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Investigation of Corrosion Behavior on High Carbon Steels and High Carbon Steel Coated with Tin Bronze in Sodium Chloride and Sulphuric Acid Solution

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Abstract— Corrosion has become an increasingly significant design consideration when components and equipments are exposed to marine environments. The predominant factors affecting corrosion are pH value, NaCl concentration of sea water and exposed time of the equipment. High Carbon steel and its alloy are widely used in services such as oil rigs and marine industries due to their high strength. But when these are exposed to sea environments their strength gets reduced due to corrosion. For Tensile strength Improvement of High carbon steel, tin bronze coating is applied. The corrosion behavior of Tin Bronze alloy (C903) is evaluated by conducting test in NaCl solution at different chloride ion concentrations, pH value, and solution flow rate and exposure time. An attempt is also made to develop an empirical relationship to predict the corrosion rate of Tin Bronze alloy and tensile strength of C903 coating on High carbon steel. Experiments are carried out when solution is at steady state and dynamic state, for estimating corrosion rate and tensile strength. Three factors, five level, central composite rotatable design matrix is used to minimize the number of experimental conditions for optimizing the values.

The empirical relation is developed by using Response Surface method. The developed relationship can be effectively used to predict the pitting corrosion rate of Tin Bronze alloy and tensile strength of tin bronze coating on High carbon steel at 95% Confidence level. The significance of each regressor (factor) in this model has been estimated and surface response is drawn using 3D mapping in MINITAB Software. This research work proves a better corrosion resistance of Tin Bronze alloy at the alkaline solution than the acidic and the neutral solutions, moreover, low corrosion rate is found at low concentrated .

Keywords— Tin Bronze, Chloride ion concentration, Corrosion rate, Optimization, Response surface Method

I. INTRODUCTION

Corrosion is responsible for the deterioration of material's properties as a result of its interaction with the environment. Industries are always suffers huge financial loss due to material deterioration which is a loss in materials directly or indirectly. A direct loss in materials of equipment, when exposed to corrosive environment, due to this corrosion of equipment will stop functioning correctly. This direct loss in materials may cause damage to parts that depend on the direct damaged part which produces the indirect loss.

The available full-scale data measured for corrosion in air environment are not adequate for design of risers that transport production, since sea environments can significantly degrade the tensile strength performance compared to that in an air environment. Higher strength steel risers have been developed recently to meet the requirements of sea water and corrosive environments. However, the optimization of alloy composition and microstructure in these steel are primarily based on mechanical properties such as tensile strength stress-strain curves and fracture toughness, along with limited corrosion testing. High Carbon steel and its alloy are widely used in services such as automobiles, marine industries due to their high strength. But when these are exposed to sea environments their strength gets reduced due to corrosion. Sea environment degrades the quality of steel and thereby reduce the life span of high carbon steel.

It is well known that the corrosion is a natural phenomenon that cannot be stopped. The seawater covers more than 70% of Earth's surface and it is considered as the most abundant natural electrolyte. A great part of metallic constructions exposed in seawater and marine surrounding are destroyed, due to the corrosion phenomenon. For the marine corrosion, the seawater is the main corrosive agent. The thermodynamic law states that every material tends to reach its lower energy state. That for metals, such as copper, corresponds to the compound state from which they are extracted. The corrosion is also referred to as metallurgy in reverse [5]. In order for copper to corrode, there are four essential constituents: an anode, a cathode, the metal itself and an electrically conducting solution. The anode is the site where the copper is corroded; the electrolyte solution is the corrosive medium; the cathode forms the other electrode of the cell and is not consumed in the corrosion process. At the anode, the corroding copper goes into solution as positively charged ions, releasing electrons that participate in the catholic process.

Generally the corrosion cells are very small, numerous and distributed in a random manner over the surface of the metal and the effects are more or less a uniform attack on the surface. The anodic and catholic reactions are the following:

$Cu \rightarrow Cu^{2+} + 2e^-$ Anodic reaction

$O_2 + 2H_2O + 4\,e^- \rightarrow 4OH^-$ Cathodic reaction

For example as shown in Figure 1 the metal ions M^{2+} are conducted towards OH^- ions, and together they form a metal hydroxide that may be deposited on the metal surface. If, for instance, the metal is Copper and the liquid is water containing O_2 but not CO_2, the pattern in the figure is followed: Cu^{2+} ions join OH^- and form $Cu(OH)_2$. When CO_2 is dissolved in the liquid a Copper is deposited. Divalent copper hydroxide, $Cu(OH)_2$, is not stable either and tends to be dehydrated to CuO [20].

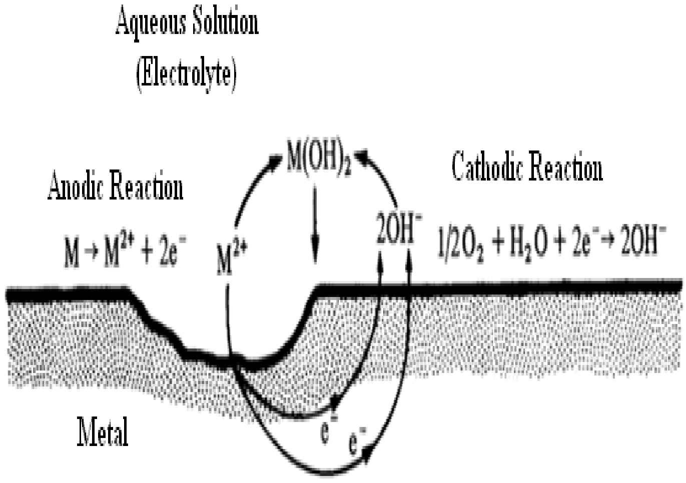


Fig. 1: Corrosion of a Divalent Metal M in an Electrolyte [20].

Reduction of oxygen is the dominating cathodic reaction in natural environments like seawater, and fresh water.

$$2H^+ + 2e^- \rightarrow H_2$$

However, under certain conditions there are also other important cathodic reactions: the hydrogen reaction reduction of carbonic acid (H_2CO_3) (in oil and gas production), reduction of metal ions etc [20].

A. *Influence of sodium chloride (NaCl)*

Other dangerous sea water components for metals' conservation are represented by saline particles. Saline particles, such as the sodium chloride, the most important constituent, accelerate the metallic corrosion process, increasing the amount of soluble corrosion products [12].

Seawater salinity typically varies from 32 to 37 g/kg (3.2 – 3.7 %), and generally, this degree of variation does not alter metal corrosion rates. Salts as sodium chloride, represent more than 90% of the solids dissolved in the seawater and its content average is of 35 g/kg (3.5%). The salinity varies according to the intensity of the evaporation of seawater or contribution of fresh water coming from rivers: dilution of the seawater in some parts of the ocean (zone of the equatorial line) and the evaporation in others (in tropical and subtropical zones) cause movement of water between these areas. The chloride ion corrosively accelerates pit and crevice corrosion initiation, and their propagation in metals [19].

In sea water, the copper and its alloys form thin layers of corrosion products, generally brown-greenish or green-bluish, known as patina, which protects the metal against subsequent deterioration. Chlorides dissolved in the layer of moisture also considerably raise the conductivity of the electrolyte layer on the metal and tend to destroy any passive film existing on the metallic surface. Chloride does not reduce the pH of the electrolyte on the metal surface but provides a rather corrosive electrolyte with high conductivity.

B. *Influence of pH*

The pH is defined as the negative of the base ten logarithm of the hydrogen ion activity. This latter quantity is related to the concentration or molarities (mol/1000 cm^3 of water) through an activity coefficient. The term is expressed as

$$pH = -\log_{10} a_{H^+} = log_{10}\, \gamma_{H^+} \mathrm{m}_{\mathrm{H}^+}$$

Where a_{H^+} is the hydrogen ion activity, γ_{H^+} is the hydrogen ion activity coefficient, and $\mathrm{m}_{\mathrm{H}^+}$ is the molarities. The value of the activity coefficient is a function of ions, non-ionized species, etc. in the solution as well as the environmental variables like temperature and pressure [15].

At the surface of open seawater, the pH value is lies in-between 7.5 to 8.3, and it depends on the amount of dissolved carbon dioxide (CO_2) that is exchanged between water and atmosphere. Plants consuming CO_2 for photosynthesis in the day can move the pH to a higher level, while some micro-organisms can increase CO_2 by their biochemical oxidation, and move the pH to a lower level [19]. Daily fluctuations in pH, from 8.0 to 8.2, which do not influence on metal corrosion behavior, practically, however, they can affect the calcareous (contain Carbonate) scale deposition on the metal surface, and this in turn, directly affects the corrosion rate. With the increment of pressure, pH value is decreased, so in the great depths of seawater, the creation of the patina (protective layers on the metal) is unlikely. The hydrogen ion concentration can influence corrosion through the equilibrium that exists with it, water, and the hydroxide or oxide formed on the alloy surface. The pH of seawater could have lowered the values because of the presence of atmospheric pollutants (acid gases) in highly pullulated coastal locations or of high industrial activity.

II. SPECIMENS AND MATERIAL PROPERTIES

A. Specimen Number 1: Bare High Carbon Steel (A641)

The material available is in the form of 0.99 mm diameter rod of high carbon steel. The chemical composition and mechanical properties of the high carbon steel are presented in Tables 1 and Table 2, respectively.

Elements	**C**	**Mn**	**Si**	**P**	**S**	**Cu**	**Fe**
Wt. %	0.7	0.55	0.24	0.01	0.008	0.72	97.53

Table 1: Chemical Composition of High Carbon Steel

Description	Breaking Load (N)	Elongation (%)	Elongation (%)
Required Standard	Above 1275	Above 3 %	5.6-5.8

Table 2: Mechanical Properties of High Carbon Steel.

B. Specimen Number 2: Bare tin bronze (C903)

Tin Bronze alloy (C903) is extruded plate of 3 mm thickness. The chemical composition and mechanical properties of the base material are presented in Tables 3 and Table 4, respectively. The specimens were cut to the dimensions of 50 mm x 50 mm to evaluate for the corrosion rates.

Elements	**Cu**	**Sn**	**Ni**	**Pb**	**Zn**	**Sb**	**P**	**S**	**Al, Si**
Wt. %	86	7.5	1	0.3	3	0.2	1.5	0.05	0.005

Table 3: Chemical Composition of Tin Bronze Alloy (C903)

Yield strength (N/mm^2)	**Ultimate Tensile Strength (N/mm^2)**	**Percentage of Elongation (%)**
152	303	18

Table 4: Mechanical Properties of Tin Bronze Alloy

C. Specimen Number 3: High Carbon Steel Coated With Tin Bronze

Tin bronze (C903) is coated uniformly on high carbon steel (specimen 1) for corrosion protection. Coating layer resist the corrosion for longer period of time to avoid rust. Tin bronze coating isolates the high carbon steel from corrosive environments. The available specimen is shown in figure 3.2. The inside material is high carbon steel and tin bronze alloy (C903) is coated as protective layer. The high carbon steel properties will be preserved in corrosive environments because tin bronze will get corroded initially **[15].** In an electrolyte solution the tin bronze layer acts as a sacrificial anode for steel. When some parts of the steel substrate are exposed, the corrosion of the tin bronze layer is accelerated by galvanic coupling with the steel. The corrosion potential of the alloy layer is between that of the tin bronze layer and that of the steel. A less defective layer exhibits potential closer to that of the tin bronze layer [16]. Thus the corrosion rate of high carbon is reduced due to the sacrificial anode of tin bronze. Also tin bronze act as barrier in between high carbon steel and corrosive medium.

III. EXPERIMENTAL SET-UP AND PROCEDURE

A. Immersion Testing

The effect of Corrosion behavior on specimens is observed by preparing different corrosive solution in glass beakers. The pH value of the solution and concentration of NaCl is varied according to experimental conditions. Immersion testing set-up consists of glass beaker in which corrosion testing is carried out as shown in figure 2.

Fig. 2: Immersion Testing Set Up.

Corrosive solution is prepared using Sodium chloride, sulpric acid, and distilled water in beaker. Specimens are immersed in solution for immersion testing. Mass loss measurement under immersion tests is carried out as per ASTM G31—72 guidelines. These guidelines for immersion testing consist of preparing bare solid metal specimen for test, removing corrosion products after test has been completed and evaluating corrosion damage that has been occurred.

B. *Measurement pH Value and NaCl Concentration of Solution*

The pH value of the solution is maintained using Sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) respectively. The pH value of Solution is measured using a digital pH meter as shown in Figure 3. pH meter consist of digital indicator for displaying pH value. Electric wired probe for dipping into solution of which pH is measured. Range of pH value is from pH 1 (acidic medium) to pH 14 (alkaline Medium) including neutral medium NaCl Concentration of solution is maintained by adding pure salt in distilled water.

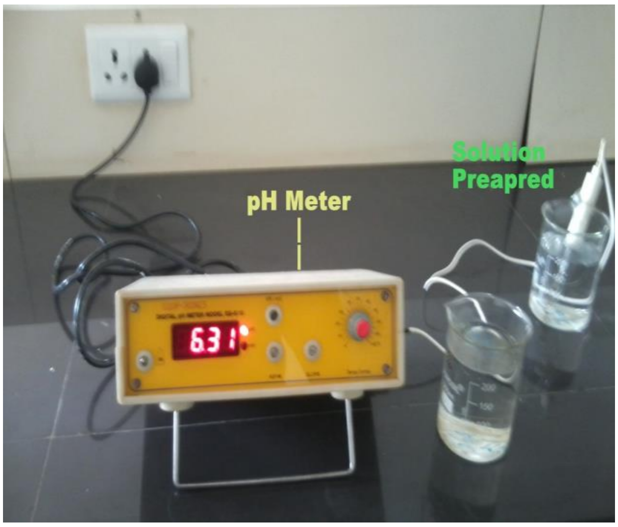


Fig. 3: pH Meter.

C. *Corrosion rate Evaluation*

The corrosion rate of the Tin Bronze (C903) alloy is estimated by mass loss measurement under immersion tests as per ASTM G31—72 [17]. The original mass (m_0) of the specimen was recorded and then the specimen is immersed into the solution of Sodium Chloride (NaCl) for different immersion time and different pH value of the solution. Finally, the corrosion products were removed by Acetone Solution. These specimens are washed with distilled water, dried and weighed again to obtain the final mass (m_1). The mass loss (Δm) could be obtained using the following relation:

$$\Delta m = m_0 - m_1$$

The corrosion rate (R) of metal region can be calculated using the following equation by,

$$R = \frac{8.76\times10^4 \times \Delta m}{A\times D\times t} \quad mm\ /year$$

Where, R = Corrosion rate in *mm/year;*

A = Exposed surface area of the specimen to corrosion in cm^2;
D = Density of the material, (for Tin Bronze 8.8 g/cm^3).
T = Immersion time in *hours*.

D. *Measurement of Tensile Strength*

Tensile strength of specimen reduced due to the corrosion medium. The protective coating is applied to reduce the corrosion effect on high carbon steel. The tensile strength of specimen before and after expose to corrosive environments is measured on tensile testing machine i.e. Universal testing machine as shown in figure 4.

The load on specimen is applied using hydraulic power. Specimens are clamped in jaw of machine and gradually load is increased due to which the specimen get break for the load that breaking load is considered for tensile strength. The tensile strength value is directly displayed on the computer attached to machine.

Fig. 4: Tensile Testing Machine.

E. *Design Variables and Response Parameters*

From the literature, and as per the previous investigation of various researchers found that, the predominant factors that have a greater influence on the corrosion behavior of copper alloys and bronzes were identified. They are: (i) pH value of the solution, (ii) chloride ion concentration (iii) immersion time. Large numbers of trial experiments were conducted to identify the feasible testing conditions using Tin Bronze alloy The following inferences were obtained:

Factor	**Notation**	**Upper Limit X_{min}**	**Lower Limit X_{max}**
pH value	*P*	3	12
Immersion time(Hr:min)	*T*	1	8
NaCl concentration(mol/L)	*C*	0.2	1

Table 5: Design Factors And Their Limits

F. *Experimental Design Matrix*

As the range of individual factor is wide, a central composite rotatable three-factor, five-level factorial design matrix is selected. The experimental design matrix consisting 20 sets of coded condition and comprising a full replication three-factor factorial is used. Table 6 represents the range of factors considered, and Table 7 shows the 20 sets of values used to conduct the experiments. The upper and lower limits of the parameters were coded as +1.682 and –1.682, respectively. Thus, the 20 experimental runs allowed for the estimation of the linear, quadratic, and two-way interactive effects of the variables. The method of designing such a matrix is dealt with elsewhere .The coded values(X_i) for intermediate levels can be calculated from the relationship.

$$X_i = \frac{1.682\,[2X - (Xmax + Xmin)]}{(Xmax - Xmin)}$$

Factor	Level				
	−1.682	−1	0	1	1.682
pH value	3	4.62	7.5	10.18	12
Immersion time(Hr:min)	1	2:42	4:50	6:58	8
NaCl concentration(mol/L)	0.2	0.36	0.6	0.84	1

Table 6: Design Factors And Their Levels

Sr.No.	Coded value			Actual Values		
	pH	Conc.	Time	pH	Conc.	Time
1	−1	−1	−1	4.82	0.36	2:42
2	1	−1	−1	10.18	0.36	2:42
3	−1	1	−1	4.82	0.84	2:42
4	1	1	−1	10.18	0.84	2:42
5	−1	−1	1	4.82	0.36	2;42
6	1	−1	1	10.18	0.36	6:58
7	−1	1	1	4.82	0.84	6:58
8	1	1	1	10.18	0.84	6:58
9	−1.682	0	0	3	0.6	6:58
10	1.682	0	0	12	0.6	4:05
11	0	−1.682	0	7.5	0.2	4:05
12	0	1.682	0	7.5	1	4:05
13	0	0	−1.682	7.5	0.6	1
14	0	0	1.682	7.5	0.6	8
15	0	0	0	7.5	0.6	4:05
16	0	0	0	7.5	0.6	4:05
17	0	0	0	7.5	0.6	4:05
18	0	0	0	7.5	0.6	4:05
19	0	0	0	7.5	0.6	4:05
20	0	0	0	7.5	0.6	4:05

Table 7: Experimental Design Matrix

IV. RESULT

A. *Experimental Results for Imerson Testing*

The Experimental Values of corrosion rate and Tensile strength are as shown in table 8.

Sr.No.	**pH**	**Concentration (mol/Liter)**	**Time (hr : min)**	**Specimen 2**	**Specimen 3**
				Corrosion rate (mm/year)	**Tensile Strength N**
1	4.82	0.36	2:42	0.051	1403.8
2	10.18	0.36	2:42	0.01	1424.4
3	4.82	0.84	2:42	0.055	1408.7
4	10.18	0.84	2:42	0.024	1433.2
5	4.82	0.36	2:42	0.041	1414.6
6	10.18	0.36	6:58	0.01	1440.1
7	4.82	0.84	6:58	0.06	1403.8
8	10.18	0.84	6:58	0.02	1438.1
9	3	0.6	6:58	0.074	1393.02
10	12	0.6	4:5	0.004	1440.1
11	7.5	0.2	4:5	0.025	1434.2
12	7.5	1	4:5	0.047	1413.6
13	7.5	0.6	1	0.058	1414.6
14	7.5	0.6	8	0.031	1432.6
15	7.5	0.6	4:5	0.038	1421.4
16	7.5	0.6	4:5	0.03	1419
17	7.5	0.6	4:5	0.034	1418.5
18	7.5	0.6	4:5	0.033	1420.5
19	7.5	0.6	4:5	0.036	1418.5
20	7.5	0.6	4:5	0.031	1419.5

Table 8: Experimental Values of Corrosion Rate and Tensile Strength

B. *Empirical Relationship*

In the present investigation, to correlate the test parameters such as pH value , NaCl concentration, immersion time and solution flow rate with the corrosion rate and tensile strength, a mathematical model is developed and for specimens under immersion testing is given below.

To correlate the immersion test parameters and the corrosion rate of C903 (specimen 2), a first order quadratic model is developed. The response (corrosion rate) is a function of pH value (*P*), immersion time (*T*) and chloride ion concentration (*C*) which can be expressed as:

$$CR = f(P,t,c)$$

The first-order polynomial equation used to represent the response surface (Y) is given by

$$Y = b_0 + \Sigma b_1 x_{1i} + \Sigma b_2 x_{2i} + \ldots\ldots + \Sigma b_j x_{ji}$$

And for three factors, the selected polynomial could be expressed as

$$CR = b_0 + b_1(P) + b_2(C) + b_3(T)$$

Where b_0 is the average of responses (corrosion rate) and b_1, b_2, b_3 are the coefficients that depend on their respective main and interaction factors,

Which were calculated using the expression given below,

$$b_i = \frac{\Sigma\,(X_i, Y_i)}{n}$$

Where *'i'* varies from *1* to *n*, in which X_i is the corresponding coded value of a factor and Y_i is the corresponding response output value (corrosion rate/Tensile strength) obtained from the experiment and *'n'* is the total number of combination considered. All the coefficients were obtained applying central composite face centered design using the Design Expert statistical software package (MINITAB). After determining the significant coefficients (at 95% confidence level), the final relationship is developed using only these coefficients.

To correlate the immersion test parameters and the Tensile Strength (*TS*) of C903 coated on High carbon steel (specimen 3), a first order quadratic model is developed. The response (Tensile Strength) is a function of pH value (*P*), immersion time (*T*) and chloride ion concentration (*C*) which can be expressed as:

$$TS = f(P,t,c)$$

The first-order polynomial equation used to represent the response surface (*Y*) is given by

$$Y = b_0 + \Sigma b_1 x_{1i} + \Sigma b_2 x_{2i} + \ldots\ldots + \Sigma b_j x_{ji}$$

And for three factors, the selected polynomial could be expressed as

$$TS = b_0 + b_1(P) + b_2(C) + b_3(T)$$

Where b_0 is the average of responses (Tensile Strength) and b_1, b_2, b_3 are the coefficients that depend on their respective main and interaction factors.

The final empirical relationship obtained by the above procedure is given below, Corrosion rate *(CR)* for Immersion testing of C903 (specimen 2)

$$(CR) = 0.0732 - 0.00708\,(P) + 0.0262(C) - 0.000273\,(T)$$

Tensile strength *(TS)* for Immersion testing of C903 coated on High carbon steel (specimen 3)

$$(TS) = 1382 + 5.01\,(P) - 2.70(C) + 0.188(T)$$

C. *Checking the Adequacy of the Model*

The Analysis of Variance (ANOVA) technique is used to find the significant main and interaction factors. It is thus conducted in this study in order to determine whether the above mentioned first order polynomial equations is significant fit with the experimental results. The results of the first order response surface model fitting as Analysis of Variance (ANOVA) are given in the Table 9.

Source	**Degree of Freedom**	**Sum of Squares**	**Mean Square**	**F value**	**Pr-value Prob > F**
Model	3	0.0054846	0.0018282	134.3	< 0.0001 Significant
Residual	16	0.0002178	0.0000136		
Lack of Fit	10	0.0001225	0.0000122	0.77	0.259 Not-Significant
Pure Error	6	0.0000953	0.0000159		
Total	19	0.0057024			
Std. dev.	0.0037				
PRESS	0.00035				
Adeq precision	29.887				
R^2	0.9620				
Adjusted R^2	0.9550				
Predicted R^2	0.9375				

Table 9: Anova Test Results for Immersion Testing.

The results of the first order response surface model fitting as Analysis of Variance (ANOVA) are given in the Table 6.1. The determination coefficient (R^2) indicated the goodness of fit for the model. The Model F-value of 134.3 implies the model is significant. There is only a 0.01% chance that a 'Model F-Value' this large could occur due to noise. Values of 'Prob > F' less than 0.0500 indicate model terms are significant. The 'Lack of Fit F-value' of 0.77 implies the Lack of Fit is not significant relative to the pure error. There is a 25.9% chance that a 'Lack of Fit F-value' this large could occur due to noise. Non-significant lack of fit is good. The 'Predicted R-Squared' of 0.9375 is in reasonable agreement with the 'Adjusted R-Squared' of 0.955. All of this indicated an excellent suitability of the regression model.

D. Surface Plot

The significance of each regressor in this model has been estimated and surface response was drawn using 3D mapping facilities in MINITAB to show the behavior of the corrosion rate of tin bronze as a function of NaCl concentration, exposed time and pH value. In MINITAB tool is available for surface plot, using same the surface Plot is plotted at Low value for pH 3, NaCl concentration at 0.2mol/lit and Immersion time as 1 hour for corrosion rate in immersion testing of bare Tin Bronze Material.

Surface plot for corrosion rate is plotted keeping pH value of solution at pH 3. NaCl Concentration Values on *x* axis and immersion time on *y* axis the corrosion rate values plotted in shaded region.

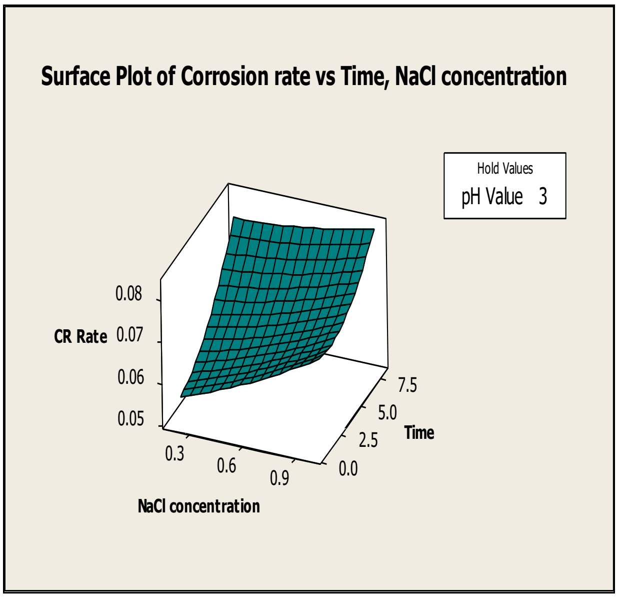


Fig.5: Surface Plot of Corrosion Rate vs. Time and NaCl Concentration

Firstly consider concentration value as 0.3, for this corrosion value goes on increasing as time also increases and reach maximum as 0.08 mm/year. As shown in figure 5. Minimum value of corrosion rate is found at the NaCl Concentration 0.3 mol/lit and time one hour.

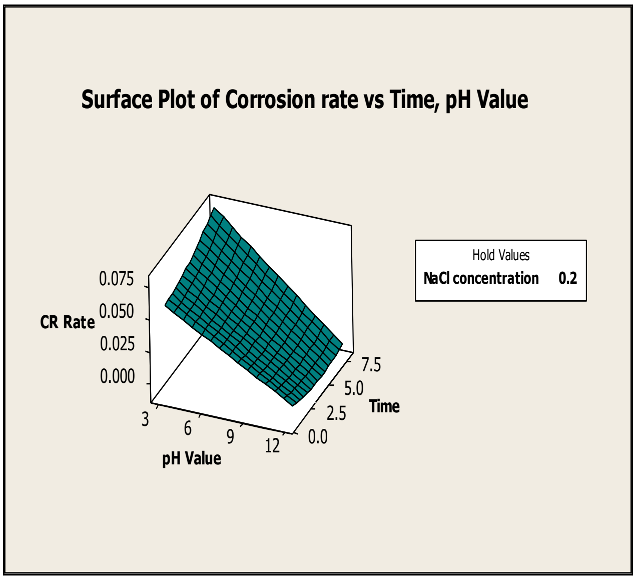


Fig 6: Surface Plot of Corrosion Rate Vs. Immersion Time And Ph Value

From Figure 6 of surface plot for the corrosion rate shows the minimum corrosion rate at immersion time 1 hour and pH value at 12. For pH 12 the corrosion rate found lower i.e. for alkaline solution corrosion rate is low as compared to the acid solution. As Solution pH value gradually increases then corrosion rate is also increasing, similar pattern found for the Immersion time in acidic medium.

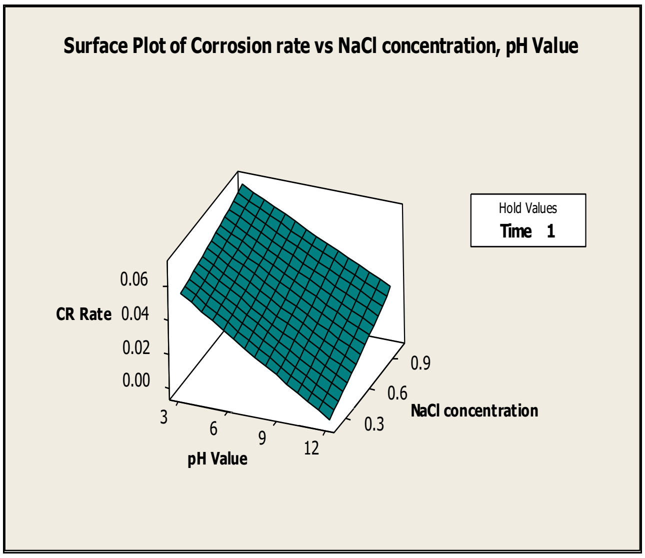


Fig 7: Surface Plot of Corrosion rate vs. NaCl concentration and pH Value

From Figure 7 Minimum corrosion rate is observed for NaCl Concentration 0.3 mol/lit and pH 12. Maximum Corrosion rate is observe at pH 3 and NaCl concentration 0.9 mol/lit. Considering pH value as constant at pH 3 then corrosion arte is increases with increase in NaCl concentration value. Similarly considering NaCl Concentration value constant at 0.3 mol/lit then as pH value decreases the corrosion rate increases.

V. CONFIRMATION EXPERIMENT

To validate the developed model, three confirmation experiments were carried out with the process parameters chosen randomly close to the range of experimental parameters. For the actual responses the average of two measured is calculated. Table 7.1 to 7.4 summarizes the experimental condition, the average actual values, the predicted values and the error. The optimum values of process parameters and the corrosion rate of C903 and tensile strength of specimen 2 show excellent agreement with the predicted values.

Sr. No.	**pH**	**Concentration (mol/L)**	**Exposure time (Hours)**	**Corrosion rate (mm/year)**		**Error %**
				Actual	**Predicted**	
1	5	0.6	2	0.051	0.053	2.84
2	7	0.4	5	0.031	0.032	2.37
3	6	0 .4	6	0.036	0.040	8.25

Table 10: Confirmation Experiment For Corrosion Rate of Specimen 2 In Immersion Testing.

Sr. No.	**pH**	**Concentration (mol/L)**	**Exposure time (Hours)**	**Tensile strength (N)**		**Error %**
				Actual	**Predicted**	
1	5	0.6	2	1296.20	1405.80	7.8
2	7	0.4	5	1346.91	1416.93	4.94
3	6	0 .4	6	1360.64	1412.1	3.64

Table 11: Confirmation Experiment for Tensile Strength of Specimen 3 In Immersion Testing.

VI. RESULT DISCUSSION

A. Effect on pH, Chloride Ion Concentration and Exposure Time on Corrosion Rate of Tin Bronze

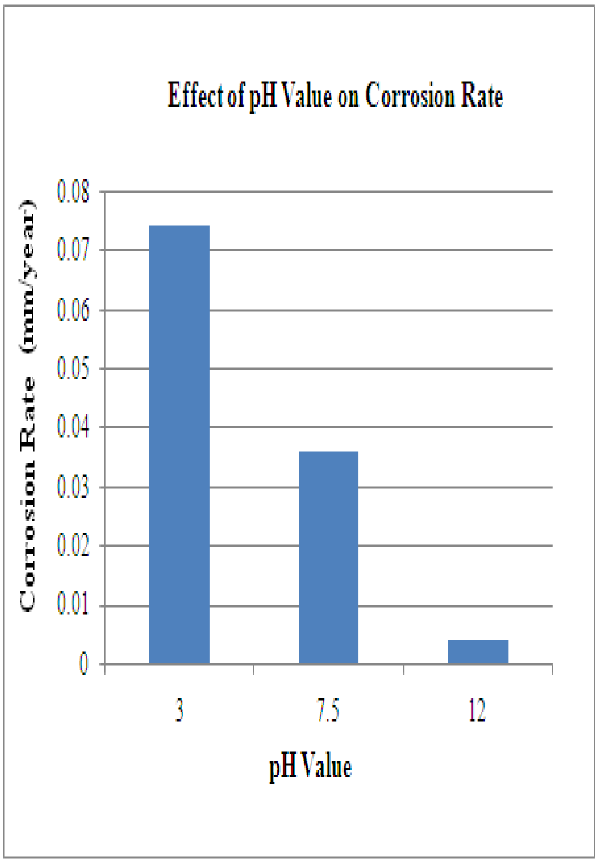


Fig.8 : Effect of Ph on Corrosion Rate

Figure 8 shows the effect of pH on corrosion rate of C903 alloy in NaCl solution. In order to study the effect of pH, the chloride ion concentration and exposure time is kept constant at 0.6 M ,4.5 hr while the pH is varied from 3 to 12. From this figure, the following points can be inferred. The pH value has an inversely proportional relationship with the corrosion rate; i.e., if the pH value increases, the corrosion rate decreases [12]. At every chloride ion concentration and time, the material usually exhibited a decrease in corrosion rate with the increase in pH. The highest corrosion rate is observed 0.074 mm/year at pH 3 and comparatively low corrosion rate 0.004 mm/year is observed in alkaline solution. It is seen that the influence of pH is more at higher concentration as compared to lower concentration in neutral and alkaline solutions.

At lower pH values, the specimen exhibited a rise in corrosion rate with an increase in chloride ion concentration. But the quantity of this rise is different in such a way that, the change in chloride ion concentration at lower concentrations affected the corrosion rate much more as compared to that of higher concentration. It showed that with the increase in chloride ion concentration, the rising rate at corrosion rate decreased that is, the influence of chloride ion concentration is much lower at higher concentrations [10].

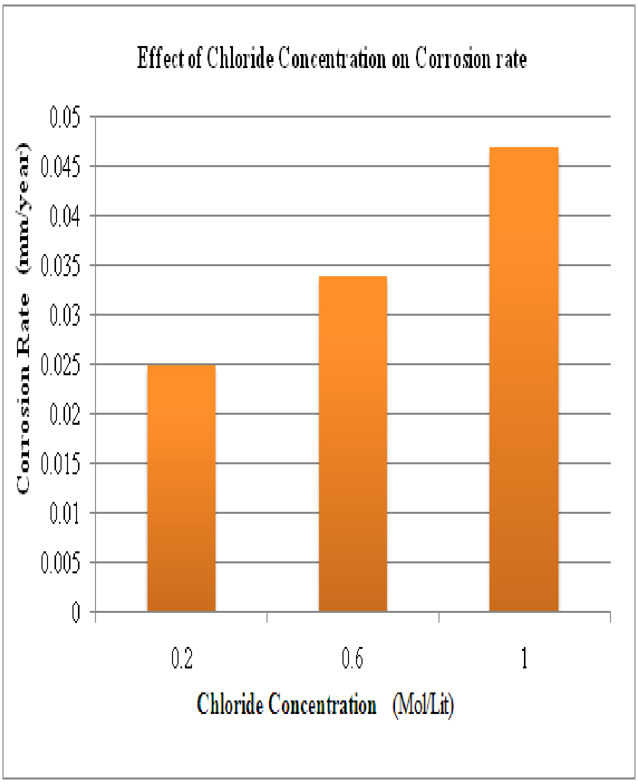


Fig. 9: Effect of Chloride Ion Concentration on Corrosion Rate

The influence of chloride ion concentration on corrosion rates of C903 alloy are displayed in the Figure 9. To investigate the effect of chloride ion concentration, the pH value and exposure time is kept constant at 7.5, 4.5 hr while the chloride ion concentration is varied from 0.2 M to 1 M. It is seen that the alloy exhibited a rise in corrosion rate with the increase in Cl^- concentration and thus the change of Cl^- concentration affected the corrosion rate much more in higher concentration solutions than that in lower concentration solutions. When more Cl^- in NaCl solution promoted the corrosion, the corrosive intermediate (Cl^-) would be rapidly transferred through the outer layer and reached the substrate of the alloy surface [10]. Hence, the corrosion rate is increased. This corrosion behavior is consistent with the current understanding that the corrosion behavior of C903 is governed by a partially protective surface film with the corrosion reaction occurring predominantly at the breaks or imperfections of the partially protective film. This is consistent with the known tendency of chloride ions to cause film break down. However, it is observed that, with the increase in chloride ion concentration, the rising rate of corrosion rate decreased.

Corrosion rate is increased from 0.025 mm/year to 0.047 mm/year when the NaCl chloride concentration is increased from 0.2 mol/lit to 1 mol/lit this shows that chloride is aggressive media for the corrosion.

The increase in corrosion rate with the increasing chloride ion concentration may be attributed to the participation of chloride ions in the dissolution reaction. Chloride ions were aggressive for C903.

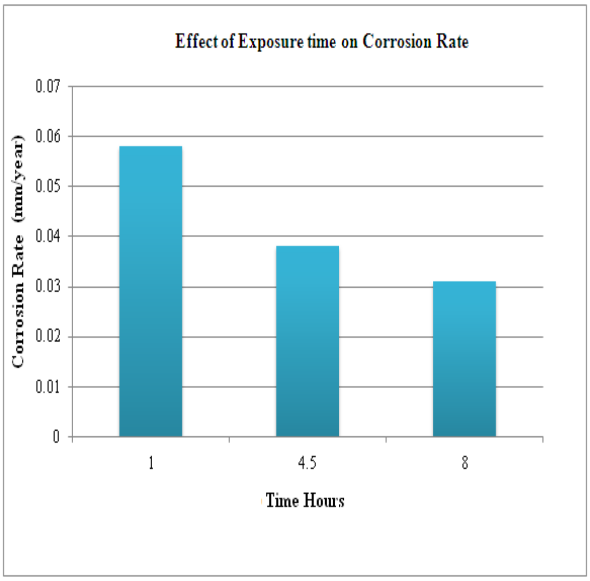


Fig. 10: Effect of Exposure Time on Corrosion Rate

Figure 10 depicts the influence of the exposure time on the corrosion rate of C903 alloy. In order to examine the effect of time, the pH value and chloride ion concentration is kept constant at 7.5, 0.6 M while the exposure time is varied from 1to 8 hr. From the figure, it can be seen that the corrosion rate decreased with the increase in time. It resulted from the decrease in hydrogen evolution with an increase in time; this is attributed to the corrosion occurring over an increasing fraction of the surface, which is the insoluble corrosion product.

The insoluble corrosion product on the surface of the alloy could slow down the corrosion rate. Initial stages of corrosion for C903 alloy exposed in NaCl solution revealed localized corrosion. Some black areas appeared initially, these areas become larger and additional similar areas appear with the increase in time.

B. Effect on Ph, Chloride Ion Concentration and Exposure Time on Tensile Strength of C903 Coated on High Carbon Steel

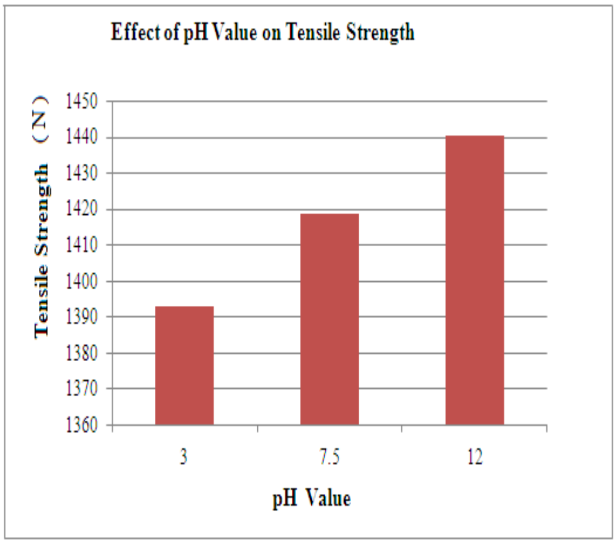


Fig.11: Effect of pH on Tensile Strength

Figure 11 shows the effect of pH on Tensile Strength of C903 coated on high carbon steel in NaCl solution. In order to study the effect of pH, the chloride ion concentration and exposure time is kept constant at 0.6 M ,4.5 hr while the pH is varied from 3-12.0. From this figure, the following points can be inferred. The pH value has a proportional relationship with the tensile strength; i.e., if the pH value decreases, the tensile strength decreases. It is seen that the influence of pH is more at higher concentration as compared to lower concentration in neutral and alkaline solutions. The corrosion rate occurs more in lower pH so the strength of specimen decreases. The opposite relation found in between corrosion rate and tensile strength.

At lower pH values, the tensile strength decreases with an increase in chloride ion concentration. But the quantity of this rise is different in such a way that, the change in chloride ion concentration at lower concentrations affected the tensile strength much more as compared to that of higher concentration. It showed that with the increase in chloride ion concentration, the large decrease in tensile strength that is, the influence of chloride ion concentration is much lower at higher concentrations. The tensile strength reduced at lower value at *1393 N* in pH 3 (Acidic) solutions and it shown lower reduction in tensile strength *1440 N* in pH 12 (Alkaline) Solution.

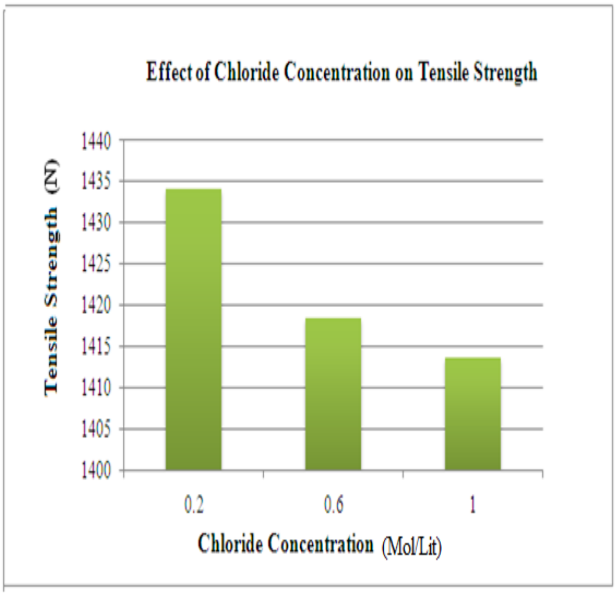


Fig.12 : Effect of Chloride Ion Concentration on Tensile Strength

The influence of chloride ion concentration on Tensile strength of C903 coated on high carbon steel is displayed in the Figure 12 To investigate the effect of chloride ion concentration, the pH value and exposure time is kept constant at 7.5, 4.5 hr while the chloride ion concentration is varied from 0.2 to 1M. It is seen that the alloy exhibited a more decrease in tensile strength with the increase in Cl^- concentration and thus the change of Cl^- concentration affected the corrosion rate much more in higher concentration solutions that leads to decrease the tensile strength than that in lower concentration solutions. When more Cl^- in NaCl solution promoted the corrosion, the corrosive intermediate (Cl^-) would be rapidly transferred through the outer layer and reached the substrate of the alloy surface [10]. Hence, the corrosion rate is increased. This corrosion behavior is consistent with the current understanding that the corrosion behavior of C903 is governed by a partially protective surface film with the corrosion reaction occurring predominantly at the breaks or imperfections of the partially protective film. However, it is observed that, with the increase in chloride ion concentration, the tensile strength decreased.

The decrease in tensile strength with the increasing chloride ion concentration may be attributed to the participation of chloride ions in the dissolution reaction. Chloride ions were aggressive for C903.

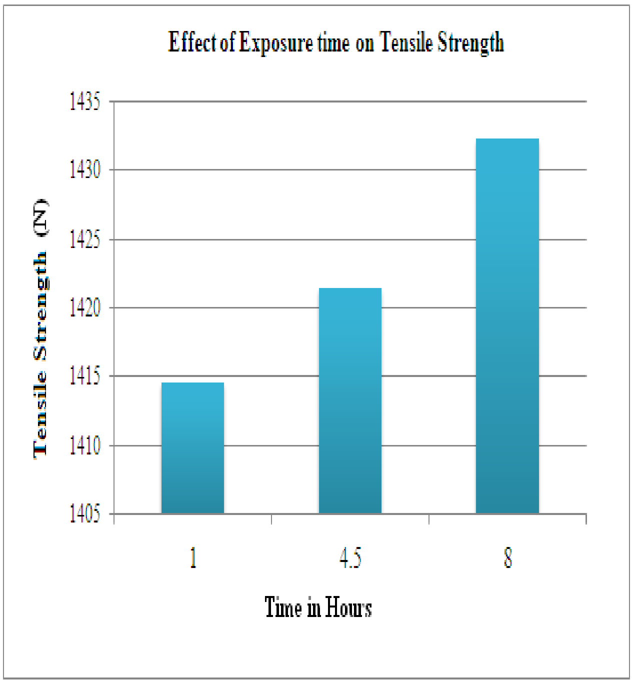


Fig.13: Effect of exposure time on Tensile strength

Figure 13 depicts the influence of the exposure time on Tensile strength of C903 coated on high carbon steel. In order to examine the effect of time, the pH value and chloride ion concentration is kept constant at 7.5, 0.6 M while the exposure time is varied from 1-8 hr. From the figure, it can be seen that the Tensile strength decreased with the decrease in time.

It resulted from the decrease in hydrogen evolution with an increase in time; this is attributed to the corrosion occurring over an increasing fraction of the surface, which is the insoluble corrosion product. The insoluble corrosion product on the surface of the alloy could slow down the corrosion rate as time increases.

C. Micro-structure of Specimens

After corrosion the specimens were viewed under microscope then corrosion process is studied. Table 12 shows the corrosion morphology and pit morphology of the corroded specimen after immersion tests at pH 3, 7.5 and 12 with chloride ion concentration of 0.2 mol/L to 0.60 mol/L and immersion time 4.5 hr respectively.

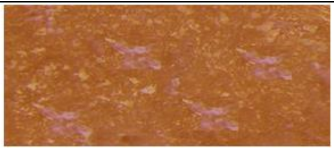
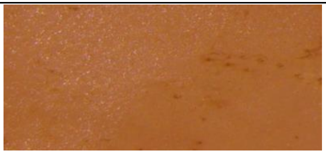
Sr. No.	Testing condition	Macro-structure
1	pH = 3 Concentration of NaCl = 0.2 M Time = 4.5 hr	
2	pH = 7.5 Concentration of NaCl = 0.2 M Time = 4.5 hr	
3	pH = 12 Concentration of NaCl = 0.6 M Time = 4.5 hr	

Table 8.1: Surface Morphology of Corrosion Tested Specimens

It is seen that, at a lower concentration of chloride ion, the surface of the specimen is relatively slightly corroded in neutral or alkaline solutions while is severely corroded at all pH values at a higher concentrations of chloride ion. The corrosion of C903 metal region is significantly influenced by pH value.

At pH 3, NaCl Concentration 0.2 M and immersion time 4.5 hr as shown in Table 8.1. On metal surface shows localized corrosion associated with dense pitted area. And small cracks developed on the metal surface. Corrosion rate find as 0.074 mm/year.

As shown in table, for pH 7.5, NaCl Concentration 0.2 M and immersion time 4.5 hr corrosion has occurred at some locations and most of metal surface not attacked by corrosion. Corrosion rate found as 0.025 mm/year.

At pH 12, NaCl Concentration 0.6 M and immersion time 4.5 hr, Corrsoion rate observed is low 0.004 mm/year. Minor pits formed on metal surface. The pit formation has been just started at this medium.

VII. CONCLUSIONS

- An empirical relationship is developed to predict the corrosion rate of C903 alloy, incorporating pH value, chloride ion concentration and exposure time. The developed relationship can be effectively used to predict the corrosion rate of C903 alloy at 95% confidence level.
- The corrosion rate and tensile strength reduction is higher in the acidic media than in alkaline and neutral media with the same chloride ion concentration and exposure time period. The corrosion potential shifted more negative values with the decrease of pH and exposure time, which is also, correlated with the increasing chloride ion concentration.
- The chloride ions are more aggressive to the C903 alloys. Since increase in the chloride ion concentration enhance the corrosion behavior. It is obvious from the Corrosion rate, which increases with the increase in chloride ions.
- The corrosion rate decreased with an increase in exposure time, which implied that the initial corrosion product impeded the passage of corrosion medium and provided protection for metal substrates.

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