Effect of surface roughness on corrosion behaviour of low carbon steel in inhibited 4 M hydrochloric acid under laminar and turbulent flow conditions

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ARTICLE INFO

Article history:
Received 22 September 2015
Received in revised form 16 November 2015
Accepted 17 November 2015
Available online 28 November 2015

Keywords:
A. Acid solutions
B. Erosion
C. Acid inhibition

ABSTRACT

The effect of surface roughness on the corrosion behaviour of low carbon steel in 4 M hydrochloric acid in the presence of corrosion inhibitor has been examined under laminar and turbulent flowing conditions. The corrosion rate increases with an increase in surface roughness in both the laminar and turbulent flow regimes. However, the effect of surface roughness is more pronounced under fully developed turbulent flow due to partial erosion of the inhibitor film caused by a high wall shear stress and turbulence eddies possessing relatively high kinetic energies.

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1. Introduction

Matrix acidizing of oil and gas reservoirs is a widely established technique to increase hydrocarbon production by the partial dissolution of reservoir rocks and fine particles which may have been introduced into near wellbore environment during drilling [1,2]. Such treatments are called “matrix” treatments because the solvent is injected at pressures below the parting pressure of the formation so that fractures are not created. The objective is to greatly enhance or recover the permeability near the wellbore, rather than affect a large portion of the reservoir. Either organic acids such as acetic acid or mineral acids such as HCl or HCl/HP mixtures are injected into the well at high concentrations to dissolve the rock while creating highly conductive wormholes that then facilitate the oil flow to the wellbore. For this application, corrosion inhibitors are enabling because the uninhibited acid would induce severe corrosion of downhole equipment. A broad range of organic film-forming corrosion inhibitors have been developed to retard the acid corrosion of low carbon steel coiled tubing through which the acidizing fluids are injected. The chemical composition and concentration of the corrosion inhibitors, the flow velocity of the injected fluids and surface roughness may have a profound effect on the corrosion rate and pitting corrosion of metal coupons in laboratory experiments as well as in tubular metal samples under oilfield conditions [3–10].

A number of studies have investigated various aspects of surface roughness in relation to the corrosion rate and pitting corrosion. These publications discussed the following effects of surface roughness on the electrochemical or mechano-chemical behaviour of metal surfaces:

(a) During corrosion, material loss occurs via electrochemical reactions which may cause pitting, intergranular or intragranular corrosion [11]. In general, surface grinding and bead blasting introduces surface defects, internal stresses, plastic deformations, micro-strains and, potentially, changes in heterogeneity via fragmentation of grains. The effect of such changes on inhibited acid corrosion rates may be greater than the effect of surface roughness [4]. Reddy et al. concluded that the residual stress stored within the material after bead blasting acts as a source of activation energy and thus enhances corrosion rate [12].

(b) Deep grooves produced by grinding may create micro-reaction sites which accommodate a very corrosive environment, and which trap corrosion products formed at the bottom of the grooves, promoting the continual growth of pits [13,14]. A smoother surface finish reduced the incidence of metastable pitting substantially by reducing the number of sites capable of being activated into metastable pit growth [15].

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http://dx.doi.org/10.1016/j.corsci.2015.11.019
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2. Rough surfaces have a larger interfacial area with the corrosive environment and therefore an increase in surface roughness is expected to enhance the rate of the corrosion processes.

(d) Roughness of the metal surface influences the corrosion potential, thereby affecting the ability of pits to form on the metal surface [15–17]. A smoother surface finish reduces the occurrence of metastable pitting by reducing the number of sites capable of being activated.

(e) Additionally, increased surface roughness affects the hydrodynamic boundary layer, the mass-transfer boundary layer, and the effect that fluid motion has on a fluid velocity-sensitive corrosion processes [18,19].

The effect of fluid flow velocity on corrosion is a subject of continuing scientific interest and practical concerns. Flow can enhance uniform corrosion or initiate and propagate localized corrosion. Corrosion that is associated with or affected by fluid flow is often called flow-dependent corrosion, which can be classified into erosion–corrosion and flow-accelerated corrosion in single phase liquid flow [8,20]. The corrosion of low carbon steel in uninhibited 4 M hydrochloric acid at elevated temperature is generally under activation control due to the high diffusivity of the hydrogen ion and flow velocity has no noticeable effect on the corrosion rate [21]. However, for inhibited acid solutions, the corrosion rate depends on flow velocity which impacts transport of the inhibitor to the corrosive surface and erosion of the inhibitor film at high flow rates.

In our previous paper [21] we studied the effect of fluid velocity on the corrosion rate of low carbon steel in 4 M hydrochloric acid in the presence of various concentrations of a film-forming corrosion inhibitor. It was demonstrated that the surface coverage of the inhibitor is a key factor controlling corrosion under laminar and turbulent flow conditions. When the inhibitor film fully covers the metal surface (coverage $\theta \geq 0.995$), the corrosion rate slightly increases with increasing flow velocity which is attributed to a partial erosion of the inhibitor film at sufficiently high wall shear stresses (7.75 Pa $\geq \tau > 2.38$ Pa). When the inhibitor film coverage is in the lower range $0.310–0.981$, 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.

In this paper we discuss the effect of surface roughness and flow conditions on the corrosion behaviour of low carbon steel exposed to 4 M HCl at 80 °C in the presence of a commercial corrosion inhibitor formulation routinely used for matrix acidizing treatments. The corrosion rates were measured by the linear polarization resistance method at a relatively high concentration of the inhibitor (0.2 wt.%) which results in an inhibitor film which fully covers the metal surface (coverage $\theta = 0.998$). In this case, the effect of the mass transport of the corrosion inhibitor to the metal surface is negligible and the dominant mechanism for metal dissolution is flow-induced erosion of the inhibitor film.

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, <0.4Cus and <0.25% Ni; iron makes up the remainder. This material has a ferrite/pearlite microstructure and ferrite grain sizes 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 parameters: dynamic viscosity $(4.8 \times 10^{-4}$ kg m$^{-1}$ s$^{-1}$), density $(1020$ kg m$^{-3}$), and diffusion coefficient $(5.25 \times 10^{-9}$ m$^{2}$ s$^{-1}$) [22,23].

In all experiments a fixed concentration (0.2 wt.%) of the corrosion inhibitor formulation was used. The proprietary inhibitor mixture contains polymerizable molecules (propargyl alcohol), an oily phase, non-ionic surfactants, and a solvent package.

2.2. Surface finish

Immediately before placing the electrode into the test solution, the specimens were bead blasted or ground with P1200, P240, P120 and P60 grit SiC paper, washed in tap water, ultrasonicated in DI water for 5 min in order to remove any residual SiC grains, degreased with acetone, rinsed with DI water and dried with an air drier. The bead blasted electrode surfaces were created using standard workshop surface finishing equipment. SiC abrasive beads were used to obtain non-directional, uniform matt surfaces with low reflectivity.

2.3. Surface characterization

The surface roughness was determined with a Mitutoyo Surftest SJ-400 contact profilometer. The roughness of the test samples was assessed by multiple 1.0 mm line measurements and a stylus velocity of 0.1 mm s$^{-1}$. Ten 1.0 mm line measurements were recorded on each sample. The average absolute deviation of the roughness irregularities, $R_a$, contour length, $R_s$, and the skewness parameter, $R_{sk}$, were used to quantify surface roughness. $R_a$ is the average absolute deviation of the roughness irregularities from the mean line. For a profile defined by $n$ measurements of surface height:

$$R_a = \frac{1}{n} \sum_{i=1}^{n} |y_i|$$

where $y_i$ is the vertical distance from the mean line to the y data point number $i$. $R_a$ does not give information about the wavelength of the irregularities and it is not sensitive to small changes in roughness.

$R_{sk}$ represents the skewness of a line profile given by the third central moment of the amplitude probability density function measured over the assessment length:

$$R_{sk} = \frac{1}{n R_q^3} \left( \sum_{i=1}^{n} y_i^3 \right)$$

where $R_q = \sqrt{\frac{1}{n} \sum_{i=1}^{n} y_i^2}$ is the root mean square roughness parameter. This parameter is sensitive to occasional deep valleys (e.g. pits) or high peaks. A symmetrical height distribution, i.e. with an equal number of equal height/depth peaks/valleys, gives $R_{sk} = 0$. Pitting corrosion is characterised by a negative skewness.

2.4. Linear polarization studies

All the electrochemical measurements were carried out in the potentiostatic mode using a three-electrode cell arrangement. An Autolab PGSTAT 302N 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 a 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
Fig. 1. Contact profilometer line measurements, surface roughness ($R_a$) and skewness parameter ($R_{sk}$) taken on low carbon steel HS80 rotating electrode for P240 (a), bead blasted (b) and P60 (c) surface finishes before and after 3 h of immersion in deaerated 4 M HCl containing the corrosion inhibitor formulation, 0.2 wt.% at 80 °C under turbulent flow.

<table>
<thead>
<tr>
<th></th>
<th>$R_a$, µm</th>
<th>$R_{sk}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>0.691</td>
<td>-0.776</td>
</tr>
<tr>
<td>After</td>
<td>0.621</td>
<td>-0.651</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$R_a$, µm</th>
<th>$R_{sk}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>4.45</td>
<td>0.001</td>
</tr>
<tr>
<td>After</td>
<td>3.24</td>
<td>-0.259</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$R_a$, µm</th>
<th>$R_{sk}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>8.71</td>
<td>0.105</td>
</tr>
<tr>
<td>After</td>
<td>7.81</td>
<td>-0.07</td>
</tr>
</tbody>
</table>

maintained at 80 ± 1 °C. Nitrogen saturation was initiated 30 min prior to the tests and was continued throughout the experiments. Corrosion tests were performed with HS80 rotating cylinder electrodes (RCE) [24] (1.5 cm diameter and 0.3 cm height). The RCE effective geometric area was 1.41 cm². Each working electrode is mounted on a polyether ether ketone sleeve, attached to a Pine Research Instrumentation Company modulated speed rotator fitted with an RCE electrode holder system. Experiments were performed using RCE rotation speeds of 5–6000 rpm. No crevice corrosion was observed under the rubber washers used to mount the RCE in the
holder. The rotation speed was maintained for 3 h. At the completion of the test period the working electrodes were cleaned and the surface roughness was examined using the contact profilometer.

Linear polarization resistance (LPR) measurements were carried out in a potential range ±10 mV with respect to the open circuit potential (OCP or $E_{\text{corr}}$) at a scan rate of 0.2 mV s$^{-1}$. The polarization resistance ($R_p$) was determined from the slope of the potential versus the current. The experimental polarization resistance data were normalized to the true surface area determined from contact profilometer measurements ($A^2$) taken after completion of the corrosion test.

2.5. Chronoamperometry

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

2.6. Electrochemical measurements

Electrochemical corrosion experiments were carried out in deaerated 4 M HCl (300 ml) at 80 °C in the presence of 0.2 wt.% of corrosion inhibitor formulation 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 at a specific rotational speed and for different surface finishes. LPR measurements were carried out after 3 h exposure in testing solution.

3. Results

3.1. Flow conditions

In this study, rotating cylinder electrodes fabricated from HS80 low carbon steel were used to monitor the polarization resistance and corrosion potential under laminar and fully developed turbulent flow conditions. The wall shear stresses and Reynolds numbers at different RCE rotation speeds, 5 and 6000 rpm, are summarized in Table 1.

The wall shear stress ($\tau_{\text{w}}$) and Reynolds number ($Re$) were calculated as follows [7–9,19]:

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

$$\tau_{\text{w}} = 4\mu \frac{u_{\text{cyl}}}{d_{\text{cyl}}}, \text{ laminar flow}$$

$$\tau_{\text{w}} = 0.0791Re^{-0.3}u_{\text{cyl}}^2, \text{ turbulent flow}$$

where $u_{\text{cyl}}$ is the electrolyte circumferential velocity (m s$^{-1}$), $d_{\text{cyl}}$ 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.

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 [7], the flow regime at 5 rpm is laminar. At 6000 rpm, the flow is highly turbulent ($Re = 1.5 \times 10^5$) and the wall shear stress of the cylinder electrode ($\tau_{\text{w}} = 50.15$ Pa) is close to that encountered during matrix acid injection at 2 bbl min$^{-1}$ (5.34 m s$^{-1}$) through coiled tubing (internal diameter 1.4 inch) [21].

3.2. Effect of flow conditions on surface roughness parameters

Five different surface finishes of low carbon steel were used. The surface roughness parameters of specimens before and after corrosion tests determined using the contact profilometer are given in Tables 2 and 3. By roughness we mean peaks above the surface of a body of arbitrary shape. These peaks are so widely separated from each other that the average distance between them is large compared with their size [25]. The typical surface roughness profiles and the average value of $R_s$ and the skewness factor $S_k$ of RCE samples before and after corrosion tests is shown in Figs. 1–3.

Corrosion in inhibited 4 M HCl results in a slight decrease in the average surface roughness as given by the $R_s$ values. This effect was more pronounced for the rougher surfaces (bead blasted and P60). This implies that protruding peaks were preferentially dissolved resulting in a smoother surface. It should be pointed out that in the present experiment, in inhibited 4 M HCl, corrosion appears to be accompanied by a slight decrease in the skewness factor ($S_k$, before and after 3 h corrosion in Fig. 2). However all changes in the roughness parameters are a fairly marginal and statistically insignificant.

3.3. Effect of surface roughness and flow conditions on corrosion rate

Fig. 3 shows a plot of the reciprocal of the polarization resistance ($1/R_p$) versus the surface roughness measured after 3 h of immersion in deaerated 4 M HCl containing corrosion inhibitor formulation, 0.2 wt.% at 80 °C. Since the polarization resistance is proportional to the corrosion current density, according to the Stern
Table 1
Correlations between angular velocity, Reynolds number, wall shear stress and electrode rotation speed (RPM) calculated for the rotating cylindrical electrode (1.5 cm diameter).

<table>
<thead>
<tr>
<th>Flow conditions</th>
<th>RPM (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>Laminar</td>
<td>5</td>
<td>0.004</td>
<td>125</td>
<td>5 × 10⁻⁴</td>
</tr>
<tr>
<td>Turbulent</td>
<td>6000</td>
<td>4.7</td>
<td>5 × 10⁵</td>
<td>50.1</td>
</tr>
</tbody>
</table>

Table 2
Average surface roughness (Rₐ), skewness parameter (Rₛ), and profile length ratio (l) measured for different surface finishes before and after 3 h of immersion in deaerated 4 M HCl containing the corrosion inhibitor formulation, 0.2 wt.% at 80 °C under laminar flow.

<table>
<thead>
<tr>
<th>Surface finish</th>
<th>Fresh surface</th>
<th>After corrosion under laminar flow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rₐ (μm)</td>
<td>Rₛ</td>
</tr>
<tr>
<td>P1200</td>
<td>0.14 ± 0.01</td>
<td>0.13 ± 0.02</td>
</tr>
<tr>
<td>P240</td>
<td>0.63 ± 0.03</td>
<td>0.59 ± 0.05</td>
</tr>
<tr>
<td>P120</td>
<td>2.87 ± 0.45</td>
<td>3.19 ± 0.30</td>
</tr>
<tr>
<td>Bead blasted</td>
<td>5.26 ± 0.16</td>
<td>4.53 ± 0.37</td>
</tr>
<tr>
<td>P60</td>
<td>7.34 ± 1.30</td>
<td>6.68 ± 0.75</td>
</tr>
<tr>
<td>P60</td>
<td>7.46 ± 1.45</td>
<td>6.84 ± 0.94</td>
</tr>
</tbody>
</table>

Table 3
Average surface roughness (Rₐ), skewness parameter (Rₛ), and profile length ratio (l) measured for different surface finishes before and after 3 h of immersion in deaerated 4 M HCl containing the corrosion inhibitor formulation, 0.2 wt.% at 80 °C under turbulent flow.

<table>
<thead>
<tr>
<th>Surface finish</th>
<th>Fresh surface</th>
<th>After corrosion under turbulent flow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rₐ (μm)</td>
<td>Rₛ</td>
</tr>
<tr>
<td>P1200</td>
<td>0.19 ± 0.06</td>
<td>0.18 ± 0.08</td>
</tr>
<tr>
<td>P240</td>
<td>0.63 ± 0.07</td>
<td>0.61 ± 0.06</td>
</tr>
<tr>
<td>P120</td>
<td>2.76 ± 0.39</td>
<td>2.81 ± 0.47</td>
</tr>
<tr>
<td>Bead blasted</td>
<td>4.31 ± 0.27</td>
<td>3.55 ± 0.46</td>
</tr>
<tr>
<td>P60</td>
<td>8.11 ± 0.85</td>
<td>7.72 ± 1.06</td>
</tr>
<tr>
<td>P60</td>
<td>6.68 ± 1.02</td>
<td>6.34 ± 1.04</td>
</tr>
</tbody>
</table>

Fig. 3. Plot of reciprocal polarization resistance (1/Rₚ) versus surface roughness Rₐ for low carbon steel HS80 electrode after 3 h of immersion in deaerated 4 M HCl containing corrosion inhibitor formulation, 0.2 wt.% at 80 °C. Polarization resistance were measured by LPR method under laminar and turbulent flow conditions.

and Geary equation, it is more convenient to use the reciprocal polarization resistance (1/Rₚ) as a measure of the corrosion rate.

Since the rougher surface has a larger surface area, surface area could contribute to the increase in the corrosion current or apparent corrosion rate. The contact profilometer measures the contour length ratio, l, which is the ratio of the contour length of the measured profile to the nominal measurement length (1 mm) (Table 4). In principle, l² is a measure of the ratio of the surface area of the sample to the perfectly smooth equivalent (1 mm²). All polarization resistance data presented in Fig. 3 were normalized to the true surface area measured at the end of the corrosion experiment.

Fig. 3 shows that the reciprocal polarization resistance 1/Rₚ increases with surface roughness Rₐ giving the following order:

P1200 > P240 > Bead Blasted ≡ P120 > P60. This trend is observed for both laminar and turbulent flow conditions. Linear relationships between the logarithm of reciprocal polarization resistance and the logarithm of the roughness parameter Rₐ, are represented by Eq. (6) and (7):

\[
\frac{1}{R_p} \sim R_a^{0.31 \pm 0.04} \quad \text{under laminar flow (5 rpm)},
\]

\[
\frac{1}{R_p} \sim R_a^{0.59 \pm 0.06} \quad \text{under turbulent flow (6000 rpm)}.
\]

Clearly, the effect of surface roughness on the corrosion rate is more pronounced under fully developed turbulent flow.

For the bead blasted surface, surface stresses may influence corrosion rate. It is known that glass bead blasting introduces stresses, plastic deformation and microstrains and induces changes in surface heterogeneity via fragmentation of grains. The residual stress acts as a source of activation energy and may enhance corrosion rate. This effect is significant when the material is corroding in uninhibited acid or in the presence of low inhibitor concentrations [4]. In contrast, as shown in Fig. 3, in the presence of a high inhibitor concentration, when the inhibitor film fully covers the metal surface, surface stresses have no effect on corrosion rate.

3.4. Film forming kinetic

Laminar and turbulent flow conditions also have different effects on inhibitor film forming kinetics. Chronoamperometry was used to investigate the formation of an inhibitor film on the metal substrate in turbulent and laminar flow regimes for P1200 and bead blasted surface finishes. Fig. 4 shows the development of the logarithmic values of the cathodic current density for the smooth (P1200) and rough (bead blasted) surface finishes a function of exposure time (recorded on polarizing surface at −0.65 V vs. Ag/AgCl) in the presence of the corrosion inhibitor formulation.
Table 4
The effect of flow regimes and surface finishes on corrosion potential (OCP) and polarization resistance ($R_p$) normalized to the true surface area for low carbon steel HS80 electrodes after 3 h of immersion in deaerated 4 M HCl containing the corrosion inhibitor formulation, 0.2 wt.% at 80 °C. Parameter $R_p$ represents the surface roughness measured after 3 h of immersion.

<table>
<thead>
<tr>
<th>Surface finish</th>
<th>Laminar flow</th>
<th>Turbulent flow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_p$ (µm)</td>
<td>OCP (V) vs. Ag/AgCl</td>
</tr>
<tr>
<td>P1200</td>
<td>0.13</td>
<td>−0.378</td>
</tr>
<tr>
<td>P1200</td>
<td>0.13</td>
<td>−0.369</td>
</tr>
<tr>
<td>P240</td>
<td>0.59</td>
<td>−0.340</td>
</tr>
<tr>
<td>P120</td>
<td>3.19</td>
<td>−0.387</td>
</tr>
<tr>
<td>P120</td>
<td>3.5</td>
<td>−0.397</td>
</tr>
<tr>
<td>Bead blasted</td>
<td>4.53</td>
<td>−0.360</td>
</tr>
<tr>
<td>Bead blasted</td>
<td>4.79</td>
<td>−0.371</td>
</tr>
<tr>
<td>P60</td>
<td>6.68</td>
<td>−0.397</td>
</tr>
<tr>
<td>P60</td>
<td>6.84</td>
<td>−0.378</td>
</tr>
</tbody>
</table>

Fig. 4. Cathodic current density recorded as function of immersion time for P1200 (a) and bead blasted (b) surface finishes of low carbon steel HS80 electrode in deaerated 4 M HCl containing corrosion inhibitor formulation, 0.2 wt.% at 80 °C under laminar and turbulent flow conditions. Electrodes were polarized at −0.65 V vs. Ag/AgCl.

For all surface finishes and flow conditions the cathodic current density’s decrease with increasing exposure time. This is to be expected as the process of forming a protective inhibitor film from inhibitor formulation is not instantaneous. Time is required for the propargyl alcohol molecules to adsorb and, subsequently, to polymerize on the metal surface. Thus, the trends reflect the kinetics of the film formation process [26,27].

For the smooth surface, a minimum in the cathodic current density, $8.18 \times 10^{-4}$ A cm$^{-2}$ and $9.26 \times 10^{-4}$ A cm$^{-2}$ is attained after 3 h exposure for laminar and turbulent flow conditions, respectively. The steepest decrease in the instantaneous rate occurs during the first ~0.5–1.0 h and, subsequently, a more gradual decreasing trend extends to 3 h exposure in inhibited 4 M HCl. The data suggest that, after the protective inhibitor film has been largely established, it undergoes a slower “maturation” process on the metal surface. It is likely that this maturation phase (~2–3 h) involves a progressive thickening of the polymeric film. Poling [27] found that the polymer film from propargyl alcohol thickens and becomes more hydrocarbon-like with increasing exposure time, giving increasingly greater protection and a film thickness of 60 Å after 24 h of exposure.

As shown in Fig. 4(a), it appears that for the smooth surface the flow velocity has no noticeable effect on the kinetics of the film formation process. In contrast, for the rough surface, the rate at which the film is established and its ultimate inhibition efficiency depend on the flow velocity.

Fig. 4(b) compare changes in the instantaneous cathodic current density with exposure time for bead blasted surface finishes under laminar and turbulent flow conditions. By comparison, the trend in the instantaneous current density with exposure time for the rough surface and laminar flow is similar in the behaviour of the smooth surface (Fig. 4(a)). However, when the flow regime is turbulent, the cathodic current density has reached its near-constant plateau value within 0.5 h of immersion ($3.9 \times 10^{-3}$ A cm$^{-2}$) and then the current density is independent of exposure time. This suggests that the turbulent flow substantially decelerates “maturation” of the inhibitor film established on the rough metal substrate.

4. Discussion

4.1. Effect of surface roughness under laminar flow conditions

Our data demonstrates that the reciprocal polarization resistance $1/R_p$ is proportional to the roughness parameter $R_p$ raised to the power of 0.31 under laminar flow conditions. Various factors that contribute to such corrosion behaviour have been discussed in the Introduction.

This is consistent with other studies [28–30] which show that under stagnant flow conditions, a rougher surface leads to a higher corrosion rate. For instance, the corrosion of copper in 3.5% NaCl solution increased with an increase in surface roughness, while the surface electron work function (EWF) decreased [28]. The EWF, which refers to the minimum energy required to remove an electron from the metal surface to a position just outside of the solid, was used to explain the observed relation between the corrosion rate and roughness. Lower EWF can improve electron activities and raise corrosion rate, while higher EWF corresponds to higher resistance to corrosion. Generally, EWF decreased with a decrease in surface roughness [31]. The EWF of a peak is lower than that of a valley and the difference in EWF between peaks and valleys may promote the formation of local corrosion cells that could further accelerate corrosion of a rough surface. The peaks with lower elec-
trode potentials or EWF are more anodic, while the valleys with higher electrode potentials or EWF are more cathodic. This implies that the dissolution of peaks is accelerated, while the corrosion in valleys is relatively slower, so that the surface became smooth when peaks were corroded [28].

In another paper [29], the reciprocal polarization resistance (1/Rp) of zinc in 0.1 M Na2SO4 solution at 25 °C was found to be proportional to the roughness parameter Rq raised to the power of 0.39, which is slightly exceeds the value 0.31 found in the present study. We note that those authors did not normalize their Rq values with respect to surface area.

Lee et al. [30] also showed that the corrosion behaviour of 21Cr stainless steel in a 1 M NaCl solution at room temperature was correlated with the reduced valley depth of the surface (Rvk). The polarization resistance is increased by more than three times when Rvk is reduced from 250 nm to 25 nm, while other roughness parameters such as roughness average Rn, root mean square roughness average, skewness Rsk, and others showed poor correlations with corrosion behaviour. The significant influence of the valleys on corrosion resistance appears to be closely related to the depth of the valleys that affect the diffusion of active ions during corrosion and to IR drops in the deep valleys.

4.2. Effect of surface roughness under turbulent flow conditions

Our data demonstrates that under turbulent flow conditions, the reciprocal polarization resistance (1/Rp) is proportional to the roughness parameter Rq to the power of 0.58, and the effect of the flow is most evident for a rough surface. The varying influence of flow velocity on the reciprocal polarization resistance for smooth and rough surfaces is correlated with different hydrodynamic conditions close to metal substrate.

Fig. 5 shows a schematic of the high-Reynolds-number boundary layer. Fully developed turbulence is observed in the bulk liquid and is characterized by a chaotic turbulence velocity field motion [25]. Close to the wall, the fluctuations are dampened that results in formation of a hydrodynamic-viscous sublayer with a nearly laminar flow profile. However, smaller scale turbulent fluctuations (eddies) are still present in the viscous sublayer and play an important role in transfer of heat and mass towards the solid surface.

By definition, in the thin layer close to the surface (the diffusive sublayer), the mass transport is controlled by only the molecular diffusion. The following equations were used to calculate the thickness of the diffusive sublayer, δ0 [25]:

$$\delta_0 = \frac{\Delta h}{\kappa^{1/3}}$$  \hspace{1cm} (8)

$$\kappa = \frac{\eta}{D}$$  \hspace{1cm} (9)

$$\Delta h = 5 \Delta h_{w}$$  \hspace{1cm} (10)

$$\Delta h_{w} = 5 \eta \sqrt{\frac{u^*}{\rho}}$$  \hspace{1cm} (11)

$$u^* = \sqrt{\frac{\tau_{w}}{\rho}}$$  \hspace{1cm} (12)

where Δh is the thickness of hydrodynamic sublayer, Δh w is the wall layer thickness, η is the Schmid number, η is the kinematic viscosity, ρ is the fluid density, D is the molecular diffusivity, $u^*$ is the friction velocity, and $\tau_{w}$ is the wall shear stress. The thickness of the diffusive sublayer under turbulent flow conditions is about 2 μm. This value was calculated for 4 M HCl at 80 °C.

We would like to note that for the fluid employed in our experiments the wall layer thickness Δh w is nearly equal to the diffusive sublayer thickness, δ0. According to the literature (e.g. [32]) the wall roughness affects the wall shear stress only when the roughness exceeds the wall boundary layer thickness. Also, it is usually considered that within the diffusive sublayer, the turbulent fluctuations do not contribute into mass transfer and can be ignored. Then, according to these views, our experimental data are split between hydraulically smooth and rough wall flow conditions. However, it is important to emphasize that Eqs. (8–12) are approximate and reliably provide only order of magnitude estimations. Because for majority of the flow regimes investigated in this work, the roughness values differ from the characteristic thicknesses $\Delta h_{w}$ and $\delta_0$ by factors smaller than an order of magnitude, only experimental data can be used for reliable conclusions. Nevertheless, the explanations of mass transfer enhancement due to surface roughness, made by using the characteristic thicknesses and provided further, are qualitatively correct and illustrative.

For the smooth surfaces ($R_{q} < 0.63 \mu m$) [P1200 and P240, Fig. 5a], when the dimensions of the peaks I are lower compared to the thickness of the diffusive sublayer δ0 > I, the flow conditions do not noticeably influence the corrosion rate and the difference between the values of corrosion rate under laminar and turbulent flow conditions is negligible (Table 4).

For the rough surface ($R_{q} \geq 2.76 \mu m$) [P120, bead blasted, and P60, Fig. 5b], the dimensions of the peaks I are large compared to the thickness of the diffusive sublayer I > δ0, and the presence of peaks has a substantial effect on the nature of the turbulent flow and the corrosion rates. In the case of a turbulent flow, the surface roughness contributes to enhancing turbulence kinetic energy. The roughness leads to an increase in fluid–wall friction that in turn causes an increase in the energy dissipation rate and the turbulence kinetic energy, respectively [33].

Nevertheless, it is most important that roughness may cause a significant enhancement in the mass transfer rate. In our experiments under turbulent conditions, the dimensions of the roughness peaks are comparable or even larger1 than the thickness of the diffusive boundary layer (δ0 ~ 2 μm at 6000 rpm). It is convenient to analyse turbulent flow behaviour in the rough wall vicinity by considering turbulence as a series of discrete turbulence eddies of different scales [25]. This analysis is based on a physically justified concept of Kolmogoroff turbulence. Turbulent eddies penetrate into cavities (valleys) between neighbouring peaks maintaining relatively high kinetic energy (Fig. 5c). An intensification of mixing, caused by these eddies, leads to a significant enhancement of mass transfer and increases partial erosion of the inhibitor film. This mixing intensification leads to thinning and, as a limiting case, to entire disappearance of the diffusive layer [32].

Let us deepen the explanation of mass transfer intensification based on analysis of behavior of discrete turbulent eddies. An eddy, which penetrates into a cavity on the wall, decelerates in the course of its motion due to viscous friction with the surface [25]. We would like to emphasize here that in absence of roughness the turbulent motion would be fully suppressed at the distance from the wall equal to the diffusive layer thickness. However, the process of eddy deceleration in a cavity is strongly non-uniform in space. This non-uniformity leads to formation of such areas inside cavities where turbulence fluctuations have relatively high kinetic energies at distances from the surface which are significantly smaller than the diffusive layer thickness calculated assuming the smooth wall. Thus, the rough surface is characterized by the local high mass transfer rates spots. This phenomenon is a major reason of mass transfer intensification due to roughness.

A simple estimate of the roughness effect on the mass transfer rate, confirming this concept, was given by Wood [34] who investigated deposition of small particles on rough walls under

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1 The maximum value of surface asperities / for P60 surface finish is above 20 μm (Fig. 1c).
Fig. 5. Schematic illustration of the hydrodynamic and the mass-transfer boundary layers for smooth (a) and rough (b) surfaces under turbulent flow and quenching turbulent eddies in micro-roughness cavity (c).

turbulent flow conditions. Note, the total diffusivity, determining mass transfer in a turbulent flow can be calculated as a superposition of the molecular and the turbulent diffusivities. According to the experiments of Lin et al. [35], the turbulent diffusivity across the hydrodynamic boundary layer changes proportionally to the third power of the distance from the surface of the smooth wall, reaching zero at the surface. As already mentioned, within the diffusive boundary layer, the turbulent diffusivity is negligible. To take into account penetration of the turbulent eddies between peaks in mass transfer calculations, Wood [34] suggested the method, according to which the wall is assumed to be smooth but shifted toward the flow at the distance equal to 45% of the wall roughness. The sought turbulent diffusivity at the rough wall is the diffusivity calculated at this artificial smooth surface assuming that the rough wall coordinate is zero. A roughness induced mass transfer intensification, evaluated by the Wood’s approach [34], for a turbulent flow in a pipe (e.g. see Eskin et al. [36]) qualitatively agrees with the experimental data of Gabe and Walsh [37]. These investigators experimentally studied mass transfer to the surface of a rotating electrode at development of roughened deposits during the process of metal extraction from aqueous solution. A significant enhancement of the mass transfer rate (by factors up to 30 times) in comparison with hydrodynamically smooth RCE was reported [37].

Thus, it is clear that the turbulent diffusivity in the rough wall vicinity may significantly exceed the molecular diffusivity that leads to an enhanced mass transfer rate. This calculation method, based on the experimental data, agrees with the concept of the mass transfer enhancement by roughness as a result of either thinning or entire disappearance of the diffusive boundary layer. In practice, according to [18] the roughness effect on the Sherwood number for a RCE flow can be taken into account by an empirical correlation:

$$Sh = \frac{kd_{cyl}}{D} = \sqrt{\frac{L}{2} Re Sc^{0.356}}$$ (13)
where $f$ is the friction factor, $k$ is the mass transfer coefficient, $Re = \frac{\omega d_{yl}^2 p}{2\eta}$ is the Reynolds number, $\omega = \pi N/30$ is the rotor angular velocity.

According to Eq. (13) is valid for both smooth and rough cylinder surfaces. Like in a pipeline flow [33], in a general case, the friction factor is a function of both the Reynolds number and the roughness. This function could be presented by a diagram, similar to the well-known Moody diagram for a pipeline flow [33]. If the roughness significantly exceeds the thickness of the viscous sublayer, the friction factor is determined by an interaction of roughness peaks with a turbulent flow and independent of the Reynolds number. The critical value of the Reynolds number, $Re_{cr}$, indicating this roughness governed regime is [18]:

$$Re_{cr} = \left( 11.8 \frac{d_{yl}}{R_k} \right)^{1.18}$$ (14)

The friction factor for this flow regime can be calculated by the analytical correlation, which has the same functional form as that for a pipe flow [33], but with the different numerical coefficients, and is written as [18]:

$$f = \frac{1.25 + 5.76 \log \left( \frac{d_{yl}}{R_k} \right)}{2}$$ (15)

A simple analysis of Eq. (13) allows concluding that for roughness governed flow regimes, a roughness increase causes a rather significant enhancement in the corrosion rate. Whereas the inhibitor film on a smooth surface ($R_k \leq 0.63 \mu m$) [P120 and P240] is subjected to only the wall shear stress effect, the inhibitor film covering a rough surface ($R_k \geq 2.76 \mu m$) [P120, bead blasted, and P60] is additionally eroded with turbulent eddies possessing relatively high kinetic energies.

5. Conclusions

The effect of surface roughness on the corrosion behaviour of low carbon steel in 4 M hydrochloric acid in the presence of corrosion inhibitor has been examined under laminar and turbulent flow conditions. We conclude:

1) Corrosion of low carbon steel in inhibited 4 M HCl for 3 h at 80 °C results in a slight decrease in average surface roughness $R_k$ and the skewness factor $R_k$. This implies that protruding cavities and peaks were preferentially dissolved resulting in a smoother surface.

2) Under laminar and turbulent flow conditions, the reciprocal polarization resistance $1/R_p$ increases with surface roughness $R_k$ giving the following order: P1200 > P240 > Bead Blasted > P120 > P60.

3) The corrosion rate is proportional to the surface roughness parameter $R_k$ to the power of 0.31 and 0.59 for laminar and turbulent flow conditions, respectively. The effect of surface roughness on the corrosion rate is more pronounced under fully developed turbulent flow.

4) For the smooth surfaces ($R_k \leq 0.63 \mu m$) [P120 and P240], the dimensions of the roughness peaks $l$ are lower compared to the thickness of the diffusive sublayer $\delta_0 > l$, the flow conditions do not noticeably influence the corrosion rate and the difference between the values of corrosion rate under laminar and turbulent flow conditions is negligible.

5) For the rough surface ($R_k \geq 2.76 \mu m$) [P120, bead blasted, and P60, Fig. 5b], the dimensions of the roughness peaks $l$ are large compared to the thickness of the diffusive sublayer $l > \delta_0$, and the presence of peaks has a substantial effect on the nature of the turbulent flow and the corrosion rates. The corrosion rate increases with an increase in surface roughness in both the laminar and turbulent flow regimes. However, the effect of surface roughness is more pronounced under fully developed turbulent flow due to partial erosion of the inhibitor film caused by a high wall shear stress and turbulence eddies possessing relatively high kinetic energies. Turbulent flow conditions and a rough surface combine to have a negative impact on the growth rate of the inhibitor film.

References


