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Corrosion of Constructional Steels in Marine and Industrial Environment

Frontier Work in Atmospheric Corrosion

 Springer

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*Dipanjana and Debosmita
... learned many things during the
compilation work*

Preface

Mild steel is used as prime constructional steel for buildings, bridges, etc. But this is very much prone to corrosion in industrial and marine environments in presence of harmful pollutants and other industrial effluents in addition to normal humid atmosphere. These corrosion problems are much severe in a tropical country like India with vast coastline. Mild steel corrodes relatively faster and thus leads to colossal loss in every year and to reduce this loss some kind of protection in the form of paints and coatings is always used. Weathering steel considerably improves its corrosion resistance in industrial and rural atmosphere. Engineers and scientists all over the world are concerned for much indepth research works at surface science and engineering of atmospheric degradation of construction steels. Endeavours have been made in the present work for better understanding of the degradation process and uses of high performance paints formulation and compare them through various AC/DC electrochemical test methods and surface characterisation through electron microscopy, XRD and Raman spectroscopy.

The protective systems and their corresponding corrosion data are available in the relevant overseas codes for reference. These data are not applicable in Indian specific context as atmospheric corrosion is location specific. Atmospheric corrosion is the frontier research area where limited work has been carried out as it comprises with three phases (solid/atmospheric/liquid environment). Therefore it is significant to study the rust on MS and WS as well as coated steels in a given atmospheric environments. This is important for the selection of more suitable materials as well as for the safety of structures, including the realisation of essential economic effect.

Weathering steel is used to protect structures from atmospheric corrosion in specific environments. Rust layers on mild steel are not protective and are permeable to air and moisture. Protective impervious rust coatings are supposed to form on weathering steel with time and due to high initial cost and sometimes unfavourable environments this steel cannot be used. Microscopic observation of rust layers on weathering steel reveals the two phases in layers parallel to the steel surface. The inner phase extends up to outer surface if exposure periods are longer than 5 years, and then it becomes the only component of the rust coating. In mild

steel, corrosion products form as two different phases, and there are two layers with a common interface allowing moistures to go in and experiences higher corrosion rate in outdoor exposure.

Present research work has been carried out in two parts: field exposure tests and accelerated laboratory tests on unexposed panels. Under field exposure test three representative sites P1: very close to sea shore and free from SO₂, P2: away from sea with presence of SO₂ and P3: industrial environment with presence SO₂ were chosen. Analytical techniques (EDX, XRD and Raman spectroscopy) were used for rust characterisation and SEM was employed for understanding the morphological state. Corrosion rates were estimated after different periods of exposure at sites. It is found that though accelerated laboratory test can predict the general trend of corrosion, actual field test data cannot be created in laboratory. So an attempt was made to simulate protective rust coating in the laboratory that is typical of field exposure protective rust formation on weathering steel.

It is my proud privilege to record a deep sense of gratitude and indebtedness to Prof. P. K. Mitra & Prof. S. Paul, Metallurgical & Material Engineering of Jadavpur University, Kolkata, India and Dr. D. D. N. Singh, Sr. Deputy Director of National Metallurgical Laboratory, Jamshedpur for their encouragement and endless support throughout the research steps. I also would like to show my gratitude to my beloved mother, gorgeous wife Mousumi, son Dipanjan and daughter Debosmita for infinite emotional support, enduring love, encouragement, patience through my hard times until this work came to completion. Finally I thank god for granting me the strength to write this book and thank editorial team of Springer publication for giving the work final shape as book.

Kolkata, India

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Abbreviations

AR	As received
MS	Mild steel
WS	Weathering steel
ZP	Zinc Phosphate system
ZR	Zinc Rich system
ZP + MS	Zinc phosphate system on MS
ZR + MS	Zinc rich system on MS
ZP + WS	Zinc phosphate system on WS
ZR + WS	Zinc rich system on WS
MIO	Micaceous iron oxide
PU	Polyurethane
CR	Corrosion rate
T	Temperature
RH	Relative humidity
R	Rainfall
AC	Alternate current
DC	Direct current
OCP	Open circuit potential
PD	Polarisation diagram
CP	Cyclic polarisation
EIS	Electrochemical impedance spectroscopy
RE	Reference electrode
WE	Working electrode
CPE	Constant phase element
CPE + D	CPE with diffusion Fit
REAP	Rapid evaluation of paints
SCE	Saturated calomel electrode
PSCT	Potentiostatic current transient
E_{corr}	Corrosion potential
I_{corr}	Corrosion current
Mod	Modulus

Z_{mod}	Modulus of impedance
Z_{img}	Imaginary part of impedance
Z_{real}	Real part of impedance
θ	Phase angle
Freq	Frequency
Z	Impedance
R_u	Solution resistance
R_p	Polarization resistance
R_{po}	Pore resistance
C	Capacitance
C_c	Coating capacitance
C_f / C_{dl}	Double layer capacitance
Y_o	Admittance
W_d	Warburg impedance
α	CPE exponent
nm	Nanometer
pA	Picoampere
μA	Microampere
μm	Micron
$\mu\text{m}/\text{yr}$	Micro meter per year
DFT	Dry film thickness
h	Hours
s	Seconds
m	Months
SEM	Scanning electron microscope
EDX	Energy dispersive X-ray
XRD	X-ray diffraction
Raman	Raman spectroscopy
α FeOOH	Goethite
β FeOOH	Akaganeite
γ FeOOH	Lepidocrocite
α Fe ₂ O ₃	Hematite
γ Fe ₂ O ₃	Maghemite
Fe ₃ O ₄	Magnetite
Fig	Figure
Ref	Reference

About the Author

Dr. Jayanta Kumar Saha is serving with Institute for Steel Development & Growth (INSDAG) as Deputy General Manager spearheading key activities like sourcing, corrosion, fire protection, tech advisory services of steel structures. He did his graduation from Bengal Engineering & Science University, Shibpur, Kolkata in Metallurgical Engineering, Post-graduation from Indian Institute of Technology Madras in Production Engineering and Ph.D. in Metallurgical & Material Engineering from Jadavpur University, India. He is an IRCA, UK accredited lead auditor for ISO 9001. He has authored 11 INSDAG books on steel applications and has credit of 20 papers published in national and 5 papers in international journals. He is representing various national bodies/committees. He had previous experience at Hindustan Aeronautics Ltd, Central Mechanical Engineering Institute and Philips India Ltd. He has visited several countries like UK, Netherlands, China, South Korea and Singapore, etc., in connection with the pioneering work in steel applications.

Introduction

Mild steel (MS) has got versatile application as structural steel for construction of buildings, bridges, flyovers, pipelines etc. But this is very much prone to corrosion in industrial and marine environments in presence of harmful pollutants and other industrial effluents in addition to normal humid atmosphere. These corrosion problems are much severe in a tropical country like India with vast coastline. MS corrodes relatively faster and thus leads to colossal loss in every year and to reduce this loss some kind of protection in the form of paints and coatings is always used. Painting is an effective means but quite costly amounting 10–15 % of the initial construction cost of superstructures besides cost of repainting at regular interval. Addition of small percent of minor alloying elements especially Cu, Cr, P etc in mild steel known as weathering steel (WS) considerably improves its corrosion resistance in industrial and rural atmosphere. While the organic coatings (paints) are invariably applied to MS structures, WS is used with or without coatings. Application of a defect-free paint to the structures improves their life. However, problems start once coatings develop defects, leading to both uniform and localized corrosion and ultimately failure of structures. Engineers and scientists all over the world are concerned for much indepth research works at surface science and engineering of atmospheric degradation of MS and WS as well as improved formulation of organic paints. Endeavours have been made in the present investigation for better understanding of the degradation process and uses of high performance paints formulation and compare them on MS and WS through various AC/DC electrochemical test methods and surface characterisation through electron microscopy, XRD and Raman spectroscopy.

WS is used to protect structures from atmospheric corrosion in specific environments. Rust layers on MS are not protective and are permeable to air and moisture. Protective impervious rust coatings are supposed to form on WS with time and due to high initial cost and sometimes unfavourable environments WS cannot be used. Studies on atmospheric influences on steels in rural, industrial and marine environments have indicated that P, Cu, Ni, Cr and Si improve the resistance to corrosion while Mn does not. In an industrial atmosphere the weathering process is rapid than rural atmosphere, whereas in coastal environment,

the protective layer does not form a conventional WS. On MS, major rust phase γ FeOOH transforms to the more stable α FeOOH with time whereas in WS after the same phase change, a continuous transformation of α FeOOH to either protective γ Fe₂O₃ or α Fe₂O₃ along with amorphous δ FeOOH with increasing exposure time takes place. On MS, this does not form in a continuous manner and the amorphous δ FeOOH formed are not protective in nature for this reason. Presence of chlorides in the atmosphere aggravates corrosion of steels leading to the formation of basic Fe²⁺, Fe³⁺ chlorides and β FeOOH on MS. In case of WS, exposure to coastal environment causes the formation of α FeOOH, β FeOOH, γ FeOOH, Fe₃O₄ and amorphous rust. In Industrial environment, formation of α FeOOH is predominant on steels which remains uniformly distributed throughout the rust layer. Concentration of α FeOOH is higher and γ FeOOH is lower on WS than on MS. Amorphous rust is found at the bottom of the rust layer on both MS and WS. On WS, the alloying elements Cu and Cr become enriched in the inner layer of rust while Si, P and Ni are not found to exhibit any characteristic distribution. The acid rain triggered atmospheric corrosion of steel and presence of SO₂ accelerates corrosion. Thus in an industrial environment, presence of humid SO₂, helps in the formation of a very thin oxide film composed of an inner layer of Fe₃O₄ covered with an outer layer of FeOOH. Investigations on atmospheric corrosion of WS in the presence of NaCl and SO₂ revealed that NaCl can accelerate the corrosion rate and their combined effect is greater than that caused by each single component. In the absence of SO₂, α FeOOH, β FeOOH, γ FeOOH, Fe₃O₄ and γ Fe₂O₃ are the dominant corrosion products, while β FeOOH, γ FeOOH, Fe₃O₄ and FeSO₄H₂O formed in the presence of SO₂. Microscopic observation of rust layers on WS reveals the two phases in layers parallel to the steel surface. The inner phase extends up to outer surface if exposure periods are longer than 5 years, and then it becomes the only component of the rust coating. In MS, corrosion products form as two different phases, and there are two layers with a common interface allowing moistures to go in and experiences higher corrosion rate in outdoor exposure.

Organic coatings are used on steels to provide an effective barrier protection. With time organic coating systems acquire dielectric properties, which cause them to act as capacitors. Corrosion occurring at the metal surface has a polarisation resistance related to the corrosion rate, and an electric double layer that also behaves as a capacitor. Rusting does not occur until the polarisation resistance fall below 10⁶ ohm cm².

The performance of protective coatings can be determined through accelerated laboratory tests but these are not the true representation of actual service conditions. Hence field tests are carried out to get reliable performance data on uncoated and coated steels. The protective systems and their corresponding corrosion data are available in the relevant overseas codes for reference. These data are not applicable in Indian specific context as atmospheric corrosion is location specific. Atmospheric corrosion is the frontier research area where limited work has been carried out as it comprises three phases (solid/atmospheric/liquid environment). Therefore it is significant to study the rust on MS and WS as well as coated steels in a given atmospheric environments. This is important for the

selection of more suitable materials as well as for the safety of structures, including the realisation of essential economic effect.

Research work has been carried out in two parts viz., field exposure tests and accelerated laboratory tests on unexposed panels. Under field exposure test three representative Indian sites like P1: very close to sea shore and free from SO₂, P2: away from sea with presence of SO₂ and P3: industrial environment with presence of SO₂ were chosen. Both uncoated and coated panels were withdrawn from field exposure sites for evaluation after different time intervals. DC corrosion measurements were carried out in different test electrolyte including exposure in humid SO₂ environment. AC impedance tests were performed on exposed panels. Analytical techniques (EDX, XRD and Raman spectroscopy) were used for rust characterisation and SEM was employed for understanding the morphological state. Corrosion rates were estimated after different periods of exposure at sites. Under accelerated laboratory experiments both DC corrosion and AC impedance tests were carried out in different electrolytes and in humid SO₂. The severity of corrosion rates were evaluated by humidity and salt spray tests. Rust formed were analysed by SEM, EDX and Raman. Comparative analysis of data generated through field and accelerated laboratory experiments has been performed. It is found that though accelerated laboratory test can predict the general trend of corrosion, actual field test data cannot be created in laboratory. So an attempt was made to simulate protective rust coating in the laboratory that is typical of field exposure protective rust formation on weathering steel.

Field exposure test is a very slow oxidation process whereas the accelerated laboratory test is a very fast oxidation process. Several months/years together are required to get measurable rust on surface of steel panels in field exposure. In accelerated laboratory test rate of oxidation is much faster and rust layers/oxides are formed, very quickly. The rust products/oxides formed in both the cases are identical but their manifestations are different. As a result corresponding morphologies and corrosion rates are vastly different.

The studies revealed that WS exhibited more pitting than on MS and deterioration of coated panels was highest at P1. Chloride ions accelerated corrosion at P1 and corrosion rate on WS is almost equal with MS. WS showed compact protective oxide film at P3 and its corrosion rate was found lower than MS for all the environments. Stable corrosion rate was found at P2 and P3 on WS and presence of SO₂ helped to prevent deterioration of weathering steels at these two sites. Performance of scribed coated panels with MS substrate was inferior with respect to WS substrate. Rust morphologies on MS showed lot of voids and micro cracks at all sites but compact, acicular oxides were formed on WS at P2 and P3 sites.

Rust formed in continuous humidity test on weathering steel was not stable and protective. Again WS developed more protective oxide than MS when exposed in humid SO₂ for longer period. No damage of coating was noted with initial exposure of 18 months on coated MS and WS. The data generated with accelerated laboratory tests on both coated and uncoated MS and WS panels have wide gap and difficult to predict the performance in field exposure.

It was envisaged that the slow oxidation of field test can be simulated in laboratory by selecting a slow scan rate in a potentiodynamic experiment. Na_2SO_4 solution was taken as test electrolyte because SO_2 was created in situ and this is also available in industrial environment at P3. Slow potentiostatic oxidation is possible at a low scan rate in Na_2SO_4 . Passivated oxide layers were found only on WS but not on MS. Results obtained were very encouraging as the corrosion rate was comparable to field test and rust morphology of WS passivated at -820 mV is quite identical to rust formed on WS exposed at P3 for 42 months. Raman characterisation of passivated WS panels showed the presence of γ FeOOH along with stable Fe_3O_4 and α Fe_2O_3 , which are very similar to the rust of WS exposed at P3 after 42 months. It was concluded that laboratory simulation by passivating WS at -820 mV for 80 min, is almost similar with the oxidation state of WS exposed for 42 months at P3.