COMPARATION OF THE ANALYTICAL AND EXPERIMENTAL MODELS OF 304SS CORROSION RATE IN 0.5 M H_2SO_4 WITH BEE WAX PROPOLIS EXTRACT

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Abstract:

Corrosion in the reservoir and transport vessel often causes a leak that leads to disaster. Data prediction and experimental corrosion in storage technology is very important to prevent damage and reduce maintenance costs. Theoretically, steel tank corrosion by sulfuric acid working medium can be minimized with the formation of sediments oxide by oxidation-reduction reaction. Behavioral inhibition of bee wax propolis on the 304SS in 0.5 M sulfuric acid was carried by potentiodynamic polarization. Based on the polarization testing the corrosion rate of the 304SS in a solution of 0.5 M H_2SO_4 *is at 0.349* g/m^2d *with the missing mass amounted 5.21* $x10^{-9}$ *g/s. In experiments, the inhibitor causing less mass loss is equal to 2.28 x* 10^{-11} *g/s. Mass lost without and with inhibitor in this study is also known by theoretical calculations. The mass losses can be used to determine the inhibition efficiency. The calculation of the efficiency theoretically and experimentally gives the same result.*

1 Introduction

The Faraday's law is often used to predict the material life service or resistance to corrosion attack. Based on the reaction process, it can be seen mole electron oxidation and corrosion rate of an element can be predicted. Generally, in applications, engineering material is a blend of several metal compounds so that the corrosion process becomes complex. However, the mass balance system in the metal alloy can be used to determine its properties. According to [1], the density of the alloy is determined by the rules of % equilibrium elements of the multiplication of the number of factions and elements. Moreover, the main element in the alloy as a base to the determination of material properties and 304SS is a stainless steel based on ferrous, chromium, and nickel. The corrosion potential of the steel depends greatly on the cathodic reaction involved in the oxide-reduction process between the elements Fe, Cr, Ni of the steel and the oxidizing species of the medium. A layer of chromium oxide in nitric acid lowers the potential of electrolytic cells and potentially becomes passive areas as from reference [2].

Based on analytical calculations, the three main elements have corrosion potential value calculation respectively. In the potential experiments the potential value is known as a potential alloy. Researches on erosion calculation using the Faraday's law have been conducted [3-4]. There are

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some differences in the calculation results explained by different causes and parameters. Parameter calculation of mass loss that has been done is the speed of the solution in the process of corrosive erosion [3]. Simulation in mass transport is also held by following the Faraday's law [4].

Metal corrosion in an aggressive environment is an important issue in cleaning and pre-treatment industries. This is due to the use of acid in the process of pickling, industry appliance cleaning, descaling process, transportation acid solution and acidification of the oil wells in the petroleum industry. The use of corrosion inhibitors is a popular method to prevent and cope with the rate of corrosion of metal surfaces in an acidic environment. This material is given in small concentrations so as to reduce and prevent the reaction between the metal and its environment [5-9]. Cr, Ni, Fe are the basic elements in SS-304 that are sensitive to corrosion by sulfuric acid. Yet, with the addition of inhibition of carbohydrate (bee wax propolis) can provide interactions of 3 materials into a thin layer of ceramic material such as oxide and carbide that electrochemically are called aberration (polarization).

The addition of inhibitors will change polarization in anodic and cathodic ways [10]. In this case, the use of bee wax propolis (BWP) as inhibitors has shown to inhibit the corrosion rate on 304SS in H_2SO_4 solution. In the inhibition of corrosion rate mixed type of polarization occurs [11]. Testing on Fourier Transform Infrared Spectroscopy (FTIR) and High Performance Liquid Chromatography (HPLC) was conducted to determine the functional groups contained in the BWP extract. Based on the preliminary research, BWP extract contains main type of compound of flavonoid namely quercetin [11]. The inhibitor of BWP extract has the ability to inhibit the rate of corrosion with physisorption. The optimum concentration of inhibitor was obtained at 2000 ppm. Inhibition efficiency (IE %) decreased as the temperature increased. The mechanism of inhibition of extract BWP on the 304SS was physisorption, following Temkin isothermal equation [11].

Linear polarization studies have been conducted to estimate the corrosion rate or to analyze the passivation of metals, corrosion protection using inhibitors, sacrificial barrier properties, and coating on metal [12-14]. Identification of the use of environmentally friendly inhibitor only in the side of polarization curve will not be sufficient. Therefore, this required theoretical calculation of how much mass is lost by the corrosion rate [15].

Corrosion current can be used to determine the corroded mass of material. It can be directly converted into the lost mass of material by using Faraday's law [12]. Based on the selection of test parameters polarization, I_{corr} and E_{corr} estimation can be calculated. Therefore, the rate of corrosion and the lost or gained mass due to passivation can be determined. Differences in mass loss before and after adding the inhibitor of BWP extract were then analyzed in this study. This study aims to compare the analytical and experimental results of calculation of the mass loss.

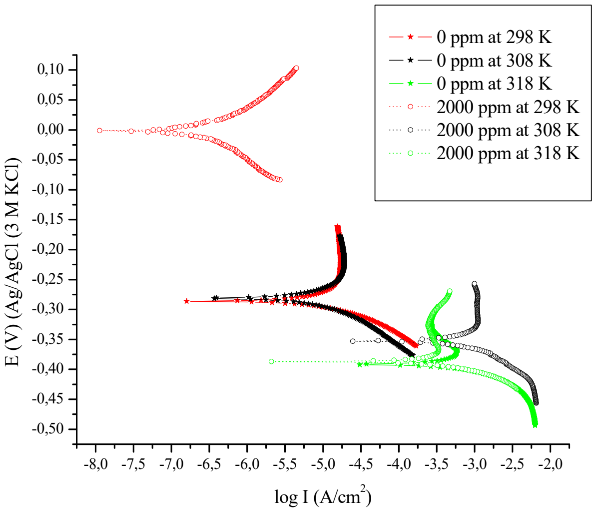


Figure 1. Polarization curve of SS 304 in the sulfuric acid 0.5 M without and with inhibitor at varied temperatures [11].

2 The method

The chemical compounds of 304SS (in % by weight) used were 0.04% C, 0.52% Si, 0.92% Mn, 0.030% P, 0.002% S, 9.58% Ni, 18.15% Cr, Bal. Fe. The density of SS 304 is 7.9 g / cm^3. Specimens were done with a size of 10 mm x 10 mm x 10 mm as the working electrode (WE).

WE was added to the epoxy resin to the geometric surface area sized 1 cm^2 connected/close to exposed electrolyte. Prior to the implementation of all of the testing, the sample surface was smoothed with sandpaper of grit 800 to 2000 alternately. BWP extract was obtained from solid-liquid extraction to get the optimum conditions.

3 Analytical and experimental setup

3.1 Analytical setup

Polarization in electrolytic sell illustrates the differences (imbalances) between the metal and the environment that cause the displacement of ion-ion anode-cathode (current flow) resulting in corrosion. In the context of corrosion, polarization refers to the potential shift of the open circuit potential (free corrosion potential) from corrosion system. If a potential shift in the direction of "positive" (above E_{corr}), it is called "anodic polarization". If a potential shift in the direction of "negative" (below E_{corr}), it is called "cathodic polarization". Moreover, this corrosion potential affects the exchange of current density in cathodic protection during the electrochemical reaction so that the current polarization (I_{corr}) is important to appear in the prevention system of corrosion passivation (inhibitor). The polarization was conducted by potentiodynamic polarization. In electrolytic cell, the inhibition efficiency (IE) of the polarization method is calculated based on the following equation (1) [16]:

$$IE\ (\%) = I\ (\%) = \frac{I_{corr} - I_{corr}(i)}{I_{corr}} \times 100\% \qquad (1)$$

Where I_{corr} and $I_{corr(i)}$ are corrosion current density in medium without and with the addition of inhibitors.
Mass calculation is based on the Faraday's law derivative [17-18]:

$$CR(mpy) = \frac{0.129 \times I_{corr} \times EW}{d} \qquad (2)$$

Where CR represents the corrosion rate, while EW and d are the equivalent weight of the material and density of material.
Other calculation of corrosion rate with and without the addition of inhibitors can be determined from the I_{corr} value in which βa and βc obtained by OCP used range is ± 0.1 V. Thus, in the Table 1, the analysis is based on βa and βc value is 0.1 [17]. Based on this, I_{corr} value was calculated by using Equation 3:

$$I_{corr} = \frac{b_a \times b_c}{2.3(b_a + b_c)} \times \frac{1}{R_p} \qquad (3)$$

in which R_{p} was obtained from Equation 4:

$$R_p = \frac{\left(\frac{d}{d_i}\right)}{A} \qquad (4)$$

where η (overpotential) = 0.22 with SHE, A is an area of exposed metal (in this experiment = 1 cm^2). Based on the Butler-Volmer equation, cathodic reaction made equation 5:

$$\left[\frac{d}{d_i}\right] = -i^o \frac{\alpha nF}{RT} \qquad (5)$$

By adding A and i polarization resistance calculations made the equation 6:

$$R_p = \frac{1}{A} \frac{1}{\left[\frac{d}{d_i}\right]} = -\frac{1}{A} \frac{RT}{nFi^o} \qquad (6)$$

Where R_p is polarization resistance, βa is anodic tafel slopes, βc is cathodic tafel slopes, T is the absolute temperature, R is the universal gas constant, n is the number of electrons involved in the redox reaction and F is Faraday constant. After getting the value of R_{p}, then the value of I_{corr} could be calculated by equation 3. Based on I_{corr} value, corrosion rate (CR) can be known in which the corrosion rate indicates the number of the oxidized mass per unit area in time. Calculation of the oxidized mass of can be completed by using the Faraday's law and is based on Faraday's equation CR derivative (equation 2). The result of theoretical mass calculation is shown in the Table 1.

3.2 Experimental setup

Corrosion testing was carried out by an electrochemical method in accordance with ASTM (American Standards and Testing) G-31 standard [19]. The batch contains 0.5 M sulfuric acid solution with and without the addition of 2000 ppm BWP extract.
Electrochemical tests were performed using an Autolab PGSTAT 128N. Specimens prepared were assembled into an electrochemical cell with platinum as auxiliary electrode and Ag / AgCl as the reference electrode. Those three electrodes were immersed in the solution for 30 minutes. The measurement of polarization in alteration -0.1 V to +0.1 V was along

the corrosion potential (OCP) with a scan rate of 0.001V / s. Test results are given in Table 2.

Fig. 4 and Table 3 shows the effect of concentration and temperature on the potentiodynamic polarization interaction of 304SS-H_2SO_4-BWP.

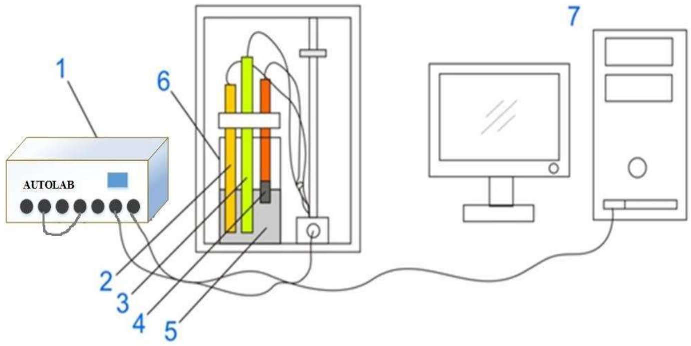
Table 1. Calculation of corrosion parameters for Fe, Cr and Ni Element

Element	Inhibitor Conc.	β_a	β_c	I_{corr}	*CR*	*m*	*IE*
	(ppm)	(V/dec)	(V/dec)	(A/cm^2)	(g/m^2·d)	(g)	%
Fe	0	0.1	0.1	10.87x 10^{-6}	0.349	5.21 x 10^{-9}	-
	2000	0.1	0.1	2.3 x 10^{-8}	7.35 x 10^{-4}	6.67x10^{-11}	98.71
Cr	0	0.1	0.1	8.76 x 10^{-6}	0.29	4.22 x 10^{-9}	-
	2000	0.1	0.1	7.61 x 10^{-8}	1.38 x 10^{-5}	5.48x10^{-11}	98.70
Ni	0	0.1	0.1	13.22 x 10^{-6}	0.42	7.11 x 10^{-9}	-
	2000	0.1	0.1	8.91 x 10^{-8}	0.14 x 10^{-2}	7.33x10^{-11}	98.96

Table 2. The potentiodynamic polarization data of 304SS in the sulfuric acid 0.5 M without and with inhibitor extract BWP

Inhibitor Conc.	β_a	β_c	I_{corr}	*CR*	*m*	*IE*
(ppm)	(V/dec)	(V/dec)	(A/m^{-2})	(g/m^2·d)	(g)	(%)
0	0.059294	-7.9582	2.19x10^{-5}	0.152 x 10^{-4}	2.28 x 10^{-11}	-
2000	0.10293	0.17181	5.93x 10^{-7}	0.428 x 10^{-6}	6.39 x 10 -13	97.09

Figure 2. Specimen 304SS used as working electrode



1.Potenstiostat,
2. Reference electrode,
3. Counter electrode,
4. Working electrode,
5. Solution,
6. Glass beaker,
7. Computer hardware

Figure 3. Research Installation

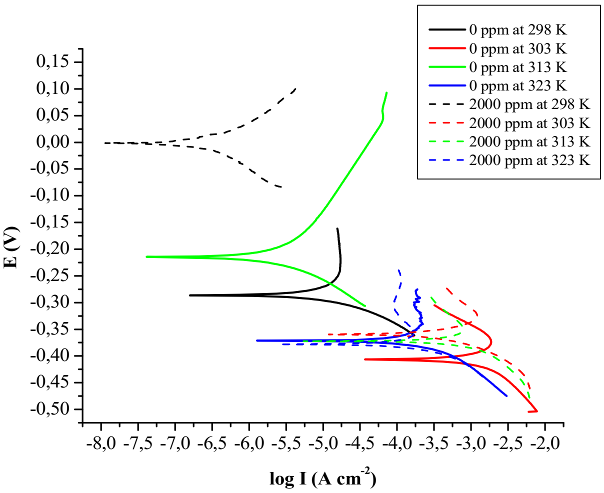


Figure 4. Tafel plots of 304 SS in the sulfuric acid 0.5 M without and with inhibitor at temperature variations.

In an electrolytic sell as reported in chapter 3.1, polarization illustrates the differences between the metal and its environment that causes the displacement of ion-ion anode-cathode (current flow) resulting in corrosion. Moreover, this affects the corrosion potential exchange of current density in cathodic protection during the electrochemical corrosion reaction so that the polarization current (I_{corr}) is important to appear in the passivation corrosion prevention system (inhibitor).

In general, organic molecules can inhibit metal corrosion by means of adsorption [20], that occurs depending on the chemical composition of molecule, temperature, and electrochemical potential on metal or interface solution/metal.

Prediction of the oxidation reaction that occurred was also done by using cyclic voltammetry (CV) as what has been done by Abdallah in 2003. The results showed oxidation reaction, reduction and passive possibility which may happen [21]. For that purpose, the electrochemical testing was resumed by using CV method. This method is used to obtain potential of oxidation and reduction reactions. CV data is used as data support to analyze the oxidation and reduction reaction of Fe,Cr and Ni.

Table 3. The potentiodynamic polarization data of 304 SSin the sulfuric acid 0.5 M without and with inhibitor at temperature variations

Inhibitor Conc.	Temperature	β_a	β_c	E_{corr}	I_{corr}	IE
ppm	K	V/dec	V/dec	V	A/cm^2	%
0	298	0.059	-7.958	-0.286	$2.19x10^{-5}$	
0	303	0.16	0.339	-0.406	$4.66x10^{-6}$	
0	313	0.095	0.430	-0.214	$5.29x10^{-6}$	
0	323	0.064	-0.218	-0.378	$6.34x10^{-4}$	
2000	298	0.103	0.172	-0.001	$5.93 \ x \ 10^{-7}$	97.27
2000	303	0.066	0.069	-0.359	$6.25 \ x10^{-7}$	86.58
2000	313	0.086	-0.517	-0.372	$2.90 \ x10^{-6}$	45.17
2000	323	0.074	-0.413	-0.371	$5.55 \ x10^{-4}$	12.46

Based on the test results in the Fig. 5, CV at the peak (a) and (c) is an oxidation reaction that is identical to the anodic area. At the peak (a) which is an anodic reaction area at a potential (E) with a value of about -0.23 V (Ag / AgCl), the reaction similar with refrence [21]. The peak (a) value with E = -0.23 is the CV datum with a scan rate of 10 mV/s. The reaction at the peak (b) with E is about -0.1 V (Ag/AgCl) and the reactions occurring based on reference [21].

Thin layer passivation mechanism of 304SS in the atmosphere inhibitors is as follows: carbohydrate + sulfuric acid to produce carbon + water + mixture of water and acid. Furthermore, water produces oxygen and hydrogen and in the final stage carbon and oxygen met with a stainless steel forming a layer of oxide and carbide. For example, in the Fig. 5, peak (b) is a passive area and peak (c) is a transpassive area in which Fe, Ni and Cr oxihydroxides were formed. At the peak (b) the formation of oxides is higher than iron and chromium as well as some thickening of nickel oxide. The formation of nickel oxide is not seen. Because of passivator property and resistance to acid, chromium oxide (Cr_2O_3) is considered a major compound of the passive layer formed [22].

Therefore, the anodic peak (b) is considered primary passive stage in the anodic polarization 304SS [21]. It seems that after the peak b) was passed by the anodic current, it began to decline until the start beginning of peak (c) formation. Throughout the peak (c) the only reaction is passive layer thickening shown with the increase in the anodic potential. The experimental results indicate a trend of 304SS becoming passive. This occurs in specimens with and without BWP inhibitors.

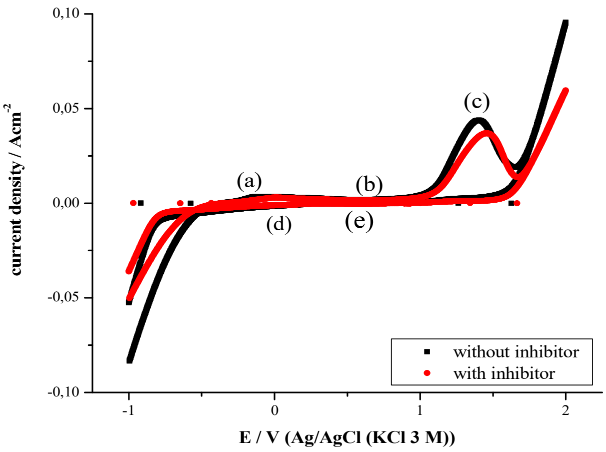


Figure 5. Cyclic voltammetry at a pH of 500 mV / s with and without inhibitors.

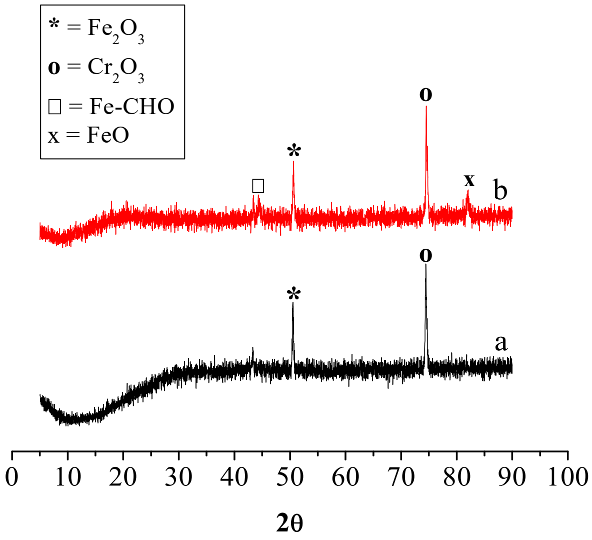


Figure 6. The result of XRD 304SS (a) without (b) with inhibitor BWP in H_2SO_4 solution 0.5M

4 Discussion

Based on the Table 1 and 2, differences in mass occur. The presence of the inhibitor indicates mass changes which are smaller than those without inhibitor. The mass changes have the same pattern theoretically and experimentally (Table 2 and Table 3). Another research found that in corrosive solution even without solid particles, the mass loss rate of sample experiment measured with the traditional weight loss method was higher than that calculated with the Faraday's law as the flowing velocity of solution was high enough [3]. Value inhibition efficiency from both the calculation of the mass and of I_{corr} comes closer. The value difference can be caused by the condition of the pH in the solution or by the corrosion mechanism occurring [3].

The difference between calculation and experiment is due to the interpretations in the calculation which differs from the experimental conditions. Greater value was obtained in experiments based on weight loss as compared with the calculation of Faraday's law [23]. On the other hand, in this study, a value was obtained in the smaller experiment. This is because of different interpretations which were analytically calculated at each main constituent element of 304SS. The analytic calculation was based on the valence of the moving ions. In this case, the valence of the element was calculated on the total ion changing for 2. Meanwhile the results of experiments were based on simultaneous conditions between 304SS alloys and good environment either containing or not containing inhibitor.

Inhibition efficiency calculation results were obtained by the lost mass. It is identical with inhibition efficiency calculations using the method of weight loss. The same relative value shows that the change in mass is equal to the current changes that occur during corrosion.

Theoretically, 304SS alloy can form an oxide layer which is a passive layer. This coating protects these alloys [24, 25]. The presence of passive layer formed can be shown in experiments in cyclic voltammetry and XRD test results.

5 Conclusion

Based on the calculation of polarization of Fe, Cr and Ni, 304SS corrosion rate in a solution of 0.5 M H_2SO_4 was obtained respectively for 0.349; 0.29; and 0.42 g/m^{2}d along with the lost mass amounted 5.01×10^{-9}; 4.22×10^{-9}; 7.11×10^{-9} g/s. In experiments, the inhibitor causes less mass loss amounted for 2.28×10^{-11} g/s. The lost mass with and without inhibitor in this study is also known as theoretical calculations and experiments. Inhibition efficiency values which are almost the same show that the change in mass is equal to the current changes that occur during corrosion.

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