

**INVESTIGATING THE EFFECT OF ISOTHERMAL AND
TEMPERED MICROSTRUCTURES ON THE PASSIVITY
AND CORROSION RESISTANCE OF STEEL REBAR IN
SIMULATED CONCRETE ENVIRONMENT**

BY

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DHAHRAN, SAUDI ARABIA

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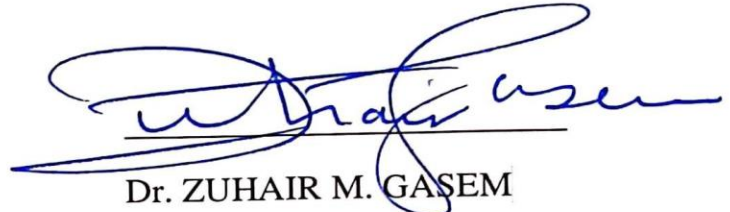
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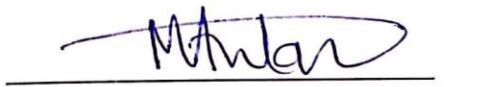
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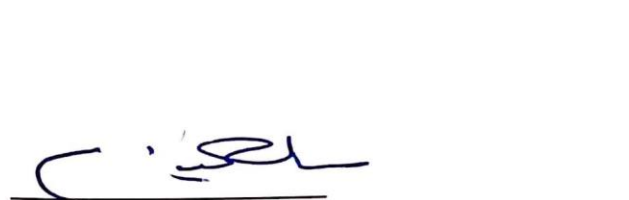
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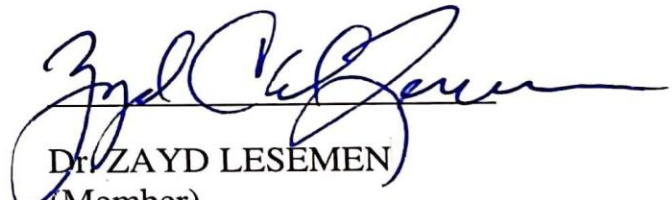
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Dedicated To
All the Hardships & Challenges
I Have Had Gone Through While Making My Way In Life...!

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LIST OF ABBREVIATIONS

GNP	: Gross National Product
TMT	: Thermo-Mechanical Treatment
QST	: Quenched and self-Tempered
AE	: Atmospheric Exposure
SCPS	: Simulated Concrete Pore Solution
CPS	: Concrete Pore Solution
SEM	: Scanning Electron Microscope
XRD	: X-ray Diffraction
XPS	: X-ray Photoelectron Spectroscopy
AC	: Alternating Current
WE	: Working Electrode
RE	: Reference Electrode
CE	: Counter Electrode
SCE	: Saturated Calomel Electrode
OCP	: Open Circuit Potential
LPR	: Linear Polarization Resistance

PDP	: Potentiodynamic Polarization Resistance
EIS	: Electrochemical Impedance Spectroscopy
PS	: Potentiostatic
E_{corr}	: Corrosion Potential (V)
I_{corr}	: Corrosion Current Density (A/cm^2)
R_p	: Polarization Resistance
R_s	: Solution Resistance
R_f	: Film Resistance
R_{po}	: Pore Resistance
R_{ct}	: Charge Transfer Resistance
CPE	: Constant Phase Element
T	: Temperature
$^{\circ}\text{C}$	: Degree Celsius
Fig.	: Figure

ABSTRACT

Full Name : Muhammad Faizan
Thesis Title : Investigating the Effect of Isothermal and Tempered Microstructures on the Passivity and Corrosion Resistance of Steel Rebar in Simulated Concrete Environment
Major Field : Mechanical Engineering
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The effectiveness of corrosion prevention of steel rebar embedded in concrete structure hinges on its passivation tendency and the ability to which it could be stable when exposed to chloride and carbonation. This study investigated the effects of isothermal (at 650, 570, 500, 450, and 400 °C) and quench and tempered (Q&T at 300 and 400 °C) heat treatments on the corrosion resistance of steel rebar immersed in simulated cement pore solution (CPS) with and without chloride addition. Electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR), and potentiodynamic polarization (PDP) techniques were utilized to assess the electrochemical characteristics. The composition of the oxide film was analyzed using X-ray photoelectron spectroscopy (XPS).

The results of various electrochemical techniques indicated that Q&T rebar samples exhibited higher corrosion resistance compared to rebar samples isothermally heat-treated in both chloride-free and chloride-containing CPS. EIS results in CPS containing chloride revealed that the Q&T 400°C rebar provided 7.2 times higher film resistance (R_f) and 2.3 times higher charge transfer resistance (R_{ct}) compared to the corresponding values of R_f and R_{ct} noted for the isothermally heat-treated rebar at 400°C. In the presence of chloride, the estimated film thickness (δ_f) of 2.5 nm was calculated for

the Q&T 400°C rebar, and 0.8 nm was calculated for the isothermal treated rebar at 400°C. In chloride, the rebar sample Q&T at 400°C showed slightly higher uniform corrosion resistance but marked enhanced pitting potential as compared to the sample Q&T at 300°C.

XPS analysis of selected samples revealed that the composition ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the naturally formed passive film varied with the substrate microstructure and correlated well with the rebar's passivation performance. For instance, spontaneously formed passive film on Q&T 400°C rebar was found to be highly protective and the quantitative analysis of the passive film composition showed a higher ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ (2.57) with approximately 72% $\text{FeO}/\text{Fe}_3\text{O}_4$ (Fe^{2+}) and 28% $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{3+}). On the contrary, the lowest $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (1.65) was exhibited by the 400°C-isothermally heat-treated rebar with approximately 62% $\text{FeO}/\text{Fe}_3\text{O}_4$ (Fe^{2+}) and 38% $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{3+}).

The second part of the study investigated calcium nitrate $\text{Ca}(\text{NO}_3)_2$ as a potential inhibitor for the corrosion of rebar in chloride-containing environments. The inhibition effect was investigated on the electrochemical performance of heat-treated rebar samples in CPS containing 2 and 4 wt.% calcium nitrate with the presence of chloride. Electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR), and potentiodynamic polarization (PDP) techniques were utilized to assess the electrochemical characteristics. The electrochemical results revealed that NO_3^- ions effectively inhibited rebar corrosion in the presence of chloride ions by suppressing localized corrosion in the form of pitting. Consequently, the charge transfer resistance (R_{ct}) was observed to be dominating in the presence of calcium nitrate inhibitors. R_{ct} enhanced 4.5 times for Q&T 400°C rebar sample in CPS solution containing 2 wt.%

calcium nitrate inhibitor compared to the rebar exposed to CPS with 0 wt.% calcium nitrate. The effective corrosion inhibition efficiency of 78% was achieved based on R_{ct} for the Q&T 400°C rebar sample in the presence of 2 wt.% calcium nitrate in CPS. The inhibition mechanism was more dominant in cathodic region as a cathodic shift was seen in PDP curves. Adsorption of nitrate ions was evident from AFM and FTIR spectra, which provided a barrier layer and possibly restricted the accessibility of Cl^- diffusion to the metal-film interface. The highest film thickness (δ_f) of 2.25 nm was estimated for the Q&T 400°C rebar in comparison to 0.5 nm calculated for Q&T 300°C rebar.

ملخص الرسالة

الاسم الكامل: محمد فيضان

عنوان الرسالة: دراسة تأثير البنية المجهرية المصلدة ومتساوية الحرارة على سلبية ومقاومة التآكل لحديد التسليح في

بيئة خرسانية مقلدة

التخصص: الهندسة الميكانيكية

تاريخ الدرجة العلمية: ديسمبر 2022

بحثت هذه الدراسة في آثار المعالجات المتساوية الحرارة (عند 400، 450، 500، 570، 650 درجة مئوية) والتبريد والمخفف (T&Q عند 300 و 400 درجة مئوية) على مقاومة التآكل لقضبان التسليح الفولاذية المغمورة في محلول مسام الأسمنت المحاكى (CPS) مع وبدون إضافة الكلوريد. تم استخدام تقنيات التحليل الطيفي للمقاومة الكهروكيميائية (EIS)، ومقاومة الاستقطاب الخطي (LPR)، والاستقطاب الديناميكي (PDP) لتقييم الخصائص الكهروكيميائية. تم تحليل تركيبة فيلم الأكسيد باستخدام التحليل الطيفي للأشعة السينية الضوئية (XPS).

أشارت نتائج التقنيات الكهروكيميائية المختلفة إلى أن عينات حديد التسليح Q&T أظهرت مقاومة أعلى للتآكل مقارنة بعينات حديد التسليح المعالجة حرارياً في كل من CPS الخالية من الكلوريد والمحتوية على الكلوريد. كشفت نتائج EIS في CPS المحتوي على كلوريد أن حديد التسليح Q&T عند 400 درجة مئوية يوفر مقاومة أعلى للفيلم (R_f) بمقدار 7.2 مرة ومقاومة أعلى لنقل الشحنة (R_{ct}) بمقدار 2.3 مرة مقارنة بالقيم المقابلة لـ R_{ct} و R_f المذكورة في حديد التسليح المعالج حرارياً متساوي الحرارة. عند 400 درجة مئوية وفي وجود الكلوريد، تم حساب سماكة الفيلم المقدرة (δ_f) البالغة 2.5 نانومتر لحديد التسليح Q&T عند 400 درجة مئوية، وتم حساب 0.8 نانومتر لحديد التسليح المعالج متساوي الحرارة عند 400 درجة مئوية. في الكلوريد، أظهرت عينة حديد التسليح Q&T عند 400 درجة مئوية مقاومة تآكل موحدة أعلى قليلاً ولكنها لاحظت ارتفاع في مقاومة تآكل النقر مقارنة بعينة Q&T عند 300 درجة مئوية.

كشف تحليل XPS لعينات مختارة أن نسبة التركيب Fe^{2+}/Fe^3 في الفيلم المتكون بشكل طبيعي تختلف مع البنية المجهرية للركيزة وترتبط جيدًا بأداء تخميل حديد التسليح. على سبيل المثال، وجد أن الفيلم الذي تم تشكيله تلقائيًا على حديد التسليح Q&T عند 400 درجة مئوية يوفر حماية عالية وأظهر التحليل الكمي لتكوين الفيلم نسبة أعلى من Fe^{2+}/Fe^3 (2.57) مع ما يقرب من 72% FeO/Fe_3O_4 (Fe^{2+}) و 28% $Fe_2O_3/FeOOH$ (Fe^{3+}). على العكس من ذلك، تم عرض أدنى نسبة Fe^{2+}/Fe^3 (1.65) بواسطة حديد التسليح المعالج بالحرارة بدرجة حرارة 400 درجة مئوية مع ما يقرب من 62% FeO/Fe_3O_4 (Fe^{2+}) و 38% $Fe_2O_3/FeOOH$ (Fe^{3+}).

الجزء الثاني من الدراسة تناول نترات الكالسيوم $Ca(NO_3)_2$ كمثبط محتمل لتآكل حديد التسليح في البيئات التي تحتوي على الكلوريد. تم دراسة تأثير التنشيط على الأداء الكهروكيميائي لعينات حديد التسليح المعالجة حراريًا في CPS التي تحتوي على 2 و 4% بالوزن من نترات الكالسيوم مع وجود الكلوريد. تم استخدام تقنيات التحليل الطيفي للمقاومة الكهروكيميائية (EIS)، ومقاومة الاستقطاب الخطي (LPR)، والاستقطاب الديناميكي الديناميكي (PDP) لتقييم الخصائص الكهروكيميائية. أظهرت النتائج الكهروكيميائية أن أيونات NO_3^- تمنع بشكل فعال تآكل حديد التسليح في وجود أيونات الكلوريد عن طريق قمع التآكل الموضعي. ونتيجة لذلك، لوحظ أن مقاومة نقل الشحنة (R_{ct}) هي المهيمنة في وجود مثبطات نترات الكالسيوم. تم تعزيز R_{ct} 4.5 مرات لعينة حديد التسليح Q&T عند 400 درجة مئوية في محلول CPS الذي يحتوي على 2% بالوزن من مثبط نترات الكالسيوم مقارنة بحديد التسليح المعرض لـ CPS مع 0% بالوزن من نترات الكالسيوم. تم تحقيق كفاءة تنشيط التآكل الفعالة بنسبة 78% لعينة حديد التسليح Q&T عند 400 درجة مئوية في وجود 2% بالوزن من نترات الكالسيوم في CPS. وكان امتزاز أيونات النترات واضحًا من أطياف AFM و FTIR، التي وفرت طبقة حاجزة وربما قيدت إمكانية وصول الكلور إلى واجهة الغشاء المعدني. تم تقدير أعلى سمك للفيلم (δ_f) يبلغ 2.25 نانومتر لحديد التسليح Q&T عند 400 درجة مئوية مقارنة بـ 0.5 نانومتر لحديد التسليح Q&T عند 300 درجة مئوية.

CHAPTER 1:

INTRODUCTION

1.1. Problem Statement

Carbon steel is the most demanding type of steel across the globe among steel families because of its enduring strength, toughness, ductility, and cost. This is the only material whose production is increasing day by day and it will not be wrong to claim that its production reflects the development and progress of a certain country. Steel rebar as a reinforcement is being used in the construction industry worldwide due to its structural strength and relatively low cost [1]–[3]. The durability of the concrete is ensured by the high alkalinity ($\text{pH} > 13$) of its interstitial pore solution. A thin protective passive film of stable oxide is formed on steel rebar which protects it from corrosion [4]–[6]. However, the deterioration of the reinforced concrete structure could take place either due to carbonation, or due to chloride depassivation. This not only reduces the structural integrity but puts human life to risk as well. Although steel rebar is designed in such a way that it could limit concrete deterioration, still many other factors limit its durability. Amongst them, corrosion of steel rebar is a substantial issue causing the most frequent degradation of reinforced concrete structures. This mechanism is usually experienced in coastal regions bearing severe environmental conditions. Consequently, a detrimental damaging situation has to be dealt with due to the formation of corrosion products on rebar which not only reduces the adherence tendency in between the metallic surface and

concrete structure but also initiates cracks due to the exertion of tensile stresses [7]. In addition, the presence of chloride in concrete makes the concrete structure even more susceptible. Structural catastrophic failure could happen once the chloride content reaches to a threshold value [8]–[10]. Because of their diffusion tendency, the chloride particles catalyze the dissolution mechanism by annihilating the outer Fe_2O_3 layer first and then the inner $\text{FeO}/\text{Fe}_3\text{O}_4$ protective layer later by the formation of pits, followed by the rapid degradation coming through the crack formation and propagation [11], [12]. The losses are reported to be 22.1 billion \$ per year in the USA [13]. In the gulf countries, the direct or indirect loss due to corrosion are more severe than in the rest of the world because of the harsh environment..

It is estimated that nearly 15-20% of losses due to corrosion can be controlled by corrosion-preventing techniques. Preventive coatings, anodic and cathodic protection, inhibitors, material selection, and improving mechanical design are some of the methods used to inhibit reinforcement corrosion [14], [15]. A significant amount of research has been directed to enhance steel rebar resistance against corrosion by several techniques. The most common are;

- (i) Hot dipped galvanizing
- (ii) Changing the alloy composition
- (iii) Developing organic/inorganic coatings (epoxies, paints etc.)
- (iv) Heat treatment
- (v) Cathodic protection
- (vi) Inhibitors

Although all of the above-mentioned protection techniques are being used but none of them is completely reliable and warrants the continuation of extensive research in order to combat this problem. Steel rebar has the tendency to passivate especially in highly alkaline environments ($\text{pH} > 13$) and the protective passive oxide layer prevents it from further corrosion and deterioration. But this passive layer degrades with time under the presence of chloride, sulfides, and carbon dioxide and thus does not offer the required long-term protection against corrosion [3], [16]. This phenomenon leads to the slow degradation of the structures.

Numerous studies [3], [17] have shown that nitrites ions act as beneficial inhibitors in concrete matrix and reduce corrosion. It is reported that these ions react with ferrous ions and produce the Fe_2O_3 layer which ultimately reduces the corrosion rate by acting as anodic corrosion inhibitors [16]. However, the addition of an inappropriate amount of these inhibitors could lead to pitting if the surface was already in a passivation state [3]. In addition to this, when concrete is surrounded by a marine environment or the concrete matrix is prepared from contaminated sand then chloride can penetrate through the pores of the concrete matrix and depassivate the oxide layer on the steel surface. As steel is embedded in concrete, having a highly alkaline environment, it develops a passive layer over it but this passive state is challenged by the presence of chloride ions, and ultimately corrosion rate depends on the chloride/hydroxyl ratio [18], [19].

Nevertheless, the electrochemical testing of steel in the solid concrete matrix is difficult to study because of the presence of high resistivity, porosity, and difficult cell design. Hence the alternate way to investigate the corrosion of steel rebar is to simulate the concrete pore solution. Many researchers have conducted studies in just $\text{Ca}(\text{OH})_2$

solution and simulated it as a concrete solution but the fact is that concrete simulated solution is much more complex [20][21] and a number of such solutions have been reported [22]–[26].

Though there is a consensus that the passivation tendency of steel rebar can be enhanced by introducing it in a highly alkaline solution simulating to concrete environment, the behavior of heat-treated rebar has never been understood in concrete systems. Besides, the inhibition tendency of the nitrate based inhibitor has also not been evaluated against the heat-treated rebar in view of corrosion resistance and passivation. So, the objectives of the current research are to investigate the effect of heat treatment with and without the presence of nitrate based inhibitor in improving the chloride-induced corrosion resistance and passivation of rebar in concrete environment.

1.2. Recent Research Work

Yilmaz et al. [27] in their recent work examined the combination of ferrite-pearlite and ferrite-martensite phases in low carbon steel and studied the characteristics of the protective layer when exposed to a 0.1 M NaOH solution. They reported that, through controlled heat treatments, similar amounts of ferrite were achieved in both ferrite-pearlite and ferrite-martensite microstructures. By subjecting the samples to potentiostatic polarization and electrochemical impedance spectroscopy (EIS), the research findings indicated that the passive films formed on the ferrite-martensite microstructure displayed weaker barrier properties compared to those on the ferrite-pearlite microstructure. This outcome was attributed to the higher concentration of charge carriers within the passive layer of ferrite-martensite specimens, a factor determined through Mott-Schottky analysis. The underlying reason for this variation was linked to the intricate

morphological structure of the martensite phase, which led to the formation of a more defective passive film.

Yelmaz et al. in another recent study [28] have investigated the effect of size of the initial austenite grains (known as prior austenite grain size or PAGS) on the characteristics of the protective layer in martensitic steels. Analysis using electron backscatter diffraction revealed that different heat treatments resulted different PAGS ranging from 5 to 66 μm . The effectiveness of the passive film's barrier properties declined as the grain size was reduced to 28 μm , which they attributed to the increased concentration of charge carriers and decreased proportion of $\gamma\text{-Fe}_2\text{O}_3$ within the passive films. However, when the PAGS is further reduced to 5 μm , the barrier properties improved due to the modifications within the martensite structure. They reported that this enhancement was a consequence of the increased proportion of $\gamma\text{-Fe}_2\text{O}_3$.

Hussain et al. [29] studied the effect of reinforcing bar microstructure on passive film exposed to simulated concrete pore solution. To enrich the understanding and insights in this realm, the authors of the study explored the protective characteristics of two specific categories of steel rebars — namely, tempered martensite (TM) and pearlite-ferrite (PF) — following their exposure to the concrete's pore solution. They conducted extensive analysis on the microstructures of both rebar types using electrochemical impedance spectroscopy and polarization techniques. Their findings disclosed that a protective film was formed on the surface of steel with a TM microstructure and exhibited a notably accelerated growth rate and greater stability in comparison to the film formed on steel with a PF microstructure. They attributed this enhanced

protectivness to the creation of a tightly compact and firmly adherent oxide film on TM steel.

Kumar et al. [30] investigated the impact of five distinct microstructures — coarse, fine, and very fine ferrite-pearlite, martensite, and tempered martensite — achieved through different cooling methods (furnace cooling, air cooling, forced air-cooling, water quenching, and tempering) of steel rebar. Their investigation delved into the corrosion behavior of these microstructures in both freely aerated conditions and in conditions involving simulated concrete pore solutions with or without chloride contamination. The corrosion performance of the steel with the five varied microstructures revealed that, in the simulated concrete pore solution (SCP), the corrosion rates of the steel were found to be quite similar. However, in the SCP solution containing chloride ions, the corrosion rates were noticed in an increasing trend in the following order: forced air-cooled steel, air-cooled steel, quenched steel, furnace-cooled steel, and tempered steel.

Pillai et al. [31] in their work investigated the microstructural and corrosion characteristics of quenched and self-tempered (QST) steel rebars. They disclosed that discontinuities in tempered martensite (TM) phase may occur due to improper quenching, and in numerous stages, defective TM phases have been detected. The influence of these defects in the TM-phase on the potential for localized corrosion was assessed through cyclic potentiodynamic polarization (CPP) test outcomes with varying chloride (Cl) concentrations. The findings indicate that ferrite-pearlite (FP) is more vulnerable to pitting corrosion compared to TM. Specifically, FP exhibits 11% and 16% lower chloride threshold (Cl_{th}) values than TM under MSP and SP conditions, respectively.

Consequently, when a discontinuity is present, there may be a preference for pitting at a lower chloride level (on FP) as opposed to the Cl_{th} in a scenario with an uninterrupted TM-phase. This signifies a 20% reduction in the service life between reinforced concrete structures using high-quality and low-quality steel.

Dong et al. [32] conducted a research on calcium nitrate ($Ca(NO_3)_2$) inhibition for rebar corrosion and provided an insights to the reactions kinetics in concrete. Their findings consolidated that calcium nitrate has proven itself as a potential inhibitor for preventing the corrosion of steel in environments with high levels of halides. They used vertical scanning interferometry to examine the changes in surface topography caused by corrosion pits and overall corrosion in solution of 10% calcium chloride ($CaCl_2$) or 10% calcium bromide ($CaBr_2$). Their findings revealed that at lower concentrations of $Ca(NO_3)_2$ (around 1%), NO_3^- ions effectively inhibited rebar corrosion in the presence of both $CaCl_2$ and $CaBr_2$ by suppressing the corrosion at rapidly corroding pitting sites. However, at higher concentrations, the effectiveness of calcium nitrate as a corrosion inhibitor was significantly diminished.

1.3. Proposed Work and Objectives

Despite acknowledging the impact of microstructure morphology on the corrosion performance of steel [33]–[40], significant work has not reported yet revealing the effect of major microstructural phases, namely, pearlite, bainite, martensite, and tempered martensite on the passivation tendency of steel rebar. Though, it has been established that cementite acts as a cathode due to the higher carbon content and ferrite is the anode in the micro-galvanic couple existing in steel [41]. However, all these studies have been done at the partial level and clear insight into the true concrete simulated structure has never been addressed so far. For instance, some have studied the effect of just heat treatment in seawater [42], [43] while others studied the effect of alkaline solution either without any heat treatment [44]–[48] or just limited to the martensitic-ferritic type of specific heat treatment [27], [28]. Similarly, some heat treated studies never went into passivation investigation at all [30], [49]. So, the effect of variation in cementite and ferrite morphologies - achieved through isothermal and Q&T microstructures- on the synergy of electrochemical and passivation characteristic of steel rebar in a concrete environment can be studied convincingly. Because it is still questionable how the heat treatment can contribute to the growth and performance of passive film under a real concrete simulating (alkaline+chloride) environment which is much more complicated compared to the individual alkaline or chloride study.

Furthermore, calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) as a corrosion inhibitor has been studied for several years and plays a vital role in enhancing the durability and service life of reinforced concrete structures in presence of chloride [50]–[53]. Long-term tests [54], laboratory models [55], as well as the theory behind simulation [56], [57] have been

studied on steel rebar. The inhibition tendency of the nitrate based inhibitor ($\text{Ca}(\text{NO}_3)_2$) may have a significant effect on heat-treated rebar samples in view of corrosion resistance, passivation and restricting the diffusion of chloride, which has never been evaluated till date.

So, the objectives of the current research work are to investigate:

1- The effect of heat treated microstructures such as coarse and fine pearlite, upper and lower bainite, martensite, and tempered martensite on the corrosion resistance and passivation tendency of steel rebar in concrete simulated environment with and without the presence of chloride.

2- The qualitative and quantitative analysis of the passive film in order to evaluate the role of each microstructure contributing in the development of protective or defective nature of film.

3- The effect of nitrate based inhibitor ($\text{Ca}(\text{NO}_3)_2$) in improving the chloride-induced corrosion resistance and passivation of heat-treated rebar in a concrete simulated environment.

The electrochemical behavior of steel rebar would be analyzed with the help of electrochemical impedance spectroscopic (EIS) and dynamic polarization tests (PDP) in freely aerated CPS, with and without the presence of calcium nitrate inhibitor. The passive film would be investigated by x-ray photoelectron spectroscopy (XPS). Nitrate adsorption would be evaluated with the help of AFM and FTIR spectroscopy.

CHAPTER 2:

LITERATURE REVIEW & BACKGROUND

2.1. Literature Review

In this era, steel rebar is produced with the latest patent technology-THERMEX. The importance of this technique is that the outer surface of the steel rebar is rapidly quenched by the water below M_s (start of martensite) temperature [58]–[61]. This phase of the process creates a hardened martensite but the inner core of the material is still at higher temperature and as a result, it remains austenite. This residual heat moves from the inside of the core to the outer hard martensitic case and starts a self-tempering mechanism in this region[58], [62], [63]. This tempering mechanism allows the partial diffusion of carbon atoms from the supersaturated martensitic structure and, as a result, hardness is reduced considerably because of the availability of slip plane. However, depending on the heat treatment process, the presence of retained austenite (RA) along with tempered martensite is likely to be transformed to different other phases, like pearlite (coarse or fine) and bainite (upper or lower) structures due to the complicated heating and cooling cycles [64]. Finally, cooling to the ambient temperature may provide somewhat a composite structure rather than a single structure [62].

Steel rebar has a passivation tendency especially in highly alkaline environments ($\text{pH} > 13$) and a protective oxide layer consisting of wustite (FeO), magnetite/maghemite ($\text{Fe}_3\text{O}_4/\text{g-Fe}_2\text{O}_3$), hematite ($\alpha\text{-Fe}_2\text{O}_3$) [64]–[66], or sometime fayalite ($2\text{FeO}.\text{SiO}_2$) [67], [68] can prevent it from further corrosion and deterioration [68]–[74]. The corrosion

potential is found to be shifted from active to passive region with low current density, and the charge transferring mechanism can be reduced with the increased embedding time in an alkaline environment [48]. This is why, owing to the high moisture content in the pore structure of concrete under the presence of $\text{Ca}(\text{OH})_2$, KOH , and NaOH , the alkalinity of the concrete structure is increased with a pH ranging in between 13-13.7 [71]–[75]. However, if concrete structures are surrounded by a marine environment or if the concrete matrix is prepared from contaminated sand, chloride can penetrate through the pores of the concrete matrix and depassivate the oxide layer of steel rebar leading to localized corrosion [76]–[79]. The corrosion rate under such circumstances depends upon the chloride to hydroxyl ratio [77], [78]. In addition to chloride, the alkalinity of the concrete starts to decrease as a result of carbonation when CO_2 and moisture from the atmosphere penetrate inside the concrete pore structure and form carbonic acid over there. As a result, pH is reduced, because of carbonation, below the critical limit ($\text{pH}=9$) and the corrosion phenomenon gets severe [79], [80].

It is inevitable that the industrial performance of a given metal significantly decreases due to the anodic dissolution or oxidation [3], [19], [81]. The corrosion behavior of the steels, which are the most widely used metallic materials, differs depending on their matrix and corrosive media[16]. Austenite, ferrite, pearlite, bainite, martensite, and tempered martensite are formed as a function of transformational conditions such as alloying content and heating-cooling rate and thus show different anodic dissolution in the same corrosive media [16], [33], [82], [83]. But each of the mentioned phases simultaneously plays a significant role in determining the mechanical stability of rebar alongside the electrochemical characteristics. Hence, a true combination

of both of the discussed properties should be balanced to meet civil structure integrity. The morphology of cementite (Fe_3C) in the ferrite matrix can affect the electrochemical properties of steel rebar. In addition, the subsequent size, shape, and distribution of different phases can also contribute in determining the electrochemical properties and thus can be altered by various heat treatments, such as isothermal transformation, quenching, and tempering mechanisms. Hence, the effect of different microstructures of steel rebar would be worth studying to understand the electrochemical behavior.

Besides other methods, the use of inhibitors is also known to be one of the most effective and economical. Though several generic and proprietary inhibitors, such as alkanolamine and its salts [84], [85], organic acid salt mixtures [86], and inorganic substances mainly containing nitrites are used for this purpose. Calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) as a corrosion inhibitor has been studied for several years and plays a vital role in enhancing the durability and service life of reinforced concrete structures, especially in corrosive environments where chloride and nitrate exposure can be significant [50]–[53]. Long-term tests [54], laboratory models [55], as well as the theory behind simulation [56], [57] have been studied. All studies demonstrated that when calcium nitrate is added to concrete, it can provide protection against the corrosive effects of chloride-containing substances. Corrosion inhibitors like calcium nitrate play a vital role in enhancing the durability and service life of reinforced concrete structures, especially in corrosive environments where chloride and nitrate exposure can be significant.

The corrosion inhibition of steel by calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) in concrete involves multiple mechanisms that help prevent or reduce the corrosion of steel

reinforcement. Calcium nitrate is commonly used as a corrosion inhibitor in concrete due to its ability to mitigate the detrimental effects of nitrates on steel corrosion. The mechanism of corrosion inhibition by $\text{Ca}(\text{NO}_3)_2$ involves both physical and chemical processes [19], [32], [87], [88]:

- i. **Passivation Enhancement:** Calcium nitrate helps enhance the passivation of steel reinforcement by promoting the formation and stability of the protective oxide layer on the steel surface. The presence of nitrate ions facilitates the formation of a denser and more stable passive film, which acts as a barrier against corrosion-causing species, such as chloride ions, towards the steel surface.
- ii. **Alkalinity Maintenance:** Calcium nitrate contributes to maintaining the alkaline environment around the steel reinforcement. As mentioned earlier, the alkalinity of concrete is crucial for the passivation process. Calcium ions released from calcium nitrate react with hydroxyl ions (OH^-) to form calcium hydroxide ($\text{Ca}(\text{OH})_2$), thereby sustaining the high pH level required for the passivation of steel.
- iii. **Nitrate Scavenging:** Calcium nitrate acts as a nitrate scavenger, reducing the concentration of nitrates in the concrete. By reacting with nitrate ions (NO_3^-), calcium nitrate forms calcium nitrite ($\text{Ca}(\text{NO}_2)_2$). Nitrites are less corrosive to steel compared to nitrates, thus helping to inhibit corrosion.
- iv. **Oxygen Reduction:** Another mechanism through which calcium nitrate inhibits corrosion is by reducing the oxygen availability at the steel surface. Calcium nitrate can consume dissolved oxygen within the concrete, limiting its diffusion to the steel reinforcement. Oxygen reduction reactions are essential in corrosion

processes, and by minimizing the oxygen concentration, corrosion rates can be reduced.

- v. Ion Blocking Effect: Calcium ions can occupy the binding sites on the steel surface, reducing the adsorption of chloride ions and other aggressive species that may promote corrosion. By blocking these binding sites, $\text{Ca}(\text{NO}_3)_2$ helps to minimize the penetration of harmful ions towards the steel reinforcement.
- vi. Electrochemical Inhibition: $\text{Ca}(\text{NO}_3)_2$ can influence the electrochemical processes occurring during the corrosion of steel. The presence of calcium ions alters the electrochemical characteristics of the steel-concrete interface, leading to a decrease in the rate of anodic and cathodic reactions involved in the corrosion process.

It's worth noting that the effectiveness of calcium nitrate as a corrosion inhibitor depends on factors such as its concentration in the concrete, exposure conditions, and the presence of other chemicals or inhibitors. The appropriate dosage and application method of calcium nitrate need to be carefully considered to achieve optimal corrosion inhibition of steel reinforcement and thus the durability and service life of concrete structures can be enhanced. It is generally accepted among scientists that nitrates do not promote steel corrosion [89]–[91]. Meland et al [92] investigated the reinforced concrete of a 22-year-old calcium nitrate (containing some ammonium) production plant where the concrete deteriorated due to an external nitrate/ammonium attack. However, concrete with up to 1.5 % NO_3^- - showed no damage. They found that the reinforcement in severely nitrate-polluted areas was in perfect condition with only surface rust and no signs of brittleness. Holm [93] noted an inhibiting effect of calcium nitrate with respect to steel corrosion but

subscribed the effect to other minor components in this commercial inhibitor. Vogelsang [94] proved that calcium nitrate and nitrite had identical corrosion-inhibiting properties by cyclovoltametry, and explained their inhibiting effect by precipitation of a calcium hydroxide layer in the alkaline solution (in such a case they would only function in an alkaline environment like concrete).

2.2. Background

2.2.1. Steel Rebar Production

Steel rebar in this era is produced by the latest patent technology - THERMEX. The important feature of this technique is the rapid quenching of the outer surface of steel rebar by water [95]. After passing through the last series of rollers, thermo-processed steel rebar is passed through predetermined pressurized water. The outer surface of steel rebar becomes harder because of the quenching mechanism and, subsequently, a thermal gradient exists (from high temperature to room temperature) inside the bar. That thermal gradient set the condition of tempering and hence the periphery, just after the hard quenched surface, provides different microstructural properties compared to the outer quenched surface. Also because of the existence of this thermal gradient, the core temperature of steel rebar becomes higher and hence the cooling mechanism is too slow in that region which leads to totally different microstructural properties than the outer discussed regions. This mechanism results in a composite structure where a peripheral zone (a transition zone of perlite and bainite), on one side, is surrounded by an outer hard martensitic case and by a soft core (a mixture of perlite and ferrite) on the other side.

Due to the combined mechanism of quenching and self-tempering, the rebar produced by the THERMEX technology is also given the name quenched and self-tempered (QST) rebar [62]. This kind of treatment is applied to those industrial steels in which the carbon content is less than 0.3% [58], [62]. This is widely used in construction of bridges, buildings, and dams. This is a highly demanding material for concrete because of its high strength (above 450MPa), ductility, and earthquake shock absorbability.

2.2.2. Rebar Production & Heat Treatment

The THERMEX technology is installed in line with the rolling milling process[58], [59]. Once the rebar leaves the finishing rolling mill, its temperature is maintained to 1000⁰C as can be seen in **Fig. 2.1**. But as this rebar passes through the cooling THERMEX system (**Fig. 2.2**), the rapid water spray quenches the outer surface below the martensitic M_s (start of martensite) temperature (**Fig.2.3**) [58], [59]. This phase of the process creates a hardened martensite but the inner core of the material is still at a higher temperature and as a result, it remains as austenite. This residual heat moves from the inside of the core to the outer hard martensitic case and starts a self-tempering mechanism in this region [58], [59], [62]. This tempering/equalization temperature is the maximum temperature that is attained by the rebar after the quenching mechanism. This tempering mechanism reduces the hardness of the supersaturated martensitic structure by phase transformation. The temperature of the surface reaches approximately 600-700⁰C due to the flow of heat from the inside to the outer surface. Finally, it cools to ambient temperature as shown in **Fig. 2.3** and the structure gained by this mechanism is somewhat a composite rather than a single phase [62].

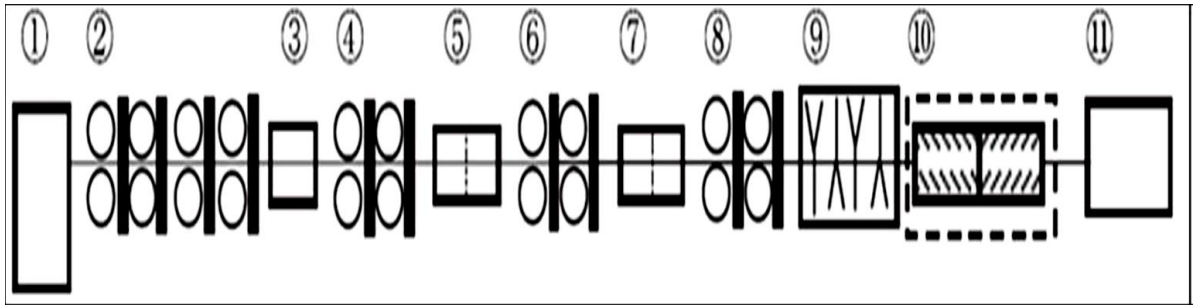


Figure 2.1: Layout of rolling mill and cooling zone in the bar product line: (1) Reheating furnace, (2) Roughing mill, (3) Rough cooling zone, (4-6) Intermediate rolling Mill, (7) Intermediate cooling zone, (8) Finish rolling mill, (9) Finish rolling mill (SCFM), (10) Finish cooling zone, (11) Cooling bed [58], [59].

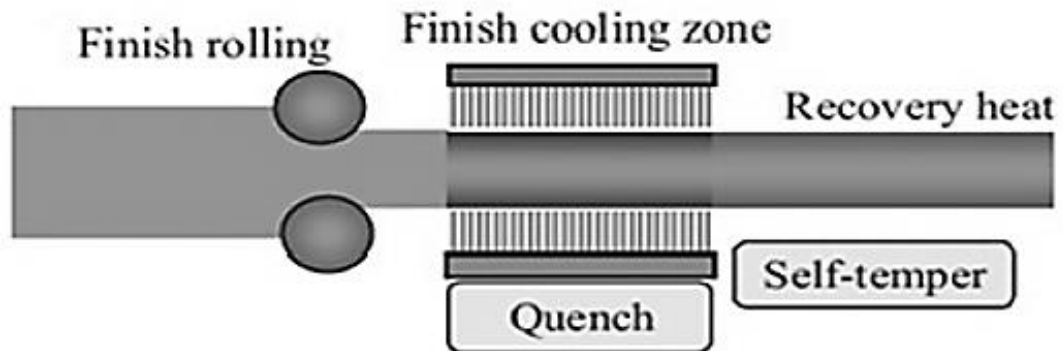


Figure 2.2: Rebar passes through the cooling THERMEX system [62].

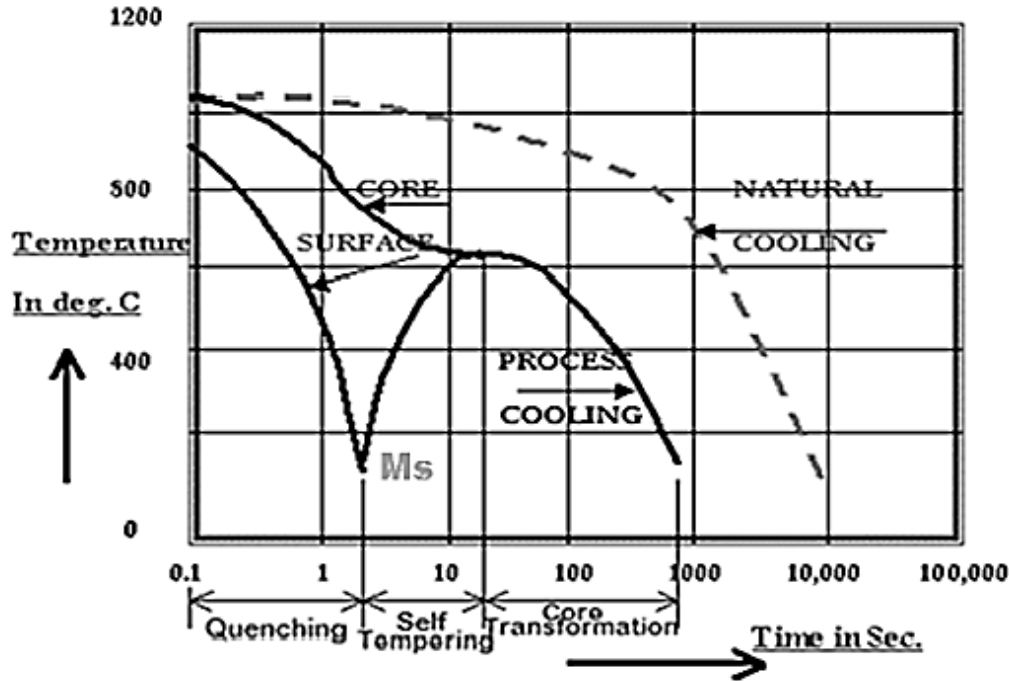


Figure 2.3: Cooling mechanism of steel rebar from outer quenched surface to core [62].

2.2.3. Corrosion Process

Steel rebar is basically an alloy of iron, as a major constituent, and carbon, as a minor constituent. Iron is found in nature as an oxide and the most abundant ores of it are magnetite (Fe_3O_4) and hematite (Fe_2O_3) [96]. For getting the pure iron from its oxides to form a desired alloy, energy is provided from the external source as a combination of many physio-chemical processes. However, pure iron is always in its unstable form and it tends to form the oxides again to reduce its free energy. Typically for iron, the corrosion products are usually iron oxides and/or hydroxides.

Corrosion is an electrochemical process or it is also called a physio-chemical process where the active part becomes an anode and releases electrons due to the

oxidation process while its counterpart acts as a cathode which accepts an electron due to the reduction phenomenon [97].

Reaction at the anode (Oxidation):



Reaction at the cathode (Reduction):



For the corrosion reaction to occur, dissolved oxygen is required in water to form the hydroxyl ions which in turn react with the iron ions and form the iron hydroxide.

Overall reaction:



Iron hydroxide formed in reaction (2.3) undergoes further oxidation reaction and forms iron oxides i.e. magnetite (Fe_3O_4) and hematite (Fe_2O_3).

2.2.3.1. Potential-pH Diagram (Pourbaix Diagram)

In an electrochemical process, the dissolution of hydrogen or oxygen affects the pH of the electrolyte. The chemical equilibrium condition in the presence of these substituents as well as the use of the Nernst equation allow us to find the thermodynamic stability region in the presence of an aqueous medium. Stability for both cathode and anode charge transfer reactions as well as of the pure chemical reaction can be a function of electrode potential, pH, and the metal ions concentration in the electrolyte. Such a diagram is known as the Pourbaix diagram [98].

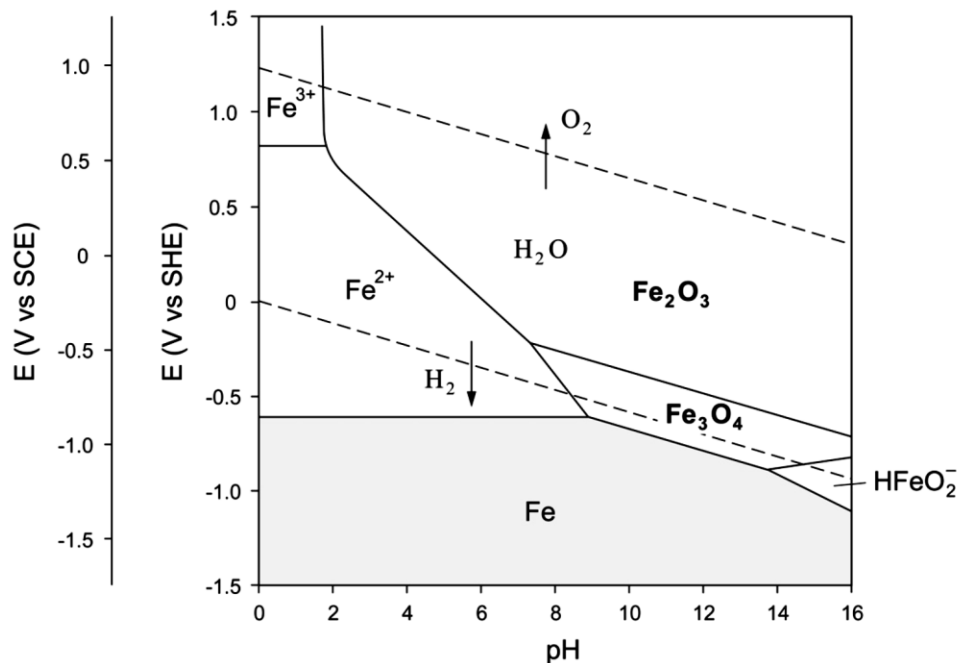


Figure 2.4: Pourbaix diagram for iron in water (for ion concentration 10^{-6} mol/lit at 25°C). Only Fe, Fe₃O₄, and Fe₂O₃ as solid products are considered [98].

Fig. 2.4 shows the stability regions of iron in the form of its oxides. The grey region defines the immunity region because in this region for a specific potential-pH combination, iron remains stable [97].

The dotted lines in the diagram represent the hydrogen (lower) and oxygen (upper) evolution and in between these lines, the water is stable. However, the water dissociates into O₂ above the oxygen line and it dissociates in H₂ below the hydrogen line. In a neutral or alkaline environment, the O₂ evolution occurs according to reaction (2.3) but for H₂ evolution, the phenomenon is as follows;

For lower pH (Acidic):



Neutral or alkaline:



2.2.3.2. Passivation

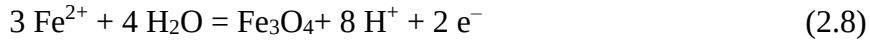
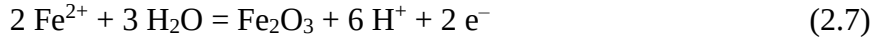
From the Pourbaix diagram, it is clear that both iron and water are not stable simultaneously unless iron is provided the more negative potential to bring it in the immunity region or it is provided a highly alkaline environment ($\text{pH} > 13.5$) where it can develop an oxide layer. In the latter scenario, iron itself is not thermodynamically stable but a passive film of a few nanometers of thickness is developed over its surface. That passive layer is dense stable and transparent in its nature and stops further dissolution of iron and hence reduces the corrosion rate to a lower extent.

2.2.3.3. Pitting Corrosion

Usually, halides, and particularly chloride present in the environment break the protective passive layer of the iron and lead to localized corrosion [99][100][101]. Unlike homogenous corrosion or general corrosion, chloride damage the protective passive layer in a localized area. Once a localized pit is formed, the area inside the pit becomes depleted in oxygen and thus acts as an anode because of the oxidation phenomenon. While the area adjacent to the pit is abundant in oxygen and hence reduction phenomenon takes place and this area acts as a cathode. As the chloride-enriched electrolyte is already inside the pit so the formation of localized cells keeps dissolving the iron under the pitting area. The dissolved iron ions form hydroxide and acidification of the electrolyte occurs inside the pit [100]. The following chemical reaction occurs:



or by the electrochemical oxidation reactions [99]:



The schematic diagram of the pitting cell is shown in **Fig. 2.5**.

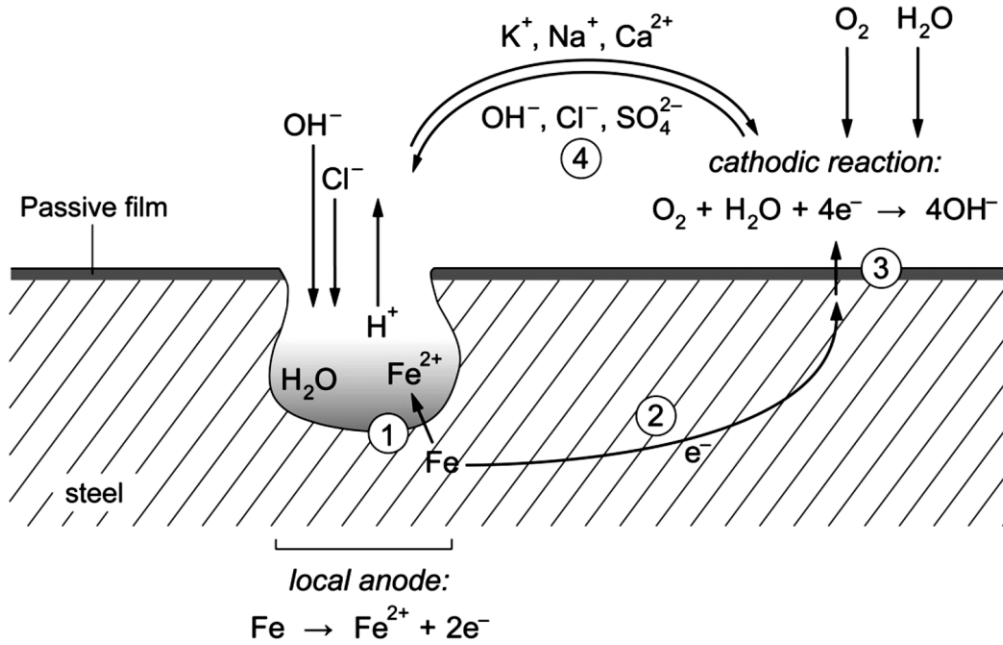


Figure 2.5: Schematic illustration of chloride-induced pitting corrosion and reaction steps: 1.

Anodic iron dissolution; 2. The flow of electrons through metal; 3. Cathodic reduction reaction;

4. Ionic current flow through the electrolyte [99], [100].

2.2.4. Steel Rebar in Concrete

In this section, it will be discussed how steel rebar is affected in a special case when it is placed in a concrete environment.

2.2.4.1. Passivation in Alkaline Environment

Owing to the high moisture content in the pore structure of concrete as well as the presence of $\text{Ca}(\text{OH})_2$, KOH , and NaOH , the alkalinity of the concrete structure is increased with a pH ranging between 13.5-13.7. This pH value agrees with the reported works in many works of literature elsewhere [76], [78], [102]–[104].

Due to the highly alkaline environment, the steel rebar embedded in the concrete structure gets passivated and the corrosion rate is decreased to many folds. However, the alkalinity of the concrete starts to decrease as a result of carbonation when CO_2 and moisture from the atmosphere penetrate inside the concrete pore structure and form carbonic acid there. As a result, from the Potential-pH diagram, it is clear that the passivation state of the steel is maintained as long as the pH of the system is above 9. Due to carbonation, the pH is reduced from this critical limit, and the corrosion phenomenon gets severe [105].

Corrosion of steel reinforcement is a major cause of premature deterioration in reinforced concrete (**Fig. 2.6**), resulting in significant economic losses [86]. Rapid deterioration can occur due to chloride ions in marine zones or from the use of thaw salts [106], as well as from carbonation in urban areas [107].

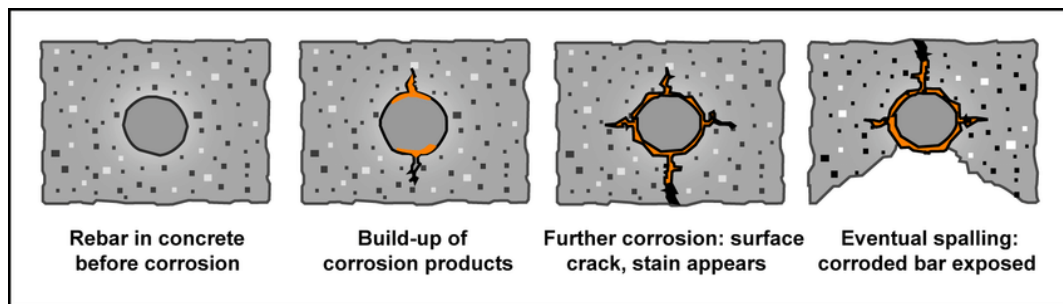


Figure 2.6: Concrete Degradation Mechanism due to corrosion at different stages [7].

2.2.4.2. Corrosion Mechanisms in Reinforced Concretes

To understand the mechanisms of action of inhibitors, it's essential to comprehend the corrosion process in reinforced concrete, as the inhibitors' effectiveness is closely linked to the corrosion cell. Corrosion in this context refers to the deterioration of material caused by chemical or electrochemical interactions with the environment, leading to material loss. The corrosion of steel reinforcement in reinforced concrete occurs due to differences in ion concentration within the concrete, creating corrosion cells with electron and ion flow between cathodic and anodic regions [3]. The anodic region, where steel corrosion happens, experiences the conversion of iron into ferrous ions and electrons, which migrate toward the cathodic region. Areas with more positive electrochemical potential act as cathodes, reducing oxygen and forming hydroxyl ions when exposed to water. In this electrochemical cell, steel bars act as electrical conductors, and the concrete's interstitial fluid serves as the electrolytic environment for ion movement [108]. This electrochemical corrosion cell in concrete is illustrated in **Fig. 2.7**.

According to Souza [3], the formation of corrosion cells with different electrochemical potentials is a result of physical or chemical variations on the metal surface. In the case of steel reinforcement, these variations are primarily caused by differences in the concentration of ions such as alkalis, chloride, and oxygen in the vicinity of the steel. Factors leading to potential differences between points on the rebar include variations in humidity, aeration, and stress within the concrete and steel. As a consequence, when an electrolyte is present, a portion of the metal becomes anodic, and another part becomes cathodic, thereby creating an electrochemical cell.

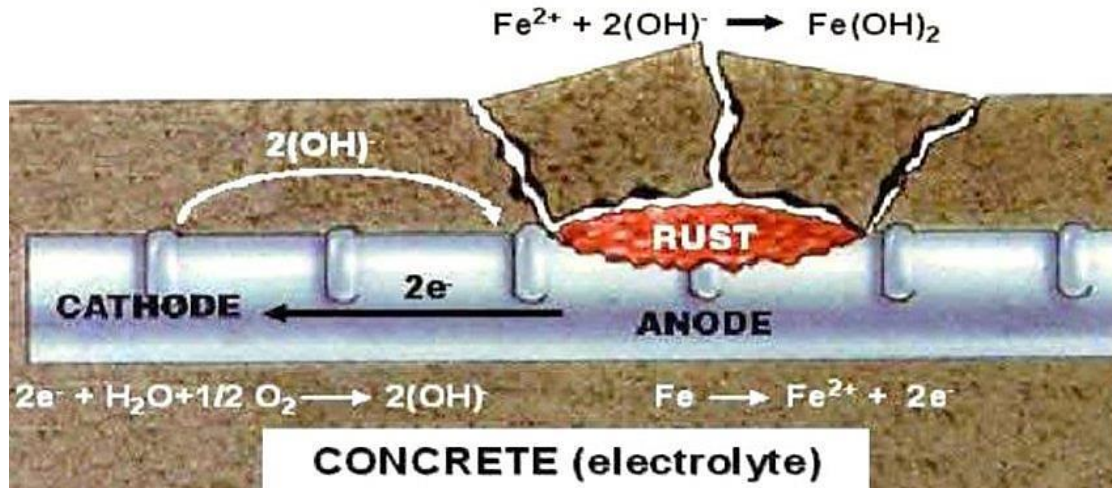


Figure 2.7: Formation of electrochemical corrosion cell of embedded steel rebar in concrete structure [108].

According to Baroghel-Bouny et al. [108], ferrous hydroxide ($2\text{Fe}(\text{OH})_2$) has the potential to undergo various oxidation reactions, leading to the formation of different hydroxides and oxides. The specific products formed depend on factors such as pH, temperature, oxygen levels, and the availability of water. Souza [3] notes that $\text{Fe}(\text{OH})_2$ is typically oxidized to insoluble ferric hydroxide ($2\text{Fe}(\text{OH})_3$), also known as rust ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). These newly formed oxides and hydroxides generally have a larger volume compared to the original steel, as illustrated in **Fig. 2.8**. The expansion in the volume of the corrosion products is compared to the initial volume of the iron (Fe) in question.

The generation of higher-volume corrosion products creates internal pressure, leading to the development of cracks. This, in turn, reduces the adhesion between the steel bars and the concrete, causing chipping and detachment of the concrete [108]. The presence of these expansive products is detrimental to the durability of concrete structures, ultimately reducing their lifespan.

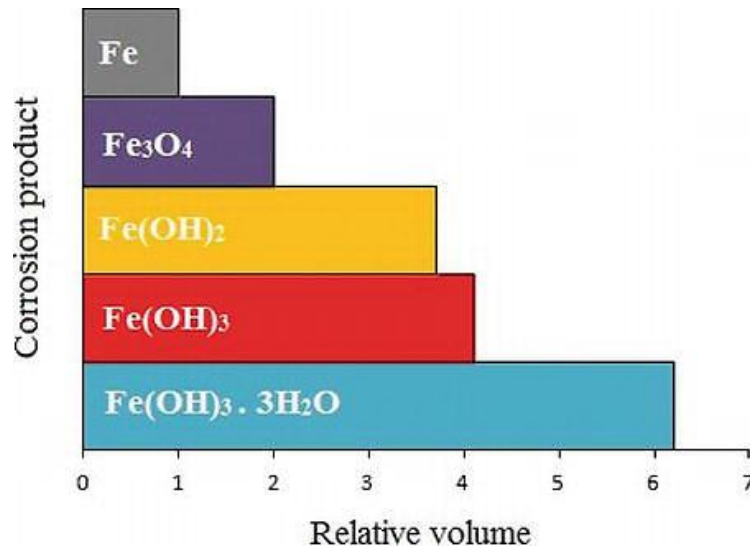


Figure 2.8: Corrosion product relative volume on embedded steel rebar in a concrete structure [109].

However, not all corrosion products negatively impact concrete structures. The formation of Fe_3O_4 , a byproduct of reinforcement corrosion, creates a compact and adherent passive film (referred to as a passivating film) on the rebar's surface. This film acts as a protective barrier, shielding the steel from the corrosion process in the absence of chloride ions [3]. This protective compound forms when the concrete is alkaline, maintains the passive state and is free from aggressive ions such as chloride. Unfortunately, this protective film can be destroyed through de-passivation, a process initiated by a decrease in the concrete's pH to values between 8 and 9 (carbonation) and/or the presence of dissolved chloride ions [110]. Once de-passivation occurs, the rebar becomes vulnerable to corrosion.

The primary factors contributing to corrosion in reinforced concrete structures are the penetration of chloride ions in marine regions and the carbonation process in urban

environments. A comprehensive understanding of these two processes is crucial for better grasping the mechanisms of corrosion inhibition.

2.2.4.3. Carbonation

In environments where chloride ions are absent, the protective film on the steel remains stable as long as the pH within the concrete pores exceeds 11.5. Due to the high alkali content and solid calcium hydroxide (approximately 20%) in Portland cement, the pH under normal conditions is even higher, exceeding 12 [111]. However, over time, reinforced concrete structures may experience a decrease in pH due to a process called carbonation, which disrupts the stability of the passivating layer, thereby initiating the corrosion process. Carbonation primarily occurs in urban areas with significant CO₂ emissions from vehicles and industrial sites [112]. An example of corrosion caused by carbonation with time lapse is illustrated in **Fig. 2.9**.

Carbonation is a process where carbon dioxide (CO₂) enters concrete through diffusion, reacting with the water in the pores and forming carbonic acid. This carbonic acid then reacts with portlandite (Ca(OH)₂), a product of cement hydration, resulting in the formation of calcium carbonate (CaCO₃) (as shown in Eq. (4)). This reaction leads to a reduction in the pH of the environment to approximately 8, as the formed product (CaCO₃) is less alkaline than portlandite. According to the Pourbaix diagram (**Fig. 2.10**), which illustrates regions of immunity, passivation, and corrosion in an iron-water system at 25°C, when the pH is reduced to 8 with the same corrosion potential, the system transitions from the passivation region to the corrosion region. This decrease in pH destabilizes the protective film, initiating the corrosive process. The summarized carbonation reaction is presented in Eq. 2.9.

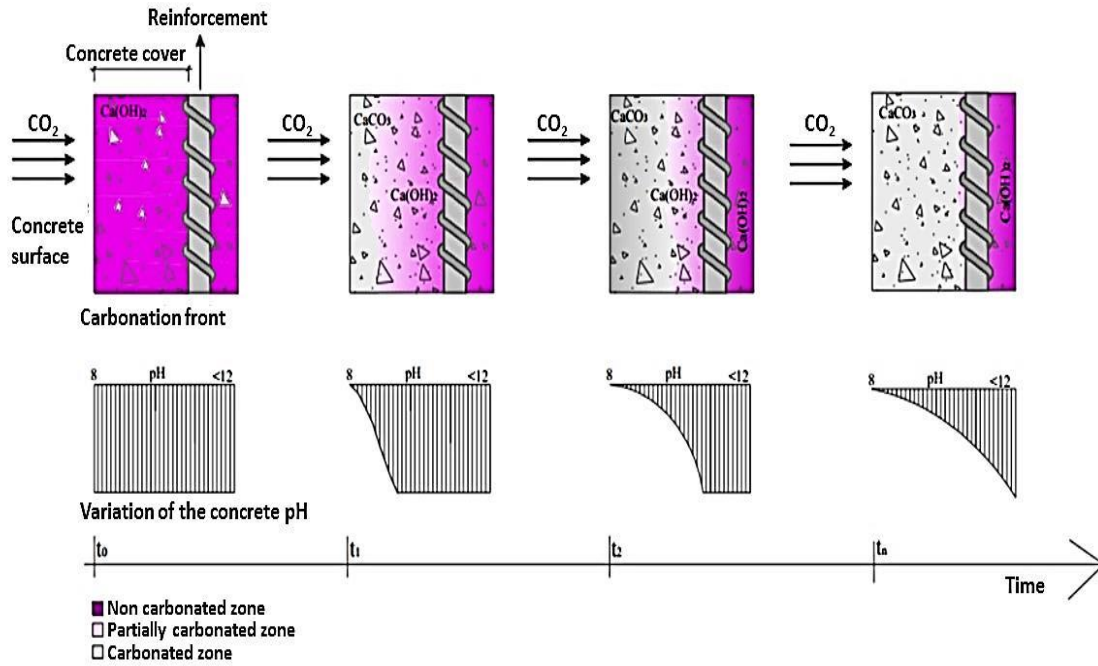
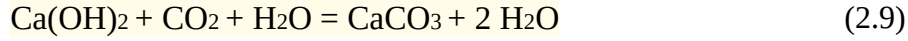


Figure 2.9: Carbonation zones emerged in concrete structures with time-lapse [113], [114].

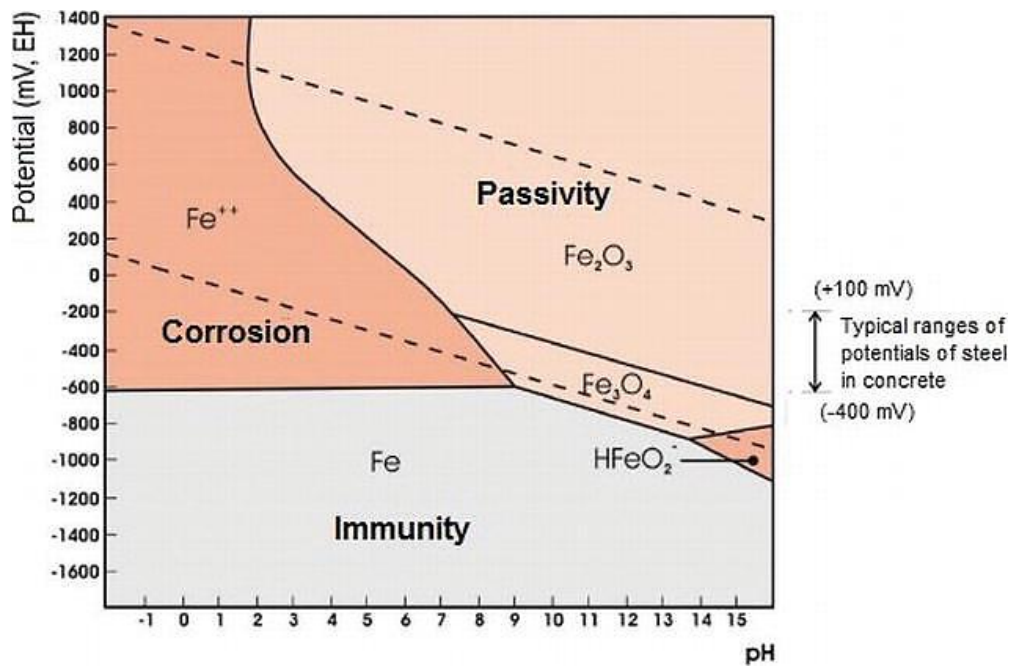


Figure 2.10: Iron-water system, without chloride, at 25°C Pourbaix diagram [115].

2.2.4.4. Chloride attack

The presence of chloride in concrete, originating from sources like seawater, marine atmosphere, CaCl_2 -containing setting time accelerators, water, or contaminated aggregates due to industrial pollutants, is a significant contributor to the corrosion of reinforcements in reinforced concrete structures [116].

In the presence of chloride, even when the pH is above 11.5, the protective film on the material's surface can be eroded. This phenomenon is influenced by the amount of hydroxides in the concrete pores. The maintenance of this protective film relies on a balance between the alkalinity (indicated by OH^- ions) and acidity (indicated by Cl^- ions). Therefore, the interplay between chloride ions and hydroxyl ions regulates the speed of pitting corrosion [111], [117]. Research by Hausmann [117] reveals that when the Cl^-/OH^- molar ratio exceeds 0.6, the protective film becomes unstable, exposing the steel reinforcement to corrosion.

The corrosion caused by chloride ions differs from that triggered by carbonation, as it leads to localized pitting rather than widespread corrosion. In chloride-induced corrosion, micro piles form, with pits acting as anodic zones and the protective film as the cathodic surface [118].

The exact mechanism of corrosion due to chloride ions isn't fully elucidated. The prevailing theory suggests that the presence of ions disrupts the passivating layer, leading to the formation of iron hydroxide through reactions (Eq. (2.10) and (2.11)). During this process, chloride ions are not consumed and remain available for further reactions.



Several factors influence the likelihood of corrosion caused by chloride ions. Decreasing the water-to-cement ratio and relative humidity of the concrete, increasing the thickness of the concrete cover, using mineral additives, and employing inhibitors all work to inhibit the occurrence of corrosion.

The impact of chloride ions on the de-passivation of reinforcement becomes evident when examining changes in the Pourbaix diagram for the iron-water system in the presence of chloride (**Fig. 2.11**). In this diagram, a reduction in the passivity region is observed compared to the Pourbaix diagram without chloride (**Fig. 2.10**). This reduction arises from the occurrence of pitting corrosion and imperfect passivity regions due to the presence of these ions. The diagram reveals that corrosion can happen across all pH values, including the range of passivity or immunity for the iron-water system in the absence of chloride ions, which typically span pH values between 8.5 and 14.

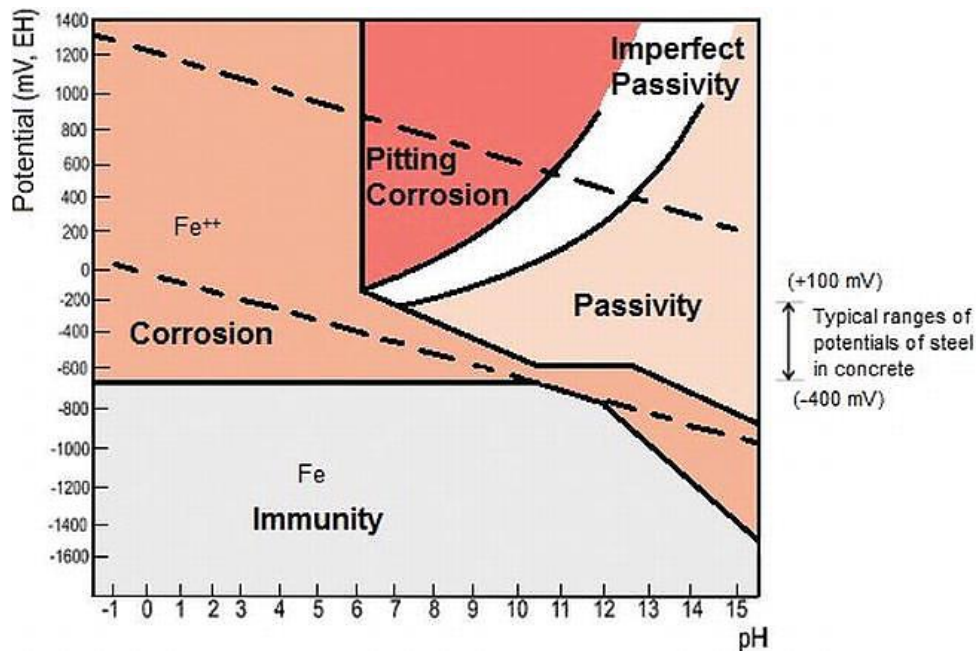


Figure 2.11: Iron-water system with the presence of chloride, at 25°C Pourbaix diagram [115].

2.2.4.5. Critical Chloride Content

The passive film of the steel in concrete under high alkaline environment suffers from localized corrosion by the presence of chloride in the concrete structure. The minimum amount of chloride required in the concrete to break the passive film of steel is termed critical chloride content or chloride threshold value. The chloride threshold value depends on many factors but the main factor is considered to be the pH of the system – more the pH, more will be the OH^- ions, and hence more chloride ions will be needed to break the passive film [46], [47].

Another factor, which affects the chloride critical value, is the quality of the concrete/steel interface. Sometimes the solid hydrates i.e. $\text{Ca}(\text{OH})_2$, stick on the surface of steel and buffer the pH of the system. These hydrates create resistance in the path of chloride ions to reach the passive layer and hence reduce the chances of localized corrosion [119], [120]. It is a consensus that this is the reason for having the high chloride threshold value in concrete [69], [121]. A detailed study of this topic can be seen elsewhere [119], [120], [122].

2.2.4.6. Corrosion Inhibitors

Corrosion inhibitors are chemicals that, when present in appropriate quantities, can reduce the rate of corrosion without significantly changing the concentration of any corrosive agent [115]. This definition excludes other methods of corrosion protection that alter the concentration of aggressive agents, such as certain mineral additives, coatings, and pore-blocking mechanisms.

Corrosion inhibitors can affect the corrosive process in two ways: by delaying the de-passivation of reinforcement, strengthening the protective film, or reducing the corrosion

rate after de-passivation [115]. When corrosion inhibitors are used in sufficient concentrations, they postpone the corrosive process, leading to an extended lifespan for reinforced concrete structures [115]. Given the growing concern about the durability of these structures, the use of corrosion inhibitor additives has been gradually increasing to extend their lifespan [123].

For newly constructed reinforced concrete structures, different products are employed for protection. Inhibitors can be added to the fresh concrete mix preventively to hinder or delay the onset of corrosion. In existing structures, inhibitors can be added to repair mortars or concrete, applied to the concrete surface, or introduced through holes or grooves in the surface to facilitate diffusion through the covering [115].

Among the inhibitors used in existing concrete structures, liquid products are common, often based on phosphate substances like monofluorophosphate [115]. For this category of inhibitors, these substances must possess the absorptive capacity to penetrate the concrete structure through the interstitial pores and reach the reinforcement.

Inhibitors, especially those combined with concrete, have the potential to alter concrete properties in both fresh and hardened states, affecting factors like setting time, strength gain rate, and other characteristics. Thus, a thorough understanding of their mechanism of action and potential side effects is essential to avoid unforeseen damage.

Anodic inhibitors also referred to as passivation inhibitors, function as oxidizing agents by gaining electrons [115]. These inhibitors operate by facilitating the oxidation of ferrous ions into ferric ions, leading to the formation of a dense and passive film on the steel surface, effectively halting the anodic reaction in the corrosion process [115]. This cohesive and insoluble film results from the interaction between the inhibitors and the

corrosion byproducts [124]. Myrdal [110] states that the impact of these inhibitors on the cathodic reaction is minimal.

According to Myrdal [110], the actions of these anodic inhibitors elevate the electrochemical potential within the anodic region, causing the anodic and cathodic curves to intersect at a lower corrosion current and a higher corrosion potential, as depicted in **Fig. 2.12**.

The effectiveness of anodic inhibitors depends on their concentration, which is determined based on the level of chloride present in the environment that the steel will encounter [125].

In the realm of reinforced concrete, calcium nitrite ($\text{Ca}(\text{NO}_2)_2$) and calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) are employed as anodic inhibitors, exhibiting comparable inhibitory characteristics, as outlined by Elsener [115].

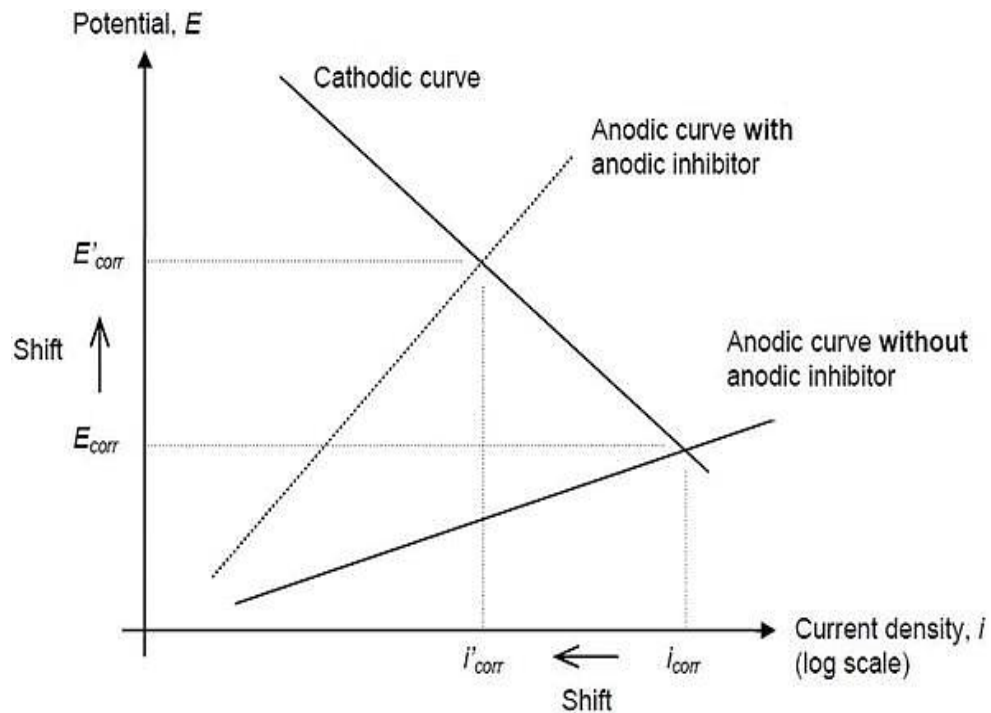


Figure 2.12: Corrosion potential with anodic inhibition effect (E_{corr} = corrosion potential and i_{corr} = corrosion rate) [95].

2.2.5. Electrochemical Techniques

2.2.5.1. Open Circuit Potential (OCP)

Before conducting the electrochemical testing, the potential of the working electrode is always measured with the help of a reference electrode under the condition that no external current or voltage is applied to the working electrode. Once the system measures the open circuit potential of the working electrode, then it applies the desired working potential in addition to the open circuit potential which was already measured.

2.2.5.2. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is measured when a sinusoidal voltage (AC voltage) is applied to the working electrode at varying frequencies. Usually, the frequency is ranged from MHz to μ Hz and the current is measured in response to applied voltage. From the applied voltages, the responded current readings and from their phase differences, many values of impedance (Z) can be recorded against each frequency. The relationship between the applied voltages, current, and the shift of phase angles are shown in the below Eq. 2.12,

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (2.12)$$

Where;

E_t = Potential at time t ,

I_t = Current at time t

E_0 = Amplitude of the signal,

I_0 = Current at time 0

$\omega = (2\pi f)$ = Radial frequency

Φ = phase shift

However, in a linear system, the response signal is shifted in phase (Φ) and has a different amplitude than I_0 as it is shown in **Fig. 2.13**.

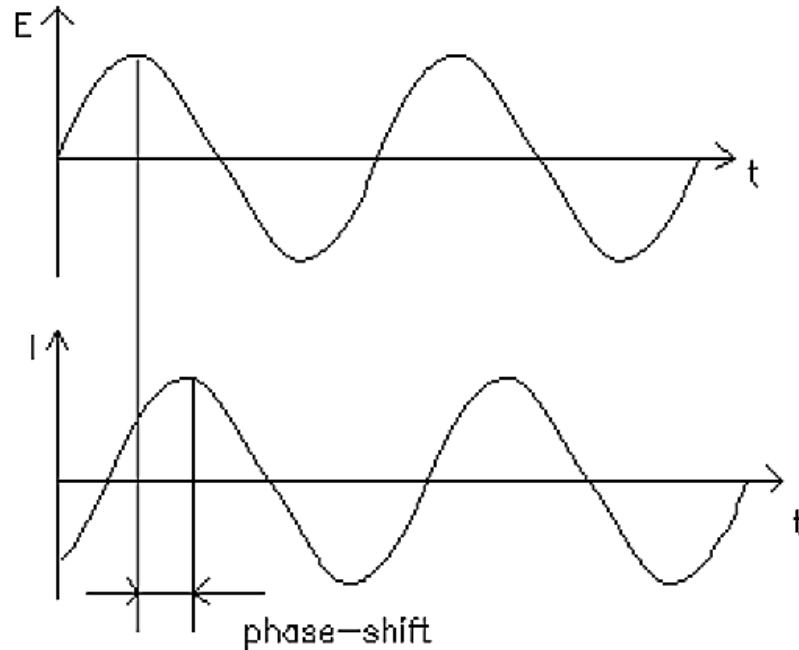


Figure 2.13: Sinusoidal current response in a linear system [126].

Let's suppose, if a capacitor and a resistor are connected in a parallel way and at a very low applied frequency, the capacitor will act as an insulator and it will keep on charging. But once it will be fully charged, the current will be forced through the resistor. At this stage, the impedance of both the capacitors and resistors will be equal. But on the other hand, if the frequency of the applied voltage is too high, then the capacitor will be short-circuited and there will be no impedance. However, if the applied frequency will be intermediate then both the capacitor and resistor will carry the AC.

By using the equivalent circuit, the measurements can be calculated. By this equivalent circuit, the charge transfer resistance, double-layer capacitance, and ohmic resistance can be measured. This will provide information about the corrosion rate and other important electrical properties of steel in concrete.

By utilizing complex notation, impedance is divided into a real, $|Z|\cos(\Phi)$, and an imaginary part, $|Z|\sin(\Phi)$. When real impedance is plotted against imaginary impedance, the plot is obtained and is called the Nyquist plot (**Fig 2.14**). However, if the relation is plotted between changing frequency and impedance/phase angle then the plot obtained is called a Bode plot (**Fig 2.15**).

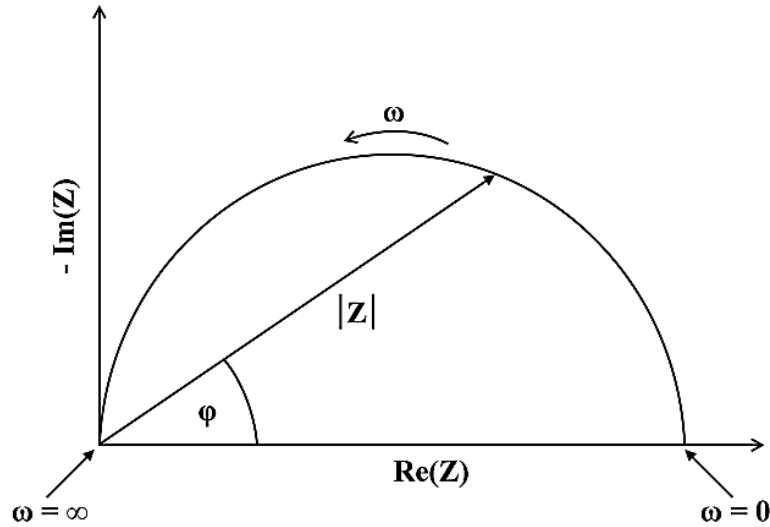


Figure 2.14: Schematic diagram of Nyquist plot [126].

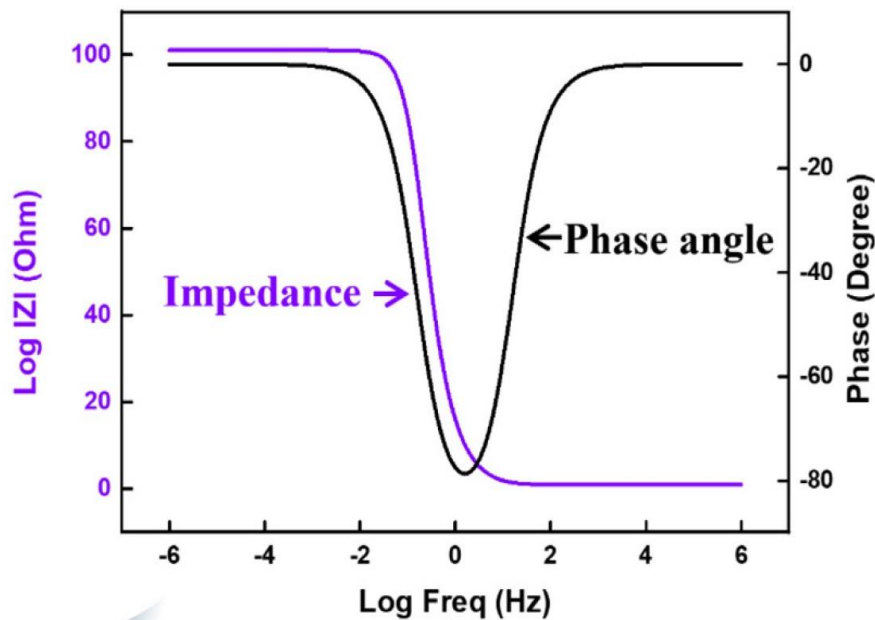


Figure 2.15: Schematic diagram of Bode plot [126].

2.2.5.3. Linear Polarization Resistance (LPR)

LPR measurements are generally used to determine the instantaneous corrosion rate of an electrode. The technique is based on the observation that within a small potential range around E_{corr} , the E-I-relationship is approximately linear [127]. The linear polarization resistance is defined as the slope of this curve ($R_p = dE/dI$) at E_{corr} and has been illustrated in **Fig. 2.16**. It can experimentally be obtained in a conventional three-electrode configuration (WE, RE, CE) by polarizing the working electrode a few millivolts (typically 10 mV) into anodic and cathodic directions and recording the required current. The well-known Stern-Geary Eq. (2.13) allows the calculation of the corrosion current [127].

$$I_{\text{corr}} = \frac{B}{R_p} = \frac{\beta_a \cdot \beta_c}{2.3(\beta_a + \beta_c)} \cdot \frac{1}{R_p} \quad (2.13)$$

Constant B contains the anodic and cathodic Tafel slopes and is, in the case of reinforcement steel in concrete, usually assumed in the range of 26 mV (corroding steel) or 52 mV (passive steel) [128].

If R_p is related to the metal area, corrosion current density i_{corr} (mA/cm²) instead of corrosion current I_{corr} (mA) is obtained. While in laboratory setups, the area of polarized steel is generally known, this is problematic in the case of field measurements where the reinforcement surface area is practically infinite. Moreover, the calculation of corrosion rate from R_p is, strictly speaking, only correct for uniform corrosion; for localized corrosion (chloride-induced corrosion), the area of actively corroding metal is normally unknown. In fact, the anodically acting surface area is variable over time. This is only

one example of reasons why the accuracy of corrosion rates (current densities) computed based on R_p measurements is, in the case of localized corrosion, highly questionable.

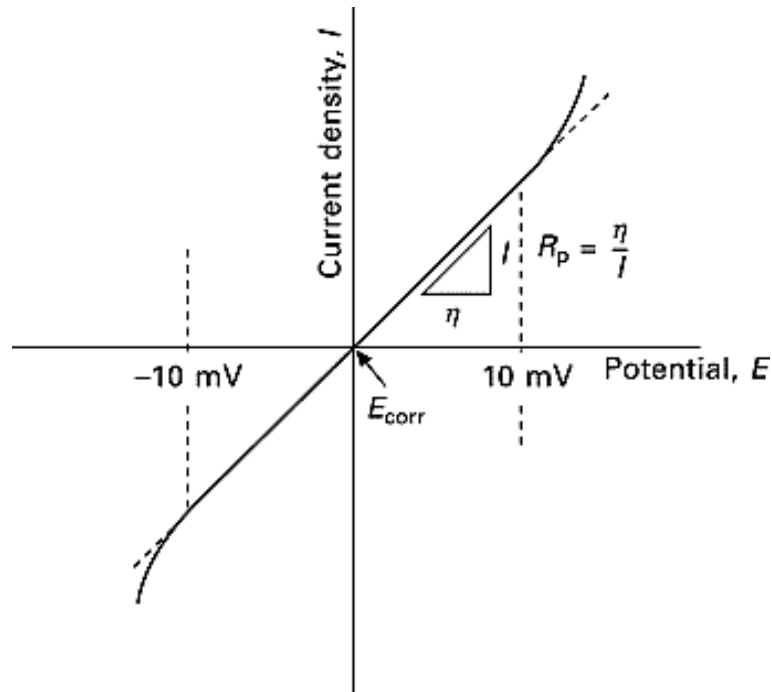


Figure 2.16: Linear polarization resistance (LPR) slope across E_{corr} region [129].

2.2.5.4. Potentiodynamic Polarization (PDP)

Potentiodynamic anodic polarization is the characterization of a metal specimen by its current potential relationship. The specimen potential is scanned slowly in the positive direction and therefore acts as an anode such that it corrodes or forms an oxide coating. These measurements are used to determine the corrosion characteristics of metal specimens in aqueous environments. A complete current-potential plot of a specimen can be measured in a few hours or, in some cases, a few minutes.

Investigations such as passivation tendencies and the effects of inhibitors or oxidizers on specimens are easily performed with this technique. With this knowledge, the corrosion characteristics of different metals and alloys can be compared on a rational

basis, and compatible specimen-environment combinations secured for further long-term testing.

When a metal specimen is immersed in a corrosive medium, both reduction and oxidation processes occur on its surface. Typically, the specimen oxidizes (corrodes) and the medium (solvent) is reduced. In acidic media, hydrogen ions are reduced. The specimen must function as both anode and cathode and both anodic and cathodic currents occur on the specimen surface. Any corrosion processes that occur are usually a result of anodic currents [127], [130].

When a specimen is in contact with a corrosive liquid and the specimen is not connected to any instrumentation – as it would be “in service” – the specimen assumes a potential (relative to a reference electrode) termed the corrosion potential, E_{CORR} . A specimen at E_{CORR} has both anodic and cathodic currents present on its surface. However, these currents are exactly equal in magnitude so there is no net current to be measured. The specimen is at equilibrium with the environment (even though it may be visibly corroding). E_{CORR} can be defined as the potential at which the rate of oxidation (anodic reaction) is exactly equal to the rate of reduction (cathodic reaction).

It is important to stress that when a specimen is at E_{CORR} both polarities of current are present. If the specimen is polarized slightly more positively than E_{CORR} , then the anodic current predominates at the expense of the cathodic current. As the specimen potential is driven further positively, the cathodic current component becomes negligible with respect to the anodic component. A mathematical relationship exists which relates anodic and cathodic currents to the magnitude of the polarization [127], [130], but a discussion of this relationship is beyond the scope of this application note. If the

specimen is polarized in the negative direction, the cathodic current predominates and the anodic component becomes negligible [130].

Experimentally, one measures polarization characteristics by plotting the current response as a function of the applied potential. Since the measured current can vary over several orders of magnitude, usually the log current function is plotted vs. potential on a semi-log chart. This plot is termed a potentiodynamic polarization plot. Note that the use of a semi-log display prevents an indication of polarity on such plots. Potentials negative with respect to E_{corr} give rise to cathodic currents, while potentials positive to E_{corr} give rise to anodic currents.

Fig. 2.17 shows the potentiodynamic anodic polarization plot of a sample of 430 stainless steel. The logarithm of the current is plotted (the abscissa) as a function of the applied potential (the ordinate). This plot is described in the following paragraphs [127], [130].

Region A in **Fig. 2.17** is the active region, in which the metal specimen corrodes as the applied potential is made more positive. At B, further increase in the rate of corrosion (as measured by the current) ceases and the onset of passivation begins. The loss of chemical reactivity under certain environmental conditions, probably due to the formation of a film on the surface of the metal, is referred to as specimen passivation. This point is characterized by two coordinate values, the primary passive potential (EPP) and the critical current density (i_c). In region C, the current decreases rapidly as the passivating film forms on the specimen. A small secondary peak is observed followed by region D, where there is little change in current as the potential is increased. The passivating film begins to break down in region E, the trans-passive region.

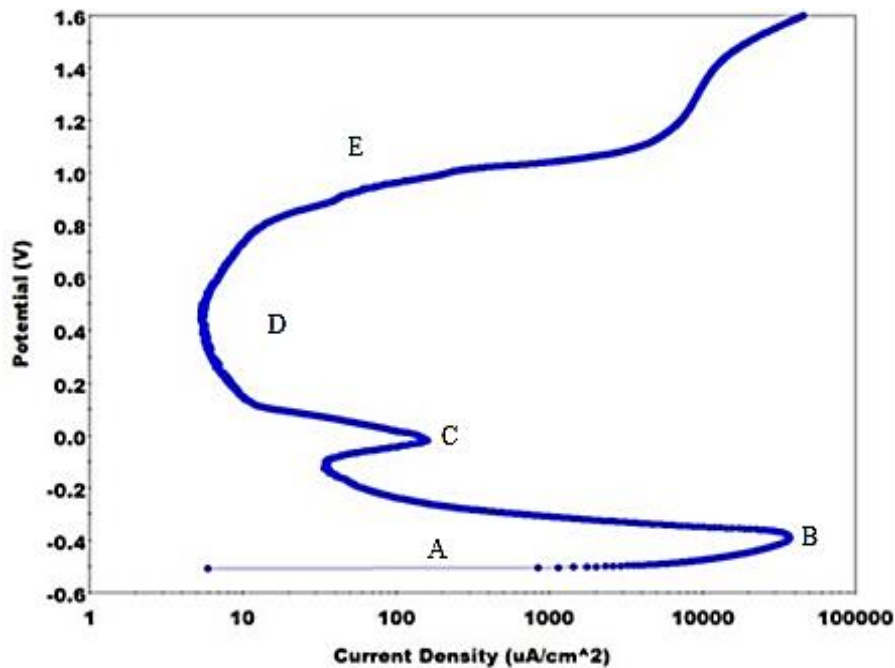


Figure 2.17: Standard potentiodynamic anodic polarization plot of 430 stainless steel.

A = Active region; B = Primary passive potential (EPP); C = Onset of passivation

D = Passivation region; E = Transpassive region [127], [130].

A potentiodynamic anodic polarization plot such as **Fig. 2.17** can yield important information such as:

- 1- The ability of the material to spontaneously passivate in a particular medium.
- 2- The potential region over which the specimen remains passive.
- 3- The corrosion rate in the passive region.

CHAPTER 3:

EXPERIMENTAL WORK

3.1. Steel Rebar

Commercial steel rebar was employed for carrying out this research work. The elemental composition of rebar was analyzed by spectrometry and given in **Table 3.1**. An average of three compositions on three different samples was obtained for precise measurement.

Table 3.1: Steel rebar composition used for heat treatment.

C	Si	Mn	P	S	Cr	Mo	Ni	Cu	Co	Al	Fe
0.192	0.13	0.721	0.007	0.0162	0.04	0.002	0.048	0.024	0.001	0.047	Balance

3.2. Heat Treatment

Rebar samples were heat treated by using state of the art “Gleeble 3500 Thermal System“. This sophisticated thermal system gives precise control over heating and cooling rate, and rapid quenching mechanism due to its in-situ heating and cooling system. The image of the thermal system, control unit, and heat treatment chamber is shown in **Fig. 3.1 (a, b)**. Prior to heat treatment, the heat treatment chamber was evacuated and backfilled with pure Argon gas to minimize oxidation of the specimens. The schematic illustration of the adopted heat treatment approach is given in **Fig. 3.1 (c)**. Rebar samples were heated at a rate of 80°C/min to reach an austenizing temperature (900°C) where the holding time was fixed to 5 minutes. For isothermal heat treatment,

rebar samples were cooled down to the required isothermal temperature with a cooling rate of 537°C/sec. The isothermal temperatures were set to 650°C, 570°C, 500°C, 450°C, and 400°C, respectively. The holding time for 650°C isothermal temperature was set to 8 minutes, whereas it was fixed to 5 minutes for the rest of the temperatures. On completion of the time limit, rebar samples were water quenched at room temperature. In the second phase of heat treatment, rebar samples were first water quenched to room temperature followed by tempering performed for 30 minutes at 300°C and 400°C. On completion of tempering treatment, rebar samples were water quenched at room temperature.

After heat treatment, test samples were wet ground with SiC grinding papers having grit sizes ranging from 240-1000. The grinding was continued until all coarse scratches were removed followed by wet polishing with 0.3-micron alumina powder. The samples were ultrasonically degreased for 5 minutes in detergent-containing water and rinsed thoroughly in distilled water followed by air drying. The microhardness of each heat-treated sample was measured using a Vickers microhardness tester (Buehler 60044-USA) under an applied load of 300 gf.

3.3. Electrochemical Testing

For electrochemical testing, rebar samples were spot welded with a conducting wire by soldering. The welded samples were cold mounted in epoxy resin where the exposed area to the electrolyte corresponded to the rebar diameter. Once the sample was mounted, it was ground up to 600 grit size and left without polishing to provide surface roughness resembling commercial rebar.

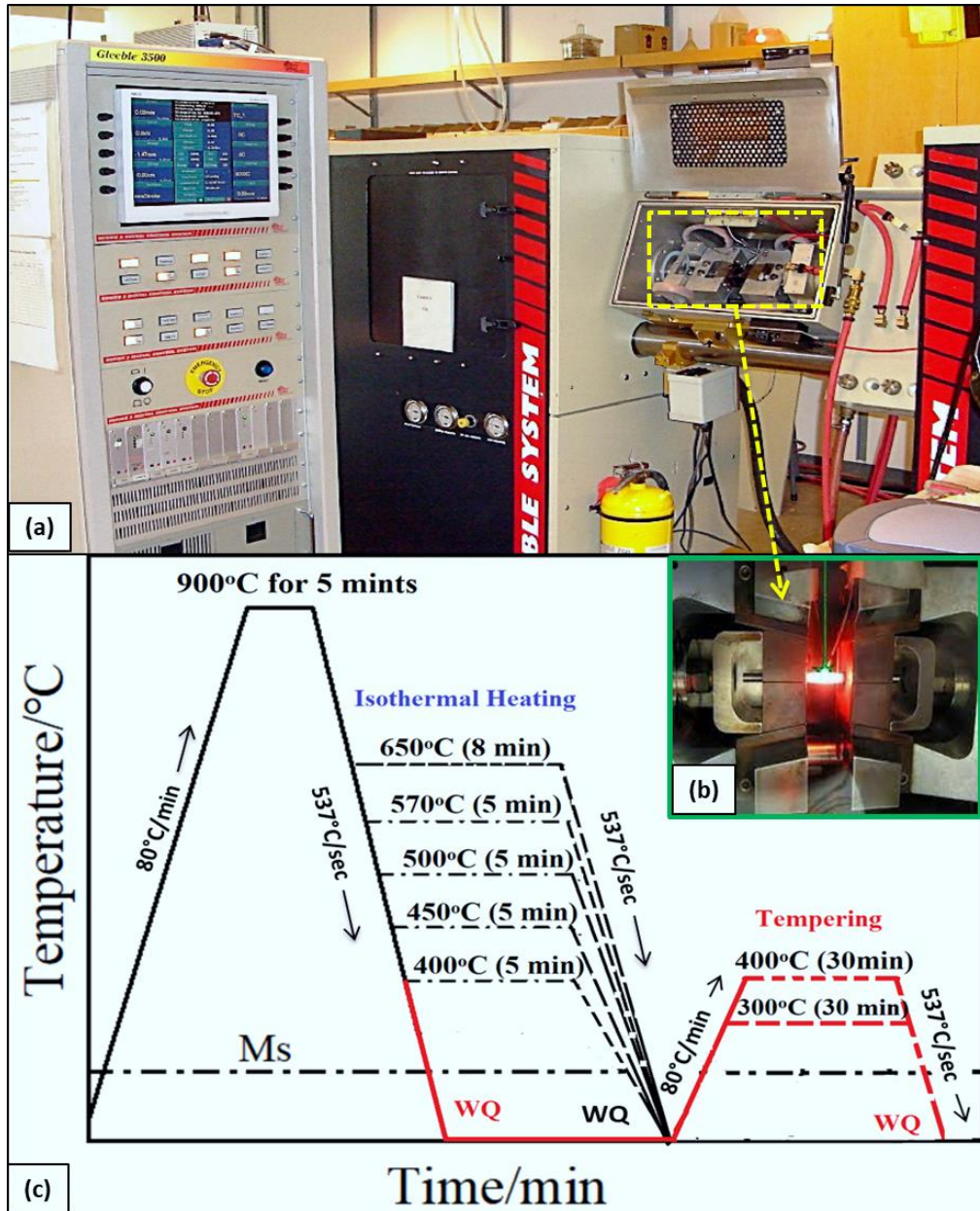


Figure 3.1: (a) Gleeble thermal system, (b) Heating treatment chamber of Gleeble, (c) Heat treatment schematic illustration of isothermal and Q&T steel rebars in combination with varying heating and cooling rates.

A concrete simulated pore solution was used to passivate the samples before electrochemical testing. The concrete simulated solution consisted of (0.6 mol/L KOH,

0.2 mol/L NaOH, and 0.01 mol/L $\text{Ca}(\text{OH})_2$) [46], [47]. The pH of the solution was continuously monitored to maintain it above 13.5. Sample coupons prepared for both electrochemical testing and surface analysis were immersed inside the concrete simulated solution for 72 hours to allow the passive layer to be developed over the exposed surface of steel rebars.

Electrochemical testing was conducted in a concrete pore solution (CPS) free of chloride. For the second phase, NaCl was added to the CPS solution to set Cl^-/OH^- ratio to 1 of electrolyte. For the third solution, calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) was introduced to CPS in the presence of chloride ($\text{Cl}^-/\text{OH}^- = 1$). The pH of the solution was measured at 13.5 for both electrolytes. For each test solution, electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR), and potentiodynamic polarization (PDP) were tested by a conventional three-electrode cell using Gamry 3000 potentiostat, a saturated calomel electrode (SCE) as a reference, and graphite as a counter electrode. Initially, open circuit potentials of all samples were monitored until achieving stability. Post OCP recording, EIS was conducted using an AC amplitude of $\pm 10\text{mV}$ while the frequency range was set from 100 KHz to 10 mHz. LPR was measured by applying $\pm 10\text{mV}$ with a scan rate of 0.2 mV/s. PDP plots were produced by setting the applied voltage from -0.8V to +1.2V with respect to OCP and the scan rate was set to 0.5 mV/s.

3.4. Microscopy and Surface Characterization

The samples prepared by metallography were used for microscopy and surface analysis. A field emission scanning electron microscope (FE-SEM) (FEI-Quanta-FEG-250) was used for microstructural analysis. To study the developed passive layer over the

surface of steel rebar, the x-ray photoelectron spectroscopy (XPS) technique was used to investigate the chemistry of the oxides. XPS spectra were recorded with V.G. Scientific ESCALAB MkII spectrometer using a non-monochromatic Al source (K, 1486.6 eV). Power out was used 130W and the pass energy of the electron analyzer was set to 50eV with an energy resolution fixed to 1eV. The binding energy of the spectrometer was calibrated by several reference lines (Cu 2p_{3/2} = 932.67 eV, Cu 3p_{3/2} = 74.9 eV, and Au 4f_{7/2} = 83.98 eV).

To understand the inhibition mechanism in the presence of calcium nitrate, Fourier transform-infrared spectroscopy (FTIR) analysis was carried out for heat-treated rebar samples in concrete pore solution (CPS). The spectra were recorded over a range of 500–4000 cm⁻¹ (wavenumbers) with a resolution of 4000 cm⁻¹ using a Thermo Scientific Nicolet iS5 spectrophotometer equipped with an FTIR instrument.

3.5. Surface Topography

Polished rebar specimens were dipped in the CPS with and without the presence of calcium nitrate Ca(NO₃)₂ inhibitor. They were allowed to stay immersed inside SCPS for 24 hours. Subsequently, they were taken out of CPS and dried at room temperature (~ 25 °C), and stored in a humidity-free (vacuum desiccator) environment prior to evaluating the surface topography. The surface topography was studied by using an Atomic Force Microscope (AFM) (Oxford C3000).

PART I:

**EFFECT OF MICROSTRUCTURE ON CORROSION
RESISTANCE AND PASSIVITY**

CHAPTER 4:

EFFECT OF MICROSTRUCTURE ON CORROSION

RESISTANCE AND PASSIVITY

4.1. Experimental Results

4.1.1. Hardness and Microstructure

Microhardness of rebar samples heat treated isothermally and under quenched and tempered (Q&T) conditions are given in **Fig. 4.1**. Highest hardness of 506 Hv was measured for the as-quenched rebar. However, the hardness started to decrease with the increase in tempering temperature and the lowest hardness was noted at 400°C Q&T temperature. For isothermally heat-treated rebar samples, the lowest hardness was measured for the sample isothermally heated at 650°C. However, the hardness started to increase gradually with the decrease in isothermal temperature.

FE-SEM microstructures of isothermally heat-treated rebar samples at 650°C, 570°C, 500°C, 450°C, and 400°C, respectively are given in **Fig. 4.2 (a-e)**. Heat treatment done at 650°C and 570°C isothermal temperature provided coarse pearlite and fine pearlite, respectively, and can be seen in **Fig. 4.2 (a, b)**. Lowering the isothermal temperature below 557°C initiates bainite formation and thus upper bainite was observed at 500°C isothermal temperature (**Fig. 4.2c**). Further lowering the isothermal temperature to 450°C and 400°C transformed the structure to lower bainite which can be validated

from **Fig. 4.2d** and **Fig. 4.2e**, respectively. On the other side, martensitic and tempered martensitic microstructures were achieved against the as-quenched, Q&T 300°C, and 400°C rebars and can be observed from the FE-SEM micrographs given in **Fig. 4.3 (a-c)**.

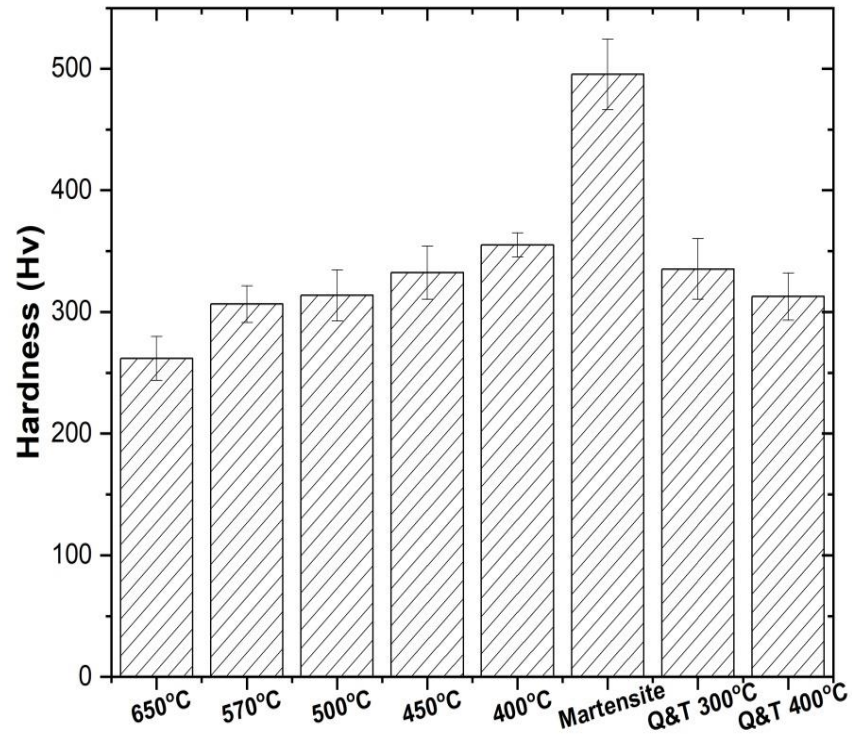


Figure 4.1: Hardness of isothermal, Quenched, and Q&T rebar samples at different temperatures.

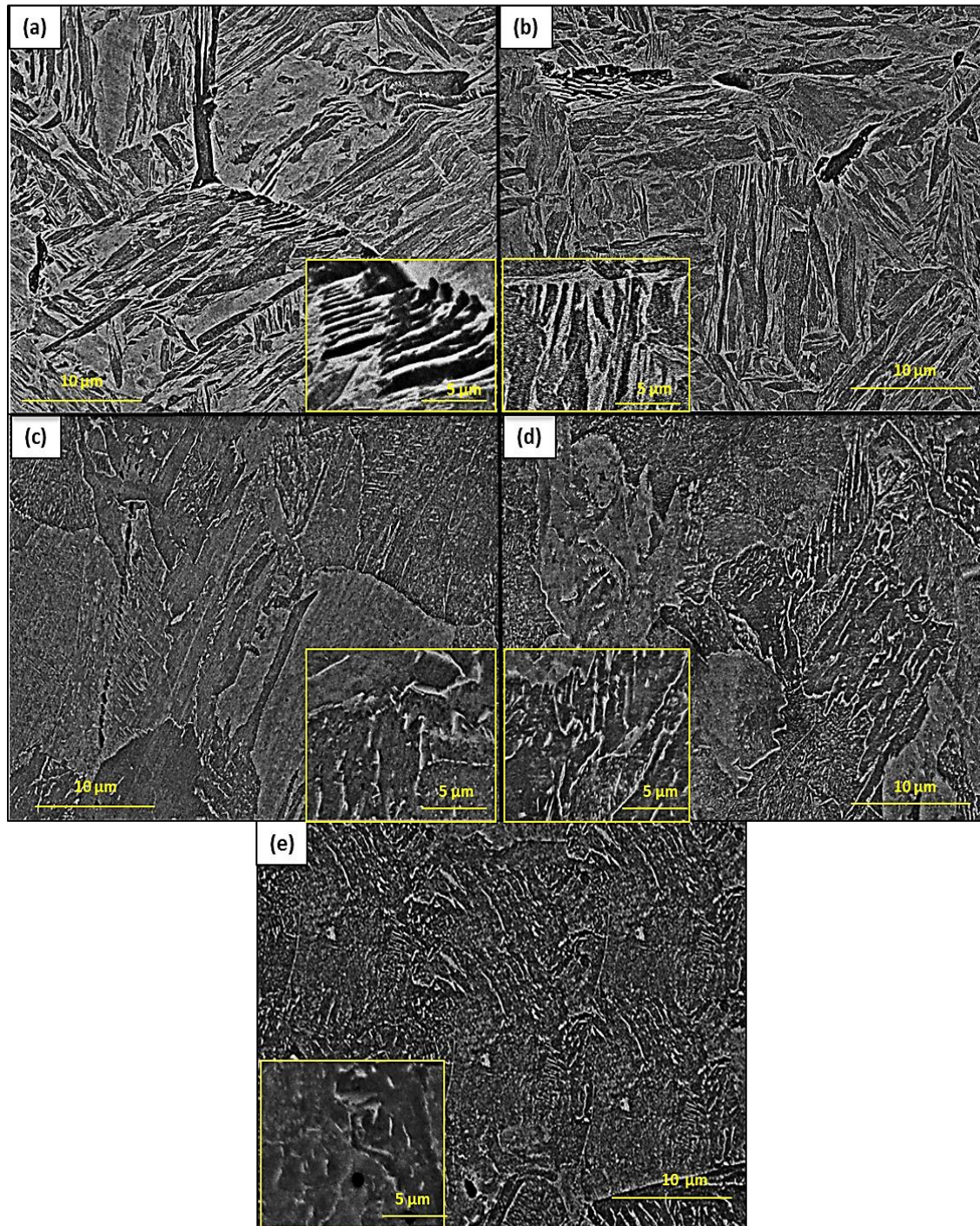


Figure 4.2: FE-SEM micrographs of austenized & isothermally heated rebar at, (a) 650°C, (b) 570°C, (c) 500°C, (d) 450°C, (e) 400°C

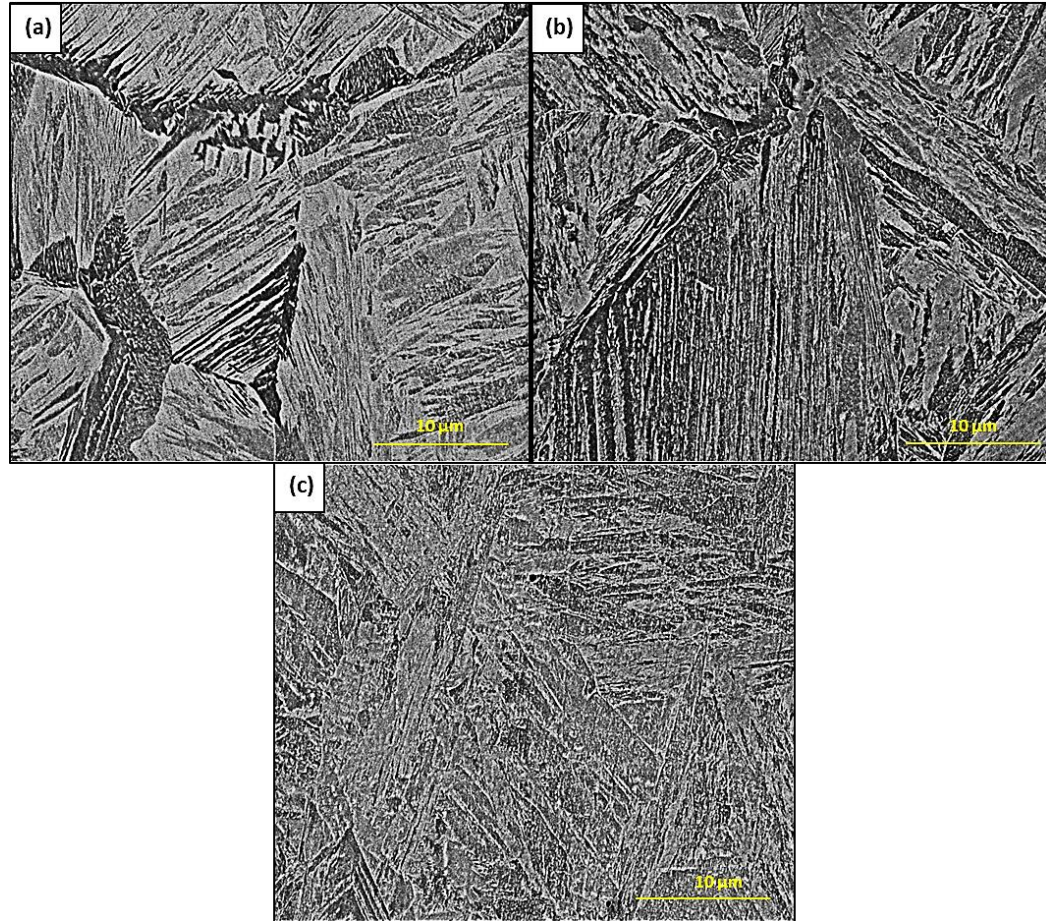


Figure 4.3: FE-SEM images of (a) quenched martensite, (b) Q&T martensite at 300°C, (c) Q&T martensite at 400°C.

4.1.2. Electrochemical Studies

Electrochemical testing of heat-treated rebar samples was conducted to study the effect of heat treatment on the passive film's composition and resistance in concrete pore solution (pH>13.5).

4.1.2.1. Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (EIS) was conducted on heat-treated rebar samples and obtained Nyquist and Bode plots are given in **Fig. 4.4 (a-d)**. The

simulated model given in **Fig. 4.5** represents the physical state of the metal-film and film-electrolyte interface with the superimposed equivalent circuit. This equivalent circuit was used for fitting the experimental data to obtain EIS parameters [45], [131], [132]. In this equivalent circuit, R_s represents the electrolyte resistance, R_{ct} represents the charge transfer resistance and R_f represents the film resistance. Two constant phase elements (CPE) were used in the equivalent circuits against all heat-treated rebar samples instead of capacitors. The capacitive element is used for the uniform or ideal film, however, if the film is heterogeneous or non-ideal due to the surface roughness then the capacitive element is replaced with the CPE to get the best fitting. So one CPE_{dl} was used parallel to the charge transfer resistance and the second CPE_f was used in parallel to the passive film resistance. The high-frequency time-constant ($R_{ct} \cdot C_{dl}$) accounts for the electrical double-layer while the low-frequency time-constant (R_f and C_f) corresponds to redox processes in the oxides film. This is why the good fitting was achieved with the presence of CPEs which could be calculated by Eq. 4.1.

$$Z_{CPE} = [Y_o (j\omega)^n]^{-1} \quad (4.1)$$

Where; Z_{CPE} is the impedance of CPE ($\Omega \cdot \text{cm}^{-2}$), Y_o is a numerical value of the admittance ($1/|Z| = s^n \Omega^{-1} \text{cm}^{-2}$), $j = (-1)^{1/2}$, ω is the angular frequency (rad s^{-1}), and n is the deviation factor from ideal behavior and exist between 0 and 1. CPE will act as an ideal capacitor if $n = 1$, or as a resistor if $n = 0$.

Z_D represents the impedance of the Warburg element and is used in series with film resistance (R_f) to account for diffusion-controlled ions transport at low frequency.

Nyquist and Bode plots of heat-treated rebar samples in concrete pore solution (CPS) can be seen in **Fig. 4.4 (a, b)**.

EIS parameters were extracted from rebar samples in CPS after fitting the experimental data on an equivalent circuit and are given in **Table 4.1**. It can be seen that the highest film resistance (R_f) ($36.8 \text{ k}\Omega\cdot\text{cm}^2$) corresponded to Q&T 400°C rebar followed by Q&T 300°C ($33.2 \text{ k}\Omega\cdot\text{cm}^2$) and martensitic sample ($14.1 \text{ k}\Omega\cdot\text{cm}^2$). For the isothermally heat-treated family, the lowest film resistances corresponded to 400°C ($11.4 \text{ k}\Omega\cdot\text{cm}^2$) whereas the highest resistance corresponded to 570°C ($25.2 \text{ k}\Omega\cdot\text{cm}^2$), a drop of 69%, and 31%, respectively, as compared to the Q&T 400°C .

The charge transfer resistance (R_{ct}) followed the same trend as that of R_f and the highest R_{ct} was noticed to be achieved against Q&T 400°C rebar ($1.73 \text{ k}\Omega\cdot\text{cm}^2$) followed by Q&T 300°C ($1.36 \text{ k}\Omega\cdot\text{cm}^2$). The lowest R_{ct} was noticed to be obtained against 400°C isothermal heated rebar ($0.44 \text{ k}\Omega\cdot\text{cm}^2$).

Nyquist and Bode plots of heat-treated rebar samples in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) are presented in **Fig. 4.4 (c, d)**. EIS parameters were extracted from rebar samples after fitting the experimental data on the same equivalent circuit and are given in **Table 4.2**. The comparison of R_f and R_{ct} before and after chloride exposure is shown in **Fig. 4.6** and it is clearly shown that the addition of chloride to the CPS solution caused a reduction in the R_f for all heat-treated rebar samples. The lowest reduction was for the martensitic sample while the rebar sample heat treated isothermally at 500°C showed the highest reduction. The chloride solution markedly decreased the overall impedances for all rebar samples. Although the presence of the chloride affected all the samples but the

highest R_f and R_{ct} were recorded for the Q&T 400°C rebar marking 21.0 $k\Omega.cm^2$ and 1.2 $k\Omega.cm^2$, respectively. The isothermal heat-treated sample at 500°C showed the lowest R_f and R_{ct} in chloride.

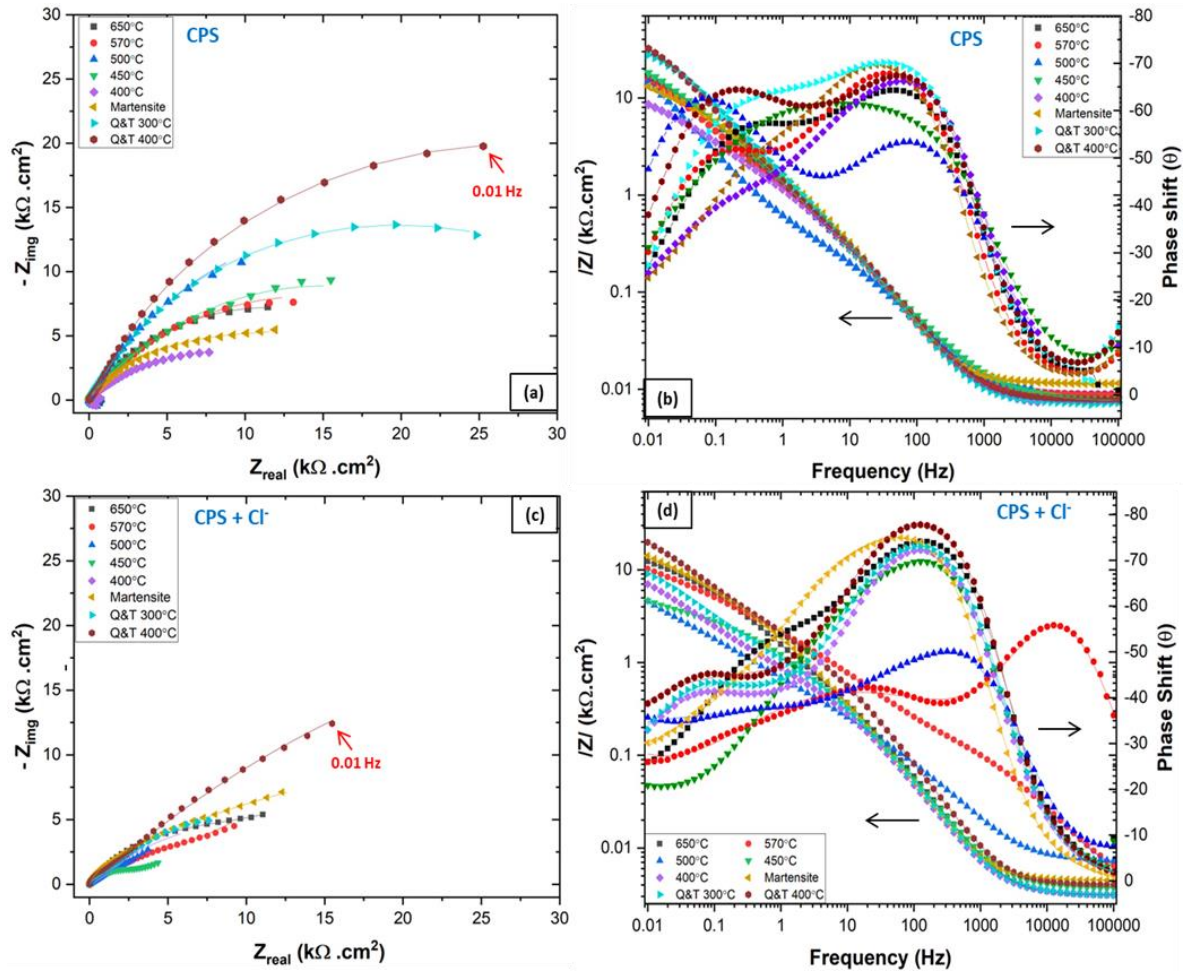


Figure 4.4: Nyquist and Bode plots of isothermal, and Q&T microstructures of steel rebar in (a, b) CPS, (c, d) CPS containing chloride ($Cl^-/OH^- = 1$).

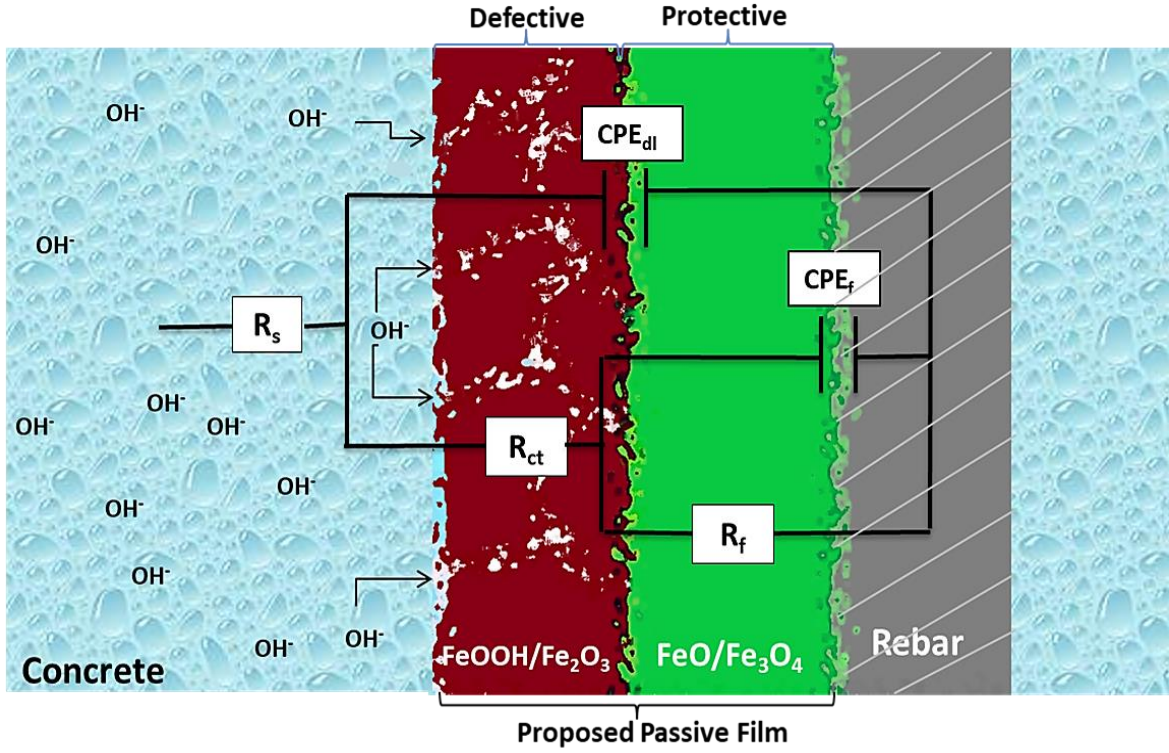


Figure 4.5: Simulated model illustrating the physical nature of metal-film and film-electrolyte interfaces after superimposing the equivalent circuit.

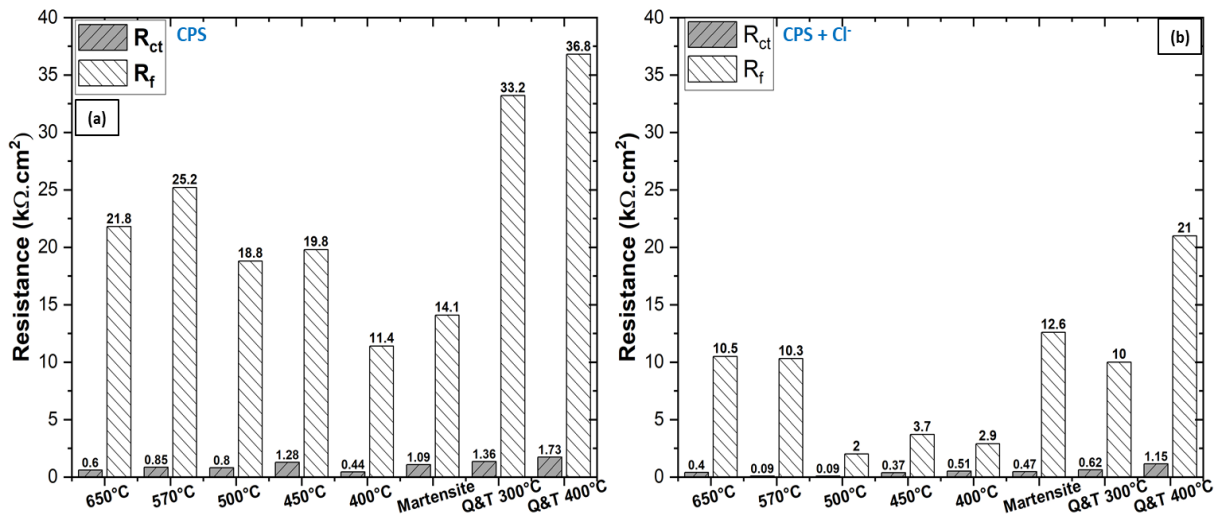


Figure 4.6: Charge transfer resistance (R_{ct}) and passive film resistance (R_f) of isothermal and Q&T heat-treated rebars in (a) CPS, (b) CPS containing chloride ($Cl^-/OH^- = 1$).

Table 4.1: EIS parameters of isothermally, Q&T steel rebar tested in CPS.

Sample	R_s	R_f	$CPE_f(Y_0)$	n	R_{ct}	$CPE_{dl}(Y_0)$	m	W
(Isotherm/ Q&T)	$(\Omega.cm^2)$	$(k\Omega.cm^2)$	$(\Omega^{-1}cm^{-2}s^n)$		$(k\Omega.cm^2)$	$(\Omega^{-1}cm^{-2}s^m)$		$(S*s^{1/2})$
650°C	8.5	21.8	3.54E-04	0.92	0.60	8.90E-04	0.90	--
570°C	8.7	25.2	3.86E-04	0.90	0.85	9.19E-04	0.91	--
500°C	9.3	18.8	3.67E-04	0.93	0.80	8.75E-04	0.92	--
450°C	7.5	19.8	3.75E-04	0.90	1.28	6.50E-04	0.95	--
400°C	7.5	11.4	4.10E-04	0.94	0.44	9.80E-04	0.87	--
Martensite	9.5	14.1	3.21E-04	0.95	1.09	6.50E-04	0.89	1.26E-03
Q&T 300°C	7.1	33.2	2.50E-04	0.92	1.36	5.50E-04	0.92	1.30E-02
Q&T 400°C	7.7	36.8	1.70E-04	0.94	1.73	4.50E-04	0.94	2.34E-04

Double-layer capacitance and film capacitance were measured by using Burg's [133] formula given in Eq. 4.2, and Hsu & Mansfeld [134] formula given in Eq. 4.3, respectively.

$$C_{dl} = CPE_{dl}^{(1/m)} (1/R_s + 1/R_{ct})^{(m-1)/m} \quad (4.2)$$

$$C_f = CPE_f^{(1/n)} R_f^{(1-n)/n} \quad (4.3)$$

Where, CPE_{dl} and CPE_f represent the CPE impedance of the double layer and the film, respectively. R_s , R_{ct} , and R_f are the ohmic resistance, the charge transfer resistance, and the film resistance, respectively. The thickness of the double layer (δ_{dl}) and the film (δ_f) were estimated from the capacitance values according to the following expression;

$$C = \epsilon \epsilon_0 / \delta \quad (4.4)$$

where ϵ is the average dielectric constant which was taken to be 6 for different iron oxides [135] in passive film calculation and 2 for double layer calculation [136], and ϵ_0 is the vacuum permittivity (8.85×10^{-12} F/m).

Table 4.2: EIS parameters of isothermally, Q&T steel rebar tested in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$).

Sample (Isotherm/ Q&T)	R_s ($\Omega \cdot \text{cm}^2$)	R_f ($\text{k}\Omega \cdot \text{cm}^2$)	$\text{CPE}_f(Y_0)$ ($\Omega^{-1} \text{cm}^{-2} \text{s}^n$)	n	R_{ct} ($\text{k}\Omega \cdot \text{cm}^2$)	$\text{CPE}_{dl}(Y_0)$ ($\Omega^{-1} \text{cm}^{-2} \text{s}^m$)	m	W ($\text{S}^* \text{s}^{1/2}$)
650°C	3.1	10.5	6.55E-04	0.89	0.402	1.60E-03	0.91	8.55E-04
570°C	4.0	10.3	6.80E-04	0.92	0.093	1.50E-03	0.95	6.09E-04
500°C	7.1	2.0	9.30E-04	0.91	0.087	1.70E-03	0.91	5.86E-04
450°C	3.7	3.7	5.40E-04	0.92	0.371	1.50E-03	0.88	1.98E-03
400°C	3.2	2.9	5.90E-04	0.94	0.506	2.10E-03	0.89	--
Martensite	4.5	12.6	5.45E-04	0.91	0.467	1.50E-03	0.91	--
Q&T 300°C	4.0	10.0	5.70E-04	0.90	0.622	9.00E-04	0.90	--
Q&T 400°C	4.1	21.0	2.00E-04	0.95	1.150	6.00E-04	0.94	--

The estimated capacitance and thickness of the double layer and passive film developed over the surface of each rebar are given in **Fig. 4.7 (a-d)**. The film capacitance (C_f) and thickness (δ_f) of heat-treated rebar samples in CPS are given in **Fig. 4.7a**, whereas C_f and δ_f estimated in CPS with the presence of chloride are given in **Fig. 4.7c**.

Since, both the capacitance and thickness are inversely proportional to each other so the trend is visible in the figures.

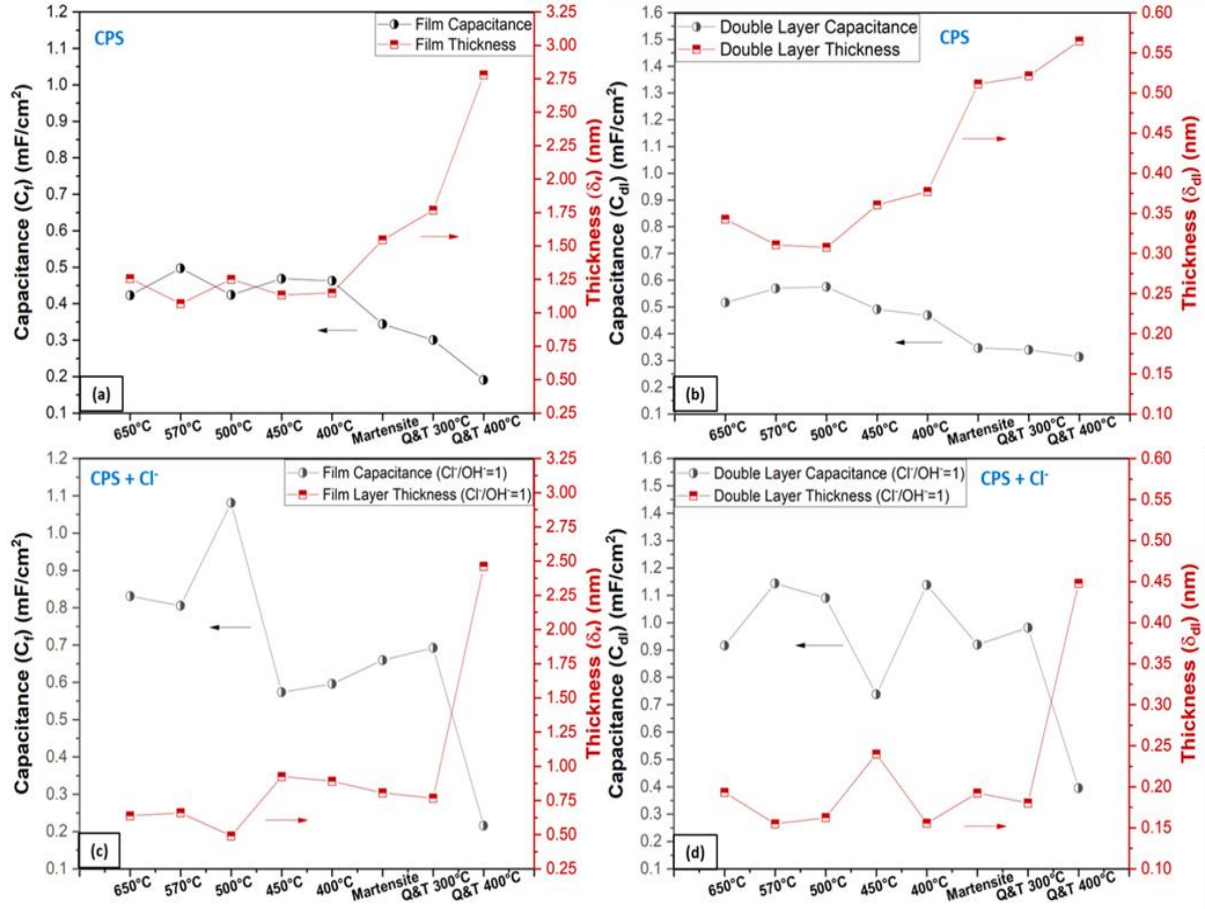


Figure 4.7: Estimated capacitances and thicknesses of (a, c) passive film, (b, d) double layer of isothermal and Q&T heat-treated rebars in CPS with and without chloride.

Out of all heat-treated samples, Q&T 400°C rebar provided the lowest film capacitance (C_f) of 0.19 mF/cm^2 with the highest film thickness (δ_f) of nearly 2.78 nm in CPS. Following this, Q&T 300°C rebar sample was found with C_f of 0.3 mF/cm^2 and δ_f of 1.77 nm. The lowest δ_f and highest C_f were noticed against 400°C- isothermal heat-treated rebar. The double layer capacitance (C_{dl}) and thickness (δ_{dl}) were found in proportionality with the film capacitance (C_f) and thickness (δ_f) and can be seen in **Fig. 4.7 (b, d)**. It

reveals that the lowest double layer capacitance (C_{dl}) of 0.31 mF/cm² and highest thickness (δ_{dl}) of 0.56 nm was achieved against Q&T 400°C rebar followed by Q&T 300°C where C_{dl} was increased to 0.34 mF/cm² and δ_{dl} was reduced to 0.52 nm. Incorporating the chloride in the CPS, however, decreased both the double layer and film thickness against all of the heat-treated samples.

4.1.2.2. Polarization and Corrosion Rates

Potentiodynamic polarization (PDP) and linear polarization resistance (LPR) of heat-treated rebar samples was first conducted in CPS solution and then under the presence of chloride at a fixed ratio ($Cl^-/OH^- = 1$). The PDP curves are presented in **Fig. 4.8 (a, b)** whereas the average corrosion rates measured from LPR based on three readings are given in **Fig. 4.9 (a, b)**. PDP curves of all heat-treated rebar samples in pure CPS reveal that the lowest corrosion current density of 0.94 $\mu A/cm^2$ and corrosion rate of 0.37 mpy was noted for the Q&T 400°C rebar sample. Furthermore, the lowest passive film current density of 9 $\mu A/cm^2$ was also observed against the Q&T 400°C rebar compared to the other heat-treated samples. The current density and corrosion rate of the Q&T 300°C rebar sample in CPS were slightly higher than that of the Q&T 400°C rebar and found to be 1.46 $\mu A/cm^2$ and 0.48 mpy, respectively. Contrarily, the highest current density and corrosion rate were noted against the rebar isothermally heat treated at 400°C temperature marking at 4.04 $\mu A/cm^2$ and 1.62 mpy, respectively. However, the pitting potentials for all samples were essentially identical at around -0.6 V.

The addition of chloride to the CPS solution was found detrimental to the localized corrosion resistance of all samples where the pitting potentials dropped to the potential range of 0.2-0.3 except for the sample Q&T at 400°C as evident in **Fig. 4.8b**.

Notably, **Fig. 4.8b** clearly differentiates between samples Q&T at 400°C and 300°C where the latter has a much lower pitting potential (< 0.4 V). Q&T 400°C rebar was seen

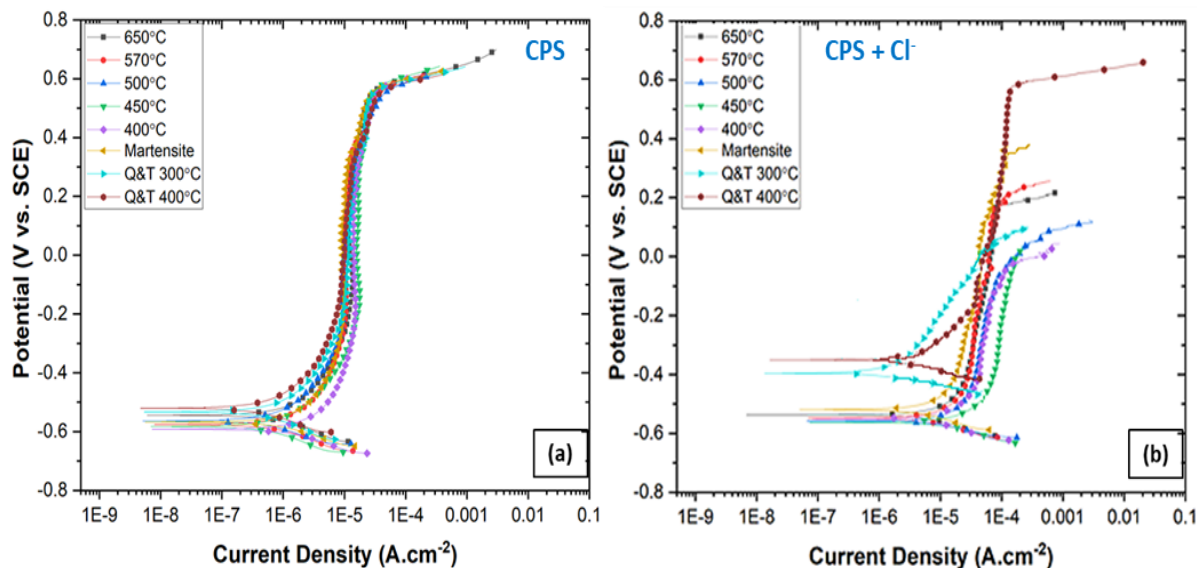


Figure 4.8: PDP plots of isothermal, Q&T heat-treated rebars measured in (a) CPS, (b) CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$).

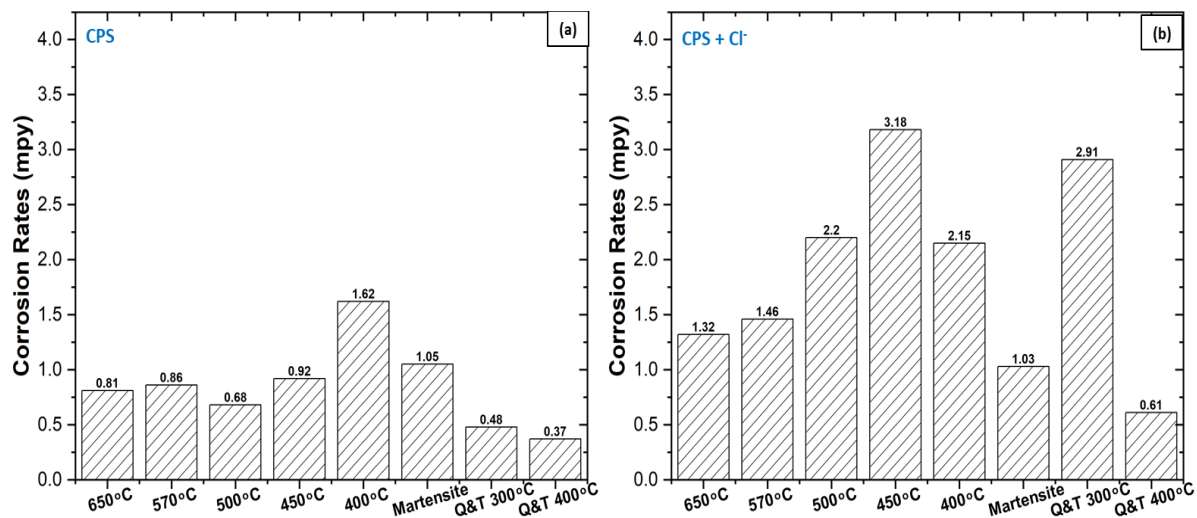


Figure 4.9: Corrosion rates (LPR) of isothermal and Q&T heat-treated rebars in (a) CPS, (b) CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$).

astonishingly resistant to the chloride ingress and hence pitting mechanism was unseen even at the higher potential of 0.6V. Chloride also deteriorated the passive film on every heat-treated rebar but again passive film formed on Q&T 400°C rebar was nearly consistent. The corrosion rates were increased to many folds against all heat-treated samples as shown in **Fig. 4.9b**. However, in comparison to its counterparts, the Q&T 400°C rebar sample provided the lowest corrosion rate even in the presence of chloride.

4.1.3. Passive Film Characterization

X-ray photoelectron spectroscopy (XPS) was employed to characterize the composition of the passive film developed on the surface of selected heat-treated rebar samples in CPS and their spectra are shown in **Fig. 4.10 (a-c)**. The high-resolution XPS spectra of Fe2p signals were deconvoluted into the most probable typical chemical states for corresponding chemical assignments. The Fe2p spectrum shown in **Fig. 4.10** is split into doublets peaks of Fe2p_{3/2} and Fe2p_{1/2}, due to the spin-orbit coupling. Deconvoluted peaks at their corresponding binding energies are given in **Table 4.3**. The peaks at 706.9 eV (2p_{3/2}) and 719.7 eV (2p_{1/2}) in the Fe XPS spectrum corresponded to the metallic state of iron (Fe). Peaks of Fe2p at 709.5 eV (2p_{3/2}) and 722.3 eV (2p_{1/2}) corresponded to the Fe²⁺ state, and reveal the formation of FeO/Fe₃O₄. Two peaks of Fe 2p at 712.6 eV (2p_{3/2}) and 725.4 eV (2p_{1/2}) corresponded to the Fe³⁺ state, and thus reflect the presence of Fe₂O₃/FeOOH in passive film [137][138].

Furthermore, Fe2p peaks detected at 716.6 eV (2p_{3/2}) and 729.4 eV (2p_{1/2}) corresponded to the satellite state. The percentage area of each peak was calculated to estimate the Fe²⁺/Fe³⁺ ratio and is given in **Table 4.3**. The passive film composition of the isothermally heat-treated rebar at 400°C in CPS (**Fig. 4.10a**) exhibited the lowest

$\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (1.65), whereas Q&T 400°C rebar (**Fig. 4.10c**) showed the highest $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (2.57) followed by Q&T 300°C rebar (**Fig. 4.10b**) with a ratio of 2.02.

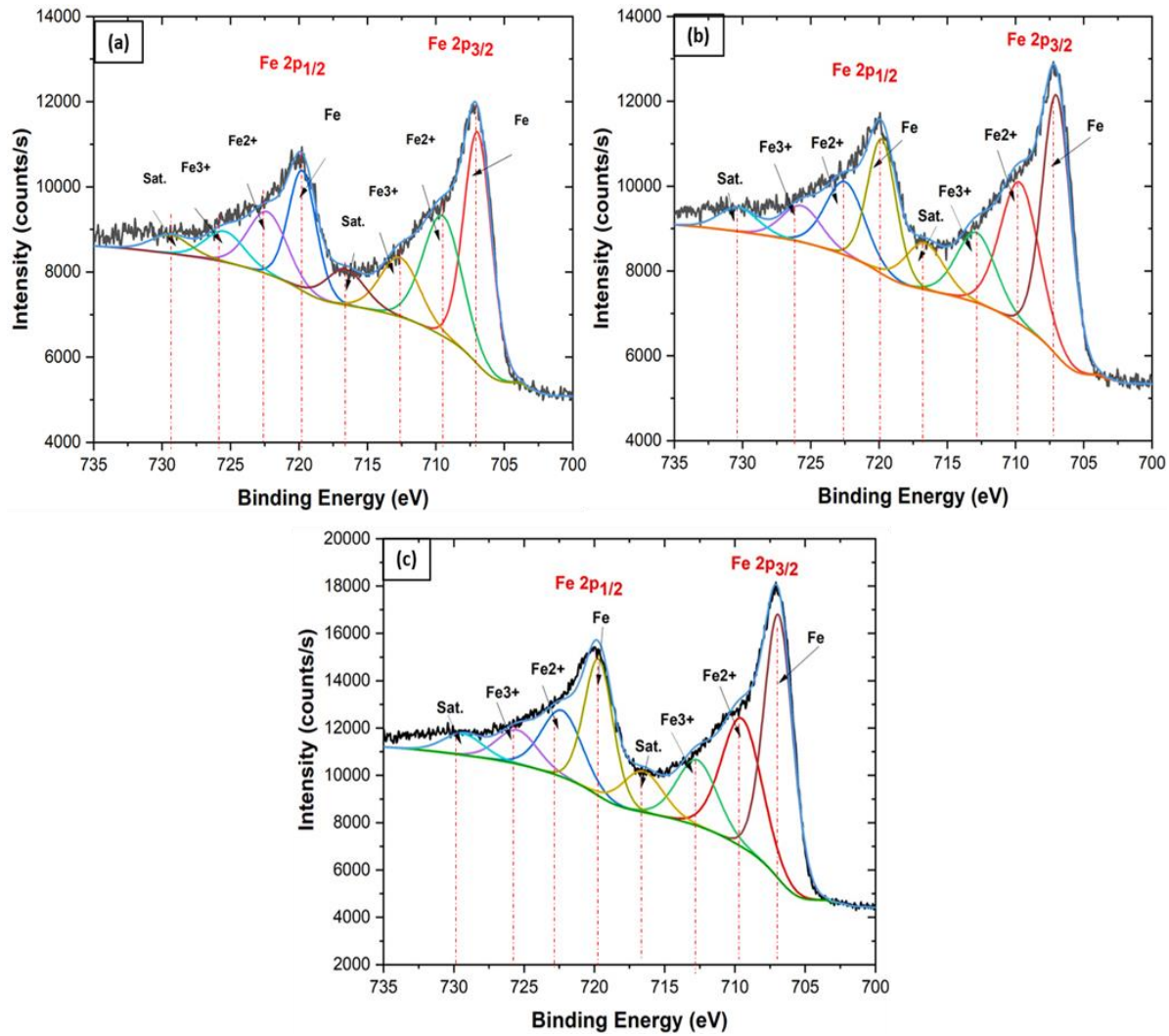


Figure 4.10: XPS spectra of passive film formed over (a) isothermally heated rebar at 400°C, (b) Q&T 300°C rebar, and (c) Q&T 400°C rebar in CPS.

Table 4. 3: Deconvoluted peak parameters of oxide species for different heat-treated samples
(NIST standard reference Database) [137][138].

Heat Treated Sample	Doublet Peaks	Peak Position (eV)	Assignment	Area (cps.ev)	Area (%)	Fe ²⁺ /Fe ³⁺
Isothermal 400°C	Fe 2p _{3/2}	706.9	Fe	14627.8	29.6	1.65
	Fe 2p _{1/2}	719.7	Fe	7570.8	15.3	
	Fe 2p _{3/2}	709.5	FeO/Fe ₃ O ₄	9286.7	18.8	
	Fe 2p _{1/2}	722.3	FeO/Fe ₃ O ₄	4806.4	9.7	
	Fe 2p _{3/2}	712.6	Fe ₂ O ₃ /FeOOH	5579.0	11.3	
	Fe 2p _{1/2}	725.4	Fe ₂ O ₃ /FeOOH	2887.5	5.8	
	Fe 2p _{3/2}	716.6	Sat.	3046.9	6.2	
	Fe 2p _{1/2}	729.4	Sat.	1576.9	3.2	
Q&T 300°C	Fe 2p _{3/2}	706.9	Fe	16308.7	27.9	2.02
	Fe 2p _{1/2}	719.8	Fe	8440.7	14.4	
	Fe 2p _{3/2}	709.6	FeO/Fe ₃ O ₄	12172.7	20.8	
	Fe 2p _{1/2}	722.4	FeO/Fe ₃ O ₄	6300.1	10.8	
	Fe 2p _{3/2}	712.8	Fe ₂ O ₃ /FeOOH	6038.1	10.3	
	Fe 2p _{1/2}	725.6	Fe ₂ O ₃ /FeOOH	3125.1	5.3	
	Fe 2p _{3/2}	716.6	Sat.	3986.2	6.8	
	Fe 2p _{1/2}	730.3	Sat.	2063.1	3.5	
Q&T 400°C	Fe 2p _{3/2}	706.9	Fe	28037.5	28.0	2.57
	Fe 2p _{1/2}	719.7	Fe	14456.6	14.4	
	Fe 2p _{3/2}	709.5	FeO/Fe ₃ O ₄	22794.3	22.8	
	Fe 2p _{1/2}	722.3	FeO/Fe ₃ O ₄	11797.0	11.8	
	Fe 2p _{3/2}	712.7	Fe ₂ O ₃ /FeOOH	8880.9	8.9	
	Fe 2p _{1/2}	725.5	Fe ₂ O ₃ /FeOOH	4596.4	4.6	
	Fe 2p _{3/2}	716.5	Sat.	6300.9	6.3	
	Fe 2p _{1/2}	729.3	Sat.	3261.1	3.3	

This suggests a higher composition of FeO/Fe₃O₄ (Fe²⁺) formed in the passive film developed at Q&T 400°C rebar and a lesser amount of Fe₂O₃/FeOOH (Fe³⁺). The lowest ratio of Fe²⁺/Fe³⁺ against isothermally heat-treated rebar at 400°C revealed that higher percentage composition of FeO/Fe₃O₄ (Fe²⁺) was transformed to Fe₂O₃/FeOOH (Fe³⁺) in the over film chemistry of passive film.

4.1.4. Potentiostatic Film Formation

Potentiostatic (PS) film was chosen to grow on Q&T 300°C and Q&T 400°C rebar samples because of their spectacular electrochemical performance in concrete pore solution (CPS). PS film was grown for 3 and 6 hours while keeping the potential constant at 100 mV against both of the heat-treated rebar samples. The electrochemical evaluation was performed of the grown passive film. EIS, LPR, and PDP were conducted for this purpose.

Nyquist and Bode plots of the PS-grown passive film are given in **Fig. 4.11**. The equivalent circuit used for fitting the experimental data of the PS-grown film at 3 and 6 hours is given in **Fig. 4.12** and the extracted parameters are given in **Table 4.4**. EIS parameters reveal that the charge transfer resistance (R_{ct}) and film resistance (R_f) was noticed to be enhanced with the increase of PS time against both Q&T 300°C and Q&T 400°C rebar samples. However, the film grown on Q&T 400°C rebar was found more resistant to corrosion than the one grown at Q&T 300°C. **Table 4.4** reveals that the R_f of the PS passive film grown for 3 hours on Q&T 400°C rebar was increased to 38 k Ω .cm² compared to the rebar where the film was grown without applying any PS potential at 0 hr (36.8 k Ω .cm²) (spontaneously formed film for 72 hrs in an open environment which was discussed in the previous section is considered as 0 hr PS film). R_f jumped even

further higher to $58.9 \text{ k}\Omega.\text{cm}^2$ once the PS time was increased to 6 hours. Film thicknesses (δ_f) were estimated by using Hsu & Mansfeld's model and are shown graphically in **Fig. 4.13a**. The film thickness was increased with the increase of PS time and a maximum δ_f of nearly 4.5 nm was estimated against the Q&T 400°C rebar when potential was applied for 6 hours.

Like film resistance, charge transfer resistance was also enhanced with the increased time of PS potential. R_{ct} of the Q&T 400°C rebar sample jumped from $9.11 \text{ k}\Omega.\text{cm}^2$ to $15.5 \text{ k}\Omega.\text{cm}^2$ once the time of applied potential was extended from 3 hours to 6 hours. The estimated double layer thickness (δ_{dl}) calculated by Burg's method is given in **Fig. 4.13b** which came in true agreement with the charge transfer resistance and it was discovered that double layer thickness was increased with the increase in time of applied PS potential. The maximum double layer thickness of 0.66 nm was noted against Q&T 400°C rebar once the PS potential was applied for 6 hours.

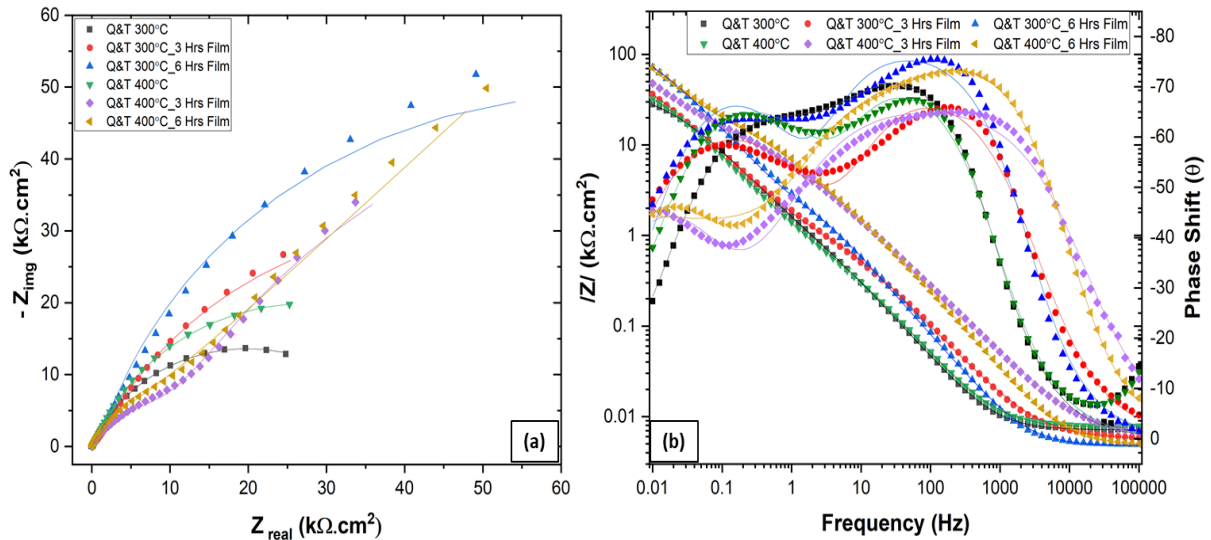


Figure 4.11: Nyquist and Bode plots of the passive film grown for 3 and 6 hours on Q&T 300°C and Q&T 400°C rebar in CPS.

Table 4.4: EIS parameters of potentiostatic-grown film on Q&T 300°C and Q&T 400°C rebar in CPS.

Specimen	Film	R_s	R_f	$CPE_f(Y_0)$	n	R_{ct}	$CPE_{dl}(Y_0)$	m
	Time	$(\Omega \cdot \text{cm}^2)$	$(\text{k}\Omega \cdot \text{cm}^2)$	$(\Omega^{-1} \text{cm}^{-2} \text{s}^n)$		$(\text{k}\Omega \cdot \text{cm}^2)$	$(\Omega^{-1} \text{cm}^{-2} \text{s}^m)$	
Q&T 300°C	0 hrs	7.11	33.2	5.50E-04	0.92	1.36	5.50E-04	0.92
	3 hrs	5.69	34.9	2.20E-04	0.91	8.79	2.75E-04	0.90
	6 hrs	4.77	55.1	2.05E-04	0.90	1.21	1.50E-04	0.93
Q&T 400°C	0 hrs	7.68	36.8	4.50E-04	0.94	1.73	4.50E-04	0.94
	3 hrs	5.86	38.0	1.95E-04	0.90	9.11	2.40E-04	0.89
	6 hrs	4.63	58.9	1.60E-04	0.92	15.5	1.40E-04	0.92

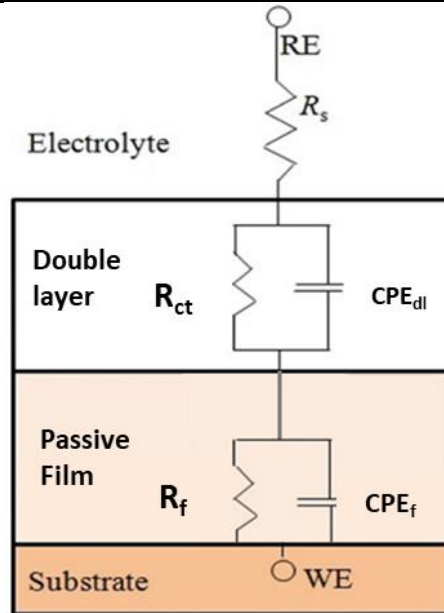


Figure 4.12: Equivalent circuit used for fitting potentiostatic-grown film on Q&T 300°C and Q&T 400°C in CPS.

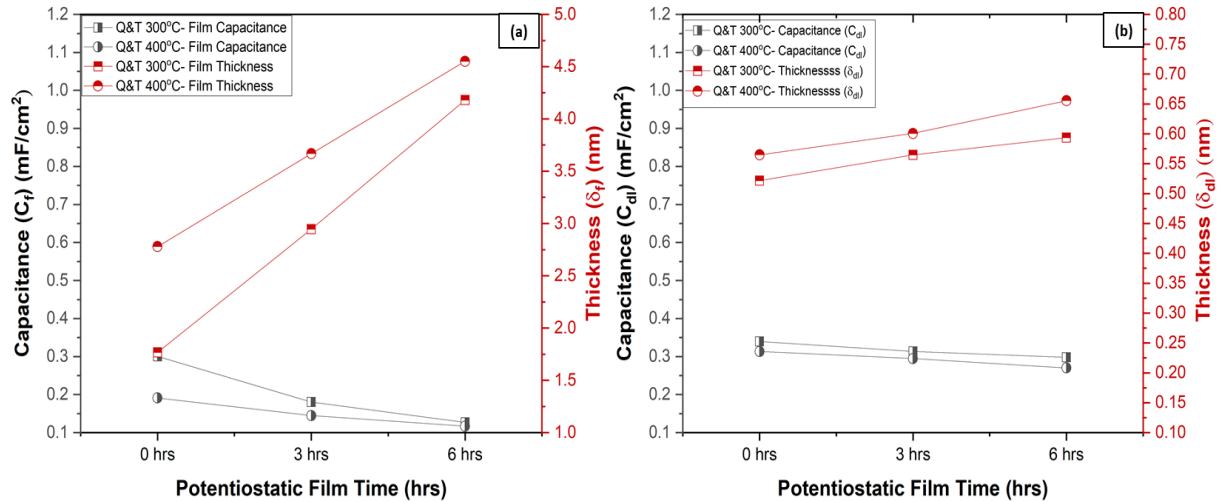


Figure 4.13: Calculated capacitance and thickness of (a) Double layer, (b) Passive film in CPS.

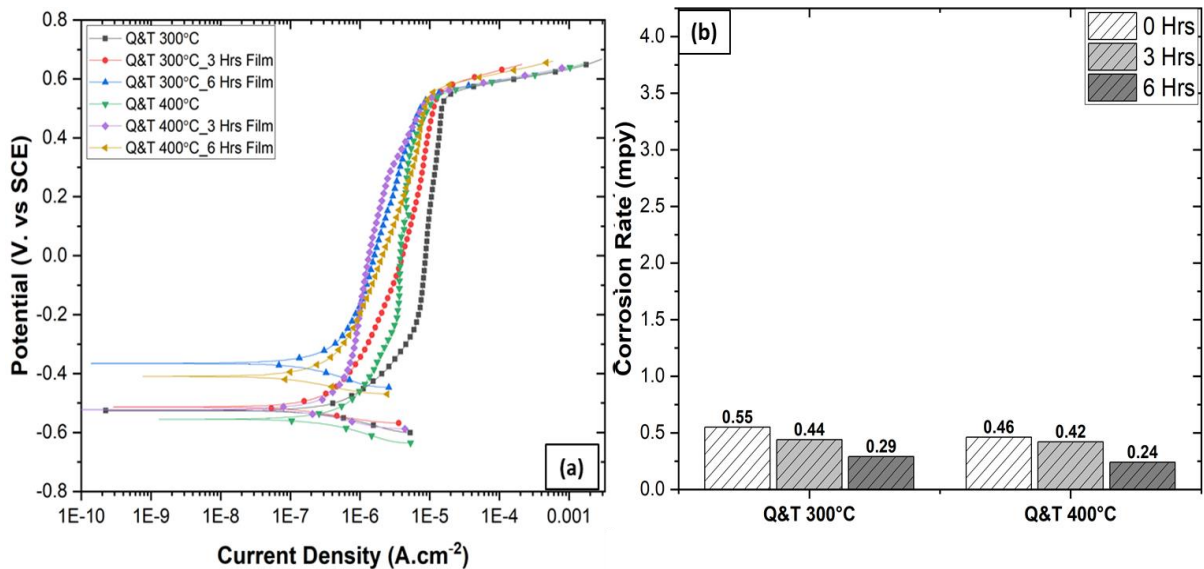


Figure 4.14: (a) PDP and (b) LPR evaluation of the passive film grown for 3 and 6 hours on Q&T 300°C and Q&T 400°C rebars in CPS.

PDP curves in **Fig. 4.14a** revealed that, for Q&T 400°C, the current density got decreased from 0.94 $\mu\text{A}/\text{cm}^2$ to 0.22 $\mu\text{A}/\text{cm}^2$ for the rebar which was provided potentiostatic potential for 6 hours compared to the rebar where no external PS potential was applied for the development of passive film. Corrosion rates measured by LPR

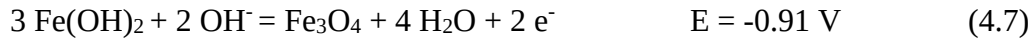
(Fig.4.14b) were also noted to be decreased from 0.46 mpy to 0.24 mpy under the applied potential for 6 hours.

4.2. Discussion

4.2.1. Passive Film Formation Mechanism

The passivity of steel rebars in the CPS environment depends largely on the cement chemistry [131], the presence of aggressive ions, composition and the structure of the passive film, and the passive film ionic and electronic transport properties. Several research groups employed a variety of electrochemical (EIS, cyclic voltammetry, anodic polarization) and surface characterization (XPS, Auger, EXAFS) techniques to investigate the composition and structure of the passive film on steel rebar immersed in high alkalinity solution in the absence of aggressive ions. The prevailing findings revealed that the passive film is typically composed of a bilayer structure of oxides and oxyhydroxides [139]–[142]. The first layer that grows at the metal/film interface is a compact inner layer rich in Fe^{+2} oxides, whereas the outer layer at the film/electrolyte interface has been characterized as porous and rich in Fe^{+3} oxides/oxyhydroxides. Magnetite (Fe_3O_4) has been found by several authors to constitute the major oxide phase in the inner layer and is the main barrier oxide responsible for the corrosion resistance of the passive film [132]. Magnetite is a mixed $\text{Fe}^{+2}/\text{Fe}^{+3}$ oxide and in its perfect state possesses the inverse spinel cubic structure ($\text{M}^{\text{II}}\text{M}^{\text{III}}\text{O}_4$) where half of Fe^{+3} cations occupy tetrahedral sites and the other half and Fe^{+2} cations occupy octahedral sites with oxygen anions occupying the close-pack cubic lattice sites. According to the point defect model, during the growth of the passive film, Fe^{+3} vacancies are generated at the film/electrolyte interface and migrate inward through the passive film, and are consumed at the

metal/film interface [143]. When sufficient Fe^{+3} vacancies are present in magnetite inverse spinel structure, the cation-deficient Fe_3O_4 behaves to a certain extent as Fe^{+2} oxide rather than a mixed oxide [Li and Lou 2007]. The possible reactions that may describe the formation of the inner layer [48], [132] can be summarized in Eq. (4.5) to (4.7) with the equilibrium potentials given at a pH = 13.2 at room temperature [144]:



The sum of Eq. (4.5), (4.6), and (4.7) are given in Eq. 4.8;



The main cathodic reaction in aerated CPS is described by Eq. (4.9):



The schematic illustration of above-described reactions is shown in **Fig. 4.15**. Initially, after the formation of Fe(OH)_2 , the first oxide which gets developed is FeO which, on further oxidation with OH^- , turns into Fe_3O_4 . The $\text{FeO/Fe}_3\text{O}_4$ transformation is a complex mechanism and, in the final stage, a lamellar oxide layer of $\text{FeO/Fe}_3\text{O}_4$ is formed and in detail can be seen somewhere else [145], [146]. Hence, magnetite (Fe_3O_4) or a film with a stoichiometry similar to it ($\text{FeO*Fe}_2\text{O}_3$) forms spontaneously at a potential of about -0.91 V, and hence a spontaneous formation of magnetite on steel rebar exposed to CPS will take place at the open circuit potential even under low oxygen condition [132].

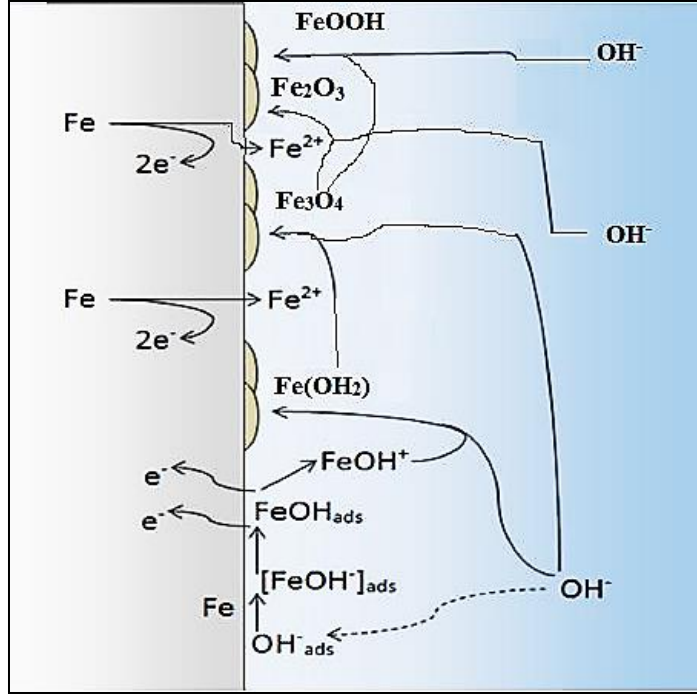
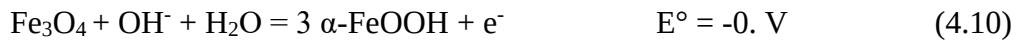
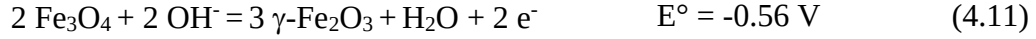


Figure 4.15: Proposed passive film formation mechanism over rebar surface in the concrete simulated environment [147].

The Fe_3O_4 layer is subjected to further oxidation in the highly alkaline solution resulting in the gradual transformation from Fe^{2+} to Fe^{3+} resulting in the formation of the porous outer layer with probably a mixed maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$). The former is a tetragonal cubic whereas the latter is orthorhombic [148]. The transformed $\gamma\text{-Fe}_2\text{O}_3$ has the same inverse spinel structure of Fe_3O_4 but does not provide corrosion protection owing to its highly porous structure as a result of precipitation via the hydrolysis of cations ejected from the inner layer [44]. The following set of reactions may possibly describe the growth of the outer layer [45], [132] along with the equilibrium potentials calculated at a $\text{pH} = 13.2$ [144]:





The peak labeled Fe^{+2} in **Figure 4.10** could possibly include FeO ($E_b = 709.3 - 710.7 \text{ eV}$) and Fe_3O_4 ($E_b = 709.6 - 711.4 \text{ eV}$) while the second peak may include $\gamma\text{-Fe}_2\text{O}_3$ ($E_b = 709.9 - 711.6 \text{ eV}$) and $\alpha\text{-FeOOH}$ ($E_b = 711.0 - 711.8 \text{ eV}$). Therefore, the XPS results shown in **Figure 4.10** are in general agreement with the abovementioned bilayer passive film composition consisting probably of an inner layer mainly comprised of divalent iron oxides including FeO and the cation-deficient Fe_3O_4 and an outer layer composed mainly of $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$. Similar bilayer passive film structure and composition have been reported for steel rebar in simulated concrete pore solution by different researchers using different techniques: cyclic voltammetry and Raman spectroscopy [132], cyclic voltammetry combined with electrochemical impedance spectroscopy [45], and angle-resolved x-ray photoelectron spectroscopy [141]. However, Gunay et al. [149] employed Electron Energy Loss Spectroscopy (EELS) and suggested that the inner layer responsible for corrosion resistance had a structure similar to that of FeO whereas the outer layer was mainly composed of oxides of $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 .

DorMohammadi et al. [150] used XPS, EIS, and reactive force field molecular dynamic simulation to study the early stage of passivity of Fe in NaOH solution and concluded that the passive film had multiple oxide structures: FeO in the innermost layers, Fe_3O_4 in the middle layers, and Fe_2O_3 in outer layers. XPS analysis showed that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio decreased with increasing distance from the metal/oxide interface. Regardless of the exact composition of the inner layer whether it is purely FeO or Fe_3O_4 or a mixture of the two oxides, the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the XPS signal of the passive film

has been employed as a measure of the ratio of the thickness of the inner barrier layer to the outer layer and has been suggested to correlate with the passive film corrosion resistance in CPS environment [151].

The calculated ratios of $\text{Fe}^{2+}/\text{Fe}^{3+}$ increase with an isothermally heat-treated sample at 400°C, Q&T at 300°C, and Q&T at 400°C. This suggests that the ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ correlates well with the corrosion rates measured by LPR, EIS, and PDP.

4.2.2. Microstructural Effect on Passive Film Formation

Steel rebar develops an oxide layer over its surface when it is introduced in a highly alkaline environment of a very high pH (>13.5). However, under such an environment, passive film seems to be dependent upon the underlying microstructural morphology of steel rebar. The passive film seems to be strongly dependent upon the underlying microstructural morphology of steel rebar. For instance, EIS parameters in **Table 4.1** reveals that the microstructure achieved at 400°C isothermal temperature provided the lowest R_f (11.4 $\text{k}\Omega\cdot\text{cm}^2$) and R_{ct} (0.44 $\text{k}\Omega\cdot\text{cm}^2$) characteristics in comparison to the microstructure achieved at Q&T 400°C, where R_f (36.8 $\text{k}\Omega\cdot\text{cm}^2$) and R_{ct} (1.73 $\text{k}\Omega\cdot\text{cm}^2$) were found to be 3.2 and 3.9 times superior to its counterpart, respectively. Hence, knowing the importance of rebar microstructure, it becomes a core interest to understand the microstructural correlation with corrosion properties. Assuming that the composition of the passive film is the same for all heat-treated rebar samples of this study, it remains to discuss the possible causes of the variation in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio with the underlying microstructure. The variation in $\text{Fe}^{2+}/\text{Fe}^{3+}$ with the heat treatment can be related to the variation in the composition and the structure of the passive film to two possibilities: surface inhomogeneity associated with the heat treatment that might

influence the nucleation and growth of the inner layer or owing to the difference in OCP of the rebar in simulated CPS and the accompanying effect on the electrochemical reactions. The difference in initial OCP of the different microstructures before reaching a fully passivated state was negligible (in the range of a few millivolts) and could not account for this behavior. This led us to focus on the effect of the underlying microstructure on the nucleation and growth of the inner layer.

The formation of passive films in austenitic and duplex stainless steels and the effects of the substrate composition and metallurgical surface state have been the subject of intensive research in the past decades. However, similar studies for mild steels are scarce in the literature. A few studies have investigated the relationship between the underlying steel rebar microstructure and the behavior of the passive film in terms of composition, thickness, and barrier properties. Yilmaz et al. [152] investigated the effect of cold- and hot-rolled microstructures on the passivity behavior of interstitial-free iron in an alkaline solution at ambient temperature. The thicknesses of the passive layers formed on the cold-rolled iron (characterized by high microstructural defect density) were estimated to be approximately 2.54 nm as compared to 1.67 nm for the hot-rolled iron (low microstructural defect density). This was attributed to lower work function and hence higher surface reactivity of the cold-rolled microstructure resulting in faster kinetic growth of the passive film.

Cementite and ferrite form a micro-galvanic couple in steel [41]. The morphology and distribution of cementite (Fe_3C) in the ferrite matrix can then influence the electrochemical properties of steel rebar. In addition, the subsequent size, shape, and distribution of different phases altered by various heat treatments can also affect the

electrochemical properties. Hence, the effect of the underlying microstructures of steel rebar would play a role in the electrochemical behavior.

The basic mechanism for corrosion in the steels with different microstructures (pearlitic, bainitic, tempered martensitic, and martensitic) is similar where the matrix phase, ferrite, acts as the anode and cementite acts as the cathode and hence forms a galvanic couple. However, the size, shape, and distribution of the constituents in the microstructures lead to a change in the length scales of the galvanic couples. The possibility of galvanic coupling may exist in two possible manners; (i)- local anodes and cathodes may be formed due to electrochemical differences between adjoining regions, and/or (b) ionic species may adhere preferentially to particular regions, due to factors such as carbide distribution, causing localized attack [153].

At isothermal temperature, austenite transformation into coarse or fine pearlite was observed. The alternate layers of ferrite and cementite could be seen at 650°C and 570°C in **Fig. 4.2a** and **Fig. 4.2b**, respectively. As 650°C isothermal temperature is very close to the eutectoid line, so lamellar layers of ferrite and cementite were noticed to be thicker as compared to those lamellar layers found at 570°C, thus distinguished as coarse pearlite and fine pearlite, respectively. With the lowering of the isothermal temperature, the geometric shape of ferrite and cementite has emerged as needle type unlike the lamellar structure found in pearlite. Hence, upper bainite, bainite (intermediate), and lower bainite were recognized at 500°C (**Fig.4.2c**), 450°C (**Fig.4.2d**), and 400°C (**Fig.4.2e**), respectively.

During the quenching mechanism, a diffusion-less transformation of austenite into martensite takes place because of the supersaturated solid solution of carbon in an iron

unit cell. In order to increase the toughness of the steel by providing the necessary driving force for the carbon atoms to diffuse out of the unit cells, tempering is performed. The resulting microstructure and toughness achieved is dependent on the tempering temperature. For instance, during stage I, transition carbides are formed and the lowering of carbon content of the martensite matrix takes place [45]–[47]. The tempering temperature of stage-I is dependent on the alloying content of the steel. For the present carbon content (0.192 %), stage I was noted to be achieved at 300°C tempering temperature as the microstructural image in **Fig. 4.3b** correlated with that of **Fig. 4.1** revealed that tempering performed at such temperature provided higher hardness than that of tempered 400°C steel rebar. It is supposed due to the formation and dispersion of fine transition carbides in the martensite matrix. However, during stage II of the tempering process, hardness drops because of two possible reasons; (i)- due to the transformation of retained austenite into ferrite and cementite and (ii)- due to martensite dissociation as newly formed cementite is considered to be formed in between the laths of martensite [45]–[47]. For the present steel rebar composition, described mechanisms can be responsible for the decreased hardness of tempered 400°C steel rebar and can be seen in **Fig. 4.3c**.

Once heat-treated rebar is immersed in an alkaline solution, OH^- ions are supposed to be adsorbed on highly active regions (more Gibbs-free energy) such as interface areas. Generally, in the presence of electrolytes, OH^- ions attack at such interface regions- known as the anodic sites [33]. The geometry and shape of such interface regions thus become the governing factors in setting the base for the growth of the passive film. Electrochemical and surface characterizations indicated that the

corrosion resistance of steel is closely related to the morphology of non-corroded iron carbide which may control the formation of passive film. It is determined by the heat treatment performed on the steel samples which also establishes the characteristics of the micro galvanic coupling between ferrite and cementite. This behavior is explained by the differences between the distribution and morphology of the non-corroded cementite which controls the intensity of the galvanic coupling between ferritic and pearlitic steel constituents and the formation of passive film [154]. As a result, due to the number of reactions involved (Eq. 4.5 - 4.11), OH^- ions start developing the passive oxide film over the surface of the steel rebar in an alkaline solution.

An alternate galvanic couple may exist in the case of pearlitic steel (**Fig. 4.2(a,b)**), whereas a distributed galvanic couple may be formed in the case of bainitic steel since cementite is not in the lamellar structure (**Fig. 4.2(c-e)**) [153]. In addition, the length of the carbide in bainitic steel was distributed on a finer length scale (nanometer) compared to that of pearlitic steel. Therefore, the density of ferrite to carbide interface regions was observed significantly higher at the lower bainitic steel (400°C isothermal temperature), which could be the ultimate reason behind obtaining the lowest film resistance (R_f) of $11.4 \text{ k}\Omega\cdot\text{cm}^2$ (**Table 4.1**) and the highest corrosion rate of 1.62 mpy (**Fig 4.9a**). The passive film chemistry formed over lower bainitic steel (**Fig. 4.10a**) provided a lower $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (1.65) which signifies that higher percentage composition of $\text{FeO}/\text{Fe}_3\text{O}_4$ (Fe^{2+}) was transformed to $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{3+}). Since, OH^- adsorption on the lower bainitic steel was on a finer length, the increased interface density might be the reason for assisting in the transformation of the initially formed $\text{FeO}/\text{Fe}_3\text{O}_4$ (Fe^{2+}) to the defective $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{3+}) at such regions in the passive film

development process. Secondly, the formed passive film over an isothermally treated rebar surface might not be continuous because those fine-distributed carbides might have provided significantly higher anchoring sites for the growth of different oxides at different locations [155]. Thus, discontinuous passive film could turn into a non-protective film.

In the case of continuous cooling heat-treated steels, as-quenched presents the highest corrosion rates, largely due to the high lattice strains/dislocation densities developed after rapid cooling from austenite. The tempering treatment brings about an improvement in corrosion resistance and a decrease in hardness. The improvement in corrosion resistance with tempering is largely a function of (i) the annihilation of dislocation density, and (ii) the coarsening of the alloy carbide precipitates (associated with relief in lattice strains and a lower net contribution to the cathodic reaction current density). Noting the correlation between hardness and corrosion rate measurements, the metallurgical tempering phenomena kinetics is deemed to be greater at the higher tempering temperatures. The combination of high-temperature tempering and long holding time would thus produce a softer but tougher alloy with improved corrosion resistance under the explored experimental conditions [156].

The more of the dispersion of carbides, the more lath interface regions are emerged which could be seen in **Fig. 4.3b** against the Q&T 300°C steel rebar. In **Fig. 4.10b**, it can be seen that, at 300°C tempering temperature, the passive film chemistry developed on the rebar surface was exhibiting $\text{Fe}^{2+}/\text{Fe}^{3+}$ to 2.02, which is higher than isothermally heated rebar (1.65) but lower than Q&T 400°C rebar (2.57). This signifies that in comparison to isothermal rebar, the lower percentage composition of $\text{FeO}/\text{Fe}_3\text{O}_4$

(Fe²⁺) was transformed to Fe₂O₃/FeOOH (Fe³⁺) which makes the passive film a bit more resilient. However, still it was less protective than the passive film formed on Q&T 400°C rebar. This is because fine martensite laths in Q&T 300°C rebar are still providing high surface-to-volume ratios and, subsequently, provide a larger number of anchoring sites to transform Fe²⁺ to Fe³⁺ at such interfaces [155]. Higher interface volume per unit area could be responsible for the growth of a discontinuous passive film over Q&T 300°C and 400°C- isothermally heat-treated rebars. Thus, the film was found to be deteriorated under the presence of chloride as PDP plots reveal its dissolution with the initiation of the pitting mechanism in **Fig. 4.8b**.

On contrary, tempering at 400°C temperature increased the driving force for carbon diffusion out of martensite and thus led to the increased dissolution of martensite. Subsequently, the surface-to-volume ratio provided by lath interfaces got decreased (**Fig.4.3c**). Also, retained austenite may have transformed into cementite and ferrite at the given tempering temperature. Hence it can be deduced that, unlike isothermal and tempered 300°C rebar, fewer anchoring sites were available against Q&T 400°C rebar. Consequently, reduced laths interfaces did not provide a supporting role, and thus lower percentage composition of the initially formed FeO/Fe₃O₄ (Fe²⁺) was transformed to the Fe₂O₃/FeOOH (Fe³⁺) (**Fig.4.10c**), which is why film resistance (R_f) got increased (**Table 4.1 & 4.2**). Structural equilibrium might have developed between newly formed ferrite, cementite, and martensite matrix in terms of size, shape, and distribution which could be the reason behind the reduced corrosion rate against Q&T 400°C rebar.

4.2.3. Microstructure-Passive Film Model

The chemistry of the passive film of the differently heat-treated rebars revealed that the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is proportional to the passive film resistance (R_f) and protective tendency in the concrete environment, and vice versa. In a comparison of isothermal 400°C and Q&T 400°C rebars, $\text{Fe}^{2+}/\text{Fe}^{3+}$ was noted to be 1.65 and 2.57, respectively, where the latter provides more robust film resistance than the former. In terms of composition, $\text{FeO}/\text{Fe}_3\text{O}_4$ (Fe^{2+}) constituted 62.42% and 71.98%, respectively against isothermal 400°C and Q&T 400°C. Similarly, $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{3+}) was constituted of 37.58% and 28.02%, respectively against isothermal 400°C and Q&T 400°C. The schematic diagram illustrating the placement of passive film on the surface of steel rebar embedded in concrete pore solution has been shown with the percentage composition and symmetry of each layer in **Fig. 4.16** [157]. From this, it can be understood that in the presence of OH^- ions, the proportionality of extended oxidation of $\text{FeO}/\text{Fe}_3\text{O}_4$ (Fe^{2+}) into $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{3+}) decides about the protective or defective nature of the passive film, and so does about the film resistance (R_f). A schematic model has been proposed by us in **Fig. 4.17** revealing the possible stages in the formation of passive film on steel rebar having two different microstructures. This model conceptualizes that the nucleation and growth of $\text{FeO}/\text{Fe}_3\text{O}_4$ (Fe^{2+}) at earlier stages, and their extended oxidation to $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{3+}) in later stages, is based on the density of lath interfaces/anchoring sites of the underlying microstructure. For instance, for the isothermal 400°C rebar, after nucleation, film growth could be restricted by the possible nearest interfaces and thus a higher number of junctions could restrict the continuous growth of $\text{FeO}/\text{Fe}_3\text{O}_4$ (Fe^{2+}). Subsequently, these junctions may provide themselves as preferential positions for the

attack of OH^- ions to oxidize $\text{FeO/Fe}_3\text{O}_4$ (Fe^{2+}) into $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{3+}) in the later stages. This could be the reason that in isothermal 400°C rebar, a higher amount of $\text{FeO/Fe}_3\text{O}_4$ (Fe^{2+}) was oxidized and resulted in 37.58% $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{3+}) in the overall passive film chemistry. Since $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{3+}) is defective, their higher amount in film composition may allow the diffusion of Cl^- ions to reach the metal- $\text{FeO/Fe}_3\text{O}_4$ (Fe^{2+}) interface. This is why; the lowest film resistance (R_f) with the highest corrosion rate was achieved against isothermal 400°C rebar. Unlikely, alteration of microstructure at Q&T 400°C lowered the density of lath interfaces to a certain level whereby martensite matrix and newly formed cementite and ferrite could come in a structural equilibrium in terms of shape, distribution, and size [154][156]. Therefore, at the initial stages, the growth of $\text{FeO/Fe}_3\text{O}_4$ (Fe^{2+}) was restricted by a lower number of interface junctions, and thus the lower number of preferential positions could be provided to the attack of OH^- ions for the extended oxidation of $\text{FeO/Fe}_3\text{O}_4$ (Fe^{2+}) into $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{2+}) (**Fig. 4.17**). This could be the result that a comparatively lower amount of $\text{FeO/Fe}_3\text{O}_4$ (Fe^{2+}) was oxidized and resulted in only 28.02% $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{3+}) in the overall passive film chemistry. Consequently, a higher percentage of $\text{FeO/Fe}_3\text{O}_4$ (Fe^{2+}) (71.98%) in the passive film could be the reason behind improved corrosion resistance and film resistance (R_f), possibly due to the lesser Cl^- ions diffusion reaching metal- $\text{FeO/Fe}_3\text{O}_4$ interface.

Now it is established that the composition of the passive film is a functionality of heat treatment and microstructure, so the possible factors governing this phenomenon are further evaluated. The significance of the geometrical shape, density, and distribution of carbides in evaluating the performance of passive film has already been described, but the

discussed factors may contribute to the current-carrying capacity against each heat-treated rebar in the cathodic reaction domain [156]. For instance, at Q&T 400°C rebar, the increased size of carbides is responsible for its decreased number density, resulting in a lower net interfacial area to bulk particle volume ratio. In addition, the tempering mechanism is also responsible for the decreased dislocation density, thus it can be speculated that the number of potential cathodic reaction sites (effective surface area) for a normalized surface area may have decreased [156]. If this was to happen, this would drop the contribution of the total cathodic current density. Consequently, lower cathodic current density might have assisted in achieving a controlled reaction kinetic, and thus lower number of vacancies and defects are expected to form in the formation of passive film. This could be the reason that FeO/Fe₃O₄ (Fe²⁺) was transformed to a lower amount of (37.58%) Fe₂O₃/FeOOH (Fe³⁺), which is justified because (Fe³⁺) is considered to have a structure with more number of defect and vacancies.

The critical role of the microstructure in governing the composition of the passive film can also be seen through another lens. The electrochemical impedance spectroscopy (EIS) spectra shown in Figure reveal the existence of two-time constants. The exponents of the CPE elements fall within a range of values (0.87-0.95) for all rebar samples which are indicative of a dominant capacitive behavior. The CPE_{dl} and the CPE_f represent the amount of charge stored in the double layer and in the passive layer, respectively. The time constant (τ) for each loop is defined as the resistance multiplied by the capacitance in the loop ($\tau = R \cdot C$) assuming that the CPE behavior is ideal. The time constant physically defines the time required to charge the capacitor in the loop. A large loop resistance implies a small current and hence it would take longer to charge the capacitor.

The time constant of the double-layer ($\tau_{dl} = R_{ct} * C_{dl}$) represents the time required to charge the double-layer (a low-frequency process) while the time-constant of the film ($\tau_f = R_f * C_f$) provides a measure of the kinetics of redox reactions taking place in the passive film (a high-frequency process). The film time-constant has been suggested frequently to describe the transformation of Fe^{2+} to Fe^{3+} oxides (Fe_3O_4 to Fe_2O_3) [45], [150]. The double layer capacitance, CPE_{dl} , for the isothermal heated samples approach $(89-98) \times 10^{-3} (\Omega^{-1} cm^{-2} s^n)$, typical values for the double layer of a spontaneous passivating film in steel immersed in alkaline solutions.

It was observed that with the increase of isothermal and tempering heat treatment temperatures, a linear decreasing trend in capacitances was noted (**Fig. 4.7a & 4.7c**). In the presence of chloride (**Fig. 4.7c**), our capacitance estimates decreased from $0.59 mF.cm^{-2}$ to $0.21 mF.cm^{-2}$ calculated against isothermal $400^\circ C$ and Q&T $400^\circ C$, respectively, as a function of heat treatment temperature. Our interpretation is that the high capacitance measurements of isothermally heat-treated samples are the consequence of severe corrosion which is resulting to roughen the interface and thus might have increased the effective electroactive area [156]. The increased effective electroactive area could rapidly enhance the reaction kinetics between Fe^{+2} and OH^- ions and thus might be the reason behind the formation of $Fe_2O_3/FeOOH (Fe^{3+})$ in the passive film. Since the reaction kinetic is sufficiently fast and the initially formed $FeO/Fe_3O_4 (Fe^{2+})$ is not getting sufficient time for film transformation, the susceptibility of vacancies and defects formation is increased to many folds. This justifies the formation of higher percentage content (37.58%) of $Fe_2O_3/FeOOH (Fe^{3+})$. Consequently, an unprotected passive film

with an estimated thickness of just 0.89 nm (**Fig. 4.7c**) was grown against the 400°C isothermal rebar, thus providing the lowest film resistance (R_f).

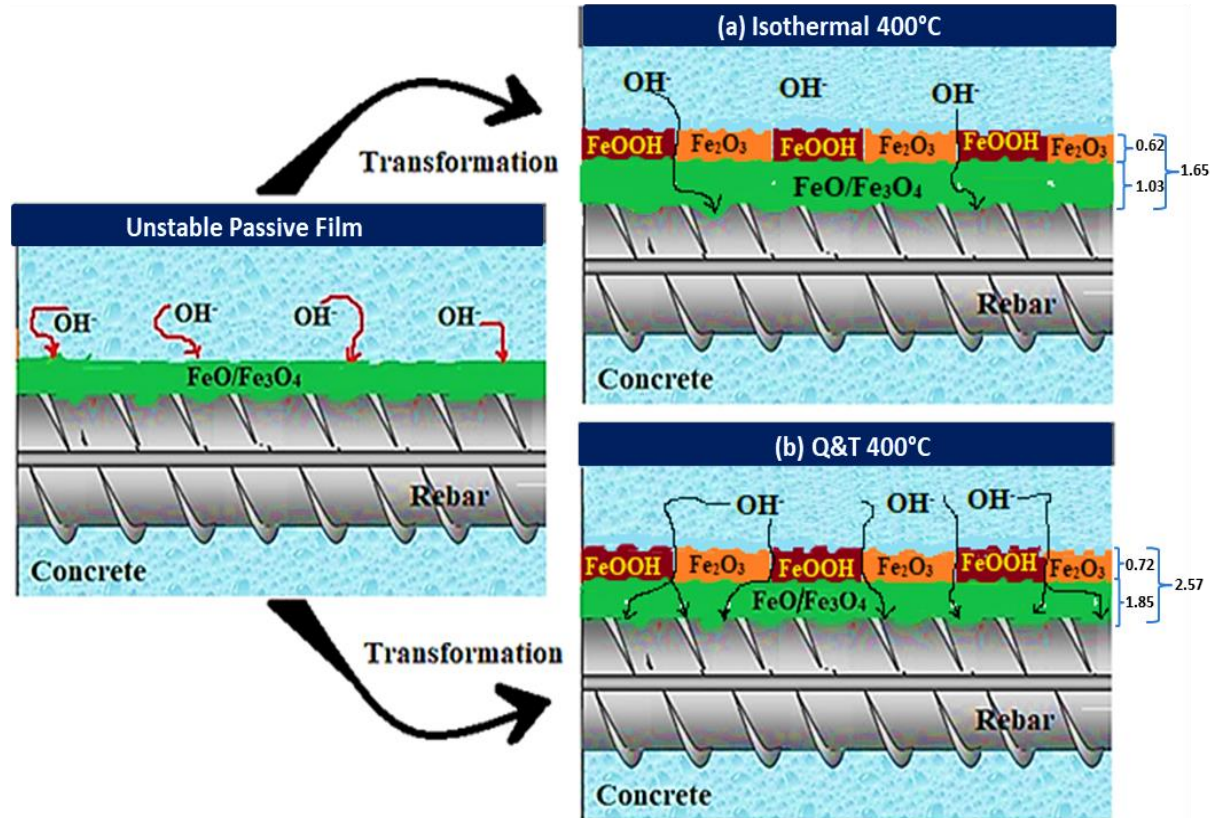


Figure 4.16: Model illustrating the effect of grain structure on the composition of passive film developed on steel rebar in concrete simulated solution (a)- Isothermal 400°C rebar, (b)- Q&T 400°C rebar.

Contrary to the isothermally heat-treated rebar, the lowest capacitance was achieved against Q&T 400°C rebar (**Fig. 4.7c**) signifying the lower effective electroactive area which might have assisted in achieving a controlled reaction kinetic, and thus lower number of vacancies and defects are expected to form. As a result, a lower amount of $\text{FeO/Fe}_3\text{O}_4$ (Fe^{2+}) was transformed to $\text{Fe}_2\text{O}_3/\text{FeOOH}$ (Fe^{3+}) (28.02%). Hence, a continuous protective passive film might have grown with higher thickness (2.46 nm),

and thus provided the highest film resistance (R_f) in **Fig. 4.6b**. Thus, we conclude it could be the effective or true electroactive surface area of carbides on the geometrically-normalized rebar surface that may control the cathodic current dynamics to a varying extent as a function of tempering.

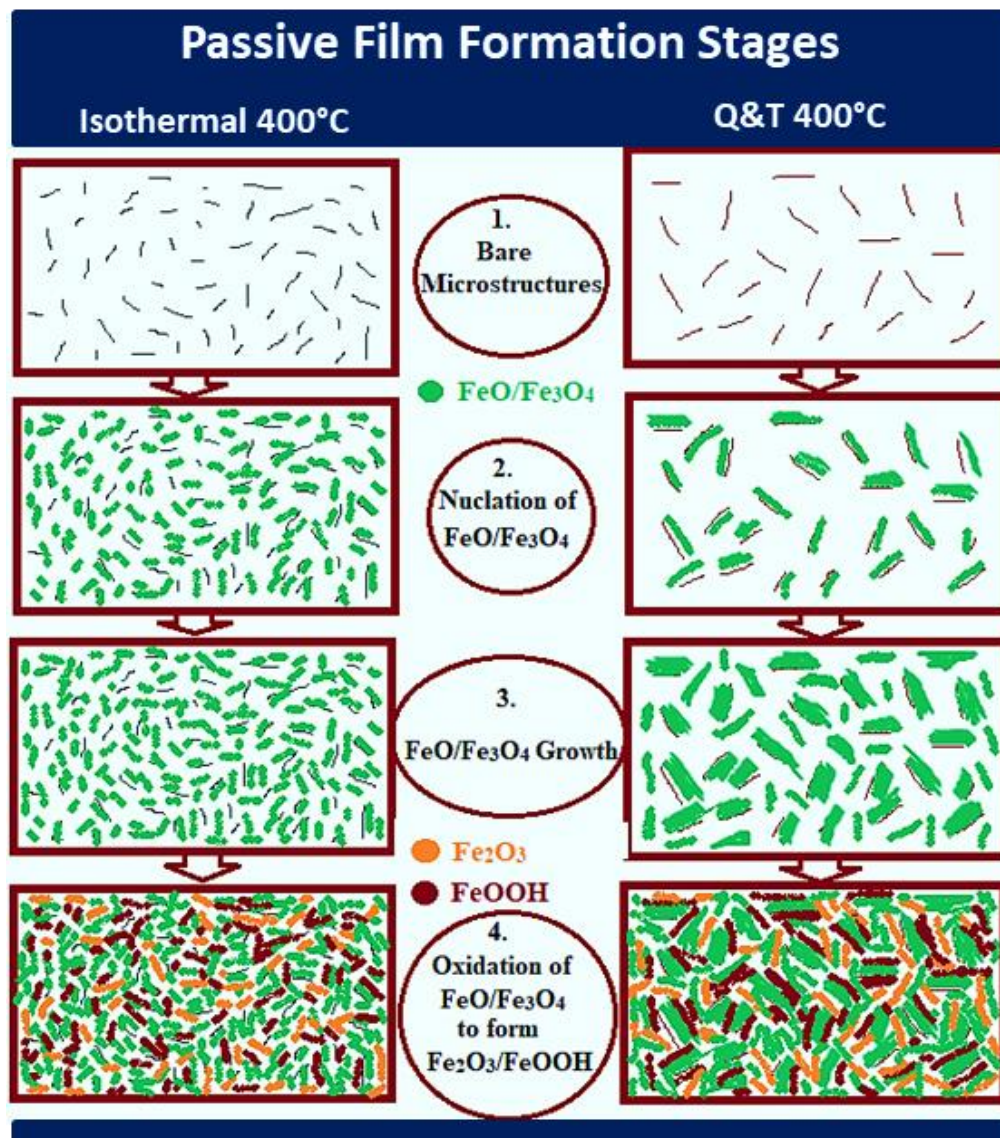


Figure 4.17: Schematic model illustrating the nucleation and growth mechanism of passive film formation under different stages.

4.3. Conclusions

Commercial-grade of carbon steel rebar was used to investigate the effect of heat treatment on corrosion resistance in concrete-simulated environments. Steel rebar was heat treated at different isothermal temperatures i.e. 650°C, 570°C, 500°C, 450°C, and 400°C, as well as quenched and tempered (Q&T) at 300°C and 400°C. Electrochemical evaluation of heat-treated samples was carried out in concrete pore solution (pH >13.5) with and without chloride addition. The main results reported in the present work support the following general conclusions:

- Isothermal and Q&T heat treatments have a significant effect on the corrosion rates and the pitting resistance of steel rebar in CPS and in CPS+Cl⁻ solutions.
- The corrosion rates calculated from the LPR technique were generally higher for rebar samples subjected to isothermal heat treatment as compared to Q&T samples at all temperatures examined in CPS solution with and without the addition of chloride. The effect of the heat treatment on the corrosion rates was higher in the chloride-containing solution. The highest corrosion rate was associated with the 400°C-isothermal rebar whereas the lowest corrosion rate was achieved against the Q&T 400°C rebar in simulated concrete pore solution.
- PDP tests indicated a significant difference in behavior when rebars were tested in CPS solution containing chloride where Q&T at 400°C showed the highest pitting resistance and the isothermally treated rebars at 400-500°C range showed the lowest pitting potential.
- EIS results in CPS containing chloride revealed that the Q&T 400°C rebar provided the film resistance ($R_f = 21 \text{ k}\Omega\cdot\text{cm}^2$) and charge transfer resistance ($R_{ct} =$

1.15 k Ω .cm²) which were 7.2 and 2.3 times higher than the corresponding values of R_f (2.9 k Ω .cm²) and R_{ct} (0.50 k Ω .cm²) for the rebar sample isothermally treated at 400°C, respectively.

- Characterization of the passive film composition by XPS revealed that the highest Fe²⁺/Fe³⁺ ratio (2.57) was achieved against Q&T 400°C rebar with 71.98% FeO/Fe₃O₄ (Fe²⁺) and 28.02% Fe₂O₃/FeOOH (Fe³⁺). Whereas, the lowest Fe²⁺/Fe³⁺ ratio (1.65) was achieved against 400°C-isothermal heat-treated rebar with 62.42% FeO-Fe₃O₄ (Fe²⁺) and 37.58% Fe₂O₃/FeOOH (Fe³⁺).
- The higher percentage content of Fe₂O₃/FeOOH (Fe³⁺) in the passive film formed on 400°C-isothermal rebar could be responsible for the reduced film resistance possibly due to a higher number of defects. Contrarily, lower percentage content of FeO/Fe₃O₄ (Fe²⁺) oxidized into Fe₂O₃/FeOOH (Fe³⁺) in the passive film formation on Q&T 400°C rebar and thus could be the reason behind achieving the remarkable film resistance.
- The composition of the passive film is dependent on the underlying microstructure of rebar. For instance, higher interface density provided a higher surface-to-volume ratio in 400°C- isothermally and Q&T 300°C heat treated rebars due to the formation of finest carbides and martensitic laths, respectively. Thus, the passive film formed on both of the rebars was not protective.
- Contrarily, martensite dissociation might have provided a structural equilibrium in between newly formed ferrite, cementite, and martensite matrix in terms of size, shape, and distribution and thus lower surface-to-volume ratio was achieved at Q&T 400°C rebar. Consequently, a protective passive film was achieved.

PART II:

CORROSION INHIBITION OF REBAR BY CALCIUM NITRATE $\text{Ca}(\text{NO}_3)_2$ INHIBITOR

CHAPTER 5:

REBAR CORROSION INHIBITION BY CALCIUM NITRATE $\text{Ca}(\text{NO}_3)_2$

5.1. Experimental Results

5.1.1. Electrochemical Results

5.1.1.1. Electrochemical Impedance Spectroscopy (EIS)

To observe the inhibition mechanism provided by calcium nitrate inhibitor, electrochemical impedance spectroscopy (EIS) was conducted in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) with the addition of 4 wt.% $\text{Ca}(\text{NO}_3)_2$. This is the similar inhibitor concentration as already has been reported by other researchers [51]. Nyquist and Bode's plots are shown in **Fig. 5.1 (a and b)**. The experimental data were fitted using the equivalent circuit shown in **Fig. 5.1a** and the extracted EIS parameters are listed in **Table 5.1**. EIS tests were also conducted in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) using 2 wt.% calcium nitrate. The Nyquist and Bode's plots are shown in **Fig. 5.1 (c and d)**, whereas the experimental data fitted on the equivalent circuit provided EIS parameters and are given in **Table 5.2**. The equivalent circuit used for fitting the experimental data has been used in several previous studies [158]–[160].

Based on **Table 5.1** and **Table 5.2**, the film resistance (R_f) and the charge transfer resistance (R_{ct}) are shown in **Fig. 5.2**. Film resistances (R_f) in **Fig. 5.2a** of heat treated

rebars decreased with the addition of 4 wt.% calcium nitrate to CPS in the presence of chloride except for the sample annealed at 450°C where R_f increased by 97%.

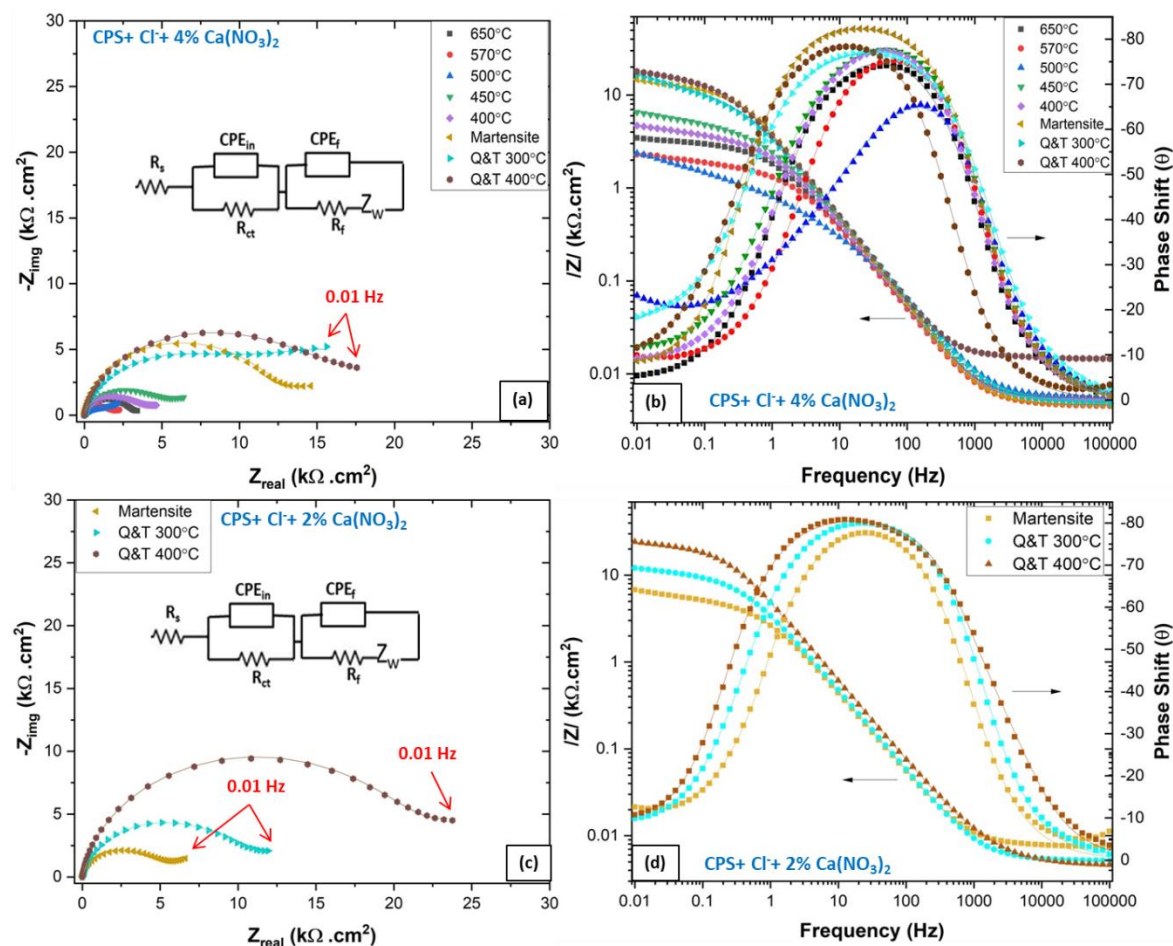


Figure 5.1: Nyquist and Bode plots of 4 wt. % Ca(NO₃)₂ (a and b) and for 2 wt. % Ca(NO₃)₂ (c and d) added as inhibitor to CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) for isothermal and Q&T heat-treated steel rebars.

Calcium nitrate effectively increased the charge transfer resistance (R_{ct}) against all heat-treated rebar samples. Nyquist plots trend was seen to be shifted into semi-circle indicating that charge transfer resistance (R_{ct}) was dominating in the impedance response. R_{ct} of isothermal heat-treated rebar samples were enhanced by multiple times in 2 wt.% calcium nitrate inhibitor. However, calcium nitrate inhibitor showed excellent inhibition

effect for the Q&T heat-treated rebar sample and R_{ct} was enhanced nearly 5 to 7 times in the presence of $\text{Ca}(\text{NO}_3)_2$. R_{ct} increased slightly as the concentration of calcium nitrate was reduced to 2 wt.%.

Table 5.1: EIS parameters of isothermally and Q&T steel rebar tested in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) and 4 wt.% calcium nitrate inhibitor.

Sample (Isotherm/ Q&T)	R_s ($\Omega \cdot \text{cm}^2$)	R_f ($\text{k}\Omega \cdot \text{cm}^2$)	$\text{CPE}_f(Y_0)$ ($\Omega^{-1} \text{cm}^{-2} \text{s}^n$)	n	R_{ct} ($\text{k}\Omega \cdot \text{cm}^2$)	$\text{CPE}_{dl}(Y_0)$ ($\Omega^{-1} \text{cm}^{-2} \text{s}^m$)	m	W ($\text{S}^* \text{s}^{1/2}$)
650°C	5.4	2.11	8.70E-04	0.71	0.77	9.91E-04	0.92	8.99E-03
570°C	4.6	1.28	8.59E-04	0.70	0.45	9.83E-04	0.94	7.11E-03
500°C	5.6	1.50	9.80E-04	0.61	0.33	9.65E-04	0.92	3.42E-03
450°C	4.9	7.32	6.05E-04	0.79	1.50	9.58E-04	0.91	3.23E-03
400°C	5.3	2.41	7.90E-04	0.75	1.42	9.89E-04	0.95	3.85E-03
Martensite	4.9	11.9	5.39E-04	0.79	3.16	6.55E-04	0.94	5.11E-04
Q&T 300°C	4.8	8.96	5.50E-04	0.75	4.23	5.97E-04	0.93	8.62E-04
Q&T 400°C	5.5	13.3	2.59E-04	0.81	5.14	4.69E-04	0.95	2.11E-04

Table 5.2: EIS parameters of Q&T steel rebar tested in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) and 2 wt.% calcium nitrate inhibitor.

Sample	R_s ($\Omega \cdot \text{cm}^2$)	R_f ($\text{k}\Omega \cdot \text{cm}^2$)	$\text{CPE}_f(Y_0)$ ($\Omega^{-1} \text{cm}^{-2} \text{s}^n$)	n	R_{ct} ($\text{k}\Omega \cdot \text{cm}^2$)	$\text{CPE}_{dl}(Y_0)$ ($\Omega^{-1} \text{cm}^{-2} \text{s}^m$)	m	W ($\text{S}^* \text{s}^{1/2}$)
Martensite	5.7	2.50	8.40E-04	0.68	3.34	6.00E-04	0.94	2.46E-03
Q&T 300°C	5.3	7.01	7.90E-04	0.85	4.49	6.15E-04	0.92	1.43E-03
Q&T 400°C	4.6	20.0	2.09E-04	0.90	5.18	4.90E-04	0.93	9.11E-04

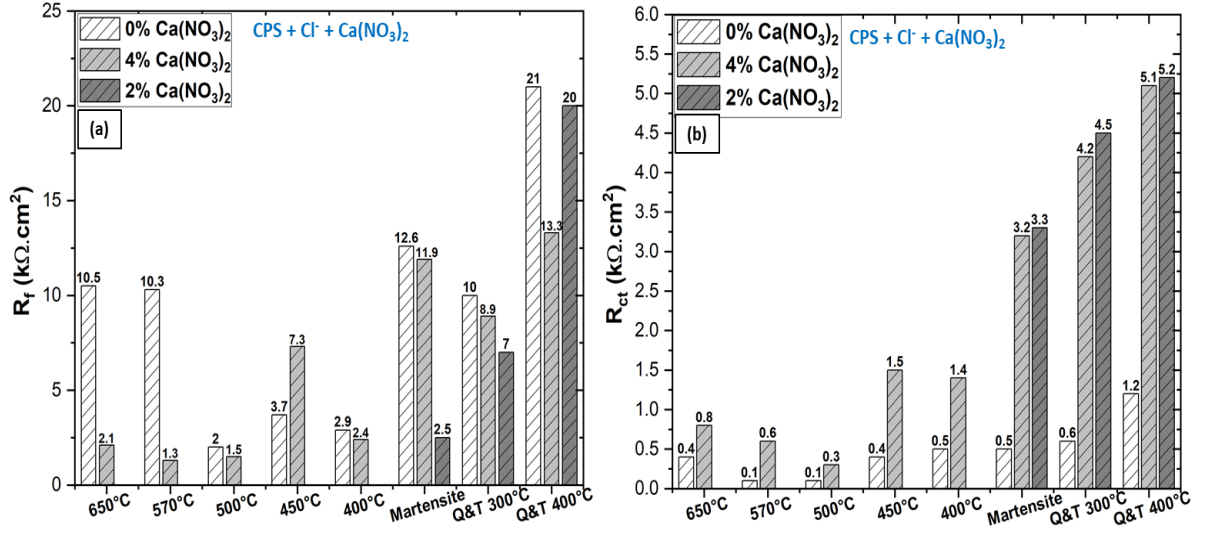


Figure 5.2: (a) Film resistance (R_f) and, (b) charge transfer resistance (R_{ct}) of isothermal and Q&T heat-treated rebars in CPS containing chloride ($Cl^-/OH^- = 1$) with two calcium nitrate inhibitor concentrations.

The inhibition efficiency (I.E.) (%) was calculated based on R_{ct} using Eq. 5.1 [161].

$$I.E. (\%) = \frac{(R_{ct,inh} - R_{ct})}{R_{ct,inh}} \times 100 \quad (5.1)$$

I.E. of 78 % was achieved against the Q&T 400°C rebar whereas 64% was achieved for the isothermal 400°C rebar in 2 wt.% of $Ca(NO_3)_2$. There appears no significant effect of varying the inhibitor concentration in the range 2-4 wt.% on the I.E. for the Q&T rebar samples.

The capacitances of the inhibitor barrier layer (C_{in}) and the film (C_f) were estimated by the same method given in Eq. 4.2 and 4.3. The capacitance and thickness of the inhibitor barrier layer and passive film developed over the surface of each heat-treated rebar sample in CPS containing chloride ($OH^-/Cl^- = 1$) and calcium nitrate ($Ca(NO_3)_2$) of two concentrations (4 and 2 wt.%) are given in **Fig. 5.4 (a-d)**. The film

capacitance (C_f) and thickness (δ_f) of heat-treated rebar samples in CPS containing chloride with 4 wt.% calcium nitrate are given in **Fig. 5.4a**, and with 2 wt.% calcium nitrate is given in **Fig. 5.4c**.

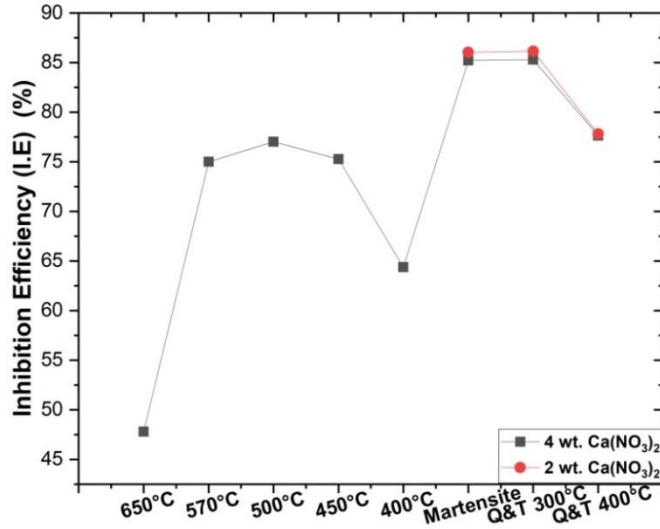


Figure 5.3: Inhibition efficiency (I.E.) based on charge transfer resistance (R_{ct}) of isothermal and Q&T heat-treated rebars in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) with two calcium nitrate inhibitor concentrations.

Out of all heat-treated samples, Q&T 400°C rebar provided the lowest film capacitance (C_f) of 0.35 mF/cm² with the highest film thickness (δ_f) of nearly 1.53 nm in the presence of 4 wt.% calcium nitrate. Reducing the content of calcium nitrate to 2 wt.% lowered the C_f to 0.25 mF/cm² and enhanced the δ_f to 2.17 nm for the Q&T 400°C rebar.

The inhibitor barrier layer capacitance (C_{in}) and thickness (δ_{in}) were found in proportionality with the film capacitance (C_f) and thickness (δ_f) and can be seen in **Fig. 5.4 (b and d)**. The lowest inhibitor barrier layer capacitance (C_{in}) of 0.34 mF/cm² and highest thickness (δ_{in}) of 0.52 nm was achieved against the Q&T 400°C rebar followed

by Q&T 300°C where C_{in} increased to 0.38 mF/cm² and δ_{in} reduced to 0.46 nm. Reducing the content of calcium nitrate to 2 wt.% in CPS with the presence of chloride was found beneficial against the Q&T heat-treated rebars where the thickness increased to 0.57 nm for the Q&T 400°C rebar.

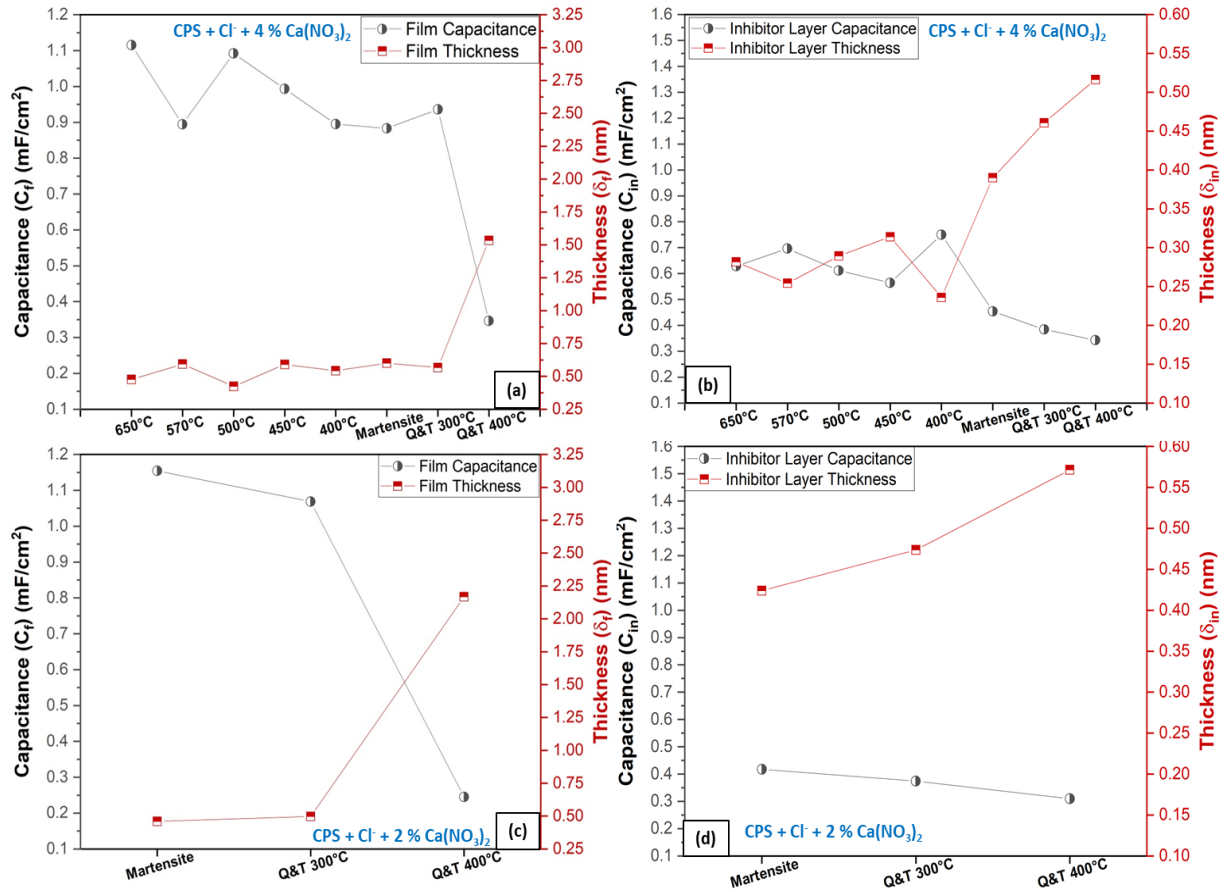


Figure 5.4: Passive film capacitance and thickness with the addition of (a) 4 wt. % Ca(NO₃)₂ and (c) 2 wt. % Ca(NO₃)₂ in CPS containing chloride ($OH^-/Cl^- = 1$). Inhibitor barrier layer capacitance and thickness with the addition of (a) 4 wt. % Ca(NO₃)₂ and (c) 2 wt. % Ca(NO₃)₂ in CPS containing chloride ($OH^-/Cl^- = 1$).

5.1.1.2. Polarization Resistance and Corrosion Rate

Potentiodynamic polarization (PDP) tests were conducted in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) with the addition of calcium nitrate $\text{Ca}(\text{NO}_3)_2$ inhibitor at 4 and 2 wt.% concentrations. PDP curves are shown in **Fig. 5.5 (a and b)** whereas corrosion rates measured by LPR are shown in **Fig. 5.6 (a and b)**.

PDP curves in **Fig. 5.5a** revealed that 4 wt.% calcium nitrate provided detrimental effect for the pitting potential as it dropped significantly with the initiation of pitting against all of the heat-treated rebar samples. A maximum pitting potential of around 0.2 V was noted against the Q&T 400°C rebar. However, reducing the content of calcium nitrate to 2 wt.% improved the pitting potential, and a maximum potential of 0.7 V was observed for the Q&T 400°C rebar sample and can be verified from **Fig. 5.5b**.

In comparison of inhibitor absence (0 wt.%) in CPS, corrosion rates (LPR) of heat-treated rebar samples increased in the presence of 4 wt.% calcium nitrate inhibitor (**Fig. 5.6a**) except of isothermal 450°C and Q&T 300°C rebar. The inhibition efficiency of 70% was achieved for the Q&T 300°C rebar. The addition of 4 wt.% calcium nitrate had a detrimental effect on the corrosion rate of martensite which increased to many folds once inhibitor concentration was reduced to 2 wt.%. The minimum corrosion rate, however, of 0.81 mpy was measured for the Q&T 400°C rebar. Reducing the concentration of calcium nitrate to 2 wt.% decreased the corrosion rate to 0.6 mpy for the Q&T 400°C rebar (**Fig. 5.6b**), which is equivalent to the corrosion rate measured in absence (0 wt.%) of inhibitor in CPS. Thus, no effect of calcium nitrate was seen on the corrosion rate of Q&T 400°C rebar.

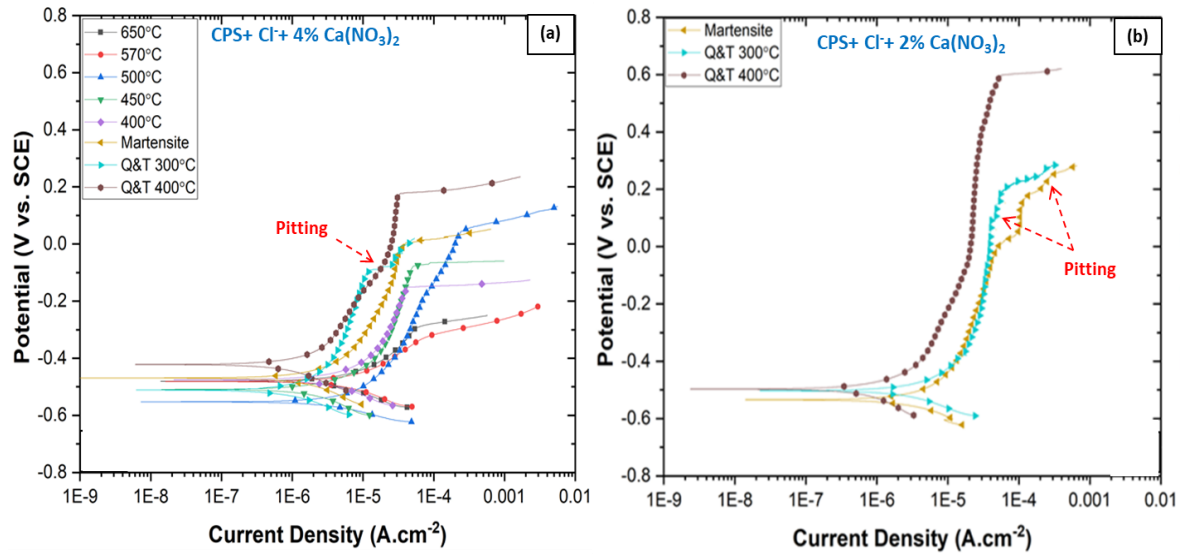


Figure 5.5: PDP curves of isothermal and Q&T microstructures of steel rebar in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) with (a) 4 wt. % and (b) 2 wt. % calcium nitrate concentrations.

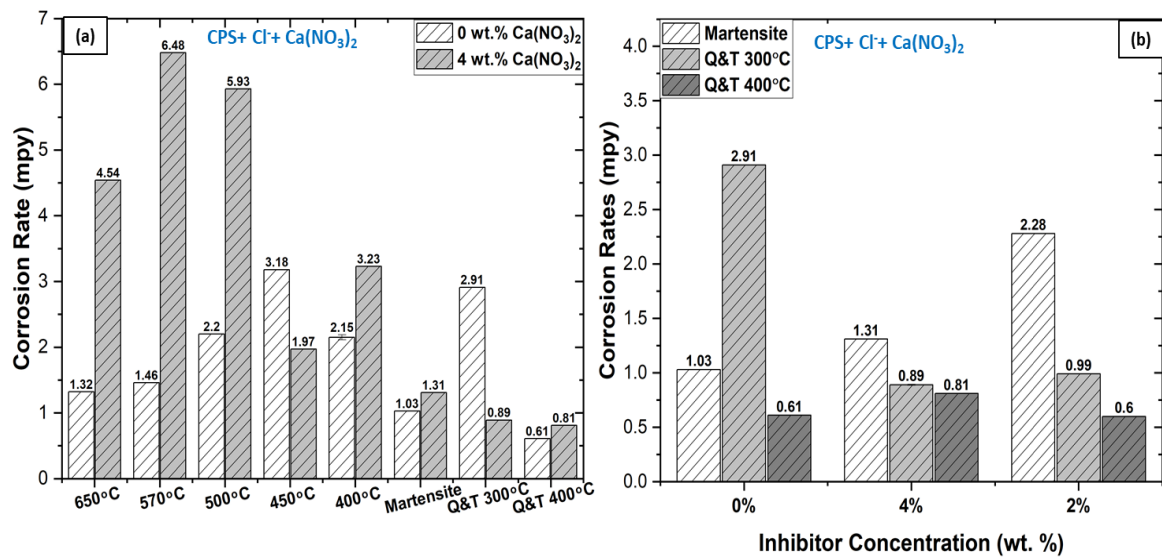


Figure 5.6: Average corrosion rates (LPR) based on three measurements of isothermal and Q&T microstructures of steel rebar samples in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) with (a) Isothermal and Q&T rebar comparison with the 0 and 4 wt.% calcium nitrate (b) Q&T rebar comparison with 0, 2, and 4 wt. % calcium nitrate concentrations.

5.1.1.3. Effect of Inhibitor Concentration on Q&T Rebars

The effect of the concentration of calcium nitrate $\text{Ca}(\text{NO}_3)_2$ inhibitor was evaluated on the electrochemical performance of Q&T 400°C rebar. EIS and PDP curves were compared in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) in the presence of 4, 2, and 0 wt.% calcium nitrate $\text{Ca}(\text{NO}_3)_2$ inhibitor concentrations. Nyquist and Bode plots are given in **Fig. 5.7 (a and b)** whereas the EIS parameters obtained after fitting the experimental data on the equivalent circuit are given in **Table 5.3**.

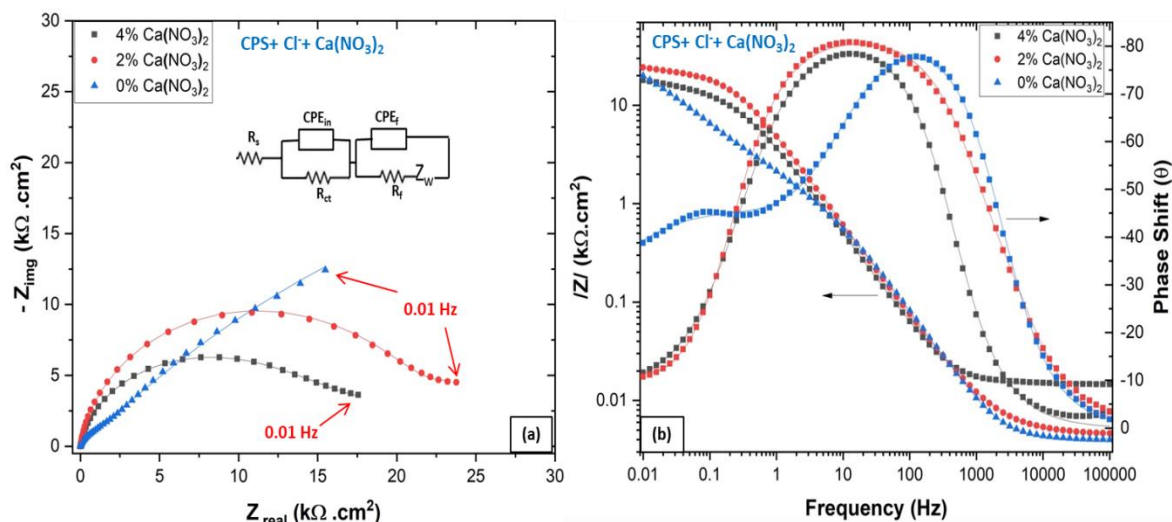


Figure 5.7: (a) Nyquist, (b) Bode Plot of Q&T 400°C heat treated rebar in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) with 0, 2, and 4 wt. % calcium nitrate concentrations.

It is visible from Nyquist plots that in the presence of calcium nitrate, impedance curves have shifted from linear to semi-circle which indicates about the enhancement in the charge transfer mechanism. R_{ct} increased nearly 5 times in the presence of 2 wt.% calcium nitrate (**Table 5.3**) compared to CPS with 0 % calcium nitrate. Subsequently, the inhibition efficiency of 78% was achieved (**Fig. 5.3**) for the Q&T 400°C rebar.

Table 5. 3: EIS parameters for the effect of calcium nitrate inhibitor on Q&T 400°C rebar.

Sample (Isotherm/ Q&T)	R_s ($\Omega.cm^2$)	R_f ($k\Omega.cm^2$)	$CPE_f(Y_0)$ ($\Omega^{-1}cm^{-2}s^m$)	n	R_{ct} ($k\Omega.cm^2$)	$CPE_{dl}(Y_0)$ ($\Omega^{-1}cm^{-2}s^m$)	m	W ($S*s^{1/2}$)
0%	4.1	21.1	2.00E-04	0.95	1.15	6.00E-04	0.94	--
4%	5.5	13.3	2.59E-04	0.81	5.14	4.69E-04	0.95	2.11E-04
2%	4.6	20.0	2.09E-04	0.90	5.18	4.90E-04	0.93	9.11E-04

PDP curves are compared in **Fig. 5.8** for martensite, Q&T 300°C, and Q&T 400°C with the addition of 0, 2 and 4 wt.% calcium nitrate inhibitor in CPS containing chlorides ($Cl^-/OH^- = 1$). For the martensitic steel rebar (**Fig. 5.8a**), increase in corrosion current density was observed with the addition of calcium nitrate inhibitor. However, unlike 2 wt. % inhibitor concentration, an adverse effect on pitting potential was seen with the addition of 4 wt.% calcium nitrate in CPS as it was dropped significantly to 0.2V. For the Q&T 300°C rebar (**Fig. 5.8b**), the corrosion current density increased to many folds with the addition of calcium nitrate inhibitor in CPS. However, with 2 wt. % inhibitor concentration, pitting potential increased slightly. On contrary, the effect of calcium nitrate concentration had a limiting role on corrosion current density for the Q&T 400°C rebar. However, the addition of 4 wt.% calcium nitrate inhibitor had an adverse effect on the corrosion potential of Q&T 400°C rebar as it lowered the pitting potential to 0.2 V. But reducing the inhibitor concentration to 2 wt.% shifted the corrosion potential to the cathodic direction (-0.5 V), and yet without compromising on the pitting potential which stood persistent at 0.6V - equivalent to the pitting potential of Q&T 400°C rebar in absence of inhibitor (0 wt. %) in CPS.

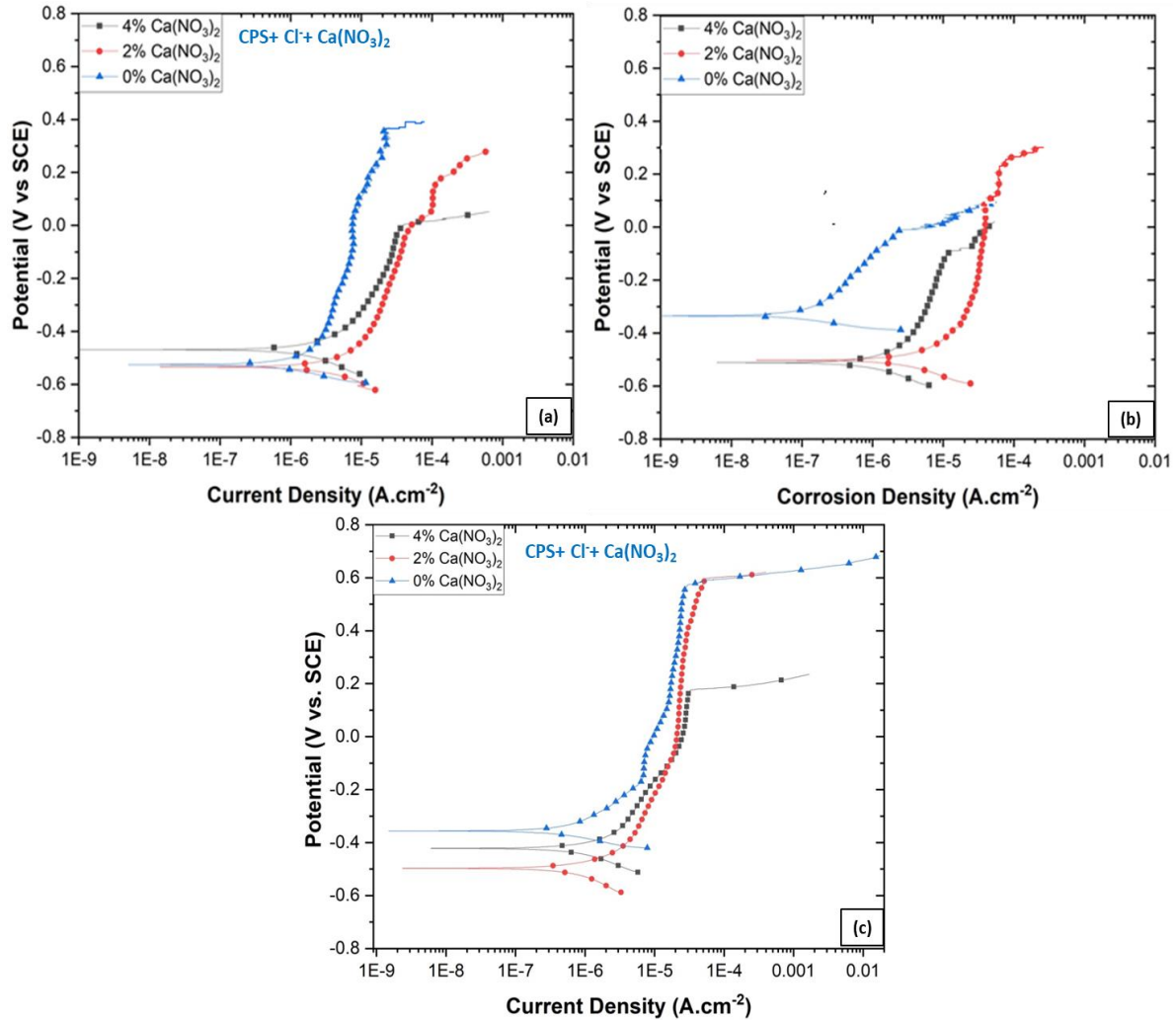


Figure 5.8: PDP curves of (a) Martensite, (b) Q&T 300°C, and (c) Q&T 400°C heat treated rebar samples in CPS containing chloride ($\text{Cl}^-/\text{OH}^- = 1$) with 0, 2, and 4 wt. % calcium nitrate inhibitor concentrations.

5.2. Discussion

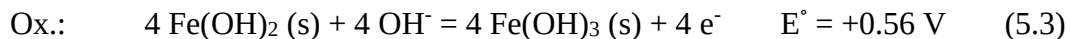
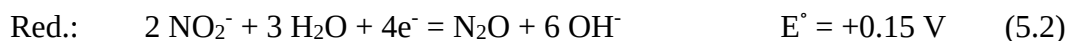
5.2.1. Calcium Nitrate ($\text{Ca}(\text{NO}_3)_2$) Inhibition Mechanism

The passive film formation mechanism of the rebar in CPS in the presence of mere OH^- ions has already been described in part I. The mechanism of corrosion inhibition of steel by calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) in concrete involves the formation of a protective

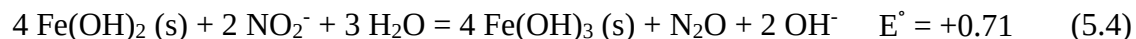
film on the steel surface, which helps prevent the corrosion process [32]. When calcium nitrate is added to concrete, it dissociates into calcium ions (Ca^{2+}) and nitrate ions (NO_3^-). The calcium ions interact with the hydroxide ions (OH^-) present in the concrete to form calcium hydroxide ($\text{Ca}(\text{OH})_2$), which is an alkaline compound [32], [87]. This reaction increases the alkalinity of the concrete near the steel surface, creating a favorable environment for passivation.

Passivation is a process in which a protective oxide film forms on the steel surface, reducing its susceptibility to corrosion. The nitrate ions (NO_3^-) from calcium nitrate facilitate the formation of a passive film on the steel surface by reacting with the iron ions (Fe^{2+} and Fe^{3+}) present in the steel. The nitrate ions act as oxidizing agents and convert the iron ions into a stable oxide/hydroxide layer, such as iron (III) oxide (Fe_2O_3) or iron (III) hydroxide ($\text{Fe}(\text{OH})_3$) [32]. This layer acts as a barrier, preventing further contact between the steel and corrosive substances in the concrete, such as chloride ions (Cl^-) and carbon dioxide (CO_2) [32]. Furthermore, the increased alkalinity near the steel surface due to the presence of calcium hydroxide helps to inhibit the de-passivation of the steel. In an alkaline environment, the formation of corrosion-promoting species, such as ferrous ions (Fe^{2+}) and carbonic acid (H_2CO_3) is suppressed [32]. This suppression limits the corrosion reactions and reduces the degradation of the steel reinforcement [32], [88]. Overall, the corrosion inhibition mechanism of steel by calcium nitrate in concrete involves the formation of a protective passive film on the steel surface, facilitated by the alkaline environment created by calcium hydroxide and the oxidizing action of nitrate ions. This mechanism helps to prevent the ingress of corrosive species and reduces the corrosion rate of the steel reinforcement in concrete.

The behavior of nitrate ions (NO_3^-) as a corrosion inhibitor/retarder can be understood through the mechanism of the related nitrite (NO_2^-) ion which is a well-known steel corrosion inhibitor [23], [24], [162]–[168]. Andrade et al. [23] suggested that steel corrosion is inhibited at $\text{Cl}^-/\text{NO}_2^- < 1.5$. Several hypotheses have been advanced for steel passivation by nitrite (El-Jazairi and Berke) [163] although without much experimental proof. Sagoe-Crentsil et al. [164] claimed that nitrite ions readily form complexing agents with Fe^{2+} that are competitive with Cl^- complexation, and thereby prevent the formation of soluble chlorocomplexes, which appear to be an essential component of the anodic corrosion processes (Sagoe-Crentsil and Glasser) [169]. Sagoe-Crentsil [164] also proposed a sacrificial reduction of nitrite (NO_2^-) to nitrogen (N_2) and a simultaneous oxidation of ferrous (oxidation state +II) to ferric (+III) iron. The formation of FeOOH (or a similar product) on the anode would then decrease iron migration as ferrous/ferric chlorocomplex, and thereby stifle iron dissolution. The proposed mechanism (Sagoe-Crentsil) [164] may be analyzed by the two half-reactions Eq. 5.2 and 5.3 with standard electrode potentials, E^0 (the equilibrium is shifted towards the right side for a positive potential);

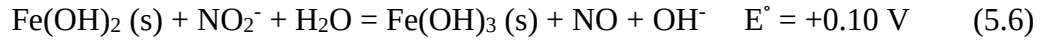


which combines to the total reaction;

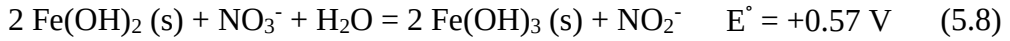
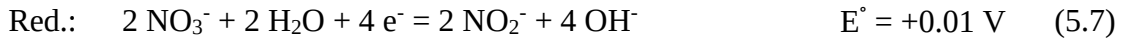


The reduction of nitrite may proceed all the way to nitrogen since the reduction potential of N_2O is so high in an acidic environment (the reduction potential of N_2O in an alkaline solution is not given in the electrochemical series). Rosenberg et al. [167]

confirmed the reduction mechanism for the nitrite inhibitor but claimed that the reduction does not proceed further than to NO (Eq. 5.5 and 5.3 combine to form 5.6), which may be due to kinetic reasons;

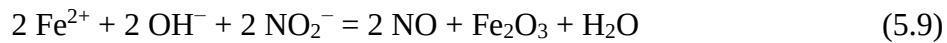


Nitrate, NO_3^- , is easily reduced to nitrite, NO_2^- , by ferrous iron in an alkaline environment as seen in Eq. 5.8 obtained by combining the half-reaction in Eq. 5.7 with Eq. 5.3;

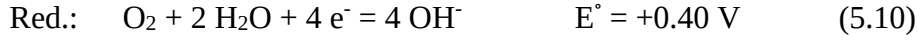


If the mechanism proposed by Rosenberg et al. [167] for nitrite inhibition of steel corrosion in concrete summed up in Eq. 5.6 is correct, Eq. 5.8 implies that nitrate, NO_3^- , should be an even better inhibitor than nitrite, NO_2^- , since three more moles of ferrous iron are oxidized to ferric per mole nitrogen oxide added (i.e. nitrate is three times as effective at an equimolar dosage). Unlike nitrite, nitrate does not appear to work when tested in a rapid solution test [170]. Even though reaction 5.8 has a greater driving force (i.e. potential) than reaction 5.6, the kinetics may be slower and a longer-term test is required. However, corrosion in practice is a slow process so this does not matter in a real structure.

Another possible reaction that may lead to the formation of Fe_2O_3 by the reduction of NO_3^- to NO_2^- (from Eq. 5.7) in the presence of ferrous ions [171] is given in Eq. 5.9.



Another hypothesis is that nitrite acts as an oxygen scavenger since NO_2^- may be oxidized in an alkaline environment, as seen from the two-half reactions Eq. 5.10 and the reverse of Eq. 5.7;



which combines to the total reaction;



However, this latter mechanism was proven (Justnes et al) [168] to only take place in acidic environments.

The formation of the passive film in the presence of NO_3^- ions as well as the adsorption of nitrate ions on the rebar surface is shown schematically in **Fig. 5.9**.

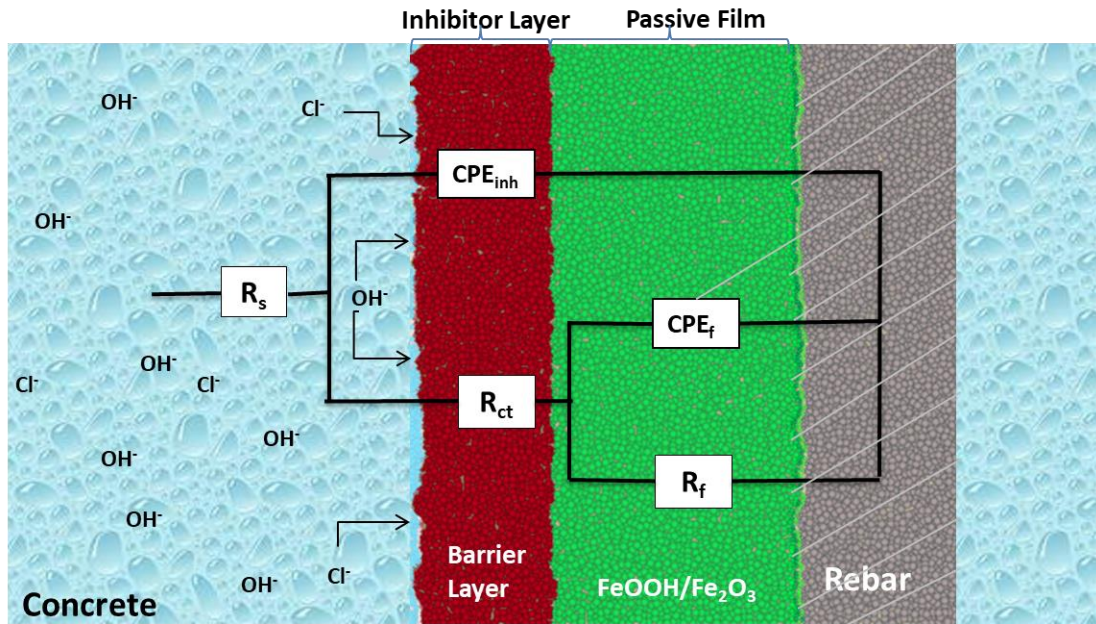


Figure 5.9: Schematic illustration of calcium nitrate inhibition mechanism hindering the diffusion of chloride ions to the steel-film interface.

5.2.2. Synergy of Heat Treatment & Corrosion Inhibition by $\text{Ca}(\text{NO}_3)_2$

R_f and R_{ct} graphs in **Fig. 4.6** of the previous chapter revealed that, in the presence of chloride, the microstructure achieved at 400°C isothermal temperature showed R_f (2.9 $\text{k}\Omega\cdot\text{cm}^2$) and R_{ct} (0.51 $\text{k}\Omega\cdot\text{cm}^2$) characteristics in comparison to the microstructure achieved at Q&T 400°C, where R_f (21 $\text{k}\Omega\cdot\text{cm}^2$) and R_{ct} (1.15 $\text{k}\Omega\cdot\text{cm}^2$) were found to be 7.3 and 2.2 times superior to its counterpart, respectively. In the presence of 4 wt.% calcium nitrate, the possible formation of an extra barrier layer might have halted the diffusion of corrosion species (Cl^-) and thus restricted their accessibility to the metal-film interface. This could be validated from the charge transfer resistance where R_{ct} increased to 5.14 $\text{k}\Omega\cdot\text{cm}^2$ (**Fig. 5.2**), and thus an effective inhibition efficiency of 78% was achieved.

The role of microstructure seems to have the same vital role in achieving inhibition efficiency as it was observed in the passive film formation mechanism in the absence of an inhibitor. The nitrate ions (NO_3^-) act as oxidizing agents and convert the iron ions into a stable oxide/hydroxide layer, such as iron (III) oxide (Fe_2O_3) or iron (III) hydroxide ($\text{Fe}(\text{OH})_3$). Cementite and ferrite form a micro-galvanic couple in steel [41]. The morphology and distribution of cementite (Fe_3C) in the ferrite matrix can then influence the passive film formation mechanism of steel rebar in the presence of a nitrate inhibition mechanism. In addition, the subsequent size, shape, and distribution of different phases altered by various heat treatments can also affect the electrochemical properties. Examination of corroded microstructures in previous studies reveals that pits are concentrated at pre-austenite grain boundaries [172], [173]. The prevailing belief is that, in the presence of Cl^- ions, sites of surface defects, such as grain boundaries and

secondary-phase inclusions, are most susceptible to pitting [172], [174], [175]. As pitting initiates, the liberation of iron in the form of Fe^{2+} triggers localized acidification within the pit via reactions: (1) $\text{Fe} + 2\text{e}^- \rightarrow \text{Fe}^{2+}$, (2) $\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})^+ + \text{H}^+$, and (3) $\text{Fe}(\text{OH})^+ + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_2 + \text{H}^+$, resulting in an acidic pH at the pit's base. The heightened presence of H^+ and Fe^{2+} at the pit's base, alongside the ensuing gradient, propels anion transport towards the pitted region. This ion concentration gradient fosters the creation of an electrochemical potential disparity between the pit's base and the steel surface, reaching levels as high as hundreds of millivolts [176], [177]. Hence, the effect of the underlying microstructures of steel rebar would play a role both in the formation of passive film as well as providing pitting resistance in the presence of calcium nitrate. This is in agreement with the electrochemical results that, unlike other heat treated microstructures, Q&T 400°C microstructure not only provided highest estimate of film thickness (**Fig. 5.4**), but also shifted the corrosion potential to the cathodic direction (-0.5 V) and provided a higher pitting potential (+0.6 V) as indicated in **Fig. 5.5b** in presence of 2 wt. % $\text{Ca}(\text{NO}_3)_2$.

The localized corrosion analysis demonstrates that the lower concentration (2 wt.%) of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) is more efficient against the pitting corrosion compared to higher concentration (4 wt.%). This outcome is in agreement with the prior findings which suggest that lower $\text{Ca}(\text{NO}_3)_2$ concentrations are better suited for achieving effective inhibition [32], [178]. Dong et al. [31] studied the effect of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) in halide enrich concrete environment. Their findings demonstrate that at lower concentrations (approximately 1 wt.%), $\text{Ca}(\text{NO}_3)_2$ effectively prevents steel corrosion in the presence of both CaCl_2 and CaBr_2 . Analysis of surface topography data

statistically indicates that the inhibition arises from the suppression of corrosion at rapidly corroding pitting sites. However, at higher concentrations, the efficacy of calcium nitrate as a corrosion inhibitor diminishes significantly. These outcomes offer a way to explain the evolution of surface topography concerning the electrochemical basis of corrosion inhibition by NO_3^- species. Furthermore, these results offer insights into the kinetics and susceptibility to degradation of the steel sheath when exposed to completion fluids enriched with halides. It is suggested that $\text{Ca}(\text{NO}_3)_2$ reduces corrosion rates by suppressing both general corrosion (i.e., bulk dissolution) and fast localized corrosion at pitting sites, although the influence on localized corrosion is more pronounced. Significantly, this indicates that low concentrations of $\text{Ca}(\text{NO}_3)_2$ inhibit corrosion processes by reducing the rate of vertical and lateral expansion of pits. Further increasing the nitrate ions concentration to beyond a certain concentration resulted in a frequency distribution that closely resembled that of the nitrate-free conditions evidencing that increasing (NO_3^-) beyond an optimal value is detrimental.

It is reported that the opening of the pits is reduced to notably a smaller size in presence of $\text{Ca}(\text{NO}_3)_2$ [32]. Furthermore, unlike scenarios where $\text{Ca}(\text{NO}_3)_2$ is absent, both the intensified corrosion area (radius) surrounding the pit and average vertical depth of this region is significantly reduced in $\text{Ca}(\text{NO}_3)_2$ containing environments [32]. A slight elevation in height around the pitting area has been reported, likely attributed to the localized creation and attachment of oxidation products [16], [178]. This observation is in agreement with the proposed mechanism of corrosion inhibition involving NO_3^- ions. Specifically, it is suggested that nitrate ions react with the released Fe^{2+} ions by oxidizing them into Fe^{3+} ions (already has been described in section 5.2.1). This chemical

transformation leads to the formation of passive film, such as Fe oxides (Fe_2O_3) and hydroxides (FeOOH). Consequently, these oxide products accumulate at the mouth of the pit, isolating the pitting site and safeguarding it from further corrosion by restricting its exposure to solution electrolytes. The deposition of these oxide products at the pit's entrance is also predicted to decrease its protrusion and the concentration of the electrical field at the pit mouth. This phenomenon results in the creation of more diffuse, albeit shallower, depressions around the pit [172]. Furthermore, the migration and concentration of NO_3^- anions toward regions undergoing anodic corrosion are projected to follow the intensity of the electric field. This process competes with the transport of Cl^- ions to the same sites. These actions alleviate the concentration of Cl^- ions at anodic sites and mitigate the occurrence of Cl^- induced localized corrosion in the vicinity of pitting sites when $\text{Ca}(\text{NO}_3)_2$ is present [179], [180]. As a result, this elucidates why the formation of shallower pits takes place in systems containing $\text{Ca}(\text{NO}_3)_2$ at moderate concentrations. However, in contrast, when the concentration of $\text{Ca}(\text{NO}_3)_2$ is further elevated (i.e. 4 wt.%), the oxidizing potential of the overall solution is also heightened. This leads to the circumstance where higher doses of $\text{Ca}(\text{NO}_3)_2$ augment the oxidative dissolution of iron and compromise the corrosion inhibition effect provided by $\text{Ca}(\text{NO}_3)_2$ additions at higher concentrations [181]. The phenomenon is clearly shown by PDP curves in **Fig. 5.5** which indicates that low pitting potentials were provided by all heat treated rebar samples in presence of 4 wt.% $\text{Ca}(\text{NO}_3)_2$ (**Fig. 5.5a**) compared to the curves achieved in presence of 2 wt. $\text{Ca}(\text{NO}_3)_2$ (**Fig. 5.5b**) with higher pitting potential.

5.2.3. Barrier Layer by Calcium Nitrate Adsorption

The adsorption mechanism could be the result of both physisorption and chemisorption. The spontaneous formation of a stable monolayer over the rebar surface by inhibitors through the chemisorption mechanism is highly desirable [182]. However, the inhibitor must tend to form bonds by sharing the electrons with the steel surface. For bonding, the metallic surface acts as an electrophile whereas the inhibitor acts as a Lewis base. Moreover, the nucleophiles, such as oxygen and nitrogen, provide free pairs of electrons which are readily available for covalent bonding. The inhibition capacity of the $\text{Ca}(\text{NO}_3)_2$ molecule could be due to the presence of electronic lone pairs of N and O heteroatoms and π -electrons which could facilitate in developing a strong interaction with the surface atoms of steel [44]. The formation of back-bonds could also be possible due to electrons sharing between d-orbitals of metal and anti-bonding orbital of $\text{Ca}(\text{NO}_3)_2$ molecules [44].

FTIR was used to characterize reactant and product composition and molecular structure. IR peak values correlate to specific bonds. **Fig. 5.10** shows the reactant IR spectra. The broad OH peak (3398 cm^{-1}) indicates a hydroxyl group [183] while the H_2O peak (1631 cm^{-1}) corresponds to water [183], and the peak (1314 cm^{-1}) indicates a nitrate (NO_3^-) group [183], [184]. Hence, the adsorption of nitrate ions is evident in the FTIR spectroscopy. It can be seen that nitrate ions (NO_3^-) adsorption on Q&T 400°C rebar provided a peak with more intensity compared to Q&T 300°C rebar when exposed to 2 wt.% calcium nitrate inhibitor in CPS.

The Bode plots in **Fig. 5.1 (b and d)** indicate a specific shift in the phase angle which is in agreement with FTIR spectra in **Fig. 5.10**. This shift in phase angle could be

attributed to the higher concentration of NO_3^- ions getting adsorbed over the surface of rebar. In other words, shifting of the phase angle is reflective of the presence of a barrier-type layer acting as a shield in mitigating the corrosion of steel [185].

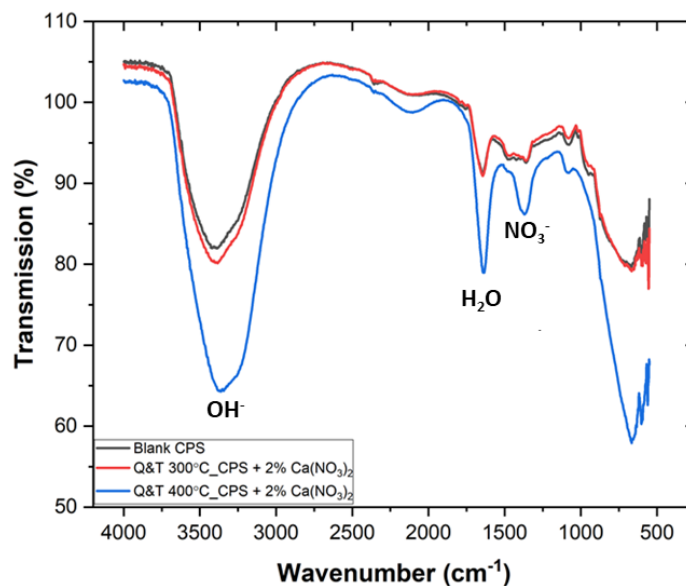


Figure 5.10: FTIR spectra of nitrate ions (NO_3^-) adsorption on Q&T 300°C and Q&T 400°C rebar in CPS containing 2 wt.% calcium nitrate inhibitor.

The barrier layer might have formed due to the adsorption of nitrate ions (NO_3^-) on the multiple sites of rebar surface and thus have delayed the oxidation reaction [186]. In addition, this could have hindered the diffusion of chloride and oxygen in reaching to the metal-film interface. Subsequently, lower charge transfer may have occurred which is in agreement with significantly improved R_{ct} . Consequently, the dissolution process of Q&T 400°C rebar was suppressed with improved inhibition efficiency of 77% in presence of 2 wt. % calcium nitrate in CPS.

Atomic force microscopic (AFM) images of the three Q&T 400°C rebar sample were compared where first sample was left in open air (**Fig. 5.11a**), second in CPS (**Fig.**

5.11b), and the third (**Fig. 5.11c**) in the CPS containing 2 wt. % calcium nitrate inhibitor. The surface profile of the rebar in **Fig. 5.11c** provides a clear indication about the presence of extra barrier layer, which thus could be attributed to the adsorption of NO_3^- ions on rebar surface [187]. Consequently, the decrease in the corrosion rate may have resulted due to the extra adsorbed layer formed over rebar because of NO_3^- ions, thus inhibiting the anodic reaction.

Bode plots in **Fig. 5.1**, FTIR spectra in **Fig. 5.10**, and AFM surface profile in **Fig. 5.11** provide the consolidated evidences of nitrate (NO_3^-) ions adsorption on the rebar surface in CPS, and has been represented through the schematic illustration shown already in **Fig. 5.9**.

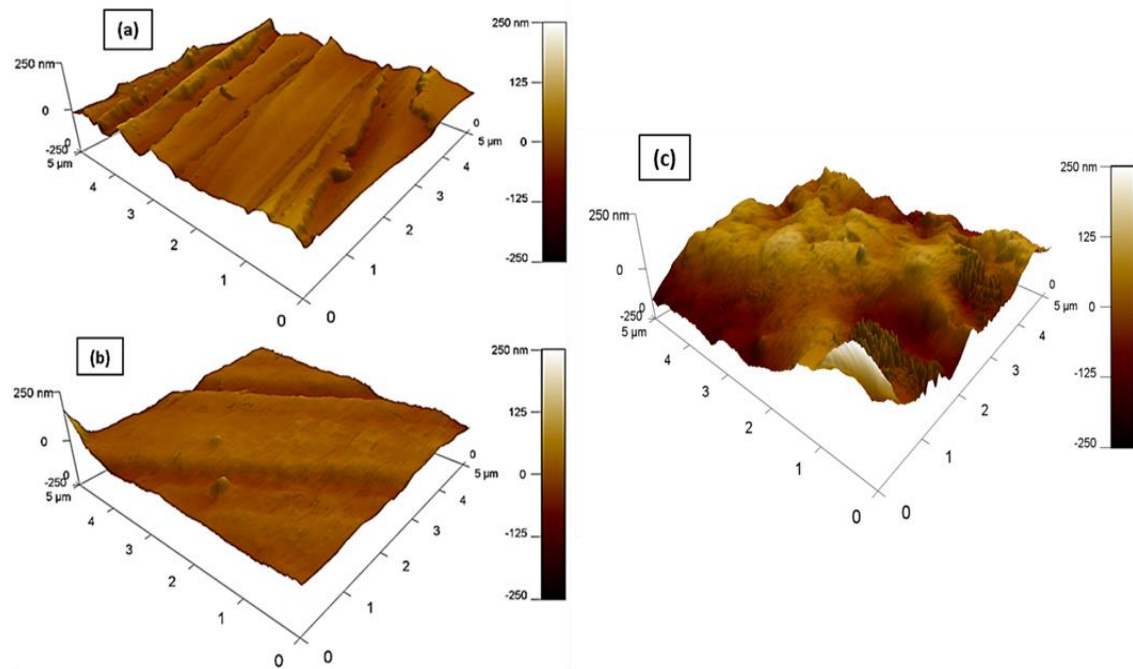


Figure 5.11: AFM images of (a) Q&T 400°C rebar left in air with no CPS exposure, (b) Q&T 400°C rebar exposed to blank CPS for 72 hrs, (c) Q&T 400°C rebar exposed to CPS with 2 wt.% calcium nitrate inhibitor for 72 hrs.

5.3. Conclusions

Commercial-grade of carbon steel was used to investigate the effect of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) inhibitor with two concentrations (2 and 4 wt. %) on the corrosion resistance of heat-treated rebar samples in a concrete-simulated environment with the presence of chloride. Steel rebar was heat treated at different isothermal temperatures i.e. 650°C, 570°C, 500°C, 450°C, and 400°C, as well as quenched and tempered (Q&T) at 300°C and 400°C. Electrochemical evaluation of heat-treated samples was carried out in concrete pore solution (CPS) (pH >13.5) containing chloride and ($\text{Ca}(\text{NO}_3)_2$). The findings of the study are:

- Based on EIS, the addition of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) inhibitor in chloride-containing CPS improved the charge transfer resistance (R_{ct}) of all heat treated rebar samples.
- Highest R_{ct} was achieved for the Q&T 400°C rebar microstructure in presence of 2 wt.% $\text{Ca}(\text{NO}_3)_2$ in chloride-containing CPS with the effective inhibition efficiency (I.E.) of 78%.
- Based on PDP, the addition of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) in CPS shifted the corrosion potential to the cathodic direction, revealing that inhibition mechanism is more cathodically dominant.
- PDP curves revealed that the addition of higher concentration (4 wt.%) of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) in chloride-containing CPS provided an adverse effect on the localized corrosion as it lowered the pitting potential of all heat treated rebar samples.

- However, reducing the concentration of inhibitor to 2 wt.% for the Q&T 400°C rebar not only provided a cathodic shift, but also increased the pitting potential to 0.6 V which is equivalent to the pitting potential measured in absence of the inhibitor in chloride-containing CPS.
- The adsorption of nitrate ions (NO_3^-) on rebar surface was evident from the peak detected by FTIR spectra.
- Nitrate ions possibly provided an additional barrier layer to the outer side of the passive film, thus restricted the diffusion of Cl^- ions and limited their accessibility to the metal-film interface.
- Rebar microstructure heat treated at Q&T 400°C assisted in achieving the maximum adsorption of nitrate ions as the maximum barrier layer thickness was achieved in presence of 2 wt.% $\text{Ca}(\text{NO}_3)_2$ inhibitor in chloride-containing CPS. The highest adsorption of nitrate ions was also confirmed by the intense peak detected by FTIR.

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Vitae

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Academic Background :My BS Engineering was in Metallurgy and Materials Engineering from University of the Punjab, Lahore, Pakistan. After that, I did approximately two years job in a multinational French Inspection company- Bureau Veritas. In September 2014, I started my MS in King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia. Here my major was Materials Science and Engineering. Here I took a number of courses of materials like, Materials Characterization, Thermodynamics, Materials Structure and Defects, Corrosion in oil and petrochemicals, Fatigue and Fracture, Tribology and Nanomaterials. Nevertheless, my research was strictly restricted to my own area of interest and that is none other than corrosion. My Thesis title was “THE EFFECTS OF COMPOSITION AND HEAT TREATMENT ON THE PASSIVATION OF STEEL REBAR IN CONCRETE SIMULATED ENVIRONMENT”.

I started my PhD in Mechanical Engineering from King Fahd University of Petroleum and Minerals in 2018. The courses I took were Advanced Mechanical Behavior of Materials, Advanced Physical Metallurgy, Advanced Corrosion Engineering, Electrical, Optical and Magnetic Properties of Materials, Welding

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Publications in Correspondence

- 1- **M. Faizan Khan**, Z. M. Gasem, “Effects of heat treatments on the corrosion resistance and passivity of steel rebar in simulated concrete pore solution”, Corrosion Science, (2023).
- 2- **M. Faizan Khan**, Z. M. Gasem, “Effect of calcium nitrate $[\text{Ca}(\text{NO}_3)_2]$ inhibitor on the corrosion resistance of isothermal and quenched & tempered steel rebar in simulating concrete pore solution”, Construction and Building Materials, (2023).

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