Original Article

Investigations on corrosion behaviors of super-strength sucker rod FG20 steel in high SO$_4^{2−}$ environment

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Abstract

In some sour reservoirs and tertiary oil recovery blocks, SO$_4^{2–}$ in the well fluid can cause the corrosion and corrosion fatigue of the sucker rods. In this paper, the corrosion behaviors of super-strength sucker rod FG20 (16Mn2SiCrMoVTiA) steel in the well fluid are investigated by electrochemical measurements, and electron probe micro-analyzer (EPMA) analysis. The results show that FG20 steel has a favorable corrosion resistance in neutral solution. When the hydrogen ions increase, the hydrolysis of SO$_4^{2–}$ greatly accelerates the corrosion of FG20 steel. The energy dispersive X-ray (EDX) results demonstrate that the corrosion process of FG20 steel in neutral well fluid is an oxygen concentration process, and the protective FeCO$_3$ and Fe$_3$O$_4$ on the surface of the samples can prevent the further corrosion. With the increase of the acidity in the well fluid, the corrosion process converts into a sulphide concentration process, and the sloppy FeS and mackinawite film cannot provide effective protection for the specimens, resulting in the increase of corrosion rate.

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1. Introduction

A comprehensive review of the world oil-gas development indicates that rod-having pump oil-production is the most traditional and most widely used method [1,2]. Approximately 75% of oil in China has been extracted by the sucker rod pumping technology. As the number of deep and ultra-deep wells increases, the pump depth and rod load of sucker rods increase accordingly. Meanwhile, due to the popularization of improved/enhanced oil recovery technologies, especially the application of chemical flooding and wastewater reinjection, the service environment of the sucker rod is worsening [3–6]. High salinity and high corrosivity of the well fluid aggravate the corrosion and failure of the sucker rods [7–10]. The conventional Chinese D and E grade sucker rods can no longer meet the exploitation of these unconventional reservoirs [11]. Hence, to develop sucker rods with super performance is imperative for most oilfields in China.

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Table 1 – Mechanical properties of FG20 steel.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_y$</td>
<td>832</td>
</tr>
<tr>
<td>$\sigma_b$</td>
<td>1036</td>
</tr>
<tr>
<td>$\delta$</td>
<td>17.4</td>
</tr>
<tr>
<td>$\psi$</td>
<td>48</td>
</tr>
<tr>
<td>$\sigma_{0.1}$</td>
<td>550</td>
</tr>
</tbody>
</table>

The corrosive well fluid is taken from the GO7-32-375 stratum of Gudong Oil Plant in Shengli Oil Field. Gudong Plant is a typical tertiary oil region. High salinity and remarkable changes in temperature, pressure and pH are the main characteristics of the underlying liquid. The corrosion behaviors of sucker rods in this reservoir are very complex, and the corrosion behaviors and mechanisms of FG20 sucker rod in different blocks are diverse. The depth of GO7-32-375 stratum is about 1200 m, and the well water temperature is about 60 °C. The chemical compositions of the solution are listed in Table 2. To analyze the effect of pH on corrosion behavior of FG20 steel in the well fluid, the dilute hydrochloric acid (5 wt%) is used to modulate the pH of the well fluid.

2.2. Tafel polarization and EIS measurement

The overall schematic of the test setup is shown in Fig. 1. The electrochemical measurements are performed in a Perkin-Elmer M283 constant potential electrochemical testing system using a three-electrode cell, where a saturated calomel electrode (SCE) is used as the reference electrode and a platinum sheet as the counter electrode. The FG20 specimen is used as the working electrode, and its size is shown in Fig. 2. The specimens are progressively grinded by a series of water sandpapers, and finally polished by a 5 µm diamond paste. Before the tests, all the specimens are successively rinsed with deionized water and acetone, and then dried.

All the electrochemical tests are conducted at 60 ± 1 °C. To maintain the experimental temperature, a specific water bath container is used, as shown in Fig. 1. The specimens are immersed in the well fluid at an open-circuit potential (OCP) for 1 h prior to the Tafel polarization measurement. Cyclic potentiodynamic polarization measurements are conducted starting from −250 mV (vs. open circuit potential), and scanned toward more positive direction with the scanning rate of 0.5 mV/s. When the current reaches 1 mA, the scanning direction turns reversely. EIS measurements are conducted at OCP with a sinusoidal perturbation of 10 mV amplitude at measurement frequency ranging from 100 kHz to 100 mHz, aided by the M1025 frequency response instrument. The data are acquired in four cycles at each frequency to provide good precision at all frequencies. All the test data are analyzed by SofrCorr III software based on the nonlinear least-square algorithm. For better reproducibility, all aforementioned electrochemical experiments are repeated more than three times.

2.3. Weight loss test

The specimens for weight loss tests (WLT) are the same as that for the electrochemical measurements and three samples used for each series are measured for good reproducibility. The test temperature is maintained at 60 ± 1 °C, and the solution is replaced weekly. Before the test, the specimens are successively washed by acetone and absolute ethanol and dried.
Table 2 – Chemical compositions (mg/L) of the selected well liquid.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Oil fraction</th>
<th>SO$_4^{2-}$</th>
<th>O$_2$</th>
<th>CO$_2$</th>
<th>Cl$^-$</th>
<th>Total salinity</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>63.7</td>
<td>724.98</td>
<td>0.02</td>
<td>0.043</td>
<td>1160.35</td>
<td>6165.24</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Fig. 1 – Schematic of the test setup.

Fig. 2 – The dimensions of specimen.

and then weighed by a digital balance with an accuracy of 0.00001 g for the original weight before immersed in the test solutions. After being immersed for 30 days and 90 days, the corroded specimens are taken out from the solutions. The corrosion products on specimen surfaces are removed using a special chemical products-cleanup liquid. Finally, the samples are weighed again to obtain the final weight. The corrosion rates of the samples are calculated by Eq. (1) [17]:

$$V_{corr} = \frac{8.76 \times 10^4 \times (W_1 - W_0)}{\mu \text{Al}}$$  (1)

After the WLT, the corrosion morphology and surface features of some corroded FG20 samples are observed by JXA-8230 EPMA, and the energy spectrum of corrosion products are analyzed to determine the corrosion mechanism in the different well fluids.

Fig. 3 – Potentiodynamic polarization curves of FG20 steel in different solutions.

Table 3 – Electrochemical parameters from polarization curve analysis in different solutions.

<table>
<thead>
<tr>
<th>pH</th>
<th>$E_{corr}$</th>
<th>$I_{corr}$</th>
<th>$b_a$</th>
<th>$b_c$</th>
<th>$R_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.8</td>
<td>-0.772</td>
<td>0.013</td>
<td>0.056</td>
<td>0.204</td>
<td>1469.514</td>
</tr>
<tr>
<td>6.0</td>
<td>-0.758</td>
<td>0.041</td>
<td>0.069</td>
<td>0.158</td>
<td>509.294</td>
</tr>
<tr>
<td>5.0</td>
<td>-0.742</td>
<td>0.148</td>
<td>0.087</td>
<td>0.129</td>
<td>152.639</td>
</tr>
</tbody>
</table>

$^a$ Polarization resistance $R_p$ is calculated by the following equation: $R_p = \frac{k_{bb}}{J_{corr}(t_1, t_2)}$ [19].

3. Results and discussions

3.1. Tafel polarization curves

The Tafel polarization curves of FG20 samples in the corrosive liquids with different pH are shown in Fig. 3. It can be seen that the polarization curves remarkably accelerates with the pH decrease of the solution. With the decrease of the solution pH, the self-corrosion potential increases, the polarization curve shifts to the right, the current density increases, and the corrosion rate increases. The electrochemical parameters obtained from the polarization curve analysis provide more details about the overall corrosion process. According to the four-point method for determining the corrosion rate developed by Jankowski et al. [18] and Tang [19], the corrosion current density, anodic and cathodic Tafel constant, and polarization resistance are determined and shown in Table 3. It is shown that the anode Tafel slopes decline with the decline of pH. The anodic reaction is inhibited because the corrosion at electrode surface is more serious and the formation of sulfide film effectively reduces the effective area of electrode corrosion, and then blocks the chemical reaction effect on the electrode surface. Cathode Tafel slopes go up and the corrosion potential becomes higher with the decline of pH. At the same time, the cathodic depolarization becomes stronger, and the electrode reaction is intense and controlled by hydrogen
evolution. However, the corrosion products on the electrode surface have poor compactness and adhesion, and no actually protective effect, resulting in the accelerated corrosion of FG20 samples.

3.2. EIS measurement

The Nyquist plots of FG20 samples in the solutions with different pH are shown in Fig. 4. Each curve contains one semi-circle, representing the Faraday resistance of the interface between the metal electrode and the solution. The shape and the diameter of the experimental impedance circle depend on the pH of the well fluids. The lower the pH, the smaller the diameter of the impedance circle. If the equivalent circuit of the corrosion system shown in Fig. 3 is adopted, where the behavior of constant phase element Q whose is attributed to the surface roughness and heterogeneities, electrode porosity, etc. [20–22], the equivalent circuit parameters in the well fluids are listed in Table 4. It can be seen from the table that $R_1$ and $R_2$ both decrease with the decline of pH, while Q varies inversely. The reaction resistance at the interface $R_2$ reflects the surface activity and corrosion resistance of the specimen. The smaller the $R_2$, the worse the corrosion resistance and the higher surface activity are. Consequently, the increasing acidity of the well fluid increases the corrosion current density, and accelerates the electrochemistry corrosion of FG20 steel.

The Bode plots of FG20 samples in different solutions are depicted in Fig. 5. With the pH decrease, the frequency corresponding to the phase angle peak changes slightly, but the phase angle increases obviously. These features demonstrate that the capacitance between the electrode and solution increases and the charge transfer resistance decreases gradually, leading to the acceleration of the corrosion. The results of EIS are consistent with those of Tafel polarization tests.

3.3. Corrosion rates

After removing the corrosion products on the WLT specimens, the corrosion rates of FG20 steel in the well fluids are calculated by equation (1) and listed in Table 5. The corrosion rate of FG20 steel increases significantly with decreasing pH of the well fluid. The corrosion rate increases up to 0.914 mmpy in the pH = 5.0 solution, which is nearly 6 times greater than that in the nearly neutral well fluid (pH = 6.8). The results indicate that the pH in the well fluid has a strong impact on the corrosion resistance of the FG20 steel, and the material shows a greater activity with the increase of acidity in the solution. The corrosion rates in the 90 days’ period are also calculated and presented in Fig. 6 for comparison. It indicates that the results of the two test periods are in good agreement, and the weight loss results of the 30 days’ test are credible.

![Fig. 4 - Nyquist plots of FG20 steel in different solutions.](image)

![Fig. 5 - Bode plots of FG20 steel in different solutions.](image)

**Table 4 - Equivalent circuit parameters in different solutions.**

<table>
<thead>
<tr>
<th>pH</th>
<th>$R_1$</th>
<th>$Q$</th>
<th>$R_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.8</td>
<td>2.11</td>
<td>$5.31 \times 10^{-3}$</td>
<td>$8.94 \times 10^{5}$</td>
</tr>
<tr>
<td>6.0</td>
<td>1.43</td>
<td>$8.82 \times 10^{-5}$</td>
<td>$1.43 \times 10^{5}$</td>
</tr>
<tr>
<td>5.0</td>
<td>0.45</td>
<td>$1.14 \times 10^{-4}$</td>
<td>$3.78 \times 10^{4}$</td>
</tr>
</tbody>
</table>

**Table 5 - Corrosion rates of FG20 steel (test period: 30 days).**

<table>
<thead>
<tr>
<th>pH</th>
<th>SP No.</th>
<th>$W_0$ (g)</th>
<th>$W_1$ (g)</th>
<th>$\Delta W$ (g)</th>
<th>$V_{corr}$ (mmpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.8</td>
<td>1#</td>
<td>4.694</td>
<td>4.625</td>
<td>0.069</td>
<td>0.143</td>
</tr>
<tr>
<td></td>
<td>2#</td>
<td>4.721</td>
<td>4.650</td>
<td>0.071</td>
<td>0.147</td>
</tr>
<tr>
<td></td>
<td>3#</td>
<td>4.679</td>
<td>4.614</td>
<td>0.065</td>
<td>0.135</td>
</tr>
<tr>
<td></td>
<td>aver</td>
<td>4.698</td>
<td>4.630</td>
<td>0.068</td>
<td>0.142</td>
</tr>
<tr>
<td>6.0</td>
<td>4#</td>
<td>4.715</td>
<td>4.509</td>
<td>0.206</td>
<td>0.426</td>
</tr>
<tr>
<td>5#</td>
<td>4.724</td>
<td>4.527</td>
<td>0.197</td>
<td>0.407</td>
<td></td>
</tr>
<tr>
<td>6#</td>
<td>4.717</td>
<td>4.523</td>
<td>0.194</td>
<td>0.401</td>
<td></td>
</tr>
<tr>
<td></td>
<td>aver</td>
<td>4.719</td>
<td>4.520</td>
<td>0.199</td>
<td>0.411</td>
</tr>
<tr>
<td>5.0</td>
<td>7#</td>
<td>4.745</td>
<td>4.297</td>
<td>0.448</td>
<td>0.925</td>
</tr>
<tr>
<td>8#</td>
<td>4.695</td>
<td>4.258</td>
<td>0.437</td>
<td>0.902</td>
<td></td>
</tr>
<tr>
<td>9#</td>
<td>4.710</td>
<td>4.267</td>
<td>0.443</td>
<td>0.915</td>
<td></td>
</tr>
<tr>
<td></td>
<td>aver</td>
<td>4.717</td>
<td>4.274</td>
<td>0.443</td>
<td>0.914</td>
</tr>
</tbody>
</table>
3.4. **Energy spectrum and corrosion mechanism**

To study corrosion mechanism of FG20 steel in the well fluid and analyze the effect of pH on the corrosion mechanism, secondary electron images (SEI) of corroded surfaces are observed after the weight loss tests. The SEI and EDX images are shown in Fig. 7. It can be seen that the corrosion morphology of the corroded sample is significantly dependent on the pH of the well fluid. In the pH = 5.0 solution, the corrosion product films are loose in structure and have deep cracks, as shown in Fig. 7(a). The corrosion products mainly contain Fe and S elements, and also contain a very small amount of O element, as illustrated in Fig. 7(b). The overall composition of corrosion products and overcome the shortage of one-point
analysis in Fig. 7(a), and region analysis is adopted and the results are presented in Fig. 8. The total corrosion products in the region marked by the red box in picture (a) are analyzed and the main elements are evaluated and listed in the right-hand table, and the main chemical composition map in this region are shown in pictures from (b) to (l), respectively. Both the point and region analysis indicate that the corrosion products are mainly composed of FeS or mackinawite FeS$_{1-x}$ [23,24], and a small amount of Fe(OH)$_2$ or FeCO$_3$. This corrosion process can be considered as the sulphide concentration process [25]. The anodic reaction proceeds according to reaction (2):

$$\text{Fe} + 2\text{H}_2\text{O} = \text{Fe(OH)}_2 + 2\text{e}^- + 2\text{H}^+$$ (2)

And the cathodic reaction is dominated by the following reaction:

$$\text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^- = \text{HS}^- + 4\text{H}_2\text{O}$$ (3)

In this reaction, Fe(OH)$_2$ is considered to be the primary corrosion product in the absence of sulfide, because the HS$^-$ produced by cathodic reaction typically interacts with the ferrous iron produced by anodic reaction and converts Fe(OH)$_2$ into FeS:

$$\text{Fe(OH)}_2 + \text{HS}^- = \text{FeS} + \text{OH}^- + 2\text{H}_2\text{O}$$ (4)

The FeS film cannot form an effective protective layer on the surface, which easily results in pitting corrosion on the surface of the samples [26]. However, with the pH increase in the solution, the corrosion behavior at the surface of the sample is restrained compared with that in pH = 5.0 solution. S, content decreases, and O and C contents increase in the corrosion products, as shown in Fig. 6(d) and (f). The figures demonstrate that the FeS content decrease and the protective FeCO$_3$ and Fe$_2$O$_3$ gradually increase, resulting in the decrease of corrosion rate. This process can be considered as the oxygen concentration process. The cathodic reaction of this process is dominated by:

$$\text{H}_2\text{O} + \text{CO}_2 = \text{H}_2\text{CO}_3^- = 2\text{H}^+ + \text{CO}_3^{2-}$$ (5)

The FeCO$_3$ is produced by the dissolution-precipitation process, reaction (6) and (7), previously presented by Gadala et al. and Castro et al. [27,28]:

$$\text{Fe}^{2+} + \text{HCO}_3^- = \text{FeCO}_3 + \text{H}^+$$ (6)

$$\text{Fe(OH)}_2 + \text{HCO}_3^- = \text{CO}_3^{2-} + \text{OH}^- + \text{Fe}^{2+} + \text{H}_2\text{O}$$ (7)

And the Fe$_2$O$_3$ is generally produced by the oxidation of the free oxygen in the solution. The conversion from Fe(OH)$_2$ to Fe$_2$O$_3$ proceeds according to reaction:

$$4\text{Fe(OH)}_2 + \text{O}_2 = 2\text{Fe}_2\text{O}_3 + 4\text{H}_2\text{O}$$ (8)

4. Conclusions

In high SO$_4^{2-}$ and Cl$^-$ well liquid, corrosion resistance of FG20 steel is good in a neutral solution; however the corrosion rate accelerates with the decrease of the solution pH.

As the solution pH decreases, corrosion potential becomes more negative, polarization resistance falls quickly, and polarization current density increases continually. Low pH aggravates both cathodic and anodic reactions of FG20 steel, leading to more serious corrosion on the sample surface.

Because of the enrichment of SO$_4^{2-}$, the concentration of hydrogen ions in solution dominates the corrosion mechanism of FG20 to a great extent. The enriched hydrogen ions accelerate the hydrolysis of SO$_4^{2-}$, and generate FeS...
or mackinawite Fe$_{51-x}$ film on the surface of the samples. FeS or Fe$_{51-x}$ film cannot prevent the further corrosion of the samples. Nevertheless, with the solution pH increase, hydrolysis of SO$_4^{2-}$ decreases, and the oxygen concentration process gradually dominates the corrosion process. The dense corrosion products, FeCO$_3$ and Fe$_2$O$_3$, can effectively reduce the reaction between FG20 and the corrosive solution, resulting in the decrease of corrosion rate.

**Conflicts of interest**

The authors declare no conflicts of interest.

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