

Operational Dependence of Galvanized Steel Corrosion Rate on Its Structural Weight Loss and Immersion-Point pH in Sea Water Environment

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Abstract The operational dependence of galvanized steel corrosion rate on its structural weight loss and immersion-point pH (pH of stagnant sea water trapped in holes and grooves of galvanized steel made structures or equipment) in sea water environment was studied. SEM analysis of the surface structure of the corroded steel revealed that the adherent and compact nature of the white rust layers absorbed on the zinc surface affected the level of corrosion attacks on the zinc and invariably on the steel structure. The corrosion rate of the galvanized steel decreased with increase in the steel weight loss and immersion-point pH. Formation and presence of $(ZnOH)_2$ in corrosion medium retarded the corrosion process because of its alkaline nature. A two-factorial model was derived, validated and used for the predictive evaluation of the galvanized steel corrosion rate. The validity of the model was rooted on the core model expression $\zeta + 5 \times 10^{-5} \ln x + 6.166 \times 10^{-5} = -1.5 \times 10^{-5} \theta^2 + 0.0001\theta$ where both sides of the expression are correspondingly approximately equal. The standard errors incurred in predicting the corrosion rate for each value of the weight loss & immersion-point pH considered as obtained from experiment, derived model and regression model-predicted results were 1.516×10^{-7} , 5.415×10^{-7} and 2.423×10^{-9} & 1.39×10^{-7} , 4.529×10^{-7} and 2.548×10^{-8} % respectively. Deviation analysis indicates that the derived model operates most viably and reliably within a deviation range of 0-15.38% from experimental results. This translated into about 84% operational confidence and response level for the derived model as well as 0.84 reliability response coefficient of the corrosion rate to the collective operational contributions of weight loss and immersion-point pH in the sea environment.

Keywords: galvanized steel, corrosion rate, immersion-point ph, weight loss, sea water environment

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1. Introduction

The growing usefulness of galvanized steel as an effective material for building and water distribution system has raised the need for research and development aimed at improving the coating of zinc on the steel substrate. Galvanized steel has dual properties; mechanical, due to steel and chemical, resulting from its enhanced corrosion resistance due to presence of zinc. [1]

Observation has shown [1] that the nature of the corrosion product deposited on galvanized steel surface following its exposure in water is waxy and white. This is referred to as white rust. The research indicates that if the

white-rust corrosion product is kept wet, it often feels waxy; if it dries it usually feels hard and brittle.

It has been revealed [1] that white rust is a rapid, localized corrosion attack on zinc that usually appears as a voluminous white deposit. Results of this work also show that there exists beneath the white deposit a localized area where the zinc has been attacked. This area appears as a shallow pit at its early formation stages.

Studies [2,3,4] have shown that the good corrosion resistance of zinc coating could be significantly improved by alloying zinc with other metal (e.g. Co, Ni, Mn, Al). Some scientists have therefore suggested that the higher protective ability of zinc results from the presence of zinc hydroxide salts $(Zn(OH)_2)$, which is formed due to interaction with the corrosion medium [5]. In addition,

corrosion current and corrosion potential are significantly sensitive to the zinc surface conditions as well as the environmental factors (pH of the solution, dissolved oxygen concentration, Cl⁻ ion concentration, temperature, etc). These factors are related to the presence of oxidized species (oxide, hydroxide and carbonate) due to the contact with aqueous solution, and to the contribution of the cathodic reduction of dissolved oxygen.

Investigations [6,7,8] on atmospheric corrosion of galvanized steel have indicated that the composition of the rust layer on galvanized steel depends on the exposure conditions, type and level of the pollutants, as well as the number of the wet- dry cycles.

It has been proposed [9] that zinc ion dissolved from the rust layer on galvanized steel prevents further corrosion of the steel substrate. The researcher [9] demonstrated the contribution of the zinc-containing rust layer to the corrosion retardation for the Fe substrate, as well as the high sacrificial anodic effect of the metallic zinc.

Galvanized steel has found application [10,11] in areas such as building, automotive body parts and water distribution systems because of its good resistance to environmental corrosion. The protection proffered by zinc coating is due to barrier and galvanic double protective effect [12,13]. However, many cases of heavy damage of galvanized pipes and tanks have been reported as being due to corrosion processes in water hanging system, as clearly evidenced by the production of rust layer in those systems after an unexpectedly short service life [14].

The aim of this research is to evaluate galvanized steel corrosion rates based on the steel's structural weight loss and immersion-point pH while serving in natural sea water. A model would be derived, validated and used for the evaluation. Structures and equipment made of galvanized steel and used in sea water evaporating system are known to have series of holes and grooves which entrap water. It is strongly believed that the corrosion rates of these areas could be predicted by substituting into the derived model, values of the galvanic steel structural weight loss (resulting from corrosion) and immersion pH (the pH of the trapped sea water).

2. Materials and Methods

Materials used for the experiments are galvanized steel pipes obtained from oil fields in Port Harcourt, Nigeria. The other materials used were acetone (analytical grade), distilled water, graduated pyrex beakers and Erlenmeyer flasks. The equipment used were Micro drilling machine (Model H), analytical digital weighing machine (Mettler 4900) and pH meter (SeaFET™ Ocean pH Sensor).

2.1. Specimen Preparation and Experimentation

The galvanized steel pipes were cleaned using 0.5M picric acid to remove any existing trace of rust. These pipes were then washed in running water, distilled water and acetone before air-drying at room temperature. The dried steel pipes were cut into test samples of cross-sectional area: 12 cm² and weight: 14 g. Each sample piece was drilled to 0.5 mm diameter to provide hole for

the suspension of the strings and submersion of the sample in the sea water.

The method adopted for this phase of the research is the weight loss technique. The test pieces were weighed and exposed to 200 cm³ of sea water contained in a beaker for 250 hrs after which they were withdrawn. The pH of the sea water was measured as each test piece was withdrawn. The withdrawn test pieces were washed with distilled water, acetone and then dried in open air before weighing to determine the final weight. The experiment was repeated with 270, 280, 290 as well as 300 hrs exposure time and the corresponding sea water pH measured.



Figure 1. Galvanized steel pipe



Figure 2. Corroded pieces of galvanized steel cut and exposed to sea water environment

3. Results and Discussion

3.1. Surface Structural Analysis of Corroded and un-corroded Galvanized Steel

The corrosion processes of the galvanized steel changed differently under the same sea water Cl⁻ concentration. Figure 3 shows the SEM images at different sampling time intervals. Figure 3 (a) presented the SEM images of the as-received sample of galvanized steel before immersion in sea water. This image (un-corroded steel) was for comparison with those of corroded samples. Evidently, the zinc coatings were compact, smooth and completely covering the substrate surface. No corrosion was found before the immersion of the test piece. Loose white rust and corrosion products were absorbed on the zinc surface after 250 hrs (Figure 3 (b)), and as time elapsed, through 270 hrs (Figure 3 (c)), designating localized corrosion attack on the zinc covering the steel

[1]. These results further support the assumption of the oxygen diffusion control step. With time, the rust layer absorbed on the zinc coating was gradually damaged under the erosion of Cl⁻. However, lots of needle-like white rust layers (Figure 3 (d)) were adherent and compactly absorbed on the zinc surface, and so reduced corrosion was observed on the zinc coating after 280 hrs. This indicates drop in corrosion attack. Figure 3 (e) also shows a reduction in the white waxy rust at 290 hrs (compared with other exposure times) due to decrease in the diffusion of oxygen. This resulted from the compact nature of the protective film formed at this particular exposure time. Corrosion attack was correspondingly reduced as a result of the highlighted hindrance to oxygen diffusion. At an exposure time of 300 hrs (Figure 3 (f)), the white rust deposit further decreased due to much significant decrease in the diffusion of oxygen, resulting from an increased compact nature of the formed protective film. This resulted to much decrease in the corrosion attack on the galvanized steel.

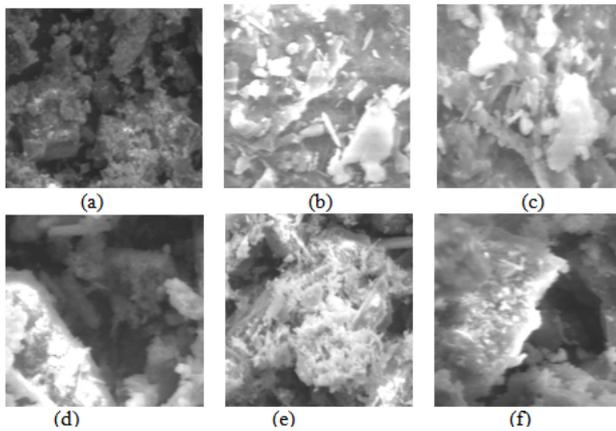


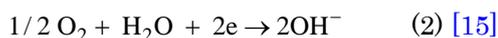
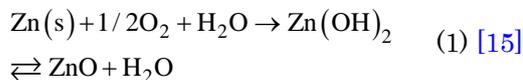
Figure 3. The SEM images of galvanized steel in sea water environment with different weight loss: (a) before immersion; (b) 250 hrs; (c) 270 hrs; (d) 280 hrs, (e) 290 hrs; (f) 300 hrs (50µm)

Table 1. Variation of corrosion rate ζ of galvanized steel with its exposure time Φ (hr) weight loss θ , and immersion-point pH \varkappa

(ζ) (mm/yr)	(Φ) (hr)	(\varkappa)	(θ) (g)
1.3010×10^{-5}	250	6.00	3.50
1.2740×10^{-5}	270	6.08	3.70
1.1261×10^{-5}	280	6.12	3.83
1.1248×10^{-5}	290	6.16	3.90
1.2360×10^{-6}	300	6.20	4.00

3.2. Variation of Corrosion Rates with Immersion-point pH and Weight Loss

Table 1 shows that the corrosion rate of the galvanized steel decreases with increase in the weight loss and immersion-point pH. It was believed that the protective film on the zinc grew, and its hardness, adherence and coherency enhanced with increased exposure time thereby reducing corrosion through oxygen diffusion.



Decrease in the corrosion rate of galvanized steel with increase in immersion-point pH stems on the formation

and presence of $\text{Zn}(\text{OH})_2$ in the corrosion medium (which reversibly gives $\text{ZnO} + \text{H}_2\text{O}$) from the reaction between OH^- and Zn^{2+} . This reaction resulted to the initial rust. Based on the foregoing, presence of $\text{Zn}(\text{OH})_2$ or ZnO in aqueous solution (around the immersed galvanized steel) during the corrosion process increases the immersion-point pH and invariably the corrosion resistance in line with past findings [15]. OH^- was formed as result of oxygen reduction at the cathodic zone as shown in equation (2).

Table 2. Variation of $\zeta + 0.00005 \ln \varkappa + 6.166 \times 10^{-5} = -1.5 \times 10^{-5} \theta^2 + 0.0001\theta$

$\zeta + 0.00005 \ln \varkappa + 6.166 \times 10^{-5}$	$-1.5 \times 10^{-5} \theta^2 + 0.0001\theta$
1.6425×10^{-4}	1.6625×10^{-4}
1.6465×10^{-4}	1.6465×10^{-4}
1.6485×10^{-4}	1.6297×10^{-4}
1.6504×10^{-4}	1.6185×10^{-4}
1.6525×10^{-4}	1.6000×10^{-4}

Computational analysis of experimental results shown in Table 2, gave rise to Table 3 which indicate that;

$$\zeta + K \ln \varkappa + S = -N\theta^2 + N_e \theta \quad (3)$$

Introducing the values of K, S, N and N_e into equation (11) reduces it to;

$$\zeta + 0.00005 \ln \varkappa + 6.166 \times 10^{-5} = -1.5 \times 10^{-5} \theta^2 + 0.0001\theta \quad (4)$$

$$\zeta = -0.00005 \ln \varkappa - 1.5 \times 10^{-5} \theta^2 + 0.0001\theta - 6.166 \times 10^{-5} \quad (5)$$

Where

$K = 0.00005$, $S = 6.166 \times 10^{-5}$, $N = 1.5 \times 10^{-5}$ and

$N_e = 0.0001$ are empirical constants (determined using C-NIKBRAN [16])

(ζ) = Corrosion rate (mm/yr)

(θ) = Weight loss (g)

(\varkappa) = Immersion-point pH (pH of stagnant sea water trapped in holes and grooves of galvanized steel made structures or equipment)

The derived model is equation (5). Computational analysis of Table 1 gave rise to Table 2. The derived model is two-factorial in nature, being composed of two input process factors: weight loss and immersion-point pH. This implies that the predicted corrosion rate of galvanized steel in the sea water environment is dependent on just two factors: weight loss and galvanized steel immersion-point pH.

3.3. Boundary and Initial Conditions

Consider short cylindrically shaped galvanized steel exposed to sea water environment, interacting with some corrosion-induced agents. The sea water is assumed to be affected by undesirable dissolved gases. The range of the exposure time was considered: 250-300 hrs, range of galvanized steel immersion point-pH considered: 6.0-6.2.

The boundary conditions are: aerobic environment for zinc coating (covering galvanized steel) oxidation (since the atmosphere contains oxygen. At the bottom of the exposed steel, a zero gradient for the gas scalar are assumed. The exposed steel is stationary. The sides of the solid are taken to be symmetries.

3.4. Model Validity

The validity of the model is strongly rooted on equation (4) (core model equation) where both sides of the equation are correspondingly approximately equal. Table 2 also agrees with equation (4) following the values of $\zeta + 0.00005 \ln x + 6.166 \times 10^{-5}$ and $-1.5 \times 10^{-5} \theta^2 + 0.00019$ evaluated from the experimental results in Table 1. Furthermore, the derived model was validated by comparing the corrosion rate predicted by the model and that obtained from the experiment. This was done using some statistical tools, graphical comparison, comparison with regression model, computational and deviation analysis.

3.4.1. Statistical Analysis

3.4.1.1. Standard Error (STEYX)

The standard errors incurred in predicting the galvanized steel corrosion rate for each value of weight loss & immersion-point pH considered as obtained from experiment and derived model were 1.516×10^{-7} and 5.415×10^{-7} & 1.39×10^{-7} and 4.529×10^{-7} % respectively. The standard error was evaluated using Microsoft Excel version 2003.

3.4.1.2. Correlation

The correlation coefficient between galvanized steel corrosion rate and weight loss & immersion-point pH were evaluated (using Microsoft Excel Version 2003) from results of the experiment and derived model. These evaluations were based on the coefficients of determination R^2 shown in Figure 4- Figure 7.

$$R = \sqrt{R^2} \quad (6)$$

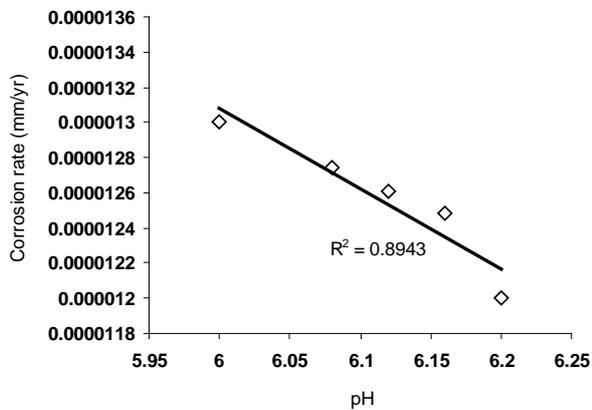


Figure 4. Coefficient of determination between galvanized steel corrosion rate and immersion- point pH as obtained from the experiment

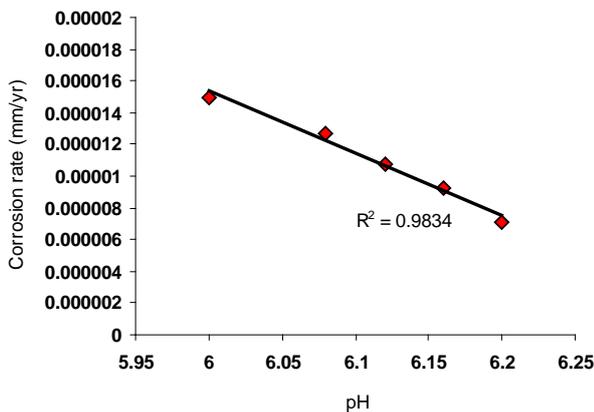


Figure 5. Coefficient of determination between galvanized steel corrosion rate and immersion-point pH as predicted by derived model

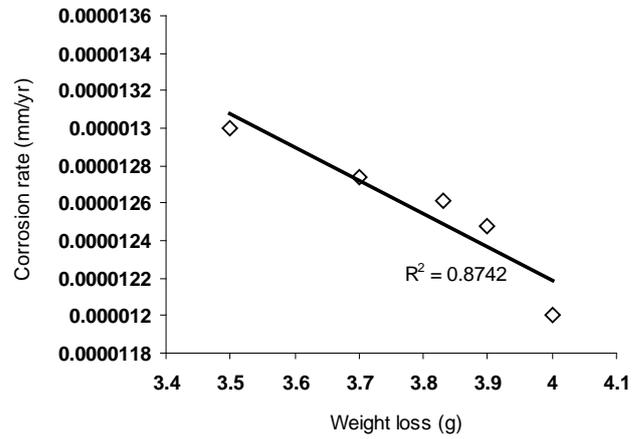


Figure 6. Coefficient of determination between galvanized steel corrosion rate and weight loss as obtained from the experiment

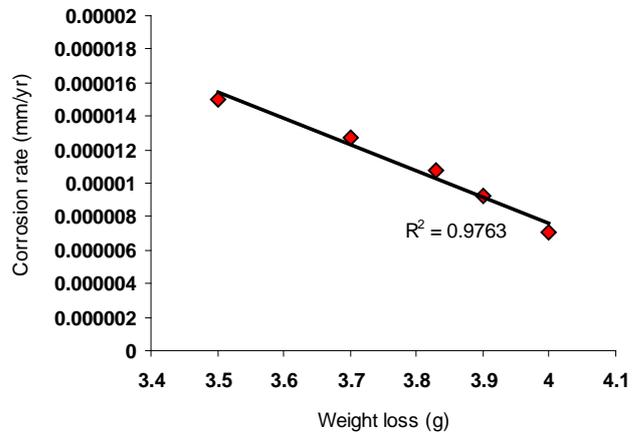


Figure 7. Coefficient of determination between galvanized steel corrosion rate and weight loss as predicted by derived model

Table 3. Comparison of the correlations between corrosion rate and weight loss as evaluated from experimental (ExD) and derived model (MoD) predicted results

Analysis	Based on weight loss	
	ExD	D-Model
CORREL	0.9350	0.9881

The evaluated correlations are shown in Table 3 and Table 4. These evaluated results indicate that the derived model predictions are significantly reliable and hence valid considering its proximate agreement with results from actual experiment.

Table 4. Comparison of the correlations between corrosion rate and immersion-point pH and as evaluated from experimental and derived model predicted results

Analysis	Based on immersion-point pH	
	ExD	D-Model
CORREL	0.9457	0.9917

3.4.2. Graphical Analysis

Figure 8 and Figure 9 show curves from derived model and experiment. Comparative analysis of these figures shows a high degree of curves alignment which indicates proximate agreement between ExD and MoD predicted results.

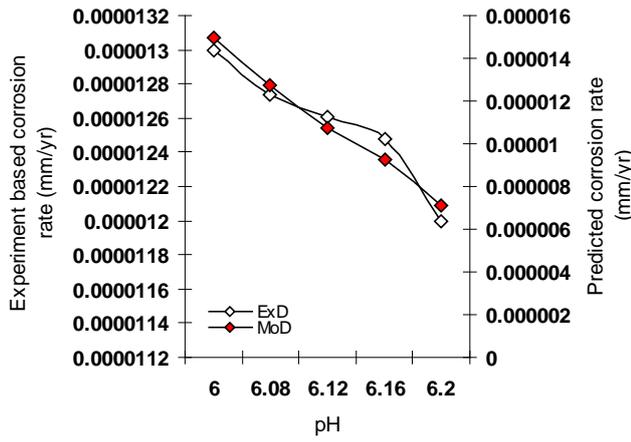


Figure 8. Comparison of the galvanized steel corrosion rates (relative to immersion-point pH) as obtained from experiment and derived model

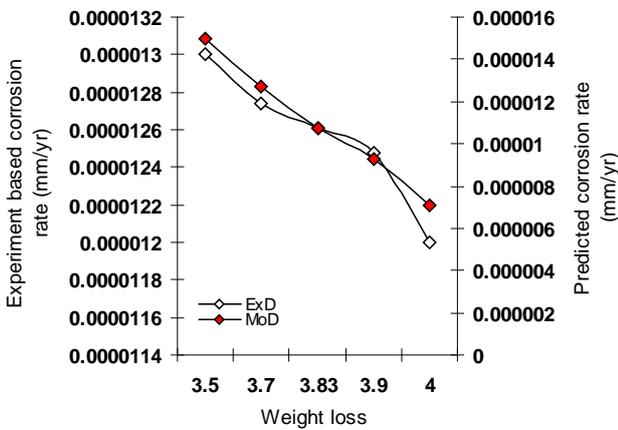


Figure 9. Comparison of the galvanized steel corrosion rates (relative to weight loss) as obtained from experiment and derived model

3.4.3 Comparison of derived model with standard model

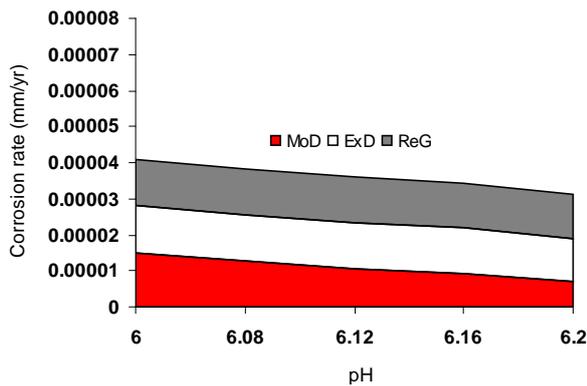


Figure 10. Comparison of the galvanized steel corrosion rates (relative to immersion-point pH) as obtained from experiment, derived model and regression model

The validity of the derived model was also verified through application of the regression model (ReG) (Least Square Method using Excel version 2003) in predicting the trend of the experimental results. Comparative analysis of Figure 10 and Figure 11 shows close dimensions of shaped areas of corrosion rates, which precisely translated into significantly similar trend of data point's distribution for experimental (ExD), derived model (MoD) and regression model-predicted (ReG) results of corrosion rates. Furthermore, the calculated correlations (from

Figure 10 and Figure 11) between galvanized steel corrosion rates and weight loss & immersion-point pH for results obtained from regression model were 1.0000 & 0.9980 respectively. These values are in proximate agreement with both experimental and derived model-predicted results. The standard errors incurred in predicting steel corrosion rates for each value of weight loss & immersion-point pH considered as obtained from regression model were 2.423×10^{-9} and 2.548×10^{-8} % respectively.

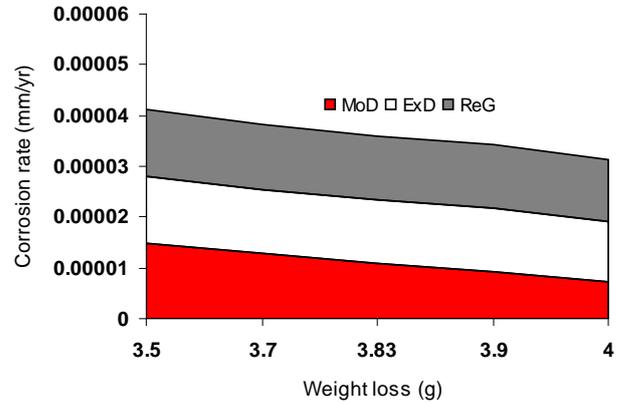


Figure 11. Comparison of the galvanized steel corrosion rates (relative to weight loss) as obtained from experiment, derived model and regression model

3.4.4 Deviation Analysis

Comparative analysis of the corrosion rates precisely obtained from the experimental data and derived model shows deviation on the part of model-predicted results. This was attributed to the fact that the effects of the surface properties of the galvanized steel which played vital roles during the corrosion process were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted corrosion rate to those of the corresponding experimental values.

The deviation D_v , of model-predicted corrosion rate from the corresponding experimental result was given by

$$D_v = \left(\frac{\zeta_P - \zeta_E}{\zeta_E} \right) \times 100 \quad (7)$$

Where ζ_E and ζ_P are corrosion rates evaluated from experiment and derived model respectively.

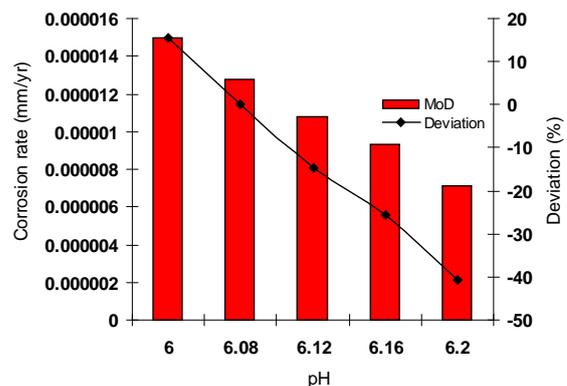


Figure 12. Variation of model-predicted corrosion rate with associated deviation from experimental results (relative to immersion-point pH)

Critical analysis of Figure 12 and Figure 13 show that the derived model operates most viably and reliably within a deviation range of 0-15.38%. This translates into over 84% operational confidence and response level for the derived model as well as over 0.84 reliability response coefficient of corrosion rate to the collective operational contributions of the weight loss and galvanized steel immersion-point pH (under service) in the sea water environment. This deviation range corresponds to corrosion rates in the range: 1.0762×10^{-5} - 1.5×10^{-5} mm/yr, exposure time: 250-280 hrs as well as galvanized steel immersion pH: 6 - 6.12 and range of weight loss: 0 - 3.5 g respectively.

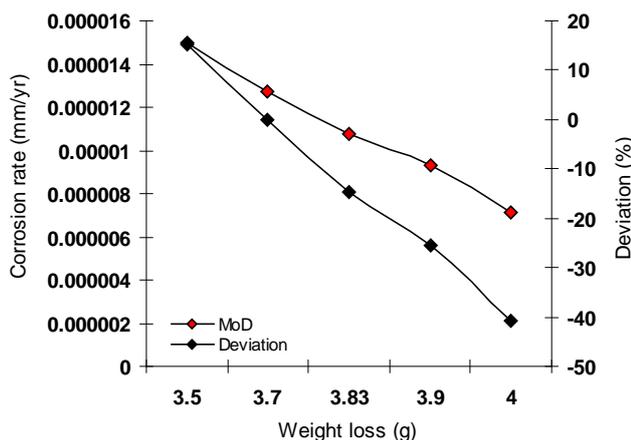


Figure 13. Variation of model-predicted corrosion rate with associated deviation from experimental results (relative to weight loss)

Correction factor, Cf to the model-predicted results was given by

$$Cf = \left(\frac{\zeta_P - \zeta_E}{\zeta_E} \right) \times 100 \quad (8)$$

Analysis of Table 5 as well as Figure 12 and Figure 13 shows that the evaluated correction factors are negative of the deviation as shown in equations (7) and (8).

The correction factor took care of the negligence of operational contributions of the effects of surface properties of the galvanized steel which actually affected the corrosion process. The model predicted results show deviation from those of the experiment because these contributions were not considered during the model formulation. Introduction of the corresponding values of Cf from equation (8) into the model gives exactly the corresponding experimental corrosion rate

Table 5. Variation of correction factor with weight loss and immersion-point pH

(θ) (g)	(γ)	Cf (%)
3.50	6.00	15.38
3.70	6.08	0
3.83	6.12	-14.66
3.90	6.12	-25.56
4.00	6.20	-40.75

Table 5 indicates that the most reliable range of correction factors to the model-predicted corrosion rates is 0-15.38%. This range correction factor also corresponds to corrosion rates in the range: 1.0762×10^{-5} - 1.5×10^{-5} mm/yr, exposure time range: 250-280 hrs as well as galvanized steel immersion pH range: 6 - 6.12 and range of weight loss: 0 - 3.5 g respectively.

It is important to state that the deviation of model predicted results from that of the experiment is just the magnitude of the value. The associated sign preceding the value signifies that the deviation is a deficit (negative sign) or surplus (positive sign).

4. Conclusion

The operational dependence of the galvanized steel corrosion rate on its structural weight loss and immersion-point pH in sea water environment has been evaluated. It was concluded that the adherent and compact nature of the white rust layers absorbed on the zinc surface affected the level of corrosion attacks on the zinc and invariably on the steel structure. The corrosion rate of the galvanized steel decreased with increase in the steel weight loss and immersion-point pH. This was so because the protective film on the zinc grew, and its hardness, adherence and coherence enhanced with increased exposure time, and so resisted corrosion process by hindering of oxygen diffusion. Furthermore, formation and presence of $(ZnOH)_2$ in corrosion medium retarded the corrosion process because of its alkaline nature. A two-factorial model was derived, validated and used for the predictive evaluation of the galvanized steel corrosion rate. The validity of the model was rooted on the core model expression $\zeta + 5 \times 10^{-5} \ln \gamma + 6.166 \times 10^{-5} = -1.5 \times 10^{-5} \theta^2 + 0.00019$ where both sides of the expression are correspondingly approximately equal. Standard errors incurred in predicting the corrosion rate for each value of the weight loss & immersion-point pH considered as obtained from experiment, derived model and regression model-predicted results were 1.516×10^{-7} , 5.415×10^{-7} and 2.423×10^{-9} & 1.39×10^{-7} , 4.529×10^{-7} and 2.548×10^{-8} % respectively. Deviation analysis indicates that the derived model operates most viably and reliably within a deviation range of 0-15.38% from experimental results. This translated into about 84% operational confidence and response level for the derived model as well as 0.84 reliability response coefficient of the corrosion rate to the collective operational contributions of weight loss and immersion-point pH in the sea environment.

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