CORROSION ANALYSIS OF NICKEL AND GOLD PLATED CARBON STEEL ORNAMENTALS IN SULPHURIC ACID MEDIUM

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ABSTRACT

This study investigated the corrosion resistance of Nickel and Gold plated carbon steels ornamentals in $0.5 mol/dm^3$ Suphuric acid (H_2SO_4) medium. Nickel plating of carbon steel was done in watts solution for 25 minutes with a current density of $3 A/dm^3$ at $60^{\circ}C$. The nickel plated carbon steel was later gold plated for 20 minutes with a current density of $0.2 A/dm^3$ at $50^{\circ}C$. The plated and unplated carbon steels were exposed to H_2SO_4 environment for 15 days. The weight loss was taken every 24 hours in order to evaluate Corrosion penetration rate (CPR). The results obtained showed that plated carbon steel generally offered a better corrosion resistance than the unplated carbon steels. The conclusion that can be drawn from this study is that Nickel plated carbon steel is found to be more reliable material to be used as ornamentals than gold plated carbon steel in H_2SO_4 environment.

Keywords: Carbon Steel, Nickel plating, Gold Plating, Corrosion Penetration Rate, H_2SO_4

1. INTRODUCTION

Equipments and infrastructures degradation as a result of corrosion is still a topical issue in most industries. The direct and indirect costs of corrosion are enormous. Corrosion has caused machines failure, economic losses, oil spillage, environmental pollution, products contamination, plant interruptions and short life span of equipments. According to *Denny (2004)*, the total annual estimated cost of corrosion in the United States was approximately $276 billion. The corrosion causes between $8billion to $128billion in economic damage per year in the United States alone degrading structures, machines and containers in the oil and gas industry. Corrosion in crude oil systems is one of the most costly problems facing oil companies, which go to great expense to effectively control the problems. Carbon steel is a very vital material in fabrication and installation of industrial machineries due to its cheapness and unique mechanical properties.   Unfortunately, corrosion has consistently dominated the major constraint degrading its highly valued mechanical properties. Quite a number of research efforts have been made towards corrosion control and prevention of steel alloys. The inhibitive action of some thiadiazole derivatives, namely 2,5-bis(2-thienyl)-1,3,4-thiadiazole (2-TTH) and 2,5-bis(3-thienyl)-1,3,4-thiadiazole (3-TTH) against the corrosion of mild steel in 0.5 M H_2SO_4 solution has been investigated using weight loss measurements, Tafel polarisation and electrochemical impedance spectroscopy (EIS) techniques (Lebrini et al,2007). The experimental results obtained revealed that these compounds inhibited the steel corrosion in acid solution. The influence of Phosphorus addition on the corrosion resistance of carbon steel for a flue gas desulphurization system has been examined (Kim et al, 2010). The authors employed electrochemical methods such as potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) in 10 wt% sulphuric acid (H_2SO_4) solution at room temperature. The results of the potentiodynamic measurements indicated that the addition of Phosphorus increased the cathodic hydrogen evolution reaction. The experimental results showed that Phosphorus has a degrading effect on the corrosion

resistance of carbon steels in H_2SO_4 solution. This is due to the increase in the activity of hydrogen. The study investigated the deterioration of mild steel in 2 M sulphuric acid solution in the presence of *Bambusa glauscescens* extract using gasometric technique (Olugbenga et al, 2011). Steel coupons measuring 4 cm by 1.5 cm were immersed in test solutions of uninhibited acid and also those containing extract concentrations of 60,100 and 140 cm^3 at a temperature of 333K for 60 minutes. The volumes of hydrogen gas evolved from the reaction were recorded and analyzed. The analysis showed that while extract concentration was increasing, H_2 evolution and percentage inhibition efficiency (% I.E) increased. There was also a corresponding reduction in corrosion rate as extract concentration increased. The decrease in corrosion rate was observed to follow in order of increasing extract concentration. Furthermore, the microstructural studies revealed that increasing the extract concentration resulted in significant reduction in the dominant coarsening of the oxide of iron phase, while the pearlite and ferrite phases became finely dispersed. A comprehensive analysis of stainless steel resistance to burning products released by heat burners has been carried out (Seifedine, 2008). Experimental tests revealed that Chloride ions, existing in combustion, decrease corrosion resistance of chromic-nickel steels. The test results also showed that the most stable steels in the aggressive environment of condensate are those with a bigger amount of titanium and molybdenum. The corrosion behaviour of low carbon steel was investigated in natural seawater and various synthetic seawaters (Möller, 2006).It was found that the steel corroded nearly four times faster in a 3.5% NaCl solution than in natural seawater for an exposure time of 21 days. The corrosion rate after immersion in synthetic seawaters (ASTM D1141 and Marine Biological Laboratory seawater) is similar to the corrosion rate after immersion in natural seawater. Calcium carbonate (aragonite) deposits were found on the surface of the steel after immersion in natural seawater and the synthetic seawaters. Some magnesium-containing deposits were also found after immersion in the natural seawater. These deposits act as a barrier against oxygen diffusion and thereby lower the corrosion rate. The morphology of the calcium carbonate deposits that formed during immersion in the natural seawater is different from those formed during immersion in the synthetic seawaters. This may explain the slightly lower corrosion rates obtained in the natural seawater. X-ray diffraction also showed that the oxy-hydroxides formed in the 3.5% NaCl solution differed from those formed in the other solutions.

The growing interest of researchers in the analysis of corrosion resistance characteristics of electroplated materials is highly encouraging. Oluwole et al in 2009 investigated the corrosion resistance of nickel-plated medium carbon steel and 18-8 stainless steel in cassava fluids (i.e. containing hydrogen cyanide).The work simulated the effect of continuous use of the materials in a cyanide environment where corrosion products are left in place. Low carbon steel sample was nickel electroplated at 4V for 35minutes.The plated sample; the unplated sample and 18-8 stainless steel were then subjected to cassava fluid environment for thirty days. The findings of the authors showed that unplated steel was found to be unsuitable for the fabrication of cassava processing machinery because of the very high corrosion rate.18-8 stainless steel was found suitable for use in this environment.

Equally, research work that investigated the corrosion resistance of nickel plated medium carbon steel in cocoa liquor was carried out by Oluwole et al, 2009. It simulated the effect of continuous use of the material in a cocoa liquor environment where corrosion products are left in place. Medium carbon steel samples were nickel electroplated at 4V for 20, 25, 30, and 35 minutes using Watts solution. The plated samples were then subjected to a cocoa liquor environment for 30 days. The electrode potentials mV (SCE) were measured every day. Weight loss was determined at intervals of 5 days for the duration of the exposure period. The result showed maximum corrosion rate on the nickel-plated steels to be 0.05mm/yr throughout the 30 days duration of the test while corrosion rate in the unplated steel was

observed to be 0.36mm/yr at the end of 30th day. Generally, it was observed that the thicker the nickel coating, the lower the corrosion rate. The pH of the cocoa liquor was acidic throughout the thirty days test duration. The conclusion drawn from this paper is that nickel plating is suitable as a protective coating for medium carbon steels in cocoa liquor environment. Ming-Gin et al (2009) investigated the Corrosion Performance of Electroless Nickel-Plated Steel. The results of the study showed excellent corrosion resistance for electroless nickel plated steel embedded in concrete specimen exposed to outdoor or seawater. The chlorine contents of concrete specimens increase as the days of immersing time in seawater pool increase during 500 days. Another steel bond strength test revealed that the electroless nickel plated steel has similar performance as the conventional one. This means that the electroplating has no significant impact on steel bond strength. In most cases, the reinforcing steel bar which was coated with an electroless nickel-plated film showed a reduction in its corrosion tendency. Olorunniwo et al (2010) has studied the performance evaluation of nickel-coated manganese steel in high-chloride low sulphate seawater environments. Structural manganese steels coated with nickel and unplated ones were tested for corrosion characteristics using weight loss technique. It was found that the nickel coat was able to resist corrosion overtime via spontaneous formation of passive oxide films at ambient temperature. The conclusion from of this study is that high-chloride low sulphate seawater (Polluted) environments are more corrosive than high chloride (Clean) seawater environments. More also; a thicker coat of electrodeposited nickel provides better corrosion resistance through formation of passivating oxide layers at the surface of the steels.

Currently, development of corrosion resistant materials for decorative purposes is attracting more researchers' interests. Titanium nitride(TiN) is a very important tribological material because of its properties. As a result of its superior mechanical properties and corrosion resistance,TiN is one of the most widely chosen coating materials (Perillo,2006). According to the author, its bright golden colour makes it appropriate for decorative purposes. Bala et al (2010) developed a decorative and corrosion resistant plasma electrolytic oxidation coating on AM50 Magnesium alloy as was shown by the potentiodynamic polarization measurements. According to the authors, the coatings produced in titania sol containing electrolytes offered an improved corrosion resistance compared to the mere phosphate PEO coating.

2. MATERIALS AND METHODS

2.1 Materials and Equipment used for Nickel plating.

Electroplating tank (Plastic in lined tanks), carbon steel to be electroplated (10cm x 20cm), Nickel Anode, Drying tray and Electrolyte. The following are the components of the electrolyte used for the experiment:
(i) Nickel Sulphate (300 g) (ii) Nickel Chloride (30 g) (iii) Nickel brightener (30g)

2.2 Materials and Equipments used for Gold plating

Rectifier, Plating tank ,Gold potassium cyanide ,Gold Anode, Drying tray Gold potassium cyanide (30g),Gold metal anode (12.5g) and Nickel plated carbon steel samples(weight of 3.3g and Area of 4.56cm^2).

2.3 Methods

2.3.1 Chemical analysis

The carbon steel used was procured from FIIRO (Federal Industrial Institute of Research, Oshodi), Lagos state. The chemical analysis of the carbon steel was carried out at the universal steel, Ikeja, Lagos state.

2.3.2 Procedures for plating carbon steel

Basically, the carbon steel substrate was plated with purified base solution is simply inside a plating tank followed by the necessary additional agents. A prepared Nickel salt was used to prepare high Sulphate Nickel base solution for Gemini and other bright and semi-bright nickel plating solutions. A standard solution of Nickel salts for electroplating of carbon steel was first prepared. A rubber lined tank was made clean and filled approximately with two-third capacity of clean water. After heating the water to 60 to 70°C, the required weight of prepared Nickel Salts was added gradually and thoroughly stirred. When dissolution of the prepared Nickel Salts was completed, the bath is then diluted with clean water of approximately 5/6ths of the final required volume. At this stage, the solution was purified to remove any traces of metallic impurity or organic contamination before the addition of the brightener additives. The base carbon steel material (10cm × 20cm) was polished and the plastic in lined tank was hot washed with dilute acid and properly rinsed out with cold water. Polished base metal (10cm × 20cm) was suspended with wires and later pickled in an hydrochloric acid. Carbon steel samples were immersed in tanks of dilute hydrochloric cleaning solutions to remove dirt and solid soil from them. The weight of sample was taken before the treatment of the sized polished specimen .This was properly rinsed in water and anodically cleaned in order to avoid drag out of the electrolyte on the material sample. The Nickel plating was done for 25 minutes at a temperature of 60°C and constant current density of $0.3A/dm^3$.After the specimen was removed from the plating tank, it was immersed into de-ionised water to avoid drag out and clogging of electrolyte on specimens. Material Sample's final weight was determined in order to know the mass of the electrolyte deposited on the work piece. This helps in determining the thickness of the Nickel plating of the sample carbon steel used in this study. The Nickel plated carbon steel was cut into three samples of dimension (24cm x 1.9cm).The three samples were used in carrying out the gold plating experiments. A little pre-treatment was done, due to the Nickel undercoat that has been done on base-metal. Proper hammering and straightening were carried out on these samples to give proper edging and smoothing. This was done in order to avoid blur and hole on the work pieces which can later result to corrosion and instability of electrolyte on work samples .The Nickel coated samples was washed in water and then with caustic soda in order to dissolve unwanted agents like hammering and working particles on the work samples that can interfere with the results of the experiment. After the clogs were dissolved away, the samples were suspended into the electroplating tank containing gold potassium cyanide (30g), gold metal anode (12.5g) and nickel plated samples (weight of 3.3g and Area of $4.56cm^2$).The samples were electroplated for 20 minutes to give enough coating thickness. All these specimens were quickly dipped in water immediately they were removed from the bath and later displayed in the drying tray for cooling. Weight of each specimen was taken by scout pro-balance in order to determine the mass of gold material deposited on the Nickel plated steels.

2.3.3 Corrosion penetration rate (CPR) Measurements Using Weight Loss

The unplated, Nickel plated and Gold plated (with nickel undercoat) carbon steels coupons were immersed in 0.5mol dm^{-3} of 100ml sulphuric acid environment for a period of 360 hours (15days).The corrosion coupons were removed from the corrosion environment with the aid of a tong . These were then properly cleaned in distilled water and dried with cotton wool. The dried samples were weighed with the electronic digital weighing balance and recorded. Weight loss measurements of coupons were recorded at interval of 24 hours. The corrosion penetration rate (CPR) were calculated from weight loss analysis using the equation (1)

$$CPR = \frac{87.6W}{\rho At} \hspace{6cm} (1)$$

Where;$CPR - Corrosion\ Penetration\ Rate\ in\ mm/yr,$ $\hspace{1cm} W - Weight\ Loss\ in\ mg$
$\rho\ is\ density\ in\ g/\ cub.cm,$ $\hspace{2cm} A\ is\ Area\ of\ exposed\ specimen\ in\ cm^2$
$t\ is\ exposure\ time\ in\ hr.$

3.0   RESULTS AND DISCUSSION

3.1 Results

Table 1: Chemical Analysis of Carbon Steel

Run	C	Si	S	P	Mn	Ni	Cr
(1)	0.3397	0.2191	0.0573	0.0620	0.8294	0.0960	0.1242
(2)	0.3426	0.2204	0.0605	0.0597	0.8343	0.0961	0.1245
Avg	0.3411	0.2198	0.0589	0.0609	0.8318	0.0960	0.1244

Mo	V	Cu	W	As	Sn	Co	A1	Pb	Ca	Zn	Fe%
0.0188	0.0057	0.2066	0.0035	0.0056	0.0252	0.0088	-0.0007	0.0001	0.0001	0.0035	97.9951
0.0191	0.0058	0.2077	0.0035	0.0059	0.0262	0.0088	-0.0007	-0.0000	0.0001	0.0038	97.9816
0.0189	0.0058	0.2071	0.0035	0.0058	0.0257	0.0088	-0.0007	0.0001	0.0001	0.0036	97.9883

Table 2: Nickel Plating Parameters

Weight(initial) (g)	Time in solution (min)	Weight (final) (g)	Temperature (^{0}C)	Current amp/dm^3
281.5	25	325.7	60	3.0

Table 3: Gold Plating Parameters

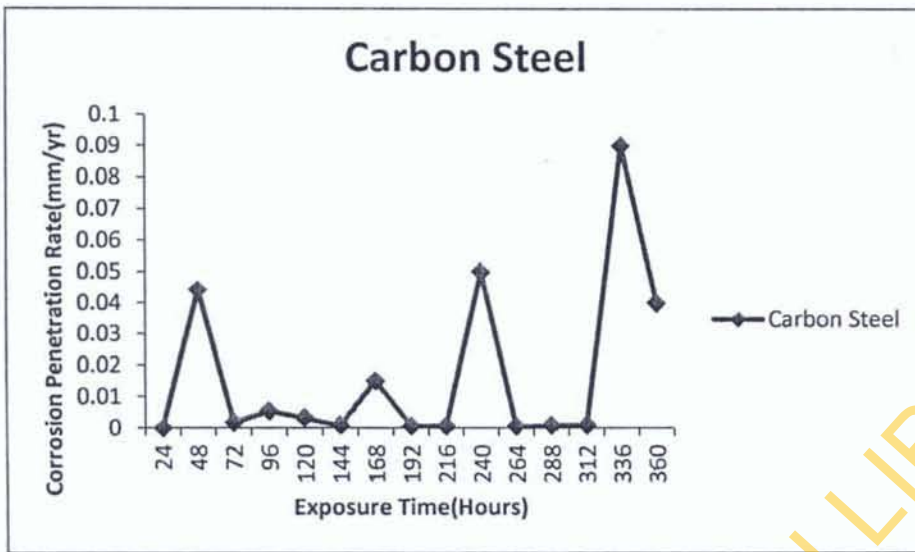| Weight(initial) (g)	Time in solution (min)	Weight (final) (g)	Temperature (^{0}C)	Current A/dm^3
15.4	20	15.9	50	0.2

Fig.1: Corrosion Penetration Rates of Carbon Steel in Sulphuric Acid Environment
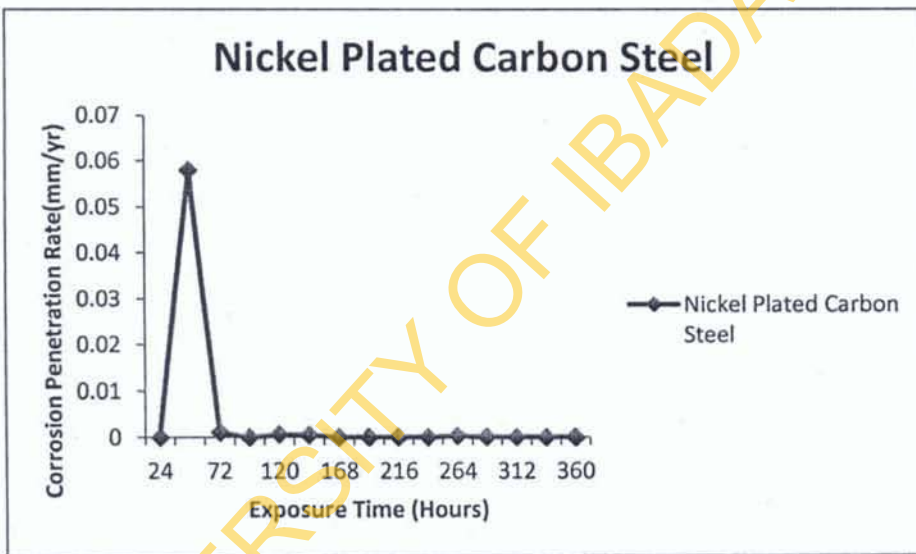

Fig.2: Corrosion Penetration Rates of Nickel Plated Carbon Steel in Sulphuric Acid Environment
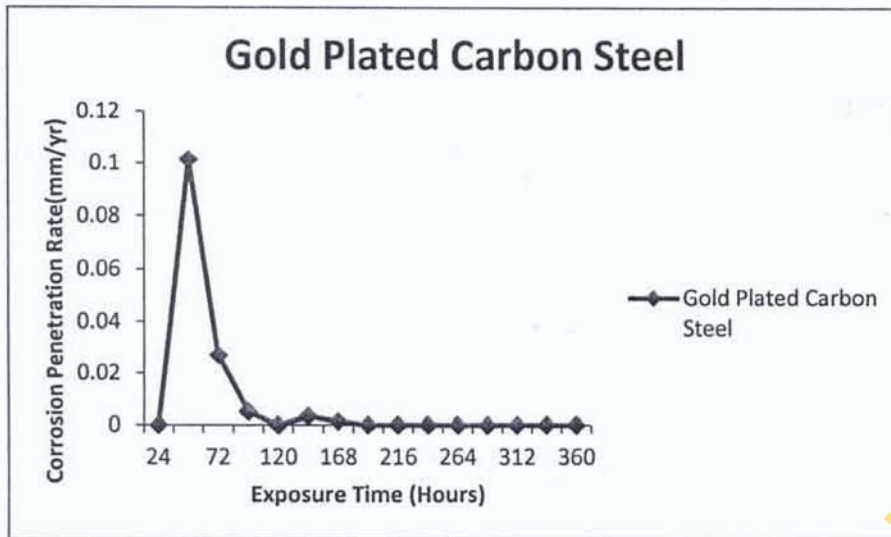
Fig.3: Corrosion Penetration Rates of Gold Plated Carbon Steel (with Nickel Underlay) in Sulphuric Acid Environment
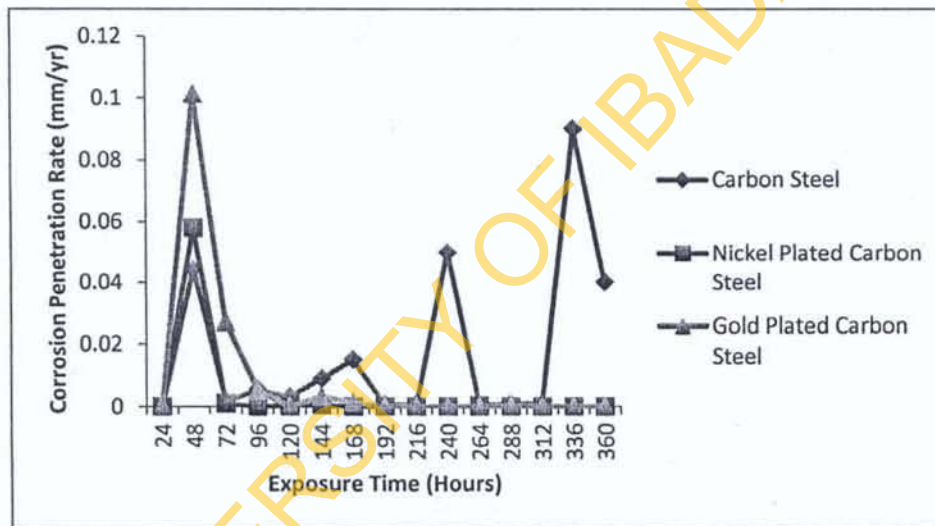

Fig.4: Chart Displaying Different Corrosion Penetration Rates of Unplated and Plated Carbon steels in Sulphuric Acid Environment

3.2 Discussions

The result from chemical analysis of carbon steel carried out at the Universal steel Ltd., Lagos state, Nigeria is shown in table 1.The average percentage of carbon content is 0.3411% which indicated medium carbon steel. Tables 2 and 3 gives the current density, plating time and increase in weight during nickel and gold plating of carbon steels. An increase in weight of 44.2g and 0.5g were obtained for nickel and gold plated carbon steels respectively.Fig.1 gives a summarized description of corrosion resistance of carbon steel in 0.5 mol/dm^3 of sulphuric acid medium. After 48 hours, the CPR increased to 4.42×10^{-2} mm/yr and then decreased to 1.8×10^{-3} mm/yr after 72 hours. A highly significant CPR is also observed

at 168 hours, 240 hours and 336 hours. The CPR at these exposure times are respectively $1.5 \times 10^{-2}\ mm/yr$, $5 \times 10^{-2}\ mm/yr$ and $9 \times 10^{-2}\ mm/yr$. The CPR of $9 \times 10^{-2}\ mm/yr$ is the highest corrosion rate recorded during the study period of 360 hours. Fig.1 clearly shows that carbon steel is unsuitable in sulphuric acid environment. Fig.2 shows that nickel plated carbon steel experiences corrosion degradation only in the first 48 hours. The CPR recorded in the second day of exposure to sulphuric acid medium is $5.79 \times 10^{-2}\ mm/yr$. At the end of 73rd hour, the CPR drastically decreased to an approximate $0\ mm/yr$. This is due to the formation of protective layer of NiO_2. This pasisive film remained stable throughout the rest parts of the study period (72 - 360 hours). The CPR experienced in these periods is highly insignificant. This result shows that nickel plating on carbon steels greatly improves its corrosion resistance. No doubt, Nickel plated carbon steel is highly suitable in sulphuric acid environment. Fig.3 illustrates the corrosion resistance of gold plated carbon steel (with Nickel coating underlay) in sulphuric acid medium. Its CPR was at the peak value of $1.013 \times 10^{-1} mm/yr$ at 48hours of immersion.

Although there was reduction in the corrosion rate between 48hours and 168hours, the CPR is however not insignificant. From 192 hours to 360 hours, no visible corrosion rate was experienced. This is surely due to the formation of passive layer. This protective layer greatly hindered the renewal in corrosion penetration behaviour. This chart has shown that gold plated carbon steel is a suitable material in sulphuric acid medium especially when exposed in this medium for a long period of time. It should however be clear that corrosion behaviour is more likely to manifest in the first 2 days. Fig.4 shows a comparison in the corrosion resistance of plated (Nickel and Gold plated) and unplated carbon steels in 0.5 mol/dm^3 sulphuric acid. The unplated carbon steel exhibited the worst corrosion resistance throughout the study period of 360 hours. The highest three CPR values recorded are $4.42 \times 10^{-2}\ mm/yr$, $5 \times 10^{-2}\ mm/yr$ and $9 \times 10^{-2}\ mm/yr$. Although nickel plated carbon steel experienced corrosion degradation in the first 48 hours of exposure, the CPR remarkably reduces to an infinitesimal level at the end of 72 hours. Between 72 hours and 360 hours, corrosion deterioration was not in any way noticeable. The reason for this is due to the formation of passivating film which created a protective layer against corrosion. This remarkably improves the corrosion resistance of nickel plated carbon steel. Equally, gold plated carbon steel experienced well significant corrosion behaviour in the first 168 hours. The highest CPR obtained in the test medium is $1.013 \times 10^{-1} mm/yr$ at the 48th hour.

The gold plated carbon steels however developed a high immunity against corrosion from 168 hours to 360 hours. This clearly implies that the formation of a protective layer is responsible for this latter improvement in its corrosion resistance. This fig.4 clearly reveals that the unplated carbon steel has the worst corrosion resistance as compared to the plated carbon steel. Nickel plated carbon steel has the best corrosion resistance of all the three alloys in the test medium. Unexpectedly, the gold plated (with nickel underlay) carbon steel has a lower corrosion resistance than the nickel plated carbon steels. This result shows that the most suitable alloy in the fabrication of ornaments meant for usage in sulphuric acid medium of all the three materials is nickel plated carbon steel.

4. CONCLUSIONS

The following conclusions can be drawn from this experimental study:

> This study has shown that as electroplating time, current density and bath concentration increases, there is a corresponding increase in the corrosion resistance of electroplated alloy materials. This qualitatively agree which what is obtainable in the literature.

✓ The results of this study have revealed that unplated carbon steel is generally unsuitable in sulphuric acid medium. It has a remarkably high corrosion rates.

✓ Nickel and gold plated carbon steels generally have high corrosion resistance in H_2SO_4 environment.

✓ Nickel plated carbon steel is the most reliable alloy for fabrication of ornamentals that will be utilized in H_2SO_4 medium. The gold plating of carbon steels with nickel underlay attracted additional costs but contrarily does not translate to its improvement in corrosion resistance.

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