Modelling the Effect of Salinity on Mild Steel Corrosion Rate in Salt Water

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Abstract
Buckingham Pi theorem has been used to develop a unique predictive corrosion rate /model for estimating the corrosion rate of materials in saline environment. The model was first developed for corrosion of mild steel in fresh water and the developed equation was validated using experimental data obtained from weight loss method and collaborated with data generated from electrochemical method. The validated model was then extended to incorporate the effect of salinity on the corrosion rate of mild steel in fresh water solutions containing different quantities of sodium chloride. The modelled corrosion rate profiles when compared with the experimentally obtained profiles had very high coefficients of correlation. This was further verified using statistical analysis of Excel-ANOVA-single factor tool, the Mean Absolute Percentage Error and the Pearson's Correlation Coefficient. These analyses confirm that there is no significant difference, statistically, between the model and experimental corrosion rates data, and a good agreement of above 95% was achieved. This unique predictive corrosion rate model relates corrosion rate constant with salinity levels and will be very useful for a more accurate prediction of corrosion rate of mild steel in sea waters.

Keyword: *Unique Predictive Model, Corrosion Rate, Buckingham Pi Theorem, Salinity, Aquatic Environment*

1.0 Introduction

Mild steel remains one of the most widely used construction materials in different fields of engineering for infrastructural development. It stands out in the midst of other materials for selection as the major construction material because of its attractive qualities such as good weld ability, adequate ductility, moderately high strength and it is relatively cheap and readily available. Generally mild steel materials, in course of their usage, are exposed to different environments with which they interact. Depending on the nature of the environment in question, material deterioration occurs and ultimately leading to their corrosion (Ikpeseni, 2012; Harishand Vikas, 2013).

Huge financial losses, running into millions of dollars are suffered by industries annually due to equipment and structural failures arising from material corrosion. Leaks of toxic materials and inflammable chemical accidents are rampant in industrial plants operating in corrosion prone environments (Anees et al, 1999) Saline environments are harsh and unfavourable for the use of steel materials in the construction of structures because of their corrosive tendencies. Sea water, whose salinity varies but has a typical range of about 33 to 37g/dm^3 (Zakowski*et al*, 2014), is corrosion prone environment, especially as the combination of salinity and temperature has a major influence on ocean currents and their impact on structures.

Service – life of equipment and structures hosted in marine environments is adversely affected by the salinity of the medium, and the knowledge of the rate of corrosion of structures in such environment would require a model equation in which the salinity factor is taken into consideration.
But presently, there seem to be no such specific model available and scientists have hitherto consistently relied only on the classical general corrosion rate equations (Perry and Green, 1997) for predicting corrosion rates. However later studies in our department (Akpa, 2013 and Chinwko *et al*, 2014) which took into consideration the physico-chemical properties of the medium (Amadi, et al, 2010), and microbial activities (Amadi,T.N.,2014), have shown that the numerical value of the corrosion rate constant in the classical general corrosion equations is environmental dependent . Hence the present study seeks to develop a model corrosion rate expression for mild steel in saline environment which will incorporate a factor that would account for the effect of salinity of the medium.

2.0 Model Formulation

Dimensional analysis is a useful mathematical modelling tool in formulating relations among physical quantities in which the significant variables in a given situation are grouped into dimensionless parameters which are less numerous than the original variables. This procedure is very helpful in handling large experimental data whereby combining the variables into a small number of dimensionless parameters, the volume of experimental data is considerable reduced. Dimensional analysis predicts the various dimensionless parameters which are relevant in correlating experimental data. The Buckingham pi theorem is one of the methods used in dimensional analysis This theorem describes how every physically meaningful equation involving $\boldsymbol{n}$ variables can be equivalently rewritten as an equation of $\boldsymbol{n-m}$ dimensionless parameters, where $\boldsymbol{m}$ is the number of fundamental dimensions used. Most importantly, it also provides a method for computing these dimensionless parameters from the given variables (Jaime, 2009).

Buckingham Pi theorem can thus be used in corrosion studies to describe the relationship between the rate of corrosion and its relation to other variables. Corrosion rate, in weight loss method, is a function of weight loss, density, and area of the metallic coupon, total exposure time, and other environmental factors like salinity (Amadi *et al*, 2015). This can be expressed mathematically, as

$$C_R = f(\Delta m, \rho, A, t, s) \qquad (2.1)$$

Choosing M, L and T as fundamental dimension for mass, length and time, implies that Number of Fundamental Dimension, $\boldsymbol{m}$ **= 3**; Number of Quantities, $\boldsymbol{n}$ **= 6.**
Therefore number of **π** terms, would be equal to **6 – 3 = 3**, hence we have $\boldsymbol{\pi_1, \pi_2}$ **and** $\boldsymbol{\pi_3}$.

Since $\boldsymbol{m}$ is **3**, there will be three repeating quantities: Geometric property (**A**). Flow property (**V**) and fluid property (**ρ**). A **π** group is a function of the repeating variables and one of the remaining variables.

Table 2.1: Dimension of Quantities'

Quantity	Symbol	Dimension
Density	ρ	ML^{-3}
Area	A	L^2
Time	t	T
Weight Loss	ΔM	M
Corrosion Rate	C_R	LT^{-1}
Salinity,	S	ML^{-3}

In order to establish the functional relationship between the various variables in equation (2.1), for the control (without the salinity term), the Buckingham Pi-groups in terms of their symbols as

2.1 Modelling for Control

$$\pi_1 = \rho^{w_1} A^{x_1} {C_{R_{mol}}}^{y_1} \Delta M \quad (2.2)$$

$$\pi_2 = \rho^{w_2} A^{X_2} {C_{R_{mol}}}^{y_2} t \quad (2.3)$$

Applying the dimensional analysis of Buckingham Pi theorem to solve for *x*, *w* and *y*, the values of π_2 and π_1 were obtained as

$$.\pi_1 = \frac{\Delta M}{\rho A^{\frac{3}{2}}} = \text{Weight loss coefficient} \quad (2.4)$$

$$\pi_2 = \frac{C_{R_{mol}} t}{A^{\frac{1}{2}}} = \text{Corrosion rate coefficient} \quad (2.5)$$

Combining π_2 and π_1 to form equation (2.6)

$$\pi_2 = k_1 \pi_1 \quad (2.6)$$

Plotting a graph of π_2 versus π_1, we can be obtain the value for k_1 as the corrosion rate constant.

Substituting equations (2.4) and (2.5) into equation (2.6) and making $\boldsymbol{C_R}$ the subject of the equation, we have

$$\boldsymbol{C_R = k_1 \frac{\Delta M}{\rho A t}} \quad (2.7)$$

Equation (2.7) is similar to the standard corrosion rate equations of the forms (Vedalakshmi, *et al*, 2009):.

$$C_R = 87.6 \times \frac{\Delta m}{\rho A t} \quad (2.7b)$$

$$C_R(mmpy) = \frac{3.27 I_{corr}(EW)}{\rho} \quad (2.7c)$$

Where the current density is related to weight loss as; $I_{corr} = \frac{nF\Delta m}{MtA}$, for the weight loss and Electrochemical Methods respectively.

Equation (2.7) can be validated using experimental data and comparing with the results calculated using equations (2.7b) and (2.7c) and ascertaining the level of significance between the various results using The Excel-ANOVA-single factor tool analysis.

2.2 Modelling for Salinity Effect

Extending the develop equation (equation 2.7) to incorporate the effect of salinity on the corrosion rate of mild steel, we have:

$\pi_3 = \rho^{W3} A^{X2} {C_R}^{Y3} S$ (2.8)

Applying dimensional analysis of Buckingham Pi theorem the values of π_3 is obtained as

$\pi_3 = \frac{S}{\rho}$ = salinity coefficient (2.9)

Combining π_1, π_2 and π_3 to form equation (2.10)

$\pi_2 = k_2(\pi_1 + \pi_3)$ (2.10)

Let $\lambda = \pi_1 + \pi_3$ = sum of weight loss coefficient and salinity coefficient (2.11)

Equation (2.11) becomes

$\pi_2 = k_2 (\lambda)$ (2.12)

Plotting π_2 against λ, we obtain graphs from which the values of k_2 are obtained as the gradients.

Substituting the values of π_2 and λ into equation (2.12) and making C_R the subject of the formula, we obtained the new generalized predictive model in terms of salinity as;

$\boldsymbol{C_R = k_2 \frac{\Delta M}{\rho A t} + s\left(\frac{k_2\sqrt{A}}{\rho t}\right)}$ (2.13)

2.3 Experiments to Validate the Model Equations

Mild steel was obtained from a building material shop along Peter Odili Road; Abuloma in Port Harcourt Local Government Area of Rivers State. The chemical composition of the mild steel, as given in Table 2.2 was analyzed using alloy detector from the Inspection Department of Indorama Eleme Petrochemical, Port Harcourt.

The mild steel was cold cut into smaller sheets (coupons) of (50$\pm$2) mm by (20$\pm$2) mm by 1mm dimension, using a cutting machine. A hole was drilled at one end of each of the coupons to allow for the passage of a suspending thread. The coupons were thoroughly surface finished with emery paper and washed. A total of 48 coupons were prepared.

Table 2.2: The Chemical Composition of the Mild Steel

Element	C	Si	Mn	S	Pt	Sn	Cr	Cu	Fe
% Composition	0.14	0.18	0.44	0.40	0.70	0.05	0.01	0.05	98.03

Eight (8) set of polished, tagged and pre-weighed mild steel coupons were immersed and kept suspended with the help of the thread into eighteen (18) transparent plastic containers labelled A to R, containing different salt solutions. Specimen A is the control, Specimen B to F were solutions of various concentrations of sodium chloride in fresh water ranging from $20gdm^{-3}$ to $40gdm^{-3}$.

After 30 days intervals one corrosion coupon from each of the experimental specimen was removed with care, with the help of the thread tied to the coupons. The corrosion products were removed using a hard plastic brush. The samples were then washed, sun dried and weighed with an electronic weighing balance to determine their new weights. The weight loss of each of the samples was determined and recorded. The processes of washing, drying, weighing and recording were repeated consistently until all the 8 coupons from the experimental medium have been exhausted. The experiment lasted for the period of eight (8) months.

The preparation of the salt solution of 20g/dm^3 NaCl was achieved by dissolving 20g of NaCl salt in 1000 cm^3 of fresh water and the flask vigorously shaken. The solution was then poured into a plastic container used for the experiment. This procedure was repeated for other concentrations of 25, 30, 35 and 40g/dm^3.

3.0 Results and Discussion

3.1 Pi Plots for the Derived Corrosion Rate Equations

3.1.1 Corrosion Rate Constant for Control

The values of л_2 against л_1 which were obtained from dimensional analysis of Buckingham Pi theorem, were plotted in Figure 3.1 and regressed to obtain the value for $\mathbf{k_1 = 87.72}$ as the corrosion rate constant in fresh water in the model equation

$$C_R = \mathbf{87.72}\,\frac{\Delta M}{\rho A t'} \qquad (3.1)$$

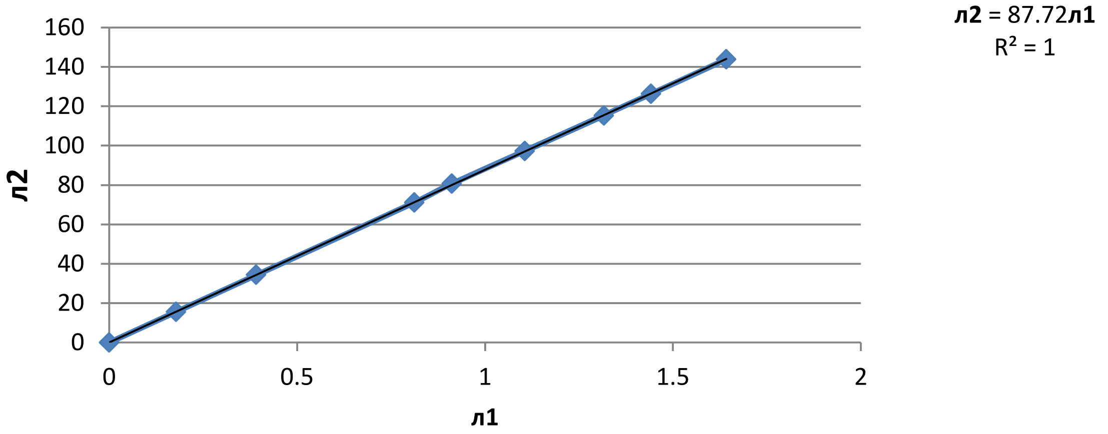

Figure 3.1: Graph of Corrosion Rate Coefficient Versus Weight Loss Coefficient for Fresh Water

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3.1.2 Validation of the Model for the Derived Corrosion Rate Equation

Equation 2.7 derived for corrosion rate of mild steel in fresh water was validated using performance plots of corrosion rates obtained from weight loss and electrochemical methods and literature data shown below in Figures 3.2 and 3.3.

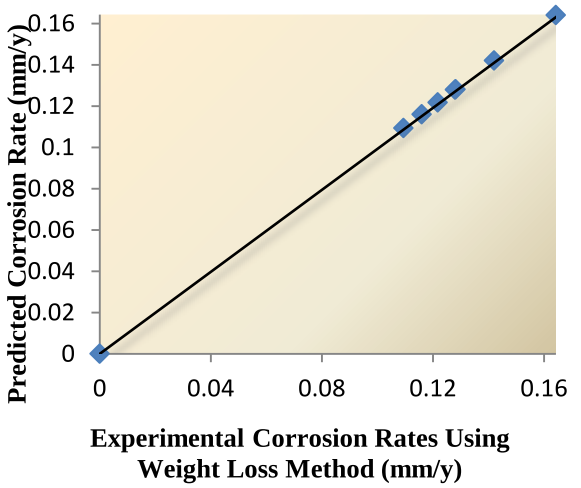


Figure 3.2: Performance Plot for Corrosion Rate

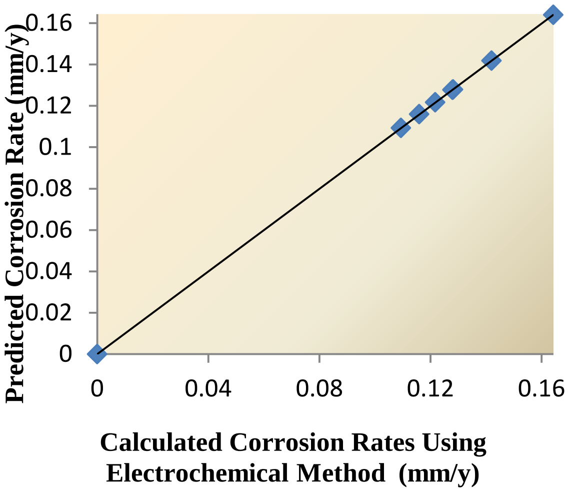


Figure 3.3: Performance Plot for Corrosion Rate

The accuracy and validation of the predictive model was further confirmed using Excel-ANOVA-single factor analysis program, the Mean Absolute Percentage Error

$$\boldsymbol{MAPE} = \left(\left(\frac{E_m - E_e}{E_m} \right) \Big/ \boldsymbol{n} \right) \quad (3.2)$$

and the relationship of Pearson's Correlation Coefficient below

$$\boldsymbol{R} = \frac{n\sum xy - (\sum x)(\sum y)}{(\sqrt{n\sum x^2 - (\sum x)^2})(\sqrt{n\sum y^2 - (y)^2})} \quad (3.3)$$

as shown in the performance measure table below

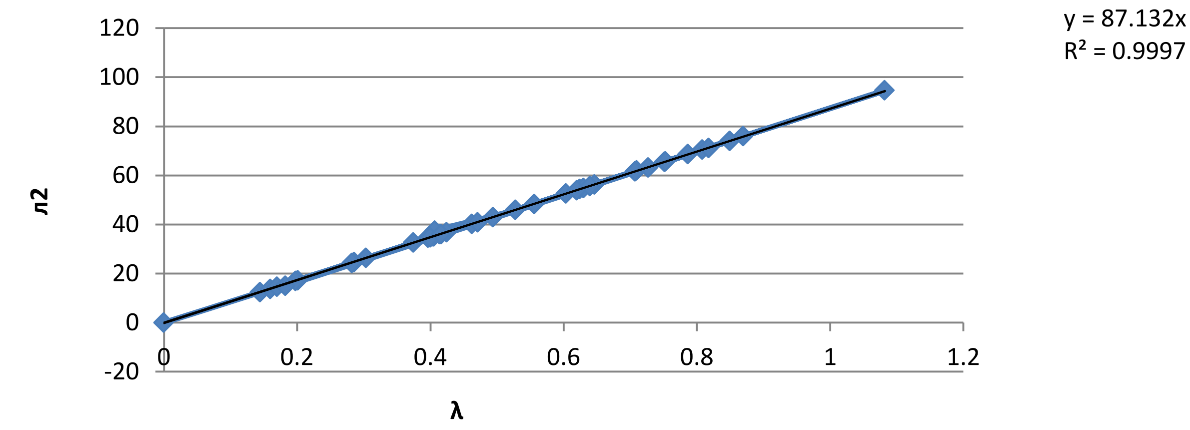
Tale 3.1: Performance Measure of the Derived Corrosion Rate Equation

Performance Measure	**Analysis**
Excel-ANOVA-single factor analysis	P-Value = 0.9824
Mean Absolute Percentage Error (MAPE)	2.46
Pearson's Correlation Coefficient	0.98

The above analysis in the table suggests that the developed model using Buckingham Pi theorem can efficiently simulate the inter relationship between corrosion rate and salinity of the environment and hence is capable of predicting the rate of corrosion of mild steel as a function of salinity with high degree of accuracy and reliability.

3.1.2 Corrosion in Rate Constant for Saline Environment

The values π_2 against λ for various concentrations of salt in fresh water were plotted as shown in Figure 3.4 to obtain the value of k_2 and the generalized model.



Figutre 3.4: Graph of л2 Versus λ for different Salinities

The new corrosion rate equation as

$$C_R = 87.13.\frac{\Delta M}{\rho A t} + s\left(\frac{87.13.\sqrt{A}}{\rho t}\right) \qquad (3.4).$$

With an average corrosion sate constant of 87.13.

This model is made up of two components, the first component, $\mathbf{k_2}\frac{\Delta M}{\rho A t}$, is similar to the standard corrosion rate equation, while the second component, $s\left(\frac{k_2\sqrt{A}}{\rho t}\right)$, is the salinity term. When there is no salinity, $\mathbf{k_2} = \mathbf{k_1}$ and the salinity term is equal to zero and the new generalized predictive model (equation 2.13) reduces to equation 2.7, the classical model, From Figure 3.4, the values of the slopes varies slightly with salinity, plotting the values of the slopes of the pi plots against salinity, as shown below

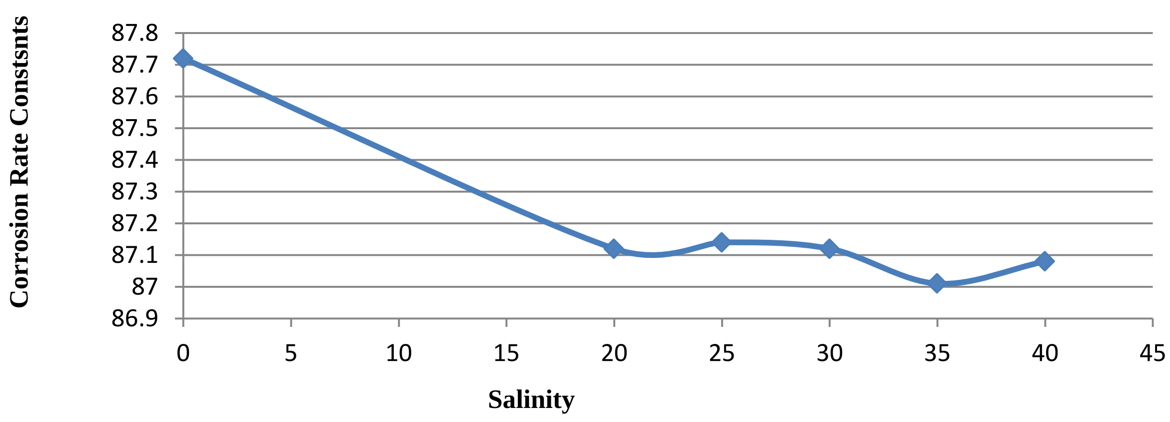


Figure 3.5: Relationship beetween Corrosion Rate Constants and Salinities

We obtain relationship between the corrosion rate constants, and salinity as

$\mathbf{k_2 = k_1 - 0.051s + 0.001s^2 - 1E\text{-}05s^3}$ (3.5).

3.1.2 Validation of the Model for the Unique Predictive Corrosion Rate Model

The accuracy and validation of the predictive model was also confirmed using Excel-ANOVA-single factor analysis, the Mean Absolute Percentage Error, and the relationship of Pearson's Correlation Coefficient, as shown in the table of performance measure,

Tale 3.1: Performance Measure of the Model Using Buckingham Pi Theorem

Performance Measure	Analysis
Excel-ANOVA-single factor analysis	P-Value = 0.6
Mean Absolute Percentage Error (MAPE)	4.67
Pearson's Correlation Coefficient	0.95

The above analysis suggests that the developed model using Buckingham Pi theorem can efficiently simulate the inter relationship between corrosion rate and salinity of the environment and hence is capable of predicting the rate of corrosion of mild steel as a function of salinity with high degree of accuracy and reliability.

Figure 3.6 to 3.7 show the comparison of the plots of the modelled and the experimental corrosion rate results.

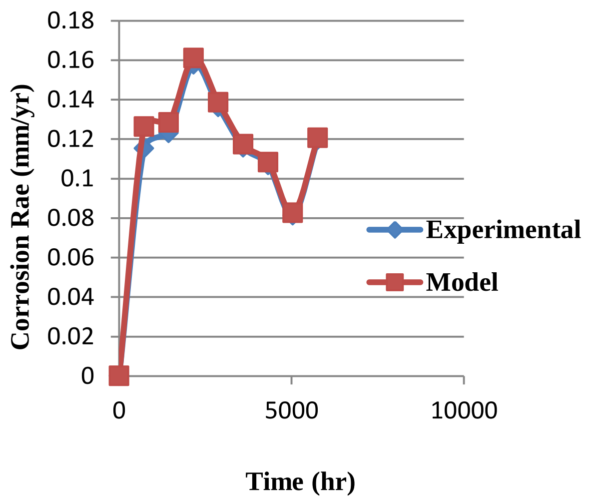


Figure 3.6: Graph of Model Corrosion Rate Versus Experimental Corrosion Rate at Concentration of 20 g/dm³

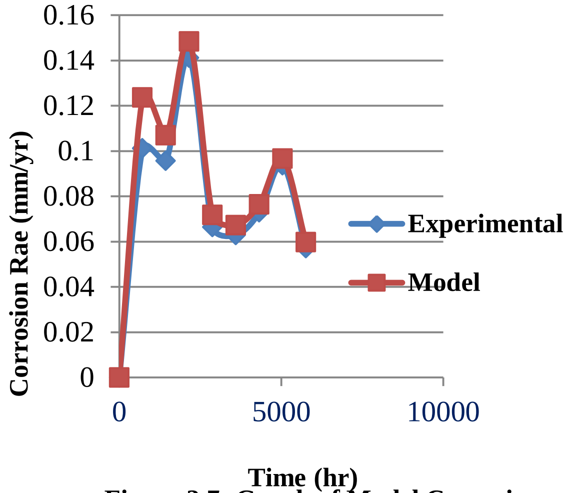


Figure 3.7: Graph of Model Corrosion Rate and Experimental Corrosion Rate Versus Time at Concentration of 40g/dm³ for Fresh Water

The plots of Figures 3.6 and 3.7 above show correlation between the unique predictive model and experimental data for the ranges of salt concentrations between $20g/dm^3$ to $40g/dm^3$

4.0 Conclusion

In this study, a unique predictive corrosion rate model that takes into account the effect of salinity has been successfully developed using Buckingham Pi theorem. The model was validated experimentally and analytically, using various statistical tools which gave a good agreement of above 95%. This unique corrosion rate model which relates corrosion rate constant with salinity levels will be very useful for a more accurate prediction of corrosion rate of mild steel in sea waters.

Nomenclature

Symbol	Definition	Unit
C_R	Corrosion Rate	$mmyr^{-1}$
FW	Fresh Water	-
L	Length of the coupon	m
Δm	Change in Mass	kg
ρ	Density	gcm^{-3}
W	Width of the coupon	cm
T	Thickness of the coupon	cm
S	Salinity	gdm^{-3}
$\pi_1 \left(\frac{\Delta m}{\rho A^{\frac{3}{2}}}\right)$	Weight Loss Coefficient	-
$\pi_2 \left(\frac{C_R}{A^{\frac{1}{2}}}\right)$	Corrosion Coefficient	-
$\pi_3 \left(\frac{S}{\rho}\right)$	Salinity Coefficient	-
λ	$\pi_1+\pi_3$	-
I_{corr}	Corrosion Current Density	Acm^{-2}
N	Valence	-
EW	Equivalent Weight	-
F	Faraday's Constant	C

M	Molecular Weight of Metal	$gmol^{-1}$
T	Time	sec

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