A comparative study of gravimetric and electrochemical techniques for the evaluation of corrosion inhibitor activity onset and efficiency in pipeline CO₂ environments

Estudio Comparativo de técnicas electroquímicas y gravimétricas para la evaluación de la actividad y eficiencia de inhibidores de corrosión en ambientes con presencia de CO₂

A. Cáceres^{1, 3*} M. Casales² L. Martínez²

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ABSTRACT

The monitoring of internal corrosion of pipelines is a critical element of the pipeline maintenance programs. A benchmarking study of enhanced techniques for real-time corrosion monitoring such as Linear Polarization Resistance and Harmonic Distortion Analysis was performed, enhanced Electrical Resistance in conjunction with standard metal coupon. The transition of the corrosion processes occurring in metals immersed in corrosive electrolytes at the onset of inhibitor action after its injection was found a revealing item for study. This study considered a 3% NaCl solution with and without 10% diesel, saturated with CO₂ at 50 °C and standard AISI 1018 coupons. A set of generic corrosion imidazoline-based inhibitors was studied. The benefits of employing real-time corrosion monitoring devices include shortened test times, increased number of inhibitors evaluated, and an increase in data quality and quantity. Results show that the corrosion rates from linear polarization resistance in the solution without inhibitor were overestimated, while the Harmonic Distortion Analysis and enhanced Electrical Resistance presented similar results to Standard Coupon. The enhanced electrical resistance monitoring also proved to be a good device to reveal the onset of corrosion protection after the inhibitor is applied.

Keywords: Internal corrosion, real time corrosion monitoring, corrosion inhibitors, linear polarization resistance, harmonic analysis, electrical resistance, coupons corrosion.

RESUMEN

El monitoreo de la corrosión interna en tuberías de transporte de crudo es un elemento crítico para los programas de mantenimiento de tuberías de transporte. En este trabajo se ha desarrollado un estudio comparativo de las diferentes técnicas utilizadas en procesos de monitoreo de corrosión interior en tiempo real, tales como resistencia a la polarización lineal (LPR), análisis de distorsión de armónicos (HDA), resistencia eléctrica (ER) junto con la técnica convencional de pérdida de peso por cupones metálicos. La transición del proceso de corrosión que ocurre en un metal inmerso en un electrolito corrosivo y la respuesta de un inhibidor de corrosión una vez inyectado en el sistema corrosivo fue evaluada mediante las técnicas antes descritas. En este estudio la solución corrosiva considerada fue al 3% de NaCl en presencia y ausencia de diesel, saturada con CO₂ a 50 °C, condiciones similares a las de transporte

¹ Departamento de Ingeniería Química Metalúrgica. Facultad de Química. Universidad Nacional Autónoma de México, 04510, México, D.F., México.

² Universidad Nacional Autónoma de México, Instituto de Ciencias Físicas, Av. Universidad S/N, Cuernavaca, Mor., México

³ Universidad ECCI, Carrera 19 N° 49-20 Bogotá-Colombia.

* Autor de correspondencia: acaceresj@ecci.edu.co

de crudos en la industria de transporte de crudo mexicano, el acero ensayado fue un AISI SAE 1018. Como inhibidor del proceso de corrosión por CO₂, se utilizó una serie de inhibidores genéricos de tipo imidazolina. El empleo de técnicas de monitoreo en tiempo real y la rápida respuesta frente al uso de inhibidores en el medio corrosivo, mostraron la eficiencia del inhibidor utilizado y su acción inmediata fue registrada con el uso de las técnicas de monitoreo en tiempo real empleadas.

Palabras clave: Corrosión interior, monitoreo de la corrosión en tiempo real, inhibidor de corrosión, resistencia a la polarización lineal, análisis de armónicos, resistencia eléctrica, cupones de corrosión.

INTRODUCTION

In the oil and gas industry, the monitoring of internal corrosion of pipelines is considered as a top priority task. This challenge has led to the evolution of corrosion monitoring tools from passive recording coupons towards real-time monitoring, which enables pipeline operators to provide immediate response and to perform proactive measures as corrosion damage is detected [1]. Corrosion monitoring is more difficult than the monitoring of most other process parameters in the industry, since different corrosion mechanisms may coexist and there is no a single measurement technique that will detect each of them. A general range of corrosion monitoring techniques and systems has grown, particularly in the last decades, for sensing, measuring, and calculating corrosion damage. The developments of effective corrosion monitoring techniques and accessible software have allowed to take to the field new techniques providing real time and nearly instantaneous evaluation of the internal corrosion phenomena caused by the transported fluids, typically containing water and other corrosive agents [1, 2].

The techniques for internal corrosion monitoring usually employed are associated with electrochemical techniques such as linear polarization resistance or harmonic distortion, and metal loss measurement employing weight loss coupons and electrical resistance probes. The corrosion coupons are only capable of providing information about month to month or larger exposures [3]. On the other hand an electrochemical approach or an electrical resistance probe may provide real time corrosion diagnostic information. The goal of this study is to evaluate comparatively the following techniques: Linear Polarization Resistance (LPR), Harmonic Distortion Analysis (HDA), Electrical Resistance (ER) and weight loss coupons in corrosion system with CO₂.

It is well known that weight loss coupons are used to evaluate the corrosion rates over long periods of time. This technique represents global corrosion rates in the system unlike electrochemical techniques through which one can follow changes in the process kinetic. However, weight loss is one of the oldest techniques and widely used in industry. Monitoring techniques such as electrical resistance (ER) and Linear Polarization Resistance (LPR) can be used to provide further quick information about instantaneous corrosion in the system. The principle of the widely used ER technique is quite simple, i.e. the electrical resistance of a sensing element increases as its cross-sectional area is reduced by corrosion damage, the electrical resistance technique (ER) by corrosion monitoring method grew quickly after the correlation with corrosion rates was recognized in the 1950's [4, 5]. In the linear polarization resistance, a small potential perturbation (typically 10-20 or even 30 mV) is applied to the working electrode and the resulting current is measured. The ratio of the potential to current perturbations is known as the polarization resistance that can be itself related to the corrosion current with the Stern-Geary relationship, where Tafel slopes are usually pre-established, this is 120 mV/dec. Harmonic distortion is a measure of the non-linear current distortion arising during the LPR measurements. The data is analyzed with the use of Fast Fourier Transform analysis, and so obtained a measure of the corrosion current and provide an on-line estimate of Stern-Geary constant. The Stern and Geary constant is calculated from the Harmonic Analysis data, with first, second and third harmonics in the sinewave signal of frequency W [6].

EXPERIMENTAL PROCEDURES

Test material and solution

AISI 1018 carbon steel samples were employed in this study. Standard three identical electrodes with a triangular configuration were used in the

Linear Polarization Resistance and Harmonic Distortion analysis techniques. The electrical resistance method used Microcor® probes in the cylindrical element form. Gravimetric coupons by Metal Samples® were used for the weight loss test. The surface samples were polished with 600 grit SiC paper and finally rinsed with distilled water, acetone and ethanol.

Experiments were performed in a 3 wt% NaCl solution, with a pH value of 4.7, in tri-distilled water and a mixture which consisted of 90 vol.% of this solution plus 10 vol.% diesel. The CO₂ gas was bubbled during 2 hours prior to testing in order to remove the dissolved oxygen from the test solution. Through the experiment, the electrolyte was kept deaerated and saturated with CO₂ by continuous bubbling with CO₂. For all experiments, the temperature was kept constant at 50 ± 2 °C. Inhibitor was added 2 hours after pre-corroding the specimen. The weight loss experiments lasted 336 h in order to follow the formation of any iron carbonate film. Additionally, the use of field measurement techniques was to evaluate the corrosion control by using inhibitors.

Weight loss and Electrochemical measurements

All the weight loss tests were obtained in a glass cell with coupons, which were removed every certain period of time; the time exposition total was 336 hours. Electrical Resistance probes were obtained by CORRDATA® Corrosion Monitoring System. Electrochemical techniques employed included, Linear Polarization Resistance, LPR, and Harmonic Distortion Analysis (HDA), which were obtained by using a SmartCET™ System. Linear Polarization Resistance and Harmonic Analysis were conducted with three electrodes mode. Linear Polarization Resistance technique involves measurements of the polarization resistance of a corroding electrode using a small amplitude polarization of the electrodes. The slope of the response at the corrosion potential, the polarization response, is then inversely proportional to the corrosion current. Harmonic Analysis technique is a measurement of the non-linear current distortion arising during the LPR measurement. The data is analyzed with the using Fast Fourier Transform analysis to provide a measure of the corrosion current, and to provide an on-line estimate of the corrosion rate calculation about the Stern-Geary constant.

Among the used inhibitors, commercial hidroxiethyl-imidazoline type inhibitors were added at a 25 ppm concentration which was found to be an optimum one to inhibit the corrosion phenomenon [7, 8, 9, 10]. Similar to the weight loss experiments, the working electrode was allowed to pre-corrode during 2 hours before the corrosion inhibitor was added. The inhibitors used were: HEIO, HEIE and HEIC. HEIO is an inhibitor whose chemical name is 1H-imidazole-1-ethanol, 4,5-dihydro,-2-C15-17 unsaturated alkyl derivatives, the inhibitor HEIE is an inhibitor whose chemical name is 1H-imidazole-1-ethanol, 4,5-dihydro, -2-nor coco alkyl derivatives and HEIC is an inhibitor whose chemical name is 1H-imidazole-1-ethanol, 2- Heptadecyl-4, 5- Dihydro.

RESULTS

Coupons Weight loss

The corrosion rate by coupons weight loss was calculated through the equation (1):

$$CR = \frac{K * W}{A * T * D} \quad (1)$$

Where CR is the corrosion rate (mpy), K is a constant ($3.45 \cdot 10^6$), W is weight loss during exposition time (g), A is exposure area (cm²), T is the exposition time (hours) and D is the density (g/cm³).

Table 1. Weight loss tests results.

Inhibitor	3% NaCl solution		3% NaCl + 10 vol.% diesel	
	Corrosion rate (mpy)	Inhibitor efficiency (%)	Corrosion Rate (mpy)	Inhibitor efficiency (%)
–	57.0	–	54.9	–
HEIO	1.44	97.47	0.951	98.27
HEIE	0.41	99.28	0.399	99.27
HEIC	1.43	97.49	0.978	98.22

Table 1 summarizes the weight loss results after exposing 1018 carbon steel during 336 hours to a CO₂-saturated 3% NaCl solution with and without 10 vol.% diesel at 50 °C with and without 25 ppmof hidroxyethyl-imidazoline. The high efficiency of these inhibitors is evident, since the corrosion rate is decreased from 57 mpy for the uninhibited 3% NaCl solution to 1.44 mpy, 0.41 mpy and 1.43 mpy

respectively, obtaining an efficiency value of 97,47%, 99.28% and 97.49% for each one of the inhibitors respectively. The corrosion products morphology of specimen in the uninhibited solution after 192 and 336 hours of exposure, consists of a porous layer of FeCO_3 , Figures 1-2, mainly siderite with equiaxial grains between 10-15 μm long.

Figure 1. XRD patterns of the carbon steel coupons covered by FeCO_3 in the uninhibited CO_2 -saturated 3% NaCl solution at 50°. All peaks can be attributed to siderite).

Electrical resistance (ER)

Corrosion rate was calculated by the electrical resistance method too. The electrical resistance of a metal or alloy element is given through the equation (2):

$$R = \frac{r \cdot L}{A} \quad (2)$$

Where L is the probe element length (cm), A is the cross-sectional area (cm^2), and r is the specific resistance of the probe metal ($\Omega \cdot \text{cm}$). Reduction or metal loss in the element cross section, A , due to corrosion will be accompanied by an increase in the element electrical resistance (R). To obtain the corrosion rate, a series of measurements are made over a period of time, and the results are plotted as a function of exposure time. The corrosion rate can be determined from the slope of the resulting plot [5, 6].

The results from the Electrical Resistance curves for 1018 carbon steel exposed to the CO_2 -saturated 3%

Figure 2. SEM micrograph of steel covered by FeCO_3 after a) 192 h and b) 336 h of exposure to uninhibited CO_2 -saturated 3% NaCl solution at 50 °C.

NaCl solution at 50 °C with and without 25 ppm of inhibitors are shown on Figure 3. In this system the average corrosion rate value for the uninhibited solution was 72.6 mpy, with inhibitor addition the average corrosion rate, and after the inhibitors addition the corrosion rates were 0.65 mpy inhibitor, 0.3 mpy and 1.24 mpy for HEIO, HEIE and HEIC inhibitors respectively. With this technique, the higher efficiency of corrosion inhibitors were clear, obtaining efficiencies values of 98.95, 99.61 and 98.39% for HEIO, HEIC and HEIE inhibitors respectively.

The electrical resistance curves for 1018 carbon steel exposed to the CO_2 -saturated in mixture of 3% NaCl + 10 vol.% diesel at 50 °C with and without hydroxyethyl imidazoline-type inhibitors are shown on Figure 4. The average corrosion rate value in the uninhibited solution was 77.3 mpy, but once the inhibitor was added the average corrosion rate was decreased down to 0.7 mpy with HEIO,

Figure 3. Metal loss data for Electrical Resistance probes with and without corrosion inhibitors type imidazoline in CO_2 -saturated 3% NaCl solution.

Figure 4. Metal loss data for Electrical Resistance probes with and without corrosion inhibitors type imidazolines in CO_2 -saturated 3% NaCl+ 10 vol.% diesel solution.

0.3 mpy with HEIE and 1.5 mpy for HEIC-type inhibitor. Similar to the obtained results in 3% NaCl without diesel, solution, the higher efficiency of these corrosion inhibitors were clear, obtaining efficiencies values of 99.07% for HEIO, 99.62% for HEIE and 98.02% by HEIC-type inhibitor.

The industrial use of ER monitoring has been documented for various authors, G.R. Cameron and L.G. Coker [11] showed that sulfide environments present difficulties for the ER technique; electrically conducting iron sulfide corrosion products cause underestimates of metal loss. Gareau [12] illustrated the use of a computerized system for data transmission from several remote sites to a central control facility.

At this central facility, the ER data were monitored in real time, manipulated, and analyzed to obtain information on corrosion at the remote sites Thierry, Thoren and Leygraf, [13] compared the weight-loss results, ER measurements, and LPR measurements in cooling water systems. They concluded that the ER measurements indicated corrosion rates greater than those observed on the coupons when there was significant localized corrosion of the coupons, concluding that ER technique is sensitive to pitting attack and provides a rate that is some intermediate value between the general corrosion rate and the penetration rate.

Electrochemical techniques

The electrochemical nature of corrosion, allows that measurements of the electrical properties of the metal solution interface. In linear polarization resistance technique, a small potential perturbation is applied to the working electrode and the resulting current is measured. The ratio between the potential and current perturbations is known as the polarization resistance (R_p). That can be related to the corrosion current through following Stern-Geary equation (3):

$$R_p = \frac{B}{i_{\text{corr}}} = \frac{\Delta E}{\Delta i}, \Delta E \rightarrow 0 \quad (3)$$

Where R_p is the polarization resistance; i_{corr} is the uniform corrosion current density and B is an empirical polarization resistance constant that is related to the anodic (b_a) and cathodic (b_c) Tafel slopes through the equation (4);

$$\beta = \frac{b_a b_c}{2.3(b_a b_c)} \quad (4)$$

The corrosion rate obtained by r by linear polarization resistance are for 1018 carbon steel exposed to the CO_2 -saturated 3% NaCl solution at 50 °C with and without 25 ppm inhibitor is shown in Figure 5, where it can be seen that the average corrosion rate without inhibitors was 150.87 mpy, but once the corrosion inhibitor was added the corrosion rate obtained were 0.81, 0.14 and 1.89 mpy for HEIO, HEIE and HEIC inhibitors respectively.

The corrosion rate obtained by linear polarization resistance are for 1018 carbon steel in the system with CO_2 -saturated 3% NaCl + 10 vol.% diesel at 50 °C, is shown in Figure 6, obtaining an average

Figure 5. Corrosion rate obtained by LPR with and without corrosion inhibitors type imidazolines in CO₂-saturated 3% NaCl solution.

Figure 6. Corrosion rate obtained by LPR with and without corrosion inhibitor type imidazolines in CO₂-saturated 3% NaCl + 10 vol.% diesel solution

corrosion rate without inhibitor of 144.47 mpy, whereas the average corrosion rates were 0.04, 0.062 and 0.16 mpy for HEIO, HEIE and HEIC-type inhibitors. It can be seen that in presence of diesel, the corrosion rates with inhibitors were much lower than those in absence of it, and, in all systems, the efficiency of inhibitor was evident, obtaining efficiency values higher than 99%. It should be noted that all tests were performed by triplicated. Arrow indicated addition of inhibitor of corrosion and your effect immediately.

In the Harmonic Distortion Analysis technique, a low frequency sinusoidal potential is applied to a three

electrode measurement system, and the resulting current is measured three different frequencies is used to verify the repeatability of the technique. The amplitude is in the range of 10-30-mV peak to peak. The frequency used is typically 0.1-10 Hz. Analyzing the primary frequency and the harmonics allow extraction of the required kinetic parameters of the corrosion process. Based on Stern-Geary model of the electrical double layer, a polarized electrode near the corrosion potential by a sinusoidal voltage of angular frequency ω and voltage amplitude U_o , over a period of time; t , gives a faradaic current density I [6, 14, 15], given through the equation (5);

$$i = i_{corr} \left(e^{2.3u_o \sin \omega t} - e^{-2.3u_o \sin \omega t} \right) \quad (5)$$

The current density of the Faradaic process will have a distorted sinusoidal form due to the non linear nature of the anodic and cathodic partial processes and will include higher harmonics having $k\omega$ angular frequency ($k = 2, 3, \dots$). This phenomenon is termed Faradaic distortion [14, 15, 16, 17, 18, 19]. The amplitudes of the harmonic components are obtained by Fourier's series expansion of the exponential terms, equation (6):

$$i_f = i_o + i_1 \sin \omega t - i_2 \cos \omega t - i_3 \sin \omega t + \dots \quad (6)$$

The first term of the series is the i_o D.C component (Faradaic rectification), the coefficients of the other terms are the amplitudes of the harmonic components. For the first three harmonic components are given by equations (7), (8), and (9):

$$i_1 = 2i_{corr} \left[I_1 \left(\frac{U_o}{\beta_a} \right) + I_1 \left(\frac{U_o}{\beta_c} \right) \right] \quad (7)$$

$$i_2 = 2i_{corr} \left[I_2 \left(\frac{U_o}{\beta_a} \right) - I_2 \left(\frac{U_o}{\beta_c} \right) \right] \quad (8)$$

$$i_3 = 2i_{corr} \left[I_3 \left(\frac{U_o}{\beta_a} \right) + I_3 \left(\frac{U_o}{\beta_c} \right) \right] \quad (9)$$

Where $\beta_a = b_a/2.303$, $\beta_c = b_c/2.303$, the first order modified Bessel functions are noted by I_n ($n = 1, 2, 3, \dots$). This formula can be simplified if U_o amplitude is limited to the extent ($U_o < \beta_a$ and $U_o < \beta_c$) that the Bessel functions could be approximated with the small arguments. Thus, the equations derivate of above formula where simplified by Devay and Mészáros as follows by equations (10, 11, 12):

$$i_1 = i_{corr} \left(\frac{1}{\beta_a} + \frac{1}{\beta_c} \right) U_o \quad (10)$$

$$i_2 = -i_{corr} \left(\frac{1}{\beta_a^2} - \frac{1}{\beta_c^2} \right) \frac{U_o^2}{4} \quad (11)$$

$$i_3 = -i_{corr} \left(\frac{1}{\beta_a^3} - \frac{1}{\beta_c^3} \right) \frac{U_o^3}{24} \quad (12)$$

Solving the equations system, Knowing amplitudes i_1 , i_2 , and i_3 , Devay and Mészáros proposed the following equations for the determination of corrosion current for the determination of i_{corr} , β_a and β_c , equations (17, 18, 19)

$$i_{corr} = \frac{i_1^2}{\sqrt{48} \sqrt{2i_1 i_3 - i_2^2}} \quad (13)$$

$$\frac{1}{b_{a,c}} = \frac{1}{4.6 U_o} \left(\frac{i_1}{i_{corr}} \pm 4 \frac{i_2}{i_1} \right) \quad (14)$$

Figures 7 and 8 show the corrosion rate obtained by using the harmonic distortion analysis. In Figure 7, the average corrosion rate without inhibitor was 53.21 mpy, but once the corrosion inhibitors were added the average corrosion rate obtained were 0.78, 0.29 and 0.86 mpy for HEIE, HEIO and HEIC-type inhibitors respectively. Figure 8 shows that, when diesel is added, the average corrosion rate without inhibitor was 54 mpy, whereas with inhibitor the average corrosion rates were 0.42, 0.088 and 0.46 mpy for HEIO, HEIE and HEIC-type inhibitors respectively. Once again, with or without inhibitors, the corrosion rates in presence of diesel were lower than those obtained without diesel, and in all systems, the inhibitor efficiency was more than 99%.

The corrosion rate obtained by using the LPR method in the uninhibited solution overestimates corrosion rates as compared to the results obtained by harmonic distortion analysis, but similar results were obtained by Durnie, Jefferson, and Kinsella [16] They demonstrated that Harmonic Distortion Analysis yields comparable corrosion rate data to LPR under a variety of carbon dioxide corrosion conditions, but a regular error of approximately 100% was evident in comparison to the HAD corrosion rates against comparable data obtained by using Linear Polarization Resistance, which was attributed to the assumed Tafel slopes in the LPR,

Figure 7. Corrosion rate measured by Harmonic Distortion Analysis with and without corrosion inhibitor type imidazolines in CO_2 -saturated 3% NaCl.

Figure 8. Corrosion rate measured by Harmonic Distortion Analysis with and without corrosion inhibitor type imidazolines in 3% NaCl + 10 vol.% diesel.

while HAD is capable of determined Tafel Slopes in each measurement cycle.

Thus, it can be concluded from all the obtained results with the different techniques, the differences in the obtained results with the SmartCET equipment is due to the fact that this is a "Black box" which does not allow us to know the used scan rate, Tafel slopes, etc. It can be said that by using these equipments the use of corrosion inhibitors can be monitored to detect its action on the metal surface and their persistency on top of the metal surface.

Finally, some polarization curves were performed for 1018 carbon steel exposed to the CO_2 -saturated 3% NaCl solution and CO_2 saturated 3% NaCl-Diesel at 50 °C with and without 25 ppm of hydroxyl ethyl type imidazolines are shown on Figures 9 and 10.

Figure 9. Effect of 25 ppm corrosion inhibitor type imidazolines on the polarization curves for carbon steel in a CO_2 -saturated 3% NaCl solution at 50 °C.

Figure 10. Effect of 25 ppm corrosion inhibitor type imidazolines on the polarization curves for carbon steel in a CO_2 -saturated 3% NaCl solution-Diesel at 50 °C.

In the solution without diesel, Figure 9, it can be seen that in both cases the data describes a distinctly active behavior, without demonstrating the existence of a passive layer. The E_{corr} value for the uninhibited solution was -740 mV, which was nobler than for

the inhibited solution (-640 mV) [20, 21]. For the uninhibited solution, the existence of a cathodic limiting current density value can be seen, give carbonic acid as follows (1):

Subsequently that the solution is de-aerated, the dominant cathodic reactions are the reduction of H^+ ions, dissociation of carbonic acid (2, 3, 4):

And water reduction as follows (5):

The main anodic reaction, in absence of inhibitor, is iron dissolution according to (6):

Though it may be through several steps. During this corrosion process, a corrosion scale of iron carbonate, FeCO_3 , would form on the surface of carbon steels according to (7):

In absence of oxygen, the primary cathodic reactions are dependent on the pH solution, and it could be the reduction of bicarbonate ions, water and hydrogen ions, equations (3), (4) and (5). At a low pH value, H^+ reduction is the governing cathodic reaction because of the high H^+ concentration. When pH increases to 4-6, as in the present case, the direct reduction of HCO_3^- and H_2CO_3 become important. At a high overpotential, the governing cathodic reaction changes to direct reduction of water. Thus, in the present case, the diffusion of HCO_3^- and H_2CO_3 ions to form iron carbonate, FeCO_3 , is the rate controlling step, which is independent of the inhibitor concentration, as shown in the cathodic branch of polarization curves in Figure 2. On top of this iron carbonate film, the inhibitor-formed film is insulating that protect the metal from the electrolyte.

The change in the corrosion rate with time, obtained from the LPR results, is shown in Figure 6, where it can be seen that for the uninhibited solution, the corrosion rate remained constant with time. However, as soon as 25 ppm of corrosion inhibitor was added, the corrosion rate decreased for more than four orders of magnitude.

In presence of Diesel, Figure 10, the E_{corr} value for the uninhibited solution was -740 mV, which was made noble for the inhibited solution and was -610 mV approximately. This shows the effect of the inhibitor, where the data exhibited that the E_{corr} was -610 mV approximately. This can be due to the fact that the inhibitor is soluble in diesel and dispersible in water, thus, a better transport is expected, and, thus improve its corrosion performance.

CONCLUSIONS

Real time corrosion monitoring, both electric resistance or electrochemical as developed for the system pertaining the current investigation has proved to be a reliable tool to predict internal corrosion with an accuracy that is very similar to that measured employing internal corrosion coupons, with the enormous advantage of enabling the pipeline operator to react with due anticipation and reactive capacities. The one-month lapse where all corrosion damage inside a pipeline, and therefore in a coupon is "averaged" as a time uniform metal loss. Real time corrosion monitoring may be useful to detect immediately a change in corrosivity due to a process distortion, such as a sudden change in the water content in the pipeline; the input of a mixture of fluids with highly corrosive agents; or in the best situation to communicate the operator that the pipeline is working steadily.

The remarkably good correlation among Electrical Resistance, Harmonic Distortion Analysis corrosivity results, and that averaged as weight loss coupons in corrosion system is apparent when the system was studied without corrosion inhibitors. The Harmonic Distortion Analysis technique present an advantage respect to Linear Polarization Resistance due the simultaneous production of Tafel slopes, eliminating the approximation imposed by using assumed Tafel slope values in Linear Polarization Resistance. The real time monitoring techniques such as Electrical Resistance, Linear Polarization

Resistance and Harmonic Distortion Analysis represent a fundamental breakthrough, since they offer the possibility of measuring changes in corrosion rate rapidly and accurately. This approach was successfully validated in a corrosive system with CO_2 -saturated in 3% NaCl solution and mixture of 90 vol.% of 3%NaCl and 10 vol.% diesel at 50 °C, both with and without the participation of corrosion inhibitors.

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