



Mechanism and kinetics of gold leaching by cupric chloride



Matti Lampinen ^{a,*}, Sipi Seisko ^b, Otto Forsström ^b, Arto Laari ^a, Jari Aromaa ^b,
Mari Lundström ^b, Tuomas Koironen ^a

^a Lappeenranta University of Technology, LUT School of Engineering Science, P.O. Box 20, FI-53851 Lappeenranta, Finland

^b Aalto University, School of Chemical Technology, Department of Materials Science and Engineering, P.O. Box 16200, 00076 Aalto, Helsinki, Finland

ARTICLE INFO

Article history:

Received 10 May 2016

Received in revised form 6 December 2016

Accepted 15 December 2016

Available online 18 December 2016

Keywords:

Leaching of gold

Cupric chloride

Reaction mechanism

Kinetics

Mechanistic modeling

ABSTRACT

A non-cyanide lixiviant for gold dissolution, cupric chloride, was studied. The work used a rotating disk electrode technique to investigate the dissolution reaction mechanism and kinetics of gold dissolution in concentrated chloride (3 M) solution with cupric ion concentration in the range 0.02–1.0 M and temperature 65–95 °C. A reaction mechanism including a disproportionation step of Au(I) is proposed. Increase in the gold dissolution rate was found to be proportional to temperature and cupric ion concentration up to 0.5 M. The dissolution rate was observed to decrease with cupric ion concentration of 1.0 M. A mechanistic kinetic model was developed to study the rate-controlling steps in the dissolution process. Uncertainties in the model parameters of the mechanistic kinetic model were studied with Markov chain Monte Carlo (MCMC) methods. The modeling results showed that the gold dissolution is mainly under mixed control, where both the intrinsic surface reaction and mass transfer have an effect on the overall dissolution rate.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Cyanidation is currently the prevailing technology in gold production. However, many factors are forcing the precious metal industry to reconsider the use of cyanide as a lixiviant. Interest in the use of non-cyanide methods for gold dissolution arises primarily from concerns regarding the toxicity of cyanide and the inability of cyanide solution to effectively leach gold from complex ores. A number of alternatives to cyanide have been presented (Hilson and Monhemius, 2006) such as thio-sulfate, halides, thiourea and thiocyanate. In recent years, thio-sulfate (Feng and van Deventer, 2010; Lampinen et al., 2015a; Xu et al., 2016), chloride (Hasab et al., 2013, 2014; Nam et al., 2008) and thiourea (Jing-ying et al., 2012; Gönen et al., 2007) have received the greatest attention.

Chloride leaching can be considered to be a promising alternative to cyanide leaching that overcomes problems regarding toxicity and offers a possibility for direct refractory ore leaching (Lundström et al., 2015). Gold production with chloride leaching has been investigated with both primary (Hyvärinen et al., 2004; Pangum and Browner, 1996) and secondary raw material (Yazici and Deveci, 2015; Nam et al., 2008). Cupric chloride leaching of gold has also been investigated as a following step for copper sulfide leaching processes such as Intec (Moyes, 2002), HydroCopper™ (Haavanlammi et al., 2007), and Nippon N-Chlo/NIKKO (Ishiguro et al., 2008). The advantage of this kind of

process is that the cupric ions can be considered a natural and self-propagating oxidant for the leaching process. Thus, chloride leaching with Cu^{2+} as the oxidant would appear to be a promising alternative to cyanidation. However, only a limited amount of published data is available about gold dissolution behavior and kinetics in chloride solutions with Cu^{2+} as the oxidant.

Nikoloski and Stockton (2000) reviewed oxidation of gold and its complexation in acidic aqueous chloride solutions and based on previous studies (Gallego et al., 1975; Nicol, 1980; Marsden and House, 1992; Schmid, 1985; Lide and Frederikse, 1997) presented that both Au(I) and Au(III) species are formed by anodic half reactions given as:



Nicol (1980) presented that electrochemical dissolution of gold in acidic chloride solutions takes place at potentials below 1.2 V with the formation of both Au(I) and Au(III) species. It has been reported that at potentials below 0.8 V gold dissolves as Au(I) species, while at potentials above 1.1 V it forms Au(III) species (Frankenthal and Siconolfi, 1982).

Several reaction mechanisms have been proposed (Diaz et al., 1993; Kozin and Melekhin, 2004; von Bonsdorff et al., 2007; Putnam, 1944; Nicol, 1980) for gold dissolution in aqueous chloride solutions. The electrochemistry of gold in acid chloride solutions has been studied to investigate corrosion behavior, to define the reactions and mechanisms involved in the electrorefining process, and to examine the leaching of

* Corresponding author.

E-mail address: matti.lampinen@lut.fi (M. Lampinen).

gold. Studies have been carried out under many different conditions and with many different solutions. Cupric chloride leaching for gold production has been studied by von Bonsdorff et al. (2005, 2006, 2007) and by McDonald et al. (1987). Von Bonsdorff et al. (2005) conducted electrochemical measurements to obtain the dissolution rate of gold in Outotec HydroCopper™ process solution and presented that the dissolution rate of gold increases with increasing cupric ion concentration, increasing chloride concentration and increasing temperature. Von Bonsdorff et al. (2007) proposed a simplified reaction mechanism for gold oxidation, in which gold is dissolved as trivalent auric ions. McDonald et al. (1987) and von Bonsdorff et al. (2007) presented that the effect of pH on the dissolution rate of gold is negligible as long as the solution is sufficiently acidic ($\text{pH} < 3$).

While the mechanism of gold dissolution is important, it is the kinetics that determines whether the dissolution can be carried out in a time frame acceptable for industrial application. Marsden and House (1992) presented that the mass transport of chloride ions to the surface is the rate-determining step, and that the chemical reaction step is fast in gold dissolution in chloride solutions. Nikoloski and Stockton (2000) argued that gold dissolution in chloride solutions is controlled by diffusion of either the chlorine (oxidant) or chloride (complexant) ion through the Nernst boundary layer to the gold surface. Jeffrey et al. (2001) presented that the chloride concentration used in chloride leaching is usually very high (~100 g/L), and hence the dissolution rate is ultimately limited by the diffusion of the oxidant. However, it was argued by von Bonsdorff et al. (2005, 2007) that the reaction rate is under mixed control and, both charge transfer and mass transfer influence the rate of gold dissolution.

It is evident that the mechanism and kinetics of gold chloride leaching are not yet fully-understood and there is thus a need for further studies. In this work, experimental data from rotating disk electrode (RDE) experiments are used to study the gold leaching mechanism and gold leaching kinetics in chloride solution in the presence of Cu^{2+} . An electrochemical technique was chosen to study the kinetics and gold leaching mechanism because such approaches enable study without undue interference from factors such as the matrix of the leaching solution and the ore/concentrate mineralogy. As presented above, it would appear that the reaction rate is under mixed control. In the case of mixed control in which the leaching rate has both intrinsic surface reaction rate and mass transfer limitations, it is necessary to separate these effects. For this purpose, a mechanistic kinetic model was developed to evaluate the intrinsic gold reaction rate at the gold surface and the mass transfer limitations. The developed model includes kinetic parameters that need to be estimated from measured data. Parameter estimates are often uncertain since they are estimated from incomplete and noisy measurements. Hence, the uncertainty of the model parameters of the developed mechanistic model was evaluated with Markov chain Monte Carlo (MCMC) methods.

2. Materials and procedures

RDE experiments were carried out to study gold dissolution phenomena and the rate controlling steps. A total chloride concentration of 3 mol/L, which can be considered to be very high, was used in all experiments, thus guaranteeing that the leach rate is ultimately limited by diffusion of the oxidant (Jeffrey et al., 2001). The solution pH was adjusted to 1.0 in every experiment by adding HCl (1.0 M). The cupric ion concentrations used were 0.02, 0.1, 0.5 and 1.0 M. The calculated concentration of the AuCl_2^- complex varied from 1.6×10^{-8} M to 8.3×10^{-7} M, which indicates that the concentration of cuprous ions formed in the leaching process (Eq. (8)) is relatively small compared to the cupric ions. Hence, it is justified to assume that the effect of cuprous ions in the current conditions is negligible. The temperatures used were 65, 75, 80, 85, 88, 92 and 95 °C. Gas was not added to the system during the experiments since it would have disrupted the RDE measurements. However, the possible effect of dissolved oxygen can

be considered to be negligible, since the average redox potential for cupric concentration range from 0.02 to 1.0 M was 0.449 ± 0.003 V with air sparge and 0.446 ± 0.004 V with nitrogen sparge at $T = 25$ °C. Furthermore, at $T = 95$ °C, the average redox potential for cupric concentration range from 0.1 to 1.0 M was 0.595 ± 0.013 V with air sparge and 0.610 ± 0.009 V with nitrogen sparge. Hence, it can be concluded that dissolved oxygen does not affect gold dissolution in the system. The chemicals used were NaCl and $\text{CuCl}_2 \times 2 \cdot \text{H}_2\text{O}$, supplied by VWR and of technical grade.

The RDE measurements were performed in a water-jacketed three electrode cell with volume of 200 mL (a water bath, Lauda M3, was used for heating). The volume of solution used was 110 mL. A gold rotating electrode (Pine Research Instrumentation Inc.) was used as the working electrode, and a pure platinum plate as the counter electrode. The diameter of the gold disc was 4.08 mm, and the disc was attached into a polytetrafluoroethylene (PTFE) sheath. An Ag/AgCl electrode from SI Analytics with a potential of 197 mV vs. standard hydrogen electrode (SHE) was used as the reference electrode (Bard and Faulkner, 1980).

Linear polarization resistance (LPR) can be determined from RDE measurement. LPR is inversely related to the corrosion current density of the working electrode. The LPR measurements were executed with ACM Instrument's Gill AC potentiostat using an LPR sweep program with Gill AC Sequencer software. The LPR measurements were performed from 10 mV below the rest potential to 10 mV above the rest potential. Three replicate measurements were conducted for every condition in order to avoid random errors. In addition, several impedance measurements were performed to ensure that uncompensated ohmic resistance did not cause errors in LPR determination.

The LPR value can be determined as the slope of the potential-current density diagram. When the LPR value increases, the current density decreases and, therefore, the dissolution rate also decreases. Eq. (3) shows the proportionality between LPR and the corrosion current density, j_{corr} , i.e. the current density at open circuit potential (OCP) (Stern and Geary, 1957):

$$j_{\text{corr}} = \frac{b_a b_c}{2.303(b_a + b_c)} \times \frac{1}{R_p} = \frac{B}{R_p} \quad (3)$$

where b_a is the Tafel slope coefficient of the anodic side (mV/decade), b_c the coefficient of the cathodic side (mV/decade), B the systematic coefficient (mV) and R_p the LPR ($\Omega \text{ cm}^2$). Since the sweep range is very short in the LPR measurements, the Tafel method cannot be used to interpret the LPR data. However, the value of B was calculated from separate Tafel measurements and its value was found to be 13.5 ± 0.5 mV. From these RDE measurements, the obtained values of the corrosion current density were converted into dissolution rates with a unit g/s/m².

3. Results and discussion

3.1. Reaction mechanism of gold dissolution

Many studies (Nicol, 1980; Frankenthal and Siconolfi, 1982; Diaz et al., 1993) have presented that gold forms aurous Au(I) and/or auric Au(III) ion complexes with chloride ions depending on the chloride concentration and electrode potential. According to Diaz et al. (1993), gold dissolves as an $[\text{AuCl}_2]^-$ complex with oxidation state +1, when the potential is 0.8 V vs. SCE and also as $[\text{AuCl}_4]^-$ complex with oxidation state +3 at higher potentials. Frankenthal and Siconolfi (1982) suggested that gold dissolves as aurous ions when the potential is below 0.8 V vs. SCE, but as auric Au(III) ions when the potential is above 1.1 V vs. SCE. Furthermore, Nicol (1976b) proposed that $[\text{AuCl}_2]^-$ complexes oxidize into $[\text{AuCl}_4]^-$ complexes in a disproportionation reaction.

Corrosion potentials and a plot of logarithmic corrosion current density as a function of logarithmic cupric concentration were used in the current work to determine the oxidation state of the gold. With cupric

Download English Version:

<https://daneshyari.com/en/article/4769316>

Download Persian Version:

<https://daneshyari.com/article/4769316>

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