Weathering Steel in Industrial-Marine-Urban Environment: Field Study

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In the present field study, we report the exposure of weathering steels in the industrial-marine-urban environment at Ennore, located near the east coast of India for 3 years. The Corrosion products viz., iron oxyhydroxides and oxides present in the rust layers were characterized using ATR-FTIR, XRD studies and quantified using TGA analysis. The specific surface area of the rust particles formed during the corrosion process were determined using N₂ adsorption isotherm studies. The morphology of the corrosion products were elucidated using SEM. ATR-FTIR and XRD studies showed that the corrosion products formed on the skyward surfaces were highly more crystalline than those on the earthward surfaces. TGA showed that the iron oxyhydroxides were major corrosion products. N₂ adsorption-desorption studies confirmed the formation of compact inner rust layers with high specific surface area (SA). SEM analysis revealed that the skyward surface was smooth and compact while the earthward surface were cracked and porous. SEM images confirmed the formation of characteristic morphological structures such as sandy crystal (lepidocrocite), needle-like (goethite), cotton ball (goethite) and cigar shaped (akaganeite) structures. Further, it revealed the formation of goethite on the skyward surface as a major constituent phase in the rust layer, which was influenced by the presence of SO₂ content in the environment. [doi:10.2320/matertrans.M2015345]

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1. Introduction

Weathering steel is widely used as a construction material due to its low cost and high corrosion resistance. The high corrosion resistance of weathering steel is attributed to the formation of dense and adherent rust layer.¹) Atmospheric corrosion studies of weathering steels in various environments such as marine, urban and industrial areas were reported.²) The corrosion parameters like chloride (Cl⁻), sulphur dioxide (SO₂), relative humidity (RH), temperature and composition of alloying elements play a crucial role in the formation of rust products during the period of exposure in different environments.³⁻⁵) The characteristic nature of the rust layer were well studied by several researchers over the last few decades.⁶⁻⁸)

Asami et al.⁹) investigated the weathering carbon steels exposed to industrial and marine environments for 17 years and concluded that the distributions of α-FeOOH phase in the inner rust layer was uniform and served as a barrier layer in the rust. Fuente et al.¹⁰) studied the morphology of corrosion products formed on mild steel, which was exposed for 13 years in various environments such as marine, industrial, rural and urban. It was found that the skyward facing surface had smooth and uniform structure with low aggressivity, whereas the earthward facing surface had irregular cracked structure. Thermogravimetric analysis were used to identify and quantify the composition of the rust and this can be achieved with a small amount of sample.¹¹) Yuxi et al.¹²) quantitatively analysed the composition of the rust formed in various environments using thermal analysis. Ishikawa et al.¹³) assessed the specific surface area of the rust layer by N₂ and H₂O adsorption studies and related this to the extent of corrosion and type of steel exposed. They showed that compact rust layers with high SA or small particle size exhibit a high corrosion resistance. Singh et al.¹⁴) have studied the long term corrosion behaviour of low alloy and plain carbon structural steel exposed to different climatic conditions for 2 years and reported the nature of rust formed, which revealed that the presence of SO₂ played a vital role in reducing the corrosion rate at Chennai site when compared to other sites.

Ennore is situated in the northern part of Chennai city at the east coast of South India near Bay of Bengal. Thermal power plants, petrochemical plants, ports, refineries, pharmaceutical companies and residential buildings are situated in Ennore and it is a marine-industrial-urban environment. There are no reports on the detailed field study of rust layers formed on weathering steels subjected to long term exposure in an industrial-marine-urban environment in India. In the present investigation, thermo gravimetric analysis and N₂ adsorption studies were used to understand the nature of corrosion products formed on the skyward and earthward rust layers of weathering steel exposed at Ennore, Chennai, India.

2. Experimental Procedure

2.1 Preparation and exposure of specimen

The composition of the exposed weathering steel is presented in Table 1. The chemical composition of alloying elements was confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES). The specimen dimensions are 100 mm × 50 mm × 3 mm. The specimens were abraded with 800 # SiC paper, rinsed with water and acetone, dried, weighed and kept in a moisture free

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>0.08</td>
<td>0.25</td>
<td>0.33</td>
<td>0.07</td>
<td>0.01</td>
<td>0.44</td>
<td>0.51</td>
<td>0.25</td>
<td>Balance</td>
</tr>
</tbody>
</table>
Table 2. Environmental conditions of exposure site (yearly average values for the period 2009–2012).

<table>
<thead>
<tr>
<th>Test site</th>
<th>Environment</th>
<th>Temperature (°C)</th>
<th>Relative humidity (%)</th>
<th>Cl&lt;sup&gt;-&lt;/sup&gt; deposition (mg/cm&lt;sup&gt;2&lt;/sup&gt;/day)</th>
<th>SO&lt;sub&gt;2&lt;/sub&gt; deposition (mg/cm&lt;sup&gt;2&lt;/sup&gt;/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ennore</td>
<td>Industrial-Marine-Urban</td>
<td>307</td>
<td>98</td>
<td>62</td>
<td>85</td>
</tr>
</tbody>
</table>

Fig. 1 Topography of the location of atmospheric corrosion exposure site of Chennai, India.

The climatic and environmental parameters viz., relative humidity, temperature were obtained from Regional Meteorological Centre, Chennai. The amounts of atmospheric deposition of Cl<sup>-</sup> and SO<sub>2</sub> content in the field were estimated using wet candle and sulphonation plate procedures prescribed in ASTM G 140-96<sup>16</sup> and ASTM G 91-97<sup>17</sup> were followed. The 3 years average environmental parameters are listed in Table 2.

2.2 Rust separation and its analysis

The easily peelable rust layers from the skyward and earthward facing surfaces were collected and labelled as skyward outer rust layer (SOL) and earthward outer rust layer (EOL). The adherent rust layers were carefully scrapped from the specimen using a sharp cut knife and were designated similarly as skyward inner rust layer (SIL) and earthward inner rust layer (EIL). The collected rust was ground and kept in a desiccator for 3 days before analysis. The adherent rust layers were carefully peeled off the specimen using a sharp cut knife and were designated as skyward inner rust layer (SIL) and earthward inner rust layer (EIL). The collected rust was ground and kept in a desiccator for 3 days before analysis.

3. Results and Discussion

3.1 Corrosive agents and environmental characteristics in the exposure site

The ISO 9223-2012 classification can be used to predict the nature of aggressiveness environment by determining the atmospheric pollutant parameters viz., SO<sub>2</sub> and Cl<sup>-</sup>. In our case study the atmospheric corrosion exposure location is closer to the industrial environment, the SO<sub>2</sub> deposits are observed in higher amount compared to the Cl<sup>-</sup>. The determined values of Cl<sup>-</sup> and SO<sub>2</sub> by wet candle and sulphonation plate confirmed the presence of SO<sub>2</sub> (85 mg/cm<sup>2</sup>/day) (S3) in the higher amount when compared to Cl<sup>-</sup> (62 mg/cm<sup>2</sup>/day) (S2). Based on the measured values of SO<sub>2</sub> and Cl<sup>-</sup> at our location, our site can be classified as C5 with reference to ISO 9223-2012 classification.<sup>18</sup> The average temperature (36°C) and RH (98%) remain throughout the year with high values. The temperature and RH varied from 30°C to 39°C, 60 to 98% respectively throughout the 3 years of exposure period. The major rainfall was observed in the months of June to December during the southwest and northeast monsoon period.

3.2 Characterization of rust layers and their products

3.2.1 Surface appearance of WS after 3 years of exposure

The physical appearance of WS surface of the skyward (Fig. 2(a)) rust layer was light red brown, adherent, compact and more uniform, whereas the earthward (Fig. 2(b)) surface of the specimens was dark brown and uneven. Also the surface was rougher and high porous in nature with the looser rust particles in EOL; but in the SOL the surface was smoother with less porous nature.

3.2.2 ATR-FTIR spectroscopic studies

The skyward (Fig. 3(a)) and earthward (Fig. 3(b)) facing rust layers were analysed using ATR-FTIR. All the ATR-FTIR spectra display the characteristic absorption peaks for water insoluble corrosion rust products namely lepidocrocite (γ-FeOOH-1020 cm<sup>-1</sup>), goethite (α-FeOOH-890 and 790 cm<sup>-1</sup>), (akaganite) (β-FeOOH-680 cm<sup>-1</sup>) maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>-560 cm<sup>-1</sup>). Water-soluble iron chloride and sulphate as residual concentration in the rust layers are hard to be detected.<sup>20</sup> In all the spectra, the absorption peak
around 1620 cm\(^{-1}\) corresponds to physisorbed water. The difference in the band intensities between 890 cm\(^{-1}\) and 1020 cm\(^{-1}\) in the skyward rust layer is attributed to the formation of goethite over lepidocrocite. The formation of goethite in the SOL is thermodynamically favourable at lower pH in the presence of sulphur dioxide which is observed at 1460 cm\(^{-1}\). Figures 3(a) and (b) reveals the presence of chloride ion favours the formation of akaganeite.\(^{21}\) The formation of stable goethite in the skyward outer rust (SOL) layer suppresses the penetration of chloride ions to the skyward inner layer (SIL) and hence less intense peak is observed for akaganeite at 680 cm\(^{-1}\) in the SIL. The protective ability index (PAI) of the rust is determined by the peak intensity ratio of the \(\alpha\)-FeOOH and \(\gamma\)-FeOOH.\(^{22}\) The skyward rust layers show the higher PAI value of 1.7 whereas the earthward rust layer shows a value of 0.98. PAI value indicates the high corrosion resistance nature of SOL when compare to EOL.

### 3.2.3 XRD analysis

Figures 4(a)–(d) shows the XRD patterns of the rust layers.
present in SOL, SIL, EOL, EIL of the exposed weathering steel. The presence of iron oxides viz., maghemite (γ-Fe₂O₃), magnetite (Fe₃O₄) and hematite (α-Fe₂O₃) and oxyhydroxides viz., lepidocrocite (γ-FeOOH), goethite (α-FeOOH), akaganeite (β-FeOOH) and ferrihydrite (δ-FeOOH) with varying intensities in all the rust layers are observed. The relative peak intensity of goethite (2θ = 21°) in the skyward surface was stronger than the earthward surface which is attributed to the presence of higher sulphur content which in turn enhances the transformation of lepidocrocite into thermally stable goethite.¹⁴) In the case of EOL relative peak intensity of lepidocrocite (2θ = 14°) is much stronger than the skyward surface. The relative peak intensity of akaganeite in the earthward layer is lower than the skyward layer due to the spallation of the earthward rust layers.²⁵) Exogeneous silica (SiO₂) is observed in all the rust layers. The cation selective ability of goethite enhances the corrosion resistance of the steel which retards penetration of chloride from the environment.²⁶) From the above results, it is inferred that the skyward surface is more corrosion resistant than the earthward surface. These results are in agreement with the ATR-FTIR studies.

3.3 Morphology of corrosion products

Scanning electron micrographs (SEM) of the skyward and earthward surfaces of exposed weathering steel are shown in Fig. 5. The presence of voids and micro cracks are significantly higher in the earthward surface when compared to the skyward surface (Fig. 5(a) and (b)). SEM-EDAX results for both skyward and earthward surfaces are represented in Fig. 5(c) and (d). It is inferred from the SEM–EDAX mapping that the distribution of relative sulphur content in the skyward rusted surface is higher than in the earthward surface. Further, it is inferred that the chloride content in the skyward surface is lower than the earthward surface. The presence of chloride influences the formation of cracks which are evident from the difference in the skyward and earthward micrographs. Chloride ion influences the formation of flaked rust in the earthward surface whereas, SO₂ plays a crucial role in the formation of less rougher morphology in the skyward surface.⁹,²⁷) Figures 6 and 7 show the typical morphologies of the rust products formed on the skyward and earthward surfaces respectively after 3 years of exposure in the marine-urban-industrial environment. Fine plate-like structure is present in the skyward surface (Fig. 6(a) and (b)) and the crystalline globule (sandy crystals) structure is present in the earthward surface (Fig. 7(a)). These structures account for the presence of lepidocrocite (γ-FeOOH). The cotton ball (Fig. 6(c)) and needle-like
structures (Fig. 6(d)) in the skyward surface and whiskery cotton ball structure (Fig. 7(b)) in the earthward surface can be regarded as the structures of goethite ($\alpha$-FeOOH).\textsuperscript{23} Akaganeite ($\beta$-FeOOH) is present in the form of cigar shaped crystals (Fig. 6(e)) and rosette morphology (Fig. 6(f)) in the skyward surface and whiskery rod shape structures (Fig. 7(c)) in the earthward surface.

It is accepted that rusting is a heterogeneous process and results in different phases.\textsuperscript{27,28} The different morphological structures of the iron rust corrosion products with same phases are attributed to the time of exposure.\textsuperscript{29} Based on Evans\textsuperscript{30} and Misawa’s Model,\textsuperscript{31} the corrosion processes and the formation of rust layers are depicted in Fig. 8. In the initial stage of rusting lepidocrocite is formed and further the presence of sulfur dioxide favors the formation of goethite through solid-state transformation.

### 3.3.1 Cross-sectional morphology of rust layers

The cross-sectional morphology of rust layers are depicted in (Fig. 9(a)–(b)) and their EDAX spectra (Fig. 9(c)–(d)) show the Cl$^-$ and SO$_2$ enrichment. The rust layers are wavy and undulating with distinguishable outer and inner layers. Among the two rust layers, the corrosion products in the skyward inner layer (SIL) is compact, dense and adherent. The Earthward inner layer (EIL) is thinner than the skyward inner layer (SIL), cracked due to spallation.\textsuperscript{32} The average thickness of the skyward and earthward rust layers are 92 and 62 µm respectively. Figure 9(b) shows that the earthward rust layers have larger number of pores and cracks through which penetration of deleterious species such as Cl$^-$ and SO$_2$ are possible. From the cross section morphological studies, it is seen that the earthward surface were highly influenced and affected by corrosive agents than the skyward surface. Figure 9(c) and (d) EDAX spectra shows the presence of chloride, sulphur and exogenous silica along with alloying elements in the rust layers. Exogenous silica also enhances the corrosion protection of the steel. Further, skyward rust layer is enriched with Cr, Mn and Ni but the earthward rust layer is enriched with Ni only. The enrichment of Cr and Ni enhances the formation of stable goethite in the skyward rust layers when compared to the earthward rust layers.\textsuperscript{33,39}
3.4 Thermal analysis of rust

Figure 10(a) shows the thermogram of the rust layers. The study reveals that weight loss of iron oxyhydroxides and oxides at different temperatures for skyward and earthward rust layers are distinct. The significant loss of weight in the temperature range 20–220°C is attributed to desorption of physisorbed water molecules. Subsequently, the second weight loss occurring at 370°C is due to the accelerated transformation of oxyhydroxides to iron oxides, with the varying weight loss (%) corresponding to their relative amounts present in the skyward and earthward rust layers. It is evident from Fig. 10(b) that the amount of oxyhydroxides in comparison to iron oxides present in skyward surface is higher than the earthward surface. Higher amounts of oxyhydroxides enhance the corrosion protection ability of the skyward rust layers.

3.5 N₂ adsorption studies of rust layers

N₂ adsorption desorption isotherms of powdered rust layers of SOL, SIL, EOL, EIL are shown in Fig. 11(a) and (b) respectively. From the Fig. 11(a) and (b) it is inferred that the adsorption and desorption behaviour of rust layers shows typical mesoporous material type IV isotherm which is attributed to the capillary condensation in mesoporous rust channels.

SOL and EOL shows the H₂ type hysteresis loop indicating the porous nature of the rust which were substantiated by the SEM results. SIL and EIL show typical H₄ type hysteresis loop attributing to the less porous nature of rust which also accounts for the morphological structures as revealed by SEM analysis. The hysteresis loop in the relative pressure \( (P/P_o) \) range between 0.4 to 0.8 and this can be attributed to the pores with narrow and wide sections and possible interconnecting channel in the rust layers. From, the BET
isotherm SA were calculated for the SIL, SOL, EIL and EOL rust layers which were found to be 107, 84, 92 and 74 m²/g respectively. The SIL and EIL shows higher SA, higher corrosion resistance which is due to the compact, adherent and porous nature of rust layers. The higher SA results in smaller rust particles of the agglomerates of iron oxide and iron oxyhydroxides with finer pore structure. EOL and SOL show less porous which is due to the low SA resulting with poor adherent nature. The compactness and protective ability of the rust layers depend on the morphology of the rust particles; smaller particles form more compact layers and sheet or plate ones make up less permeable layers by their preferred orientation.

The relative difference in the specific surface area of SOL and SIL can be inferred from the presence of a considerable amount of akaganeite (β-FeOOH) which has a tunnel structure and contributes to a high surface area and with large pore size. The enrichment of Ni and Cr influences the reduction of particle size in the rust and its structure and composition. The SA above 50 m²/g has small pores always filled with water by the adsorption and capillary condensation. Further, it prevents the transfer of corrosive ions into the pore thus leading to the formation of adherent protective layer on the skyward surface when compared to earthward surface. The results obtained from ATR-FTIR and XRD confirmed the formation of two distinct types of layers each having unique oxides and oxyhydroxides on their surfaces. The formation of goethite in the inner layer (SIL) as stable form of product with needle like structures was in other iron oxides. The BET isotherm studies confirmed the compactness and densified nature of skyward inner rust layers which prevents the ingress of chloride ions. Corrosion process with enrichment of Ni and Cr resulted in other rust particles in the skyward inner layer with higher surface area, thereby ensuring the corrosion protection of weathering steel.

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**REFERENCES**