DIFFUSION- CONTROLLED CORROSION OF AN AGITATED VESSEL UNDER FORCED CONVECTION CONDITIONS

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ABSTRACT

The rate of diffusion controlled corrosion of an agitated vessel under forced convection conditions was studied by determining the rate of diffusion controlled dissolution of the vessel wall (copper) in dilute HCI containing ferric ions. In this system the corrosion rate is controlled by arrival of ferric ions at the vessel wall where they are reduced to ferrous ions according the equation: $Cu + Fe^{+++} = Cu^{+} + Fe^{++}$. The variables studied are, the rotational speed of stirrer, the physical properties of the solutions and the HCI concentrations. For particle free solution the authors obtained the following equation $Sh = 0.01 \, Sc^{0.33} \, Re^{0.708}$ for the conditions: $65000 < Re < 170\,000$, $1680 < Sc < 1900$ where, Sh is the Sherwood number, Sc is the Schmidt number and Re is the Reynolds number.

INTRODUCTION

Agitated vessels are frequently used in the chemical industry. They usually handle corrosive fluids and suffer severely from corrosion. The rate of corrosion may be determined by the rate of dissolved oxygen to the corroding surface or the rate of diffusion of the corrosion products away from the corroding surface.

The object of the present work is to shed some light on the role played by hydrodynamic conditions in the kinetic of diffusion-controlled corrosion in agitated vessels, where the rate of corrosion is controlled by the diffusion of the dissolved oxygen to the cathodic sites of the corrosion cells as shown below:

at anode: $M \rightarrow M^{++} + 2e$ (fast)

at cathode: $1/2 \, O_2 + H_2O + 2e \rightarrow 20H^-$ (slow)
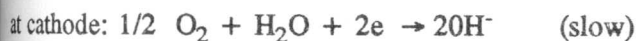
In the present work on accelerated diffusion-controlled corrosion reaction, namely the dissolution of copper in acidified $FeCl_3$ solution, was chosen to test the effect of stirring, changing of HC1 concentrations in the ferric chlorid solution, on the rate of corrosion of the vessel wall (copper) under forced convection.

EXPERIMENTAL TECHNIQUE

The experimental apparatus is schematically presented in Figure (1). It consisted of 5 liter cylindrical plastic container lined with a cylindrical copper sheet made of 99.9% pure copper. The container was fitted with a variable speed stirrer. The copper sheet was 17 cm. diameter, and 25 cm. in height. The outer surface of the copper sheet, which contacted the wall of the plastic container, was isolated with wax . The impeller which was made of pyrex glass was turbine type, with 4 blades and 3 cm.diameter. The impeller was mounted centrally on a 25 cm glass shaft of the same material, and was 6 cm from the vessel bottom. The impeller was connected to the motor shaft (0.5 HP) which run at a maximum speed of 3000 rev./min. The rotational speed of the stirrer was adjusted by the variac and measured by an optical tachometer . Samples of the solution (5c.c) were withdrawn at 3 or 5 minutes intervales. These samples were analysed by iodometry [1] to determine the concentration of the ferric ion as a function of time. Three solutions of HC1 were used in the present study: 0.1N, 1N and 2N. In all cases $FeCL_3$ concentration was kept constant at 0.0358 M. When preparing all solutions, A.R. grade chemicals and distilled water were used. The solution viscosity and density were measured using an Ostwaled viscometer and a density bottle, respectively [2]. The physical properties of the solutions used in the present work are shown in Table (1). Experiments were

carried out at $25 \pm 1°C$. The mass transfer coefficient was calculated from concentration - time data.
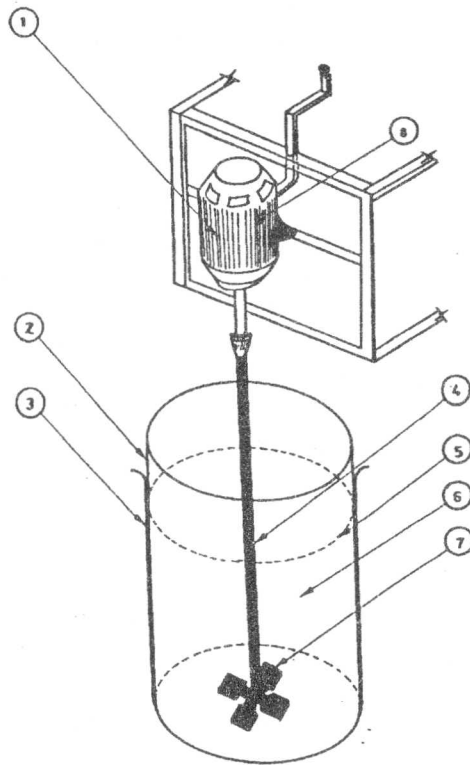
1_ Variable speed motor   5_ Solution level

2_ Copper cylinder   6_Acidified $FeCl_3$

3_Plastic cylindrical vessel   7_ Glass impeller

4_Glass stirrer (shaft)   8_ Variac

Figure 1. Experimental apparatus.

Table 1. Physical properties of the solutions used in the present work at constant temperature (25°C).

Solution Composition	g /cm³	μ poise	D cm²/s	Sc
0.0358M $FeCl_3$ + 0.1N HCI	1.0021	0.0102	$6.03*10^{-6}$	1688
0.0358M $FeCl_3$ + 1N HCI	1.0082	0.01052	$5.80*10^{-6}$	1799
0.0358M $FeCl_3$ + 2N HCLI	1.0268	0.01094	$5.61*10^{-6}$	1899

RESUITS AND DISCUSSIONS

The effect of different variables on the rate of diffusion-controlled corrosion of agitated vessels will be expressed in terms of the mass transfer coefficient of the diffusion-controlled dissolution of the copper wall of the vessel in acidified $FeCL_3$ according to the reaction:

$$Cu + Fe^{+++} = Cu^+ + Fe^{++} \qquad (1)$$

For a batch agitated vessel the rate of diffusion-controlled corrosion of the vessel wall is given by [3]

$$-V_s \, d_c/d_t = K \, A \, C \qquad (2)$$

which integrates to:

$$\ln C_o/C = KA \, t/V_s \qquad (3)$$

where V_s is the solution volume in the agitated vessel; C_o, C are the initial concentrations and the concentration at time t of $FeCl_3$; K is the mass transfer coefficient of the dissolution of the vessel wall in $FeCl_3$ solution; A is the active area (dissolving area) of the vessel wall; t is the time of corrosion.

Figures (2-4) show that the present data fit equation (3) under different rotation speeds and different HCl concentrations. The mass transfer coefficient K, was obtained from the slope of $\ln C_o/C$ vs. t lines.

Figures (2-4) show also the effect of impeller rotation speed on the mass transfer coefficient of the corrosion process. The mass transfer increases with increasing impeller rotation speed according to the equation:

$$K = a \, \omega^{0.708} \qquad (4)$$

The velocity exponent in the above equation indicates a turbulent flow mass transfer mechanism. The increase in K with increasing ω is attributed to the decrease in the diffusion layer thickness, σ at the vessel wall by the eddies generated by rotating impeller ($K = D/\sigma$). The velocity exponent 0.708 in the above equation agrees with the value obtained by Eisenberg et al [4] who studied mass transfer at rotating cylinders using the electrochemical technique. The velocity exponent in equation (4) is agreement with the value

obtained for mass transfer between suspended particles and fluids in agitated vessel [4-8]. The present velocity exponent agrees also with the value obtained for mass transfer at a rotating disc under turbulent flow conditions [3].
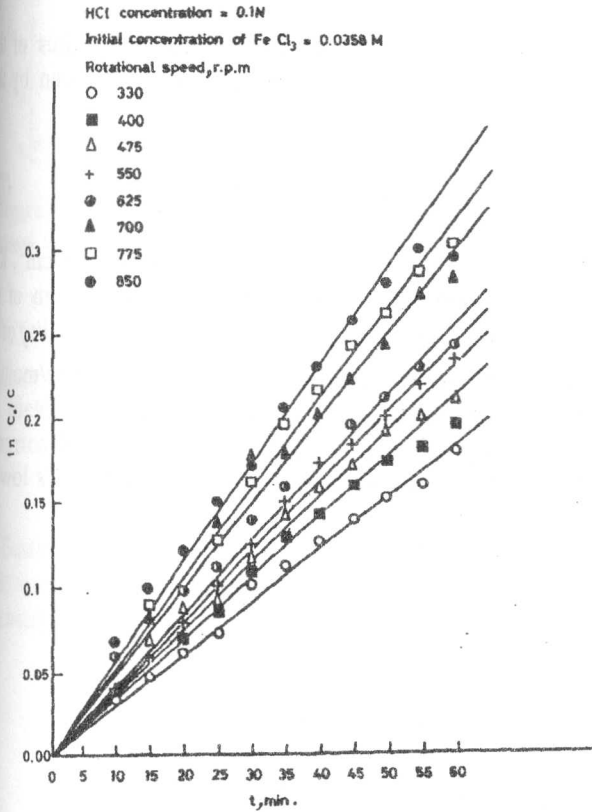

Figure 2. ln C_o/C vs t for different rotational speeds.

An overall mass transfer correlation was investigated in terms of the dimensionless groups Sh, Sc and Re usually used in correlating forced convection mass transfer. Table (2) summarizes the value of these dimentionles groups. The physical properties of the solution ($\mu, \int$) used in calculating these dimensionless groups were determined experimentally while the diffusivity (D) was taken from the literature [9] and corrected for the change of viscosity (μ) and temperature using the Stokes-Einstein equation:

$$\mu D / T = \text{constant} \qquad (5)$$

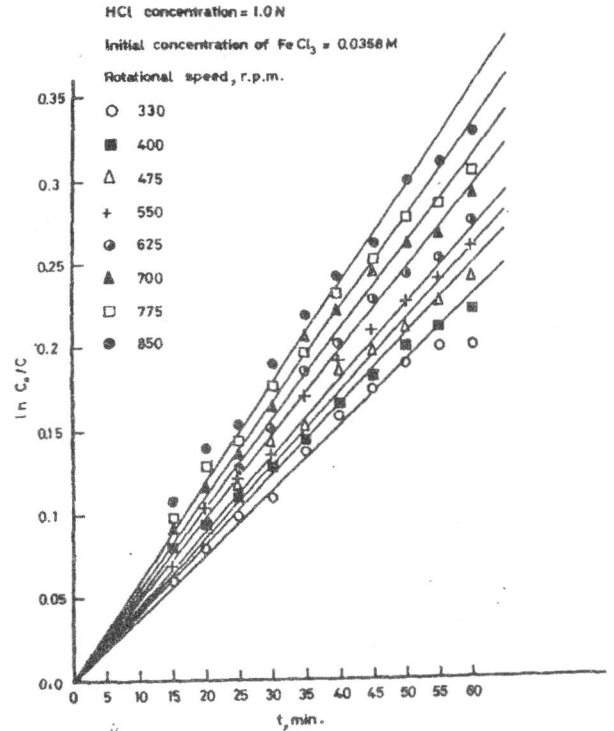In calculating Sh and Re, the impeller diameter was taken as the characteristic length.

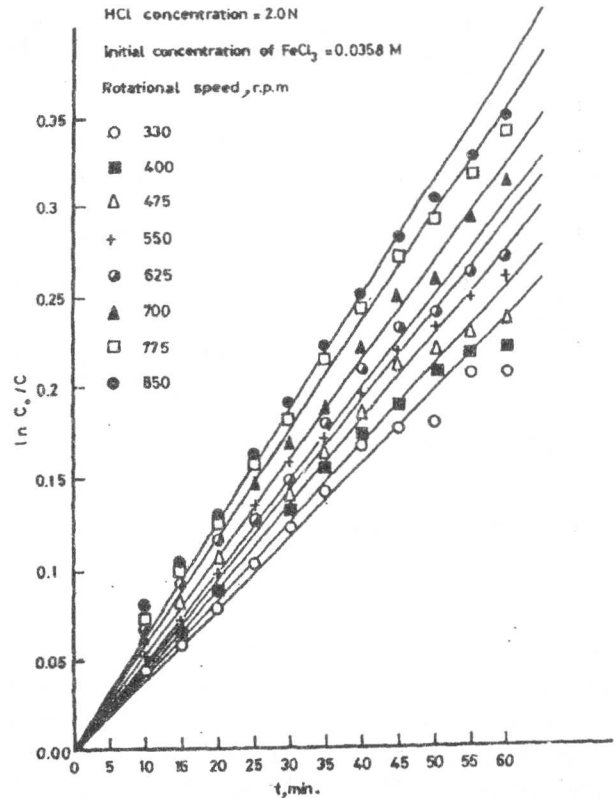
Figure 3. ln C_o/C vs t for different rotational speeds.

Figure 4. ln C_o/C vs t for different rotational speeds.

Figures. (5) and (6) show that present data for the conditions, $60\,000 < Re < 170000$ and $1680 < Sc < 1900$ fit the equation:
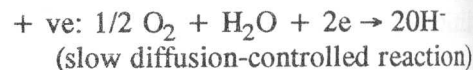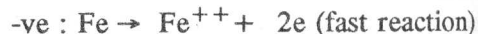
$$Sh = 0.01 \ Sc^{0.33} \ Re^{0.708} \qquad (6)$$

Table 2. Dimensionless groups used in obtaining the overall mass transfer correlation in particle free solution

initial concentration of $FeCl_3 = 0.0358$ M.

temperature $= 25°C$

HCl conc. M	V cm/s.	$K*10^4$ cm/s.	Sh	Sc	Re
0.1	107.13	2.93	301.3	1688	65255
0.1	129.85	3.38	347.5	1688	79096
0.1	154.20	3.56	359.9	1688	93926
0.1	178.50	3.91	402.0	1688	108556
0.1	202.90	4.4	542.4	1688	123584
0.1	227.20	4.6	472.9	1688	138417
0.1	251.60	5.02	516.3	1688	153247
0.1	275.90	5.12	526.4	1688	168078
1.0	107.13	3.34	356.8	1799	63655
1.0	129.85	3.81	407.3	1799	77155
1.0	154.20	3.96	423.3	1799	91623
1.0	178.50	4.19	448.2	1799	106062
1.0	202.90	4.48	479.7	1799	120560
1.0	227.20	4.96	530.2	1799	135028
1.0	251.60	5.27	563.3	1799	149497
1.0	275.90	5.44	581.9	1799	163936
2.0	170.13	3.73	404.3	1899	62340
2.0	129.85	3.97	438.8	1899	75562
2.0	154.20	4.27	472.9	1899	89731
2.0	178.50	4.39	485.2	1899	103872
2.0	202.90	4.59	507.2	1899	118071
2.0	277.20	5.26	581.3	1899	132234
2.0	251.60	5.42	599.0	1899	146410
2.0	275.90	5.63	622.2	1899	160550

with an average deviation of $\pm$ 8%. The above equation can be used in practice to calculate the rate of corrosion of the wall of agitated vessels handling aqueous solutions, where the rate of corrosion is controlled by the diffusion of dissolved O_2 (depolarizer) to the tank wall. If we consider, for instance, a steel tank. The following corrosion reactions take place during corrosion:

$$-ve : Fe \rightarrow \ Fe^{++} + \ 2e \ \text{(fast reaction)}$$

$$+ve: 1/2 \ O_2 + H_2O + 2e \rightarrow 20H^-$$
(slow diffusion-controlled reaction)

The rate of O_2 reduction the cathodic sites of the corrosion cells at the vessel walls is given by the equation:

$$i \ / \ Z \ F \ = K \ C_{O_2} \qquad (7)$$

where i is the corrosion current density, A / cm^2, K is the mass transfer coefficient of O_2 diffusion of the vessel wall, cm/s, C_{O_2} is the saturation solubility of O_2 in the solution, mole/cm^3; ZF is the charge/mole. K can be obtained from equation (6) to obtain the corrosion current density 1. The rate of steel corrosion in gm/cm^2.s can be calculated from Faraday's low:
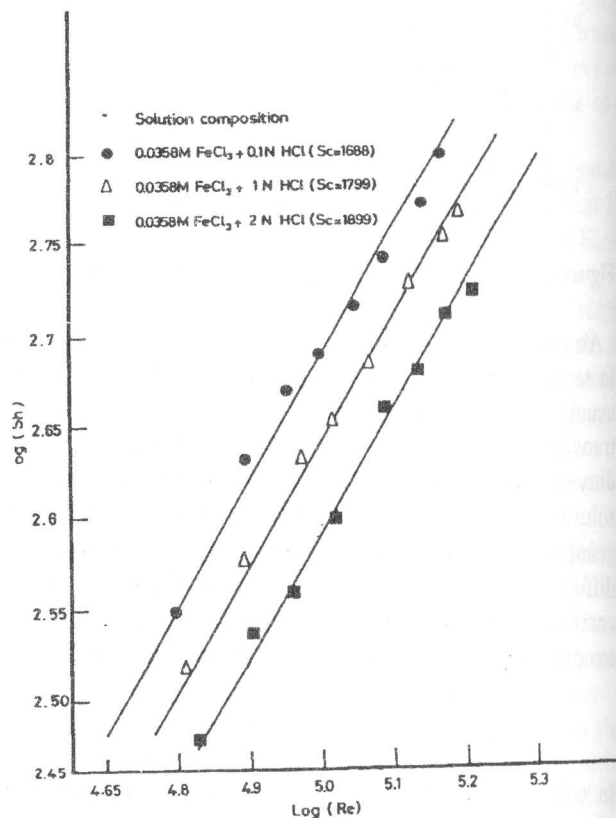
$$m = e \ i \ t \qquad (8)$$

Figure 5. log (Sh) vs log (Re) at different (Sc).

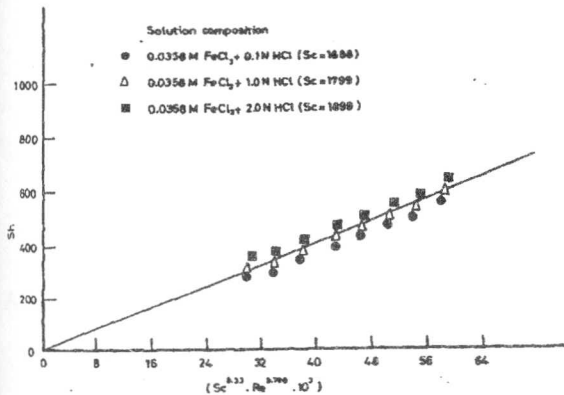$$Sh = 0.0079\ Sc^{0.356}\ Re^{0.7} \qquad (9)$$

Figure 6. Overall mass transfer correlation for the agitated vessel without suspended solid particles.

where e is the electrochemical equivalent of iron

$$(e = \frac{56}{2 \times 96500}\ g/coulomb)$$

Equation (6) is in a good agreement with the equation representing mass transfer at rotating cylinders [4], namely:

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