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Response of Aluminum-Manganese Alloy Corrosion in Sea Water to the Operational Influence of its Pre-Installed Weight and Exposure Time

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Abstract: This paper presents the response of aluminum-manganese alloy corrosion in sea water to its pre-installed weight and exposure time. The reliability of the highlighted dependence was ascertained by evaluating the response coefficient of the alloy corrosion rate to the combined influence of pre-installed alloy weight and exposure time. The alloy grain boundary morphology was evaluated through analysis of the surface structure of corroded and uncorroded Al-Mn alloys. Results of this analysis revealed in all cases widely distributed oxide film of the alloy in whitish form. A two-factorial empirical model was derived, validated and used for the response evaluation. The validity of the derived model was rooted on the core model expression $\zeta - 0.0686 = 93.077\gamma^2 - 5.0963\gamma + 0.013\vartheta^2 - 0.002\vartheta$ where both sides of the expression are correspondingly approximately equal. Results generated using regression model showed trend of data point distribution similar to those from experiment and derived model. Evaluated results indicated that the corrosion penetration depth as obtained from experiment, derived model & regression model were 2.9912 x 10^{-3}, 2.9951 x 10^{-3} & 2.7806 x 10^{-3} mm respectively. Standard errors incurred in predicting the corrosion rate for each value of the pre-installed alloy weight and exposure time considered as obtained from experiment, derived model & regression model were 0.0118, 0.0098 & 0.0164 and 0.0062, 0.0088 & 3.0614 x 10^{-5} % respectively. Furthermore the correlation between corrosion rate and pre-installed alloy weight & exposure time as obtained from experiment, derived model and regression model were all > 0.99. Maximum deviation of model-predicted corrosion rate from the experimental results was 9%. This translated into 91% operational confidence level for the derived model as well as 0.91 response coefficient of corrosion rate to the collective operational contributions of pre-installed alloy weight and exposure time in the sea water environment.

Key words: Prediction · Corrosion · Al-Mn alloys · Sea water environment · Pre-installed weight · Exposure time

INTRODUCTION

Research [1] has shown that the high level of resistance of aluminum and its alloys to corrosion in series of service environments stems significantly on their ability to passivate. The researcher reported that a change in the character of the environment (e.g., alteration in the concentration of the active corrosive species) may cause a passivated material to revert to an active state. The study revealed that a sharp increase in corrosion rate, by as much as 100, 000 times could result from subsequent damage to a preexisting passive film. This behavior is linear as it is for normal metals at relatively low potential values, within the "active" region. Furthermore, the current density suddenly decreases to a very low value that remains independent of potential with increasing potential. This is referred to as the "passive" region. Finally, the current density again increases with potential in the "transpassive" region at even higher potential values.

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Al-Mn alloys has been reported [2] to be susceptible to corrosion attack if exposed in the atmosphere because of the presence of moisture. The corrosion of this alloy stems from the strong affinity aluminium has for oxygen which results to its oxidation and subsequent formation of oxide film. Similar research [3] revealed that with time, this film becomes passive to further oxidation and stable in aqueous media when the pH is between 4.0 and 8.5. It is important to state that the passive films can break and fall of, hence exposing the surface of the alloy to further corrosion.

Studies [1, 4, 5, 6] have shown series of methods for calculating the corrosion rate.

Callister [1] reported that corrosion rate can be expressed in terms of the electric current associated with electrochemical corrosion reactions or, more specifically, current density- that is, the current per unit surface area of corroding material.

Studies [7, 6] have shown evaluations of corrosion rate of metals in atmospheric environment. Nwoye, *et al.* [6] evaluated Al-Mn alloy corrosion rate in atmospheric environment based on direct input of initial weights of the alloy and its exposure times. The validity of the two-factorial polynomial derived model;

$$\beta = -3.4674\,\alpha^2 + 0.3655\alpha - 0.0013\,\gamma^2 + 0.007\,\gamma - 0.0031 \quad (1)$$

is rooted on the core expression $0.2884\,\beta = -\,\alpha^2 + 0.1054\alpha - 3.7489 \times 10^{-4}\,\gamma^2 + 2.0186 \times 10^{-3}\gamma - 8.9396 \times 10^{-4}$ where both sides of the expression are correspondingly approximately equal. Corrosion rate per unit initial weight of exposed alloy as predicted by derived model and obtained from experiment are 1.8421 and 1.6316 (mm/yr) kg^{-1} respectively. Similarly, between exposure time: 0.0192 - 0.0628 yr, the depth of corrosion penetration on the exposed alloy as predicted by derived model and obtained from experiment are $1.5260 \times 10^{-4}$and 1.3516×10^{-4} mm respectively. Deviational analysis indicates that the maximum deviation of the model-predicted corrosion penetration rate from the corresponding experimental value is less than 11%. Statistical analysis of model-predicted and experimentally evaluated corrosion rates as well as depth of corrosion penetration for each value of alloy initial weight and exposure time considered show standard errors of 0.0014 and 0.0015 % as well as 9.48×10^{-4} and 8.64×10^{-4} %, respectively.

Nwoye *et al*. [5] predicted the open system corrosion rate of Al-Mn alloy in sea water environment based on the alloy weight loss and exposure time. A model was derived and used as a tool for the assessment. The model was made up of a quadratic and natural logarithmic function. The validity of the model;

$$C_R = 98.76\,\alpha^2 - 11.8051\alpha + 0.0445\,\ln\gamma + 0.612 \quad (2)$$

was rooted on the core expression: $1.0126 \times 10^{-2}\,C_R = \alpha^2 - 11.9538 \times 10^{-2}\,\alpha + 4.5059 \times 10^{-4}\ln\gamma + 6.1968 \times 10^{-3}$ where both sides of the expression are correspondingly approximately equal.

Corrosion penetration depth predicted by derived model, regression model and obtained from experiment were precisely 0.0102, 0.01 and 0.0112 mm respectively, while the corrosion rate per unit weight loss of the alloy as predicted by derived model, regression model and obtained from experiment are 7.7830, 7.6774 and 8.5777 mm/yr/g respectively. The maximum deviation of the model-predicted alloy corrosion rates from the corresponding experimental values is less than 27%. Statistical analysis of model-predicted, regression-predicted and experimentally evaluated corrosion rates for each value of exposure time and alloy weight loss considered shows a standard error of 0.0657, 0.0709 & 0.0715 % and 0.0190 & 2.83×10^{-5} & 0.0068 % respectively.

Predictive analysis of the possible Al-Mn alloy exposure time in sea water environment was carried out based on the alloy corrosion rates and as-cast weight in the same environment [4]. This was done using a derived empirical model. The validity of the derived model;

$$\alpha = 26.67\,\gamma + 0.55\,\beta - 0.29 \quad (3)$$

was rooted on the core expression: $0.0375\,\alpha = \gamma + 0.0206\,\beta - 0.0109$ where both sides of the expression are correspondingly approximately equal. The depth of corrosion penetration (at increasing corrosion rate: 0.0104-0.0157 mm/yr) as predicted by derived model and obtained from experiment are 0.7208×10^{-4}& 1.0123×10^{-4} mm and 2.5460×10^{-4} & 1.8240×10^{-4} mm (at decreasing corrosion rate: 0.0157-0.0062 mm/yr) respectively. Statistical analysis of model-predicted and experimentally evaluated exposure time for each value of as-cast weight and alloy corrosion rate considered shows a standard error of 0.0017 & 0.0044 % and 0.0140 & 0.0150 % respectively. Deviational analysis indicates that the maximum deviation of the model-predicted alloy exposure time from the corresponding experimental value is less than 10%.

The aim of this work is to evaluate the response of Al-Mn corrosion (in sea water environment) to its pre-installed weight and exposure time.

MATERIALS AND METHODS

Materials used for the experiment [8] are virgin aluminium of 99% purity and pure granulated manganese. The other materials used were acetone, sodium chloride, distilled water, beakers and measuring cylinders. The equipment used were lathe machine, drilling machine, crucible furnace and analytical digital weighing machine.

Specimen Preparation and Experimentation: Computation for each of the Al-Mn alloy compositions was carefully worked out and the alloying materials charged into the surface crucible furnace. The molten alloy was cast into rods and allowed to cool in air (at room temperature). The cooled rods were machined to specific dimensions, cut into test samples and weighed. Each sample coupon was drilled with 5mm drill bit to provide hole for the suspension of the strings. The surface of each of the test coupons was thoroughly polished with emery cloth according to ASTM standards [8].

The method adopted for this phase of the research [8] is the weight loss technique. The test coupons were exposed to the sea water and withdrawn after a known period of time. The withdrawn coupons were washed with distilled water, cleaned with acetone and dried in open air before weighing to determine the final weight.

Fig. 1: As-cast Al-Mn alloy

Fig. 2: Corroded pieces of Al-Mn alloy cut and exposed to sea water environment

RESULTS AND DISCUSSION

Variation of Corrosion Rate with Alloy Pre-installed Weight and Exposure Time: Tables 1 and 2 show that the corrosion rate of Al-Mn alloy increases with increase in the alloy exposure time and depicts an irregular relationship with the alloy pre-installed weight. This is attributed to the fact that the various weights of the pre-installed alloys used are insignificantly different (between 0.0001 and 0.0011kg). The tables indicate that increased alloy exposure times significantly ensured prolonged physico-chemical interactions between the Al-Mn alloy and corrosion-induced agents' resident in the sea water. Furthermore, it is suspected that subsequent film formed after the initial was not coherent and adherent. This permitted periodic inflow of oxygen into the alloy and consequently, periodic increment in the corrosion attack.

Based on the foregoing, the Al-Mn alloy corrosion rates were mainly affected by the exposure times of the alloys in the sea water environment.

Tables 1 and 2 present similar results except the conversion of alloy pre-installed weight from gramme (g) to kilogramme (Kg).

Surface Structural Analysis of Corroded Al-Mn Alloy: The control alloy is shown in Fig. 3(a) as a slightly corroded Al-Mn alloy since it was not exposed to the sea water environment. Due to absence of manganese in the control alloy, the surface structure of this alloy reveal an ash coloured background which is slightly away from the normal colour of aluminium. Inconspicuous presence of oxide film is shown in the control alloy exposed to the sea water (Fig. 3a).

Table 1: Variation of corrosion rate ζ of Al-Mn alloy with its pre-installed weight ϑ (in g) and exposure time γ

(ζ) (mm/yr)	(ϑ) (g)	(γ) (yr)
0.0048	13.2	0.0192
0.0578	12.7	0.0514
0.0649	12.8	0.0537
0.0753	12.5	0.0559
0.0829	12.1	0.0575

Table 2: Variation of corrosion rate æ of Al-Mn alloy with its pre-installed weight ϑ (in kg) and exposure time γ

(ζ) (mm/yr)	(ϑ) (kg)	(γ) (yr)
0.0048	0.0132	0.0192
0.0578	0.0127	0.0514
0.0649	0.0128	0.0537
0.0753	0.0125	0.0559
0.0829	0.0121	0.0575

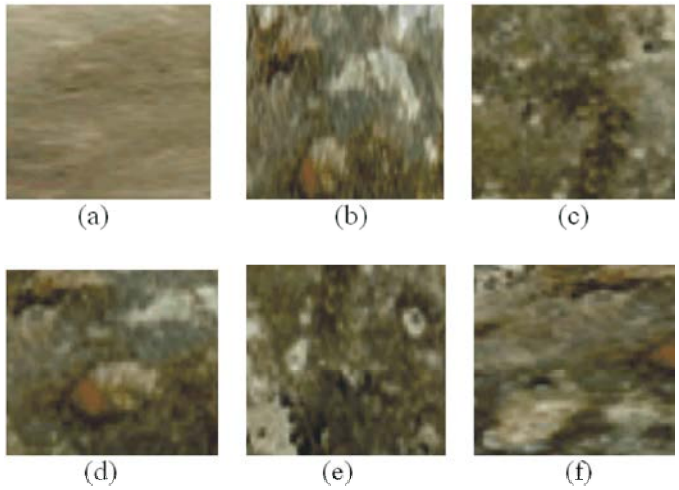

Fig. 3: Surface structure of Al-Mn alloy (a) control (b), (c) (d), (e) and (f) for exposure times: 0.0192, 0.0514, 0.0537, 0.0559 and 0.0575 yrs respectively. (x200)

Figs. 3(b- f): Clearly show various levels of corrosion attacks at different Al-Mn exposure times. The figures depict white patches strongly believed to be oxide films produced during the initial corrosion attack on the Al-Mn alloy. Furthermore, the greenish patches also observed in these figures were attributed to increased oxidation of the alloy matrix as a result of increased exposure time of the alloys in the sea water environment.

Model Formulation: Experimental data obtained from research work [8] were used for this work.

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

$$\zeta - S = N\gamma^2 - S_e\,\gamma + N_e\,\vartheta^2 - K\vartheta \qquad (4)$$

Introducing the values of K, S, N, S_e and N_e into equation (4) reduces it to;

$$\zeta - 0.0686 = 93.077\gamma^2 - 5.0963\gamma + 0.013\,\vartheta^2 - 0.002\,\vartheta \qquad (5)$$

$$\zeta = 93.077\gamma^2 - 5.0963\gamma + 0.013\,\vartheta^2 - 0.002\,\vartheta + 0.0686 \qquad (6)$$

where
K = 0.002, S = 0.0686, N = 93.077, S_e= 5.0963 and N_e= 0.013 are empirical constants (determined using C-NIKBRAN [9].

(ϑ) = Alloy pre-installed weight (kg)
(γ) =Alloy exposure time (yr)
(ζ) = Corrosion rate (mm/yr)

Table 3: Variation of ζ - 0.0686 = $93.077\gamma^2 - 5.0963\gamma + 0.013\,\vartheta^2 - 0.002\,\vartheta$

ζ - 0.0686	$93.077\gamma^2 - 5.0963\gamma + 0.013\gamma^2 - 0.002\gamma$
- 0.0638	-0.0635
- 0.0108	-0.0160
- 0.0037	-0.0074
0.0067	0.0054
0.0143	0.0147

The derived model is equation (6). Computational analysis of Table 1 gave rise to Table 3. The derived model is two-factorial in nature because it is a constituent of two input process factors: alloy pre-installed weight and exposure time. This implies that the predicted corrosion rate of the Al-Mn alloy subjected to sea water environment is dependent on just two factors: alloy pre-installed weight and exposure time of the alloy. In the previous work [8], corrosion rates were evaluated from experimental results following determination of the weight difference after alloy exposure, density of alloy, alloy specific exposure area and the constant *k*.

Boundary and Initial Conditions: Consider solid Al-Mn alloy exposed to sea water environment and interacting with some corrosion-induced agents. The sea water environment is assumed to be affected by unwanted gases and dusts. Range of exposed time considered: 0.0192-0.0575 yrs (168-503 hrs). Initial weight range considered for the experiment: 0.0121-0.0132 kg (12.1-13.2g). Purity of aluminium used: 99%. Concentration of manganese addition: 1%.

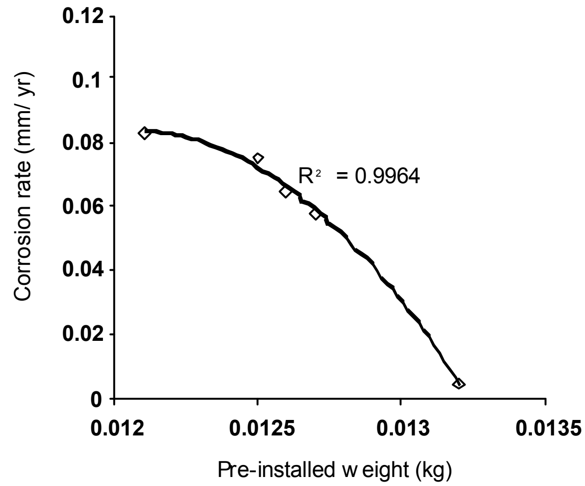

Fig. 4: Coefficient of determination between corrosion rates and alloy pre-installed weight as obtained from experiment [8]

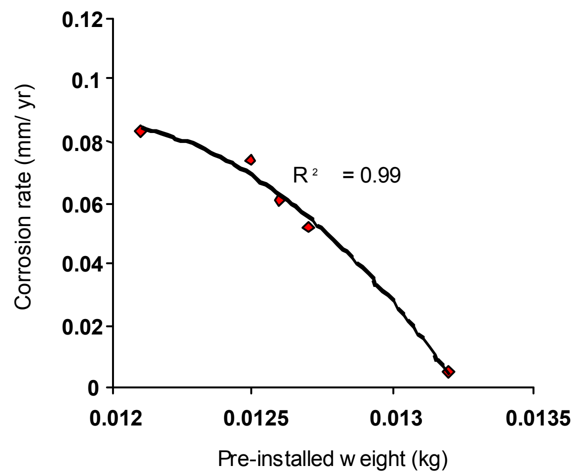

Fig. 5: Coefficient of determination between corrosion rates and alloy pre-installed weight as predicted by derived model

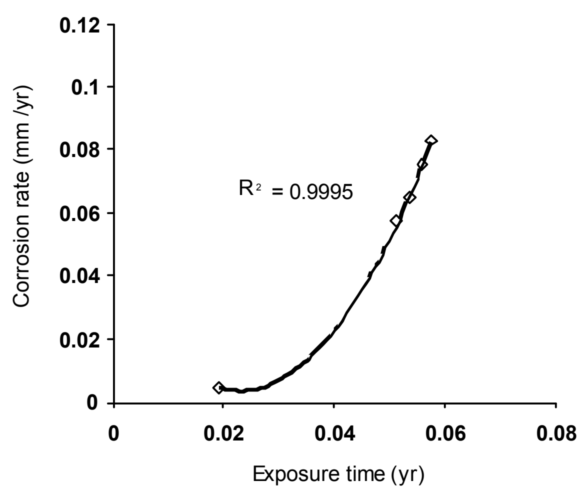

Fig. 6: Coefficient of determination between corrosion rate and exposure time as obtained from the experiment [8]

Model Validation: The validity of the model is strongly rooted in equation (5) (core model equation) where both sides of the equation are correspondingly approximately equal. Table 4 also agrees with equation (5) following the values of ζ - 0.0686 and $93.077\gamma^2 - 5.0963\gamma + 0.013\vartheta^2 - 0.002\vartheta$ evaluated from the experimental results in Table 1.

Furthermore, the derived model was validated by comparing the corrosion rates predicted by the model and that obtained from the experiment [8]. This was done using various evaluative techniques such as computational, statistical, graphical and deviational analysis.

Computational Analysis: Comparative computational analysis of the experiment based and model-predicted response of Al-Mn alloy corrosion to exposure time were carried out to ascertain the degree of validity of the derived model. This was done by comparing results of the corrosion penetration depth obtained from both cases.

The corrosion rate penetration depth C_D (mm) was calculated from the equation;

$$C_D = \zeta\Delta / \Delta\gamma \tag{7}$$

Equation (7) is detailed as

$$C_D = (\zeta_2 - \zeta_1) / (\gamma_2 - \gamma_1) \tag{8}$$

where

$\Delta\zeta$ = Change in the corrosion rates ($\zeta_2 - \zeta_1$) at two alloy exposure times γ_2, γ_1.

Considering the points (0.0192, 0.0048) & (0.0575, 0.0829), (0.0192, 0.0051) & (0.0575, 0.0833) and (0.0192, 0.0034) & (0.0575, 0.0760) as shown in Figs. 3 and 4, then designating them as (ζ_1, γ_1) & (ζ_2, γ_2) for experimental, derived model and regression model predicted results respectively and also substituting them into equation (8), gives the slopes: 2.9912×10^{-3}, 2.9951×10^{-3} and 2.7806×10^{-3} mm as their respective corrosion penetration depth.

A comparison of these two values of the corrosion penetration depths also shows proximate agreement and a high degree of validity of the derived model.

Statistical Analysis:

Standard Error (STEYX): The standard error (STEYX) in predicting corrosion rate for each value of the alloy pre-installed weight and exposure times considered as obtained from experiment and derived model are 0.0118 and 0.0098 as well as 0.0062 and 0.0088% respectively. The standard error was evaluated using Microsoft Excel (2003).

Correlations: Also the correlations between corrosion rate and alloy pre-installed weight & exposure time as obtained from derived model and experiment [8] were determined by considering Figs. 4-8 and evaluating the coefficient of determination R^2 using the equation;

$$R = \sqrt{R^2} \tag{9}$$

Results from Tables 4 and 5 suggest that the model predicts accurate and reliable corrosion rates which are in proximate agreement with values from actual experiment.

Graphical Analysis

Comparative graphical analysis of Figs. 8 and 9 shows very close alignment of the curves from model-predicted corrosion rates and that of the experiment (ExD).

The degree of alignment of these curves is indicative of the proximate agreement between both experimental and model-predicted corrosion rates.

Comparison of Derived Model with Standard Model: The validity of the derived model was further verified through application of the Least Square Method (LSM) in predicting the trend of the experimental results. Comparative analysis of Figs. 10 and 11 shows very close alignment of curves of corrosion rate, 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 rate.

Also, the calculated correlations (from Figs. 10 and 11) between corrosion rate and alloy pre-installed weight & exposure time for results obtained from regression model gave 0.9993 & 1.0000 respectively. These values are in proximate agreement with both experimental and derived model-predicted results. The standard errors incurred in predicting corrosion rate for each value of the alloy pre-installed weight & exposure time considered as obtained from regression model were 0.0164 and 3.0614×10^{-5}% respectively.

Deviational Analysis: Comparative analysis of corrosion rates from the experiment [8] and derived model revealed low deviation on the part of the model-predicted results relative to the experiment. This is attributed to the

Table 4: Comparison of the correlations evaluated from derived model predicted and experimental results based on alloy pre-installed weight

	Based on pre-installed weight	
Analysis	ExD	D-Model
CORREL	0.9982	0.9950

Table 5: Comparison of the correlations evaluated from derived model predicted and experimental results based on exposure time

	Based on exposure time	
Analysis	ExD	D-Model
CORREL	0.9997	0.9996

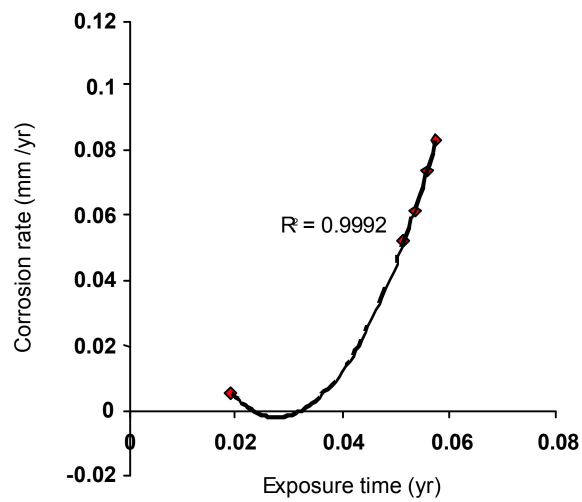

Fig. 7: Coefficient of determination between corrosion rate and exposure time as predicted by model

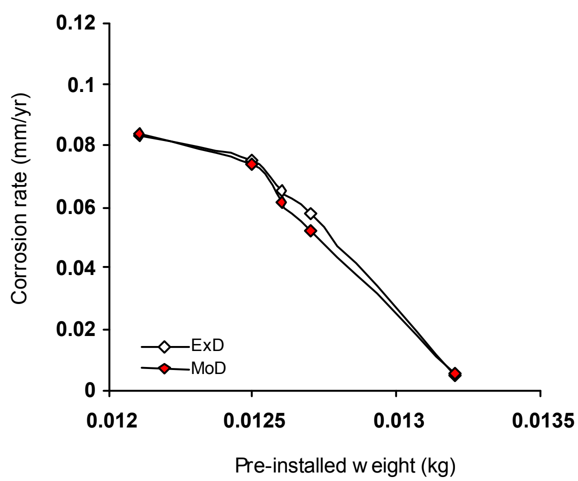

Fig. 8: Comparison of the corrosion rates (relative to alloy pre-installed weight) as obtained from experiment [8] and derived model

fact that the surface properties of the alloy and the physiochemical interactions between the alloy and corrosion inducing agents in the sea water environment which played vital roles during the process [8] 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.

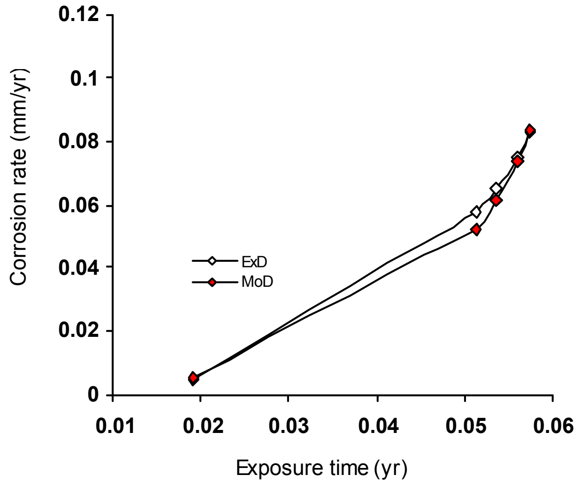

Fig. 9: Comparison of the corrosion rates (relative to alloy exposure time) as obtained from experiment [8] and derived model

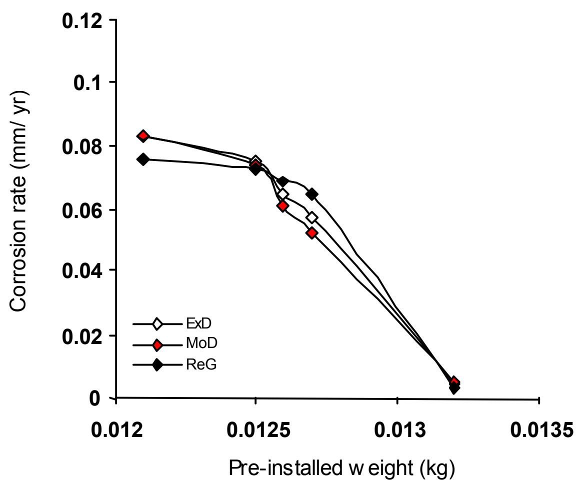

Fig. 10: Comparison of the corrosion rates (relative to alloy pre-installed weight) as obtained from experiment derived model and regression model predicted results

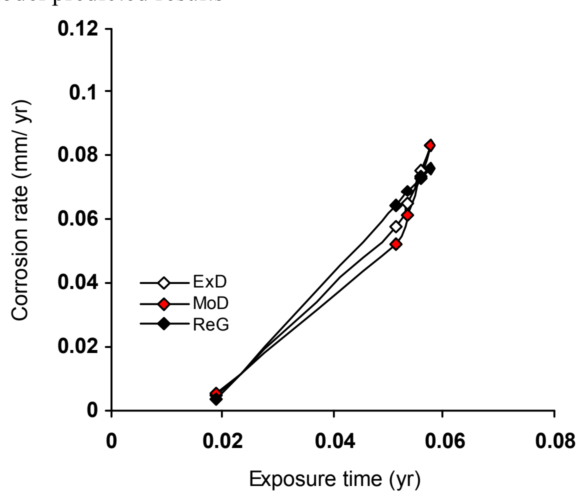

Fig. 11: Comparison of the corrosion rates (relative to exposure time) as obtained from experiment derived model and regression model predicted results

Table 6: Variation of deviation (of model-predicted corrosion rate) with pre-installed weight and exposure time

(ζ)	(γ)	Deviation (%)
0.0048	0.0192	+ 6.25
0.0578	0.0514	- 9.00
0.0649	0.0537	- 5.70
0.0753	0.0559	- 1.73
0.0829	0.0575	+ 0.48

Deviation (Dv) of model-predicted corrosion rate from that of the experiment [8] is given by;

$$Dv = \left(\frac{\zeta_{MoD} - \zeta_{ExD}}{\zeta_{ExD}}\right) x100 \qquad (10)$$

where,

ζ_{ExD} and ζ_{MoD} are corrosion rates obtained from experiment and derived model respectively.

Deviational analysis of Table 6 indicates that the maximum deviation of model-predicted corrosion rate from the experimental results is 9%. This translated into 91% operational confidence for the derived model as well as 0.91 reliability response coefficients of corrosion rate to alloy pre-installed weight and exposure time.

Table 6 show that the maximum deviation of the exact model-predicted corrosion rate from the corresponding experimental values is 9%. The table show that least and highest magnitudes of deviation of the model-predicted corrosion rates (from the corresponding experimental values) are + 0.48 and - 9% which corresponds to corrosion rates: 0.0833 and 0.0526 mm/yr, alloy pre-installed weights; 0.0121 and 0.0127 kg and alloy exposure times between; 0.0575 and 0.0514 yr respectively;

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

$$Cf = \left(\frac{\zeta_{MoD} - \zeta_{ExD}}{\zeta_{ExD}}\right) x100 \qquad (11)$$

Critical analysis of Figs. 12, 13 and Table 6 indicates that the evaluated correction factors are negative of the deviation as shown in equations (10) and (11).

Introduction of the corresponding values of Cf from equation (11) into the model gives exactly the corresponding experimental corrosion rate.

It is believed that the correction factor takes care of the effects of the surface properties of the alloy and the physiochemical interactions between the alloy and corrosion inducing agents in the sea water environment which (affected experimental results) were not considered during the model formulation. Figs. 12 and 13 indicate that

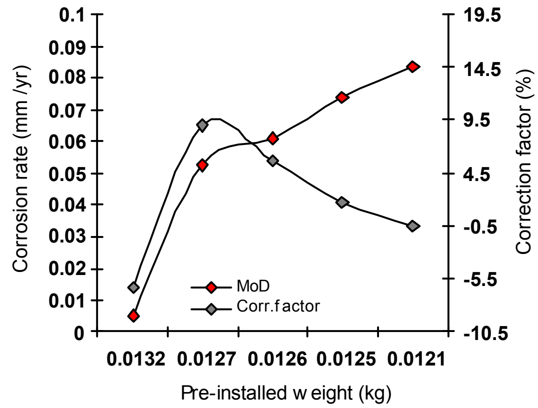

Fig. 12: Variation of model-predicted corrosion rate (relative to alloy pre-installed weight) with its associated correction factor

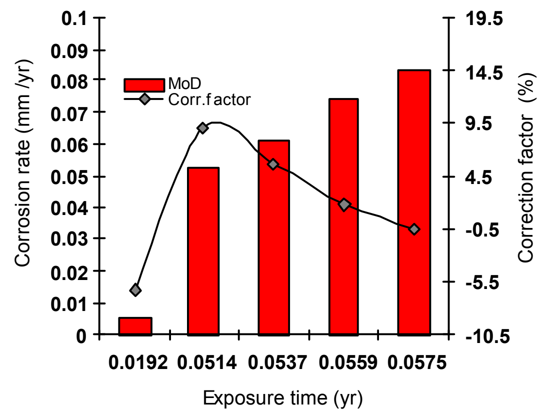

Fig. 13: Variation of model-predicted corrosion rate (relative to exposure time) with its associated correction factor

the least and highest magnitudes of correction factor to the model-predicted corrosion rate are – 0.48 and + 9% which corresponds to corrosion rates: corrosion rates: 0.0833 and 0.0526 mm/yr, alloy pre-installed weights; 0.0121 and 0.0127 kg and alloy exposure times between; 0.0575 and 0.0514 yr 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).

CONCLUSION

The response of Al-Mn alloy corrosion in sea water to its pre-installed weight and exposure time has been evaluated. The reliability of the highlighted dependence was ascertained by evaluating the response coefficient of the alloy corrosion rate to the combined influence of pre-installed alloy weight and exposure time. Surface structure of the corroded alloy depicted in all cases widely distributed oxide film of the alloy in whitish form. A two-factorial empirical model was derived, validated and used for the response evaluation. The validity of the derived model was rooted on the core model expression $\zeta - 0.0686 = 93.077\gamma^2 - 5.0963\gamma + 0.013\vartheta^2 - 0.002\vartheta$ where both sides of the expression are correspondingly approximately equal. The corrosion penetration depth as obtained from experiment, derived model & regression model were 2.9912×10^{-3}, 2.9951×10^{-3} & 2.7806×10^{-3} mm respectively. Standard errors incurred in predicting the corrosion rate for each value of the pre-installed alloy weight and exposure time considered as obtained from experiment, derived model & regression model were 0.0118, 0.0098 & 0.0164 and 0.0062, 0.0088 & 3.0614×10^{-5} % respectively. Furthermore the correlation between corrosion rate and pre-installed alloy weight and exposure time as obtained from experiment, derived model and regression model were all > 0.99. Maximum deviation of model-predicted corrosion rate from the experimental results is 9%. This translated into 91% operational confidence level for the derived model as well as 0.91 response coefficient of corrosion rate to the collective operational contributions of pre-installed alloy weight and exposure time in the sea water environment.

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