An Electrochemical Study of Gold Dissolution in Thiosulfate Solution with Cobalt–Ammonia Catalysis

Ke Li, Qian Li, Bin Xu *, Yongbin Yang and Tao Jiang

Abstract: Alkali agents could be used to enhance the extraction of zinc from solution, but excess alkali can lead to emulsification of the solution. In this study, the redox couples of Co(III)/Co(II) could be formed based on the thermodynamic analysis, and catalyze the dissolution of gold in a cobalt–ammonia–thiosulfate system. The catalytic mechanism of cobalt–ammonia for gold dissolution in the thiosulfate solution was further proposed by the analysis of polarization curves to be that NH$_3$ catalyzes the dissolution of gold in the anodic area, and Co(NH$_3$)$_6^{3+}$ catalyzes the reduction of dissolved oxygen in the cathodic area. In the dissolution of gold, the concentration of NH$_3$, Co$^{3+}$ and S$_2$O$_3^{2-}$ increased, and the dissolution of gold increased. The apparent activation energy for gold dissolution is 41.15 kJ/mol in a temperature range of 25–40 °C, and this demonstrates that gold dissolution is chemically controlled. The SEM-EDS and XPS analyses indicate that the precipitate coating on gold surfaces is mainly S$^{2-}$ in CoS and S$_8$. The decomposition of thiosulfate was also carried out in different thiosulfate solutions. Results have shown that the increase of NH$_3$ concentration can reduce thiosulfate decomposition, while the increase of Co$^{3+}$ and S$_2$O$_3^{2-}$ concentration can accelerate thiosulfate decomposition. The apparent activation energy for thiosulfate decomposition with the temperature range of 26.6–41 °C is determined to be 22.12 kJ/mol, which shows that thiosulfate decomposition is mixed chemical-diffusion-controlled.

Keywords: electrochemical study; gold dissolution; thiosulfate solution; cobalt-ammonia catalysis

1. Introduction

Cyanidation has been the dominant gold leaching technique from its ores or concentrates because of its low cost, simple process and mature technology [1]. However, this technique is harmful to the environment due to the high toxicity of cyanide. Furthermore, cyanidation has a long period of gold leaching, generally requiring more than 24 h, and gold cannot be available leached from refractory gold ores or concentrates. Due to the above environmental and technical concerns, the development of a non-cyanide technique has been focused on searching for an alternative lixivants in the study of gold extraction. There are various alternation lixiviants of cyanide being proposed for gold leaching, such as thiourea, chloride, bromide, iodine, thiocyanate and thiosulfate [2–7]. Among those lixiviants, thiourea has been widely regarded as the most promising substitute of cyanide [8–12].

The overall reaction for gold leaching in thiosulfate solution is shown in Equation (1). Actually, the gold leaching rate of the above reaction has been found to be quite slow [13]. Copper ion was found to offer a strong catalytic effect for gold leaching in the presence of ammonia, which can stabilize Cu(II) as Cu(NH$_3$)$_4^{2+}$ in alkaline thiosulfate solution [14–18]; the reaction is expressed in Equation (2). Thiosulfate is metastable and is prone to oxidize into some intermediate sulfur-containing species in ammoniacal thiosulfate solution, such as S$_4$O$_6^{2-}$, S$_3$O$_6^{2-}$, SO$_3^{2-}$ and SO$_4^{2-}$ [19–25]. The presence of Cu(NH$_3$)$_4^{2+}$ in thiosulfate solution can accelerate the thiosulfate oxidative decomposition [26–30], which
will result in a high thiosulfate consumption. For the gold recovery from its pregnant solution, resin adsorption has been considered to be the most appropriate for gold recovery due to the low requirement for water quality, high gold loading capacity, fast adsorption and easy regeneration of resin at ambient temperature [31–36]. However, the competitive adsorption of undesirable anions, predominantly including Cu(S\textsubscript{2}O\textsubscript{3})\textsuperscript{3−} and S\textsubscript{x}O\textsubscript{6}\textsuperscript{2−} with Au(S\textsubscript{2}O\textsubscript{3})\textsuperscript{2−} on the resin surface is inevitable [37–39]. As a result of this, gold adsorption on the resin is disturbed and its desorption of the loaded resin also becomes complicated. From the above, it can be concluded that the high consumption of thiosulfate and the complication of gold recovery from its pregnant solution both limit the industrial development of thiosulfate leaching.

\[ 4\text{Au} + 8\text{S}_2\text{O}_3^{2−} + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{Au(S}_2\text{O}_3)_2^{3−} + 4\text{OH}^{−} \quad (1) \]

\[ \text{Au} + 5\text{S}_2\text{O}_3^{2−} + \text{Cu(NH}_3)_4^{2+} = \text{Au(S}_2\text{O}_3)_2^{3−} + 4\text{NH}_3 + 5\text{Cu(S}_2\text{O}_3)_3^{5−} \quad (2) \]

In order to solve the problems associated with thiosulfate leaching of gold, an effective measure is the replacement of copper–ammonia catalysis with other catalysts. EDTA and oxalate both can stabilize Fe(III) in alkaline solution in the form of Fe(III)-EDTA/oxalate complexes, and formed Fe(EDAT)^−/Fe(EDTA)^3− couple and Fe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}−/Fe(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}− couple can be used to replace the traditional Cu(NH\textsubscript{3})\textsubscript{4}^{2+}/Cu(S\textsubscript{2}O\textsubscript{3})\textsubscript{3}− couple to catalyze gold dissolution [40]. Although thiosulfate consumption was negligible under the Fe(III)-EDTA/oxalate system, the gold leaching rate was very low without the addition of thiourea. Moreover, the presence of sulfide minerals in actual leach slurry can catalyze the oxidation of thiosulfate by Fe(III), leading to a lack of leaching agent [41]. The copper-ethanediamine using a synergistic additive of cetyltrimethyl ammonium bromide could be applied to catalyze gold leaching from a gold bearing ore containing high limonite, in which gold extraction reached up to 94.3%, whilst thiosulfate consumption was only 1.12 kg/t-ore [42]. Nevertheless, its development is limited because of the toxicity and corrosivity of ethanediamine. Feng and Deventer have proposed a hypothesis that the Co\textsuperscript{3+}/Co\textsuperscript{2+} couple can be used as a substitution to Cu\textsuperscript{2+}/Cu\textsuperscript{+}, but an in-depth and systematic experimental investigation has not been carried out [43]. In our previous studies, the thermodynamic calculation indicated that the dissolution of gold could be catalyzed by the Co(NH\textsubscript{3})\textsubscript{6}^{3+}/Co(NH\textsubscript{3})\textsubscript{n}^{2+} \quad (n = 1–6) couple, and the kinetics of gold leaching in thiosulfate solution with cobalt-ammonia catalysis from a gold concentrate calcine was systematically researched [44,45]. For the gold recovery in cobalt–ammonia–thiosulfate solution, gold adsorption on resin from the actual leachate and gold elution from loaded resin were also investigated. It can be concluded that cobalt–ammonia catalysis is regarded as a promising replacement to copper–ammonia catalysis for thiosulfate leaching of gold, which will solve the bottleneck problems of the traditional copper–ammonia–thiosulfate system (i.e., the high consumption of thiosulfate and the complicated gold recovery process). However, the possible mechanism of cobalt-ammonia catalysis for gold dissolution is still unclear, and electrochemical dissolution of gold in a cobalt–ammonia–thiosulfate system has rarely been reported. Moreover, the decomposition of thiosulfate has also not been reported.

Firstly, this paper used thermodynamic analysis to discuss the theoretical basis for the gold dissolution with cobalt-ammonia catalysis. Then, the catalytic mechanism of cobalt–ammonia for gold dissolution in the thiosulfate solution was investigated by drawing polarization curves. Additionally, the dissolution of gold at a constant potential in the alkaline thiosulfate solution was performed, in which the apparent activation energy of gold dissolution was obtained. Finally, the decomposition of thiosulfate was also carried out by plotting an anodic polarization curve in different thiosulfate solutions, where the apparent activation energy of thiosulfate decomposition was also determined. This study offers a theoretical basis for the development of cobalt-ammonia catalysis for thiosulfate leaching of gold.
2. Experimental Work

2.1. Electrochemical Experiments

All the electrochemical experiments were conducted on a multichannel electrochemical workstation (Princeton Applied Research, AMETEK, Berwyn, PA, USA) with a conventional three-electrode system. In the gold dissolution experiment, a gold plaque was used as a working electrode. In the thiosulfate decomposition experiment, a platinum plaque was used as a working electrode. The purity of the gold/platinum working electrode (Φ14 mm × 2 mm) was higher than 99.99%, and the exposed area of the electrode was 1 cm². Silver-silver chloride and graphite rod were used, respectively, as the reference electrode and counter electrode. Unless otherwise specified, the electrochemical experiments were conducted at the ambient temperature, and the initial pH of solution was maintained at the range of 9.98–10.02. Before each electrochemical experiment, the gold or platinum working electrode was firstly polished using P2000 grade abrasive paper, and then rinsed with ethyl alcohol, nitric acid and deionized water in sequence. For polarization curve experiments, anodic curves and cathodic curves were recorded separately, which were from linear scanning in different solutions; the scan rate was 10 mV/s. In gold dissolution experiments, 5 mL of solution sample was continually withdrawn at certain time intervals from the electrolytic tank during the electrochemical dissolution of gold in thiosulfate solution for the subsequent analysis.

2.2. Instrumentation and Chemicals

The concentration of gold was determined by inductively coupled plasma-atomic emission spectrometry (PS-6, Baird, Milwaukee, WI, USA). Morphological studies on gold/platinum surfaces were performed by a scanning electron microscope (MIRA3 LMH, TESCAN, Brno, Czech Republic) coupled with an energy dispersive X-ray analyzer (Oxford X MAX20, Britain). The XPS analysis was performed by an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Fisher, Waltham, MA, USA) to identify the surface species on gold/platinum surface.

The chemical reagents, such as hexaamminecobalt(III) chloride, thiosulfate, ammonia solution, sodium hydroxide, sulfuric acid, nitric acid and ethyl alcohol used here were all of analytical reagent grade. Deionized water prepared by a water purification system (UPR-I-5/10/15T) was used to prepare solutions, and the solutions were used immediately.

3. Results and Discussion

3.1. Thermodynamic Analysis

Thermochemical software HSC Chemistry 6.0 (AIChE, New York, NY, USA) was adopted to draw the Eh-pH diagram of the Co-NH₃-S₀₂O₃⁻-H₂O system, as presented in Figure 1. As can be seen, the stability regions of various aqueous Co(II) and Co(III) species are formed depending on pH and Eh. At 7.2 < pH < 11.4, the stability region of Co(III) is an aqueous Co(NH₃)₆³⁺. The stability region of Co(II) in the form of Co(NH₃)₆²⁺ (n is mainly 4 and 5) is in the pH range of 8.5–10.0. Thus, in the latter pH range, the stable redox couples of Co(NH₃)₆³⁺/Co(NH₃)₆²⁺ (n is mainly 4 and 5) can be generated with a potential of 0.20–0.25 V. This redox potential is greater than the oxidation potential of 0.153 V for anodic dissolution of gold in thiosulfate solution [46]. Moreover, the redox potentials of Co(NH₃)₆³⁺/Co(NH₃)₆²⁺ (n is mainly 4 and 5) are also greater than that for a potential of 0.12 V for S₄O₆²⁻/S₂O₃²⁻, but are lower than that for Cu(NH₃)₄²⁺/Cu(S₂O₃)₃⁵⁻ (i.e., 0.36 V) [47]. It can be speculated that cobalt–ammonia catalysis can be used to replace copper–ammonia for gold leaching in terms of thermodynamics.
3.2. Polarization Curve

3.2.1. Anodic Polarization Curve

Anodic polarization was performed to study the anodic behavior of gold in different thiosulfate solutions; the result is indicated in Figure 2. As reported in the literature, within the potential range from open circuit potential (OCP) value to 0.35 V, the dissolution of gold anode is observed [48,49]. In the 0.3 M thiosulfate solution, the anodic current density from 0.1 V - 0.35 V is relatively low (<0.05 mA/cm²). This demonstrated that gold is hardly dissolved in thiosulfate-only solution. When ammonia was added in the thiosulfate solution, the anodic current density apparently improved; this result is consistent with the findings of Zhang et al. and Jiang et al. [26,50]. The reason for the improvement may be that the complexing reaction between Au⁺ and NH₃ to form Au(NH₃)₂⁺ could occur with the presence of ammonia. Moreover, the anodic current density in the thiosulfate solution with the simultaneous addition of ammonia and cobalt is very close to that with the single addition of ammonia; this result is identical to the finding by Jiang for a copper–ammonia–thiosulfate system [51].
3.2.2. Cathodic Polarization Curve

Cathodic polarization was also carried out to investigate the cathodic process in different thiosulfate solutions, as illustrated in Figure 3. In our previous study, oxygen is reduced at the gold surface in the cathode process from the thermodynamic analysis [44]. In the 0.3 M thiosulfate solution, cathodic current density in the range of 0.075 to 0.175 V is very low. This may be because the diffusion rate of oxygen in solution is slow [52]. When ammonia was added in thiosulfate solution, the current density increased slightly, indicating that ammonia does not participate in the cathodic process. With the presence of cobalt in the ammoniacal thiosulfate solution, there is a noticeable reduction peak at a potential of 0.175 V. Since the diffusion rate of Co(NH₃)₆³⁺ in solution is fast [53], it is rapidly reduced to Co(NH₃)₆²⁺ (n = 1–6) on the gold surface. The formed Co(NH₃)₆²⁺ (n = 1–6) can be re-oxidized back to Co(NH₃)₆³⁺ by dissolved oxygen, as shown in Equation (3), thus, generating a strong reduction peak in this figure. In other words, Co(NH₃)₆³⁺ catalyzes the reduction of dissolved oxygen in the cathodic process.

\[
\text{Co(NH}_3\text{)}_n^{2+} + (6 - n) \text{NH}_3 + \frac{1}{4}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} = \text{Co(NH}_3\text{)}_6^{3+} + \text{OH}^- \quad (n = 1-6)
\]  

(3)

![Figure 3. Cathodic polarization for gold electrodes at 10 mV/s starting from 0.3 mV to −0.05 V in different thiosulfate solutions. Conditions: 0.3 M \(S_2O_3^{2-}\), 1.0 M NH₃ (if used), 0.02 M Co³⁺ (if used), pH 10.0 and ambient temperature.](image)

Based on the above, it can be inferred that the mechanism of cobalt–ammonia catalysis is similar to that of copper–ammonia [26,47], and a proposed catalytic mechanism of gold dissolution in the cobalt–ammonia–thiosulfate system is illustrated in Figure 4. In the anodic area, NH₃ catalyzes the dissolution of gold, and the related reactions are shown in Equations (4)–(6). In the cathodic area, Co(NH₃)₆³⁺ catalyzes the reduction of dissolved oxygen in aqueous solution as expressed in Equation (3).

\[
\text{Au} = \text{Au}^+ + e^- 
\]  

(4)

\[
\text{Au}^+ + 2\text{NH}_3 = \text{Au(NH}_3\text{)}_2^{2+}
\]  

(5)

\[
\text{Au(NH}_3\text{)}_2^{2+} + 2\text{S}_2\text{O}_3^{2-} = 2\text{NH}_3 + \text{Au(S}_2\text{O}_3\text{)}_2^{3-}
\]  

(6)
3.3. Gold Dissolution in Thiosulfate Solution

As reported in the literature, chronoamperometry was used to verify the occurrence of gold dissolution in thiosulfate solution containing ammonia [50]. To investigate the dissolution behavior of gold in a cobalt–ammonia–thiosulfate system, chronoamperometry was also carried out at a potential of 0.25 V for 1 h; the potential was chosen based on the Sections 3.1 and 3.2.1. Figure 5 shows the variation of gold dissolution as a function of time in different thiosulfate solutions. The mass of the electrode decreases with the gold dissolution; the decrease of mass can be related to the dissolution rate of gold through Equation (7).

\[ r = \frac{1}{MA} \frac{dm}{dt} \]  

(7)

where \( r \) is the dissolution rate of gold (mol cm\(^{-2}\) s\(^{-1}\)), \( M \) is the molecular weight of gold (196.97 g/mol), \( A \) is the area of the gold electrode (cm\(^2\)), and \( t \) is the dissolution time.

Figure 4. Sketch map of the mechanism for thiosulfate leaching with cobalt-ammonia catalysis.

Figure 5. The dissolution of gold as a function of time in different thiosulfate solution. Conditions: 0.3 M \( S_2O_3^{2-} \), 1.0 M \( NH_3 \) (if used), 0.02 M \( Co^{3+} \) (if used), pH 10 and ambient temperature.
It is clear from Figure 5 that the dissolution behaviors of gold were significantly different in alkaline thiosulfate solution. As can be seen, gold hardly dissolved in thiosulfate-only solution, and the amount of gold dissolution was only 0.039 mg/cm² at 1 h. When NH₃ was added in thiosulfate solution, the amount of gold dissolution increased to 0.33 mg/cm². In addition, the amount of gold dissolution increased to 0.68 mg/cm² with the simultaneous presence of ammonia and cobalt in thiosulfate solution; it was about 17.3 times that of thiosulfate-only solution. This result is basically consistent with that found in a copper–ammonia–thiosulfate system by Puente et al. [54]. It can be concluded that the gold dissolution rate can be remarkably improved only when its cathode and anode reaction are catalyzed simultaneously.

3.3.1. Effect of NH₃ Concentration

Ammonia plays a very important role in gold leaching with a thiosulfate solution, because it stabilizes cobalt(III) in the form of Co(NH₃)₆³⁺ in alkaline solution [14–18], and the formed Co(NH₃)₆³⁺ possesses a strong catalytic effect for gold leaching. As shown in Figure 6, gold dissolution increased with the increase of ammonia concentration from 0.4 M to 1.0 M; the average dissolution rate of gold increased from $3.92 \times 10^{-10}$ mol cm⁻² s⁻¹ to $7.69 \times 10^{-10}$ mol cm⁻² s⁻¹. The increase of ammonia concentration could promote the complexation of NH₃ with Au⁺, as shown in Equation (5), thus, improving the dissolution of gold.

![Figure 6. Effect of ammonia concentration on gold dissolution. Conditions: 0.01 M Co³⁺, 0.3 M S₂O₅²⁻, pH 10 and ambient temperature.](image)

3.3.2. Effect of Cobalt(III) Concentration

The gold dissolution in Figure 7 is shown as a function of time for different cobalt(III) concentrations. In the presence of 0.005 M Co³⁺, 0.01 M Co³⁺, 0.015 M Co³⁺ and 0.02 M Co³⁺, the gold dissolutions were, respectively, 0.47 mg/cm², 0.53 mg/cm², 0.60 mg/cm² and 0.68 mg/cm², and the average dissolution rates of gold were $6.63 \times 10^{-10}$ mol cm⁻² s⁻¹, $7.47 \times 10^{-10}$ mol cm⁻² s⁻¹, $8.46 \times 10^{-10}$ mol cm⁻² s⁻¹ and $9.59 \times 10^{-10}$ mol cm⁻² s⁻¹, respectively. It can be seen that the increase of cobalt(III) concentration was beneficial to gold dissolution, and the possible reason is that the increase of cobalt(III) concentration could increase the concentration of Co(NH₃)₆³⁺, acting as an oxidant for gold dissolution and, thus, improve the gold dissolution.
3.3.3. Effect of $S_2O_3^{2-}$ Concentration

Figure 8 shows the effect of thiosulfate concentration on gold dissolution. When the concentration of thiosulfate rose from 0.1 M to 0.3 M, the gold dissolution increased from 0.45 mg/cm$^2$ to 0.68 mg/cm$^2$, and the average dissolution rate of gold also went up from $6.35 \times 10^{-10}$ mol cm$^{-2}$ s$^{-1}$ to $9.59 \times 10^{-10}$ mol cm$^{-2}$ s$^{-1}$. Such a result is not surprising because the reaction between $S_2O_3^{2-}$ and Au(NH$_3$)$_2^{3+}$ to form a more stable complex of Au(S$_2$O$_3$)$_2^{3-}$, as shown in Equation (6), can be accelerated though the improvement of thiosulfate concentration.

3.3.4. Effect of Temperature

The effect of temperature on gold dissolution was investigated; the result shown in Figure 9a indicates that a higher temperature resulted in higher gold dissolution in ammoniacal thiosulfate solution. In addition, gold dissolution increased in the first 30 min, and then a slightly flat increase was observed. The decline of gold dissolution rate may have occurred because the dissolution was hindered by the sulfur-containing species deriving from oxidative decomposition of thiosulfate. Thus, the kinetics of gold dissolution in the cobalt–ammonia–thiosulfate system was studied in the first 30 min.
Figure 9. (a) Effect of temperature on gold dissolution and (b) variation of gold dissolution rate as a function of 1000/T. Conditions: 0.3 M $\text{S}_2\text{O}_3^{2-}$, 1.0 M $\text{NH}_3$, 0.02 M $\text{Co}^{3+}$ and pH 10.0.

The apparent activation energy as an important parameter to analyze the dissolution mechanism of gold in an alkaline thiosulfate solution was determined based on the Arrhenius equation shown in Equation (8). Figure 9b indicates the variation of $\ln r$ as a function of 1000/T. According to the slope of the line, the apparent activation energy was determined to be 41.15 kJ/mol in temperature between 25 °C and 40 °C. This result confirms that gold dissolution in a cobalt–ammonia–thiosulfate system is chemically controlled. The result agrees with the study of Breuer and Jeffrey for copper–ammonia–thiosulfate systems [48].

$$\ln k = \ln A - \frac{E_a}{RT}$$  \hspace{1cm} (8)

3.3.5. Effect of pH

As Figure 10 indicated, gold dissolution increased with the increase of pH from 9.0 to 10.0 and then dropped when beyond the range. The improvement of gold dissolution could be attributed to the promotion of thiosulfate stability within the pH range of 9.0–10.0. At a higher pH than 10.0, cobalt hydroxide precipitates began to form, as shown in Figure 1, resulting in the decrease of oxidant concentration for gold dissolution. As a result of this, the gold dissolution declined when beyond this pH scope.

Figure 10. Effect of pH value on gold dissolution. Conditions: 0.3 M $\text{S}_2\text{O}_3^{2-}$, 1.0 M $\text{NH}_3$, 0.02 M $\text{Co}^{3+}$ and ambient temperature.

3.4. SEM-EDS and XPS Analyses of Gold Surface

3.4.1. SEM-EDS Analysis

The SEM-EDS analysis was performed to investigate the morphology and elemental composition of the original gold plaque and the gold surfaces obtained in the cobalt/copper–
ammonia–thiosulfate solution, and the results were shown in Figure 11. Comparing Figure 11a with Figure 11c,e, it is clear that the different morphological structures were presented on the gold surface in the cobalt/copper–ammonia–thiosulfate system. As shown in Figure 11c, the gold surface in the cobalt–ammonia–thiosulfate system displayed obvious corrosion of edges and pits. In addition, the gold surface in the copper–ammonia–thiosulfate system presented significant scarring characteristics, such as cragged pitting and crevice corrosion, as depicted in Figure 11e. This demonstrates that gold can be dissolved in both of these two systems. Moreover, some precipitates seemed to form on the gold surfaces in these systems and, thus, the EDS spectra were also recorded. In the original gold plaque, only Au was found, as seen in Figure 11b. However, for the cobalt–ammonia–thiosulfate system, there was mostly Au on the surface, except for a small amount of Co and S, as shown in Figure 11d. As indicated in Figure 11f, a small quantity of Cu and S appeared on the surface, which consisted mostly of Au, for the copper–ammonia–thiosulfate system.

3.4.2. XPS Analysis

XPS analysis was carried out to record the spectra of S 2p for the gold surface obtained in the copper/cobalt–ammonia–thiosulfate solution. As indicated in Figure 12, the S 2p spectrum for the copper–ammonia–thiosulfate system was composed of two peaks centering at 162.5 eV and 168.1 eV, which might be derived from S^{2−} in Cu_{2}S and elemental sulfur S_{s}, respectively [55–57]. For the cobalt–ammonia–thiosulfate system, the peaks appeared at 162.6 eV and 168.0 eV, which might originate from S^{2−} in CoS and elemental sulfur S_{o}, respectively [57–59]. Obviously, the peak area of sulfur species for the copper–

Figure 11. SEM images and EDS spectra of the surfaces of gold electrode. (a) SEM image for original gold surface; (b) EDS spectrum for original platinum surface; (c) SEM image for cobalt–ammonia–thiosulfate system; (d) EDS spectrum for cobalt–ammonia–thiosulfate system; (e) SEM image for copper–ammonia–thiosulfate system; (f) EDS spectrum for copper–ammonia–thiosulfate system. Conditions: 0.3 M S_{2}O_{3}^{2−}, 1.0 M NH_{3}, 0.02 M Co^{3+}/Cu^{2+} (if used), pH 10.0 and ambient temperature.
ammonia–thiosulfate system was bigger than that for cobalt–ammonia–thiosulfate system, indicating that the amount of sulfur-containing species coating on the gold surface in the latter system was lower.

![Figure 12. The XPS spectra of S 2p for gold surface in different thiosulfate systems. Conditions: 0.3 M \( \text{S}_2\text{O}_3^{2−} \), 1.0 M NH\(_3\), 0.02 M Co\(^{3+}\)/Cu\(^{2+}\) (if used), pH 10.0 and ambient temperature.](image)

3.5. Decomposition of Thiosulfate

In this section, a platinum electrode was employed as a working electrode for the study of thiosulfate decomposition because of the fact that the dissolution current of gold in the ammoniacal thiosulfate solution could disturb the decomposition current of thiosulfate. In the potential range of gold dissolution, the anodic polarization was adopted to investigate the decomposition of thiosulfate on the surface of the platinum electrode. This method was reported in the literature by Liu [60].

3.5.1. Effect of NH\(_3\) Concentration

Figure 13 illustrates the effect of ammonia concentration on the thiosulfate decomposition. With the increase of ammonia concentration, the current density of thiosulfate decomposition decreased. The possible reason for the decline may be that the increase of ammonia concentration reduced the oxidability of Co(NH\(_3\))\(_6^{3+}\) [61].

![Figure 13. Anodic polarization for platinum electrodes at 10 mV/s starting from 0.1 mV to 0.3 V in different ammonia concentration solutions. Conditions: 0.3 M \( \text{S}_2\text{O}_3^{2−} \), 0.01 M Co\(^{3+}\), pH 10 and ambient temperature.](image)
3.5.2. Effect of Cobalt(III) Concentration

The effect of cobalt(III) concentration on the thiosulfate decomposition was indicated in Figure 14. It is clear that the current density of thiosulfate decomposition increased with an increase in cobalt(III) concentration. The increase in cobalt(III) concentration augmented the oxidant concentration in the solution and, thus, accelerated the oxidation of thiosulfate.

![Figure 14](image)

**Figure 14.** Anodic polarization for platinum electrodes at 12 mV/s starting from 0.15 mV to 0.3 V in different cobalt(III) concentration solutions. Conditions: 0.3 M S\(_2\)O\(_3\)\(^{2-}\), 1.0 M NH\(_3\), pH 10 and ambient temperature.

3.5.3. Effect of S\(_2\)O\(_3\)\(^{2-}\) Concentration

In Figure 15, the variation trend for the current density of thiosulfate decomposition with thiosulfate concentration was presented. It is apparent that the current density went up when thiosulfate concentration increased. The increase of current density might be because the reaction listed in Equation (9) was promoted as thiosulfate concentration rose.

\[
4S_{2}O_{3}^{2-} + O_2 + 2H_2O = 2S_{4}O_{6}^{2-} + 4OH^- \tag{9}
\]

![Figure 15](image)

**Figure 15.** Anodic polarization for platinum electrodes at 10 mV/s starting from 0.1 mV to 0.3 V in different thiosulfate concentration solutions. Conditions: 1.0 M NH\(_3\), 0.02 M Co\(^{3+}\), pH 10 and ambient temperature.
3.5.4. Effect of Temperature

As indicated in Figure 16a, the current density of thiosulfate decomposition increased at a higher temperature. This may be because the decomposition of thiosulfate is an endothermic reaction. The current density obtained at a potential of 0.25 V was used to express the decomposition rate of thiosulfate, because the dissolution of gold was carried out at this potential.

![Graph](image)

**Figure 16.** (a) Anodic polarization for platinum electrodes at 10 mV/s starting from 0.15 mV to 0.3 V in different temperature and (b) variation of current density as a function of temperature. Conditions: 0.4 M S\(_\text{2}O_3^{2-}\), 1.0 M NH\(_3\), 0.02 M Co\(^{3+}\) and pH 10.

The apparent activation energy of thiosulfate decomposition can be calculated with the method shown in Section 3.3.4. Figure 16b indicates the variation of \(\ln i\) as a function of 1000/\(T\). The apparent activation energy of 22.12 kJ/mol was obtained based on the slope in this figure, which is greater than that for a typical diffusion-controlled process (<15 kJ/mol) [62] but is lower than that for a chemically controlled process (>40 kJ/mol). This means that thiosulfate decomposition is mixed chemical-diffusion-controlled in a cobalt–ammonia–thiosulfate system.

3.5.5. Effect of pH

As shown in Figure 17, the effect of pH on thiosulfate decomposition was analogous with that on gold dissolution. The current density of thiosulfate decomposition decreased with the increase of pH from 9.0 to 10.0, and then it rose at a higher pH of 11.0. As reported in the literature, the optimal pH for the stable existence of thiosulfate in the alkaline solution is 10.0 [51], which could be responsible for the augment of current density when pH was under or beyond the value of 10.0.

3.6. SEM-EDS and XPS Analyses of Platinum Surface

3.6.1. SEM-EDS Analysis

The SEM-EDS analysis was carried out to investigate the morphology and elemental composition of the original platinum surface and the platinum surfaces obtained in the cobalt/copper–ammonia–thiosulfate system. Compared Figure 18a with Figure 18b,c, the corrosion of platinum surfaces did not appear in these systems. This may be because platinum is inert, and the dissolution of platinum in thiosulfate solution cannot occur. Similarly, the EDS analysis was implemented to identify the chemical composition of precipitate on the platinum surface, but almost only Pt was found in the spectra (data not shown). The composition of precipitate could not be identified by EDS analysis, owing to the extremely low amount of precipitate on the platinum surface.
3.5.4. Effect of Temperature

As indicated in Figure 16a, the current density of thiosulfate decomposition increased at a higher temperature. Anodic polarization platinum electrodes at 10 mV/s starting from 0.15 mV to 0.3 V in different pH solutions. Conditions: 0.4 M S_2O_3^{2-}, 1.0 M NH_3, 0.02 M Co^{3+} and ambient temperature.

**Figure 17.** Anodic polarization platinum electrodes at 10 mV/s starting from 0.15 mV to 0.3 V in different pH solutions. Conditions: 0.4 M S_2O_3^{2-}, 1.0 M NH_3, 0.02 M Co^{3+} and ambient temperature.

3.6.2. XPS Analysis

The XPS spectra of S 2p for platinum surfaces in the copper/cobalt–ammonia–thiosulfate system are shown in Figure 19. There are mainly two peaks centering at about 162.7 eV. In the copper–ammonia–thiosulfate system, two main peaks also appeared. One was centered at 162.6 eV, which might be assigned to elemental sulfur, and the other was located at 168.0 eV, which may be also attributed to S_8. The energy peak may be attributed to elemental sulfur S_8.

**Figure 18.** SEM images of the platinum electrodes’ surfaces for (a) the original platinum surface, (b) cobalt–ammonia–thiosulfate system and (c) copper–ammonia–thiosulfate system. Conditions: 0.3 M S_2O_3^{2-}, 1.0 M NH_3, 0.02 M Co^{3+}/Cu^{2+} (if used), pH 10.0 and ambient temperature.

The XPS spectra of S 2p for platinum surfaces in the copper/cobalt–ammonia–thiosulfate system are shown in Figure 19. There are mainly two peaks centering at about 162.7 eV and 168.1 eV for the copper–ammonia–thiosulfate system. The lower binding energy peak may be attributed to S_2^{2-} in the form of Cu_2S [55,56], and the higher energy peak is likely originated from elemental sulfur S_8 [57]. For the cobalt–ammonia–thiosulfate system, two
main peaks also appeared. One was centered at 162.6 eV, which might be derived from $S^{2−}$ in CoS [58,59], and the other was located at 168.0 eV, which may be also assigned to elemental sulfur S8.57 According to a comparison of peak areas, it is known that the quantity of $S^{2−}$ on the platinum surface in the cobalt/ammonia/thiosulfate system was almost equal, but the quantity of S8 in the copper/ammonia/thiosulfate system was distinctly higher. Thus, the quantity of sulfur-containing species in the copper/ammonia/thiosulfate system was more than that in the cobalt/ammonia/thiosulfate system. The XPS analysis result for the platinum surface is basically consistent with that for the gold surface.

![](image)

**Figure 19.** The XPS spectra of S 2p for platinum surface in different thiosulfate system. Conditions: 0.3 M $S_2O_3^{2−}$, 1.0 M NH$_3$, 0.02 M Co$_3^{3+}$/Cu$^{2+}$ (if used), pH 10.0 and ambient temperature.

4. Conclusions

The Eh-pH diagram has shown that the redox couples of Co(NH$_3$_n)$_2^{2+}$/Co(NH$_3$_6)$_3^{3+}$ (n is mainly 4 and 5) can be formed in the ammoniacal thiosulfate solution, and that its redox potential of 0.20–0.25 V is higher than that of Au($S_2O_3$)$_2^{3−}$/Au (i.e., 0.153 V), indicating that Co(III)/Co(II) redox couples can catalyze the dissolution of gold in a thiosulfate solution from the thermodynamics. Polarization curve studies confirmed the conclusion; the results also indicated that the mechanism of cobalt-ammonia catalysis is similar to that of copper-ammonia. Namely, NH$_3$ catalyzes the dissolution of gold at its anodic area, while Co(NH$_3$_6)$_3^{3+}$ catalyzes the reduction of dissolved oxygen at its cathodic area.

The dissolution of gold in a cobalt-ammonia–thiosulfate system was investigated by using potentiostat polarization at a potential of 0.25 V for 1 h. With the increase of reagent concentrations of NH$_3$, Co$^{3+}$ and $S_2O_3^{2−}$, the amount of gold dissolution increased. The optimum pH for gold dissolution in thiosulfate solution with cobalt–ammonia catalysis is 10.0. The apparent activation energy of gold dissolution is 41.15 kJ/mol in temperature between 25 °C to 40 °C, which indicates that gold dissolution is chemically controlled. The SEM-EDS analysis indicates that some precipitates appear on the gold surfaces in the copper/cobalt–ammonia–thiosulfate system. The XPS analysis demonstrates that the precipitate on the gold surface was mainly sulfur species, including $S^{2−}$ in CoS and S8.

The decomposition of thiosulfate was also carried out though drawing anodic polarization curves with inert platinum electrode. When NH$_3$ concentration rose, the decomposition of thiosulfate decreased; while the concentrations of Co$^{3+}$ and $S_2O_3^{2−}$ rose, the thiosulfate decomposition increased. The optimal pH for the stable existence of thiosulfate in a cobalt–ammonia–thiosulfate system is 10.0. The apparent activation energy of thiosulfate decomposition was determined to be 22.12 kJ/mol. It can be concluded that the thiosulfate decomposition is mixed chemical-diffusion-controlled in a cobalt–ammonia–thiosulfate
system. The XPS analysis has confirmed that the precipitation species on platinum surface were identical with that on gold surface.

**Author Contributions:** K.L.: Investigation, Validation, Writing–original draft. Q.L.: Conceptualization, Methodology, Funding acquisition. Writing–review and editing. B.X.: Resources, Funding acquisition, Writing–review and editing. Y.Y.: Supervision, Resources. T.J.: Supervision, Resources. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the National Natural Science foundation of China (Nos. 52174271 and 51572484), Qinghai Provincial Major Scientific and Technological Special Project of China (No. 2018-GX-A7), Hunan Provincial Natural Science Foundation of China (Nos. 1028JJ4038) and National Key Research and Development Program of China (No. 2018YFC1902006).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data that supports the finding of this study are available within the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Hilson, G.; Monhemius, A.J. Alternatives to cyanide in the gold mining industry: What prospects for the future? *J. Clean. Prod.* **2006**, *14*, 1158–1167. [CrossRef]

2. Chen, C.; Lung, T.; Wen, C. A study of the leaching of gold and silver by acidothioureid. *Hydrometallurgy* **1980**, *5*, 207–212. [CrossRef]

3. Khomologorov, A.G.; Kononova, O.N.; Pashkov, G.L.; Kononov, Y.S. Thiocyanate solutions in gold technology. *Hydrometallurgy* **2002**, *64*, 43–48. [CrossRef]

4. Mentha-Biney, R.; Reid, K.J.; Hepworth, M.T. Kinetics of gold-bromide loading onto activated carbon. *Min. Metall. Explor.* **1997**, *14*, 7–13.

5. Chai, L.; Okido, M.; Wei, W. Effect of Na2SO3 on electrochemical aspects of gold dissolution in alkaline thiourea solution. *Hydrometallurgy* **1999**, *53*, 255–266. [CrossRef]

6. Dong, Z.; Jiang, T.; Xu, B.; Yang, J.; Chen, Y.; Li, Q.; Yang, Y. Comprehensive recoveries of selenium, copper, gold, silver and lead from a copper anode slime with a clean and economical hydrometallurgical process. *Chem. Eng. J.* **2020**, *393*, 124762. [CrossRef]

7. Xu, B.; Chen, Y.; Dong, Z.; Jiang, T.; Zhang, B.; Liu, G.; Yang, J.; Li, Q.; Yang, Y. Eco-friendly and efficient extraction of valuable elements from copper anode mud using an integrated pyro-hydrometallurgical process. *Resour. Conserv. Recycl.* **2021**, *164*, 105195. [CrossRef]

8. Alzate, A.L.; Opez, E.; Serna, C.; Gonzalez, O. Gold recovery from printed circuit boards by selective breaking of internal metallic bonds using activated persulfate solutions. *J. Clean. Prod.* **2017**, *166*, 1102–1112. [CrossRef]

9. Bisceglie, F.; Civati, D.; Bonati, B.; Faraci, F.D. Reduction of potassium cyanide usage in a consolidated industrial process for gold recovery from wastes and scraps. *J. Clean. Prod.* **2017**, *142*, 1810–1818. [CrossRef]

10. Lu, Y.; Song, Q.; Xu, Z. Integrated technology for recovering Au from waste memory module by chlorination process: Selective leaching, extraction, and distillation. *J. Clean. Prod.* **2017**, *161*, 30–39. [CrossRef]

11. Muir, D.M.; Aylmore, M.G. Thiosulphate as an alternative to cyanide for gold processing-issues and impediments. *Miner. Processing Extr. Metall.* **2004**, *113*, 2–12. [CrossRef]

12. Zhang, L.; Xu, Z. A review of current progress of recycling technologies for metals from waste electrical and electronic equipment. *J. Clean. Prod.* **2016**, *127*, 19–36. [CrossRef]

13. Ter-Arakelyan, K.A.; Bagdasaryan, K.A.; Oganyan, A.G.; Mkrtchyan, R.T.; Babayan, G.G. On technological expediency of sodium thiosulphate usage for gold extraction from raw material. *Izv. VUZ Tsvetn. Metall.* **1984**, *5*, 72–76.

14. Abruzzese, C.; Fornari, P.; Masidda, R.; Vegli, O.F.; Ubaldini, S. Thiosulphate leaching for gold hydrometallurgy. *Hydrometallurgy* **1995**, *39*, 265–276. [CrossRef]

15. Breuer, P.L.; Jeffrey, M.I. Thiosulphate leaching kinetics of gold in the presence of copper and ammonia. *Miner. Eng.* **2000**, *13*, 1071–1081. [CrossRef]

16. Chen, J.; Deng, T.; Zhu, G.C.; Zhao, J. Leaching and recovery of gold in thiosulphate based system: A research summary at ICM. *Trans. Indian Inst. Met.* **1996**, *49*, 841–849.

17. Jeffrey, M.I. Kinetic aspects of gold and silver leaching in ammonia-thiosulphate solutions. *Hydrometallurgy* **2001**, *60*, 7–16. [CrossRef]

18. Zipperian, D.; Raghavan, S.; Wilson, J.P. Gold and silver extraction by ammoniacal thiosulphate leaching from a rhyolite ore. *Hydrometallurgy* **1988**, *19*, 361–375. [CrossRef]

19. Melashvili, M.; Fleming, C.; Dymov, I.; Matthews, D.; Dreisinger, D. Equation for thiosulphate yield during pyrite oxidation. *Miner. Eng.* **2015**, *74*, 105–111. [CrossRef]
20. Breuer, P.L.; Jeffrey, M.I. The reduction of copper(II) and the oxidation of thiosulphate and oxysulphur anions in gold leaching solutions. *Hydrometallurgy* 2003, 70, 163–173. [CrossRef]

21. Feng, D.; van Deventer, J.S.J.V. Leaching behaviour of sulphides in ammoniacal thiosulphate systems. *Hydrometallurgy* 2002, 63, 189–200. [CrossRef]

22. Grosse, A.C.; Dicinoski, G.W.; Shaw, M.J.; Haddad, P.R. Leaching and recovery of gold using ammoniacal thiosulphate leach liquors (a review). *Hydrometallurgy* 2003, 69, 1–21. [CrossRef]

23. Senanayake, G. Analysis of reaction kinetics, speciation and mechanism of gold leaching and thiosulphate oxidation by ammoniacal copper(II) solutions. *Hydrometallurgy* 2004, 75, 55–75. [CrossRef]

24. Dong, Z.; Jiang, T.; Xu, B.; Yang, Y.; Li, Q. An eco-friendly and efficient process of low potential thiosulphate leaching-resin adsorption recovery for extracting gold from a roasted gold concentrate. *J. Clean. Prod.* 2019, 229, 387–398. [CrossRef]

25. Xu, B.; Li, K.; Zhong, Q.; Li, Q.; Yang, Y.; Jiang, T. Study on the oxygen pressure alkaline leaching of gold with generated thiosulfate from sulfur oxidation. *Hydrometallurgy* 2018, 177, 178–186. [CrossRef]

26. Jiang, T.; Chen, J.; Xu, S. Electrochemistry and mechanism of leaching gold with ammoniacal thiosulfate. In Proceedings of the XVIII International Mineral Processing Congress, Sydney, Australia, 23–28 May 1993; pp. 1141–1146.

27. Yang, Y.; Gao, W.; Xu, B.; Li, Q.; Jiang, T. Study on oxygen pressure thiosulfate leaching of gold without the catalysis of copper and ammonia. *Hydrometallurgy* 2019, 187, 71–80. [CrossRef]

28. Xu, B.; Yang, Y.; Li, Q.; Zhang, X.; Wang, D. Improved thiosulfate leaching of a refractory gold concentrate calcine with additives. *Hydrometallurgy* 2015, 152, 87–94. [CrossRef]

29. Jeffrey, M.I.; Watling, K.; Hope, G.A.; Woods, R. Identification of surface species that inhibit and passivate thiosulfate leaching of gold. *Miner. Eng.* 2008, 21, 443–452. [CrossRef]

30. Mirza, J.; Smith, S.R.; Baron, J.Y.; Choi, Y.; Lipkowski, J. A SERS characterization of the stability of polythionates at the gold-electrolyte interface. *Surf. Sci.* 2015, 631, 196–206. [CrossRef]

31. Jeffrey, M.I.; Hewitt, D.M.; Dai, X.; Brunt, S.D. Ion exchange adsorption and elution for recovering gold thiosulfate from leach solutions. *Hydrometallurgy* 2010, 100, 136–143. [CrossRef]

32. Navarro, P.; Vargas, C.; Alonso, M.; Alguacil, F.J. Towards a more environmentally friendly process for gold: Models on gold adsorption onto activated carbon from ammoniacal thiosulfate solutions. *Desalination* 2007, 211, 58–63. [CrossRef]

33. Fotoohi, B.; Mercier, L. Recovery of precious metals from ammoniacal thiosulfate solutions by hybrid mesoporous silica: 1-Factors affecting gold adsorption. *Sep. Purif. Technol.* 2014, 127, 84–96. [CrossRef]

34. Zhao, J.I.N.; Wu, Z.; Chen, J.C.Y. Separation of gold from other metals in thiosulfate solutions by solvent extraction. *Sep. Sci. Technol.* 1999, 34, 2061–2068. [CrossRef]

35. Sullivan, A.M.; Kohl, P.A. Electrochemical study of the gold thiosulfate reduction. *J. Electrochem. Soc.* 1997, 144, 1686–1690. [CrossRef]

36. Choo, W.L.; Jeffrey, M.I. An electrochemical study of copper cementation of gold(I) thiosulfate. *Hydrometallurgy* 2004, 71, 351–362. [CrossRef]

37. Dong, Z.; Jiang, T.; Xu, B.; Yang, Y.; Li, Q. Recovery of gold from pregnant thiosulfate solutions by the resin adsorption technique. *Metals* 2017, 7, 555. [CrossRef]

38. Zhang, H.G.; Dreisinger, D.B. The recovery of gold from ammonical thiosulfate solutions containing copper using ion exchange resin columns. *Hydrometallurgy* 2004, 72, 225–234. [CrossRef]

39. Xu, B.; Kong, W.; Li, Q.; Yang, Y.; Jiang, T. A review of thiosulfate leaching of gold: Focus on thiosulfate consumption and gold recovery from pregnant solution. *Metals* 2017, 7, 222. [CrossRef]

40. Chandra, I.; Jeffrey, M.I. A fundamental study of ferric oxalate for dissolving gold in thiosulfate solutions. *Hydrometallurgy* 2005, 77, 191–201. [CrossRef]

41. Heath, J.A.; Jeffrey, M.I.; Zhang, H.G.; Rumball, J.A. Anaerobic thiosulfate leaching: Development of in situ gold leaching systems. *Miner. Eng.* 2008, 21, 424–433. [CrossRef]

42. Yu, H.; Zi, F.; Hu, X.; Zhong, J.; Nie, Y.; Xiang, P. The copper-ethanediamine-thiosulphate leaching of gold ore containing limonite with cetyltrimethyl ammonium bromide as the synergist. *Hydrometallurgy* 2014, 150, 178–183. [CrossRef]

43. Feng, D.; Deventer, J.S.J. The role of heavy metal ions in gold dissolution in the ammoniacal thiosulfate system. *Hydrometallurgy* 2002, 64, 231–246. [CrossRef]

44. Liu, X.; Xu, B.; Jiang, T.; Yang, Y.; Li, Q.; He, Y. Thermodynamic analysis of ammoniacal thiosulfate leaching of gold catalysed by Co(III)/Co(II) using Eh-pH and speciation diagrams. *Hydrometallurgy* 2018, 178, 240–249. [CrossRef]

45. Xu, B.; Li, K.; Li, Q.; Yang, Y.; Liu, X.; Jiang, T. Kinetic studies of gold leaching by thiosulfate with cobalt-ammonia catalysis and gold recovery by resin adsorption from its pregnant solution. *Sep. Purif. Technol.* 2019, 213, 368–377. [CrossRef]

46. Bard, A.J.; Ketelaar, J.A. Encyclopedia of Electrochemistry of the Elements. *J. Electrochem. Soc.* 1975, 122, 139C. [CrossRef]

47. Aylmore, M.G.; Mui, D.M. Thiosulfate leaching of gold—A review. *Miner. Eng.* 2001, 14, 135–174. [CrossRef]

48. Breuer, P.L.; Jeffrey, M.I. An electrochemical study of gold leaching solutions containing copper and ammonia. *Hydrometallurgy* 2002, 65, 145–157. [CrossRef]

49. Zelinsky, A.G.; Novgorodtseva, O.N. EQCM study of the dissolution of gold in thiosulfate solutions. *Hydrometallurgy* 2013, 138, 79–83. [CrossRef]
50. Zhang, S.; Nicol, M.J. An electrochemical study of the dissolution of gold in thiosulfate solutions Part I: Alkaline solutions. *J. Appl. Electrochem.* 2003, 33, 767–775. [CrossRef]

51. Jiang, T. *Chemistry of Extractive Metallurgy of Gold*; Hunan Science & Technology Press: Changsha, China, 1998.

52. Chanut, J.; Lagorce, A.; Lequin, S.; Gougeon, R.D.; Karbowiak, T. Fast manometric method for determining the effective oxygen diffusion coefficient through wine stopper. *Polym. Test.* 2021, 93, 106924. [CrossRef]

53. Falina, I.V.; Berezina, N.P. Diffusion of solutions in the course of the matrix synthesis of composite membranes mf-4sc—Polyaniline and their transport properties. *Polym. Sci.* 2010, 52, 244–251. [CrossRef]

54. Puente-Siller, D.M.; Fuentes-Aceituno, J.C.; Nava-Alonso, F. A kinetic-thermodynamic study of silver leaching in thiosulfate-copper-ammonia-EDTA solutions. *Hydrometallurgy* 2013, 134, 124–131. [CrossRef]

55. Feng, D.; van Deventer, J.S.J. Ammoniacal thiosulphate leaching of gold in the presence of pyrite. *Hydrometallurgy* 2006, 82, 126–132. [CrossRef]

56. Nava, D.; Ignacio, G.; Dietmar, L.; Ramos-Barrado, J.R. Surface characterization by X-ray photoelectron spectroscopy and cyclic voltammetry of products formed during the potentiostatic reduction of chalcopyrite. *Electrochim. Acta* 2008, 53, 4889–4899. [CrossRef]

57. Wagner, C.D. Photoelectron and Auger energies and Auger parameters: A data set. In *Practical Surface Analysis: By Auger and X-ray Photoelectron Spectroscopy*, Briggs, D., Seah, M.P., Eds.; Wiley: Hoboken, NJ, USA, 1990.

58. Xu, B.; Yang, Y.; Li, Q.; Jiang, T.; Li, G. Effect of common associated sulfide minerals on thiosulfate leaching of gold and the role of humic acid additive. *Hydrometallurgy* 2017, 171, 44–52. [CrossRef]

59. Liu, X.; Xu, B.; Yang, Y.; Li, Q.; Jiang, T.; Zhang, X.; Zhang, Y. Effect of galena on thiosulfate leaching of gold. *Hydrometallurgy* 2017, 171, 157–164. [CrossRef]

60. Liu, X. A Fundamental Investigation into Thiosulphate Leaching of Gold Catalysed by the Cobalt-Ammonia System. Ph.D. Thesis, Central South University, Changsha, China, 2019.

61. Nie, Y.; Yu, Q.; Hu, X.; Zi, F.; Yu, H. The effect of ammonia on the anodic process of gold in copper-free thiosulfate solution. *J. Electrochem. Soc.* 2016, 163, 123–129. [CrossRef]

62. Zhang, X.; Senanayake, G.; Nicol, M.J. A study of the gold colloid dissolution kinetics in oxygenated ammoniacal thiosulfate solutions. *Hydrometallurgy* 2004, 74, 243–257. [CrossRef]