Corrosion Inhibition Performance with the Presence of Iron Carbonate Film in CO_2 Saturated Brine Solution

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Abstract

Corrosion due to carbon dioxide (CO_2) 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 cost-effective and flexible. The objective of this research is to study the interaction between an imidazoline based inhibitor with an iron carbonate ($FeCO_3$) corrosion product film in controlling the corrosion process and reducing the corrosion rate at various concentrations of inhibitor. CO_2 saturated solution of 3% NaCl was used to study the corrosion inhibition of X52 carbon steel samples under stagnant condition at 80℃ and pH 6.6. Based on the LPR results, the addition of imidazoline based inhibitor to the test solution decreased the corrosion rate rapidly compared to the iron carbonate film itself. 100 ppm of imidazoline added to the test solution offered a great protection from the corrosion process compared to 50 ppm. Scanning Electron Microscopy (SEM) was used in the analysis of the corrosion samples in order to observe the morphology of films that were formed on the metal surface. It was observed that, the presence of corrosion inhibitor may lead to retard the growth of $FeCO_3$ film and rapidly decrease the corrosion rate.

Keywords: CO_2 corrosion, corrosion rate, imidazoline, iron carbonate, linear polarization resistance (LPR), scanning electron microscopy (SEM), X-52 carbon steel.

Introduction

Carbon dioxide (CO_2) 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 behaviour of X-52 carbon steel in CO_2 containing environment. Much work which

was focused on the protection of X–52 mild steel has already been carried out over many decades [1–4]. Among them, the inhibitor technique as the most effective and flexible one has been adopted worldwide to inhibit the CO_2 corrosion.

Commercial corrosion inhibitor consists at least one of the following surfactants: fatty acids, amines, fatty amines/diamines, imidazoline, quaternary amines, and sulphur or phosphorous containing compounds [5]. 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 [1, 4, 6–9].

Corrosion inhibitor for CO_2 corrosion is often tested in the laboratory using freshly ground specimens. However, in the field, the inhibitor 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 [10], 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 ($FeCO_3$) film.

Background

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 [6]. This could be due to the decrease of Fe^{2+} at the surface or it could be imidazoline compounds act like scale inhibitors. Also, it was found that by increasing in supersaturation level of iron decreased the corrosion rate.

Meanwhile, Kowata and Takahashi had reviewed the work done on rusted surfaces, and showed that some inhibitors are able to penetrate deep into the rust layer [11]. The studied by Kapusta et al. [12], found that one day precorrosion had a negative effect on the inhibitor performance. Addition to that, Hausler et al. concluded that four days

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precorrosion did not significantly affect the inhibitor performance in tests at high CO_2 partial pressure and high temperature [13]. 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 ($FeCO_3$), iron carbide (Fe_3C) 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 $FeCO_3$ and Fe_3C [14]. 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 [14]. 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 [11].

Experimental Procedure

Material

The sample material studied was X-52 carbon 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 ethanol.

Table 1: Chemical composition of X52 carbon 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 concentrations of imidazoline based inhibitor used in this work were 50 and 100 ppm. Before applying the inhibitor, a solution containing 3% NaCl was prepared. The testing

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solution was heated and maintained at 80 ± 1.0℃, and deaerated with CO_2 for an hour. The formation of $FeCO_3$ scale was accelerate by induced required amount of Fe^{2+} in the form of deoxygenated ferrous chloride salt (FeCl2.4H2O) solution. The analytical reagent $NaHCO_3$ was used to adjust pH value of solution to 6.6.

Electrochemical Measurement

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 electrodes glass cell. X52 cylinder carbon steel with 3 cm^2 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:

$$E(\%) = \frac{CR_i - CR_0}{CR_i} \times 100 \qquad\qquad (1)$$

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

Iron Carbonate Film Formation by addition of Fe^{2+}

Effect of Fe^{2+} concentration on the growth of $FeCO_3$ crystals size can be seen in Fig. 1 and Fig. 2.This is expected since by increasing the concentration of Fe^{2+} , 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 Fe^{2+} , gives the smaller of $FeCO_3$ crystal size [11]–[13]. Formation of $FeCO_3$ film on metal surface give a significant affect on the corrosion rate. It is observed in

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Fig. 3 by introducing Fe^{2+} into test solution lowered the corrosion rate as compared to blank test. High amount with 100 ppm of Fe^{2+} used had reduced the corrosion rate to 0.6 mm/yr. This indicates a great protection is offered by a protective film formation of $FeCO_3$ on metal surface with high Fe^{2+} [6].
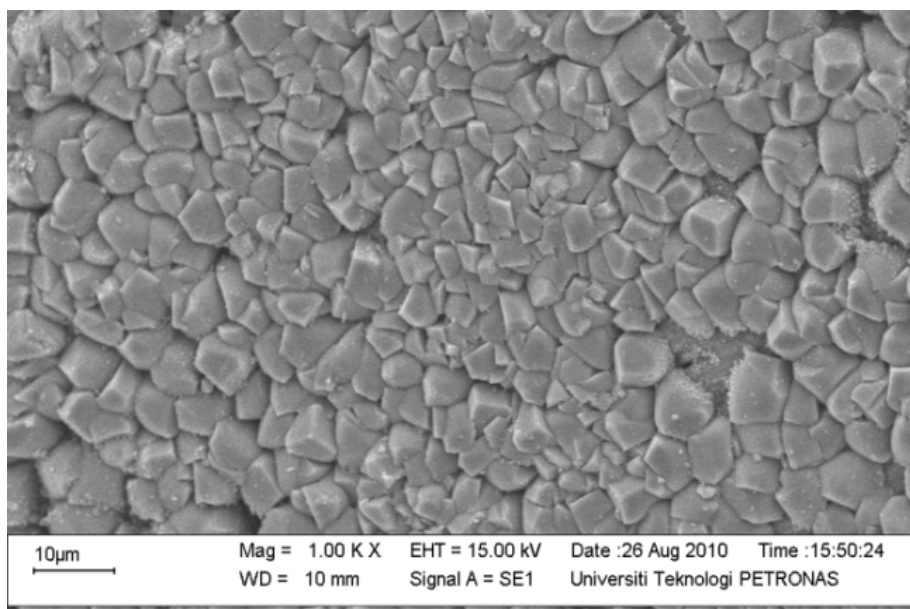

Fig. 1. The top view of the sample at 1000X, for pH 6.60, Fe^{2+} = 50 ppm, temperature = 80°C, stagnant condition
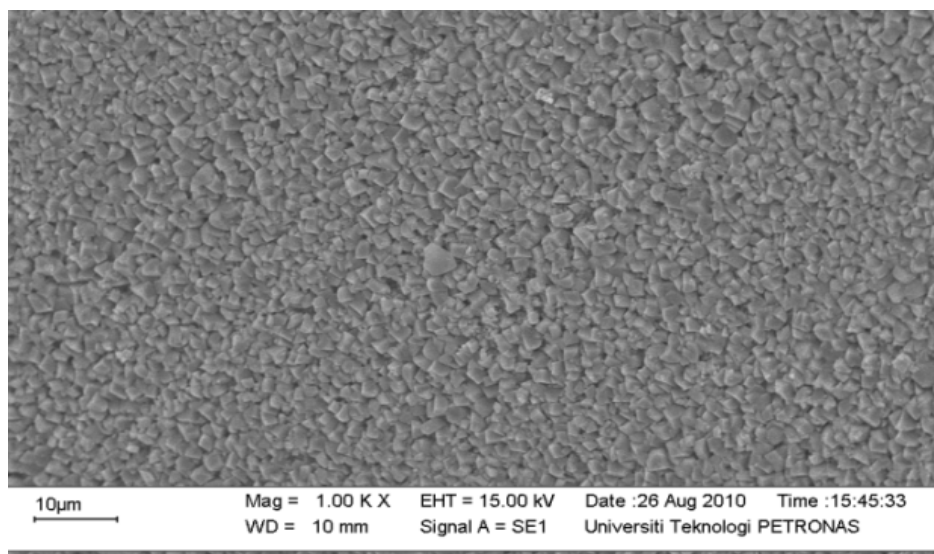

Fig. 2. The top view of the sample at 1000X, for pH 6.60, Fe^{2+} = 100 ppm, temperature = 80°C, stagnant condition

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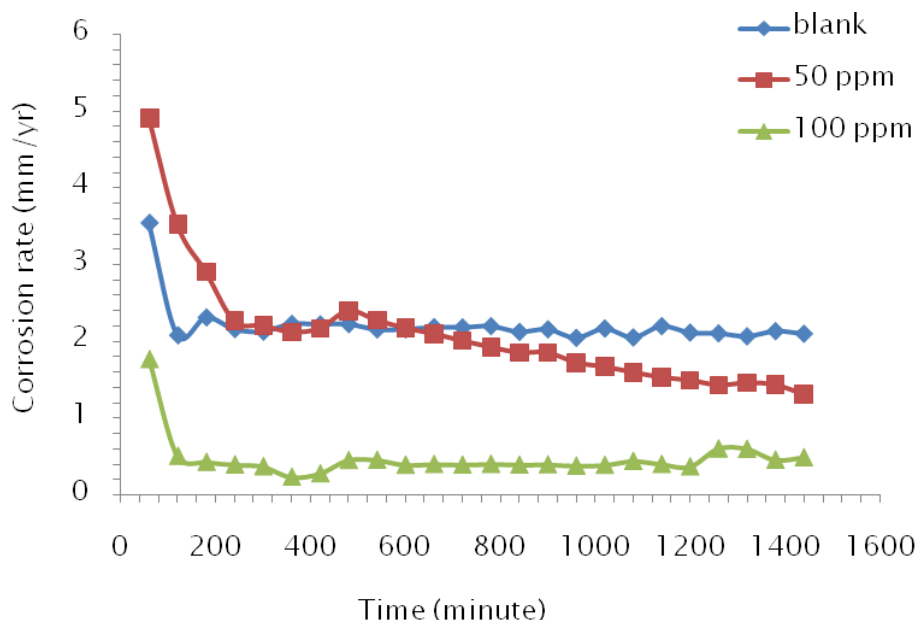
Fig. 3. Corrosion rate as a function of immersion time for (♦ = blank), (■ = 50 ppm Fe^{2+}), and (▲ = 100 ppm Fe^{2+})

Naturally Iron Carbonate Film Formation with Presence of Inhibitor

A significant effect of corrosion inhibitor presence in test solution on the formation of $FeCO_3$ film that was formed by naturally without addition of Fe^{2+} is shown in Fig. 4 and Fig. 5. It is observed the metal surface contains dispersed minute colony of $FeCO_3$ film 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 $FeCO_3$ film [15]. The free pair electrons in nitrogen atoms can be adsorbed on the metal surface and its hydrocarbon chain can form hydrophobic parts, thus providing inhibition. This protective behaviour of inhibitor film makes CO_3^{2-} ions cannot reach the surface easily. Thus, the formation of $FeCO_3$ film is less [1, 4, 6, 16–17]. However, the exact kinetics of the formation of both types of film in not quantified. The effect of imidazoline based inhibitor on the corrosion rate is shown in Fig. 6. Based on the results, it can be concluded that an imidazoline based inhibitor was efficient to reduce the corrosion rate reflecting a great adsorption of inhibitor on metal surface thus, formed a protective barrier from corrosion. A

lower of corrosion rate with 0.1 mm/yr is obtained with 100 ppm imidazoline indicates a great protection is achieved with increasing of inhibitor concentration.
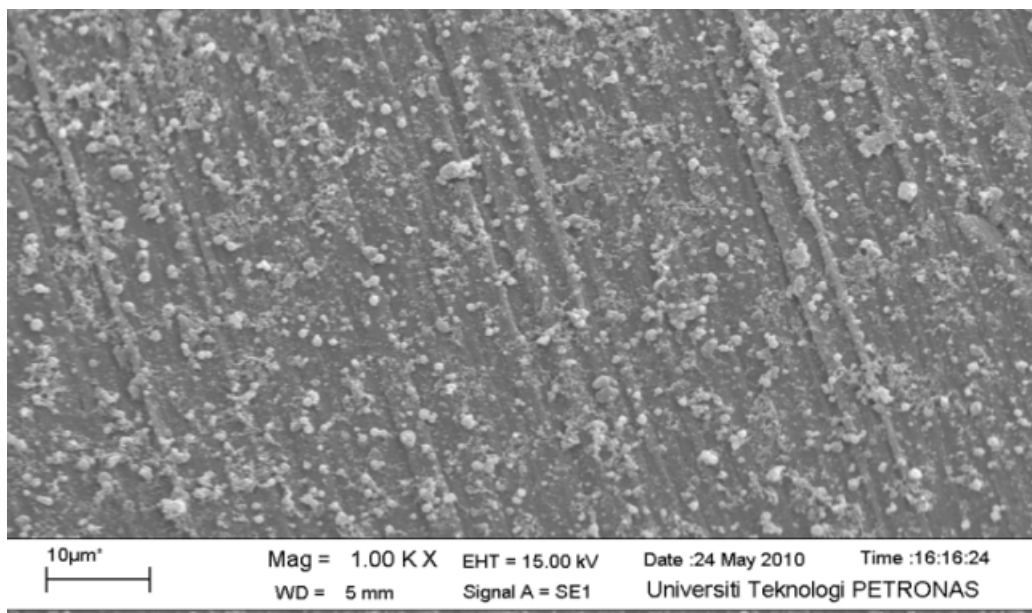

Fig. 4. The top view of the sample at 1000X, for pH 6.60, imidazoline = 50 ppm, temperature = 80°C, stagnant condition
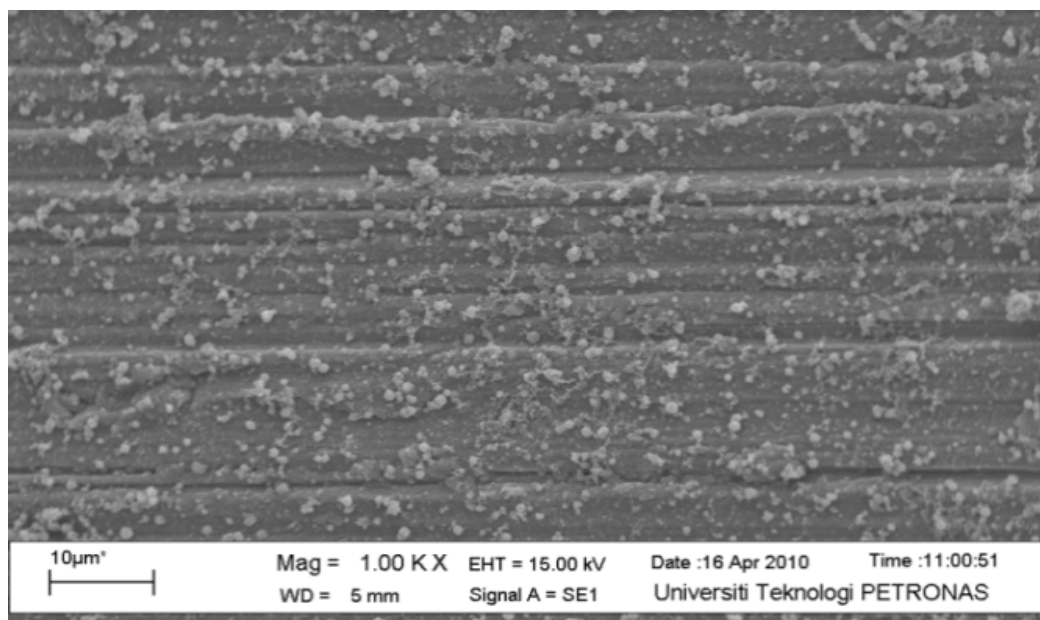

Fig. 5. The top view of the sample at 1000X, for pH 6.60, imidazoline = 100 ppm, temperature = 80°C, stagnant condition
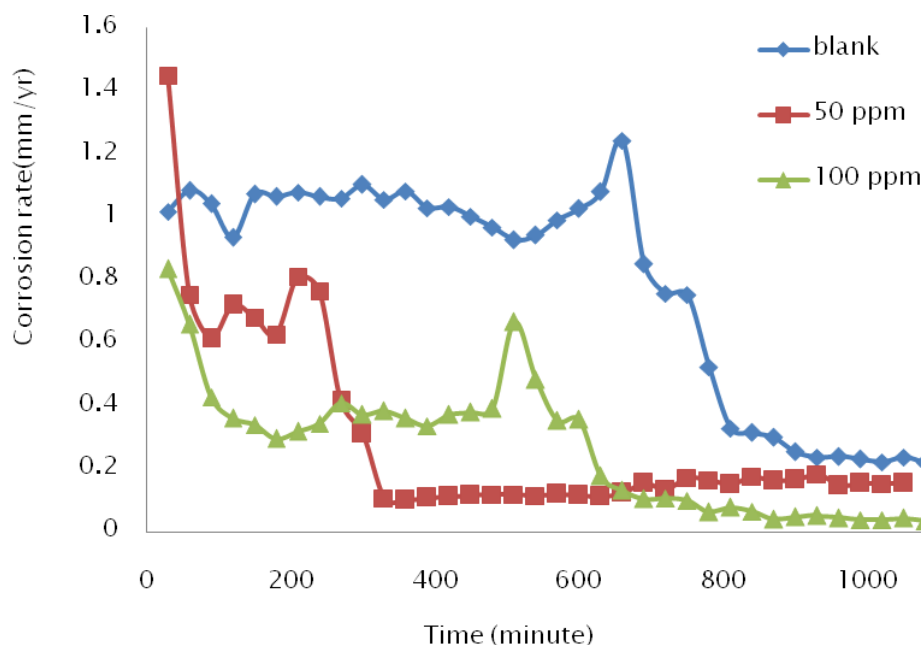
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Fig. 6. Corrosion rate as a function of immersion time for (♦ = blank), (■ = 50 ppm imidazoline), and (▲=100 ppm imidazoline)

Induced FeCO₃ Film Formation with Presence of Corrosion Inhibitor

50 ppm Imidazoline with 50 ppm and 100 ppm Fe²⁺

Presence of corrosion inhibitor together with Fe^{2+} in test solution give a great affect on the corrosion rate and the growing process of $FeCO_3$ film. This is shown in Figs. 7, 8 and 9. The images show a lack of iron carbonate film on the metal surface when low concentration of Fe^{2+} is added into test solution. However, when the concentration of Fe^{2+} added is high, the formation of a continuous iron carbonate film occurred. LPR result in Fig. 9 shows 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. At 100 ppm of Fe^{2+}, the corrosion rate is reduced to lower rate in which 0.3 mm/yr. It can be seen in both conditions, that the corrosion rate starts to be constant after 6 hours of experiment. It might be due to fully adsorption of inhibitor molecules occur after 6 hours of experiment.
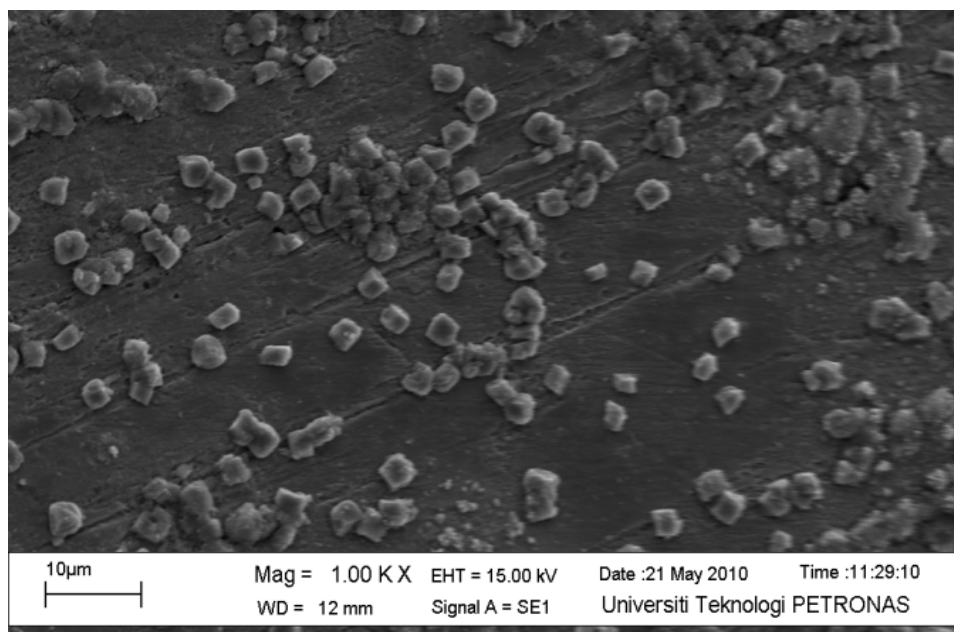
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Fig. 7. The top view of the sample at 1000X, for pH 6.60, 50 ppm imidazoline, $Fe^{2+} = 50$ ppm, temperature = 80℃.

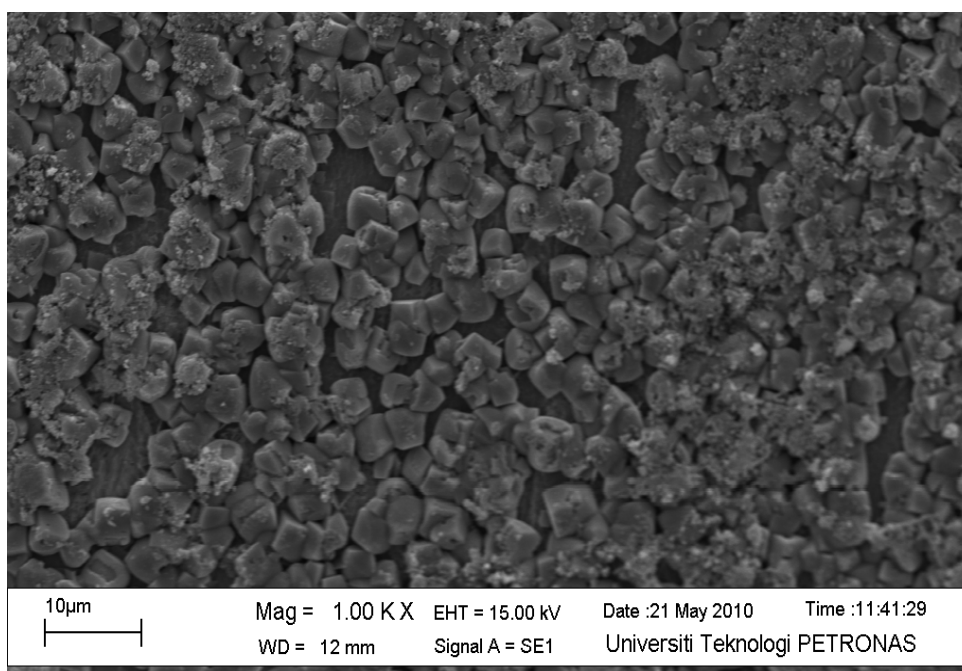

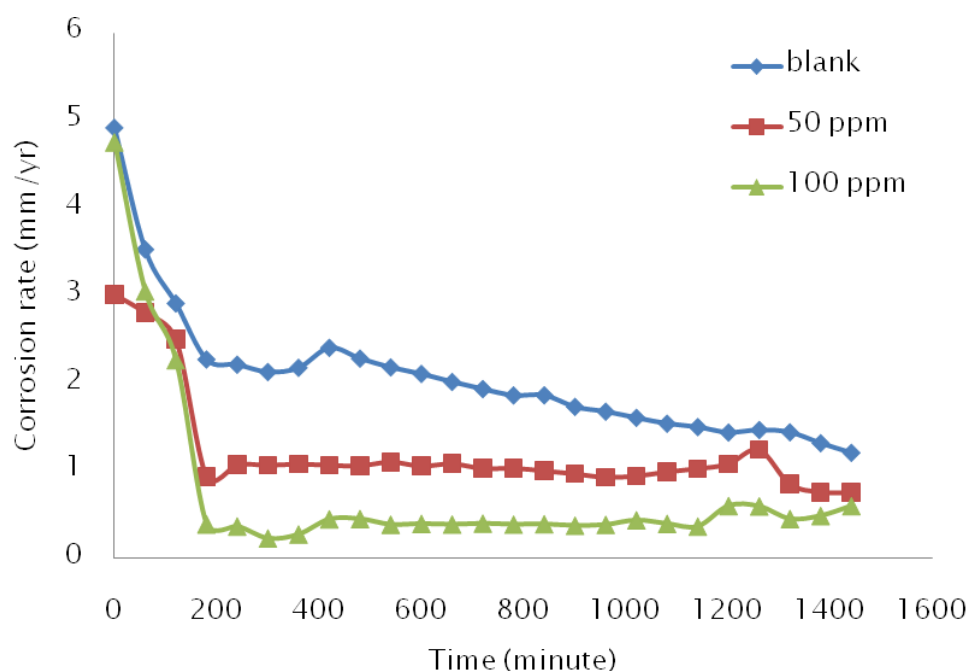Fig. 8. The top view of the sample at 1000X, for pH 6.60, 50 ppm imidazoline, $Fe^{2+} = 100$ ppm, temperature = 80℃.

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Fig. 9. Corrosion rate as a function of immersion time for 50 ppm imidazoline with presence of; ($\blacklozenge$ = blank), ($\blacksquare$ = 50 Fe^{2+}), and ($\blacktriangle$ = 100 ppm Fe^{2+})

100 ppm Imidazoline with 50 ppm and 100 ppm Fe^{2+}

Morphology of $FeCO_3$ film with addition of 100 ppm imidazoline in Figs. 10, 11 and 12 showed a similar trend with 50 ppm imidazoline. Higher amount of imidazoline, will give smaller of $FeCO_3$ crystals size. The presence of imidazoline based inhibitor into test solution retarded the growth of $FeCO_3$ film [18–19]. Combination of 100 ppm imidazoline and 100 ppm Fe^{2+} gives 0.18 mm/year of corrosion rate as compared to 0.35mm/year with 50 ppm Fe^{2+}. This is expected as higher amount of imidazoline added to the solution offered a great protection from 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 presence of 100 ppm imidazoline seems to hamper the growth of iron carbonate on the metal surface.
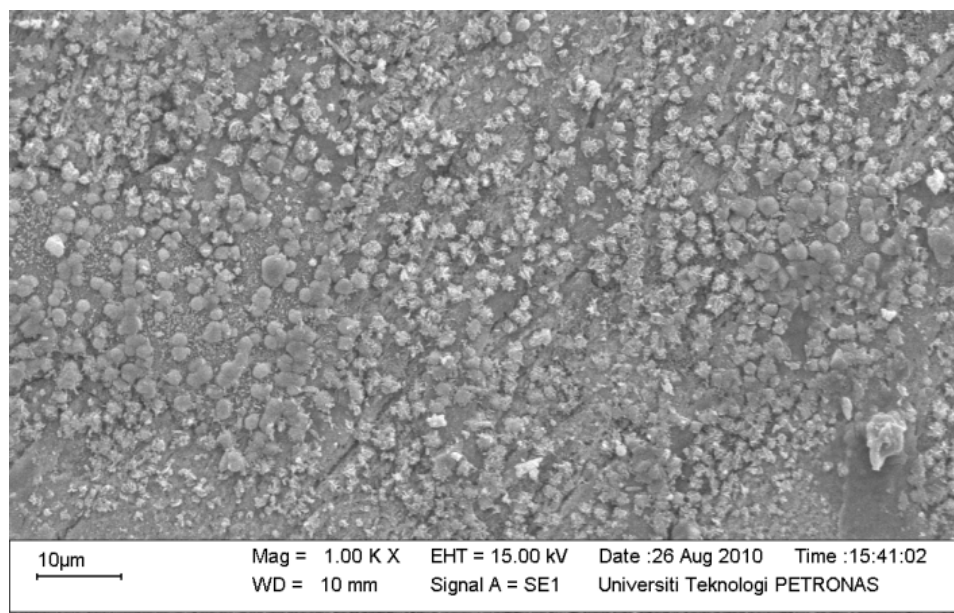
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Fig. 10. The top view of the sample at 1000X, for pH 6.60, 100 ppm imidazoline, Fe^{2+} = 50 ppm, temperature = 80℃.
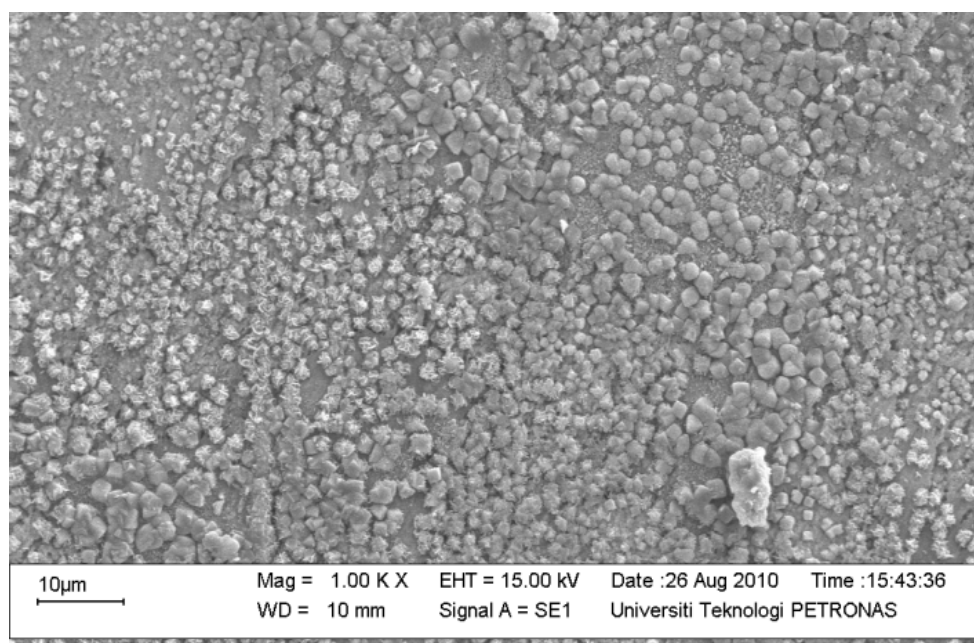

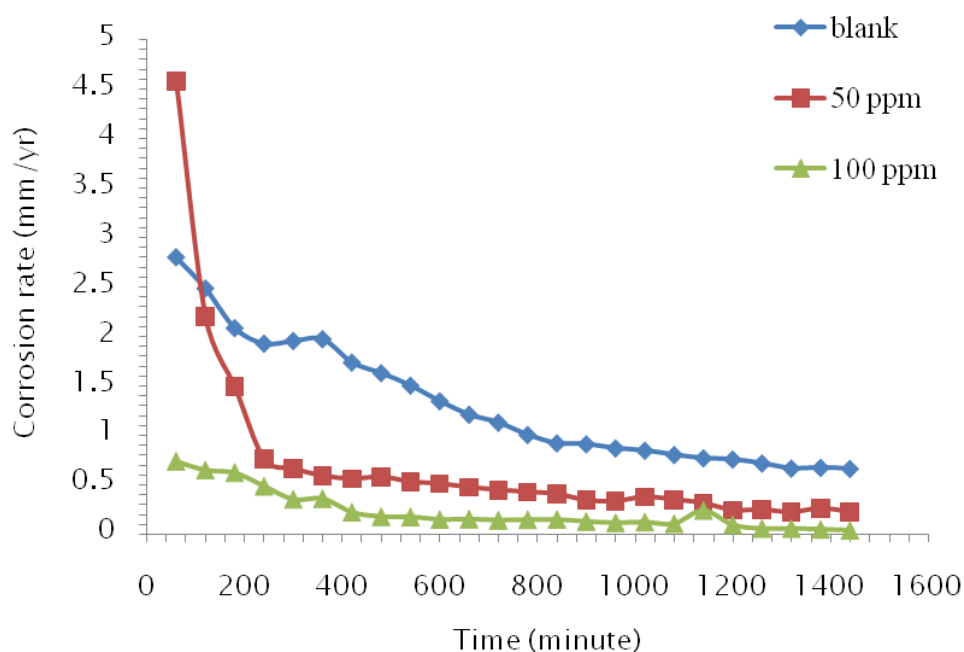Fig. 11. The top view of the sample at 1000X, for pH 6.60, 100 ppm imidazoline, Fe^{2+} = 100 ppm, temperature = 80℃.

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Fig. 12. Corrosion rate as a function of immersion time for 100 ppm imidazoline with presence of; ($\blacklozenge$ = blank), ($\blacksquare$ = 50 Fe^{2+}), and ($\blacktriangle$ =100 ppm Fe^{2+})

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 occurring at the metal surface. Thus, Fe^{2+} discharge from the metal surface and form $FeCO_3$ film [14]. Lastly, it might also be an interaction between the inhibitor films with preformed $FeCO_3$ film. As a consequence, $FeCO_3$ film is seen as a bare surface. However, this study remains open for further investigation, as some of the key questions remain unanswered.

Inhibition Efficiency

The inhibition efficiency calculated according to equation (1) is shown in Fig. 13. At high concentration of 100 ppm imidazoline, it could achieve 80 % of high inhibition efficiency. The addition of Fe^{2+} ions into solution does not inhibit the performance of imidazoline in offering a great protection to corrosion process. Combination of high imidazoline concentration and Fe^{2+} offered a great inhibition in inhibit corrosion process whereby increasing the inhibition efficiency is obtained. 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]. Corrosion product that was essentially composed of iron carbonate film might have an interaction with inhibitor film to offer a dense protectiveness film [12].
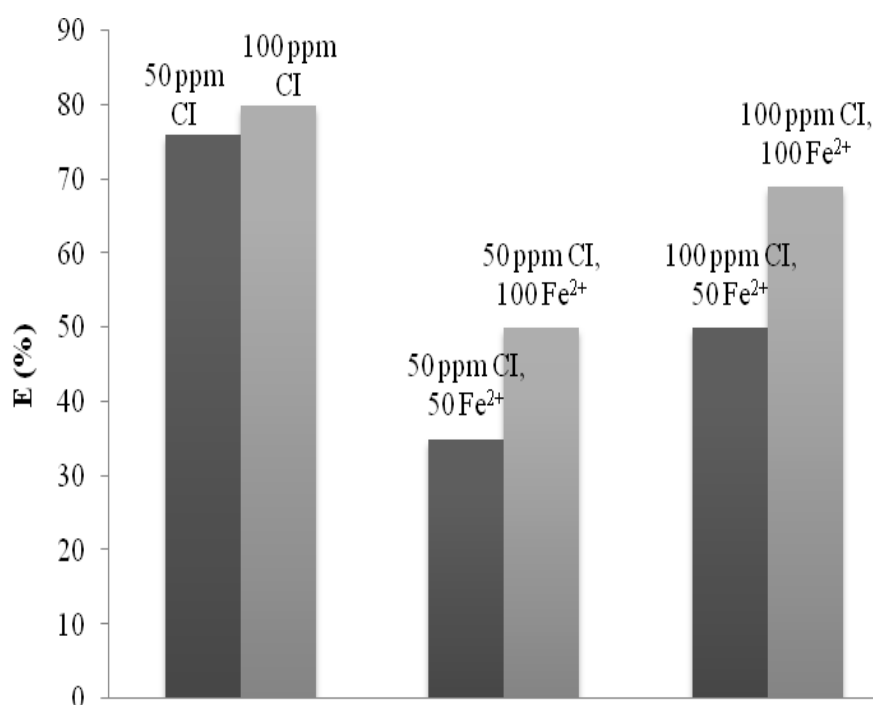

Fig. 13. Inhibitor efficiency for X52 carbon steel in CO_2 saturated 3wt% NaCl solution at various concentrations.

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Conclusion

This paper explores corrosion inhibition performance with the presence of iron carbonate film in CO_2 saturated brine solution. Based on the experimental conditions, it can be concluded that:

1) Presence of imidazoline based inhibitor together with Fe^{2+} into test solution decreased a corrosion rate to lower value than they are on own species whereby high concentration will offered a great protection to corrosion process.

2) Possibly the imidazoline portion of inhibitor forms a complex with free Fe^{2+} and this become more surface active leading to a more protective film.

3) The growth of iron carbonate film is affected by the addition of imidazoline and the resulting film is comprised of smaller crystalline formations that are tightly packed together.

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