POTENTIAL AND CURRENT DISTRIBUTION IN FLOW THROUGH POROUS ELECTROCHEMICAL REACTOR WORKING UNDER LIMITING CURRENT CONDITIONS

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ABSTRACT

This work deals with the study of porous electrochemical reactor in which electrolyte and current flows in an axial direction, flow-through configuration. The cathode consists of fixed bed of highly conductive copper particles, working under limiting current conditions. The studied electrochemical reaction was the cathodic reduction of ferric ions in the presence of sulfuric acid as a supporting electrolyte.

The influence of four parameters on the behavior of porous electrode have been studied, these are : cathode thickness (8 and 4 cm), electrolyte flow rate (100, 200, 300 and 400 l/hr), redox concentration (1, 2 and 3 mM) and electrolyte temperature (30, 40 and 50 ℃).

Metal-solution potential distributions have been determined experimentally as a function of the height in the porous electrode. Also, current distributions have been estimated using the polarization of single copper particle.

INTRODUCTION

Electrochemical reactor is defined as any device in which chemical reactions occur directly due to the input of electrical energy. Because electrochemical reactions are heterogeneous, porous electrodes have came into wide spread usage in order to provide large reaction rates per unit volume [1].

Examples of industrial applications of flow-through porous electrodes are: Electro-organic synthesis, such the synthesis of aniline, benzoquinone and p-aminophenol [2], removal of electropositive cations by electrodeposition, such as Cu, Pb, Ag and Au [3], and oxidation of organic pollutants and CN^-. Also oxidation of organic surfactant and reducing of foaming in process for manufacturing of Na_2CO_3 [4].

The basic theory of porous electrodes was established by Newman and Tobias (1962) [5], who described the behavior of one-dimensional porous electrode from a macroscopic point of view and developed a general equations to predict the current distribution and reaction rate in such electrode.

Coeuret (1976)[6] developed an analytical expression for the local metal-solution potential difference in a porous electrode working under limiting current conditions. Solution of the expression was obtained for the case where the general electrolyte flow direction is parallel to the current lines, for a given location of the current feeder and for an equipotential dispersed phase.

Metal-solution potential distributions have been determined experimentally as a function of the height in a porous electrode made of high conducting grains which are fixed or fluidized.

It was shown that the fluidized electrode should have a very low efficiency and that the problem of electrical conductivity in two-phase systems is important in the application of solid-liquid fluidized bed electrochemistry.

Gaunand, Hutin and Coeuret (1977)[7] performed an experimental study of metal-solution potential distribution in flow-through porous electrodes of fixed bed of spherical conducting particles working at limiting diffusion current (the electrolyte flows downward from the cathode to the anode). The test reaction used is the cathodic reduction of potassium ferricyanide (0.001 M) in sodium hydroxide (0.75 N).

They concluded that the metal-solution potential distribution is calculable a priori if the efficiency, *R*, the physical and chemical properties of the electrolyte entering the bed, the number of electrons in the electrochemical reaction and the bed height are known.

Olive and Lacoste (1980)[8] studied the potential drop occurring in the flow-through porous electrode, which may destroy the considered electrochemical reaction specificity or limit the electrolytic cell efficiency by changing local solution potential difference. They propose a generalized equations which permits the design of flow-through porous electrodes.

Wang, Sheu and Wan (1982)[9] studied, via experimental means, the effects of the flow rate of the electrolyte and the effects of current on potential and current distribution of the flow-through porous electrode. They studied a practical bed, which is partly activation controlled and partly mass-transfer controlled. In their study, the polarization of a single particle was used to estimate the current distribution in the electrode. They conclude that in order to make the whole electrode reach the range of limiting currents, either very thin electrode, or a very low flow rate needs to be used.

Al-Habobi and Slaiman (2000)[10] performed experimental study of flow-through porous electrode of fixed bed of highly conductive copper particles for the reduction of Ti^{+4} (or Fe^{+3}) ions in the presence of sulfuric acid as a supporting electrolyte. They proposed a method to find the current efficiency experimentally by following the solution potential with time. They found that Ti^{+4} is slightly more efficient than Fe^{+3} as a redox system (the maximum efficiency is 86% for Ti^{+4}/Ti^{+3}, while it is 84% for Fe^{+3}/Fe^{+2}). They also found that mass transfer coefficient, for single particle, is directly proportional to $Re_p^{0.5\text{-}0.525}$ in the range of $16 < Re_p < 111$.

Scope of the Work

This study is limited to:

1. Porous electrode with fixed bed, which seems to be the most promising in industrial applications [11].
2. Flow-through with axial configuration. Due to the fact that they obey one-dimensional models (one-dimensional means that the quantities such as potential, current and concentration vary only with depth within the electrode and not with lateral position), the electrode having axial configuration is very valuable in what concerns the test of theoretical analysis (as for example electrode potential distribution) and, consequently, of the hypotheses of that model [12].
3. Limiting current conditions. Because on one hand it permits the determination of the mass transfer coefficient and on the other hand the porous electrode has a maximum productivity [11,13].
4. The test electrochemical reaction is the cathodic reduction of ferric ions in acidic media (H_2SO_4 1 M) as a supporting electrolyte, because this reaction reported to be moderately fast [14,15] and because it has industrial application interest.

The aim of this study is to:

1. Investigate via experimental means the metal-solution potential distribution within the porous electrode.
2. Study the effect of various parameters (i.e. electrolyte flow rate, redox concentration, temperature and porous electrode depth).
3. Estimate the current distribution within the porous electrode by using the polarization of single copper particle.

EXPERIMENTAL WORK

The electrolytic solution used in this study was ferric sulfate in sulfuric acid solution (1 M) prepared from analytical reagent grade chemicals. Distilled water was used and had a conductivity of 5×10^{-4} $(\Omega\ m)^{-1}$.

Specifications of the chemicals used are : Analar sulfuric acid supplied by Merck company, purity 95 – 98%, and analar ferric sulfate penta-hydrate ($Fe_2(SO_4)_3\ .5H_2O$) supplied by Fluka company, purity 98%.

Description Of The Flow System

Fig.(1) is a schematic diagram of the experimental rig. The packed bed electrochemical reactor is shown in Fig.(2). The working electrode (cathode) was made of Perspex tube, 5 cm internal diameter and 4 cm (or 8 cm) long. The electrode was packed with 2.5 mm diameter, 5 mm long cylindrical copper particles. Along the electrode wall, the 4 cm thick working electrode, at equal distances labeled I, II, III, IV, V and at the surface VI the electrode was connected to calomel reference electrode through a capillary holes. For 8 cm thick working electrode nine positions were labeled, eight of them at equal distances and one at the top surface of the electrode. For single particle electrode experiments, the cathode consist of a single copper particle (2.5 mm diameter and 5 mm long) placed in the middle of the cathode chamber, and connected with isolated wire to the power supply, the cathode chamber was packed with cylindrical glass particles (2.5 mm diameter and 5 mm long).The counter electrode made of perspex tube, 5 cm internal diameter and 5 cm long. The electrode was packed with 2 mm diameter, 5 mm long cylindrical lead particles.

Procedure

Six liters of electrolyte solution was prepared from Analar grade chemicals before each run, then it was introduced into the electrolyte reservoir (R-1).

After introducing the electrolytic solution, the electrolyte was circulated through by-pass line by closing the valve leading to the reactor. Nitrogen gas was bubbled through the sparger (SP-1) for two hours to eliminate oxygen. A vacuum pump (VP-1) was operated to evacuate air from the electrochemical reactor by closing the valve (V-4), then the vacuum pump stopped and nitrogen gas introduced to the reactor (while opening V-4). This evacuation procedure was repeated several times before each run to eliminate oxygen that may be adsorbed on the cathode surface.

The complete polarization data were obtained by using the following procedure:

1. The temperature of the electrolyte was adjusted to the desired value (with accuracy ±1 °C) by using the immersed electrical heater (EH-1).
2. Introducing the electrolyte to the electrochemical reactor (ER-1) by opening the valve (V-1). The electrolyte flow rate was measured through the rotameter (RT-1) and the desired flow rate achieved using the valve (V-1).
3. The electrical circuit was switched on as soon as the electrodes were covered by the electrolyte. According to the galvanostatic technique, the voltage of the d.c. power supply (PS-1) remains constant along the experiments (12 V).
4. The desired total electrical current, which passed through the electrochemical reactor, was achieved by altering the resistance of the electrical circuit using the resistance box (RB-1).
5. The solution potential at each position was recorded. Sufficient time was allowed between each reading to reach steady state condition.
6. The complete cathodic polarization data was obtained by repeating the points 4 and 5 above for different total current. The total current increased, usually by predetermined increments, so that the solution potential readings did not exceed 50mV for successive increments. The cell voltage and solution potentials (at all positions) were recorded at each current.
7. At the end of each run the power supply was switched off, then the valve (V-5) was opened in order to drain the used electrolyte.
8. The system washed several times with distilled water to ensure that no electrolyte left.

The above procedure was repeated twice (using fresh electrolytic solution) at the same conditions to ensure the accuracy, and third run was carried out when reproducibility was in doubt.

RESULTS

Parameters Studied

90 experiments were performed to study the influence of four parameters on the behavior of the flow-through porous electrode, as follows:

- Cathode thickness: Long electrode (8 cm) and short electrode (4 cm) have been used.
- Electrolyte flow rate: Five different flow rates were studied which are 100, 200, 300, 400 and 500 l/hr.
- Redox concentration: Three different concentrations of Fe^{+3} ions were studied which are 1, 2 and 3 mM.
- Temperature: Three different temperatures were studied which are 30, 40 and 50 °C.

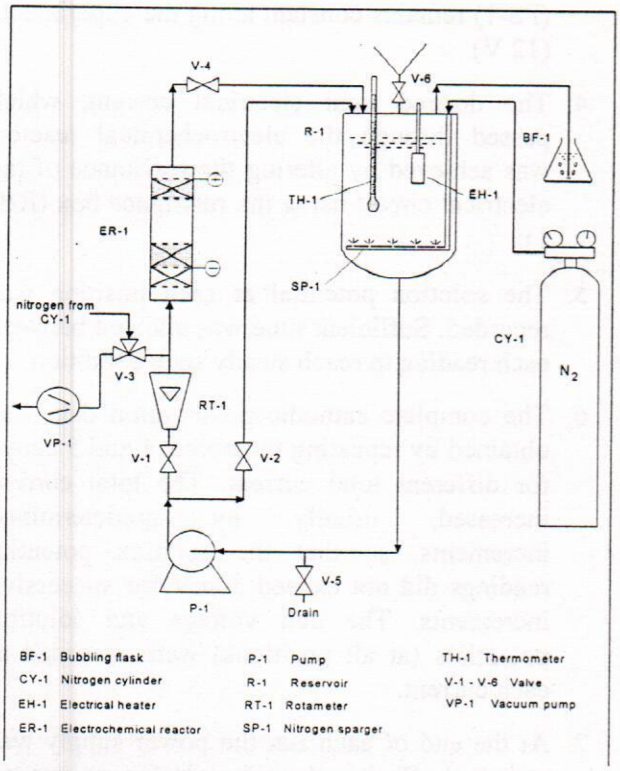

Fig. (1) Schematic diagram of flow system

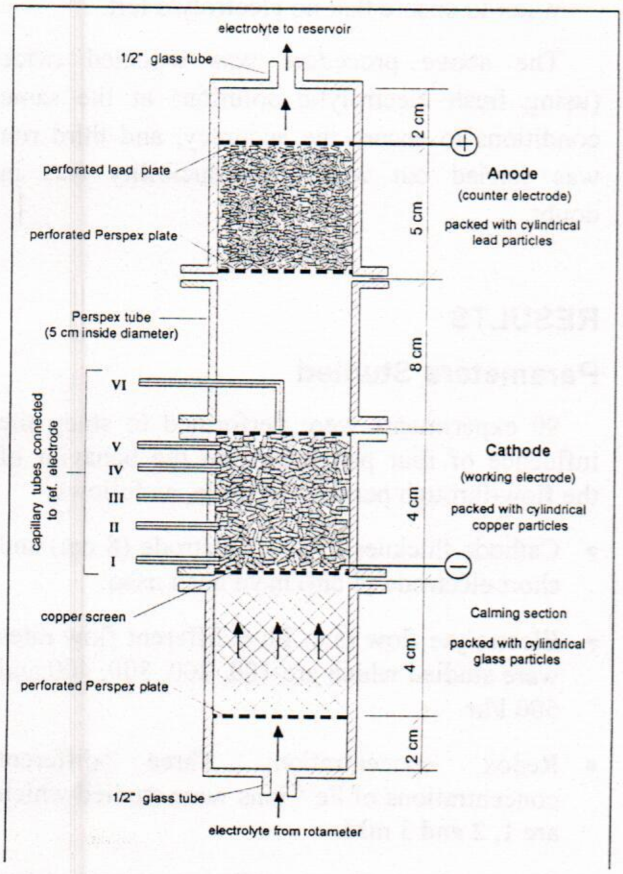

Fig. (2) Schematic diagram of experimental electrochemical reactor

Electrochemical Reactions

The electrochemical reactions occur in the cell are as follows:

Cathodic reactions:

$$Fe^{+3} + e^- \longrightarrow Fe^{+2} \tag{1}$$

$$2H^+ + 2e^- \longrightarrow H_2 \tag{2}$$

Anodic reactions:

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \tag{3}$$

$$Fe^{+2} \longrightarrow Fe^{+3} + e^- \tag{4}$$

The individual reactions at the cathode are effectively independent and the partial currents can be considered to be additive, thus [16]:

$$i_{cathodic} = i_{hydrogen} + i_{ferric} \tag{5}$$

To deduce the net polarization curves for the reduction of Fe^{+3} ions, the experiments were repeated twice once with and once without the presence of Fe^{+3} ions (at the same conditions), and a computer program was used to obtain the net polarization curves for the reduction of Fe^{+3} ions by subtracting the value of the hydrogen current from the total current (at the same potential). The polarization curves presented are the net polarization curves for the reduction of Fe^{+3} ions (the test reaction studied).

Polarization Curves

The polarization curve for long cathode (8 cm) for a selected condition is presented in Fig. (3). The ohmic loss in the electrolyte limit electro-active thickness of the electrode to a few centimeters in the direction of current and set up a potential gradient through the electrode. From Fig. (3) one can notice that intensive polarization took place in the top 4 cm of the cathode, little polarization after 6 cm from the top, and almost no polarization at the bottom of the electrode.

Since it was found that the current concentrated at the front portion of the cathode, only the 4 cm thick cathode was used in the following studies.

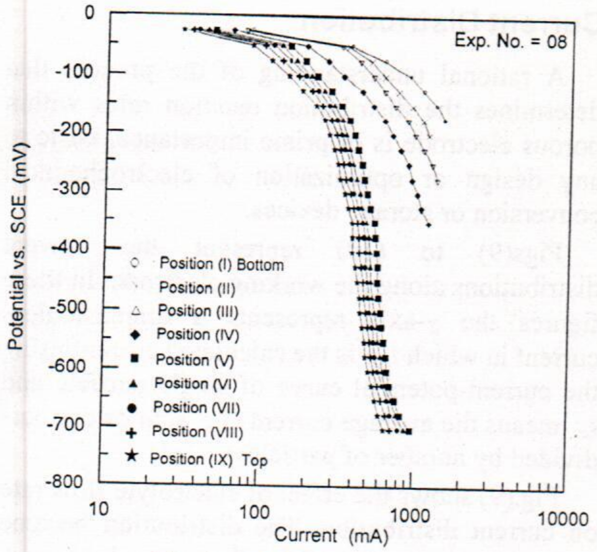

Fig. (3) Polarization curve
(Q= 300 l/hr, Fe^{+3} conc.= 2 mM, Temp.= 30 °C)

From Fig. (4) one can notice three regions. The first region at potentials greater than –150 mV in which activation energy controls the process. The third region at potentials less than –300 mV in which diffusion of Fe^{+3} ions controls the process. While in the second region (at potential between –150 to–300 mV) mixed control is observed.

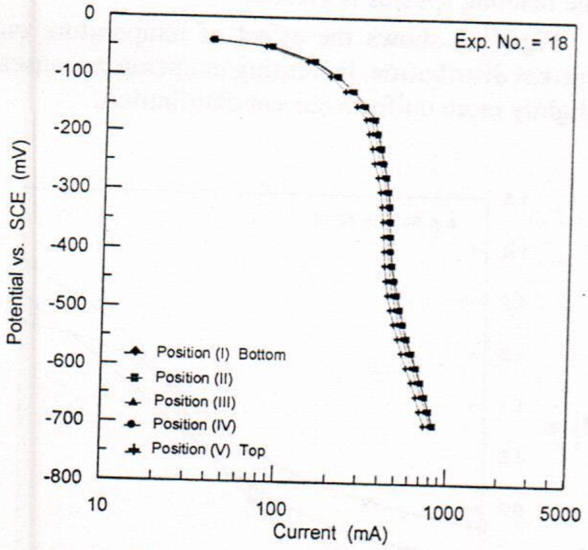

Fig. (4) Polarization curve
(Q= 300 l/hr, Fe^{+3} conc.= 2 mM, Temp.= 30 °C)

The polarization curves for cathode consists of single copper particle are presented in Fig.(5).

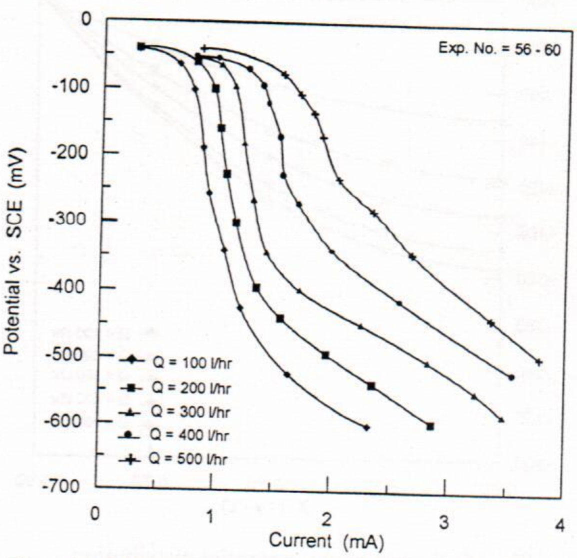

Fig.(5). Polarization curves of a single copper particle
(Fe^{+3} conc.= 2 mM, Temp.= 30 °C)

Potential Distribution

The sensitivity of reaction rate to electrode potential requires the reactor design to pay attention to potential distribution. Potential distribution depends on the electrode shape, electrolyte conductivity, electrode kinetics, mass transport and current.

In a two-dimensional electrode, it is rather easy to control the overpotential because everywhere on its surface it presents the same metal-solution potential. Nevertheless it's not true for volumetric electrodes (three dimensional electrodes). Especially for the flow-through porous electrode, the local potential drop varies in the bulk of the solution on account of the potential drop occurring in the solution.

Figs.(6) to (8) present the experimental potential distribution along the working electrode.

From these figures one can see that potential drop increased with increasing electrolyte velocity, this due to decreasing the boundary sub-layer near the cathode surface which control reaction rate.

Also one can notice that potential drop increases with increasing redox concentration. This due to the fact that increasing concentration will increase mass transfer rate which controls the process causing increase in the reaction rate.

Furthermore one can observe that potential drop slightly increases with increasing electrolyte temperature. This is due to the fact that increasing temperature will increase solution conductivity which in turn causes increase in the reaction rate.

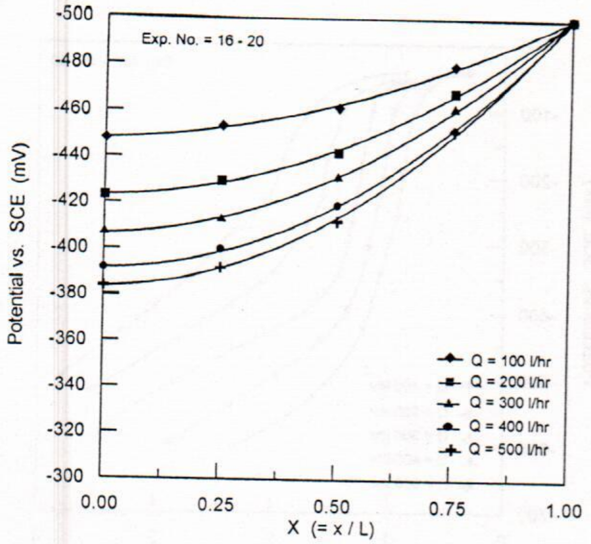

Fig. (6) Experimental potential distribution.
(Fe^{+3} conc.= 2 mM, Temp.=30 °C)

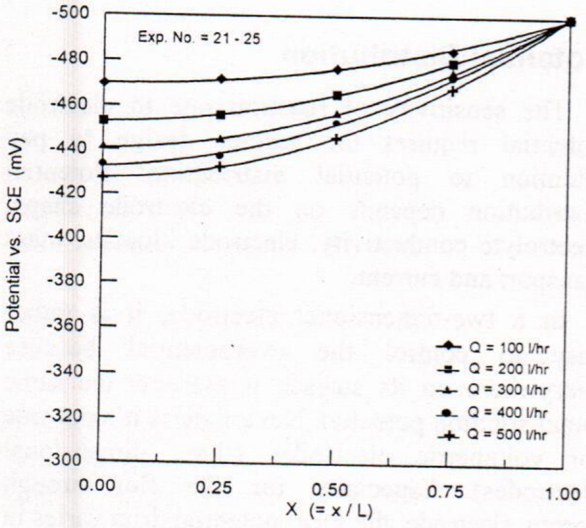

Fig. (7) Experimental potential distribution.
(Fe^{+3} conc.= 1 mM, Temp.=30 °C)

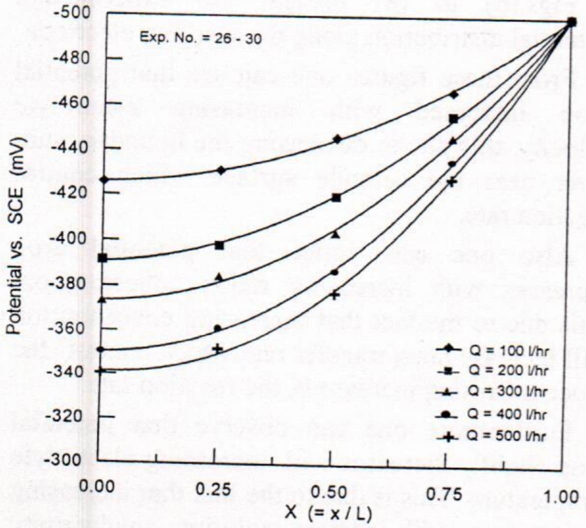

Fig. (8) Experimental potential distribution.
(Fe^{+3} conc.= 3 mM, Temp.=30 °C)

Current Distribution

A rational understanding of the process that determines the distribution reaction rates within porous electrode is of prime importance, basic to any design or optimization of electrochemical conversion or storage devices.

Figs(9) to (10) represent the current distributions along the working electrode. In these figures the y-axis represents a dimensionless current in which $i_{cal.}$ is the calculated current using the current-potential curve of single particle and $i_{av.}$ means the average current (i.e. sum of currents divided by number of particles).

Fig.(9) shows the effect of electrolyte flow rate on current distribution. The distribution became less uniform as electrolyte flow rate increased. The current concentrates at the top section of the electrode, and the current distribution shifted toward the bottom section and became more uniform as electrolyte flow rate decreased.

Fig.(10) shows the effect of redox concentration on current distribution. The distribution became less uniform as redox concentration increased. Quantitatively, the effect of variations of concentration of the redox would be expected to be the following : the species which reacts will become more depleted in the electrode, this will have the effect of shifting the reaction zone toward the electrode-solution interface at the bottom where the concentration of the reacting species is greater.

Figs.(11) shows the effect of temperature on current distribution. Increasing temperature causes slightly more uniform current distribution.

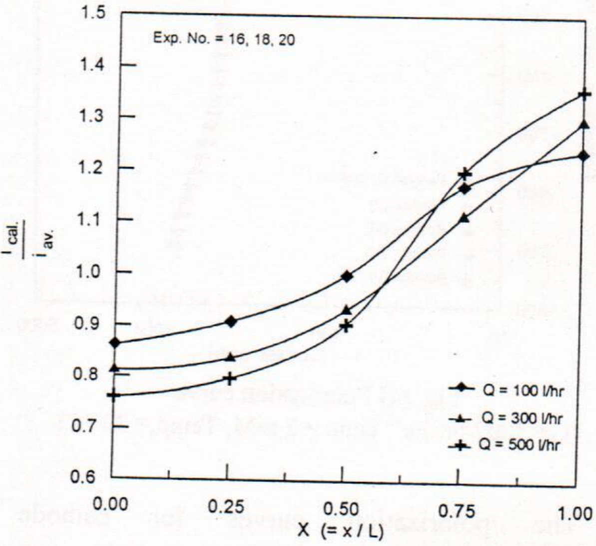

Fig. (9) Current distributions of the electrode.
(conc.=2 mM, Temp.=30 °C)

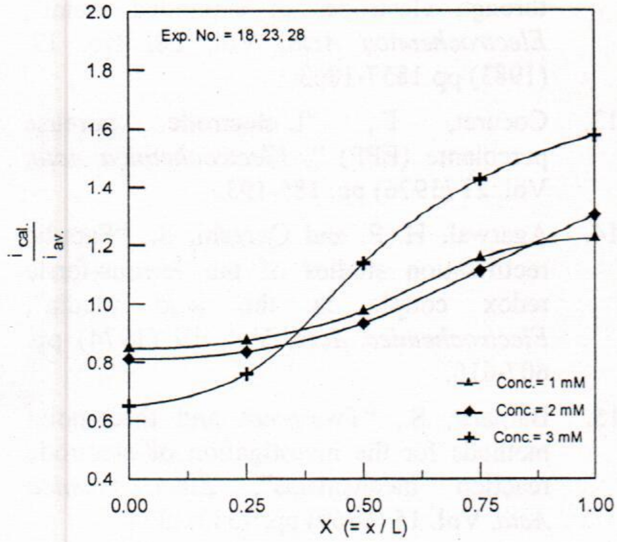

Fig. (10) Current distributions of the electrode.
(Q = 300 l/hr , Temp.=30 °C)

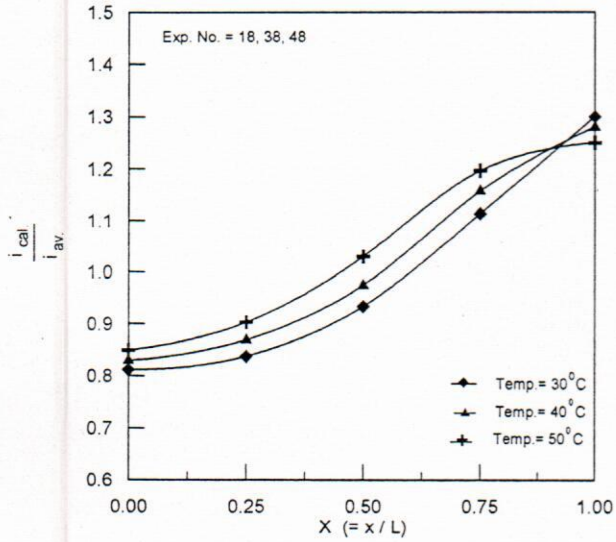

Fig. (11) Current distributions of the electrode.
(Fe^{+3} conc.= 2 mM , Q = 300 l/hr)

CONCLUSIONS

1. The electro-active bed thickness, in the range of experimental conditions used, was found to be 4 cm in the direction of current due to the ohmic losses in the electrolyte which set up a potential gradient through the electrode.
2. Increasing electrolyte flow rate improve the current at the same potential due to the diffusion boundary layer near the cathode surface become thinner. At high flow rates the system become less effected by the flow rate.
3. A substantial improvement in the current could be achieved by increasing redox concentration. This due to increasing mass transport to the cathode surface.
4. Increasing electrolyte temperature slightly improves current at the same potential. This due to increasing temperature will increase solution conductivity which in turn cause a decrease in the potential drop.
5. Current distribution curves shows that reaction concentrated at the top section of the bed. The current distributions become more uniform as increasing temperature, decreasing electrolyte flow rate or decreasing redox concentration.

NOMENCLATURE

Symbol	*Meaning*	*Unit*
C	Concentration	mole/m^3
d_p	Particle diameter	m
E	Metal-solution potential	Volt
F	Faraday's constant (= 96,487)	C/g-equivalent
I	*Current*	A
i	*Current density*	A/m^2
i_L	*Limiting current density*	A/m^2
L	Electrode thickness	m
n	Number of electron associated with the production of a molecule	
Q	Electrolyte flow rate	m^3/s
Re_b	*Reynolds number (= $d_p G_s / \mu$)*	(--)
Sc	Schmidt number (= $\mu / \rho D$)	(--)
Sh	Sherwood number (= $k_m d_p / D$)	(--)
T	*Temperature*	K
V	Voltage	Volt
x	*Distance*	m
X	*Dimensionless distance*	(--)
z	Valence	(--)

Greek Letters

ε	Porosity	(--)
η	*Overpotential*	Volt
μ	Electrolyte viscosity	kg/m s
ν	*Kinematic viscosity (= μ / ρ)*	m^2/s
ρ	Electrolyte density	kg/m^3
ϕ	Potential	Volt

Subscript

a	anode
b	bed or bulk (if specified)
c	cathode
s	solution or surface (if specified)
m	metal
p	particle