

# KINETICS OF HETEROGENEOUS MASS TRANSFER DURING METAL CORROSION IN AQUEOUS MEDIA

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## ABSTRACT

The effect of solid particles on the rate of diffusion-controlled corrosion of an agitated vessel containing suspended solid was studied. Experiments were made with inert particles ( $Al_2O_3$ ,  $SiO_2$ ) in acidified ferric chloride solution. The variables studied were; particle size, concentration of the solid particles, the rotational speed of the stirrer and the physical properties of the solution. The geometry of the impeller and its dimensions with respect to the vessel dimensions were also studied. The rate of diffusion-controlled corrosion of the vessel wall was found to increase by an amount ranging from 9% to 330% in the presence of suspended solid particles. The mass transfer coefficient was related to the impeller rotation speed by the equation:  $K = a \omega^n$  where:  $K$  is the mass transfer coefficient;  $a$  is a constant;  $\omega$  is the impeller rotation speed;  $n$  is a constant ranging from 0.4 to 0.66 depending on the particle size and the particle concentration.

## INTRODUCTION

The present study of the kinetics of metallic corrosion has revealed the fact that mass transfer plays an important role in the kinetics of corrosion.

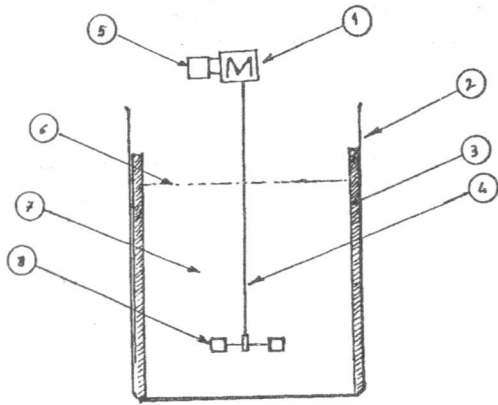
In many cases, the corrosion rate of metals is controlled solely by the diffusion [1] either of cathodic reactant to the surface, or of the soluble anodic product away from the surface. In this cases, the corrosion reaction is termed diffusion-controlled corrosion. An example for the former is the dissolution of metals such as, iron, copper or nickel in hydrochloric acid containing ferric ions. The cathodic reaction, the reduction of ferric ions, is the rate of controlling [2,3]/

Most of the attention was directed to corrosion in pipelines, but little work has been done about the corrosion behaviour of other chemical engineering equipments such as agitated vessels.

The object of the present work is to study the rate of diffusion-controlled corrosion of an agitated vessel containing solid suspension, by determining the rate of diffusion controlled dissolution of the copper wall of the vessel in acidified ferric chloride solution. The variables studied, were the effect of stirring, particle size, particle concentration and physical properties of the solution. The rate of corrosion was determined by analysing the solution at intervals of time.

## METHOD AND TECHNIQUES

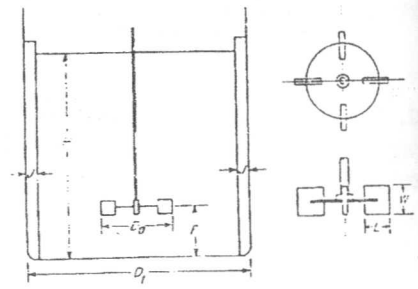
Figure (1) shows the experimental apparatus used in present work. It consists of a plastic cylindrical vessel lined with a copper cylinder made of high purity copper. The vessel was fitted with a variable speed stirrer. The outer surface of the copper cylinder, which contacted the wall of the plastic vessel, was isolated with wax. The impeller was a turbine type with 4 blades and was made of pyrex glass. The impeller geometry and dimensions were taken from the literature [4] and are shown in Figure (2). The impeller was mounted 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 which was run at a maximum speed of 3000 rev./min. The rotational speed of the motor was controlled by a variac and measured by an optical tachometer. The amount of solids in the solution was varied from 0.03 to 0.09 wt%, five particle size fractions were obtained by sieving and were used in experiments. The impeller speed was varied from 330 to 850 rev./min. in experiments.



- 1. Variable speed motor
- 2. Plastic Vessel
- 3. Copper cylinder
- 4. Glass Stirrer (Shaft)
- 5. Variac
- 6. Solution Level
- 7. Acidified FeCl<sub>3</sub>
- 8. Glass Impeller

Figure 1. Experimental apparatus.

Rates of corrosion of the copper sheet lining the wall of the plastic container were expressed in term of the mass transfer coefficient of the diffusion controlled dissolution of copper in acidified FeCl<sub>3</sub> solution containing solid particles of crushed ceramic material. Before each run, 330 c.c of acidified FeCl<sub>3</sub> solution and a certain amount of solid particles were placed in the vessel. The impeller was positioned in the center of vessel. Samples of the solution (5 c.c) were withdrawn at 3 or 5 minutes intervals. These samples were analyzed by iodometry [4] to determine the concentration of ferric ions as function of time. Experiments were carried out at 25°C ± 1. The mass transfer coefficient was calculated from the slope of ln C<sub>0</sub>/C vs.t lines. The physical properties of the solution (ρ, μ, D) needed to correlate the data, were determined experimentally. The density was measured by a specific gravity bottle; viscosity was measured by an. Ostwald viscometer and the diffusivity of copper ions in acidified ferric chloride solution was taken from the literature [6].



The relations are :

$$\begin{aligned} D_a / D_t &= 1/4 & H / D_t &= 1 & E / D_a &= 1 \\ W / D_a &= 1/5 & L / D_a &= 1/8 & J / D_a &= 1/12 \end{aligned}$$

Figure 2. Measurements of turbine.

## RESULTS AND DISCUSSIONS

The rate of the diffusion-controlled corrosion of vessel wall is given by:

$$-V_s d_c/d_t = K A C \tag{1}$$

which integrates to:

$$\ln C_0/C = K A t/V_s \tag{2}$$

where V<sub>s</sub> is the FeCl<sub>2</sub> solution volume in the agitated vessel; C<sub>m</sub><sup>3</sup>; C<sub>0</sub> and C are the initial concentration and the concentration at time t of FeCl<sub>3</sub>; K is the mass transfer coefficient of the dissolution of the vessel wall in FeCl<sub>3</sub> solution; A is the active area (dissolution area), cm<sup>2</sup>, t is the time of corrosion, s.

Figure (3) shows that ln C<sub>0</sub>/C vs.t, in the presence of suspended solid inert particles (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) in the solution obeys equation (2) for different impeller rotation speeds, different particle concentrations and different particle sizes. The mass transfer coefficient of the corrosion process was obtained from the slope of ln C<sub>0</sub>/C vs. t lines.

Figure (4) shows the effect of different particle concentration for different particle sizes on the mass transfer coefficient of the corrosion process, the data fit the equation.

$$K = a_1 \omega^n \tag{3}$$

Where  $\omega$  is the impeller rotation speed. The value of the exponent  $n$  ranges from 0.4 to 0.66 depending on particle concentration. The higher the particle concentration, The lower the value of  $n$ . The constant  $a_1$  is a function of the solid concentration for a given particle size. The higher the solid concentration, the higher the value of  $a_1$ .

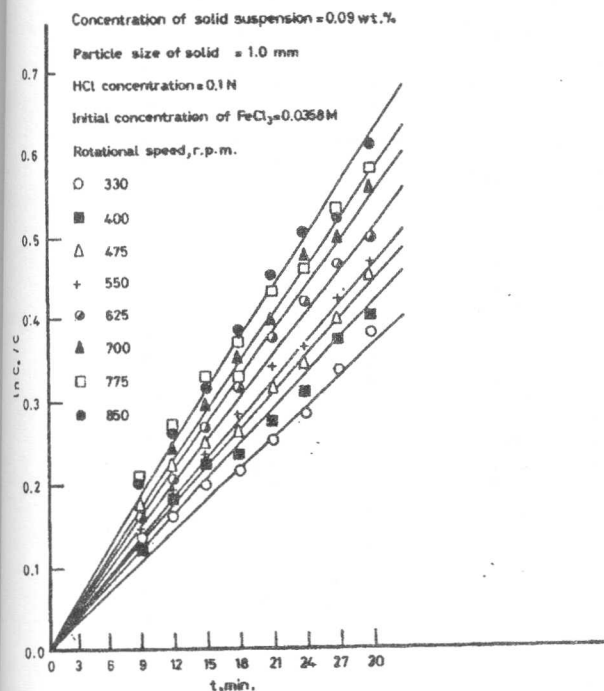


Figure 3.  $\ln C_0/C$  vs  $t$  for different rotational speeds.

Table (1) shows that the presence of suspended solid particles in the agitated vessel increases the rate of mass transfer corrosion by an amount ranging from 9% to 330% depending on the rotating speed of the impeller, particle size and particle concentration. The increase in the rate of wall mass transfer and the rate of corrosion in the presence of particles may be attributed to the following effects:

- (i) the disruption of the diffusion layer at the vessel wall, by the penetration of the solid particles, generate microconvection i.e small scale eddies the intensity of which depends on the number of particles and the kinetic energy of each particle. These turbulence penetrate the laminar sublayer of the hydrodynamic boundary layer and the diffusion layer with a consequent increase in the rate of mass transfer.

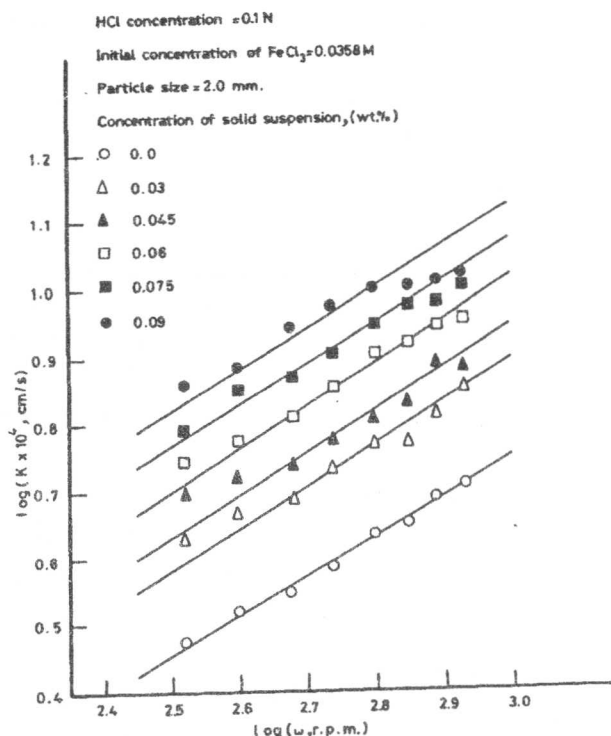


Figure 4.  $\log (K)$  vs  $\log (\omega)$  for different solid concentration.

- (ii) when particles impact with the wall, they bring with them a fresh supply of bulk solution and drag away the reacted solution. The present increase in the rate of mass transfer due to the solid particles agrees with the finding of the other authors who used different transfer gemoetries. Postlethwaite and Holdner [7] who studied the effect of suspended particles on the rate of diffusion controlled corrosion in pipelines reported an increase in the rate of corrosion. Pini and De Anna [8] who used an electrochemical technique to study the effect of solid particles on the rate of mass transfer at a rotating cylinder reported also an increase in the rate of mass transfer.

It should be emphasized that the present work which was carried a nonpassive metal (CU) dealt only with corrosion and has nothing to do erosion which takes place when passive metals such as steel, stainless steel, Ni and is alloys are subjected to particle bombardment. In case of passive metals erosion takes place as a result of the damage of the protective oxide film when bombarded with solid particles [9]. The damage of the oxide film leads to the formation of a multitude of active/passive cells.

**Table 1.** Effect of solid particles on the mass transfer coefficient in agitated vessel.

Initial concentration of  $\text{FeCl}_3$  = 0.0358 M  
 HCl concentration = 0.1N  
 Sc = 1688  
 Temperature = 25°C

Velocity(v) cm/s	Particle size mm	Solid conc. Wt. %	$K \times 10^4$ cm/s.	% increase in k
107.1 (Re=65255)	2.38	0.03	3.76	28
107.1	2.38	0.045	4.10	40
107.1	2.38	0.060	4.39	50
107.1	2.38	0.075	4.39	49
107.1	2.38	0.090	5.26	77
107.1	2.00	0.030	4.50	54
107.1	2.00	0.045	5.10	75
107.1	2.00	0.060	5.60	93
107.1	2.00	0.075	6.20	113
107.1	2.00	0.090	7.60	160
107.1	1.41	0.030	8.30	180
107.1	1.41	0.045	10.00	241
107.1	1.41	0.060	12.36	320
107.1	1.41	0.075	13.40	357
107.1	1.41	0.090	12.66	330
107.1	1.00	0.030	11.50	292
107.1	1.00	0.045	10.60	262
107.1	1.00	0.060	11.90	306
107.1	1.00	0.075	11.70	299
107.1	1.00	0.090	11.50	292
107.1	0.707	0.030	14.60	398
107.1	0.707	0.045	14.10	381
107.1	0.707	0.060	13.50	350
107.1	0.707	0.075	12.50	327
107.1	0.707	0.090	11.50	292

Table 1, (cont.)

Velocity(v) cm/s	Particle size mm	Solid conc. Wt. %	$K \times 10^4$ cm/s.	% increase in k
129.85 (Re=79096)	2.38	0.030	4.13	22
129.85	2.38	0.045	4.38	30
129.85	2.38	0.060	4.68	38
129.85	2.38	0.075	5.32	57
129.85	2.38	0.090	5.27	56
129.85	2.00	0.030	4.69	54
129.85	2.00	0.045	5.25	75
129.85	2.00	0.060	5.79	93
129.85	2.00	0.075	7.30	113
129.85	2.00	0.090	7.78	160
129.85	1.41	0.030	8.30	153
129.85	1.41	0.045	9.90	195
129.85	1.41	0.060	13.20	290
129.85	1.41	0.075	13.70	330
129.85	1.41	0.090	13.20	290
129.85	1.00	0.030	11.80	249
129.85	1.00	0.045	11.70	217
129.85	1.00	0.060	11.97	254
129.85	1.00	0.075	12.30	264
129.85	1.00	0.090	14.60	320
129.85	0.707	0.030	14.65	330
129.85	0.707	0.045	14.20	320
129.85	0.707	0.060	13.30	393
129.85	0.707	0.075	13.00	314
129.85	0.707	0.090	11.90	252
154.2 (Re=92926)	2.38	0.030	4.38	23
154.2	2.38	0.045	4.88	37
154.2	2.38	0.060	5.60	57
154.2	2.38	0.075	5.29	49
154.2	2.38	0.090	4.75	34

Table 1, (cont.)

Velocity(v) cm/s	Particle size mm	Solid conc. Wt. %	$K \times 10^4$ cm/s.	% increase in k
154.2	2.00	0.030	5.03	39
154.2	2.00	0.045	5.60	56
154.2	2.00	0.060	6.60	77
154.2	2.00	0.075	7.40	116
154.2	2.00	0.090	9.30	130
154.2	1.41	0.030	9.00	144
154.2	1.41	0.045	10.50	192
154.2	1.41	0.060	13.90	273
154.2	1.41	0.075	15.30	311
154.2	1.41	0.090	13.90	322
154.2	1.00	0.030	15.90	346
154.2	1.00	0.045	11.90	229
154.2	1.00	0.060	13.80	288
154.2	1.00	0.075	14.60	310
154.2	1.00	0.090	15.30	330
154.2	0.707	0.030	15.34	303
154.2	0.707	0.045	14.35	330
154.2	0.707	0.060	13.6	282
154.2	0.707	0.075	12.45	258
154.2	0.707	0.090	12.50	251
178.5 (Re=108556)	2.38	0.030	3.38	12
178.5	3.38	0.045	5.11	31
178.5	2.38	0.060	5.40	38
178.5	2.38	0.075	6.39	63
178.5	2.38	0.090	5.60	43
178.5	2.00	0.030	5.59	43
178.5	2.00	0.045	5.88	50
178.5	2.00	0.060	7.10	82
178.5	2.00	0.075	7.97	104
178.5	2.00	0.090	10.90	174
178.5	1.41	0.030	9.54	144

Table 1 , (cont.)

Velocity(v) cm/s	Particle size mm	Solid conc. Wt. %	$K \times 10^4$ cm/s.	% increase in k
178.5	1.41	0.045	11.40	192
178.5	1.41	0.060	14.60	273
178.5	1.41	0.075	16.10	311
178.5	1.41	0.090	16.50	322
178.5	1.00	0.030	15.95	308
178.5	1.00	0.045	12.40	217
178.5	1.00	0.060	14.80	279
178.5	1.00	0.075	15.50	296
178.5	1.00	0.090	15.60	299
178.5	0.707	0.030	14.80	299
178.5	0.707	0.045	14.60	273
178.5	0.707	0.060	15.20	288
178.5	0.707	0.075	14.10	260
178.5	0.707	0.090	13.10	235
202.9 (Re =123548)	2.38	0.030	5.39	22
202.9	2.38	0.045	5.70	30
202.9	2.38	0.060	6.58	50
202.9	2.38	0.075	6.99	59
202.9	3.38	0.090	7.30	66
202.9	2.00	0.030	5.88	33
202.9	2.00	0.045	6.17	40
202.9	2.00	0.060	8.40	91
202.9	2.00	0.075	8.99	104
202.9	2.00	0.090	11.70	166
202.9	1.41	0.030	11.00	150
202.9	1.41	0.045	11.60	164
202.9	1.41	0.060	15.30	248
202.9	1.41	0.075	16.00	241
202.9	1.41	0.090	17.30	293
202.9	1.00	0.030	16.35	272
202.9	1.00	0.045	16.10	266

Table 1 , (cont.)

Velocity(v) cm/s	Particle size mm	Solid conc. Wt.%	$K \times 10^4$ cm/s.	% increase in k
202.9	1.00	0.060	15.60	255
202.9	1.00	0.075	16.10	266
202.9	1.00	0.090	16.70	280
202.9	0.707	0.030	16.71	281
202.9	0.707	0.045	15.90	261
202.9	0.707	0.060	16.02	264
202.9	0.707	0.075	15.30	248
202.9	0.707	0.090	14.60	232
227.2 (Re=138417)	2.38	0.030	5.01	9
227.2	2.38	0.045	5.98	30
227.2	2.38	0.060	7.31	59
227.2	2.38	0.075	9.05	97
227.2	2.38	0.090	9.66	110
227.2	2.00	0.030	5.48	19
227.2	2.00	0.045	6.42	39
227.2	2.00	0.060	8.30	80
227.2	2.00	0.075	9.53	108
227.2	2.00	0.090	11.90	159
227.2	1.41	0.030	11.20	143
227.2	1.41	0.045	12.70	172
227.2	1.41	0.060	17.90	289
227.2	1.41	0.075	18.40	300
227.2	1.41	0.090	19.70	328
227.2	1.00	0.030	16.90	267
227.2	1.00	0.045	16.30	254
227.2	1.00	0.060	16.10	250
227.2	1.00	0.075	16.60	260
227.2	1.00	0.090	17.30	276
227.2	0.707	0.030	17.30	277
227.2	0.707	0.045	16.40	256
227.2	0.707	0.060	17.55	284



Table 1 , (cont.)

Velocity(v) cm/s	Particle size mm	Solid conc. Wt. %	$K \times 10^4$ cm/s.	% increase in k
227.2	0.707	0.075	18.90	246
227.2	0.707	0.090	14.90	224
251.6 (Re=153247)	2.38	0.030	5.56	10
251.6	2.38	0.045	6.27	25
251.6	2.38	0.060	8.10	61
251.6	2.38	0.075	9.65	92
251.6	2.38	0.090	10.20	103
251.6	2.00	0.030	6.02	20
251.6	2.00	0.045	7.90	57
251.6	2.00	0.060	8.70	75
251.6	2.00	0.075	9.30	85
251.6	2.00	0.090	12.30	145
251.6	1.41	0.030	11.20	123
251.6	1.41	0.045	12.70	153
251.6	1.41	0.060	17.50	256
251.6	1.41	0.075	20.00	298
251.6	1.41	0.090	19.70	252
251.6	1.00	0.030	18.30	265
251.6	1.00	0.045	16.90	237
251.6	1.00	0.060	16.90	236
251.6	1.00	0.075	16.80	235
251.6	1.00	0.090	17.70	253
251.6	0.707	0.030	17.80	252
251.6	0.707	0.045	16.60	233
251.6	0.707	0.060	17.80	255
251.6	0.707	0.075	16.30	225
251.6	0.707	0.090	15.00	199
275.9 (Re=168078)	2.38	0.030	5.40	15
275.9	2.38	0.045	6.30	23
275.9	2.38	0.060	8.30	62

Table 1 , (cont.)

Velocity(v) cm/s	Particle size mm	Solid conc. Wt. %	$K \times 10^4$ cm/s.	% increase in k
275.9	2.38	0.075	10.40	103
275.9	2.38	0.090	10.80	110
275.9	2.00	0.030	7.00	37
275.9	2.00	0.045	7.40	44
275.9	2.00	0.060	8.80	71
275.9	2.00	0.075	10.10	97
275.9	2.00	0.090	12.40	142
275.9	1.41	0.030	11.50	125
275.9	1.41	0.045	12.90	152
275.9	1.41	0.060	18.90	269
275.9	1.41	0.075	21.60	322
275.9	1.41	0.090	18.00	252
275.9	1.00	0.030	17.40	240
275.9	1.00	0.045	17.70	246
275.9	1.00	0.060	17.20	236
275.9	1.00	0.075	16.90	226
275.9	1.00	0.090	18.80	267
275.9	0.707	0.030	18.70	266
275.9	0.707	0.045	16.80	228
275.9	0.707	0.060	17.90	250
275.9	0.707	0.075	17.50	242
275.9	0.707	0.090	15.10	195

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