The effect of electrolyte additives on cathode surface quality during copper electrorefining

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Synopsis

The use of electrolyte additives to smoothen cathode deposits during copper deposition is practised worldwide. These additives absorb on the cathode surface and take part in the electrochemical crystallization process. However, these additives also affect the quality of the cathodes when they are inadequately controlled.

Electrolyte additives used by Palabora are glue, thiourea, Avitone and chloride. Their effects were determined on cathode quality, the size of the current density region that gives the desired compact morphology, and current efficiency. This was done in a small-scale cell.

Small cells have different hydrodynamics from industrial-scale cells, which makes it difficult to simulate the operation of industrial cells in a laboratory. The approach used here was to use a rotating cylinder cathode to attain controlled hydrodynamics. The rotation speed was chosen to give a diffusion layer thickness that is similar to that of an industrial-scale cell.

It was shown that even fairly small changes in the additive levels can significantly affect the cathode morphology, and the current density range over which this morphology can be obtained.

Keywords
Copper, electrorefining, glue, thiourea, avitone and chloride.

Introduction

There is a high demand for pure electrorefined copper and thus a desire to operate at high current density to improve productivity at copper electrorefining plants. Hence the dosage and control of electrolyte additives has become imperative. The electrolyte additives are organic reagents and are added to the acidic electrolyte to prevent nodulation and thus control the chemical and physical properties of copper cathodes (Andersen *et al.*, 1976). The additives level and grain refine the copper deposit to obtain a smooth, homogenous, fine grained, dense and high purity copper cathode (Conard *et al.*).

Electrolyte additives

When electrolyte additives are inadequately controlled, the cathodes produced will contain excessive amounts of nodules, dendrites and anode slimes entrapped on the surface, as in Figures 1, 2 and 3. The nodular and dendritic growths on the cathode surface cause short circuits and decrease current efficiency (Safizadeh *et al.* 2009). The electrorefined copper cathodes also show rough surfaces that cause anode slimes and suspended solids to adhere and entrap onto the cathode surface thus reducing the conductivity and ductility of the cathodic copper deposit (Safizadeh *et al.* 2009).

Bone glue is a protein colloid and is the principal levelling agent in the electroplating industry (Biswas *et al.* 1999). Glue is a hydrolysis product of connective animal tissue collagen and contains a biopolymeric structure (Figure 4). The addition of glue gives a compact deposit of copper and polarizes any nodules forming on the cathode surface (Muresan *et al.*, 1999). Excessive amounts or a deficiency of glue will cause crystalline nodulation and entrapment of slimes.

Levelling occurs on sites of higher localized current density as glue is adsorbed onto the cathode (Saban *et al.* 1992). According to Deni (1994), glue molecules adsorb on active negatively charged growth sites on the cathode. This action is shown diagrammatically in Figure 5.

Glue is added into the electrolyte solution at a rate that will give a smooth deposit of copper and minimum anode slime and electrolyte entrapment on the cathode (Biswas *et al.* 1999). With time the less active long chain molecules undergo rapid hydrolysis; this is affected by higher temperature and low pH values (Blechta *et al.* 1993). The glue degradation rate follows first order reaction kinetics (Saban *et al.* 1992).

$$\frac{1}{(Mn)_t} = \frac{1}{(Mn)_0} + k't$$

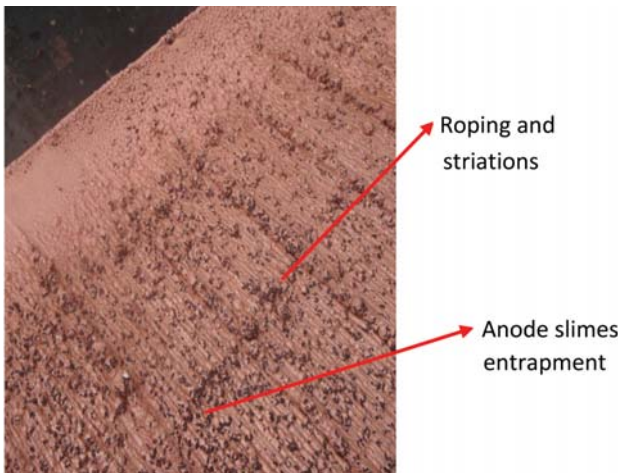Figure 1—Cathode showing nodulation on the cathode surface

Figure 2—Cathode showing anode slime entrapment and roping with striations on the cathode surface

Figure 3—Cathode showing dendrites on the edges of the cathode

$(Mn)_0$ and $(Mn)_t$ are number-average molar masses at time zero and time t respectively, and k' is the degradation rate constant. The concentration of the catalyst sulphuric acid is $[A]$. The intrinsic degradation rate constant is k.
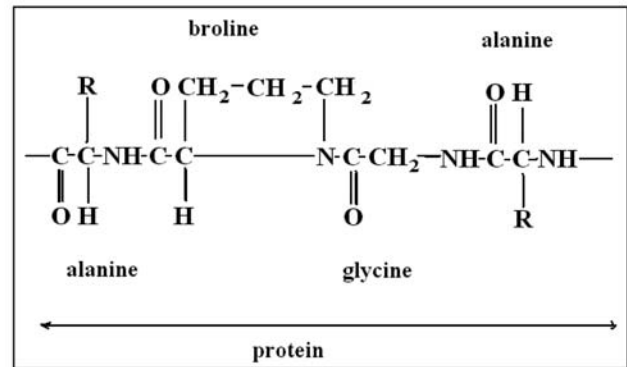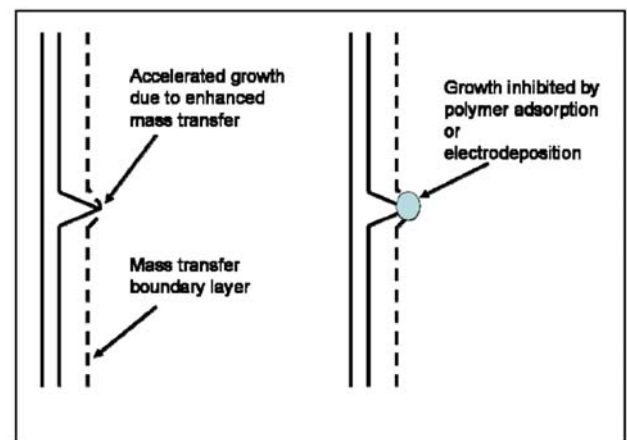

Figure 4—Chemical organic structure of bone glue

Figure 5—Dendrite growth and inhibition during copper electrorefining

$$k' = \frac{k[A]}{(Mn)_0}$$

The addition of thiourea and Avitone is based on the mass of cathode produced. Thiourea is added at 0.03 kg/ton of cathode copper produced. It gives a dense copper deposit and provides a salmon pink colour to the cathodes. If an excessive amount is added, deep prominent striations will form and entrapment of sulphur with slimes will occur (Goffman *et al.* 1985).

Thiourea has been extensively used as a grain refiner in industrial copper electrorefining processes (Muresan *et al.* 1999). Krzewska *et al.* 1984 found that the action of thiourea is one of inhibition of crystal growth processes by promoting the nucleation process. Thiourea is a small organic molecule (Figure 6) that reduces Cu^{+2} to Cu^+ forming a (Cu-thiourea)+ complex ion and dithioformamidine. The complex ion slowly hydrolyses over a period of days (Deni 1994).

High levels of thiourea are feasible: a concentration of about 5 ppm has showed satisfactory results (Goffman *et al.* 1985). This is unexpected since at high concentration it is expected that contamination of the cathode with sulfur will occur, and that the deposit will be of poor quality. However, no economic or other benefit is derived from operating at these high levels.

Thiourea is not a satisfactory additive when used by itself

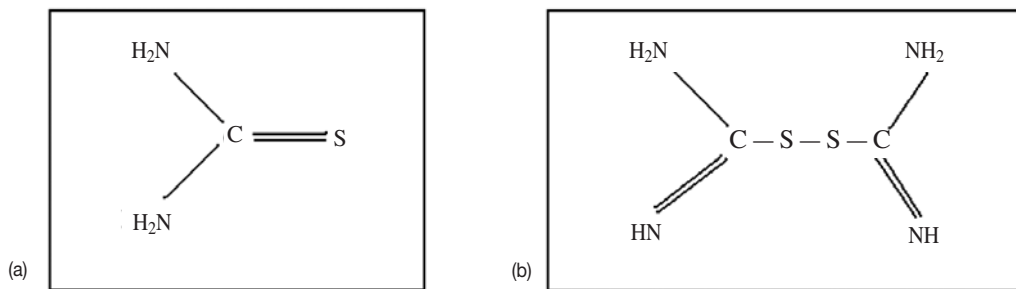# The effect of electrolyte additives on cathode surface quality

Figure 6—Organic molecule (a) thiourea and (b) dithioformamidine

in the electrolyte (Stelter *et al.* 2004). Drawbacks associated with using thiourea include contamination of up to 10 ppm sulphur in the cathodes.

Avitone is used to complement glue and acts as a detergent, removing oily patches on the electrodes (Deni 1994). It is a hydrocarbon based sodium sulphonate product which is used quite extensively in the copper refining industry to complement glue in creating a dense, smooth deposit on the cathode. Too little Avitone will cause slimes to adhere to the surface of the cathode, causing a dark colour at the bottom half of the cathode (Deni 1994).

Sodium chloride is added to precipitate silver by forming silver chloride, which settles on the bottom of the cell (Biswas *et al.*, 1999). It improves and brightens cathode deposits when combined with organic additives.

The purpose of the investigation was to determine the effect of electrolyte additives on cathode quality. This was done on laboratory scale using a rotating cylinder Hull cell.

Rotating cylinder Hull cell

The traditional Hull cell, which has a trapezoidal shape, is a test cell for electroplating. It consists of an inclined cathode, an anode and two insulating walls. The design of the Hull cell allows a wide range of current densities to be achieved along the cathode in a single experiment. The disadvantage of the traditional Hull cell is that the hydrodynamics are not the same as those in industrial plating baths. This can be improved only by stirring the electrolyte near the cathode; thus the Hull cell gives poor mass transport conditions (Madore *et al.* 1995).

A rotating cylinder Hull cell (RCH) gives well-defined and uniform mass transport conditions, and can be designed to have a similar primary current distribution to the traditional Hull cell, as shown in Figure 7 (Madore *et al.* 1995). The relative current density is seen to vary from about 3.3 to about 0.1 with distance along the cathode, as measured from the bottom tip.

The relative current densities are read off from the rotating cylinder Hull cell scale shown in Figure 8.

Figure 9 shows a commercial implementation of the rotating cylinder Hull cell.

Experimental

The electrolyte solution compositions were chosen to simulate industry practice at Rio Tinto's Palabora refinery, and are shown in Table I.

The metals were used as the sulfate salts. The concentration of the additives is calculated in practice according to the copper cathode mass produced, and the electrolyte volume.

The electrolyte temperature was 70°C.

The electrolyte additive concentrations were varied according to a factorial design matrix. The values for the high and low levels are shown in Table III.

A factorial design for 4 variables at 2 levels was used to identify which electrolyte additive effects and interactions are important.

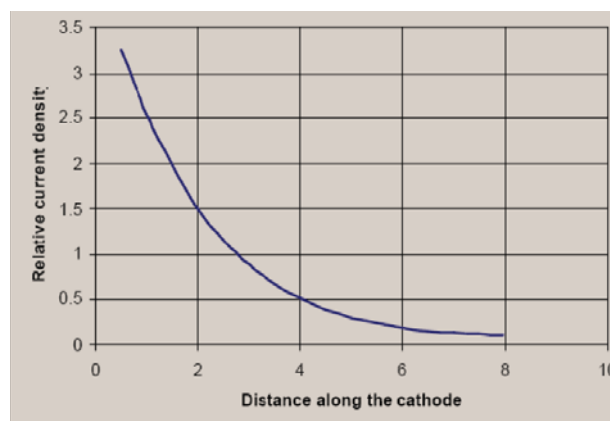The RotaHull cell was operated at 1 ampere constant

Figure 7—Primary current distribution along the cathode of the RCH cell

Figure 8—Photo showing the relative current densities and copper cathode after electrolysis

Figure 9—Rotating cylinder Hull cell Auto Lab

The effect of electrolyte additives on cathode surface quality

Table I

Electrolyte composition

Component	Concentration (g/ℓ)
Cu^{2+}	45
H_2SO_4	220
Ni^{2+}	15

Table II

Electrolyte additive concentrations, base case

Component	Concentration (mg/ℓ)
Glue	1.8
Thiourea	0.6
Avitone	0.5
Chloride	30

Table III

Electrolyte additive concentrations for the experimental matrix

	Glue (mg/ℓ)	Thiourea (mg/ℓ)	Avitone (mg/ℓ)	Chloride (mg/ℓ)
+ level	2.2	0.8	0.7	35
- level	1.5	0.3	0.3	25

current, and 80 rpm. The electrolyte was preheated to 70°C, and the cell was placed in a water bath at the same temperature. Deposition continued for one hour.

Results and discussion

Rotation speed calculation

The hydrodynamics of an experimental cell is an important parameter that should represent, as closely as possible, the hydrodynamics of the industrial cells. This is difficult in a small cell, as the convection currents due to density and temperature gradients in a full-scale cell are much greater than in a small cell. In this investigation the hydrodynamics of a large cell are approximated by using a typical Nernst diffusion layer thickness for industrial copper electrorefining. The Nernst diffusion layer thickness for a typical copper electrorefining cell is 0.02 cm (Moats *et al.* 2000). This layer thickness was used for the calculation of the rotation speed of the rotating cylinder cathode of the Hull cell.

Table IV below gives the variables used for the calculation. Values used were obtained from the physico-chemical properties of copper electrorefining- and electrowinning electrolytes by Price and Davenport, 1981.

The equations used are as follows:

$$\delta_N = 12.64 U^{-0.7} d^{0.3} v^{0.34} D^{0.356}$$

(A) Diffusion layer thickness for a rotating cylinder electrode (Madore *et al.*, 1995)
where:
- ➤ U is the peripheral velocity of the working electrode
- ➤ d the diameter of the rotating cylinder electrode
- ➤ v the kinematic viscosity
- ➤ D is the diffusion coefficient of copper ions.

$$D = RT/6\pi r \eta N$$

(B) Diffusion coefficient (Moats *et al.* 2000)
where:
- ➤ R is the gas constant,
- ➤ T is temperature in Kelvin,
- ➤ r is the radius of the ionic species, = 0.2 nm for copper electrorefining
- ➤ η is the absolute viscosity
- ➤ N is Avogadro's number.

$$v = \frac{\mu}{\rho}$$

(C) Kinematic viscosity (http://chem.wetpaint.com/page/Copper)
where:
- ➤ v the kinematic viscosity
- ➤ μ dynamic viscosity
- ➤ ρ density of Cu = 8.96 g·cm⁻³.

$$i_{\lim} = 0.0791 nFCU^{0.7} d^{-0.3} v^{-0.344} D^{0.644}$$

(D) Limiting current density (Madore *et al.* 1995)
where:
- ➤ n is the charge transfer number
- ➤ F is the Faraday constant
- ➤ d is the cylinder diameter (cm)
- ➤ U is the peripheral velocity at the rotating cylinder (cm/s)
- ➤ v is the kinematic viscosity of the electrolyte (cm²/s)
- ➤ D is the diffusion coefficient (cm²/s)
- ➤ C Bulk concentration (mol/ℓ).

$$\omega = \frac{U}{\pi d}$$

(E) Rotation speed
The rotational speed was calculated using a peripheral velocity and the diameter of the cathode.
where:
- ➤ ω is rotational speed (rpm)
- ➤ U is peripheral speed (m/min)
- ➤ d is Diameter of cathode (m).

The rotation speed required to simulate the hydrodynamics of a typical electrorefining cell was calculated to be 79.21 rpm.

Table IV

Rotation speed calculation parameters

Variables	Value	Units
Diameter of the RC electrode (d)	0.60	cm
Temperature in Kelvin (T)	343.00	K
Gas constant (R)	8.31	J/mol.k
Avogadro's number (Na)	6.02E+23	1/mol
Number of electrons transferred (n)	2.00	
Faraday's constant (F)	96485.34	C/mol
Copper electrolyte density (ρ)	1244.60	kg/m³
Radius of Ionic species Cu^{+2} (r)	2.00E-10	M
Absolute Viscosity (η)	9.93E-04	kg/m.s
Molar mass of copper	63.54	g/mol
Bulk concentration (C)	6.30E-04	mol/cm³
Cathode height (h)	8.00	cm
δ_N diffusion layer thickness	0.02	cm

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Morphology

The cathode surface morphology showed three regions had formed. The regions were identified by optical appearance, and further analysis on the cathode surface was done using SEM. The three regions can be classified as (1) dendritic at high current density, (2) compact, and (3) insufficient copper plating at lower current densities. There are transition regions of about 5 mm between the different morphologies.

Optical

The cathode on the left-hand side of Figure 10 has a long region of compact morphology and this represents a good cathode because the current density of Palabora is approximately in the middle of this region. Therefore the electrolyte used gave a large operating window, which is not the case for the right-hand electrode.

SEM

Scanning electron microscope images of the three regions are shown below.

Figure 11 shows a dendritic morphology on the copper cathode. The rough surface formed at high current density and electrolysis for 1 hour. The surface clearly shows the nodules and dendrites forming on the cathode.

In Figure 12 the desired compact morphology is shown. The surface is smooth, dense, homogenous and fine grained. The reduction in nodules and dendrites will minimize short circuits which improves the current efficiencies. The smooth surface will limit the adhesion of anode slimes and suspended solids.

Insufficient copper plating is obtained at lower current density. The SEM images in Figure 13 show this morphology.

Experimental conditions that give a long compact region are desired, as this means there is a large operating window during electrolysis. A large operating window is optimum because a compact morphological region will be attained even when the current density fluctuates.

The experiments were conducted, as shown in Table V, and the upper relative current density, lower relative current density and the current density ranges were recorded.

The graph in Figure 14 gives the relative lengths of the compact morphological regions, relative to the length of the compact region produced by a typical industry electrolyte. A compact region length greater than one will be optimal since an operating window larger than that of the standard electrolyte is achieved. The conditions used in experiments 3, 7, 8, 12, 14, 15 and 16 resulted in the desired large operating window.

Current density

Current density is the applied current during electrolysis divided by the active cathode area. During electrolysis, current density may change, and this can be caused by changes of either the active area or current fluctuations. The average current density applied during the experiment is 6.67 A/dm2 because the applied current is one ampere and the cathode active area is 0.15 dm2. The average current density of the Palabora refinery is 2.6 A/dm2. Thus at a relative current density of 0.39 in these experiments the experimental current density is the same as that of the Palabora refinery. The compact region is expected to occur at this relative current density point. The current densities of

Figure 10—Optical view of copper cathode after electrolysis showing morphological regions
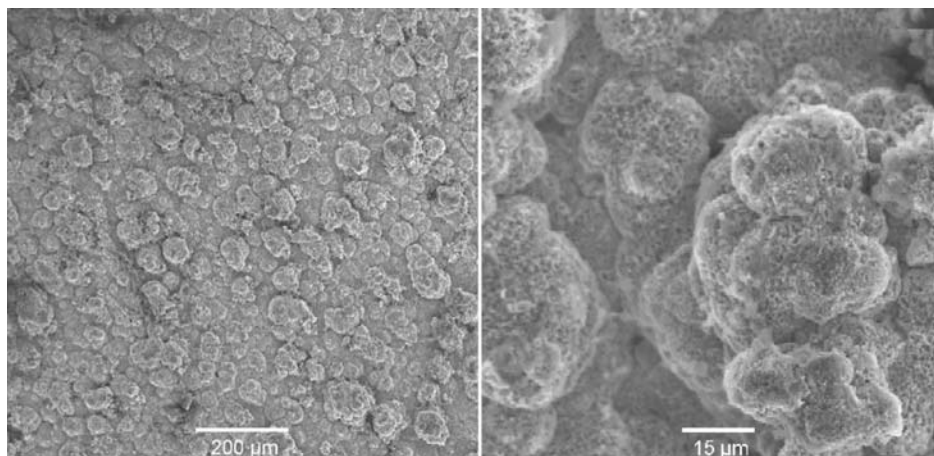
Figure 11—SEM images showing dendritic region of the cathode at high current density
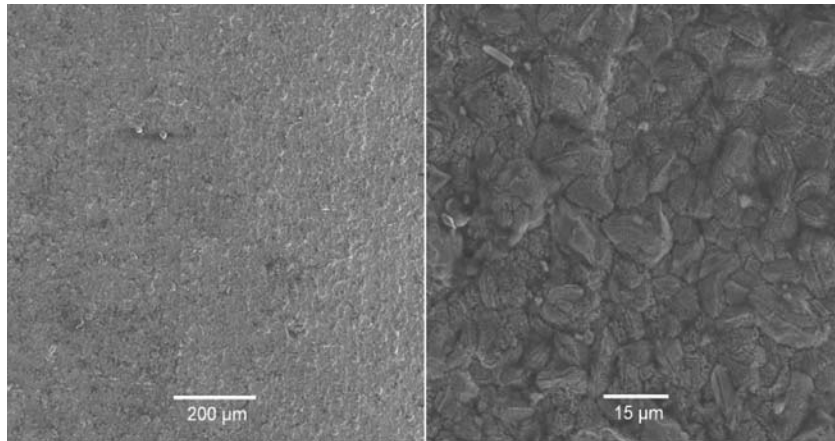
Figure 12—SEM images showing compact morphology region of the copper cathode
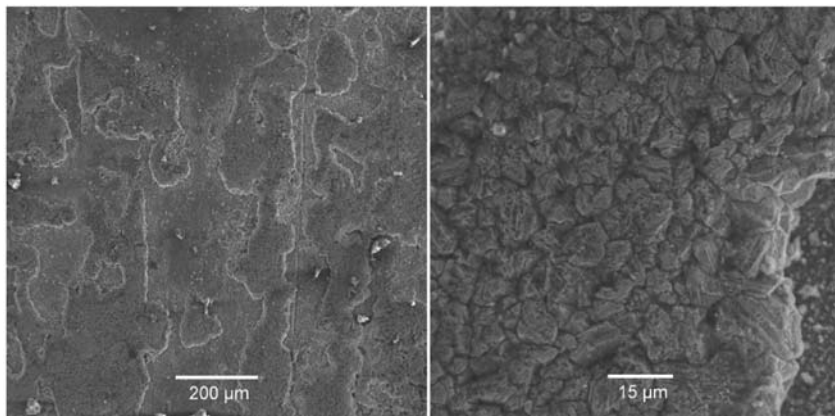

Figure 13—SEM images showing a insufficient copper plating at low current density

Table V

Factorial design experimental matrix and results

Order	Glue (mg/ℓ)	Thiourea (mg/ℓ)	Avitone (mg/ℓ)	Chloride (mg/ℓ)	Upper CD (A/dm²)	Lower CD (A/dm²)	CD Range
1	1.8	0.6	0.5	30	2.50	0.70	1.80
2	1.5	0.3	0.3	25	2.50	0.70	1.80
3	1.5	0.8	0.7	35	2.50	0.35	2.15
4	1.5	0.8	0.3	25	3.20	1.20	2.00
5	1.5	0.3	0.7	25	0.75	0.30	0.45
6	2.2	0.8	0.3	35	1.35	0.75	0.60
7	2.2	0.8	0.3	25	1.00	0.20	0.80
8	2.2	0.3	0.3	35	1.50	0.25	1.25
9	2.2	0.3	0.3	25	2.60	0.23	2.37
10	2.2	0.3	0.7	35	1.75	1.00	0.75
11	3000	1.0	0.5	30	0.75	0.30	0.45
12	3000	0.6	0.5	30	1.25	0.11	1.14
13	1.8	0.6	0.5	30	2.60	0.50	2.10
14	1.8	0.3	0.3	25	2.75	0.25	2.50
15	1.8	0.3	0.5	30	2.70	0.50	2.20
16	1.8	0.6	0.5	25	2.40	0.30	2.10
17	1.8	0.6	0.5	30	2.20	0.70	1.50
18	1.5	0.3	0.7	35	0.60	0.40	0.20
19	1.5	0.8	0.7	25	2.60	0.80	1.80
20	1.5	0.3	0.3	25	2.40	0.70	1.70
21	1.8	0.6	0.5	30	2.30	0.60	1.70

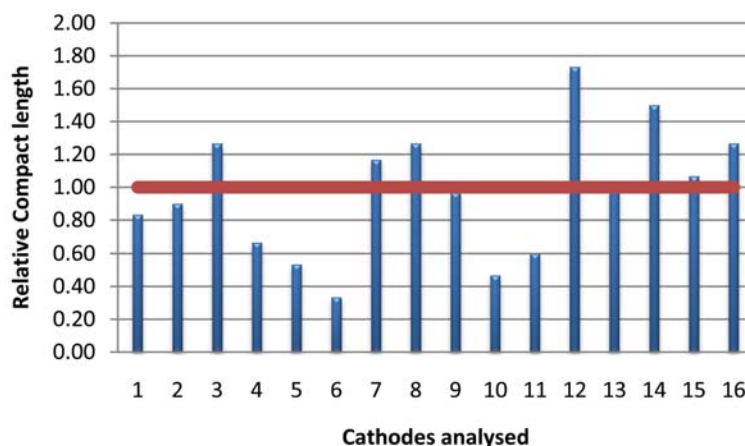# The effect of electrolyte additives on cathode surface quality

Figure 14—Relative compact length on cathodes analysed

the experiments which have a relative compact length higher than one are shown in Table VI. The measured current densities at the extremes of the compact morphology regions are calculated and tabulated. The current density range of the Palabora refinery does not fall within the compact region measured in experiment 15.

Current efficiency

Current efficiency is an important parameter in commercial electrorefining and achieving higher current efficiencies is vital. After weighing the cathodes, the current efficiencies were calculated for the cathodes that have a relative compact morphology length greater than one and with a current density range overlapping the Palabora refinery current density. It may be seen from Figure 15 that experiments 12 and 16 had the optimum electrolyte compositions for copper electrorefining, achieving 95% and 97% current efficiency respectively.

Factorial design analysis

Table V was used to generate a regression model. The current density range was used as the response parameter and the electrolyte additive levels are the input parameters. The regression model equation generated is outlined below.

CD range = b_0 + b_1*Glue + b_2*Avitone + b_3*Chloride + b_4*Glue*Thiourea + b_5*Glue*Avitone + b_6*Glue*Chloride + b_7*Thiourea*Avitone + b_8*Thiourea*Chloride + b_9*Avitone*Chloride

This is a linear regression model which intercepts on the y-axis at b_0; b_1 to b_3 are the coefficients for the main effects, and the other b-values are the coefficients for the interactive effects. Thiourea was left out of the model, as the collinearity test showed these data to be redundant.

The analysis of variance was generated at a 95% confidence level. The adjusted coefficient of determination, R^2_{adj} was determined to be 0.808, which shows that the model does not fit the experimental data very well. In fact, the R^2 for prediction was rather low, at 0.621.

The above observation was borne out by plotting a series of graphs of the response parameter (current density range) vs. the independent variable values. All showed significant scatter in the response parameter values. Inspection of the standard error associated with the coefficient values showed them to be rather high, which was confirmed by a comparison of the calculated t values with the t-critical value.

Table V shows the results obtained for four replicates of the experiment performed under the standard conditions (experiments 1, 13, 17 and 21). The response parameter is seen to vary appreciably—from 1.5 to 2.10. This likely due to the difficulty in establishing exactly where one morphological region ends and the next starts, as it is a matter of judgement.

Conclusions

The small-scale experiments conducted using a rotating electrode Hull cell were modelled to represent plant practice using a typical diffusion layer thickness value. The effects of the electrolyte additives glue, Avitone, thiourea and chloride were observed after electrodeposition of copper on the

Table VI

Table showing the allowable current density during electrolysis for Palabora

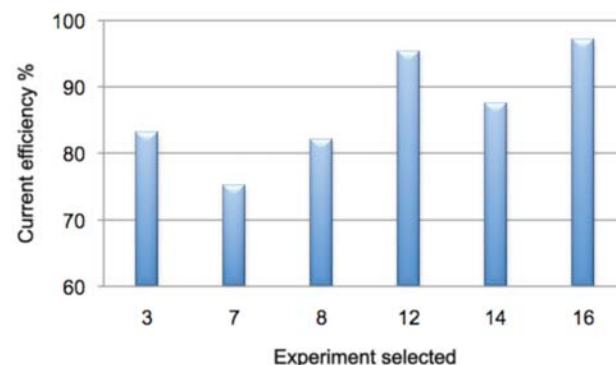| Experiment no.	Relative current density		Current density range, A/dm²	
	HCD	LCD	Upper CD	Lower CD
3	2.5	0.35	16.67	2.33
7	1	0.2	6.67	1.33
8	1.5	0.25	10.00	1.67
12	1.25	0.11	8.33	0.73
14	2.75	0.25	18.33	1.67
15	2.7	0.5	18.00	3.33
16	2.4	0.3	16.00	2.00

Figure 15—Current efficiency of the selected experiments

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cathode surface. The results show that the concentration fluctuations of electrolyte additive levels have a large effect on the cathode morphology. In this respect the small-scale work was successful in modelling the effects seen in large, industrial cells.

The cathode formed dendrites and nodules at high current density as expected. The changes in the electrolyte additive concentrations show that with proper manipulation of the additive concentration, a compact morphology can be observed even at quite high current densities. It was observed that at very high glue concentration (3 g/ℓ, experiments 11 and 12), nodules and dendrites form even at relatively low current densities. This is due to an increase in the viscosity of the electrolyte and this reduces mass transfer.

The compact morphology lengths on the cathodes were measured and compared with the measured compact morphology length obtained for the Palabora electrolyte. This was to identify which conditions give a large operating window for current density, which is desirable for easier refinery control. Current efficiencies were calculated from the cathode mass increases. Good current efficiencies were observed for laboratory experiments 12 and 16, achieving 95% and 97% current efficiency respectively.

Experiment 16 used additive levels of glue, thiourea and Avitone equal to that of the Palabora refinery, with the chloride level slightly lower. Increasing the glue level about 1000-fold to 3 g/ℓ (experiment 12) gave a larger current density operating window, but with a decreased current efficiency. This is likely to be due to the increase in electrolyte viscosity.

It was concluded that the exact current densities for the compact morphology region at the high and low current density limits are difficult to determine, as it is a matter of judgement. This significantly affected the ability to accurately determine the effects of the additive levels, over the ranges studied, on the extent of the desired compact morphology region. The determination of these values needs to be improved in future work.

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