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Full Length Research Paper

Application of statistical technique to the analysis of passivation of Al - Zn alloy systems in brine

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The high demand for light metals as engineering materials lies in their high strength - to - weight ratio with good corrosion resistance in diverse environments. Passivation phenomena in these materials especially Al - based binary alloys have well been documented. However, the present study which aims at using model equations to investigate the passivation trend in various compositions of duplex Al - Zn alloy systems subjected to different concentrations of brine is totally new. The comparative plots of the generated values from the model equations with experimental data show that it correlated well with experimental observations.

Key words: Model equations, correlation, passivation, Duplex alloy systems.

INTRODUCTION

The production of materials with high corrosion resistance and relatively low cost has been the focus of material scientists and engineers. This has largely been hampered by the composite nature of many materials even metals coupled with the complex nature of material degradation in diverse environments. Even at that, many positive results have been achieved in this regard (Kontkova et al., 1995; Feliu and Morcillo, 1993; Ekuma and Idenyi, 2006; Idenyi et al., 2006).

The intricate nature of the corrosion process may be better appreciated by recognizing that many variables are involved: environmental, electrochemical and metallurgical history of the composite etc (Ekuma and Idenyi, 2006) which is basically an electrolytic (Feliú and Morcillo, 1982; Rozenfeld, 1972) process. The electrolyte is a scale film of moisture (normally few monolayers), or an aqueous film (a thickness of hundreds of microns) when metals or composites show up perceptibly damping. Among the external factors that are determinant on the corrosion rate definition especially in aqueous environment, it is possible to mention: 1) the lifetime of the electrolytic film on the metal surface, 2) the chemical composition of environment and 3) the ambient temperature. These factors are important in corrosion measurement and general corrosion design.

The weight difference per unit area (scale film thickness) can be a good passivation monitoring parameter especially with regards to the statistical nature of passivation rate processes governed by a number of variables, though its widespread application have been hampered largely because, the use of statistics requires specialist knowledge and no reference standards exist (Ekuma et al., 2007).

However, for a passivated film to be effective, it must provide a protective barrier that keeps the corrosion current on the metal-environment interface at relatively low enough rate so that the extent of corrosion damage is reduced. An effective film is one that resists the breakdown of the passive film and if abraded, repassivates immediately (Frankenthal and Kruger, 1978); hence, the conditions that promote corrosion of aluminum and its alloys, must be those that continuously abrade the film mechanically or promote reactions that locally degrade this protective oxide film by minimizing the availability of oxygen to rebuild it (Ekuma et al., 2007).

The scale film thickness is unavoidably a good index for passivation characterization especially the statistical nature of passivation phenomenon. It clearly gives an insight into materials behaviour in a passivating media. The formation of thin protective film at metal interfaces, which could be successfully used for corrosion control, has long been the area of research for corrosion experts.

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The layers are formed either during the adsorption of corrosion inhibitors or in reactions of the cations of the metal to be protected with some components of the medium (Ekuma et al., 2008). The latter case involves not only nanosized layers formed by corrosion inhibitors but also thick conversion (oxide, phosphate, etc) coatings (Kuznetsov, 2006).

Also, the scale film deposition rate has imbedded in it the vital property of the rate at which adsorption of corrosion products occurs on the surface of any passivating material subjected to simulated corrosive environments and the stability of metals or alloys in such environments will depend on the protective properties of organic or inorganic films, as well as on the layer of corrosion products. Some film characteristics, such as chemical composition, conductivity, adhesion, solubility, hygroscopicity and morphology, determine its ability as controlling barrier to different kinds of attack and corrosion rates (Stratmann et al., 1983). On the other hand the stated characteristics depend, in turn, on chemical composition and metallurgical history of the metal, on physicochemical properties of coating and on environmental variables such as atmospheric conditions, type and amount of pollutants, wet-dry cycles, etc (Stratmann et al., 1983; Stratmann and Streckel, 1990).

The use of statistical models for predicting the passivation (by extension, corrosion) characteristics of metals and composite materials in diverse environments have been predicted for decades but its application has largely been hampered due to the special skill and above all no reference standard that is involved in the analysis. Deterministic and statistical models have both been formulated for better perceptive of the environment. Deterministic models are based on the basic mathematical descriptions of the environmental processes, in which effects are generated by causes while the statistical models are based on semi-empirical statistical relations between available data and measurements that do not necessarily reveal any relation between cause and effect, but reveals the underlying correlation between sets of input data (predictors) and targets (predictands). Example of the deterministic model is Euler models (Ekuma and Idenyi, 2007) and that for statistical models are time series analysis (Hsu, 1992) and artificial neural networks (Abdu-Wahab and Al-Alawi, 2002).

Aluminium based alloys have of recent found diverse usage in engineering industry. This can be attributed to its low density (2.71kg/cm^3); low emission, hence its frequent use as heat radiators; does not become brittle at low temperatures (strength and ductility slightly increases) like most bcc lattice materials (e.g. steel); high coefficient of linear expansivity in comparison with other metals (for instance, it is twice that of steel); specific strength with light weight as engineering materials for transportation which greatly reduces fuel consumption; good conductors of heat and electricity etc. These out lined properties of aluminium may be greatly enhanced by cold working and by alloying for instance with zinc (Callister, 1997).

In this paper, the statistical approach will be adopted to analysis the passivation trend of various alloys of aluminium - zinc alloy: Al - 2.0% Zn; Al - 2.5% Zn and Al - 3.5% Zn subjected to varying concentrations of brine: 0.1; 0.25; 0.5 and 1.0 M which are simulated from 58.5% pure assay of NaCl using standard procedure. This range of brine adequately accommodates all the positively saline environments habouring Al - based alloys as it contains the aggressive ion, chloride, which is of practical importance because, it is present in large amount both in sea water, road salts and some soils and in lower concentration in other natural sources. The aim however, will be to formulate model equations based on logarithmic regression analysis for the investigation of passivation trend in these various Al - Zn alloys. The validity of the developed model equations will be checked by plotting comparative plots of the modeled values with experimental data. It is however envisaged that the present study will aid greatly in gaining more insight into the dynamics of passivation in Al - based alloys and even in other passivating engineering materials.

DEVELOPMENT OF THE MODEL EQUATION

The rate of material degradation in any environment is better evaluated in terms of the corrosion penetration rate (CPR) which by extension gives the passivation rate (PR). This is obviously due to the fact that it gives reliable information to corrosion experts and is given mathematically as:

$$CPR = PR = \frac{k\Delta w}{\rho A t} \qquad (1)$$

Where Δw is weight difference after exposure time t, ρ and A are density and exposed specimen area respectively and k is a constant whose magnitude depends on the system of units used. For instance, when k = 87.6, CPR is in mm/yr and Δw , t, ρ and A are expressed in mg, hrs, g/cm^3 and cm^2 respectively.

From equation (1), we can have that:

$$InPR = \text{In}\left(\frac{k\Delta W}{\rho A}\right) - \text{Int} \qquad (2)$$

It is straightforward to show from equation (2) noting that $\Delta W, \rho, A$ and k are all constants that:

$$PR = \eta - \lambda \text{Int} \qquad (3)$$

Where η is a constant $= \frac{k\Delta w}{\rho A}$ ($k, \Delta w, \rho$ and A are all constants) and λ is an empirical constant which is model fitted.

Equation (3) is the compact form of the model equation used in this analysis that is in tandem with the observations made from the passivation rate profile of experimental values which utmostly forms the basis of the adoption of logarithmic model for the present study.

EXPERIMENTAL PROCEDURE

The data of Ekuma (2006), a destructive testing method which adopted the weight loss technique is used in this analysis. After the initial treatment of the samples (casting and machining to sizeable coupons; polishing of the surface according to ASTM standards), 72 test coupons were divided into three groups (of six each) with each of the alloy containing varying fractions of Zn in each of the four (4) simulated concentrations of brine. A set of coupon was withdrawn 24 hourly, washed with distilled water, cleaned with acetone and dried in an open air. The final weight of each of the test coupon was determined using the digital analytic weighing balance as to enable calculation of the passivation rate from the weight difference. In all, the samples were allowed to stand for 144 h (6-days) with a set of test coupons withdrawn 24 hourly for corrosion rate characterization.

RESULTS

Table 1 is the table of the modeled equations, coefficient of correlation (R - value) and coefficient of determination (R^2 - values) while Figures 1 - 12 show the comparative plots of passivation rate as a function of time for the experimental data and model data for the various samples: Al - 2.0% Zn; Al - 2.5% Zn and Al - 3.5% Zn in various concentration media (0.1; 0.25; 0.5 and 1.0 M of brine environment).

ANALYSIS OF RESULT

The statistical models were developed from the regression analysis of the experimental data based on the fore - knowledge of the passivation trend of the studied binary alloy system which is basically logarithmic (or exponential) in nature (Equation 2).

From the comparison plots (Figures 1 - 12) and Table 1, it can be verified that the observed experimental values correlated well with the modeled values. This is clearly significant from the high correlation coefficient values (R - values) of all the binary alloy systems being studied. For the entire composite, it can be seen that the correlation coefficient is in the range of $0.92 \leq R \leq 0.99$ (Table 1) which depicts that $R \approx 1$ hence, nearly perfect positive correlation. In order to measure the total variation in passivation rate that has been adequately accounted for by the variation in exposure time, we measured the coefficient of determination of the various duplex alloy systems being studied. It can be inferred from the table that the range of the coefficient of determination which is $0.82 \leq R^2 \leq 0.98$. The conclusion that can be drawn from this observation is that the model fit developed from the model equations is accurate and will be a good predicator of the passivation behaviour of the alloy of aluminium (in

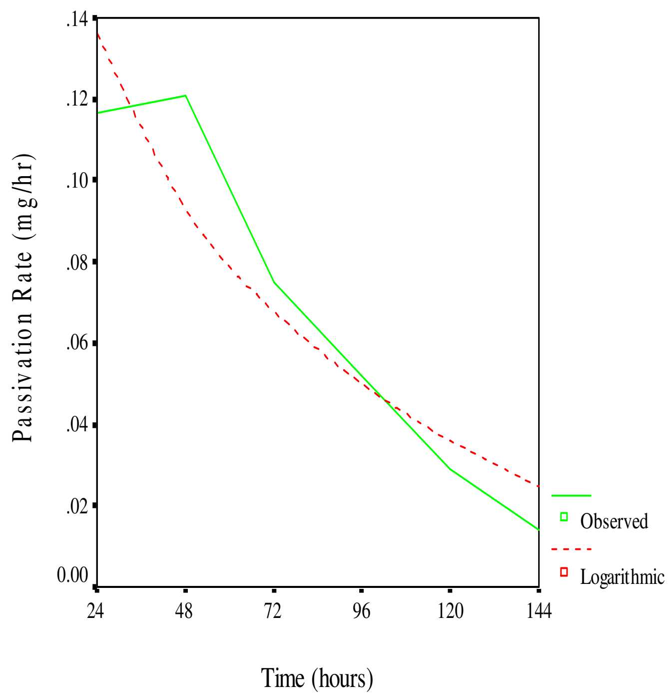

Figure 1. The graph of passivation rate (mg/h) for the experimental data and model data for Al - 2.0% Zn in 0.1 M NaCl media concentrations.

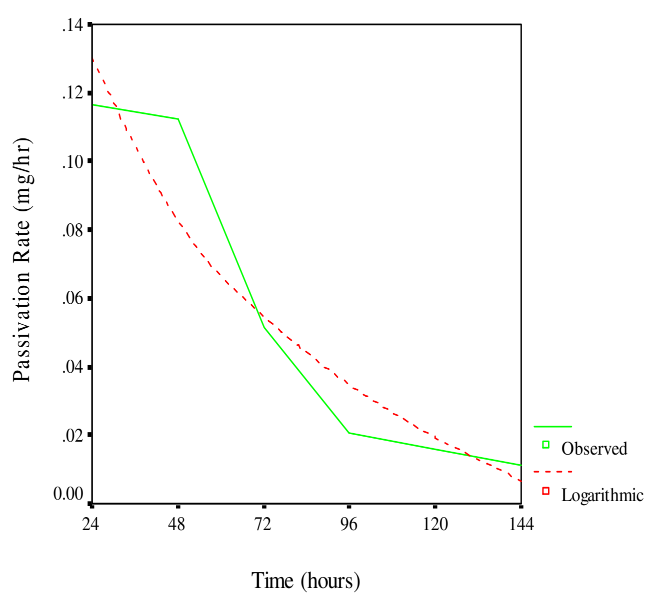

Figure 2. The graph of passivation rate (mg/h) for the experimental data and model data for Al - 2.0% Zn in 0.25 M NaCl media concentrations.

Table 1. The modeled passivation parameters for the various Al - Zn alloys in different brine environment.

Media concentration (M)	Coefficient of correlation (R - value)	Coefficient of determination (R^2 - value)	Model equation
	Al - 2.0% Zn in various concentrations of NaCl		
0.1	0.92824	0.86163	$PR = 0.334309 - 0.062312\text{Int}$
0.25	0.94223	0.88780	$PR = 0.349456 - 0.068950\text{Int}$
0.5	0.95754	0.91689	$PR = 0.163375 - 0.031833\text{Int}$
1.0	0.93007	0.86502	$PR = 0.663981 - 0.119952\text{Int}$
	Al - 2.5% Zn in various concentrations of NaCl		
0.1	0.95968	0.92098	$PR = 0.390495 - 0.063541\text{Int}$
0.25	0.92365	0.85312	$PR = 0.607812 - 0.103443\text{Int}$
0.5	0.97318	0.94708	$PR = 0.150609 - 0.025135\text{Int}$
1.0	0.94612	0.89514	$PR = 0.073447 - 0.008324\text{Int}$
	Al - 3.5% Zn in various concentrations of NaCl		
0.1	0.94362	0.89043	$PR = 0.404876 - 0.078864\text{Int}$
0.25	0.90783	0.82415	$PR = 0.305115 - 0.053806\text{Int}$
0.5	0.97666	0.95386	$PR = 0.227076 - 0.034941\text{Int}$
1.0	0.99213	0.98433	$PR = 0.262394 - 0.047547\text{Int}$

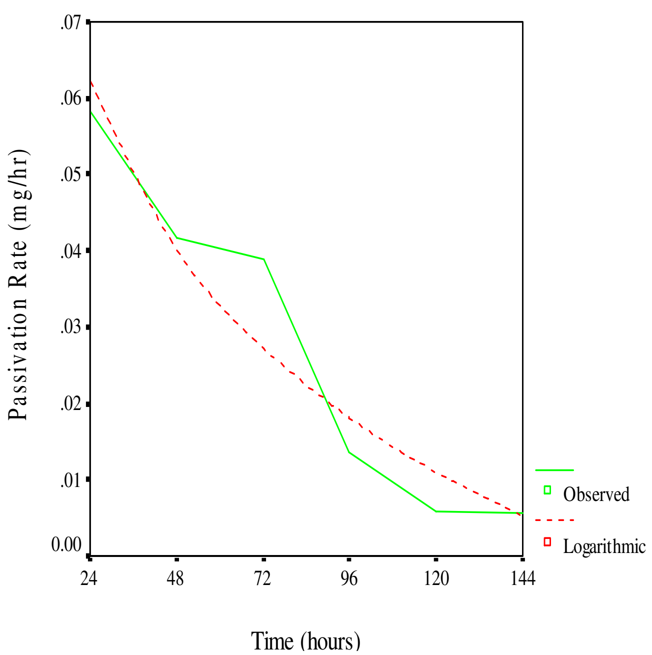

Figure 3. The graph of passivation rate (mg/h) for the experimental data and model data for Al - 2.0% Zn in 0.5 M NaCl media concentrations.

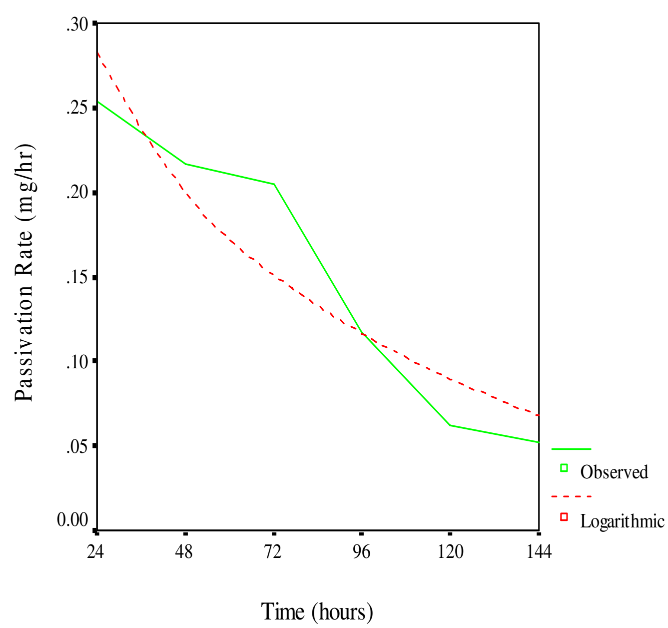

Figure 4. The graph of passivation rate (mg/h) for the experimental data and model data for Al -2.0% Zn in 1.0 M NaCl media concentrations.

this case Al - Zn) in the brine environments being studied. It further points out that approximately over 82.42 to 98.43% of the total variation in passivation rate is accounted for by corresponding variation in the exposure time while only approximately 17.58 to 1.57% are due to the influence of other factors that are not incorporated into the model equations. This model no doubt provides a

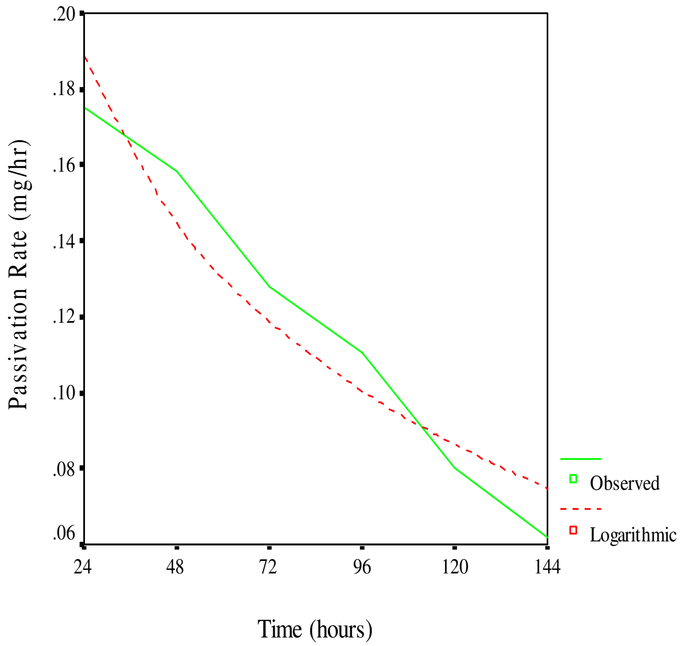

Figure 5. The graph of passivation rate (mg/h) for the experimental data and model data for Al - 2.5% Zn in 0.1 M NaCl media concentrations.

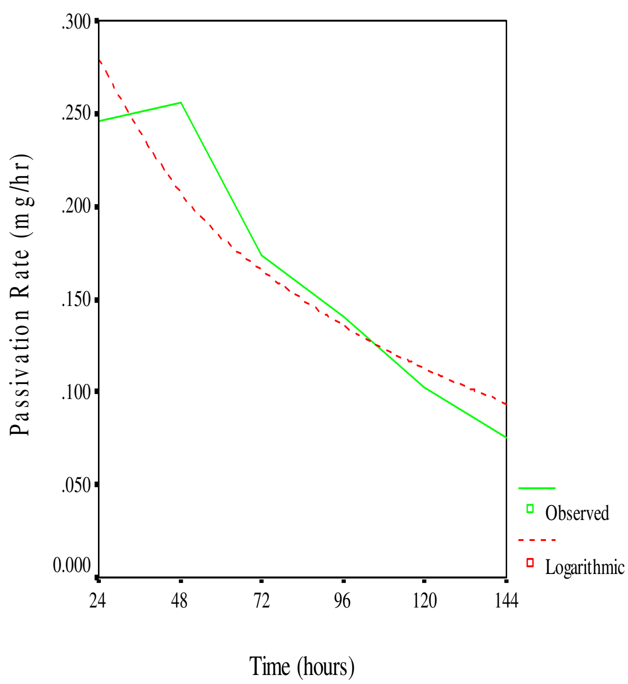

Figure 6. The graph of passivation rate (mg/h) for the experimental data and model data for Al - 2.5% Zn in 0.25 M NaCl media concentrations.

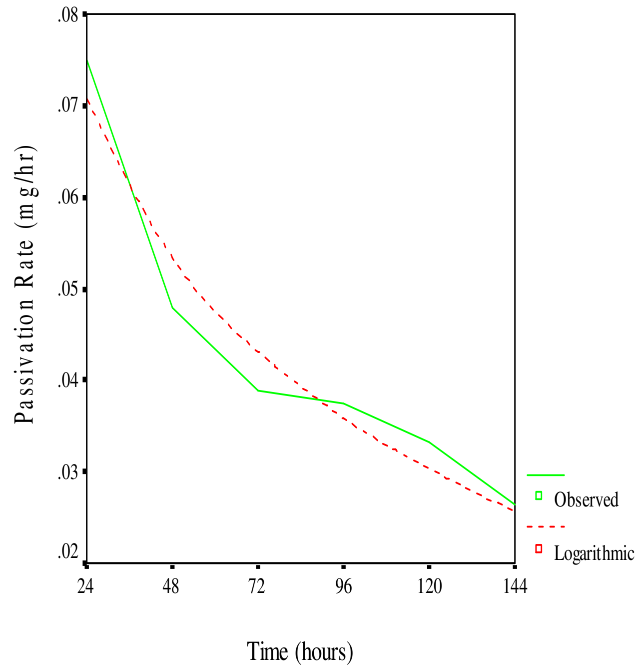

Figure 7. The graph of passivation rate (mg/h) for the experimental data and model data for Al - 2.5% Zn in 0.5 M NaCl media concentrations.

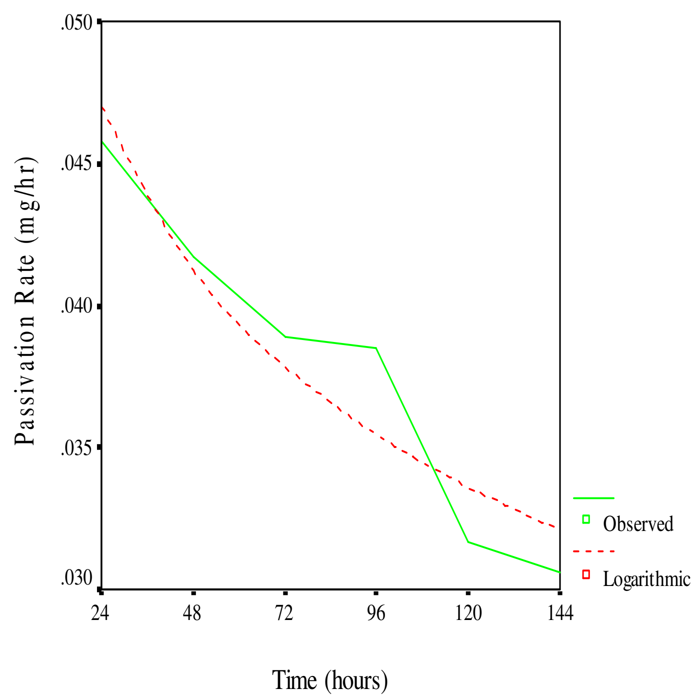

Figure 8. The graph of passivation rate (mg/h) for the experimental data and model data for Al - 2.5% Zn in 1.0 M NaCl media concentrations.

better insight into passivation trend in studied duplex aluminium alloy systems as it can be a good working tool for corrosion experts during corrosion designing of Al - Zn alloys (even other passivating light metallic alloys) in a positively saline environment.

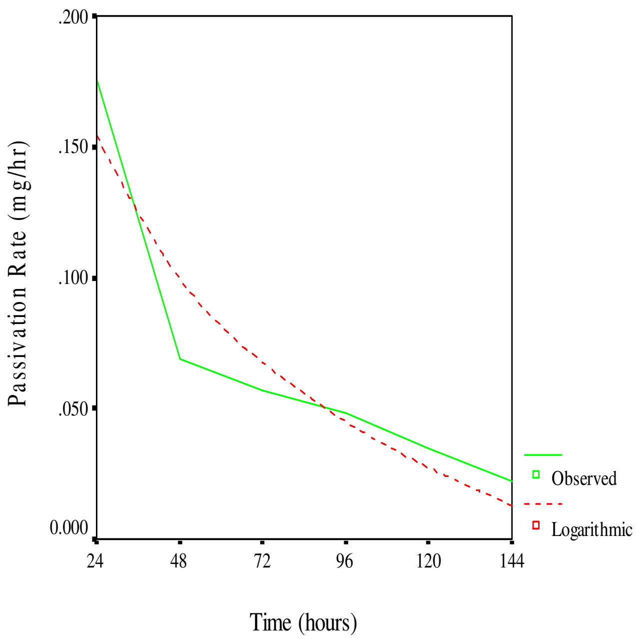

Figure 9. The graph of passivation rate (mg/h) for the experimental data and model data for Al - 3.5% Zn in 0.1M NaCl media concentrations.

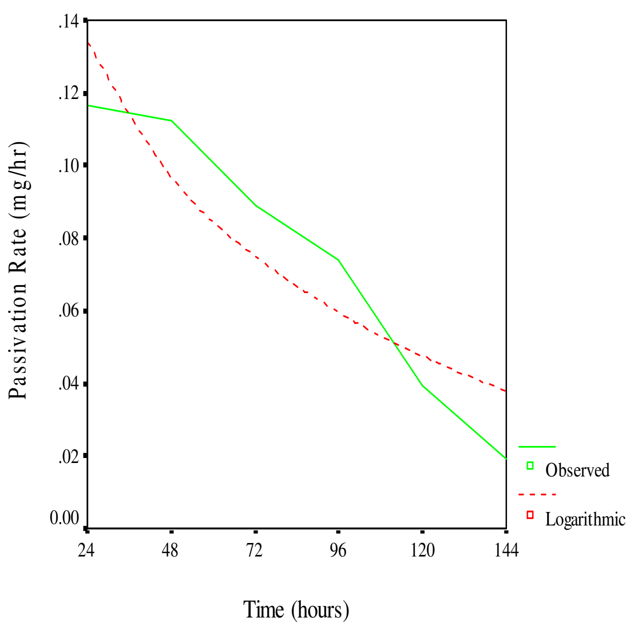

Figure 10. The graph of passivation rate (mg/h) for the experimental data and model data for Al - 3.5% Zn in 0.25 M NaCl media concentrations.

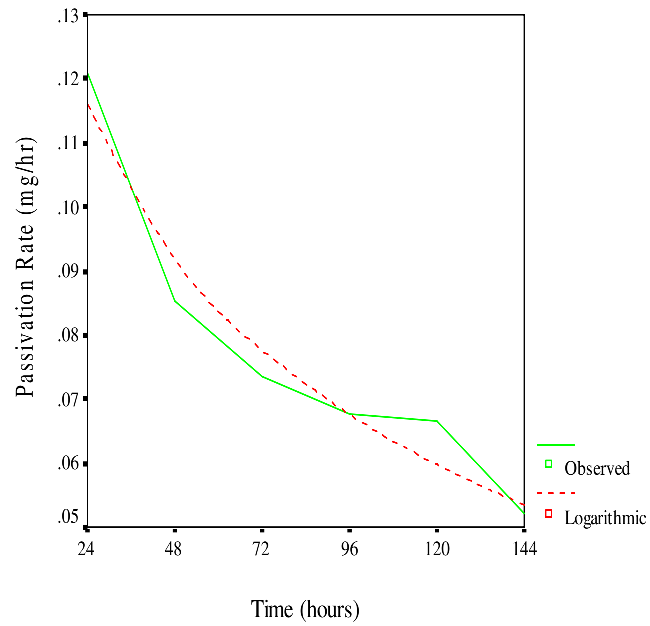

Figure 11. The graph of passivation rate (mg/h) for the experimental data and model data for Al - 3.5% Zn in 0.5 M NaCl media concentrations.

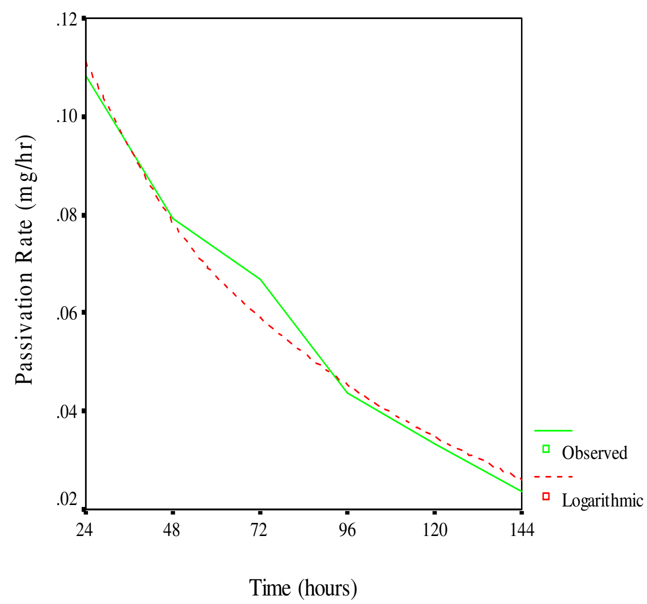

Figure 12. The graph of passivation rate (mg/h) for the experimental data and model data for Al - 3.5% Zn in 1.0 M NaCl media concentrations.

Conclusion

From the model Equations (1 - 12) developed and the statistical parameters obtained for each case (Table 1), it is evident that all the model equations are good predicators of the passivation characteristics of the studied binary alloy systems in the various media concentrations being considered. The high positive coefficient of correlation ($R \approx 1$) is consistent for all the cases and also, the high coefficient of determination for all the cases confirms this assertion. The authors wishes to state that the method used in this work is totally new and has not been used elsewhere except by the authors to their best of knowledge. Thus, we recommend that this work in itself is not conclusive and as such more elaborate work for other alloy compositions be carried out at expanded time scale to really determine the limit of validity of this technique.

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