Experimental investigation on gas–liquid two-phase slug flow enhanced carbon dioxide corrosion in vertical upward pipeline

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1. Introduction

An important consideration in oil and gas industry is multiphase transport from remote wells for much more economical transport of oil and gas combined. The multiphase transport pipelines are mostly made of carbon steel and low-alloy steel, which are able to meet many of the mechanical, structural, fabrication requirements and may offer considerable capital savings over the more expensive alloys [1,2]. However, the frequently encountered multiphase fluids may contain significant levels of CO2, which in combination with free water can make the pipeline environment corrosive, resulting in the flow enhanced CO2 corrosion, thus the damage to the interior of carbon steel pipeline walls, and the decrease in pipeline lifetime and even possible shut down of the pipeline. Over the last few decades, with the development of the crude oil exploitation technology and long distance multiphase transport technology, the problem of flow enhanced CO2 corrosion has made the economic losses increasingly serious, and it is especially true for the oil and gas multiphase transport in the offshore and deep-sea oil fields.

Corrosion is a surface damage process. Therefore, what is going on at the metal surface has a profound effect on the corrosion [3]. Many aspects of fluid dynamics related to or determined by the interactions between fluid and metal surface are of importance to corrosion. The changes in fluid hydrodynamics, turbulence, wall shear stress, mass transfer, electrochemical corrosion, the formation and the destruction of the corrosion product film, are all intimately related to the hydrodynamic boundary layer and the diffusion boundary layer in the vicinity of the metal substrate. It has been found that metallurgical characteristics of pipelines and hydrodynamic characteristics of flow are important factors influencing corrosion rate.

There are remarkably different hydrodynamic characteristics for different flow regimes, resulting in different mechanisms of flow enhanced corrosion. Among the gas–liquid two-phase flow regimes, the vertical upward slug flow is highlighted potentially as the most aggressive and commonly encountered regime, which always exists in oil and gas pipelines with higher oil and gas production rates, and causes a high corrosion rate of carbon steel [4,5]. The remarkable hydrodynamic characteristic of the slug flow is the flow intermittence, that is, the flow is pseudo-periodically alternated by Taylor elongated bubble with an annular falling liquid film around it and a portion of succeeding liquid slug, simply described as a sequence of slug unit. The Taylor bubble occupies nearly the whole cross-section of the tube with a bullet-shaped front and a flat tail profile, while the annular falling liquid film is assimilated by the succeeding liquid slug entraining many small bubbles. Although slug flow appears a well-ordered flow, it is highly complicated with an unsteady nature, which is influenced by many factors, such as the velocities of gas and liquid, void fraction, pressure shock, density wave, liquid slug frequency and the physical properties of gas and liquid.

In this paper, using the limiting diffusion current technology, conductivity probe technology and digital high-speed video system, mass-loss method, electrochemical impedance spectroscopy...
(EIS), linear polarization resistance (LPR), scanning electron microscopy (SEM), and X-ray diffraction (XRD), the vertical upward slug flow enhanced CO₂ corrosion is investigated both experimentally and mechanistically. The major characteristics investigated include the shear stress and mass transfer coefficient in the near wall zone, the effect of hydrodynamic characteristics on the corrosion process, CO₂ corrosion rate, the morphological and composition analysis of corrosion product film, the coupling characteristics of hydrodynamics and electrochemical corrosion, etc.

2. Experimental

2.1. Experimental set-up

The experiments are conducted in a two-phase flow set-up manufactured from 316L (UNS S31603) stainless steel, which is shown in Fig. 1. The detailed description of the experimental set-up has been reported in the previous paper of the authors [6].

2.2. Hydrodynamic test section

The hydrodynamic test section is a vertical 35 mm inside diameter, 5 m long Plexiglas pipe, schematically shown in Fig. 2. The experimental liquid phase is the synthetic electrolyte of 0.5 mol/L NaOH–0.01 mol/L K₄Fe(CN)₆–0.01 mol/L K₃Fe(CN)₆ by dissolving analytical-reagents in distilled water, and the experimental gas phase is CO₂. The temperature and pressure are maintained constant at 68 °C and 0.21 MPa throughout the experiments.

2.3. Electrochemical corrosion test section

The electrochemical corrosion test section is a vertical 35 mm inside diameter, 5 m long 316L stainless steel tube, schematically shown in Fig. 3. The experimental liquid phase is the synthetic solution of 0.5 mol/L NaCl by dissolving analytical-reagent in distilled water, and the experimental gas phase is CO₂. The temperature and pressure are maintained constant at 68 °C and 0.21 MPa throughout the experiments. The pH value of solution is around 4.5 and the conductivity is about 5.1 Ω⁻¹ m⁻¹. Corrosion rates are recorded using electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR), double-checked with mass-loss method. The pH is monitored throughout the experiments using standard litmus paper.

To measure the electrochemical corrosion characteristics in situ using EIS and LPR, four sets of electrochemical corrosion measurement devices with the same three-electrode configuration are flush-mounted to the wall of the pipe to minimize flow disturbances, as shown in Fig. 4. All coupons are machined from the parent tubular section into cylindrical specimens with 10 mm in diameter, 6 mm in thickness. All of the surfaces are coated with epoxy, except leaving a bottom surface exposed to the corrosive solution with an area of 0.785 cm². In each three-electrode measurement device, the working electrode (WE) is made of API N80 mild steel, the counter electrode (CE) and reference electrode (RE) are all made of 316L stainless steel. The martensitic micro-structure of sampled N80 mild steel indicates that this material has been quenched and tempered. The chemical compositions of N80 mild steel and 316L stainless steel are presented in Tables 1 and 2.

Before each test run, anaerobic grade CO₂ gas is used to deoxygenate the solution, lowering the dissolved oxygen level to less than 30 µg/L from the formation of oxides. Moreover, the dissolved iron level is controlled below 15 mg/L, avoiding the saturated iron ion effect on the corrosion process. During the experiments, the oxygen and iron ion levels are regularly monitored. The coupons are firstly polished progressively with 400-, 800- and 1200-grit silicon carbide abrasive paper, then degreased with acetone and rinsed with alcohol many times, dried, weighed, and finally flush-mounted. At the end of the electrochemical corrosion mea-

Fig. 1. Schematic diagram of experimental set-up: (1) gas storage vessel; (2) gas supplement device; (3) freezing dryer; (4) liquid supplement tank; (5) secondary separator; (6) secondary pump; (7) liquid storage tank; (8) oil bath heater; (9) primary pump; (10) liquid phase orifice flowmeter; (11) twin-screw compressor; (12) gas surge tank; (13) gas phase orifice flowmeter; (14) two-phase mixing device; (15) test section; (16) non-return valve; (17) cut off valve.
measurements in situ, these coupons are carefully disassembled from the test section, rinsed, dried, weighed, stored in a glove bag and sealed in helium gas environment, preventing the corrosion product from oxidization and destruction, to be further morphologically analyzed.

The electrochemical corrosion measurements are conducted using an EG&G Princeton Applied Research (PAR) Potentiostat/Galvanostat Model 273A and a 5210 lock-in-amplifier. The EIS measurements are carried out at the open-circuit potential with amplitude of 10 mV sinusoidal alternating current (AC) potential in the sweep frequency range of 10 mHz to 10 kHz. The acquired spectra are analyzed based on the principle of an equivalent circuit using nonlinear least-squares curve fitting algorithms provided by the accompanying software. The LPR measurements are performed by polarizing the working electrode in the range of ±20 mV from open-circuit potential with a scan rate of 0.1 mV/s, and the automatic IR drop compensation is used. In calculating corrosion rates from linear polarization measurements, anodic and cathodic Tafel slopes are assumed to be 120 mV/dec. At the end of experiments, the potentiodynamic sweeps for Tafel polarization curves are done at direct current (DC) potential range 500 mV below and 300 mV over the open-circuit potential with a scan rate of 0.1 mV/s.

3. Results and discussion

3.1. Hydrodynamic characteristics

There exist four processes in the flow enhanced corrosion as follows [3,8,9]:

1. The formation of reactants in the bulk solution.
2. The reactants transport from the bulk solution to the metal surface.
3. Electrochemical corrosion reaction at the metal/solution interface.
4. The corrosion product transport from the metal/solution interface to the bulk solution.

Since electrochemical corrosion occurs on the metal surface, the hydrodynamic boundary layer and diffusion boundary layer exert a pivotal effect on the flow enhanced corrosion [3,10]. Being decisive for the flow enhanced corrosion, the extremely complicated boundary must be simplified here. Starting from the wall, the hydrodynamic boundary layer can be further subdivided into four regions: a diffusion sublayer, a laminar viscous sublayer, an intermediate buffer layer, and an outer logarithmic turbulent layer. In the innermost diffusion sublayer, the mass is dominantly transported by molecular diffusion as a result of concentration gradient. In the laminar viscous sublayer, the velocity and turbulent stresses of the flow are damped to zero, leaves only the viscous stresses of laminar flow to act on the wall; the random movement of individual molecules and the mass is transported by convection diffusion. In this sublayer, the laminar molecular viscous forces dominate over turbulent forces and the flow is essentially laminar. In the outer logarithmic turbulent layer, turbulence plays a significant role, and mass is transported by turbulent eddy diffusion where the random movement of macro-volumes of solution controls the diffusion. In the intermediate buffer layer, the effects of both molecular viscosity and turbulence are of the equal
importance, and mass is transported by both convection diffusion and turbulent eddy diffusion.

The mass transport in the boundary layer can be measured by mass transfer coefficient $k$. The viscous energy loss within the turbulent boundary layer, namely the intensity of turbulence in the fluid acting on the wall, can be directly measured by wall shear stress $\tau_w$. The wall pressure of fluid perpendicular to the pipe wall can be measured by wall normal stress $\sigma_n$.

Consequently, the hydrodynamic characteristics, especially the transport characteristics in the near wall zone, are of significant effect on corrosion. A higher mass transfer coefficient can cause an increase in corrosion rate due to the increased transport of both reactants and corrosion products. A higher wall shear stress can lead to higher corrosion rate by preventing the protective corrosion product film from formation, or by retarding the film growth, and by removing or destroying existing film. A higher wall normal stress fluctuations can also exacerbate the corrosion rate by facilitating the turbulence formation, making the corrosion product porous. The failure of the pipelines by flow enhanced corrosion usually originates from pitting and mesa attack, and is aggravated by micro-turbulence further created by fluid flows.

To better understand the slug flow enhanced corrosion, it is necessary to have a deep insight into the transport characteristics in the near wall zone. As shown in Fig. 5, the Taylor bubble is a large axisymmetric bullet-shaped bubble with spherical cap and

Table 1
Chemical composition of N80 carbon steel (mass%)

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Nb</th>
<th>V</th>
<th>Ti</th>
<th>Cu</th>
<th>Fe</th>
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<tr>
<td>0.24</td>
<td>0.22</td>
<td>1.19</td>
<td>0.013</td>
<td>0.004</td>
<td>0.036</td>
<td>0.021</td>
<td>0.028</td>
<td>0.006</td>
<td>0.017</td>
<td>0.011</td>
<td>0.01</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Table 2
Chemical composition of 316L stainless steel (mass%)

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.80</td>
<td>1.10</td>
<td>0.02</td>
<td>17.00</td>
<td>2.00</td>
<td>14.00</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Fig. 3. Schematic diagram of electrochemical corrosion test section.

Fig. 4. Schematic diagram of electrochemical three-electrode measurement system: (1) supporting seat; (2) coupon; (3) seal packing ring; (4) built-in fitting; (5) gland nut.
nearly flat bottom occupying almost the whole cross-section of the tube. Due to the buoyancy, the Taylor bubble pushes aside the liquid phase toward the tube wall in the Taylor bubble nose zone at point A, and a falling liquid film starts to form at point B. The annular developing falling liquid film runs downward with an increased velocity all the way around the Taylor bubble, and thins as it falls, until the wall friction force is able to balance the gravitational force of the film and a terminal constant thickness and velocity of a fully developed falling liquid film are attained. When the fully developed annular falling liquid film flows over the Taylor bubble into the wake, the point C, where the annular falling liquid film plunges into the succeeding liquid slug, encountering the upward bulk liquid flow, and its velocity is diminishing until the falling liquid film is fully assimilated by liquid slug at D. The fluid flows upward in the zone from the point D to the point A at which the succeeding Taylor bubble comes.

Fig. 6 shows the instantaneous wall shear stress, wall normal stress, and mass transfer coefficient profiles in slug units at superficial velocities $U_{SG} = 0.45$ m/s, $U_{SL} = 0.344$ m/s. The acquisition voltage $U$ represents the Taylor bubble, the corresponding duration time is attributed to the length of Taylor bubble; the low level of acquisition voltage $U$ represents the liquid slug, the duration time corresponds to the length of liquid slug. Whereas the high levels of wall shear stress, wall normal stress, and mass transfer are associated with falling liquid film, the low levels are associated with the liquid slug, and the skew lines are associated with the transition from one zone to another. By comparing the profiles of acquisition voltage, wall shear stress, wall normal stress, and mass transfer coefficient, the effects of the Taylor bubble nose zone, the Taylor bubble wake zone and the penetration length of the falling liquid film in the liquid slug on the wall shear stress and the mass transfer coefficient can also be obtained. As shown in Fig. 6, although the transitions of the wall shear stress and the mass transfer coefficient from the low level to the high level are almost simultaneous, the transitions lag behind the acquisition voltage, resulting from the existence of $L_A$ in the Taylor bubble nose zone; and the transitions of the wall shear stress and the mass transfer coefficient from the high level to the low level are also almost simultaneous, the transitions also lag behind the acquisition voltage, resulting from the existence of $L_C$ in the Taylor bubble wake zone, as shown in Fig. 5.

From the above analysis of hydrodynamic structure for the slug unit, and from the validation of experimental results, the mass transfer for the slug unit can be classified as four parts as follows:

1. Mass transfer in the Taylor bubble nose zone from A to B with coefficient $k_{TBn}$.
2. Mass transfer in the falling liquid film zone from B to C with coefficient $k_{TBf}$.
3. Mass transfer in the Taylor bubble wake zone from C to E with coefficient $k_{TBw}$.

4. Mass transfer in the remaining liquid slug zone from E to A' with coefficient $k_{LS}$.

Designating the downward wall shear stress positive, the wall shear stress in the slug unit can be divided into two parts as follows:

1. Positive wall shear stress $\tau_{w}$ from B to D due to the falling liquid film, and
2. Negative wall shear stress $\tau_{wLS}$ from D to B' due to the liquid slug.

Experimental results have been found that both the mass transfer coefficient and wall shear stress in each zone increase with the increase of superficial gas velocity, and decrease with the increase of superficial liquid velocity. For the falling liquid film zone, as the superficial gas velocity is increased, the falling liquid film terminal velocity is increased and the falling liquid film thickness is reduced, which results in the increases of the velocity gradient and the concentration gradient, thus increased mass transfer coefficient and wall shear stress. Whereas as the superficial liquid velocity is increased, the falling liquid film terminal velocity is decreased and the falling liquid film thickness is increased, which results in the decreases of the velocity gradient and the concentration gradient. For the Taylor bubble wake zone, increasing the superficial gas velocity leads to an increased falling liquid film terminal velocity, resulting in more turbulent, disorderly and chaotic wake, and the mass transfer coefficient is increased; the increased superficial liquid velocity leads to a decreased mass transfer coefficient. For the liquid slug zone and the Taylor bubble nose zone, the increase of the superficial gas velocity gives rise to the increase of void fraction, resulting in increased probability of bubble impact on the wall and a larger turbulence of liquid slug, thus increased mass transfer coefficient and wall shear stress; whereas a contrary change is enhanced by increasing the superficial liquid velocity. It can also been found that the mass transfer coefficient $k_{TB}$ is maximum, the mass transfer coefficient $k_{TBw}$ is minimum; the magnitude of the wall shear stress associated $\tau_{w}$ with the falling liquid film is always larger than that of $\tau_{wLS}$ associated with the liquid slug.

Due to the complicated hydrodynamic characteristics of slug flow, there is still no widely applied normalized formula valid to accurate determination of the mass transfer coefficient and wall shear stress.

Mass transfer prediction is of great importance in computing corrosion rates, particularly for the transport based models, and is also the key for the coupling of CO$_2$ corrosion and hydrodynamics of slug flow. The global formula for mass transfer prediction in fully developed single phase liquid full-pipe turbulent flow can be expressed as

$$Sh = a \times Re^b \times Sc^c$$

where $a = 0.023$, $b = 0.8$ and $c = 0.33$ for well-known fully developed single phase liquid full-pipe turbulent flow correlation developed by Chilton and Colburn [11]. Sh is the Sherwood number $kl/D_a$, Re the Reynolds number $\rho U l/\mu$, and Sc the Schmidt number $\mu/\rho D_a$.

Based on the single phase mass transfer coefficient formula, a corrected normalized mass transfer coefficient formula for gas–liquid vertical upward slug flow is suggested as follows:

$$Sh = C \times 0.023 Re^{0.8} Sc^{0.33}$$

namely

$$k_{TP} = 0.023 CR e^{0.8} Sc^{0.33} \left( \frac{D_e}{l} \right) = 0.023 C \left( \frac{\rho U l}{\mu} \right)^{0.8} \left( \frac{\mu}{\rho D_a} \right)^{0.33} \left( \frac{D_e}{l} \right)$$

$$C = 0.27 \left( 1 + \frac{Fr_e}{\beta} \right)^{0.5}$$

where $C$ is the corrected factor considering the difference of gas–liquid slug flow from the single phase flow; $k_{TP}$ the mass transfer coefficient (m/s) in gas–liquid two-phase slug flow; $D_e$ the diffusion coefficient (m$^2$/s), for the hydrogen ion (H+) $D_e = 9.31 \times 10^{-6}$ m$^2$/s, for the ferrous ion (Fe$^{2+}$) $D_e = 7.12 \times 10^{-10}$ m$^2$/s; $l$ the characteristic length (m); $U$ the characteristic velocity (m/s); $\mu$ the characteristic dynamic viscosity (Pa s); $\rho$ the characteristic density (kg/m$^3$); $Fr_e$ the Froude number for the mixture velocity of superficial gas phase velocity $U_{Sg}$ and superficial liquid velocity $U_{S}$; and $\beta$ the Taylor bubble length fraction, ratio of Taylor bubble length $l_{TB}$ to slug unit length $l_{SG} = l_{TB} + l_{LS}$.

The experimental results show the falling liquid formation distance from the Taylor bubble nose $L_A$ is short, and the corresponding mass transfer coefficient $k_{TB}$ is minimum. Therefore, $k_{TB}$ can be neglected. The proposed expressions for calculating other mass transfer coefficient are shown in Table 3. Good agreement can be found with maximum derivation within ±10%.

The average mass transfer coefficient in a slug unit can be calculated as follows:

$$k = \sum k_f$$

where $k_f$ is the mass transfer coefficient $k_{TBf}$, $k_{TLf}$, and $k_{LS}$ in each part of a slug unit, $f$ the weight factor based on the length fraction of each part, $l_{TB}/l_{SL}$, $l_{LS}/l_{SL}$, $(l_{LS} - l_A)/l_{SL}$, respectively.

Fig. 7 shows the average mass transfer coefficient of H$^+$ for vertical upward gas–liquid slug flow at different superficial gas and liquid velocities.

The wall shear stress can be calculated as follows:

$$\tau = \frac{f \rho U^2}{2}$$

where $f = 0.046Re^{-0.2}$ is wall friction factor, $Re = \rho U l/\mu$, $U$ the characteristic velocity (m/s), $l$ the characteristic length (m), $\rho$ the characteristic density (kg/m$^3$), $\mu$ the dynamic viscosity (Pa s).

The proposed expressions for calculating the wall shear stress $\tau_w$ associated with falling liquid film and the wall shear stress $\tau_{wLS}$ associated with liquid slug are listed in Table 4. Good agreement can be found with maximum derivation within ±10%.

In Table 4, $U_{LS}$ and $U_{SL}$ are the gas bubble velocity and liquid velocity in liquid slug, respectively.

Leaving out the directions of wall shear stress, the average wall shear stress in a slug unit can be calculated as follows:

$$\tau_w = |\tau_{w} - \beta| + |\tau_{wLS} - (1 - \beta)|$$

Table 3

<table>
<thead>
<tr>
<th>$k_{TB}$</th>
<th>$k_{TBw}$</th>
<th>$k_{LS}$</th>
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<tbody>
<tr>
<td>$U (m/s)$</td>
<td>9.916(1 - $(\tau_{TBw})^{0.5}$)</td>
<td>$(U_{LS})$</td>
</tr>
<tr>
<td>$l (m)$</td>
<td>$4 \times 0.5D(1 - (\tau_{TB})^{0.5})$</td>
<td>$D$</td>
</tr>
<tr>
<td>$\rho (kg/m^3)$</td>
<td>$\mu_l$</td>
<td>$\mu_r(1 - (\tau_{LS})^0 + \mu_r(\tau_{LS}))$</td>
</tr>
<tr>
<td>$\mu (kg/ms)$</td>
<td>$\mu_l$</td>
<td>$\mu_r(1 - (\tau_{LS})^0 + \mu_r(\tau_{LS}))$</td>
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Table 4

<table>
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<tr>
<th>$k_{TB}$</th>
<th>$k_{LS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U (m/s)$</td>
<td>9.916(1 - $(\tau_{TBw})^{0.5}$)</td>
</tr>
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</table>
Fig. 8 shows the average wall shear stress for vertical upward gas–liquid slug flow. The wall normal stress \( r_n \), which represents the wall pressure of fluid perpendicular to the pipe wall, is constant with small fluctuations when the only-liquid flows in a straight smooth pipeline. In such cases, wall normal stress has a weak effect on the corrosion. However, in the gas–liquid two-phase slug flow, the larger wall pressure fluctuations are caused by the pseudo-periodical intermittence of Taylor bubble and liquid slug, exerting a large additional mechanical force onto the metal surface. Thereby, the larger wall pressure fluctuation is a very important parameter considered in the slug flow enhanced corrosion.

Fig. 9 shows the maximum wall normal stress fluctuation values for vertical upward gas–liquid slug flow. It can be seen that the maximum fluctuations are insensitive to the different superficial gas and liquid velocities.

From the above analysis, it can be seen that the intermittence of Taylor bubble and liquid slug is an essential characteristic. As shown in Fig. 6, when a Taylor bubble and the succeeding liquid slug sequentially pass through a given cross-section of the tube, the direction of wall shear stress changes twice, which also causes larger fluctuations of both mass transfer coefficient and wall normal stress. The intermittence characteristic is one of the important factors for the flow enhanced corrosion. The intermittence of slug flow can be characterized by slug frequency \( F_{SU} \).

\[
F_{SU} = \frac{N_{SU}}{\Delta T}
\]

where \( N_{SU} \) is the number of slug units at time interval \( \Delta T \).

Fig. 10 shows the slug frequency distribution at different superficial gas and liquid velocities. It is indicated that the slug frequency is generally above 2 Hz, and the slug frequency increases with increased superficial liquid velocity, decreases with increased superficial gas velocity.

3.2. CO₂ corrosion characteristics

Fig. 11 shows the corrosion rates measured by LPR for CO₂ corrosion of N80 steel at different superficial gas and liquid velocities.

| \( U (\text{m/s}) \) | \( 9.916gD(1 - (\frac{2\Delta}{L})^2)^{0.5} \) | \( U_{GLS} + U_{LLS} \)
|-------------|-----------------|----------------|
| \( L (\text{m}) \) | \( 4 \times 0.5D[1 - (\frac{2\Delta}{L})^2] \) | \( D \)
| \( \rho (\text{kg/m}^3) \) | \( \rho_c \) | \( \rho_s[1 - (\frac{2\Delta}{L})^0.5] + \rho_c(\frac{2\Delta}{L})^0.5 \)
| \( \mu (\text{kg/(m s)}) \) | \( \mu_c \) | \( \mu_s[1 - (\frac{2\Delta}{L})^0.5] + \mu_c(\frac{2\Delta}{L})^0.5 \)
The corrosion rates keep constant within the 30-h exposure to corrosion environment in all experiments due to no corrosion product film. Nevertheless, the corrosion rates remarkably decrease due to the formation of the corrosion product film for 50–85-h exposures. For instance, under the condition of the formation of the corrosion product film for 50–85-h exposures, the corrosion rates decrease continuously from 10.21 mm/yr at the beginning of the corrosion experiment to the smallest value of 16.11 mm/yr after 140-h exposure, respectively. Whereas under smaller mass transfer and smaller wall shear stress, the corrosion rate keeps lower and is prone to form the corrosion product film on the coupon.

Figs. 12 and 13 show the potentiodynamic polarization curves for CO$_2$ corrosion of N80 steel when $U_{SG} = 0.344$ m/s and $U_{SL} = 0.651$ m/s with different superficial gas velocities. It is also can be seen that the polarization currents of N80 steel are dependent on the near wall hydrodynamic characteristics. When $U_{SL} = 0.344$ m/s with $U_{SG} = 0.15$ m/s and $U_{SG} = 0.45$ m/s, except 140-h exposure, the cathodic branches of the polarization curves are similar for 1-h, 50-h and 70-h exposures. The cathodic branches of the curves exhibit limiting current, which is a direct consequence of depletion of H$^+$ ions near the surface and the slow hydration rate of CO$_2$. Right below the corrosion potential, the cathodic reaction process is controlled by activation, and the external power provides extra electrons, making the cathodic reaction accelerated; whereas farther negative to the corrosion potential, due to the adjacent active species depletion, the diffusion transport of electroactive species from the bulk solution to the electrode surface is dominated, and the cathodic reaction is diffusion controlled with the existence of explicit limiting current. However, for the anodic branch of polarization curve, the current density increases with the increase in anodic polarization potential, and unlimited supply of iron atoms is available at the interface. The anodic reaction rates do not depend on the mass transfer process. Except 75-h exposure, the anodic branches of polarization curves are similar for 1-h, 50-h and 140-h exposures. It is found that the polarization
curves gradually change from general corrosion to pitting corrosion. For 1-h and 50-h exposures, the polarization curves of N80 show the typical shape of general corrosion; whereas for 75-h exposure, the curves show the pitting type, and the small passive current densities should be attributed to the corrosion product film, although the film is not fully covered and not compact; for 140-h exposure, the corrosion product film is no longer resistant to hydrodynamic characteristics and detaches from the surface.

Table 5 shows the shifting trend of corrosion potential and the corresponding corrosion current density when \( U_{\text{gl}} = 0.344 \) m/s with \( U_{\text{gc}} = 0.15 \) m/s and \( U_{\text{gc}} = 0.45 \) m/s. Since the corrosion potential increases in the anodic direction with the formation of corrosion product film, the corrosion product film may be considered to have anodic anticorrosive capability.

The polarization characteristics when \( U_{\text{gl}} = 0.651 \) m/s with \( U_{\text{gc}} = 0.15 \) m/s and \( U_{\text{gc}} = 0.45 \) m/s are similar to those when \( U_{\text{gl}} = 0.344 \) m/s. However, due to smaller mass transfer and smaller wall shear stress, a corrosion product film is formed on the coupon when \( U_{\text{gc}} = 0.15 \) m/s, \( U_{\text{gl}} = 0.651 \) m/s for 50-h, 75-h and 140-h exposures, and the tendency of pitting corrosion is greatest.

Figs. 14 and 15 show the typical Nyquist and Bode plots of EIS spectra for CO2 corrosion of N80 steel at \( U_{\text{gl}} = 0.344 \) m/s and \( U_{\text{gl}} = 0.651 \) m/s with different superficial gas velocities. When \( U_{\text{gc}} = 0.15 \) m/s, \( U_{\text{gl}} = 0.344 \) m/s, two semicircles appear after 75-h exposure, which means a corrosion product film has been formed on the coupon. The first semicircle is so small that it merges into the second semicircle, cannot clearly distinguished from each other, namely \( R_t \) is much smaller than the charge transfer resistance \( R_{\text{ct}} \). The first semicircle at higher frequency would be due to the corrosion product film because a surface dielectric film normally has a small time constant and so has a phase angle shift in the high frequency range. The measured results validate the conclusion with \( R_t \approx 63 \) \( \Omega \) cm\(^2\), \( C_t = 1018 \) \( \mu \)F/cm\(^2\), the value of \( R_t \) being one seventh of the \( R_c \). This indicates that the corrosion product film has non-protective capacity, and further validates the results of corrosion process measured by LPR and potentiodynamic polarization.

As shown in Table 6, the charged transfer resistance increases from the 1-h exposure to 50-h exposure, and corrosion product film starts to form on the coupon. After 75-h exposure, the charged transfer resistance increases to the maximum with corrosion product film covered; however, the corrosion product film is not fully covered and non-compact. The difference for the physical property of corrosion product film from that of the metal substrate, leads to high tendency of pitting corrosion. In such a case, the corrosion product film is detached from the metal substrate due to the effect of the hydrodynamics of slug flow. Thereby, the charge transfer resistance \( R_c \) decreases to the minimum after 140-h exposure.

From the analysis of EIS spectra, it is found that the type of corrosion and the kinetics of the corrosion reaction when \( U_{\text{gc}} = 0.45 \) m/s, \( U_{\text{gl}} = 0.344 \) m/s, and \( U_{\text{gc}} = 0.45 \) m/s, \( U_{\text{gl}} = 0.651 \) m/s are similar to those when \( U_{\text{gc}} = 0.15 \) m/s, \( U_{\text{gl}} = 0.344 \) m/s. The impedances when \( U_{\text{gc}} = 0.15 \) m/s, \( U_{\text{gl}} = 0.651 \) m/s, are shown in Table 6. Since corrosion product film starts to build on the coupons at the beginning of the exposure, the angle shifts in higher frequency are very marked. The corrosion product film resistance \( R_t \) is very small, no more than one fifth of the charge transfer resistance \( R_{\text{ct}} \), which indicates that the corrosion product film
film is very porous, its anticorrosion capacity is very poor, despite the corrosion product film formation on the coupons at the initial exposure. Results of the polarization measurement and impedance measurement show that the corrosion film has limited protective exposure. Results of the polarization measurement and impedance measurement show that the corrosion film has limited protective exposure. Results of the polarization measurement and impedance measurement show that the corrosion film has limited protective exposure.

It is still difficult for a fully covered, compact, and anticorrosive corrosion product film to form due to the effect of hydrodynamics of slug flow. The hydrodynamic characteristics of vertical upward gas–liquid two-phase slug flow govern the corrosion mechanism, and are intimately related to the overall corrosion process. Mass transfer characteristic has an adverse effect on the corrosion rate, whereas the wall shear stress and wall normal stress are responsible for the final morphological consequence. Under the peculiar hydrodynamics of pseudo-periodical intermittence of Taylor bubble and liquid slug, the interactions of both the upward and downward wall shear stresses, the fluctuation of wall normal stress make the final morphological consequence of the corrosion extraordinarily serious.

Fig. 16 shows the resultant stress and included angle for wall shear stress and the fluctuation of wall normal stress. The high level of acquisition voltage $U$ represents the Taylor bubble; the low level of acquisition voltage $U$ represents the liquid slug. When a Taylor bubble passing by a given cross-section of the pipe, the positive wall shear stress $\tau_{wf}$ changes from 0 Pa to the maximum $(\tau_{wf})_{max}$, and the fluctuation of the wall normal stress changes from the 0 Pa to the maximum $(\Delta n)_{max}$ as well. Consequently, the resultant stress of the wall shear stress and the fluctuation of wall normal stress reaches its maximum, and the included angle between the resultant stress and the wall shear stress increases from 0° to the maximum (+90°) as well. When a succeeding liquid slug passes, the direction of the wall shear stress is changed upward, namely the negative wall shear stress $\tau_{wls}$ Changes from 0 Pa to the maximum $(\tau_{wls})_{max}$ and the fluctuation of the wall normal stress is changed to 0 Pa again from the maximum $(\Delta n)_{max}$. As such, the resultant stress of the wall shear stress and the fluctuation of wall normal stress changes to the minimum, and the included angle between the resultant stress and the wall shear stress decreases from +90° to the 0° as well. Due to the existence of transition from the leading liquid slug to the succeeding Taylor bubble, the direction of the wall shear stress changes with stress starting to increase, and the fluctuation of wall normal stress increases, as such, the included angle firstly changes to −90°, and then dramatically changes to 0°, further to +90°.

---

**Table 5**

<table>
<thead>
<tr>
<th>Corrosion potential (mV) (vs 316L SS)</th>
<th>Log corrosion current density log (A/cm²)</th>
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<th>Log corrosion current density log (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_{w1} = 0.15$ m/s, $U_{s1} = 0.344$ m/s</td>
<td>1 h, $-600$, $-3.018$, $-630$, $-2.77$</td>
<td>$U_{w1} = 0.45$ m/s, $U_{s1} = 0.344$ m/s</td>
<td>50 h, $-580$, $-3.14$, $-615$, $-2.78$</td>
</tr>
<tr>
<td>75 h, $-540$, $-3.27$, $-560$, $-2.86$</td>
<td>140 h, $-560$, $-2.97$, $-581$, $-2.72$</td>
<td>1 h, $-600$, $-3.018$, $-630$, $-2.77$</td>
<td>50 h, $-580$, $-3.14$, $-615$, $-2.78$</td>
</tr>
</tbody>
</table>
| 75 h, $-540$, $-3.27$, $-560$, $-2.86$ | 140 h, $-560$, $-2.97$, $-581$, $-2.72$ | Table 5 shows the potential of acquisition voltage $U$ represents the Taylor bubble; the low level of acquisition voltage $U$ represents the liquid slug. When a Taylor bubble passing by a given cross-section of the pipe, the positive wall shear stress $\tau_{wf}$ changes from 0 Pa to the maximum $(\tau_{wf})_{max}$, and the fluctuation of the wall normal stress changes from the 0 Pa to the maximum $(\Delta n)_{max}$ as well. Consequently, the resultant stress of the wall shear stress and the fluctuation of wall normal stress reaches its maximum, and the included angle between the resultant stress and the wall shear stress increases from 0° to the maximum (+90°) as well. When a succeeding liquid slug passes, the direction of the wall shear stress is changed upward, namely the negative wall shear stress $\tau_{wls}$ Changes from 0 Pa to the maximum $(\tau_{wls})_{max}$ and the fluctuation of the wall normal stress is changed to 0 Pa again from the maximum $(\Delta n)_{max}$. As such, the resultant stress of the wall shear stress and the fluctuation of wall normal stress changes to the minimum, and the included angle between the resultant stress and the wall shear stress decreases from +90° to the 0° as well. Due to the existence of transition from the leading liquid slug to the succeeding Taylor bubble, the direction of the wall shear stress changes with stress starting to increase, and the fluctuation of wall normal stress increases, as such, the included angle firstly changes to −90°, and then dramatically changes to 0°, further to +90°.
Both experimental results and previous studies by [12,13] show that the main components of the corrosion product film are iron carbonate FeCO$_3$ and iron carbide Fe$_3$C. The N80 steel is corroded away as Fe$^{2+}$, which can be precipitated out of the solution on the coupon substrate as FeCO$_3$ when the concentration of which exceeds the super-saturation level in the solution. Fe$_3$C, as the skeleton of the metal in a classical sense, is the remains on the parent metal substrate after the corrosion. Corrosion product film is brittle, compared to the metal substrate, which has plastic physical property. The brittle material is sensitive for the higher fluid impingement angle, such as 75–90°, and the plastic material is sensitive to the smaller fluid impingement angle, for example, 20–45°. Due to the higher resultant stress with included angle changing from −90° to the +90° accompanied with the frequency more than 2 Hz, the hydrodynamics make the bonding between the metal matrix and corrosion film diminish, until the corrosion film is destroyed and peeled off, leading to the exposure of partial or entire metal to the corrosive reactant and occurring localized corrosion or general corrosion.

Fig. 17 shows the corrosion product film thickness on N80 steel coupons vs different exposure time. When $U_{SG} = 0.45$ m/s, $U_{SL} = 0.344$ m/s, and $U_{SG} = 0.15$ m/s, $U_{SL} = 0.344$ m/s, and $U_{SG} = 0.45$ m/s, $U_{SL} = 0.651$ m/s, the thickness of corrosion product film firstly increases with the increased exposure time, reaching maximum after 75-h exposure; and then decreases with increased exposure time. This can be elucidated as follows: the corrosion product film starts to form on the coupons, although it is not-full covered and non-compact; however, the localized corrosion is initiated due to higher wall shear stress and wall normal stress; with the propagation of the localized corrosion, the micro-turbulent intensity increases dramatically, which sometimes may be ten orders of magnitude higher than that in the smooth pipe; then the localized corrosion further aggravates, resulting in higher corrosion rate, more damage to the corrosion product film, and more pitting. When $U_{SG} = 0.15$ m/s, $U_{SL} = 0.651$ m/s, due to the smaller wall shear stress and mass transfer of slug flow, there exists a favorable condition for FeCO$_3$ precipitation. A corrosion product film starts to form on the coupons, builds-up, and further strengthens. This makes a thicker corrosion product film, and decreases the corrosion rate.

Fig. 18 shows the average area fraction covered by corrosion product film on N80 coupons. It can be seen that the maximum area fraction covered by corrosion product film is no more than 60% due to the effect of hydrodynamics of slug flow. Fig. 19 shows the area fraction vs corrosion depth for N80 steel coupons after 140-h exposure. It can be seen that the corrosion is dominated by general corrosion with small pitting due to higher corrosion depth with smaller area fraction in each experimental conditions. Under higher wall shear stress and mass transfer of slug flow, there is higher corrosion rate, as well as more numerous and deeper pittings.

3.3. Coupling characteristics of hydrodynamics and corrosion

It is essential to develop a mechanistic model based on the simultaneous and interaction of corrosion characteristics and
hydrodynamic characteristics, such as the rate equations of both metal anodic dissolution and oxidants cathodic reductions, transport equations of reactants and products. Nevertheless, an effective mechanistic model incorporating seamlessly all of these factors is not available currently.

When the corrosion rate is electrochemical reaction controlled, mass transfer characteristic has no effect on the corrosion. However, majority of fields and laboratory investigations have shown that the corrosion are both controlled in gas–liquid two-phase slug flow enhanced CO₂ corrosion, namely the mass transfer mechanism and the electrochemical reaction mechanism are of equal importance in determining the corrosion rate. In such a situation, the flow enhanced corrosion is not merely the simple summation of the electrochemical corrosion caused by the corrosive reactants and the mechanical losses caused by the gas–liquid two-phase slug flow, the two causes are synergistical, namely there is a ‘1 + 1 > 2’ effect. There is a strong nonlinear coupling of three factors so that

$$i = D_d nF \frac{dC}{dx}$$

where \(D_d\) is the diffusion coefficient of the ionic species \((\text{m}^2/\text{s})\), \(n\) its valence, \(F\) the Faraday constant \((96,500 \ \text{C})\), and \(dC/dx\) the concentration gradient of the ion of interest.
As shown in Fig. 20, there are two scenarios for the coupling of hydrodynamic characteristics and electrochemical characteristics as follows:

1. Coupling without corrosion product film, and
2. coupling with corrosion product film.

The reduction of H⁺ is the main culprit for the CO₂ corrosion. Hence, only the H⁺ reduction is of interest in the coupling model for convenience. On the naked metal substrate surface, for Scenario 1 shown in Fig. 20, according to the Nernst’s linear concentration diffusion gradient model, the charge transport flux of H⁺ can be expressed as

\[
i = D_H \frac{nF}{\delta_d} \left( \frac{C_b}{C_0} - \frac{C_m}{C_m} \right)
\]

where \( k_{TP} \) is the H⁺ mass transfer coefficient (m/s); \( C_b = 10^{-pH} \) is the bulk concentration (mol/L); \( C_m \) is the concentration at the metal/solution interface (mol/L); \( n = 1 \) for H⁺ valence; \( \delta_d \) is the diffusion boundary layer thickness (m), which differs from the thickness of hydrodynamic boundary layer.

The Fe²⁺ mass transfer has a great effect on the formation of the corrosion product film on the metal substrate surface. The corrosion product film will not only be the diffusion barrier between the metal substrate and the corrosive medium, but also give rise to a concentration gradient of the electrochemical reactants. When super-saturation concentrations of Fe²⁺ and CO₂⁻ next to the metal substrate surface are achieved, a corrosion product film forms, as shown in Scenario 2 of Fig. 20. When the corrosion product film starts to build-up on the metal surface, the corrosion kinetics is changed, the additional mass transport through the corrosion film must be also considered. The charge transport flux of H⁺ can be expressed as

\[
i = k_{TP} nF(C_b - C_f)
\]

followed by
\[ i = k_f n F (C_i - C_m) \]  

(12)

where \( C_i \) is the \( \text{H}^+ \) concentration on the corrosion product film/solution interface (mol/L), \( C_m \) the \( \text{H}^+ \) concentration on the metal/solution interface (mol/L), \( k_f \) the mass transfer coefficient in corrosion product film (m/s).

In Eqs. (10) and (12), when the cathodic current is limited by the transport of \( \text{H}^+ \) to the surface, then the concentration at the surface is zero, \( C_m = 0 \), namely the electrochemical reactions are controlled by the mass transfer of \( \text{H}^+ \). This is valid solely for mass transfer-controlled corrosion.

There has been no advanced method to accurately determine the \( \text{H}^+ \) concentration \( C_m \) at the metal/solution interface so that it is hard to take into account the coupling of hydrodynamics in the practical corrosion process, especially when the corrosion is controlled by electrochemical reaction or by both of mass transfer and electrochemical reaction.

Double-checked by mass-loss method, based on the above analysis on Scenarios 1 and 2, as shown in Fig. 20, and based on the formula for the charge transport flux of \( \text{H}^+ \) controlled by the mass transfer, an empirical correlation for the practical charge transfer transport flux of \( \text{H}^+ \) is suggested to model slug flow enhanced CO\textsubscript{2} corrosion as follows:

\[ i = \frac{\Pi k_{TP} n F C_b}{k_{TP} + k_f} \]

(13)

\[ \frac{1}{k_{TP}} = \frac{1}{k_{TP}} + \frac{1}{k_f} \]

(14)

where \( k_{TP} \) is the total mass transfer coefficient of \( \text{H}^+ \); \( \Pi \) the empirical coefficient, \( 0 < \Pi < 1 \) for the corrosion controlled by electrochemical reaction, \( \Pi = 1 \) for the corrosion controlled by mass transfer, and \( \Pi > 1 \) for the corrosion controlled by both; Eq. (14) only has a physical rather than mathematical meaning in Scenario 1 without corrosion product film, namely \( k_{TP} = k_f \) and \( k_f = 0 \).

Fig. 21 shows the total mass transfer coefficient \( k_{TP} \) and the mass transfer coefficient \( k_f \) of \( \text{H}^+ \). It can be seen that the value of \( k_{TP} \) firstly decreases within the 95-h exposure and then increases after the 95-h exposure when \( U_{SL} = 0.45 \text{ m/s}, U_{SL} = 0.344 \text{ m/s}, \) and \( U_{SL} = 0.15 \text{ m/s} \); the value of \( k_{TP} \) reduces continuously when \( U_{SL} = 0.15 \text{ m/s} \), \( U_{SL} = 0.651 \text{ m/s} \). Nevertheless, the average value of \( k_{TP} \) at different superficial gas and liquid velocities is approximately equal to the
The gas–liquid slug flow enhanced carbon dioxide corrosion of API N80 grade steel in vertical upward pipeline has been experimentally investigated. The following conclusions can be drawn:

1. Gas–liquid two-phase vertical upward slug flow has peculiar hydrodynamics. When both the Taylor bubble and the succeeding liquid slug of a slug unit sequentially pass through a given cross-section of the tube, the direction of wall shear stress is changed twice, which causes larger fluctuations of both mass transfer coefficient and wall normal stress as well. The frequency of the pseudo-periodical alternation by Taylor bubble and succeeding liquid slug is generally above 2 Hz.

2. Experimental results validate that the hydrodynamics of slug flow have significant effects on the CO₂ corrosion. A higher mass transfer coefficient can cause the increase of corrosion rate since the transports of both reactant and corrosion product are increased. The higher wall shear stress can lead to higher corrosion rate by preventing the protective corrosion product film from formation, or by retarding the film growth, and by removing or destroying existing film. The higher wall normal stress fluctuations can also exacerbate the corrosion due to the turbulence, making the corrosion product porous.

3. Within the initial 30-h exposure, the corrosion rate keeps constant; within the 50–85-h exposure, the corrosion rate decreases due to the formation of corrosion product film; if the exposure time is further increased, due to the damage of corrosion product film, accompanied with the galvanic corrosion and pitting corrosion, the corrosion rate is increased, even larger than that at the initial exposure. The hydrodynamic characteristic plays a key role in the corrosion process, larger mass transfer coefficient and/or larger wall shear stress lead to a higher corrosion rate, smaller mass transfer and smaller wall shear stress lead to a lower corrosion rate and is prone to form the corrosion product film on the coupons.

4. A not-fully covered, non-compact, non-protective corrosion product film forms on the coupon due to the effect of hydrodynamics of vertical upward slug flow. It is found that the thickness of the corrosion product film is no more than 12 μm, the area fraction covered by corrosion product film is no more than 60%. The slug flow enhanced CO₂ corrosion is dominated by general corrosion, and the corrosion can further develop into pitting and mesa attack due to localized corrosion.

5. Based on the formula for the corrosion process controlled by mass transfer, an empirical correlation is suggested to model slug flow enhanced CO₂ corrosion. Because that there only exists a non-protective corrosion product film due to the effect of hydrodynamics of slug flow, the mass transfer in corrosion product film can be neglected. The slug flow enhanced CO₂ corrosion is dominantly controlled by mass transfer or by both of mass transfer and electrochemical corrosion reaction.

Fig. 22. Values for the empirical coefficient II.
Acknowledgments

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