient of approximately 0.919. This suggests that the variations in R_{sens} are predominantly due to temperature fluctuations, indicating minimal or potentially absent corrosion on the sensor track. This analysis also excludes the direct effect of relative humidity on R_{sens} , as no significant correlation can be observed between the trend of these two curves.

The corrosion depth obtained with Eq. 2.3 is presented in Fig. 2.5d together with the electrical resistance signal. The initial thickness is calculated to be approximately 16 μm , following Eq. 2.7. The ratio between the sensor track and the reference track is also included in the Supplementary Information under Section 2.S.6, based on which corrosion depth can be obtained directly. It must also be noticed that the corrosion depth calculated from the electrical resistance signal does not fully represent the depth of localized attack; rather, it should be considered as an averaged corrosion depth over the full sensor track.

Previous discussions have indicated that the variations in electrical resistance of the sensor track are predominantly influenced by temperature fluctuations. However, for effective temperature compensation, it is crucial to achieve a high corrosion signal to thermal noise ratio (SNR), as compensation methods can never be perfect; otherwise, residual thermal noise can significantly affect the accuracy of the corrosion signal. A high SNR indicates a clearer and more reliable corrosion measurement, because it means the desired corrosion signal is much stronger than the unwanted thermal noise, making it easier to distinguish the true corrosion signal from the background noises. This partially explains the behavior of the corrosion depth curve (depicted with the red solid curve, Fig. 2.5d) which is directly derived from the original electrical resistance signal. Theoretically, it is unrealistic for the corrosion depth curve to exhibit negative values if both reference and sensor tracks consistently maintain identical temperatures. However, in practice where corrosion is very mild, as in the current context, the corrosion depth curve is more accurately interpreted as an aggregation of thermal noises, which do not accurately represent actual corrosion depths. The observed fluctuations are within a range of $\pm 0.1 \mu\text{m}$ over an exposure duration of around 50 h, further indicating that the corrosion is indeed rather mild throughout the test. In subsequent experiments the corrosive conditions are intentionally intensified by adding salt to the electrolyte and increasing the roughness of the sample surface. This approach is taken to validate the method under conditions where the increase in the corrosion depth curve is predominantly driven by corrosion effects,

rather than by temperature fluctuations.

2.3.4. DROPLET MONITORING AND IMAGE ANALYSIS

The camera system continuously monitors electrolyte droplets during the electrical resistance signal acquisition. By monitoring the droplet's evolution in real time, it is possible to quantify the droplet size and distribution as a function of time and correlate it with the electrical resistance signal evolution.

Fig. 2.6 illustrates the processing of the image of deionized water droplets sprayed on a carbon steel sample presented before (Fig. 2.1a). Figs. 2.6a to 2.6c display the results obtained at each analysis step: (a) thresholding to isolate the droplets (b) contour filling of the identified droplets and (c) labelling of individual droplets. Notice that Figs. 2.6b and 2.6c demonstrate the successful segmentation of the droplet pattern from the background, as the majority of the droplets have been accurately identified and filled.

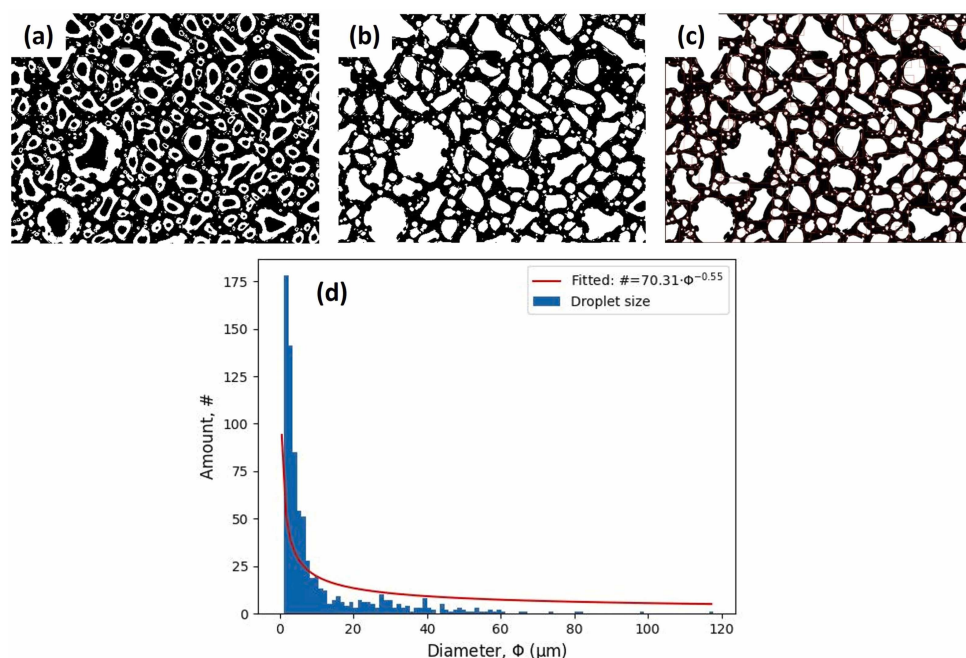


Figure 2.6: Droplet geometry and distribution analysis were conducted on Fig. 2.1a. The results after each step are as follows: (a) thresholding to isolate the droplets (b) contour filling of the identified droplets (c) labelling of individual droplets (d) histogram of droplet diameter distribution.

Following this, a droplet size histogram is also obtained, as illustrated in Fig. 2.6d. The droplet amount generally decreases with the droplet size increasing. Furthermore, the distribution can be fitted to a power law form (red curve), which partially agrees with the finding by Le Fevre and Rose[45], as described with Eq. 2.9, regarding the distribution of droplets during dropwise condensation in the absence of non-condensing gases. Here, Φ , Φ , and N represent the droplet amount at a specific diameter, the droplet diameter,

and the total amount of droplets, respectively. A is a constant related to the maximum droplet diameter.

$$\frac{\#(\Phi)}{N} = A \cdot \Phi^{-8/3} \quad (2.9)$$

Contact angle analysis was performed using the aforementioned methodology. The parameters for contact angle estimation, based on Eq. 2.5, 2.6 using droplet image Fig. 2.1a, are summarized in Tab. 2.1. The contact angle value from reflection contour (θ^l) is approximately 27.6° , whereas the contact angle obtained from the refraction contour (θ^r) is around 26.4° . In general, with an analysis of the droplets where either reflection or refraction contours can be identified, the droplet contact angle within this image is approximately between 21.2° to 28.0° .

Table 2.1: Parameters for contact angle analysis on the arrow-highlighted droplet in Fig. 2.1a. The image was acquired using a 10X lens.

Φ	d^l	d^r	n_m	n	NA	Z_0
$69\mu\text{m}$	$15\mu\text{m}$	$51\mu\text{m}$	1.00	1.31	0.21	32.2 mm

Note that the increase of surface roughness, as mentioned in the last subsection, may distort the background, potentially reducing the clarity of droplet distribution. Besides, surface roughness can increase the hydrophilicity of the metal surface, leading to a transition in droplet geometry toward a more film-like configuration. As corrosion progresses, the formation of corrosion products can further distort droplet geometry, as illustrated in Fig. 2.10a to c. To address this issue, images that cannot be efficiently analyzed by the auto-recognition program are processed using a combined approach: First, auto-recognition is performed with Python. Subsequently, areas that are not detected or misdetected are manually labelled using Label Studio, an open-source platform for image labelling. The details are described in the Supplementary Information, under Section 2.S.3.

2.3.5. VALIDATION EXPERIMENTS: CORROSION OF CARBON STEEL IN EXPOSURE TO 1 M NaCl SOLUTION

Previous investigations have reported that an increase in NaCl concentration can influence the corrosion rate of carbon steel by [46] (i) participating in the dissolution of the natural oxide layer present on the metal surface (ii) enhancing electrolyte conductivity, which enhances ion migration and (iii) decreasing oxygen solubility to limit the oxygen reduction reaction. Additionally, an increase in surface roughness can also intensify the corrosion process by (i) increasing the actual solid-liquid interface area and (ii) providing more microstructural heterogeneity (e.g. inclusions, precipitates) for corrosion to initiate.

To achieve a sufficiently high corrosion rate, 1 M NaCl solution was sprayed to a carbon steel sample characterized by high roughness (finished by grinding with 2000 grit sanding paper). The initial thickness of the sample is approximately $20\mu\text{m}$ following the calibration procedure previously described.

Fig. 2.7a shows the evolution of temperature and relative humidity within the climate chamber. The relative humidity value stays above the NaCl deliquescence point at room temperature[47, 48] for the first 12.5 h since the start of the experiment, while the fluctuation in temperature is constrained within 2 °C. Fig. 2.7b and c shows a comparison between the ambient temperature and the electrical resistance of the reference track and the sensor track, respectively. To investigate the effect of corrosion on sensor track's electrical resistance, Pearson correlation analysis is performed between the electrical resistance of both tracks with the ambient temperature. The Pearson correlation coefficient value between temperature and R_{ref} is approximately 0.904, indicating the change in reference track electrical resistance can efficiently represent the change in ambient temperature over the period of exposure. Meanwhile, the analysis conducted on temperature and R_{sens} reveals a Pearson correlation coefficient value of around 0.405, indicating the impact of temperature on electrical resistance change has decreased significantly due to an enhanced contribution from corrosion effects.

Specifically, Fig. 2.7e illustrates the evolution of the Pearson correlation between the electrical resistance of both the sensor and reference tracks with ambient temperature, which reflects the integrated effect of temperature on resistance from start of the test to each subsequent point of analysis. Initially, both tracks exhibit a high degree of correlation with temperature, as highlighted in the detailed plot-in-plot for the first hour. Notably, at the very beginning of the test, fluctuations can be observed due to an abrupt temperature change, as a result of moisture introduction. As the experiment progresses beyond the first hour, a significant divergence between the two curves appears. Specifically, the correlation coefficient for the reference track maintains a relatively stable and positive value, suggesting a consistent and direct relationship with temperature throughout the test. In contrast, the correlation coefficient for the sensor track decreases sharply after the first hour and gradually becomes negative, suggesting additional factors other than temperature. In this case, the corrosion effects start to influence the electrical resistance of the sensor track. With time, the correlation curves of the two tracks diverge increasingly until near the end of the test, the divergence starts to decrease again. This indicates the effect of temperature on the sensor track's electrical resistance has increased again, probably due to a decrease in the corrosion rate. As discussed previously, to ensure that the calculated corrosion depth accurately represents the actual value, the SNR must be relatively high. This means that the influence of corrosion on the increase in sensor track electrical resistance should exceed that caused by temperature fluctuations. In the subsequent analysis, this initial 1-hour period will be designated as the 'stabilization period'. During this period, changes in the calculated corrosion depth are likely predominantly influenced by temperature fluctuations.

Fig. 2.7d shows the temporal electrical resistance evolution under the specified experimental conditions, along with the corresponding corrosion depth. The ratio between sensor track electrical resistance to that of reference track is found in the Supplementary Information under Section 2.S.6. In general, the corrosion depth, as defined in Eq. 2.2, progressively increases with time and exceeds 1 μm after 25 h of exposure under dynamic droplet conditions. Specifically, the zoomed-in view of the plot at the start of the test shows some initial fluctuations in corrosion depth. These fluctuations primarily

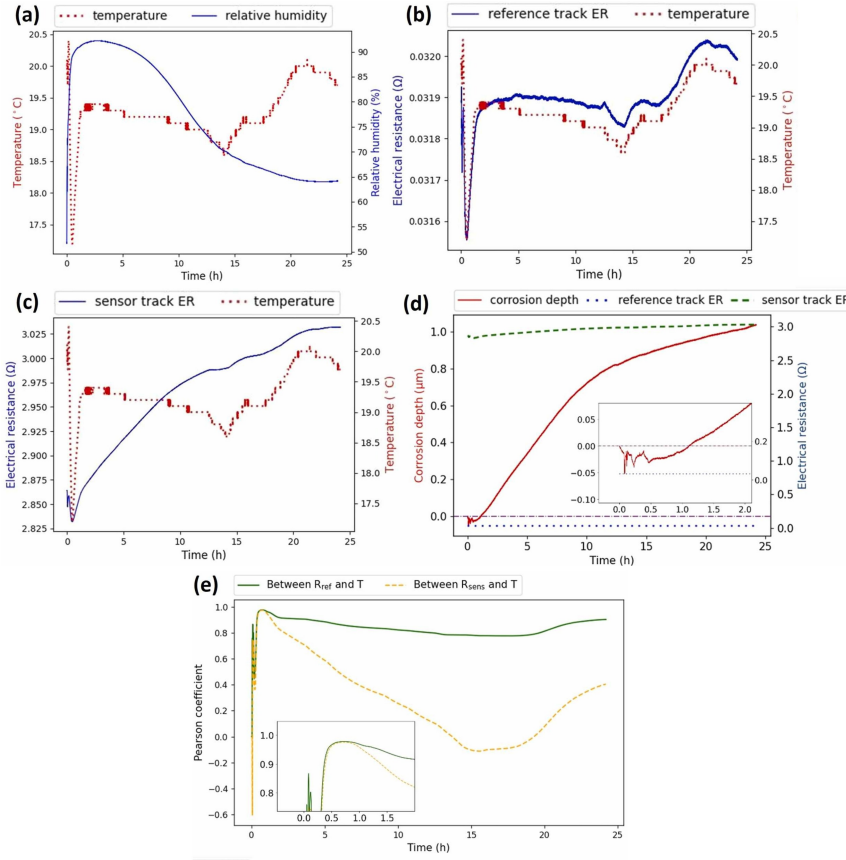


Figure 2.7: Environment parameters and electrical resistance signal monitoring were conducted during the exposure of an electrical resistance track pair to droplets of 1 M NaCl solution deposited on the surface. The tracks' surface was finished with 2000 grit SiC grinding paper. The details are as follows: (a) ambient temperature and relative humidity within the chamber (b) ambient temperature and reference track electrical resistance (R_{ref}) (c) ambient temperature and sensor track electrical resistance (R_{sens}). (d) electrical resistance of both the reference and sensor tracks, along with the corrosion depth calculated from the electrical resistance, including a zoomed-in view at the beginning of the test (e) Pearson correlation analysis results between the electrical resistance of the sensor and reference tracks with ambient temperature. The calculation is performed using data from the start to each time step of analysis. The results at the beginning of the test are shown in a zoomed-in view on the plot.

occur within the first hour and align with the analysis in Fig. 2.7e.

The corrosion rate can be obtained by analyzing the first derivative of the corrosion depth evolution over time. Fig. 2.8a and b illustrate a comparison before and after filtering the signal. Fig. 2.8a shows a high noise level, particularly pronounced at the beginning of the test. Generally, the noise observed in Fig. 2.8a is mostly internally generated by the data acquisition device throughout the test. Additionally, during the initial stage of the experiment, external noise from inadequate temperature compensation is

also playing an important role. This device-originated noise is less significant in either corrosion depth or original electrical resistance signals but becomes amplified after calculating the first derivative (i.e. corrosion rate). A detailed explanation is included in the Supplementary Information under [Section 2.S.2](#). By adopting proper filtering techniques, this device-originated noise can be removed, revealing the true trend of the corrosion rate.

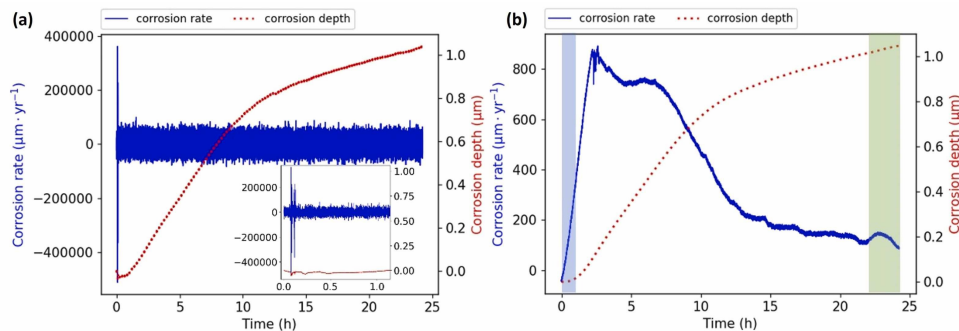


Figure 2.8: Corrosion rate corresponding to the corrosion depth in [Fig. 2.7d](#) (a) Corrosion rate without filtering, including a zoomed-in view at the beginning of the test (b) Corrosion rate after S-G filtering with $M=8000$ and $N=2$. The light blue zone at the beginning of the test corresponds to the ‘stabilization period’, during which variations in the sensor track’s electrical resistance are dominated by temperature fluctuations. Consequently, this zone might offer less reliable insights into the real corrosion rate. Details are presented in the analysis in [Fig. 2.7e](#). The light green zone by the end of the test might be affected by edge effects introduced by the filtering process and might not accurately represent the real corrosion rate of the sensor track. For details, please refer to [Section 2.S.1](#) of Supplementary Information.

The design of S-G filter is described in the Supplementary Information under [Section 2.S.1](#) and [2.S.2](#). Corrosion rate ranges from approx. $900 \mu\text{m} \cdot \text{yr}^{-1}$ ($7000 \text{ g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$) at earlier stage of exposure to approx. $100 \mu\text{m} \cdot \text{yr}^{-1}$ ($780 \text{ g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$) at longer times. Complementary weight loss tests, as described in the Supplementary Information under [Section 2.S.4](#), are also performed under a similar experimental condition to corroborate the corrosion depth and rate values found in the electrical resistance studies. The values obtained from electrical resistance measurement and weight loss are relatively similar, being in the same order of magnitude. Furthermore, the corrosion rate values are consistent with the range reported for carbon steel under coastal atmospheric conditions[46], which is also discussed in detail under [Section 2.S.4](#) of the Supplementary Information.

At the beginning of the test, the rate first increases to a local maximum, then gradually reduces to a non-zero value and remains stable until the end of the test. This non-zero stable stage suggests that by the end of the test, though relative humidity has dropped below the NaCl deliquescence point at room temperature, the surface is still partially wet. This phenomenon can likely be elucidated by the hysteresis effect associated with the deliquescence and efflorescence of NaCl. Throughout the test, the relative humidity consistently remains higher than the NaCl efflorescence point at room temperature[47, 48]. Consequently, the salt particles do not undergo full crystallization from the solution; instead, they exist in a moist state that lies between dissolution and crystallization.

The correlation between relative humidity and corrosion rate is presented in Fig. 2.9, where, in general, it is observed that the two parameters exhibit a strong correlation in their trends. This agrees with the previous investigations by Vernon[49], Peck[50] and Klinger[51], in which a strong positive dependency of corrosion rate on relative humidity was found. This correlation is particularly pronounced at the later exposure stage, where the corrosion rate exhibits an enhanced sensitivity to the relative humidity. This observation is also theoretically coherent, as the droplet electrolyte has mostly dried out at this stage, leaving behind only a thin moisture layer sustained by the presence of NaCl. The characteristics of this moisture layer, which directly impact the corrosion rate, are modulated by the ambient relative humidity near the sample surface. Nevertheless, when analyzing the results more closely, small deviations can still be found between the two terms. This phenomenon is observed, for example, at points (II) and (III) as highlighted in Fig. 2.9. The corrosion rate at the latter point substantially surpasses that at the former, despite their similarity in relative humidity. This discrepancy can be explained by the analysis into the sample surface images.

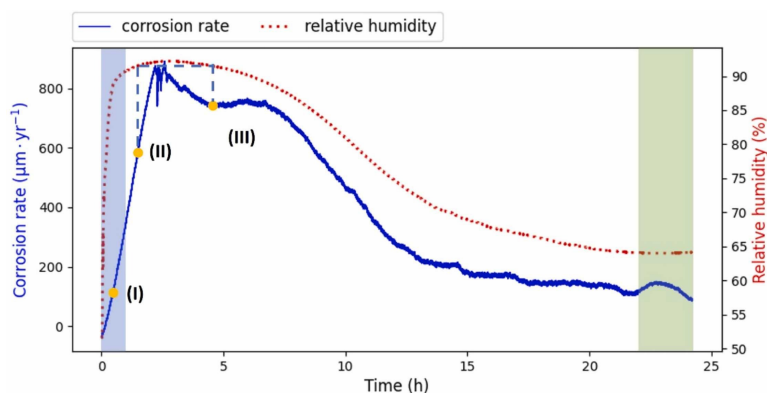


Figure 2.9: A direct comparison between corrosion rate and relative humidity was conducted based on the environment parameters and electrical resistance signal monitoring results as specified in Fig. 2.7, Fig. 2.8. The light blue zone at the beginning of the test and the light green zone by the end of the test might offer less reliable insights into the real corrosion rate. Detailed explanations are presented in Fig. 2.8.

Fig. 2.10a to c illustrate droplet distribution image and corresponding size histogram at (a) 0.5 h from the beginning of the test, by which time droplet distribution has been stabilized, (b) after approx. 1.5 h from the beginning of the test, and (c) after approx. 4.5 h from the beginning of the test.

Comparing the images in Fig. 2.10a and b, it is evident that relatively soon after the stabilization of droplets, corrosion attacks under some of the droplets become visible. As suggested by Risteen et al.[36], the probability of corrosion initiation under a known droplet is strongly correlated with both droplet size and surface roughness. This is partially consistent with the findings from this test, as it is observed that corrosion predominantly occurs under droplets with a diameter higher than 100 μm . However, further validation is needed to fully understand the quantitative relationship between droplet size and cor-

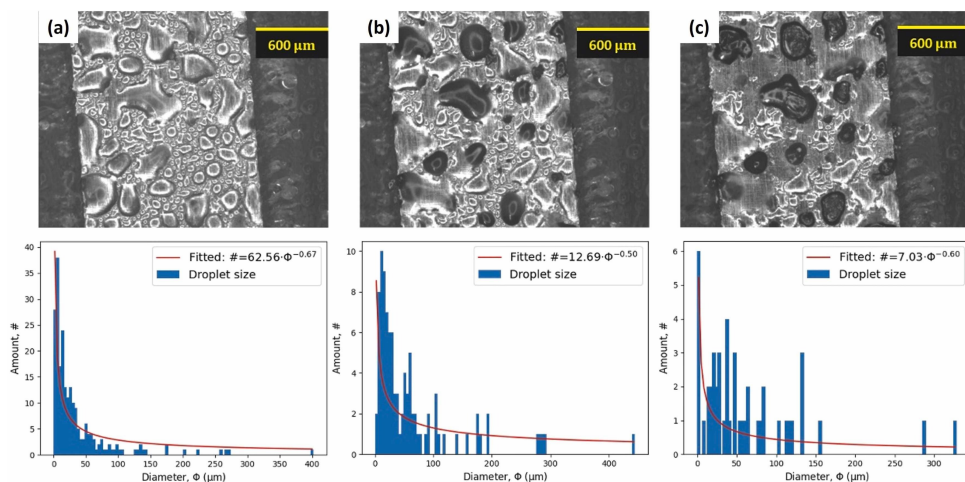


Figure 2.10: Analysis of the droplet images at the highlighted times in Fig. 2.9. Droplet image and droplet distribution at (a) 0.5 h (b) 1.5 h (c) 4.5 h of the experiment are presented. Prior to the analysis, images are first randomly cropped into 1000 pixels $\times$ 750 pixels (original image size: 2064 pixels $\times$ 1544 pixels), with coordinates for cropping being the same for all images.

rosion product formation. Comparing the images in Fig. 2.10b and c, which correspond to the periods indicated by points (II) and (III) in Fig. 2.9 where the corrosion rate is sufficiently high, the number of corrosion sites however remains almost unchanged. This suggests that corrosion propagation is primarily perpendicular to the surface, progressing deeper into the bulk of the sample rather than expanding along the surface. This observation indicates that Evans-type corrosion is dominating the process.

In terms of the analysis into the droplet size distribution in Fig. 2.10, the data in (a) can be best fit with a power law form, while a mismatch between the droplet size distribution (blue bars) and the fitted curve (red curve) becomes apparent after longer times, as seen in (b) and (c). This discrepancy is likely due to the impact of metal dissolution and the subsequent formation of corrosion products, which alter the geometry of the droplets. Moreover, from time (a) to (b), the droplet distribution curve exhibits a decrease in height and an expansion in width, indicating concurrent droplet merging and drying processes. In comparison, the curve decreases in both height and width from (b) to (c), suggesting that droplet drying is the dominant process during this period.

Following the analysis explained in the experimental section, further analysis of the droplet images can be carried out to estimate the contact angle of the different droplets. The parameters utilized are summarized in Tab. 2.2. By randomly selecting and analyzing 20 droplets from each of Fig. 2.10a to c, droplet contact angle values are calculated to be $8.3 \pm 1.1^\circ$, $5.9 \pm 1.9^\circ$ and $4.7 \pm 2.0^\circ$, respectively. The contact angle tends to decrease with time, which agrees with the previous investigations[5, 52, 53]. The analysis of the droplet contact angle enables the access of three-dimensional data from two-dimensional images, which, for example, can provide an approximation of the droplet volume values.

Based on droplet volume, it is feasible to estimate the real-time electrolyte concentration, which is expected to increase due to evaporation (Detailed discussion can be found under [Section 2.S.5](#) in the Supplementary Information). Therefore, the contact angle analysis provides a more comprehensive and complete description of droplet geometry during the monitoring of the corrosion rate.

Table 2.2: Parameters for contact angle analysis on 1 M NaCl droplets in images captured using a 3X lens.

n_m	n	NA	Z_0
1.00	1.34	0.07	20.1 mm

In summary, this novel experimental approach enables the correlation of real-time atmospheric corrosion rate with both prevailing environmental conditions and electrolyte evolution. Performing experiments under multiple-droplet conditions closely mimics common outdoor exposure and service conditions, providing a more realistic representation compared to previous studies. The primary limitation of this method is the need for environmental corrosivity to exceed a certain threshold to induce detectable corrosion. Theoretically, corrosion detection is feasible even in relatively mild corrosive environments, provided the electrolyte remains on the sample surface for a sufficient duration. However, in practice, achieving this can be quite challenging due to the dynamic behavior of droplets, making it difficult to maintain a stable multi-droplet scenario. Enhancing the sensitivity of the method may be achieved through an improved designing into the geometry of the electrical resistance tracks. Furthermore, considering the inherent limitation of the electrical resistance method, which may cause deviations from results obtained through weight loss experiments, it is feasible to offset this discrepancy by properly calibrating these two methods with additional complementary experiments. This calibration involves accounting for the distribution of corrosion products, which significantly influences the accuracy and comparability of the measurements. Consequently, this approach holds significant promise for advancing the understanding of atmospheric corrosion. This enhanced understanding can, in turn, contribute to the development of more accurate mechanistic and kinetic models for atmospheric corrosion prediction, thereby making a valuable contribution to the field.

2.4. CONCLUSIONS

This work describes the design, operation, and data processing of a novel experimental setup to study the real-time corrosion rate of metals exposed under controlled and monitored multi-droplet conditions. In this work, the atmospheric corrosion of carbon steel is studied. The following can be concluded:

- The novel experimental setup allowed simultaneous real-time monitoring of the corrosion rate and the evolution of the electrolyte geometry. The environmental conditions, including relative humidity and temperature, have also been continuously monitored.
- Real-time corrosion rate monitoring is accomplished using the electrical resistance (ER) method. In this work, a careful design of the ER track geometry and

a refined signal filtering protocol were introduced to minimize the effect of thermal noise for accurately extracting the corrosion rate signal from the background noises.

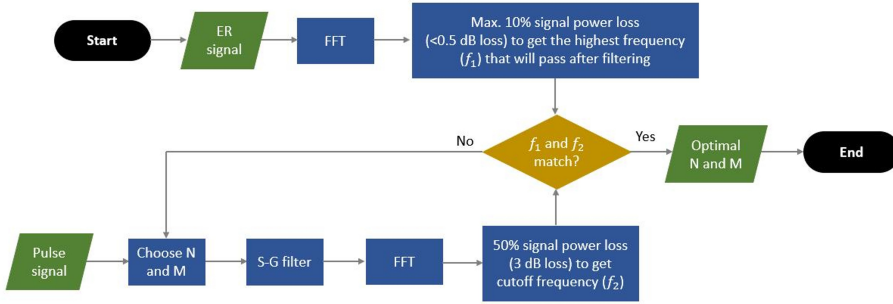
- Droplet size distribution analysis was performed on the droplet evolution images. Additionally, contact angle information was estimated from these images, which could be further used to approximate chloride concentration.
- The corrosion rate of carbon steel under a multi-droplet electrolyte (1 M NaCl) was studied as a model system. The rate values obtained from the ER system correlated well with previously reported kinetic data and additional experimental validation, confirming the reliability of this approach.
- A strong correlation was observed between the corrosion rate of carbon steel and the relative humidity in the environment chamber, aligning with findings from previous investigations. This correlation is particularly pronounced at the later stages of exposure, where the corrosion rate exhibits enhanced sensitivity to relative humidity. Nevertheless, at the earlier stage, the corrosion rate appeared less influenced by relative humidity, suggesting that other factors might be at play. Results from droplet size distribution and contact angle analysis hint that electrolyte geometry might significantly influence the corrosion kinetics, especially at an early stage of exposure.
- In general, it was observed that the corrosion under the droplets follows an Evans-type mechanism, with the attack propagating toward the bulk of the metal.
- This novel experimental approach offers valuable insights that can significantly contribute to advancing mechanistic and kinetic understanding of atmospheric corrosion, facilitating the development of mechanistic and kinetic corrosion prediction models.

SUPPLEMENTARY INFORMATION

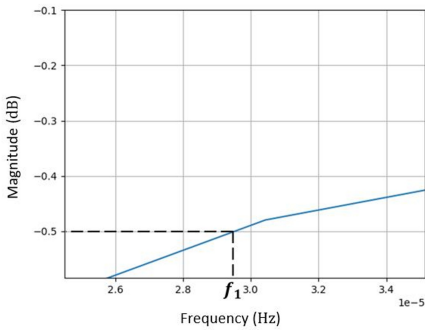
2.S.1. ER SIGNAL FILTERING METHOD

This work utilizes a frequency of 50 Hz for ER signal acquisition. Subsequently, the frequency is decreased to 1 Hz by averaging the amplitude over a temporal window of 60 seconds. This approach is adopted to reduce the processing time and memory usage. From a corrosion mechanism perspective, this low frequency aligns with the typical timescales of the atmospheric corrosion process, which are often over hours, days or years rather than seconds.

a)



b)



c)

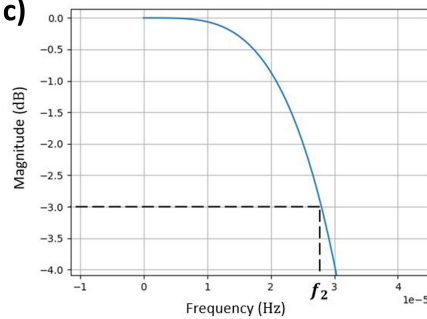


Figure 2.11: (a) Flowchart diagram describing the Savitzky-Golay (S-G) filter procedure. (b) An example of a cumulative power spectrum (converted to decibels by scaling with the total signal power) given a sequence of R_{sens} (c) An example of S-G filter ($M=19000$, $N=2$) response in the frequency domain showing a pulse signal. From f_2 on, the pulse signal starts to be significantly attenuated by the filter.

In this work, a Savitzky-Golay (S-G) low pass filter is considered, mainly due to its extremely flat pass band. The S-G filter, which is based on local least-squares polynomial approximation, is widely applied when a signal has most of its energy in the filter band[54, 55]. The filter works by minimizing the mean square error between data fitted with polynomial fitting and the original signal within the selected window. The window will then move along the whole input signal. An S-G filter is defined by two parameters, one being the highest polynomial order (N) for fitting and the other being half window length (M). A well designed S-G low-pass filter should have a proper cutoff frequency that allows most of the power in the input signal to pass. The process followed in the

application of S-G filter is presented in Fig. 2.11a. The input ER signal is analyzed to determine the highest frequency (f_1) to be passed after filtering, as presented in Fig. 2.11b. This is achieved by allowing a maximum of 10 % loss in signal power, which is equivalent to approximately 0.5 dB. The S-G filter is initialized with a random estimation into both N and M. Following this, the filter response can be tested by applying a pulse signal to the filter. The cutoff frequency (f_2) is determined by allowing a 3 dB signal power loss, which is equivalent to approximately 50 % of the power of the input signal, as presented in Fig. 2.11c. Comparing two frequencies, f_2 should match or slightly exceeds f_1 . If the criterion is not met, adjust N and M and go through the loop again until optimal N and M is found. It must be noticed that different M and N combinations can lead to the same cut-off frequency. To simplify the analysis, N is fixed to 2 throughout this work.

Also notice that S-G filters operate by fitting successive subsets of adjacent data points with a low-degree polynomial by the method of linear least square. Therefore, at the start and end of a signal, when the filter window size exceed beyond the bound of the data, the filtering can no longer be performed as there are insufficient data points to fit the polynomial. To resolve this issue, replicate padding, where the original signal is extended by repeating the nearest value, is adopted. This method physically makes sense at the start of the ER signal, this is mainly because, before the introduction of the corrosive electrolyte, the sensor track will not corrode and shall stay at its initial status. Since the ER signal is extended towards the direction earlier than the introduction of the corrosive electrolyte, it's reasonable to assume all the extended values are as the same as the first value of the incoming signal. This however might not be the case at the end of the signal, since if the experiment keeps going on, the sensor track is supposed to keep on corroding. Given the analysis above, the last 8000 data points, which is equivalent to $\frac{M}{3600}$ h given the ER signal has a frequency of 1 Hz before filtering, is discarded since this portion might not accurately represent the real corrosion rate.

2.S.2. ER SIGNAL FILTERING RESULTS AND DISCUSSION

Fig. 2.12a 2.12b and illustrate a comparison before and after filtering on corrosion rate mentioned in the main text, under the section of 'Results and discussion', subsection of 'Validation experiment: corrosion of carbon steel under 1M NaCl condition'.

The noise observable in Fig. 2.12a are mostly internally generated by the data acquisition device. Compared to either corrosion depth or original electrical resistance where the noise is less significant, the noise is amplified after calculating the first derivative. When calculating the first derivative of a signal, the change in the signal is essentially emphasized, which also amplifies any noise present, particularly high-frequency noises. In the original 1 Hz electrical resistance signal, when there is a sudden change in curve (which is caused by a sudden change in temperature on sensor track during the introduction of droplet electrolyte at the beginning of the test), this sudden change generally indicates the presence of high-frequency components in its Fourier spectrum. Denoting Fourier transform analysis as $\mathcal{F}$, original signal as $f(t)$, the first derivative of original as $f'(t)$, ω as the angular frequency, j as the imaginary unit, and signal in frequency domain as $F(\omega)$, the following equations are valid:

$$\mathcal{F}\{f(t)\} = F(\omega) \quad (2.10)$$

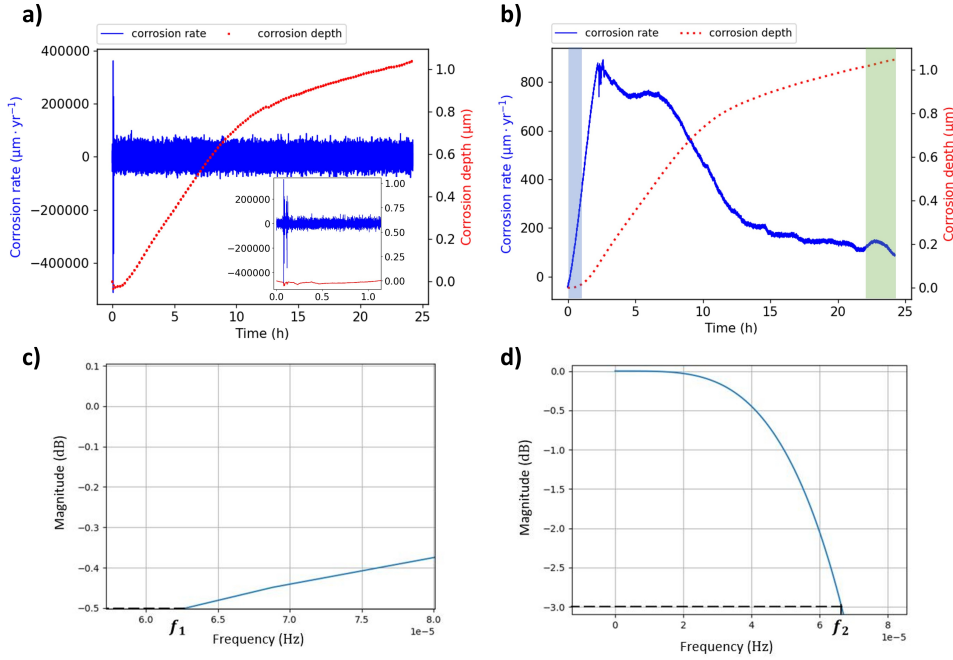


Figure 2.12: (a) Corrosion rate without filtering, including a zoomed-in view at the beginning of the test (b) Corrosion rate after S-G filtering with $M=8000$ and $N=2$, The light green zone by the end of the test and light blue zone at the beginning of the test might not accurately represent the real corrosion rate of the sensor track. For detailed explanations on light green zone, please refer to Section 2.S.1 under this Supplementary Information; Regarding light blue zone, please refer to the discussion on Figure 7 in the main text. (c) Cumulative power spectrum of R_{sens} (d) S-G filter (taking $M=8000$, $N=2$) frequency domain response when given a pulse signal. The filter cutoff frequency f_2 is slightly higher than input signal highest frequency f_1

$$\mathcal{F}\{f'(t)\} = j\omega F(\omega) \quad (2.11)$$

The factor $j\omega$ means that each frequency component of $f(t)$ is scaled by ω , implying the higher frequency components in noises are amplified more than lower ones. When converted back to the time domain, the significant amplification of high-frequency noise components are manifested as pulse-like spikes. These spikes are more pronounced at the beginning of the test where extremely high values are observed, primarily due to both internal fluctuations from the data acquisition device and external responses of the sensor track to temperature fluctuations, where electrical resistance of the sensor track is predominantly influenced by temperature changes.

Following the method in last section, the adopted S-G filter takes $M=8000$ and $N=2$ based on an analysis into the frequency spectrum of both S-G filter (Fig. 2.12d) and sensor track electrical resistance (Fig. 2.12c).

2.S.3. DROPLET IMAGE ANALYSIS METHOD

A four-step procedure achieved with Python and Label Studio, an open source platform for image labelling, is employed to analyze the droplets, as presented in Fig. 2.13.

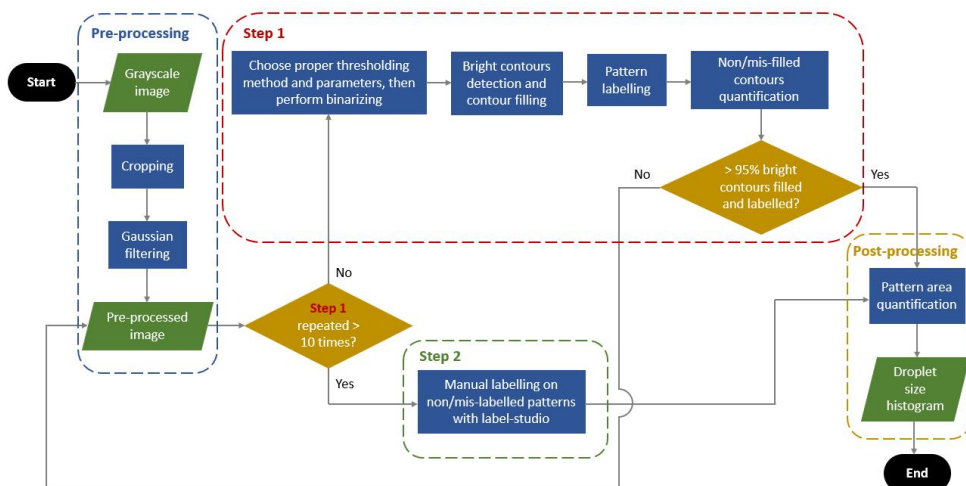


Figure 2.13: Flowchart diagram describing image processing and droplet recognition procedure. In the post-processing section where droplet size analysis is performed, since most of the droplets are irregular in shape due to varying local surface morphology and tension, the concept of equivalent diameter is employed. The equivalent diameter is calculated by converting an irregular pattern into a circle while preserving the same area. To eliminate the noises, droplets occupying an area smaller than 10 pixels ($4.10\ \mu\text{m}$ and $1.23\ \mu\text{m}$ in equivalent diameter for 3X and 10X lens) are neglected.

In general, the whole procedure is divided into four sections, including pre-processing where the original images will go through a series of steps to remove the background noises generated during acquisition; step 1 where droplets with a clear boundary against the background are labelled with the auto-recognition algorithm in Python; step 2 undetected droplets are manually labelled with Label Studio; and finally the last section, the post-processing section where droplet size distribution and corresponding distribution is quantified and visualized. Noticing that it is never ensured an optimal parameter can be obtained for step 1, to achieve a balance between efficiency and quality, step 1 will stop after 10 iterations, and step 2 will be subsequently performed.

2.S.4. WEIGHT LOSS - ER CROSS VALIDATION

The corrosion rate and depth values found in the ER studies have been corroborated by measuring the weight loss of a sample between the start and the end of an exposure. This cross-validation involved the parallel exposure of an ER sample pair with two additional small square samples measuring approx. $15\ \text{mm} \times 15\ \text{mm} \times 500\ \mu\text{m}$ for the weight loss test. All samples were placed under the same electrolyte and environmental conditions. Before exposure, all samples were surface finished down to $3\ \mu$ polishing suspension. To obtain the weight loss data for small square samples accurately, the corroded samples were cleaned following the procedures specified in ASTM G1-03[56], using chemicals

prepared according to designation C3.1 under the standard. After the cleaning procedure, the samples were dried and weighed immediately to avoid further corrosion.

The ER data was processed following the procedures as described in the main text, without adopting filtering. As shown in Fig. 2.14, after 20 h of exposure, the corrosion depth has reached $0.53 \mu\text{m}$. The average corrosion rate of ER sample within the exposure is the calculated to be approx. $236 \mu\text{m}\cdot\text{yr}^{-1}$.

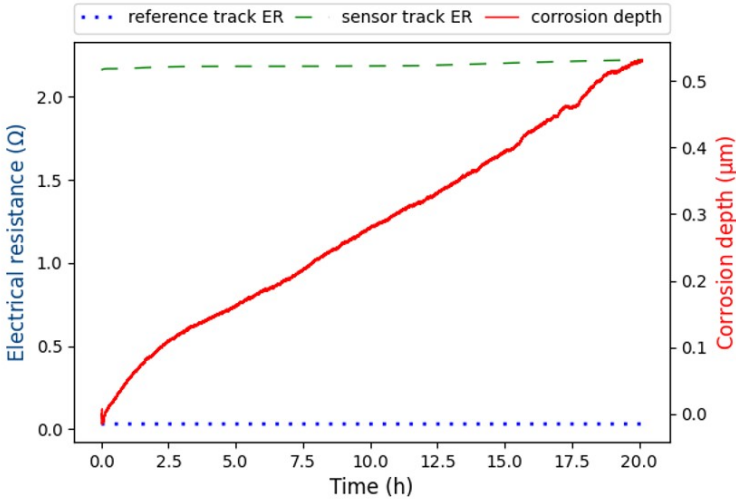


Figure 2.14: Corrosion depth of ER sample exposed under multi-droplets formed of 1M NaCl solution, for a duration of 20 h. Before exposure, ER sample is finished with 3μ polishing suspension.

Tab. 2.3 summarizes the weight loss results of the two examined small square samples exposed to multi-droplets formed of 1M NaCl solution for 20 h. The weight loss tests indicate a corrosion depth slightly higher than the ER result, $0.73 \mu\text{m}$ and $0.68 \mu\text{m}$ for the two samples, respectively.

Table 2.3: Weight loss result of two square samples exposed in parallel with ER sample pair, under same experimental conditions. Before exposure, both samples are finished with 3μ polishing suspension.

	Area (mm ²)	Weight start (g)	Weight end (g)	Weight loss (g·m ⁻²)	Depth loss (μm)	Depth loss rate (μm·yr ⁻¹)
Sample 1	14.24 × 14.51	0.9260	0.9248	5.8077	0.73	318
Sample 2	14.05 × 14.45	0.8890	0.8879	5.4181	0.68	296

Despite the observed difference, the ER-based and weight-loss-based corrosion depth values are still relatively similar, i.e. within the same order of magnitude. The difference may mainly originate from the following aspects:

- A previous investigation by Diler et al.[16] has shown the impact of corrosion prod-

uct 3D geometry and distribution on ER change through simulation, from which the correspondence of sample mass loss and ER change can be inferred. The study has highlighted that, for the two simulated corrosion product geometries (hemispherical and cylindrical), a higher distribution density correlates with a closer alignment between weight-loss-based depth and ER-based corrosion depth values. Under one circumstance, when corrosion products are sparsely distributed, the weight-loss-based depth can exceed the ER-based depth by over 40%, a discrepancy even greater than the results observed in the current study. Considering the potential complexity of corrosion product distribution and 3D geometry in real-world scenarios, variations between weight-loss-based depth and ER-based depth should be commonly accepted.

- Since the ER sample is way more elongated than the square samples, the chance to form bigger droplets should be higher in the latter than in the former. In general, corrosion tends to initiate underneath bigger droplets. Hence, it is reasonable to accept that corrosion is slightly more significant on square samples than on the ER sample.
- Because the ER sample is extremely thin, always measuring less than 25 μm , the corrosion can easily penetrate the sample thickness locally, halting perpendicular propagation of the corrosion product. Conversely, the square samples have a relatively high thickness (approx. 500 μm), making it virtually impossible for the corrosion to penetrate the full sample thickness under the current experimental conditions and duration. As a result, the sample geometry does not impede corrosion product growth, leading to a higher corrosion rate.

This result also correlates well with the previous investigations on offshore carbon steel infrastructure corrosion rates. A strong correlation between atmospheric salinity and carbon steel annual corrosion rate is observed[46, 57], and in general annual steel corrosion rate is positively proportional to atmospheric salinity (Fig. 2.15). The electrolyte deposition can be roughly converted to salinity with Eq. 2.12, where S, M, C and x represent atmospheric salinity, molar mass of chloride ion, molar concentration of the electrolyte and the height of the electrolyte layer.

$$S[\text{mgCl}^{-}\text{m}^{-2}\cdot\text{d}^{-1}] = M[\text{g}\cdot\text{mol}^{-1}] \cdot C[\text{mol}\cdot\text{L}^{-1}] \cdot x[\mu\text{m}] \quad (2.12)$$

In the current study, the 1M NaCl solution is only introduced at the beginning of the test via spraying. Taking $M = 35.3$, $C = 1$, the expression can be simplified to $S = 35.5 \cdot x$. Based on the discussion in Section 2.2.6 under the main text, x can be approximated when knowing both contact angle and droplet diameter. To simplify the analysis, the change in solid-liquid interaction is ignored when NaCl is introduced to the liquid. If considering the average x over the whole surface of the sample, x shall possess a value of several microns. This will result in a salinity value between several tens to several hundreds, which corresponds to annual corrosion rate between 100 $\mu\text{m}\cdot\text{yr}^{-1}$ to 1000 $\mu\text{m}\cdot\text{yr}^{-1}$ in Fig. 2.15.

The value remains within a comparable order of magnitude to the results from the ER

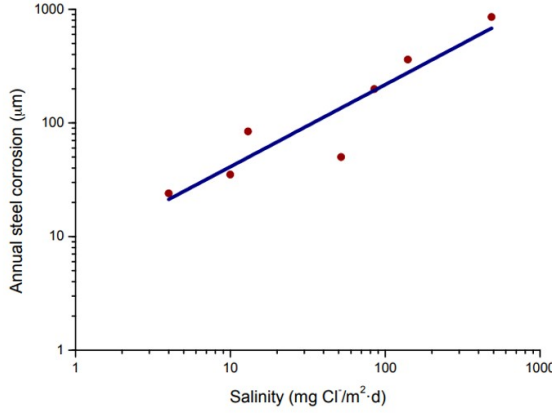


Figure 2.15: The correlation between annual steel corrosion rate and atmospheric salinity at offshore region[46].

test presented in this study, thereby cross-validating the experimental and data analysis approach presented in this study.

2.S.5. DROPLET ELECTROLYTE CONCENTRATION ESTIMATION

The concentration of the solute i.e. NaCl, can be calculated by roughly estimating droplet volume by regarding the droplet as a segment of a 3D sphere (Fig. 2.16), knowing contact angle (θ) and droplet-sample surface contact area (S).

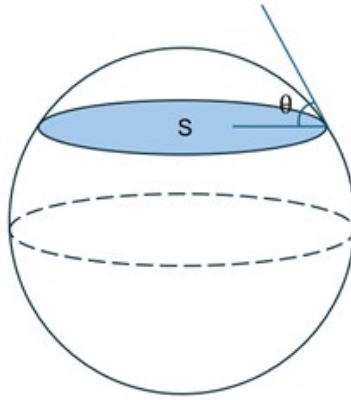


Figure 2.16: Schematic drawing showing that each droplet is regarded as a segment of a 3D sphere.

Droplet volume (V) can be correlated with θ and S with Eq. 2.13:

$$V = \frac{S^{1.5}}{3\pi^{0.5}} \frac{(1 - \cos\theta)^2 (2 + \cos\theta)}{\sin^3\theta} \quad (2.13)$$

which can be further correlated with NaCl concentration by fixing the amount of NaCl unchanged. Noticing that such estimation is aimed at providing a rough insight into the real-time NaCl concentration which would facilitate in understanding the role of NaCl in carbon steel corrosion under multi-droplet condition, rather than conducting a thorough and accurate analysis on this parameter.

2.S.6. RATIO OF SENSOR TRACK TO REFERENCE TRACK

The ratio between sensor track to reference track is presented below:

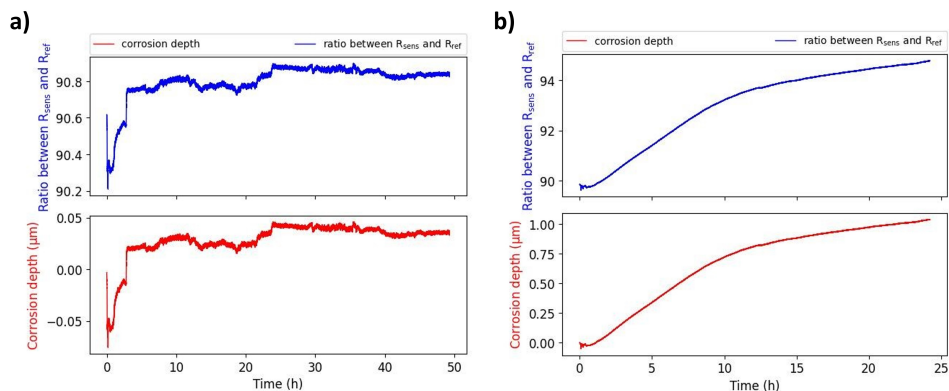


Figure 2.17: The ratio between the electrical resistance of sensor track to reference track for the tests represented by (a) Fig. 2.5 and (b) Fig. 2.7 in the main text.

BIBLIOGRAPHY

- [1] B. G. Koushik et al. "Review on modelling of corrosion under droplet electrolyte for predicting atmospheric corrosion rate". In: *Journal of Materials Science & Technology* 62 (2021), pp. 254–267. ISSN: 1005-0302. DOI: [10.1016/j.jmst.2020.04.061](https://doi.org/10.1016/j.jmst.2020.04.061). URL: [/WOS:000601221700025](https://www.wos-id.org/000601221700025).
- [2] M. Stratmann. "The Atmospheric Corrosion of Iron - a Discussion of the Physicochemical Fundamentals of This Omnipresent Corrosion Process - Invited Review". In: *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics* 94.6 (1990), pp. 626–639. ISSN: 0005-9021. DOI: [DOI10.1002/bbpc.19900940603](https://doi.org/10.1002/bbpc.19900940603). URL: [/WOS:A1990DQ48200001](https://www.wos-id.org/A1990DQ48200001).
- [3] X. Z. Ma et al. "Investigation on the initial atmospheric corrosion of mild steel in a simulated environment of industrial coastland by thin electrical resistance and electrochemical sensors". In: *Corrosion Science* 204 (2022). ISSN: 0010-938x. DOI: [ARTN11038910.1016/j.corsci.2022.110389](https://doi.org/10.1016/j.corsci.2022.110389). URL: [/WOS:000808009000003](https://www.wos-id.org/000808009000003).
- [4] U. R. Evans. "Oxygen distribution as a factor in the corrosion of metals". In: *Industrial and Engineering Chemistry* 17 (1925), pp. 363–372. ISSN: 0019-7866. DOI: [DOI10.1021/ie50184a012](https://doi.org/10.1021/ie50184a012). URL: [/WOS:000188442900132](https://www.wos-id.org/000188442900132).
- [5] V. Soulié. "Sessile droplets of salt solutions on inert and metallic surfaces: influence of salt concentration gradients on evaporation and corrosion behaviour". PhD thesis. 2015.
- [6] C. L. Li et al. "EIS monitoring study of atmospheric corrosion under variable relative humidity". In: *Corrosion Science* 52.11 (2010), pp. 3677–3686. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2010.07.018](https://doi.org/10.1016/j.corsci.2010.07.018). URL: [/WOS:000282561300012](https://www.wos-id.org/000282561300012).
- [7] S. Wan et al. "Monitoring of atmospheric corrosion and dewing process by interlacing copper electrode sensor". In: *Corrosion Science* 150 (2019), pp. 246–257. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2019.02.008](https://doi.org/10.1016/j.corsci.2019.02.008). URL: [/WOS:000462108000023](https://www.wos-id.org/000462108000023).
- [8] J. H. Ahn et al. "A Method for Estimating Time-Dependent Corrosion Depth of Carbon and Weathering Steel Using an Atmospheric Corrosion Monitor Sensor". In: *Sensors* 19.6 (2019). ISSN: 1424-8220. DOI: [ARTN141610.3390/s19061416](https://doi.org/10.3390/s19061416). URL: [/WOS:000465520200105](https://www.wos-id.org/000465520200105).
- [9] N. Fuse et al. "Methodology to Improve Corrosion Rate Estimation Based on Atmospheric Corrosion Monitoring Sensors". In: *Corrosion* 73.2 (2017), pp. 199–209. ISSN: 0010-9312. DOI: [10.5006/2234](https://doi.org/10.5006/2234). URL: [/WOS:000394444800009](https://www.wos-id.org/000394444800009).

- [10] M. Hoseinpoor et al. "Toward more realistic time of wetness measurement by means of surface relative humidity". In: *Corrosion Science* 177 (2020). ISSN: 0010-938x. DOI: [ARTN10899910.1016/j.corsci.2020.108999](https://doi.org/10.1016/j.corsci.2020.108999). URL: [%3CGo%20to%20ISI%3E://WOS:000596028600003](https://www.wos.org/wos/000596028600003).
- [11] J. T. Meng et al. "Data Mining to Atmospheric Corrosion Process Based on Evidence Fusion". In: *Materials* 14.22 (2021). DOI: [ARTN695410.3390/ma14226954](https://doi.org/10.3390/ma14226954). URL: [%3CGo%20to%20ISI%3E://WOS:000724490900001](https://www.wos.org/wos/000724490900001).
- [12] Z. B. Pei et al. "Towards understanding and prediction of atmospheric corrosion of an Fe/Cu corrosion sensor via machine learning". In: *Corrosion Science* 170 (2020). ISSN: 0010-938x. DOI: [ARTN10869710.1016/j.corsci.2020.108697](https://doi.org/10.1016/j.corsci.2020.108697). URL: [%3CGo%20to%20ISI%3E://WOS:000533523500048](https://www.wos.org/wos/000533523500048).
- [13] Y. N. Shi et al. "Data mining to online galvanic current of zinc/copper Internet atmospheric corrosion monitor". In: *Corrosion Science* 133 (2018), pp. 443–450. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2018.02.005](https://doi.org/10.1016/j.corsci.2018.02.005). URL: [%3CGo%20to%20ISI%3E://WOS:000429764100041](https://www.wos.org/wos/000429764100041).
- [14] C. Ma et al. "Electrochemical noise monitoring of the atmospheric corrosion of steels: identifying corrosion form using wavelet analysis". In: *Corrosion Engineering Science and Technology* 52.6 (2017), pp. 432–440. ISSN: 1478-422x. DOI: [10.1080/1478422x.2017.1320117](https://doi.org/10.1080/1478422x.2017.1320117). URL: [%3CGo%20to%20ISI%3E://WOS:000407560700005](https://www.wos.org/wos/000407560700005).
- [15] E. Diler et al. "Real-time monitoring of the degradation of metallic and organic coatings using electrical resistance sensors". In: *Materials and Corrosion-Werkstoffe Und Korrosion* 68.12 (2017), pp. 1365–1376. ISSN: 0947-5117. DOI: [10.1002/maco.201709655](https://doi.org/10.1002/maco.201709655). URL: [%3CGo%20to%20ISI%3E://WOS:000417217800012](https://www.wos.org/wos/000417217800012).
- [16] E. Diler et al. "Real-time corrosion monitoring of aluminium alloys under chloride-contaminated atmospheric conditions". In: *Materials and Corrosion-Werkstoffe Und Korrosion* 72.8 (2021), pp. 1377–1387. ISSN: 0947-5117. DOI: [10.1002/maco.202112302](https://doi.org/10.1002/maco.202112302). URL: [%3CGo%20to%20ISI%3E://WOS:000614700600001](https://www.wos.org/wos/000614700600001).
- [17] S. Li et al. "Application of steel thin film electrical resistance sensor for in situ corrosion monitoring". In: *Sensors and Actuators B-Chemical* 120.2 (2007), pp. 368–377. DOI: [10.1016/j.snb.2006.02.029](https://doi.org/10.1016/j.snb.2006.02.029). URL: [%3CGo%20to%20ISI%3E://WOS:000244073600003](https://www.wos.org/wos/000244073600003).
- [18] Z. L. Li et al. "Application of An Electrical Resistance Sensor-Based Automated Corrosion Monitor in the Study of Atmospheric Corrosion". In: *Materials* 12.7 (2019). ISSN: 1996-1944. DOI: [ARTN106510.3390/ma12071065](https://doi.org/10.3390/ma12071065). URL: [%3CGo%20to%20ISI%3E://WOS:000465500700064](https://www.wos.org/wos/000465500700064).
- [19] J. Orlikowski, K. Darowicki, and S. Mikolajski. "Multi-sensor monitoring of the corrosion rate and the assessment of the efficiency of a corrosion inhibitor in utility water installations". In: *Sensors and Actuators B-Chemical* 181 (2013), pp. 22–28. ISSN: 0925-4005. DOI: [10.1016/j.snb.2013.02.015](https://doi.org/10.1016/j.snb.2013.02.015). URL: [%3CGo%20to%20ISI%3E://WOS:000317941100003](https://www.wos.org/wos/000317941100003).

- [20] T. Prosek, N. Le Bozec, and D. Thierry. "Application of automated corrosion sensors for monitoring the rate of corrosion during accelerated corrosion tests". In: *Materials and Corrosion-Werkstoffe Und Korrosion* 65.5 (2014), pp. 448–456. ISSN: 0947-5117. DOI: [10.1002/maco.201206655](https://doi.org/10.1002/maco.201206655). URL: [WOS:000335981800003](https://www.wos.org/WOS/000335981800003).
- [21] T. Prosek et al. "Application of automated electrical resistance sensors for measurement of corrosion rate of copper, bronze and iron in model indoor atmospheres containing short-chain volatile carboxylic acids". In: *Corrosion Science* 87 (2014), pp. 376–382. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2014.06.047](https://doi.org/10.1016/j.corsci.2014.06.047). URL: [WOS:000341334800040](https://www.wos.org/WOS/000341334800040).
- [22] A. Rafei. "Development and evaluation of thin film electrical resistance sensors for monitoring CO₂ top of the line corrosion". In: *Sensors and Actuators B-Chemical* 346 (2021). DOI: [ARTN13049210.1016/j.snb.2021.130492](https://doi.org/10.1016/j.snb.2021.130492). URL: [WOS:000691996100007](https://www.wos.org/WOS/000691996100007).
- [23] Y. Z. Xu et al. "Experimental study on pipeline internal corrosion based on a new kind of electrical resistance sensor". In: *Sensors and Actuators B-Chemical* 224 (2016), pp. 37–47. DOI: [10.1016/j.snb.2015.10.030](https://doi.org/10.1016/j.snb.2015.10.030). URL: [WOS:000366459500005](https://www.wos.org/WOS/000366459500005).
- [24] T. Aastrup and C. Leygraf. "Simultaneous infrared reflection absorption spectroscopy and quartz crystal microbalance measurements for in situ studies of the metal/atmosphere interface". In: *Journal of the Electrochemical Society* 144.9 (1997), pp. 2986–2990. ISSN: 0013-4651. DOI: [Doi10.1149/1.1837948](https://doi.org/10.1149/1.1837948). URL: [WOS:A1997XY2000022](https://www.wos.org/WOS/A1997XY2000022).
- [25] Z. J. Liu et al. "Study of corrosion behavior of carbon steel under seawater film using the wire beam electrode method". In: *Corrosion Science* 80 (2014), pp. 523–527. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2013.11.012](https://doi.org/10.1016/j.corsci.2013.11.012). URL: [WOS:000330605200062](https://www.wos.org/WOS/000330605200062).
- [26] A. Nishikata, Y. Ichihara, and T. Tsuru. "Electrochemical impedance spectroscopy of metals covered with a thin electrolyte layer". In: *Electrochimica Acta* 41.7-8 (1996), pp. 1057–1062. ISSN: 0013-4686. DOI: [Doi10.1016/0013-4686\(95\)00438-6](https://doi.org/10.1016/0013-4686(95)00438-6). URL: [WOS:A1996UK66700014](https://www.wos.org/WOS/A1996UK66700014).
- [27] M. Stratmann and H. Streckel. "The Investigation of the Corrosion of Metal-Surfaces, Covered with Thin Electrolyte Layers - a New Experimental-Technique". In: *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics* 92.11 (1988), pp. 1244–1250. ISSN: 0005-9021. DOI: [DOI10.1002/bbpc.198800305](https://doi.org/10.1002/bbpc.198800305). URL: [WOS:A1988R362500011](https://www.wos.org/WOS/A1988R362500011).
- [28] G. A. El-Mahdy, H. A. Al-Lohedan, and Z. Issa. "Monitoring the Corrosion Rate of Carbon Steel under a Single Droplet of NaCl". In: *International Journal of Electrochemical Science* 9.12 (2014), pp. 7977–7985. ISSN: 1452-3981. URL: [WOS:000345261900099](https://www.wos.org/WOS/000345261900099).

- [29] J. Jiang et al. "Effect of length of gas/liquid/solid three-phase boundary zone on cathodic and corrosion behavior of metals". In: *Electrochimica Acta* 54.5 (2009), pp. 1426–1435. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2008.09.017](https://doi.org/10.1016/j.electacta.2008.09.017). URL: [3CGo%20to%20ISI%3E://WOS:000263006100007](https://www.wos.org/wos/3CGo%20to%20ISI%3E://WOS:000263006100007).
- [30] S. X. Li and L. H. Hihara. "The comparison of the corrosion of ultrapure iron and low-carbon steel under NaCl-electrolyte droplets". In: *Corrosion Science* 108 (2016), pp. 200–204. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2016.03.005](https://doi.org/10.1016/j.corsci.2016.03.005). URL: [3CGo%20to%20ISI%3E://WOS:000375887100020](https://www.wos.org/wos/3CGo%20to%20ISI%3E://WOS:000375887100020).
- [31] T. H. Muster et al. "The atmospheric corrosion of zinc: The effects of salt concentration, droplet size and droplet shape". In: *Electrochimica Acta* 56.4 (2011), pp. 1866–1873. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2010.09.099](https://doi.org/10.1016/j.electacta.2010.09.099). URL: [3CGo%20to%20ISI%3E://WOS:000287951600022](https://www.wos.org/wos/3CGo%20to%20ISI%3E://WOS:000287951600022).
- [32] Y. J. Tan. "Wire beam electrode: A new tool for studying localised corrosion and other heterogeneous electrochemical processes". In: *Corrosion Science* 41.2 (1999), pp. 229–247. ISSN: 0010-938x. URL: [3CGo%20to%20ISI%3E://WOS:000078779000002](https://www.wos.org/wos/3CGo%20to%20ISI%3E://WOS:000078779000002).
- [33] X. Tang et al. "Atmospheric corrosion local electrochemical response to a dynamic saline droplet on pure Iron". In: *Electrochemistry Communications* 101 (2019), pp. 28–34. ISSN: 1388-2481. DOI: [10.1016/j.elecom.2019.01.011](https://doi.org/10.1016/j.elecom.2019.01.011). URL: [3CGo%20to%20ISI%3E://WOS:000464134900006](https://www.wos.org/wos/3CGo%20to%20ISI%3E://WOS:000464134900006).
- [34] S. Lee and R. W. Staehle. "Adsorption of water on copper, nickel, and iron". In: *Corrosion* 53.1 (1997), pp. 33–42. ISSN: 0010-9312. DOI: [Doi10.5006/1.3280431](https://doi.org/10.5006/1.3280431). URL: [3CGo%20to%20ISI%3E://WOS:A1997XU78200005](https://www.wos.org/wos/3CGo%20to%20ISI%3E://WOS:A1997XU78200005).
- [35] C. Leygraf, I. O. Wallinder, and J. Tidblad. "Atmospheric Corrosion". In: John Wiley & Sons, Ltd, 2016. Chap. 1, pp. 1–6.
- [36] B. E. Risteen, E. Schindelholz, and R. G. Kelly. "Marine aerosol drop size effects on the corrosion behavior of plain carbon steel". In: *ECS Transactions* 58.29 (2014), p. 1.
- [37] N. Van den Steen et al. "Predicting the effect of droplet geometry and size distribution on atmospheric corrosion". In: *Corrosion Science* 202 (2022). ISSN: 0010-938x. DOI: [ARTN11030810.1016/j.corsci.2022.110308](https://doi.org/10.1016/j.corsci.2022.110308). URL: [3CGo%20to%20ISI%3E://WOS:000793828200001](https://www.wos.org/wos/3CGo%20to%20ISI%3E://WOS:000793828200001).
- [38] K. Popova and T. Prosek. "Corrosion Monitoring in Atmospheric Conditions: A Review". In: *Metals* 12.2 (2022). DOI: [ARTN17110.3390/met12020171](https://doi.org/10.3390/met12020171). URL: [3CGo%20to%20ISI%3E://WOS:000771927100001](https://www.wos.org/wos/3CGo%20to%20ISI%3E://WOS:000771927100001).
- [39] ISO 11844-2. *Corrosion of metals and alloys—classification of low corrosivity of indoor atmospheres—part 2: Determination of corrosion attack in indoor atmospheres*. 2005.
- [40] ASTM-G96. *Standard guide for on-line monitoring of corrosion in plant equipment (electrical and electrochemical methods)*. 2008.
- [41] ISO-4287. *Geometrical product specifications*. 1997.

- [42] N. Watanabe, M. Aritomi, and A. Machida. "Time-series characteristics and geometric structures of drop-size distribution density in dropwise condensation". In: *International Journal of Heat and Mass Transfer* 76 (2014), pp. 467–483. ISSN: 0017-9310. DOI: [10.1016/j.ijheatmasstransfer.2014.04.041](https://doi.org/10.1016/j.ijheatmasstransfer.2014.04.041). URL: [3CGo%20to%20ISI%3E://WOS:000338387800043](https://www.wos.org/wos/000338387800043).
- [43] J. M. Campbell and H. K. Christenson. "Dynamic Measurement of Low Contact Angles by Optical Microscopy". In: *Acs Applied Materials & Interfaces* 10.19 (2018), pp. 16893–16900. ISSN: 1944-8244. DOI: [10.1021/acsami.8b03960](https://doi.org/10.1021/acsami.8b03960). URL: [3CGo%20to%20ISI%3E://WOS:000432753800076](https://www.wos.org/wos/000432753800076).
- [44] M. R. Ward. "Electrical engineering science". In: McGraw-Hill, 1971, pp. 36–40.
- [45] E. J. Lefevre and J. W. Rose. "A Theory of Heat Transfer by Dropwise Condensation". In: *Chemical Engineering Progress* 62.7 (1966), pp. 86–&. ISSN: 0360-7275. URL: [3CGo%20to%20ISI%3E://WOS:A19667984300092](https://www.wos.org/wos/A19667984300092).
- [46] J. Alcántara et al. "Marine Atmospheric Corrosion of Carbon Steel: A Review". In: *Materials* 10.4 (2017). ISSN: 1996-1944. DOI: [ARTN40610.3390/ma10040406](https://doi.org/10.3390/ma10040406). URL: [3CGo%20to%20ISI%3E://WOS:000402843800081](https://www.wos.org/wos/000402843800081).
- [47] M. Langlet et al. "Caking of sodium chloride: Role of ambient relative humidity in dissolution and recrystallization process". In: *Chemical Engineering Science* 86 (2013), pp. 78–86. ISSN: 0009-2509. DOI: [10.1016/j.ces.2012.05.014](https://doi.org/10.1016/j.ces.2012.05.014). URL: [3CGo%20to%20ISI%3E://WOS:000311431800010](https://www.wos.org/wos/000311431800010).
- [48] C. Peng, L. X. D. Chen, and M. J. Tang. "A database for deliquescence and efflorescence relative humidities of compounds with atmospheric relevance". In: *Fundamental Research* 2.4 (2022), pp. 578–587. ISSN: 2096-9457. DOI: [10.1016/j.fmre.2021.11.021](https://doi.org/10.1016/j.fmre.2021.11.021). URL: [3CGo%20to%20ISI%3E://WOS:000865484800001](https://www.wos.org/wos/000865484800001).
- [49] W. H. J. Vernon. *Second experimental report to the atmospheric corrosion research committee (british non-ferrous metals research association)*. Tech. rep. 1927.
- [50] D. S. Peck. "Comprehensive model for humidity testing correlation, in: 24th International Reliability Physics Symposium". In: *IEEE*. Peck, D. S., pp. 44–50.
- [51] D. J. Klinger. "Humidity acceleration factor for plastic packaged electronic devices". In: *Quality and reliability engineering international* 7.5 (1991), pp. 365–370.
- [52] G. V. Kuznetsov et al. "Evaporation modes of LiBr, CaCl, LiCl, NaCl aqueous salt solution droplets on aluminum surface". In: *International Journal of Heat and Mass Transfer* 126 (2018), pp. 161–168. ISSN: 0017-9310. DOI: [10.1016/j.ijheatmasstransfer.2018.05.040](https://doi.org/10.1016/j.ijheatmasstransfer.2018.05.040). URL: [3CGo%20to%20ISI%3E://WOS:000442979300014](https://www.wos.org/wos/000442979300014).
- [53] V. Soulié et al. "The evaporation behavior of sessile droplets from aqueous saline solutions". In: *Physical Chemistry Chemical Physics* 17.34 (2015), pp. 22296–22303. ISSN: 1463-9076. DOI: [10.1039/c5cp02444g](https://doi.org/10.1039/c5cp02444g). URL: [3CGo%20to%20ISI%3E://WOS:000359971300060](https://www.wos.org/wos/000359971300060).
- [54] Abraham Savitzky and Marcel J E Golay. "Smoothing and differentiation of data by simplified least squares procedures." In: *Analytical chemistry* 36.8 (1964), pp. 1627–1639.

- [55] Ronald W Schafer. “What is a Savitzky-Golay filter?” In: *IEEE Signal processing magazine* 28.4 (2011), pp. 111–117.
- [56] ASTM-G1-03. *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*. 2004.
- [57] HR Ambler and AAJ Bain. “Corrosion of metals in the tropics”. In: *Journal of Applied Chemistry* 5.9 (1955), pp. 437–467.

3

DEVELOPING A DATA-DRIVEN FRAMEWORK FOR ANALYZING ATMOSPHERIC CORROSION OPTICAL RECORDING

This chapter has been published as:

Zhang, K.; Mol, A.; Gonzalez-Garcia, Y. Development of a data-driven framework for monitoring corrosion under droplets. Corros Sci 2026, 258. DOI: ARTN 113313 10.1016/j.corsci.2025.113313.

The Python code for the analysis involved in this work is available at:

<https://github.com/KeerZhang345/Droplet-Optical-Microscopy-Images-Analysis.git>

Abstract

Understanding localized corrosion under atmospheric droplets is critical, yet previous studies have mostly focused on single-droplet systems or general trends, leaving the role of individual droplets within multi-droplet environments yet to be explored. Here, we present a fully automated, image-based, data-driven framework for analyzing corrosion progression under thousands of droplets simultaneously. Using time-resolved optical imaging and pre-trained large vision models for droplet segmentation, we construct per-droplet color features and propose a probability-based representation of corrosion product formation in inner and outer regions of interest. This approach overcomes the limitations of binary classification by capturing the continuous and spatially heterogeneous nature of corrosion product formation. Applied to carbon steel exposed to over 1500 pre-sprayed 1 M NaCl droplets of various sizes, the method reveals that the probability of corrosion product presence strongly depends on droplet size, with larger droplets more likely to exhibit products both under and around the droplet footprint. Moreover, corrosion products in the outer region can appear independently of under-droplet corrosion, suggesting a role for inter-droplet interactions. By transforming raw imaging data into physically meaningful per-droplet metrics, this work offers a scalable platform for investigating localized corrosion kinetics and morphology in complex, real-world droplet populations, opening new opportunities for connecting droplet formation and population behavior to local and overall atmospheric corrosion rates.

3.1. INTRODUCTION

Droplet-based electrolytes play a crucial role in atmospheric corrosion, especially during its initial stages[1–9]. In multi-droplet systems, electrochemical activity at the solid-liquid interface is influenced not only by droplet size and shape but also by their spatial distribution[10].

Previous studies have primarily focused on single droplets, using electrochemical techniques such as polarization tests[3–5, 11], electrochemical impedance spectroscopy (EIS)[3, 11], electrochemical noise (EN)[11] analysis, and wire beam electrode (WBE)[1, 12] setups to study corrosion kinetics. These experiments often rely on precisely controlled droplet placement, with optical microscopy used to track corrosion product formation over time. For example, Rahimi et al.[11] combined EIS, polarization, and EN with optical imaging for studying corrosion kinetics under a single droplet to examine its link with electrolyte evaporation, droplet geometry, and ion concentration. Analytical models[3, 13, 14] and finite element modeling (FEM)[14, 15] simulations have also been developed to simulate electrolyte spreading, ion transport, and potential fields, although they often rely on assumptions such as fixed droplet shapes, idealized boundary conditions, or steady-state behavior.

Some studies have extended this approach to multi-droplet configurations. Larger droplets have been linked to higher corrosion probability and distinct corrosion types[6, 7]. As corrosion progresses, secondary spreading can lead to formation of a thin electrolyte layer surrounding the original droplet footprint[9], which enables inter-droplet interactions that further affect corrosion dynamics. Van den Steen et al.[10] introduced an FEM framework incorporating droplet size distributions and geometries to estimate global corrosion rates. While it accounts for heterogeneity, it assumes steady-state conditions and excludes inter-droplet interactions or time-resolved corrosion product evolution. Other works have combined imaging with kinetic measurements to study corrosion under droplet exposure[2, 7, 16, 17]. For instance, Weissenrieder and Leygraf[7] used QCM and optical microscopy to observe corrosion spreading from a single droplet to adjacent regions. While this study provided valuable mechanistic insight into corrosion spreading dynamics, the analysis was limited to isolated droplet and focused primarily on the propagation event. More recently, Zhang et al.[2] correlated electrical resistance (ER)-based corrosion depth with droplet size distributions as analyzed from in-situ optical imaging. However, this work did not resolve corrosion progression at the individual droplet level. These studies illustrate the value of image-based analysis in corrosion research and highlight the potential for a method that treats optical microscopy images as a quantitative source. A key step toward this is defining a reliable image-derived indicator that reflects corrosion activity.

Corrosion products offer such an indicator. Their visual appearance, which is usually through color and texture changes, makes them useful for non-invasive tracking into corrosion progression across large droplet populations. In the Evans model, corrosion products accumulate at the droplet center-periphery interface[18]. Other work has shown corrosion products formation both under and outside the droplet[6, 7, 12]. The distribu-

tion and appearance of corrosion products reflect localized electrochemical activity[11, 19], making them suitable for kinetic and mechanistic analysis.

To quantify these changes across thousands of droplets, a robust image analysis pipeline is required. This includes:

- Segmentation of individual droplets;
- Extraction of relevant features;
- Numerical and statistical analysis of corrosion patterns.

Traditional segmentation methods (e.g. thresholding[20, 21], connected component labeling[2, 22]) are being complemented by deep learning techniques[20]. However, such methods often require labeled data and extensive computational effort[23]. More recently, large vision models (LVM), pre-trained across diverse datasets, offer general-purpose segmentation without task-specific training[24].

This work introduces a fully image-based, automated framework for analyzing corrosion under more than 1,500 NaCl droplets on carbon steel. Using a pre-trained LVM for segmentation and unsupervised clustering of extracted features, we develop a probability-based representation of corrosion product evolution. This allows continuous tracking of localized corrosion in both inner and outer droplet regions over time.

This work serves two purposes: (1) to demonstrate a scalable, automated approach for quantifying localized corrosion from optical images, and (2) to investigate how droplet size affects corrosion initiation and progression within a multi-droplet environment.

3.2. EXPERIMENTAL METHODOLOGY

3.2.1. SAMPLE PREPARATION AND CORROSION MONITORING

Corrosion experiments were conducted on carbon steel samples under multi-droplet conditions, following the methodology described by Zhang et al[2]. The focus of the study was on droplet evolution over time; therefore, no kinetic measurements were performed.

Carbon steel specimens (1.5 cm × 1.5 cm, 500 μm thickness) were cut from an EN 10139 DC01-C950 steel sheet using cold cutting. The composition was 0.12 wt% C, 0.6 wt% Mn, 0.05 wt% P, 0.045 wt% S, with Fe as the remainder. Surfaces were mechanically ground using P800 SiC paper to a roughness of 172.68 ± 16.74 nm, measured by atomic force microscopy (AFM, Dimension Edge Scanning Probe Microscope, Bruker Corporation, USA). Samples were then stored in a drying chamber at <20 % relative humidity for 24 hours before exposure.

3.2.2. TIME-LAPSE IMAGING

Images were recorded using a Manta G319-C camera (Allied Vision Technologies GmbH, Germany) fitted with a zoom lens (Zoom 1:6.5 W.D.240mm, Unitron Ltd., USA), mounted

above the sample. Illumination was provided by an LED ring light. The zoom was fixed throughout the experiment, giving a field of view of $11.65 \text{ mm} \times 8.72 \text{ mm}$ and capturing 1600 droplets per frame.

A 1 M NaCl solution was sprayed onto the sample surface to generate droplets, followed by 4 hours of free corrosion in a climate chamber. Images were acquired at 2-minute intervals over 3 hours and 20 minutes. A total of 101 frames were selected to represent the corrosion process.

To correct for lighting variation, histogram matching was applied across the image sequence to normalize brightness levels. Minor displacements due to mechanical vibrations were corrected using Fast Fourier Transform (FFT)-based image registration, which aligned all frames to the first frame before further analysis.

3.3. RESULTS AND DISCUSSION

3.3.1. DEVELOPMENT OF A DATA-DRIVEN FRAMEWORK

To analyze localized corrosion under thousands of droplets, we developed a data-driven framework that tracks visual changes over time. The process consists of three main steps: (1) droplet identification and segmentation using a pre-trained LVM, (2) feature extraction and clustering (3) probability-based modeling of corrosion product evolution.

3.3.1.1. DROPLETS SEGMENTATION AND ROI DEFINITION

Each droplet is treated as an individual electrochemical cell that may or may not initiate localized corrosion. To analyze the formation and spread of corrosion products associated with each droplet, two regions of interest (ROIs) are defined: the inner ROI, corresponding to the initial droplet footprint, and the outer ROI, representing a surrounding annular zone with an outer equivalent diameter $9/5$ as the inner. This $9/5$ ratio is chosen as a conservative boundary based on the physical behavior of the droplets observed in our experiment, as addressed in detail under [Section 3.3.1](#) in the Supplementary Information. In cases where outer ROIs overlap with the inner ROIs of neighboring droplets, the overlapping areas are excluded from analysis to avoid ambiguity in region attribution ([Fig. 3.1e](#)).

The segmentation process ([Fig. 3.1a-e](#)) begins with the first image in the time-lapse sequence. A pre-trained vision model, Segment Anything Model (SAM)[25], identifies individual droplets from the background. As SAM occasionally merges adjacent droplets ([Fig. 3.1f](#)), we filter masks based on spatial overlap and convert the remaining masks into binary format ([Fig. 3.1b](#)). Connected component labeling assigns unique identifiers to each droplet ([Fig. 3.1c-d](#)), which are then tracked throughout the sequence using brightness-normalized and spatially aligned frames. Outer ROI are generated via morphological dilation ([Fig. 3.1e](#)).

3.3.1.2. FEATURE EXTRACTION AND CLUSTERING

The color and spatial distribution of corrosion products serve as important indicators of the underlying corrosion process. These visual features can provide insight into the severity of corrosion and the possible composition of the corrosion products[11]. The

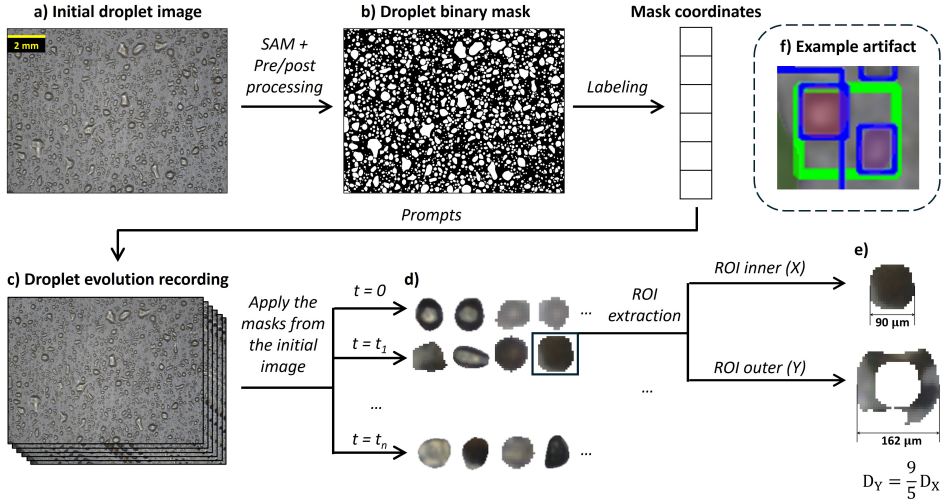


Figure 3.1: ROI extraction workflow for droplet-induced corrosion analysis: (a) Initial droplet image used for segmentation (b) Binary mask of droplet locations after post-processing (c) Time-lapse tracking of droplet-covered areas (d) Tracked droplet segments at selected exposure times (e) Inner and outer ROIs for a representative droplet, with overlapping regions excluded (f) Segmentation artifacts in SAM output, where adjacent droplets are merged.

darkening observed is a well-known characteristic of the formation of iron oxide/hydroxide layers on steel, which have low optical reflectivity. To directly validate that this optical darkening corresponds to corrosion in our experiments, post-mortem SEM-EDS analysis is performed on a representative sample (see Section 2.S.2 in the Supplementary Information), which confirms that the dark regions are composed of iron- and oxygen-rich corrosion products.

To track these changes, each ROI is first interpolated to a fixed size of 32×32 pixels using a high-quality bicubic interpolation (cv2.INTER_CUBIC) to preserve feature integrity and masked to exclude non-droplet regions (Fig. 3.2a). Three feature engineering strategies are then applied to extract color information from the inner and outer ROIs: (1) radial segmentation, where pixels are grouped by angular sectors (Fig. 3.2b); (2) concentric segmentation, where pixels are grouped based on radial distance from the droplet center (Fig. 3.2c); and (3) autoencoder-based encoding[26, 27], where unsupervised neural networks are trained separately for inner and outer ROIs (Fig. 3.2d). The feature engineering strategies are chosen to capture key physical characteristics of corrosion patterns. The concentric segmentation method aligns with the classic Evans droplet model, which describes distinct, concentric anodic and cathodic zones due to the oxygen gradient along droplet radius. The radial segmentation method emphasizes the asymmetrical nature of real-world corrosion where corrosion usually initializes at localized defects. Autoencoder is included as a data-driven approach to learn more complex spatial patterns without domain-specific assumptions. For radial/concentric methods, we compute the mean and variance of RGB channels per subgroup. To account for the obser-

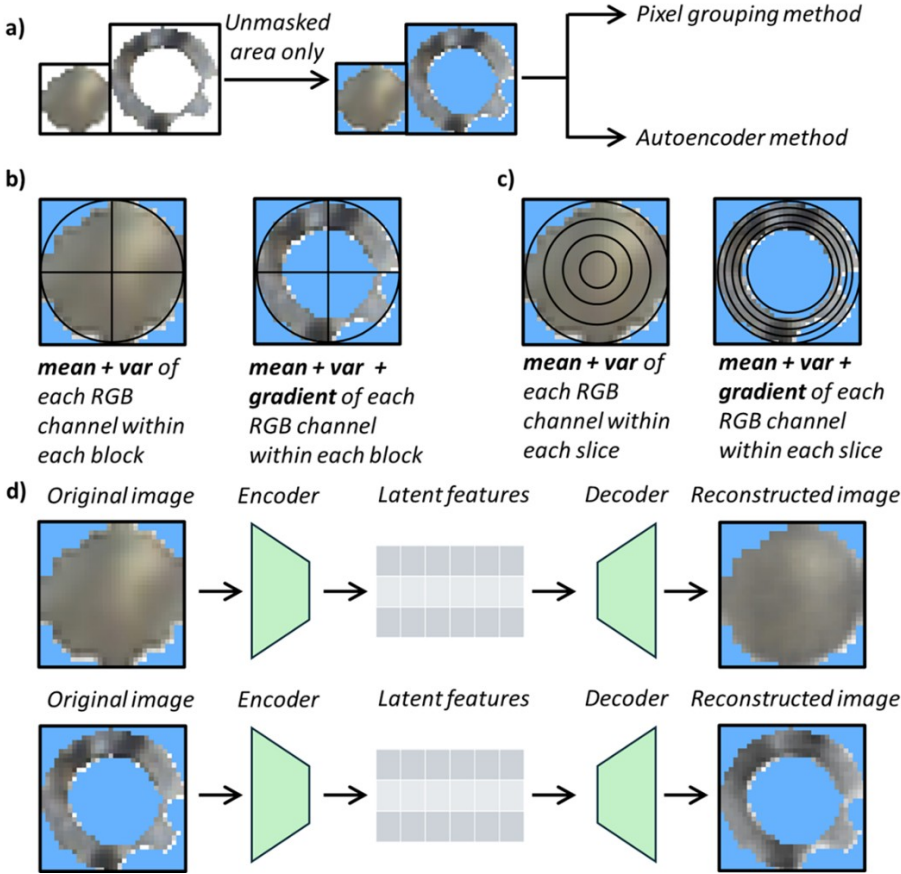


Figure 3.2: Feature engineering strategies for ROI analysis, using the final image in the time-lapse sequence. All ROIs are resized to 32×32 pixels. Only droplet-covered (unmasked) regions are included. (a) ROI masking to remove background pixels. (b) Radial segmentation of pixels by angular sector. (c) Concentric segmentation of pixels by radial distance. Regarding b and c, for illustration, each ROI is divided into four subgroups. (d) Autoencoder-based feature extraction trained separately for inner and outer ROIs.

vation that corrosion products within an outer ROI are often unevenly distributed[12], which typically appears in localized areas rather than forming a uniform ring around the droplet, we also extract grayscale gradient featured for the outer ROIs: (1) the mean and variance of all pairwise pixel intensity differences, which capture the overall variation and contrast within the region; and (2) a normalized intensity histogram computed over 5 bins spanning the full grayscale range $[0, 255]$ which provides a coarse representation of the pixel intensity distribution.

The total number of features for the segmentation-based methods therefore scales with the number of segments chosen. For the autoencoder method, two autoencoders are trained separately on inner and outer ROIs to extract the same number of features from

each ROI. A detailed description of the procedures can be found in [Section 3.3.3](#) under the Supplementary Information.

Based on a multi-stage optimization process, the concentric segmentation method is selected for final analysis. A subsequent grid search evaluated by the Silhouette score determines that the ideal parameters are 5 segments for the inner ROIs and 2 for the outer ROIs. The final number of Principal Components (PCs) is determined to be 5 for both regions to retain over 90 % of the variance from the complete dataset. The detailed methodology for the entire selection and optimization process is provided in [Section 3.3.4](#) under the Supplementary Information.

K-means++ clustering groups ROIs into corrosion and non-corrosion types. The results ([Fig. 3.3a-b](#)) show clear separation, the choice of 2 clusters is determined to be optimal as it yields the highest Silhouette score for both regions (see [Fig. 3.14](#) under Supplementary Information, [Section 3.3.4](#)). The resulting Silhouette scores of 0.72 for inner ROIs and 0.53 for outer ROIs validate the clustering quality.

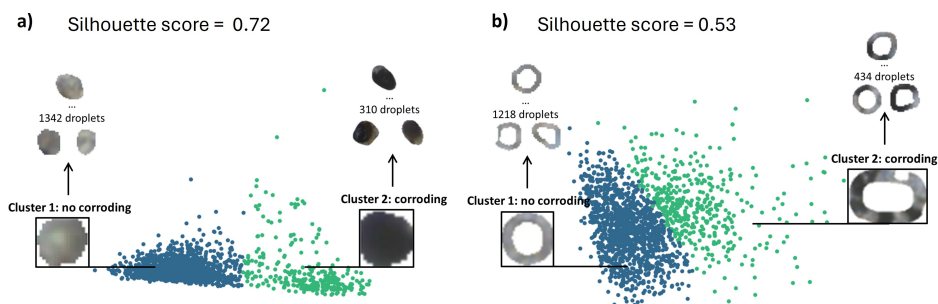


Figure 3.3: K-means++ clustering of PCA-reduced features for (a) inner ROIs and (b) outer ROIs. The plot is shown in space defined by the first two PCs for illustrative purposes. Cluster separation corresponds to corrosion vs. non-corrosion categories, normalized using MaxAbs (inner) or MinMax (outer) scaling.

Mapping the reduced feature space back to the original ROIs reveals that one cluster (green) is associated with a strong presence of corrosion products, whereas the other (blue) corresponds to droplets with minimal or no corrosion.

3.3.1.3. CONTINUOUS PROBABILITY-BASED MAPPING OF CORROSION EVOLUTION

While clustering captures final corrosion status, it does not reflect when corrosion begins or how it progresses. One potential approach to extract this kinetic information is to perform clustering on the time series of each droplet's ROI and assign a binary transition label from “no corrosion” to “corrosion”. However, this approach oversimplifies the process and is inadequate for capturing the gradual, heterogeneous evolution observed in practice (see [Section 3.3.5](#) under Supplementary Information).

To address this, we convert PCA-reduced features into continuous probability curve for each ROI over time. As illustrated in [Fig. 3.4](#), the K-Means++ classifier effectively sepa-

rates the ROIs into distinct clusters but treats all samples within a cluster equally, disregarding variations within each group. To overcome this limitation, we replace the discrete cluster labels with a probability distribution that reflects the likelihood of each sample belonging to the identified clusters.

$$\begin{aligned}\sigma_1(A) &= \frac{e^{-d(A,C_1)}}{e^{-d(A,C_1)} + e^{-d(A,C_2)}} \\ \sigma_2(A) &= \frac{e^{-d(A,C_2)}}{e^{-d(A,C_1)} + e^{-d(A,C_2)}} \\ \text{with } d(A, C_a) &= \sqrt{\sum_{i=1}^n w_i (A_i - C_{a,i})^2} \quad \forall a \in \{1, 2\}\end{aligned}\tag{3.1}$$

This probabilistic approach is based on the weighted distances between a sample and

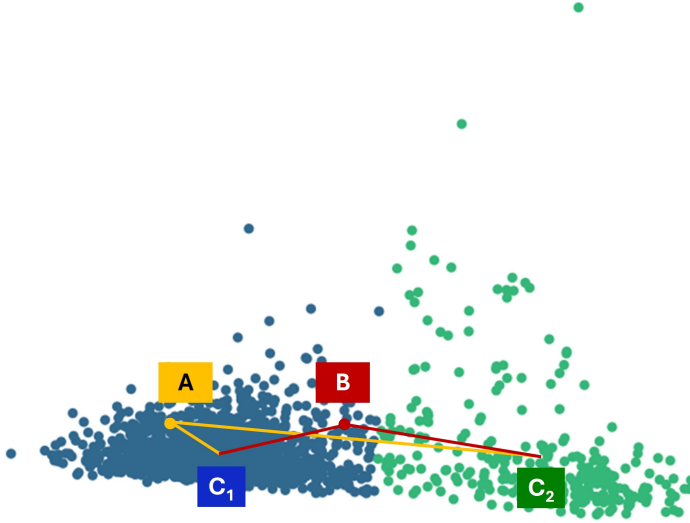


Figure 3.4: Probability-based representation of corrosion status for two inner ROI data points A and B, based on weighted distance to cluster centers (C_1 and C_2) in PCA space. Colors match cluster assignments in Fig. 3.3.

each cluster center. As shown in Eq. 3.1, the distances to the centers of the blue and green clusters, denoted as $d(A, C_1)$ and $d(A, C_2)$ are calculated using weights representing the normalized explained variance ratio obtained during PCA. A negative sign is applied to reflect the inverse relationship between distance and cluster membership probability.

A SoftMax operation is then applied to convert these opposite distances into probabilities: $\sigma_1(A)$ and $\sigma_2(A)$, representing the likelihood of A belonging to the blue or green cluster, respectively. This transformation ensures that the two probabilities sum to 1 and amplifies the contrast between samples when one cluster is clearly more likely than

the other. By extending the method to the entire droplet recording, for each droplet, we obtain a time series of probabilities:

- $p_{(X,t)}$: the likelihood of corrosion product in the inner ROI at time t
- $p_{(Y,t)}$: same for the outer ROI

The validity of using end-frame cluster centers to analyze the entire time series is confirmed with a consistency check, which is detailed in [Section 3.3.6](#) under the Supplementary Information. This yields a smooth temporal profile of corrosion product evolution ([Fig. 3.5](#)) which enables detailed analysis of initiation, progression, and stabilization on a per-droplet basis.

3.3.2. APPLICATION OF THE FRAMEWORK

With the framework, covering segmentation, feature extraction, unsupervised clustering, and probability-based tracking, in place, we now apply it to analyze the spatiotemporal behavior of corrosion across a large droplet population. We first examine representative cases, then assess population-wide corrosion kinetics, and finally investigate how droplet size influences both corrosion type and evolution.

3.3.2.1. REPRESENTATIVE CORROSION BEHAVIORS

To illustrate typical corrosion patterns, we begin with two droplets categorized as corroding or non-corroding based on the clustering results from the final image ([Section 3.3.1.2](#)). [Fig. 3.5](#) shows their probability curve (a-b: corroding, c-d: non-corroding) over time, as derived from the framework introduced in [Section 3.3.1.3](#). In [Fig. 3.5a](#), the inner ROI probability p_X (light blue solid curve) rises gradually and stabilizes near 1.0 by 50 min, indicating substantial accumulation of corrosion products. A Savitzky-Golay filter[28, 29] is applied to extract the general trend from the original data. The smoothed trend (orange curve) is consistent with image darkening over time and highlights three key kinetic features: transition onset (vertical dark blue dashed line), plateau start (vertical yellow dashed line), and midpoint between them (vertical red dashed line). From these points, we extract key kinetic descriptors: the transition interval is the duration between the onset and the start of the plateau. The transition slope is defined as the average rate of change of the probability during this interval, calculated from the smoothed curve. A steeper slope indicates a more rapid stabilization of corrosion products accumulation. Once the plateau is reached, no significant visual changes are observed, which aligns with the stabilization of p_X .

[Fig. 3.5b](#) shows the corresponding outer ROI probability p_Y , which also increases and stabilizes around 0.8, confirming corrosion product accumulation beyond the droplet footprint. This is further supported by the corresponding image sequences showing the evolution around the droplet periphery.

A comparative analysis of [Fig. 3.5a](#) and [3.5b](#) indicates that corrosion product formation begins earlier in the inner ROI than in the outer ROI. This observation aligns with the findings of Wang et al.[12], who reported that while pitting and uniform corrosion

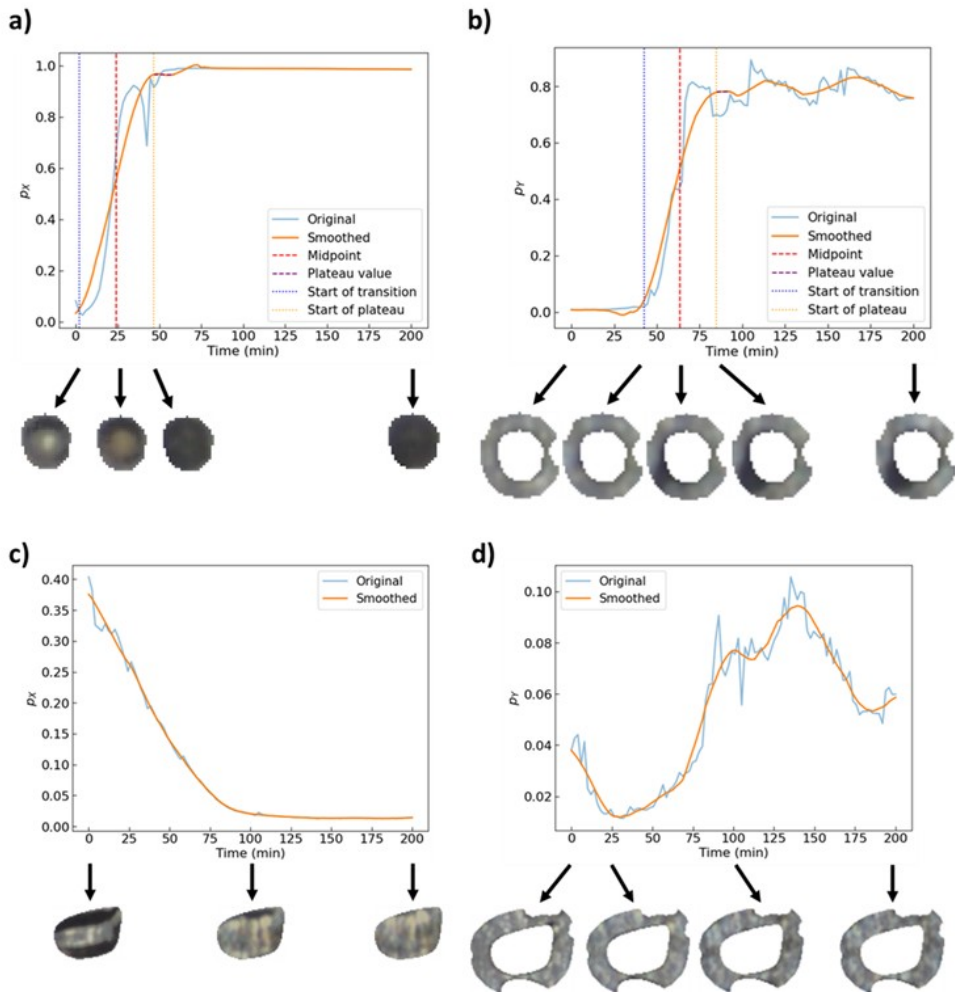


Figure 3.5: Representative corrosion probability curves and corresponding ROI images. (a) Inner ROI (p_x) for a corroding droplet, with raw (blue) and smoothed (orange) curves, and marked onset, midpoint, and plateau. (b) Outer ROI (p_y) for the same droplet. (c) Inner ROI probability for a non-corroding droplet. (d) Outer ROI probability for the same non-corroding droplet.

tend to occur within or near the droplet periphery, while minor corrosion processes may develop outside the droplet over time.

In contrast, Fig. 3.5c and 3.5d depict a droplet where no significant corrosion product formation occurs. In Fig. 3.5c, p_x curve initially rises to approximately 0.4, then declines to near zero after 100 min. Image inspection suggests that this behavior can be related to the droplet drying process. In our previous work[2], we have shown that certain contact angles can lead to optical effects such as ring-shaped illumination or re-

flection/refraction patterns that darken the droplet edge. Although these effects are not distinctly observable here due to resolution limits, the early dark rim is evident and fades over time as the droplet dries and the contact angle decreases. The p_Y curve (Fig. 3.5d) remains consistently low, fluctuating range between 0.0 and 0.1, which confirms the absence of corrosion product formation in the outer ROI of this droplet.

These representative cases illustrate the outcomes where either both ROIs show significant accumulation or neither does. Apart from that, our framework also quantitatively describes other distinct corrosion patterns reported in the literature. For example, Soulie et al.[30] observed that corrosion products under a 1M NaCl droplet is predominantly confined within the droplet footprint. This corresponds to a high p_X plateau and low p_Y in our representation. Conversely, Weissenrieder et al.[7] described corrosion that initiates at the periphery of the droplet and propagates outward, forming filiform-like corrosion morphology. Risteen et al.[6] further demonstrated that such behavior is strongly influenced by droplet size. Within our framework, this would manifest as a high final p_Y plateau and a low p_X .

While clustering on the end-of-exposure image (Section 3.3.1.2) provides an initial corrosion/non-corrosion categorization, a more physically meaningful definition based on the full time-resolved probability curves will be adopted in the following analysis, where ROI corrosion status is determined based on their long-term behavior. An ROI is considered “corroding” if its probability curve (p_X or p_Y) shows a sustained transition and stabilizes at a high plateau ($p > 0.5$) which indicates a sustained existence of corrosion products. Conversely, a “non-corroding” ROI is one where the probability remains low. The robustness of the choice regarding the probability threshold and plateau duration for end-stage plateau detection is demonstrated by a sensitivity analysis in the Supplementary Information under Section 3.S.7.

3.3.2.2. COMPARATIVE TEMPORAL ANALYSIS OF CORROSION PROGRESSION IN INNER AND OUTER ROIS

The data-driven framework allows a direct comparison of corrosion kinetics (i.e. transition midpoint, transition intervals, and transition slopes) between inner (X) and outer (Y) ROIs. We focus on ROIs that develop a clear, sustained presence of corrosion products, defined by the probability curve stabilizing at a plateau over 0.5.

Fig. 3.6 show that corrosion products on average appear earlier and accumulate faster in inner ROIs. This observation is consistent with individual cases discussed in Section 3.2.1. In Fig. 3.6a, the histogram of transition midpoints shows that the kernel density estimation (KDE) for p_X peaks earlier than for p_Y , indicating faster initiation in the inner region. Fig. 3.6b shows that the transition intervals (onset to plateau) are also shorter for p_X , suggesting a faster corrosion stabilization. This is further supported by Fig. 3.6c, where the KDE of transition slopes is steeper for p_X , confirming faster corrosion product accumulation in the inner region. Fig. 3.7a compares two representations of corrosion product occurrence over time: the “soft representation”, based on average probability values (solid curves), and the “hard representation”, based on the binary classification of whether $p > 0.5$ at each time step. Fig. 3.7a also suggests that another contributing factor

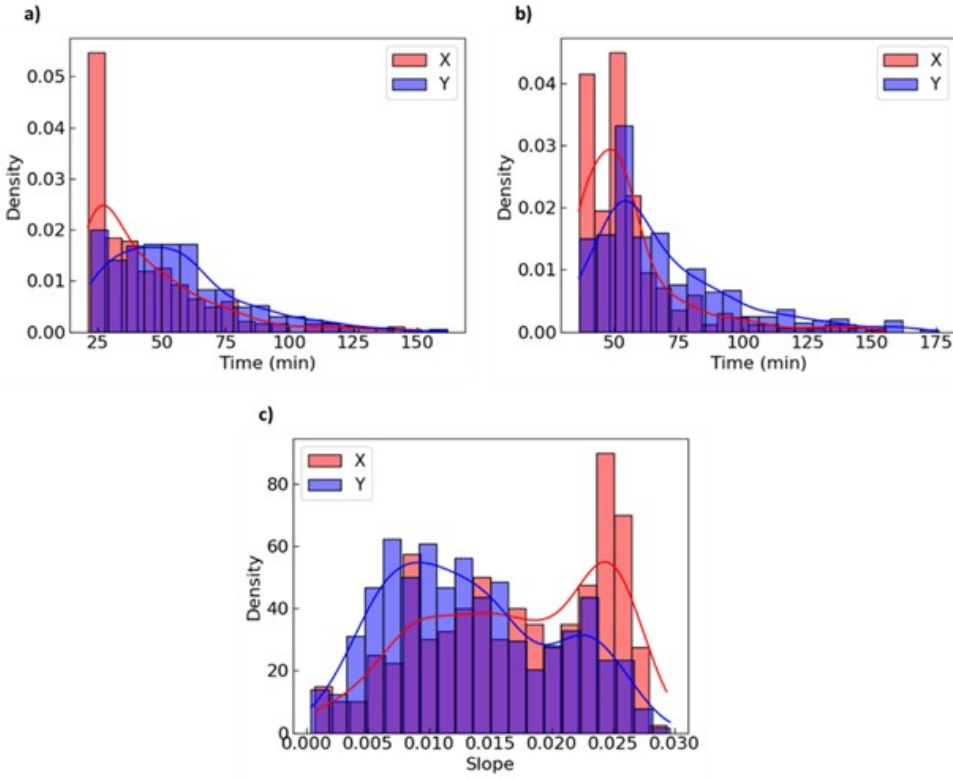


Figure 3.6: Statistical comparison of corrosion kinetics between inner (red) and outer (blue) ROIs for droplets classified as corroding at the end of the exposure. (a) Transition midpoint. (b) Transition intervals (onset to plateau). (c) Transition slopes.

of p_X peaks at a higher value than p_Y in Fig. 3.6c might be explained by the generally high values of p_X compared to p_Y . This is also theoretically valid, as corrosion product coverage is often more substantial in the inner ROI, making it more likely to exhibit either a strong presence or complete absence of corrosion products which leads to more extreme higher p_X values.

The “soft” and “hard” representation can be described with Eq. 3.2 and Eq. 3.3:

$$\overline{p_a^t} = \frac{1}{N_a} \sum_{i=1}^{N_a} p_{i,a}^t \quad \text{where } N_a = \#(a^{\text{end}} = 1) \quad \forall a \in \{X, Y\} \quad (3.2)$$

$$\text{Frac}_a^t = \frac{1}{N_a} \sum_{i=1}^{N_a} 1(p_{i,a}^t > 0.5) = \frac{n_a^t}{N_a} \quad \text{where } n_a^t = \#(a^t = 1) \quad \forall a \in \{X, Y\} \quad (3.3)$$

where N_a denotes the number of droplets containing corrosion products in the inner or outer ROI at the final stage, while $p_{i,a}^t$ represents the dynamic probability of corrosion

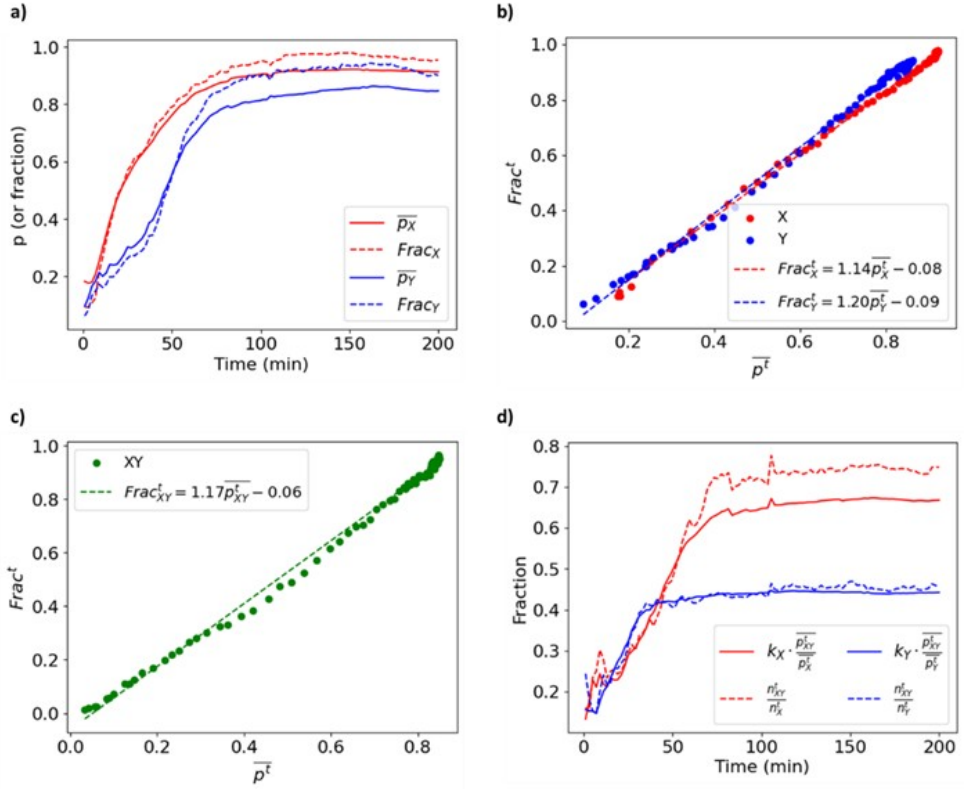


Figure 3.7: Comparison of “soft” (probability-based, solid lines) and “hard” (binary classification, dashed lines) corrosion representations. (a) Temporal evolution of average corrosion status for inner (red) and outer (blue) ROIs. (b) Correlation between soft and hard representations for droplets showing corrosion product at inner (red) and outer (blue) ROIs at the end of exposure. (c) Correlation between the two representations for droplets showing corrosion product at both inner and outer ROIs at the end of exposure (d) Co-development of corrosion in both ROIs, expressed for droplets corroding in the inner (red) or outer (blue) ROI.

product existing in the inner or outer ROI of droplet i at time t , and n_a^t stands for the number of droplets containing corrosion products in the inner or outer ROI at time t . $a^t = 1$ and $a^{\text{end}} = 1$ explicitly mean inner ($a = X$) or outer ($a = Y$) ROI shows presence of corrosion product at time t and by the end of exposure.

The close match between the two, as shown in Fig. 3.7a, confirms that the probability-based representation provides a soft yet accurate approximation of the corrosion fraction. The two curves follow a similar overall trend, with the probability-based curve initially being slightly higher and later slightly lower than the fraction-based curve. This behavior reflects the nature of the probability assignment: droplets located near cluster boundaries in feature space receive intermediate probability values rather than discrete 0 or 1 labels. As a result, the probability-based representation exhibits a smaller dynamic range compared to the binary count, while preserving the overall shape of cor-

rosion evolution. Importantly, although the global averages are similar, the “soft representation” offers finer-grained, per-droplet information, which captures gradual corrosion transitions that would be lost under “hard representation”. This relationship is further supported by Fig. 3.7b, which shows a mostly linear correlation between the two representations over time, validating Eq. 3.4:

$$\frac{n_a^t}{N_a} = \alpha_a \cdot \overline{p_a^t} + \beta_a \quad \forall a \in \{X, Y, XY\} \quad (3.4)$$

Eq. 3.4 can be further extended to droplets that show corrosion products at both inner and outer ROIs at the end of exposure, as validated by Fig. 3.7c. To explore the interaction between inner and outer ROIs, we focus on droplets that have already developed corrosion in one region at certain time and investigate the fraction that simultaneously exhibit corrosion in both regions ($\frac{n_{XY}^t}{n_X^t}$ or $\frac{n_{XY}^t}{n_Y^t}$). Within the “soft representation”, the joint probability of corrosion in both ROIs ($p_{i,XY}^t$) is approximated as the product of the individual probabilities ($p_{i,X}^t$ and $p_{i,Y}^t$) since they are separately analyzed and therefore statistically independent. Eq. 3.5 shows the correlation between the “soft” and “hard” representations by applying Eq. 3.4 to three groups of droplets: those showing corrosion in the inner ROI ($a = X$), the outer ROI ($a = Y$), and both ROIs ($a = XY$) at end of exposure.

$$\begin{aligned} \frac{n_{XY}^t}{n_a^t} &= k_a \cdot \frac{n_{XY}^t}{N_{XY}} \cdot \frac{N_a}{n_a^t} \\ &= k_a \cdot (\alpha_{XY} \cdot \overline{p_{XY}^t} + \beta_{XY}) / (\alpha_a \cdot \overline{p_a^t} + \beta_a) \\ &\approx k_a \cdot \frac{\overline{p_{XY}^t}}{\overline{p_a^t}} \quad (3.5) \end{aligned}$$

where $k_a = \frac{N_{XY}}{N_a} \quad \forall a \in \{X, Y\}$
and $p_{i,XY}^t = p_{i,X}^t \cdot p_{i,Y}^t \quad \forall i \in \{1, \dots, N_{XY}\}$

Fig. 3.7d presents the evolution of co-corrosion for inner and outer ROIs. The red curves, representing the co-development analysis regarding inner ROIs, stabilize above 0.6. This indicates that the majority of those droplets showing corrosion products at inner ROI also develop corrosion products at their outer ROI. This observation supports earlier findings by Wang et al.[12], suggesting that under-droplet corrosion often propagates outward due to electrochemical or diffusional effects.

In contrast, the blue curves show that only 40 % of the droplets exhibiting corrosion in the outer ROI also show corrosion in the inner ROI. This suggests that outer-region corrosion may occur independently of corrosion under the main droplet footprint. One hypothesis is that this is potentially due to inter-droplet interactions or diffusion of chemical species between neighboring droplets. A target analysis shows that the droplet spatially clustering behavior can both slightly increase the overall probability and accelerate the onset of outer ROI corrosion, as detailed under 3.5.8 in the Supplementary Information. Another explanation is that these independent outer corrosion events are

governed by other factors such as corrosion initiating at the three-phase boundary of a single droplet and subsequently propagating outward, as previously observed by Risteen et al.[6] and Weissenrieder et al.[7]

In summary, the comparative temporal analysis reveals distinct kinetic profiles and propagation pathways for the inner and outer ROIs. The statistical analysis of the kinetic descriptors demonstrates that corrosion product formation initiates earlier and stabilizes more rapidly in the inner region. Furthermore, the analysis of co-development fractions shows an asymmetric relationship: while under-droplet corrosion has a high probability of propagating outward, a significant portion of outer-region corrosion occurs independently. These findings suggest a primary “inner-to-outer” corrosion mechanism, supplemented by an independent initiation process at the droplet periphery.

3.3.2.3. INFLUENCE OF DROPLET SIZE ON CORROSION PROBABILITY

With the corrosion behaviors classified in a scale-invariant manner, the influence of the original, physical droplet size can now be systematically investigated. Droplet size plays a critical role in determining droplet-induced corrosion by influencing not only the likelihood of corrosion the occurrence but also the type and rate of corrosion progression[4, 6, 18, 31]. A previous study[6] has shown that for carbon steel, the probability of Evans-type corrosion increases with droplet size, with a threshold beyond which nearly all droplets exhibit this corrosion mode.

In the context of the present study, this behavior corresponds to p_X stabilizing at a high plateau, regardless of the evolution of p_Y . Conversely, corrosion products that primarily from outside the droplet footprint, represented by p_Y stabilizing at a high plateau while p_X remains low, are more frequently associated with smaller droplets. This trend is evident in Fig. 3.8.

Fig. 3.8a presents the distribution of droplets across size bins, along with the fraction exhibiting corrosion at either the inner or outer ROIs by the end of exposure. The size bins are defined as uneven ranges to avoid excessively low droplet counts in the larger size categories. A monotonic increase in corrosion fraction can be observed with increasing droplet diameter for both inner and outer ROIs. While smaller droplets dominate the population, density-normalized histograms (Fig. 3.8b) and cumulative density functions (Fig. 3.8c) confirm that this trend is not an artifact of population imbalance. Specifically, in Fig. 3.8b, the KDE curves for droplets classified as $X_{\text{end}} = 0$ or $Y_{\text{end}} = 0$ peak at much smaller value than that for either $X_{\text{end}} = 1$ or $Y_{\text{end}} = 1$. The cumulative distribution curves in Fig. 3.8c further support this trend: droplets without corrosion products in the inner or outer ROI reach a plateau at lower diameters compared to those with corrosion ($X_{\text{end}} = 1$ or $Y_{\text{end}} = 1$).

The finding that the probability of developing optically detectable corrosion increases with droplet size is a real physical phenomenon and not simply an artifact of optical detection limits. This trend is consistent with the previous study[6] that uses direct profilometry to measure metal volume loss, where the trend that the fraction of drops showing corrosion increases with drop size is also observed. This confirms that while trace electrochemical activity might exist, the likelihood of significant and visible corrosion

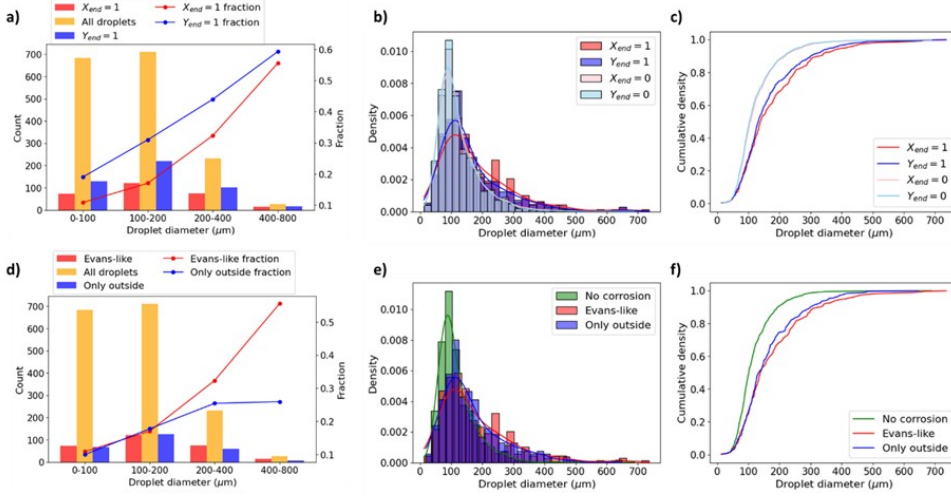


Figure 3.8: Influence of droplet size on corrosion probability and type. (a) Droplet counts (bars) and corrosion fractions (lines) by size bin for inner (red) and outer (blue) ROIs. (b) Normalized size distributions for corroding vs. non-corroding droplets in each ROI. (c) Cumulative distributions of droplet size for the same categories in (b). (d) Fractions of Evans-like (red) and outer-only (blue) corrosion types by size bin. (e) Normalized size distributions for non-corroding (green), Evans-like (red), and outer-only (blue) corrosion types. (f) Corresponding cumulative distributions shown in (e).

initiation is strongly size-dependent.

Comparing corrosion development in the inner versus outer ROIs, it is observed that the presence of corrosion products in the inner ROI is more strongly associated with larger droplet sizes. As shown in Fig. 3.8a, the fraction of droplets exhibiting corrosion at the inner ROI increases more steeply with droplet size compared to the outer ROI. In contrast, droplets exhibiting corrosion at the outer ROI appear across a broader size range, maintaining a relatively higher fraction even at intermediate droplet sizes (Fig. 3.8a). This observation is further supported by the density-normalized size distributions (Fig. 3.8b) and cumulative density functions (Fig. 3.8c), where droplets with inner ROI corrosion ($X_{\text{end}} = 1$) are shifted toward larger diameters relative to those with outer ROI corrosion ($Y_{\text{end}} = 1$), which suggests that corrosion at the outer ROI may be less dependent on individual droplet size and more influenced by inter-droplet interactions or diffusional processes.

In Fig. 3.8d-f, the droplet behavior based on ROI is categorized into three types: non-corroding ($X_{\text{end}} = 0$ and $Y_{\text{end}} = 0$), Evans-like corrosion ($X_{\text{end}} = 1$, no matter of Y), and corrosion localized outside the droplet footprint ($X_{\text{end}} = 0$ and $Y_{\text{end}} = 1$), based on the previous investigation[6]. Overall, the probability of a droplet undergoing corrosion increases with its size, with Evans-type corrosion becoming dominant beyond a critical droplet diameter. Corrosion localized only in the outer ROI may be due to inter-droplet effects or diffusion of corrosion products from neighboring droplets. This phenomenon

is more frequently observed in droplets of intermediate size. As presented Fig. 3.8f, when the droplet diameter exceeds approximately $360\text{ }\mu\text{m}$, nearly all droplets exhibit signs of corrosion, and above $650\text{ }\mu\text{m}$, all corrosion predominantly follows the Evans-like pattern.

These observations confirm that droplet size is a critical factor governing both the likelihood and the dominant mode of corrosion, with larger droplets favoring under-droplet (Evans-like) corrosion, while intermediate-sized droplets may promote corrosion in surrounding regions due to inter-droplet interactions or product diffusion.

3.3.2.4. INFLUENCE OF DROPLET SIZE ON CORROSION CHARACTERISTICS OVER TIME

The previous section focused on the influence of droplet size on whether corrosion occurs and type of corrosion by the end of the exposure, while droplet size also has a significant impact on corrosion kinetics. Jiang et al.[3] have reported that the cathodic limiting current increases linearly with the inverse of droplet radius, indicating that corrosion under larger droplets might be constrained by oxygen concentration at the solid-liquid interface. Cole et al.[14] have further showed that larger droplets exhibit a more pronounced oxygen concentration gradient along the radius, favoring cathodic reactions near the droplet edge. In addition, as droplets evaporate, their initial size influences the drying rate and thus the evolution of electrolyte concentration. Lequien et al.[32] have demonstrated that even within a single droplet, local concentration gradients might emerge due to enhanced vapor flux at the edges, which induces diffusion, capillary flow, and Marangoni flow, all strongly dependent on droplet size. Furthermore, the transport and precipitation of corrosion products, both inside and outside the droplet, are also affected by droplet dimensions[18].

In this section, we analyze the influence of droplet size on two temporal descriptors: the transition midpoint, indicating when corrosion products begin to appear, and the transition interval, reflecting how fast corrosion product accumulation stabilizes. The metrics are evaluated separately for the inner and outer ROIs to extend the previous global analysis into a size-dependent context. For consistency, droplet diameters are classified into the same ranges as presented in Fig. 3.8.

Fig. 3.9 presents normalized histograms of these characteristics across droplet size bins. In the inner ROIs, Fig. 3.9a shows that droplets of intermediate size ($100\text{ }\mu\text{m}$ to $400\text{ }\mu\text{m}$) tend to reach the transition midpoint slightly earlier than smaller ($0\text{ }\mu\text{m}$ to $100\text{ }\mu\text{m}$) or larger ($400\text{ }\mu\text{m}$ to $800\text{ }\mu\text{m}$) droplets. Similarly, Fig. 3.9b reveals that these intermediate-sized droplets also exhibit slightly shorter transition intervals, suggesting faster stabilization of corrosion product accumulation. This behavior may result from an optimal balance between oxygen solubility and ionic conductivity. Larger droplets tend to retain volume longer and maintain lower chloride concentration, enhancing oxygen solubility but reducing electrolyte conductivity. Fig. 3.9c shows the average evolution of p_x for droplets of different sizes. Larger droplets tend to stabilize at a lower plateau value, possibly due to less uniform corrosion product precipitation across the initial footprint. For outer ROIs, the trend differs. Fig. 3.9d-e show that larger droplets ($400\text{ }\mu\text{m}$ to $800\text{ }\mu\text{m}$) initiate corrosion earlier, while smaller ones ($0\text{ }\mu\text{m}$ to $100\text{ }\mu\text{m}$) stabilizes more

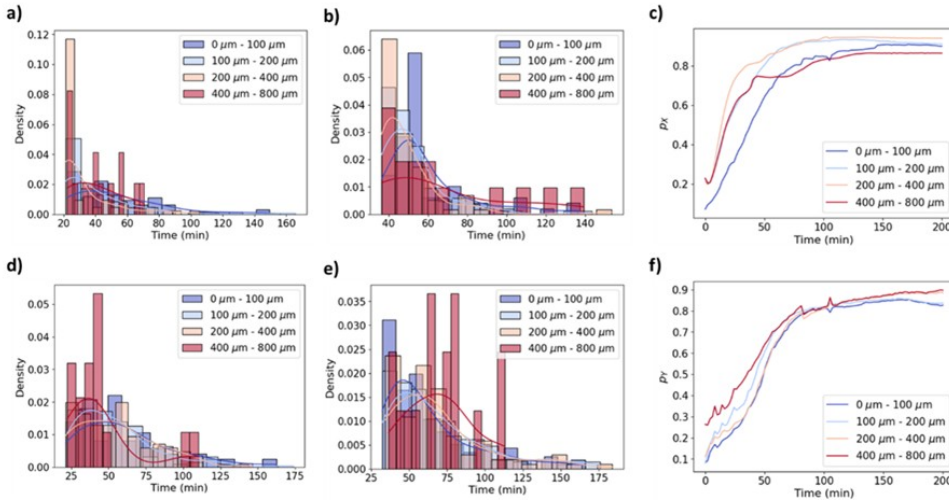


Figure 3.9: Effect of droplet size on corrosion kinetics. (a-b) Transition midpoints and intervals for inner ROIs. (c) Average p_X evolution for droplets of different sizes. Only inner ROIs with corrosion product presence at the end of exposure are included in (a)-(c). (d-e) Transition midpoints intervals for outer ROIs. (f) Average p_Y evolution for droplets with different sizes. Only outer ROIs with corrosion products presence at the end of exposure are included (d)-(f).

quickly. Earlier appearance of corrosion products in larger droplets can be attributed to enhanced evaporation at droplet edges, which results in a higher chloride concentration and thereby creating a more aggressive environment that promotes early corrosion initiation at the periphery. In contrast, the fast drying of smaller droplets cuts off electrolyte supply and accelerates stabilization.

Fig. 3.9f shows the average evolution of p_Y across size bins. Larger droplets stabilize at slightly higher plateau values than smaller droplets, possibly due to the influence of neighboring, actively corroding droplets. Corrosion products diffusing from adjacent droplets may accumulate in the outer ROI and compensate for the dilution effect caused by the larger areas. This diffusion-driven mechanism helps explain the stronger corrosion signal in the outer ROI of larger droplets.

These findings highlight that droplet size influences not only the likelihood but also the dynamics of corrosion, with distinct temporal behaviors observed between inner and outer regions.

3.4. CONCLUSIONS

This study introduced and validated a fully automated, data-driven framework for quantifying corrosion under thousands of individual droplets using time-lapse optical imaging. By converting raw image data into interpretable, probability-based metrics, the method enables a quantitative analysis of both the occurrence and kinetics of corrosion

on a per-droplet basis.

Application of this framework to carbon steel revealed that corrosion behavior is strongly size-dependent, with larger droplets exhibiting a higher probability of developing significant, optically detectable corrosion. The analysis of spatial patterns distinguished two primary corrosion pathways: a 'inside-to-outside' propagation and an independent corrosion process occurring in the periphery of the droplet. Furthermore, the kinetic analysis showed that droplet size also affects the onset and rate of corrosion product formation, with distinct behaviors observed for inner versus outer regions.

3

By translating raw pixel data into physically meaningful metrics, this work provides a scalable platform for investigating localized corrosion kinetics and morphology in complex environments. The framework is broadly applicable to other surface processes where progression can be tracked by visual changes, which offers a powerful tool for high-throughput materials analysis.

SUPPLEMENTARY INFORMATION

3.S.1. OUTER ROI REGION DEFINITION

The purpose of the outer ROI is to create a consistent area to monitor how corrosion products develop surrounding the droplet.

Previous investigations[33, 34] have suggested that salty sessile droplets evaporate in an constant contact area behavior, which is also observed in our experiment. To justify this, we have randomly picked 100 non-corroding droplets and analyzed their diameter evolution. Only non-corroding droplets are analyzed, since for corroding droplets, once corrosion products form and spread, the real edge of the droplet becomes obscured and is often impossible to define accurately.

The temporal evolution (Fig. 3.10a) shows that the droplets undergo a slight initial expansion before stabilizing at an average diameter approximately 3-4 % larger than their initial size. To quantify the full range of this behavior, we plotted the distribution of the maximum expansion ratio for each droplet (Fig. 3.10b). The histogram shows that the maximum observed expansion in our experiment was approximately 1.32 times the initial diameter.

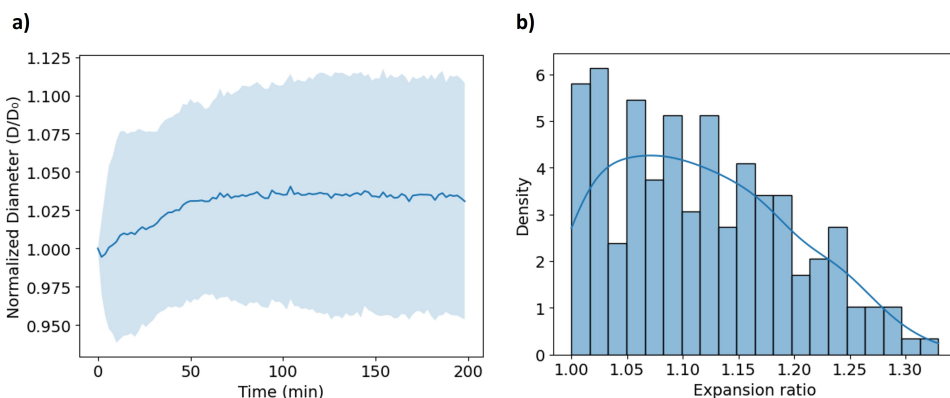


Figure 3.10: (a) Temporal evolution of normalized droplet diameter (Solid line: mean value; transparent background: standard deviation) and (b) Maximum expansion ratio histogram of the randomly selected 100 non-corroding droplets.

The outer ROI is therefore selected as 9/5 of the inner ROI diameter is a conservative boundary based on the physical behavior of the droplets.

3.S.2. POST-MORTEM SEM-EDS ANALYSIS

A complementary characterization experiment is repeated on a new sample which is prepared and tested following an identical protocol (material, electrolyte, exposure conditions) to the one described in the manuscript. After exposure, this sample is analyzed post-mortem using SEM-EDS. As presented in Fig. 3.11, the analysis confirms that the optically dark regions correspond to iron- and oxygen-rich corrosion products contain-

ing chloride.

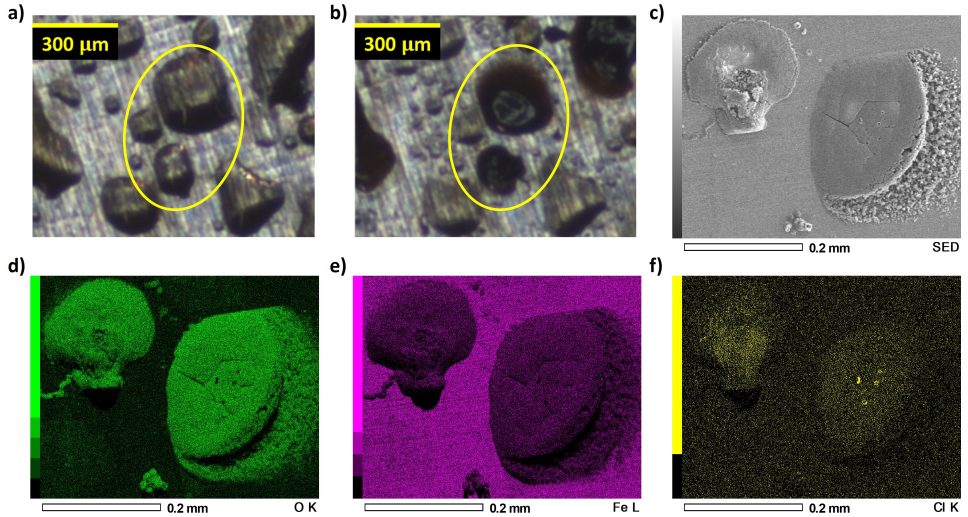


Figure 3.11: Direct experimental validation linking optical darkening to corrosion product formation. (a) In-situ optical recording of NaCl droplets on the carbon steel surface at the start of the experiment. (b) The same region after 4 hours of exposure, where significant darkening can be observed (c) Post-mortem SEM characterization of the area circled in (a) and (b). (d-f) Corresponding EDS elemental maps for oxygen (O), iron (Fe) and chloride (Cl). Together they confirm that the dark regions observed optically are composed of iron- and oxygen-rich corrosion products which also contain chloride.

3.S.3. CONVOLUTIONAL NEURAL-NETWORK-BASED AUTOENCODER FOR FEATURE EXTRACTION

A convolutional autoencoder is designed to learn compact representations of droplet ROI images, and two instances are trained separately for inner and outer ROIs to account for their distinct characteristics. The encoder consists of three convolutional layers with stride-2 downsampling and ReLU activations, reducing the input from $32 \times 32 \times 3$ to a 1024-dimensional vector, followed by a fully connected layer to compress into a N-dimensional latent space. N scales with number of subgroups in segmentation-based feature extraction methods. For example, when 4 subgroups are generated, N will be 24 for each inner ROI and 52 for each outer ROI (The details can be found in [Section 3.S.4](#)). The decoder mirrors this process, expanding the latent representation back through a fully connected layer and three transposed convolutional layers to reconstruct the original image dimensions. The model architecture diagram can be visualized in [Fig. 3.12a](#). As shown in [Fig. 3.12b-g](#), all autoencoders achieve stable convergence with low reconstruction error, confirming that the latent features preserve relevant color characteristics of the original ROIs.

This process converts each ROI into a color vector that has the same dimension as that generated with either radial or concentric segmentation method. Such latent vectors

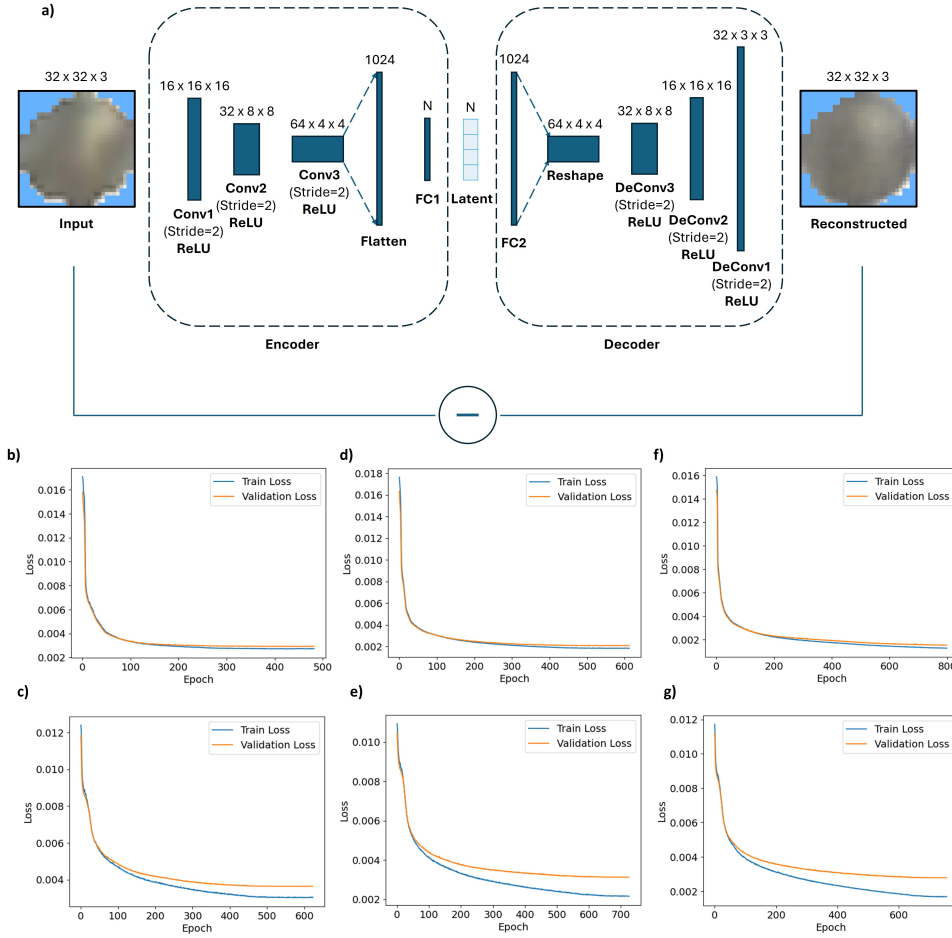


Figure 3.12: (a) Architecture of the convolutional autoencoder used to extract latent representations from inner and outer droplet ROIs. The encoder compresses the $32 \times 32 \times 3$ input into a N -dimensional latent vector through three convolutional layers and a fully connected bottleneck. The decoder reconstructs the original image using three transposed convolution layers, and reconstruction quality is evaluated using mean squared error (MSE). The training and validation loss curves for autoencoders trained on inner ROIs are presented to align with segmentation-based methods when (b) 2 segments (12 features) (d) 4 segments (24 features) and (f) 8 segments (48 features) are generated. Similarly, loss curves for autoencoders trained on outer ROIs are also included to align with segmentation-based methods when (c) 2 segments (26 features) (e) 4 segments (52 features) and (g) 8 segments (104 features) are generated. The stable convergence in both cases indicates that the latent space effectively captures key color features of the droplets.

are then processed with principal component analysis (PCA) for expressiveness analysis for comparing with the two pixel-grouping-based methods, with the results detailed in [Section 3.S.4](#).

3.S.4. THE MULTI-STAGE OPTIMIZATION PROCESS

The optimization is as follows:

- Stage 1: Selection of the optimal feature engineering method
The initial goal is to identify the most effective segmentation method. Here we have tested three feature engineering strategies, including radial segmentation method, concentric segmentation method and autoencoder method, to capture key physical characteristics of droplet corrosion. As described by the classic Evans droplet model, concentric zones of electrochemical activity would form due to the radial oxygen gradient across the droplet, with the central part being more anodic and the periphery being more cathodic. The concentric segmentation method is designed to extract features from these physically meaningful regions. Additionally, since in real-world corrosion, the development of corrosion products is usually asymmetrical and corrosion can first occur at localized defects, radial segmentation method is also evaluated where such asymmetry is emphasized. Finally, an autoencoder method, which learns more complex spatial patterns, is also included as a pure data-driven approach.

The primary criterion for this stage is information parsimony which is defined as the ability of a method to capture the maximum amount of Cumulative Explained Variance (CEV) in the fewest number of dimensions. The analyses are performed on droplets from the end-of-exposure image, as this is the moment where the visual distinction between corroded and non-corroded states is at its maximum. To ensure this selection is robust and not dependent on a specific level of segmentation granularity, we perform PCA comparison across three representative values, including a low (2 segments), a medium (4 segments) and a high (8 segments) granularity. Specifically, for the segmentation-based methods, each segment in the inner ROI generates 6 features (mean and variance for RGB channels), and each segment in the outer ROI generates 13 features (RGB stats plus gradient features). The number of latent dimensions for the autoencoder is chosen to match the total number of features generated by the segmentation methods at each level of granularity to ensure a fair comparison of their information compactness.

- Stage 2: Optimization of segmentation and clustering parameters
Once the concentric method is selected, we perform a grid search to identify the optimal number of segments and number of clusters. Again, this analysis is also performed on droplets from the end-of-exposure image. For each combination, we retain the number of principal components (PCs) required to explain 90 % of the CEV. The optimal parameters are then determined by finding the combination that maximizes the Silhouette score from a K-Means++ clustering. As a final optimization, we find that using the MaxAbs scaler for inner ROIs and the MinMax scaler for outer ROIs yields the best performance.
- Stage 3: Determination of the final number of PCs
With the feature engineering method (concentric) and its parameters (number of segments) finalized, the last step is to determine the number of PCs to be retained

for the final temporal analysis. To ensure this choice is representative of the entire corrosion process, this analysis is performed on the full dataset, including all droplets across all selected time frames. We selected the number of PCs that explained 90 % of the CEV for this complete dataset.

Since concentric segmentation method, among the three tested granularities, always requires the lowest number of components to represent the data effectively (captures the maximum amount of CEV in the fewest number of dimensions, as presented in Fig. 3.13), this method is adopted.

In Stage 2, we have found that under concentric segmentation method, the highest scores which indicate the optimal cluster quality are found with 5 segments and 2 clusters for the inner region, and 2 segments and 2 clusters for the outer region, as presented in Fig. 3.14. These combinations are therefore selected for further analysis. In Stage 3, we have analyzed the number of PCs to retain for keeping CEV over 90 %, which leads to the retaining of 5 PCs for both inner and outer ROIs, as presented in Fig. 3.15.

3.S.5. MISCLASSIFICATION ON PER-DROPLET TEMPORAL CORRODING STATUS USING BINARY CLASSIFICATION

To illustrate the limitations of binary classification in representing corrosion progression, both the temporal evolution of individual droplets and the clustering results based on dimensionally reduced features are examined. Fig. 3.16 shows a time series of ROI images from a single droplet that gradually transitions from a clean state to one with visible corrosion products. This progression visually shows the continuous nature of corrosion, where no clear-cut boundary exists between non-corroded and corroded states.

To classify droplets based on their final condition, PCA is applied to features extracted from the full time series, followed by clustering into two groups. As shown in Fig. 3.17a, the data points form two distinguishable clusters. When mapped back to droplet images, one cluster (Fig. 3.17b) largely corresponds to droplets with significant corrosion, while the other (Fig. 3.17c) contains mostly non-corroded droplets. However, several droplets with visible corrosion are also found in the non-corroding cluster, indicating that the transition is not always captured accurately through binary labeling. This reinforces that while clustering is useful for general categorization, it may not fully reflect the gradual and complex kinetics of corrosion product formation, and therefore an alternative method might be considered.

3.S.6. CONSISTENCY CHECK VALIDATING THE USE OF END-FRAME CLUSTER CENTERS

The validity of using end-frame cluster centers to analyze the entire time series is confirmed with a consistency check. This consists of two parts:

- Population Snapshots: First, we show the feature data for the entire droplet population at different time points (initial, intermediate, and late) plotted against the

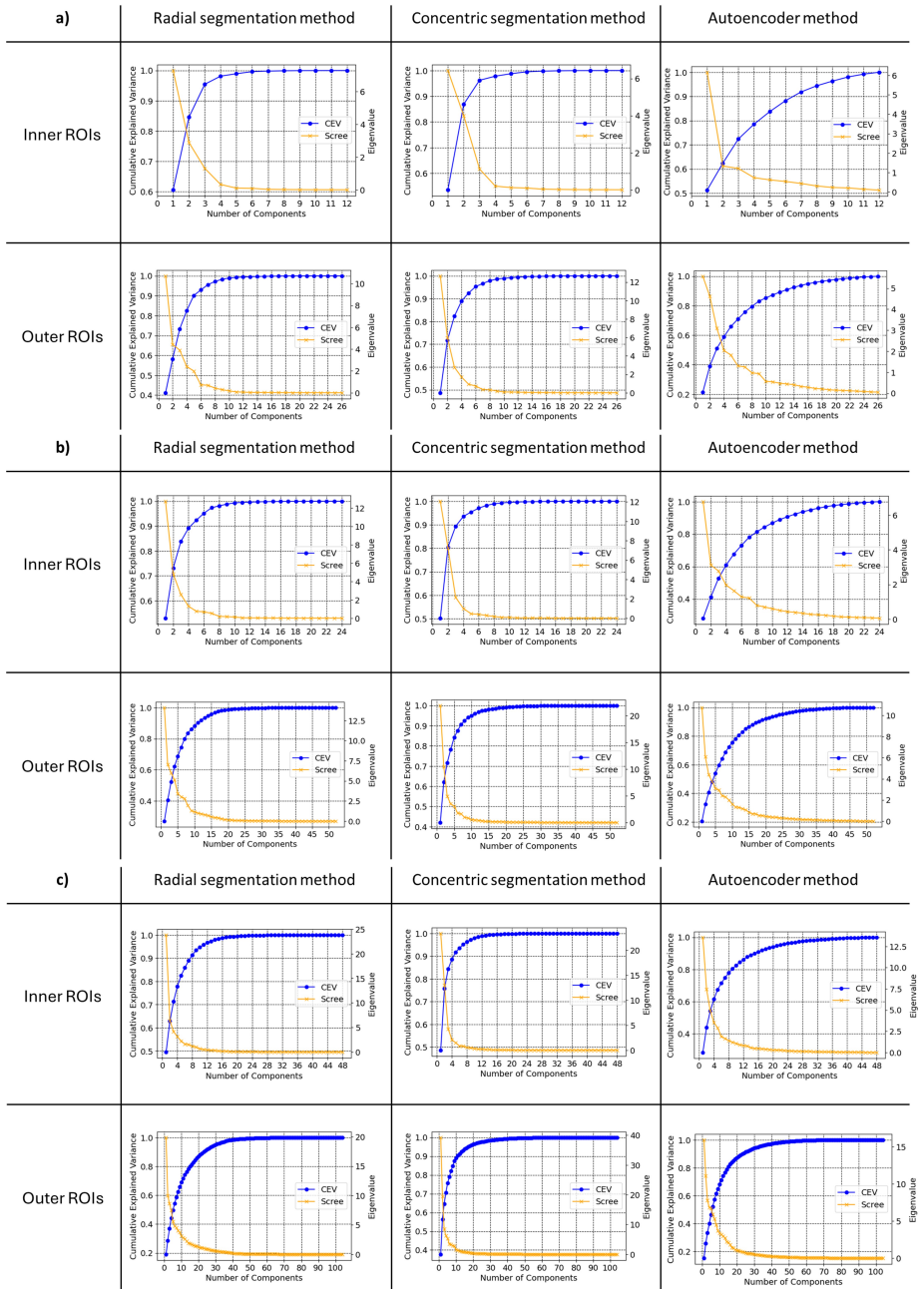


Figure 3.13: PCA results for different feature engineering methods on the end-of-exposure image. The plots show the CEV versus the number of PCs. The comparison is performed for three levels of segmentation granularity: (a) 2 segments, (b) 4 segments, and (c) 8 segments.

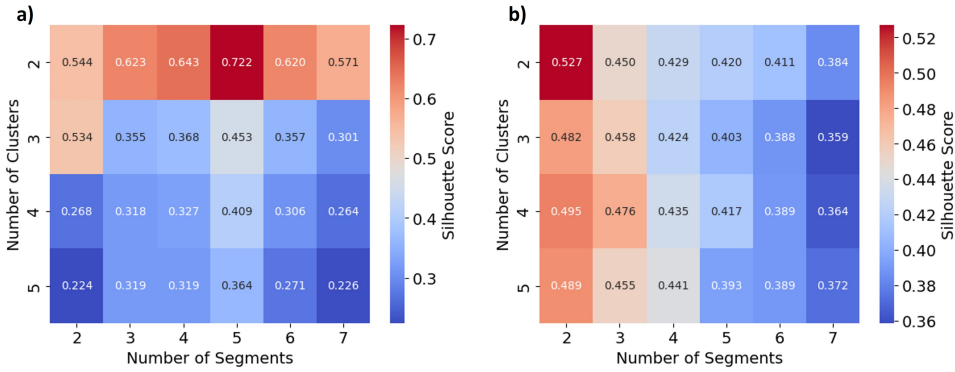


Figure 3.14: Grid search results for optimizing segmentation and clustering parameters. The heatmaps visualize the Silhouette score for the concentric segmentation method across a range of parameters. The analysis is performed separately for (a) the inner ROIs (scaled with MaxAbs scaler) and (b) the outer ROIs (scaled with MinMax scaler) using K-means++ algorithm for clustering analysis.

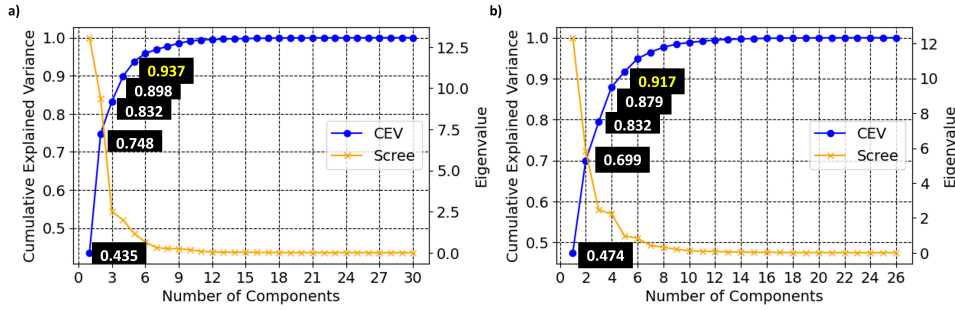


Figure 3.15: PCA on the full dataset to determine the final number of retained PCs for (a) inner and (b) outer ROIs. The analysis shows that for the inner ROIs, 5 PCs explain 93.7 % of the variance and for the outer ROIs, 5 PCs explain 91.7 %. Therefore, to capture over 90 % CEV in both cases, 5 PCs are retained for the final analysis.

two final clusters. As presented in Fig. 3.18a, the plots clearly show that for both inner and outer ROIs, the population beginning almost entirely within the “non-corroding” cluster and progressively evolving across the feature space toward the “corroding” state over time.

- **Individual Trajectories:** Second, we show the trajectories of representative individual droplets. As presented in Fig. 3.18b, these plots trace droplet ROI journey from the non-corroding cluster to the corroding cluster. The corresponding optical images to link this movement in the feature space to the physical accumulation of visible corrosion products are also provided.

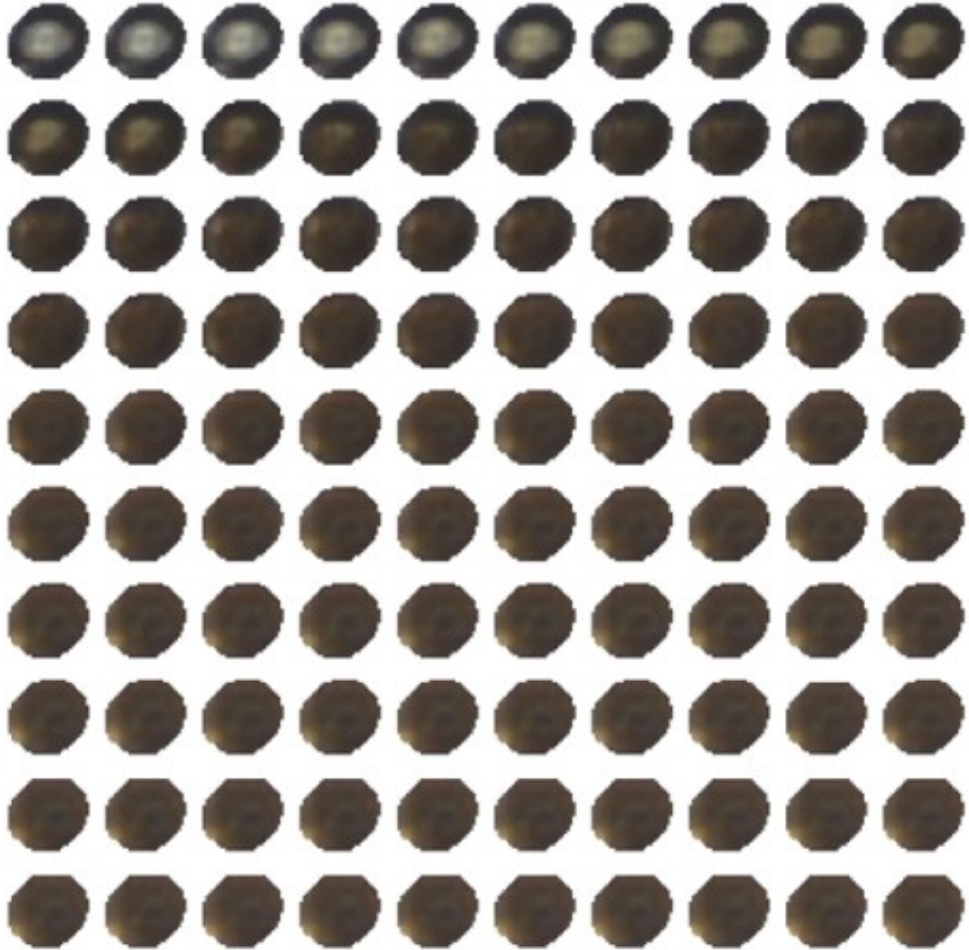


Figure 3.16: Temporal evolution of one inner ROI showing gradual corrosion product formation. Early frames show no visible corrosion, while later frames exhibit increasingly darkened regions indicative of corrosion products.

3.S.7. SENSITIVITY ANALYSIS OF THE CORROSION STATUS CLASSIFICATION CRITERIA

The robustness of the choice regarding the probability threshold and plateau duration for end-stage plateau detection is demonstrated by a sensitivity analysis.

As presented in Fig. 3.19, the results show that the final fraction of droplets classified as corroding is highly stable. Varying the probability threshold (from 0.45 to 0.55) and the minimum plateau duration (from 4 to 6 frames) has only a minor effect on the final corroding fraction for both inner and outer ROIs. For the outer ROI, the fraction varies by about 17 % across the entire tested range, and for the inner ROI, the variation is even

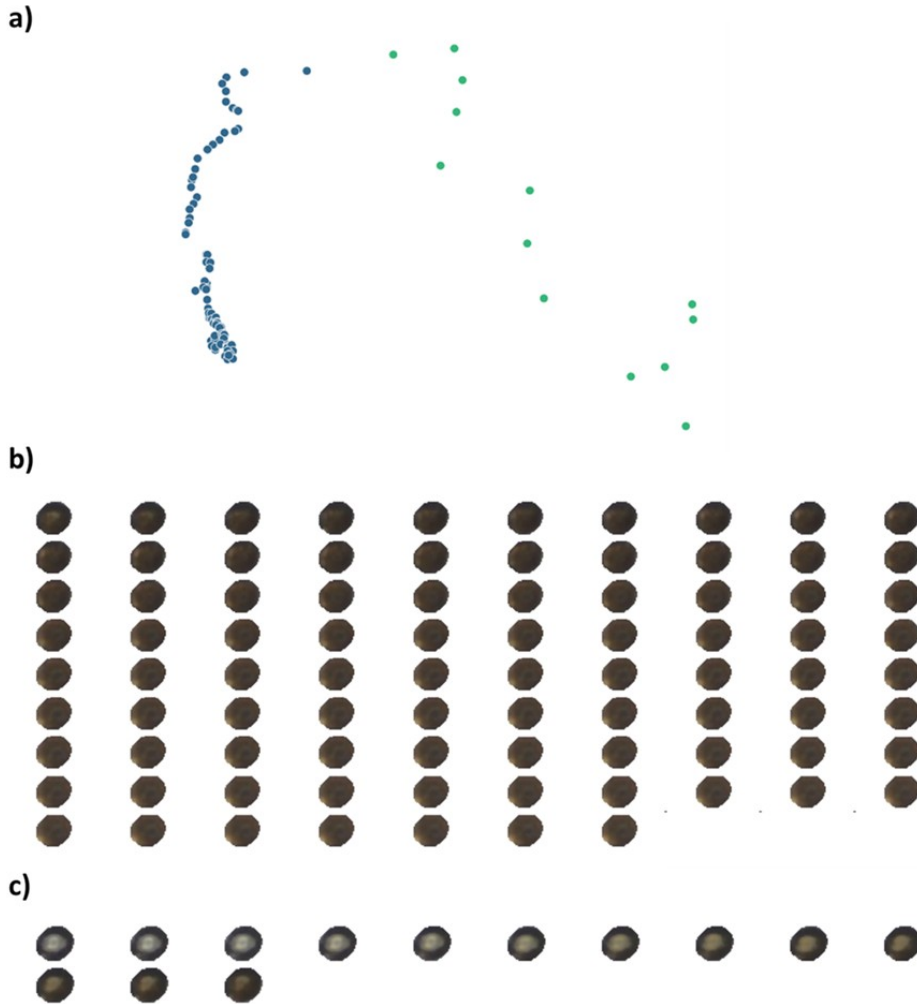


Figure 3.17: (a) PCA representation of ROI evolution as presented in Fig. 3.12, clustered into two groups. (b) Images of ROIs assigned to the 'corroded' cluster, showing significant presence of corrosion products. (c) Images of ROIs assigned to the 'non-corroded' cluster. Despite the overall grouping, some ROIs in (c) still exhibit clear signs of corrosion, which highlights the limitations of binary classification when applied to a gradual process.

smaller, at just over 7 %. This shows that the main statistical conclusions are robust and not sensitive to the specific parameters chosen for the classification.

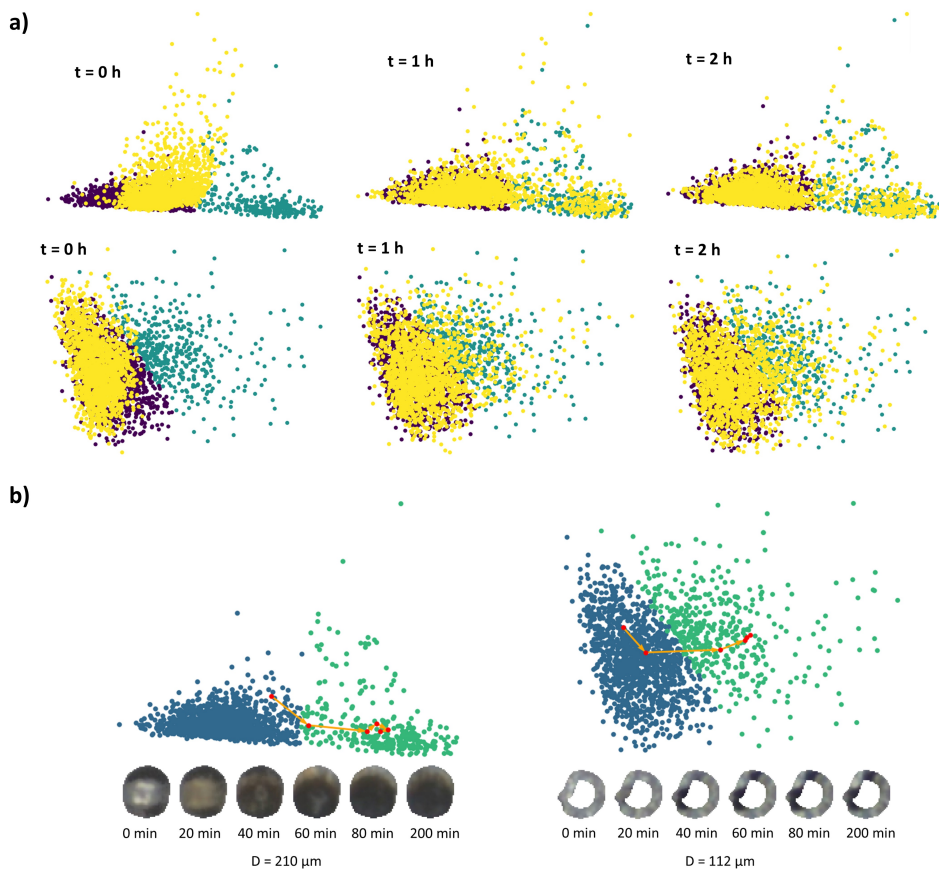


Figure 3.18: Consistency check validating the use of end-frame cluster centers. (a) Snapshots of the entire droplet population (yellow) in the feature space at different time points ($t=0\text{h}$, 1h , 2h), plotted against the final "non-corroding" (purple) and "corroding" (teal) clusters. The population begins in the non-corroding region and progressively evolves toward the corroding state. (b) The trajectories and corresponding image of a representative inner and a representative outer ROI over time, which link their path in the feature space to the physical accumulation of visible corrosion products.

3.S.8. EFFECT OF DROPLET SPATIALLY CLUSTERING BEHAVIOR ON CORROSION PRODUCT DEVELOPMENT IN OUTER ROIs

To determine if spatially isolated versus clustered droplets exhibited distinct corrosion behavior, droplets are separated into two equally sized groups ("isolated" and "clustered") using the median nearest-neighbor distance as a non-arbitrary threshold. We then compared both their final corrosion status and their corrosion kinetics. The analysis of the final corrosion status shows a slight difference between two groups, where the fraction of droplets exhibiting outer ROI corrosion is 29.9 % for the "clustered" group and 26.8 % for the "isolated" group. This indicates that the clustering behavior can slightly increase the overall probability of outer ROI corrosion. Meanwhile, an analysis of the

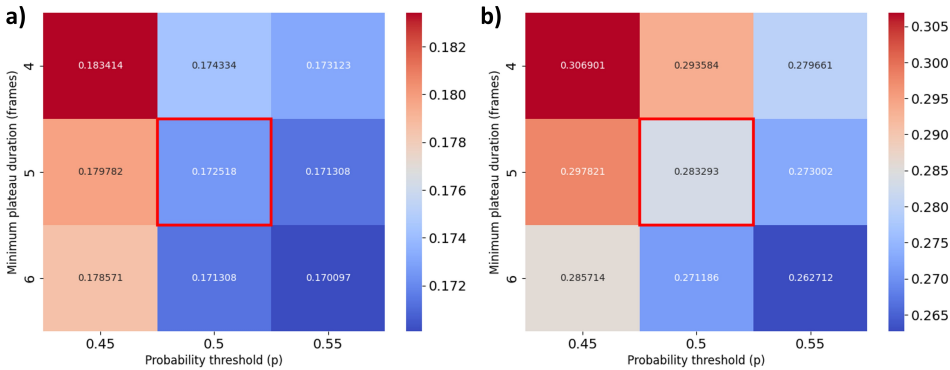


Figure 3.19: Sensitivity analysis of the corrosion status classification criteria. The heatmaps show the final fraction of droplets classified as corroding by detecting whether there is a stable high plateau appearing at the end of the probability curve in (a) the inner ROIs and (b) the outer ROIs, as a function of the probability threshold and the minimum plateau duration.

corrosion transition midpoint time shows a modest acceleration in the onset of outer ROI corrosion in the “clustered” group when compared to “isolated” droplets, as presented in Fig. 3.20.

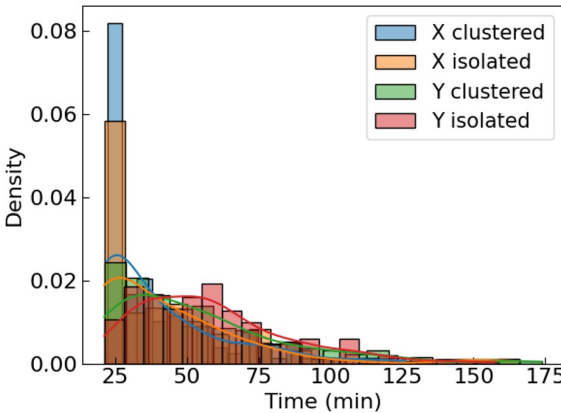


Figure 3.20: Transition midpoint for clustered and isolated droplets, classified by the median nearest-neighbor distance. The distance between two droplets is defined as their central distance extracted by their radius.

BIBLIOGRAPHY

- [1] X. Tang et al. "Atmospheric corrosion local electrochemical response to a dynamic saline droplet on pure Iron". In: *Electrochemistry Communications* 101 (2019), pp. 28–34. ISSN: 1388-2481. DOI: [10.1016/j.elecom.2019.01.011](https://doi.org/10.1016/j.elecom.2019.01.011). URL: [%3CGo%20to%20ISI%3E://WOS:000464134900006](https://www.sciencedirect.com/science/article/pii/S1388248119300006).
- [2] K. Zhang et al. "Monitoring atmospheric corrosion under multi-droplet conditions by electrical resistance sensor measurement". In: *Corrosion Science* 236 (2024). ISSN: 0010-938x. DOI: [ARTN11227110 . 1016 / j . corsci . 2024 . 112271](https://doi.org/10.1016/j.corsci.2024.112271). URL: [%3CGo%20to%20ISI%3E://WOS:001271277400001](https://www.sciencedirect.com/science/article/pii/S0010938X2400001).
- [3] J. Jiang et al. "Effect of length of gas/liquid/solid three-phase boundary zone on cathodic and corrosion behavior of metals". In: *Electrochimica Acta* 54.5 (2009), pp. 1426–1435. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2008.09.017](https://doi.org/10.1016/j.electacta.2008.09.017). URL: [%3CGo%20to%20ISI%3E://WOS:000263006100007](https://www.sciencedirect.com/science/article/pii/S001346860800007).
- [4] S. X. Li and L. H. Hihara. "Atmospheric-Corrosion Electrochemistry of NaCl Droplets on Carbon Steel". In: *Journal of the Electrochemical Society* 159.11 (2012), pp. C461–C468. ISSN: 0013-4651. DOI: [10.1149/2.035211jes](https://doi.org/10.1149/2.035211jes). URL: [%3CGo%20to%20ISI%3E://WOS:000309107200030](https://www.sciencedirect.com/science/article/pii/S001346511200030).
- [5] S. X. Li and L. H. Hihara. "The comparison of the corrosion of ultrapure iron and low-carbon steel under NaCl-electrolyte droplets". In: *Corrosion Science* 108 (2016), pp. 200–204. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2016.03.005](https://doi.org/10.1016/j.corsci.2016.03.005). URL: [%3CGo%20to%20ISI%3E://WOS:000375887100020](https://www.sciencedirect.com/science/article/pii/S0010938X1600020).
- [6] B. E. Risteen, E. Schindelholz, and R. G. Kelly. "Marine Aerosol Drop Size Effects on the Corrosion Behavior of Low Carbon Steel and High Purity Iron". In: *Journal of the Electrochemical Society* 161.14 (2014), pp. C580–C586. ISSN: 0013-4651. DOI: [10.1149/2.1171412jes](https://doi.org/10.1149/2.1171412jes). URL: [%3CGo%20to%20ISI%3E://WOS:000345975500055](https://www.sciencedirect.com/science/article/pii/S001346511400055).
- [7] J. Weissenrieder and C. Leygraf. "studies of filiform corrosion of iron". In: *Journal of the Electrochemical Society* 151.3 (2004), B165–B171. ISSN: 0013-4651. DOI: [10.1149/1.1645263](https://doi.org/10.1149/1.1645263). URL: [%3CGo%20to%20ISI%3E://WOS:000188943800029](https://www.sciencedirect.com/science/article/pii/S001346510400029).
- [8] E. Schindelholz, B. E. Risteen, and R. G. Kelly. "Effect of Relative Humidity on Corrosion of Steel under Sea Salt Aerosol Proxies". In: *Journal of the Electrochemical Society* 161.10 (2014), pp. C460–C470. ISSN: 0013-4651. DOI: [10.1149/2.0231410jes](https://doi.org/10.1149/2.0231410jes). URL: [%3CGo%20to%20ISI%3E://WOS:000341217500047](https://www.sciencedirect.com/science/article/pii/S001346511400047).
- [9] T. Tsuru, K. I. Tamiya, and A. Nishikata. "Formation and growth of micro-droplets during the initial stage of atmospheric corrosion". In: *Electrochimica Acta* 49.17-18 (2004), pp. 2709–2715. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2004.01.032](https://doi.org/10.1016/j.electacta.2004.01.032). URL: [%3CGo%20to%20ISI%3E://WOS:000221779900002](https://www.sciencedirect.com/science/article/pii/S001346860400002).

- [10] N. Van den Steen et al. "Predicting the effect of droplet geometry and size distribution on atmospheric corrosion". In: *Corrosion Science* 202 (2022). ISSN: 0010-938x. DOI: [ARTN11030810.1016/j.corsci.2022.110308](https://doi.org/10.1016/j.corsci.2022.110308). URL: [%3CGo%20to%20ISI%3E://WOS:000793828200001](https://www.sciencedirect.com/science/article/pii/S0010938X2200001).
- [11] E. Rahimi et al. "Atmospheric corrosion of iron under a single droplet: A new systematic multi-electrochemical approach". In: *Corrosion Science* 235 (2024). ISSN: 0010-938x. DOI: [ARTN11217110.1016/j.corsci.2024.112171](https://doi.org/10.1016/j.corsci.2024.112171). URL: [%3CGo%20to%20ISI%3E://WOS:001256286000001](https://www.sciencedirect.com/science/article/pii/S0010938X2400001).
- [12] M. Y. Wang et al. "Visualizing and understanding corrosion evolution beneath a condensed droplet using the multi-electrode array". In: *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 684 (2024). ISSN: 0927-7757. DOI: [ARTN13325210.1016/j.colsurfa.2024.133252](https://doi.org/10.1016/j.colsurfa.2024.133252). URL: [%3CGo%20to%20ISI%3E://WOS:001166707000001](https://www.sciencedirect.com/science/article/pii/S092777572400001).
- [13] N. Van den Steen et al. "An integrated modeling approach for atmospheric corrosion in presence of a varying electrolyte film". In: *Electrochimica Acta* 187 (2016), pp. 714–723. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2015.11.010](https://doi.org/10.1016/j.electacta.2015.11.010). URL: [%3CGo%20to%20ISI%3E://WOS:000367235600083](https://www.sciencedirect.com/science/article/pii/S001346861500083).
- [14] I. S. Cole et al. "Multiscale modelling of the corrosion of metals under atmospheric corrosion". In: *Electrochimica Acta* 56.4 (2011), pp. 1856–1865. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2010.10.025](https://doi.org/10.1016/j.electacta.2010.10.025). URL: [%3CGo%20to%20ISI%3E://WOS:000287951600021](https://www.sciencedirect.com/science/article/pii/S001346861000021).
- [15] W. C. Li et al. "Numerical simulation and experimental verification on the kinetics of droplet corrosion of carbon steel". In: *Electrochimica Acta* 514 (2025). ISSN: 0013-4686. DOI: [ARTN14560710.1016/j.electacta.2024.145607](https://doi.org/10.1016/j.electacta.2024.145607). URL: [%3CGo%20to%20ISI%3E://WOS:001399227500001](https://www.sciencedirect.com/science/article/pii/S001346862400001).
- [16] E. Schindelholtz, B. E. Risteen, and R. G. Kelly. "Effect of Relative Humidity on Corrosion of Steel under Sea Salt Aerosol Proxies". In: *Journal of the Electrochemical Society* 161.10 (2014), pp. C450–C459. ISSN: 0013-4651. DOI: [10.1149/2.0221410jes](https://doi.org/10.1149/2.0221410jes). URL: [%3CGo%20to%20ISI%3E://WOS:000341217500046](https://www.sciencedirect.com/science/article/pii/S001346511400046).
- [17] S. Wan et al. "Monitoring of atmospheric corrosion and dewing process by interlacing copper electrode sensor". In: *Corrosion Science* 150 (2019), pp. 246–257. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2019.02.008](https://doi.org/10.1016/j.corsci.2019.02.008). URL: [%3CGo%20to%20ISI%3E://WOS:000462108000023](https://www.sciencedirect.com/science/article/pii/S0010938X1900023).
- [18] B. G. Koushik et al. "Review on modelling of corrosion under droplet electrolyte for predicting atmospheric corrosion rate". In: *Journal of Materials Science & Technology* 62 (2021), pp. 254–267. ISSN: 1005-0302. DOI: [10.1016/j.jmst.2020.04.061](https://doi.org/10.1016/j.jmst.2020.04.061). URL: [%3CGo%20to%20ISI%3E://WOS:000601221700025](https://www.sciencedirect.com/science/article/pii/S100503022000025).
- [19] K. P. FitzGerald et al. "Atmospheric corrosion of copper and the colour, structure and composition of natural patinas on copper". In: *Corrosion Science* 48.9 (2006), pp. 2480–2509. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2005.09.011](https://doi.org/10.1016/j.corsci.2005.09.011). URL: [%3CGo%20to%20ISI%3E://WOS:000240767300010](https://www.sciencedirect.com/science/article/pii/S0010938X0500010).

- [20] S. Minaee et al. "Image Segmentation Using Deep Learning: A Survey". In: *Ieee Transactions on Pattern Analysis and Machine Intelligence* 44.7 (2022), pp. 3523–3542. ISSN: 0162-8828. DOI: [10.1109/TPAMI.2021.3059968](https://doi.org/10.1109/TPAMI.2021.3059968). URL: [10.1109/TPAMI.2021.3059968](https://www.wos.org/doi/10.1109/TPAMI.2021.3059968).
- [21] N. Otsu. "Threshold Selection Method from Gray-Level Histograms". In: *Ieee Transactions on Systems Man and Cybernetics* 9.1 (1979), pp. 62–66. ISSN: 0018-9472. DOI: [10.1109/TSMC.1979.4310076](https://doi.org/10.1109/TSMC.1979.4310076). URL: [10.1109/TSMC.1979.4310076](https://www.wos.org/doi/10.1109/TSMC.1979.4310076).
- [22] H. Samet and M. Tamminen. "Efficient Component Labeling of Images of Arbitrary Dimension Represented by Linear Bintree". In: *Ieee Transactions on Pattern Analysis and Machine Intelligence* 10.4 (1988), pp. 579–586. ISSN: 0162-8828. DOI: [10.1109/34.3918](https://doi.org/10.1109/34.3918). URL: [10.1109/34.3918](https://www.wos.org/doi/10.1109/34.3918).
- [23] R. Li et al. "Unsupervised Analysis of Optical Imaging Data for the Discovery of Reactivity Patterns in Metal Alloy". In: *Small Methods* 7.10 (2023). ISSN: 2366-9608. DOI: [10.1002/smt.202300214](https://doi.org/10.1002/smt.202300214). URL: [10.1002/smt.202300214](https://www.wos.org/doi/10.1002/smt.202300214).
- [24] Jiaqi Wang et al. "Review of Large Vision Models and Visual Prompt Engineering". In: *ArXiv abs/2307.00855* (2023).
- [25] A. Kirillov et al. "Segment Anything". In: *2023 Ieee/Cvf International Conference on Computer Vision, Iccv* (2023), pp. 3992–4003. ISSN: 1550-5499. DOI: [10.1109/ICCV51070.2023.00371](https://doi.org/10.1109/ICCV51070.2023.00371). URL: [10.1109/ICCV51070.2023.00371](https://www.wos.org/doi/10.1109/ICCV51070.2023.00371).
- [26] G. E. Hinton and R. R. Salakhutdinov. "Reducing the dimensionality of data with neural networks". In: *Science* 313.5786 (2006), pp. 504–507. ISSN: 0036-8075. DOI: [10.1126/science.1127647](https://doi.org/10.1126/science.1127647). URL: [10.1126/science.1127647](https://www.wos.org/doi/10.1126/science.1127647).
- [27] P. Z. Li, Y. Pei, and J. Q. Li. "A comprehensive survey on design and application of autoencoder in deep learning". In: *Applied Soft Computing* 138 (2023). ISSN: 1568-4946. DOI: [10.1016/j.asoc.2023.110176](https://doi.org/10.1016/j.asoc.2023.110176). URL: [10.1016/j.asoc.2023.110176](https://www.wos.org/doi/10.1016/j.asoc.2023.110176).
- [28] A. Savitzky and M. J. E. Golay. "Smoothing + Differentiation of Data by Simplified Least Squares Procedures". In: *Analytical Chemistry* 36.8 (1964), pp. 1627–&. ISSN: 0003-2700. DOI: [10.1021/ac60214a047](https://doi.org/10.1021/ac60214a047). URL: [10.1021/ac60214a047](https://www.wos.org/doi/10.1021/ac60214a047).
- [29] R. W. Schafer. "What Is a Savitzky-Golay Filter?" In: *Ieee Signal Processing Magazine* 28.4 (2011), pp. 111–117. ISSN: 1053-5888. DOI: [10.1109/MSP.2011.941097](https://doi.org/10.1109/MSP.2011.941097). URL: [10.1109/MSP.2011.941097](https://www.wos.org/doi/10.1109/MSP.2011.941097).
- [30] V. Soulié et al. "Salt-induced iron corrosion under evaporating sessile droplets of aqueous sodium chloride solutions". In: *Materials and Corrosion-Werkstoffe Und Korrosion* 68.9 (2017), pp. 927–934. ISSN: 0947-5117. DOI: [10.1002/maco.201609319](https://doi.org/10.1002/maco.201609319). URL: [10.1002/maco.201609319](https://www.wos.org/doi/10.1002/maco.201609319).
- [31] S. P. Knight et al. "The effect of droplet size on the localized corrosion of high-strength aluminum alloys". In: *Materials and Corrosion-Werkstoffe Und Korrosion* 67.12 (2016), pp. 1294–1307. ISSN: 0947-5117. DOI: [10.1002/maco.201609045](https://doi.org/10.1002/maco.201609045). URL: [10.1002/maco.201609045](https://www.wos.org/doi/10.1002/maco.201609045).

- [32] F. Lequien et al. "Corrosion influence on the evaporation of sessile droplet". In: *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 546 (2018), pp. 59–66. ISSN: 0927-7757. DOI: [10.1016/j.colsurfa.2018.02.047](https://doi.org/10.1016/j.colsurfa.2018.02.047). URL: [%3CGo%20to%20ISI%3E://WOS:000429302300007](https://www.sciencedirect.com/science/article/pii/S0927775718300007).
- [33] G. V. Kuznetsov et al. "Evaporation modes of LiBr, CaCl, LiCl, NaCl aqueous salt solution droplets on aluminum surface". In: *International Journal of Heat and Mass Transfer* 126 (2018), pp. 161–168. ISSN: 0017-9310. DOI: [10.1016/j.ijheatmasstransfer.2018.05.040](https://doi.org/10.1016/j.ijheatmasstransfer.2018.05.040). URL: [%3CGo%20to%20ISI%3E://WOS:000442979300014](https://www.sciencedirect.com/science/article/pii/S0017931018300014).
- [34] V. Soulié et al. "The evaporation behavior of sessile droplets from aqueous saline solutions". In: *Physical Chemistry Chemical Physics* 17.34 (2015), pp. 22296–22303. ISSN: 1463-9076. DOI: [10.1039/c5cp02444g](https://doi.org/10.1039/c5cp02444g). URL: [%3CGo%20to%20ISI%3E://WOS:000359971300060](https://www.sciencedirect.com/science/article/pii/S146390761500060).

4

A WEAKLY SUPERVISED FRAMEWORK FOR DROPLET-LEVEL CORROSION INFERENCE FROM GLOBAL MEASUREMENTS

This chapter will be submitted as:

Zhang, K.; Mol, A.; Gonzalez-Garcia, Y., A Weakly Supervised Framework for Droplet-Level Corrosion Inference from Global Measurements

The Python code for the analysis involved in this work is available at:

<https://github.com/KeerZhang345/MILcorr.git>

Abstract

In different stages of atmospheric corrosion, discontinuous electrolyte layers often form as isolated droplets, each with distinct physicochemical and geometrical characteristics. While global corrosion kinetics can be measured, the contribution of individual droplets remains unknown under realistic multi-droplet exposure conditions. In this chapter, we present a weakly supervised learning framework that extracts droplet-level corrosion behavior using only time-resolved optical imaging and global measurements of material loss from an electrical resistance sensor.

Framed as a multiple-instance regression problem, the model learns to reconstruct global corrosion curves by inferring per-droplet contributions from their spatiotemporal visual features. Despite the absence of droplet-level labels, the model reveals physically meaningful patterns: droplets with pronounced color evolution or larger initial size contribute more significantly to total damage, and inner-region corrosion often precedes spreading to outer regions.

Temporal correlation and spatial inspection confirm that predicted droplet-specific loss aligns with image-based evidence of corrosion propagation. This approach demonstrates how weak supervision can uncover localized corrosion mechanisms from global observations, providing a scalable complementary to droplet-level electrochemical methods and offering new opportunities for data-driven mechanistic studies in atmospheric corrosion.

4.1. INTRODUCTION

Corrosion of metallic materials is a pervasive and costly degradation process that accounts for an estimated 3.4% of global GDP, with atmospheric corrosion contributing approximately half of that total cost[1]. Atmospheric corrosion occurs when metallic surfaces are exposed to humid or salt-containing environments, leading to the formation of thin electrolyte layers that enable electrochemical reactions. Under outdoor or semi-controlled laboratory exposures, such as salt spray testing, these electrolyte layers are often discontinuous, especially at the early stages of exposure. The thin electrolyte layer can therefore be regarded as a collection of micro-droplets with diverse size, shape, spacing, and chemistry, each acting as a localized electrochemical cell that drives heterogeneous corrosion activity[1, 2]. Global corrosion kinetics under such multi-droplet conditions can be measured using non-electrochemical methods such as gravimetric mass loss[3, 4], or electrical resistance (ER) monitoring[5–8], and, under certain conditions, electrochemical techniques such as electrochemical impedance spectroscopy (EIS)[6, 9, 10] and galvanic coupling[11]. However, while these methods capture overall corrosion behavior, they cannot resolve the individual contribution of each droplet, whose local electrochemical effects remain experimentally inaccessible.

Understanding how individual droplets contribute to overall corrosion behavior is crucial for interpreting experimental data and validating mechanistic models, such as finite element modeling (FEM)[12–17]. Conventional FEM studies typically validate their predictions by comparing simulated and measured global corrosion losses, yet this approach overlooks localized interactions that arise when multiple droplets coexist on the same surface. In realistic multi-droplet systems, evaporation rates may differ when droplets shield one another from airflow or radiation[18, 19], and thin electrolyte layers can coalesce or form microbridges between neighboring droplets[20, 21], thereby altering local electrochemical conditions. Most existing validation data come from isolated single-droplet experiments[16, 22, 23], performed under idealized free-corrosion conditions, which do not capture these multi-droplet effects. Achieving droplet-level validation under realistic conditions would thus enhance the mechanistic fidelity and predictive capability of FEM-based corrosion models[12, 24].

Several spatially resolved electrochemical techniques, such as wire beam electrode (WBE) arrays[23, 25–27], and the scanning vibrating electrode technique (SVET)[2, 28], have been developed to probe localized corrosion behavior. However, their applicability to realistic multi-droplet systems remains limited. WBE can map current distributions under single droplets and is, in principle, also applicable to multi-droplet configurations. However, its spatial resolution is constrained by the physical size of the electrode elements, making it impractical for micrometer-scale droplets, which is the typical size range in realistic multi-droplet corrosion scenarios. SVET, which detects local ionic current density by scanning potential gradients in the electrolyte, also faces challenges under multi-droplet conditions: the probe must be immersed within each droplet, vibrations can distort droplet geometry, and positioning becomes difficult for many small, irregular droplets. Consequently, both methods are limited to idealized scenarios and cannot provide comprehensive, non-invasive mapping of corrosion activity across large

droplet populations.

To overcome these experimental limitations, we adopt a data-driven imaging approach that uses surface optical imaging[29–33] as a non-invasive probe of corrosion dynamics under realistic multi-droplet conditions. Time-resolved image sequences capture the evolution of individual droplets, allowing quantitative extraction of geometrical and color-based features that reflect the formation and spread of corrosion products. In our recent work[34], we demonstrated that these optical features can be translated into a probabilistic representation of corrosion product formation in both the inner and outer droplet regions. This confirmed that color evolution provides physically meaningful indicators of localized corrosion activity across large droplet populations.

4

Building on these findings, the remaining challenge is to quantify how individual droplets contribute to the globally measured corrosion loss during realistic multi-droplet exposures, a quantity that is experimentally inaccessible with existing electrochemical or imaging methods. The objective of this study is to recover droplet-level corrosion behaviour from solely global electrical resistance measurements by exploiting the spatiotemporal information contained in time-resolved optical imaging. Our aim is to determine whether droplet geometry and color evolution can be used to infer physically meaningful per-droplet contributions to the overall corrosion signal.

To achieve this, we formulate a multiple-instance regression (MIR) task[35–46], where each image frame is treated as a collection of droplet instances, described by static geometric properties and dynamic color descriptors. Similar formulations have been successfully applied in remote sensing[37, 38, 42, 44], and medical imaging[36, 39, 41], where global quantities are linked to collections of localized observations. A shared neural model maps these per-droplet features to latent corrosion contributions whose sum reconstructs the measured global loss. This weakly supervised framework enables us to attribute corrosion activity to individual droplets under realistic exposure conditions without requiring droplet-level labels. In doing so, the study provides a new approach for resolving localized corrosion mechanism from aggregate measurements.

4.2. EXPERIMENTAL PLATFORM AND DATASET PREPARATION

The dataset used for model development was obtained using the multi-droplet corrosion platform introduced in our previous work[5]. The system integrates in-situ ER measurements with time-resolved optical imaging to enable synchronized monitoring of global corrosion kinetics and localized droplet evolution (Fig. 4.1a). Because the experimental methodology has been validated previously, only the elements relevant to data quality and model reproducibility are summarized here.

Carbon-steel ER sensors (grade EN 10130 (DC01), nominal thickness 25 μm) were prepared following the established protocol[5] and exposed to a fine spray of 1 M NaCl inside a sealed chamber. During exposure, ER was recorded continuously and converted to corrosion depth using the standard calibration for this sensor geometry. Multiplying by the active track area yields the global corrosion-volume loss used as the model target

(Fig. 4.1b). In parallel, a fixed field-of-view covering $11.65 \times 8.72 \text{ mm}^2$ was imaged using a color camera (Manta G319-C, Allied Vision Technologies, Germany) equipped with a zoom lens (Zoom 1:6.5 W.D.240mm, Unitron Ltd., USA) and uniform ring illumination (Fig. 4.1c). The optical stream captures the spatial distribution and temporal evolution of all droplets on the surface.

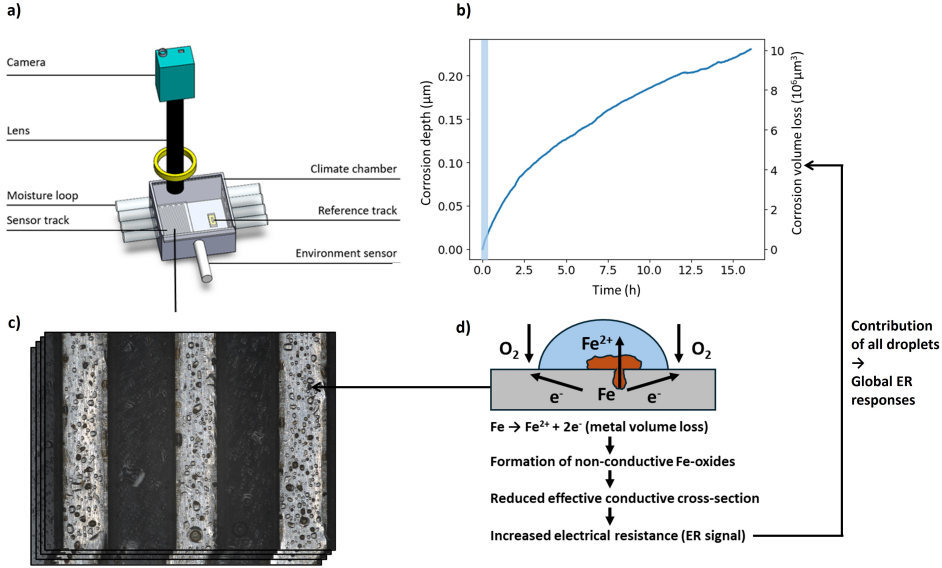


Figure 4.1: Experimental data acquisition loop. (a) Schematic of the in-situ optical imaging-ER setup used for multi-droplet corrosion experiments. (b) ER-derived corrosion evolution showing accumulated corrosion depth (left axis) and corresponding corrosion volume loss (right axis) over time. The light blue zone at the beginning of the test indicates the period when the system is not yet stabilized and is therefore excluded from subsequent analysis. (c) Optical recording of the sensor track showing evolution of droplets deposited on the ER sensor surface (d) Schematic illustration of the mechanistic link between localized corrosion beneath droplets and the global ER signal. Metal dissolution and the formation of non-conductive Fe-oxides reduce the effective conductive cross-section, leading to an increase in measured ER. Each droplet thus contributes incrementally to the total corrosion volume loss shown in (b).

To ensure stability of the ER signal, an initial 25-min period dominated by thermal equilibration was excluded following the procedure established in our previous work[5]. All subsequent analyses define this point as $t = 0$. Removing the corresponding 14 frames yields 565 candidate samples. From these, one representative mid-exposure frame and one early frame from the excluded stabilization interval were reserved as the principal component analysis (PCA) calibration set for color feature extraction (Section 4.3.1). Because the early calibration frame was already excluded, only the mid-exposure calibration frame reduces the dataset size, resulting in 564 usable samples.

Each sample contains the extracted droplet-level optical features and the corresponding global target value representing the ER-derived material loss at that time. The mecha-

nistic link between these measurements is illustrated in Fig. 4.1d: corrosion initiated beneath droplets forms non-conductive iron oxide products, which reduce the effective conductive cross-section of the sensor track and increase the measured ER signal. Simultaneously, the growth of these corrosion products alters the local optical response, enabling the extracted color and geometrical features to serve as quantitative descriptors of localized corrosion activity.

As discussed previously, corrosion products can accumulate both inside and around the initial droplet footprint. Therefore, both areas are included in the subsequent analysis and are referred to as the inner (under-droplet) and outer (surrounding) regions of interest (ROIs) (Fig. 4.2c). These two ROIs represent the primary locations of corrosion product buildup.

4

4.3. METHODOLOGY

This section outlines the framework used to model droplet-driven atmospheric corrosion from weak supervision. We first describe the imaging and ER datasets, including droplet segmentation and feature extraction. We then present the artificial neural network (ANN) model, formulated as a MIR problem, which learns to relate droplet-level features to global corrosion loss. Model interpretability is addressed through feature attribution and ablation analysis. Finally, we detail the droplet-level validation strategies used to examine the model's spatial, temporal, and geometric consistency with observed corrosion behavior.

In our framework, each time-resolved optical image constitutes a bag of droplet instances, each represented by a feature vector that combines static geometric features (such as area and aspect ratio) and dynamic color descriptors that evolve with corrosion product accumulation. The geometrical features are treated as static because previous work [34] showed that corrosion products induced by a droplet primarily form within and around its initial footprint, and that the initial droplet size has a significant impact on the kinetics of product formation. Consequently, the initial droplet geometry provides a physically meaningful reference for tracking corrosion evolution. In addition, under 1 M NaCl conditions, droplet spreading or shrinkage during exposure is minimized[47, 48], further ensuring that this static representation introduces negligible geometric bias. In contrast, the color descriptors vary over time, reflecting the progressive accumulation and spatial redistribution of corrosion products within these fixed regions.

A shared multilayer perceptron (MLP) is applied to every droplet feature vector, and the predicted per-droplet outputs are aggregated to reproduce the measured global corrosion signal. This shared-weight design maintains physical consistency across droplets while enabling the model to learn nonlinear dependencies between droplet features and corrosion volume loss. Note that the objective is to quantify how corrosion product development is associated with each droplet and how these contributions collectively determine the global corrosion volume loss within a single exposure. The study thereby emphasizes intra-run interpretability and physically consistent attribution over cross-run generalization.

4.3.1. IMAGE PROCESSING AND FEATURE EXTRACTION

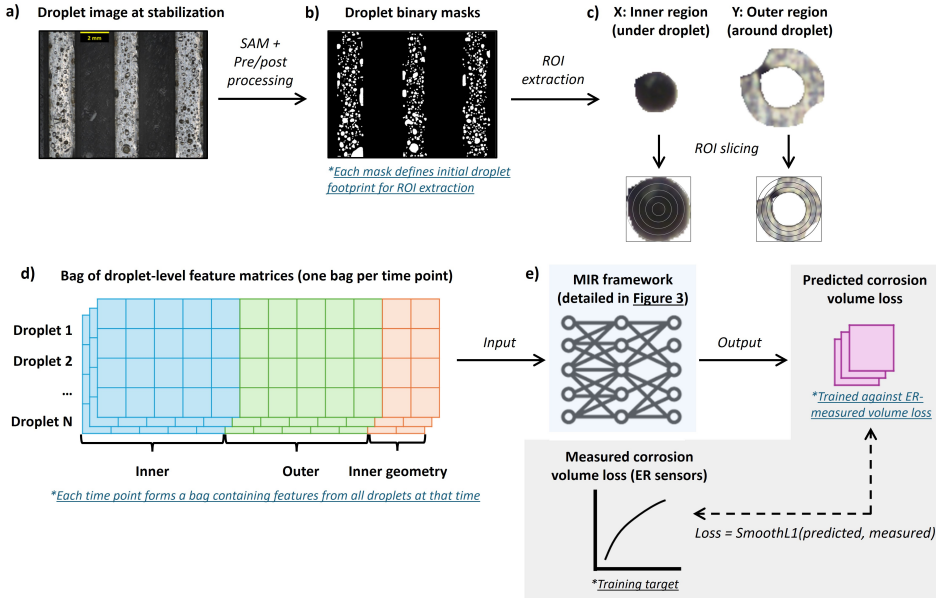


Figure 4.2: Workflow illustrating droplet-level feature extraction and MIR modeling of corrosion volume loss. Panels (a-c) are partially adapted from our previous work[34] (a) Optical image of the droplet-covered surface at stabilization. (b) Droplet binary masks obtained using the SAM model with pre- and post-processing, where each mask defines the initial droplet footprint for ROI extraction. (c) Inner (X) and outer (Y) ROIs representing regions under and around each droplet, respectively, which are further interpolated into a size of 32×32 pixels and divided into ring-shaped slices for color-based feature extraction. (d) Droplet-level feature matrices across all time points (each time point forming a bag containing all droplets) that serve as model input. (e) The MIR framework (detailed in Fig. 4.4) maps per-droplet features to the global corrosion volume loss. The model is trained in a supervised manner, using ER-measured corrosion volume loss as the target and Huber loss (SmoothL1) as the loss function.

Droplet segmentation and feature extraction follow a workflow similar to that described in our previous study[34], with modifications to accommodate the MIR framework adopted here. Each droplet in the initial optical image (Fig. 4.2a) was segmented from the background using the Segment Anything Model (SAM), a pre-trained large vision model (LVM) developed by Kirillov et al.[49] The segmentation produced binary masks that define the footprint of each droplet (Fig. 4.2b). These masks were applied across the entire image sequence as the pixel coordinates for extracting droplet-specific image segments at every recorded time point.

Corrosion product buildup occurs both inside and around the initial droplet footprints. Two regions of interest (ROIs), including an inner region (X), corresponding to the droplet footprint, and an outer region (Y), extending beyond it by a factor of 2 in equivalent diameter (Fig. 4.2c), are considered (for more details, see Supplementary Information Section 4.S.1). Overlapping outer ROIs are trimmed by subtracting intersecting inner regions from neighboring droplets, and intersections with dark inter-track areas (non-

metallic support) are excluded to prevent false detections.

Each segmented droplet is resized to 32×32 pixels using a high-quality bicubic interpolation (`cv2.INTER_CUBIC`) to preserve feature integrity, and masked to exclude non-droplet regions (Fig. 4.2c), following the same procedure as described in our previous work[34]. Within both ROIs, ring-shaped sub-regions are extracted: five rings, including the center for the inner ROI, and three rings, excluding the center for the outer ROI. The mean RGB and HSV channel values within each ring serve as the primary color descriptors: 30 features for the inner ROI and 18 for the outer ROI. Normalization ensures consistent extraction of the same number of sub-regions from droplets of different sizes. Size normalization removes absolute scale information; two geometrical descriptors, including the equivalent diameter and aspect ratio of the inner ROIs, are calculated separately from the original segmentation masks and retained as static features in the dataset (Fig. 4.2d).

Raw color descriptors often exhibit high inter-channel correlation and sensitivity to pixel-level noise. To mitigate these effects and reduce dimensionality while preserving meaningful variation, PCA is applied separately to the color features of inner and outer ROIs to enhance robustness and reduce color feature dimensionality, thereby achieving a balance with the geometrical features. PCA and scaling parameters are fitted using a fixed calibration set composed of two images, one from early frames recorded during the initial stabilization period (thus automatically excluded from the full dataset, as discussed earlier in Section 4.2) and the other at the mid-exposure stage. These frames are excluded from model training and testing to prevent data leakage.

The resulting droplet-level feature vectors, combining static geometric descriptors with dynamic PCA-reduced color components, are organized frame by frame into feature matrices that represent all droplets in the field of view (Fig. 4.2d). Each frame thus forms a “bag” of droplet instances associated with a single global corrosion measurement from the ER sensor. These instance-level features serve as the input to the MIR framework (Fig. 4.2e), which learns to map the aggregate behavior of all droplets within a frame to the experimentally measured corrosion volume loss. The architecture and training procedure of this MIR model are described in the following sections.

4.3.2. DATASET PREPARATION AND SAMPLING STRATEGY

The dataset consists of a time-ordered series of frames acquired during the 16-hour exposure experiment. Each frame provides a “bag” of droplet-level feature vectors (Section 4.3.1), together with a corresponding global corrosion volume obtained from ER measurements. Following the preprocessing described in Section 4.2, and the removal of PCA calibration frames (Section 4.3.1), the modeling dataset comprises 564 cleaned samples (Fig. 4.3a).

The overall objective is to identify how localized droplet features relate to global corrosion loss rather than to forecast temporal evolution. The samples are treated as independent observations rather than sequential time series. Therefore, the training, validation,

and test subsets are created by non-sequential random sampling rather than contiguous temporal splits.

The sampling strategy consists of two stages. First, assessing how dataset size affects model performance and second, partitioning of the clean data set for ensemble learning.

In the first stage (Fig. 4.3b), the data are repeatedly split into three subsets: training, validation, and temporary hold-out. For each random seed, a variable training proportion α_i is used, and the remaining data are split 1:1 into validation and temporary evaluation subsets. The training subset always includes two anchor frames (one early and one late exposure sample) to ensure full coverage of corrosion progression. The temporary evaluation set is used solely to compare model performance across training sizes and does not participate in model optimization.

In the second stage, partitioning is performed for ensemble modeling (Fig. 4.3c). Using a fixed random seed, the cleaned dataset is divided into a test set of proportion α^* (selected from the training-size analysis) and a training-validation pool containing the remaining $1 + \alpha^*$ proportion of samples. The test set remains unseen throughout model training and ensemble construction. The training-validation pool serves as input to the ensemble, from which each ensemble member draws its own bootstrapped training and validation subsets.

4.3.3. MODEL ARCHITECTURE

The architecture of ANN, formulated as an MIR model, is summarized in Fig. 4.4. The MIR framework employs a shared multilayer perceptron (MLP) that processes each droplet's feature vector independently using identical weights. The resulting droplet-level predictions are then summed to obtain the global (sample-level) estimate of material loss. This additive formulation reflects the physical nature of the process: since localized corrosion product buildup corresponds to underlying metal volume loss, the total material loss accumulates across all droplets, allowing the global corrosion response to be interpreted as the sum of these individual droplet contributions.

The geometrical descriptors remain constant across frames, yet they provide the contextual structure the model needs to interpret the color-based corrosion signal. Droplets with different sizes or shapes can produce distinct corrosion dynamics even when their color trajectories look similar, so the model must account for these variations. Because these descriptors do not change over time, they complicate the attribution of temporal effects. This issue is examined in detail using SHAP and targeted ablation analyses in Section 4.3.6.

4.3.4. TRAINING AND ENSEMBLE STRATEGY

The model is evaluated across 30 independent runs to determine the minimal training set size required for reliable performance. This balances the statistical reliability and computational cost for each candidate size. Each run uses a different random seed to generate a unique train-validation-evaluation split (Section 4.3.2). The same set of 30 seeds is reused across all training sizes to ensure matched and directly comparable re-

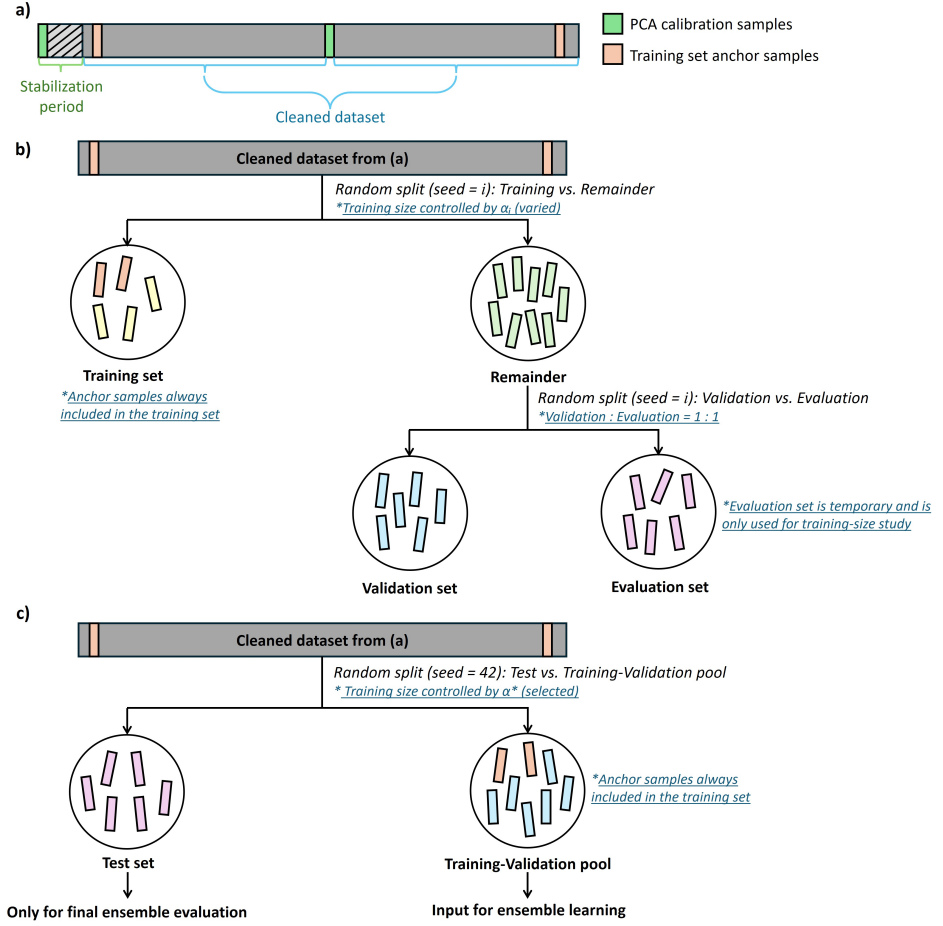


Figure 4.3: Overview of dataset preprocessing and sampling strategy. (a) Removal of the stabilization period and PCA calibration samples to obtain the cleaned dataset. Two anchor samples (one early-stage and one late-stage frame) are marked and will always be included in subsequent training sets. (b) Splitting procedure used during the training-set size analysis. For each random seed i , the cleaned dataset is first partitioned using a variable ratio α_i , which controls the training-set proportion and is varied across tested sizes. The remainder is then split 1:1 into validation and temporary evaluation subsets, resulting in an overall ratio of $1 : \alpha_i : \alpha_i$ for training : validation : evaluation. (c) Final split used for ensemble learning. A fixed random seed (seed = 42) is used to partition the cleaned dataset into a test set and a training-validation pool using the selected ratio α^* obtained from (b). The test set is used only for final ensemble evaluation, while the remaining $(1 + \alpha^*)$ proportion constitutes the training-validation pool and serves as input to the ensemble learning (Fig. 4.5).

sults. All runs share identical network architecture and training hyperparameters.

Model training employs the Adam optimizer (learning rate = 1×10^{-3} , weight decay = 1×10^{-4}) for up to 6000 epochs. Early stopping is triggered if the validation loss does not improve for 50 consecutive epochs, and the learning rate is halved after 10 stagnant

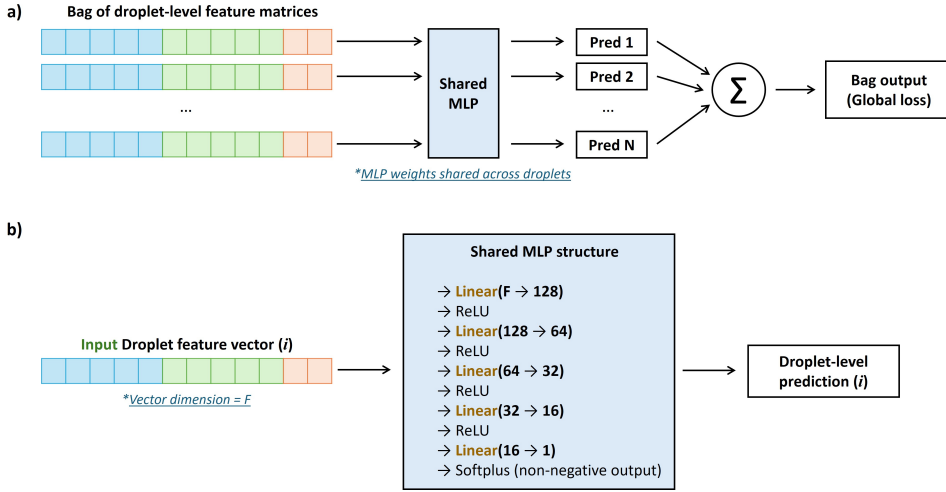


Figure 4.4: Multiple-instance regression (MIR) architecture used to link droplet-level features to the globally measured corrosion volume loss. (a) At each time point, the optical image is represented as a bag of droplet-level feature vectors, each combining PCA-reduced color descriptors and static geometrical attributes. A shared MLP processes all droplets independently and produces a droplet-level contribution. These contributions are summed to obtain the predicted global material loss. (b) Internal structure of the shared MLP, consisting of five fully connected layers, each followed by ReLU activation, except for the final Softplus output, which enforces non-negative per-droplet predictions.

epochs, down to a minimum of 1×10^{-5} . The batch size is 4 for both training and validation to maintain GPU efficiency given the large per-sample computational load, as each sample corresponds to a full droplet field which contains hundreds of instance-level feature vectors. The loss function is Smooth L1 (Huber) Loss, which is chosen for its balance between sensitivity to small deviations and robustness against occasional large errors. All models are initialized from scratch using Kaiming normal weight and zero bias, with a fixed random seed (separate from the data-split seeds) to ensure reproducibility of initialization and internal stochasticity.

The optimal training size is the smallest subset for which performance (Section 4.3.5) remains consistently high across 30 independent runs. Once this optimal size (α^*) is established, ensemble learning is used to improve robustness. The predefined training-validation pool and test set (Section 4.3.2) are used as input for the ensemble process. Each of the k ensemble models is trained on a bootstrapped subset of the training-validation pool, maintaining the training-validation ratio $1: \alpha^*$. Each subset always contains two anchor samples (shown by hatched bars) representing early and late exposure stages. All ensemble models have the same architecture and training setup. During inference, all k models generate independent predictions on the fixed test set, and their average outputs form the ensemble prediction for the final performance evaluation. The entire ensemble workflow is depicted in Fig. 4.5.

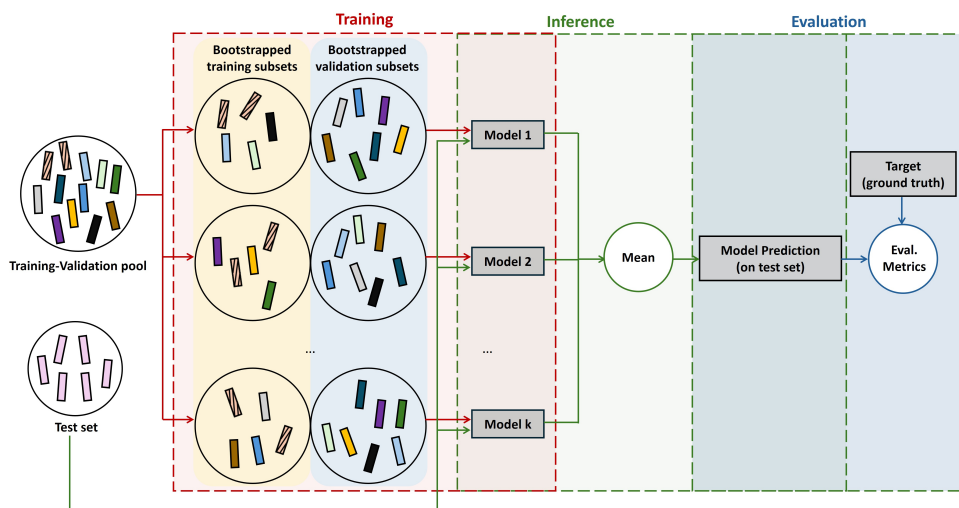


Figure 4.5: Ensemble learning workflow. The ensemble process starts from the predefined training–validation pool and fixed test set (Section 4.3.2). Each of the k ensemble models is trained on a bootstrapped subset of the training–validation pool, with training : validation ratio $1 : \alpha^*$, where α^* is the same optimal ratio used for the test split. Each bootstrapped training set always includes two anchor samples (hatched bars) representing early and late exposure stages. All models share identical architectures and training configurations. During inference, each model produces independent predictions on the fixed test set, which are averaged to obtain the ensemble prediction. Model performance is evaluated against the ground truth using standard metrics.

4.3.5. MODEL EVALUATION

Model performance is mainly measured using the coefficient of determination (R^2). For each candidate training set size, the model is trained and tested over 30 independent runs, using a fixed set of random seeds for data splitting (Section 4.3.2). The smallest training size that includes all 30 runs to achieve $R^2 \geq 0.9$ on the evaluation set is called the minimal sufficient training size. Additionally, the mean and standard deviation of R^2 , RMSE, and MAE across the 30 runs are reported to illustrate the accuracy and variability between runs for each training size.

After determining the minimal sufficient training size, ensemble learning is utilized (Section 4.3.4). Each ensemble is built by training 20 learners on bootstrap samples from the selected training set. The ensemble’s performance is evaluated using the same metrics (R^2 , RMSE, MAE), emphasizing the reproducibility of the ensemble results multiple constructions. To evaluate stability, multiple ensembles are trained with identical hyperparameters, and their performance metrics are reported individually.

4.3.6. MODEL INTERPRETABILITY

Model interpretability aims to understand how the trained model uses input features to produce the overall material loss prediction. Since the architecture processes each droplet independently through a shared MLP and adds their contributions, interpretability is assessed at the feature level rather than at the level of individual droplets.

The influence of each input feature on the global prediction is analyzed using SHAP values and ablation tests. As discussed earlier in [Section 4.3.3](#), SHAP can underestimate the importance of temporally static features over time because it attributes importance based on individual feature perturbations. To address this, an ablation experiment is conducted in which geometric features are set to zero while color features remain unchanged. Model performance metrics (R^2 , RMSE, MAE) are compared between the original and ablated inputs across 100 randomized trials, each with 200 samples.

4.3.7. DROPLET-LEVEL BEHAVIOR VALIDATION

While global interpretability explains how the model utilizes input features, it is equally important to ensure that individual droplet predictions align with physically observable corrosion processes in reality. Since the model combines droplet contributions to calculate the overall loss, analyzing droplet-level behavior serves as a validation method rather than a means of interpretability.

The following analyses are performed:

- **Classification consistency:** Droplets with predicted final material loss above a threshold are compared with those labeled as corroded via unsupervised clustering of the final-stage droplet image. Agreement is assessed using precision, recall, and F1-score, to determine if the predicted droplet activity matches visually identifiable corrosion.
- **Temporal correlation:** For each droplet, the Spearman correlation is calculated between the predicted material-loss trajectory and the related time series of aggregated color features. This determines whether predicted corrosion onset and growth align with observable changes in droplet color.
- **Spatial alignment:** For selected droplets, the evolution of predicted losses is compared qualitatively with the visual progression of their inner and outer ROIs. This analysis verifies that the predicted evolution of material loss matches the visual emergence of corrosion products.

In addition to these validation steps, we examine how the predicted material loss varies with the initial droplet size. This population-level analysis provides insight into whether the model accurately captures physical geometric effects, such as increased corrosion volume loss for larger droplets, as shown in a previous investigation[50, 51].

Collectively, these analyses assess whether the droplet-level predictions display realistic temporal and spatial patterns, complementing the global interpretability findings described in [Section 4.3.6](#).

4.4. RESULTS AND DISCUSSION

This section presents the results of the proposed weakly supervised learning framework, which integrates data-driven insights with physical understanding of corrosion behav-

ior. It starts by outlining the data statistics, then evaluates the model's global consistency by comparing predicted material loss with measurements over time. The results show that the model accurately captures corrosion kinetics even with a limited number of training samples. Next, we explore how the model interprets input features across all droplets using feature attribution and ablation studies, highlighting the importance of both localized color changes and geometric factors such as droplet size. Finally, we validate droplet-level behavior using unsupervised clustering, temporal correlation analysis, and spatial evolution analysis, and examine how the predicted loss depends on droplet geometry.

4.4.1. DATA STATISTICS

A total of 606 droplets were detected in the initial droplet-field image. Their diameter distribution is shown in Fig. 4.6a. The histogram indicates a positively skewed distribution, accurately modeled by a log-normal probability density function fitted to the data. This aligns with typical spray-deposition behavior, where small droplets are prevalent and larger droplets are less common. A kernel density estimate (KDE) is also included to provide a smooth view of the underlying distribution.

As described in Section 4.3.1, PCA was applied to the raw color features extracted from each droplet. For both the inner and outer regions of interest (ROIs), the first five principal components (PCs) account for more than 95% of the variance in the calibration set (Fig. 4.6b and 4.6c). Consequently, each droplet's color data is reduced to ten PCA coefficients (five from each ROI). Along with two geometrical descriptors, this creates a 12-dimensional feature vector for each droplet. PCA thus offers a concise, noise-reduced way to represent high-dimensional pixel data, balancing color and geometric features.

Fig. 4.6d and 4.6e show the temporal evolution of the average inner- and outer-ROI PCs across all droplets. The inner-ROI PCs exhibit slightly greater temporal variation, especially in PC1 and PC3, while the outer-ROI PCs show slightly more gradual changes except for PC1. These trends confirm that the extracted PCA features effectively capture the continuous color evolution during exposure by reflecting the ongoing formation of corrosion products.

The smooth and consistent PC trajectories also suggest a favorable signal-to-noise ratio for learning temporal patterns, which aligns with the training-size sufficiency analysis in Section 4.3.2.

4.4.2. GLOBAL PERFORMANCE COMPARISON

To find the smallest training-set size that remains sufficient, model performance was evaluated across 30 independent runs for each candidate size. As illustrated in Fig. 4.7a-d, the model rapidly improves as the sample count increases. The percentage of runs with $R^2 \geq 0.9$ increases sharply and levels off around 40 samples. Meanwhile, both RMSE and MAE decrease steadily, with confidence intervals tightening. Based on this, a training set of 40 samples (about 1/14 of the dataset) was chosen for subsequent experiments. This ensures the training data covers sufficient variations in features, as temporally close

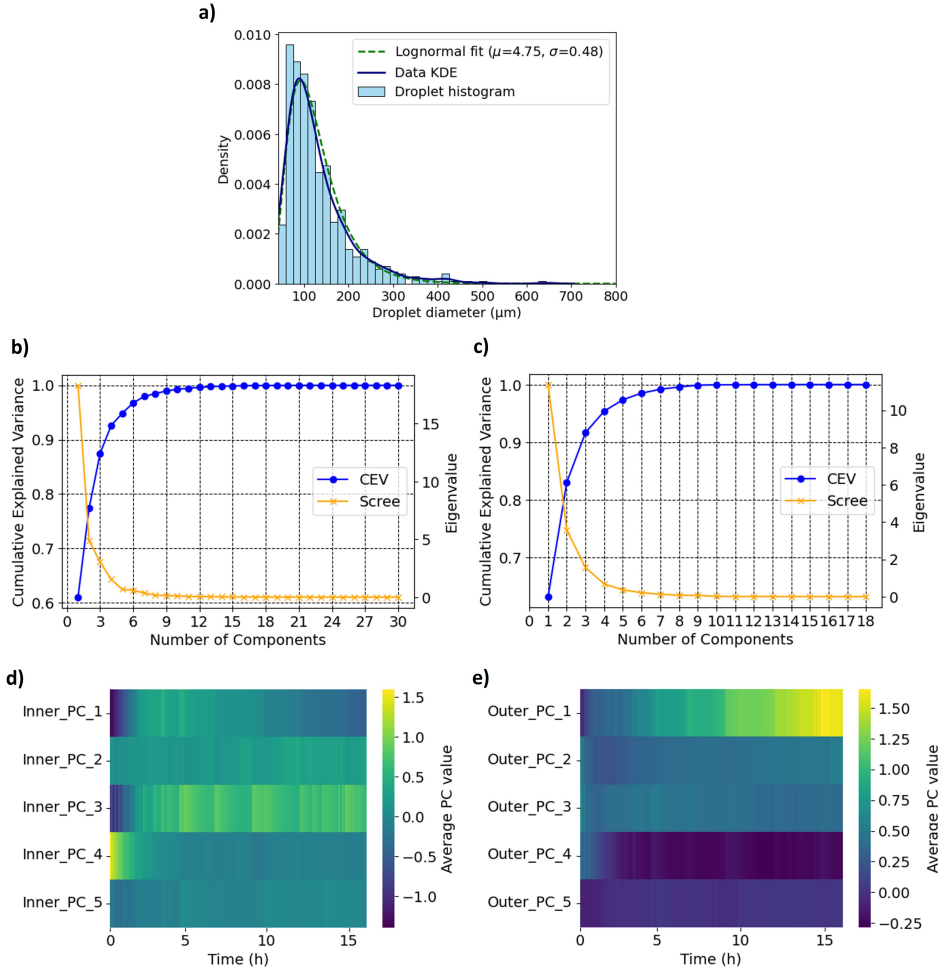


Figure 4.6: Data summary. (a) Droplet sizes distribution fitted with a log-normal function (green dashed line) and a kernel density function (dark blue line). (b) PCA of inner-ROI color features: Scree plot (orange) with eigenvalues of individual components and cumulative explained variance (CEV) (blue) showing five PCs capture over 95% variance. (c) PCA of outer-ROI color features, with similar variance capture. (d) Temporal changes of the first 5 inner-ROI PCs across droplets. (e) Temporal changes of the first 5 outer-ROI PCs across droplets.

frames change smoothly and incrementally (see [Section 4.4.1](#)), providing limited additional information when combined. After this selection, ensemble learning is utilized. [Fig. 4.7e-g](#) shows performance metrics distribution for 100 independently trained single learners versus 5 independently trained ensembles, each averaging 20 models. While individual models already perform well, ensembles consistently achieve higher R^2 scores and lower error metrics, thereby reducing the variability observed in single models. The ensemble points cluster closely, indicating better accuracy and robustness.

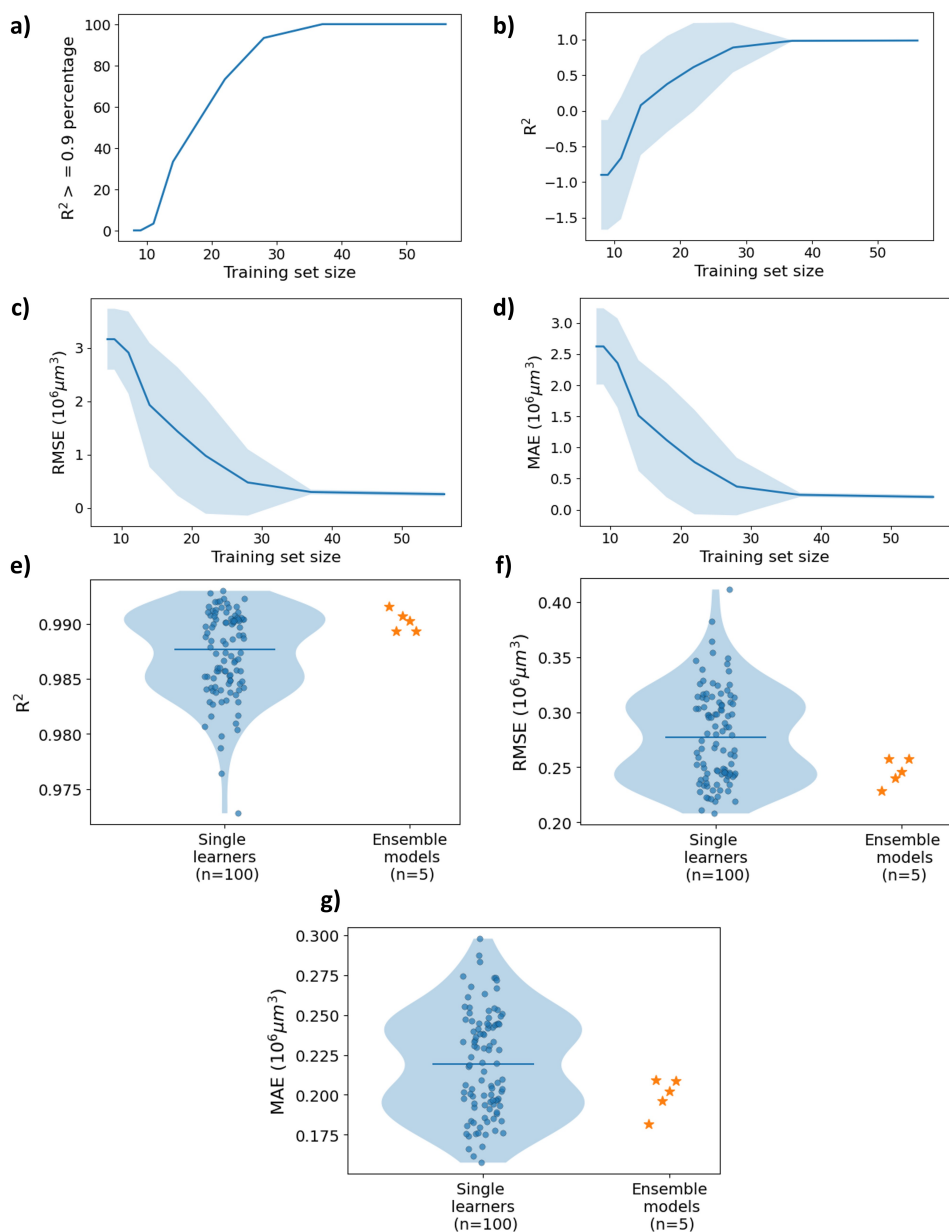


Figure 4.7: Global model performance. (a-d) Training-size sufficiency analysis across 30 runs, shown as (a) percentage of runs with $R^2 \geq 0.9$ and (b-d) mean and standard deviation of R^2 , RMSE, and MAE as training-set size varies. (e-g) 100 single learners (violins + points) versus 5 ensembles (orange stars). Ensembles outperform single learners, achieving higher accuracy and lower variability.

4.4.3. GLOBAL INTERPRETABILITY ANALYSIS

To explore how the model utilizes input features to predict global material loss, we examine feature attribution using SHAP alongside inference-time ablation testing. SHAP analysis targets the temporally varying color-feature PCs, while ablation assesses static geometrical features such as droplet diameter and aspect ratio.

The PCA-reduced color features track pixel-level changes in corrosion products within both the inner and outer ROIs. Fig. 4.8a shows the temporal progression of the summed SHAP values across all droplets. Inner-ROI PCs consistently show higher contributions, highlighting the dominance of under-droplet corrosion in influencing the global ER signal. Outer-ROI PCs contribute more slowly but steadily increase, aligning with the gradual spread of corrosion products beyond the droplet area. These trends represent average behavior across the population; individual droplets may experience corrosion only in the inner region, only in the outer region, in both regions, or in neither, depending on their local environmental conditions.

Fig. 4.8b shows SHAP values summed over all droplets and time for each PC, revealing that only a subset significantly impacts predictions. Notably, inner-ROI PCs, especially PC3 and PC4, are the most important, while outer-ROI PCs, led by PC1, contribute more modestly. Interestingly, these unimportant PCs do not always correspond to the largest temporal changes, suggesting that the model prioritizes predictive relevance over mere feature variance. Overall, the model emphasizes physically meaningful color indicators of corrosion rather than solely dynamic features.

While SHAP evaluates the marginal influence of perturbing individual inputs, it often underestimates the importance of features that remain constant within a sample, such as droplet geometry. For a given droplet, diameter and shape do not change over time, but they affect how color features evolve and therefore shape the relationship between local droplet behavior and overall material loss.

Previous studies[3, 34, 51] have emphasized the impact of droplet diameter and shape on corrosion processes. To accurately assess the contribution of these static geometric features, we performed inference-time ablation by setting either the diameter or the aspect ratio to zero, while holding all other features constant. As shown in Fig. 4.8c-e, eliminating droplet diameter causes a significant decline in model performance (R^2 drops from 0.991 to 0.683; RMSE and MAE increase by approximately 500%). Ablating the aspect ratio (Fig. 4.8f-h) results in a more moderate but still meaningful decrease, with R^2 decreasing by 0.014 and RMSE and MAE rising by roughly 60%. These findings illustrate that geometric features are critical to the model's accuracy, even though their role cannot be fully captured by SHAP analysis because they remain unchanged over time.

4.4.4. PER-DROPLET BEHAVIOR VALIDATION

To confirm that the droplet-level outputs from the model represent physically meaningful corrosion behavior, predictions are examined at the droplet scale. The aim is not to interpret the individual droplet predictions, as discussed in Section 4.4.3, but to

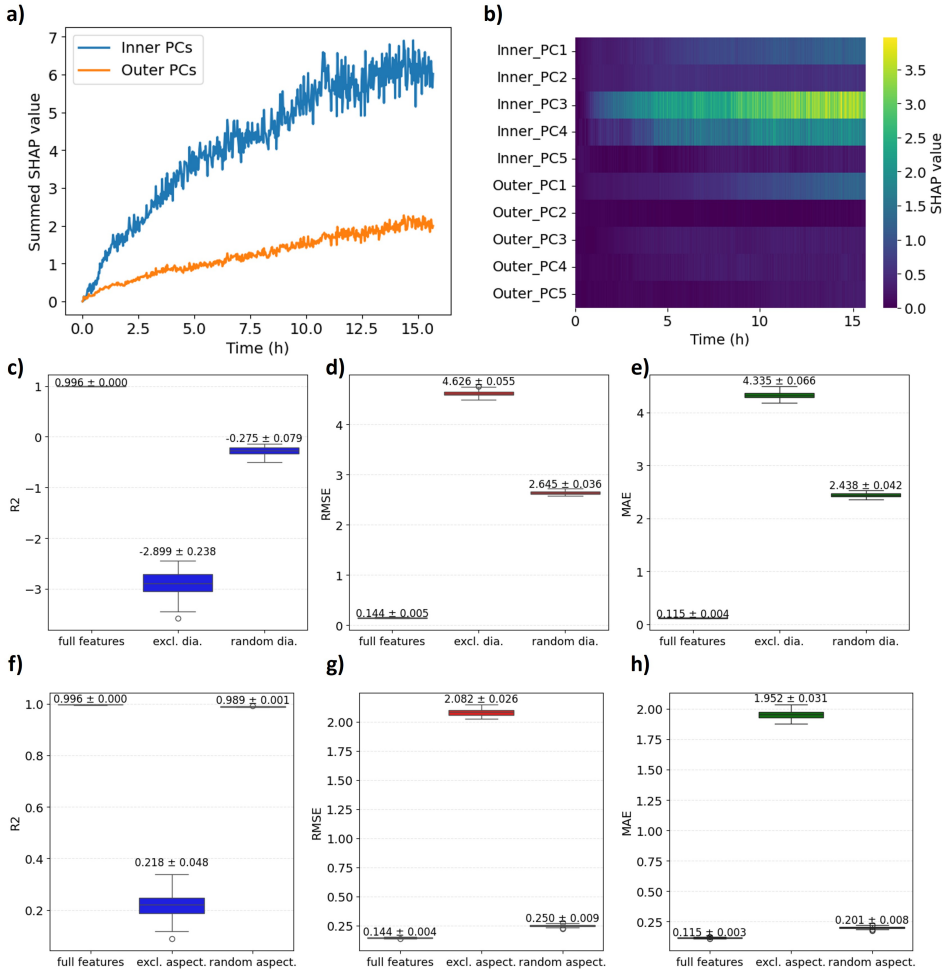


Figure 4.8: Global interpretability analysis results. Temporal evolution of the (a) summed and (b) individual SHAP values for inner and outer droplet color PCs is introduced to assess color features' attribution towards global predictions. Ablation tests on temporal static features are also included; the model performances with and without (c-e) droplet diameter and (f-h) aspect ratio information are presented.

verify whether these predictions follow observable corrosion trends such as larger predicted material loss correlating with visible corrosion products, temporal trajectories aligning with changes in droplet color features, and whether the final predicted material loss relates to droplet geometry in line with experimental observations. We compare predicted material loss with unsupervised classification obtained from final-stage droplet images. To avoid imposing an arbitrary cutoff, a two-component Gaussian Mixture Model (GMM) was fitted to the log-transformed distribution of predicted final material loss (see Fig. 4.9a). The intersection of the GMM components provides a natural threshold at around $6 \times 10^3 \mu\text{m}^3$, differentiating droplets with minor loss from those with

significant loss.

Simultaneously, K-means ++ clustering was used on PCA-reduced color features extracted from the last-frame images (Fig. 4.9b and 4.9c). The resulting clusters are well separated, with silhouette scores of 0.64 (inner ROI) and 0.69 (outer ROI). Visual inspection confirms that, in each case, one cluster predominantly contains droplets with visible corrosion products, either within the initial droplet footprint (inner ROI) or surrounding it (outer ROI), while the other cluster contains droplets with fewer visual signs of corrosion.

Using the GMM-based threshold as the model's predictor for significant loss, and the clustering labels as the reference, we compute standard agreement metrics: precision = 0.678, recall = 0.758, and F1-score = 0.716. These metrics assess how effectively the model differentiates droplets with notable corrosion activity. Precision indicates the proportion of droplets predicted to be significantly corroded that also exhibit corrosion products in the final images. Recall shows the percentage of the visibly corroded droplets correctly identified by the model. The F1-score, which balances precision and recall, indicates moderate agreement between predicted and observed corrosion behavior. Since clustering labels may be uncertain due to imaging noise and differences in corrosion morphology, an F1-score of around 0.72 suggests a meaningful match between the model's predictions and visual observations. These classification metrics are also consistent under various threshold adjustments (see Supplementary Information Section 4.S.2), confirming the robustness of this validation.

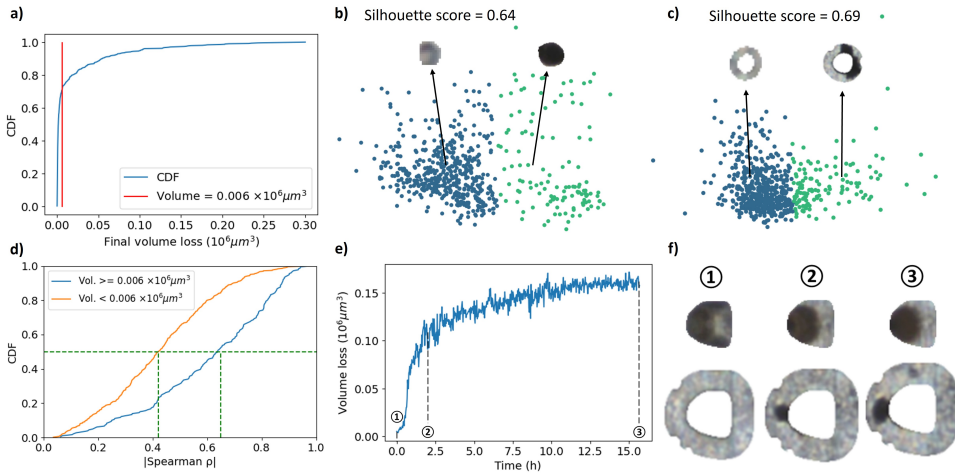


Figure 4.9: Multilevel validation of droplet predictions. (a) Cumulative distribution of predicted final material loss across all droplets, with a threshold ($6 \times 10^3 \mu\text{m}^3$) separating low- and high-loss groups. (b–c) Clustering of final-stage droplet (b) inner and (c) outer ROIs via K-means++ on PCA-reduced color (d) Spearman correlation (ρ) between predicted loss progression and color descriptor evolution. (e) Spatiotemporal evolution of a 234 μm -diameter droplet: the predicted loss curve exhibits two growth phases, corresponding to the onset of corrosion in the inner region and subsequent outward spreading. (f) Visual image of the progression of the inner and outer regions of the droplet.

A Spearman correlation analysis examined whether the model's predictions align with image-based droplet-level corrosion dynamics. For each droplet, the evolution of color features over time was represented by a weighted sum of the first five principal components, with weights proportional to each PC's explained variance (Section 4.4.1). Since corrosion can start at either the droplet center or perimeter, the correlation strength was defined as the highest Spearman's rank correlation coefficient between the predicted cumulative material loss and the color descriptor in the inner and outer ROIs.

As shown in Fig. 4.9d, droplets with higher final predicted material loss show significantly stronger monotonic correlations with their color changes (median $|\rho| = 0.64$) than those with lower predicted loss (median $|\rho| = 0.42$). This difference is statistically significant (Mann–Whitney U test, $p = 1.0 \times 10^{-19}$), indicating that the model tends to assign higher corrosion levels to droplets whose image-derived signals evolve in a manner consistent with ongoing corrosion product buildup.

To illustrate how the model assigns spatial corrosion loss over time, we analyze the temporal evolution of a representative droplet (Fig. 4.9e and 4.9f). Similar trends for additional droplets of varying sizes are presented in the Supplementary Information, Section 4.S.3. The predicted material loss curve (Fig. 4.9e) exhibits an initial rapid rise, followed by a more gradual, continuous increase. While the optical snapshots (Fig. 4.9f) capture the 2D spatial spread of corrosion products rather than direct volume loss, their progression provides important temporal context: the initial product formation within the inner ROI matches the steep early increase in the predicted loss curve, and the subsequent outward spread of products aligns temporally with the continued rise of the predictions. This temporal agreement suggests the model is responsive to the corrosion dynamics as captured in the optical images.

These findings show that the model effectively learns from color features to estimate material loss per droplet, with predictions consistent with post-exposure surface analysis. While the global interpretability results in Section 4.4.3 already highlight the influence of geometric features, especially droplet diameter, on overall predictions, their specific effect on individual droplet predictions is discussed next.

The predicted final material loss is plotted against initial droplet diameter on a logarithmic scale (Fig. 4.10). The distribution is scattered and non-monotonic, but a clear tendency is visible: most droplets below about $150 \mu\text{m}$ show minimal predicted loss, tightly clustered in the linear region near 100 to $1000 \mu\text{m}^3$, while larger droplets have a more pronounced predicted loss. This aligns with the hypothesis that larger droplets hold electrolyte for longer, enabling sustained corrosion. Conversely, small droplets evaporate quickly and have limited time to accumulate measurable products, even if corrosion begins. This diameter–loss relationship is not used as a strict validation metric. The model was not trained to enforce a size-dependent corrosion law, and the scatter reflects variability from factors such as droplet spacing, local electrolyte composition, and color evolution kinetics. Instead of strict proportionality, the plot in Fig. 4.10 shows that the model assigns higher corrosion incidence to larger droplets in a physically plausible way, not via size-independent or random predictions.

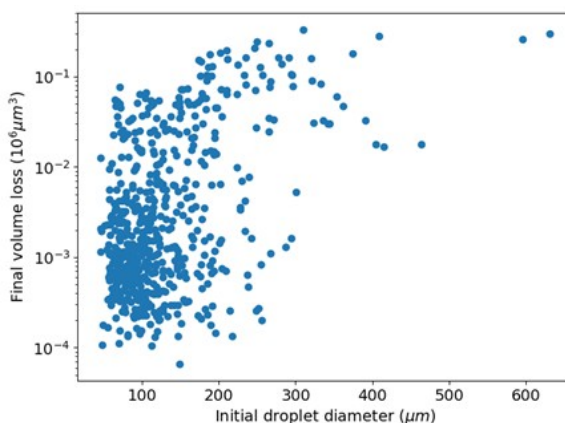


Figure 4.10: Relationship between initial droplet diameter and corrosion-induced volume loss as predicted by the model. The y-axis is presented on a logarithmic scale to clearly resolve the dense distribution of low-volume-loss data points.

These results show that the model can predict overall corrosion trends while also capturing localized, per-droplet behavior. It uses time-dependent color changes and geometric features, especially droplet diameter, to estimate material loss. The predicted values are within reasonable physical ranges. However, several assumptions should be noted. Since the method relies on optical features from RGB images, it mainly detects corrosion products visible on the surface. The possible corrosion processes occurring beneath the buildup products are underestimated in the material loss prediction. Additionally, local lighting differences, surface reflectivity, and segmentation errors can introduce noise into the color features, especially in early exposure when contrast is subtle.

Future improvements could involve enriching the model's optical inputs with hyperspectral imaging to capture chemical variations in corrosion products more precisely. Furthermore, while not feasible as real-time continuous inputs, techniques such as post-exposure surface profilometry or localized electrochemical mapping could be employed to generate high-fidelity droplet-level targets for model training and validation. Such an approach would allow future models to explicitly link surface optical features to subsurface damage and further reduce the reliance on visual color evolution alone.

4.5. CONCLUSIONS

This study presents a weakly supervised learning framework for modeling atmospheric corrosion under multiple droplet exposure, mimicking realistic conditions. By integrating time-resolved optical imaging with global material-loss measurements, the method identifies droplet-level contributions without requiring direct labels for each droplet undergoing corrosion. It effectively reconstructs global corrosion kinetics from droplet-level image features and uncovers meaningful spatiotemporal patterns that show how

individual droplets influence the measured response.

Rather than learning arbitrary data patterns, the learned per-droplet behaviors correspond to the physical spatiotemporal progression of localized corrosion. Specifically, the model detects droplets with visible corrosion products, tracks how these products accumulate over time, and differentiates between the inner and outer regions of the droplets where product buildup begins and propagates. Temporal analysis reveals that the predicted changes in material loss closely match the evolution of droplet color features. Furthermore, spatial inspection confirms that the predictions align directly with the visible accumulation of corrosion products. Additionally, the model indicates that higher corrosion volume loss for this material case correlates with larger droplets. This relationship may vary depending on material, electrolyte composition, and environmental factors.

4

This work shows that droplet-level corrosion behavior can be inferred using weak supervision. It offers a new tool for studying atmospheric corrosion under more realistic exposure conditions, where full spatial measurements of the electrolyte are often missing. Instead of replacing experimental methods, it complements them by enabling image-based reconstruction of corrosion activity across large droplet populations and over extended exposure times. More broadly, this study demonstrates how weak supervision can yield mechanistic insights from global observations, opening new avenues for data-driven corrosion analysis, accelerating testing procedures, and advancing the development of atmospheric corrosion prediction models.

SUPPLEMENTARY INFORMATION

4.S.1. OUTER ROI REGION DEFINITION

The outer region of interest (ROI) is defined to create a consistent area for monitoring the development and spread of corrosion products surrounding the initial droplet footprint. To physically justify the size of this boundary, we randomly selected 300 non-corroding droplets and analyzed their diameter evolution over time. Only non-corroding droplets were analyzed because, for corroding droplets, the development of corrosion products may obscure the true liquid boundary, making accurate edge detection impossible.

The temporal evolution (Fig. 4.11a) demonstrates that droplets undergo a slight initial expansion before stabilizing at an average diameter approximately 5% larger than their initial size. To quantify the full range of this behavior, the distribution of the maximum expansion ratio for each droplet was evaluated (Fig. 4.11b). The histogram indicates that the maximum observed expansion across the sample was approximately 1.7 times the initial droplet diameter. Therefore, setting the outer ROI diameter to 2.0 times the inner ROI diameter provides a conservative and robust boundary that safely encompasses natural droplet expansion while capturing the outward spread of corrosion products.

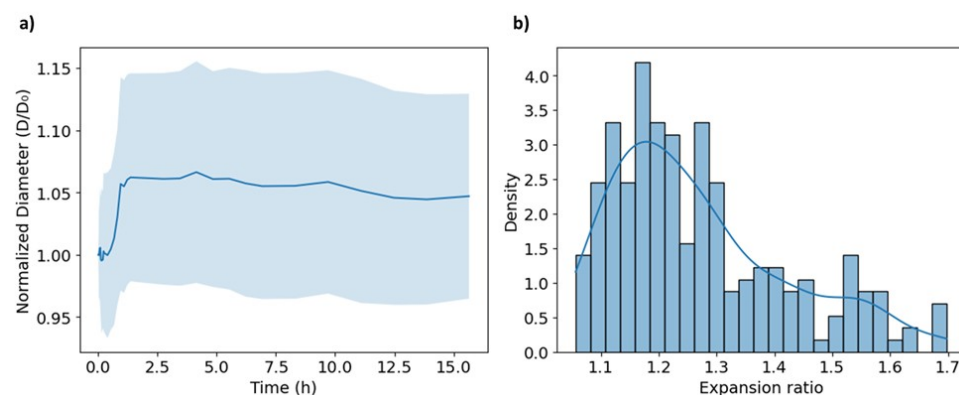


Figure 4.11: (a) Temporal evolution of normalized droplet diameter (solid line: mean value; transparent background: standard deviation) and (b) maximum expansion ratio histogram for the 300 randomly selected non-corroding droplets.

4.S.2. SENSITIVITY ANALYSIS OF THE MATERIAL LOSS VOLUME THRESHOLD

In the main text, a Gaussian Mixture Model (GMM) was used to establish a data-driven threshold of approximately $6 \times 10^3 \mu\text{m}^3$ to separate droplets with minor predicted volume loss from those with significant loss. To verify that the agreement between the model's predictions and the image-based K-means clustering is not an artifact of this specific cutoff point, a sensitivity analysis was performed. Fig. 4.12 illustrates how the classification metrics (Precision, Recall, and F1-score) evolve as the decision threshold is manually swept across a range of values. As expected, increasing the threshold makes the classification criterion stricter, which steadily increases Precision (reducing false posi-

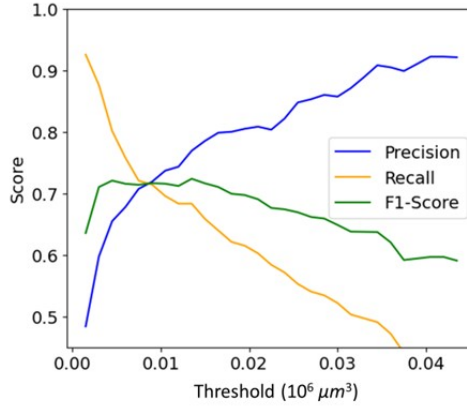


Figure 4.12: Impact of adjusting the predicted material loss threshold on classification agreement metrics (Precision, Recall, and F1-score). The reference labels are obtained from unsupervised K-means clustering of the final-stage droplet images.

tives) while proportionally decreasing Recall (increasing false negatives). Notably, the F1-score representing the harmonic mean of Precision and Recall remains relatively stable and near its peak value (around 0.70 to 0.72) across a wide threshold range from 5×10^3 to $2 \times 10^4 \mu\text{m}^3$. Therefore, the data-driven GMM threshold ($6 \times 10^3 \mu\text{m}^3$) aligns excellently with the optimal F1-score region and is therefore adopted for further analysis.

4.S.3. SPATIOTEMPORAL EVOLUTION OF ADDITIONAL DROPLETS

To verify that the model's temporal predictions consistently align with physical corrosion processes across a diverse population, the spatiotemporal evolution of several additional droplets of varying initial diameters (ranging from $68 \mu\text{m}$ to $632 \mu\text{m}$) was analyzed, as shown in Fig. 4.13. While the absolute magnitude of the predicted volume loss varies between droplets, the temporal alignment remains highly consistent, which confirms that the model reliably tracks region-specific corrosion dynamics based on optical features, rather than relying on random artifacts.

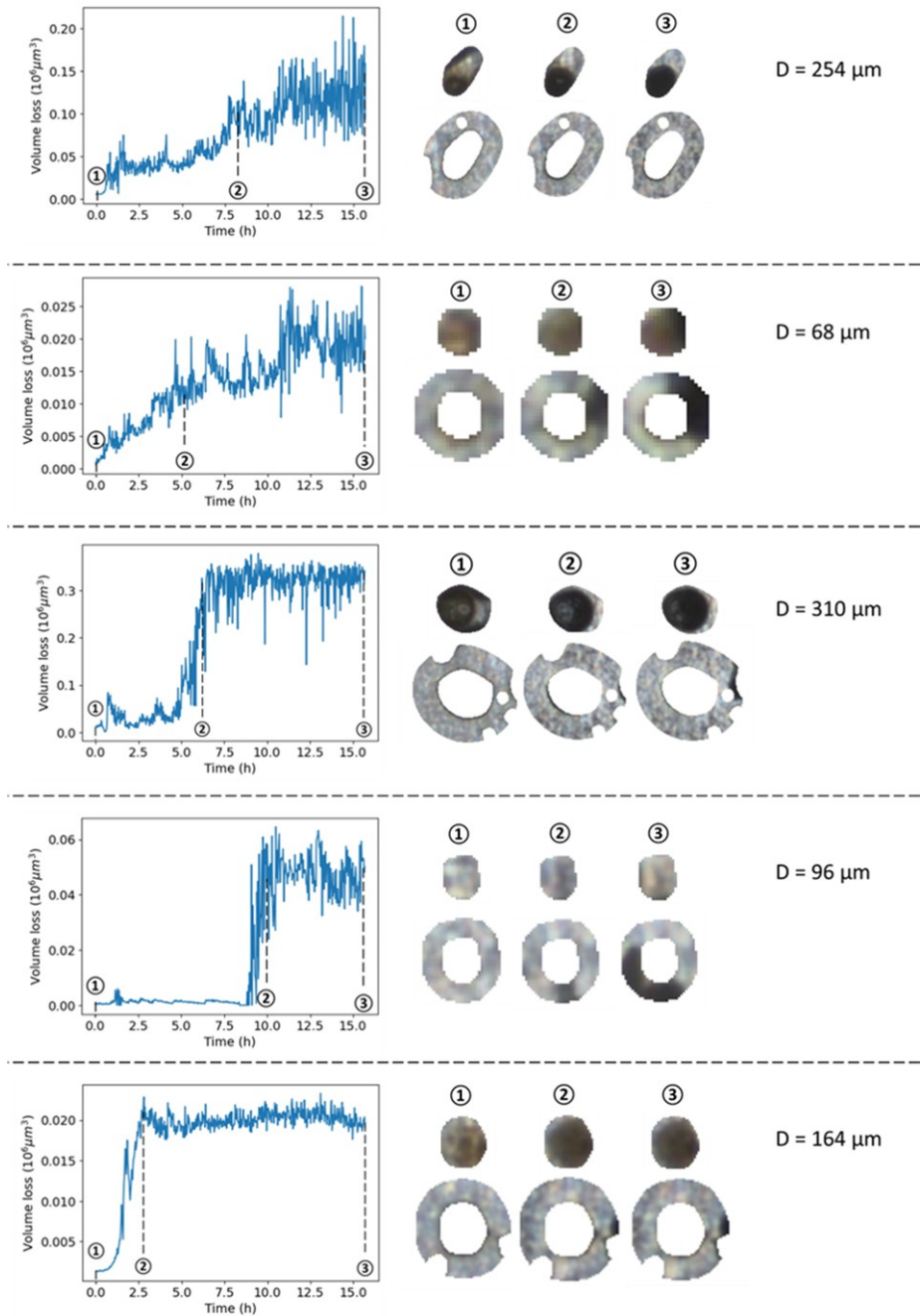


Figure 4.13: Spatiotemporal validation of model predictions for ten additional droplets with different initial diameters ($D = 68 \mu\text{m}$ to $632 \mu\text{m}$). The left column displays the predicted material volume loss curves over the exposure period. The right column presents optical snapshots of the inner and outer regions of interest (ROIs) at three distinct time points (labeled 1, 2, and 3).

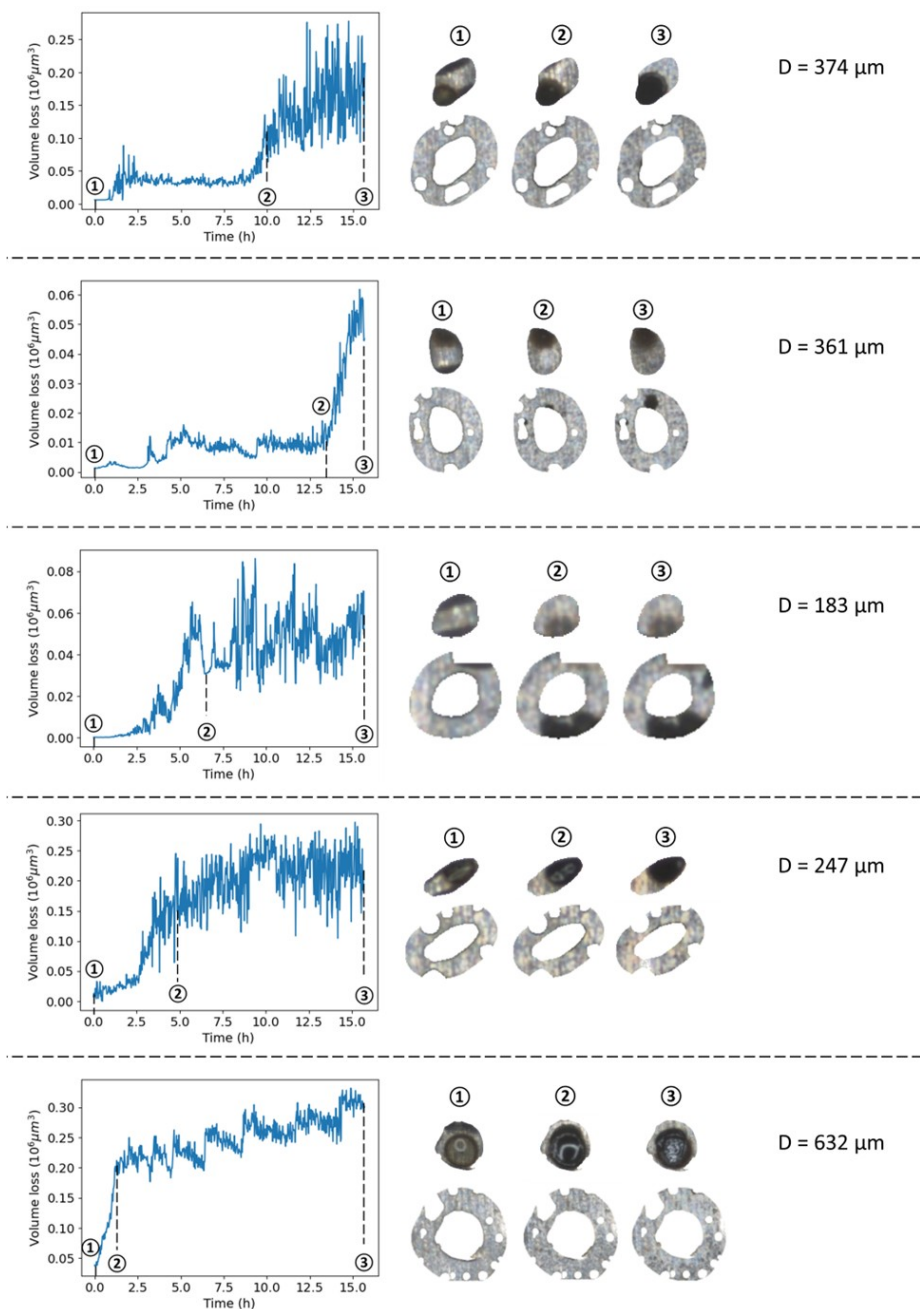


Figure 4.13: Continued.

BIBLIOGRAPHY

- [1] B. G. Koushik et al. "Review on modelling of corrosion under droplet electrolyte for predicting atmospheric corrosion rate". In: *Journal of Materials Science & Technology* 62 (2021), pp. 254–267. ISSN: 1005-0302. DOI: [10.1016/j.jmst.2020.04.061](https://doi.org/10.1016/j.jmst.2020.04.061). URL: [%3CGo%20to%20ISI%3E://WOS:000601221700025](https://www.wos.org/doi/abs/10.1016/j.jmst.2020.04.061).
- [2] J. S. Wang et al. "Observation and micro-electrochemical characterisation for micro-droplets in initial marine atmospheric corrosion". In: *Corrosion Engineering Science and Technology* 51.4 (2016), pp. 308–312. ISSN: 1478-422x. DOI: [10.1080/1478422x.2015.1110373](https://doi.org/10.1080/1478422x.2015.1110373). URL: [%3CGo%20to%20ISI%3E://WOS:000379540100011](https://www.wos.org/doi/abs/10.1080/1478422x.2015.1110373).
- [3] J. Weissenrieder and C. Leygraf. "studies of filiform corrosion of iron". In: *Journal of the Electrochemical Society* 151.3 (2004), B165–B171. ISSN: 0013-4651. DOI: [10.1149/1.1645263](https://doi.org/10.1149/1.1645263). URL: [%3CGo%20to%20ISI%3E://WOS:000188943800029](https://www.wos.org/doi/abs/10.1149/1.1645263).
- [4] T. Aastrup and C. Leygraf. "Simultaneous infrared reflection absorption spectroscopy and quartz crystal microbalance measurements for in situ studies of the metal/atmosphere interface". In: *Journal of the Electrochemical Society* 144.9 (1997), pp. 2986–2990. ISSN: 0013-4651. DOI: [Doi10.1149/1.1837948](https://doi.org/10.1149/1.1837948). URL: [%3CGo%20to%20ISI%3E://WOS:A1997XY20000022](https://www.wos.org/doi/abs/10.1149/1.1837948).
- [5] K. Zhang et al. "Monitoring atmospheric corrosion under multi-droplet conditions by electrical resistance sensor measurement". In: *Corrosion Science* 236 (2024). ISSN: 0010-938x. DOI: [ARTN11227110.1016/j.corsci.2024.112271](https://doi.org/10.1016/j.corsci.2024.112271). URL: [%3CGo%20to%20ISI%3E://WOS:001271277400001](https://www.wos.org/doi/abs/10.1016/j.corsci.2024.112271).
- [6] X. Z. Ma et al. "Investigation on the initial atmospheric corrosion of mild steel in a simulated environment of industrial coastland by thin electrical resistance and electrochemical sensors". In: *Corrosion Science* 204 (2022). ISSN: 0010-938x. DOI: [ARTN11038910.1016/j.corsci.2022.110389](https://doi.org/10.1016/j.corsci.2022.110389). URL: [%3CGo%20to%20ISI%3E://WOS:000808009000003](https://www.wos.org/doi/abs/10.1016/j.corsci.2022.110389).
- [7] A. Rafefi. "Development and evaluation of thin film electrical resistance sensors for monitoring CO top of the line corrosion". In: *Sensors and Actuators B-Chemical* 346 (2021). DOI: [ARTN13049210.1016/j.snb.2021.130492](https://doi.org/10.1016/j.snb.2021.130492). URL: [%3CGo%20to%20ISI%3E://WOS:000691996100007](https://www.wos.org/doi/abs/10.1016/j.snb.2021.130492).
- [8] K. Zhang et al. "Monitoring Atmospheric Corrosion of Carbon Steel Under Controlled Electrolyte Droplet Distributions". In: *The Electrochemical Society Meeting Abstracts* 244. Vol. 14. 2023, p. 1139. DOI: [10.1149/MA2023-02141139mtgabs](https://doi.org/10.1149/MA2023-02141139mtgabs).
- [9] S. Wan et al. "Monitoring of atmospheric corrosion and dewing process by interlacing copper electrode sensor". In: *Corrosion Science* 150 (2019), pp. 246–257. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2019.02.008](https://doi.org/10.1016/j.corsci.2019.02.008). URL: [%3CGo%20to%20ISI%3E://WOS:000462108000023](https://www.wos.org/doi/abs/10.1016/j.corsci.2019.02.008).

- [10] E. Schindelholz, B. E. Risteen, and R. G. Kelly. "Effect of Relative Humidity on Corrosion of Steel under Sea Salt Aerosol Proxies". In: *Journal of the Electrochemical Society* 161.10 (2014), pp. C450–C459. ISSN: 0013-4651. DOI: [10 . 1149 / 2 . 0221410jes](https://doi.org/10.1149/2.0221410jes). URL: [3CGo%20to%20ISI%3E://WOS:000341217500046](https://www.scopus.com/record/display.url?eid=2-s2.0-000341217500046).
- [11] D. M. Yang, H. W. Mei, and L. M. Wang. "Corrosion Measurement of the Atmospheric Environment Using Galvanic Cell Sensors". In: *Sensors* 19.2 (2019). ISSN: 1424-8220. DOI: [ARTN33110 . 3390 / s19020331](https://doi.org/10.3390/s19020331). URL: [3CGo%20to%20ISI%3E://WOS:000458569300114](https://www.scopus.com/record/display.url?eid=2-s2.0-000458569300114).
- [12] N. Van den Steen et al. "Predicting the effect of droplet geometry and size distribution on atmospheric corrosion". In: *Corrosion Science* 202 (2022). ISSN: 0010-938x. DOI: [ARTN11030810 . 1016 / j . corsci . 2022 . 110308](https://doi.org/10.1016/j.corsci.2022.110308). URL: [3CGo%20to%20ISI%3E://WOS:000793828200001](https://www.scopus.com/record/display.url?eid=2-s2.0-000793828200001).
- [13] L. Guerra-Camacho et al. "Influence of convection during droplet evaporation on corrosion product distribution in CFRP-AA2024 galvanic couple: Modeling and experimental approaches". In: *Corrosion Science* 240 (2024). ISSN: 0010-938x. DOI: [ARTN11246210 . 1016 / j . corsci . 2024 . 112462](https://doi.org/10.1016/j.corsci.2024.112462). URL: [3CGo%20to%20ISI%3E://WOS:001321801000001](https://www.scopus.com/record/display.url?eid=2-s2.0-001321801000001).
- [14] A. Sainz-Rosales et al. "Classic Evans's Drop Corrosion Experiment Investigated in Terms of a Tertiary Current and Potential Distribution". In: *Corrosion and Materials Degradation* 3.2 (2022), pp. 270–280. DOI: [10 . 3390 / cmd3020016](https://doi.org/10.3390/cmd3020016). URL: [3CGo%20to%20ISI%3E://WOS:001204371300001](https://www.scopus.com/record/display.url?eid=2-s2.0-001204371300001).
- [15] M. S. Venkatraman et al. "Modeling Corrosion of a Metal under an Aerosol Droplet". In: *Prism* 7, Pts 1-3 654-656 (2010), pp. 1650–+. ISSN: 0255-5476. DOI: [10 . 4028 / www . scientific . net / MSF . 654 - 656 . 1650](https://doi.org/10.4028/www.scientific.net/MSF.654-656.1650). URL: [3CGo%20to%20ISI%3E://WOS:000285374600404](https://www.scopus.com/record/display.url?eid=2-s2.0-000285374600404).
- [16] J. M. Vega et al. "The AA2024/CFRP galvanic couple under a dynamic electrolyte drop: modeling and experimental". In: *Electrochimica Acta* 432 (2022). ISSN: 0013-4686. DOI: [ARTN14113710 . 1016 / j . electacta . 2022 . 141137](https://doi.org/10.1016/j.electacta.2022.141137). URL: [3CGo%20to%20ISI%3E://WOS:000860974300005](https://www.scopus.com/record/display.url?eid=2-s2.0-000860974300005).
- [17] I. S. Cole et al. "Multiscale modelling of the corrosion of metals under atmospheric corrosion". In: *Electrochimica Acta* 56.4 (2011), pp. 1856–1865. ISSN: 0013-4686. DOI: [10 . 1016 / j . electacta . 2010 . 10 . 025](https://doi.org/10.1016/j.electacta.2010.10.025). URL: [3CGo%20to%20ISI%3E://WOS:000287951600021](https://www.scopus.com/record/display.url?eid=2-s2.0-000287951600021).
- [18] H. J. Lee, C. K. Choi, and S. H. Lee. "Vapor-shielding effect and evaporation characteristics of multiple droplets". In: *International Communications in Heat and Mass Transfer* 144 (2023). ISSN: 0735-1933. DOI: [ARTN10678910 . 1016 / j . icheatmasstransfer . 2023 . 106789](https://doi.org/10.1016/j.icheatmasstransfer.2023.106789). URL: [3CGo%20to%20ISI%3E://WOS:000990757400001](https://www.scopus.com/record/display.url?eid=2-s2.0-000990757400001).
- [19] Z. Y. Wang et al. "Wetting and evaporation of multicomponent droplets". In: *Physics Reports-Review Section of Physics Letters* 960 (2022), pp. 1–37. ISSN: 0370-1573. DOI: [10 . 1016 / j . physrep . 2022 . 02 . 005](https://doi.org/10.1016/j.physrep.2022.02.005). URL: [3CGo%20to%20ISI%3E://WOS:000808014400001](https://www.scopus.com/record/display.url?eid=2-s2.0-000808014400001).

- [20] T. Tsuru, K. I. Tamiya, and A. Nishikata. "Formation and growth of micro-droplets during the initial stage of atmospheric corrosion". In: *Electrochimica Acta* 49.17-18 (2004), pp. 2709–2715. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2004.01.032](https://doi.org/10.1016/j.electacta.2004.01.032). URL: [%3CGo%20to%20ISI%3E://WOS:000221779900002](https://www.wos.org/wos/000221779900002).
- [21] V. Soulié. "Sessile Droplets of Salt Solutions on Inert and Metallic Surfaces : Influence of Salt Concentration Gradients on Evaporation and Corrosion Behaviour." Soulié. PhD thesis. 2015.
- [22] E. Rahimi et al. "Atmospheric corrosion of iron under a single droplet: A new systematic multi-electrochemical approach". In: *Corrosion Science* 235 (2024). ISSN: 0010-938x. DOI: [ARTN11217110.1016/j.corsci.2024.112171](https://doi.org/10.1016/j.corsci.2024.112171). URL: [%3CGo%20to%20ISI%3E://WOS:001256286000001](https://www.wos.org/wos/001256286000001).
- [23] M. Y. Wang et al. "Visualizing and understanding corrosion evolution beneath a condensed droplet using the multi-electrode array". In: *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 684 (2024). ISSN: 0927-7757. DOI: [ARTN13325210.1016/j.colsurfa.2024.133252](https://doi.org/10.1016/j.colsurfa.2024.133252). URL: [%3CGo%20to%20ISI%3E://WOS:001166707000001](https://www.wos.org/wos/001166707000001).
- [24] H. Terryn et al. "Comparing Modelling and Experiments for Prediction of Atmospheric Corrosion Under Controlled Dynamic Thin Film and Droplet Electrolytes". In: *The Electrochemical Society Meeting Abstracts* 242. Vol. 11. Terryn. 2022, p. 712. DOI: [10.1149/MA2022-0211712mtgabs](https://doi.org/10.1149/MA2022-0211712mtgabs).
- [25] X. Tang et al. "Local electrochemical characteristics of pure iron under a saline droplet I: Effect of droplet size on electrochemical distribution". In: *Electrochimica Acta* 354 (2020). ISSN: 0013-4686. DOI: [ARTN13663310.1016/j.electacta.2020.136633](https://doi.org/10.1016/j.electacta.2020.136633). URL: [%3CGo%20to%20ISI%3E://WOS:000569143100007](https://www.wos.org/wos/000569143100007).
- [26] T. H. Muster et al. "The atmospheric corrosion of zinc: The effects of salt concentration, droplet size and droplet shape". In: *Electrochimica Acta* 56.4 (2011), pp. 1866–1873. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2010.09.099](https://doi.org/10.1016/j.electacta.2010.09.099). URL: [%3CGo%20to%20ISI%3E://WOS:000287951600022](https://www.wos.org/wos/000287951600022).
- [27] Y. J. Tan. "Wire beam electrode: A new tool for studying localised corrosion and other heterogeneous electrochemical processes". In: *Corrosion Science* 41.2 (1999), pp. 229–247. ISSN: 0010-938x. URL: [%3CGo%20to%20ISI%3E://WOS:000078779000002](https://www.wos.org/wos/000078779000002).
- [28] A. C. Bastos et al. "On the Application of the Scanning Vibrating Electrode Technique (SVET) to Corrosion Research". In: *Journal of the Electrochemical Society* 164.14 (2017), pp. C973–C990. ISSN: 0013-4651. DOI: [10.1149/2.0431714jes](https://doi.org/10.1149/2.0431714jes). URL: [%3CGo%20to%20ISI%3E://WOS:000419187700074](https://www.wos.org/wos/000419187700074).
- [29] D. Itzhak, I. Dinstein, and T. Zilberberg. "Pitting Corrosion Evaluation by Computer Image-Processing". In: *Corrosion Science* 21.1 (1981), pp. 17–22. ISSN: 0010-938x. DOI: [Doi10.1016/0010-938x\(81\)90059-7](https://doi.org/10.1016/0010-938x(81)90059-7). URL: [%3CGo%20to%20ISI%3E://WOS:A1981LA54100002](https://www.wos.org/wos/A1981LA54100002).

- [30] B. Q. Wang et al. “Advanced multi-image segmentation-based machine learning modeling strategy for corrosion prediction and rust layer performance evaluation of weathering steel”. In: *Corrosion Science* 237 (2024). ISSN: 0010-938x. DOI: [ARTN11233410.1016/j.corsci.2024.112334](https://doi.org/10.1016/j.corsci.2024.112334). URL: [%3CGo%20to%20ISI%3E://WOS:001293863900001](https://www.sciencedirect.com/science/article/pii/S0010938X24000001).
- [31] H. F. Zhang et al. “Real-time monitoring of the corrosion behaviour of the 304SS in HCl solution using BPNN with joint image recognition and electrochemical noise”. In: *Corrosion Science* 228 (2024). ISSN: 0010-938x. DOI: [ARTN11177910.1016/j.corsci.2023.111779](https://doi.org/10.1016/j.corsci.2023.111779). URL: [%3CGo%20to%20ISI%3E://WOS:001152844200001](https://www.sciencedirect.com/science/article/pii/S0010938X23000001).
- [32] M. Khayatazad, L. De Pue, and W. De Waele. “Detection of corrosion on steel structures using automated image processing”. In: *Developments in the Built Environment* 3 (2020). DOI: [ARTN10002210.1016/j.dibe.2020.100022](https://doi.org/10.1016/j.dibe.2020.100022). URL: [%3CGo%20to%20ISI%3E://WOS:000662765400008](https://www.sciencedirect.com/science/article/pii/S200662765400008).
- [33] E. Y. Son, D. Jeong, and M. J. Oh. “Corrosion area detection and depth prediction using machine learning”. In: *International Journal of Naval Architecture and Ocean Engineering* 16 (2024). ISSN: 2092-6782. DOI: [ARTN10061710.1016/j.ijnaoe.2024.100617](https://doi.org/10.1016/j.ijnaoe.2024.100617). URL: [%3CGo%20to%20ISI%3E://WOS:001321606400001](https://www.sciencedirect.com/science/article/pii/S209267822400001).
- [34] K. Zhang, A. Mol, and Y. Gonzalez-Garcia. “Development of a data-driven framework for monitoring corrosion under droplets”. In: *Corrosion Science* 258 (2026). ISSN: 0010-938x. DOI: [ARTN11331310.1016/j.corsci.2025.113313](https://doi.org/10.1016/j.corsci.2025.113313). URL: [%3CGo%20to%20ISI%3E://WOS:001597867400001](https://www.sciencedirect.com/science/article/pii/S0010938X2500001).
- [35] M. A. Carbonneau et al. “Multiple instance learning: A survey of problem characteristics and applications”. In: *Pattern Recognition* 77 (2018), pp. 329–353. ISSN: 0031-3203. DOI: [10.1016/j.patcog.2017.10.009](https://doi.org/10.1016/j.patcog.2017.10.009). URL: [%3CGo%20to%20ISI%3E://WOS:000426222800027](https://www.sciencedirect.com/science/article/pii/S003132031700027).
- [36] V. Cheplygina, M. de Bruijne, and J. P. W. Pluim. “Not-so-supervised: A survey of semi-supervised, multi-instance, and transfer learning in medical image analysis”. In: *Medical Image Analysis* 54 (2019), pp. 280–296. ISSN: 1361-8415. DOI: [10.1016/j.media.2019.03.009](https://doi.org/10.1016/j.media.2019.03.009). URL: [%3CGo%20to%20ISI%3E://WOS:000467891200022](https://www.sciencedirect.com/science/article/pii/S136184151900022).
- [37] X. X. Du and A. Zare. “Multiple Instance Choquet Integral Classifier Fusion and Regression for Remote Sensing Applications”. In: *Ieee Transactions on Geoscience and Remote Sensing* 57.5 (2019), pp. 2741–2753. ISSN: 0196-2892. DOI: [10.1109/Tgrs.2018.2876687](https://doi.org/10.1109/Tgrs.2018.2876687). URL: [%3CGo%20to%20ISI%3E://WOS:000466183500022](https://www.sciencedirect.com/science/article/pii/S00466183500022).
- [38] J. Early et al. “Extending scene-to-patch models: Multi-resolution multiple instance learning for Earth observation”. In: *Environmental Data Science* 2 (2023). DOI: [ARTNe4210.1017/eds.2023.30](https://doi.org/10.1017/eds.2023.30). URL: [%3CGo%20to%20ISI%3E://WOS:001223645700042](https://www.sciencedirect.com/science/article/pii/S2001223645700042).
- [39] M. Ilse, J. M. Tomczak, and M. Welling. “Attention-based Deep Multiple Instance Learning”. In: *International Conference on Machine Learning, Vol 80* 80 (2018). ISSN: 2640-3498. URL: [%3CGo%20to%20ISI%3E://WOS:000683379202024](https://www.sciencedirect.com/science/article/pii/S264034981800024).
- [40] S. Ray and D. Page. *Multiple instance regression*. 2001.

- [41] Ł. Struski et al. *ProMIL: Probabilistic Multiple Instance Learning for Medical Imaging*. June 2023. DOI: [10.48550/arXiv.2306.10535](https://doi.org/10.48550/arXiv.2306.10535). URL: <https://ui.adsabs.harvard.edu/abs/2023arXiv230610535S>.
- [42] Thomas Uriot. *Learning with Sets in Multiple Instance Regression Applied to Remote Sensing*. Mar. 2019. DOI: [10.48550/arXiv.1903.07745](https://doi.org/10.48550/arXiv.1903.07745). URL: <https://ui.adsabs.harvard.edu/abs/2019arXiv190307745U>.
- [43] K. L. Wagstaff, T. Lane, and A. Roper. “Multiple-Instance Regression with Structured Data”. In: *IEEE International Conference on Data Mining Workshops*. Wagstaff. 2008, pp. 291–300. DOI: [10.1109/ICDMW.2008.31](https://doi.org/10.1109/ICDMW.2008.31).
- [44] Z. Wang, L. Lan, and S. Vucetic. “Mixture Model for Multiple Instance Regression and Applications in Remote Sensing”. In: *Ieee Transactions on Geoscience and Remote Sensing* 50.6 (2012), pp. 2226–2237. ISSN: 0196-2892. DOI: [10.1109/Tgrs.2011.2171691](https://doi.org/10.1109/Tgrs.2011.2171691). URL: <https://www.wos.org/wos/doi/10.1109/Tgrs.2011.2171691>.
- [45] Z. Wang et al. *Aerosol Optical Depth Prediction from Satellite Observations by Multiple Instance Regression*. 2008. DOI: <https://doi.org/10.1137/1.9781611972788.15>.
- [46] Z. G. Wang, Z. S. Zhao, and C. S. Zhang. “Online multiple instance regression”. In: *Chinese Physics B* 22.9 (2013). ISSN: 1674-1056. DOI: [10.1088/1674-1056/22/9/098702](https://doi.org/10.1088/1674-1056/22/9/098702). URL: <https://www.wos.org/wos/doi/10.1088/1674-1056/22/9/098702>.
- [47] G. V. Kuznetsov et al. “Evaporation modes of LiBr, CaCl, LiCl, NaCl aqueous salt solution droplets on aluminum surface”. In: *International Journal of Heat and Mass Transfer* 126 (2018), pp. 161–168. ISSN: 0017-9310. DOI: [10.1016/j.ijheatmasstransfer.2018.05.040](https://doi.org/10.1016/j.ijheatmasstransfer.2018.05.040). URL: <https://www.wos.org/wos/doi/10.1016/j.ijheatmasstransfer.2018.05.040>.
- [48] F. Lequien et al. “Corrosion influence on the evaporation of sessile droplet”. In: *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 546 (2018), pp. 59–66. ISSN: 0927-7757. DOI: [10.1016/j.colsurfa.2018.02.047](https://doi.org/10.1016/j.colsurfa.2018.02.047). URL: <https://www.wos.org/wos/doi/10.1016/j.colsurfa.2018.02.047>.
- [49] A. Kirillov et al. “Segment Anything”. In: *2023 Ieee/Cvf International Conference on Computer Vision, Iccv* (2023), pp. 3992–4003. ISSN: 1550-5499. DOI: [10.1109/Iccv51070.2023.00371](https://doi.org/10.1109/Iccv51070.2023.00371). URL: <https://www.wos.org/wos/doi/10.1109/Iccv51070.2023.00371>.
- [50] S. P. Knight et al. “The effect of droplet size on the localized corrosion of high-strength aluminum alloys”. In: *Materials and Corrosion-Werkstoffe Und Korrosion* 67.12 (2016), pp. 1294–1307. ISSN: 0947-5117. DOI: [10.1002/maco.201609045](https://doi.org/10.1002/maco.201609045). URL: <https://www.wos.org/wos/doi/10.1002/maco.201609045>.
- [51] B. E. Risteen, E. Schindelholz, and R. G. Kelly. “Marine Aerosol Drop Size Effects on the Corrosion Behavior of Low Carbon Steel and High Purity Iron”. In: *Journal of the Electrochemical Society* 161.14 (2014), pp. C580–C586. ISSN: 0013-4651. DOI: [10.1149/2.1171412jes](https://doi.org/10.1149/2.1171412jes). URL: <https://www.wos.org/wos/doi/10.1149/2.1171412jes>.

5

SURFACE ROUGHNESS AND ATMOSPHERIC CORROSION: DROPLET-SCALE AND GLOBAL KINETICS

This chapter will be published as:

Zhang, K.; Mol, A.; Gonzalez-Garcia, Y. Surface Roughness and Atmospheric Corrosion: Droplet-Scale and Global Kinetics
following further modifications.

Abstract

Surface roughness is known to influence atmospheric corrosion, yet its role in multi-droplet conditions remains poorly investigated and quantified. Here, electrical resistance (ER) measurements are combined with droplet-resolved image analysis to study corrosion of carbon steel under spray-deposited 1 M NaCl droplets on surfaces grinded to P320, P800, and P1200 finishes. Rougher surfaces produced larger, more elongated droplets with slightly higher electrolyte coverage, driven by enhanced pinning and impact-driven coalescence. These differences explained the higher and earlier-developing ER-measured corrosion depth on rougher finishes. Probability-based image descriptors showed that the fraction of droplets exhibiting under-droplet corrosion increased with roughness, whereas inter-droplet corrosion displayed a more complex dependence linked to wet-area expansion and secondary thin-film formation. Time-resolved analysis further revealed earlier and stronger under-droplet corrosion on rougher surfaces, which is consistent with ER kinetics.

5.1. INTRODUCTION

Atmospheric corrosion of carbon steel is typically driven by the formation of discrete micrometer-scale electrolyte droplets or continuous thin films following salt deliquescence or the condensation of humidity[1–5]. Under ambient conditions, these individual droplets or thin films typically reach heights of tens to hundreds of micrometers. In practice, each discrete droplet acts as a tiny electrochemical cell (i.e., an Evans droplet). Within this geometry, the center of the droplet has a longer oxygen diffusion path length than the thin peripheral edge, establishing a differential aeration cell in which the center acts as the anodic site and the periphery as the cathode. While oxygen transport within these micrometric layers is rapid relative to bulk immersion, it is not instantaneous and can become rate-limiting depending on the specific electrolyte thickness and geometry. Furthermore, dynamic effects such as rapid evaporation, Marangoni flows, and capillary flows within a drying droplet can redistribute salt concentrations and create steep local gradients[3, 6–8]. Unlike bulk immersion, atmospheric corrosion is characterized by a confined electrolyte geometry, a limited electrolyte volume, strong evaporation-condensation dynamics, and enhanced transport coupling within micrometric layers.

5

Surface roughness strongly modulates the geometry and spatial distribution of deposited droplets, thereby fundamentally dictating the local electrochemical conditions for corrosion[9–20]. According to classical wetting theory on hydrophilic surfaces, increasing surface roughness enhances wettability at equilibrium by amplifying the intrinsic surface energy, thereby promoting droplet spreading and larger contact area[14–17, 20]. In practical atmospheric corrosion scenarios involving droplet deposition by spraying, wetting is primarily driven by dynamic impact and is highly non-equilibrium. During spray deposition, micro-scale roughness plays a mechanical role by limiting droplet mobility, reducing bouncing, and enhancing contact-line pinning on already deposited droplets[9, 10]. This enhanced pinning allows rough surfaces to effectively trap new incoming droplets, promoting rapid coalescence and the formation of larger, more irregular droplet shapes. Additionally, the directional micro-grooves introduced by grinding can cause droplets to elongate along specific axes[18, 19]. Larger, elongated droplets contain a greater electrolyte volume and establish longer oxygen diffusion paths from the thin, oxygen-rich periphery to the thicker, oxygen-depleted center[21]. This extended diffusion distance strengthens the differential aeration cell, which more efficiently separates the anodic and cathodic sites, promoting more severe localized dissolution. Furthermore, larger droplets increase the likelihood that the electrolyte covers surface heterogeneities and metallurgical defect sites, which are more prone to corrosion initiation. Consequently, roughness fundamentally alters the droplet size–shape–coverage statistics, thereby modulating electrolyte volume and oxygen diffusion pathways in atmospheric corrosion.

Beyond modifying the physical geometry of the electrolyte, micro-scale roughness can also influence the intrinsic electrochemical reactivity of the surface. It is important to note that while the role of surface roughness in localized corrosion is well-documented, the existing literature predominantly focuses on stainless steel[22–27] or carbon steel[28–30] in bulk immersion. Studies explicitly investigating the effect of surface roughness

on carbon steel under atmospheric multi-droplet conditions remain scarce. Nevertheless, the fundamental principles of micro-topographical activation observed in bulk systems provide a crucial mechanistic basis for droplet environments. At the micro-scale, mechanical grinding introduces physical defects such as micro-crevices, dislocations, and localized micro-deformations. When an electrolyte droplet covers the surface, these micro-crevices can act as preferential sites for electrolyte trapping. These sheltered topological features restrict local mass transport, accelerating the depletion of dissolved oxygen and facilitating localized anodic dissolution[23–26]. Furthermore, rough surfaces increase the true metal–liquid interfacial area, leading to a larger total surface area for anodic dissolution and cathodic reduction reactions to take place[27, 28]. Consequently, micro-scale roughness amplifies spatial heterogeneity through two parallel pathways by altering both the macroscopic droplet populations and the localized electrochemical active sites.

While micro-scale roughness strongly influences individual droplet geometry and local reactivity, practical atmospheric corrosion is more akin to a multi-droplet phenomenon. Historically, experimental studies have predominantly utilized single-droplet setups on smooth substrates[3, 31–36]. Population-based modeling indicates that the spatial dispersion and population statistics of these droplets matter significantly. For instance, assuming a constant contact angle, one model demonstrates that an array of small droplets yields a significantly higher global corrosion rate than a single large droplet covering the same total surface area[37]. Another study reaches the same conclusion even when the system is constrained to an equivalent total electrolyte volume[38]. Despite these theoretical insights, experimental validation under multi-droplet conditions remains scarce. The fundamental scientific challenge lies in the complexity of the system: understanding multi-droplet corrosion requires successfully linking the stochastic, highly localized nature of thousands of interacting micro-electrochemical cells (e.g., via overlapping diffusion fields or shared electrolyte pathways) to the overall macroscopic corrosion kinetic.

To overcome this complexity, our recent works established a specialized framework to quantify these localized and global relationships. Specifically, [Chapter 2](#) introduced an experimental setup that enables simultaneous optical recording of surface changes and continuous measurement of global corrosion kinetics under multi-droplet conditions. Building on this, [Chapter 3](#) proposed a data-driven approach to extract per-droplet visual evolution and quantify local corrosion development using probability-based descriptors. However, these foundational multi-droplet investigations were conducted on a single surface finish.

Consequently, the relationship between real surface micro-topography, the statistical distribution of coexisting droplets, and their collective corrosion behaviour remains insufficiently studied. Incorporating roughness effects into a multi-droplet, spatially resolved corrosion framework is therefore an ongoing challenge. This chapter aims to address this gap by systematically introducing controlled surface roughness into our framework. Building on the methodologies from earlier chapters, this work experimentally quantifies how micro-topography alters droplet population statistics and conse-

quently influences corrosion kinetics. Carbon steel samples were prepared with three different grinding finishes (P320, P800, P1200 grit), which produce measurable roughness profiles (for example, Ra) to systematically vary surface micro-topography. A custom electrical resistance (ER) sensor pair continuously records overall metal loss, while high-resolution optical imaging simultaneously captures the development of corrosion products associated with each droplet. By analysing each droplet footprint to compute per-droplet statistics and probability maps of corrosion-product formation, this work statistically correlates image-based descriptors with the ER-measured global corrosion depth to determine how roughness affects droplet size, shape, coverage, and how these aspects collectively influence atmospheric corrosion.

5.2. METHODOLOGY

5.2.1. EXPERIMENTAL CONDITIONS AND DATA ACQUISITION

The present study is based on corrosion experiments conducted under controlled multi-droplet atmospheric conditions, using carbon steel corrosion sensors with different surface finishes. A schematic overview of the experimental setup and the resulting data streams is provided in [Fig. 5.1](#). The experimental setup, corrosion sensor design and fabrication, surface preparation procedures, environmental control, and the parallel acquisition of ER signals and time-lapse optical images follow the same protocols as described in our previous work[2] ([Chapter 2](#)). Accordingly, only the aspects directly relevant to the data analyzed in this study are summarized here.

Carbon steel (grade EN 10130) samples with three different surface finishes (SiC grinding P320, P800, and P1200) were investigated, with three independent repetitions for each finish. Surface roughness values (Ra) corresponding to each finish were measured prior to exposure using atomic force microscopy (AFM, Dimension Edge Scanning Probe Microscope, Bruker Corporation, USA). For each sample, five independent $50 \times 50 \mu\text{m}$ maps were scanned at different locations to calculate the statistical mean and standard deviation, which are summarized in [Tab. 5.1](#).

Table 5.1: Ra of each repetition from each finish

	#1	#2	#3
P320	$307.9 \pm 42.2 \text{ nm}$	$282.3 \pm 39.1 \text{ nm}$	$297.2 \pm 31.2 \text{ nm}$
P800	$182.3 \pm 19.3 \text{ nm}$	$171.5 \pm 18.1 \text{ nm}$	$196.2 \pm 22.8 \text{ nm}$
P1200	$113.6 \pm 17.4 \text{ nm}$	$121.2 \pm 15.2 \text{ nm}$	$132.5 \pm 21.5 \text{ nm}$

Droplets of 1 M NaCl solution were generated by spray deposition. Within the $11.65 \times 8.72 \text{ mm}^2$ optical field of view, this resulted in a population of approximately 600–700 droplets per experiment residing on the exposed metal tracks. Accounting for the slight variations in the metal area between individual sensor samples (the average exposed track area is approximately 47.5 mm^2), this yields an initial deposition density of roughly 13–15 droplets/ mm^2 on the metal track within the observed window. A detailed quantitative analysis of how the initial droplet geometry and surface coverage vary with substrate roughness is presented in [Section 5.3.1](#). All experiments were conducted under controlled, near-identical environmental conditions in a climate chamber for 12h.

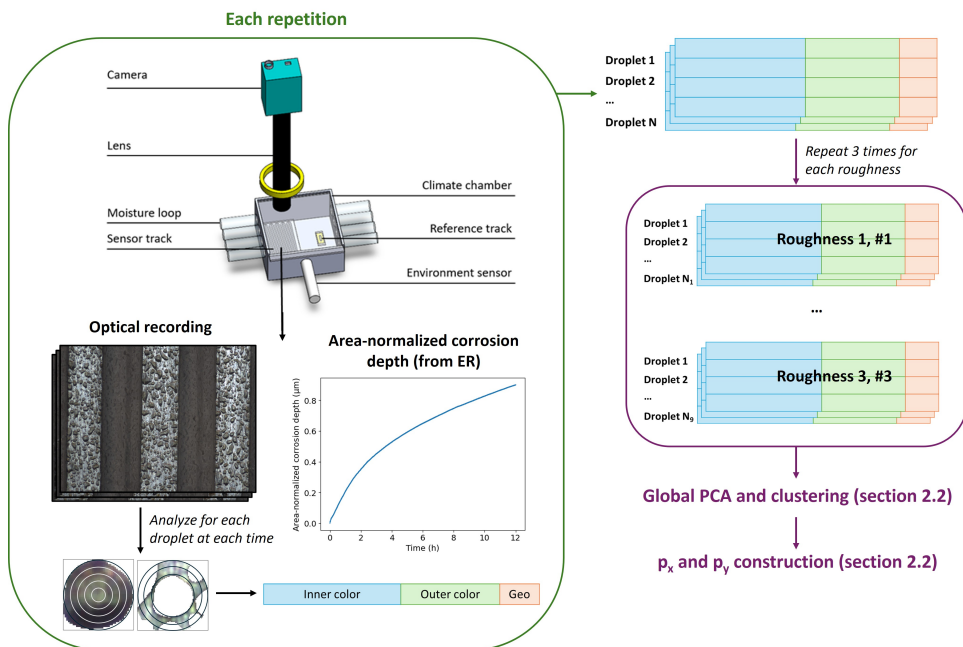


Figure 5.1: Schematic overview of the experimental setup and data streams used in this study. For each experiment, carbon-steel corrosion sensors are exposed to multi-droplet atmospheric conditions in a climate chamber, while time-lapse optical images and ER signals are acquired in parallel. Optical images are used to extract droplet-level information, including geometric descriptors and color-based features from inner and outer regions of interest (ROI), while ER measurements provide a global, area-normalized corrosion depth, from which corrosion rate is also computed. Each surface finish condition is repeated three times in independent runs.

Within each repetition, the moisture loop introducing humid air formed from a 1M NaCl solution was only enabled before the sample was placed into the climate chamber and was sealed for the rest of the duration.

Relative humidity (RH) and ambient temperature (T_a) were continuously monitored throughout all nine experiments. Fig. 5.2 shows the temporal evolution of RH and T_a , respectively, where the mean value (solid curve) with the corresponding variation (shaded area) across all runs is presented. There are only minor temperature and RH drifts during the experiments, minimizing their influence on the ER signal.

Time-lapse optical images covering an area of $11.65 \times 8.72 \text{ mm}^2$ were acquired every 2 min and were spatially aligned to the first image prior to any analysis. From these images, droplet-level features were extracted using a validated image analysis pipeline, as detailed in our previous work[4] (Chapter 3). This yielded per-droplet geometric and color descriptors. The present investigation focuses exclusively on the analysis of these derived hyper-data, without further modification into experimental procedures or raw data acquisition. Specifically, droplet geometric descriptors were defined based on the initial droplet footprint and treated as temporally constant throughout the analysis, while

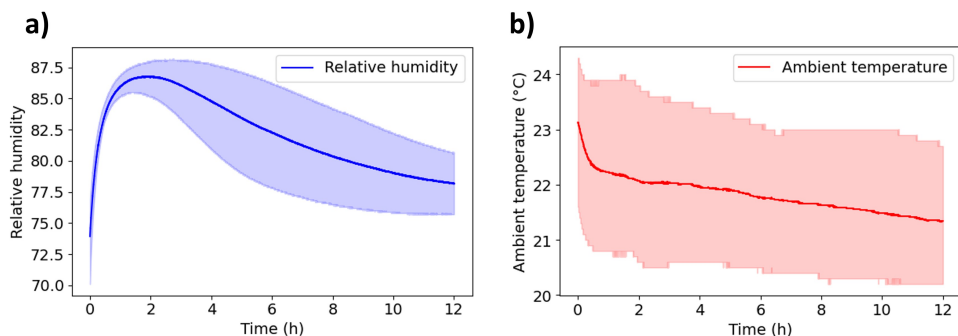


Figure 5.2: Environmental conditions evolution during all nine experiments for (a) RH and (b) Ta. The solid curve represents the mean value across all nine repetitions, and the shaded area indicates the corresponding min-max variability. The narrow spread in the shaded area confirms that the experiments were conducted under comparable and stable environmental conditions.

color descriptors capturing corrosion product development were treated as temporally dynamic. Such a choice reflects the focus of the present study on the development of corrosion products relative to the initial droplet location, rather than on the time evolution of droplet geometry, and is consistent with the approach established in our previous work[4] (Chapter 3).

In addition to the image-derived droplet-level metrics, global corrosion was measured using the ER sensors. Specifically, the ER signal was acquired at 50Hz and down-sampled to 1Hz before further processing. To enable comparison across samples with different exposed surface areas, the corrosion depth derived from the ER measurements was normalized by the initial wetting area (i.e., sample area initially covered by droplets), yielding an area-normalized corrosion depth. This value is used in the following sections as a global indicator of material loss.

5.2.2. CONSTRUCTION OF DROPLET-LEVEL FEATURE SPACE AND PROBABILITY-BASED INDICATORS

To quantify localized degradation, a time-resolved feature matrix was constructed at the droplet level based on color information extracted from two regions: the inner ROI (under the droplet) and the outer ROI (outside the droplet), as illustrated in Fig. 5.1. This image-based tracking is physically grounded in the fact that the accumulation of corrosion products can be reflected in color and textural changes, which can be directly analyzed from shifts in pixel RGB values shift[4]. For the under-droplet regions, circular segmentation into five concentric slices was applied to extract the mean and variance of the RGB channels, capturing the radial physical changes of the Evans droplet cell. For the outside-droplet regions, similar color statistics were combined with gradient-based descriptors to capture secondary spreading or thin-film corrosion, resulting in 26 features per droplet. The detailed feature construction procedure has been established in our previous work[4] (Chapter 3). To enable comparison across different repetitions

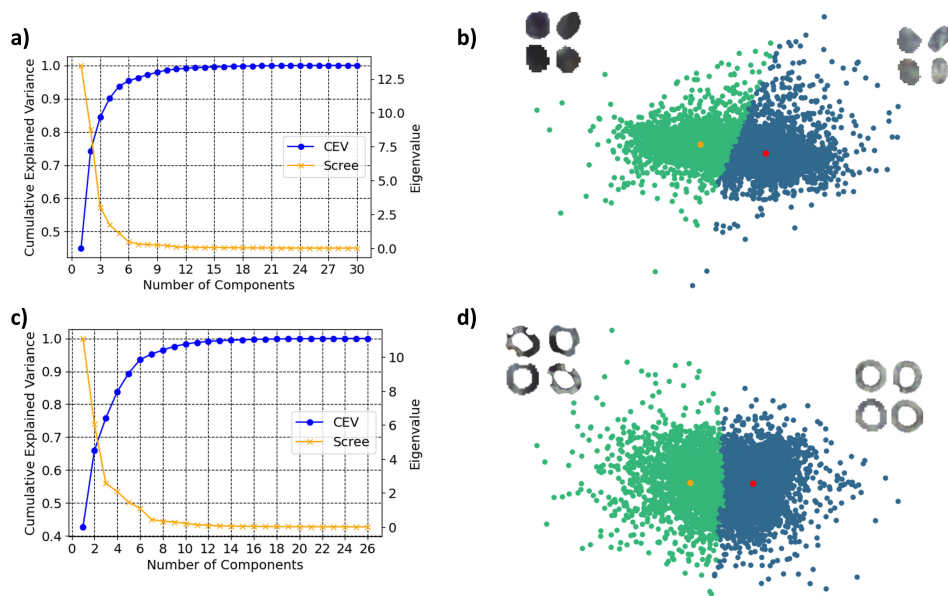


Figure 5.3: Construction of the global droplet-level feature space used for probability-based corrosion analysis. (a, c) cumulative explained variance (CEV) and scree plots obtained from PCA applied to the merged final-frame feature sets from all experimental runs, for (a) inner and (c) outer ROIs. (b, d) The corresponding PCA-reduced feature space (first two principal components shown for visualization), colored by K-means++ clustering results, with cluster centers indicated. PCA and clustering are performed globally across all runs and surface finish conditions to ensure a common reference space for subsequent cross-run comparisons and the construction of the probability-based indicators (inner ROI) and (outer ROI).

and surface finish conditions, the final-frame feature sets from all runs were merged to form a global feature space. Prior to dimensionality reduction, droplet color features were calibrated with respect to their initial state to compensate for intrinsic baseline differences in substrate appearance resulting from different surface roughness levels. Principal component analysis (PCA) was then applied separately to the under-droplet and outside-droplet feature sets. We retained 4 components for the under-droplet regions (Fig. 5.3a) and 5 components for the outside-droplet regions (Fig. 5.3c). This selection was determined by retaining principal components such that Cumulative Explained Variance (CEV) would across 90% to ensure the model captured the vast majority of physically relevant color variations.

Based on this PCA-reduced feature space, K-means++ clustering was performed to identify representative cluster centers. These cluster centers physically correspond to distinct corrosion-related appearance states which differentiate the states of “no accumulation of visible corrosion products” and states with “significant accumulation of corrosion products”, as presented separately for under-droplet (Fig. 5.3b) and outside-droplet (Fig. 5.3d) regions. The use of this global PCA and clustering framework ensures that all droplets from different runs and surface finishes are evaluated against the same physical

reference states. For each droplet at each time step, the probability-based indicators p_x (under droplet) and p_y (outside droplet) are continuously derived based on the droplet's trajectory in this feature space relative to the identified cluster centers. The reasons for using the final image for defining the feature space, the choice of PCA and clustering, and the physical interpretation and mathematical formulation of p_x and p_y have been established in our previous work[4] (Chapter 3) and are kept unchanged in the present study.

5.3. RESULTS AND DISCUSSION

5.3.1. INITIAL DROPLET GEOMETRY ACROSS SURFACE FINISHES

The geometry and spatial distribution of droplets formed upon spray deposition fundamentally influence the local electrochemical activity. Specifically, droplet size influences the available electrolyte volume and oxygen diffusion path lengths; droplet shape and elongation can introduce anisotropic diffusion gradients; and overall coverage affects the available active areas on the exposed metal surface. Because these factors play a critical role in atmospheric corrosion, the initial droplet characteristics on each surface finish are examined first to establish a physical baseline.

As visually apparent in the representative raw optical images (see Fig. 5.6a1, b1, c1), the initial droplet populations vary systematically with the substrate surface finish. Fig. 5.4 summarizes these geometric trends, illustrating both the central tendencies and the full population heterogeneity. As shown in the probability density plots (Fig. 5.4a), the droplet size distributions for all surface finishes exhibit a right-skewed lognormal profile, which is consistent with previous reports on atomized sprays where the stochastic breakup process produces a lognormal spectrum of droplet diameters[39, 40]. The detailed fitting statistics confirming this distribution are provided in Supplementary Information under Section 5.S.1. Because of this lognormal skew, the median is utilized as a robust measure of central tendency. Fig. 5.4c reveals an inverse relationship between surface finish and droplet size, with the median diameter decreasing from approximately 140 μm on the coarse P320 surface to about 110 μm on the fine P1200 surface. This shift toward a broader distribution with a higher fraction of large droplets on rougher finishes is consistent with topography-induced droplet coalescence during spray impact. As suggested in previous studies, micro-grooves created by grinding may promote the pinning of the first droplets, which subsequently act as capture sites for incoming droplets, leading to rapid coalescence[9, 10]. Note that this impact-driven coalescence process occurs on microsecond-to-millisecond timescales and should be distinguished from slower, thermodynamically driven spreading or evaporation processes that may take place during exposure.

Besides size, droplet shape is greatly influenced by surface roughness. As shown in Fig. 5.4b through the probability density distributions, the distribution for the rougher P320 finish is significantly broadened and shifted toward lower values, indicating a major shift from more elongated droplets on rough surfaces to more circular droplets on smoother finishes. Fig. 5.4d shows that the median droplet aspect ratio increases from

approximately 0.82 on the P320 surface to about 0.87 on the P1200 surface. This behavior aligns with literature on anisotropic wetting on ground surfaces, where directional grinding marks promote preferential spreading along their orientation, resulting in elongated droplet footprints on coarser finishes[18, 19]. Beyond individual droplet geometry,

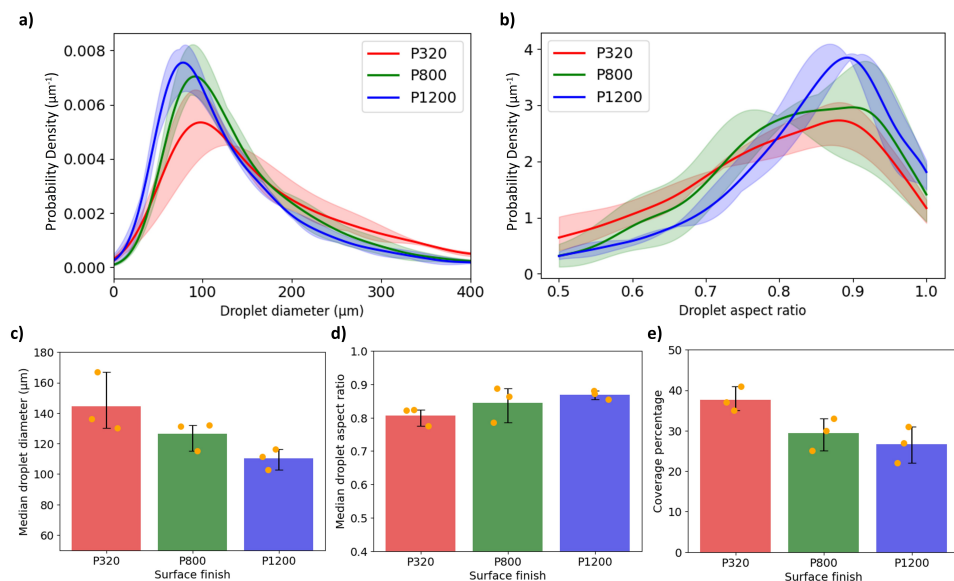


Figure 5.4: Initial droplet geometry as a function of surface finish. (a) Distribution of droplet diameter, (b) distribution of aspect ratio. Note that the y-axis represents probability density, meaning the area under the curve integrates to 1. (c) Median droplet diameter, (d) median droplet aspect ratio, and (e) surface coverage fraction for the three surface finishes (P320, P800, and P1200).

surface roughness also affects the overall electrolyte coverage. Fig. 5.4e demonstrates that the fraction of surface area covered by droplets decreases systematically with finer surface finishes. Assuming consistent total sprayed volumes and deposition conditions across experiments, the higher surface coverage observed on rougher surfaces can likely be explained by the combined effect of larger droplet sizes and increased coalescence, which together produce a greater wet area.

Overall, these observations reveal that rougher surfaces promote the formation of larger, more elongated droplets with higher overall surface coverage, whereas smoother surfaces favor smaller, more circular droplets with lower coverage. These geometric differences directly affect the local electrochemical reactions: larger droplets increase the difference in diffusion path length between the oxygen-rich droplet periphery and the oxygen-depleted center; higher surface coverage provides a larger total cathodic area to support metal dissolution; and elongation in droplets changes the spatial distribution of the electrolyte, which encourages localized corrosion to initiate and propagate at preferred locations along the grinding marks [41]. In the following sections, these systematic differences in initial droplet shape are used as a physical reference to interpret how

both global and local corrosion kinetics evolve across the different surface finishes.

5.3.2. GLOBAL CORROSION KINETICS FROM ER MEASUREMENTS

ER sensors measure resistance changes that translate into a uniform, global thickness loss across the entire exposed sensor track. However, atmospheric corrosion under spray deposition is highly localized strictly to the wetted regions. To decouple the intrinsic corrosion kinetics from the systematic differences in surface coverage established in [Section 5.3.1](#), the raw ER data were converted to an area-normalized corrosion depth. This normalized quantity was calculated by dividing the global volume loss of the sensor by the sum of the initial footprint areas of all detected individual droplets. This normalization is physically necessary to prevent coverage bias, as without it, a higher recorded global depth on the rougher P320 surface could be attributed solely to its larger wetted area. By normalizing to the initial active area, this metric would allow a direct kinetic comparison across the different surface finishes. The procedures for ER signal acquisition, calibration, and filtering follow the same methodology as described in our previous work[2] ([Chapter 2](#)) and are therefore not repeated here. [Fig. 5.5a](#) shows the evolution of the

5

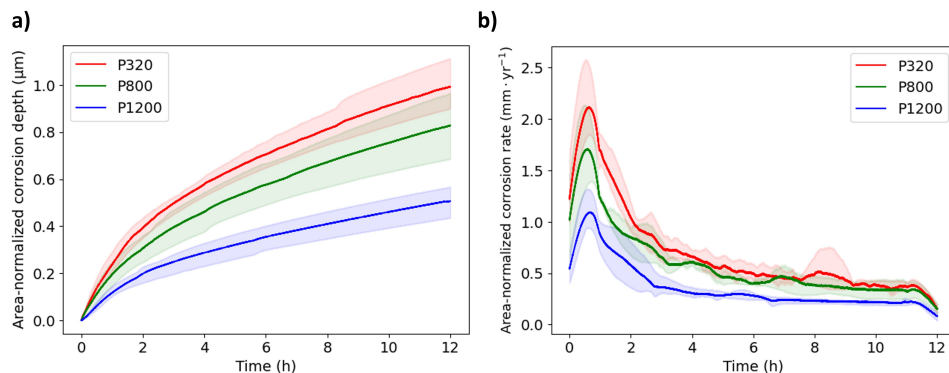


Figure 5.5: Global corrosion kinetics derived from ER measurements. (a) Area-normalized corrosion depth as a function of exposure time for the three surface finishes (P320, P800, and P1200). To eliminate bias from varying electrolyte coverage, the raw global thickness loss was normalized by the sum of the initial footprint areas of all individual droplets. No filtering is included in ER signals when computing the corrosion depth in this subplot. (b) Corresponding area-normalized instantaneous corrosion rate calculated from the derivative of smoothed area-normalized corrosion depth obtained from smoothing the raw ER reference and sensor track signals with a Savitzky-Golay filter (polynomial order 2, half-window length = 3500 data points). This is to suppress high-frequency noise without distorting physical kinetic trends (see Supplementary Information, [Section 5.5.2](#), for the mathematical derivation of the filter parameters for a representative run). The solid curve represents the mean value across three repetitions for each finish, and the shaded area indicates the corresponding min-max variability.

area-normalized corrosion depth over the exposure period for the three surface finishes. A clear dependence on surface finish is observed, with the coarse P320 surface exhibiting the highest cumulative corrosion depth, followed by P800 and P1200. The separation between the curves appears early during exposure and persists throughout the experiment, indicating that surface finish systematically influences overall corrosion severity under nearly identical exposure conditions. To further examine the temporal properties

of corrosion, the area-normalized corrosion rate (Fig. 5.5b) was obtained by calculating the first derivative of the corrosion depth with respect to time. To calculate the instantaneous corrosion rate without amplifying high-frequency instrumental noise, a Savitzky-Golay filter (polynomial order 2) was applied to the reference and sensor track ER signals prior to corrosion depth computation and further differentiation. Following the signal processing methodology established in our previous work[2] (Chapter 2), the cumulative power spectrum of the sensor track ER signals was analyzed to identify the frequency threshold retaining 90% of the signal power. Pulse analysis was then utilized to determine the optimal Savitzky-Golay half-window length whose -3 dB cutoff frequency matched this threshold (see Supplementary Information Section 5.S.2 for a representative run). Across all experimental repetitions, this calculated optimal length varied slightly between 3100 and 3900 data points, depending on the individual noise profile. To ensure uniform data treatment and prevent mathematical artifacts from skewing kinetic comparisons across runs, a constant, representative half-window length of 3500 data points was applied universally.

5

The calculated corrosion rates shows that all surface finishes exhibit a sharp initial peak right after spray deposition, which then decreases and stabilizes at a much lower level. This pattern is mainly driven by the changing physical and chemical conditions of the droplet electrolyte over time. The initial spike results from a highly localized and aggressive attack on a fresh, bare-metal surface exposed to droplets with higher oxygen levels and at their maximum initial volume. As time passes, evaporation reduces the wet area and electrolyte volume, while increasing local salt concentration. Simultaneously, solid corrosion products form and act as barriers to oxygen diffusion. These physical and chemical changes slow down the corrosion kinetics, causing the initial peak to decline and stabilize during later exposure stages. Rougher surfaces show higher initial peaks and overall corrosion rates, while smoother surfaces tend to corrode less and stabilize faster. Because ER signals are statistical and aggregate many droplet events that measure overall cumulative material loss, they do not specify where corrosion occurs or fully explain differences between surface finishes. In the following sections, we introduce droplet-level indicators (p_x and p_y) derived from optical imaging, which quantify the probability of corrosion product formation within the droplet footprint (p_x) and in the surrounding region (p_y). These indicators allow us to assess how localized corrosion activity under and around individual droplets collectively contributes to the global corrosion signal measured by ER. Since ER integrates responses across the whole surface, the relationship between the overall corrosion depth and the localised probability indicators is assessed statistically rather than attributing corrosion loss to specific droplets.

5.3.3. DROPLET-LEVEL FINAL SPATIAL DISTRIBUTION AND EXTENT OF CORROSION PRODUCT ACCUMULATION FROM PROBABILITY-BASED INDICATORS

This section focuses on the insight from the droplet-level probability-based indicators p_x and p_y the final status of corrosion within and surrounding individual droplet footprints. As detailed in our previous work[4] (Chapter 3), p_x and p_y quantify the likelihood that significant corrosion product accumulation can be detected within and outside the

droplet footprint. These indicators are first visualized to illustrate their spatial distribution, then quantified in terms of final corroding fraction. Fig. 5.6 presents qualitative

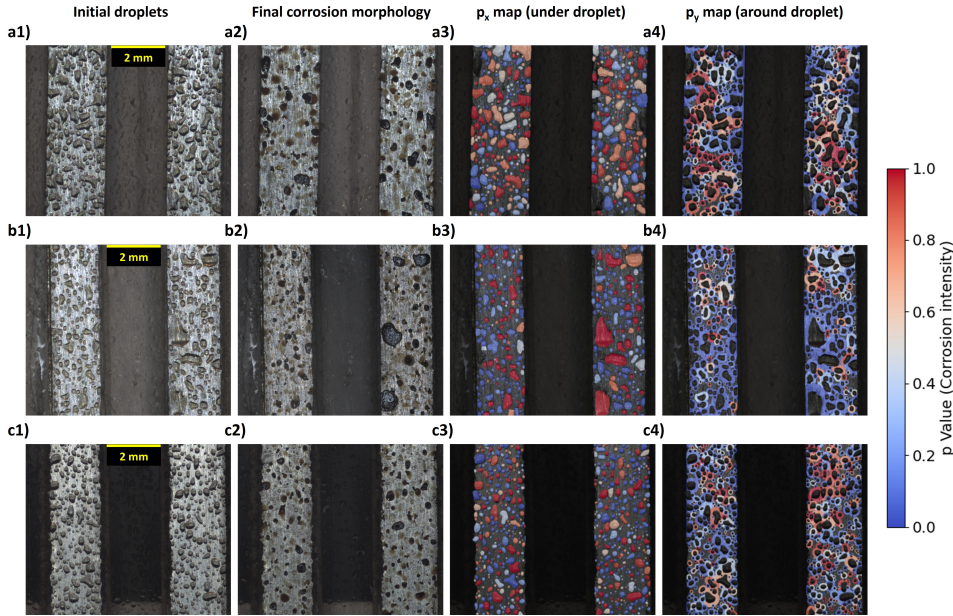


Figure 5.6: Qualitative visualization of droplet-level corrosion indicators on surfaces with different roughness (a1-a4) P320 (b1-b4) P800, and (c1-c4) P1200. The figures include: Initial raw optical images of the samples (a-c, 1); optical images after exposure (a-c, 2); corresponding color-coded maps of the probability-based indicators under the droplet (a-c, 3) and around the droplets (a-c, 4). The color scale indicates the intensity of the corrosion-related indicator, with higher values indicating stronger corrosion accumulation.

tive visualizations of the droplet-level corrosion indicators p_x and p_y for representative regions from the end-of-exposure image in a single repetition for each surface finish. Fig. 5.6a1–a4 correspond to the P320 surface, 5.6b1–b4 to P800, and 5.6c1–c4 to P1200. For each surface finish, the raw optical images and final corrosion morphology are also shown alongside the corresponding color-coded maps of p_x and p_y , which illustrate how corrosion products are spatially distributed over the exposed surface. The maps visually capture the systematic differences in corrosion product distribution across the three surface finishes. Rather than a uniform spread, the coarse P320 surface exhibits more extensive and intensely clustered regions of high p_x and p_y compared to the finer P1200 surface. However, these visualizations are intended solely to provide a qualitative intuition regarding the spatial distribution of corrosion products. Systematic differences across surface roughness conditions are quantified in the following analysis using statistical measures derived from all droplets and all experimental repetitions.

To quantify the overall extent of droplet-level corrosion at the end of exposure, the fraction of droplets exhibiting significant corrosion product accumulation was evaluated by assessing whether a plateau over a threshold value of 0.5 (with a minimum plateau

length of 5 time steps) is detected at the end of the p_x or p_y curve, as detailed in our previous work[4] (Chapter 3). This 0.5 threshold corresponds to the midpoint in the probability space between the non-corroding and actively corroding cluster centers. Furthermore, a sensitivity analysis conducted in our prior work[4] (Chapter 3) demonstrated the high robustness of this classification, showing negligible variation in the final corroding fractions when varying the probability threshold between 0.45 and 0.55, or the minimum plateau length between 4 and 6. Fig. 5.7 summarizes the final corroding fractions for the

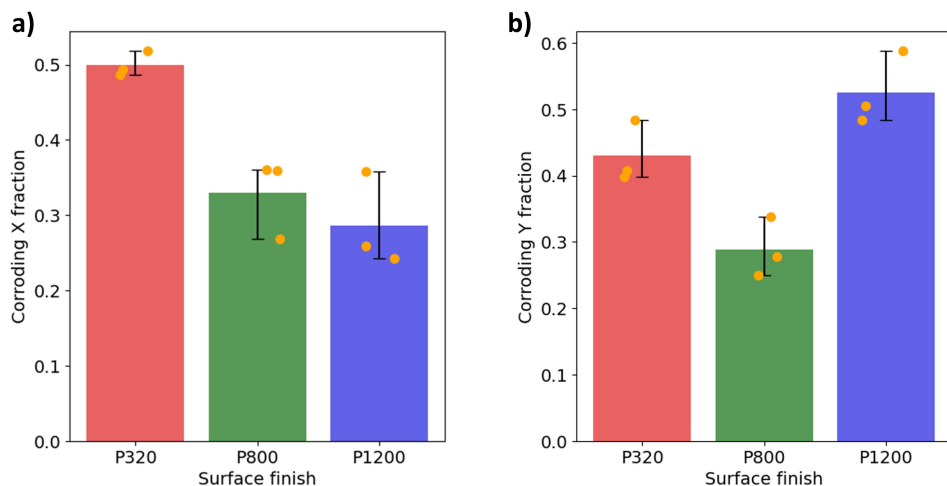


Figure 5.7: Fraction of droplets classified as corroding based on the plateau detection method at the end of exposure, based on the probability-based indicators for (a) p_x and (b) p_y for different surface finishes. Bars represent the mean values across three repeated runs for each surface finish, with error bars indicating the min-max deviation. Individual data points correspond to the results from each repetition.

three surface finishes in both inner (p_x) and outer (p_y) ROIs. For p_x (Fig. 5.7a), the corroding fraction decreases monotonically with decreasing surface finish coarse level, with the highest fraction observed on P320 and the lowest on P1200. This behavior reflects the combined influence of droplet geometry and substrate heterogeneity. As shown in Fig. 5.4a, the coarse P320 surface is associated with larger droplets and higher droplet coverage. Previous studies have shown that the probability of corrosion initiation under electrolyte droplets increases with droplet size[4, 42]. Larger droplets are more likely to promote localized corrosion under droplets through several effects. First, increased droplet size enhances the likelihood of covering surface heterogeneities[42], and this effect is especially pronounced on rougher surfaces, which inherently have a higher density of micro-grooves and defects. Larger droplets also support stable electrochemical separation between anodic and cathodic regions due to longer diffusion paths and an extended cathodic perimeter, as described in classical Evans-type droplet corrosion models[1, 43]. In addition, evaporation-driven transport can further amplify electrochemical gradients within larger droplets, as non-uniform evaporation promotes local accumulation of aggressive species and pH gradients near the droplet periphery, thereby increasing corrosion probability[4, 6, 7]. These combined effects provide a consistent explanation for the

observed highest p_x fraction in P320 and the lowest in P1200.

In contrast, p_y (Fig. 5.7b) exhibits a non-monotonic dependence on surface finish coarse level. The intermediate P800 surface shows the lowest fraction of droplets with p_y above the threshold value, the fine P1200 surface displays the highest p_y fraction among the three finishes. This behavior suggests that thin electrolyte film formation in the outer ROI is hypothesized to be governed by multiple interacting processes. Three mechanisms are possibly contributing to this behavior. First, electrochemically driven wet-area expansion, as reported in previous studies[44, 45], can promote the outward growth of thin electrolyte layers once corrosion reactions are established, particularly on surfaces with reduced contact-line pinning. This mechanism may explain the high p_y values observed on the smooth P1200 surface. Second, secondary condensation may contribute significantly. The coarse P320 surface exhibits larger, more irregular droplets and shorter inter-droplet distances, which can enhance local moisture retention and increase the likelihood of thin electrolyte layer formation between droplets under humid conditions. Such films can, in turn, support electrochemical activity outside the primary droplet footprints. Furthermore, these shorter inter-droplet distances on the coarse surface can create interacting cathodic regions near droplet edges. This proximity may enhance the accumulation of corrosion products in inter-droplet regions without requiring a continuous electrolyte film.

The combination of these effects may explain why both very rough and very smooth surfaces exhibit high p_y fractions, whereas the intermediate P800 surface shows reduced thin-film-mediated corrosion activity. While additional processes, such as capillary-driven spreading toward equilibrium, may further influence droplet boundaries at early times, the present statistical trends suggest that electrochemical spreading and secondary condensation provide dominant contributions on the timescale of corrosion development. The effect of droplet size on the final corroding fraction for each surface finish in

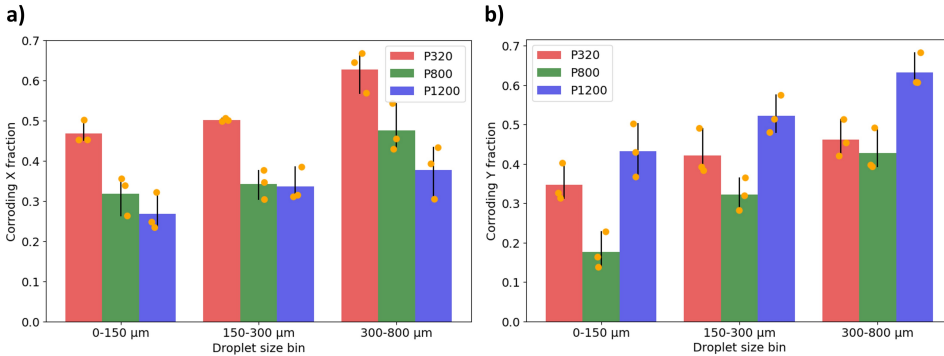


Figure 5.8: Final fraction of droplets showing corrosion products in the (a) inner and (b) outer ROIs as a function of droplet size for the three surface finishes. Bars show the mean corrosion fraction per size bin; orange markers represent individual repeat measurements, and error bars indicate the min-max deviation.

the inner and outer ROIs was also evaluated, with the results presented in Fig. 5.8. Con-

sistent with our previous work[4] (Chapter 3), larger droplets overall exhibit a higher likelihood of developing detectable corrosion products in both inner and outer ROIs, owing to their greater electrolyte volume and lateral extent. The present results show that this behavior persists across different surface finishes. While Fig. 5.7 and Fig. 5.8 separately present the influence of surface finish and droplet size on the final corroding fraction, these two variables are not independent. Surface roughness systematically modifies the droplet size distribution and surface coverage under spray deposition, as shown in Fig. 5.4. Therefore, part of the observed “roughness effect” on corroding fraction may be indirectly mediated through changes in droplet geometry and size distribution rather than arising solely from intrinsic electrochemical differences between finishes. In this sense, the apparent roughness dependence should be interpreted as the combined outcome of (i) modified droplet population statistics and (ii) altered substrate reactivity. The present analysis does not fully decouple these contributions, and the trends reported here should therefore be viewed as coupled geometric–electrochemical effects rather than as isolated mechanistic drivers.

5

5.3.4. DROPLET-LEVEL CORROSION EVOLUTION FROM PROBABILITY-BASED INDICATORS

To relate the droplet-level corrosion indicators to the ER-based corrosion response, the temporal evolution of the area-weighted average values of p_x and p_y is examined. While p_x and p_y are extracted from droplet segments that are rescaled to a common size and are therefore scale-invariant, the ER signal reflects the cumulative effect of corrosion processes occurring over the surface. Consequently, droplets with similar p -values can contribute differently to the ER signal depending on their size. The area-weighted aggregation, therefore, ensures that droplets occupying a larger fraction of the surface contribute proportionally more to the aggregated metric. However, it must be explicitly stated that this area-weighting is an approximated linear aggregation approach. It is not intended to reconstruct the physical contributions of individual droplets to corrosion depth, which may involve nonlinear relationships between a droplet’s geometry and its local chemistry (Chapter 4). Rather, it serves as an approximate, linear weighting method to aggregate local probabilities to provide a statistical approximation that aligns droplet-level scale-invariant corrosion indicators with the global corrosion measurement.

As detailed in our previous work[4] (Chapter 3), p_x and p_y (p in Eq. 5.1 provide a continuous representation of the fraction (f in Eq. 5.1) of a droplet exhibiting corrosion product, the corresponding area-weighted averages (f_A in Eq. 5.2) can therefore be interpreted as a continuous measure for the fraction of the initial wet area that exhibits significant corrosion product accumulation with high confidence. In Eq. 5.1 and Eq. 5.2, $\mathbb{I}(\cdot)$ denotes the indicator function, which equals 1 when the condition in parentheses is satisfied and 0 otherwise.

$$f = \frac{\sum_i \mathbb{I}(p_i > 0.5)}{\sum_i \mathbb{I}(1)}$$

$$p = \frac{\sum_i p_i}{\sum_i 1} \quad (5.1)$$

$$f = \frac{\sum_i A_i \cdot \mathbb{I}(p_i > 0.5)}{\sum_i A_i \cdot \mathbb{I}(1)} \quad (5.2)$$

$$p = \frac{\sum_i A_i \cdot p_i}{\sum_i A_i \cdot 1}$$

Fig. 5.9 shows the temporal evolution of the area-weighted p_x and p_y together with the corrosion depth derived from ER measurement, normalized with the initial droplet-covered area, for the three surface finishes. For all finishes, both p_x and p_y increase with time, which is consistent with the ongoing accumulation of corrosion product during exposure. Furthermore, the roughness-dependent ordering of p_x and p_y is consistent with the final corroding fractions as presented in Fig. 5.7, indicating that the area-weighted aggregation preserves the trends observed at the droplet-count level. Beyond these expected consistencies, the detailed temporal evolution of p_x and p_y reveals distinct dynamic behaviors that provide additional insight into the mechanisms that govern corrosion product development across different surface finishes. To facilitate interpretation

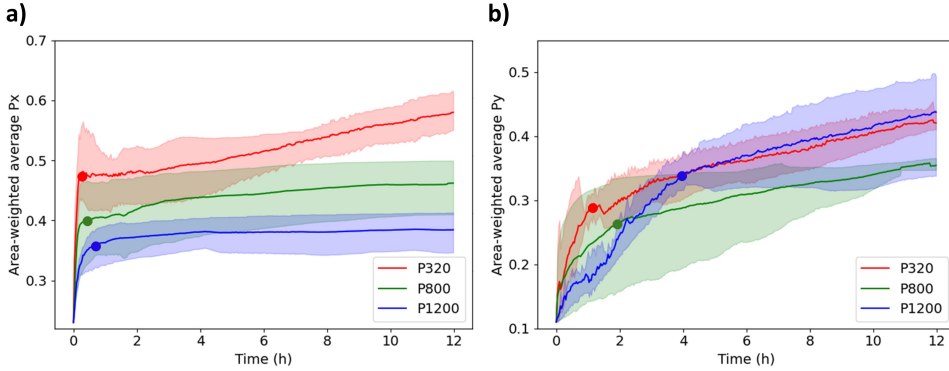


Figure 5.9: Temporal evolution of the area-weighted (a) p_x and (b) p_y for the three surface finishes, with shaded area standing for the min-max deviation across three repetitions for each surface finish. Colored markers indicate the mathematically derived characteristic turning points.

of the temporal evolution, a characteristic turning point, highlighted by red, green, and blue dots for the P320, P800, and P1200 finishes, respectively, in Fig. 5.9, can be identified in both the p_x (Fig. 5.9a) and p_y (Fig. 5.9b) curves as a noticeable change in curve slope. To ensure a reproducible and quantitative comparison across surface finishes, this turning point is defined mathematically using continuous piecewise linear regression. Specifically, a two-segment linear model is fitted to the mean p_x and p_y curves for each roughness using least-squares optimization. The intersection knot of these two linear segments serves as an approximation of the timing and magnitude of the turning point, without relying on visual estimation. In p_x , this turning point is marked by a pronounced reduction in curve slope and is consistently well defined across all surface finishes. In contrast, the corresponding transition in p_y is more gradual and spans a broader time interval, reflecting a less constrained nature of corrosion product development in outer ROIs. In the following analysis, the turning point is therefore used as a common descrip-

tor for both inner (p_x) and outer (p_y) ROIs, with its physical interpretation and associated confidence differing between the two. For p_x , and both the timing and magnitude of the turning point are employed as key quantitative descriptors of under-droplet corrosion product development. For p_y , both features are interpreted with greater caution due to the less sharply defined transition. The initial curve slope prior to the turning point can be viewed as a derived quantity, approximately reflected in the ratio of the turning-point magnitude to its timing. A higher initial slope, therefore, indicates more rapid early-stage corrosion product accumulation. Because the post-turning behavior is influenced by multiple concurrent processes, later-stage slopes are not used as independent quantitative descriptors and are discussed only qualitatively.

A clear difference is observed in the temporal evolution of p_x which rises earlier and reaches its characteristic turning point before p_y . This consistent delay in the turning point of p_y suggests that, at an aggregate level, corrosion products tend to form first within the initial droplet area before becoming significant in nearby regions. It is important to note that this does not exclude cases where corrosion products gather solely in inter-droplet zones. Instead, the delay signifies a population-level trend, where the processes most contributing to p_x cause a delayed increase in area-weighted p_y . This aligns with the mechanistic hypothesis that additional physicochemical steps such as electrolyte redistribution, thin-film formation, or micro-pools development, [42, 44, 45] are necessary for corrosion products to develop in the outer regions of interest.

For p_x , the turning-point characteristics further reveal a pronounced dependence on surface roughness. Both the timing and magnitude of the turning point follow the order $P320 > P800 > P1200$, indicating that under-droplet corrosion product development initiates earlier and reaches a higher characteristic level on the coarser surface. This behavior is consistent with the combined effects of larger initial droplet sizes and increased surface heterogeneity on rougher finishes, which promote faster initiation and spatial expansion of corrosion products within the droplet footprint. In contrast, the finer P1200 surface exhibits a delayed turning point with a lower associated magnitude, indicating slower and more gradual under-droplet corrosion development.

For p_y , the influence of surface roughness is also reflected in the turning-point timing, although the transition is less sharp than for p_x . Coarser surfaces exhibit earlier turning behavior than finer finishes, suggesting that corrosion product accumulation at inter-droplet regions occurs earlier on rougher surfaces. The corresponding turning-point magnitudes in p_y show greater variability and are therefore interpreted more cautiously, which is consistent with the more spatially distributed nature of corrosion product accumulation outside the droplet footprint. Differences in early-time curve slope observed among surface finishes can be understood as a consequence of these turning-point characteristics, with higher initial slopes mainly a result of earlier turning times. At later times, the evolution of p_y becomes more comparable across all finishes, which might be attributed to the increasing influence of multiple concurrent processes that are not uniquely attributable to surface roughness.

Summarizing the time-based changes of these probability-based descriptors, it is important to clearly acknowledge their limitations. First, the area-weighted aggregation is a linear statistical method that does not account for the nonlinear geometric-electrochemical interactions influencing individual droplet contributions. Second, since surface roughness affects various factors such as electrochemical reactivity, droplet shape, size distribution, surface coverage, and proximity between droplets, the differences observed in their temporal evolution across different finishes likely arise from these interconnected effects rather than a single dominant factor. In conclusion, although this framework offers valuable statistical insights into overall corrosion behavior, it is not designed to directly identify specific mechanistic pathways at the level of individual droplets.

5.3.5. RELATIONSHIP BETWEEN PROBABILITY-BASED DESCRIPTORS AND ER-BASED CORROSION KINETICS

The ER signal and the image-derived probability-based descriptors offer complementary insights into the corrosion process. p_x and p_y quantify the likelihood of visible corrosion product buildup both within and outside the original droplet footprint. It is important to recognize that while these quantities are related, probability-based descriptors are indirect indicators of localized activity and should not be directly interpreted as measurements of localized corrosion kinetics.

Fig. 5.10 illustrates the temporal evolution of the area-weighted p_x and p_y area-normalized corrosion depth and corrosion rate derived from ER measurements. For all surface finishes, the ER depth increases monotonically over time, consistent with continuous metal dissolution during exposure. As shown in Fig. 5.10b, the high values in the ER-based corrosion rate correspond temporally with the initial rapid rise and the characteristic turning-point observed in p_x . The temporal coincidence between the rise and the high ER corrosion rate suggests that the optical framework captures the early active corrosion regime. Furthermore, the earlier turning-point and higher magnitude of p_x the rougher P320 surface coincide with a more rapid increase in ER corrosion depth (Fig. 5.10a), suggesting that earlier and more extensive under-droplet corrosion product accumulation is found on the rougher surface. Regarding the regions outside the initial droplet footprint, the gradual increase in p_y accompanies the continued growth of the ER-measured corrosion depth at later stages of exposure (Fig. 5.10c). Furthermore, as illustrated in Fig. 5.10d, the initial spike in the global corrosion rate occurs mostly before p_y reaches its characteristic turning point. This reinforces the statistical observation that the early-stage active corrosion regime corresponds primarily to localized activity within the initial droplet boundaries, whereas the inter-droplet corrosion product accumulation (captured by p_y) develops more gradually during the later stages.

Surface roughness modulates both the ER and image-derived indicators in the same direction, such that rougher surfaces exhibit earlier and more extensive visible corrosion product accumulation, which aligns with greater ER-measured metal loss. Because surface roughness simultaneously affects droplet geometry, distribution, coverage, and intrinsic electrochemical behavior, this observed alignment likely reflects coupled geometric-electrochemical effects rather than a single dominant mechanism. The present analysis,

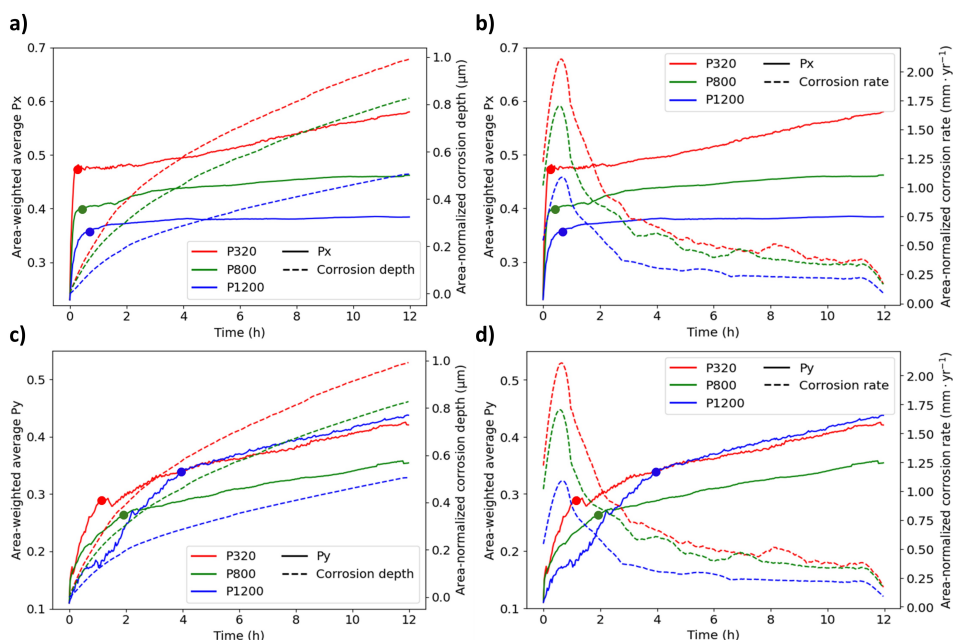


Figure 5.10: Temporal evolution of the mean area-weighted (a) p_x and (b) p_y for the three surface finishes, shown together with the mean area-normalized corrosion depth (a, c) and rate (b, d) from ER measurements, both averaged across three repetitions. Solid lines represent p_x or p_y , and dashed lines denote ER depth or rate. Shaded areas representing min-max variance have been removed for visual clarity. The full results for the ER kinetics and the optical probability indicators are shown in Figures 5 and 9, respectively.

therefore, identifies statistical correlations between optical product formation and physical metal loss without directly isolating the underlying physicochemical pathways.

5.4. CONCLUSION

This study investigated how substrate surface finish influences atmospheric corrosion of carbon steel under multi-droplet exposure across three grinding finishes: P320, P800, and P1200.

- Regarding droplet behavior and corrosion response, rougher surfaces produced larger, more elongated droplets and slightly higher initial surface coverage. ER-measured global corrosion depth and corrosion rate were consistently higher and developed earlier on rougher surface finishes.
- A primary methodological contribution of this work is the integration of continuous ER measurements with droplet-resolved optical analysis. Probability-based descriptors (p_x and p_y) were introduced to statistically characterize corrosion product development, alongside an area-weighted aggregation approach to align droplet-level descriptors with global corrosion depth. The resulting temporal analysis framework enables systematic comparison between regions within and outside initial

droplet footprints.

- Application of this framework revealed a characteristic turning point in corrosion product accumulation. For all surface finishes, the area-weighted probability of under-droplet corrosion (p_x) rose earlier and to a higher magnitude than the inter-droplet probability (p_y), indicating that corrosion products generally develop first within droplet footprints before becoming significant in surrounding regions. Furthermore, the initial rapid rise of p_x temporally coincides with the highest ER-measured corrosion rates, consistent with the early active corrosion regime being closely tied to localized activity within initial droplet boundaries.
- It is essential to acknowledge the limitations and scope of this analysis. The probability-based indicators serve as indirect proxies for visible corrosion product accumulation, not direct measurements of metal loss. Because surface roughness simultaneously modifies intrinsic substrate reactivity, droplet geometry, spatial distribution, and overall coverage, the observed differences across finishes likely reflect coupled geometric–electrochemical effects. The present approach therefore identifies aggregated statistical correlations rather than isolating single mechanistic pathways or resolving nonlinear, droplet-by-droplet interactions.
- Ultimately, the combined use of ER sensing and probability-based image descriptors establishes a framework that statistically links droplet-scale optical evolution to global corrosion kinetics. This approach enables comparative evaluation of surface finishes under complex multi-droplet conditions and can be extended to other material systems and environments where local spatial heterogeneity governs overall reactions.

SUPPLEMENTARY INFORMATION

5.S.1. LOGNORMAL FITTING OF INITIAL DROPLET SIZE DISTRIBUTION

Table 5.2: The lognormal fitting statistics for scale (μ) and shape (σ) parameters across runs

	Rep1		Rep2		Rep3	
	μ	σ	μ	σ	μ	σ
P320	4.91	0.61	4.87	0.57	5.12	0.54
P800	4.75	0.48	4.88	0.50	4.88	0.56
P1200	4.63	0.55	4.75	0.61	4.71	0.51

Section 5.S.1 details the statistical parameters derived from the initial droplet distributions. Tab. 5.2 summarizes the lognormal fitting statistics, specifically the scale (μ) and shape (σ) parameters, for the droplet diameters across all three repetitions of the P320, P800, and P1200 surface finishes.

5.S.2. DETERMINATION OF THE SAVITZKY-GOLAY FILTER WINDOW LENGTH FOR A REPRESENTATIVE RUN

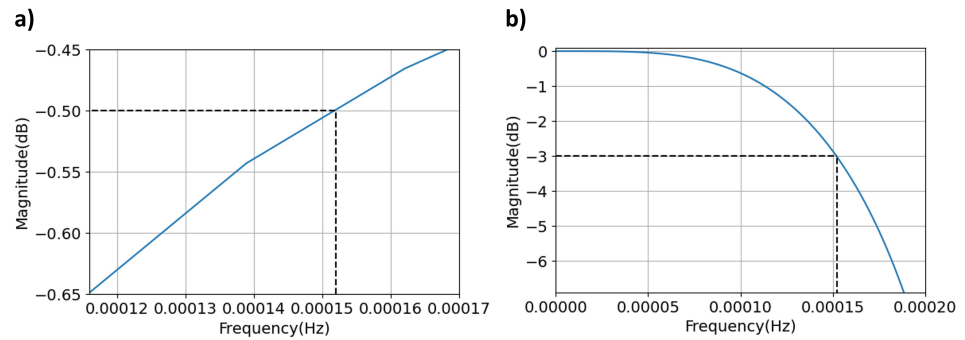


Figure 5.11: (a) Cumulative power spectrum of a representative sensor track ER signal, showing the 90% power retention threshold (-0.5 dB) at 0.000152 Hz. (b) Frequency response of a Savitzky-Golay filter (polynomial order 2, half-window length = 3500), where the -3 dB cutoff frequency for this window length perfectly matches the threshold identified in this specific run.

The overall power spectrum of the raw sensor track ER signals was examined to find the frequency that captures approximately 90% of the signal’s power (see Figure S1a). Pulse analysis was then used to identify the best Savitzky-Golay half-window length, where the -3 dB cutoff frequency aligned with this threshold (see Figure S1b). Although the optimal half-window length varied from 3100 to 3900 across the nine experimental runs, a standard value of 3500 was chosen for all datasets to ensure uniform signal smoothing during comparative kinetic analysis.

BIBLIOGRAPHY

- [1] B. G. Koushik et al. "Review on modelling of corrosion under droplet electrolyte for predicting atmospheric corrosion rate". In: *Journal of Materials Science & Technology* 62 (2021), pp. 254–267. ISSN: 1005-0302. DOI: [10.1016/j.jmst.2020.04.061](https://doi.org/10.1016/j.jmst.2020.04.061). URL: [%3CGo%20to%20ISI%3E://WOS:000601221700025](https://www.wos.org/doi/abs/10.1016/j.jmst.2020.04.061).
- [2] K. E. Zhang et al. "Monitoring atmospheric corrosion under multi-droplet conditions by electrical resistance sensor measurement". In: *Corrosion Science* 236 (2024). ISSN: 0010-938x. DOI: [ARTN11227110.1016/j.corsci.2024.112271](https://doi.org/10.1016/j.corsci.2024.112271). URL: [%3CGo%20to%20ISI%3E://WOS:001271277400001](https://www.wos.org/doi/abs/10.1016/j.corsci.2024.112271).
- [3] E. Rahimi et al. "Atmospheric corrosion of iron under a single droplet: A new systematic multi-electrochemical approach". In: *Corrosion Science* 235 (2024). ISSN: 0010-938x. DOI: [ARTN11217110.1016/j.corsci.2024.112171](https://doi.org/10.1016/j.corsci.2024.112171). URL: [%3CGo%20to%20ISI%3E://WOS:001256286000001](https://www.wos.org/doi/abs/10.1016/j.corsci.2024.112171).
- [4] K. Zhang, A. Mol, and Y. Gonzalez-Garcia. "Development of a data-driven framework for monitoring corrosion under droplets". In: *Corrosion Science* 258 (2026). ISSN: 0010-938x. DOI: [ARTN11331310.1016/j.corsci.2025.113313](https://doi.org/10.1016/j.corsci.2025.113313). URL: [%3CGo%20to%20ISI%3E://WOS:001597867400001](https://www.wos.org/doi/abs/10.1016/j.corsci.2025.113313).
- [5] V. Vangrunderbeek et al. "Corrosion and environmental sensor response delays during monitored multi-droplet wetting: Unraveling time lags in atmospheric corrosion". In: *Corrosion Science* 255 (2025). ISSN: 0010-938x. DOI: [ARTN11315410.1016/j.corsci.2025.113154](https://doi.org/10.1016/j.corsci.2025.113154). URL: [%3CGo%20to%20ISI%3E://WOS:001524798700002](https://www.wos.org/doi/abs/10.1016/j.corsci.2025.113154).
- [6] V. Soulié et al. "Salt-induced iron corrosion under evaporating sessile droplets of aqueous sodium chloride solutions". In: *Materials and Corrosion-Werkstoffe Und Korrosion* 68.9 (2017), pp. 927–934. ISSN: 0947-5117. DOI: [10.1002/maco.201609319](https://doi.org/10.1002/maco.201609319). URL: [%3CGo%20to%20ISI%3E://WOS:000408983300001](https://www.wos.org/doi/abs/10.1002/maco.201609319).
- [7] F. Lequien et al. "Corrosion influence on the evaporation of sessile droplet". In: *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 546 (2018), pp. 59–66. ISSN: 0927-7757. DOI: [10.1016/j.colsurfa.2018.02.047](https://doi.org/10.1016/j.colsurfa.2018.02.047). URL: [%3CGo%20to%20ISI%3E://WOS:000429302300007](https://www.wos.org/doi/abs/10.1016/j.colsurfa.2018.02.047).
- [8] S. R. Street et al. "The Effect of Deposition Conditions on Atmospheric Pitting Corrosion Location Under Evans Droplets on Type 304L Stainless Steel". In: *Corrosion* 74.5 (2018), pp. 520–529. ISSN: 0010-9312. DOI: [10.5006/2614](https://doi.org/10.5006/2614). URL: [%3CGo%20to%20ISI%3E://WOS:000431898500003](https://www.wos.org/doi/abs/10.5006/2614).
- [9] M. Massinon et al. "Spray droplet impaction outcomes for different plant species and spray formulations". In: *Crop Protection* 99 (2017), pp. 65–75. ISSN: 0261-2194. DOI: [10.1016/j.cropro.2017.05.003](https://doi.org/10.1016/j.cropro.2017.05.003). URL: [%3CGo%20to%20ISI%3E://WOS:000404708700009](https://www.wos.org/doi/abs/10.1016/j.cropro.2017.05.003).

- [10] M. A. Delele et al. "Predicting the dynamic impact behaviour of spray droplets on flat plant surfaces". In: *Soft Matter* 12.34 (2016), pp. 7195–7211. ISSN: 1744-683x. DOI: [10.1039/c6sm00933f](https://doi.org/10.1039/c6sm00933f). URL: [3CGo%20to%20ISI%3E://WOS:000382113400013](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000382113400013).
- [11] X. Wang et al. "A Comprehensive Review of Wetting Transition Mechanism on the Surfaces of Microstructures from Theory and Testing Methods". In: *Materials* 15.14 (2022). DOI: [ARTN474710.3390/ma15144747](https://doi.org/ARTN474710.3390/ma15144747). URL: [3CGo%20to%20ISI%3E://WOS:000832297200001](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000832297200001).
- [12] H. Kusumaatmaja and J. M. Yeomans. "Modeling contact angle hysteresis on chemically patterned and superhydrophobic surfaces". In: *Langmuir* 23.11 (2007), pp. 6019–6032. ISSN: 0743-7463. DOI: [10.1021/la063218t](https://doi.org/10.1021/la063218t). URL: [3CGo%20to%20ISI%3E://WOS:000246456700028](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000246456700028).
- [13] S. R. Yassine et al. "Impact of Droplet Wettability on Scanning Electrochemical Cell Microscopy Performance in Stainless Steels". In: *Chemical & Biomedical Imaging* 3.4 (2025), pp. 232–243. ISSN: 2832-3637. DOI: [10.1021/cbmi.4c00101](https://doi.org/10.1021/cbmi.4c00101). URL: [3CGo%20to%20ISI%3E://WOS:001444250100001](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:001444250100001).
- [14] R. N. Wenzel. "Resistance of solid surfaces to wetting by water". In: *Industrial and Engineering Chemistry* 28 (1936), pp. 988–994. ISSN: 0019-7866. DOI: [DOI10.1021/ie50320a024](https://doi.org/10.1021/ie50320a024). URL: [3CGo%20to%20ISI%3E://WOS:000188482500229](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000188482500229).
- [15] G. Wolansky and A. Marmur. "Apparent contact angles on rough surfaces: the Wenzel equation revisited". In: *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 156.1-3 (1999), pp. 381–388. ISSN: 0927-7757. DOI: [Doi10.1016/S0927-7757\(99\)00098-9](https://doi.org/10.1016/S0927-7757(99)00098-9). URL: [3CGo%20to%20ISI%3E://WOS:000082624200035](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000082624200035).
- [16] M. Razavifar et al. "Quantifying the impact of surface roughness on contact angle dynamics under varying conditions". In: *Scientific Reports* 15.1 (2025). ISSN: 2045-2322. DOI: [ARTN1661110.1038/s41598-025-01127-7](https://doi.org/ARTN1661110.1038/s41598-025-01127-7). URL: [3CGo%20to%20ISI%3E://WOS:001487815100037](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:001487815100037).
- [17] X. M. Dai et al. "Slippery Wenzel State". In: *Acs Nano* 9.9 (2015), pp. 9260–9267. ISSN: 1936-0851. DOI: [10.1021/acsnano.5b04151](https://doi.org/10.1021/acsnano.5b04151). URL: [3CGo%20to%20ISI%3E://WOS:000361935800065](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000361935800065).
- [18] J. Y. Chung, J. P. Youngblood, and C. M. Stafford. "Anisotropic wetting on tunable micro-wrinkled surfaces". In: *Soft Matter* 3.9 (2007), pp. 1163–1169. ISSN: 1744-683x. DOI: [10.1039/b705112c](https://doi.org/10.1039/b705112c). URL: [3CGo%20to%20ISI%3E://WOS:000248731700008](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000248731700008).
- [19] Y. Ding et al. "Anisotropic wetting characteristics of droplet on micro-grooved surface". In: *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 633 (2022). ISSN: 0927-7757. DOI: [ARTN12785010.1016/j.colsurfa.2021.127850](https://doi.org/ARTN12785010.1016/j.colsurfa.2021.127850). URL: [3CGo%20to%20ISI%3E://WOS:000720948000003](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000720948000003).
- [20] E. Bormashenko. "Young, Boruvka-Neumann, Wenzel and Cassie-Baxter equations as the transversality conditions for the variational problem of wetting". In: *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 345.1-3 (2009), pp. 163–165. ISSN: 0927-7757. DOI: [10.1016/j.colsurfa.2009.04.054](https://doi.org/10.1016/j.colsurfa.2009.04.054). URL: [3CGo%20to%20ISI%3E://WOS:000268059800024](https://www.wos-id.org/3CGo%20to%20ISI%3E://WOS:000268059800024).

- [21] U. R. Evans. "Oxygen distribution as a factor in the corrosion of metals". In: *Industrial and Engineering Chemistry* 17 (1925), pp. 363–372. ISSN: 0019-7866. DOI: [DOI10.1021/ie50184a012](#). URL: [%3CGo%20to%20ISI%3E://WOS:000188442900132](#).
- [22] R. H. Xu et al. "Effect of surface roughness on contact resistance and electrochemical corrosion behavior of 446 stainless steel in simulated anode environments for proton exchange membrane fuel cell". In: *Journal of Solid State Electrochemistry* 28.9 (2024), pp. 3087–3098. ISSN: 1432-8488. DOI: [10.1007/s10008-024-05864-z](#). URL: [%3CGo%20to%20ISI%3E://WOS:001191062100001](#).
- [23] Y. W. Tang et al. "Investigation of Influence of Surface Roughness on Pitting Corrosion of Duplex Stainless Steel 2205 using Various Electrochemical Techniques". In: *International Journal of Electrochemical Science* 14.7 (2019), pp. 6790–6813. ISSN: 1452-3981. DOI: [10.20964/2019.07.51](#). URL: [%3CGo%20to%20ISI%3E://WOS:000474380600068](#).
- [24] Y. W. Tang et al. "Effect of Surface Roughness on Pitting Corrosion of 2205 Duplex Stainless Steel Investigated by Electrochemical Noise Measurements". In: *Materials* 12.5 (2019). ISSN: 1996-1944. DOI: [ARTN73810.3390/ma12050738](#). URL: [%3CGo%20to%20ISI%3E://WOS:000462543700054](#).
- [25] M. H. Moayed and R. C. Newman. "Using pit solution chemistry for evaluation of metastable pitting stability of austenitic stainless steel". In: *Materials and Corrosion-Werkstoffe Und Korrosion* 56.3 (2005), pp. 166–173. ISSN: 0947-5117. DOI: [10.1002/maco.200403827](#). URL: [%3CGo%20to%20ISI%3E://WOS:000227761700003](#).
- [26] G. T. Burstein and S. P. Vines. "Repetitive nucleation of corrosion pits on stainless steel and the effects of surface roughness". In: *Journal of the Electrochemical Society* 148.12 (2001), B504–B516. ISSN: 0013-4651. DOI: [10.1149/1.1416503](#). URL: [%3CGo%20to%20ISI%3E://WOS:000172166800015](#).
- [27] F. Wang et al. "Effect of Surface Roughness on Corrosion Resistance of Mooring Chains for Offshore Floating Photovoltaics". In: *Metals* 14.10 (2024). DOI: [ARTN118110.3390/met14101181](#). URL: [%3CGo%20to%20ISI%3E://WOS:001342921300001](#).
- [28] E. M. Sherif, I. A. Alnaser, and A. T. Abbas. "Effect of surface roughness on corrosion behavior of AISI 4340 high-strength steel in sodium chloride solutions". In: *Aip Advances* 14.6 (2024). DOI: [Artn06501710.1063/5.0213527](#). URL: [%3CGo%20to%20ISI%3E://WOS:001248213700014](#).
- [29] B. Evgeny, T. Hughes, and D. Eskin. "Effect of surface roughness on corrosion behaviour of low carbon steel in inhibited 4 M hydrochloric acid under laminar and turbulent flow conditions". In: *Corrosion Science* 103 (2016), pp. 196–205. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2015.11.019](#). URL: [%3CGo%20to%20ISI%3E://WOS:000369201100021](#).
- [30] H. T. Bai et al. "Effect of Surface Roughness on Static Corrosion Behavior of J55 Carbon Steel in CO₂-Containing Geothermal Water at 65 °C". In: *Coatings* 13.5 (2023). DOI: [ARTN82110.3390/coatings13050821](#). URL: [%3CGo%20to%20ISI%3E://WOS:000996898900001](#).

- [31] C. Samarawickrama et al. "Impact of droplet conditions on corrosion inhibitor mechanisms: A case study on smallazole molecules". In: *Corrosion Science* 257 (2025). ISSN: 0010-938x. DOI: [ARTN11334010.1016/j.corsci.2025.113340](https://doi.org/10.1016/j.corsci.2025.113340). URL: [%3CGo%20to%20ISI%3E://WOS:001584759600003](https://www.wos.org/doi/abs/10.1016/j.corsci.2025.113340).
- [32] S. X. Li and L. H. Hihara. "The comparison of the corrosion of ultrapure iron and low-carbon steel under NaCl-electrolyte droplets". In: *Corrosion Science* 108 (2016), pp. 200–204. ISSN: 0010-938x. DOI: [10.1016/j.corsci.2016.03.005](https://doi.org/10.1016/j.corsci.2016.03.005). URL: [%3CGo%20to%20ISI%3E://WOS:000375887100020](https://www.wos.org/doi/abs/10.1016/j.corsci.2016.03.005).
- [33] S. X. Li and L. H. Hihara. "Atmospheric-Corrosion Electrochemistry of NaCl Droplets on Carbon Steel". In: *Journal of the Electrochemical Society* 159.11 (2012), pp. C461–C468. ISSN: 0013-4651. DOI: [10.1149/2.035211jes](https://doi.org/10.1149/2.035211jes). URL: [%3CGo%20to%20ISI%3E://WOS:000309107200030](https://www.wos.org/doi/abs/10.1149/2.035211jes).
- [34] M. Y. Wang et al. "Visualizing and understanding corrosion evolution beneath a condensed droplet using the multi-electrode array". In: *Colloids and Surfaces A-Physicochemical and Engineering Aspects* 684 (2024). ISSN: 0927-7757. DOI: [ARTN13325210.1016/j.colsurfa.2024.133252](https://doi.org/10.1016/j.colsurfa.2024.133252). URL: [%3CGo%20to%20ISI%3E://WOS:001166707000001](https://www.wos.org/doi/abs/10.1016/j.colsurfa.2024.133252).
- [35] X. Tang et al. "Atmospheric corrosion local electrochemical response to a dynamic saline droplet on pure Iron". In: *Electrochemistry Communications* 101 (2019), pp. 28–34. ISSN: 1388-2481. DOI: [10.1016/j.elecom.2019.01.011](https://doi.org/10.1016/j.elecom.2019.01.011). URL: [%3CGo%20to%20ISI%3E://WOS:000464134900006](https://www.wos.org/doi/abs/10.1016/j.elecom.2019.01.011).
- [36] W. C. Li et al. "Numerical simulation and experimental verification on the kinetics of droplet corrosion of carbon steel". In: *Electrochimica Acta* 514 (2025). ISSN: 0013-4686. DOI: [ARTN14560710.1016/j.electacta.2024.145607](https://doi.org/10.1016/j.electacta.2024.145607). URL: [%3CGo%20to%20ISI%3E://WOS:001399227500001](https://www.wos.org/doi/abs/10.1016/j.electacta.2024.145607).
- [37] J. Jiang et al. "Effect of length of gas/liquid/solid three-phase boundary zone on cathodic and corrosion behavior of metals". In: *Electrochimica Acta* 54.5 (2009), pp. 1426–1435. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2008.09.017](https://doi.org/10.1016/j.electacta.2008.09.017). URL: [%3CGo%20to%20ISI%3E://WOS:000263006100007](https://www.wos.org/doi/abs/10.1016/j.electacta.2008.09.017).
- [38] N. Van den Steen et al. "Predicting the effect of droplet geometry and size distribution on atmospheric corrosion". In: *Corrosion Science* 202 (2022). ISSN: 0010-938x. DOI: [ARTN11030810.1016/j.corsci.2022.110308](https://doi.org/10.1016/j.corsci.2022.110308). URL: [%3CGo%20to%20ISI%3E://WOS:000793828200001](https://www.wos.org/doi/abs/10.1016/j.corsci.2022.110308).
- [39] J. Heintzenberg. "Properties of the Log-Normal Particle-Size Distribution". In: *Aerosol Science and Technology* 21.1 (1994), pp. 46–48. ISSN: 0278-6826. DOI: [Doi10.1080/02786829408959695](https://doi.org/10.1080/02786829408959695). URL: [%3CGo%20to%20ISI%3E://WOS:A1994NU70400003](https://www.wos.org/doi/abs/10.1080/02786829408959695).
- [40] M. R. O. Panao. "Why drop size distributions in sprays fit the lognormal". In: *Physics of Fluids* 35.1 (2023). ISSN: 1070-6631. DOI: [Artn01170110.1063/5.0135510](https://doi.org/10.1063/5.0135510). URL: [%3CGo%20to%20ISI%3E://WOS:000912374800011](https://www.wos.org/doi/abs/10.1063/5.0135510).
- [41] M. L. Kang et al. "Effect of surface grinding on the microstructure and corrosion of Al-Mg-Si-Cu alloys". In: *Materials Research Express* 10.11 (2023). DOI: [ARTN11650610.1088/2053-1591/ad0824](https://doi.org/10.1088/2053-1591/ad0824). URL: [%3CGo%20to%20ISI%3E://WOS:001097346700001](https://www.wos.org/doi/abs/10.1088/2053-1591/ad0824).

- [42] B. E. Risteen, E. Schindelholz, and R. G. Kelly. "Marine Aerosol Drop Size Effects on the Corrosion Behavior of Low Carbon Steel and High Purity Iron". In: *Journal of the Electrochemical Society* 161.14 (2014), pp. C580–C586. ISSN: 0013-4651. DOI: [10.1149/2.1171412jes](https://doi.org/10.1149/2.1171412jes). URL: [%3CGo%20to%20ISI%3E://WOS:000345975500055](https://www.wos.org/doi/abs/10.1149/2.1171412jes).
- [43] C. Y. Chen and F. Mansfeld. "Potential distribution in the Evans drop experiment". In: *Corrosion Science* 39.2 (1997), pp. 409–413. ISSN: 0010-938x. DOI: [Doi10.1016/S0010-938x\(97\)83355-0](https://doi.org/10.1016/S0010-938x(97)83355-0). URL: [%3CGo%20to%20ISI%3E://WOS:A1997WG10700016](https://www.wos.org/doi/abs/10.1016/S0010-938x(97)83355-0).
- [44] A. K. Neufeld et al. "The initiation mechanism of corrosion of zinc by sodium chloride particle deposition". In: *Corrosion Science* 44.3 (2002), pp. 555–572. ISSN: 0010-938x. DOI: [Doi10.1016/S0010-938x\(01\)00056-7](https://doi.org/10.1016/S0010-938x(01)00056-7). URL: [%3CGo%20to%20ISI%3E://WOS:000173095500012](https://www.wos.org/doi/abs/10.1016/S0010-938x(01)00056-7).
- [45] T. Tsuru, K. I. Tamiya, and A. Nishikata. "Formation and growth of micro-droplets during the initial stage of atmospheric corrosion". In: *Electrochimica Acta* 49.17-18 (2004), pp. 2709–2715. ISSN: 0013-4686. DOI: [10.1016/j.electacta.2004.01.032](https://doi.org/10.1016/j.electacta.2004.01.032). URL: [%3CGo%20to%20ISI%3E://WOS:000221779900002](https://www.wos.org/doi/abs/10.1016/j.electacta.2004.01.032).

6

CONCLUSIONS AND OUTLOOK

This chapter concludes the dissertation by summarizing the key findings, followed by an outlook emphasizing further methodology development from both experimental and computational perspectives, the potential real-world applications, and the impacts for the future.

6.1. CONCLUSIONS

The central outcome of this research is the development and validation of an end-to-end methodology that progresses from the initial design and physical construction of the experimental platform and custom sensors, through automated multi-modal data acquisition, to quantitative kinetic analysis. Validated specifically under laboratory-scale multi-droplet conditions for carbon steel, this comprehensive framework demonstrates the capability to quantify the spatiotemporal optical evolution of droplet electrolytes and correlate these localized visual features with global macroscopic degradation.

[Chapter 2](#) established the foundational synchronized, multi-modal data acquisition pipeline. A custom climate chamber and electrical resistance (ER) sensors were designed and constructed to accurately monitor environmental parameters and corrosion kinetics. The results demonstrate that global corrosion kinetics can be continuously monitored in situ under discontinuous electrolyte conditions by coupling these ER sensors with time-lapse optical imaging of droplet evolution. While the data confirmed a strong general correlation between this global corrosion rate and the relative humidity within the chamber, the deviations observed, especially during the early stages of exposure, proved that macroscopic environmental parameters alone cannot fully explain the corrosion behavior. This motivated the spatial disaggregation approach developed in [Chapter 3](#).

6

To achieve this spatial disaggregation, [Chapter 3](#) introduced and validated a fully automated, data-driven framework for tracking corrosion under thousands of individual droplets using time-lapse optical imaging. By converting raw image data into interpretable, probability-based metrics, the method enables a quantitative analysis of both the occurrence and progression of corrosion on a per-droplet basis. Applying this framework to carbon steel revealed that droplet size strongly modulates corrosion behavior, with larger droplets exhibiting a significantly higher probability of developing optically detectable corrosion. Furthermore, the analysis categorized two primary optical manifestations of this localized attack: an "Evans-like" pattern, where corrosion initiates within the inner footprint and propagates outward, and an "outer-only" pattern, where visible corrosion products are restricted to the outer periphery. The results also showed that droplet size systematically affects the temporal development of corrosion products. Specifically, larger droplets exhibit an earlier onset and a more rapid accumulation of corrosion products within the inner footprint. In contrast, the accumulation of products in the outer periphery follows a distinct temporal trajectory, generally developing after the inner footprint has activated if both inner and outer regions show corrosion product accumulation. Together, these findings demonstrate that continuous, probability-based visual indicators can successfully quantify the gradual spatial evolution of corrosion beneath and surrounding individual droplets. This transforms complex visual observations into robust kinetic metrics that bridge macroscopic environmental exposures and localized corrosion mechanisms.

Building upon the localized visual features established in [Chapter 3](#) and the global kinetic data acquired in [Chapter 2](#), [Chapter 4](#) applied weakly supervised learning to infer per-droplet corrosion kinetics. By framing the analysis as a multiple-instance regression

problem, the data-driven model successfully disaggregated the macroscopic ER signal to infer the specific, highly localized volume loss of each individual droplet without requiring per-droplet ground-truth labels. Importantly, while Chapter 3 established visual probabilities, this machine learning approach translated those visuals into quantified physical damage. Further inspection confirmed that this predicted droplet-level material loss evolution aligned with the visual timeline of corrosion propagation. This confirmed that weak supervision can effectively extract localized kinetic information directly from global, integrated observations.

Finally, Chapter 5 validated the end-to-end framework's mechanistic sensitivity by investigating the role of surface roughness. The findings indicated that roughness modulated corrosion not merely by increasing the effective surface area, but by fundamentally altering the initial geometry and subsequent dynamics of the electrolyte population. Rougher surfaces produced larger, more elongated droplets, likely due to enhanced pinning and coalescence during spray deposition. These geometric differences were reflected in the global corrosion response: electrical resistance measurements confirmed that corrosion depth and rate were consistently higher and developed earlier on rougher finishes. Image-derived probability metrics showed that corrosion product accumulation within the inner footprint also increased systematically with roughness. Conversely, corrosion activity in the outer periphery showed a complex dependence on the combined effects of electrochemically driven wetting area expansion and secondary thin-film formation. The temporal evolution of these indicators revealed that corrosion products likely first developed within the inner footprint before becoming significant in the outer periphery, with earlier and more pronounced activity observed on rougher surfaces.

This work contributes to atmospheric corrosion prediction by establishing an experimental and computational framework that correlates local electrolyte dynamics with global corrosion kinetics. Moving beyond purely empirical, data-driven prediction models that ignore the governing electrolyte phase, this framework simultaneously monitors multi-droplet evolution and real-time corrosion rates. By integrating large-scale vision models for segmentation with weakly supervised learning to address the kinetic inverse problem, the framework quantifies corrosion evolution from visual signals and disaggregates the globally measured corrosion rate into per-droplet contributions. It is important to note that these conclusions are currently validated within a specific domain: laboratory-scale multi-droplet conditions on carbon steel, under controlled temperature and humidity, and across defined surface roughness profiles. While this approach still relies on learned data correlations rather than providing full mechanistic proof, it generates the coupled, high-resolution data needed to support the cross-validation of future physical models. Furthermore, it demonstrates how physical parameters, such as surface roughness, modulate corrosion behavior through their effect on electrolyte population dynamics.

6.2. OUTLOOK

This thesis established a foundational data-driven framework for correlating localized electrolyte dynamics with global corrosion kinetics. However, the ultimate vision for this research trajectory is the development of a unified predictive toolchain: an environment-to-damage model capable of predicting field-scale degradation based on macroscopic environmental parameters, such as ambient temperature, relative humidity, contamination composition, and precipitation. It is critical to note that this toolchain is intended for interpolating parameter combinations within a defined material class (e.g., carbon steel under specific environmental bounds), rather than claiming universal generalization across fundamentally different alloy systems. To transition toward this goal, from the perspectives of data acquisition, analysis, and computation, future research should follow a structured, three-phase roadmap (as illustrated in Fig. 6.1).

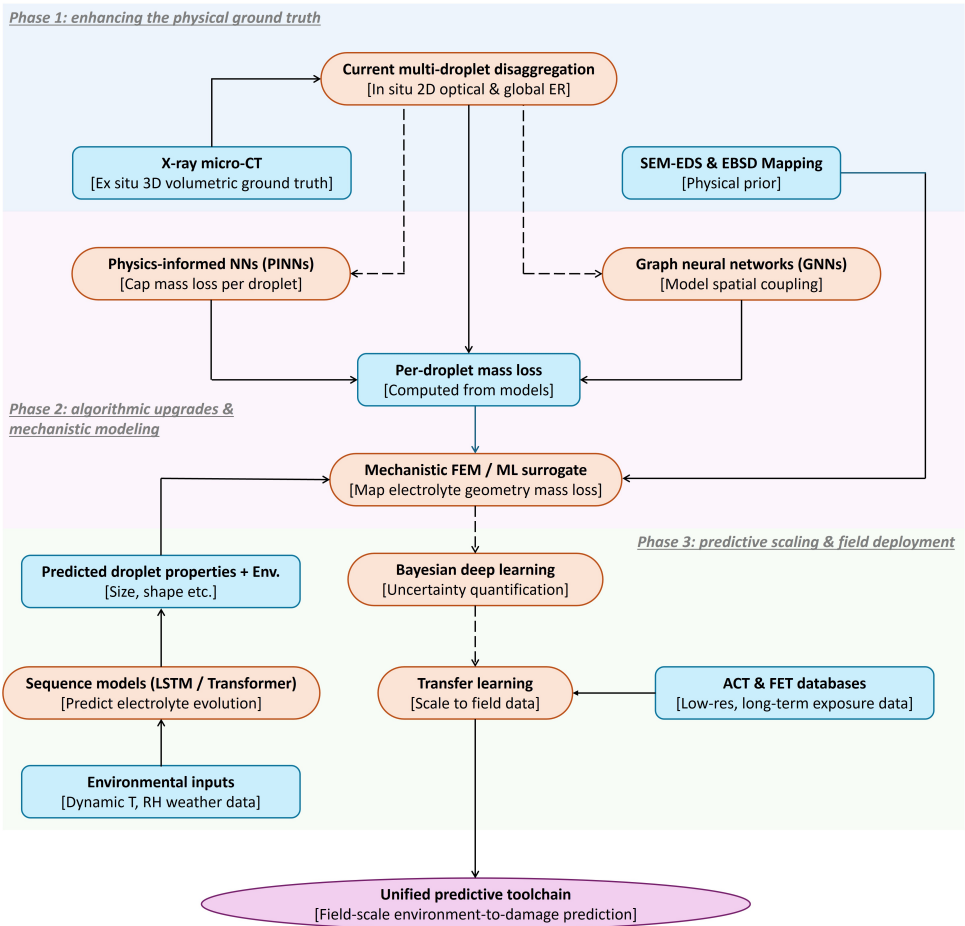


Figure 6.1: The three-phase roadmap for future work. The solid lines stand for data transmission, while the dashed lines represent model/algorithm improvement.

Phase 1: Enhancing the physical ground truth

The current machine learning framework disaggregates global macroscopic mass loss into localized per-droplet contributions using 2D in situ optical features. To rigorously validate and enrich this framework, high-fidelity ex situ data must be integrated. First, X-ray Micro-Computed Tomography (Micro-CT) should be employed post-exposure to map the final 3D topography of the localized pits. By comparing the cumulative volume loss predicted by the optical model with the true Micro-CT volume scanned at selected stages, the foundational 2D-to-3D disaggregation rules can be rigorously validated.

Second, to address the stochastic nature of corrosion initiation, pre-exposure surface characterization can provide physical prior knowledge to contextualize the data-driven model's outputs. Scanning Electron Microscopy (SEM) can identify nanoscale precipitates and inclusions that act as preferential initiation sites, while Electron Backscatter Diffraction (EBSD) can map grain orientations and (Energy Dispersive X-ray Spectroscopy) EDS can capture localized compositional gradients. Rather than attempting full spatial registration with the optical field of view, which is impractical given the huge area mismatch between SEM and optical imaging scales, these analyses would be performed on a small number of selected representative regions. The resulting microstructural insights serve as physical priors: for instance, explaining why certain surface regions systematically show earlier corrosion initiation in the optical data, or validating whether the model's inferred per-droplet kinetics are consistent with the underlying surface heterogeneity. This also well separates the role of physics-based characterization from data-driven prediction.

Phase 2: Algorithmic upgrades & mechanistic modeling

With this validated physical data, the core disaggregation algorithms can be upgraded. Currently, the weakly supervised framework infers localized material loss by mapping local optical features to per-droplet volume loss, with the only constraint being that their sum equals the total macroscopic mass loss from the ER sensor. Two algorithmic upgrades are proposed to advance this. First, Physics-Informed Neural Networks (PINNs) can embed localized geometric constraints and penalize the model if the inferred volume loss for a specific droplet exceeds the theoretical maximum mass loss allowed by its specific footprint area. Second, Graph Neural Networks (GNNs) can be implemented to model spatial electrochemical coupling. By treating droplets as nodes, the spatially aligned SEM-EDS/EBSD data can be directly fed into the GNN as localized node features, allowing the algorithm to learn how the surface heterogeneities and underlying crystallography influence both initiation and inter-droplet interactions.

Once this PINN/GNN-upgraded disaggregation model is finalized, it will extract massive, high-fidelity datasets linking droplet configurations to local corrosion rates. This localized data is then used to calibrate and validate mechanistic 3D Finite Element Models (FEM), or to train purely data-driven machine learning surrogates that establish the ultimate physical rulebook mapping any given electrolyte configuration to material mass loss for a given material class (e.g. carbon steel).

Phase 3: Predictive scaling and field deployment

To transition from spatial rule extraction to long-term temporal prediction, the mechanistic rulebook developed in Phase 2 must be coupled with dynamic environmental modeling. First, to connect macroscopic weather conditions with localized wetting, sequence models such as Long Short-Term Memory (LSTM) networks or Transformers can be trained to directly predict the transient evolution of the electrolyte itself (e.g., condensation, droplet coalescence, and evaporation cycles) directly from macroscopic environmental parameters. Second, these forecasted dynamic droplet configurations are fed sequentially into the validated FEM or ML surrogate model. This establishes a fully connected, environment-to-damage surrogate pipeline: weather parameters predict the dynamic electrolyte geometry, which in turn dictates the cumulative localized mass loss based on the spatial rules extracted in Phase 2.

Because atmospheric exposure is inherently stochastic, Bayesian deep learning can be applied to the final output of this chain to produce a probability distribution of expected corrosion depth, providing the Uncertainty Quantification (UQ) required for industrial safety margins. Ultimately, Transfer Learning can be utilized to calibrate this high-resolution predictive chain against the lower-resolution temporal databases generated by standard Accelerated Corrosion Tests (ACT) and Field Exposure Tests (FET), realizing the unified predictive toolchain for the defined material class.

6

Open-source data and community impact

The shift towards data-driven atmospheric corrosion prediction is currently hindered by the scarcity of high-quality, standardised training data. The experimental framework developed in this thesis has a unique ability to generate large, synchronised datasets of multi-droplet visual evolution and corresponding kinetic loss. A key future step is to formalise these outputs into an open-source benchmark dataset. By sharing standardised, high-resolution corrosion data publicly, this framework can provide a foundational testing platform for the broader computational materials science community, which, in turn, would speed up the global development of more robust, physics-informed machine learning models for materials corrosion prediction. This approach can support both materials selection during the initial design phase and asset maintenance throughout the product lifecycle.

EPILOGUE

This thesis is, at its technical core, a framework for extracting meaningful signal from noisy, stochastic, seemingly intractable data. It took me an embarrassingly long time to realise that the same description applies to the PhD journey that produced it.

I started this work by the end of 2020, in the middle of a pandemic, with a closed laboratory and no clear path forward. What followed was three and a half years of experiments that did not work, data that could not be quantified, and the particular kind of loneliness that comes from working on a problem there is no clear and straightforward instruction on where to go. I thought about quitting more times than I can count. I stayed, partly out of stubbornness, partly because the sunk cost felt too heavy to abandon, and partly because I could not accept the idea of leaving without something I could be proud of.

The turning point came not from inside the laboratory but from outside it. When Meta released the Segment Anything Model, something shifted. A tool appeared that made a previously impossible segmentation problem tractable, and with it, a direction I had not been able to see before. I taught myself high-performance computing, computer vision, data engineering, and machine learning architecture – fields I had no formal training in – step by step, mostly alone, mostly at night. Within eighteen months, three and a half years of mostly failed experiments had become the foundation of a coherent, novel framework. The noises had been hiding a signal all along. I had simply not yet built the instrument to find it.

I do not know whether the choices I made were the right ones. A different version of me might have left after the first year and arrived somewhere equally interesting by a shorter road. But I have come to believe that the most valuable thing this PhD gave me is not the publications, or the talks, or even the framework itself. It is the knowledge, earned rather than taught, that meaningful patterns exist even in data that looks like chaos, and that the difference between finding them and not is often simply the willingness to keep looking after everyone, including yourself, has started to doubt that anything is there.

Inspirations are like spikes hidden in noisy signals. They are easy to miss. The threshold for detecting them is not intelligence or luck. It is persistence – the decision, made quietly and repeatedly, not to go gentle.

*Keer Zhang
Delft, March 2026*

ACKNOWLEDGEMENTS

There is a particular kind of moment I have always loved. A gentle breeze on a spring night carries a fragment of a song I had not thought about in years, and suddenly everything comes flooding back – a face, a place, a smell, the specific quality of light in a room I have not stood in for a decade. I have never been someone who finds meaning in fixed monuments. My anchors are fluid, sensory, accidental. They arrive uninvited and leave when they are ready. What I have learned, over five and a half years of this PhD, is that the people who matter most work the same way: they appear at exactly the right moment, change something quietly and permanently, and become part of the signal you carry forward. This is my attempt to name some of them.

Herman, you are where this story begins. You showed me, during my master's in Brussels, that science could be genuinely fun. And then, with characteristic generosity, you handed me the key to this next chapter by recommending me for this position. I am more than grateful for what I will ever be able to properly say. The collaboration never really ended when I left Brussels, and I am glad it did not.

Yaiza, first I would like to express my greatest gratitude for having me onboard. You are the person I have talked to most during these years, and I mean that in every sense. Our conversations have ranged so far beyond science and work that I sometimes forget, sitting across from you in some cozy bar over coffee, that you are also my daily supervisor. You described me as a perfectionist, and you were right – and you helped me understand that it is both a gift and a trap. The advice you gave me about walking at my own pace and seizing the moment has stayed with me in ways I did not expect. So has what you said about daring to speak – that we, as women, can spend so long telling ourselves we are not ready, not good enough, not the right person, that we forget to simply begin. I am still working on that. But I am working on it. Thank you for showing me that was possible.

Arjan, your combination of genuine humility and quiet excellence is something I have tried to learn from throughout this PhD. The group outings at your place, with everyone bringing homemade food and Herman inevitably ending up in high spirits, are among my warmest memories of these years. Thank you for your support and for creating a group where people actually want to spend time together.

Ehsan, working alongside you for the majority of this PhD has been one of its great pleasures. You are smart, hardworking, and, perhaps most valuably, a genuinely good listener. The coffee break conversations, whether about new ideas, dead ends, or just life in general, kept me going more than you probably know. Thank you for always being there, and for having the right instincts at exactly the right moments. **Ali**, though

our time overlapping was short, thank you for the foundation you helped build. **Nils**, I wish we had had more chances to talk – the project was better for having you in it. To the industry partners of the Thincorr project – **Mohammed, Erik, Kristina, Berend, Yves, Joost, and Jeron** – thank you for teaching me to see this work from perspectives I would never have found on my own. Learning to think like an engineer, not just a scientist, has been one of the unexpected gifts of this project. **Vincent**, we go back to the master's in Brussels, which already feels like a different life. Watching you step back into academia after industry, join Herman's group, and then appear in Delft for experiments was one of the more pleasant surprises of these years. I have to say – and I mean this from a purely personal perspective – that you are genuinely cool, which does not hurt, but what I have actually learned most from you is how to hold a room. Your ability to present ideas, to talk about science in a way that makes people lean forward rather than glaze over, is something I have studied carefully and am still working on. Thank you for the visits, the conversations, and for being very good at something I needed to get better at. **Ziyu**, we shared the same office for four years, which means you tolerated my comprehensively chaotic desk for four years, and I want that acknowledged in writing. You are one of the most quietly hardworking people I have met, and your patience – with the desk, with my less organised tendencies in general – was a gift I did not always deserve. Thank you for the support, and for making that shared space feel like somewhere I could actually think. **Iftikhar** and **Santosh**, our conversations about work and life pulled me through more difficult stretches than you probably realise. Thank you for being there. **Agnieszka**, I loved the hours we spent together figuring out how to build an entirely new experimental setup from nothing but a concept and a lot of trial and error. You are extraordinary at what you do. **Reina**, your warmth, your talent for making people feel welcome, and your seemingly effortless ability to organise things that would defeat most people have made this group a genuinely lovely place to be. Thank you. To all the other colleagues, **Gaojie, Prakash, Peyman, Prasaanth, Prasad, Can, Axel, Aytaç, Arjan C., Maxine, Amir, Khaterreh, Mir, Jasper, José, Tim, Philipp, Joep, Eszter, Soroush, Alice, Gautham, Georgy, Kees, Hans, Hannah** (forgive me if I forgot naming a few), I have had the luck to share these years with – the coffee breaks, the conference dinners, the long afternoons in the lab – you know who you are, and I am glad you were here.

Boya. More than ten years now. Same faculty, then the same foreign city, the same house in that first bewildering year abroad, and then different cities, different continents, different time zones, and somehow none of it has made any real difference to what we are to each other. I think of you as the pessimistic optimist to my optimistic pessimism, which is to say that together we probably approximate one fully calibrated person. Your insights, your life philosophy, your particular way of thinking through difficult decisions, these have shaped choices I have made that I cannot fully explain to anyone who does not know you. I am enormously proud of where you are now. **Weilun**, we have eaten our way through an implausible number of Ramen Takumi branches across Rotterdam, chased a taste we, together with Boya, first found in Düsseldorf and never quite got over, played board games while waiting for tables, and seen Coldplay together twice — once in Brussels, once in Düsseldorf, because once was apparently not sufficient. These are among the best hours of the last five years. Thank you for all of them.

Xiangjun, you were my housemate, my travel companion, my morning alarm in the form of violin music drifting through the hallway, and one of my absolute favourite people. We have been to Paris, to Amsterdam, to the Texel island, back at your home in Hangzhou and my home in Ningbo, together, and every single time, without exception, the pressure lifts the moment we are in the same place. I am not sure I can fully explain that, but I am grateful for it. The distance now is real, but so are the texting, and so is every piece of meaningless but deeply beloved nonsense we send each other. **Xinxin**, the Scottish breakfast alone we had back in Edinburgh earns you a permanent place in this acknowledgement. I am already looking forward to our next trip. **Yuewen** and **Zikai** – I want it on record, in a document that will be archived in a university library, that I was there in Barcelona. I was there when Barça won, when it was my birthday, when the birthday surprise you prepared caught me completely off guard and made me happier than I could say. And I was there on that last night, when something quietly shifted between you two. You are welcome. I expect to be thanked at the wedding. Alright, and to all my dearest friends: **Zhongke, Jingjing, Li, Yun, Yuliu, Yijia, Xinrui, Xiaohui, Zhaoying, Zhaorui, Jianing, Jiaxiang, Dingshan, Kai, Shushu, Yaqi, Jiaqi, Yan, Zixiong, Sifeng, Yang** (again I sincerely apologize if I've missed anyone), you guys are more than amazing. Thank you so much for sharing part of your journey with me.

To **Taylor Swift**: your courage in the face of everything that has been thrown at you, your refusal to be diminished, your absolute devotion to the work – these are not small things. They are the kind of things that remind you, when you need reminding, that ambition and sincerity are not in conflict. Thank you for that. And to **Max Verstappen**: your line about your mother and the hypothetical ball is, I maintain, one of the most philosophically efficient statements ever made about the uselessness of regret. What has happened has happened. You race the car in front of you, not the one you wish you had. I have thought about that should be reasonable for a PhD thesis, and I think it helped.

And finally, my family. Mum, Dad, Grandma — you have been my foundation for as long as I have been anything at all. 你从未要求我成为另一个人，也从未停止相信我本来的样子已经足够好，即使很多时候我连自己也不相信自己。等一切圆满落幕，我最想做的第一件事就是回家陪你们。我爱你们。 [You have never asked me to be other than what I am, and you have never stopped believing that what I am was enough, even in the years when I was not sure of that myself. The first thing I want to do, when this is finally over, is come home and sit with you and not think about anything for a little while. I love you.]

Everything good in this thesis has you in it somewhere.

*Keer Zhang
Delft, March 2026*

CURRICULUM VITÆ

Keer ZHANG

19/05/1997 Born in Ningbo, Zhejiang, China.

EDUCATION

- | | |
|-------------------|--|
| 09/2015 – 06/2019 | BSc. Materials Science and Engineering
Northwestern Polytechnical University, China |
| 09/2018 – 09/2020 | MSc. Chemical and Materials Engineering
Vrije Universiteit Brussel, Belgium
<i>Topic: "Developing Setup and Controlling Loop for Studying Atmospheric Corrosion under Controlled Condensation"</i> |
| 09/2024 – 09/2026 | MSc. Artificial Intelligence
Katholieke Universiteit Leuven, Belgium
<i>Topic: "Flow Models for Sampling from High Dimensional Unnormalized Distribution Functions"</i> |
| 09/2020 – 09/2026 | PhD. Mechanical Engineering
Delft University of Technology, the Netherlands
<i>Topic: "Data-driven Study of Atmospheric Corrosion under Multi-droplet Conditions"</i> |

LIST OF PUBLICATIONS

1. **Keer Zhang**, Ehsan Rahimi, Nils Van den Steen, Herman Terryn, Arjan Mol, Yaiza Gonzalez-Garcia, *Monitoring atmospheric corrosion under multi-droplet conditions by electrical resistance sensor measurement*, [Corrosion Science](#) **236**, 112271 (2024).
2. **Keer Zhang**, Arjan Mol, Yaiza Gonzalez-Garcia, *Development of a data-driven framework for monitoring corrosion under droplets*, [Corrosion Science](#) **258**, 113313 (2026).
3. **Keer Zhang**, Arjan Mol, Yaiza Gonzalez-Garcia, *A Weakly Supervised Framework for Droplet-Level Corrosion Inference from Global Measurements*, under review.
4. **Keer Zhang**, Arjan Mol, Yaiza Gonzalez-Garcia, *Surface Roughness and Atmospheric Corrosion: Droplet-Scale and Global Kinetics*, in preparation.
5. Ehsan Rahimi, **Keer Zhang**, Ali Kosari, Nils Van den Steen, Axel Homborg, Herman Terryn, Arjan Mol, Yaiza Gonzalez-Garcia, *Atmospheric corrosion of iron under a single droplet: A new systematic multi-electrochemical approach*, [Corrosion Science](#) **235**, 112171 (2024).
6. Vincent Vangrunderbeek, **Keer Zhang**, Leonardo Bertolucci Coelho, Fritz Friedersdorf, Rebecca Marshall, Yaiza Gonzalez-Garcia, Mats Meeusen, Annick Hubin, Herman Terryn, Mesfin Haile Mamme, *Corrosion and environmental sensor response delays during monitored multi-droplet wetting: Unraveling time lags in atmospheric corrosion*, [Corrosion Science](#) **255**, 113154 (2025).

