

## Technical note

# The effect of gold on anode passivation and high current density operation under simulated silver electrorefining conditions



Arif Aji<sup>a</sup>, Sunara Purwadaria<sup>b</sup>, Jari Aromaa<sup>a</sup>, Benjamin P. Wilson<sup>a</sup>, Olof Forsén<sup>a</sup>, Mari Lundström<sup>a,\*</sup>

<sup>a</sup> *Hydrometallurgy and Corrosion, Dept. of Materials Science and Engineering, School of Chemical Technology, Aalto University, P.O. Box 16200, FI 00076 Aalto, Finland*

<sup>b</sup> *Institute of Technology Bandung, Department of Metallurgical Engineering, Jl. Ganesha 10, 40132 Bandung, Indonesia*

## ARTICLE INFO

## Article history:

Received 23 February 2016

Received in revised form 24 August 2016

Accepted 10 September 2016

Available online 12 September 2016

## Keywords:

Gold impurities

Current efficiency

Nitric acid electrolyte

Dissolution kinetics

High current density electrorefining

## ABSTRACT

In the silver electrorefining process, the presence of gold as an impurity in anodes can affect process performance. In the present investigation, the effect of gold on anode passivation and the kinetics of dissolution at high current density were studied. Experiments were conducted using artificial silver anodes with gold contents of 2%, 5%, 10% and 20% (w/w) and acidic nitrate electrolytes containing 40 g/dm<sup>3</sup> and 60 g/dm<sup>3</sup> of Ag<sup>+</sup>. Results obtained from potentiodynamic measurements showed that in order to have higher current densities than 50 mA/cm<sup>2</sup> and higher energy efficient operation, the gold content in anode should be limited to ≤10% with 60 g/dm<sup>3</sup> of Ag<sup>+</sup> electrolyte. In contrast, the same current density operation for 40 g/dm<sup>3</sup> electrolyte will be applicable for anodes with ≤3.2% gold content with high energy inefficiency.

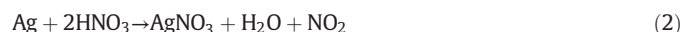
© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Silver is a noble metal which for centuries has been used in applications as diverse as medicine (Medici et al., 2015), currency and jewelry (Greenwood and Earnshaw, 1997; Silver Institute, 2015). In 2014, >50% of silver was used for industrial applications mainly in electric and electronic industries as silver is known for the highest electrical conductivity amongst all metals (Silver Institute, 2015; Cotton and Wilkinson, 1988). Production of silver as a by-product from gold mining and copper mining contributed 290 million ounces or >30% of global silver production in 2014 (Silver Institute, 2015). Refining of silver and gold as products from gold mining or the smelting of copper anode slime, is often the final process of these metal production processes (Shi and Ye, 2013; Bard and Sobral, 2008). Although there has been a significant number of studies into many aspects of the copper electrorefining processes including the effect of current density (Dabroś and Jaskula, 1978; Ntengwe et al., 2010), temperature (Owais et al., 2015), additives (Ojaghi Ilkhchi et al., 2007; Fabian et al., 2007), anode slime formation (Kilviluoma et al., 2016; Chen and Dutrizac, 2004; Chen and Dutrizac, 2008) and the presence of impurities (including silver, antimony, arsenic, bismuth) (Kucharska-Giziewicz and Mackinnon, 1996; Minotas et al., 1989; Hiskey and Maeda, 2003), in comparison, the electrorefining of silver has so far received less attention (Habashi, 1980; Ammen, 1984; Pophanken and Friedrich, 2015; Auerswald and Radcliffe, 2005).

From the binary diagram of silver and gold, it can be seen that both metals will form a single phase solid throughout the mass fraction (Okamoto and Massalski, 1983). One of the most common processes used to separate gold and silver involves nitric acid solution, a strong acid that dissociates by up to 93% at a concentration of 0.1 M (Habashi, 1980). In the absence of a complexing agent, it has been observed that on immersion in a room temperature solution of <95% nitric acid there is no appreciable corrosion of gold i.e. under these conditions gold is insoluble in nitric acid (Walkiden and Jarman, 1994).

Due to the fact that gold typically makes up the major impurity, silver refining can be conducted by (i) inquartation (addition of silver to gold to achieve at least a 3:1 ratio prior to purification) or (ii) silver electrorefining (Walkiden and Jarman, 1994). During inquartation of Ag–Au alloy, silver is dissolved in HNO<sub>3</sub> with either a concentration between 3.8 and 4.9 M of HNO<sub>3</sub> (Eq. (1)) or 4.9 to 7.1 M (Eq. (2)). In both cases although the silver dissolves to produce silver nitrate and nitric oxide or nitrogen dioxide, the gold remains as an undissolved solid residue (Habashi, 1980; Martinez et al., 1993; Ozmetin et al., 2000; Sadrnezhaad et al., 2006).



Separation of gold and silver using inquartation becomes increasingly efficient at higher Ag/Au ratios, with the optimal silver content suggested to be 75% (Habashi, 1980) or 80% (w/w) (Ammen, 1984). The dissolved silver can then be subsequently recovered from the

\* Corresponding author.

E-mail address: [mari.lundstrom@aalto.fi](mailto:mari.lundstrom@aalto.fi) (M. Lundström).

electrolyte either by cementation (Keles, 2009) or electrolytic reduction (electrowinning) (Hoffmann et al., 1976).

Silver electrorefining in acidic silver nitrate electrolytes has been widely used to produce high purity silver. Electrorefining is generally carried out using  $\text{AgNO}_3$  electrolyte with a  $[\text{Ag}^+]$  concentration in the range of 30 to 150  $\text{g/dm}^3$  and current densities between of 20–40  $\text{mA/cm}^2$  (Pletcher and Walsh, 1990). Several improvements to the silver electrorefining process have been previously reported from use of a continuous process (Auerswald and Radcliffe, 2005) to the use of high current density operation in the range of 30 to 90  $\text{mA/cm}^2$  (Claessens and Cromwell, 1999). From a cathodic deposition perspective, high current density operation will result in a high productivity although there is the drawback that impurities like copper and palladium will also be co-deposited in this current density range (Pophanken and Friedrich, 2015). In accordance with the accepted conventions, in this investigation current densities  $>50 \text{ mA/cm}^2$  will be subsequently referred as high current density and those within the range of 20–50  $\text{mA/cm}^2$  as normal current density.

It has previously been demonstrated that the current density utilized within the silver refining process can have a profound influence on the electrode potential and as a result the anodic metal dissolution and cathodic precipitation of impurities (Pophanken and Friedrich, 2015). Furthermore, the type and concentration of impurities both in the electrorefining anodes and the electrolyte bath can affect process efficiency. Gold, in particular, is a major impurity in anodes made from roasted and smelted copper electrorefinery anode slimes, with a typical Au content being between 2 and 6% of the total weight (Chen and Dutrizac, 2008). As a result of the move towards the use of higher current densities, this study investigates the effect of gold content and electrolyte concentration on silver anode passivation and high current density operation in order to determine the most suitable process parameters.

## 2. Experimental

### 2.1. Materials and methods

Artificial silver anodes containing gold with mass fractions of 2%, 5%, 10% and 20% (w/w) were prepared by smelting silver crystals (LBMA, 99.95% grade) and gold granules (LBMA, 99.99% grade) of the appropriate concentrations together. These grades were chosen as silver anodes typically contain gold as the major impurity in the range of 2% to 10%, whilst the maximum gold content (20%) was utilized in order to allow a comparison with previous studies of gold and silver separation. The anodes were prepared such that they all had a uniform surface area of 0.4775  $\text{cm}^2$  and thickness of 2 mm. Moreover, the anodes were also analyzed with XRF to determine the actual compositions and the results confirmed that the gold mass fractions were 2%, 5%, 10% and 20%, respectively.

The working electrode for the electrochemical measurements was fabricated by mounting the fabricated anodes in an epoxy resin. These anodes were polished to 2000 grit and cleaned by sonication in an ethanol bath. Two different electrolyte concentrations were used for the measurements: the first was an industrial electrolyte containing 40  $\text{g/dm}^3$  of  $[\text{Ag}^+]$  supplied by PT. Antam Tbk, Indonesia and the second was a higher concentration electrolyte that contained 60  $\text{g/dm}^3$  of  $[\text{Ag}^+]$ , which was considered as an improvement of the process. The free  $\text{HNO}_3$  concentration for both electrolytes was 10  $\text{g/dm}^3$ .

The dissolution rate was determined from the anode current density with the energy needed (W) for anode dissolution ( $\text{kWh/kg}$ ) calculated from the corresponding potentials ( $E$ ) using Eq. (3):

$$W_{\text{dissolution}} = (nFE/1000M) \quad (3)$$

where  $F$  is Faraday constant (96,485  $\text{C mol}^{-1}$ ),  $n$  is the valency number of ions and  $M$  is the atomic mass of silver.

Potentiodynamic measurements were conducted using a Gamry Instrument Reference 600 potentiostat that featured a three electrode cell set-up that included the Ag-Au anode under test, a Ag/AgCl reference electrode and a Pt wire as the counter electrode. Each anode was allowed to stabilize by immersion in the electrolyte for 1 h prior to the start of the electrochemical measurements. Potentiodynamic scans were performed from  $-50 \text{ mV}$  vs. open circuit potential (OCP) to  $+500 \text{ mV}$  vs. OCP with a sweep rate of 0.167  $\text{mV/s}$  and all measurements were performed at room temperature.

Electrochemical Impedance Spectroscopy (EIS) measurements were also conducted to measure the effect of gold content on the resistivity of the anode. EIS to measure the total impedance of the system was conducted using an ACM Instrument Gill potentiostat with a Ag/AgCl reference electrode and Pt strip counter electrode. The EIS measurement of the total impedance utilized a frequency range between 30,000–0.1 Hz with 55 readings per measurement of frequency with AC signal amplitude of 10 mV and an offset of 0 mV from rest potential.

## 3. Results and discussion

### 3.1. Polarization curves and most suitable parameters

The profile of a schematic polarization curve of a silver anode (with gold) in a  $\text{Ag}^+$  containing electrolyte is shown in Fig. 1a and it highlights the position of the key points on the curve that help determine the optimum parameters. Polarization curves of gold containing silver anodes in the two different Ag + electrolyte concentrations are shown in Fig. 1b (40  $\text{g/dm}^3$ ) and c (60  $\text{g/dm}^3$ ), respectively. As can be seen from the curves, at potentials just above OCP, there is an active region (i) where the dissolution of silver increases rapidly until a passivation potential ( $E_{pp}$ ) is reached. The dissolution rate at this potential is referred to as the critical current density ( $j_{cc}$ ). This active dissolution region is narrow, and as the potential is increased further, (ii) the current density can be observed to decrease markedly as a result of anode passivation ( $j_p$ ). Finally (iii) when a critical overpotential is reached, the current density once again increases significantly above  $j_p$ , indicating a trans-passive behavior.

The optimum parameters for the silver electrorefining process were determined based on observations from this trans-passive region, as this is where the increase in the current density becomes insignificant when compared to the increase in potential. As a result, the potential at this point is referred as the optimum process potential ( $E_{opt}$ ) and the corresponding current density as the optimum current density ( $j_{opt}$ ). Overall, Fig. 1b and c clearly demonstrate that anodes show an increased tendency to passivate with increased gold content for both electrolytes investigated.

### 3.2. Active, passive and transpassive regions

From Fig. 1b and c, the passivation potentials and critical current densities for the different anode materials studied were determined in both electrolytes. The highest critical current density ( $j_{cc}$ ) achieved in the active region was 34  $\text{mA/cm}^2$  achieved with the silver anode containing 2% Au in 60  $\text{g/dm}^3$   $\text{Ag}^+$  electrolyte. For all the other anode materials the critical current densities measured were  $<16 \text{ mA/cm}^2$  and thus rather low compared to normal current density. As a result, it can be concluded that a silver electrorefining process (with anodes having gold content of 2–20%) operating in the active region is inefficient.

From the results obtained, it is noticeable that in the passive region, the recorded current densities  $j_p$  undergo a significant reduction to very low values. Table 1 shows the trans-passive potentials, passive region current densities the length of passivation range (mV),  $E_{opt}$  and  $j_{opt}$  for the measured polarization curves in the 40  $\text{g/dm}^3$   $\text{Ag}^+$  and 60  $\text{g/dm}^3$   $\text{Ag}^+$  containing electrolytes respectively. It can be seen that an increase in gold content results in a linear increase in the extent of the passivation range for both electrolytes studied. This finding indicates that

Download English Version:

<https://daneshyari.com/en/article/4769042>

Download Persian Version:

<https://daneshyari.com/article/4769042>

[Daneshyari.com](https://daneshyari.com)