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Dissolution of Gold in Ferric and Cupric Chloride Solutions

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2) Dissolution of Gold in Ferric and Cupric Chloride Solutions (Published in European Metallurgical Conference (EMC) 2017 proceedings as a peer-reviewed conference paper + presentation)

Keywords: quartz crystal microbalance, rotating disc electrode, oxidant, oxidation state

Abstract

Currently, cyanide is the dominant lixiviant used in gold leaching. However, there is demand for non-cyanide lixiviants due to several environmental disasters, e.g. in Baia Mare in Romania in 2000 [1, 2]. The use of cyanide has been limited or forbid by legislation in many countries and/or territories [1]. Therefore, alternative leaching solutions have been investigated, and chlorides are proposed as one of the most promising lixiviants for gold due to the high dissolution rates [3]. In order to dissolve gold, strong oxidant is required [4]. When using ferric and cupric ions and/or complexes as oxidants in gold leaching, Fe(III) and Cu(II) are reduced into Fe(II) and Cu(I), respectively. These ferrous and cuprous ions can be further oxidized in the presence of oxygen, which is the major advantage of chloride leaching compared to cyanide and thiourea [5, 6].

In this study, gold dissolution in chloride solutions was investigated by quartz crystal microbalance (QCM) with ferric and cupric ions and/or chloride complexes as oxidants originating from FeCl₃, Fe₂(SO₄)₃, CuCl₂ and CuSO₄ (0.02-1.0 M). The source of oxidant and the effect of its concentration as well as the redox potential during leaching were studied, while the chloride concentration (3 M), pH (1.0) and temperature (95 °C) were fixed. With ferric ions, higher dissolution rates were achieved compared to cupric with all investigated oxidant sources. Ferric and cupric ions originating from chloride salts (FeCl₃ and CuCl₂) were shown to result in higher gold dissolution rates compared to corresponding sulfate salts as oxidant source. The redox potentials of the solutions were shown to increase with increasing oxidant concentration, from 683 to 740 mV vs. SCE with ferric and from 586 to 674 mV vs. SCE with cupric. The best gold dissolution rates, achieved with 0.5 M oxidant concentration, were 1.34·10⁻⁴ and 1.66·10⁻⁵ mol s⁻¹ m⁻² with ferric and cupric ions, respectively. Additionally, QCM results were compared to the results of rotating disc electrode (RDE)
measurements in order to investigate the oxidation state of gold in chloride leaching. It can be suggested that with both oxidants, the oxidation state of gold is +1 instead of +3.

1 Introduction

Nowadays, cyanide leaching is the dominant method to produce gold from primary raw materials [4]. However, the use of cyanide has developed as an international concern and several countries and territories has started to ban cyanidation via legislation, since there occurs an environmental risk via possible cyanide spill [7]. Therefore, many alternative solutions, such as thiourea, thiosulfate, thiosulphate, oil-coal agglomerates as well as halides have been proposed to replace cyanide as a lixiviant [1].

Gold and halogen-group elements form complex compounds such as chlorides, bromides and iodides, which are susceptible to dissolve in the aqueous solution [5]. Additionally, in order to dissolve gold into the ion form prior to complex formation, strong oxidant is required to oxide gold [4]. According to Abe and Hosaka [5], it was shown that ferric ion is an effective oxidant in chloride media for gold leaching despite lower redox potential compared to other oxidants. Abe and Hosaka [5] stated that the oxidation potential ≥480 mV (vs. Ag/AgCl) corresponding ≥435 mV (vs. SCE) is required with ferric and cupric ions for the dissolution of gold instead of ≥778 mV (vs. Ag/AgCl) corresponding ≥733 mV (vs. SCE) that is required for oxidation with chlorine or bromine gas.

Gold dissolves not only as aurous ions (Au(I)), but also auric ions (Au(III)) into aqueous chloride solution [4]. The dissolution of gold is suggested to proceed in two stages [8]. In first stage, the formation of intermediate Au(I) chloride (i.e., AuCl) occurs in the gold surface, described in equation 1. In second stage, a secondary intermediate, AuCl$_2^-$, is formed in the gold surface and it can be further oxidized into Au(III) (equation 2) or diffused into solution as AuCl$_2^-$, depending on the oxidation potential of solution [9]. Nicol [9] found out that formation of AuCl$_2^-$ occurs at lower oxidation potentials compared to the formation of AuCl$_4^-$, however, the oxidation potentials depend on the conditions of solution and process.

$$2\text{Au} + 2\text{Cl}^- \rightarrow 2\text{AuCl} + 2\text{e}^-$$

(1)

$$\text{AuCl}_2^- + 2\text{Cl}^- \rightarrow \text{AuCl}_4^- + 2\text{e}^-$$

(2)
The total reaction of gold dissolution in ferric chloride solution is described in equation 3 and in cupric chloride solution is described in equation 4, while gold is suggested to dissolve as aurous, Au(I), ions [10, 11]. However, it must be noted that with increasing chloride concentration, ferric ions form chloride complexes such as FeCl₃ [12]. The regeneration of ferrous ions back to ferric ions/chloride complexes can be conducted by oxygen purging, equation 5 presenting the reaction without complex formation [5, 6, 10]. Additionally, the regeneration of cuprous ions back to cupric ions/chloride complexes can be conducted by oxygen purging, equation 6 presenting cuprous oxidation reaction without chlorides, copper complex formation depending on chloride concentration and oxidation potential [6]. The role oxygen is significant in order to maintain the high ratio of Fe(III) to Fe(II) [10]. This reuse of oxidant (cupric or ferric) via regeneration is a major advantage compared to the other methods such as cyanidation, in which copper/iron can not be used as an oxidant for gold leaching.

\[
\text{Au} + 2\text{Cl}^- + 2\text{Fe}^{3+} \rightarrow \text{AuCl}_2 + \text{Fe}^{2+}
\]

(3)

\[
\text{Au} + 2\text{Cl}^- + \text{Cu}^{2+} \rightarrow \text{AuCl}_2 + \text{Cu}^+
\]

(4)

\[
4\text{Fe}^{2+} + 4\text{H}^+ + \text{O}_2 \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}
\]

(5)

\[
4\text{Cu}^{+} + 4\text{H}^+ + \text{O}_2 \rightarrow 4\text{Cu}^{2+} + 2\text{H}_2\text{O}
\]

(6)

In this work, the effect of oxidant source as well as the effect of oxidant concentration were investigated by the Quartz Crystal Microbalance (QCM) technology. Additionally, the Rotating Disc Electrode (RDE) measurements were performed in order to compare the results with QCM results. With this comparison, the oxidation stage of gold can be determined.
2 Experimental

2.1 QCM experiments

QCM equipment measures the resonant frequency of a quartz plate resonator which is inversely proportional to the mass of the gold layer according to the Sauerbrey equation [13]. When the frequency increases, the mass of the gold decreases, equation 7 [14].

\[ \Delta f = -C_f \cdot \Delta m \]  

(7)

In which \( \Delta f \) represents the frequency shift, \( \Delta m \) the mass change per unit surface area, \( C_f \) the sensitivity factor. For example, the sensitivity factor for a 5 MHz AT-cut quartz crystal at room temperature is 56.6 Hz \( \mu \text{m}^{-1} \text{cm}^2 \) [15].

The QCM measurements were executed in a glass reactor (1 L), which was immersed and heated in Lauda Aqualine 25 water bath. The temperature was fixed (95 °C) in every experiment. In order to avoid the thermal shock, QCM device was pre-heated in water bath for 30 min prior to immersing into heated solution. The dissolution of gold started immediately when the crystal contacted with the solution. Oxygen (with the purity of 99.9% and moisture max. 1 vol-%) sparging was used in order to enable cuprous or ferrous oxidation. However, oxygen feed was set to lowest flow rate (circa 0.2 NL min\(^{-1}\)) to avoid oxygen bubble formation, causing frequency calculation errors when hitting the gold crystal. Rotation of the system was performed with VWR Vos 16 overhead stirrer equipped with a four-blade impeller (45°) and rotational speed was fixed (50 RPM) to ensure the mixing of solution and to avoid turbulent mixing.

The QCM tests were performed using the SRS MODEL QCM 200 system and the Au/Cr QCM crystal with the frequency of 5 MHz, which was implanted into the probe of a QCM25 5 MHz crystal oscillator. In QCM measurements, the QCM crystal with the surface area of 0.40 cm\(^2\) was used as a working electrode. The redox potential of solution was investigated with a pure platinum plate as a counter electrode and a Hg/Hg\(_2\)Cl\(_2\) calomel electrode (SCE) with saturated KCl salt bridge as a reference electrode. Redox potential was measured by 16-bit USB-1608G data acquisition device. Since the mass loss rate of the crystal was set to constant, potential was measured with the frequency of 10 Hz. Redox potential data was collected with Instacal software.

Tested oxidants were iron(II) chloride, iron(II) sulfate, copper(II) chloride, and copper(II) sulfate. The chloride concentration was fixed to 3.0 M, adjusted by adding NaCl. Additionally, pH was fixed to 1.0, adjusted by adding HCl (by 1.0 M stock solution). The investigated oxidant concentration varied between 0.02-1.0 M. The used chemicals in experiments were FeCl\(_3\) (Merck Millipore, ≥ 98%), Fe(SO\(_4\))\(_3\)-7H\(_2\)O (VWR chemicals, chemically pure grade), CuCl\(_2\)-2H\(_2\)O (VWR chemicals, technical grade), CuSO\(_4\)-5H\(_2\)O (VWR chemicals, technical grade), NaCl (VWR Chemicals, technical grade)
and HCl (Merck KGaA, Ph. Eur. grade). The same chemicals were additionally used in RDE measurements.

2.2 RDE measurements

In RDE measurements, 99.99% pure gold rotating electrode (Pine Research Instrumentation Inc.) with the surface area of 13.1 mm² was used as the working electrode. Additionally, gold disc was attached into the polytetrafluoroethylene (PTFE) sheath. Pure platinum plate was used as the counter electrode and Ag/AgCl electrode as a reference electrode (SI Analytics).

RDE measurements were performed with ACM Instrument’s Gill AC potentiostat using Linear Polarization Resistance (LPR) sweep with Gill AC Sequencer software (from -10 to 10 mV vs. Open Circuit Potential (OCP) with sweep rate of 10 mV min⁻¹). The average LPR of three parallel measurements in each condition was used as LPR value. LPR \( R_p \) was determined from the slope of the potential-current density diagram, \( R_p \) being inversely proportional to the corrosion current density \( j_{corr} \), equation 8 [16].

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

in which \( b_a \) represents the Tafel slope coefficient of the anodic side (mV decade⁻¹), \( b_c \) the coefficient of the cathodic side (mV decade⁻¹), \( B \) the systematic coefficient called as Stearn-Geary constant (mV) and \( R_p \) the LPR (Ω cm²). Additionally, a separate polarization resistance measurement was performed in order to calculate Stearn-Geary constant, in which gold wire (Premion®), with the purity of 99.999%, was used as a working electrode. Stearn-Geary constant was 27.1 mV at \( [Cl^-] = 3 \) M as well as \( T = 95 \) °C.
3 Results and discussion

3.1 Effect of oxidant source and concentration

For FeCl₃, CuCl₂ and CuSO₄, concentrations investigated were 0.02, 0.1, 0.5 and 1.0 M in QCM measurements. When using Fe₂(SO₄)₃ as oxidant, concentrations higher than 0.1 M could not be prepared, since iron started to precipitate. Therefore, with Fe₂(SO₄)₃, the tested concentrations were 0.02 and 0.1 M. The dissolution rate of gold as a function of oxidant ion concentration with FeCl₃, Fe₂(SO₄)₃, CuCl₂ and CuSO₄ is presented in figure 1. Other variables in experiments were [Cl⁻] = 3.0 M, pH = 1.0 M and T = 95 °C. Figure 1 shows that oxidant originating from chloride compounds resulted in higher gold dissolution rates compared to sulfates with both cupric and ferric ions. It was shown that FeCl₃, CuCl₂ and CuSO₄ reached their maximum dissolution rate of gold with oxidant ion concentration of 0.5 M. The highest gold dissolution rate (1.34·10⁻⁴ mol s⁻¹ m⁻²) was achieved with FeCl₃ when [Fe³⁺] = 0.5 M. For cupric ion, the highest gold dissolution rate (1.66·10⁻⁵ mol s⁻¹ m⁻²) was achieved using CuCl₂ ([Cu²⁺] = 0.5 M) as a oxidant source instead of CuSO₄.

Figure 1: The dissolution rate of gold from QCM tests as a function of oxidant ion concentration. The sources of oxidant were FeCl₃, Fe₂(SO₄)₃, CuCl₂ and CuSO₄. Fixed leaching conditions were [Cl⁻] = 3M, T = 95 °C and pH = 1.0

McDonald et al. [11] presented that the dissolution of gold increases when cupric chloride concentration is increased up to 0.6 M. It was suggested that with cupric chloride concentration over 0.6 M, only a small increase in gold dissolution occurred. Therefore, the authors presented that this phenomenon occurs when the rise of cuprous concentration starts to limit the process. However, the concentration of cuprous ions can be considered to be relatively low in the current study, since the calculated concentration of AuCl₂⁻ in solution varied from 1.6·10⁻⁸ M to 8.3·10⁻⁷ M, which indicate
that the concentration of cuprous ions formed during the leaching process (equation 4) is small compared to cupric ions. Hence, with the data available it cannot be directly concluded if cuprous ions cause the lower dissolution rates with the initial cupric ion concentration of 1.0 M. However, based on the QCM dissolution rates (figure 1) the optimal initial cupric ion concentration is ca. 0.5 M.

Furthermore, Frankenthal and Siconolfi [17] concluded that the process variables such as chloride concentration, pH and rotational speed affect the passivation potential of gold. However, the mechanism of passivation is unclear as well as the effect of oxidant concentration on gold passivation. Furthermore, the passivation of gold surface by oxide layer is suggested to occur at high potentials (i.e., above approximately 1.4 V vs. NHE), which is not reached even with the highest oxidant concentration investigated in this study (1.0 M) [4]. Therefore it can be suggested that the high oxidant concentration can cause passivation already at lower potentials. Abe and Hosaka [5] stated that gold can be leached at ferric concentration ≥0.01 g L⁻¹ (0.0002 M), however, the upper limit for effective gold dissolution by ferric was not investigated.

3.2 Redox potential and reaction mechanism of gold dissolution

Redox potentials did not change during measurements, therefore, the redox potential was defined as the average value during the QCM measurement. The redox potential as a function of oxidant ion concentration, for cupric and ferric solutions when using chloride compounds as oxidant source, is described in figure 2. The redox potentials were measured during QCM measurements, therefore, the oxidant concentrations were 0.02, 0.1, 0.5 and 1.0 M, while chloride concentration (3 M), temperature (95 °C) and pH (1.0) were fixed. The redox potentials were shown to increase with increasing oxidant ion concentration. oxidant concentrations. The redox potentials in ferric solutions varied between 683-740 mV vs. SCE, whereas in cupric solutions between 586-674 mV vs. SCE. Additionally, ferric ions resulted in higher redox potentials compared to cupric ions at equal molality.
Figure 2: Redox potential of cupric and ferric solutions as a function of oxidant concentration, when using chloride compounds as the oxidant source. Fixed conditions were $[Cl^-] = 3$ M, $T = 95 \, ^\circ\text{C}$ and $pH = 1.0$

### 3.3 Comparison of QCM and RDE tests

According to QCM measurements, oxidant originating from chloride compounds resulted in higher gold dissolution rates compared to sulfates with both cupric and ferric ions. RDE measurements were performed for gold dissolution with both $\text{CuCl}_2$ and $\text{FeCl}_3$. When determining the gold dissolution rate from LPR values measured by RDE, the valence of gold ($z$) is required in calculations. Since gold dissolution rates in QCM measurements is defined from mass loss, the valence of gold does not need to be defined. In order to investigate the amount of electrons during the gold dissolution i.e. $z$ value, the gold dissolution rates from RDE measurements assuming gold either having valence of +1 or +3, were compared to the dissolution rates from QCM tests.

Figure 3 presents the comparison of dissolution rates of gold in cupric chloride solution, when using RDE method with $z = 1$ and QCM method, whereas figure 4 presents the same results, but dissolution rates from RDE measurements are calculated with $z = 3$. Other conditions were $\omega = 100$-2500 RPM, $[\text{Cu}^{2+}] = 0.5$ M, $[Cl^-] = 3$ M and $pH = 1.0$ as well as $T = 95 \, ^\circ\text{C}$. Both, LPR and QCM results indicate that gold dissolution rate decreased while cupric concentration increased from 0.5 to 1.0 M.

Figure 5 illustrates the comparison of dissolution rates of gold in ferric chloride solution, determined from LPR when using RDE with assumption that with $z = 1$ and QCM method figure 6 represents the same results, but dissolution rates from RDE measurements are calculated with assumption that $z = 3$. Experimental conditions were $\omega = 100$-2500 RPM, $[Fe^{3+}] = 0.5$ M, $[Cl^-] = 3$ M, $pH = 1.0$ and $T = 95 \, ^\circ\text{C}$. In ferric chloride leaching there is a contradiction between the methods since LPR
measurements indicate that gold dissolution rates increased with increasing ferric concentration from 0.5 to 1.0 M, whereas gold dissolution rate decreased in QCM tests in the same range.

Figure 3: Comparison of gold dissolution rates in cupric chloride solution, determined from LPR using RDE (\( \omega = 100-2500 \) RPM) with assumption that \( z = 1 \) and QCM method. Solution conditions were \([Cl^-] = 3 \) M, \( pH = 1.0 \) and \( T = 95 \) °C.
Figure 4: Comparison of gold dissolution rates in cupric chloride solution, determined from LPR using RDE ($\omega = 100$-2500 RPM) with assumption that $z = 3$ and QCM method. Solution conditions were $[Cl^-] = 3$ M, $pH = 1.0$ and $T = 95$ °C.

Figure 5: Comparison of gold dissolution rates in ferric chloride solution, determined from LPR using RDE ($\omega = 100$-2500 RPM) with assumption that $z = 1$ and QCM method. Solution conditions were $[Cl^-] = 3$ M, $pH = 1.0$ and $T = 95$ °C.
According to figures 3-6, it can be concluded that gold dissolution rate from QCM measurements match the RDE results, when the valence of gold in the calculations is assumed as +1 (i.e., $z = 1$) with both oxidants, ferric and cupric ions. When $z = 3$, the gold dissolution rates from QCM measurements exceed significantly the dissolution rates from RDE tests with similar agitation speed despite the oxidant. However, it should be noted that only the slowest rotational speed of RDE test corresponds to the stirring speed in QCM measurement. Therefore, it can be concluded that the oxidation state of gold in the investigated conditions ($[Cu^{2+}/Fe^{3+}] = 0.02-1.0$ M, $[Cl^-] = 3$ M and $pH = 1$ at 95 °C) is +1. The gold dissolution rates based on QCM experiments (solution stirred with external agitator at 50 RPM) were shown to be equal to the gold dissolution rates of RDE with rotational speeds of 100 RPM in cupric chloride and 100-300 RPM in ferric chloride solution, depending on oxidant concentration, when $z = 1$.

4 Conclusions

Chloride and sulfate compounds of ferric and cupric ions (i.e., FeCl$_3$, CuCl$_2$, Fe$_2$(SO$_4$)$_3$ and CuSO$_4$) were investigated as oxidant source of ferric and cupric ions in QCM measurement. For FeCl$_3$, CuCl$_2$ and CuSO$_4$, the tested concentrations were 0.02, 0.1, 0.5 and 1.0 M. For Fe$_2$(SO$_4$)$_3$, the tested concentrations were 0.02 and 0.1 M, since iron in the solutions started to precipitate at higher concentrations. The fixed conditions in QCM tests were $[Cl^-] = 3.0$ M, $pH = 1.0$ M and $T = 95$ °C. For all investigated oxidant sources chloride compounds resulted in higher dissolution rates of gold compared to sulfate ones.

Dissolution rate of gold was shown to increase up to 0.5 M of oxidant, however, at higher concentrations (from 0.5 to 1.0 M) the dissolution rate decreased. According to literature, this phenomenon was suggested to occur due to passivation of gold. Furthermore, the passivation of gold surface by oxide layer has been suggested to occur at high potential (i.e., above approximately 1.4 V vs. NHE corresponding 1.156 V vs. SCE), which is higher than the redox potentials of this study (in ferric solutions 0.683-0.740 V vs. SCE, and in cupric solutions 0.586-0.674 V vs. SCE) [4]. Therefore, it can be suggested that the high oxidant concentration can cause passivation already at potentials lower than 1.156 V vs. SCE. Nevertheless, the mechanism of passivation is unclear and requires further research.

Additionally, ferric ions were shown to result in higher gold dissolution rates compared to the use of cupric ions as an oxidant in QCM tests. The highest gold dissolution rate (1.34·10$^{-4}$ mol s$^{-1}$ m$^{-2}$) was achieved with FeCl$_3$ when $[Fe^{3+}] = 0.5$ M. For cupric ion, the highest gold dissolution rate (1.66·10$^{-5}$ mol s$^{-1}$ m$^{-2}$) was achieved using CuCl$_2$ as the oxidant source ($[Cu^{2+}] = 0.5$ M). Additionally, the ferric solutions were shown to have higher redox potentials compared to cupric solutions. The redox potentials in ferric solutions varied from 683 to 740 mV vs. SCE, whereas in cupric solutions the
redox potential varied from 586 to 674 mV vs. SCE. Although the redox potential was shown to increase with increasing oxidant concentration up to 1.0 M, the gold dissolution rates decreased with increasing oxidant concentration from 0.5 to 1.0 M.

The comparison of QCM and RDE methods was performed in order to define the oxidation state of gold, since QCM measurements define the dissolution rate from mass loss, whereas the gold dissolution rates defined from RDE measurements depend on the assumed valence of gold (i.e., +1 and +3). In RDE measurements, rotational speed range was 100-2500 RPM as well as other conditions were \([Cu^{2+}/Fe^{3+}] = 0.5\) M, \([Cl^-] = 3\) M and \(pH = 1.0\) as well as \(T = 95\) °C. It was shown that gold dissolution rate from QCM measurements matched the RDE results with similar agitation speed, when the valence of gold was +1 (i.e., \(z = 1\)) with both oxidants, ferric and cupric ions. When the valence of gold was assumed as +3, the gold dissolution rates from QCM measurements exceed significantly the dissolution rates from RDE tests with similar agitation speed. Therefore, it can be concluded that one electron (\(z = 1\)) is transferred during the dissolution process of elemental gold in cupric or ferric chloride solution (\([Cu^{2+}/Fe^{3+}] = 0.02\)-1.0 M, \([Cl^-] = 3\) M and \(pH = 1\) at 95 °C at redox potentials in the range of 586-674 mV vs. SCE in cupric solutions and 683-740 mV vs. SCE in ferric solutions), gold dissolving with a valence of +1.

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