

MODELING AND COMPUTER SIMULATION OF CATHODIC PROTECTION OF STEEL STRUCTURE

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ABSTRACT

Formation of calcareous deposit influences applied potential and current for long-term protection of offshore structures. A model is proposed to predict the applied potential-time history with an aim to establish mathematical correlation between applied potential on cathodically protected surface and time by computer simulation technique, following principles of electrochemical kinetics. Comparative studies between experimental and numerical analysis data show good agreement. The model opens up a method of determination of applied current and potential required to be maintained after certain period of exposure of the steel structure using simple laboratory polarization experimental data at different slope parameters and computed rate constant of calcareous deposit formation..

KEYWORDS. *cathodic protection, calcareous deposit, slope parameter, potential decay, numerical simulation, offshore structure*

INTRODUCTION

Cathodic protection for the submersed portion of steel offshore structure with or without coating is the most technically appropriate and economically viable corrosion protective method. The fundamental criteria for cathodic protection is to cathodically polarize the structure to a potential of 0.80V vs. silver-silver chloride electrode or more negative potential^{1,2}. Protection of an offshore

structure such as a petroleum production unit is normally accomplished by galvanic anode. Historically cathodic protection (CP) design procedures have been

carried out through trial and error method using a single long-term current density². During the last 10 to 15 years, CP was based on rapid polarization technique whereby a high initial current was applied for formation of protective calcareous deposit, which gives rise to a low maintenance current density⁽³⁻⁴⁾. Recently a technique based on of slope parameters is being applied for sacrificial cathodic protection of offshore structures⁵⁻⁸.

Advent of newer methods have developed the CP design systems in many respects including lower mass of anode consumption but still at times cathodic protection systems fail due to over protection or under protection. One of the major problems that people face while designing the cathodic protection is the applied potential or current change from the position of the anode over the surface of the structure. While the distributed anode arrays on space frames such as production platforms tend to provide relatively uniform polarization, the unidimensional pipe gives rise to a problem of potential attenuation with increasing distance. Computer aided mathematical models have been developed to estimate current and potential distribution using Laplace's equation $\nabla^2\Phi=0$ ^{7,11-14}.

Formation of calcareous deposit is a very important aspect for cathodic protection of offshore structure. It not only influences potential and current distribution but the kinetic aspect of its formation determines applied potential and current for long term protection of marine offshore structure⁸. In the present investigation attempts have been made to find a mathematical correlation between cathodic polarized protection potential and time. The complexity of physical, chemical and biological phenomena occurring on cathodically protected surface does not permit a simple relation to exist between them.

Thus with the aid of suitable numerical interpolation methods and computer simulation a relation is proposed.

EXPERIMENTAL PROCEDURES

Low carbon steel rod of 1 cm diameter and 10 cm long of which 2 cm was immersed in sea water collected from the Bay of Bengal, Digha region, Midnapur district. The water was allowed to flow in with a uniform velocity controlled by a pump and electrical control unit to a rectangular refractory container. The water was drained out through a hole at the other end and collected in a reservoir from where the water was pumped into the refractory vessel. Thus a water circulation was maintained with a fixed volumetric flow rate. Linear velocity of the fluid was determined at various points around the steel surface up to a distance of 1 cm. to the either side and the average of them is reported (Table-1). The conditions of the fluid were so maintained that it was very close to real system at Digha ocean in respect of fluid properties (Table-1). The system was polarized cathodically by sacrificial Zn anodes. Polarized potential of steel against a saturated calomel electrode as well as applied current were recorded with time. Some experiments were also conducted by polarizing with impressed current against a graphite auxiliary electrode. External resistances of 300, 400 600 and 800 ohms were connected to the circuit to vary the slope parameter. The polarized potential and current are recorded with time. The experimental set is illustrated in a schematic diagram in figure 1.

RESULTS AND DISCUSSION

The characteristic of cathodic polarization curves with variation of exposure time has been illustrated in figure 2. It is seen after a span of 3 months in sea water, the polarization shifts to a more

negative potential and lower current density. This is due to formation of calcareous deposits. This fact creates a major problem while estimating required applied potential and current for long term cathodic protection of offshore structures. Figure 3 illustrates variation of applied potential with time at different slope parameters. By connecting various external resistances the slope parameters have been selected in accordance with data of real offshore structures ^{6,15} from the following first principle based relation between cathodic potential (Φ_c) and cathodic current density i_c ,

$$\Phi_c = (R_t A_c) i_c + \Phi_a \quad (1)$$

Where R_t is the total circuit resistance, A_c is the cathode surface area and Φ_a is the anode potential. The slope parameter $S = R_t A_c$ for laboratory specimen is equivalent to $(R_t A_c)/N$ for actual structure ⁶. It is seen that potential decays with time for all the curves and lower the slope parameter the faster is the rate of decay. Similar trends for variation of current with time at different slope parameters are shown in figure.4.

Proposed Model

Base on the observations above an equation of following nature is proposed to predict cathodic polarized potential after a certain passage of time from its initial potential, slope parameters and others factors, influencing the fluid properties of the corrosive media.

$$E_t = E_i - \chi e^{kt} + S i_c \quad (2)$$

Where E_t is cathodic potential after t time, E_i is the initial polarized potential, t is the time, k is the rate constant (fraction reacted /hr) which is the rate formation calcareous deposits in unit time at a fixed temperature, and fluid properties of sea water and χ is a constant. Such that when $t=0$ that is no time for

deposition, E_t becomes close to E_i . Similarly if $k=0$, that is without any formation of calcareous deposits E_t tends to E_i .

The proposed equation (2) seems to be justified from the trend of the curves as depicted in figure 3. Since applied cathodic current density i_c also decreases with time exponentially from its initial value i_0 (figure 4), so i_c can also be expressed as

$$i_c = i_i - \psi e^{kt} \quad (3)$$

When ψ is another constant.

Since the effective anode diameter decreases with time due to corrosion, the slope parameter is expected to increase with time, but it is assumed constant here for the time being and its influence over the exposure time^{7,11-13} is left over for next course of study.

Combining equations (1) and (2), we have

$$E_t = E_i - \chi e^{kt} + S(i_i - \psi e^{kt}) \quad (4)$$

The above equation relates cathodic potential after formation of some calcareous deposits with kinetics of rate of formation which itself is related to chemical potentials of reactants and products, temperature, time, current density which relies on severity of corrosive fluid, applied polarized potential dependent on nature of materials, and environment, and finally slope parameter which takes care of polarization behavior and shapes of cathode and anode. Thus the proposed equation considers all the possible parameters, which are expected to influence the formation of calcareous deposits.

Numerical methods and subsequent computer programming using experimental data generated by simulating the conditions of real offshore structure with laboratory specimen solve the equation.

Numerical and Computational methods

Expansion of $e^x = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \frac{x^4}{24} + \frac{x^5}{120} + \frac{x^6}{720} + \dots$ (5)

The term e^{kt} in the equation (4) can be expanded in the above manner and then if all the terms are rearranged, then equation (4) can be expressed as polynomial of function t as follows.

$$E_t = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + \dots + a_n t^n \quad (6)$$

Provided E_i , i_i , k and S are assumed to remain fixed. The assumptions are justified for an offshore structure to be hoisted in a particular region of ocean and generating some data by few laboratory simple experiments.

The equation (6) is solved by two different numerical methods **Divided differences method and Least squares approximation for Non linear curve**. Programs are written in Microsoft Visual C++ which aim at fitting the data by thousands times iterations till a desired level of accuracy is obtained. The program also computes errors for different degree of polynomial n and compares them and hence that number as degree of polynomial where the error is minimum.

Table 2 depicts degree of polynomial with level of error for different sets. It is interesting to see that irrespective of any slope the polynomial for which the error is minimum is always 5, and hence degree of 5 is considered and accordingly the sets of -developed equation become as given in Table-3.

It is to be noted that constant term a_0 in each equation is close to its initial polarized potential (see figure 3). Figure 5 compares experimental data with those generated by computational techniques. Results obtained with the numerical method of Least Square for nonlinear curve give better matching beyond certain amount of time when a good amount of calcareous deposit has formed. While the curve with Divide difference method is more close to experimental one during the initial stage.

To find out the rate of formation of calcareous deposit k , the equation (3) is rewritten in a modified form as below.

$$\ln (S_i + E_i - E_t) = kt + \ln \lambda \quad (7)$$

Where λ is a constant here.

Plot of $\ln (S_i + E_i - E_t)$ vs. t should give straight line with a slope equal to rate constant k . Fig.6 shows the plots with regression analysis. Here all the lines are parallel with almost equal slope (Table4). The rate constant value of 0.0014 fractions reacted per hour remains same irrespective of change in slope parameter in this particular environment.

Once the rate constant k has been determined, the constant ψ can be found out from the slope of the linear plots of I_c vs. e^{kt} (see equation 3) as shown in fig. 6. It is seen the value of constant ψ for all four lines are close and mean of them has been taken as 166.45 (Table -5). Similarly the best fit linear plots of E_c vs. e^{kt} (see equation 2) produce slopes which are comparable (fig.8 and Table - 5)) and the constant χ is found out.

Substituting the equation (2) with computed determined constants the final derived proposed model equation is

$$E_t = E_i - 523.74e^{-0.0014t} + S (i_i - 166.45e^{-0.0014t}) \text{ -----(8)}$$

Validity of the derived equation

Applied potential and current density obtained after exposure of the steel structure for a fixed interval of time are calculated using above equation and their values are compared with those found in real situation¹⁶ under similar type of conditions and the results are found to be comparable.

Finally a window based software was developed , whereby applied potential and current required after 5 or 10 years from instalation could be predicted simply by feeding laboratory polarization data of of current and potential with time at a particular slope parameter .

CONCLUSIONS

A model is developed by computer simulation technique for correlating applied potential on cathodically protected surface in sea water with time with an aim to predict the applied potential that would ultimately be needed to protect an offshore structure after a good amount of calcareous deposit has formed to attain a steady state condition. It is demonstrated by the model that using polarization data generated by simple laboratory experiments under similar conditions as those in real offshore structure better methodology of estimating steady state applied potential and hence current can be obtained for long term cathodic protection. The present investigation also proposes new approach of finding rate constant of formation of calcareous deposits using polarization data. It further endeavors to show the influence of slope parameter on potential and current decay and rate kinetics.

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TABLE-1

FLUID PROPERTIES OF SEA WATER USED

Density Gm/cc	Resistivity Ω m	pH	Average Bulk linear velocity m /s	Viscosity cp	Temperature Deg. C	Dissolved 101 Mol/CM3	Reynolds Number	Nature of Fluid flow
1.0241	0.35	7.9	0.15	1.103	25	2.39	27854	Turbulent

Table-2

RESULTS OF LEASTSQUARE METHOD FOR NON-LINEAR CURVE

Degree of Polynomial	Level of Error for different Slope Parameter			
	0.90 Ω m ²	1.20 Ω m ²	1.80 Ω m ²	2.40 Ω m ²
1	0.00457363	0.000763767	0.000570586	0.00134131
2	0.00299174	0.000850436	0.00010524	0.000125383
3	0.00240196	0.000821289	0.000124958	7.10391e-005
4	0.00111055	4.6742ge-005	2. 12204e-005	4.24865e-005
5	0.00108048	3.4451e-005	1.656ge-005	3.46033e-005
6	0.00160081	5.26083e-005	2. 17335e-005	5 .34466e-005
7	0.00240256	7. 13644e-005	4.00721e-005	0.000106243
8	0.0046454	0.00011372	0.000570586	0.120785461

Table -3
RELATION BETWEEN POLARIZED POTENTIAL AND TIME

Slope Parameter Ωm^2	$E_t = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4$
0.9	$E_t = -0.723979 - 0.0153735 t + 0.000284215 t^2 - 2.34039e-006 t^3 + 6.0388e-009 t^4$
1.2	$E_t = -0.72911 - 0.0074727 t + 0.000136959 t^2 - 1.09382e-006 t^3 + 2.81452e-009 t^4$
1.8	$E_t = -0.71981 - 0.00449734 t + 5.35119e-005 t^2 - 3.12135e-007 t^3 + 1.47204e-010 t^4$
2.4	$E_t = -0.717608 - 0.00138381 t + 1.03669e-006 t^2 - 4.09036e-008 t^3 + 2.34344e-010 t^4$

T ABLE-4
DETERMINATION OF RATE CONSTANT

Slope Parameter Ωm^2	Degree of linearity R^2	Rate constant K fraction reacted lhr
0.9	0.8854	0.0014
1.2	0.9584	0.0014
1.8	0.9922	0.0014
2.4	0.9469	0.0013

Table-5
COMPUTED VALUES OF CONSTANTS ψ AND χ

Slope Parameter Ωm^2	ψ mA/m^2	Mean ψ mA/m^2	χ mV	Mean χ mV
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0.9	163.23	166.45	501.69	532.74
1.2	169.43		542.96	
1.8	171.21		546.91	
2.4	161.91		503.42	

Table-6

COMPUTED VALUES OF CURRENT DENSITY AND POTENTIAL

Slope Parameter Ωm^2	Time t hours	I_i mA/m ²	I_c mA/m ²	I_c mA/m ² (Literature) ¹⁶	E_i mV Vs. SCE	E_c mV Vs. SCE	E_c mV (Literature) ¹⁶
0.61	480	150	65.226	65.00	-980	-1207.81	-1100
1.38	1000	110	69.065	51.00	-920	-953.907	-980.00
5.82	2000	80	69.905	45.00	-750	-875.014	-850.00
0.30	480	320	235.226	218.00	-1020	-1217.03	-1105.00
0.66	500	300	217.568	187.00	-800	-916.617	-1020.50
1.20	1000	100	59.065	67.00	-790	-848.339	-998.00

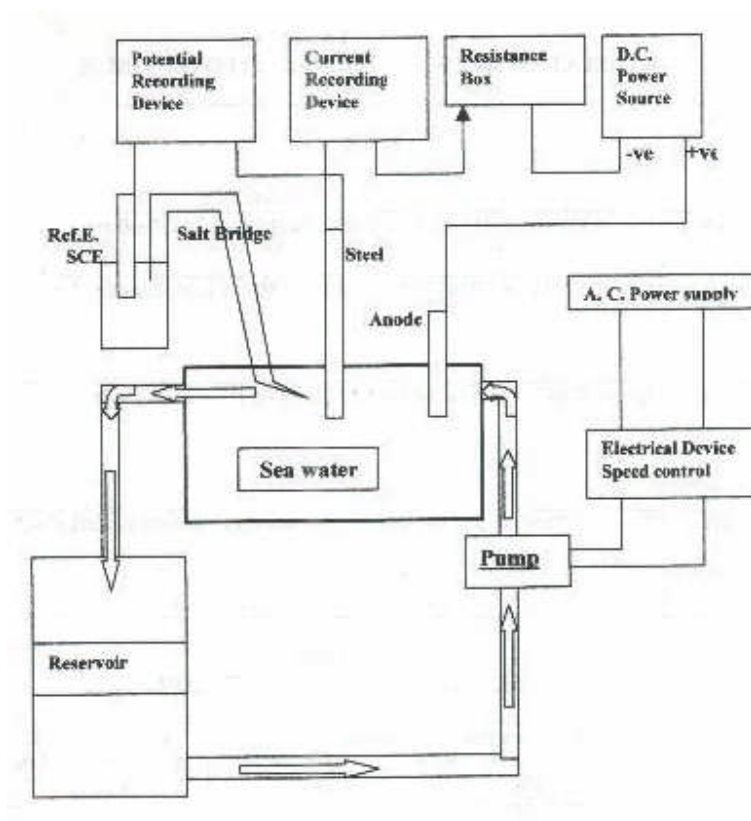


Fig.1 showing schematic diagram of the experimental setup.

