RESEARCH ARTICLE

Morphology and Composition of Corrosion Products Formed on Painted Mild Steel in Marine Atmosphere after 4, 8 and 12 Months Exposure

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Manuscript Info	***Abstract***

Corrosion is one of the few chronic issues pertaining to marine structures. It is significant to characterize the corrosion products formed on the metal surface in the order to establish the nature of corrosive attack and for the development and improvement of the material's corrosion resistance. In this study, characterization of the corrosion products formed on painted mild steel was carried out. Painted mild steel test panels were exposed to marine atmosphere in Karachi, Pakistan according to ISO 8565 norm for a period of 12 months. Morphology and composition of the corrosion products formed after four, eight and twelve months of exposure were studied by scanning electron microscopy (SEM)/energy dispersive X-ray (EDX) analysis. Lepidocrocite (γ-FeOOH) was found as major component of corrosion products formed after 4 and 8 months of exposure. After 12 months of exposure corrosion product obtained was composed of lepidocrocite (γ-FeOOH), goethite (α-FeOOH) and magnetite (Fe$_3$O$_4$). Changes in the morphology and size of lepidocrocite (γ-FeOOH) formed after 4, 8 and 12 months of exposure were noticed. Presence of very harmful form of rust that is lepidocrocite could be realted to very high corrosivity of the marine atmosphere of Karachi, Pakistan. The conversion of lepidocrocite to goethite (α-FeOOH) was also noticed.

Introduction

The word corrosion is derived from the latin word 'corrosus' which means eaten away or consumed by degrees; an unpleasant word for an unpleasant process [1]. Paint Research Association of United Kingdom has estimated that in developed countries corrosion costs about 4 % of their annual Gross National Product (GNP) and it is claimed that around one-third of this could be prevented. In the UK this would equal to about £30 billion while in United States it cost about US $300 billion [2].
Marine atmospheres are usually highly corrosive. The corrosiveness of a marine environment depends on the topography of the shore, wave action at the surf line, temperature, rainfall, prevailing winds and relative humidity. The corrosiveness decreases rapidly with increasing distance from the shore while severe storms can carry salt spray inland as much as 15 Km [3]. In marine atmosphere, salt is deposited on metal surfaces by marine fog and windblown spray droplets. This contamination induces severe corrosion due to its electrochemical boost at relative humidities exceeding about 55 %. Chloride ion is principal culprit in marine atmospheric corrosion. Chlorides are deposited mainly in the marine and marine industrial atmosphere as droplets or as crystals formed by evaporation of spray carried by the wind from the sea [4-5].
Studies have shown that corrosion can cost a country to at least 4-5 % of the GNP [6]. Design engineers essentially require corrosivity data of an area and the corrodants present in environment in order to reduce down corrosive deprivation [7]. Corrosion rate is primarily governed by the characteristics of the corrosion products. This is very

important to characterize the corrosion products formed on the surface in the order to establish the nature of corrosive attack and for the development and improvement of the material's corrosion resistance. The barrier effect of corrosion products layers depend on their thickness, compactness, uniformity, porosity, solubility, adhesion and other characteristics, and can significantly affect the corrosion rate and attack morphology through different mechanisms. Corrosion products once adequately developed and formed in adhere layers, attenuate the effects of meteorological and pollution variables [8]. Studies related to the characterization of corrosion products formed in atmospheric conditions have been reported worldwide [7-17]. Scanning electron microscopy (SEM) technique can be used to characterize the morphological structure of corrosion products [14, 16-17].

Karachi is an industrial hub and metropolitan coastal city of Pakistan. Corrosion is a key problem to all metallic installations and concrete structures situated at Karachi's coastal areas. A colossal damage to installations and equipment as well as civil property has been experienced in the past decades since the increased maintenance requirement of coastal areas. Generally marine environment is classified as high corrosivity medium while Karachi coastal environment is extremely corrosive as it has marine plus industrial anthropogenic conditions. The aim of this paper is to identify the components of the corrosion products formed on painted mild steel exposed to marine atmosphere in Karachi, Pakistan over a period of 12 months. The corrosion products formed after four, eight and twelve months of exposure were characterized by scanning electron microscopy (SEM)/energy dispersive X-ray (EDX) analysis.

Materials and Methods
Preparation and Exposure of Test Panels
Mild steel panels with a size of 10 cm x 15 cm were cut from 1.2 mm thick mild steel sheet provided by Hino Pak Motors Limited (Body Operation Plant). The panels were subjected to a surface degreasing process using a suitable detergent. This was followed by rinsing and drying. For the surface preparation each panel was pre-treated with a mixture of $Zn_3(PO_4)_2$ and H_3PO_3 solution. After surface preparation, commercially available paint coating was applied on the panels following the manufacturer's recommendations. The coated panels were left for drying and curing of the paint coating system. In order to identify the coated panels, tags were used. The bottom of each dried and cured coated panel was scribed with an X, in the coating, reaching through to the base mild steel. To prevent premature coating failure, the backside and edges of the coated panels were protected with a tape.

Prepared coated panels were exposed at the marine test site situated in Karachi, Pakistan over a period of 12 months. This test site was located at Hawke's bay of Arabian Sea coast (24° 51′ 02.63″ N, 66° 53′ 08.26″ E). Atmospheric exposure test was carried out according to ISO 8565 [18] norm. At the test site, coated panels were mounted on exposure stand facing south at an angle of 45^0 from the horizontal. During the exposure of coating at test site, visual examination of the anticorrosive performance in the scribed region was done from time to time. Data related to the anticorrosive performance of paint coating has been published [19]. In order to expose the corrosion products, paint coating was removed from the panels according to ISO 4628-8 [20] norm using paint remover.

Corrosion Products Analysis
Scanning electron microscopy (SEM) was used to study the surface morphology of the corrosion products formed on painted mild steel test panels after four, eight and twelve months of exposure. Small pieces of corrosion products were scraped from the test panels then coated with gold up to 300 A^0 using a gold coater (JEOL JFC 1500). Finally the SEM micrograph was taken by using a Scanning electron microscope (JEOL 6380A), equipped with an X-ray detector for energy dispersive X-ray (EDX) analysis. EDX technique was used for the compositional analysis of the corrosion products. The microscope was operated at 10^{-7} Torr vacuum and 30 kV accelerating voltage was applied.
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Results and Discussion

Morphology and Composition of Corrosion Product Formed on Painted Mild Steel in Marine Atmosphere after 4 Months Exposure
Figure 1a showed the scanning electron image of the corrosion product formed in marine atmosphere after 4 months of exposure. It seems that the rust formed on the surface was flowery in appearance, characteristic of lepidocrocite (γ-FeOOH). Formation of rust on iron is an electrochemical reaction. Iron oxidizes to give Fe^{+2} ions while reduction of atmospheric oxygen yields OH^- ions. Both Fe^{+2} ions and OH^- ions combine to give $Fe(OH)_2$. Further oxidation of $Fe(OH)_2$ give up $Fe_2O_3.H_2O$ or $2FeOOH$. In marine atmosphere humidity is high so iron is first corroded to lepidocrocite (γ-FeOOH) [21]. It is usually the first oxyhydroxide formed and is identified by many researchers as a part of rust developed in marine atmosphere [5, 16].

The composition of corrosion product formed in marine atmosphere after 4 months of exposure was identified by energy dispersive X-ray (EDX) analysis and is presented in Figure 1b and Table 1. EDX spectrum reveals the presence of iron and oxygen as main elements while chlorine was also found. Presence of chorine may be due to the reason that chloride ions are chief pollutant in marine atmosphere [5]. Characteristics of the rust layers are greatly influenced by the level of chloride deposition. These deposited chloride ions are ultimately responsible for the formation of lepidocrocite (γ-FeOOH) or akaganeite (β-FeOOH). It is well-known that the phase akaganeite (β-FeOOH) forms only when the chloride ion concentration is very high. In the presence of moderate amount of chloride ions formation of lepidocrocite (γ-FeOOH) takes place [5].

a) Flowery structure of Lepidocrocite (γ-FeOOH)

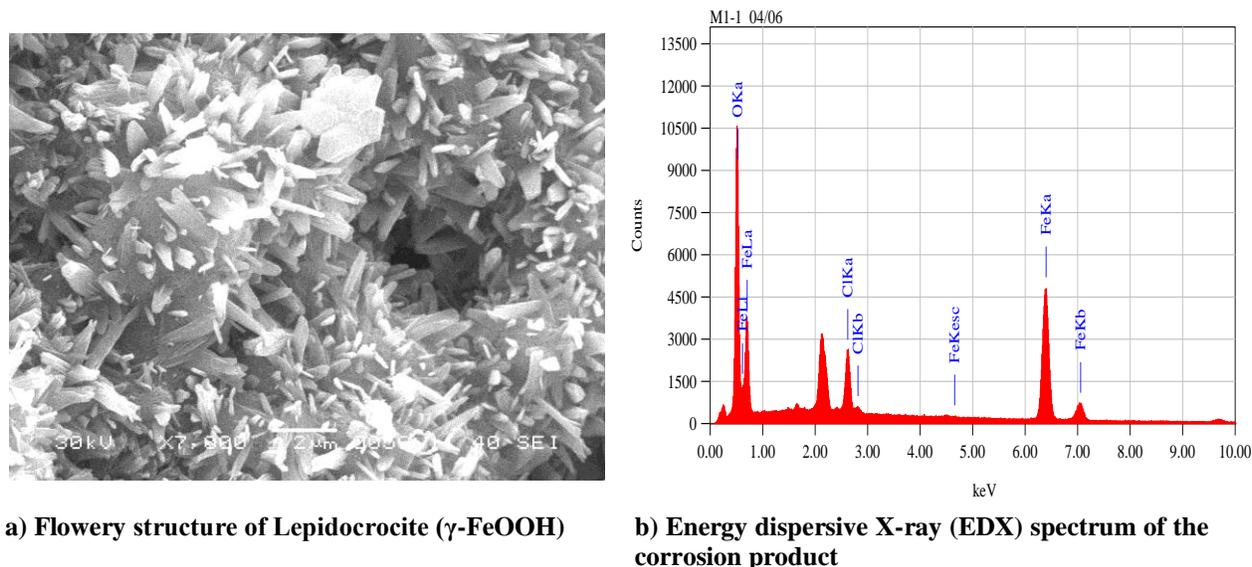**b) Energy dispersive X-ray (EDX) spectrum of the corrosion product**

Figure 1: Scanning electron micrograph (SEM) and Energy dispersive X-ray (EDX) spectrum of the corrosion product formed on painted mild steel after 4 months exposure

Table 1: Composition of the corrosion product formed on painted mild steel after 4 months exposure as determined by EDX analysis

Element	Binding Energy (kev)	Mass %
O	0.525	33.49
Cl	2.621	5.52
Fe	6.398	60.99
Total		**100.00**

Morphology and Composition of Corrosion Product Formed on Painted Mild Steel in Marine Atmosphere after 8 Months Exposure

Figure 2a showed the scanning electron image of the corrosion product formed in marine atmosphere after 8 months of exposure. It looks that the rust formed on the surface was flowery in appearance, characteristic of lepidocrocite (γ-FeOOH). Changes in the morphology and size of lepidocrocite (γ-FeOOH) formed after 8 months of exposure was noticed

The composition of corrosion product formed in marine atmosphere after 8 months of exposure was identified by energy dispersive X-ray (EDX) analysis and is presented in Figure 2b and Table 2. EDX spectrum reveals the presence of iron, oxygen and chlorine.

Lepidocrocite (γ-FeOOH) is responsible for accelerating the corrosion rate. Lepidocrocite (γ-FeOOH) is commonly porous. Electrolyte and corrosive species particularly SO_2 and NO_2 penetrate through the flowery structure of lepidocrocite (γ-FeOOH) and lower the pH. This condition accelerates the dissolution of lepidocrocite as a result concentration of Fe^{3+} increases which in turn causes further oxidation of iron because of its oxidation ability. So lepidocrocite (γ-FeOOH) is generally considered as harmful rust [21].

(a) Flowery structure of Lepidocrocite (γ-FeOOH)

(b) Energy dispersive X-ray (EDX) spectrum of the corrosion product
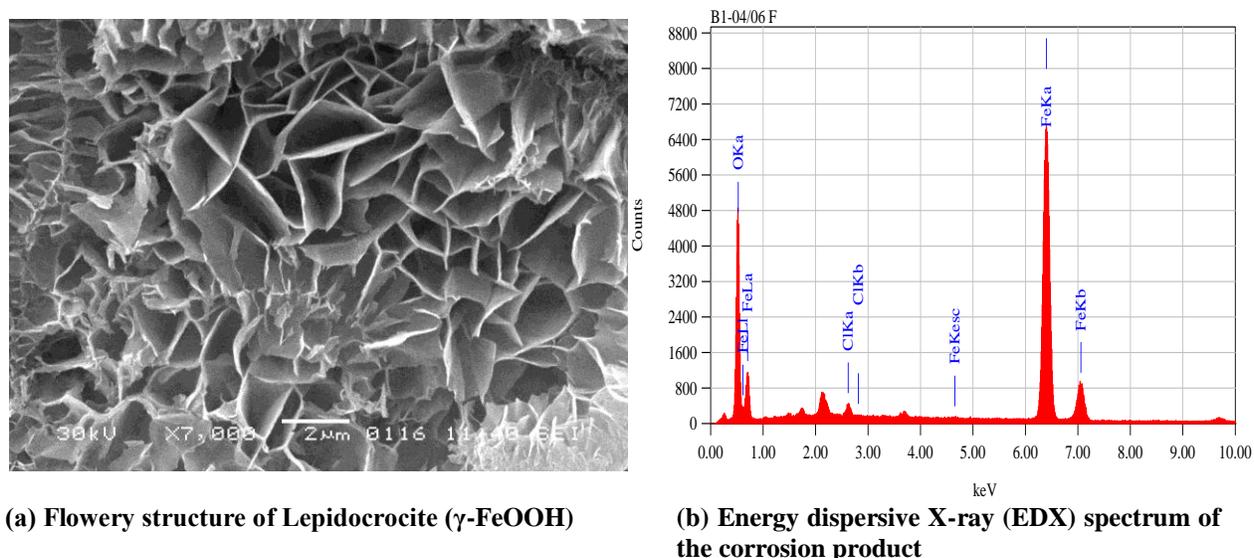
Figure 2: Scanning electron micrograph (SEM) and Energy dispersive X-ray (EDX) spectrum of the corrosion product formed on painted mild steel in marine atmosphere after 8 months exposure
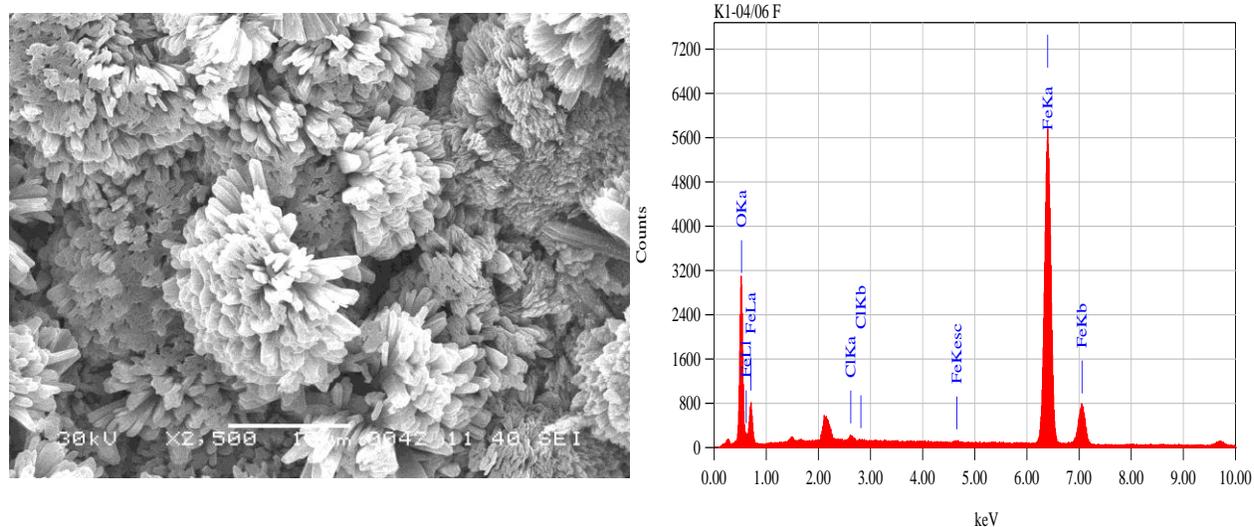
Table 2: Composition of the corrosion product formed on painted mild steel in marine atmosphere after 8 months exposure as determined by EDX analysis

Element	Binding Energy (kev)	Mass %
O	0.525	40.58
Cl	2.621	1.02
Fe	6.398	58.39
Total		**100.00**

Morphology and Composition of Corrosion Product Formed on Painted Mild Steel in Marine Atmosphere after 12 Months Exposure

Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX) analysis revealed the presence of lepidocrocite (γ-FeOOH), goethite (α-FeOOH) and magnetite (Fe_3O_4) in the corrosion product formed on painted mild steel in marine atmosphere after 12 months exposure. Figure 3a showed scanning electron image of the flowery structure of lepidocrocite (γ-FeOOH). These flowery crystals of lepidocrocite (γ-FeOOH) were larger in size as compared to the flowery crystals formed after 4 and 8 months of exposure. In general, changes in the morphology and size of lepidocrocite (γ-FeOOH) formed after 4, 8 and 12 months of exposure were noticed which has been observed by other researchers as well [16-17].

Figure 3b and Table 3 illustrated the composition of lepidocrocite (γ-FeOOH) formed in marine atmosphere after 12 months of exposure as determined by energy dispersive X-ray (EDX) analysis. EDX spectrum reveals the presence of iron, oxygen and chlorine.

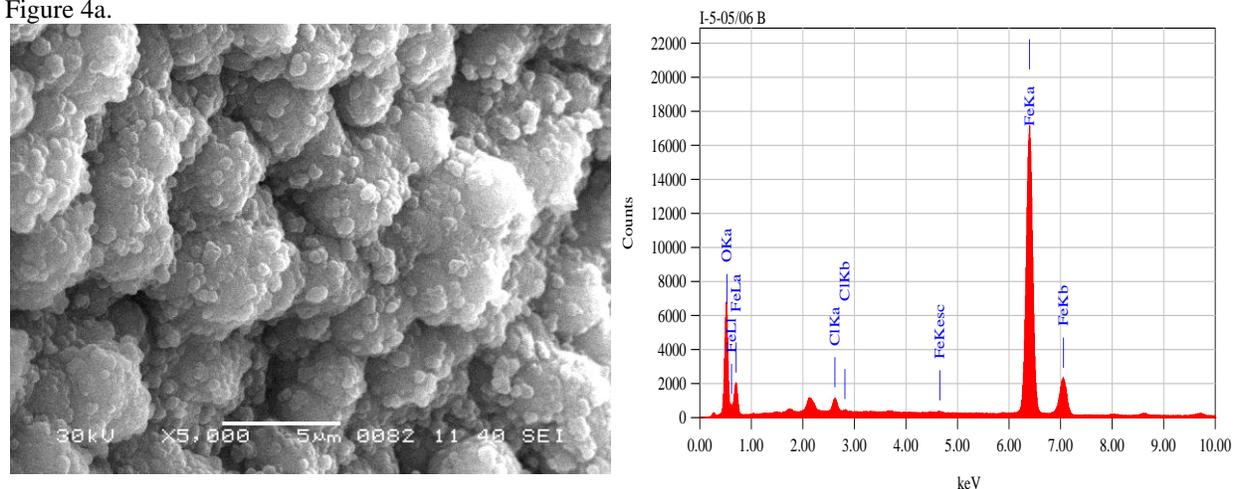**a) Flowery structure of Lepidocrocite (γ-FeOOH)**

b) Energy dispersive X-ray (EDX) spectrum of the corrosion product

Figure 3: Scanning electron micrograph (SEM) and Energy dispersive X-ray (EDX) spectrum of the Lepidocrocite (γ-FeOOH) formed on painted mild steel in marine atmosphere after 12 months exposure

Table 3: Composition of the corrosion product [Lepidocrocite (γ-FeOOH)] formed on painted mild steel in marine atmosphere after 12 months exposure as determined by EDX analysis

Element	Binding Energy (kev)	Mass %
O	0.525	35.06
Cl	2.621	0.51
Fe	6.398	64.42
Total		**100.00**

Present study showed that goethite (α-FeOOH) was present in the corrosion product formed on painted mild steel in marine atmosphere after 12 months exposure. Generally, goethite (α-FeOOH) is present in the rust of mild steel [14, 22]. Globular morphology of goethite (α-FeOOH) was noticed by scanning electron microscopy and is presented in Figure 4a.

a)   Globular structure of Geothite (α-FeOOH)

b)   Energy dispersive X-ray (EDX) spectrum of the corrosion product

Figure 4: Scanning electron micrograph (SEM) and Energy dispersive X-ray (EDX) spectrum of the Geothite (α-FeOOH) formed on painted mild steel in marine atmosphere after 12 months exposure

Chloride ions play a very important role in the transformation of lepidocrocite (γ-FeOOH) to goethite (α-FeOOH). The mechanism of accelerated effect induced by chloride ions on the atmospheric corrosion rate of carbon steel is studied by Yuantai Ma et al [5]. The results showed that the chloride ions facilitate the transformation of lepidocrocite (γ-FeOOH) to goethite (α-FeOOH) when their concentration is under critical concentration [5].

Figure 4b and Table 4 illustrated the composition of goethite (α-FeOOH) formed in marine atmosphere after 12 months of exposure as determined by energy dispersive X-ray (EDX) analysis. EDX spectrum showed the presence of iron and oxygen and chlorine.

Table 4: Composition of the corrosion product [Geothite (α-FeOOH)] formed on painted mild steel in marine atmosphere after 12 months exposure as determined by EDX analysis

Element	Binding Energy (kev)	Mass %
O	0.525	28.68
Cl	2.621	1.39
Fe	6.398	69.94
Total		**100.00**

Figure 5a showed scanning electron image of the cubic grains of magnetite (Fe_3O_4). Figure 5b and Table 5 illustrated the composition of magnetite (Fe_3O_4) formed in marine atmosphere after 12 months of exposure as determined by energy dispersive X-ray (EDX) analysis. EDX spectrum reveals the presence of iron and oxygen.
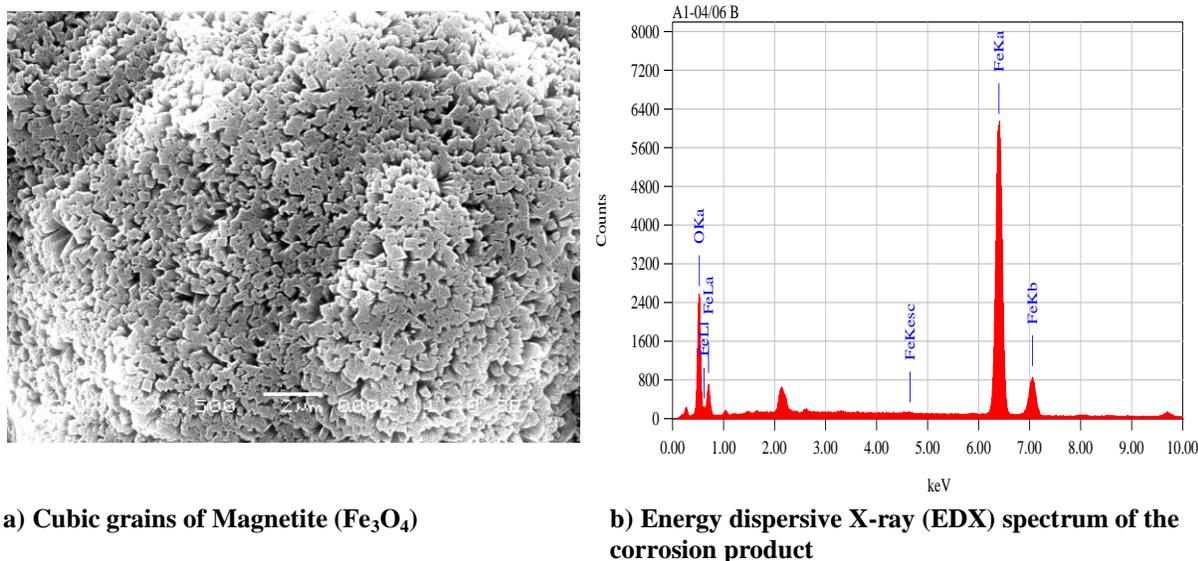
a) Cubic grains of Magnetite (Fe_3O_4)

b) Energy dispersive X-ray (EDX) spectrum of the corrosion product

Figure 5: Scanning electron micrograph (SEM) and Energy dispersive X-ray (EDX) spectrum of the Magnetite (Fe_3O_4) formed on painted mild steel in marine atmosphere after 12 months exposure

Table 5: Composition of the corrosion product [Magnetite (Fe_3O_4)] formed on painted mild steel in marine atmosphere after 12 months exposure as determined by EDX analysis

Element	Binding Energy (kev)	Mass %
O	0.525	29.15
Fe	6.398	70.85
Total		**100.00**

Formation of magnetite (Fe_3O_4) takes place when lepidocrocite (γ-FeOOH) reacts with the Fe^{+2} ions which are produced by the oxidation of iron. Iron oxide is more stable than iron oxy-hydroxides. The production free energy for magnetite (Fe_3O_4) is −117.13kJ/mol which is very less than that of lepidocrocite (γ-FeOOH) and goethite (α-FeOOH). The lattice binding energy of magnetite (Fe_3O_4) is very high. For that reason magnetite (Fe_3O_4) is considered as a harmless form of rust as it can prevent further corrosion of mild steel [21]. Formation of magnetite is

favoured by the low oxygen availability and it takes place near the surface of metal [22]. A number of researchers identified magnetite as an important constituent of rust developed on mild steel in marine atmosphere [14, 16].

The surface morphology of the corrosion products has been observed by a number of authors and it can vary considerably between different exposure sites [14, 16-17, 22]. The phases most frequently found present typical structures, for instance: lepidocrocite appears as small crystalline globules (sandy crystals) or as fine plates (flowery structures); goethite appears as globular structures known as cotton balls (semi-crystalline goethite) or even as acicular structures (crystalline goethite); akaganeite appears with cotton ball and rosette morphologies [17, 22].

Findings of the present study agreed well with the results reported by J.G. Castano et al, who studied the atmospheric corrosion of carbon steel in marine atmosphere of Colombia over a period of 14 months [16]. They reported the presence of lepidocrocite, goethite and magnetite in the coastal environment.

Conclusions

The morphology and composition of the corrosion products formed in marine atmosphere of Karachi, Pakistan were investigated by using scanning electron microscopy (SEM)/energy dispersive X-ray (EDX) analysis. Lepidocrocite (γ-FeOOH) was found as major component of corrosion products formed after 4 and 8 months of exposure. After 12 months of exposure corrosion product obtained was composed of lepidocrocite (γ-FeOOH), goethite (α-FeOOH) and magnetite (Fe_3O_4). Changes in the morphology and size of lepidocrocite (γ-FeOOH) formed after 4, 8 and 12 months of exposure were noticed. Presence of very harmful form of rust that is lepidocrocite could be realted to very high corrosivity of the marine atmosphere of Karachi, Pakistan. The conversion of lepidocrocite to goethite (α-FeOOH) was also noticed.

Acknowledgment

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