



Electrochemical dissolution of roasted gold ore in cyanide solutions



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ABSTRACT

In free corrosion tests, pure gold (Au) electrode gave more active behaviour than that of roasted gold ore (RGO) electrode. Electrochemical noise measurements of Au electrode generally showed an increasing trend in corrosion rate, while RGO plateaued after the initial 10 h until 24 h. Scanning reference electrode technique, at open circuit potential, showed higher quasi electromotive force for Au than RGO electrode. Optimal leaching conditions for RGO were found to be 0.04 M NaCN concentration, pH 10–10.5, and 250 rpm agitation speed. It was found that in cyanide solutions saturated with atmospheric oxygen, cathodic Tafel slope only ($3.30 \times 10^{-8} \pm 3.27\% \text{ mol m}^{-2} \text{ s}^{-1}$) provides representative corrosion rates of gold for RGO to that in practical cyanidation ($3.07 \times 10^{-8} \pm 7.03\% \text{ mol m}^{-2} \text{ s}^{-1}$). Considering that the anodic curve for Tafel slope or Stern–Geary methods was found to be misleading due to the presence of different constituents. The cathodic reaction on few sites of metallic conductive phase is the rate controlling one. Potentiodynamic scanning of cathodic polarization curve should go directly without cathodic cleaning from corrosion potential to more cathodic ones for both Au and RGO electrodes. SEM analysis indicated that the presence of Fe-oxide products could be the main contributor to the passivation of the gold surface.

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1. Introduction

During cyanidation, leaching of gold is reduced or retarded in some conditions. Since cyanidation is an electrochemical based process (Habashi, 2009), thus dissolution of gold can be readily studied by electrochemical techniques. Recently, Crundwell (2013) claimed that each point on the mineral surface is considered as both an anodic site and a cathodic site and concluded that there is no separation of anodic and cathodic sites on a mineral's surface. Habashi and Bas (2014) pointed out that certain experimental results demonstrated the existence of anodic and cathodic zones during the dissolution of minerals. These findings have revealed that electrochemical studies of gold still receive much attention.

Passivation of gold, diffusion control, and galvanic interactions are considered as important factors affecting the leaching of gold (Azizi et al., 2011; Filmer, 1982). Passivation of gold has been known since 1907 and gold becomes passive under certain conditions in commercial cyanide solution and assumed that the passivity is due to the formation of insoluble sodium aurocyanide film on the surface of gold (Cathro, 1961). Mrkusic and Paynter (1970) identified the passivation as the film formation of dissolved species from calcine while Nicol (1980) reported that passivation of gold mainly depends on the presence of impurities in the solution. It was suggested that gold oxides and cyanide films are responsible for the passivation of the surface of gold (Kirk

et al., 1978). The different types of dissolved minerals found in the ore may have a positive and/or negative effect on the rate of gold dissolution (Jeffrey and Ritchie, 2001; Nicol, 1980). Although many studies have been carried out, there is still a doubt on gold passive phenomenon.

In the present time, it is well known worldwide that there is an increasing trend on the treatment of refractory ores (often requires oxidation prior to cyanidation) due to the rapid depletion in free-milling gold ores (Zhou and Fleming, 2007). Till now, almost all previous electrochemical studies of gold were conducted using only sulphidic gold ores (Aghamirian and Yen, 2005; Azizi et al., 2010, 2011, 2012a,b, 2013; Cruz et al., 2005; Dai and Jeffrey, 2006; Lorenzen and van Deventer, 1992a,b; van Deventer and Lorenzen, 1987; van Deventer et al., 1990). On the other hand, there is a paucity on electrochemical interaction studies between gold and its oxide minerals. At the same time, the influence of agitation was not systematically considered in previous studies. Therefore, an increasing request of the gold mining industry for this issue is created. Furthermore, the corrosion (dissolution) rate of gold was considered from the intersections of anodic and cathodic Tafel slopes (Cerovic et al., 2005). However, Dai and Breuer (2013) showed that using only Evans' diagrams is misleading for gold dissolution estimation. These findings indicate that calculation of corrosion rate of gold is still an important issue.

Based on the above statements, the main objective of this study is to provide a detailed understanding of electrochemical behaviour and optimal leaching conditions (NaCN concentration, pH, and agitation speed) for roasted (oxidized) gold ore, as far as possible, by using conventional and more recent electrochemical techniques such as

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Electrochemical Noise Measurement (ENM) and Scanning Reference Electrode Technique (SRET). ENM is referred to as a random fluctuation of current and/or potentials that has received widely attention to study the electrochemical systems (Eden, 2011) and is used for monitoring active and passive behaviours, and type of corrosion of tested specimen (Lafont et al., 2010; Safizadeh and Ghali, 2013). Although the majority of ENM studies have been carried out in corrosion studies, there is a recent attempt using ENM in leaching studies (Bevilaqua et al., 2006). This method could potentially be an alternative in gold leaching studies for the characterization of surface products that could lead to surface passivation. SRET was considered to contribute to the electrochemical dissolution of gold since SRET in-situ provides significant information on anodic and cathodic potentials of a specimen as a function of time in free corrosion mode (Zhang et al., 2006). It is also possible to analyse the active and passive behaviours of gold with the 3D image facility of SRET. Furthermore, electromotive force of the corrosion cell is calculated by the evaluation of SRET data. This study also investigates the corrosion rate of gold by cathodic Tafel slope, Stern–Geary method, and compared to that obtained by conventional cyanidation. Concurrently, providing an appropriate understanding on the passivation phenomenon of gold is also one of the objectives.

2. Experimental conditions

2.1. Roasted gold ore sample

The gold ore sample was obtained from Barrick Gold Corp. This was the calcine after roasting of refractory gold ore. The sample (which was already reduced in size 80% passing $-75 \mu\text{m}$ (d_{80})) was riffled as portions prior to use in experiments.

Mineralogical analysis of the sample indicates that the ore sample consists predominantly of quartz, dolomite, calcite, gypsum, and iron oxides such as hematite, magnetite, and maghemite and with almost non sulphur content. Gold is mostly associated with iron oxides. Metal analysis of the ore sample by AAS for Au and Ag after hot aqua regia digestion has shown that gold and silver contents are ~ 8 and ~ 5 g/t, respectively.

2.2. Material and preparation of electrodes

NaCN ($\geq 98\%$ purity) was obtained from Thermo Fisher Scientific Company. Electrolyte medium (1 L) was prepared using distilled water and pH was adjusted at 10.5 by adding 1 M NaOH. Electrolyte was magnetically agitated (4 cm long and 1 cm diameter) during the tests. Pure gold (Au), rotating disc (RDE), roasted gold ore (RGO) and its oxide electrodes magnetite (Mag), and hematite (Hem) disc electrodes were used as working electrode while platinum (Pt) as a counter electrode and Ag/AgCl/KCl_{sat} as reference electrode.

1 cm² of gold foil (99.9% purity from Sigma Aldrich), as pure gold electrode (Au), was first polished with fine (MicroCut® 100 Grit Soft) polishing paper and then rinsed in distilled water. Then, it was introduced in aqua-regia for 10 s to clean the surface, washed with distilled water and ethanol and finally rinsed with distilled water again, to assure the reproducibility. Rotating ring disc electrode (RDE), where disc electrode was connected to a rotator, with a surface area of 0.05 cm² gold was obtained from ALS Co., Ltd. (Japan) and was used in certain tests.

Roasted gold ore (RGO), magnetite (Mag), and hematite (Hem) disc electrodes with an exposed surface area of 4.9 cm² were prepared. In each case, roasted gold ore, magnetite, hematite were mixed with graphite powder (to increase the conductivity) 3:1 and with around 0.4 g of silicone oil, for binding, till a paste was obtained. Graphite powder, which has a particle size of $< 45 \mu\text{m}$, and a 99% purity, was obtained from Sigma-Aldrich. The mixture was manually homogenized during 30 min, in general. Then, it was mechanically pressed at 20 t to have uniform sample surface. After that, all disc electrodes were kept under

nitrogen atmosphere over a night. The electrical contact was assured by an insulated copper wire, cast in acrylic resin. Although it is difficult to mimic the practical conditions in laboratory studies (for surface areas), due to the low quantity of gold in its ore, however, the chosen difference in surface areas of electrodes is considerably suitable to see the main tendencies and influences of minerals on gold dissolution.

2.3. Electrochemical test procedures

2.3.1. Open circuit potential (OCP)

In open circuit potential (OCP) or free corrosion potential tests, NaCN concentration was kept at 0.04 M and tests were carried out in 400 mL beakers. Dissolution potential of gold may be influenced either in a positive or negative way due to the presence of soluble ions in the solution. Therefore, to monitor the changes in open circuit (dissolution) potential of gold and roasted gold ore electrodes as function of soluble species, the addition of slurry into the solution was considered to mimic the real leaching conditions. When the tests were conducted in presence of roasted gold ore the solid ratio was adjusted at 35% wt/vol. All the tests were conducted for 24 h. In the case of RDE the electrode was monitored for the first hour. After that, RDE was taken off from the solution and kept under N₂ conditions for the next 22 h to prevent its corrosion. During this period the solution was continually magnetically agitated (100 rpm). After 22 h (23 h since the beginning of experiment), the RDE was again placed into the solution without any change in the potential for 1 h to complete 24 h in total.

2.3.2. Electrochemical noise measurement (ENM)

Prior to electrochemical noise measurement (ENM) tests, two working electrodes were prepared separately following the three steps: cathodic cleaning for 50 min. and potentiodynamic polarization (-0.8 to 1.2 V) and then potentiostatic measurement (at 1 V) for 2 h. The Electrochemical noise measurements were performed in employing a set-up using zero resistance ammeter (ZRA) mode in 0.04 M NaCN solution. In this mode, the electrochemical noise could be measured between two nominally identical working electrodes as the galvanic coupling kept at the same potential. The samples were immersed in the solution where the system was allowed to stand at open circuit for 5 min. Then, the potential and current fluctuations were simultaneously recorded during 24 h at a scan rate of $f_s = 10$ Hz. This scan rate is generally preferred since it is quite enough to have a clear trend in noise data. If a more precise of noise data is requested, then a higher scan rate could be applied, however, the general trend will be same and this does not affect to the noise resistance, in overall. All potentials were measured vs. Ag, AgCl/KCl saturated reference electrode (0.199 V), and reported with respect to Standard Hydrogen Electrode (SHE).

The ENM tests were carried out without agitation and exposed to atmospheric oxygen. A Gamry® PC4/300 potentiostat was used to log current and potential variations in time. The analyses were performed using a GAMRY® PC4 750/ESA400 software and analyser v. 2.35. The DC drift was removed before all analyses to eliminate the trend. At least, three series of tests were performed for each examined sample.

2.3.3. Scanning reference electrode technique (SRET) procedure

Au and roasted gold ore electrodes were mounted horizontally in the cell of SRET apparatus (EG&G Instruments-Model SVP100) for free corrosion potential measurement (Fig. 1). After ensuring that the surface of the specimen was parallel to the surface on the Perspex tripod and levelled, the probe was lowered to a distance of 100 μm above the sample surface, and then the cyanide solution was added. The basic configuration is to connect one input (+ve) to the vibrating probe and the other input (–ve) to a separate reference probe (carbon electrode in this case) placed in the solution local to the surface to be measured. After conditioning of the signal, a rectangular area (18.0 mm by 13.5 mm) was scanned, overlapping slightly the acrylic resin. The

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