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## Factors Affecting Corrosion of Steel in Pipe Lines

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**Abstract:** The corrosion behaviour of mild steel, platinum, nickel, copper and lead in 4% NaCl deaerated acidified solution was studied. Another investigation on these metals was made in solution saturated with CO<sub>2</sub> to see the effects of CO<sub>2</sub> partial pressure and temperature on the cathodic hydrogen evolution reaction. Polarization curves in different conditions were determined and different values of limiting, and exchange current densities were measured. It was found that the limiting current density  $I_L$  increases by the introduction of CO<sub>2</sub> to each one of the metals investigated. The increase is either due to a pH or a temperature effect, assuming no effect of gas bubbling. It was confirmed that the limiting current does not depend on the nature of the material used as a working electrode. The exchange current density of the cathodic hydrogen reaction was found to be metal electrode and solution pH dependent. The analysis of energy activation shows that the increase in exchange current could be due to a pH or a temperature effect, depending on the nature of the material studied. There was an increase in the exchange current density  $I_0$  by the introduction of CO<sub>2</sub> to the systems investigated. The corrosion rates on steel, nickel, copper and lead were calculated in the presence and absence of CO<sub>2</sub> and found to increase in the presence of CO<sub>2</sub>. However, platinum does not corrode but the limiting current density of the hydrogen reaction increased by the introduction of CO<sub>2</sub>.

**Keywords:** Corrosion, Mild steel, Exchange current density, Limiting current density, Activation energy

### Introduction

In oilfield operations, it is often necessary to produce oil from hydrocarbon reservoirs that contain significant amounts of H<sub>2</sub>S and CO<sub>2</sub> in addition to brine (Wang et al., 2024). The cost to the industry includes the repair of corrosion damage and associated Consequential losses, the cost of over design of protective systems and of technical effort has been estimated to be very high (Iannuzzi & Frankel, 2022). Some low alloy steels do not resist corrosion and are susceptible to cracking in environments which contain either wet H<sub>2</sub>S or wet CO<sub>2</sub>.

The assessment and the control of CO<sub>2</sub> corrosion of carbon steel tubulars and equipment is a long-standing concern of the petroleum industry. Downhole problems are particularly troublesome as they can involve removing and re-running many thousands of feet of production tubing, at a very high cost (Liu et al., 2023). The problems are caused by the corrosive effect of carbonic acid, produced by the dissolution of CO<sub>2</sub> gas in water. The corrosion related to CO<sub>2</sub> is the most significant and the corrosion problems in the produced fluids have been a major source of failure in production equipment, damage being observed in downhole equipment, pumps and tubulars, production pipework between the wellhead and the separation vessels (Solovyeva et al., 2023). Carlson reported that carbonic acid in natural waters or in steam condensate attacks materials with H<sub>2</sub>S evolution (Carlson, 1949). In all cases, water chemistry and the in-situ pH play a decisive role. When CO<sub>2</sub>, H<sub>2</sub>S, Cl<sup>-</sup> and H<sub>2</sub>O are present in the environment, rapid corrosive degradation of the exposed metal can occur (Yue et al., 2025). However, (Butler & Ison, 1966) claimed that CO<sub>2</sub> has no specific influence on the corrosion of steel since it does not participate in the cathodic reaction. It can, however, influence the corrosion rate due to its acidic character and its ability to

increase the H<sub>2</sub>S evolution type of attack by decreasing the pH of the solution. A second indirect influence is due to the fact that with an increase in CO<sub>2</sub> concentration protective calcium carbonate is not formed but remains in acid solution in the form of calcium bicarbonate. The high hydrogen ion concentrations of acid solutions promote H<sub>2</sub> evolution and make such solutions corrosive to steel even in the absence of oxygen. Generally, higher concentrations of acids and hydrogen ions are more corrosive than lower concentrations.

In the absence of water, there is no risk of corrosion. Even the presence of some free water may also be neglected under some circumstances. Fluids with up to 20% of water are considered safe in equipment as long as it contains oil and has a flow rate sufficient to entertain the water and give a continuous oil film at the steel surface. As an example, in East Texas, depending on the presence of water, the corrosion varies from mild to severe. A way to combat this corrosion economically is the use of inhibitors (Butler & Ison, 1966). At elevated temperature, the presence of CO<sub>2</sub>, oxygen or chloride accelerates the attack because they change the structure and adherence of the protective film. The presence of chloride ions Cl<sup>-</sup> in the mixture CO<sub>2</sub>-H<sub>2</sub>O accelerates the corrosion process. The corrosion rate increases proportionally with CO<sub>2</sub> partial pressures (Videm & Dugstad, 1989).

For wells producing water as a by-product, the pH at operating pressure will be an important parameter for the corrosion rate in addition to CO<sub>2</sub> partial pressure, Fe<sup>2+</sup> concentration and temperature. The overall corrosion reaction is represented by the following equation:



The rate of this reaction is affected by temperature, pressure, pH, water content and the velocity of the fluid, and although the iron carbonate corrosion product formed may give some protection to the steel, this is removed at regions of high turbulence or velocity, producing deep pitting, often seen on the sides of downhole production tubing. Detailed studies of the CO<sub>2</sub> corrosion mechanisms and associated kinetics have shown that under most conditions (above 60°C) the steel surface becomes covered with an iron carbonate layer, which totally controls all corrosion reactions including inhibition. Work is needed to produce a better understanding of this problem and clarify the role of CO<sub>2</sub> and the way in which it increases the corrosion rate (Liu et al., 2023).

## **Experimental Methods**

The parameters measured in this work include the pH of the test solution, which is affected by the introduction of CO<sub>2</sub>, the current flowing in the system between the working and counter electrodes which is affected as well.

## **Materials**

### **Solutions Preparation**

The metals investigated were mild steel, platinum, nickel, copper, and lead. The test solution was a 4% NaCl deaerated acidified solution. A second set of experiments was conducted by saturating this solution with CO<sub>2</sub> to study the effects of CO<sub>2</sub> partial pressure and temperature. Buffer solutions were also prepared for electrode calibration.

## **Measurement Techniques**

The test solutions prepared were of two types; the acid solutions prepared for polarization measurements and the buffer solutions prepared for the palladium electrode calibration. Sea water normally contains CO<sub>2</sub> in equilibrium with the atmosphere from which it comes. The total CO<sub>2</sub> content as carbonic acid, bicarbonates, and carbonates ranges from 60 to about 100 ppm. CO<sub>2</sub> present in seawater was found to have the same effect of uniform dissolution as a medium slightly acidified by carbonic acid. As a consequence, test were usually merely NaCl solutions under CO<sub>2</sub> pressure.

## **Determination of Polarization Parameters**

The corrosion rate was determined by plotting the applied potential versus the current density flowing in the cell, that is,  $E = f(\log I)$ . An extrapolation of the Tafel slopes to the reversible potential of the hydrogen reaction gives the exchange current density. The corrosion rate is calculated from the current density at the intersection of the extrapolated Tafel regions using Faraday's Law, that is,  $CR \text{ (mm/year)} = (M i_{\text{corr}} / nF\rho) \times 3.153 \times 10^7$  where, CR is the corrosion rate, M is the mass loss during corrosion (g),  $i_{\text{corr}}$  is the corrosion current,  $\rho$  is the density of steel ( $\text{g/cm}^3$ ). The other symbols have their usual meanings.

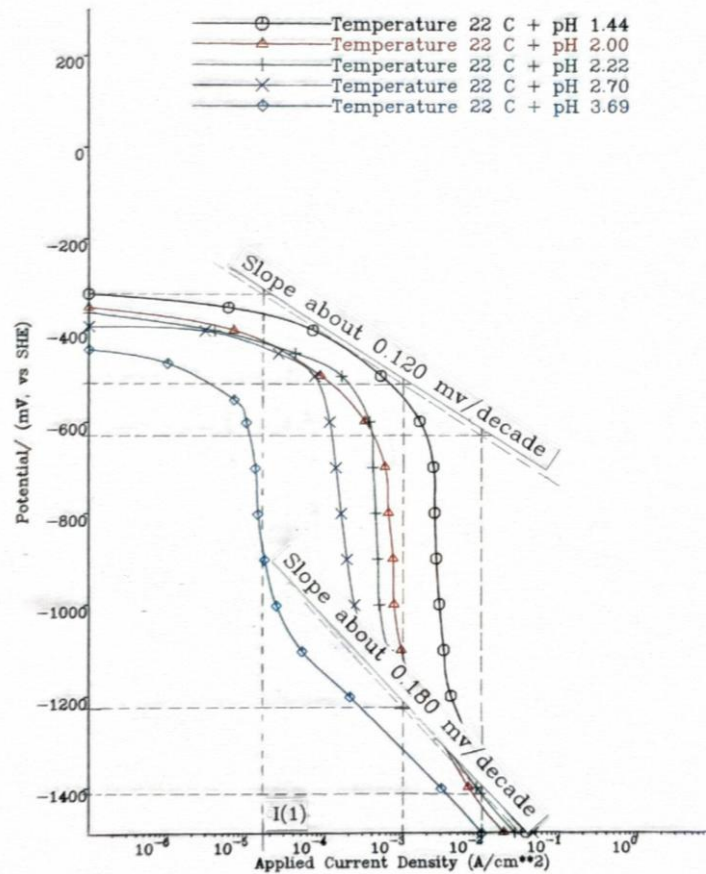
## Reproducibility

In all the electrochemical measurements, the experiment was carried out several times to assess the precision and reproducibility of the measurements. The measured potential has an accuracy of  $\pm 0.5\text{mV}$ , while the current accuracy is  $\pm 5 \times 10^{-6}\text{A}$ . The temperature controller has an accuracy of  $\pm 1^\circ\text{C}$ , while the pressure measurement is  $\pm 5\text{psi}$  (power square inch).

## Results

### Cathodic Polarization of Mild Steel in 4% NaCl Deaerated Acid Solution

The cathodic polarization curves for mild steel in 4% NaCl deaerated acid solutions are shown at two temperatures in Figures 1.a and 1.b. The cathodic parts of the curves present the three different regions. An activation control process shows a Tafel behaviour with a slope of about  $-0.120 \pm 0.010\text{V/decade}$ , which is hard to see because of steel corrosion in this region of potential, followed by a region of potential where the proton reduction rate is very high. There is a significant drop in potential. The values of the limiting current density for the hydrogen evolution reaction are found to be proportional to the proton concentration in the bulk solution. They range in the same interval given in the literature. The limiting current density is pH dependent and not dependent on the metal nature. The hydrodynamic conditions within the cell (including the bubbling effects) were not considered.



(a)

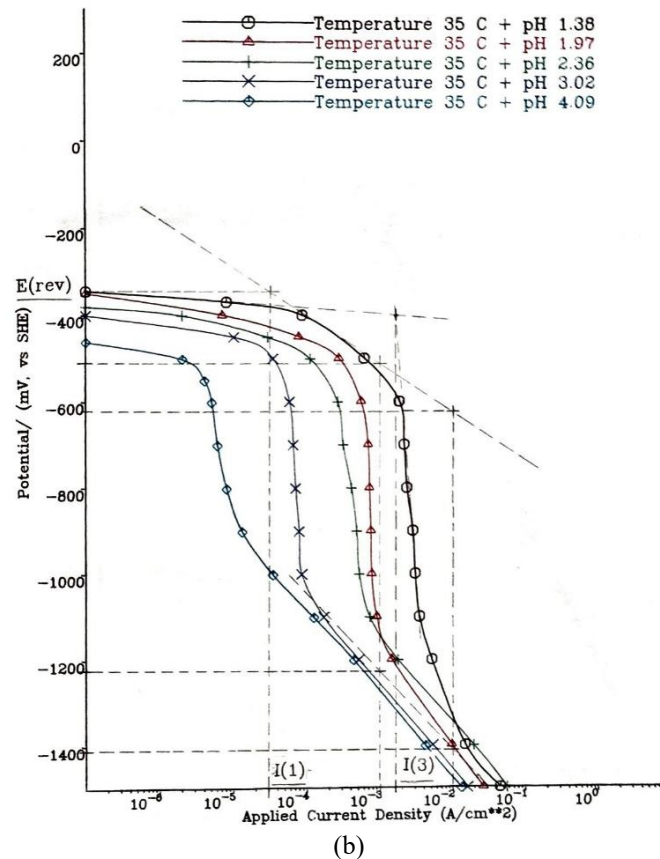


Figure 1. Cathodic polarisation of mild steel in 4% NaCl acidified solution

Another charge transfer process is observed at higher current densities. The Tafel slope found for this process is higher than that for the first one. It is about  $-0.180 \pm 0.020 \text{ V/decade}$ . The exchange current densities for the hydrogen evolution reaction are more or less in the range given in the literature, that is  $10^{-7}$  to  $10^{-5} \text{ A/cm}^2$  at  $\text{pH}=0.0$ . (Figure 2.a). The limiting current densities are in the same range as those of previous workers. They lie on the same line as for values found for steel (Figure 2.b) for comparison. As the current drawn increases, a limiting value will be formed for the previous anodic reaction due to the slow rate of  $\text{H}_2$  diffusion in water. The extrapolation of both anodic and cathodic curves to the reversible potential gives the exchange current density  $i_0$ . As expected, it is higher than the value found for steel, however, it is still in the same range found by other workers, it is about  $10^{-2}$  to  $10^{-1} \text{ A/cm}^2$  at  $\text{pH}=0.0$ .

The discussion of the results will first consider the reproducibility and accuracy of the measurements. Experiments were carried out several times to make sure that the results were reproducible. The errors on the pH were  $\pm 0.3$  pH units, on the reversible potentials  $\pm 0.005 \text{ V}$  on the exchange and the limiting currents  $\pm 5 \times 10^{-6} \text{ A}$ , on the temperature  $\pm 1^\circ \text{C}$ , and on the pressure measurement  $\pm 5 \text{ psi}$ . On all the metals studied, the cathodic part of the curve represents the hydrogen reaction, and this shows three well distinguished regions at different potentials. Apart from steel, the other metals copper, nickel, lead, an anodic polarization shows passive behaviour and film formation on the surface had occurred. At different temperatures, the polarization curves maintain a similar shape, but they were slightly displaced towards higher values of applied current densities.

### Variation of Exchange Current Density With pH on Steel

The values of the exchange current densities for the hydrogen reaction on steel were measured using the method, which consists of the extrapolation of  $-0.120 \text{ V/decade}$  theoretical Tafel slope to the reversible potential of the hydrogen reaction for each pH investigated (Figures 2.a and 2.b). When using the extrapolation method at room temperature of  $22^\circ \text{C}$ , for example, It was found that the exchange current densities lie on a straight line given by the following equation  $\log i_0 = -5.307 - 0.842 \text{ pH}$ .

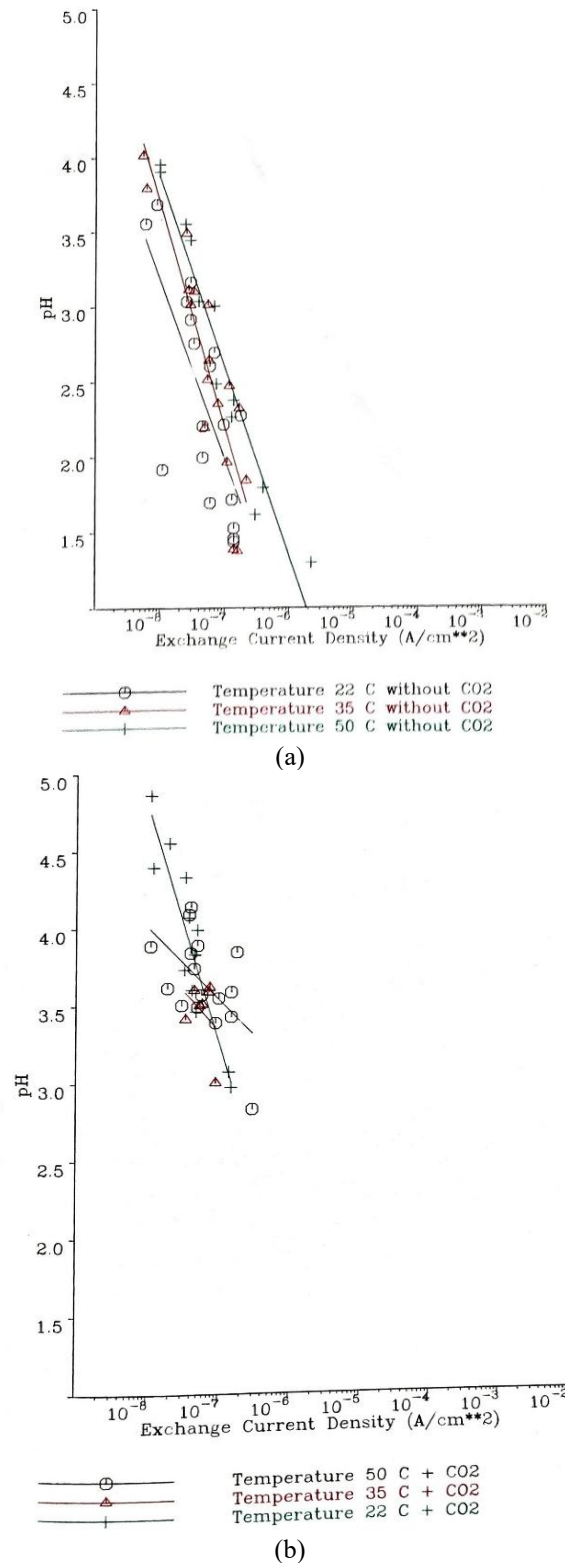
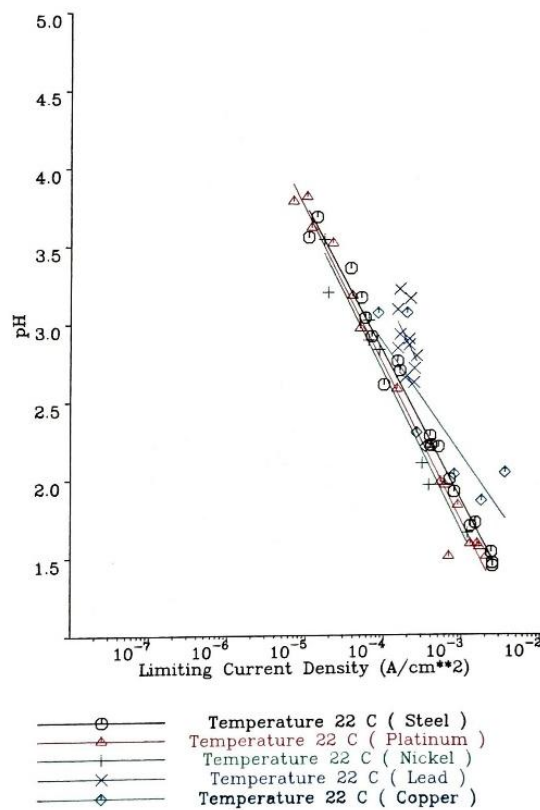
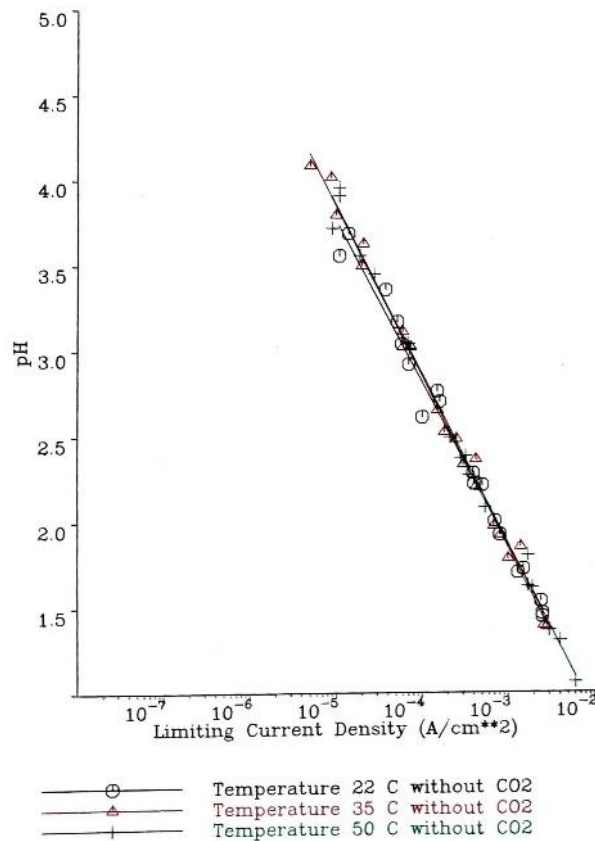


Figure 2. Variation of  $I_0$  with pH on steel

### Variation of Limiting Current Density with pH on Steel

The limiting current density for the cathodic hydrogen evolution reaction was found to vary linearly with the bulk solution pH. As was found for the other metals, it is the proton concentration in the solution which determines the magnitude of the limiting current density  $I_{L}$ . An increase in the proton concentration in the solution leads to an increase in the limiting current densities towards higher values of applied current densities. It was found that at

22°C, for instance, the variation of the limiting current density with respect to the bulk solution pH (Figures 3,4,5 and 6 ) is  $\log I_L = -1.126 - 1.020\text{pH}$ .



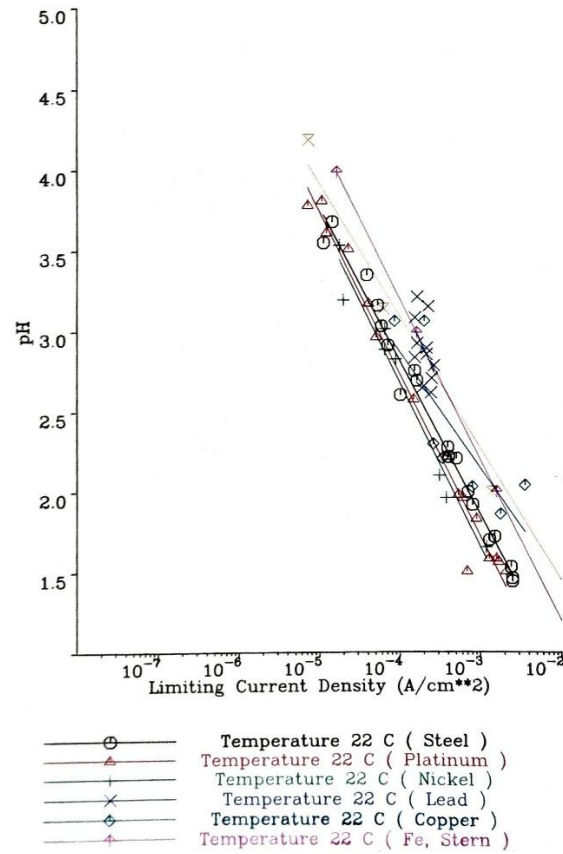


Figure 5. Variation of  $I_L$  with pH

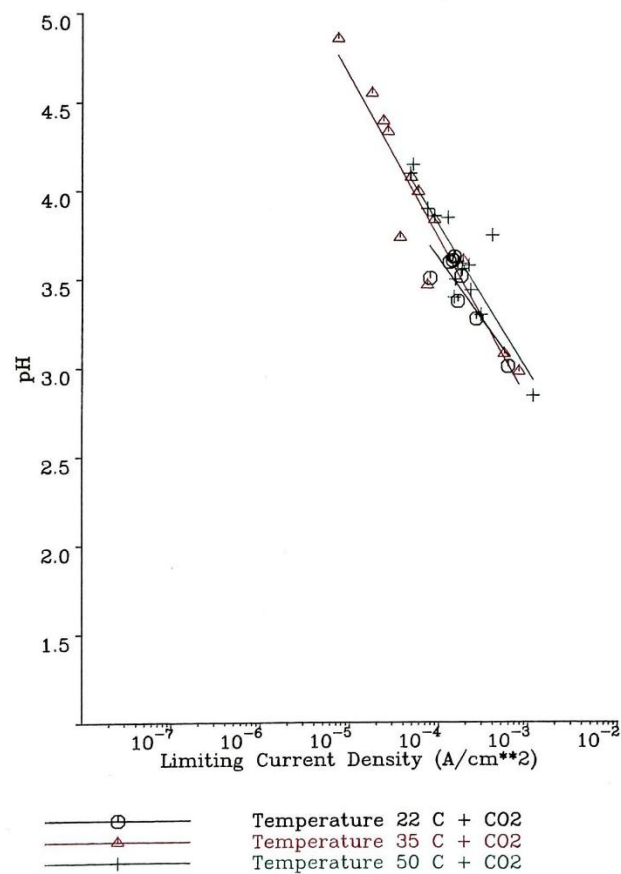


Figure 6. Variation of  $I_L$  with pH on steel



The relation given by Stern in his study of the corrosion of steel in sea water (figure 5) is  $\log i_L = -0.845 - \text{pH}$  which is close to the value found in this study. At pH 0.0, the limiting current density is  $7.482 \times 10^{-2} \text{ A/cm}^2$ , compared with  $2.735 \times 10^{-1} \text{ A/cm}^2$  and  $1.429 \times 10^{-1} \text{ A/cm}^2$ . The results are very close to each other and very reproducible. The limiting current densities are in the same range of values found for all the metals investigated, showing the independence of  $i_L$  on the nature of the working electrode material (Stern & Geary, 1957).

### Effects of Temperature

In deep gas wells, the corrosion rate is increased by  $\text{CO}_2$  partial pressure coupled with high temperature. Increasing the temperature from 22 to  $50^\circ\text{C}$  leads to an increase in both values of limiting and of exchange current densities (figure 7).

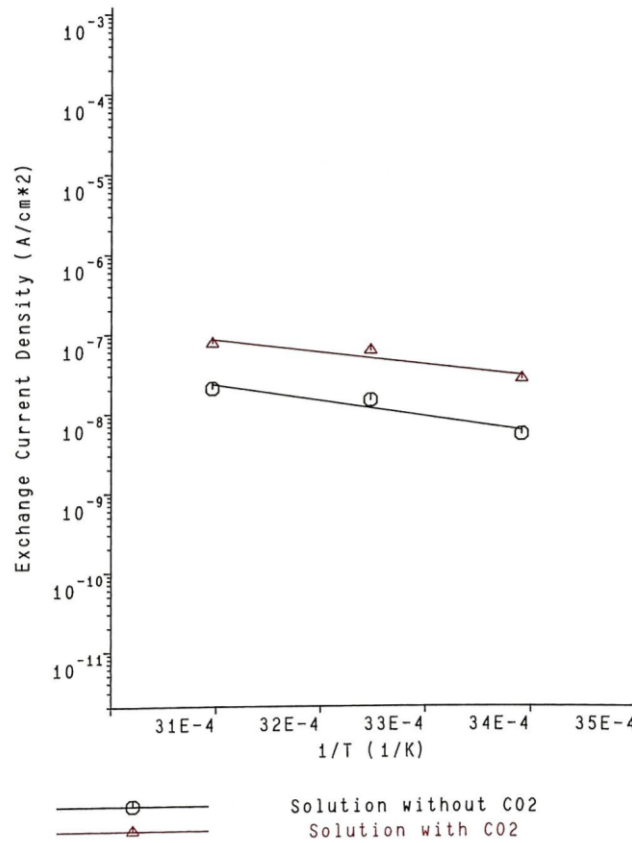


Figure 7. Variation of  $i_0$  with  $1/T$  on steel (pH 3.5)

### In $\text{CO}_2$ -NaCl Saturated Solutions

The corrosion rates obtained in this work are comparable with those of De Waard and Milliams and was found at  $22^\circ\text{C}$ , 0.48mm/year compared to 0.9 mm/year at 1 Atm. pressure  $\text{CO}_2$  and the same difference was found at for 35 and  $50^\circ\text{C}$  (De Waard & Milliams, 1975).

### Summary of Results

The hydrogen electrode reaction is the same on all the metals examined. This is modified by the exchange reaction, but the limiting current are for all the metals are in the same range. The steel used in the oil industry will be under corrosion conditions depending on those factors which affect the cathode reaction. Therefore, pH decreases and increases in temperature combine to increase the rate. The presence of concentration of  $\text{CO}_2$  increases the pH at the steel surface thereby increasing the corrosion rate. The temperature increase is shown to increase diffusion which increases the limiting current and the corrosion rate.



By studying the effect of temperature on  $I_0$  and  $I_L$  it may be possible to decide whether additions of  $\text{CO}_2$  change the activation energy for the  $I_0$  or  $I_L$  change the pre-exponential term, i.e., the frequency factor or the number of sites for the reaction to occur. This is the real meat of the discussion as different metals appear to react differently to additions of  $\text{CO}_2$  and changes in temperature.

### Activation Energy Analysis

The relation between the exchange current density  $I_0$  ( $\text{A}/\text{cm}^2$ ) and the inverse of the temperature ( $^\circ\text{K}$ ) is given by the following  $I_0 = A \exp(-\Delta G/RT)$  where  $\Delta G$  is the activation energy of the system, ( $\text{KJ}$  or  $\text{Kcal}/\text{mole}$ ),  $R$  is the gas constant ( $8.3\text{~J}/\text{mole}$ )

$T$  is the temperature in  $^\circ\text{K}$ ,

$A$  is a constant or pre exponential factor.

The variation of  $I_0$  versus  $1/T$  for mild steel in the presence and in the absence of  $\text{CO}_2$  at pH 3.5 at three different temperatures are plotted in (Figure 7). As far as the activation energy analysis is concerned, some conclusions for the metals capable of being a catalyst to the hydrogen reaction can be drawn, that is, the introduction of  $\text{CO}_2$  into each one of the systems studied results in, a noticeable change in the activation energy on Pb, and a small change on the other metals for the exchange current density, however, a big change of activation energy on Ni, Cu, and Pb, and a small change on Fe and Pt for the limiting current density.

As far as polarization curves for the hydrogen reaction on Pt, Ni, Cu and Pb in 4% NaCl acidified solution are concerned, similar relations were found for the limiting current densities. The relations agree very well with the relations given in the literature and the curves still present the same characteristics shown for steel as far as the cathodic polarization curve is concerned. The fact that the effect of  $\text{CO}_2$  on the cathodic polarization of the various metals is the same, then the role of  $\text{CO}_2$  in the corrosion of steel in oil well brines is due to the  $\text{H}^+$  ion reduction and that  $\text{CO}_2$  contributes to  $\text{H}^+$  concentration when present. Dissociation of the carbonic acid, a weak acid, has been shown to be very important in the corrosion of steel by supplying protons to the cathodic sites.

### Conclusion

The role of  $\text{CO}_2$  in the increase in corrosion rate of steel in acidified and deaerated 4% NaCl solution has been shown to be associated with the controlling cathodic reaction, i.e., reduction of hydrogen ions. This has been confirmed by the observation that the reversible electrode potential is responsive only to the hydrogen ion concentration (pH) and that the exchange current and limiting current have been increased but the electrochemical reaction kinetics measured by the Tafel slopes, i.e., reduction of hydrogen ions, is unchanged. The fact that the hydrogen reduction reaction has been changed by  $\text{CO}_2$  means that the effect on the electrochemistry should be independent of the metal electrode used. This has been shown to be the case by studying the effect on the metals, Platinum, Nickel, Copper and Lead. In these cases, although the exchange current was dependent on the metal type, the limiting current and the reversible potential were unchanged.

The work carried out has not been able to provide a complete understanding but has contributed to our knowledge in the following ways.

1. The limiting current is not a function of the electrode material, but depends only on the solution concentration in reacting  $[\text{H}^+]$ .
2. The limiting current density for each pH investigated for each metal studied in this work is increased by the introduction of  $\text{CO}_2$  into the system. Although the bulk pH did not change by introduction of  $\text{CO}_2$  ( under high pressure ), the corrosion rate increased an order of magnitude and this was shown to be due to an increase in  $I_L$  of the hydrogen reduction reaction .
3. It has been shown that there is an increase in the exchange current density of the hydrogen reaction by the introduction of  $\text{CO}_2$  for each metal investigated. For the same  $\text{CO}_2$  pressure (concentration ), the  $I_0$  for steel, platinum, nickel increased by half a decade compared to a small change for copper and lead .
4. The exchange current density for the hydrogen ion reduction reaction has been shown to be dependent on the electrode material.  $I_0$  decreases in the following order  
 $I_{0,\text{Pt}} > I_{0,\text{Fe}} > I_{0,\text{Ni}} > I_{0,\text{Cu}} > I_{0,\text{Pb}}$
5. It was confirmed that the reversible potential of the hydrogen reaction is not affected by the choice of material used, and only depends upon pH either in the bulk solution with and without  $\text{CO}_2$  in solution.

## Scientific Ethics Declaration

\* The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

## Conflict of Interest

\* The authors declare that there is no conflict of interest.

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