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CALCULUS OF THE DISTRIBUTION OF SACRIFICIAL ANODES FOR ROOF OIL TANKS CATHODIC CORROSION PROTECTION

Victor Martinez-Luaces*, **Lucia Campo, Mauricio Ohanian**

Electrochemistry Engineering Multidisciplinary Research Group, Faculty of Engineering, Udelar, Montevideo, Uruguay

Abstract. Sacrificial anodes cathodic protection (SACP) are a well-known technique widely used to protect different metallic structures. In the case analyzed, the internal maintenance of ANCAP (Uruguayan Petroleum State-owned Company) oil tanks required the re-design of their SACP. The system design implies assign the anodic material and calculate the mass number of anodes. Their position is usually determined by empiric methods or partially based corrosion potential distribution theory. Herein, we present a development of calculus for the sacrificial anodes position to ensure the total roof surface protection. In order to determine the location and number of the anodes, we started considering a mass balance which was later transformed into a charge balance. After several transformations the mathematical model resulted into an elliptic PDE problem, expressed in cylindrical coordinates with non-linear boundary conditions. The original problem was simplified by using the piecewise linearization method and applying Frumkin condition that allowed assuming unidirectional charge flux. Following these ideas, the original PDE problem was converted into a second order ODE with variable coefficients which can be solved by using power series. Taking into account the previous analysis, an iterative process was proposed to calculate the radius of the sacrificial anodes to be installed.

Keywords: Elliptic PDE, power series, cathodic corrosion protection.

AMS Subject Classification: 35C10, 35J65.

Corresponding author: Victor Martinez-Luaces, Electrochemistry Engineering Multidisciplinary Research Group, Faculty of Engineering, Julio Herrera y Reissig 565, 11300 Montevideo, Uruguay,
e-mail: *victorml@fing.edu.uy*

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1 Introduction

Sacrificial anodes cathodic protection (SACP) are a well-known technique widely used to protect different metallic structures. In the case studied here, the internal maintenance of ANCAP (Uruguayan Petroleum State-owned Company) oil tanks required the re-design of their SACP (Campo et al., 2017). The *Terminal del Este* tank farm is located in the east coast of Uruguay, near the cape named Punta José Ignacio, in the Atlantic Ocean just northeastward of the famous watering place Punta del Este. The terminal belongs to ANCAP and it has several roof oil tanks which maintenance requires the design of their cathodic protection. The oil is not an ionic conductor, although the tank bottom accumulates water precedent of the pump process or the oil segregation. This condition implies corrosive conditions whose must be controlled by periodic water purge, corrosion inhibitors dosing or cathodic protection application. It is important to mention that, the cathodic application design implies to assign the anodic material and calculate the mass and number of anodes, which position will be determined in this article by using a mathematical model. After several transformations this model results into an elliptic PDE problem, expressed in cylindrical coordinates with non-linear boundary conditions (Ohanian et al., 2014; Martinez-Luaces et al., 2018). Under certain circumstances the original problem can be simplified and converted into a second order ODE with variable coefficients which can be solved by using power series.

In this paper, we develop a mathematical model, we solve analytically the differential equations problem and we propose an iterative process to calculate the radius of the sacrificial anodes in order to ensure the total surface protection.

2 The mathematical model

The mathematical model is developed in order to evaluate the distribution of anodes inside the tank. A mass balance is carried out in a control volume (Ibl, 1983) within the electrolyte, giving for the species i the equation (1).

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_i + R_i. \tag{1}$$

The global balance for all the species can be written as:

$$\frac{\partial \sum_i c_i}{\partial t} = -\nabla \cdot (\sum_i J_i) + \sum_i R_i. \tag{2}$$

Multiplying the equation terms by the species charges (z) and also by the Faraday constant F, we obtain the following charge balance:

$$F\frac{\partial \sum_i z_i c_i}{\partial t} = -\nabla \cdot (F\sum_i z_i J_i) + F\sum_i z_i R_i. \tag{3}$$

In this case, we consider an electrochemical system with reaction at the interface and then it can be assumed that there is no generation in the control volume, so the term R_i is zero and due to the steady-state condition, the left term of Equation (3) is also null, resulting:

$$\nabla \cdot (F\sum_i z_i J_i) = \nabla \cdot j = 0. \tag{4}$$

Being j the current density vector. Expanding j taking into account migration, diffusion and advection (Newman, 1968) we have the following equation:

$$\nabla \cdot j = -\nabla \cdot (\sum_i |z_i| u_i c_i \nabla E) - \nabla \cdot (F\sum_i D_i z_i \nabla c_i) + \nabla \cdot (Fv\sum_i z_i c_i) = 0. \tag{5}$$

In this equation u_i is the ionic mobility, D_i is the diffusivity of species i and v is the local velocity of the fluid.

The solution can be considered an isotropic medium, therefore the ionic conductivity and the diffusivity of the species are homogeneous properties and so they have a null gradient. Then, Equation (5) is simplified to give:

$$\nabla \cdot j = -\chi \nabla^2 E - F\sum_i D_i z_i \nabla^2 c_i + \nabla \cdot (Fv\sum_i z_i c_i) = 0. \tag{6}$$

Being χ the electrolyte conductivity.

In the electrolyte the convective term is null due to the condition of electro neutrality and so, we can write:

$$\nabla \cdot j = -\chi \nabla^2 E - F\sum_i D_i z_i \nabla^2 c_i = 0. \tag{7}$$

In primary or secondary current distributions, we can assume that there is no concentration gradient and then, the last equation can be simplified to give:

$$\nabla \cdot j = -\chi \nabla^2 E = 0. \tag{8}$$

And then

$$\nabla^2 E = 0. \tag{9}$$

In our system, a cylindrical tank with D = 60 m and h = 0.015 m (average height of present electrolyte) it is more convenient to use cylindrical coordinates (Zill & Cullen, 2009), so we have:

$$\frac{\partial^2 E}{\partial r^2} + \frac{1}{r}\frac{\partial E}{\partial r} + \frac{1}{r^2}\frac{\partial^2 E}{\partial \theta^2} + \frac{\partial^2 E}{\partial z^2} = 0. \tag{10}$$

Due to symmetrical reasons, the derivatives with respect to the polar argument θ can be canceled to give this new equation:

$$\frac{\partial^2 E}{\partial r^2} + \frac{1}{r}\frac{\partial E}{\partial r} + \frac{\partial^2 E}{\partial z^2} = 0. \tag{11}$$

Besides, for symmetrical reasons there is no flux at the center of the tank, then

$$\frac{\partial E}{\partial r}|_{r=0} = 0. \tag{12}$$

The other boundary condition is given by polarization curves (electrochemical potential vs. current density) obtained in the laboratory and piecewise linearized. Finally, another boundary condition is obtained in the interface oil/water where there is no flux, and so:

$$\frac{\partial E}{\partial z} = 0, \ \ \textit{evaluated at} \ \ z = L. \tag{13}$$

In this system the Frumkin condition (Martinez-Luaces et al., 1949) for unidirectional flux is satisfied and so, the differential equation can be written as:

$$\frac{\partial^2 E}{\partial r^2} + \frac{1}{r}\frac{\partial E}{\partial r} = 0. \tag{14}$$

If this equation is written in terms of electrochemical potential ($\overline{\mu}$), we have:

$$\frac{\partial^2 \overline{\mu}}{\partial \mathrm{r}^2} + \frac{1}{\mathrm{r}}\frac{\partial \overline{\mu}}{\partial \mathrm{r}} = \pm \mathrm{i}_\mathrm{S}\frac{2\rho}{\mathrm{L}}. \tag{15}$$

Being i_S the normal current to the metallic surface.

The piecewise linearization of the boundary condition gives us the following:

$$\frac{\partial \overline{\mu}}{\partial z}|_{z=0} = i_s = a + b\overline{\mu}. \tag{16}$$

The change of variable $x = \frac{r}{R}$ allows writing the differential equation as:

$$\frac{\partial^2 \overline{\mu}}{\partial \mathrm{x}^2} + \frac{1}{\mathrm{x}}\frac{\partial \overline{\mu}}{\partial \mathrm{x}} = \pm \left(\frac{\mathrm{a}}{\mathrm{b}} + \overline{\mu}\right)\frac{\mathrm{bR}^2 2\rho}{\mathrm{L}}. \tag{17}$$

This equation has the form:

$$\mathrm{y}'' + \frac{1}{\mathrm{x}}\mathrm{y}' - \mathrm{Ky} = \mathrm{AK}. \tag{18}$$

In Equation (18) we defined $\frac{\mathrm{bR}^2 2\rho}{\mathrm{L}} = \mathrm{K}$ and $\frac{\mathrm{a}}{\mathrm{b}} = \mathrm{A}$ where both depend on the piecewise linearization of the experimental polarization curves, geometric characteristics and the medium conductivity.

3 The ODE analytical solution

The homogeneous ODE corresponding to equation (18) is

$$y^{''} + \frac{1}{x}\mathrm{y}^{'} - \mathrm{Ky} = 0. \tag{19}$$

We propose a solution (Somasundaram, 2001) of the form:

$$y(x) = \sum_{n=0}^{\infty} a_n x^n = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \ldots \tag{20}$$

If $y(x)$ is substituted into equation (19) we obtain:

$$\begin{array}{l} \left(2a_2 + 6a_3 x + 12a_4 x^2 + \ldots\right) + \frac{1}{x}\left(a_1 + 2a_2 x + 3a_3 x^2 + 4a_4 x^3 + \ldots\right) \\ -K\left(a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \ldots\right) = 0. \end{array} \tag{21}$$

Rearranging we have:

$$\begin{array}{l} \frac{a_1}{x} + (4a_2 - Ka_0) + (9a_3 - Ka_1)\,x + (16a_4 - Ka_2)\,x^2 + (25a_5 - Ka_3)\,x^3 \\ + (36a_6 - Ka_4)\,x^4 + \ldots = 0. \end{array} \tag{22}$$

From equation (22) it can be obtained an equation system for the odd numbers:

$$\begin{cases} a_1 = 0 \\ 9a_3 - Ka_1 = 0 \\ 25a_5 - Ka_3 = 0 \\ \vdots \end{cases} \tag{23}$$

From this system it follows that

$$a_1 = a_3 = a_5 = \ldots = 0. \tag{24}$$

From equation (22) it follows a different system for the even numbers:

$$\begin{cases} 4a_2 - Ka_0 = 0 \\ 16a_4 - Ka_2 = 0 \\ 36a_6 - Ka_4 = 0 \\ \vdots \end{cases} \tag{25}$$

Then we have:

$$a_2 = \frac{K}{4}a_0 \quad , \quad a_4 = \frac{K}{16}a_2 \quad , \quad a_6 = \frac{K}{36}a_4 \quad , \quad a_8 = \frac{K}{64}a_6 \quad , \; \ldots. \tag{26}$$

So, the corresponding recursive equation is:

$$a_{2n} = \frac{K}{(2n)^2}a_{2n-2}. \tag{27}$$

Substituting we have

$$a_2 = \frac{K}{2^2}a_0 \;,\; a_4 = \frac{K^2}{2^2 4^2}a_0 \;,\; a_6 = \frac{K^3}{2^2 4^2 6^2}a_0 \;,\; a_8 = \frac{K^4}{2^2 4^2 6^2 8^2}a_0 \;,\; \ldots. \tag{28}$$

And the general form can be written as:

$$a_{2n} = \frac{K^n}{\left[(2n)\,!!\right]^2}a_0. \tag{29}$$

Where the double factorial is:

$$(2n)!! = (2n)\,(2n-2)\,(2n-4)\ldots 2. \tag{30}$$

Then, combining the previous results we obtain the following solution of the homogeneous ODE:

$$y(x) = a_0 + \sum_{n=1}^{\infty} \frac{K^n}{[(2n)!!]^2} a_0 x^{2n} = a_0 \left(1 + \sum_{n=1}^{\infty} \frac{K^n}{[(2n)!!]^2} x^{2n}\right) = a_0 \varphi\,(x)$$

being

$$\varphi(x) = 1 + \sum_{n=1}^{\infty} \frac{K^n}{[(2n)!!]^2} x^{2n}. \tag{31}$$

Another independent solution can be obtained by using the change of variables:

$$y(x) = \varphi\,(x)\,u\,(x)\,.$$

Then:

$$y'(x) = \varphi'\,(x)\,u\,(x) + \varphi\,(x)\,u'\,(x)$$

$$y''(x) = \varphi''\,(x)\,u\,(x) + 2\,\varphi'\,(x)\,u'\,(x) + \varphi\,(x)\,u''\,(x)\,. \tag{32}$$

Replacing these results in the homogeneous equation (19) we obtain:

$$\begin{aligned} &y''(x) + \tfrac{1}{x} y'\,(x) - K y\,(x) = \varphi''\,(x)\,u\,(x) + 2\varphi'\,(x)\,u'\,(x) + \varphi\,(x)\,u''\,(x) + \\ &+ \frac{1}{x}\left[\varphi'\,(x)\,u\,(x) + \varphi\,(x)\,u'\,(x)\right] - K\varphi\,(x)\,u\,(x) = 0. \end{aligned} \tag{33}$$

Rearranging terms this equation can be written as:

$$\begin{aligned} &u\,(x)\left[\varphi''\,(x) + \tfrac{1}{x}\varphi'\,(x) - K\varphi\,(x)\right] + 2\,\varphi'\,(x)\,u'\,(x) + \varphi\,(x)\,u''\,(x) + \\ &+ \frac{1}{x}\varphi\,(x)\,u'\,(x) = 0. \end{aligned} \tag{34}$$

Since $\varphi\,(x)$ is a solution of equation (19) the first term is zero and equation (34) can be written as:

$$\varphi\,(x)\,u''\,(x) + \left[2\varphi'\,(x) + \frac{1}{x}\varphi\,(x)\right] u'\,(x) = 0. \tag{35}$$

Equation (35) is a separable differential equation, as it can be observed in the following ODE,

$$\varphi\,(x)\,\frac{d}{dx} z\,(x) = -\left[2\varphi'\,(x) + \frac{1}{x}\varphi\,(x)\right] z\,(x) \tag{36}$$

where $u'\,(x)$ was replaced by $z\,(x)$.

The solution of equation (36) is

$$\ln\left[z\,(x)\right] = -\int \left(2\frac{\varphi'\,(x)}{\varphi\,(x)} + \frac{1}{x}\right) dx = -2\ln\left[\varphi\,(x)\right] - \ln\,(x) = \ln\left[\frac{1}{x\varphi^2\,(x)}\right]. \tag{37}$$

Then, it can be written that

$$z\,(x) = \frac{1}{x\varphi^2\,(x)} \tag{38}$$

and since $z\,(x)$ is the same as $u'\,(x)$, it follows that

$$u\,(x) = \int \left(\frac{1}{x\varphi^2\,(x)} \right) dx \tag{39}$$

and so, the other independent solution of Equation (19) is

$$\psi\,(x) = \varphi\,(x) \int \left(\frac{1}{x\varphi^2\,(x)} \right) dx. \tag{40}$$

Finally, the non homogeneous ODE (18) has an obvious constant solution:

$$y(x) = -A. \tag{41}$$

Then, combining the previous results we obtain:

$$y(x) = -A + c_1\varphi\,(x) + c_2\psi\,(x)\,. \tag{42}$$

Which is the general solution for equation (18) being:

$$\varphi(x) = 1 + \sum_{n=1}^{\infty} \frac{K^n}{[(2n)!!]^2} x^{2n} \quad (\textit{see } 31)$$

and

$$\psi\,(x) = \varphi\,(x) \int \left(\frac{1}{x\varphi^2\,(x)} \right) dx \quad (\textit{see } 40).$$

4 Approximating the analytical solution

The analytical solution, given by equation (42) needs to be approximated for its practical use.

The dimensionless variable x is positive and: $x = \frac{r}{R} << 1$, the power series (31) shows a fast convergence and

$$\varphi(x) = 1 + \sum_{n=1}^{\infty} \frac{K^n}{[(2n)!!]^2} x^{2n} \approx 1 + \frac{K}{4}x^2 \tag{43}$$

then it can be written that:

$$x\varphi^2(x) \approx x\left(1 + \frac{K}{4}x^2\right)^2 = x + \frac{K}{2}x^3 + \frac{K^2}{16}x^5. \tag{44}$$

In order to obtain the integrand of (see 40)

$$\psi\,(x) = \varphi\,(x) \int \left(\frac{1}{x\varphi^2\,(x)} \right) dx$$

the long division method yields:

$$\frac{1}{x\varphi^2(x)} \approx \frac{1}{x + \frac{K}{2}x^3 + \frac{K^2}{16}x^5} = \frac{1}{x} - \frac{K}{2}x + \frac{3K^2}{16}x^3 + \ldots. \tag{45}$$

Then

$$\psi\,(x) = \varphi\,(x) \int \left(\frac{1}{x\varphi^2\,(x)} \right) dx \approx \left(1 + \frac{K}{4}x^2\right) \int \left(\frac{1}{x} - \frac{K}{2}x + \frac{3K^2}{16}x^3 + \ldots \right) dx \tag{46}$$

or

$$\psi\,(x) \approx \left(1 + \frac{K}{4}x^2\right)\left(\ln\,(x) - \frac{K}{4}x^2 + \frac{3K^2}{64}x^4 + \ldots\right) \tag{47}$$

and, if we delete powers greater than x^2, then the truncated series for series $\psi(x)$ is the following:

$$\psi(x) \approx \ln(x) - \frac{K}{4}x^2 + \frac{K}{4}x^2\ln(x). \tag{48}$$

Taking into account the previous results, the approximated solution can be written as:

$$y(x) \approx c_1\left(1 + \frac{K}{4}x^2\right) + c_2\left(\ln(x) - \frac{K}{4}x^2 + \frac{K}{4}x^2\ln(x)\right) - A. \tag{49}$$

The boundary conditions are $y(x_i) = y(Zn)$ for $i = 0, 1$ since zinc electrodes are put at radius $r_0$and r_1. These boundary conditions can be used to calculate constants $c_1$and c_2, obtaining:

$$c_1 = [y(Zn) + A]\frac{\psi(x_1) - \psi(x_0)}{\varphi(x_0)\psi(x_1) - \psi(x_0)\varphi(x_1)}$$

and

$$c_2 = [y(Zn) + A]\frac{\varphi(x_0) - \varphi(x_1)}{\varphi(x_0)\psi(x_1) - \psi(x_0)\varphi(x_1)}. \tag{50}$$

The obtained results, i.e. c_1 and c_2, are substituted in equation (49) which gives the potential for all radius between r_0 and r_1. The same procedure can be followed for radius between r_1 and r_2, between r_2 and r_3, etc., and the equation is solved approximately for all the tank.

5 Conclusion

Taking into consideration the previous equations and the experimental results– particularly the polarization curves – several proposals (see Table 1) were included in a technical report (Campo et al., 2017), being the most relevant for this article the ones about number and location of the sacrificial anodes. These recommendations can be visualized in Table 1.

Table 1: Diameters suggested for the anodes location and number of electrodes

Annulus diameter (m)	number of aluminum anodes	number of zinc anodes
16	12	17
36	48	67
54	90	100

Indeed, at present, after the design and development, our method is implemented in ANCAP, in the Terminal del Este tank farm. We are confident that further tests confirm that the present findings might help to solve the problem.

Beyond the particular ANCAP corrosion problem, our studies may improve knowledge about corrosion protection for roof oil tanks.

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