

Corrosion Inhibition Performance with the Presence of Iron Carbonate Film in CO₂ Saturated Brine Solution

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Abstract

Corrosion due to carbon dioxide (CO₂) is one of the most serious problems in the oil and gas production and transportation industry. The use of corrosion inhibitors is currently used to protect against corrosion in all petrochemical facilities in the world, because it is costeffective and flexible. The objective of this research is to study the interaction between an imidazoline based inhibitor with an iron carbonate (FeCO₃) corrosion product film in controlling the corrosion process and reducing the corrosion rate at various concentrations of inhibitor. CO₂ saturated solution of 3% NaCl was used to study the corrosion inhibition of X52 mild steel samples under stagnant condition at 80°C and pH 6.6. Based on the LPR results, the addition of imidazoline inhibitor to the solution decreased the corrosion rate rapidly compared to the iron carbonate film itself. 100 ppm of imidazoline corrosion inhibitor added to the solution offered a great protection on the samples from the corrosion process compared to 50 ppm. Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) were used in the analyses of the corrosion samples in order to observe the morphology of the iron carbonate film formed on the metal surface. It was observed that, the presence of corrosion inhibitor may lead to retard the growth of FeCO₃ film and rapidly decrease the corrosion rate.

Keywords: CO₂ corrosion, corrosion rate, imidazoline, iron carbonate, linear polarization resistance (LPR), scanning electron microscopy (SEM), X-52 mild steel

INTRODUCTION

Carbon dioxide (CO₂) corrosion has long been known to cause severe damage to the production and transportation of oil and gas. Thus, material selection is an important step in design phase in order to prevent away a corrosion process [1]. Carbon steel is widely used in the oil and gas production systems, so it has much significance to study the corrosion behavior of X-52 mild steel in CO₂ containing environments. Much work which was focused on the protection of X-52 mild steel has already been carried out over many decades. Among them, the inhibitor technique as the most effective and flexible one has been adopted worldwide to inhibit the CO₂ corrosion. It was noted that the severity of corrosion does not only depend on environmental conditions such as pH, water chemistry, CO₂ partial pressure, but also on operating conditions likes flow velocity and temperature [2].



and implemented in carbon steel piping and tubing. Almost all active inhibitor intermediates used in the oil and gas industry are nitrogen containing compounds. These compounds are excellent inhibitors because of the free pair electrons in nitrogen atoms that can be adsorbed on the metal surface and their hydrocarbon chain to form hydrophobic film on the surface, thus providing inhibition [3]-[4].

Corrosion inhibitors for CO_2 corrosion are often tested in the laboratory using freshly ground specimens. However, in the field, the inhibitors encounter steel surfaces that are covered with different kinds of corrosion products, such as rust layers from pipe production, storage and testing. As mentioned by Sastri [4], there are two processes are involved in the action of inhibitor on the metal surface. The first step involves the transport of the inhibitor to the metal surface followed by a second step involving chemical interaction between the inhibitor and the metal surface. This inhibition process may be altered due the presence of iron carbonate (FeCO₃) film.

BACKGROUND

Corrosion inhibitors for the petroleum industry have been researched extensively for years. The composition of a commercial corrosion inhibitor usually consists of a blend of an actively adsorbing chemical such as amines and imidazolines in a solvent along with a series of supporting chemicals like emulsion breakers, salting agents and many else that aid in the dispersion of the active when it is applied in the field. However, any key technological advances in their chemistries require a fundamental understanding on the interactions between the corroding surface and the inhibitor.

Although the ultimate goal of a corrosion inhibitor is to decrease the corrosion rate, the mechanism for optimal corrosion mitigation may not be thoroughly understood. Depending on the corrosion process, the addition of inhibitor to system may have potential to either slow down the formation of the corrosion products by forming a molecular film on the metal or interact with the corrosion scale to form a passivation layer and prevent further corrosion from occurring.

Chokshi *et al.* observed the prevention of iron carbonate growth due to imidazoline inhibitors [5]. In that study they used 10 and 50 ppm of Fe²⁺ to observe the effect of imidazoline inhibitors had on iron carbonate (FeCO₃) during scale formation after the scale had formed. The inhibitor was added after 15 minutes and 5 hours of starting the experiment. They concluded imidazoline inhibitors prevents the growth of FeCO₃, which could be due to the decrease Fe²⁺ ions at the surface or it could be imidazoline compounds act like scale inhibitors. This study also explained the effect of change in supersaturation of iron on the corrosion rate. It was found by increasing in supersaturation level of iron will decrease the corrosion rate.

and showed that some inhibitors are able to penetrate deep into the rust layer [6]. The research that was done by Kapusta *et al.* found that one day precorrosion had a negative effect on the inhibitor performance [7]. Addition to that, Hausler *et al.* concluded that four days precorrosion did not significantly affect the inhibitor performance in tests at high CO₂ partial pressure and high temperature [8]. From this brief overview of the existing knowledge on how precorrosion affects inhibition, it is clear that more work is needed to clarify the effects.

In oil field corrosion, corrosion product film consisting of iron sulfide (FeS), iron carbonate (FeCO₃), iron carbide (Fe₃C) and iron oxide (FeO) is formed on the steel surface. The protective properties of this film are important in determining the rates of both general and localized corrosion and also the basis of the mechanism of inhibition by inhibitors. However, based on the previous studies it pointed out that the main components of the scale are FeCO₃ and iron carbide (Fe₃C). The typical corrosion product layer in an uninhibited system is on the order of microns thick and is porous. In the presence of corrosion inhibitor, such as oleic imidazolines and phosphate esters, the inhibitor film is on a molecular level while the corrosion layer is on a microscopic order. Due to the differences in length scale, the inhibitor sees the corrosion product layer as a surface [9]. The corrosion product layer is very porous and has enough pore size for the inhibitor to migrate. Therefore, the study of inhibitor performance is always associated with the study of corrosion product film [10].

EXPERIMENTAL

Material

The sample material studied was X-52 mild steel. The sample was cut from oil production tubing with a chemical composition as given in Table 1. For all the experiments, the sample were cut into cylindrical shape and mechanically polished with silicon carbide emery paper from 180 to 600 grit. Then, it was rinsed with distilled water and degreased with acetone.

Table 1: Chemical composition of studied steel

C	Si	Mn	S	P	Cr	Ni	V	Mo	Cu	Al	Sn	Nb
0.064	0.26	1.55	0.001	0.012	0.05	0.04	0.035	0.01	0.04	0.041	0.002	0.041

Test solution

The imidazoline used as the test inhibitor in this experiment was provided by AMTECH. The concentration of imidazoline used in this work was 50 and 100 ppm. Before applying the inhibitor, a solution containing 3% NaCl was prepared. The testing solution was heated and maintained at 80 ± 1.0 °C, and deaerated with CO_2 for an hour. The formation of FeCO₃ scale was accelerate by induced required amount of Fe^{2+} in the form of deoxygenated ferrous chloride salt (FeCl₂.4H₂O) solution. The analytical reagent NaHCO₃ was used to adjust pH value of solution to 6.6.

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Electrochemical measurements

Electrochemical techniques employed included linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) measurements with rotating cylinder electrode (RCE) assembly. Measurements were obtained by using a conventional three electrode glass cell. X-52 cylinder mild steel with 3 cm² surface area was used as a working electrode. A stainless steel electrode and Ag/AgCl solution was used as the counter and the reference electrode respectively. Inhibition efficiencies (E(%)) were determined according to the following equation:

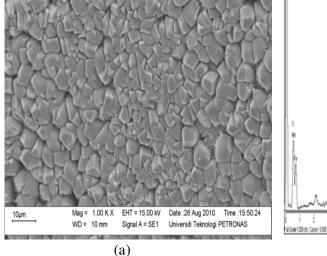
$$E(\%) = \frac{CR_i - CR_O}{CR_i} \times 100 \tag{1}$$

where CR_i is the corrosion rate without inhibitor and CR_0 is the corrosion rate in solution with inhibitor. LPR measurements were carried out by polarizing the specimen from +10 to -10 mV respect to E_{corr} at a scanning rate of 1 mV/s. While, EIS tests were carried out at E_{corr} by using a signal with amplitude of 10 mV and a frequency interval of 0.005 - 100 KHz. An ACM potentiostat controlled by a desk top computer was used for the LPR tests whereas for the EIS measurements, a model PC4 300 Gamry potentiostat was used.

RESULTS AND DISCUSSION

Formation of FeCO₃ Film under Induced Fe²⁺ Condition

The morphology and EDX spectrum of FeCO₃ film induced with 50 ppm and 100 ppm Fe²⁺ is shown in Fig. 1(a), (b) and Fig. 2(a), (b) respectively.



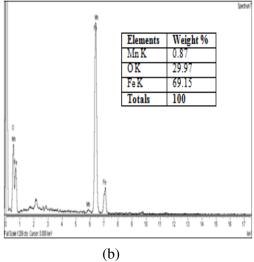


Fig. 1(a). The top view of the sample at 1000X, for pH 6.60, $Fe^{2+} = 50$ ppm, no inhibitor, temperature = 80°C, stagnant condition; (b) = EDX spectrum of FeCO₃ film

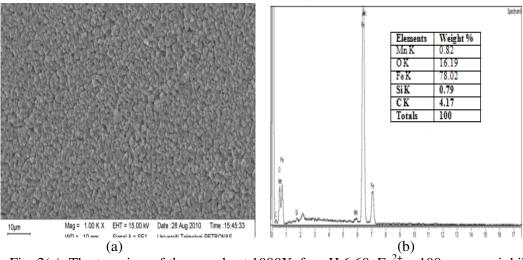


Fig. 2(a). The top view of the sample at 1000X, for pH 6.60, $Fe^{2+} = 100$ ppm, no inhibitor, temperature = 80°C, stagnant condition; (b) = EDX spectrum of FeCO₃ film

It was observed that there is a relationship between FeCO3 crystals size and Fe²⁺ concentration. This is expected since by increasing the concentration of Fe²⁺, a supersaturation and precipitation rate will be higher. The higher in precipitation rate can causes higher number of crystals nucleates on the metal surface. This close proximity of nuclei causes interference in growth of the crystals due to the adjacent crystals. Thus, higher concentration of Fe²⁺, it will give the smaller of FeCO₃ crystal size [11]-[13]. The effect of induced Fe²⁺ on the corrosion rate is shown in Fig. 3 with comparison to the natural (blank) filming condition.

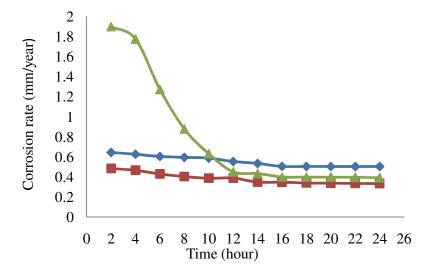


Fig. 3. Graph of corrosion rate vs. time for ($\phi = 50$ ppm Fe2+), ($\blacksquare = 100$ ppm Fe2+), and (\triangle =blank)



provides a protective layer which reduces corrosion from 2 mm/yr to less than 0.5 mm/yr. The degree of protectiveness is seemed to be dependent on the morphology of the film where 100 ppm Fe²⁺ provides a compact morphology register the lowest corrosion rate of 0.3 mm/yr.

The formation of Natural FeCO3 Film under Additional of Imidazoline Inhibitor Condition

The SEM image and EDX spectrum of the corroded coupons after were exposed to a solution containing 50 and 100 ppm imidazoline is shown in Fig. 4(a), (b) and Fig. 5(a), (b).

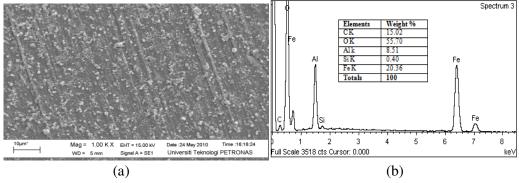


Fig. 4(a). The top view of the sample at 1000X, for pH 6.60, 100 ppm imidazoline, 0 ppm Fe^{2+} , temperature = 80°C, stagnant condition; (b) = EDX spectrum of $FeCO_3$ film

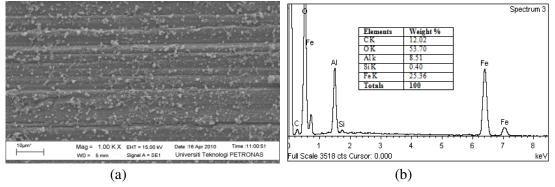


Fig. 5(a). The top view of the sample at 1000X, for pH 6.60, 50 ppm imidazoline, 0 ppm Fe^{2+} , temperature = 80°C, stagnant condition; (b) = EDX spectrum of $FeCO_3$ film

The surface of both coupons contain dispersed minute colony of iron carbonate scale in the matrix of corrosion inhibitor film. A mechanism behind this phenomenon is because the adsorption rate of inhibitor on metal surface is faster than the precipitation rate of FeCO₃ film. The free pair electrons in nitrogen atoms can be adsorbed on the metal surface and their hydrocarbon chain can form hydrophobic film on the surface, thus providing inhibition. This protective behavior of inhibitor film makes CO₃²⁻ ions cannot reach the surface easily. Thus, the formation of FeCO₃ film is lesser. However, the exact kinetics of the formation of both



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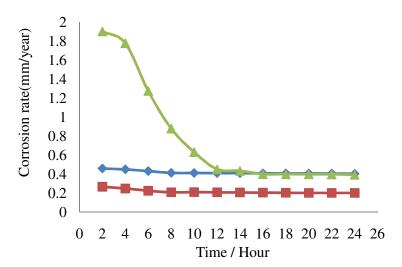


Fig. 6. Graph of corrosion rate vs. time for (♦ = 50 ppm imidazoline), (■ = 100 ppm imidazoline), and (▲=blank)

Based on the results, it can be concluded that an imidazoline corrosion inhibitor was efficient to reduce the blank corrosion rate reflecting very fast corrosion inhibitor film formation where reducing the corrosion rate to 0.3 mm/year in less than 4 hours.

The Formation of Induced FeCO $_3$ Film under Additional of Imidazoline Inhibitor with Fe $^{2+}$

50 ppm Imidazoline Inhibitor based with 50 and 100 ppm Fe²⁺

A top view and EDX spectrum of coupons for the formation of induced FeCO3 film under additional of imidazoline inhibitor with Fe²⁺ is shown in Fig. 7(a), (b) and Fig. 8(a), (b) respectively.

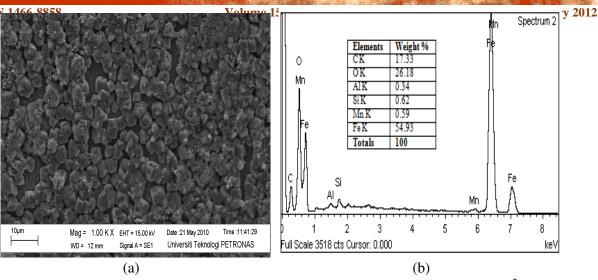


Fig. 7(a). The top view of the sample at 1000X, for pH 6.60, 50 ppm imidazoline, $Fe^{2+} = 100$ ppm, temperature = 80°C, stagnant conditions; (b) = EDX spectrum of FeCO₃ film

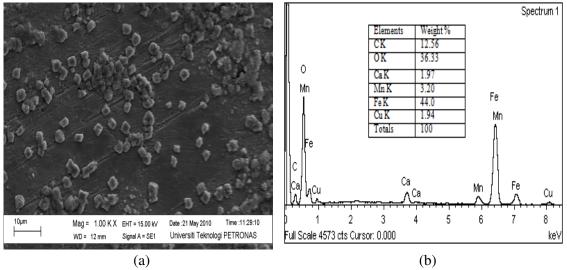


Fig. 8(a). The top view of the sample at 1000X, for pH 6.60, 50 ppm imidazoline, $Fe^{2+} = 50$ ppm, temperature = 80°C, stagnant conditions; (b) = EDX spectrum of FeCO₃ film

The images show lack of iron carbonate scale on the metal surface when low concentration of Fe^{2+} was applied. At higher concentrations of Fe^{2+} , the formation of a continuous iron carbonate scale occurred. All the data demonstrates there are interactions between imidazoline inhibitor based, the added Fe^{2+} and the surface. The effect of addition of 50 ppm imidazoline with 50ppm and 100 ppm Fe^{2+} on the corrosion rate is shown in Fig. 9.

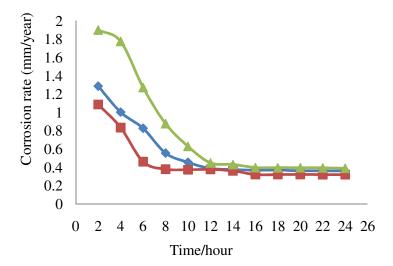


Fig. 9. Effect of 50 ppm of imidazoline on corrosion rate at pH 6.6; CO2 pressure = 1bar, temperature = 80° C, (\blacklozenge = 50 ppm Fe²⁺), (\blacksquare = 100 ppm Fe²⁺), (\blacktriangle = blank)

Based on Fig. 9 above, by comparing to blank condition it can be seen that as soon as the inhibitor is added to the system after 2 hours of starting the experiment, the corrosion rate drops rapidly for both cases. An addition of 50 ppm imidazoline into the solution brings the final corrosion rate for both concentration of Fe²⁺ to the same value which is 0.35 mm/year. Only, for the solution that contains 50 ppm of Fe²⁺, the corrosion rate starts to be constant after 8 hours of starting experiment compared to the 100 ppm Fe²⁺ which takes only three hours after addition of an inhibitor.

100 ppm Imidazoline Inhibitor based with 50 and 100 ppm Fe²⁺

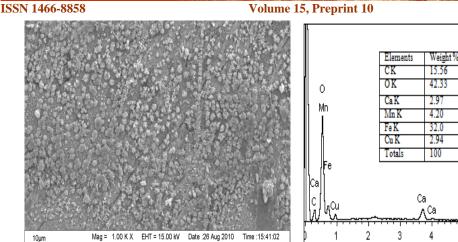
The effect of additional 100 ppm imidazoline with 50 and 100 ppm of Fe2+ on the formation of FeCO3 film is shown in top view and EDX spectrum of samples in Fig. 10(a), (b) and Fig. 11(a), (b).

Spectrum 3

Fe

6

(b)



(a)

Fig. 10(a). The top view of the sample at 1000X, for pH 6.60, 100 ppm imidazoline, Fe^{2+} = 50 ppm, , temperature = 80°C, stagnant conditions; (b) = EDX spectrum of FeCO₃ film

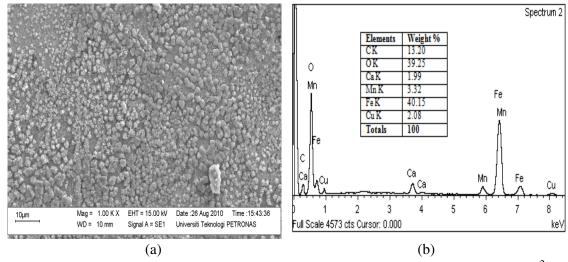


Fig. 11(a). The top view of the sample at 1000X, for pH 6.60, 100 ppm imidazoline, Fe^{2+} = 100 ppm, temperature = 80°C, stagnant conditions; (b) = EDX spectrum of FeCO₃ film

Based on the SEM images, the morphology of FeCO3 film with addition of 100 ppm imidazoline showed a similar trend with additional of 50 ppm imidazoline. At higher amount of imidazoline, will give smaller of FeCO3 crystals size. The corrosion rate for this condition test is shown in Fig.12 below.

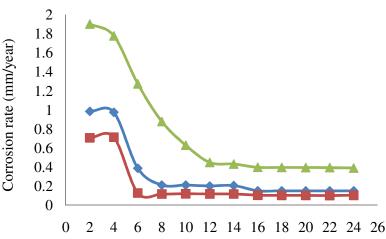


Fig. 12. Effect of 100 ppm of imidazoline on corrosion rate at pH 6.6; CO2 pressure = 1bar, temperature = 80° C, (\blacklozenge = 50 ppm Fe²⁺), (\blacksquare = 100 ppm Fe²⁺), (\blacktriangle = blank)

Time/hour

The final corrosion rate with 100 ppm imidazoline is 0.18 mm/year as compared to 0.35 mm/year from 50 ppm imidazoline. This is expected as higher amount of imidazoline added to the solution it offered a great protection on the samples from the corrosion process. However, the addition of too much concentration of imidazoline into solution cause very little iron carbonate is seen on the metal surface. Therefore, it seems that the metal surface is mainly protected due to the presence of the inhibitor and 100 ppm imidazoline seems to hamper the growth of iron carbonate on the metal surface.

The morphology of iron carbonate films that was found in this present study brings to a several assumptions. Firstly, iron carbonate crystals might have formed before the addition of the inhibitor and subsequently, the inhibitor hampered the growth of the iron carbonate scale. It can also be suggested that the inhibitor film consists porosity. This allows corrosion reaction occuring at the metal surface. Thus, Fe²⁺ ions were discharge from the metal surface and form FeCO₃ film [14]. Lastly, it might be also an interaction between the inhibitor films with preformed FeCO₃ film. As a consequence, FeCO₃ film is seen as a bare surface. However, this study remains open for further investigation, as some of the key questions remain unanswered.

Evaluation of Corrosion Inhibitor effect

An imidazoline corrosion inhibitor that was used in the study was evaluated. Fig.13 shows the Nyquist spectra of X-52 mild carbon steel that was immersed in 3wt% NaCl solution for 24 hours containing distinct concentrations of imidazoline. An increment in real and imaginary components as a function of the corrosion inhibitor concentration is observed

values. An increment in real and imaginary components giving evidence of an inhibition effect [15]. Thus, 100 ppm of imidazoline shows a good inhibition effect on the corrosion process. Besides, increasing in the semicircle diameter as a function of inhibitor concentration can be observed from the figure. This indicates the reduction in corrosion rate can be obtained once inhibitor concentration is increasing. Also, in these spectra a capacitive response appears at high frequencies and a shrunk semicircle at low frequencies is exhibited.

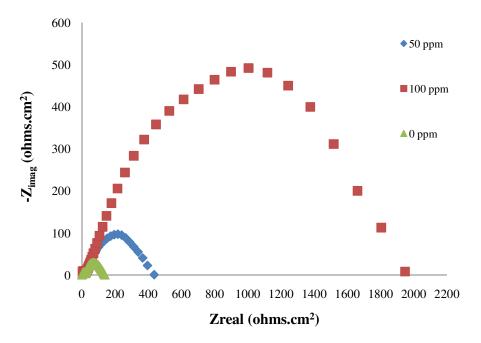


Fig. 13. Typical Nyquist diagrams of the X-52 mild steel after 24 hours immersion in 3wt% NaCl, at stagnant condition and 80°C, using different concentrations of corrosion inhibitor; (\spadesuit = 50 ppm imidazoline), (\blacksquare = 100 ppm imidazoline), (\blacktriangle = without corrosion inhibitor)

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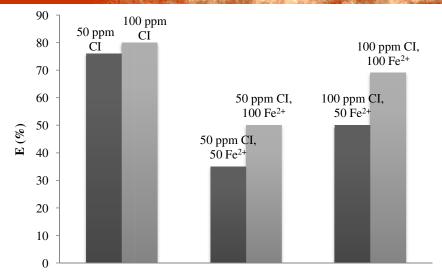


Fig. 14. Inhibitor efficiency for X-52 mild steel in CO₂ saturated 3wt% NaCl solution at various concentrations.

The inhibition efficiency calculated according to equation (1) is shown in Fig. 14. At high concentration of 100 ppm imidazoline, it could achieve the high inhibition efficiency of 80 per cent. The addition of Fe²⁺ ions into solution does not inhibit the performance of imidazoline to offer a great protection from the corrosion process. Based on the figure, a combination of high concentration imidazoline and Fe²⁺ ions offered a great inhibition in reducing the corrosion rate. It is understood that the hydrophilic part of corrosion inhibitor adsorbs onto the metal surface, whereas the hydrophobic part which is oriented towards the water phase can reduce access of the corrosive species to the metal surface [16]. All surface modifications obtained with imidazoline inhibitor corroborated by SEM are in agreement with EIS analysis. According to the EDX spectrums, the corrosion product formation on carbon steel essentially composed of iron carbonate film might have an interaction with inhibitor film to offer a dense protectiveness film [12].

CONCLUSION

This paper explores the effect of corrosion inhibitor on the formation of iron carbonate scale on the metal surface. Based on the experimental conditions, it can be concluded that:

- 1) The lowest value of corrosion rate which is 0.18 mm/yr is offered under additional of imidazoline inhibitor with Fe²⁺ than when either species are on their own.
- 2) Possibly the imidazoline portion of inhibitor forms a complex with free Fe²⁺ and this become more surface active leading to a more protective film.
- 3) The growth of iron carbonate scale is affected by the addition of imidazoline and the resulting scale is comprised of smaller crystalline formations that are tightly packed together.

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