



# Cyclic voltammetry responses of gold electrodes in thiosulphate electrolyte



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## ARTICLE INFO

### Article history:

Received 2 September 2015

Revised 7 March 2016

Accepted 8 March 2016

Available online 11 March 2016

### Keywords:

Gold oxidation and reduction in thiosulphate

Voltammogram

Peak current

Irreversibility

## ABSTRACT

The gold thiosulphate system has been studied for some time due its prospective favourable economics over the gold cyanide system when treating certain ore types. Despite the large amount of work which has been done with gold thiosulphate system, various questions (uncertainties) still remain. For example, the causes for slow gold dissolution kinetics in thiosulphate and the gold losses during leaching observed in some applications. In this study, cyclic voltammetry was used to investigate the oxidation and reduction of gold in magnesium thiosulphate electrolyte. The anodic dissolution of gold is discussed in terms of possible reactions and mechanisms involving catalysts such as thallium and thiourea. The abrupt increase in anodic current in the presence of these catalysts indicates that the passivation of gold anodic dissolution is related to surface phenomenon and not to the depletion of thiosulphate ion at the reaction interface. The Tafel-like plots identified the increase of exchange current for gold oxidation and reduction reactions for catalyst assisted systems. The large anodic to cathodic peak separation ranged between 0.25 V and 0.37 V allowed most of the leached gold to diffuse away from the electrode. This indicates the electrochemically quasi-reversible to irreversible character of this system even in the presence of catalysts. The relationship between reduction peak current and concentration of gold thiosulphate in the bulk electrolyte was estimated based on relevant equation for electrochemically irreversible reaction.

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## 1. Introduction

Cyanidation has been used as the standard practice to process free milling gold ores since the late 19th century (Marsden and House, 2006). However, with the depletion of free milling gold ores, the industry is now considering alternatives to cyanide for selected applications. The use of thiosulphate to treat gold ores containing carbonaceous matter has recently been commercialized by Barrick Gold at the Goldstrike processing plant in Nevada (Choi, 2013). The thiosulfate complex of gold is not “preg-robbed” and hence high gold extractions can be maintained (in contrast to cyanide). Despite this advantage, the thiosulfate leaching system also has limitations. Specifically, the process requires catalyst addition because gold dissolution in thiosulphate is an inherently slow reaction and, the stability of leached gold in the pulp has been an issue in some studies.

It is well known that the kinetics of leaching is dependent on particle size. In fact, the dependence has a cube relationship if it

is assumed that the particles have a sphere shapes, which means that if other kinetic factors are eliminated for simplicity, every 10-fold reduction in particle size (for example from 1  $\mu\text{m}$  to 0.1  $\mu\text{m}$ ), increases the kinetics 1000 times. Therefore, it is logical to expect that naturally fast kinetics would be achieved when leaching a sub-micron size gold particle (Fleming, 2015). Fast kinetics translates into small reactor sizes and possibly low lixiviant concentrations in the leach solution (provided there is no adverse impact on leach kinetics). For example, the Barrick Goldstrike thiosulphate plant uses low concentration calcium thiosulphate lixiviant (Aylmore, 2014) and has become the first successful thiosulphate based commercial operation in the history of gold processing. However, not every ore is similar to that of the “Goldstrike” deposit and when dealing with slow leaching kinetics there is a need for suitable catalyst for the thiosulphate process. The most studied catalyst system is a copper-ammonia assisted leaching. But it was found that the copper ammine catalyst also catalyses thiosulphate oxidation and once thiosulphate is decomposed gold is re-precipitated and lost from solution or slurry.

The biggest challenge for the gold thiosulphate leaching process is to keep the leached gold in solution. In the Goldstrike operation,

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this problem of gold instability is managed by using an ion-exchange resin which extracts the gold thiosulphate from the slurry continuously. The Goldstrike operating conditions of low thiosulfate concentration results in less competition for resin active groups (both the gold thiosulfate complex and thiosulfate and thiosulfate degradation products are anionic) and gold is efficiently recovered from leach solution. When stronger thiosulphate solution composition and high oxidative potential is required to achieve acceptable leaching kinetics (as may be the case for coarser gold particles) large amount of polythionates (tetra-, tri- and penta-thionate) form that reduce the gold thiosulphate loading on the resin and may decrease the overall recovery of gold (Fleming et al., 2003).

The dissolution of gold is an electrochemical process whether a cyanide or thiosulphate leach solution is used. However, the reduction potential for gold in thiosulphate is much more positive (0.15 V) compared to cyanide (0.01 V) (Sullivan and Kohl, 1997). This means that mild reducing agents may be used to reduce the gold from its thiosulphate complex compared to cyanide. The presence of excess thiosulphate shifts the redox potential to lower values and hence the reduction reaction is hindered and gold thiosulphate becomes electrochemically more stable (Sullivan and Kohl, 1997). However, the unstable nature of thiosulphate under conditions that is required for gold leaching makes it difficult to control the stability of leached gold. Furthermore, it was found that the gold reduction process proceeds more rapidly in the presence of potassium and ammonium as compared to sodium (Choo and Jeffrey, 2003). In fact a sharp increase in rate of gold deposition was achieved at potentials as high as  $-0.1$  V vs SHE in the presence of copper and ammonia (Choo and Jeffrey, 2003). It appears that while copper ammine catalyses the gold dissolution (Chandra and Jeffrey, 2004) it also facilitates the reduction of gold from the thiosulphate complex (Choo and Jeffrey, 2003) which means that the catalytic effect might not be unidirectional.

This study investigates the electrochemical processes involved in the use of two relatively recently discovered catalysts in order to understand their effect on gold anodic dissolution. The behaviour of gold electrodes in solutions containing magnesium thiosulphate and in the presence of thallium and thiourea is reported, covering the active dissolution, passivity regions and the electrodeposition region.

## 2. Materials and methods

The Electrochemical Quartz Crystal Microbalance (EQCM) was used to study the electrochemistry of gold oxidation and reduction from thiosulphate solutions in the presence and absence of catalysis. The quartz crystal microbalance (QCM922), electrochemical cell (RG100), and gold plated quartz crystal resonator (QA-A9M-Au) were obtained from Princeton Applied Research. The quartz crystal microbalance instrument QCM 922 was connected to a model 273A (Princeton Research) Potentiostat & Galvanostat. A typical three electrode setup was used with an Ag/AgCl reference electrode, a graphite counter electrode and a gold plated quartz crystal resonator with an exposed electrode surface area of  $0.198$  cm<sup>2</sup> as a working electrode. A newly prepared gold electrode was used for each experiment.

All experiments were conducted at room temperature in near-neutral (pH 7.8) solutions prepared from analytical grade magnesium thiosulphate hexahydrate and ultrapure  $18$  M $\Omega$  (megaohm) cm water. Other reagents used for electrochemical studies included thallium sulphate and thiourea. These reagents were both analytical grade purchased from Alfa Aesar. The solution was gently agitated during potentiodynamic cycling by bubbling nitrogen slowly through the cell. The differences in the resonant fre-

quency of the crystal electrode were recorded as a function of potential and the corresponding mass changes were calculated using the appropriate conversion factor. The potential was measured against the silver/silver chloride reference electrode and converted to the standard hydrogen electrode scale by adding  $0.197$  V to the value. Prior to each experiment, the working electrode (gold-plated crystal) was subjected to electrochemical cleaning by potential cycling in  $0.1$  M NaOH between  $0.945$  and  $-0.125$  V at  $0.1$  V/s until a stable voltammogram was obtained. The last cycle was stopped at the negative potential  $-0.125$  V in order to maintain the surface free of oxides (Pedraza et al., 1988). Each voltammogram presented in this paper has been confirmed by three overlaid voltammograms using an identical electrolyte and testing conditions.

### 2.1. Calibration

The principle of operation of the EQCM is based on recording the resonant frequency change ( $\Delta f$ ) of the quartz crystal as a function of potential. Using the proportional relationship ( $\Delta f = -C_f \Delta m$ ) known as Sauerbrey's equation, the frequency change can be converted into electrode mass change ( $\Delta m$ ). The theoretical value of the conversion factor ( $C_f$ ) is usually known but depends on the medium in which crystal is operating because the density and viscosity of a solution affect the frequency (Bard and Faulkner, 2000). Furthermore, Sauerbrey's equation is applied when the mass added or lost at the oscillator surface does not experience any shear deformation (Deakin and Buttry, 1989) which may be the case for thin, rigid (Bizzotto, 2015) layers forming on the surface. It is always recommended to compare the theoretical value with an experimentally-obtained conversion factor. In order to obtain the experimental value, the method of copper underpotential deposition (Cu-upd) was used. In this method, copper is deposited from  $2$  mM CuSO<sub>4</sub> and  $0.1$  M H<sub>2</sub>SO<sub>4</sub> solution by holding the potential at  $0.3$  V vs. SHE for  $20$  min followed by a linear anodic polarization to record the copper dissolution voltammogram (Lam et al., 2011). This linear anodic sweep for copper dissolution was performed in the potential range  $0.3$ – $1.2$  V vs SHE at  $15$  mV/s scan rate.

The cumulative charge for copper electrodisolution was calculated by integrating the current–potential and was used to determine the experimental calibration constant using the following relationship (Faraday's law applied to Sauerbrey's equation):

$$C_f = \frac{M(\text{Cu})\Delta q}{nF\Delta f} \quad (1)$$

In this relationship,  $F$  is Faraday's constant ( $96484.5$  C equiv<sup>-1</sup>);  $M$  is the atomic weight of Cu ( $63.547$  g mol<sup>-1</sup>); and  $n$  is the number of electrons ( $n = 2$ ).  $\Delta q$  was calculated as the area under the current–time curve ( $8.377\text{E}-05$  C) and  $\Delta f$  ( $30.0295$  Hz) was obtained from the EQCM apparatus. Using experimentally-obtained  $\Delta q$  and  $\Delta f$  values, the experimentally-obtained conversion factor  $C_f$  was calculated as  $1.088$  Hz ng<sup>-1</sup>. The conversion factor provided by Princeton Applied Research was  $1.068$  Hz ng<sup>-1</sup>. The experimental value is only  $1.87\%$  different from the theoretical value, which is considered acceptable.

## 3. Results and discussion

Fig. 1 presents the voltammogram obtained at the stationary gold electrode in the electrolyte of pH 7.8 containing  $0.4$  M magnesium thiosulphate. The potential scan was initiated at open circuit potential (OCP), reversed at approximately  $0.37$  V, continued to a minimum value of  $-0.2$  V, reversed again, and then stopped at the initial potential (OCP). Also shown is the calculated anodic cur-

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