International Journal of Multidisciplinary Research and Development
Online ISSN: 2349-4182, Print ISSN: 2349-5979, Impact Factor: RJIF 5.72
www.allsubjectjournal.com
Volume 3; Issue 12; December 2016; Page No. 164-170

Response of corrosion level in galvanized steel submerged in insitu sea water to the influence of contact time and iron exposure

[1] AO Ekete, [2] CI Nwoye

Department of Metallurgical and Materials Engineering, Nnamdi Azikiwe University, Awka, Nigeria

Abstract

This paper presents the response of corrosion level in galvanized steel submerged in insitu sea water to the influence of contact time and concentration of iron exposure. SEM analysis of the corroded steel surface revealed deposit of white strip-like waxy rust and dark-grey corrosion products on the zinc surface. Variation in this deposit indicates variation in the level of corrosion attacks on the zinc and invariably on the steel structure. The corrosion level of the galvanized steel increased with increase in both the contact time considered and concentration of exposed iron. This is because incessant natural agitation of the sea water does not allow formation of $(ZnOH)_2$ which is alkaline nature, due to uniformity in sea water pH. An empirical model; $\zeta = 0.0117\ \vartheta^2 - 1.7742\ \vartheta + 0.05ɤ + 109.8125$ was derived, validated and used for the response analysis of the corrosion level. The validity of the model was rooted on the core model expression $\zeta - 109.8125 = 0.0117\ \vartheta^2 - 1.7742\ \vartheta + 0.05ɤ$ where both sides of the expression are correspondingly approximately equal. The standard errors incurred in evaluating the response of corrosion level in the steel to the influence of contact time and concentration of exposed iron as obtained from experiment, derived model and regression model were 1.3, 0.65 & 1.33 and 2.83, 2.23 & 2.8 % respectively. Maximum deviational of model-predicted corrosion level from experimental results is less than 3%. This translated into about 97% operational confidence and response level for the derived model as well as 0.97 reliability response coefficient of the corrosion level to the collective operational contributions of contact time and concentration of exposed iron.

Keywords: galvanized steel, corrosion level, contact time, concentration of iron exposed, insitu sea water

1. Introduction

Yearly all over the world, millions of tonnes of steel products are protected against corrosion by the general galvanizing process. Zinc coatings provide a continuous, impervious metallic barrier that does not allow moisture to contact the steel. Without moisture, there is no corrosion, except in certain chemical atmospheres.

It has been revealed [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 further revealed that white rust is a rapid, localized corrosion attack on zinc that usually appears as a voluminous white deposit.

It has been reported [2] that zinc is chosen as a protective coating for iron and steel for two main reasons. The researcher, in deducing the reasons, posited that zinc possesses natural resistance against corrosion in most atmospheric conditions. The scientist further stated that zinc is electronegative to iron and so can protect it sacrificially.

A successful study [2] carried out on hot dip galvanized coating indicates that the thicknesses of the coating are dependent on factors such as immersion time, zinc temperature, speed of withdrawal and chemical analysis of alloy. The research indicates that zinc provides protection in two ways. It acts as a barrier that prevents access of oxygen and moisture to the protected material, and it acts as a sacrificial anode that corrodes in preference to the protected metal.

Reports [3] have shown that in air, zinc achieves significant protection itself due to the formation of a hydrated oxide $[Zn(OH)_2]$. This in turn combines with carbon dioxide in the atmosphere to form a protective zinc carbonate layer $[ZnCO_2]$ which prevents further corrosion.

Corrosion current and corrosion potential have been ascertained [4] to be 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 contact with cathodic reduction of dissolved oxygen.

Studies [5-7] have shown that during atmospheric corrosion of galvanized steel, 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.

The exquisite resistance of galvanized steel to environmental corrosion has positioned the steel for application in areas such as building, automotive body parts and water distribution systems [8, 9]. The protection proffered by zinc coating is due to barrier and galvanic double protective effect [10, 11]. 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 [12].

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 [13].

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;

$$\zeta = - 0.00005 \ln \gamma - 1.5 \times 10^{-5} \vartheta^2 + 0.0001\vartheta - 6.166 \times 10^{-5} \qquad (1)$$

was rooted on the core model expression $\zeta + 5 \times 10^{-5} \ln \gamma + 6.166 \times 10^{-5} = - 1.5 \times 10^{-5} \vartheta^2 + 0.0001\vartheta$ 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.

Deviational 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.

The aim of this research is to evaluate the response of corrosion level in galvanized steel submerged in insitu sea water to the influence of contact time and concentration of iron exposure. A model will be derived, validated and used for the evaluation.

Structures and equipment made of galvanized steel, and serving in insitu sea water are known to experience varying levels of corrosion attack at different contact time with the water and level of iron exposure due to depleted of zinc coating. It is therefore strongly believed that the response of the corrosion level of these areas to variation in the contact time and level of iron exposure could be predicted by substituting into the derived model, values of these highlighted parameters.

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 (Mettle 4900) and pH meter (SeaFET^{TM} 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: 12cm^2 and weight: 14g. Each sample piece was drilled to 0.5mm diameter to provide hole for the suspension of the strings and submersion of the sample in the sea water at Eleme, Port Harcourt.

The method adopted for this phase of the research is the X-ray mapping technique which combines SEM and X-ray diffractometry. The test pieces were submerged in insitu sea water for 30 days after which they were withdrawn. The withdrawn test pieces were washed with distilled water, acetone and then dried in open air before they were prepared for X-ray mapping which evaluates the corrosion level and corresponding level of iron exposure. The experiment was repeated with contact time: 60, 90, 120 as well as 150days and the corresponding corrosion level evaluated.

Fig 1: Galvanized steel pipe

Fig. 2: Corroded pieces of galvanized steel cut and submerged in insitu sea water

3. Results and discussion

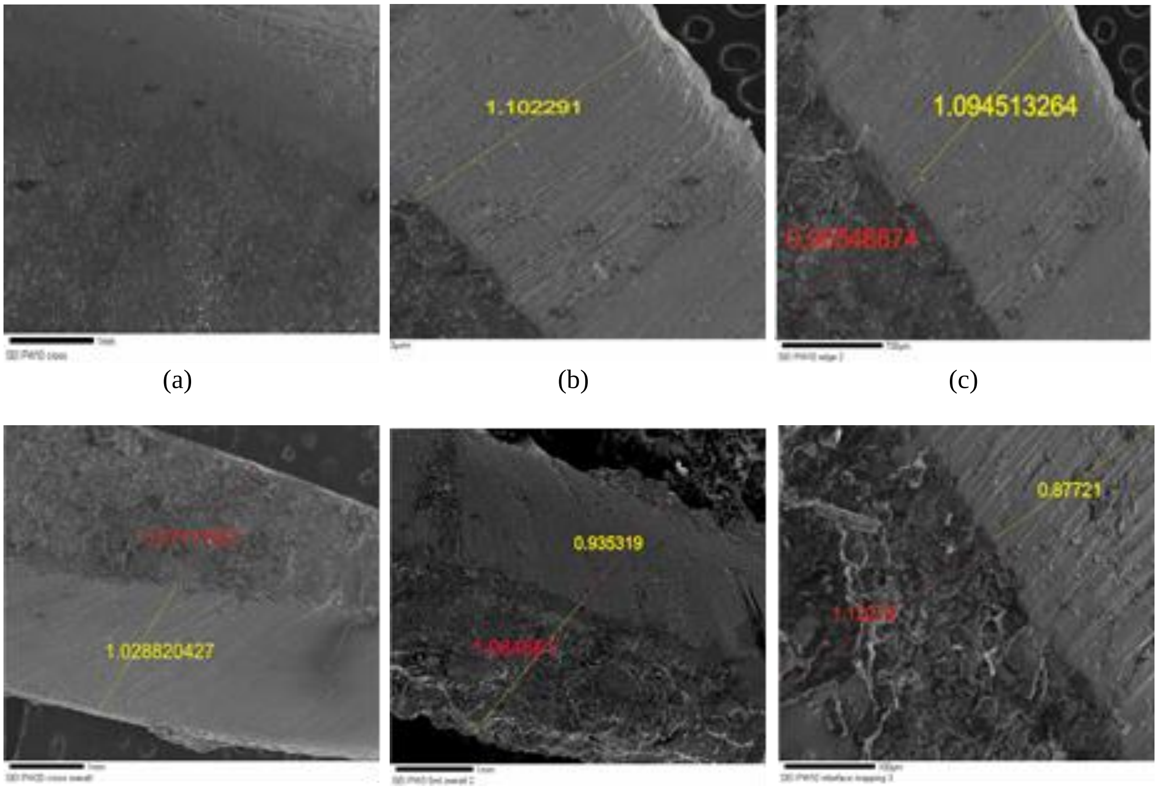
3.1 Surface analysis of corroded and un-corroded galvanized steel using X-ray mapping technique

Results of this investigation shows that the corrosion level of the galvanized steel submerged in the same insitu sea water varied with variation in the contact time and concentration of iron exposed due to attack by chloride in the water. The corrosion level of the galvanized steel increased with increase in both the contact time considered and concentration of exposed iron. This is because incessant natural agitation of the sea water does not allow formation of $(ZnOH)_2$ which is alkaline nature, due to uniformity in sea water pH.

Fig. 3 shows the SEM images at different sampling contact times. Fig. 3 (a) presented the SEM image of the as-received sample of galvanized steel before submerged in sea water. This image (un-corroded steel) was considered the control relative to the others which varied with contact time and concentration of iron exposed. This image indicates that the zinc coatings were intact and completely covering the substrate surface. No corrosion was found before the submersion of the steel piece. Loose corrosion products were absorbed on the zinc surface after 30 days (Fig. 3(b)). After 60days, white strip-like waxy rust (Fig.3(c)) was seen on the steel surface designating localized corrosion attack on the zinc covering the steel. With time, the rust layer absorbed on the zinc coating was gradually damaged under the influence of Cl^-. During this period, there was increased iron exposure. After 90 days, this is depicted in Fig. 3(d) by a section of bright shiny grey surface. Fig. 3(e) also shows increased formation of white strip-like waxy rust and dark corrosion products at 120 days due to increased eroding of zinc and iron exposure. Fig. 3 (f) Corrosion attack further increased between 120 and 150 days as a result of increased iron exposure. This is evident in the increased presence of white strip-like waxy rust and dark-grey corrosion products deposited on the steel surface.

Table 1: Variation of corrosion level ζ of galvanized steel in sea water with its contact time ɤ (days), conc. of iron exposed ϑ and depth of penetration ꞩ.

(ζ) (%)	**(ɤ) (days)**	**(ϑ) (wt %)**	**(ꞩ)**
45.00	30	68.84	0.90
45.50	60	84.23	0.91
48.50	90	90.71	0.97
53.25	120	96.63	1.07
56.15	150	99.01	1.12



(a) (b) (c)

(d) (e) (f)

Fig 3: The SEM images of galvanized steel submerged in insitu sea water for different contact time (a) before submergence; (b) 30 days; (c) 60 days; (d) 90 days, (e) 120 days; (f) 150 days

Computational analysis of experimental results shown in Table 1, gave rise to Table 2 which indicate that;

$$\zeta - K = N\vartheta^2 - S\vartheta + \text{ƀ}\text{ɤ} \qquad (2)$$

Introducing the values of K, N, and S into Equation (2) reduces it to;

$$\zeta - 109.8125 = 0.0117\,\vartheta^2 - 1.7742\,\vartheta + 0.05\text{ɤ} \qquad (3)$$

$$\zeta = 0.0117\,\vartheta^2 - 1.7742\,\vartheta + 0.05\text{ɤ} + 109.8125 \qquad (4)$$

Where;

K = 109.8125, N= 0.0117, S = 1.7742 and

ƀ = 0.05 are empirical constants (determined Using C-NIKBRAN [14]

(ζ) = Corrosion level (%)

(ϑ) = Conc. of Fe exposed (wt %)

(ɤ) = Contact time (days)

The derived model is equation (4). Computational analysis of Table 1 gave rise to Table 2. The derived model is two-factorial in nature.

Table 2: Variation of $\zeta - 109.8125 = 0.0117\,\vartheta^2 - 1.7742\,\vartheta + 0.05\text{ɤ}$

$\zeta - 109.8125$	**$0.0117\,\vartheta^2 - 1.7742\,\vartheta + 0.05\text{ɤ}$**
- 64.8125	- 65.190
- 64.3125	- 63.4330
- 61.3125	- 60.1665
- 56.5625	- 56.1938
- 53.4686	- 53.4686

3.2 Boundary and Initial Conditions

Consider short cylindrically shaped galvanized steel submerged to in insitu sea water, interacting with some corrosion-induced agents. The sea water is assumed to be affected by undesirable dissolved gases. The range of the contact time considered: 30-150 days, considered range of the corresponding concentration of iron exposed: 68.84 - 99.01 wt%.

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.

3.3 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 ζ -109.8125 and $0.0117\ \vartheta^2 - 1.7742\ \vartheta + 0.05\Upsilon$ evaluated from the experimental results in Table 1. Furthermore, the derived model was validated by comparing the corrosion level 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.

3.3.1 Statistical analysis

3.3.1.1 Standard Error (STEYX)

The standard errors incurred in evaluating the response of corrosion level in the steel to the influence of contact time and concentration of exposed iron as obtained from experiment and derived model were 1.3 & 0.65 and 2.83 & 2.23 % respectively. The standard error was evaluated using Microsoft Excel version 2003.

3.3.1.2 Correlation

The correlation coefficient between contact time and concentration of exposed iron were evaluated (using Microsoft Excel Version 2003) from results of the experiment and derived model. The results of these evaluations are 0.9730 & 0.9959 and 0.9989 & 0.9989 respectively. The evaluations were based on the coefficients of determination R^2 shown in Figs. 4-7.

$$R = \sqrt{R^2} \quad (5)$$

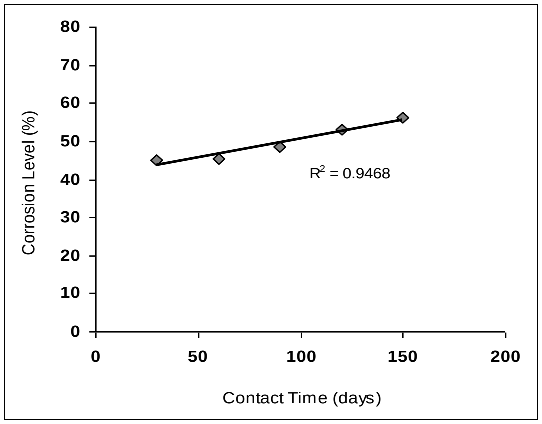


Fig 4: Coefficient of determination between galvanized steel corrosion level and contact time as obtained from the experiment

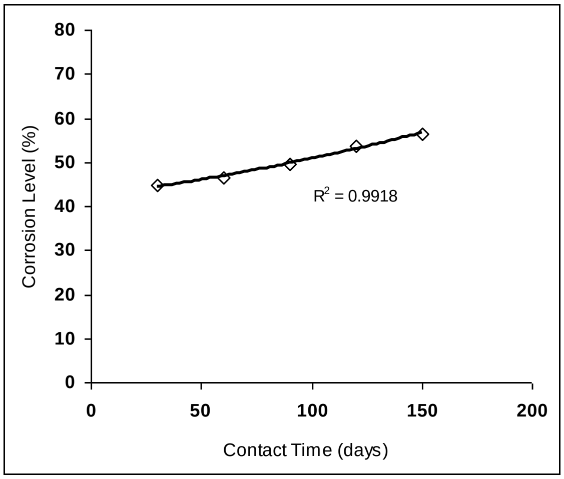


Fig 5: Coefficient of determination between galvanized steel corrosion level and contact time as predicted by model

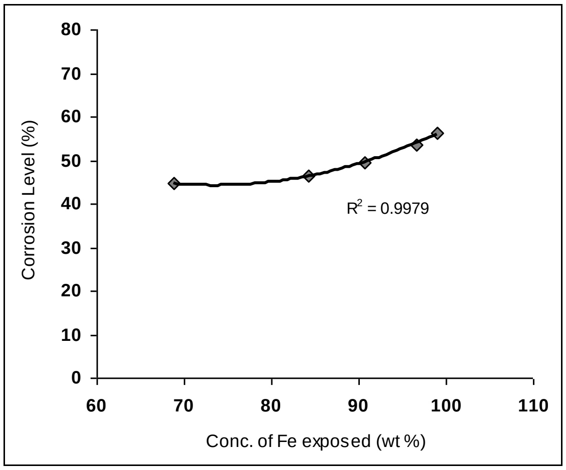


Fig 6: Coefficient of determination between galvanized steel corrosion level and conc. of Fe exposed as obtained from the experiment

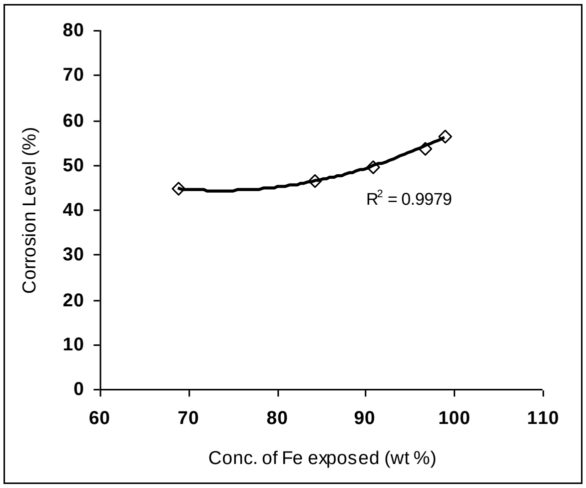


Fig 7: Coefficient of determination between galvanized steel corrosion level and conc. of Fe exposed as predicted by model

3.3.2 Graphical Analysis

Comparative analysis of Figs. 8 and 9 show curves of model-predicted and experimental results with high degree of alignment. This indicates proximate agreement between both results.

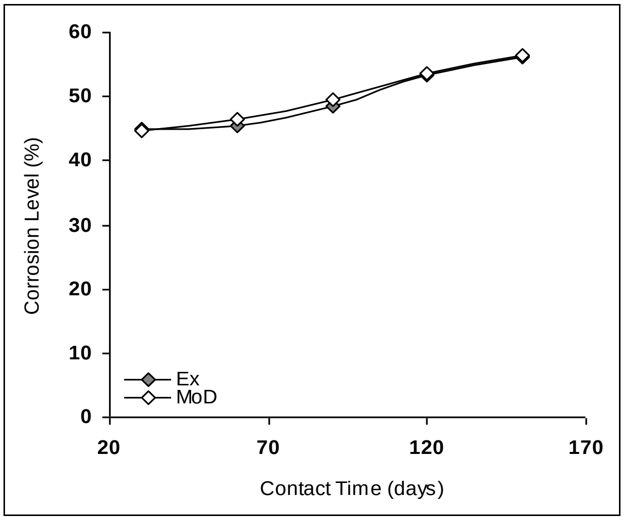


Fig 8: Comparison of the galvanized steel corrosion levels (relative to contact time) as obtained from experiment and derived model.

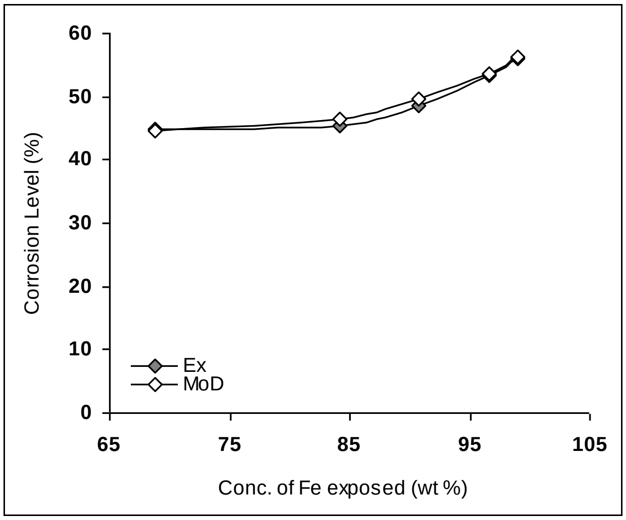


Fig 9: Comparison of the galvanized steel corrosion levels (relative to conc. of Fe exposed) as obtained from experiment and derived model

3.3.3 Comparison of derived model with standard model

The validity of the derived model was further verified by comparing model-predicted results with results generated using regression analysis (Least Square Method using Excel version 2003). Comparative analysis of Figs. 10 and 11 shows close alignment of corrosion levels, which precisely translated into significantly similar trend of data point's distribution for experimental (ExD), derived model (MoD) and regression model-predicted (ReG) results.

Furthermore, the calculated correlations (from Figs. 10 and 11) between galvanized steel corrosion levels and contact time & concentration of iron exposed for results obtained from regression model were 0.9854 & 0.9995 respectively. These values are in proximate agreement with both experimental and derived model-predicted results. The standard errors incurred in predicting the steel corrosion level for each value of the considered contact time & concentration of iron exposed as obtained from regression model were 1.33 and 2.8 % respectively.

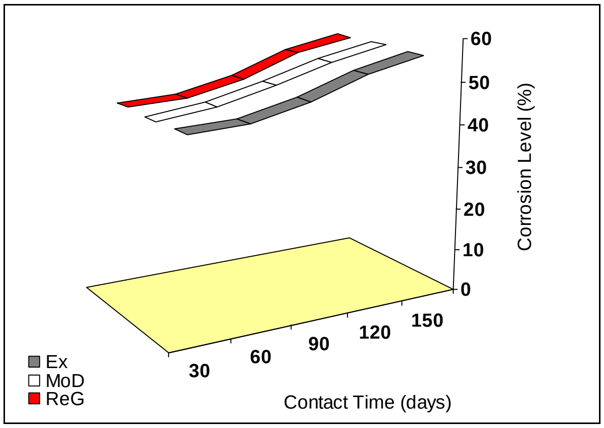


Fig 10: Comparison of the galvanized steel corrosion levels (relative to contact time) as obtained from experiment, derived model and regression model

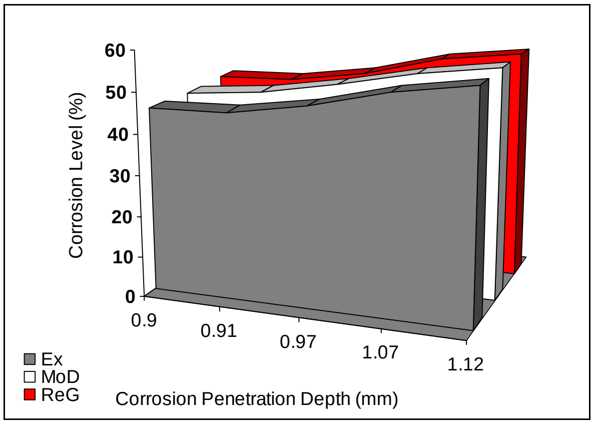


Fig 11: Comparison of the galvanized steel corrosion levels (relative to corrosion penetration depth) as obtained from experiment, derived model and regression model

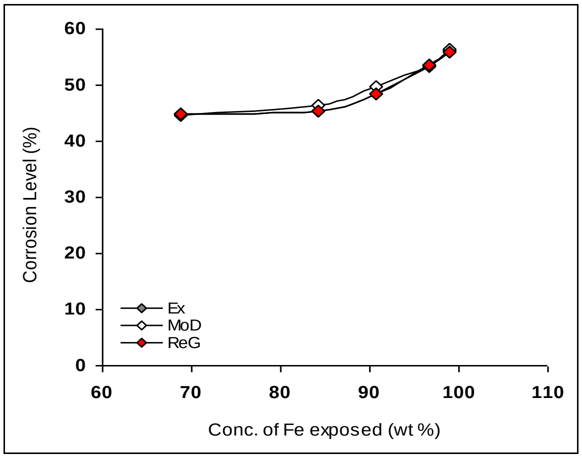


Fig 12: Comparison of the galvanized steel corrosion levels (relative to conc. of Fe exposed) as obtained from experiment, derived model and regression model

3.3.4 Deviational Analysis

Analysis of the corrosion levels 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 level to those of the corresponding experimental values.

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

$$Dv = \left(\frac{\zeta_P - \zeta_E}{\zeta_E}\right) x\ 100 \qquad (6)$$

Where

ζ_E and ζ_P are corrosion levels evaluated
From experiment and derived model
Respectively.

Table 3: Variation of deviation of model-predicted corrosion level (from experimental results) with contact time and conc. of iron exposure

(ϒ)	(ϑ) (wt%)	Dv (%)
30	68.84	- 0.84
60	84.23	+ 1.93
90	90.71	+ 2.36
120	96.63	+ 0.69
150	99.01	+ 0.35

Maximum deviation of model-predicted corrosion levels from experimental results is less than 3%. This translates into over 97% operational confidence and 0.97 reliability response coefficient of the corrosion level to the collective operational contributions of contact time and concentration of exposed iron during the corrosion process in insitu sea water.

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

$$Cf = - \left(\frac{\zeta_P - \zeta_E}{\zeta_E}\right) x\ 100 \qquad (7)$$

Comparative analysis of Table 3 as well as Figs. 13 - 15 shows that the evaluated correction factors are negative of the deviation as shown in equations (6) and (8).

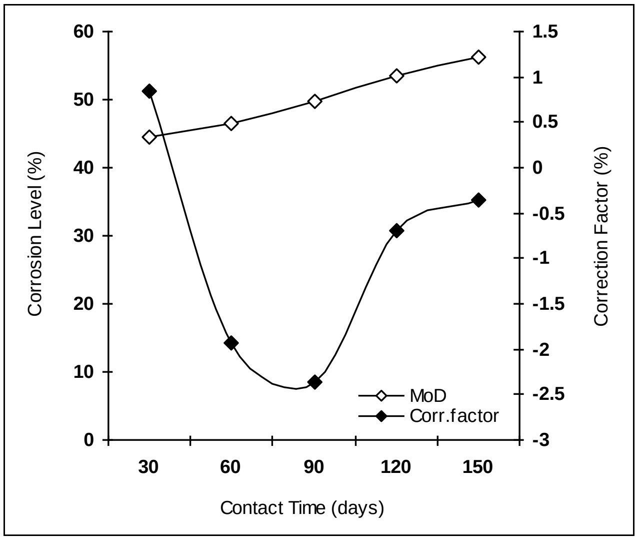


Fig 13: Variation of correction factor to model-predicted corrosion level (relative to contact time)

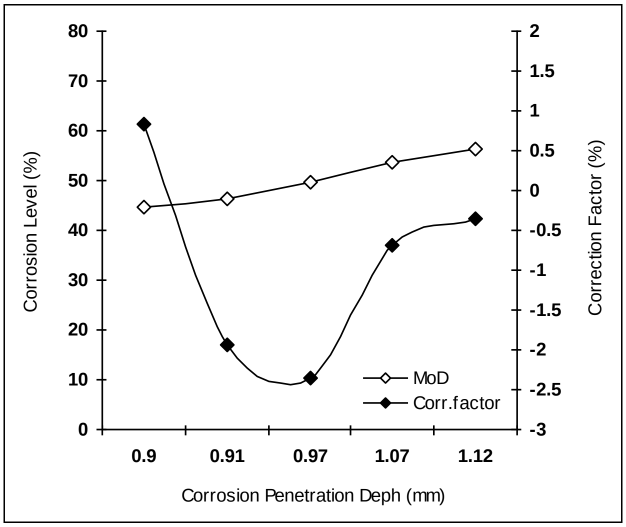


Fig 14: Variation of correction factor to model-predicted corrosion level (relative to corrosion penetration depth)

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 (7) into the model gives exactly the corresponding experimental corrosion levels

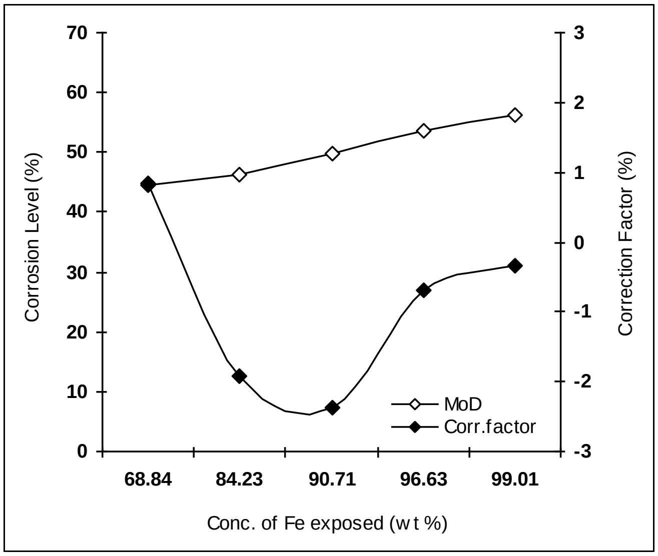


Fig 15: Variation of correction factor to model-predicted corrosion level (relative to conc. of Fe exposed)

Analysis of Table 3 as well as Figs. 13 – 15 indicates that the maximum correction factor to the model-predicted corrosion levels is also less than 3%.

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 response of corrosion level of galvanized steel submerged in insitu sea water to the influence of contact time and concentration of iron exposure was ascertained. The corrosion level of the galvanized steel increased with increase in both the contact time considered and concentration of exposed iron. This is because incessant natural agitation of the sea water does not allow formation of $(ZnOH)_2$ which is alkaline nature, due to uniformity in the sea water pH. The validity of the empirical model; $\zeta = 0.0117\ \vartheta^2 - 1.7742\ \vartheta + 0.05\text{ɤ} + 109.8125$ derived, validated and used for the response analysis of the corrosion level was rooted on the core model expression $\zeta - 109.8125 = 0.0117\ \vartheta^2 - 1.7742\ \vartheta + 0.05\text{ɤ}$ where both sides of the expression are correspondingly approximately equal. The standard errors incurred in evaluating the response of corrosion level in the steel to the influence of contact time and concentration of exposed iron as obtained from experiment, derived model and regression model were 1.3, 0.65 & 1.33 and 2.83, 2.23 & 2.8 % respectively. Maximum deviational of model-predicted corrosion level from experimental results is less than 3%. This translated into about 97% operational confidence and response level for the derived model as well as 0.97 reliability response coefficient of the corrosion level to the collective operational contributions of contact time and concentration of exposed iron.

5. References

1. Engineering Bulletin. (Evapco). White Rust on Galvanized Sheet, No. #34A, 2009,
2. Abbas HA. Corrosion and Corrosion Inhibition Study of Galvanized Steel in Salty Acidic and Basic Media. M. Sc Thesis in Chemistry, 2012, 1-96.
3. Darwin D, Browning J, O’Reilly M, Xing L. Chloride Corrosion Threshold for Galvanized Reinforcing Bars, 2007. http://www2.ku.edu/~iri/publications/ILZRO.pdf
4. Oritz ZI, Diaz-Arista P, Meas Y, Ortega-Borges R, Trejo G. Corros. Sci. 2009; 51:2703-2715.
5. Zapponi M, Perez T, Ramos C, Saragovi C. Corros. Sci. 2005; 47:923-936.
6. Azmat NS, Ralston KD, Muddle BC, Cole IS. Corros. Sci. 2011; 53:1604-1615.
7. Yadav AP, Nishikata A, Tsuru T. Corros. Sci. 2004; 46:169-181.
8. El-Sayed M, Sherif AA, Almajid B, Bairamov AK, Eissa A. Int. J.Electrochem. Sci. 2012; 7:2796-2810
9. Lin BL, Lu JT, Kong G. Corros. Sci. 2008; 4:962-967.
10. Bajat JB, Stankovic S, Jokic BM, Stevanovic SI. Surf. Coat. Technol. 2010; 204:2745-2753.
11. Kartsonakis IA, Balaskas AC, Koumoulos EP, Charitidis CA, Kordas GC. Corros. Sci. 2012; 57:30-41.
12. Zhang XG. Corrosion of zinc and zinc alloys, Corrosion: Materials, ASM Handbook, 2005, 402-406.
13. Nwoye CI, Chinwuko EC, Nwosu IE, Onyia WC, Amalu NI, Nwosu PC. Operational Dependence of Galvanized Steel Corrosion Rate on Its, Structural Weight Loss and Immersion-Point pH in Sea Water Environment, American Journal of Mining and Metallurgy, 2014; 2(4)81-87.
14. Nwoye CI. C-NIKBRAN Data Analytical Memory (Software), 2008.