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Subject

Application of Corrosion Inhibitors in the Repair of Concrete Structures Damaged by Corrosion

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Abstract

Reinforced concrete is a fundamental material in structural engineering, universally adopted to meet the demands of urbanization and guarantee the durability of infrastructures essential to daily life, such as residential complexes, transport networks, bridges… etc. Its strength and durability depend largely on the steel reinforcements. However, these latter are vulnerable to the phenomenon of corrosion (rust), when concrete structures are built in aggressive environments with a high concentration of humidity, oxygen, chloride (NaCl), or subjected to carbonation, which inevitably leads to the deterioration and rapid degradation of structures.

To avoid these structural risks, the use of corrosion inhibitors has emerged as an effective and durable solution in the field of protecting and repair of reinforced concrete structures. These inhibitors act by slowing down the chemical reactions responsible for corrosion; thereby extending the service life of structures.

Our research aims to explore methods for rehabilitating degraded structures through corrosion reinforcement by using corrosion inhibitors. It also includes recommendations aimed at best integrating corrosion inhibitors into protection and repair strategies, while ensuring continuous monitoring of structures through early defect detection, all while prioritizing environmentally friendly solutions.

In conclusion, preserving the integrity of reinforced concrete structures remains a strategic objective to guarantee their safety and durability.

Key words: Corrosion, Concrete, Inhibitors, Repair methods, Reinforcements.

Résumé

Le béton armé est un matériau fondamental dons l'ingénierie des structures, universellement adopté pour répondre aux exigences de l'urbanisation et garantir la pérennité des infrastructures, il est essentiel à la vie quotidienne, telle que les complexes résidentiels, les réseaux de transports, les ponts ….. etc. Sa résistance et sa durabilité dépendent en grande partie des armatures en acier. Cependant, ces dernières sont sujettes au phénomène de corrosion (rouille) lorsque les structures en béton armé sont réalisées dans des milieux agressifs à forte concentration d'humidité, d'oxygène, d'ions chlorures (NaCl) ou soumises à la carbonatation ce qui entraîne la dégradation et le vieillissement accéléré des structures.

Afin d'éviter ces risques structurels, l'utilisation des inhibiteurs de corrosion s'est imposée comme une solution efficace et durable dans le domaine de la protection et de la réparation des ouvrages en béton armé. Ces inhibiteurs agissent en ralentissant les réactions responsables de la corrosion, contribuant ainsi à prolonger la durée de vie des structures.

Notre recharche vise à explorer les méthodes de réfection des structures dégradées par la corrosion des armatures en utilisant les inhibiteurs de corrosion. Elle comprend également des recommandations visant à intégrer au mieux les inhibiteurs de corrosion dans une stratégie de protection et de réparation, en assurant une surveillance continue des ouvrages par la détection précoce des défauts, tout en privilégiant des solutions respectueuses à l'environnement.

En conclusion, la préservation de l'intégrité des structures en béton armé demeure un objectif stratégique pour garantir leur sécurité et leur durabilité.

Mots clés: Corrosion, Béton, Inhibiteurs, Méthodes de réparation, Armatures.

ملخص

تعتبر الخرسانة المسلحة مادة أساسية في هندسة الهياكل، حيث اعتُمدت عالمياً لتلبية متطلبات التوسع العمراني ولضمان ديمومة البنى التحتية الضرورية للحياة اليومية، مثل المجمعات السكنية، شبكات النقل، والجسور، إلخ. وتعتمد مقاومتها ومتانتها بشكل كبير على حديد التسليح. إلا أن هذا الأخير معرض لظاهرة التآكل (الصدأ) عندما يتم تشييد الهياكل الخرسانية المسلحة في بيئات ذات تركيز عالٍ من الرطوبة، الأكسجين، أيونات كلوريد الصوديوم (NaCl) ، أو تعرضها للكربنة، مما يؤدي إلى التدهور المبكر للمنشآت.

ومن أجل تجنب هذه المخاطر الإنشائية، برز استخدام مثبطات التآكل كحل فعال ومستدام في مجال حماية وترميم منشآت الخرسانة المسلحة. وتعمل هذه المثبطات عن طريق إبطاء التفاعلات الكيميائية المسؤولة عن التآكل، مما يساهم في إطالة العمر الافتراضي للهياكل.

تهدف هذه البحث إلى استكشاف طرق ترميم المنشآت المتدهورة بسبب تآكل حديد التسليح باستخدام مثبطات التآكل. كما تتضمن أيضاً توصيات تهدف إلى دمج مثبطات التآكل بشكل أمثل في استراتيجيات الحماية والإصلاح، مع ضمان المراقبة المستمرة للمنشآت من خلال الكشف المبكر عن العيوب، وكل ذلك مع إعطاء الأولوية للحلول الصديقة للبيئة.

وفي الختام، يظل الحفاظ على سلامة منشآت الخرسانة المسلحة هدفاً استراتيجياً لضمان سلامتها وديمومتها.

الكلمات المفتاحية: التآكل، الخرسانة، المثبطات، طرق الترميم، حديد الخرسانة.

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General Introduction

General introduction:

Reinforced concrete is a fundamental element in modern construction; its significance lies in its combination of two essential strengths: the high compressive strength of concrete and the high tensile strength of reinforcing steel. This integration yields a robust and resilient structural material that is resistant to earthquakes, wind loads, and various environmental factors. It also provides protection for the steel reinforcement, making structures more resistant to fire, moisture, and corrosion. Reinforced concrete is therefore considered the cornerstone of major structures, bridges, and high-rise buildings, offering low maintenance costs and a long service life.

Moreover, reinforced concrete faces durability issues, mainly related to the corrosion of its reinforcements caused by carbonation ($CaCO_3$), which leads to a reduction in the pH of concrete and chloride (Cl^-) penetration. Furthermore, deficiencies in concrete mix design and construction practices, such as a high water-cement ratio, insufficient cement content, and inadequate compaction, increase concrete porosity and permeability. This facilitates the penetration of aggressive agents, accelerates reinforcement corrosion, and ultimately reduces the long-term durability of reinforced concrete structures.

Corrosion of reinforcement is one of the most serious deterioration processes of reinforced concrete structures. The effects of reinforcement corrosion are catastrophic and have detrimental consequences on the serviceability and durability of Reinforced concrete structures. Corrosion products occupy a greater volume than the parent steel, causing internal stress and ultimately leading to debonding, cracking, or spalling of the concrete cover. This degradation leads to a decrease in the cross-section of steel, the bond between steel and concrete, and the load-carrying capacity of the attacked elements. However, this problem can be addressed through conventional repair methods.

Historically, conventional approaches to repairing reinforced concrete (RC) structures have involved using various repair techniques. For example, traditional repair and restoration processes have included patching damaged areas, installing crack injections, applying protective coatings for corrosion prevention, adding **corrosion inhibitors**, and providing additional concrete around existing structural members (concrete jackets). Traditional repair methods are often unsatisfactory, as these repair approaches do not necessarily address the underlying problems that caused corrosion to begin with (such as chloride contamination or carbonation) and can often result in poor adhesion between the newly added repair material and the old concrete. Low bond strength often leads to deterioration continuing after the repair has been made. In addition, in some cases, it is nearly impossible to completely clean off the corrosion products on steel before a repair is made, allowing the deterioration to continue after the steel has been repaired. It is not necessary to let a structure deteriorate to the point where repair becomes unavoidable.

Preventive measures can represent an effective early solution, and they are used in new concrete, which refers to incorporating anti-corrosion during construction rather than waiting for deterioration to occur. Such measures include **corrosion-inhibiting chemicals**, supplementary

cementitious materials, low-permeability concrete mixes, surface treatments, and increased concrete cover, all aimed at preventing or delaying the onset of steel corrosion. This approach helps limit chloride ingress, slow carbonation, and enhance the durability of concrete from the time it is built. By mitigating corrosion during construction, preventive strategies significantly extend the service life of reinforced concrete structures and reduce future repair costs.

After presenting the above points, we can state that the objective of this study is to investigate the use of **corrosion inhibitors** for repairing reinforced concrete structures deteriorated by corrosion and ascertaining their effectiveness in enhancing durability and reducing corrosion-induced degradation.

The main objectives of this study are as follows:

• To explain the principle reasons and development mechanisms of steel reinforcement corrosion in concrete structures.

• To study the effect of reinforcement corrosion on structural behavior and durability.

• To understand the corrosion inhibitors, such as their categories, action mechanisms, and application techniques in concrete.

• To assess the efficiency of corrosion inhibitors in cases where they are used during the repair of corroded reinforcements.

• To evaluate the effectiveness of corrosion inhibitors for prolonging service life in repaired structures exposed to aggressive environments.

The novelty of this study is in its application to existing reinforced concrete structures, most of the time subject to aggressive environmental degradation and especially in Algeria.

The structure of this master thesis comprises a general introduction, three main chapters, and a general conclusion.

The first Chapter presents the fundamental aspects of corrosion in reinforced concrete structures. It includes the definition of corrosion in concrete and discusses the different means of protection against corrosion, focusing on both steel reinforcement protection and concrete protection.

The second chapter is dedicated to concrete corrosion inhibitors. It describes their history, nomenclature and mechanisms of action, as well as their use in a preventive and repair setting.

The third chapter is devoted to corrosion inhibitors used for repairing reinforced concrete structures deteriorated by corrosion. It reviews the literature, puts forward the current best practice, outlines steps in the repair process and provides practical recommendations.

The General conclusion presents the results of this study, their importance for engineers and practitioners as they can be used as a practical guidance that will enhance the quality of repair strategies resulting in an increased service life of reinforced concrete structures subjected to aggressive local Algerian environments.

Chapter I:

Corrosion of Steel Reinforcements

I.1. Introduction:

Reinforced concrete achieves its structural performance by combining complementary material properties with well-established design principles. This combination results in ductile and load-bearing structural elements capable of resisting a wide range of actions. The same mechanical fundamentals that ensure structural efficiency also play an important role in durability and influence the failure modes discussed in this chapter.

Reinforced concrete takes advantage of the high compressive strength of concrete and the high tensile strength of steel reinforcement. Through composite action and adequate bond between the two materials, reinforced concrete elements are able to resist bending and combined stresses efficiently.However, durability problems in reinforced concrete structures are mainly associated with the corrosion of steel reinforcement.

Corrosion of reinforcement is a major cause of structural deterioration in reinforced concrete. It leads to cracking, delamination, spalling of the concrete cover, and the formation of rust products. These phenomena progressively weaken the structure and may ultimately result in partial or total structural failure.

Corrosion is generally initiated by carbonation, chloride ingress, surface cracking, and internal voids resulting from poor construction practices. In addition, chemical attack, physical deterioration such as freeze–thaw damage, and environmental factors including moisture penetration, concrete permeability, and exposure to aggressive marine or industrial environments significantly contribute to durability loss.

From a structural point of view, corrosion has serious consequences. The expansion of corrosion products generates internal stresses that cause cracking and spalling of the concrete cover. At the same time, the reduction in the cross-sectional area of steel reinforcement decreases the load-bearing capacity of structural elements. Corrosion also degrades the bond between steel and concrete, which is essential for composite action, and reduces the ductility of structures, making them more vulnerable to excessive deformation and seismic loading. In severe cases, the combined effects of section loss and bond degradation can lead to structural collapse.

The economic consequences of reinforcement corrosion are equally significant. Corrosion related damage increases maintenance and repair costs, ranging from minor surface treatments to extensive structural rehabilitation. Early deterioration reduces the service life of structures and may require premature replacement. In addition, repair works often lead to operational disruptions, such as traffic delays or temporary shutdowns, and generate indirect costs related to inspection, monitoring, and potential safety risks.

The objective of this chapter is to present the fundamental aspects of corrosion in reinforced concrete structures. It introduces the definition and mechanisms of corrosion and discusses the main protection methods used to limit its effects, including the protection of steel reinforcement

and the protection of concrete.

I.2. Overview of Corrosion:

I.2.1 Definition of Corrosion in Concrete:

ISO 8044 defines corrosion as a physicochemical interaction between a metal and its environment that leads to changes in the material's properties. It often results in degradation of the metal, the environment, or the technical system involved.

Corrosion-related damage significantly increases maintenance and repair costs, ranging from minor surface treatments to extensive structural rehabilitation. Early deterioration reduces the service life of structures and may require premature replacement. In addition, repair works often lead to operational disruptions, such as traffic delays or temporary shutdowns, and generate indirect costs related to inspection, monitoring, and potential safety risks.

In recent years, no single consistent global estimate of corrosion costs has been clearly established. However, available studies confirm that corrosion remains a major economic issue worldwide. It is reported that corrosion leads to the loss of approximately 25% of annual steel production, corresponding to nearly 150 million tons. In addition, in the United States, the cost of corrosion is estimated at around 3% of the national Gross Domestic Product (GDP), representing about 276 billion US dollars.

In reinforced concrete structures, this impact is mainly related to the corrosion of steel reinforcement, which is one of the primary causes of structural deterioration and financial loss. It has been estimated that about 20% to 25% of these costs could be avoided by applying appropriate corrosion prevention and protection techniques [36].

I.2.2 Corrosion Mechanism:

Corrosion is an electrochemical phenomenon involving simultaneous oxidation and reduction reactions. Oxidation takes place at anodic sites, where the metal loses electrons and forms metallic ions, while reduction reactions occur at cathodic sites (**FigI.1**), where the released electrons are consumed to form reduced species. The nature of the corrosion products formed depends mainly on the chemical environment, particularly its acidity or alkalinity.

In acidic environments, cathodic reactions generally lead to hydrogen evolution, whereas in alkaline or natural environments, oxygen reduction is the dominant cathodic process, resulting in the formation of hydroxide ions. The corrosion process not only causes a gradual reduction in the cross-sectional area of reinforcing steel bars but also leads to the formation of expansive corrosion products. These products generate internal stresses within the concrete, which initiate cracking and contribute to the deterioration of reinforced concrete structures [27].

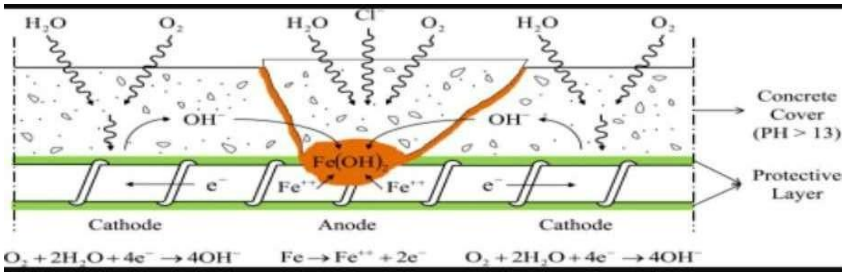


Figure I.1 : Schematic Representation of Anodic Oxidation and Cathodic Reduction During Steel Corrosion[38].

The anodic and cathodic reactions involved in steel corrosion can be expressed as follows:

$Fe \rightarrow Fe^{2+} + 2e^-$ (1.1)

$2e^- + 2H^+ \rightarrow H_2$ (in acidic environment)

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (in alkaline and natural environment) (1.2)

I.2.2.a. Influence of concrete carbonation on steel passivation:

Carbonation-induced corrosion represents another important corrosion mechanism in reinforced concrete structures. In this case, carbon dioxide diffuses into the concrete and reacts with the pore solution to form carbonic acid. This reaction reduces the alkalinity of the concrete, lowers the pH, and leads to the depassivation of the protective layer on the steel surface, thereby initiating corrosion.

The main chemical reaction of carbonation is:

$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$ (1.3)

In addition, carbonation may also involve other hydration products such as calcium silicate hydrates (C-S-H):

$CO_2 + C\text{-}S\text{-}H \rightarrow CaCO_3 + SiO_2 \cdot H_2O$ (1.4) [27].

I.2.2.b. Role of chloride ions in the initiation of reinforcement corrosion:

Chloride-induced corrosion occurs when chloride ions (Cl^-) reach the steel reinforcement and destroy the passive protective layer. Unlike carbonation, which reduces the pH of concrete, chlorides directly attack the steel surface and initiate localized corrosion (pitting).

Once the passive layer is broken, corrosion starts through electrochemical reactions:

Anodic reaction:

$Fe \rightarrow Fe^{2+} + 2e^-$ (1.5)

Cathodic reaction:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (1.6)

This type of corrosion is particularly dangerous because it leads to rapid and localized damage, reducing the cross-section of the steel and causing cracking and deterioration of the surrounding concrete [28-29].

In addition, microbiologically induced corrosion may significantly affect the integrity of concrete structures, particularly in sewer systems. Microorganisms can generate organic and inorganic acids that attack concrete and accelerate material degradation [27].

I.2.3 The aspects of corrosion:

The type of corrosion can be determined by the characteristics of the environment and the metal's behavior. In general, the various corrosion processes can be summarized as follows:

I.2.3.1 Uniform Corrosion (General):

Uniform corrosion is a type of corrosion that occurs evenly over the entire surface of the steel reinforcement (**Fig I. 2)**, resulting from uniformly distributed anodic and cathodic reactions. This form of corrosion is generally associated with carbonation, which reduces the pH of concrete and leads to the loss of the passive protective layer around the steel. As a result, corrosion develops in a relatively uniform manner.

Compared to other forms, uniform corrosion is considered less severe because its rate is more predictable, allowing a better estimation of the service life of the structure.

In contrast, corrosion caused by chloride ions leads to a non-uniform distribution of corrosion products around the reinforcement. This results in localized attack, known as pitting corrosion, which is more aggressive and can significantly reduce the cross-section of the steel in a short time.

Therefore, while carbonation generally leads to uniform corrosion, chloride penetration is mainly responsible for localized pitting corrosion, which is more dangerous for reinforced concrete structures. [22-23].

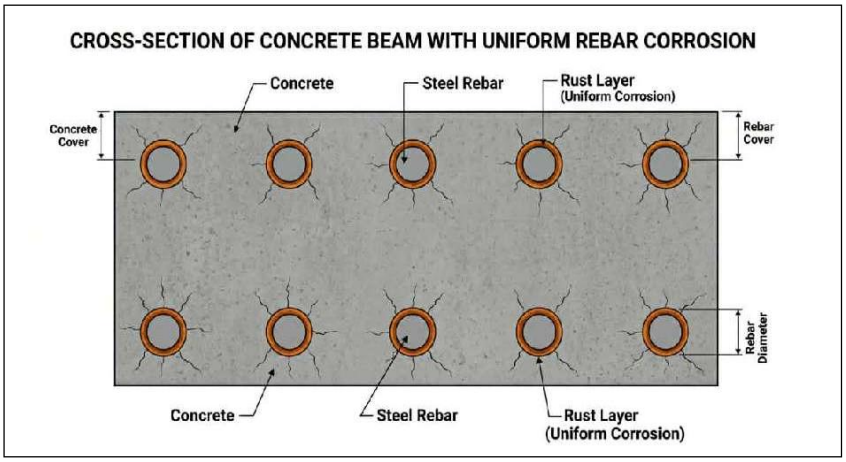


Figure I.2: Schematic illustration of uniform corrosion in reinforced concrete [41].

I.2.3.2 Pitting Corrosion:

Pitting corrosion is a localized form of corrosion characterized by the formation of small cavities or pits on the metal surface. In reinforced concrete structures, this type of corrosion mainly affects steel reinforcement when the protective passive layer is locally destroyed.

The initiation of pitting corrosion is strongly associated with the presence of aggressive anions, particularly chloride ions. These ions can penetrate the concrete cover and reach the steel surface, where they disrupt the passive film that normally protects the reinforcement in an alkaline environment. Chloride ions are especially dangerous because of their small size and high mobility, which allow them to diffuse easily toward the steel surface.

Once the passive layer is locally damaged, small anodic zones are formed, while the surrounding surface acts as a cathode. This leads to the creation of localized corrosion cells. The anodic dissolution of steel begins at these sites, while cathodic reactions occur in the adjacent areas, mainly involving oxygen reduction.

This mechanism is illustrated in (**FigI.3)**, which shows the anodic pit formation, cathodic oxygen reduction, and the transport of ions during pitting corrosion.

The initiation of pits may be promoted by several factors, such as surface heterogeneity of the steel, the presence of impurities, defects, or variations in environmental conditions at the steel–concrete interface. Deposits or debris on the steel surface can also contribute to the formation of anodic and cathodic regions, accelerating localized attack.

The pitting process starts with the destruction of the passive film at the anodic site, followed by metal dissolution according to the reaction:

$$M \rightarrow M^{n+} + ne^{-} \qquad (1.11)$$

At the cathodic zones, oxygen reduction occurs as follows:

$$O\square + 2H\square O + 4e^{-} \rightarrow 4OH^{-} \qquad (1.12)$$

As corrosion progresses, metal ions accumulate inside the pit, leading to charge imbalance. This attracts aggressive anions, especially chloride ions, which further intensify the localized corrosion. Hydrolysis reactions inside the pit cause a significant decrease in pH, creating an acidic environment that prevents repassivation of the steel surface.

The corrosion process inside the pit is self-accelerating. The continuous dissolution of metal enlarges the pit depth, increasing the local corrosion rate. This process continues until the steel section is significantly reduced or perforated, which may lead to a loss of mechanical capacity of the reinforcement.

In reinforced concrete structures, pitting corrosion is particularly dangerous because it is difficult to detect at early stages and can cause severe local damage while the surrounding steel remains apparently intact. This localized reduction in steel cross-section may result in cracking or spalling of the concrete cover and ultimately compromise the durability and structural safety of reinforced concrete elements [24].

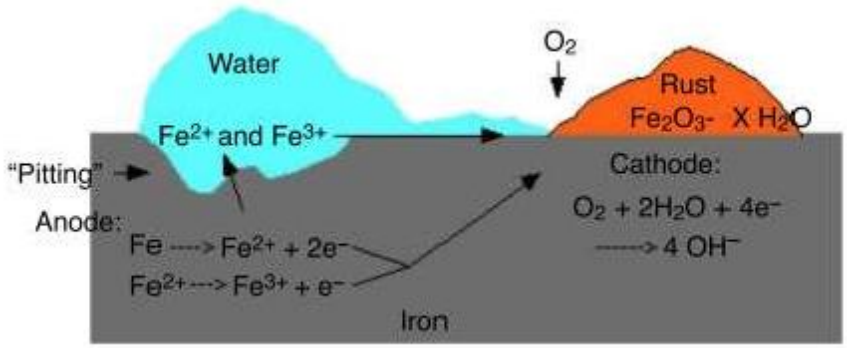


Figure I.3: Schematic representation of pitting corrosion [42].

I.2.4 The Types of corrosion:

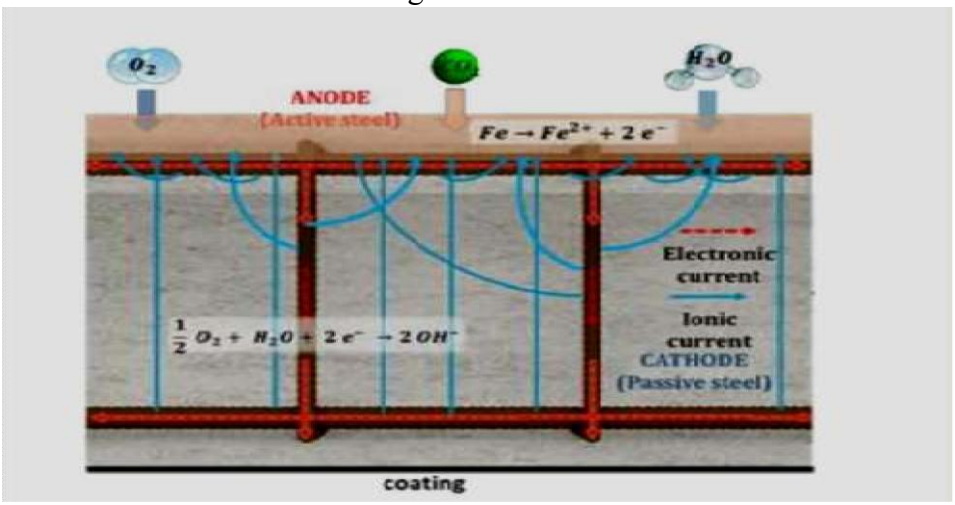
I.2.4.1 Galvanic Corrosion:

Galvanic corrosion is considered one of the main corrosion mechanisms affecting steel-reinforced concrete. This type of corrosion is particularly significant in large reinforced concrete structures, such as bridge decks, where exposure conditions are often non-uniform.

In reinforced concrete, galvanic corrosion develops as a result of differences in environmental conditions surrounding the steel reinforcement. Variations in oxygen availability, alkalinity due to carbonation, or chloride concentration can lead to uneven passivation of the steel surface. These differences create electrochemical potential gradients between different zones of the reinforcement, resulting in the formation of anodic and cathodic areas and the initiation of galvanic corrosion [21].

To better illustrate this mechanism, (**FigI.4)** shows how carbonation induced loss of passivity in the upper layer of steel bars creates anodic regions, while deeper layers still protected by high alkalinity remain passive and act as cathodes. This difference in electrochemical behavior produces galvanic coupling, accelerating steel corrosion in the carbonated zone.

Figure I.4: Schematic illustration of galvanic corrosion in reinforced concrete due to



carbonation [39].

In structures exposed to de-icing salts, chloride penetration is often uneven, which further intensifies galvanic effects and accelerates localized corrosion of steel reinforcement. This phenomenon has been identified as a major contributor to the deterioration of bridge structures, particularly in regions where de-icing salts are extensively used.

Despite the importance of galvanic corrosion in reinforced concrete durability, systematic experimental studies focusing specifically on this mechanism remain relatively limited when compared with other forms of reinforcement corrosion [21].

I.2.4.2 Chloride-Induced Corrosion:

The rate of chloride penetration is contingent upon a multitude of factors, with the principal determinants being associated with the intrinsic properties of the concrete, the transport mechanisms of chloride-laden solutions, the moisture content within the concrete matrix, and the environmental concentration of chlorides. The transport of chlorides through the concrete cover may occur as a result of an amalgamation of various transport mechanisms (diffusion, capillary suction, or permeation), and chemical binding interactions may also occur with the hydration products (**FigI. 5)**. Consequently, the modeling of chloride penetration over time constitutes a rather complex task. For instance, when a structural component undergoes cycles of wetting and drying, it experiences capillary absorption of the chloride-bearing solution during the wet phase, potentially followed by diffusion during this period, while during dry phases, the evaporation of water facilitates the accumulation of chlorides near the surface. Conversely, exposure to precipitation events may lead to the leaching of chlorides from the concrete surface. Thus, chloride penetration within a reinforced concrete structure represents a multifaceted function influenced by geometry, spatial positioning, environmental conditions, and the composition of the concrete. From a practical perspective, the ingress of chlorides into concrete is frequently characterized as a diffusion phenomenon, whereby an apparent diffusion coefficient Dapp is considered, which is influenced by the pore structure of the concrete and all factors that govern it, including the water-to-cement (w/c) ratio, compaction, curing methods, and the presence of fissures. The type of cement utilized also exerts a significant influence: transitioning from concrete composed of Portland cement to concrete with varying proportions of pozzolana or blast furnace slag can result in a substantial reduction in chloride diffusivity. The apparent diffusion coefficient tends to diminish over time, particularly in relation to slowly reacting blast furnace slag or pozzolanic cements. The Dapp derived from empirical studies or laboratory evaluations is also employed as a metric to assess the resistance of various concrete mixtures to chloride penetration, based on the premise that a lower Dapp correlates with enhanced resistance to chloride ingress. For instance, even finely ground waste glass may exhibit commendable pozzolanic characteristics and significantly enhance resistance to chloride penetration [28-29].

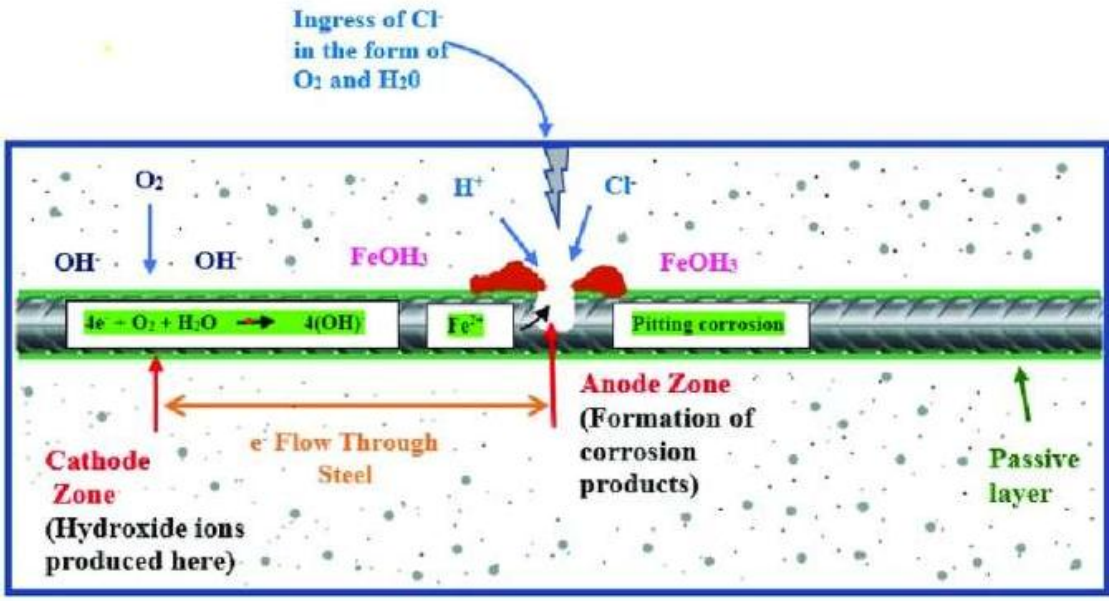


Figure I.5: Schematic representation of chloride-induced corrosion [40].

I.2.4.3 Carbonation:

Carbonation is one of the main deterioration mechanisms affecting reinforced concrete structures. It occurs when carbon dioxide (CO_2) present in the atmosphere penetrates the concrete surface through its interconnected pore system (**FigI.6)**. This penetration mainly takes place by diffusion and depends on the pore structure, moisture content, and environmental conditions.

Once inside the concrete, carbon dioxide dissolves in the pore water and reacts according to the following reactions:

$$H_2O + CO_2\ (g) \rightarrow HCO_3^-\ (aq) + H^+ \qquad (1.7)$$

$$HCO_3^-\ (aq) \rightarrow CO_3^{2-}\ (aq) + H^+ \qquad (1.8)$$

In Portland cement concrete, the pore solution is rich in calcium hydroxide, $Ca(OH)_2$, which is produced during cement hydration. Calcium hydroxide dissolves in the pore solution as follows:

$$Ca(OH)_2\ (s) \rightarrow Ca^{2+}\ (aq) + 2OH^- \qquad (1.9)$$

The calcium ions (Ca^{2+}) then react with carbonate ions (CO_3^{2-}), leading to the formation of calcium carbonate through the following neutralization reaction:

$$Ca^{2+} + 2OH^- + 2H^+ + CO_3^{2-} \rightarrow CaCO_3\ (s) + 2H_2O \qquad (1.10)$$

As a result, solid calcium carbonate ($CaCO_3$) precipitates inside the concrete pores. This process has two important consequences. First, the precipitation of calcium carbonate partially fills the pore network, which may locally densify the concrete. Second, the carbonation reaction consumes calcium hydroxide, which is responsible for maintaining the high alkalinity of the concrete pore solution [18-19].

In some cases, when calcium hydroxide becomes depleted, carbon dioxide can also react with calcium-containing hydration products such as calcium silicate hydrate (C–S–H), leading to

additional formation of calcium carbonate. The presence of water is essential for this process, since carbon dioxide must dissolve in pore water to form carbonic species [18-19].

The most critical effect of carbonation in reinforced concrete is the reduction of alkalinity. The pore solution pH decreases from highly alkaline values (pH ≈ 12–13) to values below 9. This drop in pH destroys the passive oxide layer that normally protects steel reinforcement. Once this passive film is broken, steel becomes susceptible to corrosion in the presence of moisture and oxygen.

It should be noted that the carbonation mechanism described above is characteristic of Portland cement concrete, which is widely used in reinforced concrete structures, including those commonly constructed in Algeria. Concretes containing supplementary cementitious materials such as slag or fly ash may exhibit different carbonation behavior [18-19].

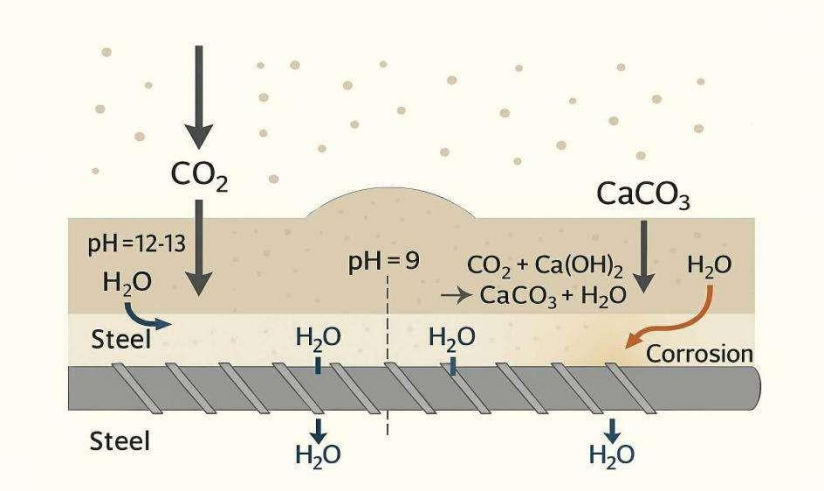


Figure I.6: Schematic representation of the carbonation process in reinforced concrete [41].

I.2.4.4 Macrocell Corrosion:

Macrocell corrosion is a form of electrochemical corrosion that develops in reinforced concrete when differences in electrochemical potential exist between steel rebars or between different zones of the same rebar. These potential differences lead to the formation of a macroscopic corrosion cell, in which anodic and cathodic regions are spatially separated within the concrete structure (**FigI.7)**.

In reinforced concrete, macrocell corrosion commonly occurs due to environmental non-uniformity or material heterogeneity. When two rebars with different electrochemical properties (such as dissimilar steel types, different surface conditions, or different exposure environments) are electrically connected through concrete, a galvanic circuit is established. The steel with the lower electrode potential behaves as the anode and undergoes oxidation, while the steel with the higher potential acts as the cathode and is relatively protected.

Another important cause of macrocell corrosion is the difference in the concentration of aggressive agents, particularly chloride ions, within the concrete. In structures exposed to marine

environments or de-icing salts, chloride ions penetrate concrete non-uniformly, creating concentration gradients. Rebars located in zones with higher chloride concentrations tend to become anodic, whereas those in less contaminated zones act as cathodic regions. This potential difference provides the driving force for macrocell corrosion, accelerating localized deterioration of steel reinforcement.

The macrocell corrosion process is governed by electrochemical reactions occurring at both anodic and cathodic sites. At the anode, iron dissolution takes place, leading to the release of metal ions into the pore solution. At the cathode, reduction reactions—primarily oxygen reduction—consume electrons generated at the anodic sites. The continuous flow of electrons through the steel and ionic current in the concrete pore solution sustain the corrosion process.

Compared to microcell corrosion, macrocell corrosion is often more severe because it can involve large areas of reinforcement and results in significant anodic dissolution at localized regions. This may cause accelerated loss of steel cross-section, cracking and spalling of the concrete cover, and a reduction in the load-bearing capacity of reinforced concrete structures.

In reinforced concrete structures, macrocell corrosion is particularly critical because it is difficult to detect and control, and its effects can propagate over long distances along the reinforcement. Understanding the mechanisms and influencing factors of macrocell corrosion is therefore essential for improving durability and ensuring the long-term performance of reinforced concrete structures [25].

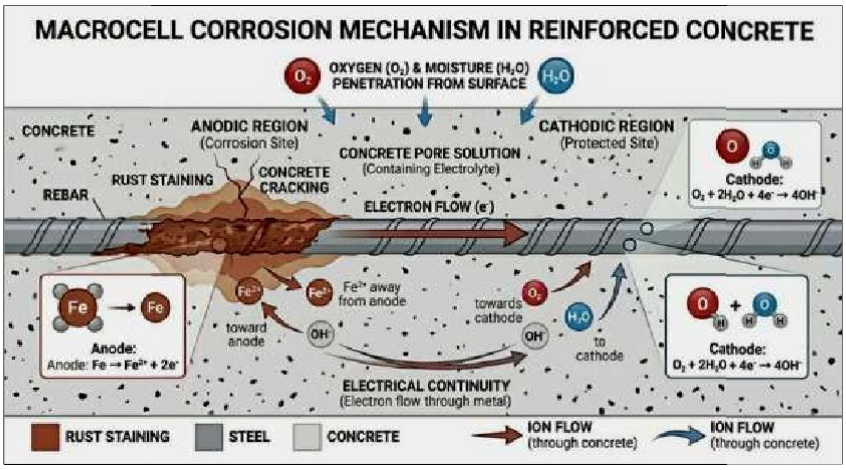


Figure I.7: Schematic representation mechanism of macrocell corrosion [41].

I.2.4.5 Microcell Corrosion:

The corrosion of steel in concrete is an electrochemical phenomenon resulting from electron transfer between anodic and cathodic sites formed on the steel surface. Microcell corrosion refers to corrosion processes that occur on a microscopic scale, where anodic and cathodic reactions take place very close to each other on the reinforcement.

At the anodic sites, iron is oxidized according to the following reaction:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1.13)$$

The ferrous ions then react with hydroxyl ions present in the alkaline pore solution to form ferrous hydroxide:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (1.14)$$

Depending on the availability of oxygen and the pH of the environment, ferrous hydroxide may further react to form hydrated iron oxides such as hydrated ferric oxide and hydrated magnetite:

$$4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3 \cdot H_2O + 2H_2O \quad (1.15)$$

$$6Fe(OH)_2 + O_2 \rightarrow 2Fe_3O_4 \cdot H_2O + 4H_2O \quad (1.16)$$

At the cathodic sites, reduction reactions occur through the consumption of electrons. In concrete, the dominant cathodic reaction is oxygen reduction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1.17)$$

Under low-oxygen conditions, hydrogen evolution may also take place:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1.18)$$

In normal concrete, the pore solution is highly alkaline, with a pH ranging between 12 and 13.5. This high alkalinity promotes the formation of a passive film on the steel surface, which significantly reduces the rate of microcell corrosion under normal conditions.

When the alkalinity of concrete is reduced and the pH drops from its initially high values (12–13) to around 9 or even 8, the protective passive layer on the steel surface becomes unstable and is gradually destroyed. This loss of alkalinity not only initiates corrosion of the steel reinforcement, but also negatively affects the concrete itself. The reduction in pH is associated with the consumption of calcium hydroxide, which plays an important role in maintaining the mechanical integrity of hardened cement paste. As a result, the concrete may lose part of its cohesion and stiffness, leading to a reduction in its durability and overall mechanical performance [26].

I.3 Different Methods for Concrete Corrosion Prevention:

Corrosion protection is essential for reinforced concrete structures to last and function well over time. Based on the element being protected, corrosion protection techniques can be broadly divided into two groups: concrete protection techniques and steel reinforcement protection techniques. Concrete-based protection techniques aim to improve the quality and impermeability of concrete to reduce the entry of aggressive agents, whereas steel-based protection techniques focus on protecting the reinforcement itself. These two techniques are commonly used to improve the overall corrosion resistance of reinforced concrete structures because they complement each other well.

I.3.1. Protection of Concrete:

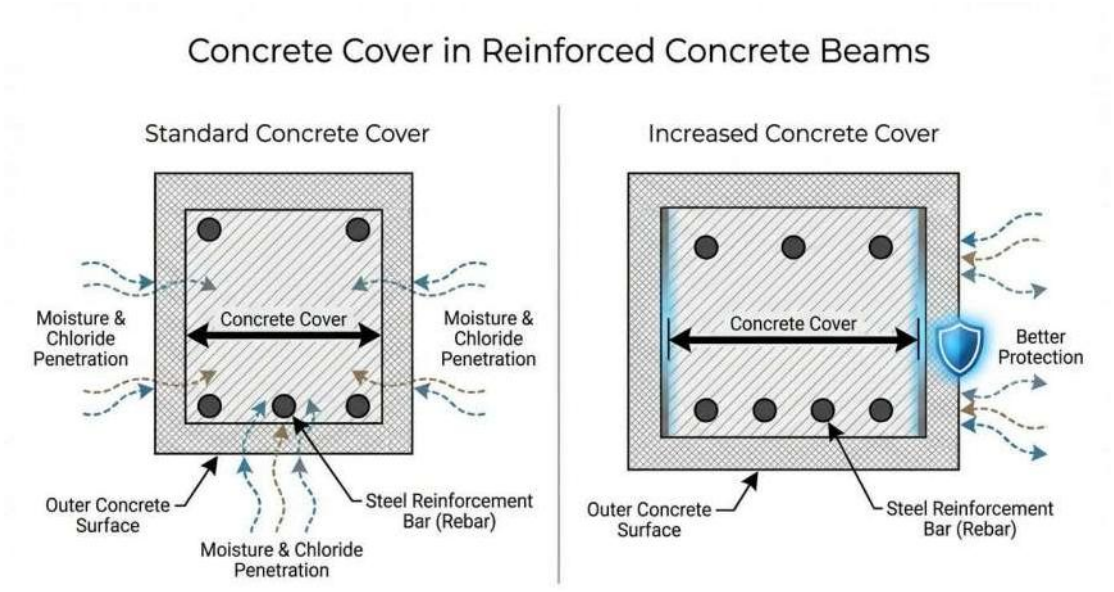
Several methods are used to protect concrete in order to increase its durability and stop it from deteriorating. These techniques cover a variety of strategies, each of which targets

particular kinds of environmental exposure and damage. The primary means of protection are:

I.3.1.1 Increasing Concrete Cover:

Rapid steel corrosion can cause a significant reduction in the service life of reinforced concrete due to cracking. Supplementary cementitious materials can change both the chemical composition of the pore solution and the environment around the steel, causing a significant decrease in the corrosion rate. For a concrete cover thickness of 20 mm, all supplementary cementitious materials led to at least a 50% reduction in the corrosion rate compared to ordinary Portland cement concrete.

Raising the crack width from 0.2 mm to 0.7 mm resulted in increased corrosion rates inall cases. However, these benefits were not observed in the samples were not seen in those using SCMs, which is due to the fact that corrosion rates in SCM-based concrete are mainly influenced by the system's resistance, in contrast to ordinary concrete where they are primarily controlled by oxygen availability. This behavior is illustrated in (**FigI.8)**, which compares standard concrete cover with increased cover thickness and shows how a thicker cover enhances protection by limiting moisture and chloride penetration.. In this case, the depth of the concrete cover offers a sufficient level of protection for both the concrete and the reinforcing steel against corrosion [37].



I.3.1.2 Low Permeability (Denser Concrete):

Several methods have been applied to protect reinforcing steel from corrosion; these methods include modifying the concrete mix design, coating the external surface of the concrete, and using inhibitors and mineral admixtures. Resorting to these admixtures is considered advantageous for several purposes, such as:

Improvingmechanical properties, increasing bond strength,reducing permeability to control

corrosion (**FigI.9)**. It is generally recognized that mineral admixtures such as silica fume and fly ash improve concrete protection against chloride□induced corrosion by reducing its permeability and diffusivity.

Figure I.9: Concrete permeability mechanism [43].

I.3.1.3 Surface Treatments and Coating:

Surface treatments and coatings help prevent harmful substances from getting into concrete.The choice to protect a surface really depends on how much it is going to be exposed to tough conditions, such as proximity to marine environments or areas where de-icing salts are used.These treatments work to limit the penetration of chlorides and other aggressive agents can get to the reinforcement.Surface protection comes in various forms including coatings, membranes, paints, polymers, and sealers.These methods are often used both to prevent problems in new structures and to fix issues in ones that are already built.Field trials have shown that surface treatments can significantly enhance the service life of concrete when appropriate materials are selected and correctly applied. Pore-blocking treatments like silane, siloxane, and other penetrating sealants are some of the most commonly used methods.These products soak into the concrete and reduce water absorption, which slows the transport of contaminants and prevent water and aggressive substances from reaching the reinforcement [7-8-9].

I.3.1.4 Waterproofing Membranes:

Waterproofing membranes are commonly used to protect against corrosion by blocking water and harmful ions from getting through.These membranes protect the steel inside mainly by keeping water and corrosive substances from passing through, pushing away liquid water, and sticking well even when under pressure or movement.Waterproofing for corrosion protection includes everything from the old asphaltic (bitumen) membranes to newer non-asphaltic polymer and fluid-applied systems.Asphaltic bitumen membranes can either be reaction-setting or applied cold, and they are usually paired with fabric or sheet layers to create a tough, crack-resistant protective system.Non-asphaltic systems, on the other hand, cover things like polymeric sheets, elastomeric membranes, fluid-applied coatings, and engineered composite systems. These are

designed to work with various substrates and suit different exposure conditions. Siloxane and polysiloxane coatings are a type of waterproofing membrane [10].

These hydrophobic coatings are put on as thin layers and are known for taking in very little water while keeping their water-repellent properties for a long time.They work well mostly because they cut down on water soaking in but still let vapor pass through.Recent progress in waterproofing technologies is mainly about making barriers work better, last longer, and be kinder to the environment.Studies show progress in making coatings that repel water really well, including spray-on surface treatments and tough composite materials. These are especially useful for hard-to-handle places like pipelines and harsh environments.Research on bio-resin-based systems and nano-additive formulations has shown good results, offering alternative waterproofing options that might have less impact on the environment [11-12].

(FigI.10) illustrates a typical waterproofing membrane system showing how multilayer barriers prevent water and chloride penetration into concrete structures.

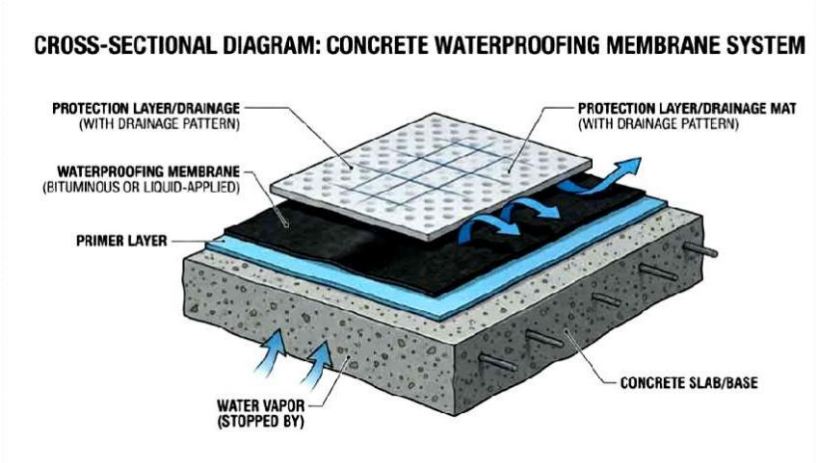


Figure I.10: Cross-Sectional View of a Concrete Waterproofing Membrane System [41].

I.3.1.5 Corrosion Inhibitors:

Corrosion inhibitors are added to reinforced concrete to help slow down when corrosion begins and to reduce how fast it spreads after it starts.Their action mostly involves changing the electrochemical reactions happening where the steel meets the concrete, either through anodic, cathodic, or a combination of both mechanisms. Inhibitors can also work by creating protective films or deposits on the steel surface.

Corrosion inhibitors mostly work on steel reinforcement, but how well they do depends a lot on the concrete's properties.Dense, low-permeability concrete helps inhibitors work better by holding them in place and keeping out harmful substances like chlorides and moisture. So, corrosion inhibitors work best when they're used alongside good-quality concrete [1-2].

I.3.2 Protection of Steel:

Protecting steel is essential to ensuring its durability and preventing structural deterioration. Steel is susceptible to corrosion when exposed to moisture, oxygen, and harsh environments such

as those rich in chlorides. Several protective methods can be employed to mitigate these effects, including:

I.3.2.1 Epoxy-coated Reinforcing Steel:

Epoxy-coated reinforcing steel is considered one of the most common methods for protecting steel from corrosion. It was first developed in the early 1970s and has been used in Scandinavian countries since the 1980s, although it did not become widely adopted there. In contrast, it is used extensively in the United States and is recommended by several transportation agencies (Federal Highway Administration 1999).

The concrete structures most susceptible to deterioration are marine structures due to their continuous exposure to aggressive environmental conditions. It has been observed that concrete bridge decks with uncoated steel reinforcement require repair every seven to ten years, whereas after using epoxy coatings in more than 100,000 structures, only a few issues were reported. Several studies have shown that epoxy-coated reinforcement significantly increases the durability and service life of concrete (Treadaway& Davies 1989; McDonald et al. 1996; Fanous& Wu 2005).

The epoxy layer acts as a barrier that prevents moisture, chlorides, and oxygen from reaching the steel surface. It also functions as an electrical insulator between bars, reducing the risk of macrocell corrosion.

Epoxy coating is applied to hot-rolled reinforcing bars either by fusion bonding or electrostatic spraying, with a typical thickness ranging from 150 to 300 μm. The surface of the epoxy is smoother and glossier than steel, resulting in a 20% to 50% reduction in bond strength compared to uncoated bars. Despite its advantages, poor performance has been observed when epoxy-coated reinforcement remains in water-saturated concrete, or when defects and damage allow aggressive agents to reach the steel surface. These defects are known as "Holidays," and they may occur during transportation, handling, fabrication, or concrete casting.

Loss of adhesion between the epoxy and the steel represents another major issue. This separation can be caused by cathodic disbandment or the formation of blisters when hydroxide ions accumulate between the coating and the steel. Despite these defects, Draper et al. (2009) found that epoxy-coated bars— even when damaged— showed only 1% of the corrosion experienced by uncoated bars.

Similarly, Darwin et al. demonstrated that conventional fusion-bonded epoxy coatings greatly improve corrosion resistance and service life compared to traditional reinforcement. A cost analysis over a design life of 75 years also confirmed that the overall cost differences were relatively small, generally favoring the use of epoxy-coated bars.[13]

I.3.2.2 Zinc Coated (Galvanized) Reinforcement:

Zinc coating, or galvanizing, is another widely used method for protecting steel

reinforcement against corrosion. It first appeared in the early 1940s.

However, its use in fresh concrete has not gained widespread popularity, especially when compared with epoxy coating, due to the similarity in cost between the two methods. The final product costs about 1.5 times the price of conventional steel reinforcement (approximately 3 USD/kg) [41].

Zinc coating acts as a protective barrier (**FigI.11)**, preventing oxygen, moisture, and chloride ions from reaching the steel surface. The thickness of the zinc layer on structural elements typically exceeds 180 micrometers.

It also acts as a sacrificial anode, since its half-cell potential is –1.004 V versus the saturated calomel electrode (SCE), which is more negative than that of steel (–0.681 V),this means that zinc is a more active than iron.

Hot-dip galvanizing is the most common method for coating reinforcement bars. The steel is immersed in a bath of molten zinc at a temperature of approximately 450°C, which results in the formation of a metallurgical bond between zinc and steel.

When zinc comes into contact with air, a fast reaction takes place between zinc and carbon dioxide, forming:

-Zinc hydroxide $Zn(OH)_2$

-Which later transforms into a relatively hard protective layer of:

-Zinc carbonate $ZnCO_2$ (after reacting with CO_2)

-Zinc is more tolerant of acidity, up to pH = 6, but it becomes more sensitive under highly alkaline conditions up to pH = 13. In concrete, where the pH ranges between 12.2 and 13.3, zinc reacts with water in the alkaline pore solution, producing zinc hydroxide and hydrogen gas:

Reaction:

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2 \quad (1.20)$$

Another reaction occurs between zinc hydroxide and calcium ions found in the concrete pore solution, forming:

Calcium Zincate (Calcium Hydroxozincate)

Final reaction:

$$2Zn(OH)_2 + 2H_2O + Ca(OH)_2 \rightarrow Ca[Zn(OH)_3]\cdot 2H_2O \quad (1.21)$$

Unlike epoxy-coated reinforcement, the durability of zinc-coated steel does not depend on keeping the surface free from scratches. It can be handled similarly to ordinary reinforcement bars, without requiring special care.

However, despite its advantages, galvanized steel will eventually corrode, and therefore it cannot be considered a permanent corrosion inhibitor. Instead, it should be viewed as a method to extend the service life of structures [13].

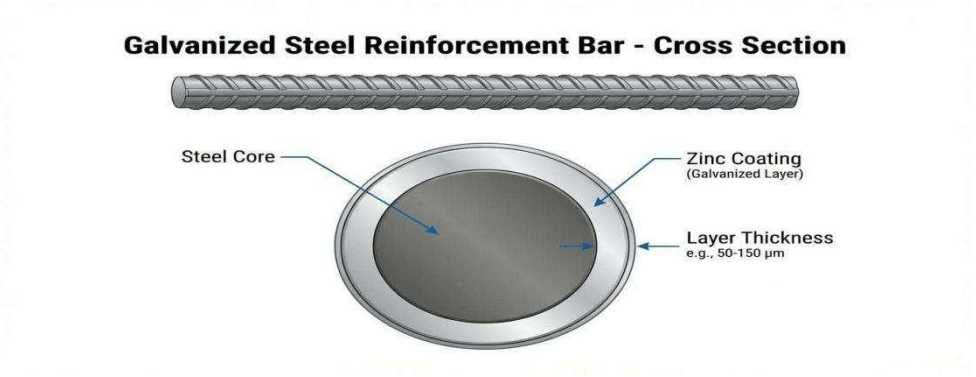


Figure I.11: Image representation of galvanized steel reinforcement [41].

I.3.2.3 Stainless Steel:

Away from coated steel, whether epoxy coated or zinc coated steel used for corrosion protection, stainless steel capable of resisting corrosion by itself—appeared in 1913 through the work of the British researcher Harry Brearley in the city of Sheffield (United Kingdom), as the first real production and application of stainless steel after earlier attempts during the 19th century (Pierre Berthier in 1821, and late□19th□century Fe–Cr research).

Stainless steel is known as an iron-based alloy, which is not composed solely of iron and carbon, but also contains several additional metals that give the alloy very high resistance to corrosion.

The alloy contains more than 12% chromium, which forms a thin oxide layer that makes the alloy highly resistant to corrosion. This protective layer can regenerate itself automatically when scratched ,contains up to 30% of elements other than iron, which strongly influence its behavior.

Studies have therefore developed and improved important properties such as tensile strength, ductility, toughness, and corrosion resistance.

For these reasons, most types of stainless steel provide excellent performance, mechanical properties, and long-term durability. Among these types:

1. Ferritic Stainless Steel (Ferritic) :

Ferritic stainless steels—characterized by their chromium content (typically 12–17%) and very low or negligible nickel levels—are generally less commonly used as reinforcement in concrete compared to austenitic (304, 316) and duplex grades. While ferritic steels offer good resistance to uniform corrosion in mildly aggressive environments, their lower toughness and reduced resistance to chloride□induced pitting make them less suitable for highly corrosive conditions, such as marine structures or de□icing salt exposure.

Despite these limitations, certain ferritic grades—such as Type 430 (EN 1.4016)—have been used in concrete elements that are exposed to moderate chloride levels or indoor environments, where corrosion risks are lower. For example, ferritic stainless reinforcement has been applied in architectural concrete elements in parts of Germany and Scandinavia, where structures require better corrosion protection than carbon steel but do not justify the higher cost of nickel□containing stainless steels. Additionally, ferritic stainless steel meshes are sometimes

used in thin precast façade panels and non□structural concrete components, benefiting from their magnetic properties, good formability, and lower cost.

Although less widespread globally, the use of ferritic stainless steel in concrete continues to develop as an economical alternative in applications demanding enhanced durability without the high price of austenitic or duplex stainless steel [30].

2. Austenitic Stainless Steel (Austenitic):

(typically 22% chromium and 8–10% nickel)

It is the most widely used type because of:

Excellent corrosion resistance

High ductility

Good workability

There are also less common grades.

Examples: 2X and 3X alloys.These were among the first alloys used in 1950 as corrosion□resistant materials.

However, alloy 3X is not considered stainless steel; it is used like conventional reinforcing steel but has higher corrosion resistance (HFX Steel 2014).

3. Ferritic–Austenitic Stainless Steel (Duplex):

Contains 4–8% nickel and around 28% chromium.

4. Martensitic Stainless Steel (Martensitic):

The main reason for the superior performance of stainless steel is the presence of a protective passive layer that prevents corrosion. This passive film is particularly important in reinforced concrete structures exposed to aggressive environments, such as marine bridges, coastal foundations, and tunnel linings, where chloride penetration is a major concern. In many of these structures—especially in Scandinavian tunnels and European harbor facilities—martensitic and other stainless□steel grades have been successfully used to ensure long□term durability.

However, when this protective layer is penetrated, two types of corrosion may occur: Pitting Corrosion and Service (Crevice) Corrosion. Such risks are especially relevant in concrete elements subjected to extreme temperature variations or welding operations during fabrication.

Factors that weaken the stainless steel surface include the presence of a scale layer caused by high temperatures, as well as discoloration produced by welding, which increases susceptibility to pitting corrosion. In construction projects such as marine piers or desalination plant structures, these effects are often mitigated through chemical treatments that restore a thin protective oxide layer composed of iron and alloying metal oxides, thereby improving long□term durability of the reinforced concrete [15].

I.3.2.4 Cathodic Protection (CP):

Cathodic protection is considered one of the most effective methods for protecting reinforcing steel from corrosion. Cathodic protection first appeared in the United States during the 1970s, and it was later applied to many concrete structures that had suffered from corrosion for over 25 years. It was implemented effectively, particularly in cases where chloride contamination leads to reinforcement corrosion. In 1982, the Federal Highway Administration (FHWA) issued a memorandum stating that cathodic protection is the only method capable of stopping corrosion on salt-contaminated bridge decks, regardless of the chloride level within the concrete.

Cathodic protection is an electrochemical technique that converts the structural element into a cathodeby supplying a continuous direct current(DC), from an external source or via a sacrificial anode. CP is classified into two main categories:

Sacrificial Anode Cathodic Protection (SACP)

Impressed Current Cathodic Protection (ICCP)

Studies by Pithouse revealed that both methods were highly successful in concrete repair applications, and a new system combining the two methods was recently introduced, known as the hybrid system.

Sacrificial Anode Cathodic Protection (SACP):

This method is used to protect steel from corrosion by connecting it to a sacrificial anode such as zinc or aluminum. The anode is electrically connected to the reinforcing steel bar, allowing it to corrode instead of the steel due to the dissolution of the anode, which provides the necessary direct current (DC) without the need for an external power source.

FigI.12 represent a schematic illustration of sacrificial anode cathodic protection (SACP).

In this method, the reinforcing steel bars are supplied with a continuous and uniformly distributed direct current (DC). This current originates from a non-corroding anode embedded within the concrete and connected to an external power source such as a rectifier, a main electrical supply, solar cells, or other power sources.

Electrons flow through the reinforcement network toward the steel–concrete interface, increasing the cathodic reaction and preventing hydroxyl ions from reacting with oxygen and water. These ions then migrate through the concrete cover toward the anode, where they oxidize and transform into oxygen and electrons. This method typically uses titanium or noble metal oxides as anodes.Regular monitoring of cathodic protection performance is required several times a year, measuring its effectiveness through polarization values. Studies have shown that the service life of such systems ranges from 10 to 15 years.

- ✧ **Disadvantages of Cathodic Protection Systems:**

Sacrificial Anode Cathodic Protection (SACP):

• Limited service life due to consumption of the sacrificial anode.

• Less effective in high resistivity concrete.

• Requires many anodes for large surfaces, increasing cost.

• Difficult to control the protection current precisely.

• Performance decreases in cracked or carbonated concrete.

Impressed Current Cathodic Protection (ICCP):

• High installation and maintenance cost.

• Requires continuous monitoring and specialized personnel.

• Risk of overprotection, which may damage the concrete.

• System failure if the power supply is interrupted.

• Electrically complex and sensitive to malfunctions.

Compared to traditional methods, cathodic protection is considered more cost□effective, easier to apply, and suitable for structures expected to suffer corrosion. This approach is known as preventive cathodic protection [14].

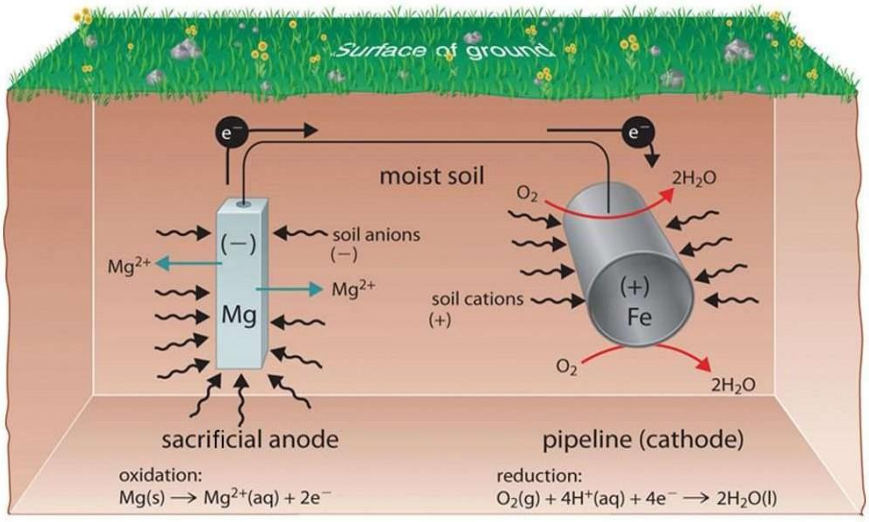


Figure I.12: Schematic representation of the cathodic protection mechanism[45].

I.4. Consequences of Reinforcement Corrosion:

The progression of reinforcement corrosion directly affects the performance and the remaining service life of reinforced concrete structures. As corrosion develops, it leads to a gradual deterioration of both steel reinforcement and surrounding concrete, resulting in several structural and durability-related consequences.

✧ **Corrosion-Induced Cover Cracking:**

During the corrosion process, products are formed on the surface of the steel reinforcement. These products are expansive in nature and can occupy two to six times the volume of the original steel. This volumetric expansion generates internal tensile stresses in the surrounding concrete, leading to cracking of the concrete cover [20].

✧ **Spalling and Delamination:**

As corrosion progresses, the continuous accumulation of expansive products causes delamination and spalling of the concrete cover. This phenomenon is often observed before a significant loss of structural capacity occurs. However, spalling reduces durability and directly exposes the reinforcement to the environment, which accelerates further corrosion [16-17].

✧ **Bond Degradation:**

Corrosion negatively affects the bond between steel reinforcement and concrete. The formation of cracks around the reinforcement reduces bond strength over time, which in turn leads to a decrease in flexural capacity and serviceability of the structure [17].

✧ **Residual Strength Deterioration:**

The loss of bond combined with the reduction of the effective steel cross-section due to corrosion results in a gradual deterioration of the residual strength of reinforced concrete members. This reduction compromises the load-carrying capacity and long-term performance of the structure [20].

I.5. Durability of Reinforced Concrete Structures:

The durability of concrete structures designed for long-term use mainly depends on their ability to resist aggressive environmental conditions, especially chemical actions. In reinforced concrete, durability is closely related to the capacity of concrete to protect the embedded steel from corrosion. Among the different deterioration mechanisms, carbonation and chloride ingress are considered the most critical factors that can reduce the protective role of concrete and initiate steel corrosion.

To ensure good durability, it is essential to limit the penetration of these harmful agents into the concrete. This is generally achieved by using high-quality materials and providing an adequate concrete cover, which acts as a physical barrier against external attacks. The effectiveness of this protection depends on both the properties of the concrete and the surrounding environmental conditions.

Therefore, improving durability requires not only proper material selection but also a good understanding of the mechanisms of chemical degradation affecting reinforced concrete structures [31].

I.6 Service Life and Corrosion Initiation of Reinforced Concrete Structures:

The service life of reinforced concrete structures refers to the period during which a structure can perform its intended function without significant deterioration or loss of safety. In recent years, this concept has become increasingly important due to environmental challenges, sustainability concerns, and the high costs associated with maintenance and rehabilitation of civil infrastructure.

One of the main factors that negatively affect the service life of reinforced concrete is steel corrosion. This phenomenon results from chemical reactions that lead to the loss of material from the steel surface, reducing the cross-sectional area of reinforcement and consequently decreasing the load-bearing capacity of the structure. Therefore, controlling corrosion is essential to extend the service life [32-33].

The initiation of corrosion is strongly related to the penetration of aggressive agents such as chlorides and carbon dioxide through the concrete cover. This stage, known as the initiation period, corresponds to the time required for these agents to reach the reinforcement. It is influenced by several parameters, including the quality of concrete, the thickness of the concrete cover, and the environmental exposure conditions. A dense and well-designed concrete cover can significantly delay this process.

Concrete naturally provides protection to steel due to its high alkalinity, which creates a passive layer around the reinforcement. However, this protection can be reduced over time due to carbonation or chloride ingress, leading to the breakdown of the passive layer and the beginning of corrosion [32-33].

To better understand and predict the evolution of deterioration, service life models are used. One of the most commonly adopted approaches is based on the division of the corrosion process into two main phases: the initiation phase and the propagation phase. The initiation phase is generally longer and represents the period before visible damage occurs, while the propagation phase is shorter but leads to rapid deterioration such as cracking and spalling of concrete. For this reason, many studies focus on accurately estimating the initiation period, as it largely determines the total service life of the structure (**FigI.13)**.

In practice, improving the service life requires considering durability measures at the design stage, such as selecting appropriate materials, increasing concrete cover thickness, and adapting the design to environmental conditions. Continuous monitoring and maintenance during the structure's life are also necessary to ensure long-term performance [32-33].

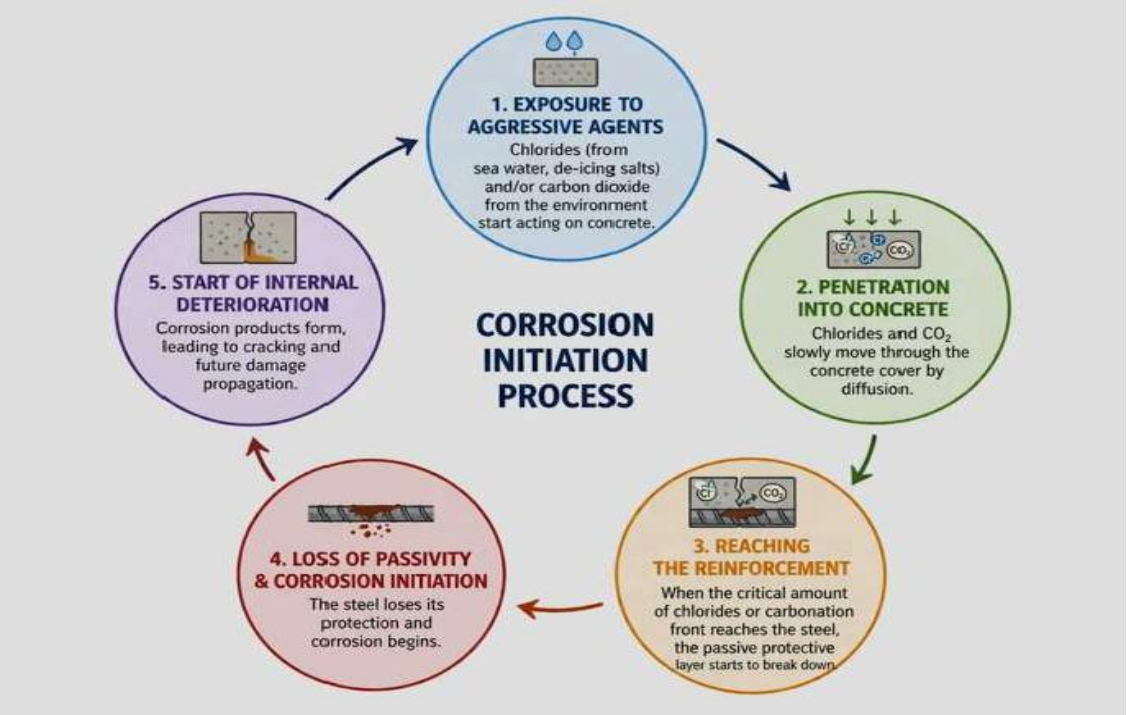


Figure I.13: Illustration of the corrosion initiation process [41].

I.7. Limitations of Conventional Repair Methods:

Although conventional repair techniques are widely used to address the deterioration of reinforced concrete structures, numerous studies have shown that these methods do not provide long-term protection for steel reinforcement, especially in aggressive environments. The major limitations of traditional repair methods can be summarized as follows:

- ✧ **Limited Ingress Resistance:**

Most conventional repair materials gradually allow the penetration of chlorides and carbon dioxide, which reactivates corrosion after a relatively short period. As a result, the repaire structure remains vulnerable to long-term degradation.

- ✧ **Lack of Direct Protection for Reinforcement:**

Traditional repairs typically involve removing damaged concrete and replacing it with new mortar. However, this approach does not address the steel–concrete interface, which is the most critical zone for corrosion initiation and propagation.

✧ **Inability to Stop the Electrochemical Corrosion Process:**

Corrosion is fundamentally an electrochemical reaction. Conventional repair methods do not alter or interrupt this mechanism, making their effect temporary rather than preventive.

✧ **Risk of Cracking and Debonding:**

Differences in physical and mechanical properties between old concrete and repair materials—such as shrinkage, elastic modulus, and thermal expansion—may lead to:

•Early cracking

•Loss of adhesion

•Premature failure of the repair system

✧ **Short Service Life and Frequent Maintenance:**

Because of the limitations above, conventional repair methods often suffer from reduced durability. This results in:

•Repeated repair cycles

•Increased maintenance costs

•Decline in structural performance

✧ **Poor Performance in Highly Aggressive Environments:**

In marine structures, wastewater treatment plants, and industrial zones, the corrosion rate is significantly higher. Under such conditions, traditional repair methods are not sufficient to ensure long-term durability.

These limitations demonstrate that conventional repair techniques often provide only temporary solutions and fail to prevent future corrosion. This clearly highlights the need for advanced protection strategies that address the root causes of deterioration rather than only treating visible damage—leading directly to the next section [34-35].

I.8. Need for Advanced Protection Strategies in Repair:

The limitations associated with conventional repair methods highlight the urgent need for advanced protection strategies that do more than simply restore the deteriorated concrete surface. Instead, these strategies aim to interrupt the corrosion process, enhance durability, and extend the service life of reinforced concrete structures exposed to aggressive environments.

Traditional repair systems often fail to prevent the reinitiation of corrosion, particularly when chloride ingress, carbonation, or moisture penetration continues after the repair. As a result, the

structural member is vulnerable to premature deterioration, leading to repeated interventions and increasing maintenance costs. Therefore, a shift toward more sophisticated and scientifically driven approaches becomes essential.

Advanced protection strategies focus on:

✧ **Targeting the Steel–Concrete Interface:**

Corrosion typically initiates at the reinforcement surface, making the steel–concrete interface the most critical region. Modern protection systems seek to:

•Restore passivity of steel

•Prevent chloride-induced depassivation

•Improve interfacial bonding

✧ **Enhancing Resistance to Aggressive Agents :**

Innovative materials and treatment techniques aim to reduce permeability and limit the ingress of harmful species such as:

•Chloride ions

•Carbon dioxide

•Sulfates

•Moisture

By minimizing exposure to these agents, the long-term stability of the repair is significantly improved.

✧ **Integrating Corrosion-Inhibiting Technologies:**

Recent advancements introduce efficient corrosion mitigation solutions, including:

•Organic and inorganic corrosion inhibitors, which chemically stabilize the steel surface

•Migrating corrosion inhibitors (MCI), capable of penetrating hardened concrete

•Protective coatings tailored for steel reinforcement

•Electrochemical treatments, such as impressed current systems, for high-risk environments

These technologies work by altering the electrochemical conditions surrounding the reinforcement, directly tackling the root cause of deterioration.

✧ **Improving Durability of Repair Materials:**

High-performance repair mortars and smart materials are designed to:

•Reduce shrinkage

•Improve compatibility with existing concrete

•Offer self-healing capabilities

•Provide enhanced adhesion to reinforcement

This results in better mechanical and long-term behavior compared to traditional mortars.

✧ **Reducing Maintenance Frequency and Life-Cycle Costs:**

By employing protection strategies that prevent rather than simply delay deterioration, infrastructure durability increases significantly. This reduces:

•Recurrent repair cycles

•Operational disruptions

•Long-term financial burdens

Given the known shortcomings of conventional repair approaches, modern engineering increasingly emphasizes protective, preventive, and durability-driven solutions. These advanced protection strategies are essential for ensuring sustained performance and structural reliability [34-35].

This naturally leads into the research focus on corrosion inhibitors and advanced materials, which will be further explored in the subsequent chapter.

I.9. Research Problem and Objectives:

Corrosion remains one of the main causes of deterioration in reinforced concrete structures, and conventional repair methods often fail to provide long term protection, as they do not adequately prevent chloride ingress or stop the electrochemical corrosion process. This creates a need for more effective solutions that can enhance durability and extend the service life of repaired elements. Therefore, the aim of this work is to evaluate the use of corrosion inhibitors as an advanced protection strategy in the repair of corrosion damaged structures, by examining their ability to reduce steel degradation and improve the overall performance of repaired concrete systems.

I.10. Conclusion:

Given the significance of the corrosion issue, numerous studies have been conducted on this flaw. In this chapter, we are interested in a bibliographic study on this phenomenon, as well as the conventional and contemporary protection strategies used. One of the techniques used in recent years is corrosion inhibitors, this method will be examined in more detail in the next chapter.

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Chapter II :

Corrosion Inhibitors in Concrete

II.1Introduction:

Corrosion of reinforcing steel within concrete is considered one of the most common issues affecting the durability of structures and their service life. To reduce or slow down this deterioration, several protection methods have been developed. Among them, corrosion inhibitors play a key role in enhancing the durability of reinforced concrete structures. In new constructions, inhibitors can be added directly to fresh concrete as a preventive measure to delay or prevent corrosion and in existing structures as a rehabilitation method, where they are applied to the concrete surface and penetrate through openings or surface channels to facilitate their penetration.

Corrosion inhibitors are chemical substances or extract of plants that function by inhibiting the corrosion process through the formation of a protective layer by increasing the polarity and lowering the corrosion potential. These substances may be organic or inorganic. Inhibitors, especially those added to concrete, can potentially affect its properties. Therefore, it is essential to understand their mechanism of action and the possible side effects in order to avoid unexpected damage. This chapter provides a general and historical overview of corrosion inhibitors used in concrete, presents a classification of different types of inhibitors, and discusses their mode of action in both preventive and rehabilitative applications. Finally, the chapter concludes with a summary of the key points discussed [1-2].

II.2 History:

The use of corrosion inhibitors dates back to antiquity (before 500 AD), when temporary and unsustainable solutions were employed to limit corrosion. These solutions consisted of primitive natural inhibitors such as oils, animal fats, and tar, which were used to protect tools, weapons, and metallic structures [3].

At the beginning of the nineteenth century (1820 -1850), the Industrial Revolution emerged, during which the use of iron and steel in various industrial facilities significantly increased. This led to major problems in maintaining the integrity of industrial installations and equipment. In fact, soluble salts, particularly chlorides are considered the main cause of corrosion in aqueous environments. From this point onward, serious attempts were made to establish a link between chemistry and corrosion.

In the late nineteenth(1880-1900) and early twentieth centuries(1900-1930), the development of electrochemistry enabled a better understanding of corrosion mechanisms. As a result, compounds such as phosphates, chromates, and nitrites began to be used as effective corrosion inhibitors, particularly in aqueous environments. However, environmental and health considerations were not taken into account at the time[3-4].

During the mid-twentieth century(1950-1970), the field of corrosion inhibitors expanded significantly expansion, especially with the development of the petroleum, chemical, and energy industries. Both organic and inorganic inhibitors were developed and classified into anodic, cathodic, and mixed inhibitors, which contributed to improved corrosion protection performance.

Toward the end of the twentieth century (1980-1990), issues related to the toxicity and environmental impact of certain traditional inhibitors, such as chromates and phosphates compounds, emerged. This led to the implementation of strict regulations limiting their use. Consequently, interest in developing safer alternative inhibitors, such as molybdate and rare-earth elements, increased [4-5].

At the beginning of the twenty-first century, scientific research shifted toward the development of environmentally friendly corrosion inhibitors (green inhibitors), derived from plants or other non-toxic biological materials, along with the use of modern techniques to better understand corrosion inhibition mechanisms. The current trend focuses on achieving a balance between efficiency, environmental safety, and cost reduction by protecting metals through the formation of a thin surface film that prevents corrosion.

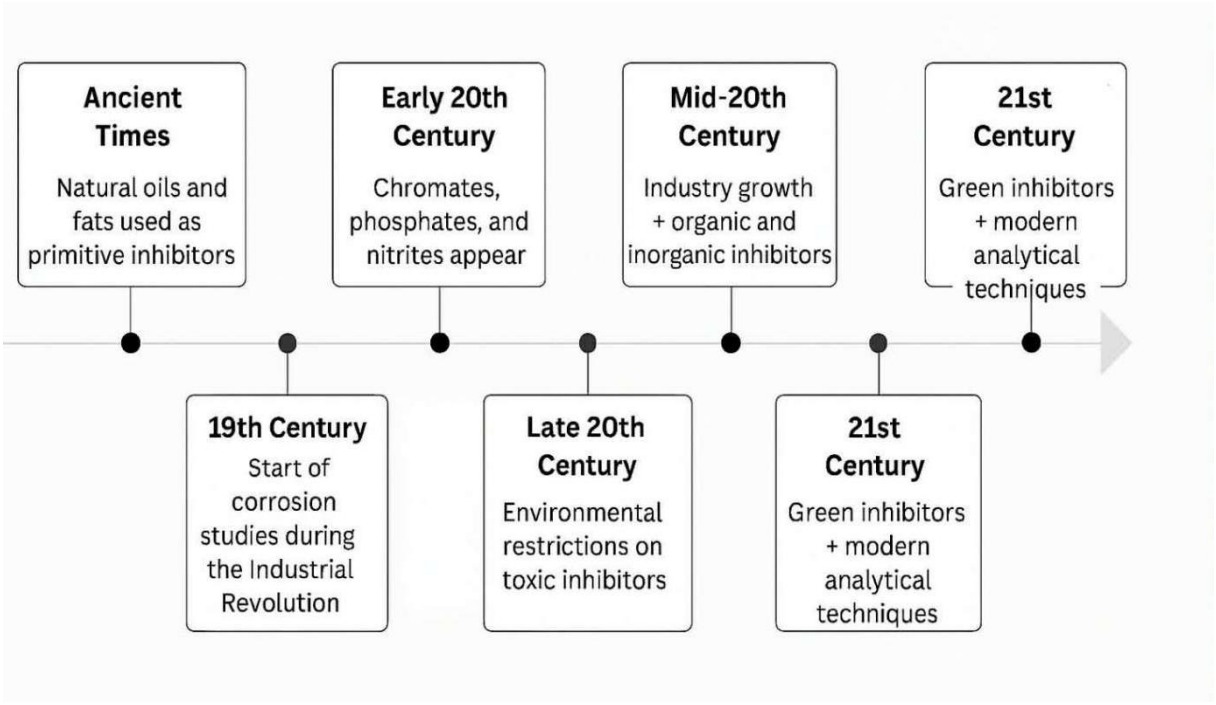

Figure II.1: Timeline of corrosion inhibitor development [6]

FigureII.1 illustrates the historical evolution of corrosion inhibitors, starting from ancient primitive substances such as oils and fats, then moving through the development of chromates,

phosphates, and nitrites in the early 20th century, and finally reaching modern green inhibitors, which that are environmentally friendly and widely used today.

II.3 Classes of Corrosion Inhibitors:

Corrosion inhibitors can be classified according to different criteria, such as their mechanism of action, chemical nature, and mode of protection [1].

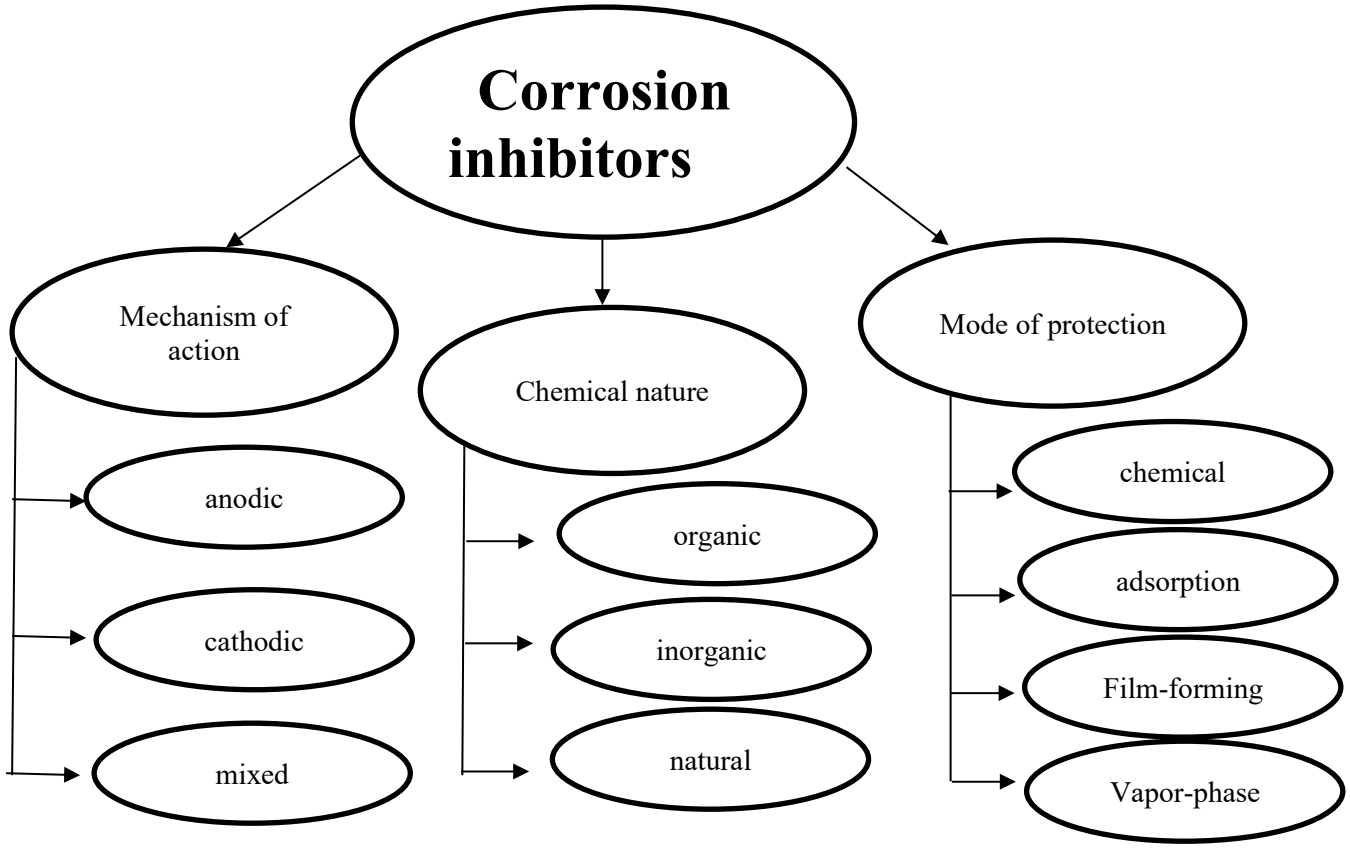

Figure II.2: Classification diagram of corrosion inhibitors [7].

Figure II.2 presents the classification of corrosion inhibitors according to their mechanism of action, chemical nature, and mode of protection.

Corrosion inhibitors can be classified according to their:

II.3.1 Mechanism of Action:

The mechanism of action describes how corrosion inhibitors affect the electrochemical reactions responsible for corrosion.

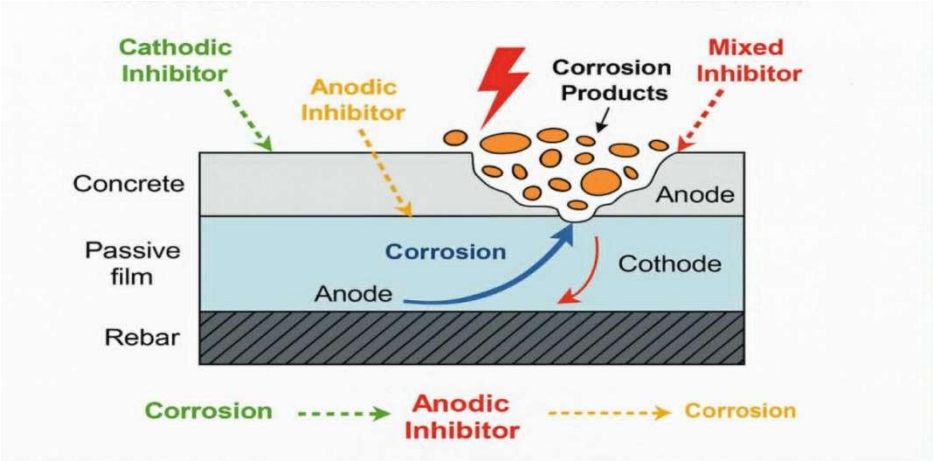

Figure II.3: Mechanism of action of inhibitors [9]

Figure II.3 illustrates the electrochemical principles that corrosion inhibitors rely on to suppress corrosion on the surface of reinforcing steel (rebar). The schematic diagram explains how these materials intervene in the 'corrosion cell,' which consists of an anode and a cathode.

According to their mode of action, inhibitors can be classified into the following types:

II.3.1.1 Anodic Inhibitors:

An anodic inhibitor, or passivating inhibitor, is so called because it increases anodic polarization. It acts by promoting the oxidation of ferrous ions to ferric ions, which then precipitate and form a dense passivating layer on the steel surface, thereby slowing down the corrosion reaction. Examples of anodic inhibitor include: chromates, phosphates, tungstates, and other compounds that form a protective layer preventing the continuation of corrosion. The effectiveness of anodic inhibitors depends on their high concentration, which is determined by the level of chlorides present in the environment. Although they are widely used, they may exhibit undesirable properties; if used in very low concentrations, they may stimulate corrosion instead of inhibiting it, causing localized attacks such as pitting [1-10].

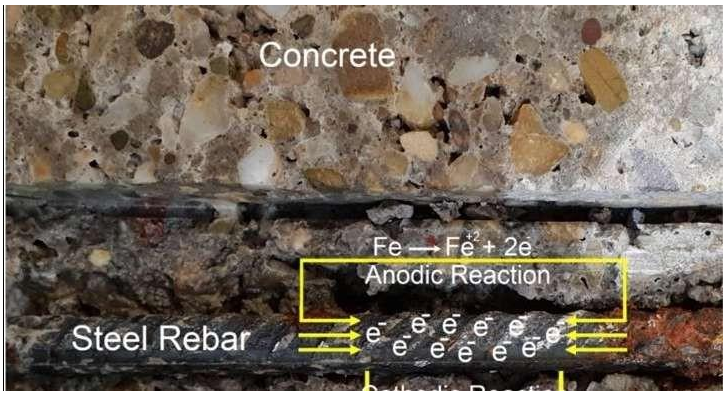

Figure II.4: Mechanism of an anodic inhibitor [11].

Figure II.4 illustrates the oxidation reaction occurring at the anodic site. At this stage, anodic inhibitors function by forming an ultra-thin protective passivation layer that prevents the migration of iron ions from the metal surface into the surrounding concrete, effectively halting the corrosion process.

II.3.1.2 Cathodic Inhibitors:

Cathodic inhibitors reduce corrosion by slowing down the cathodic reaction that occurs during the corrosion process. This is achieved by blocking the cathodic sites through the production of insoluble compounds that precipitate on the cathodic regions, forming a surface barrier that limits the diffusion of oxygen and the movement of electrons in that area. The decrease in the amount of oxygen available leads to a reduction in the corrosion and shift the corrosion potential to more negative values, indicating a lower risk of corrosion. Examples of cathodic inhibitors include: carbonates, phosphates, polyphosphates, and silicates. Sodium hydroxide and sodium carbonate are also widely used because they increase the pH around the steel, reduce oxygen transport, and form a protective film on the steel surface. Cathodic inhibitors typically require higher concentrations than anodic inhibitors because their ability to suppress corrosion is weaker. Cathodic inhibitors have three main mechanisms:

- Cathodic poisons
- Cathodic precipitates
- Oxygen scavengers[1-10]

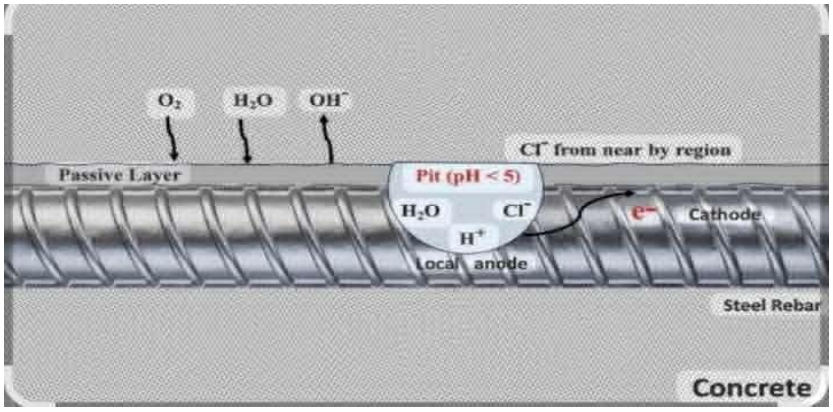

Figure II.5: Mechanism of a Cathodic inhibitor [12].

Figure II.5illustrates the electrochemical process of rebar corrosion within the concrete medium. The diagram shows how oxygen (O_2) and water (H_2O) penetrate the passive layer due to chloride ion (Cl^-) attack, leading to the formation of a 'Pit' that acts as a local anode where the pH level drops below 5.

These results in the flow of electrons (e^-) toward the cathode, causing severe localized pitting corrosion that threatens the structural integrity of the steel.

II.3.1.3 Mixed Inhibitors:

Mixed inhibitors slow down both the anodic and cathodic processes involved in the corrosion reaction. Their mechanism of action consists of adsorption onto the steel surface, where they form a protective layer that indirectly blocks anodic and cathodic reaction sites. Anodic inhibitors are generally considered dangerous, especially when their concentrations are too low, whereas cathodic inhibitors are usually safe.

Mixed inhibitors are less hazardous than pure anodic inhibitors. Among the most common inhibitors in this category are silicates and phosphates. These inhibitors are characterized by their ability to control both anodic and cathodic corrosion reactions simultaneously, making them a widely used option in corrosion protection. They can be applied either by adding them directly to fresh concrete or by using them as surface-applied inhibitors that penetrate into the concrete [1-10].

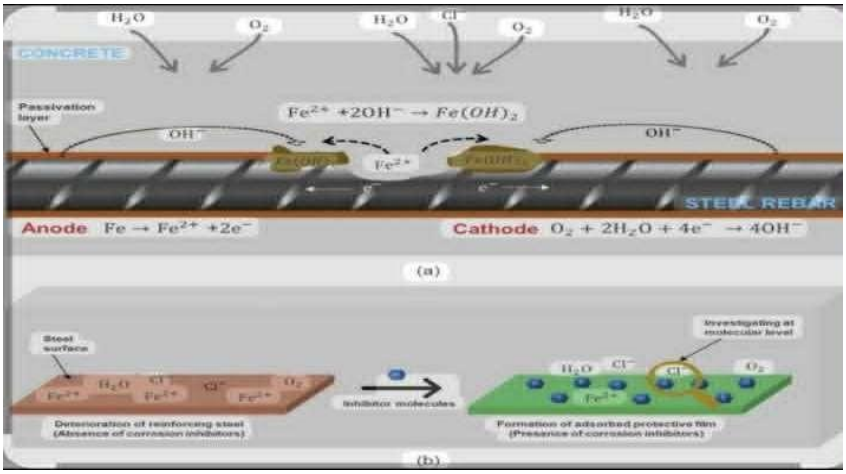

Figure II.6: Mechanism of a mixed inhibitor [13].

Figure II.6 illustrates two primary stages of corrosion study. Part (a) shows the electrochemical reactions leading to rust formation when chlorides and moisture penetrate the steel's protective layer. Meanwhile, part (b) compares metal surface deterioration in the absence of inhibitors with its protection upon their addition, where inhibitor molecules form an adsorbed layer that isolates the steel from oxygen and chlorides, effectively preventing corrosion.

II.3.2 Chemical Nature of corrosion inhibitors:

The chemical nature of corrosion inhibitors refers to the chemical composition of these substances and the types of compounds from which they are formed [2];

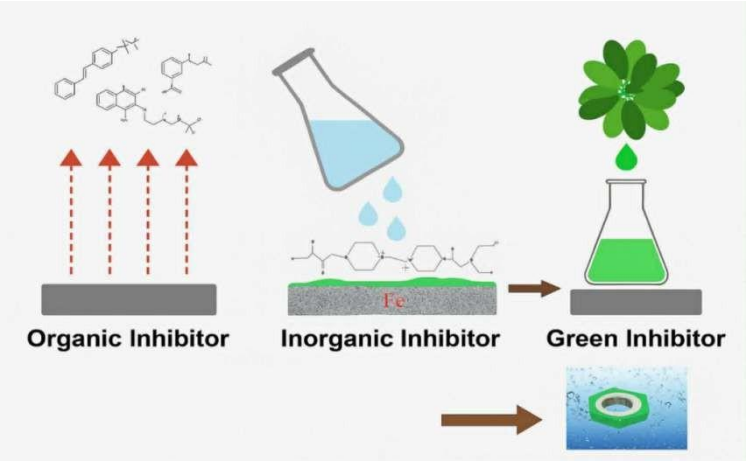

Figure II.7: Types of inhibitors [14].

Figure II.7compares three types of inhibitors:

- Organic inhibitors: forms a barrier film using chemical molecules.
- Inorganic inhibitors: reacts directly with the iron surface.
- Green inhibitors: represents a sustainable, eco-friendly natural alternative derived from plant extracts.

According to their chemical nature, corrosion inhibitors can be classified into the following types:

II.3.2.1 Inorganic Inhibitors:

Inorganic inhibitors are considered among the oldest and most widely used inhibitors for reducing metal corrosion, especially in acidic environments.

These inhibitors act by forming a thin layer on the metal, providing direct or indirect protection against corrosion. They are usually crystalline salts such as sodium chromate, phosphates, and molybdates. Nitrates are also among the most commonly used inorganic inhibitors. These inhibitors are often added to fresh concrete mixtures; however, despite their high effectiveness in reducing corrosion, some of them are classified as toxic and hazardous materials, such as chromates and nitrates.

This has led to restrictions on their use in several countries due to their health and environmental impacts. Because of these risks, many scientific studies are currently being conducted to develop alternative inhibitors that are safer and less toxic, the same corrosion resistance performance [1-15].

II.3.2.2 Organic Inhibitors:

Organic inhibitors are considered among the simplest, most widely used, and most effective means for controlling corrosion, particularly in reinforced concrete structures. In recent years, significant research efforts have been devoted to investigating the efficiency of these inhibitors and elucidating their mechanisms of action. The efficiency of organic inhibitors is mainly related to their ability to interact with the metal surface. These compounds can donate or accept electrons to or from the metallic surface, leading to the formation of covalent bonds. As a result, the inhibitor adsorbs onto the metal surface, forming a protective film that acts as a barrier between the steel and the aggressive environment, thereby reducing or preventing corrosion.

Organic inhibitors are generally composed of organic compounds containing heteroatoms such as nitrogen(N), oxygen (O), and sulfur (S), as well as multiple bonds within their molecular structure, which enhance their adsorption capacity on metal surfaces. The presence of these active sites facilitates strong interaction with the steel surface and improves inhibition performance. Among the various types of organic inhibitors, amines and alkanolamines are among the most commonly used due to their high inhibition efficiency and excellent ability to migrate through concrete. In addition, other organic compounds such as carboxylates and amino acids are also employed as corrosion inhibitors, contributing to the protection of reinforcing steel by forming an adsorbed organic layer on its surface [1-15].

II.3.2.3 Natural Inhibitors: Green Inhibitors

Natural or green inhibitors are considered low-cost and often effective, and they are environmentally friendly compared to synthetic inhibitors. Natural organic inhibitors consist of bio-molecules that bind to biological to metal surfaces or interfere with corrosion reactions, thereby reducing their activity.

Natural inhibitors are extracted from plants, animals, and microorganisms, and may contain compounds such as polypeptides, proteins, or glycoproteins. Among green inhibitors, red mud has been shown to reduce corrosion rates when incorporated into reinforced concrete, to reduce the corrosion rate of steel reinforcement. This reduction is attributed to the increase in alkalinity in the region surrounding the steel reinforcement, which promotes the re-formation of the protective passive layer on the steel. Additionally, the presence of iron oxides and aluminum oxide, along with high concentrations of aluminates, limits the diffusion of chloride ions [2].

II.3.3 Mode of Protection:

The mode of protection refers to the method by which corrosion inhibitors provide effective protection to the metal surface and prevent it from being exposed to corrosion.

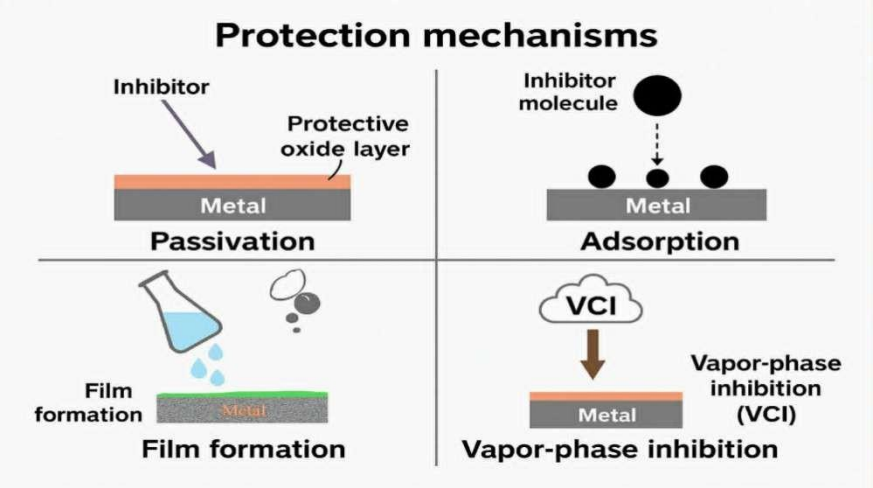

Figure II.8: Protection mechanisms of corrosion inhibitors [16].

Figure II.8 compares four fundamental protection mechanisms:

- Passivation: Stimulating the formation of a protective oxide layer.
- Adsorption: Inhibitor molecules attracting directly to the metal surface.
- Film formation: Creating a thick protective barrier to isolate the metal.
- Vapor-phase inhibition (VCI): Utilizing volatile substances for protection via the gas phase.

According to their mode of protection they offer, corrosion inhibitors can be classified into the following types:

II.3.3.1 Chemical Passivators:

Chemical passivators are substances that possess a relatively high electrochemical equilibrium potential, along with a low over potential, which leads to a reduction in the corrosion rate once the passive state is reached. Chemical passivators are widely used in various industrial systems, particularly those containing antifreeze. Chromates are also extensively employed in recirculing water systems due to their high effectiveness in corrosion control. In addition, zinc molybdate is used as a corrosion inhibiting pigment in protective coatings [1].

II.3.3.2 Adsorption Inhibitors:

Adsorption inhibitors are among the most widely used types of corrosion inhibitors. They are generally organic compounds that adsorb onto the metal surface, forming a protective layer that covers the entire surface, thereby contributing to a reduction in the corrosion rate in both

anodic and cathodic regions. In general, these inhibitors affect both anodic and cathodic reactions simultaneously; however, the extent of this effect may be changed. Adsorption inhibitors are widely used in the acid pickling of hot-rolled products, which is why they are also referred to as pickling inhibitors. The effectiveness of adsorption inhibitors depends on the presence of free electron pairs within their chemical structure, such as nitrogen atoms in amines and quinolines, sulfur atoms in these compounds, and oxygen atoms found in aldehydes [1].

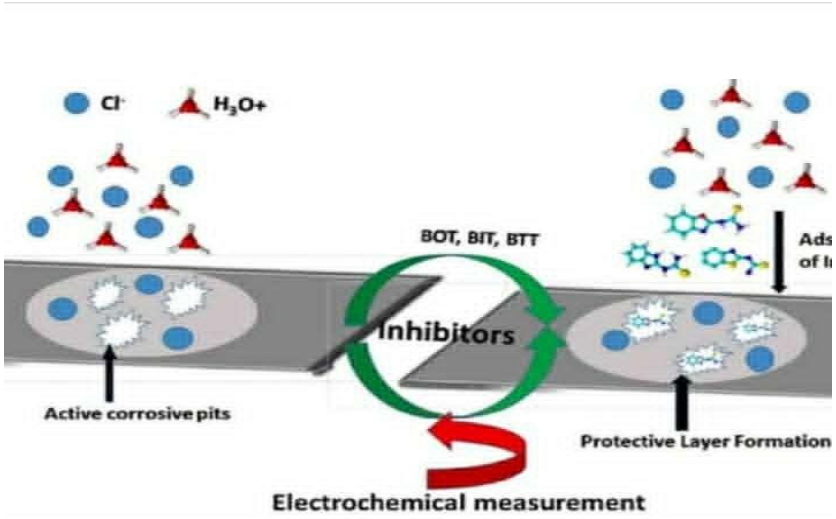

Figure II.9: Comparison between active pitting corrosion and protection via molecular adsorption by inhibitors [17].

Figure II.9 compares two states of the metal surface in a corrosive medium:

- In the Left: It illustrates the formation of 'active corrosive pits' due to chloride ion attack in the absence of protection.
- In the Right: It shows 'protective layer formation' resulting from the adsorption of inhibitor molecules (e.g., BOT, BIT) onto the surface, enhancing the metal's resistance to electrochemical corrosion and preventing deterioration**.**

II.3.3.3 Film- Forming Inhibitors:

Film -forming inhibitors differ from adsorption inhibitors in their mechanism of action, as their protective effect does not rely on the adsorption of inhibitor molecules themselves onto the metal surface. Instead, they function by forming a protective or barrier film composed of a material other than the actual inhibiting species. These films prevent the corrosive medium from reaching the metal surface, thereby reducing the rate of corrosion reactions. Such inhibitors are often designed to protect one of the electrodes, namely the cathode or anode. Zinc and calcium

salts are among the most common examples of cathodic film-forming inhibitors, whereas benzoate compounds are well-known examples of anodic inhibitors.

These inhibitors are widely used to reduce corrosion, particularly in marine applications and during marine voyages [1-15].

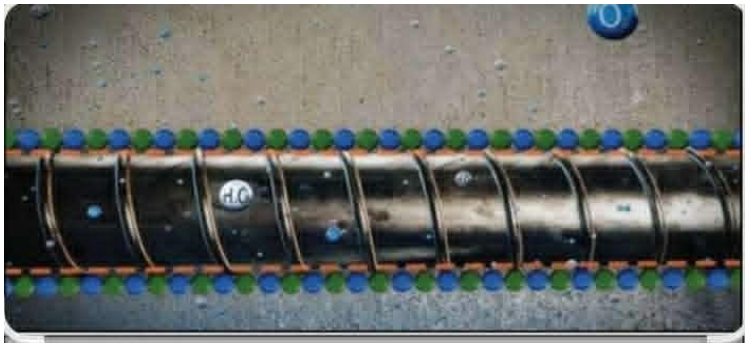

Figure II.10: Protective layer formation mechanism [18].

Figure II.10 illustrates the ability of Migrating Corrosion Inhibitors (MCI) to penetrate through concrete pores to reach the reinforcing steel. The image shows inhibitor molecules absorbing on to the metal surface to form a continuous molecular protective layer, preventing corrosive agents like oxygen and moisture from contacting the steel, thus halting electrochemical corrosion.

II.3.3.4 Vapor- Phase Inhibitors:

Vapor- phase inhibitors, also known as volatile inhibitors, are substances with a low but noticeable vapor pressure that are used in enclosed environments to reduce corrosion. The vapor comes into contact with the metal surface, where adsorption occurs, and subsequently moisture hydrolyzing the inhibitor, leading to the release of protective ions. Examples of these inhibitors include benzoates, carbonates, and nitrites. In the case of volatile nitrites, the inhibitor supplies the metal surface with a certain amount of NO_2^- ions, which contribute to the passivation of the surface. Despite the effectiveness of these inhibitors, they must be handled with caution [8].

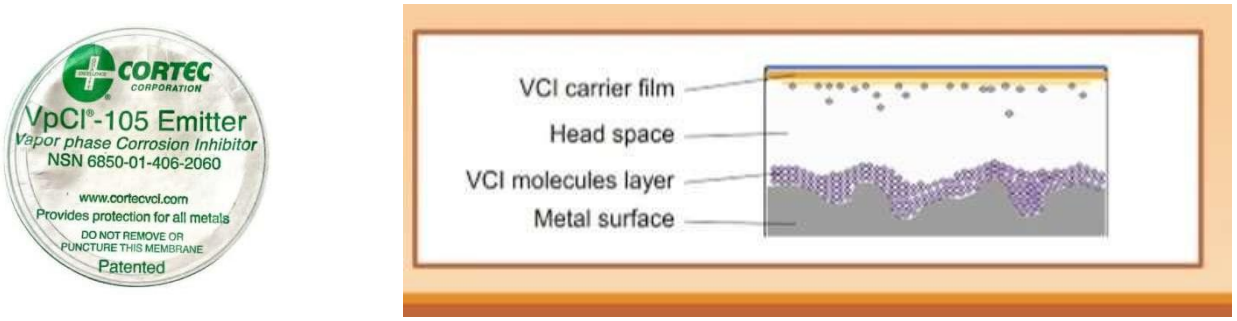

Figure II.11: Mechanism of Volatile Corrosion Inhibitors (VCI) for metal surface protection [19].

Figure II.11illustrates the mechanism of Volatile Corrosion Inhibitors (VCI), where molecules are released from the carrier film and travel through the head space to settle on the metal surface. These molecules form a protective 'adsorbed layer' that acts as a molecular barrier, isolating the metal surface from moisture and oxygen and preventing chemical reactions that cause rust.

II.4. Corrosion Inhibitors in Preventive Mode:

Corrosion inhibitors in preventive mode are used to delay corrosion initiation in new reinforced concrete structures. They are generally introduced during the construction stage, either by adding them to the concrete mixture or by applying them to surface before exposure to aggressive environmental conditions. Their main objective is to enhance the durability of reinforced concrete by protecting the steel reinforcement at an early stage. The following sections present the principle, types, mechanisms, advantages, and limitations of these inhibitors.

II.4.1 Principle of Preventive Protection:

The principle of preventive protection is based on creating a favorable chemical environment around the steel reinforcement before corrosion begins. This is achieved by:

- Forming a stable passive film on the steel surface.
- Increasing the alkalinity of the surrounding concrete matrix.
- Reducing the penetration and harmful effects of aggressive ions, especially chlorides by maintaining the steel in a passive state, the initiation corrosion is effectively delayed.
- Limiting the interaction of steel with water and oxygen. Calcium nitrite is among the most widely used inhibitors due to its strong oxidizing capability, enhancing the passivation layer on steel.

II.4.2 Types of Preventive Corrosion Inhibitors:

The main types of preventive corrosion inhibitors used in concrete include:

- Anodic inhibitors (e.g., calcium nitrite): They promote the formation of a robust passive film.
- Cathodic inhibitors: they reduce the cathodic reaction rate.
- Mixed inhibitors: they act simultaneously on both anodic and cathodic reactions.
- Organic inhibitors: they adsorb on the steel surface and improve passivation.
- Inorganic inhibitors: Such as phosphates and fluorophosphates, enhancing chemical stability.

II.4.3 Advantages of Preventive corrosion inhibitors:

Preventive corrosion inhibitors offer several advantages:

- They extend the service life of reinforced concrete structures.
- They provide early-stage protection before damage occurs.
- They are compatible with standard concrete production processes.
- They reduce long-term maintenance and repair costs.
- They improve durability in aggressive environments (marine exposure, de-icing salts…).

II.4.4 Limitations and Challenges:

Despite their benefits, preventive inhibitors also present some limitations:

- High cost of some chemical products (e.g., nitrite-based).
- Efficiency depends on proper dosage and homogeneous distribution in concrete.
- Some inhibitors may reduce workability or affect setting time. •Potential environmental and health concerns in certain chemical compounds.

II.4.5 Factors Affecting Efficiency:

The effectiveness of preventive inhibitors is influenced by:

- Dosage: Insufficient amounts decrease protection, while excessive amounts may harm concrete properties.
- Concrete permeability: Highly porous concrete reduces inhibitor performance.
- Environmental exposure: Chloride concentration, humidity, and temperature.
- Concrete cover thickness: Thicker cover improves inhibitor efficiency.
- Distribution uniformity inside the concrete matrix.

II.5 Corrosion Inhibitors in Repair mode:

With the increasing focus on the maintenance of concrete structures today , the use of corrosion inhibitor additives has gradually grown. These materials can reduce the corrosion rate of metal surfaces or delay their deterioration.

These inhibitors affect the corrosion process in two ways: either by delaying the onset of depassivation of the reinforcing steel or by reducing the corrosion rate after depassivation has occurred.

Inhibitors are added as a preventive measure to fresh concrete mixes in new structures. As for existing and older structures, they are added to repair mortar or repair mortars, or applied directly to the concrete surface. They can also be introduced through holes or channels made on the surface to accelerate their penetration through the concrete cover. Corrosion inhibitors are

typically used in combination with other repair techniques, such as removing damaged concrete, applying protective coatings, or cathodic protection.

The goal of integrating inhibitors with various repair techniques is to slow active corrosion, improve repair performance, and extend the service life of reinforced concrete structures.

Figure II.12: Simulation of Corrosion Inhibitor injection in concrete bridge beams [20].

Figure II.12 illustrates an example of a practical application of structural repair, showing the injection of a corrosion inhibitor (e.g., CORO-GUARD) into pre-drilled holes in damaged concrete. This process aims to deliver the chemical agent to the deteriorating rebar to halt electrochemical corrosion and protect the structure from failure without requiring complete removal of the concrete.

II.6. Conclusion:

Through this chapter, corrosion inhibitors are highlighted as one of the most important techniques for reducing corrosion of reinforcing steel in concrete structures. The chapter presents the definition of these inhibitors, the evolution of their use over time, as well as their classification according to their mechanisms of action and their impact on the corrosion process. The role of corrosion inhibitors in the preventive mode is also explained when they are added to fresh concrete in new structures, as well as their role in the rehabilitative mode when they are used in existing structures, either through repair concrete or by surface application.

This chapter demonstrated that inhibitors contribute to delaying the depassivation of steel or to reducing the corrosion rate after corrosion initiation, thereby improving the durability of reinforced concrete.

Additionally, integrating corrosion inhibitors with other repair techniques, such as removing damaged concrete, applying protective coatings, or cathodic protection, enhances the effectiveness of restoration processes. This contributes to extending the service life and reducing maintenance costs, making an efficient choice within sustainable maintenance strategies for concrete structures.

So that, corrosion inhibitors are a promising technology within modern maintenance strategies, given their effective role in reducing repair costs and increasing the service life of structures.
In the next chapter, repair method using corrosion inhibitors will be explained in detail.

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Chapter III:

Corrosion Inhibitors in the Repair of Structures Subjected to Corrosion

III.1. Introduction:

In recent years, reinforcement corrosion has become a global issue and one of the main causes of damage, deterioration, and, in some cases, the collapse of reinforced concrete structures. This phenomenon is strongly influenced by severe environmental and climatic conditions. When these conditions are combined with poor concrete quality and insufficient concrete cover, the corrosion process accelerates and becomes difficult to control, resulting in high maintenance and repair costs. To address this problem, various repair techniques have been developed to extend the service life of deteriorated structures and improve their durability. Among these solutions, corrosion inhibitors are considered both a preventive and corrective solutions for structures exposed to corrosion. They are chemical substances added in small quantities to concrete that work by forming a protective layer on the metal surface to reduce or limit the interaction between the reinforcing steel and its surrounding environment. The main objective of using inhibitors in repair works is to enhance structural durability of the structure and reduce the corrosion rate.

This chapter presents the application of corrosion inhibitors in repairing mode: including the state of the art, the stages of repairing corrosion-damaged structures, and the necessary recommendations.

III.2. Application of Corrosion Inhibitors in Repairing Processes:

In this chapter, different repair strategies adopted to control corrosion in reinforced concrete structures are discussed, with special focus placed on the use of corrosion inhibitors as an effective solution for repairing damaged structures and extending their service life. To facilitate the understanding of these repair approaches, a comparative overview of the various techniques reported in the literature and applied over different periods is presented in the following table:

Table 1: State of the art on the use of corrosion inhibitors in repair processes

Articles	Reference	Title of the Article	Inhibitor Used	Type of Repair Technique	Repair Procedure	Results
1	[Weyers, &. Blacksburg, 1995]	Corrosion inhibiting repair and rehabilitation treatment process for reinforced concrete structures	Corrosion inhibitors applied by injection or spraying during the repair process	Injection and spraying	1) Removal of deteriorated concrete surrounding the reinforcing steel 2) Cleaning and exposure of the corroded reinforcement 3) Multiple spray or injection application of corrosion inhibitor to the concrete and reinforcing steel 4) Optional application of insoluble or low□solubility inhibitor coatings 5) Backfilling or overlaying using repair concrete	The patented repair process significantly reduces reinforcement corrosion by delivering inhibitors directly to the reinforcing steel
2	[Batis & al,2003]	Effects of migrating inhibitors on corrosion of reinforcing steel covered with repair mortar	- Migrating corrosion inhibitors (alkanolamine□based, vapor corrosion inhibitor type) - Incorporated into polymer□modified, fiber□reinforced repair mortar	Incorporation into Repair Mortar	1). Preparation of reinforced mortar specimens with and without corrosion inhibitors. 2). Application of fiber□reinforced repair mortar containing migrating corrosion inhibitors. 3). Exposure to a corrosive environment (3.5% NaCl solution). 4). Acceleration of corrosion using an impressed anodic potential. 5). Monitoring using the strain gauge technique and galvanic current measurements.	- Significant reduction in reinforcement corrosion when migrating inhibitors are used. - Fiber reinforcement delays cracking caused by corrosion products. - Reduced corrosion rate and mass loss of steel reinforcement. - Reduced galvanic corrosion between repaired and unrepaired areas. - Improved durability of repaired reinforced concrete structures.

3	[Vaysburd& Emmons, 2004]	Corrosion inhibitors and other protective systems in concrete repair: concepts or misconceptions	Chemical corrosion inhibitors and other protective systems applied during concrete repair operations	Surface -Applied Protective Systems	1) Assessment of corrosion damage in existing reinforced concrete structures 2) Identification of corrosion mechanisms in the repaired zones 3) Application of corrosion inhibitors or protective systems during the repair process 4) Execution of concrete repair and rehabilitation works 5) Evaluation of durability and long□term performance	The study highlights that corrosion inhibitors may reduce corrosion activity in repaired concrete; however, their effectiveness strongly depends on their compatibilitywith repair materials and environmental conditions. Misuse or misunderstanding of corrosion inhibitorconcepts can lead to premature deterioration. A comprehensive corrosion□protection strategy is required to ensure durable repairs.
4	[Fedrizzi,2005]	The use of migrating corrosion inhibitors for the repair of chloride-contaminated concrete motorways structures	- Migrating corrosion inhibitor (alkanolamine□based MCI) - Applied at the concrete–repair mortar interface	Interface Application Technique	1). Casting chloride□contaminated concrete specimens containing (1% Cl^-). 2). Application of different repair mortars (standard mortar, repair mortar A, and low□porosity repair mortar B). 3). Application of a migrating corrosion inhibitor at the interface before overlay placement. 4). Exposure to a 3.5% NaCl solution using the ponding method. 5). Monitoring by corrosion potential, electrochemical impedance spectroscopy (EIS),	- Low porosity repair mortars significantly reduce chloride ingress. - MCI alone delays corrosion but is insufficient when used with porous mortars. - The best performance is achieved by combining MCI with dense, low□permeability repair mortar. - Repassivation of steel reinforcement ispossible in highly resistant repair

					porosity (MIP), and chloride penetration.	systems.
5	[Sawada &al., 2005]	Electrochemical injection of organic corrosion inhibitors into concrete	Organic corrosion inhibitors (ethanolamine and guanidine)	Electrochemical injection	Electrochemical injection, application of an electric field, and migration of inhibitors toward the steel reinforcement	Improved migration of inhibitors in carbonated concrete, and a significant reduction in the corrosion rate
6	[Larsen, 2021]	The Role of corrosion inhibitors and their applications in Concrete Repair	- Amine carboxylate. Amine□ester organic emulsion. - Calcium nitrite. - Organic alkenyldicarboxylic acid salt. - Surface-applied corrosion inhibitors.	Surface Application and Admixture techniques	1). Removal of damaged concrete and deteriorated sections. 2). Replacement or cleaning of reinforcement steel. 3). Application of a corrosion inhibitor (surface-applied or admixture type). 4). Application of a waterproofing membrane or sealer. 5). Ensuring proper curing conditions and reapplication if necessary.	- Reduction in corrosion and concrete spalling. - Increased durability of reinforcing steel. - Improved protection against chlorides and carbonation. - Extended service life of concrete structures.
7	[Kobbakaduwa& Sarno, 2024]	Effect of organic corrosion inhibitors on the behaviour of repair mortars and reinforcement corrosion	Organic corrosion inhibitors (OCs), including amino alcohol□based and gluconate□based inhibitors, used as admixtures or surface□applied inhibitors	Admixture in Repair mortar /Surface Applied	1) Preparation of different types repair mortars 2) Incorporation of organic corrosion inhibitors at various dosages 3) Application of repair mortars to reinforced concrete specimens 4) Evaluation of the properties of fresh and hardened mortar 5) Assessment of reinforcement corrosion behaviour and durability	Organic corrosion inhibitors significantly improved the corrosion resistance of the reinforcement;corrosion activity decreased with increasing inhibitor dosage. Amino alcohol□based inhibitors showed superior performance compared to gluconate□based inhibitors. However, the effects on mortar properties such as shrinkage, water absorption, and

						workability varied depending on inhibitor type and dosage.
8	[Qian& Qin, 2024]	Study on the crack repair effect of microbial self□healing concrete and the corrosion inhibition of steel reinforcement	Microbial self healing agent inducing biomineralization(micr obial mineralization for corrosion inhibition)	Microbial Self - Healing	1) Preparation of microbial self healing concrete specimens 2) Induction of cracks in concrete samples 3) Activation of microbial mineralization inside cracks 4) Evaluation of crack repair efficiency 5) Assessment of steel reinforcement corrosion resistance using electrochemical and mechanical tests	The microbial repair agent achieved excellent crack healing, with a crack repair rate up to 97.1%; ultrasonic wave velocity significantly increased, and the corrosion current density of the steel reinforcementdecreased by about 53%, indicating effective corrosion inhibition and improved durability of reinforced concrete
9	[Zhao ,2025]	Composite stabilization□assisted repair behaviour for rust layer damage of weathering steel in simulated marine atmospheric environments.	Composite stabilizer containing: - $Cu_2 (PO_4)_2$ - $CuSO_4$ - $Cr_2(SO_4)_2$ - $NiSO_2$	Composite Rust Stabilization/ Dip coating	1). Artificial corrosion of weathering steel in simulated marine atmosphere. 2). Creation of rust layer damage (cross-shaped damage). 3). Application of the stabilizer by dip coating (assisted repair). 4). Continued corrosion exposure to compare self repairvs assisted repair. 5). Electrochemical, microstructural and phase analyses using XRD, SEM, and EIS techniques	Accelerates repair during the early stages of corrosion. - Reduces corrosion tendency at later stage. - Promotes the Transformation of unstable rust phases (γFeOOH, βFeOOH) into stable αFeOOH. - Forms a dense and compact inner rust layer. - Improves corrosion resistance and inhibits chloride diffusion.

10	[Zhao ,2025]	A review of repair measures for reinforced concrete affected by chloride ion corrosion	- Corrosion inhibitors (alkali amines, TETA, HMDA, APS, and quaternary ammonium salts) - Direct repair methods (epoxy resin, flexible sealants, and repair mortars) - Electrochemical methods: ECE, BIEM, and EDT - Advanced materials: FRC, TRC, UHPC, AAMs	Integrated Direct and Electrochemical Repair	1). Diagnosis of the chloride□induced corrosion stage (latent, development, or acceleration stage). 2). Selection of an appropriate repair strategy: direct repair or electrochemical repair. 3). Crack repair using epoxy resins, flexible sealants, or dry packing techniques. 4). Structural repair using additional reinforcement or patch repair 5). Electrochemical repair methods (ECE, BIEM, EDT) for chloride extraction and steel passivation.	- Effective chloride removal and re□passivation of steel reinforcement. - Improved durability and extended service life of reinforced concrete structures. - Fiber□reinforced materials and UHPC exhibit superior corrosion resistance. - BIEM allows simultaneous chloride extraction and corrosion inhibitor introduction. - The combination of direct and electrochemical repair methods provides the best performancefor severe damage.
11	[Su & al,2025]	Investigating reinforcement corrosion of cement mortar and concrete containing fly ash and corrosion inhibitor through experimental and numerical tests	- Sodium nitrite (SN) corrosion inhibitor - Class F fly ash (FA) used as a supplementary cementitious material	Admixture of SN and Fly ash in mortar and concrete	1). Preparation of mortar and concrete specimens containing OPC, FA, and SN. 2). Evaluation of transport properties, including water absorption, RCPT, and chloride migration. 3). Acceleration of corrosion using the impressed current method. 4). Electrochemical measurements (Ecorr and Rp). 5). Mechanical tests including compressive, tensile, and rebar pull□out tests.	- Fly ash reduces chloride penetration and the corrosion rate through pore refinement. - Sodium nitrite delays steel depassivation andcorrosion initiation. - The combined use of FA and SN shows a synergistic corrosion protection effect. - Corrosion leads to crack development and reduction of bond

					6). Numerical DEM simulation of corrosion□induced cracking.	strength. - DEM simulation successfully captures the mechanisms of corrosion□induced cracking.
12	[Yao & Wen ,2025]	A review of influencing factors and evaluation systems for electromigration corrosion inhibitors in the electrochemicalrepair of concrete	Electromigration corrosion inhibitors (amine-based inhibitors, TETA, 2-aminopyridine, and ethanolamine)	Electromigration / Electrochemical injection (EICI / BIEM)	Electrochemical injection (EICI), bidirectional electromigration (BIEM), optimization of current parameters, and inhibitor migration and accumulation on steel surface	High corrosion inhibition efficiency, improved durability of reinforced concrete, and reduced corrosion rate; however,the effectivenessinfluenced by current density, exposure time, concrete properties, and inhibitor type
13	[Zeng& Zhu, 2025]	Biomineralized coating for inhibiting reinforcement corrosion in cracked concrete: A study under simulated aggressiveenvironments	Biomineralized (organic–inorganic) corrosion□inhibiting coating produced through microbially induced carbonate precipitation (MICP)	Biomineralized Coating (MICP Technique)	1) Preparation of cracked concrete specimens 2) Formation of a biomineralize-d coating on steel reinforcement using the MICP techniques 3) Exposure to simulated aggressive environmentsincluding carbonation and chloride attack 4) Electrochemical testing including OCP, polarization, and corrosion current density measurements 5) Monitoring of corrosion inhibition efficiency over time	The coating effectively protected the passive film in carbonation environments;the corrosion inhibition efficiency exceeded 95% during the early exposure period; and the corrosion current density remained below 0.1 μA/cm². Under chloride attack, corrosion was initially controlled, but the inhibition efficiency decreased from approximately 90% to 70% after prolonged exposure

14	[Kobbakaduwa&Sarno, 2025]	Experimental study on corroded reinforced concrete columns repaired with textile□reinforced mortar (TRM) and organic corrosion inhibitors	Organic corrosion inhibitors (OCIs) combined with textile□reinforced mortar (TRM)	TRM Jackets combined with corrosion inhibitors	1) Induction of corrosion in reinforced concrete columns 2) Surface preparation and removal of damaged concrete 3) Application of organic corrosion inhibitors to the reinforcement 4) Strengthening using TRM jackets reinforced with carbon or E-glass textiles. 5) Curing and testing under aggressive chloride conditions	The repair system significantly improved corrosion resistance and structural performance; TRM combined with organic inhibitors reduced corrosion activity, enhanced strength and ductility, and demonstratedsuperior durability under aggressive conditions.
15	[Fan&Duan, 2025]	Investigation of a bio□gel for concrete crack repair and corrosion inhibition of steel reinforcement	Bio□based inhibitor: sodium alginate bio□gel incorporating Sporsarcinapasteurii bacteria	Bio-gel injection / self- Healing	1) Preparation of calcium alginate gel 2) Incorporation of bacteria to produce the bio□gel 3) Injection of bio□gel into concrete cracks approximately~1mm wide 4) Cross□linking of the bio-gel using calcium ions 5) Curing under simulated marine conditions	Cracks fully sealed within ~15 minutes; chloride ion adsorption reached 118.3 mg/g and corrosion current density reduced by up to 88.7% in reinforced concrete; demonstrating effective crack repair and long□term corrosion protection

III.3. The Stages of Repairing a Structure Damaged by Corrosion:

When reinforced concrete is affected by the reinforcement corrosion, repair interventions are required to ensure the durability and safety of the structure. The repair process for deteriorated structures begins with the diagnosis stage, which represents a crucial step in determining the extent of deterioration.

During this stage, a visual inspection is conducted to identify signs of deterioration such as cracking, corrosion, and concrete spalling. In addition, the condition of both the concrete and the reinforcing steel is evaluated.

The main objective of this stage is to accurately determine the degree and causes of deterioration in order to select the most appropriate repair technique.

III.3.1 Classification of Deterioration:

The selection of an appropriate repair technique for deteriorated concrete mainly depends on the degree of deterioration. According to the studies presented in the previous table, deterioration can be classified into three main categories (see Fig III.1):

1. **Low Deterioration:**

- ✧ **Description:**

•Hairline cracks (< 0.3 mm)
•Slight rust stains on the surface
•No spalling or delamination
•Steel reinforcement remains mostly passive

- ✧ **Type of Inhibitors:**

•Sodium nitrite, Calcium Nitrite inhibitors [11].
•Organic inhibitors including Amine-carboxylate or Amine-ester organic emulsions [6].
•Admixture-type inhibitors like organic alkenyldicarboxylic acid salts [2], [6], [7], [11].

- ✧ **Application Method:**

1. Incorporation of Inhibitors into Repair Mortar:

When there are surface defects requiring repair, ordinary mortar is not sufficient, rather, a chemically developed mortar is used:

a) **Preparation mechanism:** Corrosion inhibitors, such as sodium nitrite or organic inhibitors are mixed directly with the cement repair mortar during the mixing process.
b) **Technical Application:** The damaged area is cleaned, and a repair mortar containing corrosion inhibitors is applied .These inhibitors significantly reduced the corrosion rate and

the loss of of steel mass. Studies have also shown that the use of migrating inhibitors within the repair mortar reduces galvanic corrosion, which often occurs between repaired areas and adjacent older concrete zones.

2. Supporting Additives: In some cases ,it is preferable to use fiber-reinforced mortar containing inhibitors, because the fibers help delay the formation of cracks caused by future corrosion products.

3. Surface Application and Impregnation:

This method is commonly used in cases of minor deterioration because it is non-destructive:

a) Principle of Operation: Migrating corrosion inhibitors, often based on amine-esters, are used. These materials are applied to the concrete surface and are characterized by their ability to penetrate the pores of the concrete and reach the reinforcing steel.

b) Application Procedure:

- ✓ **Surface Preparation:** Thoroughly clean the concrete surface to remove dirt, oils, and other contaminants in order to ensure proper penetration.
- ✓ **Spraying or Painting:** Apply the retarder in multiple spray applications to ensure the concrete is fully saturated, reaching the reinforcing steel.
- ✓ **Sealing:** After the retarder has dried, inject the hairline cracks with epoxy materials or apply surface sealants to prevent future moisture and chloride ingress.
- ✓ **Protective layer:** The application of a protective topcoat, such as anti-carbonation coatings or a waterproofing layer, is recommended to enhance the durability of the repair.

Application Method

Low Deterioration

Step1

Powder Component Addition

1: Adding dry components into the mortar before blending

Step2

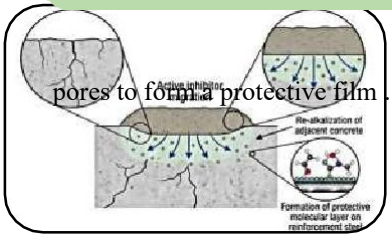
Preparation and Application

Pressing the integrated inhibitor mortar into the repaired area.

Step3

Chemical Distribution Schematic

Illustration of inhibitors migrating through concrete



pores to form a protective film .

Moderate Deterioration

Step1

Product and Dilution

preparation, showing concentration and dilution process.

Step2

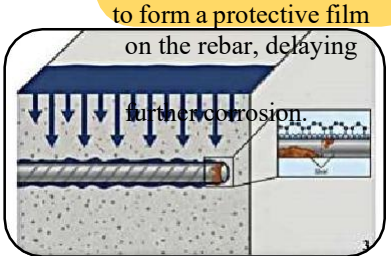
Surface Application

Low-pressure spray application to the concrete surface,

Step3

Penetration and Protection

to form a protective film on the rebar, delaying further corrosion.



Severe Deterioration

Step1

Admixture Preparation

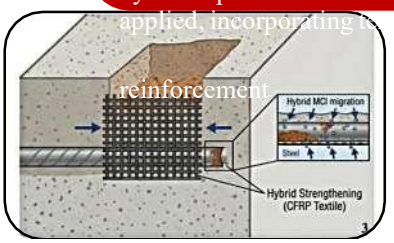
of the structural grade repair mortar with a potent with concentrated liquid and specific powder inhibitors

Deep Injection and Structural Re-alkalization

Deep pressure injection of the inhibitor directly into the crack network and around the exp
thinner bars.

Textile-Reinforced Mortar with Hybrid Support

hybrid repair mortar is applied, incorporating
reinforcement



4. Direct Injection Technique:

Figure III.1: Schematic Illustration of Deterioration Levels and Repair Strategies [17].

In cases where cracks require direct access of the inhibitor to the steel reinforcement, liquid inhibitors are injected directly into the cracks or through pre-drilled holes in the concrete cover. This method ensures direct delivery of the inhibitor to the damaged steel surface, resulting in repassivation and an immediate reduction in corrosion activity [2], [6], [7], [11].

2. Moderate Deterioration:

- ✧ **Description:**

•Visible cracks (0.3-1 mm)

•Small areas of spalling

•Partial exposure of the reinforcement

•Active corrosion of steel reinforcement

- ✧ **Type of Inhibitors:**

•Migrating corrosion inhibitors (MCI) such as alkanolamine-based VCIs [2], [4].

•Organic inhibitors including amino alcohol-based or gluconate-based inhibitors [7].

•Mixed inhibitors like ethanolamine or guanidine for targeted electromigration [3], [4], [5], [12], [13].

- ✧ **Application Method:**

1. Partial Repair by Patching:

a) ***Concrete Removal*****:** Damaged and delaminated concrete is removed until sound concrete is reached.

b) ***Steel Cleaning*****:** Exposed reinforcing steel should be cleaned using mechanical abrasion, sandpaper or a wire brush to remove rust.

c) ***Inhibitor Application*****:** Corrosion inhibitors or protective coatings are applied directly to the reinforcing steel.

2. Using injection techniques or electromagnetic methods:

a) ***Electrochemical injection:*** Organic inhibitors, such as ethanolamine, are introduced into the concrete using an electric field, which forces the inhibitor to migrate toward the reinforcing steel, even in carbonated areas.

b) ***Conventional injection*****:** Cracks are injected with epoxy materials mixed containing corrosion inhibitors in order to prevent the penetration of moisture and chlorides.

3. Use of MCIs in Repair Mortar:

Applying a repair mortar containing migrating corrosion inhibitors (MCIs) in specific dosages, in order to allow these substances to migrate from the repaired area into the adjacent “older” areas to prevent the formation of new corrosion cells [3-4-5], [12-13].

Technical Control of Dosage and Service Life Extension:

The successful repair of structures with low level of deterioration depends largely on the chemical efficiency of the inhibitors used. The effectiveness of admixture-type inhibitors is highly sensitive to dosage precision; therefore, it is essential to strictly adhere to the manufacturer's specifications. Incorrect dosages may adversely affect the fresh and hardened properties of the mortar, such as workability, water absorption, and shrinkage.

By ensuring precise application and the correct concentration of inhibitors, the reinforcement can effectively remain in its passive state. This technical precision is the keyfactor in extending the service life of the structure and preventing the progression toward more advanced stages of deterioration, thereby reducing long-term maintenance costs.

3. Severe Deterioration:

✧ **Description:**

•Wide cracks (> 1 mm)
•Extensive spalling and delamination
•Fully exposed and heavily corroded reinforcement
•Loss of cross-section and structural capacity

✧ **Type of Inhibitors:**

•Surface-applied inhibitors (such as complementary protection) like alkali amines or TETA (Triethylenetetramine) [10].
•Corrosion protection systems such as quaternary ammonium salts [10], [14].
•Innovative bio-based inhibitors including sodium alginate bio-gel or biomineralized coatings produced by MICP (Microbially induced carbonate precipitation) [13].

✧ **Application Methods**

1. Full Structural Restoration: All contaminated and delaminated concrete is removed to expose the entire circumference of the corroded reinforcement. Severely damaged reinforcing bars are replaced or supplemented with new reinforcement.

2. Inhibitors in Structural Grade Materials: High-performance repair materials, such as micro-concrete or fiber-reinforced Concrete, are used. These materials are admixed with effective corrosion inhibitors, such as sodium nitrite or advanced organic blends, in order to provide a high-alkalinity, chemically protected environment for both the new and the existing reinforcement.

3. Hybrid Strengthening Systems: Corrosion inhibitors are combined with structural strengthening techniques like Textile-Reinforced Mortar (TRM) or FRP wrapping. The inhibitors are applied to the substrate or integrated into the TRM matrix to ensure that internal corrosion does not compromise the new structural reinforcement.

4. Advanced Bio-Mineralization: Recent techniques involve injecting bio-gels containing bacteria into cracks; these gels induce mineralization that seals the crack, with efficiency reaching up to 97%,while providing a biological barrier that reduces the corrosion current density [1], [10], [14].

✧ **Mechanical Bonding:**

To ensure the structural integrity of the repair, achieving a high-quality mechanical bond between the existing substrate and the new repair material is essential. This can achieved through rigorous surface preparation methods, such as sandblasting or the application of specialized bonding agents. Furthermore, the use of mechanical anchors or dowels is recommended in severe cases to enhance adhesion and ensure that the corrosion inhibitors integrated into the repair mortar effectively protect the steel-concrete interface.

These categories are summarized and illustrated in the following figure, which highlights the relationship between the degree of deterioration, its description, and the suitable repair techniques:

III.4. Necessary Recommendations:

In order to ensure the effectiveness and durability of repair interventions in reinforced concrete structures affected by corrosion, it is essential to follow a set of key recommendations.
These recommendations provide a systematic approach that integrates proper diagnosis, the selection of suitable repair methods, the correct application of corrosion inhibitors, and continuous monitoring. By considering both structural and material aspects, these guidelines help optimize repair performance and extend the service life of the structure.

1. Understanding the Condition:

Before applying any repair method, it is important to understand the corrosion mechanism and identify the level of corrosion (low, moderate or severe). The extent of the damage must also be assessed in order to select the appropriate repair strategy [16].

2. Considering Key Parameters:

Several important parameters should be considered, including the type of loading (flexion, shear or compression), the bond between the existing structure and the repair material, and the severity

of corrosion damage [16].

3. Selection of Repair Method:

The selection of the repair method depends on the level of damage. Simple repair techniques are suitable for low damage, while FRP or ECC systems are recommended for moderate damage. In cases of severe corrosion, hybrid strengthening systems are recommended [16].

4. Performance Improvement:

To improve the performance of repaired structures, strengthening techniques such as FRP, ECC and FRCM can be used. In some cases, combining different techniques may provide better results [16].

5. Proper Application

The proper application of corrosion inhibitors is essential. This includes selecting appropriate materials, using correct application methods, and respecting the required parameters and conditions to ensure their effectiveness [16].

6. Accelerated Corrosion (for Experimental Studies)

In experimental studies, the accelerated corrosion process (ACP) can be used to simulate corrosion within a shorter time. Key parameters such as current density, exposure time and NaCl concentration must be carefully controlled [16].

7. Bond between Materials:

It is important to ensure adequate bonding between the existing structure and the repair materials. The use of anchors, dowels, or proper surface preparation can improve adhesion and enhance the overall performance of the repaired structure [16].

8. Continuous Monitoring and Maintenance:

Post-repair durability does not depend solely on the initial application; it also requires a systematic approach to continuous monitoring and maintenance. The implementation evaluation techniques and electrochemical sensors allows the real-time assessment of the inhibitor’s performance. This ongoing monitoring is crucial for the early detection of any recurrence of corrosion activity early, thereby directly contributing to the extension of the structure's service life and optimizing long-term maintenance costs [16].

III.5 Conclusion:

Corrosion of reinforcing steel remains one of the main causes of deterioration in reinforced concrete structures, especially when these structures are exposed to aggressive environmental conditions such as chlorides, humidity, and carbonation. Therefore, selecting an appropriate repair technique according to the degree of deterioration is essential to ensure the durability and safety of the structure.

The studies presented have shown that corrosion inhibitors play an important role in repair applications by reducing corrosion activity, protecting reinforcing steel, and improving the performance of repair materials. Depending on the level of deterioration, inhibitors can be applied through several techniques such as surface application, incorporation into repair mortars, electrochemical injection, or advanced bio-based repair systems.

The analysis of the different repair methods also highlighted that the effectiveness of repair interventions depends not only on the inhibitor itself, but also on proper diagnosis, adequate surface preparation, suitable repair materials, and continuous post-repair monitoring. In case of severe deterioration, combining corrosion inhibitors with strengthening systems provides better mechanical performance and longer service life.

Overall, the use of corrosion inhibitors in repair works represents an effective and durable solution for limiting the progression of corrosion, preserving reinforced concrete structures, and reducing future maintenance and rehabilitation costs.

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General conclusion

General Conclusion

This study was undertaken to contribute to addressing the issues associated with this phenomenon and to better understand its underlying mechanisms by analyzing it that directly affects the engineering field. The research focused on the corrosion of reinforcing steel within reinforced concrete structures, which represents one of the most significant challenges faced by civil engineers due to its direct impact on the durability and structural integrity of constructions over the long term.

Reinforced concrete is a fundamental component of the construction sector; however, its performance and efficiency depend largely on the condition of the embedded reinforcing steel. The exposure of this steel to corrosion, caused by various environmental and chemical factors, can lead to serious risks and potential structural failures, making it essential to mitigate and prevent its effects.

From this perspective, the objective of this work was to identify effective and sustainable solutions to reduce the corrosion of reinforcing steel. Corrosion inhibitors were investigated, which function by slowing down or limiting this phenomenon through the reduction of the electrochemical reactions responsible for it. The study examined the role of these inhibitors both as a preventive measure in new concrete and as a solution for the repair of existing and deteriorated structures. The results demonstrated the effectiveness of these materials in improving concrete durability and extending its service life compared to traditional methods, which have shown limitations over time.

On a practical level, the integration of corrosion inhibitors into maintenance and repair strategies enables engineers and professionals to make more efficient technical decisions, especially in harsh environments characterized by high humidity and the presence of salts. This is particularly relevant to many regions in Algeria, which are characterized by diverse climatic and environmental conditions. The methodology was based on a comprehensive and rigorous literature review of 15 scientific articles published between 1995 and 2025, providing a well-rounded technical insight into the dual protection of both reinforcing steel and concrete. The analyses confirmed the effectiveness of corrosion inhibitors, especially migrating corrosion inhibitors (MCI), in ensuring structural durability. Various application methods were explored, including direct injection, surface spraying, incorporation into ultra-high-performance concrete (UHPC) mortars for repair ,and advanced electromagnetic techniques (BIEM), which enable both chloride extraction and simultaneous inhibitor injection.

In light of these findings, several recommendations were proposed, most notably the need to integrate corrosion inhibitors at all stages-design, construction, and repair-due to their significant role in enhancing the sustainability of reinforced concrete structures. This study also opens promising future perspectives centered on adopting preventive maintenance strategies, along with the use of early diagnostic techniques for concrete structures and non-destructive testing (NDT) methods such as acoustic emission and electrochemical potential measurements to assess structural conditions before deterioration occurs. This approach can significantly reduce costly repair work.

Furthermore, this study advocates for the development of innovative and environmentally friendly solutions, such as self-healing crack repair technologies using bio-gels and natural corrosion inhibitors, in order to ensure the safety and sustainability of Algerian infrastructure