Cathodic kinetics of API X70 pipeline steel corrosion in H_2S containing solutions under turbulent flow conditions

S. Arzola-Peralta[1]**, J. Mendoza-Flores**[2]**, R. Duran-Romero**[2] **and J. Genesca***[1]

A study has been carried out on the effect of hydrodynamics, temperature and hydrogen sulphide (H_2S) concentration on the corrosion of API X70 steel in a flowing 3 wt-% sodium chloride (NaCl) solution. Potentiodynamic polarisation curves were used to characterise the corrosion behaviour of X70 pipeline steel in 3 wt-%NaCl solutions with H_2S concentrations 0, 100, 650 and 2550 ppm at two temperatures, 20 and 60°C, and at turbulent flow conditions. To control flow conditions, the rotating cylinder electrode (RCE) in turbulent flow regime (100–5000 rev min^{-1}) was used. It was found that the measured cathodic current is influenced by flow and therefore by a diffusion component. By comparing the theoretical and experimental cathodic currents, the H^+ reduction reaction is proposed as the main contribution to the total measured cathodic current density.

Keywords: H2S corrosion, Polarisation curves, RCE, Turbulent flow

List of symbols

C_i	Bulk concentration of species *i*, mol m^{-3}
d_{RCE}	RCE diameter, m
D_i	Diffusion coefficient in solution of species *i*, $m^2\ s^{-1}$
E_{corr}	Corrosion (mixed) potential, V
F	Faraday constant, C mol^{-1}
i	current density, A cm^{-2}
i_{corr}	corrosion current density, A cm^{-2}
i_{lim}	limiting current density, A cm^{-2}
$i_{lim,diff}$	limiting current density component associated with the diffusion of reducible species, A cm^{-2}
$i_{lim,i}$	limiting current density in turbulent conditions for species *i*, A cm^{-2}
k_i	Mass transfer coefficient for species *i*, m s^{-1}
l	characteristic length, m
n	number of exchanged electrons, dimensionless
Re	Reynolds number, dimensionless
Sc	Schmidt number, dimensionless
Sh	Sherwood number, dimensionless
u	flow velocity component in *x* direction, m s^{-1}
u_{RCE}	RCE peripheral velocity, m s^{-1}
V	flow velocity component in *y* direction, m s^{-1}
δ	hydrodynamic boundary layer thickness, m
μ	absolute viscosity, kg $m^{-1}\ s^{-1}$
v	kinematic viscosity, $m^2\ s^{-1}$
ρ	density, kg m^{-3}
τ	fluid shear stress at surface, N m^{-2}

Introduction

Corrosion of steel in hydrogen sulphide (H_2S) containing media has been investigated by several authors[1–6] using electrochemical techniques such as electrochemical impedance spectroscopy and polarisation curves in quiescent systems. Although it has been recognised for many years that hydrodynamic effects are often important in determining the rate of corrosive attack on metals, little attention has been paid to the influence of hydrodynamic factors on the analysis of the kinetics of materials degradation. Several approaches have been used to obtain some assessment of the magnitude of these hydrodynamic effects. These have included techniques such as pumping the corrosive fluid through tubular specimens, impinging the corrosive fluid onto a stationary specimen or rotating the specimens in a bath of corrosive fluid. The geometry selected in the present study was a rotating cylinder.

The rotating cylinder electrode (RCE) has been used for many years to simulate flow conditions as proposed, among others, by Silverman,[7–10] Holser *et al.*,[11] Nesic *et al.*,[12] Efird *et al.*[13] and Kim *et al.*[14] The RCE is a tool that allows working under controlled turbulent flow conditions in laboratory.[11,15] The RCE provides more uniform behaviours on the electrode surface than the rotating disk electrode (RDE) when turbulent flow conditions are reached (the central region of the RDE is always laminar). It has a well defined hydrodynamic behaviour and a uniform distribution of current.[11,16,17] The RCE also has some practical advantages such as the

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[1] Dpto. Ingeniería Metalúrgica, Facultad Química, Universidad Nacional Autónoma México (UNAM), Ciudad Universitaria, 04510 México DF, Mexico
[2] Instituto Mexicano del Petróleo, Eje Central Lázaro Cardenas No. 152, 07730 México DF, Mexico

*Corresponding author, email genesca@servidor.unam.mx

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need of relatively small quantities of test fluid and ease of cleaning. It has been demonstrated that the relative motion between metal surface and the environment influences the corrosion process.[18] This motion might increase the heat and mass transfer of the reactants from the bulk of the electrolyte to the metal surface, leading to the increase of corrosion, erosion, etc. Many industrial processes involve liquid movement throughout metallic structures such as pipelines and containers, in which the flow condition is a very important variable. In the present work, the cathodic kinetics of the corrosion mechanism of a pipeline steel was studied using potentiodynamic polarisation curves, with the RCE at turbulent flow conditions ($Re>300$).

Experimental

All electrochemical experiments were carried out with a Solartron 1280B electrochemical measurement unit, controlled by the Corrware Software. A conventional three electrode system was used. A Perkin-Elmer EG&G Model 636 RCE was used to control turbulent flow conditions. In total, 100, 1000, 3000 and 5000 rev min^{-1} rotation rates were tested. The open circuit potential E_{corr} was measured for 12 min, before each polarisation runs.

Cathodic polarisation curves were recorded by linear sweep voltammetry at a scan rate of 0·1–0·2 mV s^{-1} starting the potential sweep at the rest potential or corrosion potential E_{corr} towards more cathodic potentials. Laboratory tests indicated that slower scan rates produced no significant change on the measured current. All electrochemical tests were carried out on clean samples and in freshly prepared solutions. In each experiment, the cathodic sweeps were conducted only once for a single working electrode (WE) specimen and a given electrolyte.

A 1 L airtight three electrode electrochemical glass cell was used, as described previously.[1] The WE was machined from the parent material API X70 and had a diameter of 1·2 cm and a total exposed area of 3·071 cm^2. The counter electrode used was a rod of sintered graphite. A saturated calomel electrode was used as the reference electrode. The steel surface was first polished with 600 grit SiC paper, cleaned and degreased with acetone and finally rinsed with distilled water. The effect of abrading the steel surface with 600 grit SiC paper is thought to be minimal. Normally, a 600 grit finish is not considered to affect the surface or the underlying material to any significant degree; therefore, it is used as the standard preparation technique, insuring that a standard, film free surface was achieved according to ASTM G5.[19] Following these preparations, the polarisation tests were initiated.

The test environment was a 3%NaCl aqueous solution. Four deaereated solutions were studied containing 0, 100, 650 and 2550 ppm H_2S. The measured pH values of these solutions were 6·94, 5·34, 4·38 and 4·11 respectively. The oxygen dissolved in all solutions was removed by purging the environment with N_2 gas (99·99%) for a period of 45 min before each test.

In order to determine the purging time needed to remove all O_2 from the solution, a rotating cylindrical platinum electrode was cathodically polarised in a 1M sodium sulphate solution at room temperature and at different rotation rates. It was established that the region associated to the mass transfer reduction of oxygen on the cathodic polarisation curve disappeared after 45 min of purging time.

Just after oxygen removal, H_2S gas (99·99%) was bubbled into the solution. For the lower concentrations of H_2S, an aliquot was taken from an already saturated solution in order to prepare the concentrations of 650 and 100 ppm. All experiments were performed at the atmospheric pressure of Mexico City (0·7 bar) and at two different temperatures, 20 and 60°C. All the experiments were carried out by triplicate in order to check the reproducibility of the results. A plot of three representative measured plots is presented owing to the fact that it was found that the experimental variations of the measurements was negligible.

Experimental results and discussion

The RCE has been used extensively in corrosion research because of the fact that the flow is essentially turbulent,[20] even at low rotational velocities.[18–21] The critical Reynolds number Re for the transition from laminar to turbulent flow lies within the range of 50–300 for a smooth surface laboratory RCE.[22] The Reynolds number for a RCE is given by the following expression

$$\mathrm{Re}=\frac{u\rho d_{\mathrm{RCE}}}{\mu} \tag{1}$$

where u is the peripheral velocity of the RCE, ρ is the density of the environment, d_{RCE} is the diameter of the RCE and μ is the viscosity of the environment. It is clear from this equation that there is a linear relationship between the Reynolds number and the rotation rate of the electrode.

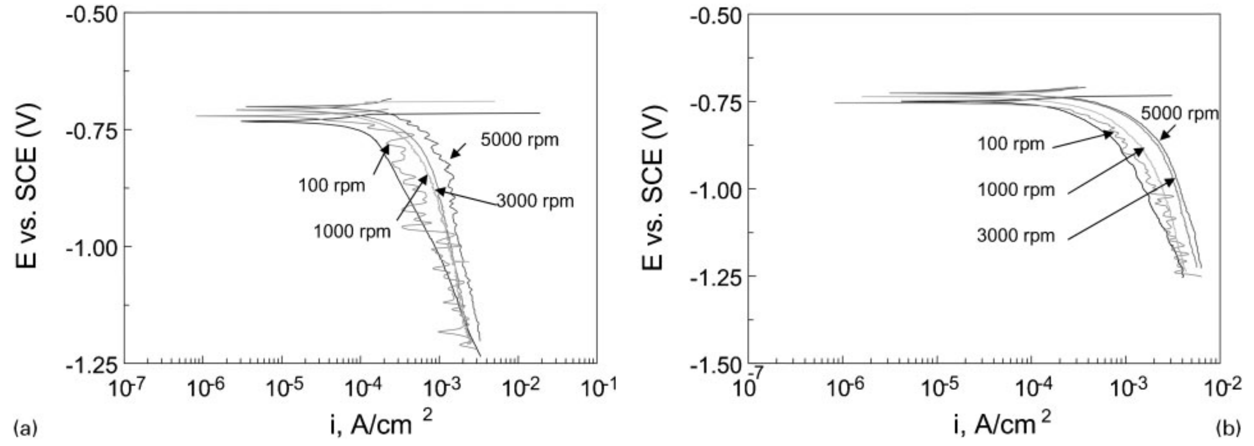
The RCE provides a relatively large surface area and is well suited for turbulent flow corrosion laboratory studies. The Sherwood number for the RCE and for a given species 'i' Sh_{i} is given by

$$Sh_{\mathrm{i}}=\frac{k_{\mathrm{i}}d_{\mathrm{RCE}}}{D_{\mathrm{i}}} \tag{2}$$

where k_{i} is the mass transfer coefficient for species 'i', d_{RCE} is the diameter of the RCE and D_{i} is the diffusion coefficient of species 'i'.

To obtain turbulent flow conditions, a rotation rate range from 100 to 5000 rev min^{-1} was selected, corresponding to a Re number range from 754 to 37 714. It has been found that for a RCE enclosed in a concentric cell, the transition between the laminar and turbulent flow occurs at low rotation rates. This transition has been suggested to occur at values of Reynolds number of $\sim$200.[16] Under the experimental conditions prevailing in the authors' study, a Reynolds value of 268 will be equivalent to a peripheral velocity of 0·024 m s^{-1} (38 rev min^{-1}) for a cylinder of 0·012 m diameter immersed in a fluid of $\nu=1\times10^{-6}$ m^2 s^{-1}, e.g. pure water.

For the RCE system used, at each Re number studied, the corrosion potential E_{corr} increased with time during the first 24 h of exposure. The effect of increasing the Re number is to increase the availability of diffusion species (H_2S and H^+) at the surface of the electrode, which in turn will polarise the corrosion reaction in the nobler direction. Therefore, the steady state corrosion potential is expected to increase as the Re increases, as observed.



1 Cathodic polarisation curves (100–5000 rev min^{-1}) of the X70 steel in a 3 wt-%NaCl solution with 2550 ppm of H_2S at *a* 20 and *b* 60°C

Figure 1 shows the cathodic potentiodynamic polarisation curves corresponding to the NaCl solution with 2550 ppm of H_2S at 20 and 60°C. The following features can be observed in this figure. At all rotation rates, a well defined cathodic limiting current density i_{lim} region can be observed. This region is clearly affected by the rotation rate of the electrode and in general terms, as the rotation rate of the electrode increases, the value of current density at which i_{lim} appears also increases. These facts can suggest that a diffusion controlled process, taking place on the surface of the electrode, is being measured.

For this hydrodynamic system, only one plateau (diffusion limited current) was observed in the cathodic region at each *Re* number. This plateau could be due to either the reduction of H_2S or H^+ diffusing through the diffusion boundary layer only or to the reduction of H_2S or H^+ diffusing through the diffusion boundary layer and an incompletely reduced surface film, depending on the value of the *Re* number. In all cases, the current plateau is controlled by mass transfer.

According to the analysis proposed by Schmitt and Rothmann[23] and Mendoza and Turgoose[24], it is possible to establish the different cathodic reactions involved in a system controlled by mass transfer and under flow turbulent conditions.

Analysis of cathodic reaction

In an H_2S containing solution, in the absence of dissolved oxygen, the cathodic reaction of carbon steel, responsible for the corrosion of iron, may be attributed to hydrogen evolution produced by the reduction of hydrogen ions, where the hydrogen ions are supplied by dissociation of H_2S as follows

$$2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

In the present testing solution, the source of H^+, which promotes the above hydrogen evolution, may be H_2S or H_2O.

Bolmer[25] showed that hydrogen evolution, in the presence of H_2S, might be represented by the overall reaction

$$2H_2S + 2e^- \rightarrow H_2 + 2HS^- \tag{4}$$

This reaction is limited by diffusion of H_2S to the electrode surface when the overpotential is far removed from the E_{corr}.[25,26]

The measured experimental cathodic current should be a consequence of all the possible reduction reactions that can occur in the NaCl H_2S system. The following reactions have been proposed[25,27] as the main cathodic reactions in H_2S containing solutions in the absence of oxygen

$$2H^+ + 2e^- \rightarrow H_2 \tag{4a}$$

$$2H_2S + 2e^- \rightarrow H_2 + 2HS^- \tag{4b}$$

$$2HS^- + 2e^- \rightarrow H_2 + 2S^{2-} \tag{4c}$$

$$H_2S + 2e^- \rightarrow H_2 + 2S^{2-} \tag{4d}$$

According to different authors,[25,26,28] reactions (a) and (b) seem to be the more probable.

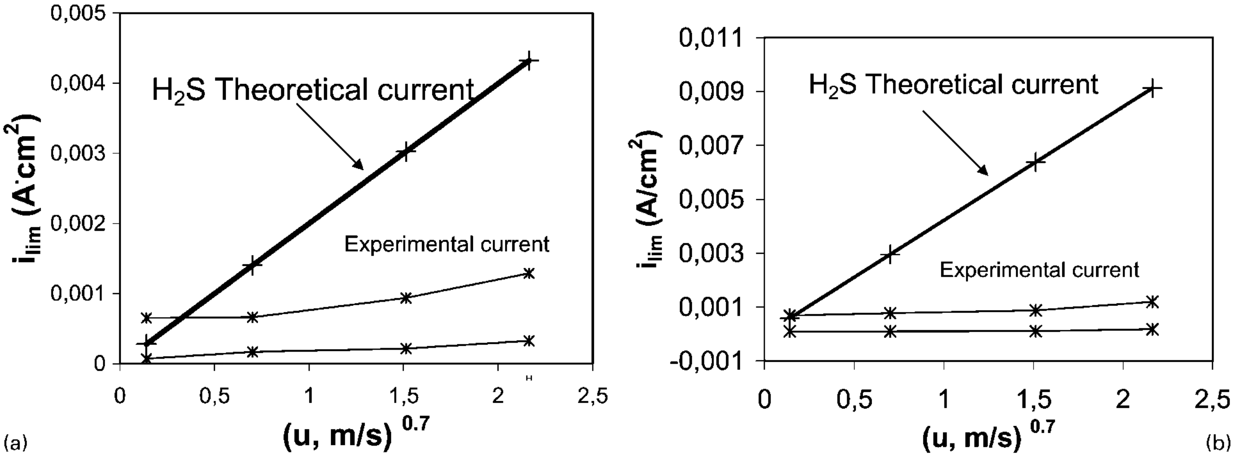
As it was proposed by Eisenberg *et al.*,[29] for the RCE, it is possible to calculate the contribution to the limiting cathodic current for a species '*i*' using the following equation

$$i_{\text{lim,i}} = 0{\cdot}0791 nFC_i d_{\text{RCE}}^{-0{\cdot}30} v^{-0{\cdot}344} D_i^{0{\cdot}644} u_{\text{RCE}}^{0{\cdot}7} \tag{5}$$

where the $i_{\text{lim,i}}$ is the limiting current density in turbulent conditions for species '*i*' (A m^{-2}), F is the Faraday constant, n is the number of electrons involved in the electrochemical reaction, d_{RCE} is the diameter of the rotating cylinder (m), v is the kinematic viscosity of the solution (m^2 s^{-1}), C_i is the bulk concentration of the chemical species '*i*' (mol m^{-3}), D_i is the diffusion coefficient (m^2 s^{-1}) of '*i*' and u_{RCE} is the peripheral velocity of the RCE (m s^{-1}).

If the above expression for the RCE proposed by Eisenberg *et al.*[29] is considered and the values of limiting current densities i_{lim} are taken from Fig. 1 at each rotation rate, then plotted *v.* the rotation rate of the electrode at a power of 0·7, $u_{\text{RCE}}^{0{\cdot}7}$, Fig. 2 for H_2S and Fig. 3 for H^+ are obtained. In these figures, the rotation rate of the electrode is expressed as peripheral velocity u_{RCE}.

In these figures, the experimental data obtained at two different potentials, selected inside the diffusion region, are indicated by the cross-markers. This analysis shows



2 Comparison between H_2S theoretical (bold line) and experimental limiting current density: 100 ppm H_2S at *a* 20 and *b* 60°C, as function of rotation rate of RCE

that the measured i_{lim} is affected by the rotation rate of the electrode and a linear relationship with $u^{0.7}$ clearly exists between both parameters, as predicted for the RCE equation proposed by Eisenberg *et al.*[29] (equation (5)), which can be expressed in a simplified form by equation (6)

$$i_{\mathrm{lim,i}} = A_{\mathrm{i}} u_{\mathrm{RCE}}^{0.7} \qquad (6)$$

where A_{i} is a constant. Concerning the flow dependent component in Figs. 2 and 3, if the concentration of dissolved O_2 is considered as negligible, then the species in solution capable of being reduced are H_2S and H^+. As the concentration of H_2O can be considered constant and the reduction rate of H^+ and H_2S slow and influenced by the diffusion of reactants, then it is possible to assume that in H_2S solution, both the H^+ ions and H_2S are reduced at the surface. Then, at a given flow rate, the total diffusion limited current $i_{\mathrm{lim,diff}}$ for a H_2S solution could be described by the addition of two components

$$i_{\mathrm{lim,diff}} = i_{\mathrm{lim,H^+}} + i_{\mathrm{lim,H_2S}} \qquad (7)$$

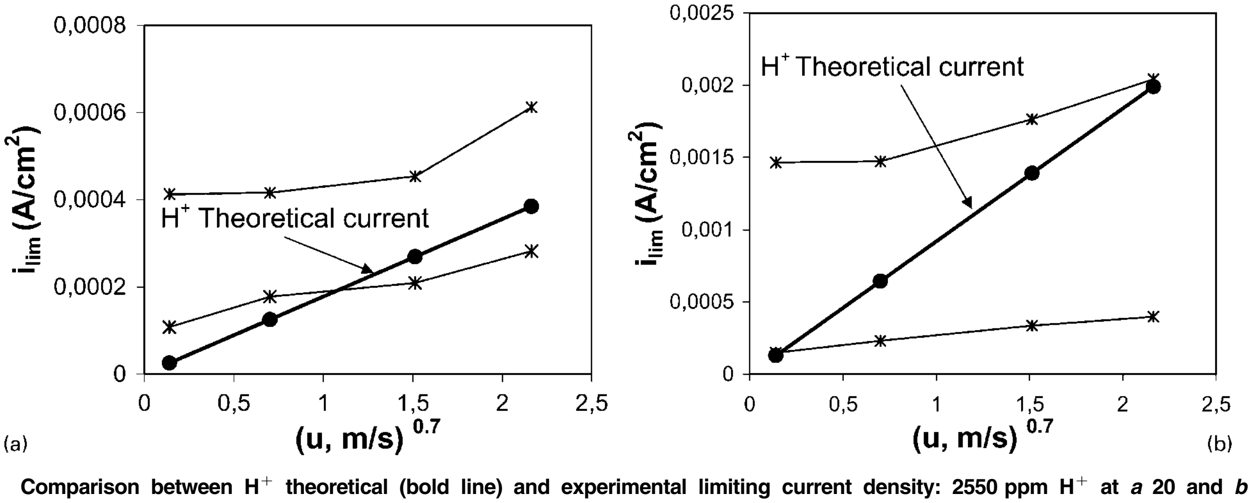
where $i_{\mathrm{lim,H+}}$ and $i_{\mathrm{lim,H2S}}$ are the limiting current densities in turbulent flow conditions for H^+ ions and H_2S molecules respectively.

These components can be defined in turbulent flow conditions in an analogous way as Schmitt and Rothmann[23] did for laminar flow conditions on the rotating disk electrode, but using the relationship proposed by Eisenberg *et al.*[29] for the mass transfer on the RCE (equation (5)).

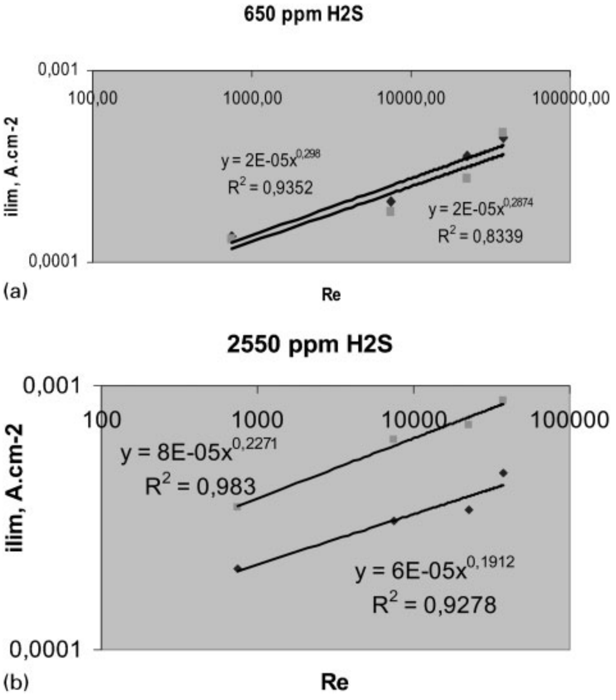
Schmitt and Rothmann[23] and Mendoza[24] proposed that the theoretical i_{lim} for H_2S and H^+ reduction calculated by equation (5) could be compared with the experimentally measured i_{lim}, in order to obtain information about the predominant cathodic reaction (kinetics).

To determine the theoretical relationship between i_{lim} and $u_{\mathrm{RCE}}^{0.7}$ for either H_2S or H^+, the values of density and kinematic viscosity were calculated according to the analysis proposed by Mendoza.[24] The other parameters, such as the H^+ and H_2S diffusion coefficients, were taken from reference.[30] Substituting these parameters for each H_2S concentration, the theoretical relationship for H_2S and H^+ reduction reaction can be obtained, as shown in Figs. 2 and 3 respectively.

From these figures, it is possible to note the linear relationship between the experimental limiting current density and the peripheral velocity of the RCE, at the two different potentials inside the mass transfer area. Although the H_2S reduction shows a linear relationship



3 Comparison between H^+ theoretical (bold line) and experimental limiting current density: 2550 ppm H^+ at *a* 20 and *b* 60°C as function of rotation rate of RCE



a 650 ppm H_2S; *b* 2550 ppm H_2S

4 Experimental limiting current density i_{lim} as function of Reynolds number *Re* at 20 (◇) and 60°C (□)

with the rotation rate of the electrode at a power of 0·7 (bold line, Fig. 2), its value does not adjust to the theoretical current, which fits better to the H^+ reduction (bold line, Fig. 3), as shown in Fig. 3. According to this analysis, one conclusion can be obtained that the dominant cathodic reaction is the reduction of hydrogen ions H^+.

As a first approximation to the possible cathodic reaction mechanism prevailing under the experimental conditions studied, it is proposed as a first step

$$H_2S_{(g)} \Leftrightarrow H_2S_{(aq)},\ K=0{\cdot}1023\ \text{mol atm}^{-1},\ pK=0{\cdot}99 \quad (8)$$

In aqueous solutions, H_2S is a weak acid. At 20°C[31]

$$H_2S_{(aq)} \Leftrightarrow H^+_{(aq)} + HS^-_{(aq)},\ pK_{a1}=6{\cdot}88 \pm 0{\cdot}02 \quad (9)$$

$$HS^-_{(aq)} \Leftrightarrow H^+_{(aq)} + S^{2-}_{(aq)},\ pK_{a2}=14{\cdot}15 \pm 0{\cdot}05 \quad (10)$$

As predicted by reaction (9), it is possible to get in solution H_2S, H^+ and HS^-. Under turbulent flow conditions, as has been experimentally demonstrated, the diffusion limited reaction is a consequence of H^+ diffusion.

The polarisation curves shown in Fig. 3 show the effect of rotation rate (*Re* number) on the cathodic limiting current density i_{lim}. Figure 4 shows the variation of the measured i_{lim} with *Re* at the two studied temperatures 20 and 60°C. It is evident that for a given temperature, i_{lim} increases as the *Re* number increases. This can be attributed to the increased supply of H^+ ions by eddy diffusion, from the bulk of solution to the metal surface, leading to a higher i_{lim} value.

As the temperature of the environment increases, the rate of H^+ diffusion to the metal surface also increases; the viscosity of solution decreases and the electrical conductivity of the solution increases. All these factors can enhance the corrosion rate. Figure 4 shows that the measured values of i_{lim} increase as the temperature of the environment increased from 20 to 60°C over all the *Re* range. This behaviour can be interpreted as follows: the temperature increment accelerates both the cathodic reaction rate and diffusion rate of H^+ by increasing the molecular movement of the ions. Additionally, one factor that plays an important role in determining the corrosion rate is *Re* number. The increment in the *Re* number enhances the eddy diffusion of H^+ ions, from the bulk of solution to the metal surface, leading to a higher corrosion rate. Figure 4 clearly indicates that measured values of i_{lim} at 60°C are higher than those measured at 20°C. When *Re* increases, the amount of H^+ supplied to the surface from the bulk will also be increased. Then the combined effect of two variables, namely, hydrogen molecular diffusivity and solution velocity (eddy diffusion), will determine the trend of the corrosion rate with increasing temperature.

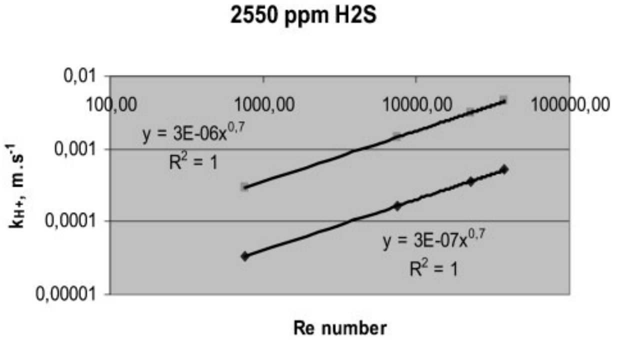
Using the fitest method on the experimental data shown in Fig. 3, the mathematical relationships between the measured i_{lim} and the *Re* number shown in Table 1 are obtained.

Mass transfer and surface shear effects may have a profound effect on the rate of material degradation, either by modifying the rate of transport of chemical species to or from the surface or by shear stripping protective films from the metal/solution interface. As a result, an accurate simulation of corrosion phenomena that occur in pipelines can be made in the laboratory only if the hydrodynamic effects are taken into account. Then, parameters such as the mass transfer coefficient k_i,[7,9,32] shear stress at the wall τ[7–13] and the Sherwood number *Sh*[33,34] can be derived from these results.

Values of limiting current density were used to estimate the mass transfer coefficients *k* for the whole range of *Re* and temperature. Experimental correlations of *k* or *Sh* with *Sc* are not necessarily simple. This is because changing *Sc* by temperature leads to the change of many physical properties that have a direct influence on *k* or *Sh*. These physical properties are mainly the hydrogen diffusivity D_{H^+}, bulk concentration C_b and kinematic viscosity v. Figure 5 shows the variation of the calculated mass transfer coefficient k_{H^+}, with *Re* as obtained from the i_{lim} in Fig. 1. Mass transfer studies of electrochemical reactions are normally carried out under

Table 1 Limiting current density i_{lim} relationships calculated for different experimental conditions studied

H_2S, ppm	Temperature, °C	Equation	Correlation coefficient
100	20	i_{lim}=1E-04 $Re^{0{\cdot}124}$	0·589
100	60	i_{lim}=1E-05 $Re^{0{\cdot}323}$	0·997
650	20	i_{lim}=2E-05 $Re^{0{\cdot}287}$	0·834
650	60	i_{lim}=2E-05 $Re^{0{\cdot}296}$	0·935
2550	20	i_{lim}=6E-05 $Re^{0{\cdot}191}$	0·928
2550	60	i_{lim}=8E-05 $Re^{0{\cdot}227}$	0·983



5 Mass transfer coefficient K_{H+} as function of Reynolds number *Re* at 20 (◇) and 60°C (□): 2550 ppm H_2S

mass transfer limited current conditions. When limiting conditions prevail, the mass transfer coefficient for a given species '*i*' k_i can be expressed as

$$k_i = \frac{i_{lim,i}}{nFAC_{b,i}} \tag{11}$$

where $i_{lim,i}$ is the mass transfer limited current (A) for species '*i*', F is the Faraday constant, n is the number of electrons involved in the reaction, A is the area of the WE (cm^2) and $C_{b,i}$ is the bulk concentration of the diffusing species "*i*".

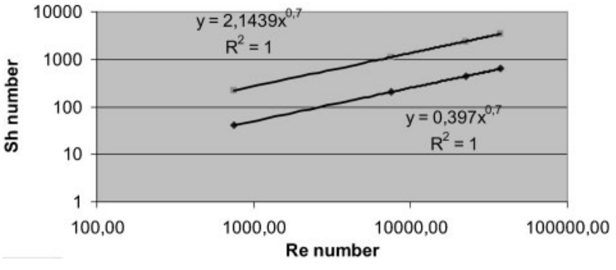
It is evident from Fig. 5 that at the two test temperatures, there is a linear relationship between k_H+ and the *Re* number. As Silverman pointed out[10], the measured mass transfer coefficient could be converted to the Sherwood number and plotted as a function of the Reynolds number. The resulting plot is in good agreement with the theoretical values calculated with the equation proposed by Eisenberg for turbulent flow conditions.

The *Sh* number is a dimensionless number that expresses mass transport under forced convective flow conditions. The *Sh* number and the mass transfer coefficient k_i are related by the equation

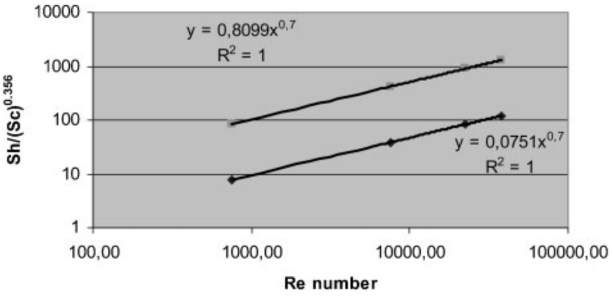
$$Sh_i = \frac{k_i d_{RCE}}{D_i} = \frac{d_{RCE}}{\delta_N} \tag{12}$$

where k_i is the mass transport coefficient of species '*i*', d_{RCE} is the outside diameter of the rotating cylinder (characteristic length), D_i is the diffusion coefficient of species '*i*', (the diffusivity of H^+ in NaCl H_2S system) and δ_N is the Nernst diffusion layer thickness. The *Sh* number expresses the size of the characteristic length in comparison with the Nernst diffusion layer.

Figure 6 shows the calculated Sherwood numbers as a function of the calculated *Re* number. From this figure, it is evident that the Sherwood number *Sh* increases as the *Re* number increases. Based on this study, the *Re* number dependence with the *Sh* number, appears to be proportional to a 0·7th power law. The coefficient of 0·7, which is the flow dependence of the *Sh* number, almost corresponds to the coefficients of the *Re* number, as indicated by the Eisenberg relationship[29] and Chilton and Coburn analogy.[35] The same information could be obtained from Fig. 7 by plotting $Sh/Sc^{0.356}$ *v.* *Re* number. Eisenberg *et al.*[29] showed that in the range of $10^3<Re>10^5$, equation (5) is a straight line approximation over a more limited *Re* number range.



6 Sherwood numbers as function of Reynolds number at *a* 20 (◇) and *b* 60°C (□)



7 Variation of dimensionless corrosion rate, expressed as *Sh* number as function of *Re* number for two temperatures studied, *a* 20 (◇) and *b* 60°C (□)

In the case of a predominating forced convection, the mass transfer correlation can be written in the form of

$$Sh = a\mathrm{Re}^b Sc^c \tag{13}$$

The values of *a*, *b* and *c* depend upon both electrode geometry and flow conditions.[22] For example, the *Re* exponent *b* tends to be greater in turbulent flow than in laminar flow. It is common to consider the Schmidt *Sc* exponent *c* to have a value of 1/3, in accordance to known hydrodynamic theory.[22]

The case of a smooth RCE was first extensively studied by Eisenberg *et al.*[29] who achieved the following empirical correlation

$$Sh = 0{\cdot}079\mathrm{Re}^{0{\cdot}70} Sc^{0{\cdot}356} \tag{14}$$

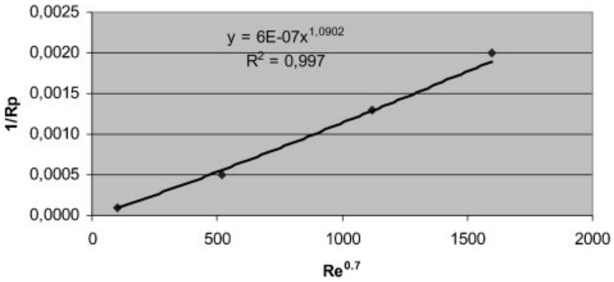
while Gabe *et al.*[21] have proposed expressions of the type

$$Sh = 0{\cdot}079\mathrm{Re}^{0{\cdot}74} Sc^{0{\cdot}356} \tag{15}$$

for the case of metal deposition.

Silverman[10] compiled various *Sh* number *v.* *Re* number relationship for a hydrodynamically smooth rotating cylinder, similar to but not equal to equation (14).

Concerning the effect of corrosion products formed on the RCE on its mass transport properties, Walsh,[22] among others researchers, stated that the enhancement of the mass transport towards the surface of a RCE, with a metal powder deposit, depends upon the increased surface area and enhanced microturbulence at the RCE surface. It may be expressed relative to a smooth cylinder as a predicted enhancement factor β, which depends on the peripheral velocity for an RCE. Although the authors have experimental evidence of mackinawite formation[1] on the RCE surface, under the experimental conditions prevailing in this study, no attempt was made to take into account the possible enhancement in mass transport to an RCE by the effect of the sulphide film formed.



8 Corrosion rate, as 1/*Rp*, as function of Reynolds number at 20°C

In the three studied H_2S concentrations, the measured cathodic current showed a linear dependence on a log log scale, with the derived parameters *Sh* number (Fig. 6) and mass transfer coefficient *k* (Fig. 5). This behaviour indicates that the cathodic current is controlled by the mass transfer rate.

For a corrosion system controlled by diffusion, the following relationship is valid

$$i_{\mathrm{lim}} \approx i_{\mathrm{corr}} \tag{16}$$

The *Sh* number is directly related to the limiting current density of an electrochemical system, according to equations (11) and (12). Then Fig. 7 shows the variation of a dimensionless parameter that can be regarded as a representative of the corrosion rate, expressed as the *Sh* number, as a function of the *Re* number for the two test temperatures. At both temperatures, a clear linear relationship can be observed, indicating that corrosion is under mass transfer control, therefore, equation (16) is valid. The corrosion rate would then coincide with the limiting current density, for the cathodic reduction of H^+. If diffusion of H^+ ions determines the corrosion rate, the process will be under cathodic control. Then, within certain limits, the corrosion current will be independent of the slope of the anodic curve in an Evans diagram. This observation can explain why the rate of general corrosion, in H_2S containing solutions, is practically the same for different types of steel.

Mass transfer theory can be applied to estimate corrosion rates for systems that are under diffusion control and not exhibiting passivity phenomena. Corrosion controlled by mass transfer rate can usually be assumed, if the slope of the straight line, when the corrosion rate is plotted against the Reynolds number, has a value of ~0·7. In Fig. 8, as the parameter 1/*Rp* directly related to i_{corr} is plotted *v. Re* number, a clear linear relationship is observed with a calculated slope value of 0·763.

Conclusions

It was observed experimentally that in the corrosion process of X70 steel in H_2S containing solutions under turbulent flow conditions, the main cathodic reaction corresponds to the H^+ reduction

$$2H^+ + 2e^- \rightarrow H_2$$

It can be assumed that corrosion is being limited by the mass transfer rate. This is because the calculated slope of the straight line found in a plot of the measured data *Sh v. Re* number is 0·7, according to the work of Eisenberg *et al.*[29] Then the above reaction can be assumed to be under complete mass transfer control.

Increasing *Re* increases the corrosion rate for the two studied temperatures, 20 and 60°C, and additionally, the dependence of corrosion rate *Sh* on *Re* varies with temperature.

Increasing the temperature from 20 to 60°C enhances the corrosion rate in the range of *Re* studied.

As the main cathodic reaction was found to be the H^+ reduction, the corrosion process in this environment will be strongly influenced by the pH value.

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