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Evaluating Corrosion Inhibitors with the Help of Electrochemical Measurements Including Electrochemical Frequency Modulation

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Electrochemical Frequency Modulation (EFM), cyclic polarization scans, potential noise measurement and long-term exposure tests have been used to evaluate the effects of green tea and tobacco against corrosion. In this work, various corroding environments were used for brass, aluminum and carbon steel materials. The level of corrosion protection by green tea and tobacco was compared with hexamethylene diamine ($C_6H_{16}N_2$) for brass and sodium nitrate ($NaNO_3$) for aluminum. The application of EFM for corrosion inhibitors has been investigated by comparing the results of EFM with different other tests. The results indicate that corrosion rate, causality factor 2 and anodic Tafel parameter can be used to evaluate and compare the performance of corrosion inhibitors. Green tea and tobacco do not always protect the chosen metals better than well-known corrosion inhibitors and mostly the level of protection is lower. Green tea was found better corrosion inhibitor than tobacco for brass in acidic environment. EFM technique applies a potential perturbation signal composed of two sine waves to generate a current response at more frequencies than the applied signal. As the corrosion phenomenon is nonlinear in nature, the ac-response will contain components at harmonic and intermodulation frequencies. Corrosion behavior can be studied by analyzing these nonlinear current components.

Keywords: EFM technique, inhibitors, causality factor, brass, aluminum, carbon steel

1. INTRODUCTION

Electrochemical frequency modulation (EFM) is a new electrochemical technique [1] for determining the corrosion rate without the preliminary knowledge of Tafel constants. Main advantages of this technique include the measurement of corrosion rate, Tafel parameters and causality factors in a single set of data. While using EFM, a potential perturbation signal composed of two sine waves is applied to any corroding specimen to get the current response. The ac-response contains more as well as higher frequencies than the applied signal due to nonlinear nature of corrosion process. Like harmonic method, EFM measures corrosion parameters with the help of nonlinearity in the voltage-current response of the electrochemical interface. EFM is relevant to harmonic method in employing lower amplitude (20 mV) sinusoidal perturbation signal but contrarily composed of two sine waves instead of one. EFM is better than harmonic method in many aspects including data validations, larger current response and insensitive to harmonics in the perturbation signal.

EFM has been used for different combinations of metals and electrolytes to measure accurately the corrosion parameters. The results obtained by Khaled [2] and Abdel-Rahim [3] demonstrate the EFM as a useful nondestructive technique for quick measurement of corrosion rate without prior knowledge of Tafel parameters. They showed a good comparison of EFM with other electrochemical techniques. Kuş and Mansfeld [4] showed that EFM can be applied successfully in case of high corrosion rates for various combinations of metals and environments. Generally the comparison between experimental and theoretical values of causality factors is used to validate the data obtained by EFM. In this study, corrosion rate, causality factor 2 and anodic Tafel parameter have been used to compare various inhibitors against corrosion.

Being economical and ecofriendly, the most common procedure to hinder the progress of corrosion involves the use of inhibitors. Organic molecules containing hetroatoms perform efficiently against corrosion typically by making protective film [5] on the matal surface. Imidazole and its derivatives represent a class of environmet-friendly inhibitors and have substituted toxic materials containing chromate and arsenic. Copper has relatively noble potential but its significant corrosion rate [6] in sea water leads to pipeline damage and causes serious economic losses. Organic corrosion inhibitors used for copper are usually azoles, amines, and amino acids. High inhibition efficiency of heterocyclic molecules is because of an insoluble physical diffusion [7] barrier on the (oxidized) metal surface. Organic compounds containing N, O, and S atoms [8] are the well-known inhibitors used to protect metals agaiinst corrosion, particularly in acidic media. Usually, N-containing inhibitor perfoms better in HCl, while S-containing inhibitor in H_2SO_4. Moreover the inhibitor with both N and S atoms simultaneously functions better than the inhibitor containing single N or S atom. Pitting potential and inhibition efficiency [9,10] for carbon steel increased with increasing concentrations of the inhibitor (a pentaerythritol glycoside compound).

Ginkgo-leaves extract [11] exhibits more efficient in 1.0 M HCl (mixed-type inhibitor) than 0.5 M H_2SO_4 (cathodic inhibitor). El-Etre [12] studied the use of natural honey to protect copper in aqueous solution. The anticorrosion effect of tea waste was shown by Sethuraman [13]. Vincent and Okhio [14] have described the green tea extract as a relatively cheap corrosion inhibitor.

The principle of EFM [15] is based on applying a potential perturbation signal composed of two since waves to obtain the current response. The ac-response will contain more and higher frequencies due to the nonlinear behavior of corrosion phenomena. Mathematical analysis of current components at various frequencies enables the calculation of corrosion rate, Tafel parameters and causality factors.

The following equations developed for EFM are used to calculate corrosion current density and Tafel parameters.

$$i_{corr} = \frac{i_{\omega 1}{}^{2}}{\sqrt{48(2 i_{\omega 1} i_{3\omega 1} - i_{2\omega 1}{}^{2})}} \tag{1}$$

$$\beta_a = \frac{i_{\omega 1} U_{\circ}}{2\sqrt{3(2 i_{\omega 1} i_{3\omega 1} - i_{2\omega 1}{}^{2})} + 2 i_{2\omega 1}} \tag{2}$$

$$\beta_c = \frac{i_{\omega 1} U_{\circ}}{2\sqrt{3(2 i_{\omega 1} i_{3\omega 1} - i_{2\omega 1}{}^{2})} - 2 i_{2\omega 1}} \tag{3}$$

Where i_{corr} is the corrosion current density, $U_{\circ}$ the amplitude of applied signal, β_a the anodic Tafel parameter and β_c the cathodic Tafel parameter.

Along with corrosion rate and Tafel parameters, EFM also measures two causality factors namely causality factor 2 and causality factor 3 that are used to validate the captured data. Theoretically, the current component at specific intermodulation frequency is a multiple of the current component at specific harmonic frequency and this multiple defines the causality factor. To obtain the causality factor 2 (shown below by equation 4), the harmonic component $\boldsymbol{i}_{2\omega 1}$ is measured at frequency $\boldsymbol{2\omega 1}$ and the intermodulation component $\boldsymbol{i}_{\omega 2\pm\omega 1}$ is measured at frequency $\omega 2\pm\omega 1$.

$$\text{Causality factor 2} = \frac{i_{\omega 2\pm\omega 1}}{i_{2\omega 1}} \tag{4}$$

Similarly causality factor 3 is measured with the help of following equation,

$$\text{Causality factor 3} = \frac{i_{2\omega 2\pm\omega 1}}{i_{3\omega 1}} \tag{5}$$

2. EXPERIMENTAL

To examine brass (63 % Cu, 35 % Zn and 1 % Pb) in both acidic and alkaline solutions, 1 % H_2SO_4 and 1 % NaOH were used with and without inhibitors. Each metallic sample having area of 1 cm^2 was connected with an electrical wire by welding and embedding in an epoxy The sample was grounded with SiC paper of 4000 grit to prepare a smooth surface. Later, the sample was washed with soap and degreased with ethyl alcohol. Green tea extract was prepared by mixing 25 g of green tea in 500 ml of distilled water and boiling for 10 min. Finally the solution was cooled and filtered to use in corrosion experiments. Tobacco infusion was prepared in the same way as the green tea extract.

Borate buffer solution (pH ≈ 6.5) and 0.1 M NaCl were used during short-term experiments for aluminum to passivate and pitting generation. For brass, 0.1 % $C_6H_{16}N_2$ (hexamethylene diamine) was used as corrosion inhibitor whereas 0.5 M $NaNO_3$ (sodium nitrate) was utilized for aluminum against pitting.

The rectangular shaped strips of carbon steel (0.2 % C, 0.045 % P and 0.045 % S) and brass (63 % Cu, 35 % Zn and 1 % Pb) having size of 10 mm x 102 mm x 3 mm were cut to perform long-term experiments. For a period of 90 days, carbon steel strips were immersed in 1 % H_2SO_4 at 25 °C and in 1 % NaCl at 35 °C whereas brass in 1 % H_2SO_4 at 25 °C. To make a comparison with the green tea, 0.1 % $NaNO_2$ (sodium nitrite) was used as corrosion inhibitor for carbon steel in 1 % NaCl at 35 °C. Brass samples were cleaned with commercially available metal cleaner known as *Sidol*, while the carbon steel samples were cleaned with 15 % HCl solution and *Sidol*.

2.1. Tests with EFM for brass

The frequencies of the perturbation signal of the EFM were used as 0.2 and 0.5 Hz with amplitude of 20 mV RMS. The tests were performed with the help of EFM for brass in 1 % H_2SO_4 to evaluate the performance of different inhibitors. The corrosion rate, causality factor 2 and anodic Tafel parameter were measured to make a comparison among different inhibitors. EFM was also utilized to see the performance of tobacco-1 to protect brass against dezincification in the acidic environment.

2.2. Cyclic polarization scans for brass

In each experiment, the parameters were kept alike to enable good comparison among the cyclic polarization scans. A slow scan rate of 0.5 mV/s vs. Ag/AgCl reference electrode was chosen for the forward and reverse scans in all experiments. Due to the reverse scan we may get positive or negative hysteresis. In case of pitting, we always get negative hysteresis, which is created by the current density difference between the forward and reverse portions of the scan at the same potential. The surfaces of the samples were visually analyzed under microscope having magnification of 40x of the original size. N_2 gas was passed through each solution to deaerate it before starting the experiment.

2.3. Potential noise measurement for aluminum

In this short-term experiment, the potential noise was measured with the help of data acquisition unit during pitting and passivation to see the performances of 0.5 M $NaNO_3$ inhibitor and green tea. For this purpose 0.2 M $Na_2B_4O_7.H_2O$ (sodium tetraborate) also known as borax was mixed with 0.2 M H_3BO_3 (boric acid). The pH of the solution was adjusted to 6.5 by adding boric acid. First, the aluminum sample was immersed into borate buffer solution. Few readings of the potential were recorded in this solution and then 0.1 M NaCl was added in borate buffer solution without stopping the experiment to observe the change in the response of the signal. Similarly, the third solution (green tea extract) was added to the previous two solutions to see the effect on the output signal. This experimental procedure was repeated by replacing green tea with 0.5 M $NaNO_3$ inhibitor.

2.4. Long-term tests

Closed glass bottles were used to put different metallic rectangular strips in different corrosive solutions for 90 days in thermostatically controlled oven. Only one third length of each sample was immersed into the solution. After 90 days, to perform visual analysis, all metallic strips were taken out of bottles, and then cleaned to remove the corrosion products.

3. RESULTS AND DISCUSSION

3.1. EFM tests to compare different inhibitors for brass

The Figure 1 shows the extent to which the corrosion rate decreases for brass by adding different green inhibitors at a temperature of 25 °C. During the course of different experiments (Figure 1), it was observed that green tea and tobacco can decrease adequately the corrosion rates for brass.

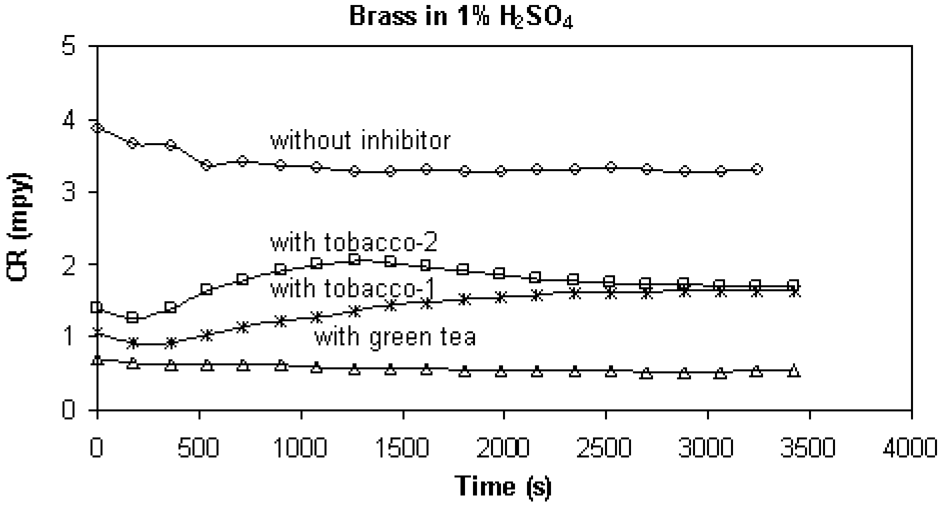


Figure 1. The effect of green tea, tobacco-1 and tobacco-2 on the corrosion rate of brass in 1 % H_2SO_4.

Kuş and Mansfeld [4] have investigated EFM and obtained promising results about corrosion rates for mild steel in 0.05 M H_2SO_4. Lenard [16] investigated the EFM as an online corrosion-monitoring instrument for copper-nickel specimens exposed to flowing seawater. He monitored the corrosion rates by using three electrochemical techniques including EFM. As supported by the electrochemical impedance measurements, the EFM showed that the corrosion rate was not under diffusion control. Lenard utilized frequencies of 20 and 50 mHz for the EFM with a base amplitude of 10 mV as an applied signal. Both techniques of LPR and EFM show a corrosion rate that quickly drops after initial immersion as protective films start to develop in the clean seawater. Due to the smaller amplitude, the EFM can be considered as a convenient method for longer durations of online corrosion monitoring because of the less perturbation applied on the surface under investigation. Lenard has mentioned that the EFM has the apparent ability to highlight the changes in corrosion mechanism. He also observed the accurate changes in corrosion rates measured by the EFM due to daily variations in oxygen concentration through biological activity.

The current experimental work suggested that corrosion rate, anodic Tafel parameter and causality factor 2 can be used to screen out various corrosion inhibitors. The advantage of using EFM is to get different corrosion parameters in a single measurement. The results shown in Figures 1-3 indicate that green tea is a better corrosion inhibitor than tobacco in the acidic environment. The values of causality factor 2 change between 1.8 and 2.4 indicating the different levels of brass protection by green tea and two types of tobacco in sulfuric acid.

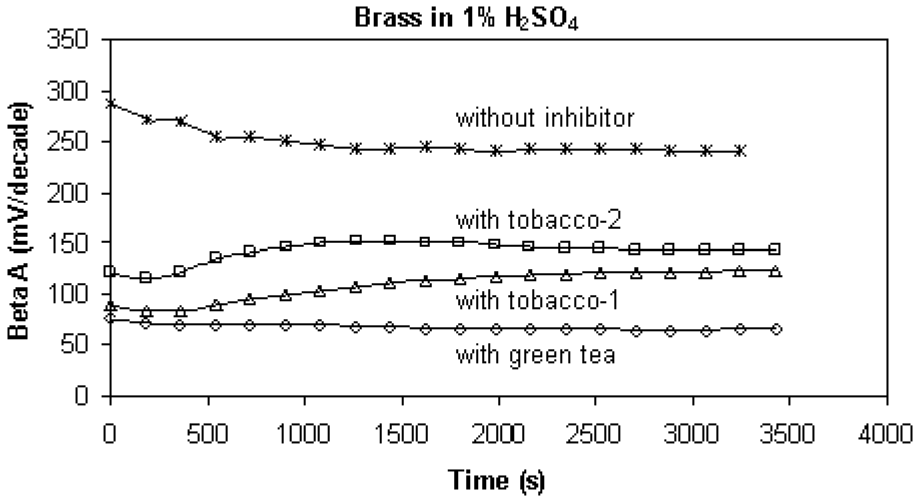


Figure 2. Anodic Tafel parameter measured for brass in 1 % H_2SO_4 with and without green inhibitors

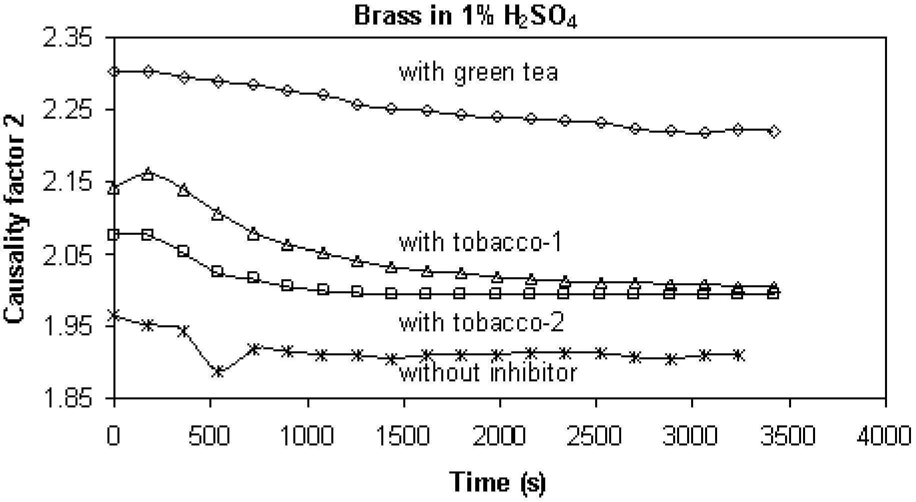


Figure 3. Causality factor 2, obtained with the help of EFM technique for brass in 1 % H_2SO_4 with and without green inhibitors

Generally during uniform corrosion, the causality factor 2 should remain stable around 2, whereas at different levels of inhibition the causality factor 2 are around 2 but vary slightly. With high corrosion rate, anodic Tafel parameter goes up while causality factor 2 goes down. These tests show that EFM can be used to compare different inhibitors.

3.2. Cyclic polarization scans for brass in alkaline solution

In the cyclic polarization scan (Figure 4A), small negative hysteresis shows the incidence of pitting corrosion. The hysteresis being the result of current density difference between the forward and reverse portions of the scan at the same potential indicates the disruption of the steady state surface structure by the increase in potential. It reflects the ease or difficulty with which that initial structure is restored as the potential is decreased back toward the corrosion potential at constant scan rate. From a practical point of view, the larger the negative hysteresis, the greater is the disruption of surface passivity, the greater is the difficulty in restoring passivity, and usually the greater is the risk of localized corrosion. In Figure 4A, much disturbance can be observed on the portion of the reverse scan due to many fluctuations in the current density as potential is ramped downwards.

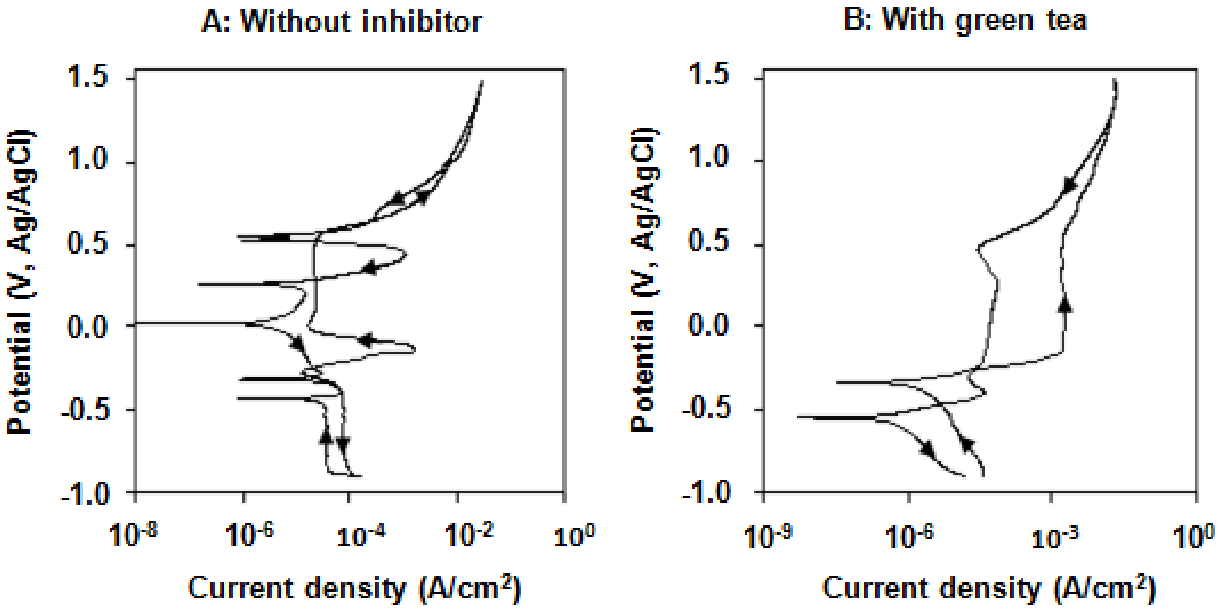


Figure 4. Cyclic polarization curves for brass in 1 % NaOH at a temperature of 25 °C with and without green tea.

After removing the black layer from the surface of the sample at the end of the experiment, a pitting like corrosion (due to dezincification of brass) was observed by inspecting the surface of the brass sample under the microscope. This suggests that alkali can be aggressive for the brass alloy to accelerate this kind of localized corrosion.

A large positive hysteresis was observed (Figure 4B) by using the green tea, indicating absence of localized corrosion. The repassivation potential is also very close to the corrosion potential showing that corrosion can be stopped by using green tea as inhibitor for brass in NaOH solution. With the addition of green tea, the corrosion potential becomes slightly noble where as the maximum current density also decreases from 2.74x10^{-2} to 2.03 x10^{-2} A/cm^2. In the portion of reverse scan, we also observed good passivation as compared to the scan without inhibitor (Figure 4A). The hysteresis area is bigger and positive suggesting the absence of trends towards localized corrosion. The microscopic view of the samples after scanning the cyclic polarization curves (Figure 5) confirms the absence of localized corrosion due to green tea.

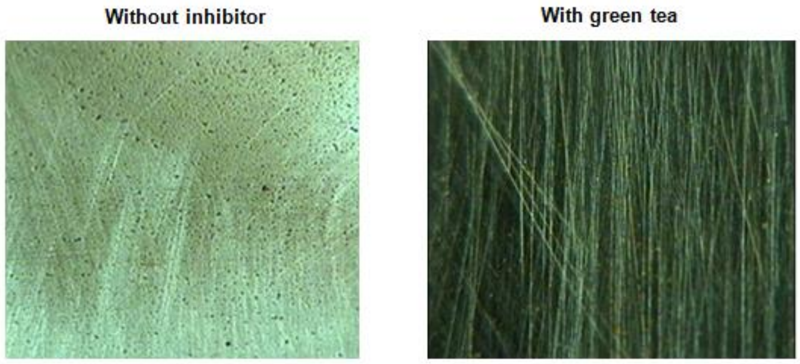


Figure 5. Images of brass surface taken by optical microscope after scanning the cyclic polarization curves in 1% NaOH. Small pits are visible in the case of no-inhibitor. Corrosion like pitting was prevented by using green tea

3.3. Cyclic polarization scans for brass in acidic solution

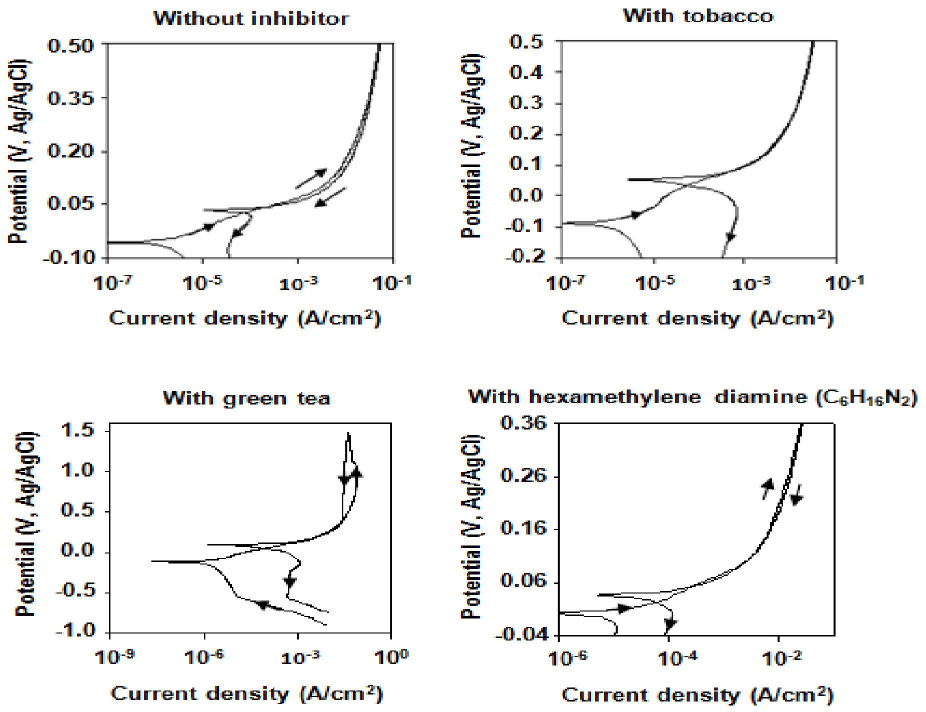


Figure 6. Cyclic polarization curves for brass in 1% H_2SO_4 with and without inhibitors

The cyclic polarization curve for brass in 1 % H_2SO_4 without any inhibitor is shown in Figure 6. The corrosion potential for brass in acidic solution without inhibitor is found to be -0.06 V vs. Ag/AgCl. After the experiment, the surface of brass was badly corroded due to the appearance of raised surfaces (shown with the help of visual microscope and SEM in Figure 7). In the scan without inhibitor, a small negative hysteresis is due to the dezincification of brass, leaving behind the raised surfaces of brass.

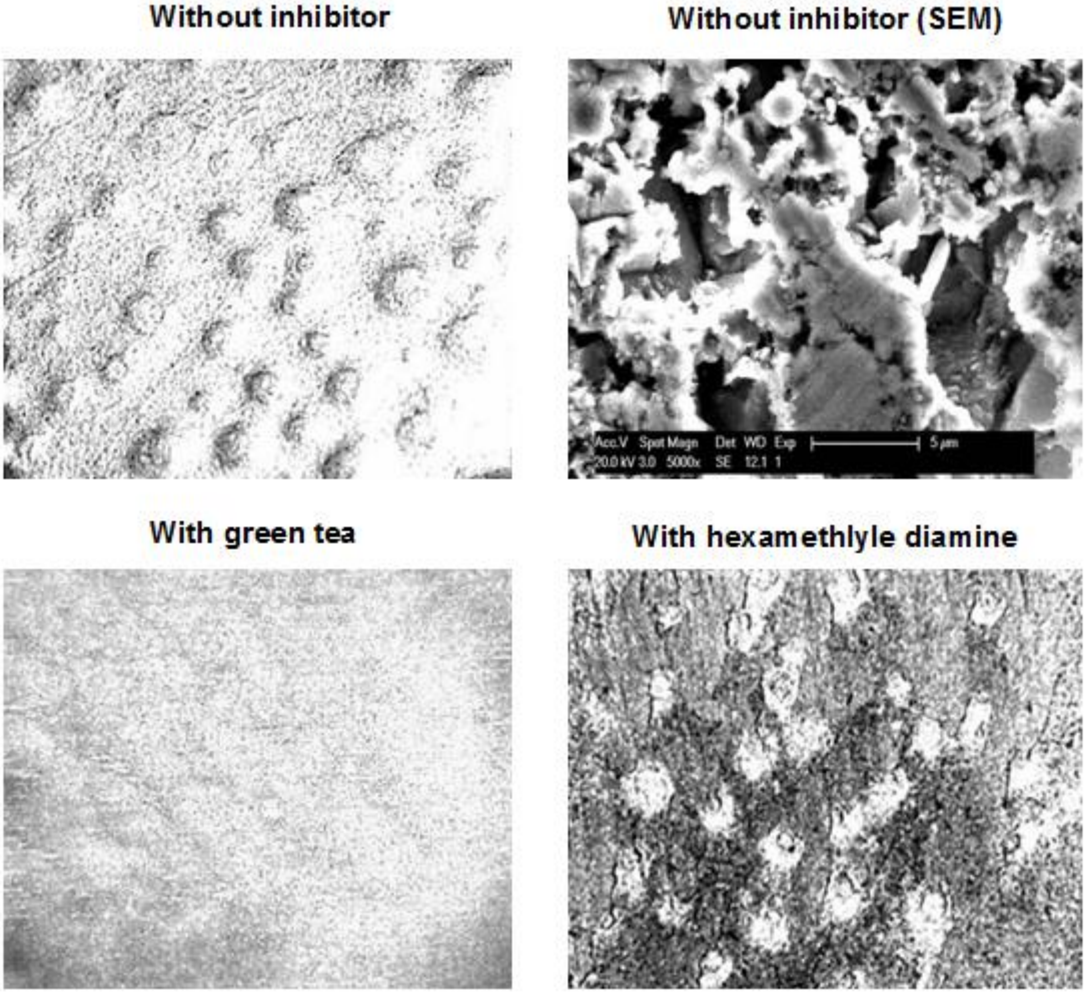


Figure 7. Microscopic images of the brass surface after scanning the polarization curves. No raised surfaces (dezincification of brass) appeared after scanning the cyclic polarization curve in 1 % H_2SO_4 only in the presence of green tea.

The cyclic polarization scan for brass in 1% H_2SO_4 with tobacco-1 (Figure 6) does not damage the metal surface significantly. The corrosion potential with tobacco-1 becomes -0.1 V vs. Ag/AgCl that is slightly more negative than the case of without inhibitor.

In the case of green tea, the hysteresis becomes positive where as the corrosion potential remains the same as with the tobacco-1. The passivation region and positive hysteresis as shown in the scan with green tea (Figure 6) indicate the protection of brass against dezincification.

The cyclic polarization curve in the presence of $C_6H_{16}N_2$ inhibitor shows that brass does not passivate completely in 1 % H_2SO_4. Some raised surfaces appear after scanning the cyclic polarization curve with corrosion inhibitor (Figure 7). The corrosion potential with $C_6H_{16}N_2$ becomes nobler (-0.002 V vs. Ag/AgCl than without inhibitors but still the metal is badly corroded as compared to the cases of tobacco-1 and green tea.

3.4. Potential noise to evaluate inhibitors against pitting

Passivation, pitting and re-passivation were deliberately created by using different solutions one after the other to get the potential noise for aluminum (Figure 8).

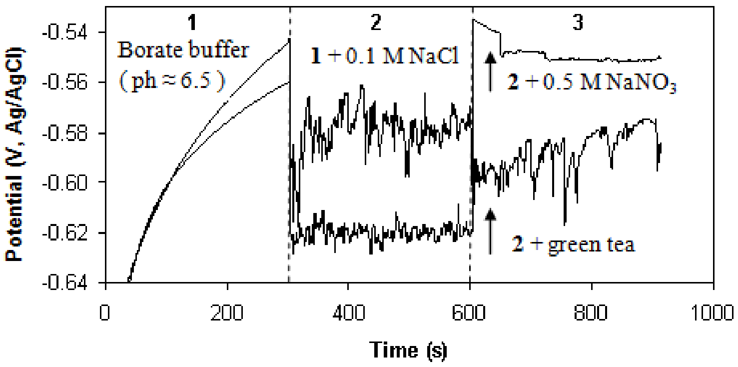


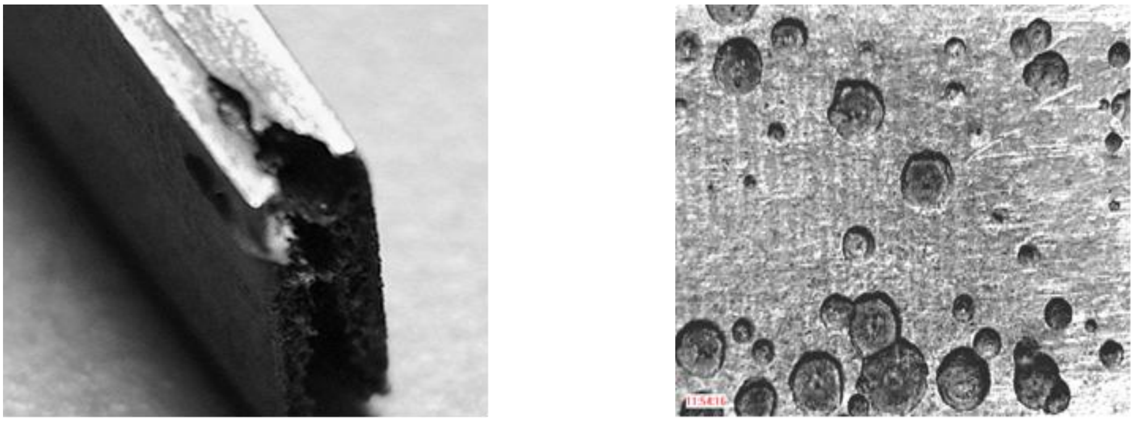
Figure 8. The change in the behavior of potential noise due to pitting and passivation for aluminum occurs due to sudden addition of different solutions in a continuous experiment.

The pitting zone is clearly characterized by rapid upward peaks. By sudden addition of 0.5 M $NaNO_3$ inhibitor the fluctuations in the potential noise reduced significantly and it moved towards a noble (more positive) direction, showing a better repassivation of aluminum. The potential noise remains noisy but with downward peaks due to the addition of green tea. Consequently, green tea neither passivates aluminum completely, nor performs better than $NaNO_3$ inhibitor (Figure 8).

3.5. Long-term tests

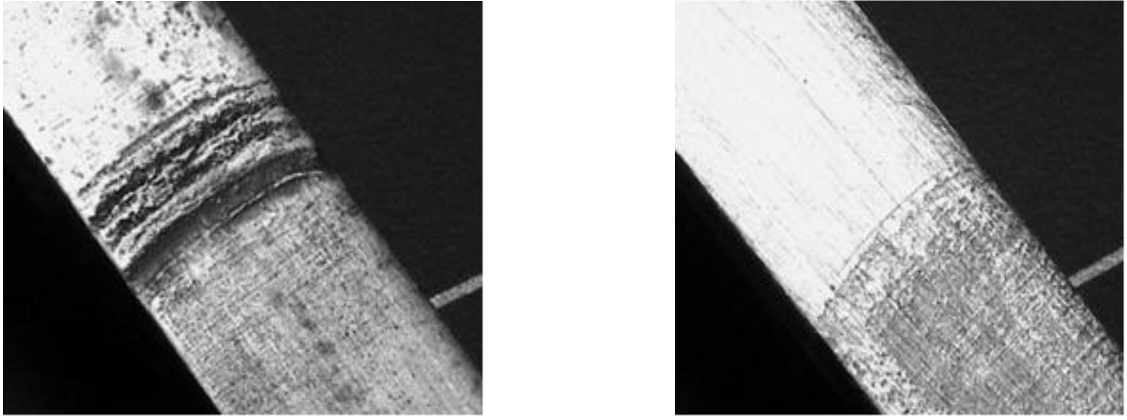
The green tea could not protect well the carbon steel and brass in 1 % H_2SO_4 at a temperature of 25 °C for 90 days. After removing the rust many pits on the carbon steel sample were found due to keeping in 1 % H_2SO_4 in the presence of green tea (Figure 9). Green tea has protected the brass to some extent in the acidic solution from acid line corrosion (Figure 10).

Figure 11 show the comparison between $NaNO_2$ inhibitor and green tea to protect carbon steel in 1 % NaCl at a temperature of 35°C.



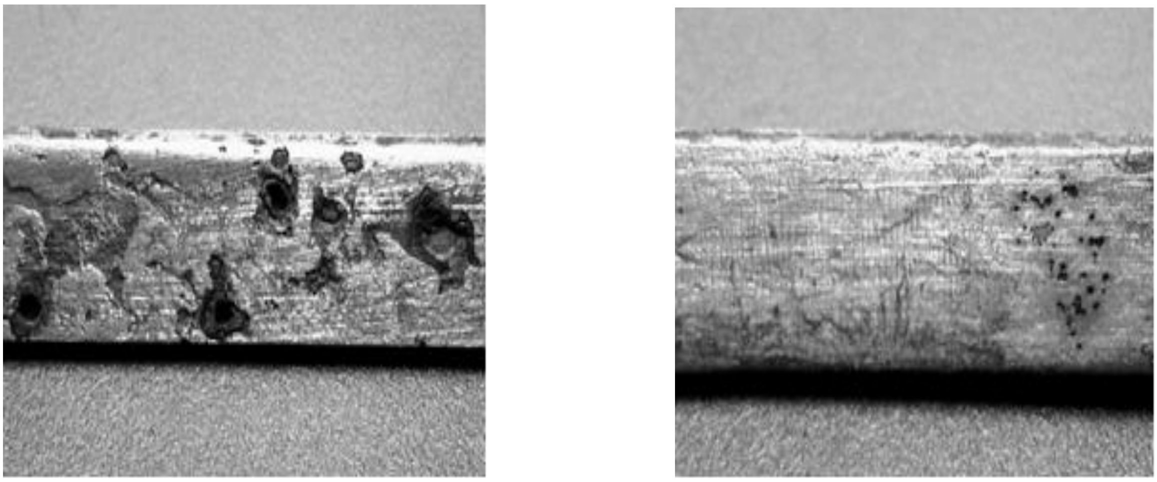
Without inhibitor With green tea

Figure 9. Carbon steel after the exposure test with and without green tea for 90 days in 1 % H_2SO_4 at a temperature of 25 °C.



Without inhibitor With green tea

Figure 10. Brass after keeping in 1 % H_2SO_4 at a temperature of 25 °C for 90 days has suffered severe acid line corrosion whereas brass with green tea experienced relatively less acid line corrosion.



Without inhibitor With green tea

With $NaNO_2$ inhibitor

Figure 11. After 90 days of exposure for carbon steel in 1 % NaCl at a temperature of 35 °C.

After removing the rust it was observed that the green tea protected the carbon steel strip partly as few pits appeared on a small portion of the sample (Figure 11). On the other hand, without inhibitor and with $NaNO_2$ inhibitor, intensive corrosion for carbon steel in saline solution occurred at a temperature of 35 °C. Therefore green tea can be used in acidic and saline solutions for carbon steel and brass to slow down the corrosion rates but sufficient protection cannot be promised by green tea.

4. CONCLUSIONS

1. EFM can be considered as a reliable technique to compare various inhibitors for their ability to protect metals against corrosion.
2. Green tea is more efficient than tobacco to protect brass in acidic environment.
3. Brass can be protected due to green tea in an alkaline solution against pitting like corrosion. In acidic environment green tea performs better than tobacco and hexamethylene diamine ($C_6H_{16}N_2$) to protect brass.
4. Sodium nitrate ($NaNO_3$) inhibitor performs better than green tea to passivate aluminum against pitting.
5. Green tea cannot protect completely the carbon steel and brass for lengthy exposure in acidic solution. Similarly green tea does not protect fully but performs better than sodium nitrite ($NaNO_2$) inhibitor for carbon steel in saline solution.

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