AC Corrosion of Cathodically Protected Pipelines

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\[(E_{\text{Iv}})'' = q - \rho A \ddot{v}\]

\[\Delta \int_a^b \varepsilon \Theta + \Omega f \equiv \chi^2 \sum \{2.71\}\]

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AC Corrosion of Cathodically Protected Pipelines

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Preface

This doctoral thesis is submitted in partial fulfilment of the requirements for obtaining the degree of PhD at the Department of Mechanical Engineering at the Technical University of Denmark (DTU). The project was part of the industrial PhD programme in which the student is employed in industry and financially supported by the Innovation Fund Denmark (project 4135-00088B) and was partially carried out at MetriCorr Aps. during the period January 2015 to October 2018. The period includes a period of leave of 10 months in total. The project was supervised by Prof. Per Møller from the Department of Mechanical Engineering, Section of Materials and Surface Engineering, at the Technical University of Denmark (DTU) and CEO Dr. Lars Vendelbo Nielsen at MetriCorr Aps.

I, Andreas Junker Olesen, declare that, if not explicitly stated, none of the presented work in this doctoral thesis has been submitted in support of an application for another degree of this or any other university. I further declare that the presented work is my own work and that I have correctly acknowledged work of others.

Andreas Junker Olesen
Kongens Lyngby, Denmark, October 23rd, 2018
Abstract

Title: "AC Corrosion of Cathodically Protected Pipelines"

This doctoral thesis presents three years of research on alternating current (AC) corrosion of cathodically protected (CP) pipelines. AC corrosion has become an increasing concern to pipeline operators worldwide during the last 30 years. This is due to a growing energy infrastructure of both buried pipelines and above ground high voltage transmission lines which results in the conditions for AC interference. The electromagnetically induced alternating voltage on pipelines may cause the existing cathodic protection to become ineffective. In fact, improper adjustment of the CP system may severely aggravate corrosion on the pipeline caused by alternating current.

AC corrosion is a multidisciplinary scientific field, requiring fundamental knowledge within the fields of electrochemistry and corrosion, material science and characterisation, as well as electrical engineering and basic geology. The approach of the present investigation is largely empirical and a wide range of parameters affecting AC corrosion have been investigated.

Effects of different coating defect geometries and their orientation has been investigated by electrochemical impedance spectroscopy (EIS) and electrical resistance (ER) probes for corrosion rate measurements. Effects of the chemical environment has been investigated by ER probes, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), ion chromatography (IC), inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray diffraction (XRD). Effects of pipeline steel grades have been investigated by polarisation scans, weight-loss coupons and ER probes. Effects of variations in AC interference levels has been investigated by ER probes. Effects of the pH level at the steel/solution interface has been investigated by pH probe measurements, ER probes and optical methods. Investigations of the formed corrosion products and mineralogical changes of the surrounding soil environment has been made by X-ray photo-electron spectroscopy (XPS), SEM, EDS, IC, ICP-OES, XRD and light optical microscopy (LOM).

All investigations have contributed to an enhanced understanding of the factors leading to and intensifying AC corrosion of cathodically protected pipelines.

The results obtained in the presented research indicate that AC corrosion is largely dependent on both AC and DC current densities. It is found that increasing levels of alternating current alone does not necessarily result in AC corrosion, but that this is highly influenced by the amount of cathodic protection current. AC corrosion may be divided into two categories: "high CP" and "low CP" AC corrosion. Many of the discrepancies in literature on AC corrosion may be explained by the fact that researches have not been aware of this fundamental difference. High CP current generates the highest AC corrosion rates. This is fully in line with present industry standards and scientific literature on the field. The importance of current densities implies that AC corrosion will be largely dependent on factors contributing to an area dependent resistance to current flow, such as coating defect size and geometry as well as soil re-
sistivity and chemistry. A direct consequence of cathodic protection is alkalisation of the environment at the steel/soil interface. The response of a soil system to elevated pH has a large influence on the soil resistivity and thus the current densities and the AC corrosion rate. Finally, AC is found to affect DC polarisation behaviour of steel significantly, causing depolarisation of both anodic and cathodic reactions as well as a shift of the corrosion potential.

One key conclusion of the present thesis is that the Pourbaix diagram for iron may be used to explain AC corrosion. This implies that pH and surface potential are important parameters when evaluating AC corrosion. Unfortunately, these are inherently difficult to measure in practical applications, especially pH. It is found that there is a strong link between DC current density and pH. AC often enhances the DC current and consequently elevates pH, but under special circumstances, i.e. a low galvanostatic DC current, a high levels of AC is shown to exhibit de-alkalisisation properties. Furthermore, AC current density strongly affects surface potential under cathodic protection, due to the strong influence of AC on the polarisation behaviour. This explains why the traditional use of current densities to evaluate AC corrosion works, although this correlation may have been completely coincidental. "High CP" AC corrosion is related to entering the high pH corrosion region (HFeO$_2^-$) and "low CP" AC corrosion is related to entering the low pH corrosion region (Fe$^{2+}$) in the Pourbaix diagram. The alternating voltage will continuously reduce or oxidise the dissolved species, thus leading to a stabilisation of these corrosion regions. Therefore, an effective corrosion mitigation strategy depends on whether the observed AC corrosion is of the low or high CP type. Numerous investigations of AC corrosion have been made without application of cathodic protection, and these fall in the category "low CP". Historically this has lead to a widespread confusion about AC corrosion because researchers observing low CP AC corrosion tend to conclude that cathodic protection will minimize corrosion, while researchers observing high CP AC corrosion will conclude that CP enhances AC corrosion. In reality an intermediate CP strategy can be used to mitigate AC corrosion. This works because the passive film on a cathodically protected surface consists of one or more of the oxides: Fe(OH)$_2$, Fe$_3$O$_4$ or a green rust type. These oxides can transfer significant amounts of alternating charge via Fe(II)-Fe(III) redox reactions within the oxide, without further oxidation of the underlying steel. Alternatively mitigation of the induced AC voltage on the interfered structure by grounding installations may lower corrosion effectively, however compared to control of the cathodic protection level, this is an extensive and costly procedure in practice.

With the publication of this thesis, hopefully researchers in the field of AC corrosion will become aware of the discrepancy between high and low CP AC corrosion, and the collective understanding of AC corrosion will be enhanced.
Resumé (dansk)

Titel: "Vekselstrømskorrosion af Katodisk Beskyttede Rørledninger"


AC korrosion er et multidisciplinært videnskabeligt område der kræver grundlæggende viden om elektrokemi og korrosion, materialelære og karakteriseringsteknikker, ligesom det også kræver kendskab til elektriske kredsløb og basal geologi. Indgangsvinklen for denne undersøgelse har været overvejende eksperimentel og en bred vifte af parametre, der har indflydelse på AC korrosion, er blevet undersøgt:


Resultaterne i den præsenterede forskning indikerer at AC korrosion er stærkt afhængig af både veksel- og jævnstrømstætheder. En observation er, at stigende niveauer af vekselstrøm alene, ikke behøver at føre til AC korrosion, men at niveauet af katodisk beskyttelsesstrøm har stor indflydelse. AC korrosion kan opdeles i to kategorier: "høj KB" og "lav KB" AC korrosion. Mange af de uoverensstemmelser der eksisterer i litteraturen kan forklares ved, at forskere ikke har været klar over denne fundamentale forskel. Høj KB strøm genererer de højeste AC korrosionshastigheder. Det er fuldt ud i overensstemmelse med gældende standarder og videnskabelig litteratur omkring emnet. Vigtigheden af strømtætheder, indebærer at AC korrosion er meget afhængig af de faktorer der påvirker den areal-afhængige modstand imod ladingsoverførsel, såsom areal og geometri af belægningsskader og jordens resistivitet og kemiske sam-
mensætning. En direkte konsekvens af katodisk beskyttelse er at pH ved stålets overflade stiger markant. Jordtypens respons på en sådan påvirkning har stor indflydelse på jordens resistivitet og således også de afledede strømtætheder og følgende korrosionshastighed. Slutteligt vises det at AC påvirker DC polariseringsmønstret af stål markant, eksempelvis ved depolarisering af både anode- og katodereaktioner og ved en forskyndning af det åbne korrosionspotentiale.


Med publiceringen af denne afhændling vil der forhåbentlig brede sig en forståelse for de beskrevne uoverensstemmelser i literaturen, samt en større samlet forståelse for fænomenet AC korrosion.
Acknowledgements

Firstly, I would like to express my sincere appreciation and gratitude towards my two supervisors Prof. Dr. Per Møller and CEO Dr. Lars Vendelbo Nielsen. They have both supported and followed my research during the project and have both contributed to the completion of this thesis.

As my university supervisor, Per Møller has been an inexhaustible source of inspiration and knowledge in the general field of corrosion (and in anything else). Every discussion with him on even the simplest topics, has lead to new ideas and things to investigate. Hopefully his enthusiasm for solving the world’s corrosion problems shines through in this thesis.

With 18 years in the field of AC corrosion, Lars Vendelbo Nielsen is among the pioneers in AC corrosion research. His chemical background and deep knowledge about AC corrosion has been invaluable in this project, but, despite his own observations and opinions on the topic, he has always allowed me to follow my own intuition and has not tried to set the scientific agenda. His strong engagement in industry has been a guide for me to keep my research relevant both from a scientific and application-minded point of view.

I would like to bring a special thank to Michael Albæk who has been an indispensable work force in the lab at MetriCorr. His solution-minded approach to the experimental work has pushed the project forward and I can honestly say that without his endless positive support and experience, this project would not have had the same experimental ballast as it does.

I am grateful for the financial support from Innovation Fund Denmark (grant no. 4135-00088B) that has made the collaboration between DTU and MetriCorr possible. This arrangement has provided me with two groups of colleagues, both of which have followed my work with interest and facilitated a positive working environment. They have allowed me to move the focus away from my project when needed, or have participated in deep and inspiring technical discussions. In particular, I would like to thank Bent Baumgarten and Michael Berggreen Petersen from MetriCorr for discussions of a more technical nature, Frances Bradfield for doing a much appreciated job on editing my texts for a better understanding, Folke Galsgaard for assistance on the electrical circuit design of my experiments, Ernesto Santana-Diaz for his input on computer modelling of AC corrosion and cathodic protection and Jens Kristoffersen for facilitating remote monitoring of my experiments. From the Department of Mechanical Engineering (DTU-MEK), laboratory technicians Marianne Burggraaf Buendia, Peter Schwenke Westermann, Steffen Munch, Rolf Jensen and Flemming Grumsen have provided support whenever needed. Furthermore I would like to thank Louise Josefine Belmonte (DTU-BYG), Sinh Hy Nguyen (DTU-ENV) and Mikael Emil Olsson (DTU-ENV) for assistance on soil analysis. Knud Dideriksen from the University of Copenhagen, Chemical Institute, has acted with sincere interest and helpfulness towards my project and has assisted in XPS analysis beyond my expertise. Last, but not least, my close PhD colleagues Felix Lampert, Frank Nießen, Nicolai Ytterdal Juul, Jacob Obitsø Nielsen, Valeriia Reveko, Mikkel Ravn Jensen and Emilie Hørdum Valente amongst many others have been a great inspiration to me with such
specialized knowledge about characterization techniques and about their respective research fields. I would also like to acknowledge the work done via the student projects that I have supervised at DTU (Corrosion, 41653) by the engineering students Lenni Helleskov Busk, Sujapragash Ramesh, Jacob Bertelsen and Christian Budden. Their work has served as proof of concept and inspiration for further experiments and valuable findings.

In my position as an industrial researcher I have had the pleasure of meeting several people from the industry. I would especially like to thank Casey Heinrich (Dominion Energy, US) and Nick Kioupis (Desfa, GR) for the fruitful collaborations resulting in valuable publications. Also Cory Mikles (OneOK), Jerry DeWitt, Len Krissa (Enbridge) and Daniel Silva (PG&E) deserve appreciation for allowing me to follow their practical work and experience with AC corrosion in the field.

Finally I am thankful for the great support that I have received from family and friends. During the course of the project I have fathered two boys, Storm and Johan and married my wife Anna. They make everything that I do meaningful and I will be forever grateful for their interference in my life.
Nomenclature

\( \alpha \)  Charge transfer coefficient
\( \alpha \)  Coating edge angle ["]
\( \alpha \)  Temperature coefficient [K\(^{-1}\)]
\( \beta \)  Tafel constant of \( k \)’th process [mV \cdot A\(^{-1}\)]
\( \chi_F \)  Faradaic fraction of alternating current
\( \eta \)  Over potential [V]
\( \lambda \)  Flux linkage [kg \cdot m\(^2\) \cdot s\(^{-2}\) \cdot A\(^{-1}\)]
\( \lambda \)  Wavelength (of x-rays) [nm]
\( C_{dl} \)  Electrochemical double layer capacitance [\( \mu F \cdot cm^{-2} \)]
\( E_{IR-free} \)  IR-drop compensated potential [V]
\( E_{OFF} \)  Off potential [V]
\( E_{ON} \)  On potential [V]
\( I \)  Current [A]
\( J_{AC} \)  Alternating current density [A/m\(^2\)]
\( J_{DC} \)  Cathodic current density [A/m\(^2\)]
\( R_{ct} \)  Charge transfer resistance [\( \Omega \)]
\( R_C \)  Resistance (corroding ER element) [\( \Omega \)]
\( R_R \)  Resistance (reference ER element) [\( \Omega \)]
\( R_S \)  Spread resistance [\( \Omega m^2 \)]
\( R_s \)  Solution resistance [\( \Omega \)]
\( R \)  Resistance [\( \Omega \)]
\( U_{AC} \)  Alternating voltage [V]
\( \nu_{vorr} \)  Corrosion rate [\( \mu m/y \)]
\( \mu \) Magnetic flux \([V \cdot s \cdot m^{-1} \cdot A^{-1}]\)

\( \omega \) Radial frequency \([\text{rad} \cdot s^{-1}]\)

\( \phi \) Magnetic flux \([V \cdot s]\)

\( \rho \) Density \([\text{g/m}^3]\)

\( \rho \) Resistivity \([\Omega \cdot \text{m}]\)

\( \sigma \) Thickness of ER probe element \([\mu \text{m}]\)

\( \theta \) Angle (of incident x-rays) \([\text{o}]\)

\( A \) Area \([\text{m}^2]\)

\( a.u. \) Arbitrary unit

\( a_n \) Anodic reaction of \(n\)'th process

\( c_n \) Cathodic reaction of \(n\)'th process

\( d \) Diameter \([\text{m}]\)

\( d \) Distance between atomic planes (XRD) \([\text{nm}]\)

\( E \) Potential \([\text{V}]\)

\( E^0 \) Standard Equilibrium potential \([\text{V}]\)

\( E_0 \) Equilibrium potential \([\text{V}]\)

\( F \) Faradays number (96485.3329 C \cdot \text{mol}^{-1})

\( f \) Frequency \([\text{Hz}]\)

\( i \) Current \([\text{A}]\)

\( i_0 \) Exchange current \([\text{A}]\)

\( i_{corr} \) Corrosion current \([\text{A}]\)

\( i_{lim} \) Limiting current \([\text{A}]\)

\( I_n(z) \) Modified Bessel function of order \(n\)

\( j \) Imaginary unit

\( l \) Length (of coating defect) \([\text{m}]\)

\( l_c \) Length (of coupon) \([\text{m}]\)

\( M \) Molar mass \([\text{g/mol}]\)

\( N \) Number of turns (coil)

\( n \) Positive integer to denote e.g. a process
\( R \quad \text{Gas constant} \quad (8.3145 \, \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \)

\( T \quad \text{Temperature} \quad [\text{K}] \)

\( t \quad \text{Thickness (of coating)} \quad [\text{m}] \)

\( w \quad \text{Width (of coating defect)} \quad [\text{m}] \)

\( z \quad \text{Number of electrons} \)

\( B \quad \text{Magnetic flux density} \quad [\text{N} \cdot \text{m}^{-1} \cdot \text{A}^{-1}] \)

\( H \quad \text{Magnetic field} \quad [\text{A} \cdot \text{m}^{-1}] \)

\( a \quad \text{Activity of species} \)

\( \text{AC} \quad \text{Alternating Current} \)

\( \text{API} \quad \text{American Petroleum Institute} \)

\( \text{AS} \quad \text{Artificial scaling Soil} \)

\( \text{BNE} \quad \text{Base Neutralising Effect} \)

\( \text{CEC} \quad \text{Cation Exchange Capacity} \quad [\text{cmol}^+ \cdot \text{kg}^{-1}] \)

\( \text{CP} \quad \text{Cathodic Protection} \)

\( \text{CSE} \quad \text{Copper-copper sulphate (Cu/CuSO}_4\text{) standard electrode.} \)

\( \text{DC} \quad \text{Direct Current} \)

\( \text{E} \quad \text{Potential} \quad [\text{V}] \)

\( \text{EDS} \quad \text{Energy Dispersive X-ray Spectroscopy} \)

\( \text{EIS} \quad \text{Electrochemical Impedance Spectroscopy} \)

\( \text{ER} \quad \text{Electric Resistance} \)

\( \text{GR} \quad \text{Green Rust} \)

\( \text{HVTL} \quad \text{High Voltage Transmission Lines} \)

\( \text{IC} \quad \text{Ion Chromatography} \)

\( \text{ICP-OES} \quad \text{Inductively Coupled Plasma Optical Emission Spectroscopy} \)

\( \text{ISO} \quad \text{International Organisation for Standardisation} \)

\( \text{NACE} \quad \text{National Association of Corrosion Engineers} \)

\( \text{NAS} \quad \text{Non-scaling Artificial Soil} \)

\( \text{OCP} \quad \text{Open circuit potential} \quad [\text{V}] \)

\( \text{rms} \quad \text{Root Mean Square} \)
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>US</td>
<td>United States</td>
</tr>
<tr>
<td>W</td>
<td>Warburg element for impedance modelling</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photo-electron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>Z</td>
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Chapter 1

Introduction

Corrosion of buried pipelines caused by alternating current, AC corrosion, was of little concern to pipeline operators, until significant corrosion damage was detected on a German pipeline in 1986, and was assigned to AC corrosion [1]. This instance and many more that followed in the sequent years occurred on cathodically protected pipelines that satisfied the cathodic protection criteria [2]. Pipelines had been protected by coatings and cathodic protection for decades, but the reason for the new threat to pipeline integrity was a growing infrastructure of both pipeline and high voltage transmission line networks which inevitably caused a growing mileage of shared right-of-way, providing the necessary prerequisites for AC interference on the buried pipelines. Initially, the induced AC voltage in metallic pipelines was treated primarily as a safety hazard for pipeline operating personnel since voltages could easily reach 50-100V, depending on the grounding conditions of the pipeline. Later when AC corrosion became an issue, the current density came into question since it was established that the current flowing through coating defects on the pipeline was the main concern from a corrosion perspective.

It was known that AC could pose a risk of accelerated corrosion of metals as early as the beginning of the 19th century [3, 4], but early investigations on the effect of AC on pipeline corrosion concluded that the threat could be addressed through enhancement of the cathodic current output from the cathodic protection system [5]. Now, it is well established that cathodic protection may be part of an efficient mitigation strategy, but that excessive cathodic protection seriously aggravates AC corrosion rates and is found to be a key influencing parameter [6–8].

Today, more than 30 years after the first recorded incident of AC corrosion on a cathodically protected pipeline, the shared knowledge about AC corrosion is extensive, but not exhaustive. Many of the prerequisites and factors leading to and enhancing AC corrosion are well understood, and effective mitigation methods have been developed. Despite this, AC corrosion still poses a serious threat to pipeline integrity, and thus both personnel and environmental safety. Still the corrosion mechanism is debated amongst researchers. This is clearly demonstrated by the fact that different national protection criteria to mitigate AC corrosion exists across the globe, despite that they deal with the same physical-chemical corrosion phenomenon [9, 10].

1.1 Research objective

This project aims at a comprehensive understanding of AC corrosion as a unique corrosion phenomenon. To accomplish this, four points of focus were chosen prior to initiation of the project. These topics include (copied from the early project description):
1. Effect of environmental/chemical conditions: Research indicates that the presence of earth alkali elements such as Mg and Ca will provide a scale-forming environment at the corroding steel surface and thus limit the corrosion; however, the influence of the chemical parameters is not well understood. The presence of high resistivity layers on the surface alters the electrical conditions. Experiments with varying chemical composition of the electrolyte (soil) in controlled environments will be conducted.

2. Effect of varying AC/DC conditions: To obtain optimum cathodic protection, the DC potential is to be kept constant at a predefined value. However, the AC influence alters the DC conditions, and since the AC current is fluctuating with night/day, summer/winter and also constantly with its frequency, it is extremely difficult to predict the AC/DC conditions on an actual pipeline and the effect on the corrosion mechanisms. Controlled environment experiments with predefined varying AC/DC patterns will be performed.

3. Effect of pipeline steel: Pipeline steels today are mainly designed for two things: weldability and strength. Corrosion protection is obtained by a combination of cathodic protection and coating systems. So far only little interest has been paid to the effect of the pipeline steel with regards to AC corrosion. It is interesting to investigate if pipeline steel types of different strengths will perform differently under AC influence. Also alternative steels might be examined.

4. Optimization of probe geometry: The project will mainly use so-called ER-probes (electrical resistance) to examine the corrosion mechanism. This technique is very sensitive to measuring the corrosion rate, while also monitoring the electrical conditions in the process. A predefined area of exposed steel simulates a coating defect. Conventionally 1 cm$^2$ is used, but since factors such as current density is highly influenced by this, it is interesting to vary this parameter and investigate the effect. The boundary layer conditions at the steel surface can also be altered by changing the design of the probe, which is also believed to play a role.

The initial project description was no more rigid than it also allowed for elaboration on particular fields of interest as they appeared along the course of the project. Such areas included:

5. AC corrosion case studies: Investigation of AC corrosion incidents observed on real interfered pipelines as opposed to laboratory studies alone is important to bridge the gap between research and applied engineering, especially in a very conservative industry such as cathodic protection in the oil and gas sector. Case studies involved detailed environment (soil) analysis and in-situ corrosion rate studies via installation of corrosion rate probes and remote monitoring stations connected to real AC interfered pipelines.

6. Effect of pH: Quite early in the project, it was established that pH appeared to be an important factor in AC corrosion. And in particular, a topic that was source of much dispute in literature. It was decided to try to resolve some of the unanswered questions on this matter by direct measurement of the pH during AC corrosion conditions. This has taken up a large part of the focus, especially in the later stages of the project.

1.1.1 Outline of the dissertation

This thesis is not made as a monograph, but as a collection of manuscripts published or submitted during the course of the research project. Chapter 1 of this thesis provides a brief historical introduction to the topic AC corrosion and a description of the contents of the thesis. This is followed by a theoretical
Chapter 2 that introduces some basic concepts to the reader and provides a literature review on the state-of-the-art knowledge about AC corrosion. Chapter 3, on the experimental methods, is included to make the reader able to evaluate the validity of the methods used. The main body of this thesis is Chapter 4 that constitutes the published manuscripts. This is equivalent to the traditional "results" chapter in any technical dissertation. Below is a numbered list of these manuscripts. Chapter 5 is a discussion of the results of all the published manuscripts. Finally, Chapter 6 outlines the main conclusions that can be drawn from the presented research in this thesis. In Chapter 7, suggestions for future work on AC corrosion of cathodically protected pipelines are made.

Published and submitted manuscripts


III  A. Junker, L. V. Nielsen, "Monitoring of the pH Evolution at a Cathodically Protected Steel Surface Subject to an AC Voltage Perturbation", CeoCor, Luxembourg, Paper no. 2017-12, 2017


V  A. Junker, C. Heinrich, L. V. Nielsen, P. Møller, "Laboratory and Field Investigation of the Effect of Chemical Environment on AC Corrosion", NACE Corrosion Conference and Expo, Phoenix, Paper no. 10488, 2018


VII  A. Junker, K. Dideriksen, L. V. Nielsen, P. Møller, "Corrosion rate measurement and oxide investigation of AC corrosion at varying AC/DC current densities", Corrosion Science, Under review 23/10/18

VIII  A. Junker, L. V. Nielsen, P. Møller, "Investigation of High pH Corrosion of Steel under Alternating Current Interference", Corrosion Journal, Under review 23/10/18

The focus of the different manuscripts with respect to the research objectives stated above can be seen in Table 1.1.

Table 1.1: Schematic overview over the investigated topics in the manuscripts I-VIII.

<table>
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<th>Research objective:</th>
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Chapter 2

Theory

This theoretical chapter is organised in two sections; one which deals with the background i.e. corrosion, cathodic protection and AC interference or similar basics, needed for understanding the following section which presents the present state-of-the-art knowledge about AC corrosion. In this chapter, no reference to the author’s own work and results will be included. Results and conclusions from other works will however be presented to outline important points or conclusions. Because AC corrosion is not entirely understood, and subject to much controversy in literature, a conclusive theory section is difficult to make, and the different sections in this chapter will reflect the uncertainties on the specific fields.

2.1 Background

2.1.1 Pipelines

Pipelines are widespread metallic structures, often buried in soil, designed to transport water, oil, gas and hazardous liquids etc. These are typically made of high-strength, low-alloyed, weld-able carbon steel. Gas pipelines especially require high strength since they are operated at elevated pressure.

![U.S. Natural Gas Pipelines](image)

Figure 2.1: Map of natural gas pipelines in the US. [Source: American Energy Mapping (AEM) 2013]
Distinction is made between smaller diameter pipelines in the distribution network from distribution stations to the end consumer, which typically operate at 0.1-1.2 MPa (1-12 bar) pressure, and large gas transmission lines, 0.72-1.42 m in diameter, operating at 1.4-10.3 MPa (14-103 bar) and transporting up to 30-35 billion cubic meters per year, typically over large distances. Millions of kilometres of pipelines are used worldwide. In the US alone, over 3.7 million km of pipeline is used [11]. Figure 2.1 shows a map of inter- and intrastate gas pipeline connections in the US in 2013. Pipelines for oil and gas play a tremendous role in modern society, i.e. in economics, national and international politics, infrastructure an environmental concerns. Damage to pipelines caused by corrosion is associated with both severe economic losses as well as safety and environmental hazards. In a 2002 report by NACE on the cost of corrosion in the United States, it is estimated that the average annual corrosion related cost amounts to $7.000.000.000 to monitor, maintain and replace pipelines for gas and liquid transmission [12]. Protection of pipelines against corrosion is thus a large industrial and scientific field, and new methods and theories about the working principles and mechanisms related to pipeline corrosion and its mitigation are continuously being developed.

2.1.2 Corrosion of Pipelines

To understand pipeline corrosion, basic knowledge about corrosion principles is required. It is not within the scope of the present work to provide this extensive background knowledge, but reference is made to several elaborate works on this topic [13–15]. Only the most fundamental principles will be explained here.

Electrochemically, corrosion can be explained by the equilibrium reaction in (2.1). Reaction from left to right represents oxidation or an anode reaction, while the reaction from right to left represents reduction or a cathode reaction.

\[ aA \leftrightarrow bB^{z+} + ze^- \] (2.1)

Any such reaction is associated with an equilibrium potential, \( E_0 \), at which the reaction may run in either direction. This is given by the Nernst equation (2.2), where \( E^0 \) is the standard equilibrium potential of the reaction, \( R \) is the gas constant, \( T \) is the absolute temperature, \( F \) is Faradays number and \( a \) is the activity of species which in most cases is given as the concentration; \( a_A = [A] \) and \( a_B = [B] \).

\[ E_0 = E^0 + \frac{RT}{zF} \ln \left( \frac{a_B^b}{a_A^a} \right) \] (2.2)

The Nernst equation (2.2) can be used to draw the Pourbaix diagram or E-pH diagram for a substance. It maps out the thermodynamic stability regions of various phases in an aqueous electrochemical system [16]. It states that at any electrochemical potential and pH, a certain phase will form, and for corrosion engineers and scientists, this is an extremely powerful tool towards understanding corrosion mechanisms. Figure 2.2 shows an example of the Fe/H\(_2\)O system at 25°C and 1 bar pressure.

The blue stippled lines indicate the stability region of water. They are marked in the diagram, but rarely commented because they are considered an inherent feature in any Pourbaix diagram. In the middle of the diagram, at 0 V and neutral pH \( \sim 7 \), H\(_2\)O is the electrochemically stable phase. At potentials above the upper line O\(_2\) is stable and below the lower line H\(_2\) is stable. The potential stability region of water can be seen to be highly pH-dependent.

The solid lines in red marks the regions of solid iron, its oxides and ions. The red lines move with varying concentrations of iron ions in the system from \( 10^{-2} \) to \( 10^{-6} \) mol/kg. Other thermodynamically stable iron oxides could in theory exist, such as e.g. FeCO\(_3\) if the presence of carbon is considered.
Figure 2.2: Pourbaix or E-pH diagram showing the thermodynamic equilibrium for iron under standard conditions (25°C, 1 bar) at different potential and pH values. The diagram is calculated for varying Fe molalities: \(10^{-2} - 10^{-6}\) mol/kg.

Placement of the lines in the Pourbaix diagram is also dependent on pressure and temperature. Looking at the Pourbaix diagram in Figure 2.2, one will note that within the stability region of water, pure iron is not stable and will dissolve as either Fe\(^{2+}\) or Fe\(^{3+}\) in acidic environments or form iron oxides; Fe\(_3\)O\(_4\) or Fe\(_2\)O\(_3\) in neutral to alkaline environments. In highly alkaline environments iron may dissolve as the dihypoferrite ion, HFeO\(_2^-\) at low potentials around the hydrogen evolution line.

The passing of electrons in equation (2.1) is associated with a current. The relation between current, \(i\), and potential, \(E\), is given by the Butler-Volmer equation (2.3)

\[
i = i_0 \left( \frac{\alpha_c zF}{RT} \exp \left( \frac{\alpha_c zF}{RT} (E - E_0) \right) \right) \cdot \frac{[A]_{\text{surf}}}{[A]_{\text{bulk}}} \exp \left( \frac{\alpha_a zF}{RT} (E - E_0) \right)
\]

(2.3)

where \(i_0\) is the exchange current and \(\alpha\) is the anodic or cathodic charge transfer coefficient denoted \(a\) or \(c\). The surface and bulk concentrations of species A and B take into account mass transfer control of the reaction, i.e. when the reaction is limited due to diffusion of reacting species to the metal surface.

Corrosion of iron in water on a freely corroding surface may proceed via the anodic reaction (2.4).

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^{-}
\]

(2.4)

The free electrons generated need to be consumed elsewhere for the reaction to continue. This can happen by several reactions, e.g. evolution of hydrogen (2.5), reduction of oxygen (2.6) or by dissociation of water in anaerobic conditions (2.7) that also causes hydrogen gas evolution. The hydrogen evolution reactions are only thermodynamically possible at a potential below the hydrogen evolution line in the Pourbaix diagram.

\[
2H^+ + 2e^- \rightarrow H_2
\]

(2.5)

\[
2H_2O + O_2 + 4e^- \rightarrow 4OH^-
\]

(2.6)
2H₂O + 2e⁻ → H₂ + 2OH⁻ \hspace{1cm} (2.7)

The movement of electrons from one reaction to the other corresponds to a corrosion current, \( i_{\text{corr}} \), and the process takes place at the open circuit potential (OCP). In Figure 2.3 a theoretical Evans or \( i/E \) diagram for iron in water is shown. It links the discussed concepts of current and potential in equation (2.3) to the possible reactions (2.4)-(2.7).

The iron reaction is coloured red and has an equilibrium potential, \( E^0_{Fe} \), above which oxidation occurs and below which reduction occurs. The same is true for the different water based reactions in blue, e.g. oxygen evolution or reduction. The black curve illustrates the measured current when scanning through a potential range (a polarisation curve). Coming from low potentials, the first recorded reaction is hydrogen evolution. Due to the high current, any oxygen in the system is depleted faster than it diffuses to the surface. At higher potentials, the current drops and when diffusion of oxygen is higher than the rate of oxygen consumption via reaction (2.6), oxygen reduction becomes feasible. The current at which this happens is called a limiting current, \( i_{\text{lim}} \) (here diffusion defines the limit). At the intersection between the blue and red curves the open circuit potential is measured. Here the recorded current goes from negative (cathodic) to positive (anodic), causing a sharp peak in the log(|\( i \)|) plot. The corrosion current \( i_{\text{corr}} \), does not appear directly from the measured curve, but can be derived by Tafel-extrapolation of the linear parts of the curve to the intersection. Following the anode curve, an increasing current flows via iron oxidation until (possibly) a passivating oxide layer forms on the surface, which again lowers the current despite a still increasing potential. There will be an increase of the anodic current when the potential for oxygen evolution is reached. Alternatively, a breakdown of the passive film is possible, causing a sharp increase in current. This is termed trans-passivity.

The described concepts in the polarisation curve in Figure 2.3 can readily be transferred to the Pourbaix diagram in Figure 2.2 at a specific pH. Polarisation curves at different pH will vary, both in terms of potentials, currents and possible passive regions.

The corrosion current can be translated into a uniform corrosion rate, \( v_{\text{corr}} \), via Faraday’s Law as given in equation (2.8), where \( M \) is the molar mass of the material, \( \rho \) is the density and \( A \) is the area of the
corroding surface.

\[ v_{corr} = i_{corr} \frac{M}{zF \rho A} \]  

(2.8)

In the case of a buried pipe, local differences in the pipes’ alloy composition, condition of the pipe surface, soil resistivity, concentration of soluble salts in the electrolyte, aeration conditions, pH and other factors which can create a potential difference between different areas of the pipe surface, will cause the formation of anodic and cathodic areas of the same pipe. A *galvanic cell* with electrical contact between an anode and a cathode through a conductor (pipe) and the flow of ions through an electrolyte (soil) can be seen in Figure 2.4.

![Figure 2.4: Anodic and cathodic areas on an unprotected pipeline, causing the formation of a galvanic cell and a flow of current indicated by red arrows. The scale is not important; the distance between anodic and cathodic sites may be anything from micrometers to several meters. The same is true for the size of the anodic or cathodic areas.](image)

A current flowing from the anodic areas into the electrolyte corresponds to corrosion. This is indicated by red arrows in Figure 2.4 and in the following.

### 2.1.3 Cathodic Protection

Cathodic protection is commonly applied to prevent corrosion of buried pipelines. This implies making the entire structure to be protected, the cathode in a large galvanic cell, including the naturally occurring anodic areas of the pipe. This can be effected by introducing a material of a lower electrochemical potential than the steel pipe, e.g. zinc or magnesium, in electrical connection to the pipeline, which will act like the anode as shown in Figure 2.5 [17].

![Figure 2.5: A sacrificial anode of e.g. Mg or Zn, connected to the pipeline will protect it from corrosion by establishing a galvanic cell. The corrosion current runs from the anode through the soil to the pipe. Having a large cathode area relative to the anode area as here implies fast consumption of the anode, and often multiple galvanic anodes are installed.](image)

The lower potential of the chosen anode material will drive down the potential of the steel to more negative than its corrosion potential and cause a current to run in the direction of the arrows. Corrosion is isolated in the anode material which can then be replaced when necessary. In Figure 2.6 the concept is illustrated by polarisation curves of the cathode and anode material which in this example is iron and zink respectively. The intersection point of the two curves defines the polarised potential of the steel and the protection current that runs via hydrogen evolution on the cathode and zink corrosion on the anode, in a simple galvanic cell. For the practical case of a buried pipeline with galvanic
anodes there are several reasons why the polarised potential and the protection current is not the same everywhere on the pipeline, but the working principle is the same.

![Diagram showing polarisation behaviour of the anode and cathode.](image)

**Figure 2.6:** Illustration of the working principle behind a galvanic anode (Zn) for cathodic protection using polarisation behaviour of the anode and cathode. The intersection of the two curves defines the protection current and the polarised potential of the pipeline.

Control of the level of cathodic protection in this configuration can be controlled by means of the following:

- Choice of anode material, in particular with respect to the corrosion potential.
- Activation of the anode material by alloying elements to avoid passivation of the surface. This is done to keep the resistance to earth low during operation.
- Increasing the active area of the anodes by anode geometry or number of anodes to lower the effective resistance to earth.
- Controlling the soil resistivity around the anodes by a conductive backfill material.
- Installation of a variable resistor in the pipe to anode connection to externally manipulate the voltage difference or the current running between the two bodies.

A cathodic protection system such as described above (Figure 2.5) is referred to as *voltage controlled CP* when it is the voltage between anode(s) and pipe that is controlled, and *current controlled CP*, when it is the current that is controlled.

A variation of this features a reference electrode, against which the potential of the pipeline with respect to soil can be measured. When the level of cathodic protection is controlled to target a desired pipeline potential, it is called *potential controlled CP*. In practice, the effectiveness of all CP systems is evaluated based on a pipeline potential measurement against a reference electrode.

The impedance of a pipeline-to-anode circuit may vary over time for numerous reasons, e.g. due to changes in the resistance to earth of the anode bed. This is associated with a change in the pipeline potential. Therefore, no matter the CP configuration, a feedback loop is required to measure the pipeline potential and adjust the CP accordingly. In its simplest form, this may be an operator with a hand-held
reference electrode and a voltmeter connected to the pipe at a test post. The operator can then adjust the variable resistor between pipe and anodes to meet the potential requirements. Automated resistor controlled cathodic protection has been developed to automate this process [18].

Modern cathodic protection systems feature a DC rectifier as shown in Figure 2.7, which allows for well defined control of the protection current, voltage or potential. Such a system is called an impressed current cathodic protection (ICCP) system. This requires a power supply, but overcomes the limitations of systems relying purely on galvanic anodes, such as being able to deliver any desired current or potential, almost unaffected by the chosen anode material. Implementation of a feedback loop for potential control is common.

![Figure 2.7: A DC rectifier between the pipe and the anode allows for control of the protection potential or the total amount of protection current. It also allows for use of e.g. scrap steel as anode material, or inert materials such as MMO coated Ti, Fe$_2$O$_3$, graphite or high Si iron, in which case the anode process becomes oxygen evolution, and replenishing of the anode material becomes unnecessary.](image)

Finally, most modern pipelines are coated with electrically insulating coatings of e.g. epoxy, polyethylene or historically bitumen or coal tar. A perfect coating would make a cathodic protection system redundant, but coating defects such as holes, pores or scratches are impossible to avoid during construction and service life of a pipeline. The cathodic protection system then covers these coating defects and protects them against corrosion. This is illustrated in Figure 2.8.

![Figure 2.8: A coated pipeline with coating holidays under cathodic protection. The current concentrates at coating holidays and the impressed current delivered by the rectifier is substantially lowered. Coating defects can arise during construction and at pipeline section joints where in-field coating application is necessary. Moving rocks in the soil or secondary construction work in the vicinity of an existing pipeline are also possible causes.](image)

Coating degradation over time will also lower the total impedance of the coating. Since the total area of exposed pipe is dramatically reduced with better coatings, and the coating impedance is increased, the necessary power from a CP system is low per unit length of pipe, and modern rectifier systems can protect hundreds of kilometres of well insulated pipeline. The protection potential output by a rectifier, $E_{ON}$, is not the same as the potential of the actual pipeline steel. The electrical resistance of the soil contributes to the so-called IR-drop, i.e. a potential drop in the soil between the pipeline and the reference electrode measuring it, caused by the current flowing through the soil. The actual IR-free pipeline steel potential, $E_{IR-free}$, is given by (2.9) and can be seen to be less negative than the ON potential, when regarding the
current I as negative (cathodic).

\[ E_{IR-free} = E_{ON} - IR \]  

(2.9)

The IR-drop is dependent on soil resistivity, but the distance over which the drop occurs is almost irrelevant because the cross-sectional area of the conductor (soil) is essentially infinite except for locally at coating defects on the pipeline where the current density, and thus the IR-drop, is high. Efforts are put into minimising the IR-drop at the anode surface, e.g. by installing them in bentonite or carbonaceous backfill materials. An alternative notation for equation (2.9) involves the cathodic current density, \( J_{DC} (A/m^2) \), and the spread resistance, \( R_S (\Omega m^2) \), which will be discussed in detail in Section 2.2.10 due to its importance in relation to AC corrosion.

\[ E_{IR-free} = E_{ON} - J_{DC} R_S \]  

(2.10)

While \( E_{ON} \) is an easily obtainable parameter from a CP system, \( E_{IR-free} \) is not. The most common method to determine the IR-free potential requires momentarily off-switching of the CP system to force the IR drop to be zero. The potential measured by this technique is often termed the off potential, \( E_{OFF} \). This technique is error prone, since immediately after interrupting the current, the pipeline will start de-polarising [15]. The obtained potential will be dependent on the time from current interruption to the reading is made. In many instances, there is also a human factor involved when analysing the on-off potential measurement. Therefore it is debated whether CP protection criteria should be based on the ON potential including the IR-drop, or the IR-free potential [19]. In the case of a superimposed AC voltage on the pipeline, a reading of the IR-free potential by the off-switching methods is difficult, if not impossible.

An \( E_{IR-free} < -850 \text{ mV}_{CSE} \) (measured against a Cu/CuSO_4 reference electrode (CSE)) criterion is common in CP standards, and refers to protection by a passivation mechanism under un-aerated conditions [19, 20]. This potential value was found empirically [21, 22], but can readily be explained with reference to the Pourbaix diagram in Figure 2.9.

![Pourbaix diagram](image)

**Figure 2.9:** Different strategies for cathodic protection: (a) through passivation obtained via alkalisation from the cathode reactions and (b) by entering the immunity region. Figures copied from [19].
When the potential of a steel surface is lowered, the hydrogen line is reached and the hydrogen evolution reactions (2.5) and (2.7) causes a local increase in pH (concentration polarisation). At moderate CP current densities, the potential and pH will follow the hydrogen evolution line, and at approximately -850 mV\textsubscript{CSE} and pH = 9, the passivity region of the Pourbaix diagram in Figure 2.9a is reached and protection by passivation is achieved. In aerated environments, this can be achieved by a small cathodic potential (-650 or -750 mV\textsubscript{CSE}, depending on the soil resistivity) due to alkalisation following the oxygen reduction reaction (2.6) [20]. In the presence of sulphate reducing bacteria, a -950 mV\textsubscript{CSE} criterion is applied. Alternatively, if passivation cannot be achieved, e.g. due to a flow of water at the electrode that hinders pH elevation, corrosion can be stopped completely by polarising to the immunity region as illustrated in Figure 2.9b (activation polarisation). This requires markedly increased cathodic current densities.

To add to the difficulty of choosing and sustaining a protection potential, a voltage drop along a pipeline may exist, caused by the pipe’s resistance and the current which is consumed at coating defects through cathode reactions. Therefore, the protection potential is not necessarily the same as the set rectifier level along the pipeline, as illustrated in Figure 2.10, and operating close to the critical protection potential of -850 mV\textsubscript{CSE} can be dangerous. Often a more conservative strategy is chosen and the on-potential is set sufficiently low to allow for some potential deviations along the pipeline.

![Figure 2.10](image)

**Figure 2.10:** Voltage drop from the set rectifier value along pipeline caused by presence of coating holidays.

The coating quality of modern pipelines is generally good, and the protection current is low. This means that the voltage drop along the pipeline is reduced. In such conditions it has been demonstrated that a CP system can be operated with potential control referring to the IR-free potential rather than the ON potential, because the potential drop along the pipeline is so small that the IR-free potential measured at a chosen site is essentially the same along the entire protected pipeline length [23].

### 2.1.4 AC Interference

AC interference on pipelines can arise from an inductive, resistive or capacitive coupling between the pipeline and an AC carrying structure. Structures typically comprise 50/60 Hz high voltage transmission lines (HVTL) or 16\textsuperscript{2} Hz AC powered trains. Originally, induced AC voltages were only considered a personnel hazard, but today it is also recognised as a serious threat to the integrity of the pipeline by corrosion. In the following the focus will be kept on interference from HVTL.
2.1. BACKGROUND

Chapter 2. Theory

**Inductive coupling**

Inductive coupling occurs when metallic pipelines are buried parallel to high voltage transmission lines as seen in Figure 2.11. This is customary when designing energy corridors, where the construction of both HVTL and pipelines for oil or gas requires large infrastructural and logistical investments, e.g. through forests, mountains, farm land or deserts. In other cases it is inevitable in areas where multiple energy supply chains are criss-crossing each other.

![Figure 2.11: Parallel construction of gas pipeline and HVTL in an energy corridor. [Source: farwestcorrosion.com]](image)

The theory behind the AC induction in pipelines can (here very simplified) be explained according to Faraday’s laws of induction [24]: A straight wire, i.e. a HVTL, carrying a current, induces a magnetic field $\mathbf{H}$ which is inversely proportional to the distance from the wire as can be seen in Figure 2.12a. The magnetic flux density $\mathbf{B}$ is related to the magnetic field according to (2.11).

$$\mathbf{B} = \mu \mathbf{H} \quad (2.11)$$

Where $\mu$ is the magnetic permeability of the material, which in the present case is free space (neglecting soil and other structures). The magnetic flux, $\phi$, passing through an area $A$, here a pipeline buried in the magnetic field, is given by (2.12).

$$\phi = \int_A \mathbf{B} d\mathbf{A} \quad (2.12)$$

This area, $A$, is directly proportional to the length of parallelism between the pipe and the HVTL. The total flux linkage to the pipeline, $\lambda$, is given by the general term (2.13).

$$\lambda = N\phi \quad (2.13)$$

Where $N$ is the number of turns in a coil situated in the magnetic field. For a pipeline without turns, $N = 1$ in the present case. According to Faraday’s law of magnetic induction, a voltage $U_{AC}$, given by (2.14) is induced in the pipe when the flux linkages are changing.

$$U_{AC} = \frac{d\lambda}{dt} \quad (2.14)$$
Because the current flow in the HVTL changes with 50Hz, this means that a voltage will be induced in the pipeline, which is proportional to the current flow in the HVTL, the length of parallelism and the frequency, and inversely proportional to the distance between the HVTL and the pipeline. Figure 2.12 visualises the basic concepts of AC induction in pipelines [25].

![Figure 2.12: Basic concepts behind magnetic AC induction in buried pipelines [25].](image)

Usually HVTL consists of one (or several) sets of three wires carrying three phase electricity. These are phase shifted by 120° to create a balanced three phase source. One of the main advantages of doing this is, that the delivered power is constant with time. If each of these current carrying wires had the same distance to the pipeline, the induced voltage would be zero, but because the distances are not equal a net voltage is induced as can be seen in phasor-notation in Figure 2.12b. The induced AC voltage on pipelines can reach hundreds of volts under the right conditions.

### Capacitive coupling

A capacitive coupling can exist between two electrically conductive materials separated by a dielectric medium capable of storing a charge. The capacitive coupling between a pipeline and an AC interference source is however merely of theoretical interest. In reality, the distance between the structures is so large that the capacitance becomes negligible and the impedance of the coupling almost infinite.

### Resistive coupling

A resistive coupling can occur via the AC interference sources grounding to earth in which a pipeline is buried. It is primarily a concern for fault currents, i.e. a short-circuit of the AC source, in which case a voltage difference of thousands of volts between the grounding and the pipeline can occur. In such a case coating damages or even damages to the metallic structure are possible, but this is not related to AC corrosion as such. An AC voltage is, however, induced in the earth wire on HVTL, and AC stray current interference can occur if the grounding sites are close to the buried pipeline and allow AC to enter the pipeline via groundings or coating holidays.
2.1.5 AC mitigation

It is possible to lower the amount of AC interference on a buried pipeline by means of an AC mitigation system [26]. Such a system constitutes a low impedance path for the alternating currents on a pipe to escape to remote earth. Either localised (lumped) or continuous (ribbon) grounding conductors of copper or zinc are installed along the interfered pipeline [27, 28]. They can be connected to the pipeline via capacitive couplings that allow the alternating current to run off the pipeline, but does not allow the direct current to pass, since this would disturb the cathodic protection system on the pipeline.

AC mitigation connected via capacitive couplings does not impair the functionality of a cathodic protection system, but obtaining the instant-off potential of a pipeline with AC mitigation by periodic switching of the cathodic protection system becomes problematic, since the capacitive AC mitigation system tends to discharge through soil and cause an error.

Retrofitting a pipeline with AC mitigation is expensive, both due to material costs and construction expenses [29]. Typically the configuration of mitigation installations is based on computer modelling and field measurements of the induced voltage on a pipeline. But even with modelling, the installation of AC mitigation in one location may cause the AC voltage to increase at other locations along the pipeline [30].

2.1.6 Pipeline Steel Systems

Pipeline steels are usually selected according to strength. Higher strength steels allows for higher operating pressure and a thinner pipe wall design, thus reducing material consumption and construction expenses due to the lower weight. Besides, when increasing the operating pressure, the efficiency of compressor station gas turbines is improved, relative to the forced gas volume flow [31]. Weld-ability is another parameter, that influences the alloy composition of the steel. Corrosion prevention is only to a limited extent addressed through the choice of the pipeline steel alloy, however, this is highly dependent on the transport medium in the pipeline. External corrosion protection is obtained through effective pipeline coating systems and cathodic protection.

![Figure 2.13: Development of pipeline steels. TM: thermomechanical treatment. Figure copied from [32].](image)

Pipeline steels are categorized according to the ISO 3183:2012 standard [33]. They are named according to yield strength. In this thesis, the API 5L (American Petroleum Institute) grading system is used to describe steels accordingly: X<sub>xx</sub>, where the ‘<sub>xx</sub>’ is the steel type identifier indicating the minimum yield
strength in kpsi. An X46 steel grade will have a minimum yield strength of 46kpsi (320MPa). Another common naming convention is Lxx where the ‘xx’ refers to the yield strength in MPa. The name may be followed by a suffix indicating any steel treatments; N: normalised, Q: quenched and tempered, M: thermomechanical treated. Figure 2.13 shows a rough overview over the pipeline steel development and the alloying elements since the 60’s. All steels grades higher than X70 are only available with a thermomechanical treatment. Today, X120M is the highest strength pipeline steel grade available, which has been under development since the early 2000’s [31].

For cathodic protection purposes there is a tendency that higher strength steels, X80-X100 are more susceptible to hydrogen embrittlement and stress corrosion cracking, and are thus more vulnerable to CP overprotection where hydrogen is developed on the exposed steel surface at coating defects [34]. The majority of installed pipelines are of an intermediate strength. In Denmark, the highest pipeline steel grade is X70, operated at 80 bar pressure.

2.2 AC corrosion

This section constitutes a review of the state-of-the-art AC corrosion theory. Due to its complicated nature, several authors have presented mechanisms for AC corrosion, not all in accordance with each other. As an introduction to the topic, some of the main guidelines from present industrial standards are presented.

2.2.1 Industry standards

Present international industry standards (ISO 18086:2015, EN15280:2013) specify the following criteria to mitigate AC corrosion [9, 35]:

- The AC voltage on a pipeline should be maximum 15 V rms.
- Compliance with general cathodic protection standards, e.g. ISO 15589-1:2015.
- Maintaining the AC current density on a 1 cm² coupon < 30 A/m².
  or
- Maintaining the DC current density on a 1 cm² coupon < 1 A/m².
  or
- Maintaining the ratio between AC and DC current density $J_{AC}/J_{DC} < 5$, preferably < 3.

Alternatively the following formula should be satisfied

$$\frac{U_{AC}}{|E_{con}| - 1.2V_{CSE}} < 3$$  \hspace{1cm} (2.15)

Effective AC mitigation can also be demonstrated by measurement of a corrosion rate. An acceptable level of corrosion is determined on a case-by-case basis but < 10 µm/y is common [20]. The above stated criteria are illustrated in Figure 2.14.

The voltage criteria of 15 V is primarily a safety guideline to protect personnel working with interfered pipelines [26]. It is a poor AC corrosion mitigation threshold, for reasons that will be elaborated on in the following.
Figure 2.14: Protection criteria outlined in ISO 18086:2015 standard for mitigation of AC corrosion. According to these both a low and high CP approach may be used.

Other standards on AC corrosion exists, e.g. the NACE standard practice SP21424-2018 [10]. This does not include a high or low CP approach to mitigate AC corrosion, but corrosion protection against AC corrosion is achieved by:

- Demonstrating effective AC corrosion mitigation by measuring a corrosion rate < 1 mpa (~25 µm/y).

Alternatively, it also specifies lowering the alternating current density on a pipeline e.g by means of grounding installations. The current density criteria according to this standard practice are given as follows:

- Maintaining the AC current density on a 1 cm² coupon < 30 A/m², if the DC current density is > 1 A/m².

or

- Maintaining the AC current density on a 1 cm² coupon < 100 A/m², if the DC current density is < 1 A/m².

The discrepancy between the NACE standard practice and the International ISO or European EN standard demonstrates, that consensus on AC corrosion has not been established on an international scale. This is also reflected in scientific literature where authors have proposed alternative AC and DC criteria for mitigating AC corrosion [34, 36].

Generally, it is difficult to evaluate current density criteria, since this is a parameter that is physically impossible to measure on an actual pipeline due to the unknown coating defect geometry, distribution, total area and local soil resistivity. In practice, current densities are measured on 1 cm² coupons connected to the pipeline and buried in the same environment since this size has been found to be particularly susceptible to AC corrosion.

A supplement to the German standard on AC corrosion, DVGW GW 28-B1, specifies modified criteria for $U_{AC}$ and $E_{on}$ that are in fact based on the current density criteria of ISO 18086:2015 through a series of assumptions and empirical data [37]. Because this is deeply rooted in the understanding of the spread resistance of coating defects, the description of the principles behind this standard are given in section 2.2.10 on spread resistance.
2.2.2 AC corrosion examples

The morphology of AC corrosion incidents is very characteristic. Figure 2.15 shows pictures from an excavation of an AC corrosion damage on a pipeline with applied cathodic protection. The surrounding soil is clearly affected.

![Figure 2.15: Characteristic morphology of AC corrosion observed on a FBE coated pipeline in clayey soil with low soil resistivity. Cathodic protection was applied. The AC interference source was overhead high voltage transmission lines. [Anonymous source].](image)

The typical indications that a corrosion incident on a cathodically protected pipeline is caused by AC are:

- Corrosion is localised and typically occurs at small coating holidays of a few centimetres in diameter.
- Corrosion products protrude from a coating defect.
- Coating disbondment of the coating surrounding a coating defect is not uncommon.
- Occasionally, the surrounding soil may form a semi-sphere of hardened soil (stone-hard-soil) that can be several tens of centimetres in diameter.
- The corrosion morphology is a smooth or dimpled surface, often a bowl-shaped attack on the pipe surface.
- An alternating voltage can be measured on the pipe.

Linhardt and Ball (2006) presented a failure analysis of an AC corrosion incident on a cathodically protected pipeline [38]. A stone-hard-soil formation was observed on top of the corrosion damage (Figure 2.16). The formation consisted of distinct phases; A, B and C, as can be seen in Figure 2.16d. These were characterised as follows:
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A. Black bitumen based material with iron oxides (mainly Fe$_3$O$_4$) and a sodium compound, presumably carbonate.

B. Grey soil based silicate material incorporating Na, K, Ca and Mg. The concentration of Na was markedly increased towards the corrosion damage.

C. White substance was an equal mixture of NaHCO$_3$ and Na$_2$CO$_3$ with a pH of 9.6.

The authors assigned the mixed appearance of the formation to high cathodic activity and hydrogen gas evolution. The observation of a re-melted appearance of the bituminous phase A, and generally good adherence of the surrounding bitumen coating, comparing to the age of the pipeline and general condition at a distance from the corrosion damage, was assigned to elevated temperatures linked to high AC current densities. The corrosion in Figure 2.16c can be seen to be very localised.

Figure 2.16: Observation of a stone-hard-soil formation from an AC corrosion damage [38].

Figure 2.17 shows another example of an excavation of an AC corrosion damage. Here, a large stone-hard-soil formation was observed on the surface of the pipeline. Also, notice the altered appearance of the pipe surface underneath the disbonded coating in Figure 2.17d with a characteristic "dotted" appear-
ance.

(a) Stone-hard-soil formation stuck on a pipeline where a corrosion damage was found.

(b) The stone-hard-soil formation seen from the pipe side. Brown corrosion products in the centre.

(c) The pipe surface after removal of the formation. Corrosion occurred at a small coating defect.

(d) Cleaned pipe surface with a small but deep corrosion site (32.8% of wall thickness).

Figure 2.17: Observation of a large stone-hard-soil formation from an AC corrosion damage [Anonymous source].

Finneran et al presented a series of AC corrosion case histories on a pipeline with low AC voltage ($U_{AC} < 2\,\text{V}$) [39]. This was done in an attempt to enhance the experience with AC corrosion from a practical point of view, and to underline the importance of assessing current densities rather than induced voltages when evaluating AC corrosion risk. Some of the examples are shown in Figure 2.18 and measured characteristics for these are listed in Table 2.1. The pipeline on which these were found was a 30.5 cm nominal diameter, X42 steel pipeline with a wall thickness ranging from 5.6 - 6.6 mm (measured close to the corrosion damages). The source of AC interference was a 345 kV and 69 kV HVTL (60 Hz) co-located with the pipeline. The AC corrosion sites were covered with hardened soil nodules, though the description of these was limited to the fact that they contained carbonates and calcareous deposits.
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Figure 2.18: Various AC corrosion features in low resistivity soils after cleaning and medium blasting of the surface. The measuring tape is in inches. Conditions for the respective features are listed in Table 2.1 [39].

From Table 2.1 it is clear that even though the induced voltage was low, the AC current densities were high because the soil resistivity at the locations was low and the defect areas were small. The reference pH of the soil at all the locations was pH = 8.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Coating</th>
<th>Depth (mm)</th>
<th>Area (cm²)</th>
<th>ρsoil (Ωm)</th>
<th>U_AC (V)</th>
<th>J_AC (A/m²)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FBE</td>
<td>3.76</td>
<td>1.8</td>
<td>3.2</td>
<td>1.5</td>
<td>80</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>Coal tar</td>
<td>4.55</td>
<td>1.9</td>
<td>0.9</td>
<td>0.8</td>
<td>160</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Coal tar</td>
<td>4.19</td>
<td>4.1</td>
<td>2.0</td>
<td>0.7</td>
<td>39</td>
<td>8.5</td>
</tr>
<tr>
<td>4</td>
<td>Coal tar</td>
<td>2.87</td>
<td>3.3</td>
<td>2.0</td>
<td>1.4</td>
<td>86</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 2.1: Characteristics of the different AC corrosion features illustrated in Figure 2.18 [39].

In a 2010 AC corrosion state-of-the-art report by NACE, several more examples of AC corrosion morphologies are presented, all in agreement with the ones included here [40].
2.2.3 The oxidation/reduction AC corrosion mechanism

A mechanistic model for AC corrosion was presented by Büchler and Schöneich in 2009 [7, 41]. It is based on cyclic voltammetry measurements from 1997 and was presented in an early version already in 2004 [42, 43]. The model is illustrated in Figure 2.19, where the fluctuating anodic and cathodic current causes a continuous degradation of a passive film on the metal surface. During the first anodic current excursion the steel oxidises and a passive film, that may be perfectly suited for protecting the steel, is formed. But, during the following cathodic cycle, this film is reduced to a non-protective porous rust layer that may not be converted to a passive film again. Instead, a new passive layer is formed via oxidation of the underlying steel and corrosion proceeds with the AC frequency.

![Figure 2.19: Model for the AC corrosion mechanism: During the anodic cycle, a passive film is formed, but during the cathodic cycle this is reduced to a non-protective rust layer. The process is repeated with the AC frequency. Büchler and Schöneich (2009) [7]. Figure copied from [44].](image)

In a 2012 paper by Büchler, the AC corrosion criteria, as outlined in ISO 18086:2015, are discussed, based on thermodynamic considerations using the model given in Figure 2.19 [44]. Apart from the anodic and cathodic reactions presented in equations (2.4-2.7) (Section 2.1.2), Büchler highlights another two reactions as important; formation of a passive magnetite film (2.16) during the anodic cycle and a ferri/ferro redox reaction (2.17) that takes place in the rust layer.

$$3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{H}^+ + 8\text{e}^- \quad (2.16)$$

$$\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + \text{e}^- \quad (2.17)$$

With reference to Figure 2.19, reaction (2.16) causes formation of a Fe$_3$O$_4$ layer during the anodic cycle. Since magnetite is a known di-electric that can conduct electricity and it consists of both Fe$^{2+}$ and Fe$^{3+}$, the redox reaction (2.17) may occur within the oxide and allow the anodic and cathodic charge to pass without progressing corrosion. This rationale can be used to understand the AC corrosion criteria [9].

- $J_{AC}/J_{DC} < 3$ (high CP): If the protection potential is very low, the anodic film formation (2.16) can be suppressed and no corrosion of the steel will be observed.
- $J_{DC} < 1 \text{ A/m}^2$ (low CP): Since the passive film formed on a steel surface can effectively accommodate the anodic and cathodic charge from an AC perturbation, corrosion can be stopped if this film is not continuously reduced due to high cathodic current densities.
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- \( J_{AC} < 30 \text{ A/m}^2 \) (low AC): Naturally, if no or limited AC is present, no AC corrosion will take place, since no anodic potential excursion will occur.

The high CP strategy is connected with a risk of cathodic coating disbondment, and possible adverse effects caused by hydrogen evolution, namely the risk for hydrogen embrittlement of the steel. Additionally, the required current from the CP system would be high, and the potential drop along a pipeline would need to be considered (Figure 2.10). Furthermore, the cathode reactions contribute to significant alkalisation of the electrolyte, which may cause a reduced solution resistivity and thus increased currents.

2.2.4 The alkalisation mechanism

Another viewpoint on AC corrosion is made by Nielsen et al (2004). According to these authors, AC corrosion involves alkalisation of the local environment around a coating defect. In combination with AC induced passivity breakdown at moderately high pH, this may lead to highly corrosive conditions in the HFeO\(_2\) region of the Pourbaix diagram [6]. Results from a soil box experiment shown in Figure 2.20 with constant AC interference of 15 V, shows the effect of varying the protection potential. At a very negative potential (day 16-48), the spread resistance (see section 2.2.10) slowly decreases due to alkalisation (Figure 2.20c), and the AC and DC current densities increase (Figure 2.20b and 2.20d). After an incubation period, corrosion initiates at day 28 and the rate gradually increases (Figure 2.20a). This is associated with a slow increase of pH until the conditions for corrosion were established. Switching of the ON potential from day 48 between -850 mV\text{CSE} and -2250 mV\text{CSE}, causes the corrosion rate to decrease and increase promptly, because the conditions for high pH corrosion are established, but can easily be interrupted.

Figure 2.20: Soil box investigation of AC corrosion with 15 V AC and varied CP potential [45].
The authors also observed general depolarisation under the influence of AC (section 2.2.7). This observation, together with the establishment of a high pH environment, lead to the formulation of "the vicious circle of AC corrosion" in Figure 2.21. This shows, that if certain pre-requisites are fulfilled, AC corrosion is possible. The circle has the unfortunate feature that the involved processes will enhance each other, making AC corrosion an auto-catalytic process, given the right conditions [46, 47].

![Vicious Circle of AC Corrosion](image)

**Figure 2.21**: Illustration of the vicious circle of AC corrosion as proposed by Nielsen et al. (2005) [47]. Figure from [10].

The standard criteria can be related to the illustrated pre-requisites: $J_{AC}$ will be small if the level of induced AC is low, or the coating defects are large. Excessive CP is the level of CP that does not generate DC current densities above $1 \text{ A/m}^2$. This is of course also related to the coating defect size.

### 2.2.5 Available models for the AC corrosion mechanism

The passive film formed under un-interfered CP conditions protects the steel from further corrosion. Under AC interference however, this film is not stable and corrosion occurs. The actual passive film degradation mechanism is largely debated and various proposals from literature are given in the following:

- **Nielsen et al (2004)** proposed that AC corrosion is closely linked to an "alkalisation mechanism" caused by excessive CP and OH\(^-\) production at the cathode. An apparent incubation time before corrosion initiates at fixed AC and DC potentials (Figure 2.20), suggests that a slow pH increase causes the steel to eventually enter the high pH corrosive region in the Pourbaix diagram. By reducing the level of CP and thus the alkalisation, corrosion could be gradually slowed down, allegedly due to a de-alkalisation at the steel surface [45]. They further highlight the auto-catalytic nature of AC corrosion in a so-called "vicious circle of AC corrosion", provided that certain pre-requisites are present (Figure 2.21) [47]. For more detail, see section 2.2.4.

- **Büchler and Schöneich (2009)** proposed the model shown in Figure 2.19 where a passive film is built up during the anodic half-wave and reduced to a non-protective rust layer during the cathodic half-wave. This process is repeated with the alternating frequency. At a frequency of 50 Hz and
assuming conversion of a single atomic layer during each anodic cycle, a corrosion rate of 100 mm/yr is obtained, which is higher than usually observed [7]. Assuming that only fractions of each atomic layer is converted during each cycle, this model may explain usually observed AC corrosion rates. For more detail, see section 2.2.3.

- Cheng et al (2010) in his group at the University of Calgary have developed an AC corrosion model, primarily based on the shift of corrosion potential observed at increasing AC interference levels. It considers a double-charge layer of a steel surface that is also covered by a passive layer or a corrosion product. In a passive state at pH 9.6, or under applied CP, the anodic cycle of alternating current up to 200 A/m² will "saturate" the double charge layer with ferrous ions, causing a positive shift of the corrosion potential. The cathodic cycle of AC currents at 200 A/m² will reduce, and at 300 A/m² break, the passive film, releasing the cations into solution and lowering the potential. The release of ferrous ions into solution, is associated with corrosion of the steel. In a non-passive state at pH 7.2, the generated ferrous ions from a corrosion process diffuse away from the surface through a layer of corrosion products, thus lowering the corrosion potential. With increasing AC levels >200 A/m², the layer of corrosion products becomes thicker and hinders diffusion. This causes a positive shift of the corrosion potential. The authors observe pitting type corrosion that is activated at a certain AC level. An AC induced vibrating effect of the charged ions in the double-charge layer may cause enhanced reaction kinetics amongst reactants and thus enhance corrosion [36, 48–51].

- Tribollet et al (2014) generally supports the corrosion mechanism in Figure 2.19 with formation of a passive, primarily magnetite and/or ferric oxide during the anodic half-wave and reduction of this to a porous ferrous oxide during the cathodic half-wave. However, based on the observation of an intermediate green rust (GR) phase \([\text{Fe}^{II}_{1-x}\text{Fe}^{III}_x\text{(OH)}_2]^{x^+} [x/n\text{Fe}^{2+}-m/n\text{H}_2\text{O}]^{x^-}\) below pH = 11, the presence of this intermediate phase is linked to maintaining the protective properties even under AC perturbation [52]. When the pH is increased to above 11 the GR is no longer stable and corrosion occurs by the above mentioned mechanism or by soluble HFeO$_2^-$ in the high pH corrosive region in the Pourbaix diagram. Alkalisation occurs via enhanced cathode reactions (2.6,2.7) caused by high CP and faradaic rectification of the alternating current, which will be discussed in detail in section 2.2.8 [53].

- Brenna et al (2016) proposed an electro-mechanical breakdown mechanism where the potential across the oxide film causes the film to physically break and expose the underlying steel to a highly alkaline environment caused by the cathode reactions. The corrosion mechanism is then purely chemical referring to the high pH corrosive region in the Pourbaix diagram (see Figure 2.2) [8]. The electro-mechanical breakdown mechanism is in line with Brennas PhD thesis on "AC corrosion of carbon steel in cathodic protection conditions" from 2011 from Politecnico di Milano [54].

- Wang et al. (2017) add to the oxidation/reduction mechanism by Büchler and Scöneich. They speculate that adsorption and permeation of hydrogen atoms into the metal, possibly due to the hydrogen evolution reaction at negative potentials, may increase the entropy and weaken the Fe-Fe bond in the metal. This could result in enhanced anodic dissolution. Furthermore, the adsorbed hydrogen atoms may react with the passive film according to reaction (2.18)$^1$ and (2.19), which impedes the film forming process and accelerates film dissolution [55].

$$\text{Fe(OH)}_2 + 2\text{H}_{\text{ads}} \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O} + 2\text{e}^- \quad (2.18)$$

$^1$The equation in the reference specified 1 electron. This has been changed to 2 to balance the charges.
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\[ \text{FeCO}_3 + \text{H}_{\text{ads}} \rightarrow \text{Fe}^{2+} + \text{HCO}_3^- + \text{e}^- \]  \hspace{1cm} (2.19)

The above viewpoints or models may not necessarily be conflicting with one another, but might help towards a more comprehensive understanding on the AC corrosion mechanism. It is, however, important to realize that these models were developed under different experimental conditions.

Büchler and Schöneichs model was hypothesized based on cyclic voltammetry scans made at 10 mV/s i.e. far below the normal excitation frequency of an AC perturbation. While this made it possible to distinguish the anodic passivation and the cathodic reduction of the passive film, as well as an alleged oxidation of Fe\(^{2+}\) in the increasingly thick oxide layer with every cycle according to the Fe\(^{2+}\) ↔ Fe\(^{3+}\) + e\(^-\) reaction in (2.17), the kinetics of these reactions may be very different from the ones at 50/60 Hz. Especially because the current recorded during the low experimental scan rate are largely faradaic, and the capacitive effects of the electrochemical double layer are ignored (see section 2.2.6).

Brennas model is based on experiments conducted largely on stainless steels known to form thin passive films, and the results are then transferred into a carbon-steel context. The passivating properties of the chromium oxide layers on stainless steels are, however, markedly different from the di-electric properties of magnetite films observed on pipeline steels under cathodic protection. The observation of an apparent break-down level of AC voltage that causes a significant increase in the AC currents (also on carbon steel) may, however, be linked to the maximum AC current that can be dissipated in the passive film as simple ferri/ferro conversion (2.17) as postulated by Büchler.

The GR phase that Tribollet observes by Raman spectroscopy of in-situ AC corrosion experiments at 50 Hz, 6 V\(_{\text{AC}}\) and -1.0 V\(_{\text{DC}}\) (CSE) may be the perfect medium for the ferri/ferro redox reaction and dissipation of substantial alternating charge that is part of the explanation by Büchler. Furthermore, it may link the model by Büchler to the alkalisation mechanism observed by Nielsen, since the increasing alkalinity destabilises the GR phase. When the pH exceeds the stability region of the GR phase, corrosion initiates which might be associated with an incubation time. Büchlers model is based on experiments in a 0.1 M NaOH solution at pH = 13, beyond the stability region of the GR phase and thus in a state which is corrosive according to Tribollet.

Tribollet states that several processes may take place on the electrode simultaneously. The faradaic current during the anodic half-wave may be used both to reverse the cathode reactions, i.e. oxidation of part or all of the adsorbed hydrogen on the surface, the transformation of metallic iron into Fe\(^{2+}\), and transformation of ferrous oxides into magnetite and/or ferric oxides. These ferrous species may leave the surface. During the cathodic half-wave, the faradaic current may include the reduction of the electrolyte and the reduction of ferric oxides or magnetite into porous ferrous oxides.

Chengs model for AC corrosion is based on results obtained at a free corrosion potential (except for two studies which includes cathodic polarisation [36, 51]). As such, it might not be directly comparable to the other mechanisms. In the two studies that do include cathodic polarisation, it was concluded that increasing levels of AC interference required more negative protection potentials to prevent AC corrosion. This is in direct contrast to the conclusions made by the other authors listed above. A negative limit of -1250 mV\(_{\text{CSE}}\) was, however, specified to avoid overprotection.

2.2.6 Equivalent Circuit Model

Nielsen and Cohn (2000) suggested an equivalent circuit model for the AC corrosion process shown in Figure 2.22 [56]. This model is used to break down the electrochemical reactions that may occur on a steel surface, into electrical equivalent elements for a better understanding of the processes that leads to AC corrosion.
They differentiate between static and dynamic elements as being independent or dependent on the frequency of an applied voltage excitation. Static elements are the solution resistance (spread resistance, $R_S$, when normalised with the area (section 2.2.10)), and the charge transfer resistance or faradaic reactions. This is symbolised by a forward and backwards diode equivalent to the cathodic and anodic Butler-Volmer reactions, $c_n$ and $a_n$ (see equation (2.3)). As mentioned in section 2.1.2, any redox reaction is associated with an equilibrium potential, $E_{0,n}$. Any products of cathode or anode reactions occurring on the surface will have a diffusion response which is illustrated by Warburg-elements, $W_n$. The impedance of such a Warburg element, as determined by electrochemical modelling, is dependent on the frequency, making this a dynamic element. Another dynamic element is the double layer capacitance, $C_{dl}$, which will act as a low impedance path for high frequency currents that can short circuit the faradaic reactions. The $n$'th faradaic process, as outlined in red, may or may not happen, depending on what is the path of the lowest impedance for the direct or alternating currents imposed on the circuit. If the redox reaction of iron in equation (2.17) is considered as one of the processes that occurs on the surface, then corrosion will occur if the current passed via the anodic reaction is greater than the current passed via the cathodic reaction [56].

Various authors have investigated the double layer capacitance of cathodically protected steel by various methods, e.g. analysis of Lissajous curves, with the purpose of predicting the corrosion behaviour under AC interference. Houban found that there’s a correlation between the extent of corrosion and the magnitude of $C_{dl}$, reporting capacitance values in the range $C_{dl} = 840-3300 \, \mu F/cm^2$ for heavily corroded samples. Xiao et al. similarly observed $C_{dl} = 1231-2475 \, \mu F/cm^2$ on corroded samples using EIS. Houban also found that $C_{dl}$ is reduced from 340-20 $\mu F/cm^2$ with more negative levels of cathodic protection from $E_{IR-free} = -1036 - -1329 \, mV_{CSE}$ [57]. Wang et al. similarly found that $C_{dl}$ is dependent on the cathodic protection potential being reduced at lower potentials, however with large fluctuations over certain potential ranges, which they assign to e.g. an oxidation stage at potentials above $\sim -850 mV_{CSE}$ and a double layer region below, where the capacitance of any passive film is neglected. They observe an increase of capacitance with increasing levels of AC from 200 $\mu F/cm^2$ - 1000 $\mu F/cm^2$ which they assign to an increase of the dielectric constant of water in the fluctuating electric field and a weakening
of the adsorption of cat- and anions that will be replaced by more neutral water molecules with a higher di-electric constant than other ions [55, 58].

The consequence of the changing double layer capacitance can be understood as a change of the impedance of this element. When the capacitance decreases with higher levels of cathodic protection, the impedance of this element increases, and a larger fraction of the alternating current is discharged via faradaic charge transfer reactions such as e.g. corrosion.

2.2.7 Effect of AC on DC characteristics

AC interference has been shown to have great influence on the DC polarisation characteristics of steel. Laboratory work with varying AC current density on carbon steel, in free corrosion condition, and anodic and cathodic polarisation by Bolzoni et al (2003), showed that AC current had an effect on the anodic and cathodic polarisation behaviour as well as on the free corrosion potential to some degree [59]. The outline of the discussion is presented schematically in Figure 2.23 and in bullet form:

- AC decreases the anodic process overpotential (Blue curve in Figure 2.23a and 2.23b).
- AC increases the limit current density for oxygen reduction, possibly due to Joule heating of the diffusion layer at the electrode (Red curve in Figure 2.23a).
- AC decreases the hydrogen overpotential causing an increase in potential for the cathode reaction (Red curve in Figure 2.23b).

For pipelines buried in soil, the amount of oxygen is limited and is consumed by cathode reaction (2.6). Under anaerobic conditions, the hydrogen evolution reaction (2.7) thus becomes dominant and as can be seen from Figure 2.23b, the presence of AC currents enhances this reaction at a given potential on the cathode curve.

Figure 2.23: Schematic effect of AC current on anodic and cathodic polarisation: (a) Effect on oxygen reduction; (b) Effect on hydrogen evolution. In both cases, the anodic process overpotential is reduced with increasing AC (blue). Figures from [59].

Polarisation scan behaviour

Several authors have recorded polarisation curves for pipeline steels under the influence of varying AC current perturbations (50/60Hz). To highlight the consistency of these investigations, a broad selection
of these have been included here in Figures 2.24 and 2.25. While some conditions, e.g. electrolyte composition and pH might vary, several general trends are visible. As Bolzoni pointed out, both the anodic and cathodic DC current density increases with overlying AC. The corrosion potential decreases with increasing AC current perturbation, until a limit of \( \sim 200-400 \text{ A/m}^2 \) (Figure 2.25c, 2.25d, 2.24b and 2.25a), after which it increases again. Xu and Goidanich explain this by increased AC corrosion at high AC current densities to a point where corrosion products cover the surface, increasing the corrosion potential [60, 61].

(a) Polarisation curves for X60 steel measured at various AC current densities and a frequency of 50Hz. Guo et. al. (2015) [62].

(b) Polarisation curves for X65 steel measured at various AC current densities (60Hz) in a neutral pH carbonate/bicarbonate solution. Kuang et. al. (2014) [49].

(c) Polarisation curves for steel measured at various AC current densities and a frequency of 50Hz. Scaling artificial soil solution (AS), Nielsen et. al. (2004) [63].

(d) Polarisation curves for steel measured at various AC current densities and a frequency of 50Hz. Non-scaling artificial soil solution (NAS), Nielsen et. al. (2004) [63].

Figure 2.24: Polarisation curves recorded by various authors.
Figure 2.25: Polarisation curves recorded by various authors.
Long term polarisation behaviour

Potentiodynamic investigations of the effect of AC on the corrosion potential are inherently dependent on the scan-rate used during the measurement. Long term polarisation behaviour of steel under various AC interference has been investigated by several authors. As can be seen in Figure 2.26, the response of the corrosion potential to an AC perturbation varies between different experiments.

In Figure 2.26a, the potential first increases, then drops with several hundreds of mV. This is explained by the authors as a passive state of the steel in the elevated pH solution. With the anodic cycles of AC, positively charged ferrous ions accumulate in the double-charge layer, thus increasing the potential. With increasing AC interference, the passive layer is destroyed and the ferrous ions released, causing a drop in potential [49]. In Figure 2.26b and 2.26c a drop in potential is observed immediately because no passive
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film is present initially. At high interference levels (>400 A/m²), the potential increases steadily due to corrosion and build up of corrosion products on the surface. This is observed in both Figure 2.26c and 2.26d.

Long term polarisation behaviour under CP

Because AC corrosion is a concern on pipelines with cathodic protection, authors have investigated the polarisation behaviour under cathodic protection. This can be carried out using the galvanostatic polarisation technique, i.e. by supplying a fixed DC current to obtain a CP potential under un-interfered conditions, and then recording the shift of potential caused by different levels of AC interference. Figure 2.27 shows the results of such an investigation by Kuang and Cheng (2017) [51]. The effect of fixing the potential and then recording the response of the polarisation current to increasing levels of AC interference was also investigated (Figure 2.28). Very similar investigations have been conducted by Du et al (2017) and Wang et al (2017) with comparable results [55, 66].

![Figure 2.27: Polarisation behaviour at different levels of CP, maintained galvanostatically in pure CP conditions, with increasing AC interference. Kuang & Cheng (2017) [51].](image)

![Figure 2.28: Current response from potentiostatic controlled CP at different levels, with increasing AC interference. Kuang & Cheng (2017) [51].](image)

While authors have several explanations for the shifting potentials, and how this is related to AC corrosion, the shifting potentials can easily be explained by comparing them to the polarisation scans. Figure 2.29 shows a generic polarisation curve based on the general trends observed in Figure 2.24 and 2.25, namely a depolarisation of the anode and cathode reactions and a negative shift of the corrosion potential.
at relatively low levels of AC interference.

Consider the galvanostatic polarisation technique: The DC current necessary to maintain a potential \( X \) is given by \( J_{DC}(X) \) and refers to the un-interfered curve (grey). With increasing AC interference, the polarisation curve will change and the recorded potential corresponds to the intersection of \( J_{DC}(X) \) with the cathode curve at a given interference level. Whether this yields a negative or positive shift of the recorded potential, depends on the potential shift and depolarisation behaviour of the polarisation curves. At still higher cathodic current, this will also induce an inversion of the order of potentials, i.e. with the most negative potential being that with the smallest AC level. This is indeed observed by both Du et al and Wang et al [55, 66].

Consider the potentiostatic technique: If the potential is held constant at \( X \) and the corrosion potential of the steel shifts negatively from \( X \) due to AC interference, then the potential will correspond to a point on the anodic branch of the respective polarisation curve and yield a positive current. In a condition with anodic current, corrosion will occur. Therefore, authors conclude that they observe AC induced corrosion, and that this is linked to the level of AC interference. The immediate conclusion will then be to increase the level of cathodic protection, and lower the protection potential to below the corrosion potential at all AC levels.

Herein lies perhaps the biggest discrepancy in AC corrosion literature. The above chain of reasoning will highlight low CP as a threat with regards to AC interference corrosion. Whereas it is also well known that high levels of cathodic protection may be a threat with regards to AC corrosion.

![Theoretical polarisation curves](image)

**Figure 2.29:** Theoretical polarisation curves, based on a large number of reported polarisation curves in literature (Section 2.2.7). They show depolarisation of both anodic and cathodic reactions, and a negative shift of the corrosion potential for the reported AC interference levels. This is used to explain the observations made by Kuang and Cheng (2017) [51].

### 2.2.8 Faradaic rectification

The alteration of the DC characteristics with an overlying AC perturbation is caused by the phenomenon *faradaic rectification*, which is well known in literature and often used in relation to AC corrosion modelling [67–69]. This gives similar results as the empirical curves in Figures 2.24 and 2.25 however based...
entirely on theoretical considerations. The basis for simulating the DC response is the Butler-Volmer equation that gives the relation between an overpotential, $\eta = E - E_0$ and the current density $i$:

$$i = i_0 \left( \frac{[B]_{\text{surf}}}{[B]_{\text{bulk}}} \exp \left( \frac{\alpha_a zF}{RT} \eta \right) - \frac{[A]_{\text{surf}}}{[A]_{\text{bulk}}} \exp \left( \frac{\alpha_c zF}{RT} \eta \right) \right)$$

(2.20)

where $i_0$ is the exchange current density, $[B]$ and $[A]$ refers to the concentration of oxidized and reduced species (ions) at the surface and in the bulk electrolyte respectively. It is identical to equation (2.3) in section 2.1.2 where the parameters of the equation are explained. Close to the equilibrium potential, the $E/\log(i)$ behavior is linear with the slope:

$$\beta_k = \frac{RT}{\alpha_k zF}$$

(2.21)

This is the Tafel constant, often expressed in mV/decade current density where $k = [a, c]$. Given an AC perturbation on the system, the voltage will consist of the original overvoltage and an added alternating voltage, i.e $\eta = \eta + U \sin(\omega t)$. Neglecting differences in the surface and electrolyte concentrations, setting $i_0 = i_{\text{corr}}$ and exploiting the relation $\exp(a + b) = \exp(a) \exp(b)$, equation (2.20) can be re-written as

$$i = i_{\text{corr}} \left( \exp \left( \frac{\eta}{\beta_a} \right) \exp \left( \frac{U \sin(\omega t)}{\beta_a} \right) - \exp \left( \frac{\eta}{\beta_c} \right) \exp \left( \frac{U \sin(\omega t)}{\beta_c} \right) \right)$$

(2.22)

Authors have used various methods to mathematically re-write this expression [67, 69] using

$$\exp(z \sin \theta) = I_0(z) + 2 \sum_{k=0}^{\infty} (-1)^k I_{2k+1}(z) \sin((2k+1)\theta) + 2 \sum_{k=1}^{\infty} (-1)^k I_{2k}(z) \cos(2k\theta)$$

(2.23)

where $I_n(z)$ is the modified Bessel function of order $n$, given by the following expression:

$$I_n(z) = \left( \frac{z}{2} \right)^n \sum_{k=0}^{\infty} \frac{\left( \frac{z}{2} \right)^{2k}}{k!(n+k)!}$$

(2.24)

When calculating the time average of the current over an AC period, i.e. by integrating equation (2.23) over the period $T_0 = 1/f$, only the first term, $I_0(z)$ is not zero. The term

$$I_0 \left( \frac{U}{\beta_k} \right) = \sum_{k=1}^{\infty} \frac{U^{2k}}{(2\beta_k)^{2k}(k!)^2}$$

(2.25)

induces the so called faradayic rectification effect. The current response according to the Butler-Volmer equation can be rewritten as

$$i = i_{\text{corr}} \left( \exp \left( \frac{\eta}{\beta_a} \right) I_0 \left( \frac{U}{\beta_a} \right) - \exp \left( \frac{\eta}{\beta_c} \right) I_0 \left( \frac{U}{\beta_c} \right) \right)$$

(2.26)

where it can be seen that depending on the Tafel constants, the current densities are dependent on the alternating voltage. At the corrosion potential, the current density is essentially zero, $i = 0$. This can be used to solve for OCP, which then also becomes a function of the Tafel constants and the alternating voltage. Any further derivations will not be included here, but illustration of the effect as shown by Bosch and Bogaerts are presented in Figure 2.30.
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(a) Simulated polarisation curves, \(i_{\text{corr}} = 1 \times 10^{-4} \text{A/cm}^2, \beta_a = 40 \text{mV/dec}, \beta_c = 120 \text{mV/dec}\).

(b) Simulated polarisation curves, \(i_{\text{corr}} = 1 \times 10^{-4} \text{A/cm}^2, \beta_a = 60 \text{mV/dec}, \beta_c = 120 \text{mV/dec}\).

(c) Simulated polarisation curves, \(i_{\text{corr}} = 1 \times 10^{-4} \text{A/cm}^2, \beta_a = 120 \text{mV/dec}, \beta_c = 120 \text{mV/dec}\).

(d) Simulated polarisation curves, \(i_{\text{corr}} = 1 \times 10^{-4} \text{A/cm}^2, \beta_a = 120 \text{mV/dec}, \beta_c = \infty \text{mV/dec}\).

Figure 2.30: Simulated polarisation curves for various Tafel constants and alternating voltages. The effect of the faradayic rectification on the corrosion potential and the current densities is clear. Bosch and Bogaerts (1998) [69].

In a recent series of papers by Ibrahim et al. (2015-2017) [70–72], the effect of the faradaic rectification is studied specifically under cathodic protection, including effects of both reduction of dissolved oxygen under diffusion or activation control and dissociation of water molecules as the cathode processes and iron dissolution as the anodic process in a so-called "three reaction corrosion mechanism". In a further step, the simulations also include the electrolyte resistance, i.e. the ohmic drop of the alternating voltage, as well as the effect of the double layer capacitance which acts as a short for high frequency AC perturbations in parallel with the charge transfer resistance. An important point in these steps is, that the Bessel function approximation relies on a linear relationship between the alternating potential and current, which is not the case when the ohmic drop is considered. As such, their model becomes increasingly complicated and relies on heavy computational power to be solved. Nonetheless, their simulation implies that the error induced in the calculations using the linear approximation exceeds 1000% at an alternating peak voltage as low as 1.52 V. In Figure 2.31, simulated polarisation curves for the linear approximation and the fully developed model (a), and the effect of varying the soil resistivity, i.e. mildly or highly aggressive soil conditions (b), are shown. The effect on both the corrosion potential and the current densities is considerable.
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(a) Simulated polarisation curves using the linear approximation (solid line) and full model (dashed line).

(b) Simulated polarisation curves using the full model for mildly aggressive soil (solid line) and highly aggressive soil (dashed line).

Figure 2.31: Simulated polarisation curves using $i_{corr} = 4 \cdot 10^{-6} \text{A/cm}^2$, $\beta_a = 43.3 \text{mV/dec}$, $\beta_c = 52.1 \text{mV/dec}$, obtained by Ibrahim et al. (2016) [71]. Note that the DC voltage here is denoted $U$, and the alternating voltage $\Delta U$.

In Figure 2.32, the effect of including the double layer capacitance in the model on the change in corrosion potential and on the corrosion current with increasing alternating voltage is indicated. The black curves represent the response for a 4 $\mu$A/cm$^2$ corrosion current without AC and a 100 $\mu$F/cm$^2$ double layer capacitance.

(a) Effects of $I_{corr,0}$ and $C_d$ on the corrosion potential shift.

(b) Effects of $I_{corr,0}$ and $C_d$ on the corrosion current density.

Figure 2.32: Effects on the alternating voltage on the corrosion potential shift and the corrosion current density. Ibrahim et al. (2016) [71].

By increasing the double layer capacitance, a bypass effect of the AC is enhanced, and the effect of the alternating voltage is diminished (solid red). Increasing the AC free corrosion current has a diminishing effect on the change in corrosion potential, especially for higher AC perturbations (dashed green). The combined effect is also outlined (dotted blue). Ibrahim et al. used the simulation to assess the effect of alternating voltage on the averaged faradic anodic current density, i.e. a measure of the dissolution of iron from the surface. Setting up an arbitrary current limit of $i_{Fa,AV} = 10 \mu$A/cm$^2$ equivalent to a uniform corrosion rate of 116 $\mu$m/yr, Figure 2.33 indicates the necessary cathodic protection potential needed to limit corrosion at different alternating voltage perturbations. The open circuit potential and current is indicated in both figures.
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It can be seen that for the mildly aggressive soil (a), a protection potential of -1 V is enough to limit corrosion if the alternating voltage is \( \Delta U \leq 1.5 \) V. In the highly aggressive soil, this only holds for \( \Delta U \leq 0.5 \) V. Ibrahim et al. states that any cathodic protection potential below 1.2 V is associated with heavy hydrogen evolution and alkalisation at the steel interface which may destabilise any protective oxide layer. Therefore, the simulation indicates that effective cathodic protection is impossible in mildly aggressive soil for \( \Delta U \geq 2 \) V, and in highly aggressive soil for \( \Delta U \geq 0.75 \) V.

It is worth noticing that alternating voltages far beyond the ones given here are often reported in actual situations, i.e. the ISO 18086:2015 standard specifies a limit \( U_{AC} = 15 \) V value, above which AC corrosion is possible. The model does also not include the effect of alkalisation or any possible alteration of the local soil chemistry with time.

2.2.9 Lissajous behaviour

Polarisation curves describe the current response at different DC potentials for a given material. For AC voltage perturbations, the current response is quite different. A pure ohmic current response to an AC voltage signal would be a straight line in a voltage/current density plot. When the voltage is moved positive to an equilibrium a positive current is produced and vice versa for negative voltage signals. Across a capacitive element, the current response to an AC voltage signal will be phase shifted by \(-90^\circ\) and, instead of a straight line in a voltage/current density plot, it will yield a circle. A steel surface/electrolyte interface is neither purely resistive or capacitive, nor is the current response linear for large voltage variations (>10 mV) as can easily be seen from the polarisation curves in Figures 2.24 and 2.25. When such a system is subjected to an AC voltage, and the current response is recorded, e.g. by an oscilloscope, a Lissajous curve is created. The Correac system, developed in 1999 at Cebelcor in Belgium allows for simultaneous recording of the current density and the true IR-free potential measured by the On-Off method for a 50 Hz voltage perturbation. The switch-off operation is repeated at slightly shifted instants of successive AC periods along with a measurement of the current density to provide multiple instantaneous \( E_{IR-free}/i \) recordings which can be put together to form a Lissajous curve for a 50 Hz AC signal [73, 74]. In theory these are cyclic polarisation curves recorded at 50 Hz, with a sinusoidal sweep rate. In Figure 2.34, Lissajous curves recorded by Gregoor, Pourbaix and Carpentiers are shown. Analysing these curves is much like analysing a classical polarisation curve with corrosion and passivity regions. The potential domain for both figures covers the entire stability region of water, with hydrogen or oxygen evolution at low or high potentials respectively. In the Lissajous curves, these reactions are illustrated as increasing current densities. The span in between, the aspect ratio of the ellipses gives an indication
of corrosion or passivity, i.e. a flattened ellipse (low phase angle) exhibiting high current densities indicates corrosion, while an upright ellipse (high phase angle) indicates passivity, resulting in low current densities.

(a) Lissajous curves for carbon steel in NaOH solution, pH = 10. Gregoor, Pourbaix and Carpentiers (2002) [74].

(b) Lissajous curves for carbon steel in NaOH solution, pH = 13.75. Gregoor, Pourbaix and Carpentiers (2001) [73]

Figure 2.34: Lissajous curves recorded with the Correac system at varying polarisation levels showing hydrogen and oxygen evolution, and the domain in between for two different pH levels.

A negative phase angle corresponds to the build-up up of a passive layer, i.e. a reduction of the current density with increasing potential. This is evident in both Figure 2.34a and 2.35, where Lissajous curves have been recorded at different polarisation and pH levels as outlined in the Pourbaix Diagram in Figure 2.35a. Together with weight loss corrosion rate measurements, this illustrates how AC can induce corrosion under conditions which would otherwise favour cathodic protection (position 3). The measurements were manually controlled to measure within the potential variations given in Figure 2.35a, so the AC voltages or current densities for the various measurements are not comparable [74]. This might be part of the explanation for the low corrosion observed in position 2 where corrosion would be expected. A potential variation across immunity, dissolution and passive regions would likely be more critical. Likewise, position 1, entirely in the immunity region, is probably closer to pure DC conditions since the AC voltage is small. In reality, AC voltages on pipelines are several volts and will effectively cause potential fluctuations much larger than in the illustrated experiments.
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(a) Measurements 1-6 conducted at different pH and potential values outlined in a Pourbaix diagram.

(b) Lissajous curves 1-6 recorded with the Correac system for various pH and potential values. The figure is edited from [74].

Figure 2.35: Corrosion rates and type for each measurement determined by weight loss after 1 week: 1) 0 µm/yr. 2) 46 µm/yr, uniform. 3) 119 µm/yr, uniform. 4) 78 µm/yr, uniform. 5) 56 µm/yr, crevice. 6) 26 µm/yr, crevice. Gregoor, Pourbaix and Carpentiers (2002) [74]

Bette did similar measurements with ER coupons and recorded the Lissajous curve for the same coupon in corroding and non-corroding conditions, shown in Figure 2.36 [75]. The only difference is the applied CP current density, which was reduced from 10 to 1 A/m² causing a change in corrosion rate from 182 µm/yr to effectively zero. The AC voltage for the two curves is similar, but the AC current density is more than doubled at higher CP levels as explained in section 2.2.7. Even though the AC frequency is only 1/3 of the 50 Hz in Figure 2.35, the corrosion curve in Figure 2.36 shows a remarkable resemblance with the corroding curve 3 in 2.35b.

Figure 2.36: Lissajous curves recorded for ER coupon in corroding and non corroding conditions. 16² Hz AC: 7.2 V/127.9 A/m² (black), 6.6 V/309.0 A/m² (red). The difference is the CP current density applied: -1 A/m² (black), -10 A/m² (red). Bette (2013) [75].
Corrosion was only observed if the IR-free potential was temporarily more negative than 1.2 V
_CSE_, as is the case for the two curves in Figure 2.36. Büchler explains this by observing the intersection between the hydrogen line in the Pourbaix diagram and the potential line for _E_on_ = -1.2 V
_CSE_, which occurs at a pH below 15 (e.g. Figure 2.9). If the cathode reaction is hydrogen evolution, the surface potential, _E_IR-free_, corresponds to a point on the hydrogen line, and therefore, as the pH increases the difference between _E_on_ and _E_IR-free_ will go towards zero, limiting _J_DC_. A steady state is established that prevents an uncontrolled increase of _J_DC_ and consequently AC corrosion. This chain of reasoning is closely related to the protection criterion in equation (2.15).

### 2.2.10 Spread resistance

The spread resistance, _R_S_, is one of the key parameters to evaluating AC corrosion risk. It relates AC and DC potential values on a pipeline to the current densities obtained at coating defects via the specific soil resistivity and the coating defect geometry. The simplest expression for _R_S_ is often given as (2.27) in literature [76].

\[
R_S = \frac{\rho}{2d} A
\] (2.27)

where _\rho_ is the specific soil resistivity and _d_ is the diameter of a circular coating defect in an infinitely thin coating. _A_ is the defect area, and is added to normalize with respect to the area. The ohmic relations are given as (2.28) and (2.29). Equation (2.28) is simply a re-formulation of equation (2.10),

\[
-J_{DC} = \frac{E_{IR-free} - E_{on}}{R_S}
\] (2.28)

\[
J_{AC} = \frac{U_{AC}}{R_S + Z_{interface}A}
\] (2.29)

The interfacial impedance, _Z_{interface}_, is given by (2.30) for a traditional Randles circuit representation of the electrode/electrolyte interface with a parallel coupling of the charge transfer resistance, _R_{ct}_, (sometimes referred to as the polarisation resistance) and the electrochemical double layer capacitance, _C_{dl}_.

\[
Z_{interface} = \frac{1}{\frac{R_{ct}}{1 + j2\pi f C_{dl}}} = \frac{R_{ct}}{1 + j2\pi f R_{ct} C_{dl}}
\] (2.30)

It is clear that for high frequency values, _f_, the impedance is low and approaches _Z_{interface} \approx 0_, independent of the value of _R_{ct}_. At 50/60 Hz this is usually the case and often equation (2.30) is simplified to (2.31) for practical applications.

\[
J_{AC} = \frac{U_{AC}}{R_S}
\] (2.31)

More detailed impedance models for the electrolyte/electrode interface exist, and will be elaborated on in section 2.2.6. The following threshold values for soil resistivity are given with respect to AC corrosion [9]:

- Below 25 Ωm: very high risk.
- Between 25 and 100 Ωm: high risk.
- Between 100 and 300 Ωm: medium risk.
- Above 300 Ωm: low risk.
This is due to the reducing effect a high resistance has on the current densities at any AC or DC voltage. Adversely, a high soil resistivity is considered a negative property for cathodic protection efficiency in general. The soil resistivity is a function of a number of parameters, in particular; soil chemistry, wetness of the soil, soil texture, temperature, aeration etc. In Figure 2.37 a map of Britain and a series of soil resistivity ranges are presented.

![Map of soil resistivity in Britain with the gas distribution network overlayed](Source: British Geological Survey)

The map illustrates the complexity of the challenge with AC corrosion, since pipelines for gas are often positioned in various resistivity soils, low resistivity soils being the biggest challenge. On a much smaller scale, the local soil resistivity can be highly influenced by e.g. de-icing salts used in countries with freezing winters. Wakelin et al. (1998) reported several cases of AC corrosion at locations where pipelines where crossing roads subject to de-icing salts that had dramatically reduced the...
soil resistivity locally to values as low as 1.3 \Omega m [77]. Using equation (2.31) and (2.27), and assuming a circular coating holiday of 1 cm², an alternating voltage of only 0.3 V AC is required to yield a current density of \( J_{AC} = 30 A/m² \). Such a low voltage is difficult to mitigate by any known mitigation methods today (section 2.1.5).

The spread resistance is also dependent on the coating defect geometry, and this has been investigated by several authors. Obviously the defect area has an effect on the AC and DC current densities, and thus the AC corrosion rate. Furthermore, there is a geometrical dependence on the spread resistance which has been modelled by Nielsen et al. [78] using equation (2.32), here normalized with respect to the area \( A \).

\[
R_S = \frac{R_{S1} R_{S2}}{R_{S1} + R_{S2}} A \tag{2.32}
\]

\( R_{S1} \) and \( R_{S2} \) for a circular coating defect are given by:

\[
R_{S1} = \rho_{soil} \frac{1}{2d} \left( 1 - \frac{d}{5l_c} \right) + \rho_{pore} \frac{4t}{\pi d^2}
\]

\[
R_{S2} = \left[ \rho_{soil} \frac{1}{2\pi} \left( 1 - \frac{d}{5l_c} \right) + \rho_{pore} \frac{2}{\pi d} \right] \frac{1}{1 - (\alpha/90)^{3/2}}
\]

\( R_{S1} \) and \( R_{S2} \) for a rectangular coating defect are given by:

\[
R_{S1} = \frac{\rho_{soil}}{\sqrt{\frac{36}{\pi} \left( l_c^2 + w^2 \right)}} \ln \left( \frac{4l_c}{w} + \frac{4w}{l_c} \right) \left( 1 - \frac{w+l}{10l_c} \right) + \rho_{pore} \frac{t}{lw}
\]

\[
R_{S2} = \left[ \rho_{soil} \frac{1}{2\pi} \left( 1 - \frac{w+l}{10l_c} \right) + \rho_{pore} \frac{2}{\pi(l+w)} \right] \frac{1}{1 - (\alpha/90)^{3/2}}
\]

In these formulas \( \alpha \) is the angle of the coating edge with respect to the steel surface, i.e. an angle of 90° corresponds to vertical coating edges as depicted in the illustrations. \( \rho \) is the resistivity of the soil and the pore medium, which can be altered considerably as previously discussed, via electrochemical reactions at the surface.

From the above expressions it can be seen that when \( \alpha \to 0° \), then \( R_{S2} \) becomes infinitely large. This means that \( R_{S2} + R_{S1} \approx R_{S2} \), and \( R_S = R_{S1} A \). For a circular defect, equation (2.32) approaches the simplified equation (2.27) when \( \alpha = 90° \), \( t = 0 \) and \( l_c \gg d \).

As already mentioned, the dependence on the soil resistivity implies that the spread resistance changes when the local environment changes, mainly due to the cathode reactions (2.5-2.7). These reactions are directly driven by the cathodic current, \( J_{DC} \), and the increased concentration of hydroxyl-ions in solution will lower the resistivity and increase the pH.

Büchler and Joos described a model for the soil resistivity at a distance \( x \) from the cathodic surface as a function of the inherent soil resistivity and the soil resistivity defined by the pH [79]. This is assumed for a circular defect with diameter \( d \).

\[
\rho(x) = \left( \rho_{pHx}^{-1} + \rho_{soil}^{-1} \right)^{-1} = \left( \left( (d + 2x)^2 \cdot \rho_{pH}/d^2 \right)^{-1} + \rho_{soil}^{-1} \right)^{-1} \tag{2.33}
\]

Here the pH dependent resistivity is given by (2.34).

\[
\rho_{pH} = \rho_0 \cdot \exp(a + b \cdot \text{pH}) \tag{2.34}
\]
The parameters \( a = 12.58 \) and \( b = 0.94 \) are empirically determined factors. The soil resistance of a hemisphere pH profile, \( R_H \), can then be determined by integrating \( \rho(x) \) from 0 to \( a_e \) which is the distance to a reference electrode. Usually this is remote earth, i.e. \( a_e = 30 \text{ m} \).

\[
R_H = \int_0^{a_e} \frac{\rho(x)}{(d+2x)^2 \cdot \pi} \, dx = \frac{\rho_{pH} \cdot \left( \tan^{-1} \left( \sqrt{\frac{\rho_{pH}}{\rho_{soil}}} \cdot (1 + 2a_e/d) \right) \right) - \tan^{-1} \left( \sqrt{\frac{\rho_{pH}}{\rho_{soil}}} \right)}{d \cdot \pi \cdot \sqrt{\frac{\rho_{pH}}{\rho_{soil}}}}
\]  
\tag{2.35}

The spread resistance is obtained by multiplying with the area of the coating defect. They further describe a correction resistance in the case of a coating thickness, but this will not be included here.

The importance of the coating defect area is however important, because they do not consider the area of the hole in the coating, but rather the surface area of the corroding steel which they find can be described by a spherical cap that may have a diameter which is larger than the coating defect. The surface area of this cap is a function of the coating defect diameter and the corrosion depth. As corrosion progresses, the area increases which causes \( R_S \) to increase. It follows that if \( U_{AC} \), \( E_{ON} \) and \( \rho_{soil} \) are known and relatively constant, then the derived current densities (2.28) and (2.31) decrease, as corrosion occurs at a coating holiday and at a certain corrosion depth for a certain defect diameter, corrosion will stop. A maximum allowable corrosion depth, that does not impair the structural integrity of the pipeline, together with a measurement of the soil resistivity, can be used to define criteria for \( U_{AC} \) and \( E_{ON} \), that are in fact based on the \( J_{AC}, J_{DC} \) criteria of ISO 18086:2015. The entire deduction of these thresholds are based on a series of assumptions and empirically determined factors that have not been included in the present description in full detail [79]. The discussed correlation do however serve as the basis for a set of modified criteria for AC voltage and ON potential for the GW 28-B1 standard on AC corrosion in Germany [37].

Depending on the chemical composition of the soil, a pH increase will cause the formation of new chemical constituents. Generally, alkaline elements (Na, K and Li) tends to form soluble species when reacting with O, H and C present in the soil, and this contributes to lowering of \( R_S \) at elevated pH, whereas the earth alkaline elements (Mg and Ca) tends to form low soluble constituents capable of increasing \( R_S \) substantially if they are formed directly on the electrode surface [35]. A more thorough discussion on the alkalisation mechanism will be made in section 2.2.11.

### 2.2.11 Alkalisation

The cathode reactions (2.5-2.7) contribute to alkalisation of the electrolyte (soil) in the vicinity of a coating defect. The degree of alkalisation, i.e. the pH level given by equation (2.36), is governed by a number of coexisting processes.

\[
pH = -\log[H^+] = -\log \left( \frac{10^{-14}}{[OH^-]} \right)
\]  
\tag{2.36}

**Production of \( OH^- \) at the surface**

Under stagnant conditions in soil, any \( H^+ \) or dissolved \( O_2 \) initially present in the soil will be consumed via reactions (2.5) and (2.6) under cathodic protection (Figure 2.38a). Alkaline hydrogen evolution (2.7) is the governing cathode reaction at a coating defect.

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^-
\]

The produced \( OH^- \) is given directly by the faradaic cathodic current

\[
\frac{d[OH^-]}{dt} = J_{DC}AzF
\]  
\tag{2.37}
where $A$ is the defect area, $z$ is the number of electrons participating in the formation of a single OH$^-$ ion ($z = 1$) and $F$ is Faraday’s number.

Under an AC perturbation, faradaic rectification of the AC current may enhance the cathodic current, $J_{DC}$, by several orders of magnitude.

**Consumption of OH$^-$**

Consumption of hydroxide ions may occur upon reaction with available cations in solution (Figure 2.38b). This is a function of the cation exchange capacity (CEC) of the soil given in cmol+/kg. Typical cations, ranked by their relative strength of adsorption to colloids (e.g. OH$^-$), are: Al$^{3+}$, H$,\text{Ca}^{2+}$, Mg$^{2+}$, K$,\text{NH}_4^+$, Na$^+$ [80]. It is well known that earth alkaline elements Ca$^{2+}$ or Mg$^{2+}$ may precipitate as carbonates or hydroxides at elevated pH upon reacting with OH$^-$ and carbon in the soil [81, 82]. In addition to the inherent soil chemistry, the dissolved iron from a corrosion process may consume hydroxide upon formation of oxides, e.g. Fe(OH)$_2$ or Fe$_3$Fe$_4$. Formation of oxides can even be associated with acidification, i.e. reaction (2.16).

**Diffusion of OH$^-$ away from the surface**

This is governed by Fick’s Laws of diffusion. The first law states that the flux, $J$, of species is dependent on the diffusion coefficient, $D$, and the concentration gradient field given by the gradient operator for a three dimensional matrix, $\nabla$.

$$J = -DV[\text{OH}^-] \quad (2.38)$$

Fick’s second law of diffusion is derived from the first law. It states that the change of concentration at a point is proportional to the second derivative of the concentration gradient.

$$\frac{d[\text{OH}^-]}{dt} = DV^2[\text{OH}^-] \quad (2.39)$$

These laws are based on mass conservation and no chemical reactions. Since $[\text{OH}^-]$ is not constant, but a function of a number of reactions as discussed above, this is not true. The main consequence of this realisation is that the concentration gradient becomes far more steep than under static conditions.

**Figure 2.38:** Various mechanisms affecting the local pH environment at a coating defect on a pipe under cathodic protection.
An illustration of the concentration gradient caused by diffusion is illustrates in Figure 2.38c. This means that the pH gradient towards a surface is correspondingly steep and a practical measurement of the true surface pH becomes difficult to obtain because conventional pH measurement techniques such as pH probe or pH paper requires a measurement volume. As stated, the OH\(^{-}\) production is directly proportional to the cathodic current. Conversely, the cathodic current is a function of the spread resistance of the soil (2.28) i.e. the resistivity, which is highly dependant on the amount of dissolved charge-carrying ions in the solution such as OH\(^{-}\). Given a sufficient driving force for OH\(^{-}\) production, i.e. a large negative polarisation, in combination with the faradaic rectification of an AC current, more OH\(^{-}\) ions will be produced than may diffuse away, or be consumed by chemical reactions in the soil. In such a case the local environment around a coating defect will become increasingly alkaline, reaching levels far beyond what is usually observed for pipelines under cathodic protection without an AC perturbation. This may cause the vicious circle of AC corrosion, as described in section 2.2.4.

2.2.12 Corrosion products

The corrosion products formed in connection with AC corrosion are not characterised consistently throughout literature. Stalder and Bindschedler reported observations of goethite (FeOOH) from analysis of field collected corrosion products [83, 84]. Fraga et al observed primarily lepidocrocite (γ-FeOOH), followed by goethite (α-FeOOH) and a minor amount of magnetite (Fe\(_3\)O\(_4\)) [85]. Büchler and Joos analysed corrosion products from a laboratory study (\(E_{ON} = -1.3\) V\(_{CSE}\), \(U_{AC} = 16\) V) and found 100% magnetite (Fe\(_3\)O\(_4\)) with a porosity ranging from 50% - 60% [79]. Tribollet et al used an in-situ Raman spectroscopy method to observe a green rust phase \(\left[Fe^{II}_{1-x}Fe^{III}_{x}(OH)_{2}\right]^{x+}\left[x/nA^{n-}m/nH_{2}O\right]^{x-}\) in a solution with pH < 11 under AC interference, that is not stable and will oxidise e.g. to lepidocrocite. For pH > 11 they observe magnetite as the primary corrosion product [52, 53]. Xiao et al conducted laboratory investigations in both scaling and non-scaling soil environments, and observed FeO(OH) and magnetite in the scaling environment and FeO(OH) in the non-scaling environment [86].

There are a number of possible explanations for the inconsistent characterisation of corrosion products:

- The chemical environment around a coating defect may have a great influence on the species formed.
- The AC and DC current and potential settings during formation may play a significant role.
- Handling of sample material, e.g. in an oxidising environment (air), prior to characterisation may alter the oxidation stage.
- Surface oxides may exist in various oxidation stages as a result of the corrosion mechanism [43].
- pH of the local environment is important, refer the Pourbaix diagram.
- The electrochemical potential at which the corrosion products are formed is important, refer the Pourbaix diagram [82].

Ruby et al. investigated precipitation of various iron oxides, upon titration by hydroxyl ions. A series of reactions leading to the formation of ferrous hydroxide (2.40), hydroxysulphate green rust (GR(SO\(_4^{2-}\)) (2.41), magnetite (2.42) and goethite (2.43) is listed [87, 88]:

\[
Fe^{2+} + 2OH^- \rightarrow Fe(OH)\_2
\]

(2.40)
CHAPTER 2. THEORY 2.2. AC CORROSION

\[ 4\text{Fe}^{2+} + 2\text{Fe}^{3+} + 12\text{OH}^- + \text{SO}_{4}^{2-} \rightarrow \text{Fe}_{4}\text{Fe}_{2}^{II}\text{OH}_{12}\text{SO}_{4} \]  

(2.41)

\[ \text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}^{II}\text{Fe}^{III}\text{O}_{4} + 4\text{H}_2\text{O} \]  

(2.42)

\[ \text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{FeOOH} + 2\text{H}_2\text{O} \]  

(2.43)

These species can be plotted in an \( \text{Fe}^{2+}-\text{Fe}^{3+} \) mass-balance diagram as in Figure 2.39. Here, \( R \) is the number of moles of \( \text{OH}^- \) consumed per mole of iron during the reactions and \( x \) is the molar fraction of \( \text{Fe}^{3+} \) of the total amount of iron. The diagram can be used to evaluate the composition of a mixed oxide with any amount of hydroxide, \( R \), and fraction of ferric iron, \( x \), by using the lever rule. If, for example, a point on the line between \( \text{Fe}_3\text{O}_4 \) and \( \text{FeOOH} \) is considered, then these two phases will exist in equilibrium. An oxide, represented by a point inside one of the drawn triangles in the diagram will consist of all three phases in equilibrium.

![Figure 2.39: Fe\(^{2+}\)-Fe\(^{3+}\) mass-balance diagram, indicating the oxidation stage of different iron oxides [87].](image)

The diagram is relevant to AC corrosion because it illustrates, in a simple manner, the oxidation stage of the respective oxides. Generally, an oxidising environment such as air will favour oxidation to \( \text{FeOOH} \) or \( \text{Fe}_2\text{O}_3 \) in the upper right corner of the diagram, almost independent on the original state of the oxide. Therefore it is important to prevent further oxidation of corrosion products in air if the type of corrosion product is to give any information on the corrosion process at all. It is worth noticing that the studies of in-field sampled corrosion products point to \( \text{FeOOH} \) as the main observed corrosion product. The \textit{in-situ} studies of AC corrosion by Tribollet showed either GR or magnetite, depending on the pH, i.e. amount of \( \text{OH}^- \) available for reaction, which corresponds nicely to the \( R \) value in the diagram. Formation of \( \text{Fe(OH)}_2 \) is possible only in a non-oxidising environment.
Chapter 3

Methods

This chapter presents the methods used in this thesis. The chapter is divided into two main sections: *in-situ* measurement techniques and characterisation techniques typically used on samples after a completed experiment.

In the field of corrosion engineering, most *in-situ* methods are electrochemical methods in which one or more of the elements; current, potential or impedance, is measured during a corrosion process. Corrosion products, or the state of a metallic surface, can also be used to characterise the rate, or seriousness, of corrosion and its mechanism.

Having a thorough understanding of the various methods and the equipment used is important in order to assess the advantages and strengths, as well as sources of errors and limitations, of the respective techniques.

Here, only the technique is described. For the actual experimental procedures, reference is made to the relevant manuscript enclosed in this thesis (Chapter 4).

3.1 Experimental set-up

The experimental set-up used for practically all investigations of AC corrosion in this thesis, is shown in Figure 3.1. A total of 9 of these set-ups were constructed at the initiation of the project, which allowed for several parallel investigations with variation of e.g. the chemical environment, AC or DC settings, etc. Minor variations to the set-up were implemented in specific experiments, but this is described in the respective manuscripts. The set-up consists of the following elements:

i. A Wenking model LB 81 laboratory potentiostat from BANK Elektronik for control of potential or current of the cathodic protection.

ii. Variable safety transformer type 260-1 from Elcanic supplied with network alternating current (50 Hz).

iii. Isolating laminated core transformer from Noratel (SU96C-23048) supplying a maximum of 48 V AC to the variable transformer. Implemented for safety reasons.

iv. Skywave unit for remote upload of data to a web-based data processing program.

v. Interference corrosion loggers (ICL-02i) from MetriCorr for logging the electrical and corrosion parameters at defined time intervals.

vi. Banana plug terminals for easy readings of the AC or DC potentials between the pipe and reference terminals on the ICL.
vii. True RMS multimeter (Fluke 83 III) for manual reading and adjustment of AC and DC potentials.

viii. 50 L plastic box containing the soil environment. Typically 50 kg of inert quartz sand (0.4-0.8 mm) and ~16 L of soil solution.

ix. Isolating toroidal transformer from Noratel (RT300-2038), giving an inductance of approximately 2 H.

x. Cornel Dubiler 947C-type polypropylene DC link capacitor of 600 µF ±10%.

Figure 3.1: Experimental setup used for investigation of AC corrosion in a controlled soil environment.

Figure 3.2 presents a principal sketch of the experimental set-up in Figure 3.1. The inductance and capacitance separates the circuit into an AC and a DC circuit, sharing the same working electrode. This configuration was chosen, based on experimental set-ups used for similar investigations [89]. One aspect in which this set-up differentiates itself from others, is the rather large soil box. This is particularly suitable for long term investigations, where the chemistry evolving at the counter electrodes could interfere with the environment around the working electrode if the distance between the two is small. As evident from the typical corrosion morphology of AC corrosion shown in section 2.2.2, the affected chemical environment around the working electrode may extend to several tens of centimetres.

The counter electrodes are 10 x 20 cm MMO coated, fine grid titanium mesh, placed at opposite ends of the soil box. In almost all investigations, the reference electrode was a Cu/CuSO₄ rod type reference electrode from M.C. Miller or Tinker & Razor, and was placed at the surface of in the soil box.
3.2 In-situ measurement techniques

3.2.1 Electric resistance corrosion rate measurements

The electric resistance (ER) technique is based on the simple relation between the dimensions of a conductor as can be seen in Figure 1, and its resistance.

This relation is given by (3.1)

\[ R = \rho(T) \frac{l}{w \cdot \sigma} \] (3.1)

Where \( \rho(T) \) is the temperature dependent resistivity of the conductor material, given by (3.2)

\[ \rho(T) = \rho_0 (1 + \alpha(T - T_0)) \] (3.2)

\( \rho_0 \) is the resistivity at a reference temperature \( T_0 \) and \( \alpha \) is a material specific temperature coefficient. If the dimensions \( l \) and \( w \) are kept constant, it is clear from (3.1) that a change in resistance can be interpreted as a change of thickness, i.e. due to corrosion of the conductor material, or a change in temperature. Temperature compensation can be effected by having a non-corroding reference element in connection with the corroding element which is exposed to the same temperature variations as the
corroding element. The thickness can then be expressed as a function of time and the two elements resistances

\[ \sigma_C(T) = \sigma(t_0) \cdot \frac{R_C(t_0)}{R_C(t)} \cdot \frac{R(t)}{R(t_0)} \]  

(3.3)

Where \( t_0 \) refers to initial conditions when the thickness is well known. Rearranging (3.1) to express the thickness as a function of resistance and differentiating with respect to time yields an expression for the corrosion rate, \( v_{corr} \) in (3.4)

\[ \sigma = \rho(T) \cdot \frac{l}{w \cdot R} \iff v_{corr} = \frac{d\sigma}{dt} = -\frac{dR}{dt} \cdot \frac{w\sigma^2}{l\rho(T)} \]  

(3.4)

From this it is clear that the corrosion rate sensitivity, i.e. the ability to measure small changes in thickness \( (d\sigma/dt) \), is a function of the original thickness of the element squared. A thinner element yields higher sensitivity but a shorter lifetime because the element will eventually corrode away. For obvious reasons, the ER technique is not applicable for all types of corrosion, e.g. pitting corrosion, but only for uniform corrosion of a surface. Considering the smooth surface of an AC corrosion attack, the ER technique is ideal for analysing AC corrosion. ER probes can be used in practically all environments and one of the key features from the technique is that it provides \textit{in-situ} real-time measurements of corrosion rate, in contrast to traditional weight-loss analysis which is time consuming and provides only average corrosion rate data for a given test period. ER data can be coupled with other experimental data such as humidity, temperature, potential, etc. to give a more comprehensive understanding of corrosion performance in various environments. A commercially available ER-probe can be seen in Figure 3.4, but designs can be varied according to application.

![Commercially available ER-probe for corrosion measurements in soil. The exposed element is a 1cm² 1:10 length/width-ratio steel element of 500 µm thickness. [Photo: MetriCorr]](image)

**Figure 3.4:** Commercially available ER-probe for corrosion measurements in soil. The exposed element is a 1cm² 1:10 length/width-ratio steel element of 500 µm thickness. [Photo: MetriCorr]

### 3.2.2 Electrical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a technique used to characterise the impedance of a metal/electrolyte interface. EIS is an alternating current technique in which a small (typically 10 mV to stay in the pseudo-linear potential and current domain) AC excitation with varying frequency is used to
CHAPTER 3. METHODS

3.2. IN-SITU MEASUREMENT TECHNIQUES

Characterise the frequency dependent impedance. The Randles circuit, with an electrochemical double layer capacitance, $C_{dl}$, and a charge transfer or polarisation resistance, $R_{ct}$, in parallel at the metal surface, coupled in series to a solution resistance, $R_s$, is the most common example of an equivalent circuit that may be characterised by EIS. This is illustrated in Figure 3.5.

\[
Z = R_s + \left( \frac{1}{R_{ct}} + j\omega C_{dl} \right)^{-1}
\]  

(3.5)

The angular frequency, $\omega = 2\pi f$, is the variable parameter, and it may be seen that for $f \to \infty$, then $Z = R_s$ and for $f \to 0$, then $R = R_s + R_{ct}$. At intermediate frequencies, the impedance will have an imaginary component. Figure 3.6a shows a Nyquist plot with the real and imaginary parts of the impedance data. The simple Randles circuit will always yield a perfect semi-circle in this plot. Figure 3.6b plots the same data in a Bode plot with the absolute impedance and the phase shift. Obtaining a value for the individual components in an electrochemical equivalent circuit is usually done by fitting a model for the circuit to measured impedance data. Very often, more complex equivalent models are necessary to obtain a satisfactory fit, e.g. the use of Warburg impedances to simulate the effect of diffusion etc.

The impedance data in figure 3.6 represents a simplified example with $C_{dl} = 200\mu F/m^2$, $R_{ct} = 1000\Omega$ and $R_s = 500\Omega$. For this specific example, it can be seen that, at 50 Hz the phase shift is small, and the impedance is mainly composed of the solution resistance. This implies that the double layer capacitance acts as a short circuit for alternating current of this frequency. The current passes primarily via charging and discharging of the double layer, and not via charge transfer as electrochemical reactions. Conversely, the impedance of the capacitance is infinite for direct current with $f = 0$, and all the current must pass...
3.3. CHARACTERISATION TECHNIQUES

As the equivalent model in section 2.2.6 indicates, a circuit model for an actual corrosion process may be much more complicated than the simple Randles circuit, making an effective EIS analysis difficult.

3.2.3 pH measurement

Measurement of pH is traditionally done by either a pH electrode or using chemical indicators. These are discussed in the following:

pH indicators

pH indicators are chemical compounds that change colour upon a change in pH. These chemicals are typically weak acids or weak bases. The colour of the conjugate acid and the conjugate base is visually different and the pH range of colour change is related to the $pK_a$ value, refer the Henderson-Hasselbach equation. Typically the colour does not change at an exact pH value, but over a range. Therefore, pH determination using chemical indicators is associated with some measurement error. Sometimes a blend of pH indicators may be used to create several colour changes over a wide pH range, such as e.g. the universal indicator. pH indicators may be added to solutions, or they may be used as pH paper that contain a pH indicator. When they are soaked with electrolyte, the paper changes color.

pH sensors

pH sensors, probes or electrodes rely on a potential reading of a material that is sensitive to the presence of $H^+$ ions, and can therefore be used to measure pH. The potential is measured against a reference electrode. For glass electrodes, conventionally used for pH measurement, the pH sensitive glass is doped with different metal cations. The potential difference between the liquid on either side of the glass membrane is then used for the pH measurement. This measurement is sensitive to temperature variations and the more extreme the pH (above or below 7), the larger the induced measurement error. Some pH electrodes are equipped with temperature sensors for compensation of this error. Because the measurement relies on a potential reading, then naturally it will also be sensitive to electrical interference and noise.

3.3 Characterisation techniques

3.3.1 X-ray diffraction

X-ray diffraction (XRD) is a technique used to characterize crystalline materials such as metals, oxides or minerals etc., i.e. materials with a regular arrangement of atoms in a repeated unit cell. Such materials have crystallographic planes that may reflect incoming x-rays capable of penetrating solid matter. Constructive interference of x-rays reflected by several parallel crystallographic planes is achieved when the wavelength of the x-rays, $\lambda$, and the $d$-spacing of the planes satisfies Bragg’s equation (3.6).

$$n\lambda = 2d\sin(\theta) \quad (3.6)$$

Here, $n$ is any number of reflecting planes and $\theta$ is the so-called Bragg angle between the incoming x-rays and the crystallographic plane. Figure 3.7a illustrates diffraction conditions. Different materials have specific combinations of reflecting crystallographic planes with well defined $d$-spacings. The background behind crystallography is well covered in literature [90]. The conditions for positive interference is a function of the angle $\theta$ which is varied in small increments in an x-ray diffractometer to create a so-called diffractogram as shown in Figure 3.7b. Whenever Bragg’s equation
is not fulfilled, destructive interference between the reflected x-rays is dominant and a diffractogram for a crystalline material yields very sharp peaks. The peak position and size of the peaks is a fingerprint for different phases in a material. Traditionally $2\theta$ values are displayed on the x-axis.

Crystalline materials have crystals oriented in all directions, but only the crystallographic planes with a normal direction ($90^\circ - \theta$) to the x-ray source and detector contributes to the diffractogram. For powder specimens, being either powders or non-textured polycrystalline materials with small crystals having a completely random orientation, both qualitative and quantitative phase analysis is possible. Depending on the x-ray sources wavelength, e.g. CuK$_\alpha$ with a wavelength of $\lambda = 0.1540598$ nm, the $2\theta$ value may be translated into a $d$-spacing, and referring to Figure 3.7a, materials having a large repeated unit cell, such as clay minerals will have peaks at low $2\theta$ values. Conversely, metals, salts and oxides have peaks at higher $2\theta$ values. Clay minerals may also have broad peaks due to irregularities in the repeated unit cell.

XRD is a very versatile characterisation technique capable of determining stress and strain or texture in materials, however this is rarely of interest in a corrosion investigation.

### 3.3.2 X-ray photoelectron spectroscopy

X-ray photo-electron spectroscopy (XPS) is used to characterise the chemical composition of a surface. The penetration depth of the technique is in the order of 10 nm, and the technique may therefore be used for e.g. oxides that are too thin for characterisation by e.g. XRD. The sample is irradiated by an Al K$_\alpha$ x-ray source, and an electron detector detects the emitted photo-electrons and their kinetic energy. The XPS spectrum is a count of the electrons as a function of their binding energies, and the peak position is characteristic to different elements, as well as the electron configuration 1$s$, 2$s$, 2$p$, 3$s$, etc. This allows for an evaluation not only of the chemical composition, but also of the chemical bonds present, e.g. C-C, C-O, C=O, etc. as well as the oxidation level, e.g. Fe$^{2+}$ or Fe$^{3+}$. 
### 3.3.3 Scanning electron microscopy

Scanning electron spectroscopy (SEM) is an electron imaging technique in which a focused electron beam in high vacuum scans the object of investigation, and a detector detects the reflected or backscattered electrons. The fine focus of the incident electron beam allows for very high resolution and a large depth of focus in a recorded image. The subject of investigation needs to be electrically conducting and properly grounded to avoid charging from the incident electrons. Besides the very high magnification that is achievable, the technique may be coupled with other techniques such as chemical analysis by EDS (see below).

#### 3.3.4 Energy dispersive x-ray spectroscopy

Energy dispersive x-ray spectroscopy (EDS) is a technique used to determine the element composition of a sample. An incident beam of high energy charged particles (i.e. electrons) is focused on the sample and causes electrons to leave the inner shells of the atoms in the sample material. Upon re-settling of the electrons from the outer shells back to the inner shells, x-rays of an element-characteristic energy are emitted and measured by a detector. Figure 3.8 illustrates the physical principle (a), and an example of an EDS spectrum of a clay sample (b). Each peak in the spectrum corresponds to a characteristic drop in energy level, e.g. $K_{\alpha}$, $K_{\beta}$, $L_{\alpha}$, etc.

The technique may be utilized inside a SEM to gain information about the chemical composition of a specific site, or an area. The technique is naturally limited to elements having two or more electron shells. A practical limit exists around carbon in the periodic table, below which the elements cannot be accurately detected.

Elemental mapping is a technique in which the incident beam scans an area, resulting in a map showing the presence of the respective elements at specific sites within the investigated area.

#### 3.3.5 Inductively coupled plasma optical emission spectroscopy

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is a chemical analysis method used for aqueous dissolved species. Sample material is sprayed directly into an ionized plasma flame and is immediately ionized itself. Upon recombining with electrons, electromagnetic radiation with a...
characteristic wavelength is emitted and recorded by a spectrometer. The intensity of the radiation from different elements can be translated into a concentration.

### 3.3.6 Ion chromatography

Ion (exchange) chromatography (IC) is used to measure concentrations of ions in aqueous solutions. The ionic species are separated based on their interaction with a resin in a column. Upon flushing the column with an ion extraction liquid (eluent), the ionic species will leave the column, but the retention time will be specific to the type of ion and its concentration. The technique may detect anions such as $\text{Cl}^-$ and $\text{SO}_4^{2-}$ or cations such as $\text{Mg}^{2+}$ or $\text{Ca}^{2+}$.
Chapter 4

Manuscripts

This chapter includes the published manuscripts that constitutes the scientific work of this thesis.

(Oral presentation at conference. Non-reviewed conference proceedings.)

(Oral presentation at conference. Peer reviewed conference proceedings.)

III A. Junker, L. V. Nielsen, "Monitoring of the pH Evolution at a Cathodically Protected Steel Surface Subject to an AC Voltage Perturbation", CeoCor, Luxembourg, Paper no. 2017-12, 2017
(Oral presentation at conference. Non-reviewed conference proceedings.)

(Peer reviewed journal publication)

V A. Junker, C. Heinrich, L. V. Nielsen, P. Møller, "Laboratory and Field Investigation of the Effect of Chemical Environment on AC Corrosion", NACE Corrosion Conference and Expo, Phoenix, Paper no. 10488, 2018
(Oral presentation at conference. Peer reviewed conference proceedings.)

(Oral presentation at conference. Non-reviewed conference proceedings.


In addition to the above listed manuscripts are a list of publications of various kinds that the author have contributed to. These are not considered part of the present thesis.


4.1 [I] CeoCor ’16

This paper investigates the effects of having different orientations of the corroding surface, simulating coating defects at the 12, 3 or 6 o’clock positions of a pipeline. It also investigates the effects of varied coating defect size, i.e. very small (0.01 cm$^2$) to large (100 cm$^2$) circular defects, and the effect of varied thickness of a coating system (0 - 10 mm). Finally, effects of the coating geometry is investigated, from a circular defect to a scratch like defect. The methods used are ER probes for corrosion rate measurement and EIS for characterisation of the boundary layer conditions at different defect geometries.
Effect of coating fault geometry and orientation in AC corrosion of buried pipelines

by A.Junker-Holst and L.V.Nielsen (MetriCorr, Denmark)
Abstract

Coupons for investigation of AC corrosion on cathodically protected pipelines acts as artificial coating defects of a well-defined area of 1 cm², typically circular, according to the EN 15280:2013 Standard. This is convenient for current density calculations, but real life coating defects can be expected to have multiple sizes and geometries, which is known to affect critical parameters such as the spread resistance, AC and DC current density and ultimately the AC corrosion rate. The effect of size, geometry, length/width-ratio, coating thickness and defect orientation is investigated at different protection levels in the present study, using electrical resistance measurements (ER) and electrochemical impedance spectroscopy (EIS). The findings suggests that smaller, scratch-like defects with a very thin adjacent coating yields the smallest spread and charge transfer resistance, and will therefore be more vulnerable to AC corrosion. The coating defect orientation also has a large influence on the AC corrosion rate, with upwards pointing defects corroding the most, and downwards pointing defects corroding the least under identical AC and DC voltage control, suggesting that the spread resistance is affected by formed species at the surface, having another density than water, or having a directional diffusion dependency.

Introduction

Coupons for investigation of AC corrosion on cathodically protected pipelines are buried in the soil next to pipelines, and electrically connected to these. In this way, they act as artificial coating defects of a well-defined area and well-known defect geometry. Such coupons can be analysed to investigate the corrosion conditions on the pipe either after an experimental period, or in situ, using ER-technology. It is customary that such artificial coating defects have an area of 1 cm², but real life coating defects can of course have multiple sizes and geometries, as well as orientation with respect to the pipe. This study investigates

- The effect of varying defect size on the spread resistance and on the AC and DC current density, which are identified as critical parameters when investigating AC corrosion [1] [2] [3].
- The effect of coating thickness known to cause a varied current density distribution across the defect surface, as well as the development of a pitting environment in defects having a large depth/width ratio [3] [4].
- The effect of varying the coating defect gradually from a circular defect to a scratch geometry having a width/length ratio of 1:100, while keeping the area constant, which influences the spread resistance [1].
- The effect of the defect orientation with respect to the pipe. Cathode reactions cause formation of hydrogen gas and hydroxyl-ions which are lighter and heavier than water respectively. Dependent on the orientation of the defect surface, these can be concentrated or transported away from the surface causing different chemical environments and thus corrosion conditions.

Figure 1 shows an overview over the variation of coating defects investigated in this study.
A total of 14 different geometries were investigated. Electrochemical impedance spectroscopy (EIS) has been used to investigate the variables; defect size, l/w ratio and coating thickness. Probes for the experiments were embedded in resin to avoid delamination of a coating or crevice corrosion. They can be seen in Figure 2. Variable coating thicknesses were made by punching a 1cm² hole in a 0.5mm thick tape and adding layers to the 1cm² circular probe until thicknesses of 1, 3 and 10mm were reached. Prior to the experiment, the probes were polished to a grid 220, obtaining a fresh metal surface.

A standard three-electrode setup was used, with the coating defect as the working electrode, an inert counter electrode mesh surrounding the working electrode and a standard calomel electrode as the reference electrode connected to the setup via a Luggin capillary placed in front of the working electrode. The working electrode was put in an upright orientation according to Figure 1. For each geometry, 400 mL of non-scaling artificial soil (NAS) solution prepared according to Table 1 was transferred to a beaker and de-aerated by bubbling through with nitrogen gas for >30 min. prior to the experiment. For the 100 cm² sample a larger beaker and 1800 mL was needed, and the bubbling time was extended. The beaker was placed in a grounded faraday cage during the experiment to minimize electromagnetic noise from the surroundings. No stirring was applied during the experiment in order to better simulate the stagnant conditions in soil.
Table 1: Non-scaling Artificial Soil (NAS) solution

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄</td>
<td>5.0⋅10⁻³ M</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>2.5⋅10⁻³ M</td>
</tr>
<tr>
<td>NaCl</td>
<td>10.0⋅10⁻³ M</td>
</tr>
</tbody>
</table>

The measurement sequence comprised 20 min. settling time at increasingly more cathodic $E_{\text{on}}$ potentials; OCP, -850 mV, -1000 mV, -1250 mV and -1550 mV vs. CSE, each followed by an EIS measurement using a 10 mV AC perturbation in the frequency range 160MHz–16mHz with 7 measurements per decade. A Gamry Instruments Reference 600 Potentiostat was used for the measurements and the data were analysed using the Echem Analyst software package from Gamry.

Electrical Resistance (ER) probes from MetriCorr with a 1cm² rectangular coating defect with a $l/w$-ratio of 10 have been used to investigate the influence of defect orientation. Unlike the impedance measurements these investigations were long-term experiments conducted in a soil-box environment; a 50L plastic box filled with 50kg of inert quartz sand and wetted (approx. 30L) with the NAS solution specified in Table 1. The probe layout in the soil box can be seen in Figure 3, at an intermediate state of filling with sand.

Two counter electrodes were implemented to separate the experimental DC and AC circuit as described by Goidanich et.al. [5]. During the entire experimental period a $U_{\text{ac}} = 20V$ AC perturbation was applied. To ensure enough cathode activity, the $E_{\text{on}}$ potential was initiated as low as -1250mV (vs. CSE) and kept there for 4 weeks while corrosion and electrical parameters where monitored with ICL-02i dataloggers from MetriCorr. Subsequently $E_{\text{on}}$ was lowered with 100mV with 3 weeks intervals until a potential of -1650mV (vs. CSE) was reached.

**EIS Investigations**

The electrochemical impedance response from the cell has been fitted to an equivalent circuit as shown in Figure 4, including a solution resistance (or spread resistance), $R_s$, connected to a parallel coupled charge transfer resistance, $R_{ct}$, and double layer capacitance represented by a constant phase element, $Q$. A Warburg
diffusion element is placed in series with $R_{ct}$, to accommodate a diffusion signal in some of the measurements.

$$\begin{align*}
Q & \quad \Rightarrow R_s \\
& \quad \rightarrow R_{ct} \quad W
\end{align*}$$

Figure 4: Randles circuit with a Warburg diffusion element.

The impedance response from the elements is given in Table 2, where $j$ is the imaginary unit and $\omega$ is the angular frequency. The real frequency is given by $\omega = 2\pi f$.

<table>
<thead>
<tr>
<th>Equivalent element</th>
<th>Impedance</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>R Resistor</td>
<td>$Z_R = R$</td>
<td>$R$</td>
</tr>
<tr>
<td>Q Constant Phase Element</td>
<td>$Z_Q = \frac{1}{Q(j\omega)^n}$</td>
<td>$Q, n$</td>
</tr>
<tr>
<td>W Warburg Diffusion Element (infinite)</td>
<td>$Z_W = \frac{1}{Y_0\sqrt{j\omega}}$</td>
<td>$Y_0$</td>
</tr>
</tbody>
</table>

Table 2: Equivalent circuit elements and their impedance

The use of a Q-element allowed for a better fitting, and instead the pseudo-capacitive response $C^*$ of the double layer is calculated as (1) for further analysis.

$$C^* = \frac{(R_{ct} \cdot Q)^{\frac{1}{n}}}{R_{ct}} \quad (1)$$

It can be seen that if the value of $n$ equals 1, the constant phase element acts as a real capacitor. Furthermore it can be seen that the Warburg element converges to a ‘short’ for large values of $Y_0$.

Figure 5 shows how impedance data presented in a) a Nyquist Plot representation and b) a Bode Plot representation.

![Graphical presentation of impedance data](image)

Figure 5: Graphical presentation of impedance data: a) Nyquist plot showing a complex plane representation. b) Bode plot showing the frequency dependent impedance and phase response.

In the Nyquist plot, a Randles circuit without the Warburg element will always produce a semi-circle in the complex plane. The constant phase element will yield a slightly suppressed semi-circle dependent on the value of $n$, and if diffusion is
predominant, the data points will align on a 45° angle line or ‘tail’ at low frequencies. The Bode plot gives a better understanding of the frequency dependent impedance response. In terms of AC corrosion, it is interesting to observe the response at 50/60Hz.

The fitted values of $R_s$ have been compared to the model reported by Nielsen et.al. [1], which for the present analysis can be simplified to (2) and (3)

$$R_s = \frac{\rho_{soil}}{2d} \left(1 - \frac{d}{5l_c}\right) + \rho_{pore} \frac{4t}{\pi d^2}$$  \hspace{1cm} (2)

$$R_s = \rho_{soil} \frac{1}{\sqrt{\frac{36}{\pi} \left(\frac{l^2 + w^2}{l}\right)}} \ln \left(\frac{4l}{w} + \frac{l}{w}\right) \left(1 - \frac{w + l}{10l_c}\right) \hspace{1cm} (3)$$

Results

Defect orientation

The corrosion rate measured by the ER-technique for coating defects having different orientations is shown in Figure 6. The data markers indicate the direction of the coating defect, i.e. : sideways vertical (P1), –: sideways horizontal (P2), ▲: upwards (P3) and ▼: downwards (P4). With increasingly negative polarisation the corrosion rate increases, but the effect is found to be highly dependent on the defect orientation. Lower corrosion rates can be seen for P2 and P4, while P1 and P3 show markedly higher corrosion rates, especially at ≥ -1450 mV. The upright facing defect corrodes at extremely high rates after ≥ -1550 mV (in the order of mm/yr) so the y-axis scale has been adjusted with a factor of 5 past 1000 µm/yr.

Figure 6: Weekly average corrosion rates for differently oriented probes, indicated by the data marker, as a function of time and $E_{cor}$ potential (arrows). Notice the change in scale of the y-axis after 1000 µm/year.
This shows in all clarity that coating defects in the same chemical environment and subject to identical AC and DC voltages responds differently to variations in the CP protection level dependent on their orientation. Figure 7a shows how the spread resistance develops with increasingly negative protection potential for the different defects, Figure 7b illustrates the immediate effect of lowering Rs, i.e. the DC current density increases. The same is true for the AC current density. Figure 7c and d illustrates the correlation between the AC and DC current densities, and the corrosion rate, and as expected the corrosion rate increases with the current densities. Interestingly there appears to be a very simple relation between the DC current density and the corrosion rate, corresponding to a straight line in a double-log plot.

\[ v_{corr} = k(-J_{dc})^2 \] (4)

Where \( k \) is a factor that moves the line up and down in the plot. Here, \( k = 1 \). This simple relation is likely too simple for universal application, but it outlines very well the 'alkalisation theory' by Nielsen that states that AC corrosion is highly dependent on the cathode reaction (5) and the following alkalisation at the steel surface, which in combination with an AC perturbation causes the steel to fluctuate in and out of the corrosive region in the Pourbaix diagram.

\[ 2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \] (5)

To understand why the defect orientation is of importance, reaction (5) is important. Hydrogen gas developing at a surface will always drift upwards, whereas the developed hydroxyl-ions will not. In fact, it is speculated whether increasing concentrations of OH\(^-\) will increase the local solution density, causing it to flow downwards.

![Figure 7](image-url)

**Figure 7:**
- a) The spread resistance drops with the protection potential, but the effect varies with defect orientation.
- b) The protection current density increases with lower values of Rs. c) The corrosion rate increases with AC current density. d) The corrosion rate falls on an almost straight line in a double-log plot being a function of the DC current density squared.
Assuming that the OH\(^{-}\) production at any of the defects is initially the same at a given CP overpotential, there will be a flow away from the downwards oriented defect, whereas the upwards oriented defect will accumulate OH\(^{-}\) and thereby dramatically increase the pH and reduce \(R_s\). With respect to the sideways oriented defects, the concentration of OH\(^{-}\) will increase with the flow direction towards the bottom. Therefore, the vertical defect will experience higher pH and lower \(R_s\) locally at the bottom, and AC corrosion rates likewise.

**Defect size**

Fitting of the large amount of impedance data to the Randles circuit model of the electrode/electrolyte interface in Figure 4, yielded values for \(R_s\), \(R_{ct}\), Q (the constant phase element) and W (the Warburg diffusion element). The latter was included to improve the fitting of the model to the data, but in most cases, no diffusion signal was present and the \(Y_0\) value was very high, giving negligible Warburg impedances according to the expression in Table 2. These are not reported in the following. Figure 8a depicts the found \(R_s\) values normalised with respect to the area (multiplied with the area) as a function of the area.

A straight line corresponding to \(R_s = 140\sqrt{A}\) is drawn. This correlation was found by Nielsen using EIS in a previous study similar to the present [6], where defect areas from 0.01cm\(^2\) to 4cm\(^2\) were investigated. A dotted line almost on top of it corresponds to the model in (2) having infinite carrier plate size, \(t = 0\) and \(\rho_{soil} = 3.5 \Omega m\). The stippled line in Figure 8a corresponds to the model in (2), with the actual values for \(l_c\).
inserted, and the factor in front of \( lc \) changed from 5 to 1.3, indicating a stronger influence from the carrier plate shielding than the model from [1] predicts. This illustrates that the coupon design is of great importance when simulating coating defects with coupons, and that the 10 and 100cm\(^2\) coupons in this study should have been designed with a bigger \( lc \) to simulate an actual pipeline defect, for which \( lc \approx \infty \). No significant effect of \( E_{on} \) on \( R_s \) is evident.

Figure 8b shows how the charge transfer resistance decreases with increasingly negative potentials. This is a simple polarisation behaviour since \( R_s + R_{ct} \) is effectively the DC resistance at \( f = 0 \), and the Ohmic relation \( U(V) = R(\Omega cm^2) \cdot J(A/cm^2) \) holds. The decrease in \( R_{ct} \), which is the resistance towards charge carrying surface reactions taking place, corresponds to passing the hydrogen overvoltage and initiation of reaction (5). This is also illustrated in Figure 8d, a potentiostatic polarisation curve from the averaged current density, \( J_{dc} \), measured during the 20 minutes polarisation prior to EIS measurements. The current density increases with decreasing \( A \), as also \( R_{ct} \) decreases with \( A \). This effect is possibly geometrical due to the surface reactions being dependent on diffusion of reacting species from the surrounding electrolyte. A small (point) defect sees diffusion from a semi-sphere, whereas larger defects see a more flat diffusion profile as illustrated in Figure 9. The volume of electrolyte providing reacting species is thus smaller per active area.

Figure 9: Effect of coating size on the current lines and diffusion profile in the surrounding environment.

Figure 8c shows the pseudo-capacitance normalised with respect to the area as a function of \( E_{on} \). The general equation for a plate capacitor is of the form (6), where \( A \) and \( d \) is the area and plate separation respectively and \( \varepsilon \) is the dielectric constant of the medium in between.

\[
C = \varepsilon \frac{A}{d}
\]  

(6)

Having this in mind, the decreasing area normalised capacitance means that either the dielectric constant of the electrochemical double layer is decreasing, i.e. due to a change in the surface chemistry, or the thickness of the double layer is increasing, e.g. by repulsion of otherwise surface active negative ions such as chlorides from the negatively charged surface, or by generation of \( H^+ \)-ions and later \( H_2(g) \) at the surface which can lift of the surface species. A decreasing capacitance causes an increased impedance of the electrochemical double layer at a given frequency according to (7)

\[
Z_C = \frac{1}{\omega C}
\]  

(7)

This means that a still larger fraction of the AC current from a given AC perturbation on a coating defect will go through the charge transfer resistance via chemical reactions in the Randles circuit in Figure 4, when the overpotential becomes increasingly negative.

Figure 10 shows the same parameters, but for varying coating thickness. Again a stippled line has been drawn in Figure 10a, corresponding to the model in (2) with \( \rho_{\text{soil}} = 3.5\Omega m^2 \) and varying coating thickness. The effect of decreasing pore resistivity
is illustrated with an arrow, where the upper line corresponds to $\rho_{\text{soil}} = \rho_{\text{pore}}$. There is a slight trend that the data points follow this trend with increasingly negative overpotential, but it is not significant. The polarisation behaviour for $R_{ct}$ in Figure 10b, for increasingly negative overpotentials, is again evident, and the decreasing $R_{ct}$ for a thinner coating can be explained by having a larger volume of electrolyte providing reactants for the surface reactions than inside a pore, analogous to the explanation given in Figure 9. The potentiostatic polarisation curves in Figure 10d supports this observation. The decrease in the double layer capacitances in Figure 10c is similar to Figure 8c, and no apparent influence by the coating thickness is evident.

Figure 10: Values from the equivalent circuit modelling for varying coating thicknesses. a) $R_s$ normalised to the area as a function of coating defect. b) $R_{ct}$ normalised to the area, as a function of $E_{on}$ potential, comparable to the polarisation behaviour of the electrode. c) Pseudo capacitance, $C^*$, normalised to the area as a function of the $E_{on}$ potential. d) Potentiostatic polarisation curve for the averaged current density measured during the 20 minutes polarisation prior to EIS measurements.

In Figure 11a the correlation between $R_s$ and the $l/w$-ratio can be seen and a simulated curve based on the model in (3) is drawn for $t = 0$ and $\rho_{\text{soil}} = 3.5\,\Omega\,\text{m}$ (top curve). The effect of decreasing the soil resistivity is indicated by the arrow. The fit to the model is satisfactory, and shows that even for a fixed coating defect area, the geometry is important in terms of a lower spread resistance for scratch like defects.
Figure 11: Values from the equivalent circuit modelling for varying l/w-ratios. a) $R_s$ normalised to the area as a function of l/w-ratio. b) $R_{ct}$ normalised to the area, as a function of $E_{on}$ potential, comparable to the polarisation behaviour of the electrode. c) Pseudo capacitance, $C^*$, normalised to the area as a function of the $E_{on}$ potential. d) Potentiostatic polarisation curve for the averaged current density measured during the 20 minutes polarisation prior to EIS measurements.

$R_{ct}$ decreases with increasing l/w-ratio, especially at large overpotentials, as can be seen in Figure 11. Again the explanation is geometrical and analogous to the one given in Figure 9. Diffusion to a long scratch occurs from a larger volume of the electrolyte, than for a point defect having the same active area. The polarisation behaviour in Figure 11d shows an increased $J_{dc}$ with higher l/w-ratios accordingly. The trend for the area normalised capacitance is similar to the defect size and coating thickness, i.e. a decreasing $C^*$ with negative overpotential, seemingly unaffected by the l/w-ratio.

Discussion and Conclusion

The investigations carried out in this study comprises two parallel investigations:

- Long-term measurements of the corrosion rate for coupons having different orientations in a soil-box setup under AC and DC voltage control, measured by the ER-technique.
- Short-term investigations of the electrochemical equivalent circuit describing the electrode/electrolyte interface of different defect geometries in a stagnant aqueous solution under DC control, using the EIS-technique.

One might argue that the latter does not provide information about AC corrosion properties, since no AC perturbation was applied, apart from a small measurement signal. However, while no direct information about AC corrosion rates are obtained, an equivalent circuit for the electrochemical double layer has been determined, and a better understanding of the response of various geometries to AC and DC perturbation is achieved. ER measurements have confirmed well known correlations
between key parameters such as the spread resistance, $R_s$, the AC and DC current densities, $J_{AC}$ and $J_{DC}$, and knowing the electrochemical equivalent circuit for an interface allows for a qualified estimation of the AC corrosion performance of this interface.

It has been established that $R_s$ is decreasing for higher levels of cathodic protection in long-term experiments (Figure 7a), and that this is highly influenced by the defect orientation. This suggests that cathode reactions can locally change the solution resistivity, and that the formed species are influenced by orientation, i.e. gravity or a directionally dependent diffusion. Upwards facing defects develops the lowest resistivity suggesting a developed species heavier than water. It is speculated whether OH$^-$-ions are the main contributor, but further experiments are needed to confirm that OH$^-$ does in fact drift downwards, and that no other species are more influential.

With decreasing $R_s$, AC and DC current densities increases, and ER measurements show increasing corrosion rates correspondingly. In fact the DC current density appears to be the most influential, showing a very strong correlation to the corrosion rate given in (4).

Investigations of the coating defect geometries have revealed that both the spread and the charge transfer resistance, $R_s$ and $R_{ct}$, are dependent on defect size, coating thickness and $l/w$-ratio. Knowing that these factors have a great influence on the AC corrosion properties, it is important to be aware of this when using coupons for AC corrosion assessments. Also the coupon design, i.e. carrier plate dimensions, have been found to have an influence, and a revision of known models [1] has been made, based on experimental data.

The findings suggests that smaller, scratch-like defects with a very thin adjacent coating yields the smallest $R_s$ and $R_{ct}$ values, and would therefore be more vulnerable to AC corrosion.

The pseudo-capacitance of the electrochemical double layer has not been found to be markedly influenced by coating defect geometry, but to a larger degree by the cathodic protection overpotential. This yields a higher impedance of the electrochemical double layer at any given frequency with increasingly negative overpotentials, and thus a larger part of the AC current density from an AC perturbation will go through charge carrying reactions. This could be iron dissolution during the anodic half-cycle of the AC perturbation, and the change in AC corrosion rate found using the ER-technique with increasing CP overpotentials could perhaps be attributed to this effect.
Bibliography


4.2 [II] Corrosion ’17

This paper investigates the effect of a varied protection potential on AC corrosion in a Ca and Mg containing soil susceptible to scale formation on the steel surface. A build-up and break-down mechanism of the calcareous deposits is observed. ER probes are used to quantify the corrosion rates and deposits are characterised by SEM and XRD. The results indicate a high pH environment at the corroding steel surface.
Effect of Chemical Environment and pH on AC Corrosion of Cathodically Protected Structures

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ABSTRACT

AC corrosion of structures under cathodic protection (CP) is a major concern for pipelines in case of even minor AC perturbations. There are indications that the specific chemical environment has a large influence on the AC mitigation current density criteria outlined in EN 15280:2013 [1]. This work investigates the effect of soil constituents, the earth alkali elements Ca and Mg, believed to have a large influence on the precipitation of hydroxides and carbonates in front of a coating damage. The formation of different polymorphous calcium carbonates, depending on the cathodic potential are observed as well as calcium hydroxides at high cathodic protection levels. This indicates a highly alkaline (pH > 11) environment locally. Corrosion rates at different cathodic potentials are measured using electrical resistance (ER) probes and a chemical and phase analysis of the calcareous deposits and corrosion products is made using scanning electron microscopy and energy dispersive x-ray spectroscopy (SEM/EDS) and x-ray diffraction (XRD). The findings suggest an AC corrosion mechanism highly dependent on the build-up and break-down of calcareous deposits at high CP, which is clearly reflected in variations in the spread resistance.

Key words: AC corrosion, SEM, EDS, XRD, Cathodic protection, Calcareous deposits,

INTRODUCTION

Perhaps the key parameter in AC corrosion of pipelines is the spread resistance, $R_S$ (Ωm²), of a coating defect. This relates the protection potential, $E_{pct}$, and induced AC voltage, $U_{AC}$, on a pipeline to the AC and DC current densities, $J_{AC}$ and $J_{DC}$, known to have a large influence on the corrosion rate [2]. For the
DC potential a significant IR voltage drop needs to be considered to obtain the IR free or true potential, \( E_{\text{IR-free}} \), of the electrode. The relations are given in equations (1-3)

\[
E_{\text{IR-free}} = E_{\text{on}} - \text{IR} = E_{\text{on}} - J_{\text{DC}} R_S \tag{1}
\]

\[
J_{\text{DC}} = \frac{E_{\text{IR-free}} - E_{\text{on}}}{R_S} \tag{2}
\]

\[
I_{\text{AC}} = \frac{U_{\text{AC}}}{R_S} \tag{3}
\]

Equation (3) may be overly simplified, since it neglects the capacitive effects of the electrochemical double layer and the charge transfer resistance. For the purpose of this explanation it is sufficient however, since at 50-60 Hz the impedance of the double layer capacitance is low, and effectively the charge transfer resistance is bypassed in a traditional Randles circuit. A more detailed explanation can be found in literature [3] [4].

EN 15280:2013 [1] current density limit values are \( J_{\text{AC}} = 30 \text{ A/m}^2 \) and \( J_{\text{DC}} = 1 \text{ A/m}^2 \) on a 1 cm\(^2\) probe, above which AC corrosion will occur. Alternatively, the AC/DC current density ratio can be kept at \( J_{\text{AC}}/J_{\text{DC}} < 3 \) to avoid corrosion [1].

\( R_S \) is both dependent on the geometry of a coating defect and the soil resistivity, \( \rho \). Equation (4) represents the simplest relation valid for a circular coating defect with diameter, \( d \), and no coating thickness, i.e. no pore geometry in front of the defect. More detailed models for the geometrical dependence are available in literature [5].

\[
R_S = \frac{\rho}{2d} A \tag{4}
\]

Low resistivity soils yields a low \( R_S \) due to the amount of dissolved species in the electrolyte. Furthermore, under cathodic protection, the cathode reaction creates an increasingly alkaline environment, either by hydrogen evolution (5) or oxygen reduction (6) in acidic or neutral to alkaline environments respectively, or by dissociation of water under anaerobic conditions (7).

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) \tag{5}
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \tag{6}
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- \tag{7}
\]

The produced hydroxyl-ions lower the resistivity, but the increased pH also alters the solubility of different species in soil. In particular the alkaline (mostly K and Na) and earth alkaline elements (mostly Ca and Mg) can precipitate as carbonates or hydroxides in high pH environments, but the earth alkaline elements form species of very low solubility [6]. Calcareous deposits will increase the spread resistance and limit the AC corrosion [7], but a thorough understanding of the interaction between different chemical constituents is lacking.

**EXPERIMENTAL PROCEDURE**

500 \( \mu \text{m} \) ER probes with a 1 cm\(^2\) exposed area and a length/width ratio of 10 have been used to measure the corrosion rate of carbon steel under cathodic protection and a 50 Hz AC perturbation of 10 V. This level was chosen below the maximal AC voltage on pipelines according to EN 15280:2013.
which is 15 V. The cathodic protection level was varied from $E_{on} = -0.85$ V to -2 V vs. a Cu/CuSO$_4$ (CSE) reference electrode according to Table 1, corresponding to low to high CP.

| Table 1: AC and DC voltages on each experiment |
|-----------------|-----------------|----------------|----------------|----------------|----------------|----------------|
| $U_{ac}$      | 10 V            | 10 V            | 10 V            | 10 V            | 10 V            | 10 V            |
| $E_{on}$ (CSE) | -0.85 V         | -0.95 V         | -1.10 V         | -1.25 V         | -1.50 V         | -1.75 V         | -2.00 V         |
| “CP level”    | Low             | Low             | Med.            | Med.            | High            | High            | High            |

The experimental setup is outlined in Figure 1 with a DC and AC circuit separated by a 600 µF capacitor and a 3 H inductance, eliminating any DC in the AC circuit and reducing the AC voltage in the DC circuit to less than 5%, measured on the setup. The setup is a modified version of that of Goidanich et.al. [8]. Each of the counter electrodes (CE) is a 200 cm$^2$ MMO coated titanium mesh and the potential is measured against a CSE routinely used for cathodic protection of buried pipelines. ER probe data is collected using an interference corrosion logger (ICL) system from MetriCorr$^\dagger$, measuring the probe element thickness, the DC on-potential ($E_{on}$), the IR corrected off-potential ($E_{IR-free}$), the DC current density ($J_{DC}$), the AC voltage ($U_{AC}$), the AC current density ($J_{AC}$) and the spread resistance ($R_s$) on the working electrode (WE). The measuring frequency is 30 min. The soil box is a 50 L plastic box filled with 50 kg of cleaned 00-grade quartz sand (0.4 – 0.8 mm) and wetted with approximately 16 L of electrolyte according to Table 2.

![Figure 1: Layout of experimental setup with an AC and DC circuit separated by an inductor and capacitor respectively. The working electrode is an ER probe connected to an ICL data logger](image)

| Table 2: Ca and Mg containing electrolyte investigated in the study |
|-----------------|-----------------|
| Species/Parameter |     |
| NaHCO3         | $2.5 \times 10^{-3}$ M |
| MgSO4-7H2O     | $2.5 \times 10^{-3}$ M |
| CaSO4-2H2O     | $2.5 \times 10^{-3}$ M |
| CaCl2-2H2O     | $5 \times 10^{-3}$ M  |
| Resistivity (pure solution) | 5.5 Ωm |
| Resistivity (solution + sand) | 18.5 Ωm |
| pH (initial)   | 7.6             |

After the experimental period, the probes were carefully excavated by draining the soil box for electrolyte and removing the surrounding sand. Electrolyte samples of ~5 ml were taken from the vicinity of the probe and in “remote earth” for all experiments for chemical analysis and pH measurement. pH measurements were made using a digital field pH-meter. After a visual inspection of

$^\dagger$ Tradename

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the probes, material present on the probe surface (corrosion products, sand particles, calcareous deposits) were removed and saved for analysis in SEM/EDS and XRD. XRD was measured using CuKα radiation from 10-70 2θ angles.

RESULTS

Visual Inspection

The ER probes were excavated after 35 days of testing. The appearance of the probes can be seen in Figure 2. It is noticed that the low CP probes (Eon = (-0.85 V, -0.95 V) vs. CSE) are covered with a black corrosion product with dispersed sand particles. The medium CP (Eon = (-1.10 V, -1.25 V) vs. CSE) appeared largely blank, the -1.25 V probe with a tendency towards miscolouring. Finally the high CP (Eon = (-1.50 V, -1.75 V, -2.00 V) vs. CSE) showed signs of red/brown corrosion and were covered with a dense layer of calcareous deposits. Based on appearance the black corrosion product is probably magnetite, Fe₃O₄, or goethite, FeOOH, whereas the red/brown corrosion product might be hematite, Fe₂O₃.

![Figure 2: Appearance of the probes immediately after excavation, after 35 days of testing. Black corrosion product with dispersed sand particles (a,b), blank metal (c,d) and red/brown corrosion and solid calcareous/sand deposits on the probe surface (e, f and g).](image)

It may also be noticed that the probes surface in Figure 2 c) to g) is fringed with a bright rim of increasing size at higher cathodic potentials. This is attributed to the increasing extent of the local high pH front, causing precipitation of carbonates or hydroxides with a white appearance. Upon excavation, this precipitation was only stable for the medium CP probes as can be seen in Figure 3, in good agreement with the white rim. This structure was removed, and was found to be a shell of a few mm thickness with non-precipitated sand inside.

![Figure 3: Solid precipitation in front of the probe surface. This structure was only stable on the medium CP probes.](image)
The upwards “cone-shape” of the precipitation is believed to be caused by an upwards drift of hydrogen gas from reactions (5) or (7) disturbing any precipitation in the upwards direction. The precipitations remained solid upon drying, but were brittle and easily broken.

**ER probe data**

ER measurements of the corrosion and other parameters are shown in Figure 4. Corrosion is clearly indicated by changes in the thickness in Figure 4a. The corrosion mechanism for the probes is however completely different, which can be realized by observing the other parameters; $R_s$, $J_{DC}$ and $J_{AC}$.

**Low CP (AC Corrosion)**

For the -0.85 V and -0.95 V (CSE) probes, an initial decrease in thickness is observed, namely for the -0.85 V probe. This is attributed to initial anodic currents as indicated in Figure 4c, i.e. insufficient cathodic protection. The explanation for this is likely the ‘faradaic rectification’ effect described in detail in literature for AC corrosion [9] [10], causing a lowering of the open circuit potential (OCP) to below the cathodic protection level under influence of AC currents. The corrosion process causes a layer of corrosion products to form on the probe surface which increases the spread resistance almost linearly (first week). Consequently the AC current density decreases, and the faradaic rectification effect decreases accordingly. The OCP increases to above the CP levels and corrosion stops. After approximately 3 weeks the spread resistance starts to decrease again for both probes. Possibly, the cathodic overpotential (i.e. the difference between the OCP and the set potential) becomes large enough to reduce or destabilize the corrosion product. Consequently the AC current density increases again. Given the total duration of these experiments, it is unclear whether corrosion will initiate again, but with respect to the above chain of reasoning, it cannot be precluded.

**Medium CP (No Corrosion)**

No corrosion is recorded for the medium CP probes, in good agreement with the appearance of the probes in Figure 2. The $R_s$, $J_{DC}$ and $J_{AC}$ values are stable throughout the period. This is an example of effective CP protection, even under the influence of an AC voltage perturbation.

**High CP (AC Corrosion)**

The initial DC current density is very high for the high CP probes, increasing with cathodic potential. This high cathodic current is directly linked to an alkalization of the solution at the surface via reactions (6) and (7), which firstly decreases the spread resistance to below the level of the low and medium CP probes due to the high amount of conductive hydroxyl ions in the solution. A high initial AC current density is a direct effect of this. The corrosion rate during the first few days appears to be proportional to the CP level, i.e. the DC current density and following alkalization by reactions (6) and (7). Due to the strong alkalization of the solution, dense calcareous deposits will form on the probe surface, dramatically increasing the spread resistance and thus reducing the AC and DC current densities. Corrosion decreases, but only as long as the calcareous deposit is stable and fully covering the surface. Arrows A and B in Figure 4 indicate incidents (not all) where the spread resistance suddenly decreases, causing $J_{DC}$ and $J_{AC}$ to increase and AC corrosion to take place. A indicates an event for the -1.5 V (CSE) probe, and B; the -2.0 V (CSE) probe. The breakdown mechanism is unknown, but given the sudden reduction in $R_s$, a slow dissolution of this film is unlikely and perhaps a brittle fracture or a ‘flake of’ mechanism due to hydrogen evolution underneath it is plausible. The cathodic reactions on the re-exposed probe surface will restart the alkalization and precipitation of calcareous deposits and with time (days) the corrosion stops again. Relying on calcareous deposits as a corrosion protection mechanism does not appear to be safe however. Especially the -1.5 V (CSE) probe shows a continuous pattern of breakdown and rebuilding of the deposits, i.e. a saw-teeth shape of the $R_s$ curve. Each cycle is associated with corrosion causing a staircase shape of the thickness curve. The CP
potential appears to have an effect on the period for this process, but given the limited duration of the present experiments, this will not be elaborated on here.

Figure 4: Thickness, $R_S$, $J_{DC}$ and $J_{AC}$ daily average values for the test period of 35 days. Corrosion and spread resistance is closely linked, especially for high CP probes. Points A and B are indicating breakdown of a shielding calcareous deposit.

Another important parameter, the IR-drop evolution during the experiment, is presented in Figure 5. Each point represents the daily average value, and the horizontal lines represent the overall average. It can be seen that in spite of large variations in currents and spread resistances for some of the experiments, the IR-drop remains markedly constant. This is because they are inversely proportional, i.e. when the resistance drops, the current increases and vice versa. The level of the IR-drop is to a
much higher degree a function of the CP potential. Essentially no IR-drop was recorded for the low CP experiments, due to the very low currents recorded on these.

![Graph showing IR-drop values recorded during the experiment. In spite of large variations in J_{AC}, J_{DC} and R_S, the IR-drop can be seen to be markedly constant. The horizontal line is the overall average.](image)

**Figure 5: IR-drop values recorded during the experiment. In spite of large variations in J_{AC}, J_{DC} and R_S, the IR-drop can be seen to be markedly constant. The horizontal line is the overall average.**

**Protection Criteria**

Visualization of the current density threshold values for AC corrosion, J_{DC} = 1 A/m², J_{AC} = 30 A/m² and J_{AC}/J_{DC} = 3, as outlined in EN 15280:2013 Annex E, is done in Figure 6 [1]. Coherent J_{AC} and J_{DC} ER-data is plotted with the marker color and size according to calculated daily corrosion rates during the five-week experimental period. Figure 6a shows that corrosion rates in the safe region are generally low. Some corrosion is recorded in the low CP (-0.85 V and -0.95 V) data due to insufficient CP, but it should be noted that the high initial corrosion rates caused by anodic (positive) DC currents are not visualized here, due to the log-scale showing only negative DC currents. The medium CP points (-1.1 V and -1.25 V) are lying in the safe and unsafe region respectively. Since no corrosion is occurring on either, this implies that the threshold values might be too conservative in the specific environment. The high CP data (-1.5 V to -2.0 V) behaved quite interestingly: initially the current densities where high, and corrosion rates likewise. But as R_S increases with time and the current densities diminish, the points move along straight lines in the diagram. Figure 6b shows a close-up of this movement indicated by arrows.

The stippled lines in the diagram have been drawn based on the AC current relations in (3), from which equation (8) can be obtained by multiplying with J_{DC}/J_{DC} and substituting J_{DC}R_S by the average IR-drop in Figure 5, which is the area independent equivalent.

\[
J_{AC} = \frac{U_{AC}}{IR} J_{DC}
\]  

(8)

Since the IR-drop for the low CP experiments is essentially zero, equation (8) breaks down here, but for the medium and high CP experiments, all data points show satisfactory agreement with the lines drawn for equation (8). It becomes clear that changes in the alternating voltage will move the data points vertically as shown in the diagram, and changes in the IR-drop (effectively E_on) will move the data points horizontally. When R_S increases, e.g. due to a build-up of calcareous deposits, the data points move downwards along the line. When R_S decreases, the opposite is observed. Especially for the -1.5 V (CSE) experiment, where the R_S value varies a lot, the data points move up and down the line and the corrosion rate is clearly associated with high current densities. The spread resistance of the -1.75 V and -2.0 V (CSE) experiments eventually becomes large enough to move the data points out of the unsafe region and stop AC corrosion, but as it can be observed for the -2.0 V (CSE) experiments, a breakdown of the resistive calcareous deposit will cause the data points to move back into the unsafe region, where corrosion is immediately observed.

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Figure 6: a) Visualization of data according to EN 15280:2013 Annex E. Each data point represents a daily corrosion rate expressed as size and color of the point. It shows that the build-up of calcareous deposits moves the $J_{DC}/J_{AC}$ point along straight lines given by the AC voltage and the IR-drop for the respective protection levels. b) Close up of medium and high CP data with each daily point connected by a solid line. Arrows indicate the time-wise evolution.

pH

Figure 7 shows the measured pH profile as a function of $E_{on}$ potential. The pH measurements are linked with a certain amount of uncertainty, due to difficulties in extracting the electrolyte exactly at the probe surface. Furthermore they represent an average value of the extracted volume, and the pH at the very surface is likely far higher. Comparing with the background pH of “remote earth” in the soil box, alkalization at the probe can be seen to be a function of the $E_{on}$ potential as expected. Some acidification is observed for the low CP levels, possibly owing to reversing the cathode reactions during anodic currents. It is however estimated, that the pH very close to the probe surface for the low CP experiments was elevated, due to cathodic currents measured during the last weeks of the experiment.

Figure 7: pH profile as a function of $E_{on}$ potential, indicating alkaline environment at high CP levels. The remote earth “background” is included, showing a neutral environment.
SEM/EDS

SEM images of the probe surface material are shown in Figure 8. Since the medium CP probes appeared blank, material from the solid precipitation in Figure 3 was analyzed instead. In all images, sand particles (quartz) were clearly distinguishable. EDS analysis confirms an atomic O/Si-ratio of 2, equivalent to SiO₂. Table 3 presents a list of minerals observed in the SEM images, along with an identifier used in Figure 8.

Table 3: List of minerals possibly observed in the SEM images. Notice polymorphous calcium carbonates.

<table>
<thead>
<tr>
<th>Name</th>
<th>Identifier</th>
<th>Quartz</th>
<th>Calcite</th>
<th>Aragonite</th>
<th>Vaterite</th>
<th>Portlandite</th>
<th>Gypsum</th>
<th>Brucite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>CaCO₃</td>
<td>CaCO₃</td>
<td>CaCO₃</td>
<td>Ca(OH)₂</td>
<td>CaSO₄·2H₂O</td>
<td>Mg(OH)₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All minerals are identified based on EDS readings and their visual appearance, i.e. crystal structure and size.

- Low CP (a-b): Calcite minerals (5-50 µm) have precipitated on the surface of the sand particles, identified by triangular/rhombic features. Iron containing powdery products covering the surface were identified as corrosion products.

- Medium CP (c-d): Spherulitic crystals containing Ca and O (50-200 µm) are observed, possibly calcium carbonates, e.g. calcite. However the spherulitic growth would be more common for gypsum crystals, which was an original constituent in the electrolyte. Atomic O/Ca-ratios from EDS were ranging from 5-2 and are thus inconclusive, but no Sulphur was detected in the crystals. The sand particles were occasionally covered by a layer of triangular crystals of a few microns’ size, most possibly brucite, in perfect accordance with an atomic O/Mg-ratio of 2 (d). This might have worked as the binder between sand grains forming the solid precipitation shown in Figure 3.

- High CP (e-g): Minerals with distinguishable hexagonal features (50-300 µm) have precipitated as a solid binder between the sand particles. EDS measurements suggest a calcium carbonate, possibly aragonite or vaterite. Though aragonite is orthorhombic in crystal structure, pseudohexagonal features can be formed by trillings of these crystals. Both minerals are metastable CaCO₃ polymorphs, indicating a higher surface energy upon formation. Investigating calcite vs. aragonite formation in caves, Murray [11] found that a temperature increase favors the formation of aragonite, but that the pH does not appear to have an effect. This could be an indication of elevated temperatures at the high CP probe surface due to Joule heating. Mg which is present in the electrolyte is also known as an aragonite stabilizer. Iron rich material was observed for -1.5 and -2.0 V (CSE) and is identified as corrosion products. This is in very good accordance with the corrosion rate measurements.

Studies of precipitation of calcareous deposits formed during cathodic protection in seawater supports the findings of calcite, aragonite and vaterite as possible calcium carbonate formations, also indicating a strong dependency on the polarization level [12].
Figure 8: SEM images of the material on the probe surfaces. (a, b) Low CP. (c, d) Medium CP. (e-g) High CP. Left: low magnification with visible sand particles (Q). Right: higher magnification of white box area showing mineral formations. Magnifications are kept constant except for (d). The $E_{\text{on}}$ potential is indicated. Arrows and letters indicate possible mineral formations according to Table 3. *) EDS Readings of Fe found in these images.

XRD

X-ray diffraction of selected surface material (same as investigated in SEM) was done for all CP levels represented by -0.95 V (low), -1.1 V (medium), -1.5 V and -2.0 V vs. CSE (high). The recorded spectra can be seen in Figure 9. None of the allegedly observed minerals in the SEM images in Figure 8 could be confirmed, probably due to the very small amounts. Instead portlandite, Ca(OH)$_2$, was detected in the surface material of the high CP probes. Portlandite minerals are hexagonal in crystal structure, and it can be debated whether the minerals observed in the SEM images are in fact portlandite and not a...
calcium carbonate. However, portlandite are typical plate-like structures, whereas the observed crystals are clearly elongated. Since the SEM images are not representative for the whole precipitated material on the probe surface, but the XRD measurements are, it is possible that portlandite existed closer to the probe surface, and was not discovered in SEM.

Figure 9: XRD spectra for four of the surface materials showing characteristic peaks for quartz (sand particles) and Portlandite (Ca(OH)$_2$) for high CP. No peaks for the A, C, G, V or B minerals allegedly observed in SEM images were detected, possibly due to too little material. Intervals indicate were typical characteristic peaks for the various minerals should have been.

In Figure 10, calculated Pourbaix diagrams for Ca and Mg are shown. The diagrams clearly show that, depending on the Ca-concentration, the occurrence of CaCO$_3$ minerals is a tracer for elevated pH, and portlandite suggests heavy alkalization above pH = 11 depending on the Ca concentration.

Figure 10: Calculated Pourbaix diagrams at 25°C and 1 bar pressure; a) for varying Ca concentrations (log values) with C [10$^{-4}$ mol/l] and S [10$^{-2}$ mol/l] present. b) for varying Mg concentrations with C [10$^{-4}$ mol/l] present. They show thermodynamically stable phases at various potentials and pH values.

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In the diagrams CaH$_2$ and MgH$_2$ were chosen as the most stable species at low potentials according to Pourbaix’s equilibria calculations [13]. The Pourbaix diagrams suggest that only a narrow pH regime around 9 allows for co-existing gypsum and brucite. Hence it is perhaps more likely that the Ca-containing spherulites in Figure 8c and d are calcite. Depending on the local Mg concentration, the existence of brucite indicates a minimum pH value where the solid precipitation was formed, i.e. alkalization is also evident for the medium CP coupons. The importance of being able to identify specific mineral formations in connection with AC corrosion becomes obvious in discussions about alkalization at the electrode under CP conditions. The pH value is difficult to measure in situ, and typically requires a certain measurable volume. As long as the chemical constituents are present, the carbonates and hydroxides will precipitate according to the Pourbaix diagrams as a function of the pH. Provided that the precipitations can subsequently be recovered, these will give a very detailed description of the pH environment and its extension in the electrolyte as demonstrated in this paper. The CP protection levels are found to be a key determining factor for mineral formation and thus the pH level, which is ultimately linked to the AC corrosion rate at high CP.

CONCLUSIONS

Investigations of AC corrosion rates in a simulated soil solution containing Ca and Mg has revealed a strong influence of the cathodic protection level, and implies that AC corrosion can be regarded as two different characteristic phenomena in good agreement with literature [2]:

- Low CP AC corrosion caused by the faradaic rectification effect, reducing the open circuit potential below the set protection level and causing anodic currents. This is recognized as “under protection”.
- High CP AC corrosion caused by high cathodic and anodic current densities as described in the EN 15280:2013 standard [1], and recognized as “over protection”. This is associated with strong alkalization of the electrolyte and consequently dense calcareous deposits are observed for these conditions.

At intermediate cathodic protection levels, no corrosion was observed. The results are not entirely in line with the DC current density threshold value of 1 A/m$^2$ [1], suggesting that this might be too conservative for the specific chemical environment.

The spread resistance, $R_s$, of the probe is identified as a key parameter, controlling the current densities, and this is highly influenced by the formation of calcareous deposits or corrosion products. An apparently cyclic increase and decrease of $R_s$ associated with notable changes in corrosion rate for high CP experiments, is attributed to build-up and break-down of the calcareous deposits by a brittle fracture or flake-off mechanism. This non-linear corrosion rate mechanism has so far been an unrecognized feature of AC corrosion in Ca and Mg containing environments, and could only be captured by the use of the ER technique for in-situ corrosion rate measurements.

The confirmed observation of Ca(OH)$_2$ in high CP condition suggests local pH values >11 which is impossible to measure by normal pH-meter measurements, since the local volume might just extend millimeters or less from the electrode surface. Such high pH values would allow for iron dissolution as HFeO$_2$ in the event of a re-exposure of the probe surface upon breakdown of the calcareous deposits. Characterization of different CaCO$_3$ polymorphs at different CP levels, i.e. calcite at low CP and aragonite or vaterite at high CP, suggests increasing surface energy and increased temperature at the probes surface caused by joule heating from the passing AC current.

ACKNOWLEDGEMENTS

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REFERENCES


4.3 [III] CeoCor ’17

This paper presents a literature review of the influence of pH on AC corrosion, as well as two experiments that allows for monitoring the pH in-situ. A visualisation experiment that illustrates the enhancing effect of AC on the cathodic current, and thus pH development, and an experiment that compares different CP and AC settings to the evolving pH which is monitored by a pH probe. ER probes are used for measurement of corrosion rate.
Monitoring of the pH Evolution at a Cathodically Protected Steel Surface Subject to an AC Voltage Perturbation

by A. Junker and L. V. Nielsen (MetriCorr, Roedovre, Denmark)
Abstract
Assessing AC corrosion with respect to an E-pH or Pourbaix diagram is widely done in literature. No common agreement on the influence of pH on the AC corrosion rate exists however. This paper presents a literature review of the effect of pH on AC corrosion, as well as an in situ investigation of pH and potential of a steel surface at different cathodic protection levels and different AC potential levels. The results are directly correlated to AC corrosion rates measured by the ER technique and discussed in relation to the current EN15280:2013 standard. Furthermore, the effect of faradaic rectification of AC currents on the pH evolution at an electrode surface is illustrated by a novel visualisation experiment.

Introduction
The mechanism of AC corrosion of cathodically protected structures is heavily debated. One factor that remains subject to debate is the effect of pH. The general understanding of cathodic protection involves the formation of a passive layer on steel due to elevated pH or bringing the steel to the immune region in the Pourbaix diagram (Figure 1) by lowering the potential [1][2]. In either case, under cathodic protection, the cathode reaction creates alkalinity, either by hydrogen evolution (1) or oxygen reduction (2) in acidic or neutral to alkaline environments respectively, or by dissociation of water under anaerobic conditions (3).

\[
\begin{align*}
2\text{H}^+ + 2e^- &\rightarrow \text{H}_2(g) \quad (1) \\
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- &\rightarrow 4\text{OH}^- \quad (2) \\
2\text{H}_2\text{O} + 2e^- &\rightarrow \text{H}_2(g) + 2\text{OH}^- \quad (3)
\end{align*}
\]

With respect to AC corrosion the typical scenario is cathodic protection of buried pipelines. Here, the natural oxygen content and acidity in the soil will be depleted and with time reaction (3) will be the governing reaction [1]. The produced hydroxyl-ions increase the ionic conductivity of the soil, which leads to a reduction of the spread resistance and consequently increased AC and DC current densities at static AC and DC voltages [3][4][5][6]. This is an autocatalytic process since increased DC current densities enhances the cathode reactions and hence the ionic conductivity and alkalisation etc. Adversely, an increased pH also alters the solubility of different species in soil. In particular the earth alkaline elements (mostly Ca and Mg) can precipitate as carbonates or hydroxides in high pH environments as species of very low solubility [7]. Calcareous deposits on a steel surface will increase the spread resistance and limit AC corrosion [8], however the effect of passing AC currents and hydrogen evolution from reaction (3) may be detrimental to the mechanical stability of these deposits, resulting in a dynamic AC corrosion mechanism with continuous build-up and break-down of the formed deposit [4]. The presence of alkaline and earth alkaline ions in solution may also act as an inhibitor for pH increase, since these will consume formed OH\(^-\) upon formation of solid hydroxides [9]. The pH buffering capabilities of the carbonate/bicarbonate system naturally occurring in many soils may also hinder the immediate pH increase until the bicarbonate is converted to carbonate [10].

In Figure 1 the Pourbaix diagram for steel is shown. It is calculated using the HSC E-pH Chemistry software at 25°C and 1 bar pressure and takes into account the effect of concentration of different Fe species in solution from \(10^{-6} – 10^{-4}\) mol/l. The present diagram favours the formation of the iron oxides Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\). It can be seen that an elevated pH contributes to passivating the steel within the stability region of water between the stippled lines, while a too high pH may cause the steel to enter the high pH HFeO\(_2\) corrosive region. The pH limits for entering this region are generally believed to be very high at pH > 13-14 [2],
but as the calculated example in Figure 1 shows, this limit is highly dependent on the concentration of iron in solution. This is often neglected in most literature on high pH corrosion. The strong dependency on the concentration of dissolved iron species must also be considered in the case of AC corrosion, where iron dissolution and the resulting increase in concentration may cause this region to shrink, unless the dissolved iron is immediately consumed by reactions with species in the electrolyte forming e.g. corrosion products.

**Figure 1:** Calculated Pourbaix diagram for 25°C and 1 bar pressure. The corrosive regions are highly dependent on the concentration of Fe in solution indicated by the log([Fe]) values.

Nielsen et.al. presented an alkalisation theory associated with an incubation period before the pH would reach a critical level and AC corrosion rates would dramatically increase. The authors linked this effect to reaching the high pH corrosion region in the Pourbaix diagram. The incubation period is a function of the OH⁻ neutralising capacity of different soils, and depending on the soil, this incubation period may be several weeks [11].

Using a retractable pH electrode, Brenna et.al. measured a pH profile in the proximity of a carbon steel surface under cathodic protection at different DC current densities (0.5-7A/m²) [12]. This is shown in Figure 2a. They found that the major pH increase occurs within the first 2 mm from the electrode surface. With higher cathodic current, the higher the pH maxima at the electrode (pH = 12-13.5) and the further the high pH region extends into the electrolyte. The effect of time is however unclear from the study. The suggested corrosion mechanism by Brenna et.al. [13] is an electromechanical breakdown mechanism of the passive film on cathodically protected steel caused by high alternating voltages, followed by an aggressive increase of pH in the formed cracks where chemical corrosion as HFeO₂⁻ is possible according to the Pourbaix diagram.

A similar strong dependence on the distance from the steel surface on the pH is reported by Gummow et.al. [14]. They report a pH increase within the first few mm of several pH values, but also take into account the pH of the bulk solution which has a high influence of the maximum obtainable pH value at the steel surface at a fixed DC current density of 0.38A/m².
Based on the findings by Thompson and Barlo [15] and Büchler and Schöneich [16] shown in Figure 2b, Büchler and Joos [3] developed an expression for the pH as a function of the DC current density shown in (4).

$$\text{pH} = \text{pH}_0 + p \cdot \log(J_{DC})$$  \hspace{1cm} (4)

They found optimized parameters for $\text{pH}_0 = 12.4$ and $p = 0.5$ and developed an empirical model that makes it possible to determine the influence of pH on the local soil resistivity and spread resistance. Surely factors such as the soils’ OH$^-$ neutralising capacity, local diffusion coefficients for the reacting species in (3) and possible convection of the solution etc. affects the developing pH and complicates this simple empirical regression, but it offers a nice understanding of the direct relationship between the current density, i.e. the amount of electrons participating in cathode reaction (3) and the amount of OH$^-$ ions being produced at the same surface, refer the general equation for pH as a function of [OH$^-$] given in (4).

$$\text{pH} = 14 + \log([\text{OH}^-])$$  \hspace{1cm} (4)

With the pH being a relatively simple function of the applied DC current density, controlling the pH should be a relatively straightforward procedure. However, the polarisation behaviour of a steel is heavily influenced by the AC current density, and the obtained DC current densities can be enhanced by orders of magnitude due to faradaic rectification of the AC current. Faradaic rectification is mathematically well described by several authors [17] [18] [19] [20] [21], and documented effects of this phenomenon are reported by several authors whether it is described as a ‘depolarisation effect’, an ‘increased exchange current effect’ or as faradaic rectification [5] [22] [23] [24] [25]. In conclusion; high DC current densities and the following alkalisation may be difficult to avoid in the special case of AC interference and AC corrosion.
In an attempt to focus the investigation on the influence of pH on AC corrosion, Tang and Du et al. designed an experiment with fixed pH solutions at pH = 6.4, 10, 11, 12 and 13, as an alternative to cathodic protection [26]. They then subjected carbon steel samples to various AC current densities (0-300 A/m²) and found that corrosion rate measured by weight-loss was proportional to the AC current density, but inversely proportional to the pH, which they attributed to passivation of the steel at high pH. This investigation however, fails to take into account that 1) pH = 13 may in fact be too low to enter the high pH corrosion region in the Pourbaix diagram. 2) The polarisation of the steel caused by cathodic protection puts the steel in a whole different place in the Pourbaix diagram. 3) The present experiment is static in terms of pH and AC current density, whereas the cathode reaction is known to contribute to the evolution of both the pH and the spread resistance, positive or negative depending on the chemical environment, and thus the AC current density. This is in line with the conclusion by Büchler and Schöneich who made a similar experiment in a pH = 14 solution at very high AC current densities (500-1200 A/m²), but found that even under these conditions no significant corrosion was observed [16]. This suggests that a high pH alone in combination with an AC current is not sufficient to induce AC corrosion.

A alternative theory on the effect of pH on AC corrosion was hypothesized by Tribollet and Meyer et al. upon the observation of an intermediate green rust corrosion product ([Fe⁹⁺, Fe³⁺(OH)₂]^[x/nA⁺ m/nH₂O]⁺) on a cathodically protected steel subject to an AC perturbation. This green rust is however only stable at pH values < 11, and the stability of this phase may be linked to maintaining a protective layer, even under AC perturbation [27]. This can easily be linked to Büchler's hypothesis of corrosion products covering the surface may be able to accommodate the alternating charge via a pseudo capacitance caused by continuous oxidation/reduction of Fe²⁺/Fe³⁺ ions in the surface film rather than at the steel surface [16] [28]. In fact such a mechanism is described by Antony et al. for green rust films [29], but the films are usually not stable and will oxidize to α- or γ-FeOOH, Fe₂O₃ or Fe₃O₄ with alternative ageing processes [30] [31], in good accordance with the analysis of corrosion products in AC corrosion cases [32] [33]. Tribollet and Meyer list two possible routes to destabilisation of the green rust phase, both triggered by high pH caused by the water reduction reaction (3): Excessive CP or faradaic rectification of high alternating currents.

Methods

Visualisation of the alkalisation

Visualisation of the alkalisation at a probe surface is done by making a transparent soil simulation with added phenolphthalein pH indicator. Commercially available ‘water beads’ made from superabsorbent polymer were soaked in a non-scaling artificial soil simulation (Table 1), causing them to swell from 1.9 mm to 10 mm diameter spheres. Consisting of ~99% solution they have approximately the same refractive index as the solution, and are thus transparent in this solution. By blending the swelled beads to a slurry, a fine grained solution is obtained. This slurry is transparent but in terms of grain structure and diffusion properties, it is estimated that it resembles a wetted sand solution, thus allowing for a visualisation of the alkalisation at an electrode by observing the change of colour of the pH indicator.

Table 1: Non-scaling artificial soil solution used in the experiments

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄</td>
<td>5.0⋅10⁻³ M</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>2.5⋅10⁻³ M</td>
</tr>
<tr>
<td>NaCl</td>
<td>10.0⋅10⁻³ M</td>
</tr>
</tbody>
</table>
The slurry of blended water beads and solution is put in a rectangular glass container to minimize the visual distortion of the image, and a 10:1 length/width-ratio, 1 cm² working electrode is placed in the field of view of a camera outside the container (Figure 3). Two counter electrodes are placed in either side of the container and connected to the working electrode via an AC generator and a 600 µF capacitor on one side, and a DC potentiostat and a 3H inductor on the other side to filter out AC on the potentiostat and DC on the AC generator. A thin oil film on top of the solution is added to hinder evaporation of the solution. A 100 mV stepwise increase of the cathodic protection level from -950 mV to -1250 mV (CSE) is applied to the coupon over a period of 11 days and the experiment is repeated two times: once without AC and once with a 10 V AC perturbation. The camera is set to take an image every minute, in order to produce an illustrative fast forward time-lapse video of the pH evolution.

**Figure 3: Experimental setup for visualisation of pH evolution at an electrode under AC and DC influence. The electrolyte is a transparent slurry simulating wetted sand, containing a phenolphthalein pH indicator with a transparent to pink colour change at pH > ~9.**

**pH monitoring**

To monitor the pH at a cathodically protected steel surface under AC perturbation, a dedicated experimental cell was designed. This setup can be seen in Figure 4. A 10:1 length/width-ratio, 1 cm² ER probe was used as the working electrode in an identical electrical circuit to that of the visualisation experiment with a separation of the AC and DC circuit. The cell was filled with sand (0.4-0.8 mm) and wetted with a non-scaling artificial soil solution given by Table 1. The resulting soil resistivity was ~18.5 Ωm. A pH electrode with a tip diameter of 3 mm and a small temperature electrode was placed ~5 mm from the probe surface. This distance was chosen to avoid disturbing the electrode surface during the experiment. A reference temperature electrode not shown in Figure 4 was placed in “remote earth” in the setup to be able to monitor the temperature increase at the surface and compensate for daily temperature variations. The temperature was recorded every 10 minutes by a Grant Squirrel data logger. The ER probe measured electrical parameters \( E_{\text{tan}}, E_{\text{IR-free}}, U_{\text{AC}}, J_{\text{DC}}, J_{\text{AC}}, R_s \) and probe element thickness, \( d \), every 15 minutes during the experimental period of 6 days. The pH was read manually from a pH meter. During the first hour of the experiment where the pH increase was particularly pronounced, the pH-measurement frequency was high (every minute).
The pH monitoring experiment was repeated three times with different potentiostatic AC and DC voltage conditions. The reason for running the experiments potentiostatically was to monitor the influence of these settings on the pH, and vice versa; the influence of the developing pH on the electrical parameters such as the spread resistance and current densities. Each experimental run was labelled I-III according to Table 2. Experiment I and II represents a cathodically protected pipeline with or without AC, allowing for a direct assessment of the effect of AC on the developing pH in front of a coating defect. Experiment II and III represents a pipeline under AC interference, but they allow for an assessment of the effect of having a medium or high CP level.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Eon (mV vs. CSE)</th>
<th>$U_{AC}$ (V RMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-1200</td>
<td>0</td>
</tr>
<tr>
<td>II</td>
<td>-1200</td>
<td>10</td>
</tr>
<tr>
<td>III</td>
<td>-1550</td>
<td>10</td>
</tr>
</tbody>
</table>

**Results**

**Visualisation of the alkalisation**

The result of the pH visualisation experiment is illustrated in Figure 5. Daily still images show a progressive change in the local pH environment and the main findings are listed below:

- The pink colouration, i.e. a pH > 9 environment, is far more pronounced for the 10 V AC experiment. For both experiments the Eon potential has a large influence on the evolving environment. Time is clearly also an influential factor in terms of the extent of the high pH environment, however difficult to evaluate properly for the relatively short term experiment.
- The experiment does not offer any information about a pH gradient field towards the electrode, i.e. the pH within the pink area may be much higher than 9.
The DC current density is increased by the presence of AC by almost one order of magnitude. This is a direct effect of faradaic rectification of the AC current.

Gas evolution at the electrode surface causes an upwards drift of the high pH environment for the 10 V AC experiment via a 'pump effect' of the upwards drifting gas bubbles. This is attributed to the high DC current that surpasses the hydrogen overvoltage. At -1250 mV the DC current for the 0 V AC experiment is just enough to produce hydrogen gas showing a small upwards tail of the pink pH environment.

The alkalisation at the electrode not affected by AC appears very localised.

No corrosion was recorded in either experiment with or without AC.

Figure 5: Visualisation of the an evolving pH > 9 environment in front of a steel surface at increasingly negative potentials from -950 mV to -1250 mV (CSE) with or without an AC perturbation. The higher DC current, caused by faradaic rectification of the AC current, is directly related to the cathode reaction and OH⁻ development.

pH monitoring

The results from the pH monitoring experiment are presented in Figure 6 for the three different experimental conditions I-III (Table 2). In Figure 6a the measured pH (5 mm) shows a rapid increase in the beginning of each experiment, after which it stabilises on a level that is highly dependent on the AC and DC voltage conditions. On the same plot, a series of calculated pH values are shown based on the recorded DC current densities and equation (4). It can be seen that these values are approximately 1 pH value higher. Taking into account that equation (4) calculates the pH at the probe surface (0 mm) it is very plausible that a pH increase towards the surface may be responsible for this discrepancy. Based on work by other authors, e.g. Figure 2a, a 1 pH value difference may even be conservative [12] [14]. Taking into account the good correlation; pH\text{calc.} = pH\text{meas.} + 1 for all three experimental conditions, equation (4) is assumed to yield a valid approximation to the actual surface pH, also in this work.
Figure 6: Data for the various experiments (I, II and III) as a function of time.  
a) pH as measured 5 mm from the surface and calculated at 0 mm by means of the current density (4) yielding approx. +1 in pH.  
b) The evolution in spread resistance, \( R_s \)  
c) Thickness (daily averages)  
d) Corrosion rate (daily averages).  
e) Both AC and DC current densities plotted as stippled and solid lines respectively. The effect of faradaic rectification is clear when comparing experiment I and II having the same on-potential of -1200 mV (CSE).
In Figure 6b the corresponding spread resistance is shown. The effect of pH on this value will be further elaborated on in the discussion. In Figure 6c and d, daily averaged thickness and calculated corrosion rates are shown. The corrosion rate can be seen to increase by approximately one order of magnitude from experiment I to II and from II to III. The large scatter of I is partially due to the logarithmic scale but all corrosion rates here were < 20 µm/yr. Towards the end of experiment II the corrosion rate decreased, however the reason for this is unknown. Figure 6e shows both the DC and AC current densities, and the faradaic rectification of the AC current is clear from the large increase of \( J_{\text{DC}} \) from experiment I to II having the same \( E_{\text{on}} \) potential. A small AC signal (~0.4 V) was applied to the I-experiment to allow for spread resistance calculation by the data logger, however this can be seen to be only 3-6 A/m², i.e. far below the AC current density threshold of 30 A/m² given by the EN15280:2013 standard, and thus not of concern with respect to AC corrosion. The DC current density of the I-experiment is also below the limit of < 1 A/m² given by the EN15280:2013 standard and the low corrosion rates confirm the effective CP. Comparing current densities from the II and III experiment, it can be seen that not only does the DC current density increase with a higher degree of cathodic polarisation, but so does the AC current density. This is related to the increased alkalisation following the enhanced cathode reaction that lowers the spread resistance and causes a higher AC current density at the same alternating voltage.

The temperature at the 5 mm distance to the electrode surface was measured during the experiment, and the difference compared to the surrounding solution was calculated as \( \Delta T \) (°C) = \( T_{\text{5mm}} \) - \( T_{\text{remote}} \). This is plotted in Figure 7a. The temperature increase is caused by joule heating of the probe surface caused by the passing AC currents as can be seen in Figure 7b where average \( \Delta T \) and \( J_{\text{AC}} \) values are plotted. This is in line with results obtained by Nielsen [34], and the limited temperature increase observed may be ignored in terms of pH correction.

![Figure 7: Temperature monitoring of the probe surface (5 mm) showing a negligible temperature change as a function of \( J_{\text{AC}} \).](image)

**Discussion**

This work investigates the effect of pH on AC corrosion of cathodically protected steel. One thing that may be concluded is that the increase in pH is linked to an increase in the ionic conductivity of the soil locally around a coating defect, and thus a decrease of the spread resistance. This is not new knowledge but confirms accepted theory, refer the introduction. In Figure 8 the measured spread resistance from the ER probe in the pH monitoring experiment is shown as a function of the measured pH values 5 mm from the probe surface.
and the calculated pH values at the surface (0 mm). The trend is a linear decrease of spread resistance with pH. These results are valid for the non-scaling artificial soil used in the present investigation having a soil resistivity of ~18.5 Ωm, and the correlation may be different for other soils. Since it is generally accepted that corrosion rate is a function of the AC current density (even in the absence of DC current) this is part of the explanation for the great dependence on the DC current density. Increased AC current density on a cathodically protected structure is a direct consequence of the alkalisation caused by the cathode reactions. That is, unless the alkalisation causes precipitation of calcareous deposits that increase the spread resistance.

If the calculated pH values at the steel surface can be accepted as true, then these may be used together with the IR-free polarised potential measured by the ER probe to map out in which stability region in the Pourbaix diagram a steel surface exists. This has been done in Figure 9 for daily averaged values, and each point has been plotted as a circle whose size and colour corresponds to a corrosion rate. This representation puts the I-experiment in the immune region of the diagram as low/no corrosion points corresponding to effective CP. In case of an AC perturbation (II and III), the hydrogen evolution cathode reaction (3) becomes enhanced by faradaic rectification of the AC current, as was also verified by the visualisation experiment, and the points fall exactly on the hydrogen line. This is remarkable since it is perfectly in line with the theory that the potential of a steel is shifted parallel to the hydrogen line towards higher pH under cathodic protection [28], and this may further verify that the calculated pH values are representative of the true pH at the surface. Observing the stability region of various species in the Pourbaix diagram it can be seen that the III-experiment falls within the log([HFeO$_2^-$]) = -4 region (much dependent on the concentration of iron species). This may be interpreted as an argument for high pH chemical corrosion being the corrosion mechanism in play, however; the present calculated stability region differ significantly from that of the vast majority of literature (that starts at pH = 13-14, but is often ignoring the effect of the concentration of the iron containing species). With high corrosion rates this region would quickly be expected to shrink towards very high pH. Since AC
corrosion is not slowing down after a period of corrosion (and increasing iron species concentration) this implies either that HFeO$_2^-$ is quickly being converted to stable oxides, e.g. during the anodic half-wave of the AC cycle, or that high pH chemical corrosion is in fact an unlikely AC corrosion mechanism.

The effects of faradaic rectification of AC currents and enhancement of the cathode reaction (3) are two-fold: alkalisation is strongly enhanced and hydrogen evolution occurs at high rates. The visualisation experiment clearly showed the great influence of an AC perturbation on steel at increasingly negative cathodic polarisation. The missing corrosion in the visualisation experiment may Perhaps be explained by a continuous removal of the high pH environment at the surface via the hydrogen 'pump effect', due to a too low viscosity of the transparent soil simulation compared to real soil.

While most literature links AC corrosion to elevated pH and high AC and DC current densities, the hydrogen evolution is rarely considered to take part in the corrosion mechanism, except for perhaps destabilising surface deposits [4]. Following the different studies conducted in high pH solutions with high AC current densities that yielded little to no corrosion [16] [26], it is interesting that the only part missing from the real case is the negative polarisation and the hydrogen evolution at the surface. Both pH and J$_{DC}$ can be interpreted as a measure of produced hydrogen as well. When observing the visualisation experiment in the present study however, plenty of hydrogen was produced at a surface with both an AC and DC current density influence above the limits given by the EN15280:2013 standard, while no corrosion was observed. Undoubtedly AC corrosion is influenced by several processes, making the mechanism particularly complicated.

**Conclusion**

The pH at a cathodically protected surface is dependent on both the DC polarisation, as well as an alternating current. This has been shown both in a novel visualisation experiment and by direct monitoring of the pH using a small pH electrode in front of a surface.
The high pH environment in front of a coating defect was visually shown to increase in size with increasing polarisation and DC current under pure CP conditions, but when 10 V AC was applied in addition to the same CP conditions, the DC current increased by an order of magnitude by faradaic rectification of the AC current and the high pH environment was increased several factors in size. Excessive hydrogen evolution was observed as a result of the increase in cathodic current.

In another experiment the pH was likewise found to be increasing with both an overlying AC perturbation by faradaic rectification, and by increased cathodic polarisation. The spread resistance decreases due to an increase in ionic conductivity of the increasingly alkaline environment which causes increased AC and DC current densities, and ultimately increased AC corrosion rates.

A satisfying correlation between measured pH values and pH values calculated from the DC current density was obtained. Plotting corrosion rates measured by ER probe in a Pourbaix diagram at calculated pH and $E_{IR}$-free positions showed that high pH chemical corrosion as HFeO$_2^-$ may be a possible corrosion mechanism, but this implies that any formed HFeO$_2^-$ must immediately be converted to stable iron oxides. The present investigation remains inconclusive on this particular matter.

**Future work**

The experimental setups used in this study have proven as powerful remedies to study the evolving pH environment at a coating defect under combined AC and DC influence, and hopefully future experiments in these setups will continue to bring forward new findings on AC corrosion. In particular three factors will be investigated further:

- The effect of extended time studies. I.e. the coupling of an incubation period of perhaps several weeks to the developing pH environment at an electrode.
- A 3 mm pH electrode was used in the present study at a distance of 5 mm to the probe surface. The use of micro electrodes having a measurement tip of $< 100 \mu m$, placed closer to the surface or moved along a profile may yield a more detailed description of the local pH environment.
- Finite element modelling of the local evolving pH environment based on experimental data may help give a better holistic view of the processes that may/may not take place at the steel surface.
Bibliography


4.4 [IV] Materials & Corrosion ’18

This paper “Investigation of stone-hard-soil formation from AC corrosion of cathodically protected pipeline” presents a detailed investigation of a hardened soil formation from an AC corrosion incident on a pipeline. The pipeline was buried in calcium rich clayey soil with low soil resistivity. Results indicate increasing alkalinity, higher contents of salts, presence of corrosion products and cement-like minerals towards the coating defect. The characterisation techniques used are XRD, SEM, EDS, IC, ICP-OES and pH measurement on aqueous soil extracts.
Investigation of stone-hard-soil formation from AC corrosion of cathodically protected pipeline

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A stone-hard-soil structure was observed on a metallic pipeline under cathodic protection and subject to alternating current corrosion at a coating defect. Using X-ray diffraction, energy dispersive X-ray spectroscopy, ion-chromatography and inductively coupled plasma optical emission spectroscopy, the stone-hard-soil was characterized as being enriched in NaCl. Local alkalization following the cathode reactions caused precipitation of calcite, believed to be partly responsible for the stability of the structure. Very close to the corrosion site at the epicenter, calcite and quartz was depleted, possibly owing to an extremely high pH. Formation of cement-like minerals and corrosion products is observed.

KEYWORDS
alternating current (AC), calcareous deposition, carbon steel, cathodic protection, pipeline, X-ray diffraction

1 INTRODUCTION

AC corrosion is well known from pipelines under cathodic protection subject to AC perturbations, e.g., induced from high voltage transmission lines.\textsuperscript{[1,2]} The corrosion attack is reported by several authors to be localized at coating defects and create a hard dome of soil and corrosion products over the corrosion site, sometimes referred to as corrosion stone or stone-hard-soil.\textsuperscript{[1,3–6]} While AC corrosion has been extensively investigated in the past 30 years, only little interest has been given to the stone-hard-soil formations, though it can provide important information on the corrosion conditions. Stalder reported weak alkalinity (9.3–9.5) of aqueous extracts of a stone-hard-soil sample, and X-ray diffraction revealed large concentrations of goethite $\alpha$-FeOOH, wegscheiderite Na$_2$CO$_3$ $\times$ 3NaHCO$_3$, and KNaSO$_4$.\textsuperscript{[3,7]} In another study, Stalder reported that lime was depleted from the close vicinity of the coating defect.\textsuperscript{[8]} Simon reported a pH as high as 11 at the pipe surface under the precipitated corrosion product.\textsuperscript{[1]} Linhardt and Ball reported increased Na concentrations in a stone-hard-soil formation as well as the presence of sodium carbonate and sodium bicarbonate owing to large cathodic activity.\textsuperscript{[4]} Furthermore they attributed a “mixed” appearance of the stone-hard-soil to evolution of gas bubbles at the coating defect due to the cathode reaction under anaerobic conditions (1) which also produces alkalinity. The main corrosion product they discovered was magnetite, Fe$_3$O$_4$. 
2H₂O + 2e⁻ → H₂(g) + 2OH⁻ \hspace{1cm} (1)

A well-documented theory for AC corrosion is that an increasingly alkaline environment at the steel surface will reduce the electric resistance to remote earth and increase the AC and DC current flowing through the coating defect at constant AC and DC voltages\(^{[9,10]}\). Adversely if earth alkaline metals such as Ca and Mg are present, these might cause the precipitation of insoluble carbonates and hydroxides at high pH, possibly covering the coating defect with an insulating layer and decreasing the currents and corrosion rate.\(^{[8,11]}\) Some authors speculate that the formed stone-hard-soil “tubercle” may be of lower resistivity and thus behave as an antenna of increased surface area that will pick up both AC and DC currents in the soil and thus escort an autocatalytic corrosion attack by increasing current densities.\(^{[6]}\) Enhancement of the cathode reaction (1) by faradaic rectification of the AC current plays a major role in comparison to pure DC conditions.\(^{[12–15]}\) The DC current may be orders of magnitude higher than at regular CP, and thus the alkalization is more pronounced in AC corrosion cases.

According to the EN 15280:2013 standard, critical current density values for AC corrosion are \(J_{DC} = 1 \text{ A m}^{-2}\) and \(J_{AC} = 30 \text{ A m}^{-2}\), above which AC corrosion is likely to occur. Smaller coating defects are thus more vulnerable to AC corrosion.

The stone-hard-soil sample investigated in this study is shown in Figure 1. It is half of the semi spherical structure that develops at a coating defect on a pipeline subject to cathodic protection and an AC perturbation. The sample is split in the direction of the pipeline. It is clear that the structure is spherical around a corrosion site (Figure 1a–c) with a clearly altered appearance toward the corrosion site in Figure 1d.

The pipeline on which the structure was discovered was a \(\varnothing = 76.2\) cm (30 inches) low alloy carbon steel with an initial wall thickness of 12.7 mm and a three-layer extruded polyethylene coating, transporting dry natural gas. It was buried in Ca rich clayey soil in the Mediterranean region in Southern Europe. The on-potential was kept at approx. \(E_{on} = -1.3\) V vs. a Cu/CuSO₄ standard reference electrode (CSE) during the service life of the pipeline. During the first 4–5 years of service an induced AC voltage in the order of \(U_{AC} = 13\) V (25 V max) was recorded but after installation of a capacitive AC mitigation device, this was reduced to average values of 0.4–1.0 V (3–4 V max) during the following 15 years of service. The corrosion site was discovered in 2012 during a magnetic flux leakage (MFL) pigging of the pipe and excavated in 2014. The corrosion site was localized at a 20 × 10 mm coating defect, with a coating lift-off exposing a 30 × 15 mm area of the steel, typical for AC corrosion. The thickness reduction was measured to be 29%, yielding an average corrosion rate of \(\sim 190\) μm per year over the service life. It is assumed that the corrosion rate was higher during the first years of high alternating voltage, but it is known that AC corrosion in similar soils can be critical even at highly reduced alternating voltages.\(^{[16]}\)

A meticulous investigation of the stone-hard-soil offers valuable insight into the long term evolving environment around a coating defect on a pipeline subject to AC corrosion.

**FIGURE 1** Stone-hard-soil semi-sphere from an AC corrosion case on a metallic pipeline. a) View of the outer surface of the sphere. b) Cross-section with indications of sites for taking samples for further analysis. c) View from the pipe surface with the corrosion site clearly visible and dimensions as shown. d) Close up of corrosion site surrounded by a white powder. The cut line for making a polished cross-section is indicated [Color figure can be viewed at wileyonlinelibrary.com]
MATERIALS AND METHODS/EXPERIMENTAL

The stone-hard-soil sample was handled in air, i.e., not in a protective atmosphere, prior to analysis. Fe(II) oxides which may have been present during corrosion can thus not be characterized in the present analysis due to oxidation to Fe(III) species.

Powder samples from the stone-hard-soil were extracted using a Ø6 mm drill along a straight line at distances of 0, 1, 2, 4, 6, 8, and 10 cm from the corrosion site on the cross-section shown in Figure 1b, assuming approximately spherical uniformity in the stone-hard-soil. Additional two samples were taken from a reference soil (REF) excavated from nearby unaffected soil close to the pipeline.

Samples (0–10, REF) were analyzed with a Panalytical X’Pert Pro X-ray diffractometer (XRD) using CuKα radiation and 2θ = 3–66° for 2 h for each sample. The powders were ground to a particle size <45 μm in an agate mortar prior to analysis. Furthermore, a scrape off of the white powdery phase shown in Figure 1d was analyzed by XRD.

Samples (0–10, REF) were analyzed for chemical composition using energy dispersive X-ray spectroscopy (EDS) in a JEOL JSM-5900 scanning electron microscope (SEM). Powder was evenly dispersed on a conductive carbon pad and carbon coated, and an approximate area of 250 · 10^3 μm^2 was measured at two different locations for each sample.

Samples (0-6, 10, REF) were analyzed for chemical composition by inductively coupled plasma optical emission spectroscopy (ICP-OES) using the US EPA 3052 method. The 8 cm sample was excluded since no additional information was expected from this region.

Samples (1–10, REF) were analyzed for pH value by dissolving 0.40 g of dry material in 2 ml of reagent water in a 1:5 soil to water relationship, due to the small amount of sample material. Insufficient sample material from the 0 cm location was available for a pH measurement. The solutions were ultrasonically mixed for 5 min to ensure full dissolution of all relevant species and subsequently left to segregate in a solid and liquid phase for 1 h before pH measurement. The pH was measured using a calibrated Radiometer PHC3359-8 Combination pH electrode until a steady value could be read.

The soil resistivity of the stone-hard-soil as well as the reference soil was measured in a 80 cm³ M.C. Miller soil box using the four electrode method. Sample material spanning from the 2 to 10 cm positions in the stone-hard-soil and the reference soil was ground to fine powders and fully wetted by de-ionized water for 24 h before measuring to ensure dissolution of relevant species.

The same samples used for soil resistivity measurements were analyzed by ion-chromatography (IC) for concentrations of dissolved ions; Cl⁻ and SO₄²⁻ using a Thermo Scientific ICS-5000 IC system.

RESULTS

The concentration of dissolved Cl⁻ exceeded the measurement range for the IC equipment >10 g L⁻¹ for both the stone-hard-soil and the reference soil, i.e., very high for soil in general. The concentration of sulphate, SO₄²⁻ was 1.385 g L⁻¹ in the stone-hard soil and 6.354 g L⁻¹ in the reference soil.

The chemical analysis made by both EDS and ICP-OES provides a profile through the stone-hard-soil along the line indicated in Figure 1b. The results are presented in Figure 2, where the concentrations have been normalized with respect to the concentrations of the reference soil sample: C/CREF. This allows for an easy overview of the alterations in the chemical composition of the soil throughout the profile. If the C/CREF of a species is larger than 1, the local concentration has increased and vice versa. Figure 2a,b or c,d are essentially showing the same results, but discrepancies arise from measurement errors from either method. The reference soil concentrations are given in Table 1. Not all elements can be detected by either method, i.e., Cl and O cannot be detected by ICP-OES, but conversely the ICP-OES technique is more sensitive and will detect species of low concentrations. Several elements, i.e., H and C cannot be detected by any of the methods, but the ICP-OES results account for only 41.4% of the total tested material (not including O for the ICP-OES) and thus many of the species may exist as oxides, hydroxides, carbonates, etc. which may be detected by other methods.

As expected, Fe concentrations are markedly increased in the close vicinity of the corrosion site (Figure 2a,b). The same is true for the alloying elements of the steel: Mn and V even though in very small quantities, verifying that this is indeed caused by steel corrosion. A general increase of both Na and Cl toward the corrosion site is observed, indicating a higher concentration of halite, NaCl (salt) in the stone-hard-soil compared to the reference soil. The concentration profiles of the earth alkaline ions Ca and Mg appear to be inverted, i.e., toward the corrosion site, Mg is high and Ca is low. At 1–2 cm Ca increases but Mg decreases. From 4–8 cm Mg is dominant and finally at 10 cm the relationship is again inverted. The proportions between Ca and Mg is not 1:1 as is clear from Table 1, but their inverse relationship is very interesting and will be elaborated on further in the discussion. Several of the elements show reduced concentrations close to the corrosion site (Na, Cl, Ca, Si, K, Ti, Al) but this may simply be caused...
by a displacement of the original soil by the corrosion products emerging from the coating defect. Figure 3 shows the results of the XRD analysis on the samples taken along the profile shown in Figure 1b. The characteristic peaks of a series of species can be seen throughout the sample, but the intensity varies. Since the profiles were made under identical conditions, this may be interpreted as variations in the concentration along the profile, but not with respect to peaks of other species. (Q) quartz; SiO₂, (C) calcite; CaCO₃, and (H) halite; NaCl is present throughout the sample and the reference soil, but the calcite and quartz signal is reduced toward the corrosion site. In the reference soil and the outer part of the stone-hard-soil a (D) dolomite; CaMg(CO₃)₂ phase is present. The XRD results support the findings of increased halite concentrations toward the corrosion site, especially in the 1–2 cm region in good correlation with the EDS and ICP-OES analysis in Figure 2. Close to the corrosion site in the 0–2 cm region, several new peaks emerge. Figure 4 shows an enhanced view of the 0–2 cm XRD spectra, and the new peaks are characterized as an aluminium substituted tobermorite: Ca₅Si₅AlO₁₇(OH) · 5H₂O, pyroaurite: Mg₆Fe₂(OH)₁₆(CO₃)(H₂O)₄·5 and a calcium iron vanadium oxide (civo): Ca₃Fe₃.₅V₁.₅O₁₂. Some peaks, in the low 2θ angle region were still unidentified. Particularly the wider peaks are characteristic to clay species or phases with similar low crystallinity, and were generally consistent throughout the sample. Therefor they were not likely to have participated in the reactions and hence not of particular interest in this analysis. A markedly increased background signal in the 0–1 cm spectra caused by fluorescence with the CuKα X-ray radiation indicates a strong enhancement of iron in these samples. An XRD spectrum of the white powder in Figure 1d has not been included here, but it was shown to consist of mainly (B) brucite; Mg(OH)₂, as well as calcite and halite.

The pH measurements were conducted on 1:5 diluted soil to water weight samples, but since the pH is typically reported for a 1:1 dilution, the equivalent pH was calculated according to Eq. (2).

\[
pH_{1:1} = -\log\left(\frac{10^{-pH_{1:1}}}{5}\right)
\]

The obtained values are shown in Figure 5, giving a clear indication of alkalization of the stone-hard-soil compared to the reference soil pH. While the reference soil is already quite

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Concentration of species in the reference soil sample measured by EDS or ICP-OES</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>EDS (wt%)</td>
<td>5.1</td>
</tr>
<tr>
<td>ICP-OES (dg kg⁻¹)</td>
<td>2.7</td>
</tr>
</tbody>
</table>
alkaline at pH = 9.8, the stone-hard-soil is as high as ∼12, 1 cm from the corrosion site. Given that the alkalinity is caused by the cathode reaction (1) at the coating defect, and observing the general increase in pH from 10 cm to 1 cm, it is anticipated that the pH at the 0 cm location may have been well beyond 12.

Soil resistivity measurements of the stone-hard-soil and the reference soil yielded very low resistivities of only $\rho = 0.3 \, \Omega \cdot m$ for both, i.e., values comparable to seawater. This is a large part of the explanation to why the pipeline corroded, even at mitigated AC levels. Assuming a circular coating defect of diameter 30 mm (conservative), the area specific spread resistance for the coating defect, $R_S$, becomes

$$R_S = \frac{\rho}{2d} A = 3.5 \times 10^{-3} \, \Omega \cdot m^2$$ (3)

Even at just 1 V AC (conservative) this yields a current density far beyond the critical $J_{AC} = 30 \, A \cdot m^{-2}$ specified by EN 15280:2013.

$$J_{AC} = \frac{U_{AC}}{R_S} = 285 \, A \cdot m^{-2}$$ (4)

The low soil resistivity is attributed to the high salt content measured by EDS and ICP-OES.

In Figure 6, a cross-sectional view of the stone-hard-soil within ∼1 cm from the corrosion site is shown. The cut is made along the line indicated in Figure 1d. The cross-section clearly shows distinct phases in terms of visual appearance. A black/brown phase is visible at the corrosion site in the lower right corner (ZONE 1), surrounded by a more red/orange phase (ZONE 2). The coloration is assumed to be caused by dissolved iron and corrosion products. A white phase is present just left of the corrosion products and toward the pipe surface in the bottom of the image (ZONE 3). Then a concentric region of dark grey matter with numerous cracks is present (ZONE 4), and finally a bright beige region which extends to the rest of the stone-hard-soil in terms of appearance (ZONE 5). Toward the pipe surface in the bottom of the image a flat pattern indicates that the stone-hard-soil at some point detached partially from the pipe, and the resulting gap was filled with corrosion products and the white powdery phase identified as Mg(OH)$_2$. This observation is supported by the circular pattern of the white phase observed in Figure 1c. Three areas within relatively homogeneous areas in the surrounding soil are marked (1–3) for chemical analysis by EDS. Furthermore a larger area across the black/brown, red and white region (ZONE 1–3) is chosen for element mapping by EDS.
EDS mapping of the marked area in Figure 6 can be seen in Figure 7 along with a closer look on some spherical structures observed in a cavity of the corrosion products, shown in secondary electron images (SEI). The EDS maps show readings of the respective elements as white spots, that clearly map out where the respective elements are present. The white phase clearly consists of mainly Mg and O in a 1:2 relationship read by a point EDS analysis, corresponding to Mg(OH)$_2$. Fe and O are present in the corrosion products. The spherulitic structure may be characteristic for siderite, FeCO$_3$ or magnetite, Fe$_3$O$_4$.[17] Magnetite is a known corrosion product in AC corrosion cases, but the EDS investigation in the area marked on one sphere in Figure 7 suggested an Fe to O atomic ratio close to 1:3, thus suggesting FeCO$_3$. The civo (Ca$_3$Fe$_{3.5}$V$_{1.5}$O$_{12}$) detected in the XRD spectra (Figure 4) may also be an option, since the mapping did show Ca present within the corrosion products, however, the point analysis showed only minor Ca concentrations and no vanadium. Since no XRD verification of the corrosion product was possible, no conclusions could be made. Due to handling of the sample in aerated conditions and the likely oxidation of Fe(II) species as previously mentioned, a true characterization of the iron oxides formed under corrosion conditions is not possible.

The EDS measurements from locations 1–3 in Figure 6, i.e., in the vicinity of the corrosion site are shown in Figure 8. By comparison to the reference soil, it is evident that the concentration profiles of the species are matching (but suppressed due to the EDS results being relative), except for Na and Cl at location 1 and 2, and Mg in location 3. This is interpreted as enrichment of halite and brucite in these locations respectively, in line with the EDS mapping in Figure 7, however, together with a clear trace of the original

FIGURE 6 Cross-section of the stone-hard-soil close to the corrosion site in the lower right corner (0–1 cm), moulded in epoxy resin. Marked areas were investigated with EDS, see Figures 7 and 8 [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 7 Close investigation of polished cross-section (Figure 6). Upper left: LOM image. Middle left: SEM image. Lower left: Close-up of corrosion products including area of detailed EDS analysis. Rest: EDS maps of the respective elements as indicated, showing distinct phases (Mg + O, Na + Cl, Fe + O, Ca + O) around the corrosion site [Color figure can be viewed at wileyonlinelibrary.com]
soil. These localized, but markedly different results within 0–1 cm from the corrosion site suggest that the chemical profile made by EDS and ICP-OES as well as XRD may be overly simplified, especially in this local region toward the coating defect. That is, no brucite was detected along the XRD-profile in Figure 3, which may simply be explained by the fact that brucite appears locally, and was by chance not present in any of the profile samples in detectable amounts.

4 | DISCUSSION

In Figure 9, Pourbaix diagrams for Fe, Ca, and Mg are shown. They are calculated using the HSC Chemistry 5 E-pH software at 25 °C and one bar pressure. In Figure 9a it can be seen that iron contains a small corrosive region at high pH where it may dissolve as HFeO$_{17-}$, often suspected to play a role in the AC corrosion mechanism. This is highly dependent on the concentration of Fe in solution, and is often pictured differently in literature. The Ca diagram shows a large calcite region from neutral to highly alkaline (pH ≈ 13) conditions. If the presence of Mg in the same system is considered, a smaller dolomite region appears. Interestingly, the reference soil (pH = 9.8) and the 10 cm position showed dolomite traces in the XRD (Figure 3), but as pH in the stone-hard-soil rises to pH>11 toward the center (Figure 5) this disappears, corresponding nicely to the calculated stability region of dolomite in Figure 9b. As the pH further increases toward the center, the quartz and calcite XRD signals are drastically reduced. This may be due to alkaline dissolution of these species, allowing for the formation of a tobermorite Ca$_5$Si$_5$Al(OH)$_{17} \cdot 5$H$_2$O-phase consuming the dissolved Ca and Si ions as well as the produced OH$^-$. Dissolution of quartz at high pH is known in literature.\[18\] The disappearance of calcite is in line with the observations by Stalder and suggests a pH value in the very center of the stone-hard-soil well above 13, confer Figure 9b, which could not be

FIGURE 8 EDS results of locations 1–3 (Figure 6) and comparison to the reference soil. Location 1 and 2 are strongly enriched with halite, NaCl, while location 3 is enriched with brucite, Mg(OH)$_2$.

FIGURE 9 Calculated Pourbaix diagrams for the Fe/H$_2$O (a), Ca/C/Mg/H$_2$O (b), and Mg/C/H$_2$O (c) system at 25 °C and 1 bar pressure. a) The corrosive regions at high and low pH increases with lower concentrations of Fe. b) The molality of C was given as $10^{-4}$, while the molality of Ca is variable. The CaCO$_3$ (calcite) region can be seen to appear at $\geq 10^{-4}$ mol/kg Ca. Higher C concentrations further stabilizes the CaCO$_3$ region. If Mg is present (10$^{-5}$ mol/kg), a small CaMg(CO$_3$)$_2$ (dolomite) region is outlined in gray and growing with increasing Ca molality. c) Brucite, Mg(OH)$_2$, is stable at elevated pH but very dependent on the concentration.
measured using conventional pH measurements in Figure 5.\[8\]

The formation of tobermorite in highly alkaline environments
is well known from investigations of the effect of an alkaline
plume from nuclear waste concrete containers on natural
clays containing both Ca and Si.\[19\] Others have synthesized
an aluminium substituted tobermorite from oil shale ash
containing among others both calcite and quartz in an alkaline
(pH = 14.9) hydrothermal (160 °C) process.\[20\] Tobermorite
formation is generally effected by the silica source and
addition of Al, as well as pH, and may contribute positively to
a soils cation exchange capacity (CEC) i.e., its ability to
accumulate cations such as H+, Al+, Ca+, and Mg+.\[21\]

Geologically, tobermorite is usually formed by metamor-
phism, i.e., at elevated temperatures or pressure in calcite
containing rocks, and thus it may be a tracer for elevated
temperatures toward the coating defect possibly caused by
high alternating current densities.

Pyroaurite, Mg₆Fe₂(OH)₁₆(CO₃)(H₂O)₄₋₅, was synthe-
sized in a near neutral pH to high pH environments by Hansen
and Taylor.\[22\] They found that in high pH environment a
possible formation path was via slow addition of Fe(II) to Mg-
rich phases, e.g., brucite or magnesite, MgCO₃. When
saturated with water, and upon the reaction with oxygen,
Fe(II) may oxidize to Fe(III) and react with Mg species in
solution. While the environment under cathodic protection is
depoleted of oxygen, it is possible that the presence of an
alternating voltage may alternate the oxidation step of
available iron from Fe(II) to Fe(III) during the anodic half-
wave, and in that way provide the conditions for pyroaurite
formation.\[23\] The observation of pyroaurite may be an
indicator for the right conditions for formation of green rust
which is also a layered double hydroxide and is found on
carbon steel under cathodic protection.\[24\]

The intertwining relation between Ca and Mg in the stone-
hard-soil may be explained by dissolution of the present
dolomite and calcite phases in the original soil making Ca and
Mg ions mobile in the soil. Even at slightly elevated pH
brucite may precipitate (Figure 9c), and as it appears on the
interface between pipe and stone-hard-soil in Figure 1c and
the cross-section in Figure 6 this phase may fill out cavities
and cracks formed, especially close to the corrosion site
causing the 0–1 cm Mg rise. Pyroaurite formation may also
play a role. The formed hydrogen gas from the cathode
reaction (1) is likely to push the stone-hard-soil away from the
steel or form pores or cracks, allowing the gas to escape.
Furthermore, the extreme alkalization from the cathode
reaction (1) at the electrode/electrolyte interface will dissolve
the calcite that may allow for some of the Ca ions to migrate
outwards in the stone-hard-soil and re-precipitate as calcite at
slightly lower pH causing the 1–2 cm Ca rise. Other Ca ions
participate in the formation of tobermorite. Even though calcite
is present in the reference soil, the XRD measurements show an
increased amount in the stone-hard-soil, suggesting that some
of the Ca in the reference soil may exist as soluble ions, and
some as calcite and dolomite. Soluble Ca ions may migrate
toward the stone-hard-soil structure as they are consumed here
by calcite precipitation, causing the increase in Ca concentra-
tion at the 10 cm position. The elevated levels of calcite may
very well contribute to the hardening of the soil. The potential
field may also contribute to electro-kinetic cementation of the
calcareous clayey soil at the cathode (and to a higher degree at
the anode, however, not investigated in this study) which
might contribute substantially to the hardness of the stone-hard-soil.\[25\]

The increased concentration of NaCl in the stone-hard-
soil is not previously reported in literature, but may support
Nielsen and Cohn’s theory that the stone-hard-soil can act as
an antenna of low soil resistivity that is able to pick up and
discharge currents in the soil, since NaCl is easily soluble and
may increase ionic conductivity.\[6\] The measured soil
resistivity for both reference soil and the stone-hard-soil
was as low as 0.3 Ωm, and thus no difference could be
measured. This is likely linked to the already high NaCl
concentrations in the reference soil (Table 1 + IC results), and
thus the effect of having a slightly higher salt concentration in
the stone-hard-soil may be insignificant in terms of
conductivity. In connection with the findings that a thin
crevace had formed between the pipe and the stone-hard-soil
structure, the low resistivity further allows for a drastic
alteration of the localized soil chemistry in this small crevace
in the center of the stone-hard-soil, because the surrounding
dense sphere slows down diffusion of formed species at the
corrosion site, e.g., OH⁻, while currents through the coating
defect may actually be enhanced. Provided the stone-hard-
soil in dry conditions for the present analysis, however, it is
uncertain what the in situ resistivity has actually been, since it
is highly influenced by the moisture content. This moisture
content is expected to be influenced by the potential gradient
field around the negatively charged pipe. It has been
demonstrated that cathodic protection increases the moisture
content of the soil/steel interface in unsaturated soils.\[24\] The
cathode will attract positive ions in solution, and thereby
water by the process of electro-osmosis, since water
molecules are attracted to the cations.\[25\] The reason for the
enhanced NaCl concentration may be explained by this
attraction of positively charged Na⁺ ions in solution. This
effect is illustrated in Figure 10. The negatively charged Cl⁻
ions should be repelled by the cathodic pipe, but may follow
the migration of cations to ensure local charge neutrality or
simply follow the water which will continuously migrate
toward the coating defect where it will be consumed by the
cathode reaction (1). The opposite observation for sulphate
ions SO₄²⁻ may be explained by higher charge of this larger
anion that enhances the influence of the electric field and
slows down diffusion, making it unable to follow the cations
toward the coating defect. The effect of an alternating voltage,
and thus changing direction of the electric field, on the migration of an- and cations respectively is unknown, but the net direction of current, i.e., toward the cathode, is expected to govern the direction of the water migration, and as it has been discussed, the cathodic current is enhanced by AC by the process of faradaic rectification.

5 | CONCLUSIONS

The investigation of a stone-hard-soil formation from an AC corroded steel pipeline under cathodic protection in a Ca-rich soil has revealed a number of findings:

- The pH of the stone hard soil was high from ~11 in the entire sample to >13 close to the corrosion site, based on pH measurements and the evident dissolution of calcite, CaCO₃, in the center. Throughout the rest of the stone-hard-soil calcite levels were increased, compared to a reference soil sample, possibly contributing to the hardness of the structure. Dolomite, CaMg(CO₃)₂, having an upper stability limit of pH ~11, was present in the reference soil, but disappeared inwards in the stone-hard-soil, confirming the measured pH values.
- Töbermorite, Ca₄Si₄Al(OH)₁₇·5H₂O, has formed close to the corrosion site where calcite and quartz, SiO₂, have disappeared. This is evidence of a very high pH environment. The kinetics for formation may have been enhanced by joule heating of the pipe-soil interface caused by passing AC currents.
- Elevated concentrations of halite, NaCl, in the stone-hard-soil were found and the soil resistivity measured as low as 0.3 Ωm. Much dependent on the moisture content, this may contribute to the stone-hard-soil being a low resistivity path for currents entering the pipe at the coating defect, while at the same time the dense stone-hard-soil may hinder diffusion of chemical species away from the corrosion site and create a crevice environment. The high concentration of NaCl is interpreted as a result of electro-osmosis of hydrated cations toward the cathodic coating defect, thus providing a high humidity and low resistivity environment.
- Brucite, Mg(OH)₂, was found as a white powder phase, especially in cracks and cavities such as between the pipe and the stone-hard-soil. It is not estimated to contribute significantly to the hardness of the stone-hard-soil, but rather to be a filler material providing cohesiveness.
- The present analysis is made >1 year after excavation of the stone-hard-soil, which has formed over several years in the soil. The conditions around the corrosion site have undoubtedly changed on a daily, seasonally or yearly basis in terms of potentials and currents, wetness levels, temperature, alkalinity, etc. during the service life of the pipeline. It is not possible to link the formation of the stone-hard-soil to a set of well-defined process conditions, but the analysis is a valuable contribution to the discussion about alkalization and the establishment of a characteristic environment around a coating defect subject to AC corrosion.

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REFERENCES


4.5 [V] Corrosion ’18

This paper presents an investigation of the effect of different chemical constituents in a soil environment by controlled laboratory experiments. The results from these experiments are compared to a field study of AC corrosion on a real pipeline where remote monitoring stations were installed and soil samples from pipe depth were taken for analysis. The results show agreement between field and laboratory investigations of AC corrosion and underline the importance of a soils resistivity and response to alkalisation.
Laboratory and Field Investigation of the Effect of the Chemical Environment on AC Corrosion

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ABSTRACT

AC corrosion is dependent on both AC and DC current densities, but only little is known about the effect of the chemical environment. In this paper, laboratory soil-box experiments are made for a better understanding of the effect of specific chemical constituents in soil on corrosion in relation to the AC and DC current densities. A field investigation of AC corrosion on an operational pipeline where AC interference and CP levels could be controlled, is presented. Soil analysis from the field study is discussed in relation to the laboratory experiments. Distinction between AC corrosion caused by anodic depolarization of the steel or by excessive cathodic protection and alkalization is made and discussed in relation to the current density criteria in industry standards.

Keywords: AC corrosion, AC interference, cathodic protection, soil, pH, pipeline.

INTRODUCTION

Present cathodic protection criteria for pipelines subject to an AC voltage perturbation are given in EN 15280:2013\(^1\) and ISO 18086:2015\(^2\) as:

- AC current density, $J_{AC} < 30 \text{ A/m}^2$, or
- DC current density, $-J_{DC} < 1 \text{ A/m}^2$, or
- $J_{AC}/J_{DC} < 3$

Alternatively, effective AC corrosion mitigation can be demonstrated by measuring corrosion rates below an acceptable level.\(^1,2\) However, many alternative protection criteria, often more conservative...
than the ones listed above, can be found in literature.\textsuperscript{3-7} The background investigations supporting these criteria often neglect the combined effect of both AC and DC and thus, the discussion on protection criteria in literature is distorted. Another factor that is rarely considered is the chemical environment and its effect on corrosion rate and protection criteria. From a literature study, Gummon et al. concluded that ‘AC corrosion appears to be dependent to a minor extent on the type of environment’.\textsuperscript{8} Some studies indicate that carbonates may increase corrosion whereas NaCl containing media seem to inhibit corrosion.\textsuperscript{4,9} Others indicate that earth alkaline elements such as Ca and Mg may precipitate as carbonates or hydroxides in alkaline environments forming shielding deposits that limit the induced current and thus the AC corrosion risk.\textsuperscript{10-12} One key indicator for AC corrosion risk used in industry standards is the soil resistivity, $\rho$ (\(\Omega\) m), which naturally reflects the soils chemistry. The spread resistance, $R_S$ (\(\Omega\) m\(^2\)) links induced AC voltage to AC current density, $J_{AC}$ (A/m\(^2\)), according to equation (1). The DC current passing through $R_S$ constitutes the IR-drop according to equation (2) where $E_{ON}$ (V) is the rectifier set potential, $E_{IR-free}$ (V) is the IR free (or polarized) potential and $J_{DC}$ (A/m\(^2\)) is the DC current density. $R_S$ is directly proportional to $\rho$ and the coating defect geometry.

$$U_{AC} = R_S \cdot J_{AC}$$  \hspace{1cm} (1)

$$E_{IR-free} = E_{ON} - IR = E_{ON} - J_{DC}R_S$$  \hspace{1cm} (2)

Detailed models for $R_S$ and its dependency of coating defect geometry are available in literature but it is impossible to evaluate on a buried pipeline where coupons or probes with a known exposed area (typically 1 cm\(^2\)) are not used.\textsuperscript{13,14} While soil resistivity is often measured as part of pipeline surveys, the local chemistry in front of a coating defect or coupon is changeable due to the primary cathode reaction which prevails under anaerobic conditions in equation (3). The hydroxyl ions generated increase pH and ionic conductivity. This reaction is directly related to $J_{DC}$, which explains the importance of this parameter in AC corrosion.\textsuperscript{15}

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$$  \hspace{1cm} (3)

The capability of a soil to neutralise (by reactions) or dissipate (by diffusion) produced alkalinity (OH\(^-\)) influences the spread resistance and hence current densities. The soil chemistry allegedly plays a role in this. As has been documented by several authors, AC and DC currents strongly influence each other.\textsuperscript{16-18} AC may affect the DC current through faradaic rectification of the alternating current, a phenomenon that is mathematically well described in literature.\textsuperscript{19-22} This has been experimentally verified by several authors whether it is described as a ‘depolarization effect’, and ‘increased exchange current effect’ or ‘faradaic rectification’.\textsuperscript{17,23-26}

The objective of the present paper is to illustrate the synergistic effects of AC and DC parameters. A series of laboratory investigations in different chemical environments seek to survey the entire (realistic) AC and DC current density regime, and to evaluate the effect of different chemical constituents. Laboratory data are compared to field data from a buried pipeline section under AC interference. A better understanding of the current density criteria and how they are related to AC corrosion, enables the authors to propose AC corrosion mitigation strategies: control of $J_{AC}$, control of $J_{DC}$ or both.

**EXPERIMENTAL**

In this study, field and laboratory experiments are compared. In both cases ER-probes are used together with data loggers to monitor corrosion rate and electrical parameters such as on and IR-free potentials, $E_{ON}$ and $E_{IR-free}$, DC voltage, $U_{AC}$, AC and DC current density, $J_{AC}$ and $J_{DC}$, as well as the spread resistance, $R_S$, a function of the local soil chemistry near the probe surface (coating defect). The ER probes have a 10:1 length to width-ratio rectangular exposed area of 1 cm\(^2\), and the initial probe element is 500 \(\mu\)m in thickness.
CHAPTER 4. MANUSCRIPTS

4.5. [V] CORROSION '18

Laboratory Experiments

Laboratory experiments were conducted in 50 L soil-box setups with separate AC and DC (Potentiostat) circuits to simulate cathodic protection and induced 50 Hz AC. The setup is described in detail elsewhere [12]. During the experimental period of 8 weeks, the on-potential was changed from -900 to -1600 mV_{CSE} in weekly steps of 100 mV. The AC voltage was increased from 0 to 20 V in daily steps of 5 V, restarting at 0 V weekly (Figure 2b). To allow the surface to polarize to each CP level and for the local soil chemistry to settle, the experiment was run for 3 days with no overlying AC.

Seven investigations were conducted in parallel, adding different electrolytes (Table 1) to inert sand (0.4 – 0.8 mm particle size) forming a fully wetted diffusion barrier, simulating soil. Conductivity, \( \rho \), and pH at the initiation of the experiment were measured using a 4-pin Miller\(^{+} \) soil-box and a handheld Hanna Instruments\(^{+} \) pH meter respectively.

The concentrations of different species in experiments 2-7 were chosen to produce similar soil resistivities \( \sim 19\pm2 \) \( \Omega \) m, while experiment 1 conducted with de-ionized (DI) water was included to illustrated the effect of low conductivity soils with a resistivity approximately 10 times larger. Experiment 2 represents a Non-scaling Artificial Soil (NAS) while experiment 7 represents an Artificial Soil (AS) capable of scale formation at high pH due to the presence of earth alkaline elements Ca and Mg. Experiments 3-5 investigate the effect of the individual constituents of the NAS solution and experiment 6 investigates the effect of having a phosphate based pH-buffer system in the solution, designed to buffer the electrolyte around pH = 7 via the \( H_{2}PO_{4}^{-} \leftrightarrow H^{+} + HPO_{4}^{2-} \) equilibrium reaction. The concentration of the buffer was such that the target conductivity of the soil was not exceeded.

The ability of the electrolytes to neutralize alkalinity formed at the cathodic probe surface was evaluated by titration, adding increasing concentrations (0-0.1 M) NaOH solution to 10 mL of electrolyte; The intersection of the titration curve with pH = 10 is reported as the ‘Base Neutralizing Effect’, BNE, given in cmol/kg. Reported BNE values are between 0-20 for different soils.\(^{27,28} \) For each experiment, two ER probes were installed for statistical verification of data.

**Table 1: Electrolyte concentration, resistivity and initial pH for laboratory experiments.**

<table>
<thead>
<tr>
<th>Concentration (( 10^{-3} ) M)</th>
<th>NaCl</th>
<th>Na(<em>{2})SO(</em>{4})</th>
<th>NaHCO(_{3})</th>
<th>NaHPO(_{4})</th>
<th>Na(<em>{2})HPO(</em>{4})</th>
<th>CaCl(_{2})</th>
<th>CaSO(_{4})</th>
<th>MgSO(_{4})</th>
<th>( \rho ) (( \Omega )m)</th>
<th>pH</th>
<th>BNE (cmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. DI</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>182.0</td>
<td>7.0</td>
<td>0.9</td>
</tr>
<tr>
<td>2. NAS</td>
<td>10.0</td>
<td>5.0</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>17.3</td>
<td>7.8</td>
<td>0.8</td>
<td>17.3</td>
<td>7.8</td>
<td>0.8</td>
</tr>
<tr>
<td>3. NaCl</td>
<td>16.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>21.0</td>
<td>6.7</td>
<td>0.9</td>
<td>21.0</td>
<td>6.7</td>
<td>0.9</td>
</tr>
<tr>
<td>4. Na(<em>{2})SO(</em>{4})</td>
<td>9.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>27.9</td>
<td>19.7</td>
<td>6.6</td>
<td>0.8</td>
<td>19.7</td>
<td>6.6</td>
<td>0.8</td>
</tr>
<tr>
<td>5. NaHCO(_{3})</td>
<td>-</td>
<td>9.5</td>
<td>15.5</td>
<td>-</td>
<td>-</td>
<td>18.2</td>
<td>8.2</td>
<td>4.0</td>
<td>18.2</td>
<td>8.2</td>
<td>4.0</td>
</tr>
<tr>
<td>6. P Buffer</td>
<td>2.5</td>
<td>9.5</td>
<td>15.5</td>
<td>-</td>
<td>-</td>
<td>18.6</td>
<td>6.4</td>
<td>5.2</td>
<td>18.6</td>
<td>6.4</td>
<td>5.2</td>
</tr>
<tr>
<td>7. AS</td>
<td>5.0</td>
<td>5.0</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>18.9</td>
<td>7.5</td>
<td>1.3</td>
<td>18.9</td>
<td>7.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>

* Base Neutralizing Effect: The amount of OH- ions needed to increase the pH of a soil to pH = 10.

Field Experiments

Field experiments were conducted at 5 remote monitoring stations installed along a high pressure gas pipeline section influenced by 60 Hz overhead high voltage transmission lines (HVTL) carrying 46, 138 and 345 kV as shown in Figure 1. The locations were chosen based on anticipated high AC interference and accessibility. The pipeline route mainly traverses farmland, interspersed with urban and industrial areas. Measurements were taken on an hourly basis and closely monitored. A four-pin soil resistivity survey at 1.5 m depth was previously conducted along the pipeline route resulting in soil resistivity measurements between 10 and 30 \( \Omega \) m (median value: \( \rho = 19.6 \) \( \Omega \) m). One ER probe was

\(^{+} \) Tradename
installed at pipe depth at each measurement site, and a soil sample (~500 g) was taken for laboratory soil characterisation. Conductivity was measured on the as-received soil using the same procedure as for the laboratory experiments. The field samples were dried for 24+ hours at 60°C and crushed to a powder. An aqueous extract of the soil was made by mixing 20 g of soil powder with 25 ml of de-ionized water for 22 hours, followed by segregation of the aqueous phase. The pH of this aqueous soil extract was measured using a Radiometer® PHC3359-8 pH electrode. Chemical analysis was conducted by energy dispersive x-ray spectroscopy (EDS) and ion chromatography (IC) analysis of dissolved ions. Sample material was evenly dispersed on a conductive carbon pad and carbon coated, and an approximate area of 200-10^3 μm^2 was measured by EDS at four different locations for each sample in a JEOL® JSM-5900 scanning electron microscope. IC analysis was performed on the same aqueous extract as for the pH measurement using a Thermo Scientific® ICS-5000 IC system. BNE_{10} was measured by adding increasing concentrations (0-0.1 M) of NaOH solution to 5 g of soil material and shaking for 22 hours. The procedure is described under laboratory experiments.

![Map illustrating the pipeline and HVAC powerline routes together with the measured soil resistivities and probe placements](image)

During the experiment, AC and DC settings for the pipeline were varied by disconnecting the AC mitigation installation (zinc ribbon installed along the entire length of the pipe) and turning the CP rectifiers up or down according to Table 2. A limit of ≤-1200 mV_{CSE} cathodic polarisation was however met due to permanently installed galvanic anodes that did not allow for less CP on the pipe. The duration of each period was continuously adjusted to gather sufficient amounts of data.

<table>
<thead>
<tr>
<th>Period</th>
<th>AC mitigation</th>
<th>CP level (mV_{CSE})</th>
<th>Duration (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>On</td>
<td>~-1600</td>
<td>7</td>
</tr>
<tr>
<td>B</td>
<td>On</td>
<td>~-1200</td>
<td>34</td>
</tr>
<tr>
<td>C</td>
<td>Off</td>
<td>~-1600</td>
<td>18</td>
</tr>
<tr>
<td>D</td>
<td>Off</td>
<td>~-1200</td>
<td>45</td>
</tr>
<tr>
<td>E</td>
<td>Off</td>
<td>~-1600</td>
<td>6</td>
</tr>
<tr>
<td>F</td>
<td>Off</td>
<td>~-1200</td>
<td>7</td>
</tr>
<tr>
<td>G</td>
<td>On</td>
<td>~-1200</td>
<td>11</td>
</tr>
</tbody>
</table>

† Tradename

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RESULTS

Laboratory experiments

Results from laboratory experiment 3 (NaCl) are presented in Figure 2. The variation in experimental settings (with increasing cathodic polarization, $E_{ON}$, and a weekly varied AC perturbation, $U_{AC}$) is clearly illustrated in Figure 2b. The resulting AC and DC current densities are shown in c). The DC current is dependent on both polarization and the AC level. Thickness and corrosion rate in a) are daily averages.

![Figure 2: 8 weeks of data from laboratory experiment 3.](image)

With increasing $-J_{DC}$, the spread resistance in d) decreases due to ionic conductivity of the hydroxyl ions produced by reaction (3), leading to high AC current densities. The combination of high $J_{AC}$ and $-J_{DC}$ causes corrosion as shown in a). It is noticed that corrosion was immediately halted when the AC level was reduced at the end of each week. But, even at high AC levels, corrosion can be controlled if the cathodic current density, $-J_{DC}$, is low. However, corrosion did occur during the short period of anodic current which is shown in the enlarged region of c) during the first week for $E_{ON} = -900$ mV vs CSE. Negative corrosion rates in a) are treated as zero in the following processing of data.

Corrosion rate and current density data from both ER probes in each of the seven chemical environments studied (Table 1) is presented in Figure 3a, where daily corrosion rates are plotted as weighted circles in the $-J_{DC}/U_{AC}$ diagram. Overlaid arrows indicate general trends for all data. Vertical arrows represent different CP potential levels with increasing AC interference. Horizontal arrows represent different AC interference levels with increasing cathodic protection. They do not correspond to specific $E_{ON}$ or $U_{AC}$ values. Several observations can be made from the AC/DC current density domain generated.

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AC and DC currents do not react linearly to changes in their respective potentials. A strong dependency on each other exists.

- At low DC levels, AC causes reduced J_{DC} and insufficient cathodic protection, despite having E_{CN} < -900 mV_{CSE} due to a potential shift of the steel. It may even cause anodic depolarization and corrosion rates >100 µm/yr. The effect is strongest at the intermediate levels of J_{AC} = 10-200 A/m² above which the currents at low CP levels became cathodic again.
- High AC levels cause significantly increased J_{DC} through faradaic rectification of the AC current. – vertical arrows in the diagram turn right at high AC.
- High J_{DC} lowers the spread resistance, R_S, through the cathode reaction (3) enhancing J_{AC} – horizontal arrows in the diagram point upwards at high J_{DC}.

Figure 3: Laboratory data for all 7 experiments. a) Daily corrosion rates. High J_{AC} and -J_{DC} causes corrosion, but also anodic depolarization may cause corrosion. b) Iso-corrosion lines of <25 µm/yr.

In Figure 3b iso-corrosion lines of 25 µm/yr (1 mpy) are shown for the different environments in the -J_{DC}/J_{AC} plot within the region of accessible data. Two paths to corrosive conditions exist with increasing AC interference: 1. Anodic depolarization, and 2. “excessive CP” leading to alkalinity and high current densities. For most environments however, an intermediate CP strategy allows for high J_{AC} while maintaining V_{corr} < 25 µm/yr, though the -J_{DC} limits may be very narrow. The variation from one environment to another illustrates the role of soil chemistry and the complexity of defining universal current density criteria. E.g. in a scaling environment (AS), the J_{DC} = -1 A/m² limit may be conservative (in accordance with previous investigations), however, in many of the non-scaling environments the J_{AC} = 30 A/m² limit is conservative and the J_{DC} = -1 A/m² limit is perhaps insufficient. One comment should be added to the high corrosion rates at low -J_{DC} caused by anodic depolarization: The data points in Figure 3 represent daily averaged values, and as it is clear from Figure 2b-c, some disturbance of the DC signal is caused by increasing levels of AC. During a day, the currents may have been both anodic and cathodic, i.e. producing high corrosion with temporary anodic currents, but giving an averaged negative DC current. After all, current densities of 10³-10² A/m² on a 1 cm² probe is only 0.1-1 µA of current.

In Figure 4 the corrosion rate data is plotted as a function of J_{AC} at different E_{CN} potential values, (notice the different corrosion rate scales). The data is plotted as daily average for the two ER probes in each environment. In a) corrosion increases and decreases over a J_{AC} interval up to a few hundreds of A/m² due to the anodic depolarization effect illustrated in Figure 3a. The chemical environment does seem to have an influence on the sensitivity to AC corrosion. The high resistivity DI environment exhibits overall lower J_{AC} and corrosion rates, but when corrosion is measured, it occurs at much lower J_{AC} values than for the other experiments. This indicates that not only the current density, but also the AC voltage itself
may be of importance in the corrosion mechanism. The scaling AS environment behaves like the others at low levels of CP (a), as the initial resistivity of the solutions were similar. However, as CP levels increase, the cathodic reaction (3) causes alkalinity and a buildup of calcareous deposits, increasing the spread resistance. This limits $J_{AC}$ in the AS environment and thus the corrosion rates at higher CP levels. Sulfate present in both the NAS and Na$_2$SO$_4$ experiment increases corrosion with higher $J_{AC}$ values, whereas chloride in the absence of sulfate appears to reduce corrosion rates at elevated $J_{AC}$ (though still unacceptably high). The same is true for bicarbonate for $E_ON < -1200$ mV$_{CSE}$ or phosphate for $E_ON < -1100$ mV$_{CSE}$ above which their presence increases the corrosion rate with higher $J_{AC}$ values. Phosphate appeared to inhibit the potential shift and anodic depolarization (Figure 4a). Another interesting observation is, that at high CP levels ($E_ON < -1200$ mV$_{CSE}$), the corrosion rate increases with $J_{AC}$until a maximum after which it decreases. Since this effect does not seem specific to a value of $J_{AC}$, it could also be an AC voltage dependent phenomenon.

![Graphs showing corrosion rate plotted as a function of $J_{AC}$ at different $E_ON$ potentials.](image)

**Figure 4:** Corrosion rate plotted as a function of $J_{AC}$ at different $E_ON$ potentials. a) corrosion due to anodic depolarization. b)-f) AC corrosion caused by high AC current density.

**Field experiments**

In Figure 5 results from the field experiments are presented in the $-J_{DC}/J_{AC}$ plot as corrosion rate measurements based on 48 hours of data. Lines connecting the points indicate the different sites and the progressing $J_{AC}$ and $-J_{DC}$ with time. Only site 4 experienced high $J_{AC}$ and corrosion rates (>100 µm/yr) in the unsafe region. Anodic depolarization caused by AC is not observed. Site 2 and site 5
momentarily entered the unsafe region without experiencing enhanced corrosion. The results follow the standard current density criteria, showing corrosion in the unsafe region, however the $J_{AC} = 30 \text{ A/m}^2$ limit may be conservative.

Figure 5: Field data from Location 1-5, corrosion rates are based on 48 hours measurements

The external parameters such as type of soil and its spread resistance, $R_S$, as well as the induced AC voltage which varies along the length of the pipe, were such that only site 4 experienced AC corrosion. Daily average values for these parameters for all 5 test sites are presented in Figure 6. It is clear that site 4 experiences the highest induced AC voltage and also has the lowest overall spread resistance. Site 2 exhibits a similar low spread resistance, but since the AC level is low at this location, no AC corrosion was measured. Site 5 also experiences high AC interference, but $R_S$ is high resulting in low current densities and thus no AC corrosion. Periods A-G of varying AC and DC levels are indicated.

Figure 6: Daily average $E_{ON}$ and $U_{AC}$ levels at all 5 sites in a), and the evolving $R_S$ in b).
Data from site 4 is shown in Figure 7. Daily and weather dependent variations in the power load on the HVTL’s can be seen. Some $U_{AC}$ peaks exceed the maximum allowable AC touch voltage of 15 V according to NACE(3) SP0177 when the mitigation is detached. However, corrosion may be evaluated based on averaged results. During periods A and B, no corrosion was recorded with $-J_{DC}$ both above or below 1 A/m$^2$ as $J_{AC}$ was below 30 A/m$^2$. In period C, the AC mitigation was detached and during the first days (30/05-01/06) at the same $E_{ON}$ potential, $-J_{DC}$ increased to ~1 A/m$^2$ due to faradaic rectification. Some days later $E_{ON}$ was changed to -1600 mV CSE, causing both $-J_{DC}$ and $J_{AC}$ to exceed the limit values, and the measured corrosion rates rose to more than 1000 µm/yr (> 40 mpy). Cold weather in the middle of period C led to lower AC interference and reduced corrosion. In period D, the potential was increased to -1200 mV CSE, resulting in $-J_{DC}$ slowly descending to < 1 A/m$^2$ as the spread resistance increased (Figure 6b) due to de-alkalization or formation of calcareous deposits. $J_{AC}$ also decreased with increasing $R_S$ to below 30 A/m$^2$ allowing non-corroding conditions to be obtained even during high AC interference. Upon lowering the potential to -1600 mV CSE (period E), corrosion

(3) NACE, National Association of Corrosion Engineers, 15835 Park Ten Place, Houston, Texas 77084
conditions were immediately re-established and corrosion rates reached > 1300 µm/yr (> 50 mpy) within a few days. When the potential was again increased to -1200 mV_{CSE} (period F), corrosion rates slowly decreased as seen in period D. Following this, all the AC mitigation was re-connected to the pipeline section (period G) resulting in an immediate reduction in U_{AC}. At this point the AC and DC voltage conditions were similar to period B, however due to the change in the soils’ spread resistance related to excursions in AC and CP, the current densities remained slightly above the criteria values. Despite this, corrosion was halted. During the experimental period, 65 µm (2.5 mil) of material was lost due to corrosion on the ER probe.

The evolving spread resistance at the different sites is plotted as a function of the cathodic current density in Figure 8 to illustrate their mutual relationship in both the a) laboratory and b) field investigations. In all cases, higher \( -J_{DC} \) yields lower \( R_S \) by alkalinization of the electrolyte and increasing ionic conductivity or inversely; higher \( R_S \) caused by drying of the soil or precipitation of shielding calcareous deposits, for example, will lower \( -J_{DC} \).

![Figure 8: Spread resistance being a function of the cathodic current density for a) laboratory and b) field experiments. The field data represent a much more complex system, but the trend is clear; increasing \( -J_{DC} \) lowers the spread resistance in all investigated environments.](image)

It was observed that different soils exhibit different \( -J_{DC}/R_S \) behavior which is important in the evaluation of the likelihood for AC corrosion in terms of the induced AC current density. Soil samples collected at site 1-5 revealed a significant difference in the chemical environment at the investigated sites. The soil texture varied from loose dirt at site 1 to clayey soil at sites 2-4 and sand at site 5 (Figure 9).

![Figure 9: Soil samples collected during probe installation. The different soils can be seen to vary in type from dirt (a) or clay (b) to sand (e).](image)

The chemical analysis of the soils is presented in Table 3. It should be noted that the EDS analysis is not exhaustive due to limitations in the measurement technique, however still presents a valid measure for comparing different soils. The IC analysis quantifies some of the dissolvable anions in an aqueous solution. It can be seen that the clayey soils 2-4 are rich in Ca, Mg and sulfate ions. Sites 2 and 4 have elevated Cl concentrations. Sites 1-3, all being in the vicinity of farmland, have elevated concentrations...
of nitrite and nitrate from fertilizers. The sandy soil at site 5 consists mainly of quartz; SiO₂. The soils’ bicarbonate content could not be measured by the techniques utilized.

Table 3: Chemistry of the soils by EDS (non-exhaustive element analysis) or IC (dissolved anions)

<table>
<thead>
<tr>
<th>EDS analysis (atomic %)</th>
<th>IC analysis (mg/L)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O  Na  Mg  Al  Si  K  Ca  Ti  Fe</td>
<td>Cl⁻  SO₄²⁻  PO₄³⁻  F⁻  NO₂⁻  NO₃⁻</td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>--------------------</td>
<td>---</td>
</tr>
<tr>
<td>Site 1  69.0 1.0 1.2 5.1</td>
<td>19.8 1.2 1.9</td>
<td>0.03</td>
</tr>
<tr>
<td>Site 2  70.4 0.4 1.8 4.3</td>
<td>16.0 1.0 5.3</td>
<td></td>
</tr>
<tr>
<td>Site 3  70.0 0.1 1.8 3.9</td>
<td>14.6 0.9 7.6</td>
<td>0.10</td>
</tr>
<tr>
<td>Site 4  69.8 0.3 2.0 3.8</td>
<td>15.1 0.9 7.2</td>
<td>0.05</td>
</tr>
<tr>
<td>Site 5  67.8 0.6 0.8 2.5</td>
<td>25.9 0.5 1.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 4 displays some of the characteristics of the different soils. The soil resistivity was measured on collected soil samples and the corresponding R_Scalc. is calculated using available geometrical models. Since R_S measured in the field varied significantly during the experimental period (Figure 6b) the minimum and maximum R_S is indicated for each site. R_Scalc. Calculated using ρ₀ is in the lower range of or below the measured R_S values. This may easily be explained by the Ca and Mg content and the initially neutral to weakly alkaline pH of the soils at sites 2-4. With cathodic protection and alkalization by reaction (3), calcareous deposits are expected to form, increasing R_S.

Table 4: Characteristics of the soil at different sites.

<table>
<thead>
<tr>
<th>ρ₀ (Ωm)</th>
<th>R_Scalc. (Ωm²)</th>
<th>R_Smin (Ωm²)</th>
<th>R_Smax (Ωm²)</th>
<th>pH₀</th>
<th>BNE (mol/kg)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>44.5</td>
<td>0.147</td>
<td>0.097</td>
<td>2.215</td>
<td>8.62</td>
<td>6.4</td>
</tr>
<tr>
<td>Site 2</td>
<td>10.4</td>
<td>0.034</td>
<td>0.038</td>
<td>0.132</td>
<td>8.50</td>
<td>9.6</td>
</tr>
<tr>
<td>Site 3</td>
<td>12.2</td>
<td>0.040</td>
<td>0.119</td>
<td>0.824</td>
<td>7.65</td>
<td>8.8</td>
</tr>
<tr>
<td>Site 4</td>
<td>12.7</td>
<td>0.042</td>
<td>0.025</td>
<td>0.718</td>
<td>7.87</td>
<td>10.8</td>
</tr>
<tr>
<td>Site 5</td>
<td>282.0</td>
<td>0.929</td>
<td>0.106</td>
<td>2.964</td>
<td>8.40</td>
<td>3.2</td>
</tr>
</tbody>
</table>

The Ca and Mg content influence the soils’ BNE due to precipitation of hydroxides in alkaline media which consumes some of the formed hydroxyl ions. Upon comparison of the evolving R_S in Figure 6b and the soils’ BNE, it can be seen that the clayey soils with a high BNE show decreasing R_S under high CP conditions whereas the opposite is true for soils with a low BNE. This is in contrast to what would be expected. The BNE characterization does not take into account the soils diffusion properties however.

**DISCUSSION**

Laboratory and field data in the present study was shown to be in good agreement with the current density criteria outlined in industry standards, though indicating that chemistry plays a role. The J_AC/J_DC < 3 threshold was not reached during experimentation and thus could not be evaluated. Investigation of this criterion has been conducted by others, however at unrealistically high CP levels. In the laboratory studies presented, a form of AC corrosion was observed under insufficient cathodic protection caused by anodic polarization of the steel under AC perturbation. Anodic depolarization caused by AC is well documented. Also as an effect observed over a limited AC current density range up to a few hundred A/m². This is not treated in the AC corrosion standards except for a mentioning of the risk of not complying with general cathodic protection standards at low DC current density. Besides, AC corrosion observed at high cathodic polarization generates far higher corrosion rates.

This study may cause a re-evaluation of the -850 mV_CSE protection criterion or alternatively introduction of a minimum (cathodic) -J_DC limit, in the special case of AC interference, supporting the findings of Xu et al. and Du et al. However, the investigations herein are in no way sufficient to present alternative criteria, as it was found that soil chemistry may also play a part in this. Furthermore, laboratory
experiments were merely screening a series of AC and DC settings (daily), but as the field experiments showed, prolonged periods (possibly weeks) in a given setting are needed to see the full development of the environment; e.g. $R_s$.

Another effect of AC interference is faradaic rectification causing significantly higher $-J_{DC}$ at static $E_{ON}$ as was shown in both the laboratory and field experiments (Figure 2 and Figure 7). $-J_{DC}$ is confirmed to have an effect on $R_s$ and thus indirectly on $J_{AC}$ at an AC voltage through equation (1). As such, a combination of both high AC and DC current densities may cause AC corrosion to become a self-perpetuating process where AC enhances DC current, and DC enhances AC current.$^{12,15-18}$

The present investigation of various chemical constituents suggests that chloride may have a reducing effect on very high AC corrosion rates but the presence of sulfate may hinder this effect. An explanation for this observation may lie in the AC corrosion mechanism suggested by Büchler and Schönreich who proposes that AC corrosion propagates by a continuous oxidation and reduction of a passive film to a porous rust layer with the AC frequency.$^{40}$ Chlorides are known to destabilize passive films on steels which will limit the passive film formation step and thus the corrosion mechanism. Sulfate ions may adsorb to the surface and inhibit the destabilizing nature of chloride ions on the passive film which will enhance the corrosion mechanism.$^{41,42}$ Sulfates may increase corrosivity of a NaCl solution steel by an increase of the corrosion current or a decrease of the charge transfer resistance, essentially the same notion.$^{43,44}$ An increased faradaic current will also increase AC corrosion. Thus, sulfates may increase AC corrosion rates, and were also found in higher concentrations at site 4 in the field study that showed AC corrosion. Chlorides are not to be understood as a corrosion inhibitor. With increasing concentrations of chlorides, $R_s$ drops as was observed at site 2 and 4 and current densities and corrosion increases.

The presence of scale forming constituents Ca and Mg or low resistivity soils were found to limit current densities and thus the prerequisites for very high AC corrosion rates. These factors did, however, alter the current density limits above which corrosion $>25 \mu m/yr$ was observed (Figure 3b and Figure 4). This indicates that the AC voltage and DC potential are also of importance to the AC corrosion mechanism. The presence of both Ca and Mg in the soil at site 4, may partially explain the higher corrosion rates in the field experiment at comparable current densities above the criteria limits when comparing the $-J_{DC}/J_{AC}$ plots (Figure 3a and Figure 5). Scale formation may also be the cause of the increasing $R_s$ during period D which stopped AC corrosion at site 4. Instability of the scale under CP + AC interference, hypothesized to be due to hydrogen evolution or alternating voltage, has previously been reported by the present authors and is in line with the observations in this study.$^{12}$

The phosphate buffer and the bicarbonate with the highest BNE showed little effect on limiting AC corrosion and at high polarization their presence was found to enhance it. It is estimated that at sufficiently high $-J_{DC}$ the rate of OH$^-$ production overcomes the capacity of the buffering reactions. In the field experiments the soils with high BNE did not stabilize the spread resistance either, which can also be attributed to limitations in the OH$^-$ consuming reactions in these soil systems. In addition, the 3 soils with high BNE also contained clay which may limit diffusion of OH$^-$ away from the surface, while also providing low initial resistivity.

The presented field study illustrates how difficult it is to evaluate AC corrosion likelihood based on soil resistivity and induced voltage only, for example. Using ER probes representing a worst-case coating defect scenario at highly interfered locations on a pipeline, the corrosion can be directly measured. CP parameters can then be controlled to stop AC corrosion even at AC or DC current densities above the standard thresholds since measuring corrosion rate is also a valid protection criterion for AC corrosion. It has been shown, in both laboratory and field experiments, that it is possible to establish AC corrosion free conditions even under high AC interference $U_{AC} > 15$ V by limiting the DC current and thus the cathode reaction (3). However, the synergetic relationship between $J_{AC}$ and $-J_{DC}$ illustrated in this paper makes it a tedious task to finetune a CP system to deliver $>-1$ A/m$^2$ when experiencing high AC interference due to faradaic rectification.

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AC mitigation installations were also proven effective in lowering the induced AC to levels where AC corrosion was stopped, however a cost assessment of the AC corrosion mitigation strategy will need to be considered. In the present field study, peak AC voltages above 15 V were measured and thus AC mitigation would be necessary nonetheless to comply with safety regulations.

CONCLUSIONS

AC corrosion experiments with varying AC and DC levels and soil chemistry were carried out in controlled laboratory settings and the results compared to field data obtained on a pipeline section influenced by AC interference. A wide range of AC and DC current densities were studied and used to verify present limit values for AC corrosion mitigation. It was found that:

- Laboratory data illustrated a form of AC corrosion up to ~150 µm/yr, caused by anodic depolarization and insufficient cathodic protection at low CP levels ≥ -900 mV\text{CSE} and intermediate AC current densities 10 A/m² < J\text{AC} < 200 A/m² not recognized by the standards.
- Both laboratory and field data confirmed very high AC corrosion rates > 1300 µm/yr under excessive cathodic protection -J\text{DC} > 1 A/m² and AC interference J\text{AC} > 30 A/m².
- Both laboratory and field data confirm a relation between -J\text{DC} and the spread resistance, R\text{s}, which is dependent on the chemical environment. R\text{s} is also influenced by moisture and buildup of calcareous deposits.
- Both laboratory and field data confirmed a strong mutual dependence between AC and DC: adjusting one will inevitably affect the other, either by faradaic rectification of AC causing high -J\text{DC}, or high -J\text{DC} influencing R\text{s} which determines J\text{AC} at any interfering U\text{AC}.
- A soil's resistivity is not a representative measure of corrosivity or response to the alkaline environment at a cathodic coating defect. The spread resistance of a coating defect is a highly dynamic parameter under AC and DC influence.
- High resistivity soils or calcareous deposits may lower the J\text{AC} threshold for corrosion, but in the case of calcareous deposits increase the -J\text{DC} threshold. In either case these environments will limit both AC and DC current that cause very high corrosion rates.
- Chlorides may reduce very high AC corrosion rates, possibly due to the destabilization of a passive film. The presence of sulfate has the opposite effect and enhances very high AC corrosion rates.
- Corrosion was only experienced at one out of five field experiments where a combination of low soil resistivity and high induced U\text{AC} caused high J\text{AC} and -J\text{DC}.
- The investigations herein illustrate that the chemical environment does alter the AC and DC current density limits for AC corrosion, however the present limits (-J\text{DC} < 1 A/m² and J\text{AC} < 30 A/m²) constitute a safe strategy in most environments.
- AC corrosion can be mitigated by either careful control of -J\text{DC} or by reducing the induced U\text{AC} by conventional AC mitigation installations as demonstrated in both laboratory and field experiments.

ACKNOWLEDGEMENTS

This work was carried out in collaboration with the Technical University of Denmark and MetriCorr. The authors would like to thank the Danish Innovation Fund for economical support of this research, and kind support with IC soil analysis by the department for environmental science at DTU.

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15. A. Junker and L. V. Nielsen, "Monitoring of the pH Evolution at a Cathodically Protected Steel Surface Subject to an AC Voltage Perturbation," in CeoCor, Luxembourg, 2017.


4.6 [VI] CeoCor ’18

This paper picks up the trail from the 2017 CeoCor paper "Monitoring of the pH Evolution at a Cathodically Protected Steel Surface Subject to an AC Voltage Perturbation" and applies micro pH electrodes to investigate the pH evolution closer to the surface. A relationship between cathodic current density and pH is established, and used to discuss a series of galvanostatic and potentiostatic CP investigations in relation to the Pourbaix diagram. A de-alkalisation mechanism is discovered, that may explain large discrepancies in literature data on the factors leading to AC corrosion.
AC Corrosion and the Pourbaix diagram

by A.Junker and L.V.Nielsen (MetriCorr, Roedovre, Denmark)
P.Moller (Technical University of Denmark, Kgs.Lyngby, Denmark)
AC Corrosion and the Pourbaix Diagram

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Abstract

AC interference on cathodically protected pipelines is of major concern due to the risk of AC corrosion. Corrosion is generally linked to AC and DC current densities, but incoherence in data from different researches is often difficult to explain. In this paper, ER-probe corrosion rate data from multiple experiments is used to illustrate how the accepted AC and DC current density criteria may, in fact, be closely linked to thermodynamically calculated Pourbaix diagrams. The concepts are illustrated by simple model experiments and discussed in a theoretical context, based on literature. AC is shown to cause de-alkalisation of steel under galvanostatic cathodic protection, possibly causing low pH corrosion. This discovery may necessitate a critical re-evaluation of literature investigations of AC corrosion under galvanostatic cathodic current.

Introduction

The Pourbaix diagram or potential/pH diagram depicts the electrochemical stability regions of different metal and mineral phases with respect to potential and pH. Once one understands the applicability of these diagrams they are extremely useful for corrosion engineers. Figure 1 shows the Pourbaix diagram for iron calculated at standard conditions (25°C, 1 bar) and the Gibbs free energy, ΔG, of the involved substances. The potentials are given with respect to the Cu/CuSO₄ electrode (CSE) (shifted -316 mV with respect to the hydrogen electrode).

<table>
<thead>
<tr>
<th>Substance</th>
<th>ΔG (kcal./mol)</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.000</td>
<td>Iron</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>-177.114</td>
<td>Hematite</td>
</tr>
<tr>
<td>Fe₂O₄</td>
<td>-242.645</td>
<td>Magnetite</td>
</tr>
<tr>
<td>Fe(OH)₂</td>
<td>-117.464</td>
<td>Ferrous hydroxide</td>
</tr>
<tr>
<td>FeO₂H</td>
<td>-116.928</td>
<td>Goethite (α)</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>-4.107</td>
<td>Ferric ion</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>-21.875</td>
<td>Ferrous ion</td>
</tr>
<tr>
<td>HFeO₂⁻</td>
<td>-95.353</td>
<td>Dihypoferrite ion</td>
</tr>
</tbody>
</table>

Figure 1: Calculated Pourbaix diagram for iron in neutral to alkaline environment. Varying concentrations (log(mol/L)) of dissolved ions influence the stability regions. Potentials with respect to Cu/CuSO₄.
The values of $\Delta G$ used here differ slightly from those originally used by Pourbaix which explains the larger HFeO$_2$ region compared to traditional Pourbaix diagrams (Pourbaix used $\Delta G = -90.627$ kcal./mol for the dihypoferrite ion). [1] The listed values are standard values in the HSC Chemistry software used for the calculation. The choice of considered species for drawing the diagram introduces a narrow Fe(OH)$_2$ region below Fe$_3$O$_4$, and a region of stability, at higher potentials, being either FeOOH or Fe$_2$O$_3$.

To be able to use the Pourbaix diagram and conclude anything about a corrosion process, one needs to be able to determine the necessary potentials and pH. Both have practical challenges:

- Potential measurements will always be an average across local surface potential variations. Even for polarised surfaces.
- For polarised surfaces, the local potential variations may be small, but here, an IR drop needs to be considered, due to the current passing through the electrode/electrolyte interface.
- One can only discuss a potential with respect to a reference potential. Several reference electrodes exist, but they may all suffer from potential drift (for various reasons) and require careful calibration and maintenance.
- Most pH measurements also rely on potential measurement, and thus the same challenges as for potential measurements exist here.
- Potential sensitive pH measurement techniques cannot be performed in the electric field of a polarised surface without introducing an error.
- pH measurement by conventional methods requires a certain measurement volume but the pH gradient towards a cathodically protected surface is very steep, yielding an infinitely small measurement volume for obtaining the true surface pH.

In this study, pH is measured using small pH glass tip electrodes and efforts have been made to minimize the effects of drifting potentials by calibration before and after and compensation of data accordingly. In addition, the electric field from cathodic protection and AC interference was periodically turned off during pH measurements. The biggest challenge with regard to pH measurement faced in this study was the limited measurement volume and the placement of the electrodes.

For comparison with large amounts of data, in which no actual pH measurement was available, the close correlation between the cathodic current density and pH is utilized. [2] Figure 2 shows measured pH as a function of cathodic current density compared to data measured by several other authors (using various techniques). This Figure is a reprint from previous work by Angst et al. (2016) with the inclusion of additional data points, especially in the high pH region. [3] [4]

![Figure 2: Achieved pH of a steel electrode as a function of the cathodic protection current density. Reprint from [3] with additional data [4]. Full line is a fit of all datapoints.](image_url)
The line is a fit of all data points with \( p = 0.714 \) and \( pH_0 = 12.318 \) in equation (1). This is very similar to the values suggested by Büchler and Joos (2016) \( (p = 0.5 \) and \( pH_0 = 12.4) \) with a slightly stronger dependence on \(-J_{DC}\) due to the higher p-value. \[ p = p_0 + p \log(J_{DC}) \] (1)

By using this simple equation, in which the current density is an easily measured parameter, one has a good approximation of the actual surface pH of steel under cathodic protection.

Surface potential measurement is a fundamental part of cathodic protection monitoring. However, it is debated whether, even under cathodic protection, each individual coating defect on an entire pipeline has its own potential, and that the measured pipeline potential is found to follow the potential of larger defects. [6] In laboratory investigations where a single simulated coating defect is investigated, this discussion is of less importance. IR drop compensation to obtain the true surface potential may be achieved by different methods, as outlined below:

- Laboratory investigations often use a Luggin capillary to provide a conductive path, in which no current runs, between the reference electrode and the surface to be measured. This method is obviously impractical for pipeline applications with coating holidays of unknown numbers and locations. Even in laboratory use, the placement of the Luggin capillary becomes important since the majority of the IR drop occurs in very close proximity to the electrode where the current density in the electrolyte is highest.

- On-Off potential measurements, in which the polarisation current is momentarily disrupted, are routinely used to determine a pipeline’s ‘polarised or instant-off potential’. This method is linked with a possible error relating to the way in which the depolarisation behaviour of the steel is interpreted. Furthermore, it requires techniques to filter out AC in the event of AC interference on the pipeline.

- Measurement of the current density and area specific spread resistance of a probe or coupon to determine the IR-free potential can also be employed. Since AC current is not subject to the same polarisation behaviour as DC, the spread resistance of a defect may be derived from Ohm’s law (2) in which the AC voltage and current density are measurable.

\[ U_{AC} = J_{AC}R_S \] (2)

This allows for the IR-free potential to be determined, via (3), since \( J_{DC} \) is also measurable.

\[ E_{IR-free} = E_{on} - IR = E_{on} - J_{DC}R_S \] (3)

This method relies on the presence of some AC, and thus for investigating AC corrosion this requirement is not an issue. Essentially, the spread resistance is a frequency-dependent impedance, but at 50/60 Hz the impedance of the double layer capacitance is low, validating the use of (3). [7] [8]

This study uses the relationship between the current density and the spread resistance and the continuous logging of these parameters (using a MetriCorr™ ICL-02/logger) to determine the IR-free potential.

As a baseline for the further discussion; the terms ‘polarised potential’, ‘instant-off potential’, ‘IR-free potential’, ‘true surface potential’ or other alternative descriptions, can be used interchangeably.

**Method**

All corrosion experiments in this study were made using 500 µm carbon steel ER probes from MetriCorr™, having an exposed area of 1 cm² with a length/width ratio of 10/1.

pH monitoring under cathodic protection was performed using different pH glass tip electrodes. To account for the steep pH gradient towards the steel surface [4], small electrodes with a tip size of 200 µm (PH-200 from Unisense®) were used (* in Figure 4). These are extremely fragile and broke upon contact with the electrode surface, thus the placement in these experiments was “as close as possible” without risking contact. In addition, a more robust 3 mm tip pH electrode (PHC3359-8 from Radiometer®), shielded on the sides with polymeric shrink sleeve, was brought into contact with the surface. In order to allow for diffusion in and out of the volume, the probe was retracted 100 µm using

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1 MetriCorr, Toerringvej 7, 2610 Roedovre, Denmark
2 Unisense, Tueager 1, DK-8200 Aarhus N, Denmark
3 Hach, Loveland, CO 80539, US
a micro-manipulator (** in Figure 4). The latter proved more unstable, probably due to gas bubbles momentarily blocking the sensitive surface or a higher sensitivity to electrical noise.

As glass pH electrodes are influenced by electric fields, the experimental setup was equipped with timers disrupting the DC and AC (if any) current in a 10/60 s open/closed sequence. The difference between pH measurements with and without current was significant, i.e. several units of pH at times. The pH electrode was logging every second using a Unisense pH/mV-meter coupled with the Sensor Trace Suite Logger software. During the 10 seconds disruption of current the pH stabilised and a value could be read. The pH electrodes were calibrated both before and after the experiment in pH = 4.01, 7.01 and 10.01 buffer solutions and any drift of the readings during the experiment was compensated for. The experimental setup can be seen in Figure 3. The AC/DC circuit for AC interference and cathodic protection is similar to that used in previous studies. [9] The 3 mm pH electrode was equipped with an internal reference electrode while the 200 µm pH electrode was coupled with an external calomel electrode (SCE).

![Figure 3: Experimental setup for AC interference of cathodically protected ER probe as well as pH measurement of the protected surface. Cathodic protection in potentiostatic or galvanostatic setting using a suitable shunt.](image)

All experiments conducted in this study were sand box experiments (0.4 – 0.8 mm, quartz sand) with a simulated non-scaling artificial soil solution (NAS) according to Table 1. In some experiments the pH was adjusted by addition of NaOH and measured using a pH electrode. The standard NAS solution mixed with sand has a soil resistivity of 17.3 Ωm and neutral pH.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td>5.0·10^{-3} M</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>2.5·10^{-3} M</td>
</tr>
<tr>
<td>NaCl</td>
<td>10.0·10^{-3} M</td>
</tr>
</tbody>
</table>

Different approaches were chosen to investigate the high pH dihypoferrite corrosive region. These are outlined in experiment I–III:

I. A pH of 13.5 was achieved by the addition of NaOH to the NAS. Applied AC interference was increased from 1.5 to 5 V. This was done, first at the free corrosion potential (exp. 1a), and secondly polarised with DC to obtain an IR-free potential of -1.11 V$_{CE}$ on the hydrogen line in the HFeO$_2$ region (exp. 1b). Additional measurements were performed at 6.3 V$_{AC}$.

II. A constant cathodic current of $J_{DC} = -30$ A/m$^2$, was introduced, theoretically yielding pH = $12.318 + 0.714\cdot\log(30) = 13.4$. AC interference was induced and increased from 1-25 V while the IR-free potential and other electrical parameters were logged.

III. A pH = 12 NAS-solution was used and a constant cathodic current of $J_{DC} = -0.3$ A/m$^2$ was induced theoretically maintaining the pH = $12.318 + 0.714\cdot\log(0.3) = 11.95$. AC interference was induced and increased from 1-37 V. while the IR-free potential and other electrical parameters were logged.

In all experiments each AC/DC setting was kept constant for a minimum of two days in order to evaluate corrosion rate on an ER probe.
Results

Monitoring of the steel surface pH under cathodic protection proved very difficult with the given experimental setup and choice of micro pH-electrodes. The results shown in Figure 4a are three readings obtained under varying conditions. In all the experiments under cathodic protection, the measured pH increased quickly to above pH = 11 proceeding to stable levels of pH = 11.95 ($J_{DC} = -0.132 \text{ A/m}^2$) and pH = 12.07 ($J_{DC} = -1 \text{ A/m}^2$) in the galvanostatic experiments. In an experiment under potential control and overlying AC ($-1.5 \text{ V}_{\text{CSE}}, 10 \text{ V}_{\text{AC}}$), pH increased to 13.37 at a final $J_{DC} = -26.3 \text{ A/m}^2$ (see Figure 5). These results are those included in Figure 2 for comparison with other studies.

Figure 4: pH evolution over time at various cathodic protection settings. a) Two experiments in galvanostatic setting and one under -1.5 V$_{\text{CSE}}$ potential control as shown in Fig. 3 with 10 V AC. b) The effect of high alternating current on pH on the -1 A/m$^2$ cathodic current probe. (*) 200 µm tip pH glass electrode. ** 3 mm tip pH glass electrode with shielded sides. See Methods.)

To investigate the influence of AC on the pH of a cathodically protected surface, increasing AC current densities $J_{\text{AC}} = 10, 35, 100, 230, 500$ and $1000 \text{ A/m}^2$ were introduced on the $J_{\text{DC}} = -1 \text{ A/m}^2$ surface, and held constant for 30 minutes at each level. No effect was visible until 1000 A/m$^2$ at which point the pH began to decline (Figure 4b). The current density was left at 1000 A/m$^2$ resulting in the pH declining to neutral pH = 8.5 after 3 hours, despite a constant cathodic current density of -1 A/m$^2$. This may be explained by consumption of hydroxyl ions (4) during the anodic cycle of AC.

$$4\text{OH}^{-} \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \quad (4)$$

The cathodic cycle of AC is likewise expected to increase the hydroxyl concentration, but differences in the kinetics of the oxygen and hydrogen evolution reactions may explain the overall lowering of pH.

$U_{\text{AC}} = 50 \text{ V}$ alternating voltage was needed to reach the high current density of 1000 A/m$^2$. This caused depolarisation of the steel to $\sim 500 \text{ mV}_{\text{CSE}}$ which is not representative of steel under cathodic protection. As pH reduced to 8.5 and settled, the IR-free potential reduced to $\sim 770 \text{ mV}_{\text{CSE}}$, which corresponds well with a point on the hydrogen-line in the Pourbaix diagram at pH = 8.5 (Figure 1).

Figure 5 shows a probe under potential controlled cathodic protection and 15 V AC interference. The potential was kept at -1500 mV$_{\text{CSE}}$ for 7 days, after which it was changed to -1000 mV$_{\text{CSE}}$. 
Figure 5: 15 V AC on an ER probe under cathodic protection at first -1500 mV to resulting in heavy corrosion, and after 7 days -1000 mV halting AC corrosion. The pH and spread resistance were monitored.

pH was measured using a shielded 3 mm electrode (**). Upon applying CP to the system, the pH immediately rose to pH > 11, thereafter increasing at a much lower rate. Although the change in potential after 7 days resulted in a reduction of the cathodic current to <1 A/m², the pH remained high. Lowering of pH relies on diffusion of OH⁻ ions away from the surface, which is a slow process. However, it is suspected that the actual pH may have changed faster than measured due to the experimental design. There is a possibility of a high response time of the shielded electrode due to the thin crevice on the sides of the pH sensitive glass sphere. Figure 5d illustrates the commonly recognized relationship between pH and spread resistance. As can be seen, corrosion is immediately stopped upon changing the potential, while the pH remains unchanged. This indicates that that it is not a pH dependent mechanism. A possible explanation of this can be found in the Pourbaix diagram in Figure 1: the IR-free potential in Figure 5b immediately changes from -1100 mV to -1000 mV, which, despite being only a difference of 100 mV, shifts the steel out of the 10⁻² mol/L stability region of HFeO₂⁻.

Figure 6 and Figure 7 show corrosion rate data from experiment I-III. The results of these experiments are outlined below:

I. In Figure 6b and Figure 7 it can be seen that no corrosion was recorded when the potential was left under free corrosion conditions (experiment Ia), despite high pH = 13.5 and increasing AC interference. When polarised to -1.11 V to (on the hydrogen line in the HFeO₂⁻ region) (experiment Ib), no corrosion was detected until the level of AC interference was increased. This may be interpreted as disappearance of the high pH corrosion region due to an initial increase of the concentration of HFeO₂⁻ ions. However, upon increasing AC, these ions are continuously oxidised during anodic polarisation or reduced during cathodic polarisation, thus the HFeO₂⁻ concentration remains low, stabilising the high pH corrosion.
Table 2 shows measured values during experiment Ia and b. The AC current densities were high despite low $U_{AC}$ levels due to the very low spread resistance of the high pH solution.

Table 2: Measured parameters in experiment I

<table>
<thead>
<tr>
<th>$U_{AC}$ ($V$)</th>
<th>$E_{ON}$ ($V_{CSE}$)</th>
<th>$E_{IR-free}$ ($V_{CSE}$)</th>
<th>$J_{AC}$ (A/m$^2$)</th>
<th>$J_{DC}$ (A/m$^2$)</th>
<th>$R_D$ (mΩm$^2$)</th>
<th>$V_{corr}$ (µm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) &quot;free&quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>-0.26</td>
<td>-0.26</td>
<td>399</td>
<td>-0.10</td>
<td>4.0</td>
<td>0</td>
</tr>
<tr>
<td>2.6</td>
<td>-0.25</td>
<td>-0.25</td>
<td>616</td>
<td>-0.09</td>
<td>4.2</td>
<td>0</td>
</tr>
<tr>
<td>3.7</td>
<td>-0.21</td>
<td>-0.21</td>
<td>781</td>
<td>-0.07</td>
<td>4.7</td>
<td>0</td>
</tr>
<tr>
<td>5.2</td>
<td>-0.12</td>
<td>-0.12</td>
<td>484</td>
<td>-0.04</td>
<td>11.4</td>
<td>0</td>
</tr>
<tr>
<td>6.3</td>
<td>-0.82</td>
<td>-0.82</td>
<td>436</td>
<td>-0.03</td>
<td>14.6</td>
<td>0</td>
</tr>
<tr>
<td>b) polarised</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>-1.11</td>
<td>-1.11</td>
<td>233</td>
<td>-0.2</td>
<td>6.4</td>
<td>0</td>
</tr>
<tr>
<td>2.6</td>
<td>-1.11</td>
<td>-1.11</td>
<td>316</td>
<td>-0.4</td>
<td>8.3</td>
<td>0</td>
</tr>
<tr>
<td>3.6</td>
<td>-1.12</td>
<td>-1.11</td>
<td>542</td>
<td>-1.8</td>
<td>6.6</td>
<td>77</td>
</tr>
<tr>
<td>5.0</td>
<td>-1.13</td>
<td>-1.11</td>
<td>810</td>
<td>-3.5</td>
<td>6.3</td>
<td>294</td>
</tr>
<tr>
<td>6.2</td>
<td>-1.18</td>
<td>-1.11</td>
<td>1138</td>
<td>-13.9</td>
<td>5.5</td>
<td>5215</td>
</tr>
</tbody>
</table>

The non-polarised experiment (Ia) exhibited an increasing spread resistance upon increasing the AC interference, lowering the AC current densities. For the polarised experiment (Ib), the artificially maintained pH allowed for high AC corrosion rates at $E_{ON}$-potentials that are not usually associated with AC corrosion. Upon increasing the AC interference of the polarised probe, the on-potential necessary to maintain the IR-free potential decreased due to depolarisation while $-J_{DC}$ increased (Table 2). An explanation may lie in de-alkalisation caused during positive AC potential excursions, necessitating an increased cathodic current to maintain high pH and the pre-set IR-free potential.

II. At a galvanostatic cathodic current of $J_{DC} = -30$ A/m$^2$ the potential was allowed to float. At zero AC interference, the IR-free potential was as low as -1.5 V$_{CSE}$, placing the steel in the immune region where no corrosion was measured. Upon increasing the AC interference, the steel de-polarised into the HFeO$_2$ stability region. Corrosion rates increased until the IR-free potential passed the $10^{-4}$ mol/L line at -1.082 V$_{CSE}$ (Figure 6b), above which the corrosion rates again declined (Figure 7). This is difficult to explain using traditional AC corrosion mechanisms [10], but has also been observed in other studies. [11] Pourbaix himself showed that the corrosion rate inside the high pH corrosion region increases towards the upper stability limit (at higher potentials). [1]

III. At pH = 12 and a galvanostatic current of $J_{DC} = -0.3$ A/m$^2$, high pH corrosion was not observed. It occurred, instead, at much higher IR-free potentials (above -0.85 V$_{CSE}$). This experiment is similar to that in Figure 4b (very high AC interference and a small constant cathodic current, but no control of the potential) that showed de-alkalisation, and a subsequent settling of the IR-free potential on the hydrogen line in the low pH corrosion region. The same mechanism is suspected to place the high measured corrosion rates inside the low pH corrosion region, by a projection of the measured IR-free potentials onto the hydrogen line (Figure 6a), provided that the constant cathodic current is due, solely or mainly, to hydrogen evolution, and not reduction of alternative species such as corrosion products. This implies that an IR-free potential more positive than the hydrogen line at a theoretical pH(-$J_{DC}$) given by equation (1) may be used as an approximate pH measurement in a galvanostatic CP experiment.

The corrosion rate in experiment Ib was extremely high: $>5$ mm/yr, measured over 3 days. This is high even for AC corrosion, but perfectly demonstrates the impact of the three factors: an IR-free potential inside the high pH corrosion region, high pH and high AC interference. The circumstances for these conditions to be fulfilled may be very dependent on the chemical system possibly explaining the variation of corrosion rate data in different studies.
Figure 6: Plot of corrosion rate data from experiments I-III. a) Pourbaix diagram. Exp. I and II illustrate how corrosion is present primarily inside the $10^{-6}$ mol/L HFeO$_2^-$ area (and not above or below). Corrosion in exp. III can be explained as low pH corrosion by projection of all points above the hydrogen line onto the hydrogen line via de-alkalisation as demonstrated in Figure 4b. b) pH = 13.5 cross-section of the Pourbaix diagram showing the effect of increasing AC: i.e. depolarisation of exp. II and stabilisation of the HFeO$_2^-$ region in exp. Ib.

Figure 7: Corrosion rate data from Exp I-III as a function of $J_{AC}$. Corrosion rate increases in exp. II upon entering the $10^{-4}$ mol/L HFeO$_2^-$ region, and decreases at higher $J_{AC}$. Exp. II illustrates how AC stabilises the high pH corrosion region.

Processing of previously published data

The correlation between $J_{AC}$ and pH in conjunction with the IR-free potential and the corrosion rate measured from ER probes, allows for mapping of corrosion rates directly in the Pourbaix diagram. Numerous experiments have been carried out in other studies reporting these parameters, but have not previously been presented in this way. Data from specific studies, as referenced, has been treated and is shown in Figure 8. Corrosion rate data measured with ER probes is presented in first the $J_{AC}-J_{DC}$ plot with indication of the EN15280:2015 criteria ($-J_{DC} = -1$ A/m$^2$, $J_{AC} = 30$ A/m$^2$ and $J_{AC}/-J_{DC} < 3$). The same corrosion rate data is presented in an adjacent Pourbaix diagram representation based on the IR-free potential and the pH calculated from $-J_{DC}$ using (1). De-alkalisation caused by AC, as demonstrated in Figure 4b, is not suspected to take place in any of the presented data. This effect has only been proven under galvanostatic controlled CP and all of the data presented in Figure 8 are from potentiostatic controlled CP experiments.
As was found in experiments I-III, the correlation between high corrosion rates and the $10^4 \text{HFeO}_2^-$ region in the Pourbaix diagram is remarkable. One is drawn towards the conclusion that the empirically determined $J_{AC}$ and $J_{DC}$ current density limits simply outline conditions that may bring the steel into the high pH corrosion region. For example, the $J_{DC} = -1 \text{ A/m}^2$ limit corresponds to $\text{pH} = 12.3$ using equation (1) and the pH value at which the $10^4 \text{HFeO}_2^-$ region begins is $\text{pH} = 12.2$ (using the stated Gibb’s free energies in Figure 1).

**Discussion**

The findings of this simple study imply that a distinction between galvanostatic and potentiostatic cathodic protection is necessary when investigating AC corrosion.

It is generally accepted that the $-0.85 \text{ V}_{\text{CSE}}$ criterion for CP is linked to passivation by alkalisation. [3] This study postulates that depolarisation of a system under galvanostatic CP can be caused by the inverse mechanism; de-alkalisation of the local environment caused by AC, as shown in Figure 4b.
The amount of data presented in this study is insufficient to establish correlations between AC interference, IR-free potential and pH. However, from this study the de-alkalisation appears to be an AC dependent phenomenon, causing a positive shift of the IR-free potential, apparently linked to the hydrogen line when a cathodic current is present.

This observation can prove important to the present understanding AC corrosion under CP. This is due to the fact that a large amount of investigations are based on galvanostatic DC currents because this provides overview of the effect of varying this parameter. [13] However, the information obtained about the influence of AC on the corrosion rate might relate to the low pH corrosion region. This is not comparable to the situation of potential controlled cathodic protection representing the vast majority, if not all of real-life CP systems.

Du et al. (2017) carried out a series of galvanostatic tests at DC current densities: \( J_\text{DC} = -0.023 \), -0.3, -1.65 and -18.16 A/m\(^2\) with increasing AC current density \( J_\text{AC} = 0, 30, 100, 200 \) and 300 A/m\(^2\). [13] They found that AC caused a strong depolarisation over 4 days and the effect was more pronounced in the high DC current experiments. In the low DC current density experiments, a maximum potential of \(~0.83\) V\( \text{CSE} \) appeared to be reached at 300 A/m\(^2\) \( J_\text{AC} \). In the light of the findings in the present study, this may be explained by de-alkalisation. As the DC current is kept constant, ensuring an IR-free potential close to the hydrogen line, this may be interpreted directly as a pH-value. This suggests a correlation between the maximum degree of de-alkalisation, and the \( J_\text{AC} \) and \( J_\text{DC} \) settings.

The above point will most likely also be true for the many studies of AC interference on steel not subject to CP that claim to investigate AC corrosion of pipelines. [14] [15] [16] [17] [18] AC interference of increasing magnitude may cause de-alkalisation and thus low pH corrosion, however this system is fundamentally different to that of steel under cathodic protection.

Potentiostatic CP will be influenced differently by increasing AC interference. In this case, AC depolarisation will cause enhancement of the cathodic current with increasing AC interference (via faradaic rectification [2]) causing an increase in pH, as well as a shift of the IR-free potential towards the hydrogen line via lowering of the hydrogen overvoltage. The combined effect may cause the steel to enter the high pH corrosion region.

If the \( E_{\text{IR-free}} \leq -850\) mV\( \text{CSE} \) criterion is fulfilled, there should theoretically be no chance of low pH corrosion under potentiostatic CP. However, due to a commonly observed shift of steels OCP to \(<-850\) mV\( \text{CSE} \) with AC interference, the presence of AC may render this criterion insufficient to avoid corrosion. This causes anodic corrosion and should not be confused with effects of de-alkalisation, nor with high pH corrosion. [9] [11]

pH is a common parameter to change in experiments, i.e. using high or neutral pH environments, often under the assumption that this is representative of steel with or without cathodic protection. [15] [10] [19] The findings of experiment I shows that the IR-free potential is significant in terms of placement in the Pourbaix diagram, proving that assumption untrue. In addition, AC seems necessary to stabilise the high pH corrosion region. Studies have been made in which it was tried to provoke AC corrosion in the high pH corrosion region, but it was not found to be significant. [20] The level of AC was low however, and might have been insufficient to provoke corrosion, as was demonstrated in experiment Ib.

The large amount of previously published corrosion rate data presented in Pourbaix diagrams in Figure 8, indicates that the high pH corrosion region plays a fundamental role in the AC corrosion process (at potentiostatic CP). The standard current density criteria (EN15280:2015) may outline the conditions necessary to bring a steel into this region by a combination of depolarisation of the IR-free potential and an increase of pH.

The corrosion regions in the Pourbaix diagram favour corrosion via dissolved ionic species, but observation of corrosion products in AC corrosion cases or experiments is easily explained. As demonstrated in experiment Ib, a potential and pH inside the high pH corrosion region is not sufficient to cause corrosion, but AC interference is necessary initiate corrosion. This suggests that the alternating polarisation continuously oxidises dissolved ions and stabilizes the high pH corrosion region. The observation of different oxides in AC corrosion cases may very well be an effect of unintentional aeration of a sample prior to analysis, rather than an indicator of the corrosion mechanism. Reaction (5) illustrates the anodic reaction in which iron is dissolved as dihypoferrite ion.

\[
Fe + 3OH^- \rightarrow HFeO_2^- + H_2O + 2e^- \quad (5)
\]
Reaction (7) and (8) represents possible anodic reaction routes to magnetite commonly observed in AC corrosion cases. Either directly via (8) or via the chemical reaction to ferrous hydroxide (6). Equation (8) is essentially a combination of equation (6) and (7) as follows: 3-(6) + (7).

\[
\begin{align*}
HFeO_2^2 + H^+ &\rightarrow Fe(OH)_2 \\
3HFeO_2^- + H^+ &\rightarrow Fe_3O_4 + 2H_2O + 2e^- \\
\end{align*}
\]

Further oxidation of the formed corrosion products may occur via reactions (9) or (10):

\[
\begin{align*}
4Fe_3O_4 + 6H_2O + O_2 &\rightarrow 12FeOOH \\
4Fe_2O_3 + O_2 &\rightarrow 6Fe_2O_3 \\
\end{align*}
\]

Despite the fact that the presented mechanism relies on dissolved dihypoferrite ions, it is clear that the corrosion products from AC corrosion cases are not soluble. Both due to continuous oxidation following the AC frequency, but also due to the steep potential and pH gradient towards the steel interface that strongly minimizes the volume at the surface where corrosion products are soluble. Hence corrosion products will accumulate on the surface as commonly observed. [5]

### Conclusion

The simple experiments presented herein as well as an illustration of previously published data implies that AC corrosion, and in particular AC corrosion of cathodically protected structures, which has been subject to much controversy in the past decades, may be partially or entirely explained using the Pourbaix diagram. The effect of AC depends on the type of cathodic protection applied.

- It is well known that AC depolarises steel under cathodic protection shifting the IR-free potential positively from the immune region towards the hydrogen line. This is true for both galvano- or potentiostatic control of the CP system. The latter typical of field applications.
- AC enhances the cathodic current density for potentiostatic cathodic protection via faradaic rectification, thus increasing the pH.
- AC is necessary for stabilising the high pH corrosion region. In a stagnant environment such as soil, the concentration of dissolved HFeO\textsuperscript{2}\textsuperscript{-} will increase and the high pH corrosion region will disappear, thus not causing progressing corrosion. Increasing AC causes corrosion in the high pH corrosion region, allegedly due to a constant oxidation or reduction of dissolved HFeO\textsuperscript{2}\textsuperscript{-}, maintaining a low concentration.
- The combined effect of; depolarisation of the IR-free potential, high pH and stabilisation of the HFeO\textsuperscript{2}\textsuperscript{-} region, due to AC on cathodically protected steel, causes high corrosion rates in the high pH region in the Pourbaix diagram.
- High levels of AC cause de-alkalisation of steel under galvanostatic CP. Evidence of the phenomenon is presented in this paper, but the available data is in no way sufficient to allow for quantitative comparisons between AC interference and de-alkalisation.
- De-alkalisation caused by AC is a novel finding that calls for a re-evaluation of numerous published papers investigating AC corrosion of pipelines under galvanostatic- or no cathodic protection, since the corrosion mechanism may be fundamentally different to the case of AC corrosion of cathodically protected pipelines under potential control (low pH vs. high pH corrosion).

The presented experiments are simple, and the results show surprisingly good correlation with the thermodynamically calculated Pourbaix diagram. Evaluation of pH is carried out according to simple relations to the cathodic current density. One experiment strongly indicates that depolarisation of steel by AC to an IR-free potential above the hydrogen line at a theoretical pH(-J\textsubscript{DC}) may be interpreted as de-alkalisation. In order to further verify the presented mechanism for AC corrosion, a more robust method of pH measurement, than that used in this study, is necessary. Only very recently, suitable pH measurement techniques for cathodic protection uses have been developed. [21]
References


4.7 [VII] Corrosion Science ’18

In this investigation, galvanostatic CP at eight different levels ranging from 0.01 A/m² to 30 A/m² cathodic current density, was applied to ER probes in a non-scaling artificial soil environment. The corrosion response to increasing levels of AC interference was analysed both in a current density and Pourbaix diagram context. High and low CP AC corrosion was observed. XPS analysis of coupon surfaces was made to evaluate the oxides being present on a surface subject to different levels of AC and DC in either corroding or non-corroding conditions. The findings suggest that Fe₃O₄, Fe(OH)₂ and possibly a green rust phase is present on the surface.

The manuscript was submitted to Corrosion Journal on September 7th 2018, and was under review by the time of submission of this thesis.
Corrosion rate measurement and oxide investigation of AC corrosion at varying AC/DC current densities

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Keywords: steel (A), galvanostatic (B), XPS (B), cathodic protection (C), oxidation (C), Pourbaix diagram (C)

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Declaration of interests: none

Abstract

Corrosion of pipelines under cathodic protection (CP) caused by induced alternating current (AC) is highly dependent on the cathodic current density. This study uses electrical resistance (ER) probes to produce a corrosion rate map of the AC/DC current density domain, using a galvanostatic CP system subject to varying AC voltage interference levels. Two corrosion domains are recognized at high or low CP respectively. X-ray photoelectron spectroscopy (XPS) is utilized for analysis of surface oxides, being primarily magnetite and ferrous hydroxide. The results are discussed in a Pourbaix diagram context.

Introduction

AC corrosion can produce high corrosion rates on pipelines even under cathodic protection. In fact, the amount of cathodic protection, in terms of cathodic current density on coating defects, is known to be an important parameter in AC corrosion; higher cathodic current densities above 1 A/m\textsuperscript{2} will accelerate AC corrosion in the presence of an alternating voltage perturbation [1, 2, 3, 4]. The reason for this is closely linked to the effect of the cathodic current on the local soil chemistry, caused by the primary cathode reaction under anaerobic conditions (1).

\begin{equation}
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- \quad (1)
\end{equation}

As the soil surrounding a coating defect becomes increasingly alkaline, two things may happen: Calcareous deposits may build on the steel surface and form an isolating layer that lowers the AC and DC currents. Alternatively, if the soil type is not prone to form deposits, the ionic conductivity will increase significantly (lowering spread resistance) and increase the AC and DC current densities. The latter scenario is particularly prone to AC corrosion in the presence of AC interference and a sufficiently negative protection potential. Furthermore, faradaic rectification of the alternating current will enhance the cathodic current (reaction (1)) at any given polarised potential, thus further decreasing the spread resistance [5, 6, 7].
One interesting observation is that at intermediate cathodic current densities below 1 A/m², e.g. 0.1 A/m², no limit of AC current is observed, above which corrosion will occur. Some corrosion is present at very low cathodic current with increasing AC interference [1].

The mechanism for AC corrosion is largely debated in literature: Büchler and Schöneich (2009) hypothesised a continuous oxidation to a passive film and reduction to a porous rust layer with the AC frequency, resulting in corrosion. A more negative protection potential will result in a higher degree of reduction of the passive film and thus increasing corrosion rate, capable of explaining the importance of the cathodic current density [1]. Nielsen et al. (2005) proposed that increasing alkalinity will cause the steel to enter and exit the high pH corrosion region in the Pourbaix diagram (HFeO₂⁻) with the AC frequency, causing corrosion. The higher the cathodic current density, the higher the pH which results in a larger potential span of the dihypoferrite region [4]. Tribollet et al. (2014) supports the oxidation/reduction corrosion mechanism, but links the observation of a green rust oxide, stable only below pH = 11, to the capability of transferring a significant amount of AC current via Fe(II)-Fe(III) conversion within the passive film i.e. not causing corrosion. Green rust is a layered double hydroxide with the general formula ([Feⁿ⁺₁₋ₓ,Fe³⁺ₓ(OH)₂]ⁿ⁺[(x/n)Na⁺/mH₂O]⁺) where A represents an anion, typically chloride, sulphate or carbonate. At higher cathodic current densities, the pH will increase and destabilise this oxide, ultimately causing corrosion [8].

This study presents an investigation of the intertwined relation between the on- and IR free cathodic protection potential (E.ON and E.RT-free), AC voltage (U.AC) and the resulting AC and DC current densities (J.AC, J.DC) via the spread resistance (R.S). See equation (2) and (3).

\[ E_{RT-free} = E_{on} - IR = E_{on} - J_{DC}R_S \]  \[ U_{AC} = J_{AC}R_S \]

This is put in relation to measured corrosion rates (v.cor) to better understand the importance of the cathodic current density on AC corrosion. Finally, formed oxides are investigated using XPS to identify the present phases and provide information about the corrosion mechanisms.

**Materials and methods**

**Mapping of AC/DC current density domain**

Mapping of the AC/DC current density domain was done using eight experimental set-ups as shown in Figure 1, having an AC and DC circuit separated by a C = 600 µF capacitor and an L = 2 H inductance with a small internal resistance. The AC source was the 50 Hz wall outlet controlled by a variable transformer and the DC source consisted of a potentiostat used in galvanostatic mode by implementation of a suitable shunt resistor, depending on the desired galvanic current flow. As counter electrodes (CE), 10x20 cm² mixed metal oxide coated titanium meshes were installed. The datalogger, an interference corrosion logger (ICL), was connected to the working electrode (WE), an ER probe, for monitoring corrosion rate and electrical parameters such as on- and IR free-potentials, AC voltage, AC and DC current density as well as the spread resistance, which is a function of the local soil chemistry near the coating defect (probe element). All parameters were measured every 20 minutes. The ER probes had a rectangular exposed area of 1 cm² (10:1 length to
width ratio), and the probe element was initially 500 µm thick. The material is a low alloyed carbon steel. The reference electrodes (RE) used in the study were Cu/CuSO$_4$ (CSE) cells tested against a laboratory calibrated calomel electrode (SCE) prior to the experiment (±10 mV including the 72 mV difference between CSE and SCE). The simulated soil environment was 50 kg of inert sand (0.4-0.8 mm) fully wetted with approximately 16 L of non-scaling artificial soil electrolyte with a composition given in Table 1. The electrolyte had a resistivity of ρ ≈ 17.3 Ωm and an initial pH ≈ 8.2.

The current supplied by the galvanostat in the eight set-ups was kept at $J_{DC} = -0.01, -0.03, -0.1, -0.3, -1, -3, -10$ and -30 A/m$^2$ respectively. A gradually increasing AC interference of $U_{AC} = 0, 0.5, 1, 1.5, 2, 3, 4, 5, 6, 8, 10, 13, 16, 20$ and 24 V was then applied to each experiment for a minimum of three days (three or four to give a weekly experimental cycle) at each voltage to allow for stabilisation of currents and potentials and a correct measurement of the corrosion rate.

**Electrical resistance probe for corrosion rate measurement**

The corrosion rate was evaluated by measuring the resistance of the thin corroding element, $R_C$, in the ER probe and translating the change of resistance into a change in thickness i.e. corrosion. To compensate for temperature dependent resistance variations, an identical but shielded reference element inside the probe, being subjected to the same temperature variations, is also measured ($R_R$). The thickness of the corroding element $\sigma$ is then given by equation (4) where $R_{C0}$ and $R_{R0}$ are the initial element resistances.

$$\sigma(t) = 500\mu m \cdot (R_{C0} \cdot \sigma(t))/((R_{R0} \cdot R_C(t))$$  (4)

The corrosion rate is given by $d\sigma/dt$, effectively measured as a linear approximation of the thickness data during every experimental AC/DC setting. Due to a very precise measurement of the resistances, changes in the element thickness can be determined at sub micrometre level.

**XPS investigation of oxide formation**

Because of requirements for the surface and sample size for XPS, coupons were created specifically for oxide investigations: A 3.16 x 31.6 mm column was machined from a piece of X65 pipeline steel. This area is identical to the exposed ER probe element of 1 cm$^2$. The column was then embedded in epoxy (30 x 50 mm$^2$) and four thin 3 mm sections were cut from this. Each of these had one face polished using grid 80, 220, 320, 500, 1000 and 4000 sand paper, followed by a 3 µm and 1 µm diamond suspension polish. The other face was electrically connected to a copper wire and was carefully shielded using waterproof but removable glue and tape.

The four coupons were tested in four set-ups identical to that given in Figure 1, except for replacement of the ER-probe with a coupon. The coupons were numbered 1-4 and were tested using: 1) $J_{DC} = -0.3$ A/m$^2$, $U_{AC} = 5V$. 2) $J_{DC} = -0.3$ A/m$^2$, $U_{AC} = 20V$. 3) $J_{DC} = -30$ A/m$^2$, $U_{AC} = 5V$. 4) $J_{DC} = -30$ A/m$^2$, $U_{AC} = 20V$. The duration of the tests were four days.

For evaluation of the oxide formation, it is important to avoid oxidation in air which can readily cause phase transformation of the sampled solid. Hence, after the test period, the coupons were carefully excavated from the soil boxes and dried in a nitrogen air flow for a few seconds while the electrical connection on the backside was removed. Thereafter the coupons were stored in a cooling container at -50°C to be transported to the XPS. Transportation time was < 30 minutes. In the
frozen state, the epoxy embedding was removed, and the coupons were mounted in the XPS which was immediately pumped down to vacuum. The visual appearance of the coupons did not change during this procedure, suggesting that the material did not oxidize.

Results

Corrosion rate mapping of AC/DC current density domain
Mapping of corrosion rates in the AC/DC current density domain is shown in Figure 2. The current density threshold values given by ISO 18086:2015 are drawn in the bottom plane of the plot, and clearly outlines a region yielding high corrosion rates, identified as high CP AC corrosion. The plot also indicates a corrosive region at low cathodic current and high AC interference identified as low CP AC corrosion. The low CP region is not recognized by the ISO 18086:2015 standard, but has been documented in several laboratory studies [1, 2, 9]. Perhaps more importantly, the plot indicates an intermediate cathodic current density domain that does not produce corrosion even at interference levels of 24 V and an AC current density of up to 600 A/m^2.

Figure 2 also illustrates that at fixed values of U_Ac (dashed lines), the resulting current density, J_Ac, is very much dependent on the cathodic current density, due to its influence on the soil chemistry and consequently spread resistance. Figure 3 plots spread resistance, R_S, as a function of -J_Dc. Above a certain cathodic current density (here, 0.1 A/m2) the spread resistance in the non-scaling artificial soil is directly proportional to -J_Dc, which may simply be interpreted as increasing pH values, i.e. increasing ionic conductivity by hydroxyl ions.

Figure 4 illustrates the potential shifting effect of AC on a polarised steel. The necessary IR free potential supplied to the probe to drive the desired galvanostatic current is strongly dependent on the AC interference level. This observation is key to understanding low CP AC corrosion, since, at a certain AC level, the probe does no longer satisfy the -850 mV_CSE criterion and corrosion is possible.

XPS investigation of oxide formation
Electrical data from the test period for the four simple coupons is presented in Table 2. Notice that while coupon 1 and 3 as well as 2 and 4 have comparable AC voltages, coupon 2 and 3 have comparable AC current densities simply due to the change in R_S caused by varying J_Dc. The R_S values are in perfect accordance with Figure 3. The IR free potential values show good agreement with Figure 4, and the differences may be explained by slightly different polarisation response of the ER-probe steel and the X65 coupon steel. The general observation of a shift of the IR-free potential due to AC interference is confirmed.

Figure 5 shows the four coupons photographed immediately before the XPS analysis. No corrosion was visible on the sides that had been embedded in epoxy, assuring that no crevice type corrosion had taken place during the test.

- Coupon 1 was bright in appearance, showing no signs of corrosion except a slight discoloration along the edges.
- Coupon 2 was covered with a dark green to yellow oxide.
• Coupon 3 was bright in appearance, with a white haze to it. Along the edges a dark brown oxide had formed.
• Coupon 4 showed a range of oxide colours from brown to black, being darkest along the edges.

The sites chosen for XPS were around the centre of the coupons to capture the dominant oxide type being representative for each coupon. Local AC and DC current densities on the coupon surface are expected to be higher along the edges [10], hence the observation of discolouration along the edges of coupon 1 and 3, that matches the oxide colours of coupons 2 and 4, is sensible.

Assignment of absolute binding energies in XPS requires reference to a peak for an element with known binding energy, for example with reference to a small amount of gold deposited on the surface. However, application of such a layer in a separate instrument would have increased the exposure time of the oxygen sensitive samples to the atmosphere. Consequently, binding energies for peaks were calibrated based on the assumption that the C1s peak with lowest binding energy represented adventitious carbon with a binding energy of 285.0 eV. Although this procedure is very widely used, uncertainties in the absolute binding energy of the adventitious carbon are large [11, 12].

Figure 6 shows the spectra for the coupons. All survey scans show peaks from Fe, O, C, Na, Si and Ca (Figure 6a). For coupon 3, the Ca2p peaks are displaced towards lower binding energy by ~1 eV compared to the values for the other coupons. Moreover, in the Fe2p detail scans (Figure 6c), the sharp peak at ~705.8 eV, representing metallic iron, is also ~1 eV lower than the values usually given [13]. Thus, it is very likely that the calibration has resulted in shifts of peaks towards too low binding energy for this coupon.

The Fe2p detail scans for coupon 1, 2 and 4 shows considerable intensity at a binding energy of ~715 eV, where the Fe2p3/2 satellite for Fe(II) is expected in oxides and hydroxides, as well as a smaller peak at ~719 eV representing the Fe2p3/2 satellite for Fe(III) [13, 14, 15]. This shows that the top 10 nm or so of the materials contains both Fe(II) and Fe(III).

Assuming that the binding energies for coupon 3 are shifted excessively towards lower values, the O1s detail scans in Figure 6d show pronounced peaks attributable to O in oxide (binding energy ~ 530 eV) and in hydroxide (binding energy ~ 532 eV) [16, 17]. Although the binding energies for O in carbonate coincide with that of O in hydroxyl, the lack of a significant C1s peak with a binding energy attributable to CO3 in iron carbonates (~290 eV) allow us to exclude that such phases are present in significant amounts [18]. In addition to peaks from O in oxide and hydroxide, the spectra for coupon 3 and 4 shows an additional, smaller peak at higher binding energy which could represent water.

Taken together, the XPS data indicates the presence of substantial amounts of mixed valent iron hydroxides and/or oxides. Green rusts are Fe(II)-Fe(III) layered double hydroxides, which contain anions in interlayers. Given that evidence for the presence of anions is sparse (small amounts of carbonate may be present), the Fe(II) bearing (hydr)oxides at the surface most likely mainly consists of magnetite and ferrous hydroxide. However smaller amounts of green rust cannot be excluded.
Discussion

Corrosion rate mapping of the AC/DC current density domain showed two corrosion domains at high AC interference levels and high and low cathodic protection respectively (Figure 2). High CP AC corrosion showed the highest corrosion rates. This is perfectly in line with observations made by others and previous studies by the present authors [1, 2, 9]. The ISO 18086:2015 standard on AC corrosion deals only with AC corrosion at DC current densities > 1 A/m², thus only with high CP AC corrosion. The same is true for the various AC corrosion mechanisms described in the introduction. Low CP AC corrosion can be explained by the observed potential shift of steel under AC interference. At a certain AC level, the IR free potential becomes less negative than -850 mV_{CSE}, thus exceeding the general CP criterion given in ISO 15589-1:2015. Since this is a prerequisite for ISO 18086:2015, it may be justified that the standard does not treat low CP AC corrosion in detail. A shift of the IR free potential to above -850 mV_{CSE} is not an explanation for corrosion in itself however, since it simply indicates that the potential is shifted. To better understand the two domains, the exact same corrosion rate data is plotted in a calculated Pourbaix diagram in Figure 7. The IR free potential is obtained directly from the data logger and the pH is calculated based on the cathodic current density via pH = 12.3 + 0.714*log(-J_{DC}) as reported by the present authors in a literature study [19]. As it is also suggested in that study, there are strong indications that AC can induce de-alkalisation on a steel subject to a galvanostatic CP current. Assuming that the galvanostatic current runs primarily via the electrochemical reaction (1), it is not a requirement that this occurs at a high pH. Only that it happens on or near the hydrogen line in the Pourbaix diagram. Hence shifting of the potential to a less negative potential (above the hydrogen potential at the theoretical calculated pH(J_{DC})) may be interpreted as a decrease in pH caused by alternating current. This hypothesis was tried in a quick test after the J_{DC} = -0.01 and -0.03 A/m² galvanostatic experiments: The soil boxes were carefully drained of electrolyte (not dried out) and the sand covering the ER probes (>10 cm) was removed. pH sensitive paper was placed directly on the face of the ER probe that was facing upwards, and the paper absorbed the moisture from the corrosion product. The result is shown in Figure 8. While the result may be difficult to interpret directly, they certainly indicate a pH much lower than the theoretical pH ≈ 11, perhaps even close to 4-5, thus supporting AC induced de-alkalisation of steel under galvanostatic CP. There is general agreement that the cathodic protection mechanism under stagnant conditions is concentration polarisation, leading to an increase in pH (following the hydrogen line), and that the -850 mV criterion correlates to passivity obtained via alkalinisation [20]. Hence, the conclusion that an IR free potential shift in the positive direction is accompanied by a decrease in pH seems obvious.

In fact, when projecting the low CP AC corrosion data onto the hydrogen line, they fall inside the low pH corrosion region in the Pourbaix diagram. Conversely, the high CP AC corrosion data fall in or near the high pH corrosion region in the Pourbaix diagram. Observing the corrosion rates in Figure 2 for the J_{DC} = -10 and -30 A/m² probes, there is even a maximum in the corrosion rates that is not at the maximum AC interference level, possibly suggesting that the still increasing AC level leads to an IR free potential above the high pH corrosion region, or alternatively, lower pH even at such high cathodic current densities. This turn in corrosion rates with increasing AC interference is difficult to explain using the oxidation/reduction AC corrosion mechanism.

The investigation of surface oxides by XPS was made such that AC corrosion would not be anticipated on coupons 1 and 2 (J_{DC} = -0.3 A/m²) but would be on coupons 3 and 4 (J_{DC} = -30
A/m²). Visually, no or little corrosion was observed on coupon 1 and 3, while coupon 2 and 4 were clearly covered with different oxides. The XPS spectra for coupons 1, 2 and 4 are quite alike, and indicate the presence of ferrous hydroxide and magnetite. The strong Fe(0) peak for metallic iron on coupon 3 in Figure 6c suggests the presence of only a very small amount of surface oxides, i.e. possibly this was polarised to the immune region. When plotting the XPS coupon data in the Pourbaix diagram in Figure 7, coupon 3 lies in the immune region in good accordance with the XPS analysis, as well as the corresponding ER probe corrosion rate data suggesting no corrosion. This is despite both JAC and JDC being above the limit values according to ISO 18086:2015, see Table 2. It is important to state that this is not a practical AC corrosion mitigation strategy however, since this very high cathodic current and IR-free potential as low as EIR-free = -1.31 V CSE (Table 2) induces alternate integrity threats such as coating disbondment and hydrogen embrittlement.

Comparing to ER probe data, no corrosion was expected on coupons 1-2 either. Visually this was confirmed on coupon 1, but coupon 2 had a greenish oxide covering the surface possibly reflecting ferrous hydroxide with small amounts of structural Fe(III) or a mixture of ferrous hydroxide and green rust. The oxides observed on coupons 1-2 may be part of the protection mechanism against AC corrosion if a significant amount of alternating charge can pass through the oxide via a Fe(II)-Fe(III) redox reaction. This would require that the oxides allow electron mobility and that changes induced by the redox reaction can be accommodated by the solid in a reversible fashion. Several aspects substantiate that this might be possible. It is well known that Fe(II) and Fe(III) in the B site in magnetite possesses delocalised electrons above the Vervey transition, conferring conductivity to the mineral. At room temperature, electron hopping occurs with a relaxation time of about a nanosecond [21]. Furthermore, magnetite transforms to isostructural maghemite upon oxidation, a rearrangement that is accompanied by diffusion of cations out of the structure (e.g. [22]). Given that the two structures are isostructural, the reverse reaction is likely to be possible. The reversible use of magenite as an electron donor and receptor by microorganisms support this [23]. If the degree of oxidation/reduction is small, such changes need only affect the surface of the particles, meaning that magnetite could undergo quick redox reaction. For ferrous hydroxide and green rust, data about electron mobility is sparse. However, a modelling study indicates that electron holes can propagate rapidly within the sheets at room temperature [24]. Ferrous hydroxide and green rust may also exist with a range of Fe(III) content without apparent changes in structure [25, 26].

The XPS analysis did not indicate a difference in the upper 10 nm of surface oxide on coupons 1 and 2, but the thickness of the oxide on coupon 2 must have been much thicker to alter the visual appearance. This may be explained by the higher AC current density (JAC = 289 A/m²). The thicker the oxide; the larger the capacity for Fe(II)-Fe(III) redox reaction.

The position of coupon 4 in the Pourbaix diagram is just above the ER probe data showing corrosion rates > 1000 µm/y and slightly above the dihypoferrite region in the magnetite region. If corrosion happened in the form of HFeO₂⁻, this dissolved ion would have formed alternative oxides on the coupon surface, i.e. Fe₃O₄ and Fe(OH)₂ as observed by XPS. Possible reaction paths are given in (5-8).

\[
\text{Fe} + 3\text{OH}^- \rightarrow \text{HFeO}_2^- + \text{H}_2\text{O} + 2e^- \quad (5)
\]
\[
\text{HFeO}_2^- + \text{H}^+ \rightarrow \text{Fe(OH)}_2 \quad (6)
\]
3Fe(OH)_2 + 2OH^− → Fe_3O_4 + 4H_2O + 2e^− \quad (7)
3HFeO_2^- + H^+ → Fe_3O_4 + 2H_2O + 2e^- \quad (8)

Magnetite is often observed in AC corrosion cases, but iron hydroxide, and green rust for that matter, are phases prone to rapid oxidation in air and thus difficult to study using more conventional methods such as XRD.

With respect to the AC corrosion mechanism, the results in this study indicate that the Pourbaix diagram can explain both high and low CP AC corrosion. This implies that corrosion is largely dependent on pH which explains the effectiveness of an intermediate CP strategy as an AC corrosion mitigation strategy i.e. keeping the pH in an interval approximately between 9.5 and 12 to maintain passivity.

**Conclusion**

- AC corrosion under cathodic protection can be split in two categories: high and low CP. The present study suggests that these are linked to the high and low pH corrosion regions in the Pourbaix diagram.
- At high CP levels a high pH value is expected. AC shifts the IR free potential from the immunity region towards the HFeO^- region where corrosion is evident.
- At low CP levels, the pH value is also high under pure DC conditions but increasing AC interference causes a significant potential shift to above the hydrogen line in the Pourbaix diagram which is interpreted as a drop in pH to the Fe^{2+} region. Low pH on the corroded probes was confirmed in a simple pH paper test.
- Fe_3O_4 and Fe(OH)_2 was found on coupons that did not experience AC corrosion, in good agreement with their position in the Pourbaix diagram. The AC corrosion mitigation mechanism is explained by the electron mobility in these oxides, allowing for a significant portion of charge to be passed without progressing corrosion.
- The surface of a coupon polarised to the immune region in the Pourbaix diagram was confirmed to be primarily metallic iron in the XPS analysis. This coupon did not experience corrosion despite a considerable amount of AC interference.
- Fe_3O_4 and Fe(OH)_2 was found on a coupon that did experience AC corrosion. This is in good agreement with the Pourbaix diagram, but it is expected that the corrosion has an intermediate step via the HFeO^- ion.

The amount of data present to support the de-alkalisation effect of AC on steel under low cathodic protection is limited, but the indications are strong. Further testing of the hypothesis is necessary to confirm the mechanism of AC corrosion at low CP.

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Data availability statement
The raw data required to reproduce these findings are available to download from http://dx.doi.org/10.17632/v97dkgy96w.1.

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**Figure captions**

Figure 1: Experimental set-up with an AC and DC circuit sharing the same working electrode.

Figure 2: Current density plot with corrosion rates showing two AC corrosion domains at low and high cathodic current.

Figure 3: Plot showing the decreasing spread resistance with increasing cathodic current density for the non-scaling soil solution.

Figure 4: IR-free potential as a function of the AC current density showing the potential shift effect of AC on galvanostatic CP.

Figure 5: Visual inspection of the four coupon surfaces after the experiment.

Figure 6: X-ray photo-electron spectra (XPS) of the four coupons. a) The entire spectrum showing distinct peaks from elements. b) Peaks for carbon. Peak positions have been calibrated assuming adventitious carbon at a binding energy of 285 eV. c) Peaks for iron. d) Peaks for oxygen.

Figure 7: Pourbaix diagram showing corrosion rates from the ER probes and the positioning of the oxide coupons.

Figure 8: pH paper measurement of the surface pH on the ER probes after the experiment had finished. a) $J_{DC} = -0.01$ A/m$^2$, $J_{AC} = 266$ A/m$^2$. b) $J_{DC} = -0.03$ A/m$^2$, $J_{AC} = 218$ A/m$^2$. 
Figures

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### Tables

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (mM)</th>
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<tr>
<td>Na$_2$SO$_4$</td>
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</tr>
<tr>
<td>NaHCO$_3$</td>
<td>2.5</td>
</tr>
<tr>
<td>NaCl</td>
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Table 1: Composition of the artificial soil solution.

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<tr>
<th>Coupon</th>
<th>$E_{ON}$</th>
<th>$E_{IR-free}$</th>
<th>$J_{DC}$</th>
<th>$U_{AC}$</th>
<th>$J_{AC}$</th>
<th>$R_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(V CSE)</td>
<td>(V CSE)</td>
<td>(A/m$^2$)</td>
<td>(V)</td>
<td>(A/m$^2$)</td>
<td>(Ω m$^2$)</td>
</tr>
<tr>
<td>1</td>
<td>-1.12</td>
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<td>-0.30</td>
<td>5.2</td>
<td>91</td>
<td>0.06</td>
</tr>
<tr>
<td>2</td>
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<td>-0.91</td>
<td>-0.31</td>
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</tr>
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<td>0.02</td>
</tr>
<tr>
<td>4</td>
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<td>-0.97</td>
<td>-30.3</td>
<td>20.6</td>
<td>1111</td>
<td>0.02</td>
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Table 2: Average voltage and current characteristics for the four coupons measured during the experiment.
4.8 [VIII] Corrosion Journal ’18

In this manuscript, high pH corrosion was investigated specifically. Polarisation curves and ER probe corrosion rate measurements in a pH = 13.5, non-scaling environment are used to evaluate HFeO$_2^-$ corrosion influenced by AC interference. It is found that, in addition to high pH and a polarised potential inside the HFeO$_2^-$ region, an alternating potential is needed to trigger the corrosion mechanism. Besides, the hydrogen evolution reaction appears to be important for the corrosion mechanism. A mechanistic AC corrosion model is proposed, based on the findings.

The manuscript was submitted to Corrosion Journal on October 1$^{st}$ 2018, and was under review by the time of submission of this thesis.
Investigation of High pH Corrosion of Steel under Alternating Current Interference

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ABSTRACT

This paper investigates the possible AC corrosion mechanism as dihydroperrite dissolution at high pH under an alternating voltage perturbation and compares the corrosion performance of three commonly used pipeline steels, X52, X65 and X70. The methods used are polarization scans at various interference levels, weight-loss coupons and ER-probe corrosion rate measurements in an artificial soil solution having high pH. It is found that AC enhances the stability region of dihydroperrite in the Pourbaix diagram, leading to corrosive conditions. Furthermore, it appears that hydrogen evolution from the cathodic protection current plays a key role in destabilization of a passive film that may otherwise provide protection of the steel, even under high AC interferences (1000 A/m²). A model for AC corrosion that considers a soluble ion is presented.

INTRODUCTION

Alternating current (AC) corrosion of pipelines under cathodic protection (CP) is an engineering topic subject to much debate. Mitigation methods have been developed and are working, but available literature on the topic points in many directions, in terms of an actual corrosion mechanism. One suggested mechanism is via HFeO₄⁻ ions (dihypoferrite) in the high pH corrosion region in the Pourbaix diagram for iron.
possible effects of varying concentration of dissolved iron species at the interface, refer the Pourbaix diagram in FIGURE 1.

To investigate the role of the dihydrite region in AC corrosion, polarization scans from -1850 mV_{CSE} to -1050 mV_{CSE} were conducted at a scan rate of 20 mV/min. The very negative interval was chosen to be sure to approach the stability region from the immunity region at low concentrations, even under high AC interference. Typically, no AC corrosion is to be expected at potentials less negative than 1100 mV_{CSE}.15

Corrosion rate experiment
To investigate AC corrosion rates in the high pH environment, weight loss coupons were made from the same Ø10x10 mm cylinders as used in the polarization scans. FIGURE 3 illustrates a cross-section of the coupon. Only the circular face was exposed, yielding an area of 0.785 cm² and a shielding “collar” (85.5 cm) was glued to the shrink sleeve to better simulate the spreading resistance of a coating defect on a large diameter pipe. In between the shrink sleeve and the steel was a layer of acetone dissolvable coating to prevent crevice corrosion. The experimental setup for the investigation was similar to the setup in FIGURE 2, only the solution (TABLE 2) was added to an inert sand (0.4-0.8 mm) to mimic diffusion conditions in soil and the potentiostat was a Bank Elektronik Wenking model LB 81. Reference electrodes were Cu/CuSO₄ type placed at the surface. Four parallel investigations were made with ER probes and a fixed AC current density of 30, 230, 500 and 1000 A/m² respectively. By varying the set rectifier potential (ON potential), the IR-free potential was adjusted as close as possible to -1450, -1350, -1250, -1150 and -1050 mV_{CSE} for minimum 5 days at each level. Interference corrosion loggers (ICL) from MetriCorr continuously recorded corrosion rate (νcorr), ON and IR-free potentials (Eon and EIR-free), AC voltage (UAC), the resulting AC and DC current densities (IAC, IDC) and the spread resistance (Rs). IR compensation was done according to equation (1) where Rs is approximated by equation (2).

\[ E_{IR-free} = E_{ON} - J_{AC} R_s \]  \hspace{1cm} (1)
\[ R_s = U_{AC}/J_{AC} \]  \hspace{1cm} (2)

The measurement interval of the data logger was 20 minutes. At EIR-free = -1250 mV, the weight loss coupons of each steel type were added to the JAC = 30 and 500 A/m² experiments, and the period was extended for 13 days to improve weight loss data. After the corrosion test, corrosion products were removed in a solution of inhibited hydrochloric acid, the total weight loss of the coupons was measured, and a corrosion rate was calculated.

RESULTS
Polarization experiment
FIGURE 4 – FIGURE 6 shows polarization curves for the different steels at varying AC levels. It can immediately be seen that the current density on the cathode curve is enhanced by orders of magnitude for high AC levels, J_{AC} > 100 A/m², due to faradaic rectification (depolaronization). The polarization scans yielded several equilibrium potentials and switching cathodic and anodic current during the scan, shown as full or dashed lines respectively in the figures. The recorded equilibrium potentials are plotted in FIGURE 5b showing a systematic behavior that appears to be characteristic for the level of AC interference and only to a minor degree dependent on the steel type. The values for no AC are plotted at J_{AC} = 0.01 A/m² in the logarithmic plot. A direct comparison with the Pourbaix diagram at pH = 13.5 is shown in FIGURE 5a.

The first equilibrium potential (lowest curve) is highly dependent on the AC current density; decreasing in potential for J_{AC} = 0-100 A/m² but increasing for J_{AC} = 230-1000 A/m². For J_{AC} = 0-100 A/m², a cathodic current interval is observed from -1120 to -1220 mV_{CSE}, however decreasing in potential range (and current density, see polarization scans) with increasing AC. For J_{AC} > 100 A/m², only one anodic interval was observed which was moving towards less negative potential values with increasing AC interference.

Corrosion rate experiment
Results from the weight loss coupons of different steels are shown in TABLE 3. The corrosion rate of the samples at EIR-free = -1250 mV_{CSE} and J_{AC} = 30 A/m² was low, in agreement with the ER probe measurement (νcorr = 2 µm/y, TABLE 4). Usually they appeared blank/metallic with a sporadic black discoloration of the surface. The higher AC (-1250 mV_{CSE}, 500 A/m²) coupons were all covered with a black/brown corrosion product. Comparing to the ER probe data (νcorr = 1728 µm/y), the corrosion rate of the coupons was at least an order of magnitude smaller. Corrosion was focused along the edges of the coupons where the current density is anticipated to be highest. The rectangular design of the ER probe element, having more edge per area, may partially explain the discrepancy.

Electrical values and corrosion rates measured by the ER probes at various AC current densities and IR-free potentials are listed in TABLE 4. The same corrosion rates are illustrated in FIGURE 8 as red columns on the same plot as shown in FIGURE 5b. Due to the very high corrosion rates measured at J_{AC} = 1000 A/m², these data are based on only 24 hours, because the ER-probe would have otherwise corroded away too quickly. Weight loss data are shown as blue columns. No significant corrosion is measured at J_{AC} < 230 A/m². Another interesting observation is the absence of corrosion at -1050 mV_{CSE}, at all investigated AC levels, even at J_{AC} = 1000 A/m².

DISCUSSION
The observation of several equilibrium potentials and switching cathodic/anodic currents during the polarization scan was surprising, but a similar behavior with multiple equilibrium potentials has been observed by Kuang and Cheng (2014) in a pH = 9.6 solution.² It may be explained by a comparison to the Pourbaix diagram in FIGURE 5 for AC interference levels < 100 A/m². The cathode reaction at the most negative potential is hydrogen evolution (3).

\[ 2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \]  \hspace{1cm} (3)

The first equilibrium potential, the corrosion potential in traditional sense, must correspond to dissolution as dihydrite (4), since at such a low potential, no other reaction is thermodynamically possible. The offset of the equilibrium potential in the negative direction may be caused by an insufficient IR-drop compensation in the experimental setup, and by further alkalization at the electrolyte interface in the non-stirred solution during the scan, following reaction (3). The latter is able to explain the negative shift with increasing AC that is observed up to 100 A/m², since this was associated with increasing cathodic current (faradaic rectification). Besides, the 10⁻⁴ mol/L minimum concentration is an arbitrary value based on typical Pourbaix diagram calculations, but the measurement may detect even lower levels.

\[ Fe + 2OH^- \rightarrow HFeO_2^- + H^+ + 2e^- \]  \hspace{1cm} (4)

The observation of first, a negative shift of the corrosion potential for J_{AC} < 100 A/m², followed by a positive shift for J_{AC} > 230 A/m² has been
observed in several other studies with a transition at about 200-400 A/m², even though none of the studies considered such a high pH environment as in this study.2,16-18 Goidanich et al. (2010) explained the positive shift of the corrosion potential at high AC levels as growth of a corrosion product and change of the double layer capacitance as well as polarization resistance.16 Xu et al. (2012) also attributed the positive shift of the corrosion potential to formation of a surface oxide film caused by oxygen evolution during high anodic polarization. The oxide was visually different from that formed at lower AC levels, but the results were not obtained under cathodic protection, which would be suspected to alter the oxidation conditions.14

At ~1200 mV_CSE, the Fe(OH)_2 and FeO_2 region is reached in the Pourbaix diagram. This allows for some deposition of the dissolved dihydroperrite ion on the surface as either of these oxides (5-6).

$$\text{HFeO}_2^+ + H^+ \rightarrow \text{Fe(OH)}_2^+ \quad (5)$$

$$3\text{HFeO}_2^+ + H^+ \rightarrow \text{FeO}_2 + 2H_2O + 2e^- \quad (6)$$

Particularly if the concentration of dihydroperrite ion has exceeded [HFeO_2] = 10^3 mol/L, which would cause this stability region in the Pourbaix diagram to shrink. Due to the conductive nature of Fe(OH)_2 and FeO_2, the cathode reaction (3) may proceed on the surface of these oxides. This creates a cathodic current in the polarization scan. Upon reaching the hydrogen evolution line at pH = 13.5 (around -1115 mV_CSE), reaction (3) is no longer possible and an anodic current is measured, either via reaction (4) again, as oxidation of Fe(II) to Fe(III) in the magnetite oxide or from ferrous hydroxide to magnetite reactions. The cathodic current at potentials > ~1080 mV is possible only via reduction of oxygen that may have diffused to the electrode during the experiment, either from the surface or from the counter electrodes where oxygen evolution takes place.

For J_{AC} = 0-100 A/m²; the anodic “loops” in FIGURE 4-FIGURE 6 were growing (higher current density and larger potential span) with increasing AC, while the cathode “loops” were shrinking (decreasing current density and smaller potential span). This is best illustrated for the X52 steel in FIGURE 4. This is indicative of stabilization of the HFeO_2 region with increasing AC, in the sense that the AC current may continuously oxidize or reduce the dissolved HFeO_2 ions, thus lowering the concentration and expanding the region in the Pourbaix diagram.

The weight loss and ER probe measurements performed in this study showed high corrosion rates at J_{AC} > 230 A/m² and E_{corr} ≤ -1150 mV_CSE, strongly supporting that corrosion and establishment of a corrosion product on the surface is responsible for the observed positive shift of corrosion potential in the polarization scans. In a corrosive state with build-up of corrosion products on the electrode surface (J_{AC} > 230 A/m²), the direct interpretation of the polarization scan with reference to the Pourbaix diagram, is impossible. But the observation of a growing HFeO_2 region in the non-corrosive state (J_{AC} = 0-100 A/m²) leading up to corrosion, supports the conclusion that this soluble ion plays a role in the corrosive state. This is contrary to the model established by Büchler and Schönich (2009) that relies on solid state oxidation and reduction of the passive film without the presence of a soluble ion.3

An AC corrosion model that considers ionic dissolution in combination with passive film degradation via chemical dissolution in an alkaline environment was proposed for aluminum as early as 1973.18 This is explained by the instability of its protective oxide layer at high pH. For steel, high pH is usually associated with passivity, even in pH > 12, e.g. steel in concrete. The HFeO_2 domain is however stabilized by the presence of alternating current and constitutes a rather narrow pH dependent potential range. Within this potential range, corrosion will progress above a certain J_{AC} threshold value. A model for the corrosion mechanism is illustrated in FIGURE 9. Below this potential range the steel is in the immunity domain. Here, hydrogen evolution (3) elevates pH further, thus expanding the HFeO_2 domain. Besides, the anodic potential excursion of high AC interference will pass through the corrosive domain causing corrosion as seen in FIGURE 10. The ER probe results at J_{AC} = 500 A/m² in FIGURE 8, showed that corrosion attenuated at lower potentials, probably because an increasingly smaller fraction of the anodic potential cycle coincided with the HFeO_2 domain. This was not observed for J_{AC} > 1000 A/m², because the potential variation here was too great. Above the HFeO_2 domain a FeO passive film is formed, as illustrated in FIGURE 11. This film will grow to a thickness where the Fe(II)-Fe(III) redox reaction within this passive film is capable of passing the alternating charge, without causing corrosion. The cathode reaction may proceed on the surface of such a film.

AC corrosion products are always observed in close contact with the corroding surface. This does not agree with corrosion as ionic dissolution, but it is important to remember that the potential and pH gradients towards a cathodically protected surface are steep.10,21 In addition, the constantly changing polarization of the AC must be considered. Diffusion will not get any far in for only 0.02 s before an AC cycle has moved the potential outside the stability region of the HFeO_2 ion. It is thus estimated that the physical volume, in which HFeO_2 may be present is limited to the surface of the steel.

An interesting observation in FIGURE 8 is that no corrosion is observed above the hydrogen evolution line at -1115 mV_CSE, even for high AC interference. Gas evolution may disturb a passive film, in particular if soluble ions at the surface “short-circuits” the electrical contact between steel and passive film. This would force the gas evolution reaction to take place in the interface between the steel and the corrosion product as illustrated in FIGURE 9 and FIGURE 10.

With the presented model it is possible to explain the industry standard protection criteria in ISO 18086:2015. The J_{AC} = 1 A/m² threshold is related to a critical pH that makes the HFeO_2 region thermodynamically possible. The J_{AC} = 30 A/m² threshold is related to stabilization of this region, due to the reasons presented in this paper. The J_{AC}/J_{p} < 3 criterion may be explained by bringing the entire AC potential variation into the immune region in the Pourbaix diagram.

**CONCLUSIONS**

- Polarization scans in a pH = 13.5 simulated soil solution from -1850 to -1050 mV_CSE with AC interference levels from J_{AC} = 0-1000 A/m² showed several equilibrium potentials and switching cathodic and anodic currents. From J_{AC} = 0-100 A/m² increasing anodic current and potential ranges is interpreted as stabilization of the HFeO_2 corrosive region at high pH, caused by continuous oxidation or reduction of the dissolved ions. A positive shift of the equilibrium potential at J_{AC} = 500-1000 A/m² is interpreted as formation of surface oxides due to corrosion.

- ER probe measurement of corrosion rates in the alkaline environment confirmed severe AC corrosion at J_{AC} = 500-1000 A/m² and an IR free potential below -1150 mV_CSE. This is related to hydrogen evolution (possible below -1115 mV_CSE) playing a role in destabilization of the passive film, that may otherwise be perfectly protective at high AC interference levels.
No significant effect of the pipeline steel grade on AC corrosion was observed, when comparing polarization scans and weight loss results. The highest AC corrosion rate was recorded for the highest steel grade investigated, X70. This was an order of magnitude lower than the ER probe measurement at similar potential and AC interference, which may be partially explained by geometrical effects.

An AC corrosion model that considers a soluble ion is presented. It may account for all the observed effects in the present and other investigations, as well as industry standard protection criteria according to ISO 18086:2015.

**References**


**FIGURE CAPTIONS**

**FIGURE 1**: Pourbaix diagram for iron outlining the high pH corrosion region (HFeO2-) being highly dependent on the concentration of dissolved species.

**FIGURE 2**: Experimental setup with a parallel AC and DC circuit.

**FIGURE 3**: Weight loss coupon with a shielding “collar” (cross-section).

**FIGURE 4**: Polarization scan (20 mV/min) of X52 steel.

**FIGURE 5**: Polarization scan (20 mV/min) of X65 steel. Legend in FIGURE 4.

**FIGURE 6**: Polarization scan (20 mV/min) of X70 steel.

**FIGURE 7**: Equilibrium potentials for switching cathodic/anodic as a function of the AC current density. The dihydrotetrane and hydrogen lines from the Pourbaix diagram at pH = 13.5 are drawn.

**FIGURE 8**: Corrosion rates at various Jcorr and IR free potentials. The base-plane is the plot of FIGURE 5b.

**FIGURE 9**: AC corrosion model considering a soluble ion at high pH. Hydrogen evolution plays an important role in destabilising the passive film.

**FIGURE 10**: At very negative potentials, hydrogen evolution is pronounced, and alkalization increases the potential span for soluble ions. The anodic cycle into this region causes corrosion. Corrosion products precipitate as ions diffuse away from the surface or the concentration becomes too great to be thermodynamically favorable.
FIGURE 11: At a potential above the hydrogen evolution line, the formation of a stable passive film facilitates passing of alternating charge without corrosion.

**Tables**

**TABLE 1:** Chemical composition of the investigated pipeline steels.

<table>
<thead>
<tr>
<th>wt%</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>V</th>
<th>Nb</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>X52</td>
<td>0.16</td>
<td>0.45</td>
<td>1.65</td>
<td>0.02</td>
<td>0.01</td>
<td>0.07</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>X65</td>
<td>0.16</td>
<td>0.45</td>
<td>1.65</td>
<td>0.02</td>
<td>0.01</td>
<td>0.09</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>X70</td>
<td>0.17</td>
<td>0.45</td>
<td>1.75</td>
<td>0.02</td>
<td>0.01</td>
<td>0.10</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>EN10130</td>
<td>0.12</td>
<td>-</td>
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<td>0.04</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**TABLE 2:** Chemical composition of the pH = 13.5 simulated soil solution.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄</td>
<td>5.0·10⁻³ M</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>2.5·10⁻³ M</td>
</tr>
<tr>
<td>NaCl</td>
<td>10.0·10⁻³ M</td>
</tr>
<tr>
<td>NaOH</td>
<td>316·10⁻³ M</td>
</tr>
</tbody>
</table>

**TABLE 3:** Weight loss and calculated corrosion rate for the coupons at -1250 mV_CSE (13 days).

<table>
<thead>
<tr>
<th>J_{AC}</th>
<th>Steel</th>
<th>Δw (mg)</th>
<th>v_{corr} (µm/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 A/m²</td>
<td>X52</td>
<td>2.9</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>X65</td>
<td>0.4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>X70</td>
<td>1.1</td>
<td>5</td>
</tr>
<tr>
<td>500 A/m²</td>
<td>X52</td>
<td>12.4</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>X65</td>
<td>13.7</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>X70</td>
<td>23.5</td>
<td>107</td>
</tr>
</tbody>
</table>

**TABLE 4:** Logged average electrical values and corrosion rates measured by the ER probes at different potential and AC interference settings.

<table>
<thead>
<tr>
<th>E_{corr}</th>
<th>J_{AC}</th>
<th>E_{CH}</th>
<th>U_{AC}</th>
<th>J_{OC}</th>
<th>v_{corr}</th>
</tr>
</thead>
<tbody>
<tr>
<td>mV_CSE</td>
<td>µA/m²</td>
<td>mV_CSE</td>
<td>V_{ref}</td>
<td>A/m²</td>
<td>µm/y</td>
</tr>
<tr>
<td>-1051</td>
<td>39</td>
<td>-1052</td>
<td>0.3</td>
<td>-0.1</td>
<td>1</td>
</tr>
<tr>
<td>-1047</td>
<td>232</td>
<td>-1065</td>
<td>2.0</td>
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<td>2</td>
</tr>
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<td>-1048</td>
<td>472</td>
<td>-1064</td>
<td>4.3</td>
<td>-1.7</td>
<td>1</td>
</tr>
<tr>
<td>-1050</td>
<td>935</td>
<td>-1063</td>
<td>6.2</td>
<td>-1.9</td>
<td>1</td>
</tr>
<tr>
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<td>32</td>
<td>-1155</td>
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<td>-0.3</td>
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<tr>
<td>-1144</td>
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<td>1.6</td>
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<tr>
<td>-1149</td>
<td>470</td>
<td>-1194</td>
<td>3.4</td>
<td>-6.3</td>
<td>154</td>
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<tr>
<td>-1156</td>
<td>962</td>
<td>-1216</td>
<td>4.7</td>
<td>-12.3</td>
<td>1888</td>
</tr>
<tr>
<td>-1251</td>
<td>30</td>
<td>-1260</td>
<td>0.2</td>
<td>-1.4</td>
<td>2</td>
</tr>
<tr>
<td>-1257</td>
<td>216</td>
<td>-1312</td>
<td>1.1</td>
<td>-10.7</td>
<td>8</td>
</tr>
<tr>
<td>-1246</td>
<td>500</td>
<td>-1400</td>
<td>2.7</td>
<td>-28.5</td>
<td>1728</td>
</tr>
</tbody>
</table>

**FIGURES**

**FIGURE 1:** Pourbaix diagram for iron outlining the high pH corrosion region (HFeO₂⁻) being highly dependent on the concentration of dissolved species.

**FIGURE 2:** Experimental setup with a parallel AC and DC circuit.

**FIGURE 3:** Weight loss coupon with a shielding “collar” (cross-section).
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FIGURE 9: AC corrosion model considering a soluble ion at high pH. Hydrogen evolution plays an important role in destabilising the passive film.

FIGURE 10: At very negative potentials, hydrogen evolution is pronounced, and alkalization increases the potential span for soluble ions. The anodic cycle into this region causes corrosion. Corrosion products precipitate as ions diffuse away from the surface or the concentration becomes too great to be thermodynamically favourable.

FIGURE 11: At a potential above the hydrogen evolution line, the formation of a stable passive film facilitates passing of alternating charge without corrosion.
Chapter 5

Discussion

Each of the included manuscripts [I-VIII] presents a detailed discussion of the observed phenomena. In this chapter, the results and observations will be discussed in a broad context, related to the existing knowledge about AC corrosion presented in Chapter 2, and in relation to the original research objectives presented in Chapter 1. One of the main points that is realised from the research [II,V] and literature is, that AC is not unambiguous, and can be considered as different phenomena under high CP or low CP. The two will be discussed individually below.

5.1 Low CP AC corrosion

5.1.1 Potentiostatic CP

Figure 5.1 is based on experiments in which the ON potential was varied from -900 mV\textsubscript{CSE} to -1600 mV\textsubscript{CSE} in steps of 100 mV and at each potential, the AC interference level was varied from 0 - 20 V in steps of 5 V [V].

![Figure 5.1: AC/DC current density map of corrosion rates recorded under potentiostatic control of AC and DC [V].](image-url)

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The responses in the current density plot are not straight lines. At low CP, the cathodic current decreases with increasing AC and even becomes anodic over an interval of AC interference $J_{AC} = 10 - 200 \text{ A/m}^2$, resulting in significant corrosion.

All the data points in Figure 5.1 correspond to averaged values over 24 hours of data and, while it was not mentioned in the paper, it was distinctive for all the points that exhibit low CP AC corrosion, that the current at some point during the period had been anodic, even if the average current density was cathodic. Therefore it can be concluded, that low CP AC corrosion in a potentiostatic CP configuration, is caused by the shift of the corrosion potential to below the set protection potential, $E_{ON}$, resulting in anodic current. This observation has been made by several authors [49–51, 61, 66, 91]. The data points denoted high CP AC corrosion will be discussed in section 5.2.

Figure 5.2 is an illustration of the shift of OCP due to AC interference, that leads to low CP AC corrosion [II, V]. The plot in Figure 5.2a is hypothesised based on trends observed in numerous experimentally recorded or mathematically modelled polarisation curves reported in literature (section 2.2.7) [49, 60–64, 67–69]. The actual AC current density at which the potential shift changes from negative to positive varies from one study to another but is generally observed between $J_{AC} = 200 - 400 \text{ A/m}^2$. It is likely, that this turning point is determined by factors that are not yet understood. Even though the experiments in [VIII] were conducted in order to investigate the phenomenon of high CP AC corrosion, the observation of the OCP pattern in Figure 5.2b was confirmed by multiple polarisation scans of different pipeline steels at increasing AC interference.

![Hypothesised polarisation behaviour with increasing AC interference.](image1)

**Figure 5.2:** Theoretical explanation for AC corrosion over an intermediate AC interference interval at low CP level as observed in Figure 5.1

A straightforward conclusion of the observed polarisation behaviour is, that the -850 mV$_{CSE}$ criterion is not sufficiently negative in the presence of AC interference. The consequences of the presented results in relation to cathodic protection will be elaborated on in section 5.5. In Figure 4 of [II] it can be seen that the corrosion rate of the low CP samples (-850 and -950 mV$_{CSE}$) is highest during the first day and slowly decreases, essentially becoming zero. Because the corrosion rate measurements in Figure 5.1 are based only on one day, it is possible that the long-term corrosion rate projection is exaggerated in this
study. Here, the effects of the scaling environment must also be considered, however, although calcite precipitation was observed to a minor degree in the low CP experiments, the increasing spread resistance was assigned to a build-up of corrosion products on the surface rather than calcareous deposits, because the increase in $R_S$ was proportional to the level of corrosion rather than the level of CP \[II\]. Besides, the results in Figure 4a in \[V\], did not show a reduced low CP AC corrosion rate in a scaling environment. Therefore, a scaling environment does not appear to limit low CP AC corrosion.

**Figure 5.3:** Visual appearance of the surface of ER coupons according to $E_{ON}$ potential. $U_{AC} = 10$ V. \[II\].

Figure 5.3 shows excavated ER probes after the experiment in an artificial scaling soil solution at 10 V AC and different ON potentials \[II\]. Corrosion products formed by AC under high and low CP are different in visual appearance. White calcareous deposits of increasing size are observed around the exposed ER element from medium to high CP (Figure 5.3c-g) clearly indicating that the pH has been elevated. An intermediate CP interval exists, in which the metal has not corroded (5.3c-d), confirmed by ER corrosion rate measurements.

**5.1.2 Galvanostatic CP**

In \[VI\] and \[VII\], galvanostatic control of the CP was applied, i.e. removing the possibility of anodic currents caused by the CP system. Still low CP AC corrosion was observed, as illustrated in Figure 5.4.
The data points denoted high CP AC corrosion will be discussed in section 5.2. The explanation of low CP AC corrosion in the case of a galvanostatic cathodic current is the phenomenon: *AC induced de-alkalisation* that was observed in [VI] and [VII]. In this case, low CP AC corrosion initiated when the potential shifted positive of the -850 mV<sub>CSE</sub> protection limit, which is commonly accepted to be the potential at which the pH is high enough to provide passivity (section 2.1.3). It therefore makes sense that when this potential is exceeded, the conditions for passivity no longer exist in terms of the surface pH. In fact, a decrease in pH was confirmed by pH-probe and pH paper measurements, when experiments of a low galvanostatic current was subject to high levels of AC interference [VI, VII]. Others have observed similar corrosion behaviour; i.e. an increasing potential of galvanostatic experiments with a small cathodic current density caused by increasing AC interference levels [7, 41, 66, 92]. Corrosion was observed when the potential approached or became less negative than -850 mV<sub>CSE</sub>. The pH evolution was not assessed in any of the studies.

Figure 5.5 shows the same theoretical polarisation curves as in 5.2a. This may also be used to explain the depolarisation behaviour that is observed under galvanostatic applied CP with increasing AC interference. The intersections of the cathode curves by lines of constant cathodic current in Figure 5.5a results in Figure 5.5b that shows how the potential of low CP samples may eventually exceed the protection limit of -850 mV<sub>CSE</sub>, which is associated with de-alkalisation into the low pH corrosion region in the Pourbaix diagram.

**Figure 5.5:** Theoretical explanation for AC corrosion at galvanostatic low CP as observed in Figure 5.4

Although low CP AC corrosion can be viewed as caused by either anodic currents under a low cathodic polarisation, or a potential shift positive of -850 mV<sub>CSE</sub> under small cathodic current, it was observed in [V], that a potentiostatic CP experiment did not show low CP AC corrosion when made in a pH buffer solution (Figure 4a, [V]). It can be interpreted, that pH may also influence the AC corrosion process in potentiostatic CP investigations.
5.1.3 Mitigation of low CP AC corrosion

Compliance with fundamental cathodic protection principles such as making the entire pipeline the cathode (i.e. no anodic currents) and satisfying the general protection potential criteria [15], will effectively stop low CP AC corrosion. Compliance with cathodic protection standards (ISO 15589-1:2015), is a criterion in the AC corrosion standard ISO 18086:2015 [9, 20]. It may be argued, that low CP AC corrosion, as discussed, is not truly representative of AC corrosion under cathodic protection, because corrosion occurs when either the current supplied by the CP system is anodic, or the polarised potential does not meet CP criteria. Therefore, the topic of the present dissertation, which is "AC corrosion of cathodically protected pipelines", should, in fact, be limited to high CP AC corrosion. It was decided to focus on all forms of AC corrosion of steel that is caused by an alternating current, including low CP AC corrosion.

The ISO 15589-1:2015 standard on cathodic protection specifies only protection potentials as criteria for protection. As several authors suggest, a revised set of protection potential criteria based on the level of AC interference may be necessary to avoid the risk of anodic currents caused by AC [36]. Alternatively, a combination of current density and potential measurements on coupons connected to the pipeline may ensure that cathodic protection is effective both in terms of current and potential, or effective corrosion protection may be documented by measurement of an acceptable corrosion rate [9, 10].

5.2 High CP AC corrosion

High CP AC corrosion is investigated in all of the manuscripts presented in Chapter 4 in one way or another. The high corrosion rates in Figure 5.1 and 5.4 clearly confirm that AC corrosion is of serious concern within the region of high AC and DC current densities outlined by the standard criteria: $J_{AC} < 30 A/m^2$, $J_{DC} < 1 A/m^2$ and $J_{DC}/J_{AC} > 3$ [9]. In Figure 8 of [VI], corrosion rate data from various experiments are shown in the $J_{AC}/J_{DC}$ plot, confirming the corrosion dependence on high AC and DC current densities [I, II, V and X] [93]. The magnitude of the AC and DC current densities is a function of the CP potential and induced AC voltage through the spread resistance of a coating defect, as described in section 2.2.10. Figure 5.6 illustrates a set of independent input parameters and their derivatives. It is fundamentally identical to "the vicious circle of AC corrosion" as presented by Nielsen et al. [47, 76].

- The CP potential, $E_{ON}$, drives the cathodic current density, $J_{DC}$.
- The induced alternating voltage $U_{AC}$, drives the alternating current density, $J_{AC}$.
- The defect geometry and the soil resistivity, $\rho_{soil}$, determines the spread resistance, $R_S$, of a coating defect.

![Figure 5.6: Illustration of the self-perpetuating nature of AC corrosion](image-url)
These derivatives are certainly not independent and affect each other in the following manner, as indicated by arrows in the illustration:

- The DC current density, $J_{DC}$, from the cathode reactions (2.5), (2.6) and (2.7), results in alkalisation of the soil locally at a coating defect that will affect $R_S$.

- Depending on the soil chemistry, the spread resistance, $R_S$, will decrease due to enhanced ionic conductivity ($OH^-$), or increase from precipitation of calcareous deposits on the steel surface at high pH. Soils with buffering capacity may stabilise pH (and $R_S$) for some time until the buffer system is exhausted. $R_S$ will affect both $J_{AC}$ and $J_{DC}$.

- The AC current density, $J_{AC}$, will affect the DC polarisation characteristics and enhance $J_{DC}$ through faradaic rectification. This can easily be seen as depolarisation of the polarisation curves in Figure 5.2a. The impact of this effect should not be underestimated.

It follows from the simple illustration in Figure 5.6, that if the soil system is non-scaling, then the spread resistance decreases, leading to enhanced currents, that will further decrease $R_S$ and the process becomes self-perpetuating. The observation of increased NaCl concentrations towards the surface in [IV] may be yet another feature of the self-perpetuating nature of AC corrosion because the spread resistance may be lowered even further. The rotational speed of this "wheel" can be understood as an analogy for the AC corrosion rate.

The strong dependence of $J_{AC}$ and $J_{DC}$ on one another is perfectly illustrated in Figure 5.1, where the AC corrosion risk area in the $J_{AC}/J_{DC}$ plot acts as a "sink" for data-points of very high corrosion rates because $J_{AC}$ enhances $J_{DC}$ and $J_{DC}$ enhances $J_{AC}$.

### 5.2.1 Mitigation of high CP AC corrosion

Using the wheel analogy for AC corrosion in Figure 5.6, mitigation of AC corrosion can be achieved by adjusting one or more of the engines that drive the wheel, i.e.:

- Modify the protection potential to comply with $J_{DC} > -1A/m^2$.

- Modify the soil resistivity and or coating defect geometries.

- Modify the induced AC voltage to comply with $J_{AC} < 30A/m^2$, e.g. by means of AC mitigation (earthing).

Of the above methods, modifying the protection potential appears to be the simplest intervention but, depending on the cathodic protection system design and condition of the coating, this may be impractical for reasons described in section 2.1.3.

Lowering the induced voltage by AC mitigation installations as described in section 2.1.5 to comply with the $J_{AC} < 30A/m^2$ criterion will solve the issue of AC corrosion in most instances, but the cost of retrospectively installing AC mitigation on a pipeline is high. In some cases with low soil resistivity, lowering the voltage to $U_{AC} < 2V$ may even be insufficient to stop AC corrosion, as is evident from the examples in Figure 2.18 [39].

The soil resistivity and coating defects are artefacts of the environment that are difficult to control. Use of a high resistivity backfill material upon construction of new pipelines could potentially limit current densities, but would impair the effectiveness of the cathodic protection system. Besides, it would be a matter of time before diffusion of the surrounding soil constituents would change the soil resistivity of the backfill material. This is not considered a valid technical solution. Use of backfill with high Ca and...
Mg content could provide the conditions for scaling, that would limit the current densities. However, the breakdown mechanism of the calcareous deposits observed in [II] leads to the conclusion that this would only limit, and not stop, AC corrosion. The use of perfectly isolating coatings would stop any electrochemical reactions on the pipeline steel surface, but this scenario is unrealistic. In the inevitable event of a coating defects or damages, the current densities will be high at these location and the conditions for AC corrosion would be worsened. On modern pipelines with high impedance coating systems, such as e.g. three layer polyethylene, the very low protection current consumed by coating defects along the pipeline, makes it possible to control the potential of the entire pipeline very accurately. As such, modification of the protection potential to comply with $J_{DC} > -1 \text{A/m}^2$ on well coated pipelines becomes easier [23].

5.3 The Pourbaix diagram

It has been found in the present research that the Pourbaix diagram may be the key explanation for AC corrosion at both low and high CP levels [III, VI, VII, VIII]. It is however difficult to assess corrosion data in the context of the Pourbaix diagram, because the parameters in the diagram are the IR free potential and surface pH, both of which are inherently difficult to determine experimentally when currents are flowing. It is implied that AC corrosion is dependent on a specific potential and pH range, but it has been found that additionally, an AC perturbation is required to trigger the corrosion mechanism [VI, VIII]. Several authors, who state that they have investigated whether or not AC corrosion was linked to the high pH corrosion domain in the Pourbaix diagram, may have falsely concluded that it is not, because one or more of the above parameters are either not considered, or inaccurately measured [7, 49, 74, 94]. Figure 5.7 shows the same corrosion rate data as in Figure 5.1 and 5.4, only plotted based on the IR free potential and a calculated pH based on the cathodic current density according to equation (5.1), where $pH_0 = 12.318$ and $p = 0.714$ as found in [VI].

$$pH(J_{DC}) = pH_0 + p \log (-J_{DC})$$  \hspace{1cm} (5.1)

*Figure 5.7: Representation of AC corrosion rate data in the Pourbaix diagram for iron.*
It can be seen that the high CP AC corrosion rate data fall inside or around the HFeO$_2^-$ region at high pH. As illustrated in e.g. Figure 5.5a, AC causes depolarisation of the cathode curve and an increase of the cathodic current, i.e. pH. It also causes a positive shift of $E_{IR-free}$ in both the $E_{ON}$ and $J_{DC}$ controlled experiment. Effectively, with increasing AC interference, the steel moves towards the HFeO$_2^-$ region in the Pourbaix diagram. The Pourbaix diagram also offers a sensible explanation for the $J_{DC} > -1\text{A/m}^2$ threshold because pH($-1$) = 12.3 according to equation (5.1), and the HFeO$_2^-$ region is thermodynamically possible for pH > 12.2.

In the two plots of Figure 5.7, low CP AC corrosion data is also illustrated. This has already been discussed in relation to Figure 5.2 and 5.5. In the case of anodic currents from a surface, corrosion is not necessarily linked to the pH but simply to the fact that the anodic current drives an oxidation reaction. Under a low cathodic current, the de-alkalisation and depolarisation is assumed to cause the steel to move up and left along the hydrogen line (opposite of the concentration polarisation mechanism in Figure 2.9a in section 2.1.3) [VI, VII]. When $E_{IR-free} > -850\text{mV}_{\text{CSE}}$ corrosion may occur as low pH corrosion (Fe$_2^+$.)

At present, no exhaustible explanation for the AC induced de-alkalisation mechanism is given, other than being related to the oxygen evolution reaction during the anodic potential cycle of the AC. Obviously the cathode reactions, which will allegedly proceed also at high AC interference levels, will increase pH. The mechanisms requires further investigation.

5.4 Proposal for an AC corrosion model

In [VIII], a mechanistic model for AC corrosion is presented. It is based on two distinct observations:

- Increasing levels of AC stabilises the HFeO$_2^-$ region in the Pourbaix diagram, allegedly due to a continuous oxidation or reduction of the dissolved ionic species.

- Hydrogen evolution plays an important role, possibly disturbing the formation of a protective passive film.

Even though the investigations in [VIII] were conducted in a pH = 13.5 environment, the described model can be used to illustrate the standard criteria.

In Figure 5.8a, the critera $-J_{DC} < 1\text{A/m}^2$ and $J_{AC} < 30\text{A/m}^2$ are both exceeded and corrosion occurs. This means that the pH is above 12.3 and the polarised potential is shifted into the HFeO$_2^-$ region due to AC interference. The passive film, here simplified as magnetite (Fe$_3$O$_4$), that would form under effective CP is dissolved at the steel interface. Hydrogen evolution will disturb the film during the negative potential wave. The dissolved species precipitate as magnetite during the positive wave, but the film is continuously disturbed and corrosion proceeds. The illustrated corrosion process corresponds to high CP AC corrosion with HFeO$_2^-$ as the dissolved ion, but the model also explains low CP AC corrosion under galvanostatic CP, where the pH is lowered and Fe$_{2}^{2+}$ is the dissolved ion. Furthermore, it is able to explain why high CP AC corrosion rates have an apparent maximum at an intermediate level of AC and decreases again at very high AC levels as observed in [V, VI, VII] as well as [X] [93]: As the IR free potential is shifted positively past the HFeO$_2^-$ region (possibly associated with a decrease in pH) corrosion will subside. Besides, at still higher AC voltages, the total time that the potential is actually within the HFeO$_2^-$ region, becomes smaller as the slope of the voltage curve around the IR free potential becomes steeper. Perhaps this is also the explanation for the extremely high corrosion rates in [VI] and [VIII], because the resistivity of the high pH soils was unrealistically low, and the AC voltage relatively small, causing a larger part of the potential variation to be within the HFeO$_2^-$ region.
In Figure 5.8b a scenario where the cathodic current density is below 1 A/m² is shown. Consequently, the pH is below 12.3 and formation of HFeO₂⁻⁻ is not thermodynamically possible. The passive film remains in contact with the steel and the alternating charge is allowed to pass via redox-reactions within the passive film [VII]. Because the passive film is conductive, the cathode reaction proceeds on the surface of the passive film. No corrosion occurs, even at AC current densities of several hundreds of A/m² [II, V, VI, VII]. The type of passive film does not need to be Fe₃O₄, but can also be Fe(OH)₂, a type of green rust or a combination of these. FeOOH or Fe₂O₃ are unlikely candidates because they contain iron in the fully oxidised state and cannot accommodate anodic charge (section 2.2.12). However, observation of these as corrosion products of AC corrosion is perfectly possible, either because the corrosion product is slowly pushed away from the reducing conditions on the cathodic steel surface, or simply due to oxidation in air during handling.

In Figure 5.9a a scenario is shown, in which the pH is above 12.3 and the polarised potential lies inside the HFeO₂⁻⁻ region. However, the amplitude of the AC interference is insufficient to oxidise or reduce the HFeO₂⁻⁻ species. Consequently, the region disappears and the conditions will resemble those in Figure 5.8b where no corrosion occurs in spite of a high pH. The illustrated example corresponds to conditions as investigated in [VI] and [VIII], in which the pH was artificially elevated and the IR-free potential was adjusted. No AC corrosion was observed until Jₐc exceeded 316 A/m² in [VIII] or 230 A/m² in [VI]. Those limits are higher than the 30 A/m² criterion, but the alternating voltage in those experiments was also small because of the artificially low soil resistivity. Under normal circumstances, a small level of AC interference will not be able to shift the steel to inside the HFeO₂⁻⁻ region, when observing the shift of E_{IR-free} and pH in Figure 5.7.
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Figure 5.9: Mechanistic AC corrosion model used to illustrate how AC corrosion is stopped at low levels of AC (a) or a very negative CP potential (b).

In Figure 5.9b a scenario is shown in which the level of CP is high enough to shift the entire potential variation into the immunity region. This represents the $J_{AC}/J_{DC} < 3$ criterion. It should be noted that this is associated with excessive hydrogen evolution and alkalinisation in a stagnant environment that will cause the $HFeO_2^-$ stability region to expand as illustrated by the slope of the lines. Depending on the soil system, it may also cause the spread resistance to decrease, yielding an increase of both $J_{AC}$ and $J_{DC}$. As such, this is not necessarily a permanent mitigation strategy. Furthermore, it is associated with a risk of overprotection, i.e. hydrogen embrittlement and coating disbondment.

5.4.1 Comments on the model

The model illustrations in Figure 5.8 and 5.9 are exaggerated for enhanced understanding. The hydrogen evolution e.g. does not happen at a rate where multiple gas bubbles are produced during each AC cycle. Active dissolution of ions does also not have to occur on the entire steel surface within each cycle, since this would be associated with extremely high corrosion rates. Corrosion will occur at the sites of highest current densities, and the actively corroding sites may move around on the surface. This can explain the surface morphology of AC corrosion that is a smooth or dimpled surface structure on a macroscale [39, 79]. Figure 5.10 shows how corrosion may initiate along edges of a coating defect where current densities are initially high, but as corrosion progresses, a bowl-shape appears. This explains the difference between observations on laboratory coupons (typically corrosion along edges [VII, VIII] and [X][93, 95]) and field observations as in section 2.2.2.
5.5 Consequences in relation to CP control

It is clear from the literature review in Chapter 2 and the manuscripts in Chapter 4, that whether experiments have been conducted with fixed potentials (potentiostatic) or with constant currents (galvanostatic), has a large impact on the results. Because the investigations deal with both alternating and direct currents, four variations of experimental AC/DC settings are possible:

1. Fixed \( J_{\text{DC}} \) and \( J_{\text{AC}} \) (galvanostatic). Potentials are allowed to vary to deliver the desired current densities.

2. Fixed \( E_{\text{ON}} \) and \( U_{\text{AC}} \) (potentiostatic). The currents are allowed to vary to sustain the desired potentials.

3. Fixed \( E_{\text{ON}} \) and \( J_{\text{AC}} \) (mixed). The DC current and the AC voltage is allowed to vary.

4. Fixed \( J_{\text{DC}} \) and \( U_{\text{AC}} \) (mixed) The DC potential and the AC current is allowed to vary.

An \( E_{\text{ON}} \) potential (or \( U_{\text{AC}} \)) controlled experiment is, in fact, not truly potentiostatic due to IR drop considerations. With respect to AC, the IR free alternating voltage experienced at the steel surface will be some fraction of the pipe-to-soil AC voltage. The magnitude of this is, however, difficult to determine and not a parameter that is usually assessed with respect to CP and AC interference. For \( E_{\text{ON}} \), as the polarisation current density and the solution spread resistance are not constant parameters (refer equation (2.10)), then neither is the true surface potential of the steel, \( E_{\text{IR-free}} \). Neglecting the IR compensated alternating voltage, this includes another two variations of the potential controlled experiment in which \( E_{\text{IR-free}} \) is controlled, as opposed to \( E_{\text{ON}} \), e.g. by minimizing the IR drop in the measurements or by measuring the IR free potential by available methods and adjusting the ON-potential accordingly.

5. Fixed \( E_{\text{IR-free}} \) and \( U_{\text{AC}} \) (potentiostatic). The current is allowed to vary to sustain the desired potentials.

6. Fixed \( E_{\text{IR-free}} \) and \( J_{\text{AC}} \) (mixed). The DC current and the AC voltage are allowed to vary.

In field applications, a pipeline is polarised to a certain ON potential either by a potential controlled rectifier or a current controlled system (refer section 2.1.3). The result of AC interference is an AC voltage that may also vary with both time as well as along the pipeline due to changes in the interference conditions. In effect: A pipeline experiencing AC interference may be considered as being in pseudopotentiostatic conditions \((E_{\text{ON}}, U_{\text{AC}})\) or \((E_{\text{IR-free}}, U_{\text{AC}})\).

Potential control of the experiments was applied in the majority of the investigations performed [I, II, III, V, VI] as well as [X][93]. This allowed for a realistic investigation of the self-perpetuating mechanism of AC corrosion, which cannot be investigated by galvanostatic methods, especially because the obvious effect of \( J_{\text{DC}} \) on \( R_S \) is not taken into account. One comment should be made to the nature of the CP
system: All the investigations used a potentiostat (equivalent to ICCP) to deliver the potential. For low CP levels ($E_{ON} = -850 \text{mV}_{\text{CSE}} - -950 \text{mV}_{\text{CSE}}$), there is a risk of inverting the polarity between anode and cathode (pipe) if the pipeline OCP is shifted negative of $E_{ON}$. In this case, the potentiostat will deliver an anodic current to pipe and cause corrosion. In the case of a galvanic anode CP system, the pipeline OCP may shift negatively with increasing levels of AC interference but as long as the $OCP_{\text{anode}} < OCP_{\text{pipe}}$, then a cathodic current will still be supplied to the pipeline (Figure 2.6 in section 2.1.3) - even if the anode system is designed to deliver "low CP" (e.g. $E_{ON} \simeq -900 \text{mV}_{\text{CSE}}$) in un-interferred conditions. Such a system can be considered as a self-regulating CP system under AC interference [54]. This observation is important with regard to the relevance of the present research and especially the findings of the mechanisms leading to low CP AC corrosion, because it may not be representative for many of the CP systems in real applications that feature galvanic anodes.

The discussion about revised CP criteria in the presence of AC interference is related to the observed shift of OCP that may become more negative than the present criterion of -850 mV$_{\text{CSE}}$. In the case of galvanostatic control of the CP system, the observation of low CP AC corrosion was associated with in-compliance with the accepted CP potential criteria of -850 mV$_{\text{CSE}}$.

### 5.6 Research objectives

The original research objectives (1-4) have been fulfilled by the investigations presented in Chapter 4. Below the individual topics are discussed.

#### 5.6.1 Chemical environment

The effect of the chemical environment has been investigated in 3 of the included manuscripts [II, IV, V]. It has been found that the presence of the earth alkaline ions will, indeed, cause formation of calcareous deposits like CaCO$_3$, Ca(OH)$_2$ and Mg(OH)$_2$ due to the alkaline environment at a cathodically protected surface. This precipitation causes an increasing spread resistance that reduces the current densities and thus, the AC corrosion risk. However, AC corrosion could not be stopped at the AC interference levels investigated. In [II], the calcareous deposits were subject to continuous build-up and break-down caused by either the alternating voltage or hydrogen evolution on the steel surface. This was clearly illustrated in the evolution of $R_S$. In effect, the overall corrosion rate was reduced, but the instantaneous corrosion rate during a break-down event was high (> 300 µm/y). This observation can be put in relation to the investigation of the stone-hard-soil formation [IV]. Here, the concentration of calcite in the stone-hard-soil formation was elevated but, in spite of this dense formation, AC corrosion was not stopped here either. This is probably due to the observed increase of NaCl concentration in the stone-hard-soil which could have, in fact, lowered the spread resistance rather than increasing it, even in a Ca-rich soil. The increase in concentration of NaCl towards the surface has been confirmed by others [86]. Additionally, the observation of different phases in the stone-hard-soil formation in [IV] was used as a pH characterisation tool that indicated a pH value >13 towards the corrosion site, which is difficult to determine by conventional methods, and may be part of an explanation for the lower pH values (pH = 8-11) observed in other investigations of similar stone-hard-soil formations [38, 39]. The investigations of individual chemical constituents in solution in [V] suggested that the higher concentration of NaCl did in fact, lower the high CP AC corrosion rates however only in the absence of Na$_2$SO$_4$.

In [V] it was found that the base neutralising effect (BNE) of a soil was not able to limit AC corrosion. In fact, the opposite was observed for very negative $E_{ON}$ potentials. Laboratory studies of a phosphate
buffer (BNE$_{10} = 5.2$) and a solution with NaHCO$_3$ (BNE$_{10} = 4.0$), as well as a field test in a clayey soil (BNE$_{10} = 10.8$), resulted in the highest corrosion rates of all investigated soil system in both the laboratory and field study at E$_{ON} \approx -1600$ mV$_{CSE}$ and high AC interference. This contradicts the alkalisation theory, but it appears that the buffering capacity of a soil system is exhausted by the produced alkalinity at a cathodically protected surface. The incubation time observed by Nielsen was also observed in the present field study [V] and is potentially related to the BNE-value of a soil, and the DC current density [46].

### 5.6.2 Varying AC/DC conditions

Investigation of varying AC/DC conditions on the AC corrosion risk was an integral part of several manuscripts due to continuous changing of the experimental settings [I, II, V-VIII]. Besides, this was the primary focus of two manuscripts which are not part of this dissertation [IX-X]. It has been found that the AC corrosion risk is indeed affected by changing the AC and/or DC settings. On the question of averaged values for interference levels being representative of conditions where e.g. the AC level is continuously increased and decreased, the study in [IX-X] concluded that the accepted AC and DC current density criteria are fully suited for average considerations of these parameters [93]. The results in [X] do suggest that an AC interference level that changes between a high level A and a low level B, will produce higher corrosion rates than stationary conditions at A (or B), at the same CP potential, E$_{ON}$. The time weighted average level, C, will then not fit into a linear model of increasing AC corrosion rates as a function of the interference level from A-B.

In the field study in [V], the AC level was changing with daily load conditions on the HVTLs. The reported AC and DC current densities are averaged values from 2 days. When comparing the $J_{AC}/J_{DC}$-plot from the field study (Figure 5, [V]) to the laboratory study (Figure 3a, [V]), the high corrosion rates are shifted towards lower values for $J_{AC}$ and $J_{DC}$ in the field study. This is in line with the observation of [X]. Consequently, laboratory investigations of the effect of AC and DC current densities made under static conditions might underestimate the seriousness of AC corrosion that is experienced under fluctuating conditions. An example is the $J_{AC}/J_{DC}$ plot in Figure 5.4 from [VII]. This suggests that the standard criteria are too conservative, however the standard criteria are based on field data that includes the effect of changing AC/DC conditions.

### 5.6.3 Pipeline steel

The effect of pipeline steel was only investigated in [VIII], and the findings did not suggest that the type of steel (X52, X65 or X70) has significant influence on the AC corrosion susceptibility. The polarisation behaviour of the steels was much more dependent on the level of AC interference than the steel type. This has the fortunate consequence that the findings of the present work can be considered as independent of the pipeline steel grade.

### 5.6.4 Coating defect geometry

Manuscript [I] investigated the effect of coating defect geometry. Three elements of the geometry were investigated in detail at different CP levels: the area, coating thickness and length-to-width ratio of the exposed steel. The results refer to essentially pure DC conditions, since only a 10 mV measurement signal was used for the EIS analysis. It was found that models available to describe $R_S$ mathematically, are in agreement with the measurements, but that the coupon design (not only the exposed steel surface) has a larger influence than originally assumed [78]. The immediate consequence hereof is that coupons
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used for pipeline corrosion studies, that are not designed as part of a larger structure, will have a lower 
$R_S$ than the coating defect it tries to mimic and will overestimate the current densities at a given CP and 
AC interference level. This knowledge was used in all of the following studies that used coupons. Here, 
the coupon dimensions were at least 3 times those of the coating defect.

The effect of varying the geometry and CP level on the double layer characteristics is illustrated in 
Table 5.1. The elements refer to the simple Randles circuit representation of a double layer interface. 
Instead of the double layer capacitance, the impedance of this element is included. This is dependent on 
the frequency of the excitation, but the comparison to the resistances becomes more simple. 
The effect of the ON potential on the spread resistance was small in the EIS investigations, due to the 
short duration of the measurement. But the long term lowering of $R_S$ due to alkalisation was found to be 
dependant of $E_{ON}$. The geometrical dependence on $R_S$ was confirmed.

The charge transfer resistance was significantly lowered by more negative $E_{ON}$ and generally lowered by 
a smaller area, thinner coating and a more scratch-like geometry. 
Finally, the double layer capacitance was fairly independent of the defect geometry, but was highly 
dependent on the polarisation level. It generally dropped an order of magnitude when the protection 
potential was decreased from $E_{ON} = -850 \text{ mV}_{CSE}$ to $-1550 \text{ mV}_{CSE}$. This is reflected in Table 5.1 as an 
increase in the impedance of this element. The values found for the $C_{dl}$ in [I] are in line with observations 
made by others [57, 58, 86].

Table 5.1: Dependence of geometry of a coating defect and CP level on the double layer characteristics in a 
non-scaling soil solution [I]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$R_S$ ($\Omega m^2$)</th>
<th>$R_{ct}$ ($\Omega m^2$)</th>
<th>$Z_{Cdl}$ ($\Omega m^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>More negative $E_{ON}$ (higher CP)</td>
<td>↓↓↓</td>
<td>↓↓↓</td>
<td>↑↑</td>
</tr>
<tr>
<td>Smaller area, A</td>
<td>↓↓↓</td>
<td>↓</td>
<td>↔</td>
</tr>
<tr>
<td>Thinner coating, $t$</td>
<td>↓↓</td>
<td>↓</td>
<td>↔</td>
</tr>
<tr>
<td>Scratch-like geometry (higher l/w-ratio)</td>
<td>↓↓</td>
<td>↑↓</td>
<td>↔</td>
</tr>
</tbody>
</table>

The following points outline the consequence of the double layer response to the parameters investigated:

- At lower $E_{ON}$ in a non-scaling environment, $R_S$ will decrease and AC and DC current densities 
will increase, following the illustration in Figure 5.6. Additionally, $R_{ct}$ drops and $Z_{Cdl}$ increases, 
forcing a larger fraction of the alternating current to flow via faradaic charge transfer reactions 
as opposed to the double layer capacitance. This will inevitably result in enhanced corrosion 
probability.

- With a decreasing defect area, the value of $R_{ct}$ is also lowered independently of the decrease in 
$R_{ct}$ caused by the CP level. This will result in enhanced faradaic reactions both from alternating 
and direct current. This implies that the polarisation behaviour of coating defects on a cathodically 
protected pipeline, will be dependent on the coating defect area.

- Thinner coatings will lower $R_{ct}$, which has the same effect as explained for a smaller defect area.

- An increasing l/w-ratio caused a slight decrease of $R_{ct}$ at more negative $E_{ON}$, which has the same 
effect as explained for the smaller defect area.

By considering the impedance of the double layer capacitance and the charge transfer resistance, the fraction, $\chi_F$, of alternating current that is transferred via faradaic charge transfer reactions can be calculated
according to equation (5.2).

\[ \chi_F = \frac{(R_{ct})^{-1}}{(Z_{dl})^{-1} + (R_{ct})^{-1}} \]  

(5.2)

The impedance of the double layer element is dependent on the frequency. In Figure 5.11, data from [I] is used to illustrate the effect of the investigated parameters on \( \chi_F \). The ON potential is set equal to the IR-free potential, \( E_{ON} = E_{IR-free} \). This can be justified because a Luggin capillary was used for the reference element. It can be seen that for an unpolarised surface, the charge transfer will be purely capacitive. With increasing CP levels to \( E_{IR-free} < -1 \text{V}_{\text{CSE}} \), an increasing fraction will become faradaic. This is highly dependent on geometrical factors such as area and \( l/w \)-ratio. The effect of increasing coating thickness had no apparent effect and is not shown here.

The very large fraction of alternating current discharge for coupons with \( A \geq 10 \text{cm}^2 \) in Figure 5.11b, does not necessarily mean that they are more prone to AC corrosion, because the fraction \( \chi_F \) refers to the current density, which is small for larger coating defects. Conversely, the rather low \( \chi_F \) for coating defects with \( A < 1 \text{cm}^2 \) may be part of the explanation to why a coating defect of \( A = 1 \text{cm}^2 \) has been found to be the most critical to AC corrosion. This may be understood in conjunction with other presented arguments [78, 79]. The large dependence of the \( l/w \)-ratio on \( \chi_F \) in Figure 5.11a may offer an explanation for the high corrosion rate of the ER probe (\( l/w = 10 \)) compared to the weight loss coupons (circular) in [VIII], when they were polarised to \( E_{IR-free} = -1250 \text{mV}_{\text{CSE}} \). Despite the fact that they had similar \( R_S \) values and AC and DC current density values. Comparison of corrosion rate on circular and rectangular ER probes in [X] also showed that rectangular probes produced higher corrosion rate at similar AC and DC potential control.

The above findings are an addition to the "vicious circle of AC corrosion" and another explanation for the effect that high CP levels and coating defect geometry have on AC corrosion rates. The EIS investigations made in [I] were conducted with a 10 mV AC excitation, to stay in the pseudo-linear potential current domain (see section 3.2.2). The response of the electrochemical double layer to AC perturbations of several volts will, undoubtedly, not be the same so the results can probably not be transferred directly to an AC corrosion context without investigating the effects of a larger excitation signal.
The influence of potential and area on the charge transfer resistance, $R_{ct}$, may also be part of the explanation to why the IR-free potential of a pipeline, measured by e.g. the instant-off method, cannot be considered representative of all coating defect sizes [96].

Another finding in [I] was that, the orientation of the probe surface had a large influence on the evolving spread resistance which caused significant differences in the AC corrosion rate. An upwards facing probe surface had the lowest $R_S$. It was speculated whether this was caused by gravity effects, e.g. a high pH environment being heavier and concentrating on the probe surface rather than diffusing away. The visualisation experiment in [III] showed that this was not the case. If anything, the hydrogen evolution at very negative potentials appeared to produce an upwards drift of the high pH environment, because the hydrogen bubbles created a "pump effect". In soils where convection is limited, this effect is anticipated to be reduced but the upwards drift of hydrogen gas may still offer an explanation for the orientation dependence: A downwards facing probe may accumulate a considerable amount of hydrogen gas on the surface that will displace the electrolyte and reduce the active area for current transfer. An upwards oriented probe surface will only be in contact with hydrogen gas during the very instance of formation, after which it will leave the surface. A sideways oriented probe surface represents a mixture because the formed hydrogen gas might travel along the probe surface for some time and effectively shield the steel surface on its way. This effect will be more pronounced for an "up-right" probe element, than for an element "lying down". For explanation of the orientations, see [I]. In fact the opposite is observed with respect to the sideways oriented probes in [I], suggesting that other factors are important.

The orientation of ER probes in [II-III] were sideways and up-right, but for the studies in [V-VIII] the insight from [I] was implemented and the probe element was facing upwards to investigate the worst case scenario for AC corrosion.
Chapter 6

Conclusion

The conclusions of the present research are listed below. The list includes overall and general observations based on the manuscripts in Chapter 4 and the discussion in Chapter 5.

1. AC corrosion is observed both at low and high levels of cathodic protection. The two can be understood as different corrosion phenomena: "Low CP" and "high CP" AC corrosion.

2. Low CP AC corrosion can be further divided in two corrosion mechanisms based on the CP control; galvanostatic or potentiostatic CP. A correlation between the two cannot be excluded.

3. Potentiostatic low CP AC corrosion occurs due to a negative shift of the pipeline OCP to below the set protection potential $E_{ON}$, which causes an anodic oxidation current, i.e. corrosion.

4. Galvanostatic low CP AC corrosion occurs due to a positive shift of $E_{IR-free}$ to above -850 mV$_{CSE}$. Results indicate that this is associated with de-alkalisation of the steel surface, and entering the low pH corrosion region in the Pourbaix diagram (Fe$_2$O$_3$).

5. High CP AC corrosion occurs for $-J_{DC} > 1$ A/m$^2$ and $J_{AC} > 30$ A/m$^2$. $-J_{DC} = 1$ A/m$^2$ corresponds to a pH above which ionic dissolution as HFeO$_2$ is thermodynamically possible. $J_{AC} > 30$ A/m$^2$ refers to the depolarising nature of AC on the IR-free potential that will cause the steel to enter the high pH corrosion region of the Pourbaix diagram. The oscillating potential will continuously oxidise the dissolved species and stabilise this region.

6. High CP AC corrosion can be described as a self-perpetuating mechanism in which $J_{AC}$ enhances $J_{DC}$ through faradaic rectification, $J_{DC}$ affects $R_S$ due to alkalisation and $R_S$ affects both $J_{DC}$ and $J_{AC}$ via Ohm’s law, at a certain CP potential and induced alternating voltage.

7. An intermediate CP level exists at which AC interference does not lead to AC corrosion.

8. The passive film on cathodically protected steel consist of one or more of the oxides Fe$_3$O$_4$, Fe(OH)$_2$ or a type of green rust. These oxides may facilitate redox-reactions of iron that allow the alternating charge to be transferred without progressing corrosion.

9. Hydrogen evolution from the cathode reaction may disturb the formation of a stable passive film when the electrical contact between passive film and steel is disrupted by ionic dissolution, forcing the hydrogen evolution reaction to occur exactly at this interface.

10. At intermediate levels of CP, the majority of alternating current is transferred via charging and discharging of the electrochemical double layer. Measurements of the charge transfer resistance and
double layer capacitance at different CP levels suggests that increasing the CP level to $E_{IR-free} \leq -1250 \text{ mV}_{\text{CSE}}$, will enlarge the fraction of faradaic charge transfer, i.e. corrosion.

11. The geometry of a defect will affect the spread resistance and the charge transfer resistance. A $1 \text{ cm}^2$, scratch-like coating defect, with the exposed steel surface oriented upwards, will be most susceptible to AC corrosion.

12. Calcareous deposits (Ca, Mg) on a cathodically protected surface may limit, but cannot stop AC corrosion due to repeated breakdowns of such a deposit caused by either the alternating voltage or hydrogen evolution.

13. The natural pH buffering capacity (BNE) of some soils may postpone, but will not stop, the pH elevation of a cathodically protected surface and thus the formation of conditions necessary for high CP AC corrosion.

14. Investigations of different pipeline steels did not suggest that the type of steel is important to the AC corrosion susceptibility. The investigation of the effect of steel grade was not exhaustive.
Chapter 7

Future work

The presented research offers an expansion of the collected knowledge that exists about AC corrosion. However, with every answered question, another two arise. Below is a short list of planned and proposed research activities for future studies on the phenomenon AC corrosion.

1. The discovery of an AC induced de-alkalisation mechanism needs further investigation by pH measurement techniques that are more suited for the environment in question. The approximation of pH according to the cathodic current density is largely based on experiments under pure CP conditions and needs verification under AC interference conditions. A modification to the ER probe design that features an iridium oxide (IrO) based pH probe, designed specifically for use in high pH environments under CP, is presently under development [97]. This will allow for simultaneous measurement of pH, $E_{\text{IR}-\text{free}}$ and corrosion rate for a comprehensive corrosion rate study of the AC and DC current density domain in the Pourbaix diagram, including a detailed investigation of the de-alkalisation mechanism under galvanostatic CP.

2. The findings of the present research suggest a strong correlation to the Pourbaix diagram of iron. This diagram typically considers iron in water. A study on the effect of other species on the stability regions could give more insight into the effect of the chemical environment on AC corrosion. Such species could include chlorides, carbonates, sulphate etc. A theoretical study based on thermodynamically calculated Pourbaix diagrams would need verification by experiments. Alternatively, calculated diagrams could be based on published investigations of different environments, in an attempt to explain the findings of others using the theory presented in this thesis.

3. Present computer models that attempt to predict AC corrosion rates via electrochemical processes are extremely time-consuming due to the small time-step resolution that is required to resolve the voltage and current fluctuations at 50 Hz [98, 99]. The presented AC corrosion model suggests that AC corrosion is a function of pH, $E_{\text{IR}-\text{free}}$ (placement in the Pourbaix diagram) and an AC interference level. These parameters are far easier to simulate than the rate of electrochemical processes, and the possibility of making more efficient computer models with experimentally determined correlations between pH, $E_{\text{IR}-\text{free}}$, $U_{\text{AC}}$ and $v_{\text{corr}}$ can be considered. It is however uncertain if the kinetics can be entirely excluded from the models.

4. Investigation of surface oxides formed under corrosion conditions and passive conditions as performed in [VII] by XPS, offer valuable information about the AC corrosion process. However, XPS did not provide conclusive results on the phases present. More, similar, investigations are needed to further characterise the passive and non-passive surface films. Such methods could include grazing incidence XRD in an inert atmosphere or SEM/EDS investigations of the surfaces.
under ultra high vacuum. It is important, that oxidation of the surface film prior to, or during, characterisation is prevented. *In-situ* methods, such as the Raman spectroscopy technique applied by Tribollet *et al.*, are also interesting candidates, however the characterisation techniques typically rely on a line-of-sight approach which is difficult to realise for AC corrosion in soil. In aqueous solutions, measures must be taken to simulate the diffusion and pH conditions that exists for a coating defect covered by soil.
Bibliography


This doctoral thesis by Andreas Junker Olesen investigates AC corrosion of cathodically protected pipelines. The research work is contained in 8 scientific papers, 5 of which are conference contributions and 3 are manuscripts submitted for publication in peer reviewed journals. The findings in this thesis suggest that much of the present knowledge about AC corrosion may be explained by fundamental corrosion science principles. A model for the AC corrosion mechanism, based on the Pourbaix diagram for iron, is proposed.