



Corrosion inhibition of carbon steel in oil and gas environments

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ABSTRACT

Oil-based corrosion inhibitors have been evaluated for carbon steel in 3.5% NaCl and saturated CO₂ gas. The corrosion rate for carbon steel was determined based on the electro-chemical method using linear resistance polarization (LPR). Specimens at various inhibitor concentrations were placed in a beaker connected to a CO₂ cylinder for CO₂ gas bubbling. The corrosion test was conducted at room temperature and high temperature (60 °C and 80 °C). Higher temperature conditions were used to study inhibitor stability. Results obtained from the LPR test indicated that the most effective corrosion inhibitor for carbon steel had between 5 to 100 ppm concentrations. The stability test showed that inhibitor efficiency was lower at higher temperature.

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1. Introduction

Pipeline is a crucial part in oil and gas industries to transport oil and gas in order for them to be processed for further steps in refineries. In this condition pipelines will experience detrimental conditions (Ridha et al., 2013). Pipelines are exposed to corrosive elements such as CO₂ gas, water vapour, NaCl, and sand particles. Corrosion will occur inside pipelines made of carbon steel or alloy steel. There will be severe forms of localized corrosion, erosion corrosion and uniform corrosion. These forms of corrosion occur when water is absorbed and collected in the local area of the pipelines. The pipelines then begin to corrode as it is exposed to water and CO₂. Corrosion will attack the bottom or upper side of the pipe surface (Azhani et al., 2014).

For long pipe service life, the protection system should provide a barrier of corrosive elements penetration. Currently, inhibitor is the preferred protection choice from corrosion damages (Ortega-Toledo et al., 2011; Makhoul, 2014). But because of fluctuations in heat, different concentration of salts (NaCl) and water vapour, the concentration of inhibitor injected to the pipelines should be in a proper quantity. Low inhibitor quantity cannot protect effectively, hence promote corrosion process. While excessive quantity of inhibitor will affect production cost. The effectiveness of an inhibitor is shown by its impact on reducing corrosion rate.

Recent researchers have used various types of inhibitor such as organic inhibitor or un-organic depending on environmental conditions (Mazumder et al., 2014). The use of petroleum-based inhibitor has been an alternative method for protection from corrosive environments. However, in situ application of liquid inhibitor requires several conditions with extra precautions. For example, an inhibitor exposed to high temperature will have lower concentration due to evaporation (Ai et al., 2006; Zhang et al., 2006).

2. Experimental set-up

2.1. Specimen preparation and test matrix

The working electrodes were made of carbon steel and the chemical composition is as shown in Table 1. The cylindrical specimens were of 12 mm diameter and 10 mm long. Before immersion, the specimen surfaces were polished successively with 240, 400 and 600 grit SiC paper, rinsed with methanol and degreased using acetone. The experiments were repeated at least twice in order to ensure reasonable reproducibility. The test matrix used to carry out the experiment is presented in Table 2.

2.2. Static test set-up

The test assembly consisted of one-litre glass cell bubbled with CO₂ gas. The electrochemical measurements were based on a three-electrode system, using a commercially available potentiostat

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with a computerized control system. The reference electrode used was Ag/AgCl and the auxiliary electrode was a platinum electrode. The linear polarization resistance (LPR) technique was used to

measure the corrosion rate. The procedure was similar as the ASTM experimental test G 5-94 (ASTM, 2004) (Fig. 1).

Table 1: Composition of 080a15 carbon steel used in the experiments

| Steel | C (%) | Si (%) | Mn (%) | P (%) | S (%) | Cr (%) | Ni (%) |
|--------|-------|--------|--------|-------|-------|--------|--------|
| 080A15 | 0.14 | 0.175 | 0.799 | 0.01 | 0.03 | 0.06 | 0.065 |

Table 2: Experimental matrix used in the test

| | |
|------------------------|--------------------------------------|
| Steel Type | 080A15 (BS 970) |
| Aqueous solution | 3 wt% NaCl, kerosin 10% and 50% |
| Purged gas | CO ₂ |
| Total pressure | Atmospheric |
| Temperature | 25°C, 60°C, 80°C |
| Rotation rate | Static |
| pH | 4 |
| Measurement techniques | Linear polarization resistance (LPR) |

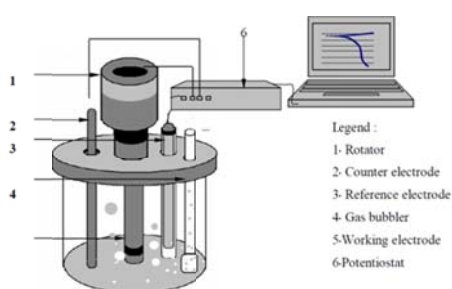


Fig. 1: Experimental set-up for static test

2.3. Cell solutions

The experiments were performed in stagnant condition. The total pressure was 1 bar, and the glass cell was filled with 1 liter of distilled water with 3% wt NaCl, which was stirred with a magnetic stirrer. Then, CO₂ gas was bubbled through the cell (at least one hour prior to experiments) in order to saturate and de-aerates the solution. After the solution was

prepared, the pH was adjusted to reach the determined pH by using NaHCO₃ as a buffer solution. During the experiment, constant concentration of gases was continuously bubbled through the electrolyte in order to maintain consistent water chemistry.

3. Results and discussions

3.1. Effect of inhibitor concentration on corrosion rate and efficiency in different types of brine solutions

The corrosion rate for carbon steel at varying inhibitor concentrations in the CO₂/kerosene system studied by LPR is presented in Table 3 and Table 4. In the experimental conditions, the inhibitor concentrations tested were ranged from 0 to 100 ppm.

Table 3: Corrosion rate (in mm/year) and efficiency of inhibitor AX1 in different types of brine solutions

| Solution | Base | 10 ppm | 20 ppm | 40 ppm |
|----------------------|------|--------|--------|--------|
| 1% NaCl-10% kerosene | 3.5 | 0.07 | 0.03 | 0.02 |
| Efficiency (%) | | 98.6 | 99.6 | 99.8 |
| 1% NaCl-50% kerosene | 2.3 | 0.02 | 0.01 | |
| Efficiency (%) | | 99.1 | 99.8 | |

The presence of inhibitor reduced the corrosion rate consistently. In other words, inhibitor concentration controlled the corrosion rate. The inhibitor reduced the corrosion rate by more than 99% with the addition of 100 ppm of inhibitor. From the tables, it can be explained that the reduced corrosion rate was caused by films formation acting as a catalyst for hydrogen evolution and governing the diffusion of proton donors. Also, It was reported that oil-based inhibitor can also increase hydrogen evolution rate without taking part in the net reaction. In further analyses, it was found that ion concentrations from inhibitor molecules can penetrate steel surface to create films which can reduce electron access to reduce corrosion rate. Indeed, when the concentration of inhibitor is

sufficiently high, the cathodic current density at the primary passivation potential becomes higher than the critical anodic current density, which causes the potential to change to a noble potential to passivate the metal. From the data recorded, it was also shown that as increasing temperature causes decreasing efficiency of inhibitor. This may relate to higher activation energy, enthalphy of activation and entropy of activation (Kairi and Kassim, 2013).

3.2. Effects of corrosion inhibitor on corrosion rate at different temperature

As seen in Fig. 2, corrosion rates measured by LPR under different temperature reached 0,01 mm/year as expected. But, experiments at 80°C, the

corrosion rate increased compared experiments at 60°C (Table 4).

Table 4: Effects of types of inhibitor on Corrosion rate (in mm/year) in 1% NaCl-10% kerosene solutions

| Inhibitor | Base | 10 ppm | 20 ppm | 40 ppm | 80 ppm | 100 ppm |
|----------------|------|--------|--------|--------|--------|---------|
| AX 2 | 1 | 0.03 | 0.01 | 0.01 | 0.01 | 0.01 |
| Efficiency (%) | | 97.0 | 99.1 | 99.2 | 99.2 | 99.4 |
| AX 3 | 1 | 0.028 | 0.01 | 0.01 | 0.01 | 0.01 |
| Efficiency (%) | | 97.2 | 99.1 | 99.2 | 99.2 | 99.4 |

This was indicated that the performance of inhibitor will change as effects of temperature. It was assumed to be caused by micro film formation was disrupted at higher temperature. The conductive film acted as an electrical barrier was interfered by corrosion process. A decrease in inhibition efficiencies with the increase temperature may relate to weakening of physical adsorption. The dependence of temperature on activation parameters for the corrosion process is expressed by the equation of transition state as proposed by Arrhenius equation (8) and transition state equation (Chetouani and Hammouti, 2014).

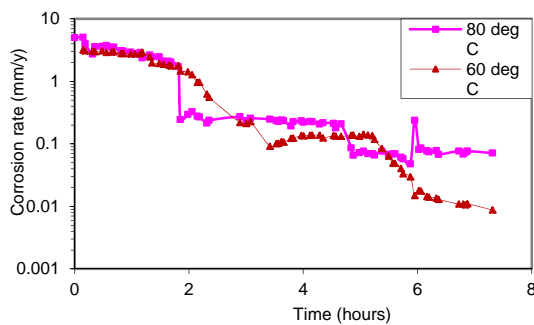


Fig. 2: Inhibitor performance at 60°C and 80°C under 3.5% NaCl and CO₂ gas

3.3. Thermal stability test

Thermal stability is the stability of an inhibitor molecule at high temperatures. An inhibitor molecule with greater stability has more resistance to decomposition at high temperatures. The effects of thermal stability of inhibitor and time are presented in Fig. 3.

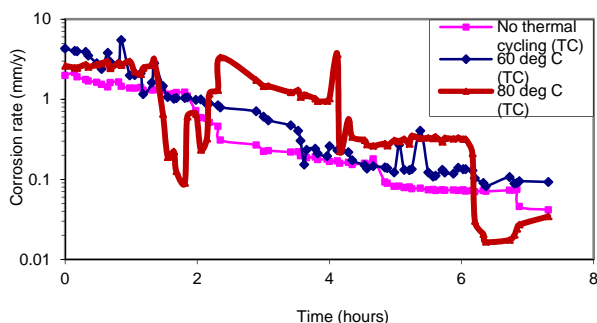


Fig 3: Inhibitor performance after 60°C and 80°C thermal stability test at 60°C bubble test under 3.5% NaCl and CO₂ gas

Fig. 3 describes the stability of the inhibitor at 60°C and 80°C. It is shown that the inhibitor still had an acceptable protection at high temperature. However, the efficiency of inhibitor at higher

temperature (80°C) was slightly reduced compared to lower temperature (60°C). At 80°C, the corrosion rate shows an unstable pattern which indicated the properties of inhibitor has degraded.

4. Conclusions

The use of corrosion inhibitor is an important aspect in reducing corrosion rate. The best corrosion inhibitor can be determined by corrosion efficiency.

Laboratory testing showed that the efficiency of an inhibitor is determined by its concentration and temperature. Higher concentration has higher inhibitor efficiency. Higher temperature cause lower inhibitor efficiency.

The properties of an inhibitor can change due to temperature. From the thermal stability test, it was shown that the inhibitor property has changed at higher temperature.

Concentration was a dominant factor governing the reaction process in CO₂/kerosene system.

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