VOL. 8, NO. 8, AUGUST 2013 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

MODELING OF THE CORROSION RATE OF STAINLESS STEEL IN MARINE OIL ENVIRONMENT

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ABSTRACT

Experimental corrosion rate data of two stainless steel grades (430 and 316) when subjected to a typical oil bearing marine environment have been generated. Empirical model equations for predicting the corrosion rates of the two steel grades were developed using the dimensional analysis of Bukinham-Pi method. Regression analysis was used to curve fit the experimental data, thus obtain the correlation factor in the model equations developed. The model equations were used to predict the corrosion rates for the two steel grades and the predicted rates were found to match the experimental rates perfectly in the time interval investigated.

Keywords: corrosion rate model, stainless steel, marine.

INTRODUCTION

Corrosion is the destruction of a metal by chemical or electrochemical or microbial reactions with its environment (Chillinger *et al*., 2008). This impact is evident in equipments made of metals when exposed to corrosion enabling environments, when corrosive reactions occur within or corrosive fluids are transported through or stored in such equipments. The cost of this destruction on the equipment/process is huge hence it is expedient that equipments are designed to withstand such impact, for safe conditions, are cost effective and fabricated with appropriate materials.

The adequate design of equipments used in corrosive environments and for corrosive processes should therefore include appropriate corrosion prevention/control measures and the selection of appropriate construction material. To do such design effectively and efficiently manage corrosion requires the availability of reliable corrosion data of materials of construction of process equipments and pipes. Most corrosion rate data in reference sources are indicative and can be very unreliable. This is because corrosion is not a property. It is a process that manifests in a variety of forms and affected by numerous factors, also Engineering materials are usually characterized by their bulk properties such as yield strength, modulus and thermal conductivity (Gosta, 1981). Thus, corrosion rates are not therefore fixed values and corrosion often remains unpredictable in a quantitative sense (Johnson, 1981). Moreover, the corrosion process is often controlled by stochastic phenomena.

Corrosion data can be obtained from on-line monitoring of corrosion processes and from mathematical models that predicts the corrosion rate of the equipments or metal of construction. On-line monitoring involves the insertion of monitoring probes through the vessel or pipes to obtain the extent and rate of corrosion as the corrosion proceeds in/on the pipe or process (Pludek, 1979); while mathematical models involves the use of appropriate mathematical equations to predict the extent and rate of corrosion in/on the pipe or process.

Different/various on-line corrosion monitoring techniques abound (Pludek, 1979), mathematical models for predicting corrosion rates of equipments/metals are also available (Faeshad and Rieke, 2008; Farshad *et al*., 2010; Garber *et al*., 2008). Such models if available would be used to predict the corrosion rates before the corrosion occurs, hence the necessary information required for designing and planning effective control/mitigating measures are obtained.

Corrosion could be as a result the reaction within the equipment or due to the impact of the environment or reaction of the environment with the metal of construction of the equipment (Robet, 1980). Studies abound (Bilogan, 1983, Garber *et al*., 1998; Farshad *et al*., 2000; Garber *et al*., 2001) on models for the rates of corrosion due to corrosive reactions of fluids within equipments, however models for the rates of corrosion due to the environmental impact or reaction with the metals of construction of equipments are sparse. This gap, this work seeks to fill.

In this work a simplified model for the determination of corrosion rates of stainless steels for the construction of equipments used in a typical marine environment where oil exploration and production activities occur was developed.

If an appropriate mathematical model is available that can accurately predict the rate of corrosion before the corrosion occurs, it will save the huge cost of combating and monitoring corrosion and enable the design of the appropriate control measures and the selection of the right fabrication material for specific application.

MATERIALS AND METHODS

The experiment was conducted in a typical oil producing marine environment in the Niger Delta area of Rivers State, Nigeria. The two steel grades (430 and 316) used in this experiment were purchased at the Mile 3 building materials market in Port-Harcourt, Rivers State

Nigeria. The experiment was conducted at oil bearing marine environment in Rivers State, in the Niger Delta region of Nigeria.

Experimental determination of corrosion rate

Two pieces of commercial steel grades 430 and 316 with composition as in Table-1 were used for the corrosion experiment.

Table-1. Composition of Specie type 430 and 316 (Nigerian Agip Oil Company, 1983).

Steel type	Element, wt.%							
	C	S	P	Si	M_n	N_i	C_r	M_o
430	0.08	0.018	0.025	0.34	0.42	0.27	16.2	0.05
316	0.04	0.017	0.026	0.42	1.55	10.80	17.7	2.70

A 50 x 50mm size test specimen of each steel grade was cut and prepared in a metallographic manner to a 1um diamond finished, glued to Bakelite spacers and labeled specimen A and B. The test specimens were weighed on an analytical balance to ascertain the weights of the specimens. These specimens were then exposed vertically to the rural oil bearing environment for a period of three (3) months. The specimens were removed from the corrosive environment; the surfaces of the specimens were cleaned with ethanol to remove oil, grease or resin and mechanically using a metal brush to remove corrosion products with minimal removal of metal. The specimens were then reweighed to obtain the weight loss. Pit depths on the steel samples were also determined using the calibrated fine focus control on a microscope after polishing.

The experiment was repeated (the specimens exposed again to the corrosive environment) and the weight loss obtained after 6, 9, 12, 15 and 18 months of exposure.

The data obtained were used to determine the experimental corrosion rate using the equation:

$$R_i = \frac{W_L}{\rho A t} \quad (1)$$

Development of theoretical model for corrosion rate

The theoretical corrosion rate model was developed using the method of dimensional analysis. An algorithm to develop the corrosion rate model by dimensional analysis using the Buckingham-Pie technique (Wan, 1989 and Gibbings, 2011) is outlined in Figure-1.

The algorithm developed in Figure-1 was followed as detailed in Appendix 1 to obtain the expression for the theoretical corrosion rate model as:

$$R_c = A_f\left(\frac{V.t.\mu}{A.\rho_o}\right) \quad (2)$$

The developed corrosion rate model equation (2) can be expressed in terms of known experimental parameters as follows:

$$R_c = A_f\left(\frac{{}^{m}/_{s}\, {}^{s.kg}/_{ms}}{A.\rho_0}\right) = A_f\left(\frac{kg}{s.A.\rho_0}\right) \quad (3)$$

$$R_c = A_f\left({}^{W_L}/_{t.A.\rho_0}\right) \quad (4)$$

Where A_f is the dimensionless corrosion rate correction factor, $W_L =$ Weight loss of the Specie (kg), $t =$ Exposure time (yrs), $A =$ Area of specie in contact with corrosive Fluid (m^2), $\rho =$ Density of the specie (kgm^{-3}).

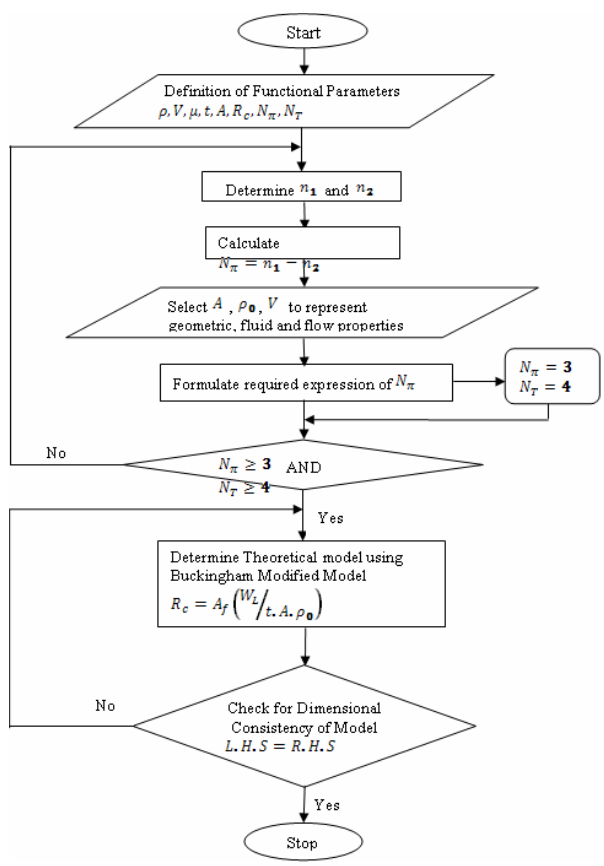

Figure-1. Algorithm for development of theoretical corrosion rate model.

VOL. 8, NO. 8, AUGUST 2013 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

Determination of dimensionless corrosion rate correction factor

The empirical/theoretical corrosion rate model developed is expected to predict the corrosion rates obtained experimentally, therefore:

$$Ri \equiv Rc \quad (5)$$

$Ri =$ Experimental corrosion rate; mmpy
$Rc =$ Predicted corrosion rate by developed model; mmpy
Hence equation (4) can be re-written as:

$$Ri = {A_f . W_L}/{A . \rho . t} \quad (6)$$

To obtain A_f, equation (6) was re-written in the form of the equation of a straight line $y = mx + c$ as:

$$\ln\left(\frac{1}{Ri}\right) = \ln\left(A . \frac{\rho}{A_f}\right) + \ln\left[\left(\frac{t}{W_L}\right)\right]$$

where m the slope of the equation corresponds to 1 and c the intercept corresponds to $\ln\left(A . \frac{\rho}{A_f}\right)$. The experimental corrosion rate data of the weight loss for the steal samples were used to plot a graph of $\ln\left(\frac{1}{Ri}\right)$ against $\ln\left[\left(\frac{t}{W_L}\right)\right]$ for the two specimens. The Newton non-linear regression method of polymath was used to fit linear equations to the experimental plots generated. The intercept from these equations were equated to $\ln\left(A . \frac{\rho}{A_f}\right)$, from which A_F values were obtained. The graphs and the corresponding linear equations are shown in Figures 2 and 3.

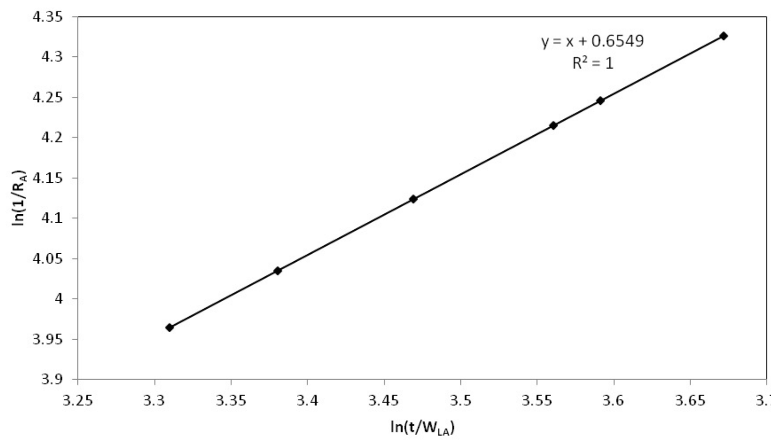

Figure-2. Determination of dimensionless correlation factor for steal grade 430.

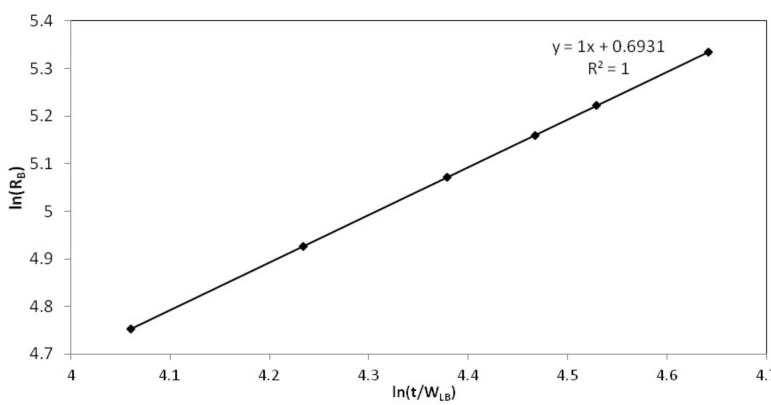

Figure-3. Determination of dimensionless correlation factor for steal grade 430.

RESULTS AND DISCUSSIONS

At the end of the eighteen months period the experiment was conducted, the following observations were made:

Pit depth on steel samples

Various interesting features were observed from examination of the steel samples under the microscope. The Pits on the steel samples due to corrosion were crystallographic in nature and hexagonal in shape. Pit grew to its maximum dimension within a relatively short period of time.

Weight loss of steel samples

The weight loss of specimen A and B (stainless steel grade 430 and 316) observed at three months interval of time for a period of eighteen months (one and a half years) are shown in Figure-4.

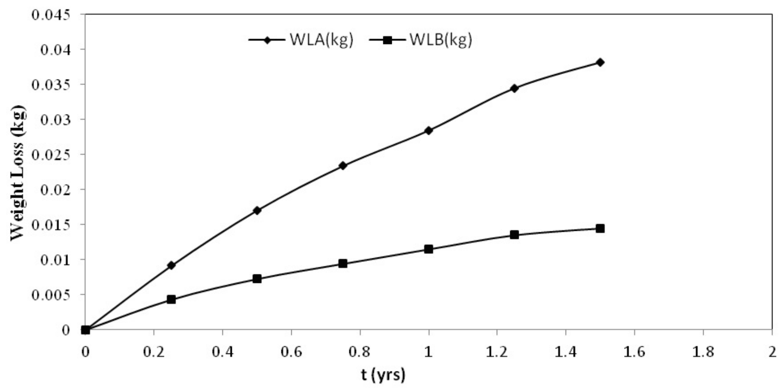

Figure-4. Weight loss of steel samples with exposure time.

Figure-4 showed an increase in weight loss with time for both stainless steel grades; however the weight loss is much more in specimen A (stainless steel grade 430).

Corrosion rate

The experimental data of weight loss were used to generate the experimental corrosion rates using equation 1. The corrosion rates are shown in Figure-3.

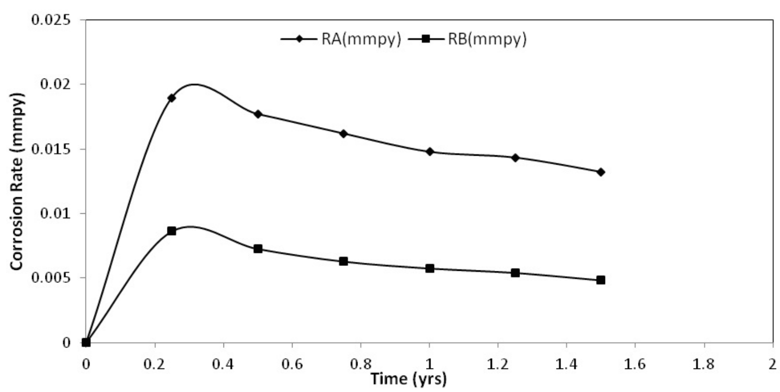

Figure-5. Experimental corrosion rate with exposure time.

Figure-5 showed that the corrosion rate of both specimens increased in the first three months, thereafter the corrosion rate gradually decreased throughout the experimental period.

The effects of corrosion rate on weight loss of the two stainless steel grades are shown in Figures 6 and 7 respectively.

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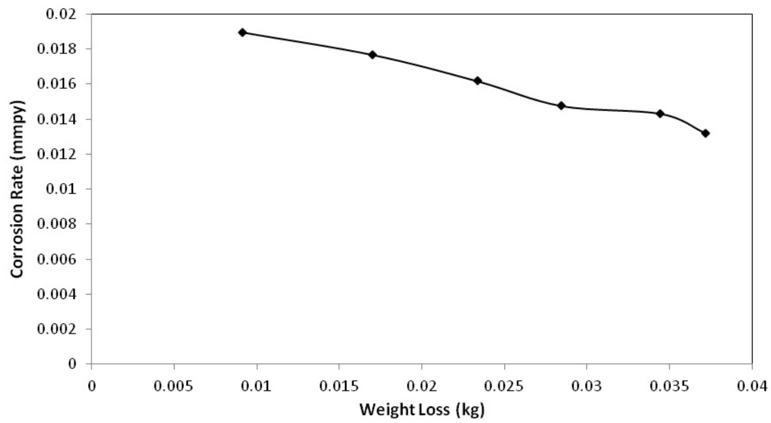

Figure-6. Corrosion rate of sample A with weight loss.

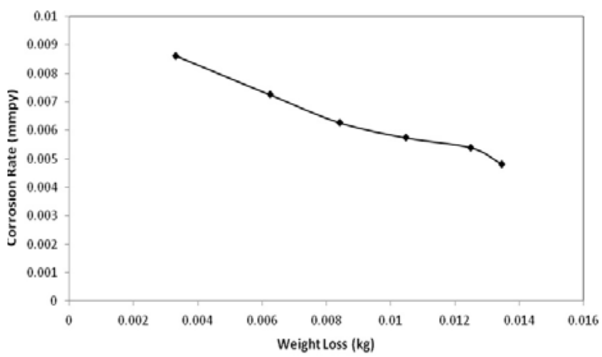

Figure-7. Corrosion rate of sample B with weight loss.

These results showed that stainless steel grade 316 were more corrosion resistant than the 430 grade. This is due to the high content of nickel (a high corrosion resistant compound) in the 316 grade as seen from the Table-1. The 316 grade also has a higher composition of molybdenum which has been found to improve resistance to pitting (Bilogan, 1983). Thus the 430 steel grade corroded more than the 316 grade in the environment they were subjected to and the time interval investigated.

COMPARISON OF EXPERIMENTAL AND THEORETICAL CORROSION RATES

The linear equations generated from Figures 2 and 3 were used to obtain the corresponding corrosion rate correction factor for the two stainless steel specimens. These corrosion rate correction factors were substituted into the developed model equations to generate the required model equations for determining the corrosion rate of the two steel grades. These equations were then used to predict the corrosion rates of the two steel specimens at the time interval under investigation. The corrosion rate predicted by the model equations were plotted alongside the corrosion rates obtained experimentally for comparison in Figure-8.

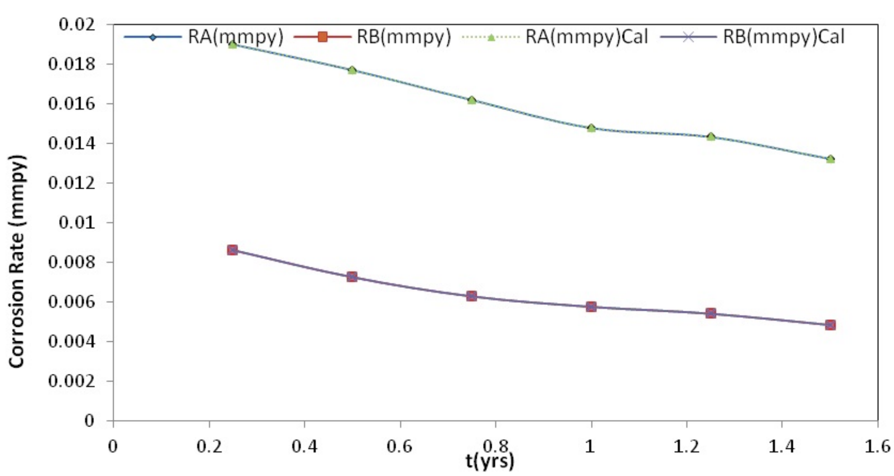

Figure-8. Experimental and model predicted corrosion rates for the two steel grades.

Figure-8 shows a perfect match between experimental corrosion rates and the corrosion rates predicted by the developed models for the two steel grades for the time interval investigated.

CONCLUSIONS

Corrosion rate data of two stainless steel grades (430 and 316) when subjected to a typical oil bearing marine environment have been generated experimentally. Empirical model equations for predicting the corrosion rates of the two steel grades were developed using principle of dimensional analysis of Bukinham-Pi. Regression analysis was used to curve fit the experimental data, thus obtain the correlation factor in the model equations developed. The model equation were used to predict the corrosion rates for the two steel grades and the predicted rates were found to match the experimental rates perfectly in the time interval investigated. The corrosion rate model equations developed can be used to predict the corrosion rate of steel structures and equipments used in the marine environments.

Nomenclature

A =	Area of specie in contact with the fluid (m^2)
A_f =	Theoretical Corrosion rate dimensionless number
N =	Number of dimensionless number
R_c =	Theoretical corrosion rate (mmpy)
R_i =	Experimental corrosion rate (mmpy)
t =	Exposure time of specie in contact with the fluid (yrs)
V =	Velocity of corrosive fluid (m/s)
W_L =	Weight loss of the Specie (kg)
μ =	Viscosity of corrosive fluid (Ns/m^2)
ρ_0 =	Density of corrosive fluid (kg/m^3)

REFERENCES

Bilogan K. 1983. Corrosion cracking phenomenon under different polarizing and microstructure conditions in a 304 stainless steel. Corrosion Journal of NACE (National Association of Corrosion Engineers). 39(12): 508-514.

Chillingar G. V., Mourhatch R. and Al-Qahtani G. D. 2008. The Fundamentals of Corrosion and Scaling, Gulf Publ. Company, Houston, TX, USA. p. 276.

Farshad F. F., Garber J. D. and Polaki V. 2000. A comprehensive model for predicting corrosion rates in gas well containing CO_2. SPE Prod. and Facilities. 15(3): 183-190.

Farshad F. F., Garber J. D, Rieke H. H and Komaravelly Sh. G. 2010. Predicting Corrosion in pipeline oil wells and gas wells, a computer modeling approach. Transaction C: Chemistry and Chemical Engineering. 17(1): 86-96.

Farshad F. F. and Rieke H. H. 2008. Gas well optimization: A surface roughness approach. CI/PC/SPE Gas Technology Symposium Joint Conference, Calgary, Alberta, Canada. p. 8.

Garber J. D., Farshad F. F. and Reinhart J. R. 2001. A model for predicting corrosion rates on oil wells containing carbon dioxide. SPE/EPA/DOE Exploration and Production Environment Conference, San Antonio, TX, USA. p. 21.

Garber J. D., Farshad F. F., Reinhart J. R., Hui Li and Kwei Meng Yup. 2008. Prediction pipeline corrosion. Pipeline and Gas Technology. 7(11): 36-41.

Garber J. D., Polaki V., Varansi N. R. and Adams C. D. 1998. Modeling corrosion rates in non-annular gas condensate wells containing CO_2. NACE Annual Meeting. p. 53.

Gibbings J. C. 2011. Dimensional Analysis, Springer, ISBN 1-84996-316-9.

Gosta W. 1981. An Introduction to Corrosion and Protection of Metals. Buttler and Tonner ltd. Publishers. pp. 62-63.

Johnson K. E. 1981. Role of inclusions in the atmospheric pitting of stainless steel. British Corrosion Journal. 15(3): 123.

Nigrian Agip Oil Company (NAOC). 1983. Characteristic of materials, maintenance technical course, Italy.

Pludek V. R. 1979. Designing and Corrosion Control, Macmillan Press Limited, London, UK. 16-33, 196-225.

Robert B. R. 1980. Metallic Materials Specification and Handbook. 3rd Ed. E and F. N Spon limited USA. p. 347.

Sinnott R. K. 2006. Chemical Engineering Design. Coulson and Richardson Series. 4th Ed. p. 6.

Wan F. Y. M. 1989. Mathematical models and their Analysis. Harper and Row Publishers, New York, USA. ISBN 0-06-046902-1.

APPENDIX

The corrosion rate of any given specie has been found to be dependent on the following parameters density of the corrosive fluid (ρ_0), velocity of the corrosive fluid (V), viscosity of the corrosive fluid (μ), exposure time of the specie (t) and area of the specie in contact with the fluid (A) (Sinnott, 2006).

Following the Buckingham pi technique (Wan, 1989 and Gibbings, 2011), the Predicted corrosion rate can be expressed as:

$$R_c = A_f[V, \mu, t, \rho_0, A] \quad (7)$$

Where

$R_c =$ Predicted corrosion rate; (ipy)

$A_f =$ Theoretical corrosion rate dimensionless number

The dimensions of the parameters in equation (7) are as follows:

$$R_c = {}^{m}/_{s} = LT^{-1} \quad (8)$$

$$V = {}^{m}/_{s} = LT^{-1} \quad (9)$$

$$\mu = {}^{Ns}/_{m^2} = {}^{kg.m.s}/_{s^2m^2} = {}^{kg}/_{ms} = ML^{-1}T^{-1} \quad (10)$$

$$\rho_o = {}^{kg}/_{m^3} = ML^{-3} \quad (11)$$

$$A = m^2 = L^2 \quad (12)$$

The algorithm of the Buckingham-Pie technique as developed in Figure-1 is implemented as follows:

The number of dimensionless numbers known as Pie groups; N_π is:

$$N_\pi = n_1 - n_2$$

$n_1 =$ Number of variables

$n_2 =$ Number of independent basic dimensions

$$N_\pi = 6 - 3 = 3$$

That is a total of three pie groups;

$$\pi_1, \pi_2, \pi_3$$

Equation (7) could be rearranged to give;

$$f_1(R_c, V, \mu, t, \rho_o, A) = 0 \quad (13)$$

In terms of the pie groups

$$f_1(\pi_1\pi_2\pi_3) = 0 \quad (14)$$

Number of terms to be placed in each pie group becomes;

$$N_T = n_2 + 1 = 4 \quad (15)$$

If 'A' represent geometric property and ρ_0 the fluid property, then:

$$\pi_1 = A^x.\rho_0^y.V^z.R_c \quad (16)$$

$$\pi_2 = A^a.\rho_0^b.V^c.t \quad (17)$$

$$\pi_3 = A^p.\rho_0^q.V^r.\mu \quad (18)$$

From equations (8), (9) (10) and (11):

$$\pi_1 = L^{2x}.(ML^{-3})^y.(LT^{-1})^z.LT^{-1} \quad (19)$$

$$\pi_2 = L^{2a}.(ML^{-3})^b.(LT^{-1})^c.T \quad (20)$$

$$\pi_3 = L^{2p}.(ML^{-3})^q.(LT^{-1})^r.ML^{-1}T^{-1} \quad (21)$$

The unknown superscripts were obtained thus:

$$M^0.L^0.T^0 = L^{(2x-3y+z+1)}.M^y.T^{(-z-1)} \quad (22)$$

$$M^0.L^0.T^0 = L^{(2a-3b+c)}.M^b.T^{(-c+1)} \quad (23)$$

$$M^0.L^0.T^0 = L^{(2p-3q+r-1)}.M^{q+1}.T^{(-r-1)} \quad (24)$$

Comparing the exponents on both sides of equation (22), (23) and (24) individually results in a set of simultaneous equations which were solved to obtain the coefficients in the equations as:

Substituting these values into equations (19), (20) and (21) gives the expressions for pie groups as:

$$\pi_1 = \frac{R_c}{V} \quad (25)$$

$$\pi_2 = \frac{Vt}{\sqrt{A}} \quad (26)$$

$$\pi_3 = \frac{\mu}{(\sqrt{A}.\rho_o.V)} \quad (27)$$

Substituting equations (25), (26) and (27) into (14) gives:

$$f_1\left(\left(\frac{R_c}{V}\right)\left(\frac{Vt}{\sqrt{A}}\right)\left(\frac{\mu}{(\sqrt{A}.\rho_o.V)}\right)\right) = 0 \quad (28)$$

Equation (28) rearranged and simplified to give the expression for determining the corrosion rate as:

$$R_c = A_f\left(\frac{V.t.\mu}{A.\rho_o}\right) \quad (29)$$