Mass Transfer Conditions in an Electrochemical Cell In the Presence of Turbulence Promoters

By T. Subbaiah, P. Venkateswarlu, S.C. Das, R.P. Das & G.J.V.J. Raju

The presence of turbulence promoters in an electrochemical cell increases the intensity of local turbulence, which enhances the limiting current density and, consequently, mass transfer coefficients. The regularity of their geometrical configuration induces a pseudo-uniformity of the spatial distribution of local transfer coefficients. Limiting current data were obtained at point electrodes fixed on the cathode support plate for the system: $CuSO_4$ - H_2SO_4. The improvements in mass transfer coefficients resulting from the presence of turbulence promoters is assessed. The effect of flow rate, promoter height and promoter spacing on mass transfer coefficient has been studied. The average mass transfer coefficient was derived from the experimental data and correlated to various operating conditions by the equation:

$$J_D = C\ Re^{-0.87}\ (S/H)^{-0.15}$$

There is continual effort to increase mass transfer for economical operation and increased output. A few investigators[1-3] have studied augmentation of ionic mass transfer rates by introducing turbulence promoters in the flow paths of the electrolytes and have reported encouraging results.

Investigations of the effect of cylindrical turbulence promoters and mesh-type eddy promoters on local and momentum transfer were reported by Storck and Hutin.[2] Leitz and Marincic[3] inserted rectangular, triangular and circular promoters near the wall of a parallelepiped electrochemical cell and identified the best type of promoter, based on local and overall mass transfer data.

In the current study, an attempt is made to determine the level of augmentation in terms of mass transfer coefficients as a result of the presence of promoters, by choosing a system nearly like that of a copper refining process. The variables covered are (i) flow rate of the electrolyte, (ii) height of the turbulence promoters, (iii) spacing of the promoters and (iv) positioning of the electrodes.

Literature Review

The growing interest in electrolytic production of copper has led to a number of significant advances in both refining and winning processes. The major techniques adopted for achieving improved mass transfer conditions are (i) increasing electrolyte circulation rate, (ii) using extended area cathodes (packed bed and fluidized bed cathodes) and placing eddy promoters. Several authors have developed model equations in presence of promoters.[4-13]

The effects of cylindrical promoters and mesh-type promoters on mass transfer and pressure drop in the electrochemical cell were reviewed by Sonin and Isaacson.[4,5] Storck and Coeuret[6] further studied the mass and momentum transfer in the channel cell, using a potassium ferro-ferricyanide system. Leitz *et al*.[3] used turbulence promoters in the fluid flow to enhance mass transfer. An instrument was developed to measure the local current densities. They also proposed a generalized correlation.

Storck and Hutin[8] noted the improvement in copper recovery in an electrochemical reactor provided with turbulence promoters. The results showed that the limit of one ppm could be obtained quite easily under usual operating conditions, using a parallelopedic channel, 1000 x 50 x 10 mm, with copper cathode of 18.5 x 3.0 cm and cylindrical promoters of 8 mm dia. and spacing of 50 mm. They suggested an experimental model cylinder for obtaining momentum and mass transfer. Dudukovic and Djurdjevic[9] used discs and spheres in their mass transfer studies and obtained 60-80 percent increase in mass transfer coefficients.

Venkateswarlu[10] used coaxially placed discs on a rod as turbulence promoters for ionic mass transfer. He observed a 4 to 12-fold increase in mass transfer coefficients because of the presence of promoters. Sujatha[11] obtained mass transfer and pressure drop data using twisted tapes, both in the absence and presence of fluidized solids. Walsh[12] obtained a generalized correlation in the presence of plate-type promoters in the range of Reynolds numbers, 1000 to 6000, yielding an equation as follows:

$$Sh = 4.01\ Re^{-0.68} Sc^{0.33} \qquad (1)$$

where Sh, Re and Sc are Sherwood, Reynolds and Schmidt numbers, respectively.

Higher current density can be used in the tanks because of the presence of promoters. Increase of current density increases the current efficiency, the production rate and reduces required building area and inventory. Higher mass transfer coefficients can be activated by operating the cell at comparatively low flow rates by employing turbulence promoters. The associated fluid friction and increased power loss from the presence of promoter elements can be offset by increased rates of mass transfer, reduced equipment size and quality of the deposit.

Experimental Procedure

Material

Analytical reagent-grade copper sulfate and sulfuric acid were used in this investigation. The electrolyte was prepared by dissolving cupric sulfate in distilled water.

Apparatus

A fiberglass-reinforced plastic electrolytic cell with dimensions of 0.594 x 0.19 x 0.23 m, and geometrically proportional to the industrial copper electrorefining cell of Hindustan Copper Ltd., Ghatsila, Bihar, India, was used. The cell was provided with an inlet of 0.027 m and three outlets, each 0.015 m in dia. at a spacing of 0.045 m at the exit end of the cell. A rectangular perspex plate of 0.005 m thickness, length 0.18 m and width of 0.15 m, on which point electrodes of 0.005 m dia. were mounted flush with its surface, served as

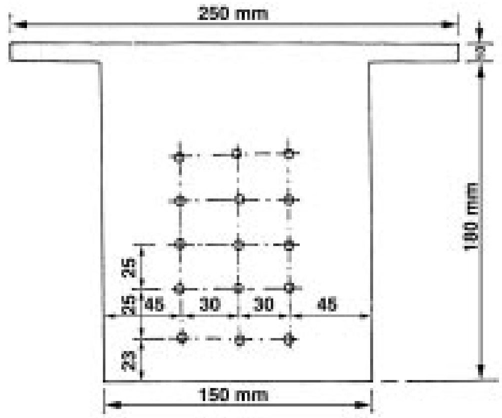

Fig. 1—Cathode support plate (dimensions in mm).

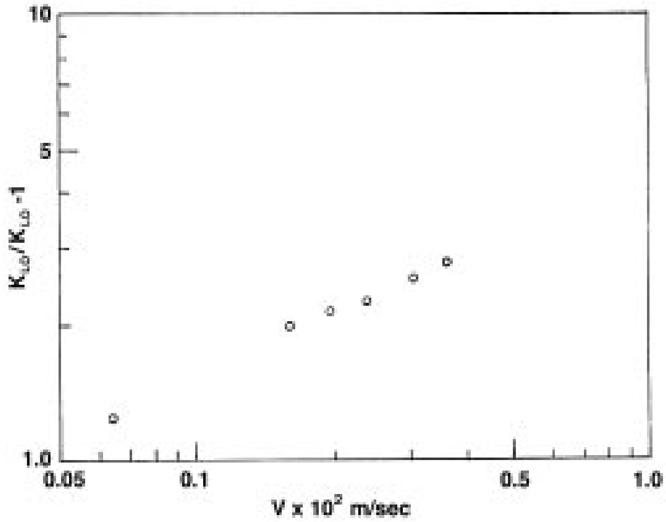

Fig. 2—Improvements in overall coefficients in absence of promoters in forced convection vs. natural convection.

a cathode support plate and were placed 0.275 m from the entrance end. A pure copper sheet anode, 0.18m x 0.15 x 0.002 m was placed 0.05 m from the exit end of the cell. A copper rod 0.003 m dia. x 0.05 m length immersed in copper sulfate solution, having the composition of the bulk electrolyte, served as a reference electrode. A metering pump was used for circulating the electrolyte in the cell. Rectangular promoters of 0.175 m in width and 0.01 to 0.07 m in height were placed at the bottom of the cell with a spacing of 0.075 to 0.30 m. A potentiostat, programmer and X-Y recorder were used for the limiting current measurements. The location of the electrodes on the inert cathode support plate is shown in Fig. 1.

Flow Procedure

The electrolyte from the recirculation tank was pumped by the metering pump to the overhead tank from which it is fed to the cell. Limiting current measurements were made at point copper electrodes for the reduction of cupric ion. The method of obtaining the limiting current is reported elsewhere.[14]

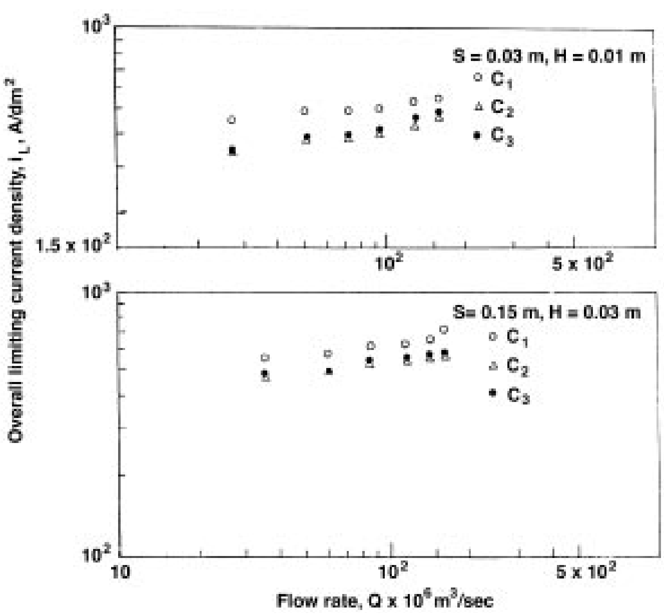

Fig. 3—Plot of overall limiting current density vs. flow rate at columns 1, 2 and 3 of CSP.

Results & Discussion

The results presented are based on the limiting current measurements obtained at point copper electrodes placed on a perspex plate vertically suspended in the electrolytic cell, on which electrodes are fixed flush with the surface. This support plate can be construed to be analogous to the cathode plate of a refining cell where the metal deposition occurs. The electrochemical reaction taking place at the point electrodes is given by

$$Cu^{+2} + 2e^{-} \rightarrow Cu \qquad (2)$$

The mass transfer coefficient is calculated as reported earlier[15] and physical properties of the electrolyte are taken from the literature.[16]

The flow conditions in the electrolytic cell can be approximated as open channel flow. The turbulence promoters placed at the bottom cause secondary flows locally and propagate upwards through the electrolyte. The cathode support plate and anode plate act on two cross-flow elements, causing considerable blockage to the flow of the electrolyte. The flow patterns developed are likely to cause vigorous mixing in the

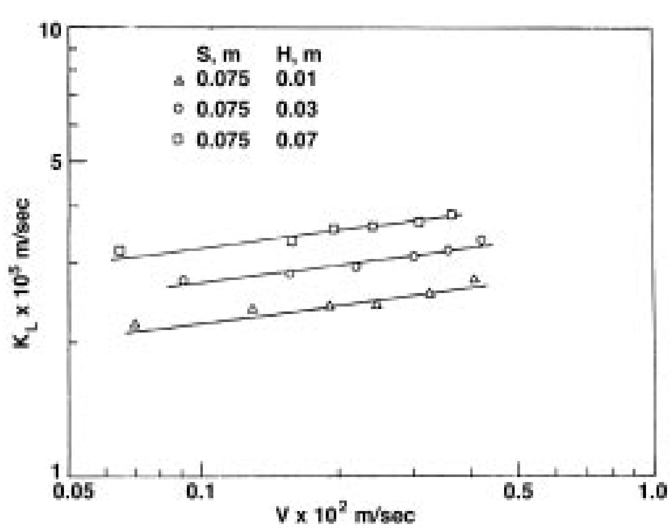

Fig. 4—Effect of propmoter height on overall coefficients at S = 0.075 m.

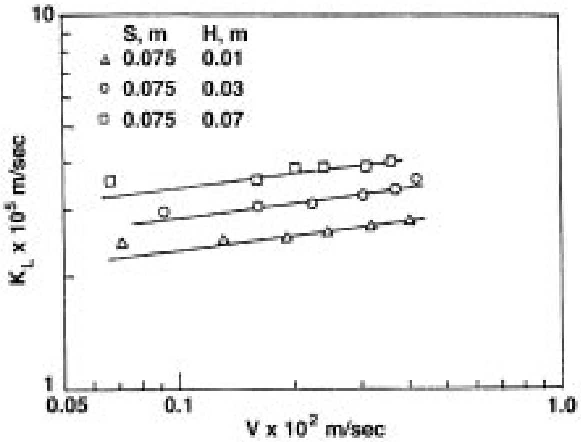

Fig. 5—Effect of promoter height on average central coefficient.

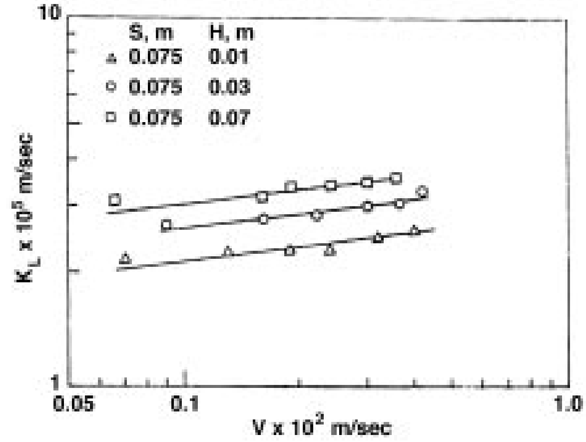

Fig. 6—Effect of promoter height on average coefficient of columns 2 and 3.

cell, resulting in favorable hydrodynamic conditions in the vicinity of the electrodes, with consequential augmentation in mass transfer coefficients.

In this study, the effects of (i) flow rate of the electrolyte, (ii) height of the promoter (H), and (iii) spacing between the promoters (S), on limiting current density and thus on the mass transfer coefficients have been considered. The electrodes on the cathode support plate were placed column-wise in five rows and numbered from 1 to 15. Limiting currents computed at columns (1, 2 & 3) against the height of the electrodes are listed in the table. In view of the fluctuating values of limiting current density because of flow interaction and narrow variations in their values, it is felt that a simple arithmetic average of the local values obtained at individual electrodes should be sufficient for subsequent analyses.

The experimental data at electrodes on the cathode support plate are then categorized as follows:

a. Average of local values of limiting current densities/mass transfer coefficients at all electrodes on the CSP— herein termed as “overall coefficient.”
b. Average of local values of limiting current densities/mass transfer coefficients at all electrodes in column 1 (electrodes 1-5)—herein termed as “average central coefficient.”
c. Average of local values of limiting current densities/mass transfer coefficients at electrodes of columns 2 and 3 taken together (electrodes 6-15)—herein termed as “average coefficient of columns 2 and 3.”

Effect of Flow Rate

With increase of electrolytic circulation, limiting current density increases and, consequently, mass transfer coefficients. The improvements in mass transfer coefficients in forced convection in the absence of promoters compared to them in natural convection are shown in Fig. 2, where the increase is by as much as a factor of 2.75.

Average values of the limiting current densities for the electrodes of central columns and outer columns are plotted against flow rate for two cases of promoters (S = 0.30 m, H = 0.01 m; and S = 0.15 m; H = 0.03 m) and shown in Fig. 3. The plots show that the average limiting current density at column (1) were found to be consistently higher. The limiting current density values for the other two cases of electrodes of columns 2 and 3 were found to be almost the same.

Effect of Promoter Height

Variation in the overall coefficient with height is shown in Fig. 4 via the plots of data with different heights (H = 0.01, 0.03 and 0.07 m) at a spacing S of 0.075 m. The data show that

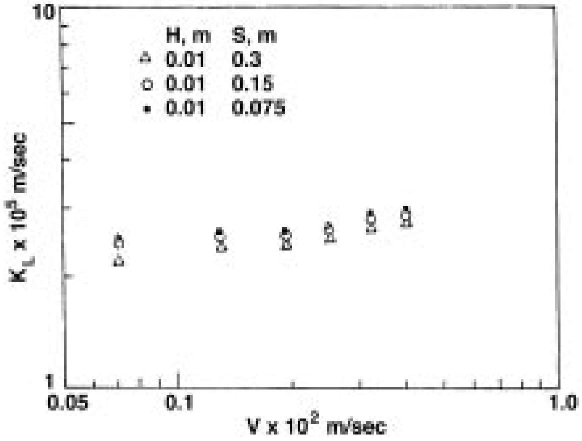

Fig. 7—Effect of promoter spacing on average central coefficient.

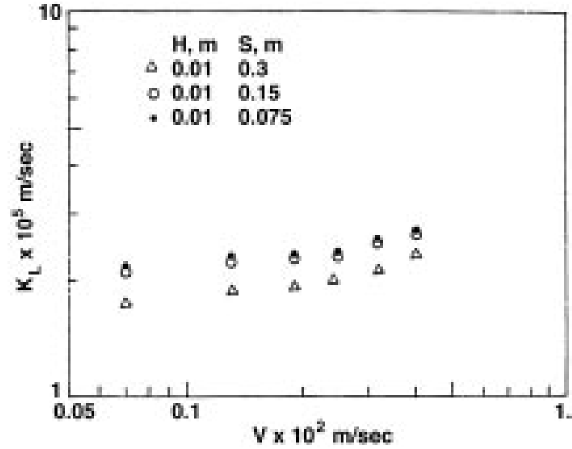

Fig. 8—Effect of promoter spacing on average coefficient of columns 2 and 3.

Limiting Currents at Cathode Support Plate				
		Limiting Currents		
S. No.	Height from bottom, cm	Central column A x 10^3	Column 2 A x 10^3	Column 3 A x 10^3
1	7.3	9.0	8.0	8.0
2	9.8	11.0	8.5	8.5
3	12.3	8.0	8.5	8.5
4	14.8	11.0	8.5	8.5
5	17.3	11.5	9.0	9.0

Electrolyte circulation rate: 38.33 x 10^{-6} m^3/sec
Concentration of copper in electrolyte C_o: 0.1067 kg mol/m^3

overall coefficients increase with increase in the height of the promoter and that the increase is as much as 60 percent in the range of height covered. Increase in the height of the promoters obstructs the flow at the bottom of the cell, altering the flow pattern. This obstruction affects the local velocities and increases the mass transfer coefficients. Similar trends were also obtained from the plots of mass transfer coefficient with height for the average coefficient of columns 2 and 3 and average central coefficient data (Figs. 5 and 6).

Effect of Promoter Spacing

The data on the average mass transfer coefficients are shown for three spacings of the promoters of a given height, H = 0.01 m, for the average central coefficient and the average coefficients of columns 2 and 3 in Figs. 7 and 8. It can be seen that the average coefficients are found to vary inversely with promoter spacing. For lower spacing, the combined effect of the ripple flow and axial flow causes turbulence, resulting in higher coefficients.

Data Correlation

It was found that the average mass transfer coefficient is proportional to H and inversely proportional to S; therefore, a geometric parameter (S/H) is taken into consideration. Mass transfer correlations for the data with homogeneous flow of electrolyte in circular conduits in the presence of promoters are generally correlated by the J_D factor with Re.

The Reynolds number is defined using the hydraulic mean diameter, D_e = 4 x cross sectional area/wetted perimeter. The constant C is evaluated by subjecting the experimental overall coefficient data to regression analysis, which yields the following equation. For average central coefficients,

$$J_D = 424\ Re^{-0.87}(S/H)^{-0.15} \tag{3}$$

Average deviation = 6.2 percent, Standard Deviation = 7.72. For the average coefficients of columns 2 and 3,

$$J_D = 371\ Re^{-0.87}(S/H)^{-0.15} \tag{4}$$

Average deviation = 7.47 percent, Standard Deviation = 10.96 The data are plotted in accordance with Eqs. (3 and 4) and shown in Figs. 9 and 10, respectively.

From the above equations, it is found that the exponential value of the dimensionless group, Re, is the same in both cases. Similarly, the exponential values of (S/H) is also the same in both cases. Comparison of the equations shows that the average central coefficients are higher by 14 percent over the average coefficients of columns 2 and 3.

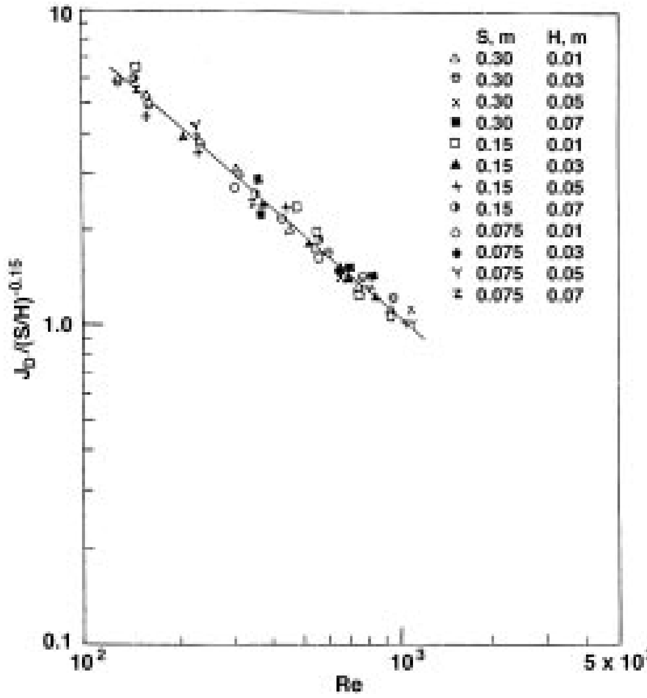

Fig. 9—Correlation plot of average central coefficient data in accordance with Eq. (4).

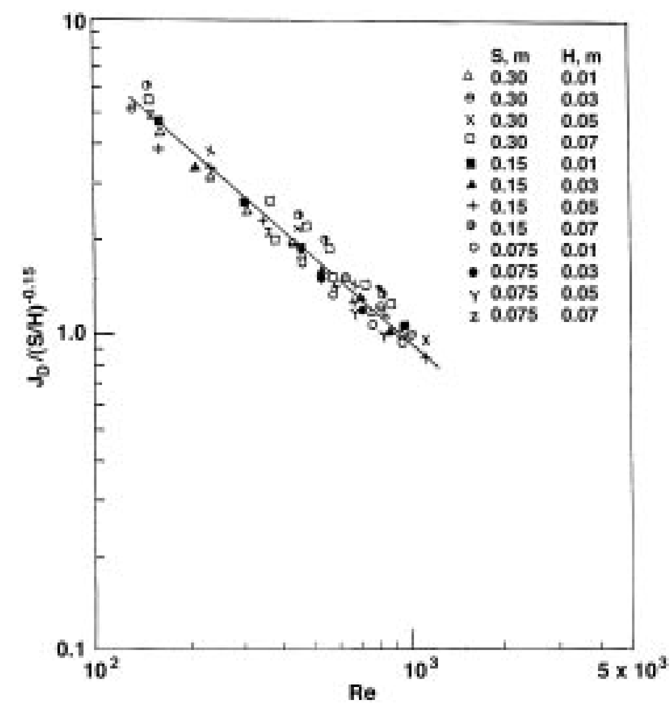

Fig. 10—Correlation plot of average coefficient of columns 2 and 3 in accordance with Eq. (4).

Findings

1. The average mass transfer coefficients at electrodes located at the center and columns 2 and 3 increase with increase of electrolyte flow rate.
2. The magnitude of augmentation in forced convection flow with natural convection is about 2.75 fold.
3. The mass transfer coefficients increase with increase of promoter height and decrease with promoter spacing.
4. The mass transfer data are correlated by the equation

$$J_D = C\ Re^{-0.87}(S/H)^{-0.15}$$

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Nomenclature

D_e—Equivalent diameter of the electrolytic cell 4 Wh/(W+2h), m
D_L—Diffusion coefficient of the electrolyte, m^2/sec
g—Acceleration of gravity, m/sec^2
h—Height of the electrolyte in the cell, m
H—Height of the promoter, m
J_D—Mass transfer factor, $K_L/V \cdot Sc^{2/3}$
K_L—Mass transfer coefficient, m/sec
R_e—Reynolds number, $V \cdot D_e/g$
S—Spacing of the promoters, m
Sc—Schmidt number, ν/D_L
Sh—Sherwood number, $K_L \cdot D_e/D_L$
V—Velocity of the electrolytes, m/sec
ν—Kinematic viscosity of the solution, m^2/sec
W—Width of the electrolytic cell, m

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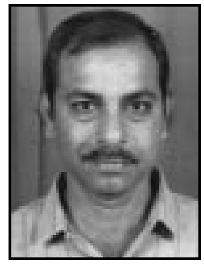
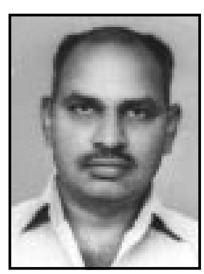
About the Authors



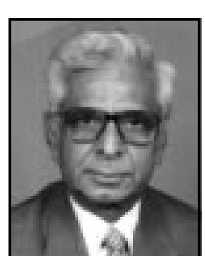
Dr. T. Subbaiah is a scientist in the Hydro & Electrometallurgy Division of the Regional Research Laboratory, Bhubaneswar 751013, India. He is a graduate of Andhra University, Waltair, India, and holds a PhD from the same university. He has published a number of papers in national and international journals that reflect his technical interests in electrowinning of aqueous and fused salts, and cell design.*

Dr. S.C. Das is a scientist in the Hydro & Electrometallurgy Division of the Regional Research Laboratory, Bhubaneswar. He is a graduate of Utkal University, Bhubaneswar, and holds a doctorate in chemistry from the Indian Institute of Technology, Kharagpur. Electrowinning, electrorefining and fuel cells are some of his areas of interest.

Dr. R.P. Das is a scientist in the Hydro & Electrometallurgy Division of the Regional Research Laboratory, Bhubaneswar. He is engaged in design and development of processes in the field of hydrometallurgy. A graduate of the Indian Institute of Technology, he holds a PhD from Penn State University. He received the National Metallurgist Day Award in 1993, given by the Ministry of Steel and Mines of the government of India.



Dr. P. Venkateswarlu is an assistant professor at Andhra University, Visakhapatnam, where he obtained undergraduate and doctoral degrees in chemical engineering. He has published in national and international journals and is interested in ionic mass transfer and fluidization.



Dr. G.J.V.J. Raju is chancellor, Sri Chandrasekharendra Saraswathy Viswa Mahavidyalaya (deemed University), Kanchipuram, India. He was awarded the DSc in chemical engineering from Andhra University, Visakhapatnam, and the DTech from the Technical University, Budapest. He was chairman of the National Board of Accreditation until October 1997.

** To whom correspondence should be addressed.*