Corrosion and protection in reinforced concrete
Pulse cathodic protection:
an improved cost-effective alternative
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an improved cost-effective alternative

Proefschrift

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CHAPTER 1
GENERAL INTRODUCTION

1.1 OVERALL AIM OF THE RESEARCH PROJECT

The research reported in this thesis was implemented in the frame of the project “Durable Building Technology, Benefiting Electrochemical Methods as a Preventive” and initially started as an EU Host-Industry Marie Curie Fellowship, EU Contract No: G5TR-CT-2001-00067. The overall objective of the integrated (research/industry) project was to contribute to an European development of a more sustainable built environment by providing a competitive infrastructure for academic and technological research development and ensuring industrial application of the generated knowledge.

Corrosion of embedded steel and thus induced degradation of concrete, subjected to aggressive environment, represents a great concern in relation to the durability of reinforced structures. The recently completed investigation in the frame of the thematic network CONREPNET (2003 – 2006), concerned with the repair and remediation of concrete structures in Europe, reported that corrosion of steel reinforcement is the main cause for reinforced structures deterioration. In this respect there is an increasing need of maintenance, repair and modernisation of new and existing concrete infrastructures, such as bridges, harbours, power plants, tunnels, as well as industrial, office and commercial buildings.

In most of the current cases the repair is considered when the need of repair is recognised at a very advanced stage of deterioration, or prevention techniques are initially not taken into account. To achieve the required durability, new civil structures must be designed and executed (performance based design) with innovative materials and construction methods, modern views on protection and service life, including plans for monitoring, inspection, maintenance and predicting the future performance. For newly built structures, innovative materials and technologies are being used, but the proper design and criteria for durability should be based on a multi-scale approach, including concrete and steel reinforcement as main materials, considering their material properties and performance with operation. Newly built structures should be assured with the proper prevention/protection techniques, relevant to engineering purposes, application and predicted or desired service life. For existing structures, the main concern is the right approach for assessment and maintenance.

Very often the arising question is: “Is concrete repair a solution or a problem?” Mostly the concern comes from the fact that before any repair of a reinforced concrete structure, the problems causing deterioration should be properly assessed and further the appropriate remediation strategy should be chosen. So as to properly choose a remediation or repair strategy, several factors should be taken into consideration: at first inspection and monitoring to establish the condition/nature of the problems is necessary (i.e. defining the cause of problems); secondly, assessment of the structure should be performed; further, prediction of the future condition,
including the progress of deterioration if no remediation takes place or intended service life if repair is performed; finally, the proper remediation technique has to be chosen and an innovative approach to evaluating economic aspects of durability design, assessment and monitoring is needed.

Normally, in achieving the above drawn schemes, generally performed monitoring techniques and engineering practices are considered. So as to be able however, to properly evaluate a current stage and estimate further performance of a reinforced concrete structure, including the proper choice of remediation, treatment etc., there should be knowledge available on how the material properties will behave after remediation and more importantly, how the intended repair will affect the material properties with time. The point here is not only to achieve the level of required repair or protection by following standards and requirements, but to be able to answer the question “Why exactly this technique works in the relevant situation”. By knowing that, we’ll be able to further optimize the remediation regime and to predict how the material properties will change with time of application or with alteration of one or another environmental factor.

To this end, the research project aimed to increase the knowledge on durability of reinforced concrete structures by means of:

- better understanding the fundamental electrochemical principles involved in corrosion and cathodic protection (CP);
- investigating the material properties of both the bulk concrete matrix and the steel reinforcement in conditions of chloride-induced corrosion and cathodic protection;
- scientifically approaching the current practices for corrosion prevention or protection, using electrochemical techniques,
- finally, suggesting an improved remediation alternative, denoted as pulse CP, which will in term minimize the repair and monitoring costs and will improve the long-term safety operation of reinforced concrete structures.

1.2 OUTLINE OF THE THESIS

The results of this study are presented in 10 chapters, in accordance to the flowchart in Fig. 1.1. The thesis comprises three parts: Introduction and technical background as Part I and two parts of experimental investigation, namely Part II, dealing with preliminary studies in mortar and reinforced mortar specimens and Part III, discussing concrete and reinforced concrete series. Part II deals with fundamental approaches to studying material properties, corrosion and cathodic protection in general, Part III aimed to clarify these mechanisms for reinforced concrete, being a system of higher-level of heterogeneity and close to practical conditions; specify the new method of cathodic protection; and support all findings with measurements in model solutions.

Chapter 2 comprises some fundamental mechanisms and technical background related to: the corrosion process in reinforced concrete, briefly introduces some main properties of cement-based materials, discusses the chlorides impact on structural morphology in conditions of
chloride-induced corrosion and finally presents a review of electrochemical methods for corrosion protection in reinforced concrete.

**Chapter 3** deals with determination of electrical properties, ion concentrations (alterations due to concentration gradients and ion migration) and investigating the pore structure characteristics of cement-based materials in the presence of aggressive substances (sodium chloride). The investigation was a preliminary study on some of the most significant properties of cement-based materials, which affect corrosion and CP application. **Motivation:** Electrical properties (e.g. electrical resistivity) determine concrete corrosivity, electrolytic paths, consequently ion transport and current flow in reinforced cement-based materials.
Chapter 4 explores the electrochemical behaviour of the steel reinforcement and presents quantitative and qualitative characterisation of the steel surface in conditions of chloride-induced corrosion, while Chapter 5 deals with evaluation of the efficiency of conventional cathodic protection, by studying its impact on morphology and microstructure (in terms of corrosion products and steel/cement paste interface). Motivation: Electrochemical principles are the fundamentals for corrosion and CP in reinforced cement-based materials. The correlation of electrochemical parameters and steel surface characterization gives complete insight into the chloride-induced corrosion process. Further, the microstructural and morphological investigations in conditions of CP, answer the question “Why CP works in general?”

The correlation of electrochemical phenomena and cement matrix microstructure in conditions of corrosion and cathodic protection for reinforced mortar allowed breakdown of the material properties to micro-level interface structures, which is discussed in Chapter 6. Motivation: The effects of corrosion and cathodic protection on material properties with time can be explored only if the cement-based reinforced system is considered as a multi-phase composite material, which is further investigated by a multi-disciplinary approach.

Chapter 7 presents the electrical and microstructural properties, cement hydration and ion transport mechanisms in plain concrete in conditions, simulating conventional and pulse CP regimes. Motivation: The concrete matrix has a significant contribution to the global performance of reinforced concrete. The physico-chemical changes, ion transport mechanisms and electrical properties are determined by the structural alterations of the pore space, induced from the CP current.

The conventional and pulse CP in terms of technical regimes and conventional monitoring in reinforced concrete are discussed in Chapter 8. Motivation: Establishing the optimal technical regimes for pulse CP and evaluating the applicability of the latter as an alternative of the conventional impressed current CP. Monitoring both CP regimes by techniques and criteria, generally applied in practice, was expected to provide evidence for effectiveness and cost-efficiency of the pulse CP, based on a more engineering, rather than a scientific approach. The performance of both CP and pulse CP was evaluated in reinforced concrete, using electrochemical approaches, morphological and microstructural investigations, presented in Chapter 9. Motivation: Determination of electrochemical parameters is essential for investigating corrosion or CP. The interpretation of the obtained corrosion parameters is not straightforward, but related to the properties of the product layers, formed on the steel surface in the different conditions.

Finally Chapter 10 deals with measurements reproducibility and presents the pre-conditioned steel oxidation/reduction behaviour in model solutions, thus supporting the findings from all previously performed investigations in embedded conditions. Motivation: Reproducibility of electrochemical measurements, thus defining corrosion parameters, is important when a new protection technique is studied. Since the formation or conversion of product layers in conditions of corrosion or CP was found to be of significant importance for evaluating the systems performance with time, the outcomes from measurements in concrete were confirmed by investigation of the pre-conditioned steel in cement extract solutions.
CHAPTER 2
FUNDAMENTALS AND TECHNICAL BACKGROUND

2.1 MECHANISMS OF STEEL CORROSION

2.1.1 Introduction. Types of corrosion. Corrosion cells

The alkaline nature of concrete, concrete pore solution respectively, generally provides corrosion protection for the embedded steel reinforcement. Concrete is a heterogeneous material with high electrical resistivity. Coupled with the high alkalinity, this forms a physico-chemical barrier for the corrosion process. The high pH (in the range of 12.6 -13.5) assures the formation of a stable passive layer on the steel surface. This ultra thin protective layer is mostly mixed oxide, composed of γ-Fe₂O₃ and Fe₃O₄, with a thickness of 10 to 100 nm [1]. The corrosion rate of any metal, steel respectively, is significantly reduced when a passive state is established. Passivity, however, is often unstable and subject to breakdown in certain conditions. As described by Tuutti [2], in the life time of a reinforced concrete structure two periods can be defined: initiation and propagation period. The initiation period is the time necessary for any aggressive substances to reach the steel surface in sufficient concentration to induce corrosion; the propagation period is related to the rate of corrosion after the steel de-passivation.

The most common depassivation agent is the chloride ion. In general, good quality concrete (low water-cement ratio, well cured), would exhibit sufficiently low permeability and thus would prevent the penetration of corrosion-inducing agents (chloride ions, carbon dioxide). This is however not always the case, since even good quality concrete is a porous material. Depending on the environmental factors (aggressiveness, humidity, oxygen supply), as well as the exploitation characteristics and maintenance, corrosion of the reinforcement can be initiated at certain point of the structure’s service life. The type and rate of corrosion will then depend on the above mentioned factors.

The broad groupings into which most aqueous corrosion activity falls and the various types of the generally formed corrosion cells [3] formed in different environments are:

- **General corrosion**: when a carbonation front reaches the surface of the steel reinforcement, the protective oxide film on the steel is progressively destroyed. If oxygen is freely available a number of corrosion cells adjacent to one another will become active. The rate of corrosion is governed by the speed at which oxygen is delivered to the steel surface and the electrical resistance of the surrounding concrete.
- **Pitting corrosion**: pitting or “localized” corrosion takes place over a more restricted area. As the deterioration is more specific to one or more spots it is also termed as “micro cell” effect. One likely method of initiation is the build-up of chloride ions leading to a localized breakdown of the passive film at isolated locations. Metal loss from the anodic side leads to the formation of a pit. As corrosion proceeds, the medium inside the pit becomes more acidic and further metal loss occurs from the bottom of the pit rather than around it. Although the growth of a pit can be retarded to a certain degree by accumulation of the corrosion product, it is a matter of time before the cross sectional area is progressively reduced to a point where the steel can no
longer withstand an applied mechanical loading for example. Unlike general corrosion, where the corrosion products are mainly forms of insoluble iron oxides, pitting attack results in the formation of soluble ferric chlorides. These can disperse into the concrete matrix, cause micro-cracking and alter the material structure much before any visual signs of structural damage take place.

Different types of corrosion cells can form, depending on the environmental conditions, the aggressiveness of the medium or the type of corrosion. For example *galvanic cells* form when two dissimilar metals are in electrical contact and share a common electrolyte. The rate and degree of steel corrosion will be a function of the potential difference, developing between the two metals as well as their relative surface area. *Concentration cells* occur in the case of varying amounts of soluble aggressive ions, which creates potential differences between different parts of the steel reinforcement. The application of de-icing salts on bridge decks for example is creating such type of corrosion cells; the upper reinforcement layers are in contact with higher chloride concentrations than the lower parts, hence a potential difference between the reinforcing layers occurs and corrosion cells are formed. Other types of corrosion cells are: *differential-aeration cell*, arising from a variation in the rate of arrival of dissolved oxygen to different parts of a metallic surface; *induced corrosion cells*, known as “stray current effects”, which in contrast to the cells mentioned above, are brought into action by the flow of external current from the environment; corrosion cells as result of *bacterial corrosion*, when at certain pH of the medium (slightly acidic), come bacteria cause corrosion in oxygen-deficient locations by converting the steel to its sulphide forms. One type or a combination of the above cases can also initiate corrosion of steel reinforcement in concrete. Hence it is necessary to investigate the cause for deterioration, to define the active areas within the structure and finally to suggest appropriate remedial strategy.

### 2.1.2 The process of electrochemical corrosion

The electrochemical corrosion is a process of self-driven metal dissolution as a result of the physico-chemical interaction between the metal surface and the surrounding environment.

![Fig.2.1 Corrosion cell – schematic presentation.](image-url)
Electrochemical corrosion is the type of corrosion which takes place in atmospheric conditions, soils and different electrolytic environments i.e. it’s also the reason for deterioration in reinforced concrete. The general corrosion cell, schematically presenting the electrochemical corrosion process, is depicted in Fig. 2.1. The performance of the corrosion cell depends on the current flow between anodic and cathodic areas i.e. on the corrosion current.

Main peculiarities of the electrochemical corrosion:

1. Interaction between the metal and the surrounding electrolytic environment, which is divided into two electrode processes, taking place simultaneously but independently:

   Anodic (oxidation): Transport of metal ions from the metal surface to the solution. As a result an equivalent number of electrons remain at the metal surface:

   \[ \text{Me} + m\text{H}_2\text{O} = \text{Me}^{m+} \cdot m\text{H}_2\text{O} + ne \]  

   (1)

   Cathodic (reduction): Assimilation of the excess electrons by ions or molecules, present in the solution i.e. reduction on the metal surface by depolarizers (D):

   \[ D + ne^- = \text{[Dne}^-] \]  

   (2)

2. The anodic and cathodic reaction rates and the corrosion rate respectively, depend on the electrode potential. A potential shift to more positive values (while applying external current) favors the anodic reaction and impedes the cathodic reaction. A shift to more negative values speeds up the cathodic reaction and impedes the anodic reaction, i.e. the corrosion process might be taken over and controlled by changing the electrode potential.

3. Non-uniform corrosion may result from a compositional variation of the metal surface and/or from ion transport limitations in the electrolyte.

2.1.3 Thermodynamics of the electrochemical corrosion process

Like all physico-chemical phenomena, corrosion obeys thermodynamics laws. Hence, thermodynamics is useful for understanding and predicting the corrosion process, since it indicates the reactions that can take place. In other words, using the laws of thermodynamics and the potential-pH equilibrium diagrams (Pourbaix diagrams) it is possible to determine which corrosion phenomena are possible and which are not under given conditions. A Pourbaix diagram for the system Fe-H$_2$O at 25°C is given in Fig.2.2a) [4]. In a metal-water system, a variety of chemical and electrochemical reaction may occur, for example dissolution of the metal as metallic cation or as a complex anion, direct oxidation to oxide or hydroxide, changes of the oxidation states of the oxides, precipitation, reduction etc. To this end, it is convenient to represent all these reactions in a single scheme, which is the Pourbaix diagram for a certain system. Nevertheless, although some reactions might be predicted as possible under given conditions from the Pourbaix diagrams, in fact they may not occur due to certain slow kinetics.

Relevant to corrosion or protection in reinforced concrete, the Pourbaix diagrams for iron (steel respectively), Fig. 2.2, reveal the regions of thermodynamic stability of Fe, its solid oxides Fe$_3$O$_4$ (magnetite) and Fe$_2$O$_3$ (hematite), and its dissolved derivates Fe$^{2+}$ (ferrous), Fe$^{3+}$ (ferric) and...
FeO$_2$H$^-$ (bihypoferrite). Consequently, the areas for iron corrosion (metal dissolving), immunity (thermodynamic stability and thus un-corrodible surface) and passivity (the surface may be covered by a more or less protective film) can be determined.

2.1.4 Steel corrosion in concrete

So as to understand why steel in concrete can sometimes undergo drastic metal loss, it is necessary to consider some chemical and physical phenomena in concrete. Portland cement, one of the principal components of concrete, reacts with water to form hydrated products, which help to bind together the other constituents, such as sand and gravel, and thus to produce a strong but porous matrix. During the hydration process, alkalinity (mainly in the form of calcium hydroxide) is produced due to the high concentration of K$^+$, Na$^+$, Ca(OH)$_2$. This excess alkaline fluid, often with a pH as high as 13, tends to remain trapped within the pores of the concrete bulk matrix. Left alone the pH of the pore solution will remain in the above range and any loss of hydroxide due to leaching will be compensated for by replenishment from the hydrated cement gels [3]. Steel in contact with an alkaline solution, such as pore water (as already mentioned) will be passivated and will behave according the following scheme:

- Steel in contact with the alkaline medium of cement paste:
  - the surface is initially active as galvanic micro-cells form due to the steel heterogeneity (cathodic and anodic areas) – Fig. 2.3a)
  - formation of passive layer – Fig. 2.3b)

As long as the water-insoluble layers formed on the surface remain intact, there will not be further corrosion of the steel. However, the pore water within the concrete can be subject to external influences, which will create loss of passivity and onset of corrosion.

Fig. 2.2 (a) Pourbaix diagrams for the Fe-H$_2$O system at 25ºC [4]; (b) Iron / unalloyed steel in the presence of Cl$^-$ [5].

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Fundamentals and Background

(a) Steel in contact with the pore solution and relevant mechanisms (corrosion cell due to steel surface heterogeneity); (b) formation of the passive layer.

- destroying the passive layer under certain conditions (ingress of Cl, CO₂), Fig. 2.4(a), where:

  At the anode sites:
  \[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]

  At the cathode sites:
  \[ \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- \]

  Further:
  \[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}\text{(OH)}_2 \]
  \[ 4\text{Fe}\text{(OH)}_2 + \text{2H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Fe}\text{(OH)}_3 \]
  \[ 2\text{Fe}\text{(OH)}_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \]

- final stage - concrete micro-cracking and spalling - Fig. 2.4(b), position (c).

Fig. 2.4 (a) onset of corrosion, formation of anodic and cathodic sites; (b) sequence of the processes up to concrete cracking and spalling (a→b→c).
A process of carbonation brings about loss of alkalinity and a more uniform (general) corrosion takes place on the steel surface. Local destruction of the protective oxide film can be initiated by the effect of aggressive ions, such as Cl\textsuperscript{-}. The corrosion products usually occupy a greater volume than the original steel. The forces generated by this expansive process can far exceed the tensile strength of the concrete, resulting in cracking and spalling of the concrete cover (Fig. 2.4b).

So as to evaluate properly the corrosion process in reinforced concrete, i.e. why and how the damage occurs and how it will proceed with time, which remediation technique will be most suitable for the given environmental conditions and the present state of the structure, etc. knowledge of the nature of the bulk concrete is essential. Physical, chemical and microstructural peculiarities of the cementitious matrix must be studied for the relevant conditions. Some main properties of cement-based materials, including definitions for parameters as porosity and pore size, used within this study, as well as the methodology for deriving microstructural parameters, will be presented in the following section.

2.2 PROPERTIES OF CEMENT-BASED MATERIALS

2.2.1 Chemical parameters. Hydration mechanism

The maintenance of steel passivity in reinforced concrete requires a high pH environment. Concrete has many special characteristics, including high alkalinity of the pore solution, high electrical resistivity and structure, acting as a barrier for mass transport. The high alkalinity is defined by the composition: concrete is a composite material, consisting of cement, sand, aggregates, water and chemical admixtures.

Detailed review of the cement chemistry and microstructural development of the cement-based materials is not in the scope of the thesis, details can be referred to [6-14], recent developments can be found in [15,16].

Ordinary Portland cement (PC) was used for the investigated in this research concrete and mortar specimens. The major phases of PC are tricalcium silicate (3CaO·SiO\textsubscript{2} or C\textsubscript{3}S), dicalcium silicate (2CaO·SiO\textsubscript{2} or C\textsubscript{2}S), tricalcium aluminate (3CaO·Al\textsubscript{2}O\textsubscript{3} or C\textsubscript{3}A) and a ferrite phase of average composition 4CaO·Al\textsubscript{2}O\textsubscript{3}·Fe\textsubscript{2}O\textsubscript{3} (C\textsubscript{4}AF). C\textsubscript{3}S and C\textsubscript{2}S together make about 75 to 80% of PC. The hydration of these main phases can be presented in a simplified way with the following reactions:

\[
2[3\text{CaO} \cdot \text{SiO}_2] + 7\text{H}_2\text{O} \rightarrow [3\text{CaO} \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}] + 3\text{Ca(OH)}_2 \quad (3)
\]

\[
2[2\text{CaO} \cdot \text{SiO}_2] + 5\text{H}_2\text{O} \rightarrow [3\text{CaO} \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}] + \text{Ca(OH)}_2 \quad (4)
\]

The hydration process, which is the reaction between the main phases and free water, results in the formation of calcium-silica-hydrate (C-S-H), calcium hydroxide (CH), ettringite and other compounds. As a result the capillary pores are filled up with hydration products, form a rigid microstructure and the bulk matrix develops strength. On the other hand the hydration mechanism and formation of hydration products is not that simple. The above reactions are approximate as
it’s not easy to estimate the exact composition of C-S-H (the C/S and S/H ratios), also not so easy to determine the exact amounts of Ca(OH)$_2$; it can be only stated that the produced Ca(OH)$_2$ by hydration of C$_2$S is less than that from C$_3$S (Eq.3), due to the slower hydration of C$_2$S in respect to C$_3$S. The C-S-H is a major phase, present both in hydrated PC and C$_3$S. It is the main bonding agent in cement based materials. Any explanation of the mechanism of hydration should take into account the following steps [15,17,18]:

- pre-induction period: the period of establishing a contact of C$_3$S and water, accompanied by high heat evolution, duration 5 to 15 min, releasing of Ca$^{2+}$ and OH$^-$ ions into solution. In this period C$_3$A is the most active phase;
- dormant (induction) period: reaction rate is very slow, duration few hours, the cement remains workable, dissolution continues and pH reaches a high value of about 12.5. The mechanisms of the dormant period are explained by the “membrane theory” or the “delayed nucleation and growth theory”, which are discussed in detail in [9];
- initial set: occurs at the time when the reaction rate becomes vigorous, continuous formation of hydration products;
- accelerating period: the rate of C$_3$S hydration accelerates with time; after reaching certain critical concentrations of Ca$^{2+}$ and OH$^-$, a rapid crystallization takes place; C-S-H and CH are formed; final set occurs before the end of the accelerating period, slow formation of products, reaction is diffusion controlled.
- post-acceleration stage: the amount of unreacted material declines, the C-S-H phase continues to be formed and the contribution of C$_2$S increases with time.

2.2.2 Evolution of microstructural properties. Definition of pore structure
The development of the pore structure affects the most important properties of concrete, e.g. physico-mechanical and chemical behavior, strength and durability. The durability of cementitious materials, especially in terms of corrosion risk, largely depends on the possibility of aggressive ions to penetrate into the cementitious porous material, where the pore water is the electrolytic medium. Porosity and pore structure are generally accepted to exert significant influence on the permeability of cementitious materials, consequently on electrical properties, electrolytic paths, corrosivity.

The pore system in cement-based materials consists of four types of pores, namely, gel pores, capillary pores, macro-pores due to deliberately entrained air, and macro-pores due to inadequate compaction. The pore sizes in cement-based materials range between nanometers and millimeters [9]. Pores with a diameter larger than 10 μm can be associated with air voids, whereas capillary pores are assumed to cover a range of 0.001 to 10 μm. Of particular interest for ordinary cement paste are the capillary pores. The pore volume is generally defined as the initial paste volume minus the volume of solid phases (the total volume of remaining anhydrated cement particles and the hydration products). Porosity $P$ is defined as the ratio between the pore volume $V$ and the initial paste volume.

**Factors affecting pore structure:** The process of cement hydration modifies the pore structure in continuous stages. Porosity and pore size distribution are functions of the water-to-cement (w/c)
ratio and degree of hydration, and are strongly influenced by the curing conditions and the cement composition. Relevant to this thesis, the main factors affecting the pore structure are the degree of hydration and the water-to-cement ratio, for a more detailed presentation of pore structure and factors affecting it see [15,16,19].

**Degree of hydration:** The total porosity decreases during the hydration process since hydration products gradually fill in the available space in the cement paste. A general trend is that the volume of the large pores significantly declines, whereas the volume proportion of the small pores (<100Å) in the total porosity dramatically increases [9]. The reduction in volume of the large pores is predominant in the early stage of hydration. It is explained that, at first, the hydration products are formed in larger pores and later on in the smaller ones, thus leaving the volume of the small pores more or less constant. Once the larger voids are filled, further hydration would affect the entire pore size distribution. It has been experimentally shown that the shape of the pore size distribution curve plotted versus the hydration degree remains fairly constant throughout the hydration process [16].

**Water to cement ratio:** It is expected that a high w/c ratio will result in a higher volume of porosity in all size ranges. An increase of the w/c ratio leads to an increase in the portion of the larger pores, and hence an increase in the mean pore size.

### 2.2.3 Image and pore structure analysis, relevant to this thesis

The pore structure analysis relevant to this study complies with the generally used methodology for pore structure analysis of cement based materials [15,16]. Scanning electron microscopy (using ESEM Philips XL30) was employed for visualization and microstructure investigations. Section images of the specimens were obtained with backscattered electron (BSE) mode (a set of SEM images were made at random locations on polished sections. The physical size of the reference region of each image is 226 μm in length and 154 μm in width, with the resolution of 0.317 μm/pixel (corresponding to a magnification of 500x). Small capillary pores play a very important role in the transport properties of cement based specimens [20]. Therefore, it is necessary to strike a balance between a representative area element revealing sufficiently large pore section, and a satisfactory resolution for detection of small capillary pores. As reported in [20], resolutions of 0.293 μm/pixel (1000x) and 0.146 μm/pixel (2000x) gave similar values, although the higher magnification could be expected to reveal more trivial and subtle changes in the pore structure. The image analysis was performed using OPTIMAS software package. The combination of SEM images and quantitative image analysis allows deriving structural information of pore space, such as the porosity and critical pore size. On the basis of mathematical morphology transformations, a pore size distribution can be obtained by using a sequence of similarly shaped structuring elements of increasing size [21]. In this study, the so-called ‘opening distribution’ is used whereby the binary image is opened by a series of squares of increasing size [20].

**Pore structure parameters.** The electrolytic path in reinforced cementitious systems is dependent on the kinetics of ions transport mechanisms. These mechanisms, in addition to the cement hydration and the morphological alterations, are affected by the pore size distribution and the pore connectivity of the bulk mortar material. Fig. 2.5(a) presents an ESEM micrograph (overview at
125x magnification) of the bulk matrix of a mortar specimen at 120 days of age. Fig. 2.5(b) presents the circled region of Fig. 2.5(a), which is the bulk cement paste at 500x magnification i.e. the reference region with resolution of 0.317 \( \mu \text{m/pixel} \).

Further, the original BSE image (or a selected area, as shown in Fig. 2.5(b), provided the analysis should exclude the aggregate particles in the image, if any) is segmented by applying a gray-level threshold to create a binary image, reflecting the pore phase.

The threshold gray level between porosity and solid phases is selected by a technique based on the shape of the histogram of the BSE image (Fig. 2.6). The anhydrous material and calcium hydroxide (CH) have fairly uniform gray levels, resulting in certain peaks in the histograms. Due to variation in composition, the gray levels of the other hydration products (basically calcium-silica-hydrate (C-S-H)) form a shallower but still identifiable peak in the histograms.

For properly choosing a threshold value of the gray level for segmentation of the pore space, it has been found that consistent results can be obtained by selecting an arbitrary point on the lower
slope of the peak produced by the other hydration products [22]. The binary image (Fig. 2.6b) is then subjected to quantitative image analysis for derivation of structural parameters (pore size distribution, critical pore size, pore connectivity etc.). Fig. 2.7a) visually presents the results after the implementation of the so called “open distribution technique” [21]. Fig. 2.7b) presents the results after pore network connectivity calculation (after skeletonization).

As aforementioned, the “opening distribution” technique was used, whereby the binary image is opened by a series of squares of increasing size. The cumulative pore size distribution curve is obtained by plotting the pore area fraction after an opening operation versus linear dimension of the structuring element. This gives a type of “size” classification in the case of an interconnected structure, like pore space in mortar. The critical pore size $l_c$ can be conceived as the diameter of the pore that completes the first interconnected pore pathway in a network, developed by a procedure of sequentially adding pores of diminishing size to this network. The critical pore size $l_c$ is a unique transport length scale of major significance for permeability properties and can be associated with the inflection point of the cumulative pore size distribution curve. For predicting the permeability of porous materials the Katz-Thompson equation Eq.(5) [23], is generally used

$$k = \frac{L_c^2}{226.0} \frac{\vartheta}{\vartheta_o}$$  \hspace{1cm} (5)

where $L_c$ is the critical pore diameter, $\vartheta$ is the electrical conductivity of the solid and $\vartheta_o$ is the electrical conductivity of the pore solution. Further, according to the Carman-Kozeny model [24], the permeability of cement paste can be predicted on the basis of geometrical properties of pore space, using Eq.(6):

$$k = -p\left(\frac{V_{pore}}{S_{pore}}\right)^{1/2}$$  \hspace{1cm} (6)

where $p$ is the porosity, $V_{pore}$ and $S_{pore}$ are the volume and surface area of pore space and $\beta$ is the tortuosity of the transport route in the cement. As it is impossible to assess the 3D distribution density directly from image analysis of 2D sections, an alternative is to determine the 2D distribution density from specimen sections and to calculate the 3D distribution density on the
basis of stereological theory [25]. The 2D distribution density \( \Gamma_{2D} \) of pore space in an image with area \( A \) encompassing \( N \) skeleton segments of length \( l \) is defined by Eq.(7):

\[
\Gamma_{2D} = \sum_{i=1}^{N} l_i^2 / A \tag{7}
\]

For application to transport studies, the parameter \( l \) has to be correlated with the length of a skeleton segment in 3D distribution, denoted as \( l_{act} \) and given by Eq.(8) [16]:

\[
l_{act} = \int_{\theta}^\pi \sin^{4.4} \theta d\theta = \pi / 4l_{act} \text{ or } l_{act} = 4/\pi l_i \tag{8}
\]

The relationship between 2D and 3D pore distribution density (PDD) is provided by stereological theory [25], using Eq.(9):

\[
\Gamma_{3D} = 2/\pi N_i l_{act}^2 = 2/\pi N_i (4/\pi)^2 l_i^2 = 32/\pi^3 \Gamma_{2D} \tag{9}
\]

where \( N_i \) represents the number of skeleton segments per unit area of the test image in 2D (i.e. the 2D PDD is converted to 3D). Finally Eq.(10), used in this study, is the refined form of the Katz-Thompson equation [16]:

\[
k = l_i^{-1} / 27800. \exp(1.7 \Gamma_{2D}) [0.001 + 0.07 p^2 + H(p - p_c)(p - p_c)^{0.5}] \tag{10}
\]

where \( p_c \) is the critical value of capillary porosity for percolation and \( H(p - p_c) \) equals 1 if \( p > p_c \), or equals 0 if otherwise. In this research, the pore interconnectivity (defined as the fraction of connected pores out of the total pore area) is used in terms of pore distribution density (PDD), as PDD contains information on both pore size and connectivity of pore space. The derived structural information allows prediction of the intrinsic permeability \( k \) of the cementitious material on the basis of above empirical relationships. Detailed information for the open distribution technique, PDD and the stereological approaches can be found in [16].

2.3 MASS TRANSPORT, WATER TRANSPORT, AGGRESSIVE ION TRANSPORT

2.3.1 Definition and transport mechanism

Corrosion of reinforcing steel in concrete is determined by three mass transport processes: oxygen diffusion, carbonation and chloride ion transport. Good quality concrete provides a physical barrier to prevent corrosion due to carbonation and chloride ingress. It also limits availability of oxygen. The moisture content affects the rate of diffusion processes of the corrosion reactants. Gradients of moisture content, hydrostatic pressure, temperature, concentration of chemicals, disturb the state of equilibrium of fluids in a porous material.

Corrosion of reinforcement could be initiated due to a variety of factors, but the main one remains the transport of aggressive ions and their arrival in the vicinity of the steel surface in the corrosion initiation period. In any transport situation, there are two points to be considered. First, there is
the force that causes the transport to occur. In migration this force is the electrical potential gradient, in permeation – the pressure gradient, in diffusion – the concentration or activity gradient. Second, there is a resistance to ion movement. The transport of a fluid flux is generally described in terms of adsorption, diffusion, absorption and permeability. In concrete both physical structure and pore solution influence those processes.

### 2.3.2 Forms of water. Transport processes in concrete

Water in concrete can be found in different forms [26]:

1. **Chemically combined (bound) water** is part of the structure of the hydration products and could be released only by decomposition of the hydrates.
2. **Interlayer water** is the water penetrating between the layers of C-S-H. Below 11% RH it will be lost, causing shrinkage.
3. **Adsorbed water** is the water close to the solid surface due to physical forces of attraction, which decreases with increasing the distance between the molecule and the solid surface. Adsorbed water can be lost by drying to 30% RH.
4. **Capillary water** is the water free from attractive forces. It is present in voids larger than $50 \times 10^{-6}$ m. Capillary water is the medium for ion transport.

Relevant to the forms of water, present in the concrete matrix, the main transport processes are: **adsorption**: molecules are adhered to the solid phases in concrete either by physical forces or by chemical binding. **diffusion**: the process of passing liquid, gas, ions through the concrete matrix due to concentration gradient. **permeability**: the ability of concrete to uptake fluid flow under pressure differential.

Although pure permeability is strictly related to flow under pressure, it’s most frequently used and includes other transport mechanisms as absorption and diffusion. It has to be bared in mind that permeability is not just the result of porosity; concrete could be porous but with low permeability in case of low pore connectivity.

### 2.3.3 Chloride ion – corrosion inducing factor. Mechanism of chloride attack

Chloride ions can be introduced into concrete as a contaminant (by exposure to the environment) or as an additive (deliberately, in the initial concrete mixture). The later case results in fast corrosion initiation; the former case involves penetration of the aggressive ions and requires longer periods. Chlorides penetrate the concrete matrix through cracks, voids, capillary pores.

The effect of chloride ions on corrosion in reinforced concrete can be explained by one or a combination of the following theories [27]: The Oxide Film Theory, according to which the chloride ions penetrate the passive film easier than other ions (e.g. $\text{SO}_4^{2-}$), thus the chloride ions may disperse in the oxide film and cause film break-down; The Adsorption Theory, according to which chloride ions are adsorbed on the steel surface in competition with dissolved oxygen or hydroxyl ions; The Transitory Complex Theory, according to which the chloride ions become incorporated in the passive film, replacing some of the hydroxides, thus increasing both the solubility and conductivity of the film. As a result the protective effect of the layer is lost and the reaction involved is mainly:
Fe(OH)$_x$ + xCl$^-$ $\rightleftharpoons$ FeCl$_x$ + xOH$^-$  

(11)

where $x$ can be 2 or 3, depending on the oxidation state of iron. The presence of chloride ions promotes the disruption of the iron oxide/hydroxide layer; the product FeCl$^+$ assists the process as well, due to its high solubility. In particular in the areas of local corrosion damage, iron chlorides react with the pore water (e.g. according the reaction FeCl$_2$ + 2H$_2$O $\rightarrow$ 2HCl + Fe(OH)$_2$), form hydrochloric acid, which in turn causes pH drop and consequently accelerates the local steel dissolution. The non-homogeneous distribution of chloride ions over the steel surface and the imperfections of the passive oxide film allow easy incorporation of the chloride ions and local breakdown of the film. What follows is the formation of micro cells on the steel surface and localized corrosion; the anodic areas are places of active corrosion, the cathodic areas remain passive locations, where reduction of oxygen takes place at higher potentials. In addition to the chloride concentration (pH value as well), the corrosion rate will depend on the cathode to anode ratio in the micro/macro cells and on the electrical resistivity of the bulk concrete between these cells.

2.3.4 Chloride binding

When chloride ions penetrate the concrete surface and ingress into the bulk material, part of them are undergoing chemical binding, part of them remain physically bound (adsorbed) and part stay free (in the pore solution).

Chemical binding. One of the factors influencing the extent of chemical binding of chlorides is the tri-calcium aluminate (C$_3$A) content in the cement. The process of chemical binding is an incorporation of chlorides in the lattice of crystalline hydration products and the formation of chloro aluminates: [3CaO·Al$_2$O$_3$·3CaCl$_2$·10H$_2$O] (Friedel’s salt) and [3CaO·Al$_2$O$_3$·3CaCl$_2$·32H$_2$O]. From 50 to 80 % of admixed chlorides can be chemically bound, depending on the amount of C$_3$A [28-30]. The amount of bound chloride ions depends on the presence and the concentration of other ions (e.g. sulphates, carbonates, Ca$^{2+}$, K$^+$, Na$^+$), pH and temperature. Bound chlorides however can be released, in case the concrete is exposed to sulphates or in case carbonation takes place [31,32]. The released chloride ions become available for pitting initiation long before the local pH drops to a value, necessary to sustain a pit growth, thus preventing re-passivation i.e. bound chloride may present a corrosion risk as well.

Physical binding is the process of adsorbing chlorides in the amorphous matrix of the calcium-silica-hydrate gel, the latter formed during the cement hydration. Physically bound (adsorbed) chlorides present a slightly lower corrosion risk, compared to free chlorides, since the movement of the former is restricted, while the latter can be freely transported in the pore water solution. It is assumed by many authors that the ingress of chloride ions into concrete can be for simplicity described with the second law of Fick. On basis of this model it is theoretically possible to calculate the time, needed for the chloride concentration to reach critical values (Section 2.3.5, Appendix I) in the vicinity of the steel surface. Such a model however is an approximation as it takes into account only the diffusion properties of the concrete, the surface concentration and the penetration depth, but does not consider the effect of chloride adsorption, binding mechanisms and micro-cracking.
Chloride binding mechanisms differ, depending on the way chlorides were introduced in the cement matrix: as admixtures, or if concrete is exposed to chloride penetration. In case of admixed chlorides, the binding mechanism is influenced by the cation type and the cement type. In case of chloride penetration, the binding mechanism is less influenced by the binder (cement) type, but depends mainly on the exposure time and the concrete permeability (Tables 2.1, 2.2, 2.3, adapted from [30] and the references therein).

Table 2.1 Binding of chlorides, added during mixing to cement paste as a function of cement type, w/b ratio 0.5, C₃A content 9% for OPC without and with replacement [30,33]

<table>
<thead>
<tr>
<th>Cement type</th>
<th>Replacement</th>
<th>Total Cl added (% by mass of binder)</th>
<th>Bound Cl (% by mass of binder)</th>
<th>Bound/total chloride %</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC1</td>
<td>1.0</td>
<td>0.385</td>
<td>0.355</td>
<td>39</td>
</tr>
<tr>
<td>OPC1 15% PFA</td>
<td>1.0</td>
<td>0.532</td>
<td>0.522</td>
<td>53</td>
</tr>
<tr>
<td>OPC1 70% GGBS</td>
<td>1.0</td>
<td>0.711</td>
<td>0.702</td>
<td>71</td>
</tr>
</tbody>
</table>

Table 2.2 Binding of chlorides as function of cement type for specimens immersed in 20г Cl⁻/l [30,33]

<table>
<thead>
<tr>
<th>Cement type</th>
<th>Replacement</th>
<th>Total Cl added (% by mass of bind.)</th>
<th>Free Cl added (% by mass of bind.)</th>
<th>Bound Cl (% by mass of bind.)</th>
<th>Bound/total chloride %</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC1</td>
<td>1.635</td>
<td>0.831</td>
<td>0.804</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>OPC1 15% PFA</td>
<td>1.887</td>
<td>0.818</td>
<td>1.069</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>OPC1 70% GGBS</td>
<td>1.750</td>
<td>0.830</td>
<td>0.920</td>
<td>53</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3 Binding of penetrated chlorides as a function of cation type, w/b ratio 0.5, OPC specimens immersed in 20г Cl⁻/l [30,33]

<table>
<thead>
<tr>
<th>Cl concentration (% by mass of binder)</th>
<th>NaCl</th>
<th>Sea-water</th>
<th>CaCl₂</th>
<th>MgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free</td>
<td>0.831</td>
<td>0.776</td>
<td>0.765</td>
<td>1.480</td>
</tr>
<tr>
<td>Bound</td>
<td>0.804</td>
<td>0.577</td>
<td>1.408</td>
<td>2.347</td>
</tr>
<tr>
<td>Total</td>
<td>1.635</td>
<td>1.353</td>
<td>2.173</td>
<td>3.827</td>
</tr>
<tr>
<td>Bound/Total (%)</td>
<td>50</td>
<td>43</td>
<td>65</td>
<td>61</td>
</tr>
</tbody>
</table>

2.3.5 Critical chloride concentration. Threshold values

There is no universal threshold value at which corrosion initiation takes place. The lowest reported threshold is 0.2 %, the highest is 2.0% by mass of binder [34]. For atmospherically exposed structures, where the steel potential is generally recorded around, or more noble than -200 mV (SCE) prior to exposure to chlorides, the risk of chloride-induced corrosion is significant when chloride levels in the vicinity of the steel bars are 0.2-0.4% by weight of cement [35-37]. For permanently soaked structures, where the steel potential is generally found to be less noble than -500 mV(SCE) prior to chloride penetration, significant corrosion activity can be expected when the chloride levels at the steel/cement paste interface reaches 1% by weight of cement, since in such structures the oxygen availability is restricted [35]. Obviously, difficulty arises when trying to exactly determine chloride concentration thresholds, since variety of factors is involved. There are several definitions for critical chloride concentration, most frequently used are [30,38]:

- 18 -
- The chloride level at the steel/cement paste interface, which initiates corrosion on the steel surface;
- The chloride level at the steel/cement paste interface, which causes corrosion and consequently, cracking and spalling (due to increased volume expansion of corrosion products) are induced;
- The chloride concentration at the steel/cement paste interface, which causes concrete deterioration at a certain stage of the service life of a structure when the need of repair is recognized.

The most likely critical chloride concentration at which corrosion will be initiated is about 0.5 % per mass of binder [30], a summary of reported critical chloride concentrations, adapted from [30], is presented in Appendix I.

2.3.6 Pore size distribution with respect to the influence of chlorides
As aforementioned, chlorides in cement based materials are found in different forms:
- bound chlorides in the form of chloro-complexes – \( \text{C}_3\text{A(F):CaCl}_2\cdot\text{H}_2\text{O} \);
- free chlorides in the pore solution;
- chemisorbed layers on the surface of the C-S-H gel.

The process of continuous cement hydration, as previously discussed in Sections 2.2.1 and 2.2.2, is a process of filling in the pore structure with hydration products. Chloride binding leads to the formation of chloro-complexes, which could be formed in the capillary pores. Thus the presence of chlorides, in addition to the cement hydration, contributes to the densification of the pore space in the bulk cementitious matrix. As reported in [39], the C-S-H morphology differs in samples with and without chlorides (NaCl), leading to the development of a different pore structure: the “chloride free” mortars have fibrous or needle shaped C-S-H, from where a considerable pore space exists, whereas the “chloride containing” mortars exhibit a modified, denser C-S-H structure, which influences the pore spaces. Other research [40] reports that the addition of 1% CaCl\(_2\) to tri-calcium silicate (C\(_3\)S) also leads to increased volume of the finer pore fraction, compared to chloride free C\(_3\)S and denotes the observations again to changed morphology of the C-S-H gel.

In the frame of this research, a difference in the morphology of the C-S-H was found as well. This is most likely one of the reasons for the obtained different pore structure parameters of the “chloride free” and “chloride containing” specimens, which in turn exerts influence on the electrical properties, ion transport and consequently electrochemical phenomena in the investigated conditions (the outcomes are presented and discussed in the experimental part of the thesis).

2.4 TESTING FOR REINFORCEMENT CORROSION
A variety of methods is available for monitoring steel corrosion in reinforced concrete. Briefly presented below are those, relevant to practical applications (also involved in this research), along with some generally accepted interpretations of the recorded data. The techniques, which are more relevant to laboratory measurements, such as Electrochemical Impedance Spectroscopy,
Potentio-dynamic polarization, Cyclic voltammetry etc., will be described in the experimental parts I and II, with relevance to the investigations, discussed in each chapter. Electrical resistance measurements are generally applied, since they provide information for concrete corrosivity i.e. for assessing the probability of reinforcement corrosion within a given structure [41]. The used techniques are dependent on an accurate measurement either of the electrical resistivity of a specific section of the concrete or of a specially introduced metallic test piece, permanently embedded in the concrete. These two techniques are referred to as: resistivity mapping and resistivity probes [3,42]. The interpretation is empirical. The following interpretations of resistivity measurements have been cited when referring to depassivated steel:

- $> 20 \, \text{K}\Omega \cdot \text{cm}$ Low corrosion rate
- $10 - 20 \, \text{K}\Omega \cdot \text{cm}$ Low to moderate corrosion rate
- $5 - 10 \, \text{K}\Omega \cdot \text{cm}$ High corrosion rate
- $< 5 \, \text{K}\Omega \cdot \text{cm}$ Very high corrosion rate

Research work [43] with the GECOR 6 device (basically performing a 2 or 4 pin measurement) reports the following relationships:

- $> 100 \, \text{K}\Omega \cdot \text{cm}$ Can not distinguish between active and passive steel
- $50 - 100 \, \text{K}\Omega \cdot \text{cm}$ Low corrosion rate
- $10 - 50 \, \text{K}\Omega \cdot \text{cm}$ Moderate to high corrosion where steel is active
- $< 10 \, \text{K}\Omega \cdot \text{cm}$ Resistivity is not the controlling parameter

Since there are numerous factors, affecting the data collection on one hand and on the other, the corrosion rate is usually controlled by the interfacial resistance between the steel and the concrete, not the bulk concrete resistivity; these measurements can be used only for orientation and always in a combination with other methods. Of course, high resistivity concrete will not sustain a high corrosion rate (since high resistivity would mean lower moisture and oxygen content due to lower permeability) while a low resistivity concrete can, if the steel is depassivated by the presence of chlorides or carbonation.

Electrochemical methods for practical applications include Half cell potential mapping, Depolarization decay, Corrosion rate measurements. Half Cell Potential Mapping: The current flow in concrete is due to an electrical field which can be measured at the concrete surface. The measurement results in recording equipotential lines, which allow determination of the location of the most corroding zones at the most negative values. Potential mapping is the principal electrochemical technique, applied in the routine inspection of reinforced concrete structures [44-46]. When the surface potentials are taken, they are measured remotely from the reinforcement, due to the concrete cover and are therefore affected by the ohmic potential drop in concrete. Several factors have a significant effect on the measured potentials: Concrete cover depth; Concrete resistivity; High resistive surface layers; Polarization effects. For example, steel in concrete structures immersed in water or placed in the earth often has a very negative potential due to restricted oxygen access [47]. In the transition region of the structure (splash zone or above ground), negative potentials can be measured due to galvanic coupling with immersed re-bars. These negative potentials are not related to corrosion of the reinforcement. The errors, arising within such measurements could be of course minimised by using embedded reference cells. The
interpretation is as follows: According to the ASTM C876 for example, corrosion can only be identified with 95% certainty at potentials more negative than -350 mV (vs CSE). Experience has shown, however, that passive structures tend to show values more positive than -200 mV and often positive potentials. Potentials more negative than -200 mV may be an indicator of the onset of corrosion. In any case, the technique should never be used in isolation, but coupled with measurements of the chloride content and its variation, concrete cover depth and carbonation.

Corrosion rate: The corrosion rate is probably the nearest the engineer can get to measuring the rate of deterioration with current technology for practical application. There are various ways for measuring the rate of corrosion, including AC impedance and Electrochemical noise measurements. However, these techniques are not widely applied in practice. A suitable field technique is the Linear polarization method, also known as Polarization resistance, which derives corrosion current density, based on the Stern-Geary equation [48]: 
\[ I_{\text{corr}} = \frac{B}{R_p} \]
where \( I_{\text{corr}} \) is the corrosion current, \( B \) is a constant, related to anodic and cathodic Tafel slopes and \( R_p \) is the polarization resistance. The problem with the practical application of this method is the slow measurement in some cases (waiting for steady state), but mostly problems arise from the not well defined area (steel surface), to which the measurements are actually related to. At low corrosion rates this can lead to errors by orders of magnitude [49]. The following broad criteria have been developed from field and laboratory investigations with the so-called sensor controlled guard ring device [50,51]:

\[
\begin{align*}
I_{\text{corr}} &< 0.1 \text{ A/cm}^2 & \text{Passive condition} \\
0.1 \text{ to } 0.5 \text{ A/cm}^2 \quad & \text{Low to Moderate corrosion} \\
0.5 \text{ to } 1.0 \text{ A/cm}^2 \quad & \text{Moderate to High corrosion} \\
> 1.0 \text{ A/cm}^2 \quad & \text{High Corrosion rate}
\end{align*}
\]

These measurements are affected by temperature and relative humidity (RH), so the conditions of the measurement will affect the interpretation of the limits defined above.

2.5 Electrochemical Methods for Corrosion Protection
The electrochemical methods for corrosion protection include cathodic protection (CP), electrochemical chloride extraction (ECE) and realkalisation (ReA). They are widely and successfully applied in practical applications, since the main principles are essentially identical to those governing the cause for corrosion i.e. electrochemical techniques and corrosion have their fundamental mechanisms in electrochemistry. The principle set-up for all electrochemical techniques comprises the following: an external anode, embedded in or in contact with (via electrolyte medium) the concrete surface; external DC power supply; a cathode, which is the steel reinforcement. The anode is connected to the positive, the cathode (the reinforcement) to the negative terminal of the power supply. The applied current density varies from mA/m² in the case of CP to A/m² in the case of ReA or ECE. In principle, the result is generating electrons for the anodic reaction while only cathodic reaction takes place on the steel surface (being the cathode). For ECE and ReA, the external anode is temporary, while for CP the anodes (embedded or external) are permanent.
The main goal of ReA and ECE is re-establishing the alkaline environment in the vicinity of the steel surface and as far as possible in the bulk concrete matrix. This would lead to steel repassivation. Impressed CP does not explicitly aim at increasing alkalinity, since the general principle is cathodically polarizing the steel reinforcement and maintaining the steel potential in the region, where corrosion does not occur (more cathodic than -850 mV CSE). The technique however has secondary beneficial effects, which actually lead to increased alkalinity in the vicinity of the steel surface (accumulation of OH\(^-\), alkali ions, Ca(OH)\(_2\)) and chloride withdrawal, since Cl\(^-\) would migrate to the anode as result of the applied electrical current. One requirement for all electrochemical treatments is the good electrical continuity, thus ensuring that current flows from the anode to all cathodic areas (i.e. all parts of the reinforcement are equally polarised).

The main side effects, accompanying the application of electrochemical techniques are: Alkali Aggregate Reaction, the most common being Alkali Silica Reaction (ASR) and bond strength degradation at the steel/cement paste interface. The ASR occurs in the presence of reactive silica in the concrete mixture, provided there is sufficient supply of alkalis and moisture. The reaction product is a hygroscopic gel, which takes up water and swells. The result is creating internal stresses, sufficient to cause concrete cracking. The phenomena of bond strength degradation, although not well understood [52], is believed to be a process of combined physico-chemical and microstructural alterations on the steel/cement paste interface, resulting from the applied electrical current flow or from ASR [53,54]. The techniques ReA and ECE use significantly high current density (in the range of A/m\(^2\)) and even if the treatments are generally applied for a few weeks to few months, they can affect the bulk concrete matrix. The same possibility holds for impressed current CP, which although using significantly lower current density (in the range of mA/m\(^2\)), can affect the bulk matrix, since it is applied for the service life of the structure. Another possible side effect is hydrogen embrittlement, which can occur for prestressed concrete, provided that safe potential limits (generally -900 mV SCE) are not taken into account [55].

More details, related to the beneficial secondary effects and the side effects of impressed current CP are presented and discussed in the experimental Parts I and II of the thesis, with relevance to the experimental observations and the outcomes from investigations of the bulk concrete matrix and the steel/cement paste interface in conditions of CP current flow.

2.5.1 Electrochemical Chloride Extraction (ECE)

Mixed metal oxide (MMO) titanium mesh is the most widely applied anode for ECE. A sacrificial anode can be used instead, e.g. copper was applied in the early 70’s, but copper (or its salts) may accelerate corrosion if it penetrates into concrete; steel mesh has been used more recently but application is restricted as it may be completely consumed in some areas before the treatment process is over. As aforementioned, the technique uses a temporary anode, placed inside a cassette shutter, containing the electrolyte (usually calcium hydroxide). This has the advantage over water of being alkaline and stops chlorine gas evolution. Additional chemicals, e.g. lithium salts, may be added to the electrolyte, so as to minimize the risk of ASR.
Of course, it is not possible to withdraw all chlorides from the concrete bulk matrix (generally the technique succeeds with maximum of 60% withdrawn chlorides). Field data shows that this treatment is effective for about six years. Although the chloride concentration in the immediate vicinity of the reinforcement can be reduced, drawbacks of the technique are the still high chloride concentrations in the bulk matrix and the high current density, which would affect the concrete microstructure. The former can lead to corrosion initiation in a short period after treatment, the latter can have effects upon concrete chemistry and therefore its physical condition. Brown staining around the rebar, for example, has been observed on specimens, when high currents and voltages are used (in excess of about 2 or 3 A/m²). This is an effect on the concrete, not the steel. Recent improvements of the ECE technique include the application of pulse current [56], but again the used current density is significantly high (in the above mentioned ranges), compared to CP.

2.5.2 Realkalisation (ReA)

The realkalisation process uses the same set-up as for the ECE technique and similar current densities. The temporary anode is placed in the same manner on the carbonated concrete surface in an alkaline electrolyte (typically sodium carbonate). The aim is to restore alkalinity within the carbonated concrete so as to establish conditions for steel re-passivation. The applied current densities are from 0.3 A/m² to 2 A/m². Since this technique uses lower current density, the risks of damage and side effects are lower, compared to ECE. A state-of-the-art report on ReA and ECE was produced in 1998 by the European Federation of Corrosion, Working Party 11, “Corrosion of Reinforcement in Concrete” [57], reviews on these techniques and relevant information can be referred also to the Final report of the European COST 521 Programme [58].

2.5.3 Cathodic Protection (CP)

A review for the development of CP form the very first proposition of this technique to more recent applications can be referred to [59]. Cathodic Protection was first proposed by Davy in 1824 [60], practical application of CP started in the USA in 1928, later a theoretical basis was given by Hoar [61] and studied and reported in 1938 by Mears and Brown [62]. The technique has been developed for reinforced concrete in the last 30 years in 3 phases. In 1973 CP was used in North America for protection of bridge decks, contaminated by chlorides. The 80’s marked an introduction of new anodes, conductive polymeric materials; the application was extended to industrial buildings. In the 90’s, improvements of the technique were reported, “Cathodic prevention”; using lower current densities, was introduced.

The conventional basis for impressed current CP relies on polarizing the steel reinforcement in a negative direction [63], which is maintaining the steel potential more cathodic than -850 mV CSE (according accepted criteria and standards), where corrosion is thermodynamically impossible [64]. The primary effect of a potential shift in negative direction is reducing the driving force for the anodic reaction (which is a thermodynamic effect) and retarding the anodic process (which is a kinetic effect). Consequently, in the case of previously corroding reinforcement (Fig. 2.8a), after cathodic polarization (Fig. 2.8b), the anodic process (or steel dissolution) will be initially impeded and further will not occur (Fig. 2.8c). In other words, initially there will be cathodic
areas and anodic areas with steel dissolution. There will be also corrosion deposits, non-uniformly distributed on the steel surface. The application of CP causes current flow, which will concentrate at the areas with lowest resistance, which are the anodic areas, so the initial effect of CP is to polarize the anodic dissolution and to decrease the corrosion rate [59]. Further, two “protection” processes might be expected, a classical thermodynamic immunity [60, 64] or “imperfect passivity” which is actually a result from restoring the alkalinity of the environment at the steel/cement paste interface.

In that sense, when CP is applied to reinforcing steel in concrete, the objective might not always be to achieve the cathodic polarization (of -850 mV CSE, as required in standards), which is the region of immunity (Fig. 2.9), but to reduce the risk of chloride-induced corrosion. Fig. 2.9a) [65] illustrates how the steel behaves for different potentials and chloride contents at temperature of about 20ºC. The evolution paths (in terms of potential and chloride content) of CP to prevent corrosion or of CP to control it, once initiated are shown in Fig. 2.9b).

**Fig. 2.8 Corrosion and CP in reinforced concrete – schematic view of: (a) corroding state; (b) CP application (initial period); (c) CP application (established protection).**

**Fig. 2.9.** (a) Schematic illustration of steel in concrete for different potentials and chloride contents; (b) Evolution paths of potential and chloride content: prevention 1 → 2 → 3; protection restoring passivity 1 → 4 → 5; protection, reducing corrosion rates 1 → 4 → 6) [65]
As illustrated in Fig. 2.9, in case CP is to be applied as a remedial treatment to reinforced concrete in which chloride-induced corrosion has already been occurring, the desired protection might be achieved by polarizing the steel from its condition of chloride-induced corrosion (or “pitting”) to the domain of “imperfect passivity”, where “pitting” is unstable i.e. in the domain where the rate of propagation of existing “pits” will be reduced considerably and the initiation of new ones will be prevented [5,65,66]. In case CP is initially applied within the construction of a structure, which is before the exposure to aggressive environments, only a modest polarization of the steel surface will be sufficient for corrosion protection, the technique being applied and denoted as “cathodic prevention” [65,67,68].

Cathodic protection, along with series of beneficial effects as chloride withdrawal, increased alkalinity around the steel bars etc., is known to have side effects. The most widely reported are: reducing anode efficiency [69,70], risk of alkali-silica-reaction (ASR) in the vicinity of the embedded steel re-bars [52,53,71], bond-strength degradation at the steel/cement paste interface [72,73], possible hydrogen embrittlement in case of prestressed concrete [53,55]. The majority of side effects result in lost of adhesion of the adjacent to the steel surface cement layer [52,53] (which can reach 60 % [74]) and bond-strength weakening by 55 % [75]. Consequently, a protection regime which uses lower current density (lower than the usually recommended range of 5 to 20 mA/m² for structures exposed to the atmosphere [68]) is expected to minimize the side effects. As aforementioned, such an alternative technique is “cathodic prevention” [5,65,68], which uses different current densities, or “intermittent protection”, which uses periods of “on” and “off” protection, with average current density of 6 mA/m², but significantly large current in the “on” regime (100 mA/m²) [76].

An improved method for CP, based on pulse technology and using a lower current density, is the primary research focus in this thesis. The pulse CP was found to have more pronounced beneficial effects and fewer side effects, compared to conventional regimes. The Chapters 8 and 9 from Part II of the thesis deal with an elaborated discussion of the technical regimes, the application and the experimental results for the pulse CP technique.

References:
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27. ACI Committee, Corrosion of metals in concrete, 222-285, ACI, Detroit (1985)
44. ASTM C-876: Standard test method for half-cell potentials of uncoated reinforcing steel in concrete (1997)
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PART II  Experimental Investigation: Mortar and reinforced mortar

CHAPTER 3
ELECTRICAL PROPERTIES, MORPHOLOGICAL OBSERVATIONS AND MICRO-STRUCTURAL ANALYSIS OF PLAIN AND REINFORCED MORTAR UNDER THE INFLUENCE OF NaCl.

Adapted from:

3.1 INTRODUCTION

This chapter presents investigations on the influence of chloride ions on the material microstructure and on the electrical properties of plain and reinforced mortars. Specifically examined are the chloride-induced changes in the morphology of the hydration products in the bulk mortar matrix, the pore structure of plain and reinforced mortars and the chemical composition of C-S-H products. Hydration and corrosion products at the steel/mortar interface are partly discussed, which will be subject to elaborated discussion in Chapter 4. Further, based on chemical analysis of the cementitious material and the investigated microstructural alterations, a correlation of ion transport (resulting from concentration gradient), chloride binding mechanisms and electrical properties (in terms of resistivity) in rest conditions was derived.

The investigations comprising this chapter were performed, since at first electrical properties (e.g. concrete resistivity) are related to predicting concrete corrosivity; secondly, aggressive ion concentrations determine the risk of corrosion and when related to electrical properties can give valuable information for predicting corrosion risks; finally, the pore structure characteristics are of significant importance, since porosity, pore size distribution and pore interconnectivity are the main factors, influencing the electrolytic path in reinforced concrete, consequently the rate of corrosion initiation or the distribution of current flow with electrochemical protection techniques (as cathodic protection, relevant to this thesis). To this end, the outcomes from the studies, discussed in this chapter (as well as the related Chapters 4 to 6), can be considered as a preliminary, fundamental investigation, relevant to the research on concrete and reinforced concrete systems, which will be presented in part II of the thesis.

3.2 MATERIALS AND SET-UP

3.2.1 Specimen groups, casting, mixtures and conditioning

The specimens investigated in this Chapter comprised two main groups: plain mortar prisms of 40 × 40 × 160 mm and reinforced mortar cylinders of d=40 mm × h=100 mm, cast from ordinary Portland cement (OPC) CEM I 32.5R from ENCI factory (Dutch cement producer). The cement
composition, physical characteristics and constituents are given in Table 3.1. Specification for specimen design, specimen groups, curing conditions, mortar mixture and some experimental procedures are summarised in Table 3.2. The group of plain mortar prisms (15 in total) comprised three sub-groups of specimens, varying in chemical compositions of the mixing water i.e. group T made with tap water, group N produced using 3% NaCl solution as mixing water and group TN, a half to half combination of the mixture for T and for N specimens (Table 3.2, point 1). The specimens were stored in a fog room, maintained at 20°C and 98% relative humidity (RH) during the whole period of 65 days of testing. Stainless steel pins were equidistantly embedded along the specimen length, each pin being embedded to a depth of 30 mm into the specimen for the purpose of resistivity monitoring (Table 3.2, point 1).

Table 3.1 Chemical properties, physical properties and constituents of CEM I 32.5 R

<table>
<thead>
<tr>
<th>Chemical Constituents</th>
<th>Physical Strength of standard mortar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide</td>
<td>Weight(%)</td>
</tr>
<tr>
<td>CaO</td>
<td>63.90</td>
</tr>
<tr>
<td>SiO₂</td>
<td>21.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.03</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.00</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.83</td>
</tr>
<tr>
<td>MgO</td>
<td>2.00</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.24</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.65</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.30</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.16</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.06</td>
</tr>
<tr>
<td>total</td>
<td>99.17</td>
</tr>
</tbody>
</table>

C₃S – tricalcium silicate; C₂S – dicalcium silicate; C₃A – tricalcium aluminate; C₄AF – ferrite.

The group of reinforced mortar cylinders (16 specimens in total) were cast using the same cement, sand and same mixing procedures as for the plain mortars (Table 3.2, point 4). Each cylinder contained a centrally located 6 mm diameter steel bar (using “as received”, cold rolled construction steel, type FeB500HKN) with exposed length of 80 mm (Table 3.2, point 1). All specimens were cured in the fog room conditions of 98% RH and 20°C for 14 days and then placed in lab air, 20°C and certain experimental conditions (Table 3.2, point 3) till the end of the testing period of 120 days. The reinforced cylinders comprised two experimental groups: reference (non-corroding) specimens denoted as R and corrosion test specimens, denoted as N (Table 3.2, point 2). A cylindrical titanium mesh served as counter electrode and saturated calomel electrode (SCE) was used as reference electrode for the electrochemical measurements, which are subject to discussion in Chapter 4.

3.2.2 Sample preparation for microstructure investigation

The samples for microscopic investigation were prepared at the end of the testing periods for both plain and reinforced mortar specimens (60 and 120 days respectively). The specimen preparation is important, since the proper and identical preparation for each investigated sample, ensures the accurate microscopical examination and further interpretation of the microstructural features (here by sample, a sample part of one specimen is meant; several samples from one and the same
specimen were normally investigated). The sample preparation includes the following steps: cutting of the specimen, drying, vacuum conditioning, epoxy impregnation, grinding and polishing. The vacuum conditioning and epoxy impregnation for the reinforced mortar were performed on several stages, repeated at least twice, thus minimising the influence on the steel/cement paste interfaces.

### Table 3.2 Specification of materials set-up, conditioning and some experimental procedures

<table>
<thead>
<tr>
<th></th>
<th>Plain mortar prisms</th>
<th>Reinforced mortar cylinders</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Specimen set-up</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>water</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>NaCl</td>
<td></td>
</tr>
<tr>
<td>TN</td>
<td>% chloride</td>
<td></td>
</tr>
<tr>
<td><strong>2. Specimen groups</strong></td>
<td>T – using tap water as mixing water</td>
<td>R – reference</td>
</tr>
<tr>
<td></td>
<td>N – using 3% NaCl solution as mixing water</td>
<td>N – corroding</td>
</tr>
<tr>
<td></td>
<td>TN – half-to-half the mixture of T and N</td>
<td>All specimens cast with demi-water</td>
</tr>
<tr>
<td><strong>3. Curing conditions</strong></td>
<td>- 60 days – fog room (98% RH, 20°C)</td>
<td>- 14 days fog room (98% RH, 20°C)</td>
</tr>
<tr>
<td></td>
<td>- 106 days lab air, 20°C in immersed conditions</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R - 1/3rd of height immersed in water</td>
<td>N - 1/3rd of height immersed in 7% NaCl solution</td>
</tr>
<tr>
<td><strong>4. Mortar mixture</strong></td>
<td>- OPC CEM I 32.5 R</td>
<td>- OPC CEM I 32.5 R</td>
</tr>
<tr>
<td></td>
<td>- w/c ratio 0.5, cement to sand ratio 1:3</td>
<td>- w/c ratio 0.6, cement to sand ratio 1:3</td>
</tr>
<tr>
<td></td>
<td>- sand of size range 125 µm to 2 mm</td>
<td>- sand of size range 125 µm to 2 mm</td>
</tr>
<tr>
<td></td>
<td>- preparation EN 196-1</td>
<td>- preparation EN 196-1</td>
</tr>
<tr>
<td></td>
<td>- embedded into 30 mm depth stainless steel pins for resistivity measurements</td>
<td>- FeB500HKN, d=6mm as embedded re-bar, exposed length 80 mm</td>
</tr>
<tr>
<td><strong>5. Chloride profile</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### 5a. Areas for pore structure analysis

Chloride concentrations determined wet chemically by sections of the prisms TN
A more detailed sequence of the aforementioned steps for sample preparation is as follows: cutting the specimens into sections of 40×40×25mm for the prisms (corresponding to sections A and B, Table 3.2, p.1) and sections of 40×25mm for the cylinders (corresponding to cross sections from the bottom and top parts of the cylinders, Table 3.2, p.1 and p.5a). The sections were dried for 60 min in a stove at 35ºC and placed in a vacuum impregnation chamber afterwards. The vacuum conditioning lasted approximately one hour before impregnation with low viscosity epoxy. After the vacuum impregnation the specimens were maintained in a stove for 24 h at 35ºC. Further, the impregnated sections were again cut into smaller sections of approximately 25×20×10mm, thus obtaining the samples for microscopic investigation. The samples were ground on a DBT Diamond Roller and Grinder/86 thin sectioning machine or on a middle-speed lap wheel with no.320, no.500, no.1200 and no.4000 grinding papers. A typical polished section (sample), as used for microscopic investigations, is shown in Fig.3.1.

![A typical polished section from reinforced mortar for microscopical investigation.](image)

### 3.3 Experimental Methods and Techniques

#### 3.3.1 Resistivity measurements of plain mortars

Resistance monitoring was conducted on specific sections of the plain mortar prisms (Table 3.2, p.1) to provide insight into ion transport due to diffusion, resulting from the concentration gradients by sections of the prisms, as schematically presented in Table 3.2, p.5 (bulk matrix mortar resistance of the reinforced mortar cylinders was determined by Impedance spectroscopy, which will be discussed in Chapters 4 and 6). Measurements of the total resistance gave information on the changes in electrical properties of specimens under various chloride ion concentrations and under various chloride concentration gradients. Resistance measurements were performed using a direct current (DC) four pin method, and alternating current (AC) two and four pin methods. For the DC measurement, a DC current of 2 mA was applied to the outer pins 1 and 5 according to the scheme shown in Table 3.2, p.1, then the voltage drop in every section was recorded. For the AC measurement, a specially designed device, referred to as R-meter was used. By applying an alternating current of 1 mA at a frequency of 1kHz, the device outputs a DC voltage, which represents the actual resistance. It was found that the different methods yielded similar outcomes with a coefficient of variation within 3 to 5%. The specific electrical resistivity was calculated from the recorded resistance values using the equation: $\rho = RA/l$, where $\rho$ is the resistivity in Ohm·m, $R$ is the resistance in Ohm, $A$ is the cross-section in m$^2$, and $l$ is the length in m.

#### 3.3.2 Chemical analysis

Wet chemical analysis for determination of ion concentrations was performed according ASTM C12218 and ASTM C1152 for free and total chloride concentrations, using Volhard titration.
method. An Inductive Coupled Plasma Spectrometer (ICP-AES) was used for determination of alkali concentrations. The chemical analysis was performed for each section of the plain mortar prisms (Table 3.2, p.1) at 1, 8, 14, 24, 30, 41 and 57 days of cement hydration. The chemical analysis aimed at monitoring ion transport due to diffusion (as result of concentration gradient) in sub-group TN for the plain mortar prisms and compare changes in concentration with sub-groups T and N (no concentration gradient). Consequently a chloride profile can be derived at the end of the test for specimens of sub-group TN, using the second law of Fick and the arrangement schematically shown in Table 3.2, p.5. The derived changes in chloride and alkali concentrations (due to concentration gradient) were further coupled with electrical resistivity measurements for the same sections of the prisms (Table 3.2, points 1 and 5), thus giving a correlation of ion transport and electrical properties in the bulk mortar matrix with aging in the present conditions.

3.3.3 Microstructural analysis

The samples for microstructural investigation of the plain mortar prisms were obtained from all sections of specimens TN (sections A and B, Table 3.2) and the edge and the middle sections of specimens T and N. The samples from the reinforced mortar cylinders were obtained from the top and bottom sections of specimens N and R (Table 3.2). The sample preparation was as described in Section 3.2.2. The low viscosity epoxy with special yellow colour epo-dye is used for distinguishing the pore fraction from the bulk matrix i.e. under fluorescent light of an optical microscope (during preparation of the samples) or in electron microscopy investigation, since due to its low atomic number, the epoxy filling the pore network appears black under ESEM (does not scatter electrons). The equipment used for imaging and microstructural investigation was environmental SEM (ESEM Philips XL30, equipped with EDX detector) in backscattered electrons (BSE) mode.

SEM imaging and EDX analysis. Pore structure analysis.

A set of BSE images were taken at randomly selected locations on the polished sections of the plain mortar prisms and in radial direction of increasing distance from the steel surface in the reinforced mortar cylinders (Table 3.2, point 5a). The image analysis was performed at magnification 500x, details for the procedure are given in Chapter 2, section 2.2.3. Morphological changes in hydration products and corrosion products were observed in SEM images but at much higher magnifications in the range of 2000 to 4000x. At the same time, EDX analysis and multi-element mapping were employed at specific positions of the image in order to analyze the chemical compositions and spatial distribution of hydration products in the plain and reinforced mortars. For the pore structure analysis, the original BSE image is segmented by applying a gray-level threshold to create a binary image reflecting the pore phase. The binary image is then subjected to quantitative image analysis for derivation of structural parameters. More detailed information for the generally performed image analysis and the determination of pore structure parameters are presented in Chapter 2, section 2.2.3. The combination of SEM images and quantitative image analysis allows determination of structural information of pore space, such as the porosity and critical pore size. Using a mathematical representation of morphology transformations, pore size distribution can be obtained by applying a sequence of similarly shaped structuring elements of increasing size [3].
3.4 RESULTS AND DISCUSSION

3.4.1 Evolution of electrical resistivity of plain mortar specimens

The mortar electrical resistivity increases with time, depicting similar trends for all groups of plain mortar specimens (Fig.3.2). For specimens T and N (no concentration gradient), the electrical properties are determined by the cement hydration mechanisms and the related microstructural alterations only. For the specimens TN (the specimens cast half-to-half the mixture of T and N specimens, Figs. 3.2c,d), Table 3.2), the chloride concentration gradient would additionally influence the bulk matrix electrical properties. When the cement hydration is a diffusion-controlled process, it strongly depends on the mobility of ions and water in the pore solution, i.e. the rate of hydration will depend on the speed of hydration products formation and their deposition in the pore space. Additives as NaCl are known as accelerators of the hydration process, thus it could be expected that the hydration process exerts less influences on the electrical resistivity in the T ("chloride free") specimens, compared to N (chloride containing) specimens.

![Sample T (Tap water)](image1)
![Sample N (NaCl)](image2)
![Sample TN (Tap Water/NaCl)](image3)

Fig. 3.2 Mortar electrical resistivity (Ohm·m) vs Time (days): a) Specimen T (using tap water); b) specimen N (using 3% NaCl as mixing water); c) Specimen TN (half-to-half the mortar mixture as for T and N); d) a comparison of resistivity values for T, N and TN specimens. The measurements are taken at different sections and as total of the prism (Table 3.2, p.1, 5).

In other investigations [4] it was claimed, that the presence of chloride ions, especially free chloride (i.e. chloride ions in the pore solution) will lead to significantly lower electrical
resistivity. This is deviating from what is observed in this study (see Figs. 3.2 and 3.3). The N specimens showed lower resistivity values up to 35 days of hydration and arrived at similar to T specimens values at 60 days of age (Fig. 3.2d). For the different sections of specimen TN, i.e. the sections free of chlorides A and the sections cast with chlorides B (Fig.3.2), similar values for electrical resistivity were recorded, despite the significantly different chloride concentrations in sections A (e.g. section A3/A4 in the range of 0.0 to 0.2 % per dry cement weight), compared to sections B (e.g. section B3/B4 about 1% per dry cement weight) (Fig. 3.3). The highest values for total electrical resistivity (Fig.3.2d) were recorded for specimen TN. It can be concluded that the electrical resistivity is not dependent on the ion concentration alone and increasing resistivity does not always mean low aggressive ion concentration, especially for high RH conditions. The latter statement is supported by the derived ion concentrations (Fig. 3.3).

Fig. 3.3 Chloride concentration (derived wet chemically in % per dry cement weight) vs time (days) for total Cl (a) and free (water soluble) Cl (b) in specimen TN (averaged data from chemical analysis of three identical specimens at same age).

3.4.2 Chloride-induced changes of hydration products in plain mortars

For the plain mortar specimens, representative ESEM images of bulk matrix morphology are given in Fig.3.4, bulk matrix porosity and pore size distribution curves are depicted on Fig.3.5.

Fig.3.4 presents the typical ESEM images and the corresponding EDX spectra for hydrated cement, indicating variations in morphology and chemical compositions of the calcium-cilica-hydrate (C-S-H) in the plain mortar specimens. The micrographs clearly reveal the differences in porosity and morphology of hydration products induced by chloride ions. The high Ca/Si ratio of at least 2.19 found for the N specimens was a chloride-induced effect. The typical Ca/Si ratio of C-S-H in Portland cements is about 1.8. The surface charge on C-S-H depends on its Ca/Si ratio: when the Ca/Si ratio is high, the surface charge of C-S-H is positive and anions such as Cl$^-$ and OH$^-$ are adsorbed on the C-S-H fibers but cations, as Na$^+$ and K$^+$, remain in the pore solution. In contrast, if the Ca/Si ratio is lower than about 1.2 to 1.3, the surface charge of C-S-H becomes negative and alkali cations are incorporated on the C-S-H, thus decreasing the alkali ion concentrations in the pore solution [5]. Therefore, in the case of relatively high Ca/Si ratio such as...
2.19 to 2.95 obtained for the N specimens, the alkali ions in the pore solution may not be suppressed by C-S-H as in the case of T specimen which had a low Ca/Si ratio of 1.4.

Although the porosity values for the N samples were significantly lower than for the T samples as seen in Fig. 3.5, similar values of resistivity measurements for the two groups of plain mortars were obtained (see Fig. 3.2).

![Fig. 3.4 ESEM images and the corresponding EDX spectrums of plain mortars: (a) without admixed chlorides (sample T) and (b) with admixed chlorides (sample N) (age 60 days, w/c 0.5)]

The negative charge of the C-S-H in specimens T (increased OH⁻ concentration in the pore solution) and the positive charge of C-S-H in specimens N (OH⁻ and Cl⁻ adsorbed on the C-S-H)
fibers, thus a decreased amount of OH⁻ and Cl⁻ will be present in the pore solution), is probably one of the reasons for similar electrical resistivity values for specimens T and N. Further, if a correlation of the measured chloride concentrations and the electrical resistivity values is performed (Fig.3.6), it is obvious that microstructural alterations and surface charge of the bulk matrix are factors, significantly contributing to the electrical properties, rather than the conductive nature of chloride ions alone.

As seen from Fig. 3.6, chloride concentration increases in section A4 (Fig. 3.6a) and decreases in section B4 (Fig. 3.6b) (as already mentioned chloride diffusion due to concentration gradient is in direction from sections B (cast with 3% NaCl) towards sections A (initially free of chlorides) in the specimens TN, Table 3.2). Electrical resistivity values however are similar in all sections (as also shown on Fig. 3.2), moreover electrical resistivity increases in both sections A4 and B4 with time, despite the differences in chloride concentration. The phenomenon is a combined effect of cement hydration with aging on one hand, the influence of NaCl as accelerator of cement hydration on the other [6, 7] and the alterations in microstructural properties of the bulk matrix. As reported in [8], bulk conductivity measurements and their respective pore fluids in comparable mortar mixtures, even if no chlorides are present in the cementitious matrix, show that changes in pore structure exert a greater influence on the measured conductivity. Hence, the electrical properties at early ages of cement hydration are determined mainly by changes in the pore structure, rather than the changes in the pore solution. To this end, resistivity is not only dependant on the presence of conductive ions (as chlorides) in the pore solution, but is also a function of the pore structure and the physico-chemical changes in the C-S-H matrix (as discussed above), thus influenced by the movement of the pore solution ions in the pore network.

3.4.3 Permeability prediction for plain mortars

Relevant to the morphological aspect of pore structure the specific surface area, \( S_V \), is a widely used parameter. It is defined as the surface area of pore phase per unit test volume in standard stereological terms, and can be derived from the total perimeter length of pore features per unit
test area on a statistical basis [9]. This parameter was measured for all the plain mortar specimens in this study.

### Table 3.3 Structural information derived from SEM images for the plain mortars (age 60 days; w/c 0.5)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>T (using tap water)</th>
<th>N (using NaCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (%)</td>
<td>30.46</td>
<td>13.54</td>
</tr>
<tr>
<td>Critical pore size $l_c$ (µm)</td>
<td>1.585</td>
<td>0.951</td>
</tr>
<tr>
<td>Specific surface area $S_V$ (µm⁻¹)</td>
<td>1.088</td>
<td>0.410</td>
</tr>
<tr>
<td>Pore distribution density PDD (µm²)</td>
<td>1.454</td>
<td>0.199</td>
</tr>
<tr>
<td>Intrinsic permeability $k$ (m²)</td>
<td>5.77x10⁻¹⁷</td>
<td>1.04x10⁻¹⁹</td>
</tr>
</tbody>
</table>

Another characterizing parameter, the so called pore distribution density (PDD) was also measured for the two groups of plain mortar samples. The pore distribution density is a three-dimensional structural parameter derived from the skeleton length of pore features observed on two-dimensional section images. For details of the definition and measurement procedures of this parameter, see Chapter 2 and [10]. This parameter has been found to show a higher degree of correlation with water permeability of cement pastes than the conventional parameters of porosity and critical pore size often used for characterizing the pore structure [10]. The good correlation can be attributed to the fact that this new parameter PDD contains information on both pore size and connectivity of pore space. Results of the pore structure analysis are summarized in Table 3.3 for the plain mortars. The derived structural information allows prediction of the intrinsic permeability, $k$, of the mortars on the basis of empirical relationships between pore structure and permeability. For this purpose, an upgraded version of the Katz-Thompson equation was employed (Chapter 2, [11]), which incorporates the PDD and has been demonstrated to be capable of significantly improving the quality of predicted values [10]. Calculated values of permeability are also given in Table 3.3. Results reveal clearly that permeability of the mortars decreased by two orders of magnitude for the specimens prepared using admixed chlorides. The estimation is generally in line with the experimental measurements, reported in other research [12] under comparable conditions. Furthermore, the outcomes discussed in this Chapter 3 for plain mortar are consistent with investigations for the bulk matrix of reinforced mortar (Chapters 4 and 6), plain concrete (Chapter 7) and reinforced concrete (Appendix III). These results confirm the close relationship between pore structure and permeability of cementitious materials.

As discussed in Section 3.4.1, the similar resistivity measurement results for the two groups of plain mortars, given in Fig. 3.2, imply that pore solution chemistry is not the only decisive factor affecting the resistivity of mortars and concretes, but a combined effect of ion transport mechanisms and the resulting alterations in the pore structure are inducing the development of the electrical properties. As reported in [13], there is a linear relationship between the diffusion chloride coefficient, $D_{Cl}$ and inverse of resistivity, $1/\rho$ which is the conductivity. Although the diffusion of chloride ions into mortars and concretes is known to contribute to the overall electrical properties, the relationship between chloride concentration and electrical resistivity is apparently not always linear i.e. increased resistivity does not always mean low chloride concentration. The factor which influences the electrical resistivity in cement based materials at most, is the moisture content. When chlorides are present in the bulk cement-based matrix,
Electrical properties, morphology and microstructure of plain and reinforced mortar

significantly contributing factors become the chemical binding mechanisms and microstructural properties. The former contribute to morphological alterations in hydration products and surface charge of the bulk matrix i.e. the influence of the pore solution ions can be quite significant. The latter determine the electrolytic path in the system and the pore interconnectivity i.e. the ease of aggressive ion penetration and further ion transport.

The TN specimens were used to determine the chloride coefficient of diffusion, $D_{Cl}$ in the plain mortars. One longitudinal half of the specimen was mixed using tap water, while the other half was mixed using NaCl solution. This arrangement sets up a chloride concentration gradient between the two halves of the same mortar specimen (see Table 3.2, p.5). A non-steady state condition is applicable here and the second law of Fick was used, $\frac{\partial^2 c}{\partial x^2} = \frac{1}{D} \frac{\partial c}{\partial t}$, where $D$ is the diffusion coefficient. The Crank’s solution to this equation was employed for estimating, $D_{Cl}$. The Crank’s solution is given as

$c = c_0 \left[ 1 - \text{erf} \left( \frac{x}{2 \sqrt{D t}} \right) \right]$, where $c$ is the chloride concentration at distance $x$ (kg/m$^3$), $c_0$ is the chloride concentration at the exposed surface (kg/m$^3$) (in this case $c_0$ is the concentration in section B2 in specimens TN, Table 3.2), $x$ is the distance from the exposed surface. The values of $\text{erf} \left( x/2 \sqrt{D t} \right)$ vs $x/2 \sqrt{D t}$ are available in standard tables. Based on the chloride profiles obtained along the longitudinal direction of TN specimens, $D_{Cl}$ was calculated to be 6.5x10$^{-10}$ m$^2$/s. This approach and the performed calculations however are an approximation (so is the usage of the second law of Fick for ion transport in concrete), since what is taken into account are the diffusion properties of the concrete, the surface concentration and the penetration depth, but the effects of chloride adsorption, binding mechanisms and micro-cracking are not considered.

Along with the high chloride concentrations, in the range of 0.73 % to 0.93 % per mass of binder, in the separate sections of specimens TN (reported threshold values are varying from 0.2 to 2 w.% per mass of binder [1,14]), the group of plain mortar prisms would have been a highly corrosive environment if reinforcement was present in the prisms. Hence, in terms of corrosion risks, the similar electrical resistivity values in specimens T (no chlorides) and specimens N and TN (with admixed chlorides) would not mean low corrosion risk in the latter two groups.

3.4.4 Chloride-induced microstructural changes in reinforced mortars

The formation of corrosion products in corroding specimen N and lack thereof in the reference specimen R can be seen in Figs. 3.7 and 3.8, while Fig. 3.9 provides a comparison of bulk mortar microstructure between the corroded and reference specimens.

Fig. 3.7a) shows the steel/mortar interface in the upper part of specimen N, revealing the presence of corrosion products. This is the part of the specimen where the bulk mortar had showed a higher degree of shrinkage cracking due to exposure to air, and cracks appeared to be interconnected through voids as seen in Fig. 3.9a).

It is known that the volume of corrosion products is larger than the volume of the reactants, thus the excessive formation of the products results in expansive pressure causing cracking in hardened cementitious systems. The newly formed cracks tend to connect with other existing
cracks forming a percolating network, which in turn promotes further ingress of chloride ions into the mortar.

Fig. 3.7 BSE images of the steel/mortar interface in reinforced mortar N (under chloride ingress). The section images are taken at: (a) the upper part (exposed in air) and (b) lower part (immersed in NaCl solution) of the specimen. The bright white regions represent steel bar (specimens’ age 120 days, w/c 0.6).

Fig. 3.8 BSE images of the reference reinforced mortar R (without external chloride ingress) at different locations on the steel/mortar interface (circled and zoomed areas in Fig.3.8(b) represent Hadley grains in specimen R) (specimens’ age 120 days, w/c 0.6).

Fig. 3.9 BSE images of bulk cement paste in: (a) corroding N and (b) reference R mortars (specimens’ age 120 days, w/c 0.6)
Hadley grains, the hollow hydrate shells such as seen in Fig. 3.8b), were evident in the reference mortar. Its thin shells consist of C-S-H. The reasons for this phenomenon are not well understood, but it appears that the aluminate phase has an important influence. The formation of a possibly amorphous product of C_3A hydration on the surface of the cement grains might inhibit the precipitation of C-S-H on the grain surface and lead to the formation of the separated shells [15]. These are a common feature in all cement pastes. The reference specimen which had a lower hydration rate and a more porous steel/mortar interface than the N specimen showed more Hadley grains.

Fig. 3.10 Elemental mapping, suggesting possible presence and distribution of Friedel’s salt (c), corrosion products composed of iron oxides and iron oxy-chloride complexes (d).

Elemental mapping was employed for evaluating chemical composition of hydration and corrosion products in the mortar/steel interfacial transition zone, within 100 µm distance away from the reinforcement surface. Fig. 3.10a) is an SEM image of the interface revealing the existence of corrosion products in sample N and lack thereof in group R (Fig. 3.10c). Figs. 3.10b) and (f) indicate the spatial distribution of calcium (Ca) and silica (Si) in the vicinity of the steel bar in specimens N and R respectively.
The presence of Si is mainly from aggregates, while Ca is from hydration products. The regions indicated on Figs. 3.10d show lack of Ca and Si at the reinforcement/mortar interface where the chloride-induced corrosion products are found. Fig. 3.10c is the elemental mapping of the image shown in Fig. 3.10a) for Al\(^{3+}\), Ca\(^{2+}\), Na\(^{+}\), Cl\(^{-}\), suggesting a possible formation of Friedel’s salt under chloride ingress. It is known that when NaCl comes in contact with free tri-calcium aluminate, the following chemical reaction will lead to Friedel’s salt formation:

\[
2\text{NaCl(aq)} + [3\text{CaO.Al}_2\text{O}_3.6\text{H}_2\text{O}(s) + \text{Ca(OH)}_2(s) + 4\text{H}_2\text{O} \Rightarrow [3\text{CaO.Al}_2\text{O}_3.\text{CaCl}_2.10\text{H}_2\text{O}(s) + 2\text{NaOH(aq)}
\]

However, Friedel’s salt can also form through chloride attack on existing ettringite [16]. Figure 3.10d) presents the mapping of elements Fe and O, indicating the presence of iron oxidation products. It should be noted that the corrosion products in the upper part of Fig.3.10d), indicated as A, and the lower part, indicated as B, had significantly different chemical compositions. In part A of Fig. 3.10d), elemental mapping and EDX both indicate a significant amount of chloride, suggesting the presence of iron oxy-chloride complexes.

The corrosion products in part B are mainly composed of Fe and O, with negligible Cl. It suggests that the corrosion products may consist of iron oxides/hydroxides, Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), and FeOOH. The portion of FeOOH in corrosion products reportedly increases significantly when the concentration of NaCl solution changes from 0.5\% to 1\% [17], hence, the content of FeOOH could be relatively high in the region B. In contrast, Figs. 3.10e) and (f) show the steel/cement paste interface in specimens R that were free of corrosion products.

### 3.4.5 Microstructural characterisation of reinforced mortar

Fig. 3.11 shows the pore size distribution at the steel/mortar interface in reinforced mortars groups N and R at the age of 120 days.

*Fig. 3.11 Pore structure changes in the steel/cement paste interface of reinforced mortars, exposed to chloride ingress (120 days of age); (a) pore size distribution; (b) critical pore size.*
It is clear that the reference specimen R, had a coarser pore structure, characterized by a porosity of 12.68% and critical pore size of 2.8 µm for the top sections and porosity of 8.8% and critical pore size of 1.27 µm for the bottom section of the specimen. The porosity and critical pore size decreased to 10.87% and 1.27 µm respectively, for the top section and to 4.04% and 1.27 µm for the bottom section of the corroding specimen, N (Fig. 3.11).

The bottom sections of both specimens, being submerged in NaCl solution for specimen N and water for specimen R, have lower porosity compared to the relevant top aerated sections, which is due to moist conditions provided by the solutions. The finer pore structure of the bottom section of specimen N however, demonstrates that the chloride ions promote cement hydration, evidenced by the much lower porosity of 4.04% in the bottom section of specimen N, compared to the porosity of 8.80% in the bottom section of R specimen. These results are also consistent with the observations for the influence of NaCl on the microstructure in reinforced mortar (Chapters 4 and 6), in plain concrete (Chapter 7) and for reinforced concrete (Appendix III).

Fig. 3.12 Pore structure changes in the radial direction of reinforced mortars, exposed to chloride ingress (locations presented in Table 1, p.5a): (a) and (c) - pore size distribution of specimen N and R respectively; (b) and (d) – critical pore size of specimens N and R respectively (specimens’ age 120 days, w/c 0.6).
Chapter 3

Fig. 3.12 shows the variation of the pore structure of the corroding specimen N (Fig. 3.12a,b) and the reference specimen R (Fig. 3.12c,d) in the radial direction of increasing distance from the steel surface (schematically presented in Table 3.2, p.5a). For both specimens N and R, the bulk and edge parts of the specimens (both immersed and aerated sections) have similar porosity values and approximate pore size distribution curves. The steel/mortar interface is expected to be more porous in both specimens, characterised by much higher values of porosity and critical pore size. However, for the bottom section of N specimen, the porosity distribution is much more uniform, without an obvious gradient in the radial direction (Fig.3.12a). The phenomenon confirms the influence of NaCl in refining the pore network (as also reported in [18,19] and consistent with the observations for plain mortar specimens, discussed previously in Section 3.4.3) i.e. significantly reducing the porosity and critical pore size of the submerged (bottom) section and also inducing pore refinement in the aerated (top) section of the specimen N, compared to specimen R. The reduction in porosity from top (aerated) section to bottom (immersed) section for specimen R is due to continuous cement hydration with aging for both sections and the additional moist conditions for the bottom section. The reduction is in the range of: 30 % from top to bottom in the interfacial zone, 37 % from top to bottom for the bulk and 46 % from top to bottom for the edge locations. The reduction in porosity and critical pore size for the corroding specimen N is a result of the combined effects of hydration (in both sections), moist conditions for bottom section and the influence of NaCl in both sections (due to capillary suction chlorides can exert influence in the top aerated section as well). Thus, the reduction in porosity in specimen N is far more significant, compared to specimen R and is in the range of: 65 % from top to bottom for the interfacial zone, 57 % from top to bottom for the bulk and 62 % for the edge locations.

3.5 CONCLUSIONS

This Chapter 3 was focussed on microstructural analysis and electrical and microstructural properties of plain and reinforced mortars in the presence of chlorides. Admixed chloride ions were found to induce changes in chemical compositions of hydration products resulting in the formation of C-S-H with a high Ca/Si ratio in the range of 2.19 to 2.95. The corrosion products observed mainly consisted of iron oxides and iron oxychloride complexes of different compositions and morphological features. The use of quantitative pore structure characteristics of mortars, determined from SEM micrographs with the support of image analysis have been explored in relation to durability-related physical properties of mortars.

Mortars with and without admixed chlorides gave similar electrical resistivity values at early ages. It is likely that the pore refining effect of accelerated hydration due to admixed chlorides in the plain mortars (consequently pore network structural changes) is affecting the electrical properties at most, which is in addition to the physico-chemical alterations in the C-S-H matrix.

Evidenced by the microstructural analysis of the reinforced mortar cylinders, chloride ingress exerts similar effects of pore refinement, but electrical properties here are determined by a
combined influence of chloride binding mechanisms and corrosion process i.e. the denser pore structure of the bulk matrix in corroding specimens is counterbalanced by the percolating network of interconnected cracks (appearing as result of volume expansion of corrosion products). Hence, electrical resistivity, electrolytic paths and chloride-induced corrosion respectively, are not only dependent on the presence of conducting ions (as chlorides) in the pore solution, but are also a function of the pore structure of the bulk cementitious matrix.

References:
CHAPTER 4
ELECTROCHEMICAL BEHAVIOUR OF THE STEEL REINFORCEMENT AND QUANTITATIVE CHARACTERIZATION OF THE STEEL/CEMENT PASTE INTERFACE IN CONDITIONS OF CHLORIDE-INDUCED CORROSION IN REINFORCED MORTARS

Adapted from:

4.1 INTRODUCTION

The corrosion resistance of reinforced cement-based materials represents one of the most important factors in structures durability. Chloride-induced corrosion of steel reinforcement has been a focus of interest for decades in the field of civil engineering. Conventional monitoring techniques include methods and measurements related to the concrete bulk material and related to the steel reinforcement. In terms of corrosion risk assessment, Chapter 3 discussed generally accepted monitoring techniques such as electrical resistivity measurements and determination of chloride concentration. Related to evaluation of the steel reinforcement, potential measurements, polarisation resistance (PR) measurements, electrochemical impedance spectroscopy (EIS) are commonly used, which will be discussed in this Chapter 4. The electrochemical parameters will be further correlated with certain morphologies and quantitative characterisation of the steel/cement paste interface. The electrical and electrochemical methods provide information on the global corrosion situation, therefore an additional quantitative characterisation of the chemical compositions and the spatial distribution of the corrosion products in local areas are of significant importance.

4.2 APPLICABILITY OF ELECTROCHEMICAL TECHNIQUES TO REINFORCED CEMENT-BASED MATERIALS

The assessment of the condition of reinforced structures in terms of: time to initiation of reinforcement corrosion, the level of damage, the performance of the system related to mechanical properties, evaluation of efficiency of protection techniques etc. is always related to estimating corrosion rates i.e. to determination of electrochemical parameters for the steel reinforcement in certain technical and environmental conditions. The electrochemical behavior of steel reinforcement has been extensively studied and outcomes are reported in literature [1-16]. The intention of the investigation in this Chapter 4 is to show how well different electrochemical techniques agree for reinforced cement-based materials, rather than obtaining absolute quantitative parameters (as corrosion rate for example) and further to correlate results with structural and morphological observations of the steel/cement paste interface.

Different approaches hold for the performance of electrochemical (EC) measurements and their applicability, along with possible errors occurring in measuring corrosion parameters related to
reinforced concrete \[7,13,16-20\]. A recent study \[21\] presents comprehensive information on the application of EC techniques in investigating the corrosion of steel reinforcement, emphasizing the fact that all known techniques are applicable and useful for such systems and the inevitable errors in deriving quantitative results are mainly due to inaccurate performance of the techniques, but not the techniques themselves, as for example doubted in \[22-24\]. Generally all EC techniques use simple models which might not always completely apply to all corrosion systems. Therefore the applicability of these techniques, especially in reinforced cement-based materials, being relatively more complex than purely aqueous systems \[25\], are subject to certain limitations, as already reported and discussed in numerous works \[13,16,17,19,20,26-30\].

Relevant to the application of EIS for example, problems occur in the shape of the response of reinforcing steel in concrete (mortar) in Nyquist format, i.e. showing open and incomplete arcs when a capacitive behavior of the steel is observed or various semi- to depressed semi-circles and further appearance of additional time constants due to corrosion and certain chemistry of the bulk material \[2,4\]. Composing complex equivalent electrical circuits, consisting of more time constants is not always a solution in the latter cases, as it is often difficult to attribute them to a good physical model \[3\]. For deriving the polarization (or charge transfer) resistance in EIS applications for reinforced concrete and mortar, the system response at lowest frequency is generally considered for calculations as reported in \[15,16,31-34\] and used in the present study as well. Some studies indicate that this response can also include redox reactions in the product layers \[3,4\]. Additional complications and errors might appear in EIS measurements when high AC frequency is applied, in case of inadequate polarization hold period, high solution resistance etc \[27\]. Despite the above mentioned, the EIS technique remains a powerful tool for investigations in reinforced concrete and mortar systems, as it gives information for the interfacial phenomena and electrical and electrochemical properties of the materials involved, taking into consideration both the bulk cement-based matrix and the steel reinforcement \[4,35\].

Relevant to DC measurements, like PR, the above considerations for possible errors, applicability and reliability hold as well, reported elsewhere \[e.g. 2,3,11,16,36,37\]. In case corrosion rates have to be derived from PR measurements, complications and errors arise related to the following factors \[17,18\]: not known Tafel slopes, lack of linearity of the polarization curve in the region of corrosion potential, lack of steady state, equilibrium potentials of anodic and cathodic reactions very close to the corrosion potential etc. Although the drawbacks of the technique are well known, it is widely applicable for fast evaluation of electrochemical behavior (for example deriving the polarization resistance \(R_p\), as in this study) for reinforced concrete or mortar systems \[10,21,38,39\]. The arising errors can be minimized by establishing a correct sweep rate and waiting time during the measurements, e.g. potentiodynamic measurement using 2.5 to 10 mV/min sweep rate according \[17, 21, 27, 29, 40\] is giving reliable results.

The aim of this Chapter 4 is to investigate the applicability and reliability of a combination of techniques, which at first take into consideration both materials in a reinforced concrete system i.e. the bulk cement-based material and the steel surface. Further, to investigate the relevant interfaces, like the interfacial transition zones (ITZs) in the bulk matrix (cement paste/aggregate) and the interface steel/cement-based material, both bearing significant alterations in conditions of
Electrochemical behavior and quantitative characterization

chloride induced corrosion. Both interfacial zones are considered to have significant contribution to ion transport in the system. The former (the ITZ in the bulk matrix) represents a zone of 15 – 20 μm cement paste, adjacent to the large aggregate particles (sand and gravel). Although it could appear minor, compared to the bulk cement paste, this zone is comparatively more porous than the original bulk, makes up about 20-30% of the total paste volume [58], hence it contributes to the overall mechanisms of ion and pore water transport. The latter interface (steel/cement paste) is of particular interest in reinforced cement-based materials, since this is the zone, relevant to the formation and/or transformations of product layers on the steel surface and its’ properties determine the bond strength degradation in conditions of corrosion for example.

Finally, an attempt was made to correlate derived electrochemical behavior of the steel surface in corroding and non-corroding conditions with microstructural properties and moreover to visualize the relevant alterations of product layers, using morphological investigations. To this end, the combination of techniques was intended to approach in a more fundamental way the understanding of corrosion of steel in concrete and further to enable proves for the efficiency of improved steel protection, using electrochemical methods, which will be subject to discussion in Part II of the thesis.

4.3 MATERIALS, EXPERIMENTAL METHODS AND TECHNIQUES

4.3.1 Specimen groups and experimental set-up
The investigation in this Chapter 4 was performed on reinforced mortar specimens, prepared as already described in Chapter 3, Table 3.2. All specimen groups, the mortar mixture, the curing and experimental conditions are as specified in Chapter 3, the corroding specimens, group N, are here represented by specimens A and B, which are identical in specimen preparation and conditioning, but are separately discussed due to the different steel surface performance with conditioning. The poor mortar quality, the high water/cement ratio and the relatively high NaCl concentration (using 7% NaCl) are designed to accelerate the corrosion process. A group denoted as R, as previously described (Chapter 3), were investigated as reference (control) specimens. The ordinary construction steel bar (“as received” steel, type FeB500HKN (d=6 mm) i.e. no preliminary treatment) was centrally located (embedded length of 80 mm) in all specimens. The electrochemical measurements were performed in immersed conditions (ensuring conductivity of the medium), using MMO Ti mesh as counter electrode and external SCE or (for verifications of results and monitoring, embedded Mn/MnO₂) as reference electrode. The chosen set-up (Fig. 4.1) is found to be appropriate for measurements on steel in mortar (concrete) as generally used in the frame of this research [41, 42] and as also reported in [31].

4.3.2 Experimental techniques
4.3.2.1 Electrochemical measurements: Potential mapping, Polarization Resistance (PR) and Electrochemical Impedance Spectroscopy (EIS) were performed at open circuit potential (OCP) for all groups of specimens. For PR measurement, an external polarization in the range of ±20 mV vs OCP was used at scan rate 0.15 mV/s; EIS was carried out in the frequency range 50 kHz.
to 10 mHz by superimposing an AC voltage of 10 mV. The used equipment was EcoChemie Autolab - Potentiostat PGSTAT30, combined with FRA2 module, using GPES and FRA interface.

Fig. 4.1 Experimental set-up and measurement configuration (the solid dots in the cross-section view (left) represent the locations for microstructural analysis)

4.3.2.2 Wet chemical analysis for determination of alkali and chloride concentrations was performed according standards (ASTM C1218 and ASTM C1152). The data obtained are not subject to extensive discussion in this Chapter. Relevant to the here presented results and discussion is just mentioning the derived total chloride concentration, between 5.7 and 6.0 wt.% per dry cement weight, in the immediate vicinity of the steel bar in the corroding specimens.

4.3.2.3 Scanning electron microscopy (using ESEM Philips XL30) combined with energy dispersive X-ray analysis (EDXA) has been employed for visualization, morphological and microstructure investigations. For measuring structural properties, a set of ESEM section images in radial direction around the steel bar (Fig. 4.1) were obtained with backscattered electrons (BSE) mode, physical size of the reference region of each image is 226 µm in length and 154 µm in width, with a resolution of 0.317 µm/pixel, corresponding to magnification of 500x. Main outcome from a quantitative image analysis, as previously described in Chapter 3, is deriving parameters as porosity, pore size distribution, critical pore size. Further, based on mathematical morphology and stereology approaches, obtaining information for pore distribution density, which corresponds in physical meaning to pore connectivity and permeability. A correlation of pore network parameters and electrochemical behavior is partly presented in this Chapter (Section 4.4) and will be subject to elaborated discussion in Chapter 6.

4.3.2.4 X-ray diffraction (XRD). The steel surface for all investigated specimens (including the “as received”, i.e. non-conditioned and not cast in mortar bar) was analyzed by scanning representative areas of about 1 cm² (directly on the surface) of the test specimens, using a D8 Advance Diffractometer, “Bruker AXS”. A VANTEC position sensitive detector (window 6 deg.) was used for detection. Energy source was CoKα (1.789A) and the tube settings were 45 kV and 35 mA.
4.4 RESULTS AND DISCUSSION

4.4.1 Potential mapping and polarization resistance

In general, open circuit potential readings for steel embedded in cement-based materials are widely used [30,43-45], aiming at determination of the time-to-initiation of corrosion and evolution with time. In chloride containing environments, corrosion initiation is related to the passive layer breakdown, hence is due to exceeding certain threshold levels of chloride in the vicinity of the steel surface, consequently potential mapping is used for determination of chloride thresholds as well [43]. Although the potential readings can be significantly influenced by environmental conditions and the resistivity of the bulk material, also by the degree of pore network saturation [46, 47], they can give valuable qualitative information for the electrochemical behavior of the steel surface in such systems, hence corrosion potential readings were used in the present study as supportive information.

![Fig. 4.2](image)

Fig. 4.2 Evolution of open circuit potential with time for non-corroding specimens (R) and corroding specimens A and B (group N).

Fig. 4.2 depicts the trends of the open circuit potential evolution with time for corroding (specimens A and B, group N) and reference (group R) specimens (up to 120 days of age). As expected, the open circuit potential for corroding specimens A and B (recorded in the potential intervals of -400 to -650 ± 40 mV vs SCE) are beyond the threshold of passivity, which is generally accepted to be -200±70 mV vs SCE for reinforced mortar (concrete) systems [43-45, 48]. Since potential mapping is strongly influenced by the different phenomena in the bulk cementitious matrix and gives only qualitative information, quantification of the corrosion process can be obtained only by polarizing the steel surface, thus deriving parameters as polarization resistance ($R_p$) for example. In the present study, $R_p$ was derived from PR and EIS, taking into considerations all requirements and aspects related to reliable calculation and performance of the measurements [4,16,40,49].

Fig. 4.3 depicts the recorded $R_p$ values from PR measurements, the $R_p$ values for non-corroding specimens (group R) being, as expected, about one order of magnitude higher than corroding specimens (group N) at the end of the test. A slight deviation from the passive threshold (potential of -250 mV vs SCE) was recorded for the reference (non-corroding) specimens, reflected by a
drop of $R_p$ values (Fig. 4.3) between 35 and 60 days of age. Calcium carbonate and iron hydroxy-
carbonates were detected in small amounts on the steel surfaces (Fig. 4.4). The carbonate
compounds are formed most likely in the process of initial hardening of the mortar mixture and
the presence of CO$_2$ in the mixing water or due to very slow penetration of atmospheric CO$_2$
through the mortar cover. This penetration is additionally promoted by the poor quality of the
investigated mortar (w/c ratio of 0.6, large air voids), small dimension of the sample, small cover
depth and high degree of structural heterogeneity of the system.

The XRD observations (Fig. 4.4) support the above statements but a uniform carbonation front
can not be expected in this case. These observations, along with the fundamental behavior of steel
in alkaline solution, explain the shift of the $R_p$ for non-corroding specimens to lower values but
still considerably higher comparing to corroding specimens (Fig. 4.3 and Table 4.1, Section
4.4.2).

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*Fig. 4.3 Evolution of polarization resistance ($R_p$) with time for non-corroding specimens (group R) and
corroding specimens A and B (group N) (values are derived using PR method).*

*Fig. 4.4 X-ray diffraction (using CoK$_\alpha$ radiation) patterns for the steel surface in reinforced mortars from
reference group R and blank sample (as received) steel.*
4.4.2 Electrochemical Impedance measurements

A schematic presentation of the systems under study is presented on Fig. 4.5.

Fig. 4.5 Schematic model of involved interfaces (a) and corresponding equivalent electrical circuit, used to fit the experimental EIS data (b) for the specimens under study.

At least three interface regions should be considered in interpretation of the impedance response (Fig. 4.5a) i.e. the interface of electrolyte and concrete bulk (incorporating concrete cover) – region 1, the inner bulk matrix – region 2 and the steel/cement paste interface – region 3. The equivalent circuit used in the present study (Fig. 4.5b) comprises two time constants in series with the electrolyte resistance. The elements of the equivalent circuit are suggested to have physical meaning as follows: $R_{el+b}$ is the electrolyte (7%NaCl in the case of corroding groups or demineralised water in case of reference group), including contribution of the mortar overall bulk resistance; the first time constant ($R_{pn}$ and $CPE_{pn}$) is attributed to the properties of the cementitious matrix in terms of pore network; the second time constant ($R_{ct}$ and $CPE_{dl}$) deals with the electrochemical reaction on the steel surface. The experimental impedance response in Nyquist and Bode formats for all groups is presented in Figs. 4.6 to 4.8. Summarized data for the best-fit parameters are presented in Table 4.1.

<table>
<thead>
<tr>
<th>Age(days)</th>
<th>$R_{el+b}$ ($\Omega$)</th>
<th>$Q_{pn}$ ($\Omega$)</th>
<th>$R_{pn}$ ($\Omega$)</th>
<th>$Q_{dl}$ ($\Omega$)</th>
<th>$n$</th>
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<tr>
<td>35</td>
<td>400</td>
<td>5.44E-09</td>
<td>0.6596</td>
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<td>70</td>
<td>768</td>
<td>2.62E-09</td>
<td>0.6607</td>
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<td>90</td>
<td>881</td>
<td>1.70E-09</td>
<td>0.6302</td>
<td>512</td>
<td>450</td>
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<tr>
<td>120</td>
<td>1397</td>
<td>9.87E-10</td>
<td>0.6241</td>
<td>755</td>
<td>420</td>
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</table>

Table 4.1 Summarised data for the best-fit parameters, derived on basis of the experimental EIS results, using simulation and fitting procedures, and the equiv. circuits: $R_{ct}$($Q_{dl}$($R_{pn}$($Q_{pn}$($R_{el+b}$)$^n$))), shown in Fig. 4.5.

Gr. R

<table>
<thead>
<tr>
<th>Age(days)</th>
<th>$R_{el+b}$ ($\Omega$)</th>
<th>$Q_{pn}$ ($\Omega$)</th>
<th>$R_{pn}$ ($\Omega$)</th>
<th>$Q_{dl}$ ($\Omega$)</th>
<th>$n$</th>
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<tr>
<td>35</td>
<td>202</td>
<td>4.90E-07</td>
<td>0.6232</td>
<td>22</td>
<td>171</td>
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<tr>
<td>70</td>
<td>208</td>
<td>8.35E-10</td>
<td>0.3643</td>
<td>27</td>
<td>36</td>
</tr>
<tr>
<td>90</td>
<td>230</td>
<td>7.56E-10</td>
<td>0.4213</td>
<td>38</td>
<td>35</td>
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<tr>
<td>120</td>
<td>264</td>
<td>6.93E-06</td>
<td>0.5744</td>
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<td>30</td>
</tr>
</tbody>
</table>

Gr. N, sp. A

<table>
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<th>Age(days)</th>
<th>$R_{el+b}$ ($\Omega$)</th>
<th>$Q_{pn}$ ($\Omega$)</th>
<th>$R_{pn}$ ($\Omega$)</th>
<th>$Q_{dl}$ ($\Omega$)</th>
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</tr>
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<td>35</td>
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<td>1.38E-07</td>
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</tr>
<tr>
<td>70</td>
<td>216</td>
<td>2.82E-09</td>
<td>0.4662</td>
<td>36</td>
<td>44</td>
</tr>
<tr>
<td>90</td>
<td>224</td>
<td>1.56E-10</td>
<td>0.4103</td>
<td>63</td>
<td>59</td>
</tr>
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<td>120</td>
<td>307</td>
<td>1.27E-07</td>
<td>0.4709</td>
<td>74</td>
<td>81</td>
</tr>
</tbody>
</table>
Fig. 4.6 EIS response for non-corroding specimens (group R) for the time domain 35 to 120 days of age: (a) Nyquist format; (b) enlarged area of high frequency response; (c) Bode plots

The shape of the experimental curves for all specimens is reflecting typical response of reinforcing steel in the alkaline medium of cement paste and in conditions of chloride present at the steel/paste interface, as reported also in [21, 31, 32]. Since the specimen geometry is equal for all groups and specimens, the diagrams apply for the total electrode, without conversion for surface area. The same holds for the fit-parameters in Table 4.1, except the charge transfer resistance \( R_{ct} \), calculated in kOhm.cm\(^2\) (electrode surface area is 16 cm\(^2\)). The replacement of pure capacitance \( C \) with constant phase element (CPE) in the equivalent circuits (Fig. 4.5) is widely accepted for systems as in this study [2, 5, 16, 50], being denoted to inhomogeneities at different levels i.e. steel surface roughness, bulk matrix heterogeneity etc. The CPE is an empirical mathematical description of the observed impedance response and is defined by [51] as:

\[
Z = j\omega^{-n}/Y_0
\]

being further quantified by the parameters \( Y_0 \) and \( n \) (CPE constant and CPE factor respectively).
At low frequencies (0.01 Hz) close to capacitive behaviour was observed for group R, indicating situation of passivity (Fig. 4.6) in contrast to the inclined to the real axis semi-circles for the corroding group N, specimens A and B (Figs. 4.7 and 4.8), reaching a shape of a semi-depressed circle in case of group A (Fig. 4.7).

**Fig. 4.7 EIS response for corroding specimens A (group N) for the time domain 35 to 120 days of age: (a) Nyquist format; (b) enlarged area of high frequency response; (c) Bode plots.**

The response for group N reflects the evolution of corrosion with time, also evidenced by the more significant phase angle drop for these specimens, compared to the reference group R (Bode plots in Figs. 4.6 to 4.8). The impedance response in the low frequency domain was used for deriving the charge-transfer resistance of the steel bars [15,16,31-34]. The recorded $R_{ct}$ for group R was at least one order of magnitude higher than the $R_{ct}$ for group N (Table 4.1).

The high frequency arcs (incorporated plots of enlarged area – up right of the Nyquist plots for each group, Figs. 4.6b to 4.8b) and the response evolution with time, suggest that $R_{el+b}$ is the
electrolyte resistance, including contribution of the mortar bulk resistance, as the derived values increase with time due to cement hydration (cement hydration modifies the microstructure of the bulk matrix as hydration products gradually fill in the available space in the cement paste).

Fig. 4.8 EIS response for corroding specimens B (group N) for the time domain 35 to 120 days of age: (a) Nyquist format; (b) enlarged area of high frequency response; (c) Bode plots.

The derived values for \( R_{el+b} \) for the reference group are in the range of 400 to 1390 Ohm (from 35 to 120 days of age) and about 200 to 300 Ohm for the corroding groups (Table 4.1), which is consistent with observations in similar research [3], reporting resistance of 900 Ohm for free of chloride and 450 Ohm for mortar containing 1% chlorides (about 6% total chloride per dry cement weight was found at the steel/cement paste interface, hence lower resistivity was observed for the relevant specimens in this study).

In modeling the steel/cement paste interface, several researchers [13,16,52] have proposed the equivalent circuits to include elements for diffusion in addition to the CPE, coupled with the charge transfer (\( R_{ct} \)). Including diffusion elements normally explains low frequency tails which
could appear in some impedance diagrams [2], however such response was not observed in the present study. The EIS measurements were performed up to 10 mHz as lowest frequency for both corroding and non-corroding groups, hence the charge process of CPE predominates in the response and no diffusion effects (which will be at frequency lower than 1 mHz for passive and lower than 5 mHz for active state [16]) were recorded. The proposed circuit (Fig. 4.5) gives generally good fitting results. Additional components were not included, taking into consideration the time of exposure and test conditions of only 4 months.

Looking at the equivalent circuit (Fig. 4.5) and the fit parameters (Table 4.1), the first time constant (for all groups) is definitely related to the pore network of the bulk material, as the power of CPE is mostly in the range of 0.4 to 0.6, pseudo capacitance values are very low ($Y_\infty$ in the range of $1.3e^{-7}$ to $9.8e^{-10}$), hence can not be denoted to the electrical double layer on the steel surface or to redox-reactions [53]. The second time constant is related to the charge transfer resistance and double layer capacitance at the steel surface, as the CPE power in the range of 0.69 to 0.86 is related to the electrochemical reaction, the pseudo capacitance is stable with time for the reference group and increases for the corroding groups, which is consistent with the drop of the derived $R_c$ of the latter two.

Obviously an equivalent circuit with a single capacitor is not in harmony with the response of all specimens. On the other hand, it is questionable if phase shifts originating from phenomena very different from real capacitance, especially in such systems, can be modelled with complicated electrical circuits [3]. Hence, the proposed relatively simplified equivalent circuit is believed to be satisfactory for evaluation of the system parameters, where the components have clear physical meaning. This consideration is supported by the values obtained from the fitting procedures (Table 4.1), which correspond well to values reported in similar research [3,7,31,53-55] and evidenced by an acceptable error – Fig. 4.9. The sine shape indicates that obviously the equivalent circuit can be further improved; however more complicated circuits are not subject to this paper. The relative error in the frequency domain 100 Hz to 0.01 Hz (corresponding to the frequency region for calculation of $R_c$) is almost zero, hence the determined values for charge transfer resistance can be considered as reliable. Moreover, the derived values for $R_c$ are consistent with the derived $R_p$ values from PR method – Fig. 4.10. Table 4.1 comprises the best-fit values for the rest of the components from the equivalent circuits, including pore network resistance and charge transfer resistance, which will be further discussed in correlation with microstructural properties of the bulk material.
4.4.3 Microstructural analysis

The electrolytic path in reinforced mortar and concrete systems is dependent on the kinetics of aggressive ions transport mechanisms which are affected by pore size distribution and pore connectivity. Porosity and ionic conductivity are related to main physicochemical processes, which affect the material properties. Hence, pore structure is highly relevant to the electrical properties of materials (as previously discussed in Chapter 3) and consequently influences the electrochemical phenomena in systems as in the present study.

The structure parameters in the present study were derived on basis of microstructural investigation in radial direction around the steel bar (Fig. 4.1). Graphical presentation was presented and partly discussed in Chapter 3 and reported in [56, 57]. Generally, the interfacial zone at the steel surface, exhibits a high connectivity and a coarser pore structure than the bulk matrix. Fig. 4.11 clearly shows that for the reference group R, the interfacial porosity is the highest, the bulk and edge porosity are...
similar to the corroding groups. The pore connectivity of group R is lower than the corroding group N, specimens A and almost equal to specimens B. The phenomena are attributed to the formation of hollow hydrate shells surrounded by a thin shell of calcium-silica-hydrate (C-S-H). As previously discussed in Chapter 3, the reasons for this phenomenon are not well understood, it is believed that the formation of possibly amorphous hydration product on the surface of the cement grains might inhibit the precipitation of C-S-H on the grain surface and lead to the formation of the separated shells [58], which contribute to the total porosity, but do not significantly affect the structure permeability and connectivity.

Hence, ion and water transport can not be determined by only one parameter alone, but should be considered as a function of a combination of structural parameters. These parameters bare alterations in conditions of chloride ingress, chloride binding and corrosion at the steel/paste interface, which is the main reason for the different electrochemical behavior of the steel surface in specimens of group N (specimens A and B), being otherwise completely identical in mixture, set-up and specimens geometry. This consideration is evidenced by the significant difference in pore structure parameters of specimens A and B at the end of the testing period – Fig. 4.11 and supports the experimental results from all electrochemical methods.

4.4.4 Electrochemical behavior and microstructural properties
As aforementioned, the high frequency impedance response in EIS measurements is attributed to bulk matrix properties.

Fig. 4.12  Evolution of bulk matrix and pore network resistivity for specimens group R (a) and corroding specimens A and B (b), calculated using geometrical parameters of the cell and the data obtained from EIS measurements (Table 4.1).

Fig. 4.12 depicts the evolution of the bulk matrix resistivity and the pore network resistivity in Ohm.m for group R (a) and group N, specimens A and B (b), derived from the EIS data and in particular the resistance $R_{el+b}$ (including electrolyte) and the resistance $R_{pn}$. It is evident that the non-corroding group (R) exhibits higher values of bulk and pore network resistivity, increasing with time, despite the more open pore structure and lower rate of cement hydration. In contrast,
the corroding specimens A and B are characterized by much lower bulk and pore network resistivity values, although it is known that NaCl is accelerator of cement hydration, hence lower porosity, denser pore structure and higher resistivity would be expected [56, 59-61].

The phenomenon in the non-corroding specimen is attributed to the already discussed above presence of certain features of the pore network, which do not contribute to ion and water transport, hence despite the highest porosity of 12.68 % at the interface region and critical pore size of 2.8 µm (Fig. 4.11), the non-corroding group R has high resistivity (increasing from 60 to 180 Ohm.m for the bulk matrix and 25 to 85 Ohm.m for the pore network). The corroding specimens A and B have much lower resistivity, partly ascribed to the presence of NaCl. Although having identical mixture and set-up, specimens A and B exhibit significant differences in microstructural parameters (Fig. 4.11) at the end of the test, consequently they vary in resistivity values as well: for the bulk matrix between 26 and 34 Ohm.m for specimens A and 26 and 39 Ohm.m for specimens B (increased resistivity for specimens B at the end of the test), in accordance with the pore network resistivity of 3 to 7 Ohm.m for A and 3 to 10 for specimens B.

The resistivity values are consistent with the microstructural parameters for both specimens (Figs. 4.11, 4.12). The interface region for specimens A is characterized by 10.87 % porosity and 1.27 µm critical pore size, while specimen B has lower interface porosity of 10.20 % and 0.9 µm critical pore size. More significant differences apply for the structural parameters at bulk and edge regions (schematic points on Fig. 4.1), where for specimens A, porosity is 5.25 %, critical pore size 0.78 µm and for specimen B – porosity is 1.55 % with critical pore size 0.63 µm. The denser pore structure of specimen B and lower connectivity determines the higher resistivity values, compared to specimen A, although both specimens are corroding samples from one and the same group. This confirms the intimate relationship between pore structure and permeability of reinforced cementitious materials which determines the chloride ingress in the systems under study and the corrosion process with time respectively.

Structural alterations relevant to the corrosion process are contributing as well: the volume of corrosion products is larger than the metallic ions; their excessive formation results in expansive pressure and causes cracking (as discussed and schematically presented in Chapter 2). The newly-formed cracks tend to connect with the existent cracking and form a percolated network, which in turn promotes the further ingress of chloride ion into the steel surface (as expansion and cracking are multiplying the amount of connected channels for Cl\textsuperscript{-} movement). This process is obviously more pronounced in specimens A than in specimens B, as connectivity in group B is lower, consequently the structural parameters determine the electrochemical behaviour to be different than group A.

The above observations on structural changes and electrical properties are supported by: the open circuit potential values (shifting of \(E_{corr}\) for specimens B to more noble values at the end of the test (Fig. 4.2); the derived polarization resistance from RP measurements (higher \(R_p\) for specimens B compared to specimens A at the end of the test (Fig. 4.3) and evidenced by the EIS measurements.
The pseudo-capacitance on the steel surface (Table 4.1) can provide sufficient information for the electrochemical process, in order to compare the present study with literature data however, it is also presented as double layer capacitance in µF/cm² (Fig. 4.14), using the following [62]: for a given frequency ω the following relation between the imaginary part of the impedance of the CPE (Z_{CPE}) and the impedance of the fitted capacitance (Z_C) is valid: \[ \text{Im}(Z_{CPE}) = Z_C \cdot \text{Im}[1/Y_0(j\omega)^n] = \frac{\omega}{C}. \]
Chapter 4

Evolution of interfacial capacitance $C_{dl}$ for specimens A and B, group N and for specimens group R

Fig. 4.14 Evolution of interfacial capacitance with time (calculated on basis of pseudo-capacitance in the low frequency domain – Table 4.1) for non-corroding group R and corroding specimens A and B.

Using the relationship: $(j\omega)^n = \omega^n \cos(n.\pi/2) + j\sin(n.\pi/2)$, the relation between the CPE parameters $Y_o$ and $n$ and the capacitance C is: $C = Y_o \omega^{-n}/\sin(n.\pi/2)$. The change of the derived capacitance values with time is depicted on Fig. 4.14. The derived values for reference group R are almost constant with time, in the range of 37 to 39 µF/cm$^2$. In contrast, the corroding specimens exhibit higher values of $C_{dl}$ being in the range of 65 to 73 µF/cm$^2$ average for the whole period, with increasing trend for specimens A and decreasing trend for specimens B at the end of the period (about 42 µF/cm$^2$). As mentioned, the transition in electrochemical behavior of specimen B is reflected also by the derived $C_{dl}$, the latter showing a decreasing trend at the end of the test. The derived values for $C_{dl}$ correspond well to reported in literature for similar systems and conditions [4,7,21,31] and are denoted to the electrochemical reaction on the steel surface.

4.4.5 Microstructural and morphological observations on the steel/cement paste interface;
Quantitative characterizations of corrosion products

The corrosion resistance of reinforced cement-based materials is due to the chemical nature and physical conditions operating at the steel-paste interface. The composition of the passive film, normally formed on reinforcing steel in the alkaline medium of cement-based materials, and the mechanism of its breakdown by chlorides can be explained by more than one model. However, it can be assumed that chloride ions form soluble complexes with iron, leading to localised acidification and consequent pit growth. Hence, chloride induced corrosion is a very local and non-uniform phenomenon on the steel surface.

In this study, in addition to observations on cross sections of the steel/cement paste interface, the steel reinforcement was removed from the mortar specimen, showing layers of red and brownish-red colored rust in different amounts and positions on the steel surface. These positions are subjected to SEM observations, EDX analysis and identified by XRD patterns. A magnification of about 500x (corresponding to an image resolution of 0.3 µm/pixel) is enough for conventional microstructural analysis by SEM images. The morphological observations of hydration products and corrosion products are realized at much higher magnifications up to 2000x. At the same time,
multi-element mapping is employed at certain positions on the images in order to analyze the chemical compositions and spatial distribution of specific ions, hydration or corrosion products.

4.4.5.1 XRD diffractogram

Fig. 4.15 shows the XRD pattern for a representative area of about 1 cm² on the surface of the corroding steel bar. The two extremely strong peaks from the iron substrate are truncated so as to highlight the detected iron oxides and iron oxy-hydroxides. Contributions of quartz (SiO₂, deriving from the sand in mortar) and calcite (CaCO₃) are found; calcite is represented by a relatively shallow peak at 2θ of 34°, which is attributed to the penetration of a small amount of atmosphere CO₂ into the steel surface. Iron oxyhydroxides (FeOOH) vary in chemical compositions and present different morphologies, according to which they can be categorized as goethite (α-FeOOH), lepidocrocite (γ-FeOOH), akaganeite [Fe³⁺(O,OH,Cl)], denoted as G, L and A, respectively (Fig. 4.15).

4.4.5.2 SEM and EDX observations

SEM photographs of representative locations on the rust spots at steel-mortar interface are in agreement with the findings from XRD. Fig. 4.16 (left) shows the unetched steel (bright white) in the left part of the image, with some loose (low density, highly porous) hydration gels (C-S-H) deposited on the steel surface. Multi-element mapping indicates very high concentration of NaCl (bright white crystals) in the right part of the image, revealing the arrival of chloride ions at steel surface. Chloride arrival at the steel/cement paste interface was detected by EIS as well (see Section 4.4.2) in terms of changed shape of the plotted response curves from almost straight line to a depressed semi-circle. The chloride concentration in this case is about 6% per cement weight, significantly exceeding the threshold value for corrosion initiating, reported as 0.2 - 0.4% per cement weight (Chapter 2, Annex I).
Fig. 4.16 Overview (BSE image, 125x) of the steel reinforcement surface in mortars (w/c=0.6, subjected to external 7% NaCl ingress for 120 days), revealing the steel/mortar interface (top left) and EDAX elemental mapping.

Fig. 4.17 provides direct visualization (left) and quantification (right) of corrosion products distributed in the bulk mortar. The significantly different morphologies of the corrosion products are clearly revealed in Fig. 4.18, displaying flower-like and globular products of various dimensions.

Fig. 4.17 Overview (BSE image, 125x) of steel reinforcement surface (left) in mortars (w/c=0.6) subjected to external chloride ingress (7% NaCl solution) for 120 days and EDAX quantification (right).

Fig. 4.18 (right) highlights the corrosion products in the centre part of Fig. 4.18 (left) at a higher magnification (500x). EDX (Fig. 4.19) reveals that lamellar and globular crystals are both iron oxycloride complexes, whereas the different morphology can be attributed to different mass ratio of iron and chloride ions. When the Fe/Cl ratio is in the range of 3-3.5, the complexes present a general lamellar shape. In contrast, at a much higher ratio of 6.5-7, a globular shape is
observed – Fig. 4.20. The former type is expected to be responsible for volumetric expansion rather than the delicate, globular and whiskery minerals.

Fig. 4.18 Overview (BSE image, 100x) of steel surface showing variety of corrosion products (left) and higher magnification (500x) of the corrosion products in the centre part (right), depicting formations with different morphology (A, B and C).

Fig. 4.19 EDX spectrums of the corrosion products shown on Fig. 4.18 (right), different in morphology and Fe/Cl ratio (quantification shown in Table 4.2).

Fig. 4.20 (left) 1000x magnification of region C in Fig. 5 (right), displaying iron oxochloride complexes of globular morphology and (right) the corresponding EDX spectrum.

Table 4.2 presents the chemical composition (in mol %) of oxides for the circled regions in Fig. 4.18 (right) and Fig. 4.21. As mentioned above, the different Fe/Cl ratio determines different morphology of the corrosion products. EDX analysis of the flower-like region in Fig. 4.21
demonstrates the existence of goethite ($\alpha$-FeOOH) crystals, which are generally grown on a relatively flat surface mainly composed of lepidocrocite ($\gamma$-FeOOH).

Table 4.2. EDX quantification of circled regions on Fig. 4.18 (right) and Figs. 4.20 and 4.21 - steel surface in mortar ($w/c=0.6$), subjected to external chloride ingress for 120 days.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>mol. %</th>
<th>Type A (Fig. 4.18)</th>
<th>Type B (Fig. 4.18)</th>
<th>Type C (Figs. 4.18;4.20)</th>
<th>Type D (Fig. 4.21)</th>
<th>Type E (Fig. 4.21)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>1.19</td>
<td>3.81</td>
<td>2.29</td>
<td>4.90</td>
<td>8.51</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>1.18</td>
<td>4.88</td>
<td>3.58</td>
<td>2.34</td>
<td>3.29</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.54</td>
<td>1.75</td>
<td>1.35</td>
<td>0.97</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.83</td>
<td>2.75</td>
<td>2.72</td>
<td>2.45</td>
<td>2.20</td>
<td></td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.35</td>
<td>1.49</td>
<td>2.83</td>
<td>1.89</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>Cl$_2$O (Cl-containing compounds)</td>
<td>20.78</td>
<td>19.89</td>
<td>11.47</td>
<td>1.20</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.14</td>
<td>0.13</td>
<td>0.44</td>
<td>0.14</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.71</td>
<td>0.62</td>
<td>1.09</td>
<td>4.71</td>
<td>5.83</td>
<td></td>
</tr>
<tr>
<td>Fe$_2$O$_3$ (iron oxides/hydroxides)</td>
<td>74.28</td>
<td>64.69</td>
<td>74.23</td>
<td>81.41</td>
<td>77.53</td>
<td></td>
</tr>
</tbody>
</table>

The right picture in Fig. 4.21 shows a magnified (2000x) detail of the flat (light grey) region at the centre-bottom part of Fig. 4.21(left). At a higher magnification level (2000x), it is evident that the flat region consists of minerals with nesty and foam-like morphologies. The foam-like products are attributed to lepidocrocite, nested by some lamellar type crystals in the bottom-right region of Fig. 4.21 (circled region). This nest area indicates an evident lamellar growth, with a larger lamellar size at the centre than in the periphery, which is typical for iron oxychloride. Their face-to-edge intergrowth and, in some cases, their exfoliation, favors a very large volume representative both of a high specific surface area and expansive product. Similar forms have been found and reported in [63] as ‘rose-like crystallisation’ products in presence of chloride. The expansive character of these rose-like crystals can account for the clearly visible microcracks on the dense structure of the product layer formed on the steel surface (see Fig. 4.21 right).

Microscopic observations reported two layers of corrosion products in concrete subjected to carbonation [64]: an inner one composed mainly of non-stoichiometric magnetite and probably Ca substituted magnetite, and an outer one composed of $\alpha$-FeOOH and $\gamma$-FeOOH. This is in
agreement with the SEM investigations on local areas in this study. As reported in [65], the structure of α-FeOOH is more porous because of its tendency to grow in needles. The morphological observation in this study reveals non-adherent layer of corrosion products, mainly consisting of porous and crystallised goethite and lepidocrocite, as confirmed by the XRD analysis. The investigated steel surface did not show significant evidence of formation of high-valent iron oxides (e.g. magnetite).

Although the oxidation and reduction of corrosion products are dependent on oxygen availability, in this case, this is not influencing the iron oxides transformation to a considerable extent. At first, oxygen availability is limited at the steel/mortar interface (comparing to aqueous solutions); secondly, the contribution of direct oxygen electro-reduction at the underlying steel surface to the cathodic reaction of high-valent oxide formation is negligible at the stage of magnetite formation (because of the slow diffusion of oxygen into the pores of the rust layer). Furthermore, ESEM and XRD did not detect obvious formation of magnetite on the steel surface; the investigated steel surface was corroding with formation of mainly low-valent iron oxides (wustite, see Fig. 4.15)

The mortar specimens were subjected to chloride ingress, hence, the presence of akaganeite \([\text{Fe}^{3+}(\text{O,OH,Cl})]\) can be expected. The XRD pattern (Fig. 4.15) reveals sharp peaks at 2θ=66° (representative for akaganeite with CoKα radiation, corresponding to planar spacing of d=1.64 Å), which confirms the presence of crystalline akaganeite in the rust layer. SEM observation (Fig. 4.22) depicts a typical needle-like morphology and intensive growth of akaganeite in the vicinity of the steel/paste interface (Fig. 4.22 left) and in air voids (Fig. 4.22 right).

Akaganeite is normally present in less adherent rust layers [66] on a steel surface, exposed to chloride environment. This oxide is not accommodating in the rust layer, thus is impeding the formation of a film with good protective properties. The formation of less adherent akaganeite is always accompanied by increased corrosion rates.
In the case of chloride ingress, chlorides partly react with the cement paste, the rest remaining free in the cement pore solution, the latter initiating localised corrosion on the steel surface. Free chlorides in the form of NaCl crystals were observed both in the cement paste and in the vicinity of the steel bar (Fig. 4.23).

![Fig. 4.23 Cement paste in the corroding specimen (polished section) at magnification of 1000x (left), revealing the accumulation of free NaCl crystals of cubic morphology (right, 2000x, non-polished section) incorporated in the cement paste on the steel/mortar interface.](image)

The chemically-bound chlorides form chloro-aluminate complexes, e.g. 3CaO·Al₂O₃·CaCl₂·10H₂O (Friedel’s salt). The formation of Friedel’s salt depends on the amount of tricalcium aluminate (C₃A) phase in the cement.

![Fig. 4.24 Friedel’s salt formation (circled region) in the vicinity of steel/mortar interface (left) and the corresponding EDX analysis (right), showing the typical composition for Friedel’s salt (Ca-chloro-aluminate).](image)

When chlorides react with the cement paste and form Ca-chloro-aluminates, they incorporate in the cement hydrates, thus forcing portlandite to release OH⁻ so as to reach equilibrium with the alkali ions in the pore solution. Binding mechanisms can impede the transport of free chloride, thus delays the corrosion initiation. Friedel’s salt was detected in the vicinity of the steel/mortar interface in the investigated mortars (Fig. 4.24).

According to [67], the formation of Friedel’s salt will lead to recombination of ion charges in the pore solution. Thus the OH⁻ ions from Ca(OH)₂ crystals are the main source of anions to balance...
the charge. As reported in [59], the mechanism of chloride binding is not that simple. A differentiation has to be done between chloride binding with and without OH release. In the latter case, an equivalent amount of Na$^+$ incorporates in the C-S-H lattice, hence, the Na$^+$ concentration is decreasing after a certain hydration time (approximately 60 days). This is in accordance with the findings from studies on ion transport in plain mortar prisms, part of the research project [56], previously discussed in Chapter 3. The sodium ions concentration is decreasing as a result of binding with the C-S-H in the cement paste, thus achieving ion equilibrium. However, the limit of chloride binding capacity depends on the type of cement and of the cation type. As reported in [59] reported that the amount of bound chlorides does not increase with further increase of the chloride concentration (from 0.75 up to 1.5 M NaCl) in the mixing water. Although chlorides can bind in concrete and thus become partially immobilized in the matrix, bound chloride may participate in the corrosion process if the pH drops, leading to dissolution of the chloride complex phases and releasing chloride ions in the pore solution. Such a breakdown of the chloroaluminates can be due to carbonation. In this study, calcite (calcium carbonate) formation, Fig. 4.25, of “dog tooth” morphology (typical for calcite, see e.g. [68]), will contribute to an accelerated corrosion along with the free chlorides. As previously mentioned, calcium carbonate and iron hydroxy-carbonates were detected in small amounts on the steel surfaces. This penetration is additionally promoted by the poor quality of the investigated mortar (w/c ratio of 0.6, large air voids) and the small geometric dimension of the specimens (small cover depth and high degree of structural heterogeneity of the mortar system).

According to comparable experimental conditions in literature [69], diffusion coefficient of oxygen $D_{O2}$ is around $3.2\times10^{-8}$ m$^2$/s in the present case, leading to an estimated carbonation depth of 5 mm for the reinforced mortar exposed for 9 months. In view of the small dimension of the mortar specimen in this study, carbonation may exert influence on the corrosion process of the reinforcement steel. SEM observations (Fig. 4.25) and XRD (Fig. 4.15) reveal that a small amount of CO$_2$ penetrates through the mortar cover and arrives at the steel surface, but a uniform carbonation front can not be expected in this case. XRD analysis reveals the existence of higher amounts of aragonite and calcite in the cement paste around the steel bar, indicating the
involvement of carbonation process in the corroding specimen. The aragonite could be formed directly or by transformation of the thin layer of calcite on the cement paste.

The significantly different morphology of the corrosion products accounts for the formation of rust layers with varying composition in aspect to ratios of iron, oxygen and chloride ions. A basic iron chloride $3\text{Fe(OH)}_2\cdot\text{FeCl}_2$ is formed at the early stage of corrosion, which later decomposes to produce akaganeite. As a result, in local areas where pH is relatively low, bound chloride may be released and initially-formed iron chloride tends to decompose; the produced goethite will grow in flower-like pattern on the relatively flat surface of foam-like lepidocrocite (discernible at a high magnification of 2000x). The iron oxychlorides are easily identified at a relatively low magnification level (500x) according to their typical lamellar or globular morphologies. The non-protective corrosion products, goethite and lepidocrocite (Fig. 4.21) are formed either by a dissolution–precipitation mechanism, or due to a direct dissolution of steel, leading to an etched irregular cross-section of metallographic rebar (as shown in Fig. 4.22).

The general relationship between the iron compounds and the conditions under which they have been deposited have been widely discussed [70]. The frequent occurrence of Green Rust, magnetite and lepidocrocite is associated with an ample supply of Fe$^{2+}$ ions. Due to the fact that the presence of Fe$^{2+}$ ions is often combined with alkaline conditions in concrete, Green RUSTs are common corrosion products and depending on the concentration of carbonate ions in the system, they transform either to goethite or to lepidocrocite. As result of carbonation and chloride ingress, pH is lowered from about 12.5 to 8 and the passivity of iron is lost. In this case, Fe$^{2+}$ ions are originated, and then, they are transformed by hydrolysis and oxidation to Green Rust compound ($\text{Fe}_2\text{O}_3\text{(OH)}_2\cdot\text{Y}\cdot\text{xH}_2\text{O}$, where Y = CO$_3^{2-}$, SO$_4^{2-}$, etc.). Afterwards, Green Rust is oxidized at low temperature to lepidocrocite ($\gamma$-FeOOH), and finally lepidocrocite yields $\alpha$-FeOOH via an intermediate compound Fe(OH)$_{\text{x}+\text{Y}}$ [71]. All the above-mentioned reactions (oxidation) are electro balanced by the reduction of oxygen.

The lower part (1/3 of its length) of the mortar specimen is submerged in NaCl solution, whereas the upper 2/3 part is exposed in air. Due to capillary suction, water tends to move upwards to the top of the cylindrical specimen, a part of which later evaporate in the lab environment. Thus the upper part of the rebar (embedded in mortar) may undergo alternating wet and dry conditions during the testing period due to the high w/c ratio of 0.6 (corresponding to a relatively poor quality of the mortar) and the lack of waterproofing membranes on the specimen surface. In this case, it is known that the oxide films support a mechanism for the increased corrosion rate under cyclic conditions based on FeOOH reduction accruing at the steel surface, as suggested in [72]. The SEM observations in this study provide supporting evidences for these oxidation and reduction reactions.

The behavior of the corroding mortar specimens was compared with a group of reference mortars (being conditioned in the same lab environment, without chloride ingress) in the present study. The comparison encompasses electrochemical condition of the steel surface, microstructure of the bulk mortar and morphological alterations of products at the steel/paste interface. The reference
specimens were investigated using the same monitoring techniques, basically revealing a passive state of the reinforcement.

In concrete without aggressive ion attacks, the steel/cement paste interfacial regions are already different from the bulk material both in the composition and in the morphology aspects. During the hydration, a layer very rich in Ca(OH)$_2$ separates from the bulk and moves towards the steel hydrophilic surface. The distribution of such a layer depends on, for example, the nature of the cement, the w/c ratio, etc, and is not uniform. In some zones it can have a thickness of 20-25 μm, but may be absent in others [73].

**Fig. 4.26** Cross section of steel/mortar interface of the reference specimen, magnification 125x (left) and EDX multi-element mapping (right), revealing the calcium rich layer in the steel/cement paste interface.

**Fig.4.27** Ca-rich layers (CH) of plate morphology in the reference specimen (left, 1000x), preventing the steel reinforcement from corrosion; C-S-H gel and needle-shape ettringite (circled region) formation in the reference specimen (right, 2000x).
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Fig. 4.26 depicts the intact steel/cement paste interface in the reference (non-corroding) specimen, evidenced by the EDX mapping (Fig. 4.26 right), revealing the passive state of the reinforcement. The steel surface was mainly covered by calcium-rich layer in the form of calcium oxide/hydroxide plates – Fig. 4.27 (left) and C-S-H gels from the cement paste – Fig. 4.27 (right). The SEM observations of the reference specimens reveal the presence of ettringite $[3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ or $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_12 \cdot 26\text{H}_2\text{O}$], (Fig. 4.27, right), which is not present in the corroding samples. This is attributed to the substitution of FeS phases by the formed goethite in the corroding mortars [74].

The microstructural and morphological observations for corrosion products in reinforced mortar are consistent with those for reinforced concrete (Chapter 9). Additionally, a comparison of EDX mapping results at the steel cement/paste interface for all investigated conditions for both reinforced mortar and concrete is given in Appendix II.

4.5 CONCLUSIONS

The aim of this Chapter 4 is to quantitatively characterise the electrochemical process of steel corrosion in concrete by means of electrochemical techniques (EIS, LPR) and microstructural analysis (SEM, XRD and EDX).

The polarization (charge transfer) resistance reflects the electrochemical phenomena at the steel/cement paste interface. Microstructure investigations and quantitative image analysis support the experimental results from EIS. Moreover, it is evident that the applicability of EC techniques, EIS in particular, can supply additional information in terms of electrical properties and bulk matrix characteristics.

Microstructural changes are a factor, significantly affecting the global performance in reinforced concrete systems and hence the electrochemical behaviour of the steel surface. The chemical composition and morphological aspects of the corrosion products were quantitatively investigated and correlated to electrochemical measurement results of the systems response. For the corroding mortar specimen, subjected to chloride ingress, the corrosion products mainly consist of highly crystallized goethite, lepidocrocite and akaganeite, confirmed by sharp and representative peaks of the respective products in the XRD patterns. Depending on the ratio of iron and chloride ions, the iron oxychlorides and iron oxyhydroxides present different morphologies and exert influence on the steel/mortar interface microstructure and on material behavior. The typical lamellar type of iron oxychlorides is more responsible for volumetric expansion than the delicate, globular and whiskery minerals. The formation of dominant corrosion products, i.e., flower-like goethite and foam-like lepidocrocite is additionally promoted by penetration of CO2 through the mortar specimen. The arrival of chlorides at the steel surface leads to formation of needle-like akaganeite, particularly in voids. The EIS and LPR measurements provide supporting evidence to the microstructural observations, indicating a gradually increasing corrosion current density for the corroding specimens and a relatively constant and low value for the reference specimens.
The combination of electrochemical measurements with quantitative microstructure analysis of the steel-paste interface constitutes a reliable and useful tool for quantitative characterization of the interface microstructure and of the various corrosion products, and thereby offers better insight into the electrochemical phenomena during corrosion of the steel reinforcement in concrete structures. Furthermore, the combined techniques can be applied to cementitious materials subjected to different technical conditions (e.g. local or uniform corrosion, protection) for more accurate and complete assessment of new protection and prevention techniques.

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CHAPTER 5
CATHODIC PROTECTION – IMPACT ON MORPHOLOGY.


5.1 INTRODUCTION

Cathodic protection (CP) has been found as one of the most viable techniques for inhibiting chloride induced corrosion of steel in concrete structures. Since CP is generally evaluated according empirical criteria only, the need was to investigate what exactly is the principle of a working CP technique and how it influences the material properties i.e. why CP works in general. Only based on such evaluation, and in addition to a comparative investigation with conventional regimes and corroding conditions, we can further reveal the performance of a new CP technique, which was the prime objective of the research. To this end, this Chapter 5 specifically pursues exploring the morphological alterations of corrosion products in reinforced mortars under cathodic protection. For this purpose, scanning electron microscopy (SEM) techniques are combined with energy dispersive X-ray analysis (EDX) and X-ray diffraction (XRD) for microstructural analysis and quantification of the corrosion products. The combined characterization provides important insight into the structural alterations induced by cathodic protection, and therefore, help to explain the efficiency of CP techniques. The beneficial microstructural alterations result in better corrosion resistance of the protected specimens, and turn out to be the mechanisms underlying the efficiency of CP techniques.

5.2 TECHNICAL BACKGROUND

Various protective methods, including epoxy-coated steels, overlays, membranes, impregnations or inhibitors, are used to prevent corrosion in reinforced concrete structures. The positive effects of cement blending in terms of reducing diffusion coefficients of oxygen and aggressive ions have been generally accepted in concrete technology [1,2]. However, some negative aspects of blended cement concrete, specifically in aggressive environments, deserve particular attention. For example, blended cement mortar specimens exposed to MgSO₄ environment showed more substantial strength reduction compared to ordinary Portland cement (OPC) mortar [1]. In addition, an adequate and continuous supply of water is necessary for the long term strength development and durability performance of concrete with fly ash (FA) and blast furnace slag (BFS); the inadequacy of curing, in some cases, may result in a situation worse than that without the addition of FA and BFS [2]. According to other literature data the presence of NaCl salts in fly ash blended concretes has shown decline in the alkalinity of hardened concretes, yielding detrimental consequences to corrosion resistance of steel reinforcement [3].

The general principle with the application of impressed current CP is polarizing the steel reinforcement in such a way that the steel surface is in an “immune” region, where corrosion is thermodynamically impossible to occur [4] (exceptions for CP in concrete, in terms of required
cathodic polarization, were mentioned in Chapter 2 and will be discussed in Chapter 10. This is achieved by supplying impressed direct current (DC) to the steel embedded in concrete structures; the negative terminal being connected to the steel to be protected and the positive terminal to an external (or embedded in the concrete/mortar cover) anode. The repulsion of anions (e.g. chloride) which takes place along with the protection itself is a beneficial one as far as the corrosion risk of the steel is concerned. Firstly the chloride level near the steel surface will be reduced as chlorides will tend to migrate to the positively charged anode, and secondly, the concentrations of alkali ions in the vicinity of the reinforcement will increase as cations will migrate towards the negatively charged steel surface. Hence, the cathodic protection current is promoting beneficiary effects in terms of ion migration in the systems under CP. However, chloride repulsion from the steel surface can be achieved on variety of levels and for longer periods (as the current normally used in CP is not as high as in desalination techniques), and accumulation of cations on the steel/paste interface can have a variety of side effects. For example, CP current successfully reduced the chloride concentration at the steel surface from 0.17% to 0.08% for concrete mixed with 0.2% NaCl by weight of concrete [5]. But the increased cation concentrations (K⁺, Ca²⁺, Mg²⁺) at the steel/paste interface are reported to cause bond degradation between steel and concrete [6,7]. So, caution should be bestowed on current densities and protection regimes. Investigation on pulse current for CP applications provided promising results, which will be further discussed in Part II of the thesis.

In terms of assessing the efficiency of cathodic protection, generally accepted methods for practical applications are potential mapping and depolarization measurements of the reinforcing steel (e.g. ASTM C876-91). Electrochemical methods are also used, but mainly as techniques for the determination of corrosion probability or corrosion stage. These are the linear polarization resistance measurements (PR) and electrochemical impedance spectroscopy (EIS). Both PR and EIS methods (as discussed in Chapter 4) were employed to monitor the corrosion situation under different technical conditions. In this study, the electrochemical methods are also applied to monitor the steel performance after CP application i.e. the combination of techniques (both electrochemical and microstructural) was used to assess the CP efficiency. A detailed discussion and data presentation on the applicability of electrochemical techniques in monitoring CP in reinforced concrete will be presented in Part II, Chapters 8 and 9. This Chapter 5 deals with the efficiency of CP techniques in terms of favorable microstructural alterations and the related morphological observations at the steel/cement paste interface as consequence of CP application.

5.3 MATERIALS AND EXPERIMENTAL TECHNIQUES

5.3.1 Materials and set-up
Reinforced mortar cylinders (40 mm in diameter and 100 mm long) were cast according to standard experimental procedures, using OPC CEM I 32.5R, water to cement ratio of 0.6, with a construction steel bar, type FeB500HKN “as received” (d=6 mm), embedded in the centre of the specimen. The specimens’ set-up, curing and environmental conditions are identical to those described in Chapter 3. In addition to the corroding groups N and the reference groups R (as
specified in Chapter 3 and also discussed in Chapter 4), a group of cathodically protected (denoted as P) specimens, maintained in identical to groups N environmental conditions, is subject to investigation in this Chapter 5, in comparison with group N. Cathodic protection current (mixed metal oxide Ti serving as external anode, current density of 10 mA/m² steel surface) was applied to group P from 60 days of cement hydration. At this testing stage, the N group specimens are already actively corroding. The electrochemical performance of all specimens was monitored by electrochemical means (both LPR and EIS). A cylindrical titanium mesh served as counter electrode and saturated calomel electrode (SCE) as reference electrode (the set-up for electrochemical measurements is as previously presented in Chapter 4).

5.3.2 Experimental techniques
The electrochemical parameters used to characterise the corrosion behaviour of steel in reinforced mortars include corrosion potential (E_corr), polarization resistance (R_p) and corrosion current density (I_corr). The advantage of electrochemical monitoring techniques is that they are fast to perform and do not influence the electrochemical behaviour of the steel surface. The corrosion current can be estimated according a simplified Stern-Geary equation on the basis of R_p [8]. The electrochemical methods (LPR, EIS) employed in the present investigation are identical to those described in Chapter 4, where a discussion for the limitations of the techniques, when applied to reinforced cement-based materials, is also presented. Relevant to the cathodically protected specimens, group P, all electrochemical measurements were performed at open circuit potential after depolarization (i.e. before and in the time of the measurement the protection current was interrupted).

The corrosion resistance of reinforced cementations materials is due to their chemical nature and physical conditions operating at the steel/paste interface. For the purpose of exploring the alterations in morphological aspects and chemical compositions of the corrosion products, associated with cathodic protection, environmental SEM Philips XL30 equipped with energy dispersive X-ray analysis (EDX) was used. X-ray Diffraction (XRD) was also performed on the steel surface of corroding N and protected P specimens (compared to reference R and “as received” steel bars, AR), allowing qualitative determination of various iron oxide compounds in each group of mortars. The quantitative characterisation is expected to provide fundamental understandings of the electrochemical processes occurring in reinforced cement-based materials under cathodic protection.

5.4 RESULTS AND DISCUSSION

5.4.1 Electrochemical parameters
Corrosion current density was calculated using the Stern-Geary equation. The conditions/ assumptions, relevant to these calculations were discussed in Chapter 4. The electrochemical behaviour of reinforced mortar in conditions of corrosion, compared to reference conditions has been discussed in Chapter 4 as well.
Fig. 5.1 presents the $R_p$ (obtained by LPR method) and $I_{corr}$ values for corroding specimens (group N), protected specimens (P) and reference specimens (R) up to 120 days of hydration. Literature suggested a value of 1 and 0.01 µA/cm$^2$ of corrosion current density, respectively, for active and passive status of steel reinforcement [9]. Hence, the steel reinforcement in specimens N can be classified as actively corroding.

After application of CP current (from 60 days), the corrosion current density of protected P specimen declines in the period of 65 to 80 days and continues to decrease slightly to 0.03 µA/cm$^2$ at 120 days of cement hydration. Some discrepancies however can be also observed in terms of derived corrosion current density. The slight change of corrosion current density values with time for group P, although a decreasing trend was observed, can be interpreted in two ways. On one hand a decreasing trend of corrosion current density could be denoted to increased corrosion resistance i.e. the CP, applied to this group, is effectively working. On the other hand, such a slight decline in corrosion current densities for group P (also being significantly lower than the values for passive steel in specimens R) can be explained with certain electrochemical phenomena at the steel surface while measuring, which will be discussed in more detail for reinforced concrete in Chapter 8. The aim of this Chapter is mainly to explore the efficiency of CP in reinforced mortar in terms of secondary beneficial effects on morphology and composition of corrosion products and favourable alterations in the cement chemistry around the steel bars, as consequence of CP.

5.4.2 Microstructural investigation

Scanning electron microscopy (SEM) images were made either on cross-section of the mortar specimen to visualize the steel/paste interface, or on the longitudinal surface of the steel reinforcement to investigate morphologies of the corrosion products, XRD measurements were
performed on longitudinal sections of the steel surface or the adjacent layers of cement paste (the experimental procedures, the used equipment and the methods of investigation are identical to those described in Chapter 4).

5.4.2.1 XRD diffractograms

XRD analysis of the steel reinforcement surface clearly revealed the presence of the common iron oxides and iron (oxy)hydroxides in all investigated specimens.

Figure 5.2 shows the XRD patterns (using CoKα radiation) for an "as-received" bar (AR), for a reference (non-corroding) bar from group R at 120 days of age and for a specimen from group P at 45 days of age, which is before CP application. As seen from Fig. 5.2, the AR bar shows mainly the relevant peaks for iron and a small contribution of wustite at 2θ 49.3º. The same observation holds for the reference specimen R (middle pattern). As for the specimen group P before CP application (top pattern P(45d), Fig. 5.2), i.e. at this time being a corroding specimen, peaks for goethite (2θ 39.8º, 41º, 73º) and wustite (2θ 42º, 49.3º) are attributed to the presence of corrosion products on the steel surface. This comparison aimed on one hand to provide evidence for the already initiated corrosion on the steel surface in specimens N and specimens P before CP application (at 45 days of age); and on the other hand to serve for comparison with the XRD patterns for corroding bar (from group N) and protected bar (from group P) at 120 days of age. The XRD patterns for the latter two conditions are depicted on Fig. 5.3.

The extremely strong peaks of iron substrate are truncated to highlight the intensity signals for various corrosion products. Contributions of quartz (SiO₂) and calcite (CaCO₃) are detected as well, which are derived from relicts of mortar paste. Quartz is corresponding to sand grains, and calcite attributed to carbonation products on the steel surface, (as already discussed in Chapter 4). This investigation focuses on the difference in chemical compositions and morphological aspects of corrosion products between the P and N groups of specimens.
Fig. 5.3 X-ray diffraction patterns for corroding specimen N (top) and protected specimen P (bottom) at 120 days of age, using CoKα radiation: C - calcite, G - goethite, MG - magnetite, L - lepidocrocite, Q - quartz, W - wustite, AG - aragonite, A - akaganeite, H - hematite

The intensity of the peaks is corresponding to the amount of specific corrosion products, rendering possible a qualitative comparison between the different specimens. The group of iron oxyhydroxides (FeOOH) varies in crystal structure and chemical compositions and presents different morphologies, according to which they can be identified as goethite (α-FeOOH), lepidocrocite (γ-FeOOH), akaganeite [Fe\textsuperscript{3+}(O,OH,Cl)], denoted as G, L and A, respectively (Fig. 5.3). Goethite and lepidocrocite are prominent as corrosion products in rust. Akaganeite is an iron oxide which has been identified as a part of the rust layer formed through the corrosion of steel exposed to chloride environments. These common products are present in both the P and N specimens; however, cathodic protection is expected to induce changes in the morphologies and proportions of these corrosion products. In general, N specimen reveals sharper peaks for the corrosion products (Fig. 5.3) than P specimen, implying a higher crystallinity of corrosion products in the unprotected mortar. The main differences between XRD patterns of the two specimens are:

1) The protected steel bar (P) presents more goethite, corresponding to the peaks at 39.8°, 46.1°, 50.3°, 60.5° and 74°, respectively;
2) Compared to the P specimen, the corroding steel bar (N) shows a relatively high amount of lepidocrocite (represented by the peak at 31.1°, 41°, and 54.5°) and a considerably higher amount of akaganeite (with a pronounced peak at 66.0°).
3) The proportions of high-valent iron oxides, particularly hematite, maghemite and magnetite are higher in the P specimen, corresponding to the peaks at 35°, 42.7°, 67.8°, 71.8° and 73°, whereas the iron oxides are mainly FeO in the corroding sample (see the peaks for FeO at 49.3° and 72.3°). The high-valent iron oxides contribute to the formation of more protective and adherent layer on the steel surface.

5.4.2.2 Spatial distribution of corrosion products
Scanning electron microscopy imaging and elemental (EDX) mapping was employed for evaluating chemical composition and distribution of corrosion products in the steel/paste interfacial transition zone (within 200 μm away from the steel surface). Fig. 5.4(left) shows a
cross-section image (100x) of a corroding specimen (non-polished section), clearly revealing the existence of corrosion products on the steel/mortar interface. Fig. 5.4(right) depicts the spatial distribution of chloride (Cl), calcium (Ca) and silica (Si) in the vicinity of the steel reinforcement (Fe), indicating high concentration of chlorides at the etched (irregular) reinforcement surface.

Fig. 5.4 (left): Cross-section image (100x) of the steel/paste interface in freely corroding specimen (w/c=0.6) subjected to external chloride ingress (partially submerged in 7% NaCl solution) for 4 months, the bright white region represent the steel surface; (right) multi-element mapping, revealing the existence and distribution of corrosion products, mainly composed of iron oxides and iron oxy-chloride complexes.

Fig. 5.5 Overview (250x, left) and corresponding multi-elemental mapping (right) of cross-section displaying steel/paste interface in cathodic-protected reinforced mortar (w/c=0.6) subjected to external chloride ingress (partially submerged in 7% NaCl solution) for 4 months.

Fig. 5.5 provides an overview of a cross-section (250x) of a protected specimen (P), visualizing different corrosion and hydration products at the steel/paste interface. The corresponding multi-elemental mapping results (Fig. 5.5, right) clearly reveals the existence of Ca(OH)₂ layer (Ca mapping) in the immediate vicinity of the steel surface in the P specimen. It remains intact after 4 months of exposure to external chloride ingress, thus efficiently prevents further corrosion on the reinforcement surface. The effectiveness of cathodic protection can be further visualised by SEM image made directly on the steel surface as in Fig.5.6, which presents the plate morphology of the calcium hydroxide (CH) protection layer on the steel surface, along with calcium-silica-hydrate (C-S-H) gels and ettringite. SEM observations and mapping results prove that the CP current
successfully mitigate the accumulation of chloride ions on the steel surface, hence, the CH layer continues to act as a protection barrier, so that there is no local pH drop, resulting further in corrosion prevention (additional EDX mapping results and comparison for all conditions (reference, corroding and protected) is given in Appendix II).

Scanning electron microscopy observations on the P specimen indicate the presence of Friedel’s salt in the bulk paste. As previously discussed in Chapter 4, the C\textsubscript{3}A phase of Portland cement has the ability to complex with the dissolvable chloride, resulting in formation of insoluble Friedel’s salt (3CaOAl\textsubscript{2}O\textsubscript{3}•CaCl\textsubscript{2}•10H\textsubscript{2}O or 3CaOAl\textsubscript{2}O\textsubscript{3}•NaCl•10H\textsubscript{2}O). The binding of C\textsubscript{3}A phase with free chlorides in hydrated cement results in the reduction of the corrosion-inducing dissolvable chlorides in the pore solution, and thereby retards further ingress of chloride ions into the concrete.

Of course, the distribution of a protective CH layer, surrounding the steel surface, is not uniform, hence, it is absent in some regions. Fig. 5.7(left) is an example of this case. The irregular edge of the steel reinforcement implies a relatively higher amount of corrosion products in this local area.
Fig. 5.7 (right) presents the EDX mapping for Ca, Si, Cl and Fe elements. The mapping reveals a clear strip of about 100 μm wide in the immediate vicinity of the steel surface with dominant presence of Fe and O, implying the corrosion products to be iron (oxy)hydroxides. The mapping for Cl proves that the CP current successfully keeps chloride ions 100 μm away from the steel surface.

As aforementioned, the CP current was expected to induce an increased cation concentration (e.g. Na⁺) on the steel surface. Element mapping indicates existence of Na⁺-rich local regions in the 200 μm wide interfacial zone bordering the steel surface in the protected (P) specimen. The higher alkali concentrations were observed on a relatively flat and dense layer composed of iron oxides and hydration products (Fig. 5.8 left). In local areas with the presence of various corrosion products, a rough surface is observed as shown in Fig. 5.8 (right). The corrosion products mainly consist of iron oxides and iron oxyhydroxides. CP current efficiently prevents accumulation of chloride ions on the steel surface (Figs. 5.5 to 5.7); hence, the chloride ions concentration on the steel surface is lower in the P specimen than in the N mortar, corresponding to a relatively lower salinity in the protected mortar. Compared to P mortar, a relatively uniform distribution of alkali ions (i.e., Na⁺) was detected in the corroding (N) specimens. It was suggested that Na⁺ interacts with iron hydroxides to form ion pairs that may have interfered with the surface mobility of the adsorbed growth units and thus multi-domainic goethite crystals were formed [8]. As previously discussed in Chapter 3, a higher Cl⁻ concentration will increase the Ca/Si ratio in the C-S-H gel [10], so that the surface charge of C-S-H is positive and as a consequence, cation movement cannot be suppressed by the C-S-H gel [11]. This can explain the relatively uniform distribution of Na⁺ in the N specimens, which tends to encourage the formation of multi-domainic goethite in the N specimens, where goethite exhibits a typical flower-like morphology.

5.4.2.3 Morphologies of various corrosion products in conditions of CP, compared to corroding conditions.

Alkaline media favour the precipitation of magnetite and the crystallization of hematite. Crystallisation from Fe²⁺ solutions usually involves crystallisation of Fe(OH)₂, which transforms to magnetite at moderately alkaline solutions (pH>8). Under slightly alkaline conditions, green rust phases are formed and upon further oxidation they are transformed into goethite and lepidocrocite [12]. In the case of CP, chloride ingress into the steel surface is suppressed by the protection current; hence, the Ca(OH)₂ layer, produced by cement hydration, accumulates on the steel reinforcement and remains intact (Fig. 5.5). Thus Ca(OH)₂ is able to provide a relatively high degree of reserve basicity for the steel protection.

In contrast, the pH value in the corroding (N) specimen was reduced as a result of the reaction between Ca(OH)₂ and Cl⁻, which promotes the crystallization of akaganeite. Hence, the amount and crystallinity of akaganeite is expected to be higher in the N mortar. This is confirmed by the clearly visible and sharp peak (corresponding to planar spacing of d=1.64 Å, 2θ=66°) for akaganeite in the XRD patterns of the N sample (Fig. 5.3).
In the protected (P) specimen, the peak for akaganeite has lower intensity and is partially overlapping with the peaks for hematite ($2\theta = 64^\circ$), magnetite and maghemite ($2\theta = 67.5^\circ$), leading to a shallow and multi-peak patterns (in the 20 range of $64^\circ$ to $68^\circ$) in the XRD diffractogram (Fig. 5.3). Fig. 5.9 is a comparison of akaganeite morphology between the N and P specimens, clearly revealing a much larger dimension and a higher crystallinity of akaganeite in the N mortar. The growth of needle-like akaganeite was found in voids or in areas where considerable cracking was observed in the outer layer, indicating that the relatively high chloride concentrations (ingress through the cracking and voids) in the porous regions favour the formation of akaganeite.
In the protected (P) specimen, CP current prevents complete oxidation of iron, hence, magnetite and siderite precipitate, accompanied by goethite and lepidocrocite. In the unprotected (N) mortar, solubility of $O_2$ is reduced and its distribution is limited, leading to co-precipitation of lepidocrocite, akaganite and goethite. Depending on pH value, oxidation rate and oxygen mobility, goethite, akaganite and lepidocrocite can vary widely in morphologies and dimensions. In addition, salinity also exerts significant effects on crystallinity of goethite and lepidocrocite. It was reported that increase in salinity improves crystallinity of goethite. For example, lepidocrocite crystallinity is reported to increase in all axial directions with salinity, its morphology also changes from plates through rods to multi-domainic crystals due to enhanced crystal growth along the $c$ axis [13]. Goethite and lepidocrocite are dominant corrosion products of reinforcement steel. In what follows, various morphologies of goethite and lepidocrocite in the protected (P) mortar will be explored and compared to those in the unprotected (N) specimen.

![Fig. 5.10 SEM (500x) images of the protected (left) and unprotected (right) specimens reveal significantly different dimension and morphologies of corrosion products. The iron oxychloride complexes of lamellar morphologies (circled region in the right image) in the N specimen are responsible for volumetric expansion and cracking initiation in the reinforced mortars.](image)

The significantly different morphologies of the corrosion products between the protected (P) and unprotected (N) specimens are clearly revealed in Fig. 5.10. Fig. 5.10(left) is a magnification (500x) of Fig. 5.5(left), displaying lamellar morphology of iron oxychloride (left-bottom part of the image) and a relatively flat and compact layer of iron oxidization products. Fig. 5.10(right) displays the iron oxychloride complexes of lamellar type deposited on the steel surface in the N specimen (discussed in more detail in Chapter 4) at the same magnification level. The lamellar morphology is expected to be responsible for volumetric expansion and crack initiation. It can be seen that in the P mortar, the dimension of iron oxychloride complexes is much smaller than in the N specimen. In particular, further magnification of the flat iron oxidization products (circled...
region in Fig. 5.10 left) present a whiskery and delicate morphology. This type of crystals is less detrimental than the lamellar iron oxychloride complexes in terms of inducing volumetric expansion and cracking propagation.

The flat products in Fig. 5.10(left) are attributed to magnetite, nested by some very small (linear dimension of 2–3 μm) star-like crystals. This nest area indicates an evident lamellar growth, with larger lamellae size at centre than in periphery, which is typical for iron oxyhydroxides. Their face-to-edge intergrowth and, in some cases, their exfoliation, favours a large volume representative both of a high specific surface area and expansive product. Similar forms have been found by Hachemi et al. [14] as ‘rose-like crystallisation’ products in presence of chloride. The expansive character of these rose-like crystals can account for the clearly visible cracks on the layered structure (see Fig. 5.10 left). The XRD patterns imply a higher percentage of hematite, magnetite and maghemite out of total iron oxides in the protected (P) group (compared to N). It should be mentioned that XRD can not and should not be used to distinguish between magnetite and maghemite due to the similar lattice parameter for each oxide. SEM observations provide supporting evidences to the more substantial existence of magnetite in the protected mortar.

![Image of goethite and lepidocrocite morphologies](image)

Fig. 5.11 Morphologies of goethite and lepidocrocite (left) in the P mortar. A relatively flat surface (right) mainly composed of magnetite and nested by a small amount of residue of iron oxyhydroxide.

Fig. 5.11(left) visualises typical flower-like structure of goethite and star-like lepidocrocite with very small dimensions in the P mortar. Fig. 5.11(right) shows the layer mainly composed of magnetite and maghemite. As reported in [15] the structure of goethite is more porous because of its tendency to grow in needles, whereas magnetite grows in layers. This is in accordance with the morphological observations in this study. The right image in Fig. 5.11 presents the growth of goethite on the magnetite substrate on the surface of the steel reinforcement. This picture is made on the cross-section of the mortar specimen, displaying the outward growth of goethite crystals in the radial direction of the steel bar. SEM observations directly on the steel surface clearly reveal the precipitation of flower-like goethite on a relatively flat and dense substrate of magnetite.

The lower part (1/3 of its length) of the mortar specimen is submerged in NaCl solution, whereas the upper 2/3 part is exposed in air. Due to capillary suction, water tends to move upwards to the top of the cylindrical specimen, a part of which later evaporate in the lab environment. Thus the
upper part of the rebar (embedded in mortar) may undergo alternating wet and dry conditions during the testing period due to the high w/c ratio of 0.6 (corresponding to a relatively poor quality of the mortar) and the lack of waterproofing membranes on the specimen surface. In this case, the oxide films support a mechanism for the increased corrosion rate under cyclic conditions based on FeOOH reduction to magnetite which occurs at the magnetite-oxyhydroxide interface [16]. The SEM observations in this study provide supporting evidences to these mechanisms, represented by the small amount of residue of oxyhydroxide (Figs. 5.10 and 5.11). Energy dispersive X-ray analysis for this layer structure shows atomic percentages of 33% Fe, 53% O and 6% Ca, and the Fe/O ratio is 0.62. This indicates the substrate layer to be mainly composed of non-stoichiometric magnetite (Fe₃O₄), partially substituted by calcium.

It is clear that the morphologies of corrosion products as well as the material microstructure are heterogeneous in nature. Figs. 5.11(left) and 5.12 present different morphologies of goethite. The left picture in Fig. 5.11 indicates the typical flowery and multi-domainic morphologies. In the corroding (N) specimen, most of the goethite crystals are multi-domainic, yet in the protected (P) specimen, amorphous goethite (see Fig. 5.12) appeared. This can be at least partially attributed to the decreased salinity in the case of cathodic protection. Summarising, goethite and lepidocrocite are observed in large amounts and with large dimensions (10-15 µm) in the N specimens, and the main morphology is flower-like structure. In the protected (P) specimens, this typical morphology for iron oxyhydroxide is also found (Fig. 5.11 left), but with smaller dimensions (less than 5 µm). In particular, many local areas in the steel/paste interface present cloudy or clustering microstructures as in Fig. 5.12. These spots can be attributed to the presence of poorly crystalline goethite, displaying the amorphous cotton-ball structures typical for semi-crystalline goethite, interconnected by formations as nests. The lower crystallinity of goethite in the protected specimens can be associated with the lower salinity (resulting from lower chloride concentration around the steel surface) since higher salinity will promote crystallinity of goethite and lepidocrocite.
5.5 CONCLUSIONS

This Chapter 5 explores the morphological and microstructural differences between unprotected and protected (under cathodic protection) reinforced mortars subjected to chloride ingress. The research demonstrates that cathodic protection current can efficiently prevent further corrosion on the steel surface and successfully decrease the chloride concentration around the steel bar. In local areas with a protective layer of Ca(OH)$_2$, the latter remains intact after 4 months exposure to 7% NaCl solution, maintaining high pH of the environment, surrounding the steel reinforcement. In the regions where CH layer is absent, the cathodic protection technique can keep the chloride ions 100 μm away from the steel surface, thus efficiently protecting the steel reinforcement.

It was expected that the common corrosion products, i.e. iron oxyhydroxides (goethite, akaganeite, lepidocrocite) are present in both groups of specimens. However, X-ray diffraction analysis and SEM observations (combined with EDX) have revealed that the amount of hematite and magnetite (also maghemite) is much higher in the protected specimens (group P), with less akaganeite and lepidocrocite at the same time. Another important aspect is the dimension and crystallinity of corrosion products. The iron oxychlorides in the N specimens display lamellar type and much larger dimensions than in the P mortars. The lamellar morphologies are responsible for volumetric expansion and cracking initiations in the reinforced mortars. Instead of the typical flowery structure of goethite (as observed in N specimens), cotton-ball structures of goethite are revealed to a wide extent in the P specimens. This semi-crystalline goethite is less detrimental to the material structure. The favourable morphology (lower crystallinity) of goethite can be attributed to the relatively high pH value and lower salinity (i.e., lower concentration of chloride ions) in the protected mortar. The morphological and microstructural analysis shed light on the fundamental mechanisms underlying the efficiency of cathodic protection. The protection current could modify the material structure (including the amounts and morphologies of different corrosion products) to a favourable trend in terms of corrosion protection and prevention. Further study will be conducted in the future concerning the proper operation of improved cathodic protection techniques with respect to specific deteriorating conditions.

References:
CHAPTER 6
CORRELATION OF ELECTRICAL PROPERTIES, PORE STRUCTURE
AND ELECTROCHEMICAL PHENOMENA.
BREAKDOWN TO MULTIPHASE INTERFACE STRUCTURES.

Adapted from:

6.1 INTRODUCTION

Since reinforced mortar is a multi-phase composite material at different levels of aggregation, a combination of techniques, namely electrochemical impedance spectroscopy (EIS) (for investigating the electrochemical phenomena on the steel reinforcement) and microstructure analysis (for qualifying and quantifying the composite bulk material), was expected to provide insight into the macro- and micro-level interactions, involved in conditions of corrosion and cathodic protection for the here investigated reinforced mortar specimens.

This Chapter presents some additional morphological aspects, chemical composition and distribution of corrosion and hydration products in terms of modifying the material characteristics as consequence of the conditioning regimes of corrosion and CP. Further, the elements of the equivalent electrical circuit from EIS measurements are discussed in correlation to the evolution of porosity, pore size distribution and pore interconnectivity of the bulk matrix, during corrosion and CP application. The results indicate that different parameters in the EIS modeling concept correspond well to specific interface microstructures.

The correlation between EIS measurements and microstructure investigations allows breaking down the electrical properties of reinforced mortar and the electrochemical performance of the steel reinforcement during the corrosion process and during CP application to the micro-level.

6.2 TECHNICAL BACKGROUND

As already mentioned in the previous Chapters, various side effects of CP and detrimental effects of chloride-induced corrosion are known and reported in [1-6]. Investigations in the framework of this project and other research [2,6-9], show that the unfavorable pore structure alterations in cement-based materials yield non-uniform electrical properties and thereby possibly result in disturbance of the electrolytic path due to heterogeneities and instabilities inherent to the bulk matrix. In reference (non-corroding) conditions, cement hydration is the factor, responsible for the development of the structural properties of cementitious materials. When chloride induced corrosion is involved, on one hand the material structure is influenced by physico-chemical mechanisms (NaCl is known to accelerate the hydration process [10,11]). On the other hand, a
corroding steel surface determines various structural changes (e.g. the formation of corrosion products and further volume expansion induces micro-cracking, consequently influences ion transport, electrical properties, bulk material permeability etc.). Finally, in conditions of CP, along with the cement hydration and the influence of environmental conditions (as NaCl in this study), the current flow is a contributing factor to the modified structural properties, ion transport mechanisms and global performance of the system.

On macro-level, the electrical properties (material behavior) of the bulk mortar matrix as well as the electrochemical performance of the steel reinforcement in aggressive environment are monitored by electrochemical methods, as EIS in this case, being a widely used technique [12-15], applicable to low conductivity media, such as reinforced mortar (concrete). On micro-level, material microstructure is investigated by scanning electron microscopy (SEM) of the steel-paste interfaces, of the bulk mortar and of the paste-aggregate interface.

In summary, the electrical properties and the material microstructure undergo continuous changes due to complicated cement hydration and steel corrosion process. These effects are far more complicated when CP is involved. Global electrical resistivity and dielectric properties of mortar and cement paste have been investigated before [16-18]. The correlation between electrical properties, pore solution chemistry and local microstructure of the material (in terms of porosity, pore size distribution, pore connectivity, etc.) has not been studied in details. This Chapter investigates the origin of material behavior in the relevant conditions of steel passivity, corrosion and protection. The study pursues to decompose the equivalent circuit of EIS measurements in reinforced mortar into various components and to correlate these components to specific structure elements. Microstructural characteristics in combination with morphological investigation and quantitative and qualitative study on corrosion and hydration products for corroding, protected and reference specimens were evaluated at first, thus providing information for the fundamental reasons of altered material structure. Second, a correlation of morphological and microstructural investigation with electrochemical parameters of the steel reinforcement was performed.

6.3 Some remarks for Electrical Double Layer and Double Layer Capacitance

The theory of the electrical double layer (EDL) has been widely applied to various physicochemical and electrochemical processes in cement based materials [19]. Basically, in the case of contact between two phases (liquid-gas, solid-liquid, liquid-liquid etc.), their interface presents a layer of accumulated charge species, distributed in a certain way along that interface [20]. Although mortar is an insulating material and a significant charge separation is restricted, the accumulation and distribution of these charged species i.e. the excess charge in the bulk matrix and pore walls, will behave as an EDL. Hence, the interfacial microstructures in the reinforced mortar systems can be described by the capacitance of the formed electrical double layers: in the bulk material, at the interface between pore walls and pores solution, in the interfacial transition zone (ITZ) between aggregate and cement paste, and at the interface between pore water and product layers on the surface of steel reinforcement.
6.4 EXPERIMENTAL

6.4.1 Materials
The reinforced mortar specimens used in this study, comprised three main groups: reference (non-corroding) group R, corroding group C and protected group P (totally 15 specimens were cast for this investigation). Specimen set-up and details, curing conditions and mortar mixture are summarized in Table 6.1 and are identical to those described in Chapters 3, 4 and 5 (cement chemical composition, constituents and physical properties are given in Chapter 3).

Table 6.1. Specification of materials set-up, conditioning and some experimental procedures.

<table>
<thead>
<tr>
<th>Reinforced mortar cylinders</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Specimen set up:</td>
</tr>
<tr>
<td>- Dimensions mortar cylinder: $d = 40\text{mm}, h = 100\text{ mm}$;</td>
</tr>
<tr>
<td>- Reinforcement: FeB500HKN (C &lt;0.22 w.%), $d = 6\text{mm}$, exposed length $80\text{ mm}$, cast “as received”; All specimens used demi-water as mixing water.</td>
</tr>
<tr>
<td>2. Specimen details and groups:</td>
</tr>
<tr>
<td>- $R$ – reference group</td>
</tr>
<tr>
<td>- $C$ – corroding group</td>
</tr>
<tr>
<td>- $P$ – protected group</td>
</tr>
<tr>
<td>- Dimensions mortar cylinder: $d = 40\text{mm}, h = 100\text{ mm}$;</td>
</tr>
<tr>
<td>- Reinforcement: FeB500HKN (C &lt;0.22 w.%), $d = 6\text{mm}$, exposed length $80\text{ mm}$, cast “as received”; All specimens used demi-water as mixing water.</td>
</tr>
<tr>
<td>3. Curing conditions:</td>
</tr>
<tr>
<td>- 14 days fog room (98% RH, 20°C);</td>
</tr>
<tr>
<td>- 106 days lab air, 20°C in immersed conditions:</td>
</tr>
<tr>
<td>- Groups $R$ - $1/3^{rd}$ of height immersed in water</td>
</tr>
<tr>
<td>- Groups $C$ and $P$ - $1/3^{rd}$ of height immersed in 7% NaCl solution</td>
</tr>
<tr>
<td>4. Mortar mixture:</td>
</tr>
<tr>
<td>- OPC CEM I 32.5 R</td>
</tr>
<tr>
<td>- $w/c$ ratio 0.6, cement to sand ratio 1:3</td>
</tr>
<tr>
<td>- sand of size range 125 µm to 2 mm</td>
</tr>
<tr>
<td>- preparation EN 196-1</td>
</tr>
</tbody>
</table>

The reference group R was used as a control (non-corroding, non-protected) group. Group C were specimens, in which corrosion was initiated in environmental conditions (7% NaCl), as specified in Table 6.1. The specimens were maintained in a “freely corroding” state till the end of the test of 120 days of age. The steel reinforcement (Table 6.1) was embedded “as received” i.e. there was no preliminary treatment before casting. The poor mortar quality, the high water cement ratio and the relatively high NaCl concentration are designed to accelerate the corrosion process.

Group P comprised specimens, maintained in equal conditions as for group C till the end of the test, but cathodic protection current was applied after corrosion was initiated at 60 days of age (the presence of corrosion and the CP efficiency further on, were evaluated by potential mapping and electrochemical measurements on the reinforcement). Impressed CP current was applied on the P specimens at 60 days of cement hydration, using a CP current of 10 mA/m² (steel surface) and an externally positioned mixed metal oxide (MMO) Ti mesh, serving as anode (the CP application and set-up for electrochemical measurements are identical to those discussed in Chapters 4 and 5).
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Open circuit potentials (OCP) for specimens group C ranged from -400 to -650 mV vs Saturated Calomel Electrode (SCE), open circuit potentials for specimens group R were around –260 mV vs SCE throughout the test. The former readings indicate a corrosion state, the latter indicate passive behavior according to accepted criteria [ASTM C876, NACE RP0290-2000]. The OCP values for group P before CP application were in the same range as for the specimens group C; after 60 to 65 days of age i.e. after CP was applied, the on-potentials (potentials under cathodic polarization i.e. working CP) for group P were more cathodic than -850 mV SCE, mostly about -920 mV. (Detailed discussion for the electrochemical performance of corroding and reference specimens was presented in Chapter 4; morphological observations for corrosion products and product layers transformations as consequence of CP were discussed in Chapter 5).

6.4.2 Electrochemical Impedance Spectroscopy (EIS)
The used measurement set-up (Table 6.1) is found to be appropriate for electrochemical measurements on steel in mortar (concrete) as generally used in the frame of this research [21,22], also reported by [23] and as discussed in Chapter 4. The centrally located construction steel bar served as working electrode; the cylinder of MMO Ti, positioned around the mortar cylinder, served as counter electrode; a saturated calomel electrode (SCE), immersed in the solution between the titanium mesh and the mortar cylinder, served as reference electrode. The EIS measurements were performed in the frequency range of 50 kHz to 10 mHz by superimposing an AC voltage of 10 mV. All measurements were performed at OCP (for group P after 48 to 96 h depolarization i.e. CP current was interrupted and not running in the time of measurements), in immersed conditions (ensuring electrical conductivity of the medium) and using EcoChemie Autolab instrument – Potentiostat PGSTAT30, combined with FRA2 module and GPES and FRA software package.

6.4.3 SEM imaging and pore structure analysis
Scanning electron microscopy (SEM) and Energy-dispersive X-ray (EDX) investigations were performed with environmental SEM, ESEM Philips XL 30, equipped with secondary, backscattered electron and large field detectors, operating at an accelerating voltage of 20 to 25 kV for imaging and 7 to 20 kV for x-ray analysis of the product layers. For EDX analysis in the bulk material, an accelerating voltage of 20 kV was used, for composition analysis directly on the steel surface, 7 to 15 kV was used. The ESEM and EDX analysis were performed as already specified in Chapters 3 and 4. The technical background for the pore structure analysis is presented in Chapter 2, the experimental procedures are as presented in Chapters 3 and 4.

6.5 RESULTS AND DISCUSSION
6.5.1 Morphological observations and EDAX analysis of product layers
Scanning electron microscopy (using ESEM) images were made either on cross-sections of the mortar specimens to visualize the steel/mortar interface, or on longitudinal sections of the steel surface and the corresponding locations in the cement paste, aiming to investigate corrosion and hydration products. Chapter 3 discussed the morphological observations of corrosion and some
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Hydration products in corroding and reference conditions, Chapter 5 presented the observations in protected specimens. Hereby in Chapter 6, a comparison of corrosion and hydration products for corroding, non-corroding and protected conditions is briefly presented, aiming to support the microstructural observations and bulk matrix parameters, which will be further hereby correlated with electrochemical performance of the steel surface.

Fig. 6.1 ESEM images of product layers, deposited on the steel surface and the relevant “prints” of the same region in the cement paste in: corroding specimen C, steel surface (a) and cement paste (b); protected specimen P, steel surface (c) and cement paste (d).

Figures 6.1a) and 6.1b) provide ESEM images of the product layers, deposited on the steel surface (2000x), and the corresponding steel “print” in the mortar (4000x) at the steel-mortar interface in corroding specimen from group C. Figs. 6.1c) and 6.1d) present similar locations for the protected specimen P respectively (steel surface at 1000x (Fig.6.1c) and corresponding cement paste at 4000x (Fig.6.1d)). Generally, the corrosion products are formed on the steel surface and further penetrate into air voids and openings in the restricted space of the steel/cement paste interface. The corrosion products, prominent in these conditions (lepidocrocite, goethite, akaganeite, as defined by XRD (see Chapter 5) and detected by ESEM), further volume expand and deposit in the cement paste layer (evidenced by ESEM investigation – Figs.6.1b)d)), which normally causes micro-cracking in the bulk matrix.
Relevant to the corroding group C is the formation and volume expansion of corrosion products, which exhibit higher crystallinity and low adherence to the steel surface, whereas the product layers in protected group P are expected to have different properties and morphology. Since CP in group P was applied after corrosion initiation (as already mentioned at 60 days of age), the initially formed wustite, goethite, lepidocrocite will transform into the more stable high valent oxides (mainly hematite and magnetite), thus forming a product layer, adherent to the steel surface. Hence CP brings about lower crystallinity and favorable morphology (relatively flat layers on the steel surface - Fig. 6.1(c) and compact deposits in the cement paste – Fig. 6.1(d)). The transformation of product layers in group P to a more favorable morphology and better adherence is favored by the lower salinity of the cement paste layers, adjacent to the steel surface in CP applications (more details for the fundamentals and efficiency of CP in such systems are reported in [24] and discussed in Chapter 5).

In contrast, chloride ions are concentrated at the immediate vicinity of the steel surface in the C specimens (see EDX maps for Fe, Cl, Ca and Si in Fig. 6.2(right), corresponding to the steel/paste interface of Fig. 6.2(a)), which promotes higher crystallinity of goethite and lepidocrocite and accumulation of akaganeite (Fig. 6.2(b)). The presence of akaganeite supports the hypothesis for high salinity in the corroding specimens C, as akaganeite is found only in chloride containing environments [25-27]. As previously discussed in Chapter 4, akaganeite is mainly responsible for micro-cracking in reinforced mortar (concrete) as it is less adherent and not accommodating in rust layers [25], thus impeding the formation of a film with good protective properties. It is found to grow in the weak zones of the paste/gravel or the steel/paste interfaces (Fig. 6.2(b)), which along with its typical needle like structure additionally promotes micro-cracking.

As mentioned, ESEM observations provide supporting evidences to the more substantial existence of magnetite in the protected mortars (Figs. 6.1c) and 6.3a)). As reported in [28], the
structure of goethite is more porous because of its tendency to grow in needles, whereas magnetite grows in layers. The ESEM investigation, supported by XRD (see Chapter 5), in this study is consistent with the latter statement, revealing tiny flower-like goethite growing on a relatively dense layer which is mainly composed of non-stoichiometric magnetite (partially substituted by calcium) and magnetite (Fig. 6.1(c) lower right corner, Fig. 6.3a)).

Table 6.2 summarizes the EDX results for the corrosion products, depicted on Figs. 6.3 and 6.4. (although the drawbacks of EDX analysis, applied directly on the steel surface, are well known, the local area EDX analysis, performed in the regions of the typical product morphologies and in combination with XRD measurements, is considered reliable and is a supporting evidence for the composition and morphology of the here investigated product layers). In addition to the different proportions of corrosion products between the C and the P specimens (evidenced by XRD and EDX), another important aspect is the crystallinity of iron oxy-chloride and goethite.

Table 6.2 EDX quantification of marked regions in Figs. 6.3 & 6.4 (corrosion products on the steel surface, previously embedded in mortar of w/c ratio 0.6, subject to external chloride ingress and CP application)

<table>
<thead>
<tr>
<th>Element</th>
<th>Location A, Fig. 6.3</th>
<th>Location B, Fig. 6.3</th>
<th>Location C, Fig. 6.3</th>
<th>Location D, Fig. 6.4</th>
<th>Location E, Fig. 6.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1.86 0.05 1.14 2.49 1.05 2.36 0.48 0.83 1.50 1.77</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.58 1.18 0.87 1.78 0.65 1.39 0.58 0.95 0.71 0.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.73 1.35 0.82 1.52 0.48 0.93 0.49 0.72 0.46 0.46</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>2.18 2.89 1.24 2.20 0.62 1.14 2.19 3.08 0.61 0.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.62 0.97 0.52 0.81 0.09 0.14 0.08 0.09 0.14 0.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.30 0.43 8.11 11.45 5.29 7.71 0.24 0.27 2.95 4.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.18 0.23 0.12 0.16 0.00 0.00 0.12 0.12 0.05 0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>6.56 8.18 1.97 2.46 1.78 2.30 90.46 89.35 2.57 1.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>86.43 77.38 84.99 76.17 89.85 83.21 5.05 3.58 49.70 24.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the P mortar, iron oxychlorides are whiskery and form a relatively compact layer (Fig. 6.3b), exhibiting much lower crystallinity (compare Figs. 6.2(b) and Fig. 6.3, location C). In contrast, iron (oxy)hydroxides and oxy(hydroxy)chlorides of lamellar and globular types are found in the C mortar, Fig. 6.1(a), (more detailed information is presented in Chapter 4), the lamellar type being of much higher crystallinity, compared to P mortar (compare Figs. 6.1(a) and Fig. 6.3, location B). In the P mortar, calcium rich deposits are relatively intact (Fig. 6.4a), location D), while goethite and lepidocrocite, are of semi-crystalline characteristics (Fig. 6.4b). The favorable products’ morphology (smaller dimension and lower crystallinity) can be attributed to the relatively high pH value and lower salinity (i.e. lower concentration of chloride ions) in the protected sample.

6.5.2 Hydration products in the bulk mortar
ESEM observations show the presence of platy crystals of Friedel’s salt (Fig. 6.5(a), points 1), in the vicinity of the steel surface and in the bulk matrix in both P and C mortars, surrounded by hydration products (in case of P specimens, calcium-rich plates are normally found existing along with Friedel’s salt – Fig. 6.5(a), points 2). Table 6.3 summarizes the EDX quantification of the marked areas in Fig. 6.5.
Fig. 6.3 SEM (2000x) images reveal the relatively dense and flat magnetite layer (a) and various (flower-like goethite, star-like lepidocrocite and needle-like akaganeite), low crystalline corrosion products (b) in the protected mortars.

Fig. 6.4 ESEM images of the steel surface in the protected mortar, reveal presence of relatively large and intact protective Ca-rich deposits (a), location D; (b) product layer morphology of goethite (cotton-ball) and tiny flower-like structures (lepidocrocite).

Fig. 6.5 BSE images of bulk mortar matrix in the vicinity of the steel surface, depicting Friedel’s salt (a) in specimen P and lumps of platy AFm phase in specimen R (b).
Electrical properties, pore structure and electrochemical phenomena

Table 6.3  EDX quantification of marked areas in Fig. a) (P group) and b) (R group)

<table>
<thead>
<tr>
<th>w.%</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>p.1</td>
<td>0.80</td>
<td>0.78</td>
<td>0.64</td>
<td>1.52</td>
<td>1.44</td>
<td>6.97</td>
<td>0.17</td>
<td>35.66</td>
<td>2.83</td>
</tr>
<tr>
<td>p.2</td>
<td>0.71</td>
<td>0.50</td>
<td>0.76</td>
<td>1.22</td>
<td>0.52</td>
<td>0.33</td>
<td>0.20</td>
<td>50.77</td>
<td>1.25</td>
</tr>
<tr>
<td>p.3</td>
<td>0.65</td>
<td>0.66</td>
<td>12.07</td>
<td>3.93</td>
<td>3.10</td>
<td>0.11</td>
<td>0.53</td>
<td>57.10</td>
<td>21.54</td>
</tr>
<tr>
<td>p.4</td>
<td>1.59</td>
<td>2.12</td>
<td>5.44</td>
<td>20.39</td>
<td>5.37</td>
<td>0.00</td>
<td>0.42</td>
<td>58.23</td>
<td>6.45</td>
</tr>
</tbody>
</table>

As previously discussed, the C\textsubscript{3}A phase of Portland cement has the ability to complex with the dissolvable chloride, resulting in formation of stable Friedel’s salt 3CaO.Al\textsubscript{2}O\textsubscript{3}.CaCl\textsubscript{2}.10H\textsubscript{2}O or 3CaO.Al\textsubscript{2}O\textsubscript{3}.NaCl.10H\textsubscript{2}O. The chemical binding of C\textsubscript{3}A phase with free chlorides in hydrated cement results in the reduction of the corrosion-inducing dissolvable chlorides in the pore solution and also retards further ingress of chloride ion in the concrete. In the reference (R) mortar, well crystallized ettringite (Fig.6.5b, points 4) is the primary sulphoaluminate phase detected at early ages. Two possible mechanisms have been suggested for the reactions between ions in pore solutions and cement paste components to form ettringite [29], i.e., topochemical (replacement of preexisting mineral phases) and through solution (i.e. direct precipitation from solution). Monosulphate was not detected by XRD at early ages in the reference mortar, though this does not necessarily indicate its absence, as much of the monosulphate at early ages is likely poorly crystalline and not detectable by XRD. The outer hydration products in R mortar are hardly of single phases and likely contain small amounts of other phases, such as calcium hydroxide, ettringite, monosulphate (AF\textsubscript{m}), etc., which are intermixed with the C-S-H gel (spherules formations in Fig.6.5(b)). Interpretation of these data is not straightforward.

Evidenced by ESEM investigation, monosulphate is present in the R mortar. Some of the monosulphate was deposited in small cavities or in the hollow shells remaining from the complete dissolution of very small cement particles, but much of the monosulphate observed were platy lumps occluded by the fibrillar C-S-H in the outer product (see Fig.6.5(b), points 3). The conversion of the AF\textsubscript{m} phase, monosulphate to Friedel's salt, can be discussed in terms of the structural similarities between the phases. Friedel's salt and monosulphate are both members of the AF\textsubscript{m} family of structurally related phases, which have layered structures (Fig.6.5), the basic building unit of which has the constitution \([\text{Ca}_4\text{Al}_2(\text{OH})_12]^{2+}\). The net positive charge of this layer is balanced by anions: either monovalent, e.g., OH\textsuperscript{−}, Cl\textsuperscript{−}, or divalent, e.g., CO\textsubscript{3}\textsuperscript{2−}, SO\textsubscript{4}\textsuperscript{2−}, etc. To maintain charge balance, the number of interlayer anions may be variable; for example, 2Cl\textsuperscript{−}~SO\textsubscript{4}\textsuperscript{2−}. The different numbers of anions required for charge balance, as well as their different sizes and polarisabilities, control the variable interlayer water contents and control the exact layer stacking sequence. Hence, Friedel's salt (in which the balancing ion is mainly Cl\textsuperscript{−}) is readily distinguished from monosulphate, the main AF\textsubscript{m} type phase occurring in Cl\textsuperscript{−}-free cement pastes.

6.5.3 Pore structure parameters

The electrolytic path in reinforced mortar systems is dependent on the kinetics of ions transport mechanisms. These mechanisms, in addition to cement hydration and morphological alterations (as discussed in the previous sections), are affected by pore size distribution and pore connectivity of the bulk mortar material. Further, the bulk matrix contributes to the corrosion behaviour of the
reinforcing steel, evaluated by electrochemical techniques (as EIS measurements). As mentioned, the correlation of derived electrochemical parameters from EIS measurements with structural parameters from the investigation of the bulk material is meant to provide more detailed information for the related phenomena, associated with the corrosion process and the CP application in the investigated systems.

The microstructural analysis is performed on polished sections of the specimens, in BSE mode (sample preparation is presented in Chapter 3). Equal experimental procedures were used for all investigated locations and for each specimen (it should be noted that all pore structure investigations were averaged from at least 25 locations for “edge”, “bulk” and “interface” positions, shown in Table 6.1, p.1. The “interface” location relates to a zone of 15 to 50 µm wide from the steel surface into the bulk material). Further, the original BSE image is segmented by applying a grey-level threshold to create a binary image, reflecting the pore phase. The binary image is then subjected to quantitative image analysis for derivation of structural parameters (pore size distribution, critical pore size, pore interconnectivity etc.).

![Porosity distribution for specimen C2, “edge”, “bulk” and “interface” locations](image1)

![Pore size distribution for specimen C2, “edge”, “bulk” and “interface” locations](image2)

Figs.6.6 and 6.7 present an example for the data presentation after the performed analysis, depicting the calculated porosity, pore size distribution and critical pore size for a corroding specimen C2 from the investigated group C. The cumulative pore size distribution curve is obtained by plotting the pore area fraction after an opening operation versus linear dimension of the structuring element (Fig.6.6(b)). For predicting the permeability of porous materials, a revised form of the Katz-Thompson equation [30], is generally used in the frame of the research. The pore interconnectivity (defined as the fraction of connected pores out of the total pore area) is used in terms of pore distribution density (PDD), as PDD contains information on both pore size and connectivity of pore space. Detailed information for the techniques, performed in the microstructural analysis, the PDD and the stereological approaches are given in Chapter 2 and can be found in [31].
Figure 6.7 presents a comparison of derived porosity and critical pore size for corroding and protected specimens (a) and corroding and reference specimens (b) at the steel/cement paste interface. Table 6.4 presents summarized data for the “edge”, “bulk” and “interface” regions parameters of the specimens.

Based on the pore structure analysis and the derived parameters from Table 6.4, the following can be stated: In general, a higher porosity is corresponding to higher pore connectivity; however, this is not necessarily the case. For example, the porosity in the steel-mortar interfacial zone is higher in the R (12.68%) than in the C (10.28%) mortar, that latter is resulting from the accelerated hydration in the presence of chloride ions [32,33]. However, the pore connectivity (a dimensionless parameter, for definition, see [31]) in the R mortar (at 120 days of hydration) is 0.18, significantly lower than in the C specimen (0.27). This can be partially attributed to the presence of a large amount of Hedley grains [34,35] in the R mortar (Fig. 6.8a, circled regions),
which contribute to the total porosity but are isolated from the pore network (phenomena already partly discussed in the previous chapters). The average porosity at the steel-mortar interfacial zone is 8.53% for the P mortar (Fig. 6.8b) at 120 days of hydration, accompanied by a pore connectivity of 0.06. At this stage, volume expansion of corrosion products already initiated cracks in the C mortar; hence, the connectivity of void space is about 0.27 (Fig. 6.9), significantly higher than the P mortar (0.06). Additionally, the corrosion products in specimen C, penetrate and deposit in the bulk matrix (Fig. 6.9b), causing further increase of micro-cracking and thus contributing to raised interconnectivity of the pore network in specimens C.

In structural morphology aspect it was observed that monosulphates were accumulated to a significant extent on the steel surface in the R mortar as discussed in the previous sections. At the hydration stage of around 3(4) months, monosulphate is well crystallized into plate structures, with relatively large size of a few micrometers. This morphology is responsible for the relatively coarser pore structure (e.g. critical pore size is 2.85 µm at the steel-mortar interfacial zone, at 120 days of cement hydration) in the R mortar. At the same hydration stage, the critical pore size is 0.95 to 1.23 µm for the C group and 0.95 for group P.

Fig. 6.8 ESEM images of the steel-mortar interface microstructure in specimen R (a) and specimen P (b) at 120 days of hydration.

Fig. 6.9 ESEM images (BSE mode i.e. steel and corrosion products appear brighter) of the steel-mortar interface (a) in C specimens (120 days of hydration) revealing corrosion-induced cracks. Corrosion products, deposited in the bulk matrix (b), contribute to increased interconnectivity.
Further, a detailed discussion of the pore structure parameters is not subject to this Chapter (more details for similar groups to the here investigated specimens were presented in Chapter 3; pore structure parameters will be further discussed in Chapter 7 for concrete specimens, in terms of the influence of NaCl alone and the combined effects of NaCl and current flow on the material structure). Relevant to this Chapter 6 is only the combination of the derived values with obtained electrochemical parameters, thus correlating bulk matrix material properties with certain responses from electrochemical point of view (which will be discussed in what follows).

6.5.4 Electrochemical impedance spectroscopy and interface microstructures

The electrochemical processes in reinforced cement-based materials are closely associated with structural alterations that take place at different interfaces, such as the one between mortar and aggressive media, between cement paste and aggregate, and the one between cement paste and the steel reinforcement (Fig. 6.10a).

In general, EIS measurements use certain equivalent models that might not apply for all corrosion systems, especially steel in concrete, which is a very complex one [36]. Further, different electrical circuits with equally good fit results can be used to model the EIS response of a system to applied signals [12-15].

As aforementioned, the EIS measurements were performed in the frequency range of 50 kHz to 10 mHz. The elements from the equivalent electrical circuit are attributed to definite physical parameters, corresponding to each interface. As presented in Fig. 6.10b), the model is composed as follows: Resistance \( R_{el+b} \) (also denoted as \( R_1 \)), corresponding to the high frequency domain (between 50 kHz and 1 kHz), is related to the mortar bulk resistance, including the electrolyte resistance (the electrolyte resistance \( R_0 \) is negligible compared to concrete bulk resistance). \( R_{el+b} \) might also include contributions of the electrolyte/mortar cover interfacial effects, which are considered to be minor, compared to the mortar bulk resistance, especially after 30 days of cement hydration. The resistance \( R_{pn} \) (denoted \( R_2 \)), corresponding to the intermediate frequency domain (range of 1 kHz to 40 Hz), is employed to represent the pore solution resistance, the latter having a significant contribution to the overall impedance response in the reference samples and negligible effect in the corroding and protected samples. The corresponding \( Q_{pn} \) represents the non-ideal capacitance of double layers in the pore network and cement paste/aggregate interfacial transition zones (ITZs).

The low frequency domain (40 Hz to 10 mHz) is normally used to evaluate charge transfer process in combination with mass transport process [13] and corresponds to resistance \( R_{ct} \); \( Q_{dl} \) is used to determine the non-ideal interfacial capacitance of the steel surface. Figure 6.10c) depicts a representative plot of the freely corroding (C) and reference (R) mortars (EIS measurements were discussed in detail in Chapter 4). The reference mortars show a line comparatively more inclined to the vertical axis in the low frequency zone throughout the investigation period, indicating relatively passive state of the steel reinforcement. In contrast, the C mortars present a depressed semi-circle at the end of the test, typical for active corrosion state.
Fig. 6.10 (a) Schematic of the interface microstructures in reinforced mortar (concrete) exposed to aggressive environments (7% NaCl solution); (b) Equivalent circuit used to model and fit the experimental EIS data, comprising resistances, attributed to the corresponding interfaces and physical properties: $R_{el+b}$ (or $R_1$) (resistance of mortar bulk, incl. $R_0$ of electrolyte), $R_{pn}$ (or $R_2$) (resistance of pore solution & ITZ between cement paste and aggregate), $R_{ct}$ (or $R_3$) (charge transfer resistance at the steel surface); (c) Complex impedance response – a representative plot for corroding C and reference R samples in the frequency range of 50 kHz – 10 mHz.

6.5.5 Impedance measurements in the high frequency domain

The global impedance of the system can be obtained from EIS measurements, thus deriving electrical and electrochemical parameters for the mortar matrix and the steel reinforcement respectively. Additionally, an evaluation of certain domains from the impedance response can be correlated to properties of the bulk cementitious material and denoted to different interfacial structures. This study aims at exploring the microstructure alterations and specific interfacial
zones, related to which, porosity and ionic conductivity are main structural and physicochemical parameters, defining ion transport and current flow, with regard to corrosion and protection respectively. Investigation of the system response in the high frequency domain will describe the microstructure phenomena in the bulk cementitious material.

Figure 6.11 depicts a representative example of the impedance response in the high frequency domain (similar to lower left corner of the full complex plane plot of Fig. 6.10c) for the reference and corroding specimens. In this domain (Fig.6.11), the complex impedance plot comprises two distinct regions, i.e. the bulk mortar response and the beginning of the electrode (steel surface) response. The cusp between the high frequency arcs and the semi-straight lines represents the transition in system response from bulk mortar (including pore network and ITZs, see Fig.6.10a, region 2) to the electrode response.

The high frequency arcs for reference (R) and corroding (C) specimens differ in patterns, the latter presenting a distinct ‘plateau’ region in the response. This implies that the microstructure changes in the C mortar result in enhancement of double-layer polarization effects on the pore walls surface, as reported in case of other inclusions in cementitious materials [37]. The plot however is not shifted to higher, but to lower impedance values. This indicates that the bulk mortar in specimen C does not become more resistive as expected due to faster hydration and reduced porosity (normally chloride additions in ordinary Portland-cement materials increase the pore volume of finer pores and decrease the fraction of coarse pores i.e. shift the porosity to a finer one [32,33]). This observation can be explained with the pore network parameters, derived from micro-structural analysis (Section 6.5.3), which will be further discussed in the following sections.
Based on the aforementioned analysis, the derived porosity of mortars C (containing NaCl) in the mortar bulk is 4.37%, slightly lower than that of R (4.91%), accompanied by critical pore size of 0.78 and 1.59 µm, respectively. The electrical properties and impedance response for the bulk mortar are mainly dependent on the specific surface area (per volume of mortar) of the pore space (0.041 µm⁻¹ for group C and 0.038 µm⁻¹ for group R, at 120 days of hydration), and the pore interconnectivity (0.134 for C and 0.048 for R). Hence, the electrical properties of the specimens are determined to a significant extent by pore network characteristics. The double layer polarization in the C specimens is additionally influenced by microstructure alterations associated with chloride binding/de-binding mechanisms. Thus the influences of NaCl ingress in terms of stimulating hydration and lowering bulk porosity are counteracted by the effects of increased pore surface area and interconnectivity. This explains the lower electrical resistivity i.e. higher pore network capacitance for mortar C, which will be elaborated in the following sections.

6.5.5.1 Correlation between EIS and interface microstructure in the high frequency domain

As mentioned, EIS measurements were performed for all specimens in each technical condition. In this section, some data for the elements of the equivalent circuits, corresponding to the high frequency domain in EIS measurements, will be correlated to specific interfaces, morphological aspects and composite microstructure in terms of the influence of corrosion and hydration products. Fig. 6.12 presents a schematic presentation of the bulk mortar matrix (corresponding to regions 2 and 2’ in Fig.6.10).

6.5.5.2 Interface between pore solution and solid phase in bulk mortar

The resistance of the bulk mortar and the pore network (represented by $R_1$ and $R_2$, Fig.6.10b) are mainly dependent on the properties of the pore solution and of the ITZs between the cement paste and the aggregate. Relevant to microstructure properties, Song [38] proposed a theoretical model of an equivalent circuit for interpreting the experimental Nyquist plots for concrete systems. According this model, there are basically three types of paths in a concrete structure, i.e., continuous conductive paths (CCPs), discontinuous conductive paths (DCPs), as sketched in Fig. 6.12, and ‘insulator’ conductive paths (ICPs).
Theoretically, current conduction through CCP occurs by ion migration in the pore solution. Therefore, the total impedance of all the CCPs in the mortar could statistically be described as a resistance $R_{CCP}$. It can be expected that $R_{CCP}$ is inversely proportional to porosity and pore connectivity, whereas positively proportional to the resistivity of the pore solution, and to the tortuosity of the transport paths (CCPs) (mainly dependent on the volume fraction and the shape of aggregate grains). It is also related to the geometry of the concrete specimen (e.g. thickness, geometrical shape of the mortar specimen). The specimen geometry and the mortar mixing proportions are constant in this study, so only the porosity, the pore connectivity and the resistivity of the pore solution are relevant to $R_{CCP}$ in this case. The resistance of CCPs (denoted as $R_{CCP}$) can be associated with the experimental values of $R_1$ and $R_2$ by $R_{CCP} = R_1 + R_2$.

Compared to CCP, DCP has a more complicated impedance expression because of the discontinuous points (DPs). The impedance of DCP can be considered consisting of two parts: the continuous portion of DCP and the discontinuous point (i.e. the cement paste layers). At the DP point, current has to "penetrate" through the cement paste layer. However, the cement paste has high resistivity and is usually regarded as an "insulator," so a DC current is difficult to "penetrate" through such a layer. The "discontinuous point" can also be treated as a double parallel plate capacitance ($C_{DP}$) with the cement paste as its dielectric. The continuous portion of DCPs would have an impedance similar to that of CCP, and can be described as the resistance $R_{CP} = (R_1 + R_2)R_2/R_1$. For theoretical details of this equivalent circuit model, see [38].

During the process of cement hydration, a large amount of hydration products (C–S–H gels) are generated, which will block the CCP paths, will narrow the DCP paths or thicken the DP layers (cement paste). All these changes in CCP and DCP paths would increase $R_{CCP}$ and $R_{CP}$, resulting in a gradual increment of $R_1$ and $R_2$ with hydration time. In the reference mortar, substantial existence of monosulphate was evidenced. In the freely corroding (C group) and protected (P) mortars, monosulphate would bind with chloride ions and transform into Friedel’s salt (Fig. 6.5).

![Fig. 6.13 BSE image and the relevant EDAX analysis](image-url)  

The mechanism of Friedel's salt formation in cement pastes has not been unambiguously identified. Literature suggested two mechanisms underlying the conversion from monosulphate to Friedel's salt [39]. The conversion of hydroxy-AFm to Friedel's salt by ion exchange or by the
absorption of Cl\(^-\) as Friedel's salt forms by precipitation. Friedel's salt consists of two principal \([\text{Ca}_2\text{Al(OH)}_6\cdot2\text{H}_2\text{O}]^+\) layers that require balancing negative charge for stability. The availability of Cl\(^-\) (from NaCl ingress) would satisfy charge neutrality in the solid but this would disturb the ionic charge balance in the pore solution. To compensate for this, an equivalent amount of Na\(^+\) ions would be required to leave the pore solution, i.e. be absorbed into solid phases. In a cement paste system, the main ions in the pore solution are OH\(^-\), K\(^+\), Na\(^+\), and Ca\(^{2+}\). Ions migrate to the interface from the pore solution, and pass through the interface, and then continue to travel in the solid phase. In this case, the solid is usually an ion conductor; otherwise the ions would be accumulated in the vicinity of the interface in the solid side (Fig. 6.13) and would finally minimize the current conduction. At the interface between the pore solution and cement gel, the cations K\(^+\), Na\(^+\), and Ca\(^{2+}\) would be "piled up" in the cement solid, which would change the electrical properties of the latter.

Figure 6.14 reveals that mortar resistance of the R specimen is gradually increasing, in correspondence to the continuous hydration process. Porosity and pore connectivity are further reduced at a more matured hydration stage. The much higher value of \(R_{CCP}\) for the R mortar (see Fig. 6.14c) is partly attributed to the fact that the R mortars were submerged in water. In contrast, the C and P mortars (both submerged in 7% NaCl solution) present much lower resistance, reflecting the effects of chloride ingress on the electrical property of concrete. The C mortar

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![Graph showing resistance evolution versus time of the investigated mortars](image-url)
witnessed a sharp drop in both $R_{CCP}$ (Fig. 6.14a) and in $R_{CP}$ (Fig. 6.14b) around 90 to 100 days of cement hydration. A simplified model was proposed in [40] to correlate the valence of iron ions in corrosion products, volume expansion of the corrosion products, as well as porosity and thickness of the steel-paste interfacial zone with mechanical aspects of reinforced cementitious materials. According to this model, the estimated crack initiation period for the C mortar is about 130 days. This is in line with the time of the sharp drop in mortar resistance for the C specimen and implies that the corrosion-induced cracks yield formation of channels and networks of CCPs.

As seen from Fig. 6.14, the $R_{CCP}$ of the P specimen maintains relatively stable throughout the investigation period and the value of $R_{CP}$ indicates an obvious trend of increase since 100 days of cement hydration. The estimated crack initiation period for the P mortar (keeping in mind that CP was applied at 60 days i.e. after corrosion was initiated) is about 4.23 years. This (along with the protection itself) can be attributed to the favourable morphologies of corrosion products (very small dimensions and semi-crystalline) in the P mortars. The transformation of small amounts of these tiny oxides can migrate through the porous structure of the bulk mortar, pile up in empty space (as pores or voids), and locally reduce the porosity. Hence, the estimated crack initiation period for the P mortar is 4.23 years, compared to 130 days for the C mortar [41].

6.5.6 EIS response in the intermediate and low frequency domains

Determination of double layer (DL) capacitance in terms of bulk, pore network or interfacial capacitance, involves properties of the double layers formed in the pore structure, in the ITZs and at the steel/cement paste interface, hence capacitance values can be correlated to the specific interface microstructures in the system. Capacitance can be calculated from the impedance response in certain frequency domains (derived from experimental Nyquist plots, theoretical considerations, fitting procedures and according the relation $C=1/\omega Z''$). In some fitting procedures, the capacitance $C$ was replaced with constant phase element (CPE), which is widely accepted for systems as in this study [14,42,43]. The replacement of C with CPE is denoted to inhomogeneities i.e. steel surface roughness, bulk matrix heterogeneity etc. The CPE is an empirical mathematical description of the observed impedance response and is defined by [44] as: $Z=(j\omega)^{-n}Y_0$, being further quantified by the parameters $Y_0$ and $n$ (CPE constant and CPE factor respectively).

As described in Section 6.5.5.2, relevant to microstructure properties, three types of paths in mortar structure can be basically distinguished [38], i.e. continuous conductive paths (CCPs), discontinuous conductive paths (DCPs) and ‘insulator’ conductive paths (ICPs). All these paths contribute to the overall ion transport and thereby to the electrolytic and current transport in the system. Hence, the DL capacitance values, attributed to these paths, determine the electrical properties of the bulk materials and those of the interfaces.

The system response in the high frequency domain (50 kHz to 1 kHz) corresponds to interfacial properties associated with the electrolyte/mortar cover zone, overlapping with bulk mortar characteristics. The correlation of derived resistance values in this frequency domain (as $R_1$ and $R_2$, Fig.6.10b) with structural parameters was discussed in Section 6.5.5. Further, in the
intermediate frequency domain, using the best fit parameters of the experimental EIS data and considering the first time constant of the equivalent circuit (Fig. 6.10a,b), the bulk in terms of pore network capacitance (using pseudo-capacitance values) can be derived. Evolution of the latter with time is presented in Fig. 6.15.

The electrical capacitance for the reference group R is significantly lower than the capacitance values for corroding specimens. The observed decreasing trend for $Q_{pn}$ (Fig. 6.15), can be denoted to the cement hydration process (densification of the pore network and increased electrical resistance with aging). Specimens $C_1$ and $C_2$ (which are different corroding specimens from group C, equal in composition, specimen geometry and set-up) exhibit a general trend of decline of pseudo-capacitance values for all paths until 90 days of hydration. The differences in capacitance values for the two corroding specimens (which are otherwise equal in composition and conditioning) can be attributed to the combined effects of non-uniform chloride binding reactions (the formation of calcium-chloro-aluminates) and de-binding mechanisms as chloro-aluminate complexes become unstable in certain conditions, e.g. CO$_2$ penetration into the cement matrix. Since mortar is a highly heterogeneous material (especially on micro level), these physico-chemical alterations (already discussed in Sections 6.5.1. and 6.5.2.) can not be expected to take place in exactly the same manner in different specimens from one group, although the same mortar mixture was used. On later stages of hydration, the behaviour of specimens $C_1$ and $C_2$ becomes closer, the capacitance values for both specimens exhibiting an obvious trend of climb since 90 days (Fig. 6.15). The increase for bulk/pore network capacitance at 120 days for group C,

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**Table: Pseudo-capacitance Values**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$Q_{pn}$ (1/Ohm)</th>
</tr>
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<tbody>
<tr>
<td>R</td>
<td>5.44E-09 2.62E-09 1.70E-09 9.87E-10</td>
</tr>
<tr>
<td>P</td>
<td>1.30E-07 6.30E-08 2.06E-08 4.00E-08</td>
</tr>
<tr>
<td>C1</td>
<td>1.38E-07 2.82E-09 1.56E-10 5.27E-07</td>
</tr>
<tr>
<td>C2</td>
<td>4.90E-07 8.35E-10 7.56E-10 6.93E-07</td>
</tr>
</tbody>
</table>
can be denoted to crack initiation and propagation as a result of volume expansion of corrosion products (as evidenced by morphological observation (Section 6.5.3, Fig.6.9). These observations are consistent with the observed drop in bulk/pore network resistivity values at about 100 days of age (Fig.6.14). Hence, micro-cracking contributes to the overall ion transport and thereby affects electrical properties of the mortar system.

In contrast to the freely corroding reinforced mortars (group C), the pseudo-capacitance of the protected specimens (group P) in the intermediate frequency domain, does not show significant change after 80 days of age. In particular, the pore network capacitance (Fig.6.15) is shifting towards lower values since 80 days of hydration, which proves the efficiency of CP technique. The underlying mechanisms are the favourable changes in structural morphology of hydration and corrosion products (as discussed in Sections 6.5.2 and 6.5.3, as well as Chapter 5). As mentioned, the presence of NaCl in cement-based materials (as in this study) is causing structural modifications [32], similar to the influence of additions with pozzolanic effects [37]. In the present study, a combined effect is likely taking place in specimens group P, taking into consideration the current flow in these specimens. The protection current brings about additional alterations in the surface charge of the calcium silica hydrate (C-S-H), which is influenced by the chloride ion impulsion away from the steel surface (see Chapter 3). In this case the free chloride ions will be bound, the C-S-H will trap the charge carriers (Na⁺, K⁺, OH⁻). Together with reduced porosity and connectivity (Table 6.4.) and lower electrical capacitance in the pore network, the resistivity in the bulk matrix will be improved. (The combined influence of NaCl and current flow on concrete microstructure and electrical properties is reported in [9] and will be discussed in Chapter 7).

In summary, comparing capacitance values at the end of the test, specimens C exhibit an increasing trend after 90 days of age, in contrast to the decreasing trend for group P till the end of the test at 120 days (Fig.6.15). The bulk and pore network capacitance (denoting CCPs, ICPs, DCPs) for the reference sample (R) are the lowest, (corresponding to the highest resistance values, Fig.6.14) and are much lower than those for the corroding group (specimens C). Comparing specimens C and P, the bulk and pore network capacitance of specimens C is higher than for specimen P after the CP application (supporting evidence for the effective performance of CP on specimen P), corresponding to lower resistance, the latter attributed to micro-cracking in specimens C, which results from propagation of corrosion products in the pore network.

6.5.7 Correlation capacitance/microstructure

Ion transport mechanisms and electrical properties are strongly dependent on material microstructure, the pore structure is highly relevant to the electrical properties of materials. However, porosity and pore size distribution are not the only determining factors. Another important factor is the pore network connectivity (dimensionless parameter [31], derived from PDD, Chapter 2).

Figure 6.16 depicts the relationship between pore interconnectivity and the critical pore size. The data are presented for the “edge”, “bulk” and “interface” locations (Table 6.1) for all investigated groups R, C and P at the end of the testing period.
Generally, the interfacial zone at the steel surface (solid symbols in Fig.6.15), exhibits high connectivity and coarser pore structure than the bulk matrix (as depicted also in Figs.6.6 and 6.7, Table 6.4). The critical pore size in the interfacial and bulk zones for R is higher than the mortars C under NaCl ingress, the pore interconnectivity however is much lower; hence the pseudo-capacitance of pore network and the interfacial capacitance are expected to be lower for specimens R, compared to specimens C.

Fig. 6.17(a) presents the correlation of pore network capacitance (derived from $Q_{pn}$, as already described above) with bulk critical pore size and bulk porosity, confirming the aforementioned statements. It is expected that the specimen R (without chloride ingress) exhibits the lowest capacitance for the bulk regions among the investigated mortars. For specimens R, ion transport is restricted and results in high electrical resistance (see Fig.6.14, despite the coarser pore structure (porosity higher than specimens C and P, critical pore size is highest as well -Table 6.4, Fig.6.17a). The phenomena are partly attributed to certain structural peculiarities in the reference specimens (as previously discussed) and microstructure (Section 6.5.3)). In addition, it should be mentioned that the surface charge of the C-S-H influences the pore network properties and electrical parameters. As discussed in Chapter 3, the typical Ca/Si ratio of C-S-H in Portland cement is about 1.8. The surface charge on C-S-H depends on its Ca/Si ratio: when the Ca/Si ratio is high, the surface charge is positive and anions (such as Cl$^-$ and OH$^-$) are adsorbed on the C-S-H fibers (but not cations as Na$^+$ and K$^+$, which remain in the pore solution); in contrast, if the Ca/Si ratio is lower than about 1.2-1.3, the surface charge of C-S-H becomes negative and alkali ions are incorporated in the C-S-H, thus decreasing the alkali ion concentrations in the pore solution [45]. Therefore, in the case of relatively high Ca/Si ratio as in the C specimens, being in the range of 2.19 - 2.95, the ion movement cannot be suppressed by C-S-H as in the case of R specimen (Ca/Si ratio of 1.4). Thus the unfavourable effects of high Ca/Si ratio counteract the positive...
aspects of a lower porosity and critical pore size in the C specimens. In addition, the pore connectivity in group C is higher than group R (both in the bulk matrix and the interface, Fig.6.16), despite the smaller critical pore size for group C (Figs.6.16,6.17). As a result, along with the influence of the electrochemical phenomena on the steel surface, the pseudo-capacitance of the pore network in corroding specimens C, also determined by the surface charge of the C-S-H in the bulk matrix, is higher than the reference mortars R (Figs.6.17a).

Figure 6.17b) depicts the correlation of interfacial capacitance (values derived by EIS and already presented and discussed in Chapter 4) and pore connectivity at the steel/paste interface. The observed relationships are as expected: highest interfacial capacitance and highest pore interconnectivity for groups C, corresponding to enhanced corrosion on the steel surface and the consequently formed corrosion-induced cracks; lower interfacial capacitance and pore connectivity at the steel interface for the reference group R, confirming the passive state in this group; and even lower capacitance and connectivity values for protected group P, reflecting the efficiency of CP in these specimens.

With regard to the lower capacitance and pore connectivity for specimens P, compared to specimens R, the following deserves attention: as already discussed, NaCl accelerates cement hydration and alters the pore structure. Specimens P, being maintained in the same conditions as specimens C, will undergo densification of the pore network, similar to group C, which explains the lower pore interconnectivity in group P at the end of the test, compared to group R. On the other hand, CP application at 60 days of age, will further maintain group P protected from corrosion, consequently the interfacial capacitance becomes lower for specimens P, compared to specimens C and the bulk matrix will be maintained un-cracked (as there is no further formation of corrosion products, as this would proceed in specimens C). Therefore, the already denser (compared to R) pore structure remains unchanged and there are no other factors (as micro-cracks) which would cause increase in pore interconnectivity, hence group P exhibits lowest pore
network connectivity at the steel interface at the end of the testing period. A contributing factor is the constantly flowing CP current, the latter found to contribute to densification of the bulk cementitious matrix as well [9,46].

A comparison on basis of derived structural parameters can be done for all conditions, corresponding well to microstructural observations on the steel/cement paste interface and derived electrochemical parameters. In the reference specimen (group R) – Fig.6.18b, there is no detrimental influence of chlorides, the steel/paste interface exhibits the highest porosity, but relatively low connectivity (Fig.6.18a). For the corroding specimens (group C), the presence of a significant amount of cracks due to corrosion and expansion of corrosion products is evident (Fig.6.18c), corresponding to the highest connectivity at the interface for C (Fig.6.17, 6.18a). The microstructure analysis of protected specimens P (interface is clear from cracks – Fig.6.18d) and the EIS measurements, evidence the effect of CP technique, since specimens P exhibit the lowest interfacial capacitance and lowest connectivity at the steel/paste interface (Fig.6.17b, 6.18a).
6.6 CONCLUSIONS

This Chapter aimed at exploring reinforced mortar as a multi-phase composite material, underlying the effects of corrosion and cathodic protection on material structure; further, to correlate the structural properties of the involved materials with electrical and electrochemical parameters. For this purpose, certain component elements of the equivalent electrical circuit of EIS measurements were discussed in correlation to the evolution of specific interfaces and pore structure parameters during the corrosion process and during CP.

Although mortar is an insulating material, hence a significant charge separation is restricted, the accumulation and distribution of charge species, especially in conditions of corrosion and CP, will behave as an electrical double layer (EDL). Therefore, a correlation of derived electrochemical parameters and pore network characteristics provides more detailed information for the evolution of the material behavior in the relevant conditions. The pore inner space was described with microstructure parameters as critical pore size; the alterations in the EDL capacitance and the influence of the hydration/corrosion products were associated with the pore size distribution and the changes in size of the structuring element; the pore interconnectivity was related to the capacitance of the EDL in the pore network.

The bulk and pore network pseudo-capacitance for reference specimens R are the lowest and are relatively constant in time, which corresponds to the highest bulk resistance, despite the highest porosity for these specimens. For the freely corroding mortar specimens, the resistance of continuous conductive paths (CCPs) is increasing in the first 2(3) months as a result of cement hydration in combination with the influence of NaCl. However at about 90 to 100 days of age, the excessive volume expansion of corrosion products of lamellar and needle-like morphologies (generally in the 10 – 20 µm regions of steel/paste interface), leads to cracks in the steel-mortar interfacial zone. The cracks further propagate into the bulk mortar (up to 2000 µm away from the steel surface for this age) and yield a sharp drop in the resistance of CCPs.

The cathodic protection induces favorable microstructure changes in the specimens, in terms of dimension and morphological aspects of the product layers. The low crystalline corrosion products, formed prior to CP application, initially migrate through the material structure and fill in voids and open space, thus block a part of the conductive paths. Further, the product layers on the steel surface transform into a stable and adherent film of high valent iron oxides. As a consequence, the resistance of CCPs is maintained at a stable level and after 100 days of cement hydration, displays a trend of increase.

Microstructure investigations (by means of scanning electron microscopy) and morphological studies of pore structure characteristics (by means of quantitative image analysis) support the experimental results of EIS. In terms of the steel electrochemical behavior, correlated to the properties of the mortar matrix at the steel/cement paste interface, the following can be concluded: the interfacial capacitance reflects the electrochemical phenomena at the steel-paste interface; the highest interfacial capacitance and the highest interfacial pore connectivity were
recorded for the corroding group C, which corresponds to the enhanced corrosion of the steel surface and consequently corrosion-induced cracking in this group; lower interfacial capacitance and pore interconnectivity were recorded at the steel/cement paste interface for the reference group R, confirming the passive state of the reinforcement and unaffected mortar microstructure in this group; comparing all specimens, lowest capacitance and pore connectivity values at the steel/cement paste interface were derived for the protected group P, reflecting the CP effectiveness in these specimens.

The combination of electrochemical methods and microstructure characterizations allows breaking down the EIS measurements to different interface structures in concrete composites, and sheds light on the fundamental mechanisms underlying the efficiency of cathodic protection techniques.

References:
PART III Experimental Investigation: Concrete and reinforced concrete

CHAPTER 7
ELECTRICAL AND MICROSTRUCTURAL PROPERTIES OF PLAIN CONCRETE IN CONDITIONS, SIMULATING CONVENTIONAL AND PULSE CATHODIC PROTECTION.

7.1 INTRODUCTION

The concrete matrix has a significant contribution to the global performance of reinforced concrete. In conditions of current flow (as in the case of impressed current cathodic protection (ICCP)) through the concrete bulk material, the latter undergoes alterations in chemical composition, electrical properties and microstructure, thus influencing the overall response of the system. Aiming at optimization of the ICCP technique, a comparative study is carried out in this Chapter 7 between pulse and conventional ICCP in terms of bulk matrix (concrete) response to applied current regimes. Ordinary Portland cement concrete blocks were cast, differing in experimental set-up and chloride concentrations. All specimens were subject to resistance monitoring and ion concentrations determination. The favorable effects of pulse-CP current flow on the concrete matrix were additionally explained by microstructural analysis of the specimens. It is found out that physico-chemical changes due to ion transport as well as electrical properties of the concrete are attributed to the structural alterations of the pore space induced by the CP current.

7.2. TECHNICAL BACKGROUND

Impressed current cathodic protection (ICCP) is used for corrosion protection in reinforced concrete since the 1970s. So far it is proven to be the only technique that is able to minimize or stop corrosion in salt contaminated environments [1]. The repulsion of aggressive anions (e.g. chloride) which takes place along with the protection itself is a beneficial one as far as corrosion risk of the steel is concerned. An excessive overprotection current however, will result in alkali ions (K\(^+\), Ca\(^{2+}\), Mg\(^2+\)) accumulation at the steel/rebar interface, thus causing softening of the C-S-H gel, alkali silica reaction (ASR) and bond degradation [2]. Along with ion migration and diffusion due to the CP current, the heterogeneities and instabilities inherent in the concrete material may lead to non-uniform distribution of the current and thus might result in localized overprotected areas. In addition, CP current was found to induce structural alterations in the bulk concrete and in the pore space, to cause micro-cracking which along with softening of the C-S-H leads to reduced concrete durability, as discussed for mortar specimens in Chapters 4 and 6 and reported also in [3]. The main negative effect in terms of concrete microstructure is enlarging the gap between cement paste and aggregate in the interfacial transition zones (ITZs), thus yielding micro-cracks. These unfavorable microstructure alterations can lead to concrete degradation; however, the underlying mechanisms are not well explained for civil structures. Furthermore,
concrete resistance increases with aging. As investigated in the frame of this research [4,5] and discussed in the previous chapters for mortar specimens, microstructure alterations in cement-based materials yield non-uniform electrical properties and thereby possibly result in disturbance of the electrolytic path (i.e. the current demand is increasing). This constitutes an additional feature that should be overcome in engineering application of the CP techniques.

This Chapter explores the applicability of pulse current as alternative of conventional steady DC current for corrosion protection in reinforced concrete. The investigation was performed on different stages, and hereby summarized for the total duration of the test (210 days of cement hydration). The Chapter focuses on the influences of conventional and pulse CP current on ion transport, electrical properties of concrete material, and on microstructural alterations in the concrete specimens. In particular, the study aims at correlating electrical properties with the concrete microstructure changes (in pore structure and the ITZ) associated with the CP current. The properties of the ITZ are of significant importance for the electrolytic path in the concrete system and the manner of current distribution. The research reveals that the cost-effective pulse CP applications can successfully minimize the side effects on material structure and promote beneficial ion transport (particularly chloride withdrawal), while more efficiently overcoming the concrete resistance and thus suggesting for better performance compared to conventional CP current applications.

7.3 EXPERIMENTAL MATERIALS AND METHODS

7.3.1 Materials
Concrete prisms (100x100x300 mm) were cast by mixing Ordinary Portland Cement CEM I 32.5R with sand and gravel (ratio 1:2:4, aggregate size ranging from 125 µm to 16 mm), with water-to-cement ratio (w/c) of 0.6. The specimens were de-mould 24 hours after casting and placed in a fog room (98% RH and 20°C) for a curing period of 60 days. Afterwards they were maintained in a climate room (50% RH, 20°C) till the end of the testing period (210 days). Table 7.1 indicates the differences in compositions between the three groups of specimens. Group D used de-mineralized water as mixing water, whereas 1.25M NaCl solution was used for the group N. Half of the DN specimen was mixed with de-mineralized water and the rest half with 1.25M NaCl solution. All the specimens were subjected to no-current, pulse CP and conventional CP current flow, respectively. The design of DN group aims at monitoring ion transport due to concentration gradient (in no-current condition) or ion migration due to the applied CP current (under pulse or steady CP current condition). Table 7.1 also presents the experimental set-up for electrical resistance measurements, i.e., MMO titanium plates were cast on both sides of the prisms for applying the electrical current; five MMO titanium pins were embedded equidistantly at 90 mm depth for monitoring the voltage drops along the longitudinal direction of the prisms. In what follows, no-current condition is denoted as ‘rest’, conventional and pulse CP current coded as ‘DC’ and ‘pDC’, respectively.
### Table 7.1 Experimental set-up

<table>
<thead>
<tr>
<th>Specimen code</th>
<th>Composition</th>
<th>Experimental set-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (x10 specimens)</td>
<td>Demineralised water</td>
<td>![Demineralised water Diagram]</td>
</tr>
<tr>
<td>N (x10 specimens)</td>
<td>1.25M NaCl solution as mixing water</td>
<td>![1.25M NaCl Solution as Mixing Water Diagram]</td>
</tr>
<tr>
<td>DN (x12 specimens)</td>
<td>Demineralised water NaCl</td>
<td>![Demineralised Water NaCl Diagram]</td>
</tr>
</tbody>
</table>

### Table 7.2 Technical specification: resistance monitoring and CP current regimes.

<table>
<thead>
<tr>
<th>Resistance measurement</th>
<th>Cathodic protection current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measuring current: 100µA balanced alternating square wave</td>
<td>DC current: 100µA (per cell)</td>
</tr>
<tr>
<td>Frequency: 120 Hz</td>
<td>Current source impedance: 300 kΩm</td>
</tr>
<tr>
<td>Current source impedance: &gt;10 MΩhm</td>
<td>Pulse DC: 1kHz</td>
</tr>
<tr>
<td>Voltage diff. input range: max + or –4 Volt, 12 bit</td>
<td>Duty cycle 12.5 % to 50 %</td>
</tr>
<tr>
<td>A/D conversion</td>
<td></td>
</tr>
<tr>
<td>Voltage diff. input impedance: &gt;100 MΩhm</td>
<td></td>
</tr>
</tbody>
</table>

#### 7.3.2 Electrical resistance measurements and simulation CP current regimes

The resistance measurement was performed by AC 4 pin method, performed with a specially designed device in certain regimes (Tables 7.1,7.2). The advantage of the AC methods is that the mean value of the AC current is zero, i.e. the polarization effects due to the measurement could be minimized, thereby guaranteeing relatively high accuracy. The measurement was performed via the embedded plates (at both ends of the specimens, see Table 7.1) and the embedded pins. Thus several potential differences can be recorded, depending on configuration. A multiplexer is used to select a specific section from a number of cells. Another multiplexer selects two electrodes (pins) to measure the potential difference. For the resistance measurement an alternating square wave current is applied to the cell via one of the current electrodes, whereas the other is grounded. The potential difference between two of the five electrodes (pins) is recorded at the moment just before the transition in the current source for the purposes of reducing the effects of cabling and other parasitic capacities. The resistance is then computed from the current and the measured potential difference.

![Resistivity Measurement Diagram]
The current supply (CP current of 10 mA/m²) was involved in two regimes, i.e. DC and pulse DC. The current was applied to the side electrodes of the cells, with one connected to the current source and the other to ground (same as for the resistance measurement). The current source is a real voltage source with a series resistor for each cell that determines current. This set-up has a minor disadvantage that the voltage over the cell will influence the current; however, this effect can be neglected in view of the quite high voltage (30V). The frequency and duty cycle for the pulse DC regime was set out by an external function generator. The specification for the resistance monitoring and the CP current regimes are given in Table 7.2.

7.3.3 Chemical analysis
Chemical analysis was performed for the different sections (Table 7.1) of the specimens at 14, 50 and 128 and 210 days of cement hydration. Additionally, ion concentrations were determined at 64, 86 and 109 days of hydration for the specimens under the three technical regimes (rest, DC and pulse DC) by drilling cores, thus monitoring the changes in ion concentration for a specific section in one and the same specimen with time. The samples for chemical analysis (including determination of hydrated cement and hydrated water) were prepared according to ASTM C114-77 (wet chemical measurement of chloride concentrations using Volhard titration method). For the water-soluble chloride, the analysis conforms to ASTM C1218, for the acid-soluble chloride according to ASTM C1152. Alkali ion concentrations were determined by plasma spectrometry using Inductive Coupled Plasma spectrometer (ICP-AES). The chemical analysis aims at monitoring ion transport associated with diffusion and migration under electrical field (DC and pulse DC).

7.3.4 SEM imaging and pore structure analysis
Section images of the specimens were obtained by scanning electronic microscopy (SEM) with backscattered electrons mode (BSE), using environmental SEM, ESEM Philips XL 30. The ESEM and EDX analysis were performed as already specified in Chapters 3 and 4. The technical background for the pore structure analysis is presented in Chapter 2, the experimental procedures are as presented in Chapters 3 and 4.

7.4 RESULTS AND DISCUSSION

7.4.1 Electrical properties – changes due to hydration and CP current
The electrical resistivity of concrete is claimed to be one of the main parameters characterizing the possibility of displacement of charged particles under the influence of an external electrical field or under the influence of concentration gradients. The moisture content in concrete significantly influences its electrical resistivity. The concrete conductivity (reciprocal of resistivity) is characterized through the motion of ions such as Na⁺, K⁺, OH⁻, SO₄²⁻, Ca²⁺ in the pore solution. In concrete, ionic (or electrolytic) conduction is the main phenomenon of electricity transport [6]. So, the value of concrete conductivity and resistivity will be influenced by the ions concentration in the pore system. The electrical conductivity and resistivity are correlated with the concentration of aggressive ions, such as Cl⁻, being a main cause for pitting corrosion in
Electrical and microstructural properties of concrete materials in conditions of current flow

Some studies claimed that the chloride ions will reduce the resistivity of wet concrete (i.e. increase concrete conductivity) and thus lead to corrosion risk [7,8]. It is reported that reinforcement corrosion can be predicted from concrete resistivity, taking into account that chloride diffusivity is proportional to concrete conductivity [8]. Other studies [6,9] found an inversed correlation between concrete resistivity and chloride diffusion rate. According to Polder [7] the corrosion rate is inversely proportional to the concrete resistivity.

Total Resistivity (KOhm cm) vs Time(days), samples N1 rest, N2-pDC and N3-DC

Total Resistivity (KOhm cm) vs Time(days), samples D1 rest, D2-pDC and D3-DC

Total Resistivity (KOhm cm) vs Time(days), samples DN1, DN2-pDC, DN3-DC

Fig. 7.1 Evolution of total resistivity vs. time (days of cement hydration) for different concrete specimens (D- mixed with de-mineralized water, N- mixed with 1.25M NaCl solution, DN- half-to-half combination of D and N) under three technical conditions: rest- no-current conditions, pDC- under pulse CP current, DC- under conventional CP current. Details of the experimental set-up are indicated in Table 1.

Resistance monitoring was performed during a period of 210 days of cement hydration. The total electrical resistivity and local resistivity at various sections are calculated using the equation: $\rho = RA/l$, where $\rho$ is the resistivity (in Ohm-cm), $R$ is the resistance (in Ohm), $A$ is the cross section area (in cm$^2$) and $l$ is the length (in cm). Fig. 7.1 depicts the evolution of total electrical resistivity for all groups in different technical conditions, i.e. in rest conditions (only cement hydration is involved), under pulse and conventional CP current with the current flowing through the cell as an additional influencing factor. Fig. 7.2 presents the changes in electrical resistivity for various sections in all groups of specimens under these technical conditions.

Concrete resistivity increases with time as a result of cement hydration, a mechanism involved in all the investigated specimens. For the N and DN specimens under pulse and conventional CP current, electrical properties are additionally influenced by the presence of NaCl and by electrical current flow through the specimens. In the initial testing period of 30 days of cement hydration, all specimens were in the same conditions (fog room) without CP applications; during this period, only the chloride ions play a role in addition to cement hydration. Fig. 7.1 reveals that all specimens follow the same pattern of resistivity increase during this initial period despite the significant concentration of NaCl (1.25M NaCl solution used as mixing water) in groups N and DN. The fact is attributed to the accelerated cement hydration in case of NaCl additions, represented by the following chemical reaction:
\[
2\text{NaCl}_{\text{aq}} + [3\text{CaO.Al}_{2}\text{O}_3\cdot6\text{H}_2\text{O}]_{\text{s}} + \text{Ca(OH)}_2_{\text{s}} + 4\text{H}_2\text{O} \rightarrow [3\text{CaO.Al}_{2}\text{O}_3\cdot\text{CaCl}_2\cdot10\text{H}_2\text{O}]_{\text{s}} + 2\text{NaOH}_{\text{aq}}
\]

(1)

As a consequence, the so called Friedel’s salt is formed \([3\text{CaO.Al}_{2}\text{O}_3\cdot\text{CaCl}_2\cdot10\text{H}_2\text{O}]\), accompanied by release of NaOH, which leads to increase of the pH in the pore solution. This will further accelerate the hydration process and consequently modify the pore structure towards a finer pore size distribution. The observations are consistent with the experimental findings for mortar specimens, discussed in Part I of the thesis and will be further demonstrated by the pore structure analysis (Section 7.4.4) for the here investigated concrete specimens. The chloride ions promote cement hydration and reduce the pore connectivity, hence, the electrical resistivity for all of the specimens during the first 30 days of testing are similar and do not show a significant dependence on ion concentrations.

The electrical current was applied after 30 days of cement hydration to part of the concrete specimens (simulating CP current) and aimed at investigating the relationships between electrical properties and microstructure changes induced by the current flow. Figs. 7.1 and 7.2 reveal that in fog room conditions, all the specimens (under both steady and pulse current) show a smooth and gradual pattern of climb of the electrical resistivity. However, the current is influencing the cement hydration as the amount of hydrated cement in some sections of DN (half-to-half mixed specimen) is slightly higher than those in no-current conditions. This is attributed to enhanced ion migration which takes place along with the ion transport due to concentration gradient in the DN specimens. From this point of view, the pulse CP presents better performance than the steady current, this will be further discussed in Section 7.4.2.

After 60 days of cement hydration, all specimens were placed in climate room (50% RH). As expected the electrical resistivity shows a considerable shift towards higher values as specimens were drying out. The influences of current flow on electrical properties for specimens D and N are lower compared to specimens DN, the latter showing a significant increase in electrical resistivity due to the applied current (Fig. 7.1). The reason is that the Cl concentration gradient in the DN specimen additionally promotes ion transport and accelerates the hydration process. Changing the pulse pattern (see Table 7.2 and Fig. 7.1) at about 120 days leads to a slight decline in the resistivity for pulse current conditions. This is beneficial for the concrete microstructure, since lower resistivity will ease ion and current flow in the concrete systems. Moreover, the pulse CP yields lower electrical resistivity in specimens DN compared to steady CP current (Fig. 7.1), the trend becomes more obvious at a later stage with a changed pulse pattern. At the end of the testing period (210 days in Fig. 7.1), specimens DN revealed the highest electrical resistivity, in contrast to the lowest values in specimens N. However, the difference of about 5 to 15 kOhm.cm between specimens D (free of chlorides) and N (with chlorides) is not dramatic taking into account the considerable chloride concentration (2.6% total and 1.87 % free chloride per dry cement weight). The literature recommended chloride threshold values of 0.2 % to 2.0% by mass of binder \([10,11]\); ACI 201.2R-77 suggested a limit of 0.10 - 0.15% free chloride by weight of cement for above ground structures. Hence, the chloride concentration in the investigated concrete is relatively high.
On the other hand, electrical resistivity values (>20 kOhm.cm) are good as well, in view of the recommended thresholds for evaluating corrosion risk (Table 7.3). It is evident that caution should be bestowed on interpretation of such experimental results, as high chloride concentration in DN specimens will cause local corrosion in reinforced concretes; therefore, high electrical resistivity does not guarantee a low corrosion risk. These research outcomes are in agreement with the observations for electrical properties of mortar specimens (discussed in Chapter 3) at earlier ages, hence confirm the aforementioned mechanisms, although concrete is a cement-based material with higher level of structural heterogeneity.

Table 7.3 Electrical resistivity thresholds for evaluation of corrosion risk in reinforced concrete structures.

<table>
<thead>
<tr>
<th>Empirical interpretation (after [12])</th>
<th>Interpretation using Gecor 6 device (after [13])</th>
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<tbody>
<tr>
<td>&gt; 20 kOhm.cm</td>
<td>No risk</td>
</tr>
<tr>
<td>10–20 kOhm.cm</td>
<td>Low to moderate corrosion risk</td>
</tr>
<tr>
<td>5 – 10 kOhm.cm</td>
<td>High corrosion risk</td>
</tr>
<tr>
<td>&lt; 5 kOhm.cm</td>
<td>Very high corrosion risk</td>
</tr>
<tr>
<td></td>
<td>Resistivity is not the controlling parameter</td>
</tr>
</tbody>
</table>

Figure 7.2 depicts the influence of electrical current (in addition to concentration gradients) on all specimens at different sections. Figs.7.1 and 7.2 indicate that electrical resistivity is not influenced by ion concentration gradients for the period of fog room curing, but by the moisture content (up to 60 days of cement hydration), which implies that the high RH of the surrounding environment plays a decisive role. After this stage (in climate room, but still with high humidity of 50% RH) the influence of ion diffusion and migration becomes more evident, particularly confirmed by the changes of electrical resistivity at different sections of the prisms (Fig. 7.2). A comparative study between the specimens without and with current applications allows separately evaluating the influences of ion migration and electrical current. For specimens without current application (the rest group), the only influencing factor is cement hydration (i.e. aging) and for specimens DN, also including concentration gradient. Fig. 7.2 clearly reveals the non-uniform values of resistivity for all the specimens under steady current, particularly in DDC, NDC and DNDC specimens. This can be attributed to non-uniform binding/de-binding mechanism of chlorides in the cement matrix (reported in [4] and discussed in Chapter 3) and to the alterations in pore connectivity in the bulk material.

Except ion concentration and moisture content, the electrical properties are also influenced by concrete microstructure and material heterogeneity. The electrical resistivity for all sections of all the specimens in rest conditions vary in the range of 25 – 40 kOhm.cm. With respect to aforementioned criteria for corrosion risk, all sections fall in the ‘moderate to high corrosion risk’ category. However, in view of the high chloride concentration in specimens N and sections B of specimen DN, corrosion risk can be considered as very high. Hence, a direct correlation between electrical resistivity and chloride concentration cannot be derived.
Fig. 7.2 Evolution of electrical resistivity with time of cement hydration for various sections (see Table 7.1) in concrete specimens under no-current (denoted as rest specimens), conventional CP (DC specimens) and pulse CP (pDC specimens) techniques.

In the case of absence of a concentration gradient (i.e. D and N specimens), steady DC (conventional CP) current increases the electrical resistivity, compared to the rest conditions. Pulse DC current (specimens DpDC and NpDC) exerts slight influences on the electrical properties; lower resistivity is recorded for both groups in the sections B (around the negative pole of the cell). Basically, decline in electrical resistivity could be explained by two main reasons, i.e., the presence of micro-cracking or easy water and ion transport. In the former case, damaged microstructure will further reduce overall resistance of the concrete material and consequently increase the conductive paths. The latter case is strongly related to structural parameters of the bulk concrete matrix. Microstructure analysis (Section 7.4.4) demonstrates higher extent of detrimental effects by the steady DC current compared to the pulse current. The favorable structural alterations, together with possible electro-osmotic effects [14] are underlying the positive effects of the pulse current regime.

The mechanisms are more complicated for the mixed specimens (DN) under steady and pulse DC. Here, the steady current significantly increases the resistivity in the middle sections A/B, in contrast to the less dramatic effects of the pulse DC (Fig. 7.2), exhibiting behavior, similar to rest
conditions. It should be noted that the section B4 (close to the negative terminal of the cell, with NaCl addition) in the pulse DC condition shows higher electrical resistivity than sections A (initially free of chloride). The phenomenon can be denoted to a considerably accelerated hydration process in section B (right half of the specimen) as result of enhanced ion migration under the influence of current flow. Chemical analysis (Section 7.4.3) of amounts of hydrated (bound) water by sections of the specimens provides supporting evidences. The favorable effect of pulse DC (compared to steady DC) is additionally envisaged by the much more uniform values of electrical resistivity among various sections of the specimen.

7.4.2 Hydration mechanism and electrical properties
As previously discussed in Chapter 2, the hydration process (the reaction of main phases with free water) results in the formation of calcium silicate hydrate (C-S-H, being the main bonding agent in cement-based materials), calcium hydroxide (CH), ettringite and other compounds. During the hydration process, the capillary pores are gradually filled up with hydration products; the solid phases form a rigid microstructure with increasing strength. However, the hydration mechanism and formation of hydration products are very complicated. Relevant to the present study, the presence of NaCl is involved in hydration mechanisms, and thereby also influences the ion and electrical current flow through the specimens. Water plays a decisive role with respect to transport process. Being the main source for mass transport in concrete, water can be classified into different forms in the porous structure of concrete material [15]. Chemically bound (hydrated) water is part of the hydration products, and could be released only with decomposition of hydrates; interlayer water is the water penetrating between layers of C-S-H; absorbed water is the water close to the solid surface due to physical forces of attraction, which decrease with the distance between the molecule and the solid surface. The last category, i.e., capillary water is the water free from attractive forces. Capillary water is present in voids larger than 50 Å and is the medium for ion transport.

![Hydration Water Distribution](image_url)

**Fig. 7.3(a)** Distribution of hydrated (bound) water by sections (middle sections and charged poles) in % per dry cement weight in specimens D in rest conditions (Drest), under steady (DDC) and pulse (DpDC) current; **(b)** distribution of bound water (% per dry cement weight) in middle sections and charged poles for samples N in rest conditions (Nrest), under steady (NDC) and pulse (NpDC) current.
The amount of bound water indicates the degree and rate of cement hydration, hence is related to electrical resistivity and ease of ion transport. The percentage of bound water for D specimen in rest conditions (Drest) is 18%, climbing to an average value of 25% at 210 days for the specimens under current flow (DDC and DpDC) (Fig.7.3a). The plot depicts the amount of bound water at different sections (middle part and around the positively and negatively charged poles) for specimens D under steady (DDC) and pulse (DpDC) current, respectively. The percent of bound water is the highest in section B3 of specimens DDC and lowest in section B3 of specimen DpDC. These results correspond well to the electrical resistivity measurements (Fig. 7.2). Hence, the amount of interlayer, absorbed and capillary water in those regions is higher which determines the lower resistance. The same observations are found for samples N (with addition of NaCl) for both current regimes: the lower amount of bound water at the negative pole for specimens under pulse DC (NpDC, see Fig.7.3b) corresponds to the lowest electrical resistivity for the same section. The higher bound water content in the middle section and in section B4 for specimen N under steady current (NDC) corresponds to higher electrical resistivity for the same section (Fig.7.2).

The relationship between bound (hydrated) water content and concrete resistivity for the mixed specimen DN under pulse current regime (DNpDC) follows a similar trend as for specimens D and N, but additionally affected by ion transport as a combined influence of concentration gradient and electrical fields – Fig.7.4.

NaCl increases the rate of hydration (higher electrical resistivity respectively) for sections B of all specimens DN (the negatively charged poles), consequently higher percentages of hydrated water are recorded for these sections. The electrical current flow is additionally promoting cement hydration, especially under DC conditions, as evidenced by the chemical analysis for hydrated water – Fig.7.4, revealing highest percentages of bound water in specimen DND. The specimens DN under pulse DC conditions (DNpDC) behave similarly to rest conditions (DN rest), with
slightly higher values of hydrated water in the middle section A and even lower values for the positively charged pole (A’ed+”). These phenomena will be further elaborated with respect to chloride-induced accelerated hydration and microstructural properties in what follows.

Specimens DN, under steady current (DNDC) and no-current conditions (DNrest), exhibit similar behaviour, in terms of larger variations in electrical resistivity by sections. The amount of hydrated water is basically relevant to the amount of hydrated cement, and the sections with highest percent of hydrated water would correspond to the sections with highest resistivity, as recorded for specimens DNDC and DNpDC (Fig. 7.2 and Fig. 7.4). For specimen DN in rest condition, sections B3(mid) and B4(ed-) contain higher amount of hydrated water (due to the chloride-induced acceleration of the hydration process), but exhibit lower electrical resistivity compared to sections A. Diffusion is the rate limiting process in the advanced stage of cement hydration. When current flow is involved, the hydration process is accelerated (as in DNDC and DNpDC). The current flow influences the direction of ion transport: anions (chloride and OH− ions) should move to the positive pole, cations (Na+, K+, Mg2+) to the negative one. Chemical analysis, by sections of all specimens for all technical conditions, reveals higher mobility of chlorides under current flow, more pronounced for pulse conditions (DNpDC) - Fig. 7.5(left) and no significant change in sodium concentrations by sections of the prisms – Fig. 7.5(right).

The free ion movement can undergo in counteracting streams, e.g. Na+ ions are normally surrounded by water dipoles (hydration shell), and thus they can migrate to the negative pole. In case of counter transport of OH− and Na+ in the pore solution, water content will possibly be reduced at the negative terminal. Thus, the material microstructure is externally changed by the electrical current due to its influences on ion and water transport. Moreover, the electrical properties of the different interfacial zones in the concrete matrix can be directly correlated with resistivity of the materials. As discussed in Chapter 6, according to [16], there are basically three types of paths in concrete structure, i.e. continuous conductive paths (CCPs), discontinuous conductive paths (DCPs), and ‘insulator’ conductive paths (ICPs), respectively. The CCPs consist
of connected micro-pores, which could be a series of capillary cavities connected through pore necks. If the micro-pores in the concrete are blocked by the cement paste layers, these discontinuous pores constitute the DCPs. Apart from the DCPs and CCPs, the continuous concrete matrix composed of cement paste, acts as ‘insulator’ paths (ICPs) in the concrete system. All these paths contribute to the overall ion transport and thereby to the electrolytic and current transport in the system. An enhanced ion movement will lead to faster hydration and filling up of the pore network. This explains the higher resistivity in section B4 of DN specimen under pulse current.

The involvement of electrical current (both steady and pulse) will stimulate the hydration process by accelerating ion transport, in this case, the conductive CCPs and non-conductive ICPs will transform from one to the other. In general, the portion of CCPs will decrease and DCPs increase with cement hydration and physicochemical reactions. Hence, both current regimes will reduce the portion of CCPs and thereby increase the total electrical resistivity. However, in case of pulse current, there is a favorable mechanism of charge-discharge cycling and the ions are prevented from ‘piling up’. Hence the portion of conductive CCPs is more than that of the DCPs. This is supported by the much more uniform resistivity values at various sections in specimens under pulse DC compared to those under steady DC (Fig.7.2) and ease of ion transport (mainly chlorides) – Fig.7.5, which will be discussed in the following section.

7.4.3 Chemical composition – influence of hydration and current regimes on ion transport

When chloride ions penetrate through the concrete surface and ingress in the bulk material, part of them undergo chemical binding, part of them remain physically bound, and the others stay free in the pore solution. Bound chlorides can be released when carbonation takes place [17]. Physically bound chlorides are found as absorbed in the C-S-H gel, they could participate in diffusion processes, moving towards the chloride-free spaces in the bulk matrix. However, the diffusion of chloride is very slow, so, physically bound chlorides hardly exert influences on the diffusion process. The chemical binding of chloride ions is a process of incorporation into the lattice of crystalline hydration products in the form of 3CaO·Al₂O₃·3CaCl₂·10H₂O (Friedel’s salt) and 3CaO·Al₂O₃·3CaCl₂·32H₂O. The amount of C₃A has significant influences on the chloride binding mechanism and thereby on the amount of chlorides remaining free in the pore solution [18,19]. There is also a process of chemisorptions of chloride ions on the surface of the C-S-H hydration products. The amount of bound chloride ions is dependent on the concentrations of other ions as sulphates, carbonates, Ca²⁺, K⁺, Na⁺, pH as well as on temperature.

The aforementioned mechanisms are slow in no-current conditions due to slow diffusion and ion transport. When an electrical field is applied, ion migration will take place along with diffusion mechanisms and consequently speed up all related chemical transformations. Hence, ion exchange is closely related to electrical resistivity properties of the specimens.

In addition to the chemical analysis (ion concentrations, hydrated water) of the concrete prisms by sections (Table 7.1, Figs.7.4,7.5), monitoring was performed on cell couples (DC and pDC), in one and the same sections of the specimens by drilling cores, thus recording information for one
and the same section of the prisms with time. Fig. 7.6 presents the chloride and alkali concentrations measured from drilled cores of the specimens DN at different stages of hydration.

In the specimens under pulse CP current regime (DNpDC), the current flow is accelerating the ion transport towards sections A (initially free of chloride) where the ion-exchange capacity is higher, thus increasing the hydration rate and filling up of the pore system. It is followed by reduction in the portion of CCPs in the system and increased electrical resistivity. In this case, the physicochemical process is taking place more uniformly throughout the specimens than the specimens under steady DC, evidenced by the local resistivity measurements (Fig. 7.2). This effect can be additionally proved by the lower and almost uniform chloride concentrations in specimen DNpDC at the middle part and negatively charged pole of the specimens, accompanied by a higher chloride concentration around the positively charged pole, compared to the specimens under steady DC current (Fig. 7.6a). Furthermore, when chloride ions diffuse through hardened cement paste, Ca(OH)$_2$ crystals are identified on the surface of the hydrated cement. This is due to the counter diffusion of Cl$^-$ and OH$^-$ between the solution and the cement paste. Such counter diffusion can be expected in the case of NaCl additions as well. The hydrated cement behaves as a semi-permeable membrane; the diffusion coefficients for the cations being lower than those for

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**Fig. 7.6** Total chloride (a), sodium (b), potassium (c) and magnesium (d) concentration in mMol per dry concrete weight at different sections of specimens DN under steady (left of the plots) and pulse DC current (right of the plots).
the associated chloride ions, [20]. The alkali ion migration is much slower than that of chlorides, consequently for the period of testing, a considerable change of alkali ions concentration cannot be expected (as demonstrated in Fig. 7.6b,c,d) for sodium, potassium and magnesium).

Cations, like Na⁺ (along with K⁺, Mg²⁺ etc.), will migrate towards the negative pole of the cells (the negative pole being initially with high concentration of NaCl). However, such enhanced transport is only minor for sodium in the specimens under pulse DC whereas potassium and magnesium concentrations were maintained relatively constant in all sections (Fig. 6). On one hand, this migration could be favorable if steel is embedded in the concrete, as it is supposed that alkali ions will accumulate on the steel surface. On the other hand, an increased accumulation of alkalis will cause, already mentioned in Chapter 2, side effects such as reduction in bond strength between the steel reinforcement and concrete. In the specimens under pulse current, the pulse electrical current will enhance the electro osmotic effects and hence withdraw water to the negative pole in the system. A possible mechanism here is transport of Na⁺ ions with a water molecules hydration shell.

All aforementioned mechanisms and hypothesis aim at establishing a correlation between electrical properties of concrete with the changes in chemical composition and microstructure of the materials under various external influences, including the effect of CP current. However, a thorough and fundamental understanding and possible solutions for effective performance of CP technique remain to be solved. A clear statement though can be suggested for the microstructure of the concrete material and the positive or negative aspects of these factors. The presence of chloride will induce decrease in porosity and a finer pore size distribution since chloride binding leads to the formation of chloro-complexes in the capillary pores. As reported in [18], the C-S-H morphology differs in the mortars with or without chloride additions. In the chloride-free mortars, C-S-H gel is of fibrous or needle shape, accompanied by a coarse pore structure. In contrast, the chloride-contaminated mortars exhibit denser C-S-H gel and a finer pore size distribution. These observations are reported in [21] and discussed in Chapter 3 for mortar specimens.

7.4.4 Microstructure observations

The development of the pore structure in hardening concrete is fundamental to the overall behavior of concrete exposed to aggressive environments. It influences mass transport of ions into the material and their interaction with concrete as well as its diffusion characteristics. Furthermore, electrical current flow (as in CP applications) will additionally affect the material structure (including pore structure) and engineering properties of concrete, which will be elaborated in what follows.

The electrolytic path in concrete systems is dependent on the kinetics of aggressive ions transport mechanisms, the latter affected by pore size distribution and pore connectivity. Figs. 7.7, 7.8 and 7.10 present the pore size distribution and critical pore size of the investigated specimens. The critical pore size can be conceived as the diameter of the pore that completes the first interconnected pore pathway in a network developed by a procedure of sequentially adding pores
of diminishing size to this network. Details for the opening distribution technique and pore structure analysis are given in Chapter 2 and can be referred to [22].

Relevant to morphological aspects of the pore structure and ion transport, the characterising parameter pore distribution density (PDD) is employed in the microstructural investigations for all specimens in the present study (as also applied for the structural analysis of mortar specimens, discussed in Part I of the thesis). The PDD is a three dimensional parameter, derived from the skeleton length of pore features, observed on two-dimensional section images. For details of the definition and measurement procedures of this parameter see Chapter 2 and [22,23].

Table 7.4 Summarized data for structural parameters for all specimens and sections.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>DC</th>
<th>Pulse DC</th>
<th>DC</th>
<th>Pulse DC</th>
</tr>
</thead>
<tbody>
<tr>
<td>D in rest, DC and pulse DC conditions, 210 days of cement hydration</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity bulk [%]</td>
<td>10.84</td>
<td>10.82</td>
<td>10.39</td>
<td>10.30</td>
</tr>
<tr>
<td>Porosity ITZ [%]</td>
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<td>11.20</td>
<td>12.2</td>
<td>12.2</td>
</tr>
<tr>
<td>Critical pore size [μm]</td>
<td>0.95</td>
<td>0.95</td>
<td>1.27</td>
<td>1.27</td>
</tr>
<tr>
<td>Pore connectivity (PDD)</td>
<td>0.12</td>
<td>0.12</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>Permeability [μm]</td>
<td>3.5e-08</td>
<td>4.5e-09</td>
<td>5.6e-09</td>
<td>6.6e-09</td>
</tr>
<tr>
<td></td>
<td>1.5e-08</td>
<td>2.5e-09</td>
<td>6.5e-09</td>
<td>7.5e-09</td>
</tr>
</tbody>
</table>

Fig. 7.7 Pore size distribution and critical pore size (peak of the curves in the right figure) for specimen D under various conditions, no-current (denoted as 'rest'), pulse (denoted as PDC), and steady (denoted as DC) current, respectively.

The PDD is strongly connected to water permeability and is found to have higher correlation with ion transport than the conventional parameters for pore structure characterisation (such as porosity, critical pore size). This parameter contains information on both pore size and connectivity of pore space. The derived structural information allows prediction of intrinsic permeability of the specimens on the basis of empirical relationships between pore structure and permeability. For this purpose an upgraded version of the Katz-Thompson equation [24] is...
employed, incorporating the PDD, which has been demonstrated to be able to improve to a significant extent the quality of prediction in a comparative study with experimental measurements [25]. Table 7.4 presents summarized data for porosity, critical pore size, permeability and connectivity for all investigated specimens.

Fig. 7.8 Pore size distribution and critical pore size for the bulk matrix and ITZ regions for specimen D under pulse (denoted as PDC), and steady (denoted as DC) current, respectively.

The DC current regime causes an obvious decrease in total porosity for all conditions. Comparing specimens D and N with specimens DN allows determination of the influence of current flow on concrete microstructure separately, apart from the combined effects of concentration gradient and ion migration, (since specimens D and N have the same concrete mixture along the whole specimen in contrast to specimens DN).

Fig. 7.7 reveals the decrease of porosity in specimen D under steady current (DDC) and almost equal porosity for specimens D in rest and pulse DC conditions (Drest and DpDC), however accompanied by a coarser pore structure in pulse DC conditions (critical pore size for DpDC is 1.268 μm) than no current conditions (Table 7.4, Fig.7.7 right). Along with refined bulk porosity, the DC current causes increased heterogeneity in the concrete matrix, evidenced by the microstructure analysis in the bulk material and in the interfacial transition zone (ITZ) of cement paste/aggregate.

The analysis in ITZ refers to investigation of the 50 – 80 μm cement paste zone, adjacent to the aggregate particle. Fig.7.8 reveals the significant difference in bulk porosity (~9 %) and porosity in the ITZ region (~17 %) for specimen D under steady DC in contrast to more uniform structural performance for the specimen under pulse DC (DpDC), exhibiting bulk porosity of ~ 10.8% and ITZ porosity of ~12.2%. The critical pore size for both conditions in the ITZ region (compared to bulk matrix) is increased from 0.951 to 1.268 μm for DC conditions and from 1.268 to 1.584 μm for pulse DC conditions.
The most significant side effect of current flow (along with densification of the bulk porosity) is enlarging the interfacial gap between aggregate and cement paste in DC conditions – Fig. 7.9, while the pulse DC has minor influence on this weak zone and specimens behave similarly to rest conditions (compare Figs. 7.9a,c,e).

Similarly to specimens D, for the N specimens, the current flow causes a decrease in the total porosity. In addition to the effects of current flow, specimens N exhibit a denser pore structure as result of the influence of NaCl (as discussed in the above sections) and lower critical pore size, compared to specimens D (Table 7.4). Fig. 7.10 illustrates the previous observation, presenting a
comparison of porosity and pore distribution density for specimens N and D in rest and pulse DC conditions.

Fig. 7.10 Pore size distribution and critical pore size (peak of the curves in the right figure) for specimens N and D in rest conditions (denoted as Nrest, Drest) and pulse DC conditions (denoted as NpDC and DpDC).

Along with derived porosity and critical pore size, structural parameters as permeability and pore connectivity were derived for all specimens according above described techniques. The pore connectivity and permeability are directly related to ion transport and electrical properties respectively. Fig. 7.11 presents the summarized data for these parameters for specimens D and N (no concentration gradient) and specimens under current flow (DDC, DpDC, NpDC). As seen from the plot, specimens N exhibit significantly lower values of permeability and connectivity, compared to specimens D, which correspond well to the lower electrical resistivity values for the latter (Fig. 7.2) and the pore structure characteristics (Table 7.4 and Fig. 7.10).

Fig. 7.11. Bulk matrix permeability and pore interconnectivity for specimens group D in rest (Drest), steady DC (DDC) and pulse DC (DpDC) current and specimens N in rest (Nrest) and pulse DC current (NpDC) conditions.
The data for specimens N in Fig. 7.11 reflect the minor effects on the bulk matrix of the pulse current in specimens N, additionally supported by the derived conventional parameters (critical pore size for rest and pulse conditions 0.634 μm and similar porosity – Table 7.4). The specimens from group D vary in pore connectivity and permeability depending on technical conditions. Despite the almost equal porosity (~10%) for rest (Drest) and pulse DC (DpDC) conditions, specimen DpDC has higher permeability, corresponding to the lowest electrical resistivity in the group of D specimens (Fig. 7.2). The higher permeability of specimen DDC (compared to Drest) and almost equal connectivity, counteract the lower porosity of specimen DDC (Fig. 7.7), hence the latter shows higher electrical resistivity (Fig. 7.2), compared to rest and pulse DC conditions of D specimens.

The above observations generally hold for the specimens DN as well. The derived structural parameters, reflecting the properties of the bulk matrix in these specimens, are additionally influenced by the ion transport due to concentration gradient only (specimen DN in rest conditions) or due to concentration gradient and ion migration (specimens DNDC and DPDC).

Fig. 7.12 presents the pore size distribution and critical pore size for sections A (initially free of NaCl) and sections B (initially cast with NaCl) for specimens DN in all conditions (rest, steady DC and pulse DC). Sections A of all specimens DN exhibit higher porosity, compared to sections B in the same specimens (as consequence of induced hydration in the B sections as already discussed above). The trend of increased structural heterogeneity (as observed and discussed above for specimens D and N) is more pronounced in the specimens under steady DC: porosity of section A ~10.2%, section B – 8.2 %. The result is attributed to current-induced micro-cracking and enlarged gap between aggregate and cement paste in DC conditions (Fig. 7.13), compared to rest and pulse DC, similarly to those observed in specimens D and N (Fig. 7.9).
Fig. 7.13. The interfacial transition zone (ITZ) between cement paste and aggregate in section B (top row) and section A (bottom row) of specimen DN in rest (left), under pulse DC (middle) and under steady DC (right) conditions. The SEM image magnification is 1000x.

Despite the higher porosity in sections A of specimen DNrest (~13%, compared to 10.4% for sections B), the electrical resistivity recorded for sections B of these specimens is significantly lower (Fig. 7.2). The fact can be attributed to the combined effects of: structural parameters – permeability in sections A is lower (Fig. 7.14), ion concentrations in sections A of specimen DN rest is significantly lower as well (chloride and alkali – Fig. 7.5). Hence, the combination of higher permeability and higher chloride and alkali concentrations in sections B of specimen DNrest determine lower electrical resistivity of these sections, compared to sections A (Fig. 7.2).

In the DN specimens under current flow, the steady current yields a much higher extent of structural heterogeneity in the material, supported by the largely diverging values in electrical resistivity (Fig. 7.2) and corresponding well to the derived values for pore connectivity and permeability (Fig. 7.14). In contrast, the pulse current induces only minor changes in the pore structure (Figs. 7.12, 7.14), and the different sections exhibit similar resistivity (Fig. 7.2). Therefore, pulse DC is beneficial for the bulk matrix properties, since it is promoting ion transport (Fig. 7.6) and current flow in the system on one hand and maintains structural parameters similar to that in no-current condition (Fig. 7.14).

The sections B in pulse condition have higher permeability than the counterpart in steady current condition and the latter is of much higher structural heterogeneity with respect to permeability properties (compare values for sections A and B in specimen DNDC, Fig. 7.14). Although the current flow decreases total porosity in the sections B of DNDC and DNpDC specimens (Fig. 7.12), the gap between cement paste and aggregate (Fig. 7.13) counteract the positive effects of lower porosity, resulting in a lower resistivity at sections B3 for specimen DNDC (Fig. 7.2). The phenomena is more pronounced under steady DC conditions, attributed to comparatively
larger gap in DNDC (between 2 and 6 μm for DC and 1 to 3 μm for pulse DC – Figs. 7.9, 7.13), resulting in lower electrical resistivity in section B3 for DC, compared to section B3 for pulse DC. The section B4 in the steady current condition shows highest resistivity among all the sections of the specimens (Fig. 7.2), attributed to the highest amount of hydrated water (Fig. 7.4), lowest porosity (7.8%), connectivity (0.07) and permeability (1.68e-9) in this section (Figs. 7.12, 7.14).

The discussed in this Chapter results from microstructural analysis for plain concrete in conditions, simulating CP (conventional, as specimens DC and pulse, as specimens pDC) were confirmed by investigation in reinforced concrete. Since the former results are completely in line with the latter, the microstructural investigation for reinforced concrete is not discussed in a separate chapter, but briefly described in Appendix III.

7.5 CONCLUSIONS

In conclusion, this Chapter explores the effects of pulse and steady current on material structure and electrical properties of concrete specimens. The research reveals that the pulse current is less detrimental to concrete microstructure and beneficial for electrical properties and ion transport mechanisms. A steady current (as normally used in conventional ICCP applications) tends to bring about unfavourable modifications of the material structure both in the bulk (reducing porosity) and in the interfacial transition zone (enlarging the gap at aggregate surface) to a significant extent, leading to a high level of structural heterogeneity of the materials. In addition
steady current yields non-uniform electrical properties and thereby results in disturbance of the electrolytic path in the materials under study. Both current regimes reduce the portion of connected conductive paths in the material microstructure and thereby increase the total electrical resistivity. However, in case of pulse regime with alternating periods of ‘on’ and ‘off’ current, there is a favourable mechanism of charge-discharge cycling, and the ions are prevented from ‘piling up’. Hence the pulse regime is in favour of the ease of ion migration mechanisms. This comparison study demonstrates that pulse current can efficiently reduce the negative effects of steady current applications, evidenced by relatively uniform resistivity at all sections of the concrete prisms. Microstructure observations and chemical analysis reveal the underlying mechanisms to be a more homogenous material microstructure (including slightly refined pore structure), a dense ITZ (small gap) structure, and the promoted ion and water transport. The latter induces alterations towards a favourable trend with respect to the electrolytic paths in the concrete systems. The positive effects of these chemical and microstructure changes account for achieved better global performance of the concrete materials.

References
CHAPTER 8
CONVENTIONAL AND PULSE CATHODIC PROTECTION IN REINFORCED CONCRETE. TECHNICAL REGIMES. CONVENTIONAL MONITORING, “OPEN CIRCUIT POTENTIAL PASSIVITY”

8.1 INTRODUCTION

Since the cause of the steel corrosion in concrete is an electrochemical reaction, a variety of techniques, which use electrochemical methods for prevention, protection or repair have been developed and are presently applied [1,2]. Cathodic protection (CP) is one of the electrochemical techniques, used for prevention and protection from corrosion in reinforced concrete [1-8]. The widespread use of CP is well established, some developments in the field have been reported elsewhere [3,5]. As discussed in Chapter 2, the application of CP however is accompanied by side effects, some of them reviewed in [1,5]. Hence, any improvements of the CP techniques, which will minimize the variety of side effects, are an important aspect in corrosion control and corrosion protection of reinforced concrete structures. Moreover, elucidation of the fundamental basis of CP in terms of the influence of DC current flow on both the steel reinforcement and the bulk concrete matrix, is essential for the evaluation of any new or improved CP technique.

A fundamental approach to the basic principles of the influence of a conventional CP regime, both on the steel reinforcement and the bulk cementitious matrix, in terms of hydration and corrosion products, was presented in Chapters 5 and 6 for reinforced mortar specimens and will be subject to discussion for reinforced concrete in Chapters 9 and 10. Chapter 7 discussed the side effects of DC current flow (as conventional CP) on the bulk concrete matrix and some beneficial effects of the introduced alternative, based on pulse DC current (denoted as “pulse CP”), both regimes investigated as model conditions of CP.

The aim of this Chapter 8 is to show the applicability and effectiveness of the pulse CP as an alternative of impressed current CP for reinforced concrete. The Chapter presents details on the technical regimes for both CP and pulse CP and the outcomes from conventional i.e. generally applied in practical applications, monitoring techniques for CP effectiveness. Additionally, Chapter 8 deals partly with some fundamental aspects from electrochemical point of view, which will be subject to elaborated discussion in Chapters 9 and 10.

The hereby presented technique, denoted as pulse cathodic protection (CP), was evaluated on the basis of a comparative analysis to reference (non-corroding), corroding and conventional CP conditions in terms of monitoring the corrosion behavior and defining the electrochemical parameters for the embedded steel with time of corrosion and protection. Both CP regimes were applied after corrosion was initiated (using corrosion medium of 5% NaCl), at different time intervals (hereby reported are starting points 60 and 150 days of age). Both CP regimes used current density of 2 to 20 mA/m² steel surface. The pulse CP was achieved by applying a pulse shaped current (block pulse) with the current itself being the feedback control signal, using 12.5%
to 50% duty cycle at 100 Hz to 100 KHz frequency. In equal environmental conditions the pulse CP was found to perform as effectively as the conventional CP with regard to electrochemical behavior of the steel reinforcement.

8.2 TECHNICAL BACKGROUND

As previously mentioned, impressed current CP is used for corrosion protection in reinforced concrete since the 1970’s and so far it is proven to be the only technique that is able to minimize or stop corrosion in salt contaminated environments [4]. The conventional basis for impressed current CP relies on inducing a negative steel potential shift [7,9] i.e. more cathodic than -850 mV SCE, where corrosion is thermodynamically restricted [10]. When CP is applied to reinforcing steel in concrete however, the objective might not always be to achieve immunity but to reduce the risk of chloride-induced corrosion. In case CP is to be applied as a remedial treatment to reinforced concrete in which chloride-induced corrosion has already been occurring, then the desired protection might be achieved by polarizing the steel from its condition of chloride-induced corrosion (or “pitting”) to the domain of “imperfect passivity”, where “pitting” is unstable i.e. in the domain where the rate of propagation of existing “pits” will be reduced considerably and the initiation of new ones will be prevented [4,5,11]. In case CP is initially applied within the building of a structure, i.e. before exposure to aggressive environments, then only a modest polarization of the steel surface will be sufficient for corrosion protection, the technique being applied and denoted as “cathodic prevention” [4,12,13]. Hence, the application of CP will be determined by the environmental factors, the engineering properties and the age of the structure to be protected.

It was previously discussed, that there is a variety of side effects, normally accompanying CP applications, the most widely reported are: reducing anode efficiency [1,14], risk of alkali-silica-reaction (ASR) in the vicinity of the embedded steel re-bars [15-17] and consequently bond-strength degradation at the steel/cement paste interface [18,19], possible hydrogen embrittlement in case of prestressed concrete [16,20]. The majority of side effects result in lost of adhesion of adjacent to the steel surface cement layer [16,17], which can reach 60% [21], the bond-strength can weaken by 55% [22]. The reason for bond-strength degradation is still unclear, despite the reported data for changes in microstructure, pore size distribution and micro-cracking [16,23,24]. In the frame of this research (Chapters 6, 7) it was generally found that CP current induces structural alterations in the bulk cementitious matrix, the pore space and the bulk hydration products, to cause micro-cracking, which along with softening of the calcium-silica-hydrate (C-S-H) leads to reduced concrete durability, as reported also in [22]. By all means, a protection regime which uses lower current density (i.e. lower than the usually recommended range of 5 to 20 mA/m² for structures exposed to the atmosphere [13]) is expected to minimize the side effects. As aforementioned, such an alternative technique is “cathodic prevention” [4,12,13], which uses different regimes. For example 0.4 to 2 mA/m² steel surface can be applied within the construction of the structure, the lower current being sufficient for achieving the required CP criteria since the structure has not been yet exposed to aggressive environment i.e. the steel is still
passive. Using 0.2 to 2 mA/m² for immersed conditions is also reported as sufficient and this would be the case, since saturated concrete provides limitation for oxygen supply and lower diffusivity. Finally an effective “cathodic prevention” system can use 2 to 5 mA/m² steel surface in chloride containing environment, but the reported chloride concentrations do not exceed 2 wt.% per cement weight in these applications. Moreover, using the latter regime, the authors of these works [12,13] report the need of a waiting period of more than a few months, before the level of protection could be achieved, and even report insufficient protection when carbonation is involved, although using 10 mA/m² current density.

As suggested by Glass et al. [25], an intermittent CP, applied to reinforced concrete in the presence of up to 3 wt.% chlorides per cement weight and using average current density of 6 mA/m² is able to arrest further corrosion of the steel reinforcement. Further, the research [25] reports that the intermittently applied CP promotes beneficial effects in terms of enhancement of the OH⁻ concentration and reduction of the chloride concentration near the steel surface. The locally elevated concentration of OH⁻ caused by cathodic polarization results in substantial additional deposition of portlandite around the steel [26], which would be expected to have further beneficial effects in stabilizing the “passivity” of the steel re-bars for reasons that have long been recognized [27].

The experimental evidences to support the aforementioned suggestions for these secondary beneficial effects in terms of morphology, crystallinity, cement composition or oxide layers composition etc., along with the microstructural properties of the steel/cement paste interface however, are rather limited [5] and still very restricted. As mentioned in the introduction part of the thesis, this research aimed to provide such experimental evidence for the suggested beneficial secondary effects of CP on one hand, to prove the applicability and effectiveness of the introduced pulse CP, evaluated by conventional and used in practice criteria, on the other and further to provide additional experimental evidence in terms of the fundamental principles for effectively working CP, using electrochemical studies and characterization of the involved materials (steel and concrete).

It should be stressed, that the pulse CP regime, studied in the frame of this research, differs from the reported and already mentioned CP alternatives “Cathodic prevention” or “Intermittent CP” in the way of technical application and the testing environmental conditions. The former technique “Cathodic prevention”, was discussed above. The latter i.e. “Intermittent CP” [25], being more close as application and outcomes to the here investigated “pulse CP”, actually presents CP with intervals of “on” and “off” protection in certain schemes, but not really a pulse technique. Although the average current density is reported to be 6 mA/m², the resulting beneficial effects are most likely due to the rather high current density during the “on” regime (100 mA/m² steel surface, pointed out as an optimum regime) and performance in relatively low chloride concentrations (of up to 3 wt.% per cement weight, using admixed chlorides). The performance of the investigated “pulse CP” was tested in higher chloride concentrations and more severe environmental regimes, which will be presented in the following Section 8.3.

Table 8.1 Experimental set-up, concrete mixture, curing and experimental conditions.
Chapter 8

8.3 EXPERIMENTAL

8.3.1 Materials

The materials used in the present study were reinforced concrete cylinders, cast from OPC CEM I 32.5 R, using water to cement ratio 0.6, with dimensions: H = 25 cm, D=12 cm, containing embedded construction steel (type FeB500HKN ribbed bars, d=12mm), used “as received” (no
preliminary treatment, no mill scale present) for all technical conditions. Details of the experimental set-up, curing conditions, concrete mixture, chemical composition and constituents of the used cement are given in Table 8.1.

After curing in fog room conditions (98% RH and 20°C) for 28 days the specimens were placed in a salt spray cabinet (SSC), aiming at initiation of corrosion before applying CP. The SSC used 5% NaCl spray, additionally the cylinders were immersed 1/3rd of height in 5% NaCl (except for the non-corroding cells, maintained in the same RH and temperature conditions, but immersed in water – Table 8.1, point 4). The maintained temperature was 35°C for 30 (or 60) days, followed by 20°C afterwards and till the end of the test (460 days), with certain intervals of drying and wetting. As seen from Table 8.1, four main groups of specimens were investigated: a freely corroding group (further in the text represented by specimen C), a non-corroding group (represented by specimen R), a group with applied conventional CP (represented by specimens A) and a group with applied pulse CP (specimens B). The specimens from groups A and B comprised certain sub-groups, differing in the starting point for CP application and in the applied CP current density as well (Table 8.1, point 3).

8.3.2 Methods

Electrical Resistivity: since concrete electrical resistance is an important factor in the determination of concrete corrosivity, as well as a contributing factor in deriving electrochemical parameters, electrical resistance monitoring was performed for all cells from 15 to 240 days of cement hydration. The method used was a 2 pin AC method (using the embedded steel bars, Table 8.1), recording resistance values was done automatically 4 times in 24 h. The method and measurements are analogical to those, described in Chapter 7 for plain concrete. The specification of the method is given in Table 8.2, the experimental results from this measurement will be subject to elaborated discussion in Chapter 9 in correlation with data, obtained from EIS measurements.

<table>
<thead>
<tr>
<th>Resistance measurements:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Measuring current: 100 µA balanced alternating square wave</td>
</tr>
<tr>
<td>- Frequency: 120 Hz</td>
</tr>
<tr>
<td>- Current source impedance: &gt; 10 MOhm</td>
</tr>
<tr>
<td>- Voltage diff. input range: max ±4V, 12 bit A/D conversion</td>
</tr>
<tr>
<td>- Voltage diff. input impedance: &gt; 100 MOhm</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Cathodic protection:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Current source impedance: 300 kOhm;</td>
</tr>
<tr>
<td>- DC current for conventional CP: 2 to 20 mA/m² steel surface;</td>
</tr>
<tr>
<td>- DC current for pulse CP: 2 to 20 mA/m² steel surface at 500 Hz to 1 kHz frequency and duty cycle: 50%, 25%, 12.5%;</td>
</tr>
<tr>
<td>- Anode: MMO (mixed metal oxide) Ti mesh;</td>
</tr>
</tbody>
</table>
Cathodic protection: The specification for both CP regimes, along with the patterns for the pulse CP regime, is presented in Table 8.2. Cathodic protection was applied as impressed current CP, using MMO (mixed metal oxide) Ti mesh as anode. The CP current was in the range of 2 to 20 mA/m² steel surface (in some cases 30 mA/m² was tested), using two regimes, conventional CP and pulse CP. As aforementioned, the pulse CP used the same current density, but applied as a block pulse signal (square wave), tested frequency 100 Hz to 100 KHz (rise time of the pulse shaped current larger than 100 A/m² s), duty cycle of 1% to 50 %, preferably less than 25 %, at certain frequencies [28] i.e. the effective CP current density in case of pulse CP was always 50% of the CP current density in the relevant conventional CP regime (electrical schemes are given in Appendix VII). The protection was applied at different intervals to different cell couples, aiming at investigating the efficiency of both regimes with time and with current density (a cell couple presents two identical in geometry, concrete mixture and set-up specimens, one of them under CP, the other one under pulse CP, both CP applications using the same current density regime). For example there were cell couples on which CP (both regimes) was applied after 28 days of age, when corrosion was still not initiated, thus evaluating both techniques as “cathodic prevention” at lower current densities, but still in a relatively severe environment. On other cell couples both CP regimes started after corrosion was initiated at 60 days, 120 or 150 days and were monitored up to 270, 380 or 460 days. The environmental conditions for all protected cells were identical to those for the corroding cells i.e. all specimens were maintained in the highly aggressive environment, as above described in Section 8.3.1.

Conventional monitoring: in terms of assessing corrosion initiation and cathodic protection efficiency, the generally accepted methods are potential mapping and depolarization measurements, aiming at monitoring the level of steel surface polarization in accordance with standard requirements (e.g.BSEN12696). Half-cell potential mapping and Polarization Development /Decay were performed for the reinforced concrete cylinders according ASTM C876 and NACE RP0290-2000 respectively.

Electrochemical methods involved were potentio-dynamic polarization (PDP) and polarization resistance method (PR), which will be subject to extensive discussion in the following Chapters 9 and 10. Data from PR and PDP measurements are partly presented in this Chapter 8, aiming to provide evidence for some fundamental aspects from electrochemical point of view for the so called “open circuit potential passivity”. The measurements were performed at open circuit potential (OCP) for all cells (after 24 h depolarization of the reinforcement for the protected specimens i.e. protection current was interrupted before and in the time of the measurement). For PR an external polarization in the range of ±20 mV vs OCP was used at scan rate 0.16 mV/s, for the PDP measurements an external polarization in the range of -0.15 V to +1.2 V vs OCP at 0.5 mV/s scan rate was applied. The used equipment was EcoChemie Autolab - Potentiostat PGSTAT30, combined with FRA2 module, using GPES and FRA interface.
8.4 RESULTS AND DISCUSSION

As aforementioned, the aims of this Chapter 8 are to provide evidence for the effective performance of both CP regimes, especially the pulse CP regime, using conventional monitoring techniques as a first step for monitoring corrosion and CP in reinforced concrete structures. It is widely accepted, that the conventional techniques have certain limitations. For example experimental set-up, electrodes positioning, re-bars location, moisture and specific electrical resistivity of the concrete matrix etc. are affecting the measurements, when applied in practice. For laboratory investigations, most of these limitations are avoided by using known and justified geometry of the specimens and measuring set-up, but identical environmental conditions should also be assured each time when performing potential readings or decay measurements, thus providing reliable information for the behavior of the system with time. To this end, the reinforced concrete specimens in this study were subject to conventional monitoring techniques throughout the test, providing practical information for the onset and development of corrosion in the corroding specimens and CP performance for the protected specimens (as well as evidencing the passive state of the reference, non-corroding cells). The data from the conventional monitoring were further correlated with the more fundamental approach of investigating the systems by electrochemical techniques, which will be subject of Chapters 9 and 10 and are only partly discussed in this Chapter in terms of steel potential shift with CP application.

8.4.1 Conventional techniques

8.4.1.1 Potential/time history. Fig. 8.1 presents the recorded electrode potentials (OCP for groups C, R, A and B and “under current potentials” after CP application for groups A and B) for the different specimens with time.

![Fig. 8.1 Potential/time history for specimen groups: corroding (C); reference (R); CP and pulse CP using 5 mA/m², applied at 60 days of age (A1,B1); CP and pulse CP using 20 mA/m², applied at 150 days of age (A2,B2); CP and pulse CP applied as prevention (2 mA/m² at 28 days of age).](image-url)
The potential mapping was performed in accordance with ASTM C876, using embedded Mn/MnO\(_2\) reference electrodes and additional comparative measurement with external SCE electrode. The potential mapping gives information for the time to initiation of corrosion in case of corroding specimens, or provides information if the achieved polarization of the steel surface falls in the region of thermodynamic stability (i.e. more cathodic than -850 mV SCE) for the protected specimens. As seen from the plot (accdg. potential readings), specimens group C are actively corroding; the protected specimens fall in the region of thermodynamic stability since 80 days for groups A1 and B1 (CP was applied at 60 days, using 5 mA/m\(^2\) steel surface), since about 170 days of age for groups A2 and B2 (CP applied at 150 days of age, using 20 mA/m\(^2\) and maintain stable potential values further on. Specimens group R, being non-corroding cells, fall in the region of passivity.

8.4.1.2 Polarization decay measurements. Fig. 8.2 presents depolarization (decay) measurements, performed according generally accepted criteria (e.g. NACE RP0290-2000). The decay was determined by interrupting the CP current and monitoring the potential of the steel bars, relative to embedded (and alternatively external) reference electrodes (Mn/MnO\(_2\) and SCE). The decay according criteria should be at least 100 mV for 4h (24 h), which determines effective CP. All measurements were performed in equally controlled for all cells environmental conditions.

As seen from the plots, at 460 days of age both types of CP are considered to be effectively performing, since the polarization decay is more than 200 mV within 4 h and minimum 500 mV within about 16h (Fig.8.2). The difference between “on-potential” and “instant-off potential” (both given in Fig.8.2) is in the range of 40 to 210 mV (values are presented vs Mn/MnO\(_2\) electrode, which is +140 mV vs SCE). Further, the polarization decay is more steep for specimens A2 and B2 (using 20 mA/m\(^2\) CP current), compared to specimens A1 and B1 (using 5 mA/m\(^2\) CP...
current); the pulse CP protected specimens from both regimes (B1 and B2) exhibiting a more significant decline of potential with time of depolarization. In all specimens the decay is sufficient according criteria, reaching a more or less stable state at about 15h after interrupting the CP current.

Figure 8.3 presents a comparison of performed depolarization measurements for specimens A2 and B2 at different ages (which is at different periods of CP duration, after the application at 150 days of age). As seen from the plot, the decay at 220 days of age (which is 70 days running CP) is significantly lower, compared to the decay at 460 days (which is 310 days running of CP) for both regimes (pulse and conventional CP). The decay at 220 days is however sufficient, being 85 mV for specimen A2 and 100 mV for specimen B2 in 4 h, and 127 mV for A2 and 180 mV for B2 in 22 h. At later stage already (460 days of age) the decay is more significant for 4h and 22 h, a stable OCP being established after about 15h. Similar observations are recorded at earlier ages for other cell couples from parallel groups at different CP current densities (for 200, 270 and 380 days of age), reported in [29,30] and are consistent with findings on comparable specimens and conditions, reported in [25].

Except verifying the efficiency of CP for all regimes, the decay measurements provide information for changed electrochemical behavior of the steel surface with time of CP application. As seen from Fig.8.3, there is a shift in the OCPs to more noble values with time, which is more evident for the pulse regime (specimens B). The observation confirms the effectiveness of both pulse and conventional CP in terms of achieving the so called “open circuit potential passivity” [25], which will be discussed in what follows.

8.4.2 Electrochemical approach
8.4.2.1 Efficiency of CP and pulse CP – steel open circuit potential passivity
As aforementioned, the fundamental basis of CP relies on a negative steel potential shift. The maintained cathodic potential (according the criteria for CP efficiency, generally in the region where corrosion is thermodynamically restricted i.e. more cathodic than -850 mV vs SCE) is expected to be accompanied by a decrease of corrosion rates. In this potential range and for pH from 8 to 13.5 (relevant to the present conditions), there should be no anodic reaction on the steel surface i.e. there will be no iron dissolution. It should be taken into consideration however, that the steel surface in concrete environment, even if maintained cathodic, is never completely bare steel i.e. locally there is always a product layer, undergoing relevant conversions under conditions of running CP or in the time of interruption of the protection current as a result of the high pH medium. Hence, the conventional understanding for CP efficiency needs to be extended to include, except sustained negative OCP after CP interruption, possible polarization of the anodic reaction kinetics on parts of the steel surface [31].

Corrosion initiation on passive steel would normally suggest a local decrease in pH and increase of chloride concentration (or carbonization due to CO₂ penetration) where the passive film breaks down. First, as suggested by Glass [25], and illustrated in Chapter 7 for plain concrete specimens, the cathodic current is rendering less aggressive environment, consequently increased pH in the
medium surrounding the anodic sites. Hence in case of reinforced concrete, locally induced passivity can occur on the steel surface; the pitting potential will be more positive if the pH is stabilized at high values and the chloride content is reduced at the steel surface [32,33]. Second, as reported also by [34] and evident from the present study, the positive shift in OCPs (after CP application and in depolarized conditions), suggests that the protective effects of CP are predominantly due to increased pH and less aggressive environment around the steel surface, as secondary beneficial effect, rather than the sustained (current induced) negative potential, as a conventional basis of CP. The latter statement is supported by the experimental data from the potentiodynamic polarization tests in this study and will be discussed in what follows.

8.4.2.2 Potentiodynamic polarization and summarized data for $R_p$ values
Electrochemical measurements (PDP and PR introduced above) were performed for deriving the polarization resistance $R_p$ (inversely proportional to the corrosion current density).

![Graph showing open circuit potential values in NHE scale for non-corroding (R), corroding (C), CP protected (A1 at 5 mA/m² and A2 at 20 mA/m²) and pulse CP protected (B1 at 5 mA/m² and B2 at 20 mA/m²).

Fig. 8.5 Open circuit potential values in NHE scale for non-corroding (R), corroding (C), CP protected (A1 at 5 mA/m² and A2 at 20 mA/m²) and pulse CP protected (B1 at 5 mA/m² and B2 at 20 mA/m²).

A comparison of all open circuit potential values (before external polarization) for the presented cells is given on Fig.8.5 vs NHE. Here again, the positive open circuit potential shift for the cells under cathodic current (A1, B1, A2, B2, compared to C) supports the consideration for induced passivity as result of the secondary effects of CP, hence evidences its efficiency. The obtained polarization resistance ($R_p$) values (after IR drop correction) for all investigated specimens are presented on Fig.8.6. The $R_p$ values for the non-corroding cell are the highest (R), followed by the corroding cell (C) and the protected cells (A1, A2, B1, B2). The $R_p$ values of A1 and B1 (CP current 5mA/m²) being lower than those for A2 and B2 (CP current 20mA/m²), corresponding to the lower current densities of the latter (Fig. 8.4).

![Graph showing polarization resistance $R_p$ derived from PR method.

Fig. 8.6 Polarization resistance $R_p$ in Ohm.cm², derived from PR for non-corroding (R), corroding (C), CP protected (A1, A2) and pulse CP (B1, B2) specimens.

In the present conditions (measurements after interruption of the CP current and only 24h depolarization of the steel surface), a low $R_p$ does not imply that the steel surface is not protected. In this case, $R_p$ will reflect the rate of oxidation of previously reduced species on the steel surface [34]. For example, low $R_p$ may be determined by cathodic reduction of Fe$^{3+}$-compounds, formed prior to reduction of previously oxidized species – e.g. reduction of Fe(OH)$_3$ to Fe(OH)$_2$ may start...
at potentials below the equilibrium potential of this half reaction, which range between -400 and -700 mV vs SCE as the pH changes from 6 to 12 [10]. Hence, although expected that the protected steel surface will exhibit lower corrosion rate and higher $R_p$ values respectively, this is not always the case, as determination of $R_p$ depends on the condition of the steel surface and the chemical nature of the surrounding medium.

Generally, two mechanisms are most likely responsible for the lower $R_p$ values of the protected specimens, compared to non-corroding and corroding conditions: First, as already mentioned, maintaining the steel surface cathodic (in the time of CP application) would result in relatively clean “bare” steel surface i.e. the product layers formed prior to CP application would only bear conversions, but no further formation and growth of product layers will occur. Consequently, the product layers on the protected steel surface would be relatively thinner, not entirely uniform and homogeneous. Therefore, in the time of measuring $R_p$ after depolarization for 24 h (which is after a transition of the steel potential from strongly cathodic to natural potential), there are conditions for iron dissolution on sites, where the surrounding environment is still aggressive and hence the protected specimens (in conditions of interrupted CP) exhibit higher corrosion current compared to non-corroding and corroding specimens. In addition to high chloride concentration (from 0.25% to 2.5% chloride per dry cement weight, determined wet chemically), CO$_2$ has obviously penetrated to the steel surface and caused drop in pH and more aggressive environment. The latter is proved by XPS analysis performed on the steel surface (Fig.8.7), ESEM observations (Figs.8.7 and 8.8) and EDAX analysis (Fig.8.8) in the 200 µm region away from the steel/paste interface.

![Fig. 8.7 Morphology of product layer on the steel surface (longitudinal section after removing the concrete surrounding, (270 days of age) depicting carbonate compounds (a), and the relevant XPS analysis (b).]

As previously mentioned, a secondary effect of CP is rendering less aggressive environment in the vicinity of the steel surface, which along with the open circuit potential shift towards positive values (after interruption of CP), will finally lead to “healing” of the steel surface and possible re-passivation. This process however is very slow, due to the highly aggressive environment in the present study.

The nature of the product layers in the three conditions (corroding, non-corroding and protected surface), would also have a significant influence on the electrochemical response and the derived electrochemical parameters respectively. It is well known that the product layer on steel in Ca(OH)$_2$ containing environment (as in this case concrete environment) is composed of several layers [35], regardless the presence or absence of aggressive substances as chlorides. Ca(OH)$_2$ can be incorporated in the outer plane of the inner layer and increase the protective abilities of the product layers when no chlorides are present [35, 36]. In the absence of chlorides, the first adherent layer is much thinner (~1nm), compared to much thicker films (~20 to 86 nm) in the presence of chlorides [35]. The film thickness increases and its protective ability decreases with increasing the chloride concentration.

Relevant to the reference (non-corroding) conditions, the product layer on the steel surface in the specimens R will be much thicker and composed of inner, metal adhering film of most probably Fe(OH)$_2$ and an outer layer, being a colloidal mixture of FeOOH and Ca(OH)$_2$, which will determine reduced anodic current in conditions of external polarization (in the time of measuring $R_p$). The presence of high chloride concentration in the corroding specimens (C), will induce thicker product layers formation but will retard the formation of the gelatinous outer layer of FeOOH in addition to preventing adherence of Ca(OH)$_2$. The inner layer will be thicker, non-protective and exhibit rough morphology. For the protected specimens (A and B) the following mechanisms most likely take place: an initial product layer will be present on the steel surface, formed prior to CP application. After applying CP, no oxidation of iron occurs, hence the initial layers are only bearing conversions. In conditions of external polarization (in the time of
performing PDP or PR), there are less limitations for the oxidation process, hence lower $R_p$ is recorded in the protected specimens. In contrast, in the corroding specimens, gradual formation of product layers occurs and in conditions of external polarization, the oxidation process is retarded first due to higher product layer thickness and second due to the diffusion limitations through the highly heterogeneous surface layers, deposited on significantly larger surface area, compared to protected specimens. Consequently higher $R_p$ is recorded for corroding compared to protected specimens. The product layers properties, transformations and their influence on the electrochemical behavior of the steel reinforcement; hence their impact on corrosion process or CP performance will be discussed in Chapters 9 and 10.

8.5 CONCLUSIONS

From the data, obtained from conventional monitoring and external steel polarization, presented in this Chapter, it becomes evident that in all cases, when a positive potential trend in open circuit potentials (Figs. 8.4 and 8.5), or sustained negative potential (not presented, but discussed in Chapter 5 for reinforced mortar) are observed, corrosion induced deterioration is arrested, as evidenced by the present research and also reported in [25,31,34]. It is not possible to definitely determine which direction the “healing” process will take, as the system as a whole is extremely heterogeneous in nature. The present results however, allow proving the effectiveness of CP by correlating experimental evidences and empirical criteria, thus revealing the phenomena of cathodic protection as a fundamental mechanism in addition to some secondary beneficial effects.

In other words, an effective CP is achieved in two ways: polarizing the steel reinforcement cathodically and maintaining steel potentials in the “immune” region, according Pourbaix diagrams, where corrosion is thermodynamically restricted. This regime is effective in aggressive environments and can minimize or practically stop even previously advanced stages of steel corrosion. On the other hand, only a modest polarization of the steel surface is required for environmental conditions with much lower aggressiveness, thus maintaining the steel reinforcement in the region of “imperfect passivity” where corrosion propagation is restricted. In both cases, the beneficial secondary effects, which render “healing” environment as consequence from beneficial cement chemistry in the vicinity of the steel-paste interface, will be the reason for effectively performing CP. The result is a shift toward more noble values of the steel open circuit potentials with time of application, or the so-called “open circuit potential” passivity.

The introduced cost-effective CP, based on a block-shaped, current pulse signal, is at least as effective as the conventional CP in terms of achieving the required steel polarization, thus providing adequate protection of the steel reinforcement. Potentio-dynamic polarization determines similar electrochemical parameters for both types of protection and, taking into consideration the at least 50 % less CP current density used in pulse regime, confirms the efficiency and cost-effectiveness of the latter.
Based on previously discussed investigations and established beneficial effects of pulse DC current in terms of bulk matrix alterations and concrete microstructure (Chapter 7), it is expected that the lower cathodic current density, as in pulse CP applications for reinforced concrete, will possibly lead to reduced side effects and more pronounced beneficial secondary effects, compared to conventional CP. The former are mainly related to bond/strength degradation on the steel/cement paste interface; the latter are in terms of enhanced chloride withdrawal, calcium-rich layers accumulation, favorable morphology and crystallinity of the product layers on the steel surface and electrochemical response, which will be subject to the following Chapters 9 and 10.

References:
34. Glass, G.K., “Advances in CP”, UMIST, Manchester, Feb’ 2006, UK
CHAPTER 9
CONVENTIONAL AND PULSE CATHODIC PROTECTION IN REINFORCED CONCRETE. ELECTROCHEMICAL PROPERTIES AND SURFACE ANALYSIS OF THE STEEL REINFORCEMENT.

Adapted from:

9.1 INTRODUCTION
Corrosion and cathodic protection (CP) in reinforced concrete are electrochemical processes with high complexity. The corrosion state or the performance of CP techniques can be evaluated by conventional monitoring techniques as Potential mapping or Depolarization/decay measurements. The previous Chapter 8 discussed the conventional and pulse CP in terms of technical regimes and conventional monitoring, thus providing evidence for the performance of both techniques in reinforced concrete and consequently their efficient application for steel protection in conditions of chloride-induced corrosion. However, when a more scientific approach to these processes is to be achieved, or in the case when a new or an improved technique for corrosion protection has to be assessed, which is to provide experimental evidence for the fundamentals of a working CP technique, conventional monitoring is not sufficient to provide the necessary knowledge and understanding. Moreover, the monitored protection regimes have to be investigated in a comparison with corroding and control (non-corroding, non-protected) cases. To this end, electrochemical methods i.e. EIS, PR, PDP, are essential for describing the corrosion behavior of the steel reinforcement in condition of corrosion or CP. Further, if the obtained electrochemical parameters are correlated with steel surface analysis, a better insight into the mechanisms of corrosion and protection is achieved.

This Chapter 9 deals with a fundamental approach to understanding the principles of CP in terms of performance and efficiency, compared to corroding and reference (non-corroding, non-protected) conditions, by discussing the electrochemical behavior of the steel reinforcement and the steel surface characteristics.

9.2 TECHNICAL BACKGROUND
The chloride-induced corrosion process on steel reinforcement has been largely studied in concrete and in simulated pore solutions as well [1-21]. Along with the localised corrosion on the steel surface, physico-chemical and structural transformations are taking place on the steel/cement paste interface. Further, the morphological alterations and certain distribution of product layers are influencing the mechanical properties of the reinforced concrete system as a whole. The mechanisms of steel corrosion in concrete were discussed in more detail in Chapter 2.
Relevant to the discussion in this chapter, some brief introductory remarks are as follows: in a simplified way, corrosion of steel in reinforced concrete can be represented by two electrochemical reactions: dissolution of iron at anodic sites (Eq. 1) and the corresponding oxygen reduction at local cathodes, using the electrons generated by the metal dissolution (Eq. 2).

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

The products of the above reactions normally interact and in a final stage transform into a stable protective film on the steel surface. In the simplest case, a two layer structure of the film can be assumed, where the inner layer, ascribed as Fe₃O₄, acts as a barrier layer, strongly adhering to the steel surface and limiting further film growth [22]. Passivity though, is assigned to the outer, gelatinous type layer, composed of outer hydrous Fe₂O₃. The protective layer is additionally supported by the presence of a Ca-rich outer layer, which adheres to the steel as well. According to some researchers, the calcium rich layer provides only limited protection, the inner (two layer) film of iron oxide/hydroxides is the one passivating the steel [23]. Other investigations [22,24] attribute increased protective ability of the passive layers to incorporated Ca(OH)₂ in the outer atom layers of the inner passivating film. The mechanism is denoted to adsorption of Ca²⁺ ions in the inner film of iron oxide/hydroxides.

The protective abilities of the passive films are strongly dependent on the electrode potential, pH of the adjacent solution and the presence of aggressive ions (as chloride in this study). In general pH in concrete is about 12.5 – 13.5 and oxygen availability is comparatively restricted in case of sound concrete layer on the steel surface, hence passivity could be stable with time. However, in the presence of aggressive substances, moisture and microcracks, which favor oxygen and aggressive ions penetration to the vicinity of the steel surface, breakdown of passivity occurs and corrosion is initiated. The passive layer breakdown mechanisms were extensively studied by numerous authors [e.g. 25-28] and a number of models are already proposed and described, for example: the adsorption-displacement, the chemico-mechanical and the migration-penetration mechanism. Whatever the mechanism of protective film breakdown, the final stage is exposure of small areas from the metal surface to the electrolyte (in this case to the pore solution). Once corrosion is initiated, film transformations or formation of new product layers occur. There are several possibilities for the formation sequence of these layers, depending on the environmental conditions. The steel surface is generally found to be covered by a layered, non-homogeneous formation of products, differing in crystallinity and composition, comprising an inner layer, similar to Fe₃O₄, and an outer layer, composed of iron (oxy)hydroxides and iron (oxy)hydroxy-chlorides (i.e. a combination of α, β, γ – FeOOH, Fe(O,OH,Cl) and Fe₂O₃). The product layer in corroding specimens is a combination of low valent oxides and iron-oxy(hydroxy)chlorides, exhibiting a relatively rough morphology. In conditions of CP, transformations of the product layers, formed prior to protection, occur as well, mainly in terms of lowering the products crystallinity. The surface layers in the protected specimens are far more compact, the inner product layer (mostly Fe₃O₄) remains more uniform, whereas the outer layer exhibits reduced crystallinity. The favorable conversions are more pronounced under pulse CP conditions compared to conventional CP and are attributed to the beneficial effects of pulses in reducing pore water salinity and favorable physico-chemical and microstructural alterations in the bulk.
cement paste. A simplified scheme and discussion of the formation of product layers, relevant to the present conditions will be presented in Section 9.3.3.

Summarizing, electrochemical measurements are readily applicable for evaluating electrochemical behavior of the steel surface not only for a corroding or passive state, but also in conditions of cathodic protection. This Chapter presents the applicability of electrochemical techniques (EIS, PDP, PR) in monitoring the steel parameters in conditions of corrosion and cathodic protection in reinforced concrete. Further, based on the obtained results, the aim is to evaluate if the introduced pulse CP is as effective as the conventional CP, thus fundamentally supporting the findings from conventional monitoring, described in Chapter 8. The interpretation of the obtained parameters however is not straightforward and is related to the properties of the product layers, formed on the steel surface in the different conditions. This evaluation should take into account the crystallinity, morphology and composition of the surface layers. Hence, additionally, this chapter presents a correlation of the steel surface behaviour and electrochemical parameters in concrete with those in model medium (cement extract solution) and finally, the morphological and structural observations of the product layers on the steel surface, formed as consequence of each investigated technical regime are presented, thus supporting the findings from electrochemical measurements. The correlation of techniques and results provides evidence for the fundamental mechanisms of CP efficiency, and in particular the pulse CP regime, which is normally evaluated according empirical criteria only.

9.3 EXPERIMENTAL

9.3.1 Materials

The materials used in the present study were reinforced concrete cylinders, cast from OPC CEM I 32.5R (casting according EN 196-1), water to cement ratio 0.6, cement to sand to gravel ratio 1:2:4 (sand range: 125 µm to 2 mm; gravel range: 2mm to 12 mm). The reinforced concrete cylinders had dimensions: H=25cm, D=12 cm, containing embedded construction steel (FeB500HKN ribbed bars, d=12mm), used “as received” (no preliminary treatment) for all technical conditions. After curing in fog room conditions (98% RH and 20°C) for 28 days the specimens were placed in a salt spray cabinet (SSC), aiming at initiation of corrosion before applying CP. The SSC used 5% NaCl spray, additionally the cylinders were immersed 1/3rd of height in 5% NaCl (except for the non-corroding cells, maintained in the same RH and temperature conditions, but immersed in water). The maintained temperature was 35°C for 30 (or 60) days, followed by 20°C afterwards and till the end of the test (460 days), with certain intervals of drying and wetting. The concrete mixture, experimental set-up and environmental conditions are as described in Chapter 8, Table 8.1. Cathodic protection was employed in the two regimes (conventional and pulse), using DC current in the range of 5 to 20 mA/m² steel surface; duty cycle for the pulse regime was 12.5% to 50 % at 1KHz frequency; MMO Ti mesh, embedded in the concrete cover served as anode (more details for the CP regimes are given in Chapter 8, Table 8.2). This Chapter 9 presents the results for four groups from all studied specimens, on which CP was applied at 120 days (i.e. in the time of applying protection, corrosion was already in an advanced stage) and the specimens were maintained in the relevant conditions up to 270 days.
These four groups are as follows: freely corroding group (further in the text represented by specimen 3), a non-corroding group (represented by specimen R), a group with applied conventional CP (represented by specimen 6) and a group with applied pulse CP (specimen 7).

9.3.2 Experimental techniques

The experimental techniques, used for studying the specimens described in this Chapter are:

Electrical resistivity measurements, Electrochemical measurements, ESEM, EDX, XRD and XPS measurements.

**Electrical resistivity:** Specification of the 2 pin AC 2 pin resistance measurement is as follows:

- Measuring current: 100µA balanced alternating square wave
- Frequency: 120 Hz
- Current source impedance: >10 MΩm
- Voltage: 4 Volt
- Voltage input range: ±4 Volt
- Voltage input impedance: >100 MΩm

A multiplexer was used to select a specific cell from all investigated specimens and measure the potential difference. The potential difference between the electrodes was recorded at the moment just before the transition in the current source for the purposes of reducing the effects of cabling and other parasitic capacities (the measurements is as described in Chapter 8).

**Electrochemical methods:** this study involved electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP) and polarization resistance method (PR). The measurements were performed at open circuit potential (OCP) for all cells (after 24 h depolarization of the reinforcement for the protected specimens i.e. protection current was interrupted before and in the time of the measurement) and in immersed condition (mentioned above), assuring electrical conductivity of the medium. For LPR an external polarization in the range of ±20 mV vs OCP was used at scan rate 0.16 mV/s, PDP was performed in the range of -0.15 V to +1.2 V vs OCP. The EIS measurements were carried out in the frequency range of 50 KHz to 10 mHz by superimposing an AC voltage of 10 mV. The used equipment was EcoChemie Autolab - Potentiostat PGSTAT30, combined with FRA2 module, using GPES and FRA interface.

In addition to the electrochemical measurements in concrete, sample electrodes from the steel, previously embedded in the concrete, were subject to EIS, PDP and PR measurements in cement extract (CE) solution (pH 12.6). The tests in solution aimed at investigating the electrochemical parameters of the previously embedded steel and were performed in a common 3-electrode cell, using SCE as reference electrode, Pt or MMO Ti mesh (surrounding the working electrode) as counter electrode. Monitoring was performed after allowing stabilisation of OCP (generally 45 min immersion in the solution).

**Steel surface analysis (ESEM, EDX, XRD, XPS):** Relevant to the morphological aspects of the product layers, formed on the steel surface in every technical condition, section images of the specimens were obtained by scanning electronic microscopy, using environmental SEM, ESEM Philips XL 30, equipped with secondary, backscattered and large field detectors, operating at accelerating voltage of 20 to 25 kV for imaging and 10 to 20 kV for x-ray analysis of the product layers. The ESEM is equipped with EDX detector. In addition to general EDX measurements, X-
ray point analysis (using local area of 5x5 µm at magnification 2000x or spot analysis at magnification 500x) were performed in radial direction of the steel bar, starting at 0 µm (the steel surface) up to 5000 µm into the bulk material (direction the edge of the specimen). For EDX analysis in the bulk material, accelerating voltage of 20 kV was used, for composition analysis directly on the steel surface, 7 to 15 kV was used.

For the XRD measurements, X-ray powder diffractometer DRON-3 (Bragg-Brentano arrangement, CuKα radiation and scintillation counter) was used. The XPS measurements were carried out using ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the analysis chamber of 5x10⁻¹⁰ mbar (during the measurement - 1x10⁻⁸ mbar). The photoelectrons were excited using AlKα X-ray source (excitation energy hν=1486.6 eV). The pass energy of the analyzer was 20 eV (for Fe 2p – 50 eV). The instrumental resolution measured as the full-width at a half-maximum (FWHM) of the Ag3d5/2, photoelectron peak is 1 eV. The energy scale is corrected to the C1s peak maxima at 285 eV.

9.4 RESULTS AND DISCUSSION

9.4.1 Electrochemical methods
Electrochemical impedance spectroscopy (EIS) has emerged as an effective method to distinguish fundamental processes occurring during corrosion and is used as a useful technique for obtaining detailed knowledge of the steel/concrete system [29, 30]. It provides information on a number of parameters, such as the presence of surface films, bulk concrete characteristics, interfacial corrosion or transformation of corrosion product layers, mass transfer phenomena.

The aim of this chapter is to compare the electrochemical behaviour of the steel surface in conditions of corrosion and CP, using EIS and supportive PDP and PR measurements. The derived parameter was mainly polarization resistance (R_p), which can be associated with the corrosion process (the anodic oxidation of steel) as well as other electrochemical processes involving corrosion products, thus providing information for the overall reaction rates. The measurements were performed in concrete (steel embedded in the concrete cylinders) and in cement extract solution (steel electrodes from the previously embedded steel used as working electrodes). The equivalent circuits used in the present study comprise two (three) time constants in series with the electrolyte resistance – Fig. 9.1. The elements of the equivalent circuit present the following physical meaning: R_con is the concrete resistance including the contribution of electrolyte resistance in case of measurements in concrete, R_c is the cement extract resistance for measurements in model medium. The first time constant (R_p, C_p, R_c, C_c) is attributed to the properties of the concrete matrix in terms of pore network (Fig. 9.1a) or properties of product layer on the steel surface (R_p, C_p, R_c, C_c). The second time constant (R_c, R_c, C_c, C_c) for both conditions deals with the electrochemical reaction (or oxi-redox reactions) on the steel surface. The third time constant in the equivalent circuit for concrete (R_red, C_red) is attributed to redox processes, taking place in the product layers.
9.4.1.1. Electrochemical measurements in concrete

For deriving $R_p$ from EIS measurements in reinforced concrete, the low frequency limit of the impedance spectra is generally considered for calculations as reported in [15,16,31-34] and used in the present study as well.

Fig. 9.2 EIS response in Nyquist (a) and Bode (b) format for non-corroding (R) and corroding specimen (3) in concrete at 270 days of age ($E_{corr}=-220$ mV SCE for specimen R, $E_{corr}=-440$ mV SCE for specimen 3).

Fig. 9.2 presents the impedance response for non-corroding and corroding specimens (measurements in concrete) in Nyquist and Bode format. Fig. 9.3 depicts an overlay of the impedance response for the corroding specimen and the two types of protected specimens (conventional CP (6) and pulse CP (7)). Summarized data for the best fit parameters are given in Table 9.1.
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Fig. 9.3 EIS response in Nyquist (a) and Bode (b) format for corroding specimen (3) and protected specimens (6 – CP and 7 – pulse CP) in concrete at 270 days of age (E_{corr}=-388 mV SCE for specimen 6, E_{corr}=-250 mV SCE for specimen 7, E_{corr}=-440 mV SCE for specimen 3).

Table 9.1. Best fit parameters from experimental EIS results in concrete, using the equivalent circuit presented on Fig. 1a and the CDC: R_{el+b}(C_{pn})(R_{pn}(C_{f}(R_{ct}(C_{red}(R_{red}))))).

<table>
<thead>
<tr>
<th>Concrete</th>
<th>R_{el+b}</th>
<th>C_{el+b}</th>
<th>R_{cor}</th>
<th>C_{te}</th>
<th>R_{p}</th>
<th>C_{red}</th>
<th>R_{red}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP (6)</td>
<td>70.90</td>
<td>18.00</td>
<td>13.90</td>
<td>244</td>
<td>1.49</td>
<td>2210</td>
<td>11.60</td>
</tr>
<tr>
<td>pCP (7)</td>
<td>121.10</td>
<td>13.70</td>
<td>11.59</td>
<td>248</td>
<td>3.30</td>
<td>1454</td>
<td>17.70</td>
</tr>
<tr>
<td>Corr (3)</td>
<td>95.04</td>
<td>2.38</td>
<td>20.02</td>
<td>239</td>
<td>7.30</td>
<td>509</td>
<td>36.20</td>
</tr>
<tr>
<td>Ref. (R)</td>
<td>142.40</td>
<td>1.07</td>
<td>9.80</td>
<td>88</td>
<td>36.60</td>
<td>86</td>
<td>423.00</td>
</tr>
</tbody>
</table>

The high frequency arcs for all specimens correspond to the concrete bulk resistance including the contribution of electrolyte resistance. The derived R_{el+b} values (Table 9.1) are consistent with derived concrete resistance from AC 2 pin method (generally accepted method for measuring concrete electrical resistance, Fig. 9.4a). The AC 2 pin resistance measurement was performed with specially designed for this study device. The advantage of the AC methods is that the mean value of the AC current is zero, i.e. the polarization effects due to the measurement could be minimized, thereby guaranteeing relatively high accuracy. Using the steel electrodes as pins, the potential differences were measured. The resistance is then computed from the current and the measured potential difference. The concrete electrical resistivity was further calculated based on derived values from EIS and AC 2 pin and the geometry of the cells.

Fig. 9.4b presents the concrete electrical resistivity on Ohm.m, derived from EIS (R_{el+b} + R_{p,netw}) and AC 2 pin measurement. As expected, due to volume expansion of corrosion products and micro-cracks initiation, lower resistance (R_{el+b} + R_{p,netw}) was recorded for the corroding specimen, compared to reference specimen.
Generally, in terms of cement chemistry and development of microstructural properties with aging, concrete hydration is the main factor influencing the concrete resistance. At the age of 270 days however, more significantly contributing factors are the environmental and technical conditions. As seen from Table 9.1, the lowest resistance is recorded for the specimen under conventional CP (about 84 kOhm.cm²), denoted to the influence of current flow on the bulk matrix and bond-strength degradation. In this respect, the pulse CP has beneficial effects, as concrete resistivity in specimen 7 (pulse CP, 133 kOhm.cm²) is close to non-corroding conditions (specimen R). The slight deviation between values obtained by the two methods (Fig. 9.4b) is attributed first to the 30 days difference in age (AC 2 pin method was performed up to 240 days of age) and second – due to the AC 2 pin measurement itself. The measuring device recorded resistance values automatically 4 times per day, hence the CP current flow through the protected cells might have influenced the recorded resistance values, as the deviation for corroding (3) and reference (R) specimens is lower. On the other hand, the resistance for specimen R, being non-corroding, is not expected to give large deviations for 30 days difference at this age, as it is supposed to happen with the other cells as consequence from internal micro-cracking (due to volume expansion of corrosion products or alterations in mechanical properties due to current flow). Hence, it is assumed that microstructural changes due to corrosion and current flow, along with the difference in age, are the reason for the slight deviation in recorded values by EIS and AC methods. Main outcome from the correlation of the two methods is that EIS is able to provide reliable data for electrical properties of concrete bulk matrix as well, along with describing the electrochemical behavior of the steel surface, which will be discussed in what follows.

As mentioned, the EIS response in the low frequency domain was used for deriving electrochemical parameters related to the steel electrode. Fig. 9.2 shows the significant difference of the impedance response for corroding (3) and non-corroding (R) specimens in the low frequency domain, attributed to accelerated corrosion state in the former and passive condition in the latter case. The derived $R_c$ for corroding specimen is significantly lower compared to non-corroding specimen (Table 9.1). The corresponding interfacial capacitance ($C_f$) for corroding specimen is higher (239 µF/cm²), compared to non-corroding specimen (88 µF/cm²), attributed to spreading the corrosion damage on a large surface area.
Dependence of $R_{ct}$ and $C_f$ (derived from best fit parameters)

$R_{ct}$ [kOhm.cm$^2$]

$C_f$ [uF/cm$^2$]

$R_{red}$ [kOhm.cm$^2$]

$C_{red}$ [uF/cm$^2$]

Fig. 9.5 Correlation of $R_{ct}$ and $C_f$ (a) and $R_{red}$ and $C_{red}$ (b) for all investigated specimens (in concrete): 3 – corroding, R – reference, 6 – CP and 7 – pulse CP protected.

The equivalent circuit used for fitting the experimental data from measurements in concrete allowed separately deriving charge transfer resistance ($R_{ct}$) and resistance $R_{red}$ attributed to redox processes in the product layers. Fig. 9.5 presents a correlation of $R_{ct}$ ($R_{red}$) and $C_f$ ($C_{red}$) for all specimens. The values for interfacial capacitance $C_f$ of the reference specimen R tend towards the values for the capacitance $C_{red}$ (88 μF/cm$^2$ and 86 μF/cm$^2$ respectively), which corresponds to the low rate of oxidation process for this specimen. The significantly higher values of $C_f$ for all other specimens are consistent with the lower $R_{ct}$ (Fig. 9.5a) and hence higher corrosion rates will be expected for these specimens. Compared to $C_f$, the derived values for $C_{red}$ for specimens 3, 6 and 7 are significantly higher (Fig. 9.5b) and can be only denoted to modifications in the structure of product layers.

Fig. 9.6 Potentio-dynamic curves for all investigated specimen-groups in concrete (a) and comparison of derived $R_p$ values (b) (IR drop corrected for all conditions).

Although EIS allows separate characterization of charge transfer and other processes related to the corrosion phenomena, the comparison of the investigated specimens in the present conditions is believed to be more accurate if the overall reaction rates are compared i.e. the specimens in this study were discussed mainly using global $R_p$ values. $R_p$ values can be either lower or higher than pure $R_{ct}$ (associated with the corrosion reaction only). $R_p$ equals $R_{ct}$ when there are no mass transport limitations. When absorbed intermediate layers start undergoing transformations
(contributions of the product layers), the overall reaction rate is given by \( R_p = R_{ct} + R_{red} \) where \( R_{red} \) is related to redox transformations, mass transfer phenomena etc. [35]. Hence, the discussions for \( R_p \) in this study is relevant to describing the overall response and reaction rate of the systems in each technical condition.

Comparing the impedance response for protected specimens and corroding specimen (Fig. 9.3), it is obvious that the magnitude of impedance (Fig. 9.3a) and phase angle (Fig. 9.3b) are higher for the corroding specimen. The derived \( R_p \) (from EIS measurements in concrete) for the corroding specimen is higher (about 43 kOhm.cm\(^2\)), compared to protected specimens (in the range of 13 to 21 kOhm.cm\(^2\)) (Table 9.1). The observation is consistent with PDP measurements, giving \( R_p \) values in the same range and same trend of change (Fig. 9.6).

Fig. 9.7 presents a comparison of \( R_p \) values, derived from polarization resistance measurements (PR) and EIS measurements in concrete. The \( R_p \) values from EIS were calculated using the derived values for \( R_{ct} \) and \( R_{red} \). Fig. 9.7 shows consistency of obtained results and similar trends for each investigated system, derived from both methods.

Although it was expected that the protected specimens will exhibit higher impedance and higher \( R_p \) values respectively, apparently this is not the case. Generally two mechanisms are most likely responsible for the lower \( R_p \) values in protected conditions. First, maintaining the steel in protected specimens cathodic during the time of the experiment (270 days), with interruptions of the protection current only in the time of depolarization and electrochemical measurements, suggests a relatively “clean” steel surface in the protected cells. Any layers, formed prior to CP application (as mentioned CP was applied at 120 days) would only bear conversions, but further oxidation of the steel will not occur in the time of protection. In the time of interrupting the CP however, and after depolarization for 24 h, allowing establishment of a steady OCP, the steel gradually slips to a more “active” state (as result of shifting the steel potential from strongly cathodic to natural for the present conditions potential). Taking into consideration the cement...
chemistry around the re-bars (chloride concentration above the thresholds of 0.15 w.% to 2.5 % per dry cement weight [1]), in the period of electrochemical measurements, there will be conditions for steel dissolution on isolated locations, hence the recorded averaged corrosion current density might end up higher (lower $R_p$ values respectively), comparing to corroding and non-corroding conditions. As a second hypothesis, the nature of the product layer, formed on the steel surface (for each technical condition), is contributing to the performance of the systems and influencing the electrochemical response. Based on fundamentals, the measured corrosion current density will be controlled by the kinetics of the electrochemical reactions during the measurement and the diffusion of reactants both towards and away from the electrode. Hence, higher diffusion limitations, as in the corroding specimens, will result in effectively higher $R_p$ values.

The above consideration is supported by the PDP measurements (Fig. 9.6a): the most significant anodic control in the region of 100 mV after $E_{corr}$ is observed for the non-corroding specimen, followed by the corroding specimen (see incorporated in Fig. 9.6a zoomed area of anodic region after $E_{corr}$). The impeded anodic reaction in the non-corroding specimen R is expected, as the steel surface is in passive state. Comparing corroding specimen (3) and protected specimens (6 and 7) in the 100 mV region around $E_{corr}$ in anodic direction, specimen 3 exhibits the highest limitations of the anodic reaction as result of heterogeneous and rough product layer on the steel surface. Basically, after the corrosion potential $E_{corr}$ an accelerated metal dissolution takes place at first. Considering that specimens 6 and 7 were protected before the time of the measurements, and the surface was initially preserved (less corrosion products than specimen 3), steel dissolution after $E_{corr}$ is faster and formation of corrosion products takes place. Following the formation of these new layers, the dissolution is impeded due to diffusion limitations i.e. difficulties in the transport of pore solution to fresh metal surface on one hand and slower transport of soluble corrosion products back into the pore solution on the other. With anodic polarization further on (Fig. 9.6a) a trend towards continuous increase of current density is recorded. Further, approaching the region of maximal diffusion current and diffusion control (at relatively higher current densities) a steady state of the described process would take place. As conclusion, the higher $R_p$ values for corroding specimen 3 are obviously attributed to diffusion limitations in conditions of external polarization and the product layers composition, which will be further discussed in Section 9.4.2 below.

9.4.1.2. Electrochemical measurements in model solutions
As aforementioned, a series of steel samples ($S=3.7cm^2$) from the reinforcing steel, previously embedded in concrete for 270 days (from each technical condition i.e. non-corroding, corroding and both protection regimes), were used as working electrodes for electrochemical measurements in model solutions, namely cement extract (CE) solution. The outcomes from electrochemical measurements in CE solutions, along with an elaborated discussion in terms of steel surface oxidation/reduction behavior after re-bars conditioning for the whole period of the test (460 days) will be presented in Chapter 10.

The CE solution was prepared by mixing (for 24 h) ordinary Portland cement (the same used for mixing the concrete specimens, section 1) and water, ratio 1:1, filtrating and thus obtaining a model pore solution with pH 12.6. The measurements in model solutions were expected to
provide information for the behavior of the already formed in concrete product layers on the steel surface. The previously described equivalent electrical circuit (Fig. 9.1b) and time constants (Section 9.3.1) apply for EIS measurements in CE. Figure 9.8 presents the impedance response for steel electrodes from non-corroding (R), corroding (3) and protected (6 and 7) specimens in CE solution, Table 9.2 summarizes the best fit parameters for the experimental EIS data.

### Table 9.2: Best fit parameters from experimental EIS results in CE solution, using the equivalent circuit, presented on Fig. 9.1b and the CDC: \( R_g(\sigma_{P,E}(R_p,C_f)) \)

<table>
<thead>
<tr>
<th>CE</th>
<th>( R_p ) [kOhm.cm²]</th>
<th>( C_{\sigma} ) [µF/cm²]</th>
<th>( R_{el} ) [kOhm.cm²]</th>
<th>( C_f ) [µF/cm²]</th>
<th>( E ) [mV, SCE]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP (6)</td>
<td>10.65</td>
<td>20</td>
<td>3.23</td>
<td>370</td>
<td>19.10</td>
</tr>
<tr>
<td>Pulse CP (7)</td>
<td>10.30</td>
<td>4</td>
<td>5.27</td>
<td>220</td>
<td>23.56</td>
</tr>
<tr>
<td>Corroding (3)</td>
<td>11.30</td>
<td>180</td>
<td>86.18</td>
<td>110</td>
<td>2.86</td>
</tr>
<tr>
<td>Reference (R)</td>
<td>10.50</td>
<td>70</td>
<td>6.29</td>
<td>50</td>
<td>412.00</td>
</tr>
</tbody>
</table>

As seen from the plots, the response and derived parameters in CE for specimens R (non-corroding) and protected (both CP – 6 and pulse CP – 7) are consistent with the data obtained from EIS measurements in concrete (embedded conditions): the non-corroding specimen R exhibits the highest \( R_p \) due to passive steel surface, the protected specimens (6 and 7) depict similar behavior as in embedded conditions – \( R_p \) in the range of 19 to 24 kOhm.cm². The derived \( R_p \) values for corroding specimen 3 are again significantly lower compared to non-corroding conditions, as in concrete, but completely different behavior is observed with regard to protected specimens. While in concrete \( R_p \) values for specimen 3 are higher than specimens 6 and 7, in CE solution, the opposite trend appears i.e. for the corroding specimen 3 the recorded \( R_p \) values are about one order of magnitude lower (~ 3 kOhm.cm²) compared to protected specimens (19 kOhm.cm² for CP (6) and 24 kOhm.cm² for pulse CP (7)). Obviously, the properties of the product layers on the
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Steel surface, as well as in the steel/cement paste interface (in embedded conditions and in CE solution conditions), are responsible for the observed differences. The CE extract solution (representing the concrete pore solution) will not affect the steel surface in terms of corrosion initiation (pH 12.6). Hence, the difference in electrochemical behavior, comparing to concrete surrounding, will be attributed to the chemistry of the cement paste adjacent to the steel surface in concrete conditions, the lower diffusion limitation in case of CE solutions (compared to concrete) and the solubility, adherence, crystallinity, composition and compactness of the product layers formed on the steel surface, which will be further discussed in Section 9.4.2.

The data derived from EIS measurements in CE solution are supported by PR and PDP measurements in the same medium. Figure 9.9(a) presents the potentio-dynamic curves for the specimens under study, Fig. 9.9(b) depicts a comparison of $R_p$ values, derived from PDP and PR measurements in CE. As seen from Fig. 9.9(a) the protected specimens (pulse CP -7 and CP – 6) depict similar behavior with external polarization, the lowest corrosion current density is recorded for non-corroding specimen R, the highest for the corroding specimen 3.

In the region of the corrosion potential $E_{corr}$, namely 100 mV in anodic direction, the most significant anodic control is for specimen R (incorporated in Fig. 9.9a) zoomed area of anodic region around $E_{corr}$, followed by specimen 3 (as observed in concrete), while the protected specimens 6 and 7 exhibit close to mixed anodic-cathodic control (typical for steel in passive condition). Further, approaching the region of diffusion control, a trend towards increased current density is observed for all specimens, the curves pass through a “plateau” region and reach the potential of oxygen evolution. The almost identical behavior of specimens 6 and 7 (except the slight difference in corrosion potential) denotes for at least similar effectiveness of the pulse CP (specimen 7), compared to the conventional CP (specimen 6), which is also observed in embedded conditions. Although PDP measurements in embedded conditions (in concrete) are not comparable with measurements in cement extract solutions, in terms of electrolyte medium, both investigations present the electrochemical behavior of the steel surface as result of the previous maintenance in certain technical conditions (corroding, non-corroding and both regimes of conditions).
protection). Hence, the response of the systems, related to product layers and behavior with external polarization is expected to give similar trend of the overall reaction rates. Figure 9.10 presents a comparison of \( R_p \) values derived from PDP measurements in concrete and CE (the data are computed after IR drop corrections for both media). As seen from the plot, consistent results for the global corrosion behavior of the systems is observed, except for the corroding specimen 3, which was mentioned above and will be discussed in what follows in terms of microstructural observations of the steel/cement paste interface.

![Comparison of \( R_p \) values for steel in concrete and cement extract, derived from PDP measurements in concrete and CE (results corrected for IR drop in both media)](image)

**Fig. 9.10** Comparison of \( R_p \) values for specimens 3 – corroding, R – reference, 6 – CP and 7 – pulse CP, derived from PDP measurements in concrete and CE (results corrected for IR drop in both media)

### 9.4.2 Microstructural and morphological observation at the steel/cement paste interface: properties of the product layers in correlation with electrochemical parameters

The steel bars in all investigated specimens were initially equal in surface preparation (“as received”, depicted on Fig. 9.11(b). As reported in [36], “as received” steel bars behave similarly to “pre-rusted” bars and exhibit even higher corrosion current densities, compared to “sandblasted” bars in equal conditions similar to the present study (pH ~12.6 and sufficiently high chloride concentration). Thus, presuming equal appearance of the steel surface before conditioning, the comparison of product layers after maintaining the steel reinforcement in the relevant technical conditions is considered accurate (as the comparison reflects the changes with conditioning time of initially same specimens).

Cross sections of the steel/cement paste interface in a conditioned (e.g. protected case) and “as received” (not conditioned) steel bars are presented on Fig. 9.11, revealing the product layer, formed on the steel surface with time of the experiment in the former case and lack of product layer on the surface of the “as received” (and never cast in concrete) specimen in the latter case. Visualization of the steel/cement paste interface was obtained using ESEM in BSE mode (steel appears bright in the images), at different magnification up to 4000x. The investigation gives information for the adherence, thickness and distribution of the product layers on the steel surface. Furthermore, the chemical composition of the layers, along with composition of the
immediately adjacent hydration product (in the region 1 to 5 µm away from the product layer) were obtained using EDAX analysis (Section 9.4.3.4. below will discuss in more detail the product layers on longitudinal sections of the steel surface, as well as the hydration products from the steel/paste interface into the bulk concrete matrix).

**Fig. 9.11** Cross section images of the steel/cement paste interface in a protected specimen (a), and “as received” specimen (b), revealing the product layer formed on the steel surface after conditioning for 270 days (a) and the lack of product layer (b) in the “as received” specimen.

Figure 9.12 presents the steel/cement paste interface for non-corroding (R), corroding (3), CP protected (6) and pulse CP protected (7) specimens at equal magnification (4000x).

**Fig. 9.12** Cross sections (magnification 4000x) of the steel/cement paste interface in specimen 6 (CP) (a), specimen 7 (pulse CP) (b), corroding specimen 3 (c) and non-corroding specimen R (d)
As seen from the micrographs, the most compact and adherent layer on the steel surface is the one in the non-corroding specimen R (Fig. 9.12d). The product layers in the protected specimens exhibit similar compactness and adherence, the specimen 7 (pulse CP) however, characterized by a thinner and denser product layer (~2 µm), compared to the product layer in specimen 6 (under conventional CP). In the former case the product layer is obviously more homogenous (Fig. 9.12b), while in the latter case, the product layer is thicker (~10 µm) and in addition presents a kind of multi-layered appearance (Fig. 9.12a): a denser phase adhered to the steel (as in specimen 7) of about 3 µm, followed by a rough almost compact formation of ~ 4µm and a final non-compact, rough outer layer with low adhesion to the previous two of about 2 µm thickness. The product layer in the corroding specimen 3 (Fig. 9.12c) exhibits the lowest adherence to the steel surface, very rough morphology, low density and lack of compactness i.e. exhibits the highest heterogeneity along with varying thickness of 3 to 12 µm (the appearance of the product layers on the steel surface at later stage of 460 days is given in Annex IV).

The different appearance and properties of the product layers is obviously influencing the electrochemical response of the systems, described in the previous sections, and is responsible for the different behavior with respect to model medium when performing electrochemical measurements. It is known that the product layers on steel surface in Ca(OH)$_2$ environment (as in concrete or CE) are composed of several layers and in the simplest case are being considered as inner and strongly adherent formation, with composition similar to Fe$_3$O$_4$ and a gelatinous outer layer of iron hydroxides, where Fe$^{2+}$ or Fe$^{3+}$ can be detected [37-39]. Calcium ions can be incorporated in the outer atom layers of the inner layer and increase the protective ability of the product layers when no chlorides are present [39]. Such case is relevant to the non-corroding specimen R. In the presence of chlorides, as in corroding specimens 3 and protected specimens 6 and 7 (both CP regimes were applied at 120 days after conditioning in SSC), the film thickness increases but the protective abilities decrease. Obviously with this respect, the pulse CP is more effective, compared to conventional CP, as specimen 7 exhibits more compact, thinner and adherent layer compared to specimen 6 (Figs. 9.12ab), which proves the beneficial effects of the pulse current in terms of chloride withdrawal from the steel surface. This consideration is supported by EDAX analysis and wet chemical analysis of the adherent cement paste as well – Figs. 9.13 to 9.15.

![Fig. 9.13 Concentration of iron (w.%) (a) and chloride and sodium concentration (w.%) (b) in the product layer on the steel surface (legend key p.1) and in the immediate vicinity of the steel surface (legend key p.5)](image-url)
The X-ray spot analysis was performed, using local area of 5x5 µm at magnification 2000x at accelerating voltage of 7 to 15 kV for the steel surface and the product layers and 20 kV for the adjacent cement paste. The data presented on Figs. 9.13, 9.14 are averaged for all EDAX measurements, performed in radial direction of the whole perimeter of steel bar. The data presented by legend key p.1 in the plots present the chemical composition in the product layer, the data for p.5 - the composition of the cement paste immediately surrounding the product layer (marked spots in the micrographs Fig. 9.12). As seen form the plots, the highest iron concentration in the product layer is in specimens 6 and 7 (protected cells) and the non-corroding specimen R, the lowest in corroding specimen 3. The highest iron concentration (Fig. 9.13a), along with lowest amount of chlorides in the reference and protected specimen (Fig. 9.13b), denotes for a layer of iron oxides/hydroxides in specimens R, 6 and 7 and higher concentration of iron oxy(hydroxy)chlorides in the corroding specimen 3. In addition, the calcium (as well as silica, aluminum) concentration in the region, adjacent to the product layers, is highest in specimens 6, 7 and R (Fig. 9.14), while the same region in corroding specimen 3 (along with the outer part of the rough product layer on the surface) contains highest amounts of chlorides (Fig. 9.13b).

Fig. 9.14 Concentration of calcium (w.%) (a) and aluminum and silica (w.%) (b) in the product layer on the steel surface (legend key p.1) and in the immediate vicinity of the steel surface (legend key p.5).

Fig. 9.15 Chloride and alkali concentration in the cement paste adjacent to the steel surface in w.% per dry cement weight, determined wet chemically (ASTM C1218).
Comparing the iron concentration in the cement layer, adjacent to the steel surface (which means corrosion products penetration or product layer roughness and distribution into the bulk matrix), the lowest amounts of iron are detected in the non-corroding specimen, similar to the pulse CP protected specimen 7. The highest amounts of iron in the adjacent paste are in specimen 3 (corroding) and 6 (conventional CP), attributed to the rough and non-adherent outer layer of the latter and corrosion products penetration into the bulk material for the former. The EDAX analysis is supported by wet chemical analysis of the cement paste around the steel bars, revealing similar observations – Fig. 9.15. The alkali ions concentrations around the steel bar are higher and the chloride concentration lower in the pulse CP conditions, compared to conventional CP. Here again, the observation supports the hypothesis for the beneficial effects of the pulse CP current, compared to conventional CP technique.

The above statements suggest that the cement chemistry, as well as the composition of the product layers, have significant influence on the electrochemical parameters derived by EIS, PDP and RP measurements. The product layers composition, obtained by XRD and XPS, as well as the surface layers morphology, using longitudinal sections of the steel surface from each technical condition, will be discussed in the following Section 9.4.3.

Relevant to the relationship of product layers parameters and composition with derived electrochemical parameters, the following could be considered: There are several aspects that one should take into account when evaluating electrochemical performance of systems as in the present study in terms of product layers formation: One aspect is the substitution of iron oxides/hydroxides layers with calcium. This would cause structural changes in the oxide/hydroxide layers and will probably lead to different catalytic activity [4], hence will give difference in electrochemical parameters obtained in different media (as concrete and CE in the present study). Second aspect is the thickness, morphology and adhesion of the product layers. The protected specimen 7 for example, exhibits a thinner layer, composed of most likely Fe$_3$O$_4$, while specimen 6 exhibits a multi-layered formation, the outer layer being similar to the one in the corroding specimen 3. The outer layer of the corroding specimen 3 is most likely composed of non-adherent compounds as akaganeite and predominance of goethite and lepidocrocite, while for specimens 6, 7 and R magnetite/hematite are the predominant products [40]. These observations are consistent with reported results from similar research [41], where the presence of α- and γ- FeOOH are detected in the outer product layers, and Fe$_3$O$_4$ and α-FeOOH in the inner layers. In addition to this sequence, β-FeOOH·2Cl$_2$ (akaganeite), being a needle shape formation at earlier age or bundles of rods of hollow subcrystals at later ages, is non-adherent compound, which does not accommodate in the product layer. Hence, although the derived $R_p$ values for the corroding specimen in concrete are higher than the protected cells, lowest $R_p$ values are recorded in CE solutions, as the iron(oxo)chlorides are most likely released in the solution in the time of external polarization i.e. there is no adherent, protective rust layer on the steel surface in specimen 3. Additionally, along with the already discussed reasons for diffusion limitations in the corroding specimens, there is a larger surface area of the products, composing the surface layer in specimen 3, contributing to the overall process (as reported by [42], the surface area in m$^2$/g decreases in the sequence of: Fe$_3$O$_4$, $\alpha$H$_2$O $>$ β-FeOOH·2Cl$_2$ $>$ α-FeOOH $>$ α-Fe$_2$O$_3$).
Along with the above considerations, another aspect is the conductivity (electron, ionic, electrical) of the formed layers. For example, electrical conductivity of goethite, hematite and magnetite is decreasing in the order: magnetite-hematite-goethite [43], which suggests that the layers containing mostly magnetite (as in specimens under pulse CP) will exhibit lower limitations to current flow (as in the time of electrochemical measurements), while specimens with high amounts of goethite (oxy-hydroxides are in higher amounts in the corroding specimens as consequence of more oxygen supply via micro-cracks) will exhibit a higher resistivity.

Apparently the product layers’ physical and electrical properties, composition, crystallinity, adherence etc. are of significant importance for the interpretation of the electrochemical measurements on steel specimens in concrete or in model medium. The investigation of the above said features of the product layers on the steel surface in corroding, non-corroding and cathodically protected conditions in correlation will be presented in what follows.

9.4.3. Morphology and composition of the product layers on the steel surface

9.4.3.1 Formation of product layers – Some fundamental mechanisms
Several mechanisms will be presented for the Fe-H$_2$O system in what follows, not taking into consideration the cement chemistry for simplicity. The reaction products in the Fe-H$_2$O system are normally determined not only by thermodynamic relationships [44], but by the oxidation rate of Fe$^{2+}$ and the structure and composition of initial and intermediate iron species, as reported in [45]. In conditions of chloride induced corrosion, intermediate compounds are inevitably formed in the vicinity of the steel reinforcement, which further decompose or influence the formation of the “final” product layers, as further oxidation or reduction is governed by their existence. According to [45], the intermediate compounds are formed either by precipitation from the so called “green complexes”, the latter produced by coexisting anions as chloride ions during oxidation of FeOH$^+$, or by solid state transformation of Fe(OH)$_2$ with oxidation. The mechanisms for products formation are complicated and depend on a variety of environmental factors and oxidation stages.

A simplified scheme, based on the transformations suggested by [45] is presented on Fig. 9.16. The formation of Fe$_3$O$_4$ from Fe(OH)$_2$ can be classified into two routes (1 and 3a, Fig. 9.16). Route 1 of slow oxidation, ending up with mainly Fe$_3$O$_4$ as final product, is more likely for reinforced concrete systems, where oxygen availability is reduced and especially for such systems under cathodic protection, where the negative (cathodic) potential and the consumption of oxygen due to the CP are promoting mainly Fe$_3$O$_4$.

The intermediate compounds can be converted to γ-FeOOH as well, consequently to amorphous oxy-hydroxide layer or α-FeOOH (path 2). This transformation is more likely for the corroding specimens in the present study, as the hydroxides and amorphous products would be dominant for the potential range (mostly more anodic than -650 mV SCE), the locally low pH and higher
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oxygen supply to the steel surface (through the formed cracks due to volume expansion of corrosion products) for these specimens.

As reported in [45], a direct spontaneous transition from Fe(OH)$_2$ to Fe$_3$O$_4$ or γ-FeOOH, although thermodynamically possible [44], seems difficult in terms of transition from hexagonal closed-packed structure of oxygen (Fe(OH)$_2$) directly to cubic closed-packed structure (Fe$_3$O$_4$ and γ-FeOOH). Hence, the transformation occurs via intermediate compounds (complex compounds, similar to green rusts, denoted as Fe$_x$O$_y$.GR(CO$_2^-$)), having both structures. Such intermediate compounds are identified in the corroding specimens in this study, exhibiting granularly-porous or layered deposits. These deposits are most probably Fe$_3$O$_4$.GR(CO$_2^-$), (which forms in the conversion process of Fe(OH)$_2$ to Fe$_3$O$_4$ or γ-FeOOH), being composed of Fe(OH)$_2$:Fe(OH)$_3$ with intercalated CO$_2^-$, also reported by [46].

In conditions of relatively poor oxygen supply (as in reinforced concrete), the oxidation of the intermediate compounds proceeds slowly, hence Fe$_3$O$_4$ can be directly formed, which explains the expected (and identified) higher amounts of magnetite in the protected specimens in this study (protection was applied at 120 days of age, when corrosion was in an advanced stage already). In case of more rapid oxidation (as in the corroding specimens), the structural re-arrangement is not following the formation of Fe$_3$O$_4$, but formation of γ-FeOOH via amorphous oxyhydroxides (path 2). Similar mechanisms for neutral and alkaline solutions, account for the formation of Fe$_3$O$_4$ and γ-FeOOH from FeOH$^+$ (paths 3a to 3c), with predominant formation of Fe$_3$O$_4$ for the protected specimens (thermodynamically and CP favored) and γ-FeOOH formation in the corroding specimens. It is also possible for the final γ-FeOOH to precipitate directly by oxidation of ferrous solutions i.e. in conditions of enriched of Fe$^{2+}$ pore solution in the vicinity of the steel reinforcement in corroding conditions, accompanied by acidification due to passivity breakdown on the anodic sites (path 3c). α-FeOOH and amorphous ferric oxyhydroxides can be found as precipitates from Fe$^{2+}$ (direct transformation from Fe(OH)$_3$) in strongly basic solutions, as in the systems under study (path 4 and 4a). Indeed in all types of specimens, α-FeOOH is present, in much lower amounts and crystallinity though for the protected specimens, compared to corroding
specimens. In addition, possible formation of α-FeOOH is favored by the high solubility of the ferrous hydroxo-complex Fe(OH)$_3$(HFeO$_2$), the latter being dominant in the pH region 12 – 14 along with electrode potential range more cathodic than -1V vs SCE (as recorded in CP applications). The Fe(OH)$_3$$_{aq}$, participating in the former transformation (path 4a) is electro neutral and after polymerization to colloidal [Fe(OH)$_3$]$_n$ and in the presence of OH in the pore solution, (OH always available at the steel surface in the protected specimens due to the cathodic reaction), it precipitates to amorphous ferric oxyhydroxide (FeO$_x$(OH)$_{3-2x}$), which converts to α-FeOOH [47,48]. In the presence of chlorides, as in this study, β-FeOOH (akaganeite) can be formed as well by hydrolysis of ferric solutions containing Cl$.\beta$-FeOOH and iron oxy(hydroxy)compounds were found in the corroding specimens and only at earlier stages in the protected specimens.

9.4.3.2 X-ray diffraction analysis
This Chapter investigates the difference in chemical composition and morphological aspects of corrosion products between corroding and protected specimens. In addition the comparison among the protected specimens (under pulse CP and conventional CP) aims at revealing the beneficial effects of the pulse technique in terms of favorable transformations of product layers on the steel surface. The peak intensity in the XRD diffractograms is generally corresponding to the amount of specific crystalline corrosion products, thus rendering possible a qualitative comparison between different specimens. The common products on the steel surface, in the conditions under study, include iron oxides, iron (oxy)hydroxides and oxy(hydroxy)chlorides in the presence of chlorides. Wustite (FeO), Hematite (Fe$_2$O$_3$), Magnetite/Maghemite (Fe$_3$O$_4$) are categorized in the group of oxides, while the iron oxyhydroxides vary in crystal structure ($\alpha$-, $\beta$-, $\gamma$-, $\delta$-FeOOH) or in composition in the case of akaganeite (Fe$_3$$^+$$^{}$OOHCl). Goethite ($\alpha$-FeOOH) and Lepidocrocite ($\gamma$-FeOOH) are prominent corrosion products in rust layers, akaganeite has been identified only in layers formed through corrosion of steel in chloride environment (as in the present study). These products are present in both corroding and protected specimens, however CP is expected to induce changes in proportions and morphology of the product layers.

Fig. 9.17 shows the XRD patterns (using CuKα radiation) for corroding (IIIN, Fig. 9.17a) and protected specimens (pulse CP (pDCVII middle) and conventional CP (DCVI-bottom)). In general the XRD pattern for the corroding specimen (IIIN, Fig. 9.17a) reveals sharper peaks for low valent oxides (e.g. wustite –W) and shallower peaks for magnetite (MG). In addition, akaganeite (A) is identified mainly in the corroding specimens (characteristic peak at 20 = 56°). Contributions of Quartz - Q (SiO$_2$), Portlandite –P(CaOH$_2$) and Calcite/Aragonite – C/Ar (CaCO$_3$) were detected along with the iron oxides and hydroxides. Quartz (Q) is corresponding to sand grains; Portlandite (P) is both derived from relicts from the cement paste or from the Ca-rich layer adhered to the steel surface. The former case is, valid mostly for the corroding specimen as the P peaks are relatively shallow. The latter case of a Ca-rich layer more adhered to the steel surface is valid for the protected specimens, particularly for pulse CP (middle pattern) as the portlandite peaks are much sharper (e.g. the peaks at 20 = 34.2° and 46.5°). CO$_2$ is obviously
contributing to the products formation as the peaks at 20 29.17° (and 20 43° partly overlapping with the magnetite peak) are present in all specimens. The CO₂ penetration seems however to have been more pronounced in the corroding specimen (IIIN) as supported by the additional peaks at 20 45.6° for Aragonite and 20 54° for Siderite. The siderite peak is overlapping with a shallow peak for akaganeite, leading to a multi-peak pattern in the range of 20 54° to 54.6° for the corroding specimen.

The main characteristic differences in the XRD patterns for the three specimens are:
1. The patterns for the protected specimens (Fig. 9.17b,c) present more magnetite (MG, MH), corresponding to peaks 20 35.5°, 43°, 57°, 62.5° and 67° respectively.
2. Compared to the protected specimens, the corroding specimen (Fig. 9.17a) shows relatively high amount of wustite (W) at 20 42°, presence of lepidocrocite (L) and goethite (G) at 20 36.5° (overlapping partly with magnetite) and a characteristic peak for akaganeite (20 56°). Siderite and aragonite (S, Ar) are present in the corroding specimen, which along with L, G and A are barely detected in the protected specimens.
3. The proportions of high valent oxides, particularly magnetite for the protected specimens are higher. Compared to conventional CP, the specimens under pulse CP show favorable composition of the product layers, evidenced by the relatively sharper peaks for magnetite, in addition to the
absence of a distinguished peak for goethite at 20 37° and sharper peaks for portlandite at 20 34.2° and 20 46.5°.

Hence, the pulse CP brings about favorable modifications of the corrosion products in terms of higher amounts of protective Fe₃O₄ adhering to the steel surface, which along with the Ca-rich layer (evidenced by adhered portlandite) and oxy(hydroxy) chlorides, non detectable by XRD, denotes for better efficiency, compared to the conventional CP.

9.4.3.3 X-ray photoelectron spectroscopy
The XPS analysis supports the findings from XRD in terms of amounts and composition of corrosion products. The XPS spectra are presented on Fig. 9.18, the identified compounds are summarized in Table 9.3. The fitting of O1s, Ca2p and C1s spectra revealed the presence of CaCO₃ in all specimens. Iron oxyhydroxides and iron oxides are present in different amounts as well, the former enriching the product layers in corroding specimens and conventionally protected specimens (IIIN and VIDC), the latter (the iron oxides) more pronounced in specimens under pulse CP (VIIpDC).

The most intensive peak for Fe is the one for the corroding specimen, shifted toward lower binding energy, corresponding to Fe²⁺ in FeO at 709.6 eV, while for the protected specimens, the corresponding peaks are at 710.2 eV for Fe₂O₃ or α-Fe₂O₃ which is consistent with the observations according the O1s spectrum. There is a high energy broadening of the O1s spectrum for the corroding specimen (IIIN), which can be attributed to higher chloride concentration and denoted to bound water on the surface layer. Consequently, the formation of more hydrated iron compounds is more likely for the corroding specimen, hence the amount of iron oxyhydroxides (FeOOH) is higher, as identified by XRD. Such distribution is also reported by [52] for similar systems, where the presence of chlorides results in thicker films in which the contents of FeOOH and water tend to increase. The binding energy of 531.87 eV for the corroding specimen (Fig. 9.17a) is attributed to OH-M bonds, while binding energies 530.26 eV and 530.46 eV for the protected specimens (pulse CP and CP respectively) are attributed to O-M bonds. Hence the presence of Fe₂O₃ and Fe₃O₄ in protected specimens is more pronounced.

The Fe2p spectra (Fig. 9.17e) reveals the following: for corroding specimen (IIIN), binding energy 709.3 eV and 709.6 eV correspond to FeO and Fe₂O₃ respectively; for the protected specimens, binding energy 710.2 eV and 710.4 eV correspond to Fe₂O₃ and 712 eV to FeOOH. Fe₂O₃ is most likely more pronounced in specimen under pulse CP (higher intensity of the peak at the relative binding energy – VIIpDC), while FeOOH is most likely in higher amounts in the corroding specimen and the protected specimen VIDC as they depict wider peaks, with larger surface area at this relevant binding energy (712 eV). The oxidation states of iron could correspond to a Fe₂O₃ or to a mixture of FeO and γ-Fe₂O₃. As Fe₂O₃ (an inverse spinel) is structurally similar to the mixture of FeO and γ-Fe₂O₃ [53], no difference between the two oxides can be measured with XPS [54]. However, the broadening of the Fe2p peaks for both protected specimens towards binding energy of 715 eV can be interpreted as an indication of the change in relative concentration of the Fe³⁺ and Fe²⁺ ions in the Fe₂O₃ structure.
Fig. 9.17 XPS spectrums O1s (a), Ca2p (b), C1s (c), Si2p (d) Fe2p (e), and for corroding (IIIN), pulse CP (VIIpDC) and conventional CP (VIDC) specimens, using AlKα X-ray source (excitation energy $h\nu=1486.6$ eV).

Table 9.3 Compounds according Fe2p, O1s, Ca2p and C1s spectra and relevant binding energy.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fe (2p)</th>
<th>O (1s)</th>
<th>Ca (2p)</th>
<th>C (1s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSn</td>
<td>707.5</td>
<td>528.7</td>
<td>344.8</td>
<td>FeCO3</td>
</tr>
<tr>
<td>Fe3O4</td>
<td>708.1,708.2</td>
<td>529.1</td>
<td>CaO</td>
<td>346.1</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>709</td>
<td>529.4</td>
<td>Ca(OH)2</td>
<td>346.7</td>
</tr>
<tr>
<td>FeO</td>
<td>709.3-709.6</td>
<td>529.5-529</td>
<td>CaCO3</td>
<td>346.7</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>709.6,709.9</td>
<td>529.7</td>
<td>CaCO3</td>
<td>346.8</td>
</tr>
<tr>
<td>Fe3O4</td>
<td>710.2-710.4</td>
<td>529.8</td>
<td>CaSO4</td>
<td>347.04</td>
</tr>
<tr>
<td>FeO2</td>
<td>710.3</td>
<td>530.1</td>
<td>CaCO2</td>
<td>347.8</td>
</tr>
<tr>
<td>FeCO3</td>
<td>710.4</td>
<td>531.2</td>
<td>Ca(OH)2</td>
<td>351.8</td>
</tr>
<tr>
<td>FeOOH</td>
<td>710.7</td>
<td>531.3</td>
<td>CaO</td>
<td>350.9</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>710.8</td>
<td>531.4</td>
<td>Ca(OH)2</td>
<td>351.8</td>
</tr>
<tr>
<td>FeO2</td>
<td>710.9</td>
<td>531.5</td>
<td>CaO</td>
<td>350.9</td>
</tr>
<tr>
<td>FeOOH</td>
<td>724.3</td>
<td>531.7</td>
<td>FeOOH</td>
<td>351.8</td>
</tr>
</tbody>
</table>
9.4.3.4 Morphological and microstructural observations of the product layers on the steel surface (specimens after 270 days of conditioning)

SEM imaging was employed for evaluating the morphology of product layers and their distribution in the vicinity of the steel/cement paste interface (the immediately adjacent layers were discussed in Section 9.3.2. above). The investigations were performed on cross sections of the specimens, which visualize the characteristic changes relevant to bond strength and mechanical properties respectively. Longitudinal sections of the steel surface and the corresponding “steel prints” on the cement paste were investigated as well. The analysis was coupled with energy dispersive X-ray (EDAX) for evaluation of the chemical composition of corrosion and cement hydration products from the steel/paste interface into the bulk matrix.

Fig. 9.18 Cross section images of the steel/cement paste interface in corroding specimen ((a), at 250x) and protected specimen ((b) 200x) in BSE mode. The white bright regions represent the steel surface.

Fig. 9.18 presents the cross section of the steel/cement paste interface of the corroding and protected specimens. The significant corrosion attack on the steel surface in the corroding specimen (Fig. 9.18a) is clearly visible along with micro-cracking of the cement paste.

Fig. 9.19 Higher magnification (2000x) of the steel/cement paste interface in corroding (a) and protected specimens (b), revealing the significant bond strength degradation due to corrosion products penetration into the bulk paste (a) and calcium-rich layer, adhered to the steel surface in the protected specimen (b).
The microcracking is a result from the volume expansion of the corrosion products which at first occupy the restricted space around the steel bar, fill in cracks and voids and penetrate further into the bulk material. In contrast, the protected specimen presents a compact steel/paste interface (Fig. 9.18b), with no visible significant damage, although CP was applied at 120 days of age i.e. after corrosion was certainly initiated on the steel surface taking into consideration the extreme environmental conditions. The corrosion process on the steel surface of the protected specimens was obviously arrested and no further growth of corrosion products occurred, resulting in a dense layer, enriched in calcium (Fig. 9.19b), in contrast to the cracks and voids as consequence from corrosion products growth and further penetration into the bulk material, as observed in the corroding specimens at the same age (Fig. 9.19a).

Longitudinal sections of corroding and protected specimens (steel surface) are presented in Fig. 9.20. The severe corrosion damages on the steel surface of the corroding specimen are evident (Fig. 9.20a), whereas the steel surface of the protected specimens (Fig. 9.20b) is comparatively uniform.

![Fig. 9.20](image_url)

**Fig. 9.20** Longitudinal sections of the steel surface in corroding (a), pulse CP protected (b) and conventional CP protected (c) specimens – overview.

Table 9.4 Summarized data from EDAX analysis of the corrosion products, depicted on the micrographs (the w.% do not equal 100% as the table contains only compounds, relevant to the discussion).

<table>
<thead>
<tr>
<th>Fig. No.</th>
<th>Products</th>
<th>Composition (most relevant compounds), w.%</th>
<th>Cl₂O</th>
<th>FeO₃</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig.9</td>
<td>Lepidocrocite [γ-FeOOH]</td>
<td>0.67</td>
<td>77.46</td>
<td>12.29</td>
<td></td>
</tr>
<tr>
<td>Fig.10 (a)</td>
<td>Akaganite [Fe²⁺(O,OH,Cl)]</td>
<td>3.56</td>
<td>75.18</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Fig.12 (b)</td>
<td>Goethite (α-FeOOH)</td>
<td>0.60</td>
<td>75.09</td>
<td>4.21</td>
<td></td>
</tr>
<tr>
<td>Fig.13 (flat regions)</td>
<td>Magnetite (Fe₃O₄)</td>
<td>0.21</td>
<td>83.11</td>
<td>2.57</td>
<td></td>
</tr>
<tr>
<td>Fig.14 (&quot;pit&quot;) Corroding sample</td>
<td>Inner product</td>
<td>1.02</td>
<td>66.29</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Outer layer (pit wall)</td>
<td>1.15</td>
<td>62.89</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Adjacent flat (carbonated layer)</td>
<td>0.86</td>
<td>70.46</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(32.4%CO₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fig.14 (&quot;pit&quot;) Protected sample</td>
<td>Inner product</td>
<td>0.11</td>
<td>41.67</td>
<td>6.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Outer adjacent layer (Magnetite)</td>
<td>0.20</td>
<td>77.97</td>
<td>2.63</td>
<td></td>
</tr>
</tbody>
</table>
Comparing specimens under pulse CP (Fig. 9.20b) and specimens under conventional CP (Fig. 9.20c) it is seen that for the specimen under pulse CP a more adherent layer of cement paste (enriched in calcium) covers the steel surface. The observation is consistent with the higher amounts of portlandite, detected by XRD analysis. Of course the distribution of calcium-rich layers (e.g. CaO and Ca(OH)$_2$) is not uniform, however, cement paste layers more adhered to the steel surface mean lower amount of corrosion products which normally increase the bond degradation process.

As mentioned, the CP was expected to bring about changes in crystallinity and morphology of product layers on the steel surface. The findings from the XRD and XPS analysis were confirmed with microscopical observations of these layers, revealing higher amounts and crystallinity of the corrosion products in corroding specimens, compared to protected specimens, both at same age of 270 days. The observations are supported by energy dispersive X-ray analysis, results of the latter for the most relevant compounds are summarized in Table 9.4.

Fig. 9.21 presents layers of lepidocrocite ($\gamma$-FeOOH) in the corroding specimen (a) and the protected specimen (pulse CP) (b). Fig. 9.22(a) presents the needle-like morphology of akaganeite, identified in the corroding specimen only. The presence of akaganeite supports the hypothesis for high salinity in the corroding specimens as it is found only in chloride containing environments [49-51].

Akaganeite is mainly responsible for micro-cracking in reinforced concrete as it is less adherent and not accommodating in rust layers [49], thus impeding the formation of a film with good protective properties. It tends to grow in the weak zones of the paste/gravel or the steel/paste interfaces (Fig. 9.22b), which along with its typical needle like structure additionally promotes microcracking. The microstrutural observations are supported by the XRD analysis with the characteristic pick for akaganeite at 20 56°, corresponding to planer distance d=1.64 Å.
Additional micrographs of the hereby discussed products (in terms of morphology and higher crystallinity of akaganeite, lepidocrocite and goethite in corroding specimens) and product layer distribution for all investigated conditions, but at 460 days of age are given in Appendix IV.

Fig. 9.22 Needle like morphology of akaganeite (a) in the corroded specimen, growing preferentially in voids or weak zones, as cement paste/aggregate, thus causing significant de-bonding and microcracking (b).

Along with the formation of certain corrosion products as consequence of the presence of chlorides, the carbonate compounds contribute to the overall process of product layers formation, especially in the corroding specimens. The findings from XRD and XPS analysis were supported by morphological observations. Fig. 9.23 presents carbonate containing compounds on the steel surface of a corroding specimen (a) and on a "print" in the cement paste adjacent to the re-bar (b). Fig. 9.23(a) presents variety of corrosion products on the steel surface, depicting a large formation of siderite (left side of the image, zoomed region incorporated in the micrograph), along with colonies of lepidocrocite and goethite (Fig. 9.23(a) – middle zone). The different morphology, presented on Fig. 9.23(b) is attributed to the higher chloride concentration in the adjacent paste and the formation of complex compounds with the calcium containing cement.

Fig. 9.23 Steel surface morphology of corroding specimen (a), revealing globular shape of siderite (zoomed area) and intermediate, carbonate containing compounds, deposited on the cement paste in the vicinity of the steel surface in the corroding specimen (b).
Goethite was expected to be present in both corroding and protected specimens with more significant formations in the corroding specimens. A formation of goethite (most probably mixed with lepidocrocite) is presented on Fig. 9.24b (the right side of the image), depicting needles growing in globular (“flowery”) forms. The layer of mixed oxyhydroxides is adjacent to a large local damage on the steel surface, filled in with amorphous layer of most likely intermediate compounds. Figure 9.24a) presents the formation of low crystalline goethite in the protected specimen, showing the typical globular, but whiskery and finer structure, compared to the corroding specimen. The formation of the product layer, adherent to the steel surface, comprises at least 2 layers (as already introduced above). In the protected specimens, the inner layer contains Fe$^{2+}$ and Fe$^{3+}$, forming magnetite (as evidence by XRD and XPS). The outer layer will contain mainly Fe$^{3+}$ and will have a more porous structure and poor conductivity. This hypothesis is evidenced by the poorly crystalline goethite in the protected specimen (Fig. 9.24a). For the corroding specimens, the crystallinity of lepidocrocite (Fig. 9.21a) and goethite (Fig. 9.24b) is higher.

Another significant difference in the morphology of product layers in protected and corroding specimens is the appearance of the so called “inner” layer, composed from Fe$_3$O$_4$. Figure 9.25 presents magnetite deposits in protected (a) and corroding specimens (b). The images were taken on longitudinal sections of the adherent to the steel bar concrete layer, on a “print” from the steel surface in the cement paste i.e. the top layer is the one adhering to the steel (marked area). The
magnetite layer in the protected specimen is far more compact (Fig. 9.25a), while the product layer in the corroding specimens is rough from the steel-side and “spongy” in the direction of the paste. The former feature would denote for lower protective properties, the latter will favor restructuring and conversion of these layers in case of changed environment.

Certain product morphology is observed on the surface of the corroding specimens in the regions of localized corrosion. Fig. 9.26a) shows local corrosion damage, grown on a layer enriched in carbonates (plate morphology on the right side of the image). The centre of the figure depicts the growth of corrosion products (most likely akaganeite and lepidocrocite) outwards of the formation, surrounded by a perpendicularly grown amorphous layer of oxy(hydroxy)chlorides, initially formed on the steel surface. In contrast, such local damages in the protected specimens reveal completely different morphology and composition of the products, filling in the “pits” (Fig. 9.26b). Local disruptions of the product layers in the protected specimens were expected as cathodic protection was applied at 120 days of age, however as seen from Fig. 9.26b), these local areas are significantly smaller, are filled in with iron (oxy)hydroxides with CaO contributions (Table 9.4), there is no crystalline product growth as in the corroding specimen, hence due to the changed cement chemistry as consequence from the cathodic current, these local areas in the protected specimens are “healed”. With prolonged CP application (at the stage of 460 days) a well adhered, Ca-rich layer, deposits on the steel surface, as evidenced by XRD and XPS investigations (Chapter 10) and EDX and ESEM observations (Appendix V).

Finally, a comparison of crystallinity of corrosion products in corroding, protected (pulse CP) and protected (conventional CP) is presented in Fig. 9.27. It is obvious that the crystallinity of corrosion products (namely nested lepidocrocite and goethite in the relatively flat layers of magnetite) for the protected specimens is much lower in the specimen under pulse CP (Fig. 9.27a, Appendix V), compared to the conventionally protected specimen (Fig. 9.27b). Of course, the crystallinity of the same products in the corroding specimen is much higher (crystal length of at least 12 μm -Fig. 9.27c). As supported by the XRD and XPS analysis, the specimen under pulse CP presents higher amounts of relatively flat magnetite. Small residues (circled regions Fig.
9.27a) of iron-(oxy)hydroxides (crystal length about 2 to 5 µm) are detected nested in the adhered magnetite layers, while the specimens under conventional CP are characterized by higher amounts of (oxy)hydroxides with higher crystallinity (crystal length about 10 µm – Fig. 9.27b). The different crystallinity, morphology and distribution is denoted to the more favourable cement chemistry under pulse CP conditions, as supported by EDAX analysis as well, which will be presented in what follows.

9.4.3.4 X-ray local area (spot) analysis from the steel/paste interface into the bulk matrix
As aforementioned EDAX analysis was performed locally for the different corrosion products on the steel surface (previously presented in Section 9.3.2), as well as those deposited in the cement paste (subject to this Section) for all specimens. The EDAX analysis was performed as “spot” analysis on cross sections, using accelerated voltage of 20 eV at 500x magnification, in radial direction from the steel bar (starting at the edge of the steel surface as distance “0 µm” in direction the edge of the specimen up to distance 5000 µm away from the steel surface). The aim was to investigate the change in composition of the products, penetrating the bulk matrix (in case of corroding specimens) and the change in ion concentrations (of main interest chlorides and alkali) for the protected specimens. In the former case, information for how far from the steel surface corrosion products are spreading into the bulk and consequently the extent of volume expansion and microcracking can be obtained. In the latter case, the efficiency of CP in terms of
chloride withdrawal and alkali ion accumulation in the vicinity of the steel surface can be estimated.

Fig. 9.28 Mounted ESEM images (cross section) of corroding specimen, depicting the penetration of corrosion products into the bulk concrete matrix up to ~2000 µm from the steel surface (a); scheme (bottom of (a)) for the spot analysis and summarized data for ion concentrations (up to 5000 µm from the steel surface into the bulk material) (b).
Figure 9.28a) presents a schematic draw for the spot-analysis around the steel bar, along with mounted micrographs (up to 2000 µm only are presented, starting from the steel surface in direction of the bulk material) for the corroding specimen (mounted micrographs for specimens from all investigated conditions are given in Appendix III). Figure 9.28b) presents the derived information for ion concentrations in w% (summarized trends, up to 5000 µm from the steel surface into the bulk matrix). As seen from Fig. 9.28a), the corrosion products have penetrated into the bulk matrix, occupying at first empty space (like pores or voids), preferentially depositing around the weakest zones (the paste/aggregates interfaces) and causing significant bond degradation as well (the black area around the steel surface). The plots (Fig. 9.28b), reveal higher amounts of iron and chloride ions close to the steel surface and up to about 1600 µm. From this point further into the bulk the iron concentration is decreasing and alkali ions concentration increasing, i.e. accumulation of corrosion products is reduced. Oxygen distribution is more or less uniform along the whole tested area and calcium is increasing in direction of the bulk.

The same analysis (as presented above for the corroding specimen) was performed for the protected specimens, with main interest distribution of chloride and alkali concentrations around the steel bars. As seen from the plots on Fig. 9.29 (representing summarized trends), the chloride concentration in the immediate vicinity of the steel surface is lowest in the case of pulse CP and remains lower up to the end point of the analysis. Calcium concentration in the same areas for the pulse CP is lower than the conventional protection, but higher than the corroding specimen. Hence, the pulse CP promotes chloride transport away from the steel surface and thus renders favorable changes of the cement chemistry in the vicinity of the reinforcement (some additional evidences for the secondary beneficial effects of CP, and pulse CP in particular, are given in Appendix V, while some side effects in terms of bulk matrix microstructure and steel/cement paste interface are given in Appendix VI).

Fig. 9.29 Chloride and calcium concentrations around the steel bars of corroding and protected specimens in w%, derived by EDAX spot analysis, performed from 0 to 5000 µm away from the steel surface.
9.4 CONCLUSIONS

This Chapter aimed to provide a fundamental approach to understanding the principles of CP in terms of performance and efficiency of both investigated regimes (conventional and pulse) in comparison to corroding and reference conditions. The applicability of electrochemical measurements, namely EIS, PDP and PR for reinforced concrete not only with regard to corroding and non-corroding conditions but also in case of cathodic protection were discussed. Along with deriving polarization resistance values for the steel surface, EIS in concrete was found to be a useful technique for accurately describing the electrical properties of the bulk matrix and additionally gives information for the product layers formed on the steel surface in the different technical conditions, data readily applicable to modeling approaches in terms of mechanical behavior of such systems.

The effectiveness of CP, especially pulse CP, was additionally proven by electrochemical measurements in simulated pore solution i.e. in cement extract solution, revealing best performance (lower corrosion current density) of the steel surface, previously maintained under pulse CP conditions, compared to corroding and conventional CP.

The interpretation of the obtained corrosion parameters was found to be not straightforward, but related to the properties of the product layers, formed on the steel surface in the different conditions. The investigation revealed the close dependence of cement chemistry and the formation, conversion, amounts, morphology and crystallinity of the product layers on the steel surface in reinforced concrete systems. The product layer in corroding specimens is a combination of mainly low valent oxides and iron-oxy (hydroxy)chlorides, exhibits rough morphology and higher crystallinity. Cathodic protection reduces salinity around the previously corroded steel bars, hence the product layers are more uniform and compact, exhibit lower crystallinity and are composed predominantly of high valent iron oxides, consequently a more adherent and protective layer is formed. The transformation phenomena are found to be more apparent under pulse CP conditions, hence the pulse regime is able to arrest corrosion as efficient as the conventional CP technique on one hand, and is more favorable for the steel surface and cement chemistry in terms of morphology and microstructure on the other. The combination of methods reveals the fundamentals for cathodic protection effectiveness, which is normally evaluated according to empirical criteria only and additionally proves the efficiency of the introduced cost effective pulse CP as alternative of the conventional techniques.

References:

CHAPTER 10
THE EFFECTIVE PERFORMANCE OF PULSE CP, EVIDENCED BY MEASUREMENTS' REPRODUCIBILITY IN CONCRETE AND SUPPORTED BY EVALUATION OF THE STEEL OXIDATION/REDUCTION BEHAVIOR IN MODEL SOLUTIONS

10.1 INTRODUCTION

One of the main goals of this thesis was to define a new or improved method for corrosion protection in reinforced concrete. So as to claim reliability of the collected data, the research on an improved corrosion protection technique should be performed in comparison with non-protected conditions on one hand and with conventional protection techniques on the other, therefore all investigations in the frame of the thesis were performed in this manner. Regarding the former case, protected specimens were compared to corroding specimens in terms of electrical parameters, electrochemical behavior and microstructural and morphological observations of corrosion and hydration products (i.e. both the embedded steel and the bulk cement-based matrix were studied). The latter case of comparing the performance of the improved pulse CP technique to conventional CP regimes was studied in plain concrete, by simulating CP model regimes and in reinforced concrete, using variety of current densities for both conventional and pulse CP application. The presented results and discussions in the previous Chapters were reproducible with the time of the relevant investigations, generally comprising stages of 210 to 270 days of conditioning. To this end, the aims of Chapter 10 are to show the effective performance of the introduced pulse CP technique in reinforced concrete, but already presenting the whole period of the implemented tests (460 days) in comparison with earlier stages, as well as with various CP current densities. Additionally, the discussion in this chapter aims to provide supporting evidence for the better performance of pulse CP by evaluation of the oxidation/reduction behavior of the pre-conditioned in concrete steel but in model solutions.

10.2 TECHNICAL BACKGROUND

The understanding of corrosion and CP in reinforced concrete lies in understanding electrochemical principles. The assessment of the condition of steel re-bars in concrete in terms of time to initiate corrosion in aggressive environments, the level of corrosion damage or the evaluation of the effectiveness of protection techniques is usually related to the estimation of corrosion rates i.e. to determination of the electrochemical parameters of the steel reinforcement. The chloride-induced corrosion process on steel reinforcement has been largely studied in concrete and in simulated pore solutions by using electrochemical methods [1-21]. The performance of CP protection techniques however, is generally determined according: empirical criteria only, according criteria, established in standards for CP application (e.g. ASTM C876 and NACE RP0290-2000 (for half-cell mapping and polarization decay), or BS EN 12696 for CP in...
Chapter 10

reinforced concrete) and more recently, the performance of CP applications has been studied, using some electrochemical techniques as polarization resistance or impedance spectroscopy [22 - 24].

As previously discussed in Chapter 4, different approaches hold for the performance of the electrochemical measurements and their applicability to reinforced cement-based materials, including possible errors, occurring in such systems when measuring corrosion parameters [7, 13, 16 -20]. Therefore the applicability of electrochemical techniques, especially in systems like reinforced cement-based materials, being relatively more complex [25], are subject to certain limitations, as already reported and discussed in numerous works [13, 16, 17, 19, 20, 26-30]. The reliability of electrochemical techniques has been recently discussed in [21], was also experimented evaluated in the frame of this research (Chapters 4 and 9).

Hence, although the corrosion behaviour of steel re-bars is well determined in cement-based materials, there are a lot of works in simulated pore solutions, or simply alkaline solutions, aiming to characterise the steel passivation/depassivation performance in such medium and to relate these research outcomes to the behavior of steel in concrete. Investigations on steel passivation in model solutions (e.g NaOH or Ca(OH)₂) are considered to be very close to the real conditions of steel passivation in concrete [31-33], other research outcomes [34, 35] show that a more resistant layer is formed on the steel surface in cement extract solutions, due to its distinctive composition, higher homogeneity, thickness and porosity. As also reported in [36-38], investigations in cement extract solution or cement layers directly applied on the steel surface, as environmental medium, are far more representative and close to the behavior of steel in concrete. However, anodically grown films are found to be significantly different, compared to those grown in natural conditions [34, 39]. The differences in appearance, properties and composition of product layers, formed on the steel surface in conditions of corrosion and protection, determine the electrochemical response of the reinforcing steel, hence significantly contribute in the evaluation of results, obtained for corrosion behavior or CP performance in reinforced concrete. CP contributes to a higher complexity of the mechanisms of product layers formation and stability in such systems.

In the frame of the research project, the fundamental principles of chloride induced corrosion and cathodic protection in terms of distribution, morphology, crystallinity of corrosion and hydration products, as well as the microstructural changes at the steel/cement paste interface and in the bulk cement-based material were initially investigated in mortar specimens and discussed in Chapters 3 to 6. Wet chemical analysis (according ASTM1218 and ASTM1152) for chloride and alkali concentrations in the bulk material and in the immediate vicinity of the steel re-bars was performed for all studied conditions. The influence of both CP current regimes i.e. the alterations which CP current induces on the bulk pore structure and physico-chemical properties of hydration products were investigated as well and presented in Chapter 7. Further, electrochemical response in all conditions (corrosion, protection and reference) was derived from electrochemical measurements in reinforced concrete (Chapters 8 and 9). All observations were also supported by the aforementioned conventional and generally applied in practice half-cell potential mapping and
polarization decay (Chapter 8). In other words, both regimes of protection were evaluated and pulse CP was found beneficial in all aspects.

It was found out however, that the electrochemical measurements, although readily applicable for evaluating electrochemical behavior of the steel surface not only for corroding or passive state, but also in conditions of cathodic protection, exert some discrepancies in the obtained parameters. For example polarization resistance ($R_p$) values, derived from electrochemical measurements in concrete for corroding specimens, were higher than the $R_p$ values for protected specimens, the latter derived after 24h depolarization of the steel surface, while the same measurements in cement extract solution gave the contrary results (i.e. higher $R_p$ for protected and lower $R_p$ for corroding cells). This latter study was performed after 270 days of conditioning and was presented in Chapter 9.

As previously discussed and based on fundamentals, the measured corrosion current density will be controlled by the kinetics of the electrochemical reactions during the measurement and the diffusion of reactants both towards and away from the electrode. In that case, higher diffusion limitations, as in the corroding specimen, will result in effectively higher $R_p$ values in the time of the measurement and compared to protected specimens, since the product layer in these specimens exhibits very rough morphology and the highest heterogeneity, along with varying thickness of 3 to 12 µm (Chapter 9). Hence, the product layers’ composition, adherence, compactness, solubility, crystallinity, surface area, conductivity (electron, ionic, electrical) etc. are influencing the electrochemical parameters and should be taken into account in such systems.

Thus, the interpretation of derived parameters (like $R_p$) is not straightforward and is related to the properties of the product layers, formed on the steel surface in the different conditions. Additionally, the properties of these layers will be influenced by the chemical alterations in the cement layers, adjacent to the steel surface, with time of corrosion or CP application. As previously discussed in Chapter 8, CP promotes beneficial effects in terms of enhancement of the OH⁻ concentration and reduction of the chloride concentration near the steel surface. The locally elevated concentration of OH⁻ caused by cathodic polarization results in substantial additional deposition of portlandite around the steel, which would be expected to have further beneficial effects in stabilizing the “passivity” of the steel re-bars. Therefore, a comparison of the obtained electrochemical parameters with time of corrosion or CP will elucidate the above mentioned mechanisms of product layers alterations as consequence of corrosion products accumulation or as a result of the beneficial secondary effects of CP application. Furthermore, an additional investigation of the pre-conditioned steel surface in model solutions will give information for the properties of the product layers, formed as consequence from each technical regime. The study in model solutions aims to clarify some fundamental issues, related to the steel surface properties, the application of electrochemical techniques and the derived electrochemical parameters; to finalize the research on already proved pulse CP effectiveness and further to improve the understanding for some fundamental aspects of the pulse CP technique.

To this end, the present Chapter 10 comprises two sections: first the electrochemical behavior of the steel reinforcement in embedded in concrete conditions is discussed, providing information
for the systems response with time of conditioning till the end of the test of 460 days in comparison with earlier stages; second, the surface properties of the pre-conditioned in concrete steel re-bars are discussed for the stage of 460 days and further their electrochemical parameters are investigated in model solution of cement extract, thus providing evidence for effectively working pulse CP regime on one hand and explaining the aforementioned and discussed fundamental issues on the other.

10.3 EXPERIMENTAL

10.3.1 Materials

The discussion in this Chapter 10 concerns two groups of specimens: the reinforced concrete cylinders and steel electrodes from the previously embedded and conditioned in concrete reinforcing steel. Section 10.4.1 below deals with the former group, in particular electrochemical measurements for earlier and the latest stage of the experimental conditioning. Section 10.4.2 deals with the investigation of the latter group in model solution of cement extract, using electrochemical methods and steel surface analysis techniques.

**Reinforced concrete cylinders**: cast from OPC CEM I 32.5 R, water-to-cement ratio 0.6, with dimensions: H=25 cm, D=12 cm, containing embedded construction steel (type FeB500HKN ribbed bars, d=12 mm), used “as received” (no preliminary treatment) for all technical conditions. Corrosion was initiated before applying CP, by maintaining the specimens in a salt spray chamber (SSC using 5% NaCl spray, 25°C to 35°C) for 460 days after curing in fog room conditions (98% RH and 20°C) for 28 days. Additionally, the specimens were immersed in 5% NaCl for the whole period of the SSC conditioning (except for the non-corroding cells, maintained in the same RH and temperature conditions, but immersed in water). Details of the experimental set-up, curing conditions, concrete mixture, chemical composition and constituents of the used cement are given in Chapter 8, Table 8.1.

Four groups of reinforced concrete cylinders are hereby discussed: a freely corroding group (further in the text represented by specimen C), a non-corroding group (represented by specimen R), a group with applied conventional CP (represented by specimens A) and a group with applied pulse CP (specimens B). The specimens from groups A and B comprised certain sub-groups, differing in the starting point for CP application and in the applied CP current density as well: A1 and B1 are CP and pulse CP, applied at 60 days of age, using 5 mA/m² current density; A2 and B2 are CP and pulse CP applied at 150 days of age, using 20 mA/m² current density. C is corroding and R – reference specimen (conventional monitoring techniques, applied to these groups of specimens were presented in Chapter 8).

**Steel electrodes**: cylindrical parts (h=15 mm, d=12 mm) from the previously (for 460 days) embedded and conditioned in concrete re-bars (the conditioning regimes in embedded conditions are as aforementioned and presented in Chapter 8), comprising three main groups: samples from a previously corroding group reinforced cylinders (denoted as C), samples from a non-corroding (or
The effective performance of pulse CP. Steel behavior in model solution

reference) group reinforced cylinders (denoted as R) and samples from a previously protected group cylinders (denoted as P). Group P comprises 4 subgroups: P1a and P2a are specimens which were previously under CP and pulse CP, using current density of 5 mA/m² steel surface, applied at 60 days of age (i.e. these are samples from the aforementioned reinforced concrete groups A1 and B1). Groups P1b and P2b are specimens, initially maintained under CP and pulse CP, but using higher current density – 20 mA/m², CP both regimes being applied at 150 days of age (i.e. these are samples from the aforementioned reinforced concrete groups A1 and B1).

The top and bottom cross sections of the steel electrodes were isolated and used as working electrodes in a common 3-electrode cell arrangement; the working electrolyte was cement extract solution of pH 12.6, prepared from ordinary Portland cement OPC CEM I 32.5R (the same cement type, used previously for the concrete mixture). The cement extract was prepared by mixing water and cement (ratio 1:1) for 24h and filtrating the mixture through a glass filter. The solution was stored in closed containers before using, thus avoiding absorption of atmospheric CO₂. Reference electrode was a saturated calomel electrode (SCE), counter electrode was a cylindrical Pt mesh (positioned around the working electrode).

10.3.2 Experimental techniques

Electrochemical measurements (generally as described in the previous Chapters):

For the reinforced concrete: the measurements were performed at open circuit potential (OCP) for all cells (after 24 h depolarization of the reinforcement for the protected specimens i.e. protection current was interrupted before and in the time of the measurement).
- Electrochemical Impedance Spectroscopy (EIS), carried out in the frequency range of 50 KHz to 10 mHz by superimposing an AC voltage of 10 mV;
- Polarization resistance (PR), using external polarization in the range of ±20 mV vs OCP at scan rate 0.16 mV/s;
- Potentio-dynamic polarization (PDP) in the range of -0.15 V to +1.2 V vs OCP at scan rate 0.5 mV/s.

For the steel electrodes: the measurements were performed for all investigated specimens in cement extract solution (CE), pH 12.6, at room temperature and after allowing for OCP stabilization before each measurement (~ 40 min).
- EIS, PR and PDP as described above;
- Cyclic voltammetry (CV) was carried out at 200 mV/s scan rate, starting at -1.6 V and first vertex potential of 0.9 V (SCE).

For all electrochemical measurements the used equipment was EcoChemie Autolab - Potentiostat PGSTAT30, combined with FRA2 module, using GPES and FRA interface.

Chemical analysis (for the reinforced concrete): performed for the cement paste adjacent to the steel surface in each technical condition according ASTM C1218 and ASTM C1152 for free and total chloride concentration and using plasma spectrometry (Inductive Coupled Plasma Spectrometer (ICP-AES) for determination of alkali concentrations.

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Steel surface morphology, composition of product layers (performed for the steel electrodes):
The product layers on the initially corroding, non-corroding and protected steel surfaces were observed using the following techniques: X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray (EDAX) analysis and scanning electron microscopy (SEM).

XRD measurements were performed by scanning representative areas of about 1 cm² (directly on the surface) of the test specimens, using D8 Advance Diffractometer, "Bruker AXS". A VANTEC position sensitive detector (window 6 degr.) was used for detection. Energy source was CoKα (1.789 Å) and the tube settings were 45kV and 35mA.

XPS measurements were carried out using ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the analysis chamber of 5x10⁻10 mbar (during the measurement 1x10⁻8 mbar), using AlKα X-ray source (excitation energy hν=1486.6 eV). The pass energy of the hemispherical analyzer was 20 eV (for Fe 2p – 50 eV), 6 mm slit widths (entrance/exit). The instrumental resolution measured as the full width at a half maximum (FWHM) of the Ag3d₅/₂ photoelectron peak is 1 eV. The energy scale is corrected to the C1s - peak maxima at 285 eV for electrostatic charging. The fitting of the recorded XPS spectra was performed, using a symmetrical Gaussian-Lorentzian curve fitting after Shirley-type subtraction of the background.

SEM and EDAX investigations were performed with environmental SEM, ESEM Philips XL30. The research outcomes for morphology and composition (XRD, XPS and ESEM observations) of the product layers on the steel surface for 460 days of age are consistent with previous observations for 270 days of age (Chapter 9), hence surface morphology and microstructural observations (ESEM) will not be discussed in this Chapter, details can be referred to Chapter 9 and Appendices III-VI.

10.4 RESULTS AND DISCUSSION

10.4.1 Electrochemical measurements in reinforced concrete
This Section deals with RP, PDP and EIS measurements in reinforced concrete (i.e. steel in embedded conditions), presenting the collected data as a comparison of: earlier stages (190, 210, 270 days) with final results for 460 days on one hand and the electrochemical response with respect to different CP current density on the other.

Potentio-dynamic polarization. The previously discussed in Chapter 8 positive shift of OCP with time of CP application (after depolarization), is supported by the observed behavior of the steel reinforcement with external polarization. Fig. 10.1(a) presents polarization curves for all investigated specimens at 460 days of age (A1 and B1 are CP and pulse CP, applied at 60 days of age, using 5 mA/m² current density; A2 and B2 are CP and pulse CP applied at 150 days of age, using 20 mA/m² current density C is corroding and R – reference specimen). The measurements were performed after 24 h depolarization and awaiting for the establishment of a stable OCP of
the steel bars in groups A and B (i.e. 24h before and in the time of all electrochemical measurements there was no CP current flowing through the cells).

As seen from Fig. 10.1(a), the secondary effects of CP in terms of increased pH and less aggressive environment around the steel surface in protected conditions, are reflected by the behavior of the steel electrodes with external polarization. The anodic shift of corrosion potential is more evident for the specimens A2 and B2, previously maintained under higher CP current (consistent with the previous observations for the OCPs after decay measurements, discussed in Chapter 8). Fig. 10.1(b) presents the calculated corrosion current density $I_{corr}$ (after IR drop correction and using Tafel and Butler-Volmer equation fit of the Autolab interface) for all specimens. The $I_{corr}$ values for the reference group R are the lowest, for the rest of the specimens $I_{corr}$ is increasing in the order of: corroding specimen C, specimens A2 and B2 (CP 20 mA/m$^2$), specimens B1 and A1 (5 mA/m$^2$). As previously discussed, the expected lower corrosion current density in the protected specimens (groups A and B), compared to corroding specimens (group C), was not observed. These results are consistent with recorded parameters in parallel cell couples for earlier ages and at different CP regimes (270 days, discussed in Chapter 9) and can be explained on the basis of several possible mechanisms. As mentioned in the previous Chapters, maintaining the steel in protected specimens cathodic during the time of the experiment (460 days, with interruptions of the protection current only in the time of depolarization and electrochemical measurements), suggests a relatively “clean” steel surface in the protected cells, compared to the corroding cells. Thus, any layers formed prior to CP application (which was 60 days for A1 and B1 and 150 days for A2 and B2) would only bear conversions but further oxidation of the steel will not occur in the time of protection. In the time of interrupting the CP, and after depolarization for 24 h, allowing establishment of a steady OCP, the steel gradually slips to a more “active” state (as result of shifting the steel potential from strongly cathodic to natural for the present conditions potential). Taking into consideration the cement chemistry around the re-bars (Fig. 10.2), the chloride concentration still being above the thresholds of 0.15
w.% per dry cement weight [1] at 460 days (higher chloride concentration and carbonates detected at earlier stages, discussed in Chapter 8), in the period of electrochemical measurements, there will be conditions for steel dissolution on isolated locations; the recorded averaged corrosion current density for protected specimens ends up higher, comparing to corroding and non-corroding conditions.

As a second hypothesis, the nature of the product layer, formed on the steel surface (for each technical condition), is significantly contributing to the performance of the systems and influencing the electrochemical response, which was presented in Chapter 9 for 270 days and will be elaborated in Section 10.4.2. below for 460 days of conditioning.

Despite the more significant anodic potential shift, observed for the specimens under conventional CP (groups A) for 460 days of age (Fig. 10.1(a)), the pulse CP is expected to achieve better performance with time and with respect to inducing "open circuit potential passivity" as result of rendering less aggressive environment. The latter is confirmed by the chemical analysis of the cement paste, surrounding the steel reinforcement (Fig. 10.2).

The chloride concentration at 460 days of age in all cells (A1,B1,A2 and B2) is still higher than accepted thresholds (being more than 0.4 w% chlorides per dry cement weight), but specimens B2 (pulse CP) exhibit lower chloride concentration, compared to specimen A2 (CP). Although CP was applied at 150 days for specimens A2 and B2, the pulse CP is obviously more beneficial for chloride withdrawal away from the steel surface in the case of regime, using 20 mA/m\(^2\) current density (group B2). The latter observation is consistent with the results for chloride withdrawal in a regime of 20 mA/m\(^2\), CP applied at 120 days of age, where even better efficiency of the pulse CP was recorded, compared to conventional application (details given in Chapter 9). Finally, the chloride withdrawal, recorded as consequence of CP application using 5 mA/m\(^2\) and applied at 60 days of age gives the best results in terms of lowest chloride concentration around the steel bar. In this regime however, the derived chloride concentration after pulse CP is slightly higher, compared to the corresponding conventional CP. What should be taken into account here, is that a
pulse CP operating at 5 mA/m² actually means effective current density of 2.5 mA/m². Thus, the pulse CP is far more beneficial, since this latter regime, operating at lowest current densities is achieving almost the same results in terms of chloride withdrawal as the corresponding conventional regime (see Fig. 10.2).

Taking into consideration the discussed above “open circuit potential passivity” i.e. shifting of the steel potential to more noble values with time of CP application, it will be expected that the recorded at 460 days of age corrosion current densities for specimens A and B will further decrease with time of protection as consequence of reducing the aggressive ion concentrations around the steel bars. Therefore, although higher corrosion current densities are always recorded for the protected cells, compared to corroding cells, the results do not suggest that CP is not working effectively. So as to evaluate the effects of CP in the protected specimens or the increasing corrosion rate in specimens C, there must be a comparative investigation of electrochemical parameters at different stages in the overall run of the experiment.

The expected decrease of $I_{corr}$ with time of CP application would be as a consequence of the evolution of the steel electrochemical behavior, where the pulse CP would have better performance, compared to conventional CP, taking into consideration the secondary beneficial effects of the pulse regime (as recorded from 190 to 270 and 360 days - Fig. 10.3).

In order to illustrate the above discussed behavior, Fig. 10.3 presents polarization curves for specimens from parallel groups, analogical to the discussed hereby groups A and B, but for earlier stages (190 and 290 days), using CP current density of 20 mA/m² for both the pulse and conventional regime, CP applied at 120 days. As seen from the plot, the anodic shift of corrosion potential, along with a decrease of corrosion current with time is more obvious for the specimen under pulse CP (the anodic shift for pulse CP condition is about 600 mV in anodic direction.
compared to about 70 mV shift for CP conditions). Along with the more significant anodic shift in pulse CP conditions, it should be noted that the pulse CP achieves 4 to 5 times larger anodic shift with time, using twice lower CP current density (both regimes are at 20 mA/m² steel surface, but pulse CP uses 50 % duty cycle, hence the effectively running CP current is 10 mA/m²), hence the pulse CP can be considered as more efficient and moreover cost-effective regime.

The former observations are consistent with the specimens behavior on later stages (the hereby discussed groups A and B). Fig. 10.3(b) depicts a comparison of steel behavior with external polarization for specimen B2 (using pulse CP 20 mA/m²) and specimen A1 (using CP 5 mA/m²). As seen form the plot, the pulse CP regime (B2) again exhibits a significantly larger anodic potential shift with time (from 190 to 360 days of age), compared to specimen A1. If we consider that B1 uses 20 mA/m² CP current density (which is effectively 10 mA/m², being pulse regime at 50 % duty cycle) and A1 uses 5 mA/m² CP current density i.e. the effective current density in B1 is twice larger than in A1, we would expect about twice larger anodic shift in group B2 compared to group A1. The observation however is different from expected (Fig. 10.3b), the anodic shift for group B2 is 4 times (instead of twice) larger than the one for group A1. Taking also into consideration that CP was applied for specimen B2 later than for specimen A1 (150 days for the former and 60 days for the latter case), which means significantly shorter time of protection for specimen B2, here again the pulse CP can be considered more efficient compared to the conventional CP regime.

In contrast to the shift of corrosion potential to more noble values with time for the protected specimens (groups A and B), the corroding specimens (group C), depict increase of corrosion current density with time and shift of the corrosion potential to more cathodic potentials (Fig. 10.4(a) and 10.4(b)).

![Fig. 10.4 Polarization curves for corroding specimen C with time (from 120 to 460 days of age) – (a); Evolution of corrosion current density for specimen C with time, derived from PDP measurements (b) ](image)

After an earlier drop of corrosion current density (Fig. 10.4b) and anodic shift from 120 to 240 days of age (Fig. 10.4a), the corrosion current is increasing with time (up to 460 days of age) and
the corrosion potential shifts cathodically. The observed behavior of the steel reinforcement with external polarization is consistent with investigations using electrochemical impedance spectroscopy, which will be discussed in what follows.

**Electrochemical Impedance Spectroscopy (EIS).** The EIS measurements were performed at certain intervals for all investigated specimens at OCP (after 24 h depolarization and awaiting for stable OCP for the protected cells). As previously discussed in Chapters 4 and 9, EIS is a useful technique for obtaining detailed knowledge of the steel/concrete system as it provides information for both the steel surface (electrochemical parameters) and the concrete bulk matrix (concrete bulk, pore network resistance) [40,41]. Using EIS for the here investigated specimens aimed to evaluate the electrochemical behavior of the steel surface in conditions of corrosion and CP, compare to reference conditions and support the data derived from other techniques (as PDP and PR).

**Fig. 10.5** Equivalent electrical circuit, used for all specimens.

**Fig. 10.6** Comparison of impedance response for reference specimen (R) and corroding specimen (C) at 460 days of age, Nyquist (a) and Bode (b) plots.

The generally derived parameter was polarization resistance ($R_p$), which can be associated with the corrosion process (the anodic oxidation of steel) as well as other electrochemical processes involving corrosion products, thus providing information for the overall reaction rates. Fig. 10.5 presents the equivalent circuit, used for the interpretation and data fitting for each reinforced
concrete specimen. The elements of the equivalent circuit present the following physical meaning: $R_{el+b}$ is the concrete resistance including the contribution of electrolyte resistance, the latter being negligible compared to the concrete resistance. The first time constant $(R_{el+b}, C_{el+b})$ is attributed to the properties of the concrete matrix in terms of pore network; the second time constant $(R_{ct}, C_{ct})$ deals with the electrochemical reaction on the steel surface; the third time constant in the equivalent circuit $(R_{red}, C_{red})$ is attributed to redox processes, taking place in the product layers on the steel surface.

Fig. 10.6 presents the impedance response at 460 days of age for non-corroding (R) and corroding (C) specimens in Nyquist and Bode format. Fig. 10.7 depicts an overlay of the impedance response for the corroding specimen (C) and the protected specimens A1, B1 (CP and pulse CP using 5 mA/m² current density) and A2, B2 (CP and pulse CP using 20 mA/m² current density) at 460 days of age. Summarized data for the best fit parameters are given in Table 10.1.

The high frequency arcs (starting at 50 KHz frequency) for all specimens correspond to the concrete bulk resistance including the contribution of electrolyte resistance. The obtained $(R_{el+b})$ values (Table 10.1) correspond to the overall concrete resistance, for deriving $R_{ct}$ from EIS measurements in reinforced concrete, the low frequency limit of the impedance spectra is generally considered for calculations as reported in [15, 16, 42-45] and hereby used as well.

Fig. 10.6 shows the significant difference of the impedance response for corroding (C) and non-corroding (R) specimens in the low frequency domain, attributed to accelerated corrosion state in the former and passive condition in the latter case. The derived $R_{ct}$ for corroding specimen is significantly lower compared to non-corroding specimen (Table 10.1), corresponding to the interfacial capacitance ($C_{ct}$) values: much higher for corroding specimen (370 µF/cm²) compared to non-corroding specimen (30 µF/cm²). Comparing the impedance response for protected
specimens and corroding specimen (Fig. 10.7), it is obvious that the magnitude of impedance (Fig. 10.7a) is higher for the corroding specimen, the phase angle (Fig. 10.7b) is almost equal to protected specimen B1, but higher than the rest of the specimens.

The used equivalent circuit (Fig. 10.5b) allowed separately deriving charge transfer resistance \(R_{ct}\) and resistance \(R_{red}\), attributed to redox processes in the product layers. Fig. 10.8 presents a correlation of \(R_{ct}/C_f\) and \(R_{red}/C_{red}\) for all specimens at 460 days of age. The values for interfacial capacitance \(C_f\) of the reference specimen R tend towards the values for the capacitance \(C_{red}\) (30 \(\mu\)F/cm\(^2\) and 50 \(\mu\)F/cm\(^2\) respectively), which corresponds to the low rate of oxidation process for this specimen. The significantly higher values of \(C_f\) for all other specimens are consistent with the lower \(R_{ct}\) (Fig. 10.8a) and hence higher corrosion rates will be expected for these specimens. Compared to \(C_f\), the values obtained for \(C_{red}\) of specimens C, A1, B1, A2 and B2 are significantly higher (Fig. 10.8b) and can be only denoted to modifications in the structure of product layers.

Although EIS allows separate characterization of charge transfer and other process, related to the corrosion phenomena, the comparison of the investigated specimens is relevant to describing the overall response and reaction rate of the systems in each technical condition in terms of discussing global \(R_f\) values (this approach is generally used in the thesis). The \(R_f\) values from EIS were calculated using the values for \(R_t\) and \(R_{net}\) (Table 10.1). The \(R_f\) values for the corroding specimen is higher (about 22 kOhm.cm\(^2\)), compared to protected specimens (in the range of 11 to 15 kOhm.cm\(^2\)). The observation is consistent with PDP measurements, where lower corrosion
current density values were recorded for specimen C, compared to protected specimens groups A and B (Fig. 10.1).

Fig. 10.9 Comparison of corrosion current density for the investigated specimens, derived from all performed measurements at 460 days of age

Fig. 10.10 Comparison of impedance response for the reference specimen (R) with time (210 and 460 days of age), Nyquist (a) and Bode (b) plots.

Fig. 10.9 presents a comparison of $I_{corr}$ values, derived from PR, EIS and PDP measurements (values are calculated after IR drop compensations for all methods), showing consistency of obtained results and similar trends for each investigated system, derived from all methods.

Figs. 10.10 to 10.13 present the evolution of impedance response for all investigated specimens with time (for 210 and 460 days of age). The magnitude of impedance and the phase angle (Figs.10.10, 10.12, 10.13) are increasing for all specimens with time except for the corroding specimen C, where the opposite trends are recorded (Fig. 10.11).
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Fig. 10.11 Comparison of impedance response for the corroding specimen (C) with time (210 and 460 days of age), Nyquist (a) and Bode (b) plots.

Fig. 10.12 Comparison of the impedance response for protected specimens (A1 (CP) and B1 (pulse CP), using 5 mA/m²) at 210 and 460 days of age, Nyquist (a) and Bode (b) plots.

The increase in impedance and phase angle for specimens R, A1, B1 and A2,B2 (Figs. 10.10, 10.12, 10.13) is denoted to increasing the protective properties of the passive layer on the steel surface for specimen R and less aggressive environment around the steel bars (as consequence of CP application with time) for the protected specimens (A and B groups), the latter suggesting “healing” effects for the steel surface in protected conditions. The continuous corrosion process in specimen C (although higher $R_p$ and lower $I_{corr}$ values, compared to groups A and B, were recorded at the end of the test and the reasons already previously discussed), cause decrease of impedance and phase angle with time (Fig. 10.11).
The EIS response is consistent with the previously discussed findings from PDP measurements (Figs. 10.3 and 10.4). Summarized trends of $R_p$ values, calculated on basis of EIS measurements with time are presented on Fig. 10.14.

As can be observed (Fig. 10.14), the polarization resistance values for corroding specimen C were higher and still remain highest at 460 days of age, but exhibit a decreasing trend with time. In contrast, the $R_p$ values for the reference R and the protected specimens A1 and B1 tend to increase with time, suggesting increased protective properties of the product layers on the steel surface with time of CP operation.
Relevant to the EIS response in the high frequency domain, which as previously discussed corresponds to the properties of the bulk concrete matrix, for the time period of 210 days to 460 days, there is almost no change in concrete electrical resistance for specimen R (Fig. 10.10). This is expected, since at the age of 210 days and further up to 460 days, the bulk matrix resistance is already not significantly influenced by the factor “cement hydration”, provided that there is no other external influence on the cement chemistry and the pore microstructure (as in the case of R specimen). At this age, the concrete bulk matrix resistance would be influenced more substantially by other factors, as expansion of corrosion products in case of specimens C, chloride binding/de-binding mechanisms, electrical current flow as in case of the protected specimens.

As seen from Fig. 10.11, the concrete bulk resistance increases in the time period of 210 to 460 days of age for the corroding specimen C. The fact is attributed to the influence of NaCl as accelerator of cement hydration [46, 47] and microstructural changes, induced by altered pore structure and pore distribution density, as consequence from the continuous chloride ingress on one hand and modified pore interconnectivity on the other (discussion on these combined effects and phenomena were presented in Chapters 3 and 6). Although concrete resistivity increases with time, the change is not as significant as in the case of protected specimens, since a contributing factor in specimen C is the ease of ion transport through the percolated network of increasing with time number of micro-cracks, formed as a result of volume expansion of corrosion products.

The bulk concrete matrix is less influenced in the time period of 210 to 460 days for specimen B1 (which is pulse CP, using 5 mA/m² steel surface). The rest of the specimens exhibit similar behavior, with a shift towards higher values of bulk matrix resistance. The changed microstructural properties of the protected specimens are influenced to a significant extent from the CP current flow, in addition to the presence of NaCl. As discussed in Chapter 7 for plain concrete prisms, the electrical current flow is significantly contributing to altered microstructural properties, pore network connectivity and pore distribution density, which in turn influences ion transport and CP efficiency. The research on plain concrete revealed that the pulse current is less detrimental to concrete microstructure and beneficial for electrical properties and ion transport mechanisms. A steady current (as normally used in conventional ICCP applications) tends to bring about unfavorable modifications of the material structure both in the bulk (reducing porosity) and in the interfacial transition zones (enlarging the gap at aggregate) to a significant extent, leading to a high level of structural heterogeneity of the materials. Similar observations were recorded in the case of the reinforced concrete specimens, presented in this Chapter and are given in Appendix III.

Summarizing, the above presented comparison of results from electrochemical measurements in concrete at different stages of corrosion or CP, reveals the effective performance of CP, and in particular the pulse CP, with time of application. This effectiveness is mainly denoted to the secondary beneficial effects of CP current in terms of rendering less aggressive environment and favorable chemistry of the cement layers, adjacent to the steel reinforcement. Consequently, with time of application (for example as here investigated from 190 to 460 days) these effects will become more apparent and, evident from the here presented relatively short period of
investigation, the corrosion current density for protected specimens will decrease, while corrosion current density for corroding specimens will increase. In other words, the electrochemical parameters in corroding and protected conditions, measured at one and the same stage of conditioning, might give discrepancy of results and we might end up with higher corrosion rates for protected conditions, which does not mean that CP is not working effectively, but is as a result of the steel/cement paste interfacial interactions or certain properties of the product layers, deposited on the steel surface. So as to properly evaluate the electrochemical phenomena in corroding or protected conditions, a comparison of the parameters derived at different stages within one group of specimens has to be performed and further compared with the other groups, thus we end up with the expected increasing trends for corrosion current density for specimens C and decreasing trends for specimens A and B. Of course, all parameters are influenced by the alterations in cement chemistry on one hand and the properties of the formed product layers on the other, which modify with time and as a consequence from maintaining regimes and will be discussed in the following Section 10.4.2.

10.4.2 Steel surface analysis and electrochemical measurements in model solutions
As previously discussed, the differences in appearance, properties and composition of product layers, formed on the steel surface in conditions of corrosion and protection, determine the electrochemical response of the reinforcing steel, hence significantly contribute in the evaluation of results, obtained for corrosion behavior or CP performance in reinforced concrete systems.
This section deals with investigation of the pre-conditioned in concrete reinforcing steel in cement extract solution, as model concrete pore solution of pH 12.6. The aim was to comparatively investigate the naturally formed (during steel embedment in concrete) surface layers after 460 days of initial conditioning, thus allowing evaluation of the performance of both CP regimes in terms of steel surface oxidation/reduction behavior in model alkaline solutions. (The specimens assignation is given in section “Materials”, the below discussed specimens P1a and P2a, being steel electrodes from specimens A1 and B1, presented in the above section; the specimens P1b and P2b, being steel electrodes from specimens A2 and B2) 

10.4.2.1 Surface analysis – XRD
The peak intensity in the XRD diffractograms is generally corresponding to the amount of specific corrosion products, thus allowing a qualitative comparison between different specimens. Fig.10.15 shows the XRD patterns for corroding (C) specimens and protected specimens (P1a (CP) and P2a (pulse CP)) after 460 days of initial conditioning in concrete (using CoKα radiation). In general the XRD patterns for the corroding specimens reveal sharper peaks for low valent oxides (e.g. wustite –W) and shallower peaks for magnetite (MG). In addition, akaganeite (A) is identified only in the corroding specimens (at 2θ 31.2°), overlapping with the peak for lepidocrocite (L); goethite (G) and hematite (H) are detected at 2θ 39.5°, 41°, 49.1°, 50.5°, 62.5°, 67°,74° are sharper for the protected specimens, in contrast the peaks for wustite at 2θ 42.5°, 49.1°, 72.5° are more pronounced for the corroding specimen. A quantification for the main oxides/hydroxides (FeO, Fe₂O₃, Fe₃O₄ and Ca(OH)₂) is presented in Table 10.2 for specimens C (corroding), P1a (CP) and P2a (pulse CP). The XRD results are
consistent with previous observations for parallel groups of specimens after 270 days of conditioning (Chapter 9) and are also in line with reported results for the composition of the product layers on the steel surface in similar environments [48-51], as well as reported data for the properties of these layers [52, 53]. A layer, enriched in magnetite and hematite, as in the protected specimens (and particularly pulse CP), will have better performance in terms of adherence, compactness and homogeneity, whereas a layer composed from wustite, akaganeite, lepidocrocite (as in the corroding specimens) will have lower protective properties, lower adhesion (especially in the presence of akaganeite) and reduced corrosion resistance.

![X-ray diffraction patterns for corroding specimens (C) and protected specimens P1a (CP) and P2a (pCP), using CoKα radiation: C - calcite, G - goethite, MG - magnetite, L - lepidocrocite, Q - quartz, W - wustite, Ar - aragonite, P - portlandite, A - akaganeite, H - hematite](image)

*Fig. 10.15 X-ray diffraction patterns for corroding specimens (C) and protected specimens P1a (CP) and P2a (pCP), using CoKα radiation: C - calcite, G - goethite, MG - magnetite, L - lepidocrocite, Q - quartz, W - wustite, Ar - aragonite, P - portlandite, A - akaganeite, H - hematite.*

<table>
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<tr>
<th>Specimen</th>
<th>FeO %</th>
<th>Fe₂O₃ %</th>
<th>Fe₃O₄ %</th>
<th>Ca(OH)₂ %</th>
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</thead>
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<td>17.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Specimen P1a (CP)</td>
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<td>1.2</td>
</tr>
<tr>
<td>Specimen P2a (pCP)</td>
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<td>0.1</td>
<td>30.4</td>
<td>2.9</td>
</tr>
</tbody>
</table>

### 10.4.2.2 Surface analysis – XPS

The XPS results for the here discussed specimens (stage 460 days) are consistent with the previous XPS investigations for earlier stages of 270 days conditioning (Chapter 9), hence will not be subject to extensive discussion and only the high resolution spectra for iron will be presented here. Fig. 10.16 depicts the Fe2p spectrums for all investigated specimens (the dashed lines are for orientation of the reader).

A general interpretation of Fig. 10.16(a) (Fe2p spectrums for specimens R, C, P1a and P2a) is the following: The most intensive peak for Fe is the one for the corroding specimen C, shifted toward lower binding energy, corresponding to Fe²⁺ in FeO at 709.2 eV, while for the protected specimens P1a and P2a, the corresponding peaks are at 710.2 eV for Fe₂O₃ or α-Fe₂O₃, which is consistent with the observations according the O1s spectrum. For the corroding specimen C, binding energies 709.2 eV and 709.5 eV correspond to FeO and Fe₂O₃, respectively; for the
protected specimens, binding energy 710.2 eV and 710.4 eV correspond to FeO$_4$, the shoulder peaks at 712 eV correspond to FeOOH [54,55].

Quantification of the collected data was obtained after fitting the recorded high resolution spectra by following the aforementioned procedures, taking into account the peak parameters (binding energy E (eV), the FWHM (eV) and the corresponding satellites) and considering reported procedures and results [56,57]. The data are consistent with the results, derived from XRD measurements (Table 10.2), bearing in mind however that for XPS, the data interpretation after fitting can vary, since the oxides on the steel surface are complex in nature. The product layers consist not only from iron oxides, but are mostly a mixture of calcium and silica substituted such in combination with iron oxides/hydroxides. An example of a fitted spectrum is depicted on Fig.2b) for the Fe2p$_{3/2}$ high resolution signal for specimen R, showing four contributions: a divalent oxide peak at 709.6 eV, a trivalent oxide peak at 711.1 eV and the corresponding satellites at 714 eV and 718.6 eV respectively.

![Fig. 10.16 (a) XPS spectrums for Fe 2p for specimens R,C,P1a and P2a, using AlK$_\alpha$ X-ray source (excitation energy h$\nu$=1486.6 eV); (b) a representative plot for the performed fitting procedure, the plot depicts the Fe2p$_{3/2}$ spectrum for specimen R.](image)

By performing the aforementioned data collection for all specimens, the following can be summarized: the area of the peaks, corresponding to FeO in each Fe2p$_{3/2}$ spectrum, is the largest in the corroding specimen C (26%), followed by specimens P1a and R (3 times less than specimen C) and specimen P2a (6 times less than specimen C) i.e. the data are consistent with the amounts of FeO derived from XRD (although for these experiments XRD is a bulk technique, while XPS is relevant to the product layers), showing higher amounts of FeO in specimen C, compared to specimens P.

Further, different ratios of Fe$^{2+}$: Fe$^{3+}$ can be approximated. For example the ratio FeO : Fe$_2$O$_3$ for the investigated specimens is as follows: 1.93 for specimen C, 0.28 for specimen R, 0.15 for specimen P1a and 0.23 for specimen P2a i.e. the ratio Fe$^{2+}$ to Fe$^{3+}$ is highest in the C specimen, corresponding to higher amounts of wustite and lower amounts of hematite/magnetite in this
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specimen, as derived from XRD measurements as well. Since magnetite is a mixture of wustite and hematite, exact values can’t be derived, but a relative ratio can be approximated. For example, the ratio of \((Fe_2O_3+Fe_3O_4)\) for specimens P2a to \((Fe_2O_3+Fe_3O_4)\) for specimen P1a is 1.6, which is again consistent with the XRD measurements, where higher amounts of these oxides were detected for specimen P2a.

Summarizing, the surface analysis shows conformable results from both XRD and XPS measurements, in terms of composition and amounts of corrosion products. Obviously, and as expected, CP brings about favorable modifications of the corrosion products in terms of higher amounts of protective and adhering to the steel surface \(Fe_3O_4\), which along with the Ca-rich layer (evidenced by adhered portlandite) and non detectable by XRD oxy(hydroxy) chlorides, denote for the CP efficiency and supplies evidence for the fundamental reasons underlying the CP mechanisms, in particular for the pulse CP regime, as far as product layers formation and conversion are concerned.

10.4.2.3 Electrochemical measurements in cement extract

As already mentioned in the section “materials”, the samples in the present study were cylindrical parts from the previously embedded in concrete reinforcing steel, from each technical condition (at 460 days of age), i.e. the studied specimens were steel electrodes with equal geometrical surface of 5.65 cm\(^2\). The specimens from each group (as previously defined: reference R, corroding C, protected P1a, P2a, P1b and P2b) were subject to electrochemical testing in cement extract solutions. The applicability and limitations of electrochemical measurements with regard to systems as in this study were already discussed in Chapters 4 and 9 and briefly mentioned in Section 10.2 above.

Potentio-dynamic polarization

Fig. 10.17a) presents polarization curves for all investigated specimens, recorded after OCP stabilization (~40 min) in cement extract solution of pH 12.6 and after IR drop correction (the solution resistivity was defined about 3 ohm, geometry of the experimental cell and working electrode geometrical surface were identical in each test). The scans were performed from -0.15 V to approx. +1.8 V vs OCP. As seen from the plot, all protected specimens (groups P) depict similar behavior with external polarization. The lowest corrosion and anodic currents are recorded for specimen R (non-corroding specimen). The corrosion current density for all protected specimens (groups P) is similar (Fig. 10.17b), slightly higher anodic currents are observed for specimen P1a (CP, 60d, Fig. 10.17a). The highest corrosion current density is recorded for specimen C (previously corroding surface), along with significantly higher anodic current density for the -0.6 V to 0.6 V region. Basically the PDP measurements on steel specimens in cement extract solution would not give information about the pitting potentials or show significant differences in the slopes of the anodic curves or in the potentials of oxygen evolution, since cement extract is a highly alkaline solution and for this test, there was no additional contamination with NaCl. Chlorides can only be present at the steel surface in the form of iron oxy/hydroxy-chloride complexes in the product layers, previously formed in the relevant conditions (e.g. akaganeite for specimen C, as detected by SEM and XRD investigation; chlorides...
were not found in the solutions after performing the electrochemical measurements). These compounds however, will hardly exert changes in electrochemical behavior during the PDP (EIS or CV) measurements. The influence of Cl⁻ ions on steel depassivation, even at high pH levels, can be seen as a function of the net balance between two competing processes on the metal surface i.e. stabilization (and repair) of the film by OH⁻ ions and disruption of the film by Cl⁻ ions (if present) [58,59]. When the activity of OH⁻ ion overcomes that of Cl⁻ ion, the pitting initiation or growth would be halted [58-60]. Hence, especially in the case of the present experiments, information for pitting potentials or depassivation will not be observed for specimen C. The results however support the observations for lower corrosion resistance of the films on specimen C, for which the most active corrosion potential (~0.7V) and the highest anodic current in the potential region 0V to 0.6V were recorded. The potential shift to more anodic values for protected specimens P, along with the lower passive current density (compared to specimen C) is an additional evidence for effectively working CP [22], as previously discussed in Section 10.4.1 and will be further elaborated in relation to the CV measurements.

Figs. 10.18 to 10.20 present the EIS response of the investigated specimens, after OCP stabilization in CE solution (in all Nyquist plots, imaginary and real impedance are presented in Ohm, since geometrical surface and experimental set-up were identical for all specimens). Using EIS in this study aimed to evaluate the electrochemical behaviour of the steel surface in CE solution as result of the different products formations after 460 days of conditioning (the observations are consistent with EIS results for earlier stage of 270 days, discussed in Chapter 9). The varying product layers’ characteristics, relevant for each (previously maintained) technical condition, were expected to exert influence on the corrosion behaviour of the steel electrodes in the model pore solution and further to allow collecting evidence for the performance of the CP techniques. The discussed parameter is the polarization resistance ($R_p$), which can be associated
with the overall corrosion process, since $R_p$ is inversely proportional to the corrosion current $I_{corr}$ i.e. we do not claim exact values for corrosion rates.

Figure 10.18 presents the impedance response for a steel electrode from non-corroding group (R) and corroding group (C) in Nyquist and Bode format, illustrating the used equivalent electrical circuit (incorporated in Fig. 10.18a). The elements of the equivalent circuit present the following physical meaning: $R_{ce}$ is the cement extract resistance; the first time constant ($R_p, C_{f}$) deals with the electrochemical reaction on the steel surface; the second time constant ($R_{p,l}, C_{p,l}$) is attributed to resistance and properties of the product layers (or redox transformations in the product layers). The parameters (elements) assignment depends on electrode potential, especially for magnetite based product layers [4, 61], but in the passive domain (where all here investigated specimens fall in, as OCP values were between -226 and -573 mV (SCE) in solution of pH 12.6), $C_f$ would correspond to the interfacial capacitance and $C_{p,l}$ to redox capacitance, $R_p$ is associated with charge transfer processes, $R_{p,l}$ with redox transformations (mainly Fe$^{2+}$/Fe$^{3+}$) in the product layers.

The replacement of pure capacitance (C) with constant phase element (CPE) in the equivalent circuits is largely accepted for systems as in this study [2, 5, 6, 40], being denoted to inhomogeneities at different levels i.e. steel surface roughness, product layer heterogeneity etc. Although CPE element is widely used, in order to compare the present study with literature data, and mostly to be able to directly compare this investigation with studies in identical conditions but for earlier ages of 270 days (Chapter 9), capacitance values are hereby presented [in µF/cm$^2$], taking into consideration the following [62]: for a given frequency $\omega$ the following relation between the imaginary part of the impedance of the CPE ($Z_{CPE}$) and the impedance of the fitted capacitance ($Z_C$) is valid: $\text{Im}(Z_{CPE}) = Z_C \cdot \text{Im}[1/Y_0(j\omega)^n] = 1/j\omega C$. Using the relationship: $(j\omega)^n = \omega^n [\cos(n\pi/2) + j\sin(n\pi/2)]$, the relation between the CPE parameters $Y_0$ and $n$ and the capacitance $C$ is: $C = Y_0 \cdot \omega^{-n}/\sin(n\pi/2)$.

Figure 10.19 depicts an overlay of the impedance response for the protected specimens P1a and P2a, which are steel samples from previously protected for 400 days reinforcing steel (CP both
conventional (P1a) and pulse (P2a), was applied at 60 days of age, using CP current density of 5 mA/m². The shape of the experimental curves and the recorded parameters after fitting procedures (Table 10.3) for specimens P1a and P2a (Fig. 10.19) are very similar to those depicted on Fig. 10.20 for specimens P1b and P2b, which are steel samples from previously protected for 310 days reinforcing steel (CP both conventional (P1b) and pulse (P2b), was applied at 150 days of age, using CP current density of 20 mA/m²). The previously CP protected specimens (index “1”) from all groups exhibit a slightly higher low frequency impedance limit, compared to the pulse CP protected specimens.

Fig. 10.19 A comparison of impedance response for protected cells P1a (CP) and P2a (pulse CP), (working electrode at 460 days of age, CP both regimes applied at 60 days of age) in cement extract solution, after OCP stabilization only.

Fig. 10.18 shows the significant difference of the impedance response for corroding (C) and non-corroding (R) specimens in the low frequency domain, attributed to accelerated corrosion state in the former and passive condition in the latter case. The $C_f$ values for specimen R tend towards the values for $C_{pl}$ (42 µF.cm⁻² and 39 µF.cm⁻² respectively), which corresponds to the low rate of oxidation process for this specimen. The derived $R_p$ for corroding specimen C is much lower compared to non-corroding and protected specimens (Table 10.3). The corresponding $C_f$ is significantly higher (520 µF.cm⁻²) compared to protected specimens P (23 to 52 µF.cm⁻²), attributed to spreading the corrosion damage on a larger surface area. The $C_{pl}$ values for all specimens are higher than the $C_f$ values and can be only denoted to modifications in the structure of the product layers.

Comparing the impedance response for protected specimens and corroding specimen (Fig. 10.20), it is obvious that the magnitude of impedance and the phase angles are higher for all protected specimens, compared to specimen C, which denotes for effectively working CP in all previously maintained protected conditions and the formation of a more corrosion resistive film. What should be noted here, is again the observed discrepancy between results, obtained when the measurements are performed in concrete (Section 10.4.1) and those in solutions (as also discussed for 270 days in Chapter 9). The different electrochemical performance of the steel surface (which
The effective performance of pulse CP. Steel behavior in model solution is contrary to expected in concrete and as expected in cement extract) is as a result of diffusion limitations and cement chemistry when measuring in concrete and influenced by the properties of the product layers, when measuring in both concrete and cement extract (the phenomena were already discussed in Chapter 9 and mentioned hereby, consequently the more broad range of electrochemical measurements, presented in this Chapter is to elucidate the effects of product layers properties and performance).

The pulse CP (both regimes of lower and higher CP current density) is obviously at least as effective as the conventional CP technique, evidenced by the similar to conventional regimes EIS response and previously supported by very close performance with external polarization, as shown on Fig. 10.17 from PDP measurements. The parameters $R_{p.l}$ and $C_{p.l}$ indicate the properties of the product layers formed on the steel surface. The capacitance $C_{p.l}$ for corroding specimen C is the highest among the investigated specimens. It can be denoted to the capacitance associated with redox processes of product layers containing chlorides (as in specimen C) and can be attributed to: the easier oxidisability of the product layer in the presence of Cl$^{-}$ and the initially high corrosion rate, consequently thicker (but not protective) layers are quickly formed, thus high

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$R_{p}$</th>
<th>$C_{p}$</th>
<th>$R_{p.l}$</th>
<th>$C_{p.l}$</th>
<th>$E_{ocp}$</th>
<th>$E_{corr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1a</td>
<td>24.4</td>
<td>52</td>
<td>7.1</td>
<td>60</td>
<td>-502</td>
<td>-502</td>
</tr>
<tr>
<td>P2a</td>
<td>20.9</td>
<td>23</td>
<td>25.9</td>
<td>48</td>
<td>-417</td>
<td>-417</td>
</tr>
<tr>
<td>P1b</td>
<td>37.6</td>
<td>26</td>
<td>12.5</td>
<td>191</td>
<td>-480</td>
<td>-480</td>
</tr>
<tr>
<td>P2b</td>
<td>27.7</td>
<td>50</td>
<td>5.2</td>
<td>184</td>
<td>-472</td>
<td>-472</td>
</tr>
<tr>
<td>C</td>
<td>1.8</td>
<td>520</td>
<td>120</td>
<td>974</td>
<td>-573</td>
<td>-573</td>
</tr>
<tr>
<td>R</td>
<td>363.5</td>
<td>42</td>
<td>8.5</td>
<td>39</td>
<td>-226</td>
<td>-226</td>
</tr>
</tbody>
</table>

$R_{p}$ for all specimens is approx. 3 Ohm (cement extract solution resistance, varying between 2.8 and 3 Ohm, geometry of the cell and experimental set-up, as well as geometrical surface of all specimens is identical).
values of $R_{p,l}$ and $C_{p,l}$ can be observed even at an earlier stage (as for example 3 months reported in [4]). In addition to the low protective properties of this product layer, evidenced by the low $R_p$ values, the high values of $C_{p,l}$ denote for a rough and porous film with a large surface area, which is supported by the behavior of specimen C with cycling during the CV measurements, subject to discussion in the following section 5.3.3. In contrast, the capacitance related to product layers ($C_{p,l}$) for specimens P and R is much lower, also is $R_{p,l}$, which corresponds to thin layers of products and higher $R_p$ values (lower corrosion rate).

**Cyclic voltammetry**

Cyclic voltammetry is a useful method for investigating the mechanisms of surface oxidation/reduction behavior of steel in an alkaline environment, as the concrete pore solution, and as such has been extensively used in studying the performance of bare steel in model solutions [31-33, 39, 63-66].

In this study, by using CV (in combination with the above discussed EIS and PDP measurements) the aim was to observe the properties of the layers, already formed on the steel surface and their electrochemical behavior in the alkaline medium of cement extract of pH 12.6 (being model pore solution). In this way, we correlate results and compare properties of the previously “naturally” formed product layers (in the time interval of 460 days), rather than investigating any further passivation of the steel surface in contact with the model solution.

![Steel electrode (as received) in CE solution: overlay of CVs at different scan rates](image)

**Fig. 10.21 CVs appearance with respect to scan rate.**

A series of cyclic voltammograms (CVs) was acquired for steel samples from each technical condition (aforementioned and described groups C, R and all P groups) in model solution, after allowing for OCP stabilization (~ 40 min). The stabilized electrode potentials varied between -220 mV SCE for specimens R to -570 mV SCE for specimen C, the groups P showed minor variation, stabilized OCP values were about -420 mV SCE. The different steel potentials in the model solution (pH 12.6) are denoted to the different properties of the initially formed product layers. The scan rate for performing the CV measurements was 200 mV/s, allowing for well
distinctive peaks in the voltammograms, which was not the case at lower scan rates (Fig. 10.21). When the scan rate was decreased from 100 to 20, 5 and 1 mV/s, the cathodic reduction peak shifts cathodically, while the anodic peaks practically disappear, the passive potential region becomes much extended and almost no other features can be easily observed (Fig. 10.21). Hence, a scan rate of 200 mV/s was used in the present study, as also used in similar research [31,34] and previously reported for measurements in alkaline solutions at lower but still significantly high scan rates [67-69].

Cyclic Voltammetry in cement extract solution after OCP stabilization.

Fig. 10.22 depicts an overlay of the 1st (left) and the 15th (right) scans for all here investigated specimens. Figs. 10.22a) and b) present an overlay for specimens R (reference) and all groups of protected specimens (P1a, P2a, P1b, and P2b); Figs. 10.22c) and d) present a comparison of the 1st and 15th scans for corroding specimen C, reference specimen R and the couple of protected specimens, on which CP was applied at 60 days of age (P1a and P2a). The voltammograms are obtained, as mentioned, at scan rate 200 mV/s after allowing for OCP stabilization (approx. 40 min). The peaks II (-0.99 V to -1.1 V) and III (-0.6 V to -0.5 V) in the forward scan and peaks IV (approx. 0.51 V) and V (approx. -1.25 V) in the reverse scan are mainly distinguished (all potentials are vs SCE). As seen from the plots, with cycling the previously protected specimens (groups P) behave similarly to reference (previously non-corroding) conditions. The best performance in terms of product layer corrosion resistance with cycling is for specimen P2a, which is steel surface, previously pulse CP protected (pCP applied at 60 days of age). This is evidenced by the lowest cathodic and anodic currents with cycling in addition to the highest hydrogen and oxygen evolution overpotentials. In what follows, the main characteristics of the cyclic voltammograms will be discussed along with separate presentation of scan overlays for the different conditions.

Figures 10.23a) and b) depict an overlay of 2nd to 15th scans for specimens R and C, Figs. 10.24 and 10.25 present overlay of CV scans for the couple of protected specimens P1b (conventional CP) and P2b (pulse CP). For specimens R (Fig. 10.23a) the anodic peak II reaches almost constant height after 2 to 5 cycles, while the second anodic peak (III), associated with the oxide film development, increases with increasing the number of cycles. The same observation holds for the corresponding reduction peak V. Peak IV becomes more distinct after the 5th cycle, both reduction peaks achieving a stable height in the last few cycles. Although the peak current densities at peaks III and V increase with cycling, the slope of the curves becomes stable after the 5th cycle and approaches relatively constant values i.e. there is a tendency to reach a steady state, as reported in similar research [36, 63]. This behavior is attributed to the thickening of the hydrous oxide film, which results from a slightly incomplete reduction at the cathodic peak on each cycle. The observation is supported by the change in peak potential, as the potential of the anodic peak increases (becomes more anodic) with time, while the change in cathodic peak potential to more anodic values is less pronounced. This would suggest that oxidation becomes more difficult, while reduction remains almost unchanged.
Further, a steady state thickness of the oxide film can be possibly reached as result of diffusion limitations of the transport of water molecules and hydroxide ions through the oxide layer i.e. the film permeability will decrease [70].

Another important observation is, that the passive current, in the potential region of 0V to 0.6 V remains almost unchanged after the 5th cycle, hence the protective properties of the product layer, initially formed on the steel surface of specimen R, before immersion in cement extract, remain unchanged, moreover, thickening of the film with cycling does not influence the corrosion resistance of the previously formed layer. In specimen C (which was the previously corroding specimen) a shoulder peak (IIIa at about –300 mV) is observed (Fig. 10.23b), denoted to a more active dissolution process in this specimen, which along with the strong distortion of the voltammogram, compared to the other specimens (Figs. 10.22c,d, 10.23b), suggests a very low corrosion resistance of this film, evidenced by the high currents in the normally passive region at potentials anodic to peaks III and IIIa. Consequently, a completely different behavior is observed.
The effective performance of pulse CP: Steel behavior in model solution

for corroding specimen C. After the 1st and 2nd scan, there is a drop of the current in the region of peak IIIa, but almost no change is observed for the peak current III (see also Fig. 10.26).

Fig. 10.23 Overlay of the 2nd to 15th scans for group R (a) and for group C (b) in cement extract solution, after OCP stabilization only.

In the region of peak IV, which for specimen C is anodic, a shift towards cathodic current is observed, but the peak remains in the anodic region till the 15th scan and further on with cycling (data not presented). After the 5th scan, the anodic current in the region -0.3V to 0.6 V again increases and reaches stable, significantly higher values, compared to specimens R. The observations could be probably attributed to some limitations in the beginning of cycling, related to rapid formation of corrosion products with larger surface area in the first scan, which is evidenced by the highly distorted curves and high currents. There are almost no limitations in the cathodic region of hydrogen evolution (region I), peak II is hardly distinguishable due to the very steep slope of the transition from peak II to peak III.

In contrast to specimen C, significantly lower currents of the anodic, cathodic peaks and in the passive region are recorded for the protected specimens P; the similar behavior of all protected specimens (groups P) with cycling is evidenced by Figs.10.24 and 10.25. The overlay of 2nd to 15th scans for both groups (Figs 10.24a and 10.25a) shows similar behavior and peak current ranges as for the reference specimen R (Fig. 10.23a) i.e. a tendency to reach a steady state with change of peak currents height, denoted to thickening of the oxide layer. Moreover, an increase in the peak current only, not accompanied by anodic shift of the peak potential (as otherwise observed for specimens R, Fig. 10.23a), suggests that the product layer in the protected specimens is more homogeneous and compact. These observations are supported by further cycling (from 15th to 45th cycles), depicted on Figs. 10.24b and 10.25b), showing almost constant values of anodic and cathodic currents in the potential region of 0V to 0.6V, which again is consistent with the observations in specimen R.
Relevant to all investigated specimens are the anodic/cathodic reactions, as summarized below [71, 72], corresponding to the observed peaks.

**Region I** — hydrogen evolution reaction

**Peak II** (approx. -990mV): Fe + 2OH⁻ → Fe(OH)₂ + 2e⁻

**Peak III** (approx. -554mV): Fe(OH)₂ + OH⁻ → [FeOOH] + H₂O + e⁻, followed by a chemical reaction of:

2[Fe(OOH)] → [Fe₂O₃·H₂O]

**Peak IV** (approx. 510mV): poorly defined, formation of calcium substituted layers [4].

**Peak V** (approx. -1250mV): FeOOH → Fe(OH)₂; Fe₃O₄ → Fe(OH)₂
Although the electrochemical reactions, corresponding to the various peaks in alkaline solutions have been discussed and reported by previous investigations [e.g. 4, 73-79], they have not been strictly identified. There is a general agreement however, which is as follows: Peak II is generally attributed to steel dissolution i.e. to the formation of ferrous hydroxide from the base steel surface. The current densities at peak III are characteristic of the onset of passivation, at which point Fe$^{2+}$ is being oxidized to insoluble Fe$^{3+}$. This peak is associated with the transformations in the outer hydroxide oxide layer and the relatively intact inner anhydrous oxide layer. At peak III, the increasing rate of oxidation to insoluble Fe$^{3+}$, or possibly substituted layer of CaFe$_3$O$_4$[36, 73] is further overtaken by the increasing impermeability of the passivating layer. Hence the properties in terms of compactness, permeability, corrosion resistance of the product layers at potentials anodic to peak III are determined by the current densities in this region (a comparison of the values for anodic current at 0V for the investigated specimens is presented on Fig. 10.27).

As depicted on Figs. 10.22 and 10.23 the product layer in specimen C is less corrosion resistant than groups P and R. Further, the potential of oxygen evolution varies for the different specimens, which suggest certain structural properties for the oxide layers, formed initially in the different conditions of groups P, C and R. Additionally, the potential of oxygen evolution shifts for some specimens with cycling, suggesting different catalytic activity of the product layers. Following the potential of oxygen evolution, peaks IV and V are further observed, peak IV is poorly defined for some specimens and becomes more apparent with cycling; it is most likely associated with the formation of calcium substituted layers [4]. Peak V is generally ascribed to reduction of the compact, anhydrous inner layer.

With regard to the increasing anodic current at peak III with cycling and the observed changes in cathodic current at peak V, the following should be taken into consideration: With cycling, there is most likely a formation of a different type of oxides/hydroxides layers on the steel surface. The very low solubility of Fe$^{3+}$ and the formation of Fe(OH)$_2$ in highly alkaline solutions may determine a solid-state conversion reaction of Fe$^{3+}$ to Fe$^{2+}$ [80, 81]. The well distinctive anodic peak III and not well pronounced cathodic peak V in the first cycles (especially for specimen R) however, can be also attributed to oxidation/reduction reactions, accompanied by a significant change in absorption. Similar phenomena is recorded for iron in NaOH solutions and reported in [82], where the behavior of the product layers with cycling is supported by absorption data from reflectance techniques.

The increase of the peak III current densities in this study with cycling is related to the oxidation of Fe(OH)$_2$ in this potential region. This oxide/hydroxide layer however, although electrochemically active, will not have the properties of the initially formed passive layer and can not be considered as such. This must be the case as a growth of this deposit layer is not influencing the barrier (passive) layer i.e. the deposit layer, which becomes thicker with cycling, will not contribute to passivity, since a contribution to passivity would result in a delay of film growth [83]. This would mean that the layer formation at peak III for group R and the protected groups P is mainly relevant to oxidation of Fe$^{3+}$ to Fe$^{3+}$ instead of the formation from metallic iron. At cathodic potentials (peak V), the product layer is converted from Fe$^{3+}$ to Fe$^{2+}$, the Fe$^{2+}$
film being the deposit layer. After each cycle the thickness of Fe(OH)$_2$ increases as iron from possible reduction of the passive layer is added.

Similar mechanisms hold for the behavior of the previously corroding surface of specimen C with cycling, which can be correlated to the EIS measurements and the derived highest values of $R_{p,l}$ and $C_{p,l}$, (as previously discussed in terms of EIS, the highest values for $R_{p,l}$ and $C_{p,l}$ are denoted to higher roughness, porosity and surface area of the product layer in specimen C). As mentioned, after the first cycle there is initial drop in the anodic current at peak IIIa, which is probably associated with an attempt to re-pair the initially formed product layer and re-passivation in the high alkaline medium of pH 12.6. Rust layers however (as in specimen C) in alkaline solutions, even without the presence of Cl$^-$, may produce active corrosion on the steel surface [83-85]. Thus competing mechanisms of passivation and de-passivation are most likely responsible for the almost constantly high currents at anodic and cathodic peaks III and V in specimen C with cycling, since the rust interferes in some way with the passivation process. This is due to the locally broken continuity of the product layer on the steel surface in specimen C (as supported by previous investigation of the steel surface, (Chapter 9) in addition to possibly low pH inside the points of local attack, where the steel surface remains permanently active [86, 87]. Hence, the peak currents in specimen C remain significantly high, but almost constant with cycling, whereas the peak currents in specimens R and P increase with cycling, due to aforementioned mechanisms.

**Variation of peak current density, peak potential and passive current with cycling**

The development and properties of the oxide layers can be related to the recorded peak current densities and peak potentials with cycling. Fig. 10.26 shows the development of the peak current density and peak potential for the anodic peak III, a characteristic feature in the CVs for all investigated specimens.

![Graph](image_url)

**Fig. 10.26** Evolution of peak potential (E) and peak current density (I) for all investigated specimens with cycling: (a) comparison for corroding C and reference R; (b) comparison for pCP and CP protected cells.
The peak III, as already discussed, is most prominent as oxidation peak and related to the onset of passivation after the peak maximum. The peak potential initially shifts anodically for all specimens, except the potential of peak III in corroding specimen C, where the opposite trend is observed. The latter observations support the previous discussion for a product layer in specimens C with low corrosion resistance. The peak potential for all specimens reaches a steady state with cycling. The same trend is recorded for the peak currents with number of cycles. The highest peak current recorded for corroding specimen C (Fig. 10.26a), the lowest for the protected specimen P1a (Fig. 10.26b).

The approach to steady state with cycling (shortly after the first few cycles) for all specimens is confirmed further by the anodic current density at 0V (Fig. 10.27). In this region, specimen C exhibits significantly higher current densities, compared to the rest of the specimens. The observation is consistent with the recorded steel surface behavior with external polarization from PDP measurements (Fig. 10.17) and in line with the highest $R_p$ and $C_p$ for the corroding specimens C, obtained from EIS measurements (Table 10.3).

The best performance of the pulse CP protected surface with cycling (specimen P2a) is evidenced by the lowest current density at 0V (Fig. 10.27). Obviously, the product layer, formed in the previously protected by pulse CP (60 days) specimens P2a is more stable and with better properties, compared to the CP protected specimen P1a. Fig. 10.28 supports the previous statements, showing the better performance of specimen P2a, compared to specimen P1a (Fig. 10.28a) (lower anodic and cathodic currents with cycling and not well distinguished peaks). The opposite trend is however valid for pulse CP protected specimens, when the protection was applied at 150 days of age. Fig. 10.28(b) shows overlay of CV scans for CP and pCP protected specimens, P1b and P2b respectively. As seen from the plot, 150 days as starting point for CP application results in similar, but not better performance of the product layers in pCP, compared to CP conditions.

The above discussed performance of the initially formed product layers on previously corroding, reference and protected steel surface in cement extract solutions and mainly, the better properties, in terms of corrosion resistance, of previously pulse protected specimens, compared to the other
conditions, is evidenced by observations of the steel surface response with cycling after exposure to cement extract for longer periods.

Fig. 10.28 Overlay of 15th CV scans for specimens P1a and P2a (CP and pCP applied at 60 days of age) (a); overlay of 15th scans for specimens P1b and P2b (CP and pCP, applied at 150 days), cement extract solution, after OCP stabilization only.

Fig. 10.29 (a) Overlay of 15th, 30th and 45th CV scans for specimen P1b (CP applied at 150 days), in cement extract solution, after OCP stabilization only (black lines) and after 12h exposure to cement extract (gray lines); (b) Overlay of 1st (solid lines) and 15th (dashed lines) scans for specimen C before and after 12h exposure to cement extract.

Figure 10.29 presents overlay of CV scans for protected group P1b and corroding group C before and after 12h exposure to cement extract solution. Generally, it is assumed that the corrosion resistance of the product layer on the steel surface will be increased with exposure to alkaline medium of pH 12.6 due to additional passive film repair, physico-chemical reactions between the deposited layer and the solution, absorption mechanisms. However, this is obviously not exactly the case. Fig. 10.29a) presents a comparison overlay of 15th, 30th and 45th cycles after OCP stabilization only.
The effective performance of pulse CP. Steel behavior in model solution stabilization (~40 min) only (black lines) and after exposure for 12h in cement extract solution (gray lines). As seen from the plot, exposure to cement extract for 12 h does not exert significant influence on the anodic and cathodic currents, as well as peak currents with cycling. There is a slight increase of anodic current at peak III and cathodic current at peak V, but the anodic current in the normally passive region i.e. between 0V and 0.6V remains the same before and after conditioning in the cement extract. The observations suggests, that exposure of the steel surface to the highly alkaline medium does not result in increased corrosion resistance i.e. the initially formed films are with good performance and properties.

The same observation holds for corroding group C (Fig. 10.29k), where significantly higher currents are observed before as well as after immersion in cement extract for 12h. The anodic current initially drops after the first cycle, before exposure to the cement extract (as already aforementioned), probably due to limitations from absorbed species or attempts for repair. After 12h exposure, the 1st cycle presents lower currents, but with further cycling the current again increases to the initial values (15th cycles before and after immersion of the specimen present identical result). The observation suggests that the product layer in specimen C is with low corrosion resistance and is difficult to repair even after exposure to cement extract of pH 12.6.

Summarizing, the measurements in cement extract solutions aimed to investigate the performance of “naturally” formed product layers on the steel surface of pre-conditioned in concrete steel re-bars, and maintained in different technical regimes for 460 days. The study further allowed evaluation of the CP performance in terms of steel surface oxidation/reduction behavior in the alkaline medium of cement extract. The CV measurements (supported by EIS and PDP results) reveal the higher corrosion resistance of protected specimens, proving the efficiency of both protection regimes, which is as expected compared to corroding conditions, but hereby experimentally evidenced. This behavior is denoted to better adherence, higher compactness and homogeneity of the product layers in these specimens (since they are mainly consisting of Fe₂O₃ and Fe₃O₄), whereas the product layers (mainly FeO, α-FeOOH, γ-FeOOH, β-FeOOH.Cl₂) in the previously corroding specimens do show rough morphology, high heterogeneity and low adherence, and consequently low protective properties.

10.5 CONCLUSIONS

This Chapter reveals that the introduced cost-effective CP, based on a block-shaped, current pulse signal, is at least as effective as the conventional CP in terms of achieving the required steel polarization, thus providing adequate protection of the steel reinforcement. The effective performance of pulse CP is further evidenced by a more significant open circuit potential shift of the steel surface towards noble values. Potentio-dynamic polarization and impedance spectroscopy, determine similar electrochemical parameters for both types of protection and taking into consideration the at least 50% less CP current density used in pulse regime, confirms the efficiency and cost-effectiveness of the latter.
The interpretation of electrochemical parameters (like $R_p$) is not straightforward and is related to the properties of the product layers, formed on the steel surface in the different conditions. Additionally, the properties of these layers will be influenced by the chemical alterations in the cement layers, adjacent to the steel surface, with time of corrosion or CP application. The electrochemical parameters, when derived from measurements in concrete, can give reliable information only if recorded and compared within one group of specimens with time of conditioning (for example protected or corroding group of specimens) and further compared with other groups of specimens (for example corroding to protected specimens). The evaluation of data, derived in-between differently conditioned and maintained specimens at equal stage might give discrepancy in obtained parameters.

A better insight in the phenomena involved in corrosion or CP is achieved if the electrochemical parameters are correlated to material properties at the steel/cement interface. The pulse protection regime is found to be more efficient as far as ion transport is concerned and achieves the so called “open circuit potential passivity” more effectively, which is found to be dependent on the secondary beneficial effects of favorable cement chemistry around the steel bars in pulse CP conditions. Moreover, the surface film, formed in pulse CP conditions appears to be more homogeneous and resistive, compared to the conventional CP regime.

These observations are experimentally confirmed by investigation of the pre-conditioned steel in cement extract solutions. The specimens, on which pulse CP was applied at 60 days of age, exhibit the best performance with external polarization and cycling in cement extract. The observation suggests that pulse CP, using 50% of the current density applied in the relevant CP regime, is sufficient for cathodic protection in reinforced concrete, subjected to chloride ingress. Further, CP and pulse CP using higher current densities (20 mA/m$^2$) but applied at a later stage of 150 days (which suggests relatively higher corrosion rates in these specimens before protection), lead to similar results in terms of electrochemical behavior of the steel electrodes. However, pulse CP applied at 150 days does not show better performance compared to the relevant conventional regime, as it was found for pulse CP applied at 60 days of age.

Exposure to cement extract for longer periods does not result in increased corrosion resistance i.e. the initially formed films on the surface of protected specimens are with good performance and better properties. The product layers in the previously corroding specimens are with very low corrosion resistance and are difficult to repair, even after longer periods of exposure to cement extract of pH 12.6.

References:
The effective performance of pulse CP. Steel behavior in model solution

CHAPTER 11
CONCLUSIONS AND RECOMMENDATIONS

11.1 CONCLUSIONS, RELATED TO THE PRIMARY OBJECTIVE

This chapter comprises the main outcomes from the research project and some recommendations for future research, which could be initiated on the basis of the experimental findings from the thesis.

The primary objective was to investigate the possibilities for improving the application of impressed current cathodic protection for reinforced concrete, to establish the technical regimes for the improved technique and to assess its applicability and effective performance. The drawn conclusions are as follows:

1. **Effective protection**: in equal environmental conditions, the Pulse CP achieves the required cathodic polarization of the steel reinforcement at least as effectively as the conventional CP regime.

2. Pulse CP has a superior performance, compared to conventional CP regimes, in terms of achieving more pronounced beneficial secondary effects:
   - more effectively overcoming the high concrete resistance;
   - consequently, enhanced chloride withdrawal away from the steel surface;
   - accumulation of a more uniformly distributed calcium rich layer on the steel surface, maintaining alkalinity of the steel environment;
   - consequently the crystallinity of the previously (before pulse CP application) formed corrosion products is lower, they exhibit favourable morphology and composition, which leads to the formation of a strongly adherent, uniform and corrosion resistant product layer;
   - further, the calcium-rich deposits are most likely in favour of impeding the possibility of hydrogen development on the steel surface;

3. Pulse CP achieves better performance in terms of reduced side effects:
   - minor influence on electrical properties, which maintain close to the reference (control) conditions;
   - minor influence on the concrete bulk matrix in terms of maintaining porosity and pore size distribution, as well as the properties of the interfacial transition zones in the bulk matrix close to reference (control) conditions;
   - additionally, pulse CP is less influencing the microstructure and properties of the inner and outer bulk hydration products of the concrete matrix, which will probably determine better mechanical properties of the system as a whole;
• affecting the steel/cement paste interface to a lower extent, compared to conventional CP, thus reducing the effects on bond strength degradation;

4. Pulse CP appears to be a cost-effective technique. Since the pulse CP involves the application of a block-shaped DC current signal (square wave), the used effective current density is always 50% lower than in the conventionally applied cathodic protection.

11.2 FUTURE RESEARCH - RECOMMENDATIONS

In view of the above drawn conclusions, there are at least several aspects, which could serve as a basis for future investigations:

1. A more comprehensive study on the cement hydration and ion transport mechanisms in conditions of electrical current flow, in particularly different pulse regimes.

As investigated in the frame of the thesis, current flow has a significant influence on the bulk matrix in terms of structural properties, morphology and composition of hydration products. A more deep investigation (on micro and even nano-level), starting at very early ages (e.g. immediately after concrete mixing) will give insight on: how the electrical properties, and ion transport respectively, will perform with time; how the current flow will affect the hydration mechanisms and thus the mechanical properties; the possibilities for defining the positive and negative effects of current flow in applications as cathodic prevention for example (in the time of the construction of a structure) or the influence of stray currents (an important aspect, related not only to the steel reinforcement, but the bulk concrete matrix as well) can be investigated and result in significant improvement of available prevention/protection or repair techniques.

2. Investigation of different types of cements (e.g. fly ash cements, slag cements) and various water-cement ratios will result in a more broad verification for the application of the improved pulse CP regime.

3. Investigation for different grades of construction steel, which behave differently in terms of localized corrosion, but also in terms of susceptibility for hydrogen embrittlement (due to residual stresses for example, or in the case of prestressed concrete).

The corrosion and cathodic protection mechanisms were investigated in ordinary Portland cement-based system, since this type of cement has lower chloride binding capacity. The latter, in addition to the high water-to-cement ratios was intended to accelerate the monitored processes with time, but still maintaining the conditions as close as possible to real practice. Hence, investigation of the pulse CP technique could be performed for longer periods and using different concrete mixtures or steel grades.
4. A study on the possibility for minimizing the number and surface area of the anodes (since pulse CP results in better current “throw” and overcomes more effectively the concrete resistance, it is possible to significantly reduce the surface area of anodes, which will result in even better cost-efficiency).

5. Testing of pulse CP in concrete mixtures, containing different admixtures and additives, as for example polymer nano-particles (also particles, incorporating a metal core), will possibly result in the formation of a more stable product layer on the steel surface on one hand and could improve the properties of the bulk cement-based matrix on the other.

6. The study did not include modeling approaches. However, based on the already derived real experimental data, numerical modeling for predicting the combined effects of cement hydration, corrosion, ion transport and cathodic protection should be possible and even more realistic, compared to existing models, which rely to a significant extent on literature, empirical data or presumptions.
### APPENDIX I

Review of critical chloride concentration thresholds for atmospherically exposed structures, data only for OPC as relevant to the present research. (adapted from “Gaal G.C.M, Prediction of deterioration of concrete bridges, PhD thesis, Delft University of Technology, Delft (2004)”).

<table>
<thead>
<tr>
<th>Author</th>
<th>condition</th>
<th>salt</th>
<th>Definition</th>
<th>Salt added</th>
<th>Cl (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluge, 2001</td>
<td>OPC, sea exp.</td>
<td>NaCl</td>
<td>Initiation (1)</td>
<td>no</td>
<td>0.47</td>
</tr>
<tr>
<td>Breit, 1997</td>
<td>OPC</td>
<td></td>
<td>Initiation (1)</td>
<td>no</td>
<td>0.48</td>
</tr>
<tr>
<td>Gaal, 2001</td>
<td>OPC</td>
<td>NaCl</td>
<td>Initiation (1)</td>
<td>no</td>
<td>0.50</td>
</tr>
<tr>
<td>Polder, 2002</td>
<td>OPC</td>
<td>NaCl</td>
<td>Initiation (1)</td>
<td>no</td>
<td>0.50</td>
</tr>
<tr>
<td>Polder 2002</td>
<td>OPC, sea exp.</td>
<td>NaCl</td>
<td>Initiation (1)</td>
<td>no</td>
<td>0.50</td>
</tr>
<tr>
<td>Mohammed, 2001</td>
<td>OPC</td>
<td>NaCl</td>
<td>Initiation (1)</td>
<td>Yes(free Cl-)</td>
<td>0.50</td>
</tr>
<tr>
<td>Li, 2002</td>
<td>OPC</td>
<td>NaCl</td>
<td>Initiation (1)</td>
<td>no</td>
<td>0.53</td>
</tr>
<tr>
<td>CUR 2000</td>
<td>OPC, w/b 0.5</td>
<td></td>
<td>Initiation (2)</td>
<td>no</td>
<td>0.50</td>
</tr>
<tr>
<td>CUR 2000</td>
<td>OPC, w/b 0.4</td>
<td></td>
<td>Initiation (2)</td>
<td>no</td>
<td>0.80</td>
</tr>
<tr>
<td>Fluge, 2001</td>
<td>OPC, sea exp.</td>
<td>NaCl</td>
<td>Initiation (2)</td>
<td>no</td>
<td>0.80</td>
</tr>
<tr>
<td>CUR 1992</td>
<td>OPC</td>
<td>CaCl₂</td>
<td>Propagation (3)</td>
<td>yes</td>
<td>1.00</td>
</tr>
<tr>
<td>Fluge, 2001</td>
<td>OPC sea exp.</td>
<td>NaCl</td>
<td>Propagation (3)</td>
<td>no</td>
<td>1.20</td>
</tr>
</tbody>
</table>

### National Standards

- **ACI, Code 318, 1999** - Free chlorides: 0.15
- **SAA 1990 (AS 3600)** - Total chlorides: 0.22
- **BSI 1972(UK, CP 119)** - Total chlorides: 0.35
- **NNI 2001(NEN-EN206-1)** - Total chlorides: 0.40
- **NSF 1999 (Norway NS3474)** - Total chlorides: 0.60

1 – initiation without visible damage  
2 – initiation + propagation until visible damage  
3 – initiation + propagation until repair needed
APPENDIX II

1. EDX mapping at the steel/cement paste interface in reference, protected and corroding conditions (reinforced mortar, 120 days of age)
2. Steel/cement paste interface in reinforced concrete for all investigated conditions:

- Reference (non-corroding, non-protected, 460 days)
- Corroding (460 days)
- Pulse CP protected (460 days)
- CP protected (460 days)
3. EDX mapping of steel/cement paste interface in reinforced concrete:
- Reference specimen (460 days)

- Pulse CP protected specimen (270 days)

- Pulse CP protected specimen (460 days)

- CP protected specimen (270 days)
APPENDIX III

Microstructural analysis of reinforced concrete specimens (after 460 days of conditioning).

Generally, the main purpose of the microstructural analysis, performed in the frame of the thesis and in particular for specimens, subjected to current flow (as plain concrete in model CP conditions (discussed in Chapter 7) and further on the reinforced concrete specimens under CP and pulse CP (discussed in Chapters 8 to 10), was to evaluate the alterations in the bulk matrix and in the interface regions cement paste/aggregate or steel/cement paste as consequence from corrosion and both types of cathodic protection. In addition to cement hydration with aging, there are three main mechanisms/processes, influencing the microstructural properties: the influence of NaCl which accelerates cement hydration and causes densification of the bulk porosity (discussed in the chapters of Part I of the thesis), the influence of current flow (both CP and pulse CP), which is also found to cause bulk matrix densification, but might also influence the interfacial transition zones (ITZs) in direction of enlarging interfacial gaps (Chapter 7) and third – the corrosion process itself (volume expansion of corrosion products induces microcracking). The investigations confirmed that in addition to environmental influences (NaCl) and corrosion, the cathodic current is strongly affecting the bulk matrix in terms of changed electrical properties, altered porosity and pore size distribution, enlarging interfacial gaps. To this end, the alternative pulse CP has better performance, as the pulse current is found to have minor influence on structural properties, thus minimising the extent of side effects. The already discussed observations (Chapters 3, 4, 6 and 7) were confirmed also for reinforced concrete (the plain concrete in Chapter 7 and the reinforced concrete, discussed in Part II of the thesis were prepared, using identical concrete mixture and water-to-cement ratio).

![Graphs showing pore size distribution and critical pore size](image_url)

Fig. 1 shows that the specimen R (reference, non-corroding and non-protected specimen) has highest bulk porosity (~7% at 460 days of age), while the corroding specimen C and the conventionally protected specimen CP exhibit lowest bulk porosity (~3 to 4%). In the interfacial region (steel/cement paste) the corroding specimen exhibits highest porosity as contributing factor is the corrosion induced cracking (~7%); specimen CP has lower interfacial porosity (~3%) but still higher than specimens R and pCP (~2.5%). This proves the minor influence of pulse current, which maintains the material properties close to reference conditions. Supporting evidence is the derived critical pore size distribution as well, the specimens R and pCP having critical pore size of 0.951 µm while specimens C and CP – 0.634 µm.
Apparently, the CP current flow, in addition to corrosion induced changes in the bulk matrix (as CP was applied at 90(120) days of age), is affecting the material properties. Fig.2 presents the calculated porosity in the immediate vicinity of the steel surface (50 μm), interface region (150 μm away from the steel surface) and bulk material (more than 700 μm away from the interface). It is evident, that the current flow causes densification of the bulk matrix in both regimes (specimens CP and pCP), compared to rest conditions, while the interface region is maintained coarser, compared to rest conditions and denser, compared to specimens C, the latter influence by corrosion induced cracking. The coarser pore structure in the 50 μm region for specimens CP and pCP, compared to specimen R, is denoted to de-bonding mechanisms as result of CP current flow (Fig.5).

Fig.2 A schematic presentation of the steel/cement paste interface and bulk concrete matrix and porosity distribution in these zones for specimens C, R, pCP and CP (specimens' age 460 days, w/c 0.6).

Reinforced concrete is a highly heterogeneous material. Taking into consideration the variety and complexity of external influences in this study, it is difficult to claim absolute values for each parameter. Hence, the analysis would be better considered as comparative investigation between the different regimes, considering that all measurements were performed in exactly the same manner for each specimen.

Fig.3 Frequency of occurrence (% distribution) vs class of parameter (porosity %) for specimens R (reference), pCP (pulse CP), CP (conventional CP) and C (corroding) in the 50 μm region, adjacent to the steel surface.
The structural parameters were averaged from at least 90 locations in the bulk matrix and the interface regions. The final data were considered after performing a statistical evaluation in terms of frequency of occurrence (distribution) vs class (porosity in %) for the samples in each regime. An example is shown on Fig.3 for the 50 μm porosity distribution in the investigated conditions. For example, for specimen R, the recorded data (from 90 locations around the re-bar, d=12 mm) show variations from 1.5 to 8 % porosity. The curve presents the % distribution variation for the total number of locations. Thus, averaged porosity in the 50 μm region is taken to be 1.1 %, which is the porosity with highest % of distribution (30 %) compared to the other locations (e.g. 8 % porosity has only 10% distribution over the total interface). Similarly, the porosity data for the other specimens were calculated as shown on Fig.3.

Relevant to morphological aspects of the pore structure and ion transport, a characterising parameter, the so-called pore distribution density (PDD), is implied in the microstructural investigations for all specimens. The PDD is a three dimensional parameter, derived from the skeleton length of pore features, observed on two-dimensional section images (details were discussed in the chapters of the thesis).

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Fig. 4 Permeability vs pore connectivity (a) and porosity vs pore connectivity (b) for all investigate specimens (index “b” is denoted to “bulk matrix”, index “f” to interface steel/cement paste).

Fig. 4a) shows the calculated (averaged) permeability in correlation with pore network connectivity, Fig. 4b) depicts the pore connectivity in correlation with derived porosity for the interface regions and bulk matrix for all investigated specimens. As seen from the plots, the highest pore connectivity and highest permeability are recorded for the interface region of the corroding specimen C. The observation is expected, since the volume
expansion of corrosion products causes microcracking, thus increasing the volume fraction of connected channels at the steel/cement paste interface of the specimen. In addition, the critical pore size of the interface region (Fig.1) is higher (0.951 µm), compared to that in the bulk matrix (0.634 µm), which corresponds well to the derived permeability and connectivity values for specimen C.

The lowest permeability and connectivity in the interface region is recorded for the non-corroding specimen R. The relatively low permeability in the bulk matrix is counteracting the high bulk porosity in specimen R, which in addition to lowest values for porosity, connectivity and permeability in the interface, account for the highest electrical resistance in non-corroding conditions, as evidenced by EIS response and AC 2 pin measurements (discussed in Chapter 9). The observations in specimen R are due to certain formations in the bulk matrix, which contribute to the total porosity but are not influencing ion transport and current flow, since they are not connected (discussed in Chapters 3 and 6).

Comparing specimens CP and pCP, the current flow, causes densification of the bulk matrix and brings about changes in the pore network, permeability and connectivity. Contribution to these alterations however, has the influence of CP current on interfacial gaps, mainly in the interface of steel/cement paste in the investigated specimens. These alterations are consequently influencing the bond strength. As seen from the plots (Fig.4) the specimen under pulse CP exhibits higher bulk and interfacial porosity compared to specimen CP (Figs.1 and 2), accompanied by higher permeability in the bulk matrix, the latter almost equal to reference conditions (Fig. 4b). The pore interconnectivity for CP and pCP in the interface regions are higher than the reference R but significantly lower than corroding condition, the pCP again showing better performance with lower connectivity and permeability, compared to specimen CP (i.e. less influence on bond strength degradation compared to conventional CP).

**Better performance of the pulse CP compared to conventional CP in terms of structural alterations at the steel/cement paste interface**

![Image](image-url)

Fig.5 BSE images (from cross sections) of the steel (white regions)/cement paste interface, at magnification of 100x, for corroding (a), reference R (b) pulse CP protected (c) and CP protected (d) specimens

Figs.5 (a-d) presents the steel/paste interface (mounted ESEM images) for corroding, reference, CP protected and pulse CP protected specimens. Here again, the CP current yields much higher influence on material
properties, compared to pulse CP conditions. As aforementioned, the porosity data are averaged over 90 sub-areas (physical size of each image is 226 µm in length and 154 µm in width) located at the peripheral interface around the steel reinforcement (radius of the steel bar = 0.6 cm). The sub-areas are selected following a systematical sampling strategy so that the porosity measurement is representative for the whole paste immediately surrounding the rebar. As seen from the micrographs on Fig.5, the most damaged interface is as expected in the corroding specimen (Fig.5a), where due to volume expansion of corrosion products and filling up the pore network, the interfacial gap is increasing and at 460 days of age is in the range of 200 – 500 µm away from the steel surface. For the specimens under CP, an adhered to the steel surface layer of 100 to 200 µm cement paste is observed, after which in radial direction (almost all around the steel cross section) an irregular gap of 200 – 300 µm appears (Fig.5d). These observations suggest for increased material heterogeneity, possible bond-strength degradation and detrimental effect of the CP current flow. In contrast, the specimens under pulse CP do not exhibit such large gaps and separated layers of cement paste material, the structure is more homogeneous and uniform (Fig.5c), compared to CP and corroding conditions and appears close to reference conditions (Fig.5b). The latter considerations are supported by the above discussed results for pore structure parameters as gradient of porosity from the steel surface into the interface and bulk material. At the steel-paste interfacial zone, the paste density is higher in the concrete protected by conventional CP than the one protected by the pulse technique. Hence, the latter paste has a better ability to absorb strain energy, induced by volume expansion of corrosion products or structural alterations as consequence of the effects of electrical current flow on cement hydration. This implies that the pulse protected concrete provides better conditions for energy dissipation mechanisms.
APPENDIX IV

Morphology of corrosion products on the steel surface of a corroding specimen (reinforced concrete cylinders, w/c ratio 0.6), after 460 days of conditioning.

(A and B – well crystallized akaganeite; C and D – carbonates, goethite/lepidocrocite)
Product layers at the steel/cement paste interface for all investigated conditions after 460 days of conditioning.

Fig. E below presents the product layers on longitudinal sections of the steel reinforcement for each investigated condition (left column) and cross sections of the steel/paste interface for these conditions (right column).

The reference specimens R (Fig.Ea) is characterized by a clean from corrosion products steel surface, with strongly adhered calcium-silica-hydrate (C-S-H) and Ca(OH)$_2$, whereas well defined, local corrosion damages (Fig.Eb), were found distributed to a significant extent throughout the whole steel surface in corroding specimens C. In contrast, the steel surface in all protected specimens is comparatively clean (Figs. Ec and d) present the surface of pulse CP and conventional CP protected specimens). The typical, relatively flat, morphology of uniformly distributed magnetite layers was mainly observed, along with adhered portlandite, defined also by XRD and XPS (as discussed in Chapters 9 and 10). Strongly adhered to the steel surface cement paste layers (enriched of C-S-H and portlandite, as also evidenced by XRD and visualized by EDX observations, Appendix II) denote for lack of (or lower amount of) corrosion products, the latter would normally cause micro-cracking (when steel is in embedded conditions) and increase the bond degradation process.

The homogeneity and compactness of the product layers on the steel surface in specimens R and the protected specimens P is supported by observations of these layers on cross sections of the steel samples – Fig. E, right column. At 460 days of age, the most compact and adherent layer on the steel surface is the one in the non-corroding specimen R (Fig.E(a), right), with a thickness of about 3 µm, while in contrast, the layer in the corroding specimen C (Fig.E(b),right) is highly inhomogeneous and with rough morphology. The product layer in specimen C is non-uniform and much thicker, with a minimum thickness of 5-10 µm (reaching 20 µm for the inner layer, in the vicinity of the steel surface, and locally reaching 200 µm thickness, already penetrating into the bulk concrete matrix, Appendix II). The product layers in the protected specimens exhibit similar compactness and adherence, the specimen pulse CP (Fig.E(c), right) characterized by a thinner and denser product layer (~2.5 µm), compared to the product layer in the specimen under conventional CP, ~ 3.5 µm (Fig.E(d), right). These observations are consistent with the observations for 270 days (Chapter 9). A comparison of the product layer appearance and morphology for 270 days and 460 days reveals the following: for non-corroding specimens R, the product layers at 270 days (Chapter 9) exhibit similar thickness to the layers for the here reported 460 days (~3 to 5 µm); for parallel groups of corroding specimens C, lower thickness (max 10 µm) of the inner product layers was observed at 270 days of age, in contrast to the min 5 to 20 µm at 460 days of age; for parallel specimens to the here protected groups P, higher thickness (4 to 6 µm), along with multilayered appearance for some protected specimens (mainly specimens under CP conditions) were observed at 270 days, whereas at 460 days the layers in specimens P are more compact and thinner (specimens in pCP regime exhibiting thinner layers, compared to CP regime on both ages). The evolution of the product layers with time for each condition, reaching the here presented results for 460 days can be interpreted as follows: the groups R, being non-corroding specimens, do not exhibit significant change in properties within this time interval; the corroding groups (previously discussed in Chapter 9 at 270 days and here presented for 460 days) will show increase in the product layers thickness as consequence from the continuous corrosion process, which is as observed. The protected specimens undergo transformations of the product layers as result of the CP current flow; the layers become more homogeneous and compact, denoted to transformation of the previously formed products to high valent, stable and compact oxides, hence the thickness of the layers decreases slightly and compactness increases. The latter observation is especially relevant to pulse CP conditions, where no significant changes from 270 to 460 days were observed, which means that the steel polarization (i.e. protection) is likely more efficient under pulse CP conditions compared to conventional regimes.
Fig. E  ESEM micrographs, showing the morphology (left column) and cross sections (right column) of the product layers on the steel surface in: (a) reference (R) specimen; (b) corroding (C) specimen; (c) pulse CP protected specimen and (d) CP protected specimen, after 460 days of conditioning.
APPENDIX V

Beneficial secondary effects of CP applications.

1. Crystallinity of corrosion products.

The various morphologies and chemical compositions of the corrosion products determine different extent of volume expansion and penetration in the cement paste, filling in pores or voids. Since lower corrosion products penetration and lower micro-cracking at the steel/cement paste interface will be expected in case of lower crystallinity, the crystallinity of corrosion products itself is an important material characteristic as far as mechanical properties are concerned. Salinity is the factor, responsible for the crystal structure and crystal growth of akaganeite, goethite and lepidocrocite.

Figure 1 depicts high magnifications of corrosion products detected on the steel surface for corroding and protected specimens at the stage of 460 days of conditioning. The highest crystallinity of FeOOH (goethite + lepidocrocite) is detected in the corroding specimen (Fig. 1a), crystal length is about 18 µm. The same products are expected to appear in the protected specimens as well, since they have been formed before applying the CP (CP started at 120 days of age), however with much lower crystallinity. The specimens under CP exhibit higher crystallinity of corrosion products (about 5 to 8 µm) – Fig. 1b), compared to pulse CP (about 2 to 3 µm) – Fig. 1c), hence the pulse CP is more efficient in terms of morphology and spatial distribution of product layers on the steel surface.

Fig. 1 BSE images of typical corrosion products (different phases of FeOOH), formed on the steel surface in corroding (a) at 2000x, CP protected (b) at 4000x and pulse CP protected (c) at 4000x specimens (left) and EDX quantification (bottom).

EDX observations (Fig. 1 bottom) support the better performance of pulse CP and prove the expected beneficial effects on ion transport as well. As seen from the analysis, the highest chloride concentration was detected (as expected) on the corroding steel surface (17.42 w%), the lowest – on the pulse CP protected steel surface (0.17 w%). For the conventional CP, the chloride concentration detected in the product layer is significantly lower than the corroding one, but still higher than the pulse CP conditions (3.96 w%). The EDX analysis was confirmed wet-chemically as well (discussed in the chapters of the thesis).

2. Calcium-rich “healing” layers.

As aforementioned and experimentally evidenced, lower crystallinity of the typical corrosion products on the steel surface in protected conditions was observed, attributed to lower salinity of the cement layers, adjacent to the reinforcement. These observations are confirmed by ESEM and EDX investigation of the strongly adhered calcium-rich layers on the steel surface of the protected specimens P in both CP and pulse CP conditions and also supported by wet chemical analysis of the adjacent cement layers, XRD and XPS analysis, which are in detail discussed in the chapters of the thesis. Figure 2 depicts the morphology and distribution of these layers in specimen P under conventional CP (Fig. 2a) and specimen P under pulse CP (Figure 2c) after 460 days of conditioning; Table 1 summarizes the EDX analysis of the marked
regions in Fig. 2. As seen from the micrographs (Fig. 2(a,c)), these layers are not entirely uniform and are mainly deposited on locations where the steel surface was previously locally damaged (Fig. 2(c)), left part of the image; the very bright locations in the images depict bare steel surface). The observations denote for the "healing" effects, promoted on the steel surface as consequence from CP application. The latter are more pronounced in pulse CP condition (Fig. 2(c,d)), evidenced by the higher concentration of Ca-containing compounds (Table 1) and the presence of well crystallized portlandite (Fig. 2(d)).

Table 1: EDX analysis of marked locations in Figure 2(b,d)

<table>
<thead>
<tr>
<th>Composition (most relevant compounds), w.%</th>
<th>Figure 2b(CP)</th>
<th>Figure 2d(pulse CP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>49.15</td>
<td>62.57</td>
</tr>
<tr>
<td>NaO</td>
<td>0.70</td>
<td>1.00</td>
</tr>
<tr>
<td>Fe₂O₃(oxy)hydroxides</td>
<td>1.41</td>
<td>1.71</td>
</tr>
<tr>
<td>Cl₂O</td>
<td>0.47</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Fig. 2: Calcium-rich product layers, deposited on the steel surface in CP protected specimens (a,b) and pulse CP protected specimen (c,d) (specimens after 460 days of conditioning).
APPENDIX VI

Side effects of CP application
Some research outcomes on the potentially better performance of pulse CP in terms of inner and outer hydration products in the bulk matrix and retarding hydrogen evolution on the steel surface in reinforced concrete after 460 days of conditioning.

As discussed in the chapters of the thesis, certain side effects are normally accompanying CP applications in reinforced concrete. They are generally discussed in the literature in terms of possible softening of C-S-H and bond-strength degradation, but very limited information is available on the influence of CP current flow on the bulk matrix microstructure and the influence of hydrogen evolution, although hydrogen embrittlement is generally referred to as a “threat” for prestressed concrete only.

The effects of electrical current flow on the bulk cementitious matrix were presented in the thesis in terms of altered microstructural parameters in plain and reinforced mortar and in plain concrete. This Appendix briefly describes some additional observations, related to “inner” and “outer” hydration products of the bulk matrix as well as observation on the steel/cement paste interface in reinforced concrete.

1. Observations of bulk microstructure
A more thorough investigation of the hydration products in the bulk matrix, reveals interesting observations. Figures 1 to 3 depict typical and representative morphology of bulk hydration products in protected specimens at the same age of 460 days. Figure 1 presents a protected specimen P under conventional CP, with regime of application 5 mA/m².

Figure 1: Bulk hydration products, specimen group P, conventional CP, 5 mA/m²

Figure 2: Bulk hydration products, specimen group P, pulse CP, 5 mA/m²
Figure 2 depicts the hydration products for protected specimen P, using pulse CP in regime of 5 mA/m², which is an effective current density twice lower i.e. 2.5 mA/m². Fig.3 shows the hydration products in protected specimen P, using 4 times higher current density i.e. 20 mA/m² in conventional CP regime. As seen from the micrographs, micro-cracks appear in the inner and outer hydration products to a more significant extent in CP conditions, compared to pulse CP conditions (compare Figs.1 and 2). The current flow is influencing the cement hydration and consequently alters the morphology and composition of the hydration products. Apparently, the pulse CP condition causes minor influence on the bulk microstructure, whereas the most significant micro-cracking appears in the specimens with highest current density (20mA/m²) in conventional CP application (compare Figure 3 with Figures.1 and 2). EDX analysis of the marked regions in Figures 1-3 reveals different Ca/Si ratio of the inner and outer hydration products, which is also varying depending on the used CP current regime – Table 1.

| Table 1: Ca/Si ratio of the inner and outer hydration products. |
|-----------------|---|---|---|---|---|---|
|                | Ca  | Si  | K   | Na  | Mg  | Al  |
| Fig. 1 (CP, 5mA/m²) |    |    |    |    |    |    |
| p.1             | 43.58 | 9.14 | 1.56 | 0.00 | 0.20 | 0.88 |
| p.2             | 43.69 | 9.77 | 1.50 | 0.09 | 0.33 | 1.19 |
| p.1a            | 35.07 | 11.48 | 1.47 | 0.60 | 0.74 | 1.48 |
| p.2a            | 37.62 | 11.28 | 1.66 | 0.75 | 0.53 | 1.56 |
| p.3             | 50.76 | 7.07 | 1.57 | 0.22 | 0.26 | 1.39 |
| Fig. 2 (pulse CP, 5mA/m²) |    |    |    |    |    |    |
| p.1             | 33.95 | 12.45 | 1.22 | 0.23 | 0.81 | 1.37 |
| p.2             | 33.17 | 12.55 | 1.35 | 0.38 | 0.72 | 1.65 |
| p.3             | 33.89 | 12.37 | 1.3 | 0.37 | 0.78 | 1.80 |
| p.4             | 32.67 | 13.08 | 1.31 | 0.31 | 0.87 | 1.28 |
| p.1a            | 36.15 | 12.29 | 1.18 | 0.14 | 0.62 | 1.26 |
| p.2a            | 35.47 | 12.23 | 1.61 | 0.25 | 0.45 | 1.65 |
| Fig. 3 (CP, 20 mA/m²) |    |    |    |    |    |    |
| p.1             | 30.25 | 14.12 | 1.17 | 0.32 | 0.97 | 1.48 |
| p.2             | 32.79 | 12.65 | 1.42 | 0.22 | 0.81 | 1.57 |
| p.1a            | 28.61 | 13.70 | 1.34 | 0.28 | 1.00 | 1.87 |
| p.2a            | 29.72 | 12.72 | 1.29 | 0.25 | 1.19 | 1.74 |
| p.3             | 50.15 | 10.61 | 0.87 | 0.10 | 0.35 | 0.92 |

The typical Ca/Si ratio of C-S-H in Portland cements is about 1.8 and as discussed in Chapter 3, a high Ca/Si ratio of at least 2.19 is a chloride-induced effect. Since all investigated specimens, including all protected groups P, were in conditions of chloride ingress (which is also before and in the time of CP application for groups P and till the end of the test), it was expected that chlorides will be present in different amounts, determined by the technical regimes, in all specimens. Apparently this is the case, since the Ca/Si ratio for the above presented (Figures 1-3) specimens is higher than 2.19. The Ca/Si ratio
however is lower in the specimen under pulse CP in regime 5 mA/m² (Fig.2) compared to the relevant conventional CP specimen (Fig.1). The observation suggests that lower amounts of chloride will be detected in the bulk cementitious matrix in case of pulse CP specimen, which is actually the case, as proved by chemical analysis and EDX observations of product layers. What can be concluded is that the microstructural properties of inner and outer hydration products are less affected in pulse CP conditions (lack of micro-cracks), whereas in conventional CP regime the current flow exerts obvious micro-cracking on one hand and is less effective in chloride withdrawal on the other, supported by the derived higher Ca/Si ratios and previously evidenced by a number of techniques. Although such a level of micro-cracking is not reported to have influence on mechanical properties of cement-based materials, it would most likely have impact on the behavior of the system as a whole. The observed micro-cracking can be of course a combined effect of leaching, drying shrinkage etc., along with the aforementioned mechanisms, which were however not subject to investigation in the thesis. Moreover, since all specimens were conditioned in equal environmental conditions, samples for ESEM analysis were prepared in identical manner and tested at same age as well, the differences in microstructural observations will be denoted only to different technical conditioning (pulse CP and conventional CP in this case).

2. Steel/cement paste interface (steel cross section). As previously mentioned, the effects of hydrogen embrittlement are considered in CP applications in reinforced concrete only, when the steel reinforcement is high tensile steel. Some preliminary observations on cross sections of the reinforced concrete specimens, discussed in this thesis, in terms of hydrogen induced or hydrogen facilitated crack growth will be presented in what follows. Figure 4 depicts typical cracks, observed in the steel cross-section of specimens under CP and pulse CP conditions (using 5 mA/m²). The cracks observed in the former case (Figure 4a) are generally about 300 to 500 µm in direction the centre of the cross section (i.e. the centre of the steel bar), whereas the cracks, observed in the latter case (pulse CP) are significantly lower as a number (the whole perimeter of the cross sections was observed, which is ~90 locations at magnification 200x) and are maximum of about 100 µm, extending in direction the centre of the steel bar (Figure 4b) (note that magnification of Fig.4b is 10 times higher than Figure 4a). Another important observation is that the cracks observed in the specimen under pulse CP, except significantly smaller as dimensions, are generally filled in with products (mainly magnetite or calcium-substituted magnetite), while the cracks under conventional CP are generally empty (shortly, about 40 µm, after the crack initiation point and towards the crack tip). The hypothesis is that these cracks are either as result of developed hydrogen, trapped in the vicinity of the steel surface and further crack growth was assisted by hydrogen evolution (as consequence of the CP); second, due to initial corrosion, inhomogeneities etc. on the steel surface, and consequently CP application, hydrogen develops, which assists in crack propagation on the place of initial damage.

Figure 4: Cracks, observed on cross-sections of the steel re-bars in conventional CP conditions (5 mA/m²) – (a) and in pulse CP conditions (5 mA/m² i.e. effective 2.5 mA/m²) – (b).
It is known that increased crack growth rates under cathodic protection are most probably due to hydrogen embrittlement, caused by hydrogen formation during cathodic protection, consequently the higher the cathodic current density, the higher will be the risk of embrittlement and rate of crack growth [1]. This statement however, as aforementioned, is generally accepted for high tensile strength steel. On the other hand it is also known, that cold rolled construction steel (as the one used in this experiment), could be susceptible to hydrogen assisted cracking, or more unlikely to embrittlement, due to the internal residual stresses after manufacturing [1]. Since the re-bars in this investigation war not under load, the aim is not to discuss embrittlement of the steel, but the hypothesis for hydrogen assisted cracking, which seems very likely, as consequence from the experimental conditions. Three are the most common hydrogen sources: 1) hydrogen, induced during the welding cycle; 2) hydrogen developed during cathodic protection or galvanic corrosion and 3) hydrogen development due to internal corrosion, localized corrosion or corrosion due to H2S. All three sources can be considered as generally available in the present study.

The following are some main features/mechanisms related to hydrogen entry, transport and trapping after [2].

**Entry of hydrogen:** the hydrogen atoms are developed on the surface due to electrochemical reactions, or they are transported to the surface as molecules. After being adsorbed on the metal surface, the atoms may either recombine to molecules and leave the surface, or the atoms can enter the metal. A clean metal surface, and especially a freshly formed surface (e.g. crack growth) is a very attractive location for hydrogen entry;

**Transport of hydrogen:** the reason why hydrogen is so detrimental to metals, is the high mobility of hydrogen. The coefficient of diffusion D, is orders of magnitude above the coefficient of other interstitially solved atoms as carbon and nitrogen.

**Trapping of hydrogen:** the phenomena can be expected at grain boundaries, dislocations, matrix-precipitate interfaces etc. Even small variations in chemical composition and thermo-mechanical cycles, may cause considerable changes in trapping and diffusivity of hydrogen in steel.

What is also reported and found relevant to the possibly “hydrogen assisted” growth of cracks observed in this study, is the transport of hydrogen in media as 3% NaCl and sea-water. As investigated by [2] in 3 % NaCl solution the hydrogen penetrates every segment of the crack surface and the damaging effect is due to hydrogen, liberated mainly at the crack tip. In contrast, in artificial sea-water calcareous deposit are formed on the crack surfaces and prevent hydrogen formation and/or hydrogen penetration of the steel.

These latter statements support the here presented observations of cracks and crack growth in conditions of CP or pulse CP. The calcium containing deposits are found in higher amounts in pulse CP conditions (in the form of Ca-rich layers or Ca(OH)2 plates, as discussed in the chapters of the thesis and also presented in Appendix V), along with lower amounts of chlorides and lower crystallinity of corrosion products (hence lower salinity in the cement layers adjacent to the steel reinforcement). The lower current densities, operating in pulse CP conditions, compared to conventional CP will determine lower amounts of formed hydrogen (hydrogen forms due to the cathodic reaction) and lower extent of hydrogen development on the steel surface. Taking all aforementioned into consideration and moreover, keeping in mind the observation that the amount and growth of cracks is different and obviously depending on the different regimes of protection (of initially identical steel bars, maintained in identical environmental conditions) i.e. significant amount and largely extending cracks related to the conventional CP regime, compared to the pulse CP regime, the suggestion for hydrogen assisted crack growth seems likely indeed.

References:
APPENDIX VII

Electrical schemes of the experimental set-up for measuring electrical resistance and the application of both conventional and pulse CP regimes in reinforced concrete cylinders (the measurements are discussed in Chapter 8)
Summary
Corrosion and protection in reinforced concrete
Pulse cathodic protection: an improved, cost-effective alternative

The increasing focus on durability aspects requires developing high knowledge-based materials, systems and technologies, which will yield improved or new functionalities and superior performance. Durability of reinforced concrete structures is a main concern in terms of performance and current industrial practice. There is always a need of developing new concepts, which are more flexible, safe and ecologically friendly, thus optimizing the civil structures performance, the relevant technologies, the life-cycle and service-life.

In non-damaged reinforced concrete, steel remains passive due to the high alkalinity of the concrete pore solution. If the concrete cover and the concrete bulk matrix are damaged, depending on the aggressiveness of the environment, corrosion of the steel reinforcement will be initiated. Impressed current cathodic protection (CP) is one of the protection techniques, applied to such systems. Along with minimizing the corrosion process, CP is known to have secondary positive effects in terms of enhancement of the OH− concentration and reduction of the chloride concentration near the steel surface. The locally elevated concentration of OH− caused by cathodic polarization results in substantial additional deposition of portlandite around the steel, which would be expected to have further beneficial effects in stabilizing the “passivity” of the steel rebars. Side effects however are known in these applications as well e.g. bond-strength degradation, alkali ion accumulation and concrete degradation due to alkali-silica reaction, and possible hydrogen embrittlement in case of prestressed concrete. Hence, the aim of this research was to study the possibilities for establishing a new or improved electrochemical method for corrosion prevention/ protection for reinforced concrete. The main objective was to develop an alternative for the impressed current CP, based on pulse technology. The new technique, denoted as pulse CP, was expected to achieve and address the following:

- To be able to achieve sufficient protection of the steel reinforcement on one hand and minimize the known side effects of the conventional CP techniques on the other;
- Since the principles of CP are electrochemical, a proper execution lies in the thorough understanding of the electrochemical mechanisms which cause the damage itself i.e. the corrosion process. Therefore, the performance of the pulse CP technique was evaluated after a comprehensive research on electrochemical and microstructural phenomena, related at first to the corrosion process in reinforced concrete;
- Further, elucidating the fundamental basis of CP in terms of the influence of current flow on both the steel reinforcement and the bulk concrete matrix, was essential for the evaluation of any new or improved CP technique, which is the pulse CP in this study;
- Finally, the main objective, in terms of establishing an improved CP technique, was achieved by implementing a multi-disciplinary approach i.e. correlating certain fields of science (electrochemistry and concrete materials science) and engineering applications (generally accepted criteria and standards for CP monitoring and control).

The evaluation of a new or improved technique for corrosion protection in reinforced concrete should at first take into consideration the fundamental electrochemical principles of the cause of
damage and the protection itself, thus being able to answer the questions: “Why exactly this technique works?; How the material properties will change with application of cathodic protection and how this will affect the protection process in time?”. The results of this thesis are as follows.

   - It is likely that the pore refining effect of accelerated hydration due to admixed chlorides in the plain mortars (consequently pore network structural changes) are affecting the electrical properties at most, which is in addition to the physico-chemical alterations in the C-S-H matrix. Electrical resistivity, electrolytic paths and chloride-induced corrosion respectively, are not only dependent on the presence of ions (as chlorides) in the pore solution, but are also a function of the pore structure of the bulk cementitious matrix.

   - The corrosion resistance of reinforced cement-based materials is due to the chemical nature and physical conditions operating at the steel/cement paste interface. Electrochemical techniques provide reliable results in determination of corrosion parameters for embedded steel in cement-based materials and can supply additional information (EIS in particular) in terms of electrical properties and bulk matrix characteristics.

   - The investigation of morphological alterations of corrosion products in reinforced mortars under cathodic protection provides important insight into the structural alterations induced by cathodic protection, and therefore, help to explain the efficiency of CP techniques.

   - Cathodic protection current efficiently prevents further corrosion on the steel surface and successfully decreases the chloride concentration around the steel bar. The result is significantly lower crystallinity and smaller dimensions of the corrosion products in protected conditions.

   - The correlation between EIS measurements and microstructure investigations allows breaking down the electrical properties of reinforced mortar and the electrochemical performance of the steel reinforcement during the corrosion process and during CP application to the micro-level.

   - The combination of techniques constitutes a reliable and useful tool for quantitative characterization of the interface microstructure and of the various corrosion products, and thereby offers better insight into the electrochemical phenomena during corrosion of the steel reinforcement in concrete structures.

2. Material properties in conditions of CP current flow.
   - A steady current (as normally used in conventional CP applications) tends to bring about unfavorable modifications of the material structure both in the bulk (reducing porosity) and in the interfacial transition zone (enlarging the gap at the aggregate surface) to a significant extent, leading to a high level of structural heterogeneity of the materials. In
addition steady current yields non-uniform electrical properties and thereby results in disturbance of the electrolytic path in the materials under study.

- Both current regimes (conventional and pulse) reduce the portion of connected conductive paths in the material microstructure and thereby increase the total electrical resistivity. However, in case of pulse regime there is a favorable mechanism of charge-discharge cycling, and the ions are prevented from ‘piling up’. Hence the pulse regime favors ion transport.

- Microstructure observations and chemical analysis reveal the underlying mechanisms to be due to a more homogenous material microstructure (including slightly refined pore structure), dense interfacial transition zones, and promoted ion and water transport.

3. Pulse CP – an improved, cost effective alternative.

- The introduced pulse CP, based on a block-shaped, current pulse signal, is at least as effective as the conventional CP in terms of achieving the required steel polarization, thus providing adequate protection of the steel reinforcement.

- Potentio-dynamic polarization determines similar electrochemical parameters for both types of protection and, taking into consideration the at least 50 % lower CP current density used in the pulse regime, the efficiency and cost-effectiveness of the latter are confirmed.

- The pulse protection regime is found to be more efficient as far as ion transport is concerned and achieves the so called “open circuit potential passivity” more effectively, which is found to be dependent on the secondary beneficial effects of favorable cement chemistry around the steel bars in pulse CP conditions. Moreover, the surface film, formed in pulse CP conditions appears to be more homogeneous and resistive, compared to the conventional CP regime.

- The lower cathodic current density, as in pulse CP applications for reinforced concrete, will lead to reduced side effects and more pronounced beneficial secondary effects, compared to conventional CP. The former are mainly related to bond/strength degradation on the steel/cement paste interface; the latter are in terms of enhanced chloride withdrawal, calcium-rich layers accumulation, favorable morphology and crystallinity of the product layers on the steel surface.

- Pulse cathodic protection is an efficient, cost-effective and superior alternative for corrosion protection in reinforced concrete structures.
Samenvatting
Corrosie en bescherming van gewapend beton
Puls kathodische bescherming: een verbeterd, kostenbesparend alternatief

De toenemende belangstelling voor duurzaamheidsaspecten vereist de ontwikkeling van hoog ontwikkelde materialen, systemen en technologieën, die voor verbeterde of nieuwe functionaliteit en superieure prestaties zorgen. Duurzaamheid van gewapend betonnen constructies is een belangrijk aspect waar het prestaties en de huidige industriële toepassingen betrekking op hebben. Het blijft altijd nodig om nieuwe concepten te ontwikkelen die flexibeler, veiliger en milieuvriendelijker zijn en om daarmee het gedrag van civiele constructies, de relevante desbetreffende technologieën, de levenscyclus en de levensduur te optimaliseren.

In onbeschadigd gewapend beton blijft staal passief vanwege het hoge alkaligehalte van de poriënoplossing van het beton. Als de betondeklaag en de beton matrix beschadigd zijn, zal afhankelijk van de mate van agressiviteit van het milieu, corrosie van de staalwapening gaan ontstaan. De huidige kathodische bescherming (CP) via opgedrukte gelijkstroom is een van de technieken die worden toegepast om zulke systemen te beschermen. Naast het minimaliseren van het corrosieproces staat CP bekend om zijn secundaire positieve effect voor wat betreft verhoging van de OH⁻ concentratie en verlaging van de chloride concentratie aan het staaloppervlak. De plaatselijk verhoogde OH⁻ concentratie door kathodische polarisatie resulteert in een aanzienlijke afzetting van portlandite rondom het staal, waarvan mag worden verwacht dat het nog meer gunstige effecten heeft op het stabiliseren van de ‘passiviteit’ van het staal. Er zijn bij deze toepassingen echter neveneffecten vastgesteld, zoals bijvoorbeeld afgenomen hechtkracht, alkali ion ophoping en achteruitgang van de betonkwaliteit door alkali-silica reactie, en verder ook, in geval van voorgespannen beton, mogelijk door waterstof veroorzaakte broosheid. Daarom was het doel van deze studie het bestuderen van de mogelijkheden voor het vinden van een nieuwe of verbeterde elektrochemische methode voor corrosie preventie/bescherming voor gewapend beton. Het voornaamste doel was een alternatief te ontwikkelen voor de huidige gelijkstroom CP, die is gebaseerd op puls technologie. Van de nieuwe techniek, aangeduid als puls CP, werd verwacht dat daarmee het volgende zou kunnen worden bereikt:

- Enerzijds de mogelijkheid om voldoende bescherming van de staalwapening te verkrijgen en anderzijds om de bekende neveneffecten van de conventionele CP technieken te minimaliseren.
- Daar CP op elektrochemische principes berust, is een goede uitvoering afhankelijk van een grondig inzicht in de elektrochemische mechanismen die de schade veroorzaken, namelijk het corrosieproces. Daarom is de werking van de puls CP techniek geëvalueerd na omvangrijk researchwerk op elektrochemisch en microstructurele verschijnselen die allereerst zijn gerelateerd aan het corrosieproces bij gewapend beton.
- Voorts, meer licht laten schijnen op de fundamentele basis van CP voor wat betreft de invloed van een elektrische stroom op zowel de staalwapening als de beton matrix, essentieel

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voor de evaluatie van elke nieuwe of verbeterde CP techniek. In deze studie is dit de puls CP studie.

Het hoofddoel tenslotte, het vinden van een verbeterde CP techniek, is gerealiseerd door het implementeren van een multidisciplinaire aanpak, het bijeenbrengen van bepaalde gebieden van wetenschap (elektrochemie en betonmaterialen) en bouwkundige toepassingen (algemeen aanvaarde criteria en normen voor CP besturing en controle).

De evaluatie van een nieuwe of verbeterde techniek voor corrosiepreventie bij gewapend beton dient zich allereerst te richten op de fundamentele elektrochemische principes waar het de oorzaak van de schade en de aanwezige bescherming betreft, teneinde de volgende vragen te kunnen beantwoorden: “Wat is het precies waarom deze techniek werkt? Hoe zullen de materiaaleigenschappen veranderen bij toepassing van kathodische bescherming en op welke manier zal dit in de loop der tijd invloed hebben op het beschermingsproces?” De resultaten van dit promotie-onderzoek zijn de volgende.


- Het ligt voor de hand dat het poriënverfijnende effect van versnelde hydratie door bijgemengde chlorides in (ongewapende) mortels (met als gevolg structurele veranderingen in het poriënnetwerk) de meeste invloed uitoefenen op de elektrische eigenschappen, naast de fysio-chemische veranderingen in de C-S-H matrix. Elektrische weerstand, electrolytisch transport door chloride in gang gezette corrosie zijn niet alleen afhankelijk van de poriënstructuur van de cement matrix.

- De weerstand tegen corrosie van gewapende op cement gebaseerde materialen is te danken aan het chemische karakter en de fysische condities bij het staal/cement hechtlvlak. Elektrochemische technieken verschaffen betrouwbare resultaten bij het opstellen van corrosie parameters voor staalwapening in op cement gebaseerde materialen en kan aanvullende informatie (in het bijzonder EIS) verschaffen waar het elektrische eigenschappen en matrix karakteristieken betreft.

- Het onderzoek van morfologische wijzigingen van corrosieproducten in gewapende mortels onder kathodische bescherming geeft belangrijk inzicht in de structurele wijzigingen, veroorzaakt door kathodische protectie, en helpen daardoor de werkaanheid van CP technieken te verklaren.

- Kathodische bescherming beschermt tegenwoordig verdere corrosie op het staaloppervlak en verlaat de chloride concentratie rond de stalen wapening op succesvolle wijze. Het resultaat is een aanzienlijk lagere kristallisatie en kleinere afmetingen van de corrosieproducten onder beschermende omstandigheden.

- De correlatie tussen EIS metingen en onderzoek naar de microstructuur maakt het mogelijk de elektrische eigenschappen van gewapende mortel en de electrochemische
prestatie van de staalwapening bij het corrosieproces en tijdens de CP toepassing op micro niveau precies in kaart te brengen.

- De combinatie van technieken levert een betrouwbaar en nuttig gereedschap op voor kwantitatieve karakterisering van het raakvlak van de microstructuur en van de diverse corrosieproducten, en biedt daardoor een beter inzicht in de elektrochemische verschijnselen gedurende het corrosieproces van de staalwapening in betonconstructies.

2. Materiaaleigenschappen onder elektrische stroom condities bij CP
- Een gelijkstroom (zoals gewoonlijk bij CP toepassingen gebruikt) heeft in belangrijke mate de neiging om ongunstige wijzingen te veroorzaken in de materiaalstructuur, zowel in de bulk (verminderde porositeit) als in de overgangzone tussen het toeslagmateriaal en de cementsteen (hetgeen de porieruimte bij het aggregaatoppervlak vergroot). Dit leidt tot een grote structurele heterogeniteit van de materialen. Voorts geeft gelijkstroom niet-uniforme elektrische eigenschappen en resulteert daardoor in een verstoring van het elektrolytische pad in de bestudeerde materialen.

- Zowel de huidige regimes (conventionele en puls) reduceren het gedeelte van met elkaar verbonden geleidepaden in de microstructuur van het materiaal en verhogen daardoor de totale elektrische weerstand. In het geval van het puls regime echter, is er een gunstig mechanisme van een opladings- en ontladingscyclus, en de ionen kunnen zich niet meer ‘ophopen’. Daarom is er bij het puls regime voorkeur voor ionentransport.

- Microstructuur observaties en chemische analyse onthullen dat de mechanismen die eraan ten grondslag liggen veroorzaakt worden door een homogenere materiaalstructuur (incl. enigszins verfijnde poriënstructuur), “dichtere” overgangszones en bevordering van ionen- en watertransport.

3. Puls CP – een verbeterd, kostenbesparend alternatief
- De hier geïntroduceerde puls CP, gebaseerd op een blokvormig elektrisch pulssignaal, is minstens zo effectief als de conventionele CP voor wat betreft het bereiken van de benodigde staalpolarisatie en verschaf aldus adequate bescherming van de staalwapening.

- Potentiaal dynamische polarisatie bepaalt overeenkomstige elektrochemische parameters voor beide soorten protectie, en, de minstens 50% lagere CP stroomdichtheid die bij het puls regime gebruikt wordt, in aanmerking nemend, worden de efficiëntie en kostenbesparing van de laatste bevestigd.

- Het puls protectie regime is efficiënter bevonden waar het ionentransport betreft en bereikt de z.g. ‘open circuit potentiële passiviteit’ doeltreffender. Vastgesteld is dat deze
afhankelijk is van secundaire voordelige effecten van gunstige cementchemie rondom de bewapening onder puls CP omstandigheden. Bovendien blijkt het passiveringslaagje aan de staaloppervlakte, dat onder CP omstandigheden wordt gevormd, homogener te zijn en meer weerstand te bieden dan onder het conventionele CP regime.

- De lagere kathodische stroomdichtheid, zoals in puls CP toepassingen voor gewapend beton, zal, vergeleken met conventionele CP, tot minder nevenwerkingen leiden en tot meer uitgesproken gunstige secundaire effecten. Eerstgenoemde zijn hoofdzakelijk gerelateerd aan hechting/sterkte verminderen op de staal/cement hechting grensvlakken. De laatstgenoemde in termen van verhoogde chloride onttrekking, accumulatie van kalkrijke lagen, gunstige morfologie en kristallisatie van de productlagen op het staaloppervlak.

- Puls kathodische protectie is een efficiënt, kostenbesparend en superieur alternatief voor corrosiebescherming in gewapend betonnen constructies.
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