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Computerized scaled cells to study the effect of additive ratios and concentrations on nodulation during copper electrorefining

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Abstract

Scaled copper electrorefining cells were designed, built and computerized to simulate as closely as possible industrial conditions at three Canadian copper refineries. The industrial dimensions of Falconbridge, Kidd Metallurgical Division, were considered while designing scaled cells. Anode width to cell width ratio, anode width to cathode width ratio, anodic surface to cathodic surface ratio, as well as electrolyte volume to cathodic surface ratio, which was about 60 L m^{-2}, were consistent with Kidd's industrial ratios. However, the cell design also allowed simulation of INCO's Copper Cliff Copper Refinery (CCCR) or Noranda's Canadian Copper Refinery (CCR). Electrorefining cells were 135.0 cm deep by 14.7 cm wide. Electrolyte flow rate was parallel to the electrodes. Electrolyte was circulated from the lower part of the electrorefining cells to the top where there was an overflow going to the electrowinning circuit. The equipment was computer controlled using Labview software. Experiments were conducted using this scaled electrorefining set-up to evaluate the effect of various ratios and concentrations of additives on nodulation during copper electrorefining under high current densities. Cathodic polarization curves, SEM micrographs, porosity analyses and copper grain analyses were used to characterize the cathodes produced.

1. Introduction

Electrorefining is used to produce high quality copper cathodes from anodes containing a variety of impurities. Copper electrorefining is conducted in an aqueous bath containing sulfuric acid, copper sulfate and nickel sulfate at a temperature close to 65 °C. During electrolysis, anodes are dissolved and metallic copper is deposited on the cathode. Copper cathodes must meet quality criteria such as a smooth cathodic deposit (without nodule and dendrite), a low content of impurities (high purity copper $>$ 99.99%) and a low porosity level (a porous deposit corresponds to the presence of frequent pores observed under 50×). In reality, the control of the quality criteria can be estimated by chemical analysis of the deposit. Smooth, non-nodular and non-porous deposit contains very few impurities.

This must be achieved under high current efficiency (>90%). This is a complex task since the growth of the cathode is influenced by many parameters such as current density, electrolyte temperature, electrolyte composition ($H_2SO_4, Cu^{2+}, Ni^{2+}$), anode composition, anode/cathode spacing, electrolyte flow rates and probably more importantly by the ratios and concentrations of the additives [1].

Precise knowledge concerning the individual influence of additives on the cathode deposit and metallographic structure is still lacking [2]. The combined influence of additives on cathode quality is far greater than the influence of each additive added separately [3]. Moreover, most of the research on additives was conducted in small vessels using synthetic electrolyte at different temperatures. Additives were generally added in small quantities (a few ppm) once at the beginning of short-term experiments. From an industrial point of view, it is then very difficult to correlate this research to actual industrial practices where additives are continuously added to the electrolyte as a function of the copper production (e.g., 40 g of Thiourea (TU) are added to the electrolytic bath for each metric ton of copper produced, (40 g t^{-1}, otherwise 40 mg kg^{-1})).

Today, copper electrorefining under high current density is required to improve the profitability of the refineries. However, various drawbacks arise when current density is increased. A decrease in cathode quality and current efficiency due to nodulation problems are probably the principal ones. Keeping all other variables constant, ratios and concentrations of additives that produced good cathode quality under a lower current density are not necessarily suitable under a higher current density. In fact, they may even decrease cathode quality and cause nodulation.

Increasing current density without decreasing cathode quality is one of the problems faced by copper refineries.

A National Sciences and Engineering Research Council of Canada (NSERC) strategic research program was initiated at Laval University in collaboration with CANMET and the three Canadian copper refineries, which were Falconbridge, Kidd Metallurgical Division, INCO's Copper Cliff Copper Refinery (CCCR) and Noranda's Canadian Copper Refinery (CCR). The first objective of this research program was to design, build and computerize scaled copper electrorefining cells that would simulate industrial conditions as close as possible. This pilot plant was then used to study the effect of different additives' ratios and concentrations on nodulation during copper electrorefining. The ultimate goal of the project was to identify a combination of additives that would prevent nodulation under high current densities (>300 A m^{-2}). This paper presents the computerized scaled electrorefining set-up that was built. Some of the cathodes obtained so far are presented and characterized using cathodic polarization curves, SEM micrographs, porosity analyses and copper grain analyses.

2. Experimental details

2.1. *Scaled copper electrorefining set-up*

Electrorefining cells were built in polycarbonate. Cell dimensions were based on Kidd's industrial electrorefining cells. Anode width to cell width ratio, anode width to cathode width ratio, anodic surface to cathodic surface ratio as well as electrolyte volume to cathodic surface ratio, which was about 60 L m^{-2}, were all considered when designing the cells. All these parameters were consistent with those of Kidd. However, it is worth mentioning that the cell's design also allowed simulation of CCCR or CCR industrial ratios. Electrorefining cells were 135.0 cm deep by 14.7 cm wide. Electrolyte flow rate was parallel to the electrodes to simulate flow in jumbo tanks as in Kidd. It was also possible to have perpendicular flow to simulate conventional cells as in CCCR or CCR. Electrolyte was circulated from the lower part of the electrorefining cells to the top where there was an overflow going to the electrowinning circuit.

Electrowinning cells were used during long-term experiments (seven days or more) to prevent a build up of copper concentration. Based on previous experiments conducted at the Noranda Technology Centre (NTC) with a similar set-up, it was found that operating the electrowinning cells at 1% of the current density applied to the electrorefining cell maintained a constant copper concentration. Electrowinning cells were built in polycarbonate and had a volume of about 1/5 that of electrorefining cells. Lead anodes and 316L stainless steel cathodes were used.

Each electrorefining cell contained three 10.5 cm wide and 0.3 cm thick 316L stainless steel cathodes and two 10.0 cm wide and 2.2 cm thick Hazelett copper anodes. Full-length industrial electrodes were used. Distance from the centre of an anode to the centre of the next anode was 8.4 cm, which corresponded to the distance found in Kidd's industrial tank house. Cathodes positioned at the extremity of each electrorefining cell had one side insulated. Hence, there were four anodic and four cathodic surfaces. Parallelism between electrodes was maintained by a special mechanism. Characteristics of the scaled copper electrorefining set-up are presented in Table 1.

The electrorefining cells were electrically linked in series. A model EMS 10-200-5D-RSTL power supply controlled through a GPIB interface was used to apply the desired current density. Voltage and current were monitored continuously while data was logged at the frequency specified by the user. Experiments could be conducted at current densities as high as 500 A m^{-2} considering the cathodic surface mentioned in Table 1. As with the electrorefining cells, electrowinning cells were electrically linked in series. A model HP E3633A power supply was used to apply the desired current density. This power supply was also controlled through a GPIB interface which is a common protocol (IEEE-488.2) used to communicate with various types of electronic instruments.

Voltage and current were monitored continuously while data was logged at the frequency specified by the user.

Two multiple head variable speed peristaltic pumps model Masterflex L/S® with computerized drives were used with the scaled copper electrorefining set-up. The first pump was used to circulate the electrolyte from the electrorefining cells to the electrowinning cells. The

Table 1. Characteristics of the scaled copper electrorefining set-up

Characteristics	Cells	
	Electrorefining	Electrowinning
Number	3	3
Depth	1.35 m	0.18 m (ϕ)
Width	0.15 m	
Length*	0.17 or 0.21 m	
Electrolyte		
Flow	$\|\|$ or $\perp$	$\|\|$ or $\perp$
Inlet	bottom	top
Outlet	overflow	bottom
Volume	~20 l	~2 l
Composition	$[Cu^{2+}] = 42$ g l^{-1}	$[H_2SO_4] = 160$ g l^{-1}
	$[Ni^{2+}] = 18$ g l^{-1}	$[Cl^{-}] = 40$ mg l^{-1}
Electrodes	Cathodes	Anodes
Number/cell	3	2
Length (m)	1.04	1.10
Width (m)	0.105	0.100
Thickness* (cm)	0.3	2.0 or 4.2
Material	316L SS	~99% Cu
Anodes spacing*	–	8.4 or 10.2 cm

*These parameters depend on which industrial partners conditions are being simulated.

speed of this pump was adjusted to reproduce industrial electrolyte residence time. Each electrorefining cell had its individual electrolyte circuit. Additives' ratios and concentrations could then be different from one cell to the next during the same experiment. The second pump was used to add additives to the three distinct electrolyte circuits. Both pumps were computer controlled through a RS-232 interface. Norprene® tubing was used as pipe material.

Electrolyte temperature was logged for each electrorefining cell using type K thermocouples and a National Instrument's data acquisition card model AT-MI0-64E-3. Electrolyte was circulated through heat exchangers that were put into a tank filled with water. The water was heated until the electrolyte reached the desired temperature. Heaters were computer controlled using solid-state relays that turned on and off the electric power depending on the values returned by the thermocouples. Control of the electrolyte temperature in the electrorefining cells was within ±1 °C. Finally, the voltage of one cathode by electrorefining cell was monitored continuously while data was logged at the frequency specified by the user. A schematic of the scaled copper electrorefining set-up is shown in Figure 1.

All the instruments described previously were computer controlled using National Instrument Labview 5.0®. A 'Virtual Instrument' was built for each instrument using graphical programming. Experimental parameters (electrolyte temperature, speed of the pumps, current density, data acquisition frequency, experiment's length etc.) were set at the beginning of each experiment. Labview controlled the various instruments and made sure that the specified conditions were fulfilled throughout the experiment.

2.2. *Materials*

The supporting electrolyte was CCR's industrial electrolyte containing 42 g l^{-1} of Cu^{2+}, 18 g l^{-1} of Ni^{2+}, 40 mg l^{-1} of Cl^- and 160 g l^{-1} of H_2SO_4. Electrolyte was renewed before each experiment. Concentration of chloride ions (Cl^-) was fixed at 40 mg l^{-1} and the temperature was maintained at 65 °C for all experiments reported in this paper. Hazelett copper anodes were used and renewed before each experiment. Copper cathode deposits were manually stripped from the supporting 316L stainless steel cathodes after each experiment. Additives were first diluted in water then a defined volume was added every 30 min throughout the duration of the experiments. Faraday's Law was used to calculate the quantity of additives to add in order to reflect industrial practice. Concentration of thiourea (TU) was varied from 20 to 60 grams per metric ton of copper produced (g t^{-1}) and gelatin (G) from 50 to 150 g t^{-1}. The scaled copper electrorefining set-up was a significant enhancement over previous studies since it made possible to simulate closely the addition of additives to the electrolytic bath and their consumption during copper electrorefining. Experiments were conducted at different current densities ranging from 200 to 450 A m^{-2}. Depending on the current density applied, the duration of the experiments was adjusted to deposit the same amount of copper. For example, the duration of experiments conducted at 250 A m^{-2} was 48 h, 40 h at 300 A m^{-2}, 30 h at 400 A m^{-2} and so on. The individual effect of Cl^- under various current densities was investigated first. Binary systems thiourea–Cl^- and gelatin–Cl^- were both studied as well as the ternary system thiourea–gelatin–Cl^-.

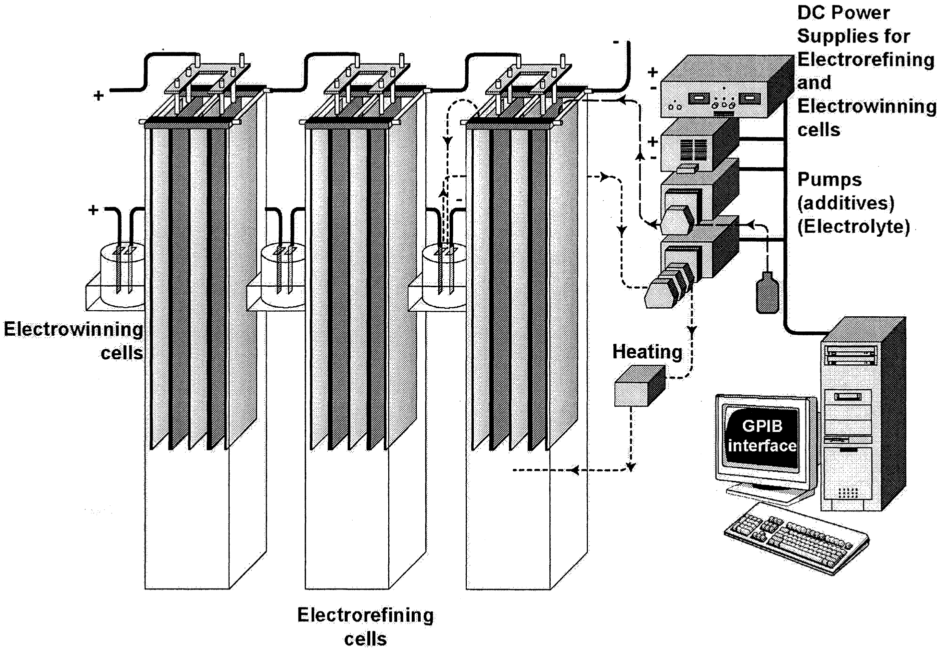

Fig. 1. Schematic of the scaled copper electrorefining set-up built to simulate industrial conditions.

2.3. *Instrumentation*

Silver chloride electrodes Ag, AgCl/KCl_{sat} (0.202 V vs SHE) were used as reference electrodes. All potentials are given with respect to SHE electrode.

At least three tests (cathodic potential against time) were made in each condition presented in this paper. SEM analyses were conducted using Jeol JSM-25s III model scanning electron microscope equipped with a TN 5700 model energy dispersive X-ray analyser. Porosity analyses were made on cathode samples that were mechanically polished with SiC paper (240 to 600 grit) and diamond powders (1–0.1 μm). After porosity analyses, cathode samples were acid etched in $FeCl_3 \cdot HCl$ solution for 20–30 s to reveal the copper grain structure. Porosity analyses and copper grain analyses were conducted using Clemex Vision software controlling a Nikon Epiphot microscope linked to a Sony CCD camera.

3. Results and discussion

3.1. *Potential curves*

The scaled electrorefining set-up is useful in characterizing cathodic polarization depending on additive ratios and concentrations. Typical cathodic polarization curves for cathodes produced at 250 A m^{-2} over 40 h with 40 mg l^{-1} of Cl^- and two concentrations of thiourea (20 and 60 g t^{-1}) are presented in Figure 2. Cathodic potentials increase rapidly at the beginning and reach a plateau around 300 mV vs SHE after 24 h. Addition of thiourea to an electrolyte containing 40 mg l^{-1} of chloride ions has a depolarizing effect on copper electrodeposition. The depolarization becomes stronger as the thiourea concentration increases. The cathodic potential is about 20 mV higher when the thiourea concentration is increased from 20 to 60 g t^{-1}.

Typical cathodic polarization curves for cathodes produced at 250 A m^{-2} over 40 h with 40 mg l^{-1} of Cl^-, 20 g t^{-1} of thiourea and three concentrations of gelatin (50, 100 and 150 g t^{-1}) are presented in Figure 3. The cathodic polarization increases by about 50 mV when the gelatin concentration is increased from 50 to 150 g t^{-1}. Similar potential values and behaviours were also observed during short-term galvanostatic and potentiodynamic experiments using a 700 ml electrochemical cell. It is thus clear that increasing gelatin concentration also increases cathodic polarization when Cl^- and thiourea are present in the electrolytic bath.

3.2. *SEM micrographs*

The scaled electrorefining set-up is indicated to characterize cathode surface smoothness depending on additives' ratios and concentrations. Cathodic defects (nodules, dendrites, edge effect) produced using the scaled electrorefining set-up are similar to the ones generally found in industrial tank houses. Typical SEM micrographs of cathodes produced at 300 A m^{-2} over 40 h under various combinations of additives are presented in Figure 4. With only Cl^- (see Figure 4(a)), the copper deposit consists of pyramidal grains, which get more field oriented and coarser as the current density increases (columnar structure). The edge effect is always present when only chloride ions are present in the electrolyte, even on cathodes produced under a current density as low as 200 A m^{-2}. Edge quality rapidly deteriorates into big dendrites as the current density increases. Furthermore, small and round defects appear randomly under high current densities (350 and

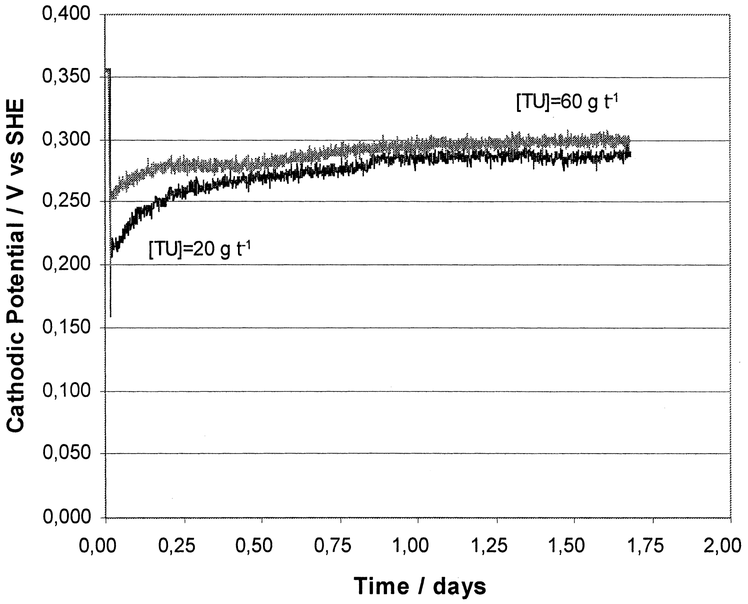

Fig. 2. Effect of two concentrations of thiourea on the evolution of cathodic potential for cathodes produced at 250 A m^{-2} over 40 h with an electrolytic bath containing 40 mg l^{-1} of Cl^-.

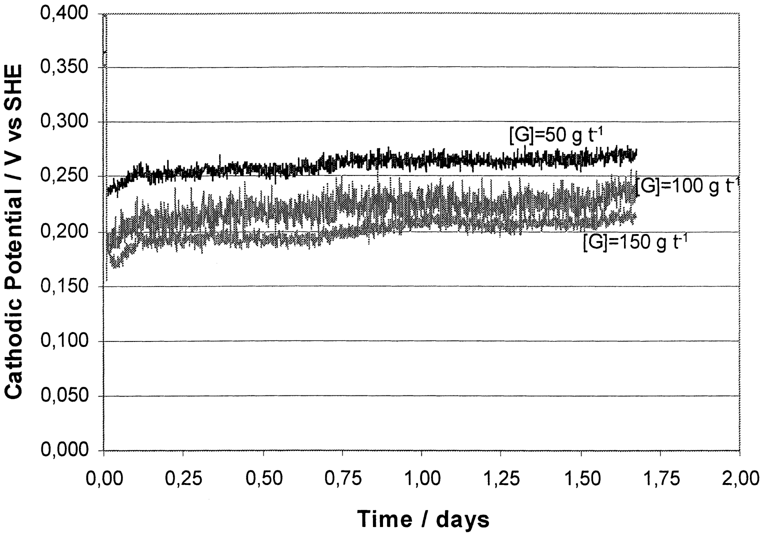

Fig. 3. Effect of three concentrations of gelatin on the evolution of cathodic potential for cathodes produced at 250 A m^{-2} over 40 h with an electrolytic bath containing 40 mg l^{-1} of Cl^{-} and 20 g t^{-1} of thiourea.

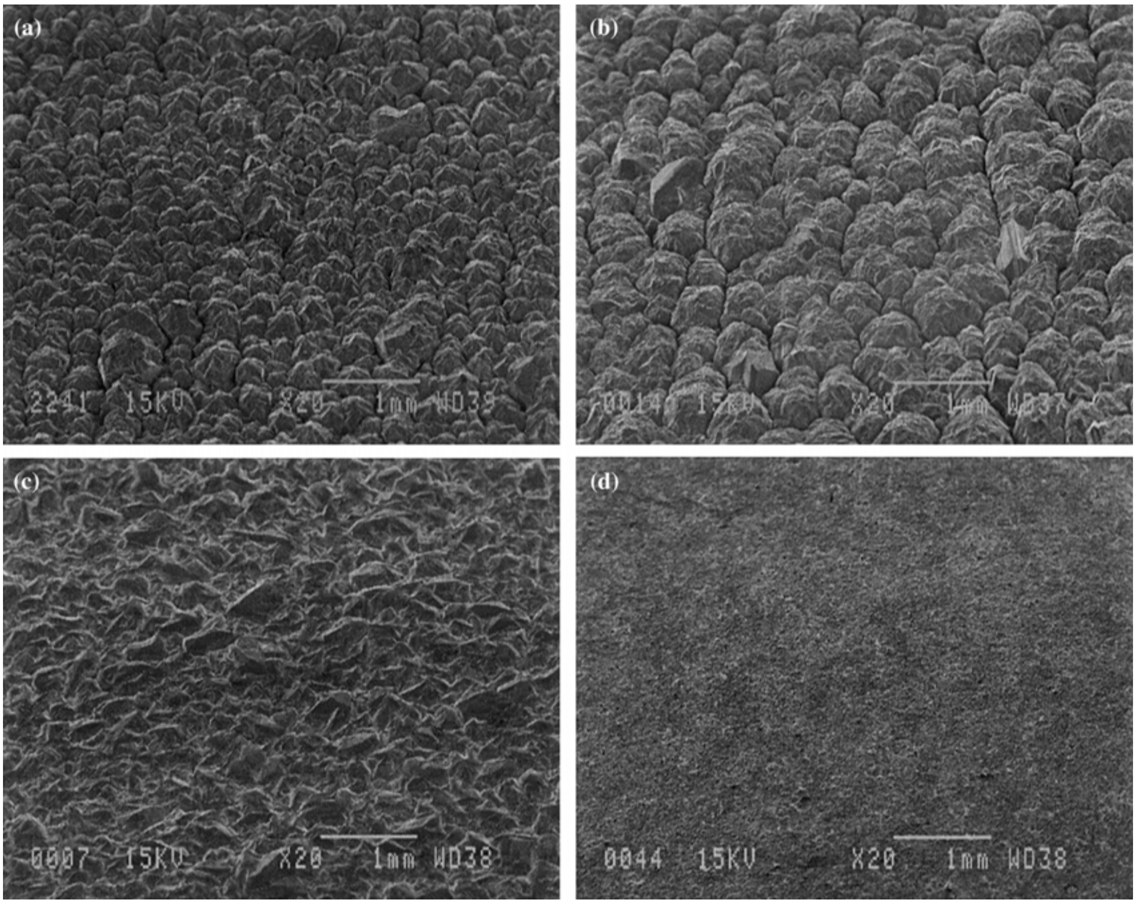

Fig. 4. SEM micrographs of cathodes produced at 300 A m^{-2} over 40 h with (a) only 40 mg l^{-1} of Cl^{-}, (b) 60 g t^{-1} of thiourea and 40 mg l^{-1} of Cl^{-}, (c) 100 g t^{-1} of gelatin and 40 mg l^{-1} of Cl^{-} and (d) 40 g t^{-1} of thiourea, 100 g t^{-1} of gelatin and 40 mg l^{-1} of Cl^{-}. Magnification 20×.

400 A m^{-2}). These might eventually deteriorate into nodules or dendrites.

Adding small amounts of thiourea (20 g t^{-1}) to an electrolytic bath containing chloride ions produces more brilliant copper cathodes. However, cathodes become darker as thiourea concentration increases. Figure 4(b) shows a typical SEM micrograph of a cathode produced with 40 mg l^{-1} of Cl^{-} and 60 g t^{-1} of thiourea. Copper electrodeposition is more field oriented. Pyramidal grains are coarser and sharper compared to the ones obtained with only Cl^{-}. An increase in thiourea concentration increases pyramid size slightly. Nodules and dendrites are observed on cathodic surfaces for all thiourea concentrations and all current densities studied.

Figure 4(c) shows a typical SEM micrograph of a cathode produced with 40 mg l^{-1} of Cl^- and 100 g t^{-1} of gelatin. Copper electrodeposition is not field oriented. Cathodes obtained are smoother than the previous ones for all current densities studied (up to 350 A m^{-2}). The copper deposit consists of small pyramidal grains, but this time the pyramid edges become smoother as the gelatin concentration increases. None or very few nodules appear when gelatin and Cl^- are present in the electrolyte. Gelatin has a strong improving effect on edge quality. Edge effect is not observed under a low current density (250 A m^{-2}). However, edge quality deteriorates into dendrites for current densities higher than 300 A m^{-2}.

The best cathode quality is obtained when gelatin, thiourea and Cl^- are present in the electrolyte. On the other hand, we have also obtained the worse cathode quality when the [gelatin]/[thiourea] ratio is not appropriate. With an electrolytic bath containing 40 mg l^{-1} of Cl^-, 40 g t^{-1} of thiourea and 100 g t^{-1} of gelatin, as can be seen in Figure 4(d), copper electrodeposition is not field oriented and the cathodic surface is significantly smoother than all the previous results. The copper deposit consists of very fine grains. Nodules are not observed on the cathodic surface and edges for current densities up to 350 A m^{-2}. Based on the SEM results, it is thus clear that all three additives are required to obtain high surface smoothness.

3.3. *Porosity analyses*

Cathodes produced with the scaled electrorefining set-up are thick enough to evaluate their porosity level. This is another very useful technique used to characterize the cathodes quality depending on the additive ratios and concentrations. Typical optical metallographs of cathodes produced at 300 A m^{-2} over 40 h under various combinations of additives are presented in Figure 5. Cathodes have been cut to show copper deposit growth throughout experiments' duration. Each picture represents a top view of a cathode where it is possible to see the deposit evolution from left (0 h, initial deposition on SS cathode) to right (end of the test, after 40 h). Copper growth, see extreme right of Figure 5(a), is very rough when only 40 mg l^{-1} of chloride ions are present in the electrolyte. Small and round porosities appear all over the cathodes' thickness. More damageable are the large closed porosities (~300 μm) appearing along grain boundaries.

Small and round porosities are still present when 60 g t^{-1} of thiourea are added to an electrolytic bath containing 40 mg l^{-1} of Cl^- (see Figure 5(b)). They are concentrated at grain boundaries where they combine and form large cracks (~600 μm). Copper growth is

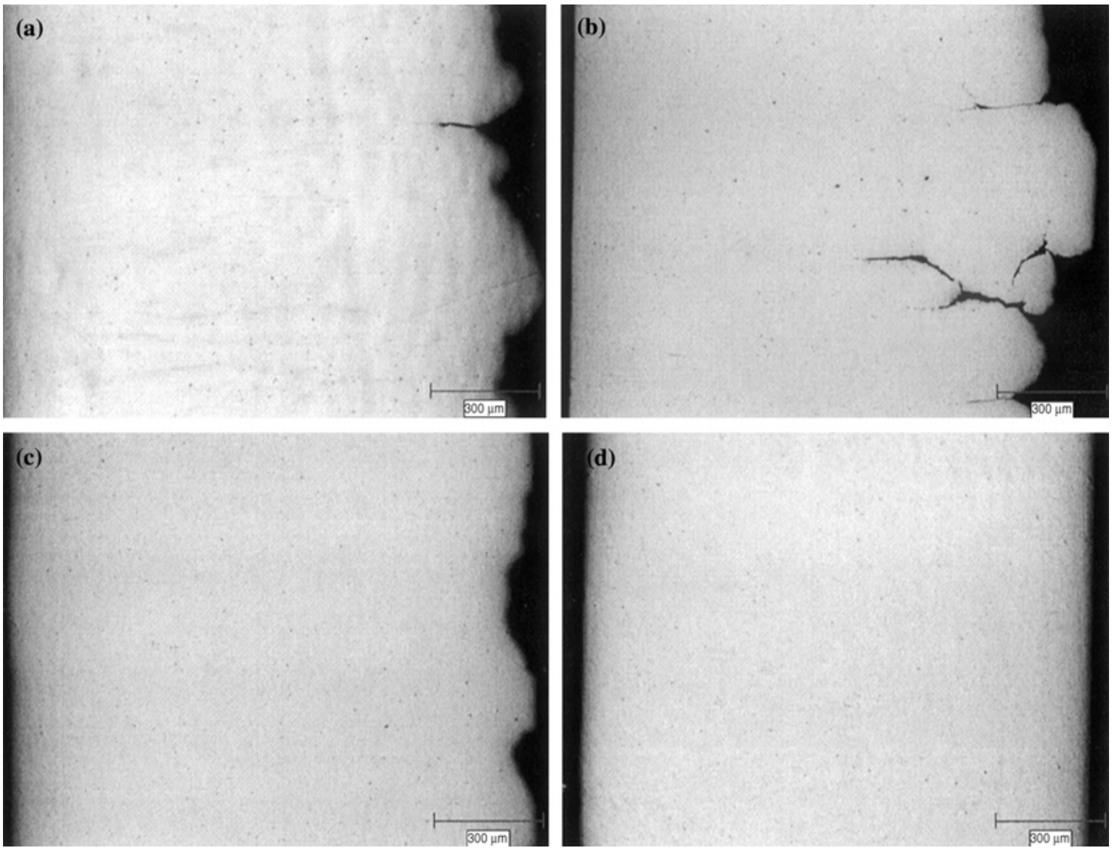

Fig. 5. Optical metallographs of cathodes produced at 300 A m^{-2} over 40 h with (a) only 40 mg l^{-1} of Cl^-, (b) 60 g t^{-1} of thiourea and 40 mg l^{-1} of Cl^-, (c) 100 g t^{-1} of gelatin and 40 mg l^{-1} of Cl^- and (d) 40 g t^{-1} of thiourea, 100 g t^{-1} of gelatin and 40 mg l^{-1} of Cl^-. Magnification 50×.

rough and similar to the cathodes produced with only Cl^-. Adding thiourea to an electrolyte containing only Cl^- does not reduce the porosity level.

When both 40 mg l^{-1} of Cl^- and 100 g t^{-1} gelatin are present in the electrolytic bath, the porosity level is very low. Small and round porosities are present but they are finer than those observed before. Copper growth (see extreme right of Figure 5(c)) is still pretty rough. When 40 mg l^{-1} of Cl^-, 40 g t^{-1} of thiourea and 100 g t^{-1} of gelatin are present in the electrolyte (see Figure 5(d)), porosities appear randomly and they are significantly fewer and finer than the ones observed before. Copper growth is also greatly improved.

3.4. *Growth structures*

It is also possible to observe the evolution of the copper grain structure from the cathodes produced with the scaled electrorefining set-up. This technique is also used to characterize copper deposit quality depending on the additive ratios and concentrations. Optical metallograph samples presented in Figure 5 were acid etched to reveal copper grain boundaries. As can be seen in Figure 6(a), with only 40 mg l^{-1} of Cl^-, the initial copper growth pattern consists of small grains formed on stainless steel cathodes. After a few hours, these grains gradually transform to the FT structure (field-oriented texture-type) according to the generally accepted classification proposed by Fisher [4]. As the current density increases, copper grain growth deteriorates to the BR structure (basis reproduction). Initial small grains are still present when both 40 mg l^{-1} of Cl^- and 60 g t^{-1} of thiourea are present in the electrolyte (Figure 6(b)). However, the copper growth pattern changes directly to the BR structure. When both 40 mg l^{-1} of Cl^- and 100 g t^{-1} of gelatin are present in the electrolytic bath, initial grains are somewhat different from those observed before. They are fewer, bigger and more elongated. After a few hours of deposition, the copper growth pattern consists of a mix between FT and BR structures (Figure 6(c)).

An obvious observation from Figure 6(d) is that grain size is definitively much finer when 40 mg l^{-1} of Cl^-, 40 g t^{-1} of thiourea and 100 g t^{-1} of gelatin are present in the electrolyte. Small and round grains are still present initially. After a few hours of deposition, the copper growth pattern consists of a mix between FT and UD (unoriented dispersion-type) structures. This type of structure assures a dense copper deposit as was confirmed by porosity analyses.

4. Conclusions

Scaled copper electrorefining cells were designed, built and computerized using Labview® software to control

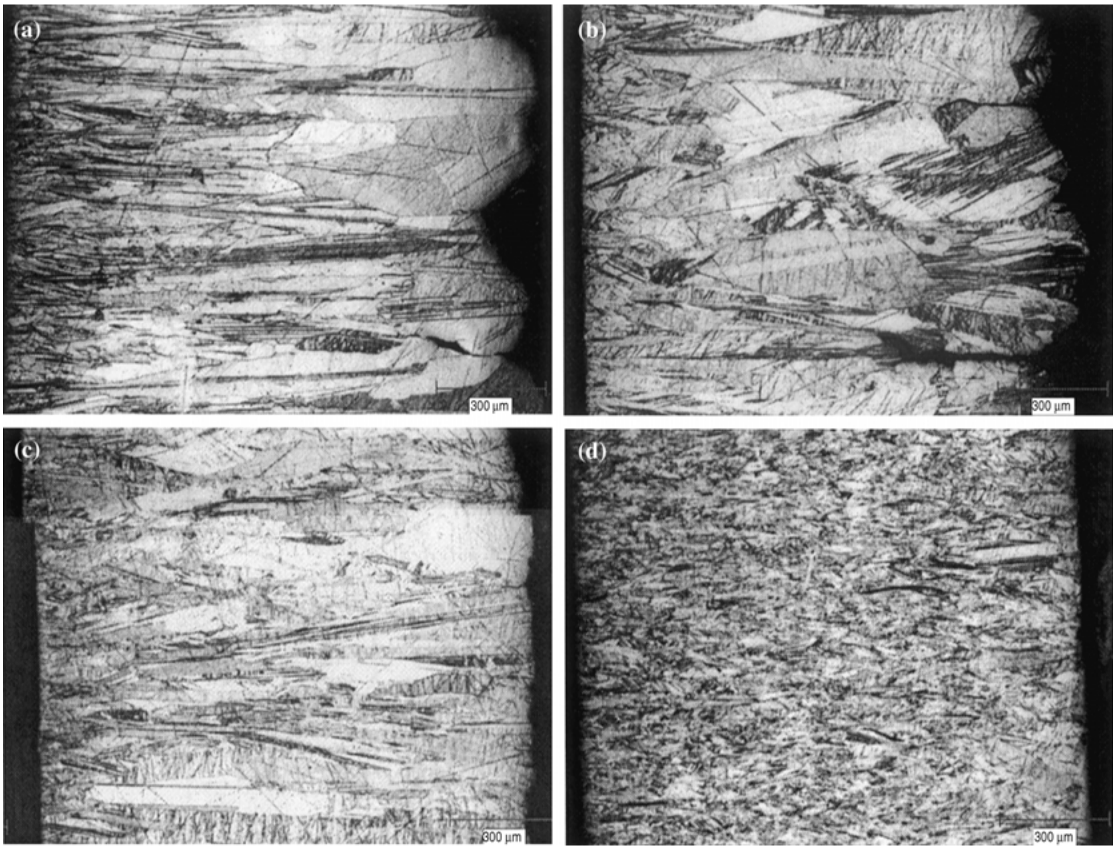

Fig. 6. Optical metallographs of acid etched cathodes produced at 300 A m^{-2} over 40 h with (a) only 40 mg l^{-1} of Cl^-, (b) 60 g t^{-1} of thiourea and 40 mg l^{-1} of Cl^-, (c) 100 g t^{-1} of gelatin and 40 mg l^{-1} of Cl^- and (d) 40 g t^{-1} of thiourea, 100 g t^{-1} of gelatin and 40 mg l^{-1} of Cl^-. Magnification 50×.

all instruments. Industrial ratios were considered and respected when designing the scaled cells. This was a major improvement over previous studies since it allowed a closer simulation of industrial conditions. It was particularly useful in simulating addition of additives to the electrolyte and their consumption during copper electrorefining. The scaled electrorefining set-up was used extensively to simulate Kidd's industrial conditions. Surface defects obtained were similar to the ones found industrially. The copper cathodes produced with various additive ratios and concentrations were characterized using cathodic polarization curves, SEM micrographs and optical analyses. Cathodes were thick enough to allow porosity analyses and copper grain analyses throughout the duration of experiments. These analyses are very relevant to fully characterize cathode quality.

Keeping all other conditions constant, results presented in this paper have clearly demonstrated that cathode quality is greatly influenced by additive ratios and concentrations contained in the electrolytic bath. Addition of thiourea to an electrolyte containing 40 mg l^{-1} of Cl^- has a depolarising effect on copper electrodeposition. Depolarization is somewhat stronger as thiourea concentration increases. With an electrolyte containing 40 mg l^{-1} of Cl^- and 20 g t^{-1} of thiourea, cathodic polarization increases with gelatin concentration. With an electrolytic bath containing only 40 mg l^{-1} of Cl^- or both 40 mg l^{-1} Cl^- and 60 g t^{-1} of thiourea, SEM micrographs have shown that the copper deposit consists of pyramidal grains, which get field oriented and coarser as the current density increases. The copper deposit is smoother with 40 mg l^{-1} of Cl^- and 100 g t^{-1} of gelatin and significantly smoother when all three additives are present ($Cl^- = 40$ mg l^{-1}, thiourea = 40 g t^{-1} and gelatin = 60 g t^{-1}). Optical metallographs have shown that big closed porosities are present along grain boundaries when the electrolytic bath contains only 40 mg l^{-1} of Cl^- or both 40 mg l^{-1} of Cl^- and 60 g t^{-1} of thiourea. Cathodes produced with 40 mg l^{-1} of Cl^- and 100 g t^{-1} of gelatin or with all three additives simultaneously have very low porosity levels. With only 40 mg l^{-1} of Cl^-, FT structure type deteriorates to the BR structure as the current density increases. When both 40 mg l^{-1} of Cl^- and 60 g t^{-1} of thiourea are present in the electrolyte, the copper growth pattern gradually changes to the BR structure. When both 40 mg l^{-1} of Cl^- and 100 g t^{-1} of gelatin are present in the electrolytic bath, the copper growth pattern consists of a mix between FT and BR structures. The copper grain size is much smaller when all three additives are present in the electrolyte. The copper growth pattern consists of a mix between FT and UD structures. This type of structure produces dense cathodic deposits and good cathode quality.

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