Rotating Cylinder Electrode Study on the Influence of Turbulent Flow, on the Anodic and Cathodic Kinetics of X52 Steel Corrosion, in H₂S Containing Solutions

Ricardo Galván-Martínez(1), Juan Mendoza-Flores(2), Rubén Durán-Romero(2) and Juan Genescá-Llongueras *(1)


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RESUMEN

En este trabajo se presentan los resultados obtenidos durante el estudio del mecanismo y de la cinética de corrosión de un acero API X52 en soluciones acuosas que contienen H$_2$S bajo condiciones de flujo turbulento, utilizando un electrodo de cilindro rotatorio (ECR). El estudio se ha realizado a cinco diferentes velocidades de rotación: 0 (condiciones estáticas), 1000, 3000, 5000 y 7000 rpm. Se ha encontrado que bajo condiciones de flujo turbulento aumenta significativamente la velocidad de corrosión y el mecanismo de corrosión está controlado por el proceso de difusión que tiene lugar en la reacción catódica.

Palabras clave: Acero API X52. Electrodo cilindro rotatorio. Flujo. H$_2$S. Transferencia masa.

SUMMARY

This work presents the electrochemical kinetics results measured during the corrosion of API X52 pipeline steel immersed in aqueous environments, containing dissolved hydrogen sulfide (H$_2$S) under turbulent flow conditions. In order to control the turbulent flow conditions, a Rotating Cylinder Electrode (RCE) was used. Five different rotation rates were studied: 0 (or static conditions), 1000, 3000, 5000 and 7000 rpm. It was found that the turbulent flow increases the corrosion rate and the corrosion mechanism for X52 steel exhibits a significant dependence on mass transfer on the cathodic kinetics.

Key words: API X52. Flow. Hydrogen sulfide. Mass transfer. RCE.

Dedicat al Prof. Dr. Lluís Victori, S.J., amb motiu del seu 70è aniversari

RESUM

En aquest treball, es presenten els resultats obtinguts durant l’estudi del mecanisme i de la cinètica de corrosió d’un acer API X52 en dissolucions aquoses que contenen H$_2$S sota condicions de flux turbulent, utilitzant un Electrode de cilindre rotatori (ECR). L’estudi s’ha realitzat a cinc velocitats diferents de rotació: 0 (condicions estàtiques), 1000, 3000, 5000 i 7000 rpm. S’ha trobat que sota condicions de flux turbulent augmenta significativament la velocitat de corrosió i el mecanisme de corrosió està controlat pel procés de difusió que té lloc en la reacció catòdica.


* Corresponding author: genesca@servidor.unam.mx
INTRODUCTION

In the oil industry, H₂S has been associated to damages by corrosion and stress corrosion cracking (SCC) induced by sulphides or hydrogen. H₂S gas can dissolve in aqueous solutions turning them in corrosive solutions, known as «sour». The increment of temperature and/or pressure can increase the aggressiveness of H₂S solution to carbon steel. Corrosion of steel in H₂S containing solutions can be represented according to:

\[ \text{Fe} + \text{H}_2\text{S}_\text{aq} \rightarrow \text{FeS} + \text{H}_2 \]  

(1)

The majority of studies on the corrosion of steels in environments containing dissolved H₂S, have been carried out under static conditions\(^{(7)}\). The main objective of these studies, is the determination of the resistance of different alloys to combined conditions of corrosion and mechanical stresses. In many real situations, H₂S corrosion occurs under flowing conditions, for example, in transport of hydrocarbons in pipelines\(^{(23)}\). Therefore, the influence of flow on the corrosion processes is an important issue to be considered in the design and operation of industrial equipment. The most common type of flow conditions found in industrial processes is turbulent; however, few corrosion studies in controlled turbulent flow conditions are available. With the increasing necessity to describe the corrosion of metals in turbulent flow conditions some laboratory hydrodynamic systems have been used with different degrees of success\(^{(22-25)}\). Among these hydrodynamic systems, rotating cylinder electrodes (RCEs), pipe segments, concentric pipe segments, submerged impinging jets and closed-circuit loops have been used and have been important in the improvement of the understanding of the corrosion process taking place in turbulent flow conditions\(^{(10-17)}\). The use of the rotating cylinder electrode (RCE), as a laboratory hydrodynamic test system, has been gaining popularity in corrosion studies\(^{(10-15)}\). This popularity is due to its characteristics, such as, its operation mainly in turbulent flow conditions, its well-defined hydrodynamics, ease of assembly and disassembly, smaller volume of fluid used, and easier flow and temperature control\(^{(18-21)}\).

It has been found that for a RCE enclosed in a concentric cell, the transition between the laminar and turbulent flow occurs at values of Reynolds number (Re) of 200 approximately\(^{(22-24)}\). The RCE in corrosion laboratory studies is a useful tool for the understanding of mass transfer processes, effects of surface films, inhibition phenomena, etc\(^{(25-27,38)}\), taking place in turbulent flow conditions. However, the use of the RCE has been questioned by some researchers\(^{(23)}\), due to the differences found between the values of corrosion rates measured on pipe flow electrodes and on the RCE. The reasons for this difference are still not well understood. However, some works have provided ideas on the explanation of this apparent difference\(^{(30-34)}\).

Dimensionless analysis using mass transfer concepts showed that the corrosion when controlled by diffusion of one of the species between the bulk fluid and the surface, could be modeled completely by the rate of mass transfer of the rate limiting species and the Re and Schmidt numbers (Sc)\(^{(37-38)}\). In general, the effect of flow can be used to determine if corrosion is under activation, diffusion or mixed control.

EXPERIMENTAL

Test Environment

All experiments were carried out at 20 °C and at the atmospheric pressure of Mexico City (0.7 bar). Two aqueous solutions were used: (a) NACE brine specification 1D196\(^{(26)}\) and (b) 3.5 % NaCl solution. These two test environments were selected due to the fact that, most of the H₂S corrosion laboratory testing is carried out in one of these solutions and the electrochemical behavior has not been reported. In order to remove oxygen from the solution, N₂ gas (99.99%) was bubbled into the test solution for a period of 20 minutes. The measured dissolved O₂ content was lower to 10 ppb. After oxygen removal H₂S gas (99.99%) was bubbled into the test solution until saturation was reached. The measured saturation pH was 4.2 for NACE brine and 4.1 for the 3.5 % NaCl brine.

Experimental Set up

An air-tight three-electrode electrochemical glass cell was used. Cylindrical working electrodes were used in all experiments. These cylinders were made of API X52 steel.\(^{(7)}\) The total exposed area of the working electrodes was 5.68 cm² and 3.4 cm² for static and dynamic conditions, respectively. As reference electrode a saturated calomel electrode (SCE) was used. A sintered graphite rod was used as auxiliary electrode. Prior to each experiment, the steel working electrode was polished up to 600 grit SiC paper, cleaned in deionised water and degreased with acetone. All electrochemical tests were carried out on clean samples and in freshly prepared test solutions. Hydrodynamic conditions were controlled using a Perking-Elmer EG&G Model 636 Rotating Cylinder Electrode (RCE) system. In dynamic conditions, the rotation speeds tested were 1000, 3000, 5000 and 7000 rpm.

Electrochemical Measurements

A Solartron\(^{(22)}\) SI 1280B Potentiostat / Galvanostat was used in all the electrochemical tests. Potentiodynamic polarization curves were recorded at a sweep rate of 1 mV per second. In order to minimize the effect of the solution resistance a Lugging capillary was used.

EXPERIMENTAL RESULTS AND DISCUSSION

Previous work on these systems has shown that the corrosion mechanism for carbon steel exhibits a significant dependence on mass transfer. This has lead various workers to suggest the use of dimensionless analysis as a means of relating laboratory-scale experiments to plant-scale corrosion behavior. For an accurate study of the influence of flow velocity upon the corrosion rate of fluids in motion, the hydrodynamic conditions must be well-defined. The Reynolds number (Re), a dimensionless number dependent on the fluid velocity or the electrode rotation rate, as the case may be, density and viscosity of the fluid, and a characteristic dimension is used to define the type of flow. At low velocities, i.e. at low Re, a stable or laminar flow is encountered. Assuming the fluids under consideration to be Newtonian and incompressible in nature, the shear stress at any point in a laminar flow is given by

\[ \tau = \frac{du}{dy} \]  

(2)

If the velocity is increased, at a critical Reynolds number (Reₐₗₙ), the flow becomes turbulent and an additional mechanism of momentum mass transfer appears, which is caused by rapid and random fluctuations of velocity about its average value. The Reₐₗₙ for the transition between laminar and turbulent flow will vary depending on the geometry and Reₐₗₙ for pipe flow has been experimentally found to be around 2100. The Reynolds number for the RCE (Reₐₗₙ) is given by the expression:
Where \( u_{RCE} \) is the peripheral velocity of the RCE, \( d_{RCE} \) is the RCE diameter, \( \nu \) is the kinematic viscosity of the environment, \( \mu \) is the viscosity of the environment \( (1 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) \) considered for both environments, and \( \rho \) is the density of the environment \( (1.024 \times 10^{3} \text{ kg m}^{-3}) \) considered for both environments. Figure 1 shows the correlation between the rotation rate of the electrode and the equivalent Reynolds number.

Figure 2 shows the measured values of corrosion potential \( (E_{corr}) \) as a function of Reynolds number. \( E_{corr} \) was obtained on the API X52 steel cylindrical samples immersed in NACE brine and 3.5% NaCl solution saturated with hydrogen sulfide (H2S) at different rotation rates \( (0, 1000, 3000, 5000 \text{ and } 7000 \text{ rpm}) \) and \( 20^\circ \text{C} \). This Figure shows that the measured values of the \( E_{corr} \) are affected by the increment of the rotation rate. In both NACE brine and 3.5% NaCl solution, as the \( Re_{RCE} \) (and therefore the rotation rate) increases, \( E_{corr} \) also increases. The measured \( E_{corr} \) corresponding to the 3.5% NaCl solution increased from a value of \( -0.768 \text{ V} \) (at 0 rpm) to a value of \( -0.700 \text{ V} \) (at \( Re_{RCE} = 5.34 \times 10^{4} \), equivalent to 7000 rpm) approximately. The measured \( E_{corr} \), corresponding to the NACE brine, increased from a value of \( -0.750 \text{ V} \) (at 0 rpm) to a value of \( -0.695 \text{ V} \) (at \( Re_{RCE} = 5.34 \times 10^{4} \), equivalent to 7000 rpm) approximately.

In order to obtain an estimation of the corrosion current densities \( (i_{corr}) \) for each system, an extrapolation of the cathodic and anodic branches of the polarization curves was made for each case, in a region of \( \pm 0.150 \text{ V} \) of overpotential, approximately, with respect to the corresponding value of \( E_{corr} \).

Figure 3 shows the estimated values of \( i_{corr} \) for both 3.5% NaCl and NACE brines, as a function of the calculated \( Re_{RCE} \). This Figure demonstrates that there is a clear influence of flow on the measured corrosion rate.

Figure 4 shows the cathodic polarization curves (CPC) obtained on API X52 steel cylindrical electrodes, in the NACE brine saturated with H2S at \( 20^\circ \text{C} \) and at 0.7 bar, as a function of the rotation rate. In this Figure it is possible to see that all CPC (at all rotation rates) have a region where a diffusion process is influencing the overall cathodic current. It is clear that the measured cathodic current is affected by the rotation rate of the electrode. At a constant value of \( E \), as the rotation rate of the electrode increases the measured values of current density also increase.

It is important to note that these features can suggest...
that a diffusion process is taking place on the surface of the cylindrical electrode. If H\(^+\) ions are considered to be the main diffusing species in the environment, it is possible to calculate the cathodic current density due to H\(^+\) reduction (\(i\_{\text{corr}}\)). In order to do this, the expression proposed by Eisenberg, Tobias and Wilke\(^{32}\) was used:

\[
\begin{align*}
    i_{\text{corr}} & = 0.0791 \, n \, F \, C_{\text{H}^+} \, D_{\text{H}^+}^{0.644} \, u_{\text{RCE}}^{0.7} \, \nu^{-0.344} \, R C E
\end{align*}
\]

Where: \(n\) = number of electrons; \(F\) = Faraday constant; \(C_{\text{H}^+}\) = bulk concentration of H\(^+\); \(D_{\text{H}^+}\) = diffusion coefficient; \(\nu\) = kinematic viscosity; \(u_{\text{RCE}}\) = RCE peripheral velocity. This expression indicates a direct relationship of the calculated limiting current density \(i_{\text{corr}}\) to the peripheral velocity of the RCE \(u_{\text{RCE}}\), to a power of 0.7.

Figure 5 compares the different measured and calculated current densities as a function of \(u_{\text{RCE}}\) to a power of 0.7 in NACE brine. The values of cathodic current densities \(i_c\) were taken from the corresponding cathodic polarization curves in Figure 4, at a constant potential of \(-0.860 \text{ V (SCE)}\). The estimated values of corrosion current densities \(i_{\text{corr}}\) correspond to NACE brine showed in Figure 3. The values of cathodic limiting densities \(i_{\text{lim}}\) for H\(^+\) diffusion were calculated with equation (4).

This analysis demonstrates that the measured cathodic current is affected by flow and this current can be associated to the diffusion of H\(^+\) ions from the bulk of the solution to the surface of the electrode, where they reduce to H\(_2\) gas. It also demonstrates that the flow dependency of the \(i_{\text{corr}}\) can be associated to this diffusion process.

Figure 6 shows the cathodic polarization curves (CPC) obtained on the X52 steel cylindrical samples, in 3.5% NaCl solution saturated with H\(_2\)S at 20\(^\circ\)C and 0.7 bar, at different rotation rates. These cathodic curves show a similar behaviour to that one observed in Figure 4. All CPCs (at all rotation range) show a region where a diffusion process is influencing the overall cathodic current. It is clear that the measured cathodic current is affected by the rotation rate of the electrode. At a constant value of potential, as the rotation rate of the electrode increases the measured values of current density also increase.

Figure 7 compares the different measured and calculated current densities as a function of \(u_{\text{RCE}}\) to a power of 0.7 in 3.5% NaCl solution. The values of cathodic current densities \(i_c\) were taken from the corresponding cathodic polarization curves in Figure 6, at a constant potential of \(-0.860 \text{ V (SCE)}\). The estimated values of corrosion current densities \(i_{\text{corr}}\) correspond to 3.5% NaCl solution showed in Figure 3. The values of cathodic limiting densities \(i_{\text{lim}}\) for H\(^+\) diffusion were calculated with equation (4).

The analysis of this Figure 7 confirms the influence of flow on the cathodic kinetics. As the rotation rate of the electrode increases the measured cathodic current also increases. It is also possible to suggest that the measured cathodic current can be associated to the diffusion and reduction of H\(^+\) ions. It is also demonstrated that the flow dependency of the \(i_{\text{corr}}\) can be associated to this diffusion process.
Silverman\textsuperscript{14} has suggested that the method of quantitatively relating the mass transfer relations must also ensure that the interaction between the alloy surface and the transfer of momentum is equivalent for both pipe and rotating cylinder geometries. Then, for the same alloy and environment, laboratory simulation allows to duplicate the velocity-sensitivity mechanism found in the plant geometry. The shear stress is one such measure of the alloy surface-fluid interaction. The shear stress at the wall can be estimated for many geometries so that the following equation may be written\textsuperscript{32, 33}:

\[ \tau_{LAB} = \tau_{PLANT} \]  

Then, for a given system, the mechanism by which fluid velocity affects corrosion rate in the plant is proposed to be identical to that which affects corrosion rate in the laboratory.

Figures 8 to 11 show the dimensionless number analysis as a function of the wall shear stress (\( \tau_{w} \)) and the Reynolds number (\( Re \)). The \( H^+ \) ions are considered to be the main active specie in the environment, in this analysis.

Figures 8 and 9 compare the measured cathodic current density (\( i_c \)) and the corrosion current density (\( i_{corr} \)) as a function of the wall shear stress (\( \tau_{W,RCE} \)) in NACE and 3.5\% NaCl solution. The expression used in the calculation of \( \tau_{W,RCE} \) for the RCE was\textsuperscript{14, 15, 23, 34-37}:

\[ \tau_{W,RCE} = 0.079 Re_{RCE}^{–0.3} \rho_{RCE} \]  

Figure 8 shows \( i_c \) and \( i_{corr} \) as a function of \( \tau_{W,RCE} \) in NACE brine. In this Figure it is possible to see that as measured \( i_c \) and \( i_{corr} \) increases the \( \tau_{W,RCE} \) also increases. These results suggest that the corrosion rate increases as the wall shear stress increases. Figure 9 shows \( i_c \) and \( i_{corr} \) as a function of \( \tau_{W,RCE} \) in NACE brine. This Figure shows the same behavior that the Figure 8, because the measured \( i_c \) and \( i_{corr} \) increase when the \( \tau_{W,RCE} \) also increases. These results also suggest that the corrosion rate increase as the wall shear stress (\( \tau_w \)) increases.

Figure 10 shows the mass transfer coefficient of \( H^+ \) ion, in the form of a dimensionless group, Sherwood number, (\( Sh \)) as a function of the Reynolds number (\( Re_{RCE} \)). The Sherwood number for the RCE (\( Sh_{H^+, RCE} \)) is given by the expression\textsuperscript{35}:

\[ Sh_{H^+, RCE} = \frac{i_{lim,H^+}}{n F D_{H^+} C_{H^+}} \]  

Where the \( k_{H^+, RCE} \) is given in m s\textsuperscript{–1}.

Figure 10. Sherwood number of the specie \( H^+ \) (\( Sh_{H^+} \)) as a function of the Reynolds number. API X52 steel immersed in NACE brine and 3.5\% NaCl solution, saturated with H\(_2\)S at 20 °C and 0.7 bar.
Figure 11 shows the same behavior that the Figure 10, because the mass transfer coefficient increases when the Re_RCE also increases.

The behaviour show in Figures 10 and 11 can suggest that the mass transfer coefficient (ShH+ and kH+) is flow dependent, because it increases as the rotation rate also increases.

Figure 12 shows the measured anodic polarization curves (APC) obtained on API X52 steel cylindrical electrodes immersed in the NACE brine, saturated with H2S at 20 °C and 0.7 bar, for different rotation rates. In this figure, it is possible to observe that the anodic Tafel slopes (b_a) are high. This fact indicates a passivation process, taking place on the surface of the electrode. It is important to note that the APCs measured from 3000 to 7000 rpm are not as influenced by rotation rate of the electrode.

Figure 13 shows the APC obtained on API X52 steel cylindrical electrodes, immersed in the 3.5% NaCl solution saturated with H2S, at 20 °C and 0.7 bar, for different rotation rates. In this figure, it is also possible to observe that the anodic Tafel slopes (b_a) are high. These observations also suggest a passivation process taking place on surface of the electrode. It is important to note that the measured APCs are influenced by the rotation rate of the electrode.

Figure 14 shows the estimated anodic Tafel slopes (b_a) as a function of Re_RCE, on API X52 steel cylindrical electrodes immersed in NACE brine and 3.5% NaCl solution, saturated with H2S at 20 °C and 0.7 bar. The slopes were calculated on each anodic polarization curve, in the region from +0.150 V of overpotential, to the corresponding E_corr. All the estimations of the Tafel slopes, in the NACE brine, were higher than 0.180 V/decade. The calculated Tafel slopes, in the 3.5% NaCl solution, also were higher than 0.180 V/decade.
CONCLUSIONS

1. In both test environments (NACE brine and 3.5% NaCl solution), the cathodic polarization curves show a region that is influenced by a diffusion process, at all rotation rates.

2. All cathodic polarization curves are affected by the rotation rate of the cylindrical electrode. In general, when the rotation rate of the cylindrical electrode increases, the measured cathodic current density also increases.

3. The anodic polarization curves corresponding to 3000, 5000 and 7000 rpm obtained in NACE brine are not affected by the rotation rate.

4. In both test environments (NACE brine and 3.5% NaCl solution), the cathodic polarization curves and the corrosion current density increase as the wall shear stress increases.

5. The mass transfer coefficient \( k_{H^+} \) and \( S_{H^+} \) is flow dependent, because it increases as the rotation rate also increases.

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BIBLIOGRAFÍA


