Efficiency of film-forming corrosion inhibitors in strong hydrochloric acid under laminar and turbulent flow conditions

Evgeny Barmatov *, Trevor Hughes, Michaela Nagl

Schlumberger Gould Research, High Cross, Madingley Road, Cambridge CB3 0EL, UK

ABSTRACT

The effect of fluid velocity on the corrosion rate of low carbon steel in inhibited 4 M HCl at 80 °C has been examined. When the inhibitor film fully covers the metal surface, the corrosion rate slightly increases with increasing flow velocity which can be attributed to a partial erosion of the inhibitor film. When the inhibitor film coverage is in the lower range, the corrosion takes place at the diffusion limit and an increase in flow velocity results in a strong decrease in corrosion rate due to an increased rate of mass transport of the corrosion inhibitor to the metal surface.

1. Introduction

Acidizing treatments of oil and gas wells are commonly used to create artificial flow channels in carbonate formations and to increase permeability by dissolving clays and other pore plugging materials near the wellbore [1]. Either organic acids such as acetic acid or mineral acids such as HCl or HCl/HF mixtures are injected into the reservoir via the wellbore.

For this application, corrosion inhibitors are enabling because uninhibited acidizing treatment fluids would induce severe corrosion of both downhole casing completions and coiled tubing strings. Basically, the inhibitor films protect the bare metal from corrosion by providing a “barrier” between the aggressive acid solution and the metal surface. A broad range of organic film-forming corrosion inhibitors have been developed to retard the acid corrosion of downhole equipment and coiled tubing strings [2]. Commercially available acid corrosion inhibitor formulations are complex mixtures containing of film-forming inhibitor molecules (e.g. various nitrogen heterocycles, quinoline-based quaternary ammonium compounds and polymerizable acetylenic alcohols), an oily phase, and a solvent package. Often surfactants are included to aid dispersion of the inhibitor in the acid. For high temperature applications, critical components in the inhibitor cocktail are polymerizable inhibitors. Acetylenic alcohols, (\(\alpha\))-alkenylphenones and (\(\alpha,\beta\))-unsaturated aldehydes are typical polymerizable inhibitors [3–6].

Coiled tubing is used to inject highly corrosive acidizing fluids directly into the target zones/formations bypassing most of the client’s casing and completion hardware. Coiled tubing can be defined as any continuously-milled tubular product manufactured in lengths that require spooling onto a take-up reel during the primary manufacturing process [7]. The tube is straightened prior to being inserted into the wellbore and is recoiled for spooling back onto the reel. Tubing internal diameters normally range from 0.75 in. to 4 in. and single reel tubing lengths in excess of 9 km are available commercially.

In coiled tubing acidizing, a variety of fluids are pumped through coiled tubing into the producing formations. Since the acidic fluids are pumped at fairly high rates, flow velocity may influence the corrosion and inhibition process. In this paper, the effect of fluid velocity on the corrosion rate of low carbon steel in 4 M hydrochloric acid at 80 °C in the presence of a commercially available inhibitor formulation has been examined.

2. Experimental

2.1. Material

All electrodes for electrochemical testing were prepared from field grade tubular goods. Tenaris coiled tubing HS80 low carbon steel was used. The composition of this steel is 0.1–0.15% C, 0.6–0.9% Mn, <0.03% P, <0.005% S, 0.3–0.5% Si, 0.45–0.7% Cr, <0.4 Cu% and <0.25% Ni; iron makes up the remainder. This material has a ferrite/pearlite microstructure and ferrite grain sizes are in the range of 5–10 µm. The pearlite phase is composed of alternating ferrite–cementite layers.

Analytical reagent grade 4 M HCl was supplied from Sigma-Aldrich. The following physico-chemical parameters of 4 M HCl...
at 80 °C were used to calculate the flow velocity parameters: dynamic viscosity (4.8 × 10⁻⁴ kg m⁻¹ s⁻¹), density (1020 kg m⁻³), and diffusion coefficient (5.25 × 10⁻⁹ m² s⁻¹).

In all experiments varying concentrations of the corrosion inhibitor formulation were used. The proprietary inhibitor mixture contains polymerizable molecules (alkenylphenones), a quaternary salt of a nitrogen-containing heterocyclic aromatic compound (quinolinium salt), nonionic surfactants and a solvent package (alcohols) [4].

2.2. Surface finish

Immediately before placing the electrode into the test solution, the surface of specimen was ground with P1200 grit SiC emery paper, washed in tap water, ultrasonicated in DI water for 5 min in order to remove any residual SiC grains, rinsed again with DI water, degreased in acetone, rinsed with DI water and dried with an air drier. The average surface roughness parameter, \( R_a \) was determined to be 0.14 ± 0.01 μm.

2.3. Electrochemical equipment

All the electrochemical measurements were carried out in the potentiostatic mode using a three-electrode cell arrangement. An Autolab PGSTAT 302 N Potentiostat was used. The setup comprises a 0.5 L glass container with a thermostatic water-jacket and a glass top designed to be fitted with an Ag/AgCl (3 M KCl) reference electrode, a graphite counter electrode, a thermometer and a gas two-way purge tube. A fine Luggin capillary was placed close to the working electrode to minimize ohmic resistance effects. The experiments were carried out under dynamic flow conditions in de-aerated solutions saturated with nitrogen. The temperature was maintained at 80 ± 1 °C. Nitrogen saturation was initiated 30 min prior to the tests and was continued throughout the experiment.

Corrosion tests were performed with HS80 rotating cylinder electrodes (RCE) (1.5 cm diameter and 0.3 cm height). The RCE effective area was 1.41 cm² and this value has been used throughout for corrosion rate calculations. Each working electrode is mounted on a polyether ether ketone sleeve, attached to a Pine Research Instrumentation Company modulated speed rotator (model AFMSRCE) fitted with an RCE electrode holder system. Experiments were performed in the RCE rotation range from 5 to 6000 rpm. No crevice corrosion was observed under the rubber washers used to mount the RCE in the holder. The rotation speed is usually maintained for 3 h. At the end of the test period the working electrodes were cleaned and examined under a high magnification optical microscope.

2.4. Electrochemical measurements

Corrosion experiments were carried out in deaerated 4 M HCl at 80 °C in the presence of various concentrations of the corrosion inhibitor, 0.0065–0.2 wt.%, under laminar (5 rpm, 0.004 m s⁻¹) and fully developed turbulent (6000 rpm, 4.7 m s⁻¹) flow conditions. The standard testing period was 3 h. Experiments were started by monitoring the corrosion potential (every 30–180 s) at a specific rotational speed and measuring the polarization resistance every 20–30 min. Finally the cathodic potentiodynamic sweep was recorded. This procedure was repeated for a variety of flow velocities and for different corrosion inhibitor concentrations.

2.5. Linear polarization studies

Linear polarization resistance (LPR) measurements were carried out in a potential range ±10 mV with respect to the open circuit potential (OCP or \( E_{corr} \)) at a scan rate of 0.2 mV s⁻¹. The polarization resistance (\( R_p \)) was determined from the slope of the potential vs. the current. The Tafel slope determined from the potentiodynamic polarization tests and the polarization resistance was used to calculate the corrosion current using the Stern–Geary equation:

\[
i_{corr} = \frac{B}{R_p} = \frac{b_a b_c}{2.303} \frac{1}{R_p}.
\]

where \( b_a \) and \( b_c \) are measured or estimated. Knowledge of \( R_p \), \( b_a \) and \( i_{corr} \), enables direct determination of the corrosion rate at any instant in time using Eq. (1). Faraday’s Law was used to calculate the corrosion rate in terms of a penetration rate:

\[
\text{Corrosion Rate (nm year}^{-1}) = \frac{M}{nF\rho} i_{corr} = K \cdot i_{corr},
\]

where \( M \) is the atomic weight of the metal, \( \rho \) is the density, \( n \) is the charge number which indicates the number of electrons exchanged in the dissolution reaction, \( F \) is the Faraday constant, \( i_{corr} \) is current density (mA cm⁻²) and \( K \) is constant (\( K = 11.527 \)).

2.6. Potentiodynamic polarization

Potentiodynamic polarization tests were carried out after LPR experiments and served to determine the corrosion current (\( i_{corr} \)), OCP, and Tafel slopes of the cathodic (\( b_c \)) curve. These cathodic Tafel curves were obtained by changing the electrode potential automatically from OCP to −200 mV at a potential sweep rate of 1 mV s⁻¹. They were corrected for the ohmic drop, previously determined by electrochemical impedance measurements. The cathodic corrosion current was conventionally determined by extrapolation of the cathodic Tafel slope to the OCP.

2.7. Chronoamperometry

Chronoamperometry tests were carried out by applying a constant potential to the electrode and recording the current density as a function of time, for periods from 1 s to 300 min. A constant potential, typically −0.65 V vs. Ag/AgCl, was applied to the working electrode which was rotated at speeds of 5 and 6000 rpm.

3. Results and discussion

3.1. Oilfield and laboratory testing conditions

The majority of matrix acidizing jobs are pumped at a rate of two barrels per minute, which corresponds to a linear flow velocity of 5.34 m/s, a wall shear stress of 49.44 Pa and a Reynolds number of 403,000 for a standard coiled tube with inner diameter 1.4 in. (Table 1). The flow in pipe is transitonally turbulent at \( Re \approx 2000 \) and is fully turbulent at \( Re \approx 100,000 \) [8].

It is critical to choose a suitable laboratory method to match or mimic the corrosive and flow conditions found in the field environment. A number of experimental techniques are available to investigate flow effects under laboratory conditions [9,10]. Pipe flow loops, rotating electrochemical probes and jet impingement experiments are established methods to simulate a variety of flow conditions and to cover a broad temperature range. Corrosion testing in strong inorganic acids like hydrochloric acid at elevated temperature is usually associated with rapid reaction rates and safety concerns.

In this study, the effect of flow velocity on the inhibition of low carbon steel in hot hydrochloric acid was assessed using a rotating cylinder electrode. A critical issue when attempting to use the RCE to simulate realistic flow conditions is to choose the correct electrode rotation speeds at which to perform electrochemical mea-
measurements. Several solutions to this problem have been proposed over the years [9,11–14]. Most involve operating the RCE at a rotation speed where the wall shear stress matches that found in the field, or alternately, at a rate where the mass transport coefficient at the RCE matches that observed in the field.

For the RCE configuration, the wall shear stress ($\tau_{cyl}$) and Reynolds number ($Re$) was calculated as:

$$Re = \frac{u_{cyl}d_{cyl}\rho}{\mu},$$

$$\tau_{cyl} = 0.0791\rho Re^{-0.3}u_{cyl}^2,$$

where $u_{cyl}$ is the electrolyte velocity ($m s^{-1}$), $d_{cyl}$ is the outer diameter of electrode ($m$), $\rho$ is the density ($kg m^{-3}$) and $\mu$ is the dynamic viscosity ($kg m^{-1} s^{-1}$) of 4 M hydrochloric acid at 80 °C.

The wall shear stress and Reynolds number for different RCE sample rotation speeds are summarized in Table 2. Taking into account that for a rotating cylinder the critical Reynolds number for the transition from laminar to turbulent flow regime was found to be approximately 200 [11], the flow regime at 5 rpm can be considered as laminar. At the maximum acceptable electrode rotation speed, 6000 rpm, the flow is highly turbulent ($Re = 1.5 \times 10^5$) and the wall shear stress of the cylinder electrode ($\tau_{cyl} = 50.15 Pa$) is similar to the value of the wall shear stress in a typical coiled tube ($\tau_{pipe} = 49.44 Pa$, Table 1) during fluid injection rate at 2 bbl min$^{-1}$ (5.34 m s$^{-1}$).

### Table 2

<table>
<thead>
<tr>
<th>Rotation rate (min$^{-1}$)</th>
<th>Angular velocity (m s$^{-1}$)</th>
<th>Reynolds number</th>
<th>Wall shear stress (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.004</td>
<td>125</td>
<td>0.0003</td>
</tr>
<tr>
<td>100</td>
<td>0.078</td>
<td>2503</td>
<td>0.048</td>
</tr>
<tr>
<td>1000</td>
<td>0.78</td>
<td>$2.5 \times 10^4$</td>
<td>2.38</td>
</tr>
<tr>
<td>2000</td>
<td>1.57</td>
<td>$5.0 \times 10^4$</td>
<td>7.75</td>
</tr>
<tr>
<td>4000</td>
<td>3.14</td>
<td>$1.0 \times 10^5$</td>
<td>25.17</td>
</tr>
<tr>
<td>6000</td>
<td>4.71</td>
<td>$1.5 \times 10^5$</td>
<td>50.15</td>
</tr>
</tbody>
</table>

3.2. Potentiodynamic polarization measurements and corrosion potential

Fig. 1 shows, as an example, the steady state polarization curves obtained for two different electrode rotation speeds after 3 h of immersion in deaerated 4 M HCl solution containing the corrosion inhibitor formulation (0.2 wt.%) at 80 °C.

In this particular case, the cathodic current densities increased with increasing electrode rotation speed and the corrosion potential shifted in the cathodic direction. This suggests that the hydrogen reduction current density depends on flow velocity. Such polarisation measurements were used to determine the corrosion current density, $i_{corr}$, by extrapolation of the cathodic part of the polarization curve to $E = E_{corr}$. The values of corrosion current densities ($i_{corr}$), corrosion potential ($E_{corr}$), cathodic Tafel slope ($b_c$), polarization resistance ($R_p$), and corrosion rate are summarized in Table 3.

For these measurements we did not consider the anodic polarization curves since they do not exhibit a well-defined Tafel behaviour. A detailed analysis of the anodic region at 5 rpm showed that in the presence of corrosion inhibitor within a certain anodic potential range, the current increases steeply, which is usually associated with the onset of desorption of absorbed species [15]. The phenomenon may be due to the obvious metal dissolution, which leads to desorption of the inhibitor molecules from the electrode surface. If the desorption rate of the inhibitors is higher than its adsorption rate, the corrosion current increases more obviously with rising potential [16].

Fig. 2 represents the typical behaviour of the corrosion potential in V vs. Ag/AgCl as a function of time for two different inhibitor concentrations and at laminar and turbulent flow conditions. Under laminar flow conditions, the corrosion potential increases as the inhibitor concentration increases. This suggests that the inhibitor formulation is a mixed type inhibitor influencing both the reduction of hydrogen as well as the oxidation of the metal with a predominant effect on the anodic reaction. The shift of the OCP towards a more positive value in strong hydrochloric acid is very typical for cationic surfactants, quinoline derivatives, and acrylenic alcohols [2,17,18].

In addition, the flow velocity affects the corrosion potential. At both inhibitor concentrations, after an initial peak, the OCP becomes more negative under fully developed turbulent flow (Fig. 2, compare curve 2 with curve 1 and curve 4 with curve 3). The corrosion potential shifts by 50 mV in the cathodic direction when 0.2 wt.% corrosion inhibitor is present. It is apparent that increased surface flow rates results in the surface becomes less noble (Table 3) which is probably due to an increased rate of the anodic reaction at high flow velocities.

3.3. The effect of corrosion inhibitor concentration on corrosion rate

Fig. 3 shows the corrosion rates measured by the potentiodynamic polarization method for HS80 in deaerated 4 M HCl solutions at different concentrations of the corrosion inhibitor at 80 °C and at 5 and 6000 rpm after 3 h of immersion in a double logarithmic plot. It is obvious that the inhibitor concentration has a strong effect on corrosion. At low inhibitor concentrations (0.003–0.01 wt.%) the corrosion rate decreases rapidly reaching a minimum at concentrations >0.05 wt.%. This type of data would be used to decide on the inhibitor dosage for a 4 M hydrochloric acid solution.
and represent the equation: 

\[ \theta = 1 - \frac{R_p}{R_{p0}}, \]  

where \( \theta \) is surface coverage by the inhibitor, \( R_p \) and \( R_{p0} \) represent the polarisation resistances with and without inhibitor in the system, respectively.

**Fig. 4** shows the surface coverage \( \theta \) at different concentrations of the inhibitor at the electrode rotational speeds of 5 and 6000 rpm. At low inhibitor concentrations (<0.05 wt.%), the surface is not completely covered with inhibitor, but at inhibitor concentrations ranging from 0.05 to 0.2 wt.% the degree of surface coverage is very high (0.995 coverage for 0.2 wt.%).

The results shown in Figs. 3 and 4 also suggest that under our particular experimental conditions the flow velocity has a different effect on the corrosion rate depending on the inhibitor dosage. At moderate to high inhibitor concentrations (0.05–0.2 wt.%), laminar and turbulent flows have a negligible effect on corrosion rate. Corrosion rates remain very low for both flow regimes. However, at very low concentrations of inhibitor (0.0065–0.01 wt.%), the flow velocity has a significant influence on the corrosion rate.

In the following two paragraphs, the corrosion behaviour of HS80 at two distinguished ranges of the corrosion inhibitor concentrations will be considered separately.

### 3.4. Effect of flow velocity on corrosion rate of HS80 at relatively high (0.2 wt.%) corrosion inhibitor concentration

In **Fig. 5** the relationship between corrosion rate and electrode rotation speed of HS80 in 4 M HCl with 0.2 wt.% inhibitor at acid treatment pumped through HS80 coiled tubing into a reservoir with an initial reservoir temperature of 80 °C. Conventional field practice would be to maintain the selected inhibitor dosage (0.05–0.2 wt.%) throughout the total volume of acid pumped.

This behaviour is typical for film forming inhibitors and reflects surface coverage by the inhibitor. The degree of protection is assumed to be directly proportional to the fraction of the steel surface covered by the inhibitor. Surface coverage can be calculated based on polarisation resistance data from LPR test results using the equation:

\[ \text{Surface coverage (\%) = } \theta \times 100 \]

Table 3: Potentiodynamic polarization parameters and polarization resistance for the corrosion of HS80 in 4 M HCl solution containing different concentrations of corrosion inhibitor at 80 °C (immersion time is 3 h for inhibited acid and 1 h for uninhibited acid).

<table>
<thead>
<tr>
<th>Inhibitor concentration (wt.%)</th>
<th>Electrode rotation rate (RPM)</th>
<th>( E_{corr} ) (mV vs. Ag/AgCl)</th>
<th>( i_{corr} ) (mA cm(^{-2}))</th>
<th>( -b_i ) (nV dec(^{-1}))</th>
<th>( R_p ) (( \Omega ) cm(^{-2}))</th>
<th>Corrosion rate (mm year(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>No inhibitor</td>
<td>6000</td>
<td>-398 ± 2</td>
<td>-</td>
<td>0.39 ± 0.07</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.003</td>
<td>6000</td>
<td>-382 ± 4</td>
<td>-</td>
<td>0.43 ± 0.08</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.0065</td>
<td>6000</td>
<td>-372 ± 3</td>
<td>49.0 ± 4.9</td>
<td>248 ± 14</td>
<td>0.57 ± 0.08</td>
<td>565 ± 48</td>
</tr>
<tr>
<td>0.01</td>
<td>6000</td>
<td>-381 ± 3</td>
<td>3.1 ± 0.3</td>
<td>231 ± 17</td>
<td>9.4 ± 1.6</td>
<td>36 ± 4</td>
</tr>
<tr>
<td>0.05</td>
<td>6000</td>
<td>-408 ± 5</td>
<td>0.25 ± 0.09</td>
<td>262 ± 8</td>
<td>83 ± 8</td>
<td>2.94 ± 0.9</td>
</tr>
<tr>
<td>0.2</td>
<td>6000</td>
<td>-398 ± 3</td>
<td>0.237 ± 0.005</td>
<td>285 ± 14</td>
<td>94 ± 24</td>
<td>2.75 ± 0.8</td>
</tr>
<tr>
<td>0.0065</td>
<td>5</td>
<td>-368 ± 3</td>
<td>58.5 ± 3.7</td>
<td>238 ± 9</td>
<td>0.48 ± 0.03</td>
<td>675 ± 42</td>
</tr>
<tr>
<td>0.01</td>
<td>5</td>
<td>-369 ± 2</td>
<td>6.6 ± 2.3</td>
<td>254 ± 16</td>
<td>5.35 ± 0.64</td>
<td>76 ± 27</td>
</tr>
<tr>
<td>0.05</td>
<td>5</td>
<td>-379 ± 3</td>
<td>0.13 ± 0.05</td>
<td>248 ± 11</td>
<td>196 ± 17</td>
<td>1.55 ± 0.6</td>
</tr>
<tr>
<td>0.2</td>
<td>5</td>
<td>-351 ± 5</td>
<td>0.031 ± 0.009</td>
<td>257 ± 13</td>
<td>752 ± 34</td>
<td>0.36 ± 0.11</td>
</tr>
</tbody>
</table>

**Fig. 2.** Variation of open circuit potential vs. time for low carbon steel HS80 electrode under laminar (5 rpm) and turbulent (6000 rpm) flow conditions in deaerated 4 M HCl containing corrosion inhibitor, at 0.01 wt.% and 0.2 wt.% at 80 °C.

**Fig. 3.** Effect of the corrosion inhibitor concentration on the corrosion rate obtained for low carbon steel HS80 electrode under laminar (5 rpm) and turbulent (6000 rpm) flow after 3 h of immersion in deaerated 4 M HCl at 80 °C. Corrosion rates were measured by potentiodynamic method.

**Fig. 4.** Surface coverage as a function of the concentration of corrosion inhibitor for low carbon steel HS80 electrode under laminar (5 rpm) and turbulent (6000 rpm) flow after 3 h of immersion in deaerated 4 M HCl at 80 °C. The surface coverage was calculated using Eq. (5).
80 °C is shown. At relatively high concentrations of the inhibitor, 0.2 wt.%, the low carbon steel can be satisfactorily inhibited under laminar conditions resulting in a corrosion rate of 0.36 mm year\(^{-1}\). The corrosion rate under fully developed turbulent flow is 2.75 mm year\(^{-1}\) [at 6000 rpm]. The latter corrosion rate is still very low and lies considerably below internal oilfield internal standards established for acid stimulation treatments [2]. However, we observe that fully developed turbulent flow increases the corrosion rate by a factor of 7.6 relative to the rate under laminar flow conditions.

Generally, flow conditions may have several different effects on the corrosion rate (Fig. 6) [19]. The dissolution of iron in hydrochloric acid is a heterogeneous process and corrosion kinetics are influenced by the following different steps:

(i) rate of diffusion of corrosive species onto the metal surface;
(ii) the rate at which molecules adsorb at the metal surface;
(iii) the rate of chemical reactions on the surface (reduction of protons to hydrogen and oxidation and dissolution of metal);
(iv) the desorption rate of reaction products.

The overall rate for a multi-step chemical process is controlled by the slowest or rate-limiting step. Assuming the diffusion controlled process is the slowest step, the overall corrosion rate can be influenced by the availability of corrosive species involved in the corrosion reaction at the metal surface. Corrosion occurs in a very thin fluid layer at the metal surface (the so-called diffusion sublayer). The thickness of the diffusion sublayer is a function of the flow rate and can be estimated to be in the order of a few micrometres for fully turbulent flow [20]. The effect of increasing velocity is to increase the surface concentration of corrosive species and corrosion inhibitor or to decrease the surface concentration of corrosion products. Therefore, the rate of corrosion increases with increasing flow velocity. At higher velocities the corrosion process is under charge transfer (activation) control and the rate of mass transfer exceeds the rate of corrosion reaction at the metal surface rendering the corrosion rate independent of flow velocity (Fig. 6). Finally, at still higher velocities, erosion–corrosion may occur if the surface shear stress of the impinging liquid is high enough to strip the protective inhibitor film from the surface, leading to an increase in corrosion rate. In this context, the word erosion refers to a partial hydro-mechanical removal of the protective film by the flow while the main mode of metal loss is caused by corrosion [21].

First, the effect of flow velocity on the corrosion of HS80 in a blank solution (in the absence of corrosion inhibitor) will be considered. Only a limited amount of reports studying the corrosion of iron in strong hydrochloric acid (\(\geq 4\) M) and at temperatures above 60 °C have been published in the literature. High values of uninhibited corrosion rates cause substantial changes in the properties of the electrode surface, e.g. roughness, localised corrosion, formation of acid-insoluble corrosion products, etc. The most relevant study was conducted by Mazanek and Bala [22]. These authors demonstrated that the flow velocity has no influence on the corrosion rate of pure iron at acid concentrations \(\leq 2\) M. However, at [HCl] \(\geq 4\) M the corrosion rate initially increased slightly, but reached a plateau with an additional increase in the sample rotational speed. It is worth noting these studies were performed under laminar flow and at relatively low temperature (25 °C).

Table 3 shows the polarisation resistance obtained for a low carbon steel HS80 electrode after 3 h of immersion in uninhibited 4 M hydrochloric acid at 80 °C (blank solution). Within the accuracy of the polarisation resistance method, the flow velocity has no a noticeable effect on the \(R_p\) and corrosion rate. The polarisation resistance \(R_p\) values were 0.39 ± 0.07 Ω cm\(^{-2}\) and 0.43 ± 0.08 Ω cm\(^{-2}\) for 6000 and 5 rpm, respectively. We can conclude that the corrosion of low carbon steel in 4 M hydrochloric acid at elevated temperature is generally under activation control. Meanwhile, a slight increase \(R_p\) with an increase of flow velocity may indicate surface screening by hydrogen bubbles [22–24]. Under turbulent flow hydrogen bubbles formed during corrosion are removed faster from the metal surface, which may slightly increase the corrosion rate.

Fig. 7 displays the effect of angular rotation rate on HS80 corrosion rate in a double-logarithmic plot. This graph serves to determine the dependence of the corrosion rate on the flow velocity.
at a concentration of corrosion inhibitor, 0.2 wt.%. The results were fitted to simple power law relationships:

\[
\text{CR} \sim \omega^{0.00 \pm 0.00}, \quad \text{for flow velocities ranging from 0.004 to 0.78 m s}^{-1}, \quad \text{and} \quad \text{CR} \sim \omega^{1.12 \pm 0.13}, \quad \text{for flow velocities of 1.57–4.71 m s}^{-1}.
\]

Two main flow regimes can be distinguished. In the first region, wherein the flow velocities vary from 0.004 to 0.78 m s\(^{-1}\) (5–1000 rpm) the corrosion rate is independent of flow. In the second region, 1.57–4.71 m s\(^{-1}\) (2000–6000 rpm) the corrosion rate increases abruptly with flow velocity. In the latter case, the corrosion rate is proportional to the angular velocity to the power of 1.12 ± 0.15, which indicates a strong contribution of the flow erosion process to the overall corrosion rate.

Erosion-corrosion is a complicated phenomenon and many factors affect this mechanism \cite{25}. In our case, erosion-corrosion is associated with a flow-induced partial mechanical removal of the inhibitor film that results in a subsequent increase of iron dissolution. Fig. 7 can be used to estimate the critical shear stress at which a protective film is partially removed and becomes less effective. The critical wall shear stress \(\tau_c\) lies in the range (see also Table 2):

\[
7.75 \text{ Pa} \geq \tau_c > 2.38 \text{ Pa}.
\]

Thus, we can conclude that the corrosion rate of low carbon steel HS80 in deaerated 4 M HCl at relatively high concentration of the corrosion inhibitor, 0.2 wt.\% is increased due to a partial removal of the protective film by erosion-corrosion at sufficiently high wall shear stresses (7.75 Pa \(\geq \tau_c > 2.38 \text{ Pa}\)). A reduced hydrogen screening effect is also partially responsible for a higher total corrosion rate at high flow velocities.

### 3.5. Effect of flow velocity on the corrosion rate of HS80 at relatively low (0.0065 and 0.01 wt.\%) corrosion inhibitor concentration

Fig. 8 compares the corrosion rates measured by potentiodynamic polarization method for a HS80 electrode after 3 h of immersion in deaerated 4 M HCl solution at two different concentrations of the corrosion inhibitor (0.0065 and 0.01 wt.\%) at 80°C as a function of the electrode rotational speed. It is shown that, under laminar conditions (5 rpm), the average corrosion rate is 675 ± 42 and 76 ± 27 mm year\(^{-1}\) for inhibitor concentrations of 0.0065 and 0.01 wt.\%, respectively. However, an increase in flow velocity results in a significant decrease in corrosion rate. For example, for the inhibitor concentration of 0.0065%, the corrosion rate decreases by one order of magnitude, from 675 ± 42 mm year\(^{-1}\) at 5 rpm to 36 ± 4 mm year\(^{-1}\) at 6000 rpm.

As mentioned above, at relatively low inhibitor concentrations (0.0065–0.01 wt.\%) the surface is not completely covered with inhibitor and the corrosion rate is strongly dependent on the inhibitor concentration. This means that the main role of flow velocity is to enhance transport of corrosion inhibitor molecules from the bulk to the metal surface, resulting in improved inhibitor film formation. This behaviour leads to a substantial decrease in the corrosion rate as illustrated in Fig. 8.

Data analysis shows that the corrosion rate is proportional to the angular velocity in the following manner:

\[
\text{CR} \sim \omega^{0.41 \pm 0.11}, \quad \text{at inhibitor concentration, 0.0065 wt.\%, and} \quad \text{CR} \sim \omega^{0.28 \pm 0.07}, \quad \text{at inhibitor concentration, 0.01 wt.\%.}
\]

For both concentrations of corrosion inhibitor the exponent of \(\omega\) is negative, because flow velocity reduces the corrosion rate. If a corrosion process is limited by mass transport, it is expected that the corrosion rate would vary linearly with the angular velocity raised to the 0.7 power \cite{9}. However, the calculated exponents (−0.41 and −0.28) are less than for a purely diffusion controlled reaction and this indicates a strong contribution of other mechanisms to the overall corrosion rate. The hydrodynamic factor causes two conflicting effects. On the one hand, high flow velocity benefits the mass transport of the corrosion inhibitor from bulk solution to the metal surface, resulting in an improved surface coverage of protective inhibitor film. On the other hand, high wall shear stresses can erode part of the inhibitor film. The balance of these opposing effects is critical. In our particular corrosion system, improved transport of inhibitor molecules to the metal surface seems to outweigh the surface erosion effect resulting in an overall decrease of the corrosion rate at high electrode rotational speed.

To our knowledge, such a “positive” effect of flow velocity has not been previously reported for film-forming organic inhibitors. Ghereba and Omanovic \cite{26} reported the influence of electrolyte flow on the inhibitor efficiency of 12-aminoodeodecanoic acid in CO\(_2\)-saturated 0.5 M HCl. Flow velocity did not significantly change the corrosion rate of carbon steel at 3 mM of inhibitor. However, when lowering the concentration to 1 mM a decrease in inhibition efficiency was noticed at higher Reynolds numbers which was explained by the partial desorption of inhibitor at higher wall shear stresses. A similar effect was reported for other chemi-sorbed inhibitors, 2-hydradino-4,7-dimethylbenzothiazole \cite{27} and 4-amino-5-phenyl-4H-1, 2, 4-trizole-3-thio1 \cite{28}.

A positive beneficial effect of flow on inhibition efficiency was reported by Ashassi-Sorkhabi and Ashgari \cite{29} for mild carbon steel in 1 M H\(_2\)SO\(_4\) solution at 25°C using L-methionine as a “green” organic inhibitor. The results showed that the corrosion rate is higher in the presence of flow for both blank and inhibited solutions compared to static systems. However, the inhibition efficiency improved when increasing the electrode rotational speed, suggesting that the inhibited solution is more resistant to flow than the uninhibited system. The authors identified three different flow controlled factors which can influence the overall inhibition efficiency: (i) inhibitor mass transport to the metal surface, (ii) desorption of adsorbed inhibitor molecules, and (iii) removal of [Fe-Inh]\(^{2+}\) complex.

In summary, our data indicate that at relatively low inhibitor concentrations, the corrosion takes place at the diffusion limit and an increase in flow velocity results in a strong decrease in corrosion rate due to increased rate of mass transport of the corrosion inhibitor to the metal surface. However, it has to be noted that this effect does not lead to sufficient protection of the metal surface to be used in acid stimulation jobs and does not mean that metals can be fully protected with low inhibitor concentrations at high flow rates.
3.6. The effect of exposure time on the corrosion rate

Fig. 9 compares changes in the instantaneous corrosion rate as a function of exposure time as determined by LPR data at different inhibitor concentrations under laminar and turbulent flow conditions. At a relatively high concentration of the corrosion inhibitor, 0.2 wt.% the corrosion rate decreases with increasing exposure time (Fig. 9b). This is to be expected as the process of forming a protective film from polymerizable inhibitor is not instantaneous. Time is required for the polymerizable molecules to adsorb and, subsequently, to polymerize on the metal surface [30]. Literature data shows that polymerizable inhibitors form a relatively thick polymeric film. For example, a film produced in the presence of propargyl alcohol (0.087 M) ranges from a monolayer formed in a few minutes to films up to 50 Å thick after a period of 24 h exposure of steel in 10% HCl at 65°C [31].

Fig. 9(a) summarizes results obtained at relatively low concentrations of the corrosion inhibitor (0.01 wt.%) under various flow conditions. At any rotational speed we observe an increase in instantaneous corrosion rate with time. This effect is most pronounced under laminar flow (5 rpm): the corrosion rate increases from 48 mm year\(^{-1}\) at exposure time \(t = 18\) min to 52 mm year\(^{-1}\) at \(t = 180\) min. Under laminar flow conditions, the corrosion inhibitor seems to begin to form an inhibitor film, but it takes > 120 min to reach its full maturity. The film forming kinetics are quite different under turbulent flow as compared to laminar flow conditions. At electrode rotational speeds \(> 1000\) rpm, an improved transport of the inhibitor molecules from the bulk solution to the metal sub-

3.7. Film persistence and reversibility of inhibitor film under flow

Film persistence is the ability of an inhibitor to resist detachment from the surface under specific conditions, e.g. in the presence of the fluid from which the inhibitor film is established, as a function of the chemistry and composition of the inhibitor product, as a function of physico-chemical conditions prevailing during film formation, as a function flow conditions (Reynold’s number, wall shear stress), etc. Film persistency is one of the crucial parameters used to identify the effectiveness of corrosion inhibitors in oilfield environments.

As shown by the present studies, the properties of the inhibitor film are controlled by at least two main factors, namely (i) the concentration of inhibitor molecules in the acid solution and (ii) the flow regime. Taking into account a high sensitivity of the corrosion
The situation changes dramatically when vice versa conditions are used (Fig. 10b). In this case the inhibitor film was established under turbulent flow (6000 rpm), followed by laminar (5 rpm) flow conditions. In this case, the corrosion rate increases with time from 12.4 ± 2.9 mm year$^{-1}$ at $t=0$ min to 51.0 ± 2.0 mm year$^{-1}$ at $t=120$ min. Under laminar flow conditions the surface concentration of inhibitor in the solution is too low to maintain the inhibitor film formed under turbulent flow, i.e. at higher surface concentrations of inhibitor molecules. This indicates that insufficient concentration of inhibitor begins to play a major role in the mechanism of degradation of protective inhibitor film.

A similar mechanism of inhibitor film failure was proposed in the publications from Growcock, Frenier et al. [32,33]. They proposed that for reliable long term protection, the concentration of inhibitor in the treatment solution should be maintained above a critical level. The surface area covered by the inhibitor and the inhibitor efficiency as calculated from analysis of charge transfer resistance and the capacitance of the interface double-layer suddenly decreases with exposure time in strong 28% hydrochloric acid solution because the polymer film consumes polymerizable inhibitor (1-octyn-3-ol), leaving none for inhibition.

Fig. 11 shows the film persistence at high inhibitor concentrations (0.2 wt.%). As expected an opposite trend was observed. The corrosion rate of the inhibitor film established under laminar flow slightly increases under turbulent flow conditions due to erosion mechanism under high wall shear stress (Fig. 11a). Switching from turbulent to laminar flow is accompanied by a decrease in the corrosion rates (Fig. 11b). The inhibitor film becomes more robust with prolonged immersion time, and then the corrosion rate reaches a steady state within 70–120 min.

Chronoamperometry was also used to investigate the formation of an inhibitor film on the metal substrate and to further study the reversibility of the corrosion rate in turbulent and laminar flow regimes. Fig. 12 shows the development of the logarithmic values of the cathodic current density with exposure time (recorded on polarizing surface at −0.65 V vs. Ag/AgCl) in the presence of the corrosion inhibitor formulation. The experiment was started with a rotational speed of 6000 rpm (region AB). After approximately 4 h the rotational speed was reduced to 5 rpm (region BC) and the experiment was continued for another 3 h. While at 6000 rpm the cathodic current density decreases with time for both inhibitor concentrations (0.01 and 0.2 wt.%) an increase in cathodic current density can be observed when changing to laminar flow for low inhibitor concentrations (region BC, curve 1 in

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**Fig. 11.** Reversibility of corrosion rate under changing flow conditions (see explanation in the text). Corrosion rates were measured by LPR in deaerated 4 M HCl solution in the presence of corrosion inhibitor, 0.2 wt.% at 80 °C. The total experiment lasted 5 h.

**Fig. 12.** Cathodic current density recorded as function of immersion time for low carbon steel HS80 electrode in deaerated 4 M hydrochloric acid containing corrosion inhibitor, at 0.01 wt.% (1) or 0.2 wt.% (2) at various flow conditions. Interval A ... C was laminar (5 rpm). Electrodes were polarized at −0.65 V vs. Ag/AgCl.
Fig. 11). This behaviour indicates a progressive deterioration of inhibitor film at low surface concentrations of inhibitor.

On the contrary at high inhibitor concentrations (0.2 wt.%) the cathodic current densities continue to fall even at laminar flow (5 rpm) and reaches a low, almost constant value within 30 min (region BC, curve 2 in Fig. 12). Because flow-induced erosion is basic mechanism of the film degradation at high inhibitor concentration, a low wall shear stress under laminar flow (5 rpm) completely eliminates erosion of the inhibitor film, which manifests itself in a decrease in the cathodic current density.

4. Conclusions

The effect of fluid velocity on the corrosion rate of low carbon steel HS80 in 4 M hydrochloric acid at 80 °C in the presence of the corrosion inhibitor formulation has been examined. Using rotating cylinder electrodes, the corrosion rates were monitored under laminar and turbulent flow regimes at wall shear stresses and Reynolds numbers corresponding to a flow velocity in the range 0.004–4.71 m/s. We conclude:

1. Two main effects of flow conditions can be distinguished depending on the surface coverage of the inhibitor molecules.
   a. When the inhibitor film fully covers the metal surface (coverage θ > 0.995), as given by the use of inhibitor concentrations in the range 0.05–0.2 wt.%, laminar and turbulent flows have a negligible effect on corrosion rate. The low carbon steel is satisfactorily inhibited under laminar conditions resulting in a low corrosion rate 0.36 ± 0.11 mm/year. The corrosion rate slightly increases with increasing flow velocity which can be either attributed to a decrease in the density of hydrogen bubbles formed on the surface of the metal (the so-called “screening” effect) or to a partial erosion of the inhibitor film at sufficiently high wall shear stresses (7.75 Pa > τc > 2.38 Pa).
   b. When the inhibitor film coverage is in the lower range θ = 0.31–0.981, as given by the use of inhibitor concentrations in the range 0.003–0.01 wt.%, the flow velocity has a strong influence on the corrosion rate. In this case, the corrosion takes place at the diffusion limit and an increase in flow velocity results in a strong decrease in corrosion rate due to an increased rate of mass transport of the inhibitor film to the metal surface.

2. Flow conditions have an effect on inhibitor film formation kinetics. For high inhibitor concentrations (0.2 wt.%), the instantaneous corrosion rate decreases with increasing exposure time under laminar or turbulent flow conditions. However, at relatively low inhibitor concentrations (0.01 wt.%), the corrosion rate increases with exposure time and the film takes much longer to reach its full maturity. At the same time, turbulent flow significantly reduces the corrosion rate and accelerates film formation kinetics by improving transport of the inhibitor molecules from the bulk solution to the metal surface.

3. The corrosion rate is sensitive to rapid changes in the flow regime. For relatively low inhibitor concentration, 0.01 wt.%, switching from turbulent to laminar flow is accompanied by an immediate response of the system (increase in corrosion rate). For relatively high inhibitor concentration, 0.2 wt.%, the change from turbulent to laminar flow has a lesser effect on the corrosion rate as the initial film is more robust.

4. Generally turbulent flow conditions serve to enhance the efficiency of acid corrosion inhibitors. Such an effect has been observed for passivating inorganic films but, to our knowledge, the effect has not been previously reported for film-forming organic inhibitors. However, it should be noted that this effect was only observed at inhibitor concentration which are too low to provide sufficient protection under realistic oilfield conditions; the observation does not imply the effect can be used to provide full protection with low inhibitor concentration at high flow rates.

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References


