



# Experimental studies on impurity particle behavior in electrolyte and the associated distribution on the cathode in the process of copper electrorefining



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## ARTICLE INFO

### Article history:

Received 3 November 2014

Received in revised form 27 April 2015

Accepted 10 June 2015

Available online 20 June 2015

### Keywords:

Impurity particle

Particle distribution

Copper electrorefining

Fluid velocity

Settling velocity

## ABSTRACT

A three factor 2-level designed set of experiments was performed to determine the effects of inlet flow rate, temperature, and current density on impurity particle behavior in electrolyte and the associated distribution on the cathode in copper electrorefining. Laser-Induced Breakdown Spectroscopy (LIBS) was used to measure the concentration of impurities on the cathode. The results of the experiments were statistically analyzed using Minitab. The inlet flow rate was identified as the most significant factor. All three factors and their two-factor interactions have a significant effect on impurity concentration on the cathode. The impurity concentrations in corner positions of cathodes had higher impurity levels than those in the center position of cathodes. The current density exerts more effect on both impurity concentrations at corner positions than at the center position. A possible explanation for the phenomena observed is proposed.

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## 1. Introduction

Anodes consisting of copper with its inherent silver, lead, nickel, bismuth, antimony, and arsenic impurities are common in copper electrorefining. Although arsenic and antimony can exert positive effects in producing copper cathodes of better quality and thus might be added intentionally, impurities existing in anodes generally tend to jeopardize the quality of cathodes (Free, 2013). Group 15 elements (As, Sb, and Bi) are impurities that are potentially detrimental in many metallurgical processes and to the environment (Brent Hiskey, 2012). Therefore, the plating characteristics of Group 15 elements are significant in copper electrorefining. During the process of copper electrorefining, these impurities are typically transferred to the electrolytic solution as soluble species or impurity particles as the anode dissolves. These impurities can co-precipitate, if the concentration of these impurities in the electrolytic solution reaches saturation levels. Some of these precipitates are floating slimes and can be a major source of cathode contamination (Brent Hiskey, 2012). The elements such as Pb, As, Bi, Sb, and Se are the most significant impurities (Cifuentes et al., 2012). From previous studies it is proposed that reducing the tendency for antimony oxidation could prevent the formation of floating slimes and help maintain cathode quality (Brent Hiskey, 2012).

Cast anode inclusions within the copper matrix result from the existence of impurities within the copper melt. When the copper anodes dissolve in electrorefining, many of these inclusions are liberated, to

form anode slimes. Chen and Dutrizac (1993) have carried out detailed investigation of the phases and structures existing in the anode slimes, such as kupferglimmer, euhedral NiO crystals,  $(\text{Cu,Ag})_2\text{Se}$  rings,  $\text{PbSO}_4$ , Ni–Fe oxides, silicates, and a variety of complex oxides (Chen & Dutrizac, 1990; Chen & Dutrizac, 1989; Chen & Dutrizac, 1991; Chen & Dutrizac, 2005; Chen & Dutrizac, 1988). The majority of anode slimes settle to the bottom of the cells. However, anode slimes that do not settle can be transported and incorporated into cathodes (Free, 2013; Davenport et al., 2002; Baker & Kershaw, 2010). Therefore, anode slimes are a major potential source of impurities in the cathode (Abe et al., 1980; Ling et al., 1994; Sedzimir & Gumowska, 1990; Srinivasan et al., 1982).

It is helpful to study anode slime behavior in the flowing electrolyte. Unfortunately, few flow studies involving slimes can be found in the literature (Gu et al., 1995; Sawicki et al., 1993; Chen & Dutrizac, 1993) and the effect of major electrorefining parameters on slime transport in electrolyte is not well known.

In this study, electrorefining testing was performed to understand the behavior of anode slimes in flowing electrolyte and their distribution on the cathode using tracer impurity nanoparticles.

## 2. Experimental procedures

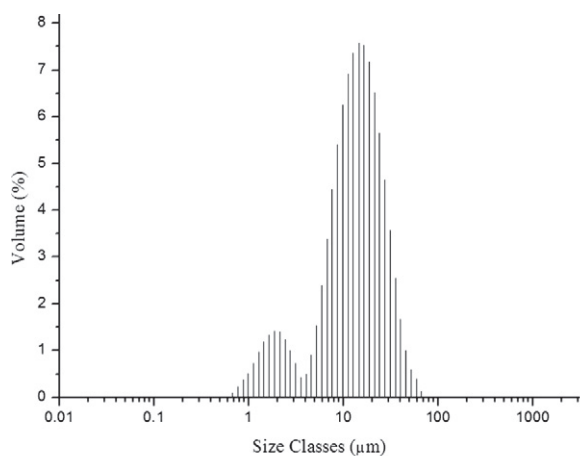
Laser-Induced Breakdown Spectroscopy (LIBS), which can analyze the localized concentration of impurities on the cathode, was utilized. The analysis using LIBS works by firing a high powered laser beam onto a metal sample. The focused thermal energy produced by the laser beam creates plasma. This plasma ionizes the atoms which emit

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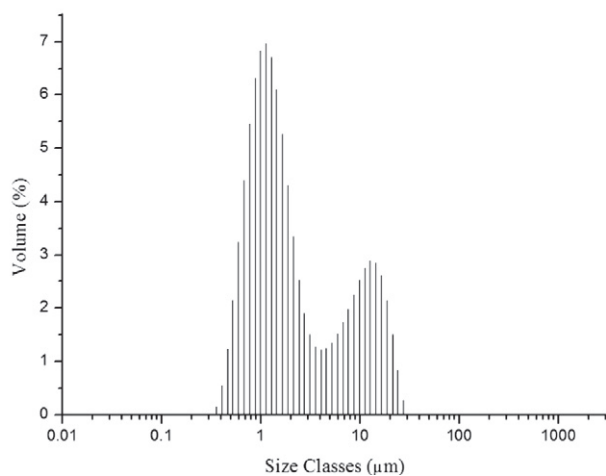
E-mail address: [michael.free@utah.edu](mailto:michael.free@utah.edu) (M.L. Free).

different colors of light that are unique to each atom's outer electrons in proportion to concentration (Reinhard, 2012; Vadillo & Javier, 2004; Lee et al., 2004). If a spectrometer is used to measure the exact wavelengths of emitted light, these wavelengths are compared to standard wavelengths and signal intensity to calculate the chemical composition of the tested sample.

A series of copper electrorefining tests were performed using two different types of tracer nanoparticles: titanium dioxide nanoparticles (200 nm) and silver nanoparticles (100 nm). The particle size distribution analyses of the particle aggregates (added to and stirred in water, and injected into the size analyzer through a syringe pump) were performed before the experiments. The results of the analyses are shown in Fig. 1a & b. The TiO<sub>2</sub> particle sizes are distributed mostly at 14.5 μm, and the Ag particle sizes are distributed mostly at 1.13 μm. The two kinds of particles are added to and stirred in water and pumped into the cell through a syringe pump. Each test was performed for 5 h with 45 g/L Cu(II) as CuSO<sub>4</sub>, 2 g/L Fe(II) as FeSO<sub>4</sub>, 180 g/L H<sub>2</sub>SO<sub>4</sub>, 30 mg/L Cl<sup>-</sup> as HCl, and 100 mg/L Co(II) as CoSO<sub>4</sub>. Eight tests were performed for the 3-factor 2-level experimental design (high and low inlet flow rate (pumping rate), high and low temperature, and high and low current density). Another 8 tests were performed using the same experimental design to verify the reproducibility of the tests. The total number of tests completed was sixteen, which includes eight original tests and eight repeated tests.



a) Particle size distribution analyses of TiO<sub>2</sub>



b) Particle size distribution analyses of Ag

Fig. 1. a. Particle size distribution analyses of TiO<sub>2</sub>. b. Particle size distribution analyses of Ag.

The test cell consists of a 12.5 × 10 × 10 cm vessel that is continuously fed electrolyte and tracer particles at specified levels through an inlet and an outlet as shown in Figs. 2 and 3. The cathode is a stainless steel sheet that is approximately 8 × 9.5 × 0.1 cm with a corresponding Cu anode that is about 5 mm shorter than the cathode sheet. The current was supported by a power supply. An isothermal bath and heater were used to maintain the temperature. A peristaltic pump was used to move the electrolyte solution from the containment system to the cell. The electrolyte solutions were prepared in a 5-liter container and the amount of the solution is calculated on a 6-hour basis to supply the solution required for 5 h of testing. A syringe pump was used to supply the two kinds of impurity particles at a rate equal to 500 mg/L TiO<sub>2</sub> nanoparticles and 200 mg/L Ag nanoparticles over each 5-hour period.

Plates were collected after 5 h of testing. Pictures of each plate were taken: one example is shown in Fig. 4. Samples were then stripped from the cathode plates and cut into 9 equivalent pieces as shown in Fig. 5, but only the 4 corner pieces and the center piece (the shaded pieces in Fig. 5) were analyzed later. Once cut, odd numbered pieces were analyzed by LIBS to determine the localized concentration of the added impurities. Ten points were analyzed randomly over each piece and the average intensities were calculated with reasonable standard variations among the ten points. Examples of the resulting spectrum are presented in Fig. 6. To determine the concentration of the impurities, calibration curves for each impurity were performed. After the impurity concentrations were measured on the five sections of each cathode deposit, concentration data were collected, compiled, and statistically analyzed using Minitab.

### 3. Results

LIBS calibrations for titanium dioxide particles and silver particles were performed, based on the calibration methods described in published books (Cremers & Radziemski, 2006; Miziolek et al., 2006). The results of the calibrations are shown below.

The linear relationship between TiO<sub>2</sub> normalized intensity and concentration can be described by:

$$\begin{aligned} \text{Normalized Intensity}(\%) &= 8.601 * \text{Concentration of TiO}_2 \text{ (wt.\%)} \\ \text{R-Sq(adj)} &= 99.9\%. \end{aligned}$$

Similarly, there is a conversion equation for Ag nanoparticles:

$$\begin{aligned} \text{Normalized Intensity}(\%) &= 5.432 * \text{Concentration of Ag (wt.\%)} \\ \text{R-Sq(adj)} &= 99.9\%. \end{aligned}$$

Based on the above two equations, the impurity concentrations were calculated for the five sections of each sample (Tables 1 and 2), after the normalized intensity data were measured using LIBS.

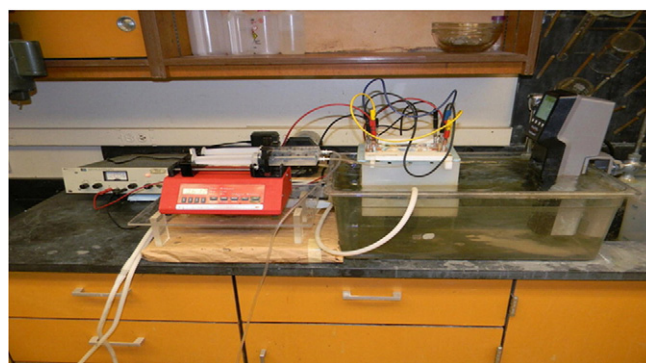


Fig. 2. The electrorefining cell and associated equipments used in the experiments.

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