Study on Atmospheric Corrosion for Two Different Marine Environments in India

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In any developing nation major investment goes for infrastructure and it is not exception in India. Good numbers of buildings, bridges, shopping malls, car parks etc. are coming up with steel for sustainable development. Thus protecting the structures from corrosion are the challenges faced by professionals for all types of steel structures. About 3% of GDP is accounted for loss due to corrosion. To combat this up to date corrosion map is called for as the country has wide variation of climatic zones with vastcoastline. Logically organic paint system can be prescribed based on the corrosion rate on bare steel with respect to environment. Present paper will emphasis on the study conducted on two types of structural steel coated with organic paint located in twomarine environment having been exposed for three years, Test coupons made from steels both bare and coated are deployed at two field stations having marine (Digha) and industrial marine (Channai) environments. Various tests like AC impedance DC corrosion, polarisation, salt spray test, SO₂ chamber and Raman spectroscopy were carried out both in laboratory on fresh as well as coupons collected from exposure sites. Rust formed on the bare and scribed coated coupons are investigated. It is found that normal marine environment at Digha exhibits higher corrosion rate than polluted marine environment in Channai. Rust analysis indicates formation of ∝-FeoOH protects or reduces corrosion rate at Channai and formation of non-protective y-FeoOH increases corrosion rate at Digha. The slower corrosion rate in Channai than at Digha is attributed due to availability of SO₂, in the environment, which converts non protective rust γ -FeoOH to protective rust \propto -FeoOH. While comparing the damage on the coated panels it is found that low alloy structural steel provides less damage than plain carbon steel. From the experimentations a suitable paint system specification is drawn for identical environments for low medium and high durability.

Keywords : coupons, organic paint, plain carbon steel, low alloy steel, durability, weathering steel, atmospheric corrosion, paint system

1. Introduction

Structural steel in general is vulnerable with respect to corrosion and to reduce this effect alloying elements (Cu, Cr) cathodic in nature are added in grade like Weathering Steel. These steels perform better with respect to plain carbon steel both at normal and polluted inland. These steels demonstrate poor corrosion resistant at marine environment and this is due to formation of unstable oxide rust layer. It is expected that that painted weathering steel should perform better with respect to plain carbon steel in all types of environment. This is true for non-polluted inland environments. However in polluted marine environments, the corrosion protection properties found to be identical or less. This again is a function of humidity, temperature, rainfall, sulphar dioxide, salinity etc. To derive scientific explanation kinetics, mechanism and morphology of corrosion products are to be examined. The present work findings are derived from pan Indian project to find out corrosion map for structural steel using generic type of paints.

2. Experimental set up:

2.1 Materials:

Two grades of structural steels like plain carbon steel (IS 2062) and high strength low alloy/weathering steel (IS 11587) were chosen. The steel test coupons 150X100X4 mm³ were prepared from hot rolled plates.

2.2 Coatings:

The generic paint systems used were taken from two leading paint companies (AK & AM) having identical formulations. The total dry film thickness will vary with

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	t System Used								
Coastal									
Sa (l	Low Durability) 2 - 5 yea	ars for Normal Coastal (DFT in Micron	s)	Total				
Epoxy (75)	Epoxy (100)	poxy (100) - Polyurethane (50)							
AM Epoxy (50) Epoxy (100) Epoxy (50) P.U. (50)									
Sb (Medium Durability) 5 - 10 years for Normal Coastal (DFT in Microns)									
Epoxy-Zinc Rich (50)	Epoxy (150)	-	Polyurethane	250					
Epoxy (50)	Chlorinated Rubber (100)	Epoxy (50)	Chlorinated 1	Rubber (50)	250				
Sc (High Durability) > 10 years for Normal Coastal (DFT in Microns)									
Epoxy-Zinc Rich (75)	Epoxy (150)	-	Polyurethane (50)		275				
AM Epoxy-Zinc Rich (50) Epoxy M10 (100)		Epoxy (50)	P U (100)	300					
Coastal									
Sd - (Low Durability) 2 - 5 ye	ars for Polluted coastal	(DFT in Micro	ns)	Total				
AK	Epoxy (75)	Epoxy (125)	- Polyurethane (50)		250				
AM	Epoxy (50)	Epoxy (100)	Epoxy (50)	P U (50)	250				
Se (Me	dium Durability) 5 - 10	years for Polluted coasta	l (DFT in Mici	rons)	Total				
Epoxy-Zinc I	Rich (75)	Epoxy (150)	-	Polyurethane (50)	275				
Epoxy (50)		Epoxy (100)	Epoxy (50)	P U (50)	250				
Sf (1	High Durability) > 10 ye	ars for Polluted coastal	(DFT in Micro	ns)	Total				
Epoxy-Zinc I	Rich (75)	Epoxy (200)	-	- Polyurethane (50)					
Epoxy-Zinc I	Rich (50)	Epoxy (50)	Epoxy (50)	P U (50)	200				
	Coastal Sa (1) Epoxy (75) Epoxy (50) Epoxy (50) Sb (Me Epoxy-Zinc Rich (50) Epoxy (50) Sc (1) Epoxy (50) Sc (1) Epoxy-Zinc Rich (75) Epoxy-Zinc Rich (50) Coastal Sd - (AM Se (Me Epoxy-Zinc I Epoxy-Zinc I AM Se (Me Epoxy (50) Sf (1) Epoxy-Zinc Sf (1) Epoxy-Zinc Sf (1)	Sa (Low Durability) 2 - 5 yeaEpoxy (75)Epoxy (100)Epoxy (50)Epoxy (100)Sb (Medium Durability) 5 - 10 yeaEpoxy-Zinc Rich (50)Epoxy (150)Epoxy (50)Chlorinated Rubber (100) Sc (High Durability) > 10 yeaEpoxy-Zinc Rich (75)Epoxy (150)Epoxy-Zinc Rich (50)Epoxy (150)Epoxy-Zinc Rich (50)Epoxy (150)CoastalEpoxy M10 (100)CoastalEpoxy (75)AMEpoxy (50)Se (Medium Durability) 5 - 10 yeaEpoxy (50)Epoxy (50)	CoastalSa (Low Durability) 2 - 5 years for Normal Coastal (Epoxy (75)Epoxy (75)Epoxy (100)-Epoxy (50)Epoxy (100)Epoxy (50)Sb (Medium Durability) 5 - 10 years for Normal CoastalEpoxy (150)-Epoxy (50)Chlorinated Rubber (100)Epoxy (50)Sc (High Durability) > 10 years for Normal CoastalEpoxy-Zinc Rich (75)Epoxy (150)-Epoxy-Zinc Rich (50)Epoxy (150)-Epoxy-Zinc Rich (50)Epoxy (150)-Epoxy-Zinc Rich (50)Epoxy M10 (100)Epoxy (50)CoastalEpoxy (75)Epoxy (125)AMEpoxy (50)Epoxy (100)Se (Medium Durability) 5 - 10 years for Polluted coastalAKEpoxy (50)Epoxy (100)Se (Medium Durability) 5 - 10 years for Polluted coastalEpoxy (50)Epoxy (100)Se (Medium Durability) 5 - 10 years for Polluted coastalEpoxy (50)Epoxy (100)Se (Medium Durability) 5 - 10 years for Polluted coastalEpoxy (50)Epoxy (100)Se (Medium Durability) 5 - 10 years for Polluted coastalEpoxy (50)Epoxy (100)Se (Medium Durability) 5 - 10 years for Polluted coastalEpoxy (50)Epoxy (100)Se (Medium Durability) 5 - 10 years for Polluted coastalEpoxy (200)Epoxy (200)	CoastalSa (Low Durability) 2 - 5 years for Normal Coastal (DFT in MicronEpoxy (75)Epoxy (100)-PolyurethaneEpoxy (50)Epoxy (100)Epoxy (50)P.U. (50)Sb (Medium Durability) 5 - 10 years for Normal Coastal (DFT in MicronRich (50)Epoxy (150)-Epoxy (50)Chlorinated Rubber (100)Epoxy (50)Chlorinated IEpoxy (50)Chlorinated Rubber (100)Epoxy (50)Chlorinated ISc (High Durability) > 10 years for Normal Coastal (DFT in MicronRich (75)Epoxy (150)-Epoxy-Zinc Rich (75)Epoxy (150)-PolyurethaneEpoxy-Zinc Rich (50)Epoxy (150)-PolyurethaneEpoxy-Zinc Rich (50)Epoxy (100)Epoxy (50)P U (100)CoastalEpoxy (150)-Epoxy (50)P U (100)CoastalEpoxy (75)Epoxy (125)-AMEpoxy (50)Epoxy (100)Epoxy (50)Se (Medium Durability) 5 - 10 years for Polluted coastal (DFT in MicroAMEpoxy (50)Epoxy (100)Epoxy (50)Se (Medium Durability) 5 - 10 years for Polluted coastal (DFT in MicroEpoxy (50)Epoxy (100)Epoxy (50)Se (Medium Durability) 5 - 10 years for Polluted coastal (DFT in MicroEpoxy (50)Epoxy (100)Epoxy (50)Se (Medium Durability) 5 - 10 years for Polluted coastal (DFT in MicroEpoxy (50)Epoxy (100)Epoxy (50)Se (High Durability) > 10 years for Polluted coastal (DFT in MicroEpoxy (50)	CoastalSa (Low Durability) 2 - 5 years for Normal Coastal (DFT in Microns)Epoxy (75)Epoxy (100)Epoxy (50)P.U. (50)Epoxy (50)Epoxy (100)Epoxy (50)P.U. (50)Sb (Medium Durability) 5 - 10 years for Normal Coastal (DFT in Microns)Polyurethane (50)Epoxy-Zinc Rich (50)Epoxy (150)-Polyurethane (50)Epoxy (50)Chlorinated Rubber (100)Epoxy (50)Chlorinated Rubber (50)Sc (High Durability) > 10 years for Normal Coastal (DFT in Microns)Polyurethane (50)Epoxy-Zinc Rich (75)Epoxy (150)-Polyurethane (50)Epoxy-Zinc Rich (50)Epoxy M10 (100)Epoxy (50)P U (100)CoastalEpoxy (75)Epoxy (125)-Polyurethane (50)AKEpoxy (75)Epoxy (100)Epoxy (50)P U (50)AKEpoxy (50)Epoxy (100)Epoxy (50)P U (50)Se (Medium Durability) 5 - 10 years for Polluted coastal (DFT in Microns)Polyurethane (50)AMEpoxy (50)Epoxy (100)Epoxy (50)P U (50)Se (Medium Durability) 5 - 10 years for Polluted coastal (DFT in Microns)Polyurethane (50)Epoxy (50)Epoxy (150)-Polyurethane (50)Se (Medium Durability) 5 - 10 years for Polluted coastal (DFT in Microns)Epoxy (50)P U (50)Se (Medium Durability) 5 - 10 years for Polluted coastal (DFT in Microns)Polyurethane (50)Epoxy (50)Epoxy (100)Epoxy (50)P U (50)Se (Medium Durability) 5 - 10 years for Polluted coastal				

Table 1 Congris Paint System Used

respect to the expected life of structures. The paint system criteria and typical formulations are given in Table 1.A two to three coat system is applied over a clean, blasted surface (Sa 2.5). Systems applied are high-build, high solids, good-wetting epoxy/chlorinated rubber primer with aliphatic polyurethane topcoat.

2.3 Exposure centre:

Both bare and painted (scribed & non scribed) test coupons were deployed in places like Digha (normal costal having latitude 21.68, longitude 87.55 & altitude 22') and Chennai (polluted coastal having latitude 13.04, longitude 80.17 & altitude 20'). The meteorological and pollution data are indicated in Table 2.

2.4 Test racks:

The test coupons were exposed at an <45° facing south

and were fixed to the rack with the help of porcelain and brass nuts & bolts. Painted test coupons deployed in two conditions scribed and unscribed along with bare coupons. The typical field stations are shown in Fig. 1.

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3. Controlled laboratory environment tests:

Coupons were exposed in salt spray, SO₂ chamber, dip/dry tests, DC corrosion tests (EIS, Polarisation), Raman Spectroscopy and EDXA.

3.1 Salt spray and dry chamber test:

The painted (scribed) and unpainted panels were put to chamber at 45 $^\circ\!\! C$ with 5% NaCl solution sprayed with compressed air at a pressure of 6-8 bar as per ASTM B-117. The spraying continued for 8 hours with the freshly prepared brine solution and the spraying was discontinued

Table 2. Meteorological and Pollution Data of Field Stations	Table	2.	Meteorological	and	Pollution	Data	of	Field	Stations
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Parameters		Che	ennai		Digha				
Lizita	20	04	2005		20	04	2005		
Units	Min	Max	Min	Max	Min	Max	Min	Max	
Av Temp (°C)	29.95	34.44	30.37	34.69	21.65	29.85	22.29	28.40	
Av Humidity (%)	58.52	70.97	66.72	76.12	76.10	88.66	76.95	81.68	
Yearly Rain Fall (mm)	106	106.95		193.60		81	171.06		
$SO_2 (\mu g/m^3)$	15		12.2		3.	7	3.6		
No _x ($\mu g/m^3$)	26		20	0	3	0	34		



Fig. 1. View of Field Stations Digha (Left) & Chennai (Right)

Table 3. Salt Spray Exposure (5000 hours) for AM & AKPanels on LAS and PCS

Sample	LAS	PCS
Ss	Rust at scribed part spread by 0.5 mm for AM. Rust at scribed lines by 1.5 mm for AK.	Rust across the scribed line by 0.5 mm. Less severe than LAS of the same category.
Sb	No effect observed on both AM & AK	No effect observed on both AM & AK
Sc	No effect observed on both AM & AK	No effect observed on both AM & AK
Sd	Rust on the scribed lines (<0.5 mm) for AM. Rust on scribed lines by 1.5 mm for AK.	No effect observed on both
Se	No effect observed on both Am & AK	Rust deposited at the edge n the scribed lines.

for sixteen hours and allowed to dry for same duration. The tests continued for 5000 hours and observations are summarized in Tables 3.

No correlation on spreading of rust across the scribed lines with durability of is found system as low durability system S-b & S-c provide superior performance than Sd & Se. Thus this spray tests do not provide exact nature of the coating and they were tested for deterioration by EIS technique.

3.2 Electrochemical impedance study (EIS):

EIS were performed by imposing sinusoidal voltage (10 mv) with reference to open circuit potential at the working electrode and varying the frequency from 100 KHz to 0.001 Hz. Gamry Potentiostat used for EIS in a flex cell fitted with two graphite rods at two sides of the working electrode, which acted as auxiliary electrodes. The reference electrode was a saturated calomel electrode (SCE). A luggin capillary was used to provide electrolytic contact between the calomel electrode and electrochemical cell. The electrolyte used as per SAEJ-2334 (to simulate the atmospheric conditions) comprised of NaCl {5gms/lit (0.5%) + CaCl₂ {1gm/lit (0.1%)} + NaHCO₃ {2.5gm/lit (0.25%). The corrosion rate experienced by the substrate due to their exposure in test electrolyte was assessed at different intervals of time (instant & after 120hrs). Polarization resistance (R_P) technique was used to determine the corrosion rate. The parameters derived from these studies are incorporated in Table 4 & 5.

The scribed portion provides improved protection for AM coating in the order of 10⁵ times higher than AK. The corrosion products of AM coating, gives resistant to penetration of electrolyte. Sb & Sc provide better Rp value w.r.t Se.

The AM coated panels are found to deteriorate faster in comparison to AK coated panels.

4. Uncontrolled field environments tests:

Exposed samples were withdrawn from both field stations at different time interval for evaluation the corrosion rate (by weight loss measurement) and the values are given in the Table 6. The corrosion rate for both LAS & PCS is higher in Digha than Chennai. Again loss of thickness for PCS is higher in both the places. Corrosion rate of Chennai is lower due to availability of SO₂. These coupons were taken for EIS and cyclic polarisation studies to find out the degree of deterioration under the coatings. Exposed specimens were also tested in 3.5% and 1% solution of chloride ions.

4.1 Salt spray test:

No change was noted during the first 1400 hrs of exposure on both the panels and after that spreading of rust was more for LAS. The spread of rust on PCS & LAS after 5000 hours of salt spray exposures is shown in Fig. 2 and it is evident that the spreading of rust is more severe on LAS than on PCS.

Paint type	EOC (-V)	Rp (Ohm Cm ²)	Cf (F/cm ²)	۵	Paint type	EOC (-V)	Rp (Ohm Cm ²)	Cf (F/cm ²)	۵
LAS AK-Sa	0.4779	$1.00 \text{x} 10^3$	9.85x10 ⁻²	0.76	LAS AM-Sc	0.2314	2.57×10^8	4.04×10^{-8}	0.85
LAS AM-Sa	0.2758	2.98×10^{8}	2.07x10 ⁻⁹	0.9	PCS AM-Sc	0.1960	$1.36 \text{x} 10^7$	3.61×10^{-8}	0.85
PCS-AK-Sa	0.5215	1.24×10^{3}	9.87x10 ⁻¹	0.66	LAS AK-Se	1.1064	6.11x10 ⁹	1.23×10^{-9}	0.9
PCS-AM-Sa	0.3246	2.86×10^7	2.48x10 ⁻⁸	0.76	LAS AM-Se	0.4220	9.37×10^{6}	1.35x10 ⁻⁹	0.83
LAS-AK-Sb	0.0998	5.02×10^8	1.45x10 ⁻⁹	0.9	PCS AK-Se	0.4301	1.22×10^5	4.09×10^{-8}	0.7
PCS-AK-Sb	2.7294	4.52×10^9	4.33x10 ⁻⁸	0.8	PCS AM-Se	0.0043	5.53×10^{6}	1.83x10 ⁻⁹	0.96

Table 4. Instant Exposure of EIS of Panels after 5000 hrs in Salt Spray

Table 5. 120 Hrs Exposure of EIS after 5000 hrs of Salt Spray

Paint type	EOC (-V)	Rp (Ohm cm ²)	Cf (F/cm ²)	α	Paint type	EOC (-V)	Rp (Ohm cm ²)	Cf (F/cm ²)	α
LAS AK Sa	0.546	$7.88 \text{x} 10^3$	1.56x10 ⁻⁸	0.76	LAS AM S-c	0.3974	5.93x10 ⁶	2.73x10 ⁻⁸	0.9
LAS AM Sa	0.2102	$1.81 \text{x} 10^8$	5.73x10 ⁻⁸	0.8	PCS AM S-c	0.6774	$1.16 \text{x} 10^6$	2.32×10^{-8}	0.85
PCS-AK Sa	0.6137	2.96×10^7	5.06×10^{-2}	0.55	LAS AK Se	0.6295	2.11×10^8	5.15x10 ⁻⁸	0.85
PCS-AM Sa	0.3357	2.72×10^7	3.28×10^{-8}	0.76	LAS AK Se	0.4904	4.52×10^9	5.57x10 ⁻⁸	0.99
LAS AK S-b	0.3253	$1.88 \text{x} 10^8$	5.52x10 ⁻⁸	0.85	PCS AK Se	2.6439	355x10 ⁹	8.9x10 ⁻⁸	0.96
PCS AK S-b	0.1438	9.55x10 ⁸	5.51x10 ⁻⁸	0.9	PCS AM Se	0.70291	$4.34 \text{x} 10^7$	4.14x10 ⁻⁸	0.86

Table 6. Corrosion Rate in (mpy) of Steels Exposed

Place	PCS	LAS	Place	PCS	LAS
Digha	0.953	0.79	Chennai	0.748	0.53

4.2 Cyclic polarisation:

After salt spray exposure of 5000 hrs the samples were taken up for cyclic polarisation at scan rate of 0.5 mv/sec. The same samples the plot of LAS is observed to be in higher current density region than the plot of PCS. This indicates faster attack at the surface of LAS than PCS. This result corroborates the visual observations where surface of LAS was observed to deteriorate faster than the PCS as shown in Fig. 3.

4.3 SO₂ test:

This was carried out as per G87-84 to understand the phenomenon of deterioration and kinetic of corrosion of underneath surface. The moist SO₂ test generates high humidity and acid at the test panels and this condition is normally encountered in humid and industrial polluted environments. The photograph has shown in Fig. 4 the spread of rust across the scribe lines on PCS & LAS after 6400 hrs of exposure. The exposure of coated steels in humid SO₂ atmosphere also confirms the findings of salt spray tests .The appearance of rust on the surface of LAS was found within 700 hrs and same was 1500 hrs for PCS and also the spreading of rust was faster on LAS than on PCS.



Fig. 2. Salt Spray Exposure (5000 hrs)

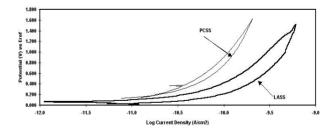


Fig. 3. Cyclic Polarisation of Coated Steel After Salt Spray

The SO₂ exposed samples were subjected to EIS and cyclic polarisation studies. Fig. 5 shows the EIS real vs imaginary impedance plots for both steels exhibit one incomplete semicircle at higher frequencies followed by a complete semicircle at intermediate and a diffusion tail at lower frequencies. The diameter of the intermediate fre-



Fig. 4. Rust on PCS & LAS in SO₂

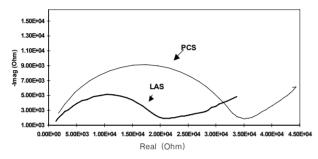


Fig. 5. Nyquist Plots of coated PCS & LAS after SO₂

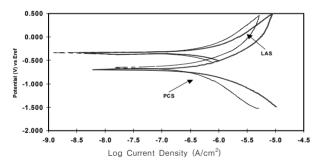


Fig. 6. Cyclic Polarisations coated LAS & PCS after SO₂ exposure

quency semicircle corresponds to charge transfer reaction at the metal/rust/electrolyte interface. This is observed lower for LAS in comparison to PCS, indicating more deterioration of LAS than PCS.

Fig. 6 shows cyclic polarisation where the curve of PCS falls in lower current density zone than for LAS. All these tests indicate that in accelerated tests LAS coated specimens deteriorate faster than PCS.

The above observations in accelerated test were surprising in view of generally reported behaviour of coated LAS performing superior in comparison to PCS in normal rural/industrial dry environments. In order to determine the behaviour of two types of coated steels in industrial envi

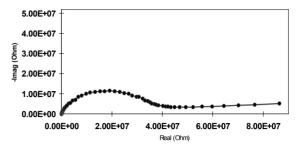


Fig. 7. Nyquist plot of coated PCS in Industrial Town

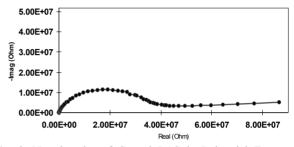


Fig. 8. Nyquist plot of Coated LAS in Industrial Town

ronment both samples were exposed at industrial town Jamshedpur, India. Coupons were taken to EIS and polarization studies after 18 months of exposure. The EIS plots for the two-coated steels are shown in Figs. 7 and 8. For both the steels the plots exhibit semicircle of smaller diameter in high frequency range, which are attributed to the coating's properties. In intermediate ranges of frequency, the semicircles of diameter having considerable variations are observed for the two steels. The diameter on real impedance axis for LAS is appreciably bigger than of PCS. These observations suggest that LAS in normal industrial environment was performing far superior than PCS.

5. Rust analysis scribed painted panels:

Atmospheric corrosion rate of steels on long term basis is dependend on the oxide layers formed on their surface. The main constituents of oxides are γ -FeOOH (lepidocrocite), α -FeOOH (goethite), β -FeOOH (akaganite) and δ -FeOOH (feroxyhite). Out of these, goethite is the most stable phase. During the initial stages, lepidocrocite (γ -FeOOH) is formed which is subsequently oxidized to goethite in presence of proper climatic conditions at the exposure sites. Once a stable layer of goethite on a steel surface develops, the corrosion of the steel is completely stopped. The factors that facilitate the transformations of unstable γ -FeOOH to stable α -FeOOH are the chemistry of steels and atmospheric conditions. It is reported that the presence of salinity encourages the formation of β -FeOOH, which is an unstable phase of iron oxide.

5.1 Corrosion characteristics of bare steels:

It is further suggested that the ratio of α/γ^* in the oxide controls the corrosion rate of steels. Here γ^* is the sum of β -FeOOH, γ -FeOOH and Fe₃O₄ and α is α -FeOOH. This ratio is normally 1 for LAS exposed during 5-10 years and higher than 2 for steels exposed for more than 10 years. Most of studies for characterization of corrosion products reported in the literature pertain to the oxides formed after longer duration of exposure of steels. These studies do not throw any light on the type of oxides that are generated during the initial exposure of steels having different type of chemistry and climatic conditions. A recent study by Antunes et.al conducted for the characterization of rust formed on carbon and weathering steels during 1-3 months of their exposure in urban, industrial and humid atmospheres have shown that the oxides formed were mixed in character. This was not surprising in view of the fact that initial rusting of steels is controlled by many factors such as heterogeneity of their surface, climatic conditions etc. The nature of oxides gets stabilized and provides real characteristics of the steels and climatic effects only after they meet to all cycles of changes of climate. The long-term corrosion rates of steels are controlled by the type of rusts formed during the initial stages of exposure of their virgin surface. The initial exposure data, therefore, are very important to predict the long-term performance of steels

Raman spectroscopy of these rusts established the presence of ∞ -FeOOH on LAS and β -FeOOH on PCS. Rust developed identified as stable α -FeOOH at Chennai is more protective than that of at Digha. It is further seen from these spectra that for almost all conditions of exposures, certain unidentified peaks are also observed as shown in Table 7.

Examination of the peaks reveals that many unidentified peaks are recorded for the rusts of LAS exposed at locations where salinity and humidity dominate in the environment (Digha and Chennai). For PCS, however, these peaks are absent. These facts indicate that the unidentified peaks should be attributed to a rust compound having Chlorine and other minor elements present in the steel.

5.2 EDXA:

It is also observed that steel surfaces were having pitting attack and its severity varied with the climatic conditions & steel chemistry. The LAS exhibits lesser pitting on its surface than PCS. These rusts were subjected to energy dispersive X-ray analysis (EDXA) to find the presence of elements and no traces of the presence of Cl, Cu or Cr, was noted in the rust. EDXA of these rusts showed in Figs. 9 & 10 the presence of Al, Mn, Si, and S. The absence of alloying elements of steels (Cu, Cr) and Chlorine in the rust is probably due to the limitations in detecting ability of the instrument. As the exposure of steels in the environments was only for a shorter duration (2 years), the micro alloyed elements (Cu & Cr) in rust should be present in ppm level. The instruments based



Fig. 9. Rust Morphology on LAS (Scale 20 µm)

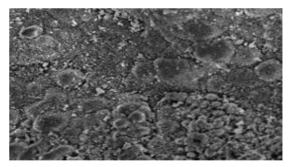


Fig. 10. Rust Morphology on PCS (Scale 20 µm)

Table 7.	Raman	Shifts	for	Rust	Formed	on	Panels	(2	years	exposure)	
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Place		LAS	PCS		Place		LAS	PCS	
	Peaks	Compounds	Peaks	Compounds		Peaks	Compounds	Peaks	Compounds
	392.92	δ-FeOOH	694.9	Fe(OH) ₃		384	δ-FeOOH	687.5	δ-FeOOH
	1292.1	-	1307	γ-FeOOH		1292	-	391.6	δ-FeOOH
Digha	591	-	375	γ-FeOOH	Chennai	589.6	-	298.9	γ -Fe ₂ O ₃
	276	-	251	γ-FeOOH		272.7	-	548	Fe ₃ O ₄

on energy dispersive X-ray analysis are unable to detect the elements present in ppm levels. Silicon and Sulphur in the rust are coming from the environments and got entrapped in the rust layer. Out of these elements, the role of S, which has come from SO_2 present in the environment, is more important in changing the characteristics of the rust formed on the steels.

Many researchers in the past have shown that the rust formed on weathering type of steels having Cr, Cu, P etc considerably differ from normal oxides formed on PCS. While characterizing the rust of LAS, Fujiwara et.al. observed that Cr and Cu were present in the inner layer of the rust and chloride in its outer layer. It was confirmed by Yamashita et.al. that the rust developed on LAS incorporates Cr^{3+} co-ordinated with O^{-2} . The shift in the Raman peaks observed for LAS exposed in saline environment towards lower value (1292 cm⁻¹) than the peaks assigned to pure lepidocrocite (γ -FeOOH, 1303 cm⁻¹), therefore, may be attributed to the above changes in the lattices of rust of LAS.

5.3 Salt spray tests:

In order to assess the performance of these steels in salt spray, they were exposed for 5000 hrs in salt spray chamber and then their corrosion rate was evaluated. The results are summarized in Table 8. It is evident that both the steels corroded at a very high rate which is many fold higher than their rates in normal environment (8-24 μ m/year). Further, the variation in the corrosion rate of the two steels exposed in salt spray chamber was negligible. This indicates that in saline environments, the chemistry of the steels has little role to play in controlling their corrosion rate. This finding is also corroborated by the thickness loss data of the two steels exposed on coastal saline environment of Digha where both the steels exhibit almost the same thinning rate (24 and 20 μ mpy respectively for PCS and LAS).

Table 8. Corrosion Rate in (µmpy) in Salt Spray Chamber

Steel	Corrosion rate	Steel	Corrosion rate		
PCS	373.4	LAS	345.7		

5.4 SO₂ test:

To confirm this fact in the laboratory, LAS & PCS specimens were subjected to exposure in humid environments having 4 ppm of SO₂ for 6 months and Raman Spectroscopy analyzed the rusts generated on their surface. Interestingly, in these cases also, the majority of peaks corresponded to α -FeOOH. Scanning of the literature re-

vealed that many earlier workers have also proposed that the presence of SO₂ in the environments facilitates the formation of α -FeOOH rust. The above results indicate that during longer duration of exposures, the steels exposed at Chennai should experience significantly lower rate of corrosion than exposed at Digha despite of the fact the environment heavily loaded with salinity and humidity.

5.5 Raman spectroscopy:

The rusts formed during the salt spray exposure of LAS and PCS were subjected to Raman Spectroscopy and the results are shown in Figs. 11 (a), (b) & Figs. 12 (a), (b) respectively.

In both the cases, peaks of β -FeOOH are recorded. This is in agreement with the results of earlier researchers who reported the formation of this type of rust in saline environments.

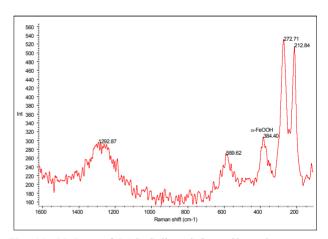


Fig. 11. (a) Rust of LAS Collected from Chennai

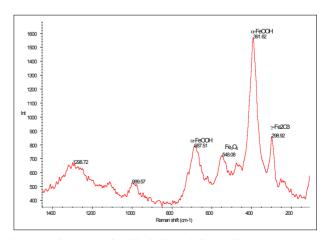


Fig. 11. (b) Rust of PCS Collected from Chennai

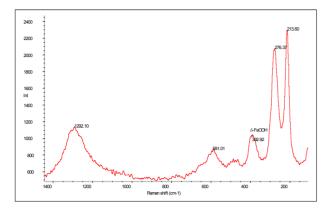


Fig. 12. (a) Rust of LASS Collected from Digha

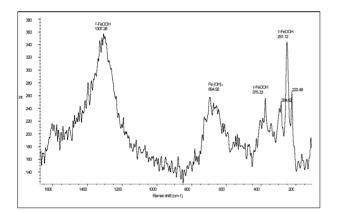


Fig. 12. (b) Rust of PCSS Collected from Digha

6. Conclusions

AM coatings give better performance during the observed period and coating applied appears to be over specified. During the atmospheric exposure tests, the coating on LAS performs superior than on PCS, for the same category of the coating. Digha exhibits the higher corrosion rate for bare steels followed by Chennai. LAS exhibit higher corrosion resistance in all atmosphere. The formation of α -FeOOH rust on steel surface exposed at Chennai reduces the corrosion rate of steel in comparison to Digha, although, the former's atmosphere is more hostile than the latter one. The slower corrosion rate at Chennai than at Digha is attributed to the presence of SO₂ in the environment, which helps in transformation of rust from non protective γ -FeOOH to the protective α -FeOOH.

Many investigators had reported that LAS out performs PCS in rural and industrial dry environments. However, in humid and saline climate the longevity of LAS is ques tioned and in many reports this type of steel is rated either equal or inferior to PCS as found in place like Digha and Chennai. This is mainly attributed to the inhibition in formation of protective patina on low alloy steels caused by high humidity and salinity. The deterioration of painted surface of steels exposed in humid and saline environments is expected to follow the same pattern. The results of accelerated tests where LAS is performing inferior to PCS, therefore, are not surprising. In humid and high salinity accelerated test chambers the protective patina on LAS is not formed. The corrosion rate is rather accelerated due to the presence of cathodic alloying elements in LAS (Cu, Cr, P etc.). The faster appearance of rust along the scribe lines of LAS than PCS confirms this mechanism of deterioration. The nature of the rust formed on two steels is also different. Less stable rust like \propto -FeOOH is found in LAS and stable rust like β -FeOOH is found on PCS.

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References

- 1. L.D. Vincent, Materials Performance 1999 October 62.
- 2. N. Schwartz, Werkst. Korros. 16, 208 (1965).
- 3. M. Yamashita and T. Mishawa, Corrosion Eng., **49**, 159 (2000).
- 4. Ph. Dillmann, F. Mazandier, and S.Hoerle, Corrosion Scie., 46, 1401 (2004).
- M. Yamashita, H. Miyuki, Y. Masuda, H. Nagano, and T. Misawa, Corros. Sci., 36, 283 (1994)
- R.A. Antunes, I.Costa, D.L.A. de Faria, Materia 8, 27 (2003).
- 7. Practice for conducting atmospheric corrosion metals, ASTM G50-76 (1992)
- Practice for operating salt spray (fog) testing, ASTM B-117 (1994)
- 9. Practice for preparing, cleaning and evaluating corrosion test specimens, ASTMG1-90
- 10. DDN Singh and A.Kumar, Corrosion, 59, 1029 (2003).
- H. Fujiwara, T.Sugano, M. Aosawa, and T. Nagatans, Corros. Eng., 49, 145 (2000).
- M. Yamashita, T. Mishawa, S.J. Oh, R. Balasubramanium and D.C. Cork Corros. Eng., 49, 133 (2000).