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Modeling corrosion of carbon steel in global marine environment from experimental electrochemical polarization data

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ABSTRACT

Corrosion study of structural steel in marine environment is an important parameter for design engineers to predict life of structure. Marine corrosion of steel is a complex process as it is influenced by so many parameters of salinity, sulphate, bicarbonates ions, pH, temperature, dissolved oxygen content etc. These parameters also vary quite lot depending geographical locations of the structure as well as various depths of sea water in which parts of the structures are immersed. It would be interesting to find and predict rate of corrosion of structural steel with any combinations of those variables by performing few laboratory experiments. In the present paper attempt has been made to develop a software to find corrosion rate of steel as functions of combinations of so many variables data fit for a given geographical location in an ocean., by performing some laboratory experiments based on factorial design of experiments. 3D mapping of corrosion of steel as function of two variables, (keeping other variables fixed) have been generated. Endeavors have also been made to predict corrosion rate of mild steel at a particular geographical location and compare it with real field study from literature. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Chloride;
Sulphate;
pH;
Dissolved oxygen;
Temperature;
Corrosion rate;
3D mapping.

INTRODUCTION

The geographical variation in the corrosivity of natural sea water results from variation of salinity, temperature, dissolved oxygen concentration and presence of various other salts. Chloride ion (Cl^-) has strong influence on the corrosivity of structural steel. The chloride (Cl^-) concentration of sea water varies from about 5.8gm/Kg to about 24g/Kg, sulphate (SO_4^{2-}) concentration varies from 0.8gm/Kg to 3.4 gm/Kg and the

bicarbonate (HCO_3^-) concentration varies from 0.01gm/Kg to 0.2gm/Kg^[1], across the different ocean and sea. Increase of temperature and dissolved oxygen [O] concentration are known to aggravate degradation rate of the structural material. Though the pH of sea water is in the range of neutral to slightly alkaline, local acidity developed due to corrosion products as well as crude petroleum products results in lowering of pH to around pH 4. It is interesting to find the effect of sulphate (SO_4^{2-}) which also influence corrosion rate of

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steel.

There have been some laboratory studies^[2] and fields studies^[3-5] of corrosion of mild steel in sea water. Melchers et al. conducted field tests at Swansea Public Wharf and at Pelican Marina^[3] and reported 1.3 mm/day as the rate of material loss at Swansea Public Wharf. N Sridhar et. al^[6]. developed a model to predict localized corrosion of steel in sea water. They predicted Repassivation potential and corrosion potential of stainless steel. Temperature is also known to have a strong effect on marine corrosion of carbon steel. It is reported by Melchers^[7] in his study of marine immersion of mild and low alloy steel, corrosion rate of mild steel of different geographical locations with data of temperature, salinity, PH, sulphate concentration and dissolved oxygen. M L Free^[8,9] developed a mathematical model based on thermodynamic, kinetics and mass transport equations to predict corrosion of steel in aqueous media as variations of solution compositions

In the present investigation endeavors have been made to find corrosion rate of low carbon structural steel and 304 stainless steel in artificially prepared sea water, covering full range of constituents salts, temperature, pH and dissolved oxygen by 2^k Factorial design of experiments.

EXPERIMENTAL PROCEDURE

Rectangular samples of 1X2 cm² were cut from 304 stainless steel and low carbon steel steels. They were ground carefully in order to make the edges blunt and to give a near rectangular cross section. The samples were then further ground by belt drive and polished up to 3/0 emery paper. Polishing provides a uniform surface, removes surface defects that could serve as pit sites. Following this, the samples were washed with acetone and then left to be air-dried. The samples were observed with low magnification microscope to observe whether there is any pit or deep scratch on the polished surface. If any deep scratch or pits were observed, the samples were further polished. This procedure continues till the samples become pit free.

The base solution was prepared with 0.67 gm/L KCl, 1.36 gm/L CaCl₂, 0.18 gm/L NaHCO₃ in double distilled water. Fresh solutions were prepared before each experiment. Using this base, several solutions were

TABLE 1 : Composition of different variables in 2⁵ factorial design of experiments

Reagents	Maxima Z _j ^{max}	Minima Z _j ^{min}	Average for Z _j ⁰
Chloride	24 gm/l	15 gm/l	19.5 gm/l
Sulphate	3.4 gm/l	0.8 gm/l	2.1 gm/l
Dissolved Oxygen	5 ppm	12 ppm	8.5 ppm
Temperature	40 °C	10 °C	25 °C
PH	8	4	6

prepared for each experiments with various combinations of maxima and minima of chloride, sulphate, dissolved oxygen contents, temperature and pH as shown in TABLE-1. There were 2⁵=32 nos. of experiments plus three experiments were conducted with solution of average composition.

Let Z_j^{max} = Upper limit of the variable j and Z_j^{min} = Lower limit of the variable j (See TABLE 1)

$$Z_j^0 = (Z_j^{\max} + Z_j^{\min})/2 \quad (1)$$

$$\Delta Z_j = (Z_j^{\max} - Z_j^{\min})/2 \quad (2)$$

$$\text{Dimensionless variable } X_j = (Z_j + Z_j^0)/\Delta Z_j \quad (3)$$

Where j= 1,2,.....k. Here k =5.

Using this factorial design, the regression equation

$$Y = f(\mathbf{b}_j, \mathbf{X}_j) = \mathbf{b}_0 + \mathbf{b}_1 X_1 + \mathbf{b}_2 X_2 + \dots + \mathbf{b}_{12} X_1 X_2 + \dots + \mathbf{b}_{123} X_1 X_2 X_3 + \dots + \mathbf{b}_{12345} X_1 X_2 X_3 X_4 X_5 \quad (4)$$

Where b are the interaction coefficient and X are dimensionless variables

The significance of the interaction coefficients are tested by student t distribution with 95% confidence limit. The regression equation is adequately fit by F distribution test with 99% confidence limit

Standard Corrosion Cell has been used to perform the electrochemical potentiostatic polarization tests on standard flat metal specimens. Polarization experiments have been carried out as per ASTM ST72 using Gamry Potentiostat. The software used is Gamry Echem Analyst. The potentiodynamic experiment is done with stainless steel and mild steel, and corrosion and corrosion potential were determined by Tafel's extrapolation method as well as linear polarization method. A software was developed based on equations estimated and 3D mapping of corrosion with variables was generated by the software.

RESULTS AND DISCUSSIONS

The regression equation of the form of equation

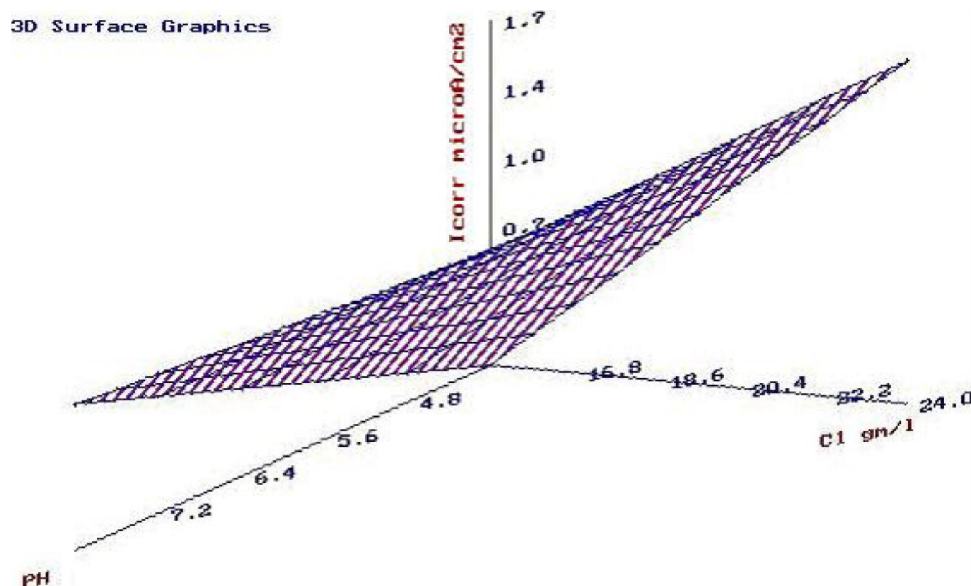


Figure 1: Corrosion rate of stainless with variation of chloride and pH in artificial sea water at 25°C

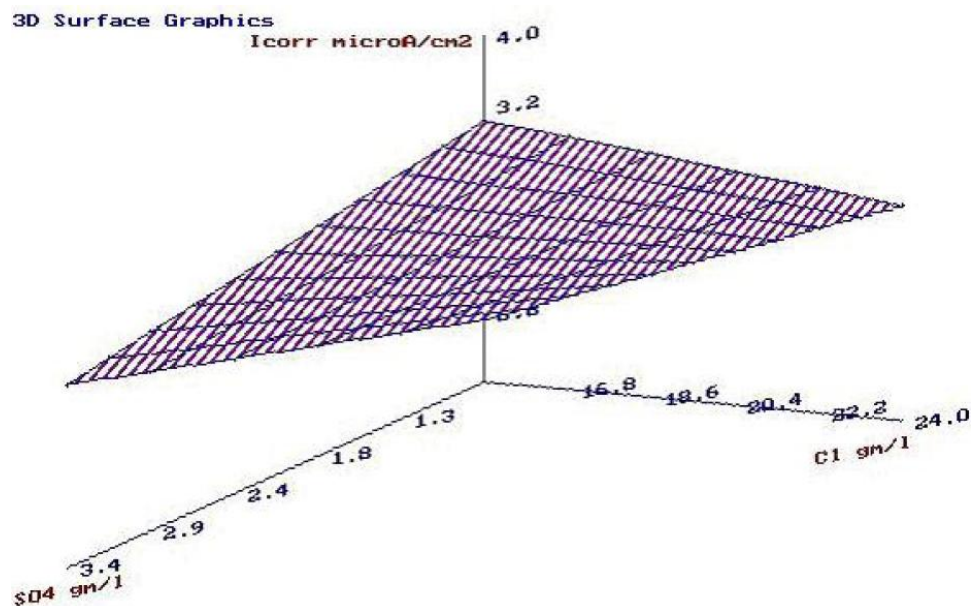


Figure 2 : Corrosion rate of stainless steel with variation of chloride and sulphate concentration , pH in the alkaline range

(4), generated from the experimental data and subsequent computation based on student T test with 95% confidence limit adequately fit F distribution test with 99% confidence limit. A software was built by C++ programming to generate 3D corrosion mapping, based on regression equation.

Regression equation stainless steel

$$I_{corr} = 1.186 + 0.659 * ((Cl-19.5)/4.5) + 0.189 * ((SO_4-2.1)/1.3) + 0.354 * ((pH-6)/2) + 0.213 * ((SO_4-2.1)/1.3) * ((pH-6)/2) + 0.219 * ((Cl-19.5)/4.5) * ((SO_4-2.1)/1.3) * ((pH-6)/2)$$

Regression equation low C steel

$$I_{corr} = 64.225 + 28.05 * ((Cl-19.5)/4.5) + 1.43 * ((pH-6)/2) + 27.03 * ((T-25)/15) + 20.96 * (([O]-6)/4) - 3.71 * ((SO_4-2.1)/1.3) * ((pH-6)/2) - 2.09 * ((Cl-19.5)/4.5) * ((pH-6)/2) - 4.66 * ((Cl-19.5)/4.5) * ((SO_4-2.1)/1.3) * ((pH-6)/2) + 20.89 * ((Cl-19.5)/4.5) * ((T-25)/15) + 18.98 * ((T-25)/15) * (([O]-6)/4) + 11.17 * ((Cl-19.5)/4.5) * (([O]-6)/4) + 11.65 * ((Cl-19.5)/4.5) * ((T-25)/15) * (([O]-6)/2)$$

Figure 1 depicts 3D surface of corrosion of 304 stainless steel in sea water with variation of chloride and pH, keeping all other variables fixed. It is seen corrosion rate increases with increase in chloride concen-

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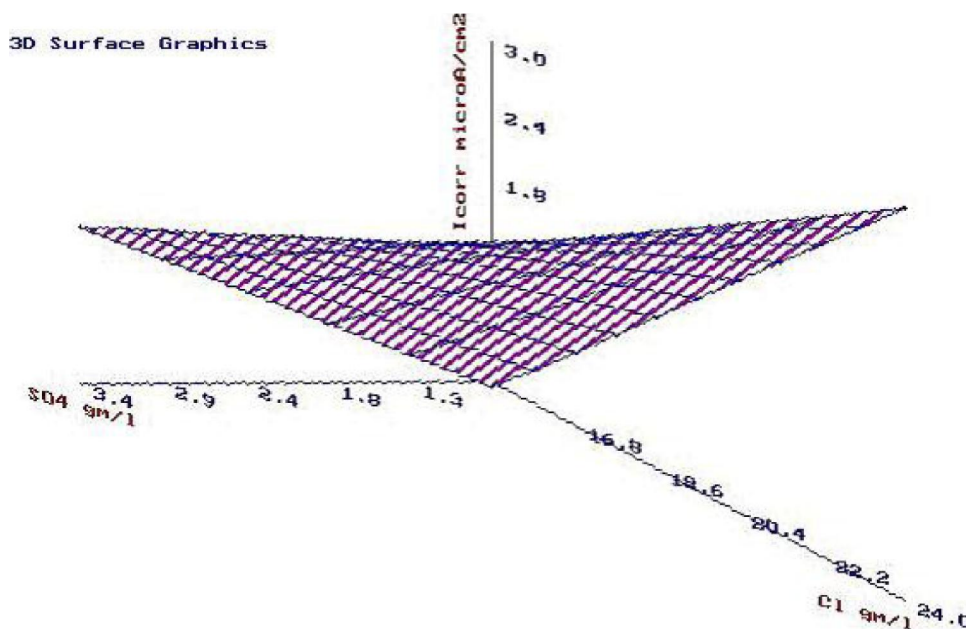


Figure 3 : Corrosion rate of stainless steel with variation of chloride and sulphate concentration in acidic range

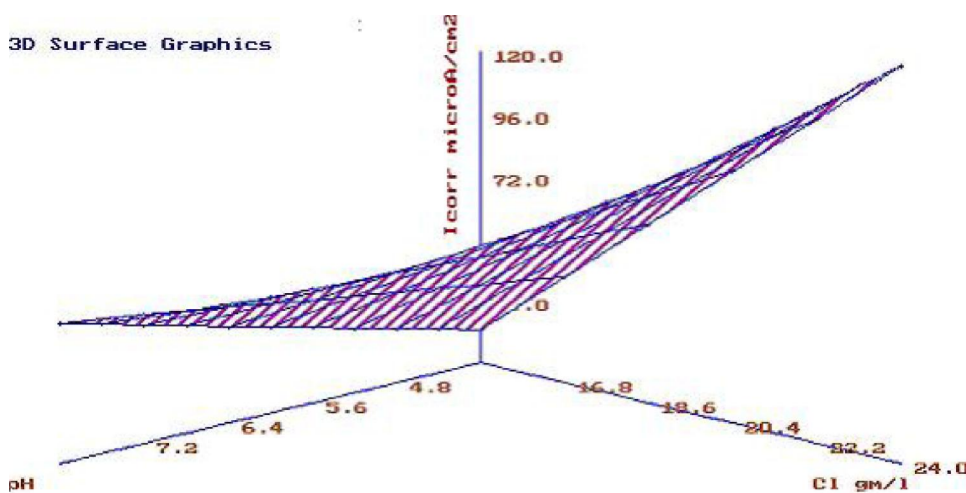


Figure 4 : Corrosion rate of low C steel as function of chloride content and pH

tration and decreases with increase in pH. This is due to fact alkalinity helps in formation of passive layer on stainless steel surface. The effect of sulphate (SO_4^{2-}) and chloride ion Cl^- concentration with pH 8, alkali region is shown in Figure 2.. Both the ions as expected have positive effect on corrosion rate. It is seen at lower pH 4 that is in the acidic region (Figure 3) the effect of chloride (Cl^-) ion is much more pronounced than that of sulphate (SO_4^{2-}) ion concentration. While combined effect of Cl^- and SO_4^{2-} (both concentrations are increased), increases the corrosion rate in alkaline region (Figure2), it decreases in acidic region (Figure3). This may be due to fact, excess H^+ ions remove free Cl^- and SO_4^{2-} ions from the system to restore the ionic equilib-

rium.

The following figures display 3D corrosion mapping of low carbon structural steel with effect of several parameters.

It is seen from Figure 4 the corrosion rate increases sharply within increasing :chloride (Cl^-), while increase of pH enhances the corrosion rate marginally. Figure5 illustrates effect of chloride (Cl^-) and sulphate (SO_4^{2-}) on corrosion rate of structural steel. It is seen chloride (Cl^-) has a very strong influence in enhancing corrosion, compared to it, the effect of sulphate (SO_4^{2-}) is negligible.

Figure 6 is an interesting diagram showing the effect of pH and sulphate (SO_4^{2-}) ion concentration at

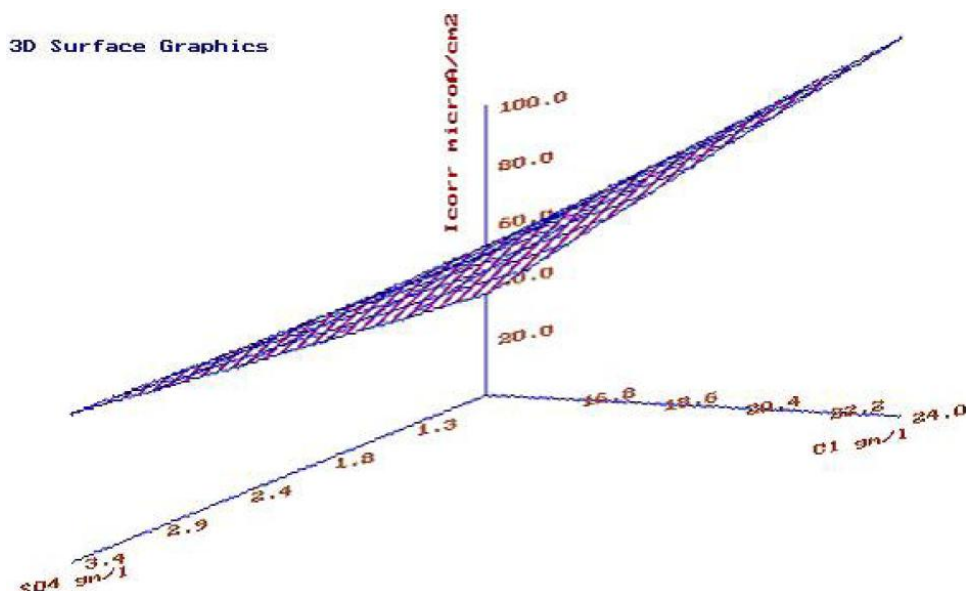


Figure 5 : Corrosion rate of low C steel with variation of chloride and sulphate concentration with neutral PH

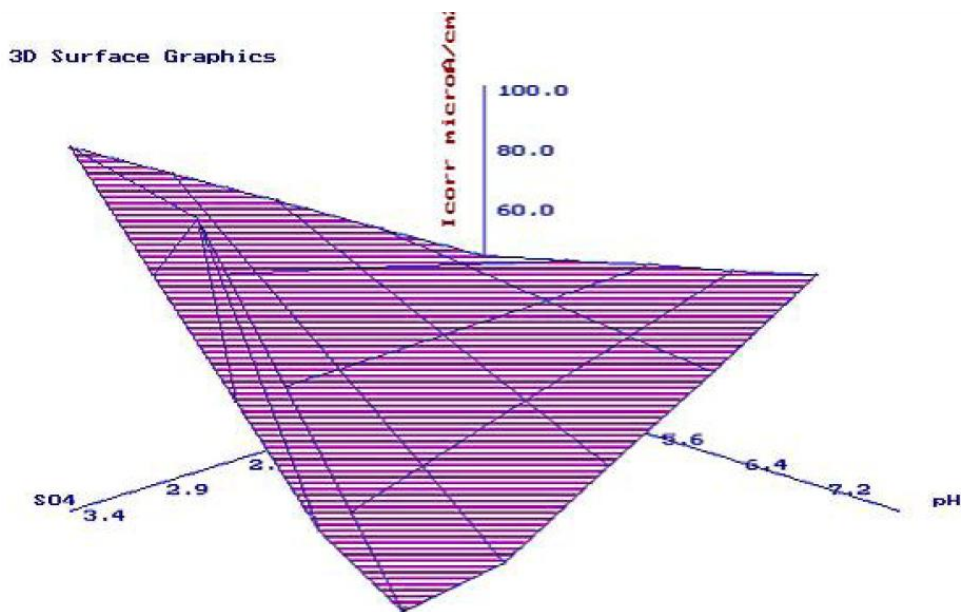


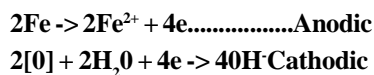
Figure 6 : Corrosion rate of low C steel with variation of sulphate ion concentration and pH

fixed chloride (Cl⁻) concentration. It is seen that the effect of increment of pH and sulphate (SO₄²⁻) jointly together bring down corrosion rate of the structural Steel. Whereas individually they have a positive effect on corrosion rate. This is due to formation of calcareous deposit on the steel surface under favorable conditions of high sulphate (SO₄²⁻) ion concentration in the alkaline region.

Figure 7 depicts the effect of chloride (Cl⁻) ion concentration and temperature at fixed [O] concentration. The diagram shows both temperature and Cl⁻ have a strong influence on the corrosion rate. The effect of

chloride (Cl⁻) and dissolved oxygen ([O]) content together at a fixed temperature 25^o C is shown in the Figure 8. It is seen dissolved oxygen [O] has very strong influence on a corrosion rate of structural Steel. Hence corrosion rate is strongly enhanced by dissolved oxygen ([O]) and chloride ion concentration.

The electrochemical corrosion of plain carbon steel in aqueous environment like seawater takes place by the following anodic and cathodic reaction.



It is seen that the concentration of dissolved oxy-

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3D Surface Graphics

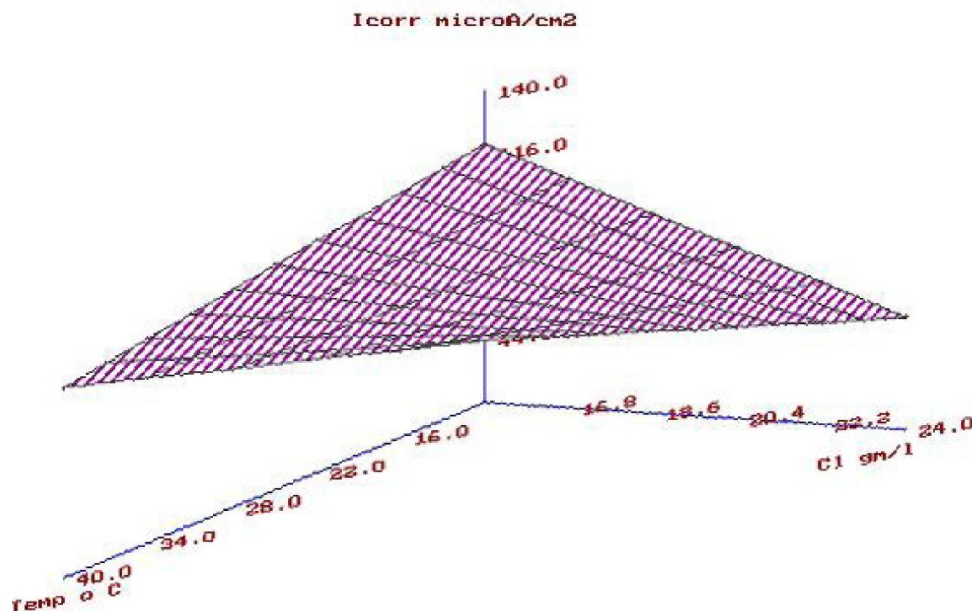


Figure 7 : Corrosion rate of low carbon steel with variation of temperature and chloride content

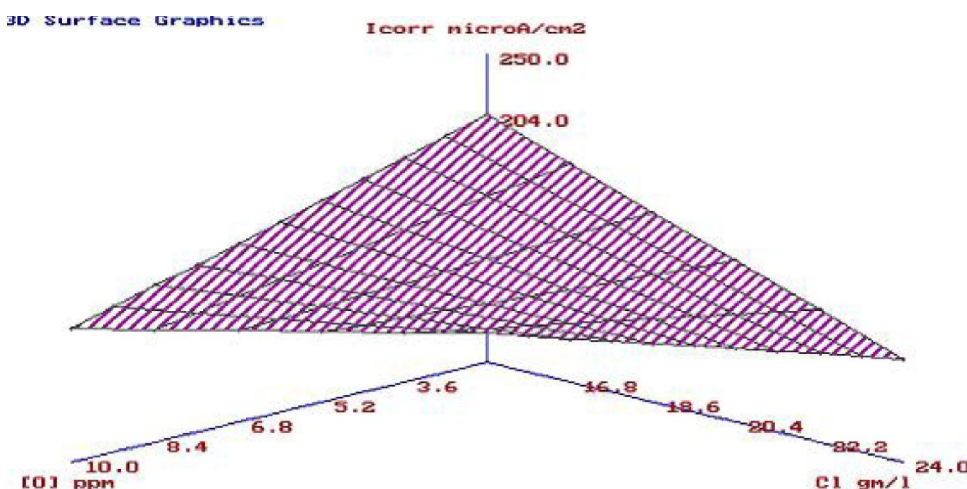


Figure 8 : Corrosion rate of low C steel with variation of dissolved oxygen and chloride

gen [O] has a positive influence on the rate of cathodic reaction. Moreover it is found from the polarization diagram of steel in aqueous environment that the anodic line cuts at concentration polarization region of the cathodic polarization curve at $E_{corr} - I_{corr}$ point. The rate of cathodic reaction is controlled by I_L , the limiting Current density, which is a strong function of concentration and diffusion of oxygen [O] from the bulk solution to the interface. These explain the enhancement of corrosion rate with increase of dissolved. oxygen [O] concentration. The limiting current density is also very much influence by temperature and agitation, both of which increases the diffusion rate. It is due to the fact that the corrosion rate of Mild Steel increases at higher tem-

perature (Figure 8). However at lower temperature of 4° C, corrosion rate is found to decrease (Figure 9) with the concentration of dissolved. oxygen [O] and chloride (Cl). The reason may be explained as mobility of both species chloride (Cl) and dissolved. oxygen [O] decreases at lower temperature (Figure 9). Finally Figure 10 displays the effect of dissolved. oxygen [O] and temperature together at fixed chloride (Cl) ion concentration. As expected both of them increases corrosion rate markedly.

Steel is known to get passivity in aqueous environment in the alkaline region. Because of higher chromium in Stainless Steel the passive oxide layer is compact adherent and corrosion resistance. However pres-

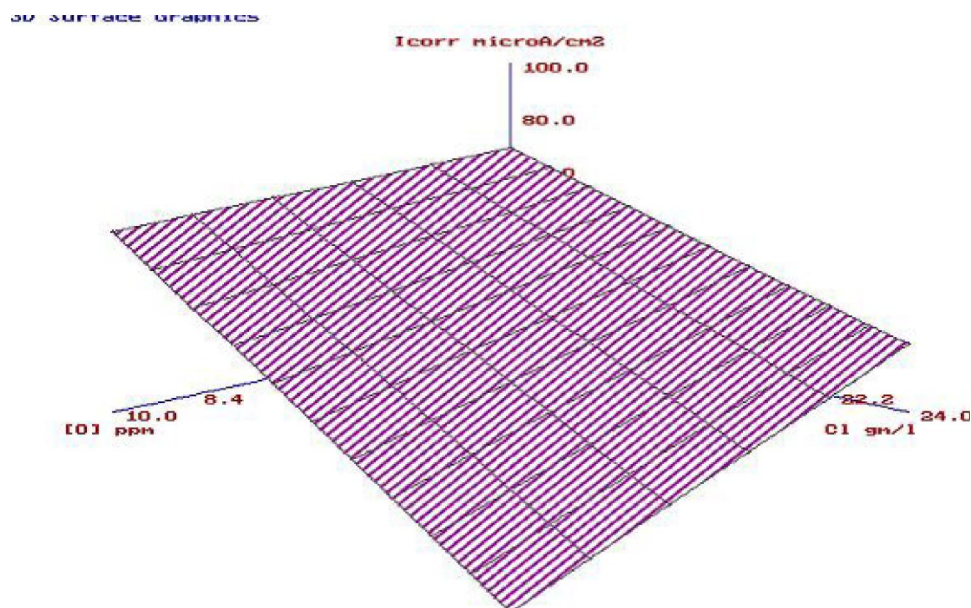


Figure 9 : Corrosion rate of low c steel with variation of dissolved [O] and chloride at 4°C

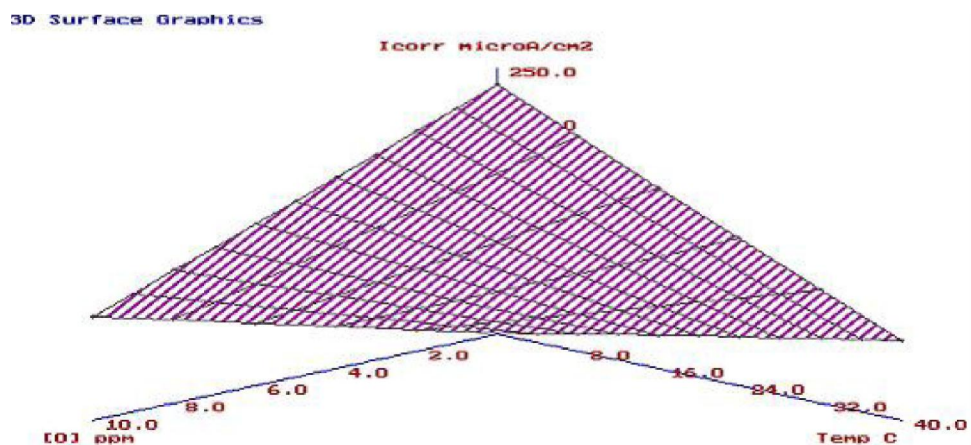


Figure 10 : Corrosion rate of low C steel with variation of dissolved and temperature

ence of chloride (Cl⁻) concentration cause the passive layer to break at some points of weakness giving rise localized corrosion. Seawater containing a god amount of chloride (Cl⁻) ion concentration thus agitate the Stainless Steel.

In case of plain carbon steel, the passive oxide layer does form, but the layer is not as much compact and adherent as that produced on Stainless Steel. So here effect of chloride (Cl⁻) on corrosion rate may be breaking of passive layer at local points as well as attack of chloride (Cl⁻) ion on expose metal.

In the present investigation the effect of chloride (Cl⁻) in artificially made seawater has been revealed in Stainless Steel as well as Mild Steel. The conjoint effects of pH and sulphate (SO₄²⁻) on corrosion rate have been formed. The effect of temperature and dissolved

oxygen ([O]) content on corrosion rate of Mild Steel have also been found to support the electrochemical theory and polarization of steel in aqueous system

Prediction of corrosion rate

Attempts have been made to predict corrosion of real structures submerged in seawater at Geographical location, from the derived equation.

It is found from the literature^[3,7] that the corrosion rate of low carbon structural steel at a specific in the ocean (Swansea Wharf) with average composition of 29.8 to 34.9 gm salinity, 2.4 gm/L SO₄²⁻ and pH 8, corrosion rate is 0.471 mm/year.

With above constituents in sea water, the corrosion rate comes out from our derived equation in the present investigation is 0.435 mm/year. It is interesting to find

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the computed corrosion rate is very close to one determine the real situation.

CONCLUSION

Corrosion rate of low carbon steel and stainless can be visually studied from 3D mappings as functions of various combinations of concentration of Cl^- , SO_4^{2-} ions, PH, temperature and Dissolved [O], depending on the geographical location of the marine structure. A prediction of corrosion rate and hence life of the structure can be computed within some limits, given the data of those variable at the particular location.

REFERENCES

- [1] Dechema Handbook of Corrosion, (Weinheim, NY: VCH publishers, **11**, 66 (1992).
- [2] U.R.Evans; The corrosion and Oxidation of metals: Scientific principles and practical applications, Edward Arnold (publishers) Ltd., London, (1960).
- [3] R.E.Melchers, R.Jeffrey; Influence of water velocity on marine corrosion of mild steel, Corrosion (NACE), **60**, 84-94 (2004).
- [4] L.A.Terry, R.G.J.Edyvean; Influences of microalgae on corrosion of structural steel. In : J R Lewis and AD Mercer, Editors, Corrosion and Marine growth on offshore structures, 38-44 (1984).
- [5] B.D.Craig; Handbook of Corrosion data, ASM, international, Ohio, (1989).
- [6] N.Sridhar, C.S.Brossia, D.S.Dunn, A.Anderko; Predicting Localized corrosion in Seawater. Corrosion (NACE), 915 (2005).
- [7] R.E.Melchers; Effect of temperature on the marine immersion of corrosion of Carbon steels, Corrosion (NACE), 762 (2002).
- [8] M.L.Free; Tri service, Corrosion Conference, 1 (2005).
- [9] M.L.Free, W.Wang, D.Y.Ryu; Prediction of Corrosion Inhibition Using Surfactants Corrosion, **60**, 837 (2004).