RECREATION OF MARINE ATMOSPHERIC CORROSION CONDITION ON WEATHERING STEEL IN LABAROTORY

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Abstract-- Salt spray test, autoclave corrosion test, SO_2 salt spray test, and Relative humidity test are generally used to assess atmospheric corrosion in laboratories at accelerated rates. However no test can absolutely simulate the service condition. One can get only approximate corrosion rates using the aforesaid tests which serve as an indicative of corrosion behavior of the material in a service condition. The present work is aimed at creating specific environmental condition in laboratory to get the corrosion test done in short duration to compare with on field exposure test which would otherwise take years to complete. In this work recreation of atmospheric environment of DIGHA was tried and it was tried to simulate in such a manner that the results of laboratory test could be compared with long time field exposure at Digha. Weathering steel was taken for experimentations. Potentiostatic electrochemical tests route was adopted to simulate atmospheric condition of Digha. Laboratory test results compared well with 18 month field exposure data in terms of corrosion rate, SEM and Ramon Spectroscopy matching.

Key Words: Weathering steel,Laboratory simulation, Corrosion, Field test, SEM, Raman Spectroscopy

1. INTRODUCTION

Panossian, Z. et al. showed that weathering steels (WS) have 1-2.5% of alloying elements especially Cu, Cr, P etc and have a tendency to form a specific type of rust which helps in decreasing the corrosion rate after long exposures.[1] The rate of rust formation depends on the access of oxygen in the presence of moisture and air. According to J.K.Saha rust formation process slows down as the process progresses because the rust layers acts as a barrier to the ingress of the oxygen[2]. In weathering steels the rust layer is more adherent in nature and reduces the rate of rust growth. From M.Pourbaix concept, it has been seen that the typical behavior of weathering steel is due to the passivation during drying and lack of activation during wetting[3]. S.Feliu et al reported that air borne chloride ($0.5mg/100cm^2/day$), average wetness time < 60 %, industrial pollutants (SO2< $2.1 mg/100cm^2/day$) are the favorable parameters to formed a stable rust on weathering steel, like [4-5].

Marine atmosphere have high percentage of relative humidity and airborne salt. Corrosion rate in chloride environment gets reduced in special grade weathering steel. Many authors have studied the corrosion products formed on carbon and weathering steels (WS) when they are exposed to different atmosphere[6-14]. On WS, major

rust phase lepidocrocite (γ-FeOOH) transforms to the more stable goethite (α-FeOOH). With increasing exposure time continuous transformation of α -FeOOH occurs to either protective γ Fe$_2$O$_3$ or α Fe$_2$O$_3$ as well as amorphous δ FeOOH[2]. Pourbaix diagram[3] for iron-Na$_2$SO$_4$ shows passivity between pH 9 to 12.5 due to formation of iron hydroxide. Jayanta K Saha[2] reported that when weathering steels are exposed to the Digha a protective layer of α Fe$_2$O$_3$, γ Fe$_2$O$_3$, γ FeOOH, δ FeOOH and α Fe$_2$O$_3$, α FeOOH, γ FeOOH are formed during 18 months and 42 months on field explosion respectively.

 Since passive layer formation is supposed to cause the decreasing corrosion rate of weathering steels with increasing exposure time, it was envisaged to induce on weathering steel formation of passive layer corresponding to Digha. Digha exhibits a typical marine atmosphere in India. Passive layer on weathering steel was formed potentiostatically in the laboratory. Aqueous solution corresponding to Digha environment was taken for the Potentiostatic experiments.

2. EXPERIMENTAL & RESULTS

   The composition of WS used for this purpose is given in the table 1.a.

Table.1.a: chemical composition of WS

Composition (wt%)	C	Mn	Cu	Cr	Ni	S	P	Si	Fe
WS	0.09	0.38	0.35	0.45	0.27	0.01	0.11	0.41	balance

Test sample of WS as per ASTM Standard was exposed at Digha which is a marine site having trace amount of SO$_2$ in the environment with appreciable amount of chloride ions. The samples were exposed for 18 months and their corrosion rate were measured by DC corrosion using Gamry potentionstat (fig.1.a) Rust morphology was characterized by scanning electron microscope (SEM) model JEOL S3400, Japan (fig1.b.),
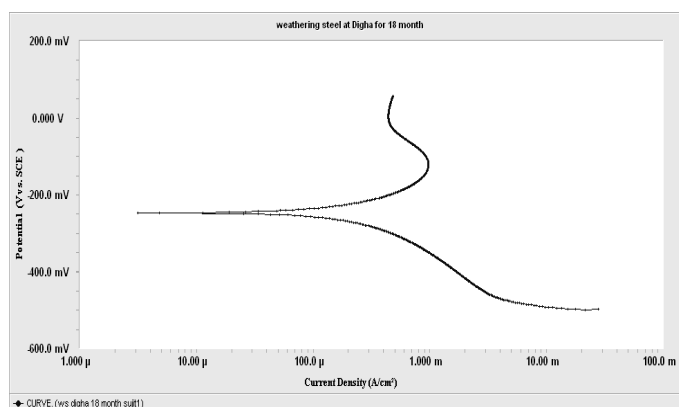

Fig 1.a. PD tests of 18 month on field WS in 3.5% NaCl solution , scan rate 1 mV/s
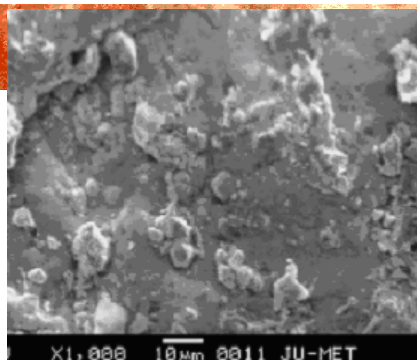
Fig.1.b. SEM of Rust Exposed for 18 month at Digha WS

Raman spectroscopy was used to identify the phases present in rust using Nicolet Almega dispersive Raman Spectroscope by exciting the laser beam of He-Ne of 532 nm focused through Olympus microscope at 50X. Raman peaks were identified according to spectra for the various iron oxide and hydroxide compounds from the references (Table 1.d).

The weathering steel samples were cut into number of pieces and were polished through 120, 180, 1/0, 2/0 emery papers and were finally cloth polished. To accelerate corrosion process electrolyte 0.01 N chloride solution was taken. For making the solution near neutral its pH was adjusted to 8.8 by adding KOH solution. The Potentiodynamic polarization of the sample in this solution was done to find out the passive region using GAMRY POTENTIOSTAT. Scanning rate used was 1mV/s (fig.1.c).
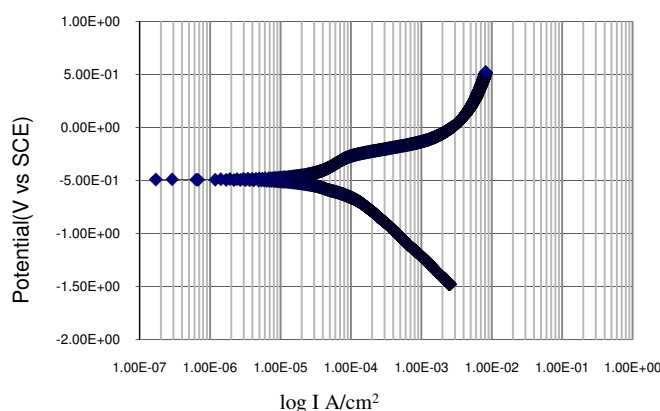

Fig 1.c.: Polarization curve of Weathering Steel in 0.01 (N) KCl solutions at pH 8.8

Once the passive region was found, a number of Potentiostatic current transient experiments at E=400mV and at 450 mV vs. SCE were carried out for different time durations i.e 30 mins, 60 mins, 110 mins. Once the passivation was done, it was then exposed to 3.5% NaCl solution for Potentiodynamic test to get the electrochemical corrosion rate (table 1.c). Potentiodynamic tests of exposed WS samples were also done in 3.5% NaCl solution. The details of results are given in the table.2.b. SEM of the both fields exposed and

laboratory simulated samples are shown in fig (2.b & 2.h). Raman spectroscopy of these samples also did (table 1.d & 1.e).
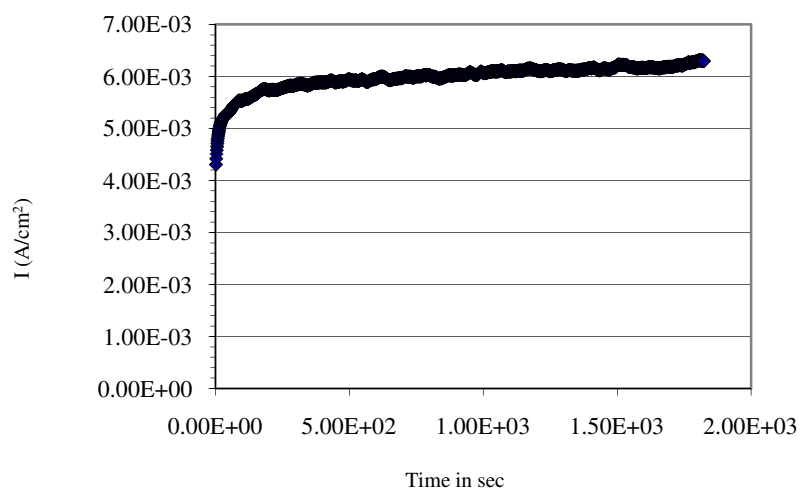
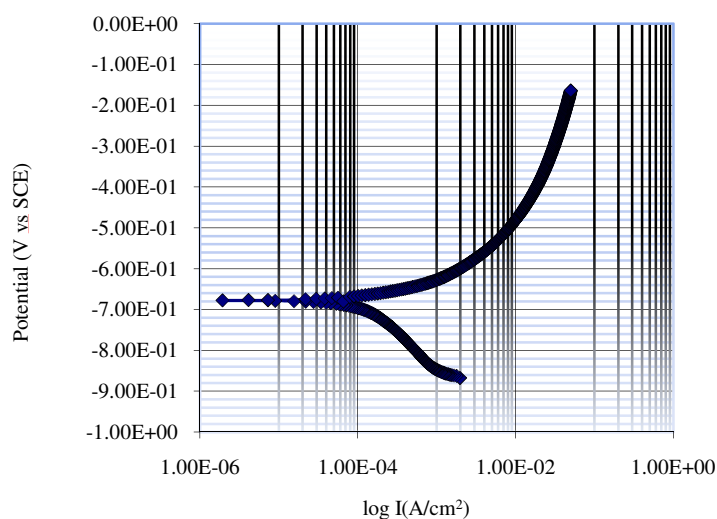Fig.1.d. Current transient in 0.01(N) KCl(pH 8.8) at a passivation potential of 400mV for 30 mins

Fig.1.e. PD of WS in 3.5% NaCl solution after passivation for 30   mins at E=400 mV

Table.1.b. Polarization Data of Digha WS sample after 18 months exposed

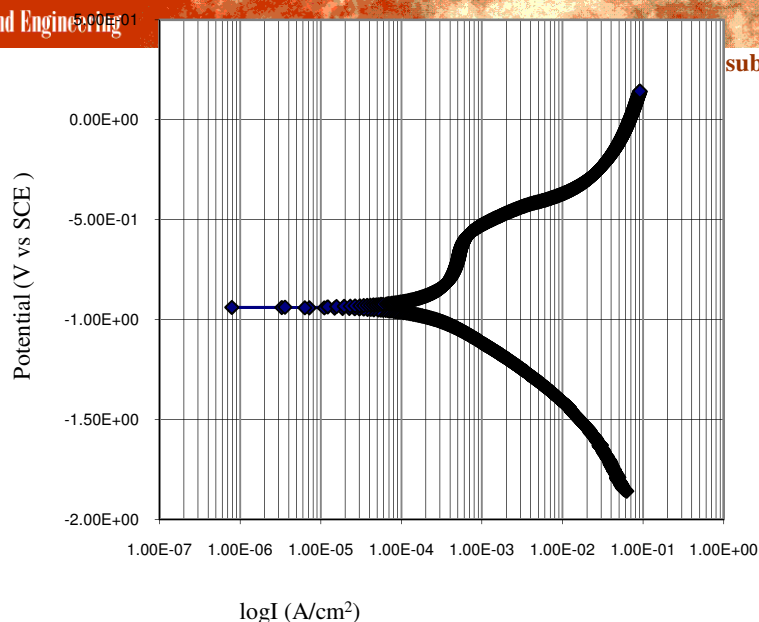| Site	Icorr ($\mu A/cm^2$)	Ecorr (mV)
Digha	102.1	-251.8

Fig 1.f. Polarization curve of WS in 0.01(N) KCl(pH 8.8) after passivation for 60mins at E=400mV
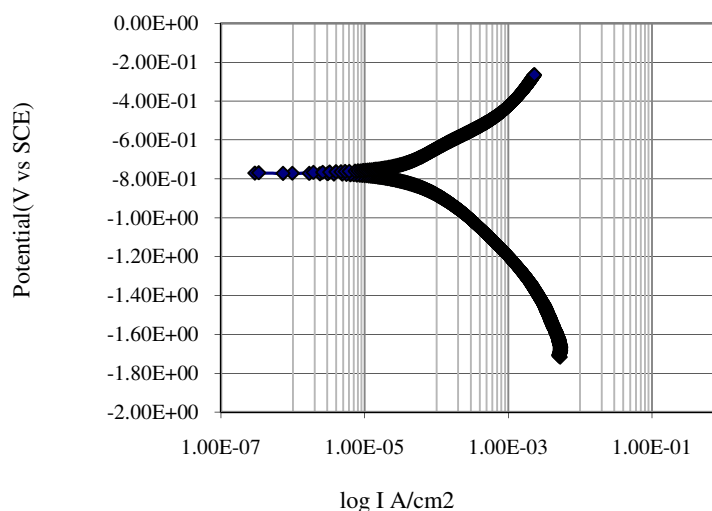
Fig.1.g.PD of WS in 3.5% NaCl solution after passivation for 110mins at E=400mV

Table1.c. Polarization Data of WS after Passivation

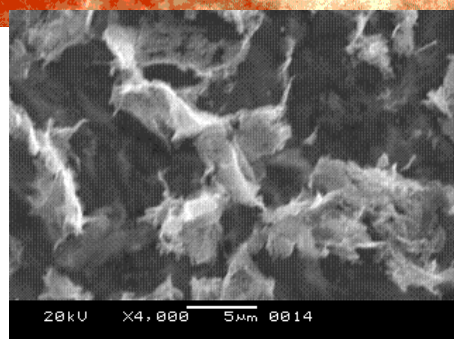| After passivation for selected time at 400mV		
Time	Icorr ($\mu A/cm^2$)	Ecorr (mV)
110 mins	40	-770
60 mins	220	-807
30 mins	102	-690

Fig.1.h .SEM of WS Passivation at 400 mV for 30 minute in 0.01 KCl (pH 8.8).

Table.1.d Raman Phases of Digha WS sample after 18 months exposed

Phase	Raman Shift (cm^{-1})
$\gamma\ Fe_2O_3$	265.37
$\delta\ FeOOH$	392.92
$\gamma\ FeOOH$	241.60
$\gamma\ FeOOH$	1292.10
$\alpha\ Fe_2O_3$	491.01

Table.1.e. Raman Phases of Digha WS sample after passivation for 30 mins at 400 mV

Phase	Raman Shift (cm^{-1})
$\alpha\ FeOOH$	302.07
$\delta\ FeOOH$	392.84
$\alpha\ FeOOH$	687.82
$\alpha\ Fe_2O_3$	1319.01
$\gamma\ Fe_2O_3$	1425.63
$\gamma\ FeOOH$	313.94
$\gamma\ Fe_2O_3$	395.69
$\beta\ FeOOH$	723.40
$\gamma\ Fe_2O_3$	1422.78

3. DISCUSSION:

The objective of passivating the sample in 0.001 (N) KCl solutions at pH 8.8 was to effect formation of oxide/hydroxide layer similar to field exposure. From fig 1.c. it can be seen that 0.4V vs. SCE is well within the passive region. Fig 1.d shows the current transient curve at 0.4V vs. SCE while fig 1.e-1.g are the polarization curve in 3.5% NaCl solutions after passivation at 0.4V vs. SCE for 30 minutes, 60 minutes, and 110 minutes respectively. It can be seen that I_{corr} and E_{corr} of the sample passivated for 30 minutes is closest to the sample which was field exposed for 18 months (table 1.b & 1.c).

The morphology of the oxide/hydroxide layer formed after passivation at 0.4V vs. SCE for 30 minutes is shown in fig 1.h and compares well with that of 18 months field exposed sample shown in fig.1.b.

 After 18 month exposure at Digha Raman spectroscopy detected major peaks γ Fe_2O_3 (265.37 cm^{-1}), δ FeOOH (392.92 cm^{-1}), γ FeOOH (241.60 cm^{-1} and 1292.1 cm^{-1}),α Fe_2O_3 (491.01 cm^{-1}) (table 1.d). WS sample shows better corrosion resistance property due to the presence of δ FeOOH phase. But there is evidence on the presence of γ FeOOH phase on the WS. As the time of exposure is increased, there is a tendency of β FeOOH getting converted to γ FeOOH and reduction of severity of corrosion environment. According to N.Sato,γ FeOOH is the top layer of passive film as claimed by most investigators[15-16]. Rust morphology of the laboratory simulated sample was also analyzed by Raman spectroscopy. The major phases are very similar to the on field exposed sample. The major phases are α FeOOH (302.07 cm^{-1}, & 687.82 cm^{-1}), δ FeOOH (392.84 cm^{-1}), α Fe_2O_3 (1319.01 cm^{-1}), γ Fe_2O_3 (395.69, 1425.63, 1422.78 cm^{-1}), γ FeOOH (313.94 cm^{-1}), β FeOOH (723.4 cm^{-1}) (Table 1.e). Laboratory accelerated corroded WS sample consist α FeOOH, which is formed from the first oxy hydroxide γ FeOOH phase. These two phases are less protective against corrosion and further phase transformation takes place. β FeOOH phases present due to the presence of chloride ion present in the solution.

4. CONCLUSION

WS forms passive layers in Na_2SO_4 solution. Rust morphology and analysis of simulated weathering process on weathering steels compared well to field exposed weathering steels at Digha. Raman characterization of passivated WS panels showed the presence of γ FeOOH along with α Fe_2O_3, γ Fe_2O_3, δ FeOOH and α Fe_2O_3, α FeOOH, which are very similar to the rust of WS exposed after 18 months. Laboratory simulation by passivating weathering steel at 400 mV for 30 min was almost similar with the oxidation state of weathering steel exposed for 18 months at Digha with respect to Icorr & Ecorr values .It is thus concluded that laboratory simulation by passivating WS at 400 mV for 30 minutes, is almost similar with the oxidation state of WS exposed for 18 months at Digha.

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