



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Seisko, Sipi; Aromaa, Jari; Lundström, Mari

# Features affecting the cupric chloride leaching of gold

Published in: Minerals Engineering

DOI: 10.1016/j.mineng.2019.03.030

Published: 15/06/2019

Document Version Publisher's PDF, also known as Version of record

Published under the following license: CC BY-NC-ND

Please cite the original version:

Seisko, S., Aromaa, J., & Lundström, M. (2019). Features affecting the cupric chloride leaching of gold. *Minerals Engineering*, 137, 94-101. https://doi.org/10.1016/j.mineng.2019.03.030

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

Contents lists available at ScienceDirect





# Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

# Features affecting the cupric chloride leaching of gold

### Sipi Seisko, Jari Aromaa, Mari Lundström\*



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

#### ARTICLE INFO

Keywords: Gold dissolution RDE Cyclic voltammetry Mixed potential theory ABSTRACT

The current study investigated gold dissolution in cupric chloride solution, which is one of the most promising alternatives to replace cyanide, although not yet in operation on industrial scale. In this paper, the gold dissolution reaction rate and mechanism were studied by varying the process variables of temperature (28-95 °C), cupric concentration (0.02-1.0 M), chloride concentration (1-5 M), rotational speed (100-2500 RPM), and pH (0.5-2.0). The parameters affecting either the anodic or cathodic reaction, or both, were identified for the first time to the best of the authors' knowledge in this wide range and with these parameter intervals. Tafel and linear polarization methods as well as cyclic voltammetry were used for pure gold with both rotating disk and stationary gold electrodes. An increase in the gold dissolution rate was observed with an increase in temperature, chloride concentration, and rotational speed. Additionally, an increase in cupric concentration  $([Cu^{2+}] = 0.02 - 0.75 \text{ M})$  promoted the gold dissolution rate, whereas the gold dissolution rate decreased with  $[Cu^{2+}]$  from 0.75 to 1.0 M. The conditions for maximizing the gold dissolution rate in cupric chloride solution were concluded to be T > 55 °C,  $[Cu^{2+}] = 0.5-0.75$  M,  $[Cl^{-}] = 5$  M, and pH = 1.0 and the highest gold dissolution rate  $(2.9 \cdot 10^{-4} \text{ mol m}^{-2} \text{s}^{-1})$  was achieved at 95 °C with  $[Cu^{2+}] = 0.5 \text{ M}, [Cl^{-}] = 5 \text{ M}, pH = 1.0$ , and  $\omega_{cvc}$  = 2500 RPM. The pH was shown not to affect the gold dissolution rate at all, but only to affect the solubility of the oxidant. It was suggested that gold dissolved as aurous species in the conditions of this study, although the increase in chloride concentration promoted the dissolution of gold as both, auric and aurous, species.

The reaction mechanism was interpreted using mixed potential theory. An increase in temperature was shown to promote only the cathodic reduction of cupric ion to cuprous at lower temperatures (28–55 °C); however, both the anodic gold dissolution reaction and cathodic cupric reduction reaction were enhanced at higher temperatures (65–95 °C). The cathodic reaction was also enhanced with an increase in cupric concentration (0.02–0.5 M), whereas the anodic reaction was promoted when the cupric concentration was increased from 0.5 to 0.75 M. When the cupric concentration was increased from 0.75 to 1.0 M, the cathodic reaction rate decreased. However, the reason for the decrease in the cathodic reaction rate was not clear. An increase in cubric concentration are specifically at low rotational speed (i.e., improved mass transfer) increased the anodic gold dissolution rate, specifically at low rotational speeds.

#### 1. Introduction

Nowadays, cyanide leaching is the predominant process in gold production from primary raw materials (Adams, 2016; Aylmore, 2005; Marsden and House, 2006). Alternative gold leaching methods are being intensively investigated and developed, since there is only one cyanide-free process currently operating with thiosulfate at Barrick in the USA (Helm et al., 2009). Due to a possible environmental risk in the form of an unacceptable cyanide spill, the use of cyanide has raised international concern and several countries and territories have started to ban it via legislation (Laitos, 2012). Although many alternative solutions, such as thiourea, thiosulfate, ammonia, oil-coal agglomerates as well as halides, have been investigated in order to replace cyanide as a lixiviant, chloride solutions have been suggested to be among the most promising (Adams, 2016; Aromaa et al., 2014; Aylmore, 2005; Hilson and Monhemius, 2006). According to Aylmore (2005), 4% of publications on alternative lixiviants to cyanide in gold leaching were classified as oxidative chloride processes. Further, some patents have been filed for cupric chlorides in gold leaching (Abe and Hosaka, 2010; Lundström et al., 2016). Cupric chloride complexes have been shown to provide the high oxidative power required for gold oxidation (Abe and Hosaka, 2010; Lundström et al., 2016), whereas chlorides can complex

\* Corresponding author.

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

https://doi.org/10.1016/j.mineng.2019.03.030

Received 13 December 2018; Received in revised form 18 March 2019; Accepted 27 March 2019

0892-6875/ © 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/BY-NC-ND/4.0/).

the gold ion (Aromaa et al., 2014). Cupric chloride, as a halide leaching method, has an advantage over cyanidation as it is capable of leaching refractory gold minerals, without pre-treatment like pressure oxidation or roasting (Angelidis et al., 1993; Lundström et al., 2015; Marsden and House, 2006; van Meersbergen et al., 1993). Chloride solutions are also known to pose challenges with corrosive and oxidative nature, which increases the cost related to construction materials on industrial scale. Lundström et al. (2015) found Ti Gr. 2 being resistant towards uniform and localized corrosion in highly aggressive chloride solution ([*HCl]* = 10 g dm<sup>-3</sup>, [*Cu*<sup>2+</sup>] = 100 g dm<sup>-3</sup>, [*Fe*<sup>3+</sup>] = 5 g dm<sup>-3</sup>, [*Cl*<sup>-</sup>] = 230 g dm<sup>-3</sup>, [*NaBr*] = 100 g dm<sup>-3</sup>, *T* = 90 °C) during 4 weeks immersion. In addition, chlorides may challenge the process water balance. Therefore, the costs related to the processing may motivate the applications with higher grade raw materials.

Gold can be present in aqueous chloride solution either in monovalent aurous Au<sup>+</sup> or trivalent auric Au<sup>3+</sup> form (Marsden and House, 2006). Many studies (Putnam, 1944; Nicol, 1980; Frankenthal and Siconolfi, 1982; McDonald et al., 1987; Diaz et al., 1993) have shown that gold forms aurous and/or auric ion complexes with chloride ions depending on the chloride concentration and electrode potential. Frankenthal and Siconolfi (1982) suggested that in [NaCl] = 0.1-5.4 M  $([Cl^-] = 0.06-3.28 \text{ M})$  gold dissolves as aurous ions when the potential is below 0.8 V vs. saturated calomel electrode (SCE), but as auric ions when the potential is above 1.1 V vs. SCE. These reactions of gold dissolution in cupric chloride solution are described in Eqs. (1) and (2) (McDonald et al., 1987). The regeneration of cuprous species back to cupric can be conducted by oxygen purging as represented in Eq. (3) (Abe and Hosaka, 2010). This reuse of oxidant via regeneration is a major advantage of chloride leaching (Abe and Hosaka, 2010). McDonald et al. (1987) concluded that cupric ions could be described to act as a catalyst for oxidation as the regeneration of cuprous ions is reasonably fast in the presence of oxygen and acid. Therefore, combined overall reactions are described in Eqs. (4) and (5), in which  $Cu^+/$  $Cu^{2+}$  reactions (Eqs. (1)–(3)) are implicitly included.

$$Au + 2Cl^{-} + Cu^{2+} \rightarrow AuCl_{2}^{-} + Cu^{+}$$
(1)

 $Au + 4Cl^{-} + Cu^{2+} \rightarrow AuCl_{4}^{-} + Cu^{+}$ <sup>(2)</sup>

 $4 Cu^{+} + 4H^{+} + O_2 \rightarrow 4 Cu^{2+} + 2 H_2O$ (3)

 $4 \text{ Au} + 4\text{H}^{+} + \text{O}_{2} + 8\text{Cl}^{-} \rightarrow 4 \text{ Au}\text{Cl}_{2}^{-} + 2 \text{ H}_{2}\text{O}$ (4)

$$4 \text{Au} + 12\text{H}^+ + 3 \text{O}_2 + 16\text{Cl}^- \rightarrow 4 \text{AuCl}_4^- + 6 \text{H}_2\text{O}$$
 (5)

However, it should be noted that the equations above are simplifications, as cuprous and cupric copper prevails commonly in chloride solutions in a complex form. The prevailing complex depends on temperature (Collings et al., 2000) and chloride concentration (McDonald et al., 1987). Zhang et al. (2014) stated that the amount of cupric complexes, such as CuCl<sup>+</sup>, CuCl<sub>2</sub><sup>0</sup>, CuCl<sub>3</sub><sup>-</sup>, and CuCl<sub>4</sub><sup>2-</sup>, increased as the chloride concentration increased from 0 to 5.57 M, when  $[Cu^{2+}] = 0.0005 \text{ M}$  and  $T = 25 ^{\circ}\text{C}$ . The relative increase in complex concentration was smaller when the complex contained a higher amount of chlorides. Cu<sup>2+</sup> was suggested to be the predominant cupric species up to  $[Cl^{-}] = 3$  M. According to Bjerrum (1987), the cupric ions occurred as  $CuCl_2^0$ ,  $CuCl^+$ ,  $CuCl_3^-$ ,  $Cu^{2+}$  and  $CuCl_4^{2-}$  in decreasing order of magnitude in acidic conditions when [NaCl] = 5 M. Further, cupric ions were suggested to occur as CuCl<sub>2</sub><sup>0</sup>, CuCl<sup>+</sup>, and Cu<sup>2+</sup> with the species containing the highest amount of chlorides predominating more when  $[Cu^{2+}] = 0.1 \text{ M}$ ,  $[Cl^{-}] = 6 \text{ M}$ , and T = 25 °C (Wilson and Fisher, 1981).

The formation of auric species can occur through the disproportionation of aurous species. In previous research, this reaction has often been described as a reaction of gold cations. Schalch and Nicol (1978) stated that the disproportionation reaction, in which gold is presented as cations (Eq. (6)), is extremely slow. However, more recently, Diaz et al. (1993) proposed that  $AuCl_2^-$  complexes could oxidize into AuCl<sub>4</sub><sup>-</sup> complexes by a very slow disproportionation reaction (Eq. (7)). Hiskey and Atluri (1988) stated that this disproportionation reaction occurs with low chloride concentration (i.e.,  $10^{-2}$  M) based on the value of equilibrium constant  $K = 1.3 \cdot 10^8$  at T = 25 °C. However, it was suggested that gold remained in aqueous solution predominantly as AuCl<sub>2</sub><sup>-</sup> species when [*Cl*<sup>-</sup>] > 0.1 M (Hiskey and Atluri, 1988). Further, according to Eq. (7), an increase in chloride concentration promotes the stability of AuCl<sub>2</sub><sup>-</sup> (Diaz et al., 1993). Since the disproportionation reaction will cause back precipitation of the dissolved gold, it should be avoided by minimizing the amount of produced aurous gold that could react through disproportionation (Nicol et al., 1987).

$$3 \operatorname{Au}^+ \to 2 \operatorname{Au} + \operatorname{Au}^{3+} \tag{6}$$

$$3 \operatorname{AuCl}_{2}^{-} \rightarrow 2 \operatorname{Au} + \operatorname{AuCl}_{4}^{-} + 2\operatorname{Cl}^{-}$$

$$\tag{7}$$

The dissolution of gold can be affected by process variables, such as temperature, oxidant (e.g., cupric and iron) and chloride concentration, rotational speed/solution flow as well as pH. Several authors have investigated the effect of process variables on the gold dissolution rate in cupric chloride media (von Bonsdorff, 2006; von Bonsdorff et al., 2005; Lampinen et al., 2017; McCaughey, 1909; McDonald et al., 1987). Additionally, McDonald et al. (1987) studied the effect of process variables on the solubility of gold.

Many authors have reported that temperature has a positive effect on gold dissolution (Abe and Hosaka, 2010; von Bonsdorff, 2006; von Bonsdorff et al., 2005; Lampinen et al., 2017; Lundström et al., 2016; McCaughey, 1909; McDonald et al., 1987). In the early studies of McCaughev (1909), it was stated that the dissolution rates of gold increased 29-42 times when the temperature was raised from 38 to 43 °C to 98-100 °C. Further, temperature has been reported to increase the gold dissolution rate in the following ranges: 65–95 °C (Lampinen et al., 2017), 70-90 °C (von Bonsdorff, 2006), and 80-95 °C (von Bonsdorff et al., 2005). Different temperature ranges have been investigated and/ or suggested for the cupric chloride leaching process: ≤85 °C (Abe and Hosaka, 2010) and 90-100 °C (Lundström et al., 2016). McDonald et al. (1987) stated that the dissolution rate of gold as well as the solubility of gold increased with increasing temperature in cupric chloride solutions. The solubility of gold increased from 10 to  $130 \text{ mg dm}^{-3}$  when the temperature was increased from 63 to 102 °C.

Cupric concentration has been reported to have a positive effect on the gold dissolution rate (McCaughey, 1909; McDonald et al., 1987; von Bonsdorff, 2006; von Bonsdorff et al., 2005; Lampinen et al., 2017). According to McCaughey (1909), the dissolution of gold increased when the cupric concentration was raised from 1 to  $2 g dm^{-3}$ (0.016-0.031 M), when  $[Cl^{-}] = 2.33-4.66 \text{ M}$  at 38–43 °C. According to Lampinen et al. (2017), an increase in cupric concentration from 0.01 to 0.5 M improved the gold dissolution rate fourfold. Additionally, von Bonsdorff et al. (2005) stated that an increase in cupric concentration from 0.372 to 40 g dm<sup>-3</sup> (0.006–0.63 M) increased the gold dissolution rate almost linearly. A higher cupric chloride concentration was noted to result in lower polarization resistance, while McDonald et al. (1987) achieved similar results with a cupric concentration from 6 to 38 g dm<sup>-3</sup> (0.09–0.60 M). However, Lundström et al. (2016) suggested that cupric as low as 9–20 g dm  $^{-3}$  (0.14–0.31 M) may be enough for an industrial gold chloride leaching process. According to McDonald et al. (1987), the increase in cuprous ion concentration can limit the gold dissolution rate at cupric concentrations higher than 0.6 M. This result is in agreement with von Bonsdorff et al. (2005), who showed that with higher cupric concentrations, the dissolution rate of gold approached a plateau. However, gold dissolution has been found to decrease when the cupric ion concentration is increased from 0.5 M to 1 M (Lampinen et al., 2017). von Bonsdorff (2006) suggested that the increase in cupric concentration promoted the cathodic reaction according to the mixed potential theory by Stern and Geary (1957), since an increase in cupric concentration from 0.372 to  $40 \text{ g} \text{ dm}^{-3}$  (0.006–0.63 M) increased the

open circuit potential and gold dissolution rate.

Chloride concentration is known to have a positive effect on gold dissolution (von Bonsdorff, 2006; von Bonsdorff et al., 2007; Lundström et al., 2016; McDonald et al., 1987; Nicol, 1976). The chloride concentration has a positive effect on the solubility of gold when  $[Cl^{-}] = 1.98-5.3 \text{ M}, [Cu^{2+}] = 0.6 \text{ M}, \text{ and } T = 102 \text{ °C} (McDonald et al., )$ 1987). Nicol (1976) concluded that the gold dissolution rate increased with the increasing chloride concentration ( $[Cl^{-}] = 0.05-5$  M) originating from HCl, while the open circuit potential (OCP) decreased. Therefore, it can be suggested, according to the mixed potential theory, that the increase in chloride concentration originating from the HCl promoted an anodic reaction, von Bonsdorff (2006) and von Bonsdorff et al. (2007) reported that an increase in sodium chloride concentration from 2.8 to  $280 \text{ g} \text{ dm}^{-3}$  ([Cl<sup>-</sup>] = 0.05–4.79 M) and even up to  $300 \text{ g dm}^{-3}$  ([Cl<sup>-</sup>] = 5.13 M) promoted the gold dissolution rate, while Lundström et al. (2016) stated that gold leaching is also possible at lower chloride concentrations  $> 1 \text{ g dm}^{-3}$  (> 0.03 M).

In the study of von Bonsdorff et al. (2007), it was stated that the mass transfer affected the gold dissolution rate more than temperature, cupric and chloride concentration, and pH (T = 70-95 °C,  $[NaCl] = 2.8 - 280 \,\mathrm{g} \,\mathrm{dm}^{-3}$  $[Cu^{2+}] = 0-30 \,\mathrm{g} \,\mathrm{dm}^{-3}$ (0–0.47 M),  $([Cl^{-}] = 0.05-4.79 \text{ M})$ , and pH = 1-2.5). This study was conducted electrochemically with a stationary gold electrode. In their investigations, the flow rate, which was adjusted with a pump, was varied from 0 to 300 ml min<sup>-1</sup> resulting in a tenfold increase in the gold dissolution rate. Therefore, von Bonsdorff et al. (2007) suggested that it would be important to consider efficient stirring in order to maximize the gold dissolution rate. Lampinen et al. (2017) concluded that an increase in the rotational speed (i.e., improved mass transfer) of a gold electrode (rotating disc electrode) increased the gold dissolution rate up to 1000 RPM, whereas with  $\omega_{cyc}$  = 1000–2500 RPM, the gold dissolution rate was almost constant.

The main role of pH is to keep oxidants (i.e., cupric) soluble during leaching (Abe and Hosaka, 2010; von Bonsdorff et al., 2005; McDonald et al., 1987). Therefore, McDonald et al. (1987) suggested that adequately acidic conditions (pH < 3) should be maintained to avoid the precipitation of Cu<sub>2</sub>(OH)<sub>3</sub>Cl, which would decrease the dissolution of gold, due to a reduction in the oxidation power of the solution. According to Haavanlammi et al. (2010), pH values should be between 0.5 and 2.5, while Abe and Hosaka (2010) suggested that the desirable pH should be between 0.5 and 1.9. However, according to von Bonsdorff et al. (2005) and McDonald et al. (1987), the pH did not affect the OCP nor the dissolution rate of gold when the pH was below 3.

The effect of process variables on gold dissolution in cupric chloride leaching is not yet fully understood. This paper continues the research of Lampinen et al. (2017) using a wider range of temperature and cupric concentration using smaller intervals, as well as chloride concentration and pH as new parameters. Electrochemical methods, such as linear polarization resistance (LPR) measurements using a rotating disk electrode (RDE), polarization measurements (Tafel method), as well as cyclic voltammetry (CV), were performed for pure gold in cupric chloride media. The effect of temperature, cupric and chloride concentration as well as pH on the open circuit potential and gold dissolution rate was investigated. The behavior of gold dissolution in cupric chloride media was further explored by comparing the gold dissolution rate and OCP according to the mixed potential theory by Stern and Geary (1957). The parameters affecting either the anodic or cathodic reaction, or both, were identified. The dissolution of gold as auric and aurous gold was studied using cyclic voltammetry.

#### 2. Experiments

#### 2.1. Experimental set-up and materials used

RDE measurements were performed in a water-jacketed three-electrode cell (V = 200 m) heated in a water bath (Lauda M3) with a

solution volume of 145 ml. The working electrode was a 99.99% pure gold RDE (d = 5 mm,  $A = 19.6 \text{ mm}^2$ ) covered in a polytetrafluoroethylene (PTFE) sheath (Pine Research Instrumentation Inc.), the counter electrode was a platinum plate ( $A = 7.1 \text{ cm}^2$ ), and the reference electrode was Ag/AgCl (REF251, SI Analytics) with a potential difference of 197 mV vs. standard hydrogen electrode (SHE) (Bard and Faulkner, 1980). For the polarization measurements, a stationary gold wire (Premion<sup>®</sup>, purity of 99.999%,  $A = 1.6-2.8 \text{ mm}^2$ ) was used as the working electrode in a three-electrode cell. CV measurements were performed in a three-electrode cell (V = 50 ml) with a 99.99% pure gold wire (d = 0.14 cm, A = 0.455 cm<sup>2</sup>, Kultakeskus Oy) as a working electrode, SCE reference electrode (B521, SI Analytics), and a platinum plate as the counter electrode. All the potentials in this paper are presented vs. SCE. The chemicals used in the experiments were technical grade NaCl (VWR Chemicals), NaOH (Sigma-Aldrich), and CuCl<sub>2</sub>·2H<sub>2</sub>O (VWR Chemicals), and Ph. Eur. grade HCl (Merck KGaA).

#### 2.2. Parameters investigated

The parameters were investigated by varying one parameter at a time, while the other parameters were fixed to T = 95 °C,  $[Cu^{2+}] = 0.5$  M,  $[Cl^{-}] = 3$  M, and pH = 1.0. Further, the rotational speed of the RDE was varied in the range of 100–2500 RPM for every condition. The temperatures investigated were 28, 35, 45, 55, 65, 75, 85, and 95 °C, cupric concentrations 0.02, 0.1, 0.5, 0.75, and 1.0 M, chloride concentrations 1, 2, 3, 4, and 5 M and pH values 0.5, 1.0, 1.5, and 2.0, adjusted by HCl (4 M) or NaOH (2 M). HCl was used since it does not interfere with the process chemistry (Abe and Hosaka, 2010). The measured responses were the LPR from the RDE measurement as well as the Tafel slope coefficients of the anodic and cathodic side from the Tafel measurement in order to calculate the Stearn-Geary constant for LPR dissolution rate calculations. CV measurements were performed in NaCl solution with chloride concentrations of 1, 3, and 5 M and pH values of 1, 2, and 3 at T = 20 °C. pH was adjusted with 1 M HCl.

#### 2.3. Electrochemical methods

RDE measurements were performed with an ACM Instruments Gill AC potentiostat using an LPR sweep with Gill AC Sequencer software (from -10 to 10 mV vs. OCP with a sweep rate of  $10 \text{ mV} \text{ min}^{-1}$ ). The average LPR of three parallel measurements in each condition was used as the LPR value. The LPR ( $R_p$ ) was determined from the slope of the potential-current density diagram,  $R_p$  being inversely proportional to the dissolution current density ( $j_{corr}$ ), as presented in Eq. (8) (Stern and Geary, 1957).

$$j_{corr} = \frac{b_a b_c}{2.303(b_a + b_c)} \cdot \frac{1}{R_p} = \frac{B}{R_p}$$
(8)

where  $b_a$  represents the Tafel slope coefficient of the anodic side (mV decade<sup>-1</sup>),  $b_c$  the coefficient of the cathodic side (mV decade<sup>-1</sup>), B the systematic coefficient known as the Stearn-Geary constant (mV), and  $R_p$  the LPR ( $\Omega$  cm<sup>2</sup>). The Stearn-Geary constant was determined from separate Tafel measurements at  $[Cl^-] = 0.7$ , 1.5, 3, and 5 M as well as T = 27, 65, and 90 °C. The Stearn-Geary constant (presented in Eq. (9)) was shown to vary from 17.2 to 30.0 mV and increased when the temperature and chloride concentration was increased.

$$B = 8.00 + 0.14 \cdot T + 1.89 \cdot [Cl^{-}] \tag{9}$$

The dissolution rate can be calculated according to Eq. (10) when the dissolution current density and the number of transferred electrons during the reaction are determined. The number of transferred electrons can be defined by comparing the measured OCPs on the equilibrium potentials of Au/AuCl<sub>2</sub><sup>-</sup> and Au/AuCl<sub>4</sub><sup>-</sup> as presented in Fig. 1. The equilibrium potentials of Au/AuCl<sub>2</sub><sup>-</sup> and Au/AuCl<sub>4</sub><sup>-</sup> were calculated in solution with  $[Cl^-] = 1-5$  M and  $[Au^+/Au^{3+}] = 3.2 \cdot 10^{-8}$ -4.6  $\cdot 10^{-6}$  M at T = 28-95 °C as a function of



**Fig. 1.** Equilibrium potentials of Au/AuCl<sub>2</sub><sup>-</sup> and Au/AuCl<sub>4</sub><sup>-</sup> in solution with  $[Cl^-] = 1-5$  M and  $[Au^+/Au^{3+}] = 3.2 \cdot 10^{-8}-4.6 \cdot 10^{-6}$  M at T = 28-95 °C as a function of temperature. Additionally, OCPs were measured when T = 28-95 °C,  $[Cu^{2+}] = 0.5$  M,  $[Cl^-] = 3$  M, and pH = 1.0.

temperature. Standard electrode potential, E°, values were calculated by HSC 9.2.6 and equilibrium potentials were calculated with the Nernst equation (Eq. (11)), and they were compared to the measured OCPs when T = 28-95 °C,  $[Cu^{2+}] = 0.5$  M,  $[Cl^{-}] = 3$  M, and pH = 1.0. Regardless of the temperature, the measured OCPs were always higher than the equilibrium potentials of Au/AuCl2<sup>-</sup>, but lower than the equilibrium potentials of Au/AuCl<sub>4</sub><sup>-</sup>. The only exception was observed at low temperatures (T < 35 and 45 °C) with the rotational speed of 2500 and 100 RPM, in which OCPs were below the equilibrium potentials of Au/AuCl2<sup>-</sup>. However, at low temperatures, the dissolution rates of gold were low, therefore, OCPs at low temperatures should be equilibrium potentials compared to calculated with  $[Au] = 3.2 \cdot 10^{-8}$  M, which are lower than the OCPs. Further, OCPs closer to the equilibrium potentials of Au/AuCl2<sup>-</sup> suggested that the gold oxidation state of +1 was predominant in the investigated conditions. The results were in agreement with previous studies suggesting that gold dissolves as aurous gold at lower open circuit potentials and as auric gold at higher potentials (Diaz et al., 1993; Frankenthal and Siconolfi, 1982; Nicol, 1980).

$$\frac{dn}{A \cdot dt} = \frac{J_{corr}}{z \cdot F}$$
(10)

$$E = E^{\circ} - \frac{R \cdot T}{z \cdot F} \cdot ln \frac{[Cl^{-}]^{x}}{[AuCl_{x}^{-}]}$$
(11)

where  $\frac{dn}{A \cdot dt}$  represents the dissolution rate (mol m<sup>-2</sup> s<sup>-1</sup>), z the number

of transferred electrons during the reaction, F Faraday's constant (96,485 C mol<sup>-1</sup>), *E* the potential of the electrochemical reaction, in this case the equilibrium potential of the gold oxidation (V),  $E^{\circ}$  the standard electrode potential (V) calculated by HSC 9.2.6, R the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), *T* the temperature (K), *[AuCl<sub>x</sub>]* the concentration of AuCl<sub>2</sub><sup>-</sup> or AuCl<sub>4</sub><sup>-</sup>, *x* the number of chloride ions involved in the reaction, and *[Cl<sup>-</sup>]* the concentration of free chlorides.

Cyclic voltammetry measurements were performed in order to determine the effect of chloride concentration and pH on gold dissolution. Additionally, the ratio of auric and aurous reaction products can be defined from cyclic voltammetry measurements. An Ivium 24-bit CompactStat potentiostat was used with a scan rate of  $20 \text{ mV s}^{-1}$  and step size of 2 mV. In order to avoid hydrogen and oxygen evolution, the initial potential range of cyclic voltammetry measurements was from -0.5 to 2.0 V vs. SCE. The passivation of the gold surface was observed to occur at 1.47-1.71 V vs. SCE with  $[Cl^-] = 1-5 \text{ M}$ . Therefore, the effect of chloride concentration was investigated with potentials of 0.85 and 1.0 V vs. SCE at the highest in order to avoid the passivation of the gold surface.

#### 3. Results and discussion

#### 3.1. Effect of temperature

Temperature as well as rotational speed (i.e., improved mass transfer) were shown to promote the dissolution rate of gold, see Fig. 2(a). The effect of temperature was in line with the literature (von Bonsdorff, 2006; von Bonsdorff et al., 2005; Lampinen et al., 2017; McCaughey, 1909). Fig. 2(b) presents OCP as a function of temperature showing that the OCPs increased significantly at T > 45 °C, although the OCPs moderated to 0.59 V vs. SCE when the temperature exceeded 75 °C. The logarithm of gold dissolution rate showed quite a linear dependency to OCP, although showing the limiting OCP value to be around 0.59 V vs. SCE, see Fig. 3. This phenomenon can be explained by the powerful increase in anodic gold dissolution at higher temperatures. The result was in line with the results presented by Diaz et al. (1993), which showed that the dissolution of gold is accelerated significantly when the potential of the system exceeded approximately 0.55 V vs. SCE. However, according to the mixed potential theory, it can be suggested that up to 55 °C, an increase in temperature promoted the cathodic cupric reduction reaction, as both the OCP and gold dissolution rate increased. However, at higher temperatures (i.e., 65-95 °C), the OCP was almost constant but the dissolution rate increased significantly. Assuming that the cathodic reaction rate continues to increase with temperature, the anodic reaction rate increases more rapidly at temperatures above 55 °C. It can be suggested that in order to promote efficient gold leaching, the temperature should be set to at



Fig. 2. (a) The logarithm of gold dissolution rate as a function of temperature and (b) the OCP as a function of temperature, when T = 28-95 °C,  $\omega_{cyc} = 300, 1000$  and 2500 RPM,  $[Cu^{2+}] = 0.5$  M,  $[Cl^{-}] = 3.0$  M, and pH = 1.0.



**Fig. 3.** The logarithm of gold dissolution rate as a function of OCP, when T = 28-95 °C,  $\omega_{cyc} = 300$ , 1000 and 2500 RPM,  $[Cu^{2+}] = 0.5$  M,  $[Cl^{-}] = 3.0$  M, and pH = 1.0.

#### least 65 °C.

#### 3.2. Effect of cupric concentration

Fig. 4(a) shows that the gold dissolution rates increased when the cupric concentration increased from 0.02 to 0.75 M at all rotational speeds. In previous studies by McDonald et al. (1987) and von Bonsdorff et al. (2005), it was also observed that an increase in cupric concentration up to 0.6 and 0.63 M increased the gold dissolution rate: however, higher cupric concentrations were not investigated. In this study it was found out that the gold dissolution rate decreased when the cupric concentration was further increased up to 1.0 M. Additionally, crystal microbalance previous quartz (OCM) results  $([Cu^{2+}] = 0.02 - 1.0 \text{ M}, \omega_{cvc} = 50 \text{ RPM}, T = 95 \text{ °C}, [Cl^{-}] = 3.0 \text{ M}, \text{ and}$ pH = 1.0, Seisko et al., 2017) are shown in Fig. 4(a), and these results suggested that gold dissolved as aurous gold, since the magnitude of OCM dissolution was similar to RDE when the number of transferred electrons during the reaction was one. Although Lampinen et al. (2017) and Seisko et al. (2017) observed that the gold dissolution rate decreased at high cupric concentration (1.0 M), it should be noted that they did not study any cupric concentrations between 0.5 and 1.0 M in more detail. Fig. 4(b) shows that the OCP increased up to  $[Cu^{2+}] = 0.5$  M, but then decreased slightly up to  $[Cu^{2+}] = 1$  M to 0.59 V vs. SCE.

The logarithm of gold dissolution rate was shown to increase linearly when the OCP increased as a function of cupric concentration, see Fig. 5. The OCP as well as gold dissolution rate increased as a function of cupric concentration from 0.02 to 0.5 M. This may be due to an



**Fig. 5.** The logarithm of gold dissolution rate as function of OCP, when  $[Cu^{2+}] = 0.02-1.0 \text{ M}$ ,  $\omega_{cyc} = 300$ , 1000 and 2500 RPM,  $T = 95 \degree \text{C}$ ,  $[Cl^{-}] = 3.0 \text{ M}$ , and pH = 1.0.

enhanced cathodic reaction, in this case the reduction of cupric ion. With  $[Cu^{2+}] = 0.5-0.75$  M, the OCP decreased, but the gold dissolution rate increased, which indicates that anodic gold dissolution was promoted. At  $[Cu^{2+}] = 0.75-1.0$  M, OCP and gold dissolution rate decreased. According to the mixed potential theory, this means that the cathodic reaction rate ( $Cu^{2+}$  reduction) decreased. It can be concluded that the optimal initial cupric ion concentration is around 0.5–0.75 M according to gold dissolution rates.

#### 3.3. Effect of chloride concentration

Fig. 6(a) shows that the gold dissolution rate increased as the chloride concentration (1-5 M) and rotational speed (300-2500 RPM) increased with a reaction order of approximately 1.6. A positive correlation between chloride concentration and gold dissolution rate was in line with previous studies by von Bonsdorff (2006) and von Bonsdorff et al. (2007). Fig. 6(b) shows that the OCP also had a linear dependency on chloride concentration, increasing up to 5.0 M. Fig. 7 represents the dependency of the gold dissolution rate on the OCP, showing that the logarithm of gold dissolution rate had a linear dependency on the OCP when the chloride concentration was changed from 1 to 5 M. Additionally, an increase in rotational speed (i.e., improved mass transfer) increased the gold dissolution rate. Further, an increase in chloride concentration resulted in the formation of cupric chloride complexes, such as  $CuCl_2^0$ ,  $CuCl_3^-$  and  $CuCl_4^{2-}$ , which have a higher standard electrode potential ( $E^{\circ}$ ) when compared to the  $E^{\circ}$  of Cu<sup>2+</sup> reduction. Hence higher equilibrium potentials also supported higher kinetics in gold leaching. Therefore, it can be suggested that the cathodic reaction,



Fig. 4. (a) The logarithm of dissolution rate as a function of the logarithm of cupric concentration from RDE. when  $[Cu^{2+}] = 0.02 - 1.0 \,\mathrm{M},$  $\omega_{cyc} = 100-2500$ RPM,  $T = 95 \,^{\circ}\text{C}$ ,  $[Cl^{-}] = 3.0 \,\text{M}$ , and pH = 1.0 as well as QCM results according (2017), Seisko et al. when  $[Cu^{2+}] = 0.02 - 1.0 \text{ M}, \quad \omega_{cyc} = 50$ RPM.  $T = 95 \,^{\circ}\text{C}, [Cl^{-}] = 3.0 \,\text{M}, \text{ and } pH = 1.0 \text{ and}$ (b) OCP as a function cupric concentration, when  $[Cu^{2+}] = 0.02 - 1.0 \text{ M}, \quad \omega_{cyc} = 300,$ 1000 and 2500 RPM,  $T = 95 \,^{\circ}\text{C},$  $[Cl^{-}] = 3.0 \text{ M}$ , and pH = 1.0.



**Fig. 6.** (a) The logarithm of gold dissolution rate as a function of the logarithm of chloride concentration and (b) the OCP as a function of the logarithm of chloride concentration, when  $[Cl^-] = 1.0-5.0 \text{ M}$ ,  $\omega_{cyc} = 300$ , 1000 and 2500 RPM,  $[Cu^{2+}] = 0.5 \text{ M}$ , T = 95 °C, and pH = 1.0.



**Fig. 7.** The logarithm of dissolution rate as a function of OCP, when  $[Cl^-] = 1.0-5.0 \text{ M}$ ,  $\omega_{cyc} = 300$ , 1000 and 2500 RPM,  $[Cu^{2+}] = 0.5 \text{ M}$ , T = 95 °C, and pH = 1.0.

in this case the reduction of cupric ion, was enhanced at higher equilibrium potentials.

Additionally, CV measurements were performed in order to investigate the effect of chloride concentration on current density (i.e., gold dissolution rate). The maximum potential was 0.85 V vs. SCE and no copper as oxidant or rotation was used in these tests. As presented in the results of Diaz et al. (1993), the anodic peaks of auric and aurous gold overlap, since they occur within a similar potential range. A similar result was observed in this study, since there occurred only one anodic peak, but two cathodic peaks, as presented in Fig. 8. An increase in chloride concentration was shown to increase the current density of the anodic peak, therefore, it can be suggested that total gold dissolution is promoted at higher chloride concentrations. However, it is not still clear whether both the aurous and auric dissolution of gold, or only one of them is enhanced.

Since the anodic peaks overlapped, the cathodic peaks of gold should be considered when investigating the occurrence of aurous and auric dissolution. The reduction of aurous gold was observed at potentials of 0.3–0.58 V vs. SCE as well as peak maxima at 0.48–0.52 V vs. SCE, see Fig. 9(a). The reduction potential of aurous gold was similar to that reported in Diaz et al. (1993), who found it to be 0.437 V vs. SCE when  $[Au^+] = 0.244 \text{ mol m}^{-3}$ ,  $[Au^{3+}] = 0.085 \text{ mol m}^{-3}$ ,  $[NaCl] = 0.99 \text{ kmol m}^{-3}$  ( $[Cl^-] = 0.99 \text{ M}$ ), and  $[HCl] = 0.01 \text{ kmol m}^{-3}$  ( $[Cl^-] = 0.01 \text{ M}$ ) at T = 295 K. The increase in chloride concentration promoted the cathodic peak of aurous gold, therefore, it can be suggested that chloride concentration enhanced the dissolution of gold as aurous species. Further, the reduction of auric gold was



**Fig. 8.** Cyclic voltammogram, in which the current density is described as a function of potential, when E = -0.5-0.85 V vs. SCE,  $[Cl^-] = 1-5$  M, and pH = 1.0 at T = 20 °C.

observed at potentials of 0.58–0.75 V vs. SCE as well as a peak maximum at 0.66–0.72 V vs. SCE, see Fig. 9(b). The reduction potential of auric gold was similar to that reported in Diaz et al. (1993), who found that it occurred at 0.595 V vs. SCE. The increase in chloride concentration also promoted the cathodic peak of auric gold, therefore, it can be suggested that chloride concentration also enhanced the dissolution of gold as auric species. Fig. 9(a) and (b) show that the reduction peaks of aurous gold were larger compared to the reduction peaks of auric gold when  $[Cl^-] = 1-5$  M; therefore, it can be suggested that gold dissolves mainly as aurous gold at potentials up to 0.85 V vs. SCE.

#### 3.4. Effect of pH

The effect of pH on the gold dissolution rate and OCP was investigated and the results suggested that the gold dissolution rate was not affected by the pH in the range tested, see Fig. 10(a). In addition, the OCP was shown to have a constant value at all pH values, see Fig. 10(b). The dissolution rate was dependent on the mass-transfer conditions (rotational speed), whereas this did not affect the measured OCP.

Additionally, CV measurements were performed in a potential range between -0.5 and 1.0 V vs. SCE, when pH = 1-3, T = 20 °C, and  $[Cl^-] = 3$  M, in order to investigate the effect of pH on the anodic and cathodic peaks when the maximum potential of 1.0 V vs. SCE was kept constant, as presented in Fig. 11(a). According to the results, pH was



**Fig. 9.** (a) 2nd cathodic peak of aurous gold reduction and (b) 1st cathodic peak of auric gold reduction, in which the current density is described as a function of potential, when E = -0.5-0.85 V vs. SCE [*Cl*<sup>-</sup>] = 1-5 M, T = 20 °C, and pH = 1.0.

shown not to affect the gold dissolution rate under the investigated conditions. Similar results were achieved with the RDE and CV methods. Additionally, Fig. 11(a) shows that the reduction peak of aurous gold was larger than the reduction peak of aurous gold; therefore, it can be suggested that gold dissolves mainly as aurous gold also at potentials up to 1.0 V vs. SCE. The gold dissolution did not have any dependency on OCP in the investigated pH range, see Fig. 11(b). However, it should be considered that the importance of the pH value is that it provides the conditions in which cupric ions and chloride complexes remain in soluble form (Abe and Hosaka, 2010; von Bonsdorff et al., 2005; McDonald et al., 1987).

#### 4. Conclusions

In this study, the effect of the process variables of temperature  $(28-95 \,^{\circ}\text{C})$ , cupric concentration  $(0.02-1.0 \,\text{M})$ , chloride concentration  $(1-5 \,\text{M})$ , rotational speed  $(100-2500 \,\text{RPM})$ , and pH (0.5-2.0) were investigated to determine their effect on the gold dissolution rate as well as the behavior of gold dissolution. To the best of the authors' knowledge, this was done for the first time over such a wide range and with these parameter intervals. The electrochemical methods used were linear polarization and Tafel methods as well as cyclic voltammetry using pure gold as a rotating disk electrode and stationary wire electrodes. An increase in the gold dissolution rate was observed with an increase in temperature, chloride concentration, and rotational speed. Further, the dissolution of both auric and aurous gold was promoted by increasing the chloride concentration. Gold was shown to dissolve mainly as aurous gold according to the gold reduction peaks at

maximum potentials of 0.85 and 1.0 V vs. SCE regardless of the chloride concentration. Additionally, an increase in cupric concentration promoted the gold dissolution rate when  $[Cu^{2+}] = 0.02-0.75$  M, although the gold dissolution rate decreased when the cupric concentration was increased from 0.75 to 1.0 M. However, the gold dissolution rate was not affected by the pH values.

The reaction mechanism was discussed according to the mixed potential theory. In the system, the dissolution of aurous gold represents an anodic reaction, while the reduction of cupric ion represents a cathodic reaction. An increase in temperature promoted the cathodic reaction rate at lower temperatures (28-55 °C); however, the anodic reaction rate was enhanced notably at higher temperatures (i.e., 65-95 °C). The cathodic reaction rate was enhanced with an increasing cupric concentration (0.02-0.5 M). When the cupric concentration was increased from 0.5 to 0.75 M, the anodic reaction was promoted. When the cupric concentration was increased from 0.75 to 1.0 M, the cathodic reaction rate decreased. However, the reason for this reduced gold dissolution rate is not clear. An increase in chloride concentration enhanced the cathodic reaction in the investigated range (1-5 M), since the OCP as well as the gold dissolution rate increased. Additionally, cupric ions form cupric chloride complexes at higher chloride concentrations with increased reduction potentials, which results in higher dissolution rates of gold. An increase in rotational speed (i.e., improved mass transfer) promoted the gold dissolution rate; however, the increase was the most significant at low rotational speeds. pH is the only parameter that did not affect the dissolution rate of gold directly, however, it has an inverse effect on oxidant concentrations. The conditions for maximizing the gold dissolution rate in cupric solution can



**Fig. 10.** (a) The logarithm of dissolution rate of gold as a function of pH and (b) OCP as a function of pH, when pH = 0.5-2.0,  $\omega_{cyc} = 300$ , 1000 and 2500 RPM,  $[Cu^{2+}] = 0.5$  M, T = 95 °C, and  $[Cl^{-}] = 3.0$  M.



be concluded to be T > 55 °C,  $[Cu^{2+}] = 0.5-0.75$  M,  $[Cl^{-}] = 5$  M, and pH = 1.0. Additionally, an adequate rotational speed was beneficial for gold dissolution due to enhanced mass transfer.

#### Acknowledgements

This work was funded by the School of Chemical Engineering, Aalto University; therefore, the authors are grateful to the Dean of the School of Chemical Engineering at that time. Additionally, "RawMatTERS Finland Infrastructure" (RAMI) supported by the Academy of Finland and Outotec's AuChloride research project supported by Business Finland, are acknowledged. "GoldTail" (Grant 319691) funding by the Academy of Finland is also acknowledged.

#### References

- Abe, Y., Hosaka, H., 2010. US 7682420 B2. Method for Leaching Gold, Nippon Mining & Metals Co., Ltd., 12. Cited on 13.12.2018 from: < http://www.google.com/patents/ US7682420#forward-citations > .
- Adams, M.D., 2016. Chloride as an alternative lixiviant to cyanide for gold ores. In: Adams, M.D., 2016. Gold Ore Processing - Project Development and Operations, Ch. 29, Elsevier, Amsterdam, pp. 525–534.
- Angelidis, T.N., Kydros, K.N., Matis, K.A., 1993. A fundamental rotating disk study of gold dissolution in ionide-ionide solutions. Hydrometallurgy 34, 49–64.
- Aromaa, J., Rintala, L., Kähäri, M., Forsén, O., 2014. Dissolution of gold with cyanide replacing reagents. Physicochem. Probl. Min. Process. 51 (1), 269–279.
- Aylmore, M.G., 2005. Alternative lixiviants to cyanide for leaching gold ores. In: Adams, M.D., 2016. Gold Ore Processing - Project Development and Operations, Ch. 27, Elsevier, Amsterdam, pp. 447–484.
- Bard, A.J., Faulkner, L.R., 1980. Electrochemical Methods: Fundamentals and Applications. Wiley, New York.
- Bjerrum, J., 1987. Determination of small stability constants. a spectrophotometric study of copper(II) chloride complexes in hydrochloric acid. Acta Chem. Scand. A41, 328–334.
- von Bonsdorff, R.C., Aromaa, J., Barker, M.H., Hyvärinen, O., 2005. Dissolution of gold in cupric chloride solution. EMC, Dresden, Germany, pp. 237–245.
- von Bonsdorff, R., 2006. The Use of a Quartz Crystal Microbalance in Determining the Dissolution Rate of Gold in Cupric Chloride Solution. Licentiate thesis, Helsinki University of Technology, Espoo, Finland.
- von Bonsdorff, R.C., Aromaa, J., Forsén, O., Barker, M.H., 2007. The rate of gold dissolution in concentrated cupric chloride solutions. In: Proceedings of Copper 2007, pp. 121–131.
- Collings, M.D., Sherman, D.M., Vala Ragnarsdottir, K., 2000. Complexation of Cu<sup>2+</sup> in oxidized NaCl brines from 25°C to 175°C: results from in situ EXAFS spectroscopy. Chem. Geol. 167, 65–73.
- Diaz, M.A., Kelsall, G.H., Welham, H.J., 1993. Electrowinning coupled to gold leaching by electrogenerated chloride: I. Au(III) · Au(I)/Au kinetics in aqueous Cl<sub>2</sub>/Cl<sup>-</sup> electrolytes. J. Electroanal. Chem. 361, 25–38.

**Fig. 11.** (a) Cyclic voltammogram, in which the current density is described as a function of potential, when E = -0.5-1.0 V vs. SCE, pH = 1-3 M,  $[Cl^{-}] = 3$  M at T = 20 °C, and (b) the logarithm of dissolution rate as a function of OCP, when  $\omega_{cyc} = 300$ , 1000 and 2500 RPM, pH = 0.5-2.0,  $[Cu^{2+}] = 0.5$  M, T = 95 °C, and  $[Cl^{-}] = 3.0$  M.

- Frankenthal, R.P., Siconolfi, D.J., 1982. The anodic corrosion of gold in concentrated chloride solution. J. Electrochem. Soc. 129, 1192–1196.
- Haavanlammi, L., Hyvärinen, O., Tiihonen, M., Tontti, R., 2010. US 7799114 B2. Method for Recovering Gold, Outotec Oyj. Cited on 13.12.2018 from: < https://patents. google.com/patent/US7799114 > .
- Helm, M., Vaughan, J., Staunton, W.P., Avraamides, J., 2009. An investigation of the carbonaceous component of preg-robbing gold ores. World Gold Conf. 2009, 139–144.
- Hilson, G., Monhemius, A.J., 2006. Alternatives to cyanide in the gold mining industry: prospects for the future? J. Clean. Prod. 14, 1158–1167.
- Hiskey, J.B., Atluri, V.P., 1988. Dissolution chemistry of gold and silver in different lixiviants. Min. Process. Extr. Metall. Rev.: Int. J. 4 (1–2), 95–134.

HSC 9.2.6, 2018. < www.outotec.com > .

Laitos, J.G., 2012. The current status of cyanide regulations. Eng. Min. J. 213 (2), 34–40. Lampinen, M., Seisko, S., Forsström, O., Laari, A., Aromaa, J., Lundström, M., Koiranen, T., 2017. Mechanism and kinetics of gold leaching by cupric chloride. Hydrometallurgv 169. 103–111.

Lundström, M., Ahtiainen, R., Laihonen, P., Lindgren, M., 2015. Possibilities and challenges in gold chloride processing. In: Proceedings of ALTA 2015, pp. 269–280.

- Lundström, M., O'Callaghan, J., Haakana, T., Ahtiainen, R., Karonen, J., 2016. WO 2016066905 A1. Process for recovering gold, Outotec (Finland) Oy. Cited on 13.12. 2018 from: < https://patents.google.com/patent/WO2016066905A1/en > .
- Marsden, J., House, I., 2006. The chemistry of gold extraction, vol. 2. Littleton (CO), USA: Society for Mining, Metallurgy and Exploration (SME), 651.
- McCaughey, W.J., 1909. The solvent effect of ferric and cupric salt solutions upon gold. J. Am. Chem. Soc. 31 (12), 1261–1270.
- McDonald, G.W., Saud, A., Barger, M., Koutsky, J.A., Langer, S.H., 1987. The fate of gold in cupric chloride hydrometallurgy. Hydrometallurgy 18, 321–336.
- van Meersbergen, M.T., Lorenzen, L., van Deventer, J.S.J., 1993. The electrochemical dissolution of gold in bromide medium. Min. Eng. 6 (8–10), 1067–1079.
- Nicol, M.J., 1980. The anodic dissolution of gold. Part I. Oxidation in acidic solutions. Gold Bull. 145 (13), 70–75.
- Nicol, M.J., Fleming, C.A., Paul, R.L., 1987. The chemistry of the extraction of gold. In: Stanley, G.G. (Ed.), The extractive metallurgy of gold in South Africa, 2, SAIMM, Johannesburg, pp. 831–905.
- Nicol, M.J., 1976. An electrochemical and kinetic investigation of the behaviour of gold in chloride solutions. II. The anodic dissolution of gold. National Institute for Metallurgy, Johannesburg, Report no. 1844, 1–20.
- Putnam, G.L., 1944. Chlorine as a solvent in gold hydrometallurgy. Eng. Min. J. 145 (3), 70–75.
- Schalch, E., Nicol, M.J., 1978. A study of certain problems associated with the electrolytic refining of gold. Gold Bull. 11 (4), 117–123.
- Seisko, S., Forsström, O., Aromaa, J., Lundström, M., 2017. Dissolution of gold in ferric and cupric chloride solutions. In: Proceedings of EMC 2017, 19–30, June 25–28, Leipzig, Germany.
- Stern, M., Geary, A.L., 1957. Electrochemical polarization. I. A theoretical analysis of the shape of polarization curves, J. Electrochem. Soc. 104 (1), 56–63.
- Wilson, J.P., Fisher, W.W., 1981. Cupric chloride leaching of chalcopyrite. J. Metals 33 (2), 52–57.
- Zhang, N., Zhou, Q., Yin, X., Zeng, D., 2014. Trace amounts of aqueous copper(II) chloride complexes in hypersaline solutions: spectrophotometric and thermodynamic studies. J. Solution Chem. 43, 326–339.