

Enhancement of the Instantaneous Mass-Transfer Coefficient in Large Diameter Pipeline under Water/Oil Flow

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A mass-transfer study was carried out in water and water/oil flow in a large diameter flow loop by a limiting current density technique using oxidation of $\text{Fe}(\text{CN})_6^{4-}$ in 1 M NaOH. High-frequency and high-magnitude mass-transfer coefficients were found by potentiostatic measurements and may account for the corrosion rate enhancement in water/oil flow. The effect of oil droplets on the mass-transfer enhancement is highlighted and a mechanism of mass-transfer coefficient oscillation is proposed.
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Internal corrosion of carbon steel pipeline is a substantial problem encountered in the oil and gas industry. Efrid¹ *et al.* pointed out the importance of using flow loops to simulate pipeline conditions for corrosion study. Such importance was further shown in studies²⁻⁵ at our center. These studies emphasized that the results obtained from small diameter (e.g., 2.54 and 5 cm) flow loops cannot be easily extrapolated to large diameter pipeline, as the flow mechanisms in both systems can be entirely different. So large diameter pipeline (e.g., 10 cm) becomes an imperative condition for internal corrosion studies.

Water/oil two-phase flow is very common in oil transport pipeline. The results of a corrosion study in water/oil two-phase flow by Kanwar and Jepson⁴ showed that the corrosion rate unexpectedly increases with the increment of oil from 0 to 60% (v/v) at low velocity. They observed that the two components, shear forces and mass transfer, contribute to the enhancement of corrosion rates. However, these two components have not been distinguished.

Mass-transfer coefficients of reactant ions to and from the pipeline walls are important in studying corrosion. Mass-transfer studies in pipe mainly have focused on single-phase flow and small diameter pipe.⁶⁻⁸ Very few studies exist on multiphase flow and large diameter pipe (e.g., 10 cm). Therefore, the mass-transfer studies in multiphase flow in large diameter pipe have important significance and may be applicable to many industries, such as power generation, oil, and gas exploration.

In the present work, experiments were carried out in a large diameter flow loop at two levels of oil, 0 and 20% (v/v), at 1.0 m/s fluid velocity. Potentiodynamic and potentiostatic measurements were performed to determine the limiting current density^{9,10} from which the mass-transfer coefficient was calculated. The results of this work provide an explanation as to the enhancement of the corrosion rate in water/oil flow.

Experimental

The experiments were carried out in 10 cm inner diameter (i.d.) Plexiglas™ pipe. The overall layout of the system is shown in Fig. 1. This system had been used and described by Jiang and Gopal.¹¹ The solution used in the experiments was 0.018 M potassium ferri/ferrocyanide in 1.0 M NaOH electrolyte, stored in a 1 m³ stainless steel tank. The solution was pumped through a 10 cm i.d. PVC pipe by a variable-speed Moyno™ multiphase pump. The liquid flow rate was measured by means of an orifice plate.

LVT 200 oil was used which includes 60% cycloparaffinic hydrocarbon, 20% isoparaffinic hydrocarbon, 19% normal paraffinic hydrocarbon, and 1% other hydrocarbon. It has 3 cp viscosity and

850 kg/m³ density at 25°C. Nitrogen gas, stored in pressured cylinders, flowed through the tank. A regulator and valve controlled the gas flow rate. Nitrogen was used to deoxygenate the system before the test.

The test section is shown in Fig. 2. The reference electrode, working electrodes, and counter electrode were placed in the direction of the flow, respectively. All electrodes were made from Hastelloy C-276. The counter was a ring electrode mounted flush with the pipe wall. The working and reference electrode pins were inserted in the Plexiglas block along a line at the bottom of the pipe wall. The diameter of each pin was 1.5 mm and the distance between the consecutive working electrodes was 4.5 mm.

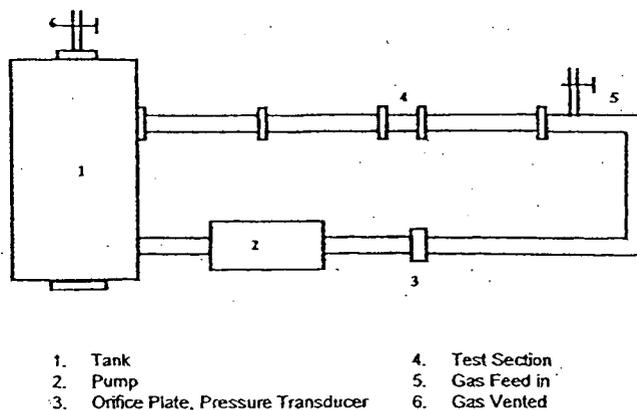


Figure 1. System layout (not to scale).

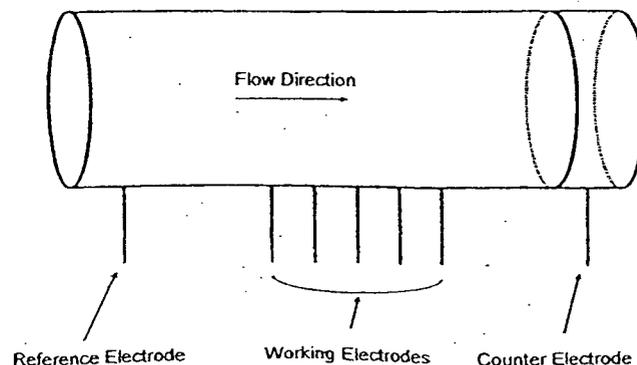


Figure 2. Test section layout, part 4 in Fig. 1.

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In multiphase systems, once the standard reference electrode becomes fouled with oil, it is almost impossible to get valid readings. Therefore, pseudo reference electrodes are becoming increasingly popular in multiphase systems, e.g., 316L stainless steel has been recommended as a pseudo reference electrode in electrical impedance spectroscopy (EIS) studies in multiphase flow conditions.¹² Sedahmed *et al.*¹³ have used nickel wire as a pseudo reference electrode in the mass-transfer at rough gas-sparged electrodes. The dimensionally stable anode (DSA) has been applied as pseudo reference electrode in the study of two-phase mass transfer in channel electrolyzers with gas-liquid flow.¹⁴ In the present electrolyte solution, the Hastelloy C276 can also provide a stable potential considering that it is better than stainless steel or nickel in terms of metal stability. Thus, it was employed in these mass-transfer studies in water/oil and other multiphase systems in large diameter pipeline.

Prior to each set of experiments, the working electrodes were prepared using a combination of several techniques. First the electrode surface was sanded with progressively finer grades of 600 and 1500 grit paper (Master Mechanic), followed by 45 and 9 μm Meta-di diamond compound (Buehler), and finally polished with 1.0 μm γ -alumina micropolish (Buehler). Next the electrodes were rinsed with dilute H_2SO_4 . Then each electrode was treated cathodically at 20 mA/cm^2 for 20 min with 5% H_2SO_4 as an electrolyte. The test section was then installed into the system after rinsing with demineralized, distilled water.

Gamry software CMS 105 was used for the potentiodynamic and potentiostatic measurements. All experiments were performed at 25°C and under a full pipe flow at fluid velocity of 1.0 m/s.

Results and Discussion

The one-electron oxidation of ferrocyanide was studied at the working electrodes. The limiting current density was obtained from the potentiodynamic curve and the instantaneous limiting current density was measured from the potentiostatic curve at a given potential. The mass-transfer coefficient was calculated from the following equation

$$K = I_L / (nFAC_b) \quad [1]$$

Since the $\text{Fe}(\text{CN})_6^{4-}$ was not soluble in LVT 200 oil, its concentration was not corrected for the volume fraction of the oil when calculating the mass-transfer coefficient. According to the results obtained by Shi *et al.*,¹⁵ in water/oil flows in large diameter horizontal pipelines, the emulsion of water/oil does not exist at low velocity less than 2.6 m/s. Therefore, in the case of this work, there should be no emulsion at the velocity of 1 m/s.

Figure 3 shows the polarization curves obtained from potentiodynamic measurements in water flow and water/oil two-phase flow.

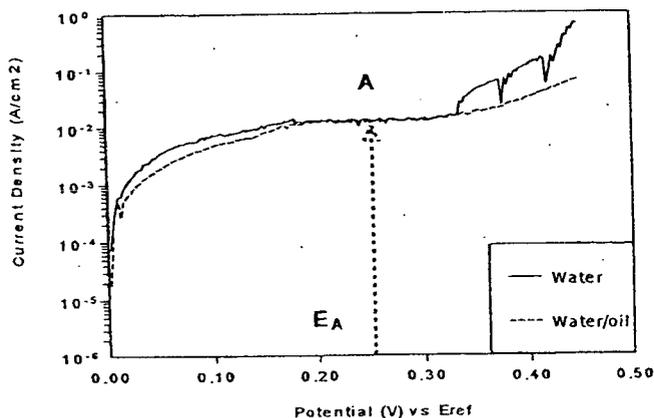


Figure 3. Limiting current density in water and water/oil flow at velocity 1 m/s. Point A is in the middle of the limiting current plateau. E_A (0.25 V) is the applied potential in the potentiostatic experiments.

Limiting current densities were observed on the two curves after 0.25 V (point A). The values are nearly equal at $1.10 \times 10^{-2} \text{ A}/\text{cm}^2$. According to Eq. 1, the mass-transfer coefficient is $6.30 \times 10^{-5} \text{ m/s}$.

Kanwar and Jepson⁴ observed that the corrosion rate unexpectedly increases with the increment of oil from 0 to 60% (v/v) at low velocity. However, the mechanistic reason was not explained completely. In general, fluid velocity has two effects on corrosion, the mass-transfer effect and the surface shear stress effect.^{16,17}

The experimental results from Fig. 3 show that the measured time-averaged mass-transfer coefficient is nearly the same in water and water/oil. Zhang *et al.*¹⁸ showed that the CO_2 corrosion rate is mass transfer controlled in low velocity from 0 to 3 m/s through experimental studies. It is unlikely that the mass-transfer coefficients are the same between water and water/oil flows because the corrosion rates are different in these two kinds of fluids. Thus, the difference in the instantaneous mass-transfer coefficient in water and water/oil can be considered as a main reason for the different corrosion rates. In this work, the instantaneous limiting current density was measured to determine the instantaneous mass-transfer coefficient. The potential in the middle of the limiting current plateau ($E_A = 0.25 \text{ V}$), as shown in Fig. 3, was selected for making the potentiostatic measurements to record the instantaneous limiting current density shown in Fig. 4 and 5 for water and water/oil flows, respectively. Under these conditions the surface concentration is expected to be close to zero. The responses in Fig. 3 show that the limiting current density has some small fluctuations, which have been amplified in the potentiostatic experiments shown in Fig. 4a and 5a. The response between limiting current density and time in water flow (Fig. 4a) shows a relatively flat baseline, although there is a low level of fluctuation. These fluctuations may have resulted from a surface oxidation film on the electrode. However, large current spikes in water/oil flow are observed as shown in Fig. 5a. If it is assumed that these spikes are only a short fraction of the whole time period tested, then it can still be considered that the zero surface concentration is valid.

Based on Eq. 1, the instantaneous mass-transfer coefficient can be obtained, and the results for water and water/oil phases are shown

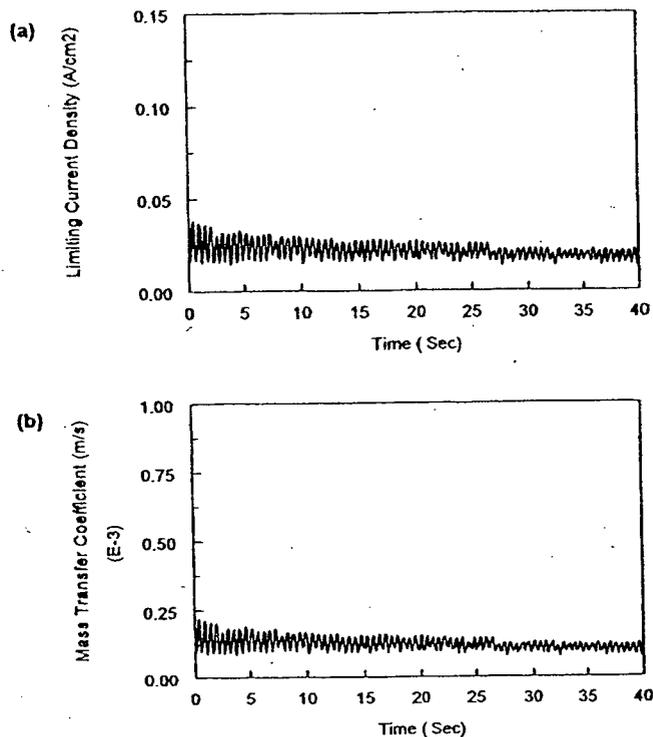


Figure 4. (a) Instantaneous limiting current density and (b) instantaneous mass-transfer coefficient in water flow at 1 m/s velocity.

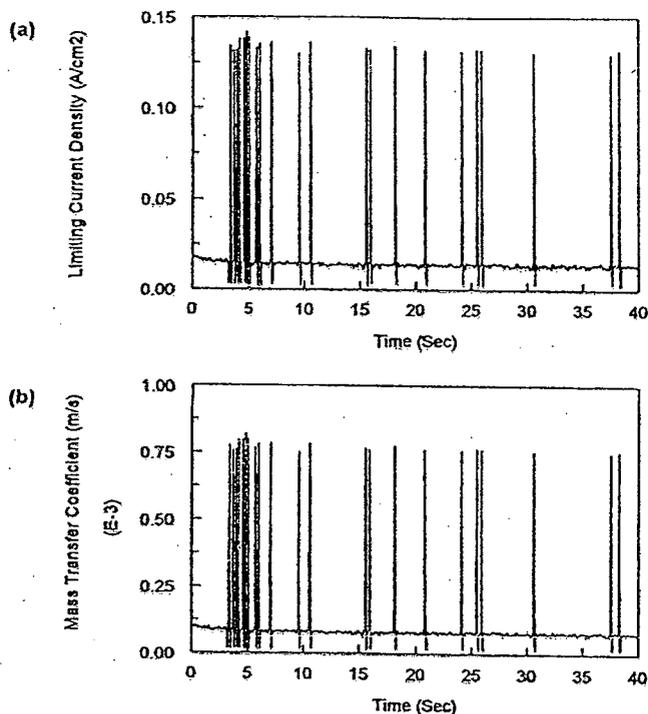


Figure 5. (a) Instantaneous limiting current density and (b) instantaneous mass-transfer coefficient in water/oil flow at 1 m/s velocity.

in Fig. 4b and 5b, respectively. The average value of the instantaneous mass-transfer coefficient in water flow is 1.10×10^{-4} m/s. The average value of the instantaneous mass transfer coefficient at the spikes in water/oil flow is 7.65×10^{-4} m/s, and the average value of the baseline instantaneous mass-transfer coefficient in water/oil flow is 8.06×10^{-5} (Fig. 5b). Adding oil to water flow enhanced the instantaneous mass-transfer coefficient about seven times. Kanwar and Jepson⁴ had considered that shear forces and the effects of turbulence contribute to enhanced corrosion rates under water/oil flow. The former includes a scouring type of corrosion while the latter can account for the increase in mass-transfer rate to and from the pipeline wall. They concluded that the effect of each component could not be distinguished at that time. Therefore, the high-frequency and high-magnitude instantaneous mass-transfer coefficient found in the present study may answer this question and may result in the enhancement of the corrosion rate in water/oil flow.

Several recent studies have addressed the effects of ultrasound on mass transfer.¹⁹⁻²² In those studies it was found that the collapsing bubbles renewed the surface concentration which was not zero during the period of bubble formation and collapse. Further, it was shown that microjets or forced convection produced when cavitation bubbles impinge on, or near, the electrode increase the mass transport of electrolyte to the electrode. Through such comparison, the impingement of an occasional oil droplet corresponds to the spikes of limiting current density and may have increased the mass transfer in this study.

Similar current spikes (or oscillatory phenomena) to those observed in Fig. 4 in the oxidation of $\text{Fe}(\text{CN})_6^{4-}$ ions have been observed by Li *et al.*^{23,24} However, their experiments were performed in quiescent solutions. They also considered that oscillations would disappear with agitation. In the present flow system under higher turbulence, the low level of fluctuation of current oscillations exists and can only be attributed to the fluctuation of turbulent flow itself in water flow and possibly the influence of a surface film on the electrode (Fig. 4). Li considered that the oscillations are attributed to the occurrence of bistability, *i.e.*, $\text{Fe}(\text{CN})_6^{4-}$ oxidation and oxygen production at different potentials, coupled with convective feedback induced by oxygen evolution. This bistability theory con-

sidered that it is the overlap of the positive and negative feedback between the bistable states [$\text{Fe}(\text{CN})_6^{4-}$ oxidation and oxygen production] that accounts for the oscillations. It had been described through a circuit model.²³ The positive feedback emphasizes the determination of oxygen evolution to raise the limiting current to the level of the peaks under the initial high voltage. This is because the growth, detachment, and movement of oxygen bubbles produce a forced convection, which replenishes the surface concentration of the anions. However, the oscillation found in the water/oil system does not include the influence of oxygen evolution because no oxygen was produced under the voltage corresponding to the limiting current. Therefore, the high-frequency and high-magnitude current oscillations encountered in water/oil flow (Fig. 5) cannot be explained directly by this bistability theory.

A new qualitative explanation may be given, as follows, after considering the influence of an oil droplet and revising Li's theory. When a constant voltage (V) is imposed in the circuit,²⁵ it is divided into two parts: one part $I(R_c + R_s)$, where I is the circuit current, R_c is the external series resistance, and R_s is the solution resistance, and another is E , the potential of the cell. At the beginning of the imposition of the potential, E drives the current over the limiting value of the $\text{Fe}(\text{CN})_6^{4-}$ anions in a stationary state, so the surface concentration of the anions is depleted and maintained at zero because this potentiostatic experiment is carried out at the selected voltage E_A . The movement of oil droplets produces a forced convection, which replenishes the surface concentration of the $\text{Fe}(\text{CN})_6^{4-}$ anions, and raises the limiting current plateau over the stationary one to the spiked level. This may be called a positive feedback because it increases the current. In the meanwhile, a negative feedback comes from two aspects: one is the depletion of the surface concentration of the $\text{Fe}(\text{CN})_6^{4-}$ anions by oxidation; and the other is a decrease in E because of the increase of I and so $I(R_c + R_s)$ under constant voltage. This reduces the current to the minimum until the oil droplet influences it again. It is believed that the combination of positive feedback and negative feedback accounts for the oscillation of the instantaneous limiting current. Chaos analysis^{24,25} could be used to prove if the oscillation of limiting current is of deterministic chaos. This work is currently under study.

Conclusion

The effect of oil droplets on mass transfer in large diameter pipeline has been discussed in this work. A high-frequency and high-magnitude instantaneous mass-transfer coefficient found in water/oil flow may explain the enhancement of the corrosion rate in low fluid velocity (1 m/s).

The current oscillations are explained by the influence of oil droplets in water/oil flow. The combination of positive and negative feedback results in the current oscillations and the spikes in the instantaneous mass-transfer coefficient.

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List of Symbols

A	surface area of the electrode, m^2
C_b	bulk concentration of potassium ferrocyanide, mol/m^3
E_A	applied potential (obtained from potentiodynamic plot)
F	Faraday's constant
I	circuit current
I_L	limiting current, A
K	mass-transfer coefficient, m/s
n	number of moles reacted
R_c	external series resistance
R_s	solution resistance
V	voltage

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