Journal of Applied Electrochemistry **33**: 1093–1098, 2003.

The use of electrochemical noise measurements to detect bad copper electrorefining conditions

B. VEILLEUX[1], A.-M. LAFRONT[1,*], E. GHALI[1] and P.R. ROBERGE[2]
[1]*Department of Mining, Metallurgical and Materials Engineering, Laval University, Ste-Foy, Quebec, Canada G1K 7P4*
[2]*Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Ontario, Canada K7K 7B4*
*(*author for correspondence)*

Received 1 July 2001; accepted in revised form 12 June 2002

Key words: additives, chloride, copper electrorefining, electrochemical noise measurements (EN), frequency domain transforms, gelatin, glue, kurtosis, skewness, statistical analysis, thiourea

Abstract

Additives like thiourea, gelatin and chloride are used during copper electrorefining to promote a smooth deposit. However, additives can also facilitate nodule formation when their ratios and/or concentrations are inadequate. A preliminary investigation was conducted to determine if electrochemical noise (EN) measurements could be used to monitor and detect inefficient copper electrorefining conditions due to improper ratios and/or concentrations of additives. EN measurements were carried out in the laboratory under simulated industrial conditions. Galvanostatic experiments were conducted using a synthetic electrolyte containing different concentrations of additives. A 316L SS cathode and industrial copper anodes were used. The effects of three different data acquisition frequencies were also investigated. EN signals obtained as potential time record series were studied using statistical analyses and frequency domain transforms. The different calculated parameters gave similar results for all conditions studied except when additives present in the electrolyte led to nodule formation. Results also showed that the data acquisition frequency must be at least 10 Hz to detect improper ratios and/or concentrations of additives.

1. Introduction

In industrial copper electrorefining, additives like thiourea (TU), gelatin (G) and chloride (Cl) are added to the electrolytic bath to maintain cathode quality and promote a smooth cathodic deposit [1, 2]. These additives, which act mostly as inhibitors, adsorb on the cathode surface where they take part in the electrochemical crystallization process [3, 4]. The need for these with regard to the cathodic deposition is clearly established, although their mechanisms during electrolysis are not completely understood [3]. However, additives can also facilitate nodule formation when their ratios and/or concentrations are inadequate [5–7]. Knowing the active concentration of each individual additive in the electrolytic bath is therefore extremely important to ensure a better control over the electrochemical crystallization process and therefore on the cathode quality. Unfortunately, this task is difficult since the different techniques available are sensitive and/or time consuming. Moreover, results may differ significantly depending on the technique employed [8].

As part of a broader study [8] on the effect of various additives on cathode quality, electrochemical noise (EN) techniques were used to study copper electrodeposition during copper electrorefining. The sensitivity of these electrochemical techniques is relatively well established for the detection of spontaneous changes in localized corrosion processes, in particular pitting, cavitation attack and certain types of stress corrosion cracking (SCC) [9]. The objective of the present study is to determine if EN techniques can identify different cathodic potential behaviors depending on the concentration of additives in the electrolytic bath during copper electrorefining. EN could then be a powerful tool to monitor, detect and eventually control bad industrial copper electrorefining conditions due to improper ratios and/or concentrations of additives.

2. Experimental procedure

The methodology followed in this study was designed according to the principles described in a recent publication on EN techniques [10]. The emphasis was put on statistical analyses for time domain curves (skewness and kurtosis) and on the slope of the power spectrum for frequency domain curves.

2.1. *Experimental setup*

Galvanostatic experiments were conducted over 25 min using conventional 700 ml electrochemical cells. A square 316L SS cathode with a surface area of 1.0 cm^2 and an industrial copper anode were used. The anode to cathode distance was 2.5 cm. A thermostatic bath was used to maintain the electrolytic temperature at 65 ± 1 °C. The synthetic supporting electrolyte contained 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. The electrolyte was renewed before each experiment. A GAMRY® PC4/300 potentiostat linked to a personal computer was used to log potential and current values. EN experiments and data treatment were conducted using GAMRY® ESA400 software. At least four experiments were made in each condition presented in this paper.

Additive concentrations in the electrolytic bath were based on previous work conducted at Laval University on copper electrorefining [11]. A condition that has clearly resulted in nodulation, two conditions that have resulted in a nodule free deposit and an additive-free electrolyte were investigated at 500 A m^{-2} (see Table 1). Additives were first diluted in water and then added at the beginning of the experiments. The influence of data acquisition frequency on EN values was also investigated. Experiments were conducted at 1, 10 and 20 Hz for conditions previously presented.

2.2. *Instrumentation*

A silver chloride electrode Ag,AgCl/KCl_{sat} (0.202 V vs SHE) was used as reference. All potentials are given with respect to this electrode. SEM analyses were conducted using a JEOL JSM-25s III model scanning electron microscope equipped with a TN 5700 model energy dispersive X-ray analyzer.

2.3. *Data analysis*

EN signals obtained as potential and current time records were analyzed by using a variety of methods. First, potential time records were examined to identify short-term transients in the data. These transients are usually indicative of spontaneous changes in mechanism. Statistical analyses were then calculated on batch data from potential time records. The following statistics were calculated: mean, variance, standard deviation, root mean square, coefficient of variance, skewness, kurtosis and noise resistance (standard deviation of potential divided by standard deviation of the current). Details on calculation of these parameters can be found in the literature [9].

EN analyses were also conducted in the frequency domain. To do so, time domain curves were first expressed in the frequency domain using Fast Fourier Transform (FFT). The slope of the Fourier Power Spectrum was then calculated (FPS). Slopes of power spectra were also calculated by the Maximum Entropy Method (MEM).

Each parameter discussed here after is calculated on blocks of data containing 5 min of experiments (3000 point experiments using sample rate of 10 Hz). An average of these results is then calculated for each parameter. Observations are based on the differences between these averages from one experimental condition to another. All data treatment was done using GAMRY® ESA400 EN software.

Table 1. Galvanostatic copper electrorefining EN experiments conducted at 500 A m^{-2} under different data acquisition frequencies (1, 10 and 20 Hz) with an electrolytic bath containing various concentrations of additives (TU = thiourea; G = gelatin; Cl^{-} = chloride)

Experimental conditions	Additives mg l^{-1}			Deposit
	[Cl^{-}]	[TU]	[G]	
A	–	–	–	Nodule free
B	40	4	2	Nodule free
C	40	4	6	Nodule free
D	40	4	11.5	Nodules

3. Results and discussion

Figure 1 presents typical experimental curves obtained from galvanostatic EN experiments conducted at 500 A m^{-2} with various additive concentrations. As expected, since the current is imposed, no short-term transients are observed throughout galvanostatic experiments.

Figure 2 presents typical SEM micrographs of cathodes obtained from galvanostatic EN experiments conducted at 500 A m^{-2} for 25 min with a bath containing different concentrations of additives. Nodules developed only on cathode D (bath containing 40 mg l^{-1} of Cl^{-}, 4 mg l^{-1} of TU and 11.5 mg l^{-1} of G). The deposited copper is smoother in all other conditions tested although it is somewhat rougher with an additive-free electrolyte (Figure 2A). However, in this latter case, this does not lead to nodule formation [11].

3.1. *Effect of different concentrations of additives*

3.1.1. *Statistical analysis*

Skewness and noise resistance statistical parameters calculated from galvanostatic EN experiments conducted at 500 A m^{-2} over 25 min with a bath containing different concentrations of additives are presented in Figure 3. The values calculated are significantly different in conditions where nodulation occurs. The skewness parameter is only positive for condition D, which is the only condition leading to nodule formation. The physical meaning of such signal behavior is that the shape of the distribution of the potential signal is very different when electrochemical conditions result in nodulation. The noise resistance value increases steadily with gelatin concentration. The value calculated is significantly

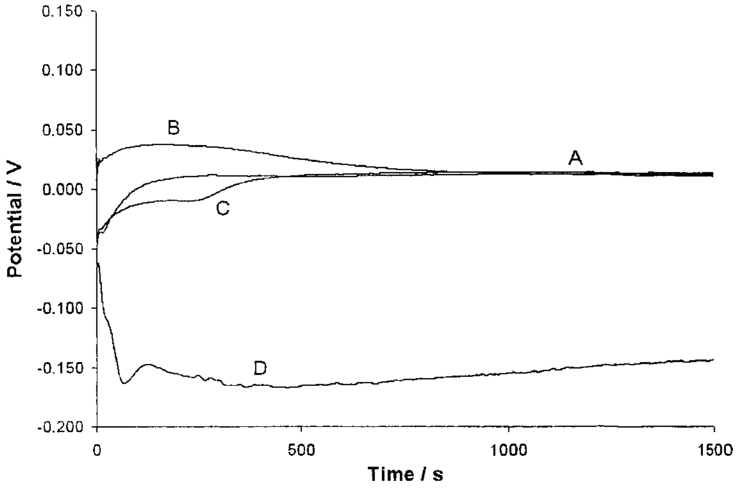

Fig. 1. Typical experimental curves of galvanostatic EN experiments conducted at 500 A m^{-2} and 10 Hz.

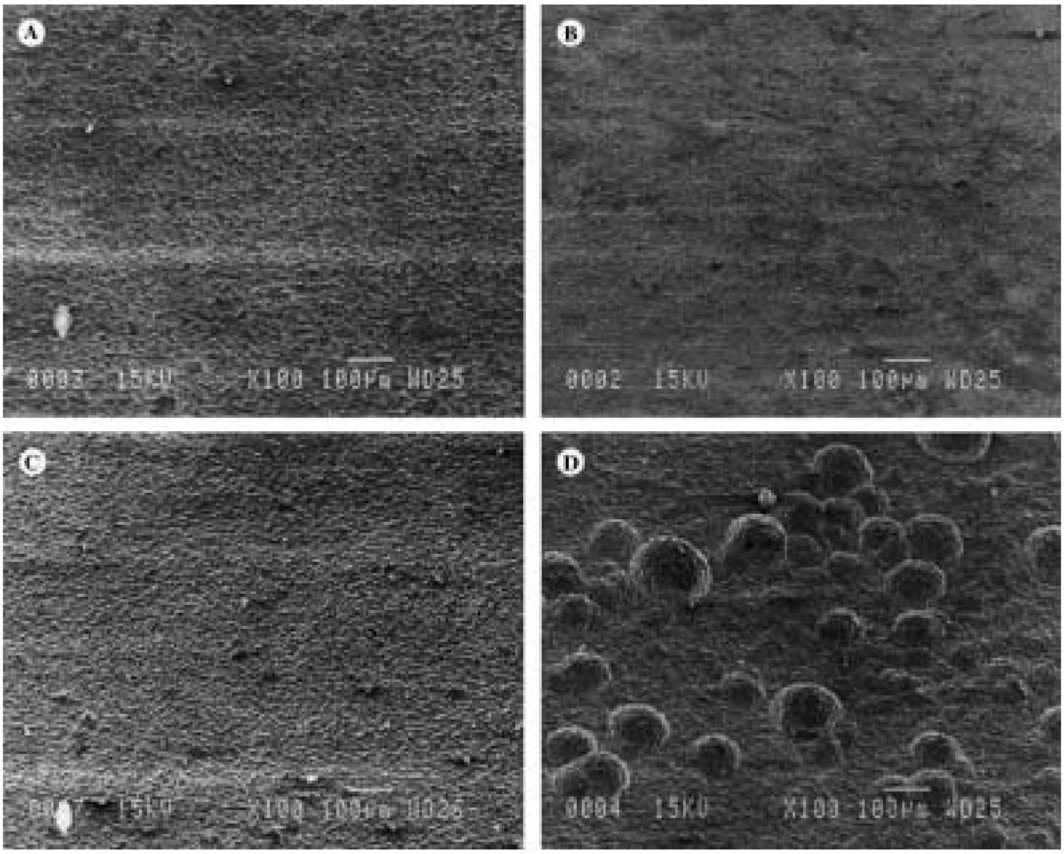

Fig. 2. Typical SEM micrographs obtained from deposition of copper during galvanostatic EN experiments conducted at 500 A m^{-2} for 25 min with an electrolytic bath containing different concentrations of additives.

higher (about three times higher) when nodulation occurs. It can be atgued that the noise resistance corresponds to the polarization resistance. Gelatin has a strong polarizing effect on copper electrodeposition. The polarization increases with gelatin concentration. The resistance noise can thus be used to characterize and determine high polarization levels during copper electrorefining.

3.1.2. *Frequency domain transforms*

Slopes of frequency domain curves calculated by FFT and MEM from galvanostatic EN experiments conducted at 500 A m^{-2} for 25 min with an electrolytic bath containing different concentrations of additives are presented in Figure 4. Results calculated are similar for both FFT and MEM when experimental conditions do not lead to nodulation (conditions A, B and C).

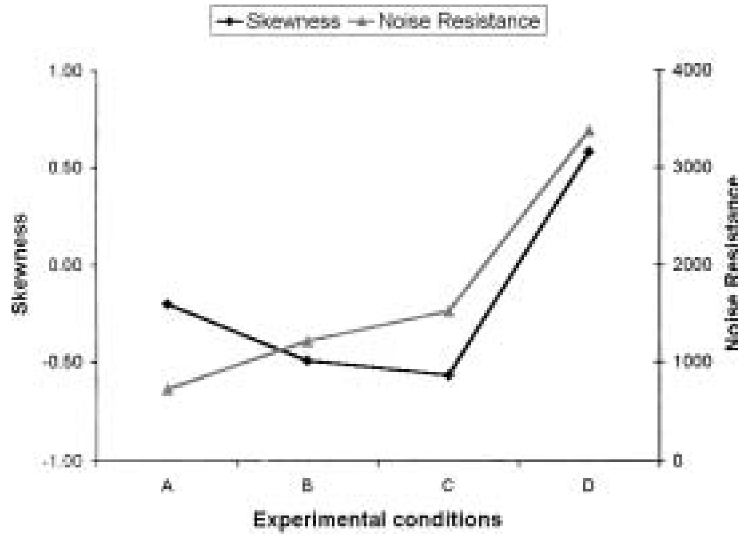

Fig. 3. Skewness and noise resistance statistical parameters calculated from galvanostatic EN experiments conducted at 500 A m^{-2} for 25 min with an electrolytic bath containing different concentrations of additives (10 Hz).

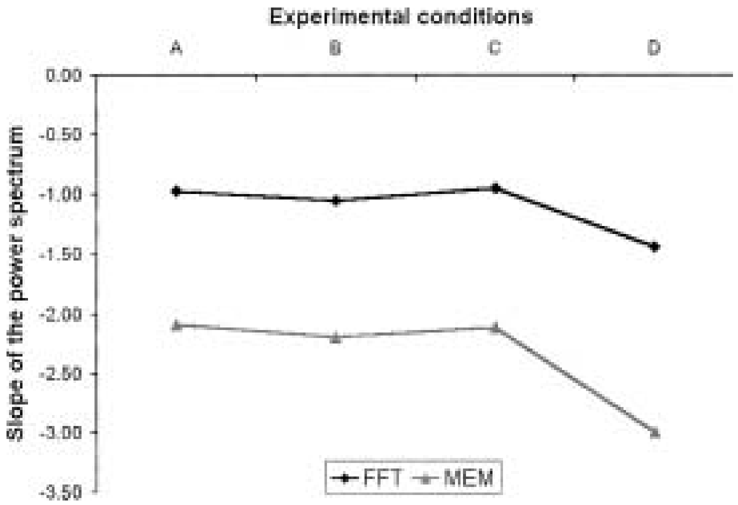

Fig. 4. Slopes of frequency domain curves calculated by using FFT and MEM from galvanostatic EN experiments conducted at 500 A m^{-2} for 25 min with an electrolytic bath containing different concentrations of additives (10 Hz).

However, the slopes of the power spectra decrease drastically when the concentration of the additives in the bath produces nodules (condition D). The effect of increasing gelatin concentration is to increase the amplitude of low frequencies present in the signal. These low frequencies are related to the interface impedance. Hence, under high gelatin concentrations, the impedance of the interface changes in a manner that leads to the formation of nodules.

3.2. *Effect of different data acquisition frequencies*

EN techniques require high precision instruments that can log current and potential values very rapidly. The influence of data acquisition frequency was investigated using statistical analyses and frequency domain transforms to determine the optimum data acquisition speed.

3.2.1. *Statistical analysis*

Skewness, kurtosis and noise resistance statistical parameters calculated from galvanostatic EN experiments conducted at 500 A m^{-2} for 25 min with an electrolytic bath containing 40 mg l^{-1} of Cl^{-}, 4 mg l^{-1} of thiourea and 2 mg l^{-1} of gelatin are presented in Figure 5 for various data acquisition frequencies. The skewness values are very similar no matter what the data acquisition frequency is. However, the kurtosis and the noise resistance values calculated under high data acquisition frequencies (10 and 20 Hz) are very different from those obtained under low data acquisition frequency (1 Hz). Thus, 10 Hz is the minimum data acquisition frequency required to distinguish different mechanisms using statistical analyses.

3.2.2. *Frequency domain transforms*

Slopes of frequency domain curves calculated by FFT and MEM from galvanostatic EN experiments conduc-

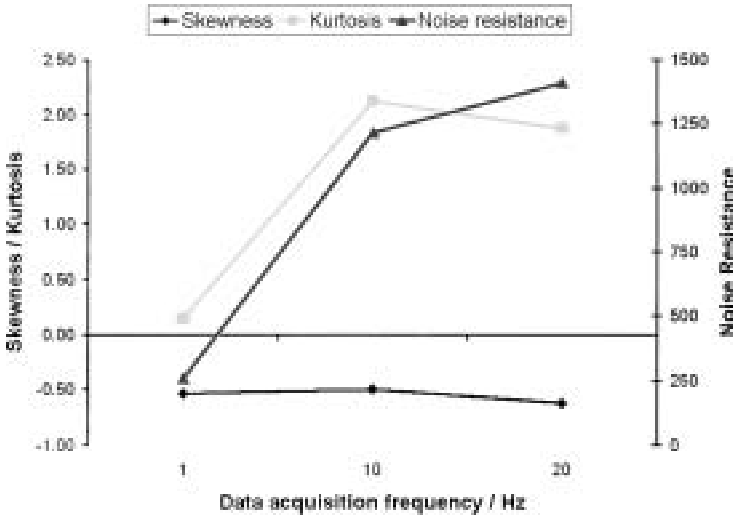

Fig. 5. Skewness, kurtosis and noise resistance statistical parameters calculated from galvanostatic EN experiments conducted at 500 A m^{-2} for 25 min under various data acquisition frequencies ($[Cl^-] = 40$ mg l^{-1}, $[TU] = 4$ mg l^{-1} and $[G] = 2$ mg l^{-1}).

ted at 500 A m^{-2} for 25 min with an bath containing 40 mg l^{-1} of Cl^-, 4 mg l^{-1} of thiourea and 11.5 mg l^{-1} of gelatin are presented in Figure 6 for various data acquisition frequencies. FFT and MEM slopes calculated for 1 Hz experiments are significantly different from those calculated for 10 and 20 Hz experiments, which are similar. Moreover, at 1 Hz, the slopes calculated are almost identical for all experimental conditions. It is thus not possible to identify any characteristics under low data acquisition frequencies. Consequently, a data acquisition frequency of 1 Hz is not fast enough to clearly identify different electrorefining conditions. On the other hand, there is no advantage of conducting experiments at data acquisition frequencies higher than 10 Hz since the values obtained at 10 and 20 Hz are similar.

4. Conclusions

EN techniques have been applied to a copper electrorefining system. Galvanostatic experiments were conducted at 500 A m^{-2} under various additive concentrations and various data acquisition frequencies. Statistical analyses and frequency domain transforms were calculated from potential time records.

At 10 Hz, statistical results calculated are significantly different when additives present in the electrolytic bath result in the nodulation phenomenon. The skewness parameter is positive only for conditions leading to nodule formation. The noise resistance value increases with gelatin concentration. This value is about three times higher when nodulation occurs. The noise resistance value is related to the polarization, which increases

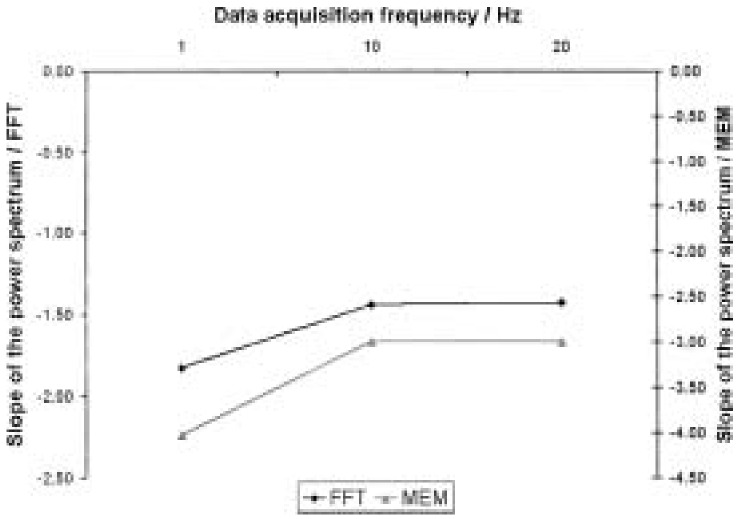

Fig. 6. Slopes of frequency domain curves calculated by using FFT and MEM from galvanostatic EN experiments conducted at 500 A m^{-2} for 25 min under various data acquisition frequencies ($[Cl^-] = 40$ mg l^{-1}, $[TU] = 4$ mg l^{-1} and $[G] = 11.5$ mg l^{-1}).

with gelatin concentration. This parameter can thus be use to characterize and determine high polarization levels during copper electrorefining.

Values calculated from frequency domain curves gave similar results for all conditions studied except when nodulation occurs. In this case, the slope values decrease drastically when the experimental conditions lead to nodule formation. Hence, increasing gelatin concentration increased the amplitude of low frequencies present in the signal. These low frequencies are related to the impedance of the interface. In these conditions, the impedance of the interface changes in a manner that leads to the formation of nodules.

A data acquisition frequency of 10 Hz is deemed appropriate for studying copper electrorefining using EN techniques. Lower data acquisition frequencies (1 Hz) are insufficient to differentiate between the various electrorefining conditions. On the other hand, 20 Hz data acquisition frequency gave similar results to those obtained at 10 Hz. There is thus no interest in conducting experiments under data acquisition frequencies higher than 10 Hz.

Results have shown that EN techniques can identify different cathodic potential behaviors, which depend on the composition of the electrolyte. EN techniques are an interesting avenue of study and characterize copper electrorefining conditions. These techniques could be used to monitor, detect and eventually control bad industrial copper electrorefining conditions due to improper ratios and/or concentrations of additives. However, further research on the influence of additives using EN techniques is required.

Acknowledgements

The support of the Natural Sciences and Engineering Research Council of Canada (NSERC), Mr J. Dutrizac from CANMET, Mr J. Lenz and Mr G. Morin from Falconbridge, Kidd Metallurgical Division, Mr D. Kerfoot, Mrs L. Skelton and Mrs C. Clement from INCO's Copper Cliff Copper Refinery (CCCR), Mr V. Baltazar from Noranda Technology Centre, Mr J. Thiriar and Mr T. Whitton from Noranda's Canadian Copper Refinery (CCR) and Mr M. Lefrançois from Laval University are gratefully acknowledged.

References

1. X. Cheng and J.B. Hiskey, *Metall. Trans. B* **27B** (1998) 53.
2. C. De Maere and R. Winand, Proceedings of copper 95–cobre 95 International Conference, Vol. III – Electrorefining and Hydrometallurgy of copper (1995) pp. 267–284.
3. O. Forsen, Copper '90 Refining, fabrication, markets (1990) pp. 189–197.
4. D.F. Suarez and F.A. Olson, *J. Appl. Electrochem.* **22** (1992) 1002.
5. E. Ilgar, Ph.D. Thesis, University of Missouri (1993) pp. 53–117.
6. B. Veilleux, A.-M. Lafront and E. Ghali, *Can. Metall. Quart.* **40** (2001) 343.
7. B. Veilleux, A.-M. Lafront and E. Ghali, *Can. Metall. Quart.* **41** (2002) 47.
8. B. Veilleux, Ph.D. Thesis, Laval University (2000).
9. D.A. Eden, *Electrochem. Noise* (2000) 1227.
10. R. Cottis and S. Turgoose, *Electrochem. Impedance Noise* (2000).
11. A.-M. Lafront, B. Veilleux and E. Ghali, *J. Appl. Electrochem.* (2000) in press.