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Study of the Mass Transport on Corrosion of Low Carbon Steel Immersed in Sour Solution Under Turbulent Flow Conditions

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1. Introduction

A corrosion process can be influenced, in different ways, by the relative movement between the metal and the corroding environment. This relative movement can increase the heat and mass transfer of reactants towards and from the surface of the corroding metal, with a consequent increase in the corrosion rate. Also, if solid particles are present, removal of protective films, erosion and wear on the metallic surface can occur. The corrosion of the metallic structure under turbulent flow is complex, but this problem has been studied mainly in the oil industry (Garnica-Rodriguez et al., 2009; Genesca et al., 2010; Mora-Mendoza et al., 2002; Papavinasam et al., 1993; Poulson, 1993), where, the flow and some gases are very important in the behaviour of the phenomenon processes. This oil industry has processes that involve the movement of corrosive liquids in metallic structures, for example, the transport of mixtures of liquid hydrocarbons and gas with water through pipes. Therefore the influence of flow on the corrosion processes is an important issue to be considered in the design and operation of industrial equipment. This influence is complex and many variables are involved. Many observations of flow-accelerated corrosion problems have been documented (Dean, 1990; Garverick, 1994; Poulson, 1993). One aim that has been so much studied in the petroleum industry is the effect of flow and dissolved gases, such as hydrogen sulphide (H_2S) and carbon dioxide (CO_2).

The most common type of flow conditions found in industrial processes is turbulent and according to increasing of the necessity to describe the corrosion of metals in turbulent flow conditions some laboratory hydrodynamic systems have been used with different degrees of success (Poulson, 1983, 1993, 1994). Among these hydrodynamic systems, rotating cylinder electrodes (RCE), pipe segments, concentric pipe segments, submerged impinging jets and close-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 (Liu et al., 1994; Lotz, 1990; Schmitt et al., 1991; Silverman, 1984, 1988, 1990).

The use of the RCE, as a laboratory hydrodynamic test system, has been gaining popularity in corrosion studies (Nesic et al., 1995, 2000). This popularity is due to its characteristics, such as, it operates mainly in turbulent flow conditions; it has a well understood mass transfer properties and it is relatively easy to construct and operate (Gabe, 1974; Schlichting & Gersten, 1979; Gabe & Walsh, 1983; Poulson, 1983). The critical Reynolds number, *Re*, for the transition from laminar to turbulent flow is 200 approximately, for a smooth surface laboratory RCE (Gabe, 1974; Gabe & Walsh, 1983; Poulson, 1983, 1993; Galvan-Martinez et al., 2010). This Reynolds value will be equivalent to a rotation rate $\approx$ 38 rpm, for a cylinder of 0.01 m of diameter immersed in a fluid of ν = 1.0E-06 m²s⁻¹ (e.g. pure water). When the RCE is immersed in a fluid and rotated at a very low rotation rate the fluid moves in concentric circles around the cylinder (laminar conditions). As the rotation rate of the cylinder increases the flow pattern is disrupted, cellular flow patterns, known as "Taylor vortices", appear and the turbulent condition develops. These vortices enhance the mass, momentum and heat transfer at the rotating electrode (Gabe, 1974; Gabe & Walsh, 1983). In 1954, some researchers published what it is now considered as the basic study on the mass transfer characteristics of the RCE (Eisenberg et al., 1954).

The Reynolds number for a RCE is given by the following expression

$$Re_{RCE} = \frac{\mathrm{u}_{RCE} d_{RCE}}{\nu} = \frac{\mathrm{u}_{RCE} d_{RCE} \rho}{\mu} \qquad (1)$$

Where u_{RCE} is the peripheral velocity of the RCE, d_{RCE} is the diameter of the RCE, ρ and μ are the density and viscosity of the environment, respectively. It is clear from this equation that there is a linear relationship between the Reynolds number and the rotation rate of the electrode. Figure 1 shows the correlation between the rotation rate of the electrode and the equivalent Reynolds number.

The RCE in corrosion laboratory studies is an useful tool for the understanding of mass transfer processes, effects of surface films, inhibition phenomena, etc., (Galvan-Martinez et al., 2010; Mendoza-Flores et al., 2002) taking place in turbulent flow conditions. However, the use of the RCE has been questioned by some researchers (Efird et al., 1993), due to the differences found between the values of corrosion rates measured on pipe flow electrodes and on the RCE. The reasons for these differences are still not well understood. However, some works have provided ideas on the explanation of this apparent difference (Mendoza-Flores, 2002; Mendoza-Flores & Turgoose, 2002; Turgoose et al., 1995). One of the main objectives of using hydrodynamic test systems in laboratory studies of turbulent flow is to obtain a series of criteria, aimed to help in the explanation and prediction of real life situations. In order to attain this, the data measured in one hydrodynamic system has to be compared, somehow, with the data measured in other hydrodynamic systems or with data obtained in real life systems. It has been suggested that the comparison among the results obtained in different hydrodynamic systems can be made by means of the wall shear stress (τ_w). This suggestion considers that, when two hydrodynamic systems are at the same value of τ_w, at the same flow regime (turbulent or laminar), the same flow velocities near the surface and mass transfer conditions, prevail (Silverman, 1990).
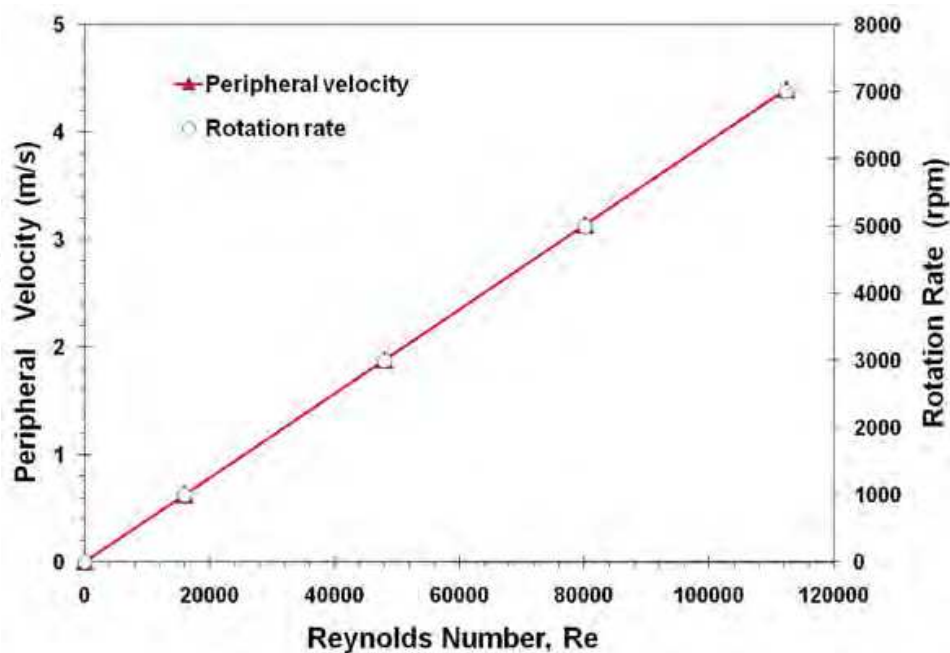
Fig. 1. Equivalence of rotation rate (rpm) and peripheral velocity (m/s) of the electrode and the calculated Reynolds number.

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 modelled completely by the rate of mass transfer of the rate limiting species and the Reynolds (*Re*), Sherwood (*Sh*) and Schmidt numbers (*Sc*) (Dean & Grab, 1984; Ellison & Schmeal, 1978; Ross et al., 1966). In general, the effect of flow can be used to determine if corrosion is under activation, diffusion or mixed control.

2. Experimental

2.1 Test environment

All experiments were carried out at 60°C, under static conditions (0 rpm) and turbulent flow conditions and, at the atmospheric pressure of Mexico City (0.7 bars). Two aqueous solutions were used as test environment: NACE brine (National Association of Corrosion Engineers, 1996) and a 3.5 % NaCl solution. These test environments were selected due to the fact that most of the H_2S corrosion laboratory tests are carried out in this solutions. The solutions were prepared using distilled water and reagent grade chemicals. In order to remove oxygen from the solution, N_2 gas (99.99%) was bubbled into the test solution for a period of 30 minutes before each experiment was carried out. After oxygen removal, H_2S gas (99.99%) was bubbled into the test solution until saturation was reached. H_2S bubbling was maintained during all the experimentation.

The measured saturation pH was 4.4 for the NACE brine and a pH of 4.5 for the 3.5% NaCl solution. In order to determine the purging time needed to remove all O_2 from the solution, a rotating cylindrical platinum electrode was cathodically polarized in a 1 M 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 polarization curve, disappeared after 30 minutes of purging time.

2.2 Experimental set up

All electrochemical measurements were carried out in an air-tight three-electrode electrochemical glass cell. Cylindrical working electrodes were used in all experiments. These cylinders were made of API X52 steel (American Petroleum Institute, 2004). The working electrode (WE) was machined from the parent material API X-52 and it had a diameter of 0.0012 m. The total exposed area of the working electrodes was 5.68E-04 m^2 and 3.4E-04 m^2 for static and dynamic conditions respectively. As reference electrode (RE) a saturated calomel electrode (SCE) was used and a sintered graphite rod was used as auxiliary electrode (AE). The experimental set up is schematically shown in Figure 2.
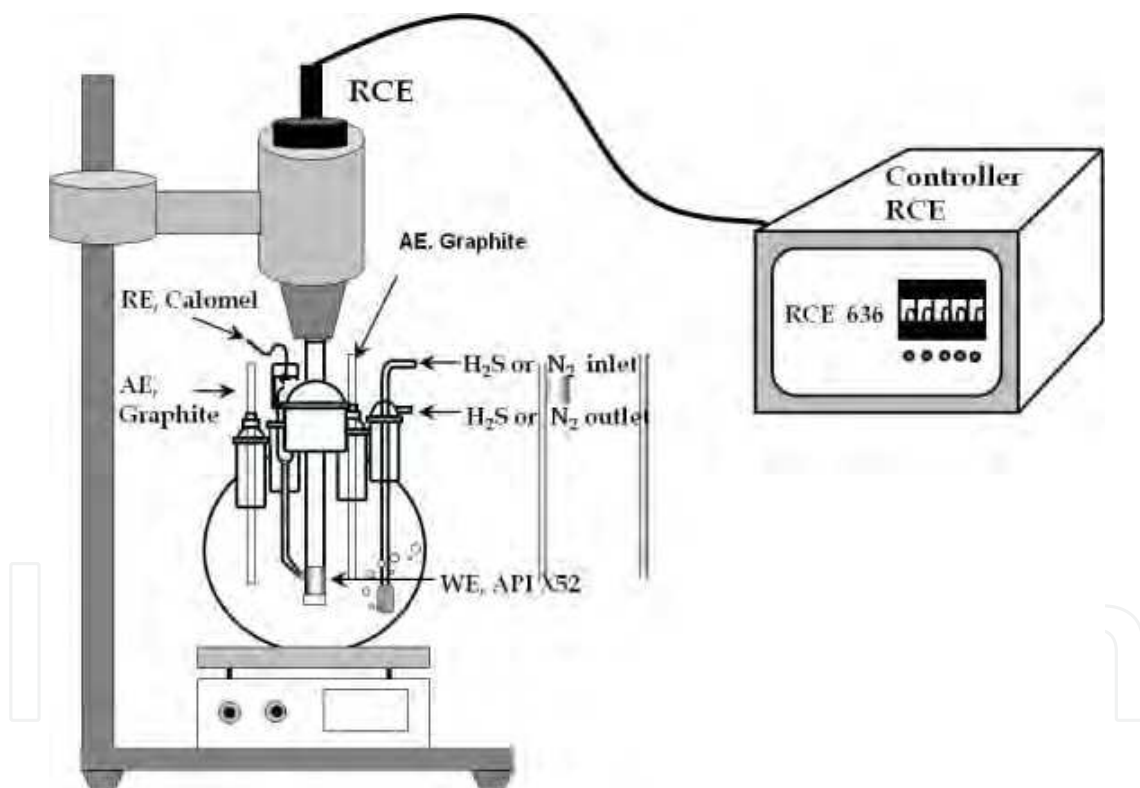
Fig. 2. Experimental set-up used in the electrochemical measurement.

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.

Hydrodynamic conditions were controlled using a Perking-Elmer EG&G Model 636 Rotating Cylinder Electrode system. In dynamic conditions or turbulent flow conditions, the

rotation rates tested were 1000, 3000, 5000 and 7000 rpm. It is important to point out that the electrochemical measurements were carried out also at static condition or 0 rpm.

2.3 Electrochemical measurements

A Potentiostat / Galvanostat was used in all the electrochemical tests. Potentiodynamic polarization curves were recorded at a sweep rate of 0.001 mVs⁻¹, starting the potential sweep at the rest potential or corrosion potential (E_{corr}) towards more cathodic potentials. It is important to mention that in order to get a better cathodic study, the cathodic polarization curve (CPC) and anodic polarization curve (APC) were made by separated.

The overpotential range used in the CPC was from +0.015 V to -0.5 V versus to corrosion potential (E_{corr}), on the other hand, the APC was recorded using an overpotential range between -0.015 to 0.5 V versus E_{corr}.

Laboratory tests indicated that, slower scan rates produced have not significant change on the measured current. In order to minimize the effect of the solution resistance a Lugging capillary was used. 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; this is due to the fact that it was found that the experimental variations of the measurements were negligible.

3. Experimental results and discussion

The corrosion of low carbon steel in brine solution containing H_2S has been investigated by several authors (Arzola et al., 2003; Galvan-Martinez et al., 2005; Vedage et al., 1993) using electrochemical techniques such as linear polarization resistance, electrochemical impedance spectroscopy and polarisation curves in quiescent systems. Even though 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. Many hydrodynamic systems have been applied in the corrosion studies and one of these hydrodynamic systems is the RCE.

Researches about these hydrodynamic systems (Arzola, 2006; Galvan-Martinez, 2005, 2007) have shown that the corrosion mechanism for carbon steel exhibits a significant dependence on mass transfer. This has led various workers to suggest the use of dimensionless analysis as a means of relating laboratory- scale experiments to industrial-scale corrosion behaviour.

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 is a dimensionless number dependent on the fluid velocity or the electrode rotation rate according to the density and viscosity of the fluid. It is a characteristic dimension in order 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 (τ) at any point in a laminar flow is given by:

$$\tau = \mu \frac{d\mathrm{u}}{dy} \tag{2}$$

If the velocity is increased, at a critical Reynolds number (Re_{crit}), 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 Re_{crit} for the transition between laminar and turbulent flow will vary depending on the geometry and Re_{crit} for usual pipe flow has been experimentally found to be around 2100 (Rahmani & Strutt, 1992).

Figure 3 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 H_2S at different rotation rates (0, 1000, 3000, 5000 and 7000 rpm) and 60 °C. This figure shows that, for both solutions, E_{corr} has the general trend to increase with Re_{RCE}, with exception of the range 50000< Re_{RCE} <80000 approximately, where it decreases.

The measured E_{corr} corresponding to the 3.5% NaCl solution increased from values of –0.739 V to –0.714 V approximately, whereas in NACE brine increased from values of –0.734 to –0.719 V approximately.
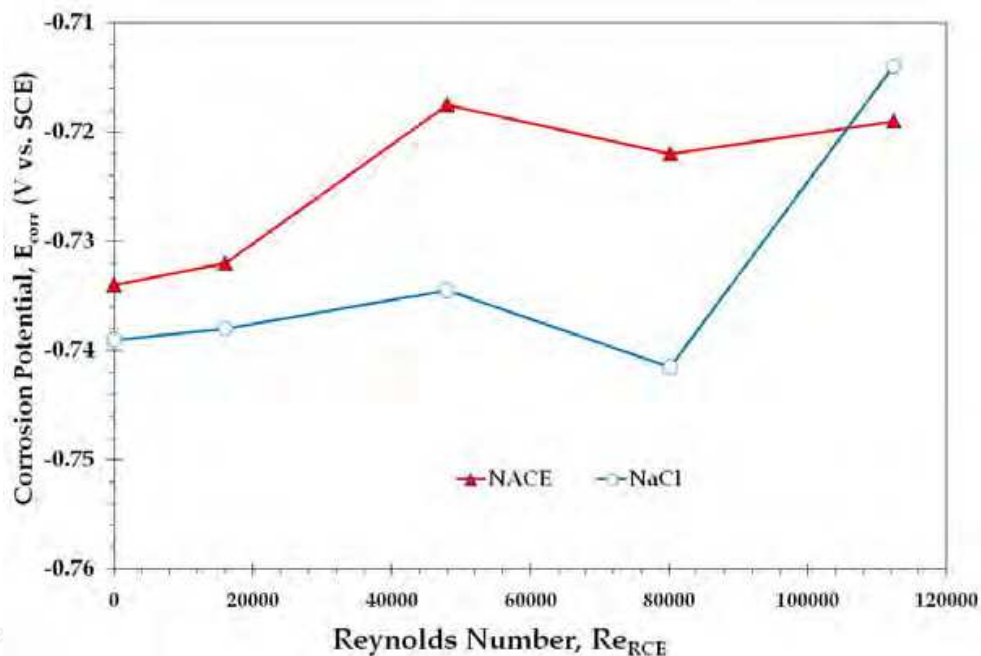

Fig. 3. E_{corr} as a function of different Re numbers of the cylindrical electrode in NACE brine and 3.5% NaCl solution at 60°C and 0.7 bars.

In order to obtain an estimation of the corrosion current densities (i_{corr}) for the API X52 steel immersed in both solutions containing H_2S, an extrapolation of the cathodic and anodic branches of the polarization curves was made for each case, in a region of ± 0.150 V of overpotential, approximately, with respect to the corresponding value of E_{corr}.

Figure 4 shows the estimated values of i_{corr} as a function of the calculated Re_{RCE}. According this figure, the i_{corr} values in both solutions increased and fell as the Re number increased. This figure demonstrates that the influence of flow on the measured corrosion is not a linear relationship.

Figures 5 and 6 show the cathodic polarization curves (CPC) obtained on API X52 steel cylindrical electrodes, in the NACE brine and 3.5 % NaCl solution saturated with H_2S at 60

°C and at 0.7 bars, as a function of the rotation rate. In these two figures are possible to see that all CPC (at all rotation rates) have a region where a diffusion process, taking place on the surface of the electrode, is influencing the overall cathodic current. It is to say, a region with well defined cathodic limiting current density, i_{lim} can be observed.
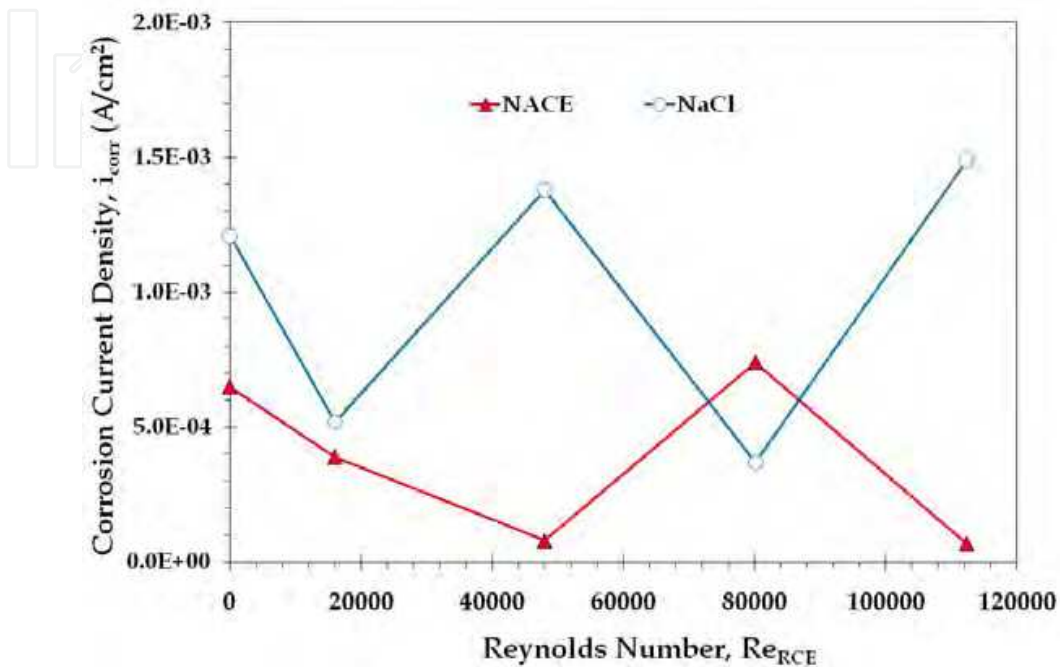

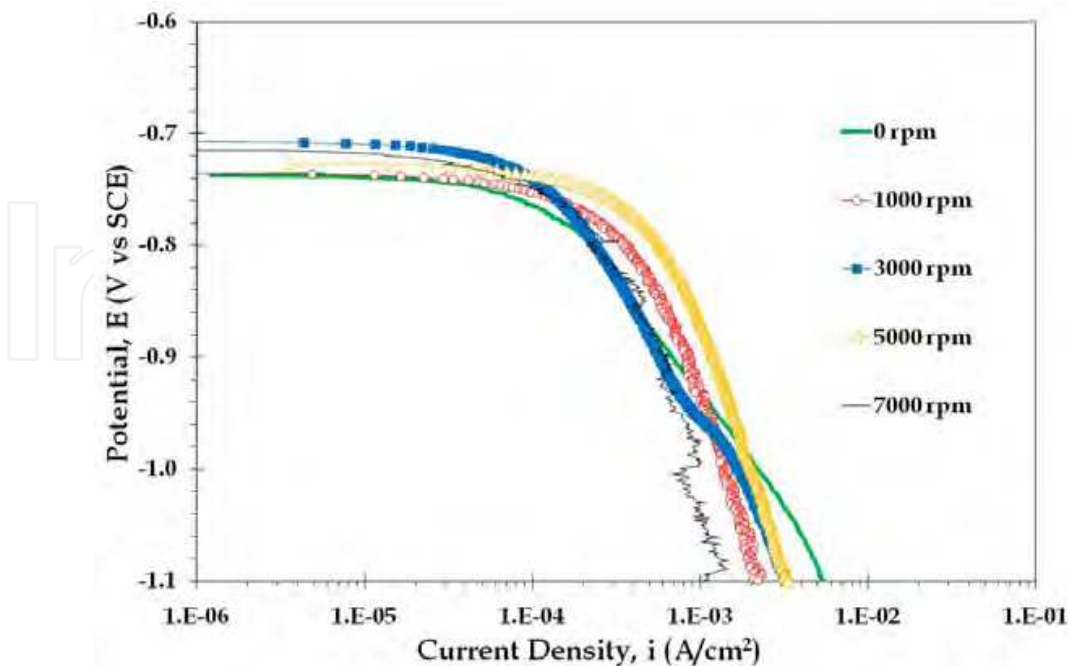Fig. 4. Corrosion current density as a function of Re_{RCE}.

Fig. 5. Cathodic polarization curves as a function of the different rotation rate. API X52 steel immersed in NACE brine saturated with H_2S at 60°C.
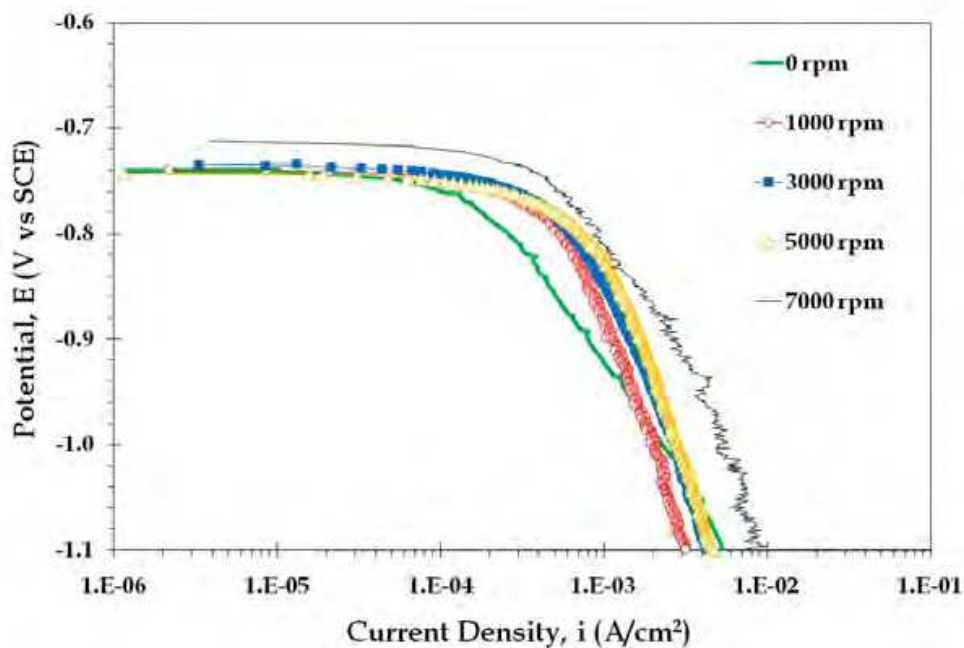
Fig. 6. Cathodic polarization curves as a function of the different rotation rate. API X52 steel immersed in 3.5% NaCl solution saturated with H_2S at 60°C.

In general, for these two hydrodynamic systems, only one plateau (i_{lim}) can be observed in the cathodic branches at each rotation rate. This behaviour could be attributed to the H^+ diffusing either, through the corrosion products layer or from the bulk of the solution towards to the surface of the electrode and the reduction of H_2S (Arzola, 2006; Galvan-Martinez, 2004). In both cases, the current plateau is controlled by mass transfer.

According to the analysis proposed by Schmitt (Schmitt & Rothmann, 1977) and Mendoza (Mendoza-Flores, 1997), it is possible to establish the different cathodic reactions involved in a system controlled by mass transfer under flow turbulent conditions.

Previous work about the steel corrosion in a sour solution say that, in a 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.

The hydrogen evolution can occur as follow:

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

It is important to note that in sour media, the source of the H^+, which promotes the hydrogen evolution, may be the H_2S or H_2O.

Some researchers like Shoesmith (Shoesmith et al., 1980) and Pound (Pound et al., 1985) propose that the cathodic reaction in the presence of H_2S, might be represented by the follow 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} (Ogundele & White, 1986). It is important to point out that in this work, the measured experimental cathodic current should be a consequence of all the possible reduction reactions that can occur in the NACE and 3.5% NaCl solution saturated with H_2S. According to different researchers (Ogundele & White, 1986; Vedage et al., 1993), the main cathodic reactions in H_2S containing solutions in the absence of oxygen are:

$$2H^+ + 2e^- \rightarrow H_2 \tag{5}$$

$$H_2S + e^- \rightarrow H + HS^- \tag{6}$$

At a constant potential (E) value, as the rotation rate of the electrode increase 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.

According to previous cathodic analysis, it is important to define which process is controlling the cathodic reaction, the diffusion of the H^+ or H_2S. This fact can define the main reduction reaction.

With the equation proposed by Eisenberg et al., (Eisenberg et al., 1954) for the RCE is possible to calculate the cathodic current density or limiting cathodic current due to the reduction for a species i ($i_{lim,i}$). The equation is:

$$i_{lim,i} = 0.0791 nFC_i d_{RCE}^{-0.3} \nu^{-0.344} D_i u_{RCE}^{0.7} \tag{7}$$

Where the $i_{lim,i}$ is the limiting current density in turbulent conditions for species i (A/m^2), n is the number of electrons involved in the electrochemical reaction, F is the Faraday constant, C_i is the bulk concentration of the chemical species i (mol/m^3), d_{RCE} is the diameter of the rotating cylinder (m), ν is the kinematic viscosity of the solution (m^2/s), D_i is the diffusion coefficient of i (m^2/s) and u_{RCE} is the peripheral velocity of the RCE (m/s). This expression indicates a direct relationship of the calculated limiting current density ($i_{lim,H+}$) to the peripheral velocity of the RCE (u_{RCE}), to a power of 0.7.

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. According to these facts and at given flow rate, the total diffusion limited current $i_{lim,t,diff}$ for a H_2S solution could be described by the addition of two components.

$$i_{lim,t,diff} = i_{lim,H^+} + i_{lim,H_2S} \tag{8}$$

Where i_{lim,H^+} and $i_{lim,H2S}$ are the limiting current densities for the H^+ and H_2S under turbulent flow condition.

In order to obtain the i_{lim,H^+} and $i_{lim,H2S}$ Mendoza and Schmitt (Mendoza-Flores, 1997; Schmitt & Rothmann, 1977) proposed that the theoretical i_{lim} for H_2S and H^+ reduction

could be compared with the experimentally measured i_{lim}, in order to obtain information about the predominant cathodic reaction (kinetics). In order to get the theoretical relationship between i_{lim} and u_{RCE} to a power of 0.7 for either H_2S or H^+, the values of density and kinematic viscosity were calculated according to the analysis proposed by Mendoza (Mendoza-Flores, 1997).

Figure 7 compares the different measured and calculated current densities as a function of u_{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 5, at a constant potential of –0.860 V (SCE). The estimated values of corrosion current densities (i_{corr}) correspond to NACE brine were showed in figure 4. The values of calculated current densities, for the H^+ (a) and H_2S (b) reduction, were calculated with equation (7).

Figure 7(a) shows that the experimental cathodic current density increased and decreased as the rotation rate of the electrode at a power of 0.7 also increase. On the other hand, the corrosion current density has the same behaviour that the i_c. According to these facts are possible to conclude that the H^+ reduction reaction and iron oxidation reaction are no flow dependent. It is important to note that, although the i_c corresponding to H^+ reduction reaction has not a linear relationship with respect to the peripheral velocity of the RCE, it has a better adjust to the theoretical current obtained by the equation of Eisenberg et al., with respect to the i_c corresponding to the H_2S reduction reaction (see figure 7b). In general, the theoretical (i_{lim} obtained by equation of Eisenberg et al.) and experimental (i_c and i_{corr}) densities corresponding to the H^+ reduction have a fits better than the theoretical and experimental densities corresponding to the H_2S. According to this analysis, one conclusion should be obtained: the dominant cathodic reaction is the reduction of hydrogen ions.
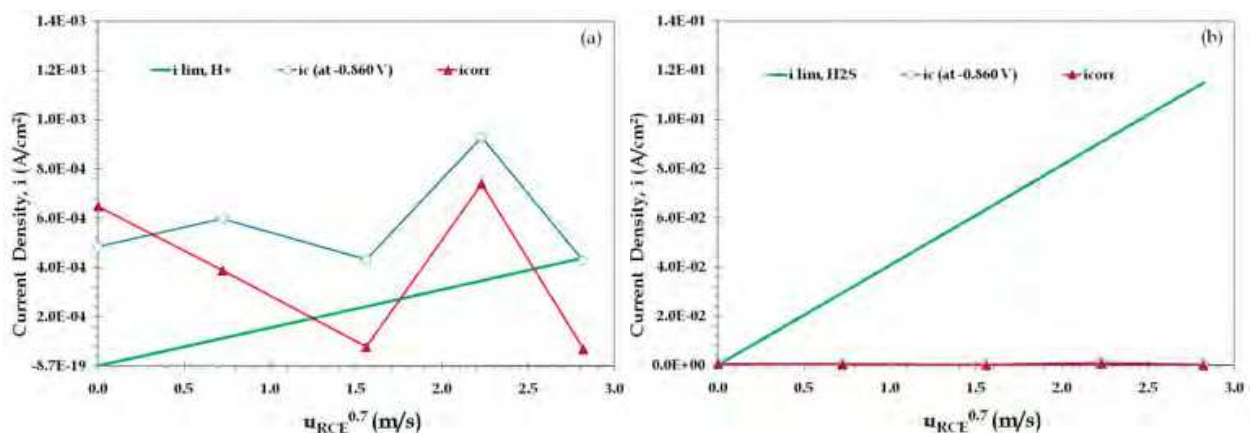

Fig. 7. i_{lim,H^+} (a) and $i_{lim, H2S}$ (b) as a function of u_{RCE} to a power of 0.7 in NACE brine.

In figure 8 is possible to see the comparison of the different measured and calculated current densities as a function of u_{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 V (SCE). The estimated values of corrosion current densities (i_{corr}) correspond to NACE brine were showed in figure 4.
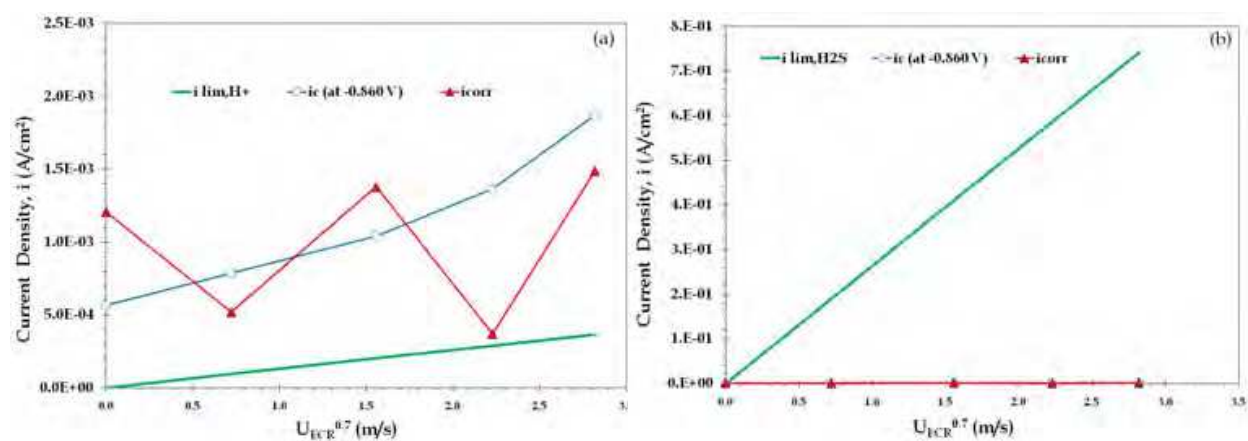
Fig. 8. $i_{lim,H+}$ (a) and $i_{lim,H2S}$ (b) as a function of u_{RCE} to a power of 0.7 in 3.5% NaCl solution.

From the figure 8a, it is possible to note the linear relationship between the experimental limiting current density of the H+ reduction and the peripheral velocity of the RCE. This fact suggests that a mass transfer phenomenon can occurs in the cathodic reaction. According to this analysis is possible to say that the measured cathodic current is affected by flow and this current can be associated to the H+ diffusing through the corrosion products layer, where they are reduced to H_2 gas. For that reason, the H+ reduction is flow dependent. In figure 8b is possible to see that the comparison of the theoretical ($i_{lim,H2S}$) and experimental (i_c) current densities of the H_2S reduction have not good correlation. In general, the best fit of the theoretical and experimental current densities correspond to H+ reduction. Finally and according to the analysis of the figure 8, is possible to say that in the corrosion of the steel immersed in 3.5% NaCl solution, 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 was proposed by Mellor (Mellor, 1930):

$$H_2S_{gas} \leftrightarrow H_2S_{aq} \tag{9}$$

In aqueous solutions, H_2S is a weak acid (Widmer & Schwarzenbach, 1964):

$$H_2S_{aq} \leftrightarrow H^+_{aq} + HS^-_{aq} \tag{10}$$

$$HS^-_{aq} \leftrightarrow H^+_{aq} + S^-_{aq} \tag{11}$$

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

Silverman (Silverman, 1984) 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 simulations allow duplicating the velocity- sensitivity mechanism found in the industrial geometry. The shear stress is a measure of the interaction between metallic surface and fluid. The shear stress at the wall can be estimated by the following equation (Bolmer, 1965):

$$\tau_{LAB} = \tau_{PLANT} \tag{12}$$

Then, for a given system, the mechanism by which fluid velocity affects corrosion rate in the industry is proposed to be identical to that which affects corrosion rate in the laboratory. Figures 9 to 12 show current densities and the dimensionless number analysis as a function of the wall shear stress ($\tau_{W,RCE}$) and the Reynolds number (Re). In this analysis, the H$^+$ ions are considered to be the main active specie in the cathodic reaction in the environment. 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 $\tau_{W,RCT}$ for the RCE was (Denpo & Ogawa, 1993; Efird et al., 1993; Johnson et al., 1991):

$$\tau_{W,RCE} = 0.079 Re_{RCE}^{-0.3} \rho \, u_{RCE}^2 \tag{13}$$

Mass transfer and surface shear effects may have an important effect on the corrosion rate, either by modifying the rate of transport of chemical species to surface or from the surface, or by shear-stripping protective films from the metal/solution interface. So that, 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. For that reason, parameters such as the mass transfer coefficient, k_i, shear stress at the wall, $\tau_{W,RCE}$, and the Sherwood number, Sh, can be derived from these results.

Figure 9 shows i_c and i_{corr} as a function of $\tau_{W,RCE}$ in NACE brine. This figure shows that the measured i_c and i_{corr} increases and decreases as the $\tau_{W,RCE}$ increases. This behaviour suggests that the corrosion rate and the cathodic reaction are no dependent to the wall shear stress. This result confirms the behaviour presented in figure 7a, where the i_c and i_{corr} are no dependent of the flow.
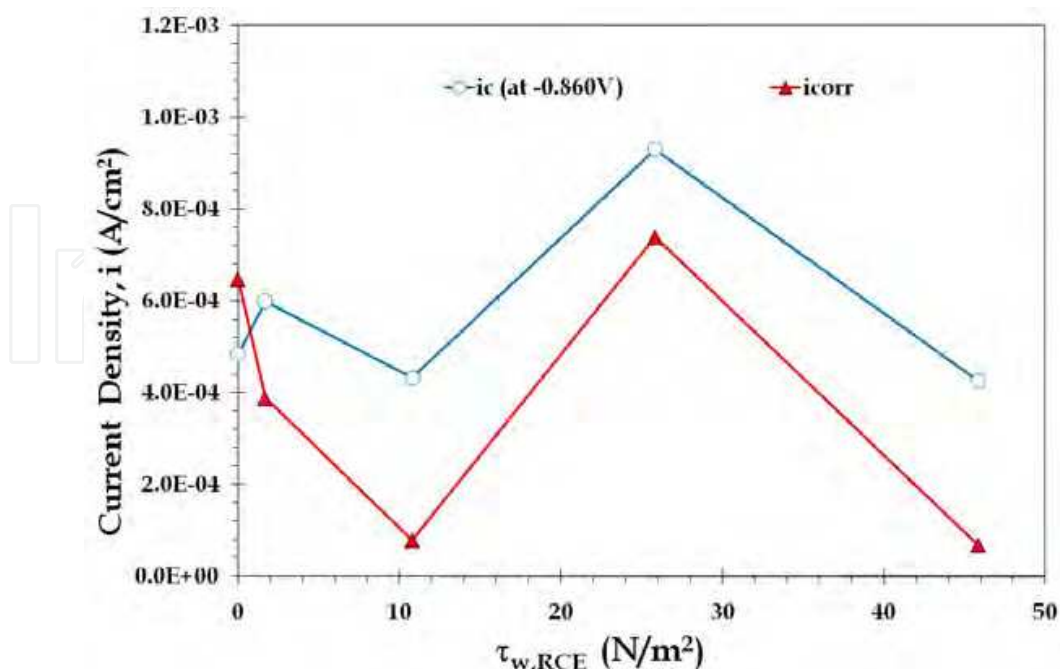
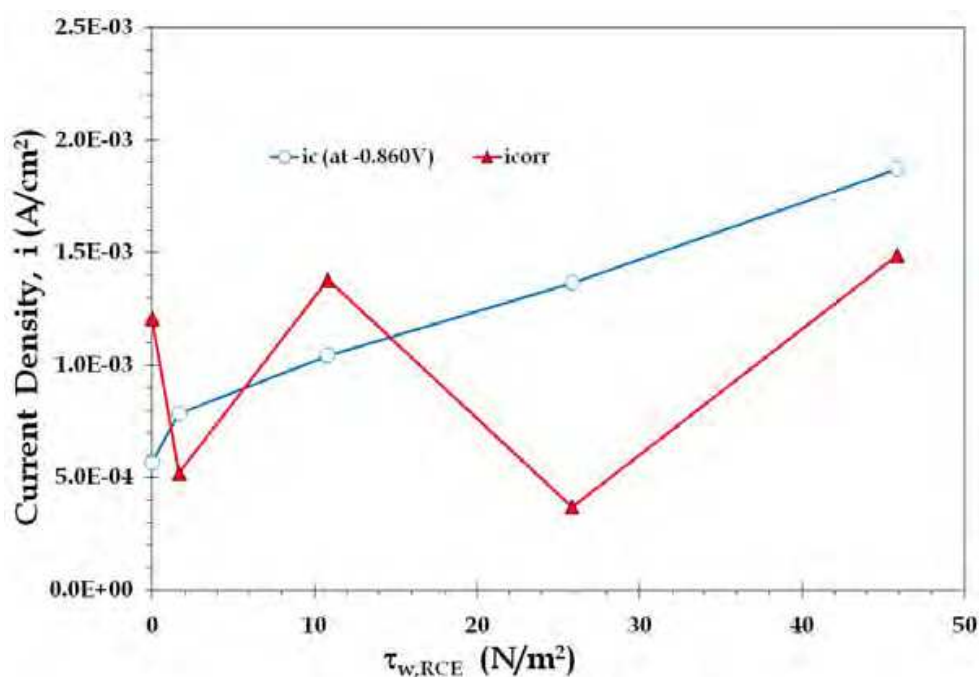

Fig. 9. Cathodic current density obtained at –0.860 V(versus SCE) on the CPC in figure 5 and corrosion current density as a function of $\tau_{W,RCE}$.

Figure 10 shows i_c and i_{corr} as a function of $\tau_{W,RCE}$ in 3.5% NaCl solution. In this figure, it is possible to see that as measured i_c increase the $\tau_{W,RCE}$ also increases. This result suggests that the cathodic reaction increased as the $\tau_{W,RCE}$ also increased. Mass transfer studies of electrochemical reactions are normally carried out under mass transfer limited current conditions. When limiting conditions prevail, the mass transfer coefficient for a given species H+, k_{H+}, can be expressed as (Galvan-Martinez, 2004):

$$k_{H^+} = \frac{i_{\lim,H^+}}{nFC_{H^+}}$$
(14)

Fig. 10. Cathodic current density obtained at –0.860 V(versus SCE) on the CPC in figure 5 and corrosion current density as a function of $\tau_{W,RCE}$.

Where: $i_{\lim,H^+}$ is the mass transfer limited current for species H+, F is the Faraday´s constant, n is the number of electrons involved in the reaction and C_{H+}, is the bulk concentration of the diffusing species H+. It is important to mention that Silverman pointed out (Silverman, 2004) the measured mass-transfer coefficient could be converted to the Sherwood number and plotted as a function of the Reynolds number (Galvan-Martinez, 2004). The Sherwood number for the RCE (Sh_{H^+}) is given by the expression:

$$Sh_{H^+} = \frac{i_{\lim,H^+} d_{RCE}}{nFD_{H^+}C_{H^+}}$$
(15)

Where: d_{RCE} is the outside diameter of the rotating cylinder, D_{H^+} is the diffusion coefficient of specie H^+, it is the diffusivity of H^+ in the 3.5% NaCl solution -H_2S system (or NACE brine-H_2S system).

In figure 11, in the 3.5% NaCl solution is possible to see that the Sherwood number increases as the Reynolds number increases. This behaviour indicates that the cathodic reaction is controlled by the mass transport rate. 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 equation of Eisenberg et al., (Eisenberg et al., 1954) and, Chilton and Colburn analogy (Chilton & Colburn, 1934). Eisenberg et al. (Eisenberg et al., 1954) showed that in the range of 1.0E03 < *Re* > 1.0E05, the equation (7) is a straight line approximation.
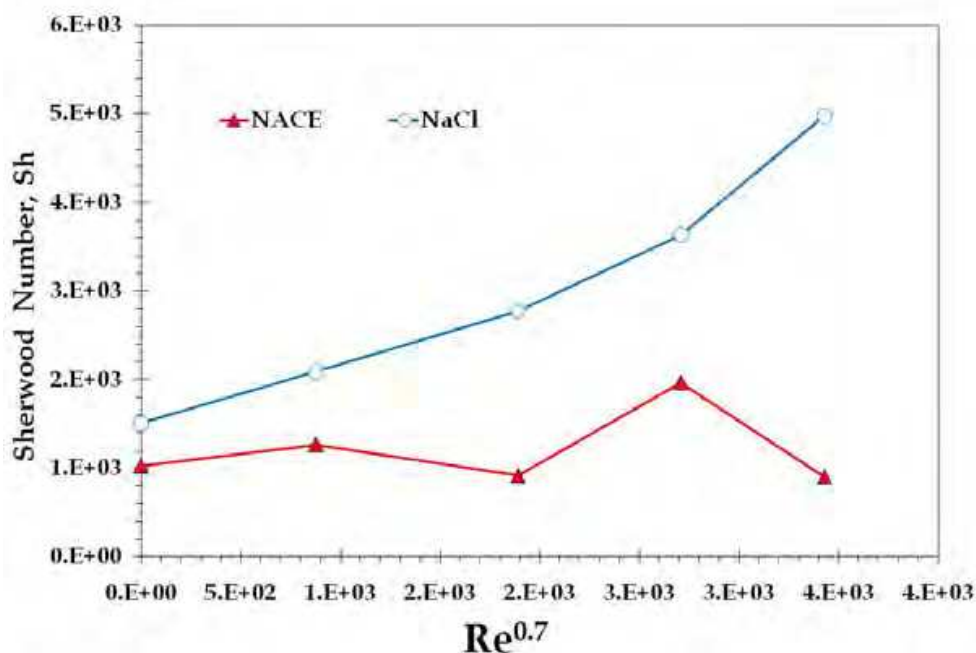

Fig. 11. Variation of dimensionless corrosion rate, expressed as the *Sh* number versus *Re* number to a power of 0.7.

Figure 12 shows the k_{H^+} as a function of *Re* number to a power of 0.7. On the 3.5% NaCl solution, the behaviour of the k_{H^+} is the same behaviour that showed the *Sh* number in figure 11 because the mass transfer coefficient increases when the Re_{RCE} also increases.

The behaviour shown in figures 11 and 12 can suggest that the mass transfer coefficient (Sh_{H^+} and k_{H^+}) is flow dependent, because it increases as the rotation rate also increases. In general, the behaviour presented by Sh_{H^+} and k_{H^+} indicates that the cathodic current is controlled by the mass transfer rate. On the other hand, the behaviour of Sh_{H^+} and k_{H^+}, in NACE brine, confirm the behaviour presented by the current densities, the cathodic process that happens in the corrosion of the steel immersed in NACE brine is not flow dependent. It is because the Sh_{H^+} and k_{H^+} increase and decrease as the *Re* number also increase.
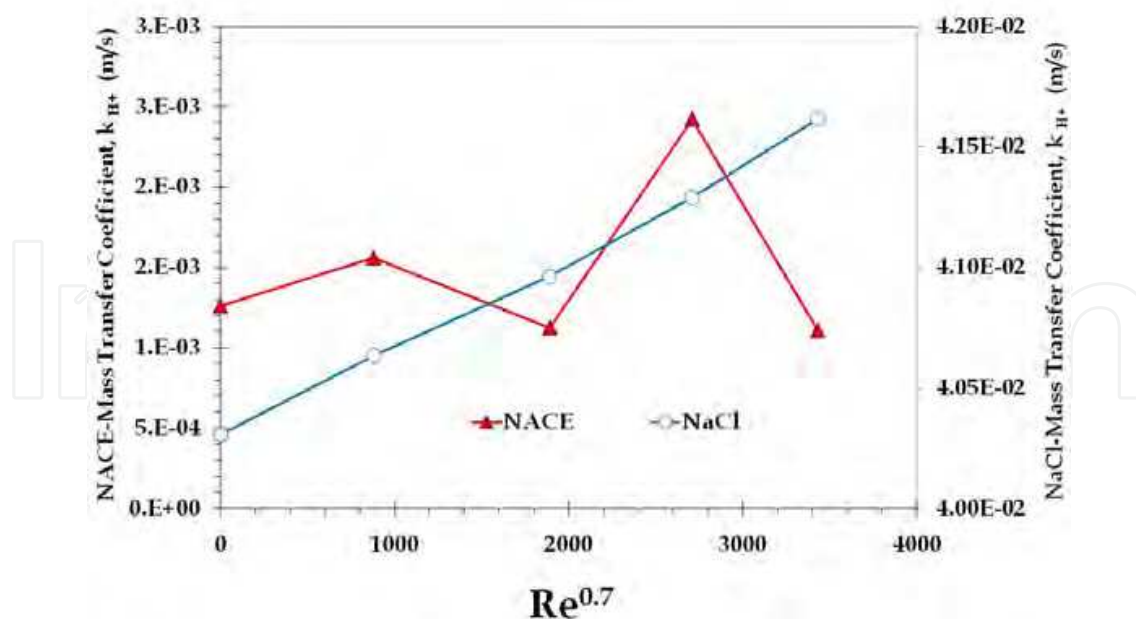
Fig. 12. Variation of mass transfer coefficient (k_{H^+}) versus *Re* number to a power of 0.7.

Figures 13 and 14 show the measured anodic polarization curves obtained on X52 steel cylindrical electrodes immersed in the NACE brine and 3.5% NaCl solution, respectively, saturated with H_2S at different rotation rates.
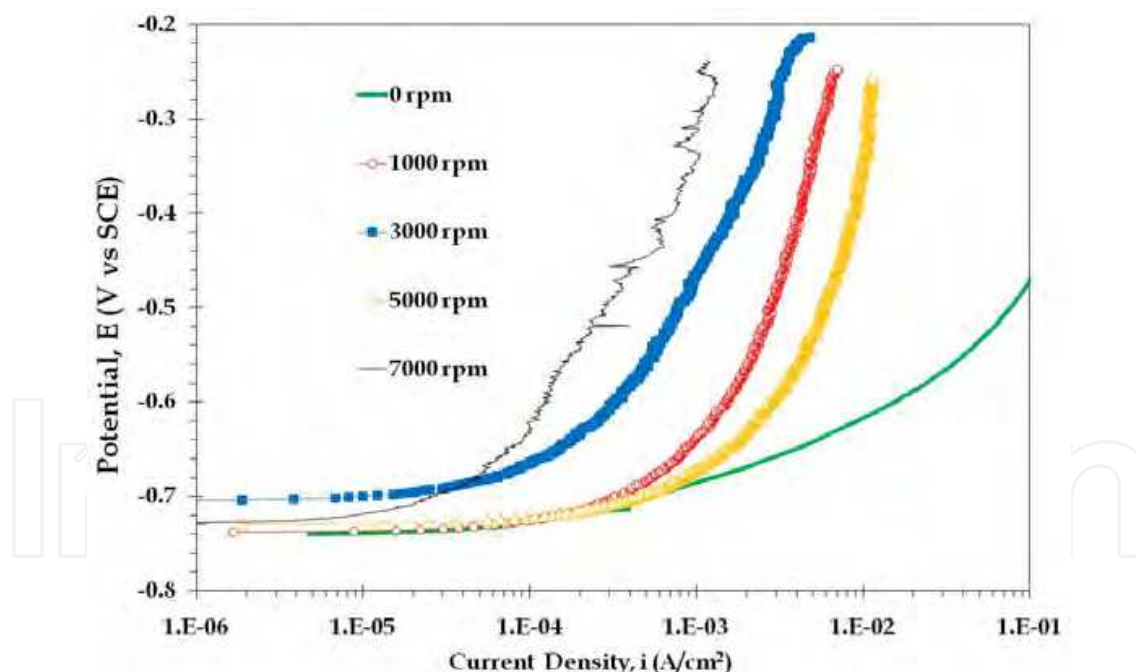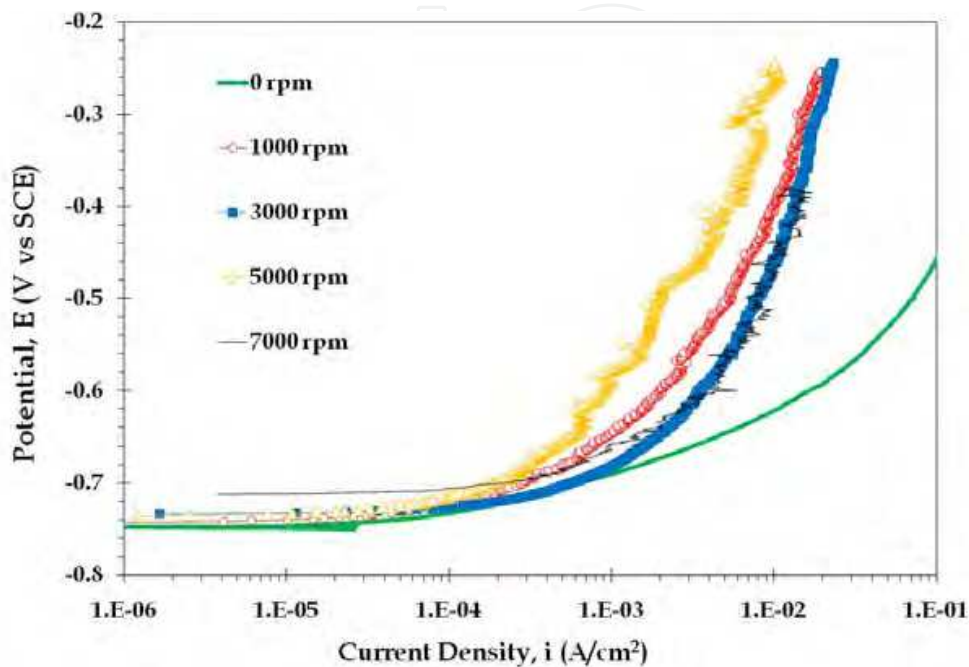

Fig. 13. Anodic polarization curves as a function of different rotation rates. X52 steel electrode immersed in NACE brine saturated with H_2S.

In both figures, it is possible to observe that the anodic Tafel slopes (b_a) are relatively high. This fact indicates a passivation process, taking place on the surface of the electrode. It is important to note that at 0 rpm the anodic polarization curve shows a b_a with values from 115 to 135 V vs. SCE approximately, where these values correspond to an activational or charge transfer process.

Figure 15 shows the estimated anodic Tafel slopes (b_a) as a function of Re_{RCE}, on cylindrical X52 steel electrodes immersed in NACE brine and 3.5% NaCl solution saturated with H_2S. 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 NACE brine and 3.5% NaCl solution, carried out from 1000 to 7000 rpm were higher than 0.250 V/decade. This fact can be suggested that a passivation process can be influence in the anodic reaction.

Fig. 14. Anodic polarization curves as a function of different rotation rates. X52 steel electrode immersed in 3.5% NaCl solution saturated with H_2S.
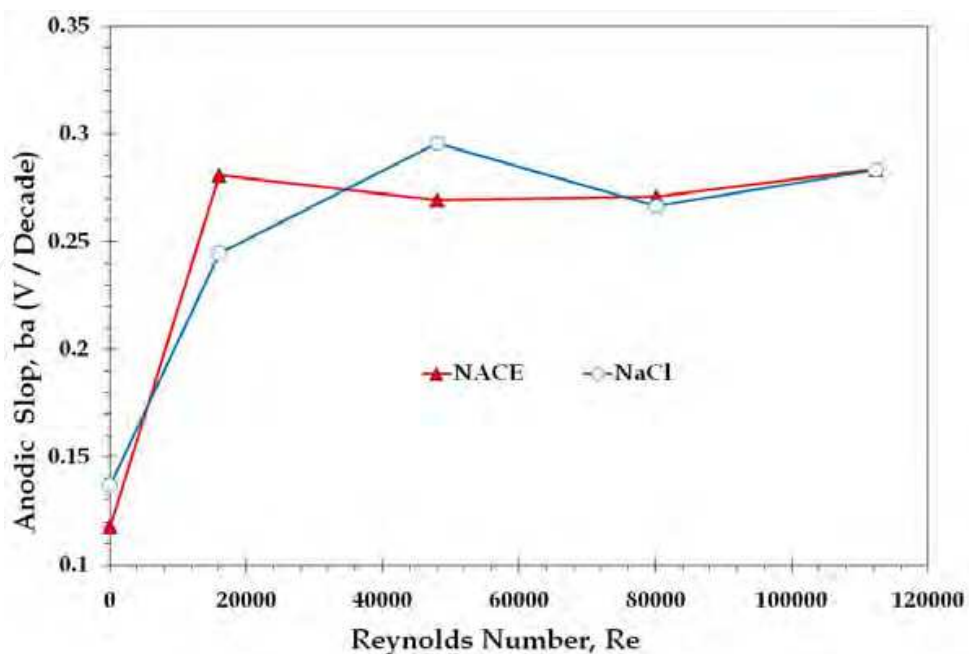

Fig. 15. Calculated anodic Tafel slopes as a function of Reynolds number. Cylindrical API X52 steel electrode immersed in NACE brine and 3.5% NaCl solution saturated with H_2S.

4. Conclusions

According to the experimental results is possible to conclude that the corrosion process of the X52 steel immersed in NACE brine and 3.5% NaCl solution at 60°C and turbulent flow condition, the main cathodic reaction correspond to the H+ reduction.

$$H^+ + e^- \rightarrow H$$
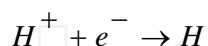
All cathodic polarization curves, in 3.5% NaCl solution, were affected by the rotation rate of the cylindrical electrode because all CPC show a region that is influenced by a diffusion process, at all rotation rates. In general, when the rotation rate (or *Re* number) of the cylindrical electrode increases, the measured cathodic current density also increases. X52 steel in NACE brine, the cathodic polarization curves shows a region that is influenced by a diffusion process, at all rotation rates, but the current densities are not flow dependent.

In the corrosion process of the X52 steel immersed in 3.5% NaCl solution, the analysis of the current densities (i_c at 0.860 V vs. SCE and i_{lim,H^+}) and the mass transport (Sh_{H^+} number and mass transport coefficient ,k_{H^+}) can be assumed that the 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* vs *Re* number is 0.7. In addition, the above reaction can be assumed to be under complete control of mass transfer and, it is a flow dependent reaction. On the other hand, the corrosion process of the X52 steel immersed in NACE brine, the analysis of the current densities and the mass transport is can be assumed that the corrosion is being limited by the mass transfer rate, but the cathodic reaction is not flow dependent because the theoretical and experimental current densities and mass transport coefficients increased and decreased as the Re number also incremented.

All the estimations of the anodic Tafel slopes in NACE brine and 3.5% NaCl solution, carried out at flow condition (1000, 3000, 5000 and 7000 rpm), were higher than 0.250 V/decade. This fact can suggest that a passivation process can be influence in the anodic reaction.

5. Acknowledgment

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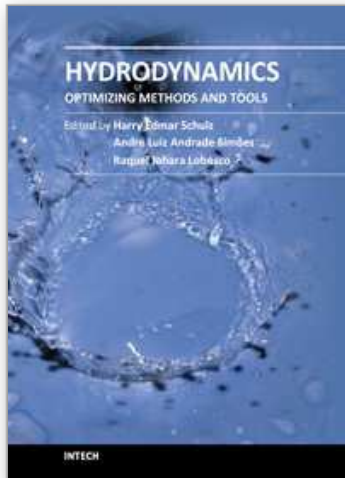
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