

# Evaluation of soil aeration as applicable to underground metal corrosion

Rukshan Maliq Azoor

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> Department of Civil Engineering Monash University Australia

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To my Mother For her unwavering support and belief in me

# Abstract

This research was conducted to ascertain the influence of soil aeration properties on the patterns and levels of corrosion experienced by buried assets such as pipelines. The work stemmed from a larger body of work examining the factors that contribute to failures of buried pipelines in water supply networks. Previous research indicated that corrosion is a major contributor towards pipe failures and that soil aeration is one of the main governing factors influencing corrosion.

The main objective of this study was to identify and characterise the main mechanisms responsible for the key phenomenological observations in underground corrosion. Guided from previous research informing the importance of soil aeration, a field case study was conducted during initial stages of this research to gather field evidence from sites where failures in water supply networks occurred. The field case study corroborated research literature and provided first hand evidence of some of the phenomena involving soil aeration, including the effects of differential aeration.

Based on these findings, multiphysics finite element numerical models were developed to simulate field conditions for corrosion. New methods were developed for implementing time dependent corrosion behaviour by coupling corrosion electrochemistry to soil aeration and moisture properties. The numerical models were validated with published corrosion data from a field exposure study conducted by the U.S. National Bureau of Standards. A multidisciplinary experimental framework was devised to investigate the varying influence of soil aeration and moisture conditions on corrosion. Three soil types, sand silt and clay, spanning the general soil spectrum were used for all experiments. Electrochemical experiments including potentiodynamic polarisation, time lapse polarisation resistance measurement and electrical conductivity were performed. Soil aeration and moisture properties and standard compaction tests. Micro X-ray CT imaging was used to analyse the microstructure and the pore network that facilitates corrosion.

All experimental results indicated that the optimum moisture for corrosion in soil occurs at the air transition point, identified as the inflection point of the soil water retention curve. The mechanisms leading to this behaviour were for the first time, attributed to soil hydraulic properties which are easily obtained through standard water retention tests. It was further identified that standard engineering compaction practices may result in the highest levels of corrosion in buried assets. Finally, the new insights obtained were incorporated into improved numerical models that illustrate the simultaneous effect of diffusion and moisture migration on corrosion, in addition, enabling climatic coupling. The developments made through this research are expected to be useful in field assessments of underground corrosion and its mitigation.

# Declaration

This thesis is an original work of my research and contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Signature:

Name: Rukshan Maliq Azoor

Date: 19.06.2019

# **Publications during enrolment**

- **R.M. Azoor**, R.N. Deo, N. Birbilis, J. Kodikara, *On the optimum soil moisture for underground corrosion in different soil types*, Corrosion Science. 159 (May 2019) 108116, https://doi.org/10.1016/j.corsci.2019.108116
- **R.M. Azoor**, R.N. Deo, N. Birbilis, J.K. Kodikara, *Coupled Electro-Chemical-Soil Model to Evaluate* the Influence of Soil Aeration on Underground Metal Pipe Corrosion, Corrosion. 74 (2018) 1177– 1191. doi:https://doi.org/10.5006/2860
- **R.M. Azoor**, R.N. Deo, N. Birbilis, J.K. Kodikara, *Modelling the Influence of Differential Aeration in Underground Corrosion*, in: COMSOL (Ed.), Proc. 2017 COMSOL Conf. Bost., Boston MA, 2017
- **R.M. Azoor**, R.N. Deo, B.M. Shannon, J.K. Kodikara, *Using soil moisture retention curves and corrosimetry to characterise the role of soil moisture in underground corrosion*, in: 13th Aust. New Zeal. Conf. Geomech., Perth WA, 2019
- **R. Azoor**, R. Deo, J. Kodikara, *Modelling and testing of optimum soil moisture levels in the corrosion of underground pipelines*, in: 7th Int. Symp. Deform. Charact. Geomaterials, Glasgow, 2019
- **R. Azoor**, R. Deo, J. Kodikara, *The influence of soil moisture retention properties on oxygen diffusion in soils of different textures* (In preparation)
- **R. Azoor**, R. Deo, D. Wijewickreme, E. Asselin, J. Kodikara, *Corrosivity characterisation of Fraser River Silt* (In preparation with UBC collaboration)
- **R. Azoor**, R. Deo, J. Kodikara, *Numerical modelling of coupled phenomena in underground corrosion* (Planned)
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- R.N. Deo, R.M. Azoor, C. Zhang, J.K. Kodikara, *Decoupling pipeline influences in soil resistivity measurements with finite element techniques*, J. Appl. Geophys. (2017). doi:10.1016/j.jappgeo.2017.11.009
- R.N. Deo, C. Zhang, S. Rathnayaka, B. Shannon, D. Weerasinghe, **R.M. Azoor**, J.K. Kodikara, *A Method for Identification of Pipe failure Hotspots*, Geotech. Eng. J. SEAGS AGSSEA. 50 (2019).

# **Presentations and Awards**

- Postgraduate Publications Award (PPA) 2019, Monash University
- 1st Place at the 10th Annual Brian Cherry Award (for excellence in post graduate/student research in corrosion), organized by the Victorian branch of the Australasian Corrosion Association. (AECOM Melbourne Oct 2018)
   Presentation title: "When does maximum corrosion happen in underground metal infrastructure? Should we consider this in geotechnical engineering design?"
- Graduate Research International Travel Award (GRITA), Faculty of Engineering Monash University (Travel grant to conduct research at the University of British Columbia Vancouver Canada)
- Semi-finalist (Victoria) FameLab Australia, Organized by the British Council Australia (Melbourne Museum March 2018)
   Presentation title: "A predictive model for underground corrosion"
- **2nd Place at the 9th Annual Brian Cherry Award** (for excellence in post graduate/student research in corrosion), organized by the Victorian branch of the Australasian Corrosion Association Presentation title: "*A unified electro-chemico-soil mechanical model for underground corrosion*"
- Best Seminar presentation, Department of Civil Engineering, Monash University (Nov 2017 Civil Engineering Conference 2017 held at Engineers Australia Melbourne)
  Presentation title: "A Multiphysics model for underground Corrosion"

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# **Chapter 1: Introduction**

### 1.1 Underground corrosion and pipeline failures

Corrosion of buried infrastructure such as pipelines is a problem that causes significant economic losses. Corrosion-induced pipe failures are increasingly encountered by water utilities with ageing pipe networks around the world [1,2]. Corrosion in soils is a complex problem involving interrelationships between the electrochemical activity on the pipe, soil properties, and other external factors [3–5]. Underground corrosion is usually classified into uniform corrosion and localised corrosion [3]. Uniform corrosion leads to spatially uniform loss of metal by the action of closely-placed and randomly-oriented anodic and cathodic regions, known as micro cells, while the spatial separation of anodes and cathodes, known as macro cell formation, leads to localised metal loss [6,7]. Aeration and moisture retention in soils have been shown to be important factors governing the rate of corrosion [4], while macro corrosion cells formed due to differential aeration in soil cause significant levels of localised patch corrosion, leading to the relatively rapid loss of structural integrity of buried pipelines [3]. It is almost impossible to locate and predict regions undergoing destructive corrosion due to the lack of relevant information and access to underground assets. Furthermore, it is not possible to develop purely empirical predictive equations, due to the difficulty in collecting sufficient data which are accurate and span a range of variables of influence.



Figure 1.1: A reticulation pipeline failure in a residential suburb in Melbourne, captured during a field visit

Figure 1.1 shows a pipe failure in a residential suburb in Melbourne. Such failures typically result in flooding of streets, causing inconvenience to residents and occasionally leading to serious damage to the surroundings, especially if high-pressure lines are involved. More than 70% of buried water pipelines in Australia are of some form of ferrous metal [5] and are susceptible to corrosion [5]. In a study conducted on the water supply networks in Melbourne Australia by Kodikara et al. (2012) [8], corrosion was identified as the major contributor to pipe failure. However, information about the levels of corrosion experienced by a pipeline asset and its remaining lifetime is not readily available. Maintenance of this ageing pipe network would benefit from timely information which would point to high priority areas termed "hotspots" [9]. With data on these pipelines only available after failure, and acquisition of pipe condition data before failure being an expensive process, a mechanistic understanding of the effect of soil properties on underground corrosion is invaluable. As indicated by previous studies [3–5,10,11], the conditions of aeration and moisture in soil play a significant role in the development of such mechanistic models.

### 1.2 Importance of soil aeration in underground corrosion

The important influence of soil aeration and moisture levels on underground corrosion has already been established. Results from previous studies also place considerable significance on the aeration level of soil in modelling long-term corrosion damage in soils [4,12]. In particular, data from a long-term environmental exposure project presented by Romanoff indicated strong evidence of the importance of soil aeration [4].

Furthermore, the pattern of corrosion mass loss for all soils shows a consistent exponential increase with time, as proposed by some researchers [12,13], with the level of aeration being the major factor governing the shape of the exponential model. It is also observed that in some cases, soils with very poor aeration show an unusually high level of corrosion, despite being in waterlogged condition. A possible reason for this behaviour may be the action of macro cell corrosion, which results in intense levels of localised corrosion in poorly aerated regions. Difference in the availability and diffusion of oxygen in soil, termed differential aeration, is one of the main reasons for the formation of macro cells. The formation of macro cells in the field is also impacted by the electrical conductivity/resistivity of the soil, which is also governed by soil aeration and moisture conditions. Figure 1.2 schematises some of the conditions of soil aeration and moisture, including differential aeration which may lead to corrosion hotspots impacting buried pipelines and therefore should be prioritised in condition assessment. It is noted here that these corrosion hotspots are similar to the stress hotspots presented by Weerasinghe (2018), and the effect of stresses compounded with that of corrosion is therefore detrimental to the condition of the buried pipeline, if not mitigated.



Figure 1.2: Schematic representation of corrosion hotspots along a pipeline. The red shapes along the pipeline indicate corrosion at the anode and the cyclic arrows indicate macro cell formation due to differential aeration.

Another important phenomenological observation pertaining to corrosion in soils is the existence of an optimum level of soil moisture for underground corrosion at which the rate of corrosion achieves its maximum value. The reason for this behaviour is the effect of the increasing soil-metal contact area, termed the active area, and oxygen diffusion through soil, both of which are functions of the aeration and moisture regimes in soil. A mechanistic understanding of this phenomenological observation therefore requires a detailed analysis of the aeration and moisture regimes in soil.

The aeration and moisture regimes of soil and the hotspots as applicable to underground corrosion are best observed under actual field conditions. Evidence for the importance of soil aeration and its associated effects were obtained through a case study programme detailed below in Section 1.3.

# 1.3 Observations from a field case study program

A field case study program was conducted during the initial stages of the present research to observe the effects of soil aeration on the corrosion of failed pipelines in the field. This study was conducted as part of another study on reactive soils and their effects on pipeline failures [14]. This case study was conducted with the support of City West Water (CWW) in Melbourne, which is the organisation responsible for the operation and maintenance of the water pipeline networks in the western suburbs of Melbourne. The CWW pipe failure case study provided valuable insights into the corrosion process and into factors that accelerate pipe deterioration. Observation of the pipe in the field allowed for a better assessment of the conditions under which corrosion occurred. The analysis of the failed pipe specimen in the laboratory also yielded valuable insights. The main observations gathered from this case study are summarised below with relevant figures acquired from the field and subsequent laboratory analyses.

1. Pipe failures tend to occur at driveway edges where sharp gradients in sub-soil oxygen concentrations are present



Figure 1.3: Corrosion- induced pipe failure at driveway edge, possibly caused by differential aeration corrosion.

2. Pipe failures close to trees are a common occurrence. Tree root zones can cause differential aeration cells to develop, in addition to imparting stresses on the pipe.



Figure 1.4: Pipe failure next to tree root. The failed pipe that was recovered showed high levels of corrosion

3. Corrosion patterns show that certain areas of the pipe surface are more prone to corrosion. Bottom surfaces which are more likely to be poorly aerated, show significantly higher levels of corrosion. A 51-year-old 300 mm diameter failed pipe obtained from the field was gritblasted to reveal the corrosion patterns to illustrate this observation. The corroded pipe surface was scanned in the laboratory using a laser scanner, and the results shown in Figure 1.5.



Figure 1.5: Images of top and bottom surfaces of corroded pipeline and surface scan of pipe highlighting different patterns of corrosion on top and bottom surfaces. The heat map indicates depth of corrosion. (Red deepest and green shallowest)

4. Cast iron undergoes graphitic corrosion, which is the leaching of iron for participation in the corrosion reactions while leaving behind the carbon (graphite) matrix [15,16]. Graphitic corrosion was present in all failed pipe samples which were examined and the samples showed evidence of chemical species movement during the corrosion process. As the iron leaches though the internal cement lining of the pipe, oxidation reactions occur creating green and brown rust, as shown in Fig. 1.6.



Figure 1.6: Cross section of failed pipe specimen showing corroded graphite layer (grey-coloured region), and iron oxide (brown and green colour) migration within cement lining

5. A soil crust which is visibly different to the surrounding soil, and tightly adhered to the pipe shows that, in addition to facilitating the physical corrosion process, the surrounding soil also participates chemically in the corrosion reaction and undergoes changes in soil properties. The soil crust as identified in the field and separated from the corroded pipe in the laboratory are shown in Fig. 1.7.



Figure 1.7: Pipeline coated by layer of soil with different chemical composition to that of surrounding soil, seen as an orange coloured crust.

The observations from the case study program indicated that soil aeration, and in particular differential aeration, is important in underground corrosion. The observations made at driveway edges, tree roots and the higher levels of corrosion present at the bottom of the pipe indicate that soil aeration plays a major role in pipe failures caused by corrosion. While only a single figure supporting each observation has been provided here, a complete analysis of the case studies and conducted on small-diameter pipe failures, with classifications of failures due to the causes and surrounding conditions noted above including some reference to corrosion has been previously by Weerasinghe (2018) [14]. Other observations regarding soil crust formation and graphitic corrosion gathered in this field case study yielded valuable evidence on the chemical processes involved in the corrosion of cast iron in soil.

# 1.4 Aims and objectives of the research

With the importance of aeration and moisture conditions for underground corrosion having been established by previous research and supported by the case study, the present study was formulated to develop a mechanistic understanding of the influence of soil aeration on underground corrosion, and to create a model capable of simulating the important phenomenological observations.

Due to the inherent difficulties in exhuming, extracting and grit-blasting pipe sections to obtain corrosion data, the collection of a reasonable dataset requires significant time and resources. Therefore, there is a need for a model of underground corrosion with a theoretical basis. Carefully formulated laboratory experiments which are multidisciplinary in nature can be used for detailed analysis of key phenomenological observations and to obtain input parameters for numerical models. The overall aims and objectives of this study are as follows:

• Identify and characterise the mechanisms responsible for the key phenomenological observations in underground corrosion

- Develop a mechanistic model capable of predicting underground corrosion in the field, based on aeration regimes
- Develop a multidisciplinary experimental framework to gather the required data and for detailed analysis of the main phenomenological observations
- Provide quantitative assessments of the role of aeration, differential aeration and moisture in underground corrosion
- Formulate findings from experiments into practically actionable methods and knowledge regarding corrosion assessment and control in the field.

The research plan formulated to achieve the above objectives is summarized in Fig. 1.8. The overall plan has of three main sections consisting of an initial numerical modelling exercise based on field observations and information from the research literature, a comprehensive experimental program and the implementation of fully-coupled numerical models.



Figure 1.8: Summary of research plan for work presented in this thesis. The sections shaded in green are the planned work while the red sections are the main outcomes.

# **1.5 Thesis structure**

This thesis details the work carried out in this research project in nine chapters. Most chapters are self-contained with the necessary background being provided at the beginning. However, the findings presented in these diverse chapters are interconnected and are discussed together with cross references, to formulate the new knowledge resulting from this work. The chapters and their contents are summarised below:

#### **Chapter 1: Introduction**

The first chapter details the background of the research and outlines the field case study program which helped to formulate the main research questions to be addressed in this research project. The aims and objectives of the research, together with a summary of the research plan and thesis structure are also presented.

#### **Chapter 2: Literature review**

The literature review is very brief and refers only to the past literature on the influence of soil aeration and moisture content and other main phenomenological observations pertaining to underground corrosion. The literature relevant to the other multidisciplinary components of this work are presented at the beginning of their respective chapters. The main knowledge gaps pertaining to the overall project are identified at the end of this chapter.

# Chapter 3: Finite element simulations of pipeline corrosion in the field

This chapter presents the numerical models developed to assess the levels of metallic corrosion of buried pipelines in the field. The model was validated with field exposure data from the United States National Bureau of Standards (NBS) corrosion exposure study report [4]. Important outcomes include the development of a novel approach to the accurate simulation of field aeration conditions in the field and modelling mechanisms which lead to localised patch corrosion through naturally evolving macro cells. The effects of differential aeration are quantified and the mechanisms of the phenomenological observation of the bimodal trend are explained.

#### Chapter 4: Measurement and characterisation of electrochemical properties of soils

This chapter outlines the electrochemical experiments conducted to evaluate the corrosivity of three diverse soil types: sand silt and clay. A new electrochemical cell design is developed and 3-D-printed to conduct these tests on compacted, unsaturated soils. Other tests on the soil include electrical resistivity, chemical element analysis, active area measurements and time- lapse polarisation

resistance measurements. Important outcomes are the identification of a different optimum moisture level for three soil types, the correspondence of the chemical properties to the magnitudes of corrosion rates and the correspondence of soil physical properties to the levels of moisture at which the highest corrosion rate is achieved. An approach to numerically model the optimum moisture content is presented.

#### Chapter 5: Investigation of aeration and moisture retention characteristics of soil

The soil physical properties that determined the level of moisture at which the highest corrosion rate was achieved, was found to be the aeration and moisture retention properties of soil and this chapter discusses these properties. Soil water retention experiments were conducted for the three soil types prepared to the same specifications as the electrochemical tests. An important outcome of this chapter is the identification of the inflection point of the soil water retention curve as the air transition point, where the continuity of the water and air phase changes. The degree of saturation at the inflection point was found to be the same degree of saturation at which the corrosion rates are maximised. The effect of soil compaction on the inflection point is examined in detail through standard compaction tests and high-resolution micro X-ray CT imaging.

#### Chapter 6: Developments in determination of oxygen diffusion properties of diverse soil types

Since oxygen diffusion is an important factor in underground corrosion, this chapter outlines the oxygen diffusion experiments conducted on the same three soil types prepared to the same specifications. Transient numerical models were developed to supplement the experiments and the results indicate that the inflection point of the water retention curve is also related to the diffusion coefficient-degree of saturation relationship in soils. A new semi-empirical equation is proposed to capture these mechanistic effects and shows a good to fit to the experimental data obtained in this work and previous studies.

#### Chapter 7: Mechanistic view of optimum soil moisture for underground corrosion

This chapter combines the findings from the previous three chapters to develop a mechanistic understanding of the optimum soil moisture for underground corrosion. The change in continuity of the air phase at the air transition point, denoted by the inflection point on the soil water retention curve, results in a rapid change to oxygen availability for corrosion, resulting in the characteristic optimum. It is further shown with results from Chapter 5 that the optimum conditions for corrosion are the same as the optimum moisture conditions for soil compaction in usual geotechnical engineering practice. Another important finding is that the variations in measured corrosion rates are also the highest in the same optimum region, creating the highest likelihood of localised damage due

to macro cells in soils compacted to standard engineering practice. The immediate practical implications of these findings are discussed.

#### Chapter 8: Modelling coupled phenomena in underground corrosion

The findings from the previous chapters relating to the importance of the aeration and moisture retention properties for underground corrosion were incorporated into coupled numerical models and the results are detailed in this chapter. The experimental water retention curves and oxygen diffusion coefficients are used to solve the governing equations corresponding to moisture flow in unsaturated media, and the results are then related to oxygen diffusion and the active area to model the optimum moisture for corrosion more accurately. The new model results show better agreement with the experimental data. The new fully-coupled model is extended to field conditions to evaluate the climatic effects and the effect of pipe size on localised corrosion due to differential aeration. The coupled flow phenomena implemented in the new model are found to be more accurate in simulating field conditions such as differential aeration. The coupled influence of pH and salinity are also evaluated.

#### **Chapter 9: Conclusion and recommendations**

This chapter summarises the main findings and contributions of this research project. The main outcomes in advancing the understanding of corrosion in soils and developing a mechanistic corrosion model which will be of use to a broad range of engineering practitioners are discussed. Overall, the importance of multidisciplinary studies which break the boundaries between traditionally-isolated fields of study, such as geotechnical engineering and applied electrochemistry, is highlighted in this work, for the first time to the author's knowledge.

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# **Chapter 2: Literature Review**

Corrosion in soils is a complex process dependent on multiple variables. Understanding the main processes and their inter-relationships is important to evaluate the corrosivity of metal under field conditions. This information is useful for the prediction of the remaining lifetime of buried metal assets with reasonable accuracy. Information on the properties of soil which influence corrosion is also useful for new installations of buried assets, where engineering controls can be used to provide the soil conditions which prolong the lifetime of the asset. This chapter summarises existing research pertaining to underground corrosion and identifies the gaps addressed by the present study.

### **2.1 Basics of corrosion**

Corrosion is often seen as the return of metal to its original form. This is because a certain amount of energy is used to convert metallic ore taken from earth into metals and when left for nature to take its natural course, this energy is dissipated and the metal returns to its natural stable state.

Corrosion is an electrochemical reaction with anodic and cathodic half-cell reactions occurring simultaneously.

The anodic reaction is the oxidation of iron as shown in Eq. 2.1:

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
 (2.1)

The most common cathodic reaction which occurs in almost all cases of underground corrosion (under near-neutral conditions) is oxygen reduction and the reaction is given in Eq. 2.2:

$$O_2 + 2 H_2O + 4 e^- \rightarrow 4 OH^-$$
(2.2)

However, other reduction reactions can also occur at the cathode [1]. While not common in underground corrosion, these reactions occur in other types of aqueous corrosion. The anodic and cathodic reactions need to occur simultaneously for corrosion to occur. In a metal corroding in an ideal electrolyte, such as a highly conductive liquid, the anodic and cathodic sites are randomly

distributed in approximately equal amounts [2]. This means that no net current flows through the electrolyte, and direct measurement of the corrosion current is not possible. However, electrochemical methods can be used to measure the corrosion rate indirectly, as detailed in the following section.

#### 2.1.1 Polarisation and corrosion rate measurement

The uniform corrosion current of a metal cannot be measured under equilibrium conditions. Therefore, to measure the uniform corrosion rate, the electrode potential is varied from the equilibrium potential to induce currents to flow through the metal electrolyte. This process is called polarisation, and is discussed in more detail in Chapter 4. Polarisation shifts the potential of an electrode away from its equilibrium and results in a net current flow through the electrolyte. This net current can be measured and forms the basis for electrochemical measurements in corroding systems. Potentiodynamic polarization and linear polarisation resistance measurement are two methods which can be used to obtain the uniform corrosion of a system and are discussed in later sections of this thesis. The Butler-Volmer equation and the Tafel equations can be used for corrosion rate determinations in the above methods. The Butler-Volmer equation is given in Eq. 2.3 [2]:

$$i = i_{corr} \left[ \exp\left(-\frac{\alpha n F \eta}{RT}\right) - \exp\left(\frac{(1-\alpha)n F \eta}{RT}\right) \right]$$
(2.3)

where,  $i (\mu A/cm^2)$  is the external current density flowing through the electrolyte due to polarisation,  $i_{corr}(\mu A/cm^2)$  is the corrosion current density (at open circuit potential), R (J K<sup>-1</sup> mol<sup>-1</sup>) is the universal gas constant, T (K) is the temperature, n is the number of electrons involved in the reaction, F (C/mol) is the Faraday constant,  $\alpha$  is the charge transfer coefficient and  $\eta$  (V) is the overpotential. The Tafel equations (see Chapter 3) can be derived from the Butler-Volmer equations and are useful for modelling corrosion with some basic electrochemical parameters such as the equilibrium potential and exchange current density.

In the case of localised corrosion where the anodes and cathodes are spatially separated, due to selective passivation, causing accelerated metal loss such as pitting, standard electrochemical measurements cannot be accurately performed. In such cases, numerical modelling can be performed to assess the localised corrosion from parameters obtained from uniform corrosion experiments. Numerical modelling of corrosion in soils is discussed in detail in Chapter 3. However, it is noted that laboratory measurements of localised corrosion in soils have been conducted using electrode array techniques such as the wire beam electrode (WBE) [3]. These electrode array techniques were used to examine the influence of electrode surface area, and moisture content in systems subjected to

the disruptions in cathodic protection [4,5]. Such techniques may also possibly be used after further development and modification to obtain useful information regarding localised corrosion under field conditions.

#### 2.1.2 Corrosion of buried assets under field conditions

As detailed in the previous section, for corrosion to occur both these reactions need to occur simultaneously and form a couple between the anodic and cathodic regions. The formation of this couple depends on the electric potential difference on the metal surface, which in turn depends on other factors. Anodes and cathodes located very close to each other result in the formation of micro couples and the metal surface undergoes uniform corrosion, while spatially separated anodes and cathodes result in macro couple formation, which can lead to highly localized and rapid corrosion at the anode. This is one of the mechanisms of pit formation, which in turn is responsible for most corrosion-induced structural failures in buried infrastructure such as pipelines. Tomashov (1966) [6] has provided a thorough account of the action of micro and macro corrosion couples. Tomashov postulates that micro couples arise due to the non-homogeneity of the metal, while macro couples arise due to variations of the soil structure, in particular differences in oxygen penetration, termed differential aeration. As stated previously, macro cell corrosion takes precedence in corrosion rate assessment and damage prediction.

### 2.2 Influence of soil aeration

The importance of aeration in the process of corrosion is a direct consequence of oxygen being a primary reactant in the cathodic reaction in corrosion (Eq. 2.2). In soils, aeration usually depends on moisture content and the two are inversely related. The interplay between aeration and the moisture content in soils and their effects on corrosion have been discussed by Rossum (1969) [7] and Levlin (1996) [8]. The general consensus is that in well aerated soils, high initial corrosion rates gradually decrease, whereas in poorly aerated soils the corrosion rates continue to proceed. The reason for this is that, the abundant supply of oxygen promotes the cathodic process, but also causes the corrosion products formed to readily oxidise, thus shielding the metal from further corrosion. In contrast, poorly aerated soils, owing to their larger moisture content, have higher conductivity and allow the corrosion products to migrate away from the corrosion site. This does not create a shielding effect, thus allowing the reaction to proceed. Metals in very poorly aerated (waterlogged) soil with high moisture content

eventually stop corroding due to the lack of oxygen. Such cases have been reported by Romanoff (1962)[9]. In most situations it is a combination of these two cases that tends to be most corrosive. The ample availability of oxygen at the cathode coupled with a poorly aerated, highly moist anode coupled along a conductive path is the most suitable combination for corrosion.

Romanoff (1957) [10] in his report on an extensive National Bureau of Standards (NBS) study on metal exposure in buried environments provided field corrosion observations over a relatively long period of time for several types of ferrous pipe material. Fig. 2.1 summarises the data extracted from this report for cast iron under four classes of aeration described by Romanoff as good, fair, poor and very poor aeration.



Figure 2.1: Cast iron corrosion in soil of four different classes of aeration-good, fair, poor and very poor, modified from Romanoff (1957)

The corrosion data in Fig. 2.1 for good, fair and poor aeration are consistent with the mechanisms presented by Rossum [7], while the data for very poor aeration do not show the low corrosion rates expected. The possible reasons for this behaviour are discussed in Chapter 7. It is also noted that the fair aeration regime, in addition to showing generally high corrosion rates, also shows great variations in the measurements. These great variations in corrosion rates may be due to macro cell activity, possibly caused by differential aeration.

# 2.3 Differential aeration and localised corrosion

Macro corrosion couples may arise from variations of several soil properties, of which differential aeration plays a significant role [6,9]. Tomashov (1966) [6] highlights that the reason for aeration playing a major role in corrosion is the influence of oxygen on the equilibrium potentials of metals.
Iron is ennobled by the presence of oxygen, thus favouring the formation of a cathode at a wellaerated region coupled with an anode in a relatively poorly aerated area. Therefore, spatial variations in soil properties which affect aeration, such as particle size, porosity and moisture content, induce the formation of corrosion cells. In addition to the soil properties, external features that promote or restrict soil aeration may also result in the formation of differential aeration cells. Impermeable covers, such as surface paving and the presence of vegetation and root zones, can be cited as examples.

Once formed, the rate of corrosion in a macro couple may be significantly increased by a high ratio of cathode-to-anode surface area, as it increases the corrosion current of the cell [8,11]. This is also the reason why a wet clay inclusion in contact with a metal laid in a well- aerated sandy medium is deemed to be highly corrosive. The area of the clay inclusion with poor aeration becomes the anode, while the region of pipe exposed to the spatially extensive, well-aerated medium becomes the cathode. As pointed out by Romanoff (1964) [11], differential aeration may arise due to the backfilling of the trench in which the pipe was laid. If the bottom of the pipe rests on undisturbed ground, compared to backfill which is more aerated, a differential cell ensues with a corroding anode at the bottom of the pipe. Such a case has been reported by Makar (2000) [13] in which the top of the pipe had bare metal exposed with the bottom having a significant graphitic layer, with a pit penetration depth of 6.1mm (56% of wall thickness). The pipe in this case had been laid on a rock bedding with a backfill of clay and granular material. A similar situation with the bottom of the pipe showing high levels of corrosion was observed in the field case study conducted in the present work which was reported in Chapter 1. While corrosion due to differential aeration is well accepted, a precise quantification of the effects of differential aeration is still elusive. Laboratory experiments examining localised corrosion as influenced by differential aeration have been conducted [4,14]. However, the applicability of these experiments in the scales usually encountered in the field is yet to be seen. Numerical modelling is a useful tool that could be used in conjunction with laboratory data to examine field scale situations. The effects of differential aeration discussed above have been incorporated into a numerical model which is presented in Chapter 3.

# 2.4 Soil properties governed by aeration and moisture

# 2.4.1 Oxygen diffusion

Under isothermal and isobaric conditions, oxygen transport in soil occurs mainly through diffusion [6]. Modelling diffusion through a variably-saturated porous medium requires an effective diffusion coefficient to be defined for the soil medium. Since oxygen diffusion takes place through both the water and air phase, the effective oxygen diffusion coefficient needs to include both phases, and depends on the fractions of water and air in the soil pore network. According to Aachib et al. (2004) [15], the effective diffusion coefficient of oxygen for variably saturated soils can be described by Eq. 2.4:

$$D_{e} = \frac{1}{n^{2}} \cdot \left[ D_{a}^{0} \theta_{0,a}^{p} + H D_{w}^{0} \theta_{0,w}^{p} \right]$$
(2.4)

where,  $D_e$  (m<sup>2</sup>/s) is the effective oxygen diffusion coefficient,  $D_a^0$ (m<sup>2</sup>/s) is the diffusion coefficient of oxygen in free air,  $D_w^0$ (m<sup>2</sup>/s) is that of free water,  $\theta_{0,a}$  and  $\theta_{0,w}$  are volumetric air and water contents (dimensionless) respectively, *H* is the dimensionless Henry's equilibrium constant, n is the porosity and *p* is a calculated or approximated exponent. Writing the volumetric water contents in terms of the porosity (*n*) and degree of saturation (*S<sub>r</sub>*), the following relationship (Eq. 2.5) is obtained. The value of *p* is approximated to be 3.4, as it is a typical value for most soils naturally encountered [15].

$$D_{e} = \frac{1}{n^{2}} \left[ D_{a}^{0} \left( n \left( 1 - S_{r} \right) \right)^{p} + H D_{w}^{0} \left( n S_{r} \right)^{p} \right]$$
(2.5)

Plotting  $D_e$  against and  $S_r$  using Eq. 2.5 yields the following 3-D surface for the oxygen diffusion coefficient (Fig. 2.2), which can be used as an input function for a numerical model. The values for  $D_a^0 D_w^0$  and *H* under standard conditions were used (See Table 3.1).



Figure 2.2: Oxygen diffusion coefficient given by Eq. 2.4 as a function of n and Sr

#### 2.4.2. Electrical conductivity

Soil moisture determines the electrical conductivity which in turn controls the current conduction in soils. Therefore, to model the soil as an electrolyte which facilitates corrosion, the electrical conductivity also needs to be expressed in terms of soil moisture and aeration.

Considering the similarities between electrical and groundwater flow, and building upon previous work by Rhoades et al. (1976) [16], Mualem & Friedman (1991) [17] proposed the following equation (Eq.2.6) to relate soil electrical conductivity to moisture content:

$$\sigma = \sigma_{w} \cdot \frac{\theta^{n+2}}{\theta_{sat}} + \sigma_{s}$$
(2.6)

where,  $\sigma$  (S/m) is the electrical conductivity of the bulk soil solution,  $\sigma_w$  (S/m), is the conductivity of the pore water,  $\sigma_s$  (S/m) is the surface conductivity of soil particles and *n* is the porosity,  $\theta$  and  $\theta_{sat}$  are the volumetric water content and the saturated volumetric content respectively, corrected for bound water so that  $\theta = \Theta - \Theta_0$ , where  $\Theta_0$  is the bound water content and  $\Theta$  is the volumetric water content of the bulk soil. Following these definitions, Eq. 2.6 can be rewritten as Eq. 2.7:

$$\sigma = \sigma_w \cdot \frac{\left(n.S_r - \Theta_0\right)^{n+2}}{n - \Theta_0} + \sigma_s \tag{2.7}$$

Bound water content ( $\Theta_0$ ) and surface conductivity ( $\sigma_s$ ) are soil-dependent properties. Therefore, the electrical conductivity of the soil medium is based on the soil type and moisture distribution. A plot of Eq. 2.7 with typical values for the soil-dependent parameters is shown in Fig. 2.3



Figure 2.3: Electrical conductivity for typical soil given by Eq. 2.5 as a function of n and Sr

#### 2.4.3 Optimum soil moisture for corrosion

The existence of an optimum soil moisture for underground corrosion has been reported previously by several researchers [5,6,18,19]. Gupta and Gupta (1979) [18] provided the most widely recognised results for three different natural soil types exhibiting an optimum moisture content at which their corrosivities become the highest. Fig. 2.4 shows the levels of corrosion levels in the three soil types re-drawn from the data reported by Gupta and Gupta (1979).



Figure 2.4: Corrosion levels obtained for three soil types with different moisture contents, exhibiting optimum moisture levels for all three soils (Modified from Gupta and Gupta (1979))

Fig. 2.4 shows that the three different soils show different gravimetric moisture contents at which their corrosivities attain the highest value. The three soil types were of natural origin and the following properties (Table 2.1) were provided for the three soil types:

	Sand (1-2mm)	% particle Sand (0.05- 1mm)	size distribut Silt (0.002- 0.05mm)	ion Clay (0.002mm)	Water holding capacity (%)	рН	Chlorides (ppm)	Saturated resistivity (Ω cm)
Jabalpur	68	20	1	11	39	7.3	15	1270
Tejpur	6	56	22	16	46.2	6.3	16	3302
Bareilly	7.5	30	45.5	18	53.2	7.6	18	1778

Table 2.1: Properties of soils tested for optimum moisture for corrosion by Gupta & Gupta (1979)

Gupta & Gupta (1979) [18] reported that although the moisture contents at the optimum were different for each soil type, when the optimum water content was expressed as a percentage of the waterholding capacity, all three soils showed approximately the same value. This value was identified by the authors as 65% of water-holding capacity. However, the authors did not mention the method used to calculate the water-holding capacity of the soils.

# 2.5 Effect of pH and salinity

By definition, the pH value of soil gives an indication of the ionic concentration in the soil. It is known that a high H<sup>+</sup> ion concentration in low pH soils make it acidic and promotes the corrosion reaction, while in high pH soils, the high dissolved salts reduce soil resistance and promote corrosion [4,20,21]. Rossum's analytical model for the corrosion rate [7] is derived assuming that pH is the main contributor to cell potential through the Nernst equation. According to Rossum, the corrosion cell potential *E* is given by Eq. 2.8:

$$E = K(10 - pH) \tag{2.8}$$

and the pit depth p is given by Eq. 2.9:

$$p = K_n \left[ \frac{(10 - pH)t}{\rho} \right]^n \tag{2.9}$$

where, K and K<sub>n</sub> and *n* are constants,  $\rho$  is the soil resistivity, and *t* is time. Rossum states that the corrosion mechanisms modelled by this equation are only valid over the *pH* range 5 to 9. It has been assumed that the iron is passive beyond a *pH* value of 10.

Padilla et al. (2013) [22], in their numerical model of galvanised steel corrosion incorporated the effect of pH on the cathodic equilibrium potential for oxygen reduction, as given in Eq. 2.10:

$$E_{O_1}^{eq} * = E_{O_2}^{eq} - 0.0592(pH - 14)$$
(2.10)

where,  $E_{O_2}^{eq}$  is the modified cathodic equilibrium potential and  $E_{O_2}^{eq}$  is the standard cathodic equilibrium potential. The authors reported that the model yielded lower corrosion rates with increasing *pH*.

Soil salinity affects underground corrosion primarily in two ways [22,23]. The first and most widely reported mechanism is the increase in electrical conductivity (decrease in soil resistivity). High electrical conductivity facilitates the acceleration of corrosion reactions especially macro cell corrosion. The influence of conductivity on corrosion rates has been modelled by Padilla et al. (2013,2014) [24,25]. According to Song et al. (2017) [23], the presence of chloride ions also alters the pathways of the possible corrosion reactions by participating in the reactions. It was reported that the iron oxides formed in carbon steel under different levels of chloride were different. The authors also reported that localised corrosion is more likely in soils with high chloride content.

Padilla et al. (2014) [25] also considered the effect of soil resistivity in addition to pH and reported the results of a parametric study using the numerical model developed previously [24]. The model reported consists of three time-dependent stages of galvanised steel corrosion. During the first stage, ZnO coating dissociation is modelled, in stage two, the iron corrodes along with ZnO dissociation, while in stage 3 the primary oxidation reaction is the corrosion of iron. The results of the parametric study of the influence of pH and resistivity reported by Padilla et al. (2014) for stage 3 are shown in Fig. 2.5.



Figure 2.5: Influence of pH and resistivity obtained from numerical model as reported by Padilla et al. (2014)

As Fig. 2.5 shows, the usual trend of increasing corrosion rate with decreasing resistivity is observed. Padilla et al. (2014) considered the effect of resistivity according to Eq. 2.11 presented in the following section. Since salinity primarily influences the resistivity or conductivity of soil, similar trends can be expected with changing soil salinity. The effect of pH implemented according to Eq. 2.10 gives rise to a trend where lower pH leads to higher corrosion rates and vice versa.

# 2.6 Numerical modelling for corrosion

In usual practice, the anodic and cathodic reactions are expressed as current densities according to Butler-Volmer reaction kinetics, and are coupled with activation and/or concentration controls. These reactions are coupled with reactant diffusion mechanisms and the finite element method is used to solve the resulting equations.

Most numerical models prescribe activation control for the anodic reaction and combined activation and concentration control for the cathodic reaction.

#### 2.6.1 Steady-state models

For underground corrosion, the anodic reaction is under activation control and the cathodic reaction is under concentration control [6,26]. Hence, the corresponding current densities for the above two reactions are expressed as:

$$i_{Fe} = i_{Fe}^{0} \times 10^{\frac{\eta_{Fe}}{A_{Fe}}}$$
 (2.11)

for the anodic reaction, and

$$i_{O_2} = \frac{C_{O_2}}{C_{O_2}^{ref}} \times i_{O_2}^0 \times 10^{\frac{\eta_{O_2}}{A_{O_2}}}$$
(2.12)

for the cathodic reaction, where,  $i_{Fe}^0$  and  $i_{O_2}^0$  are the respective exchange current densities ( $\mu$ A/cm<sup>2</sup>). The concentration polarization effect is included in the cathodic current density expression as described by Kranc & Sagues (1994) [27], where  $C_{O2}$ (mol/m<sup>3</sup>) is the concentration of the diffusing oxygen and  $C_{O_2}^{ref}$  (mol/m<sup>3</sup>) is the reference oxygen concentration (atmospheric),  $A_{Fe}$  (V) and  $A_{O2}$  (V) are the Tafel slopes and  $\eta_{Fe}$  (V) and  $\eta_{O2}$ (V) are the respective over-potentials given by

$$\eta_{Fe} = -\phi - E_{Fe}^{eq} \tag{2.13}$$

and

$$\eta_{O_2} = -\phi - E_{O_2}^{eq} \tag{2.14}$$

where,  $\phi$  is the electrolyte potential of the soil medium and  $E_{Fe}^{eq}$  and  $E_{O_2}^{eq}$  are the equilibrium potentials for the cathodic and anodic reactions, respectively.

With the above boundary conditions on the corroding metal surface, the electrolyte potentials in the soil are solved for. Assuming that the soil medium obeys Ohm's law with conductivity ( $\sigma$ ), the governing equation for the electrolyte potential ( $\phi$  (V)) is:

$$\nabla . (\sigma \nabla \phi) = 0 \tag{2.15}$$

The steady-state governing equation for the oxygen concentration is given by Eq. 2.16:

$$\nabla \cdot \left( D_e \nabla C_{O_2} \right) = 0 \tag{2.16}$$

where,  $D_e$  (m<sup>2</sup>/s) is the effective diffusion coefficient for oxygen and  $C_{o_2}$  is the oxygen concentration in the soil, and  $D_e$  is input as a function obtained from the aforementioned experimental results. A constant concentration boundary condition is imposed at the surface exposed to the atmosphere and the oxygen diffusing to the corroding metal surface is assumed to be consumed by the cathodic reaction, as shown by Eq. 12:

$$i_{O_2} = -D_e \left( \mathbf{n} \cdot \nabla C_{O_2} \right) zF \tag{2.17}$$

where, z is the number of electrons involved in the reaction and F is the Faraday constant. The oxygen flux coupled with the cathodic corrosion current density together capture the diffusion limitation conditions in underground corrosion.

#### 2.6.2 Time-dependent models

Time-dependent models are useful for modelling long-term corrosion rates and different timedependent stages of corrosion. Models which consider or evaluate corrosion product formation need to be solved at successive time steps, to identify the evolution of related effects. These time-dependent numerical modelling exercises have been performed for concrete reinforcement corrosion to evaluate the crack formation in concrete due to corrosion product deposition [28].

In time-dependent simulations the oxygen concentration at each time step is calculated using Fick's second law given in Eq. 2.18:

$$\frac{\partial C_{o_2}}{\partial t} = \nabla \cdot \left( D_e \nabla C_{o_2} \right) \tag{2.18}$$

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The time-dependent oxygen concentration and the resulting current densities are then used to model other time-dependent phenomena, such as corrosion product deposition and passivation. In usual practice, the anodic reaction is modified to include the effect of passivation. Passivation renders the metal inactive and inhibits corrosion. Hines (1983) [29] has proposed the following method to include the effect of passivation (Eq. 2.19):

$$i_{Fe} = S.i_{active} + (1-S).i_{passive}$$
(2.19)

where,  $i_{active}$  and  $i_{passive}$  are the active and the passive current densities and S is a transition function.

However, some researchers have used other methods to factor in the effect of passivation. For example, Chang et al. (2014) [30] have used the precipitates deposited during the corrosion process to effect passivation according to the following equation:

$$i_{Fe} = (1 - \gamma).i_{Fe} \times 10^{\frac{\eta_{Fe}}{A_{Fe}}} + \gamma.i_{passive}$$
(2.20)

where,  $\gamma$  (dimensionless) is the fractional coverage of corrosion products. The above approaches in modelling corrosion have been utilised in aqueous corrosion and concrete re-bar corrosion, but are not currently used for underground corrosion. This means that soil- dependent corrosion parameters, mass transport and passivation mechanisms have not yet been included in models.

# 2.7 Knowledge gaps and areas investigated in this study

Current studies in underground corrosion rely on single definitions of soil moisture, and accurate descriptions of soil moisture and aeration according to soil hydrology theories have not been incorporated in soil corrosion studies.

Although differential aeration is accepted as a significant factor in corrosion, and laboratory techniques have been developed to assess its impact, currently no method exists to quantify its effects in a field scale. Finite element modelling incorporating soil physics principles governing aeration and moisture in soils has not been used in underground corrosion to date, and this research project aims to create a model which is able to capture the effects of various controls, including differential aeration. The resulting model will enable the understanding of various facets of underground corrosion.

The natural evolution from uniform corrosion to localized corrosion is not seen in models. Present models require prior definitions of anodic and cathodic regions for localized corrosion. In relation to this, it is also noted that numerical implementations of mechanisms such as passivation are not fully developed in underground corrosion models.

While the phenomenon of the optimum soil moisture has been reported previously, the mechanisms giving rise to it in relation to the soil properties that govern them have not been presented.

This study addresses each of these identified gaps.

The brief literature review presented in this chapter complements the further results obtained from the research literature under each section and is presented at the beginning of each subsequent chapter.

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# Chapter 3: Finite element simulations of pipeline corrosion in the field

This chapter presents the development and validation of a numerical model to assess the levels of corrosion under field conditions. A realistic method of simulating field conditions of aeration and moisture is presented, along with the relatively long-term effects of differential aeration. The contents of this chapter were published in *Corrosion* **74** (2018) 1177–1191. [1].

# 3.1 Introduction

As the excavation and long-term monitoring of buried pipes is highly resource-intensive and sometimes not practical, in most instances the necessary information on corrosion damage is not available. A viable alternative is to utilise mechanistic models of underground corrosion based on fundamental principles and validated with field observations. Such mechanistic models can then be applied to practical pipeline asset management. Information about the level of corrosion as a function of soil properties would enhance condition assessment efforts [2]. It should be noted that most older pipelines (>50years) had natural soil placed as the compacted backfill and therefore the soil surrounding the pipe has stabilised to almost natural conditions [3]. However, for recent pipelines (from the 1960s) engineered sandy backfill was used. Regardless of the soil surrounding the pipe, the following theoretical analysis is valid since it embodies general principles of soil physics.

Corrosion in soil may be modelled by coupling the electrochemical activity at the soil/pipe interface, the corrosion product build-up, soil properties and interface mechanics and the influence of external environmental factors [4,5]. However, to date no such model encapsulating all these variables has been developed. While soil parameters such as pH, chloride ion concentration and temperature are important in corrosion assessment, their influences appear to be highly variable among different metal/electrolyte systems [6,7]. Nevertheless, these parameters influence corrosion kinetics, as shown in past studies [8,9] and their influences can be modelled, provided their relevant mechanisms are known. Previous studies have indicated that soil aeration is an important parameter to characterise corrosion in soils [5,10–12]. While the mechanics of aeration are understood, models incorporating

the influence of soil aeration on underground metal corrosion from a soil physics perspective are not presently available.

Soil aeration characteristics, while influencing the overall rate of corrosion, can also lead to localized corrosion, especially if differential aeration [10,13] is present. Aeration and moisture regimes in soil influence a range of mechanisms [11] and these need to be modelled simultaneously to determine their inter-dependencies. In this regard, soil hydrology concepts can be utilised to describe soil aeration and moisture retention characteristics.

Soil particles constitute a capillary porous structure and air and water occupy the pore network (Fig. 3.1). The soil pore network facilitates the transport of oxygen to the corroding pipe surface and the soil water within the pores acts as the electrolyte that facilitates corrosion reactions at the pipe surface. To model the bulk soil as an electrolyte, both air and water phases need to be quantified. Therefore, the degree of saturation ( $S_r$ ), which is the ratio of the volume of water to the volume of the voids in soil, is a suitable parameter to describe soil moisture.



Figure 3.1: Schematic of three-phase soil over buried metal, identifying the main mechanisms modelled.

The soil water retention curve (SWRC) is the relationship between soil suction ( $\psi$ ) and  $S_r$  (Fig. 2). Soil suction is a measure of the thermodynamic energy state of soil water and is considered as a state variable in unsaturated soil mechanics [14]. The SWRC depends on the soil type, and characterises the amount of water the soil can hold under different levels of soil suction, and therefore is a useful relationship to characterize soil as an electrolyte. The SWRC can be obtained in the field or in laboratory-prepared soil samples using equipment such as a pressure plate apparatus and tensiometers. Interested readers can refer to Fredlund & Rahardjo [14] for detailed experimental methods and the underlying theory.



Figure 3.2: Soil water retention curves for three soil types considered in this model

Soil suction is generally expressed as a pressure deficit between the air and water interface, typically in kPa. Due to the large range of values involved (0 to 10<sup>6</sup> kPa), it is usually expressed on a logarithmic scale in units of pF, where 1 pF =  $log(10.2\psi)$ . When expressed in units of pF, suction is commonly denoted by the symbol *u*. Climatic influences through evaporative and infiltration fluxes and soil physical properties affect the ground suction profiles with depth [14]. The suction profiles determine the moisture distribution and the level of aeration of the soil medium [15]. Climatic variations can perturb the suction profiles up to a certain depth, known as the active zone depth  $(H_s)$ , after which an equilibrium suction  $(u_e)$  is normally established (Fig. 3.3). The development of this equilibrium condition highlights the importance of using suction in contrast to soil moisture for evaluating the influence of aeration subject to climatic influence. This equilibrium suction depends on the soil type and the overall ambient climate, including the depth to the groundwater table. Relationships between the climate, characterised by the Thornthwaite Moisture Index (TMI) [16] and the equilibrium soil suctions for different soil types have been presented by Russam and Coleman [17]. Assuming the surface suction varies in a sinusoidal manner due to climatic variations, Mitchell [18] derived equations for soil suction variations with soil depth. These relationships can be used to define conditions of soil moisture and aeration depicting certain climatic conditions, which can then be coupled with the corrosion processes.



Figure 3.3: Typical suction profiles showing equilibrium suction  $(u_e)$  established after the active zone depth  $(H_s)$  where  $u_0$  is the amplitude of the suction variation at the surface

Several approaches have been taken to model the time-dependent behaviour of the corrosion process. The first approach is to assume different stages of corrosion and to assign uniform corrosion rates at the different stages, as demonstrated by some studies [19,20]. However, this approach requires prior knowledge of the initiation times and durations of the different phases. The second approach is to use mathematical relationships to model the shape of the corrosion mass loss curve, as described in some analytical and empirical models [11,21]. It is also noted that the basis for accounting for the differences in the corrosion mass loss curves in most such models is soil aeration, since aeration defines the rates of the reaction as well as the oxide/corrosion product formation. The main basis here is that the rate of corrosion diminishes with time as corrosion products are deposited on the metal surface [5,11,22], while the rate of product deposition itself depends on soil moisture and aeration [11]. This approach to modelling time dependency is selected in this study.

This chapter presents a mechanistic underground corrosion model with emphasis on the influence of soil aeration. The finite element method (FEM) is used to solve the coupled equations arising from the various mechanisms considered. The model is capable of simulating both micro- and macro-cell corrosion and their natural evolution with time without prior specification of anodic and cathodic areas. The model is verified with field data reported in NBS circular 579 [10]. It is also demonstrated that the model is consistent with observations regarding differential aeration and influence of soil type, as reported in [10,13,23,24].

## **3.2 Numerical model of corrosion**

The time-dependent model in this study utilises the deposition of corrosion products over time to simulate macro-cell activity. Therefore, prior assumptions of anodic and cathodic regions are not necessary, since the model naturally evolves from micro-cell-induced uniform corrosion to localized corrosion due to macro-cells.

The anodic half-cell reaction in ferrous pipes is iron oxidation. The cathodic half-cell reaction is usually oxygen reduction, as underground environments are generally circumneutral pH conditions [25]. These half-cell reactions are given by Eqs. 3.1 and 3.2, as discussed in Chapter 2.

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
 (3.1)

$$O_2 + 2 H_2 O + 4 e^- \rightarrow 4 O H^-$$
(3.2)

The hydroxide ions from the cathodic reaction combine with the cations from Eq. 3.1 to form a corrosion product precipitate. The most common corrosion product observed in iron corrosion is iron (III) hydroxide ( $Fe(OH)_3$ ) [26]. Hence, the following reactions are assumed to be responsible for corrosion product formation, which is deposited on the pipe [22,27]

$$\operatorname{Fe}^{2+} + 2 \operatorname{OH}^{2} \to \operatorname{Fe}(\operatorname{OH})_{2}$$
 (3.3)

$$\operatorname{Fe}(\operatorname{OH})_2 + \operatorname{OH}^2 \to \operatorname{Fe}(\operatorname{OH})_3 + e^2$$
 (3.4)

According to Eqs. 3.3 and 3.4, the hydroxide ions from the cathodic reaction (Eq. 3.2) are utilised in the formation of  $\text{Fe}(\text{OH})_3$ . Therefore, the rate of formation of the corrosion product was coupled with the cathodic current density with appropriate stoichiometric coefficients. This coupling implies that the spatial variations of the cathodic current density result in variations of the corrosion product layer thickness on the pipe.

#### 3.2.1 Micro-cell and macro-cell corrosion

Micro-cell corrosion occurs when the entire surface of the metal corrodes uniformly with no net current flowing through the electrolyte [5,28]. In reality, due to spatial differences in electrode potentials caused by inhomogeneous soil/pipe interface features, macro-cells can form, resulting in a net current flowing from the anodic to the cathodic region through the soil electrolyte. This macro-

cell current,  $i_{macro}$  (A/m<sup>2</sup>), is the difference between the anodic ( $i_{Fe}$ ) and cathodic ( $i_{O_2}$ ) current densities at a given point on the pipe surface, as given by Eq. 3.5:

$$i_{macro} = i_{Fe} - i_{O_2} \tag{3.5}$$

#### 3.2.2 Potential distribution and electrode polarisation

The potential ( $\phi$  in V) distribution in the electrolytic soil medium is governed by Eq. 3.6:

$$\nabla \cdot \left( \sigma \nabla \phi \right) = 0 \tag{3.6}$$

where,  $\sigma$  is the electrical conductivity of the soil (S/m). The current density vector through the soil electrolyte,  $\mathbf{i}_{l}$  (A/m<sup>2</sup>), is governed by Ohm's law and is given by Eq. 3.7:

$$\mathbf{i}_{l} = -\sigma \nabla \phi \tag{3.7}$$

Note that the soil conductivity,  $\sigma$  is not a homogeneous soil property but rather varies, depending on the spatial and temporal changes in the degree of saturation and the soil type [29].

Since both the anodic and cathodic current densities are specified on the pipe surface, the net current density, or the macro-cell current, should equal the total electrolyte current flux normal to the soil/pipe interface. Hence, the following condition is imposed on the pipe surface.

$$i_{macro} = i_{Fe} - i_{O2} = \mathbf{n}.\mathbf{i}_l = \mathbf{n}.(-\sigma\nabla\phi)$$
(3.8)

where,  $\mathbf{n}$  is the unit vector normal to the pipe surface. On all other surfaces, a zero-current flux boundary is specified as follows:

$$\mathbf{n} \cdot \left( -\sigma \nabla \phi \right) = 0 \tag{3.9}$$

Since anodes are under activation polarization and cathodes are under both activation and concentration polarization, the anodic and cathodic current densities can be modelled using Eqs. 3.10 and 3.11, respectively [30].

$$i_{Fe} = i_{Fe}^{0} \times 10^{\frac{\eta_{Fe}}{A_{Fe}}}$$
 (3.10)

$$i_{O_2} = \frac{C_{O_2}}{C_{O_2}^{ref}} \times i_{O_2}^0 \times 10^{\frac{\eta_{O_2}}{A_{O_2}}}$$
(3.11)

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where,  $i_{Fe}^{0}$  (A/m<sup>2</sup>) and  $i_{O_{2}}^{0}$  (A/m<sup>2</sup>) are the exchange current densities for the anodic and cathodic reactions respectively,  $C_{O_{2}}$  (mol/m<sup>3</sup>) is the concentration of the diffusing oxygen (at the pipe level),  $C_{O_{2}}^{ref}$  (mol/m<sup>3</sup>) is the reference oxygen concentration (atmospheric),  $A_{Fe}$  (V) and  $A_{O_{2}}$  (V) are the anodic and cathodic Tafel slopes respectively, and the  $\eta_{Fe}$  (V) and  $\eta_{O_{2}}$  (V) are the anodic overpotentials respectively, and are given by Eqs. 3.12 and 3.13.

$$\eta_{Fe} = -\phi - E_{Fe}^{eq} \tag{3.12}$$

$$\eta_{O_2} = -\phi - E_{O_2}^{eq} \tag{3.13}$$

where,  $\phi$  is the soil potential at the pipe surface, and  $E_{O_2}^{eq}$  (V) and  $E_{Fe}^{eq}$  (V) are the equilibrium potentials for the cathodic and anodic reactions respectively. The Tafel slopes and the other parameters were sourced from the literature (Table 1).

Parameter	Value	Units	Reference
Tafel slope iron oxidation	0.06	V	[28]
Tafel slope oxygen reduction	-0.12	V	[28]
Oxygen reference concentration	8.6	mol/m <sup>3</sup>	calculated
Iron oxidation equilibrium potential	-0.76	V	[31]
Oxygen reduction equilibrium potential	0.189	V	[31]
Iron oxidation exchange current density	7.1 x 10 <sup>-5</sup>	$A/m^2$	[31]
Oxygen reduction exchange current density	7.7 x 10 <sup>-7</sup>	$A/m^2$	[31]
Oxygen diffusivity in air	1.8 x 10 <sup>-5</sup>	m <sup>2</sup> /s	[32]
Oxygen diffusivity in water	2.5 x 10 <sup>-9</sup>	m <sup>2</sup> /s	[32]
Electrical conductivity of pore solution	0.2	S/m	[29]
Dimensionless Henry's equilibrium constant	0.03	-	[32]
Porosity of material	Soil-dependent	-	-

Table 3.1: Parameter constants used in model

#### 3.2.3 Oxygen reduction and diffusion coupling

Since oxygen transport through soil under isothermal and isobaric conditions occurs mainly through diffusion [5], the time-dependent oxygen concentration can be described using Eq. 3.14.

$$\frac{\partial C_{O_2}}{\partial t} = \nabla \cdot \left( D_e \nabla C_{O_2} \right) \tag{3.14}$$

where,  $D_e$  (m<sup>2</sup>/s) is the effective diffusion coefficient of oxygen and is a function of soil properties [32]. Since the oxygen at the pipe surface undergoes a reduction reaction (Eq. 2), the oxygen flux can be equated to the cathodic current density using Faraday's laws of electrolysis as follows:

$$i_{O_2} = -D_e \left( \mathbf{n} \cdot \nabla C_{O_2} \right) zF \tag{3.15}$$

where, z is the number of electrons involved in the reduction reaction found from Eq. 3.2 and F (96485 C/mol) is the Faraday constant. At the soil surface exposed to the atmosphere, a constant concentration boundary is imposed with a concentration of  $C_{O_2}^{ref}$  equal to 8.6 mol/m<sup>3</sup>, which is the average atmospheric oxygen concentration. For all other surfaces, a zero-flux condition is specified as follows:

$$\mathbf{n} \cdot \left( D_e \nabla C_{O_2} \right) = 0 \tag{3.16}$$

Since the oxygen diffusion coefficient  $D_e$  is a function of soil properties, the coupling between oxygen diffusion and corrosion causes the corrosion kinetics to be soil-dependent. This dependency is illustrated in Fig. 3.4, which presents the theoretical polarization curves showing the influence of the soil degree of saturation on cathodic polarization. It is clear that the diffusion limitation becomes prominent at higher saturations.



Figure 3.4: Theoretical polarisation curves for active corrosion of metal showing cathodic limitation with increasing soil saturation. Solid lines indicate the polarisation curves without diffusion limitation effects

#### 3.2.4 Active area of uniform corrosion

Note that for corrosion to take place, and liberate ions in the aqueous phase, the metal surface needs to be covered with moisture [33–35]. Soils with low moisture levels show isolated areas of corrosion, and the total corroding surface area increases with increasing levels of moisture [33–35]. In this context, the actual area undergoing corrosion under predominantly anodic regions is known as the active area [34]. The global corrosion rate, the ratio of the corrosion current to the entire working electrode surface area measured in electrochemical experiments, does not consider the effect of the active area.

The active area is identified in terms of predominantly cathodic and predominantly anodic regions being formed under thin films of water and relatively thick regions of capillary water, respectively. This situation is similar to the water droplet corrosion experiment performed by Evans [36] and as discussed recently by Cole et al. [37] where it was shown that parts of the drop with good access to oxygen turn cathodic, whereas the thicker centre portion of the drop turns anodic with loss of metal observed in the centre region. As shown in Fig. 3.1, such a situation can arise in unsaturated soil, where areas under capillary water and thin films formed by condensation lead to the same effect. This factor is taken into account in some corrosion simulations as the ratio of anode to cathode [19,20], while it is termed the active area in other studies [33,34]. In the present model, the active area is simply considered as the actual area undergoing corrosion.

Since corrosion takes place in areas with electrolyte contact, or areas in which soil water is held by capillary action, the active area may be approximately equal to the degree of saturation of the soil. This hypothesis was confirmed in a series of corrosion experiments, as part of another study, as follows. Potentiodynamic polarization scans were conducted on cast iron working electrodes with  $2 \text{cm} \times 1.5 \text{ cm}$  exposed surface area. Sand was compacted at different degrees of saturation into a specially-designed electrochemical cell to conduct the standard three-electrode polarization test [38]. The working electrodes were digitally imaged after the test. The images were then processed and subjected to a thresholding algorithm to separate corroded regions from the uncorroded sites. The fractional coverage of the active area was calculated as the ratio between the total corroded area and the total surface area of the electrode and compared against the degree of saturation. Figure 3.5 shows that the active area ratio and the degree of saturation are highly correlated, exhibiting a nearly 1:1 relationship. This result is also consistent with soil mechanics principles, where a similar concept of area of water contact is related to the degree of saturation in the calculation of the effective average soil skeleton stress in unsaturated soils [39]. However, it was later observed that the relationship between soil saturation and the active area may take a sigmoidal shape, especially in soils with

colloidal properties. This observation is discussed further in Chapter 4 and Chapter 8. It was also shown that the criteria simulated in the present simulation are not impacted significantly by this difference.



Figure 3.5: Fractional coverage of active area against degree of saturation showing a 1:1 relationship. Also shown are digital images of electrode surfaces and thresholded binary images for Sr=0.2 and 0.5

The results of this study indicate that the soil degree of saturation,  $S_r$ , can be used to determine the active area. Therefore, to correct the anodic current density, adjusting for the active area, Eq. 3.10 was multiplied by  $S_r$  to convert it to the global corrosion rate. In the case of a sigmoidal dependence, the anodic current density is simply multiplied by the  $S_r$  dependent sigmoid equation.

#### 3.2.5 Corrosion product dynamics and metal loss due to corrosion

Most of the corrosion products deposited on the pipe surface resulting from corrosion processes are insoluble and have low permeabilities [5]. The result of deposition of such products is a shielding of the metal surface from further corrosion [5,40]. It is also known that the formation of certain hydroxides on the metal surface has the effect of passivating the metal thermodynamically [41]. The overall result of these mechanisms is the hindrance of oxidation half-cell reaction due to corrosion product build-up. To include this phenomenon, the thickness of corrosion products formed on the metal surface was calculated from the cathodic half-cell reaction according to Faraday's laws. It was assumed that the corrosion product is iron (III) hydroxide, in which case the rate of the cathodic reaction  $R_{OH}$  (mol/m<sup>2</sup> s) can be expressed by Eq. 3.17.

$$R_{OH} = \frac{\upsilon_{Fe(OH)_3} \cdot i_{O_2}}{z F} = \frac{\upsilon_{Fe(OH)_3} \cdot i_{O_2}}{3 F}$$
(3.17)

where,  $v_{Fe(OH)_3}$  is the stoichiometric coefficient of Fe(OH)<sub>3</sub>, and z is the number of electrons. Therefore, the thickness gain  $V_{Fe(OH)_3}$  (m/s), due to Fe(OH)<sub>3</sub> deposition on the metal surface is given by Eq. 3.18.

$$V_{Fe(OH)_{3}} = \frac{R_{OH} \ m_{Fe(OH)_{3}}}{d_{Fe(OH)_{3}}}$$
(3.18)

where,  $m_{Fe(OH)_3}$  (kg/mol) and  $d_{Fe(OH)_3}$  (kg/m<sup>3</sup>) are the molar mass and density of Fe(OH)<sub>3</sub> respectively.

The formation of corrosion products depends, among other factors, on the level of moisture of the surrounding soil [11]. In dry soils the ions formed by the reactions combine to form corrosion products which are deposited on the surface. With increasing levels of moisture in the soil, these ions migrate away from the pipe surface before they combine to form insoluble corrosion products [11]. Therefore, in soils with high moisture levels the shielding effect of corrosion products is lower than in soils with low moisture levels. To incorporate the dependence of corrosion product deposition on soil moisture, a sigmoid function was used to modify the stoichiometric coefficient for  $Fe(OH)_3$  formation as per Eq. 3.19.

$$\nu_{FeOH3} = \frac{1}{1 + \exp(25(S_r - 0.75))}$$
(3.19)

The effect of ionic migration becomes significant when a continuous water phase is formed. Hence, the activation for the sigmoid in Eq. 19 was chosen as  $S_r = 0.75$ , since this is approximately the degree of saturation for which a continuous water phase is established in most compacted or uncompacted soils [3,42].

The effect of passivation was modelled using the time-dependent thickness of the  $Fe(OH)_3$  calculated in the above manner. It is known that the thickness of the corrosion product layer in either long-term natural or accelerated corrosion tests is generally 100-150 µm [43,44]. Therefore, it can be safely assumed that the rate of corrosion product growth diminishes after the thickness of the product layer exceeds ~150 µm, after which a consistent corrosion rate is achieved. Passivation was modelled in this manner by modifying the anodic current density expression with a sigmoid function. The anodic current density modified to include the active area and passivation mechanisms can now be given by Eq. 3.20:

$$i_{Fe} = i_{Fe}^{0} \times 10^{\frac{\eta_{Fe}}{A_{Fe}}} \times S_{r} \times \frac{1}{1 + \exp\left(5 \times 10^{4} \left(t_{Fe(OH)_{3}} - 1.5 \times 10^{-4}\right)\right)}$$
(3.20)  
Tafel kinetics Active area Passivation

where,  $t_{Fe(OH)_3}$  (m) is the time-dependent corrosion product layer thickness given by:

$$t_{Fe(OH)_3} = \int_0^t (V_{Fe(OH)_3}) dt$$
(3.21)

The loss of iron due to the anodic half-cell reaction was calculated in a similar manner, with the respective stoichiometric coefficients and material properties of iron. The reaction rate ( $R_{Fe}$ ) or the molar flux of iron consumed by the reaction can be expressed as:

$$R_{Fe} = \frac{\upsilon_{Fe} \, i_{Fe}}{z \, F} = \frac{1 \cdot i_{Fe}}{2F} \tag{3.22}$$

where,  $v_{Fe}$  is the stoichiometric coefficient. The rate of change of metal thickness, or the corrosion penetration rate was calculated using Eq. 3.23:

$$V_{Fe} = \frac{R_{Fe} \ m_{Fe}}{d_{Fe}}$$
(3.23)

where,  $m_{Fe}$  (kg/mol) and  $d_{Fe}$  (kg/m<sup>3</sup>) denote the molar mass and density of iron, respectively. Integrating Eq. 3.23 over time gives the depth of penetration  $t_{Fe}$  (m) at a given time and location on the surface of the pipe:

$$t_{Fe} = \int_{0}^{t} (V_{Fe}) dt$$
 (3.24)

The mass lost at a given time  $w_{Fe}$  (kg/m<sup>2</sup>) can be computed in a similar manner using Eq. 3.25:

$$w_{Fe} = \int_{0}^{t} (V_{Fe} d_{Fe}) dt$$
 (3.25)

The local mass loss was calculated on a given point on the pipe and also averaged over the entire pipe area to determine the total average mass lost ( $W_{Fe}$  in units of kg/m<sup>2</sup>) due to corrosion as per Eq. 3.26:

$$W_{Fe} = \frac{\int w_{Fe} \, dA}{A} \tag{3.26}$$

where, A is the total area  $(m^2)$  of the exposed pipe, given as the pipe circumference multiplied by the out-of-plane unit thickness in the 2-D model, or the actual surface area in the 3-D model.

#### **3.3 Modelling the soil medium**

#### 3.3.1 Soil moisture profiles

Typical soil water retention curves given in Fig. 3.2 were used to define the water retention characteristics of the three soil types investigated in this study, *viz.*, sand, silt and clay. Ignoring cyclic climatic variations [18], Eq. 3.27 was used to define the sub-surface suction profiles:

$$u(y) = u_e + u_0 \exp\left[\left(\frac{\pi}{\alpha}\right)^{0.5} y\right]$$
(3.27)

where, *u* is the soil suction at depth *y* (m), *u*<sub>0</sub> is the amplitude of suction variation, *u*<sub>e</sub> is the equilibrium suction and  $\alpha$  (m<sup>2</sup>/year) is the moisture diffusion coefficient. The moisture distribution profiles in terms of *S*<sub>r</sub> were obtained by interpolating from the SWRC pertaining to the suction profiles obtained from Eq. 3.1. The other soil properties were described in terms of *S*<sub>r</sub>.

#### 3.3.2 Oxygen diffusion and electrical conductivity

As oxygen diffusion can occur both in the air and the water phase, the following relationship was used to define the effective diffusion coefficient for oxygen in soil [32]:

$$D_{e} = \frac{1}{n^{2}} \cdot \left[ D_{a}^{0} \left( n \left( 1 - S_{r} \right) \right)^{p} + H D_{w}^{0} \left( n S_{r} \right)^{p} \right]$$
(3.28)

where,  $D_e$  (m<sup>2</sup>/s) is the effective oxygen diffusion coefficient,  $D_a^0$  (m<sup>2</sup>/s) and  $D_w^0$  (m<sup>2</sup>/s) are the diffusion coefficient of oxygen in free air and water respectively, *H* is the dimensionless Henry's equilibrium constant (0.03), *n* is the porosity, and *p* is usually ~ 3.4 for most naturally encountered soils [32].

The soil electrical conductivity was defined using Eq. 3.29 [29]:

$$\sigma = \sigma_{w} \cdot \frac{\left(n.S_{r} - \theta_{0}\right)^{n+2}}{n - \theta_{0}} + \sigma_{s}$$
(3.29)

where,  $\sigma$  (S/m) is the electrical conductivity of the bulk soil solution,  $\sigma_w$  (S/m) is the conductivity of the pore water,  $\sigma_s$  (S/m) is the surface conductivity of soil particles, and  $\theta_0$  is the bound water content (dimensionless). The bound water content  $\theta_0$  and surface conductivity  $\sigma_s$  are soil-dependent properties. Therefore, the electrical conductivity of the soil medium is based on the soil type and the moisture distribution. The effect of soil salinity on electrical conductivity can be included using this equation, provided the soil solution conductivity ( $\sigma_w$ ) is given as a function of the chloride concentration.

Typical values for  $\sigma_s$  and  $\theta_0$  sourced from the literature (Table 3.2) were used for the modelling conducted in this study. Figure 3.6 summarises the mechanistic approach undertaken to model soil as an electrolyte.

Table 3.2 : Bound water content (volumetric) and surface conductivity values used in the model

Parameter	Value				Reference
i arameter	Sand	Silt	Clay		Reference
Surface conductivity	0.018	0.032	0.045	S/m	[45]
Bound water content	0.02	0.05	0.1	-	[29]



Figure 3.6: Process and mechanisms developed to model bulk soil as an electrolyte that facilitates corrosion reactions

#### 3.3.3 Model geometry

Numerical simulations were conducted for a pipe buried at the usual depth in Australia of 1 m. Most of the study was conducted in 2-D space, since dominant aeration and moisture effects are well captured. Further verification of the effects of aeration and the examination of lateral variations were conducted with a 3-D model. The 2-D geometry included a soil domain of  $3 \text{ m} \times 3 \text{ m}$  with a buried pipe (radius = 0.15 m) aligned into the plane, while the 3-D geometry extended this section by 10 m laterally. A mesh sensitivity analysis was conducted for optimum mesh size identification. Figure 3.7 shows the final mesh size selected after this exercise. Note that the finite elements closer to the pipe surface are smaller in size to capture local gradient effects around the pipe.

The top boundary of the soil domain was assumed to be exposed to the atmosphere, allowing oxygen to diffuse down through the soil to the pipe surface, where it is consumed by the corrosion reactions. Figure 3.7 summarises the relevant boundary conditions specified on the pipe surface and soil boundaries.



Figure 3.7: Model geometry for 2-D model and boundary conditions imposed on soil medium

#### 3.3.4 Simulation of field conditions of soil aeration

The NBS dataset [10] contains data on a diverse range of factors that affect underground corrosion. As identified in that report and subsequent analyses [46], due to the scatter caused by the diverse competing factors, interpretations of the data should be done over a restricted scope of variables. For this reason and due to the importance of soil aeration highlighted in the NBS study, comparison of the model results was performed primarily on soil aeration.

To enable verification of model results with the NBS dataset [10], typical field conditions, as described by Romanoff [10], were implemented in the suction and water retention curves for the three different soil types. The NBS report contains information on the four aeration regimes, which were categorised with corrosion data. These aeration regimes, viz., good, fair, poor and very poor, were simulated with implementations summarised in Table 3.3. Corrosion data corresponding to low alloy cast iron pipes exposed for the same periods of time were extracted from the NBS dataset for comparison with the model results. Cast iron was selected for the analyses because it is the most common material used in old pipelines and it is nearing its critical lifetime [21]. High alloy cast iron was not included because of the unusually low corrosion rate due to alloying, and it would not correspond to the mechanisms presented in this work.

Category	NBS report description		Implementation in model		
	Soil description	Water table level	SWCC type	Suction profile	
Good aeration	Coarse sands, sandy loams and porous loams	Very low	Sand	Typical profile based on TMI (Neutral climate, TMI – 0)	
Fair aeration	Silt loams or sandy loams with mottling at depth	Low	Silt	Typical profile based on TMI (Neutral climate, TMI – 0)	
Poor aeration	Clay loams or clays (soils with heavy texture)	At pipe depth	Clay	Profile with equilibrium suction of zero	
Very poor aeration	Extremely impermeable	At surface	Clay	Soil suction zero throughout soil profile ( $S_r$ =1)	

Table 3.3 : Aeration regimes used in model to simulate conditions in NBS study for validation.

For good and fair aeration, the water retention curves for sand and silt respectively were selected. For both these soils, a suction profile obtained from Eq. 3.27, deviating towards the dry side from the respective equilibrium suctions ( $u_e$ ), was used. The equilibrium suction values for the respective soil types were obtained from the TMI-equilibrium suction curves [17]. For consistency, a TMI value of 0, indicating neutral climatic conditions (being neither arid nor humid), was chosen for all aeration regimes in this study. The moisture diffusion coefficient ( $\alpha$ ) was selected on the basis that it gave an active zone depth ( $H_s$ ) of around 2 m. The amplitude of the suction variation,  $u_0 = 0.85$  pF, was used, which is half of the suction difference in pF between the field capacity and the wilt point of soil. For poor and very poor aeration regimes, the water retention curve for clay was used. According to the NBS report, the water table was approximately at pipe burial depth in the poor aeration regime. Since the suction profiles used in this work cannot be utilised in shallow water table situations, Eq. 3.30 was used to define a suction profile to establish a water table at pipe level. This equation effectively incorporates the effects of the groundwater in the poor aeration regime:

$$u(y) = \frac{3.35}{1 + \exp\left(-5\left(y + y_p\right)\right)}$$
(3.30)

where,  $y_p$  (m) is the approximate depth to the water table. For the very poor aeration regime, the suction throughout the soil medium was set to zero to simulate full water saturation ( $S_r$ =1).

According to Cole and Marney, [4] a model to accurately describe corrosion in soils should encompass the following five levels of phenomena:

- Anodic/cathodic activity
- Oxide effects
- Pore water/pipe interface
- Soil moisture/air dynamics
- Macro environment

The model presented in this chapter includes all of the above five levels in some form. The previous sections illustrate these modelled phenomena, the modes of implementation and their coupling. The finite element method was used to solve the main governing equations with non-linear boundary conditions using the COMSOL 5.3 Multiphysics® software. The soil water characteristic curves (SWCCs) and the suction-TMI relationships were implemented as interpolated functions, while other equations, discussed in earlier sections, were incorporated as analytical functions. Table 3.1 provides a complete summary of the parameters used in the model.

#### 3.3.5 Solution method used

COMSOL Multiphysics provides a range of solvers to solve the set of equation set up during model creation. Direct solvers such as MUMPS, PARDISO and SPOOLES and iterative solvers based on the conjugate gradient method are built in and available in COMSOL [47]. Once the domain is discretised, parameters approximated and equations assembled, COMSOL automatically selects the best solver for the problem depending on physics being solved, the size of the domain and memory requirements [47]. The corrosion simulations presented in this chapter were conducted in two stepsan initialisation step followed by the transient simulation. The initialisation step uses the provided initial values to solve only for the electrode and electrolyte potentials and global variables. All other dependent variables are not solved in this step. In the transient simulation, all the coupled equations such as mass movement and resulting concentrations are solved together with the electrochemistry using the results from the initialisation step as initial values. This approach was taken for all corrosion simulations conducted and presented in this thesis. The direct MUMPS solver was used for the most of the simulations and where moisture migration equations are solved, MUMPS together with the iterative GMRES (generalized minimal residual method) was used. Error minimisation, solver settings and convergence criteria were determined using the automatic optimisation methods in COMSOL.

# 3.4 Results and discussion

#### 3.4.1 Model verification with NBS data on soil aeration

For verification purposes, the model results were compared with corrosion mass loss data for different aeration regimes published in the NBS circular [10]. The corrosion mass losses given in oz/ft<sup>2</sup> were converted to standard units of kg/m<sup>2</sup>. The mean cumulative mass losses with time for the collection of low alloy cast iron pipes within each aeration regime are shown in Figs. 3.8-3.11. Note that the error bars represent one standard deviation from the mean. The model results are also given in the same figures. The corrosion rate along the circumference of the pipe was different, since the suction profile results in non-uniform moisture distribution in most of the aeration regimes. For most cases, the bottom of the pipe shows enhanced mass loss, as evidenced in Figs. 3.8-3.11. For this reason, both the corrosion mass losses at the top and bottom of the pipe are reported, along with the total average mass loss of the pipe. Note that the average mass loss calculated using Eq. 3.26 equates to the mass loss measurements reported in the NBS study.



Figure 3.8: Model results and mass loss data for average cast iron pipe from NBS study for good aeration regimes. Local losses at the top and bottom of the pipe are equal to the total average loss in the model and show agreement with field data

The corrosion mass loss for the good aeration regime (Fig. 3.8) is consistent with the model results, appearing to stabilise within  $2 \text{ kg/m}^2$  over the long term. Moreover, the model mass losses at the top and bottom of the pipe are equivalent to the average mass loss over the entire pipe surface. This indicates that the corrosion rate is uniform over the entire pipe surface. The corrosion rate, given by the gradient of the model curve, is relatively high initially and stabilises to a relatively small steady-

state level over a period of time. This observation can be explained as follows. Initially, corrosion progresses without any hindrance from corrosion product build-up. However, over time, the formation and subsequent deposition of corrosion products on the pipe surface in well-aerated soils leads to an attenuation of the reaction kinetics. This attenuation is further exacerbated if insufficient moisture is available for the diffusion of the corrosion products from the pipe surface [10,11], as is the case in most well- aerated soils.



Figure 3.9: Model results and mass loss data for average cast iron pipe from NBS data for fair aeration regime. Local losses at top and bottom vary considerably, but total average loss compares well with field data

In contrast, the fair aeration regime (Fig. 3.9) reveals that the highest mass loss occurs at the bottom of the pipe compared to the top. In addition, compared to the good aeration regime, the mass loss at the bottom of the pipe is nearly an order of magnitude greater. This behaviour can be attributed to the presence of optimum corrosion conditions in this aeration regime. It follows that with sufficient moisture, the corrosion products diffuse away from the metal surface, leaving it susceptible to further corrosion. Since it is a fair aeration regime, sufficient oxygen is available to continue corrosion. Note that the mass loss data reported in the NBS study do not distinguish between pipe top and bottom mass loss. Rather, the figures provide an overall mass loss for the entire pipe surface. In this regard, the NBS data agree well with the total average mass loss obtained from the model simulations. It is also clear that the fair aeration regime leads to differential aeration cells, resulting in further alteration of corrosion rates and giving rise to a bimodal trend in the corrosion accumulation curve.



Figure 3.10: Model results and mass loss data for average cast iron pipe from NBS study for poor aeration regime. Local losses at top and bottom are different but total average loss compares well with field data

Soils in the poor aeration regime have relatively high levels of moisture, which allow most of the corrosion products to diffuse away from the pipe surface. The low product deposition results in a poor shielding effect, permitting corrosion to proceed unhindered. Reduced passivation due to migration of corrosion products explains the quasi-linear mass loss model curve, implying a constant corrosion rate, as shown in Fig. 3.10. The model results generally conform to the NBS data, as shown in the figure. However, compared to the fair aeration regime, the overall mass loss is relatively low. This observation can be explained by the reduced oxygen availability at the pipe surface in the poor aeration regime. The presence of relatively high moisture levels hinders the diffusion of oxygen to the pipe level [32], resulting in a reduction in the cumulative mass loss. Since corrosion product formation is dependent on the moisture level in the model (see Eqs. 3.17-3.19), good agreement between the model simulations and the NBS data is observed, as shown in Fig. 3.10.



Figure 3.11: Model results and mass loss data for average cast iron pipe from NBS study for very poor aeration (water-logged) regime. Model results do not agree with NBS data, showing an almost order of magnitude difference (note: mass loss is in log scale)

Finally, the very poorly aerated regime implies pipes laid in fully saturated media (waterlogged soil). According to the NBS data, relatively high cumulative mass losses were observed in this category. In contrast, model simulations revealed very low levels of cumulative mass loss, as shown in Fig. 3.11. The significant disagreement between the NBS data and model simulations can be attributed to possible bacterial corrosion and (or) other phenomena, such as hydrogen ion reduction [5,11,48]. Nevertheless, it is also noted that in a separate study by Penhale [23,24] low corrosion levels in highly waterlogged soils were reported, which is consistent with the model observations presented here. The identification and mechanistic treatment of the possible mechanisms causing the conflicting behaviours, in the NBS study and that by Penhale, are beyond the scope of the present study and should be investigated further. However, recent experimental studies on localised corrosion in sand [48], have indicated that relatively lower pH values that occur under fully saturated regions could result in changes to the passivation behaviour of the metal, influencing localised corrosion. It is possible that such changes to corrosion mechanisms under saturated conditions are responsible for the above the discrepancy between the numerical model and field data, but this aspect requires further research. While the mechanistic influence of pH on corrosion reactions are beyond the scope of the present work, the localisation of pH values in soil around a corroding pipeline is modelled and discussed in Chapter 8.

As the cast iron pipes in the NBS study were primarily 1.5 inches in diameter (0.02 m radius) an investigation was conducted on the potential effects of pipe sizes on the model results. The results are presented in Fig. 3.12. It is evident that pipe size has a less significant impact when considered against other important properties, such as soil type and aeration. Therefore, for the purposes of validation of the present work, the effect of pipe size was considered to be irrelevant.



Figure 3.12: Effect of pipe radius on mass loss for different aeration regimes. While slight variations are present, in the context of soil aeration, the pipe size effect is less significant.

#### 3.4.2 Macro-cell corrosion caused by differential aeration

Differential aeration at the pipe surface can arise due to differences in moisture, soil type and other external factors such as driveways and soil covers [47]. The model developed in this work naturally incorporates the effects of differential aeration due to the differences in moisture distribution around the pipe. This effect is evident in the case of the fair aeration regime, and as shown in Fig. 3.13, there is a clear difference between the mass loss curves between the top and bottom of the pipe, indicating that corrosion rates are different at these locations. Differences in corrosion rates indicate the possibility of a macro-cell forming between the top and bottom of the pipe. In Fig. 3.13, the model results for the electrode potentials and the electrolyte currents at different times are also illustrated. The colour scale on the pipe circumference denotes the electrode potential. The arrows indicate the electrolyte current density vectors, and their sizes are proportional to the vector magnitude.



Figure 3.13: Effect of differential aeration in fair aeration regime. Natural evolution of macro-cells alters corrosion rates at bottom of pipe, giving rise to a bi-modal characteristic in the corrosion mass loss curve

The figure shows that the electrolyte current density at the bottom of the pipe is maximum when t = 4 yrs. The anodic pipe bottom results in a relatively large macro-cell current, implying a larger anodic current density  $i_{Fe}$  at the bottom portion of the pipe, according to Eq. 3.5, and as observed in the field (see Chapter 1). The resulting high levels of corrosion are evident during the period t = 2 years to t = 6 years with the maximum at t = 4 years, as seen in the electrolyte current densities. During the same interval  $2 \le t \le 6$  years, the gradient of the mass loss curve of the pipe bottom initially increases, reaching a maximum at t = 4 years before gradually decreasing again. The agreement between the macro-cell current and the gradient of the mass loss curve implies that the corrosion rate at the pipe bottom is enhanced by macro-cell activity.

It is further observed that an increase in the corrosion rate due to macro-cells leads to a bi-modal characteristic in the mass loss curve. Variations in the electrode potential with time suggest that the pipe bottom always remains anodic, although the relative magnitude of the potential varies. Micro-cell corrosion dominates over the entire pipe surface until macro-cell corrosion emerges, and increases the corrosion rate at the more anodic bottom portion of the pipe, leading to elevated levels of corrosion as time progresses. The bi-modal trend has been observed in marine and atmospheric corrosion studies [49]. It has also been shown to be applicable to underground corrosion [47]. The
present study shows that the transformation from micro- to macro-cell corrosion leads to the bi-modal characteristic in the mass loss curve. However, there may be other rate controlling factors which influence this, and these mechanisms need to be investigated further.

## 3.4.3 Influence of soil type

The model developed in this study also allows the comparison of the levels of corrosion in different soil types. This comparison is performed by utilising the suction profile corresponding to dry, equilibrium, and wet conditions consistently throughout the three different soil types and later comparing the levels of corrosion amongst them. The results suggest that clay is the most corrosive soil type, followed by silt, and then sand, as shown in Table 3.4.

Soil type	Total average mass loss (kg/m2)						
	Wet suction profile	Equilibrium suction profile	Dry suction profile				
Sand	1.76	1.71	1.69				
Silt	2.25	6.56	9.13				
Clay	5.99	10.7	13.7				

Table 3.4: Corrosion in different soil types

Clay and silt reveal consistently high corrosion rates, especially with a suction profile denoting dry conditions. However, it should be noted that "dryness" at the pipe depth is more subtle than at the ground surface. Therefore, high levels of corrosion in these soils are expected, since high levels of moisture hinder corrosion by oxygen limitation, whereas a balance between the level of moisture and oxygen concentration leads to the best combination for the progression of corrosion. Clay and silt, due to their structure and water retention characteristics, retain more water under high suction [14] and therefore, have the right conditions for corrosion under equilibrium and dry conditions. In addition, the presence of two or more different soil types together can cause large variations in moisture, as can be inferred from Fig. 3.14. The resulting differential aeration cells under these conditions can give rise to an increase in corrosion rates in soil types that have poor access to oxygen (i.e. they hold more water) *viz.*, clay and silt. These situations are consistent with field observations and assessments, in which clay and silt soils have been found to be the most corrosive [24,50,51].



Figure 3.14: Moisture profiles for different soil types. Clay and silt soil have moisture profiles that tend to produce higher levels of corrosion under equilibrium conditions.

## 3.4.4 Model extension to 3-D

To ascertain any potential longitudinal effects on corrosion due to oxygen concentration differences, a 3-D model simulation was also conducted by extending the relevant equations presented in this paper into 3-D space. An impermeable soil cover (such as a concrete driveway) covering half of the soil domain was simulated to examine lateral variation in oxygen penetration and its effects on corrosion. This was achieved by enforcing a no-flow condition on the region of the soil cover so that it had zero oxygen permeability and also ensuring that the soil underneath the cover had the equilibrium suction profile throughout its depth, as is usually observed in soil covers [14]. The section open to the atmosphere was similar to the top boundary of the 2-D model. Fig. 3.15 shows the model geometry and the corrosion mass loss curves at the highest corrosive points on the pipe surface. The figure indicates that the bottom part of the pipe close to the edge of the soil cover is the most corrosive, with a bi-modal trend similar to that observed in the fair aeration group in the 2-D model. It is also noted that the mass loss in this edge region is slightly higher than that of the bottom portion of the pipe in the open region. In addition, the corrosion behaviour in the region of soil open to the atmosphere behaves identically to the 2-D model with the exact mass loss curves being produced.



Figure 3.15: Model geometry and corrosion mass loss curves in 3-D model. Corrosion is identical to the 2-D model in open region while localised high corrosion is seen in the bottom portion of the pipe under the edge of cover

## 3.4.5 Modelling directions identified to expand upon

The model presented in this chapter has been shown to agree well with the observations presented in the literature. The major mechanism implemented is the aeration/moisture distribution and its influences on oxygen diffusion, soil conductivity, and passivation. The moisture distribution itself is implemented based on firm soil physics concepts. Consequently, the present model serves as a baseline model for further work. Further work could be carried out on the effects of soil salinity, pH [52] temperature and moisture movement, along with factors such as coating and cathodic protection [53], which are known to be of importance in underground corrosion. Some of these effects are addressed in Chapter 8.

According to research to date, soil salinity influences corrosion in two ways [2,7]. It can alter the soil's electrical conductivity, thereby influencing macro-cell corrosion [2]. This influence can be directly incorporated into the present work, as stated previously. Moreover, soil salinity can also directly influence the electrochemistry of the system, which is beyond the scope of the present work.

The effect of pH has been included in previous soil corrosion models [19,20] in a simplistic manner through modification of the equilibrium potential for the oxygen reduction reaction. However, the effect of pH in underground corrosion is known to be more complex [54]. Therefore, a thorough study investigating the possibility of incorporating pH in a mechanistic manner to the current model will be very beneficial. Similar comments are applicable to the effects of temperature and moisture migration in unsaturated soil media. For the latter, coupling of matric suction to emulate climatic variations or to other hydraulic boundary conditions will further enhance the model's capabilities. Moreover, the present work has not considered cases where pipelines are coated and/or under cathodic protection. The influence of these protection methods in reducing corrosion deterioration is an important study in its own right, but is beyond the scope of the present work. Nevertheless, in future, these studies can be implemented as extensions to the initial model developed here.

The development emanating from this work is that the thermodynamic concept of soil suction is used to govern the moisture distribution in soils, which ultimately influences the processes of underground corrosion. The manner in which the effects of soil suction are transformed to pipe deterioration through corrosion is evident in the differences within the different aeration regimes and around the pipe (top and bottom). Notably, for future development, soil suction can be used to model the effects of climatic variation on underground corrosion, as discussed in more detail in Chapter 8.

# **3.5 Conclusions**

The present model was developed to realistically couple the essential factors pertaining to the soil medium involved in the underground corrosion process. Equilibrium and transient soil suction profiles and water retention curves were used to develop different soil aeration regimes and the corrosion characteristics in these regimes were investigated. This approach enabled a quantitative assessment of soil moisture and aeration conditions on underground corrosion using qualitative descriptions of field conditions. Comparison of model results in the different aeration regimes with the NBS dataset indicated that soil aeration and moisture distribution are able to explain the important observations commonly encountered in the field.

In the model simulations it was observed that differential aeration leads to the formation of macrocells, which evolve naturally and without any prior definition in the model, and enhance corrosion rates. In addition, investigation of the different soil types in the underground corrosion process revealed clay to be the most corrosive, followed by silt and then sand. Although the ranking of soils in this order of corrosiveness is well known, it was demonstrated that the origin of this ranking arises from the water retention characteristics. An extension of the model to 3-D confirmed the previous observations, while also highlighting the influence of lateral variations in oxygen concentration.

The model presented captures the main physical controls influencing underground corrosion along with the coupled mechanisms. Soil aeration and suction profiles, moisture distribution, corrosion product effects, active area and localized anodic/cathodic activity are the phenomena which were modelled. However, other influential factors, such as pH, temperature, salinity and moisture migration, are possible expansions to the model, provided a mechanistic understanding of the processes is developed. The interrelationships, physical coupling and the mode of implementation of these phenomena are potential directions for further research, as identified in the present study. The proposed model could be improved by incorporating moisture migration in soils to simulate the aeration regimes instead of the approach presented here. This implementation is expected to improve the capabilities of the model, allowing for natural simulation of climatic effects. These improvements along with the results are presented and discussed in Chapter 8 of this thesis.

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# Chapter 4: Measurement and characterisation of electrochemical properties of soils

# 4.1 Introduction

Since corrosion is an electrochemical process, it is possible to use electrical measurement techniques to quantify the corrosion process. The sensitivity of electrical measurements using modern instruments also makes it possible to accurately measure levels of corrosion, even if no metal loss is visible, or no weight loss is recorded on an analytical balance [1]. A system undergoing corrosion is identified as a metal electrolyte system, where the electrolyte is defined as an aqueous medium containing dissolved ions or gases such as oxygen [1]. The metal undergoes oxidation during corrosion, which involves the loss of metal as ions into the electrolyte, creating an abundance of electrons at the metal surface. This generation of electrons is counter-balanced by a reduction reaction, which consumes the excess electrons by means of a reduction reaction. The oxidation half of the reaction is known as the anodic reaction and the reduction half of the reaction is known as the anodic reactions are the oxidation of iron and the reduction of oxygen. Both the anodic and cathodic reactions need to occur simultaneously for corrosion to occur.

#### 4.1.1 Electrochemical polarisation

A metal immersed in an electrolyte and corroding has a certain electric potential with respect to a reference electrode. This potential is named the open circuit potential (OCP), since no measurable electric current flows between the metal and the electrolyte in this situation. The anodic and cathodic reactions occur at the same rate and the metal and electrolyte together in this situation are electrically neutral. Therefore, under such conditions the rate of corrosion cannot be quantified using electrical measurements. However, if an external potential is applied to the metal, the anodic or the cathodic activity will dominate, depending on the polarity of the applied potential, in an attempt to re-establish electrical neutrality [1]. This shift in electrode potential from the OCP is known as polarisation, and the deviation of the electrode potential from the equilibrium is known as over-potential  $\eta$  (V) [2].

Figure 4.1 shows a schematic with the Evans diagram used commonly for numerical modelling of corrosion and the experimentally-measured Stern diagram [2].



Figure 4.1: Schematic illustrating electrode polarisation using Evans diagram and Stern diagram. Modified from Perez (2004) [2].

The subscripts *WE* in the axes denote the working electrode, which is the metal that undergoes corrosion. The logarithm of the working electrode current (*i*) is plotted against the working electrode potential (*E*).  $E^{eq}$  values with subscripts *Fe* and  $O_2$  denote the standard equilibrium potentials for iron oxidation and oxygen reduction respectively, while the  $i^0$  values with the same subscript denote the exchange current densities for the same reactions. *A* and  $\eta$  denote Tafel slopes and the over-potentials for the anodic and cathodic reactions. The coordinates of the point where the lines intersect, *E*<sub>corr</sub> and *i*<sub>corr</sub>, denote the corrosion potential and the corrosion current density respectively.

During polarisation, a current flows either to or from the electrode, making measurements possible. In electrochemical testing, the current flowing to and from the corroding working electrode (WE) is counted at each potential level by means of a counter electrode (CE). Therefore, this process of polarisation provides a dataset of potential (voltage) versus electric current, which can be used for measuring corrosion rates and other electrochemical quantities. As Fig. 4.1 shows, the Stern diagram represents such a dataset known as the polarisation curve which can be obtained experimentally. The polarisation behaviour of a metal can be mathematically represented using the Butler-Volmer equation introduced in Chapter 2. A model fit known as the Tafel fit [3] can be performed on the experimental data to obtain the corrosion current and potential and the Tafel slopes.

#### 4.1.2 Standard electrochemical test

The standard electrochemical test consists of three electrodes known as the working electrode (WE), counter electrode (CE) and the reference electrode (RE). A standard three-electrode electrochemical cell is schematised in Fig. 4.2.



Figure 4.2: Schematic of three-electrode electrochemical cell connected to potentiostat showing electrical connections

In the three-electrode cell schematised in Fig. 4.2, the working electrode is polarised by supplying or withdrawing current from it. The current flows through the electrolyte between the working electrode and the counter electrode. The voltage of the working electrode is measured against the reference electrode, which is defined as electrode polarisation. No current flows between the potentiostat and the reference electrode and the reference electrode provides a fixed point from which voltages can be measured [1]. The reference electrode is also used to provide feedback to the potentiostat in order to adjust the working electrodes in a three-electrode cell are used to withdraw or supply current through the electrolyte, while the reference electrode is used to monitor and control the potential of the reference electrode. Therefore, the output from a polarisation test is the working electrode potential and the electrode current (either flowing into or out of the working electrode).

#### 4.1.3 Electrochemical properties of soil

#### 4.1.3.1 Soil as an electrolyte

In the process of corrosion in soils, soil acts as the electrolyte. Therefore, in laboratory measurements using techniques such as polarisation, soil should be used as the electrolyte. Due to the three-phase nature of soil whereby water and air are distributed in a porous solid soil structure, electrochemical measurements in soil are not as straightforward as in aqueous solutions. Some previous studies used the soil water extracted from soil as the electrolyte solution [4]. While this approach can account for the chemical species in soil and their influences on corrosion, the effect of the soil physical structure is not considered.

The capillary porous nature of soils results in many problems during electrochemical measurements, the most important of which is the large resistivity in bulk soil. In addition, the lack of continuous pathways for ionic conduction between the working and counter electrodes, especially in low moisture conditions, can result in potentiostat overloading with no measurements being made. Such problems in soil can be overcome to a certain extent by the placement of electrodes during electrochemical measurement. To visualise the contribution and effects of soil resistivity to the electrochemical measurement, the soil electrolyte-metal interface can be represented as an equivalent circuit, as shown in Fig. 4.3 [1,5].



Figure 4.3: Simple circuit diagram for soil-metal interface system. Soil resistance together with double layer properties are shown.

The capacitor ( $C_{dl}$ ) and the resistor ( $R_p$ ) which are in parallel, as shown in Fig. 4.3, are the electric double-layer (EDL) properties, while the single resistance on the left ( $R_{\Omega}$ ) is the soil resistance. The EDL forms a corroding metal surface due to charge separation and facilitates the corrosion reactions [1,3,5]. Due to the charge separation, this interface exhibits capacitor- like behaviour. The localisation of charges also leads to resistance to electron transfer, giving it a resistive property known as charge transfer resistance, or polarisation resistance ( $R_p$ ). Therefore, the corroding metal interface can be defined using a parallel arrangement of  $R_p$  and  $C_{dl}$ .

#### 4.1.3.2 Effect of soil resistance in electrochemical measurements

Although the corroding interface in a metal-electrolyte system can be defined using the parallel circuit of  $R_p$  and  $C_{dl}$ , the additional soil resistance term of  $R_Q$  may lead to erroneous estimations of corrosion rates during electrochemical measurements [6]. As discussed in Section 4.1.2, in polarisation testing to indirectly assess the uniform corrosion rate, the electrode potential is recorded against the corresponding electrode current. The potential is measured against a reference electrode, and the potential drop between the reference electrode and the working electrode introduces an additional term to the applied voltage in addition to the over-potential. Since the applied voltage is used for the recorded measurement, this effect introduces an error to the electrochemical measurement. This effect is illustrated in Eq. 4.1, where the different contributions of the potential measured by the potentiostat are shown [1]:

$$V_{applied} = \eta + V_{\Omega} \tag{4.1}$$

where,  $V_{applied}$  is the applied potential,  $\eta$  is the over-potential and  $V_{\Omega}$  is the potential drop due to the soil resistance  $R_{\Omega}$ . Therefore, the measured over-voltage does not represent the actual system undergoing uniform corrosion. The effect of soil resistance can be minimised to counter this effect. Soil resistance  $R_{\Omega}$  can be defined as shown in Eq. 4.2:

$$R_{\Omega} = \frac{d.\rho_{soil}}{A} \tag{4.2}$$

where, d (m) is the distance between the reference and working electrodes,  $\rho_{soil}$  ( $\Omega$  m) is the soil resistivity and A (m<sup>2</sup>) is the electrode surface area. It can be seen from Eq. 4.2 that minimising d reduces soil resistance, leading to reduced error in measurement [6]. This can be achieved by the electrode arrangement and electrochemical cell design, as discussed in Section 4.2.3. In addition, it is possible to measure soil resistance during measurement and then correct the potential according to Eq. 4.1. In this study, soil resistance is minimised by cell design and electrode arrangements.

Note that the effect of soil resistance is important in this case for the electrochemical measurement of uniform corrosion and not the actual process of uniform corrosion itself. However, soil resistivity or the associated resistance is significant in macro-cell corrosion where a net current flows through soil. Therefore, the measurement of soil resistivity or conductivity is essential to define the governing equations for numerical simulations conducted to assess the effects of macro-cell corrosion.

In this chapter, the aforementioned factors are considered in developing a systematic experimental programme to investigate the electrochemical properties of soils. A wide variety of instrumentation and tools were utilised, and the experiments were supplemented with numerical modelling. The following sections detail the adopted methodology and results.

# 4.2 Experimental methods

The corrosivity characteristics of the soil were established using two different electrochemical methods to assess levels of uniform corrosion and other supplementary information was obtained from chemical tests, electrical conductivity tests and active area measurements. The supplementary results obtained were used for numerical simulations and further analysis.

## 4.2.1 Chemical tests of the soil

The cations and anions present in soil water solutions were analysed using inductively- coupled plasma optical emission spectrometry (ICP-OES) using a Thermo iCAP Duo 7000 and ion chromatography (IC) using a Thermo Dionex ICS-1100, respectively. Air-dried samples of sand, silt, and clay were mixed thoroughly with de-ionized water at a 1:5 ratio by mass and left to equilibrate for 24 hours. The soil solutions were filtered and diluted to the required level (1/10 or 1/100) with the appropriate standards and reagents added. For major cation analysis using ICP-OES, the diluted solutions were acidified with HNO<sub>3</sub> and an Yt-In internal standard was added. For the anion analysis, the solutions were not acidified and only the standard was added. External standardisation was carried out using USGS standard reference material AGV-2 and commercially available stock solutions.

The pH and conductivity of the filtered 1:5 soil solutions and that of 0.001M NaCl were measured using a commercially available water quality probe for reference.

#### 4.2.2 Electrical conductivity tests in soil

The electrical conductivity of the sand samples at similar dry densities, as in the oxygen diffusion tests, was measured using a 4-electrode set-up described by Deo & Cull (2015) [7] and shown in Fig. 4.4. This set-up conforms to the design criteria given by Zimmerman et al. (2008) [8] and applies a current pulse between two end-cap copper electrodes and measures the potentials between two middle non-polarisable electrodes (E-Daq Ag/AgCl leak-less miniature reference electrodes). The current/potential response was transformed to the soil conductivity (reciprocal of resistivity) using the geometrical factor of the sample holder. The data analysis procedure used was the same as that detailed by Deo & Cull (2015) [7]. Prior to the measurement of sand samples, the experimental set-up was calibrated with solutions of known conductivity for quality control purposes. The soil was compacted into the sample tube (Fig. 4.4) to the required dry density at varying levels of saturation before securing the top end-cap.



Figure 4.4: Schematic of electrical resistivity measurement cell and image showing test in progress

The soil conductivity/resistivity values were plotted against degree of saturation for analysis. The conductivity saturation relationships were also used as inputs for numerical modelling (see Section 4.4.5 and Chapter 8).

# 4.2.3 New electrochemical cell design for soil tests

As detailed in Section 4.1.3.2, possible errors due to soil resistivity were minimised by electrode arrangement.

## 4.2.3.1 Cell Design

To minimise  $R_{\Omega}$ , the distance between the reference and working electrodes must be as low as possible. However, if the reference electrode rests on the working electrode, the reference blocks the current flow to (or from) the working electrode and may also induce other effects such as pitting [1]. Therefore, the reference electrode needs to be placed at a sufficient distance in order not to block the working electrode. Since miniature reference electrodes were used for testing, it was decided to position the reference electrode at a distance of 1 mm from the working electrode. The electrode arrangements are indicated in the new cell design shown in Fig. 4.5. The working electrode was positioned at the bottom of the cell, ensuring a flush surface on which the soil could be compacted. The counter electrodes with no obstructions. Therefore, a side slot was created in the cell cap (Fig.4.5(a)) so that the counter electrode could be inserted once the soil was compacted.



*Figure 4.5: (a)* New electrode design with allowances for required arrangements of electrodes to minimise soil resistance effects and (b) Schematic showing electrode placement in compacted soil

This new electrochemical cell allowed for free compaction of soil to the required dry density and degree of saturation so that the electrodes could be inserted after compaction. This cell design was 3-D printed using PLA polymer with an infill density of 85% with a honeycomb structure and smooth outer finish to ensure strength and water-tightness.

## 4.2.3.2 Electrode design

The working, counter and reference electrodes used for electrochemical tests are shown in Fig. 4.6.



Figure 4.6: Miniature leak-less Ag/AgCl reference electrode, titanium-coated mesh counter electrode and working electrode constructed from cast iron from old pipeline.

The cast iron working electrodes (Fig.4.6) were prepared from an out-of-service cast iron pipe, and used for the corrosion tests in this study. The elemental composition of the cast iron specimen was measured in an earlier study [9] and is summarised in Table 4.1.

Table 4.1: Chemical composition of cast iron specimen used for tests

Element	С	Mn	Si	S	Р	Ni	Cr	Cu
Percentage by	3 52	0.43	1 83	0.1	0.57	<0.001	0.01	0.2
weight	5.52	.52 0.45 1	1.05	0.1	0.57	<0.001	0.01	0.2

The cast iron specimen was cut into 20 mm  $\times$ 15 mm  $\times$ 5 mm blocks which were then encased in an epoxy resin in a circular mould 38.5mm in diameter, as shown in the cell design (Fig. 4.5(b)). One of the sides, with dimensions 20 mm  $\times$ 15 mm, was left uncovered for the electrochemical tests.

A titanium-coated mesh electrode was used as the counter electrode. The larger surface area compared to the working electrode ensures that the potentiosat current can flow freely between the counter and working electrodes.

A commercially-available miniature leak-less Ag/AgCl reference electrode (eDAQ) was chosen as the reference electrode. Due to its small diameter and rigid polycarbonate casing, the reference electrode can be readily inserted into compacted soil.

#### 4.2.4 Potentiodynamic polarisation

The working electrode was progressively wet ground using emery papers of grit size 400 to 2000, ultrasonically cleansed in ethanol and air-dried prior to each test. The prepared working electrode was placed in the working electrode compartment as shown in Fig, 4.5. Soils were prepared with varying degrees of saturation ( $S_r$ ), with fixed amounts of solids to maintain the same dry density, with varying amounts of 0.001M NaCl solution. The soil was prepared by mixing 0.001M NaCl with dry soil. Prior to the main tests, trials were conducted on sand prepared by mixing de-ionised water. These tests were not successful, as the potentiostat could not supply enough current for polarisation. The reason for this was identified as the low conductivity in sand mixed with de-ionized water, as verified with the results presented in Table 4.3. Such potentiostat overload conditions were avoided by mixing the soil with 0.001M NaCl solution. This concentration was chosen to increase the conductivity to a sufficient amount without significantly influencing the corrosion reactions. However, even then at

very low moisture contents, the same situation occasionally arose, and no measurement was made. In such cases, the test was re-started with a fresh electrode and soil.

To ensure uniform compaction, the soil samples were compacted in layers in the electrochemical cell with the working electrode affixed, with scarification between layers to ensure homogeneity. The three-electrode set-up described in Section 4.1.2 was used for the experiments. The leak-less Ag/AgCl miniature reference electrode was inserted through the compacted soil column in the centre to rest ~1 mm above the working electrode. The titanium mesh counter-electrode was inserted through the side slot in the cell assembly. All electrochemical tests were conducted using commercially-available potentiostats. Fig. 4.7 shows the cell assembly and electrode arrangement within the compacted soil during a potentiodynamic polarisation test.



Figure 4.7: Electrochemical cell and electrode connections during polarisation test

Prior to each test, the open circuit potential (OCP) was monitored for at least 30 minutes to ensure equilibrium conditions. The polarisation scans were conducted in the range of -0.4 V against OCP to 2 V against reference at a scan rate of 0.2 mV/s. A Tafel-type fit [3] (see Section 4.1.1) was performed on the resulting polarisation curves to determine the corrosion current ( $i_{corr}$ ) and the corrosion potential ( $E_{corr}$ ). This complete procedure was repeated for each soil at different degrees of saturation. Furthermore, several tests were conducted for each soil to ensure reproducibility.

#### 4.2.5 Time-lapse polarisation resistance measurements

In addition to the potentiodynamic polarisation experiments, time-lapse measurements of the polarisation resistance,  $R_p$ , were also conducted. Polarisation resistance is a non-destructive measurement of a metal's ability to resist corrosion in a conductive environment. A low  $R_p$  indicates a (relatively) higher corrosion rate and vice versa. It is defined by Eq. 4.3, where  $\Delta E$  (V), is the change in potential from the corrosion potential ( $E_{corr}$ ), and  $\Delta i$  ( $\mu$ A/cm2) is the resulting change in corrosion current density:

$$R_{p} = \left(\frac{\Delta E}{\Delta i}\right)_{\Delta E \to 0} \tag{4.3}$$

The soils were initially fully saturated ( $S_r = 1$ ) and allowed to dry under standard laboratory conditions. The same electrochemical cell and electrode arrangements described in Section 4.2.2 were used. The electrochemical cell was placed on an electronic balance programmed to monitor its weight at 10-minute intervals. After an initial 30-minute resting period at OCP, the  $R_p$  was determined at 10-minute intervals. Based on the initial weight of the soil and the electrochemical cell, and the initial moisture content, the change in weight as measured by the electronic balance was converted to the change in the degree of saturation. Time-lapse  $R_p$  measurements were conducted using a commercially-available software suite [10], which utilises the polarisation resistance analysis method [11].

The equipment assembly used for time-lapse measurement is shown in Fig. 4.8.



Figure 4.8: Equipment assembly used for time-lapse polarisation resistance measurement

## 4.2.5 Active area measurements

The area on the working electrode which undergoes corrosion is known as the active area [12,13]. This area corresponds to the electrolyte contact area in the soil-metal interface. To ascertain the active area, the corroded electrode surfaces were digitally imaged after each polarisation test. Subsequently, the images were thresholded using Otsu's algorithm [14] and the active area, normalised to the total electrode area, was determined [15]. The relationship between the active area and the degree of saturation was established in this manner. Since the active area influences the corrosion current densities [12,13], it is considered in the numerical model equations presented in this section and in Chapter 8. Fig 4.9 shows the set-up used for active-area imaging.



Figure 4.9: Equipment assembly used for active-area measurements

The active area was determined for sand with good accuracy, but the colloidal nature of silt and clay and particle aggregation caused difficulties in conducting active area tests on silt and clay. The results obtained for silt and clay did not display a significant pattern, unlike the case of sand, and it is hypothesised that the difficulties in measuring the active area are due to the colloidal nature of these soil types. However, based on the active-area results obtained for sand, and the other tests for silt and clay, reasonable assumptions can be made regarding the active area of silt and clay. These observations and assumptions are discussed in Section 4.4.

# 4.3 Numerical modelling of optimum moisture content

A steady-state numerical model was developed to simulate the effects of varying degrees of saturation on the corrosion rate. The aim of this exercise was to compare the experimental results with the identified mechanisms and to reconcile the observations of the optimum soil moisture conditions for corrosion. The experimental results from the oxygen diffusivity and electrical conductivity tests were used as input functions to characterise the soil medium as an electrolyte which facilitates corrosion. A 1-D model was developed to scrutinise factors pertaining to the optimum moisture content for corrosion.

#### 4.3.1 Electrochemistry modelling

Assuming that the anodic and cathodic reactions are given by Eqs. 4.4 and 4.5,

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
 (4.4)

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
(4.5)

the following equations were used to define the anodic and cathodic current densities:

$$i_{Fe} = \frac{1}{1 + \exp(10 \times (0.4 - S_r))} i_{Fe}^0 \times 10^{\frac{\eta_{Fe}}{A_{Fe}}}$$
(4.6)

$$i_{O_2} = \frac{C_{O_2}}{C_{O_2}^{ref}} \times i_{O_2}^0 \times 10^{\frac{\eta_{O_2}}{A_{O_2}}}$$
(4.7)

where,  $S_r$  is the degree of saturation,  $i_{Fe}$  (A/m<sup>2</sup>) and  $i_{O_2}$  (A/m<sup>2</sup>) are the anodic and cathodic current densities respectively,  $i_{Fe}^0$  (A/m<sup>2</sup>) is the exchange current density for the anodic reaction,  $i_{O_2}^0$  (A/m<sup>2</sup>) is the exchange current density for the cathodic reaction,  $A_{Fe}$  (V) and  $A_{O_2}$  (V) are the anodic and cathodic Tafel slopes respectively,  $C_{O_2}$  (mol/m<sup>3</sup>) is the oxygen concentration in the soil electrolyte,  $C_{O_2}^{ref}$  (mol/m<sup>3</sup>) is the atmospheric reference oxygen concentration,  $\eta_{Fe}$  (V) is the anodic overpotential, and  $\eta_{O_2}$  (V) is the cathodic over-potential, which are given by Eqs. 4.8 and 4.9 respectively:

$$\eta_{Fe} = -\phi - E_{Fe}^{eq} \tag{4.8}$$

$$\eta_{O_{2}} = -\phi - E_{O_{2}}^{eq} \tag{4.9}$$

where,  $\phi(V)$  is the electrolyte potential.  $E_{O_2}^{eq}(V)$  and  $E_{Fe}^{eq}(V)$  are the equilibrium potentials of the cathodic and anodic reactions respectively. The anodic current density (Eq. 4.6) includes the active area concept [12,13] (Section 4.4.5.1), while the cathodic current density expression includes the concentration polarisation effect [16]. In this manner, both the anodic and cathodic reactions relate to the practical observations in underground corrosion.

The electrolyte potential ( $\phi$ ) in the soil electrolyte is governed by Eq. 4.10:

$$\nabla . \left( \sigma \nabla \phi \right) = 0 \tag{4.10}$$

where,  $\sigma$  (S/m) is the soil electrical conductivity. The current in the electrolyte,  $\dot{\mathbf{i}}_{l}$  (A/m<sup>2</sup>), is governed by Ohm's law (Eq. 4.11) and is related to the anodic and cathodic current densities, as shown in Eq. 4.12.

$$\mathbf{i}_l = -\sigma \nabla \phi \tag{4.11}$$

$$\mathbf{n.i}_l = i_{Fe} - i_{O2} \tag{4.12}$$

#### 4.3.2 Oxygen diffusion

The steady-state governing equation for the oxygen concentration is given by Eq. 4.13:

$$\nabla \cdot \left( D_e \nabla C_{O_2} \right) = 0 \tag{4.13}$$

where,  $D_e$  (m<sup>2</sup>/s) is the effective diffusion coefficient for oxygen and  $C_{o_2}$  is the oxygen concentration in the soil.  $D_e$  is input as a function obtained from the experimental results. A constant concentration boundary condition is imposed at the surface exposed to the atmosphere, and the oxygen diffusing to the corroding metal surface is assumed to be consumed by the cathodic reaction, as shown by Eq. 4.14:

$$i_{O_2} = -D_e \left( \mathbf{n} \cdot \nabla C_{O_2} \right) zF \tag{4.14}$$

where, z is the number of electrons involved in the reaction and F is the Faraday constant. The oxygen flux coupled with the cathodic corrosion current density together capture the diffusion limitation conditions in underground corrosion.

## 4.3.3 Geometry and boundary conditions

A 1-D model was developed to scrutinise the mechanisms giving rise to the optimum moisture conditions observed in experiments and a 3-D model was created to assess possible practical outcomes.

The initial 1-D model was created with the same model geometry as the experiments, *i.e.*, a constant oxygen concentration boundary condition and the corrosion current density equations imposed on either side of a 0.033 m interval. Oxygen diffusion was coupled to corrosion electrochemistry with the degree of saturation as the controlling variable. The electrical conductivity-saturation relationship was defined for sand using Eq. 4.15 and the oxygen diffusion coefficient-saturation relationship was defined using a curve fit to experimental data (see Chapter 6).

The 3-D model was created to simulate a length of pipeline buried in variably-saturated soil. A hypothetical situation of a homogeneous sand subsurface variably saturated in the range  $0 \le S_r \le 1$  (linearly in the x direction, as shown on the top surface) was simulated with a constant concentration boundary condition imposed on the top surface (z=0 plane). A ferrous pipe traversed this sand medium and the corrosion rate on the pipe surface was assessed. Note that in the present work the gravity effects on moisture distribution and the variations in S<sub>r</sub> with depth are not considered. Fig. 4.10 shows the model geometry and the boundary conditions imposed.



Figure 4.10: 3-D model geometry and boundary conditions

The pipeline is shaded in green and the varying degree of saturation is denoted by the blue gradient. Oxygen concentration is constant on the surface (z=0).

# 4.4 Results and discussion

## 4.4.1 Soil solution chemistry and conductivity properties

The major cations and anions present in the 1:5 soil solutions as identified by ICP-OES and IC are given in Table 4.2 Note that only the element of the major cation is identified by ICP-OES and the valance state of the cation is not identified. It is clear that overall sand has very low concentrations of cations and anions when compared with clay and silt. In particular, silt shows high levels of cations in comparison with the other two soils.

Soil type	Cl <sup>-</sup> (mg/L)	NO <sup>3-</sup>	SO <sup>4-</sup> (mg/L)	Fe	Al	Mn
		(mg/L)		(ppb)	(ppb)	(ppb)
Sand	4.2	15.7	0.8	11	40	1
Silt	1.9	51.8	16.36	173	291	812
Clay	37	17	160	16	49	6

Table 4.2: Chemical components present in 1:5 soil solutions

The pH values and conductivities determined using the water quality probe are given in Table 4.3. The table shows that the pH values decrease from sand silt to clay, with sand having a pH closest to neutral with silt and clay being progressively more acidic. The influence of pH on the rate of corrosion is not studied in detail in the present study. However, the mechanistic influence of pH on underground corrosion is discussed and implemented in the fully-coupled numerical models presented in Chapter 8.

Solution type	Sand 1:5	Silt 1:5	Clay 1:5	0.001M NaCl	Deionised water
рН	6.2	5.6	4.1	5	-
Conductivity (µS/cm)	6.4	218.6	447	122.1	4.7

Table 4.3: pH and electrical conductivity values of 1:5 soil solutions, 0.001M NaCl and de-ionised water

The soil solution conductivity values given in Table 4.3 show increasing conductivity from sand, silt to clay, and are consistent with the anion concentrations given in Table 4.2. Anions generally have higher ionic mobilities than metal cations [17]. Due to their high mobilities, anions such as chlorides and nitrates contribute to increasing solution conductivity. Note that the concentration of chlorides and nitrates in clay and silt are significantly higher than in sand. In clay, it is further noted that the chloride concentration is even higher (37 mg/L). Chlorides, due to their small ionic radius, have very

high mobility and therefore have a significant effect in increasing the conductivity of the solution [17]. In this manner, the variations in electrical conductivity between the three soil solutions can be explained by the ion concentration of the respective soil solutions.

The cation concentrations in solution are significantly higher in silt than in sand and clay. The high cation concentrations may be an indication of the presence of oxidisable species and therefore may be influential in the magnitudes of the corrosion rates, as discussed in Section 4.4.3.

The 0.001M NaCl solution showed a conductivity value of 122.1  $\mu$ S/cm, which is higher than the sand solution but lower than the solutions of silt and clay. This means that this NaCl solution used in preparing bulk soil for testing would significantly increase the conductivity of the bulk soil, thus improving the soil conditions for carrying out polarisation measurements, especially in sand. The addition of NaCl in soil preparation would change the bulk soil conductivity and this is discussed in the following section.

# 4.4.2 Electrical conductivity/resistivity of the bulk soil

The electrical conductivity/resistivity values for bulk soils at varying levels of saturation were measured using the technique described in Section 4.2.2.

The electrical conductivity of bulk soil can be expressed as the summation of the conductivity of the soil solution and the soil matrix conductivity, also known as surface conductivity [18,19]. Since soil solution conductivity depends on the moisture content or the degree of saturation of soil, and the potential pathways for ionic conduction, bulk soil conductivity can be viewed as a function of soil solution conductivity, the degree of saturation, the porosity and the surface conductivity of the soil. This relationship is illustrated in the Mulaem & Friedman equation [19] presented in Eq. 2.7 (Chapter 2).

While the surface conductivity values for the three soils are unavailable, the soil solution conductivity (0.001M NaCl) used for preparing the soils for electrochemical testing is known to be 122.1  $\mu$ S/cm. Table 4.3 shows that the soil solution in sand has a conductivity value very close to that of de-ionised water. Together with the results from Table 4.2, which show very low ion concentrations for the sand solution, it can be assumed that the surface conductivity of sand is close to zero. Therefore, using the measured soil porosity values and the NaCl solution conductivity, the experimentally-measured values can be compared against the predicted conductivity values from the Mualem & Friedman equation (values are in S/m). The bound water content was assumed to be zero.



Figure 4.11: Experimental conductivity values for sand and conductivities given by Mualem & Friedman equation for varying degree of saturation

Fig. 4.11 indicates that with the Mualem and Friedman equation it is possible to approximate the general trend of the experimental results, albeit with significant differences at higher saturations. The assumptions of zero surface conductivity and bound water content may be the reason for the difference between the equation and the experiments.

Given that the other three soils types have inherent conductivities before the addition of NaCl (Table 4.3), it can be expected that the bulk soil conductivities for silt and clay would be significantly higher than that of sand. The measured bulk conductivities for all three soils are given in Fig. 4.12.



Figure 4.12: Electrical conductivity against degree of saturation for sand silt and clay, showing significantly higher values for silt and clay compared with sand

Fig 4.12 shows the experimentally-determined electrical conductivity values with degree of saturation for sand, silt and clay. As expected, the conductivities for silt and clay are significantly higher than that of sand. Since insufficient information with regard to surface conductivity is available, a simple power law fit similar to Archie's law [20] was used to fit the experimental data. The conductivity-saturation relationship can now be explained by Eq. 4.15:

$$\sigma = a S_r^{\ b} \tag{4.15}$$

where,  $\sigma$  is the electrical conductivity (S/m),  $S_r$  is the degree of saturation and a and b are fitting coefficients.

In the case of electrical resistivity, which is the inverse of the conductivity and widely used for corrosion assessments in the field, the same equation can be used with coefficients 1/a and -b. The values for coefficients *a* and *b* are given in Table 4.4.

Parameter value	Sand	Silt	Clay
а	0.007386	0.0648	0.1456
b	2.247	1.132	1.753

Table 4.4: Fitting parameter values for power law relationship for conductivity/resistivity



Figs. 4.13 and 4.14 show the power law fit for electrical conductivity and resistivity, respectively.

Figure 4.13: Electrical conductivity for sand silt and clay with their respective curve fits



Figure 4.14: Electrical resistivity for sand silt and clay with their respective curve fits

The electrical conductivity-saturation relationships for the three soils given by Eq. 4.15 and depicted in Fig. 4.13 were used as inputs for defining the soil electrolyte in numerical modelling.

#### 4.4.3 Potentiodynamic polarisation test results and critical region for corrosion

The results from the potentiodynamic polarisation resistance measurements yielded the corrosion current density,  $i_{corr}$  (A/m<sup>2</sup>), and the corrosion potential,  $E_{corr}$  (V), with the degree of saturation, along with other parameters through the Tafel fitting process. The variations of  $i_{corr}$  and  $E_{corr}$  with the degree of saturation and the mechanisms giving rise to the observed trends are described in this section.

Typical polarisation curves for sand, silt, and clay are shown in Fig. 4.15. The data in Fig. 4.15 correspond to  $S_r \approx 0.5$ , 0.7, and 0.8 for sand, silt, and clay, respectively. The Tafel fitting process was conducted as indicated by the dashed lines to obtain the  $i_{corr}$  and  $E_{corr}$  values.



Figure 4.15: Typical polarisation curves for sand, silt and clay and schematic representation of Tafel fitting process

The  $i_{corr}$  for the three soils types at different levels of saturation are shown in Figs. 4.16-4.18. The  $i_{corr}$  values measured over the range of saturations including the repetition tests were grouped into  $S_r$  bins and the respective means and standard deviations of the grouped bins are presented in these figures.

The mean corrosion current density and the standard deviations indicating the variation in measured  $i_{corr}$  are given in Fig. 4.16:



Figure 4.16: Measured icorr values for sand, indicating means and standard deviations of measurements

Fig. 4.16 shows that the maximum  $i_{corr}$  of 4.5  $\mu$ A/cm<sup>2</sup> is achieved at  $S_r$ =0.5, while the variations in this region around the maximum are also the highest.

Fig. 4.17 shows the same results for silt:



Figure 4.17: Measured icorr values for silt, indicating means and standard deviations of measurements

Similar to the trend seen in sand, an optimum saturation at  $S_r=0.7$  is observed for silt, although with considerably larger  $i_{corr}$  of 100  $\mu$ A/cm<sup>2</sup>. The variations around the optimum also show proportionally larger values.

The results for clay are given in Fig. 4.18:



Figure 4.18: Measured icorr values for clay, indicating means and standard deviations of measurements

The highest  $i_{corr}$  of 38  $\mu$ A/cm<sup>2</sup> is observed at  $S_r$ =0.8. The magnitude of corrosion lies between sand and silt, while the degree of saturation at which the optimum takes place is the highest.

The reason for the large differences in magnitudes of corrosion rates may be the presence of various oxidisable species in the soil. This means that, in addition to the metal undergoing oxidation, these chemical species are also oxidised, liberating an electric current. This effect increases the measured corrosion rate. Table 4.2 indicates that silt contains a significantly higher amount of cations followed by clay and sand. The relatively large amount of Fe cations observed in the silt solution possibly indicates the presence of elemental iron in equilibrium with the solution. If this is the case, the iron in the soil will also oxidise in addition to the working electrode during polarisation, giving a higher measurement of  $i_{corr}$ . Similar comments are applicable to other cations such as Al and Mn. However, this cannot be verified with certainty with the present results, and additional testing is necessary.

Observation of the variations in measurements reveals that in all three soil types, the variations are significantly higher close to the optimum degree of saturation for each soil type. Therefore, critical regions of saturation where the variations and the overall mean corrosion rate are high can be

identified. These critical regions were demarcated by taking the mean of all the measurements and selecting the region of saturation at which the upper bound of the measurement (i.e mean plus standard deviation) is above the overall mean. The critical regions identified in this manner are given in Table 4.5.

	Sr	Mean i <sub>corr</sub> (μA/cm <sup>2</sup> )	Std. Dev. (μA/cm <sup>2</sup> )	Ecorr (mVAg/AgCl)	Std. Dev.
Critical region for	0.4	2.4	1.5	-352	35
sand	0.5	3.2	1.1	-423	74
	0.6	2.5	1.4	-462	78
Critical region for silt	0.44	18.1	13	-353	16
	0.51	25.3	17.2	-339	60
	0.62	57.2	21.8	-409	49
	0.72	82.4	20.8	-551	49
	0.82	68.7	33.9	-623	66
Critical region for clay	0.53	13.6	6	-459	87
	0.62	15.9	6.5	-444	51
	0.69	24.7	8.1	-485	106
	0.8	32.3	5.4	-638	8

Table 4.5: Critical regions for sand, silt and clay and mean and standard deviations of measured icorr and Ecorr

As identified in Table 4.5, the critical region for sand is  $0.4 \le S_r \le 0.6$ , that for silt  $0.4 \le S_r \le 0.8$ , and for clay  $0.5 \le S_r \le 0.8$ .

As noted from Figs. 4.16-4.18 and Table 4.5, the optimum saturation regimes for the three soil types yielding the highest corrosion rates differ. Following further experimentation, it was identified that the soil physical properties of aeration and moisture and the mechanisms involved resulted in this difference. The variations of the measured corrosion rates were also related to the oxygen diffusion process, which is controlled by the moisture retention properties of the soil medium. The oxygen diffusion process is a bulk soil property and variations in  $i_{corr}$  are influenced by the bulk soil properties just as much as the metal-soil interface properties.

These results demonstrate that, while the magnitudes of the corrosion rates in soil are controlled by the chemical composition and electrolytic properties of the soil, the degree of saturation at which the highest corrosion is achieved is a function of the soil's physical properties. The reason for the measurement variations is also explained by soil-related mechanisms. The soil experiments relating to moisture retention and oxygen diffusion and their influence on corrosion rates are discussed in Chapters 5 and 6. The results from this chapter and those of Chapters 5 and 6 are combined to discuss the mechanistic influence of soil in underground corrosion in Chapter 7.

The  $E_{corr}$  values with the degree of saturation for the three soils are presented in Fig. 4.19.



Figure 4.19: Ecorr vs saturation for all three soil types

Fig. 4.19 shows that, although some scatter is observed, unlike the  $i_{corr}$  variations, the  $E_{corr}$  – saturation relationship does not vary significantly between soil types. It appears that the same general trend of decreasing  $E_{corr}$  with increasing saturation occurs in all three soils. This means that the  $E_{corr}$  is not as sensitive to variations in oxygen diffusion and the continuity of the bulk transport processes, but is a function of the interfacial properties which depend on the moisture level at the surface of the metal. This is in contrast to  $i_{corr}$  where in addition to the interfacial properties, the bulk transport also plays a significant role.

# 4.4.4 Time-lapse polarisation resistance measurements

The results of the time-lapse polarisation resistance ( $R_p$ ) measurements for sand silt and clay are shown in Figs. 4.20-4.22. The results show the variation of  $R_p$  vs time and after an initial decrease to a minimum, the  $R_p$  continues to rise with increasing time.



Figure 4.20: R<sub>p</sub> vs. time from time-lapse polarisation measurement for sand



Figure 4.21: R<sub>p</sub> vs. time from time-lapse polarisation measurement for silt



Figure 4.22: R<sub>p</sub> vs. time from time-lapse polarisation measurement for clay

As Figs. 4.20 to 4.22 indicate, the magnitude of the polarisation resistance is the highest in sand, followed by clay and silt. Since the polarisation resistance is inversely proportional to the corrosion rate, this observation confirms the results of the potentiodynamic polarisation measurements.

The  $R_p$  vs. time results were converted to  $R_p$  vs. saturation using the weight loss data measured by the electronic balance and the initial weights of the soil and cell assembly. These results are given in Figs. 4.23 - 4.25.



Figure 4.23: R<sub>p</sub> vs. degree of saturation results for sand from time-lapse measurement


Figure 4.24: R<sub>p</sub> vs. degree of saturation results for silt from time-lapse measurement



Figure 4.25: R<sub>p</sub> vs. degree of saturation results for clay from time-lapse measurement

Figs 4.23-4.25 show that the minimum  $R_p$  is achieved at a degree of saturation of 0.5 for sand, 0.7 for silt, and 0.8 for clay, consistent with the polarisation measurements. Furthermore, the minimum  $R_p$  for the same three soils is ~5000  $\Omega$  cm<sup>2</sup>, 1500  $\Omega$  cm<sup>2</sup> and 900  $\Omega$  cm<sup>2</sup>, respectively. These values also indicate that the corrosion rates are the highest in silt, followed by clay and sand. The results from the time-lapse polarisation measurements are consistent with the polarisation measurements, showing three distinct degrees of saturation at which the corrosion rate is maximised in the three soil types.

#### 4.4.5 Numerical modelling results

#### 4.4.5.1 Active area

The active area of corrosion is an essential component required to model the anodic current density, as described in Section 4.3.1. Active area images for sand at varying degrees of saturation are presented in Fig. 4.26.



Figure 4.26: Active areas of corrosion obtained using digital imaging

The active area when plotted against the degree of saturation yields a sigmoidal shape, as shown in Fig. 4.26. A sigmoid curve fit was performed on the data obtained for sand, and the following equation was used to describe the active area-saturation relationship:

$$\frac{1}{1 + \exp(10 \times (0.4 - S_r))} \tag{4.16}$$

Equation 4.16 was used to modify the anodic corrosion current density in the numerical model as shown in Eq. 4.6. Previously (see Chapter 3), it was assumed that the active area-saturation relationship is linear. However, in the light of more experimental results, the above equation was found to better define this relationship. The sigmoidal shape of the active area is also supported by some studies of soil water distribution and the electrical properties of soil [21,22].



Figure 4.27: Active area variation with degree of saturation and sigmoidal curve fit

As evident in Figs. 4.26 and 4.27, in the region of saturation between 0.4 - 0.6, the variations in the active area are the largest. The coalescing of smaller areas into larger ones dominates in this region, leading to large variations. This observation is similar to the variations in *i*<sub>corr</sub> in the same saturation region for sand, and provides evidence for the possible behaviour of the active area-saturation relationship in other soil types. This is discussed further in Chapter 8.

#### 4.4.5.2 Modelling optimum soil moisture for corrosion

The equations presented in Section 4.3 were used to model the optimum moisture content for uniform corrosion in sand, with the boundary conditions described in Section 4.3.3.

Fig. 4.28 shows the  $i_{corr}$  (A/m<sup>2</sup>) values computed form the numerical model overlaid on the experimental results of  $i_{corr}$ . In the case of uniform corrosion simulated here, the increase in corrosion current density with soil water saturation is attributed to the effect of the active area [13], since the electrolyte contact on the metal surface increases with increasing moisture levels. The subsequent decrease in the current density after reaching the peak point is due to the restriction of oxygen diffusion to the metal surface brought about by the filling of the air pore space with water, making the air phase discontinuous [23]. As diffusion of oxygen through the water phase is several orders of magnitude smaller than in the air phase, the corrosion rate starts to decrease with insufficient oxygen at higher saturations. These two competing factors are modelled, giving rise to the characteristic shape of the curve and the optimum point.



Figure 4.28: Results from numerical model overlaid with experimental values for sand exhibiting optimum saturation for corrosion

While the model results show similarity with the experimental results, a notable difference in the peak point of the corrosion rates is noted. The experimental values show a clear peak at around  $S_r = 0.5$ , while the numerical model results attain the peak much later ( $S_r \approx 0.8$ ). A possible reason for this behaviour is that at relatively high saturations, water settles down at the bottom of the cell due to gravity, thereby increasing the degree of saturation close to the working electrode compared with the rest of the cell. This means that the oxygen deficiency occurs much earlier, leading to a decrease in corrosion rates at relatively lower overall saturations. Gravity drainage effects and soil suction-based water movement are not modelled in the present model; hence, these effects are not discussed in detail. The effects of soil suction and moisture re-distribution in the optimum moisture content in reporting optimum moisture content in soil are modelled in the fully-coupled numerical models presented in Chapter 8, and it will be shown that the model curves better simulate the experimental results.

#### 4.4.5.3 Soil depth effects and practical applications

A parametric sweep of the length of the 1-D mode was conducted to simulate the variations of burial depth of metallic infrastructure such as pipelines on corrosion behaviour. Figure 4.29 shows the results of the parametric sweep of the soil electrolyte length in the 1-D model.



Figure 4.29: Results of parametric sweep changing diffusion length (L) for sand. Variations in current density with diffusion length shows a shift in the optimum conditions.

The figure shows that both the maximum corrosion rate and the degree of saturation at the optimum point decrease with increasing depth. This result can be explained by the diffusion control in soil corrosion. Since one of the competing factors controlling the optimum point is oxygen diffusion, any factor which influences the process of diffusion in turn influences the rate of corrosion. This means that the burial depth of the corroding metal is an important factor that needs to be reported when dealing with the optimum moisture content. For the sand considered in this chapter, at a typical burial depth of 1 m the optimum corrosion occurs at around Sr = 0.6. The decrease in corrosion rate with increasing depth has been observed in practice and was reported in early studies by Tomashov [24]. However, to the author's knowledge, the dependency of the optimum moisture level on burial depth has not been reported previously.

Figure 4.30 shows the results of the 3-D model to assess a possible practical scenario. The corrosion current density on the pipe surface and the net current density in the soil electrolyte are depicted. For clarity, the variation of the degree of saturation imposed as a boundary condition is also depicted by the shaded blue gradient.



Figure 4.30 Corrosion current density on pipe surface and electrolytic current flowing through soil denoted by arrows. The Sr distribution is shown on the top surface (z=0 plane). Note that gravity drainage effects are not considered.

The maximum corrosion rate was observed at the location of the pipe corresponding to the optimum degree of saturation reported earlier. The electrolyte current shows that macro-cell currents are established due to the effects of differential aeration (variably saturated). The highly saturated area turned anodic with a net current leaving the pipe surface. These macro- cells can evolve into intensely localised corrosion through the spatial separation of anodes and cathodes. Soil electrical conductivity plays a significant role in macro-cell corrosion. However, this study does not consider factors that accentuate such effects, such as passivation and corrosion product deposition. These effects and their time-dependent influence on corrosion are discussed in Chapter 3 and published as a journal paper [15].

3-D simulation involving a hypothetical saturation distribution shows that the level of corrosion becomes a maximum corresponding to the optimum point, while also highlighting the development of macro-cells due to differential aeration. This means that even waterlogged areas need to be considered as high priority areas in corrosion assessment, due to the possibility of coupled macro-cell corrosion. The subsurface moisture levels in soil can be ascertained by several geophysical methods, such as electrical resistivity tomography and ground penetrating radar (GPR) [5,25] and their applications have been discussed previously [25]. GPR can also be used for the remote assessment of

corroded pipes [26], and can be used in conjunction with other assessment methods for testing the corrosivity of soil in field conditions.

The steady-state numerical models described in this chapter were shown to capture the phenomenological behaviour of the optimum soil moisture for underground corrosion with reasonable accuracy. However, moisture migration in soil was identified as a key mechanism which may further improve the model's performance. These effects are addressed by the development of fully-coupled numerical models which are presented in Chapter 8. The models were also used to simulate the effect of soil depth on corrosion, and to highlight a possible practical consequence of corrosion in a pipeline buried in variably saturated conditions. It was shown that such conditions may lead to macro-cell formation and this result is consistent with the results of the time-dependent simulations presented in Chapter 3.

## 4.5 Conclusions

Electrochemical tests were conducted on the three soil types: sand, silt and clay investigated in this project. Potentiodynamic polarisation tests were conducted at various degrees of saturation to assess corrosion rate variations with saturation in the three diverse soil types. Time-lapse measurements of polarisation resistance were obtained in soil which was drying under laboratory conditions, starting from the fully-saturated state. A new electrochemical design to minimise soil resistance effects was used for these tests. The electrical conductivity of bulk soil was measured separately at varying levels of saturation for the soils and chemical tests were conducted on extracted soil solutions.

Both the polarisation experiments and time-lapse polarisation resistance measurements indicated that the corrosion rate achieved its maximum level at a distinct degree of saturation ( $S_r$ ) for sand, silt and clay. These degrees of saturation were identified as  $S_r=0.5$  for sand,  $S_r=0.7$  for silt, and  $S_r=0.8$  for clay. The magnitudes of the corrosion rates also varied significantly between the three soil types. Silt showed the highest levels of corrosion ~110 µA/cm<sup>2</sup>, followed by clay with a maximum rate of 38 µA/cm<sup>2</sup> and sand with the lowest rate of 4.5 µA/cm<sup>2</sup>. It was also observed that variations in the measurements were the highest in the region of saturation close to the optimum. The presence of oxidisable species in soil, as identified by chemical analyses, was identified as a possible reason for the variation in magnitude of the corrosion rate. It was identified that while the magnitude of the corrosion rate at the optimum depends on soil chemistry, the degree of saturation at which the optimum is achieved depends on the soil's physical properties. The variations in  $E_{corr}$  were observed to be due to interfacial mechanisms, while  $i_{corr}$  was influenced by bulk soil properties such as oxygen diffusion in addition to interfacial mechanics. The soil properties that govern these behaviours are discussed in detail in subsequent chapters on soil moisture retention and oxygen diffusion.

The active area of corrosion was determined through digital imaging and the results were used as input for numerical modelling along with electrical conductivity and oxygen diffusion results. The numerical models which coupled oxygen diffusion to corrosion electrochemistry were able to simulate the behaviour of the optimum moisture content with reasonable accuracy, albeit with some key differences. Areas to improve the mechanistic modelling efforts were identified and these will be addressed in Chapter 8. The numerical models were also used to illustrate the effect of soil depth on corrosion behaviour along with some preliminary practical considerations that may be useful for corrosion rate assessment in the field.

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# Chapter 5: Investigation of the aeration and moisture retention characteristics of soil

# **5.1 Introduction**

Unsaturated soil is a three-phase system and the proportions of the air and water phases affect the properties of the soil. The soil structure and pore spaces determine the total amount of air or water the soil can hold, while the mineralogy determines the physico-chemical interactions with the water. The relative amounts of air and water also determine the level of aeration and the transportation of various chemical species through soil. This chapter introduces concepts relating to aeration and moisture in soil and presents the results of several experimental approaches used to investigate aeration and moisture regimes in the three diverse soils tested. The findings and mechanisms revealed are then related to previous findings on corrosion in soils.

#### 5.1.1 Basic weight-volume relationships

As the proportions of air and water affect the properties of soil, definitions for quantifying these proportions are important to characterise the soil medium. These relationships are most often given in terms of the weight and volume of the phases and are hence named the weight- volume relationships. A phase diagram for soil is shown in Fig 5.1, where  $V(m^3)$  denotes volume and W(kg) denotes weight. The subscripts *a*, *w s* and *v* denote air water solids and voids, respectively.



Figure 5.59: Phase diagram for soil

The gravimetric moisture content (*w*), the volumetric moisture content ( $\theta$ ), and the degree of saturation (*S<sub>r</sub>*) are parameters which are commonly used to quantify soil water and are given in Eqs. 5.1-5.3:

$$w = \frac{W_w}{W_s} \tag{5.1}$$

$$\theta = \frac{Vw}{V} \tag{5.2}$$

$$S_r = \frac{Vw}{Vv} \tag{5.3}$$

Of these relationships, the degree of saturation ( $S_r$ ) is most appropriate for this study, since it provides information regarding the relative proportions of water to air present in soil voids, and most transport phenomena related to corrosion depend on the relative fractions of water and air occupying soil voids. The void ratio (e) and porosity (n) are relationships which are used to quantify the proportion of voids to soil solids:

$$e = \frac{V_{\nu}}{V_s} \tag{5.4}$$

$$n = \frac{V_v}{V} = \frac{e}{1+e} \tag{5.5}$$

The density of soil (kg/m<sup>3</sup>) can be expressed in terms of bulk density ( $\gamma_b$ ), which is the density of wet soil, or the dry density ( $\gamma_d$ ), which considers only the weight of dry solids:

$$\gamma_b = \frac{W_s + W_w}{V} \tag{5.6}$$

$$\gamma_d = \frac{W_s}{V} \tag{5.7}$$

In addition to the above basic definitions, the following derived relationships were used for calculations in the experimental work in this project.

$$\gamma_d = \frac{\gamma_b}{1+w} \tag{5.8}$$

$$e = \frac{G_s \gamma_w}{\gamma_d} - 1 \tag{5.9}$$

$$S_r = \frac{G_s w}{e} \tag{5.10}$$

where,  $\gamma_w$  is the density of water and  $G_s$  is the specific gravity of soil solids.

#### 5.1.2 Soil mineralogy classification and structure

Soil consists of a mixture of crystalline minerals of various sizes, non-crystalline clay material organic matter and salts [1]. Depending on the size of the solid particles, soil can be classified into either sand, silt or clay. Soil particles smaller than 2  $\mu$ m are said to be in the clay size range. In addition, the term clay is used also to refer to the mineral type, which has a net negative electrical charge and exhibits plasticity when mixed with water [1]. According to the ASTM system [2], soils with particles less than 2  $\mu$ m are termed clays, soils with a particle size range between 2  $\mu$ m to 75  $\mu$ m are termed silts, and soils with solid particles between 75  $\mu$ m and 4.75 mm in size are called sands. Particle sizes larger than 4.75 mm belong to the class of gravel which are generally not classified as soils. Due to their plasticity, clay soils show different properties to sands and silts.

#### 5.1.3 Particle- size distribution

The particle-size distribution curve or the grain-size distribution is the curve plotted between the particle size or mesh size of a sieve and the percentage of particles passing through that sieve. This relationship is usually presented on a semi-log graph and is widely used for engineering purposes. The shape of the particle size distribution and the range it covers on the particle size scale provides information about the soil type. The particle size distribution curves for sand silt and clay used in this study are given Fig. 5.2:



Figure 5.2: Particle-size distribution curves for soils used in this study

The particle size distribution in a soil can also be expressed as a density function, where the soil particle size is plotted against the frequency of the respective particle sizes. The particle- size density

functions (normalised) together with the particle size distribution curves for sand silt and clay used in this work are shown in Figs 5.3-5.5.



Figure 5.3: Particle-size distribution and density curves for sand showing that peak particle size corresponds to inflection point of particle- size distribution curve



Figure 5.4: Particle size distribution and density curves for silt showing that peak particle size corresponds to inflection point of particle-size distribution curve



Figure 5.5: Particle-size distribution and density curves for clay showing that peak particle size corresponds to inflection point of particle- size distribution curve

Since the particle size distribution is a cumulative curve obtained by integrating the particle density curve, the particle density curve can be obtained by differentiating the particle size distribution. Figs 5.3-5.5 show that the peak particle sizes in these soils correspond to the inflection point in the particle size distribution when plotted in the log scale. Since the particle volume in soil plus the voids in soil add up to the total volume of soil, it can be expected that the particle size distribution and the void distribution have a complementary relationship [3]. Further, the void distribution of soil is directly related to the water retention curve [4], and has the same general shape when plotted in the semi-log scale.

#### 5.1.4 Soil structure and void distribution

The void spaces in soil and their distribution govern the structure of the soil skeleton and influence the distribution and movement of air and water in soil. As the total soil volume is made up of soil particles plus the voids, the void distribution in soil can be expected to be similar to that of the particle distribution. However, this assumption neglects the effects of soil aggregation on void distribution. Similar to the particle density curves depicted in Figs. 5.3-5.5, the void/pore size distribution can be schematically illustrated, as shown in Fig. 5.6. While some soils may show a bimodal or multimodal distribution of pore sizes with distinct peaks [5], other soils show a unimodal distribution, as depicted in Fig. 5.6. In such cases the demarcation between the structural pores and the textural pores, also termed inter-aggregate and intra-aggregate pores, can be approximated by the modal pore diameter of the distribution [6,7] as indicated in Fig. 5.6.



Figure 5.6: Schematic depiction of void distribution in soil

The pore size distribution in soil depends on the texture of the soil, including its particle size and the nature of interactions between particles. The pore size distribution in soil can be obtained by several methods. As stated in Section 5.2.1, the shape of the particle distribution curve can be taken as indicative of the pore size distribution, based on the assumption that the pore sizes and particle sizes are similarly distributed. Alternatively, the water retention curve can be used to approximate the particle size distribution curve. The pore sizes which drain under a given level of suction can be approximated by the capillary rise equation which relates the radius of the water meniscus formed in a pore to the surface tension of the pore fluid. Therefore, the quantity  $\frac{dS_r}{d\log\psi}$  when expressed in a log scale with equivalent diameter  $d_e$  gives the pore size distribution, as indicated in Fig. 5.6. This method of obtaining the pore size distribution is performed and discussed in Section 5.4.4.

The pore size distribution scan also be experimentally determined. Mercury intrusion porosimetry (MIP) and micro-imaging are the most popular techniques. Micro X-ray computed tomography (Micro X-ray CT) is an emerging technique which can be used to obtain images with resolutions in the order of several microns and can be used for pore size analysis in sands and silts. As detailed in Section 5.3.3, X-ray CT scanning of silt and subsequent pore size analysis was performed, while the generation of pore size distribution based on the experimental water retention curves was conducted for all three soil types tested in this project.

### 5.2 Soil water retention curve

The soil water retention curve is the relationship between the soil suction and the degree of saturation or the moisture content. Soil suction represents the energy state of the soil water and is usually given in units of kilo Pascal (kPa). Soil suction is generally expressed as a pressure deficit between the air and water interface  $(u_a - u_w)$ . As discussed in Section 5.1.4, the soil water retention curve depends largely on the pore size distribution and the pore connectivity of soil. A typical soil water retention curve is schematised in Fig 5.6:



Figure 5.65: Schematic diagram of typical soil water retention curve

Three characteristic points are identified in a water retention curve: the air entry point, the inflection point and the residual point. The air entry point is defined as the value of suction at which air just starts to enter the soil under drying conditions. In the case of wetting, this point is called the air expulsion point. The residual point is the point after which further increase in suction has very little effect on the moisture level of the soil. The inflection point in the transition region between the above points is an important point with physical significance [8]. It is the state of soil at which air has completely entered the soil in drying or when water has completely entered in wetting, or in other words, the complete air entry or the complete water entry points [9]. Therefore, this is the state at which both the air phase and water phase are continuous and are in transition to either side of the point. This transition point is termed the air transition point (ATP) and is denoted by the inflection point on the water retention curve. The inflection point is identified on the water retention curve as the point at which the gradient changes from an increasing value to a decreasing value, or where the rate of change of the gradient is zero ( $d^2S_r/d \log \psi^2 = 0$ ). The ATP also corresponds to the peak of

the pore size distribution curve [4] and therefore can be considered as a property of the soil's physical structure. Due to the transition in water/air phase continuity, the inflection point has implications for water and air movement in soil and the related processes in corrosion.

#### 5.2.1 Models of water retention curves

Several models and equations have been proposed to describe water retention curves. Of these models, the van Genuchten [10] and Fredlund & Xing [4] equations, which are two of the most widely-used models, are reviewed here. Of the characteristic points in the water retention curve, the inflection point is of considerable importance in this work. Therefore, the determination of the inflection point using the above equations is described here.

#### 5.2.1.1 Van Genuchten equation

The van Genuchten (1980) equation for water retention curves [10] is given in Eq. 5.11:

$$S_r = \frac{1}{\left(1 + \left(\frac{\psi}{a}\right)^n\right)^m} \tag{5.11}$$

where,  $\psi$  is the suction in kPa,  $S_r$  is the degree of saturation and *a m* and *n* are fitting parameters. The value of *a* is chosen such that it has a value of suction in units of kPa. As the water retention curves are presented and the characteristic points are determined in a semi-log scale, differentiation is performed with respect to  $\log \psi$ :

$$\frac{dS_r}{d\log\psi} = \frac{dS_r}{d\psi} \times \psi \times \ln 10 = -\left(mn\left(\frac{\psi}{a}\right)^n \left(\left(\frac{\psi}{a}\right)^n + 1\right)^{-m-1}\right) \ln 10$$
(5.12)

At the inflection point, the second derivative is equal to zero. Therefore:

$$\frac{d^2 S_r}{d \log \psi^2} = \left(mn^2 \left(\frac{\psi}{a}\right)^n \left(\left(\frac{\psi}{a}\right)^n + 1\right)^{-m-2} \left(m \left(\frac{\psi}{a}\right)^n - 1\right)\right) (\ln 10)^2 = 0$$
(5.13)

Hence, the suction value at the inflection point is given by Eq. 5.14:

$$\psi_i = am^{-\frac{1}{n}} \tag{5.14}$$

#### 5.2.1.2 Fredlund & Xing equation

The Fredlund & Xing (1994) [4] equation for water retention is given by :

$$S_{r} = \left(\frac{1}{\left(\ln\left(e + \left(\frac{\psi}{a}\right)^{n}\right)\right)^{m}}\right) \cdot \left(1 - \frac{\ln\left(1 + \frac{\psi}{h}\right)}{\ln\left(1 + \frac{10^{6}}{h}\right)}\right)$$
(5.15)

where, *a m n* and *h* are fitting parameters.

Differentiating the equation yields:

$$\frac{dS_r}{d\log\psi} = \ln^{-m}\left(\left(\frac{\psi}{a}\right)^n + e\right) \left(-\frac{mn\left(\frac{\psi}{a}\right)^n \left(1 - \frac{\ln\left(\frac{h+\psi}{h}\right)}{\ln\left(\frac{h+1000000}{h}\right)}\right)}{\psi\left(\left(\frac{\psi}{a}\right)^n + e\right)\ln\left(\left(\frac{\psi}{a}\right)^n + e\right)} - \frac{1}{(h+\psi)\ln\left(\frac{h+1000000}{h}\right)}\right)\psi\ln 10 \quad (5.16)$$

Therefore, at the inflection point:

$$\frac{d}{d\log\psi}\left(\ln^{-m}\left(\left(\frac{\psi}{a}\right)^{n}+e\right)\left(-\frac{\ln\left(\frac{h+\psi}{h}\right)}{\ln\left(\frac{h+1000000}{h}\right)}-\frac{1}{\left(h+\psi\right)\ln\left(\frac{h+1000000}{h}\right)}-\frac{1}{\left(h+\psi\right)\ln\left(\frac{h+1000000}{h}\right)}\right)\psi\ln(10)=0$$
(5.17)

As differentiation leads to a complex expression that cannot be solved in closed form, an approximation for the inflection point is made in the case of the Fredlund & Xing equation. The parameter a has been identified as an approximate value for the inflection point by Fredlund & Xing

(1994) [4]. The value of a has also been used directly for the inflection point in some analyses [11,12]. Although a full characterisation of the inflection point in terms of the parameters a, m, n, and h is warranted, in the present study, the a parameter is used as the inflection point to analyse the properties of the soils tested in the experimental program.

#### 5.2.2 Trends in soil textural properties observable from water retention curves

Substitution of the suction value at the inflection point in the van Genuchten equation (Eq. 5.14) in Eq. 5.11 gives the degree of saturation at the inflection point ( $S_{ri}$ ):

$$S_{ri} = \frac{1}{\left(1 + \left(\frac{1}{m}\right)\right)^m} \tag{5.18}$$

Note that the degree of saturation at the inflection point depends only on the m parameter.

The variation of degree of saturation at inflection  $(S_{ri})$  with the *m* parameter is given below:



Figure 5.8: Plot of m parameter in van Genuchten equation vs. degree of saturation at inflection point as related by Eq. 5.18

Fig. 5.8 shows that with the increasing value of m, the degree of saturation at the inflection point decreases and eventually approaches a value close to 0.4.

Table 5.1 provides the estimated values of *m*,  $\alpha$  ( $\alpha = 1/a$ ) and air entry values (assuming *m*=1-1/*n*) for 75 soil samples of different textural classes obtained from the UNSODA database [13], as reported by Ghanbarian-Alavijeh et al [14].

Soil texture	Number of	Ι	И	$\alpha = 1/a$		
	samples	Max	Min	Max	Min	
Sand	6	0.85	0.47	1.28	0.2	
Loamy sand	8	0.68	0.16	1.3	0.3	
Sandy loam	6	0.73	0.11	5.61	0.09	
Sandy clay loam	5	0.39	0.07	1.6	0.2	
Sandy clay	3	0.26	0.11	0.24	0.01	
Loam	8	0.34	0.34 0.08		0.09	
Silt loam	7	0.29	0.09	1.47	0.13	
Silty clay loam	10	0.48	0.09	1.51	0.01	
Clay loam	5	0.26	0.05	2.46	0.21	
Silt	1	0.25	-	0.1	-	
Silty clay	8	0.5	0.05	16.3	0.04	
Clay	8	0.13	0.02	50.3	0.01	

Table 5.1: Estimated van Genuchten parameters reported by Ghanbarian-Alvijeh et al. [7]

As Table 5.1 indicates, the *m* values tend to decrease when moving from sands to clays along the textual spectrum of soils. When the corresponding *m* values are checked against Fig. 5.7, as a general observation, the degree of saturation at the inflection point ( $S_{ri}$ ) for sands is around  $S_{ri} \approx 0.5$ , whereas for clays,  $S_{ri} \approx 0.8$ , with silty soils having a value between these, at around  $S_{ri} \approx 0.7$ .

This same observation can be made using a different model for the water retention curve. In an analysis performed on the performance of the tangential model for the water retention curve (TANMOD), by Thuyet et al. [15], 399 soils from the UNSODA [13] database were used to estimate model parameters. The tangential model requires nine parameters to describe the water retention curve. These parameters are the coordinates ( $\psi$ ,  $S_r$ ) of the air entry point, the inflection point, and the residual point and their corresponding tangential slopes. As one of the parameters of this water retention model is the degree of saturation at the inflection point ( $S_{ri}$ ), the authors plotted the estimated values for  $S_{ri}$  for each of the soil texture classes examined. Fig. 5.9, redrawn from Thuyet et al. [15], presents this information:



Figure 5.9: Degree of saturation at inflection point of water retention curve (re-drawn from Thuyet et al. [8])

Fig. 5.9 reveals that the degree of saturation at the inflection point increases for soil textures changing from sand to clay, consistent with the previous observation.

The parameters in the Fredlund & Xing (1994) equation can also be used to infer the variations of soil structural properties. The same exercise performed above can be repeated with mean Fredlund & Xing (1994) equation parameter values across the general soil types to obtain trends in the degree of saturation at the inflection point. This exercise also indicates the validity of assuming the *a* parameter to be the suction value at the inflection point in the water retention curve.

To verify the suitability of parameter *a* as the inflection point with respect to the above observations, mean fitting parameters for the Fredlund & Xing (1994) [4] equation reported by Sillers & Fredlund (2001) [16] were used to find the saturation at the inflection point. This was done by assuming the inflection point to be the "*a*" parameter i.e.:  $\psi_i = a$  (kPa). Table 5.2 shows the mean values of the fitting parameters given by Sillers & Fredlund (2001) and the calculated degree of saturation at the inflection point.

Soil type	Number of	Mean val	$S_r$ at inflection			
	samples	Α	n	m	h	point
Clay	12	506.3	9.27	0.626	3000	0.82
Clay loam	24	172.6	2.418	0.492	3000	0.87
Loam	18	20.3	2.365	0.562	3000	0.86
Loamy sand	12	6.684	3.398	0.874	3000	0.79
Sand	50	17.27	6.537	4.428	3000	0.30
Silt	25	188.4	4.286	0.949	3000	0.76
Silty loam	23	63.14	2.188	0.665	3000	0.83
Sandy loam	36	16.37	5.53	2.608	3000	0.49

Table 5.2: Mean fitting parameters for Fredlund & Xing (1994) equation and corresponding degree of saturation at inflection point computed assuming  $S_{ri} = a$ 

The calculated saturation values show that for sand the degree of saturation at the inflection point in general is around  $S_{ri} \approx 0.5$ ,  $S_{ri} \approx 0.8$  for clay and  $S_{ri} \approx 0.7$  for silt. This observation is consistent with that in the case of the van Genuchten equation and the tangential model (TANMOD) for the water retention curve. In general, it can be concluded that the degree of saturation at the inflection point depends on the textural properties of the soil, with clayey soils showing inflection at higher saturation than silts or sands. The reason for this observation, where the degree of saturation at the inflection point of the water retention curve increases across the soil textural classes moving from sands to clays, is the colloidal properties of soil.

Soil colloids are defined as clay particles less than 1 micron in diameter [17]. This clay fraction has a very large specific surface area and a net negative charge. The resultant effect is that water is tightly bound to the surface and is relatively immobile compared to the capillary water. The amount of water held by the colloids in a soil increases with increasing fines or clay content, and therefore, the effective saturation at which capillary water is available (held in structural pores) is much higher in clay soils. The bound water content (held in textural pores) in such soils is considerably higher. This means that the inflection point, which marks the transition of drainage from structural pores to textural pores, occurs at much higher saturation in soils with a significant clay fraction.

# 5.3 Experimental methods

# 5.3.1 Soil water retention curves

Experiments were conducted to develop the water retention curve for the three diverse soils types (sand, silt and clay) examined in this thesis.

Soil moisture retention curves were developed for quartz sand and kaolin clay. The low-range suction profile was measured using the HYPROP test equipment, while the higher suction measurements were conducted using the WP4C dew-point potentiometer. The suction range measured using the HYPROP (0 to 150 kPa) was adequate to generate the entire range of the water retention curve for sand, while the WP4C set-up was used for the higher suction ranges (>150kPa) required for silt and clay.



Figure 5.10: Left: HYPROP test assembly Right: WP4C equipment

The HYPROP apparatus consists of two tensiometers positioned at different heights and measures the soil suction at consecutive time steps (10-minute intervals) under laboratory drying conditions [18]. The two tensiometers were saturated with de-gassed water under a vacuum prior to the test. Quartz sand was compacted to the required dry density and left to saturate in the sample holder for a period of 24 hours. The sample and the tensiometer were placed in the base, and the test was initiated. The test was stopped once the tensiometers cavitated. The suction readings and the calculated moisture content readings were used to generate the water retention curve for the quartz sand. For silt, the sample was compacted and saturated in a water bath for 24 hours. The test was conducted similar to that for sand until the HYPROP tensiometers cavitated. Samples of silt were progressively dried to different moisture content tests were conducted at each stage. For clay, a consolidated sample (100 kPa) was used. After preparing the tensiometers, the set-up was assembled, and the test was conducted upto the point of cavitation. Suction measurements beyond the measurable region of

HYPROP were made using the WP4C test set-up, similar to that of the silt sample. The test results from the HYPROP set-up and WP4C were combined to generate the full water retention curve for the kaolin clay.

#### 5.3.2 Soil compaction

Standard Proctor compaction tests were conducted to obtain the optimum moisture for compaction (OMC) and the maximum dry density for the three soils tested. It has been reported that, at the OMC, the air phase becomes discontinuous due to entrapment [19,20], leading to a build-up of pore air pressure [19,21]. This mechanism has been used in the theoretical modelling of the compaction curve [21]. As it was shown previously that air entrapment happens at the inflection point of the water retention curve, the objective of these tests was to identify the degree of saturation at the OMC and to relate it to the degree of saturation at the inflection point.

The method outlined in the Australian Standards for standard compaction [22] were used to determine the compaction curves for sand and silt. Previously published [23,24] compaction curves were used for the kaolin (Eckalite) clay. After each stage of compaction with different moisture contents, the gravimetric moisture content was determined. The degree of saturation was also determined using the volume of the compaction mould. The saturation curves were determined using weight-volume relationships to identify the levels of saturation at the OMC.

#### 5.3.3 Micro X-Ray CT imaging of compacted silt

A high-resolution 3D X-ray microscope (Zeiss Xradia XRM520 Versa) was used for imaging compacted silt specimens. It is possible to perform X-ray computed tomography scans of 0.7 microns using this instrument. However, the resolution drops with increasing scanned specimen size, and a resolution of 3.38 microns was used for the work described here. This resolution was the optimal setting to accommodate a reasonably small compacted specimen representative of the bulk medium. The purpose of these scans was to identify the pore structure of the soils and to establish the changes to the pore size distribution during compaction.

#### 5.3.3.1 Sample preparation

Compacted silt specimens were imaged at each stage of the Proctor compaction process. Small cubic samples of silt were carefully extracted from the centre of the compacted mass after carefully

removing it from the compaction mould. Care was taken not to disturb the compacted soil fabric. These samples were weighed for moisture content and left to air-dry for 72 hours. Silt was chosen for this purpose as it is known to retain its structure after drying with negligible change in volume. It was assumed that no physical changes to the fabric occurred during the process of air drying. While the accuracy of this assumption cannot be guaranteed, for the purposes of the present study, since only the relative pore structures were considered and since all samples were subjected to the same conditions, the assumption is reasonable. After air drying and ensuring that the weights of the samples did not change further, small roughly cylindrical specimens were carefully chiselled from the dried cubic samples of silt. These specimens were carefully inserted into clear plastic tubes 5 mm in diameter (internal) and 200 mm high and the specimens were secured by capping the ends of the tubes paper plugs. The soil samples secured in this manner were imaged using the Zeiss Xradia instrument with a resolution of  $3.38 \,\mu$ m. The acquired images were visualised using Drishti and detailed analysis was performed using Avizo.

#### 5.3.3.2 Image analysis

The image processing was performed on the Avizo software package (Thermo Fisher Scientific 2018). After importing the raw image into Avizo, a region of interest (ROI) ~ 1.8 mm × 1.8 mm × 2 mm in size was selected as representative of the entire sample across all the scanned specimens. The ROI was filtered to remove noise using the non-local means algorithm, and segmented using Otsu's [25] method of segmentation. The segmented binary image was refined to remove isolated small spots and holes using Avizo's built in modules. The segmented image was separated using the watershed algorithm implemented in Avizo's separate objects module. Due to the creation of non-pore objects during the separation process, the removal of small spots and holes was repeated with a smaller cutoff value (5 pixels). Once the image was rectified in this manner, a volume calculation was performed, and the porosity of the ROI region of the scanned soil was determined. The calculated porosity values were compared against the experimental porosities obtained from the standard compaction test. In most cases a good match was obtained between the porosities of the image and the experiments. However, some samples with higher initial moisture contents showed a difference, and the images were therefore re-thresholded to match the experimental porosities. This was performed by repeating the process after the thresholding step mentioned above until the volume calculation yielded the required porosity. The attributes of the separated objects were extracted and the pore volume distribution functions were generated using a spreadsheet program.



Figure 5.11: Rendered volume of region of interest (ROI) in micro--Xray CT scan of silt specimen. Dark regions indicate pore spaces, and textural pores (micro) and structural (macro) pores are clearly visible.

Fig. 5.11 shows the 3-D volume constructed from the filtered ROI of the scanned image for the silt with an initial moisture content of 0.2. The compacted sample was wet of optimum and had a degree of saturation of  $S_r$ =0.9. Similar ROIs for the other samples were also created and the subsequent analyses were performed as described above.

# 5.4 Results and discussion

The results of the experiments relating to the aeration and moisture distribution of soil are discussed in this section. The observations made from the various experiments are reconciled and related mechanisms which contribute to corrosion in soils are presented.

#### 5.4.1 Water retention curves

The water retention curves generated for sand silt and clay are given in Figs. 5.12-5.14. The Fredlund & Xing (1994) and van Genuchten (1980) equations described previously were fitted to the experimental data and are depicted in solid lines. The Fredlund & Xing equation showed an overall better fit, especially for the experimental values for silt and clay. The range of soils suction values ranged significantly between soil types, with sand showing most of its moisture variations between 0-30 kPa, while silt and clay showed suction values up to 200000 kPa.



Figure 5.12: Experimental values of soil suction vs Sr with Fredlund and Xing (1994) and van Genuchten (1980) water retention curve fits for sand



Figure 5.13: Experimental values of soil suction vs Sr with Fredlund and Xing (1994) and van Genuchten (1980) water retention curves fits for silt



Figure 5.14 Experimental values of soil suction vs S<sub>r</sub> with Fredlund & Xing (1994) and van Genuchten (1980) water retention curves fits for clay

Table 5.3 provides the fitting parameters used for the two water retention equations used to fit the experimental data. In both cases, that the inflection point of the water retention curve is around 4 kPa for sand, 40 kPa for silt and 100 kPa for clay, and the corresponding degrees of saturation are,  $S_{ri}$  =

0.5 for sand,  $S_{ri} = 0.7$  for silt and  $S_{ri} = 0.8$  for clay. These values are consistent with the values obtained from the research literature for soils of similar textures, as shown in Tables 5.1 and 5.2.

Fitting parameters	Fredlund & Xing (1994)				V	van Genuchten (1980)				
	<i>a=(ψ<sub>i</sub>)</i>	т	n	hr	Sri	a	т	n	Ψi	Sri
Sand	3.9	1.4	11.8	4	0.6	3.7	0.5	11.3	4	0.5
Silt	41	0.2	15	2.2	0.72	12.9	0.2	1.5	38	0.7
Clay	100.2	0.76	0.85	396.1	0.79	30	0.1	2.5	75.4	0.79

Table 5.3: Fitting parameters used for water retention curves and inflection point  $\psi_i$  and degree of saturation at inflection point  $S_{ri}$  from both fitting methods

As stated in Section 5.2 and the subsequent discussion, the inflection point of the water retention curve has significance in terms of aeration and moisture distribution and can be considered a physical property of soil. This significance of the inflection point in light of the experimental results is discussed in the following sections.

#### 5.4.2 Inflection point and soil air/water continuity

The inflection point on the water retention curve is the point at which the gradient of the curve changes from an increasing value to a decreasing value. As discussed previously and reported in the experimental results, the inflection point can be determined from the equations used to describe the water retention curve. The values in Table 5.3 indicate that the inflection point and the degree of saturation of the inflection point vary significantly among the three soil types tested. A closer examination of the inflection point will provide a better understanding of these observations.

Since the gradient of the water retention curve represents the rate at which water is drained, and the drainage rate depends on the continuity of the water flow channels in soil, the inflection point can be viewed as the point at which the continuity of the water phase changes. Being complementary, the water and air phases occupy the pore space and the following could be said regarding the inflection point of the WRC:

- During drying, the water phase becomes discontinuous and the air phase becomes continuous at the inflection point in the WRC.
- During wetting, the water phase becomes continuous and the air phase becomes discontinuous at the inflection point.

The above statements are supported by the work by Dexter 2004a, b, c [6,8,26] and Reynolds et al. 2009 [7]. Dexter proposed a parameter known as the S index, which is the slope of the water retention curve at the inflection point. The S index has been shown to relate to important soil properties such as hydraulic conductivity, compaction and tillage. These soil properties are dependent on the pore volume and the drainage characteristics of soil, while the slope of the water retention curve also depends on the pore network characteristics, as the slope of the retention curve denotes the rate of drying or wetting of the soil. The inflection point is important in this context because it represents the point at which the slope or the gradient of the curve changes from an increasing value to a decreasing value. i.e., the rate of change of the gradient becomes zero. This indicates a change in the drainage process. The physical reason for this phenomenon, as explained by Dexter [6,8,26] and later expanded upon by Reynolds et al. [7], is the presence of two types of pores in soil. These pores are named structural pores and textural pores. The structural pores are relatively larger pore spaces which are more likely to form inter-connected 3-D networks in soil, examples of which are micro-cracks, interaggregate spaces and fractures. In contrast, textual pores are smaller in size and are the pores between individual particles of sand silt or clay which are dependent on the texture of the soil. Textural pores are more likely to be disconnected from each other, while structural pores are said to drain or fill in the region between full saturation and the inflection point and the same happens for textural pores in the drier side of the inflection point, as illustrated in Fig. 5.15:



Figure 5.15 : Effect of drying or wetting of structural pores and textural pores on either side of inflection point in water retention curve (drawn after Reynolds et al. (2009))

The pore volume distribution function of a soil also shows a peak at the pore size that drains at the level of suction corresponding to the inflection point. This is the basis for deriving the equation for the soil water retention curve from the pore side distribution function [4]. For a soil that is drying, the water content corresponding to the inflection point is schematically denoted in the pore volume distribution function in Fig 5.16:



Figure 5.16 : Water content at inflection point denoted in terms of pore distribution function. (Drawn after Dexter (2004))

However, the situation during and wetting is different. The effect is known as hysteresis and the hysteretic effects on the inflection point are discussed in the following section.

#### 5.4.3 Hysteresis effects

During drying and wetting, the WRC follows different paths with respect to suction. This effect is known as hysteresis. The main branches in a water retention curve exhibiting hysteresis are known as the boundary drying curve and the boundary wetting curve. There can be an infinite number of scanning curves within the hysteresis loop [27]. The hysteretic nature of soil is caused by four main factors [27]:

- The "ink bottle effect" caused by the irregular cross sections of the voids
- The contact angle in an advancing meniscus being larger than that of a receding meniscus
- The effect of entrapped air
- The thixotropic gain or ageing due to the drying or wetting history of soil



Figure 5.17: Schematic of water retention curve exhibiting hysteresis and showing shift in inflection point

In the case of water retention curves exhibiting hysteresis, the inflection point shifts along the suction axis (see Fig.5.17). In this case, the shift in the inflection point is used as a measure of hysteresis [3].

Soil consists of pores of many sizes and distributions, and while the largest pores drain first, they are the last to fill. The corresponding suction at the peak in the pore size distribution is taken as the inflection point of the WRC [4]. However, this value of suction is different for drying and wetting curves. Drying and wetting processes also depend on pore connectivity, and certain pores may not drain or fill as quickly as others. The processes of drying and wetting at the inflection point can be illustrated on a schematic pore size distribution curve as shown below. The pore size distribution contains only information on the pore sizes and not their connectivity. Certain pores may not be drained or filled due to their lack of connectivity at a corresponding level of suction.



Figure 5.18: Schematic illustration of water and air entrapment during drying and wetting of soil using pore-size distribution graph

As Fig. 5.18 shows, when drying, the air phase becomes continuous at a suction value lower than the suction value for when the air phase becomes discontinuous during wetting. The inverse is true for the water phase. However, the water content in each case when taken as the total of the undrained and unfilled pores may be equal for drying and wetting at the inflection point. This effect is consistent with the drying and wetting water retention curves displaying hysteresis explained using Fig. 5.17. While the suction value at the inflection point is different for the drying and wetting cases, the water content, or the overall degree of saturation can be considered the same at the inflection point for both cases.

#### 5.4.4 Pore size distributions from water retention curves and micro X-Ray CT

As discussed previously, the water retention characteristics are a direct consequence of the pore distribution and the pore connectives in soil. Many of the equations for the water retention curves are derived based on the pore size distribution in soils [4]. Therefore, the pore size distribution can be estimated using the water curves for a given soil.

The water retention curve expressed in terms of volumetric water content and suction can be used to obtain the pore size distribution function. This is achieved by plotting the slope of the water retention curve against the equivalent diameter in a semi log plot [7]. The equivalent diameter is the diameter of the pore corresponding to a given level of suction according to the Young-Laplace equation for capillary rise given in Eq. 5.19:

$$d_e = \frac{4T\cos\theta}{\psi} \tag{5.19}$$

where, *d* is the diameter of the pore (m), *T* is the surface tension of water (N/m),  $\theta$  is the contact angle between water and the soil surface, and  $\psi$  is the soil suction (Pa). It should be noted that this method assumes that soil is a collection of unconnected tubes of varying sizes which progressively drain with changing suction. The tortuosity of the pore spaces is disregarded in this case. A surface tension value of 78.2 mN/m and a contact angle of 0 degrees [7] was used to calculate  $d_e$  using Eq. 5.19. The pore size distribution functions obtained in this manner are given in Figs 5.19-5.21.



Figure 5.19: Pore size distribution calculated from water retention curve for sand



Figure 5.20: Pore size distribution calculated from water retention curve for silt



Figure 5.21: Pore size distribution calculated from water retention curve for clay

Figs. 5.19 to 5.21 reveal that the peak pore size (modal pore diameter) varies over orders of magnitude in the three soils. Sand has a peak pore size of around 70  $\mu$ m, whereas in silt and clay the peak pore sizes are 7  $\mu$ m and 0.8  $\mu$ m, respectively. A similar trend was observed in the particle size distributions for the three soils (Figs. 5.3-5.5), although the particle sizes were much larger than the pore sizes, as expected.

The pore size distributions for silt were obtained from X-ray CT imaging, as stated in Section 5.3.3. The normalised pore density vs. the equivalent pore diameter for silt as calculated from the water retention curve and extracted from X-ray CT image analysis are given in Fig. 5.2.2. The X-ray CT image shown here corresponds to a silt sample compacted just wet of optimum. According to the figure, the two approaches yield approximately similar results. It is noted that while the calculated peak pore size is around 7  $\mu$ m, the peak pore size from image analysis is 10  $\mu$ m. Since several assumptions were made in the calculation, (neglecting tortuosity etc.), the similarity in the results for the two approaches is remarkable.


Figure 5.22: Normalised pore density calculated from water retention curve and X-ray CT image analysis for silt showing consistent results

Fig. 5.22 further reveals that the pore distribution obtained from the X-ray CT imaging indicates that silt has a bi-modal pore distribution. This trend is not observed in the distribution calculated from the water retention curve, as the values were obtained in this method through numerical differentiation of the fitted Fredlund & Xing equation, which describes a unimodal soil. However, closer examination of the experimental values for silt given in Fig. 5.13 reveals that changes in the gradient of the water retention curve also take place at 1 kPa and around 6 kPa in addition to the main inflection point at 40 kPa. Of these secondary inflections, that at 6 kPa is more significant and corresponds to an equivalent diameter of 48 µm when calculated using Eq. 5.20. Incidentally, this is approximately the pore size at which the second peak is observed in the results obtained from X-ray CT imaging, which may indicate that the bi-modality of silt is supported experimentally. However, it is not clear whether the secondary inflections observed in the experimental data reflect the actual pore structure of the silt or whether they are experimental errors. This observation should be studied in detail with further experiments for verification purposes.

## 5.4.5 Effect of compaction and changes to pore distribution

## 5.4.5.1 Compaction test results

Standard compaction test results for the three soil types tested are given in Fig. 5.23. It is noted that in all three soils, the degree of saturation at the optimum moisture content (OMC) is the same as that of the inflection point for the three soils reported above.



Figure 5.23: Standard compaction curves for sand, silt and clay showing that  $S_r$  at OMC is the same as that of inflection point  $S_{ri}$ 

Compaction results in a decrease of the total void space in soil, and soil compaction is usually assessed in practice using the compaction curve. The compaction curve is the relationship between the gravimetric moisture content and the dry density. The compaction curve shows an optimum moisture level for which the dry density is maximised. The compaction process and the mechanisms giving rise to this behaviour have been explained by Kodikara (2012) [19] and Kodikara et al. (2018) [20]. The mechanism giving rise to the optimum dry density, beyond which the density decreases again, has been identified as the entrapment of air at the OMC. Fig. 5.24 depicts the compaction curves at varying compaction efforts and the corresponding information in the void ratio (e) moisture rato ( $e_w$ ) space. The figure shows that the degree of saturation at the OMC remains constant throughout, and changes to the continuity of the air phase to either side of the line of optimums are indicated.



Figure 5.24: Effect of compaction on degree of saturation at optimum point (adapted from Kodikara 2012) [19]

The entrapment of air at the OMC suggests that similar mechanisms are in action in regard to moisture distribution at the inflection point of the water retention curve. The implication here is that the degree of saturation at the inflection point and the degree of saturation at the OMC are the same value for all soils. However, it should be noted that, as shown in Fig. 5.24, the void ratio changes during compaction. Since the soil water retention curve is typically given for a constant void ratio, it is necessary to evaluate the changes to pore distribution indicating whether the structural and textural pores are altered.

#### 5.4.5.2 Changes to pore density and water retention curves

The X-ray CT images acquired at each point in the compaction curve were analysed to ascertain the changes to the pore distribution during compaction. Fig. 5.25 shows the compaction curve for silt with imaged samples labelled S1-S8, and Fig. 5.26 shows a representative slice of the ROI for each compacted specimen (S1-S8). The compaction curves expected for higher compaction efforts are schematised in dotted lines in Fig. 5.25. While the  $S_r$  at OMC remains roughly the same for different compaction efforts, it is necessary to evaluate the changes to the pore structure at each point of compaction for different initial moisture contents and initial void ratios to check the assertion that the  $S_r$  at the inflection point is independent of void ratio and remains the same for any state of compaction for a given soil.



Figure 5.25: Standard compaction curve for silt with schematic depiction of expected curves for higher compaction efforts



Figure 5.26: Representative slices of ROI of X-ray CT images obtained at each corresponding point of compaction curve, showing evolution of pore structure during standard compaction

As Fig. 5.26 indicates, for the standard compaction effort, the pore structures for different initial moisture contents vary significantly, in particular showing large structural pore (macro pore) formation due to aggregation with increasing moisture content. It is also noteworthy that samples S2 and S8 have the same dry density (Fig. 5.25) and therefore the same void ratio but significantly different pore structures (Fig. 5.26). S2 shows a generally well- distributed pore structure, while S8 contains a few significantly larger structural pores distributed among a relatively more compact soil fabric. It is also noted that prominent structural pores form beyond the OMC (S4-S8), with the size

of the macro pores gradually increasing. The orientation of some of the structural pores may indicate that they were formed due to air pressure build-up in the compacted soil, and this is consistent with the mechanism of compaction explained by Kodikara (2012) [19].

To quantify the evolution of the pore structure, pore density functions for each sample were plotted from segmented pore volume information extracted from the processed X-Ray CT images. Fig. 5.27 shows the pore density functions plotted for selected samples (S1, S2, S4, S5, and S7) to illustrate the evolution of pore sizes with compaction. It can be seen that in the bi-modal pore distribution exhibited by silt, smaller pores with diameters ~ 10  $\mu$ m remain the same size, whereas changes take place primarily in larger pores with diameters in the range 40 -100  $\mu$ m. It is also noted that the peak structural pore diameters (secondary peak in distribution) in the samples compacted up to the optimum (S1-S4) show a gradually reducing trend and starts to increase again in samples compacted after the optimum (S5 and S7).



Figure 5.27: Pore density functions for selected samples in compaction curve

As noted in Fig 5.27 and the above discussion, the diameter range of the smaller textural pores remains mostly unchanged during compaction, while the structural pores change in size, as shown by the horizontal shift in peak structural pore diameters. Furthermore it can be shown that despite the total areas under each curve being different, the area ratios of regions under the curve belonging to the textural and total pore volumes are approximately the same. Since the area under the pore density

curve is proportional to the pore volume, this implies that the ratio between the textural pore volume and the total pore volume remain constant ( $V_{vt}/V_v = C$ , where  $V_{vt}$ ,  $V_v$ , and C are textural pore volume, structural pore volume and a constant respectively). Note that this means that the ratio between the textural pores and structural pore also remain same. Since water fills the textural pores first, this means that the degree of saturation at the threshold between drainage of textural and structural pores is the same ( $S_{ri} = V_{vt}/V_v = C$ ). This observation implies that the degree of saturation at the inflection point ( $S_{ri}$ ) remains constant and is therefore not influenced by compaction, and as previously discussed, during hysteresis.

Similar observations can also be made for the unimodal pore size distribution of sand. Fig. 5.28 shows the pore density curves calculated for sand at no load and at a load of 7 MPa. Note that unlike in Fig. 5.27, the pore volumes are plotted in the horizontal axis and in linear scale (data from Mahbub and Haque (2016) [28]). Particle crushing was not observed and the compression of larger structural pores was primarily responsible for the change in the shape of the curve. Note that the peak pore volume shifts along the horizontal axis indicating that the most dominant pore size (highest frequency) reduces in size. The smaller pore volumes however do not change significantly. Similar to the previous case, despite the total area under the curves being different, the area ratios between regions of textural and total pore volumes are approximately equal, indicating as before, the equivalence of the degree of saturation at the inflection point, irrespective of compaction.



Figure 5.28: Change to pore size distribution due to compression

As the water retention curves are dependent on the pore distribution of the soil, these changes should be reflected in the water retention curves. As small pore sizes are associated with larger suction values 129 according to the Young-Laplace equation for capillarity, the shift in the water retention curves is to the high suction side. Further, as associated with the changes to the pore size density curve, the water retention curve may also exhibit a change in gradient in the low suction region (wet side of the inflection point), whereas the higher suction region predominantly remains the same.

These effects are illustrated by results from Vanapalli et al. (2001) [29], who reported changes in water retention curves with soil compaction. Fig. 5.29 shows the soil water retention curves for specimens compacted at different initial water contents (dry of optimum, at optimum and wet of optimum)



Figure 5.29: Water retention curves for specimens compacted at different initial water contents (redrawn after Vanapalli et al 2001) [29]

According to Vanapalli et al., the water retention curves with repacked soil before, at and after the optimum resulted in changes only in the low suction regions, indicating the drainage influence of only the macro pores (structural pores). The authors also identified that the boundary between the occluded and open pore conditions occurs at the OMC. This means that the degree of saturation at the inflection point, which is the point of transition in drainage in textural and structural pores, remains constant, irrespective of the compaction conditions of a given soil type, as observed previously in the pore distributions.

# 5.5 Conclusions

The aeration and moisture distribution characteristics of three soil types, sand silt and clay, were investigated in this chapter. Water retention curves for the three soil types were developed, and the respective pore distributions were analysed based on the Young-Laplace equation for capillary rise applied to the water retention curves and micro X-ray CT imaging. Standard compaction tests were conducted to ascertain the influence of compaction on the three soil types.

The inflection point of the water retention curve, which is significant in terms of continuity of the air and water phases, was investigated in detail. The inflection point is identified as the point at which the drainage processes change from occurring in structural pores to textural pores and vice versa. In a unimodal pore size distribution, the inflection point is identified as suction corresponding to the modal pore size (highest frequency or density). In a bi-modal pore distribution, the demarcation of structural and textural pores is more pronounced. The silt investigated in this work exhibited a bimodal pore distribution, as identified by micro X-ray CT imaging. The inflection points for sand, silt and clay were found to be 4kPa, 40kPa and 100kPa, respectively. The degree of saturation at the respective inflection points ( $S_{ri}$ ) was found to increase from sand to clay, with values of  $S_{ri} = 0.5$ ,  $S_{ri}$ = 0.7 and  $S_{ri} = 0.8$  for sand, silt and clay, respectively. This observation is consistent with results reported in the research literature and the colloidal nature of soils was identified as the reason for this trend. It was shown that the  $S_{ri}$  value is independent of hysteretic effects and compaction. It is reasonable to assume that while the suction at the inflection point may change, the degree of saturation at the inflection point,  $S_{ri}$  remains approximately the same and equal to the optimum moisture content (OMC) for compaction for a given soil type.

The equivalence of the degree of saturation at the OMC and that of the inflection point and the conditions of moisture and aeration regimes in this region are important for underground corrosion. As the continuity of the air and water phases impacts the level of corrosion in soils, and standard backfill compaction is performed at the OMC, these findings are important in assessing the corrosion of buried metallic infrastructure. The influence of the inflection point of the water retention curve on oxygen diffusion and corrosion is discussed in subsequent chapters.

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# Chapter 6: Developments in determination of oxygen diffusion properties in diverse soil types

# **6.1 Introduction**

The evaluation of oxygen transport in soil is important in various fields of study. The adsorption of oxygen by plant roots is an important step in plant respiration and oxygen availability is therefore an indicator of soil quality and crop yield in agriculture [1,2]. In the mining industry, soil covers are used to contain mine tailings and the covers act as a barrier to oxygen flow to avoid oxidation and subsequent leaching of harmful chemicals into the ground [3]. In underground corrosion, oxygen is a primary reactant and oxygen reduction is a rate-determining process [4] which plays a role in overall corrosion damage to buried metal infrastructure. For these reasons, it is important to understand the transport of oxygen in soil and its dependency on soil type and structure. Under isothermal and isobaric conditions, oxygen transport in soil takes place by diffusion [4]. While temperature and pressure differences may result in oxygen transport through advection, under normal conditions it is well accepted that diffusion is the dominant mode of oxygen transport in soils [4,5]. In this chapter, oxygen diffusion coefficients are determined experimentally using the diffusion chamber method. Numerical modelling is used to supplement experimental work. New relationships between the soil water retention curve and the oxygen diffusion coefficient and degree of saturation are revealed and discussed in light of their influence on underground corrosion.

#### 6.1.1 Oxygen diffusion

Diffusion is the movement of a substance due to a concentration gradient. The diffusion process in soil is different to that in free air or water due to the inherent tortuosity of the pore space in soil through which oxygen has to diffuse. The process of diffusion in any medium can be described by Fick's law:

$$J = -D\frac{\partial c}{\partial x} \tag{6.1}$$

where,  $J \pmod{m^2 s^{-1}}$  is the diffusive flux,  $c \pmod{m^{-3}}$  is the concentration of the diffusing species (oxygen) and  $D \pmod{m^2 s^{-1}}$  is the diffusion coefficient. Under transient conditions, Fick's second law is used to describe the change in concentration with time:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{6.2}$$

where, t (s) denotes time. In porous media such as soils, the effective porosity and tortuosity are usually incorporated into the diffusion coefficient to obtain an effective diffusion coefficient.

#### 6.1.2 Effective oxygen diffusion coefficient in soil

The oxygen diffusion coefficient in soils is commonly expressed as an effective diffusion coefficient taking into account correction factors such as the porosity and tortuosity of the soil medium. Soil pores are occupied by both air and water and oxygen diffuses through both media. In unsaturated soils, the gas-filled pore space contributes most to the effective diffusion coefficient. However, as the degree of saturation increases and the air phase becomes occluded, the diffusion of the component through the water phase also needs to be considered. In this context, single-phase models refer to models which consider only the air- filled pore space in describing the effective diffusion coefficient, while dual-phase models refer to those which consider both air and water phases.

#### 6.1.2.1 Single-phase models

Single-phase models, such as those by Penman (1940) [6], and Millington and Quirk (1961) [7], relate the effective oxygen diffusion coefficient to air-filled porosity. These models are given in Eqs. 6.3 and 6.4 respectively:

$$D_e = 0.66\theta_a D_a^0 \tag{6.3}$$

$$D_{e} = \frac{\theta_{a}^{10/3}}{n^{2}} D_{a}^{0}$$
(6.4)

where,  $D_e$  (m<sup>2</sup> s<sup>-1</sup>) is the effective oxygen diffusion coefficient,  $D_a^0$  (m<sup>2</sup> s<sup>-1</sup>) is the oxygen diffusion coefficient in free air,  $\theta_a$  is the volumetric air content, and *n* is the porosity. Equations 6.3 and 6.4 can be written in the form below, where  $T_a$  (dimensionless) is the gas phase tortuosity [8]:

$$D_e = T_a \theta_a D_a^0 \tag{6.5}$$

where,  $T_a$  for the Penman (1940) and Millington & Quirk (1960) models are given by Eqs. 6.6 and 6.7, respectively:

$$T_a = 0.66$$
 (6.6)

$$T_a = \frac{\theta_a^{\frac{\gamma_3}{\gamma_3}}}{n^2} \tag{6.7}$$

Note that in these single-phase models, under full saturation ( $S_r = 1$ ), which corresponds to  $\theta_a = 0$ , and the effective diffusion coefficient becomes zero. However, it is known that this is not the case, and that diffusion through the water phase contributes to the value of  $D_e$ . This effect is considered in dual-phase models of  $D_e$ .

#### 6.1.2.2 Dual-phase models

Dual phase models of  $D_e$  consider the influence of both air and water phases under parallel diffusion paths [9]. Similar to the form given in Eq. 6.5, the dual-phase effective diffusion coefficient, which considers the water-filled pore space, can be written as shown in Eq. 6.8:

$$D_e = T_a \theta_a D_a^0 + H T_w \theta_w D_w^0 \tag{6.8}$$

where, H is the dimensionless Henry's equilibrium constant,  $T_w$  (dimensionless) is the tortuosity of the water-filled pores,  $\theta_w$  is the volumetric water content and  $D_w^0$  (m<sup>2</sup> s<sup>-1</sup>) is the oxygen diffusion coefficient in free water. Equations for  $T_a$  and  $T_w$  have been provided by Collin & Rasmuson [9] and Aachib et al. [8]. Based on these equations and experimental observations, a simplified, semiempirical relationship for  $D_e$  was provided by Aachib et al. [8], given by Eq. 6.9:

$$D_e = \frac{1}{n^2} \cdot \left[ D_a^0 \theta_a^{\ p} + H D_w^0 \theta_w^{\ p} \right]$$
(6.9)

where, the exponent *p* can be determined using polynomial functions of  $\theta_a$  and  $\theta_w$ [8]. However, it has been proposed that a value of *p* = 3.4 gives the best fit to data observed in practice.

Note that, in some studies, the effective diffusion coefficient is defined by decoupling the porosity term c.f. [3,10–12]. Then this diffusion coefficient  $D_e^*$  is defined in terms of  $D_e$  as  $D_e = \varepsilon_{ea} D_e^*$ , where

 $\varepsilon_{eq}$  is the equivalent porosity [13]. In the present work, the diffusion coefficient  $D_e$  is defined by Eq.6.8, which includes the porosity term.

In comparing diffusivities in different types of soil, in addition to water distribution and diffusion through the water phase, the effects of the interaction of water with soil particles are also important. The colloidal properties of soils together with the distribution of water through textural and structural pores, *i.e.* intra and inter-aggregate pore spaces, need to be accounted for. The effective diffusion coefficient in aggregated porous media is discussed in the following section to account for these factors.

# 6.1.2.3 Effective diffusion coefficient in aggregated porous media

Millington & Shearer [14] provided a single-phase model for the diffusion coefficient in aggregated porous media. This model considers the contribution of the intra-aggregate porosity ( $n_A$ ) and the inter-aggregate porosity ( $n_P$ ) to diffusion. The Millington & Shearer model is given in Eq. 6.10:

$$D_{e} = \left[\frac{(1-S_{rA})^{2} \left[\frac{n_{A}-\theta_{A}}{n_{A}+n_{S}}\right]^{2x_{1}} \left(1-n_{P}^{2x_{2}}\right) \cdot \left[\left(n_{P}-\theta_{P}\right)-\left(n_{P}-\theta_{P}\right)^{2x_{3}}\right]}{(1-S_{rA})^{2} \left[\frac{n_{A}-\theta_{A}}{n_{A}+n_{S}}\right]^{2x_{1}} \left(1-n_{P}^{2x_{2}}\right) + \left[\left(n_{P}-\theta_{P}\right)-\left(n_{P}-\theta_{P}\right)^{2x_{3}}\right]} + \left(1-S_{rP}\right)^{2} \cdot \left(n_{P}-\theta_{P}\right)^{2x_{3}}\right]} \cdot D_{a}^{0} \quad (6.10)$$

where,  $n_A$  and  $n_P$  are the intra-aggregate and inter-aggregate porosities respectively,  $S_{rA}$  and  $S_{rP}$  are the degrees of saturation in the intra-aggregate and inter-aggregate pore spaces, and  $\theta$  with subscripts A and P are the volumetric water contents of the same and given by  $\theta = n.S_r$ .  $n_S$  is defined as the volume of solid per total volume (the inverse of the specific volume). The total porosity is:  $n = n_A + n_P = 1 - n_S$ . The values  $x_1$ ,  $x_2$  and  $x_3$  are determined using the equations given in [14].

In using the model by Millington & Shearer to estimate  $D_e$  for aggregated porous media, in addition to the intra- and inter-aggregate porosities of the medium, the respective saturations (the distributions of water) within these pore spaces should also be known. According to Collin and Rasmuson [9], these two extreme water distributions can be explained as follows:

- 1. Water occurs in pores between aggregates (inter-aggregate) only when the pores in the aggregate (intra-aggregate) are fully saturated ( $S_{rP} = 0$  for  $S_{rA} < 1$ ). This assumes that the intra-aggregate pores are significantly smaller than the inter-aggregate pores.
- 2. The degree of saturation in both intra- and inter-aggregate pores is equal. ( $S_{rP} = S_{rA}$ ). This assumes that both intra-aggregate and inter-aggregate pore sizes are equal.

Since most soils have a log-normal pore size distribution [15], it can be inferred that most natural soils have a water distribution closer to case 1 above, where smaller pores are filled before larger pores fill.

Considering the above extreme water distributions (cases 1 and 2) and two different intra-aggregate porosities, the following plot (Fig. 6.1) for single-phase  $D_e$  vs.  $S_r$  has been presented by Collin and Rasmuson [9].



Figure 6.1: Estimated  $D_e$  values from Millington & Shearer model [10] for two different intra-aggregate porosities. As indicated by the numbers, the lines above are for water distribution case 1 and the lines below are for water distribution case 2. (Modified from Collin and Rasmuson [9])

For water distribution case 1, a discontinuity is seen at the degree of saturation equal to the value of  $n_A/n$ . Prior to this discontinuity, the diffusion coefficient remains approximately the same at its maximum value, and after the discontinuity,  $D_e$  rapidly decreases with increasing saturation. Water distribution case 2 shows no such discontinuity, as the intra-aggregate and inter-aggregate pores are of equal size and drain together.

The single-phase Millington Shearer model has been shown to be consistent with experimental data for aggregated media such as pumice [14], and models the discontinuity in the  $D_e$  -  $S_r$  relationship well, as shown above. In natural soils with unimodal pore distribution, such a sharp discontinuity is not expected, as a range of pore sizes exists and a sharp demarcation of intra- and inter-aggregate porosity is not observed. However, as detailed by Dexter (2004a,b)[16,17], the pore spaces in soils can be classified as structural pores and textural pores, analogous to inter-aggregate and intraaggregate pore spaces. Furthermore, Dexter (2004b) [17] and subsequently Reynolds et al. (2009) [18] noted that the peak in the pore size distribution marks the demarcation between primarily structural pores and primarily textural pores. The peak pore size in the pore size distribution function also corresponds to the pore size which drains or fills up corresponding to the inflection point in the water retention curve. In soils with bi-modal or multimodal distributions, the demarcation between structural and textural pores is distinct [19,20]. It is also noted that structural pores are the first to drain and the last to fill, similar to water distribution case 1 described above.

Fig. 6.2 shows a schematic pore size distribution (similar to that introduced in Fig. 5.6 in Chapter 5) with the pore classes of textural pores and structural pores, as identified by Dexter [16,17] and Reynolds [18]. Accordingly, the pore volumes of the two pore classes can be calculated by their respective areas under the pore size distribution curve.



Pore volume

Figure 6.2: Schematic pore size distribution curve identifying structural and textural pores and respective pore volumes

Considering the similarity between the intra- and inter-aggregate pores to textural and structural pores, the break point seen Fig.6.1 at  $n_A/n$  can be written in terms of the information given in Fig 6.2 as:

$$\frac{n_A}{n} = \frac{\frac{V_{VA}}{V_T}}{\frac{V_V}{V_T}} = \frac{V_{VA}}{V_V} = \frac{A_t}{A_t + A_s}$$
(6.11)

The ratio at the right side of Eq. 6.11 corresponds to the degree of saturation at the inflection point in the water retention curve  $(S_{ri})$  [17]. This means that, although a sharp discontinuity in the  $D_e$ - $S_r$  relationship may not be present in most soils, the degree of saturation at which the value of  $D_e$  starts

to drastically decrease can be identified as that of the inflection point in the water retention curve. If the soil exhibits aggregation during compaction, for example in compacted clays, a reasonably sharp discontinuity at the  $S_{ri}$  value also can be expected.

Collin and Rasmuson [9] modified the Millington & Shearer [14] model for aggregated porous media to include diffusion through the water-filled pore space. This was done by assuming parallel diffusion paths, as given in Eq. 6.8. The effective diffusion coefficient was given as:

$$D_e = D_a + H.D_w \tag{6.12}$$

The  $D_a$  was found using the usual Milling & Shearer model given in Eq. 6.10. Since the derivation for the water phase diffusion is tedious, the authors presented a simplified method as follows. Since the right side of Eq. 6.10 is fluid-independent, the following equivalency was established:

$$\left(\frac{D_w}{D_w^0}\right)_{S_r=1} = \left(\frac{D_a}{D_a^0}\right)_{S_r=0}$$
(6.13)

Next the diffusivity through the water phase  $D_w$  was assumed to be proportional to the degree of saturation:

$$\left(\frac{D_w}{D_w^0}\right) \approx S_r \cdot \left(\frac{D_w}{D_w^0}\right)_{S_r=1}$$
(6.14)

Based on Eqs. 6.12, 6.13, and 6.14, the dual-phase effective diffusion coefficient for aggregated media is given by Collin & Rasmuson [9] as:

$$D_{e} = D_{a} + H.S_{r}.D_{w}^{0} \left(\frac{D_{w}}{D_{w}^{0}}\right)_{S_{r}=1}$$
(6.15)

Eq. 6.15 shows that this dual-phase model has considerable complexity, especially since Eq. 6.10 is still used to calculate  $D_a$  to be used as a predictive model.

According to the theoretical model equations presented by Millington & Shearer and Collin and Rasmusson, the point at which the oxygen diffusion coefficient starts to rapidly decline in the oxygen diffusion-degree of saturation relationship, where the intra-aggregate pores are completely filled and the inter-aggregate pores just start to fill. Therefore, the degree of saturation at this point is given by the ratio of intra-aggregate porosity over total porosity.

Work by Dexter (2004 a, b) and subsequently by Reynolds et al (2009) showed that this relationship between intra-aggregate pores and inter-aggregate pores, termed textural and structural pores respectively, is related to the water retention properties of soils, and that the point corresponds to the degree of saturation at the inflection point of the water retention curve. Since different soils have different pore distributions and varying levels of demarcation between structural and textural pores, it follows that the diffusion-saturation relationship in diverse soils differs, similar to the inflection points of the water retention curve.

Based on experimental results from oxygen diffusion tests presented in this chapter and the soil water retention experiments presented in Chapter 5, in this chapter, a semi-empirical model for the oxygen diffusion-saturation relationship is proposed, based on the soil water retention characteristics discussed above.

# **6.2 Experimental methods**

Oxygen diffusion through soil depends on soil moisture and has a direct impact on corrosion. The oxygen diffusion properties for the three soil types tested in this study: sand, silt and clay under varying degrees of saturation were evaluated. Since oxygen diffuses simultaneously through the air and water phases, the effective diffusion coefficients considering both phases were determined through experiments. The relationship between the effective diffusion coefficient and soil properties such as moisture retention and compaction were also studied.

#### 6.2.1 Materials and apparatus

# 6.2.1.1 Soil properties

Pure sand, silt and clay samples were used in this study to cover the spectrum of general soil types. The sand and clay samples were acquired from a local supplier (Clayworks, Melbourne), while the silt sample was sourced from the Fraser River estuary in Vancouver, British Columbia, Canada. The particle size distribution and the experimentally-determined water retention characteristics were provided and described in detail in Chapter 5. As the water retention characteristics are important for the ensuing discussion, the water retention curves for all three soil types are summarised in Fig 6.3.



Figure 6.3: Water retention curves for sand silt and clay used in this work showing inflection point for each soil type. Dotted lines denote inflection point for each soil

#### 6.2.1.2 Diffusion chamber set-up

The oxygen diffusion coefficients for soil samples prepared to the same specifications as the previous tests (see Chapter 5) were measured using the UMS-G experimental set-up [21] developed in accordance with the diffusion chamber method [22]. A schematic of the experimental set-up is given in Fig. 6.4.



Figure 6.4: Schematic of oxygen diffusion experimental set-up

The experimental set-up consists of three chambers. The top chamber is open to the atmosphere, the middle chamber contains the compacted soil sample and the bottom chamber (diffusion chamber) collects and measures the oxygen which diffuses from the top chamber through the soil sample into the bottom chamber. The top chamber and middle chamber can be isolated from each other by means of a sliding metal disc. The set-up contains O-rings at all joint locations and is sealed using petroleum jelly. Prior to the test, all oxygen is purged from the bottom chamber using nitrogen gas. Next, the divide between the top and middle chamber is removed allowing oxygen to diffuse through the soil. The oxygen concentration in the diffusion chamber was recorded at 1-minute intervals through a data acquisition system.

#### 6.2.1.3 Sample preparation

A sample holder modified with a 3-D printed mesh was used to compact soil samples to the required dry density. Fig. 6.5 shows the modified sample holder. Due to the very low thickness of the mesh

and the relatively large size of the mesh opening, the modification does not result in significant additional diffusion resistance.



Figure 6.5: Modified sample holder used for compacted soils

The prescribed amount of sand was measured and the required amount of water was added and mixed thoroughly and allowed to equilibrate for a few minutes. The sand was packed into the sample holder with varying compactive efforts, ensuring that the mixed dry mass occupied the entire volume of the sample holder. The degree of saturation was calculated based on the mass measurements of sand and water. The silt and clay were prepared differently. Due to the longer time taken for the soil moisture to equilibrate, after mixing approximately 15% more dry weight than the mass required for the target dry density with water, the soil was sealed in a container and left for 24 hours. The equilibrated soil was then compacted, the weights of the empty and full sample holder recorded, and a moisture content test was conducted to calculate the degree of saturation. The compacted sample holder was installed into the upper chamber and the set-up was assembled for the experiment. Due to the design of the apparatus, very little moisture loss occurred during the diffusion tests. Moisture content tests were performed before and after the experiment to ensure that no significant change in moisture content occurred in the compacted sample.

## 6.2.2 Data analysis

#### 6.2.2.1 Single-phase effective diffusion coefficient

The recorded oxygen concentrations were converted to relative concentrations according to Eq. 6.16:

$$C_{r} = \frac{C(t) - C_{ref}}{C_{0} - C_{ref}}$$
(6.16)

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where,  $C_r$  is the relative concentration (dimensionless),  $C_0$  is the initial concentration (mol m<sup>-3</sup>) in the diffusion chamber (z > L) at time *t*=0,  $C_{ref}$  (mol m<sup>-3</sup>) the atmospheric concentration (source) and C(t) the concentration in the diffusion chamber at time t > 0. The solution to the relative concentration detailed by Carslaw and Jaeger [23] given by Eq. 6.17 was used to calculate the effective oxygen diffusion coefficient considering the air-filled pore space ( $D_p$ ) for the soil samples:

$$C_{r} = \frac{C(t) - C_{ref}}{C_{0} - C_{ref}} = \sum_{n=1}^{\alpha} \frac{2h \exp(-D_{p} \alpha_{n}^{2} t / \varepsilon_{a})}{L(\alpha_{n}^{2} + h^{2}) + h}$$
(6.17)

where, *L* (m) is the thickness of the sample, and *h* is defined as  $h = \varepsilon_a / L_a$ , where  $L_a$  (m) is the length of the diffusion chamber plus the space below the compacted sample,  $\varepsilon_a$  is the air-filled porosity, and  $\alpha_n$  with n=1,2,..., are the first positive roots of  $h=\alpha \tan \alpha L$ .

Equation 6.17 can be written in the form of a linear equation by ignoring the terms for which  $n \ge 2$ . Then the natural logarithm of  $C_r$  can be expressed as:

$$\ln C_{r} = \ln \left( \frac{C(t) - C_{ref}}{C_{0} - C_{ref}} \right) = \frac{D_{p} \alpha_{1}^{2}}{\varepsilon_{a}} t + \ln \left( \frac{2h}{L(\alpha_{1}^{2} + h^{2}) + h} \right)$$
(6.18)

As Equation 6.18 shows, a plot of  $\ln C_r$  vs *t* gives a straight line with a gradient given by  $\frac{D_p \alpha_1^2}{\varepsilon_a}$  where

 $\alpha_l$  depends only on the geometry of the experimental set-up. The oxygen diffusion coefficient considering the air-filled pore space,  $D_p$  is therefore obtained using the gradient of the experimental values of ln  $C_r$  vs. time and the geometry of the set-up.

#### 6.2.2.2 Dual-phase effective diffusion coefficient

For zero air-filled porosity (full saturation), the term  $\frac{D_p \alpha_1^2}{\varepsilon_a}$  when equated to the gradient of ln *Cr* vs *t*, gives zero for the oxygen diffusion coefficient. However, it is known that this is not the case and that the diffusion of oxygen through water gives a non-zero diffusion coefficient under fully saturated conditions. While the contribution from the water phase is very small and negligible in unsaturated conditions, it is required to accurately define the diffusion coefficient in fully saturated conditions.

To include the effect of the water phase, it is assumed that the oxygen in air and water phases are in equilibrium according to Henry's law, and instead of the air-filled porosity term in the above calculations, an equivalent porosity ( $\varepsilon_{eq}$ ) is defined as follows [8,13]:

$$\mathcal{E}_{eq} = \mathcal{E}_a + H \mathcal{E}_w \tag{6.19}$$

where, H is the dimensionless Henry's equilibrium constant and  $\varepsilon_w$  is the water-filled porosity. The above calculation procedure can then be repeated with the equivalent porosity instead of the air-filled porosity to find the effective diffusion coefficient which includes both the air and water phases. In this case Eq. 6.18 is written as:

$$\ln C_{r} = \ln \left( \frac{C(t) - C_{ref}}{C_{0} - C_{ref}} \right) = \frac{D_{e} \alpha_{1}^{2}}{\varepsilon_{eq}} t + \ln \left( \frac{2h}{L(\alpha_{1}^{2} + h^{2}) + h} \right)$$
(6.20)

where,  $D_e$  is the dual-phase effective diffusion coefficient and  $\varepsilon_{eq}$  is the equivalent porosity defined above, and h is defined as  $h = \varepsilon_{eq} / L_a$ .

The results presented in Section 6.4 were obtained by adopting this dual-phase approach, as oxygen diffusion in saturated conditions is important for the assessment of corrosion in waterlogged soil media.

# **6.3 Numerical Modelling**

A numerical modelling exercise was conducted to compare the solution to the analytical equation based on Fick's law with the experimentally-observed concentration-time curves.

# 6.3.1 Model set-up

As detailed in Section 6.2.3, Fick's law can be solved only for the compacted soil domain with a constant concentration boundary condition imposed on the top surface (z=0). However, in the finite element simulation presented here, three separate domains were created to closely approximate the actual diffusion chamber set-up with real dimensions. A 2-D axisymmetric model with axial symmetry across the r=0 axis (Fig. 6.6) was created to simulate the three cylindrical chambers of the diffusion chamber set-up. Fig. 6.6 shows the geometry and the mesh of the model. The middle chamber (compacted soil domain) was modelled as a domain with the effective diffusion coefficients  $(D_e)$  obtained from the experiments, whereas the upper chamber and diffusion chamber were modelled as domains with the free diffusion coefficient of oxygen in air  $(D_a^0)$ .



Figure 6.6: Model geometry, mesh and diffusion coefficients used for each domain for simulation

The time-dependent concentration (C(t)) through the domains was solved for using Fick's second law (Eq.6.2) using the COMSOL Multiphysics software package. A constant concentration boundary condition equal to the atmospheric concentration,  $C_{ref} = 8.6 \text{ mol/m}^3$  was imposed ion the top surface of the upper chamber (z = 0.22 m). The time-dependent simulation was initialised with initial concentration values of  $C_{ref} = 8.6 \text{ mol/m}^3$  for the upper and middle chambers and  $C=2.26 \text{ mol/m}^3$  for the diffusion chamber, to simulate experimental conditions after purging with nitrogen gas.

The reason for selecting an initial value of  $C=2.26 \text{ mol/m}^3$  for the diffusion chamber instead of  $C=0 \text{ mol/m}^3$  was the initial jump in concentration in the diffusion chamber which occurs during the experiment when the sliding disc is opened to allow oxygen to diffuse. The gap between the sliding metal disc and the compacted sample (Fig.6.4) contains oxygen at atmospheric concentration and once the disc is opened this oxygen diffuses and rapidly raises the concentration in the diffusion chamber by mixing. In the data analysis detailed above, only the data points measured after this initial jump were used. For the numerical simulations, the average value of the concentration in the diffusion chamber after this occurrence was used. Fig. 6.7 shows typical measured concentration values from the beginning and the jump in concentration after the disc is opened.



Figure 6.7: Typical measured O2 concentration vs. time, stages of testing and data used for analysis

As Fig. 6.7 shows, the mixing of oxygen within the gap with the nitrogen in the diffusion chamber causes a sudden jump in concentrations when the metal disc is opened. Only the data beyond line 4 shown in Fig. 6.7 were used for analysis and numerical modelling, as stated above.

## 6.3.2 Simulations conducted

The experimentally-obtained dual-phase effective diffusion coefficients for the three soil types were simulated separately. The time-dependent simulation was conducted for 14000 seconds with time steps of 60 seconds and the concentration profiles at each time step were obtained.

A typical concentration profile at the end of the simulation depicted in the 3-D model domain is shown in Fig. 6.8. According to the figure, at the end of the simulation, the concentrations in all three chambers are very close to each other.



*Figure 6.8: Typical final concentration profile obtained from simulation (time = 3.8 hours)* 

The evolutions of the concentration profiles with time in the two chambers and across the samples were examined to validate the assumption that no significant concentration gradients are present in the upper and diffusion chambers. As the calculations presented in the data analysis concern only the concentration gradients across the sample, and assume that there was sufficient turbulence in the gases to eliminate concentration gradients in the chambers [22], this verification was necessary to ensure the accuracy of the adopted method. The evolution of the concentration profile with time is provided in the following sections.

The concentration of a point corresponding to the location of the oxygen sensor in the experimental set-up was monitored with time and concentration vs. time plots were generated for each effective diffusion coefficient simulated. The experimental concentration vs. time plots were compared against those for the numerical model.

# 6.4 Results and discussion

The results of the experiments and numerical models are presented in this section. A comparison is made with the numerical model results and it is shown that the calculation procedure adopted gives reasonably similar results to those of the numerical model.

## 6.4.1 Calculation of effective diffusion coefficients

#### 6.4.1.1 Concentration in diffusion chamber

The concentrations in the diffusion chamber vs. time and the corresponding values for  $\ln C_r$  at each degree of saturation tested for the three different soils types are given in Figs. 6.9-6.11. It can be seen that at higher degrees of saturation in all three soil types, the concentration in the diffusion chamber changes very little, due to the very low diffusion coefficients under saturated conditions.



Figure 6.9: Experimentally-measured concentration vs. time and ln Cr vs. time for sand



Figure 6.10: Experimentally-measured concentration vs. time and ln Cr vs. time for silt



Figure 6.11: Experimentally-measured concentration vs. time and ln Cr vs. time for clay

The slope of  $\ln C_r$  vs. time plots for each degree of saturation in each soil type was used to calculate the effective diffusion coefficient, as detailed in Section 6.2.3.2.

## 6.4.1.2 Comparison with numerical model

The calculated effective diffusion coefficients were used for the numerical simulation described in Section 6.3 and the resulting concentration vs. time curves were compared with the experimental values. Apart from minor differences at low degrees of saturation, the experimental and numerical model curves were similar. Figs. 6.12-6.14 show the concentration-time curves obtained from the numerical model and the experimental data side by side, for the calculated diffusion coefficients.



Figure 6.12: Experimental data and oxygen concentration vs time curves calculated from numerical model for different degrees of saturation in sand



Figure 6.13: Experimental data and oxygen concentration vs time curves calculated from numerical model for different degrees of saturation in silt



Figure 6.14: Experimental data and oxygen concentration vs time curves calculated from numerical model for different degrees of saturation in clay

Note that the experimental data are comparable with the numerical model curves. Although minor differences are seen at low degrees of saturation between the two, it is concluded that the method of calculation of  $D_e$  from concentration-time curves presented in Section 6.2.3 is reasonably accurate, despite the assumptions made. To improve the calculation it is possible to fit the numerical model curves into the experimental data to back-calculate  $D_e$ . Since Fick's laws are numerically solved without simplifying assumptions, it is expected that this method will be more accurate. However, given the similarities in the two methods shown in this study, the simplified calculation is used for the subsequent analyses.

# 6.4.1.3 Concentration profiles

The numerical model was also used to examine the concentration profiles in each of the chambers of the simulated experimental set-up. This exercise was performed to evaluate the assumptions made in the calculations and to check whether significant concentration gradients are present in either of the chambers. Figs. 6.15 and 6.16 show the evolution of the concentration profile over time for two diffusion coefficients,  $D_e=1 \times 10^{-6} \text{ m}^2/\text{s}$  and  $D_e=1 \times 10^{-9} \text{ m}^2/\text{s}$ . These values are typical of the highest and lowest diffusion coefficients respectively observed in soils. In both figures, time steps of 10 minutes are indicated from the start to the end of the test.



Figure 6.15: Concentration profile evolution with time for diffusion coefficient of  $1x10^{-6}$  m<sup>2</sup>/s



Figure 6.16: Concentration profile evolution with time for diffusion coefficient of  $1x10^{-9}$  m<sup>2</sup>/s

The figures show in both instances the gradient of concentration in the upper and lower (diffusion) chambers is insignificant compared with the concentration gradient across the sample. This effect is

pronounced at lower diffusion coefficients, as observed in Fig. 6.16, and also increases with time. Fig. 6.15 indicates that by the end of the tests, the oxygen concentration in the diffusion chamber reaches the same concentration (atmospheric) as that in the upper chamber. This effect is not observed in the case of the lower diffusion coefficient, (Fig.6.16) where the concentration in the diffusion chamber remains almost the same due to the very low rate of diffusion. It is also observed that the concentration gradients in the sample with lower diffusion coefficient are much sharper and primarily occur across the bottom half of the sample. These observations indicate that, although concentration gradients are present in the upper and lower chambers, they are insignificant compared with the concentration gradient across the sample. Further, according to Currie (1960), [22], the gases behave as a well stirred fluid with sufficient turbulence to eliminate concentration gradients in the chambers. Experimental evidence has been presented for this claim by Currie [22]. The numerical simulation does not simulate turbulence effects and it can therefore be assumed that the actual concentration gradients in the air-filled chambers are much lower than indicated in Figs. 6.15 and 6.16. Therefore, the assumptions made in performing the calculation presented in Section 6.2.3 can be deemed valid.

# 6.4.1.4 Calculated effective diffusion coefficients

Based on the dual-phase calculation procedure described in Section 6.2.3 with verified assumptions as discussed above, the effective diffusion coefficients for sand, silt and clay were determined. Fig. 6.17 shows the experimental effective diffusion coefficients ( $D_e$ ) determined at varying degrees of saturation for sand, silt and clay. As expected, in all three soils, the effective diffusion coefficient decreases with increasing saturation. This behaviour is typical for all porous media [3,11] and is attributed to the pore space filling with water, decreasing the rate of diffusion due to the very low diffusion coefficient in water compared to that of air. It is also observed that all three soil types show approximately the same  $D_e$  of ~1x10<sup>-6</sup> m<sup>2</sup>/s at low degrees of saturation. This indicates that the three soil types behave similarly at low degrees of saturation when diffusion is relatively rapid.



Figure 6.17: Effective diffusion coefficients at varying levels of saturation for sand, silt, and clay

Fig. 6.17 reveals that, although the three soils show similar diffusion coefficients at low saturations, the pattern diverges for the three soils at high saturations, and the "turning point" beyond which  $D_e$  starts to drastically decrease is different for the three soils. The reason for this behaviour can be attributed to the soil textural properties and this matter is discussed in the following sections.

#### 6.4.2 Differences in $D_e$ between sand silt and clay

## 6.4.2.1 Experimental results

A non-parametric fit to the experimental data presented above shows that the degree of saturation after which the  $D_e$  starts to drop rapidly is different for the three soil types. This value of saturation is around  $S_r \approx 0.5$  for sand and  $S_r \approx 0.7$  and  $S_r \approx 0.8$  for sand, as shown in Fig. 6.18. The dotted lines in Fig. 6.18 denote these degrees of saturation. Note that these saturation values for sand, silt and clay are the same as that of the inflection point in the water retention curve ( $S_{ri}$ ) for the three soils, as described in Chapter 5. Note that the inflection points of the water retention curves for the soils used in this study are marked in Fig. 6.3. The physical importance of  $S_{ri}$  in terms of oxygen diffusion is discussed in Section 6.4.3



Figure 6.18: Experimental data with non-parametric fit. Dotted lines denote degrees of saturation beyond which De starts to rapidly decrease

The differences in the three soil types can also be explained by aggregate formation, as discussed in Section 6.1.2.3, as some soils are more likely to form aggregates than others. As Fig. 6.1 indicates, the differences in drainage between intra- and inter-aggregate porosities may cause a pattern similar to that seen in the clay data in Fig. 6.18. Similar observations from the research literature are discussed in the following section.

## 6.4.2.2 Results of previous studies

Previous studies have shown variations in the oxygen diffusion coefficient in various types of porous media. For example, Bouazza and Rahman (2008) [11] reported the oxygen diffusion coefficients for two types of geosynthetic clay liners (GCLs). Fig. 6.19 shows the oxygen diffusion coefficients with the degree of saturation for needle-punched GCLs and stitch-bonded GCLs. Note that the effective diffusion coefficient given in this figure is  $D_e^*$ , which as stated in Section 6.1.2.2, does not include a soil porosity term. However, this detail does not affect the comparison of trends observed in the effective diffusion coefficients and the arguments which follow.



Figure 6.19: Oxygen diffusion coefficients for two types of GCLs (modified from Bouazza & Rahman 2008[11])

According to Bouazza & Rahman [11], the reason why the stitch-bonded GCLs show a higher diffusion coefficient at relatively high saturation is the changes to the uniformity of the bentonite layer. The bentonite in zones along the stiches in stitch-bonded GCLs tends to swell freely, creating zones with less bentonite available for mitigating gas diffusion. In needle- punched GCLs, the bentonite has been observed to swell uniformly and effectively block the diffusion process.

Similar mechanisms causing the changes in  $D_e$  due to structural changes in GCLs can be observed in soils which exhibit aggregate behaviour. The structural pore spaces in soil can lead to similar situations where preferential pathways for diffusion are established along the connected structural pores until they are blocked at relatively higher degrees of saturation. It was stated in Chapter 5 that, due to the colloidal nature of some soils, the point at which the drainage processes transition from occurring in structural pores to textural pores is higher than in non-colloidal soils. This transition point, identified as the degree of saturation at the inflection point in the water retention curve ( $S_{ri}$ ), is therefore much higher in silts and clays than in sands. In clay soils in particular, the saturation at which the structural pores are blocked is therefore higher. Aggregation of clay soils, which leads to the formation of large structural pores, enhances this effect. MacKay (1997,1998) [12,24] conducted experiments to determine the soil water retention curve and oxygen diffusion for sand and silt. Two curves for sand and three curves for silt were reported by this researcher, and a representative curve of each soil starting at full saturation is given in Fig. 6.20.



Figure 6.20: Water retention curves for sand and silt reported by MacKay (modified from MacKay 1979 [24])

The effective diffusion coefficients  $D_e^*$  vs. saturation for sand and silt are given in Fig. 6.21:



Figure 6.21: Effective diffusion coefficients reported by MacKay for and silt (MacKay 1997[24])

It is clear from Fig. 6.21 that although the data are limited, the diffusion coefficient for silt is generally greater than that of sand and drops rapidly after a relatively high saturation to that of sand. As observed in the data from the present study, this pattern may indicate the influence of the inflection point of the water retention curve shown in Fig. 6.20 on the effective diffusion coefficient.

MacKay (1997) [24] also reported oxygen diffusion coefficients from several other sources. Fig. 6.22 shows all data reported by MacKay, including data from other sources cited therein. MacKay noted that some of the diffusion coefficients presented are not for oxygen diffusion but for other gases such as nitrogen or radon. Hence, the author normalised the diffusion coefficient by the respective free air diffusion coefficient of the appropriate gas. (The diffusion coefficient in this case is also  $D_e^*$  and  $D_0$  is the free air diffusion coefficient of the appropriate gas).



Figure 6.22: Gas diffusion coefficients normalised by free air diffusion coefficients from various sources for a variety of soils types, as reported by MacKay (modified from MacKay 1997 [12])

In Fig. 6.22 a great deal of scatter is present in the data in the high saturation region compared with the low saturation region. In particular, the scatter is largest after  $S_r = 0.6$ . MacKay attributed this scatter to the variability of the connected and occluded pore space, noting that even at the same total porosity and degree of saturation, the effective porosity differs, giving a different diffusion coefficient. MacKay further noted that the scatter may mask any difference in diffusion coefficient caused by variations in soil type. In the present work, it is shown that the drainage processes giving rise to occlusion of the air phase vary with soil type (see Chapter 5) and therefore also vary the oxygen diffusion coefficient of the soil.
#### 6.4.3 Relationship of $D_e$ to water retention curve and soil compaction

The effective oxygen diffusion coefficient presented in this and previous studies has been shown to decrease differently with the degree of saturation, based on the differences in structural and textural properties of the soil media. The results of the present work show that with increasing  $S_r$  the  $D_e$  starts to drastically decrease after the  $S_r$  corresponding to the inflection point ( $S_{ri}$ ) of the water retention curve. As discussed in Chapter 5, the inflection point of the water retention curve is the point at which the continuity of the air phase and water phase change during drainage processes in soil. It was shown that towards the dry side of the inflection point, the air phase is continuous and towards the wet side of the inflection point, the air phase is occluded. As it is the air phase that contributes most to diffusion in soils, this results in a sharp decrease in  $D_e$  at saturations greater than  $S_{ri}$ .



Figure 6.23: Schematic illustrating relationship between inflection point of water retention curve, moisture regimes involved, and oxygen diffusion coefficient-saturation relationship.

Fig. 6.23 shows the relationship between the inflection point of the water retention curve and the relationship between the oxygen diffusion coefficient and degree of saturation. The moisture regimes involved during each stage are also schematically represented. The importance of the inflection point

of the water retention curve in regard to soil properties has been previously discussed by Dexter (2001-2004) [2,16,17,25] and Reynolds (2009) [18]. According to Dexter and subsequently Reynolds, the inflection point of the water retention curve corresponds to the point at which the drainage process changes from occurring in structural pores to textural pores, or vice versa. These authors also note that the structural pores are more likely to form 3-D interconnected networks. This means that the connected pathways in soil are more likely to be blocked at degrees of saturations higher than the value of  $S_{ri}$ . In a soil which is being progressively saturated, first the textural pores fill. Although the textural pores are filled, the availability of connected structural pore spaces means that the diffusion coefficient does not change significantly. However, with further increasing saturation, beyond  $S_{ri}$  when the connected pathways are filled with water, the oxygen diffusion coefficient starts to drastically decrease due to the occlusion of the air pore space. The decrease in  $D_e$  caused by the occlusion or blocking of pore paces was discussed by MacKay (1997) [24].

The difference in the degree of saturation at the inflection point between soil types was identified as the colloidal and structural properties of the soils (Chapter 5). Soils with higher colloidal properties, such as clay, tend to adsorb more water due to their larger specific surface area before filling up structural pores. The result is that the saturation at which structural pores start filling up is higher than in soils without colloidal properties, such as clean sands. It was shown in Chapter 5 that the saturation at inflection increased from sand to silt to clay with values of  $S_{ri} \approx 0.5 S_{ri} \approx 0.7$  and  $S_{ri} \approx 0.8$ , respectively. Furthermore, colloidal soils tend to form aggregated structures that enhance the wellconnected aggregate pore space that would be blocked only at higher degrees of saturation. The effect of aggregate pore structures was discussed in Section 6.1.2.3, and it was shown that the drop in the degree of saturation can be sharp at the location corresponding to the saturation at which the larger inter-aggregate pore spaces start filling up. The mechanisms presented here are able to explain the differences in the diffusion coefficient-saturation relationship observed in this study between the soil types of sand, silt and clay and also in previous studies of soils and geosynthetic clay liners.

It was further shown in Chapter 5 that the  $S_r$  at the optimum moisture for compaction (OMC) is the same as that of the inflection point. It was shown that the mechanisms of air entrapment which take place at the OMC [26,27], are the same as those which take place at the inflection point in the water retention curve. Despite the change in density and therefore void ratio and also moisture content in compacted specimens, the degree of saturation at the optimum remains the same for a given soil type. Fig. 6.24 shows the experimental standard compaction curves obtained for the sand, silt and clay soils tested in the present study.



Figure 6.24: Experimental standard compaction curves for sand, silt and clay used in this study and expected schematised curves for higher levels of compaction

Figure 6.24 also schematically shows the expected compaction curves at higher compaction efforts, where although the density and moisture content change, the degree of saturation at OMC remains approximately the same. As explained in detail in Chapter 5, the degree of saturation at the inflection point ( $S_{ri}$ ) and the degree of saturation at the OMC are the same and influence the aeration and moisture retention properties of the soil. In the present chapter it has been shown that the same properties also influence the oxygen diffusion coefficients in soils.

#### 6.4.4 Development of a new semi-empirical equation to model $D_e$ in different soils

As the inflection point of the water retention curve has been shown to govern the diffusion coefficientsaturation relationship in soils, in this section a new semi-empirical equation incorporating  $S_{ri}$ , is presented. It is envisioned that by using this equation it will be possible as a first approximate to establish the D<sub>e</sub> -  $S_r$  relationship for soil if basic information about the water retention or compaction of the soil is known.

The value for  $S_{ri}$  can be found using Eqs. 6.21 and 6.22 if the fitting parameters for either the van Genuchten (1980) or the Fredlund & Xing (1994) equations are known (see Chapter 5 for derivations).

 $S_{ri}$  derived using van Genuchten (1980) model can be written as:

$$S_{ri} = \frac{1}{\left(1 + \left(\frac{1}{m}\right)\right)^m} \tag{6.21}$$

 $S_{ri}$  approximated using Fredlund & Xing (1994) model can be written as:

$$S_{ri} = \left(\frac{1}{\left(\ln\left(e+1\right)\right)^{m}}\right) \cdot \left(1 - \frac{\ln\left(1 + \frac{\psi}{h}\right)}{\ln\left(1 + \frac{10^{6}}{h}\right)}\right)$$
(6.22)

where, *m* and *n* are curve-fitting parameters. Alternatively, if compaction data are available, the degree of saturation at OMC can be calculated to find  $S_{ri}$ .

With this information on  $S_{ri}$ , the following equation (Eq. 6.23) is proposed for the  $D_e$  vs.  $S_r$  relationship:

$$D_{e} = \frac{D_{a}^{0} \varepsilon T_{a}}{\left(1 + \exp(m(S_{r} - S_{ri}))\right)^{n}}$$
(6.23)

where,  $D_e$  is the oxygen diffusion coefficient,  $S_r$  is the degree of saturation,  $S_{ri}$  is the degree of saturation at the inflection point of the water retention curve (or at OMC) and *m* and *n* are fitting parameters (not the same as those in the water retention curve models). The term  $D_a^0 \theta_a T_a$  (where  $D_a^0$  is the free diffusion coefficient in air,  $\varepsilon$  the porosity and  $T_a$  the tortuosity) is identified as the

experimental value of  $D_e$  when  $S_r = 0$ . Hence, for the present study, the value of  $D_a^0 \theta_a T_a$  is,  $1 \times 10^{-6}$ , as shown in Fig. 6.18. The equation can be written as:

$$D_e = \frac{1 \times 10^{-6}}{\left(1 + \exp(m(S_r - S_{ri}))\right)^n}$$
(6.24)

Fig. 6.25 shows the above equation fitted to the experimental  $D_e$  values obtained in this study.



Figure 6.25: New equation given by Eq. 6.2 and its fit to experimental De values

It is clear from Fig. 6.25 that the new equation fits reasonably well the experimental  $D_e$  values obtained in this study for the diverse soil types of sand, silt and clay. The fitting parameters used for fitting Eq. 6.24 are given in Table 6.1. It is noted that the values for  $S_{ri}$  well approximate the values obtained from the water retention tests (Chapter 5).

Table 6.1: Parameters used for fitting Equation 6.24 to experimental data

	Sand	Silt	Clay
S <sub>ri</sub>	0.6	0.7	0.85
m	10	11	17
n	2.5	2.3	2.3

Fig. 6.26 shows the new equation fitted to experiemental data for two types of GCLs reported by Bouazza & Rahman 2008 [11].



Figure 6.26: New equation fitted to experimental data for GCLs reported by Bouazza and Rahman (2008 [11])

Fig. 6.27 shows the equation fitted to the experimental data from MacKay (1997) [24].



Figure 6.27: New equation fitted to experimental data reported by MacKay (1997 [24])

The new equation incorporating the inflection point of the water retention curve provides a reasonably good fit to experimental data.

#### 6.5 Conclusions

The oxygen diffusion characteristics of three diverse soil types, sand, silt and clay, were examined. The diffusion chamber method was used for conducting oxygen diffusion tests and the data were analysed using a dual-phase approach that included the contributions of both the air and water phases to the effective diffusion coefficient. Sand, silt and clay samples compacted to the same dry density at varying levels of saturation were used in the tests. The concentration-time curves were modelled numerically to evaluate the assumptions used in the calculation, and it was concluded that the calculation and numerical model yielded similar results. The numerical modelling exercise also provided additional information about the concentration profiles within the three chambers of the experimental set-up, which cannot be easily evaluated experimentally.

The effective oxygen diffusion coefficients ( $D_e$ ) calculated for sand, silt and clay were plotted against the degree of saturation ( $S_r$ ) and it was observed that the  $D_e$ - $S_r$  relationships for the three soils were different. It was further observed that the point at which the  $D_e$  starts to drastically decrease corresponds to the  $S_r$  at the inflection point of the water retention curve ( $S_{ri}$ ). The change in continuity of the air and water phases at the inflection point was identified as the reason for this behaviour. Findings presented in Chapter 5 were incorporated into the diffusion mechanisms and it was shown that the well-connected structural pores which primarily influence oxygen diffusion in soil start to fill with water when the degree of saturation exceeds that of the inflection point. As soils with colloidal properties such as clay adsorb more water before the structural pores are filled, this transition happens at a higher level of saturation for such soils. This mechanism explains the  $D_e$ - $S_r$  relationship exhibited by sand, silt and clay in relation to inflection points and their respective water retention curves.

A new equation to model the  $D_e$ - $S_r$  relationship which takes into account the influence of the inflection point was presented. The proposed equation shows a good fit to the experimental data from this study and also fits well to the experimental diffusion coefficients for different types of soils and geosynthetic clay liners (GCLs), obtained from the research literature. The results reported in this and the previous chapter elucidate the important soil properties that affect underground corrosion and are combined with the corrosion test results from Chapter 4 and are presented in the following chapter, which discusses the optimum levels of soil moisture and aeration for underground corrosion.

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## Chapter 7: A mechanistic view of the optimum soil moisture for underground corrosion

This chapter combines the findings from Chapters 4-6 to determine the influence of soil aeration and moisture on underground corrosion. The presence of an optimum soil moisture is demonstrated and the mechanisms leading to this phenomenon are discussed in detail, on the basis of experimental evidence.

## 7.1 Introduction

Previous studies have revealed that an optimum moisture level exists at which a maximum corrosion rate is attained in soil environments [1–4]. The reasons for this phenomenon are generally attributed to the coupled influences of electrical conductivity and oxygen diffusion [1,5,6], or the active area [2,7] and oxygen diffusion. The active area is the soil-metal contact area and is dependent on the soil structure and moisture distribution. Oxygen diffusion is also a soil moisture-dependent property that directly influences underground corrosion [3,8]. Although the reason for an optimum moisture level for corrosion in soil media is generally explained on the basis of the aforementioned mechanisms, the variations in optimum moisture level for different soil types in synergy with these mechanisms have not been presented or explained to date.

The moisture retention and distribution characteristics of unsaturated soils are ascertained using the relationship between the soil suction ( $\psi$ ,) negative pore water pressure, measured in kPa), and the degree of saturation. This relationship, known as the soil water retention curve (SWRC) or the soil water characteristic curve (SWCC), was described in detail in Chapter 5. [9]. The use of the SWRC in the interpretation of the variations in corrosion rates in soils has not been attempted before to the author's knowledge. Since corrosion in soil media depends on the water retention properties of soil [4,10], a detailed inspection of the SWRC and the the optimum moisture level for corrosion may provide indications of the causes of the latter.

In this chapter, the basis for the existence of the optimum moisture level, which leads to relatively high corrosion rates in soils, is provided. For this purpose, the corrosion rates of cast iron in sand, silt,

and clay were interpreted in terms of the water retention properties in these soils after measurement of their respective SWRCs.

## 7.2 Effect of degree of saturation on corrosion rates in different soil types

It was reported in Chapter 4 that the results of polarisation measurements in sand, silt and clay revealed different trends of corrosion current density with the degree of saturation ( $S_r$ ).

Fig 7.1 shows typical polarisation curves for the three soils. The data in Fig. 7.1 correspond to  $S_r \approx 0.5, 0.7, \text{ and } 0.8$  for sand, silt, and clay, respectively.



Figure 7.1: Representative polarisation curves for sand, silt and clay. These curves were obtained at the respective optimum degrees of saturation

Fig. 7.1 shows that  $E_{corr}$  and  $i_{corr}$  for the three soils at their optimum levels are different. It was also reported in Chapter 4 that while  $E_{corr}$  is influenced by interfacial properties,  $i_{corr}$  is influenced by both interfacial and bulk soil properties.

The corrosion current densities ( $i_{corr}$ ) for the three soils types at different levels of saturation are shown in Fig. 7.2. Note that the  $i_{corr}$  values are grouped into  $S_r$  bins and the respective means and standard deviations of the grouped bins are presented in Fig. 7.2. The shaded regions in Fig. 7.2 also indicate the critical regions of corrosion as identified by the experiments reported in Chapter 4.



Figure 7.2: Corrosion current density (*i*<sub>corr</sub>) for **a**) sand **b**) silt and **c**) clay at varying degrees of saturation. The regions shaded in red denote critical regions for corrosion identified by experiments

The three soil types show different levels of corrosion with  $S_r$  and the maximum corrosion rate also varies. Sand and silt exhibit the lowest and highest levels of corrosion, respectively, while clay shows intermediate levels of corrosion. Although the magnitudes of the corrosion rates are influenced by the ions present in the different soils (Table 7.1), this is not necessary for the arguments that follow in this chapter. The influence of the ionic concentrations on magnitudes of corrosion was discussed in Chapter 4, where it was argued that the presence of oxidisable species in soil may result in a higher corrosion rate due to oxidation reactions taking place in addition to the oxidation of the working electrode. This was reason identified for the high corrosion rates in silt, as evidenced by the presence of relatively high concentrations of oxidisable species, as shown in Table 7.1.

Table 7.1: Summary of major and trace ions measured in the 1:5 soil solutions for three different soils studied. Note that the valence states of the ions are not known

Soil type	<b>Cl</b> <sup>-</sup> ( <b>mg/L</b> )	NO <sup>3-</sup>	<b>SO</b> <sup>4-</sup>	Fe	Al	Mn
		(mg/L)	(mg/L)	(ppb)	(ppb)	(ppb)
Sand	4.2	15.7	0.8	11	40	1
Silt	1.9	51.8	16.4	173	291	812
Clay	37	17	160	16	49	6

Note that all three soils show a characteristic initial rise in  $i_{corr}$  with increasing  $S_r$  until a certain optimum level is reached, beyond which  $i_{corr}$  starts to decrease with further increase in saturation. This trend in corrosion rate with soil moisture has been reported previously, and the moisture level corresponding to the highest rate of corrosion was termed the critical moisture [1–4,7]. However, the results of a study across different soil types with different textural properties and their effect on the optimum moisture content have been unreported to date. The results of this study indicate that, apart from the different rates of corrosion in the three different soils, the  $S_r$  at which the optimum is reached also varies with soil type.

Fig. 7.2(a) and 7.2(b) indicate that the maximum corrosion rate in sand and silt is achieved at  $S_r = \sim 0.5$  and  $S_r = \sim 0.7$ , respectively. For clay (Fig. 7.2(c)) the maximum corrosion rate occurs at  $S_r = \sim 0.8$ . It was concluded in Chapter 4 that while variations in  $i_{corr}$  depend on bulk soil properties, the optimum degrees of saturation observed are related to the moisture retention and aeration characteristics of the soils.

## 7.3 Variations in corrosion rates and critical regions

As highlighted by the red regions in Fig. 7.2, the three soil types exhibit regions in the  $S_r$  domain, where  $i_{corr}$  is higher than at other degrees of saturation. These critical regions were demarcated by taking the mean of all the measurements and selecting the region of saturation at which the upper bound of the measurement (i.e mean plus standard deviation) is above the overall mean. The critical regions for sand, silt, and clay were  $0.4 < S_r < 0.6$ ,  $0.6 < S_r < 0.8$ , and  $0.5 < S_r < 0.8$  respectively. The highest variations in the measured  $i_{corr}$  values, denoted by the standard deviations, also occur in these critical regions. Table 7.2 summarises the mean  $i_{corr}$  and  $E_{corr}$  values along with their standard deviations measured in the critical regions.

	Sr	<i>Mean icorr</i> (μA/cm <sup>2</sup> )	Std. Dev. (μA/cm <sup>2</sup> )	$E_{corr}$	Std. Dev.
				(III V Ag/AgCI)	
	0.4	2.4	1.5	-352	35
Critical region for	0.5	3.2	1.1	-423	74
sand	0.6	2.5	1.4	-462	78
	0.62	57.2	21.8	-409	49
Critical region for	0.72	82.4	20.8	-551	49
SIIt	0.82	68.7	33.9	-623	66
Critical region for	0.53	13.6	6.0	-459	87
	0.62	15.9	6.5	-444	51
clay	0.69	24.7	8.1	-485	106
	0.8	32.3	5.4	-638	8

Table 7.2: Mean icorr, Ecorr and normalised icorr with respective standard deviations in critical regions.

The critical regions are identified as regions of degrees of saturation where the highest variability in the measured corrosion rates were observed, and these regions are therefore seen as transitional regions where small changes in saturation result in large variabilities in corrosion rates. The reasons for this phenomenon are discussed in terms of aeration and moisture regimes in soil in the following sections.

## 7.4 Soil water retention properties and their influence on corrosion behaviour

A typical water retention curve for soils and the water regimes involved at each stage as discussed in Chapter 5 are schematised in Fig. 7.3.



Figure 7.3: Schematic of soil water retention curve (SWRC) identifying continuity/discontinuity regions of air and water phases as the structural and textural pores fill or drain. Moisture retention zones and water regimes in different sections of the SWRC are also illustrated.

Three different zones are noted in each case: the boundary effect zone, the transition zone, and the residual zone. These zones are typical of all water retention curves [9] and depend on the soil's textural and structural properties [11,12]. The boundary effect zone is the region where the water is held by capillary forces with an occluded air phase. The water in this zone is said to be in the capillary regime and is relatively free to move within the largest interconnected pores known as structural pores. The residual zone is the region where water is tightly held by physico-chemical forces. The term pendular regime is given to the state of water in this zone and this water is relatively immobile [13]. Textural pores [11,12] are dominant in this regime and the residual zone can be identified in the

water retention curve by a gradual change in moisture with changing suction. The transition zone is the region where the largest change in moisture takes place for a given change in suction. The water in this zone is said to be in the funicular regime and is characterised by a change in continuity of the air and water phases. The air transition point (ATP) located in the transition zone indicates the suction or degree of saturation at which both phases are continuous and is denoted by the inflection point of the water retention curve. The connectivity of the air and water phases and the availability of the water for corrosion in these three regimes, especially the funicular regime, identified through the inflection point of the water retention curve are necessary for understanding observations regarding variations in corrosion. The effect of water phase connectivity in the funicular regime on electrical conductivity and corrosion modelling has been discussed previously [5].

The experimental SWRCs for the three soil types were generated as detailed in Chapter 5. Figure 7.4 shows the SWRCs for sand, silt, and clay. The inflection points for the water retention curves were obtained from the curve-fitting parameter "*a*" in the Fredlund-Xing equation [14], as described in Section 2.4. The inflection point of the water retention curve for sand corresponds to  $S_r = 0.5$  (Fig. 7.4(a)), which is also the saturation at which the maximum rate of corrosion was noted in sand (Fig. 7.3(a)). For silt and clay, the inflection point of the water retention curve corresponds to a saturation of  $S_r = 0.7$  (Fig.7.4(b)) and  $S_r = 0.8$  (Fig. 7.4(c)) respectively. Note that the optimum degree of saturation coincides with the inflection point of the water retention curves for the three soil types.



Figure 7.4: Soil water retention curves for (a) sand (b) silt and(c) clay showing inflection point and critical region for corrosion in each case

In all these soils, the  $i_{corr}$  becomes a maximum at the saturation corresponding to the inflection point  $(S_{ri})$  of their respective water retention curves. Furthermore, the variations in  $i_{corr}$  across all three soil types increase within the range of saturations in the vicinity of the inflection point in their respective SWRCs. The critical regions with high variations in  $i_{corr}$ , in the funicular regime are denoted by the shaded regions in the  $S_r$  scale  $(\Delta S_r)$  in Figs. 7(a)-(c). These results indicate that, while the corrosion rates tend to increase in the vicinity of the ATP (funicular regime), the maximum corrosion rate occurs at the ATP, given by the inflection point of the water retention curve. These features have not been reported to date and provide a firm basis for the importance of soil retention properties in underground corrosion.

#### 7.5 Importance of ATP and transition zone

The ATP is established as the inflection point on the water retention curve, and the inflection point is identified as the location at which the gradient of the curve changes from an increasing value to a decreasing value, or where the rate of change of the slope is  $\operatorname{zero}(d^2S_r/d\log\psi^2=0)$ . Since the gradient of the water retention curve  $(dS_r/d\log\psi)$  denotes the rate of drainage or infiltration, a change in gradient implies a change in the mechanisms related to drainage or infiltration. A major reason for this behaviour is the different moisture regimes involving two different types of pore spaces in the soil: structural pores and textural pores [11,12,15,16]. Structural pore spaces are larger and more likely to form interconnected 3-D networks [16] and are quicker to drain or fill up under the capillary regime. On the other hand, textural pores are smaller and less connected and are slower in drainage or infiltration with tightly-bound water in the pendular regime.

The inflection point in the water retention curve is the location where the drainage or infiltration changes from occurring in primarily structural pores to primarily textural pores or vice versa in the funicular regime (Fig 7.3). Therefore, the ATP given by the inflection point corresponds to the situation where both the air and water phases can be considered continuous. Since water is tightly bound to the soil particles under the pendular regime, the ionic movements are slow, resulting in reduced corrosion rates. An increase in  $S_r$  towards the funicular regime results in relatively high ionic movement, due to the freely available water. However, beyond the ATP and towards the capillary regime, oxygen availability decreases, causing a reduction in the corrosion rate. In this manner, the optimum conditions for corrosion are achieved at the ATP, where sufficient water and oxygen are freely available for corrosion to proceed.

Since the funicular regime close to the ATP is where the continuity of the air and water phases is in transition, the connective pathways for continuous air movement and the continuous water contact areas on the electrode are highly variable. This situation can be contrasted with the pendular regime, where a continuous air phase is always present, and the capillary regime, where the water phase is consistently continuous. A slight deviation of  $S_r$  from  $S_{ri}$ , can drastically change the oxygen diffusion coefficient ( $D_e$ ) in the bulk soil medium. For  $S_r < S_{ri}$ , the oxygen diffusion coefficient changes very little due to the presence of a continuous air phase. Hence, within the transition region and in the vicinity of the ATP, minor perturbations in  $S_r$  can lead to either an occluded or continuous air phase in the soil, as indicated by  $D_e$ . This was the reason presented in Chapter 6 for the different diffusion characteristics in the three soil types tested. It was shown in Chapter 6 that the  $D_e - S_r$  relationship depends on the pore structures of the soil and that the point at which De rapidly declines relates to  $S_{ri}$ .

Since underground corrosion is generally under diffusion control [17] and the oxygen flux is directly related to the corrosion current [18], variations in  $D_e$  lead to corresponding variations in  $i_{corr}$ . However, beyond a lower threshold of  $D_e$ , where oxygen flux is severely limited, the variations no longer influence corrosion rates. For this reason large variations in  $i_{corr}$  are seen only in the vicinity of the inflection point, and postulated as critical regions in underground corrosion. Figure 7.4 shows the values of  $D_e$  under different degrees of saturation for the sand, silt, and clay soils in semi-log space. For the purpose of clarity, non-parametric fits to the experimental data are also shown. The figure clearly shows that the  $D_e$  drops sharply immediately after  $S_{ri}$  for the three soils. All three soils show generally the same oxygen diffusion coefficient at low degrees of saturation, since the airflow is unhindered with continuity maintained. However, with increasing saturation, the  $D_e$  in sand drops significantly around  $S_r \approx 0.5$ , while for silt and clay significant reductions occur at  $S_r \sim 0.7$  and  $\sim 0.8$  respectively.



Figure 7.5: Oxygen diffusion in sand, silt and clay used in present study and non-parametric fit to experimental data, showing sharp drop in oxygen diffusion coefficient in region corresponding to inflection point for water retention curves of respective soils.

As the three different soils exhibit different  $S_{ri}$ , it is important to consider the properties that may cause this feature. Sand contains no colloids and has a relatively small specific surface area compared to silt and clay. The  $S_{ri} = 0.5$  for sand means that most of the water is contained within the pore space and is not utilised for any colloidal-related processes. In contrast, in silt and clay an appreciable amount of water is used for colloidal-related processes (*e.g.*, adsorption, plasticity *etc.*) [4,13]. Hence, a relatively large fraction of the water is required to overcome the colloidal-related properties of silt and clay, before free water is available to fill the pore space. This may explain the presence of the inflection point at relatively high saturation in silts and clays compared to sand. These results imply that an increase in the colloidal nature of soils tends to increase the degree of saturation at the inflection point, which corresponds to an increased optimum degree of saturation for corrosion. Although this assertion cannot be confirmed with certainty based solely on the present study, it serves as an important feature which deserves to be investigated in detail in the future. On this basis, it is expected that when sand is well graded with a mixture of particles (as commonly found in nature),  $S_{ri}$  will shift above 0.5.

#### 7.6 Further evidence from time-lapse polarisation resistance measurements

To provide further evidence of the significance of the degree of saturation at the inflection point and its variation in different soil types, results of the time-lapse polarisation resistance ( $R_p$ ) measurement are shown in Fig. 7.6. It can be clearly seen that the minimum  $R_p$  for sand, silt and clay is achieved at  $S_r$  of ~0.5, ~ 0.7, and ~ 0.8 respectively (Fig 7.6(a)). As presented in Chapter 4, the results are consistent with the potentiodynamic polarisation test results. The minimum  $R_p$ , corresponding to the maximum corrosion rate is achieved at  $S_r$ , corresponding to the inflection point of the water retention curve ( $S_{ri}$ ). This is demonstrated in Fig 7.6(b), where the measured water retention curves were used to transform the degree of saturation into soil suction. The figure shows that the suction values corresponding to the minimum  $R_p$  are 4 kPa, 71 kPa and 100 kPa for sand, silt, and clay, respectively. These suction values at the inflection points ( $\psi_i$ ) for the respective soils are obtained at the minimum  $R_p$ . Results from the polarisation resistance measurements complement the notions developed thus far regarding the importance of ATP denoted by the inflection point.



Figure 7.6: Variation in polarisation resistance with (**a**) degree of saturation and(**b**) soil suction (where vertical dashed lines correspond to suction values at respective inflection points).

## 7.7 Significance for geotechnical engineering and future outlook

The inflection point and the gradient at the inflection point of the water retention curve have been shown to correlate with many soil properties, such as hydraulic conductivity, optimum water content for tillage, plant water availability, soil structural stability and soil compaction [11,12,15,16,19]. In the case of soil compaction, it has been shown that air entrapment takes place at the optimum moisture content, giving maximum dry density for Proctor compaction (OMC) [20,21], which corresponds to the degree of saturation at the inflection point.

The present study has systematically shown that the degree of saturation corresponding to the inflection point in the SWRC ( $S_{ri}$ ) gives rise to the maximum corrosion rate possible within the entire saturation range. Fig. 7.10 shows the standard Proctor [22] compaction curves for sand, silt and clay used in this study. According to the figure the  $S_r$  at OMC are similar to the  $S_{ri}$  for all three soils. Although the dry densities vary during compaction depending on the compaction energy imparted to the soil, it has been shown that the degree of saturation at OMC remains the same with different compaction efforts and the resulting different dry densities [20,23].

The compaction curves at varying compaction efforts are schematised by the dashed lines of the same colour in Fig. 7.7. With consideration of the effect of air entrapment at the OMC during wetting [20], the implication is that the same mechanisms responsible for the optimum moisture for corrosion are in action during compaction. In addition, due to the large variations in corrosion rates observed within this optimum region, it is believed that under field conditions, the potential to form macro cells [17,24] which lead to localised damage is also the highest within the optimum moisture levels presented in the present work. Since localised damage causing patch corrosion is the main mode of pipe failure [25–27], this means that compacting to the optimum conditions is the worst scenario for a buried asset in regard to corrosion.

These observations have immediate implications for the manner by which current pipelines are installed in the field. The usual geotechnical engineering practice is to compact soils to the OMC with a view to achieving maximum density. This implies that the current practice inevitably creates the most conducive environment for corrosion damage to occur. The results presented in this chapter are expected to be useful to the wider geotechnical engineering community and enable this practice to be addressed.



Figure 7.7: Compaction curves for sand, silt and clay, showing same S<sub>r</sub> at OMC as S<sub>ri</sub> Values for soils. Also depicted in dotted lines are the expected compaction curves at higher compaction efforts, showing same OMC

The pure sand, silt and clay soil types used in this study covered the broad soil spectrum. Given the trends observed in relation to the degree of saturation at the inflection point on the SWRC and its correspondence to the maximum corrosion rate possible in that soil type, the question arises whether this is applicable to soils with mixed proportions of sand, silt, and clay. This is as an important research area that needs to be investigated further in. If it is applicable, then the  $S_{ri}$  is an important soil parameter that can serve as a good proxy for potential soil corrosivity. Furthermore, the increase in  $S_{ri}$  in different soil types with increasing colloidal features is an interesting observation. A detailed investigation of this observation in regard to the maximum corrosion rates possible in soil should be conducted in future. This will enable a mechanistic treatment of the colloidal influence on corrosion rates in soils.

## 7.8 Conclusions

The present study sought to identify the mechanisms responsible for the presence of the optimum moisture content in soil which leads to a maximum corrosion rate. Potentiodynamic polarisation and soil moisture retention experiments were conducted on sand, silt, and clay soils. It was observed that for all the soils the maximum corrosion rate occurred at the degree of saturation corresponding to the inflection point of the SWRC ( $S_{ri}$ ). It was also noted that the variations in measured corrosion current density ( $i_{corr}$ ) were the highest in the transition zone of the water retention curve in the vicinity of the inflection point. Time-lapse polarisation resistance ( $R_p$ ) and oxygen diffusion measurements were consistent with the overall significance of the degree of saturation at the inflection points on the SWRCs of the three soil samples.

Observations regarding the variations in corrosion rate with the degree of saturation were explained on the basis of the different moisture regimes, viz., pendular, funicular, and capillary. The results suggested that soils with moisture in the funicular regime cause the highest level of corrosion damage to ferrous material compared with soils with moisture in the pendular and capillary regimes. It was also found that there is a general increase in the degree of saturation at the inflection point from sand, silt, to clay. A clear correspondence of this feature with the optimum moisture content for maximum corrosion rate possibly indicates the role and importance of soil colloidal properties in underground corrosion.

Similarities in the mechanisms giving rise to the optimum moisture level in soil compaction and underground corrosion were also noted. This observation has consequences for usual geotechnical engineering practices in pipeline installation, particularly if typical compaction practices may create conditions for the highest levels of corrosion. The mechanisms explained here in light of electrochemical polarisation, soil water retention, oxygen diffusion and soil colloid properties may elucidate previous observations in the research literature.

## 7.9 References

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# Chapter 8: Modelling coupled phenomena in underground corrosion

#### **8.1 Introduction**

Underground corrosion is a process with several inter-related and coupled mechanisms. As identified in previous chapters, corrosion reactions consume water and oxygen as the primary reactants. While the consumption of oxygen is highly significant and the rate at which it is supplied controls the corrosion rate, the consumption of water is less significant. However, water plays a significant role in controlling other influential factors in soil. The amount of soil water present and its spatial and temporal distribution govern the oxygen diffusion coefficient in soil, the electrical conductivity, the metal-electrolyte contact area (active area) and the corrosion product deposition processes. The effects of soil moisture and other phenomena are coupled together and need to be considered in unison to analyse the overall consequences in terms of corrosion. As discussed previously by Mitchell (1991) [1], the coupled flow laws, including Darcian, Fickian and Laplacian, taken together are required to assess complex problems in geotechnical engineering. Underground corrosion is a problem which is influenced by these coupled phenomena. For example, the flow of water can result in a greater flux of oxygen than diffusion alone while altering the oxygen diffusion coefficient in certain areas. The flow of water also influences the electrical conductivity of the media and the electric field, which in turn governs the movement of charged species in the soil. This chapter presents a fully-coupled numerical model which connects the important features identified in the previous chapters in the process of corrosion. The aeration and moisture characteristics of soil are implemented using water retention curves and the moisture movement is considered in addition to oxygen diffusion. Therefore, the variation of the degree of saturation due to moisture flux is also directly taken into account. The new model results are compared against the results of experiments conducted on the optimum moisture content, and this model is also extended to field scale for comparison with previous models of corrosion rates in the field. Additional investigations regarding the effect of pipe size on differential aeration and the climatic influence on corrosion rates are also reported using moisture flow boundary conditions coupled with climatic changes. Finally, the effects of pH and salinity on the localisation of corrosion are investigated based on the coupled ionic movement of H<sup>+</sup> and OH<sup>-</sup>

ions under the influence of electric potential, pressure and concentration fields in the simulated soil domain. This chapter presents only the additional equations concerning the implementation of the additional mechanisms. The other governing equations are given in Chapter 3 and where modifications are made, the relevant references to the previous sections are provided.

#### 8.2 Coupling moisture flow in unsaturated soil to corrosion process

The numerical models presented previously coupled oxygen diffusion through the medium based on the degree of saturation. The degree of saturation was assumed to be homogenous throughout the soil medium and moisture movement was not considered. Moisture movement in soil may occur through gravity drainage, soil water evaporation, and also as a relatively small flux due to the consumption of water in the corrosion reactions. The movement and distribution of moisture through the soil medium influence the mechanisms of oxygen diffusion, thereby affecting the rate of corrosion.

#### 8.2.1 Modelling moisture flow in unsaturated porous media

Darcy's law is used for modelling the flow of water through saturated porous media. Darcy's law is given by Eq. 8.1:

$$v = -K(\theta)\frac{\partial H}{\partial z} \tag{8.1}$$

where, v (ms<sup>-1</sup>) is the flow rate of water, K (ms<sup>-1</sup>) is the hydraulic conductivity and  $\frac{\partial H}{\partial z}$  (dimensionless) is the hydraulic head gradient in the vertical (*z*) direction. Darcy's law has also been shown to be valid for unsaturated porous media [2,3]. In such cases, the hydraulic conductivity is not a constant but a function of the water content or the degree of saturation of the porous medium. Darcy's equation for unsaturated porous medium re-written by separating the pressure and elevation head terms (H=p+z) is given in Eq. 8.2:

$$v = -K(\theta) \frac{\partial}{\partial z} (p+z)$$
(8.2)

where, p is the pressure head and z is the elevation head. In the case of unsaturated soils, p is the head due to matrix suction ( $\psi$ ). Equation 8.2 can be solved with the appropriate boundary conditions to calculate the mass flux of water moving through soil. Similar to the oxygen consumption coupling presented in Chapter 3, the water consumed by the corrosion reactions can be coupled as a flux term through Faraday's laws. Darcy's equation can be combined with the continuity equation to derive the equation for time-dependent moisture movement [4]:

$$\frac{\partial \theta}{\partial t} = -\frac{\partial v}{\partial z} \tag{8.3}$$

Substituting Eq. 8.2 in 8.3, and rewriting the pressure head in terms of matrix suction head ( $\psi$ ) leads to Eq. 8.4:

$$\frac{\partial\theta}{\partial t} = -\frac{\partial}{\partial z} \left( -K(\theta) \frac{\partial}{\partial z} \left( \psi + z \right) \right)$$
(8.4)

which upon simplification yields Eq. 8.5:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left( K(\theta) \left( \frac{\partial \psi}{\partial z} + 1 \right) \right)$$
(8.5)

Equation 8.5 is widely known as Richards's equation and is used to model moisture flow through unsaturated soil [2].

#### 8.2.2 New coupled numerical model

#### 8.2.2.1 Equations for moisture flow and dependent phenomena

Under steady-state conditions in which uniform corrosion is taking place, the cathodic half-cell reaction consumes water, as given in Eq. 8.6:

$$O_2 + 2 H_2 O + 4 e^- \rightarrow 4 O H^-$$
(8.6)

According to the stoichiometry of Eq. 8.6, the mass flux of water lost due to corrosion can be found and related to the flux calculated from Eq. 8.1. This coupling between the moisture flow and corrosion is given by Eq. 8.7:

$$\rho . v = -\rho K(\theta) \frac{\partial H}{\partial z} = \frac{i_{02}}{zF} v_{H_2 0} m_{H_2 0}$$
(8.7)

where,  $\dot{l}_{0_2}$  (A/m<sup>2</sup>) is the cathodic current density, *F* (C/mol) is the Faraday constant, *z*=4 is the number of electrons participating in the reaction,  $m_{H_2O}$  (kg/mol) is the molar mass of water,  $V_{H_2O}$ = -2, is the stoichiometric coefficient and  $\rho$  (=1000 kg/m<sup>3</sup>) is the density of water.

Quantitatively, the mass flux of water consumed by the reaction is very small and results only in a small flow field through the soil medium. However, this flow field contributes to the oxygen transport process through advection. This means that in addition to diffusion, the Darcian velocity field also contributes to the transport of oxygen to the corroding electrode surface. The flux of oxygen reaching the corroding surface can now be expressed by Eq. 8.8:

$$J_{O_2} = -D_e \frac{\partial C_{O_2}}{\partial z} + vC_{O_2} = -D_e \frac{\partial C_{O_2}}{\partial z} - K(\theta) \frac{\partial}{\partial z} (p+z)C_{O_2}$$
(8.8)

where,  $J_{O_2}$  is the total flux of oxygen reaching the corroding metal in the vertical direction and the two additive terms are the diffusive flux and the flux due to Darcian movement, respectively.  $D_e$  is the effective diffusion coefficient of oxygen. Therefore, the new coupling between oxygen and the cathodic current density is:

$$i_{O_2} = \left(-D_e\left(\frac{\partial C_{O_2}}{\partial z}\right) - K(\theta)\frac{\partial}{\partial z}(p+z)C_{O_2}\right)zF$$
(8.9)

An important role of moisture in facilitating corrosion is the dependency of  $D_e$  on the level of moisture, which subsequently impacts the rate of corrosion according to Eq. 8.9. The gravity drainage effects and the changes in pressure between the top and bottom of the soil therefore lead to differences in saturation which in turn lead to spatial differences in the diffusion coefficient. These effects are considered in the equation presented above and improved upon in the numerical models presented previously.



Figure 8.1: Schematic representing components in fully-coupled numerical model

Figure 8.1 is a schematic illustrating the component couplings of the numerical model described above. The arrows indicate the direction of influence of the mechanisms. The dual arrows indicate cyclic dependence. For example, oxygen diffusion governs the corrosion rate, which in turn controls the flux of oxygen reaching the metal. The two arrows pointing to the same direction from the moisture movement to oxygen transport indicate the two mechanisms of transport involved *i.e,* diffusion and advection, from Darcian flow.

#### 8.2.2.2 Model set-up

The equations presented above were solved using the COMSOL Multiphysics software. An 1-D model was created to simulate the electrochemical experiments on optimum moisture content. The optimum moisture content for the three soil types was investigated and a model similar to that presented in Chapter 4, with the additional equations presented above, was implemented. The equations for oxygen and corrosion current coupling are modified according to Eq. 8.9 while the rest of the equations are the same as those presented in Chapter 4. To define the soil water retention properties that govern the moisture movement, the simplified van Genuchten equation (where m=1-1/n) was used. The Mualem criterion of m=1-1/n reduces the number of parameters associated with the equation and allows for direct input into the numerical modelling software. This simplified water retention equation is given in Eq. 8.10, where  $\psi$  is the suction head (m), and  $\alpha$  (1/m) the modified van Genuchten parameter.

$$S_r = \frac{1}{\left[1 + \left(\alpha\psi\right)^n\right]^{\left(1 - \frac{1}{n}\right)}}$$
(8.10)

where,  $S_r$  is the degree of saturation and *n* is a fitting parameter. The parameter  $\alpha$  is the inverse of the *a* parameter presented in Chapter 5 and 6 and is given as a pressure head (m) similar to the soil suction head  $\psi$  (m). The relative conductivity of soil is given by Eq. 8.11[5]:

$$K_{r} = S_{r}^{l} \left[ 1 - \left( 1 - S_{r}^{\frac{1}{m}} \right)^{m} \right]^{2}$$
(8.11)

where,  $K_r$  is the relative hydraulic conductivity (dimensionless) and l is an empirical pore parameter related to pore connectivity. The hydraulic conductivity is related to the relative conductivity as:

$$K = K_{sat}K_r \tag{8.12}$$

where,  $K_{sat}$  is the saturated hydraulic conductivity (m s<sup>-1</sup>). The  $K_{sat}$  values for sand, silt and clay were approximated using the van Genuchten parameter  $\alpha$  as detailed by Guarracino (2007) [6]. Eq. 8.13 gives the equation proposed by Guarracino (2007) after unit conversions, where  $\varepsilon$  is the porosity:

$$K_{sat} = 5.382 \times 10^{-7} \times \varepsilon \times \alpha^2 \tag{8.13}$$

The experimental water retention data fitted to Eq. 8.10 are depicted in Fig. 8.2.



Figure 8.2: Simplified van Genuchten equation fitted to experimental data and used for coupled model

The oxygen diffusion coefficients for the three soil types were defined using the new semi-empirical equation proposed in Chapter 6:

$$D_e = \frac{1 \times 10^{-6}}{\left(1 + \exp(m(S_r - S_{ri}))\right)^n}$$
(8.14)

and the electrical conductivity was defined using the power law fit presented in Chapter 4:

$$\sigma = a S_r^{\ b} \tag{8.15}$$

While the electrical conductivity does not influence uniform corrosion modelling in this section, it becomes vital for macro-cell corrosion, which is discussed in the following sections. Therefore, the

electrical conductivity-degree of saturation relationship was used as an input to the model as an important equation, regardless of the type of corrosion simulated.

The boundary conditions for oxygen and the corroding metal are the same as in the models presented previously. In addition, a pressure head boundary condition (negative pressure or suction head for unsaturated soil) was applied to the top surface of the soil to simulate different suction conditions and a parametric sweep was conducted with different levels of suction to simulate and identify the optimum moisture conditions over the simulated range of saturations.

#### 8.2.2.3 Active Area

The active area, which is the ratio between the soil electrolyte-metal contact area and the total electrode area, is a soil moisture-dependent property which has a significant impact on corrosion. In Chapter 4 it was shown that the active area for sand follows a sigmoidal trend with the degree of saturation. Findings from Chapter 7 highlighted that the water regimes and the degrees of saturation at which free water becomes available in soils are different. Therefore it was assumed that the active area sigmoid would also vary with the soil type. Sigmoids of the type given in Eq. 8.16 were used for the three soil types simulated.

$$\frac{1}{1 + \exp(c(d - S_r))} \tag{8.16}$$

where, c and d are constants (dimensionless) which vary with soil type. It is hypothesised that the parameters c and d are related to the texture and the colloidal properties of the soil. Since it was established in Chapters 5 and 7 that the inflection point of the water retention curve marks the degree of saturation at which free water becomes well connected in soil, it can be assumed that the sigmoid function given in Eq. 8.15 starts to plateau around the degree of saturation at the inflection point for the three soil types. To achieve this, the cut-off point of the sigmoid, given by d needs to have a value lower than that of the saturation of the infection point. It was shown in Chapter 4 that a model fit performed on the experimental data for sand gave a value of 0.4 for d. Therefore, the d values for sand, silt and clay were chosen to be 0.4, 0.6 and 0.7, which are 0.1 less than their respective inflection points. It is further hypothesised that the parameter c, which indicates the sharpness of the sigmoid, is related to the colloidal nature of the soil. Since sand has the lowest colloidal properties with silt and clay showing increasing colloidal nature, and since the curve fit presented in Chapter 4 yielded a value of c=10, the c values for silt and clay were chosen as 15 and 20, respectively. It should be noted that while experimental active area data for sand were used as a guide to infer the possible behaviour

of the active areas of silt and clay, this behaviour cannot be verified with certainty in the present study. However, as the following section shows, these assumptions yield reasonable estimates of the experimental results for current density for the three soils tested in this study. The active area behaviour for silt, clay and other colloidal soils is an area warranting further investigation.

Table 8.1 gives the parameters used to define the additional soil moisture-related mechanisms simulated in the proposed fully-coupled model.

	Dovomotor		Soil type		
rarameter		Sand	Silt	Clay	
Electrochemistry _	Anodic Tafel slope $A_{Fe}(V)$	0.13	0.0480	0.066	
	Cathodic Tafel slope $A_{O2}(V)$	-0.12	-0.12	-0.12	
	α (1/m)	2.41	0.5	0.16	
-	n (van Genuchten)	11	1.4	1.3	
Water retention – properties _ –	$K_{sat}$ (ms <sup>-1</sup> )	1×10 <sup>-6</sup>	5×10 <sup>-8</sup>	8×10 <sup>-9</sup>	
	Porosity	0.37	0.4	0.6	
	l	0.5	0.5	0.5	
Oxygen diffusion –	Sri	0.6	0.7	0.85	
	т	10	11	17	
	<i>n</i> (diffusion)	2.5	2.3	2.3	
Electrical	а	0.007386	0.0648	0.1456	
conductivity <sup>–</sup>	b	2.247	1.132	1.753	
Active area	С	10	15	20	
sigmoid	d	0.4	0.6	0.7	

Table 8.1: Parameter values used for fully-coupled simulation

#### 8.2.3 Model Results



Figure 8.3: Experimental results and numerical simulation results showing optimum moisture level for (**a**) sand (**b**) silt and (**c**) clay, showing reasonable agreement

Figure 8.3 shows the experimental results of the potentiodynamic polarisation tests overlaid with the results of the fully-coupled numerical simulation. Reasonable agreement between the model and the experiments is observed, and the mechanisms of moisture and aeration implemented in this model capture the trend in optimum moisture content better than the previous model presented in Chapter 4. This is evident in comparing the results for sand presented in Fig. 5.27 with those in Fig. 8.3(a). The reason for this good agreement is the ability of the model to capture the variations in the degree of saturation with depth due to gravity effects, and accurate descriptions of oxygen diffusion through variably saturated soil which depend on soil type. The water retention characteristics input into the model captured this behaviour accurately, along with the active area variations between the soil types. It was observed that the active area relationship together with the oxygen diffusion equation governs the shape of the optimum corrosion characteristic curve for the three soil types. Therefore, it is possible to change these input curves to fit the model curve to the experimental data as required. A better fit to the experimental data can be obtained using this method. This approach shows that in the absence of experimental data for oxygen diffusion and active area, a fitting process can be undertaken to find the parameters  $S_{ri}$ , m, n, c and d to obtain estimates of these relationships using the measured corrosion data alone.

As shown in Table 8.1, the anodic Tafel slopes were changed for the simulation of different soil types. The anodic Tafel slope is an indicator of the reaction kinetics for the anodic half-cell reaction, while the measured and modelled corrosion rates are the anodic current densities. Therefore, changing the Tafel slopes to match the magnitude of the measured corrosion rates was deemed to be valid. As discussed in Chapter 4, the presence of oxidisable species such as elemental iron in the soil influences the corrosion kinetics of the anodic reaction, leading to a change in the anodic Tafel slope. This was evident especially in silt, where evidence of such oxidisable species was identified using chemical analysis and related to the relatively high corrosion rate compared with the other soil types. Therefore, the anodic Tafel slope was assumed to be the parameter controlling the magnitude of the corrosion rates in these simulations.
### 8.3 Time-dependent numerical models

A 2-D time-dependent model was developed to examine the effects of moisture movement around the pipe and the effects of climate variations on underground corrosion. The effects of differential aeration due to pipe size effects were also analysed. In time-dependent models, Richard's equation is solved for the moisture flux through the soil domain, while Fick's second law is solved for oxygen diffusion together with the relevant boundary conditions and couplings described in Chapter 3 and Section 8.2.2.1 of this chapter.

As discussed in Chapter 3, the stoichiometric coefficient of  $Fe(OH)_3$  deposition was modified to depend on the spatially-varying degree of saturation to model the effects of ion migration due to the presence of a continuous water phase [7]. A value of  $S_r$ =0.75 for typical soils was chosen, as given by Eq. 3.19. The results presented in Chapter 5 showed that the degree of saturation corresponding to the point at which a continuous water phase is formed is the saturation at the inflection point of the water retention curve, denoted by  $S_{ri}$ . Hence, in the new improved coupled models, the stoichiometric coefficient  $U_{FeOH3}$  as influenced by the spatially varying degree of saturation is expressed as:

$$\nu_{FeOH3} = \frac{1}{1 + \exp(25(S_r - S_{ri}))}$$
(8.17)

where,  $S_{ri}$  is the inflection point degree of saturation and varies between the soil types of sand, silt and clay. In addition, the degree of saturation profiles also varies temporally, in contrast to the previous model, as moisture migration is calculated at each time-step.

#### 8.3.1 Influence of climatic variations on underground corrosion

As the moisture movement in soil in the coupled model is solved using pressure boundary conditions (suction head) on the soil surface, climatic variations can be simulated by representing the surface boundary conditions as time-dependent variations of surface suction. This approach was adopted by Mitchell (1979) [8] in conducting structural analyses of footings in expansive soil. It was assumed that surface suction has sinusoidal variation with time [9], with one cycle over a period of 360 days, with the lowest suction indicating wet conditions occurring during winter and dry conditions occurring during summer. Equation 8.18 was used to describe the cyclic variations in surface suction. Note that the suction value ( $u_s$ ) is in units of pF, indicating the logarithm of suction, and t is time in days:

$$u_s = 1.5\sin\left(\frac{\pi t}{180}\right) + 3.5\tag{8.18}$$

For the ensuing simulations, the silt soil type was selected and the model parameters are given in Table 8.1. Although the simulations presented in Chapter 3 utilised generic water retention curves, the present simulation utilises the experimental water retention curves, oxygen diffusion coefficients and electrical properties of silt. Silt was chosen, as it is the soil type that lies in the middle of the soil spectrum (i.e., between sand and clay) tested in this project. This approach helps bind the model results to the previously-discussed aeration and moisture retention properties of soil, and also enables comparison with the previously simulated fair aeration regime, which utilised a generic silt water retention curve in the model presented in Chapter 3.

It was observed that the time-dependent corrosion rates obtained from the model are sensitive to initial conditions of pressure head (soil suction), especially if a constant value is used throughout the soil domain. Therefore, to best approximate field conditions, where the soil at pipe level is compacted to the optimum (see Chapter 7), the pressure head profile given by Eq. 8.19 was used as the initial condition:

$$u(y) = 2 + 1.5 \exp(1.772 y) \tag{8.19}$$

Note that Eq. 8.19 is in fact in the same as Eq. 3.27 with the appropriate numerical values substituted. u(y) is the soil suction given in values of pF, and y (m) is the soil depth.

The pressure head in meters is then defined using u(y) as follows:

$$H_p = -10^{(u(y)-2)} \tag{8.20}$$

where,  $H_p$  is the pressure head (m), and the negative sign indicates negative pressure or suction. The initial degree of saturation around the pipe defined by Eq. 8.19 and 8.20 is shown in Fig. 8.4:



Figure 8.4: Initial degree of saturation for simulation of influence of time- dependent climatic effects on corrosion

Note that as shown in Fig. 8.4, the pipe is buried at a depth of 1 m and the initial conditions of degree of saturation more accurately represent field conditions of burial with the degree of saturation close to the optimum.

When the time-dependent simulation is conducted it is observed that similar to the simulation presented in Chapter 3, the onset of macro-cell corrosion causes an increase in the corrosion rate, leading to bimodal behaviour in the corrosion accumulation curve. In addition, the cyclic climatic variations appear to perturb the corrosion rates, especially at the initial stages of corrosion. During later stages, *i.e.*, beyond 6 years, a steadier rate of corrosion is observed. Fig. 8.5 shows the corrosion accumulation curve for the overall average corrosion loss, and local corrosion losses at the top and bottom of the pipe.



Figure 8.5: Corrosion accumulation curves for time-dependent simulation over period of 14 years, showing bi-modal behaviour in bottom portion of pipe and climatic perturbations during initial stages

Note that significant differences in levels of corrosion are seen at the top and bottom of the pipe due to the effects of differential aeration. Furthermore, the overall levels of corrosion observed in this simulation are higher than those reported in Fig. 3.9 in Chapter 3, where the highest levels of corrosion were observed for the fair aeration regime. It appears that climatic variations give rise to an overall increased corrosion rate. This is possibly due to the variation between high and low corrosion rates with time as opposed to a high corrosion rate from the beginning which would lead to faster passivation. The use of experimental data as inputs to the model may also have contributed to the high corrosion rates.

It can be further observed that at time t=3 years, the corrosion rate at the bottom of the pipe undergoes an increase, giving rise to the previously explained bi-modal behaviour. The reason for this effect is evident in Fig. 8.6, where the anodic bottom surface of the pipe and the current flow in soil, denoted by arrow vectors, indicate macro-cell corrosion occurring approximately 3 years from installation.



Figure 8.6: Electrolyte potential and current density vectors indicating onset of macro-cell corrosion around t=3 years

If instead of initialising the simulation with a suction profile given by Eq. 8.19, a fully- saturated condition is simulated, simular results are obtained, although with lower corrosion rates due to the lower availability of oxygen. However, the degree of saturation at pipe level gradually approaches that of the optimum condition with the continuing cyclic climatic variations. This effect is shown in Fig. 8.7.



Figure 8.7: Degree of saturation at pipe level for simulation initialised with fully-saturated conditions

However, for the approximation of field conditions, for the initial values, the pressure head profile given by Eq. 8.19 is preferred, as it better approximates the optimum conditions of compaction in a newly installed pipeline and also assists in model convergence.

#### 8.3.2 Differential aeration and pipe size effect

The macro-cell corrosion observed in the above simulation occurs due to the difference of moisture and aeration between the top and the bottom of the pipe. It follows that if the spatial separation between the top and bottom increases, the electric potential difference also increases, leading to different levels of corrosion (see Chapter 3). Once such macro-cells are established, soil resistivity comes into effect and governs the flow of the net electrolyte current through the soil. To examine these effects, a parametric sweep of the pipe diameter for a simulation without climatic perturbations was conducted. The moisture distribution was modelled using Richard's equation with a constant negative pressure head boundary condition, and gave similar results to the previous simulation, albeit without climatic effects. The different pipe sizes were assumed to be buried at the same depth with the crown of the pipe located at a depth of 1m from the ground surface. The steady-state corrosion rate after 12 years and the net electrolyte current density were examined.

Figure 8.8 shows the electrolyte potential and the current density vectors denoting the macro- cell current for two pipe sizes – 300 mm diameter and 600 mm diameter at 12 years after installation. Note that the lengths of the current arrow vectors are proportional to the magnitude of the macro-cell current.



Figure 8.8: Electrolyte potential and macr- cell current vectors for pipes of diameter 300 mm and 600 mm demonstrating effect of pipe size on differential aeration corrosion

Fig. 8.8 shows that although the crowns of the two pipes are at the same level, the differences between the top and bottom of the pipe, particularly in conditions of aeration and moisture, give rise to large potential differences (0.0.2 V potential difference in the 300 mm diameter pipe vs, 0.07 V difference in the 600 mm diameter pipe), leading to the formation of a differential aeration cell. Due to the larger electric potential differences and the supportive influence of soil conductivity, larger magnitudes of macro-cell currents are observed in the larger diameter pipe. The increase in macro-cell currents coincides with an increase in the anodic current density, which is the corrosion rate.

Figure 8.9 shows the anodic current density indicating the corrosion rate after 12 years for the different pipe diameters simulated. The corrosion rates at the top and bottom of the pipe are given.



Figure 8.9: Local corrosion current density at t=12 y, at top and bottom of pipe with varying pipe diameter showing that corrosion levels at bottom increase with increasing pipe diameter

As Fig. 8.9 reveals, the corrosion current density at the top of the pipe does not show a significant change with increasing diameter. The effect is attributed to passivation, which protects the pipe from further corrosion as described below. Passivation was modelled with the same corrosion product dynamic mechanisms presented in Chapter 3.

The increase in corrosion rate at the bottom of the pipe is caused by macro-cell activity, as stated previously. Due to the difficulty for oxygen to reach the pipe bottom, the bottom remains anodic while the passive top portion of the pipe becomes the cathode. This imbalance causes the net anodic current from the pipe to flow around the pipe (see arrow vectors in Fig. 8.8) to the cathodic top portion. This corrosion couple allows the anodic bottom to corrode further, while the top portion of the pipe, instead of undergoing corrosion, supports the corrosion of the bottom portion by reducing the oxygen which is easily diffused to the top of the pipe. With increasing pipe diameter, conditions at the top remain the same while the bottom portion becomes deeper, the anodic effects at the bottom of the pipe therefore become more pronounced, leading to higher levels of corrosion only at the bottom surface of the pipe.

## 8.4 3-D models for assessing localised corrosion in pipelines

A 3-D coupled model with moisture migration effects was developed to assess the influence on corrosion of longitudinal variations of soil conditions around the pipe. As an initial starting point, this model allowed the more accurate simulation of differential aeration effects due to a soil cover than the previous simulation presented in Chapter 3.

#### 8.4.1 Differential aeration under soil cover

The effects of differential aeration under a soil cover such as a driveway can more accurately be modelled with moisture migration equations. The moisture distribution of a pipe traversing a driveway subject to climatic conditions can be modelled using the equations presented previously. The same geometry as that given in Section 3.4.4 in Chapter 3 was used, with a partly-covered section hereafter referred to as the closed section. Figure 8.10 shows the model geometry with the closed and open surfaces and the relevant boundary conditions. The portion open to the atmosphere is referred to as the open surface (shaded in green in Fig.8.10). In addition to the zero flux boundary condition for oxygen on the closed surface, the same for water flow was also implemented to simulate the driveway. A constant negative pressure head (suction) was imposed on the open surface, to simulate a fairly aerated condition. Cyclic variations due to climate were not considered in this model.

Surface open to the atmosphere



Figure 8.10: Geometry of 3-D model highlighting main boundary conditions. Surface shaded in green is open to the atmosphere with constant concentration and pressure head boundary conditions imposed

The model was initialised with a saturated condition and was run for a period of ~14 years with a surface suction of 100 kPa (10.2 m head) corresponding to fairly aerated conditions for the silt soil type. The same water retention parameters and hydraulic conductivity for silt as in the previous simulations were used. Figure 8.11 shows the degree of saturation and the moisture flux (given by arrow vectors) at 12 yrs.



Figure 8.11: Degree of saturation and moisture flux at time t = 12 yrs. for 3-D differential aeration simulation

Fig. 8.11 indicates that the portion under the soil cover remains more highly saturated after 12 years, while the soil under the surface open to the atmosphere has a significantly lower degree of saturation. The effects of differential aeration are therefore naturally simulated by solving the equations of unsaturated water flow instead of explicitly specifying the aeration and moisture conditions as was done in the previous numerical model presented in Chapter 3. Therefore, the coupled numerical model proposed here is an improvement over the previously-presented model and is expected to closely simulate actual conditions.

Figure 8.11 also shows the water flux by means of the red arrow vectors. The water flow occurs from underneath the bottom of the soil cover towards the open surface. The water reaching the open surface is expected to be lost to processes such as evaporation. In fact, the surface boundary condition imposed on the open surface is a function of climate conditions, direct evaporation, and evapotranspiration by plants, as detailed by Rajeev et al. (2012) [10], in modelling long-term ground moisture conditions. Therefore, the present model can be viewed as a baseline model to include further effects of evapotranspiration and climatic conditions on localised corrosion due to differential aeration.

The localised corrosion due to differential aeration showed results similar to the model presented in Chapter 3 (Fig. 3.15). The corrosion loss, as in the previous model, showed the same general pattern where the bottom portion of the pipe underneath the covered region close to the edge of the cover was identified as the location with the highest cumulative loss, and therefore the most likely area for failure. Therefore, the corrosion accumulation curves were generated for the present model at four points in this critical region. However, compared with the previous model (see Fig 3.15), the critical region tended to be more spread out on the pipe surface in the present simulation. Figure 8.12 shows the corrosion accumulation curves for the four selected points in the critical region and the pipe surface with the cumulative mass loss mapped into a colour scale in the inset.



Figure 8.12: Critical region of corrosion (corrosion hotspot) and corrosion mass loss curves for three points within critical region in fully-coupled differential aeration simulation

Figure 8.12 shows that the total levels of corrosion are higher on the bottom surface of the pipe than on the top, and this is consistent with the previous observations. The bi-modal feature observed in the mass loss curves for the bottom portion of the pipe is more prominent in the present simulation than in the previous simulation, while also showing an overall higher rate of corrosion.

#### 8.4.2 Inferences on coupled effect of salinity and pH in underground corrosion

The same simulation presented above was used to evaluate the coupled influence of pH and salinity. This exercise was conducted with the goal of identifying the possible influence of salinity and pH in the localisation of corrosion. Instead of evaluating the direct influences of salinity and pH on the magnitude of the corrosion rates, as has been reported previously [11,12], the present approach is to evaluate the possibility of the pH and salinity leading to the formation of localised corrosion patch. This is achieved by modelling the local variations of pH and salinity under the soil conditions created in the model.

Since pH and salinity are essentially the ionic concentrations of  $H^+$  and  $Cl^-$  ions within the soil medium, the time-dependent concentrations of these ionic species as they mobilise due to the concentration and electric potential gradients can be established. Based on the spatial variations of the concentrations, and the known effects of pH and salinity on corrosion rates [12,13], inferences regarding the extent of local damage can be drawn. The equations for the mechanistic influence of pH and salinity on the actual corrosion reactions are not included in this model due to their complexity and will be discussed in future work. However, the present model enables the evaluation of the possible effects of pH and salinity under realistic field conditions and their role in pipeline degradation.

pH is defined as the negative logarithm of the molar concentration of  $H^+$  ions in solution. It is assumed that the soil domain initially has a neutral pH corresponding to an  $H^+$  concentration of  $10^{-7}$  M and this only changes due to the migration of  $H^+$  under the electric field created by the corrosion process. The soil water solution is assumed to the same electrolyte as that used for the electrochemical experiments (Chapter 4) and therefore was assumed to have a Cl<sup>-</sup> concentration of  $10^{-3}$  M. The chloride ions would also migrate under the same electric field, changing the spatial concentration within the soil. The ionic migration effect can be included in the overall mass transport equation and is called the Nernst-Planck equation [14].

The Nernst-Planck equation for the vertical direction for a given chemical species gives the total flux of a chemical species as the summation of diffusion, advection and ionic migration, and is given by Eq. 8.21:

$$J_{i} = -D_{i} \frac{\partial C_{i}}{\partial z} + vC_{i} + z_{i}u_{i}C_{i} \frac{\partial \phi}{\partial z}$$
(8.21)

where, similar to Eq. 8.8,  $J_i$  (mol m<sup>-2</sup>s<sup>-1</sup>) is the total flux of the chemical species *i*,  $C_i$  (mol m<sup>-3</sup>) is the concentration, v (m s<sup>-1</sup>) is the velocity of the electrolyte (Darcian flow from Richard's equation),  $z_i$  (dimensionless) is the charge number,  $u_i$  is the ionic mobility, and  $\phi$  (V) is the electric potential. Using the Nernst-Einstein relationship [14], the ionic mobility can be directly related to the diffusivity, as given by Eq. 8.22:

$$u_i = D_i \frac{F}{RT} \tag{8.22}$$

where, F (C mol<sup>-1</sup>) is the Faraday constant, R (J K<sup>-1</sup> mol<sup>-1</sup>) is the universal gas constant and T (K) is the temperature in Kelvin. By substituting the Nernst-Einstein relation into Eq. 8.21, the following final equation for mass transport of chemical species in the soil medium is obtained (Eq. 8.23):

$$J_{i} = -D_{i}\frac{\partial C_{i}}{\partial z} + vC_{i} + z_{i}D_{i}\frac{F}{RT}C_{i}\frac{\partial\phi}{\partial z}$$
(8.23)

Eq. 8.23 was used together with the equations described Section 8.2 to model the time- dependent spatial concentrations of the  $H^+$  and  $Cl^-$  ions influenced by diffusion, advection and ionic migration in the soil medium.

The free solution diffusivities for the H<sup>+</sup> and Cl<sup>-</sup> ions were obtained from the research literature [14] and were converted to effective diffusivities by multiplying them by the volumetric water content  $(n \times S_r)$ , assuming the effective diffusivity relationship proposed by Shackelford and Daniel (1991) [15] with tortuosity and fluidity factors equal to 1, for simplicity. Note that the degree of saturation and therefore the volumetric water content is not a constant value and varies spatially and temporally according to the solution to Richard's equation.

The negative logarithm of the H+ concentrations expressed in terms of molarity is the pH value. Figure 8.13 shows the calculated spatial variation of pH within the soil at time t=12 yrs.



Figure 8.13: Spatial variation of pH after t=12 yrs. beginning from neutral pH conditions at time t=0. (Top surface extending from x=0 to x=5 is covered region similar to previous simulations)

Fig. 8.13 shows that the pH in soil under the covered region approaches alkaline values while under open conditions it approaches acidic values. Given that acidic conditions result in overall higher rates of corrosion, it can be deduced that the open region is more susceptible to corrosion. However, the variations are only slight and therefore the overall effect on corrosion may be less significant than other processes.



Figure 8.14 shows the spatial variation of the Cl<sup>-</sup> concentration at t=12 yrs.

Figure 8.14: Spatial variation of Cl<sup>-</sup> concentration after t=12 yrs. (Top surface extending from x=0 to x=5 is covered region similar to previous simulations)

Figure 8.14 shows that the chloride concentration is highest at the bottom portion of the pipe under the covered region. Since chlorides are known to break down the passive layer and participate in corrosion reactions [13,16], while also leading to an increase in the electrical conductivity of the electrolyte, it can be concluded that the presence of higher levels of salinity in soil supports the localisation of corrosion in the anodic region. In addition, note that the Cl<sup>-</sup> concentration at the top surface at the edge of the soil cover is slightly higher than the rest of the soil. This is due to the effect of advection by the Darcian velocity field which transports Cl<sup>-</sup> with moving water (see Fig 8.11). This illustrates the capabilities of the coupled model presented here.

While the actual influence of pH and chlorides on the magnitude of the corrosion rates is not simulated in this model, the spatial variations arising from the coupled flow processes yield important insights about the expected levels of localisation. The overall effect of pH and chlorides subjected to coupled flow is likely to accentuate the corrosion localisation trends observed previously. Furthermore, the interaction of Cl<sup>-</sup> and H<sup>+</sup> ions with the corrosion products formed and the surrounding soil are greater in these localised regions and their mechanistic implementation forms the basis for future research.

## 8.5 Scope for future work

The work presented here has yielded additional directions for future work in the simulation of the coupled phenomena related to underground corrosion. These areas and the possible methods of application are discussed in this section.

The effect of soil salinity on corrosion is two-fold. Salinity has a direct influence on electrical conductivity and also participates in the corrosion reaction and leads to the breakdown of the passive layer. It was shown in the previous section that salinity varies spatially based on the coupled flows occurring in the soil medium. This effect must be included in the soil moisture- dependent electrical conductivity equation. The equations that quantify the effects of the chloride concentration on the breakdown of the passivity effects and the interaction with the surrounding medium are not fully developed, but and once they are available they can be implemented in a similar fashion to the moisture-dependent corrosion product dynamics equations. Similar comments are applicable to pH. In using the existing equations relating pH to the equilibrium potential for oxygen reduction the influence pH can be included, but these equations need to be verified experimentally.

As local variations in electrical conductivity affect macro-cell corrosion, it is necessary to evaluate the changes to soil conductivity in the vicinity of the pipe by the diffusing ionic species created by the corrosion reactions. These ions tend to deposit in the soil around the pipe, changing the properties of the soil, including its conductivity and water retention properties. Soil which undergoes this change manifests as a cemented soil crust that surrounds the pipe in very old pipelines and this has been observed in several cases in the field (see Chapter 1).

It was shown in Chapter 7 that due to variations in the funicular regime in the vicinity of the inflection point, any small variations in moisture may lead to drastic alterations to the continuity of the air phase and therefore large variations in corrosion rates. This effect was identified as one of the mechanisms leading to localised corrosion due to macro-cells in the absence of external factors such as driveways or the water table. The implication was that the natural variations in soil compacted close to optimum alone may lead to such macro-cells. This hypothesis can be tested using the fully-coupled numerical model presented here if the natural variations in soil properties are implemented. This could be achieved by inputting the soil properties into the model as random fields instead of using static soil properties as inputs. This would allow the testing of the likelihood of macro-cell corrosion occurring close to optimum conditions, further reinforcing experimental observations.

## 8.6 Conclusions

This chapter has presented a fully-coupled numerical model for corrosion in soils coupling moisture flow, oxygen diffusion, ionic migration, electrochemistry and their inter-relationships. Solving the governing equations for moisture flow and advection is an improvement over previous models, where soil moisture conditions were explicitly input into the model. The new coupled model has been shown to better approximate the experiential results for the optimum moisture content for the three soils. The limitations identified in Chapter 4 in modelling the optimum moisture experiments were overcome by including gravity drainage effects. The moisture retention properties of the three soil types obtained from experiments were used as inputs into the model, yielding very good agreement with the experimental corrosion data.

The corrosion model with moisture migration equations was extended to the field scale to simulate field conditions for moisture and aeration. In the previous models presented in Chapter 3, the moisture profiles were static input parameters based on the SWRCs. By solving Richard's equation with the appropriate boundary conditions, it was shown that the modelled moisture profiles are very similar to the approximated ones, and that similar levels of corrosion are obtained by simulating a fairly aerated regime using silt. Climatic variations and their influence on underground corrosion were simulated by implementing cyclic boundary conditions for surface soil suction. It was observed that the climatic effects perturb the corrosion rates in the initial stages while a steady corrosion rate independent of climatic variations is achieved after a certain period of time. The effect of pipe size on the severity of differential aeration corrosion leading to localised corrosion on the bottom portion of the pipe was also investigated. Increasing pipe size was shown to be detrimental in terms of damage due to differential aeration cells.

A 3-D numerical model to evaluate differential aeration due to partial soil cover such as a driveway was developed similar to that presented in Chapter 3. Comparable results were obtained, although with slightly higher levels of corrosion. The bi-modal trend observed and explained previously was found to be more pronounced in the new coupled simulation. The same 3-D model was used to observe the effects of pH and salinity localisation due to the coupled flows arising due to differential aeration corrosion. It was concluded that the overall effect of pH and salinity is to accentuate already-established trends. The mechanistic influence of pH and salinity along with the implementation of other factors were identified as possible areas for future research.

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## **Chapter 9: Conclusions and recommendations**

#### 9.1 Conclusions and contributions of this study

This study was conducted with the objective of evaluating the influence of the aeration and moisture properties of soil in relation to underground corrosion. Since corrosion in soil is a multidisciplinary problem, a multifaceted research approach was undertaken to reconcile the main phenomenological observations. The experiments and modelling work undertaken helped to bridge the gap between geotechnical engineering and applied electrochemistry, and yielded important findings. The main conclusions and contributions of this study can be summarised as follows:

- A mechanistic understanding of underground corrosion was developed and incorporated in numerical models. Soil moisture and aeration properties were found to influence the main governing processes, including the active area, electrical conductivity and oxygen diffusion in underground corrosion. Realistic simulation of these influential mechanisms paved the way for numerical models validated by field observations. New methods of simulating metal passivation leading to the natural evolution of corrosion from uniform micro-cell corrosion to localised macro-cell corrosion were developed for these numerical models.
- 2. The mechanisms of the optimum moisture content for underground corrosion were identified. It was shown that corrosion is maximised at the air transition point given by the inflection point of the soil water retention curve. The change in continuity of the air phase at this air transition point was identified as the main mechanism leading to the observed optimum moisture content. Results from two different electrochemical measurements, potentiodynamic polarisation and time-lapse polarization resistance, were used to reach this conclusion. The time-lapse polarisation resistance measurement is a new development arising from this work and a novel method of assessing the corrosivity of different soil types. It was further shown that the variations in measured corrosion rate are also highest at a region in the vicinity of the air transition point termed the critical region for corrosion. New findings relating moisture retention properties to corrosion were incorporated into improved coupled numerical models.

- 3. The combined findings of oxygen diffusion experiments and soil water retention tests further verified these reasons for the phenomena of optimum moisture for corrosion. Oxygen diffusion tests indicated that the degree of saturation at the inflection point of the water retention curve is the same degree of saturation beyond which the oxygen diffusion coefficient starts to rapidly decline. The relationship between the diffusion coefficient and the degree of saturation was found to vary between the three diverse soil types and a new semi-empirical equation was proposed to model this soil- dependent relationship. The soil water retention curve is a property unique to a given soil type, irrespective of the level of compaction. It was also found that this degree of saturation tends to increase from sand through silt to clay, and the reason for this trend was identified as the colloidal properties of the soils.
- 4. Results of standard compaction tests of the three soils revealed that the degree of saturation at the optimum moisture content for compaction, (OMC), is the same as the degree of saturation at the inflection point, and the highest corrosion observed in electrochemical tests. The previously-reported mechanisms relating to the compaction curve of soil were consistent with those identified through the water retention curves and it was concluded that the degree of saturation at the optimum moisture content remains the same, irrespective of the level of compaction of the soil. Indirect evidence for this was obtained from pore size distributions extracted from micro X-ray CT images of compacted silt.
- 5. Based on this multidisciplinary study, possible weaknesses in current soil compaction practices in underground metallic infrastructure were reported. Results of electrochemical, oxygen diffusion, soil moisture retention and soil compaction tests indicated that the moisture content to which soil is compacted in usual practice with the intention of maximising the dry density is the same moisture content for which the highest levels of corrosion are observed for a given soil type. It was further observed that the region around this optimum is also where the highest variations in corrosion rates occur, which eventually lead to macro-cell formation. This implies that compacting soil to optimum conditions as in standard practice creates the most conducive conditions for failure in buried metallic infrastructure. Therefore, this common practice of geotechnical engineering needs to be re-evaluated.

## 9.2 Directions for future research

The present work was conducted on three diverse soil types spanning the general soil spectrum. Several areas were identified which would further extend the findings of this work to provide a general and complete description valid for all soil types. These areas are identified as follows:

- 1. The degree of saturation at the inflection point on the water retention is found to increase from sand, silt to clay and the reason is the colloidal nature of the soils. A detailed analysis of the influence of soil colloids on corrosion could be conducted, especially by combining varying fractions of sand, silt and clay, and testing natural soils for the inflection points of their water retention curves and levels of corrosivity. Soils with varying levels of salinity could also be tested to ascertain the influence on corrosion, along with the moisture retention characteristics due to variations in osmotic suction.
- 2. The air transition point was identified as the point at which the continuity of the air and water phases change in a soil undergoing drainage or infiltration. It was noted that at the air transition point the drainage or infiltration changes from occurring primarily in structural pores to occurring in textural pores, and vice versa. This change reflects a change in the gradient of the water retention curve and the inflection point therefore denotes the air transition point. While indirect evidence for this claim was obtained using oxygen diffusion tests and micro X-Ray CT imaging, this phenomenon could be verified by imaging both the air and water phases in soil and establishing their degrees of connectivity for varying moisture contents.
- 3. The coupled numerical models presented in the final chapter ended with the assessment of the possible mechanistic influence of pH and salinity of soil. The influence of pH and especially salinity on corrosion is complex, with several inter-related factors. While the some of the mechanisms, such as passive layer breakdown, catalytic reactions and soil property modifications are known, the equations governing these behaviours are not fully defined as yet. If mechanistic or empirical equations approximating these complex features are developed, they could also be incorporated in the fully-coupled model, providing a complete description of corrosion in soils.
- 4. The inherent variability of soil leading to variations in transport mechanisms and therefore corrosion rates within the funicular regime in soil can be factored into the numerical models

by using random fields for soil property inputs instead of constants. These random field inputs will manifest as variations in corrosion rates due to natural ground variations through the equations in the coupled model. This approach would be a realistic estimation of field conditions of corrosion and could explain the creation of corrosion hotspots in soil where no external factors such as soil covers or tree roots are present. In addition to closely approximating natural ground conditions such stochastic efforts would also be useful in pipeline condition assessment in the field.

5. While localised corrosion under field conditions was primarily assessed using numerical models in this thesis, recent experimental developments on electrode array techniques such as the wire beam electrode are expected provide further insights into the mechanisms of localised corrosion. These laboratory electrode array techniques could be extended and modified to investigate phenomena such as corrosion patch formation on pipelines in field scale. Such methods could be used for assessing model predictions, and also for investigating the effects of pH, salinity, soil type and pipe metal passivation behaviour and their influence on localised corrosion.

# Appendices

## Appendix A: Electrochemical measurement data

A1 - Selected polarisation curves for clay silt and sand from  $S_r=0$  to  $S_r=1$ 

Key:  $E_{WE}$  (V) – Working electrode potential  $i (\mu A/cm^2)$  – Working electrode current density  $\log|i(\mu A/cm^2)|$  – logarithm of the absolute value (ignoring the sign of the anodiccathodic current) of the working electrode current density

Clay





## A2 – All Polarisation test data for clay silt and sand

Clay

empty	filled cell		Moisture	Content		Den	sity			Corro	sion
cell weight (g)	weight (g)	bulk+tin (g)	dry+tin (g)	Tin (g)	moisture content	bulk density (kgm <sup>-3</sup> )	dry density (kgm <sup>-3</sup> )	Void ratio	Sr	i <sub>corr</sub> (μAcm <sup>-2</sup> )	Ecorr (mV)
282.43	366.13	13.69	12.8	7.01	0.154	1067.57	925.33	1.86	0.22	5.1	-308
282.21	365.5	16.57	15.36	7.36	0.151	1062.34	922.77	1.87	0.21	1.4	-244
259.9	340.9	15.96	14.76	6.7	0.149	1033.13	899.25	1.95	0.20	7.7	-286
284.52	384.28	17.07	15.15	7.01	0.236	1272.41	1029.56	1.57	0.40	3.2	-284
283.99	390.63	16.16	14.54	7.37	0.226	1360.16	1109.48	1.39	0.43	4.4	-297
259.72	366.15	15.8	14.1	6.72	0.230	1357.48	1103.33	1.40	0.44	8.3	-309
286	367.31	15.61	15.24	7.01	0.045	1037.09	992.47	1.67	0.07	6.7	-332
287.47	373.98	14.62	14.28	7.37	0.049	1103.41	1051.66	1.52	0.09	6.1	-356
263.04	342.18	13.98	13.71	6.71	0.039	1009.41	971.92	1.73	0.06	2.1	-332
284.63	395.75	16.95	14.84	7.01	0.269	1417.30	1116.45	1.37	0.52	12.8	-402
286.69	405.09	20.93	17.99	7.38	0.277	1510.16	1182.49	1.24	0.59	14.1	-455
262.68	371.68	18.63	16.09	6.71	0.271	1390.26	1094.02	1.42	0.50	14.6	-499
286.08	425.64	21.2	17.29	7.01	0.380	1780.05	1289.56	1.05	0.96	6.8	-763
289.97	426.27	23.37	18.96	7.38	0.381	1738.47	1259.00	1.10	0.91	7.5	-781
262.49	403.94	20.38	16.64	6.7	0.376	1804.15	1310.91	1.02	0.98	8.0	-749
286.18	390.45	14.68	13.65	7.01	0.155	1329.93	1151.34	1.30	0.32	7.3	-272
287.61	386.44	17.56	16.25	7.38	0.148	1260.55	1098.34	1.41	0.28	4.0	-281
261.69	363.08	13.45	12.59	6.71	0.146	1293.20	1128.19	1.35	0.29	6.2	-312
286.76	401.99	15.23	13.31	7.01	0.305	1469.73	1126.43	1.35	0.60	13.2	-439
288.56	399.19	18.88	16.23	7.41	0.300	1411.05	1085.05	1.44	0.55	16.8	-530
263.4	368.7	14.48	12.75	6.71	0.286	1343.07	1044.03	1.54	0.49	21.0	-548
284.62	405.56	18.7	15.81	7.01	0.328	1542.55	1161.20	1.28	0.68	31.9	-327
260.09	379.96	18.01	15.24	6.7	0.324	1528.91	1154.45	1.30	0.66	33.9	-531
282.57	406.19	18.78	16	7.26	0.318	1576.74	1196.24	1.22	0.69	20.2	-576
281.67	415.86	19.35	15.89	7.26	0.401	1711.55	1221.73	1.17	0.91	7.4	-737
284.66	406.38	14.87	13.16	7.26	0.290	1552.50	1203.65	1.20	0.64	26.6	-512
283.7	412.78	17.12	14.48	6.76	0.342	1646.38	1226.84	1.16	0.78	38.2	-645
261.1	350	15.5	14	7.23	0.222	1133.89	928.23	1.85	0.32	0.8	-244
260.96	331.66	13.14	12.45	7.12	0.129	901.76	798.40	2.32	0.15	3.3	-267
263	354.1	16.85	14.76	6.76	0.261	1161.95	921.27	1.88	0.37	1.0	-282
261.7	404.35	22.97	18.74	8.77	0.424	1819.46	1277.47	1.07	1.05	3.5	-759
263.6	353.56	14	12.92	7.26	0.191	1147.41	963.56	1.75	0.29	1.5	-278
261.41	361.43	13.39	12.34	7.23	0.205	1275.73	1058.27	1.50	0.36	3.2	-291
263.14	373.38	18.82	16.33	8.55	0.320	1406.08	1065.17	1.49	0.57	3.0	-318
260.82	387.68	14.36	12.4	7.25	0.381	1618.06	1172.01	1.26	0.80	33.5	-626
263.03	389.86	12.72	10.48	6.76	0.602	1617.68	1009.69	1.62	0.98	3.7	-865
260.86	362.98	16.11	14.79	8.76	0.219	1302.51	1068.59	1.48	0.39	1.9	-302
263.37	391.56	13	10.91	7.26	0.573	1635.03	1039.69	1.55	0.98	3.4	-878
260.44	387.96	15.35	13.42	8.53	0.395	1626.48	1166.20	1.27	0.82	25.1	-642
262.94	379.68	16.2	13.9	7.12	0.339	1488.99	1111.82	1.38	0.65	9.5	-370
260.02	378.91	15.43	13.4	7.21	0.328	1516.41	1141.92	1.32	0.66	11.8	-395
262.75	384.71	16.49	14.04	7.37	0.367	1555.56	1137.68	1.33	0.73	25.9	-597

Silt											
empty	filled		Moistur	e Content		Der	isity	Void	$S_r$	Corros	sion
cell weight	cell weight	bulk+tin	dry+tin	tin	moisture content	bulk density	dry density	ratio		i <sub>corr</sub> (μAcm <sup>-2</sup> )	Ecorr (mV)
285.73	434.28	29.93	26.82	10.91	0.20	1894.7	1584.9	0.67	0.77	58.0	-567
293.84	416.57	25.74	24.21	10.82	0.11	1565.4	1404.9	0.89	0.34	11.0	-394
293.94	407.56	27.7	26.81	10.7	0.06	1449.2	1373.3	0.93	0.16	12.8	-325
292.98	415.58	27.87	26.78	10.88	0.07	1563.7	1463.4	0.81	0.22	10.2	-343
292.14	425.67	33.71	30.4	10.89	0.17	1703.1	1456.1	0.82	0.55	30.7	-423
292.1	429.55	40.25	32.49	10.7	0.36	1753.1	1292.8	1.05	0.90	4.1	-724
299.06	444.97	45.03	38.24	10.81	0.25	1861.0	1491.8	0.78	0.84	5.4	-757
285.28	404.02	26.37	25.3	10.77	0.07	1514.5	1410.6	0.88	0.22	2.7	-352
290.64	429.92	31.77	28.64	10.81	0.18	1776.5	1511.2	0.75	0.62	31.2	-377
290.71	422.38	27.99	25.76	10.89	0.15	1679.4	1460.4	0.81	0.49	56.3	-341
285.83	411.68	30.23	28.28	10.76	0.11	1605.2	1444.4	0.83	0.35	9.2	-361
286.15	438.14	37.2	32.9	10.81	0.19	1938.6	1622.7	0.63	0.81	46.3	-639
285.64	409.93	29.39	28.02	10.69	0.08	1585.3	1469.1	0.80	0.26	3.9	-349
286.7	435.06	39.29	33.44	10.65	0.26	1892.3	1505.8	0.76	0.90	6.3	-783
288.06	426.48	30.63	27.97	10.78	0.15	1765.5	1528.9	0.73	0.56	37.3	-375
287.5	432.09	38.68	34.56	10.89	0.17	1844.2	1570.8	0.69	0.67	91.7	-471
287.73	432.57	37.69	33.55	10.82	0.18	1847.4	1562.8	0.70	0.69	111.7	-560
288.6	439.9	93.5	83.1	31.4	0.20	1929.8	1606.6	0.65	0.82	77.3	-627
288.14	410.33	29.43	28.4	10.89	0.06	1558.5	1471.9	0.80	0.19	7.2	-341
283.09	416.69	31.77	29.41	10.91	0.13	1704.0	1511.2	0.75	0.45	43.7	-372
282.73	408.36	31.03	29.26	10.91	0.10	1602.4	1461.4	0.81	0.31	9.8	-317
283.95	422	40.2	36.85	10.79	0.13	1760.8	1560.2	0.70	0.49	9.8	-356
283	420.21	33.12	30.59	10.9	0.13	1750.1	1550.8	0.71	0.48	12.9	-366
282.64	427.13	37.96	34.07	10.9	0.17	1842.9	1578.0	0.68	0.65	67.3	-460
283.44	420.46	29.55	27.11	10.8	0.15	1747.7	1520.2	0.74	0.53	18.5	-336
282.33	400.62	30.47	29.4	10.68	0.06	1508.8	1427.2	0.86	0.18	4.5	-333
283.15	429.09	30.1	27.53	10.78	0.15	1861.4	1613.8	0.64	0.63	92.0	-477
283.93	406.98	31.83	30.43	10.9	0.07	1569.5	1464.5	0.81	0.23	7.1	-328
285	429	33.4	30.3	12.2	0.17	1836.7	1568.1	0.69	0.66	58.3	-357
282.52	402.13	26.45	25.87	10.77	0.04	1525.6	1469.2	0.80	0.13	14.0	-301
284.89	436.88	36.6	32.45	10.81	0.19	1938.6	1626.6	0.63	0.81	103.7	-581
285.1	402.3	34.8	33.8	12.2	0.05	1494.9	1428.7	0.85	0.14	5.1	-308
281.95	403.32	29.28	27.96	10.81	0.08	1548.0	1437.4	0.84	0.24	11.2	-318
282.95	416.29	32.82	30.5	10.91	0.12	1700.7	1520.6	0.74	0.42	8.4	-345
286.13	418.98	28.6	26.68	10.81	0.12	1694.5	1511.6	0.75	0.43	15.9	-354
283.23	419.11	28.23	26.07	10.83	0.14	1733.1	1518.0	0.75	0.50	11.3	-237
282.03	401.88	29.85	29.18	10.81	0.04	1528.7	1474.9	0.80	0.12	5.6	-290
283.88	402.96	31.68	30.4	10.82	0.07	1518.8	1425.6	0.86	0.20	5.8	-307
286.53	412.95	28.15	26.52	10.91	0.10	1612.5	1460.0	0.82	0.34	6.5	-360
284.3	415.83	32.2	29.88	10.88	0.12	1677.6	1495.1	0.77	0.42	9.8	-327
282.32	429.83	36.97	32.76	10.88	0.19	1881.4	1577.8	0.68	0.75	68.3	-604
283.16	434.36	32.84	29.3	10.83	0.19	1928.5	1618.3	0.64	0.80	99.7	-569
281.97	433.2	32.07	28.59	10.81	0.20	1928.9	1613.2	0.64	0.81	79.7	-563

#### Sand

Sr	Corrosion					
	icorr	Ecorr				
0.1	3.129	-400.929				
0.1	2.867	-384.377				
0.1	0.074	-427.292				
0.2	4.642	-369.658				
0.2	3.941	-259.883				
0.2	1.313	-460.922				
0.3	2.269	-336.19				
0.3	4.447	-377.878				
0.3	4.659	-496.929				
0.4	3.177	-309.465				
0.4	13.327	-396.108				
0.4	5.2	-351.117				
0.5	10.002	-430.236				
0.5	5.028	-329.178				
0.5	13.35	-509.146				
0.6	2.931	-387.886				
0.6	6.54	-429.006				
0.6	13.195	-570.151				
0.7	5.982	-697.003				
0.7	3.566	-837.373				
0.7	2.683	-715.066				
0.8	3.403	-824.961				
0.8	4.413	-683.41				
0.8	2.725	-737.599				
0.9	2.392	-863.962				
0.9	6.339	-753.322				
0.9	4.403	-768.283				
1	4.469	-886.356				
1	3.376	-810.392				
1	2.918	-741.287				

Since the fine sand used in these experiments was quick to equilibrate with water, unlike silt and clay, a different preparation method was used. For each test 115 g of dry sand was measured and thoroughly mixed with predetermined volumes of water measured with a pipette to achieve the required degree of saturation.

The void ratio (*e*) and dry density ( $\rho_d$ ) for sand are as follows:

*e* =0.85

 $\rho_d = 1450 \text{ kg/m}^3$ 

### A3 – Adopted experimental preparation methods for electrochemical tests

#### Electrical conductivity tests (Using IP test cell)

Sample holder Diameter = 39.4mm Height=120mm Volume: 1.4631e-4 m3

Required properties: e = 0.85,  $\rho_d = 1450 \text{ kg/m}^3$ 

#### Sand preparation Method

- Measure 210g of sand using electronic balance
- Pour sand onto the glass sheet in a circular pattern with some space in the centre
- Measure out the required volume of water using the pipette.
  - The volume of water depends on the required degree of saturation such that,
  - Volume of water = Sr\*67ml
  - Eg: for Sr=0.5, Volume required = 0.5\*67 = 33.5ml
- Pour the water into the centre region of the sand so that no water is lost due to flowing out of the glass sheet
- Mix well with the spatula until the sand is wetted uniformly
- Pack the wet sand into the sample holder in layers compacting each layer using the back of the spatula and scarifying between each layer to ensure good contact
- Secure the top of the sample holder to make good contact with the sand
- Insert electrodes and carry out the test



#### Polarisation, LPR and IP tests (Using 3D printed cell)

Sample holder

Diameter = 55 mm Height= 33 mm Volume: 7.84024e-5 m<sup>3</sup>

Required properties: e = 0.85,  $\rho_d = 1450 \text{ kg/m}^3$ 

#### **Cell preparation**

• Insert the working electrode wire through the grove at the bottom of the cell and pull it out

through the wire channel

• Secure the working electrode in the circular space so that the

metal surface is exposed and the surfaces are level



#### Sand preparation Method

- Measure 115 g of dry sand using electronic balance
- Pour sand onto the glass sheet in a circular pattern with some space in the centre
- Measure out the required volume of water using the pipette.
  - The volume of water depends on the required degree of saturation such that,
  - Volume of water =  $S_r$ \*36.14ml
  - Eg: for  $S_r=0.5$ , Volume required = 0.5\*36.14 = 18.1 ml
- Pour the water into the centre region of the sand so that no water is lost due to flowing out of the glass sheet
- Mix well with the spatula until the sand is wetted uniformly
- Pack the wet sand into the cell in 3 layers compacting each

layer using compacting rod and scarifying between each layer to ensure good contact

• Secure the top of the cell cap and insert electrodes in the spaces in the cap and conduct test

#### Silt and clay preparation method for all tests

• Measure a weight of approximately 15% more than the dry soil solids required for

maintaining dry density for the particular test\*, using an electronic balance.

• Add the required amount of water to the approximate moisture content for the test



- Mix well with the spatula until the soil is wetted uniformly
- Leave for 24 hours to equilibrate, in an air-tight and sealed container
- Measure the empty soil container before filling with soil
- Compact the wet soil into the sample holder (different for each test)\* in layers (3 for 3D printed cell, 5 for conductivity tube) compacting each layer using the appropriate tamping rod and scarifying between each layer to ensure good contact
- Measure the weight of the container with compacted soil in it
- Remove the extra 15% of soil and use for a standard gravimetric moisture test.
- Calculate moisture content, bulk density, dry density, void ratio and degree of saturation using weight measurements

\* The same soil preparation method was used for the other soil tests (Oxygen diffusion, electrical conductivity where the only variable is the soil holder volume and therefore the mass of dry soil required to maintain the same dry density

#### Appendix B – X-Ray CT imaging data for compacted silt

## B1 – Representative slices, segmented 3D pore volume and volume statistics



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## B2 – Histogram data from segmented label analysis

SI		S2	2	<b>S</b> 3	;	S4	1	SS	i	Se	5	S7	7	S8	3
vol	freq	vol	freq	vol	freq	vol	freq	vol	freq	vol	freq	vol	freq	vol	freq
8.10	80	8.10	38	8.13	52	8.08	72	5.80	1	8.41	95	8.50	229	8.84	607
9.05	895	9.06	409	9.14	614	9.01	486	6.82	0	9.98	211 8	10.27	681	11.27	880
10.00	239	10.02	103	10.15	751	9.95	117	7.85	42	11.55	125	12.03	398	13.71	277
10.96	156 1	10.97	735	11.17	449	10.88	646	8.88	266	13.12	570	13.79	161	16.15	84
11.91	911	11.93	446	12.18	306	11.81	602	9.90	651	14.69	266	15.56	70	18.58	38
12.86	661	12.89	349	13.19	168	12.74	318	10.93	410	16.26	125	17.32	32	21.02	18
13.82	373	13.85	175	14.21	124	13.67	242	11.96	277	17.83	69	19.08	24	23.45	16
14.77	276	14.81	145	15.22	66	14.60	157	12.98	167	19.40	37	20.85	10	25.89	17
15.72	131	15.77	82	16.23	52	15.53	94	14.01	105	20.98	19	22.61	7	28.33	47
16.67	103	16.73	56	17.25	24	16.46	55	15.03	69	22.55	4	24.38	3	30.76	73
17.63	60	17.68	30	18.26	30	17.39	42	16.06	42	24.12	6	26.14	15	33.20	98
18.58	25	18.64	25	19.28	12	18.32	27	17.09	32	25.69	13	27.90	10	35.63	153
19.53	24	19.60	17	20.29	15	19.25	11	18.11	19	27.26	15	29.67	14	38.07	185
20.49	17	20.56	7	21.30	11	20.18	15	19.14	12	28.83	19	31.43	35	40.50	208
21.44	7	21.52	7	22.32	12	21.11	8	20.17	9	30.40	23	33.20	33	42.94	256
22.39	8	22.48	6	23.33	11	22.04	6	21.19	9	31.97	26	34.96	39	45.38	275
23.35	14	23.44	9	24.34	16	22.97	10	22.22	10	33.55	40	36.72	41	47.81	307
24.30	12	24.39	8	25.36	13	23.90	4	23.25	2	35.12	48	38.49	55	50.25	402
25.25	14	25.35	12	26.37	14	24.83	2	24.27	3	36.69	67	40.25	91	52.68	353
26.20	18	26.31	17	27.38	21	25.76	8	25.30	3	38.26	60	42.01	120	55.12	381
27.16	15	27.27	14	28.40	16	26.69	7	26.33	5	39.83	112	43.78	127	57.56	397
28.11	23	28.23	23	29.41	23	27.62	9	27.35	4	41.40	90	45.54	128	59.99	383
29.06	28	29.19	24	30.42	40	28.55	4	28.38	6	42.97	127	47.31	169	62.43	341
30.02	36	30.15	28	31.44	47	29.48	15	29.41	9	44.54	176	49.07	193	64.86	374
30.97	37	31.11	38	32.45	66	30.41	10	30.43	12	46.12	131	50.83	203	67.30	344
31.92	43	32.06	42	33.46	83	31.34	15	31.46	16	47.69	168	52.60	215	69.74	308
32.88	61	33.02	38	34.48	100	32.27	21	32.49	26	49.26	143	54.36	207	72.17	333
33.83	43	33.98	71	35.49	102	33.20	24	33.51	20	50.83	172	56.13	268	74.61	303
34.78	53	34.94	53	36.51	111	34.13	28	34.54	28	52.40	195	57.89	217	77.04	281
35.73	63	35.90	60	37.52	126	35.06	36	35.56	37	53.97	206	59.65	234	79.48	241
36.69	63	36.86	73	38.53	140	35.99	36	36.59	33	55.54	191	61.42	264	81.92	258
37.64	78	37.82	100	39.55	149	36.92	40	37.62	51	57.11	204	63.18	236	84.35	204
38.59	91	38.77	89	40.56	147	37.85	48	38.64	55	58.68	195	64.94	230	86.79	219
39.55	99	39.73	104	41.57	156	38.78	47	39.67	64	60.26	207	66.71	250	89.22	179
40.50	92 70	40.09	104	42.59	140	39.71	64 50	40.70	04	62.40	193	70.24	200	91.00	101
41.45	79	41.00	107	43.60	146	40.64	00 104	41.72	07 110	64.07	109	70.24	102	94.10	159
42.41	91	42.01	122	44.01	201	41.57	104	42.75	90	66 5 <i>1</i>	176	72.00	217	90.55	100
44.31	97	44 53	118	46 64	199	43.43	113	44 80	121	68 11	175	75.53	206	101 4	99
45.26	101	45 48	127	47.65	187	44.36	116	45.83	126	69.68	195	77 29	188	0	94
10.20	440	40.44	405	40.07	400	45.00	404	10.00	120	74.05	400	70.05	100	4	400
46.22	110	46.44	135	48.67	192	45.29	131	40.80	132	71.25	183	79.05	192	106.2 8 108.7	76
47.17	107	47.40	131	49.00	104	40.22	119	47.00	157	72.03	145	00.02	17.1	1	70
48.12	112	48.36	119	50.69	189	47.15	146	48.91	180	74.40	154	82.58	166	111.1 5	70
49.08	109	49.32	132	51.71	192	48.08	114	49.94	175	75.97	136	84.35	148	113.5 8	73
50.03	112	50.28	132	52.72	188	49.01	144	50.96	200	77.54	140	86.11	130	116.0 2	52
50.98	112	51.24	148	53.73	197	49.94	151	51.99	207	79.11	146	87.87	150	118.4 5	65
51.94	134	52.19	133	54.75	177	50.87	170	53.01	227	80.68	130	89.64	113	120.8 9	42
52.89	120	53.15	123	55.76	204	51.80	190	54.04	198	82.25	116	91.40	107	123.3 3	36

53.84	111	54.11	152	56.78	196	52.74	181	55.07	208	83.82	112	93.17	104	125.7	42
54.80	120	55.07	151	57.79	189	53.67	167	56.09	192	85.40	99	94.93	96	6 128.2	22
55.75	118	56.03	148	58.80	189	54.60	181	57.12	207	86.97	97	96.69	78	0 130.6	16
56.70	121	56.99	173	59.82	186	55.53	206	58.15	199	88.54	83	98.46	97	3 133.0	20
57.65	135	57.95	151	60.83	214	56.46	196	59.17	182	90.11	84	100.2	71	135.5	20
58.61	116	58.90	158	61.84	198	57.39	207	60.20	188	91.68	71	2 101.9	64	1 137.9	20
59.56	127	59.86	134	62.86	189	58.32	178	61.23	205	93.25	64	9 103.7	72	4 140.3	16
60.51	116	60.82	143	63.87	202	59.25	207	62.25	174	94.82	65	5 105.5	71	8 142.8	14
61.47	148	61.78	163	64.88	203	60.18	176	63.28	217	96.39	72	1 107.2	68	1 145.2	7
62.42	135	62.74	168	65.90	172	61.11	197	64.31	182	97.97	67	8 109.0	65	5 147.6	11
63.37	128	63.70	157	66.91	235	62.04	181	65.33	208	99.54	59	4 110.8	46	9 150.1	13
64.33	134	64.66	147	67.92	210	62.97	173	66.36	167	101.1	60	0 112.5	53	2 152.5	12
65.28	134	65.61	152	68.94	182	63.90	201	67.39	159	102.6	57	7 114.3	38	6 154.9	8
66.23	138	66.57	157	69.95	211	64.83	185	68.41	177	8 104.2	46	3 116.1	39	9 157.4	8
67.18	134	67.53	160	70.96	192	65.76	177	69.44	155	5 105.8 2	52	117.8	47	3 159.8 7	9
68.14	147	68.49	147	71.98	183	66.69	170	70.47	163	107.3	38	119.6	35	162.3	3
69.09	174	69.45	161	72.99	194	67.62	177	71.49	142	9 108.9 7	37	121.3	26	164.7	3
70.04	163	70.41	173	74.01	197	68.55	159	72.52	149	/ 110.5	37	9 123.1	27	4 167.1 7	4
71.00	148	71.37	170	75.02	196	69.48	168	73.54	148	112.1 1	31	124.9 2	22	, 169.6 1	7
71.95	150	72.32	170	76.03	172	70.41	127	74.57	149	113.6	38	126.6	24	172.0	5
72.90	160	73.28	165	77.05	168	71.34	146	75.60	150	115.2 5	22	128.4 4	19	174.4 8	4
73.86	152	74.24	135	78.06	162	72.27	145	76.62	123	116.8 2	35	130.2 1	19	176.9 2	1
74.81	152	75.20	156	79.07	150	73.20	150	77.65	129	118.3 9	24	131.9 7	23	179.3	7
75.76	163	76.16	149	80.09	183	74.13	158	78.68	122	119.9 6	31	133.7 3	24	181.7 9	3
76.71	165	77.12	162	81.10	139	75.06	129	79.70	122	121.5 4	24	135.5 0	16	184.2 2	0
77.67	165	78.08	167	82.11	143	75.99	146	80.73	122	123.1 1	20	137.2 6	11	186.6 6	4
78.62	151	79.03	168	83.13	119	76.92	108	81.76	110	124.6 8	22	139.0 3	6	189.1 0	4
79.57	121	79.99	143	84.14	146	77.85	120	82.78	97	126.2 5	23	140.7 9	21	191.5 3	1
80.53	157	80.95	134	85.15	132	78.78	120	83.81	96	127.8 2	15	142.5 5	10	193.9 7	2
81.48	137	81.91	168	86.17	136	79.71	113	84.84	102	129.3 9	20	144.3 2	17	196.4 0	3
82.43	160	82.87	127	87.18	110	80.64	101	85.86	72	130.9 6	24	146.0 8	15	198.8 4	2
83.39	147	83.83	135	88.19	115	81.57	103	86.89	76	132.5 3	15	147.8 5	15	201.2 8	1
84.34	148	84.79	152	89.21	103	82.50	96	87.92	89	134.1 1	10	149.6 1	11	203.7 1	4
85.29	155	85.74	134	90.22	95	83.43	88	88.94	75	135.6 8	13	151.3 7	8	206.1 5	1
86.24	121	86.70	123	91.24	96	84.36	87	89.97	90	137.2 5	23	153.1 4	9	208.5 8	3
87.20	131	87.66	124	92.25	103	85.29	82	91.00	72	138.8 2	20	154.9 0	9	211.0 2	2
88.15	143	88.62	124	93.26	92	86.22	113	92.02	71	140.3 9	15	156.6 6	10	213.4 6	1
89.10	112	89.58	126	94.28	78	87.15	98	93.05	65	141.9 6	22	158.4 3	5	215.8 9	3
90.06	135	90.54	123	95.29	90	88.08	89	94.07	71	143.5 3	13	160.1 9	7	218.3 3	0
91.01	136	91.50	107	96.30	80	89.01	59	95.10	62	145.1 0	12	161.9 6	12	220.7 6	0
91.96	113	92.45	105	97.32	80	89.94	66	96.13	56	146.6 7	5	163.7 2	5	223.2 0	0
92.92	122	93.41	87	98.33	80	90.87	70	97.15	55	148.2 5	13	165.4 8	6	225.6 4	1
93.87	111	94.37	96	99.34	72	91.80	66	98.18	57	149.8 2	12	167.2 5	12	228.0 7	0

94.82	119	95.33	95	100.3	65	92.73	70	99.21	48	151.3	7	169.0	3	230.5	1
95.78	93	96.29	93	101.3	78	93.66	68	100.2	56	9 152.9	10	170.7	5	232.9	1
96.73	90	97.25	75	102.3	58	94.60	60	3 101.2	33	154.5	10	7 172.5	3	4 235.3	1
97.68	106	98.21	79	103.4	49	95.53	49	102.2	51	3 156.1	16	174.3	3	237.8	1
98.63	93	99.16	91	104.4	44	96.46	59	9 103.3	45	157.6	12	176.0	2	240.2	0
99.59	118	100.1	69	105.4	42	97.39	48	104.3	54	159.2	10	7 177.8	4	5 242.6	0
100.5	97	101.0	69	106.4	39	98.32	40	4 105.3	40	4 160.8	8	3 179.5	1	9 245.1	0
4 101.4	96	102.0	54	4 107.4	43	99.25	44	106.3	36	162.3	3	9 181.3	7	247.5	0
9 102.4	66	4 103.0	64	5 108.4	35	100.1	41	9 107.4	29	9 163.9	6	6 183.1	7	249.9	0
5 103.4	60	103.9	81	109.4	40	0 101.1	38	108.4	40	165.5	4	184.8	3	9 252.4	0
0 104.3	72	104.9	55	0 110.4	37	102.0	37	5 109.4 7	40	3 167.1	9	9 186.6	2	3 254.8 7	0
5 105.3	65	105.8	44	9 111.5	29	4 102.9	40	110.5	35	168.6	4	5 188.4	4	257.3	0
106.2	66	106.8	53	112.5	24	103.9	41	111.5	32	170.2	10	190.1	2	259.7	2
0 107.2	73	3 107.7	55	113.5	39	104.8	39	3 112.5	23	4 171.8	7	0 191.9	2	4 262.1	1
108.1	65	9 108.7	51	3 114.5	29	3 105.7	32	5 113.5	33	173.3	6	4 193.7	0	264.6	1
109.1	49	109.7	32	115.5	15	106.6	49	114.6	29	9 174.9	3	195.4	4	267.0	1
2 110.0 7	58	110.6	35	116.5	19	107.6	36	115.6	28	176.5	3	197.2	2	269.4	0
, 111.0 2	49	, 111.6 3	37	, 117.5 9	18	108.5	25	116.6 6	28	178.1	4	199.0	0	271.9 2	1
111.9 8	46	112.5 9	45	118.6	23	109.4	29	117.6 8	16	179.6 7	6	200.7	1	274.3	1
112.9 3	49	113.5 4	34	119.6 1	15	110.4 1	31	118.7 1	23	, 181.2 4	5	202.5 2	3	276.7 9	0
113.8 8	35	114.5 0	36	120.6 3	14	111.3 4	23	119.7 4	19	182.8 1	6	204.2	4	279.2	0
114.8 4	43	115.4 6	22	121.6 4	12	112.2 7	28	120.7 6	18	184.3 8	4	206.0	1	281.6 6	0
115.7 9	48	116.4 2	34	122.6 5	11	, 113.2 0	20	121.7 9	31	185.9 6	3	207.8 2	3	284.1 0	1
116.7 4	28	117.3 8	28	123.6 7	9	114.1 3	29	122.8 2	19	187.5 3	3	209.5 8	2	286.5 3	0
117.7 0	41	118.3 4	33	124.6 8	11	115.0 6	17	123.8 4	11	189.1 0	4	211.3 4	0	288.9 7	1
118.6 5	39	119.3 0	29	125.7 0	14	115.9 9	17	124.8 7	19	190.6 7	3	213.1 1	0	291.4 1	0
119.6 0	29	120.2 5	25	126.7 1	12	116.9 2	26	125.9 0	12	192.2 4	3	214.8 7	0	293.8 4	1
120.5 5	31	121.2 1	15	127.7 2	9	117.8 5	21	126.9 2	25	193.8 1	4	216.6 3	0	296.2 8	0
121.5 1	26	122.1 7	10	128.7 4	8	118.7 8	18	127.9 5	11	195.3 8	6	218.4 0	1	298.7 1	0
122.4 6	28	123.1 3	22	129.7 5	9	119.7 1	16	128.9 8	13	196.9 5	4	220.1 6	0	301.1 5	0
123.4 1	25	124.0 9	18	130.7 6	3	120.6 4	12	130.0 0	14	198.5 3	4	221.9 3	0	303.5 8	0
124.3 7	30	125.0 5	19	131.7 8	5	121.5 7	20	131.0 3	13	200.1 0	3	223.6 9	1	306.0 2	0
125.3 2	25	126.0 1	19	132.7 9	3	122.5 0	8	132.0 6	6	201.6 7	3	225.4 5	0	308.4 6	0
126.2 7	18	126.9 6	20	133.8 0	7	123.4 3	23	133.0 8	16	203.2 4	2	227.2 2	3	310.8 9	0
127.2 3	19	127.9 2	10	134.8 2	6	124.3 6	11	134.1 1	11	204.8 1	4	228.9 8	1	313.3 3	2
128.1 8	15	128.8 8	17	135.8 3	5	125.2 9	14	135.1 3	10	206.3 8	0	230.7 5	0	315.7 6	0
129.1 3	16	129.8 4	13	136.8 4	5	126.2 2	16	136.1 6	12	207.9 5	3	232.5 1	0	318.2 0	1
130.0 8	20	130.8 0	13	137.8 6	2	127.1 5	5	137.1 9	10	209.5 2	6	234.2 7	1	320.6 4	0
131.0 4	14	131.7 6	17	138.8 7	0	128.0 8	10	138.2 1	8	211.1 0	0	236.0 4	0	323.0 7	0
131.9 9	12	132.7 2	8	139.8 8	4	129.0 1	14	139.2 4	12	212.6 7	1	237.8 0	0	325.5 1	1
132.9 4	18	133.6 7	4	140.9 0	8	129.9 4	12	140.2 7	6	214.2 4	2	239.5 6	1	327.9 4	0
133.9 0	12	134.6 3	8	141.9 1	3	130.8 7	10	141.2 9	10	215.8 1	1	241.3 3	0	330.3 8	0
134.8 5	9	135.5 9	4	142.9 3	3	131.8 0	12	142.3 2	6	217.3 8	2	243.0 9	1	332.8 2	0

135.8	10	136.5	8	143.9	3	132.7	12	143.3	7	218.9	5	244.8	0	335.2	0
0 136.7	10	5 137.5	1	4 144.9	2	3 133.6	10	5 144.3	8	5 220.5	3	6 246.6	1	5 337.6	0
6 137.7	13	1 138.4	4	5 145.9	3	6 134.5	10	7 145.4	12	2 222.0	2	2 248.3	1	9 340.1	0
1 138.6	7	7 139.4	4	7 146.9	1	9 135.5	8	0 146.4	7	9 223.6	1	8 250.1	0	2 342.5	0
6 139.6	8	3 140.3	5	8 147.9	0	3 136.4	5	3 147.4	6	7 225.2	0	5 251.9	0	6 345.0	1
1 140.5	9	8 141.3	5	9 149.0	1	6 137.3	10	5 148.4	5	4 226.8	0	1 253.6	0	0 347.4	0
7 141.5	5	4 142.3	2	1 150.0	0	9 138.3	7	8 149.5	5	1 228.3	1	8 255.4	0	3 349.8	0
2 142.4	7	0 143.2	2	2 151.0	3	2 139.2	6	1 150.5	6	8 229.9	2	4 257.2	0	7 352.3	0
7 143.4	5	6 144.2	2	3 152.0	1	5 140.1	5	3 151.5	4	5 231.5	2	0 258.9	1	0 354.7	1
3 144.3	3	2 145.1	3	5 153.0	2	8 141.1	7	6 152.5	3	2 233.0	3	7 260.7	0	4 357.1	0
8 145.3	5	8 146.1	1	6 154.0	1	1 142.0	6	8 153.6	5	9 234.6	3	3 262.4	0	8 359.6	0
3 146.2	5	4 147.0	1	7 155.0	0	4 142.9	5	1 154.6	6	6 236.2	2	9 264.2	1	1 362.0	0
9 147.2	6	9 148.0	1	9 156.1	0	7 143.9	2	4 155.6	3	4 237.8	2	6 266.0	2	5 364.4	0
4 148.1	6	5 149.0	2	0 157.1	1	0 144.8	3	6 156.6	3	1 239.3	1	2 267.7	0	8 366.9	0
9 149.1	7	1 149.9	1	1 158.1	0	3 145.7	3	9 157.7	4	8 240.9	0	9 269.5	0	2 369.3	0
4 150.1	4	7 150.9	3	3 159.1	0	6 146.6	10	2 158.7	5	5 242.5	0	5 271.3	0	5 371.7	0
0	1	3 151.8	2	4 160.1	0	9 147.6	2	4	2	2 244.0	1	1 273.0	0	9 374.2	0
5 152.0	2	9 152.8	2	6 161.1	1	2 148.5	5	7	3	9 245.6	0	8 274.8	0	3 376.6	0
0	2	5	0	7	0	5 149 4	3	0	3	6 247 2	1	4 276.6	0	6 379 1	0
6 153.9	-	0	1	8	0	8 150 4	4	2	0	3	0	1 278.3	0	0	0
1	3	6 155 7	4	0	1	1	4	5	5	1 250.3	1	7 280 1	0	3	0
6 155.8	5	2	1	1	1	4	2	8	1	8 251 9	0	3	0	7	0
2	3	8	1	2	1	7	-	0	1	5 253 5	0	0	0	1	0
7	2	4	2	4	0	0	3	3	2	2	1	6 285.4	0	4	0
2	2	0	2	5	0	3	4	6 167 9	3	9 256.6	1	2	0	8	0
8	0	6 160 5	0	6 160.2	0	6 155 0	1	8	0	6 258.2	0	9	0	1	0
3 160 5	0	1 1 161 4	0	8	0	9	2	170.0	2	250.2 3 259.8	0	5 290.7	1	5 398 5	0
8	1	7 162 /	0	9	0	2	0	4	2	0	1	2	0	9 401.0	0
3 162.4	0	3	0	0	0	5	1	6	2	201.3 8 262.0	1	8 204.2	0	401.0 2 402.4	0
9	2	9	0	2	0	8	1	9	1	202.9 5 264.5	0	4	0	6	0
4	1	5	0	3	0	1	5	173.1	0	204.5	0	290.0	0	405.8 9	0
104.3 9 165.2	1	105.5	1	4	0	4	0	4	2	200.0 9 267.6	0	297.7 7 200.5	0	400.3 3 410.7	0
105.5 5	י ר	100.2 7 167.2	1	6 176.2	0	101.5 7 162.5	0	7	3	207.0 6 260.2	0	299.5	0	410.7	0
0	2	2	0	170.3 7 177.2	0	0	2	9	0	209.2	0	0	0	413.2 0 415.6	1
5	1	8	0	9	0	163.4 3	4	2	0	270.8 0	0	303.0 6	0	415.6	1
168.2	1	169.1 4	0	178.4 0	1	164.3 6	1	178.2	1	272.3	0	304.8	0	418.0	0
169.1 6	2	170.1	0	179.4	0	165.2 9	0	179.2 7	1	273.9 5	0	306.5 9	0	420.5	0
170.1 1	0	171.0 6	0	180.4 3	0	166.2 2	0	180.3 0	1	275.5 2	0	308.3 5	0	422.9 4	0
171.0 6	0	172.0 2	0	181.4 4	0	167.1 5	2	181.3 3	1	277.0 9	0	310.1 2	0	425.3 8	0
172.0 2	0	172.9 8	0	182.4 5	0	168.0 8	1	182.3 5	1	278.6 6	0	311.8 8	0	427.8 2	0
172.9 7	0	173.9 3	0	183.4 7	0	169.0 1	1	183.3 8	1	280.2 3	1	313.6 5	0	430.2 5	0
173.9 2	0	174.8 9	0	184.4 8	0	169.9 4	2	184.4 1	0	281.8 0	0	315.4 1	1	432.6 9	0
174.8 8	0	175.8 5	0	185.4 9	0	170.8 7	3	185.4 3	0	283.3 7	0	317.1 7	0	435.1 2	1
175.8 3	1	176.8 1	0	186.5 1	0	171.8 0	1	186.4 6	0	284.9 4	0	318.9 4	0	437.5 6	0

176.7	1	177.7	0	187.5	0	172.7	0	187.4 o	1	286.5	2	320.7	1	440.0	0
177.7	1	178.7	1	188.5	0	173.6	0	188.5	0	288.0	1	322.4	0	442.4	0
4 178.6	1	179.6	0	189.5	0	174.5	0	189.5	1	289.6	0	324.2	1	3 444.8 7	0
9 179.6	0	9 180.6	0	5 190.5	0	9 175.5	0	4 190.5	0	291.2	0	325.9	1	447.3	0
4 180.5	1	4 181.6	0	6 191.5	0	2 176.4	1	7 191.5	1	292.8	0	9 327.7	0	0 449.7	1
9 181.5	1	182.5	0	192.5	0	177.3	0	9 192.6	1	294.3	0	329.5	0	4 452.1	0
182.5	0	183.5	0	193.6	0	178.3	1	193.6	0	295.9	0	331.2	0	454.6	0
183.4	0	184.4	0	194.6	0	179.2	0	4 194.6	0	297.5	0	333.0	0	457.0	0
184.4	1	o 185.4	0	195.6	0	180.1	0	195.7	0	299.0	1	334.8	0	459.4	0
185.3	1	186.4	0	196.6	0	0 181.1	1	196.7	0	300.6	1	336.5	0	6461.9	0
186.3	1	187.3	0	4 197.6	0	182.0	0	197.7	0	302.2	0	338.3	1	464.3	0
1 187.2	0	5 188.3	0	6 198.6	0	4 182.9	0	5 198.7	0	3 303.8	0	4 340.1	0	6 466.7	0
7 188.2	1	1 189.2	0	7 199.6	0	7 183.9	0	8 199.8	0	0 305.3	0	0 341.8	1	9 469.2	0
2 189.1	0	7 190.2	0	8 200.7	0	0 184.8	0	0 200.8	0	7 306.9	0	7 343.6	0	3 471.6	0
7 190.1	0	3 191.1	0	0 201.7	0	3 185.7	0	3 201.8	1	4 308.5	0	3 345.3	0	6 474.1	0
2 191.0	0	9 192.1	1	1 202.7	0	6 186.6	0	6 202.8	1	1 310.0	0	9 347.1	0	0 476.5	0
8 192.0	0	5 193.1	0	2 203.7	0	9 187.6	0	8 203.9	0	8 311.6	0	6 348.9	0	4 478.9	0
3 192.9	0	1 194.0	0	4 204.7	0	2 188.5	0	1 204.9	0	6 313.2	0	2 350.6	0	7 481.4	0
8 193.9	0	6 195.0	0	5 205.7	0	5 189.4	0	4 205.9	0	3 314.8	0	9 352.4	0	1 483.8	0
4 194.8	0	2 195.9	0	6 206.7	0	8 190.4	0	206.9	0	0 316.3	0	5 354.2	0	4 486.2	0
9 195.8	2	8 196.9	0	8 207.7	0	191.3	0	208.0	0	317.9	0	355.9	0	88.7	0
4 196.8	0	4 197.9	1	9 208.8	0	4 192.2	0	209.0	0	4 319.5	0	8 357.7	0	491.1	0
0 197.7 5	1	198.8 6	1	209.8 2	1	7 193.2 0	1	4 210.0 7	1	321.0 8	1	4 359.5 1	1	5 493.5 9	1

## Appendix C – Oxygen diffusion test calculations

### Clay: Test1







Calibratio	n Equatio	n	y=a*x+b		Moisture Calculation			
conc	a=	0.832849119	b=	-0.14991	Specific gravity =			
percent	a=	2.028762347	b=	-0.36518	Mould volume (m^3) =			
c0 =	8.6	5	20.949		Water density (kgm-3)=			
Calculatio	'n				Wet+tin Dry+tin			
Dry densi	ty =		1185.038		tin Moisture Content:			
porosity (	n)=		0.552816		filled also succeeded			
Henry's e	quilibrium	constant =	0.03		Empty ring weight			
volumetri	c air conte	ent (ɛa) =	0.299957		Bulk density			
vol. water	r content (	εw) =	0.252858		Void ratio			
equivaler	t porosity	(ɛeq) =	0.307543		1			
Sample h	eight (L) =		0.019					
Diff. Chan	nber lengt	h (a) =	0.127					
	α tan(a	$\alpha L) = \frac{\varepsilon}{a}$						
function f	or a							
α*tan(α*	L) - ε/a =	7.5204E-05						
α =		11.20381364						
Diffusion	coefficien	t						
slope =		-0.00029502						
De =		7.22806E-07						

Test2







Calibratio	on Equation	ı	y=a*x+b					
conc	a=	0.850390586	b=	-0.15222				
percent	a=	2.071492139	b=	-0.3708				
c0 =	8.6	i	20.949					
Calculatio	on							
Dry densi	ty =		1313.309					
porosity (	n)=		0.504412					
Henry's e	quilibrium	constant =	0.03					
volumetr	ic air conte	ent (εa) =	0.182472					
vol. wate	r content (	εw) =	0.32194					
equivaler	nt porosity	(ɛeq) =	0.19213					
Sample h	eight (L) =		0.019					
Diff. Char	nber lengt	h (a) =	0.127					
	α tan(a	$rL) = \frac{\varepsilon}{a}$						
function	for a							
α*tan(α*	L) - ε/a =	1.71558E-05						

8.880701056

-0.00025982

6.32945E-07

α =

slope = De =

Diffusion coefficient

Moisture Calculation	
Specific gravity =	2.65
Mould volume (m^3) =	8.63E-05
Water density (kgm-3)=	1000
Wet+tin	16.87
Dry+tin	14.98
tin	7.27
Moisture Content:	0.245136

2.65

1000

18.76 16.75

7.33 0.213376

> 207.49 83.41

1.44E+03

1185.038 1.236215 0.457401

8.63E-05

 filled ring weight
 224.33

 Empty ring weight
 83.22

 Bulk density
 1.64E+03

 Dry density
 1313.309

 Void ratio
 1.017804

 Sr
 0.638247








Calibratio	on Equatio	y=a*x+b				
conc	a=	0.845957112	b=	-0.13874		
percent	a=	2.060692504	b=	-0.33795		
c0 =	8.6	5	20.949	)		
Calculati	on					
Dry dens	ity =		1337.304	Ļ		
porosity	(n)=		0.495357	,		
Henry's e	quilibrium	constant =	0.03			
volumeti	ric air conte	ent (εa) =	0.097867	,		
vol. wate	r content (	εw) =	0.39749	)		
equivale	nt porosity	(ɛeq) =	0.109792			
Sample h	eight (L) =		0.019	)		
Diff. Cha	mber lengt	:h (a) =	0.127	,		
	α tan(a	$\alpha L) = \frac{\varepsilon}{a}$				
function	for α					
α*tan(α*	'L) - ε/a =	4.86679E-05				
α =		i				
Diffusion coefficient						
slope =						
De =						

2.65
8.63E-05
1000
18.05
15.58
7.27
0.297232
233.14
83.44
1.73E+03
1337.304
0.981599
0.802431

Test 4







Calibratio	on Equation	y=a*x+b		
conc	a=	0.837635142	b=	-0.13486
percent	a=	2.040420766	b=	-0.32851
c0 =	8.6	20.949	)	
Calculatio	on			
Dry densi	ty =		1393.243	3
porosity (	(n)=		0.474248	3
Henry's e	quilibrium	constant =	0.03	3
volumetr	ic air conte	ent (εa) =	0.027011	L
vol. wate	r content (	εw) =	0.447237	,
equivaler	nt porosity	0.040428	3	
Sample h	eight (L) =	0.019	Ð	
Diff. Char	nber lengt	0.127	7	
	α tan(a			

function for $\boldsymbol{\alpha}$	
$\alpha$ *tan( $\alpha$ *L) - $\epsilon$ /a =	0.000285491
α =	4.090912255
Diffusion coefficient	
slope =	-4.16776E-05
De =	1.00681E-07

Moisture Calculation	
Specific gravity =	2.65
Mould volume (m^3) =	8.63E-05
Water density (kgm-3)=	1000
Wet+tin	17.26
Dry+tin	14.83
tin	7.26
Moisture Content:	0.321004
filled ring weight	242.3
Empty ring weight	83.48
Bulk density	1.84E+03
Dry density	1393.243
Void ratio	0.902037
Sr	0.943044







Calibration Equation		y=a*x+b		Moisture Calculation	
conc	a=	0.823833701	b=	-0.13264	Specific gravity =
percent	a=	2.006801418	b=	-0.3231	Mould volume (m^3) =
c0 =	8.6	i	20.949	1	Water density (kgm-3)=
Calculatio	on				Wet+tin Dry+tin tin
Dry densi	ty =		1260.264		Moisture Content:
porosity (	n)=		0.524429		<i></i>
Henry's e	quilibrium	constant =	0.03		Empty ring weight
volumetr	ic air conte	ent (εa) =	0.434521		Bulk density
vol. water content (ɛw) =		0.089908	1	Void ratio	
equivalent porosity (ɛeq) =		0.437218	1	21	
Sample height (L) =		0.019	1		
Diff. Char	nber lengt	h (a) =	0.127		
	α tan(a	$tL) = \frac{\varepsilon}{a}$			
function	for a				
$\alpha^*$ tan( $\alpha^*$ L) - $\epsilon$ /a = -5.0827E-06					
α =		13.31577189			
Diffusion	coefficien	t			
slope =		-0.00036517			
De =		9.00443E-07			

2.65

1000

15.98

15.4 7.27

0.071341

200.14

83.63

1.35E+03

1.35E+03 1260.264 1.102734 0.17144

2.65

1000

23.28

18.07 7.27

0.482407

253.43

83.81

1.97E+03

1325.975 0.998529

1

8.63E-05

Moisture Calculation Specific gravity =

Mould volume (m^3) =

Water density (kgm-3)=

Moisture Content:

filled ring weight

Empty ring weight

Bulk density

Dry density Void ratio

Sr

Wet+tin

Dry+tin

tin

8.63E-05

### Test 6





1

# $\ln(\mathcal{C}r) = -\frac{D_p \alpha^2 t}{\varepsilon} + \ln\left[\frac{2h}{L(\alpha^2 + h^2) + h}\right]$



Calibratio	on Equatio	y=a*x+b				
conc	a= 0.835194717		b=	-0.13948		
percent	a=	2.034476061	b=	-0.33976		
c0 =	8.0	5	20.949	)		
Calculatio	on					
Dry densi	ty =		1325.975	i		
porosity	(n)=		0.499632			
Henry's e	quilibrium	i constant =	0.03	1		
volumetr	ic air conte	C	)			
vol. wate	r content (	εw) =	0.499632	!		
equivale	nt porosity	(seq) =	0.014989	)		
Sample h	eight (L) =	0.019	)			
Diff. Char	nber lengt	0.127	,			
	α tan(e					
function for $\alpha$						
α*tan(α*L) - ε/a = 0.000192247						

2.493434466 α =

### Diffusion coefficient

-6.73939E-07 slope =

De = 1.62479E-09









### $\ln(Cr) = -\frac{D_p \alpha^2 t}{\varepsilon} + ln \left[\frac{2h}{L(\alpha^2 + h^2) + h}\right]$



Calibration Equation			y=a*x+b		Moisture Calculation
conc	a=	0.823045267	b=	-0.1284	Specific gravity =
percent	a=	2.00488085	b=	-0.31276	Mould volume (m^3) =
c0 =	8.6		20.949	)	Water density (kgm-3)=
Calculation	on ity =		1357.886	ō	Wet+tin Dry+tin tin Moisture Content:
porosity	(n)=		0.48759	)	
Henry's e	quilibrium	constant =	0.03	8	filled ring weight Empty ring weight
volumetric air content (ɛa) =		0.055406	5	Bulk density	
vol. water content (εw) =		0.432184	Ļ	Dry density Void ratio	
equivale	nt porosity	(ɛeq) =	0.068371		Sr
Sample h	neight (L) =		0.019	)	
Diff. Cha	mber lengtl	h (a) =	0.127	,	
$\alpha \tan(\alpha L) = \frac{\varepsilon}{a}$					
function	for α				
α*tan(α*	"L) - ε/a =	0.0001886	3		
α =		5.3148963	3		
Diffusion	coefficien	t			

slope = De =

y=a\*x+b Calibration Equa ion a= 0.827320827 b= -0.12823 conc percent a= 2.015295815 b= -0.31237 c0 = 8.6 20.949 Calculation 1385.577 Dry density = 0.477141 porosity (n)= Henry's equilibrium constant = 0.03 volumetric air content (ɛa) = 0 vol. water content (ɛw) = 0.477141 equivalent porosity (ɛeq) = 0.014314 Sample height (L) = 0.019

0.127

Diff. Chamber length (a) =

function for  $\alpha$ 

Diffusion coefficient

α =

slope = De =

 $\alpha \tan(\alpha L) = \frac{\varepsilon}{a}$ 

 $\alpha^{*}tan(\alpha^{*}L) - \epsilon/a = 0.000388745$ 

2.438918852

-3.10813E-07

7.4795E-10

-9.33779E-05

2.26011E-07

Moisture Calculation	
Specific gravity =	2.65
Mould volume (m^3) =	8.63E-05
Water density (kgm-3)=	1000
Wet+tin	18.77
Dry+tin	15.63
tin	7.26
Moisture Content:	0.375149
filled ring weight	247.74
Empty ring weight	83.32
Bulk density	1.91E+03
Dry density	1385.577
Void ratio	0.91256
Sr	1.089403

2.65

1000

19.79 16.76 7.24

0.318277

237.78 83.31

1.79E+03

1357.886 0.951563 0.886368

8.63E-05







Calibration Equation		v=a*x+b		Moisture Calculation	
		,			
conc	a=	0.824307486	b=	-0.122	Specific gravity =
percent	a=	2.007955526	b=	-0.29718	Mould volume (m^3) =
c0 =	8.6		20.949	I	Water density (kgm-3)=
Calculatio	on				Wet+tin Dry+tin tin
Dry densi	ty =		1269.331		Moisture Content:
porosity (	n)=		0.521007	,	
Henry's e	quilibrium	constant =	0.03	i	filled ring weight Empty ring weight
volumetr	ic air conte	nt (εa) =	0.31814	Ļ	Bulk density
vol. water content (εw) =		0.202868	1	Void ratio	
equivalent porosity (ɛeq) =		0.324226	i	Sr	
Sample height (L) =		0.019	1		
Diff. Char	nber lengtl	h (a) =	0.127	,	
$\alpha \tan(\alpha L) = \frac{\varepsilon}{a}$					
function	for α				
α*tan(α*	L) - ε/a =	4.94451E-06	5		
α =		11.49877122	2		
Diffusion	coefficien	t			
slope =		-0.000304259	)		

2.65

1000

8.63E-05

17.71 16.27 7.26 0.159822

> 210.95 83.91

1.47E+03 1269.331 1.087714 0.389376

De = 7.46085E-07





Silt:

Test 1



### Test 2







Calibration Equation			y=a*x+b		Moisture Calculation
conc	a=	0.829155418	b=	-0.12272	Specific gravity =
percent	a=	2.019764751	b=	-0.29893	Mould volume (m^3) =
c0 =	8.6	5	20.949	I	Water density (kgm-3)=
Calculatio	on				Wet+tin Dry+tin tin
Dry densi	ity =		1478.519	I.	Moisture Content:
porosity	(n)=		0.442068	:	
Henry's e	quilibrium	constant =	0.03	i	filled ring weight Empty ring weight
volumetr	ic air conte	ent (εa) =	0.285687		Bulk density
vol. water content (ɛw) =		0.156382		Void ratio	
equivalent porosity (εeq) =		0.290378	:	51	
Sample height (L) =		0.019	1		
Diff. Char	mber lengt	h (a) =	0.127	,	
	α tan(a	$\alpha L) = \frac{\varepsilon}{a}$			
function	for α				
α*tan(α*	'L) - ε/a =	-0.000401081	L		
α =		10.89017412	2		
Diffusion	coefficien	t			
slope =		-0.000479295	5		

1.17354E-06 De =

y=a\*x+b Calibration Equat tion a= 0.832849119 b= -0.12743 conc percent a= 2.028762347 b= -0.3104 c0 = 8.6 20.949 Calculation 1563.116 Dry density = 0.410145 porosity (n)= Henry's equilibrium constant = 0.03 volumetric air content (ɛa) = 0.165576 vol. water content (ɛw) = 0.244569 equivalent porosity (ɛeq) = 0.172913 Sample height (L) = 0.019 Diff. Chamber length (a) = 0.127  $\alpha \tan(\alpha L) = \frac{\varepsilon}{\alpha}$ 

#### function for $\alpha$

$\alpha^*$ tan( $\alpha^*$ L) - $\epsilon$ /a =	3.2564E-05
α =	8.428934783

### Diffusion coefficient

-9.34287E-05 slope =

De = 2.27385E-07

### Moisture Calculation Specific gravity = Mould volume (m^3) =

2.65

1000

15.31 14.54 7.26

0.105769

224.05 82.97

1.63E+03

1478.519 0.792334 0.35375

2.65

8.63E-05

8.63E-05

Water density (kgm-3)=	1000
Wet+tin	10.66
Dry+tin	10.2
tin	7.26
Moisture Content:	0.156463
filled ring weight	239.66
Empty ring weight	83.67
Bulk density	1.81E+03
Dry density	1563.116
Void ratio	0.695332
Sr	0.596299







#### 0.03 Henry's equilibrium constant = volumetric air content (ɛa) = 0.002178 vol. water content (ɛw) = 0.436692 equivalent porosity (ɛeq) = 0.015279 Sample height (L) = 0.019 Diff. Chamber length (a) = 0.127 $\alpha \tan(\alpha L) = \frac{\varepsilon}{\alpha}$ function for $\boldsymbol{\alpha}$ $\alpha^* \tan(\alpha^* L) - \epsilon/a = 0.000606736$ 2.521713841 α = Diffusion coefficient -8.0137E-07 slope = De = 1.92548E-09

**Calibration Equation** 

8.6

conc a=

c0 =

percent a=

Calculation

Dry density =

porosity (n)=

y=a\*x+b

20.949

1486.993

0.438871

-0.12836

-0.31267

0.844461901 b=

2.057050275 b=

### Test 4







Calibration Equation		y=a*x+b		
conc	a=	0.839106254	b=	-0.11999
percent	a=	2.044004293	b=	-0.29229
c0 =	8.6	5	20.949	
Calculatio	on			
Dry densi	ty =		1465.22	
porosity (n)= 0.447087				
Henry's equilibrium constant =			0.03	l
volumetric air content (ɛa) =		0.378805	i	
vol. water content (ɛw) =		0.068282		
equivalent porosity (εeq) =		(ɛeq) =	0.380853	
Sample height (L) =			0.019	1
Diff. Chamber length (a) =		0.127	,	
$\alpha \tan(\alpha L) = \frac{\varepsilon}{a}$				
function for $\alpha$				

α =

### Diffusion coefficient

slope = -0.000419545

 $\alpha^{*}$ tan( $\alpha^{*}$ L) -  $\epsilon/a = 4.14791$ E-06

12.44514072

De = 1.0317E-06

Moisture Calculation	
Specific gravity =	2.65
Mould volume (m^3) =	8.63E-05
Water density (kgm-3)=	1000
Wet+tin	15.85
Dry+tin	13.9
tin	7.26
Moisture Content:	0.293675
filled ring weight	249.73
Empty ring weight	83.73
Bulk density	1.92E+03
Dry density	1486.993
Void ratio	0.78212
Sr	0.995037

	Moisture Calculation	
1999	Specific gravity =	2.65
9229	Mould volume (m^3) =	8.63E-05
	Water density (kgm-3)=	1000
	Wet+tin	12.65
	Dry+tin	12.41
	tin	7.26
	Moisture Content:	0.046602
	filled ring weight	215.93
	Empty ring weight	83.6
	Bulk density	1.53E+03
	Dry density	1465.22
	Void ratio	0.808603
	Sr	0.152727







Dry density =		1472.784
porosity (n)=		0.444232
Henry's equilibriun	n constant =	0.03
volumetric air cont	ent (ɛa) =	0.203778
vol. water content	(ɛw) =	0.240455
equivalent porosity	y (ɛeq) =	0.210991
Sample height (L) =	:	0.019
Diff. Chamber leng	th (a) =	0.127
α tan(	$\alpha L) = \frac{\varepsilon}{a}$	
function for $\alpha$		
$\alpha^*$ tan( $\alpha^*$ L) - $\epsilon$ /a =	0.000104657	
α =	9.30228654	
Diffusion coefficie	nt	
slope =	-0.000199868	
De =	4.87336E-07	

**Calibration Equation** 

8.6

conc a=

c0 =

percent a=

Calculation

y=a\*x+b

20.949

0.843385309 b=

2.054427773 b=

#### Moisture Calculation -0.11807 Specific gravity = 2.65 -0.28762 Mould volume (m^3) = 8.63E-05 Water density (kgm-3)= 1000 11.82 Wet+tin 11.18 7.26 Dry+tin tin Moisture Content: 0.163265 filled ring weight Empty ring weight 231.07 83.23 1.71E+03 Bulk density Dry density Void ratio Sr 1472.784 0.799313 0.541281

Calibration Equation		y=a*x+b			
conc	a= 0.844959717		b=	-0.13097	Spe
percent	a=	2.05826292	b=	-0.31903	Mo
c0 =	8.0	5	20.94	19	Wa
Calculation	on				We Dry tin
Dry dens	ity =		1473.2	6	Mo
porosity (n)=			0.44405	i3	
Henry's equilibrium constant =		0.0	13	Em	
volumetric air content (ɛa) =			0.25610	16	Bul
vol. water content (ɛw) =		0.18794	7	Dry Voi	
equivalent porosity (εeq) =			0.26174	15	Sr
Sample height (L) =			0.01	.9	
Diff. Chamber length (a) =			0.12	7	

Moisture Calculation	
Specific gravity =	2.65
Mould volume (m^3) =	8.63E-05
Water density (kgm-3)=	1000
Wet+tin	15.48
Dry+tin	14.55
tin	7.26
Moisture Content:	0.127572
filled ring weight	226.91
Empty ring weight	83.56
Bulk density	1.66E+03
Dry density	1473.26
Void ratio	0.798732
Sr	0.423253

## Test 6



### $\ln(Cr) = -\frac{D_p \alpha^2 t}{\varepsilon} + ln \left[\frac{2h}{L(\alpha^2 + h^2) + h}\right]$





function for  $\alpha$ 

α =

-0.000276755 slope =

 $\alpha^{*}tan(\alpha^{*}L) - \epsilon/a = 0.000450149$ 

10.34864978

De = 6.76402E-07

 $\alpha \tan(\alpha L) = \frac{\varepsilon}{a}$ 















Calibration Equation		y=a*x+b		Moisture Calculation	
conc	a=	0.853598015	b=	-0.18352	Specific gravity =
percent	a=	2.079305211	b=	-0.44705	Mould volume (m^3) =
c0 =	8.6	5	20.949	)	Water density (kgm-3)=
Calculati	on				Wet+tin Dry+tin
Dry dens	ity =		1522.6	5	tin Moisture Content:
porosity	(n)=		0.425434	Ļ	
Henry's e	quilibrium	constant =	0.03	1	filled ring weight Empty ring weight
volumetr	ic air conte	ent (εa) =	0.113464	Ļ	Bulk density
vol. wate	r content (	εw) =	0.31197	,	Void ratio
equivale	nt porosity	(seq) =	0.122823	3	31
Sample h	eight (L) =		0.019	)	
Diff. Cha	mber lengt	:h (a) =	0.127	,	
	α tan(	$(\alpha L) = \frac{\varepsilon}{a}$			
function	for α				
α*tan(α*	'L) - ε/a =	0.000137036	5		
α =		7.113187375	5		
Diffusion	coefficier	ıt			
slope =		-4.54648E-05	5		
De =		1.10364E-07	,		

Calibration Equation			y=a*x+b	
conc	a=	0.846040334	b=	-0.11929
percent	a=	2.060895229	b=	-0.29059
c0 =	8.6	5	20.949	9
Calculatio	on			
Dry densi	ity =		1543.202	2
porosity	(n)=		0.41766	5
Henry's equilibrium constant =			0.03	3
volumetric air content (ɛa) =			0.079938	3
vol. wate	r content (	εw) =	0.337722	2
equivalent porosity (εeq) =			0.090069	9
Sample height (L) =			0.019	9
Diff. Chamber length (a) =			0.12	7
$\alpha \tan(\alpha L) = \frac{\varepsilon}{a}$				

function for $\boldsymbol{\alpha}$	
------------------------------------	--

 $\alpha^{*}tan(\alpha^{*}L) - \epsilon/a = 0.000945738$ 

α = 6.099916015

### Diffusion coefficient

slope = -2.06645E-05 De =

5.00212E-08

Specific gravity =	2.65
Mould volume (m^3) =	8.63E-05
Water density (kgm-3)=	1000
Wet+tin	11.19
Dry+tin	10.52
tin	7.25
Moisture Content:	0.204893
filled ring weight	241.9
Empty ring weight	83.59
Bulk density	1.83E+03
Dry density	1522.6
Void ratio	0.740444
Sr	0.733298

Moisture Calculation				
Specific gravity =	2.65			
Mould volume (m^3) =	8.63E-05			
Water density (kgm-3)=	1000			
Wet+tin	11.25			
Dry+tin	10.53			
tin	7.24			
Moisture Content:	0.218845			
filled ring weight	245.86			
Empty ring weight	83.55			
Bulk density	1.88E+03			
Dry density	1543.202			
Void ratio	0.717209			
Sr	0.808606			







#### 0.433548 porosity (n)= 0.03 Henry's equilibrium constant = volumetric air content (ɛa) = 0.010844 vol. water content (ɛw) = 0.422704 0.023526 equivalent porosity (ɛeq) = Sample height (L) = 0.019 Diff. Chamber length (a) = 0.127 $\alpha \tan(\alpha L) = \frac{\varepsilon}{\alpha}$ function for $\boldsymbol{\alpha}$ α\*tan(α\*L) - ε/a = 0.000181637 α = 3.122114005 Diffusion coefficient -7.30683E-07 slope = De = 1.76348E-09

**Calibration Equation** 

8.6

conc a=

c0 =

percent a=

Calculation

Dry density =

y=a\*x+b

20.949

1501.097

-0.1623

-0.39534

0.832284912 b=

2.02738798 b=

### Test 10







Calibratio	on Equation	y=a*x+b			
conc	a= 0.827718961		b=	-0.15727	
percent	a=	2.01626564	b=	-0.38309	
c0 =	c0 = 8.6			)	
Calculatio	on				
Dry densi	ty =		1495.763	5	
porosity	(n)=		0.435561		
Henry's e	quilibrium	constant =	0.03	8	
volumetric air content (ɛa) = 0.321686					
vol. wate	r content (	εw) =	0.113875	i	
equivale	nt porosity	(ɛeq) =	0.325102	!	
Sample height (L) = 0.019					
Diff. Char	nber lengt	0.127	,		
function for a					
$\alpha^{*}$ tan( $\alpha^{*}$ L) - $\epsilon/a = 7.60263$ E-05					

α	=	11.51421788

### Diffusion coefficient

slope = -0.000425208

De = 1.04268E-06

Moisture Calculation	
Specific gravity =	2.65
Mould volume (m^3) =	8.63E-05
Water density (kgm-3)=	1000
Wet+tin	13.02
Dry+tin	11.75
tin	7.24
Moisture Content:	0.281596
filled ring weight	249.23
Empty ring weight	83.22
Bulk density	1.92E+03
Dry density	1501.097
Void ratio	0.765375
Sr	0.974987

Moisture Calculation						
7	Specific gravity =	2.65				
9	Mould volume (m^3) =	8.63E-05				
	Water density (kgm-3)=	1000				
	Wet+tin	12.48				
	Dry+tin	12.11				
	tin	7.25				
	Moisture Content:	0.076132				
	filled ring weight	222.84				
	Empty ring weight	83.94				
	Bulk density	1.61E+03				
	Dry density	1495.763				
	Void ratio	0.771671				
	Sr	0.261444				







Calibratio	n Equatio	y=a*x+b			
conc	onc a= 0.8322849		b=	-0.1623	
percent	a=	2.02738798	b=	-0.39534	
c0 = 8.6			20.949		
Calculatio	on				
Dry densi	ty =		1545.5	i	
porosity (n)=			0.416793	5	
Henry's equilibrium constant =			0.03	3	
volumetr	ic air conte	ent (εa) =	0.043358	3	
vol. wate	r content (	εw) =	0.373434	Ļ	
equivalent porosity (εeq) =			0.054561		
Sample height (L) =			0.019	)	
Diff. Chamber length (a) =			0.127	,	
	α tan(a				

Moisture Calculation	
Specific gravity =	2.65
Mould volume (m^3) =	8.63E-05
Water density (kgm-3)=	1000
Wet+tin	11.89
Dry+tin	10.88
tin	6.7
Moisture Content:	0.241627
filled ring weight	249.14
Empty ring weight	83.55
Bulk density	1.92E+03
Dry density	1545.5
Void ratio	0.714656
Sr	0.895971

function for  $\alpha$  $\alpha^* tan(\alpha^*L) - \epsilon/a = -1.80868E-05$ 

α = 4.748587205

Diffusion coefficient

slope = -1.03068E-06 De = 2.49391E-09

xlvi







Degree of saturation Sr = 0.2







Calibration Equation			y=a*x+b	
conc	a=	0.743301642	b=	-0.14271
percent	a=	1.810630942	b=	-0.34764
c0 =	8.	6	20.949	9
Calculatio	on			
Dry densi	ity =		1427	7
porosity	(n)=		0.46	5
Henry's e	quilibriun	n constant=	0.03	3
volumetr	ic air cont	ent (εa) =	0.414	1
vol. wate	r content	(εw) =	0.046	5
equivale	nt porosity	(seq) =	0.41538	3
Sample height (L) =			0.019	9
Diff. Chai	mber leng	th (a) =	0.127	7
	α tan(	$\alpha L) = \frac{\varepsilon}{a}$		
function	for α			
α*tan(α*	L) - ε/a =	-4.3884E-05		
α =		12.9858729	I	
Diffusion coefficient				
slope =		-0.00043774	Ļ	
De =		1.07825E-06	;	

Calibration Equation			y=a*x+b	
conc	a=	0.741507156	b=	-0.1357
percent	a=	1.8062597	b=	-0.33055
c0 =	8.6	5	20.949	1
Calculatio	on			
Dry densi	ity =		1427	,
porosity	(n)=		0.46	
Henry's e	quilibrium	constant=	0.03	
volumetr	ic air conte	ent (εa) =	0.368	:
vol. wate	r content (	0.092	1	
equivalent porosity (ɛeq) =			0.37076	i
Sample h	eight (L) =		0.019	i i
Diff. Chai	mber lengt	:h (a) =	0.127	,
	α tan(a			
function	for a			
α*tan(α*	L) - ε/a =	-0.00030292		
α =		12.28154558	:	

Diffusion coeffi	cient
slope =	-0.00039652



## Sand: Test 1







Degree of saturation Sr = 0.4



# $\ln(\mathcal{C}r) = -\frac{D_p \alpha^2 t}{\varepsilon} + ln \left[\frac{2h}{L(\alpha^2 + h^2) + h}\right]$



Calibration Equation			y=a*x+b	
conc	a=	0.756442959	b=	-0.16869
percent	a=	1.842642273	b=	-0.41091
c0 =	8.6	i	20.949	
Calculatio	on			
Dry densi	ty =		1427	
porosity (	n)=		0.46	
Henry's e	quilibrium	constant=	0.03	
volumetr	ic air conte	nt (εa) =	0.322	
vol. water content (εw) =			0.138	
equivalent porosity (ɛeq) =			0.32614	
Sample h	eight (L) =		0.019	
Diff. Char	nber lengt	h (a) =	0.127	
	α tan(a	$\alpha L) = \frac{\varepsilon}{a}$		
function f	or α			
α*tan(α*	L) - ε/a =	-6.3883E-05		
α =		11.53197177		
Diffusion	coefficien	t		
slope =		-0.00033509		

8.21785E-07

De =

conc	a=	0.765192633	b=	-0.13238
percent	a=	1.863955868	b=	-0.32246
c0 =	8.6	5	20.949	)
Calculatio	on			
Dry densi	ity =		1427	,
porosity	(n)=		0.46	5
Henry's e	quilibrium	0.03	3	
volumetric air content (ɛa) =			0.276	5
vol. wate	r content (	0.184	Ļ	
equivalent porosity (ɛeq) =			0.28152	<u>!</u>
Sample height (L) =			0.019	)
Diff. Chamber length (a) =			0.127	,
$\alpha \tan(\alpha L) = \frac{\varepsilon}{a}$				
function for $\boldsymbol{\alpha}$				
$\alpha^{*}$ tan( $\alpha^{*}$ L) - $\epsilon/a = 0.000355578$				
α =		10.7269094		

Diffusion coefficient slope = '-0.00025743

De = 6.29827E-07







Calibration Equation		y=a*x+b		
conc	a=	0.75537989	b=	-0.11935
percent	a=	1.8400527	b=	-0.29073
c0 =	8.	6	20.949	J
Calculatio	on			
Dry dens	ity =		1427	,
porosity	(n)=		0.46	i i
Henry's e	quilibrium	n constant=	0.03	
volumetr	ic air cont	ent (εa) =	0.23	
vol. wate	r content	(ɛw) =	0.23	
equivale	nt porosity	(seq) =	0.2369	J
Sample height (L) =			0.019	J
Diff. Chamber length (a) =			0.127	,
$\alpha \tan(\alpha L) = \frac{\varepsilon}{a}$				
function	for α			
$\alpha^{*}$ tan( $\alpha^{*}$ L) - $\epsilon$ /a = 0.00025902				
α =		9.85093385		
Diffusion coefficient				
slope =		-0.0001673		
De =		4.0843E-07		

### Test 6

#### Degree of saturation Sr = 0.6







Calibration Equation			y=a*x+b			
conc	a= 0.751682545		b=	-0.12553		
percent	a=	1.831046237	b=	-0.30578		
c0 =	c0 = 8.6			)		
Calculatio	on					
Dry densi	ity =		1427	,		
porosity	porosity (n)=			0.46		
Henry's equilibrium constant=			0.03	3		
volumetric air content (ɛa) =			0.184	1		
vol. water content (εw) =			0.276	5		
equivalent porosity (ɛeq) =			0.19228	3		
Sample height (L) =			0.019	)		
Diff. Chamber length (a) =			0.127	,		
$\alpha \tan(\alpha L) = \frac{\varepsilon}{a}$						

### function for $\boldsymbol{\alpha}$ $\alpha^{*}$ tan( $\alpha^{*}$ L) - $\epsilon/a = 4.22312E-05$ α = 8.884197652 Diffusion coefficient

Diridsion coeffici	
slope =	-9.89984E-05
De =	2.41171E-07

Degree of saturation Sr = 0.7







Calibration Equation			y=a*x+b	
conc	a=	0.757042254	b=	-0.1181
percent	a=	1.844102113	b=	-0.28768
c0 =	8.0	6	20.949	)
Calculatio	on			
Dry densi	ity =		1427	,
porosity	(n)=		0.46	5
Henry's e	quilibrium	n constant=	0.03	3
volumetr	ic air cont	ent (εa) =	0.138	3
vol. water content (ɛw) =			0.322	2
equivalent porosity (ɛeq) =			0.14766	5
Sample h	eight (L) =		0.019	)
Diff. Chamber length (a) =			0.127	7
$\alpha \tan(\alpha L) = \frac{\varepsilon}{a}$				
function	for α			
α*tan(α*	L) - ε/a =	0.000492933	3	
α =		7.795584476	5	
Diffusion coefficient				
slope =		-3.07401E-05	5	
De = 7.46915E-0			3	

# Test 8

Degree of saturation Sr = 0.8







Calibration Equation			y=a*x+b	
conc	a= 0.844876707		b=	-0.16898
percent	a=	2.058060713	b=	-0.41161
c0 =	c0 = 8.6		20.949	
Calculatio	on			
Dry densi	ity =		1427	,
porosity	(n)=		0.46	i
Henry's equilibrium constant=			0.03	
volumetric air content (ɛa) =			0.092	!
vol. wate	vol. water content (ɛw) =			3
equivalent porosity (εeq) =			0.10304	Ļ
Sample height (L) =			0.019	)
Diff. Chamber length (a) =			0.127	,
	α tan(	$\alpha L) = \frac{\varepsilon}{a}$		
function for $\alpha$				
** ( **) (				

u tan(u L) - c/a -	0.0001/00/9
α =	6.518643301
Diffusion coeffici	ent
slope =	-2.36017E-06

slope -	2.500172 00
De =	5.72314E-09

Degree of saturation Sr = 0.9



# $\ln(\mathcal{C}r) = -\frac{D_p \alpha^2 t}{\varepsilon} + ln \left[\frac{2h}{L(\alpha^2 + h^2) + h}\right]$



Calibration Equation			y=a*x+b	
conc	a=	0.781179035	b=	-0.11171
percent	a=	1.902897629	b=	-0.27211
c0 =	8.	6	20.949	)
Calculation	on			
Dry dens	ity =		1427	,
porosity	(n)=		0.46	5
Henry's e	quilibrium	constant=	0.03	3
volumetr	ric air conte	0.046	5	
vol. wate	vol. water content (ɛw) =			1
equivalent porosity (ɛeq) =			0.05842	2
Sample height (L) =			0.019	9
Diff. Cha	mber leng	th (a) =	0.127	,
	α tan(	$\alpha L) = \frac{\varepsilon}{a}$		
function	for a			
α*tan(α*L) - ε/a = 6.75514E-05			5	
α =		4.913623082	2	
Diffusion	coefficier	nt		
slope =		-1.67242E-07	,	
De = 4.04673E-1			)	

End of thesis