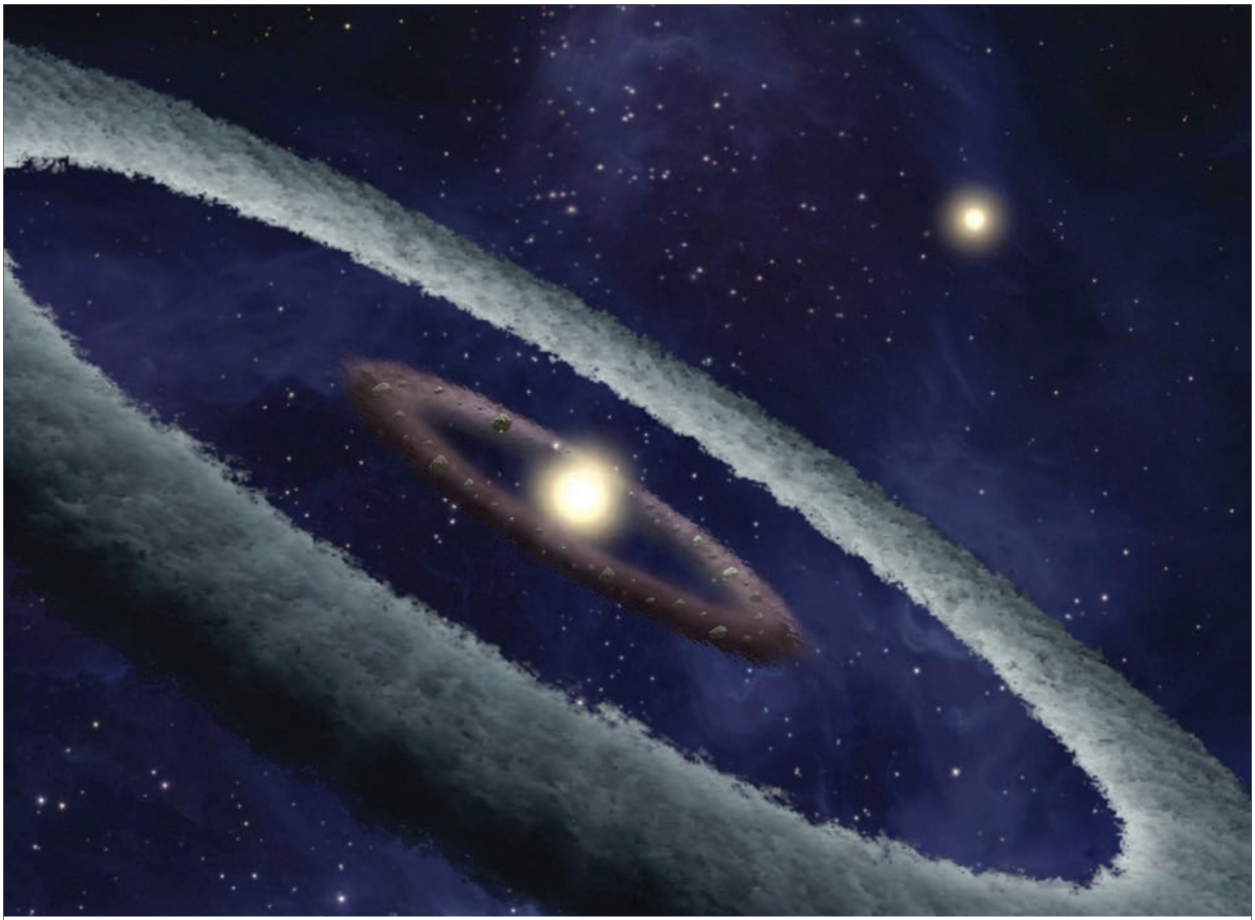

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Statistical Analysis of the Influence of Environment on Prediction of Corrosion from its Parameters*

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Abstract: Statistical analysis of the corrosion characterization of Al-2.5% Zn binary alloy system has been carried out. Preweighed test coupons were subjected to seawater and atmospheric environments, respectively. The set up were allowed to stand for 480 h with a set withdrawn 120-hourly for corrosion rate characterization. The model equation developed using regression technique revealed that the model could be used for effective and accurate determination of corrosion trend in seawater and atmospheric environments as it showed good correlation with the experimental data.

Key words: CPR, statistical analysis, corrosion characterization, binary alloy, model equation

INTRODUCTION

Corrosion generally, is a statistical effect governed by a number of variables including environmental, electrochemical and metallurgical aspects. For example, anodic reactions and rate of oxidation, cathodic reaction and rate of reduction, corrosion inhibition, polarization or retardation; passivity, effect of oxidizers, effect of velocity, temperature, corrosive concentration, galvanic coupling and metallurgical structure all influence the type and rate of the corrosion process; and its statistical analysis can take different forms due to the varied forms of corrosion. Its application to corrosion characterization to improve the estimation of corrosion rate has been suggested for over 50 years and has been applied but in few isolated cases. This is due largely because, the use of statistics requires specialist knowledge and no reference standards exist (Idenyi *et al*., 2006).

Basically, seawater is a complex composition of different dissolved minerals (Laque, 1993), but, a single parameter of greatest interest in defining the complexity of seawater is the chlorinity which is a measure of the amount of chlorine, bromine and iodine replaced by chlorine as measured in grams per kilogram of seawater. The higher the chlorinity, the higher the concentration of salts. Chlorinity can be directly related to passivity, which is the material parameter of interest in this analysis.

The stability of metals or alloys in an aggressive environment 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 (Stratmaun *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). In this sense, a common example is galvanic protection of steel by zinc, due, not only to the preferential corrosion of zinc, but also to the barrier effect of corrosion products.

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The effects of atmosphere on the corrosion behaviour of metals are well known and quite understood. It is probably the most common form of corrosion and is defined as the corrosion or degradation of material exposed to the air and its pollutants. Therefore, it is important to know the specific corrosion rate in a given application environment in order to effectively use metals in outdoor structures. Most of the broad forms of corrosion occur in the atmosphere and some appear to be largely restricted to it (Ekuma, 2006). Since the corroding metal is not bathed in large quantities of electrolyte, most atmospheric corrosion operates in highly localized corrosion cells (Kenneth, 1970). Most aluminum alloys have excellent resistance to atmospheric corrosion (often called weathering) and in many outdoor applications, such alloys do not require shelter, protective coatings or maintenance.

A common method for estimating the useful life of metals has been the use of various types of metals and alloys for the different types of atmospheres. Recognition of marked differences in corrosivity has made it convenient to divide atmospheres into types. The major types are rural, urban, industrial, marine, or a combination of these. Earlier researchers Kontkova *et al.* (1995) and Kucera and Fitz (1995) have examined the corrosion rates of various metals exposed to different atmospheres as to evaluate the relative corrosion resistance of various metals in different atmospheric environmental conditions. It was observed that the relative resistance of metals to atmospheric corrosion changes with location. For instance, galvanized iron performs well in rural atmospheres but it is relatively less resistant to industrial atmospheres (Uhlig and Revie, 1985).

Many models have been formulated for predicting the corrosion damage of metals in the atmosphere which are useful for answering such questions as the durability of metallic structures, determining the economic costs of damages associated with the degradation of materials (Feliu and Morcillo, 1993) and acquiring knowledge about the effect of environmental variables on corrosion kinetics (Ekuma, 2006).

Deterministic and statistical models have both been developed for better understanding of the environment. Deterministic models are based on fundamental mathematical descriptions of atmospheric processes, in which effects (air pollution) are generated by causes (emissions). Examples of the deterministic types are Euler models (Zannetti, 1983) and Gaussian models (Zannetti, 1990). 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. Basically, statistical models attempt to determine the underlying relationship between sets of input data (predictors) and targets (predictands). Examples of statistical models are regression analysis (Abdul-Wahab and Al-Alawi, 2002), time series analysis (Hsu, 1992) and artificial neural networks (Abdu-Wahab *et al.*, 1996; Elkamel *et al.*, 2001).

In this research, the regression analysis (Y_{CPR}: X_t) will be used to develop an exponential model equation for the Corrosion Penetration Rate (CPR) as a function of time. Also, a model equation (Y_{PR}:X_t) will be developed. A correlation analysis for the observed corrosion parameters will also be carried out. It is envisaged that these analysis will be of uttermost importance in both material selection and in general corrosion design since these parameters are known to furnish corrosion experts with vital information on corrosion trend in general corrosion design. An attempt will also be made to compare the experimental results with the data generated using the developed model equations, which will be plotted for proper comparison.

MATERIALS AND METHODS

Study Area

This research was carried out in Abakaliki, Ebonyi State, located centrally in southeastern part of Nigeria in the month of November 2006.

Materials

The materials used for the work were scraps of aluminium (99% pure Al) purchased from aluminum smelting and melting company, in Enugu, Nigeria and pure zinc ingot procured from scientific construction company, Enugu, Enugu state. The other materials used were: acetone, seawater gotten from Ndibe beach here in Abakaliki, emery paper, distilled water, laboratory beakers, measuring cylinders, etc.

Equipments

The equipments used were: lathe machine, drilling machine and a surface crucible furnace. The fundamental equipment used an analytic digital weighing machine X21-0014 KERN 770-15,15402301, which measures to an accuracy of 0.000000 mg. This was used to weigh the test coupons before and after exposure to the study envirouments as to ascertain the exact weight difference.

Sample Preparation

After the aluminium scraps and zinc ingot have been thoroughly cleaned, the composition for each of the Al-Zn alloy were carefully worked out and charged into the surface crucible furnace, the molten alloys were cast into rods after melt down (at 700°C), machined to sizeable dimensions and consequently, cut into coupon samples of dimension range of 54.40×47.60×22.40 mm and initial specific surface area of about 1468.00 mm^2. Each sample coupon was drilled with a 5 mm drill bit to provide hole for the suspension of the strings. The surface of each of the coupon specimen was thoroughly polished according to ASTM standard.

Simulation of Test Environments

The envirouments for this work were seawater and natural atmosphere. The seawater was obtained from Ndibe beach located in Afikpo in Ebonyi state.

Design Setup and Experimentation

The test coupons were divided into two groups of 4 test coupons each. The first group was exposed to atmospheric enviroument while the other was immersed in seawater enviroument. The set up was allowed to stand for 480 h with a set of coupon withdrawn 120 hourly, (washed with distilled water, cleaned with acetone and dried before weighing to determine the final weight using the digital analytic weighing machine) for corrosion characterization.

The degree of corrosion progress in the samples, most conveniently evaluated in terms of the Corrosion Penetration Rate (CPR) expressed mainly in mils/year or mm year^{-1} was evaluated based on the mathematical formula:

$$\mathrm{CPR} = \frac{k\Delta W}{\rho A t} \tag{1}$$

where ΔW is weight loss after exposure time t, ρ and A are density and exposed specimen area, respectively and k is a constant that has a magnitude which depends on the system of units used. However, for this work, k = 87.6 then, CPR is in mm year^{-1} and w, t, ρ and A are expressed in mg, hrs, g cm^{-3} and cm^2, respectively (Idenyi *et al*., 2006; Callister, 1997).

RESULTS AND DISCUSSION

Regression Analysis: Corrosion Rate

The multiple regression analysis of the corrosion penetration rate as a function of time was carried out. From the initial knowledge of the trend of the corrosion rate profile, the exponential multiple regression analysis Y_{CPR}: X_t for the two environments: atmosphere and seawater were determined.

For atmospheric environment, recalling (1) and taking the natural log of both sides, we obtain that:

$$\text{In CPR} = \text{In k+In } \Delta\text{W-In } \rho\text{-In A-In t}$$

$$= \text{In}\left(\frac{\text{k}}{\rho\text{A}}\right) - \text{In}\left(\frac{\Delta\text{W}}{\text{t}}\right)$$

Let η= k, ρ and A since they are all constants. Thus, we obtain that:

$$\text{In CPR} = \text{In}(\eta) - \text{In}\left(\frac{\Delta\text{W}}{\text{t}}\right) \tag{2}$$

The model equation developed is thus:

$$Y_{CPR} = 0.5430 - 0.0879 \text{ In t} \tag{3}$$

with r-value of 0.99719 and r-square value of 0.99439. Where Y_{CPR} is the corrosion penetration rate and t is the exposure time. The negative sign is as expected which can easily be verified from (2).

From (3), modeled values were plotted with the experimental values to check the validity of the developed model equation. From Fig. 1, it can be seen that the experimental values fitted well with the modeled values, hence giving a good insight into the material behaviour in the atmospheric environment being studied. The coefficient of correlation (r-value) of 99719 shows high positive correlation. The coefficient of determination (r-square value) shows that 99.72% of the variation in the corrosion penetration rate is caused by change in time.

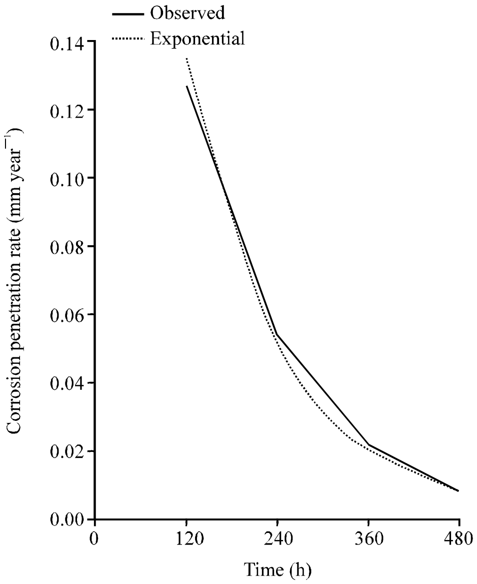

Fig. 1: Corrosion penetration rate as a function of time for the experimental data and observed model data in atmospheric environment

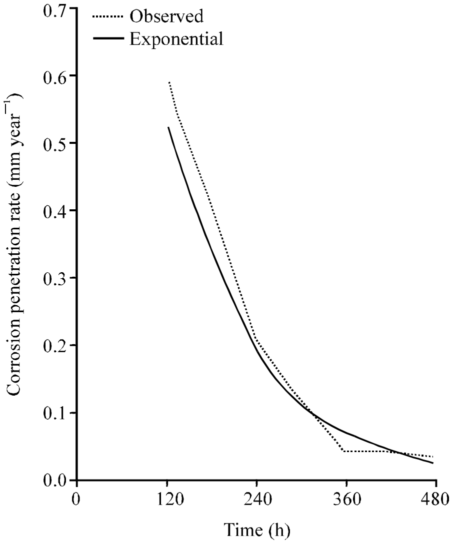

Fig. 2: Corrosion penetration rate as a function of time for the experimental data and observed model data in seawater environment

For the seawater environment, the model equation is:

$$Y_{CPR} = 2.5896 - 0.4241 \ln t \tag{4}$$

with r-value of 0.96368 and r-square value of 0.92868. This again is a good observation as it can be inferred from (4) that on comparing the modeled values with the experimental data, it fitted well as can be observed from Fig. 2.

Uttermostly, this shows a good observation as it can be seen that there is high positive correlation as can be seen from the high value of the coefficient of correlation (r = 0.96368). The coefficient of determination depicts that 96.37% of the change in corrosion penetration rate depends on exposure time.

Passivation Rate

The scale film deposition rate (passivation rate) has imbedded in it the important property of the rate at which adsorption of corrosion products occurs on the surface of any passivating material subjected to any environment.

For the atmospheric environment, the model equation is:

$$Y_{PR} = 24.6659 - 3.9924 \ln t \tag{5}$$

with r-value of 0.99712 and r-square value of 0.99425. Where Y_{PR} is the passivation rate and t is the exposure time.

To check the validity of the model equation, we compare the experimental data with the modeled values. From Fig. 3, it can be inferred that the observed values correlates well with the modeled data. This can also be inferred from the high coefficient of correlation value. The coefficient of determination (r^2) shows that 99.71% of the variation in the passivation rate is caused by the exposure time.

For the seawater environment, the model equation is:

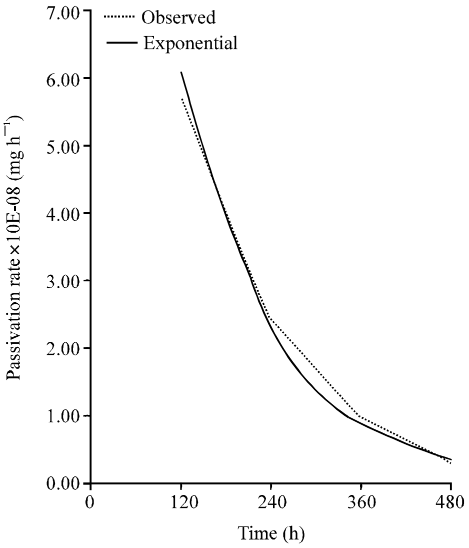

Fig. 3: Passivation rate as a function of time for the experimental data and observed model data in atmospheric environment

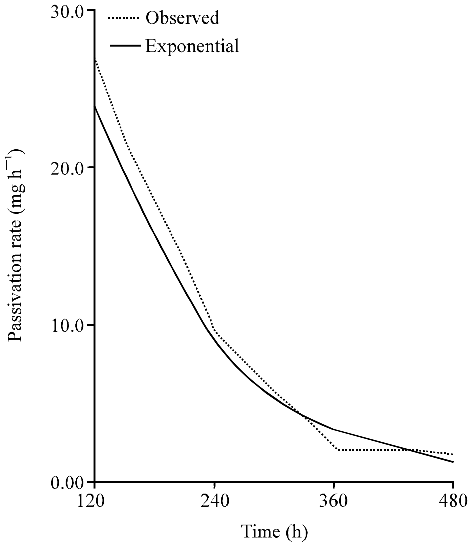

Fig. 4: Passivation rate as a function of time for the experimental data and observed model data in seawater environment

$$Y_{PR} = 117.602 - 19.261 \text{ In } t \tag{6}$$

with r-value of 0.96385 and r-square value of 0.92900. Again, to check the validity of this result, a comparison graph was plotted. From Fig. 4, it can again be inferred that the model equation can be used in corrosion characterization, as there is close proximity between the plotted experimental data and the data generated from the model equation. The coefficient of correlation, r = 0.96385 uttermoslty shows high correlation value. The coefficient of determination (r^2 = 0.92900) shows that 92.90% of the passivation rate does that with time.

Correlation Analysis

The correlation analyses of the observed corrosion parameter data (Table 1) were carried out. The Spearman correlation analysis, which is a nonparametric test analysis, was deployed.

For the atmospheric environment, there were perfect correlation for the correlation between weight difference and corrosion rate; weight difference and passivation rate; passivation rate and corrosion penetration rate ($r \approx 1$), which are all significant at 0.01 levels.

For the observed corrosion parameters of samples immersed in seawater, the correlation value $r \approx 0.800$ for weight difference and corrosion penetration rate was observed; for weight difference and passivation rate, it is, which are both significance at 0.200 level of correlation. A perfect correlation ($r \approx 1$) however existed between corrosion penetration rate and passivation rate, which is significance at 0.01 level of correlation. The high level of correlation observed in the correlated corrosion parameters are as expected and this agrees with the regression analysis earlier carried out. Significance of mention is the perfect correlation that existed between corrosion penetration rate and passivation rate. This is not unusual as the passivation rate by extension, corresponds to the corrosion penetration rate.

CONCLUSIONS

From the foregoing discussions, it can be concluded that model equation developed using regression analysis can be employed in the determination of the influence of time on corrosion parameters (in this case, the corrosion penetration rate and the passivation rate). It can be inferred however that the relationship between the observed corrosion parameters with time are not linear but an exponential one. This can be verified from the plots (Fig. 1-4). The model Equations (3-6) clearly show that the equation can be used to evaluate material behaviour in corrosion design which can further be validated by the comparison plots (Fig. 1-4) that show good correlation between the experimental data and the modeled data. The almost perfect correlation ($0.8 \le r \le 1$) existing between the correlated corrosion parameters studied using correlation analysis is in agreement with the model equations. However, it is envisaged that an elaborate work on other materials: alloys, metals etc be carried out on expanded time scale to determine the limit of the validity of the technique.

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