CORROSION PROTECTION METHODS OF STRUCTURAL STEEL AGAINST ATMOSPHERIC CORROSION

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Abstract: The aim of this study is to examine the anticorrosive performance of two different primers, one based on VpCI technology and the other based on rust converter technology, against atmospheric corrosion of steel reinforcement exposed to the atmosphere, prior to its installation into concrete. The performance against atmospheric corrosion of the aforementioned corrosion inhibitor was evaluated by means of microscopy techniques and corrosion rate measurements (electrochemical and weight loss measurements). Electrochemical parameters such as corrosion current density, Icorr, and linear polarization resistance, Rp were evaluated. In addition, Measurements of the bond strength between concrete and steel treated with the corrosion inhibitor primers were performed in order to investigate their effect on bond strength between the steel surface and concrete. Furthermore, visual observations were used to identify the rust strains and the corrosion product morphology of steel reinforcement before its installation into the concrete. The results indicate that both primers exhibit satisfactory protective behavior under the specified conditions.

Keywords: Vapour phase corrosion inhibitors- rust converters- atmospheric corrosion

Introduction

The process of atmospheric corrosion is a natural action of a material, in most cases a metal, returning to its original state through an electrochemical process caused by a reaction with the surrounding environment. Even though it is a natural process, there are certain environmental conditions to which metals are exposed during manufacture, processing, storage, or shipment that can aggressively accelerate the degradation. In normal atmospheres containing pollutants, metals begin to corrode at this accelerated rate when the relative humidity of the air layer next to the surface exceeds about 75%, mostly in coastal areas where the main factor of corrosion is the presence of chloride ions [1,2]. Greece is a country surrounded by sea, with high average temperatures and high relative humidity during the summer. The sea spray and wind driven salt leads to the formation of corrosion products on the surface of steel reinforcement, which many times is left exposed during transportation and storage at buildings sites for a long period prior to its installation in concrete structures. When these weathered steel bars are to be used, the presence of corrosion products affects the concrete/steel bond strength and the chemical composition of the cement. If they are going to be considered viable as a construction material, these weathered reinforcement bars should be used only if their corrosion products do not have any detrimental effect on the mechanical and chemical properties of concrete. As a result of the concerns mentioned above, the question, that emerges is when such corroded steel rebar can be used without causing harmful effects on the mechanical and corrosion behavior of reinforced concrete structures [3].

The protection of steel rebar prior to its installation into the concrete is of great importance for the durability of concrete structures and prevents great economic loss.

Among the available protection systems for steel, the use of coatings is the most popular and economical method. Over the last decade, the need for environmentally safe coatings gave rise to many research studies with significant results that promoted the use of anticorrosive coatings containing vapor phase corrosion inhibitors commercially.

VpCIs are organic compounds (such as amine based compounds) that have *sufficient vapor pressure* under ambient atmospheric conditions to essentially travel to the surface of the metal by diffusion and physically adsorb onto it, including recessed areas and cavities not reached with conventional methods. In the presence of moisture, the VpCI molecule becomes polarized and is attracted to both anodes and cathodes on the metal. Once the VpCI protective ions have adsorbed onto the surface, the electrochemical process of corrosion is interrupted as *the ions create a protective barrier to contaminants* such as oxygen, water, chlorides, and other corrosion accelerators. With the protective barrier in place, the corrosion cell cannot form and corrosion is halted. That barrier self-replenishes through further condensation of the vapor [4, 5, 6].

VpCI technology focuses on the metal itself, actually passivating the metal's surface. In fact, VpCI molecules use the same mechanism that accelerates corrosion to accelerate the release of protection molecules as a built-in defense mechanism. Whereas many methods of corrosion protection alter the metal (i.e., stainless versus carbon steel, cathodic protection, and treatment of metal), VpCIs do not alter the surface as the protective ions are *adsorbed* to the surface rather than becoming *permanently attached* [7].

Electrochemical behavior investigations show that these VpCI compounds belong to mixed or "ambiodic" inhibitors capable of slowing both cathodic and anodic corrosion processes. The reduction of the cathodic reaction results from a decrease in oxygen concentration caused by the formation of an adsorbed film that acts as a diffusion barrier for oxygen. Strong inhibition of the anodic reaction results from the inhibitor's two acceptor-donor adsorption centers that form a chemical bond between the metal and the inhibitor. Adsorption of mixed VpCI compounds changes the energy state of metallic ions on the surface, diminishing the tendency of metal to ionize and dissolve [8].

The two important properties of VpCIs are the functional groups linked to the nucleus of the inhibitor molecule, which are responsible for the adsorption, thickness and inhibition efficiency of the absorbed film, and the hydrophobic properties of VpCIs, which allow them to act as buffers to hold the pH at the metal inhibitor interface on the alkaline side for optimum corrosion protection.

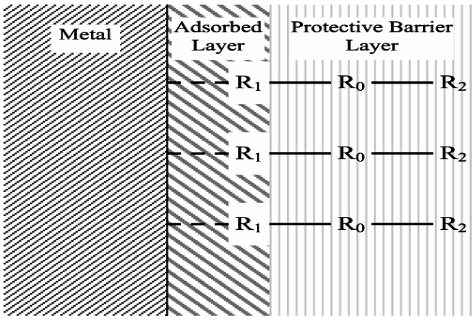


Figure 1: Proposed inhibition mechanism

The functional group (R1), linked to the nucleus (R_0) of the inhibitor molecule, is responsible for establishing a stable bond with the metal surface and controls how firmly the inhibitor is adsorbed on the metal. The functional group (R2), also linked to the nucleus, controls the thickness and penetrability of the film, which is important in resisting the penetration of aggressive ions. As the inhibitor molecules are adsorbed on the metal surface, the R_2 groups form a continuous line of defense to protect the metal from corrosive species [9].

In this work the performance against atmospheric corrosion of reinforcing steel rebar of two primers was evaluated, a neutral rust converter and an organic primer coating containing VpCI corrosion inhibitor. These primers are available in the market for coating metallic surfaces which are already corroding. The rust converter has a pH of 7, can be directly applied to rust and also combines with existing rust to form a permanent protective layer of a ferro-organic-acid-free coating. Rust is reduced to pure iron and the liberated oxygen molecules are bound together to form a black protective layer which prevents any new corrosion [10].

$$Fe^0 \leftrightarrows Fe^{+2} \leftrightarrows Fe^{+3}$$

The experimental procedure was built to simulate three typical exposure conditions for storage areas and building sites of reinforcing steel located in coastal and urban regions, where the weather is characterized by pollutants such as: sulphur dioxide (SO_2), salt particles (Cl^-) and carbon dioxide (CO_2), high temperatures and relative humidity. In the present study the interest in atmospheric corrosion of reinforcing steel lies in the fact that Athens has a marine environment (Cl^-) with a combination of urban contaminants, for example SO_2 and CO_2.

The experimental method used to assess the condition of the steel rebar included weight loss measurements throughout the experimental period. Measurements of the bond strength between concrete and steel rebar were performed in order to investigate the effects of the corrosion products on steel surface.

Materials and evaluation methods

For all test specimens S500s Temcore reinforcing steel was used. The steel rebar specimens had a cylindrical shape (100 mm long and 12 mm ∅).

Table 1 : Chemical compositions (% atom) of steel rebar S500s, type of Tempcore

C	Mn	S	P	Si	Ni	Cr	Cu	V	Mo
0.18	0.99	0.047	0.023	0.15	0.09	0.09	0.21	0.002	0.021

Prior to exposure, the surface of the steel rebar was washed with water, then immersed for 15 min in strong solution of HCl (500 ml HCl in 1000 ml distilled water, density 1.19 g/ml^3) with organic corrosion inhibitor (3.5 g hexamethylene tetramine in 1000 ml distilled water) washed with distilled water to eliminate traces of the corrosion inhibitor and chloride ions (according to ISO/DIS 8407). Following that, they were cleaned with alcohol and acetone and then weighed to 0.1 mg accuracy.

The two above mentioned primers were then applied to the steel rebar specimens and left in a drying chamber (T = 40°C, RH = 50%) for 7 days.

The test specimens were exposed to atmospheric conditions over a period of 18 months on the roof of the Chemical Engineering building at Zografou campus in Athens.

The performance against atmospheric corrosion of the aforementioned corrosion inhibitor and rust converter was evaluated by means of corrosion rate measurements (electrochemical and weight loss measurements). Electrochemical parameters such as corrosion current density, I_{corr} and linear polarization resistance, R_p, were evaluated. In addition, measurements of the bond strength between concrete and steel treated with corrosion inhibitor were performed in order to investigate the effect of corrosion inhibitor on bond strength between the steel surface and concrete.

For all the electrochemical measurements, a standard corrosion cell was used. The corrosion cell consisted of a reference electrode which was a Saturated Calomel Electrode (*SCE*) in a luggin capillary filled with electrolyte (NaCl), a working electrode which was the reinforcing steel and a counter (auxiliary) electrode. A carbon electrode was used as the counter electrode.

In the LPR technique, the reinforcing steel bar is polarized to ± 20mV of the open circuit potential (E_{corr}), the potential at which the current varies linearly with applied potential. In the Tafel technique, the reinforcing steel bar is polarized to ± 250mV of the open circuit potential (E_{corr}). The potential scan rate used for both techniques was 0.1mV/sec.

Steel pull out testing was carried out according to ASTM C-234, to investigate the difference in bond stress and rebar slip behavior.

Results and discussion

1. Weight loss measurements

After 6, 12 and 18 months of exposure the test specimens were removed and cleaned according to the standard (ISO/DIS 8407.3). The weight loss of the steel rebar was determined and the corrosion rate evaluated using the following equation:

$$\text{Corrosion Rate } (\mu\text{m/year}) = 8.76 \times 10^{7} \frac{W}{A \times T \times D} \qquad (1)$$

Where W: weight loss (g), A: area of steel specimen (cm^2), T: exposure time (h), D: density of steel (7.8g/cm^3).

The results of the mass loss (%) and corrosion rate measurements for the 6, 12 and 18 months of exposure are given in Fig. 2 and 3.

The results of the rust converter primer are not shown in these figures because of the excellent adhesion of the rust converter to the steel surface and the extremely low values of weight loss.

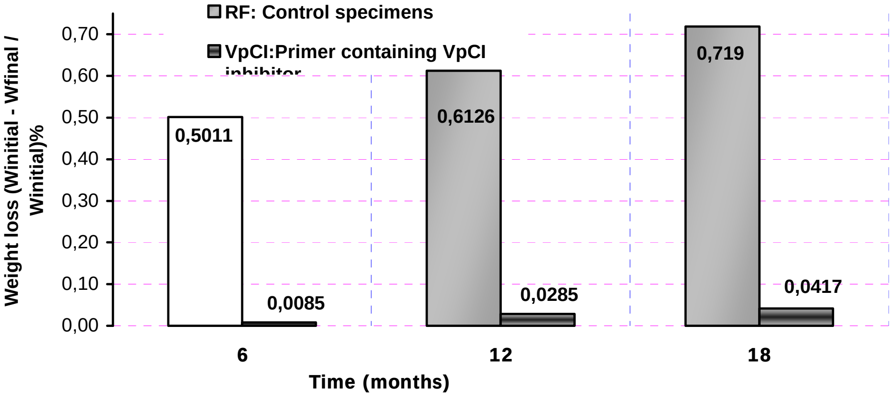


Figure 2: Gravimetric weight loss measurements after 6, 12, and 18 months of exposure for the control (RF) and VpCI primer coated specimens.

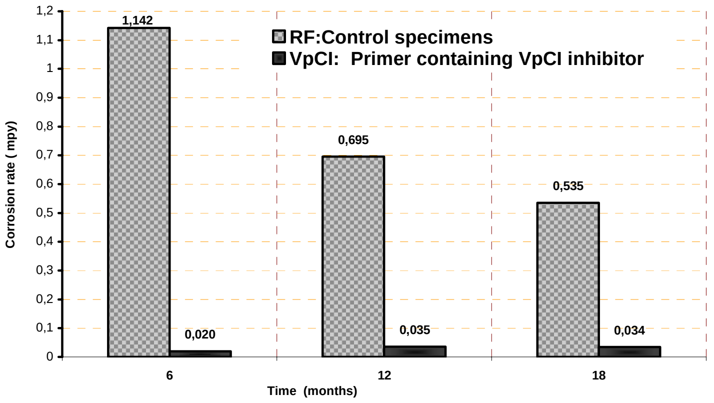


Figure 3: Corrosion rate measurements of control (RF) and VpCI primer coated reinforcement after 6, 12 and 18 months of exposure.

2. Electrochemical measurements

Linear polarization and Tafel techniques were used in this study for the determination of the anticorrosive performance and the rate of protection against atmospheric corrosion examining electrochemical parameters.

The results from electrochemical measurements are summarized in Table 2, and it can be seen that both techniques show similar responses and both coatings provide significant corrosion protection. The Icorr vs. exposure time values of the polarization technique are displayed in Figure 4.

Table 2: Linear polarization and Tafel technique electrochemical parameters evaluated during the exposure time.

Specimens type	**Exposure time (months)**	**Linear polarization technique**			**Tafel technique**	
		I_{corr} ($\mu A/cm^2$)	**R_p** (kOhms)	**Corrosion Rate** (mpy)	**I_{corr}** ($\mu A/cm^2$)	**Corrosion Rate** (mpy)
RF	6	4451	6,265	132,16	3705	110,0
RU		41,72	536,9	1,239	20,25	0,6013
VpCI		29,33	784,1	0,871	49,03	1,4560
RF	12	5615	3,896	166,75	5430	161,4
RU		216,1	133,7	6,416	103,8	3,082
VpCI		104,8	342,3	3,113	50,53	1,5010
RF	18	4373	5,0335	144,4	6033	184,9
RU		189,8	117,8	5,763	57,66	1,712
VpCI		174,2	228,9	5,130	62,06	1,8960

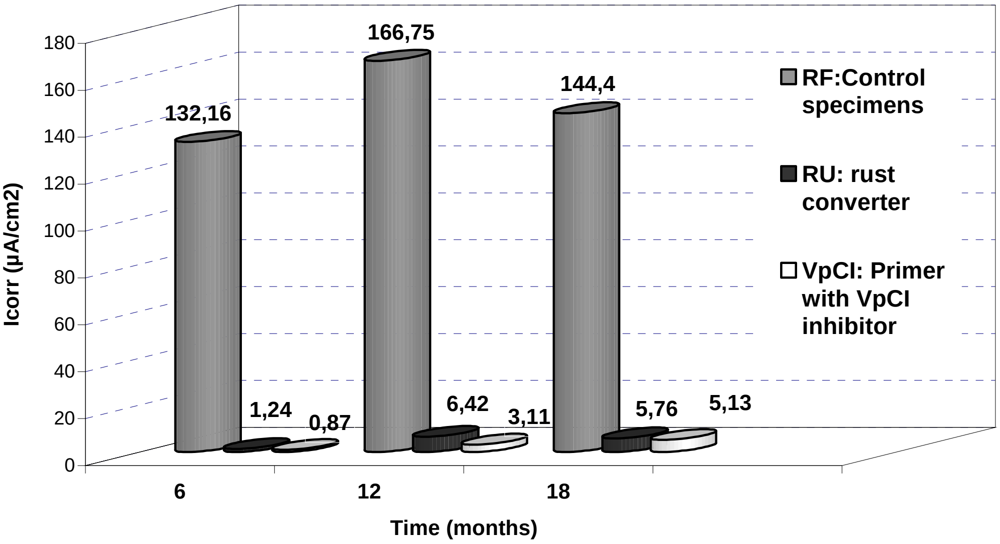
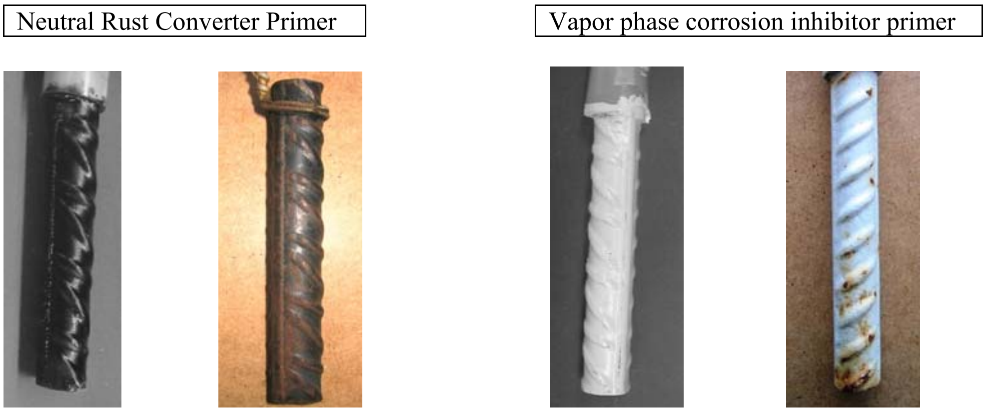


Figure 4: Corrosion current density for the 6, 12 and 18 months of exposure

3. Visual Observation



t = 0 days t = 18 months exposure t = 0 days t = 18 months exposure

Figure 5: Images of the state of corrosion on steel reinforcement coated with the neutral rust converter and the vapor phase corrosion inhibitor coating, present at the beginning of exposure and after 18 months.

CONCLUSIONS

The results show that both primers offered significant protection against atmospheric corrosion, especially the VpCI primer.

Visual observation of the rebar after 18 months of exposure in atmospheric conditions show that corrosion products appear mainly at the neurons of the rebar on the specimens coated with the RU primer, whereas those coated with the VpCI primer show pitting corrosion over a small area of the specimens.

The electrochemical measurements listed in Table 2 shows that the VpCI primer provided better corrosion protection and 23 times better corrosion resistance than the control specimens.

There is not a considerable difference between the two coatings on the effect they cause on the bond strength between the concrete and the rebar in pull-out measurements. There was also no significant difference between measurements on the coated specimens versus the control.

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