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Effect of redox potential and OCP in ferric and cupric chloride leaching of gold

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A R T I C L E I N F O	A B S T R A C T			
Keywords: Gold dissolution Cyanide-free Modeling Optimization Process parameter	The research presented contributes to the global goal of responsible production by providing robust tools for the optimization of gold dissolution in cyanide-free gold leaching solutions, which represent emerging non-toxic gold technologies. In the current study, gold dissolution was investigated in ferric and cupric chloride solutions. The effect of the redox potential on the open circuit potential (OCP) and dissolution rate of gold was investigated experimentally in the parameter range of $T = 25-95$ °C, $[Fe^{3+}/Cu^{2+}] = 0.02-1.0$ M, $[Cl^{-}] = 1-5$ M, $pH = 0.0-2.0$, and $\omega_{cyc} = 2500$ RPM. A high rotational speed was chosen to minimize the effects of limited mass transfer rate. The aim was to provide tools for estimating the gold dissolution rate in ferric and cupric chloride solutions, using the solution properties. The results showed that redox potentials, OCPs, and dissolution rates were constantly higher in ferric chloride solutions compared to corresponding cupric chloride solutions. The multilinear regression models for redox potential in ferric chloride solutions. However, an increase in the chloride concentration decreased the redox potential in ferric solutions, whereas the effect was the opposite in cupric solutions. A rise in the pH value increased the redox potential in ferric solutions, but this was found to be an insignificant variable in cupric chloride leaching within the investigated parameter range. The redox potential had a positive correlation with OCP and the logarithm of the gold dissolution rate in both investigated systems. The results suggest that, in the chloride leaching systems examined, the solution properties can be used to determine the redox potential, and furthermore, the redox potential can be used to estimate the gold dissolution rate in chloride systems.			

1. Introduction

Although cyanide leaching has been dominantly employed in primary gold production (Marsden and House, 2006), it has raised international concern due to its toxic nature, which may threaten ecological entities, such as in the Baia Mare disaster in Romania in 2000 (Hilson and Monhemius, 2006; UNEP/OCHA, 2000). Several countries, e.g., Costa Rica, Czech Republic, Germany, Hungary, and Turkey, have legislated to ban or limit cyanidation (Laitos, 2012). Alternative solutions, such as thiourea, thiosulfate, oil-coal agglomerates as well as halides, have been suggested to substitute cyanide as lixiviant (Aromaa et al., 2014; Aylmore, 2005; Hilson and Monhemius, 2006). Halide leaching methods, such as ferric and cupric chloride in aggressive leaching conditions, have also been reported as being capable of leaching refractory gold minerals, without requiring pre-treatment such as roasting or pressure oxidation (Angelidis et al., 1993; Lundström et al., 2015; Marsden and House, 2006; van Meersbergen et al., 1993). Additionally, chloride leaching has been proposed as one of the most promising alternatives due to its high dissolution rates of gold compared to cyanidation (Aromaa et al., 2014) as well as the easy oxidant (Cu^{2+}/Fe^{3+}) regeneration via oxygen/air sparging (Abe and Hosaka, 2010; Liu and Nicol, 2002; Lu and Dreisinger, 2013; Senanayake, 2004).

In aqueous chloride solutions, it has been proposed that gold occurs in either monovalent aurous, Au⁺, or trivalent auric, Au³⁺, form (Marsden and House, 2006). Many studies have stated that gold forms aurous and/or auric chloride complexes: AuCl₂⁻ dominating at potentials < 0.8 V vs. SCE and AuCl₄⁻ at higher potentials (Diaz et al., 1993); more specifically above 1.1 V vs. SCE (Frankenthal and Siconolfi, 1982). According to Gammons et al. (1997), it has been suggested that gold dissolves mostly as AuCl₂⁻ rather than AuCl₄⁻ in acidic chloride solutions.

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Putnam (1944) suggested that the dissolution of gold proceeds in two steps: First, gold reacts into intermediate AuCl at the gold surface, Eq. (1). Second, AuCl reacts further into a more stable complex, AuCl₂⁻, Eq. (2). Further, Diaz et al. (1993) suggested the possibility for the oxidation of Au⁺ as AuCl into Au³⁺ as AuCl₄⁻ via an intermediate, AuCl₃, Eqs. (3) and (4). Direct oxidation reactions into AuCl₂⁻ and AuCl₄⁻ could also occur, Eqs. (5) and (6). Additionally, the direct oxidation of AuCl₂⁻ into AuCl₄⁻ may occur, Eq. (7) (Gammons et al., 1997).

 $Au + Cl^{-} \rightarrow AuCl + e^{-}$ (1)

 $AuCl + Cl^{-} \rightarrow AuCl_{2}^{-}$ ⁽²⁾

 $AuCl + 2 Cl^{-} \rightarrow AuCl_{3} + 2 e^{-}$ (3)

 $AuCl_3 + Cl^- \to AuCl_4^- \tag{4}$

 $Au + 2 Cl^{-} \rightarrow AuCl_{2}^{-} + e^{-}$ (5)

$$Au + 4 Cl^{-} \rightarrow AuCl_{4}^{-} + 3 e^{-}$$
(6)

$$AuCl_2^- + 2 Cl^- \rightarrow AuCl_4^- + 2 e^-$$
(7)

The dissolution of gold can be affected by several process parameters, such as temperature, oxidant and chloride concentration, as well as pH. An increase in temperature, chloride concentration, and the ferric to ferrous ratio or cupric to cuprous ratio enhances gold dissolution in ferric/cupric chloride leaching (von Bonsdorff, 2006; Liu and Nicol, 2002; McDonald et al., 1987; Seisko et al., 2018; Seisko et al., 2019). Redox potential, as a consequence of the above-mentioned parameters, has an obvious impact on chloride leaching (Liu and Nicol, 2002; Zhao et al., 2013). Redox potential is also known as oxidation/ reduction potential (ORP). The competitive edge of ferric/ferrous and cupric/cuprous leaching is that the redox potentials in these chloride solutions are higher compared to, for example, sulfate media (Muir, 2002). The potential of the redox pair can be kept high by the regeneration of the oxidant e.g., by oxygen sparging. Further, Abe and Hosaka (2010) stated that ferric/cupric chloride species can dissolve gold even at lower redox potentials, i.e., ≥0.480 V vs. Ag/AgCl $(\geq 0.435 \text{ V vs. SCE})$, compared to bromine/chlorine gas or aqua regia leaching, in which higher redox potentials, i.e., ≥ 0.778 V vs. Ag/AgCl $(\geq 0.733 \text{ V vs. SCE})$, are required for gold dissolution.

However, Lundström et al. (2016) found that a low redox potential can result in slow gold dissolution rates. Further, low redox potentials can be detrimental to the process, since the gold chloride complex may be less stable and preg-rob, i.e., reduce back to several substances such as carbonaceous concentrates (Ahtiainen and Lundström, 2016). On the other hand, at higher redox potentials, the surface of gold may be passivated, which can prevent dissolution (Abe and Hosaka, 2010). In one patented application, the operative redox potential range for gold chloride leaching was suggested to be 0.400–0.750 V vs. Ag/AgCl (0.355–0.705 V vs. SCE) (Lundström et al., 2016). Further, Ahtiainen and Lundström (2019) observed that gold dissolved from a non-pregrobbing and quartz-rich raw material even at a low redox potential (at 0.460 V vs. Ag/AgCl i.e., 0.415 V vs. SCE).

The overall redox potential can be determined as the weighted average of all occurring redox pairs, since each pair of metal ions and metal chloride complexes has a specific redox potential (Zhao et al., 2013). According to the literature, suggested possible ferric species are Fe^{3+} , $FeCl^{2+}$, $FeCl_2^+$, $Fe(H_2O)Cl^{2+}$, and $FeCl_3(aq)$ (Strahm et al., 1979) and ferrous $FeCl_2(aq)$, $FeCl^+$, and Fe^{2+} (Wilson and Fisher,

1981). Suggested cupric species are Cu^{2+} , $CuCl^+$, $CuCl_2(aq)$, $CuCl_3^-$, and $CuCl_4^{2-}$ (Bjerrum, 1987; McDonald et al., 1987; Zhao et al., 2013), and cuprous Cu^+ , CuCl(aq), $CuCl_2^-$, $CuCl_3^{2-}$, $Cu_2Cl_4^{2-}$, and $Cu_3Cl_6^{3-}$ (Zhao et al., 2013). The complex formation of ferric/cupric ions depends on the free chloride concentration (Muir, 2002; Wilson and Fisher, 1981), oxidant concentration (Zhao et al., 2013), and temperature (Collings et al., 2000; HSC 9.4.1, 2018).

Ferric ions occur predominantly as FeCl_2^+ , but FeCl^{2+} species are also present as well as ferrous ions, mainly as FeCl_2 , in the conditions of this research (HSC 9.4.1, 2018; O'Melia, 1978; Strahm et al., 1979; Wilson and Fisher, 1981). Many studies have suggested that cupric ions occur most probably as CuCl⁺ species in the conditions of this research (von Bonsdorff, 2006; Collings et al., 2000; Lundström et al., 2007; Sato and Kato, 1977; Wilson and Fisher, 1981, and Zhang et al., 2014). It has been stated that the occurrence of cuprous chloride complexes is improbable, since cuprous ions oxidize easily in chloride solution (Fritz, 1980). According to von Bonsdorff (2006), Lundström et al. (2007), McDonald et al. (1987), Wilson and Fisher (1981), and Zhao et al. (2013), cuprous ions occur mainly as CuCl₂⁻ and CuCl₃²⁻ at room temperature, although it has been suggested that CuCl₃²⁻ is more dominant than CuCl₂⁻ at higher temperatures (T = 90-102 °C).

This work focuses on the relationship between the gold dissolution rate, open circuit potential (OCP), and redox potential. In this work, previously defined gold dissolution rates from the papers of Seisko et al. (2018) and Seisko et al. (2019) are utilized. The effect of temperature, as well as oxidant and chloride concentration on gold dissolution rate, OCP, and redox potential were investigated. The effect of pH was examined only on redox potential, since pH had been found not to correlate with the gold dissolution rate in ferric and cupric chloride solutions (Seisko et al., 2018; Seisko et al., 2019). Multilinear models for redox potential in ferric and cupric chloride solutions were built using ferric/cupric and chloride concentrations, temperature, and the pH in ferric chloride solution. Models for gold dissolution rates in ferric and cupric chloride solutions were built using the redox potential. The aim was to provide robust experimentally verified tools, which can be used to estimate the gold leaching rate in ferric and cupric chloride solutions solely based on solution properties.

2. Experiments

2.1. Experimental set-up, materials used, and parameters investigated

The electrochemical dissolution rate experiments were done using a jacketed glycol-heated glass reactor (V = 200 mL) with a solution volume of 145 mL. The rotating disk working electrode was pure gold, with a purity of 99.99%, RDE (Pine Research Instrumentation Inc., $d = 5 \text{ mm}, A = 19.6 \text{ mm}^2$), the counter electrode was a platinum plate (Kultakeskus, Finland, $A = 7.1 \text{ cm}^2$), and the reference electrode was an Ag/AgCl electrode (REF251, SI Analytics). The OCP was measured between the working and the reference electrode, while the redox potential was measured between the counter and the reference electrode. Further, all experimental potential values were reported vs. SCE reference. In separate Tafel measurements, a stationary gold wire, with a purity of 99.999% (Premion[®], $A = 1.6-2.8 \text{ mm}^2$), was used as the working electrode. The chemicals in the experiments were NaCl (VWR Chemicals, technical grade), CuCl₂·2H₂O (VWR Chemicals, technical grade), FeCl₃ (Merck Millipore, \geq 98%), HCl (Merck KGaA, 37%, Ph. Eur. grade), and NaOH (Sigma-Aldrich, reagent grade). All the solutions

Table 1

Investigated parameters and their values in ferric and cupric chloride solutions. Fixed parameters marked with *.

Solution/parameter	<i>T</i> (°C)	$[Fe^{3+}/Cu^{2+}]$ (M)	[<i>C</i> l ⁻] (M)	рН
Ferric chloride solution	25, 35, 45, 55, 65, 75, 85, 95*	0.02, 0.1, 0.25, 0.5*, 0.75, 1.0	2.0, 3.0*, 4.0, 5.0	0.0, 0.5, 1.0*
Cupric chloride solution	28, 35, 45, 55, 65, 75, 85, 95*	0.02, 0.1, 0.5*, 0.75, 1.0	1.0, 2.0, 3.0*, 4.0, 5.0	0.0, 0.5, 1.0*, 1.5, 2.0



Fig. 1. a) *OCP as a function of redox potential*, and b) logarithm of gold dissolution rate as a function of redox potential and OCP with a rotational speed of 2500 RPM when T = 25-95 °C, $[Fe^{3+}] = 0.5$ M, $[Cl^{-}] = 3.0$ M, and pH = 1.0. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. a) OCP as a function of redox potential, and b) logarithm of gold dissolution rate as a function of redox potential and OCP with a rotational speed of 2500 RPM when $[Fe^{3+}] = 0.02-1.0 \text{ M}$, T = 95 °C, $[Cl^-] = 3.0 \text{ M}$, and pH = 1.0. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

were prepared with distilled water.

The parameters were investigated by varying one parameter at a time, see Table 1, while the other parameters were fixed to T = 95 °C, $[Fe^{3+} \text{ or } Cu^{2+}] = 0.5 \text{ M}, [Cl^{-}] = 3 \text{ M}, \text{ and } pH = 1.0 \text{ using a rotational speed of 2500 RPM. HCl was used to adjust the pH of the solution, if pH was desired to be reduced, because it has been stated that it does not interfere with the process chemistry (Abe and Hosaka, 2010). Additionally, NaOH was used to adjust pH, if it was desired to be raised. Solutions were prepared with distilled water just before performing the experiments. The measured responses were the linear polarization resistance (LPR) from the rotating disk electrode (RDE) measurement as well as the Tafel slope coefficients of the anodic and cathodic side from the Tafel measurement to determine the Stern-Geary constant for LPR dissolution rate calculations (Stern and Geary, 1957).$

2.2. Electrochemical methods

RDE experiments were done with a Gill AC potentiostat (ACM Instruments) and Gill AC Sequencer software using an LPR sweep from -10 to +10 mV vs. OCP with a sweep rate of 10 mV min⁻¹. The LPR was determined as a slope of potential vs. current density plot and the

average value from three repeat measurements was used in further analysis. The dissolution current density was calculated using 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 j_{corr} represents the dissolution current density (mA cm⁻²), b_a the anodic Tafel slope coefficient (mV decade⁻¹), b_c the cathodic Tafel slope coefficient (mV decade⁻¹), *B* the systematic coefficient known as the Stern-Geary constant (mV), and R_p the LPR (Ω cm²).

According to the Tafel experiments, the Stern-Geary constant increased when the temperature and chloride concentration increased at T = 27-90 °C and $[Cl^-] = 0.7-5$ M. The Stern-Geary constants outside the temperature range (i.e., < 27 and > 90 °C) are extrapolated using Eq. (9).

$$B = 8.00 + 0.14 T + 1.89[Cl-]$$
(9)

The dissolution rate was calculated according to Eq. (10) as the dissolution current density and the number of transferred electrons in the reaction are known. The number of transferred electrons was defined by comparing the results from the RDE and QCM measurements



Fig. 3. a) OCP as a function of redox potential, and b) logarithm of gold dissolution rate as a function of redox potential and OCP with a rotational speed of 2500 RPM, when $[Cl^-] = 2.0-5.0 \text{ M}$, $T = 95 \degree \text{C}$, $[Fe^{3+}] = 0.5 \text{ M}$, and pH = 1.0. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Predicted redox potentials according to the model as a function of measured redox potentials in ferric chloride solution.

(Seisko et al., 2017; Seisko et al., 2019), which suggested that gold dissolves mainly as aurous gold in the current conditions both in ferric and cupric solutions.

$$\frac{dn}{Adt} = \frac{j_{corr}}{zF}$$
(10)

where *T* represents the temperature (°C), $[Cl^{-}]$ the concentration of chlorides (M), $\frac{dn}{Adt}$ the dissolution rate (mol s⁻¹ m⁻²), *z* the number of transferred electrons during the reaction, and F Faraday's constant (96,485 C mol⁻¹).

The Nernst equation can be used to determine the equilibrium potential of a reduction reaction in solution, Eq. (11), describing the redox potential when only one redox pair is present in the system. The Nernst equation (in a form of reduction reaction) was utilized to describe the anodic oxidation of Au into AuCl₂⁻ or AuCl₄⁻ as well as the cathodic reduction of Fe³⁺ into Fe²⁺ or Cu²⁺ to Cu⁺, see Eqs. (12) to (14). However, it should be noted that Eq. (13) is valid when ferric or cupric ions are present in solution as Fe³⁺ or Cu²⁺ as well as ferrous or cuprous ions as Fe²⁺ or Cu⁺, not as chloro complexes.



Fig. 5. Sensitivity analysis of the redox potential model in ferric chloride solution indicating the effect of a change in a parameter value on the change in redox potential.

$$E = E^0 - \frac{RT}{zF} * \ln\left(\frac{a_{Red}}{a_{Ox}}\right)$$
(11)

$$E = E^{0} - \frac{RT}{zF} * ln \frac{a_{[Au]} \cdot a_{[Cl^{-}]^{x}}}{a_{[AuCl_{x}^{-}]}}$$
(12)

$$E = E^{0} - \frac{RT}{zF} * \ln \frac{a_{[Fe^{2+}]}}{a_{[Fe^{3+}]}}$$
(13)

$$E = E^{0} - \frac{RT}{zF} * ln \frac{a_{[Cu^{+}]}}{a_{[Cu^{2+}]}}$$
(14)

where *E* represents the redox potential (V), *E*^o the standard electrode potential (V), R the molar gas constant (8.314 J K⁻¹ mol⁻¹), *T* the temperature (K), a_{Ox} and a_{Red} the activities of the oxidized and reduced species, respectively, $a_{[AuCl_x^-]}$ the activities of AuCl₂⁻ or AuCl₄⁻ (M), *x* the number of chloride ions involved in the reaction, $a_{[Cl-1]}$ the activity of free chlorides (M), $a_{[Fe^{2+}]}$ and $a_{[Cu^{2+}]}$ the activities of ferrous or cuprous ions (M), and $a_{[Fe^{3+}]}$ and $a_{[Cu^{2+}]}$ the activities of ferric or cupric ions (M).



Fig. 6. Logarithm of dissolution rate as a function of OCP with a rotational speed of 2500 RPM when T = 25-95 °C, $[Fe^{3+}] = 0.02-1.0$ M, $[Cl^{-}] = 2.0-5.0$ M, and pH = 0–1.0.



Fig. 7. Logarithm of dissolution rate as a function of redox potential with a rotational speed of 2500 RPM when T = 25–95 °C, $[Fe^{3+}] = 0.02–1.0$ M, $[Cl^-] = 2.0–5.0$ M, and pH = 0–1.0.

3. Results and discussion

3.1. Ferric chloride leaching

Gold dissolution was investigated using ferric species as the oxidant. The effect on gold dissolution of the process parameters, i.e., temperature, ferric and chloride concentration, as well as pH, was interpreted based on the mixed potential theory (Stern and Geary, 1957). Furthermore, the correlation between the redox potential and the OCP with the gold dissolution rate was determined when each process parameter was changed separately. Finally, a redox potential model was built consisting of the process parameters and its sensitivity was analyzed. Additionally, a gold dissolution rate equation was generated based on the measured redox potential.

3.1.1. Effect of temperature

In ferric chloride leaching, the temperature had a positive effect on the gold dissolution rate. According to Seisko et al. (2018), increasing



Fig. 8. Redox potential as a function of temperature when T = 28-95 °C, $[Cu^{2+}] = 0.5$ M, $[Cl^{-}] = 3.0$ M, and pH = 1.0.

temperature was shown to result in an increase in redox potential, and to follow the Nernst equation. The measured redox potentials varied between 0.64 and 0.73 V. The OCP and the redox potential increased as the temperature rose from 25 to 55 °C, although the OCPs reached a steady value of 0.66 V despite the redox potential increase at temperatures > 55 °C, see Fig. 1 a). A simultaneous increase in the OCP and the dissolution rate (Fig. 1 b)) indicated that cathodic reaction (i.e., the reduction of ferric ions) was dominant at T = 25-55 °C. However, at T = 55-95 °C, the anodic reaction (i.e., the dissolution of gold) was also enhanced in addition to the cathodic reaction, since the gold dissolution rate increased while the OCP remained constant, see Fig. 1 b). Furthermore, the logarithm of the gold dissolution rate had a positively linear dependency on the redox potential at T = 25-95 °C, see Fig. 1 b).

3.1.2. Effect of ferric concentration

In our previous research (Seisko et al., 2018), the increase in ferric concentration was shown to increase the redox potential and to follow the Nernst equation. The measured redox potentials varied between 0.68 and 0.74 V. Similarly, Liu and Nicol (2002) stated that the higher ratio of Fe^{3+} to Fe^{2+} promoted gold dissolution. The OCP had a linear dependency on the redox potential, see Fig. 2 a). Above a redox potential of 0.72 V ($[Fe^{3+}] \ge 0.5$ M), the gold dissolution rate became constant and the OCPs remained at approximately 0.66 V $([Fe^{3+}] \ge 0.5 \text{ M})$, see Fig. 2 b). A simultaneous increase in the OCP and the dissolution rate (Fig. 2 b)) indicated that the cathodic reduction of ferric ions was promoted at $[Fe^{3+}] = 0.02-0.5$ M. However, the anodic dissolution of gold was reduced, since the gold dissolution rate did not increase, even though the OCP continued to increase at $[Fe^{3+}] = 0.5-1.0$ M. The reason for the constant gold dissolution rate is not clear, therefore, further investigation is required. The logarithm of the gold dissolution rate increased linearly with increasing redox potential at $[Fe^{3+}] = 0.02-0.5$ M, see Fig. 2 b).

3.1.3. Effect of chloride concentration

In ferric chloride leaching, the chloride concentration has a linear negative correlation with the redox potential, and measured redox potentials varied between 0.70 and 0.74 V (Seisko et al., 2018). This agrees with Lundström et al., (2016), where the redox potential of Fe^{3+}/Fe^{2+} decreased with increasing chloride concentration. The redox potential and the OCP had a linear correlation and the OCP also decreased with increasing chloride concentration, see Fig. 3 a). However, the gold dissolution rate increased with increasing chloride concentration up to $[Cl^{-}] = 4.0$ M, but decreased at $[Cl^{-}] = 5.0$ M.



Fig. 9. a) *OCP as a function of redox potential*, and b) logarithm of gold dissolution rate as a function of redox potential and OCP with a rotational speed of 2500 RPM when T = 28-95 °C, $[Cu^{2+}] = 0.5$ M, $[Cl^{-}] = 3.0$ M, and pH = 1.0. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 10. Redox potential as a function of the logarithm of cupric concentration when $[Cu^{2+}] = 0.02-1.0$ M, T = 95 °C, $[Cl^{-}] = 3.0$ M, and pH = 1.0.

Generally, the effect of chloride concentration on the gold dissolution rate was not that significant compared to the other process variables. A simultaneous decrease in the OCP and increase in the gold dissolution rate (Fig. 3 b)) indicated that the anodic dissolution of gold was promoted at $[Cl^{-}] = 2.0-4.0$ M. At higher chloride concentrations, the cathodic reduction of ferric ions decreased, as the OCP and gold dissolution rate decreased at $[Cl^{-}] = 5.0$ M. The reason for the reduced cathodic reaction is not clear, but it may be related to the chloro complexes that are formed, since the amount of ferric chloride complexes increases when the chloride concentration increases (Muir, 2002; Sato and Kato, 1977; Strahm et al., 1979). According to Muir (2002), the reduction potentials of ferric chloride complexes decrease when the chloride concentration increases. However, the effect of high chloride concentrations (i.e., $[Cl^{-}] > 4.0 \text{ M}$) on gold dissolution requires further investigation. Furthermore, the gold dissolution rate in this research had a negative linear dependency on the redox potential at $[Cl^{-}] = 2.0-4.0$ M, see Fig. 3 b).

3.1.4. Redox potential model

As a result of these findings, a multilinear redox potential model was

built using the temperature, ferric and chloride concentration, as well as the pH with unscaled individual coefficients, see Eq. (15). However, it should be noted that the addition of reduced species of oxidant would describe the redox potential of the system more accurately. Therefore, this tool describes the leaching system only with pure gold in the leaching conditions, in which ferric species are dominant compared to ferrous species. The pH was shown to be a statistically significant parameter in ferric leaching, therefore it was included in the model. The measured redox potentials varied between 0.64 and 0.74 V. Additionally, replicate redox potentials were measured in order to test the reproducibility of the model. Three replicate redox potentials in the middle point of the parameter ranges (i.e., T = 55 °C, $[Fe^{3+}] = 0.25$ M, $[Cl^-] = 3.0$ M, and pH = 0.5) varied from 0.639 to 0.643 V, while four redox potentials in selected conditions (i.e., T = 95 °C, $[Fe^{3+}] = 0.5$ M, $[Cl^-] = 3.0$ M, and pH = 1.0) varied from 0.723 to 0.726 V.

 E_{REDOX} (V vs. SCE) = 5.75 $\cdot 10^{-1}$ + 1.27 $\cdot 10^{-3}$ T (°C) + 5.99 $\cdot 10^{-2}$ [Fe³⁺] (M)

$$-9.94 \cdot 10^{-3} [Cl^{-}] (M) + 2.61 \cdot 10^{-2} pH$$
(15)

According to the validation metrics of regression analysis such as the confidence level (95%), adjusted goodness of fit (adjusted $R^2 = 97.2\%$), goodness of prediction ($Q^2 = 94.9\%$), relative standard deviation (*RSD* = 0.58%), and reproducibility (99.7%), as well as a predicted vs. measured redox potential plot (Fig. 4), the redox potential model is reliable. Every parameter was shown to be statistically significant. The sensitivity analysis (Fig. 5) of the model suggests that an increase in temperature affected the redox potential most, compared to the ferric concentration and pH in the investigated range. The comparison point (i.e., zero point) was chosen to be at T = 60 °C, $[Fe^{3+}] = 0.5$ M, $[Cl^-] = 3.0$ M, and pH = 0.5. Furthermore, it should be noted that only an increase in chloride concentration decreased the redox potential.

3.1.5. Relationship of OCP, redox potential, and gold dissolution rate

As presented previously, the redox potential and OCP had a linear dependency on the temperature range of 25–55 °C, the ferric concentration range of 0.02–1.0 M, and the chloride concentration range of 2.0–5.0 M. At higher temperatures (i.e., T = 55-95 °C), OCP was constant, even though the redox potential was increased. However, the OCP did not have a significant correlation with the gold dissolution rate (Fig. 6), and therefore cannot be used to estimate gold dissolution.

The logarithm of the gold dissolution rate and redox potential



Fig. 11. *a)* OCP as a function of redox potential, and b) logarithm of gold dissolution rate as a function of redox potential and OCP with a rotational speed of 2500 RPM when $[Cu^{2+}] = 0.02-1.0 \text{ M}$, $T = 95 \degree C$, $[Cl^{-}] = 3.0 \text{ M}$, and pH = 1.0. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 12. Redox potential as a function of the logarithm of chloride concentration when [Cl⁻] = 1.0–5.0 M, T = 95 °C, [Cu²⁺] = 0.5 M, and pH =1.0.

increased linearly with a temperature of 25–95 °C and a ferric concentration of 0.02–0.5 M, but both decreased linearly with a chloride concentration of 2.0–4.0 M, as presented previously. A positive linear dependency was observed between the logarithm of the gold dissolution rate and the redox potential, and Fig. 7 shows all the tested parameter combinations. However, it should be noted that the logarithm of the gold dissolution rate settled above a redox potential of 0.71 V at a value of -3.2 (i.e., $6.3 \cdot 10^{-4}$ mol s⁻¹ m⁻²). The correlation coefficient was 0.88 for the correlation up to 0.71 V, therefore, the linear correlation is clear with these factors and indicates the normality of the response data (Gardiner, 1997). This suggests that the gold dissolution rate can be estimated according to Eq. (16), at redox potentials between 0.64 and 0.71 V, whereas higher redox potentials (i.e., up to 0.74 V) resulted in a gold dissolution rate of $6.3 \cdot 10^{-4}$ mol s⁻¹ m⁻².

$$\frac{dn}{Adt} (mol \ s^{-1} \ m^{-2}) = 10^{21.4E_{REDOX} \ (V \ vs.SCE) - 18.4}$$
(16)

3.2. Cupric chloride leaching

The effect of the process parameters of temperature, cupric and

chloride concentration on gold dissolution was investigated. The correlation between the redox potential and the OCP with the gold dissolution rate was studied when each process parameter was changed separately. A redox potential model was built using the above-mentioned process parameters and its sensitivity was analyzed. Additionally, a gold dissolution rate equation was generated using the measured redox potential.

3.2.1. Effect of temperature

In cupric chloride leaching, the temperature was shown to increase the redox potential and to follow the Nernst equation (Fig. 8). The measured redox potentials varied between 0.53 and 0.67 V. The similar effect was also observed with increasing temperature from 25 to 85 $^{\circ}$ C (Lundström et al., 2009).

The OCP and the redox potential increased as the temperature increased from 28 to 65 °C, although the OCP became nearly constant between 0.58 and 0.59 V even when the redox potential increased between 65 and 95 °C, see Fig. 9 a). However, the OCP and the redox potential had a positively linear correlation. The simultaneous increase in the OCP and dissolution rate indicated that the cathodic reduction of cupric ions was promoted at T = 28-55 °C (Seisko et al., 2019). However, at higher temperatures (i.e., T = 65-95 °C), the anodic dissolution of gold was also enhanced in addition to the cathodic reaction, since the gold dissolution rate was increased while the OCP remained constant, see Fig. 9 b). Furthermore, the logarithm of the gold dissolution rate had a positive linear dependency on the redox potential at T = 28-95 °C, Fig. 9 b).

3.2.2. Effect of cupric concentration

An Increase in cupric concentration increased the redox potential linearly, and followed the Nernst equation, see Fig. 10. The measured redox potentials varied between 0.62 and 0.68 V. The similar effect was shown with increasing cupric concentration from 10 to 40 g L^{-1} (i.e., 0.16–0.63 M) (Lundström et al., 2009).

The OCP and redox potential increased as the cupric concentration increased from 0.02 to 0.5 M, although the OCP settled to 0.59 V and decreased slightly despite the fact that the redox potential also increased at $[Cu^{2+}] = 0.5-1.0$ M, see Fig. 11 a). According to Seisko et al. (2019), the simultaneous increase in OCP and dissolution rate indicated that the cathodic reduction of cupric ions was promoted at $[Cu^{2+}] = 0.02-0.5$ M. However, at $[Cu^{2+}] = 0.75$ M, the anodic dissolution of gold was also enhanced in addition to the cathodic reaction, since the gold dissolution rate was increased while the OCP



Fig. 13. *a)* OCP as a function of redox potential, and b) logarithm of gold dissolution rate as a function of redox potential and OCP with a rotational speed of 2500 RPM when $[Cl^{-}] = 1.0-5.0 \text{ M}$, $T = 95 \degree C$, $[Cu^{2+}] = 0.5 \text{ M}$, and pH = 1.0. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 14. Predicted redox potentials according to the model as a function of measured redox potentials in cupric chloride solution.

decreased slightly. At $[Cu^{2+}] = 1.0$ M, the cathodic reduction of cupric ions was decreased, since the OCP and the gold dissolution rate decreased, see Fig. 11 b). The logarithm of the gold dissolution rate had a positively linear dependency on the redox potential at $[Cu^{2+}] = 0.02-0.75$ M, Fig. 11 b).

3.2.3. Effect of chloride concentration

In cupric chloride leaching, an increase in chloride concentration increased the redox potential linearly, Fig. 12. The measured redox potentials varied between 0.64 and 0.68 V. The positive effect of chloride concentration on redox potential has been suggested previously by Muir (2002) as well as Lu and Dreisinger (2013), as a higher chloride concentration results in a lower concentration of cuprous ions.

The OCP and the redox potential increased as the chloride concentration increased from 1.0 to 5.0 M, see Fig. 13 a). The OCP at $[Cl^-] = 2.0$ M was considered to be a random error. According to Seisko et al. (2019), a simultaneous increase in OCP and dissolution rate indicated that the cathodic reduction of cupric ions was promoted at $[Cl^-] = 1.0-5.0$ M, see Fig. 13 b). Further, the gold dissolution rate



Fig. 15. Sensitivity analysis of redox potential model in cupric chloride solution indicating the effect of change in a parameter value on the change in redox potential.

increased with the redox potential at $[Cl^-] = 1.0-5.0$ M, Fig. 13 b).

3.2.4. Redox potential model

A multilinear redox potential model was successfully built using temperature, cupric and chloride concentration with the investigated parameter range and consisting of unscaled individual coefficients, Eq. (17). The pH was shown to be statistically insignificant in the pH range of 0.0–2.0, therefore it was excluded from the model. The measured redox potentials varied from 0.53–0.68 V. Four replicate redox potential measurements in selected conditions (i.e., T = 95 °C, $[Cu^{2+}] = 0.5$ M, $[Cl^{-}] = 3.0$ M, and pH = 1.0) varied from 0.654 to 0.665 V.

$$E_{\text{REDOX}} (\text{V vs. SCE}) = 419 \cdot 10^{-3} + 1.77 \cdot 10^{-3} T (^{\circ}\text{C}) + 66.7 \cdot 10^{-3} [Cu^{2+}] (\text{M}) + 13.3 \cdot 10^{-3} [Cl^{-}] (\text{M})$$
(17)

According to the validation metrics of regression analysis such as



Fig. 16. Logarithm of gold dissolution rate as a function of redox potential with a rotational speed of 2500 RPM when T = 28-95 °C, $[Cu^{2+}] = 0.02-1.0$ M, $[Cl^{-}] = 1-5$ M and pH = 1.0. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 17. Logarithm of gold dissolution rate as a function of redox potential with a rotational speed of 2500 RPM when T = 28-95 °C, $[Cu^{2+}] = 0.02-1.0$ M, $[Cl^{-}] = 2-5$ M and pH = 1.0. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$\frac{dn}{Adt} (mol \ s^{-1} \ m^{-2}) = 10^{12.9E_{REDOX} \ (V \ vs.SCE) - 12.5}$$
(18)

the confidence level (95%), adjusted R^2 (98.0%), Q^2 (96.4%), RSD (0.65%), and reproducibility (99.7%), as well as a predicted vs. measured redox potential plot (Fig. 14), the created linear redox potential is reliable. A sensitivity analysis of the model (Fig. 15) suggests that the increase in temperature increased the redox potential more, compared to the cupric and chloride concentration.

3.2.5. Relationship of OCP, redox potential, and gold dissolution rate

The redox potential and OCP had a positive dependency on the temperature range of 28–85 $^{\circ}$ C, the cupric concentration range of 0.02–0.5 M, and the chloride concentration range of 1.0–5.0 M, as presented previously. However, the OCP did not have a significant correlation with the gold dissolution rate (Fig. 16) and therefore it cannot be used to estimate gold dissolution.

As presented previously, the logarithm of the gold dissolution rate

was positively linear with the redox potential with the temperature range of 25–95 °C, the cupric concentration of 0.02–0.75 M, and the chloride concentration of 2.0–5.0 M. As a conclusion, a positive linear correlation was observed with the logarithm of gold dissolution rate and redox potential with all the investigated parameter ranges (excluding $[Cl^-] = 1$ M), Fig. 17. However, the pH was not considered, since its effect was statistically insignificant. The correlation coefficient was 0.96; therefore the linear correlation is clear with these factors and it indicates the normality of the response data (Gardiner, 1997). The gold dissolution rate can be estimated according to Eq. (18) when the redox potential varies between 0.53 and 0.68 V vs. SCE.

4. Conclusions

The aim of this study was to investigate the effect of process variables on the redox potential, OCP, and further on the gold dissolution rate in ferric and cupric chloride solutions. The second aim was to provide tools that can be used to estimate the gold leaching rate in ferric and cupric chloride solutions using solution properties. In ferric chloride solutions, the investigated redox potentials were found to vary between 0.64 and 0.74 V vs. SCE, gold OCPs of between 0.60 and 0.69 SCE, V vs. and dissolution rates of $1.7 \cdot 10^{-5}$ -7.3 $\cdot 10^{-4}$ mol s⁻¹ m⁻². In contrast, the corresponding values in cupric chloride solutions were all lower: redox potentials of between 0.53 and 0.68 V vs. SCE, OCPs of between 0.53 and 0.60 V vs. SCE, and gold dissolution rates of $2.5 \cdot 10^{-6}$ - $2.9 \cdot 10^{-4}$ mol s⁻¹ m⁻².

Linear regression models were built for redox potential, including the process parameters of temperature, oxidant and chloride concentration, as well as pH. In the ferric chloride solution, all the parameters were found to be statistically significant, but in cupric chloride leaching, the effect of pH in the investigated region (i.e., T = 25-95 °C, $[Fe^{3+}/Cu^{2+}] = 0.02-1.0$ M, $[Cl^{-}] = 1-5$ M, pH = 0.0-2.0, and $\omega_{cyc} = 2500$ RPM) was insignificant. Temperature was shown to be the most influential parameter on the redox potential in comparison with the oxidant and chloride concentrations, and the pH. Additionally, the increase in chloride concentration decreased the redox potential in the ferric system, whereas the effect was the opposite in the cupric system. Furthermore, according to the sensitivity analyses, the process variables had more effect on the redox potential in cupric solution.

A linear positive correlation was observed between the redox potential and the logarithm of the gold dissolution rate in both oxidant systems, therefore the linear redox potential model could be used to estimate the gold dissolution rate of system with the solution parameters (i.e., T, $[Fe^{3+}/Cu^{2+}]$, $[Cl^{-}]$, and pH) as model variables. However, the OCP did not have a significant correlation with the gold dissolution rate, therefore it cannot be used to estimate gold dissolution. In the ferric system, the presented dependency is valid with redox potential values of between 0.64 and 0.71 V vs. SCE, while higher redox potentials (i.e., up to 0.74 V vs. SCE) resulted in a gold dissolution rate of $6.3 \cdot 10^{-4}$ mol s⁻¹ m⁻². In the cupric system, the dependency is valid throughout the entire investigated redox potential range (i.e., 0.53–0.68 V vs. SCE).

As a conclusion, the study showed that the solution properties can be used to predict the redox potential and furthermore the redox potential can be used as an estimator for the gold dissolution rate in ferric and cupric chloride solutions. In future, this can provide tools for the optimization of leaching behavior with industrial gold-containing raw materials, although they should be subjected to separate research and optimization. Currently, the gold dissolution rate tool presented in this study was built for pure gold and synthetic solutions, but can potentially be more applicable industrially in systems where gold dominates in elemental form, for example for free-milling gold ores with no significant amounts of other leachable components.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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