Arch. Metall. Mater. **70** (2025), 2, 1039-1054

DOI: https://doi.org/10.24425/amm.2025.153510

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# CORROSION BEHAVIOR OF FLY ASH-BASED GEOPOLYMER CONCRETE

This review paper investigates the corrosion characteristics of geopolymer concrete, which is considered a sustainable and environmentally friendly substitute for conventional concrete made with Portland cement. This study aims to consolidate the current understanding of corrosion mechanisms, the various factors contributing to corrosion, strategies for preventing corrosion, and the latest developments in this field. Geopolymer concrete has garnered considerable attention owing to its capacity to mitigate environmental impact and enhance the durability of concrete structures. A comprehensive understanding of a material's vulnerability to corrosion is paramount to guaranteeing its sustained effectiveness over extended periods in diverse environmental conditions. Insights into the mechanisms of corrosion initiation and progression in geopolymer concrete have been derived from critical findings from experimental and theoretical studies. This paper examines the mechanisms of electrochemical corrosion, the characteristics of pore structure, permeability, and chemical composition, and the various factors that influence corrosion, such as environmental exposure and microstructural characteristics. This paper examines various methods for assessing corrosion, including electrochemical techniques, non-destructive testing, and microstructural analysis.

Additionally, preventive measures such as material selection, coatings, sealants, cathodic protection, and inhibitors are discussed. Geopolymer concrete's performance and challenges are exemplified through real-world case studies. The review provides a comprehensive summary of significant findings, implications, and areas for further research. It is a valuable resource for researchers and practitioners interested in utilizing the potential of geopolymer concrete while ensuring its corrosion resistance.

*Keywords:* Geopolymer concrete; corrosion behavior; mechanisms; influencing factors

## 1. Introduction

Geopolymer concrete, an environmentally sustainable alternative to traditional cement-based concrete, utilizes industrial byproducts like Fly Ash (FA) and slag to create a binder matrix [1-4]. Unlike traditional concrete, geopolymer concrete significantly reduces carbon emissions and energy consumption during manufacturing, making it a more environmentally responsible choice for building structures [2,3,5,6]. Its lower environmental impact stems from the reduced natural resource extraction and processing need.

While geopolymer concrete presents numerous advantages, its viability as a building material hinges on its ability to resist corrosion [7,8]. Corrosion of embedded reinforcement steel poses a significant challenge that can compromise the structural integrity and durability of geopolymer concrete structures [9-11]. With effective corrosion mitigation strategies, geopolymer concrete may withstand harsh environments and fulfill its potential as a sustainable building material [12,13]. Understanding the corrosion mechanisms and implementing preventative measures are crucial for ensuring geopolymer concrete's long-term durability and performance.

The initial protective alkaline environment provided by geopolymerization offers inherent resistance to corrosion. However, pore structure, chemical composition, curing conditions, and environmental exposure can weaken this protection over time. Thus, an in-depth examination of the corrosion mechanisms is necessary to address potential deterioration [12-15]. Overall, unraveling these complexities is fundamental in fighting against geopolymer concrete corrosion.

The corrosion susceptibility of geopolymer concrete is governed by various influencing factors that dictate its response

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to aggressive environments. The mineralogical composition of source materials, the type and concentration of activators, curing methods, and exposure conditions all impact the material's corrosion behavior. Researchers and practitioners can tailor geopolymer concrete formulations to optimize corrosion resistance and longevity by systematically dissecting and understanding these factors.

Half-cell potential measurements, electrical resistivity tests, and microscopic analysis are some of the most common evaluation techniques for assessing corrosion in geopolymer concrete. Half-cell potential measurements involve measuring the electrical potential between a reference electrode and the reinforcement steel to determine the likelihood of corrosion. Electrical resistivity tests assess the ability of concrete to resist the flow of electrical current, indicating its corrosion resistance. Microscopic analysis, such as scanning electron microscopy, can provide detailed insights into corrosion products and mechanisms at the microscopic level [7,16-19]. These evaluation techniques help to understand corrosion initiation, progression, and severity and guide maintenance and repair strategies for geopolymer concrete structures.

Preventive measures are essential to achieve environmentally responsible building practices and resilient infrastructure [20]. The use of geopolymer concrete offers a blank slate for the development of novel approaches, such as the incorporation of reinforcement that is resistant to corrosion and the creation of surface coatings that are tailored to specific needs [8,21,22]. These measures extend the service life of geopolymer concrete structures, aligning with the overarching goal of utilizing sustainable construction practices. This is accomplished by directly addressing the challenges posed by corrosion.

This article demonstrates that an in-depth understanding of corrosion mechanisms, influencing factors, assessment methods, and preventative measures in geopolymer concrete has significant implications for environmentally responsible construction practices. If corrosion challenges are confronted head-on and preventative measures are implemented, geopolymer concrete structures can have longer service lives. This will reduce the frequency of maintenance and replacement. This is consistent with the overarching objective of sustainable construction, which is to minimize resource consumption and reduce construction's environmental impact. The continuation of geopolymer concrete corrosion research and development will refine and optimize the performance of this cutting-edge material, paving the way for its widespread adoption and contributing to the resilience and durability of the built environment.

## 2. Geopolymer Concrete: Composition and Properties

### 2.1. Geopolymerization Process

In recent years, several researchers have examined the geopolymerization process, which involves a complicated procedure [23]. Currently, there are numerous theories, and the evolution of their article-generating processes is accelerating. Glukhovsky was among the first to write in the 1950s about alkaline activation mechanisms. Duxson et al. [24] proposed a polymerization process that involves several steps proposed in the conceptual model. There are three stages: destruction-coagulation, coagulation-condensation, and condensation-crystallization. A general mechanism of geopolymerization is shown in Fig. 1.

Initially, the dissolution of the amorphous components occurs, leading to the release of silicate and aluminate monomers, specifically $[Si(OH)_4]^-$ and $[Al(OH)_4]^-$. This reaction, depicted

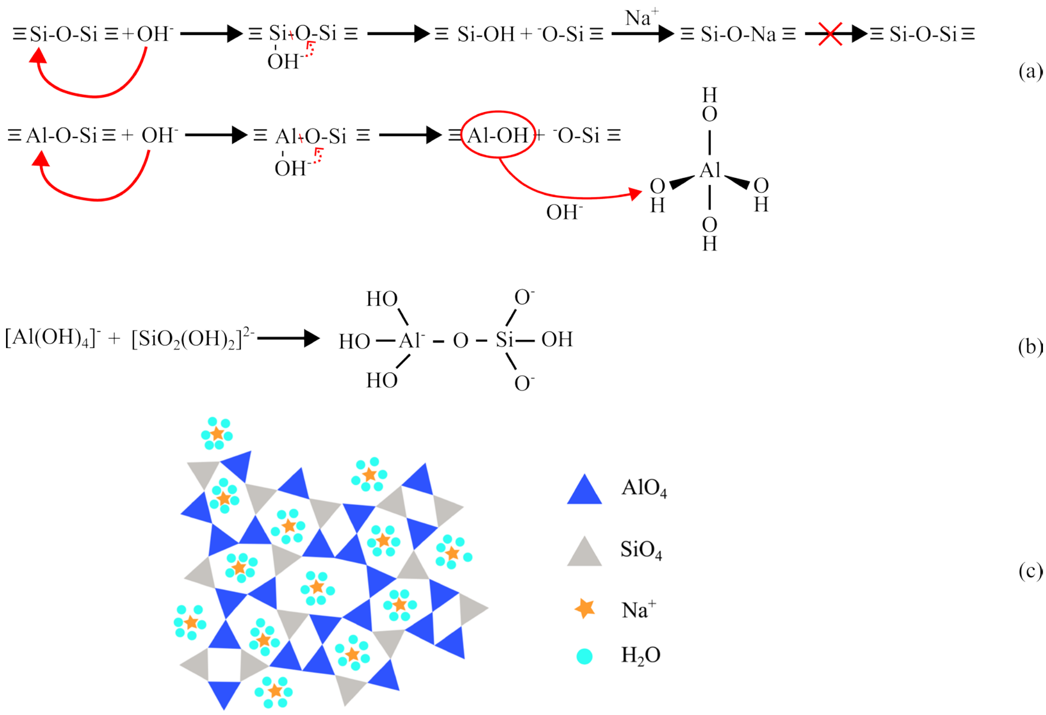

Fig. 1. Geopolymerization process (a) destruction-coagulation, (b) coagulation-condensation, (c) condensation-crystallization

in Fig. 1(a), is triggered when the $OH^-$ ions from the alkaline activator break the Si-O-Si bonds and reposition themselves around the silicon atoms, resulting in the formation of silanol (-Si-OH) and sialate (-Si-O). The alkaline cations in the solution, such as $Na^+$ or $K^+$, neutralize the negative charge, leading to the formation of $Si\text{-}O\text{-}Na^+$ or $Si\text{-}O\text{-}K^+$ bonds, which prevent the return to the siloxane (Si-O-Si) structure [25]. When $OH^-$ ions target the Si-O-Al bonds, the dissolved aluminum species form complex bonds, primarily releasing $Al(OH)_4^=$ anions. In the second stage, the condensation process occurs, where the reactive silicate and aluminate monomers bond by sharing oxygen atoms to create a more crosslinked system. During this stage, water is removed from the structure through the hydrolysis process, as illustrated in Fig. 1(b) [26,27].

In the final stage, known as condensation crystallization, the presence of unreacted particles in the initial solid phase promotes the precipitation of the polymerization reaction product. These alkali-activated products form an amorphous matrix with cementing properties, referred to as N-A-S-H (hydrated sodium aluminum silicate), which has a crystalline structure similar to zeolite [26]. Ultimately, the material hardens and develops mechanical properties. Fig. 1(c) displays the final structure of the 3D network formed in the composition of the geopolymers. The final composition of geopolymers is influenced by several factors, including the chemical composition of precursors and activators, mineralogy, and cure, among others [26].

Geopolymers are synthesized from aluminosilicate sources, rich in amorphous $SiO_2$ and $Al_2O_3$, and a highly alkaline solution . These substances are inorganic polymers with a composition akin to zeolites but are fundamentally amorphous polymers [15,28]. The term “geo” in the name is associated with its resemblance to geological materials, and “polymer” is linked to the chemistry of silico-aluminates [29].

As per Davidovits [30], geopolymer materials have a broad spectrum of applications in various industries, such as construction, aerospace, and plastics. The usage of geopolymer material is contingent on the chemical structure in terms of the atomic ratio of Si: Al in the polysilane. The application classification of geopolymer material based on the Si: Al ratio is depicted in TABLE 1. A low Si: Al ratio of 1, 2, and 3 signifies a rigid polymer network, whereas a Si: Al ratio greater than 15 exhibits a polymeric nature of the geopolymer material.

TABLE 1

Application of geopolymer material based on Si:Al ratio

| Si:Al Ratio | Applications |
|---|---|
| 1 | Bricks |
| | Ceramic |
| | Fire Protection |
| 2 | Cement and concrete |
| | Toxic waste management |
| 3 | Fire protection fibre glass composite |
| | Heat resistant composite (200°C-1000°C) |
| >3 | Sealants for industry (200°C-600°C) |
| 20-35 | Fire resistant and heat resistant fibre composites. |

The raw material is a crucial factor in the geopolymer formulation process. Various materials are employed for geopolymerization, which may lead to different properties of geopolymers [4,31]. An essential prerequisite for geopolymerization is that the material must be abundant in silica and aluminum contents. Additional materials can be used as fillers to improve the properties of angeopolymer as per the requirements [32-34]. Therefore, the composition of each material must be regulated based on the concrete application.

### 2.2. Mechanical and Durability Properties

Geopolymer concrete exhibits superior mechanical properties to Ordinary Portland Cement (OPC), with improved compressive strength attributed to the development of chemically stable aluminosilicate gels [35]. The robust interlocking structure enhances load-bearing capacity, making geopolymer concrete suitable for high-strength applications. Geopolymer concrete is recognized for its exceptional durability, demonstrating resilience against chemical assaults like acids and sulfates [36]. Calcium-aluminium-silicate-hydrate (C-A-S-H) and sodium-aluminosilicate-hydrate (N-A-S-H) gels reduce permeability, restricting the penetration of harmful substances and enhancing resistance to sulfate exposure [33,37-39]. The material’s low water absorption and reduced penetration of chloride ions further contribute to its durability.

The current research on mechanical and durability are summarized in TABLE 2 [3,40,41]. Studies by researchers such as Shaikh [3] and Ghafoor et al. [40] have provided valuable insights into the influencing factors of geopolymer concrete. Shaikh [3] investigated the impact of Natural Coarse Aggregates (NCA) and Recycled Coarse Aggregates (RCA) and revealed a significant 9% enhancement in compressive strength with NCA over 28 days. However, introducing RCA led to a gradual decline of 15% when the content reached 50%. The study emphasized the need for customized geopolymer concrete models to accommodate RCA, highlighting a positive correlation between the geopolymer binder and RCA and suggesting a promising bond between the two materials. These insights contribute to a comprehensive understanding of the mechanical properties of geopolymer concrete and the influencing factors in research.

In contrast, Ghafoor et al. [40] thoroughly examined the effects of various variables on the properties of geopolymer concrete. Various parameters, such as the molarity of NaOH, the ratio of $Na_2SiO_3$ to NaOH, and the ratio of Alkaline Activator to Fly Ash (AA/FA), were investigated. The compressive and flexural strength were found to be significantly increased with higher molarity of NaOH, reaching its maximum at a concentration of 14 M. This improvement can be attributed to the enhanced dissolution of silicon and aluminum. Initially, the excessive ratios of AA/FA contributed to increased flexural strength. However, when the ratios became overly high, it resulted in a decrease in strength. The importance of water in the process of geopolymerization was highlighted. It is worth mentioning that geopolymer

TABLE 2

Summary of the previous finding on mechanical and durability properties

| Researcher | Aspect of Study | Key Findings |
|---|---|---|
| Shaikh [3] | Compressive Strength | Compressive strength increased by 9% from 7 to 28 days for 100% NCA, decreased with increasing RCA content; |
| | | Optimum compressive strength at 16 M NaOH. |
| | Indirect Tensile Strength | Tensile strength decreased with higher RCA content: |
| | | Longer curing improved tensile strength by 11-21%. |
| | Elastic Modulus | Elastic modulus decreased with increasing RCA content. |
| | Empirical Models | Existing models showed discrepancies for geopolymer concrete with RCA. |
| Ghafoor et al. [40] | Effect of NaOH Molarity | Compressive strength increased up to 14 M NaOH, reduced at 16 M due to hydroxide ion congestion. |
| | Effect of $Na_2SiO_3$/NaOH Ratio | Compressive strength decreased with higher Na2SiO3/NaOH ratio. |
| | Effect of AA/FA Ratio | Complex effect on compressive strength based on NaOH molarity. |
| | Modulus of Elasticity | M.O.E. increased with molarity up to 14 M, decreased at 16 M NaOH. |
| | Effect of NaOH Molarity | Flexural strength increased with higher NaOH molarity. |
| | Effect of $Na_2SiO_3$/NaOH Ratio | Flexural strength decreased with higher Na2SiO3/NaOH ratio. |
| | Effect of AA/FA Ratio | Complex effect on flexural strength based on NaOH molarity. |
| | Comparison with OPC Concrete | Flexural strength of GPC significantly higher than OPC for similar compressive strength. |
| Prusty et al. [41] | GGBS Replacement Level | Compressive strength affected by GGBS content, higher GGBS improved early and 28 days strength. |
| | NaOH Solution Molarity | Higher molarity improved compressive strength through increased geopolymerization rate. |
| | Binder Content | Binder content influenced compressive strength. |
| | SS/SH Ratio | Varied effects on compressive strength, possibly due to different factors. |
| | ANOVA Analysis | GGBS replacement level had significant impact on compressive strength. |

concrete exhibited higher flexural strength than OPC concrete, even though their compressive strengths were similar.

The study conducted by Prusty et al. [41] provided significant insights into the various factors that influence the compressive strength of Geopolymer Concrete (GPC). The replacement level of Ground Granulated Blast Furnace Slag (GGBS) has been identified as a crucial factor influencing the mechanical performance of GPC in its early and later stages. A positive correlation was observed between the amount of GGBS used and the level of compressive strength achieved. This can be attributed to the calcium content in GGBS, which promotes the geopolymerization process and the formation of calcium-silicate-hydrate (C-S-H) gel. Achieving an optimal balance between FA and GGBS resulted in significant increases in strength during the period from the 7th to the 28th day. In a specific molarity, NaOH has enhanced geopolymerization. This is achieved by assisting in the dissolution of the components involved, ultimately increasing the strength of the resulting material. The amount of binder and the Silica/Sodium Silicate (SS/SH) ratio influenced the compressive strength. However, it is essential to note that the effects of these factors may vary depending on the specific context. The importance of the replacement level of GGBS in influencing the strength properties of GPC was emphasized, indicating significant progress in the development of sustainable construction materials.

In summary, the extensive research conducted by Shaikh [3], Ghafoor et al. [40], and Prusty et al. [41] have highlighted the impact of factors on the mechanical properties of geopolymer concrete. Shaikh found that NCA positively influences compressive strength, while Ghafoor et al. highlighted the importance of NaOH molarity and AA/FA ratios. However, it also emphasized the potential decrease in performance as the content of RCA increases. Prusty et al. found a positive relationship between GGBS and compressive strength, highlighting the potential of sustainable building materials. However, it is essential to keep improving models and considering context variables to progress in geopolymer concrete. Research has also shown how important it is to address permeability to make geopolymer concrete last longer and be less affected by the environment.

Durability in concrete is crucial for its resistance to disintegration and decay, with permeability playing a significant role in influencing these properties. Geopolymer concrete, or Geocrete, enhances durability through practices like achieving complete compaction of admixtures and ensuring sufficient curing. Permeability measures how water and corrosive substances can infiltrate concrete, affecting its resistance to potential deterioration [28,42]. Geopolymer concrete's reduced permeability limits the penetration of acids, enhancing its ability to withstand acid attacks [43,44]. Various factors impact permeability in geopolymer concrete. The appropriate polycondensation process, spherical morphology, and particle size of the alumino-silicate precursor in fly ash (FA) contribute to reduced permeability, resulting in a 6% increase in strength [45]. Conversely, using metakaolin (MK) increases permeability, leading to a 34% decrease in strength due to increased moisture penetration [46].

Studies by Wongpa et al. [47] show that increased liquid content decreases compressive strength and enhances water permeability. Water-repellent materials, like silane-siloxane, can increase chloride diffusion, but they may be ineffective in preventing water entry. Achieving low permeability in concrete involves appropriate cement amount, low water-cement ratio, and thorough compaction. Specific practices, including slag replacement, increased MK content, limestone and silica fume ash incorporation, higher amounts of FA and rice husk ash, and proper curing contribute to low permeability. In geopolymer concrete, water content, binder content, water/binder ratio, aggregate content, and curing method significantly contribute to matrix weakness and increased permeability. The permeability evaluation in geopolymer concrete is crucial for assessing its durability and long-term performance, directly impacting its ability to resist aggressive external agents and complex mechanisms involved in corrosion processes.

## 3. Corrosion Mechanism in Geopolymer Concrete

Extensive discussions on the corrosion mechanisms of steel in concrete can be found in various sources [7,48]. Nevertheless, this section will provide a concise overview to equip readers with the requisite background knowledge to understand the subsequent sections on corrosion detection and protection methodologies. In the concrete context, Healthy concrete's pore solution has a pH level of 13 due to calcium hydroxide as the dominant phase, facilitating the formation of a slender passive film on the rebar surface, providing steel corrosion protection [49]. However, the pH level is not the sole determining factor in forming various chemical species of metals. The electrochemical potential is an essential determinant in governing it. The Pourbaix diagram, also known as a potential-pH diagram, is a tool that combines the Nernst equation to represent potential and pH in an aqueous electrochemical system. Fig. 2 illustrates the Pourbaix diagram for the Fe-$H_2O$ system, depicting thermodynamically stable scenarios [50]. The vertical axis represents the electrochemical potential, where positive potentials indicate metal oxidation and negative potentials suggest reduction, particularly of oxygen atoms. The x-axis represents pH, with values below 6 being acidic, around 7 being neutral, and above 6 being alkaline or basic. The immunity region, below the line a-b-j, signifies where metal corrosion does not occur. Above the line g-f-h, the corrosion region indicates metal oxidation into FeO42- in an aqueous solution. Passivation involves oxidation, forming a protective $Fe_2O_3$ oxide layer that prevents further reactions.

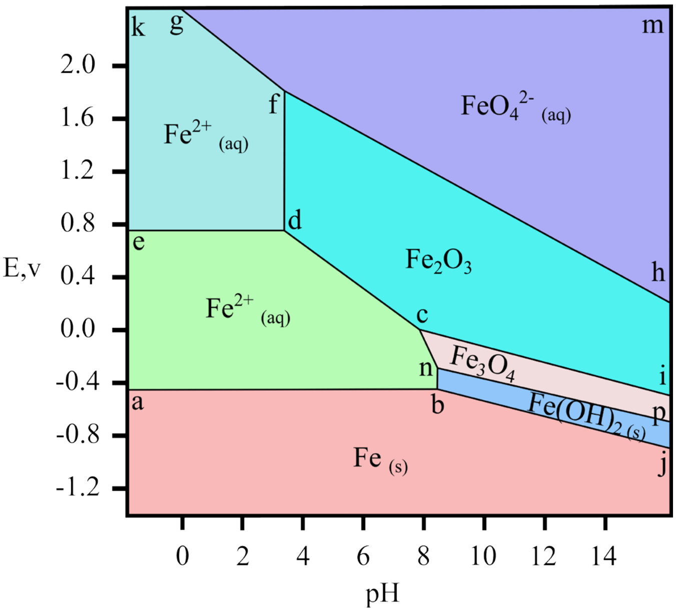

Fig. 2. Pourbaix diagram

The presence of aggressive ions of $Cl^-$, such as in seawater, can destroy the film and lead to pitting corrosion in steels. Other passivation zones include e-i-p-n and n-p-j-b, where solid oxides formed are $Fe_3O_4$ and $Fe(OH)_2$, respectively. The Pourbaix diagram in Fig. 2 demonstrates that the passive film can remain intact and prevent corrosion within the range where solid $Fe_2O_3$ and $Fe_3O_4$ are stable. Nonetheless, it is essential to note that the Pourbaix diagram only offers thermodynamic information for a specific system condition, such as concentration, temperature, and pressure. It does not provide information on kinetics [51]. Steel corrosion in concrete is an electrochemical process involving half-cell reactions [7]. At the anode, iron releases electrons and dissolves in a ferrous state, as illustrated in Eq. (1). These electrons then move to the cathode, where oxygen reduction takes place in the presence of oxygen, as shown in Eq. (2). The cathode reaction can also involve water reduction in the absence of oxygen, as demonstrated in Eq. (3).

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{1}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{2}$$

$$2e^- + 2H_2O \rightarrow 2\ OH^- + H_2 \tag{3}$$

The composition of corrosion products formed on steel surfaces is heavily influenced by environmental factors, such as exposure duration and chloride concentration, as noted in previous research [52,53]. A study on weathering steel exposed to atmospheric corrosion found that the rust layer consisted of an inner α-FeOOH-rich layer and an outer layer predominantly composed of γ-FeOOH. The transformation from γ-FeOOH to α-FeOOH was attributed to amorphous ferric oxyhydroxide resulting from acid rains and wet-dry cycles. In contrast, steel rebar in concrete experiences the formation of goethite (α-FeOOH) and lepidocrocite (γ-FeOOH) in carbonated concrete. The presence of high chloride ion concentrations leads to the creation of akageneite (β-FeOOH) [53-55]. The passive film on steel in concrete is disrupted when chloride ion concentration near the rebar surface exceeds a critical value or when concrete carbonation lowers the pH below nine [22].

## 3. Corrosion Detection Methods

Accurately predicting the residual service life, developing suitable strengthening and repair strategies, and implementing effective anti-corrosion measures are crucial in detecting corrosion conditions in geopolymer concrete structures. The evaluation methods employed for corrosion detection in geopolymer concrete have undergone significant development over the years. The methods can be classified into direct and indirect techniques, depending on the type of information they yield. Direct methods encompass monitoring various corrosion parameters, such as corrosion potential, corrosion rate, and the quantity of steel corrosion. Electrochemical and physical methods are two distinct subsets of direct methods, each employing unique testing principles.

In contrast, indirect methods are employed to evaluate parameters associated with the corrosion process, such as chloride concentration, pH levels of the concrete pore solution, depth of concrete carbonation, concrete resistivity, and the resulting damages caused by corrosion, such as concrete cracking and redistribution of steel strain. These indirect methods offer valuable information regarding the degree of steel corrosion. This article focuses on the latter category and does not include coverage of the former indirect methods. Specifically, the following methods of finding corrosion are explained in detail: half-cell potential measurements, electrical resistivity tests, and microscopic analysis. TABLE 3 comprehensively summarizes these methods' underlying principles, measured parameters, and critical characteristics for reference.

### 3.1. Half-Cell Potential Measurement

Half-cell potential (HCP) is also called open circuit potential (OCP) and corrosion potential (Ecorr). Its measurement is the easiest and most common way to find out about corrosion in the field, besides looking for rust stains and cracks caused by corrosion. As shown in Fig. 3, it is measured with a working electrode (the steel reinforcement) and a reference electrode. Based on ASTM C876 and TABLE 4 [56,57], the HCP of steel can be used to determine how likely it is to rust. The ASTM C876 HCP values are based on the copper/saturated copper sulfate electrode (CSE), the most common reference electrode used in the field. Standard silver/silver chloride electrodes (SSCE) and saturated calomel electrodes (SCE) are often used in lab tests. TABLE 4 shows the HCP vs. SSCE, HCP vs. SCE, and HCP vs. standard hydrogen electrode (SHE) for each corrosion risk.

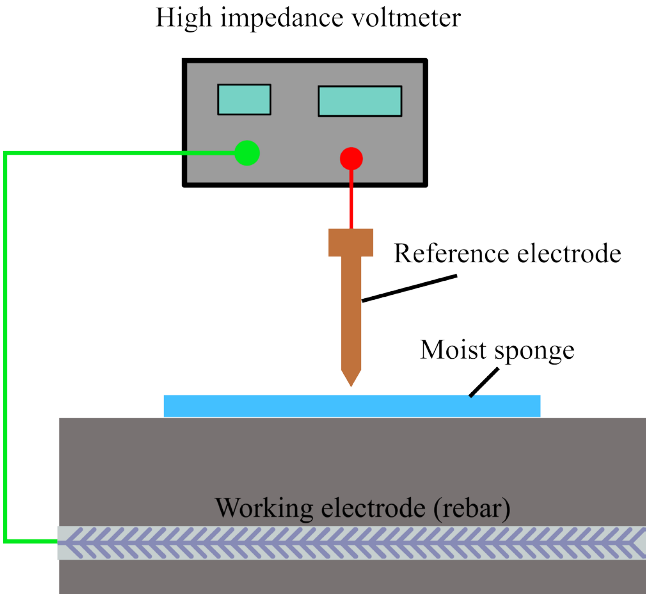

Fig. 3. Configuration to measure corrosion potential of steel

The HCP method is primarily utilized for conducting initial and early field assessments to identify areas at risk of corrosion. However, the interpretation of its meaning can be intricate, as

TABLE 3

Summary of Corrosion Detection Methods

| Methods | Principle | Measured Parameter | Remarks |
|---|---|---|---|
| Half-cell Potential (HCP) | HCP is the potential difference between steel and reference electrode, also known as corrosion potential and open circuit potential (OCP). | Corrosion potential, from which corrosion probability is estimated. | Fast measurement;<br>Allow the identification of the main defect points with high corrosion risk; No quantitative information of the corrosion rate;<br>Absolute value is highly affected by concrete conditions, the condition of the steel rebar, the availability of oxygen near the steel surface and environmental factors;<br>Potential gradient is recommended instead of absolute potential to reduce errors. |
| Electrical resistance probe (ER) | The resistivity of a metal depends on its geometry. Thickness reduction of steel due to corrosion leads to an increase of its electrical resistance. | Resistance of corrosion coupon. Corrosion amount can be deduced from the resistance changes. | Straightfoward principle;<br>Simple setup;<br>Accurate detection for corrosion amount;<br>The estimated corrosion rate is an averaged value over a certain period and consequently incapable to indicate localized corrosion;<br>Reasonable arrangement of ER point sensors before embedding;<br>Effects of temperatures must be compensated. |
| X-μCT tomography | Different materials have different X- ray adsorption capabilities, thereby steel rebar, corrosion products, cementitious materials, and defects in concrete can be identified and distinguished. | Corrosion distribution, geometry, amount, and the time variation of these quantities can be obtained. | Nondestructive;Accurate detection for corrosion amount;<br>Visualization of morphology of both general and localized corrosion; Restrict limitation on the dimension of tested sample;<br>Unportable equipment;<br>High costs. |

TABLE 4

The relationship between HCP of steel and corrosion probability

| HCP Values | | | | Corrosion Probability |
|---|---|---|---|---|
| (mV vs. CSE) | (mV vs. SSCE) | (mV vs. SHE) | (mV vs. SCE) | |
| < –350 | < –256 | < –34 | < –276 | > 90% probability corrosion is occuring |
| –350 to –200 | –106 to –256 | +116 to –34 | –126 to –276 | Uncertain |
| > –200 | > –106 | > –116 | > –126 | > 90% probability no corrosion |

it is influenced not only by the level of corrosion but also by various factors such as the thickness of the concrete covering, resistivity, and oxygen availability [58]. Although it is non-destructive and only necessitates an electrical connection to the steel reinforcement, there are certain limitations associated with this method. These include the labor-intensive process of mapping larger surfaces and difficulty accessing specific structural elements [58]. A prospective gradient method was proposed to solve this matter, which employs two reference electrodes to obviate the necessity of a direct linkage to the steel. This approach entails the relocation of the reference electrodes to determine an equivalent potential gradient [59].

Recent developments have introduced novel solutions to surmount additional challenges and broaden the method's practicality. Researchers have successfully created a flying robot with electrochemical sensors [60]. These sensors can measure both the half-cell potential and concrete resistance. This technology effectively tackles the challenges associated with labor-intensive tasks involving large surfaces and structurally complex components that are hard to access. Nevertheless, despite progress in this area, the HCP method still faces certain constraints that impede its widespread and regular implementation. This highlights the necessity for continuous innovation in corrosion detection techniques.

### 3.2. Electric Resistance

The detection of corrosion using the Electrical Resistance (ER) method is based on a fundamental principle, which states that the electrical resistivity of a metal is influenced by its geometry [61]. The decrease in steel thickness caused by corrosion leads to an elevation in its electrical resistance. As a result, the alterations in electrical resistance, as detected by ER probes, can be converted into the cumulative loss of steel mass. In the case of uniform corrosion, it is possible to calculate the average corrosion rate within specific time intervals [62]. Nevertheless, as temperature impacts the resistance of a metal, it is necessary to make adjustments to the measured resistance values to eliminate the influence of temperature. In order to compensate for temperature variations, an uncorroded ER probe is placed within the same environment.

Electrochemical impedance spectroscopy (EIS), specifically Electrochemical Resistance (ER) probes, is proficient in detecting general corrosion but less effective in identifying localized corrosion [62]. Severe localized corrosion may lead to minimal overall metal loss, making sensor resistance changes inconspicuous. ER probes have historically faced limitations in response time, requiring weeks to detect low corrosion rates. Recent material and electrical circuitry advancements have improved ER probe sensitivity [63]. While ER probes are commonly used in petrochemical engineering, their application in cementitious materials, mainly concrete, is less explored. Studies by Zivica [64] ella, and Taylor [62] demonstrated the practicality and accuracy of ER in measuring mass loss and corrosion depth in concrete structures, surpassing other electrochemical techniques. Despite its benefits, ER probes are limited to point sensors, requiring strategic planning for installation. Gartner et al. [65] monitored corrosion in marine-exposed Reinforced Concrete (RC) columns over 52 months using ER probes, emphasizing the importance of installation location planning. Legat et al. [66] used a combination of ER and electrochemical noise techniques to effectively monitor cumulative and localized corrosion levels in concrete subjected to wet-dry cycles.

It is crucial to acknowledge that when using electrical resistance (ER) probes in reinforced concrete (RC) structures, the measured corrosion level corresponds to the sensing material on the probes rather than the rebar itself. This discrepancy in corrosion conditions may arise between the probes and the actual rebar when exposed to the same environmental conditions. Not withstanding these challenges, electrochemical impedance spectroscopy (ER) techniques exhibit potential for corrosion monitoring and continuously advance through materials improvements and innovative application methods.

### 3.3. Microscopic Analysis

Microscopic analysis, mainly through X-ray micro-computed tomography (X-ray μCT), is a corrosion assessment method that examines materials at a microscopic scale to identify and characterize corrosion-related features, defects, and structural changes. X-ray μCT is an advanced imaging technique that provides non-destructive, three-dimensional visualization of internal structures [67-74]. This method relies on various materials' distinct X-ray absorption capabilities, with internal images represented by varying shades of grey based on X-ray intensity mapping. Brighter regions indicate higher attenuation coefficient values, while darker regions indicate lower values.

Recent applications of X-ray μCT in monitoring corrosion processes in steel within cementitious materials have been introduced. The technique identifies and differentiates steel rebar, corrosion products, cementitious materials, and concrete defects such as voids, pores, and cracks. Various studies have demonstrated the ability to quantify cross-sectional areas of different targets, including steel loss, corrosion products, and cracks [70,72,75]. Fig. 4(a) illustrates the principle of X-ray CT observation, and Fig. 4(b) depicts the quantification of cross-sectional areas in a sample [72].

X-ray micro-computed tomography (μCT) enables the visual and quantitative monitoring of corrosion progression in steel embedded in concrete, providing real-time in-situ observations. By utilizing 3D images of corroded steel reinforcements, it is possible to obtain information regarding the distribution of corrosion and the accumulated amount of corrosion [67,70]. Additionally, the temporal changes in these quantities can also be determined. Other corrosion detection techniques often struggle to achieve this level of difficulty. The X-ray μCT's capability renders it a highly suitable instrument for investigating the processes of corrosion accumulation, corrosion-induced internal deterioration of concrete, and the infiltration of rust into pores and cracks [70,71]. This makes it an invaluable tool for laboratory research.

Nevertheless, the X-ray μCT technique requires the tested samples to be minor, typically less than a few hundred millimeters, to achieve a high resolution. Moreover, the exorbitant expenses and specific prerequisites associated with existing X-ray μCT instruments limit its utilization. In order to evaluate the current structures, it is necessary to extract small samples from the site and transport them to laboratories for analysis. These methods serve a dual purpose of predicting the remaining service life of structures and providing guidance for maintenance strategies. This aids in preventing expensive repairs and ensures the overall structural integrity. However, prevention is also an equally crucial aspect of corrosion management. Implementing suitable corrosion prevention measures can significantly enhance the durability of materials subjected to corrosive environments.

## 4. Corrosion Prevention Methods

Methods for preventing existing reinforced concrete (RC) structures can be classified into passive prevention solutions and active therapy solutions. Various actions, including protective coatings, are implemented to preserve the current condition and hinder or postpone additional degradation. The concept of "therapy solutions" aims to effectively mitigate or halt corrosion processes, such as electrochemical rehabilitation techniques, although achieving complete cessation is challenging in practical applications. First, the passive "prevention solutions" are presented, followed by the active "therapy solutions." TABLE 5 comprehensively summarizes the various protection methods and their advantages and disadvantages. In the case of structures that have experienced severe corrosion, there is a significant requirement to restore their structural performance. Specific protection methods serve a dual purpose of enhancing structural integrity and safeguarding against corrosion. The relevant sections are highlighted.

### 4.1. High-performance fiber-reinforced Cementitious Composite Overlay

High-performance fiber-reinforced cementitious composite (HPFRCC) is a type of HPC with random fiber distribution [76]. HPC improves workability, mechanical properties, and durability by adding FA, silica fume, and blast-furnace slag and reducing the water-binder ratio. Due to fiber bridging, HPFRCC outperforms HPC in fracture toughness and crack width control. Engineered cementitious composites (ECC), or SHCC or UHTCC, are stretch-hardening HPFRCC. The product was developed by adding a 1.5-2% volume fraction of polymeric fibers and micromechanics to the fiber, matrix, and interface [76].

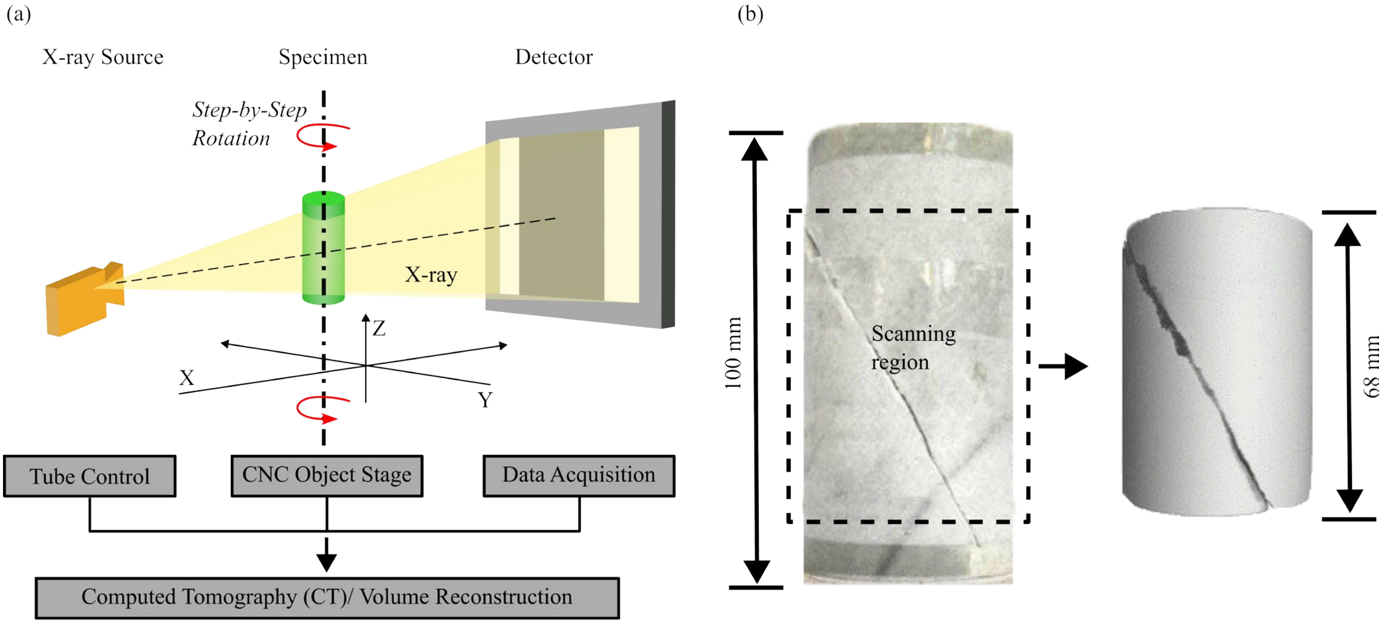

Fig. 4. Principle of the X-ray micro-CT observation and illustration of the scanning region. (a) The principle of X-ray CT observation and (b) the obtained cross-sectional area with respect to different targets

TABLE 5

Summary of Prevention Methods against corrosion

| Methods | Advantages | Disadvantages |
|---|---|---|
| High-performance fiber-reinforced cementitious composite (HPFRCC) overlay | Good durability in adverse service condition;<br>No maintenance required;<br>Dual function as an anti- corrosion barrier and a strengthening overlay; Suitable for corrosion-damaged structures needing strengthening. | The anti-corrosion effects are limited as HPFRCCs are still a porous material;<br>Risk of galvanic coupling. |
| Anti-corrosion coating | Convenient application; No maintenance required. | Organic coating has problems of poor fire resistance, crack, delamination, ultraviolet ageing, uneasy to remove;<br>Inorganic coating performs not as good as organic coating as a physical barrier;<br>Not suitable for heavily contaminated concrete. |
| Corrosion inhibitors | Convenient application; Lower cost;<br>Multiple alternative inhibitors are available towards different corrosion mechanism. | High requirement of penetrability when applied on the hardened concrete surface; Dosage is crucial otherwise it will backfire sometimes. |
| Sacrificial anode cathodic protection (SACP) | Simple installation, design and low maintenance;<br>No external power source required;<br>Low risk of hydrogen embrittlement and consequently SACP is feasible to apply to prestressed structures; Availability of wide range of anodes. | Lack of control system and knowledge of protection degrees; Limited service life; Low driving voltage, thus can be used only in less resistive concrete and may be inadequate to provide full protection; Anodes can be large and intrusive compared to ICCP. |
| Impressed current cathodic protection (ICCP) | Protection current is controllable;<br>Effective for high resistive environment like concrete;<br>Longer lifespan; Secondary benefits, such as increasing pH values near steel rebar and repelling chlorides; Low maintenance cost in the long run. | The need for permanent external power source and constant monitoring; Risk of hydrogen embrittlement of steel, concrete softening, and steel/concrete bond degradation;<br>Electrical connection of all the rebars should be insured, or rebars that are skipped will corrode more severely;<br>Lifelong running; Anodic acidity. |

Strain-hardening before crack localization produces small crack widths, close spaces, high ductility, and 2-5% stain capacity. When strain exceeds 1%, ECC cracks are tens of microns. According to research, cracked ECC has similar water permeability to sound concrete but delayed chloride penetration.

Maximum packing density theory, ultrafine reactive mineral admixtures, and a low water/binder ratio can give ultra-high performance concrete (UHPC) compressive and tensile strengths over 150 and 10 MPa, respectively [77]. UHPFRCC improves cracking resistance and ductility by adding short discrete fibers (usually steel) to UHPC at a 2-6% volume fraction [78,79]. UHPC has a durability of <2 mm carbonation depth for up to 3 years, 4.5 times lower than regular concrete [80], and a chloride diffusion coefficient of 0.2 to $4.1\times10^{-13}$ $m^2/s$, at least one order lower than ordinary concrete [80,81]

HPFRCC's mechanical properties and durability make it ideal for harsh environments. Recent studies have examined pure HPFRCC or hybrid HPFRCC-RC structures [80,82]. HPFRCC is used in hybrid structure cover layers due to its crack control and chemical resistance. HPFRCC overlays have been studied for strengthening and corrosion protection on corroded RC beams and slabs [83-85]. These materials are more robust than steel plates and have better bond compatibility, more accessible construction, lighter weight, and corrosion-free properties. The strengthened system improves flexural, tension, shear, and durability [85]. Most HPFRCC strengthening studies have shown mechanical performance benefits, but the authors are unaware of long-term corrosion protection studies. These materials are more corrosion-resistant than conventional concrete, but galvanic coupling between the old, degraded concrete and the new strengthened layer may affect their effectiveness in corroded structures [86,87].

### 4.2. Anti-Corrosion Coating

An anti-corrosion coating is a surface treatment used on reinforced concrete and steel. Previous research suggests coating the surface to control corrosion in reinforced concrete (RC) structures [88]. Besides anti-corrosion protection, this component is decorative and prevents concrete degradation from ultraviolet light. The typical method for preventing concrete surface coating corrosion is to reduce aggressive substances like carbon dioxide, chloride ions, oxygen, and water. There are also efforts to reduce concrete conductivity and corrosion [89]. Organic coatings create a seamless film on concrete, making it chemically resistant to aggressive substances. Silanes, siloxy silanes, and chemically similar compounds can infiltrate concrete pores and react with water to form a hydrophobic layer that repels water. The water repellency of organic coatings is essential because water carries harmful ions. Acrylate, polyurethane, chlorinated rubber, and epoxy are standard organic coating matrices. Organic coating loses effectiveness over time due to concrete's alkalinity and the erosive environment [90].

The durability of inorganic coating makes it more popular than organic coating. According to Al-Zahrani et al. [91], the inorganic coating is a cement-based material with low permeability and a thickness of less than 10 mm. The fine-grained mortar is enhanced with polymers to reduce permeability and improve concrete adhesion. In recent years, geopolymer coatings with high chemical resistance have garnered attention. Several scholarly articles have suggested and investigated this topic [92,93]. Due to the coating's thinness, the reinforcing function of cement materials can be ignored in studies on mechanical strength.

### 4.3. Corrosion Inhibitor

ISO 8044-1989 defines a corrosion inhibitor as "a chemical substance that reduces the corrosion rate when present in the corrosion system at a suitable concentration without significantly altering the concentration of other corrosion agents." Oil and gas industries use corrosion inhibitors that work up to 95-99% in uniform, slightly acidic, or nearly neutral media around corroding steel [94]. Due to the high alkalinity of concrete pore solution, complex concrete matrix, and carbonation, chloride, or sulfate corrosion, RC systems vary. Add corrosion inhibitors to fresh concrete or transport them through hardened concrete for RC structures. The admixed inhibitor allows precise dosage control. Migrating inhibitors in rehabilitation systems struggle to dose and diffuse from concrete to rebar [95].

$$2Fe^{2+} + 2OH + 2NO_2^- \rightarrow Fe_2O_3 + 2NO\uparrow \quad (4)$$

$$Fe^{2+} + OH^- + NO_2^- \rightarrow NO\uparrow + \gamma\text{-}FeOOH \quad (5)$$

Anti-corrosion inhibitors are anodic, cathodic, or mixed. Anodic inhibitors increase steel corrosion potential by reacting with its dissolution. Calcium nitrite is the most common anodic inhibitor. Sodium nitrite, benzoate, and chromate are used. Nitrite's oxidizing properties make it the main active component. Nitrites compete with chloride ions to oxidize $Fe^{2+}$ at film defects, strengthening passive film (Eq. (4) and (5) [94,96]. Regardless of the product ($Fe_2O_3$ or $\gamma$-FeOOH), a dense passive film can form on steel surfaces, even with chloride. The nitrate/chloride molar ratio determines inhibition. For corrosion prevention, use values from 0.8 to 1 [97]. Unfortunately, nitrite consumption and inhibition reduce concentration gradually. Low nitrite concentration is a harmful corrosion inhibitor that accelerates steel dissolution [98].

$$\underset{\text{(ester)}}{RCOOR'} + \underset{\text{(base)}}{OH^-} + \underset{\text{(carboxylic acid)}}{RO_2^-} + \underset{\text{(alcohol)}}{R'OH} \quad (6)$$

By preventing electron migration or lowering oxide concentration, cathodic inhibitors slow corrosion. The cathodic inhibitors are phosphates and fatty acid esters. Representative production is sodium monofluorophosphate. $PO_3F_2$ reacts with $Ca(OH)_2$ to form $Ca_3(PO_4)_2$, an indissoluble salt and a barrier layer [99]. This barrier layer prevents oxygen intrusion and increases cathodic resistance. MFP is used as an admixed inhibitor instead of a migrating inhibitor because it penetrates hardened concrete poorly [100]. Eq. (6) shows that concrete pore solution esters hydrolyze to carboxylic acid and its alcohol. The carboxylic acid anions quickly combine with free calcium to form an insoluble calcium salt of the fatty acid, creating a barrier layer on steel rebar like MFP. Second, fatty acids and calcium salts hydrophobicize concrete pores. Water escapes pores due to contact angle changes, preventing oxygen and chloride intrusion. Cathodic inhibitors include sodium hydroxide, carbonate, zinc oxide, silicate, and polyphosphates. A mixed inhibitor inhibits anodic and cathodic corrosion. Performance should be better than anodic or cathodic inhibitors alone. Zinc oxide and calcium nitrite are used [101]. An insufficient nitrite/chloride molar ratio can increase corrosion. Zinc oxide lowers chloride levels around steel rebar, reducing nitrite risks.

### 4.4. Cathodic Protection

Cathodic protection uses polarized steel reinforcement as an electrochemical cell cathode [102]. The main methods are the main methods for sacrificial anode cathodic protection (SACP) and impressed current cathodic protection. SACP steel rebar is connected to a lower metal. The sacrificial anode must have a lower potential than the cathode steel rebar to prevent corrosion. SACP unanimously chose zinc as the sacrifice anode. There are titanium, magnesium, and zinc alloy anodes like 85Zn-15Al. SACP is better for prestressed RC structures without hydrogen embrittlement than Impressed Current Cathodic Protection (ICCP) because it requires less maintenance and no DC power [103]. Short-circuiting's poor controllability, short lifespan, frequent anode replacement, and low self-driving voltage may not be enough to protect a larger structure, especially high-resistance concrete.

The Federal Highway Administration claims ICCP is the only effective chloride-containing concrete corrosion rehabilitation method [104]. It works as shown in Fig. 5. The external electrical field "primary effect." negatively polarizes immunity zone rebar. This process moves chloride ions from rebar to concrete or outdoor anodes. Rebar's surface produces hydroxyl by reducing oxygen. The benefits are "secondary effects" [105,106]. Research shows that ICCP's "secondary effects" – raising pH and repelling chlorides – work [102,107,108]. Long-term use of steel in concrete can cause passivation or re-passivation, resulting in a dense ferric oxide ($Fe_3O_4$) layer [109] and a sublayer and $\gamma$-$Fe_2O_3$ layer [105]. The type of anode and chloride presence affect anodic reactions. The acidification of anode materials and interfaces leaches solids from hardened cement paste [110]. Passive steel is more accessible to polarize and requires less negative potential for cathodic protection [111]. ICCP improves pH and reduces chlorides to keep steel reinforcement passive longer after the current is reduced or turned off, eliminating the need for a high-density current to corrode [87,112]. High charge until steel re-passivates, then low current maintains passivity for corroding sites [102].

The study by Glass et al. [108] proposes intermittent impressed current cathodic protection (ICCP) and highlights the need for low integrated protection current densities. Koleva et

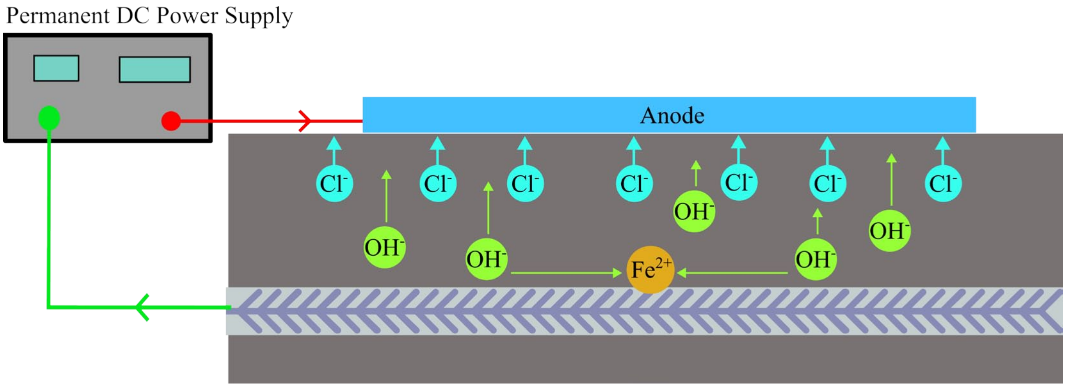

Fig. 5. Schematic illustration of impressed current cathodic protection (ICCP) of reinforcing steel in concrete

al. [113] introduce pulse current advanced ICCP, emphasizing its safety and effectiveness compared to conventional methods. While ICCP reduces corrosion, it can adversely affect reinforced concrete (RC) elements by altering concrete microstructure, causing hydrogen embrittlement, and degrading the steel-concrete bond [114-117].

ICCP protection efficiency is anode-dependent, with Ge et al. [118] suggesting a minimum total charge density for anodes at 38,500 A·h/m$^2$ (over its surface area). The success of ICCP systems over decades depends on the reliability of the anode-concrete interface, necessitating more research [110]. Durable anode systems are crucial, and conductive cement overlay anodes, particularly with carbon fibre content near the percolation threshold, are recommended. Carbon fiber fabric anodes in various shapes are gaining popularity due to their mechanical, electrical, and electrochemical properties. CFRP composites strengthen and serve as anodes in ICCP systems [119-121].

Studies by Gadve and Lu [122] propose a CFRP and concrete bonding matrix with a conductive polymer and graphite in epoxy resin, addressing issues with the insulating CFRP matrix. Zhu et al. utilize conductive cement on carbon fiber fabric anodes, reinforcing and anodizing concrete with prefabricated CFRP bars. Lambert et al. [123] suggest U-shaping CFRP to enhance concrete-CFP bonding and flexural strength.

Research findings indicate that CFRP/ICCP-strengthened RC beams exhibit lower mass losses, corrosion rates, and flexural strengths than controls. However, active protection may decrease CFRP-concrete bond strength, highlighting the need for careful consideration in applying these techniques.

## 5. Conclusions

This study aimed to investigate the existing knowledge on corrosion mechanisms, the diverse elements contributing to corrosion, methods for corrosion prevention, and recent advancements in this domain. The conclusions drawn from the literature reviews presented in this study are as follows:

A. The mechanical and durability performance of geopolymer concrete are dependent on geopolymerization. Factors such as water content, binder content, water/binder ratio, aggregate content, and curing method determine the material's durability and performance.

B. Healthy concrete forms a passive film on steel due to its alkaline pore solution, providing essential protection. However, corrosion can also be influenced by electrochemical potential and pH. Environmental factors like exposure duration and chloride concentration affect steel corrosion product composition.

C. HCP is a standard field corrosion measurement method. However, it is labor-intensive and can be challenging to access certain structural elements. Recent developments use two reference electrodes to determine an equivalent potential gradient, improving the method's effectiveness.

D. ER is another corrosion detection method based on metal resistivity. It struggles to detect localized corrosion and has a slow response time. However, ER techniques have the potential for corrosion monitoring and are improving through material improvements and new application methods.

E. X-ray micro-computed tomography (X-ray μCT) is used to visualize and quantify corrosion progression in steel embedded in concrete. This method provides real-time in-situ corrosion distribution and accumulation data. However, it is limited by high costs and specific requirements, requiring small samples for high resolution.

F. Corrosion prevention include passive and active methods. Protection coatings preserve the current condition and delay degradation in passive prevention solutions. Electrochemical rehabilitation is an active therapy that reduces or stops corrosion.

G. Chemical corrosion inhibitors work 95-99% in uniform, slightly acidic, or nearly neutral media around corroding steel. Anodic inhibitors increase corrosion potential by reacting with steel dissolution, while cathodic inhibitors slow corrosion by preventing electron migration or lowering oxide concentration.

H. Polarized steel reinforcement is used as an electrochemical cell cathode in SACP and impressed current cathodic protection. Carbon fibre fabric anodes' mechanical, electrical, and electrochemical properties make them popular. Carbon Fiber Reinforced Polymer (CFRP) and carbon fibre fabrics are ICCP anodes and strengthening materials.

### Acknowledgments

The authors gratefully acknowledge the Ministry of Higher Education, Malaysia, through the Fundamental Research Grant Scheme (grant number: 9008-00009). The authors would like to acknowledge Geopolymer and Green Technology, Centre of Excellence (CEGeoGTech), University Malaysia Perlis (UniMAP), Faculty of Chemical Engineering Technology UniMAP for the support.

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