

PERFORMANCE EVALUATION OF Al-Mn ALLOY IN SEA WATER ENVIRONMENT AND PREDICTION OF EXPOSURE TIME BASED ON ITS CORROSION RATE AND INITIAL WEIGHT

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ABSTRACT

The performance of aluminium-manganese alloy in sea water environment has been evaluated by submerging the alloy produced at varying Mn input range: 1- 4 wt % into a 99% purity aluminium powder. It was observed that increased concentration of Mn in Al-Mn alloy (1-3%) resulted in increase in corrosion rate of the alloy (in presence of sea water) due to the strong affinity between aluminium and oxygen which enabled oxygen to significantly oxidize aluminium, forming oxide films. This implied that oxide film formation occurred simultaneously with corrosion attack. A model was derived to predict the alloy exposure time based on its initial weight and corrosion rate in the same environment. The validity of the derived model;

$T_{xp} = - 5638.5 \gamma^2 - 64.35 \beta^2 + 125.29 \gamma + 2.9279 \beta - 0.653$ was rooted on the core expression $T_{xp} + 0.653 = - e_1 \gamma^2 - e_2 \beta^2 + e_3 \gamma + e_4$ where both sides of the expression are correspondingly approximately equal. Comparative statistical analysis of results from a standard model (regression model) derived model and experiment shows that the standard error in predicting the alloy exposure time for each value of the initial weight and alloy corrosion rate are 3.6752×10^{-5} & 0.017%, 0.0096 & 0.0217% and 0.0084 & 0.0203% respectively. Similarly, the F-test results are 2.47×10^{-5} & 0.3471, 2.29×10^{-5} & 0.3298 and 2.01×10^{-5} & 0.3024 respectively. Furthermore the correlation between exposure time and corrosion rate & initial weight as obtained from experiment, derived model and regression model were all > 0.97. Computational analysis of results generated from regression model, derived model and experiment shows that the depths of corrosion penetrations are 9.5288×10^{-4} , 9.8728×10^{-4} and 9.89×10^{-4} mm respectively. Deviation analysis indicates that the maximum deviation of the model-predicted alloy exposure time from the corresponding experimental value is less than 14.58%. This translated into over 85% operational confidence for the derived model as well as over 0.85 reliability response coefficient for the dependence of the alloy exposure time on corrosion rate and initial weight of alloy.

Keywords: Performance Evaluation, Al-Mn Alloys, Sea Water, Exposure Time, Initial Alloy Weight, Corrosion Rate.

1.0 INTRODUCTION

Corrosion of storage tanks, vessels, pipelines and other structures involving transfer of oil and other fluids has posed a great problem in metallurgical and oil industries due to damages encountered as a result of rupture and abrupt failure of these structures. This has raised the need to assemble high corrosion resistant metals and alloys for a high efficiency fluid transfer from one location to another.

Report [1] has shown the need to know the specific corrosion rates of different metals and alloys in different application environments in order to know the materials that can withstand outdoor structural applications.

Studies [2] have shown that the stability of metals or alloys in an aggressive environment basically depends on the

protective properties of organic or inorganic films as well as on the layer of corrosion products. The researcher concluded that the ability of films to act as controlling barriers against different kinds of corrosion attack is dependent on film properties such as chemical composition, adhesion, conductivity, solubility, morphology and hygroscopicity.

Researchers [1,3] reported that the highlighted characteristic of films in turn depends on environmental variables such as atmospheric conditions, type and amount of pollutants as well as wet-dry cycle, the chemical composition and metallurgical history of the metals or alloys and physicochemical properties of coating.

Tragic carelessness in plumbing, equipment manufacture and installation, with possibility of explosion, fire and spread

of toxic materials in living environment has been seen to cause malfunctioning of engineering structures and equipment due to corrosion [4]. This invariably goes with some expenses such as costs of replacing corroded equipment, disturbance in processes due to equipment corrosion, shut down of plants due to replacement of corroded equipment, impurity in processed products due to corrosion as well as waste of the products of those vessels which are attacked by corrosion.

Commercial Al-Mn alloys contain up to 1.25% manganese although the maximum solid solubility of this element in aluminium is as high as 1.82%. This limitation was caused by presence of iron as impurity which reduces the solubility. There is a danger that local ductility is disastrously affected by large primary particles of $MnAl_6$.

Report [5] has shown that $MnAl_6$ formed from Al and Mn has almost the same electrode potential as aluminium and this compound is capable of dissolving iron which reduces the detrimental effect of Mn. Al-Mn alloys have been known to belong to the 3xxx series of alloys which are used for the manufacture of *roofing sheets* [5]. The presence of moisture and oxygen in the atmosphere renders these sheets susceptible to corrosion. The corrosion of the alloy results from the strong affinity aluminium has for oxygen which leads to its oxidation and subsequent formation of oxide film. It was observed [6] 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.

Corrosion management has been found [4] to offer preventive strategies in two technical and non-technical domains. Technical domains as preventive strategies include: (1) improving corrosion technologies via research and development. Corrosion can be controlled in most industries by using scientific methods and new technological achievements. (2) upgrading planning methods and using advanced planning to better corrosion

management and so prevent avoidable corrosion costs. Furthermore, planning methods must change and the best corrosion technologies must be available for planners.

Non-technical domains as preventive strategies include: (1) Instruction to employees about corrosion problems and their identification as well as introduction of techniques of corrosion control

(2) Changing and amending wrong belief about not being able to do anything about corrosion and making new decisions in preventing this phenomenon. (3) Enhancing the employees' awareness about the high costs of corrosion and about saving costs that result in correct application of existing technologies and corrosion costs. A lot of corrosion problems are due to lack of awareness about corrosion management and accountability of people in exchanging operations, inspection and maintenance of management system. (4) changing guidelines, protocols, standards and management methods to reduce corrosion costs by correct corrosion management resulting in effective control of corrosion and safe operation and increase in shelf life of equipment.

The aim of this work is to evaluate the performance of Al-Mn alloy in sea water environment and also predict the alloy exposure time based on its initial weight and corrosion rate in environment. The model to be derived is expected to evaluate and predict directly the exact time (exposure time) for which the Al-Mn alloy should be exposed in the sea water environment putting into consideration its initial weight and corrosion rate in such environment.

The essence of this work is to determine the exact exposure time for a weighed Al-Mn alloy whose corrosion rate in the sea water environment is already known. This rules out exposure of the alloy to the corrosive environment longer than necessary, a situation that could result to very disastrous, undue corrosion penetration on the alloy and invariably, failure. It is expected that the success of this work would eventually reduce abrupt failure of Al-Mn alloys in sea water environment due to over exposure.

2.0 MATERIALS AND METHODS

Materials used for the experiment 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.

2.1 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.

The method adopted for this phase of the research is the weight loss technique. The test coupons were exposed to the sea water atmosphere 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. The corrosion rate was calculated using the formula;

$$\text{CPR} = k\Delta w / \rho A t \quad (1)$$

Where Δw (mg) is weight difference after exposure time t (hr), ρ (g/cm³), A (cm²) and CPR (mm/yr) are density, corrosion rate and specific exposure area of specimen respectively. For this work, k is a constant equal to 87.6.

3.0 RESULTS AND DISCUSSION

3.1 Performance of Al-Mn Alloy in Sea Water

Table 1 shows that increased concentration of Mn in Al-Mn alloy (1-3%) resulted to increase in corrosion rate of the alloy (in line with previous work [7]) due to the strong affinity between aluminium and oxygen which enabled oxygen (in presence of sea water) to significantly oxidize

aluminium, forming oxide films. This implies that while oxide film was being formed corrosion was taking place.

Table 1: Variation of Mn addition to Al and Al-Mn alloy initial weights with corrosion rates

Mn (%)	(γ) (g)	(β)(mm/yr)
1	11.7506	0.0099
2	12.5408	0.0115
3	12.0890	0.0829
4	12.4775	0.0159

Table 1 also indicates that beyond 3% Mn addition, the corrosion rate dropped. This is attributed to formation of passive films at 4% Mn addition which hindered further corrosion attack. And so the greatest corrosion attack was observed at 3% Mn addition. Furthermore, the alloy corrosion rate was observed to be unaffected by its initial weight.

3.2 Model Formulation

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

$$T_{xp} + e_5 = -e_1 \gamma^2 - e_2 \beta^2 + e_3 \gamma + e_4 \beta \quad (2)$$

$$T_{xp} = -e_1 \gamma^2 - e_2 \beta^2 + e_3 \gamma + e_4 \beta - e_5 \quad (3)$$

Introducing the values of e_1 , e_2 , e_3 , e_4 and e_5 into equation (3)

$$T_{xp} = -5638.5 \gamma^2 - 64.35 \beta^2 + 125.29 \gamma + 2.9279 \beta - 0.653 \quad (4)$$

Where

(β) = Corrosion rate (mm/yr)

(T_{xp}) = Exposure time (yr)

(γ) = Initial weight of alloy (kg)

e_1 , e_2 , e_3 , e_4 , and e_5 = Empirical constants (determined using C-NIKBRAN [8])

$e_1 = 5.6385 \times 10^3$, $e_2 = 0.6435 \times 10^2$, $e_3 = 1.2529 \times 10^2$, $e_4 = 2.9279$ and $e_5 = 0.653$

3.3 Boundary and Initial Conditions

Consider solid Al-Mn alloy exposed to sea water environment and interacting with some corrosion-induced agents. The sea water is assumed to be affected by unwanted dissolved gases. Range of exposed time considered: 0.0192 - 0.0767 yrs (168-672 hrs). Initial weight range considered: 0.0109-0.0134 kg (10.8676-13.3548g). Purity of aluminium used: 99%. Concentration of manganese addition: 2 wt

%. The boundary conditions are: aerobic environment to enhance Al-Mn alloy oxidation (since the sea water contains oxygen). At the bottom of the exposed alloy, a zero gradient for the gas scalar are assumed. The exposed alloy is stationary. The sides of the solid are taken to be symmetries.

The derived model is equation (4). The model is two-factorial in nature because the predicted exposure time for the Al-Mn alloy in sea water environment is dependent on just two factors: alloy corrosion rate and its initial weight.

Table 2: Variation of corrosion rate of Al-Mn alloy with its initial weight and exposure time

(β) (mm/yr)	(T _{xp}) (yr)	(γ) (kg)
0.0440	0.0192	0.0134
0.0412	0.0274	0.0132
0.0376	0.0384	0.0129
0.0115	0.0575	0.0125
0.0268	0.0767	0.0109

3.4 Model Validation

The validity of the model is strongly rooted on equation (2) (core model equation) where both sides of the equation are correspondingly approximately equal. Table 3 also agrees with equation (2) following the values of T_{xp} + e₅ with - e₁ γ² - e₂ β² + e₃ γ + e₄ β evaluated from the experimental results in Table 2. Furthermore, the derived model was validated by comparing the exposure time predicted by the model and that obtained from the experiment. This was done using various analytical techniques.

Table 3: Variation of T_{xp} + e₅ with - e₁ γ² - e₂ β² + e₃ γ + e₄ β

T _{xp} + e ₅	- e ₁ γ ² - e ₂ β ² + e ₃ γ + e ₄ β
0.6722	0.6707
0.6804	0.6827
0.6914	0.6970
0.7105	0.7103
0.7297	0.7281

3.4.1 Computational Analysis

Computational analysis of the experimental and model-predicted exposure time was carried out to ascertain the degree of validity of the derived model. This was done

by comparing the depth of corrosion penetration obtained by calculations involving experimental results, and predicted directly by the model.

The depth of corrosion penetration for Al-Mn alloy during the period of exposure in the sea water environment C_D (mm) was calculated from the equation;

$$C_D = \Delta\beta \times \Delta T_{xp} \tag{5}$$

$\Delta\beta$ = Change in the corrosion rates β_2, β_1 within a range of exposure time: $T_{xp1} - T_{xp2}$.
 ΔT_{xp} = Change in alloy exposure times T_{xp1}, T_{xp2} ,

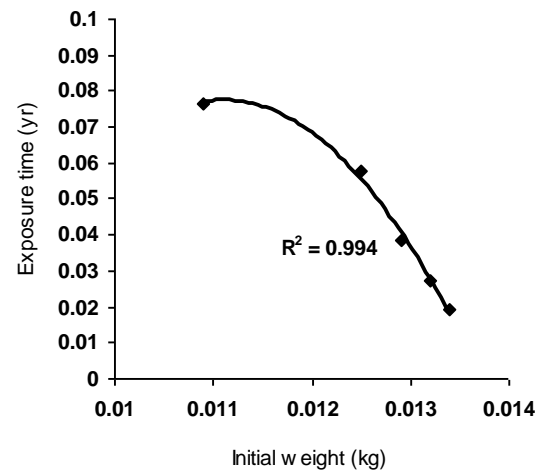


Fig.1: coefficient of determination between alloy exposure time and its initial weight as obtained from experiment.

Considering experimental results of points (0.044, 0.0192) and (0.0268, 0.0767) for (β₁,T_{xp1}) and (β₂,T_{xp2}) respectively (as in Fig. 3) and substituting them into equation (5),

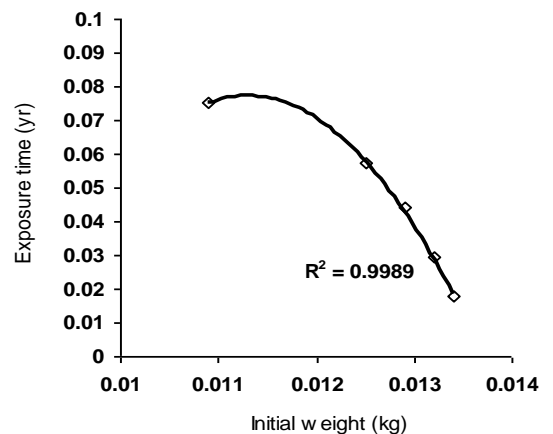


Fig. 2: Coefficient of determination between alloy exposure time and its initial weight as predicted by derived model.

gives -9.89×10^{-4} mm as the depth of corrosion penetration on the alloy during the actual corrosion process. Also similar plot (as in Fig. 5) using model-predicted results of points (0.044, 0.0177) and (0.0268, 0.0751) for (β_1, T_{xp1}) and (β_2, T_{xp2}) respectively, and substituting them into equation (5) gives the depth of corrosion penetration on the alloy as -9.8728×10^{-4} mm. This is the model-predicted depth of corrosion penetration on the alloy.

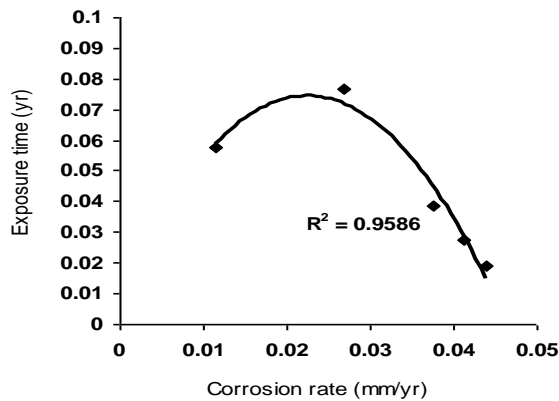


Fig. 3: Coefficient of determination between alloy exposure time and its corrosion rate as obtained from the experiment. The negative signs preceding the magnitudes of the depth of corrosion penetration do not indicate that the depth of the penetration is negative, but that the corrosion penetration occurred when the alloy corrosion rate was decreasing and so are discarded.

Based on the foregoing, the depths of corrosion penetration during the period corrosion rate was decreasing as obtained from experiment and derived model are 9.89×10^{-4} mm and -9.8728×10^{-4} mm.

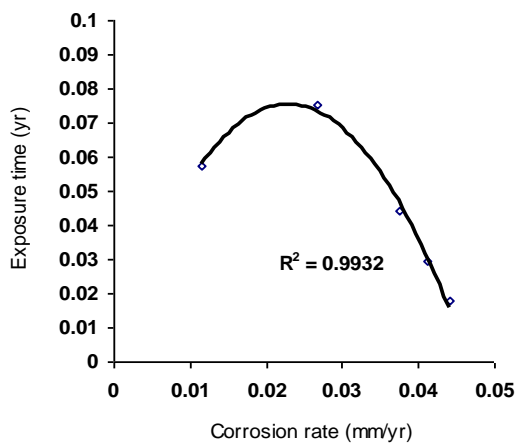


Fig. 4: Coefficient of determination between alloy exposure time and its corrosion rate as predicted by derived model

3.4.2 Statistical Analysis

Standard Error (STEYX)

Statistical analysis of model-predicted and experimentally evaluated exposure time for each value of alloy initial weight and corrosion rate considered shows a standard error (STEYX) of 0.0096 & 0.0217 % and 0.0084 & 0.0203 % respectively. The standard error was evaluated using a Microsoft Excel 2003 Version.

F-Test

The F-test evaluated from derived model and experiment relative to the alloy initial weight and corrosion rate were 2.29×10^{-5} & 2.01×10^{-5} and 0.3298 & 0.3024 respectively.

Correlation

The correlations between exposure time and initial weight as well as exposure time and corrosion rate as obtained from derived model and experimental results were calculated. This was done by considering the coefficients of determination R^2 from Figs. 1-4, using the equation;

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

Table 4: Comparison of the correlations between exposure time and alloy initial weight as evaluated from experiment and derived model

Analysis	Based on alloy initial weight	
	ExD	D-MoD
CORREL	0.9970	0.9994

The evaluated correlations are shown in Tables 4 and 5. The model was validated by comparing its results of evaluated correlations between exposure time and initial weight as well as exposure time and corrosion rate with that evaluated using experimental results. These tables show that the correlation results from experiment (ExD) and derived model (D-MoD) are in proximate agreement.

Table 5: Comparison of the correlations between exposure time and alloy corrosion rate as evaluated from experiment and derived model

Analysis	Based on alloy corrosion rate	
	ExD	D-MoD
CORREL	0.9791	0.9966

3.4.3 Graphical Analysis

Comparative graphical analysis of Figs. 5 and 6 shows very close alignment of the curves from derived model and experiment. It is strongly believed that the degree of alignment of these curves is indicative of the proximate agreement between ExD and D-MoD predicted results.

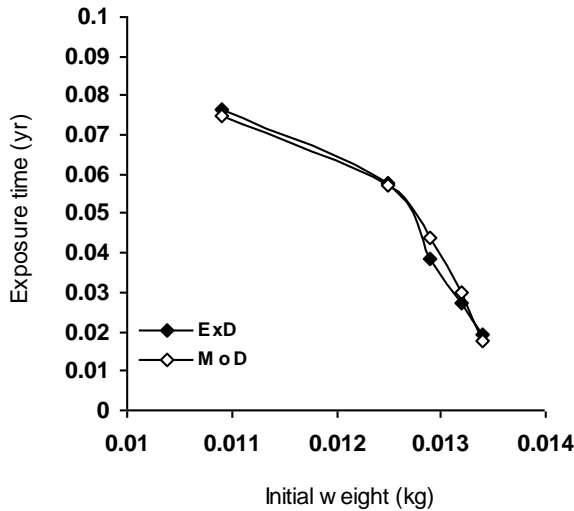


Fig. 5: Comparison of the alloy exposure times (relative to its initial weight) as obtained from experiment and derived model.

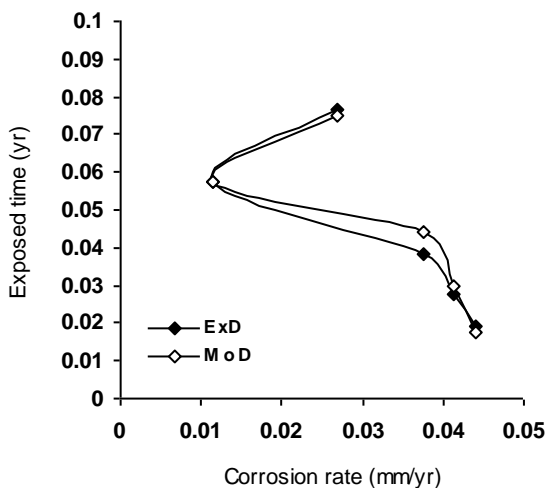


Fig. 6: Comparison of the alloy exposure times (relative to its corrosion rate) as obtained from experiment and derived model.

Comparison of Derived Model with Standard Model

Results predicted by the regression model (Least Square Method (ReG)) were plotted; exposure time against alloy initial weight and corrosion rate respectively along with results from the experiment and derived model to analyze its spread and trend relative to results from experiment and derived model.

The validity of the derived model was further verified through comparative analysis of curves from the experimental, derived and regression model predicted results. The comparative analysis of Figs. 7-10 (which includes a 3-D plot of process parameter interaction) shows very close alignment of curves and significantly similar trend of data point's distribution for experimental (ExD), derived model-predicted (MoD) and regression model predicted (ReG) results of exposure time.

Furthermore, values of F-test, standard error and corrosion penetration also generated from regression model predicted results for alloy initial weight and corrosion rate are ; 2.47×10^{-5} & 0.3471 , 3.6752×10^{-5} & 0.017% and 9.2888×10^{-4} mm respectively. These values are in proximate agreement with the corresponding values from experimental and derived model-predicted results.

3.4.4 Deviation Analysis

Comparative analysis of exposure time from the experiment and derived model revealed deviations on the part of the model-predicted values relative to values obtained from the experiment. This is attributed to the fact that the surface properties of the alloy and the physiochemical interaction between the alloy and corrosion induced agents (in the sea water) 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.

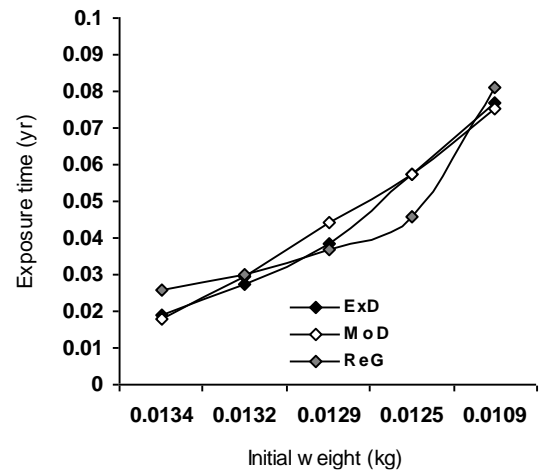


Fig. 7: Comparison of the alloy exposure times (relative to its initial weight) as obtained from experiment, derived and regression model.

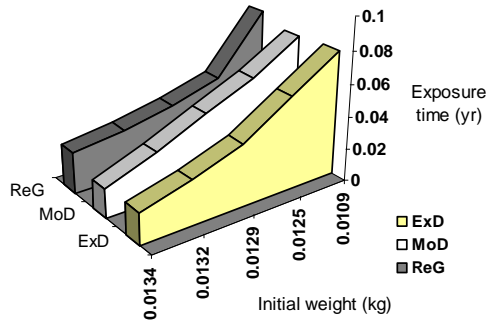


Fig. 8: 3-D comparison of the alloy exposure times (relative to its initial weight) as obtained from experiment, derived and regression model.

Deviation (Dn) of model-predicted corrosion rate from that of the experiment is given by

$$Dn = \left(\frac{Pe - Ee}{Ee} \right) \times 100 \quad (7)$$

Correction factor (Cr) is the negative of the deviation i.e

$$Cr = -Dn \quad (8)$$

Therefore

$$Cr = - \left(\frac{Pe - Ee}{Ee} \right) \times 100 \quad (9)$$

Where

Pe = Model-predicted exposure time (yr)

Ee = Exposure time obtained from experiment (yr)

Cr = Correction factor (%)

Dn = Deviation (%)

Introduction of the corresponding values of Cr from equation (9) into the model gives exactly the corresponding experimental exposure time.

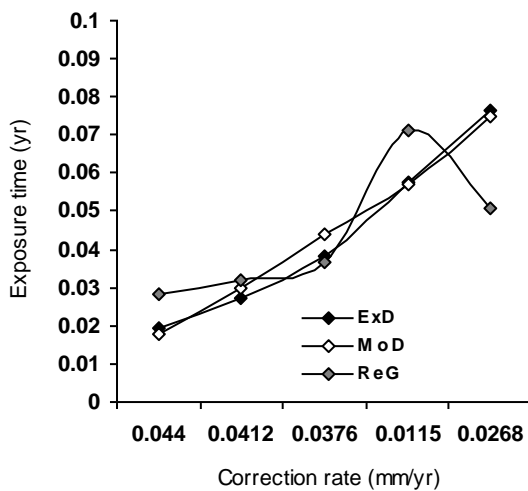


Fig. 9: Comparison of the alloy exposure times (relative to its corrosion rate) as obtained from experiment, derived and regression model.

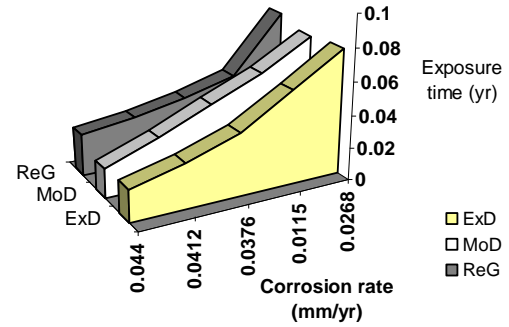


Fig. 10: 3-D comparison of the alloy exposure times (relative to its corrosion rate) as obtained from experiment, derived and regression model.

Equation (6), Figs. 11 and 12 show that the correlations between exposure time and alloy initial weight as well as exposure time and corrosion rate for results obtained from regression model gives 1.000 as well as 1.000 respectively.

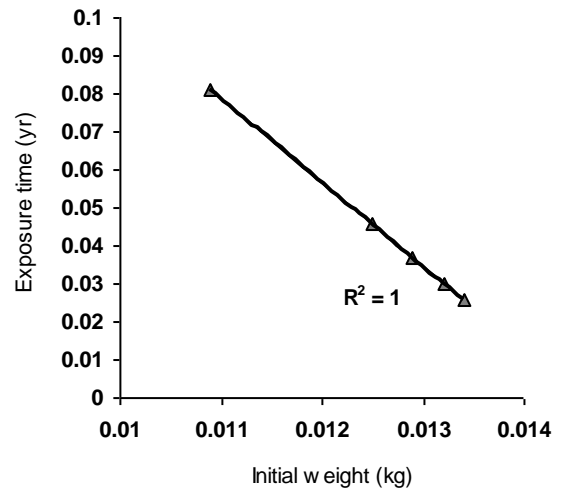


Fig. 11: Coefficient of determination between alloy exposure time and its initial weight as predicted by regression model.

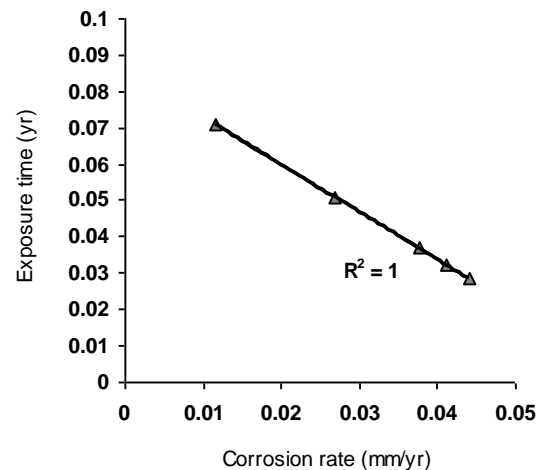


Fig. 12: Coefficient of determination between alloy exposure time and its corrosion rate as predicted by regression model

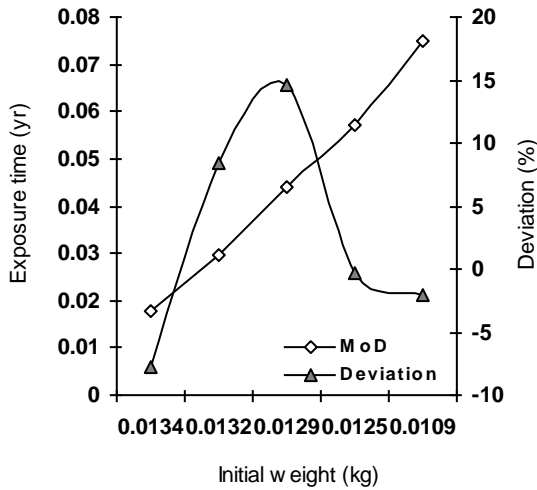


Fig. 13: Variation of model-predicted alloy exposure time (relative to its initial weight) with its associated deviation from experimental values

Figures 13 and 14 show that the maximum deviation of the model-predicted exposure time from the corresponding experimental values is less than 15% and quite within the acceptable deviation limit of experimental results.

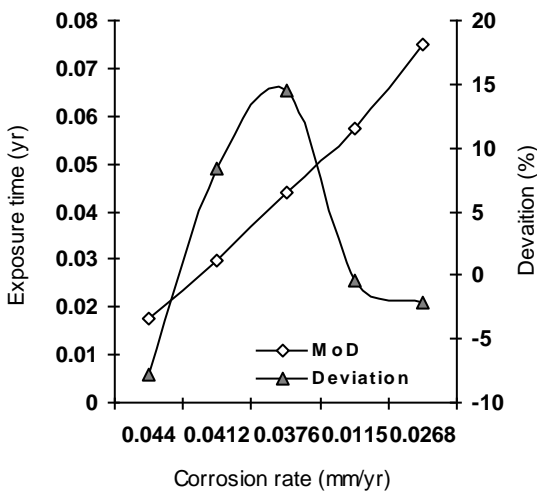


Fig. 14: Variation of model-predicted alloy exposure time (relative to its corrosion rate) with its associated deviation from experimental values

These figures show that least and highest magnitudes of deviation of the model-predicted exposure time (from the corresponding experimental values) are -0.35 and +14.58% which corresponds to exposure times: 0.0573 and 0.044 yr, alloy initial weight; 0.0125 and 0.0129 kg and alloy corrosion rates between; 0.0115 and 0.0376 mm/yr respectively.

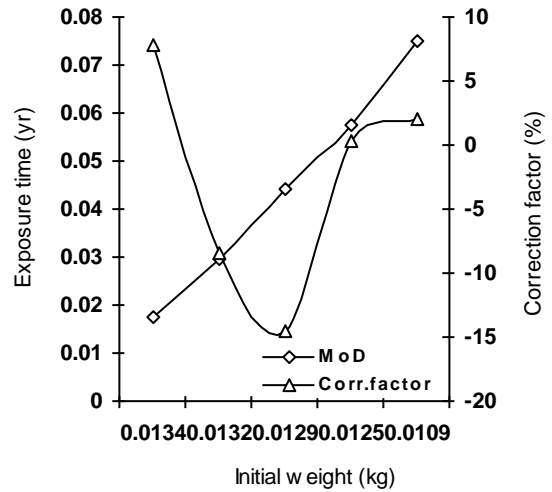


Fig. 15: Variation of model-predicted alloy exposure time (relative to its initial weight) with its associated correction factor

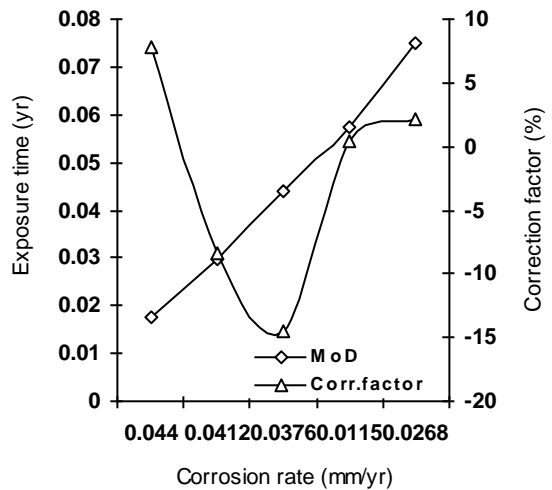


Fig. 16: Variation of model-predicted alloy exposure time (relative to its corrosion rate) with its associated correction factor

Comparative analysis of Figs. 13-16 indicates that the orientation of the curve in Figs. 15 and 16 is opposite that of the deviation of model-predicted exposure time (Figs. 13 and 14). This is because correction factor is the negative of the deviation as shown in equations (8) and (9).

It is believed that the correction factor takes care of the effects of the surface properties of the alloy which were not considered during the model formulation. Figures 15 and 16 indicate that the least and highest magnitudes of correction factor to the model-predicted exposure time are 0.35 and -14.58 % which corresponds to exposure times: 0.0573 and 0.044 yr, alloy initial weight; 0.0125 and 0.0129 kg and alloy

corrosion rates between; 0.0115 and 0.0376 mm/yr respectively.

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 deficit (negative sign) or surplus (positive sign).

4.0 CONCLUSION

Increased concentration of Mn in Al-Mn alloy (1-3%) resulted to increase in corrosion rate of the alloy (in presence of sea water) due to the strong affinity between aluminium and oxygen which enabled oxygen to significantly oxidize aluminium, forming oxide films. This basically implied that oxide film formation occurred simultaneously with corrosion attack. A derived model accurately predicted the alloy exposure time based on its initial weight and corrosion rate in the same environment. The validity of the derived model; was rooted on the core expression $T_{xp} + 0.653 = -e_1 \gamma^2 - e_2 \beta^2 + e_3 \gamma + e_4$ where both sides of the expression are correspondingly approximately equal. Results from a standard model (regression model) derived model and experiment showed that the standard error in predicting the alloy exposure time for each value of the initial weight and alloy corrosion rate are 3.6752×10^{-5} & 0.017%, 0.0096 & 0.0217% and 0.0084 & 0.0203% respectively. Similarly, the F-test results are 2.47×10^{-5} & 0.3471, 2.29×10^{-5} & 0.3298 and 2.01×10^{-5} & 0.3024 respectively. Results generated from regression model, derived model and experiment indicates 9.5288×10^{-4} , 9.8728×10^{-4} and 9.89×10^{-4} mm as the depths of corrosion penetrations respectively. Deviation analysis indicates that the maximum deviation of the model-predicted alloy exposure time from the corresponding experimental value is less than 14.58%. This translated into over 85% operational confidence for the derived model as well as over 0.85 reliability response coefficient for the dependence of the alloy exposure time on corrosion rate and initial weight of alloy.

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