PROTECTIVE NATURE OF THE SURFACE FILM FORMED ON THE WEATHERING STEEL

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INTRODUCTION

Weathering steel containing Cu, P, etc., has been widely used for various steel structures such as, bridges, buildings, towers, etc., because of its maintenance free characteristics resulting from the formation of a protective and adhesive film during the exposure of the structure to the atmosphere. This feature facilitates the weathering steel to be used without any surface treatment. It is well known that rate of atmospheric corrosion depends upon: i) the length of time, the moisture is in the contact of the surface ii) the extent of pollution in the atmosphere in which the material is exposed and iii) the chemical composition of the iron and steels. Here, i and ii both are of great importance. It is seen that sample of the same material exposed in a similar manner lost hundred times as much weight in the humid industrial atmosphere of England, as in the dry semi-tropical atmosphere of Khartoum, Egypt.Variation in the composition of iron or steel (i.e., factor iii) may play as important role as atmospheric environment. For example, during exposure in an industrial atmosphere, a structural steel with 0.04% Cu lost 13.8g/sq.dm after 8 years of exposure, whereas a similar specimen of steel containing 11.4% Cr lost only 0.16g/sq.dm[1]. Figure 1, is a time-corrosion plot[2] of three steels in marine and industrial atmospheres. It is seen from the figure that the loss in weight of copper steel during the first 0.5 and 1.5 years is considerably less in marine than in industrial atmosphere, but from the shape of the curves it is probable that the corrosion losses in marine atmosphere will eventually be higher than in industrial atmosphere. Though the metal loss in 3.5% Ni steel is low it behaves in the similar manner as Cu steel. Opposite is true in case of more complex Ni- Cu-Si-P steel i.e., metal loss is less in industrial atmosphere to that of marine atmosphere. It was suggested that such a reduced loss in weight was due to a very thin and adherent film formation on the latter surface.

Figure 2 shows the typical time-corrosion curves for various steels mentioned in Table 1. In order to obtain metal loss well below the band, it is necessary to add alloying elements in amount disproportionate to their value. This is due to the fact that when steels are exposed as mentioned above, a loss in weight of about 3 g/sq dm of most alloy steels is used up in providing a protective oxide film on the surface. Thus the corrosion rates shown by the lower limit of the band in the figure appear to be about the optimum value which can be achieved economically for this type of steel.

Several reports have been introduced about the structure of the protective rust form on the weathering steel. Okada et.al.[3-5] reported that a protective layer was formed with two layers. They showed that the inner layer of protective rust was optically isotropic and consisted of amorphous

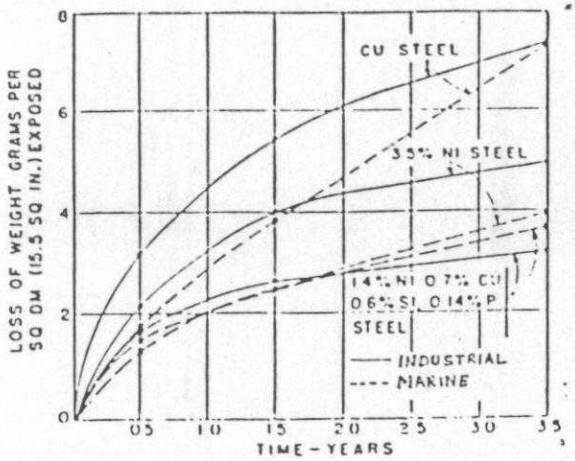

Fig. 1. Time-corrosion curves for steels in Marine and industrial atmosphere

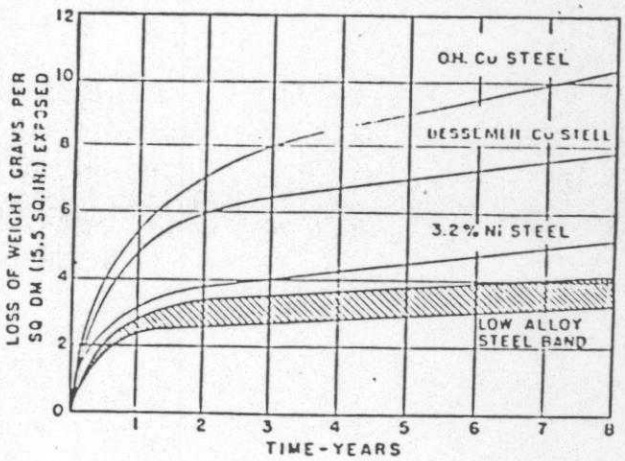

Fig. 2. Time corrosion curves for steel in industrial atmosphere

or very fine spinal type iron oxide. Some introduced the enrichment of alloy elements and thus the nature of the rust layers[6-10]. Their analyses were almost based upon the protective rust formed on weathering steel in a mild environment

Table. 1 Chemical composition of steels (Fig. 2)

Steel	C	Mn	P	S	Si	Cu	Ni	Cr	Mo
O.H.Cu	0.02	0.30	0.006	0.018	0.005	0.20	0.00	0.07	-
Bessemer Cu	0.01	0.04	0.112	0.059	0.018	0.21	0.003	0.03	-
Ni steel	0.19	0.53	0.016	0.022	0.009	0.07	3.23	0.10	-
Low Alloy Steel									
Ni-Cu	0.05	0.36	0.054	0.016	0.008	1.14	1.99	0.01	-
Cu-Ni-Mn	0.09	0.86	0.008	0.025	0.019	1.41	0.95	0.03	0.09
Cr-Si-Cu-P	0.09	0.24	0.154	0.024	0.80	0.43	0.05	1.07	-

Present topic deals with the atmospheric corrosion testing of weathering steel and nature and mechanism of protective rust formation on the surface.

ATMOSPHERIC CORROSION TESTING

Atmospheric corrosion studies are usually carried out for a period of month or even years to ascertain the environmental effect on the degradation of the materials evaluated. Therefore, it is important to select standard or reference material(control specimen) that will be exposed alongside of the materials, alloys, or coatings of interest. Exposure of control specimen is extremely important for comparison purpose and for monitoring the corrosively of the site. For atmospheric corrosion testing, specimens are normally exposed on a rack similar to that shown in Fig. 3. The rack is the attached to a frame or stand (ASTM G 50 or ISO DP 8565). Specimen sizes are normally 100 x 150 mm (4 x 6 in), but it can be of any size, necessary to evaluate the behavior properly. All the specimen should be isolated from each other and also from the exposure rack by

some non-conducting materials such as the porcelain insulator as shown in the figure. The normal convention used for specimen orientation is as follows:

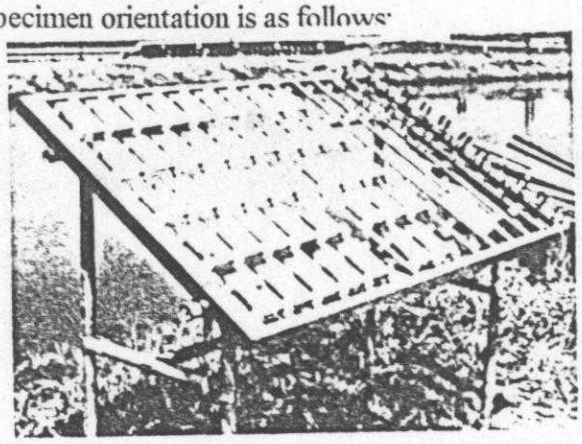

Fig.3. Test rack for atmospheric corrosion

Specimen exposed in the northern hemisphere, normally faces south and the specimen exposed in the southern hemisphere faces north. Also, it is common practice to exposed specimens facing the most corrosive direction if the exposure site is close to a source of corrodent such as, sea water or power plant stack. To study the effect of rain fall a similar exposure test is generally conducted under shelter and thus a comparative result could be obtained to evaluate the nature of surface film when material is kept in store or not exposed to rain.

CHARACTERISTICS OF THE PROTECTIVE OXIDE FILM

It has been observed that during night when dew point is reached, atmospheric moisture condenses on the metal surface and thus provide more rusting. On an average, a 5.5 to 8.3^{0}C drop in temperature, when in daytime relative humidity is around 75%, is sufficient to result in condensation at night. Here, the atmospheric moisture absorbs the gaseous contaminants present in the local atmosphere and nucleates around the dust particle and thus brings an acidic droplet to the metal surface[11] The thin acidic moisture film is capable to dissolve steel and generate iron salt which has tendency get hydrolysed and peptized to produce very thin and dense film of rust in the form of gel. By Morning, the sun and the moving air dry the gelatinous ferric hydroxide compound that form and the oxide begins to consolidate itself on the surface. This process of film formation is presented in pictorial form below:

Step 1	Moisture + Gases	→	Acidic moisture
Step 2	Acidic moisture + Dust particle	→	Acidic droplet
Step 3	Metal Surface + Droplet	→	Fe^{2+} salt solution
Step 4	Fe2+ + Water + H+	→	Gelatinous Film
	Dried		
Step 5	Gel Film	→	Adherent oxide film
	in the Sun		

This alternate cycle is repeated again and again to produce a dense and protective oxide film on the surface of the weathering steel. The characteristics of rusts formed on the low alloy steels after long exposure to the atmosphere is given below[12].

(1) The rust on the weathering steel consists of two layer. An outer layer and an inner amorphous, compact adhesive layer. Inner layer is generally much finer in grain.
(2) Enrichment of Cu, P etc., was found in the inner layer of the rust film (analysed by electron-probe microanalyser).
(3) Weathering steels are used in the atmosphere containing SO_2 and show higher corrosion resistance to atmospheric corrosion in comparison to mild steel.

Mechanism of rust formation is as follows:

i) $Fe \rightarrow Fe^{2+} + 2e^-$ Anodic Reaction

ii) $2H^+ + \frac{1}{2} O_2 \rightarrow H_2O - 2e^-$ Cathodic Reaction

iii) Corrosion of metal ceases with the enrichment of the surface with alloying elements i.e., Cu, Ni, etc.

$$Fe^{2+} + 2H_2O \xrightarrow[\text{formation depends on anion}]{H^+ \text{ as catalyst}} \text{Fe(II) hydroxo-complex}$$

$$\text{Fe-Hydroxo complex} + O_2 \rightarrow \text{Green Rust}$$

$$\text{Green Rust} \rightarrow FeOOH$$

iv) γ FeooH may transform to α FeooH by dissolution and reprecipitation in slightly acidic solution. It has been seen that in industrial atmosphere the test pieces contained mainly α FeooH and γ FeOOH in same ratio. Misawa, et.al. have shown that in presence of Cu^{2+} and PO_4^{3-}, the Fe-hydroxo complexoxidised to Amorphous δ FeOOH by the diffused O_2 to the surface. This transformation was considered to be caused by the marked catalytic activity of Cu^{2+} and PO_4^{3-} in oxidation Fe-hydroxo complex.

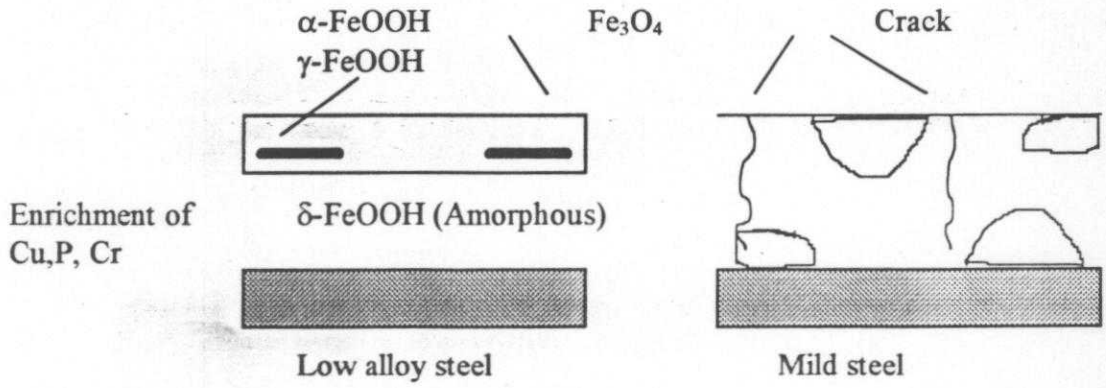

Fig.4: Schematic representation of the rust layers on steels after exposer to the atmosphere for long periods.

On the basis of the above informations, a schematic representation of rust the film formation is shown in Figure 4. Experimental verification is given in Figure 5, using polarization

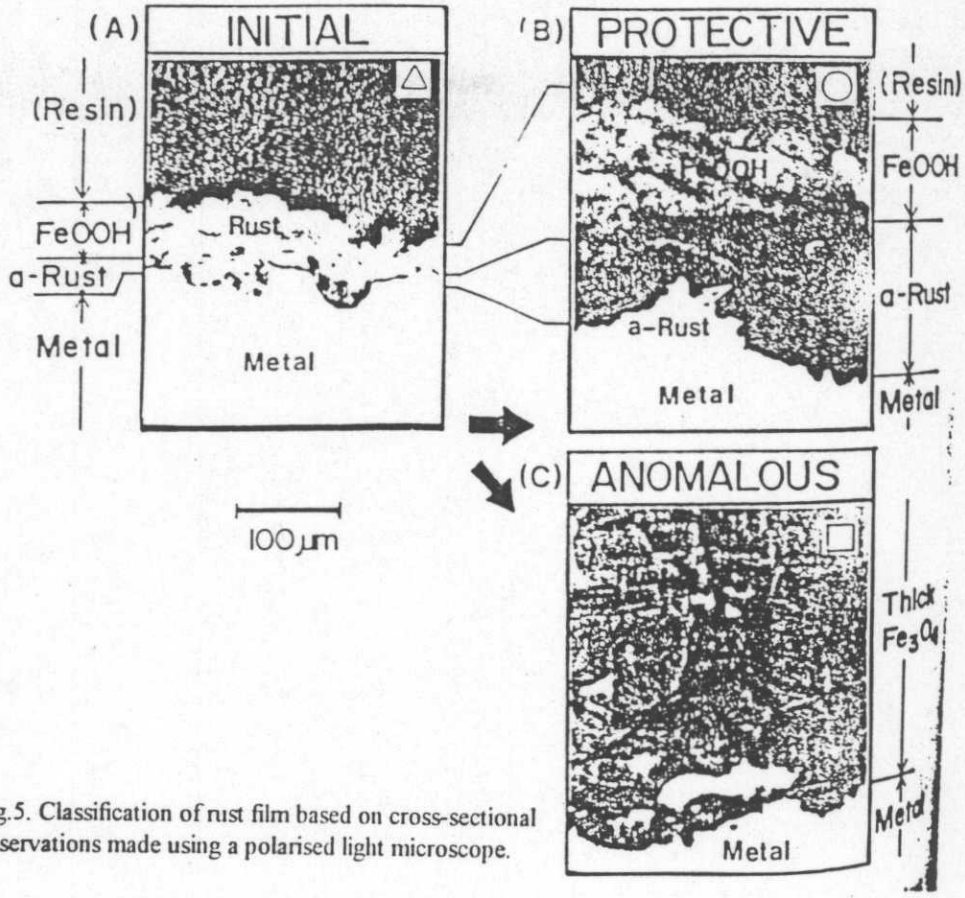

Fig.5. Classification of rust film based on cross-sectional observations made using a polarised light microscope.

light microscopy[8]. Figure 5 (a) shows an island of amorphous rust at the steel-rust interface under crystalline rust layer. This is obtained during initial exposure. Usually rust thickness is less than 270 μm.. Figure 5 (b) represent the form of protective rust. An amorphous rust layer covers the whole surface area under the crystalline rust layer (FeOOH). Total thickness of this layer is between 40 and 380 μm.Lastly, the Figur 5 (c) shows the anomalous rust layer as crystallin Fe_3O_4.

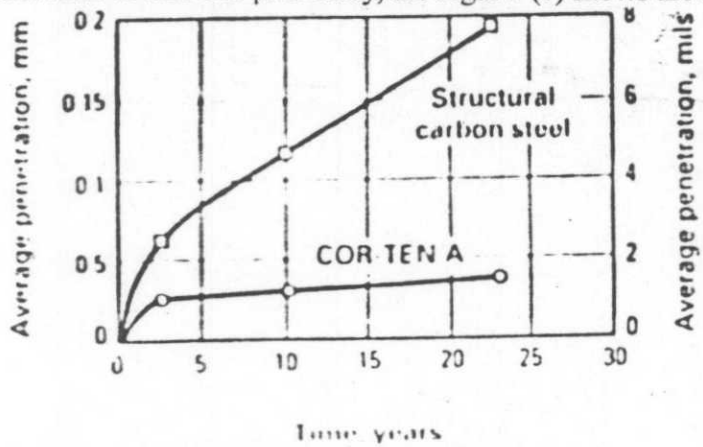

Fig.6. Time-corrosion plot showing relative performance in semi-industrial environment

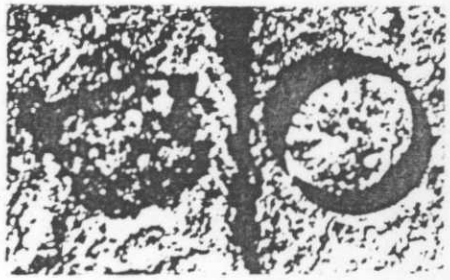

Fig.7. Water droplet wetted out and penetrated C-steel rust (left) but ailed to penetrate sealed restive weathering steel (right)

This kind of rust is found during excessive wetting period and/or accumulated salt is present. Raman spectroscopy and infrared studies[7] have also revealed that the protective film formed on the weathering steel is made up of two layers and thus it corrborates the finding obtained by polarization light microscopy.

Effect of alloying elements on the corrosion behaviour can be understood by the time-corrosion plot shown in Figure 6[12]. From the figure it can be clearly seen that formation of protective film almost reduced the corrosion rate to that of carbon steel.A porous and nonprotective film is form on the carbon steel whereas, weathering steel possess a nonporous and protective film. With aging of the film sealing action increases. Figure 7 shows a water droplet on a weathering steel panel,[13] where it is seen that droplet retains its spherical shape because of the sealed surface. But in contrast, the porous rust film on the carbon steel surface allows the droplet to wet out and penetrate the rust film.

As indicated above, the key to the development of the protective oxide film is the alternate wetting and drying cycle typified by the normal night and day exposure. Under conditions of long term immersion of in fresh water or sea water, corrosion rate is same as that of carbon steel - about 0.13 mm/yr. Similarly ,burial in the soil having varying moisture levels results in behaviour similar to that of carbon steel. Thus it is easy to understand that the lack of drying cycle inhibits the formation of the characteristic oxide film. The implication then is, to avoid features in any structure, such as pockets, that can retain water for lengthy periods and to paint any portion of a structure, such as column, that will be in soil subject to rain.

Yamamoto and co-workers[14] performed to study the effect rain on the protective film formation on the steel surface. Results are shown in Figures 8-13 for three different steels having composition shown in Table 2. Tests were conducted in two coastal areas of Japan, at six different sites, under ordinary (exposed to the sun, rain and dew) and sheltered exposure conditions. From the figures 8 and 9, which are for mild steel (steel A), it seems that corrosion depth is greater for sheltered exposure whereas, it is much less for ordinary exposure tests in each coastal area. When mild steel A including two weathering steels, B and C (C, a modified steel) were exposed in coastal regions under above conditions (Fig.10 & 11) , it was observed that in ordinary exposure

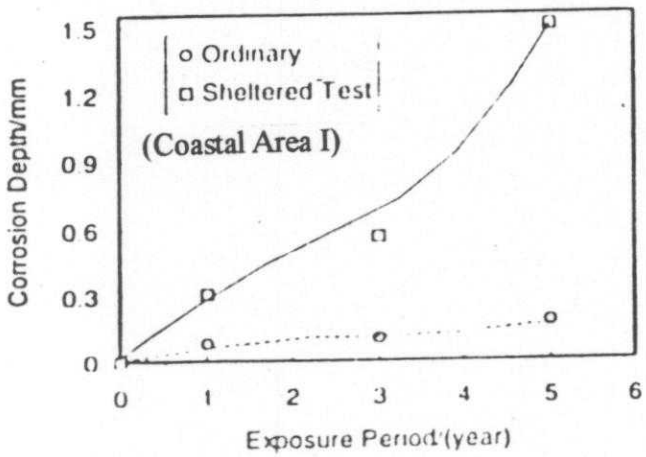

Fig.8. Difference in corrosion depth by exposure method

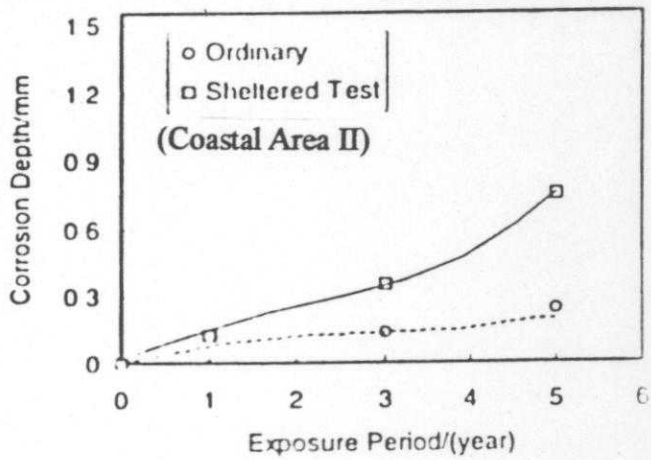

Fig.9. Difference in corrosion depth by exposure metho

Table.2 Chemical composition of steel exposed (Mass %)

Steel	C	Si	Mn	P	S	Cu	Cr	Ni	Ca
A	0.16	0.42	1.40	0.016	0.002	0.02	0.03	0.02	-
B	0.09	0.45	0.43	0.090	0.003	0.33	0.78	0.19	-
C	0.06	0.03	1.37	0.094	0.003	0.37	0.03	0.58	40ppm

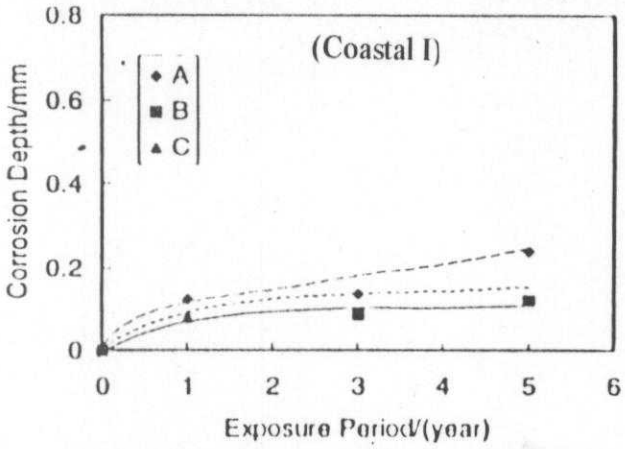

Fig.10. Corrosion depth of ordinary exposure test

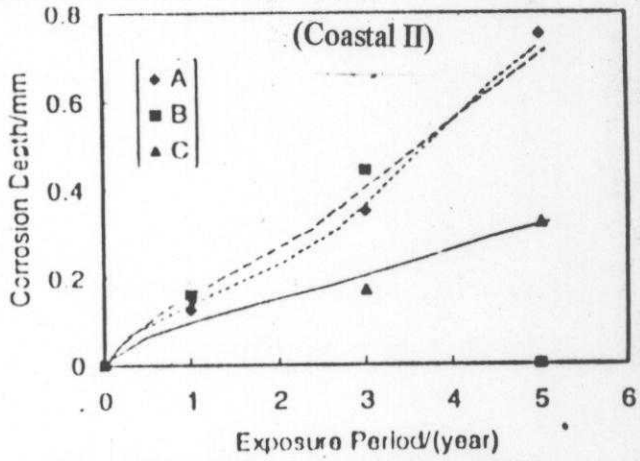

Fig.11. Corrosion depth of sheltered exposure test

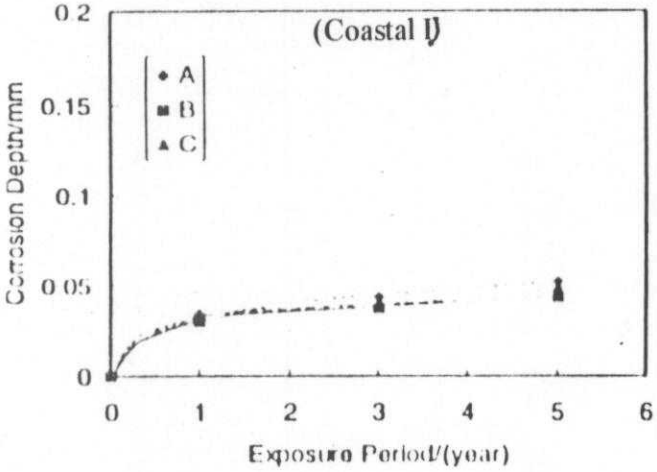

Fig.12. Corrosion depth of ordinary exposure test

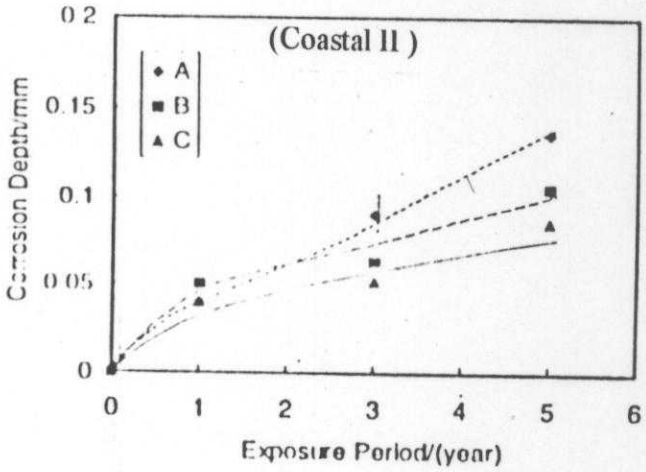

Fig.13. Corrosion depth of sheltered exposure test

test the corrosion depth for mild steel was greater than the other two steels. Likewise, the trends of corrosion of the weathering steels B & C was not very different. Besides, the corrosion depths of mild steels A and the weathering steel B were almost same under sheltered condition, the modified weathering steel C has better preformance in this environment. Similar results were also obtained in other coastal area (Fig. 12 & 13).

Sheltered exposure tests were utilized to clarify the effect of rain on atmospheric corrosion. These results indicate that the corrosion in the sheltered condition is more severe to that of ordinary exposure test. Thus, on combining the drying effect on the thin film and rain we can say that the lack of drying in the sun and the lack of washing by the rain limit the service life of the structures. Therefore, ideal exposure conditions are those in which the surface is washed frequently to remove contaminates and the sun is present to dry the surface.

CONCLUSIONS

Weathering steel possesses two layers on the surface. an outer layer and an inner amorphous, dense and adhesive layer. Inner layer is made up of amorphous δ FeOOH whereas, outer layer is build up of α and γ FeOOH. Inner layer is formed from Fe(II) hydroxo complex under the catalytic action of copper, phosphorous, nickel. This layer provides a non-porous protective barrier during atmospheric corrosion. Increase in concentration of Cu, P, and Ni is due to the acid droplets formed on the surface. The wet-dry cycle favours the formation of a adhesive layer. The ideal exposure conditions are those in which the surface is frequently washed to remove the contaminates/salts and the sun is present to dry the surface.

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