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Quadra-Statistical Modeling Of Corrosion Penetration Rate (CPR) Of Martensitic and Annealed Stainless Steel in H_2SO_4 and HCl.

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Abstract
A lucid quadratic model graphs and equations has been successfully generated after corrosion characterization behavior analysis of cast stainless steel (70.90% Fe, 19% Cr 10%Ni, 0.08% C) alloys in (0.25M- 0.5M) H_2SO_4 and (0.25M- 0.5M) HCl using SPSS computer software. The cast stainless steel specimen were sectioned into three sets labeled M, A, U and machined to the same cross sectional area. M and A were subjected to a temperature of 900^{o}C (1173K or 1652^{o}F) where the grains formed austenitic phase which was further heat-treated to form martensitic stainless steel (M) and annealed stainless steel (A) test coupons respectively. Then, (U) was left untreated as a control test coupon sample. These pre-weighed test coupon samples were immersed in 0.25M and 0.5M simulated tetraoxosulphate (vi) acid (H_2SO_4) and Hydrochloric acid (HCl) respectively. The experimental process was allowed for a total of 168hrs with each set withdrawn at 24hr interval for weight loss analysis. Using the formula $CPR = \frac{k(W_b - W_a)}{PA(\Delta t)}$, the corrosion penetration rate values were calculated. The findings showed those of passivating metals with initial steady rise in corrosion penetration rate (CPR) followed by gradual decrease in CPR which increases as molar concentration increases for the annealed specimen(A) in H_2S0_4. Based on the computed values for CPR, a computer software SPSS version 17.0 was employed to generate the quadratic model graphs and equations that will enhance future prediction of corrosion penetration rate without necessarily carrying-out weight loss technique (WLT) analysis for the material under services condition.

Key words: Quadra-Statistical Modeling, Quadratic modeling, Passivation, Corrosion kinetics, Stainless Steel, Acidic Environment, Martensitic, Annealing, Weight Lose Techniques, Austenitic Phase, Martensitic Phase.

INTRODUCTION

In metallurgy, stainless steel is regarded as an alloy consisting majorly of iron, carbon, chromium and hence defined as a steel alloy with a minimum of 11.5 wt % chromium content (Scheil, 2006). It is believed that stainless steel does not stain, corrode or rust as ordinary steel (it is stainless) but not stain proof (Krugar, 2001) and it is useful in numerous engineering application. Also, corrosion can be defined as the environmentally induced degradation of a material that involves a chemical reaction (Duquette et al., 2011). Some of the deleterious effects of corrosion are known to include among others sudden failure of material under service condition, poor outward appearance of material surface, high maintenance and operating costs, frequent plant shutdowns, contamination of end products, loss of valuable products, hazardous effects on safety and reliability as well as burdensome product liabilities. The unpredictable degradation of these engineering material recently have been a cause for worldwide concern, consequently upon its huge financial loses (about 4-24% metal produced annually are destroyed by corrosion) and many mechanical failure results from it (Revie, 2000). Hence the recent resurgence in studying the corrosions characterization behavior of these engineering material.

In this paper, we presents the effect of heat treatment process on the corrosion penetration rate of stainless steel with composition (70.90% Fe, 19%Cr, 10%Ni 0.08%C) which has been made martensitic and also annealed by heat treatment processes. Using weight lose technique (WLT). Further discussion on the x-ray diffraction analysis as well as optical micrographic analysis will be considered due to grain boundary structural analysis as a site for corrosion kinetics and dislocation movement.

MATERIALS AND METHODS

Study Area

The research: Quadra-Statistical Modeling Of Corrosion Penetration Rate (CPR) Of Martensitic and Annealed cast Stainless Steel with percentage composition (70.90% Fe, 19%Cr, 10%Ni 0.07%C) in H_2SO_4 and HCl in acidic and basic media was carried out in Ebonyi State University Abakaliki and River State University of Science and Technology in southeastern and south-south region of Nigeria in April, 2013.

Materials and Equipments

The material used for this research work includes: cast stainless steel bar with percentage composition of (70.90% Fe, 19%Cr, 10%Ni and 0.08%C). This cast stainless steel was produced successfully at Union Founding Engineering Service, River State Nigeria. Other materials includes (0.25M, 0.5M) H_2SO_4, (0.25M, 0.5M) NaOH, Emery papers, distilled water, laboratory cylinders and beakers, retord stand.

\The equipments involved includes lathe machine, electronic weighing machine, vernier caliper and analytic digital weighing machine KERN 770 with serial number xx21-0014 and laboratory number EBSU/FPS/ICH/016 located in industrial Chemistry Department, Ebonyi State University, Nigeria.

Sample Preparation

The cast stainless steel bar is thoroughly cleaned with emry paper of different grit size to avoid surface pitting and remove carbonize layer. Using lathe machine, the sample is machine to a sizeable dimension and subsequently cut into a coupon samples with dimension range of 25.1mm x 24.1mm x 10mm and specific surface area of 22.78cm^2. A groove is drilled on both sides of the specimen to allow for string suspension with regards to the ASTM immersion standard specification.

Preparation of Test Environment

Basically, the environment for this research work includes; Acidic and basic environment of different concentration prepared from its stock. The (0.25M and 0.5M) H_2SO_4 is produce from its stock solution with 98% purity assay while the NaOH is produce from its stock of 46% purity assay.

Measurement and Weighing

Using vernier caliper, the dimensions of the test specimen were measured as 25.1mm x 24.1mm x 10mm while the specific area is calculated using the formula

$$Sa = 2[(xy + x\varepsilon + y\varepsilon) - \pi rh] \quad (1)$$

where h is height of groove, r is radius of groove, Sa is specific area, x, y and ε are length, width and thickness respectively(Oshionwu et al.). Furthermore, using analytic digital weighing machine prior to immersion, the initial weights of the test coupons is ascertain.

Design Setup and Procedure

The test coupons are divided into three groups which comprises of 6 test specimen each. The first group is allowed as a control sample. The remaining two groups are subjected to a temperature of 900^{o}C where austenitic phase are formed. One group are withdrawn and quenched in distilled water rapidly to produce martensitic specimen (M) while the second group is allowed to be furnace cooled to produce the annealed specimen (A) (Ashby, 2007, Antropov, 1975). One test coupons from each of these groups is immersed in a solution of H_2SO_4 and NaOH of different concentration with exposure time of 168hr. Then, one test coupon in each set are withdrawn, washed with acetone and dried at 24hr interval. Prior to corrosion penetration rate analysis, the digital analytic weighing machine is used to determine the final weight. The degree of corrosion progress is conveniently evaluated using the corrosion penetration rate expressed in miles/year or mm/yr and its mathematical computation is based on the formula.

$$CPR = \frac{k(W_b - W_a)}{\rho A(\Delta t)} \quad (2)$$

where Wa and Wb are initial and final weight respectively, while t, ρ and A are exposure time, density and area respectively. K is a constant with a value of 87.6mm/yr (callister, 1997, Idenyi et al, 2006 Landrum, 1990).

RESULTS AND DISCUSSION

The results of the experiment shown in the graphs below, are in conformity with those of passivating metal but are more pronounced on some of the heat treated specimen as discussed below.

Observation in 0.25M H_2SO_4 and 0.5M H_2SO_4

Close observation of the corrosion penetration rate values of the heat treated specimen plotted in the graphs (figure 1-2) revealed that the annealed specimen witness the highest rate of material removal while the martensitic specimen exhibited high rate of passivity with minimal corrosion penetration rate. This variation in corrosion penetration rate and passivity is due to the different heat treatment administered to the specimen. Having observed this, the nature of the quadratic model graph generated will be discussed is subsequent paragraphs.

Observation in 0.25M HCl and 0.5M HCl.

A perusal at the corrosion penetration rate(CPR) profile in figure 3-4 reviews weight loss which increases with time in the stainless steel alloy. This trend is in conformity with the fact that media concentration has direct consequence on the degradation of materials in acidic environment (Oshionwu et. al). However, the overall trend of the corrosion profile clearly depicts that of passivating metal subjected to simulated environment. In this case, the drift shows an initial increase in corrosion rate which depict the active region of the stainless steel until a limit is attained where passivation phenomenon sets in leading to a gradual decline in corrosion rate as exposure time increases (passive region attained). Hence in the solution of 0.25M HCl, it was observed that the annealed specimen (A) exhibit high passivity with the lowest corrosion penetration rate of 0.007mm/yr while the control sample has the highest corrosion penetration rate of 0.0450mm/yr. The annealed specimen (A) witness the lowest CPR due to the compact nature of the grain boundaries as a result of heat

treatment as well as media saturation. In the same vein, the annealed specimen witnesses high passivity in 0.5M HCl and low corrosion penetration rate (CPR) while the martensitic specimen witness sharp increase in penetration rate due to it initial active state.

Based on the above analysis, it becomes imperative to generate a model graphs and equations that will enhance future prediction of corrosion penetration rate as the concentration of the acid increases or decreases with time. In other to achieve this, a computer software SPSS was employed. In figure 1-2, the observed values for the corrosion penetration rate for the martensitic was combined to generate a single quadratic curve with model equation. This model graph with the equation will help to determine the CPR of a stainless steel that has been made martensitic through heat treatment without necessarily carrying out weight loss techniques (WLT) analysis. The curve generated possesses R-Square value of 0.44 ie the goodness of fit of the curve as well as significance value of 0.780. This is shown in figure 5 below. In the same vein, quadratic model graph and equation for annealed stainless steel was generated as shown in figure 6 below. In this case, the goodness of fit and significance value is 0.1281 and 0.471 respectively. This depicts how the model graphs fits in for the corrosion penetration rate.

Fig. 1 Graph of CPR vs Time for **$0.25MH_2SO_4$**

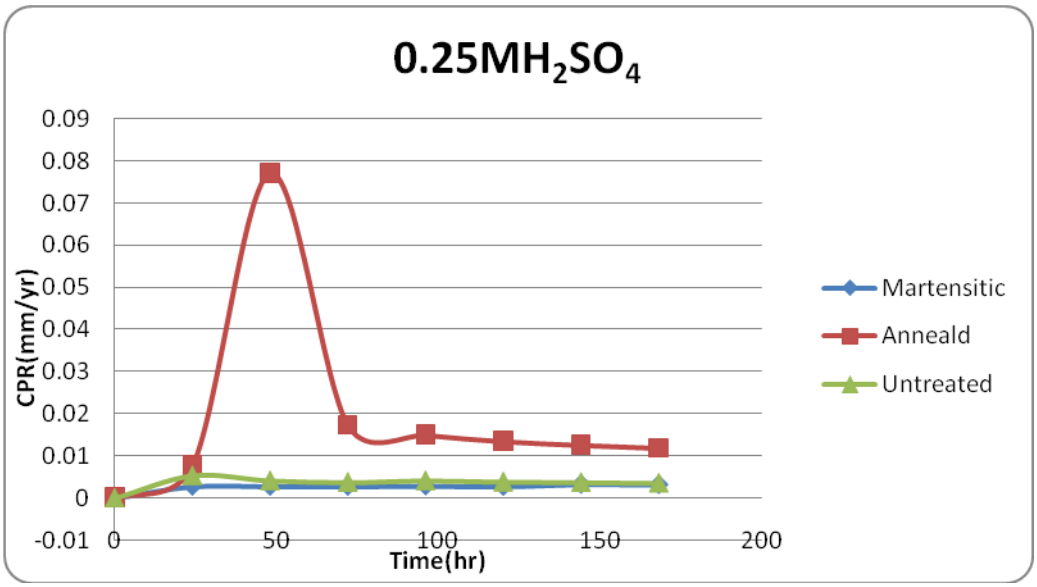


Fig. 2 Graph of CPR vs Time for **$0.5MH_2SO_4$**

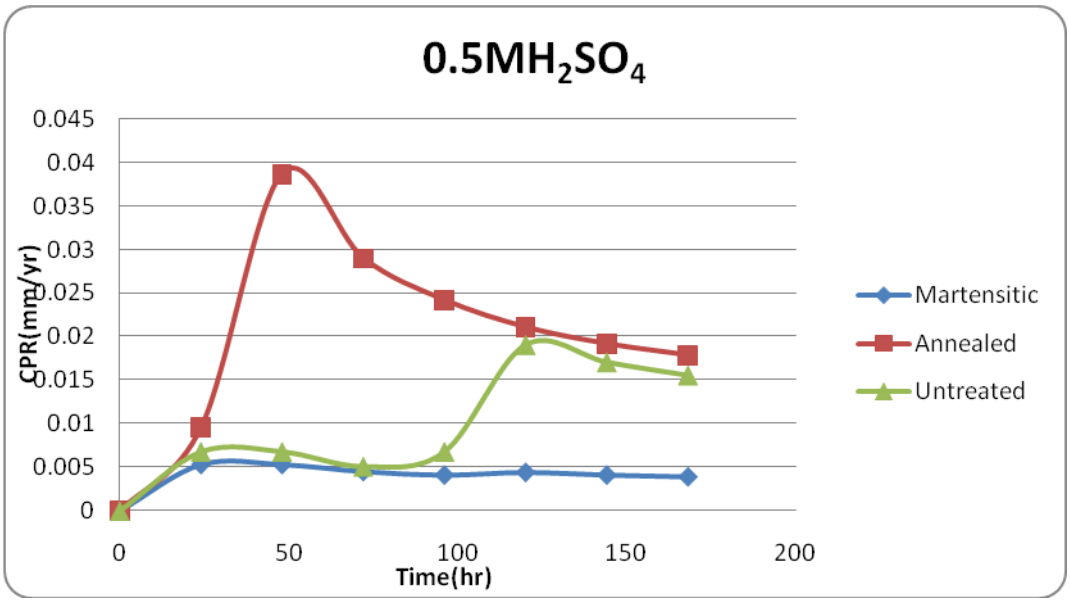


Fig. 3 Graph of CPR vs Time for 0.25MHCl

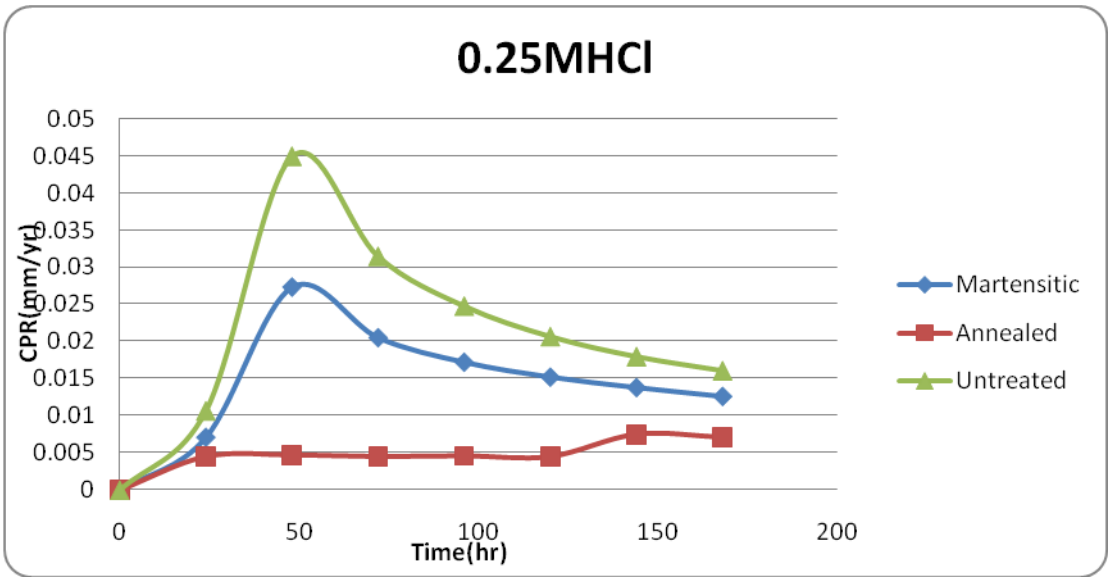


Fig. 4 Graph of CPR vs Time for 0.5MHCl

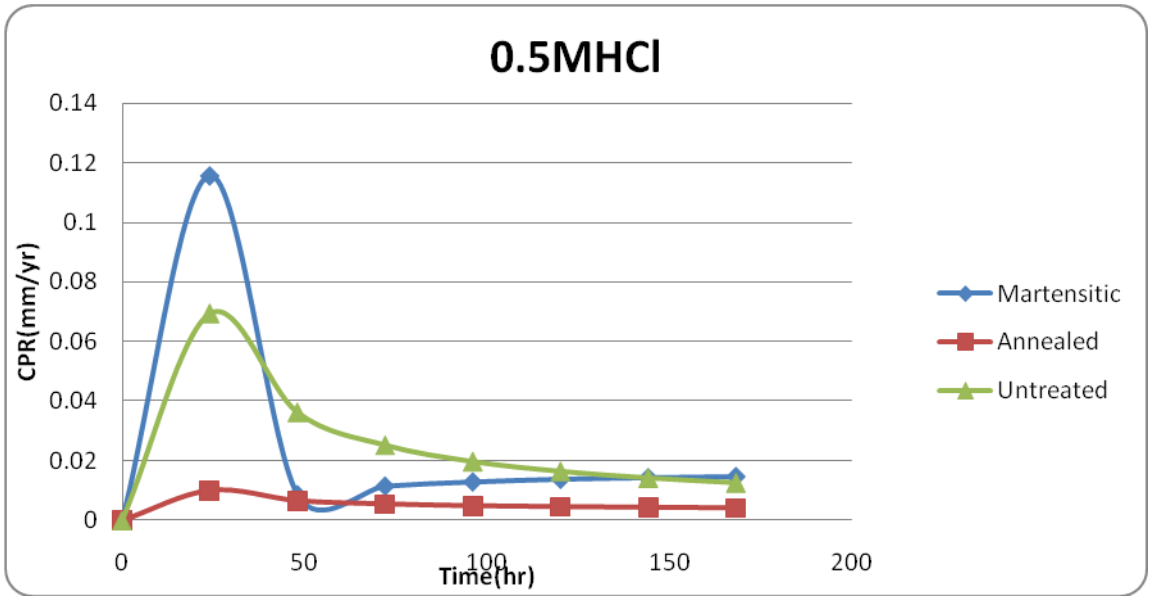


Fig. 5 Quadratic Model Graph correlating Martensitic specimen in(0.25-0.5)M H_2SO_4

Model Summary and Parameter Estimates

Dependent Variable:CPR1.HSO

Equation	Model Summary					Parameter Estimates		
	R Square	F	df1	df2	Sig.	Constant	b1	b2
Quadratic	.044	.255	2	11	.780	.004	-1.228E-5	4.650E-8

The independent variable is T.

$$CPR1.HSO = 0.074 - 1.23\times10^{-5}T + 4.65\times10^{-8}T^2 \quad (3)$$

H_2SO_4

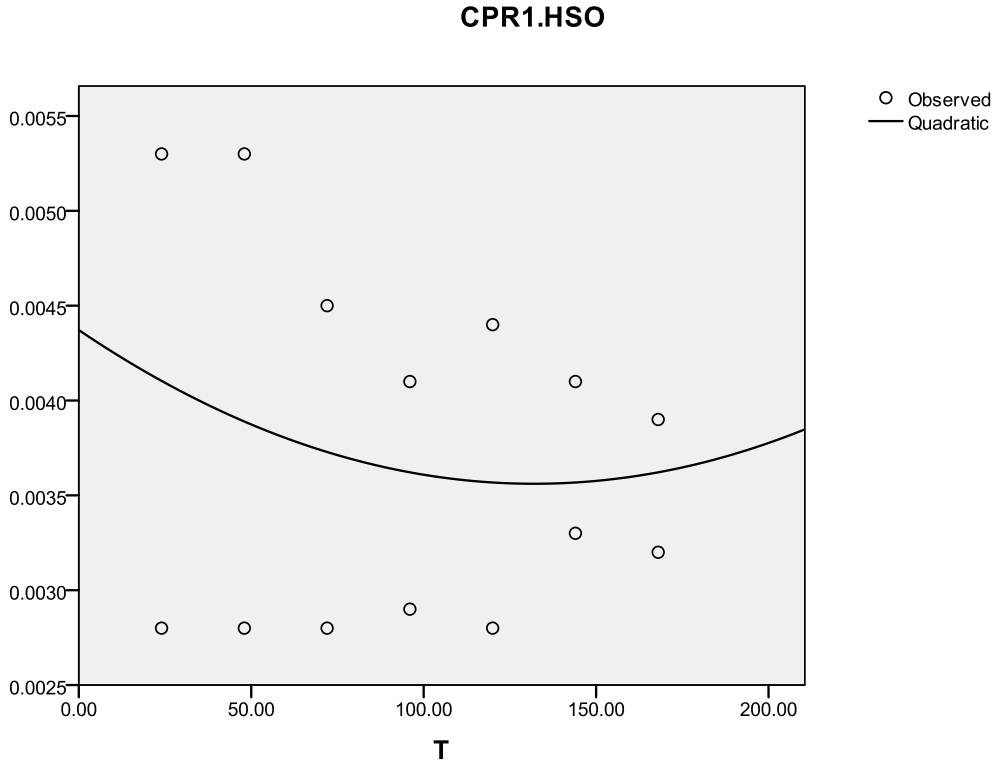


Fig. 6 Quadratic Model Graph correlating Annealed specimen in (0.25-0.5)M H_2SO_4

Model Summary and Parameter Estimates

Dependent Variable:CPR2.H_2SO_4

Equation	Model Summary					Parameter Estimates		
	R Square	F	df1	df2	Sig.	Constant	b1	b2
Quadratic	.128	.808	2	11	.471	.021	.000	-1.693E-6

The independent variable is T.

$$CPR2.HSO = 0.021 - 2.19\times10^{-4}T - 1.69\times10^{-6}T^2 \quad (4)$$

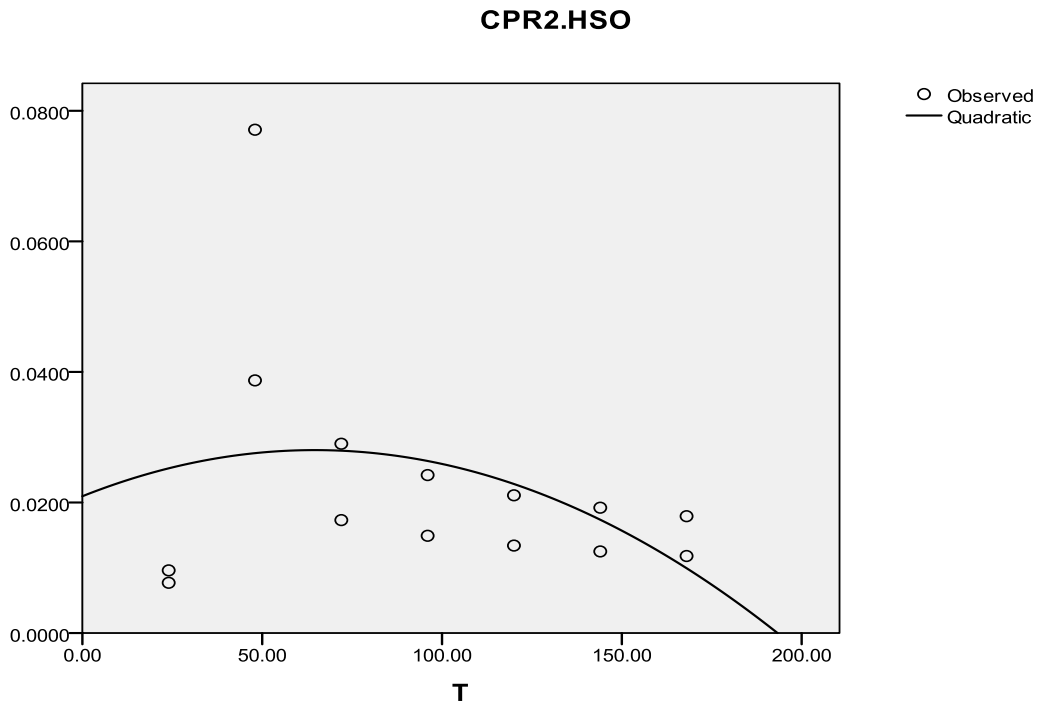


Fig. 7 Quadratic Model Graph correlating Martensitic specimen in(0.25-0.5)M HCl

Model Summary and Parameter Estimates

Dependent Variable:CPR1.HCl

Equation	Model Summary					Parameter Estimates		
	R Square	F	df1	df2	Sig.	Constant	b1	b2
Quadratic	.278	2.121	2	11	.166	.074	-.001	4.457E-6

The independent variable is T.

$$CPR1.HCL = 0.074 - 0.001T + 4.46\times10^{-6}T^2 \quad (5)$$

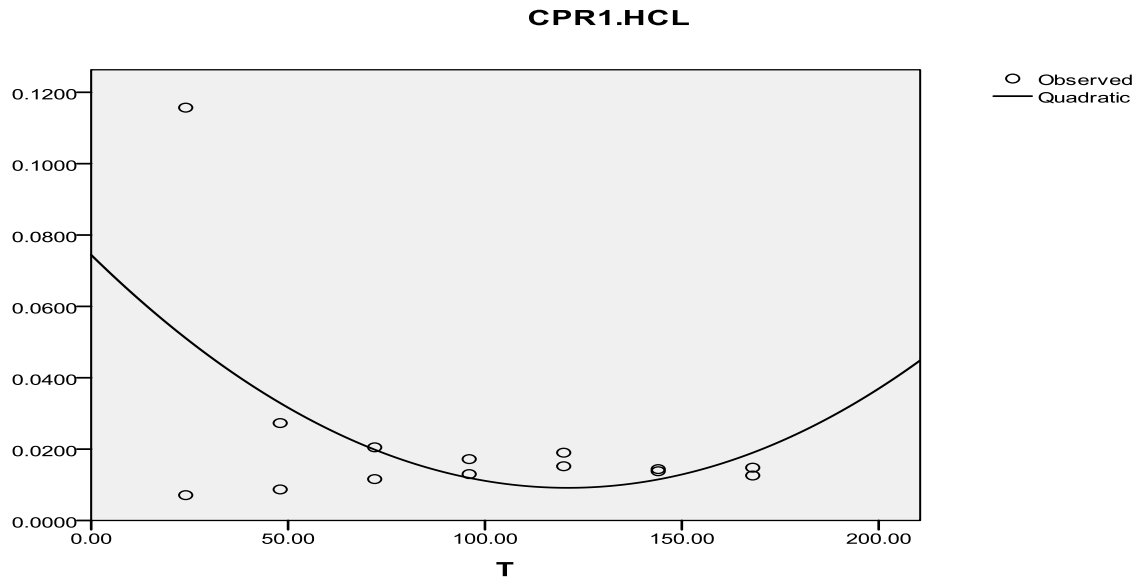


Fig. 8 Quadratic Model Graph correlating Annealed specimen in(0.25-0.5)M HCl

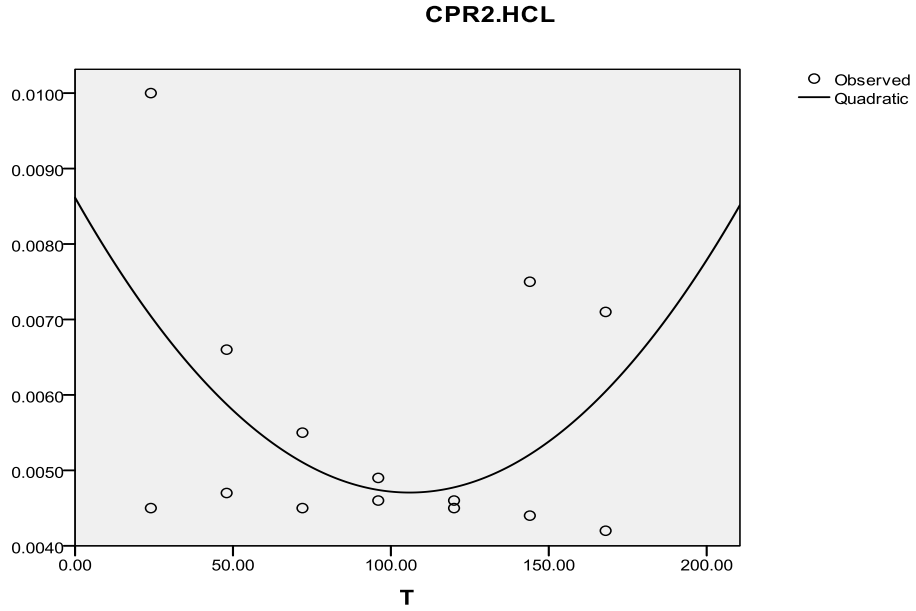
Model Summary and Parameter Estimates

Dependent Variable:CPR2.HCl

Equation	Model Summary					Parameter Estimates		
	R Square	F	df1	df2	Sig.	Constant	b1	b2
Quadratic	.227	1.619	2	11	.242	.009	-7.378E-5	3.483E-7

The independent variable is T.

$$CPR2.HCL = 0.009 - 7.38\times10^{-5}T + 3.48\times10^{-7}T^2 \quad 6$$



Furthermore, in figure 3-4, the observed values for the corrosion penetration rate for the martensitic and annealed stainless steel were combined to further generate two quadratic curve and model equation. This model graph(figure 7-8) with the equation will help to determine the CPR of a stainless steel that has been made martensitic and annealed through heat treatment without necessarily carrying out weight loss techniques (WLT) analysis. The curve(figure 8) generated has R-Square value of 0.227 ie the goodness of fit of the curve as well as significance of 0.242. These sets of equations enhances future prediction of corrosion penetration rate.

CONCLUSION

The Quadra-Statistical Modeling Of Corrosion Penetration Rate (CPR) Of Martensitic and Annealed Stainless Steel in (0.25M-0.5M) H_2SO_4 and (0.25M-0.5M) HCl have been successfully studied using weight lose techniques (WLT) and software SPSS. In general, it can easily be inferred that the phenomenon of passivation is predominant in the various media concentrations for the acidic media. The effect of heat treatment on the cast stainless steel (annealed and martensitic) has resulted in the reduction to the extent of passivation especially in the annealed specimen. This factor may be attributed to the compact nature of the grain boundaries as a result of redistribution in the grain boundaries as well as slip dislocation movement of grains(Oshionwu et. al). Furthermore, it becomes obvious that an acidic environment of H_2SO_4 and HCl with molar concentration ranging from 0.25-0.5 has adverse effect on cast stainless steel (70.90% Cr, 10%Ni 0.08%^oC) product which can be minimize by heat treatment process.

Finally, sets of quadratic model equations were generated in other to enhance future prediction of corrosion penetration rate without conducting weight lose analysis of the specimen under services condition. These equation for each sets of heat treated specimen are stated below:

(a) $CPR.H_2SO_4 = 0.074 - 1.23\times10^{-5}T + 4.65\times10^{-8}T^2$ for Martensitic in (0.25-0.5)M H_2SO_4

(b) $CPR.H_2SO_4 = 0.021 - 2.19\times10^{-4}T + 1.69\times10^{-6}T^2$ for Annealed in (0.25-0.5)M H_2SO_4

(c) $CPR1.HCL = 0.074 - 0.001T + 4.46\times10^{-6}T^2$ for Martensitic in (0.25-0.5)M HCl

(d) $CPR2.HCL = 0.009 - 7.38\times10^{-5}T + 3.48\times10^{-7}T^2$ for Annealed in (0.25-0.5)M HCl

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