



## PERFORMANCE OF CORROSION INHIBITOR WITH SAND DEPOSIT IN CO<sub>2</sub> ENVIRONMENT

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### ABSTRACT

The performance of corrosion inhibitor on API X65 carbon steel covered by sand deposit under CO<sub>2</sub> environment is presented. The effect of corrosion inhibitor concentration on a constant sand deposit thickness was analyzed using Linear Polarization Resistance (LPR) electrochemical method. In addition, the effect of each element alone on corrosion behaviour was also studied for comparison purpose. The results indicated that both corrosion inhibitor and sand deposit could retard the corrosion rate either by working alone or exist together in a system. The overall performance of inhibitor with or without deposit is almost similar suggesting that the controlling factor for corrosion rate in this experiment was the rate of absorption towards the metal surface through sand deposit by corrosive species and inhibitor.

**Keywords:** CO<sub>2</sub> corrosion, corrosion inhibitor, sand deposits, linear polarization resistance.

### INTRODUCTION

Integrity of pipelines is one of the most important aspects to be focused in oil and gas industry. In exploration and production of oil and gas, one of the main threats to the integrity of the pipeline is the Carbon Dioxide (CO<sub>2</sub>) corrosion. To control this threat, proper mitigation methods are implemented such as Corrosion Inhibitor (CI) injection. However, there is no assurance that the CI would work effectively on every occasion due to various factors such as the existence of deposit on the inner pipewall. There are several occasions of malfunction CI have been reported such as the crude leaked from a corroded transit pipeline at the state's northern tip Prudhoe Bay pipelines, Alaska and under deposit corrosion of Halfdan, Denmark production tubulars [1-3]. It was reported that the presence of this deposit could limit the inhibitor excess to the metal surface which can initiate severe localized corrosion.

Many studies have been conducted in the past to study the performance of inhibitor with deposit. Many argued that the performance of corrosion inhibitors was reduced due to a few factors such as environmental changes under the sand deposit, absorption of inhibitor from solution to the deposit surface which is known as parasitic consumption, slow diffusion of corrosion inhibitor through the sand deposit layer and galvanic effect between clean and deposited region [4,5]. On the other hand, Huang *et.al.* [6] also reported that the reduction in inhibitor performance was due to the adsorption of inhibitor from underneath the sand deposit thus leaving the metal unprotected. The main mechanism for inhibitor performance deficiency may varies by type of inhibitors and deposit used in the investigations [5,7]. In addition, deposit properties such as deposit porosity, thickness and type were also have been investigated in details by previous researchers [8,9]. There was also a research conducted to develop a corrosion inhibitor for specific application such as reported by M.B Kermani *et.al.* [7]

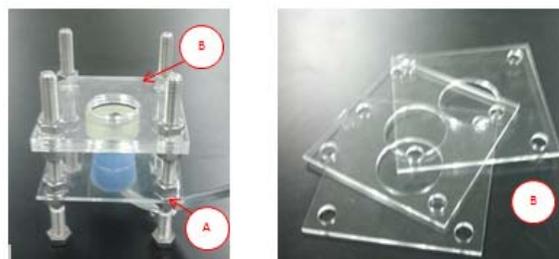
which had superior sand penetration and low absorption losses to sand.

As a conclusion, the literature review shows that the understanding of under deposit corrosion is still scarce and may vary on numerous factors. Thus research on under deposit corrosion is still needed to provide sufficient data for further understanding. Therefore, in this paper, performance of corrosion inhibitor concentration on API X65 carbon steel covered by sand deposits under CO<sub>2</sub> environment was investigated. In addition, the effect of each element alone on corrosion behaviour was also studied for comparison purpose.

### METHODOLOGY

#### Preparation of specimens

Test specimens were prepared by cutting the API X65 carbon steel pipe to 10mm by 10mm. The specimens were spot welded to insulated flexible copper wire and hot mounted with epoxy resin. The samples were ground with silicon carbide grit paper of 180, 240, 320 and 600, cleaned thoroughly, rinse in ultrasonic cleaner, dried and kept in desiccators for further test.



**Figure-1.** (A) Base and specimen holder and (B) sand holder.

A plastic specimen holder was fabricated from acrylic according to Huang J. *et.al.* [4] to provide an easy



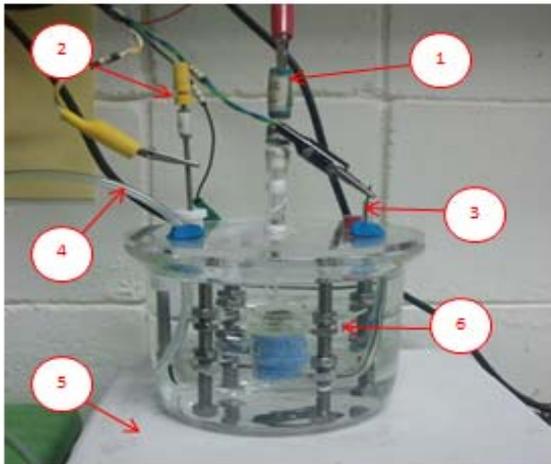
way to place a bed of sand on top of the specimen. Stainless steel bolts and nuts were used to secure the holder together. The exposed surface area of the specimen was 8cm<sup>2</sup>. Figure-1 shows the specimen and sand holder used in the experiment. In this experiment, 2mm and 4mm thicknesses of sand were deposited on the specimen by varying the deposit holder thickness.

### Preparation of deposits

Inorganic silica sand particles were used in the experiment. Size of the sand particles was 212µm which is categorized as fine sand to simulate the average sand particle size found in oil production area in Malaysia. The sands were pre-treated by washing with 5M acid hydrochloric (HCl) solution, rinsed with deionized (DI) water, neutralized by sodium hydroxide (NaOH) solution and rinsed again with DI water before dried in oven for 2hours at 200°C to remove the impurities. After that the sand particles were stored in CO<sub>2</sub> saturated test solution prior to the experiment.

### Test setup

Experiments were conducted at 1 bar in three electrode glass cell setup as shown in Figure-2. The glass cell consists of silver- silver chloride (Ag/AgCl) reference electrode, platinum counter electrode, and a working electrode. The working electrode was the mounted specimen placed inside the fabricated holder under different thicknesses of sand deposit bed. The test solution was stagnant throughout the test and temperature was controlled by a heater. The test solution was 1wt% of sodium chloride (NaCl) in 2L of DI water. Dissolved oxygen was removed by bubbling an oxygen-free CO<sub>2</sub> gas for a minimum of half an hour prior to the test. Then pH value was measured to confirm the CO<sub>2</sub> saturation in the solution. CO<sub>2</sub> gas bubbling was continued throughout the experiment to simulate the CO<sub>2</sub> environment.



**Figure-2.** Three electrode glass cell setup: (1) reference electrode, (2) counter electrode, (3) working electrode, (4) CO<sub>2</sub> gas inlet, (5) heater and (6) specimen and sand holder.

### Test procedure

For baseline test (blank), specimen was initially exposed to test environment for 24hours without sand deposit covering the metal surface. The electrochemical response LPR of the bare steel was monitored at two different temperatures for every half an hour. For under deposit corrosion experiments, the specimens were first exposed to the test environment without any deposit for an hour (pre-corrosion) while corrosion rates LPR were recorded. After that, pipette was used to add a bed of sand to the dedicated sand deposit holder area in the solution. After deposit was added, LPR was continuously monitored for every half an hour until the end of the test. For inhibited test, correct amount of inhibitor was injected only after 4 hours of pre-corrosion period. LPR was used to record the corrosion rate with the same interval period. Experiment conditions are summarized in Table-1.

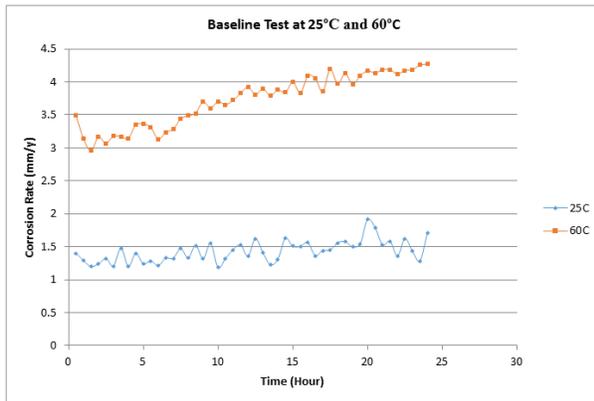
**Table-1.** Experimental conditions.

Parameter	Conditions
Test material	API X65 carbon steel
Test solution	2L DI water + 1wt% NaCl
CO <sub>2</sub> partial pressure	1 bar
Solution pH	4
Temperature	25°C and 60°C
Deposit type	Inorganic silica sand particles (212µm size)
Silica sand thickness	2mm and 4mm
Corrosion inhibitor type	Imidazoline based
Dosage of corrosion inhibitor	25ppm, 50ppm
Test duration	24 hours
Linear polarization resistance	±10mV vs. E <sub>oc</sub> (sweep rate: 0.125 mV/s)

## RESULTS AND DISCUSSION

### Effect of temperature on blank specimens

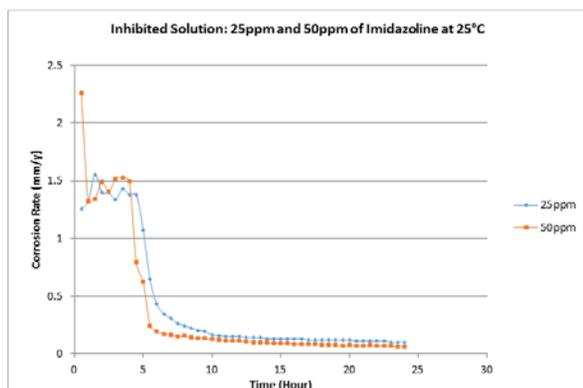
Figure-3 shows the variation of corrosion rate with time at two different temperatures. The corrosion rate of steel specimen at 25°C was consistent throughout the experiment with final corrosion rate of 1.7 mm/year. On the other hand, specimen tested at 60°C shows increment in corrosion rate with final corrosion rate of 4.3 mm/year. High and increasing trend of corrosion rate at a higher temperature was observed may be due to the quicker rate of revealing Fe<sub>3</sub>C network. This is due to the fast mass transfer and charge transfer rate at high temperature as reported by M.B Kermani *et.al.* [7].



**Figure-3.** LPR corrosion rate over time at test conditions: T=25 °C, 60 °C, 1wt% NaCl solution, pH4.0, CO<sub>2</sub> saturated, 1 bar.

### Corrosion inhibitor performance

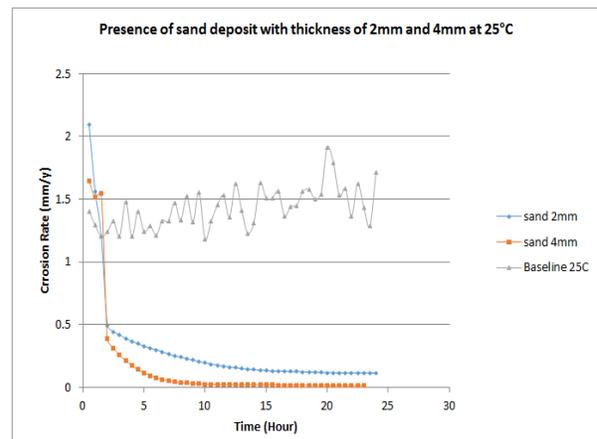
Figure-4 shows the performance of two different concentrations of corrosion inhibitor with time. It was noticed that the corrosion rate decreased dramatically for both concentrations upon injection of corrosion inhibitor to the solution. The final corrosion rate was 0.1mm/year and 0.06mm/year for injection of 25ppm and 50ppm corrosion inhibitor respectively. It was found that both inhibitor concentration effectively reduced general corrosion rate with 94% and 96% inhibitor efficiency were obtained for injection of 25ppm and 50ppm respectively. This may be due to the highly dispersible, stable emulsion-like inhibitor solutions obtained at these concentrations which may exceed the critical micellar concentration (CMC) of the system. It is known that at or above this CMC, the surfactant molecules in the solution may form an ordered structure (micelle) resulting in the formation of an adsorbed surfactant monolayer or bilayer on the metal surface. At hydrophilic surfaces of this sample, it is expected that more than one layer of corrosion inhibitor molecules may form thus effectively reduce the corrosion rate. [10]



**Figure-4.** LPR corrosion rate over time at test conditions: T=25 °C, 1wt% NaCl solution, pH=4.0, corrosion inhibitor (imidazoline):25ppm and 50ppm. CO<sub>2</sub> saturated, 1 bar.

### Effect of sand deposits

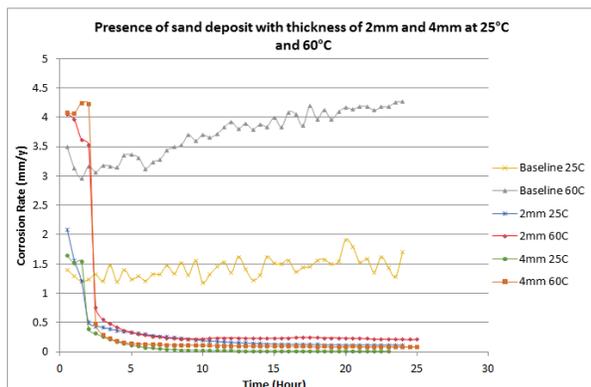
Figure-5 shows corrosion rate of specimens covered by different sand thicknesses with time. Both sand addition resulted in a reduction of corrosion rate and then remained stable up to 24 hours. The final general corrosion rate of samples covered by 2mm and 4mm sand thickness was 0.11mm/year and 0.02mm/year respectively in comparison to the final corrosion rate of bare steel which was 1.7mm/year at a similar condition. It was also observed that corrosion rate for sample covered with 2mm deposit gradually decreased to steady state while sample with 5mm addition of sand deposit drop instantly upon addition of sand deposit. The main mechanism for the reduction of corrosion rate observed is may be due to the slower diffusion rate of corrosive species to the metal surface covered by deposit layer. It was reported that as the deposit density increase or porosity decrease and or increase in deposit thickness as in this case, this will slow down the diffusion of corrosive species and the corrosion products on the metal surface [11]. As a result, instant drop of corrosion rate and lower corrosion rate were achieved at a thicker sand deposit as observed in this experiment.



**Figure-5.** LPR corrosion rate over time at test conditions T=25 °C, 1wt% NaCl solution, pH=4.0, sand particle size=212µm, sand deposit thickness= 2mm and 4mm. CO<sub>2</sub> saturated, 1 bar.

### Effect of temperature with sand deposits

Figure-6 shows corrosion rate of specimens covered by 2mm and 4mm deposit at 25 °C and 60 °C. At both temperatures, addition of both sand thicknesses resulted in dramatic reduction of corrosion rate. The final corrosion rate for specimen covered with 2mm sand deposit was 0.11mm/year and 0.21mm/year at 25°C and 60 °C respectively. While 0.02mm/year and 0.08mm/year of corrosion rate were recorded at 25 °C and 60 °C respectively for specimen covered with 4mm sand deposit.

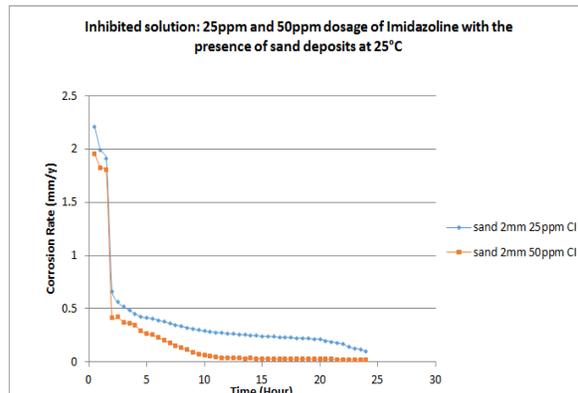


**Figure-6.** LPR corrosion rate over time at test conditions  $T=25^{\circ}\text{C}$  and  $60^{\circ}\text{C}$ , 1wt% NaCl solution, pH=4.0, sand particle size= $212\mu\text{m}$ , sand deposit thickness= 2mm and 4mm.

It was found that, both sand thicknesses indicate a higher corrosion rate when exposed to a higher temperature. In addition, it was also found that at a higher temperature the corrosion rate reach plateau much faster in comparison to the metal exposed to a lower temperature. These indicate that the sand deposit did not effectively reduce the diffusion rate at a high temperature. However, the corrosion rates were still less in comparison to the blank test at  $60^{\circ}\text{C}$ , thus demonstrate the integrated effect of both parameters i.e. sand thickness and temperature in determining the new mass and charge transfer rate to the metal surface. However, results by Jin Huang et.al.[12] reported that corrosion rate change for metal with deposit at  $80^{\circ}\text{C}$  was similar as  $25^{\circ}\text{C}$ . The contradict result may be due to the deposit properties such as the porosity of the sand deposit which in that case more dominant to control the rate of diffusion of corrosive species to reach the metal surface.

#### Effect of sand deposits on inhibitor performance

Figure-7 shows the performance of different concentration of corrosion inhibitor on specimen covered with 2mm thickness of sand deposit. Higher dosage of corrosion inhibitor contributes to a lower corrosion rate as expected. However, the performance of corrosion inhibitor was delayed where both corrosion rate approaching plateau stage only after 10 minutes while reaction by inhibitor alone would result in instant decrement of corrosion rate. This explains the slow rate of inhibitor diffusion towards the metal surface due to the existence of sand deposit. There was no significance different in term of final inhibitor performance either with or without sand deposit. This suggest that the sand deposit was the main controlling factor for corrosion rate in this experiment which provided mass transfer barrier thus reducing the rate of absorption towards the metal surface regardless of corrosive species or inhibitor. This bed of sand retards both corrosion rate and performance of inhibitor.



**Figure-7.** LPR corrosion rate over time at test conditions  $T=25^{\circ}\text{C}$ , 1wt% NaCl solution, pH=4.0, sand deposits thickness=2mm, corrosion inhibitor (imidazoline) =25ppm and 50ppm.

#### CONCLUSIONS

Based on the results discussed in this work, the summary are as follows:

- Higher solution temperature results in higher corrosion rate of specimen with a different trend in comparison to exposure at room temperature.
- Both inhibitor dosage worked effectively under the given conditions (without sand deposit presence).
- General  $\text{CO}_2$  corrosion rate decreased significantly underneath the sand deposits.
- Inhibitor did not work effectively with the presence of sand deposit.

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