

The Corrosion of (Fe,Zn,Cu) Metals in 3.5%Nacl Solution Under Different Flow Conditions

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Abstract

As the practical importance of protection of industrial equipments from corrosion the need arises to study the corrosion of different metals as Carbon steel, Zinc and Copper measured their corrosion current and potentials have been investigated in 3.5% NaCl solution at 40°C for different flow conditions ($Re = 5000, 10000$ and 15000), by using commercial metal pipe as test specimens cylindrical. Potentiodynamic polarization studies have been performed for single metals. It was found experimentally that the corrosion of metals (Fe, Zn, Cu) is under diffusion control since the corrosion current density (i_L) increases and corrosion potential ($E_{corr.}$) shifts to less negative with increasing velocity, the limiting diffusion current density is independent of the nature of the cathode material, but it depends on the Reynolds number.

The corrosion current density of metals (Fe, Zn, Cu), shows a good agreements with other works, and reasonable agreement with Culburn –Chilton and Paulson correlations are also observed at different Re.No.

تأكل معادن الحديد والخراسين والنحاس في محلول ملح الطعام 3.5% وتحت حالات جريان مختلفة

الخلاصة

بسبب الاهمية العملية في حماية المعدات الصناعية من التأكل ظهرت الحاجة لدراسة التأكل للفولاذ الكربوني وللخراسين والنحاس بالحالة المنفردة في محلول كلوريد الصوديوم 3.5% عند درجة حرارة 40°م، ومن دائرة الجريان المستمر، بأستخدام انبوب بقطر مقداره (2.6)سم حيث تم بحث حالات التأكل تحت ظروف الجريان المضطرب وبقيم مختلفة ل ($Re.no.$) (5000,10000,15000).

تم استخدام جهاز الأستقطاب (Potentiostatic) لدراسة ميكانيكية التأكل للمعادن اعلاه وبينت النتائج ان تأكل معادن (Zn, Cu, Fe) يكون تحت سيطرة تفاعل الانتشار للاوكسجين (Diffusion Control), على سطح المعدن وليس هناك تأثير لنوعية المعدن بالنسبة لتفاعل الاوكسجين الكاثودي على سطح المعدن وتم استخدام برنامج (Grapher win and Regression), للحصول على معادلات تربط بين معامل انتقال المادة ومعدل الجريان وكان هناك تطابق تقريبي لهذه العلاقات مع كثير من العلاقات المكتشفة من قبل الباحثين الاخرين.

Introduction

Corrosion is the deterioration of materials by chemical interaction with their environments. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals ^[1]. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion are ^[1]: reduction of metal thickness, hazards or injuries to people arising from structural failure, loss of time, reduced value of goods, contamination of fluids in vessels and pipes, perforation of vessels and pipes, loss of technically important surface properties of a metallic component. Mechanical damage to valves, pumps, etc, adds complexity and expense of equipment which needs maintenance to protect it from corrosion ^[1]. Almost all corrosion problems and failures encountered in service can be associated with one or more of the eight basic forms of corrosion: general corrosion, galvanic corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, stress

corrosion cracking, dealloying, and erosion corrosion ^[2].

The study of controlled mass transfers of electrochemical and corrosion processes is of fundamental importance that allows the provision of the corrosion data for various metals in a process plant. In industrial chemical processes, there are many parts or units which involve heat input or extraction such as heat exchangers units, refrigeration units, power plant units, etc. The corrosion process involved in these units is to be under the influence of action of mass transfer.

Cohen ^[3] showed that the natural water pipe corrosion increased with increasing velocity up to 1.6 m/s and then decreased with further increase of flow. Copson ^[4] found that corrosion, in general, increased with increase in velocity.

Eliassen et al. and Romeo et al. ^[5,6] state that the velocity of the water, degree of turbulence, geometry of pipes, and other physical factors have a direct influence on the movement of dissolved O₂ through the fluid.

Vilambi and Chin ^[7] carried out an experimental and theoretical

investigation on turbulent mass transfer to a rotating cylinder. They analyzed the reduction of ferricyanide ion on the rotating cylinder as a mass transfer operation to express the corrosion rate in terms of mass transfer parameters and obtained the following equation for $800 < Re < 80000$ and $Sc=1900$,

$$Sh = 2.79Re^{0.61} \dots (1)$$

they found that Eq. (1) agrees with Equation of Eisenberg et al. [8] to within $\pm 12.5\%$. The following expression for the Nernst diffusion layer was obtained

$$\delta_d = 0.36\left(\frac{d}{Re^{0.61}}\right) \dots (2)$$

Poulson [9] studied the influence of fluid flow on the corrosion rate for different geometries (rotating disk, rotating cylinder, impinging jet, nozzle, and tube) using electrochemical technique. For pipe flow he obtained the following correlation for fully developed turbulent flow.

$$Sh = 0.0165Re^{0.86}Sc^{0.33} \dots (3)$$

This predicts entrance effects to decrease with increasing Re and even at Re of 10^4 they will have disappeared

before 1 diameter. The author states that the corrosion rates, even when controlled by diffusion, are not always simply related to mass transfer.

Fluids flowing past a corroding surface often affect the way an alloy corrodes in an environment. An acceleration of the corrosion rate caused by fluid moving past the alloy surface would make corrosion rate predictions based on stagnant tests inaccurate [10]. For reaction rate that is diffusion controlled, the limiting current density (LCD) is obtained from Eq. (4)

$$i_{lm} = \frac{D n F C_b}{\delta_m} \dots (4)$$

Where: **D** = diffusion coefficient of reacting ion (m^2/s). **n** = number of electrons transfer. **C_b** = bulk concentration of reacting ion ($moles/m^3$). **d_m** = thickness of the diffusion layer (m).

$$i_L = Z F k \Delta C \dots (5)$$

Thus the basis of the LCD technique in determining k (mass transfer coefficient) is to measure LCD at fixed ΔC . Also if k is known then measuring i_L allows the determination of ΔC , which will be the bulk concentration. If this approach can

be applied to a corrosion process in which both an anodic and cathodic reaction occur, if either reaction is diffusion controlled then the rate of corrosion will be given by

$$\text{Corrosion Current} = ZFk \Delta C \dots (6)$$

The value of ΔC will be the bulk concentration of cathodic reactant for systems which are cathodically controlled and will equal the solubility limit of the relevant product when the anodic reaction is diffusion controlled. It is found from dimensional analysis that [9]:

$$Sh = \text{cons. } Re^x Sc^y \dots (7)$$

x is usually between 0.3 and 1, y is typically 0.33. Substituting for k yields

$$\text{Corrosion Current} = zF\Delta C \frac{D}{d} \left(\frac{ud}{v}\right)^x \left(\frac{D}{v}\right)^y \dots (8)$$

i.e. corrosion current can be predicted without any tests if the relevant parameters are known. However this would predict no corrosion at zero velocity and natural convection would have to be added at low to zero flow velocities [5].

Nesic et al. [11], using rotating cylinder electrode, studied the effect of velocity on the limiting current density.

For temperature of 22°C and Re up to 26000, the cathodic polarization curves show that the limiting current density increases with velocity increase, and the anodic polarization curves shows that the velocity slightly affects the magnitude of the current densities.

Shrier [12] also points out that increased velocity usually increases corrosion rates by removing corrosion products which otherwise might stifle the anodic reaction and by providing more oxygen, may stimulate the cathodic reaction.

Kolman et al. [13] found that increasing the oxidizer concentration increases the corrosion potential, while increasing the NaCl decreases the corrosion potential.

Kim [14] carried out electrochemical tests conducted to study the external corrosion of a steel pipeline beneath the disbanded insulation from synthetic groundwater. The corrosion rate of pipeline steel under the insulated condition was much lower than that under the uninsulated condition. The better corrosion property of the insulated steel was attributed to the formation of a

protective rust layer under the insulation. This is mainly because the mass transfer or the thickness loss rate through the insulation was small compared to the connective mass transfer directly to the electrolyte without insulation.

Experimental Work

Throughout this investigation the corrosion of Carbon Steel, Zinc and Copper metals in single condition was studied in 3.5% sodium chloride solution under flow conditions at constant temperature ($40^{\circ}\text{C} \pm 0.2$). Two kinds of electrochemical measurements were conducted: Corrosion potential measurement and Potentiodynamic polarization measurement. Three different Metals were using C.steel, Zinc and Copper. The Metals specimens dimension of (2.6cm) inside diameter, (2.8cm) outside diameter and (2.4cm) length and were used as received. The test section was mounted horizontally and preceded Entrance region (i.e., $L/d=10$) of Q.V.F. tube to ensure fully developed velocity profile before the solution reaching the

specimens ^[15, 16, 17]. The test section was followed by (35cm) exit length to avoid disturbance at the outlet ^[18, 19]. The flow system was designed to contain the following items as shown in Fig. (1).

3.1 Corrosion Potential Measurements

In Corrosion Potential Measurements, the test section was composed of the following components, as shown in Fig. (2).

3.2 Polarization Measurements

In the polarization measurements, the test section was composed of the following components, as shown in Fig. (3).

The sodium chloride solution was supplied to the system and circulated through the by-pass, going through the heat exchanger until the required temperature (40°C) was achieved, after that the electrolyte was allowed to pass through the corrosion cell and the flow was adjusted at the desired Reynolds number value. Two sets of experiments were performed:

In the first sets, for three metals, the corrosion potential was measured using digital Multirange Voltmeter.

In the second set, for three metals, Potentiodynamic polarization techniques studies was carried out. At the beginning of the test the potential was measured every minute, along the period of polarization. The specimen was cathodically polarized from (-1000 mV) for copper, (-1100 mV) for c.steel and (-1500 mV) for zinc.

Result and Discussion

The polarization method by using Potentiodynamic technique was used to study the behavior of the metals (Carbon Steel, Zinc and Copper) in 3.5% NaCl solution at 40 °C and for different Reynolds numbers [ranging from (5000-15000)]. The open circuit potential method was used to predict the corrosion potential.

4.1 Corrosion Potential of Single Metal

The corrosion potential was monitored by measuring the open circuit potential at a variable Reynolds number (5000-15000). Fig. (4) Shows the effect of Reynolds number on the corrosion potential of carbon steel, zinc and copper measured at the end of 4 hour exposure. It is observed that the corrosion potential of carbon steel and zinc increases to the positive direction slightly with increasing Reynolds number, but the corrosion potential of copper is observed to be nearly constant with increasing Reynolds number^[11, 9 and 19].

4.2 Potentiodynamic Polarization Curve

The polarization curves provide information about the effects of changes

in potential on the corrosion behavior of the metals. Cathodic polarization behavior was studied by using Potentiodynamic technique for the individual metals (carbon steel, zinc and copper) in 3.5% NaCl solution at 40°C with different flow rate (Re) as shown in Figs. (5) to (7). These diagrams show two regions, the cathodic and anodic regions. The behavior of the cathodic reaction on all metals is found under diffusion control. The results and discussion of this section will be split into two items, i.e., corrosion potential and limiting current density.

4.2.1 Corrosion Potential (E_{corr})

As the electrode potential is raised, the corrosion potential (E_{corr}) is reached eventually at which no net current can be measured. The corrosion potential values for different metals at various flow rates in 3.5% NaCl solution at 40°C are presented in Figs. (5) to (7) and tabulated in Table (1).

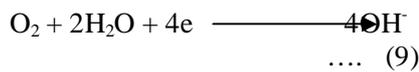
Table (1) generally shows that the corrosion potential increases slightly in positive direction with increases in Reynolds number, except for copper metal which increase slightly in negative direction as the Reynolds number increases. This is in agreement with the results of many workers^[19, 20, 21, 22]. The cathode reaction which is under mass transfer control is increased by increasing velocity i.e. the limiting current density is increased, while the anodic reaction which is under activation control is not affected by velocity^[23, 24].

4.2.2 The Limiting Current Density i_L

The limiting current density (i_L) values of the oxygen reduction reaction

are the most important characteristic of the cathodic region at the various Reynolds number for Cu, Fe and Zn shown in Table (2).

Table (2) present the limiting current densities calculated from the polarization curves of different metals at different flow conditions. The values of the limiting currents of the metals are not significantly different which indicates that they are independent of the nature of the metal electrodes as shown in this table. The value of Re. in 3.5%NaCl solution at 40°C affects mass transfer controlled oxygen reduction Eq. (9). Since the corrosion of Cu, Fe and Zn in aerated 3.5% NaCl solution is under mass transfer control, the cathodic partial process of the oxygen reduction reaction is controlled by the rate of oxygen diffusion. Therefore, the corrosion current density is equal to the absolute value of the limiting current density for the cathodic partial process, Eq. (10)^[23, 8].



$$i_{corr} = i_L = nF K C_b \quad \dots (10)$$

Fig. (8) Shows the variation in oxygen limiting current density (i_L) with Reynolds number for clean surface. It is clear that as Reynolds number increases i_L increases for all metals. This behavior is in accordance with mass transfer theory and previous studies, e.g. rotating cylinder and rectangular duct^[15]. This is attributed to the increase in the amount of oxygen arriving to the metals surface and hence leads to a higher (i_L).

Increasing the velocity leads to shift the intersection point between the decreasing cathodic polarization curve of O_2 reduction and increasing anodic polarization curve of metal dissolution in polarization curve. Hence the limiting current density will be increased. Higher Reynolds number leads to remove the corrosion product on the metal surface causing clean surface to appear to the solution and hence increasing the corrosion current.

4.2.3 Calculation of Mass Transfer Coefficient

The mass transfer coefficient can be estimated using Eq. (11).

$$K = i_L/nFC_b \quad \dots (11)$$

where:

n is charge transfer=4.0

F is Faraday constant=96487 (Coulombs / mole).

C_b is the oxygen concentration = 0.14016 (mole / m^3) (measured by Oxygen meter at 40 c°). i_L is the limiting current density (A / m^2).

Fig. (9) Shows the variation in mass transfer coefficient with Reynolds number for different metals. It is clear that (k) increases with increasing Re. for (cons. Sc.No.). The increase in k with Re. can be explained according to the following Eq. (12)^[19, 19, 22]:

$$k = \frac{D + \epsilon_D}{\delta_d} \quad \dots (12)$$

As Reynolds number increases the convective mass transport of O_2 will increase, i.e., mass transfer by eddy diffusion (ϵ_D) due to the increased turbulence. Increasing turbulence leads to decrease in the thickness of the viscous sub-layer (δ_d) and the diffusion

layer that represents the main resistance to momentum and mass transport respectively [9, 11, 27], hence the O₂ concentration gradient at the surface will be increased leading to increase in mass transfer coefficient (k).

4.2.4 Calculation of the Sherwood Number

Fig. (10) Shows the relationship between Sherwood number and Reynolds number for different metals, increasing Re increases the Sh, because the increase in Reynolds number would lead to increase in the mass transport by convection (or eddy diffusion) over that by molecular diffusion so that Sherwood number is the ratio between the mass transfer velocity and diffusion velocity.

4.2.5 Mass Transfer Correlation

Using Sherwood number values from Fig.(10) and the physical properties of 3.5% NaCl solution at 40 °C, employing **the grapher-win and regression techniques**, the following correlations are obtained (see Eq. (7)) assuming the dependence of Sh on Sc is raised to power (0.33) as customarily found by others^[28,9].

$$\text{For Carbon Steel (R = 0.86)} \quad \text{Sh} = 0.0184 \text{Re}^{0.975} \text{Sc}^{0.33} \quad \dots (12a)$$

$$\text{For Zinc (R = 0.88)} \quad \text{Sh} = 0.0371 \text{Re}^{0.934} \text{Sc}^{0.33} \quad \dots (12b)$$

$$\text{For Copper (R = 0.84)} \quad \text{Sh} = 0.0125 \text{Re}^{0.967} \text{Sc}^{0.33} \quad \dots (12c)$$

R= Coefficient of determination (R-squared).

Many correlations of such type are available in the literature which is

satisfactorily applied for electrochemical processes under turbulent flow conditions.

Many workers [20, 29] agree that the surface roughness enhances the mass transfer. It is important to realize that velocity dependent corrosion is normally an unsteady process, the interaction between this surface and the corroding fluid will most likely result in non-uniform metal loss and also in the formation of the corrosion product layer. This progressive modification of the metal surface will affect its physicochemical interaction with the fluid. It follows that there will always be a two coupling between the corrosion morphology and the local flow geometry at the metal/liquid interface. In general, the constants a and b depend on Reynolds number and the latter depends on physical properties at fixed velocity.

Examining literature reveals a variety of *i_L* dependence on Re (or u) that was found by authors for various geometries. The manner in which velocity affects the limiting diffusion current is a marked function of the physical geometry of the system [30]. This dependence depends on the nature of the system under consideration, i.e., geometry, roughness of the surface, viscosity, and temperature [31, 9, 30, 27] but it generally ranges from 0.2 to 1 [31, 9, 30] as evidenced by the present findings. In the present section it is desired to investigate the influence of Re and metals on mass transfer groups mentioned above for clean surface. This section also aims to propose adequate correlations for mass transfer coefficient (or Sh) with Re at various metals and investigate the influence of the

developing roughness on the dimensionless groups.

Experimental correlations of k (or Sh) with Sc can not be simple.

1- This is because changing Sc by temperature leads to change in many physical properties that have a direct influence on k (or Sh). These physical properties are mainly the oxygen diffusivity (D), bulk concentration (C_b), and kinematics viscosity (ν)^[16].

Conclusions

From this study the following points can be concluded:

- 1- The corrosion of single metals (zinc, carbon steel and copper) in 3.5% NaCl solution at 40°C is under diffusion control, the corrosion current density increases with increasing velocity.
- 2- The limiting diffusion current density is independent of the nature of the cathode material, but it is dependent on the Reynolds number.
- 3- The results of polarization experiments for single metals, give the following arrangement of metals to combat corrosion in the environment of 3.5%NaCl solution: $Cu > Fe > Zn$.
- 4- Generally, the experimental results for corrosion current show good agreement with others. Reasonable agreement with Colburn - Chilton and Paulson correlations are also observed at different Reynolds number.

6. References

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Table (1) E_{corr} of Cu, Fe and Zn under Different Re.

Metal	Corrosion Potential ,mV ,vs. SCE		
	Re = 5000	Re= 10000	Re= 15000
Copper	-240	-260	-280
Carbon Steel	-600	-580	-560
Zinc	-1080	-1060	-1040

Table (2) The LCD of Cu, Fe and Zn under Different Re.

Metal	Limiting Current (A/m ²)		
	Re = 5000	Re = 10000	Re = 15000
Copper	1.155	2.424	4.219
Carbon Steel	1.88	3.395	5.314
Zinc	3.175	4.844	8.713

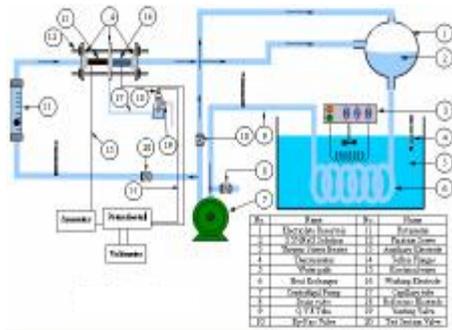


Fig. (1) Experimental Apparatus.

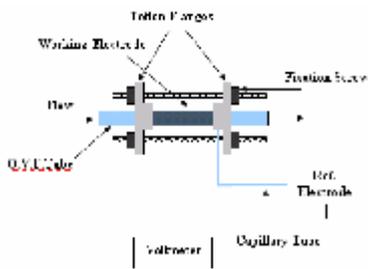


Fig. (2) Test Section for Corrosion Potential Experimental for Single Material

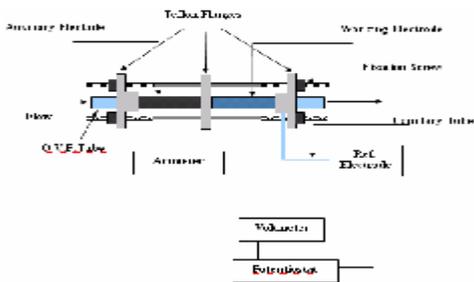


Fig. (3) Test Section for Polarization Experiments

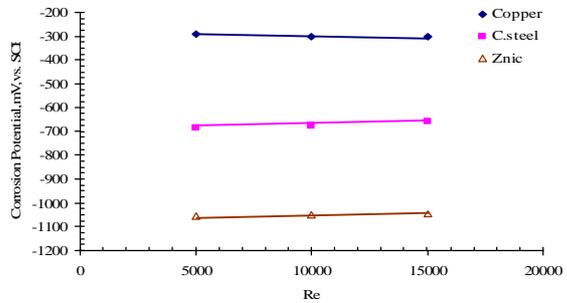


Fig. (4) Effect of Re on the E_{corr} . Of Zinc, Carbon Steel And Copper after 4 h exposure.

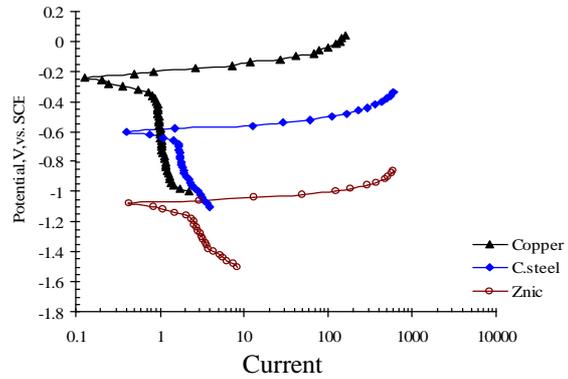


Fig. (5) Cathodic polarization curves of Copper, Zinc and C.steel at Re= 5000.

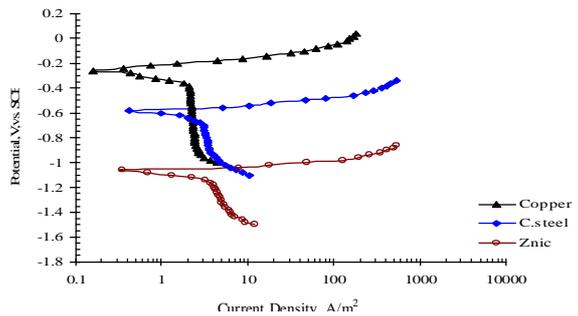


Fig. (6) Cathodic polarization curves of Copper, Zinc and C.steel at Re= 10000

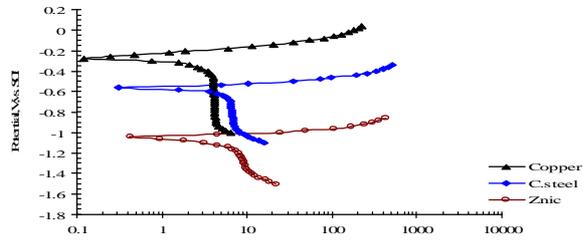


Fig. (7)Cathodic polarization curves of Copper, Zinc and C.steel at Re= 15000.

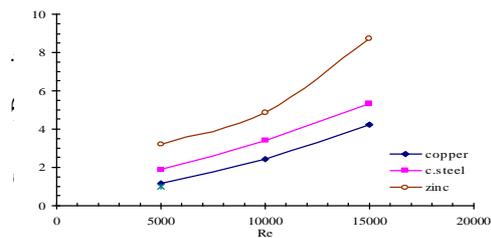


Fig. (8)The LCD of Oxygen Reduction vs. Re for different Metals.

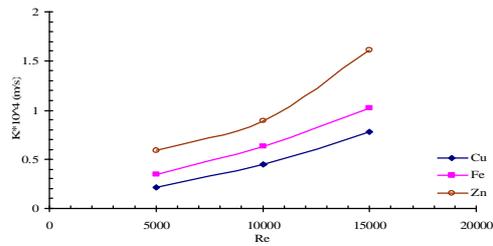


Fig. (9) Variation in k with Re for different Metals.

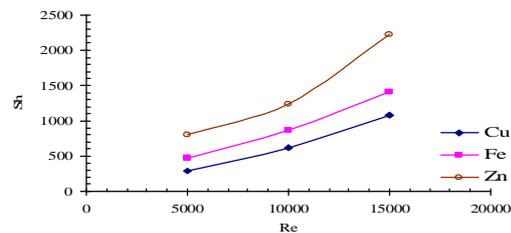


Fig. (10) Variation in Sh with Re for different Metals.