In-situ measurement of chloride ion concentration in concrete

Yawar Abbas

IN-SITU MEASUREMENT OF CHLORIDE ION CONCENTRATION IN CONCRETE

Yawar Abbas

20th November 2015

The research described in this thesis was performed at the BIOS – Lab on a Chip group, which is part of MESA+ Institute for Nanotechnology, and MIRA Institute for Biomedical Technology and Technical Medicine, at the University of Twente. This work was funded by the Dutch Technology Foundation (STW), within the Perspectief program “Integral Solution for Sustainable Construction (IS2C)” project 10968.

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Title: In-situ measurement of chloride ion concentration in concrete

Cover: Inspection of the Nijkerk bridge, The Netherlands, during the IS2C workshop (www.is2c.nl).

Author: Yawar Abbas

ISBN: 978-90-365-3991-3

DOI: 10.3990/1.9789036539913

URL: <http://dx.doi.org/10.3990/1.9789036539913>

Printed by: Gildeprint, Enschede, The Netherlands

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DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
prof. dr. H. Brinksma,
on account of the decision of the graduation committee,
to be publicly defended
on Friday, 20 November 2015 at 14:45 hrs.

by

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in Karachi, Pakistan

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Promotor: Prof. dr. ir. Albert van den Berg

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to

Dr. Abdus Salam

Nobel Laureate in Physics 1979

who has been an inspiration during my academic and research career

“Scientific thought and its creation is the common and shared heritage of mankind”

“You cannot escape knowledge; Science is knowledge”

Dr. Abdus Salam

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Chapter 1.

Introduction

In this chapter, the motivation, background and aim of this work are presented. A brief description of the theory of chloride-based corrosion also known as pitting corrosion is discussed. At the end of this chapter an outline of this thesis is given.

1.1. Motivation

Reinforced concrete is an important part of infrastructures around the world due to its cost effectiveness and high compressive and tensile strength [1]. The tensile strength comes from the reinforcement steel. The reinforcement steel used in such structures suffers from corrosion over time, lowering its strength and causing deterioration. This deterioration is more acute in structures near marine and industrial environment [2, 3]. This has been a major concern for both the asset owner and the construction engineers. In 2011, the U.S.A. Federal Highway administration stated that 11% of the national bridges are structurally defective [4, 5]. This can result in fatal accidents such as the collapse of I-35W Mississippi river bridge on 1st of August 2007 [6]. The collapsed bridge is shown in Figure 1.1. This not only causes human casualties but also economic impact due to additional travel cost [7]. Therefore, monitoring such deterioration is crucial for determining the life time and maintenance cycle of reinforced concrete (RC) structures.

Figure 1.1: Snapshot of the collapsed I-35W Mississippi river bridge on 1st of August 2007. The bridge was Minnesota's second busiest, carrying 140,000 vehicles daily [8].

Other than reinforcement corrosion, there are different deterioration mechanisms of RC structures such as alkali silica reaction (ASR), freezing and thawing, acid attack, abrasion/erosion and mechanical loading [9, 10]. However, corrosion of reinforcement steel is one of the most frequent and prime deterioration mechanism [11, 12]. There are two main causes for corrosion of steel in concrete; carbonation and chloride attack. Carbonation is caused by the reaction of the environmental CO_2 with the alkaline constituent, reducing the pH around the steel. In contrast,

chloride ions infiltrate from ambient sources and break the passive film of steel. Both carbonation and chloride attack drastically increase the corrosion rate of reinforcement steel [9, 13]. In this work we treat the deterioration due to chloride attack and evaluate techniques to measure its concentration in concrete.

Figure 1.2: (a) Deterioration of the concrete bridge cover near the splash zone due to the corrosion of steel inside [14] (b) Splash zone of the pillar of concrete bridge. Considerable corrosion of embedded steel is observed in the splash zone [15] (c) De-icing salt is dispensed on roads and bridges to melt the ice during snow in winter [16] (d) Reinforcing bar (16mm) with pitting corrosion. The corrosion was caused by chloride (salt), which had migrated through the concrete surface up to the reinforcement [17].

1.2. Deterioration due to chloride

Mainly, there are two types of corrosion in reinforcement steel; normal corrosion and pitting corrosion. In normal corrosion a passive layer of corrosion product is formed at the surface of steel, reducing further corrosion [9]. This type of corrosion is not that critical as the passivation film protects steel from further deterioration [9, 12]. When the amount of

chloride ions increases beyond a certain threshold, it breaks the passivation film causing pitting corrosion. Pitting corrosion is more rapid and noxious as it prevents the formation of a passivation layer on the steel surface [13, 18]. Structures near to sea water such as bridges are prone to pitting corrosion. The most critical area in these structures is the splash zone. This is the area near the air/water interface. Due to abundant supply of oxygen from the atmosphere and chloride from sea water, the electrochemical process of corrosion cell is accelerated. Such deteriorations are shown in Figure 1.2a and b. Due to the large volume of the corrosion product the concrete cover is detached in the splash zone. Delayed maintenance could result in the collapse of these structures and human casualties, but unnecessary upkeep increases both costs and CO₂ emissions. To precisely predict the optimal time for maintenance of these structures, a service-life model of the concrete is required [19] and the chloride ion concentration is an essential parameter.

In the Netherlands, where most of the infrastructures are near sea water, pitting corrosion is the most frequent and fatal deterioration mechanism [20]. An example of such deterioration is shown in Figure 1.3, which is a snapshot of the Nijkerk bridge through N301 road, the Netherlands. According to the Ministry of infrastructure and the environment (Rijkswaterstaat, The Netherlands), the concentration of chloride near the reinforcement beam has reached its threshold value (0.2 % by weight of concrete) and the condition of the bridge was considered critical as it was closed for heavy traffic.

1.2.1. Ingress of chloride in concrete

Chloride ions in concrete may arise from both internal and external source. Internal sources are the chloride salt in aggregates and mixtures during casting of concrete. External sources include sea water for structures near marine environment and de-icing salt, commonly used for melting ice on road and bridges, see Figure 1.2c.

Figure 1.3: (a) Snapshot of the pillars of the Nijkerk Bridge at N301 road, The Netherlands. (b) On 27th of April 2012, the IS2C workshop team inspected the beams at the bottom of the bridge. The steel inside the beam expanded due to corrosion and removed the concrete cover as visible in the red circle. The inspection report showed high chloride content in the beams.

Figure 1.4: The chloride ion concentration profiles at different time of exposure to a saturated concrete sample [21].

The ingress of chloride ions from an external source occurs in liquid phase with the diffusion of chloride ions due to a concentration gradient. The diffusion of Cl^- in concrete is a function of the humidity inside and the pore size distribution, in other words the water to cement ratio (w/c). The ingress of chloride ions occurs progressively in concrete which is exposed to both wet and dry conditions [13]. A typical chloride profile ingress at different exposure time is shown in Figure 1.4 [21]. In wet condition Cl^-

diffuses into the concrete and once it gets dry the chloride remains inside the concrete. In the next wetting cycle the water brings more chloride inside the concrete. Over time the concentration gradient of chloride ion decreases and some salt may diffuse back to the surface. Therefore, typical chloride ingress follows a non-linear profile with a decrease in the chloride content along the depth of the concrete cover.

1.2.2. What chloride does in concrete – the chemistry behind pitting corrosion

When reinforcement steel is immersed in a concrete paste, it undergoes oxidation with the formation of $\gamma\text{-Fe}_2\text{O}_3$ due to the high alkalinity of the paste [13]. This is known as the normal corrosion of reinforcement steel. This forms a tight passive layer of $\gamma\text{-Fe}_2\text{O}_3$ film on the steel surface causing self-inhibition of corrosion. Due to the local differences in the electrical potential along a steel bar, an electrochemical cell is formed with the partition of cathodic and anodic reactions. Such a localized difference in electrical potential arises due to small differences in local environment around the area of the steel bar. These reactions are as follows:

Anodic reaction:

Cathodic reaction:

At the anodic region the steel oxides and pass positively charged ferrous ions (Fe^{2+}) to the solution while leaving electrons behind in the conducting steel. These electrons travel through the conducting steel and reach the cathodic area enriched with water and oxygen. At the cathode both water and oxygen are reduced to hydroxide ions. At the anodic region the ferrous ions react with hydroxide ions in the pore solution to form ferric hydroxide which eventually forms ferric oxide (Fe_2O_3) which is the corrosion product. So the main ingredients of such corrosion are oxygen and water. There is no corrosion in dry concrete where the humidity is below 60%; nor in the absence of oxygen [13]. Therefore the rate of corrosion is higher at the water/air interface of immersed steel.

The formation of the oxide film at the surface of steel restricts the transport of ions to the steel, inhibiting the corrosion rate. In such condition the reinforcement steel remains intact and the structure lives to its projected lifetime. However, once a threshold amount of chloride ions

are present in concrete, they destroy the passivation film at a local position on the steel bar and causes rapid corrosion, forming pits at the localized areas. A typical pit is shown in Figure 1.2d. Chloride ions are known as a specific and unique destroyer of reinforcement steel as described by Verbeck [22]. The formation of a pit and the whole pitting corrosion cell is shown in Figure 1.5. A macro-cell is formed as a result of a pit with the pit being an anode because of the de-oxygenation (due to the constriction of the pit) and the passivated area next to the pit acts as a cathode. The aggressive anions such as Cl^- migrate towards the anode (pit) and prevent the formation of a passivation film. The electrons from the oxidation site travel to the cathode site where reduction of oxygen takes place. The following electrochemical reaction results in the formation of pits:

In the intermediate step ferric(III) chloride is formed but overall Cl^- is regenerated as the rust contains no Cl^- . The processes involved in this macro-cell are also shown in Figure 1.5.

Figure 1.5: Schematic illustration of chloride induced pitting corrosion and reaction steps: 1. Anodic iron dissolution; 2. Flow of electrons through metal; 3. Cathodic reduction reaction; 4. Ionic current flow through the electrolyte [23].

In the presence of high alkalinity, chloride ions are not that aggressive due to the readily available hydroxide ions that repair the broken passivation layer. But in the presence of the threshold chloride content, the breakage of the passivation film is sustained due to enough supply of chloride ions. Low pH and high Cl^- concentration is the lethal combination to initiate

pitting corrosion [9, 24]. Pitting corrosion is localized and rapid as compared to normal corrosion. Therefore, there are two main consequences of such corrosion. First, due to the formation of pits the cross sectional area of the steel reduced at localized places reducing its strength (load carrying capacity). Second, the rapid increase in the corrosion product results in the crack in the concrete structure, thereby reducing the strength and making it vulnerable to more aggressive ions, initially protected by the cover of concrete.

1.2.3. Free, bound and acid soluble chloride

Chloride exists in two different forms in concrete namely; free and bound chloride. The sum of both gives the total chloride content. This will also be discussed in detail in chapter 2. Bound chloride is either attached chemically to the hydration product of cement in the form of calcium chloroaluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10 \text{H}_2\text{O}$) also known as Friedel's salt or physically at the surface of gel pores [13]. On the other hand free chloride ions remain in the ionic form in the pore solution and contribute to the pitting corrosion. Therefore, for the durability purpose, measuring the concentration of free chloride is of main interest.

1.3. Critical chloride content in concrete

As discussed in previous sections, pitting corrosion is initiated when the chloride ion concentration in concrete reaches its threshold value, which is also known as the critical chloride content, C_{crit} [23, 25]. There are two different ways of defining C_{crit} : (1) based on theory i.e. the chloride ion concentration required for de-passivation of the steel, (2) based on the visible or acceptable deterioration of the concrete structure [25]. The concepts of these definitions are shown in Figure 1.6. There are two stages of deterioration due to corrosion; initiation and propagation stage. In the initiation phase no significant deterioration is observed, whereas in the propagation stage large deterioration and increase in corrosion rates are observed. According to the first definition the amount of chloride to initiate the propagation stage is C_{crit} , whereas, according to the second definition the amount of chloride to observe the acceptable or visible deterioration in propagation stage is C_{crit} .

Although several studies have been performed to evaluate C_{crit} [25], there is no universal value so far, since it depends on several factors like pH, temperature, humidity, oxygen availability and steel concrete interface [13, 25]. Many of the influencing factors are still not completely understood [13]. Moreover, the non-uniformity inside concrete structures misleads the value of C_{crit} . Angst et al. 2009 evaluated several conditions

and reported values for critical chloride content. A crucial parameter for C_{crit} was found to be the ratio between the concentration of Cl^- and OH^- with the most accepted value of $[Cl^-]/[OH^-] = 0.6$ in the literature [26]. The effect of pH and the chloride ion concentration on the corrosion rate is shown in Figure 1.7. From visual inspection, higher corrosion rates are observed for low pH and high chloride contents.

Figure 1.6: Deterioration of a concrete structure due to the pitting corrosion of the reinforcement steel based on Tuutti's model [25, 27]. At the critical chloride content the degree of corrosion enters the propagation state with an increasing in corrosion rate.

Figure 1.7: Snapshots of steel wires immersed in different electrolytes for 3 months. Higher corrosion product (brown rust) is visible in case of lower pH and higher chloride ion concentration.

1.4. Integral solution for sustainable construction (IS2C)

This work is a part of a Perspectief STW program “Integral Solutions for Sustainable Construction (IS2C)”. It encourages new technologies and innovation on durability and service-life assessment of constructions and sets a new standard for sustainable construction. These innovations will be used in the development of a next generation “*predictive Simulation Model for service-LIFE assessment (SIMLIFE)*”. The building blocks to such a model are the key performance indicators, degradation mechanisms, sensors for degradation and structural performance monitoring, materials performance and structural deterioration, and data management. The three main research directions of the IS2C program are Sensing & Monitoring, Degradation mechanisms and Materials & Structures. This concept of integral approach is shown in Figure 1.8.

Chloride ion concentration is a key parameter for the SIMLIFE model to determine the health of a structure. Developing a chloride ion sensor falls under the category of Sensing and Monitoring. To reliably measure the chloride ion concentration the sensor should be embedded inside concrete. The critical requirements of the sensor, keeping in mind the state of the art technologies, are stated in section 6 of this chapter.

Figure 1.8: The concept of integral approach of the STW IS2C Perspectief program. This program is demanded to comply with the integral multidisciplinary approach for sustainable construction and to emphasize the three overlapping research fields, i.e. Sensing & Monitoring, Degradation mechanisms and Materials & Structures [28].

1.5. In-situ chloride ion measurement in concrete

For the last two decades chloride ion concentration has been measured in concrete using electrochemical techniques such as potentiometry [29-31]. Here, the open circuit potential (OCP) of a silver/silver chloride (Ag/AgCl) electrode is measured with respect to a reference electrode at equilibrium. The OCP is measured in the extracted pore solution which is acquired by drilling holes (destructive sampling) in concrete structures [5, 32, 33]. The extraction of pore solution destroys concrete structure by drilling cores for sampling and gives unreliable intermittent measurements. For reliable and continuous measurement, the sensor (Ag/AgCl electrode) should be embedded inside concrete and the OCP should be measured wirelessly and displayed on a readout device as illustrated in Figure 1.9 [34, 35]. This method requires both the working and reference electrode to be embedded inside concrete (near each other) to reduce errors due to diffusion potential [36]. The limiting factor of this approach (for in situ measurement in concrete) is the long term stability (more than 10 years) of the reference electrode [37]. Different techniques for in situ measurement of chloride ion in concrete are discussed in chapter 2 in detail.

1.6. Sensor requirements

There are some requirements of the sensor for long-term, reliable and in-situ measurement of chloride in concrete. Following are the main requirements:

- The sensor should work as a stand-alone system embedded in concrete with a remote readout device.
- It should give reliable and long-term measurement results of the concentration of chloride ions in concrete

The sensor will be embedded at critical area of bridges and structures such as splash zones. Furthermore, the sensor should have a potential of miniaturization, cost effectiveness and integration. Figure 1.9 shows the artistic illustration of an embedded chloride ion sensor for measurement inside concrete.

Figure 1.9: Artistic illustration of the concept of in-situ chloride ion measurement in concrete. For reliable and continuous monitoring of chloride ions the sensor should be embedded inside concrete and the data should be transferred wirelessly to a readout unit.

1.7. Focus of this work

We have studied different electrochemical approaches to measure chloride ion concentrations in concrete. Our research was mainly focused to solve the challenges of the in-situ measurement of chloride in concrete structures. For the state of the art electrochemical measurements such as potentiometric measurement of a silver-silver chloride electrode, the drift from the reference electrode for long-term measurement was critical. So the focus of this work is to solve the challenge of the reference electrode, either by removing it or making a better one. Furthermore, investigating corrosion monitoring and wireless data communication techniques are treated in this work.

1.8. Thesis outline

We covered three different themes in this thesis i.e. the challenge of a long-term stable reference electrode, corrosion monitoring and passive-wireless communication in concrete. These themes are presented in the experimental chapters. In chapter 2, a brief description of all the existing techniques regarding in-situ measurement of chloride in concrete is presented. The scheme of the chapters coming up is shown in Figure 1.10.

There are different approaches to solve the problem of the stability of the reference electrode, either by removing it or by making a better reference electrode. These are discussed in chapter 3 and 4, respectively. In chapter 5 a corrosion monitoring approach using transient time measurement is presented. This is a rigorous sensing approach which indicates the active and passive corrosion status of reinforcement steel. To complete the sensor system a passive wireless approach for measurement inside concrete is presented. Here, the OCP of an Ag/AgCl electrode is measurement using a near field electromagnetic coupling. Finally, the main findings and outlook are summarized in chapter 7.

Chapter 2: Non-destructive techniques to measure chloride ions in concrete - a review	<ul style="list-style-type: none"> • Reviewing the existing literature on non-destructive measurement techniques of chloride ions in concrete
Chapter 3: Dynamic measurement of chloride ions	<ul style="list-style-type: none"> • A chronopotentiometric approach to measure chloride ions using potential gradient and transition time of a Ag/AgCl electrode
Chapter 4: Activated carbon as a pseudo-reference electrode in concrete	<ul style="list-style-type: none"> • In search for a long-term stable reference electrode in concrete • Kynol based activated carbon as a pseudo-reference
Chapter 5: Corrosion monitoring of reinforcement steel	<ul style="list-style-type: none"> • Corrosion monitoring of reinforcement steel using galvanostatically induced potential transients
Chapter 6: Connecting to concrete	<ul style="list-style-type: none"> • A passive-wireless measurement of chloride ion in concrete using near field electromagnetic coupling
Chapter 7: Conclusion	

Figure 1.10: Scheme of the upcoming chapters and their short descriptions.

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Chapter 2.

Non-destructive techniques to measure chloride ions in concrete - a review

The techniques for non-destructive in situ measurement of chloride ions are presented. Non-destructive (ND) in situ measurement is crucial for reliable and continuous concentration determination of chloride ions in concrete. Over the last 20 years, several studies have been performed on the ND measurement. These were mainly focused on electrochemical and electromagnetic techniques. Each of the techniques has its advantages and disadvantages. Depending on the requirement of the assets manager and constructor, these techniques can favorably be applied, as discussed in this chapter.

2.1. Introduction

Chloride ion concentration is one of the most important indicators of the deterioration of reinforced concrete (RC) structures [1-6]. In the presence of a critical amount of chloride ions, also known as critical chloride content, the reinforcement steel undergoes rapid corrosion. Due to the local formation of pits, such corrosion is called pitting corrosion [7-9]. As compared to normal corrosion, pitting corrosion is more fatal [10, 11], as it drastically reduces the strength of reinforced concrete. In normal corrosion, a passive film of iron oxide is formed at the surface of steel, inhibiting further corrosion, whereas in pitting corrosion, this passive film is broken, forming high volume corrosion products. This results in the crack formation and detachment of the concrete cover. Structures near marine environment or those exposed to de-icing salt are prone to pitting corrosion. Specially, the splash zone near sea water, which is the area near the air/water interface, undergoes such deterioration, due to readily available oxygen, water and chloride [12-14]. On-demand maintenance of these structures not only preserves them but also reduces unnecessary costs and CO₂ emissions [15]. The chloride ion concentration in concrete is measured to estimate the risk of corrosion and therefore predicting the lifetime and maintenance cycle of RC structures [16-19].

The present review summarizes different techniques reported so far for non-destructive in-situ measurement of chloride ions in concrete. For more than two decades in-situ measurement of chloride inside concrete has been reported in literature [20-22]. These techniques are characterized into two main approaches i.e. electrochemical and electromagnetic. The description of these techniques along with their advantages and disadvantages are presented.

2.2. Types of chloride in concrete

In concrete, the chloride exists in different forms, namely free and bound chloride. Before moving to the measurement techniques, it is important to describe these types.

Free chloride is in the ionic form in the pore solution and can diffuse to the steel through the pores. On the other hand, bound chloride is either chemically or physically attached to the hydration product, also known as chemically and physically bound chloride, respectively [23].

In hydrated cement-based materials, the chloride is free if its concentration in the pore solution cannot exceed that of the storage solution (external chloride solution). The physically bound chloride

adsorbed (loosely bound) to calcium silicate hydrate gel (C-S-H), it is released into the pore solution expressed under pressure. On the other hand, the chemically bound chloride is extracted in acidic environment to the pore solution [24, 25].

Chemical binding is the result of chemical reactions between chloride ions and certain cement hydration products, leading to the binding of chloride ions. It is believed that chloride ions are chemically bonded mostly in the hydrated phases of tricalcium aluminate (C_3A) to form calcium chloroaluminate hydrate or Friedel's salt [26]. However, Friedel's salt is not the only phase responsible for chloride binding [27] and other phases including Calcium-Silicate-Hydrate (C-S-H), hydration product of alite (C_3S) and belite (C_2S), [28, 29] and the ferrite analogue of Friedel's salt should also account [30-32].

The chloride adsorption on the surface of C-S-H controls physical binding of chloride. It is due to electrostatic or Van der Waals forces between the chloride ions and the surface of the C-S-H. The physically and chemically bound chlorides are dependent on each other concentrations. A linear relationship between the amount of Friedel's salt and the total amount of bound chlorides has been suggested [6, 33]. The traditional methods for free chloride ion determination involve expressing the pore solution from the cement-based materials by applying pressure, leaching of chloride from the concrete sample by a solvent or achieving equilibrium between the external solution of known concentration and the pore solution. The pore-water expression is often regarded as the most accurate method [34]. The advantages of this method are obvious as comprehensive information can be obtained not only on the chloride content but also the type and concentration of all substances dissolved in the pore water. However, its application is limited to rather porous samples. Certain minimal water content is required to obtain enough pore liquid for further analysis. Therefore, this technique is not applicable to practical concrete samples in dry state condition, with low water to cement ratios and coarse aggregate. Moreover, the chloride ion concentration measured by this method is the free chloride ions in the bulk solution and a part of physically bound chloride. It has been stated that this technique may overestimate the free chloride concentration by 30% to 200% [24]. Surprisingly, two times more chloride concentration than the expected value is also reported some time [24].

If water is used as solvent, the leached out amount of chloride is often called "water soluble chloride" and assumed to be equal to the free chloride ion concentration. This is prone to errors resulting from the reversible nature of some binding reactions, the agitation time of the powder/solvent

mixture, solvent temperature and quantity of water used. Moreover, the concrete powder should be immediately analyzed after grinding, because carbonation may reduce chloride binding which subsequently increases the water-soluble chloride content. Therefore, the amount of released chloride ions into the solution depends on the applied test procedure.

2.3. Critical chloride content

The pitting corrosion in RC is initiated when the chloride ion concentration reaches its threshold value, which is also known as the critical chloride content, C_{crit} [35, 36]. There are two different ways of defining C_{crit} : (1) based on theory i.e. the chloride ion concentration required for de-passivation of the steel, (2) based on the visible or acceptable deterioration of the concrete structure [36]. There are two stages of deterioration due to corrosion; initiation and propagation stage. In the initiation phase no significant deterioration is observed, whereas in the propagation stage large deterioration and increase in corrosion rates are observed. According to the first definition the amount of chloride to initiate the propagation stage is C_{crit} , whereas, according to the second definition the amount of chloride to observe the acceptable or visible deterioration in propagation stage is C_{crit} .

Regarding the type of chloride responsible for pitting corrosion, some literature consider total chloride content [37, 38] and others free chloride [36, 39]. Mostly, the free chloride is reported to be responsible for pitting corrosion. Although several studies have been performed to evaluate C_{crit} [36], there is no universal value so far, since it depends on several factors like pH, temperature, humidity, oxygen availability and steel concrete interface [36, 40]. Many of the influencing factors are still not completely understood [40]. Moreover, the non-uniformity inside concrete structures misleads the value of C_{crit} . Angst et al. 2009 evaluated several conditions and reported values for critical chloride content. A crucial parameter for C_{crit} was found to be the ratio between the $[Cl^-]$ and $[OH^-]$ with the most accepted value of $[Cl^-]/[OH^-] = 0.6$ [41].

2.4. Measurement techniques for chloride ingress

There are different approaches to measure chloride ion concentration in concrete depending on the application, i.e. determining the chloride ingress profile for quality control of new structures or chloride ion concentration in existing structures. The most routinely used techniques are potentiometry and the Volhard method, measuring the free and total content in extracted pore solutions, respectively [42]. An overview of the available techniques is shown in Figure 2.1.

The techniques are broadly categorized into laboratory and field methods. The laboratory methods are used to validate the concrete-chloride penetration models and the quality of concrete before it is casted. These techniques are focused on determining the diffusion coefficient and ingress profile of chloride over time. These studies use different descriptions and theories such as Fick's law, Nernst-Planck expression [43], binding isotherms [6], moisture transport [17] and temperature variation [42, 44]. On the other hand the field methods are focused on measuring chloride in existing concrete for determining its durability and maintenance cycle.

The field methods are further divided into destructive and non-destructive measurements. The state-of-the-art Volhard [45-47] and potentiometric methods [21, 38, 48, 49] are both destructive and require extracted pore solution. Such destructive sampling can result in significant measurement errors [50], resulting in under or over-estimations. This can lead to a wrong maintenance decision. Furthermore, such destructive approaches bring additional indirect costs due to road closures and traffic delays [15, 42]. These techniques are mostly used for short term decisions regarding maintenance and model updating [16, 42, 51].

The non-destructive methods are characterized by their non-invasive nature, i.e. they do not alter the properties of the measuring sample. These techniques work by either using external contactless measurement or embedded sensors inside concrete [42, 52]. The non-destructive methods are mainly divided into electrochemical and electromagnetic approaches. Although some of the electromagnetic approaches seem destructive and laborious, such as Nuclear Magnetic Resonance (NMR), X-ray and Prompt Gamma Neutron Activation (PGNA) analysis, these methods have potential for non-invasive measurements without destroying the structure. The focus of this review is the non-destructive measurement techniques which are indicated in the red-solid-lined boxes in Figure 2.1. A brief description of each of the techniques along with their strengths and weaknesses is presented in Figure 2.1.

Figure 2.1: An overview of available techniques of measuring chloride ions in concrete. The blocks with solid-red-outline list different non-destructive techniques, which are discussed in this work.

2.5. Non-destructive in-situ measurement

Non-destructive (ND) measurement of chloride ions in concrete is not a straightforward task. A perfect method must obey several conditions: it must be stable, non-invasive, invariant to chemical and thermal changes in concrete, able to pass small currents with a minimum of polarization and hysteresis effects (for electrochemical methods), display long-term performance, cost effective and result from an environmentally safe manufacturing procedure [53]. However, concrete is a heterogeneous material with perm-selective properties of pore walls of cement hydration products, high alkaline pore solution with different compositions and pore systems with various porosity and pore size distribution [54, 55]. These properties induce challenges for the available chloride measurement techniques to be employed in the concrete environment. However, many attempts have been made to describe and overcome the limitations in the concrete environment. These efforts are discussed in the following section.

2.6. Electrochemical techniques

2.6.1. Potentiometric measurement

Ion selective electrodes are well established over the last decades and have been used for analytical applications. For concrete applications the first attempt to use embedded Ag/AgCl electrodes was done in the 1990s [20, 21, 52, 56, 57]. Potentiometric measurement, using a Ag/AgCl electrode, is the state of the art standard electrochemical technique to measure free chloride in concrete [20, 21, 39, 52, 53, 58]. The Ag/AgCl electrode is a chloride ion selective electrode (ISE) whose half-cell potential is a function of the Cl^- ion concentration [39]. The calibration curve of various concentrations of Cl^- ion, along with the standard deviation, σ , in synthetic pore solution, reported by Angst et al. 2010, is shown in Figure 2.2a [39]. The uncorrected values curve is the measured potential response, which is then adjusted for the activity coefficient and theoretical junction potential to give the corrected values curve.

In the field, the Ag/AgCl electrode can be embedded inside concrete and its potential can be measured with respect to an external reference electrode. Angst et al. 2010 measured the half-cell potential of an embedded Ag/AgCl electrode over a period of one month for 0.1 and 0.5 M Cl^- concentration in various alkaline media, as shown in Figure 2.2b. Indeed the potential remains stable and the Ag/AgCl is a rigorous and reliable Cl^- ion sensor in concrete.

Figure 2.2: (a) Calibration curve of chloride sensors in synthetic pore solution (mean values and corresponding line fit by linear regression analysis) [39] (b) Long-term stability: Average potential of three parallel sensors in solutions of various pH and chloride concentration versus time (white symbols = initially no chlorides; grey symbols = 0.1 M NaCl; dark symbols = 0.5 M NaCl) [39].

2.6.2. Chronopotentiometric measurement

An alternative for classical potentiometry is chronopotentiometry; a dynamic electrochemical method where the response of the system is measured to an applied stimuli. Abbas et al. 2014 reported this approach to counteract the drift issues in potentiometric response [59, 60].

When a current pulse is applied to a Ag/AgCl working electrode (WE), its potential change as a function of the Cl^- concentration in the electrolyte.

The schematic of this process is shown in Figure 2.3 [59]. The Cl^- is consumed during the applied current pulse due to the faradaic reaction ($\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl}$). This change in concentration changes the half-cell potential of the Ag/AgCl working electrode, region A as shown in the potential response in Figure 2.3. After some time the Cl^- will deplete completely near the surface of the Ag/AgCl electrode, followed by a sharp increase in its potential. This moment is called transition time, given by the Sand equation [61], region B in Figure 2.3. Therefore, the Cl^- concentration can be measured, either by measuring the potential change (Differential potential) in region A [60] or by measuring the transition time in region B [59].

Figure 2.3: (a) Schematic of the Cl^- ion detection approach. During an applied current pulse at the WE w.r.t a CE (not included in this figure), chloride ions deplete at the Ag/AgCl WE, resulting in the illustrated Cl^- ion concentration profile. (b) Schematic figure of the ΔV and $d\Delta V/dt$ response. The solid line (—) and dashed line (--) represent ΔV and $d\Delta V/dt$, respectively. t is the transition time and t is the duration of the applied current pulse [59].

The calibration curves obtained from both chronopotentiometric approaches are shown in Figure 2.4a and b. In Figure 2.4a, the potential change, ΔV , decreases with the increase in Cl^- concentration [60]. Figure 2.4b, the transition time increases with the increase in Cl^- concentration [59].

Figure 2.4 (a) The calibration curve of the potential difference, ΔV , at different Cl^- concentration is given. [60] (b) Calibration curve showing the square root of the transition time versus the Cl^- ion concentration, in a 0.5M KNO_3 background electrolyte. The circular points (o) are the measured data and the solid line (—) is the linear fit. The dashed line (--) is the theoretical curve from the Sand equation. The applied current pulse is $10 \text{ A} \cdot \text{m}^{-2}$ and the ambient temperature is 20.8°C . D and D_a are the theoretical and apparent (measured) diffusion coefficients, respectively [59].

2.6.3. Electrical resistivity and impedance analysis

The electrical resistivity (ER) is a measure of the ionic and moisture content of a concrete sample [62-64]. In ER measurement, a potential (V) is applied between two electrodes and the current (I) is measured. From this, the electrical resistance and resistivity can be computed. An increase in chloride ion concentration in concrete decreases its resistivity, provided that other factors remain constant [64-66].

Figure 2.5: (a) Schematic of the resistivity testing setup by two electrode method [67] (b) Relationship between chloride diffusivity and the electrical resistivity of concrete [67].

This method is used mainly to determine the diffusion coefficient of Cl^- in concrete. The diffusion coefficient is related to its electrical resistivity by the Nernst-Einstein equation [68]. Ozkan [67] measured the diffusion coefficient of Cl^- using ER measurements. The experimental setup and the measurement results are shown in Figure 2.5 [67]. In Figure 2.5a, the concrete sample is placed between two electrode are embedded and a dc potential is applied. The resistivity is obtained according to the standard ASTM C1760 method, which is based on Ohm's law . In Figure 2.5b, the measured relationship between the chloride diffusivity and the electrical resistivity is shown. This shows an exponential relation between the resistivity of concrete and the diffusivity of Cl^- [67].

Impedance analysis, on the other hand, utilizes both the resistive and capacitive changes in concrete due to chloride ingress. An alternating current is applied to an electrode with a range of frequency sweeps, the (complex) impedance is measured. The curve is then compared with the equivalent model of the electrode in concrete, keeping other parameters constant, and the chloride profiles are calculated [69, 70].

2.7. Electromagnetic techniques

2.7.1. Fiber optic sensor

Embedded fiber optic chloride sensors allow a non-destructive method of determining the Cl^- penetration into concrete structures [71-74]. Over the last decade, several groups have developed fiber optic sensors to measure the free chloride content in concrete. The principle is based on the changing optical properties of an opto-chemical transducer as a function of the Cl^- concentration. Therefore, the fiber optic sensors have three critical parts: (1) Opto-chemical transducers (2) optical signal carrier (3) Light source and spectrometer. Generally, optical fibers are used as signal carriers. The standard light sources and spectrometers are commercially available. Fiber optic sensors offer several advantages when compared to electrochemical techniques, such as better stability against interfering ions, sensitivity and inertness to electromagnetic noise and electrical cross-talk [71]. However, the long-term fiber material degradation, protection of the transducing element in aggressive environment, geometrical stability of the fiber, mechanical stability in a stressed concrete and temperature dependence are some critical issues which should be solved. Mostly, research has been done on the opto-chemical transducing part as it defines the sensitivity, selectivity and long-term performance of the sensor [74-77]. There are two approaches for opto-chemical transduction: (a) fluorescence-based and (b) optical grating (refractive index) based. These are briefly discussed below.

a. Fluorescence-based optical sensors

This sensing mechanism is based on the collisional quenching of the fluorescence molecule by chloride ions [77]. Such an opto-chemical transducer is also referred to as an optode. The determination of the concentration with opto-chemical probes is made possible by recent developments of fluorophores. Collisional quenching is a reversible process where the emitted intensity of fluorescence molecules decrease nonlinearly with increasing quencher concentration, in this case chloride ions.

Figure 2.6: (a) The principle of fluorescence quenching in the presence of chloride ions in the electrolyte [77]. (b) The instrumentation of fluorescence based detection of chloride ions in concrete. The transducing element (optode) is embedded in the concrete sample and the quenching effect is analyzed with a spectrum analyzer [77].

The extinction mechanism is explained by a close collision between the excited state of fluorophores (indicator dyes) and the quencher as shown in Figure 2.6a. Laferrière et al. 2008 used Lucigenin dye from molecular probes [77]. This molecule is impregnated in Sol-gel along with alginate polymer to form the chloride ion sensitive optode. The complete instrumentation of the fluorescence-based detection is shown in Figure 2.6b. The optode is placed at one end of the fiber bundle which will be embedded in concrete. The optodes are excited by a blue LED (light source) whereas the emission spectra from the optodes is analyzed at the spectrometer. The experimental setup of the sensor at various depth of concrete is shown in Figure 2.7a. The sample was simulated for hot marine (harsh) environment with varying temperature cycle and

immersion in 3% NaCl solution. For comparison, results from a standard destructive test are also plotted (i.e. Test-total Cl^- mentioned in the legend). The free chloride was calculated to be within the range of 10 % and 25 % of total chloride (dashed line). Figure 2.7b shows that the optodes values are similar to the free chloride range of the standard test which indeed proves the applicability of this device for in-situ chloride measurement in concrete.

Figure 2.7: (a) The optodes along with the optical fiber are embedded in concrete sample at a distance of 5, 10, 15 and 20 mm. (b) The comparison between measured and control results. After 30 days measurements the chloride ions (total chloride) were destructively measured by the standard Volhard method as control experiment [77].

b. Optical grating

The optical grating sensor is based on the modification of the grating portion of a long-period fiber grating (LPG). This sensor is extremely sensitive to any changes in Refractive Index (RI) of the grating surrounding, therefore the selectivity toward chloride is enhanced by incorporating a monolayer of self-assembled gold colloids with the LPG [78]. Tang and Wang 2007 [73] used this approach to measure chloride ion concentration in concrete.

Long-period grating is a opto-induced periodic modulation of refractive index along the core of fiber. It has a typical index perturbation of $\Delta n \sim 10^{-4}$ period between 100 and 1000 μm and length of 2 to 4 cm. It couples light from guided mode into forward propagating mode (in cladding) where it is lost due to absorption and scattering. There resonance can only be observed in transmission spectra. The transmission spectrum has a sharp decrease in gain at the resonance with various cladding modes.

Figure 2.8: (a) Schematic representation of the experimental setup used to make measurements with the LPG. Apparatus used to obtain transmission spectra: A, Amplified Spontaneous emission (ASE) light source; B, liquid cell; C, sensing LPG; D, optical spectrum analyzer; E, magnified view of a sensing LPG [73]. (b) The wavelength shift of a bare LPG sensor in sodium chloride aqueous solution with increasing weight concentration [73].

The center wavelength, λ_m , is a function of the refractive index of the core, cladding and surrounding medium. If the concentration of the surrounding medium changes, the RI of the grating material also changes, shifting the resonance frequency in the transmission spectrum. The sensitivity of center wavelength to index of refraction can be adjusted by the fiber parameters and the grating period. The selectivity to specific ions/molecule can be enhanced by affinitive coating on the cladding active area. The experimental setup of the measurement is shown in Figure 2.8a. The active cladding area is immersed in a aqueous solution containing sodium chloride. The wavelength shift of an LPG sensor with changing chloride ion concentration in aqueous solution is shown in Figure 2.8b.

The sensitivity and the lower detection limits of the optical grating sensor can be improved by depositing gold nanoparticles at the active side of the grating [73, 78].

Figure 2.9: (a) Experimental setup of LIBS technique [79]. (b) A snapshot of the plasma on the surface of a building material during LIBS measurement [80].

2.7.2. Laser breakdown spectroscopy

This method is able to detect the total chloride content in a concrete sample. Laser-induced breakdown spectroscopy (LIBS) allows the measurement of elements on the surface of solids, liquids and gases. In this technique first a laser pulse evaporates a small amount of elements from the surface forming plasma plume. This plasma radiation is then analyzed through spectroscopic technique to detect its composition [79, 81-84].

The LIBS setup to measure chloride in concrete samples is shown in Figure 2.9. A high energy Laser beam (Nd-YAG laser, pulse duration 10 ns, energy 300 mJ/pulse) is focused on the sample through a lens. The high energy density (> 2 GW/cm²) produced plasma with the evaporation of a small amount of the sample. The relaxation spectra of the atomic emission is observed at the detector. The optical signal is directed through a fiber optic cable to the detector. Due to other contamination from building material the spectral peak of chloride is weak, which can be enhanced by flushing the sample with helium gas. The atomic emission spectrum of a concrete sample with and without helium flushing is shown in Figure 2.10a. The chloride spectral line at 837.6 nm is reported to have

repeated peaks. The integral of the chlorine spectra gives the content of total chloride which is the measured response for calculating chloride ion concentration. The calibration curve of normalized response at various chloride contents is shown in Figure 2.10. The response increases with the increase in chloride ions in the sample.

Figure 2.10: (a) Comparison of measurements on cement mortar samples accomplished under air and helium atmosphere [79]. (b) Correlation between chloride content of the cement mortar samples and normalized integral of Cl spectral line [79].

2.7.3. Near-infrared, millimeter and microwave spectroscopy

The electromagnetic waves below the THz frequency range (near infrared, micro and millimeter wave) are known to have higher penetration and spatial resolution in concrete material [85]. These waves can be used to measure chloride content in concrete sample non-destructively [86]. The principle of millimeter wave (MMW) is presented here, which is similar to near-infrared and microwave spectroscopy. In this approach a MMW is focused to a concrete sample through a prism. The reflected wave is then collected at a Gunn oscillator. This forms an attenuated total reflection (ATR) measurement system to measure chloride ions in concrete. The refractive index of the reflecting medium should be larger than the concrete sample [87, 88]. The MMW creates an evanescent wave at the interface of prism and sample which penetrates into the sample.

Figure 2.11: (a) Schematic diagram of a millimeter wave attenuated total reflection (ATR) measurement setup. (b) Schematic diagram of a silicon prism used as total internal reflection medium. (c) ATR of samples with different Cl^- concentrations [86].

The schematic of the experimental setup is shown in Figure 2.11. The MMW penetrates into the sample as defined by the penetration depth. When a material absorb MMW the beam loses its energy according to the sample dielectric properties. The ratio of the sample power and reference power gives the ATR. The measured ATR for various chloride ion concentrations is given in Figure 2.11.

2.7.4. Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) is used for detailed analysis of concrete samples at atomic scale. The NMR technique is able to determine the presence and concentration of different nuclei due to the magnetic behavior of the nuclei of atoms.

In this method the non-zero spin nuclei of the material placed in a relatively big uniform magnetic field B_0 start to precess around the direction of B_0 with the specific frequency related to the gyromagnetic ratio of nuclei, called Larmor frequency ω_0 . Another radio frequency pulsed

magnetic field, B_1 , perpendicular to the static field is also utilized to generate small excitation in the sample and also receiving signal back from the sample[89, 90].

The possibility of detection of chloride with NMR in addition to the possibility of quasi-simultaneously measuring moisture, sodium and chloride makes NMR a suitable method to obtain chloride profiles as a function of time and position [91]. A typical NMR setup to detect chloride profiles is shown in Figure 2.12a. The salt solution absorption profiles of Cl^- for two different types of mortar at different time steps is shown in Figure 2.12b. Here, the sample is moved by a step motor and the signal is collected in different cross-sectional positions.

The poor limit of detection of chloride is an issue which limits the detectable concentration range. One way to improve this limit is averaging over many recorded signals. However, the random noise level also increases by a factor of the square root of the number of scans but it is a considerable improvement in signal to noise ratio. Another way to improve the signal for chloride is increasing the static magnetic field, B_0 , or improving the RF coil. The signal to noise ratio (SNR) measurement is always required to find the lowest chloride concentration possible to detect [92].

Figure 2.12: (a) Schematic of NMR setup with birdcage RF coil and distribution of ^{93}Cl during NaCl solution absorption in mortar specimens at 5(●), 22.2(■) and 72(▼) hours, for $w/c=0.3$ and 0.6 [92].

2.7.5. X-ray diffraction analysis

X-ray fluorescence is a general method to analyse the chemical composition of inorganic materials. The X-ray beam produced by micro capillary optics excites the different atoms in the target material, the transient excited atoms decay to a lower energy state by emitting a characteristic X-ray which is detected by an X-ray detector. Analysis of the results with data taken from highly controlled conditions determine the proportion of each element in the material. The quantitative X-ray analysis accuracy is highly dependent on homogeneity of the sample, but cement is heterogeneous in all scales, so the cement specimen can be prepared in the form of a glass bead or a pellet of pressed powder. In case of grinding cement few more issues must be considered as the X-ray intensity then is not only depended on chloride concentration but also on powder grain size, degree of compaction and chloride binding [94].

Figure 2.13: The X-ray image of chloride gradient in cement paste where red, green and blue represent, highest, moderate and lowest concentrations [95].

Sudbrink et al. 2012 studied the chloride gradient imaging by X-ray fluorescence analysis for cement paste, as shown in Figure 2.13 [95]. This image is taken by moving the sample in a raster pattern under stationary X-ray radiation with a spacing of 50 μm .

2.7.6. Prompt Gamma Neutron Activation (PGNA)

Prompt Gamma Neutron Activation (PGNA) is based on the detection of γ -rays emitted by specific nuclei in the target which are excited by neutron capture. The system consists of a portable neutron source, usually ^{252}Cf radioisotopes producing high energy neutrons in range of 1-3 MeV, a polyethylene moderator to slow down the neutrons to thermal energy and a high-purity germanium detector. The thermal neutrons can penetrate a long distance in the target until they are captured by the element nuclei in the material. The excited nuclei then decay with the characteristic γ -ray to its ground state. The emitted γ -rays are then detected by the germanium detector [96, 97]. The schematic of the experimental setup is shown in Figure 2.14a.

Figure 2.14: Schematic representation of the MP320 portable neutron generator used to measure the Prompt Gamma-ray yield. Integrated yields of 6.11 MeV Prompt Gamma-rays as a function of chlorine concentration in concrete specimens. Solid line represents the calculated yield obtained through Monte Carlo simulations.

The measured γ -line can be used for both qualitative and quantitative measurements. The qualitative analysis to determine the nuclei is not always easy as a mixture of elements gives a complex spectrum of many γ -rays, in addition of Compton scattering background noises. Naqvi et al. 2012 reported the calibration curve of the Prompt Gamma yield to various Cl^- concentrations. The intensity of the γ -line is related to the number of elemental nuclei, but to convert the intensity to concentration a calibration function is required [98].

The large cross-section of H and Cl for thermal neutron capture makes PGNA a suitable method to measure moisture and salt concentration in building materials. In addition, as the emitted γ -rays can be measured by a detector in a hemispherical volume of radius 15-20 cm, this method can

be used to measure chloride to the depth of the reinforcement bars in concrete [99-101].

The sample volume in this case can be very large, by moving the neutron source from point to point a concentration distribution map can be provided to obtain the chloride profile in depth of the concrete. Mohamed et al developed a model to determine the chloride concentration change due to diffusion of salt [98, 102].

2.7.7. GPR technique

Ground penetrating radar (GPR) is another non-destructive technique to investigate the concrete condition. In this method a transmitted electromagnetic pulse (with microwave frequency range) propagates in the material. Depending on the dielectric properties of the concrete, these are different optical responses of the electromagnetic pulse [103-106].

The amplitude of the emitted signal or the damping of the radar signal can be utilized not only to collect information about the level and location of corrosion, cracks and pore structure of the concrete, but also about moisture and chloride content, which is because of the influence of chloride and moisture on permittivity and conductivity [106, 107]. Kalogeropoulos et al. used ray-based inversion to obtain the average values of permittivity and conductivity, and full-waveform inversion for conductivity gradient estimation [108].

Figure 2.15: (a) The experimental dataset was obtained by placing GPR antennas above a concrete slab containing chloride ions distributed in gradients. (b) Free chloride % gradients of all specimens with respect to concrete mass. The gradients are analyzed using slices of 1 cm from cores probed on the specimens [108].

2.8. Comparison of non-destructive techniques

Each of the presented non-destructive techniques have their strengths and weaknesses. There are different factors which influence the selection of a technique for an application. These factors are listed in Table 2.1. The comparison among these techniques is based on the measurand, ease of embedding in concrete, long-term stability, robustness, ease of fabrication, cost effectiveness, and accuracy, see Table 2.1.

The electrochemical techniques such as potentiometry and chronopotentiometry are direct measurement techniques, measuring the concentration of free chloride. The chemical stability in aggressive environments, ease of fabrication, cost effectiveness and rigorous nature of Ag/AgCl electrodes make them one of the mostly used techniques. However, the stability of the reference electrode, cross-selectivity for OH^- and errors due to diffusion potentials in concrete restrict the long-term in-situ measurement in concrete. The effect of pH is more pronounced when concentration of OH^- is 10 times more than the $[\text{Cl}^-]$. Then, the Ag/AgCl electrode serves like a pH sensor sensitive to OH^- [39, 60]. Furthermore, the optimal sensitivity, i.e. 59 mV/decade, causes a change of 8.9 mV in reference potential means a two-fold error in the determination of concentration [109]. The chronopotentiometric technique, on the other hand, has tunable sensitivity and better long-term stability due to its dynamic nature. [59]. In the chronopotentiometric approach, a long-term stable reference electrode is not required which makes it feasible for long-term measurement in concrete. However, the interference from OH^- at high pH (pH >12) restricts these measurements in fresh concrete samples.

Electric resistivity and impedance spectroscopy techniques are indirect techniques to measure the Cl^- and depends on different factors such as temperature, ionic composition, porosity and moisture. Although these techniques are robust, cost effective and easy to use, the poor selectivity to chloride ions restrict their feasibility to measure Cl^- concentration in concrete. It can be used to determine the chloride diffusion coefficients after a comprehensive calibration.

Electromagnetic techniques in general have bulky setups and poor selectivity to Cl^- . It is difficult to embed the electromagnetic based sensors in concrete. The optical sensor based on fiber optic material can be embedded in concrete but due to leaching of dyes (transducing element), it has poor long-term stability as compare to electrochemical techniques. Moreover, the development of an optical setup is complex and labor intensive. As compared to electrochemical techniques the fiber optic sensors require extra protection by insulating the optical fibers from water, high alkalinity and mechanical stresses. Therefore, fiber optic sensors are less robust.

The other electromagnetic techniques using an external excitation, such as LIBS, x-ray analysis, PGNA and NMR, generally lack selectivity. These measurements are either based on changing the dielectric constant of the concrete due to chloride or exciting elements in concrete to detect elements signatures. Although these techniques are non-invasive, the complexity of the setup, labor intensiveness, non-selectivity and

expensiveness constraint these approaches in laboratory for detailed analysis. These techniques require a higher number of calibrations in different concrete conditions to counter the non-selectivity of chloride ions. These techniques have a potential of non-invasive, non-destructive and on-field analysis but so far this is not the case. In laser-induced breakdown spectroscopy (LIBS) the main issue lies with the low selectivity for chloride, the peaks of chloride ions are sometime not visible due to background noises. This is due to the low chloride content as compare to other elements in concrete. As compare to other contactless excitation techniques, LIBS has better portability and higher practical impact. This is evident from the number of studies performed using the LIBS technique. In case of the NMR technique, the biggest issue is the portability and the labor intensiveness. This also holds true for X-ray analysis. Both of these techniques are highly accurate and are used for modelling and testing purpose. Unlike X-ray analysis, NMR requires cores from the structures and generates chloride diffusion profile along the core. The x-ray technique requires specialized sampling methodology and sample preparation. These techniques are mostly used for quality control and pore chemistry of casting concrete.

Near-infrared, millimeter (MMW) and micro waves spectroscopy are other non-invasive electromagnetic techniques. The portability and implementation is better than other electromagnetic techniques. Moreover, MMW technology is matured and well established, where high power MMW emitters and sensitive detectors such as a Gunn oscillator and a Schottky barrier diode, respectively, are easily accessible. The low sensitivity to chloride ions and ambient interference limits its feasibility. This method is sensitive to moisture and ionic composition of the concrete sample. These measurements are valid in extreme control conditions with carefully obtained calibration curves. These techniques are capable of analyzing very large samples. They are helpful for qualitative analysis of chloride in concrete and to perform some initial quick investigation of structures.

Table 2.1: Comparison of different non-destructive techniques to measure chloride ions in concrete. In this comparison, +, ++ and +++ corresponds to fine, good and excellent and -, -- and --- corresponds to not good, bad and worse, respectively. Here N.A stands for “not available”.

classification	Techniques	Measurand	Ease of implementing in concrete + portability	Long-term stability	Robustness	Ease of Fabrication + cost effectiveness	selectivity
Electrochemical	Potentiometric measurement	Free Cl^-	+++	+	++	+++	+++
	Chrono-potentiometric measurement	Free Cl^-	+++	+++	++	+++	+++
	Electrical resistivity and impedance spectroscopy	Cl^- diffusion coefficient	+++	+++	++	+++	--
Electromagnetic	Fiber optic sensor	Free Cl^-	--	--	+	--	++
	Laser breakdown spectroscopy	Total chloride content	-	N.A.	-	-	-
	Near infrared, millimeter and micro waves spectroscopy	Free and Total chloride content and diffusion coefficient	+	N.A.	--	--	--
	Nuclear magnetic resonance	Free Cl^- and diffusion coefficient	---	N.A.	+	---	++
	X rays analysis	Total chloride content	---	N.A.	+	---	+
	Prompt gamma neutron activation	Total chloride content	---	N.A.	-	---	+
	Ground Penetrating Radar (GPR)	Free chloride content	++	N.A.	-	--	--

The GPR technique shows low selectivity towards chloride ions. The signal is affected by moisture, geometric position and ionic conductivity in concrete. These are the factors which affects the permittivity of electromagnetic waves in concrete. Moisture causes the reduction of relative permittivity and conduction [104] while chloride increases the conductivity and permittivity at low frequencies [85]. The rebar position also affects the GPR measurements and it is recommended to keep them as far as possible from the measurement points [110]. In construction industries, GPR has been routinely used for locating metallic rebar, pores and pore distribution, cracking, delamination and interfaces [42, 105, 110]. To obtain better resolution higher frequencies are needed which reduces the penetration depth. Therefore, GPR is a technique for subsurface and cover concrete imaging. Many different papers suggested GPR as a suitable technique to study bridge decks [111-114].

2.9. Strategies for in-situ chloride measurement

In the previous section, the electrochemical and the electromagnetic techniques were compared and their pro and cons were briefly discussed. When applying these techniques in real life testing, the application, asset condition, measurement type (qualitative or quantitative) and the cost should be kept in mind. Of course, it is not sensible to spend more resources on monitoring than on the maintenance of the structures. Depending on the requirement and the asset management of the structures an efficient strategy should be outlined to measure chloride ions with the existing techniques. The outline of such strategy is given in Figure 2.16.

The monitoring protocols are different for future structures as compare to existing structures. In case of existing structures, embedding the sensor by drilling cores and applying new concrete paste changes the actual condition of concrete around the sensor. This results in an erroneous signal, underestimating the Cl^- concentration in the existing structure.

In existing structure the first monitoring step is visual inspection. In the late propagation stage, when $[\text{Cl}^-]$ is higher than the critical concentration, C_{crit} , cracks and huge corrosion products are visible on the concrete cover, depicting an acute deterioration. Such structures requires maintenance straight away. In the absence of visual deterioration the next step is the qualitative analysis using GPR/near-infrared/micro or millimeter wave spectroscopy. This will give a rough estimation of the $[\text{Cl}^-]$. In general, electromagnetic techniques are expensive and labor intensive. Some techniques such as NMR, X-ray analysis and LIBS are accurate and more suitable for detailed investigation. Other techniques such as GPR,

millimeter and micro wave spectroscopy are suitable for a quick qualitative analysis of the chloride penetration in concrete. If there is no chloride or only low chloride concentrations are present then the structure is healthy and does not require maintenance at this stage.

Figure 2.16: The strategy for measuring chloride ion concentration in concrete using the existing techniques.

In the presence of Cl^- in concrete, quantitative analysis is required to precisely determine the concentration. This can be done by the potentiometric measurement on the extracted pore solution (acquired by drilling cores of the sample). Now if the chloride concentration is below the critical content, the structure is healthy and has no chloride based deterioration. If the concentration is above the critical value, the decision on the maintenance should be taken by the construction management. In case of new structures for future construction the electrochemical approach with multiple sensors; potentiometric, chronopotentiometric and electrical resistivity sensor should be embedded in concrete and the chloride ion concentration should be monitored continuously to assess the deterioration due to chloride ions.

2.10. Conclusion

The presence of chloride ions is a major cause of reinforcement steel corrosion in concrete, resulting in its deterioration. The chloride ion concentration has been measured both at the laboratory and in the field. At the laboratory, it is measured to develop an ingress model to determine the quality of pre-casted concrete, whereas in the field, it determines the deterioration of the existing structures. In field methods, the state of the art techniques are destructive and required the extraction of the concrete pore solution. For real time, reliable and continuous monitoring of the chloride-based deterioration, a non-destructive measurement technique is required. Over the last 20 years, several studies have been performed for non-destructive in-situ chloride ion measurement. These non-destructive approaches are divided into electrochemical and electromagnetic techniques.

As electrochemical techniques, potentiometry and chronopotentiometry, using a Ag/AgCl chloride ion selective electrode, have been used. In potentiometric measurements, which is a zero-current technique, the open circuit potential of an embedded Ag/AgCl electrode is measured against a reference electrode. The stability of the reference electrode potential, low sensitivity, interference from other anions and the errors due to diffusion potential limit the long-term use of this approach. Moreover, geometric positioning and temperature also affects the results. Chronopotentiometry is a dynamic measurement method which shows better stability for long-term measurements. This method does not require a classical reference electrode. The interference from hydroxide ions at high pH ($\text{pH} > 12$), limits the use of this technique in fresh concrete.

The electromagnetic techniques can be characterized into embedded and non-embedded techniques. In embedded techniques, a fiber optical sensor with optical transducer, sensitive to chloride is embedded in concrete. They are relatively inert to environmental factors, ion interference and geometric factors. Nevertheless, the lifetime of optical transducers, extra protection of fibers and the bulky measurement setup restrict their use for long-term in-situ measurements. On the other hand, the non-embedded techniques with an external excitation seem ideal due to the complete non-invasiveness and contactless nature. Nevertheless, these methods lack selectivity, portability and local chloride ion measurement.

The assets management and construction industries are still struggling for a reliable and non-destructive technique to continuously monitor the structural integrity of concrete. Depending on the specific demands of the measurements, a strategy can be implemented with the existing

techniques. In this strategy, decision making on maintenance is based on the measurements from multiple approaches. Depending on the severity and the monitoring vs. maintenance cost one of the available techniques can be used.

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Chapter 3.

Dynamic measurement of chloride ions

This chapter is divided into two sections; 3a and 3b. Both sections present a dynamic electrochemical technique to measure chloride ion concentration. The focus of this chapter is to avoid the use of a conventional reference electrode. In both sections, a chronopotentiometric approach, where a current is applied and potential difference is measured, is presented. Section 3a is based on measuring the potential difference, while section 3b is based on measuring the transition time during an applied current pulse. A short summary of each approaches is given before each sections.

Section 3A.

A chronopotentiometric approach for measuring chloride ion concentration

In this section, a novel approach is reported for the electrochemical measurement of chloride ions in aqueous solution. This sensor is based on the stimulus/response principle of chronopotentiometry. A current pulse is applied at the Ag/AgCl working electrode and the potential change is measured with respect to another identical Ag/AgCl electrode in the bulk electrolyte. The potential difference is related to the Cl^- ion concentration via the Nernst equation and follows an inverse logarithmic trend. By varying the applied current pulse, the sensitivity of the sensor is tunable to different concentration ranges. The potential response is also influenced by the pH of the electrolyte, this effect is pronounced at lower concentration of Cl^- ions (<1 mM KCl) and at high pH values (>12 pH). The advantage of this approach is the use of a bare Ag/AgCl electrode as a pseudo-reference electrode, which enables this system for long-term application such as the in situ measurement of Cl^- ions in concrete.

3A.1. Introduction

The major cause of deterioration in reinforcement concrete is due to the presence of chloride ions in the concrete itself [1, 2]. When the amount of chloride ions increases beyond a certain threshold, pitting corrosion of the steel reinforcements initiates and ultimately results in localized structural failure [3]. This is particularly a problem in structures near salt water or which are exposed to de-icing salt. In 2011, the U.S.A. Federal Highway Administration stated that 11% of the national bridges are structurally defective [4] mainly due to degradation from chloride ions. Delayed maintenance could result in the collapse of these structures and human casualties, but unnecessary upkeep increases both costs and CO₂ emissions. To precisely predict the optimal time for maintenance of these structures, a service-life model of the concrete is required [5] and the chloride ion concentration is an essential parameter.

The well-established method for chloride ion detection in concrete requires destructive sampling of structures and time-intensive laboratory processing [6, 7]. In contrast, a non-destructive in-situ monitoring provides fast measurements, data reliability and real time ingress profile without destroying the structures [8]. In recent years many groups have investigated in-situ measurement of chloride in concrete using mainly electrochemical [9-11] and optical methods [12-14]. However, optical methods have bulky setups, are difficult to integrate as a standalone system and have other disadvantages such as the photo bleaching of dyes (optical transducers) and the leaching of transducer (polymer matrix) due to the high pH environment inside concrete.

While electrochemical sensing is the preferred and most researched method, many devices are only suitable for in-situ measurements in a laboratory setting and no solution for long-term measurements in concrete structures currently exists (with a required sensing period of 20 years or more). Most of the reported electrochemical sensors use potentiometry [8, 11, 15-17] where the half-cell potential of a silver/silver chloride (Ag/AgCl) electrode is measured with respect to a reference electrode at equilibrium. This method requires the reference electrode to be embedded inside concrete (near the Ag/AgCl working electrode) to reduce errors due to diffusion potential [18]. The limiting factor of this approach (for in-situ measurement in concrete) is the long term stability of the reference electrode and the drift in potential [19]. Therefore, to design an electrochemical sensor capable of measuring a real-time Cl⁻ ion concentration in concrete over the span of decades, a system that is not dependent on a stable reference electrode is desired.

Potentiometry is a static (zero current) approach and the alternative to this is a dynamic measurement approach (e.g. chronopotentiometry) which involves measuring the response of an equilibrated system to an applied stimulus [20, 21]. In this technique, a controlled, chemical stimulus defines the condition at the working electrode, depending on the analyte concentration (in this case, Cl^- ions). A chemical stimulus approach provides improved sensitivity and system robustness by avoiding drift of the potentiometric response [19-22]. Moreover, the dynamic measurement technique can eliminate the dependence of potential measurement on the stable reference electrode.

The aim of this work is to develop a Cl^- ion sensor based on chronopotentiometry, where the conventional (liquid junction) reference electrode is replaced by a bare Ag/AgCl pseudo-reference electrode. A current stimulus is applied at the Ag/AgCl working electrode and the corresponding potential difference is measured simultaneously. This resulting potential difference will vary depending on the Cl^- ion concentration in the bulk electrolyte, thereby enabling long-term, in-situ measurement of Cl^- ions in concrete structures without the need for stable reference electrodes. This method can be used for the in-situ measurement of Cl^- ions in concrete structures. The theoretical background of this approach along with the experimental evaluation in aqueous solution containing chloride ions are presented in detail.

3A.2. Theory

A Ag/AgCl electrode is a redox electrode of the second kind. When immersed in a solution containing Cl^- ions, electrochemical equilibrium occurs between AgCl salt and Cl^- ions at the electrode surface, which gives rise to the half-cell potential. The concentration of Cl^- ions in the electrolyte determines the half-cell potential, given by the Nernst equation, equation 3.1:

$$V_{\text{Ag/AgCl}} = V_{\text{Ag/AgCl}}^{\circ} - \frac{RT}{nF} \ln a_{\text{Cl}^-} \quad 3.1$$

Here, $V_{\text{Ag/AgCl}}^{\circ}$, R , F , T , a_{Cl^-} are the standard electrode potential of Ag/AgCl, general gas constant, Faraday constant, absolute temperature (K) and activity of the Cl^- ions, respectively. In chronopotentiometry, a constant current is applied at the working electrode (WE) and the potential change is measured with respect to a reference electrode; the measured potential response is called chronopotentiogram. In the case of a Ag/AgCl WE, an anodic current pulse initiates the Faradaic reaction, equation 3.2, at the surface of the WE. The Cl^- ions near the WE are consumed during this

reaction, locally depleting Cl^- ions near the electrode surface [23]. This results in a concentration gradient that gives rise to a potential difference (ΔV) at the WE with respect to the RE. The expression for ΔV , in the case of high background electrolyte concentration (0.5 M KNO_3) is given in equation 3.3, from the Appendix I.

$$\Delta V = -\frac{RT}{F} \ln \left(1 - \frac{2j}{FC^*} \sqrt{t/D\pi} \right) \quad 3.3$$

Here, C^* is the bulk Cl^- ion concentration in the electrolyte, j the current density, t the pulse time and D the diffusion coefficient. Since the potential difference, ΔV , in equation 3.3 does not depend on the reference potential, a bare Ag/AgCl electrode in the bulk electrolyte can serve as a pseudo-reference electrode. The schematic of this approach is shown in figure 3.1. Both Ag/AgCl electrodes are in the same bulk electrolyte. At zero current condition (figure 3.1a), the potential difference is ideally zero (same half-cell potential). During the current pulse (figure 3.1b) applied via a counter electrode (CE), the potential at the WE changes due to the depletion of Cl^- ions whereas the half-cell potential of the Ag/AgCl pseudo-reference electrode remains the same. This change in potential, ΔV , is a function of Cl^- ion concentration in the bulk electrolyte, as elaborated from equation 3.3.

However, this approach is only valid if the potential difference is measured within the time it takes for the Cl^- ion concentration at the electrode surface to reach zero, defined as the transition time (τ) [23]. After the transition time, additional Faradaic reactions occur (e.g. oxide formation) which invalidate equation 3.3. The selection criteria for the current densities, j , and the current-pulse time, t , to ensure measurements within the transition time is outlined in equation 3.4.

$$j < 0.5 FC^* \sqrt{t/D\pi} \quad 3.4$$

This boundary condition is evaluated from the logarithmic-term ($1 - \sqrt{t/D\pi} 2j/FC^*$) of equation 3.3. The theoretical curve of this logarithmic-term versus the Cl^- ion concentrations of the bulk electrolyte is shown in figure 3.2 for three different current densities. The logarithmic-term values between 0 and 1 give the operational range of this sensor. The sensitivity changes at different values of the Cl^- ion concentration. In this work the concentration range of the Cl^- ions are selected for values between 0.13 and 0.9 of the logarithmic term to achieve relatively high sensitivity. The sensor then has different sensitivities for specific Cl^- ion concentration

ranges depending on the applied current density. The detection ranges of Cl^- ion concentrations and the corresponding optimal current densities are given in table 3.1 for current-pulse time, $t = 5$ s.

Figure 3.1: The schematic of the chronopotentiometric approach with Ag/AgCl as pseudo-reference electrode. (a) At zero current condition, the half-cell potential of the WE and pseudo-reference electrode is the same, therefore the potential difference, ΔV , is zero. (b) During the anodic current pulse at the WE, applied w.r.t. a counter electrode, not included in this figure, the Cl^- ions deplete near the WE surface, resulting in a concentration profile w.r.t the bulk electrolyte.

Figure 3.2: The theoretical curve of the logarithmic term of equation 3.3 for different current densities versus the Cl^- ion concentrations. The detection range for relatively high sensitivity is defined as the concentration range which corresponds to the values between 0.13 and 0.9 of the logarithmic term.

Table 3.1: The selected current densities, j , for different Cl^- ions detection range, at the actuation time of $t = 5$ s, elaborated from equation 3.4 and figure 3.2.

No.	$[\text{Cl}^-]$ range (mM)	Current density, j ($\text{A}\cdot\text{m}^{-2}$)
1	0.1 to 1	0.15
2	1 to 10	1.5
3	10 to 100	15

The Ag/AgCl electrode is an ion selective electrode which has higher selectivity to Cl^- ions than other interfering anions (for instance Br^- , I^- , OH^- ions) [8]. These interfering ions also contribute to the half-cell potential of the Ag/AgCl electrode. The influence of interfering ions is quantified by the selectivity coefficient. For analytical applications the selectivity coefficient of interfering ions is preferably small (ideally zero), but when the interfering ions are more abundant than primary ions this effect becomes more pronounced [8]. In concrete pore solution, the most notable interfering ions are OH^- ions (pH of the electrolyte), which are hydration product from $\text{Ca}(\text{OH})_2$, NaOH and KOH [8]. As long as the ratio of $[\text{Cl}^-]$ to $[\text{OH}^-]$ is much greater than the selectivity coefficient, see equation 3.5, the effect of pH is trivial. For a Ag/AgCl electrode the selectivity coefficient OH^- ions in aqueous solution, $k_{(\text{Cl}, \text{OH})}$, is reported as $2.4 \cdot 10^{-2}$ [24].

$$[\text{Cl}^-]/[\text{OH}^-] \gg k_{\text{Cl}, \text{OH}^-} \quad 3.5$$

3A.3. Experimental

3A.3.1. Ag/AgCl electrode fabrication

The Ag/AgCl electrode was fabricated by electro-deposition of silver chloride over a silver wire (0.5 mm dia. and ca. 19.5 mm^2 area). Prior to the electro-deposition, the silver wire was immersed into the acetone bath for 20 min, and then immersed into the concentrated ammonium hydroxide for 2 hours to remove any organic contamination and oxide film at the surface, respectively [11, 17]. The Ag wire was then chloridized in 0.1 M HCl solution for 20 min at a current density of $13.3 \text{ A}\cdot\text{m}^{-2}$, to form a AgCl layer (thickness ca. $5 \mu\text{m}$) on the surface. The non-anodized area of the electrode was protected through heat shrink tubing. The Ag/AgCl electrode was then stored in 1 M KCl solution.

3A.3.2. Chemicals

The Ag wire ($\geq 99.99\%$ trace metals), potassium chloride (BioXtra, $\geq 99.0\%$), potassium hydroxide (90% pure reagent grade) and potassium nitrate ($> 99\%$ reagent grade) were ordered from Sigma Aldrich, the Netherlands. The KCl and KNO_3 electrolyte solutions were prepared with Milli-Q water.

Figure 3.3: Schematic representation of the experimental setup for the chronopotentiometric measurements. Here, CE, WE and RE stands for counter electrode, working electrode and reference electrode, respectively.

3A.3.3. Measurement setup

The chronopotentiometric measurements were performed using a VSP potentiostat from Biologic Instruments, France. The working electrode (WE) terminal of the potentiostat was connected to the Ag/AgCl electrode (19.5 mm^2), the reference terminal was connected to another identical Ag/AgCl electrode (pseudo-reference electrode) and the counter electrode (CE) terminal was connected to 60 mm^2 Pt counter electrode. The schematic of the measurement setup is shown in figure 3.3. The current pulse is applied between the WE and the CE, and the potential difference, ΔV , of the WE is measured w.r.t to the Ag/AgCl pseudo-reference electrode. The distance between the Ag/AgCl WE and the Pt CE is ca. 1 cm whereas the distance between the WE and the pseudo-reference electrode is ca. 2.5 cm in a glass beaker of 5 mL capacity. All the measurements were performed in a Faraday cage and the measurement parameters were controlled via the user interface of the potentiostat (EC-lab). The pulse time for each applied current was 5 s and the corresponding values of the applied current pulses were derived from equation 3.4. The analytic solutions were composed of various concentrations of KCl in a 0.5 M KNO_3 background electrolyte, and the pH

was adjusted by the addition of KOH. All the measurements were carried out at regulated room temperature (22 °C).

3A.4. Results and discussion

3A.4.1. Chronopotentiogram of Ag/AgCl electrode

Figure 3.4a shows a typical chronopotentiogram of the Ag/AgCl WE electrode w.r.t to another Ag/AgCl electrode in 10 mM KCl solution. Prior to the current pulse, the electrode potential of the Ag/AgCl electrode is ca. 5 mV (ideally zero) due to a nearly identical half-cell potential of the WE and the pseudo-reference electrode in the bulk electrolyte. A current pulse of $35 \text{ A}\cdot\text{m}^{-2}$ is applied at $t = 0 \text{ s}$ which results in a rapid ohmic drop of ca. 100 mV. The rate of increase in the potential then slows due to the Cl^- ion depletion near the WE electrode surface, indicated as region A (first plateau) in figure 3.4a. As the Cl^- ions deplete completely near the WE, the slope of ΔV reaches its maximum (region B in figure 3.4a), which corresponds to the transition time. After this point a new plateau (region C in figure 3.4a) is reached (after 2.6 s); this plateau is attributed to the other faradaic reaction, i.e. the formation of silver oxide (Ag_2O). Of these three regions indicated in figure 3.4a, region A is of prime interest as the potential change here is a function of the Cl^- ion concentration. The theoretical curve, based on equation 3.3, is also plotted in figure 3.4a, offset from the initial ohmic drop (100mV). The transition time measured experimentally is 2.0 s, whereas the theoretical value from equation 3.3 is 1.2 s. This deviation is attributed to the uncertainty in the current density, caused by the roughness of Ag/AgCl electrode surface. The roughness of the Ag/AgCl WE increases the surface area, therefore the actual current density is lower than the applied current density. Consequently the transition time, in the experimental curve, is higher than the theoretical one.

Figure 3.4b shows the potential response for different Cl^- ion concentrations with an applied current pulse of $15 \text{ A}\cdot\text{m}^{-2}$. For this current density and concentration range, the current pulse can be applied for 5 s and the potential response still remains within the transition time (region A of figure 3.4a). The ohmic drop at this current density is in the range of 30 to 40 mV. Prior to the current pulse ($t < 0$), the potential difference is nearly zero for all Cl^- ion concentrations. After the applied current pulse ($t > 0$), the potential changes as a function of locally decreasing Cl^- ion concentration; as the number of Cl^- ions in the bulk solution increases, the potential difference between the Ag/AgCl electrode increases. The potentials are measured at the end of the current pulse ($t = 5 \text{ s}$).

Figure 3.4: The potential response of the Ag/AgCl working electrode w.r.t another Ag/AgCl pseudo-reference electrode during the applied current pulse w.r.t a CE, not included in this figure. (a) The experimental and theoretical chronopotentiometric response of the Ag/AgCl WE at a current pulse of 35 A·m⁻² in a 10 mM KCl and 0.5 M KNO₃ bulk electrolyte. (b) The potential difference, ΔV , response for different Cl⁻ ion concentrations in the bulk electrolyte at 15 A·m⁻² current pulse of 5 s. The ΔV decreases with the increase in Cl⁻ ion concentration.

Figure 3.5: The theoretical and the experimental calibration curve for different Cl^- ion concentrations at different applied current densities. The electrolyte is composed of different KCl concentration in a 0.5 M KNO_3 solution. For the theoretical curves, $D = 2 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ and $T = 22^\circ\text{C}$.

3A.4.2. Calibration curve for chloride ions measurement

Figure 3.5 shows the calibration curves for different Cl^- ion concentrations at two current densities: 1.57 and 5.2 $\text{A}\cdot\text{m}^{-2}$. The theoretical curves from equation 3.3 are also plotted with their respective experimental curves. The experimental curves follow the trend of the theoretical curves, as the potential difference decreases with increasing Cl^- ion concentration. Comparison of the experimental curve with the theoretical one is only relevant for the part of the experimental curve that is on the right hand side of the vertical asymptotic part of the theoretical curve, according to equation 3.4. Only then is the data from region A of figure 3.4a. On the left hand side from this asymptote, silver oxide formation start to occurs (region C in figure 3.4a). As the applied current density increases, the detection window shifts to higher concentrations of Cl^- ions as is evident by the location of the vertical asymptotes in figure 3.5. In the theoretical expression we neglected the ohmic drop due to the high background electrolyte concentration (0.5 M KNO_3). However, there is some ohmic drop which increases with the increase in the applied current pulse.

The Cl^- ion detection range of the sensor is tunable and is a function of the applied current pulse. Figure 3.6 shows the calibration curve, measured experimentally, for the particular concentration ranges at the corresponding current densities, given in table 3.1. These detection ranges have relatively higher sensitivity at specific current densities as shown in figure 3.2. The corresponding theoretical curves are also plotted in figure 3.6a, 3.6b and 3.6c from equation 3.3, at the respective current densities,

specified on each curve. The experimental curves in each follow the trend of the theoretical curves, as the potential difference shows an inverse logarithmic response for different Cl^- ion concentrations in the bulk electrolyte. The deviation from the theoretical curve is due to the ohmic drop at high current densities, e.g. in case of figure 3.6b and figure 3.6c the ohmic drop is ca. 30 mV and ca. 55 mV, respectively.

Figure 3.6: The calibration curve of the potential difference, ΔV , at different Cl^- ion concentration range. For each concentration range the corresponding current densities, for optimal sensitivity, were calculated from equation 3.4 and given in table 3.1.

3A.4.3. Effect of the pH

Figure 3.7 shows the effect of pH on the measured potential difference at four different Cl^- ion concentrations. In this experiment (figure 3.7), the change in ΔV , for the change in pH of the electrolyte, is investigated and the absolute value of ΔV (at different concentrations) is trivial. The applied current densities are selected according to the condition stated in equation 3.4. Consequently, for the lower concentrations, e.g. 0.1 M KCl, relatively low current density is chosen ($0.1 \text{ A} \cdot \text{m}^{-2}$), resulting in relatively low ΔV as

well as low ohmic drop. Although a decrease in the Cl^- ion concentration increases the potential difference (see equation 3.3), a decrease in current density along with a lower ohmic drop decreases the potential difference, significantly. The effect of pH is evident at low Cl^- ion concentrations ($[\text{Cl}^-] < 1\text{ mM}$) for a high pH ($\text{pH} > 12$), see figure 3.7. This is due to the fact that the condition stated in equation 3.5 no longer holds true, e.g. at 0.1 mM $[\text{Cl}^-]$ and pH 12, $[\text{Cl}^-]/[\text{OH}^-] = 1 \cdot 10^{-4}/1 \cdot 10^{-2} = 1 \cdot 10^{-2}$ is being smaller than $k_{(\text{Cl}^-, \text{OH}^-)}$ (ca. $2.4 \cdot 10^{-2}$, [24]). For this setup, the lower detection limit for Cl^- ion concentrations in aqueous solution at $\text{pH} > 12$ is 1 mM . For in-situ measurement in concrete this lower detection limit moves to even lower value due to relatively smaller value of $k_{(\text{Cl}^-, \text{OH}^-)}$ in concrete (ca. $4 \cdot 10^{-3}$, [8]). The change in potential at high pH, for low Cl^- ion concentration, is also attributed to damage of the AgCl membrane from the formation of oxides [8].

Figure 3.7: Effect of pH on the potential difference, ΔV , of the Ag/AgCl electrode. Different current densities were used for different Cl^- ion concentrations of the electrolyte, to satisfy equation 3.4.

3A.5. Conclusion

A chronopotentiometric approach, without a conventional liquid-junction reference-electrode, can be successfully used for the detection of Cl^- ions in aqueous solution. When a current pulse (stimulus) is applied at the Ag/AgCl WE electrode, the change in the electrode potential (response), due to the depletion of Cl^- ions, is a function of Cl^- ion concentration in the bulk electrolyte. In such an approach, a bare Ag/AgCl can serve as a pseudo-reference electrode, enabling this sensor for long term

applications. The theoretical expression for the potential difference was derived from the Nernst equation, and the expected inverse logarithmic behavior was observed in experimental measurements. Deviation from the theoretical curve is attributed to the ohmic drop during the applied current pulse. The potential difference for different concentrations of Cl^- ions showed an inverse logarithmic behavior; i.e. the potential decreases with the increase in Cl^- ion concentration. The sensitivity of the response is tunable with the applied current pulse at the corresponding detection range of Cl^- ion concentration. The pH of the electrolyte has an influence on the sensor response. The potential response is not stable at high pH values ($\text{pH} > 12$) for low Cl^- ion concentrations ($< 1 \text{ mM}$). Thus, the lower limit of detection of the Cl^- ion sensor is defined by the pH of the electrolyte and is expected to be even lower when measured inside concrete. We conclude that this measurement approach is very promising to monitor chloride concentrations inside concrete structures.

Section 3B.

Transition time for determining chloride ion concentration

This section presents a chronopotentiometric approach to minimize drift and avoid the use of a conventional reference electrode for measuring chloride ion concentration. An anodic current pulse is applied to a Ag/AgCl working electrode which initiates a faradaic reaction that depletes the chloride ions near the electrode surface. The rate of change in potential at the Ag/AgCl electrode, due to chloride ion depletion, reaches an inflection point once the chloride ions deplete completely near the electrode surface. The moment of the inflection point, also known as the transition time, is a function of the chloride ion concentration and is described by the Sand equation. It is shown that the square root of the transition time is linearly proportional to the chloride ion concentration. The moment of inflection determines the response, and thus is independent of the absolute potential of reference electrode.

Above figure: Schematic of the chip and the working principle of transition time measurement. The typical transition time response is also shown.

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This section has been published as “No more conventional reference electrode: Transition time for determining chloride ion concentration”, Yawar Abbas, Derk Balthazar de Graaf Wouter Olthuis, and Albert van den Berg. *Analytica Chimica Acta*, 2014, 821, pp 81-88. The above schematic is the graphical representation of this section.

3B.1. Introduction

Ion selective electrodes (ISE) are one of the most prevalent electrochemical sensors in analytical chemistry and date back to the early 20th century [25, 26]. Their high selectivity toward specific ions make them suitable for many analytical applications. The half-cell potential of ISEs is a function of the ionic activity in the electrolyte, as derived from the Nernst equation [23]. Typically, the open circuit potential of the ISE is measured with respect to a reference electrode, which is called potentiometry [27]. This method is routinely used in some clinical [28, 29] and environmental applications [30, 31]. Despite the simple measurement setup and the low energy consumption of the potentiometric method, it is unfeasible for long-term and remote sensing applications [19]. This is due to the requirement of a long-term-stable reference electrode and drift in the potential response over time [32].

Dynamic electrochemical measurements (DEM) are well known for counteracting drift in electrochemical measurements because they measure a system's response to an applied stimulus [19, 32, 33]. Chronopotentiometry is an example of DEM, where an applied current pulse stimulates a faradaic reaction which depletes ions near the working electrode and changes its the potential [34]. This measured potential change relates to the applied current pulse and the concentration of the electrolyte [35]. When the ions involved in the reaction at the electrode surface have completely depleted, the potential increases rapidly and jumps to a higher value (creating an inflection point), where a second faradaic reaction then occurs [20]. The moment of this inflection point, also known as the transition time [36, 37], is a characteristic of the analyte concentration [23, 38] and is given by the Sand equation. This approach has been used to determine different ions concentration [37-39] and the pH of electrolytes [21, 40].

Chloride ions are one of the major contributors to degradation of reinforcement-concrete [1, 41]. The presence of these ions initiate pitting corrosion in the reinforcement steel and ultimately results in the failure of the construction [2]. Thus, the chloride ion concentration inside concrete is a crucial parameter to predict the service life of a structure [42, 43]. Several groups have investigated the in-situ measurement of chloride using potentiometry based on Ag/AgCl ISE [8, 9, 11]. Despite promising results, this approach is limited to lab-scale measurements because drift in the reference potential causes flawed data. A transition time approach based on DEM as described could counteract such drift. This approach has been previously reported by Meyer *et al.* [37]. Here, we demonstrated the advantage of this approach by shunning the liquid-junction reference

electrode and instead using any metal wire as a pseudo-reference electrode. This allows the detection of chloride ions concentration for long term and in-situ applications, e.g. measurement inside concrete structures.

This work presents a chloride ion concentration sensor based on chronopotentiometry using the transition time of a Ag/AgCl WE. A current pulse is applied between the Ag/AgCl WE and CE and the potential is measured w.r.t a pseudo-reference electrode. The maximum of the first derivative of the potential response during the applied current pulse gives the transition time. Since only the rate of change in the potential is of interest, the absolute potential values are irrelevant. Therefore, any conducting electrode can be used as a pseudo-reference electrode. The feasibility of this approach will be demonstrated by using several electrodes as pseudo-REs to measure the transition time. Furthermore, the effect of Cl^- ion concentration and current density is discussed. Measurements are also taken to ensure the technique appropriately avoids inherent drift.

3B.2. Chronopotentiometric response of a Ag/AgCl electrode

The half-cell potential of a Ag/AgCl electrode is a function of chloride ion concentration, as described by the Nernst equation. When an anodic current pulse is applied to a Ag/AgCl WE (in a Cl^- ion containing electrolyte), the faradaic reaction given in equation 3.2 takes place, consuming Cl^- ions at the electrode surface. Depletion of Cl^- ions at the Ag/AgCl WE occurs when the electrochemically imposed ion flux can no longer be maintained by the Cl^- ions near the electrode surface [44]. The time it takes for the Cl^- ions to deplete completely near the Ag/AgCl WE surface is called the transition time [23], τ .

Beyond the transition time, the Cl^- ion flux to the electrode surface is not sufficient to satisfy the applied current. Therefore, the electrode potential shifts to a higher value where another faradaic reaction occurs, e.g. the formation of silver oxide. A schematic of the Cl^- ion concentration profile near the WE during the applied current pulse is shown in figure 3.8a. The corresponding potential response of the Ag/AgCl WE along with its first derivative are illustrated in figure 3.8b. There are three distinct regions of the response curve, each corresponding to different conditions near the WE. Region A depicts the change in the potential due to the depletion of Cl^- ions (corresponding to equation 3.2). The change in potential in this region is a function of Cl^- ion concentration in the bulk electrolyte. Region B is characterized by the steep rise in the potential and contains the

transition time. Here, the rate of change of the potential is maximum (inflection point) [39] as given by the peak of the first derivative of the potential response (see Appendix II). Region C denotes the beginning of a second faradaic reaction and the potential jumps to another plateau.

Figure 3.8: (a) Schematic of the Cl^- ion detection approach. During an applied current pulse at the WE w.r.t a CE (not included in this figure), chloride ions deplete at the Ag/AgCl WE, resulting in the illustrated Cl^- ion concentration profile. (b) Schematic of the ΔV and $d\Delta V/dt$ response. The solid line (—) and dashed line (--) represent ΔV and $d\Delta V/dt$, respectively. τ is the transition time and t is the duration of the applied current pulse.

The transition time is related to the Cl^- ion concentration in the bulk electrolyte and the applied current pulse, as given by the Sand equation in equation 3.6. Here, C^* is the bulk Cl^- ion concentration, F is the Faraday constant, j is the current density, t_{cr} is the transport number and D is the diffusion coefficient. In case of high concentration of the background electrolyte, t_{cr} approaches zero and can be neglected.

$$\tau = \left(\frac{FC^*}{2j(1 - t_{\text{cl}^-})} \right)^2 D\pi \quad 3.6$$

The diffusion coefficient, D , is a function of electrolyte temperature and so is the transition time, increasing by 2 to 3% per degree rise in temperature [45].

3B.2.1. Selection criteria of the current pulse and Cl^- ion concentration range

The applied current pulse is critical for the transition time measurement, as apparent from equation 3.6. A decrease in current density of one order increases the transition time by two orders. However, the higher and lower

value of the transition should be limited. At higher transition times the measurement can be interfered by convection. On the other hand for extremely small transition times (τ less than 10 ms), a non-negligible part of the current pulse is used for charging the double layer capacitance at the electrode-solution interface. An upper limit of τ_{max} equal to 6 s and lower limit of τ_{min} equal to 10 ms are selected. The selection criterion for applied current pulse is stated as a ratio of current density and the Cl^- ion concentration in equation 3.7.

$$0.5F \sqrt{\frac{D\pi}{\tau_{max}}} < \frac{j}{C^*} < 0.5F \sqrt{\frac{D\pi}{\tau_{min}}} \quad 3.7$$

The diffusion coefficient value of Cl^- ions is obtained from literature to be $2 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ at 25 °C [20, 45]. The limits for the value of j/C^* is between 1.56 and 38.23 $\text{A} \cdot \text{m} \cdot \text{mol}^{-1}$ (for 6 s and 10 ms, respectively). Table 3.2 depicts the selection of the current density for a Cl^- ion concentration range of 1 to 6 mM to justify equation 3.7.

Table 3.2: The selected current density for a Cl^- ion concentration range of 1 to 6 mM, evaluated from equation 3.7. The corresponding values of the ratio j/C and transition time is also given.

$[\text{Cl}^-]$ range (mM)	Current density, j ($\text{A} \cdot \text{m}^{-2}$)	$(j/C^*)_{\min}$ ($\text{A} \cdot \text{m} \cdot \text{mol}^{-1}$)	$(j/C^*)_{\max}$ ($\text{A} \cdot \text{m} \cdot \text{mol}^{-1}$)	$\tau_{\min}$ (s)	$\tau_{\max}$ (s)
1 to 6	10	1.66	10	0.146	5.26

The analytical application of this technique relies on diffusional mass transport. In case of additional convective mass transport, a clear depletion of the ions near the electrode is prevented and leads to spurious transition times [46]. Thus, measurement in stagnant solution is preferred [38] and detection for higher concentrations (more than 1 M $[\text{Cl}^-]$) should be avoided due to expected high transition times. Furthermore a high concentration background electrolyte must be used to minimize the migrational transport of Cl^- ions during the applied current pulse. Another issue is the sensitivity of AgCl membrane to other interfering ions, such as Br^- , I^- , OH^- ions, etc. [8, 23]. However, the OH^- ion, which is the hydration product from $\text{Ca}(\text{OH})_2$, NaOH and KOH, is the pronounced interfering ion in concrete. If the concentration of OH^- ion is 10 time more than the Cl^- ion, this interfering effect is dominant [35].

3B.3. Materials and method

3B.3.1. Fabrication of Ag/AgCl electrode – Chip fabrication

The chip used in this work is shown in figure 3.9a and was previously reported by our group [47]. All electrodes were fabricated on a Borofloat glass chip using standard cleanroom processes, including conventional photolithography, metal deposition and lift-off. The fabrication process is schematically given in Appendix III. The silver electrodes are deposited on a Borofloat glass chip and are then chloridized in 0.1 M FeCl_3 solution for 30 s to form a AgCl layer over the surface. The Ag/AgCl WE (area = 9.812 mm^2) is located in the center, surrounded by the Ag/AgCl pseudo-RE. To ensure the proper formation of the AgCl layer, the surface is analyzed by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX).

Figure 3.9: (a) The Cl^- ion sensor chip with Ag/AgCl electrodes on a glass substrate and electrical connection pads. (b) The complete electrochemical cell (chip holder) with the mounted chip. The middle circular area shows the area of the chip exposed to the electrolyte.

3B.3.2. Chemicals and equipment

The platinum wire ($\geq 99.99\%$ trace metals), potassium chloride (BioXtra, $\geq 99.0\%$), potassium hydroxide (90% pure reagent grade) and potassium nitrate ($> 99\%$ reagent grade) were ordered from Sigma Aldrich, the Netherlands. The Ag/AgCl liquid junction reference electrode (model MF-2079) was ordered from BASi, USA. The KCl and KNO_3 electrolyte solutions were prepared with Milli-Q water.

An in-house designed and constructed Teflon chip holder is used, see figure 3.9b. The holder provides easy electrical connections via push-pins

(or spring-loaded pins) and contains an electrochemical cell. The measurements were performed using a VSP potentiostat (Biologic Science Instruments, France). The WE and RE terminals of the potentiostat are connected to the two on chip Ag/AgCl electrodes. The CE terminal is connected to an external Pt electrode. A schematic of the actual measurement setup is shown in figure 3.10. All the measurements were performed in a Faraday cage and the operational parameters were controlled via the user interface of the potentiostat (EC-Lab).

Figure 3.10: Schematic representation of the experimental setup and the electrode arrangement for the transition time measurement. The background electrolyte is 0.5 M KNO_3 .

3B.3.3. Data analysis

The potential response of the Ag/AgCl WE during an applied current pulse is measured for different concentrations of chloride ion. The measurement data were stored as a mpt file with the EC-lab software and subsequently analyzed in MATLAB version 2012B. The potential response is plotted and the data points corresponding to Region B in figure 3.8b are selected. The first derivative of the selected region of interest is then also plotted, with its maximum indicating the transition time. The MATLAB program codes are provided in the Appendix IV.

3B.4. Results and discussion

3B.4.1. Chronopotentiogram of a Ag/AgCl electrode

The potential response of a Ag/AgCl WE plotted versus the time of an applied current pulse gives a chronopotentiogram. A typical chronopotentiogram of a Ag/AgCl WE in a solution containing 5 mM Cl^- ions under an applied current pulse of $10 \text{ A}\cdot\text{m}^{-2}$ is shown in figure 3.11. The ambient temperature is 20.9°C and the background electrolyte is 0.5 M KNO_3 . Prior to the current pulse, the potential difference, ΔV , is nearly zero, due to the identical half-cell potential of the Ag/AgCl WE and Ag/AgCl pseudo-RE electrode. The current pulse is applied at $t = 0$ which causes a change in the potential response. In figure 3.11, the initial rapid rise of the potential is due to the ohmic drop of ca. 10mV across the electrolyte. After this ohmic drop the potential changes at a slower rate corresponding to the depletion of chloride ions near the electrode surface. Once the chloride ions deplete completely, the potential change inflects and indicates the transition time. The theoretical value for the transition time under these conditions is 3.75 s, as calculated from the Sand equation, whereas the experimental value is 4.28 s. This deviation is attributed to uncertainty in the current density due to the surface roughness of the electrode (see SEM image in figure 3.18). For the theoretical transition time the literature value of $D = 2\cdot 10^{-9} \text{ m}^2\text{s}^{-1}$ at 25°C is used [45].

3B.4.2. Chronopotentiogram for various chloride ion concentrations

To observe the effect of Cl^- ion concentration on the transition time, solutions containing 4, 5 and 6 mM of Cl^- ions in a 0.5 M KNO_3 background are measured. The applied current pulse is $10 \text{ A}\cdot\text{m}^{-2}$ and the ambient temperature is 20.9°C . Figure 3.12 shows the potential responses and their first derivatives. The measured transition times are 2.69, 4.28 and 5.92 s, respectively. As predicted by the Sand equation (equation 3.6), the transition time increases with higher Cl^- ion concentration. This is expected as more Cl^- ions present in the bulk electrolyte means the longer it will take to completely deplete the Cl^- ions near the WE surface.

Figure 3.11: The measured chronopotentiogram (solid line) and its first derivative (dashed line) of the Ag/AgCl WE w.r.t another Ag/AgCl pseudo-RE electrode. A current pulse of $10 \text{ A}\cdot\text{m}^{-2}$ (not shown) was applied at $t = 0$. The electrolyte contains 5 mM Cl^- ions in a 0.5 M KNO_3 background electrolyte at 20.9°C . The maximum value (indicated by the dotted line) gives a transition time of 4.28 s .

Figure 3.12: The chronopotentiograms (solid line) and their first derivatives (dashed line) of the Ag/AgCl electrode w.r.t another Ag/AgCl pseudo-RE electrode in solutions of 4 , 5 and 6 mM Cl^- ions. The background electrolyte is 0.5 M KNO_3 , the applied current pulse is $10 \text{ A}\cdot\text{m}^{-2}$ and the ambient temperature is 20.9°C . The maximum slopes of the potential responses are indicated by the dotted lines.

From the Sand equation, (equation 3.6), the square root of the transition time is expected to be linearly proportional to the Cl^- ion concentration, when the other variables are kept constant. Figure 3.13 shows the square root of the measured transition times plotted w.r.t the Cl^- ion concentration, which indeed shows a linear behavior. Three measurements at each concentration were performed with an interval of 1 hour in between, at 20.8 °C. The red solid line in figure 3.13 shows the linear fit of the measured data with a correlation coefficient of $R = 0.998$.

Figure 3.13: Calibration curve showing the square root of the transition time versus the Cl^- ion concentration, in a 0.5 M KNO_3 background electrolyte. The circular points (o) are the measured data and the solid line (—) is the linear fit. The dashed line (--) is the theoretical curve from the Sand equation, equation 3.6. The applied current pulse is $10 \text{ A}\cdot\text{m}^{-2}$ and the ambient temperature is 20.8 °C. D and D_a are the theoretical and apparent (measured) diffusion coefficients, respectively.

The corresponding theoretical curve from the Sand equation is also plotted. Back calculating from the Sand equation using the linear fit of the measured data, the apparent diffusion coefficient, D_a , is found to be $2.280 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$. This value is in good agreement with the theoretical value, $D = 2 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$. The slope and the y-intercept of the data points are $0.41 \pm 0.0165 (1 \cdot 10^3 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \sqrt{\text{s}})$ and $0.033 \pm 0.043 (\sqrt{\text{s}})$ with 95% confidence interval. The deviations from theory is 2% of the confidence limits, which is acceptable for concrete application. Deviation can be attributed to uncertainty in the current density value. The non-zero value

of the y-intercept is due to the displacement currents from charging the double layer capacitance at zero $[\text{Cl}^-]$. The data presented are from solutions containing 1 to 6 mM of Cl^- ions. At higher concentrations, the deviation in transition time from the expected behavior is large (in the order of seconds). For example, the corresponding transition time at 7 mM of Cl^- ions is 6.59 s, which does not fulfil the requirements as set in equation 3.7. This is attributed to the relatively large thickness of the concentration profile, which makes it more sensitive to convection. This deviation can be prevented by increasing the current density, and thus, keeping the transition time within 6 s. The detection range of the $[\text{Cl}^-]$ can be adjusted by the applied current density. In concrete application, the required detection range of $[\text{Cl}^-]$ is from 1 to 500 mM, typically, in the presence of 400 mM $[\text{OH}^-]$. The Cl^- ions are exponentially distributed over the depth of concrete [48]. The depth of concrete is defined as the distance from the concrete cover to the steel rebar. The sensor should be placed near the steel rebar to locally detect the $[\text{Cl}^-]$. Typically for Portland cement, the $[\text{Cl}^-]$ reduces to 2% of the exposed concentration at a depth of 50 mm one year after the exposure to the chloride media. At the same depth in concrete the variation of $[\text{Cl}^-]$ is within 10%, typically.

3B.4.3. Effect of the current density

The transition time versus Cl^- ion concentration is a function of the applied current pulse, as described by the Sand equation, equation 3.6. Figure 3.14 shows the curve of the square root of the transition time versus the reciprocal of the applied current pulse, j^{-1} , at a fixed Cl^- ion concentration of 3 mM. In these measurements the applied current pulses range from 5 to 17 $\text{A}\cdot\text{m}^{-2}$ (or j^{-1} from 0.2 to $0.0588(\text{A}\cdot\text{m}^{-2})^{-1}$), respectively. The measured data points are fitted through linear regression with correlation coefficient of $R = 0.993$, which indicates good linear fit as predicted. The apparent diffusion coefficient, back calculated from the fitted curve, is found to be $2.77\cdot 10^{-9} \text{ m}^2\text{s}^{-1}$. The linear trend of the measurement points and the apparent diffusion coefficient are in good agreement with the theoretical values. The slope of the data points is $13.533 \pm 0.798 (\text{A}\cdot\text{m}^{-2}\cdot\sqrt{\text{s}})$ with 95% confidence interval. The deviation from theory is 8% of the confidence limits, which is acceptable for concrete application. The transition time decreases as the current density increases because higher current densities result in faster depletion of Cl^- ions, and thus, shorter transition times. Current densities larger than $100 \text{ A}\cdot\text{m}^{-2}$ should be avoided as the AgCl layer over the Ag surface was found to peel off or degrade, in such case measurements are meaningless.

Figure 3.14: The curve of the square root of the transition time and the reciprocal of the applied current pulse. The Cl^- ion concentration in all measurements is 3 mM, with a background of 0.5 M KNO_3 and an ambient temperature of 21.8 °C. Here, the circular points (o) are the measured data and the solid line (—) is the linear fit. The dashed line (--) is the theoretical curve from the Sand equation, equation 3.6. D and D_a are the theoretical and apparent (measured) diffusion coefficients, respectively.

3B.4.4. Pseudo-reference electrode

Since the transition time is the time to reach the inflection point, it is theoretically independent of the reference potential. In the previously shown measurements (figure 3.12, 3.13 and 3.14), a bare Ag/AgCl electrode was used as a pseudo-RE. The Ag/AgCl pseudo-RE gives a stable potential at a given Cl^- ion concentration. In principle, any metal wire can be used as a pseudo-reference for transition time measurements, provided that its potential does not drift significantly during the measurement time (i.e. within 6 s). Different pseudo-references such as a Ag/AgCl wire, a platinum wire and a steel wire are tested to measure the transition time.

Figure 3.15 shows the transition time measurement using different pseudo-reference electrodes in a solution of 4 and 5 mM Cl^- ions, at a current density of 15 $\text{A}\cdot\text{m}^{-2}$. For comparison, the transition time measurement using a proper reference electrode (Ag/AgCl RE) is also shown. The half-cell potentials of these pseudo-reference electrodes are stable (drift within 1 mV) for more than 6 s. In figure 3.15, the response does not change significantly for different pseudo-REF electrodes; the transition time varies within 80 ms ($\pm 75 \mu\text{M}$ at 4 and 5 mM Cl^- ions). The

95 % confidence limit of the transition time for 4 and 5 mM $[\text{Cl}^-]$ plots are 0.873 ± 0.105 and 1.794 ± 0.063 , respectively. This confidence limit leads to the detection error of up to $\pm 6\%$ in concentration. This is an acceptable analytical tolerance for concrete application. Thus, any conducting wire can be used as a pseudo-reference electrode for transition time measurements in concrete application. The theoretical values of the transition time (from equation 3.6) for 4 and 5 mM of Cl^- ions at a current density of $15 \text{ A}\cdot\text{m}^{-2}$ are 1.03 and 1.624 s, respectively.

Figure 3.15: Measured transition times using pseudo-REs composed of a Ag/AgCl liquid junction RE, Ag/AgCl wire, platinum wire and steel wire. The applied current pulse is $15 \text{ A}\cdot\text{m}^{-2}$ and the ambient temperature is 21.2°C . Here, + and o marks show the measured data for 4 and 5 mM of Cl^- ions in a 0.5 M KNO_3 background, respectively.

3B.4.5. Drift measurements

To observe the long term stability of the sensor response, a drift analysis was performed with the transition time measured over two weeks. Figure 3.16 shows the transition time of a solution containing 1 mM Cl^- ions and an applied current pulse of $10 \text{ A}\cdot\text{m}^{-2}$. The transition times were recorded every other day, with 3 measurements each day and an interval of 3 hours between measurements. The solution was refreshed on each day of measuring. The ambient temperature varied between 20 to 21.5°C during the measurement period. The linear fit (dashed line) in figure 3.16 shows a decreasing trend in the transition time of 0.51 ms/day , which

corresponds to $59 \mu\text{M}/\text{day}$. However, this variation is small and could be attributed to handling errors (systematic error), changing Cl^- ion concentration due to evaporation, change in apparent current density and temperature variation over the measurement period. In figure 3.16, the 95% confidence interval of the transition time is $0.15625 \pm 3\%$. The deviation is within the systematic error range (within 10% for concrete application). Therefore we can conclude that there is no inherent drift in these measurements. The deviation of the measured data from the theoretical one (0.16 s from the Sand equation using $D = 2.0 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$) is within 40 ms which corresponds to the concentration of 0.12 mM at 1 mM Cl^- ions.

Figure 3.16: Drift analysis: subsequent measurements of the transition time over two weeks. Each measurement was carried out every other day, with 3 measurements performed each day and 3 hours between each same-day measurement. The electrolyte contains 1 mM of Cl^- ions in a 0.5 M KNO_3 background and the applied current pulse is $10 \text{ A}\cdot\text{m}^{-2}$. The data points and linear fit are denoted by (+) and a dashed line, respectively.

3B.4.6. Ag/AgCl surface analysis

Beyond the transition time, the AgCl surface might be damaged due to oxide formation from the second faradaic reaction. The validity of the results depend on the surface composition of the WE; the Ag surface must be covered by a uniform AgCl layer for the Sand equation (equation 3.6) to hold. A SEM image of the electrode surface will show its topography and an EDX analysis will give the surface composition. Figure 3.17a and b

shows a SEM image and EDX analysis of the WE before the experiment. The SEM image shows a compact layer and EDX analysis indicates that this layer is composed of AgCl. After the first series of chronopotentiometric experiments (the calibration curve shown in figure 3.13), another SEM image and EDX analysis were taken; see figure 3.18a and b. Most importantly, the EDX analysis does not show the formation of silver oxides; thus, the measurements performed during this work are valid as the WE is still covered with the AgCl layer. However, the surface is not completely unaffected, as the SEM image shows an increase in surface area due to the formation of porous AgCl crystals. Note that the life time of the sensor depends upon the consumption of the Ag during the galvanostatic pulse. This consumption can be counteracted by the reduction of the Ag/AgCl electrode after the oxidation current [37], which was not attempted in this work.

(a) SEM image

(b) EDX analysis

Figure 3.17: Surface analysis of the Ag/AgCl electrode before any experiments were performed; (a) SEM image and (b) EDX analysis of the surface composition. The WE surface is composed of Ag and Cl elements.

(a) SEM image

(b) EDX analysis

Figure 3.18: Surface analysis of the Ag/AgCl electrode after current pulses have been applied (measurements taken); (a) SEM image and (b) EDX analysis of the surface composition. The WE surface is still primarily composed of Ag and Cl elements.

For usage in concrete the sensor electrode should be fabricated on a substrate which is stable in concrete environment. Mostly reported sensors in concrete are fabricated on PCB substrates [49, 50]. Prior to use, the electrode area should be pre-casted to give mechanical strength.

3B.5. Conclusion

An ISE sensor based on transition time measurement has been developed to measure the Cl^- ion concentration in aqueous solutions. When a current pulse is applied to the Ag/AgCl working electrode, the half-cell potential of the electrode changes due to the depletion of Cl^- ions near the electrode surface. The transition time (the moment at which the Cl^- ions deplete completely at the electrode surface) is indicated by the first inflection point of the potential response and is a function of the Cl^- ion concentration in the bulk electrolyte. The calibration curve of the square root of the transition time versus the Cl^- ion concentration depicts a linear line, as predicted by the Sand equation. A deviation exists between the theoretical and experimental values, which was attributed to uncertainty in the current density and diffusion coefficient values used to calculate the theoretical times. Proper selection of the current density for a particular concentration range is crucial for optimal device operation. Low current densities lead to higher transition times, and thus, subsequent mass transport by convection (which must be prevented). Conversely, high current densities (larger than $100 \text{ A}\cdot\text{m}^{-2}$) may damage the AgCl layer. The transition time shows an inverse relationship with the current density, as expected. Thus, transition time can be tuned to a particular Cl^- ion concentration range by varying the applied current pulse, giving a wide

possible detection range of the sensor. Since the transition time does not depend on the absolute reference potential, any metal wire may be used as a pseudo-reference electrode. Furthermore, there was no inherent drift in the transition time over two week measurement period. This measurement approach is promising for Cl^- ion sensing in applications where the integration of a conventional liquid junction reference electrode is not possible; such as, the measurement of Cl^- ions inside concrete structures.

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Chapter 4.

Activated carbon as a pseudo-reference electrode in concrete

In this chapter, the application of Kynol based activated carbon (KAC) as a pseudo-reference electrode for potentiometric measurement inside concrete is presented. Due to its high surface area the activated carbons has a large electrical double layer capacitance ($EDLC > 50Fg^{-1}$) and are used as electrode material for super capacitors. The change in potential of an electrical double layer capacitor is given by $\Delta E = dQ/C_{DL}$, where E [V] is the potential, Q [C] is the charge and C_{DL} [F] is the EDLC. Therefore any small amount of oxidation/reduction reaction as well as adsorption/desorption of charge (dQ) at the KAC will be neutralized by its large capacitance C_{DL} and its potential will not change significantly. The AC electrode is proposed as a feasible alternative for a pseudo-reference electrode in concrete.

Above figure: The SEM image of a single tube of Kynol based activated carbon. We call it the micro-cannon.

4.1. Introduction

In electrochemical measurements a long-term stable reference electrode has always been a topic of interest [1-4]. This is even more pronounced in the case of potentiometric measurements where the half-cell potential of a working electrode is measured against a reference electrode [2, 5-7]. The drift in reference potential adds an error to the measurements [8]. In regard to a redox electrode, such as an Ag/AgCl electrode (Nernstian slope = -59 mV/decade), a change of 8.9 mV in reference potential means a two-fold error in the determination of concentration [9].

For a continuous long-term potentiometric measurement a stable reference electrode is inevitable [9-11]. Such an application is the in-situ monitoring of chloride ions and corrosion in concrete structures. The chloride ion concentration is one of the major indicators of concrete structural degradation [12]. A threshold amount of chloride ions triggers rapid corrosion of reinforcement steel, resulting in ultimate failure of the structure [13, 14]. Currently, to determine the $[\text{Cl}^-]$ [15, 16] and corrosion [17-19], the half-cell potential of an Ag/AgCl electrode and the reinforcement steel is measured against a reference electrode (usually a liquid junction reference), respectively. The working electrodes (Ag/AgCl and reinforcement steel) are embedded inside the concrete whereas the reference electrode is kept outside since its reference solution should be refreshed over time to keep a stable potential. This adds a dynamic diffusion potential to the measurement [20] and furthermore restricts this method to the lab scale. For in-situ potentiometric measurement in real concrete structures a stable embeddable reference electrode is crucial.

Recently, several solutions of embeddable pseudo-reference electrodes in concrete [21] have been proposed such as metal/metal oxide (MMO) electrodes (e.g. Mn/MnO₂ [22, 23] and metal oxide activated titanium rod electrodes [24]). Limitation of these electrodes is their pH sensitivity which is not compatible with the pH variations encountered inside concrete. Due to carbonation the pH inside concrete may vary from 12.5 to 9 [25]. Still, for some onset corrosion measurement, while the pH remains constant, these electrodes can be used as a pseudo-reference. However, for long term monitoring the pseudo-reference should be inert to the change in pH and ionic composition in the concrete pore solution. The concrete pore solution is composed mainly of saturated Ca(OH)₂ [15, 26]. This high ionic concentration of the pore solution can be utilized for designing a stable pseudo-reference electrode.

(a) Snapshot of the rolled activated carbon fabric. This material can be compacted into small volumes

(b) SEM image of the activated carbon material at micro-scale. The carbon tubes of ca. 10 μm diameter woven like a fabric are visible

(c) Magnified SEM image of a single carbon tube. Micro pores of less than 1 μm diameter are visible

(d) Further SEM magnification of the micro pores on a single carbon tube. Nano-pores of up to 10 nm diameter are visible.

Figure 4. 1: Kynol based activated carbon electrode (a) Snapshot of the rolled activated carbon fabric (b–d) SEM image of the micro and nano pores of the material.

Carbon material is well known for its inert behavior in the presence of aggressive ions in concrete such as hydroxide and chloride [21, 27]. When activated at elevated temperature (typically above 700 °C) this material becomes highly porous, also known as activated carbon (AC) [28]. Due to its higher surface area, the activated carbon electrode, when immersed in an electrolyte, forms a huge electrical double layer capacitance (EDLC > 50 Fg⁻¹) [29]. Activated carbon electrodes are therefore commonly used as an electrode material for super capacitors [30]. The high surface area of an AC electrode comes from its micro and nano-porosity. The large EDLC can be utilized to stabilize the potential of AC electrode in high ionic electrolytes. The potential change, ΔE , across the double layer capacitor is given by $\Delta E = dQ/C_{DL}$, where dQ and C are the change in charge and the capacitance, respectively. Any change in the charge due to any small amount of oxidizing/ reducing species or adsorption/desorption reaction (dQ) will be neutralized by the large C_{DL} in the denominator. Therefore, the electrode potential of an AC electrode will remain relatively steady against the change in the concentration of ions in a higher ionic electrolyte as compared to commonly used MMO electrodes. Ruch et al. 2009 reported the use of AC electrode as a pseudo-reference electrode in ionic liquid by using the same principle [31]. The use of an AC electrode as a pseudo-reference electrode can be justified in high ionic electrolyte, especially in the absence of potential determining redox species. We demonstrated the feasibility of an AC electrode as a pseudo-reference electrode for potentiometric measurement inside concrete. The EDLC and characterization, stability of electrode potential toward ionic composition and pH of the electrolyte are evaluated. Furthermore, the long-term measurement in concrete pore solution is studied.

4.2. Materials and method

4.2.1. Activated carbon material

In this work a Kynol based activated carbon of type ACF-1603-15 from Kynol GmbH Hamburg is used. According to the manufacturer this activated carbon contains 100 % carbon which is derived from a novoloid fiber precursor [32]. It is a fabric-like material with a specific surface area larger than 1500 m²g⁻¹. Unlike most of the available AC material [28, 33] it consists of 100 % carbon with no polymeric impurity added. According to the supplier the novoloid fiber is first sewed together to form polymer fabric and then carbonized and activated at elevated temperatures (typically up to 2000 °C). The resulting AC material is a porous carbon flexible fabric which can be compacted into small volumes, as shown in figure 4.1a. The SEM image of the Kynol AC fabric at different

magnifications is shown in figure 4.1b-d. The spaghetti of micro carbon tubes of ca. 10 μm is visible in figure 4.1b which gives the bulk-porosity to this material. When zooming in on a carbon tube the micro-pores and nano-pores are clearly visible, see figure 4.1c and d. Each carbon tube shows randomly distributed micro and nano-pores of diameter down to ca. 1 nm. The pores on each carbon tube are not connected within the bulk material which will reduce any intercalation problem for such electrode.

Figure 4.2: Preparation of the AC electrode. (a) AC electrode fabric with graphite rod. Rolling of AC electrode fabric around the graphite rod, here carbon paste is used for adhesion of the fabric to the graphite rod. (b) The AC electrode ready to be used.

4.2.2. Electrode fabrication

The Kynol AC fabric is compacted to form an electrode for electrochemical measurement. A graphite rod (2 mm diameter, 5 cm length) is used as a current collector. The electrode fabrication process is shown in figure 4.2. The fabric is rolled around the carbon rod and a graphite/carbon paste is used for adhesion between the fabric and the carbon rod and also among the different layers of fabric as shown in figure 4.2a and b. The graphite paste should be carefully applied as an excess amount of graphite/carbon paste can block the pores and decrease the specific surface area of the electrode. The finished electrode is shown in figure 4.2c and will be referred to as AC electrode from now on. The AC electrode is dried at room temperature for 24 hours followed by an immersion step into DI water for 24 hours. Finally N_2 purging is applied to remove the trapped oxygen.

4.2.3. Measurement in concrete

To evaluate the performance of the AC electrode in concrete, it was embedded inside a concrete sample. The sample was prepared at Microlab TU Delft, The Netherlands according to the recipe mentioned in table 4.1 with a water to cement ratio (w/c) of 0.5. During casting, the AC electrodes of various sizes (350 and 30 F) are immersed in the concrete sample. Moreover, for comparison a graphite rod (1.2 cm²) and an Ag/AgCl electrode are embedded in the same sample. After drying, the concrete sample is placed in an electrolyte (pore solution = sat. Ca(OH)₂) and the open circuit potentials (OCP) of the electrodes are measured against a double junction Ag/AgCl reference electrode, see figure 4.3.

Figure 4.3: The open circuit potential measurement of the three electrodes, embedded inside concrete, with respect to an external reference electrode.

Table 4.1: The concrete paste recipe used in this work. The casting of concrete sample was performed in Microlab TU Delft, The Netherlands.

Material	Type	Mass (g)
Cement	CEM III	400
Water	Tap water	200
sand	Coarse (0–2 mm)	1200

4.2.4. Chemicals and equipment

Calcium hydroxide (99.995% trace metal basis), potassium nitrate (>99% reagent grade), potassium chloride (BioXtra, $\geq 99.0\%$) and potassium hydroxide (90% pure reagent grade) were ordered from Sigma–Aldrich, the Netherlands. A double junction Ag/AgCl reference electrode Z113107 model is ordered from Sigma–Aldrich, the Netherlands. The carbon rods (Ultrafine 1-5 μm , 99.997 %, model C007911) were ordered from Goodfellow Cambridge Ltd., UK. The graphite/carbon paste model C10903P14 is ordered from Gwent group, UK. The electrochemical characterization and measurements were performed using a VSP potentiostat from Biologic Science Inst., France. The Ag/AgCl electrode was made by anodization an Ag wire in 0.1 M HCl electrolyte for 20 mins. at a current density of 0.5 mA cm^{-2} . The Ag wire model 265608 (wire, diam. 1.0 mm, 99.9% trace metals basis) was ordered from Sigma–Aldrich, the Netherlands. All measurements were carried out at room temperature (ca. 21 °C) unless stated otherwise.

4.3. Results and discussion

4.3.1. Cyclic voltammogram of AC electrode (capacitance measurement)

The EDLC of the AC electrode is determined from cyclic voltammetry measurements. A potential range of -0.5 to 0.5 V is applied to the AC working electrode at various scan rates (1 and 0.1 mVs^{-1}) in 3 M KCl electrolyte. Another AC electrode is used as a counter electrode and an Ag/AgCl wire is used as a reference electrode. The CV curve is normalized by dividing all the current values by the scan rate[29, 34]. After normalization the y-axis of the CV corresponds to the capacitance of the AC electrode as $C = i/(dV/dt)$. The normalized CV of the AC electrode at scan rate of 1 and 0.1 mVs^{-1} is shown in figure 4.4a.

Figure 4.4: Scan-rate-normalized CV curve in 3 M KCl electrolyte (a) At various scan rates 0.1 and 1 mV/s. The EDL capacitance of the AC electrode in this case is ca.45 F (b) For 350 F EDLC electrode with 0.1 mVs⁻¹ scan rate.

Theoretically, the scan-rate-normalized CV curves should be the same for both scan rates, which is not the case. The EDLC is determined to be ca. 40 F (93 Fg⁻¹) and ca. 45 F (104 Fg⁻¹) for 1 and 0.1 mVs⁻¹ scan rates, respectively. The decrease in capacitance at higher scan rate can be explained by the kinetics limitation of the adsorbing/desorbing ions and/or by the transmission line behavior of the porous electrode [29, 35]. At lower scan rate (0.1 mV/s) ions have more time to reach the nano-pores and thereby accessing the larger surface area of the electrode thus increasing the EDLC. Moreover, the corners of the scan-rate-normalized CV in figure 4.4a are rounded and show variations depending on the scan rate. The higher the scan rates the lower the rise time of the CV curve which is (again) due to the transmission line (equivalent series resistance) behavior of the nano-pores. There is a small peak around 0.25 V in figure

4.4a for 0.1 mVs^{-1} scan rate. Activated carbon is known to have a redox peak for the quinone group [36] at its surface but this occurs at a higher potential. Therefore, the observed peak can be due to some potential dependent adsorption/desorption reaction especially at lower scan rates. The CV of another AC electrode with higher EDLC is shown in figure 4.4b at 0.1 mVs^{-1} scan rate. No prominent peak is visible in case of 350 F EDLC for the defined potential window.

4.3.2. Drift in open circuit potential

To observe the long-term potential stability of the AC electrode, its open circuit potential (OCP) is measured against an Ag/AgCl liquid junction reference electrode over 21 days. The measurement result is shown in figure 4.5. To avoid drifting of the reference electrode it was preconditioned overnight after each measurement (after each day). The OCP of the AC electrode stabilizes over time and drifted within $\sim 9 \text{ mV}$ over 21 days (drift = 0.4 mV/day). In the first 10 days of the measurement the potential decreases relatively fast and drifted with a rate of 0.8 mV/day . After 10 days the potential remains relatively steady with a drift of 0.1 mV/day . This value is in agreement with the literature [31]. This drift in potential can be due to adsorption/desorption of ions near the electrode surface. The drift can be concealed by the pre-conditioning of the AC electrode. After the CV measurement the AC electrode should be precondition in the electrolyte for at least one week. This is because the electrode is charged to a certain potential during the CV and it takes a while for it to self-discharge. The self-discharging of the EDLC should not be confused with the drift in the OCP.

4.3.3. OCP dependence on the nature of ions

In the absence of any redox active species the OCP of the AC electrode depends on the adsorption/desorption (charging/discharging) of ions in the electrolyte. Therefore, the nature of ions (i.e. the size and charge) plays a vital role in defining of the OCP. The concrete pore solution is typically composed of Ca^{+2} , K^{+} , Na^{+} and OH^{-} , Cl^{-} ions. In the pore solution the adsorption/desorption of Ca^{+2} and OH^{-} ions will dominantly effect the potential of the AC electrode. The effect of Cl^{-} ions on the OCP in concrete pore solution is shown in figure 4.6a. It can be observed that there is no significant effect of Cl^{-} ions on the OCP untill 100 mM but at a concentration of about 500 mM the OCP starts to decrease drastically ($dV/d[\text{Cl}^{-}] \sim -12 \text{ mV/decade}$). Typically in concrete the Cl^{-} ion concentration reaches concentrations up to 0.5 M [14]. Therefore this electrode can still be applied for measurement in concrete.

Figure 4.5: Open circuit potential measurement of the AC electrode for 21 days immersion in the concrete pore solution. The potential is relatively steady after 10 day of immersion and the drift is less than 0.2 mV/day.

4.3.4. Effect of pH

In concrete structures the pH of the pore solution changes gradually (depending on conditions) over time from 12.5 to 9 due to carbonation [25]. As a long term pseudo-reference in concrete, the OCP of the AC electrode should therefore not be affected by this change in pH. The measurement results of the OCP of the AC electrode as a function of pH is shown in figure 4.6b. The pH is varied between pH 7.5 and 13 in a 1 M KCl + 2 M KNO₃ solution, satisfying the condition of high ionic concentration. The effect is pronounced at higher pH (pH > 12) as the potential decreases significantly (~ 20 mV) as compare to pH change from pH 8 to 12 ($\Delta V < 1$ mV). Compared to common metal and metal oxide pseudo-reference electrode, the AC electrode shows better pH stability. This is due to the absence of faradaic reactions at the AC electrode during the pH change in contrast to metal/metal oxide electrodes. The observed variation in potential is due to the decrease in the adsorption isotherm of ions at higher pH, which is more pronounced at higher pH of the electrolyte.

Figure 4.6: The stability of OCP of the AC electrode (a) Effect of changing the $[Cl^-]$ on the OCP of the AC electrode in the pore solution (b) The OCP of the AC electrode for different pH in 1 M KCl + 2 M KNO_3 background electrolyte.

4.3.5. Measurement inside concrete

The concrete sample was immersed in sat. $Ca(OH)_2$ solution for 72 days and the OCP of the different embedded electrodes was measured against a liquid junction reference electrode. After each measurement, the externally placed reference electrode was conditioned in its reference solution overnight. The Cl^- ions (0.5 M KCl) were added to the pore solution after 57 days, as shown in figure 4.7.

The activated carbon electrodes (Double layer capacitance 350 and 30 F) showed a steady OCP (Change in OCP < 1 mV/day) after the first month of the measurement. The OCP remained steady around -110 mV. Both AC electrode of 350 F and 30 F showed more or less the same stability. After

the introduction of Cl^- ions, the OCP of the 350 F electrode remained relatively stable (Change in OCP ca. 21 mV) as compared to the 30 F electrode (ca. 60 mV). Therefore, the AC electrode with large double layer capacitance has a relatively better OCP stability. The OCP measurement of the graphite rod showed a random value spreading from ca. -60 to +70 mV. The OCP changes drastically and no stable potential is achieved after 3 months of measurements. On the other hand, the OCP of the Ag/AgCl electrode remains relatively steady. In the absence of Cl^- ions the OH^- is the potential determining ion for this Ag/AgCl electrode [16]. In the absence of Cl^- , Ag/AgCl can be used as a reference electrode in concrete. Once the Cl^- ions are introduced in the pore solution (after 57 days of measurement) its OCP changed drastically (ca. 115 mV), corresponding to the change in the concentration of Cl^- ions. Due to the high porosity of this concrete sample the Cl^- penetrates rapidly. Within one day the Cl^- concentration inside concrete equals the pore solution concentration (0.5 M Cl^-) derived from the calibration curve of the Ag/AgCl electrode (65 mV).

Figure 4.7: Open circuit potential of different electrodes embedded in concrete sample over a period of 72 days.

4.3.6. Comparison with the state-of-the-art reference electrodes

Keeping in mind the dependence of the OCP of AC electrode upon the nature of ions and higher pH values in the electrolyte the activated carbon electrode does not seem an ideal solution for a pseudo-reference electrode inside concrete. Furthermore, in contrast to the existing metal/metal oxide pseudo-reference the AC electrode does not has a defined electrode potential. However, the AC electrode does carry some advantage: the OCP is relatively stable over time and is less sensitive to the pH change at lower pH values. The comparison of the AC electrode with state -of-the-art reference electrodes, such as the liquid junction and metal metal oxide pseudo-reference electrode is summarized in table 4.2. Plus and minus signs indicate comparative advantages and disadvantages, respectively. The ease of fabrication, material cost, potential stability and inert behavior of the AC electrode make it an inexorable contender for reference electrode inside concrete.

Table 4.2: Comparison of the AC electrode with the state-of-the-art liquid junction reference electrode and the metal/metal oxide pseudo-reference electrode in concrete. Here + and –sign mean comparative advantages and disadvantages, respectively. The characteristics of liquid junction reference and MMO reference electrode in concrete is evaluated from literature [21].

Reference electrode	OCP Stability against interfering ions	Stability against pH change	Material degradation	Embedded inside concrete	Cost effective-ness
Liquid junction reference electrode	+	++	–	–	–
Metal/metal oxide (MMO) pseudo-reference	–	–	–	+	+
Activated carbon pseudo-reference electrode	–	+	+	+	++

4.4. Conclusion

The feasibility of activated carbon as a pseudo-reference electrode for measurement inside concrete is evaluated. Kynol based activated carbon is used which is renowned for its high surface area and inertness to aggressive ions. The scan-rate-normalized CV of material showed a specific capacitance of 93 to 110 Fg^{-1} . The high capacitance is due to micro and nano porosity of the activated carbon. The currents in the CV were from the non-faradaic reaction (adsorption/desorption) at the AC surface. This is only valid in the absence of any redox species which is the case of concrete pore solution (sat. $\text{Ca}(\text{OH})_2$ and Cl^- ions). The OCP of the AC electrode remains steady for higher ionic concentration of the electrolyte. The drift measurement in pore solution showed a drift of within 0.2 mV/day. This stability is due to the high EDLC of the AC electrode. Therefore, any change in adsorption/desorption of ions is neutralized by the high EDLC. The nature of the ions in the solution, i.e. the charge and size, affects the OCP behavior of the AC electrode. In the pore solution the OCP changes significantly (-12 mV/decade) when changing the $[\text{Cl}^-]$ from 0.5 to 1 M. The OCP is not affected by the $[\text{Cl}^-]$ up to 0.5 M. The OCP is relatively steady (inert behavior) against pH changes from pH 8 to 12 of the electrolyte as compare to the MMO pseudo-reference electrode. PH higher than 12 resulted in a significant change in the OCP (20 mV for pH change from 12 to 13). The AC electrode showed better stability and inert behavior in pore solution as compare to the existing metal and metal oxide pseudo-reference electrode. Moreover, the OCP of the AC electrode embedded in concrete showed steady values over 3 months of measurement (OCP change < 1mV/day). Therefore, the AC electrode can be an attractive alternative to the existing metal and metal oxide pseudo-reference electrode inside concrete. Moreover, the AC electrode can be used as a pseudo-reference in case of high ionic (saturated) electrolyte in the absence of redox species.

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Chapter 5.

Corrosion monitoring of reinforcement steel

A sensor for determining the status of corrosion of reinforcement steel is presented. The sensing method is based on the measurement of the time constant of the relaxation of the current-induced polarization potential. This time constant corresponds to the polarization resistance and therefore the amount of corrosion. The polarization resistance decreases from 655 to 10 $\text{k}\Omega \text{ cm}^2$ and from 670 to 300 $\text{k}\Omega \text{ cm}^2$ for pore solutions with and without chloride ions, respectively. This is a dynamic measurement to determine the status of corrosion i.e. active or passive corrosion where a long-term stable reference electrode is not required. Furthermore, *a priori* knowledge of the actual surface area of the steel is not required.

5.1. Introduction

Corrosion of reinforcement steel in concrete is one of the most devastating phenomena causing concrete degradation [1-3]. The formation of rust during corrosion reduces the tensile strength of the reinforcement steel along with volume expansion inside concrete, resulting in cracks and accordingly structural failure [1]. Corrosion sensors embedded inside these structures can give early warning of structural failure, thereby saving human lives and unnecessary maintenance cost.

The steel inside concrete structure undergoes corrosion with the formation of an oxide layer (rust) due to the alkaline environment. This oxide layer acts as a passivation film and inhibits the corrosion rate [4]. The structure can therefore live for its projected lifetime. The problem arises when Cl^- ions make their way inside the concrete. When the $[\text{Cl}^-]$ reaches a threshold value inside concrete [5], the passivation film breaks down at localized areas, known as pits. This results in a drastic increase in the corrosion rate [6], resulting in sudden failure of structures. This type of corrosion is termed pitting corrosion.

Electrochemical techniques are commonly used to assess the corrosion rate since the corrosion process is itself an electrochemical process. Several groups have reported the monitoring of corrosion rate by using electrochemical techniques [7] such as half-cell potential measurement [8], DC linear polarization resistance and the AC impedance method [9-13]. These existing methods require knowledge of the actual steel rebar area in concrete which is not easy to estimate. Furthermore, for long-term on-site measurement, a stable reference electrode is required. Therefore, a feasible method for measuring the corrosion rate, when the area of reinforcement steel is unknown and a stable reference electrode is not required, would be of great assistance. Such a method has been proposed by J. A. Gonzalez et al. [14] and Glass et al. [12], who studied the polarization behavior of a steel by applying brief current pulses. The polarization behavior of steel can provide information about its corrosion status [15, 16]. During a current pulse applied to the reinforcement steel, the potential of the steel changes to a certain constant (the decay time). The time constant incorporates information of the polarization resistance of the corroding steel [17-19]. This is a dynamic measurement technique, and therefore a stable (conventional) reference electrode is not required. Any metal wire can act as a pseudo-reference electrode. This work further investigates the use of galvanostatic pulses to evaluate the corrosion status of reinforcement steel, without any knowledge of the area of the steel rebar. This method is feasible for the indication of active/passive corrosion under harsh conditions. Thus, it is only a semi-quantitative

indicator of the corrosion process, differentiating between active and passive corrosion. The determination of the time constant, the effect of the magnitude of current pulse and the utility of an arbitrary electrode as a pseudo-reference electrode will be discussed in this paper.

5.2. Theory

When a current pulse is applied through a reinforcement steel bar, the half-cell potential of the steel changes due to its polarization. The electrical equivalent of such an electrochemical process is given by a simple Randles circuit; see figure 5.1. In figure 5.1, C_{dl} is the double layer capacitance, R_p is the polarization resistance of the steel rebar and R_{el} is the resistance of the electrolyte (or concrete specimen). During the applied current pulse, the C_{dl} is charged to a certain potential and the potential response of the steel changes by ΔV . Once the current is interrupted, the C_{dl} discharges through R_p using the corrosion current, i_{corr} [14, 16]. The potential of the reinforcement steel then relaxes to its initial value. The expression for the relaxation potential, V_{relax} is expressed as:

$$V_{relax} = \Delta V e^{-t/\tau} \quad 5.1$$

Where τ is the time constant (decay time) of the relaxation potential, V_{relax} , and the time constant, τ , is the time for the potential response to reach 37% of the ΔV . The time constant is given by:

$$\tau = C_{dl} R_p \quad 5.2$$

The corrosion current is inversely proportional to the polarization resistance. Therefore with the progression of corrosion, the polarization resistance decreases, consequently decreasing the time constant, τ . Figure 5.2a shows a typical polarization of a reinforcement steel bar during an applied current pulse and the relaxation after the current pulse is interrupted. The time interval from the moment the current was interrupted, t_1 to the time t_2 at which the potential response, V_{relax} , reaches 37% of ΔV [12, 14] gives τ ; see figure 5.2a. The natural log (ln) of the normalized potential (relaxation potential) is also plotted. Indeed the linear relation of the natural log of relaxation potential vs. measurement time indicates the expected exponential decay of the potential, see figure 5.2a.

Figure 5.1: Randle's circuit: Model of the equivalent electrical circuit for the polarization response of the reinforcement steel in electrolyte.

To determine the polarization resistance from the time constant, an estimated value of C_{dl} for reinforcement steel is required. For the reinforcement steel wire, the capacitance per unit area can be approximated between 10 and 150 $\mu\text{F}/\text{cm}^2$ [14, 20]. In this work, we used 150 $\mu\text{F}/\text{cm}^2$. Once the time constant, τ , is known, the polarization resistance, R_p , can be calculated from equation 5.2. The corrosion rate is inversely proportional to the polarization resistance and the time constant, τ . Note that for the determination of τ , ΔV and V_{relax} must be measured. This only requires a pseudo-reference electrode that is stable for the total measurement of ca. 20 s in figure 5.2a. Furthermore the IR drop, which occurs during measurements inside concrete, is neglected. This is allowed due to the fact that the time constant, τ , is measured after the current pulse is interrupted i.e. $I = 0$. Therefore IR drop is irrelevant in this approach. Note also that C_{dl} is proportional to the area of the steel wire and R_p is inversely proportional to that area, rendering time constant, τ , independent of the area of the steel wire.

5.3. Materials and method

The reinforcement steel wires were received from the Microlab, TU Delft, The Netherlands. Potassium chloride from BioXtra, $\geq 99.0\%$, potassium hydroxide 90% pure reagent grade, calcium hydroxide 99.995% trace metals basis and sodium hydroxide reagent grade $> 98\%$, pellets (anhydrous) were obtained from Sigma Aldrich, The Netherlands. The Ag/AgCl liquid junction reference electrode was also obtained from Sigma Aldrich, The Netherlands.

The galvanostatic measurements were performed using a VSP potentiostat from Bio-Logic Instruments, France. The reinforcement steel wire (area = 0.5 cm^2) is connected to the working electrode (WE) terminal of the potentiostat. Another steel wire (area = 5 cm^2) is used as a counter (CE). A bare Ag/AgCl wire is used as a pseudo-reference electrode. The

measurement parameters were controlled via the user interface of the potentiostat (EC-lab).

Figure 5.2: (a) Typical polarization curve of a steel wire. The current pulse is applied between $t = 0$ and t_1 . After the interruption of the current pulse at t_1 the potential relaxes (decreases), t_2 is the point at which the potential reaches 37% of ΔV . Time constant τ is the difference between t_2 and t_1 . (b) Schematic of the experimental setup for measuring the potential response during the applied current pulse. WE, CE and RE stand for the working, counter and reference electrodes, respectively.

Figure 5.2b shows the schematic of the experimental setup. Two electrolytes A and B were used; Electrolyte A is sat. $Ca(OH)_2 + 0.1$ M NaOH with pH 13 and Electrolyte B is 1 mM $Ca(OH)_2 + 1$ M KCl with pH 9. The beakers with the electrolytes were then stored in a container partially filled with water to avoid evaporation of the electrolyte. The container was

covered with aluminum foil, this setup is known as the ‘poor man’s humidor’. All measurements were performed at the room temperature ($\sim 20^\circ\text{C}$).

5.4. Results and discussion

5.4.1. Polarization of reinforcement steel

The steel wires are polarized using the galvanostatic pulse in electrolytes A and B. The typical polarization curve of the steel wire, for a current pulse of $10\ \mu\text{A}/\text{cm}^2$ for 1 s, is shown in figure 5.2a. The magnitude and the duration of the pulse must be carefully selected to avoid erroneous data. Current pulses that are too low result in a lower signal to noise ratio, which make it difficult to separate the polarization response from the background noise. While the higher current pulses improve the signal to noise ratio, it also causes undesirable oxidation reactions leading to self-induced corrosion. The applied current pulse must be chosen to give an adequate polarization ($\Delta V = 10$ to $60\ \text{mV}$ [14]) so that the time constant can be measured reliably. Figure 5.3 shows the effect of the applied current pulse on the potential response. The background noise is dominant at the lower current pulse ($I_{app} = 0.2\ \mu\text{A}/\text{cm}^2$), see figure 5.3a, whereas at a higher current pulse ($I_{app} = 20\ \mu\text{A}/\text{cm}^2$), the potential response shows a plateau due to the faradaic reaction; see figure 5.3c. For large reinforcement steel inside concrete the applied current pulse would not be uniform over the electrode area [14]. This non-uniformity can be reduced by applying low current pulse for longer time and placing the counter electrode relatively far from the reinforcement steel. Once the current pulse is within an adequate range (between 1 and $15\ \mu\text{A}/\text{cm}^2$) there will be no significant effect of I_{app} on the time constant. The time constant measurement for various current pulses is shown in figure 5.4. Two series of measurements were performed. It was found that the time constants, τ , for different I_{app} (5 , 8 and $10\ \mu\text{A}/\text{cm}^2$ for $10\ \text{s}$) are quite similar (48 , 53 and $51\ \text{s}$, respectively).

(a)
At I_{app} of $0.2 \mu\text{A}/\text{cm}^2$ the background noise is dominant.

(b)
At I_{app} of $4 \mu\text{A}/\text{cm}^2$ the polarization is sufficient (50 mV) and the time constant can be easily measured

(c)
At I_{app} of $20 \mu\text{A}/\text{cm}^2$, the polarization is 100 mV and the potential reaches a plateau where it undergoes an undesirable Faradaic reaction

Figure 5.3: The effect of the magnitude of the current pulse on the polarization measurement. In this work, the range for the galvanostatic pulse in this work is selected to be between 1 and $15 \mu\text{A}/\text{cm}^2$.

Figure 5.4: The polarization measurement of steel wire in electrolyte A for three current pulses in two series of measurements. The time constant, τ , is calculated from the relaxation potential response (37% of ΔV). The magnitude of current pulse has no significant effect on the time constant, τ .

5.4.2. Determination of τ

The polarization measurements for the evaluation of τ were performed under humid conditions over a period of one month. It was observed by visual inspection that the steel wire immersed in electrolyte A corroded at lower rate than the steel wire in electrolyte B. The higher pH of electrolyte A, without chloride ions, causes a stable passivation film which inhibits rapid corrosion, whereas the lower pH and the presence of chloride ions in electrolyte B cause rapid corrosion (pitting corrosion) with the formation of rust [21]. Another observation we made is the relatively fast corrosion of the steel wire just below the air/electrolyte interface. This is due to the difference in oxygen concentration just above and below the air/electrolyte interface. This is also known as differential aeration corrosion [22]. The area of steel just below the interface (lower oxygen concentration) acts like an anode whereas the area above (higher oxygen concentration) acts as cathode [22]. Therefore, a dark brownish rust is visible near the air/electrolyte interface.

Figure 5.5 shows the response of multiple time constant measurements taken at 146, 176, and 184 hours after the immersion of the steel wire in electrolyte B. The x-axis of figure 5.5 shows the measurement time at different immersion conditions (after 146, 176, and 184 hrs of immersion). The time constant, τ , decreases (from 29 to 22 s) over time (span of 16 hours) due to the progression of corrosion. This is due to the fact that the

polarization resistance decreases over time under an active corrosion condition. In these measurements, a bare Ag/AgCl wire is used as a pseudo-reference electrode. This wire gives a relatively stable half-cell potential depending on the concentration of Cl^- ions [23] but in principle any metal wire can be used as a pseudo-reference electrode as long as it remains stable over the time of measurement (being < 100 s for figure 5.5). In the absence of Cl^- ions, the OH^- ions determine the half-cell potential [24].

Figure 5.5: Measurement results of the time constant. Before the measurement, the steel wire was immersed in electrolyte B for the time indicated in this figure. The time constant decreases with the progression of corrosion. The magnitude of the current pulse is $10 \mu\text{A}/\text{cm}^2$ for 10 s.

The time constant measurements, over a period of one month in both electrolytes A and B are shown in figures 5.6a and b. The measurements were performed at a current pulse I_{app} of $10 \mu\text{A}/\text{cm}^2$ for 10 s. Each day, three sets of measurements were taken and then plotted versus time. The corresponding polarization resistance versus time, based on equation 5.2, is also plotted in figure 5.6. The pH of the electrolytes did not change significantly due to carbonation over one month of measurements. The time constant, τ and the polarization resistance, R_p for the steel wire immersed in electrolyte A (figure 5.6a) does not show such a large change as that for electrolyte B. Here the polarization resistance is calculated from the measured time constant and estimated double layer capacitance and can therefore not be used to precisely quantify the corrosion rate. The time constant method serve as the indication of active and passive corrosion. Over a span of one month, the R_p changes from 670 to 300 $\text{k}\Omega \text{ cm}^2$ and τ changes from 105 to 50 s; see figure 5.6a. These values are comparable to those reported by Gonzalez et al. 2001 for passive corrosion, i.e up to 190

s [14]. The typical value of R_p , for actively corroding steel is less than 250 $\text{k}\Omega \text{ cm}^2$.

Figure 5.6: Measurement results of the time constant and calculated polarization resistance. (a) Plot of the time constant and the corresponding polarization resistance vs. immersion time for electrolyte A. (b) Plot of the time constant and the corresponding polarization resistance vs. immersion time for electrolyte B. The approximated C_{dl} value used to calculate the polarization resistance is $150 \mu\text{F}/\text{cm}^2$.

Initially (first week after immersion), the R_p changes significantly after then it remains relatively steady. In this first week, the steel wire undergoes

rapid corrosion, producing iron oxide which then forms a passivation film. This passivation film then inhibits further corrosion resulting in a steady polarization resistance.

Figure 5.7: (a) Effect of various pseudo-reference electrodes on the time constant. The time constant is plotted with respect to the Ag/AgCl liquid junction reference electrode, Ag/AgCl wire and steel wire. (b) Effect of the area of the corroding steel wire on the time constant. The time constant is plotted against various areas of steel wire immersed in the electrolyte. Ag/AgCl wire was used as a pseudo-reference.

In the case of steel wire immersed in electrolyte B, as shown in figure 5.6b, the time constant drastically changed with a decrease by two orders of magnitude, from 98 to 1.6 s. Gonzalez et al. 2001 reported time constant value up to 3 s for active corrosion of reinforcement steel [14] which are comparable to our measurement results. The corresponding reduction in polarization resistance is from 655 to 10 $\text{k}\Omega \text{ cm}^2$. The large change of R_p in electrolyte B is due to the increase in corrosion rate over time. This is due to the presence of aggressive ions, such as chloride ions, in the electrolyte which breaks down the passivation film.

Finally, the effects of (pseudo-) reference electrodes and the area of the corroding steel wire on the time constant were evaluated, as shown in figure 5.7. In figure 5.7a, three different (reference) electrodes were applied to assess the time constant, namely an Ag/AgCl liquid junction reference electrode, an Ag/AgCl wire and a steel wire. It is shown that the reference electrode has no systematic and significant effect on the time constant. The difference from the mean value is within $\pm 3\%$, which is an acceptable error range. In this work, a precise measurement is not crucial, because the order of the time constant values indicates the status of corrosion. Within this experimental error range, active and passive corrosion can still be distinguished. In case of the steel-wire reference, the standard deviation is relatively large. This can be due to some change in its potential during the measurement period. Any metal wire that gives a stable potential during the measurement period ($< 100 \text{ s}$) can be used as a pseudo-reference electrode. The effect of the surface area of the corroding steel wire on the time constant is shown in figure 5.7b. During these measurements, three different areas of the steel wire were exposed to the solution, namely 63, 27 and 5 mm^2 . It is shown that the exposed area has no significant effect on the time constant as predicted in the theory section. The smaller surface area, i.e. 5 mm^2 , shows a relatively lower time constant which can be attributed to the higher ohmic drop. Overall, the differences can also be explained by the inhomogeneity of the corrosion process.

5.5. Conclusion

The status of corrosion of the reinforcement steel can be determined by the time constant (decay) of the relaxation potential of the current-induced polarization potential. This time constant is a function of the polarization resistance of the corroding steel. It gives the corresponding corrosion status (active or passive corrosion) of the reinforcement steel. Steel wires were immersed in two electrolytes; (1) sat. $\text{Ca}(\text{OH})_2$ + 0.1 M NaOH with pH 13 and (2) $\text{Ca}(\text{OH})_2$ + 1 M KCl with pH=9, for a month and the time

constants were measured. The electrolyte without any chloride ions shows an increase in the corrosion rate for the first week of immersion. The corrosion rate then remains constant at a polarization resistance of $300 \text{ k}\Omega \text{ cm}^2$ owing to the formation of a stable passivation film (passive corrosion). On the other hand, the steel wire in the electrolyte with a high concentration of chloride ions shows higher corrosion rates with a drastic decrease in polarization resistance. Over a period of one month, the polarization resistance decreases from 655 to $10 \text{ k}\Omega \text{ cm}^2$. The magnitude of the applied galvanostatic pulse has no significant effect on the time constant measurement, provided that the pulses are within an adequate range, namely between 1 and $15 \text{ }\mu\text{A}/\text{cm}^2$ for 10 s. This is a dynamic measurement where the absolute potential of the WE is not relevant. Any metal wire, the potential of which remains steady for 100 s (the maximum measurement period), can be used as a pseudo-reference electrode. Furthermore, the area of the steel wire has no significant effect on the time constant, therefore the corrosion status of the reinforcement steel can be evaluated without prior knowledge of its area. This approach can rigorously determine the active and passive status of corrosion of reinforcement steel embedded inside concrete.

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Chapter 6.

Connecting to concrete: Wireless monitoring of chloride ions in concrete structures

In this chapter, a passive wireless monitoring technique to measure the half-cell potential of a Ag/AgCl electrode in concrete is presented. Wireless communication is achieved by an inductive coupling (reflected-impedance) between a sensor and a readout coil. The resonance frequency of the sensor coil (resonator) changes due to the change in the capacitance of a varactor element connected to the Ag/AgCl electrode. The resonance frequency of the sensor coil is reflected on the readout coil, giving the wireless sensor response. The capacitance of the varactor increases with the increase in chloride ion concentration (20 pF/decade). This approach is feasible for a short range wireless detection of chloride ion concentration in concrete.

This work was conducted as a bachelor B2 assignment of the electrical engineering program by student Bas ten Have, Idzard Hoekstra, Arjan Douma and Douwe de Bruijn. In above picture, Arjan Douma is depicting the concept of wireless chloride ion sensor in concrete.

6.1. Introduction

Chloride ions in concrete, when reaching a threshold amount, are one of the major causes of deterioration of concrete structures [1-3]. It is a crucial parameter determining the service life and maintenance cycle of concrete structures [4, 5]. Potentiometry using a Ag/AgCl electrode is one of the state-of-the-art techniques to measure the Cl^- concentration in concrete [6-9]. The open circuit potential (OCP) of the Ag/AgCl electrode is a function of the Cl^- concentration in electrolyte, expressed by the Nernst equation [10]. The OCP is measured in the extracted pore solution which is acquired by drilling holes (destructive sampling) in concrete structures [5, 11, 12]. Moreover, it gives an unreliable and intermittent result. By embedding the sensor inside concrete, a non-destructive, reliable and continuous measurement can be achieved. Accordingly, a wireless measurement of the OCP of the Ag/AgCl electrode is required for long-term measurement inside concrete [13, 14].

A passive-wireless communication (i.e. without external power source) using an electromagnetic coupling can be used for such application [14-16]. In this approach, a change in the resonance frequency of a sensor resonator is reflected (impedance matching) on a nearby readout coil [17-19]. Several groups have worked on this approach to measure the impedance characteristics of a sensor resonator [14-19] for biomedical, environmental and industrial applications. If an electrical element, which impedance is a function of the open circuit potential of a Ag/AgCl electrode, is introduced in the sensor resonator, the readout can be correlated to the chloride ion concentration. Such an element can be a varactor. Varactors are p-n junction diodes operated in a reverse-biased state [20, 21] to develop a capacitance due to the depletion zone. Its capacitance is inversely proportional to the applied (bias) voltage. We propose a passive-wireless-sensor resonator based on the changing capacitance of a varactor, connected to a Ag/AgCl electrode. The schematic of the approach is shown in Figure 6.1. The sensor resonator has an LC-network with a characteristics resonance frequency. The Ag/AgCl electrode provides the bias potential for the varactor. The change in the Cl^- ion concentration changes the OCP (bias potential), changing the capacitance of the varactor. Consequently, the resonance frequency of the LC-network changes which is reflected on the readout coil. This approach is inspired by the AquaTag device from SensorTag solution B.V, The Netherlands [22].

In this chapter, a passive-wireless-potentiometric approach to measure the chloride ion concentration in concrete is presented. The calibration curve and the effect of distance between sensor and readout coil is

measured. The measurements are performed in both electrolyte and concrete sample.

Figure 6.1: The schematic of the near field coupling between a sensor (secondary) and a readout (primary) coil. There is variable capacitor (varactor + fixed + trimmer capacitors) in the LC-network of the sensor coil. The capacitance of the varactor is a function of its bias potential supplied by the OCP of a Ag/AgCl electrode.

6.2. Materials and method

6.2.1. AquaTag device

AquaTag is a hand held device which is used to measure moisture in soil for agricultural purpose. The schematic of the working principle of this device is shown in Figure 6.2 [22]. According to the manufacturer there are two antenna coils on both the sensor and readout unit: receiver and transmitter coils. The receiver of the sensor unit receives two signals frequencies through a mixer (2.4×2.427 GHz) from the readout unit. The transmitter coils at the sensor unit is an element of an LC-network which resonates at the received frequency spectrum (near 27 MHz) through the mixer. The LC-network consists of the transmitter coil, the resonance circuit. The change in the capacitance changes the resonance frequency of the LC-network. The resonance frequency is reflected at the readout due to the impedance matching [23]. The readout device is a portable version of an impedance analyzer with limited frequency range; it samples five frequencies around 27 MHz received after the mixer. The device can reliably measure a capacitance change up to 20 pF around the base capacitance of 180 pF.

Figure 6.2: Schematic of the working principle of the AquaTag device. In the modified version (m-Aquatag) a Ag/AgCl electrode along with a reference electrode is connected to the varactor, which resonates in the LC-network [22].

6.2.2. Sensor circuit adapting to potentiometric sensor

The AquaTag device has been modified to measure the OCP of a Ag/AgCl electrode. The sensing element in the AquaTag device is replaced by a varactor, which is connected to a Ag/AgCl electrode and a reference electrode. The schematic of the circuit diagram of the modified unit is shown in the LC-network of Figure 6.1 with the varactor. There are four capacitors in the LC-network, i.e. decoupling capacitor, fixed capacitor, trimmer capacitor and varactor. The decoupling capacitor blocks any dc current in the circuit whereas the fixed and the variable capacitor provides a base capacitance of around 180 pF. The selected values of all the capacitors are shown in Table 6.1. The varactor gives a change of around 20 pF for the corresponding Cl^- concentration. The detection range of the $[\text{Cl}^-]$ can be adjusted through the trimmer capacitor (screw-adjustable). The Ag/AgCl working and the reference electrode are connected to the varactor in reverse biased configuration. From here on we will name this sensor module as m-AquaTag (modified AquaTag for potentiometric sensing), unless stated otherwise.

Table 6.1: Selected components for the sensor resonator circuit.

Component	Type	Capacitance value	Manufacturer
Varactor	BB201	Measured: 130–140 pF for 0–200 mV potential change which is the relevant range in our measurements	NXP semiconductors, The Netherlands
Ceramic Trimmer Capacitor	TZY2R250A C01	Range: 5.5 to 25 pF	Murata manufacturing Co. Ltd., Japan
Fixed capacitor	MC0805N3 90J500A2.5 4MM	39 pF	Multicomp electronics
Decoupling capacitor	MC0805B1 53K500A2. 54MM	15 nF	Multicomp electronics

6.2.3. Measurement setup

The calibration curve of the Ag/AgCl electrode is measured in various chloride ion concentrations. The capacitance measurement is performed with the readout placed near the transmitter coil of the sensor module with the Ag/AgCl working and reference electrode immersed in the electrolyte as shown in Figure 6.3. The readout device is connected to a computer through a universal serial bus (USB) and the capacitance value is displayed on the HyperTerminal interface and later analyzed.

6.2.4. Chemical and equipment

Potassium chloride salt (BioXtra, $\geq 99.0\%$) is ordered from Sigma-Aldrich, The Netherlands. It is dissolved in Milli-Q water to form 1 M KCl stock solution. A Ag wire with a 1.5mm diameter ($\geq 99.99\%$ trace metals) is coated with a thick layer of Ag/AgCl paste (Code: C2651014P10, from

Gwent group, UK). A ca. 500 μ m thick layer of Ag/AgCl paste is used in this work.

The potentiometric measurements were performed using a VSP-300 potentiostat from BioLogic Instruments, France. For capacitance measurements Agilent u1733c capacitance bridge is used. The Keithley 2200-72-1 programmable power supply is used as a voltage source. The AquaTag readout device was ordered from Sensortag solution, The Netherlands [22]. The varactor (BB201) was ordered from NXP semiconductors, The Netherlands. All the measurements involving potentiometry were performed in a Faraday cage and the measurement parameters were controlled via the user interface of the potentiostat (EC-lab v.10.37).

Figure 6.3: Measurement setup for Cl^- measurements. The handheld readout device is provided by SensorTag Solutions, The Netherlands [22]. The Ag/AgCl electrode is immersed in an aqueous solution and its OCP is measured against a reference electrode.

6.2.5. Concrete sample preparation

The m-AquaTag sensor module along with the Ag/AgCl electrode was embedded in concrete. The concrete casting recipe is mentioned in Table 6.2. The sample was casted and cured for one week in a closed humid chamber. After curing, the sample was immersed in 0.5 M KCl electrolyte to measure the change in Cl^- ion concentration over time. The snapshots of the sample preparation are shown in Figure 6.4. The active part of the sensor is laminated with epoxy resin to achieve a sealed package. The sensor is placed at ca. 30 mm inside from the surface cover of concrete. The Ag/AgCl reference electrode was kept outside the concrete to get a stable reference potential.

Table 6.2: The recipe of concrete casting used in this work.

Material	Type	Mass (g)
Cement	CEM III	400
Water	Tap water	200
Sand	Coarse (0–2 mm)	1200

Figure 6.4: The concrete sample casting and embodiment of the sensor along with a Ag/AgCl electrode in the concrete paste. After curing for one week the sample was immersed in a 0.5 M KCl electrolyte.

6.3. Results and discussion

6.3.1. Capacitance measured by the m-AquaTag readout

The Ag/AgCl electrode system is connected to the sensor unit and the electrodes are immersed in the electrolytes with varying $[Cl^-]$. The $[Cl^-]$ is varied from 0.01 to 1 M and the capacitance is measured by the m-AquaTag readout, as shown in Figure 6.5. The corresponding calibration curve of the Ag/AgCl electrode is also plotted along with the capacitance. The capacitance measurement is reliable up to 0.2 M $[Cl^-]$ with a linear increase in capacitance from 180 to 200 pF for a change in $[Cl^-]$ from 0.01 to 0.2 M, respectively. This is due to the limited detection range of the m-

AquaTag readout; it is designed to measure a change in capacitance of 20 pF. The measured capacitance is in agreement with our expected total capacitance value (total capacitance = varactor + variable capacitor + fixed capacitor) given in Table 6.2. The detection window of the $[\text{Cl}^-]$ in Figure 6.5 can be adjusted by varying the capacitance of the trimmer capacitor. For higher detection limit, the capacitance of the variable capacitor should be increase and vice versa.

Figure 6.5: The calibration curve between the Cl^- concentration and the measured capacitance (at the readout). The corresponding OCP of the Ag/AgCl electrode is also given.

6.3.2. Effect of distance

The distance between the sensor coil and the readout coil is crucial in passive monitoring. The larger the distance the higher the attenuation in the impedance matching, resulting in data losses. The capacitance measurement at various distances in air between sensor and readout coil is shown in Figure 6.6. The $[\text{Cl}^-]$ is 25 mM in all measurements. The measurements are repeatable and similar (deviation within 1 pF) up to a distance of 35 mm. After 35 mm, the measurements are not reliable as evident by the big error bar at 40 and 45 mm. When measuring inside concrete, although not tested inside concrete, the sensor coil should not be placed more than 35 mm deep.

Figure 6.6: Effect of the distances in air between the sensor and readout coil on the measured capacitance. The Cl^- concentration is 25 mM for all measurements.

Figure 6.7: The capacitance measurement by the *m-AquaTag* sensor module embedded in concrete sample. The sample with the embedded electrode is immersed in 0.5 M KCl electrolyte.

6.3.3. Measurement inside concrete

The capacitance measurement using the m-AquaTag sensor module embedded in concrete is shown in Figure 6.7. These measurements were performed over a period of two months. It was difficult to acquire a signal from the sensor node unless the sensor coil and readout coils are perfectly aligned. Furthermore, the circuitry on the sensor module should be carefully sealed to avoid any defect. As expected, the change in the capacitance shows a non-linear ingress of chloride in concrete. The detection range of this sensor is between 180 to 200 pF, measurements outside this range are unreliable. Therefore, from the initial results, when no chloride is present in the concrete and the capacitance is below 180 pF, nothing can be concluded. After the first week of immersion, the concentration reaches 10 mM KCl. The concentration inside concrete reaches 200 mM, i.e. near to the bulk concentration, after forty days. The measurements after 200 mM reliable due to the upper detection limit of the m-AquaTag.

6.4. Conclusion

A wireless communication method to measure the open circuit potential (OCP) of a Ag/AgCl chloride ion selective electrode is presented. The wireless communication is achieved by a near field coupling of a sensor resonator and a readout coil. The OCP is translated into a capacitance by using it as a bias potential for a varactor. This varactor is an impedance element in the LC-network of the sensor resonator. Therefore, the change in $[Cl^-]$ is translated into the change in resonance frequency. This change in the resonance frequency is reflected on to the near readout coil. The readout measures the change in capacitance due to changing Cl^- concentration. The chloride ion concentrations were measured in aqueous solution as well as in concrete. The detection range of the device is between 0.01 to 0.2 M $[Cl^-]$. This range is tunable by adjusting the trimmer capacitor in the sensor circuit. The capacitance of the sensor unit increases with the increase in chloride ion concentration. We measured a change of capacitance to 20 pF/decade to the change in $[Cl^-]$. Moreover, measurements were reliable up to a distance of 35 mm in air. The measurements inside concrete showed a change in capacitance over time with the ingress of chloride in concrete. Over a period of 50 days the $[Cl^-]$ inside concrete approximately reaches the bulk concentration. This passive monitoring approach can be used for short range wireless data acquisition of a potentiometric sensor inside concrete.

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Chapter 7.

Conclusion and outlook

The conclusions of each chapter are given at the end of the respective chapters. This chapter presents the overall conclusion of this work. Moreover, the existing challenges and the outlook of this work are also presented.

7.1. Conclusion

This work is a part of an integral solution for sustainable constructions with a focus on the sensing and monitoring of chloride ion concentration in concrete. The focus of this work is the non-destructive and in-situ measurement of chloride ions in concrete.

In chapter 2, a brief overview of all the existing non-destructive techniques along with their pros and cons are presented. These techniques are categorized into electrochemical and electromagnetic methods. The electromagnetic (EM) techniques seem to be an ideal solution for in-situ and non-destructive measurements due to their non-invasiveness, especially the techniques which use external EM excitation. However, the poor limit of detection and poor selectivity for chloride ions reduces the reliability of these measurements. Moreover, the EM techniques require a bulky setup in controlled experimental conditions with a trained operator. On the other hand, the electrochemical techniques, such as potentiometry, have better selectivity to chloride ions, are easy to embed in concrete and are cost effective. The challenges with electrochemical techniques lie in the drifts of the half-cell potential of the reference electrode when embedded in concrete. To date there is no such reference electrode which is long-term drift free. Moreover, the interference from hydroxide ions at high pH causes errors in chloride measurements.

In chapter 3, a dynamic electrochemical technique, to remove the need for a reference electrode, is presented. Drift in the state-of-the-art potentiometric approach is due to its static nature (zero current), relying on the absolute potential of the working electrode measuring against a stable reference electrode. An alternative to this is chronopotentiometry, which is a dynamic electrochemical approach. It is proposed as a reference free technique. A current pulse is applied to a Ag/AgCl electrode and its potential change is measured. In this case, the change in potential is due to the concentration gradient near the electrode. Once the chloride is depleted completely, the potential change reaches an inflection point, also called the transition time. The change in potential and the transition time do not depend on the absolute reference potential and any metal wire can be used as a pseudo-reference electrode. The only limitation is the poor potential stability at high pH with low chloride ion concentration i.e. when $[\text{OH}^-]/[\text{Cl}^-]$ is greater than 10. In such condition, the interference from hydroxide ions is significant. Therefore these approaches should be applied in conditions where the pH is below 12.

Another alternative for a long-term reference electrode, discussed in chapter 4, is a Kynol based activated carbon (AC) pseudo-reference

electrode. This is due to the fact that activated carbon has huge double layer capacitance (in the order of tens of Farad per gram) and has good material stability in concrete environment. The high double layer capacitance countervails any small changes in adsorption/desorption reaction (non-faradaic) which would cause a change in its electrode potential. Therefore, the potential of a Kynol based activated carbon with a double layer capacitance around 100 F remains stable in concrete. The drift measurement was within 0.2 mV/day over 22 days. Moreover, the OCP of the AC electrode embedded in concrete showed steady values over 3 months of measurement (OCP change < 1mV/day). Therefore, the AC electrode can be an attractive alternative to the existing metal and metal oxide pseudo-reference electrode inside concrete.

Along with the chloride ion concentration, the corrosion status of steel is an additional aspect for determining the structural deterioration. A rigorous corrosion sensor which indicates the active or passive state of corrosion is presented in chapter 5. The time constant of a decaying potential, after a current pulse is interrupted, gives the status of corrosion of reinforcement steel. It is a rigorous system where *a priori* knowledge of the area of steel and a stable reference electrode is not required. Furthermore, due to its dynamic nature no reference electrode is required and the system can easily be embedded inside concrete. Overall, the combination of the chloride measurement system presented in chapter 3 and 4 and the corrosion sensor presented in chapter 5 can be used for complete characterization of the pitting corrosion and its relation to chloride ion concentration in concrete.

A wireless communication, preferably passive, is needed for data acquisition for an embedded sensor inside concrete, as discussed in the requirements of an embedded chloride sensor in section 1.6 of chapter 1. A near field electromagnetic coupling between sensor and a readout coil can be used to wirelessly monitor the open circuit potential of a Ag/AgCl electrode. The chloride ion concentrations were measured in aqueous solution as well as in concrete. The detection range of the device in aqueous solution is between 0.01 to 0.2 M $[Cl^-]$, which can be tuned. The distance between the sensor and receiver unit is limited up to 35 mm in air. The measurements inside concrete showed a change in capacitance over time with the ingress of chloride in concrete. Over a period of 50 days the $[Cl^-]$ inside concrete nearly reaches the bulk concentration. This method is limited to potentiometry. For dynamic electrochemical approaches such as those discussed in chapter 3, an active wireless method is required.

Overall this work demonstrates some solutions to the challenges in the measurement of chloride ion in concrete, especially when using a long-term embedded reference electrode. This will help in building a new type of chloride sensor system for concrete based on dynamic electrochemical measurement with embedded corrosion sensors and a better pseudo-reference electrode.

7.2. Existing challenges for non-destructive in-situ measurements

Several techniques to measure the chloride ion concentration have been reviewed in this work. However, a long-term reference electrode for electrochemical measurement was the main focus of this work. We investigated a dynamic electrochemical technique and an activated carbon electrode as a (pseudo-) reference electrode as a possible solution. However, there still are some challenges to acquire an ideal chloride ion sensor for long-term measurement in concrete. These challenges are discussed as follows:

- a. The **material durability** of sensor against the aggressive chemical and mechanical environment of concrete is crucial for sensor design. Most structures have a projected lifetime between 50 and 100 years. Thus, the sensor and its sealing material should have the same or longer lifetime. So far, no focus has been given to this area.
- b. The **interference** from other environmental conditions, such as moisture content, temperature, presence of sulphate and CO_2 , has not been incorporated in the measurements. All the measurements were performed in controlled environment. For reliable data the sensor should compensate for these environmental factors.
- c. The **wireless data acquisition** in the presence of reinforcement steel would be difficult as steel would itself acts like an antenna. Therefore, long range wireless data acquisition is still a challenge.
- d. For measurements at different locations in concrete, a **multiple sensor array** is required, this is only feasible in case of a cheap and a miniaturized sensor. The manufacturing and installation cost should not dominate the maintenance cost of the RC structure.

7.3. Outlook

7.3.1. Material degradation

In this work we did not discuss the degradation of sensor material itself. Degradation of sensor material is a critical issue which restricts the practical implementation of these sensors. Different polymer materials, which are chemically and physically inert in a concrete environment, have been reported to protect sensor from such degradation. For example epoxy and PolyTetraFluoroEthylene (PTFE, Teflon) can be used as a substrate and lamination material. PTFE showed better stability as compare to epoxy as a substrate. Moreover, parylene C can also be used for lamination purpose.

7.3.2. Proposing a generic multi-sensor for corrosion based degradation (chloride/pH/corrosion sensor)

With all the techniques developed in this work, we can monitor the corrosion based degradation in concrete. We only need to tailor our device to the desired regime of sensor operation. In regard to corrosion monitoring, the most relevant question is: are we interested in determining whether active corrosion is occurring or do we precisely want to measure the corrosion rate? Similarly, do we want to only roughly estimate chloride ingress or measure the precise concentration? Of course the answer differs for different users of the sensor. In our opinion, for assessing degradation we are mostly interested in determining the active or passive status of corrosion and roughly measuring the chloride ion concentration. This will give an initial status of the integrity of the structure. Once the structure is found to be critical with active corrosion and high concentrations of chloride ions then more precise measurements such as destructive sampling for potentiometric and chemical analysis can be done. For a rigorous long-term measurement a qualitative approach is more beneficial at this stage. The ideal approach is to use a multiple sensor which includes a corrosion sensor based on the time constant (presented in chapter 5), dynamic chloride sensor (presented in chapter 3), potentiometric sensor based on AC as a pseudo-reference electrode (chapter 5) and a pH sensor. The measurement results from such a sensor can be processed to construct different regimes of deterioration status, relating them to the health of a structure. Such a multi-sensor gives the complete picture of chloride based deterioration.

Appendices

A.1. Derivation potential response

Potential response of a Ag/AgCl electrode during an applied current pulse

During the anodic current at the Ag/AgCl WE, the Cl^- ions near the WE are consumed (Faradaic reaction), resulting in a local depletion of Cl^- ions near the electrode surface. The temporal and spatial gradient of Cl^- ions near the Ag/AgCl electrode, during an applied current pulse, is expressed in equation A.1 [1].

$$C(x, t) = C^* + \frac{j(1 - t_{\text{Cl}}^e)}{FD} \left\{ 2 \left(\frac{Dt}{\pi} \right)^{1/2} \exp \left(-\frac{x^2}{4Dt} \right) - x \operatorname{erfc} \left[\frac{x}{2(Dt)^{1/2}} \right] \right\} \quad \text{A.1}$$

Here, C^* is the bulk Cl^- ion concentration in the electrolyte, j the current density, t_{Cl}^e the transport number of Cl^- ion in the electrolyte, x the distance from the electrode surface and D the diffusion coefficient. The expression for the concentration of Cl^- ions at the surface of Ag/AgCl WE ($x = 0$) is given in equation A.2, as follows from equation A.1.

$$C(0, t) = C^* \left(1 - \frac{2j(1 - t_{\text{Cl}}^e)}{FC^*} \sqrt{t/D\pi} \right) \quad \text{A.2}$$

The applied current pulse and the corresponding concentration gradients give rise to a potential difference (ΔV) at the WE with respect to the reference electrode (RE). This potential difference is the sum of: the ohmic drop due to the impedance of electrolyte ($V_{\Omega, e}$); the growing layer of AgCl salt on the WE ($V_{\Omega, a}$); and, the half-cell electrode potential ($V_{\text{Ag/AgCl}}$) due to the change in Cl^- ion concentration. Therefore:

$$\Delta V = V_{\Omega, e} + V_{\text{Ag/AgCl}} + V_{\Omega, a} \quad \text{A.3}$$

The ohmic drop, $V_{\Omega, e}$, is contributed by the bulk electrolyte and the diffusion layer near the electrode surface. The half-cell potential, $V_{\text{Ag/AgCl}}$, is given by the Nernst equation. The expression for the overall potential drop, ΔV , at the surface of the Ag/AgCl is expressed by equation A.4 [2].

$$\Delta V = \frac{j \cdot (d - \sqrt{\pi Dt})}{\lambda C^*} - (\pi t_{\text{Cl}}^* + 1) \frac{RT}{F} \ln \left(1 - \frac{2j(1 - t_{\text{Cl}}^e)}{FC^*} \sqrt{t/D\pi} \right) + V_{\Omega, a} \quad \text{A.4}$$

Here, λ is the conductivity of the electrolyte [$\Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$] and d is the distance between WE and RE. For high background-electrolyte concentration (0.5 M KNO_3), the ohmic drop ($V_{\Omega, e}$) can be neglected, also

resulting in a Cl^- ion transport number of $t_{\text{Cl}} \approx 0$. The ohmic drop due to the AgCl deposition, $V_{\Omega,a}$, depends on the initial thickness of the AgCl layer. The additional increase in this potential during the current actuation is very small (ca. $1 \text{ mV} \cdot \text{s}^{-1}$) at a current density of $25 \text{ A} \cdot \text{m}^{-2}$ [2], therefore this potential change can also be neglected. The remaining expression for ΔV is given in equation A.5.

$$\Delta V = -\frac{RT}{F} \ln \left(1 - \frac{2j}{FC^*} \sqrt{t/D\pi} \right) \quad \text{A.5}$$

A.2. Derivation transition time

Inflection point in the chronopotentiogram

The potential response of a Ag/AgCl electrode during an applied current pulse is given in equation A.5. This equation is differentiated with respect to the pulse time to obtain the rate of change of the potential response, as shown in equation A.6:

$$\frac{d\Delta V}{dt} = \frac{RT}{F} \left[\frac{j/FC^* \sqrt{D\pi t}}{\left(1 - \frac{2j}{FC^*} \sqrt{\frac{t}{D\pi}} \right)} \right] \quad \text{A.6}$$

Let $m = d\Delta V/dt$, such that $m \rightarrow \infty$. From equation A.6 the time of the response, at which $d\Delta V/dt$ is maximum (inflection point), is calculated. Putting variable m and rearranging equation A.6:

$$\left(1 - \frac{2j}{FC^*} \sqrt{\frac{t}{D\pi}} \right) = \lim_{m \rightarrow \infty} \frac{RT}{F} \left(\frac{j/FC^* \sqrt{D\pi t}}{m} \right) \quad \text{A.7}$$

Applying the limit:

$$\left(1 - \frac{2j}{FC^*} \sqrt{\frac{t}{D\pi}} \right) = 0 \quad \text{A.8}$$

Rearranging equation A.8:

$$t = \left(\frac{F C^*}{2j} \right)^2 \cdot D\pi \quad \text{A.9}$$

According to the Sand equation, the value at the right hand side of equation A.9 is equal to the transition time (τ). Therefore:

$$t = \tau \quad \text{A.10}$$

Hence, the time at which the slope of the potential response is maximum is equal to the transition time, τ , of the corresponding faradaic reaction.

A.3. Chip fabrication

Mask layout

Figure 7.1: The layout of the chip. Here, green color is platinum layer and blue color is silver layer.

Schematic process flow

The Ag electrode is deposited on a glass substrate (Borofloat wafer) by the standard cleanroom processes. Following is the process flow of the chip fabrication with schematic representation; the figures are not scaled.

Process	Process details	Schematic
<div>Lithography</div> <div><div></div> Glass wafer</div> <div><div></div> Metal (Ag)</div> <div><div></div> Positive</div> <div><div></div> photoresist</div> <div><div></div> Photo mask</div> <div><div></div> Adhesion layer (Ti)</div>	Wafer cleaning: Wet cleaning of the borofloat wafer with KOH and conc. HNO3 bath.
	Photo resist coating: Spin coat the borofloat wafer with positive resist and prebake the resist at 95 °C.
	UV Exposure: Expose the wafer with UV light for 5 s through the glass mask	<div>UV light exposure</div>
	Development of the resist.
Glass etching	Borofloat wet etching in KOH bath

Metal deposition (Sputtering)	Sputter Titanium (Ti) as an adhesion layer (20 nm) and Pd (70 nm) as a diffusion barrier between Ti and Ag
	Sputter electrode metal Ag (500 nm).
Lift off	Remove the resist in acetone bath. The chip is ready to be used.

A.4. Matlab code

Matlab program to calculate the transition time:

The data analysis of potential response is performed by the Matlab2012 program. The potential response data from the EC-lab (the user interface of the Biologic potentiostat) is imported into the Matlab file and then transition time is calculated from the maximum of the first derivative of the potential response. Following are the names of the three Matlab programs to calculate the transition time.

1. ReadEClab.m:

This program reads the text data file from EC-lab and store into Matlab data

2. FindTransition.m:

This program plot the potential response from the data given by ReadEClab.m program and then determines the maximum of its first derivative.

3. DataAnalysisWithFunction.m:

This program is the main program which specify the data files and then call the program findTransition.m to calculate the transition time of multiple data files.

Following are the codes along with the respective comment of the Matlab program mentioned above.

1. ReadEClab

```
function data=readEClab(fileName)
%data = readEClab(fileName)
%Imports data from EC-Lab MPT files. Written to import files that are the
result of chronopotentiometry. MPT files from other types of experiments
probably need adaptations in this function
%fileName: string containing file to import
%Author: Derk de Graaf
% open the file, exit function if file does not exist
fid=fopen(fileName);
if fid<0
data=[];
return;
end
% ignore first line
fgets(fid);
% read line and extract number of header lines.
headerInfo=fgets(fid);
headerLine=textscan(headerInfo,'%s%s%s%s%s%u');
% read file again and convert commas to dots
fileData=strrep(fileread(fileName),',','.');
% extract two colums with data out of the file, ignoring the header lines
data=textscan(fileData,'%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f', ...
'headerlines',headerLine{1});
% close the file
fclose(fid);
end
```

2. FindTransition.m

```
function [ transitionPoint ] = findTransition(data,titleData)
%FINDTRANSITION Summary of this function goes here
% Detailed explanation goes here
span=10;
lowerThreshold=0.05;
upperThreshold=0.23;
```

```

% lowerThreshold=0.1;
% upperThreshold=0.45;
startPoint=1;
while data(startPoint,1) < 10.01
    startPoint = startPoint + 1;
end
%startPoint=find(data(:,2) > lowerThreshold, 1, 'first');
endPoint=find(data(:,2) < upperThreshold, 1, 'last');
dataSubset{1}=data(startPoint:endPoint,1);
dataSubset{2}=data(startPoint:endPoint,2);
[fitp,fitS,fitmu]=polyfit(dataSubset{1},smooth(dataSubset{2},span),15);
dataFit=polyval(fitp,dataSubset{1},fitS,fitmu);
dydt=diff(dataFit)./diff(dataSubset{1});
dt = diff(dataSubset{1}(1:end)) + dataSubset{1}(1:end-1);
[peakFit,locsFit] = findpeaks(dydt);
[~, maxIndex] = max(peakFit);
peakLocation=locsFit(maxIndex);
%[temp peakLocation]=max(dydt);
transitionPoint=dt(peakLocation);
figure;
%plot(dataSubset{1},dataFit,'r')
hold on;
[AX,H1,H2] = plotyy(data(:,1),data(:,2),dt,dydt,'plot');
% plot(data(:,1),data(:,2),'b:');
% plot(dt,dydt,'r');
line([dt(peakLocation) dt(peakLocation)],[0 1],'color','k','linestyle',':');
text(dt(peakLocation), .2, num2str(dt(peakLocation)));
xlabel('time [s]');
set(get(AX(1),'Ylabel'),'String','potential [V]')
set(get(AX(2),'Ylabel'),'String','first derivative of potential [V/s]')
% ylabel('potential [V]');
title(strcat({'Measurement data and first derivative for: ',titleData)));
hold off;
%second derivative
dydt2=diff(dydt)./diff(dt);
dt2=diff(dt(1:end)) + dt(1:end-1);

figure;
%plot(dataSubset{1},dataFit,'r')
hold on;
[AX,H1,H2] = plotyy(data(:,1),data(:,2),dt2,dydt2,'plot');
%plot(dt2,dydt2,'r');

```



```

%line([dt(peakLocation) dt(peakLocation)],[0
max(dataSubset{2}),'color','k','linestyle',':');
%text(dt(peakLocation), .2, num2str(dt(peakLocation)));
xlabel('time [s]');
set(get(AX(1),'Ylabel'),'String','potential [V]')
set(get(AX(2),'Ylabel'),'String','second derivative of potential [V/s^2]')
%ylabel('potential [V]');
title(strcat('Measurement data and second derivative: ',titleData));
hold off;
end

```

3. DataAnalysisWithFunction

```

close all;
clear
values=[1 2 3 4 5 6];
%output=zeros(numel(values),2);
figure()
for repeat=[1,2,3]
for i=1:numel(values)
fileName=(strcat('2013-07-25-',num2str(values(i)), 'mMKCl-62uA-
',num2str(repeat), '_C02.MPT'));
%fileName=(strcat('..\experiments\Yawar\2013-05\2013-05-03\2013-
05-03-transition-time-',num2str(values(i)), 'mMKCl-0_5MKNO3-5A_m2-
Ag_AgCl-ref-electrode-2_C02.MPT'));
F=readEClab(fileName);
transition=findTransitionChips([F{1,1}
F{1,2}],strcat(num2str(values(i)), 'mM KCl',strcat(num2str(repeat))),10);
if isempty(transition)==false
output(i,repeat,2)=transition;
output(i,repeat,1)=values(i);
end
end
end
[p,ErrorEst] = polyfit(output(:,1),sqrt(output(:,2)),1);
fit = polyval(p,output(:,1),ErrorEst);
plot(output(:,1),fit,'-
',output(:,1),sqrt(output(:,2)),'+b','markersize',6,'LineWidth',1);
eqn = ['y = ' sprintf('%3.3fx^%1.0f + ',p ;length(p)-1:-1:0)];
eqn = eqn(1:end-3);
R=corrcoef(output(:,1),sqrt(output(:,2)));
%plot(output(:,1),sqrt(output(:,2)), 'or','markersize',6);
% title('Calibration curve');

```

```
ylabel('$$\sqrt{\tau}$$ [$$\sqrt{s}$$]', 'interpreter', 'latex');
xlabel('Cl ion concentration [mM]');
hold on;
```

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Samenvatting

Dit werk draagt bij aan een oplossing voor duurzamere constructies met de focus op het detecteren en monitoren van chloride concentraties in beton. In dit werk komen de niet-destructieve en in-situ metingen van chloride in beton aan bod.

In hoofdstuk 2 wordt een overzicht van de voor – en nadelen van de bestaande niet-destructieve technieken gegeven. Deze technieken worden onderverdeeld in electrochemische en electromagnetische methoden. De electromagnetische (EM) methode lijkt een ideale oplossing voor in-situ en niet-destructieve metingen vanwege het niet invasief meten. Met name technieken welke gebruik maken van een externe EM bron. De lage detectie limiet en lage selectiviteit van chloride ionen vermindert de betrouwbaarheid van deze metingen. Daarbij komt dat bij EM metingen een relatief grote opstelling en getraind personeel noodzakelijk is.

Aan de andere kant hebben elektrochemische methoden zoals potentiometrie een betere selectiviteit voor chloride ionen, eenvoudiger in beton aan te brengen en kostendekkend. De uitdaging bij elektrochemische methoden ligt in de signaal drift van het *half-cell potential* van de referentie electrode wanneer deze in beton wordt aangebracht. Tot nu toe bestond er nog geen referentie electrode welke op de lange termijn drift vrij was. Chloride metingen kunnen hinder ondervinden van hydroxide ionen bij hogere pH waarden.

In hoofdstuk 3 wordt een dynamische electrochemische methode gepresenteerd waardoor de er geen referentie electrode meer nodig zal zijn. Drift in de huidige potentiometrische aanpak is een gevolg van een statische benadering gebaseerd op het absolute potentiaal van de werk electrode welke meet tegenover een stabiele referentie electrode. Alternatieven hiervoor zijn chronopotentiometrie, een dynamische electrochemische aanpak. In de benadering zonder referentie electrode, zal een stroom pulse worden aangebracht op een Ag/AgCl electrode waarna het potentiaalverschil gemeten wordt. In dit geval zal de verandering in potentiaal een gevolg zijn van een concentratie gradiënt dichtbij de electrode.

Wanneer de chloride geheel opgelost is zal de potentiaal verandering een buigpunt bereiken, ook wel bekend als de transitie tijd. De verandering in het potentiaal en de transitie tijd hangen niet af van de absolute referentie potentiaal en vrijwel ieder metaal draad kan worden gebruikt als een psuedo-referentie electrode. De enige limitering is de lage potentiaal

stabiliteit bij hoge pH met lage chloride ionen concentratie, bijvoorbeeld wanneer $[\text{OH}^-]/[\text{Cl}^-]$ groter is dan 10. In zo'n geval is de invloed van hydroxide significant. Daarom geldt deze methode alleen voor pH waarden lager dan 12.

Een alternatief voor de lange-termijn referentie electrode is een Kynol actieve koolstof (AC) pseudo-referentie electrode, genoemd in hoofdstuk 4. Dit is interessant vanwege het feit dat actieve koolstof een zeer hoge dubbel laag capaciteit (in de orde van tientallen Farad per gram) heeft en een goede materiaal stabiliteit in beton omgeving. De hoge dubbel laag capaciteit compenseert veranderingen in de adsorptie/desorptie reactie (niet-faradayisch) welke een verandering in het electrode potentiaal zou geven. Het potentiaal van de Kynol actieve koolstof met een dubbellaag capaciteit van circa 100 F blijft hierdoor stabiel in beton. De drift meting was binnen 0,2mV/dag gemeten over 22 dagen. De *open circuit potential* (OCP) van de AC electrode in het beton toonde stabiele waarden gedurende 3 maanden (OCP verandering < 1mV/dag). Hierdoor zou de AC electrode een aantrekkelijk alternatief zijn voor bestaande metaal en metaal oxide psuedo-referentie elektroden in beton.

Tegelijk met de chloride concentratie is de corrosie van staal een aspect voor structurele afbraak. Een sensor welke de actieve en passieve staat van corrosie aangeeft wordt gegeven in hoofdstuk 5. De tijdsconstante voor een uitdovend potentiaal, na de stroompulse geïnterrumpeerd is, geeft de status van de corrosie van bewapeningsstaal.

Het is een systeem waarbij *a priori* kennis over het oppervalk van het staal en stabiele referentie elektroden niet specifiek vereist is. Daarbij komt gezien de dynamische aard van het systeem dat een referentie electrode niet nodig is en hierdoor gemakkelijk in beton geplaatst kan worden. De combinatie van de chloride meet opstelling gegeven in hoofdstuk 3 en 4, en de corrosie sensor gepresenteerd in hoofdstuk 5 kunnen worden gebruikt voor het compleet karakteriseren van put-corrosie en de relatie met chloride concentratie in beton.

Draadloze communicatie, bij voorkeur passief, is nodig bij data acquisitie wanneer de sensor ingebed in beton is zoals besproken in de specificaties voor een ingebedde chloride sensor in sectie 1.6 van hoofdstuk 1. Een *near field electromagnetic coupling* (NFC) tussen de sensor en de uitlezing antenne van worden gebruikt voor het draadloos monitoren van de OCP van een Ag/AgCl electrode. De chloride ionen concentratie zijn zowel gemeten in vloeistof als in beton. De detectie reikwijdte van de sensor in vloeistof is tussen 0,01 en 0,2 M $[\text{Cl}^-]$ welke aangepast kan worden. De afstand tussen de sensor en de ontvanger is gelimiteerd tot 35 cm in lucht.

De metingen in beton lieten een verandering in capaciteit zien met toename van chloride in het beton. Gemeten over 50 dagen zal de $[Cl^-]$ in het beton bijna de bulk concentratie bereiken. Deze methode is gelimiteerd tot potentiometrie.

Dit werk laat draagt een aantal oplossingen aan voor de uitdagingen in het meten van chloride ionen in beton, met name wanneer een lange-termijn ingebedde referentie electrode wordt gebruikt. Dit zal een bijdrage leveren voor de bouw van nieuwe chloride sensor systemen voor beton, gebaseerd op dynamische elektrochemische metingen met ingebedde corrosie sensoren en een verbeterede psuedo-referentie electrode.

List of publications

Journal contributions

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Acknowledgements

I bet you will be reading this part before even reading the title of this thesis. For years I have been doing the same and hoping to write this part someday, which at some point seemed improbable. I am glad that I made it to this part. I must admit that I have been lucky throughout my life, finding right people at the right time and because of them I made it to this point. I owe them a lot for guiding me, both in academic and social aspects. I thank all of them for bearing me these years. It will be unjust not mentioning their names.

Specially, I would like to thank you, Albert, for giving me the opportunity to pursue my research career. You have always been an inspiring figure for me. You motivated me to think out of the box. The social atmosphere you gave in the BIOS group was the factor behind my personal growth. I will miss our BIOS Workweek and yearly mountain biking events, although it was difficult to keep up with you during mountain biking.

Wouter, thank you for your patience for past four years. It was not easy to work with a person like me from a very different cultural background. You are the finest scientist as far as I know. You ask me the right questions at the right time and kept me motivated. I have learned a lot from you, specially, the positive attitude in research. Your words “you can plan experiments but can’t plan the outcomes” will always be engraved in my mind. Thank you for keeping me on the track. Only now do I realize how unreasonable some of my ideas were during our brainstorm sessions. I must say you are a very good listener, a very fine critic and a sharp observer. It was not easy to convince you, I still recall some of our intense discussions about the non-faradaic electrochemistry of Mr. Cheng. Finally, the freedom in research, you gave me, has transformed me from a learner to a proactive thinker.

I would also like to thank the technology foundation STW, The Netherlands for their financial support. Specially, the coordinators of the Perspectief program, Integral Solution for Sustainable Construction (IS2C), Stefan and Monique for taking care of all the administrative and financial business. Another person without which the IS2C program was not possible is Prof. Eddy Koenders. Eddy, your organization skills have always an impact on me. The way you organized all the IS2C workshop, venue, speakers, food and excursions were all impressive.

I would also like to thank Prof. Klaas van Breugel from TU Delft for guiding me in this project and asking critical questions during our user committee

meetings to keep us on the right track. Moreover, I would like to thank all the User committee members and my project partners, specially Leo Pel, Dessi Koleva, Farhad Pargar, Raheleh Pishkari.

I have to write a separate paragraph to thank Wim, Max and Marcel from Sensortag solution. Their active collaboration results in a successful student assignment and a chapter of this thesis (chapter 6). Thank you for lending me your “AquaTag” device and having confidence in me.

There are some people who helped me shaped my early research career. I would like to thank Prof. Roland Zengerle, Junichi Miwa and Felix von Stetten, from University of Freiburg, for confining my scattered mind into research aptitude.

Bundle of thanks to the people in BIOS group who have been like a team and helped me out now and then. Special thanks to Johan, Hans, Paul, Justyna, Mathieu and Jan van Niewkastele. Many thanks to Hermine for taking care of all the administrative issues. Thank you Allison, Susan and Adithya for taking time in reading my horrible manuscript all along. Adthiya, you have been a catalyst in keeping me socially active. Your pointless jokes and horrible captaincy (in cricket) make me think there are more worst people than me in this world.

Anne and Haimanti, thank you for being so active around me and accepting to be my paranymphs. You both injected social energy in my life. Haimanti, you kept me motivated and made sure that I have things to bother about other than research. After listening to your complex issue I used to think “well! I am doing good in my life”. Anne, if there is any natural button to deactivate you, I would have definitely done that. You have been my motivation to visit the BIOS coffee corner.

The most amazing thing that happened to me during these years is my officemates. I bet, you won’t get such a diverse, interactive and dynamic mates. Trieu, thank you for being so proactive. Your presence lift the spirit of our office. Bjorn, our most technical and sportive guy, he kept us technically alert. Rogier, our fun boy, kept smile on our faces and asking what we did on our weekend and sharing all kind funny videos. Sertan, our boss and star footballer, made sure that we are doing good in the office. Thank you guys for keeping a relax atmosphere. Taking about the relax environment, I would also like to thank Lennart for arranging technical discussion meetings, sailing weekends and weekly futsal. I would also like to thank the BIOS football team.

Some chapters in this thesis were part of some student assignments and were possible due to some hardworking and dedicated students. Many thanks to Arjan, Izhard, Bas, Douwe, Derk, Jorrit, Xiao and Vasilis for working with me and producing some fine results.

Next, I would like to thank all of my friends in Enschede, specially friends from the great Macandra building, Pakistani Student Association and MCC Hengelo cricket club. Particularly, I would like to mention Faizan, Khurram, Mohsin, Rahim, Bishal and Timmi. I would also like to thank Saif and his family for taking care of me and keep me inviting for food and never ending discussions.

During my stay in the Netherlands I have encountered the most notorious friends in my life; Shoaib, Tauseef and Usman. They tried their level best to keep me away from research. Shoaib, unfortunately happens to be my flatmate (more landlord of the house), kept me updated with all the craps on the internet and TV. He is a kind of buddy no one wants but need to have. Tauseef, our big brother, is the most experience personal in my circle. He has his own theory of happiness. Usman, Phathar, tries his level best to mess things up and makes sure everyone is having fun. Thank you all.

Last but not least, I would like to thank my family members back in Pakistan. They are the reason I made it so far. Totti, you are great, I just want to say “Salamun alikum lae gulzari mindook”. If there is one person, who I owe the most, it is you. Tau, you made it sure everything is there when we needed it. Moreover, Rana sahib, Taru, Baji, and Cheena are the gravitational force in my life. I wish you all the best. Finally, the story is not completed without mentioning the greatest man on earth, his excellency Kaka Ghulam. His vision and pure love gave me the power to proceed further. I love you all.

Yawar

Some words about Prof. Salam:

Dr Abdus Salam (29 January 1926 - 21 November 1996) was a theoretical physicist who won the Nobel prize in physics in 1979 for his contribution to electroweak unification. In particle physics, the electroweak interaction is the unified explanation of two of the four known fundamental interactions of nature: electromagnetism and the weak interaction. His main contribution was directed to the theory of the unified weak and electromagnetic interaction between elementary particles, including, inter alia, the prediction of the weak neutral current.

He hailed from a poor family in a small village called Jhang in Pakistan. From his childhood he was a keen learner, in his 10th grade he scored the highest ever marks at state level. When he cycled home, the whole village turned out to welcome him. He won a scholarship to Government college, University of Punjab, and took his master's degree in mathematics. At the age of 17, he published his first scientific paper titled "A problem of Ramanujam" where he proposed a technique to rapidly solve a system of equations. He was rewarded a scholarship to St. John's college, Cambridge. In 1950 he received the Smith's Prize for the most outstanding pre-doctoral contribution to physics. His doctoral research, in Cambridge 1951, was on quantum electrodynamics which already gained him an international reputation. In 1960 he became the professor of Theoretical Physics at Imperial College London.

Frustrated from his own experience, he was determined to offer scientists from third world countries an alternative to migration. In 1964, with the help of the Italian government, he founded International Centre for Theoretical Physics (ICTP) in Trieste, Italy. At the ICTP, Trieste, the deserving young physicists from developing countries are allowed to spend their vacations in invigorating atmosphere, in close touch with their peers, losing their sense of isolation in research. In 1983, he founded Third World Academy of Science (TWAS) in Trieste, with the purpose to recognize, support and promote excellence in scientific research and encourage the pursuit of the same in developing countries. In November 1996- after his death- the ICTP was renamed "the Abdus Salam International Centre for Theoretical Physics".