JOURNAL OF SMART SCIENCE AND TECHNOLOGY

Journal of Smart Science and Technology

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A Review on the Application and Morphology of Organic Corrosion Inhibitors

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Abstract
Corrosion is a major challenge in construction technology and manufacturing industry. It does not only reduce the aesthetics of a building but also weakens the structure. Structural weakness caused by rust leads to the reduction in the durability of reinforced concrete. Various efforts and research ranging from prevention to maintenance process are being carried out globally to overcome this problem. Due to the increased awareness of the importance of preserving the environment for health and ecological system, studies are increasingly focused on the use of environmentally friendly corrosion inhibitor. This paper discusses several conditioning methods of using organic corrosion inhibitors in concrete reinforcement. It also takes a close look at the effect of every conditioning method towards the reinforced concrete strength and the mechanism to improve it. The migrating and admixed corrosion inhibitors (MCI) conditioning methods is considered as the best solution so far to enhance corrosion resistance performance that contributes to superior reinforced concrete mechanical strength.

Keywords
Corrosion; Organic; Biosurfactant; Concrete reinforcement; Conditioning

1 Introduction

Corrosion of reinforced concrete is one of the major durability issues faced by construction industry around the globe. The main concern is the corrosion of steel reinforcements that could severely affect concrete strength and durability. Corrosion is the deterioration of metal by chemical attack or reaction to its environment. It is a constant and continuous problem, often difficult to eliminate completely. This leads to rust formation, cracking, spalling, delamination and degradation of structures that may threaten its performance and aesthetic of the concrete structures, thus lead to earlier failure.

Therefore, to address these issues, research around the globe is geared towards developing methods and materials to prevent corrosion of reinforced concrete structures. Among various methods of preventing and avoiding the degradation and destruction of concrete reinforcement, the corrosion inhibitor is one of the best-known methods of corrosion protection. Historically, inhibitors have great acceptance in industries. However, many have shown negative side effects that caused damage to the environment.

This has led to the search for eco-friendly organic corrosion inhibitors that are biodegradable, do not contain heavy metals or other toxic compounds that could damage the environment and its inhabitants. In addition to being eco-friendly and environmentally acceptable, these organic surfactants are known as inexpensive and renewable.

In 1928, the American Society for Testing and Material (ASTM) recognized rust as a major problem in construction involving metal. Various efforts were done to address the problem and thus numerous guidelines and specification were published. Table 1 shows the evolution of steel coating in America from 1910 to 2015.

Table 1. The evolution of coated reinforcing bars

Year	Events	Specifications
1910	The first reinforcing bar specifications was issued.	
1928	The first hot-dip galvanized reinforcing bar specifications was published.	ASTM A123
1973	Epoxy-coated rebar was first used in U.S. bridge.	
1979	The specification for zincs-coated (galvanized) rebars was published.	ASTM A767
1981	The specification for epoxy-coated rebars was published.	ASTM A775
1981	The specification for handling of epoxy coated bars was published.	ASTM D3963
1997	The American Association of State Highway and Transportation Officials (AASHTO) published specification for epoxy-coated rebars.	M 284
1990	ASTM A775/A775M was revised with provisions for repairing damaged coating.	ASTM A775/A775M
1991	The Concrete Reinforcing Steel Institute (CRSI) began a certification program for epoxy-coating applicator plants.	
1992	ASTM A775/A775M was revised to change the coating thickness.	ASTM A775/A775M
1995	The specification for prefabrication epoxy-coated rebar was published.	ASTM A934/A934M
1995	ASTM A775/A75M was revised to allow a chemical wash for surface preparation.	ASTM A775/A775M
1997	Cathodic debonding was introduced in ASTM A775/A775M and A934/A934M.	ASTM 775/A775M/ ASTM A934/A934M
2008	The specification for zinc and epoxy dual coated rebars was published.	ASTM A1055
2012	ASHTO discontinued AASHTO M 284M/M 284. It was replaced by ASTM A775/A775M.	
2015	The specification for continuous hot-dip galvanized steel rebars was published.	ASTM A1094/A1094M

2 Corrosion of Concrete Reinforcements

Corrosion is defined by ASTM terminology (G15) as an electrochemical or chemical process between materials, usually metals, with their environment that causes the materials and their qualities to deteriorate. The process involves two electrochemical reactions; oxidation occurs at an anodic site and reduction occurs at the cathodic site. The corrosion layer does not form on the reinforcement in the absence of oxygen and water. Corrosion occurs as a result of defects that allow water or oxygen to infiltrate the reinforced concrete. Several most common defects occur due to high water cement ratio, concrete shrinkage, low material quality, concrete permeability, environmental condition, concrete strength, loss of alkalinity due to carbonation, sulphate, and chloride attacks.

Usually, concrete reinforcement is in an inactive and noncorroding state. However, steel reinforced in concrete is frequently used in harsh environment that contain salt or seawater. When chloride enters the concrete, it causes the passive layer that protects the steel to be disrupted, resulting in rust and pitting.

Concrete carbonation occurs when carbon dioxide, moisture and calcium hydroxide, which is found in cement, react electrochemically to produce calcium carbonate. Concrete's alkalinity is reduced by calcium carbonate from pH 12 to 13 to around pH 9. This hardens the concrete and increases its compressive strength but the protective passivation layer covering the reinforcing steel begins to break down at this lower pH level, exposing the steel to corrosion.

Understanding the corrosion process and its mechanism is important when designing concrete structures that will be exposed to hostile environments and deciding the most effective corrosion inhibitor and its conditioning method.

2.1 The Mechanism of Corrosion in Concrete Reinforcements

The concrete reinforcement corrosion is among the main cause of the deterioration of existing reinforced concrete structures. When corrosion occurs, corroded bars lose their original shape and deformed bars will lose their bond with concrete. Corrosion reduces the cross-sectional area of steel, thus decreasing capacity and ductility. These phenomena have a long-term detrimental effect on structural and mechanical performance and integrity.

Corrosion of steel bars results in the formation of rust materials that are significantly larger in volume than the original steel. As a result of volume expansion, splitting stresses act on the concrete, resulting in cracking that leads to the concrete cover spalls. Such damage accelerates the rate of corrosion. Meanwhile, the mechanical properties of the reinforcement bars deteriorate due to the decrease of cross-sectional area. This also impairs the bond mechanism and causes cover cracking and spalling. Figure 1 illustrates the corrosion mechanism and its consequences.
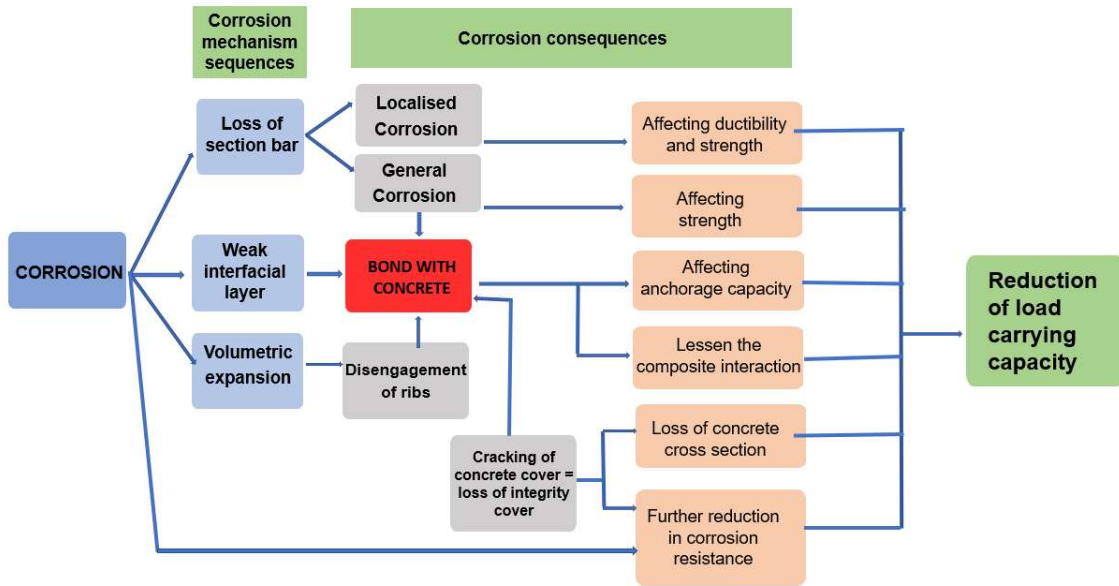
Figure 1. Sequences and consequences of corrosion on reinforcements. Reproduced from Cairns et al. (1999)[43]

Reduced cross-sectional area of reinforcement caused by corrosion results in decreased in structural stiffness, shear and moment capacities. This will ultimately reduce the load bearing capacity of the structure[1]. The detached components reduce the cross-section and cover of the concrete. Spalling or delamination of the concrete cover due to the erosion of reinforcement reduces the bending capacity of the concrete element. Reduced confinement affects the interaction of reinforcement and the concrete, thereby reducing anchorage capacity. The cracked concrete surrounding corroded reinforcements and stirrups influences the anchorage and shear capacity of a beam. When the concrete in this region is cracked due to corrosion, it reaches its tensile strength maximum. As a result, any additional loading on the structure induces environmental elements. This condition in time will eventually impair bonding and thus reducing the shear and loading capacities of the structure[2]. Depending on their direction, the cracks may alter the stiffness of the structure, thereby altering the force distribution within it. Figure 2 illustrates the direct relation of reinforcement corrosion on the mechanical properties of reinforced concrete structure.

Figure 2. The relation of reinforcement corrosion on the mechanical properties of reinforced concrete structures

3 Corrosion Inhibitors

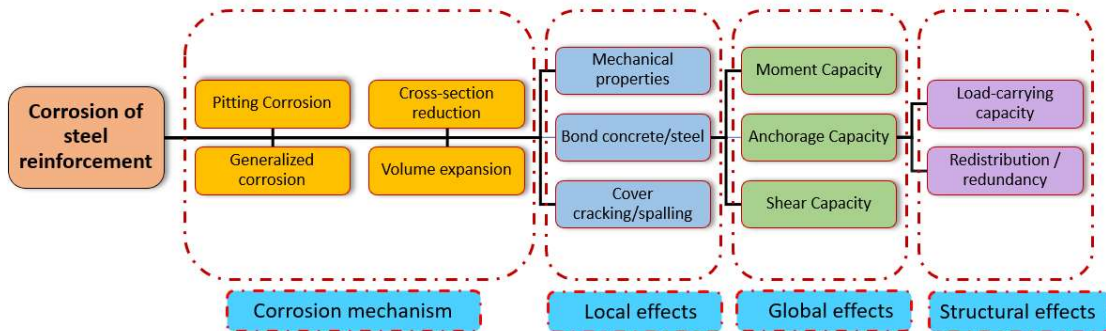Corrosion inhibitors are substances, either organic or inorganic, in the form of liquid or powder, that when present in the corrosive environment at a suitable concentration, will minimize, slow down or prevent corrosion attack on steel reinforcement. Corrosion inhibitors can be categorised according to their application methods, mechanism of protection, or their composition[3], which can be organic and inorganic. They prevent corrosion by forming a passivating coating (anodic inhibitors) or enhancing polarity and lowering the corrosion potential (cathodic inhibitors). There are other inhibitors that work both ways (mixed inhibitors). These inhibitors can be directly applied as protective coatings on the reinforcement. This can be done by adding an inhibitor solution to the kneading water during the concrete mixing process and pre-treating the reinforcement by immersing it in an inhibitor solution, or the application of an inhibitor solution to the surface of a hardened reinforced concrete structure (migrating inhibitors)[39]. This process allows the inhibitor solution to penetrate the concrete via capillarity.

Anodic inhibitors when applied as anodic surfaces increases the layer of the natural oxide layer on the surface of metal components. An application of anodic inhibitors forms a protective layer through electrolysis decreases the rate of corrosion. These inhibitors alter the anodic reactions in a chemical cell, forcing the metallic surface into the passivation region.

The passivating inhibitors come in two types: oxidizing anions and non-oxidizing ions. The purpose of oxidizing anions is to render steel inert in the absence of oxygen. This is accomplished with chemicals such as nitrates and chromates. Non-oxidizing ions on the other hand require oxygen and different chemicals such as molybdates, tungstate and more commonly used phosphates are used. The maximum effectiveness of anodic inhibitors can be gained when optimum concentrations are utilized[4]. The factor to be considered in establishing the concentration required is by determining the chloride level present in the environment. Since the work of an inhibitor is to decrease the anodic process rate, the corrosion potential changes after the inhibitor has been added, indicating a retardation in the process.

Cathodic inhibitors retard corrosion on metal surfaces by reducing the capacity of the metal to react with corrosive elements in the environment. A protective film is developed around the cathodic areas when cathodic inhibitor is applied. These are referred to as cathodic precipitation inhibitors[5]. Cathodic precipitation normally uses zinc, calcium and magnesium precipitated on the metal surface to form a protective layer. Although cathodic inhibitors are the most effective in preventing pitting, they are less effective in the prevention of other types of damage by corrosion as compared to anodic inhibitors[6].

The combination of both cathodic and anodic inhibitors suppresses both anodic and cathodic corrosion. It slows the rate of corrosion by adsorbing a thin protective moisture repelling layer onto the entire surface of the metal[7]. Corrosion inhibitors are typically applied in the following ways: i) as an admixture to fresh concrete, ii) as migrating corrosion inhibitors (MCI) to harden concrete and damaged structures, iii) as an additive that can be used for mortars, and iv) as a treatment to rebar[8] surface prior to the formation of concrete. Figure 3 shows the classification of corrosion inhibitors.
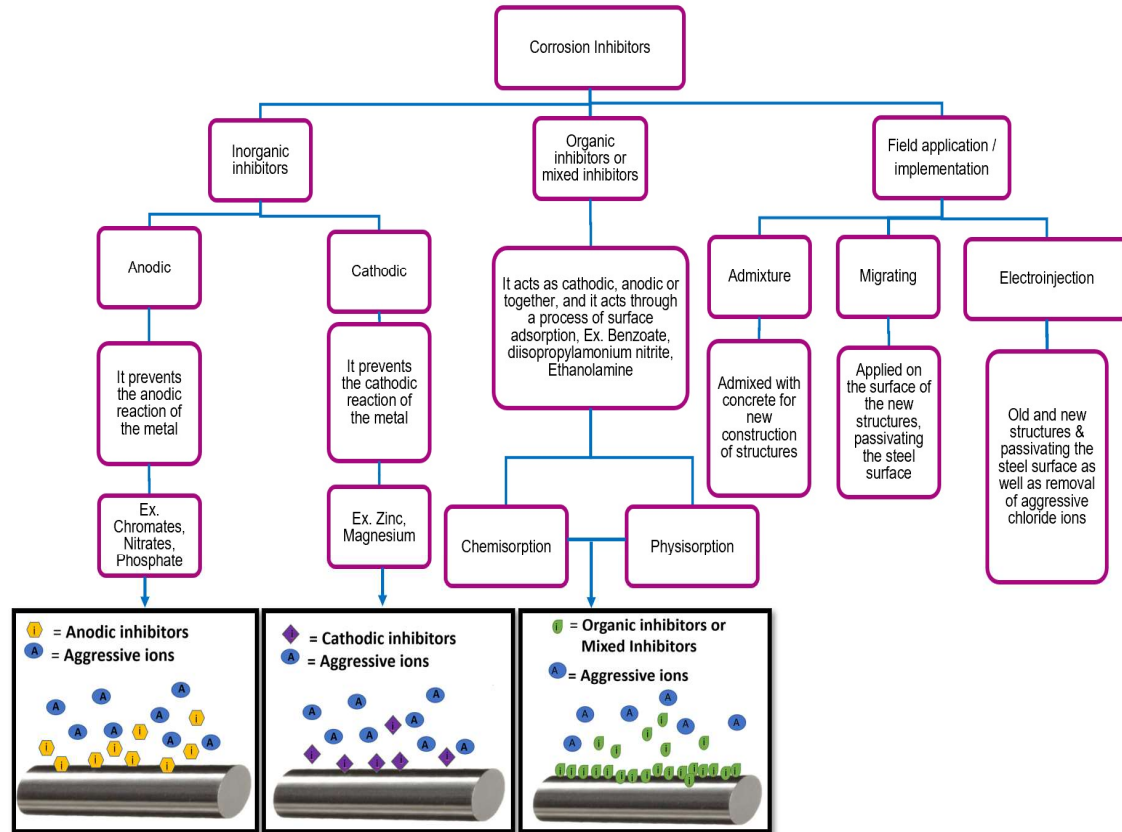
Figure 3. Classification of corrosion inhibitors. Reproduced from Hosseinalipour et al. (2010)[44]

Several factors including cost and amount, easy availability and most important safety to environment and its species need to be considered when choosing an inhibitor.

3.1 Organic Inhibitors

Organic compounds are used as inhibitors, act as cathodic, anodic or combination of both, as cathodic and anodic inhibitors, act through a surface adsorption process known as film formation. The presence of molecules exhibits a high affinity for metal surfaces, high inhibitory efficiency and lower risk to the environment[9]. These inhibitors form a protective hydrophobic layer on the metal surface, adsorb molecules which acts as a barrier to the dissolution of the metal in the electrolyte. They must be soluble in or dispersible in the media in which the metal is suspended[10]. The most common organic corrosion inhibitors are phosphate esters, quaternary ammonium salts, amidoethylimidazolines and thioglycolic acid.

The interest in biosurfactants as organic corrosion inhibitors has significantly increased in the last decade. Biosurfactants are microorganism-produced surface-active biomolecules. They are found to be an eco-friendly approach as they are produced through biological processes. Therefore, they are also categorized as biodegradable and renewable[40,41]. This review includes the application of biosurfactants as an organic corrosion inhibitor. Table 2 shows the biosurfactants classification and application.

Table 2. Biosurfactant classification and application

Biosurfactant	Strain	Type of metal	References
Lipopeptides	*Bacillus* sp.	Carbon steel	Purwasena et al. (2019)[45]
Rhamnolipids	*Pseudomonas* sp. PS-17	Alluminium alloy	Zin et al. (2018)[46]
Glycolipids	*Pseudomonas mosselii* F01	Carbon steel	Punniyakotti et al. (2018)[47]
Lipopeptides	*Pseudomonas fluorescens*	Stainless steel	Dagbert et al. (2006)[48]
Lipopeptides	*Pseudomonas fluorescens*	Carbon steel	Shubina et al. (2015)[49]
Fatty Acid	*Halomonas meridiana*	Carbon steel	Sari et al. (2017)[50]
Lipopeptides	*Bacillus* sp.	Mild steel	Jayaraman et al. (1999)[51], Zuo et al. (2004)[52]
Lipoprotein	*Bacillus subtilis*	Heavy Metals	Saranya et al. (2014)[53]

4 Application of Organic Corrosion Inhibitors in Concrete

4.1 Migration Corrosion Inhibitors

The corrosion inhibitors applied to the surface can migrate to the inside of the concrete until they are absorbed by capillary pores and subsequently adsorbed on the metallic surface[11]. These are also known as migration corrosion inhibitors (MCI) and are regarded as an efficient method for inhibiting and retarding the corrosion of the reinforcement and the concrete structure[12,14]. Studies conducted by Lan et al.[12,13] in the implementation of this strategy is quickly becoming one of the most popular methods, owing to its easy application method.

These inhibitors work by producing an adsorbed coating on the surface of the reinforcement, preventing the depolarizing agents (O_2 and Cl^-), preventing them from coming into direct touch with the reinforcing surface, and so avoiding the onset of the corrosive process[15]. Fei et al.[15] claim that this protective layer is formed by the inhibitors and prevents the electrons from flowing on the concrete or metal interface, acting as a barrier to the aggressive ions, making the reinforcement less corrosive. The inhibitor's effectiveness in shielding the steel against corrosion is largely determined by the inhibitor's interaction with the metallic surface[16].

Among the organic corrosion inhibitors used for the concrete are alkanolamines and amines, which can infiltrate the concrete's capillary and micropores[12]. Lan et al.[13] found that inhibitors of amino alcohol and carboxylates applied on the high resistance concrete contaminated with chlorides are efficient in inhibiting the corrosive process in medium and low concentrations of chloride ions.

MCI applied to the surface are frequently used to repair chloride-contaminated concrete. In concrete terms, chloride and inhibitor ions exert their effects via three distinct mechanisms, namely natural diffusion, electrical migration and transport via capillary suction or pressure gradient-induced movement of pore solution. Typically, MCI are derived from commercial organic compounds, amines and alkanol amines and their salts[17]. Amino alcohols penetrate the concrete pores rapidly and protect the reinforcement by using physical or chemical adsorption to form a hydrophobic layer. An insoluble compound forms that closes the pores in the concrete when inhibitors are introduced due to its reactions with the cement particles[11]. Due to their ease of use, low cost and safety, application of this type of inhibitors are the suitable and effective solutions for rehabilitating reinforced concrete structures. MCI are applied topically to chloride-contaminated concrete surfaces prior to the application of patches and overlays. Another study demonstrated that inhibitors based on amino alcohols are more effective on mortar than on other compositions containing furnace slag[4]. Additionally, it was observed that the corrosion rate was reduced in samples with a lower chloride concentration but it was ineffective in mortar specimens with a higher chloride concentration[18].

4.2 Admixed Corrosion Inhibitors

The promising potential of organic corrosion inhibitors as admixtures in

concrete composition to provide enhanced corrosion prevention at lower cost are gaining attraction in the construction industry[19].

While additives are typically used to improve the qualities of fresh or hardened concrete, corrosion inhibitors work primarily on the steel surface. Inhibitors are mixed into the fresh concrete at the time of concreting.

By right, these inhibitors should not compromise the concrete's properties. However, they are added in the fresh state and hence they usually contribute additional characteristics to the concrete, other than inhibiting corrosion. To assess the effects of corrosion inhibitors on the concrete properties, Gaidis[20] in his research concluded that concrete hydration process, the gain in mechanical resistance, and other properties are influenced by the inhibitors.

Corrosion inhibitors as admixture to concrete mix can prevent steel corrosion by forming a protective layer on the surface of the rebar through adsorption mechanism that acts as a barrier against corrosion. Amines and alkanol amines, as well as their salts, are some of the compounds used as organic inhibitors in concrete[17]. Alkanol amine-based inhibitors have been found to be able to reduce the corrosion rate of reinforcement subjected to carbonation-induced corrosion as well[21].

According to Ormellese et al.[22], the corrosion inhibitory effect of amines and alkanol amines on steel when used in chloride-containing alkaline solutions is minimal. They also discovered that pitting corrosion can be prevented effectively with polycarboxylates[22]. The same study compared carboxylates to amines or alkanol amines and amino acids, and the results indicate that amines or alkanol amines were only moderately effective, whereas carboxylates exhibited the most effective behaviour at low and moderate levels of chloride. Increasing the dosage of amines reduced the effectivity and the compressive strength of cement paste[23]. Heren et al.[24], in her research, demonstrated that increasing the concentration of corrosion inhibitor concentration resulted in the decrease of concrete strength[24].

According to Elsener and Angst[25], monofluorophosphate (MFP) reacts with fresh concrete, making it not suitable to be used as mixed corrosion inhibitor. It extracts the active material from the pore solution of the concrete and retards its hydration. Therefore, it is recommended only for surface application. Sodium nitrite or potassium nitrites reduce the compressive strength of concrete and increase the risk of an alkali-aggregate reaction (AAR). On the other hand, calcium nitrite accelerates cement hydration, requiring the addition of a water reducer and a setting retarder to the concrete mix.

According to a study conducted by Olsson et al.[26], certain organic inhibitors are adsorbed more effectively in the active state on the iron surface compared to in the passive state[26].

4.3 Solution Gelling (Sol-Gel) Coating

The sol–gel process can be defined as the result of an oxide network by successive condensation reactions of molecular precursors in a liquid media[27]. The formation of sol–gel occurs in four stages known as (a) hydrolysis, (b) condensation and polymerization of monomers to create particles and chains, (c) particles growth, (d) agglomeration of polymer structures followed by the creation of networks that span throughout the liquid medium, resulting in a thickening form of a gel.

Various techniques can be used to apply a sol–gel coating to a metal substrate. The two most common techniques are spin-coating and dip-coating. Corrosion inhibitors are incorporated into the sol–gel system with the purpose of increasing the corrosion resistance of metal substrates[27]. Sugama[28] developed hybrid coatings to protect steel and aluminium from corrosion by adding about 20% concentration of cerium acetate (by weight) as corrosion inhibitor into 3-aminopropyl trimethoxysilane (APS) solution[28]. The cerium compound may reduce the content of unreacted water-soluble APS and generate a passive Ce(III) oxide coating on the metal surface that is insensitive to Cl dissolution. The coating thickness was around 2.5 μm, and it increased the lifetime of steel exposed to salt fog in the salt chamber from 10 to 768 hours, and of aluminium panels from 40 to 1440

hours. Duran et al.[29] also studied cerium ions loaded hybrid silica sol–gel coatings deposited on stainless steel AISI 304 substrates[29]. Coatings prepared with the Ce(III) salt improve the corrosion resistance through a barrier effect, but developed faults later in the immersion period, indicating that there were no apparent inhibitory effects. Simultaneously, coatings derived from Ce(IV) compounds improved the coating performance. This is most likely owing to the surface production of Ce(OH)$_3$ via a chemical or electrochemical mechanism involving a redox interaction between Cr and Ce ions. From these studies of sol–gel coatings on steel substrates (stainless steel, carbon steel and zinc steel), it was clear that sol–gel coating can effectively protect against corrosive media in practical service conditions. As a result, the corrosion resistance of steel substrates has been significantly enhanced.

Other than that, the merits associated with sol-gel coatings are their process flexibility (e.g., ambient spraying or immersion application), highly cross-linked coating structure that acts as an excellent physical barrier to retard the ingress of water or corrosive species, covalent bonding to metals substrates to provide strong adhesion at metal or coating interface, and the use of environmentally friendly sol-gel precursors[30]. Figure 4 shows the schematic steps and processes to obtain sol–gel, adapted from Hosseinalipour et al.[44]. Figure 5 shows the Illustration of a sol-gel process and a variety of sol-gel derived materials, adapted from Zhu et al.[30].
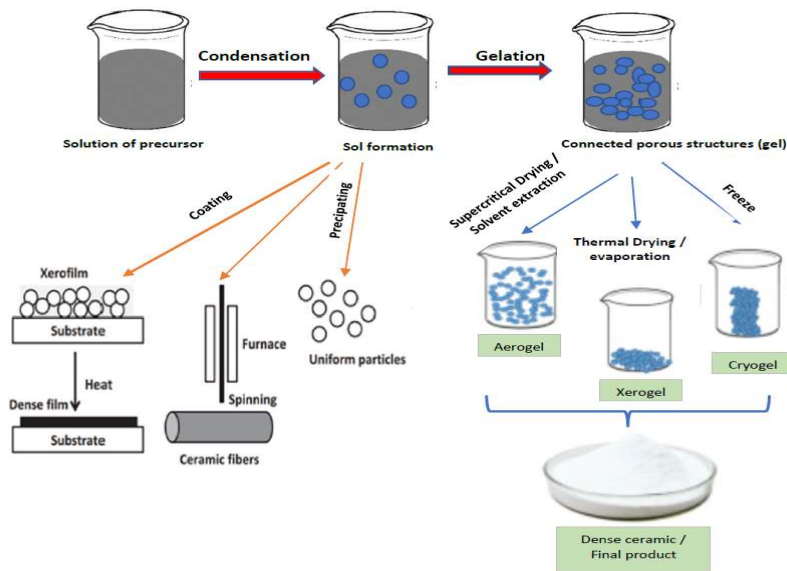

Figure 4. Illustration of a sol-gel process and a variety of sol-gel derived materials
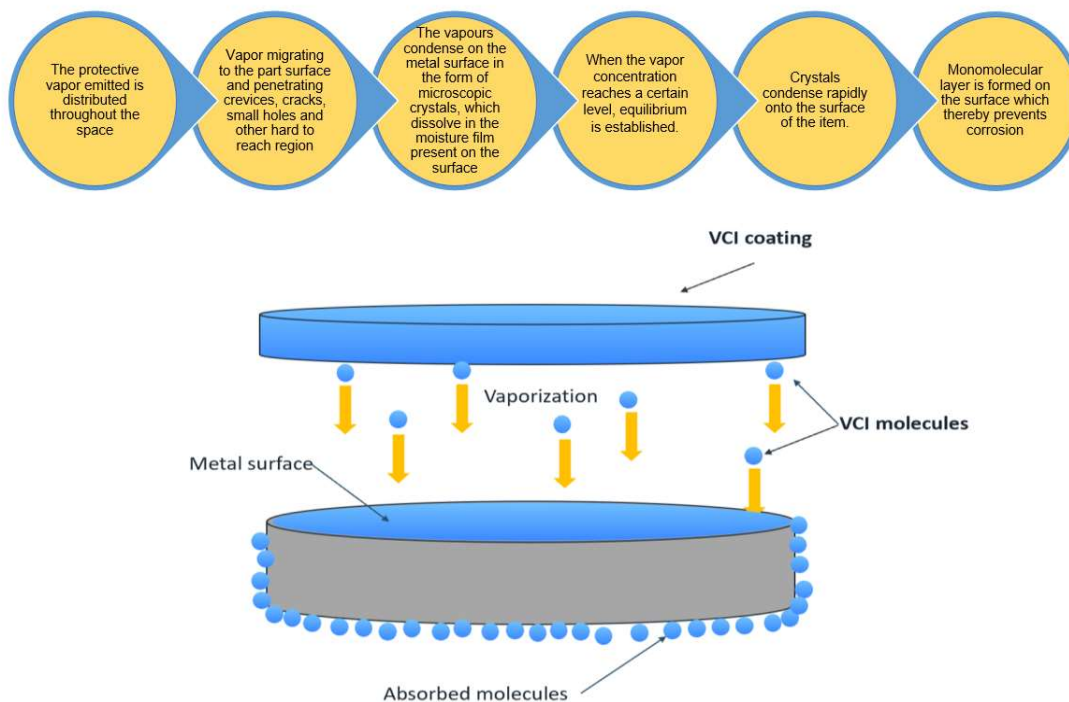
Figure 5. VCI working mechanism. Adapted from Gangopadhyay et al. (2018)[34]

4.4 Volatile/Vapor Corrosion Inhibitors (VCI) Coatings

VCI coating is a user-friendly replacement for solvent and oil-based corrosion inhibitors. It is a water-based system that is safe to be used on ferrous metals and stainless steel. Volatile corrosion inhibitors vaporize at a significant pressure and then are adsorbed on the metal surface, forming a thin corrosion protection layer. These molecules are not necessarily being in direct contact with the metal surface but by condensing on the metal surface. The invisible protective layer prevents oxygen, moisture and other corrosive elements from making contact with the metal surfaces on the metal surface, forming a thin corrosion protection layer.

The main advantage of these VCI is they are gas-phase transported, which enables them to reach the exposed metallic surfaces anywhere. As it is a vapour, it works well in confined areas that are inaccessible by traditional coating treatments and treats intricate internal components without having to be physically touched or exposed. Most VCI are amino carboxylates—products of reaction between organic acids with an amine or amine derivatives. The amino group-derivative compounds are commonly used as VCI because they are generally volatile and their chemical structures have high electronic density, in the presence of oxygen, sulphur, nitrogen and/or unsaturated bonds. VCI commonly used for steel are nitrite of amines, carboxylate of amines, chromate of amines and ester of carboxylic acid.

The selection of the most suitable inhibitor for a particular metal and environment depends on the vapor pressures of compounds. The vapor pressure of an effective VCI should be less than 1 mmHg to prevent too rapid evaporation of the VCI. Previous researchers studied the effective use of VCI for mild steel under various conditions[31,32,33].

The protective vapor emitted is distributed throughout the space migrating to the part surface and penetrating crevices, cracks, small holes and other

hard-to-reach regions. The vapor condense on the metal surface in the form of microscopic crystals, which dissolve in the moisture film present on the surface.

When the vapor concentration reaches a certain level, equilibrium is established, and some crystals condense rapidly onto the surface of the item and a monomolecular layer is formed on the surface which thereby prevents corrosion[34] as shown in Figure 5. VCI molecules also decrease the diffusion of oxygen to the metal surface and control the pH level in the electrolyte. The attraction of the VCI molecules is stronger than that of water molecules, thereby repelling moisture and preventing corrosion, as shown in Figure 6[34].

Figure 7[34] shows the case of corrosion of an unprotected metal surface, without VCI protection. The water molecules condense on the metal surface and thereby initiate electrochemical reaction, leading to corrosion.
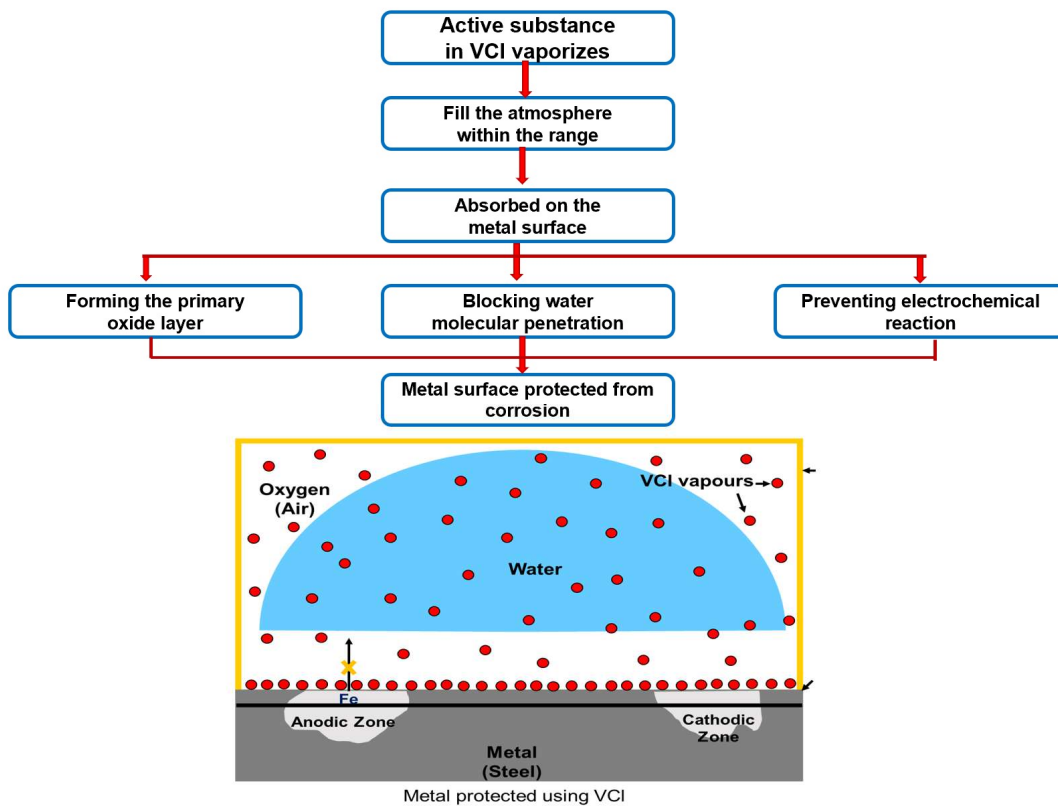

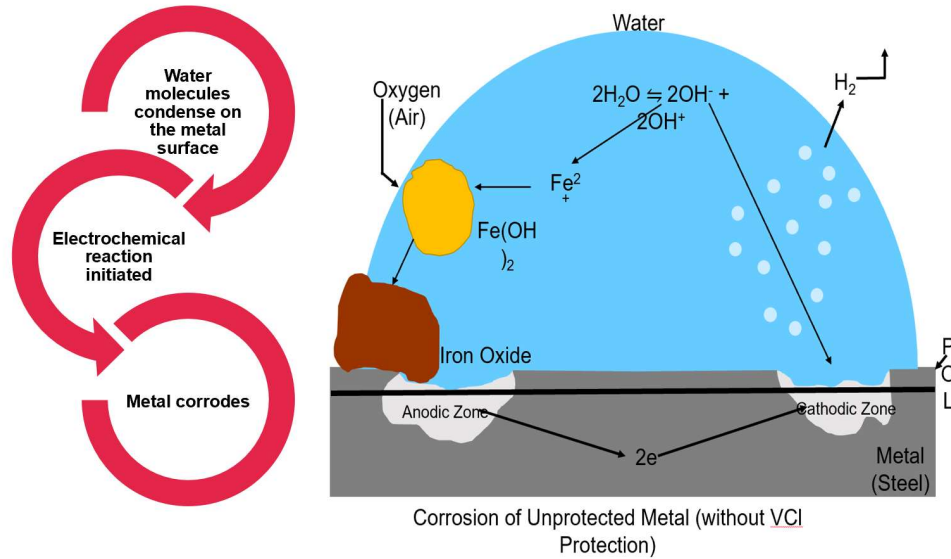Figure 6. Process of metal protection using VCI. Reproduced from Gangopadhyay et al. (2018)[34]

Figure 7. Corrosion of an unprotected metal surface, without VCI. Adapted from Gangopadhyay et al. (2018)[34]

VCI coatings are useful for corrosion prevention during the working hours of metal, at the place of its installation. They provide protection to the metal surface or equipment against both corrosion and mechanical damage such as scratch when it is in use. The main advantage of such coatings is that they continue to protect the metal against corrosion even if there is a small scratch on the coated surface due to the presence of a protective layer on the metal.

The application of VCI coatings provide excellent indoor protection but are not recommended for outdoor use unless they are used in combination with other VCI products that contain UV inhibitors[34].

4.1 Electrochemical Injection of Corrosion Inhibitors (EICI)

Numerous repair techniques have been used to restore damaged concrete structures due to corrosion of reinforcements. Partial replacement of the concrete cover, surface application of corrosion inhibitors, re-alkalization, electrochemical chloride extraction and cathodic protection are some of the methods employed to mitigate the damage[35]. In improving the durability of carbonated and chloride-contaminated reinforced concrete structures, electrochemical injection of corrosion inhibitors (EICI) was found to be an effective method in preventing corrosion in existing structures that are also effective to prevent further corrosion. Kubo et al. mentioned that the EICI technique was used in the repair of a carbonated reinforced concrete railway viaduct in Tokyo that was 40 years old. They discovered that ethanolamine, which is an organic based corrosion inhibitor, was applied through electrochemical injection into an existing aged, carbonated concrete allowed for sufficient inhibitor penetration near the steel. It was discovered that the pH level near the steel was altered as a result of the inhibitor's buffering action. Additionally, an uneven injection treatment was applied as it was discovered that the current density distribution was impacted, resulting from variation in the concrete cover as is the common case in real concrete structures[36]. Additionally, to develop a reasonable treatment strategy for successful inhibitor injection, detailed information on the distribution of concrete cover within the structure must be determined.

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Mangaiyarkarasi et al.[37] studied the efficacy of inhibitors application through electrochemical injection in chloride-admixed concrete containing ordinary Portland cement and Portland pozzolana cement. The results showed that the multi-component inhibitor injection demonstrated greater than 95% efficiency in terms of reduction in corrosion rate, regardless of chloride content in various concretes at a current density of 0.5 Am^{-2} by using Portland slag cement (Table 3)[36]. Lee et al.[38] investigated the injection of corrosion inhibitors by injecting the same type of inhibitor at a current density of 0.5 Am^{-2} into a chloride-contaminated old concrete slab[38]. The inhibitor formulation's efficiency was determined by using a variety of electrochemical tests. The mechanism of inhibition was determined by Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDAX) and Mercury Intrusion Porosity (MIP) studies. The FTIR studies indicated that the inhibiting reaction was achieved due to the migration of inhibitors' functional groups, namely $-NH_2$, C–H, and C, towards the cathode of embedded rebar that adsorbed on the metal surface. MIP studies demonstrated reduction in porosity of a nearly 50% in concrete samples after injection of corrosion inhibitors. According to the SEM analysis, the formulation of a hybrid inhibitor acts as a pore blocking agent when applied to concrete structures. They discovered that treatment via injection of corrosion inhibitors significantly reduced the rebar's corrosion rate due to the shifting of the rebar potential around (+300 mV) towards the passive region of the potentiodynamic polarisation curve. The tests results are shown in Figure 8[54].

Table 3.   Polarization parameters for the corrosion of rebar embedded in Ordinary Portland Cement (OPC), Portland Pozzolana Cement (PPC) and Portland Slag Cement (PSC) concretes with and without electro injection process

System	Cement	Ecorr (mV vs. SCE)	Icorr (mA.cm^{-2}) x 10^{-5}	Corrosion rate (mmpy) x 10^{-3}	Inhibitor efficiency (%)
Without electro-injection	OPC	−591	91.910	10.650	-
	PPC	−567	82.080	9.512	-
	PSC	−476	30.690	3.556	-
With electro-injection	OPC	−282	6.034	0.699	93.43
	PPC	−3[45]	2.276	0.263	97.22
	PSC	−295	2.024	0.234	93.40

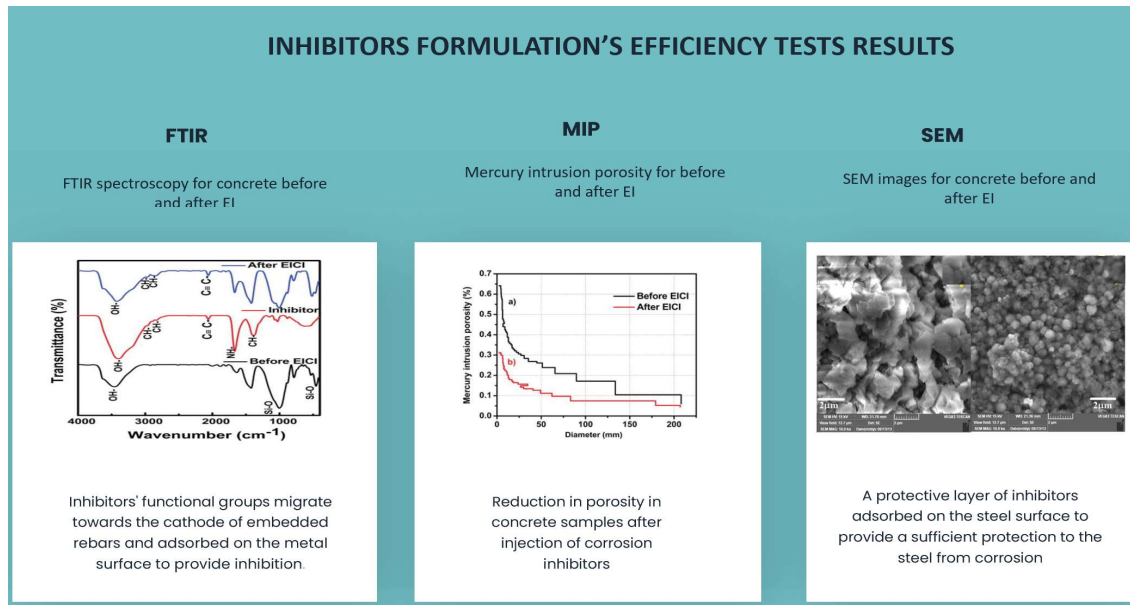Source: Mangaiyarkarasi et al. (2014)[37]

Figure 8. The inhibitor formulation's efficiency determined using a variety of electrochemical tests. Adapted from Karthick et al. (2016)[54]

5   Conclusion

Understanding the corrosion process and its thermodynamic and kinetic nature is important for designing a suitable protection strategy. This review summarizes the most commonly applied organic corrosion inhibitors such as admixed and MCI, VCI, EICI and sol-gel coating were systematically studied for their property's improvement of metallic concrete reinforcement. These various common applications were also examined for their effects and suitability for organic inhibitor.

The most used corrosion inhibitors around the globe are the MCI as they are easier to apply. However, these types of inhibitors are less effective in mortar specimens with a higher chloride concentration. Admixed corrosion inhibitors mixed in fresh concrete were reported to reduce the compressive strength of hardened concrete. However, this can be improved by reducing the dosage of the inhibitors.

It was found that sol-gel coatings enhance the corrosion resistance through a barrier effect, but developed defects later with immersion time, showing no apparent inhibiting effects. The performance of the coating can be enhanced by minimizing the

Ce(III) salt, at the same time, adding Ce(IV) chemicals into the solution. Other than that, the advantages of using sol-gel coatings are their flexibility such as ambient spraying or immersion application.

As the VCI application are gas-phase transport, this process enables corrosion inhibitors molecules to reach the expose metal surface in confined areas that are inaccessible by traditional coating treatments and treats intricate internal components without having to be physically touched or exposed. This treatment is highly recommended to continue to protect the metal against corrosion during storage. VCI coatings provide excellent indoor protection but are not suitable for outdoor use unless used in combination with other VCI products that contain ultraviolet inhibitors. EICI is mainly used for repair techniques to restore concrete structures damaged due to corrosion of reinforcements. To improve the corrosion inhibition of organic inhibitors, it is highly recommended to combine the inhibitors – organic and non-organic. The mixture should have lower solubility for long term protection.

In Malaysia, the use of biosurfactants in large-scale construction projects are still new and not widely used. Very little is known about its efficacy and reliability in long term under different environments. Optimistically,

with current advancements in the production and application of biosurfactants, additional information about their properties, behavior, and reaction could be uncovered, thus allowing for the potential discovery of new strains, application methodologies, and new designs of concrete structures in the future.

Conflict of Interest

The authors declare that there is no conflict of interest.

Acknowledgment

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