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Study on the Effect of Surface Finish on Corrosion of Carbon Steel in CO, Environment

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Abstract: The effect of the surface roughness is believed to contribute on corrosion rate and on corrosive wear in CO₂ gas system. Surface roughness affects the hydrodynamic and mass-transfer boundary layer which can influence electrochemical and mechanic-chemical behavior of a surface. Study effects of surface finish is important to predict corrosion rate that happen in the as-delivered internal pipe surface condition. In this research, the influence of surface morphology, represented by roughness, was used to study effect of surface roughness on corrosion rate in CO₂ gas condition. The experiments used the specimens which were abraded using SiC abrasive paper of 60, 240, 400, 600, 800 and 1200 grit on the surface. The specimen used was carbon steel BS 970 (070M20). The specimen was tested at pH 5.5, 3 wt.% NaCl, in static and turbulent flow solution saturated with CO₂ gas condition. The corrosion rate was measured by the three corrosion measurements methods: Linear Polarization Resistance (LPR), weight loss and Electrochemical Impedance Spectroscopy (EIS). Experimental results showed that the corrosion rate increased with increasing surface roughness either in static or in turbulent flow condition. The corrosion rate in the turbulent flow was higher than in static condition for all surface finish.

Key words: Surface roughness, CO2 gas system

INTRODUCTION

Laboratory test practice standards for corrosion measurement such as NACE and ASTM try to obtain accurate reproducibility of the results. To study effects of surface condition, it can be, generally, conducted by removing a substantial layer of metal from the test specimens. This method should be done to eliminate effect of metallic surface variations. However, the lack of specific guidelines leads to variations in surface roughness which can affect the corrosion rate measurement. According to NACE (NACE Standard TM0169-2000, 2000), a common and widely used surface finish is produced by polishing with No. 120 abrasive paper or its equivalent. Ideally, in laboratory test, the surface of the specimen should be identical with the surface of actual equipment to be investigated. However, this is usually not possible as the surfaces of field equipment vary as fabricated and due to its interaction nature with environment. Since many interactions factors may govern corrosion behaviour, sometimes, there is a different result between experimental data and field data. One of the factors that might cause those differences is surface conditions. It was described theoretically that surface roughness can influence electrochemical or mechano-chemical behavior of a surface. Such conditions

could promote different interaction in the micro-electrical behavior and will impact on corrosion rate. Thus, effect of surface roughness is important factor that should be considered in verifying corrosion rate of carbon steel from the laboratory experiments and corrosion rate of as-delivered internal pipe line. This study investigated the correlation between various surface roughness conditions on corrosion rate in CO_2 environment.

Literature review of surface roughness: A number of studies have been carried out to investigate various aspects of surface roughness in relation to the corrosion rate. Cheng and Roscoe (2005) investigated the influence of surface polishing on the electrochemical behavior of titanium. The research concluded at high anodic potential range (>2.0V), the 1 µm diamond paste polished electrode gave a much higher anodic current than the rough sandpaper polished. Klein *et al.* (2005) investigated the erosion/corrosion resistance of chromium nickel steel in the as-delivered condition and the surface roughness of the heat treated version in a multiphase CO₂ corrosion. The results indicated that one of the heat treated versions of the steel has higher wear resistance.

According to Fogg and Morse (2005), steel pipedelivered to the coating yard has a relative roughness in order of 20 μ m and may exceed 50 μ m, depending on

the corrosion products formed on the surface. This, in turn, affects the fluids in motion. Friction occurs between the fluid and the pipeline wall will affect on corrosion rate.

Fogg and Morse (2005) have also done a research in 2005 on the effect of surface roughness on the maximum flow rate of a subsea gas export line. They concluded that the maximum flow rate decreases with increasing internal surface roughness. It was due to turbulent flow of natural gas transportation in pipelines can form a laminar film at the pipe wall which reduce the friction between the fluid and pipe wall. Increased roughness would also affect the hydrodynamic boundary layer, mass-transfer boundary layer, thus affecting the fluid-velocity sensitive corrosion mechanism.

CO₂ corrosion: Corrosion in oil and gas industries mainly deals with CO₂ gas as it is the main species presenting in oil field. The hydration of CO₂ to carbonate acid causes corrosion on mild steel. Carbonate acid decreases pH of the medium. Degree of corrosiveness due to CO₂ gas is influenced by environmental conditions such as; temperature, CO₂ partial pressure, corrosion film properties and flow conditions (De Waard and Milliams, 1975; Silverman, 2006). In aqueous environment, CO₂ corrodes carbon steel through an electrochemical process involving anodic dissolution of iron and cathodic evolution of hydrogen (Nesic, 2007; Nordsveen *et al.*, 2003). When water reacts with CO₂ gas, it will produce carbonic acid as shown in the following reaction equation:

$$CO_2 + H_2O \rightarrow H_2CO_3$$
 (1)

On the anodic site, the anodic dissolution of iron in acid solutions occurring as follows (Nesic, 2007):

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
 (2)

Then, on the cathodic side, there are two possibilities reactions are independent and the net cathodic current is the sum of the currents for the two reactions:

$$2H^{+}+2e^{-} \rightarrow H_{2}$$
 (3)

$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^-$$
 (4)

The overall reaction is:

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2$$
 (5)

From the reaction in Eq. 2, anodic process of iron oxidation could produce FeCO₃ and/or Fe₃O₄ film which can be protective or non protective depending on the conditions when it forms (Schmitt and Papenfuss, 1999).

MATERIALS AND METHODS

Electrochemical set-up: A typical schematic three-electrode set-up used in all electrochemical experiments is presented in Fig. 1. A rotating cylinder electrode with a speed control unit was used as the working electrode. Glass cell was fitted with graphite electrodes as auxiliary electrode and a Ag/AgCl as a reference electrode.

Specimen preparation: The working electrodes were carbon steel and the chemical composition is as shown in Table 1. The cylindrical specimens have diameter of 12 and 10 mm length. Before immersion, the specimen surfaces were polished successively with 60, 240, 400, 600, 800 and 1200 grit SiC paper, rinsed with methanol and decreased using acetone. The experiments were repeated at least twice in order to ensure reasonable reproducibility.

Cell solutions: The experiments were performed both in stagnant and flow solutions condition. The total pressure was 1 bar, the glass cell was filled with 1 L of distilled water and 3% wt. NaCl which was stirred with magnetic stirrer. Then, CO₂ gas was bubbled through the cell (at least one h prior to experiments) in order to saturate and de-aerates the solution. Temperature was set using a hot plate. After the solution was prepared, the pH was adjusted to reach the pH set by using NaHCO₃ as buffer solutions.

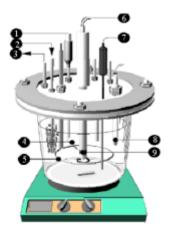


Fig. 1: Schematic RCE corrosion test cell (George, 2007); 1: Reference electrode 2: Gas in; 3: Gas out; 4: Luggin capillary; 5: Counter electrode; 6: Rotator; 7: Temperature probe; 8: pH probe; 9: Working electrode

Table 1: Composition of 080a15 (Bs 970) carbon steel used in the experiments

| | OZ ED OZ ZZZ | Dit Del IIII et les | | | | | | |
|--------|--------------|---------------------|-------|------|------|-------|-------|--|
| 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: Surface profiles for different surface finishes

| | Surface finish (grit) | | | | | |
|-----------------|-----------------------|-------|-------|-------|-------|-------|
| Surface profile | 60 | 240 | 400 | 600 | 800 | 1200 |
| Average Ra (µm) | 8.45 | 13.03 | 25.56 | 22.78 | 20.07 | 15.87 |
| Average Rz (µm) | 38.02 | 26.56 | 22.01 | 21.96 | 19.98 | 18.95 |

| Table | 3. | Experimental | test | matrix |
|-------|----|--------------|------|--------|
| | | | | |

| Table 5: Experimental test mad ix | | |
|-----------------------------------|---------------------------------|--|
| Parameter | Value | |
| Steel type | BS 970 (070M20) | |
| NaCl (wt.%) | 3 | |
| pН | 5.5 | |
| Temperature (°C) | 25 | |
| Rotational Velocity (rpm) | 0, 1000 | |
| Surface Finish (grit) | 60, 240, 400, 600, 800 and 1200 | |
| Measurement Techniques | LPR, Weight Loss, EIS | |

Simulation of flow condition was conducted using Rotating Cylinder Electrode (RCE). A cylindrical working electrode was screwed onto an electrode holder at the center of the cell for rotating in the RCE. The Linear Polarization Resistance (LPR) technique was used to measure the corrosion rate. The procedure is similar to ASTM Experimental test G 5-94 (ASTM G 5-94, 2004).

The Mitutoyo Surface Profiler was used to measure the roughness as Ra and Rz parameter, the arithmetic average and depth of the peak-to-valley height of surface asperities in micrometers (μ m). An average of six random readings is taken, as shown in the subsequent Table 2. More detail results regarding to the surface condition and SEM investigation can be seen in Appendix.

Test matrix: The corrosion evaluations in this study will be performed under stagnant and dynamic conditions, with the use of static electrodes and RCE apparatus. Table 3 was test matrix used to do experiments.

RESULTS AND DISCUSSION

Corrosion rate in static condition: Effects of surface roughness on corrosion in CO₂ saturated solution is presented in Fig. 2. The figure shows that increase of corrosion rate as a decrease surface roughness. Figure 2 was also seen that material with rough surface will prone to be stable compared to smooth surface during 2 h measurement. At 1200 grid surface finishing, corrosion rate fluctuate from 1.5-2.5 mm year⁻¹. But, variation of corrosion rate occur around 1 mm year⁻¹ for material with 60 grid surface finishing. The effects of surface roughness on contributing an increase of corrosion rate were also investigated by (Li and Li, 2006).

Measurement corrosion rate with different corrosion measurements method is presented in Fig. 3. It can also be shown that generally the corrosion rate of the rough surface is higher than the smooth surface finish. Rough surface increases corrosion rate by increasing surface

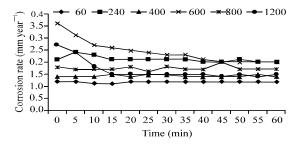


Fig. 2: Average corrosion rate of carbon steel in CO₂-saturated NaCI solution at pH 5.5,22°C, static condition at several surface roughness

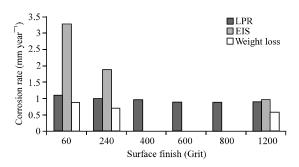


Fig. 3: Corrosion rate (mm year⁻¹) for variation surface finishes at static condition as measured using different corrosion measurements method (EIS, LPR, and weight loss)

area which involves in distribution of electrochemical reaction. Corrosion measurement using EIS and weight loss showed a consistence decrease of corrosion rate for rough surface and smooth surface. But, LPR presented fluctuating results.

Corrosion rate in flow conditions: From Fig. 4, there is a trend that corrosion rate is higher at rougher surfaces. It can be concluded that a rise in surface roughness intensifies corrosion processes by increasing the surface contact of the specimen subjected to corrosion, as can be seen in the Rz surface profile (Appendix 1). These effects may relate with increasing distribution of fluid phase, mass transport species and giving mechanical forces that could wash away corrosion products.

Figure 5 is presented comparison different corrosion methods in measuring corrosion rate on flow condition. Results from all measurement methods suggested that the corrosion rate calculated by EIS and LPR did not vary significantly in turbulence flow condition. There was also indication that the corrosion rate did not much different along the surface roughness tested. However, using LPR method, the corrosion rate showed a meaningful decreased.

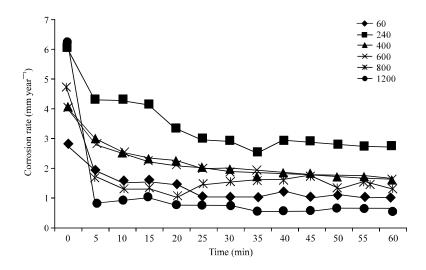


Fig. 4: Average corrosion rate of mild steel in CO₂-saturated NaCl solution at pH 5.5, 22°C, 100° rpm several surface roughness

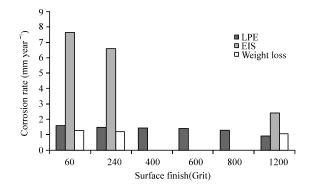


Fig. 5: Corrosion rate for variation surface finishes at flow simulated condition (1000 rpm) as measured using different corrosion measurements method (EIS, LPR and weight loss)

CONCLUSION

- Based on surface profiles and corrosion rate measured, the practice of 400, 600 and 800 grit surface finish is acceptable in representing the 'as-delivered' in laboratory
- As the corrosion rate varies at different roughness, the abrasive paper used for surface polishing must be consistent throughout the experiment. Too rough or fine finish should be avoided as it may induce high inaccuracy in predicting field corrosion behavior

- Rough surface, as shown by the surface profile, has larger area of surface contact with the corrosion environment. Thus, a rise in surface roughness intensifies corrosion processes by increasing the surface contact of the specimen subjected to corrosion
- It can also be concluded that generally, the corrosion rate of the turbulent flow is higher than static condition for all surface finish.
- The corrosion rate difference between surface finishes at static condition is relatively small and insignificant

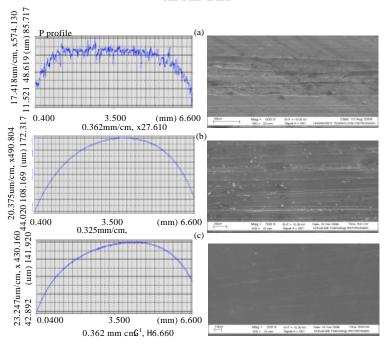
RECOMMENDATION

The results leave a gap between the corrosion rate measured by EIS with weight loss and LPR. Since the EIS results show significant corrosion rate deviation in turbulent flow, it can be further investigated in the future. This study can also be further improved by conducting experiments at higher temperatures and by including the effect of film formation at the surface.

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APPENDIX



Appendix 1: Surface Profiling and SEM Imaging (500x Magnification); (a)60 Grit, (b) 400 Grit and (c) 1200 Grit

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