Int. J. Electrochem. Sci., 3 (**2008**) 56 - 66

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

EIS Evaluation of the Effect of Neutralizing and Inhibitor Compounds on Corrosion Process of 1018 Carbon Steel in Acid Solutions Typical of Atmospheric Distillation Plants

L. Quej-Aké[1,2], *R. Cabrera-Sierra*[2], *E. Arce-Estrada*[2], *J. Marín-Cruz*[1,*]

[1] Instituto Mexicano del Petróleo, Coordinación de Ingeniería Molecular. Competencia de Química Aplicada. Eje Central Lázaro Cárdenas Norte 152, C. P. 07730, México, D. F. (MEXICO)
[2] Instituto Politécnico Nacional, Escuela Superior de Ingeniería Química e Industrias Extractivas, Departamento de Ingeniería Metalúrgica. UPALM Ed. 7, C.P. 07738, México, D.F. (MEXICO)
[*]E-mail: jmarin@imp.mx

Received: 22 December 2006 / *Accepted:* 25 October 2007 / *Online published:* 20 November 2007

The effect of monoethanol amine (MEA) as neutralizing and a corrosion inhibitor (IC) on carbon steel corrosion process in typical environments of petroleum refining distillation plants was evaluated using electrochemical impedance spectroscopy (EIS). The EIS analysis showed that the carbon steel corrosion process in HCl solution is favored by the presence of H_2S reaching maximum activity at 500 ppm dosage. The EIS analysis using a Randles circuit allows to identify that under the experimental conditions considered here (pH = 2) all MEA dosages result in a contrary effect accelerating the corrosion process of the carbon steel in sour medium (0.05 M HCl + 500 ppm of H_2S). However, an important inhibition effect was observed when IC compound was added to the same sour solution. This fact could be associated to the formation of a passive film composed by corrosion products and IC molecules on steel surface. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) confirmed the EIS results obtained in presence and in absence of MEA and IC compounds.

Keywords: Corrosion, Carbon steel, hydrochloric acid, hydrogen sulfide, atmospheric distillation.

1. INTRODUCTION

Corrosion process of carbon steel in acid sour environments, representative of atmospheric distillation plants, is a very important scientific and technological topic in the oilfield industry [1-10]. Due to different crude oil qualities and the increment in heavy oil recovery, oil refining is every time more difficult. After desalting process, salts and sulphide compounds dissolved in crude can provoke the formation of a corrosive aqueous solution whose chemical composition involves the presence of both hydrochloric acid (HCl) and hydrogen sulfide (H_2S) [3-8]. This solution is very aggressive causing varied damages on carbon steel surface during plant operation.

Several works have been performed related to the corrosion process of carbon steel, stainless steel and other metals in acid solutions [11-19]. These papers describe the influence of temperature, immersion time of electrode and corrosion inhibitors dosage on the corrosion phenomena. However, chemical composition of these solutions (1 and 5.5 M hydrochloric acid, no H_2S) is different to those found in real-life operation of distillation plants in oil refining, and the neutralizing and inhibitor effects on the corrosion process are not addressed. To mimic the corrosion process of 1018 carbon steel immersed in an oil distillation environment where hydrochloric acid is the main undesirable compound, it was necessary to identify statistically the concentration of HCl and H_2S which are the main corrosive species in this environment. Furthermore H_2S influences remarkably the corrosion process of carbon steel in HCl, and it is well known that neutralizing compounds and corrosion inhibitors are commonly used to control it.

Therefore, the aim of this work is to evaluate –by means of Electrochemical Impedance Spectroscopy (EIS)- the effect of both a neutralizing compound and a commercial corrosion inhibitor on carbon steel corrosion process in acid solutions typical of Mexican crude oil distillation plants.

2. EXPERIMENTAL PART

2.1. Experimental device

A typical three electrode cell was used including a recirculation bath (THERMOMIX 1460) in order to control temperature to 30 and 40 ± 0.05°C. The reference was a saturated calomel electrode (SCE) and the counter electrode was a graphite bar, both arranged within a separate compartment. The working electrode was a 1018 carbon steel disc with a surface area of 0.5 cm^2. The steel surface was prepared by mechanical polishing using different emery papers and a silicon carbide paper No. 600 as the last, and rinsed in acetone for 5 min. in ultrasonic bath. This treatment was done before every electrochemical characterization using EIS technique.

2.2. Preparation of the electrolytic environments

Both 0.05 M HCl and 0.05 M HCl + Na_2S solutions were prepared by utilizing deionized water (18.2 MΩ cm) and adding reagent analytical grade chemicals. The latter was prepared varying the sodium sulfide amount to study the H_2S effect on the corrosion process of carbon steel. The chemical composition of hydrochloric acid solution was obtained based on an analysis of water content in the feed to an atmospheric distillation plant [10]. It was determined that in drastic conditions the concentration of HCl is 0.05 M and its pH is approximately 2.

To study the influence of a neutralizing compound and/or corrosion inhibitor on 1018 carbon steel corrosion process, various alcoholic solutions were prepared using isopropyl alcohol. Mono Ethanol Amine (MEA) was employed as neutralizer and a commercial corrosion inhibitor –identified as IC -hereafter- was utilized as well. Both chemicals are commonly used in the Mexican oilfield industry and were added using diverse dosages to the test solution.

2.3. EIS Characterization

EIS characterization was carried out under the following conditions: ±10 mV in amplitude, frequency range from 10 kHz to 10 mHz, working electrode rotation to 2000 rpm and 3 h immersion time of the carbon steel electrode in the acid solutions. All experiments were performed using AUTOLAB model PGSTAT30 potentiostat/galvanostat.

3. RESULTS AND DISCUSSION

3.1. EIS Characterization

To study the effect of neutralizing compound and corrosion inhibitor on carbon steel corrosion process the electrochemical behavior of carbon steel–0.05 M HCl interface was first characterized. This electrochemical response was taken as a reference behavior for further evaluation of H_2S, neutralizing compound and corrosion inhibitor effects.

3.1.1. Temperature and rotation speed effect

Figure 1 shows the Nyquist diagrams obtained in the carbon steel – 0.05 M HCl interface. Relative to temperature effect, in figure 1a (30 and 40 °C) the electrochemical response is similar; the formation of a capacitive loop from intermediate to low frequency region can be observed. The loop diameter decreases when the temperature is increased, manifesting an activation of the corrosion process of carbon steel in acid solution [13, 17]. Also, a negligible formation of an inductive loop at low frequencies is visible. The EIS responses shown in figure 1a are similar to those found in the literature [17, 18, 20, 21] using higher concentrations of hydrochloric acid.

On the other hand in figure 1b, the influence of different rotation speeds in the corrosion process of the carbon steel - acid solution interface [22] is evident. Decrease in the semicircle diameter as a function of the rotation speed indicates a greater activity at 2000 rpm.

3.1.2. Influence of hydrogen sulfide

To evaluate the influence of H_2S on the corrosion process of carbon steel in acid solution, 50, 100, 150, 300 and 500 ppm of H_2S were added to 0.05 M HCl solution (sour solution). According to a previous statistical analysis, 100 ppm of H_2S is a typical concentration in atmospheric distillation plants [10].

Figure 2 shows the Nyquist diagrams obtained for 1018 carbon steel immersed in acid sour solutions with several H_2S concentrations at 40 ^{o}C. A similar electrochemical response is displayed compared to those shown in figure 1a. In presence of H_2S (figure 2), a decrease in real and imaginary impedance values is observed (Figures 2a-e). This electrochemical behavior had also been observed by H. Ma et. al. who found that a solution containing sulfide ions (sour medium) can accelerate or inhibit the steel corrosion [23] depending on the stoichiometric iron sulfides formed on the carbon steel [2,8,25,26]. However, under experimental conditions used here (pH=2 for all cases), corrosion process of carbon steel is favored as a function of hydrogen sulfide concentrations hence iron oxides are mainly formed. Thus, at 50 ppm concentration (figure 2a) the semicircle diameter is maximum while the minimum occurs at 500 ppm (figure 2e), showing a greater activity for upper H_2S concentrations.

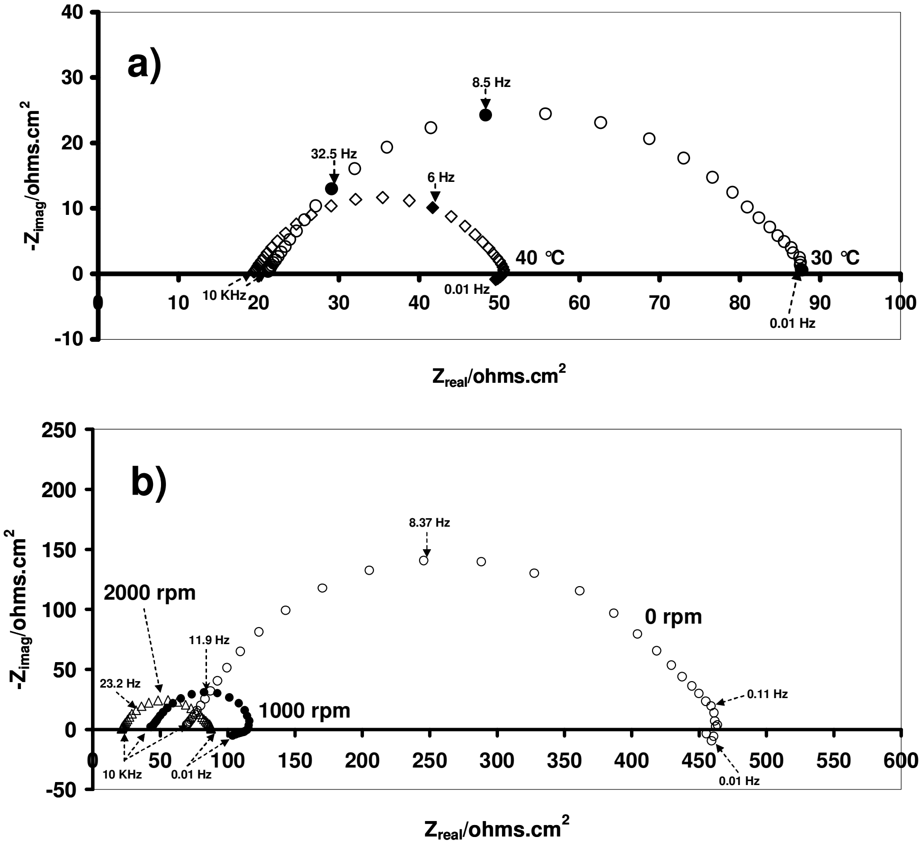

Figure 1. Typical Nyquist diagrams obtained for the carbon steel after 3 hours of immersion in 0.05 M HCl. a) temperature effect at 2000 rpm; b) rotation speed effect.

In all the Nyquist plots, it can be noted that a capacitive behavior appears at high frequencies. In the intermediate region, depressed loops are present, whereas in low frequencies an inductive response is poorly defined. This behavior can be mainly associated to the removal of corrosion products from carbon steel surface as a consequence of the hydrodynamic conditions [27, 28]. The magnitudes of the impedance diagrams suggest the formation of corrosion products with non-protective properties (easily removed).

Based on these results, the most aggressive conditions were chosen to evaluate the corrosion inhibition properties of various chemical compounds commonly used in the oil industry. These conditions yield an acid solution (0.05 M HCl) containing 500 ppm of H_2S, 40 ºC, 2000 rpm and 3 h immersion time.

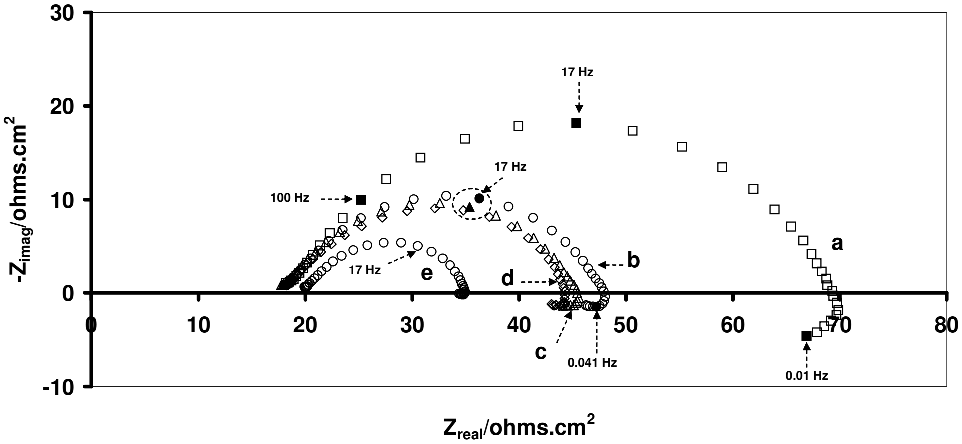

Figure 2. Typical Nyquist diagrams obtained for the carbon steel after 3 hours of immersion in a sour solution (0.05 M HCl + X ppm H_2S), using a rotation speed of 2000 rpm and 40°C. Effect of the H_2S concentration: a) 50 ppm, b) 100 ppm, c) 150 ppm, d) 300 ppm and e) 500 ppm.

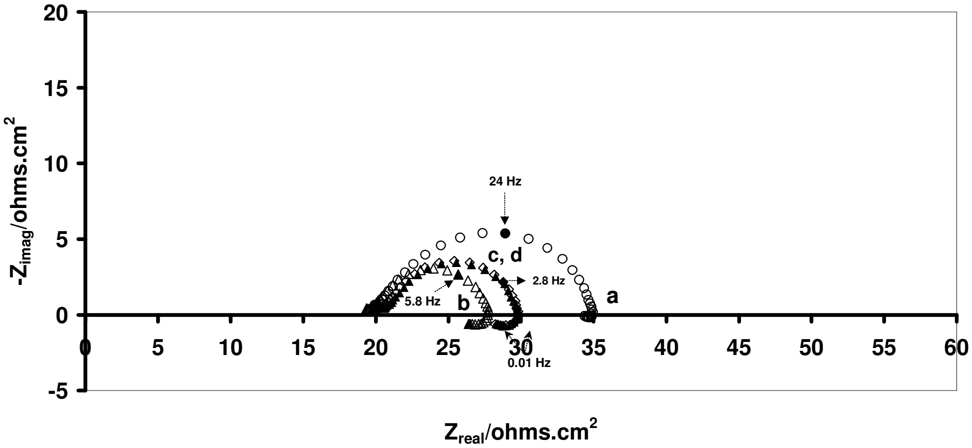

Figure 3. Typical Nyquist diagrams obtained for the carbon steel after 3 hours of immersion in sour solution (HCl + 500 ppm of H_2S), rotation speed of 2000 rpm and 40°C, using different concentrations of MEA. a) without MEA, b) 5 ppm, c) 15 ppm and d) 30 ppm of MEA.

3.1.3. Evaluation of amine neutralizing effect

EIS diagrams obtained for carbon steel in sour solution containing varied Mono Ethanol Amine (MEA) concentrations are shown in figure 3. These spectra are very similar to those displayed in figures 1 and 2. However, in figure 3a the maximum values correspond to the environment without neutralizing amine. The real and imaginary impedance values obtained in solutions containing MEA (figures 3b-d) reveal that the corrosion process is favored by amine presence. A visual inspection of carbon steel surfaces after the electrochemical experiments leads to prove the formation of a poor-adherence black layer. There was evidence of metal dissolution underneath the corrosion products as well. This dissolution process could possibly be involved in the not-well-defined inductive effect observed at low frequencies (figures 1, 2 and 3).

3.1.4. Evaluation of corrosion inhibitor effect

In the same way, a corrosion inhibitor used in primary distillation plants was evaluated. Figure 4 shows the Nyquist diagrams of carbon steel in an acid sour solution containing distinct concentrations of IC. An increment in real and imaginary components as a function of the IC concentration is observed in figure 4 giving evidence of an inhibition effect. In these diagrams, a capacitive response appears at high frequencies and a shrunk semicircle connected to an inductive behavior at low frequencies is exhibited. Such behavior is better defined in this figure in comparison with those shown in figures 1 to 3. The inductive response in Figure 4 can be associated to a removal of corrosion products or to a dissolution process -as suggested above- and/or to an adsorption process of IC. However, the assumptions one and two are disregarded because a visual examination of the surface of carbon steel allows identifying a poor formation of corrosion products. Furthermore, the inductive response increases as a function of IC dosage. In previous papers had been reported the evaluation of the the corrosion inhibition to iron in hidrocloric acid solution using organic compounds such as polyethylene glycols and thiourea [29-31]. In these works the inductive loop (at low frequencies) had been related to the adsorption relaxation of intermediates. Thus, it is most plausible to consider the IC adsorption which could be related to an inhibition effect of this compound in the environment (see below).

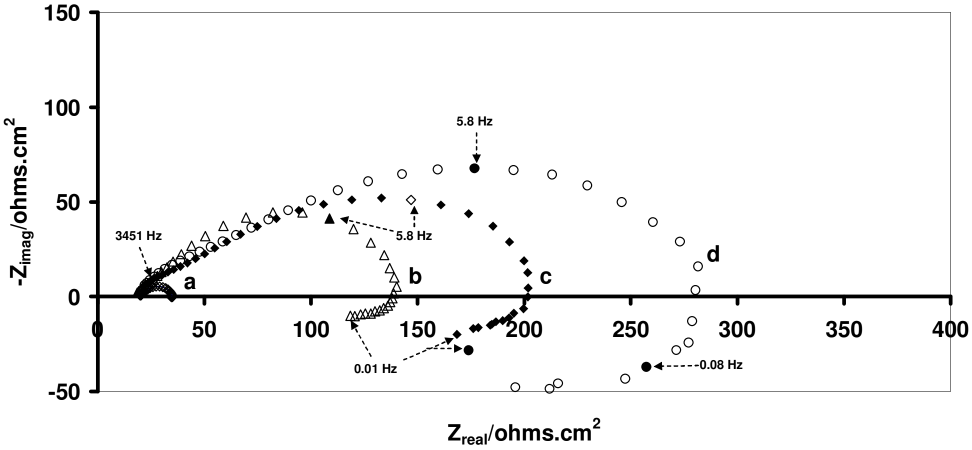

Figure 4. Typical Nyquist diagrams of the carbon steel after 3 h of immersion in sour solution (HCl + 500 ppm of H_2S), rotation speed of 2000 rpm and 40°C, using different concentrations of corrosion inhibitor (IC). a) without IC, b) 5 ppm, c) 15 ppm and d) 30 ppm of IC.

A comparative analysis of the electrochemical interfaces investigated is presented in figure 5 using the most aggressive conditions for each case. Nyquist spectra displayed major modifications. It is evident that the solution containing 30 ppm of MEA (figure 5c) remains the most aggressive because impedance values are the smallest.

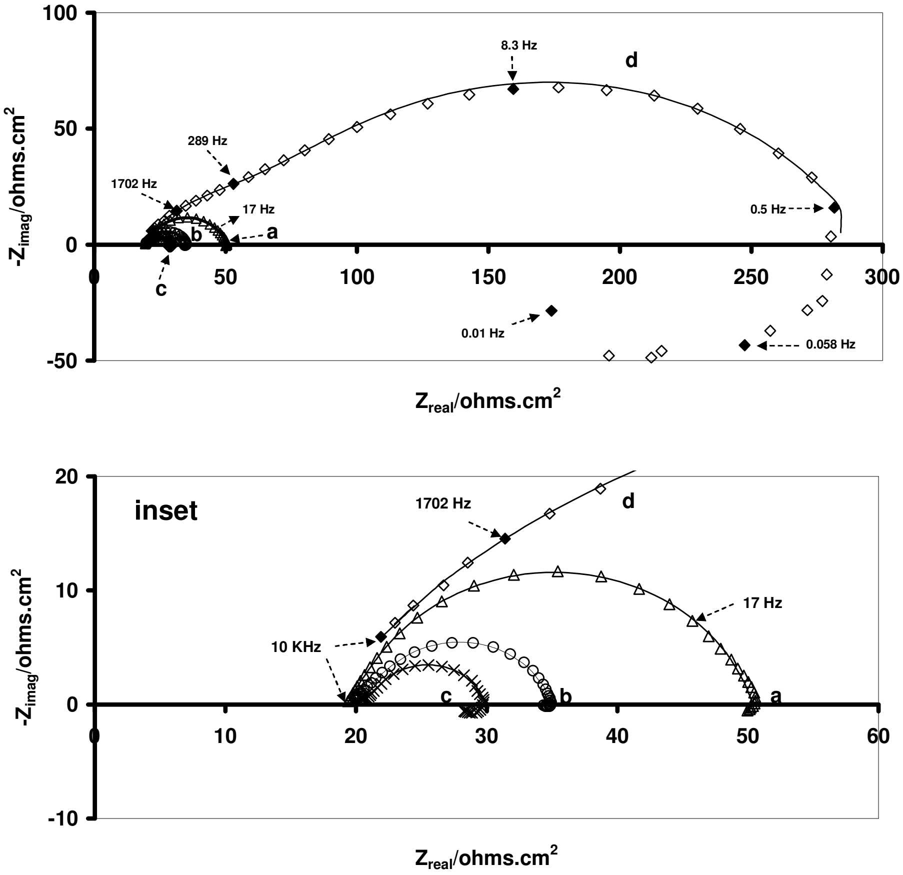

Figure 5. Typical Nyquist diagrams of the carbon steel after 3 hours of immersion in different solutions using a rotation speed of 2000 rpm and 40°C. a) 0.05 M HCl, b) 0.05 M HCl + 500 ppm of H_2S, c) 0.05 M HCl + 500 ppm of H_2S + 30 ppm of MEA and d) 0.05 M HCl + 500 ppm of H_2S + 30 ppm of IC. The continuous line represents the fitting obtained using the Randles equivalent circuit and the program of Boukamp.

The complex plot attained for 30 ppm of IC in acid sour solution (figure 5d) displays the maximum real and imaginary impedance values, showing an inhibition effect on the corrosion process. In this spectrum, two capacitive loops can be observed, being better defined from high to intermediate frequencies (figure 5d). The above-mentioned inductive response at low frequencies is more evident for the acid sour solution in presence of IC (figure 5d). As a first approach, the EIS diagrams shown in figure 5 were analyzed using a Randles circuit [17, 20] taking into account two time constants. According to this equivalent circuit, the corrosion mechanism occurring at the different interfaces can be related to the charge transfer resistance associated with carbon steel oxidation in these environments (R_1), the capacitive contribution, C, was evaluated from a Constant Phase Element (CPE, Q_1) of the films grown on the carbon steel surface, and the arrangement (Q_2-R_2) used to describe the impedance response of a diffusion process, where the R_2 element could be linked to the diffusion of iron ions of the corrosion products (mainly iron oxides) to the solution.

In figure 5, the continuous line represents the data fitting which ensure the quality of the simulation using the equivalent circuit program developed by Boukamp [32]. The fitting procedure was performed based solely on the capacitive response in a frequency interval from 10 kHz to 100 mHz. The reasons for this are the poor definition of the inductor shown in figures 5a, 5b and 5c and/or the adsorption process of IC (figure 5d). Table 1 summarizes the electric parameter values obtained by the best fitting of the experimental data.

Table 1. Parameter values of the electric elements obtained after the best fitting of the experimental data using the equivalent circuit program of Boukamp.

MUESTRA	R_s (ohms.cm^2)	C (μF)	Y_{01} x 10^6	n_1	$\mathbf{R_1}$ (ohms.cm^2)	$\mathbf{R_2}$ (ohms.cm^2)	Y_{02} x 10^6	n_2
HCl	19	201	652	0.82	7.2	24	372	0.84
HCl + H_2S	19	108.5	410	0.83	3.7	12	653	0.83
30 ppm MEA	20	212.1	778	0.84	1.4	8.0	22.5	0.85
30 ppm IC	17	7	113	0.63	78	201	310	0.67

* The pseudocapacitance values shown in Table 1, were evaluated using the following expression $C=((Y_{o1}*R_1)\^(1/n_1))/R_1$ [24]. The terms Y_{o1} and n_1 were obtained using a constant phase element (Q_1).

The ionic conductivity of the different solutions is very similar (R_s). Pseudocapacitance values (C) related to the corrosion products formed on the carbon steel surface in presence of HCl and HCl plus H_2S (201 and 108 μF, respectively) can be caused by the formation of iron oxides with a porous nature and non protective properties. Note that these values are smaller than those reported in the literature [25]. The formation of iron sulfides are not considered in sour solution because they are soluble in acid pH [26]. In MEA solutions, an increment of pseudo-capacitance value (212 μF) is observed. This value is quite similar to that obtained for HCl solution. However, given the smallest impedance values obtained in presence of MEA, the formation of diverse iron compounds (mainly composed by oxides) could be suggested. The formation of such products can increase the corrosion process activity due to surface heterogeneity enlargement, thus provoking an increment in the layer thickness as compared to those acquired in HCl and HCl plus H_2S solutions. Contrary to this finding, when the IC is used an opposite tendency is observed supported by the smaller values in the capacitance (7 μF) in comparison with the other interfaces. The capacitance value obtained for the last solution suggested the formation of a modified iron oxide film originated by the IC compound.

The resistance values (R_1 and R_2) attained for the different interfaces contribute to determine the aggressiveness of the acid solutions. The most critical appears when the neutralizing amine is present. This means that this compound is fairly effective under the conditions used in this work (pH=2 for all environments). On the other hand, an inhibition behavior is observed in presence of IC (increasing the R_1 and R_2 terms) which can be related to competition between the electroactive species and the IC adsorption at the active sites of the carbon steel surface. To corroborate the EIS analysis a SEM characterization was carried out.

3.2. SEM and EDS Characterization

SEM images and EDS analysis of carbon steel immersed in corrosive solutions are shown in figure 6. To compare the surface modifications induced on carbon steel, a freshly polished surface image is shown in figure 6a including its EDS plot. A homogeneous surface with some scratches is observed on the carbon steel after mechanical treatment (figure 6a). As was expected, EDS analysis corroborated only the presence of iron (figure 6a'). In the SEM image for the steel immersed in the hydrochloric acid solution (figure 6b) a rough surface is visualized which can be associated to the aggressiveness of the solution. This change in morphology implies that according to the EDS plot shown in figure 6b', the corrosion product formation on carbon steel is essentially composed of iron oxides which points toward a minor contribution of chloride peak being slightly visible.

The rough surface for the acid sour solution is also observed when the hydrogen sulfide is added (500 ppm, figure 6c). It is interesting to note that roughness is slightly higher in presence of H_2S. This fact could be a hint to the corrosive feature of this compound. Moreover, the formation of iron oxides at medium pH (pH=2) are not protective and can be easily dissolved. Also the presence of iron sulfides is almost negligible in the EDS analysis (figure 6c'). The morphological surfaces shown in figures 6b and 6c are detected by the EIS analysis using the Randles equivalent circuit, where the porous nature of the corrosion products was established.

Conversely, when carbon steel is immersed in the sour solution in presence of the neutralizing amine, figure 6d, similar surface damages are observed compared to those shown in figures 6b and 6c. Nevertheless, the carbon steel surface exhibits a more serious deterioration. The EDS analysis shows the existence of iron compounds such as oxides, sulfides and/or chlorides suggesting the formation of heterogeneous corrosion products on the carbon steel -as mentioned above. The formation of these iron compounds can be related to the aggressiveness of the MEA environment. As for the IC, it has been stated that it has an inhibition effect on the corrosion process of carbon steel immersed in a sour solution. This assumption is confirmed by the SEM image shown in figure 6e where a homogenous corrosion film on the carbon steel was perceived. This film is mainly comprised by iron oxides; the influence of H_2S (figure 6e') is negligible. Finally, the formation of this corrosion film could be produced by the interaction between the IC and the corrosion products formed in sour environments.

4. CONCLUSIONS

The corrosion process of the selected carbon steel immersed in an acid (HCl) and acid sour (HCl-H_2S) solutions characteristic of atmospheric distillation units in the Mexican oil refining industry was evaluated using the EIS technique. The EIS analysis showed that the carbon steel corrosion phenomena in HCl solution is enhanced by H_2S. Furthermore, it was possible to investigate the influence of several chemical compounds commonly used in the refining processes such as a neutralizing amine (MEA) and a corrosion inhibitor (IC). Based on these evaluations, it was found that MEA dosages result in a contrary effect accelerating the corrosion process of carbon steel under the experimental conditions considered here. Additionally, an inhibition effect was observed using the IC compound. All surface modifications obtained with and without chemicals were corroborated by SEM characterization and are in agreement with EIS analysis.

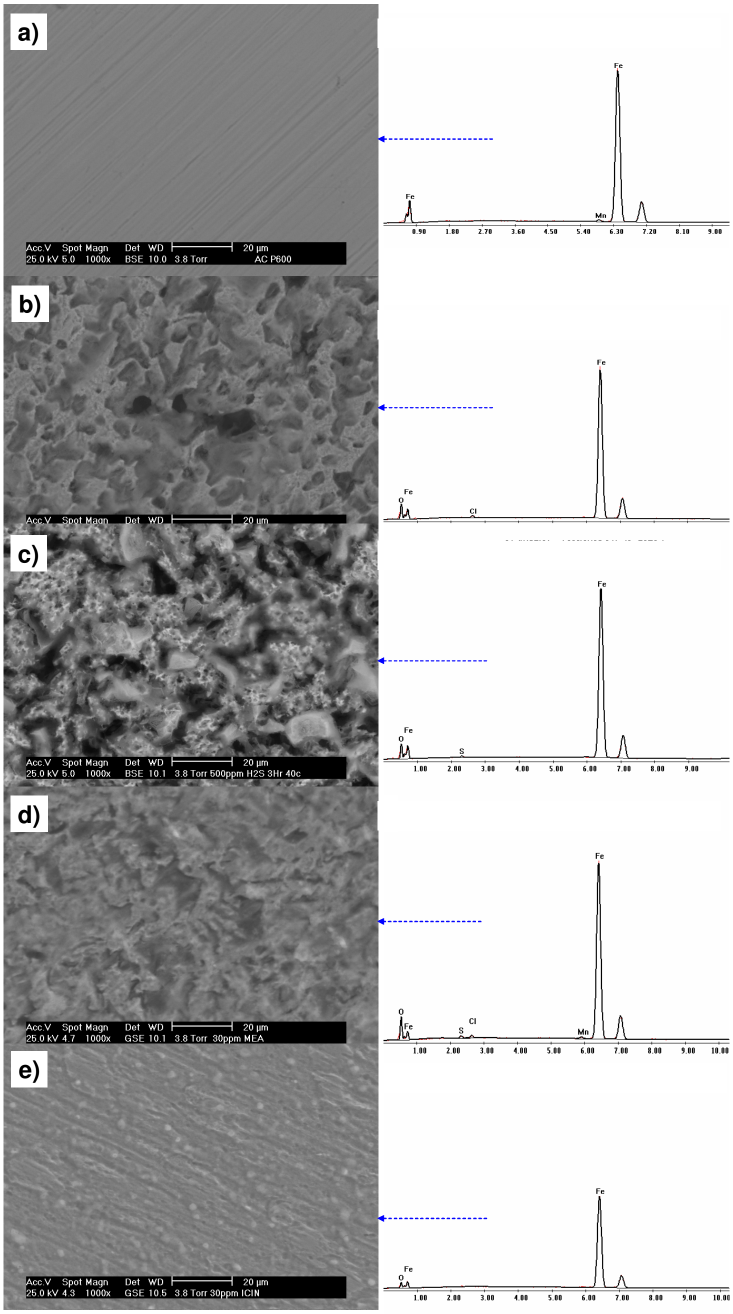

Figure 6. SEM images and EDS analysis obtained for the carbon steel surfaces immersed for 3 h in different aggressive solutions using a rotation speed of 2000 rpm at 40 ^{o}C. a) Freshly polished surface, b) 0.05 M HCl, c) 0.05 M HCl + 500 ppm of H_2S, d) 0.05 M HCl + 500 ppm of H_2S + 30 ppm of MEA and e) 0.05 M HCl + 500 ppm of H_2S + 30 ppm of IC.

ACKNOWLEDGEMENTS

L. Quej-Aké wishes to thank CONACYT-México for granting his PhD scholarship and IPN – ESIQIE for the academic support on the doctoral program.

References

1. J. T. Powell, J. R. Rue, M. M. Mansouri, *Oil & and Gas Journal*, Mar 20 (1989)60.
2. I. García, E. Sosa, R. Cabrera-Sierra, M. T. Oropeza, I. González, *Proceedings of XIV SIBAE Meeting* (2000), Oaxaca, México.
3. H. Vedage, T. A. Ramanarayaran, J. D. Munford, S. N. Smith, *Corrosion* 49 (1993)114.
4. R. Viswanath, *Industrial Corrosion*, 47 (1972)77.
5. R. D. Kane and M. S. Cayard, InterCorr International, Inc., Houston Texas, *Hidrocarbon Processing*, October, (1998)97.
6. Q. J. M. Slaiman and H. J. Nasouri, *Materials Performance*, 8 (1984)38.
7. D. W. S. and J. E. Boggs, Corrosion-National Association of corrosion Engineers 15 (1959)33.
8. Z. A. Foroulis, *corrosion prevention & control* 8 (1993)84.
9. B. E. Wilde, C. D. Kim, and E. H. Phelps, *Corrosion* 36 (1980)625.
10. L. Quej-Aké, R. Cabrera-Sierra, J. Marín-Cruz, Proceedings of 210 Joint Internacional Meeting of The Electrochemical Society, Cancún, Quintana Roo, México, October 29 to November 3 (2006).
11. L. F. Li, P. Caenen, M. Daerden, D. Vaes, G. Meers, C. Dhondt, J. P. Celis, *Corrosion Sci.* 47 (2005)1307.
12. K. Brunelli, M. Dabalá, I. Calliari and M. Magrini, *Corroson Sci.* 47 (2005)989.
13. Z. A. Chikh, D. Chebabe, A. Dermaj, N. Hajiaji, A. Srhiri, M. F. Montemor, M. G. S. Ferreira and A. C. Bastos, *Corrosion Sci.* 47(2005)447.
14. M. Lebrini, M. Legrenée, H. Vezin, L. Gengenbre and F. Bentiss, *Corrosion Sci.* 47 (2005)485.
15. L.-G. Quiu, A.-J. Xie and Y.-H. Shen, *Corrosion Sci.* 47 (2005)273.
16. H.-L. Wang, R.-B. Liu and J. Xin, *Corrosion Sci.* 46 (2004)2455.
17. A. Popova, E. Sokolova, S. Raicheva and M. Christov, *Corrosion Sci.* 45 (2003)33.
18. Sk. A. Ali, M. T. Saeed and S. U. Rahman, *Corrosion Sci.* 45 (2003)253.
19. F. Bentiss, M. Traisnel, H. Vezin and M. Lagrenée, *Corrosion Sci.* 45 (2003)371.
20. A. Popova, S. Raicheva, E. Sokolova and M. Christov, *Langmuir* 12 (1996)2083.
21. C. Cao, *Corrosion, Sci.* Vol. 38 (1996)2073.
22. L. Quej-Aké, M. Lozano-Rodríguez, G. Hernández-García, J. Marín-Cruz, Proceedings of XX SMEQ Meeting, Puente de Ixtla, Morelos, México, 22-27 de Mayo, 2005.
23. H. Ma., X. Cheng, G. Li, S. Chen, Z. Quan, S. Zhao, *Corrosion Sci.*, 42 (2000)1669.
24. M. A. Pech-Canul, L. P. Chi-Canul, *Corrosion*, 55 (1999)948.
25. A. Bonnel, F. Dabosi, C. Deslouis, M. Duprat, M. Keddam, B. Tribollet, *J. Electrochem. Soc.* 130 (1983)753.
26. H. Her-Hsiung, Tsai Wen-Ta, L. Ju-Tung, *Electrochim. Acta*, 41 (1996)1191.
27. S.U. Koh, J.S. Kim, B.Y. Yang, and K.Y. Kim, *Corrosion*, 60 (2004)244.
28. H.-H. Huang, W.-T. Tsai, and J.-T. Lee, *Corrosion*, 52 (1996)708.
29. M. El Azhar, B. Mernari, M. Traisnel, F. Bentiss, M. Lagrenée, *Corrosion Sci.*, 43 (2001)2229.
30. C.B. Shen, S.G. Wang, H.Y. Yang, K. Long, F.H. Wang, *Corrosion Sci.*, 48 (2006)1655.
31. H. Ashassi-Sorkhabi, N. Ghalebsaz-Jeddi, F. Hashemzadeh, H. Jahani, *Electrochim. Acta*, 51 (2006)3848.
32. B. A. Boukamp, Users Manual Equivalente Circuit, Versión 4.51, Faculty of Chemical Technology, University of Twente, The Netherlands, 1993.