



# A comparison of electrochemical methods and the rotating electrochemical quartz crystal microbalance for measuring hydrometallurgical reaction kinetics

M.I. Jeffrey\*, W.L. Choo, P.L. Breuer

*Department of Chemical Engineering, Monash University, Vic, 3800, Australia*

Received 29 November 2001; received in revised form 25 June 2002; accepted 7 August 2002

Available online 9 August 2005

## Abstract

As cementation and most leaching processes are electrochemical in nature, there is an interest in the use of electrochemical methods to estimate the rate at which these reactions occur. Despite this, there has been little work published evaluating methods such as linear polarisation resistance (LPR) in hydrometallurgical applications. In the present paper, the kinetics of a range of different metal leaching and cementation reactions was measured using the rotating electrochemical quartz crystal microbalance. The measured reaction rates were then compared to those calculated using Evans' diagrams and LPR. The accuracy of the Evans' diagrams is limited to instances where the constituent half reactions are independent of each other; examples will be provided where this assumption is valid and invalid. LPR will be shown to be problematic, as the polarisation resistance is a measure of both the Tafel slopes and the reaction rate. Examples will be given where the Tafel slope either varies or is difficult to obtain; in these cases, LPR is of limited value. Another problem with LPR which will be highlighted is when the mixed potential is close to the open circuit potential of one of the constituent half reactions; this leads to the polarisation resistance being a combination of the reaction rate and the exchange current density.

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*Keywords:* Electrochemistry; Leaching; Cementation; Kinetics

## 1. Introduction

It is well known that electrochemistry is a very important aspect of hydrometallurgy. This is because two of the main hydrometallurgy processes, cemen-

tation, and electrowinning, are electrochemical in nature; in most instances, leaching is also an electrochemical process. Of these processes, leaching and cementation are spontaneous reactions, and examples of importance in hydrometallurgy include:

- 1) the leaching of gold in cyanide solutions to form the stable gold cyanide complex (Kudryk and Kellogg, 1954);

\* Corresponding author. Tel.: +61 3 9905 1873; fax: +61 3 9905 5686.

E-mail address: [matthew.jeffrey@eng.monash.edu.au](mailto:matthew.jeffrey@eng.monash.edu.au) (M.I. Jeffrey).

- 2) the removal of cobalt from zinc electrowinning electrolyte using zinc cementation (Raghavan et al., 1999); and
- 3) the recovery of gold from cyanide solutions by zinc cementation (Nicol et al., 1979).

Often one is interested in how rapidly leaching and cementation reactions occur, as this determines the residence time, and hence size of equipment required. Traditionally, leaching and cementation kinetic studies are undertaken using solution analysis, in which the reaction rate is followed by measuring the appearance/disappearance of one or more species to/from solution. The disadvantages of this method include: 1) the rate measured is an average over the sample interval; 2) when using a small rotating disc, long periods are required in order to produce measurable changes in concentration; and 3) the accuracy of the data is limited by the analysis method. As a result of these problems, there has been an interest in electrochemical methods for estimating the reaction rate. The two methods discussed in the present paper are the use of Evans' diagrams, and linear polarisation resistance (LPR). The results obtained using these methods for a variety of systems will be compared to the reaction rate measured using the rotating electrochemical quartz crystal microbalance (REQCM).

## 2. Experimental methods

All experiments were carried out using solutions prepared from analytical grade reagents and distilled water. The composition of the solutions utilised in the present study is shown in Table 1. All experiments were conducted at a rotation speed of 300 rpm, and temperature of 30 °C, with the exception of the cyanide leaching experiments, which were carried out at 25 °C.

Mass changes were measured using the REQCM, which is described elsewhere (Jeffrey et al., 2000). The frequency of the quartz crystal was measured using an Optoelectronics 3000A TCXO hand-held frequency counter, and the mass was simply calculated from the changes in frequency using the Sauerbrey equation. This equation has been found to be accurate when utilising thin rigid metallic films (Jeffrey et al., 2000). Prior to each experiment, the appropriate metal was electrodeposited onto the platinum

Table 1  
Solution conditions utilised in the present study

System	Other conditions
Gold/silver leaching in 20 mM CN <sup>-</sup>	0.05 M NaHCO <sub>3</sub> , pH 10.3, 2 ppm lead, 20 mM NaCN.
Gold/silver leaching in 2 mM CN <sup>-</sup>	0.05 M NaHCO <sub>3</sub> , pH 10.3, 2 ppm lead, 2 mM NaCN.
Gold leaching in 2 mM CN <sup>-</sup>	0.05 M NaHCO <sub>3</sub> , pH 10.3, 2 mM NaCN.
Silver cementation from thiosulfate	0.1 M Na <sub>2</sub> SO <sub>4</sub> , 0.01 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 0.1 M NH <sub>3</sub> , 0.93 mM AgNO <sub>3</sub> (100 ppm Ag(I)).
Silver cementation from cyanide	0.05 M NaClO <sub>4</sub> , 4 mM K <sub>2</sub> CO <sub>3</sub> , 7.7 mM KCN, 0.93 mM AgCN (100 ppm Ag(I)).
Gold cementation from thiosulfate	0.1 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 0.1 M NH <sub>3</sub> , 0.76 mM Na <sub>3</sub> Au(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O (150 ppm Au(I)).

coated quartz electrode. The plating conditions for each metal used in the present paper are shown in Table 2. The alloy containing 95% gold and 5% silver will be referred to as gold/silver for simplicity.

The linear sweep voltammetry and linear polarisation resistance (LPR) experiments were performed using an EG and G PAR 362 potentiostat connected to a data acquisition card and PC. During LPR measurements, the potential was varied by 10 mV negative and positive of the mixed potential at a scan rate of 0.2 mV s<sup>-1</sup>. The polarisation curves were recorded at a scan rate of 0.5 mV s<sup>-1</sup>. All potentials were measured relative to the saturated calomel electrode (+0.242 V vs. SHE), but are reported relative to the SHE. A platinum wire was used as the counter electrode.

## 3. Results and discussion

### 3.1. Gold/silver leaching in solutions containing 20 mM cyanide and 2 ppm lead

The first system which was studied was the leaching of a gold/silver sample in a solution containing 20 mM cyanide and 2 ppm lead. This system was chosen, as the leaching reaction is oxygen diffusion controlled (Jeffrey and Ritchie, 2000b), and as will be shown, electrochemical methods for estimating the reaction rate are more reliable when the reaction is diffusion limited. The first task was to measure the actual reaction rate using the REQCM; other studies

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