Chapter 8

Vapor Inhibitors for Corrosion Protection in Humid and Saline, Natural, and Industrial Environments

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Additional information is available at the end of the chapter

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Abstract

Corrosion is a pernicious phenomenon that appears in engineering materials, infrastructure assets, and industrial equipment exposed to the atmosphere, water, and soil. The aim of this chapter is to produce a body of knowledge on the theory and practice of corrosion inhibition so it can be used in the selection of corrosion inhibitors, to prevent and/or minimize corrosion in natural environments and industrial facilities. Corrosion inhibitors are employed in different forms such as emitters, pellets, powders, films, paints, aerosols, and aqueous and solvent solutions, depending on their chemical composition: organic or inorganic. They are impregnated on papers or plastics; closed in pouches and sachets; or added to coatings and paints to form a barrier against the attack of corrosive agents. They are employed in many industries: automotive, offshore/onshore, water, military, marine, manufacture, oil and gas, electronics, and concrete structures. A special group of corrosion inhibitors are extracted from vegetables or derived from industrial vegetable wastes, which are related to the advanced field of "Green Chemistry." The use of vapor corrosion inhibitors (VCI) has expanded rapidly in the last decades, and is frequently mentioned in the relevant literature, in particular in professional congresses and conferences, organized by international and national corrosion associations.

Keywords: corrosion, corrosion inhibitors, natural environments, industrial facilities, impregnated papers

1. Introduction

The global potable water scarcity, clean efficient energy, and environmental quality are recognized as central disciplines in modern science, engineering, and technology. Today, they are linked to the critical problems of climate change, worldwide warming, and greenhouse gas emissions, all interrelated phenomena [1, 2].

In recent years, advances, discoveries, and developments related to corrosion management, including theory and practice, have been made by universities, research institutes, international and national laboratories, and private industrial enterprises [3–5]. The importance and relevance of corrosion is evident by the periodical publication of 20 scientific and technical journals, in many languages, devoted to corrosion, materials, coatings, paints, structures, fouling, and scaling. Moreover, the economic and social value of the use of VCI for corrosion control in many critical industrial fields is graphically demonstrated in **Figure 1**.

The VCI triangle shows the harmful action of corrosive agents encountered in water bodies, atmosphere and land environments, and in industry facilities. The VCI are actively implemented to prevent, mitigate, and control corrosion in numerous industries and natural locations.

A special electronic newsletter is published weekly by NACE Corrosion Press describing corrosion events, corrosion problems and their solutions, novel instruments for corrosion detection and measurements, application of nanoparticles in corrosion devices, and repair and rehabilitation of bridges and infrastructure assets.

The influence of VCI technology is expressed by many international and national patents gathered in recently published reviews [6, 7].

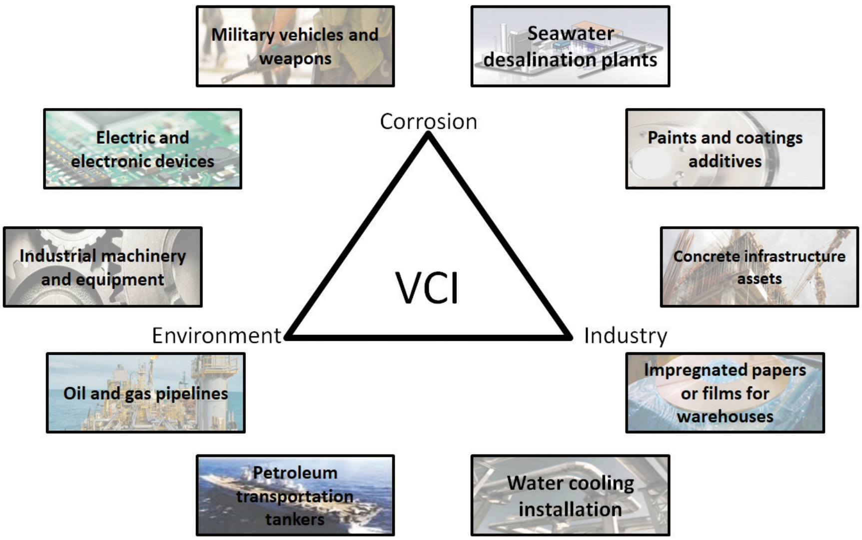

Figure 1. Schematic illustration of the great variety of VCI applications.

2. Corrosion and pollution

Corrosion and deterioration of industrial equipment occurs by an interaction between the surface of the material and the corrosive factors of its environment. Localized corrosion happens on parts of these equipment with a geometry prone to corrosion. Prevention and mitigation of these forms of corrosion require adequate methods and techniques, including VCI. Corrosion and pollution are harmful processes that are strongly intertwined since many pollutants, e.g., SO_X, NO_X, H_2S, NH_3, CH_4, CO_X, O_3, and acids, accelerate corrosion, and corrosion products such as rust, oxides, and soluble salts pollute water bodies such as lakes and rivers. Both are noxious phenomena that destroy the environment, impair the productivity of industry, and affect the durability of the materials and infrastructure assets [1–3].

The surface of a metallic piece of a machine or a vehicle reacts with the corrosive factors of its environment such as humidity and salinity, regulated by anodic and cathodic electrochemical reactions, as follows:

$$\text{Anodic} \quad 2Fe \rightarrow 2\,Fe^{+2} + 4\,e^{-} \tag{1}$$

$$\text{Cathodic} \quad O_2 + 2\,H_2O + 4\,e^{-} \rightarrow 4\,OH^{-} \tag{2}$$

The total corrosion process is

$$2Fe + O_2 + 2\,H_2O \rightarrow 2Fe\,(OH)_2 \tag{3}$$

Moreover, a posterior oxidation transforms the ferrous hydroxide into ferric oxide $Fe_2O_3xH_2O$, which covers the steel piece as rust.

Corrosion may appear in several forms: as general, uniform, covering the whole surface or as localize corrosion in special spots and sometimes producing perforations called pits.

3. VAPPRO corrosion inhibitors

Magna International, with headquarters in Singapore, consists of several enterprises located in Australia, Canada, Indonesia, China, and South Korea. The company is one of the world's leaders devoted to the critical field of corrosion-preventive technology. One of its main products is Vapor Corrosion Inhibitor, known as VAPPRO, which stands for Vapor-Phase-Protection, suitable for environmental, industrial defense, and commercial fields.

VAPPRO products conform to U.S. Military specifications, especially for the protection of weapons and vehicles. NACE International, the Worldwide Corrosion Authority partners with the U.S. Department of Defense (DOD) to launch CorrDefense, and online e-magazine highlighting corrosion control efforts of the DOD, the Coast Guard and the National Aeronautical and Space Administration (NASA) as well as projects the agency shares with laboratories, universities, research institutions, and private companies.

Magna VAPPRO products are accessible through the North Atlantic Treaty Organization and its Master Cross Reference List (NATO MCRL). These VCI are assigned NATO Stock Numbers, to facilitate their quoting.

The VAPPRO products conform to the requirements of the European Union (EU) Directive on Restriction of Hazardous Substances (RoHS), which control the use of harmful chemicals that may be noxious to the environment and consumer's well-being.

VAPPRO VCI have been tested and certified by the Bureau Veritas, a well-known organization dealing in quality, health, safety, and environment (QHSE) for the benefit of the general public.

Magna International cooperates with NACE International, with headquarters in Houston, U.S. and having a membership of about 30,000 experts on corrosion management and with the World Corrosion Organization (WCO) which associates many national corrosion organizations, with its central office in China.

Magna International maintains a cooperation relation with the American Chemical Society (ACS), U.S. using the correct chemical definitions and terms for the chemical molecules and reactions.

The North American Free Trade Agreement (NAFTA), which associates the United States, Mexico, and Canada, is familiar with the VAPPRO VCI, being widely applied in natural environments, industrial facilities, and military assets. The NAFTA trilateral trade deal is now being renegotiated an experts believe that an upgrade to this deal is possible, including new rules on digital trade and e-commerce.

Magna worldwide operations are based on the application of the International Standards Organization-ISO 9001-2000, ISO 14001-2004, and ISO 9001-2008 that satisfy the requirements of the VAPPRO consumers. Magna provides VCI and service in many countries including the NATO countries, NAFTA region, the Asia Pacific, and Europe zones, maintaining a high level of science, technology, and innovation, for the creation of novel products in the demanding twenty-first century. Magna International marketing executives are conducting an expansion of their organization and enhancing their knowledge and strategy. All these multiple activities generate a drive towards intense work and useful achievements.

Magna International, as a global enterprise, is committed to social and environmental concerns, to promote greater awareness that minimizes or eliminates harmful corrosion and pollution.

4. Corrosion inhibitors

Practical methods that minimize or eliminate corrosion in the chemical, mineral, fertilizer, electrons, food and beverages, energy, and manufacture industries include:

- Selection of corrosion resistant construction materials, metallic, plastic, ceramic, and composites for fabrication of the plants equipment, machinery, and structures.

- Application of paints, coating, and linings for protection of the industrial plants and energy facilities.
- Cathodic protection (CP) applying sacrificial anodic metals such as aluminum and magnesium and their alloys. An additional CP system employs impressed direct electrical current.
- Corrosion inhibition is a technique widely accepted, the vast industry of corrosion inhibitors (CI) is fast spreading worldwide for various technological and industrial applications such as petroleum oil and natural gas facilities, structures built from steel reinforced concrete, pickling and cleaning steel vehicles during production, protected transportation, and storage of electronic and military equipment; for cooling water systems; as additives for paints, coatings, elastomers, and plastics, to avoid corrosion in natural gas pipelines, to control corrosion in desalination plants [8–12].

To prevent atmospheric corrosion, in particular in humid environments, military equipment, vehicles, and weapons are covered, during long times, with papers, canvas, and plastic sheets fully impregnated with VCI.

Three types of CI, with different inhibition mechanisms, are known:

a. CI that are adsorbed on the metal surface, avoiding metal deterioration. They comprehend organic chemicals such as waxes, oils, and amines.

b. CI that hinder the anodic reaction of metal dissolution and, frequently, for a passive layer.

c. The cathodic CI controls corrosion, for example, by the reduction of dissolved oxygen (O_2).

In the last decade, a new family of inhibitors has emerged, called green corrosion inhibitors, which are relevant in this crucial time of energy problems and economic havoc since they will extend the life of the water infrastructure and save large expenses in materials, equipment, and structures. They belong to the advanced field of green chemistry, also known as sustainable chemistry, which involves the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substance [13, 14].

Types of VCI include nitrite of amines, amine carboxylates, heterocyclic compounds (thiazole, triazole, pyrrole, mercaptans, imidazoline, etc.), carboxylic acid esters, amines, acetylenic alcohols, mixtures, and reaction products of these substances. **Figure 2** shows four molecular structures of synthetic chemicals, developed in modern laboratories, that are the base of the well-known VCI.

In this time of energy crisis, with petroleum prices up and down, and economic global turmoil, it is necessary to develop and implement safe "green" VCI. The oil inventories in many industrialized countries are weighing on oil prices. But frequent filling and emptying of these huge storage tanks, permitting access to humid air, can lead to harmful corrosion events, which, logically, should promote the application of useful corrosion inhibitors.

4.1. Natural corrosion inhibitors

In the context of this section on CI it is worthwhile to present a particular group of CI, called natural CI, which are obtained applying the chemical technology of extraction from vegetables

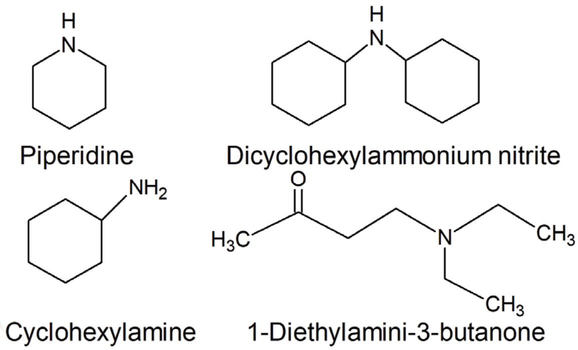

Figure 2. Molecular structures used for production vapor corrosion inhibitors.

using water or organic solvents as extractors. The ancient human communities located around forests and jungles, especially in tropical and arid areas, discovered and extracted medicines from parts of plants, shrubs, and trees such as roots, leaves, flowers, fruits, and seeds. These people took them orally or applied them as oil, cream, or ointments, to prevent and cure diseases, to relieve pain, and to improve their quality of life—in short, to attain the highest possible level of health.

Some natural CI are under experimental development stage and others are applied to prevent, diminish, or control corrosion damage [15–29].

5. Protection mechanisms

VAPPRO VCI protects ferrous and nonferrous metals, including their alloys and multimetals, machinery, structures, and devices. VCI molecules penetrate in recessed areas, voids, crevices, and cavities exposed to saline water and to humid atmospheres.

The protection mechanism of VCI depends on two basic chemical processes described in the following examples.

Ionization is the formation of ions as a result of chemical breakdown of molecules:

$$\underset{\text{Molecule}}{NaCl} \rightleftarrows \underset{\text{Cation}}{Na^{+}} + \underset{\text{Anion}}{Cl^{-}} \tag{4}$$

Hydrolysis is a chemical decomposition involving the splitting of water in hydrogen cation and the hydroxide anion:

$$NaCl + H_2O \rightleftarrows Na^{+} + Cl^{-} + H^{+} + OH^{-} \tag{5}$$

Figure 3 describes how the VCI molecule ionizes and hydrolyzes in the presence of moisture, forming a protective layer on the metal surface.

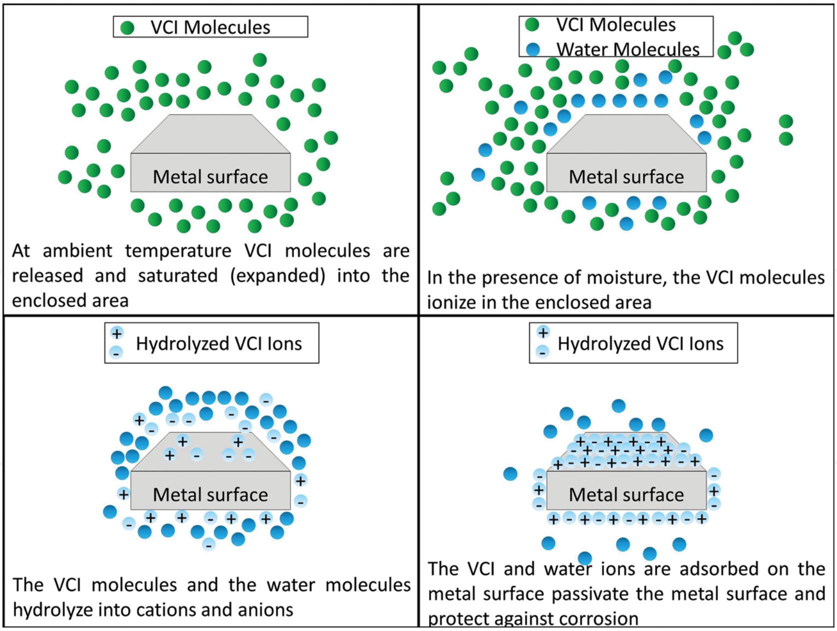

Figure 3. VCI molecule ionizes and hydrolyzes in the presence of moisture, forming a protective layer on the metal surface.

6. Practical applications

VCI products in solid and liquid forms are widely applied to protect components and parts of many industry products: automotive, oil, and gas, offshore and onshore, water supply and cooling, marine including oil tankers, military vehicles, and weapons, manufacture machines and tools, electronic and electrical devices, and concrete structures. These VCI are presented, packaged, and distributed in accordance to the form, size, and characteristics of the system being protected against corrosion.

6.1. Emitters and foams

Emitters consist of a piece of plastic foam impregnated with VCI, particularly suitable for the protection of enclosures holding electrical gear, relays, contactors, switches, and connectors. (**Figure 4**) The vapor does not increase the electrical resistance of these devices. Diverse foam types are used to produce emitters such as breathable polyurethane which is utilized as a tape with a self-adhesive backing. A VCI foam pad combines the resiliency and light weight of the inhibitor impregnated foam.

6.2. Pouches

Pouches are made from DuPont Tyvek, plastic material, to meet packaging applications for electronic devices, military parts of weapons, and protection against atmospheric corrosion factors. Other pouches are prepared from spun-bonded polyethylene fibers, which are located in the enclosed space holding the metallic parts to be protected (**Figure 5**).

6.3. Films

Thin antistatic polyethylene film containing VCI to protect metal parts from rust, tarnish, stains, water spots, and sulfide attack. They appear as custom size bags, sheets, tubing, sleeves, and roll stock. They are appropriate for protection during shipment and storage. Their UV stabilization extends the film life making it useful for outdoors, corrosive environment [30].

6.4. Impregnated papers and canvas

Military assets require implementation of corrosion control and monitoring techniques, in particular during long periods of storage, under the open skies, sometimes with falling rains and snow. Special papers such as kraft and stone, plastic sheets, and textile canvas, well impregnated with VCI, are applied to cover equipment, vehicles, and weapons [31].

The U.S. armed forces under the guidance of the U.S. Department of Defense (DOD) and its Office of Corrosion Policy and Oversight (CPO) maintain a Website (www.CorrDefense.org) and

Figure 4. Foam emitter device with VCI.

Figure 5. Breathable pouches containing vapor corrosion inhibitor.

publish an electronic magazine that features content on corrosion and corrosion control of military facilities. The diverse VCI impregnated sheets have proven to work for long periods [32].

Delicate machinery parts are kept in warehouse in closed VCI impregnated paper envelopes, cardboard boxes, or wrapped with textiles.

Most of the military equipment and arms are continually kept in reserve, so it is important to protect them while maintaining their original properties such as reliability and readiness for warlike operations. Heavy cannons on wheels, military hardware on wood pallets, and large weapons are wrapped with distinct fabrics, all impregnated with VCI. These covers are easy to install and are resistant to UV radiation, moistures, rain, snow, dust, and mold and are durable (**Figure 6**).

6.5. Coatings and paints

VCI are used as additives to improve their function as a barrier that impedes to reach the metal surfaces by the corrosive parameters and damage the machines and structures.

A wax coating, containing VCI, is particularly useful in marine and industrial rust proofing application in ferrous and nonferrous metals. A paint made from an acrylic polymer with an added nontoxic, organic VCI offers corrosion protection in outdoor environments. Magtan is an unpigmented primer that converts the rust into a more stable iron compound. Pro-Disc is a water-based coating that combines VCI with a nonslip, safe material. It was developed to protect brake disks of military vehicles during short storage or long mothballing without affecting the braking efficiency of the vehicle. Electrospray provides protection for circuit boards, relays, and electrical equipment without changing electrical properties of installations (**Figure 7**).

6.6. Powders

VCI in the form of powder are water soluble, do not contain phosphates and chromates, are used in low dosage for closed loop cooling system, hydrotesting, and marine fields.

These polymolecular VCI are added to seawater as a powder; then it converts into a colloidal suspension with nanoparticles dissolved in the water. These particles are adsorbed on the steel wall, forming a thin protective film. Their performance depends on physical, biological, and chemical factors.

Figure 6. Steel combustible tanks, ready for covering with a VCI protective cloth.

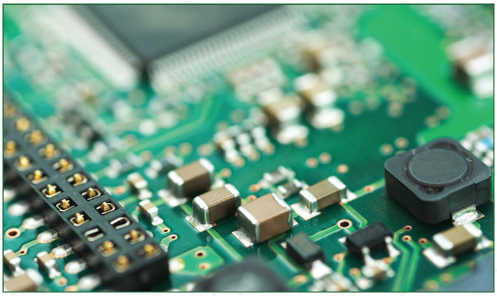

Figure 7. Printed circuit board protected by VCI electrospray.

Petroleum tankers (**Figure 8**) are ships specially designed and constructed at American and Asian shipyards for the bulk transportation of crude oil from extraction sites to the refineries. In its way back the tanker holds are full of seawater to provide it adequate stability. VCI are added to this ballast water to provide protection against corrosion. According to U.S. federal mandate all tankers in U.S. waters should have double hulls to diminish oil spill and damage to the environment, in case of hull rupture accident. Pipes, fire-water storage tanks, and hydrotest water are dosed withe these powder VCI [33].

6.7. Gun lubricants

Weapons, small and personal such as pistols and rifles, and big, installed and operated on land, sea and air vehicles should be kept clean and well lubricated for an efficient action. Arm-Kleen, which includes VCI, was specially developed for the cleaning of small arms and for automatic weapons mounted in all kinds of vehicles. The weapons should be cleaned before and after firing, learning a temporary protective coating for a period of several weeks. Once applied, the removal of VCI is unnecessary [34].

Such anticorrosive gun lubricant fuses itself into the metal gun barrel, smoothening out the metal surface of the asperities, and greatly reducing the coefficient of friction. The lubricant

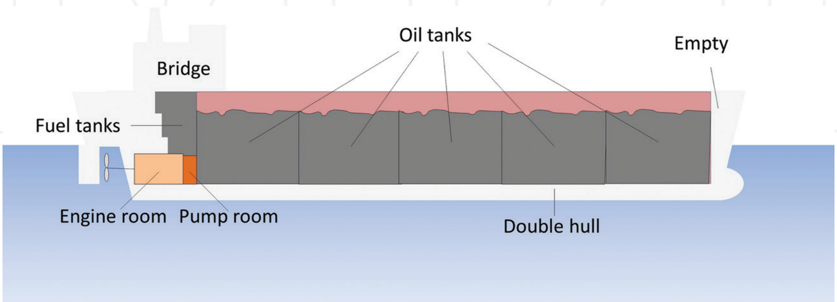

Figure 8. Petroleum transportation tanker showing holds containing ballast water with VCI powder.

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that cleans also displaces moisture of the weapon's internal parts. These products conform to military standards: MIL-SPEC:MIL-PRF-634600 and MIL-C-372.

6.8. Aerosols

These VAPPRO aerosols, fortified with VCI, that protect electrical equipment, are presented in a variety of forms. Electrospray avoids corrosion against humid environments. A light oily liquid gives off an invisible vapor to protect machine tools, hand tools, and weapons subject to rusting and atmospheric corrosion. A penetrant dissolved in a solvent provides reliability in locating surface flaws; it is easily removed at the end of testing. It conforms to MIL-I-25135-E.

6.9. Master batch additives

The master batch VCI, identified as MB, are often dissolved in many media: water, oil, solvent, and kerosene, in accordance to their intended application, e.g., metal working fluids, inks, rust inhibitors and removers, gears, and engine and machine oils. Some are tacky, emulsifiable, viscous liquids with film forming properties.

VCI MB can be produced for special objectives, e.g., a low density polyethylene (LDPE), a resin to protect equipment functioning in aggressive, corrosive environments such as petroleum refineries and chemical plants.

6.10. Concrete rebar inhibitors (CRI)

Concrete is a composite material, useful for the construction of structures in land, water, and seas. It is made of mixture of water, Portland cement, sand, and mineral aggregates. Steel reinforced concrete is generally very durable; nevertheless concrete infrastructure, in particular in marine environments, can undergo visible damage due to penetration of seawater, reaching the steel reinforcement [35, 36].

Concrete and steel are the primordial engineering materials for the construction of the infrastructure of a nation, including bridges, buildings, highways, tunnels, parking garages, breakwaters, port piers, dam walls, offshore oil platforms, sport stadia, and electric transmission tower foundation. The principal cause of degradation of the steel reinforced structure is the corrosion attack to the rebar embedded in the concrete by CO_2 dissolved in seawater, increasing its pH to about 8.0, in conformance with the following equilibria:

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+ \tag{6}$$

$$CaCO_3 + H_2O \rightleftarrows Ca^{+2} + HCO_3^- + OH^- \tag{7}$$

CO_2 and chlorides enter into the concrete body, reach the steel rebar, leading to the breakdown of passivity, a process called carbonation. The rebar loses thickness and, consequently, its strength, being the primary cause of damage and the collapse of the concrete structure. CRI-VCI have the ability to prevent and/or mitigate this event (**Figure 9**).

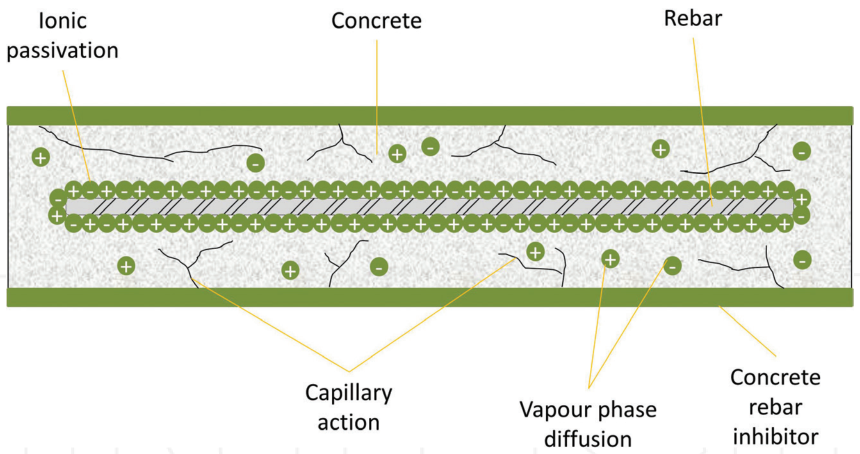

Figure 9. Protection mechanism of the concrete steel rebar.

VAPPRO concrete rebar inhibitors (CRI) are produced in special physical form and chemical composition, in accordance with their intended application, as follows:

- Concrete surface treatment (CST), to assure an impervious concrete surface, to avoid penetration of noxious agents present in the environment.
- VAPPRO rebar coating (VRC), to impart a protective coating on the rebar, that will be stable in contact with humid and dry concrete.
- Concrete repair products, to rehabilitate damaged concrete structure, covering them with fresh, alkaline concrete, providing conditions of its stable curing.
- Concrete additive treatment, adding to fresh concrete VCI soluble in solvents, specially designed for corrosion control in high humidity and high salinity environments.

7. Corrosion testing

The determination of the protection properties of the VCI and their corrosion avoidance performance are done by laboratory tests, simulating the relevant environmental and industrial conditions. ASTM and NACE standards were applied based on gravimetric, electrochemical, and surface examination methods and instruments, as recorded in the following.

ASTM standards detailed in:

- G1, preparing, cleaning, and evaluating corrosion test specimens.
- G3, electrochemical measurements in corrosion testing.
- G4, conducting corrosion test in field applications.

- G5, potentiostatic and potentiodynamic anodic polarization measurements.
- G31, laboratory immersion corrosion testing of metals.
- G59, conducting potentiodynamic polarization resistance measurements.

NACE standards:

RP 0300	Corrosion of metals and alloys
TM 0169	Laboratory corrosion testing of metals
SP 0308	Inspection methods for corrosion evaluation of conventionally reinforced concrete structures
TM 0208	Laboratory test to evaluate the vapor-inhibiting ability of volatile corrosion inhibitor materials for temporary protection of ferrous metal surfaces

8. Conclusions

The VAPPRO corrosion inhibitors are designed and produced, taking into account the metallic materials and the structures to be protected and the physical, chemical, biological, and thermal conditions of the natural or industrial environment in which they operate.

VCI are utilized in diverse forms such as emitter devices, pellets, powders, additives to coatings and paints, aerosols, gun lubricants, master batch additives, impregnated papers and textiles, for concrete rebar protection, aqueous and solvent solutions, and in pouches and sachets.

The proper use of VCI in combination with a system of automated corrosion sensors is an effective means of preserving machinery, equipment, vehicles, and weapons, during long-term storage, with savings in maintenance costs.

The selection of the most appropriate VCI for a corrosion-prone system is based on its cost, ease of availability, workers safety, chemical stability, and saving in maintenance. The choice should be made in accordance with the corrosion expert knowledge and experience, and it is a compromise between technological and economic criteria.

Magna executives, designers, organizers, and employees know that to progress the key is to keep learning and improving and to increase knowledge and enrich experience to constantly renew themselves.

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