ChE *laboratory*

LOW-COST EXPERIMENTS IN MASS TRANSFER

Part 7. Natural Convection Mass Transfer on a Vertical Cylinder with Sealed Ends

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Chemical engineers commonly use dimensionless correlations for predicting heat and mass transfer coefficients needed to design heat and mass transfer equipment operated under natural as well as forced-convection conditions. This paper describes a simple electrochemical technique to establish a correlation for natural-convection mass transfer in which the dimensionless group Sherwood number (Sh) is expressed as a function of Grashof (Gr) and Schmidt (Sc) numbers in the form

$$\mathrm{Sh}=\alpha(\mathrm{Gr\ Sc})^{\beta} \qquad (1)$$

Such a condition is useful for predicting the mass transfer coefficient[1] that is needed in the design and operation of chemical and electrochemical reactors used in conducting liquid-solid diffusion controlled reactions.

This laboratory experiment introduces chemical engineering students to the basic theories of mass transfer, dimensional analysis, and electrochemistry, and at the same time provides training and skills in electrochemical techniques that are quite important for processes such as corrosion, electrowinning of metals, electrorefining, electroplating, electroforming, electrochemical machining, electrodialysis, and effluent treatment for environmental purposes.

THEORY

Electrolytic cell solutions used for mass-transfer studies usually contain a certain concentration (C_b) of an electroactive species (such as Cu^{2+}) and a relatively large concentration of a supporting electrolyte (such as H_2SO_4). The supporting electrolyte ionizes

$$\left(H_2SO_4 \leftrightarrow H^+ + HSO_4^- \leftrightarrow 2H^+ + SO_4^{2-}\right)$$

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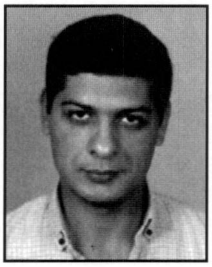

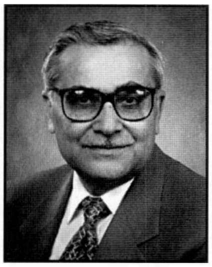

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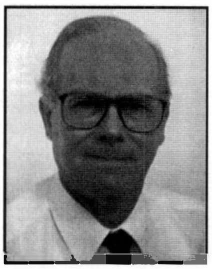

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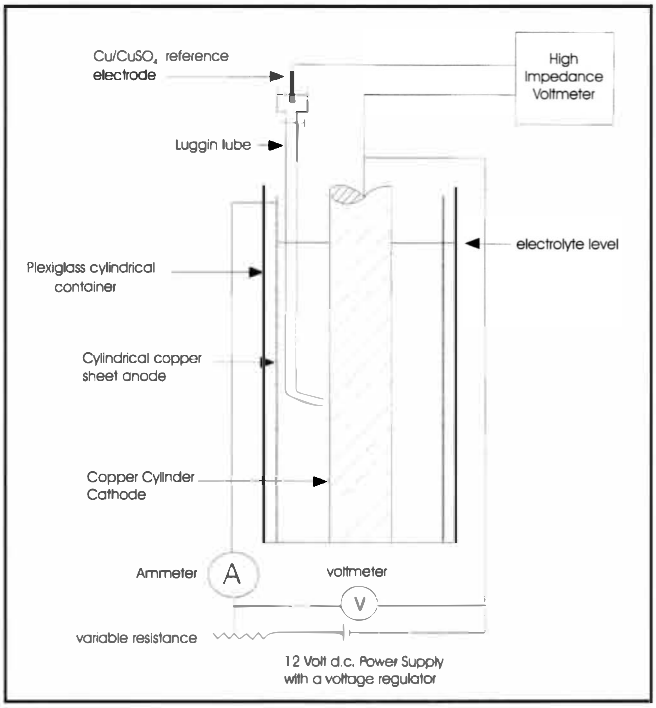

***Figure 1.** Apparatus*

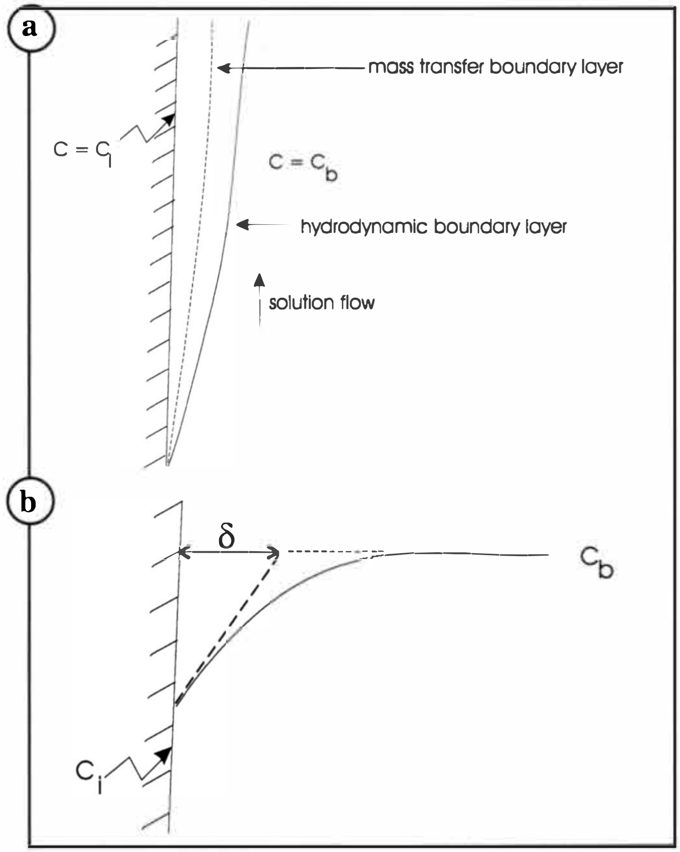

Figure 2.
***(a)** Buildup of hydrodynamic and mass transfer boundary layers along the cathode surface.*
***(b)** Concentration distribution of Cu^{++} at the cathode surface.*

to provide high solution conductivity (low Ohmic resistance, R_Ω) and a large number of ions that act as the actual current carriers within the electrolytic solution. Therefore, the transfer of Cu^{2+} to the cathode surface by electrical migration is eliminated. In the presence of a supporting electrolyte such as H_2SO_4, Cu^{++} ions are transferred to the cathode surface by other mechanisms such as diffusion and convection.

When a small potential difference (V) is applied across the electrodes, the ions move within the solution toward the oppositely charged electrodes and accumulate near the respective electrodes (see Figure 1 for the apparatus). An ammeter placed in the circuit detects a small amount of current (I) known as the residual current. As the applied voltage is increased further, a high enough value of the cathode potential, known as the *discharge potential of the electroactive species* (E), is reached. At 25°C and 1.0 mol/L concentration of electroactive species, this potential is known as the *standard electrode potential* (E_o) evaluated against standard hydrogen reference electrode ($H_2|H^+$). Values of the standard electrode potentials are tabulated in the literature as *standard electrochemical series.*[2] When the discharge potential is reached, an electrode reaction sets in and the ammeter records a sudden jump in current. This is due to the increased flow of electrons in the circuit because of the exchange of electrons between the electrodes and the electroactive ions, *i.e.,* the electrode reactions. For the reduction of Cu^{2+} ions, the cathodic reaction may be expressed by the following equation (the students should be encouraged to comment on the anodic reaction)

$$Cu^{2+} + 2e \rightarrow Cu \tag{2}$$

The equilibrium deposition potential is given by the Nernst equation

$$E = E_o + \frac{RT}{nF} \ell n C_b \tag{3}$$

The value of the equilibrium potential of the system $Cu|CuSO_4$ can be determined by measuring the potential difference between the copper electrode ($Cu|CuSO_4$) and a suitable reference electrode by means of a high impedance voltmeter.

Due to the discharge of some Cu^{2+} ions, the concentration of Cu^{2+} ions in the immediate vicinity of the cathode is decreased to C_i. Accordingly, the interfacial solution density decreases from ρ_b to ρ_i and this density difference gives rise to a buoyancy force, $g\Delta\rho$, which causes upward solution flow at the electrode surface. This flow enhances the transfer of Cu^{2+} from the solution bulk to the edge of the diffusion layer.

A boundary layer (known as the Nernst diffusion boundary layer and also as the effective mass transfer boundary layer) of thickness δ is established between the bulk solution and the electrode (see Figure 2b). The value of δ is determined by the magnitude of the upward flow (natural convection) as well as solution physical properties. The effective mass transfer boundary layer thickness (δ) is defined in such a way that the concentration gradient at the electrode surface, $(C_b - C_i)/\delta$, is as shown in Figure 2b. The concentration gradient causes the transfer of Cu^{2+} ions across the diffusion layer from bulk solution to the electrode surface by molecular diffusion.

As the applied cell voltage is gradually increased, the corresponding current increases owing to the increase in the rate of Cu^{2+} deposition at the cathode. This is followed by a further decrease in the interfacial Cu^{2+} concentration (C_i) and an increase in the cathode potential above the equilibrium deposition potential E (see Eq. 3). Assuming that reaction (2) is fast, *i.e.,* there is no activation polarization and there is no ohmic drop in measuring the cathode potential, the difference between the actual deposition potential and the equilibrium deposition potential is known as concentration polarization (η_c) and its magnitude is given by

$$\eta_c = \frac{RT}{nF} \ell n \frac{C_i}{C_b} \tag{4}$$

If the cell voltage is sufficiently increased, a state is reached where the interfacial Cu^{2+} concentration becomes zero and the rate of mass transfer becomes maximum. Under this condition, the current attains a constant value known as the limiting current (I_L). In the meantime, the cathode potential increases to a high value where H_2 gas starts to evolve simultaneously with copper deposition according to the reaction

$$2H^+ + e \rightarrow H_2 \tag{5}$$

Obviously, the value of I_L will depend on the value of the limiting driving force gradient, *i.e.,* C_b/δ. In the absence of any mechanical agitation (assuming transfer of Cu^{2+} by electrical migration is eliminated by H_2SO_4 supporting electrolyte), the flux of Cu^{2+} ions ($N_{Cu}{}^{2+}$) may be obtained from

$$N_{Cu^{2+}} = \frac{I_L}{nF} = \frac{D}{\delta}\Delta C = K\Delta C = KC_b \tag{6}$$

or

$$\frac{I_L}{nF} = KAC_b \tag{7}$$

which yields

$$K = \frac{I_L}{nFAC_b} \tag{8}$$

where $N_{Cu}{}^{2+}$ is the diffusional flux of Cu^{2+} ions, i_L is the limiting cathodic current density (limiting cathodic current per unit cathode area, I_L/A), n is the number of electrons involved in the electrode reaction (2 for the reduction of Cu^{2+} ions according to Eq.2), F is Faraday's constant (96,500 Coulomb/equivalent), and A is the active surface area of the electrode.

Knowing the physical properties of the solution [viscosity (μ) and bulk (ρ) and interfacial (ρ_i) densities] the diffusion coefficient of electroactive ions (D) and the characteristic length dimension of the electrode (l), the dimensionless groups

$$Sh(= Kl / D), \quad Gr\left(= gl^3 \Delta\rho / v^2 \rho_b\right), \quad \text{and} \quad Sc(= \mu / \rho D)$$

can be determined. Hence the constants α and β of Eq. (1) can be evaluated.

There are a variety of cathode shapes to choose from, but the easier ones to work with are vertical cylinders with ends made inactive by coating with wax or epoxy resin. In this case, the characteristic length l is the cylinder height.

EXPERIMENTAL PROCEDURE

A typical apparatus using a 5-cm diameter cylindrical copper cathode is shown in Figure 1. A plexiglass container of 14-cm diameter and 55-cm height is used as the cell. The anode is a pure copper sheet rolled to fit in the container. Using an anode made of pure copper ensures the constancy of $CuSO_4$ bulk concentration (C_b) in the cell at the initial value owing to the fact that copper dissolves from the anode at a rate equal to that of cathodic copper deposition during electrolysis. The circuit consists of 12-volt d.c. power supply with internal voltage regulator and a multirange ammeter connected in series with the cell. The cathode (cylinder) is connected to the negative pole of the power supply, while the anode is connected to its positive pole. Polarization curves from which the limiting current is determined are obtained by increasing the current stepwise through the variable resistance (see Figure 1) and measuring the corresponding steady-state cathode potential against a reference Cu/ $CuSO_4$ electrode placed in the cup of a Luggin tube whose tip is placed 0.5-1 mm from the cathode surface. The Luggin tube is filled with the same cell solution. A high impedance voltmeter should be used to measure the potential difference between the cathode and the reference electrode.

The cell solution contains 1.5 mol/L H_2SO_4 (supporting electrolyte) containing different concentration of $CuSO_4$, viz., 0.05, 0.1, 0.15, 0.2, and 0.25. The experiment can be conducted at room temperature. The physical properties of the solution needed for data correlation are shown in Table 1.[3,4] If a 12-volt d.c. power supply with internal voltage regulator is not available, a 12-volt automobile battery and a rheostat can be used. Also, the plexiglass container and the long electrodes can be replaced by a glass beaker and short electrodes.

TABLE 1
Physical Properties of Copper Sulphate Solution in 1.5 M H_2SO_4 at 24°C

$[CuSo_4]$ (mol/L)	Viscosity (cp)	Diffusivity x 10^6 (cm^2/s)	Density (g/cm^3)	$(\rho - \rho i)$ (g/cm^3)
0.01	1.197	6.28	1.09	0.0014
0.0498	1.260	5.93	1.093	0.0068
0.0688	1.242	6.04	1.092	0.0093
0.0966	1.263	5.94	1.097	0.013
0.1890	1.300	5.80	1.103	0.025

RECOMMENDED LABORATORY SETUP

1. The class may be divided into five groups.
2. A cylinder of 60-cm length should be cut from copper rods of available diameters (10-50 mm). The active cylinder height can be changed by isolating the upper part of the cylinder by wrapping a Teflon tape on it. Alternatively, epoxy resin or molten bee's wax can be used to control the active part of the cylinder.
3. All solutions should be prepared by the laboratory technologist prior to the scheduled lab hour.
4. Each group should obtain the polarization data (current vs. cathode potential) by increasing the applied current stepwise and recording the corresponding cathode potential until the onset of hydrogen evolution (see Figure 3 for a typical experimental curve) for one cylinder height but different [$CuSO_4$]. Each experiment will take about 20-25 minutes. The students should be advised to clean the cathode surface with a fine emery paper before each test to remove any adhering copper powder from previous experiments.

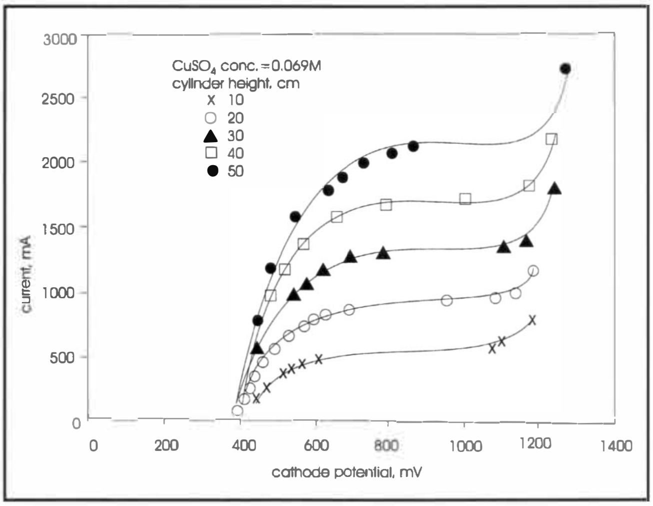

Figure 3. Typical polarization curves at different cylinder heights.

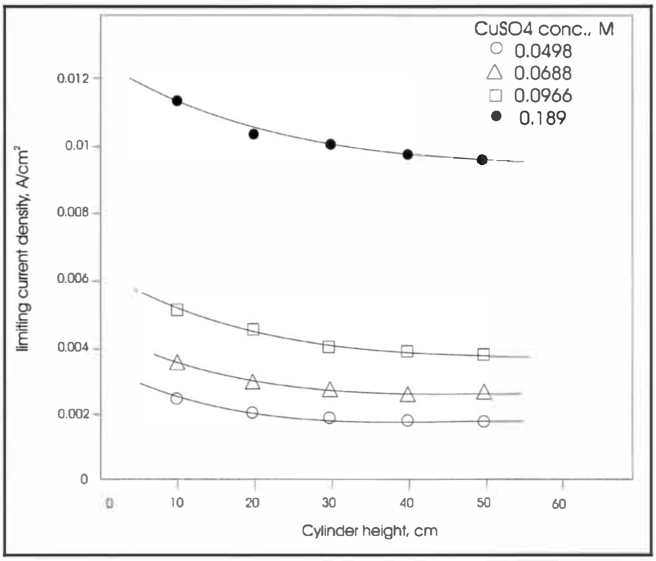

Figure 4. Effect of cylinder height on limiting current desities.

5. Different groups should study the effect of cathode height on limiting current and mass transfer coefficient (see Figures 4 and 5, respectively, for typical experimental data).

ANALYSIS OF RESULTS

1. Notice the decrease in the limiting current and the mass transfer coefficient with increasing cylinder height owing to the increase in the thickness of the hydrodynamic boundary layer and the mass transfer boundary layer as the solution moves along the cylinder (see Figure 2a). Determine the relation between the mass transfer coefficient and cylinder height and compare it with the prediction of the hydrodynamic boundary-layer theory.[3,5,6]
2. Calculate Sh, Gr, and Sc numbers using the experimental limiting current date, the electrode height, and the physical properties given in Table 1.
3. Determine values of α and β for Eq. (1) (see Figure 6 for typical experimental results indicating that for this case, for the range $1.8 \times 10^{10} < \text{Sc Gr} < 4 \times 10^{13}$, $\text{Sh} = 0.64\,(\text{Sc Gr})^{0.258}$ with an average deviation of ±7.2%).
4. Compare the above-mentioned values of the constants α and β with those of the corresponding mass and heat transfer equations reported in the literature.[1,5]
5. Calculate the mass transfer coefficient using Eq. (1) and compare this predicted value with the experimental value determined from Eq. (8).
6. Discuss what happens at a current value slightly larger than the limiting current for copper deposition.
7. Check the electrodes for surface smoothness after the experiment to see whether the anode is smoother than the cathode, and give a possible explanation.
8. Record your observations on the structure of the deposited

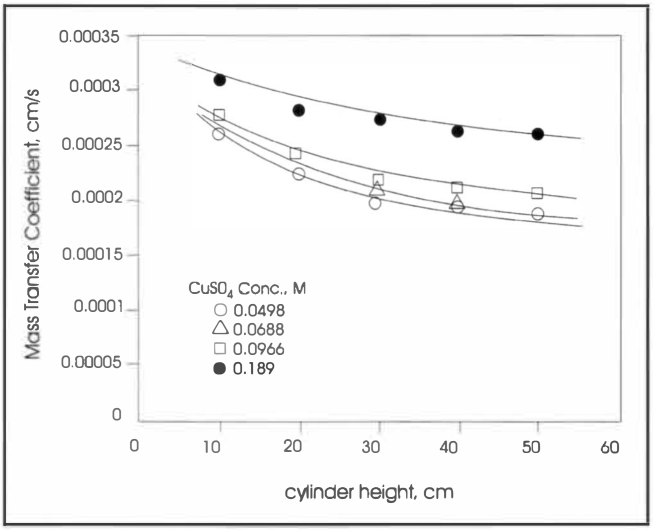

Figure 5. Effect of cylinder height on the mass transfer coefficient.

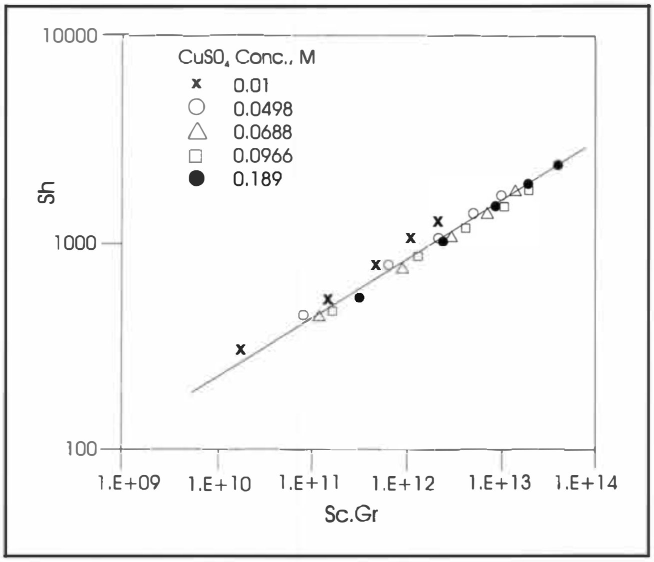

Figure 6. *Overall mass-transfer correlation for the range* $1.8 \times 10^{10} < Sc\ Gr < 4 \times 10^{13}$, $Sh = 0.64\,(Sc\ Gr)^{0.258}$ *with an average deviation of ±7.2%*

copper at different current densities, noticing that below the limiting current a compact adherent copper deposit is obtained, while at the limiting current copper powder starts to deposit. The effect of current density on deposit structure has an important industrial implication in electrochemical industries such as electrowinning of metals from their natural ores, electrorefining of metals, electroforming, and electroplating. Usually an operating current density below the limiting value is used to obtain a compact adherent deposit. Operation at the limiting current density is used in industry only when it is required to produce metal powder. Metal powders are needed in the metallurgical industry for fabricating objects by the powder metallurgy technique (see Reference 6 for the mechanism of metal powder formation at the limiting current).

9. Comment on the possible sources of error, *e.g.*, surface roughness due to copper deposition at limiting current density, especially at high copper sulphate concentrations in solutions, and the slight incline usually found in the limiting current plateau.
10. Using Faraday's law as given by Eq. (9) below, calculate the daily rate of copper production (m) that is carried out in industry at a current density 30-50% of the limiting value[7] in the form of compact adherent deposit:

$$m = e\,I\,t \tag{9}$$

$$e = \text{electrochemical equivalent} = \frac{\text{equivalent weight}}{96500} \tag{10}$$

11. Calculate the electrical energy consumed in the electrolytic production of copper in kWh/kg from the formula

$$\text{energy consumption} = \frac{\text{Total cell voltage (V)} \times I}{1000 \times \text{amount produced in kg/h}} \tag{11}$$

The cell voltage at the operating current density can be measured by connecting a voltmeter in parallel with the cell, as shown in Figure 1.

NOMENCLATURE

A	cathode area, cm^2
C	concentration of copper sulphate, mol/cm^3
D	diffusion coefficient, cm^2/s
d	cylinder diameter, cm
e	electrochemical equivalent, g/Coulomb
E, E_o	equilibrium and standard deposition potentials, respectively, V
F	Faraday's constant (96500 Coulomb/equivalent)
g	acceleration due to gravity, cm/s^2
I_L	limiting current, A
i_L	limiting current density, A/cm^2
K	mass transfer coefficient, cm·s^{-1}
l	characteristic length dimension in Sherwood and Grashof numbers, cm (cylinder height in the present case)
m	mass production, g
N	diffusional flux of electroactive species, mol/cm^2·s
n	number of electrons involved in the reaction
R	gas constant, Joule/deg. mole
R_Ω	Ohmic resistance, ohms
T	temperature, K
t	time, s
V	cell voltage, V

Dimensionless Groups

Gr	Grashof number $\left(g l^3 \Delta\rho / \nu^2 \rho_b\right)$
Sc	Schmidt number $(\mu/\rho D)$
Sh	Sherwood number (Kl/D)

Greek Symbols

α, β	constants
ν	kinematic viscosity of the bulk solution, μ/ρ, cm^2/s
ρ	density of the bulk solution, g/cm^3
$\Delta\rho$	density difference between the bulk and the interfacial solution, g/cm^3
δ	thickness of mass transfer boundary layer, cm
η_c	concentration polarization, V

Subscripts

b	bulk
i	interfacial
c	cathodic

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