The Effect of Flow Rate on the Preferential Weld Corrosion of X65 Pipeline Steel

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Abstract

Large galvanic currents occurring in a weld between the parent metal, weld metal and heat affected zone can sometimes lead to serious localised corrosion. In practice, the galvanic currents are generally controlled by the addition of a corrosion inhibitor and by ensuring that the composition of the weld metal is selected to make it slightly more noble than the parent material. However, it has been shown that in some circumstances, a current reversal takes place which results in the weld metal becoming more active than the parent metal and severe attack of the weld occurs. The corrosion inhibitor appears to have a role in this current reversal. It has been proposed that the inhibitor may be selectively removed from the weld metal at the high flow rate but this needs further investigation.

The aim of the research described in this paper is to study the effect of flow rate on preferential weld corrosion in X65 pipeline steel by investigating the hydrodynamic conditions under which current reversal takes place. A submerged jet-impingement flow loop was used to investigate the corrosion behaviour of the steel in stagnant and flowing brine, saturated with CO\textsubscript{2} at 1 bar. The galvanic currents between the weldment samples in each hydrodynamic region were recorded simultaneously using zero-resistance ammeters and analysed to investigate the impact of galvanic effects on the overall corrosion rate.

Key words: Preferential weld corrosion; carbon dioxide; electrochemical measurements; submerged jet impingement

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1. Introduction

Preferential weld corrosion (PWC) is a serious form of attack in which the corrosion rates of the weld metal (WM) and heat affected zone (HAZ) exceed that of the parent metal (PM). Figure 1 shows an example of severe PWC in a carbon steel pipeline which failed after only a few months in service [1].
Preferential weld corrosion occurs by a galvanic corrosion mechanism caused by differences in the composition and microstructure of the metal in the three weld regions [2]. It can be controlled by alloying the weld metal so that it is slightly cathodic to the parent metal and therefore benefits from partial corrosion protection [3]. In addition, oilfield corrosion inhibitors, which operate by adsorbing onto the metal surface, are an effective way of reducing the corrosion rate to acceptable levels [4]. However, inhibitor adsorption is affected by the flow rate of the fluid in the pipeline. It has been shown that at high flow rates a current reversal can take place, with the weld metal changing from being more cathodic than the parent metal to being more anodic, and severe PWC results. This attack is exacerbated by the now large cathodic area of the parent metal, relative to the small area of the anodic weld metal. Figure 2 shows galvanic currents measured in rotating electrode studies of a X65 pipeline steel weldment tested in inhibited brine containing CO₂ [5]. The current reversals that occurred first at 4000rpm and again at 5000rpm are thought to be caused by the inhibitor being removed selectively by the flow from different regions of the weld in turn.
This important finding needs further investigation and the aim of the work described in this paper is to investigate in detail the influence of fluid flow on current reversal. A new weld is being studied, having been produced by a different process and using different welding parameters from those employed in previous work [7]. The paper describes progress in this current research project to date.

2. Experimental Procedure

Materials

A Submerged Jet Impingement (SJI) target was prepared from a sample of X65 pipeline steel with a weldment from a multi-pass welding process. The chemical composition of the parent metal and weld metal is shown in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Al</th>
<th>Cu</th>
<th>Mo</th>
<th>Ni</th>
<th>Cr</th>
<th>Nb</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pipe (%)</td>
<td>0.07</td>
<td>0.30</td>
<td>1.51</td>
<td>0.01</td>
<td>&lt;0.005</td>
<td>0.05</td>
<td>0.04</td>
<td>0.26</td>
<td>0.01</td>
<td>0.39</td>
<td>0.02</td>
<td>0.02</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Weld (%)</td>
<td>0.07</td>
<td>0.30</td>
<td>1.59</td>
<td>0.01</td>
<td>0.007</td>
<td>0.005</td>
<td>&lt;0.01</td>
<td>0.1</td>
<td>0.11</td>
<td>0.27</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

The weldment plate (Figure 3), of area 210 x 60 mm² and 30 mm thickness, was polished using different grades of abrasive paper from 240 to 1200 grit, rinsed with deionized water, isopropanol then etched in 10 % Nital. The detailed macrostructure of X65 weldment is shown in Figure 3C with parent metal (PM), weld metal (WM) and heat affected zone (HAZ).

![Figure 3](image)

*Figure 3. (A) Welded plate, (B) plate etched in 10 % Nital and (C) PM, WM and HAZ macrostructure*
Design and Construction of the Submerged Jet Impingement Target

The SJI target design used in this study is adopted from previous work by Adegbite et al. [7] and shown in Figure 4A. The target for this current research is constructed from carefully selected sections, extracted with electrical discharge machining (EDM) from the X65 carbon steel pipeline weldment of three weld metal (WM), three heat affected zone (HAZ) and three parent material sections (PM) with surface areas in the ratio 2:1:8 respectively (Figure 4B).

Figure 4. (A) Design of jet impingement target [7], (B) the sections of weldment cut using electrical discharge machining (EDM).

Each of the nine metal pieces were attached to a connector and then later an electrical wire to create an electrode. The target was formed of three concentric circles, each with a section of parent metal, weld metal and heat affected zone, isolated from neighbouring sections with PTFE to avoid electrical contact (shown in Figure 5A and 5B). The concentric circles are placed so as to experience different hydrodynamic effects from an impinging water jet [7]. The target form was filled with insulating resin. Wires connected to the electrodes were combined and protected in an insulated cable as shown in Figure 5C.
Experiment Procedure

The SJI target was polished using different grades of abrasive paper from 240 up to 1200, rinsed with deionized water and isopropanol then dried. All tests were performed in both static conditions and with a flow rate of 5 m/s in artificial seawater saturated with CO₂.

The experimental layout of submerged jet impingement used in this research is shown schematically in Figure 6. The SJI target is placed in a glass cell within a flow loop, beneath a 5 mm water jet nozzle. The cell also contains reference and auxiliary electrodes and is connected to a zero resistance ammeter to monitor the corrosion process.

Initially, brine solution is deaerated with N₂ in a glass cell for 4 hours to remove the dissolved oxygen in the system. Then CO₂ is sparged into the flow loop for 12 hours for effective saturation. After 12 hours brine solution saturated with CO₂ flowing at 5 m/s is applied with the jet onto the submerged target. The flow loop temperature is maintained at 32°C while CO₂ is bubbled into the system continuously for the experiment duration.
Electrochemical Measurements

Galvanic currents: The galvanic currents between each weld region were recorded every minute using a multichannel zero resistance ammeter (ZRA), ACM Instrument Galvo-Gill 12) connected to a data logging PC. For the nine electrode sections in each hydrodynamic region of the target, currents from the parent material (PM) to the heat-affected zone (HAZ) and from the weld metal (WM) to the HAZ were recorded on six channels of the ZRA. The working electrodes were coupled, with the HAZ short-circuiting all channels. The reference electrode (SCE) was connected to all channels in the same way as the HAZ. Since the three working electrodes (PM, HAZ, WM) were in the short circuit condition, the sum of their individual galvanic currents will be zero, such that their individual galvanic currents (IpM, IHAZ, IWM respectively) are established from the following relationship:

\[ I_{PM} + I_{HAZ} + I_{WM} = 0 \]  \hspace{1cm} (1)

Self-Corrosion Rates:

Self-corrosion rates of the Submerged Jet Impingent (SJI) target were analysed from linear polarisation resistance measurements of each working electrode. The LPR was determined by using every single section in the SJI target as a working electrode with a standard calomel reference electrode (SCE) and an auxiliary platinum electrode. A cyclic sweep technique is
used to scan each uncoupled electrode from 10 mV (SCE) below the open circuit potential (OCP) to 10 mV (SCE) above the OCP and back to the starting potential. Changes of current during the process were recorded every second.

The resulting potential/current density plot exhibited a straight line where the gradient is inversely related to the corrosion rate. This results in the polarisation resistance $R_p$, which is related to the corrosion current using equation 2:

$$R_p = \frac{\Delta E}{\Delta I} = \frac{\beta}{I_{corr}}$$  \hspace{1cm} (2)

Where:
- $R_p$ = polarisation resistance ($\Omega \text{cm}^2$)
- $I_{corr}$ = corrosion current ($\text{A/cm}^2$)
- $\beta$ = Stern-Geary constant related to the anodic ($b_a$) and cathodic ($b_c$) Tafel slopes

**Electrochemical Impedance Spectroscopy (EIS)**

Electrochemical impedance spectroscopy was used to complement the LPR measurements and confirm the self-corrosion rates. The potential was scanned +/- 10mV of the open circuit potential, as in the LPR measurements, at frequencies ranging from 20kHz to 0.05 Hz and the corresponding currents were recorded and used to calculate the impedance of the corrosion processes. In addition, EIS can be used to investigate the corrosion mechanism and the influence of surface films result from either the corrosion process or action of the inhibitor.

3. **Results and Discussion**

Typical results are reported here for the corrosion measurements on the outer ring of the SJI target at a flow rate of 5m/s and a temperature of 32 °C.

**Galvanic Current Measurements**

The results of the galvanic current measurements are given in Figure 7. During the initial deaeration stage with nitrogen (a), the galvanic currents are small and slowly decrease. The deaeration is monitored by recording the electrode potentials, which become more electronegative as dissolved oxygen is removed. Figure 8 shows that the potentials of the PM/HAZ and WM/HAZ couples are lowered to approximately -640mV(SCE) during this period. The brine is considered to be well deaerated when the potential reaches -730mV(SCE) so in these initial experiments there was still some dissolved oxygen present.

When CO$_2$ is bubbled into the cell (b), there is a further active shift in the electrode potentials to -754 mV(SCE) as the steel electrodes are attacked by the carbonic acid (Figure 8) accompanied by an increase in the galvanic currents (Figure 7). At this stage, the PM is slightly anodic to the other two weld regions (a positive current) and the WM and HAZ are both cathodic (negative currents) and therefore partially protected from corrosion.

After flowing CO$_2$ into the solution for 6h, the pump is started and the brine impinges on the target electrodes at 5m/s (c). There is a large transient increase in the galvanic currents, which quickly stabilises, leaving a reversal in the current direction on the WM. Whereas the WM has been cathodic in static conditions, it now becomes anodic, providing corrosion protection
mainly to the HAZ. If sustained over long periods, this current reversal would result in the preferential corrosion of the WM.

Figure 7. Galvanic current density in the weld sections exposed to (a) static deaerated brine solution, then (b) saturated with CO$_2$, and (c) flowing at 5 m/s and 32 °C

Figure 8. Corrosion potential of PM-HAZ and WM-HAZ galvanic couples in (a) stagnant brine solution (b) saturated with CO$_2$ and (c) flowing at 5 m/s and 32 °C
Self-Corrosion Measurements

Linear polarisation resistance (LPR) measurements for all of the electrodes are recorded after the galvanic measurements were completed and typical potential/current density plots for the outer ring are shown in Figure 9. The open circuit potentials of the electrodes (where current density is zero) confirm that the WM was the most electronegative of the three weld regions and therefore it behaves as the anode in the galvanic current measurements.

![Figure 9. The plot of cyclic sweep measurements for weld sections of the outer ring in brine saturated with CO₂, 5 m/s flow rate and 32 °C](image)

For each electrode, the polarisation resistance was calculated from the gradient of the potential/current density plot and used to obtain the corrosion current density and the self-corrosion rate using Equation 2. The rates for the three weld regions were similar, with the value for the HAZ (the steepest plot and the highest polarisation resistance) being marginally lower than the other two. The self-corrosion rate results are compared in Figure 11.

Electrochemical Impedance Spectroscopy (EIS)

Nyquist plots for the three weld regions in the outer electrode ring are shown in Figure 10. Essentially, each consists of a single, complete semicircle indicating that corrosion occurred by an activation controlled process. There was no evidence of a second semicircle at high frequencies, which would suggest the presence of a corrosion product film on the metal surface.

The diameter of the semicircle represents the charge transfer resistance, Rt, (broadly equivalent to the polarization resistance measured in the LPR technique) from which the corrosion current density and self-corrosion rate can be obtained using Equation 2. The
resistance values obtained by the two methods show good agreement. In this example, the HAZ had the lowest charge transfer resistance (smallest semicircle), indicating the highest rate of self-corrosion.

![Nyquist plots of weld sections of the outer ring in brine saturated with CO$_2$, 5 m/s flow rate and 32°C](image)

**Figure 10.** Nyquist plots of weld sections of the outer ring in brine saturated with CO$_2$, 5 m/s flow rate and 32°C

**Total Corrosion Rate**

The overall corrosion rate of each weld region is the sum of its individual galvanic and self-corrosion contributions

$$CR_{Total} = CR_{Galv} + CR_{Self}$$  \hspace{1cm} (3)

These total corrosion rates for the electrodes in the outer ring are shown in Figure 11. In all cases, the galvanic rates were calculated from the currents at the end of the galvanic measurements, immediately before the start of the LPR measurements. At this time, the PM was slightly cathodic and therefore partially protected. As a result, its total corrosion rate was less than the rate of its self-corrosion alone. In contrast, both the WM and HAZ were anodic and the galvanic contributions added to their total corrosion rates.

Figure 11 indicates that the total corrosion rates of the WM and HAZ exceeded that of the PM and in these circumstances some preferential weld corrosion would occur. It should be noted that the rates of 6mm/y are higher than would be expected in deaerated brine at this temperature (typically 1-2mm/y) [8], and are the result of some dissolved oxygen being present. This was confirmed by the relatively noble open-circuit potential measurements at the end of deaeration, as described above and shown in Figure 8. These results have a very important practical significance as they demonstrate the serious effect that air leaking into a CO$_2$ containing system, at a pump or valve, can have on the corrosion rate of steel [7]
Figure 11. Total corrosion rate in weld sections of the outer ring in brine saturated with CO$_2$, 5 m/s flow rate and 32 °C

Conclusions

[1] Small differences in composition and microstructure between adjacent regions of a weld can lead to galvanic currents, which can either partially protect or increase their total rate of corrosion.

[2] It is preferable that the PM should be slightly anodic to the WM and HAZ but some circumstances, including flowing conditions, have been shown to cause a current reversal with the onset of preferential weld corrosion.

[3] The presence of even small quantities of dissolved oxygen in brine containing carbon dioxide can increase the overall rate of corrosion of steel and this can result in serious damage in pipework systems from leaks at pumps and valves.

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References


