

Kinetics and mechanisms of gold dissolution by ferric chloride leaching

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

^a Aalto University, School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, P.O. Box 16200, 00076 Aalto, Helsinki, Finland

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

ARTICLE INFO

Keywords:

Gold leaching
RDE
Oxidant concentration
Modeling
Markov chain Monte Carlo

ABSTRACT

Gold dissolution was investigated in ferric chloride solution, being one alternative cyanide-free leaching media of increasing interest. The effect of process variables ($[Fe^{3+}] = 0.02\text{--}1.0\text{ M}$, $[Cl^-] = 2\text{--}5\text{ M}$, $pH = 0\text{--}1.0$, $T = 25\text{--}95\text{ }^\circ\text{C}$) on reaction mechanism and kinetics were studied electrochemically using rotating disk electrode with $\omega_{cyc} = 100\text{--}2500\text{ RPM}$ and Tafel method. The highest gold dissolution rate ($7.3 \cdot 10^{-4}\text{ mol m}^{-2}\text{ s}^{-1}$) was achieved at $95\text{ }^\circ\text{C}$ with $[Fe^{3+}] = 0.5\text{ M}$, $[Cl^-] = 4\text{ M}$, $pH = 1.0$ and $\omega_{cyc} = 2500\text{ RPM}$. Increase in gold dissolution rate was observed with increase in temperature, ferric ion concentration and chloride concentration, but gold dissolution rate did not have a clear dependency on pH. Redox potential was found to vary between 636 and 741 mV vs. SCE during experiments. According to the calculated equilibrium and measured open circuit potentials, gold was suggested to dissolve as aurous ion Au^+ and form $AuCl_2^-$, rather than auric ion Au^{3+} and form $AuCl_4^-$. Further, it is suggested that $AuCl_2^-$ does not oxidize to $AuCl_4^-$ under the investigated conditions. Levich plot and the calculated activation energies suggested that gold dissolution was limited by mass and electron transfer. According to a mechanistic kinetic model developed in the current work, intrinsic surface reaction mainly controls gold dissolution, especially at higher rotational speeds ($> 1000\text{ RPM}$). Uncertainties in the model parameters of the mechanistic kinetic model were studied with Markov chain Monte Carlo methods.

1. Introduction

Cyanide leaching is the predominant method used in gold production from primary raw materials (Marsden and House, 2006) regardless of the toxic nature of the chemical posing a significant health threat if exposed to the ecological entities (Hilson and Monhemius, 2006). Since the Baia Mare disaster in Romania in 2000, the use of cyanide has been the subject of international concern (UNEP/OCHA, 2000). Moreover, several countries have started to ban cyanidation via legislation, e.g., Costa Rica, many states of the USA and provinces within Argentina (Laitos, 2012). Therefore, alternative solutions, such as thiourea, thio-sulphate, oil-coal agglomerates as well as halides have been proposed to replace cyanide (Adams, 2016; Aromaa et al., 2014; Aylmore, 2005; Hilson and Monhemius, 2006; Lampinen et al., 2015a).

Halide gases (Cl_2 and Br_2) have been industrially used since the 19th century in gold ore leaching due to their oxidative nature and ability for gold complexation by Cl^-/Br^- ions in solution originating from Cl_2 and Br_2 gases (Kirke Rose, 1898). The disadvantage in the use of halide gases is that they are expensive, strongly corrosive, and requires high focus on safety and storing during operation. In addition, the use of halide gases can induce high redox potentials that result in gold passivation (Abe and Hosaka, 2010).

Chloride leaching provides major advantages for hydrometallurgical processing, as it supports high metal solubility, enhanced redox potentials and high leaching rates (Liddicoat and Dreisinger, 2007). According to Abe and Hosaka (2010), ferric ion can be an effective oxidant in chloride media for gold leaching, gold dissolution occurring at lower redox potentials compared to chlorine and aqua regia leaching. A redox potential of $\geq 480\text{ mV}$ (vs. Ag/AgCl) is required in ferric chloride leaching compared with typical redox potentials of $\geq 778\text{ mV}$ (vs. Ag/AgCl) in chlorine/bromine gas leaching (Abe and Hosaka, 2010). Ferric and cupric chloride leaching can have advantage over cyanidation being capable for refractory gold mineral leaching, without pre-treatment like pressure oxidation or roasting (Angelidis et al., 1993; Marsden and House, 2006; Lundström et al., 2014; van Meersbergen et al., 1993). According to Aylmore (2005), 4% of publications for alternative lixivants to cyanide in gold leaching were under category oxidative chloride processes including aqua regia and acid ferric chloride. Further, some patents have been subjected for ferric chlorides for gold leaching (Abe and Hosaka, 2010; Lundström et al., 2016).

Gold can be present in aqueous chloride solution as either in monovalent aurous form Au^+ or trivalent auric form Au^{3+} (Marsden and House, 2006). Putnam (1944) suggested that the dissolution of gold proceeds in two steps: formation of intermediate $AuCl_2^-$ occurs by

* Corresponding author.

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

Nomenclature

List of symbols

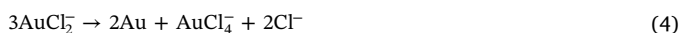
A	area of the electrode (mm^2 or cm^2)
b_a	Tafel slope coefficient of the anodic side (mV decade^{-1})
b_c	Tafel slope coefficient of the cathodic side (mV decade^{-1})
B	systematic coefficient (mV)
C_O^*	concentration of oxidant in bulk solution (mol cm^{-3})
$c_{\text{Cl}^-,\text{blk}}$	concentration of the chloride ion at liquid bulk phase (mol L^{-1})
$c_{\text{Fe}^{3+},s}$	concentration of the oxidant at the disc surface (mol L^{-1})
d	rotating disc diameter (m)
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
D_O	diffusion coefficient of oxidant ($\text{cm}^2 \text{s}^{-1}$)
E_a	activation energy (J mol^{-1})
E^0	standard potential (V)
F	Faraday's constant (C mol^{-1})
i	sum of the currents (mA cm^{-2})
i_K	electron transfer-limited current (mA cm^{-2})
$i_{\text{lim},c}$	diffusion-limited cathodic current (mA cm^{-2})
j_{corr}	corrosion current density (A cm^{-2})
k	reaction rate constant
k_L	mass transfer coefficient through the boundary layer

k_{mean}	rate constant at the reference temperature ($(\text{m}^3 \text{kmol}^{-1})^{n-1} \text{m s}^{-1}$)
n	reaction order for the oxidant
ω_{rad}	angular speed of the electrode (rad s^{-1})
ω_{cyc}	rotational speed of the electrode (RPM)
$n_{\text{Fe}^{3+}}$	mass transfer of the Fe^{3+} through the boundary layer ($\text{mol m}^{-2} \text{s}^{-1}$)
r_s	surface reaction rate ($\text{mol m}^{-2} \text{s}^{-1}$)
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
Re	Reynolds number
R_p	linear polarization resistance (LPR) (Ωcm^2)
Sc	Schmidt number
Sh	Sherwood number
T	temperature (K)
T_{mean}	reference temperature (K)
z	the number of transferred electrons during reaction

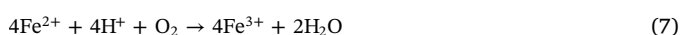
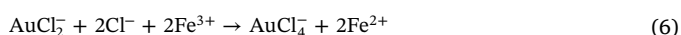
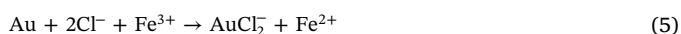
Greek symbols

γ	stoichiometric coefficient of Fe^{3+} to oxidize 1 mol of gold
μ	solution dynamic viscosity (mPa s)
ν	solution kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$)

anodic reaction at the gold surface, Eq. (1), after which AuCl forms a more stable complex AuCl_2^- , Eq. (2). AuCl_2^- is the prevailing species at oxidation potentials < 1.2 V vs. Standard Hydrogen Electrode (SHE), whereas oxidation further into AuCl_4^- can occur at oxidation potentials > 1.2 V vs. SHE (0.956 V vs. SCE), Eq. (3) (Nicol, 1980). According to Diaz et al. (1993), gold dissolves as an AuCl_2^- complex with an oxidation state +1, when the potential is 0.8 V vs. Saturated Calomel Electrode (SCE) (1.044 V vs. SHE) and also as AuCl_4^- complex with oxidation state +3 at higher potentials. Frankenthal and Siconolfi (1982) also suggested that gold dissolves as aurous ions Au^+ , when the potential is below 0.8 V vs. SCE, but as auric Au^{3+} ions, when the potential is above 1.1 V vs. SCE. Furthermore, Diaz et al. (1993) proposed that AuCl_2^- complexes can oxidize into AuCl_4^- complexes by a very slow disproportionation reaction (Eq. (4)).



The net reaction of gold dissolution in ferric chloride solution is described in Eq. (5) according to the gold dissolution steps by Putnam (1944) and Liu and Nicol (2002). Furthermore, the net reaction of AuCl_2^- oxidizing into AuCl_4^- ions is presented in Eq. (6) (Liu and Nicol, 2002). The regeneration of ferrous ions back to ferric ions or ferric chloride complexes can be achieved by oxygen purging, Eq. (7) (Abe and Hosaka, 2010; Liu and Nicol, 2002; Lu and Dreisinger, 2013; Senanayake, 2004). This reuse of oxidant via regeneration is a major advantage in chloride leaching (Abe and Hosaka, 2010).



Ferric ion can exist in chloride solutions in ionic form, but also with increasing chloride concentration as chloride complexes such as FeCl_2^+ , FeCl_2^+ and $\text{FeCl}_3(\text{aq})$ (Muir, 2002). Further, Strahm et al. (1979) demonstrated that the amount of Fe^{3+} species reduced and the

amount of FeCl_2^+ , FeCl_2^+ , $\text{Fe}(\text{H}_2\text{O})\text{Cl}_2^+$ as well as $\text{FeCl}_3(\text{aq})$ species increased, when chloride concentration increased. Their results suggested that Fe^{3+} species are predominant with chloride concentration from 0 to 2 M, FeCl_2^+ from 2 to 5 M and $\text{FeCl}_3(\text{aq})$ above 5 M (Strahm et al., 1979). According to O'Melia (1978), ferric ions occur predominantly as chloro complexes, when ferric ion concentration is between 0 and 1 M and pH below 2. In the temperature range 0–100 °C, the equilibrium constant (K) for FeCl_2^+ formation is 29–72 and for FeCl_2^+ formation $K = 10^{13}$ – 10^{15} (HSC 8.1, 2015). This suggests that as long as enough chloride ions are present the ferric iron will be in chloride complexes.

Many process variables, such as temperature, ferric iron and chloride concentration as well as pH, can affect the dissolution of gold. According to Liu and Nicol (2002) increase in temperature, chloride concentration and ferric to ferrous ratio improves gold dissolution in ferric chloride pressure leaching. Different temperature ranges have been investigated and/or suggested for ferric chloride leaching: ≤ 85 °C (Abe and Hosaka, 2010), 90–100 °C (Lundström et al., 2016) and 25–200 °C in pressurized conditions (Liu and Nicol, 2002). Abe and Hosaka (2010) suggested the optimal ferric ion concentration in chloride leaching being 0.01–0.26 g L^{-1} (0.0002–0.0047 M), whereas Lundström et al. (2016) suggested ferric ion concentration of 9–20 g L^{-1} (0.16–0.36 M) being advantageous. In chloride solutions, the oxidation of base metal sulfides generally results in elemental sulfur formation at pH values close to 1.5 (Lundström et al., 2008; Lundström et al., 2009). This may result in the formation of layers that prevent gold dissolution (Abe and Hosaka, 2010).

von Bonsdorff (2006) used a maximum chloride concentration of 5.0 M for gold leaching, while Lundström et al. (2016) stated that the chloride concentration in ferric chloride leaching process can be below 120 g L^{-1} (< 3.39 M). However, it must be noted that the optimal chloride concentration depends on raw material, with increasing impurities present, higher amount of chlorides are complexed with base and precious metals dissolved into the solution.

Investigations by Abe and Hosaka (2010), also showed that pH lower than 1.9 favors soluble iron during ferric chloride leaching, whereas at higher pH iron precipitates as hydroxides. The solubility of iron increases with decreasing pH, and it has been stated that the pH must be ≤ 1.9 in order to ensure that the iron is at least partially soluble

Download English Version:

<https://daneshyari.com/en/article/6672656>

Download Persian Version:

<https://daneshyari.com/article/6672656>

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