

Article

Leaching of Gold and Silver from a Complex Sulfide Concentrate in Copper-Tartrate-Thiosulfate Solutions

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Abstract: The leaching behaviors of gold and silver from a complex sulfide concentrate in copper-tartrate-thiosulfate solutions were investigated in this paper. Experimental parameters, including temperature, initial pulp pH, and concentration of copper, tartrate, and thiosulfate, were systematically studied. The copper-tartrate-thiosulfate leaching system exhibits promising performance in dealing with the complex sulfide concentrate. Thiosulfate consumption could be greatly reduced due to the in-situ generation of thiosulfate derived from sulfur or disulfide ions. Increasing the temperature and concentrations of copper, tartrate, and thiosulfate can promote gold leaching. A low tartrate content and a moderate increase in temperature and copper and thiosulfate concentrations can accelerate silver leaching, but a higher temperature or copper content may depress silver extraction. A suitable pulp pH is critical for gold and silver leaching in copper-tartrate-thiosulfate solutions. An extraction of 74.50% Au and 36.33% Ag was obtained with the direct leaching of the concentrate, while the percentages can be significantly increased up to 82.60% and 70.38%, respectively, when leaching the calcine following the oxidative roasting pretreatment. The recycling of leaching solutions demonstrates that a suitable free tartrate content is of great significance in maintaining the stability of the novel system. As an alternative to the traditional cyanide or copper-ammonia-thiosulfate leaching processes, the copper-tartrate-thiosulfate leaching system provides an environmentally friendly, nontoxic, and relatively low-cost method for gold and silver leaching from ores or concentrates.

Keywords: gold; silver; thiosulfate; tartrate; sulfide concentrate; leaching



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1. Introduction

Due to the high toxicity of cyanide, more than 30 alternative leaching reagents have been developed in the past half century, but only a few have attracted serious attention [1–6]. Thiosulfate is one of the most promising substitutes with the characteristics of nontoxicity, high efficiency, and low cost. Moreover, thiosulfate exhibits excellent performance in dealing with carbonaceous or copper-bearing gold ores or concentrates where gold recovery by cyanidation is poor or cyanide consumption is high [7–11]. Accordingly, numerous studies have been carried out on the kinetics and mechanism of gold and silver leaching in thiosulfate-based solutions [12–17]. However, with many years of progress and development, traditional copper-ammonia-thiosulfate leaching systems still have some urgent problems to be solved, such as high consumption of thiosulfate, ammonia nitrogen wastewater, and difficulty in gold recovery [18–20]. Some researchers developed non-ammonia thiosulfate leaching systems to completely avoid the potential hazards caused by the use of ammonia [21–24], while others attempted to replace the copper-based catalyst

with other transition metals, such as nickel, cobalt, and ferric, to reduce the consumption of thiosulfate and benefit gold recovery [25–30]. A recent review reported by Xie et al. systematically summarized and illustrated the current research status of gold thiosulfate leaching systems [31].

Non-ammonia copper-based thiosulfate leaching systems are believed to be an attractive route for gold and silver leaching, especially using organic carboxylic acids to replace ammonia. The introduction of citrate in copper-thiosulfate solutions provides an environmentally viable method for gold extraction in dealing with carbonaceous and free-milling oxide gold ores [32–34]. The consumption of thiosulfate can be significantly reduced due to the lower potential of the $\text{Cu}_2\text{Cit}_2\text{H}_{-2}^{4-}/\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$ redox couple. Moreover, the author proposed a copper-catalytic glycine thiosulfate collaborative system for gold leaching and believed that this novel leaching system could offer a wider pH range and lower thiosulfate consumption [35]. With the copper-tartrate-thiosulfate solutions, the capacity of gold leaching is comparable to that of cyanidation or copper-ammonia-thiosulfate leaching systems. The consumption of thiosulfate can be dramatically reduced due to the strong chelating effect of tartrate on copper ions [36]. Tartrate performance, in terms of gold leaching from a carbonaceous gold concentrate, is encouraging. Accordingly, the leaching behaviors of gold and silver from a sulfide concentrate with copper-tartrate-thiosulfate solutions were studied in this work.

Conventional direct leaching processes are unsuitable for treating complex sulfide concentrates because the minerals in the ore are very fine and coexist closely with each other. Pretreatments such as roasting, chemical oxidation, pressure oxidation, ultrafine grinding, and biological oxidation are generally used to disrupt sulfide crystals to enhance the rate of gold and silver leaching [37–39]. Table 1 summarizes the application of some pretreatments in gold thiosulfate leaching systems. It is worth mentioning that pretreatments, such as chemical oxidation or physical activation, can effectively expose the encapsulated gold or silver and improve metallic recovery with thiosulfate solutions. Xu et al. reported that 98.2% Cu, 95.8% Zn, 95.7% Pb, 96.8% Ag, and 94.7% Au can be obtained by staged oxygen pressure leaching processes from a complex polymetallic sulfide concentrate in nickel-ammonia-thiosulfate solutions [40]. The author compared pretreatments of permanganate oxidation and oxidative roasting on gold cyanidation from a high carbon-, arsenic- and antimony-bearing sulfide gold concentrate and achieved considerable gold extraction [41]. Feng and Deventer used an oxidative ammonia leaching pretreatment to enhance the rate of gold leaching from sulfide ores in copper-ammonia-thiosulfate solutions. Gold extraction can be effectively promoted from 69% to 94% following 22 h of pretreatment, and thiosulfate consumption can be reduced from 2.37 kg/t-ore to a negligible extent [42]. Zhao et al. proposed a process combining bio-oxidation followed by thiosulfate leaching for gold extraction from a refractory gold concentrate. A maximum gold leaching rate of 85.05% can be obtained under the optimal conditions of 0.18 M thiosulfate, 0.02 M copper (II), 1.0 M ammonia, and 0.24 M sulfite [43]. Wang et al. adopted microwave roasting pretreatment to leach a copper-bearing sulfide ore with copper-citrate-thiosulfate solutions. The results indicate that 94.5% Au was obtained after roasting at 500 °C for 30 min in comparison to a leaching rate of 69.7% Au without pretreatment. The consumption of thiosulfate was simultaneously reduced from 33.20 kg/t-ore to 11.38 kg/t-ore [44]. Mechanical activation was proven to be an appropriate pretreatment for CuPbZn complex sulfide concentrate. The gold extraction can be rapidly increased up to 99% in a copper-ammonia-thiosulfate solution [45]. Moreover, Gui et al. used ultrasound to enhance the kinetics of gold leaching in cobalt-ammonia-thiosulfate solutions. The gold leaching efficiency significantly increased from 70% to 89% with the assistance of ultrasound [46].

Table 1. Application of pretreatment in gold thiosulfate leaching systems.

Materials (Gold Content)	Pretreatment	Optimal Conditions	Gold Extraction
Sulfide gold concentrate with high Fe, As and Sb (12.6 g/t)	Oxygen pressure leaching	0.03 mol/L NiSO ₄ , 1.0 mol/L NH ₃ ·H ₂ O, 0.3 mol/L Na ₂ S ₂ O ₃ , 6 h	94.7% [40]
Sulfide gold concentrate with high C, As and Sb (31.1 g/t)	Alkaline pressure oxidation	0.012 mol/L CuSO ₄ , 1.2 mol/L NH ₃ ·H ₂ O, 0.2 mol/L Na ₂ S ₂ O ₃ , 5 h	86.1% [41]
Sulfide gold ore (4.3 g/t)	Oxidative ammoniacal leaching	0.006 mol/L CuSO ₄ , 0.8 mol/L NH ₃ ·H ₂ O, 0.1 mol/L Na ₂ S ₂ O ₃ , 22 h	94% [42]
Sulfide gold concentrate (28.9 g/t)	Bio-oxidation	0.02 mol/L CuSO ₄ , 1.0 mol/L NH ₃ ·H ₂ O, 0.18 mol/L Na ₂ S ₂ O ₃ , 0.24 mol/L Na ₂ SO ₃ , 24 h	85.05% [43]
Sulfide gold concentrate (47.8 g/t)	Microwave roasting	0.10 mol/L CuSO ₄ , 0.20 mol/L Na ₃ Cit, 0.10 mol/L Na ₂ S ₂ O ₃ , 7 h	94.5% [44]
Sulfide gold concentrate with high Cu, Pb and Zn (353 g/t)	Mechanical activation	10 g/L CuSO ₄ , 0.5 mol/L (NH ₄) ₂ S ₂ O ₃ , 403 kWh/t, 45 min	99% [45]
Gold calcinate (27.5 g/t)	Ultrasound	0.03 mol/L CoSO ₄ , 1.0 mol/L NH ₃ ·H ₂ O, 0.2 mol/L Na ₂ S ₂ O ₃ , 750 W, 8 h	89% [46]

It is expected that biological oxidation is a promising route for treating complex sulfide ores because it is cheap and eco-friendly. The mineral itself can be used as a rich nutrition resource; however, it is inefficient and sensitive to the operating conditions. Chemical oxidation can easily eliminate the encapsulation phenomenon using strong oxidative reagents, but it is expensive and has high corrosivity. Microwave, mechanical activation, and ultrasound exhibit wide application prospects in the gold hydrometallurgy leaching process, but they require high capital cost and energy consumption. Pretreatment of oxidative roasting is the most extensive method used in China due to its simple operation, high efficiency, and good processing capacity, and flue gas (SO₂) can be used as the raw material of sulfuric acid (H₂SO₄). Thus, oxidative roasting pretreatment was conducted in this experiment, and the leaching results were compared to the cyanide or copper-ammonia-thiosulfate leaching processes.

The main objective of this study is to examine the capacity of gold and silver leaching from a sulfide concentrate with copper-tartrate-thiosulfate solutions. Experimental parameters, including temperature, initial pulp pH, and copper, tartrate, and thiosulfate concentrations, were systemically studied. Based on the results obtained, the feasibility and economy of the novel leaching system in treating complex sulfide concentrate were discussed and analyzed in detail.

2. Experimental

2.1. Sample and Reagents

The gold concentrate was obtained from Henan Gold Co. of China (Zhengzhou, China) with a particle size of 99% passing 75 µm. The sample was first dried in an oven at 80 °C for 12 h prior to any analysis and experiments. Then, the dried concentrates were split and weighed after three hours of stirring in an electric mixer (Gongyi Yuhua Instrument Co., Ltd., Gongyi, China) to obtain representative samples (25.0 g per bag).

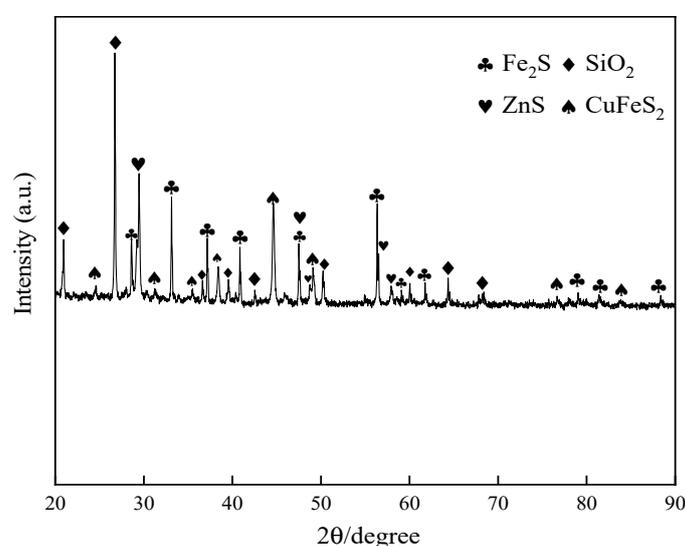
The analysis of the gold concentrate is shown in Table 2. The gold and silver contents were found to be 33.5 g/t and 152.9 g/t, respectively. The contents of valuable metals such as Cu, Fe, Zn, and nonmetallic elements containing C, As, and S were found to be 5.12%, 22.5%, 0.98%, 2.45%, 0.26%, and 26.3%, respectively. Gold is quite stable and typically exists in metallic form, while silver readily combines with sulfur and is generally found in the form of silver sulfides or argentojarosites [40,41]. Table 3 illustrates the X-ray fluorescence (XRF, ZSX Primus II, Rigaku, Tokyo, Japan) analysis of the complex polymetallic sulfide concentrate. Figure 1 shows the X-ray diffraction (XRD, X'Pert Pro, Philips, Amsterdam, Netherlands) analysis of the sulfide gold concentrate. The mineralogical phase detected indicates that the gold concentrate mainly consists of pyrite (FeS₂), chalcopyrite (CuFeS₂), sphalerite (ZnS), and quartz (SiO₂).

Table 2. Quantitative analysis of the main elements in the complex sulfide gold concentrate (ω , %).

Element	Au	Ag	Cu	Fe	Zn	C	As	S
Content	33.5 g/t	152.9 g/t	5.12	22.5	0.98	2.45	0.26	26.3

Table 3. X-ray fluorescence analysis of the complex sulfide gold concentrate (ω , %).

Element	Fe	Si	S	Cu	Al	Ca	Pb
Content	31.77	25.32	14.57	9.29	5.88	3.29	2.27
Element	K	Zn	Mg	As	Ti	Mn	Bi
Content	2.18	1.96	1.38	1.28	0.31	0.15	0.09
Element	P	Co	Mo	Sr	Ni	Zr	Rb
Content	0.08	0.06	0.05	0.02	0.02	0.02	0.02

**Figure 1.** X-ray diffraction analysis of the sulfide gold concentrate.

The analytical grade reagents used in this study included copper sulfate pentahydrate, sodium tartrate dihydrate ($C_4H_4Na_2O_6 \cdot 2H_2O$, $Na_2L \cdot 2H_2O$), sodium thiosulfate pentahydrate, ammonium hydroxide, sodium hydroxide, sulfuric acid, ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) and formaldehyde. Deionized water was used throughout all experiments.

2.2. Leaching Tests

The leaching tests were carried out in 250 mL beakers provided with an overhead mechanical stirrer (IKA RW 20, IKA Instrument Equipment Co., Ltd., Guangzhou, China) and a PTFE impeller (IKA Instrument Equipment Co., Ltd., Guangzhou, China). For each test, a 25.0 g gold concentrate sample was leached in 100 mL copper-tartrate-thiosulfate solution within a set time. The agitation speed was agitated at 300 rpm during leaching tests. The lixiviant was accurately prepared by mixing the required contents of copper sulfate, sodium tartrate, sodium thiosulfate, and deionized water prior to any experiments. The order of adding the reagents is important to minimize the oxidation of thiosulfate and to prevent copper precipitation. Oxidative roasting experiments were carried out in an electrical resistance furnace (YFX6.5/13Q-YC, Shengke Instrument Equipment Co., Ltd., Shanghai, China) at different temperatures. Samples were withdrawn within a predetermined time and then washed with 1.0 mol/L NaOH and deionized water. The solution pH was measured by a standard pH probe (PB-10) and adjusted by the addition of 1.0 mol/L NaOH and 1.0 mol/L H_2SO_4 . The slurry was filtered under a vacuum, and

then the volume of the filtrate was measured. The residue was dried at 80 °C for 12 h and ground into fine particles for subsequent testing.

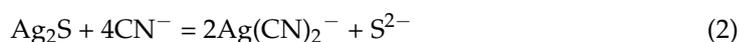
2.3. Analysis

The oxidative reductive potential (ORP) of the solution/pulp was measured by a potentiometer (PHS-3E, INESA, Scientific Instrument Co, Ltd., Shanghai, China). Unless otherwise stated, all the ORPs are referenced to the standard hydrogen electrode (SHE). The XRF and XRD analyses of the gold concentrate samples were conducted by X-ray fluorescence spectrometry (ZSX Primus II, Rigaku, Rigaku, Tokyo, Japan) and X-ray diffraction (X'Pert Pro, Philips, Amsterdam, The Netherlands), respectively. The thiosulfate concentration in the leaching solution was measured by standard iodine titration using the Vitex indicator (Sinopharm Chemical Reagent Co, Ltd., Shanghai, China) [28,33]. A certain amount of EDTA-2Na (Sinopharm Chemical Reagent Co, Ltd., Shanghai, China) and formaldehyde (Sinopharm Chemical Reagent Co, Ltd., Shanghai, China) were added to eliminate the potential interference of copper tartrate complexes and sulfite ions prior to titration. The concentration of free cyanide was detected by a silver nitrate titration method using rhodamine as the indicator. The content of gold and silver in the leaching solution or residue was analyzed by atomic absorption spectrophotometry (AAS), model Hitachi Z-2300 (Hitachi Limited, Tokyo, Japan). An ultraviolet–visible spectrophotometer (L5S, INESA, Scientific Instrument Co, Ltd., Shanghai, China) was used to determine the concentration of copper-tartrate complexes in the leaching solutions. Moreover, standard solutions prepared by the analytical reagent grade of copper sulfate and sodium tartrate were used to draw a standard curve of the absorbance and concentration.

3. Results and Discussion

3.1. Diagnostic Cyanidation

Previous studies indicated that 41.80% Au can be obtained following 24 h of leaching in 0.04 mol/L sodium cyanide solutions at room temperature. This means that the sample used in this leaching test was a typically refractory polymetallic sulfide gold concentrate [47]. Accordingly, a higher initial cyanide concentration (0.50 mol/L) was used to enhance the rate of gold and silver leaching, and the results are shown in Figure 2. The rate of gold and silver extraction dramatically increases initially and then attains a steady state with prolonged leaching time. The silver leaching rate is slightly lower than that of gold due to the low solubility and low reactivity of silver sulfide. The mechanism of gold and silver leaching in cyanide solutions can be expressed by Equations (1) and (2).



Gold can be oxidized to aurous ions under the catalytic effect of dissolved oxygen, while silver sulfide can be substituted into solutions in the presence of cyanide ions. The sulfur ions (S^{2-}) from Ag_2S can be further oxidized to S_x^{2-} , S, SCN^- , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , and SO_4^{2-} , promoting the dissolution of silver sulfide in the solutions [48]. It was found that 92.06% Au and 71.07% Ag can be obtained after 24 h of leaching in 0.50 mol/L cyanide solutions at 25 °C. However, cyanide consumption dramatically increased to 84.68 kg/t-ore. Reactive minerals, such as chalcopyrite (CuFeS_2), pyrite (FeS_2), and sphalerite (ZnS), could greatly consume the leach reagents in side reactions, leading to insufficient cyanide and/or oxygen in the pulp to leach gold [2]. This outcome seems catastrophic for the gold cyanide leaching process in dealing with complex sulfide gold ores or concentrates. The massive wastewater or tailings containing cyanide may cause great damage to the surrounding environment. The detoxification process of cyanide oxidation is extremely costly as well.

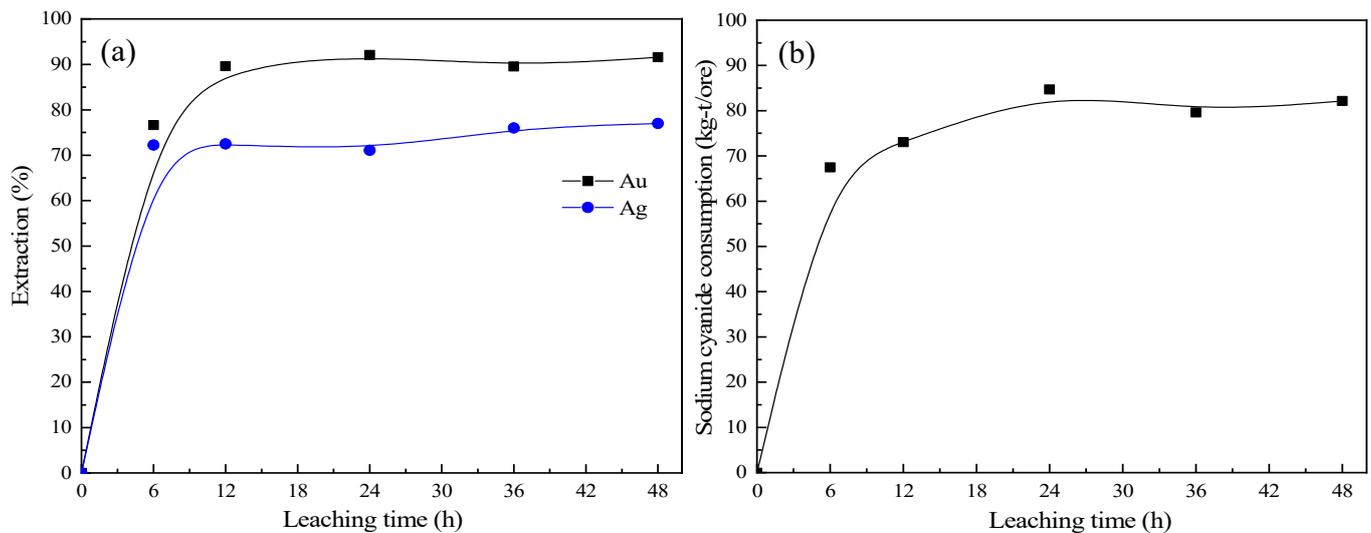


Figure 2. Effect of leaching time on (a) gold/silver extraction and (b) cyanide consumption (0.5 mol/L sodium cyanide, pH = 11.0, and 25 °C).

3.2. Direct Leaching with Copper-Tartrate-Thiosulfate Solutions

3.2.1. Effect of Leaching Time

Figure 3a illustrates the effect of leaching time on gold and silver extraction from the complex sulfide concentrate. The gold extraction increases with increasing leaching time and then tends to be stable, while the leaching rate of silver fluctuates with extended leaching time. This shows that the silver thiosulfate complex exhibits less stability in leaching solutions than the gold thiosulfate complex. Equations (3)–(6) explain the mechanism of gold and silver leaching in copper-tartrate-thiosulfate solutions.

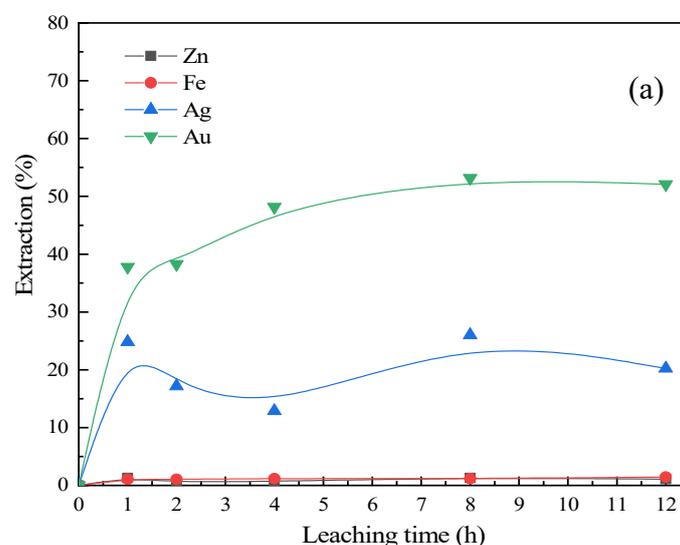
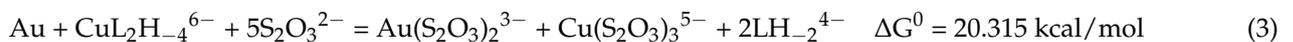


Figure 3. Cont.

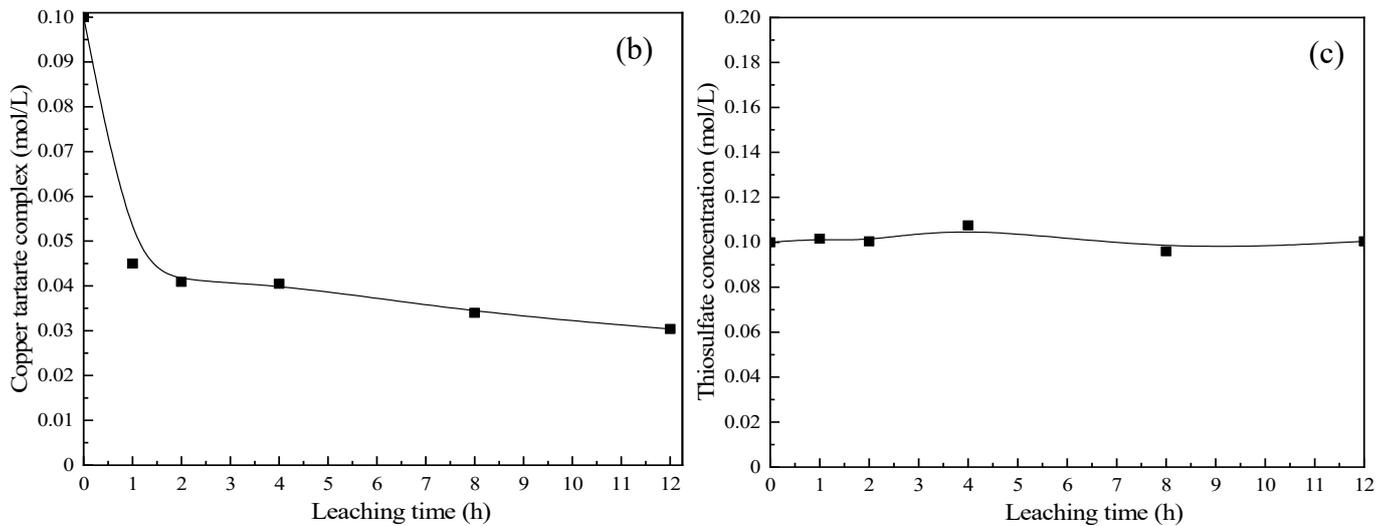


Figure 3. Effect of leaching time on (a) gold/silver extraction, (b) copper tartrate complex, and (c) thiosulfate concentration (0.1 mol/L CuSO₄, 0.3 mol/L Na₂L, 0.1 mol/L Na₂S₂O₃, 75 °C, initial pulp pH 11.0).

Gold can be oxidized to aurous ions under the catalytic effect of the oxidants (O₂ and CuL₂H₄⁶⁻) and stably exist in leaching solutions by the formation of the Au(S₂O₃)₂³⁻ complex, while silver sulfide can be substituted by thiosulfate ions to form the Ag(S₂O₃)₂³⁻ complex. Sulfide minerals, such as FeS₂, CuFeS₂, and ZnS, can partly dissolve into the solutions, as shown in the following reactions. The newly generated sulfur or disulfide ions may affect the stability of the silver thiosulfate complex, leading to a loss of silver ions in aqueous solutions, as depicted in Equation (10). Another factor accounting for the low silver extraction can be attributed to the reactions between cupric/cuprous ions and Ag₂S that may be reversible with a small free energy change.

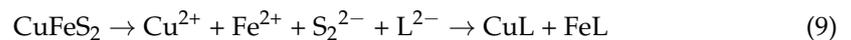


Figure 3b shows the variation in the copper tartrate complex concentration during the leaching process. The concentration of the copper tartrate complex decreases rapidly in the first 1 h and then slightly decreases with increasing leaching time. In the initial stage of leaching, the copper ions are gradually reduced to cuprous ions by thiosulfate as gold dissolution proceeds. The associated minerals also exhibit detrimental effects on the stability of copper tartrate complexes, leading to a loss of copper ions in solutions Equations (11) and (12). Subsequently, the cuprous thiosulfate complex can be reoxidized to the copper tartrate complex under the catalytic effect of dissolved oxygen, leading to a low decomposition rate of the copper tartrate complex. The thiosulfate concentration slightly increases with increasing leaching time. The in-situ generation of thiosulfate may be derived from the oxidation of sulfur and disulfide ions, as depicted in Equations (13) and (14).





With copper-ammonia-thiosulfate solutions, the capability of gold and silver leaching is comparable to that of the copper-tartrate-thiosulfate leaching system. However, the thiosulfate consumption significantly increased up to 19.42 kg/t-ore under the conditions of 0.05 mol/L CuSO₄, 1.0 mol/L NH₃·H₂O, 0.1 mol/L Na₂S₂O₃, 50 °C and following 8 h of leaching. Apparently, as an alternative to ammonia, tartrate is more efficient in complexing with cupric ions. The negligible thiosulfate consumption from the complex sulfide gold concentrate is encouraging. The copper tartrate complex (CuL₂H₋₄⁶⁻) is equipped with a high negative charge, which can weaken the affinity of associated mineral surfaces to thiosulfate. Moreover, it can prevent passivation species from coating gold surfaces through electrostatic repulsion. Thus, the catalytic effect of minerals on thiosulfate consumption or decomposition could be effectively relieved.

3.2.2. Effect of Tartrate Concentration

Figure 4a illustrates the effect of tartrate concentration on gold and silver extraction in copper-tartrate-thiosulfate solutions. The gold extraction increases with an increase in tartrate concentration in the range of 0.1 mol/L to 0.5 mol/L, while the silver leaching rate decreases as the tartrate content increases. The formation of CuL₂H₋₄⁶⁻ in copper-tartrate-thiosulfate solutions before the leaching process is shown in Equation (15), which is the dominant species of the copper tartrate complex under alkaline conditions [36]. Increasing the tartrate content is expected to promote the formation of the copper tartrate complex, thereby enhancing the stability of thiosulfate and accelerating the gold and silver leaching rate. Figure 4b shows the variation in the content of the copper tartrate (CuL₂H₋₄⁶⁻) complex in the leaching solutions at different tartrate concentrations. The concentration of the copper tartrate complex following 8 h of leaching increased with increasing tartrate content. This implies that a moderate increase in tartrate content is beneficial for enhancing the stability of mixed solutions. However, excessive tartrate content may significantly narrow the region of stability of the cuprous thiosulfate complex and cause a decline in the cuprous ion concentration, as shown in Equations (16) and (17). This outcome may depress the dissolution of silver sulfide in copper-tartrate-thiosulfate solutions. Thus, cuprous ions would be favored over copper ions for substitution into the residue due to the chemical and structural orthorhombic similarities between Ag⁺ and Cu⁺ ions [49].

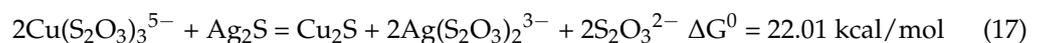
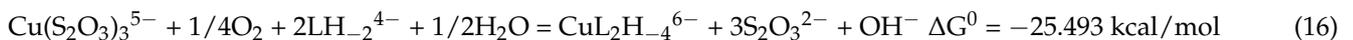


Figure 4c shows the variation in thiosulfate concentration during the leaching process. It can be seen that there was a slight consumption of thiosulfate in 0.1 mol/L tartrate solutions. Such an observation can be attributed to the catalytic effect of free ferric and copper ions on thiosulfate. The associated minerals may also play a catalytic role in accelerating the consumption or decomposition of thiosulfate in copper-tartrate-thiosulfate solutions due to the lack of tartrate. Thus, 0.4 mol/L tartrate was used to conduct the following tests.

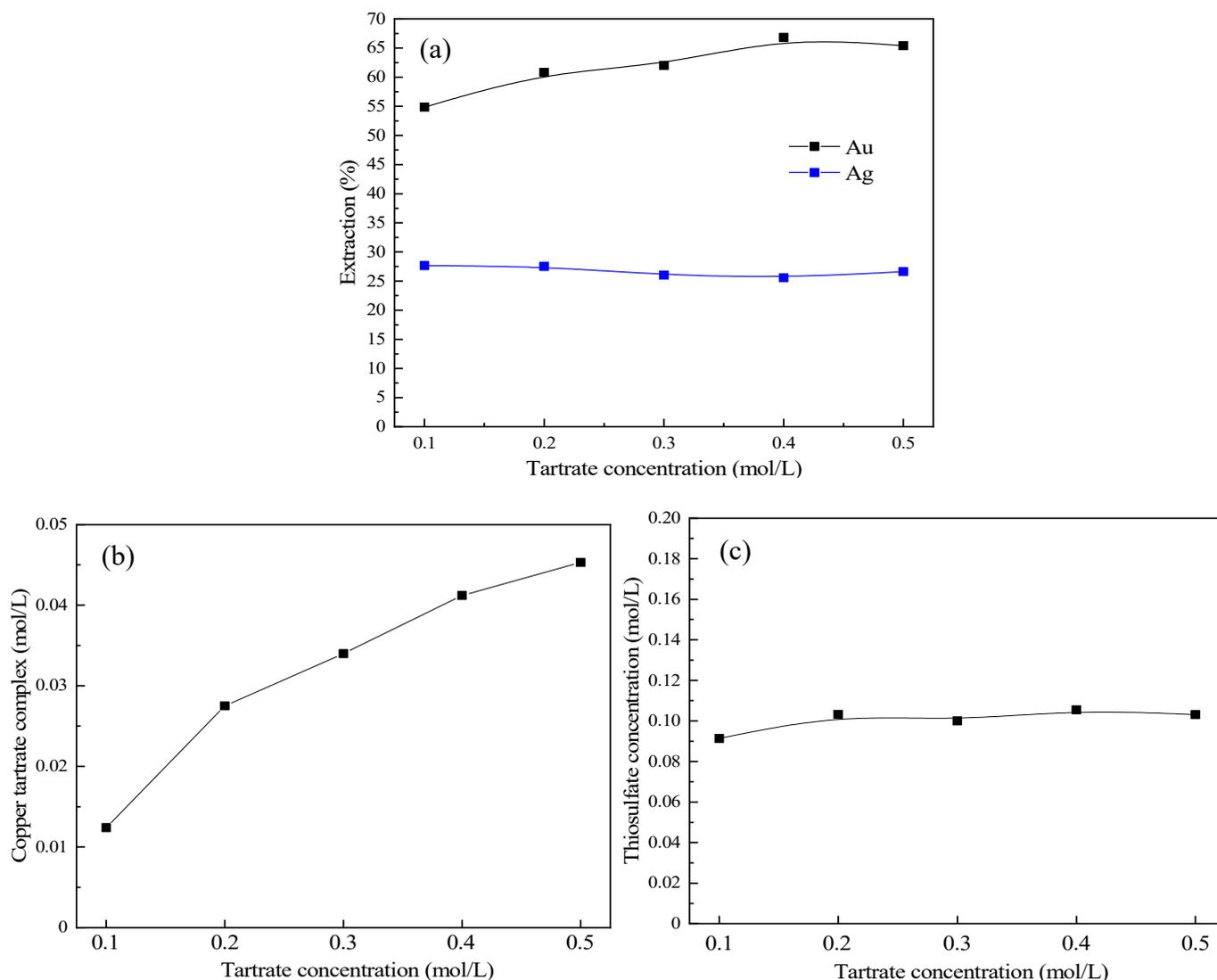


Figure 4. Effect of tartrate concentration on the (a) gold/silver extraction, (b) copper tartrate complex and (c) thiosulfate concentration (0.1 mol/L CuSO_4 , 0.1 mol/L $\text{Na}_2\text{S}_2\text{O}_3$, 75 °C, initial pulp pH 11.0, and 8 h).

3.2.3. Effect of Copper Concentration

Figure 5a shows the effect of copper concentration on gold and silver extraction in copper-tartrate-thiosulfate solutions. The gold extraction dramatically increases with a moderate increase in the copper concentration (0.01 to 0.1 mol/L) and then tends to be stable when the copper concentration further reaches 0.4 mol/L. The silver leaching rate increases with increasing copper concentration in the range of 0.01 mol/L to 0.1 mol/L and then slightly decreases as the copper concentration increases to 0.4 mol/L. The results indicate that a moderate increase in copper concentration is beneficial for gold and silver leaching, but excessive copper content may cause a lower silver extraction.

Figure 6 illustrates the XRD analysis of the leaching residue at different copper ion concentrations. The peak areas of Cu_2S and CuO gradually increase with increasing copper ion concentrations. The loss of silver ions may be ascribed to the precipitation of the silver thiosulfate complex in the presence of Cu_2S , according to Equation (18). This result supports the notion proposed by Zipperian and Raghavan that the precipitation of copper sulfide results in silver losses from solutions [50]. The presence of CuO may be derived from the hydrolysis of copper ions liberated from the associated minerals. Figure 5b shows

the variation in the copper tartrate complex content during the leaching process. Based on thermodynamic analysis, increasing copper ion concentrations will narrow the stability region of the $\text{CuL}_2\text{H}_4^{6-}$ complex, thereby causing a significant loss of copper ions as the copper ion concentration increases [36]. The thiosulfate concentration slightly increases with increasing copper ion concentration and then tends to be stable, as shown in Figure 5c. A moderate increase in the copper ion concentration is beneficial for enhancing the potential of the mixed solutions, thereby promoting the oxidation of sulfur or disulfide ions. Thus, 0.1 mol/L copper ion was used to conduct the following leaching tests.

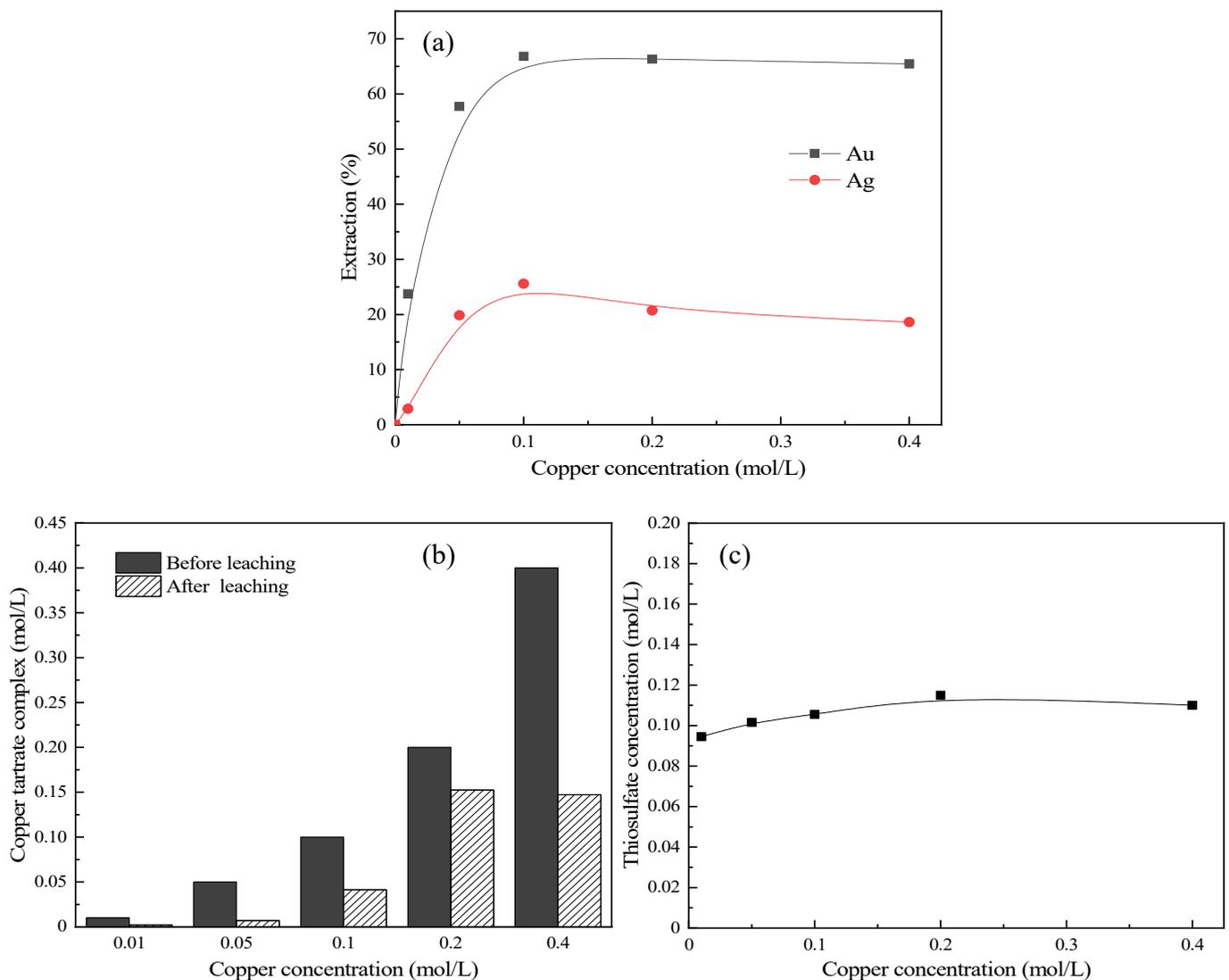


Figure 5. Effect of copper concentration on (a) gold/silver extraction, (b) copper tartrate complex and (c) thiosulfate concentration (0.4 mol/L Na_2L , 0.1 mol/L $\text{Na}_2\text{S}_2\text{O}_3$, 75 °C, initial pulp pH 11.0, and 8 h).

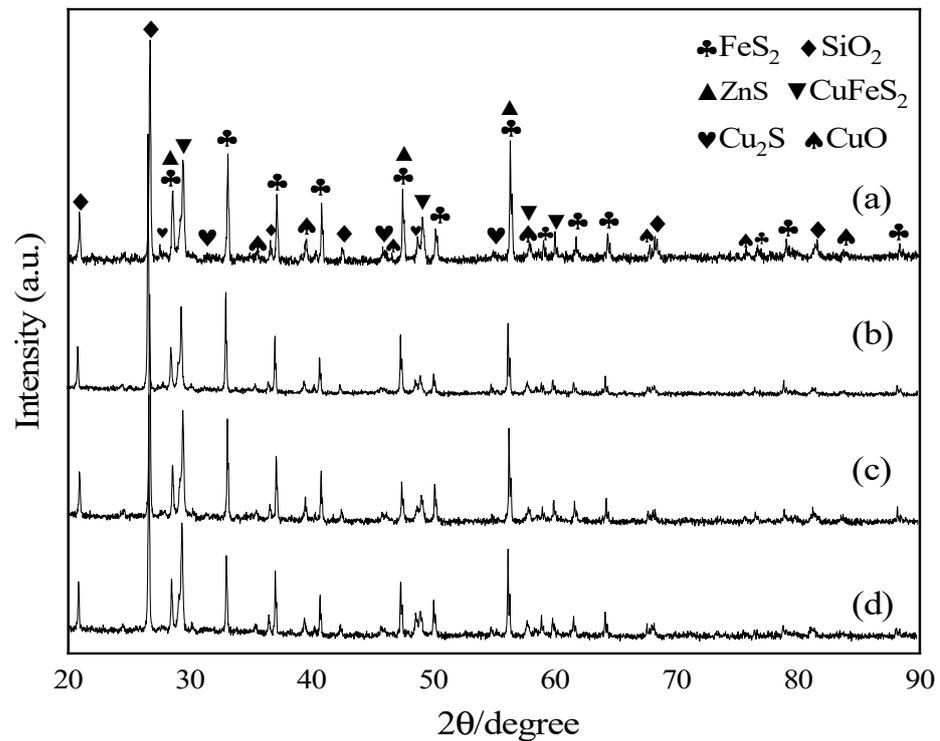
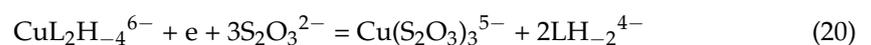
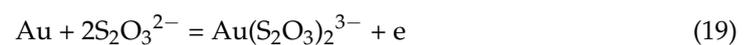


Figure 6. XRD analysis of the leaching residue at different copper ion concentrations: (a) 0.01 mol/L CuSO_4 , (b) 0.05 mol/L CuSO_4 , (c) 0.10 mol/L CuSO_4 , and (d) 0.40 mol/L CuSO_4 .

3.2.4. Effect of Thiosulfate Concentration

Figure 7a illustrates the effect of thiosulfate concentration on gold and silver extraction during the leaching process. The gold and silver extraction increases with increasing thiosulfate concentrations in the range of 0.01 to 0.4 mol/L. A moderate increase in thiosulfate concentration promotes the half-reactions of gold leaching in thiosulfate-based solutions, as shown in Equations (19) and (20). Moreover, the rate of silver extraction can be simultaneously enhanced due to an increase in cuprous thiosulfate complexes ($\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$). However, according to Equation (20), increases in thiosulfate concentration may have a detrimental effect on the stability of the $\text{CuL}_2\text{H}_{-4}^{6-}$ complex, leading to a lower content of the copper tartrate complex. Figure 7b shows the variation in copper tartrate complex content at different thiosulfate concentrations. The concentration of the copper tartrate complex in the leaching solutions dramatically decreases as the thiosulfate concentration increases. Figure 7c indicates that the thiosulfate concentration following 8 h of leaching slightly increases with increasing thiosulfate concentrations. A moderate increase in thiosulfate content can elevate the potential of the mixed solutions, which promotes the in-situ generation of thiosulfate derived from the oxidation of sulfur or disulfide ions in the leaching solutions. Therefore, 0.2 mol/L thiosulfate was used to conduct the following tests.



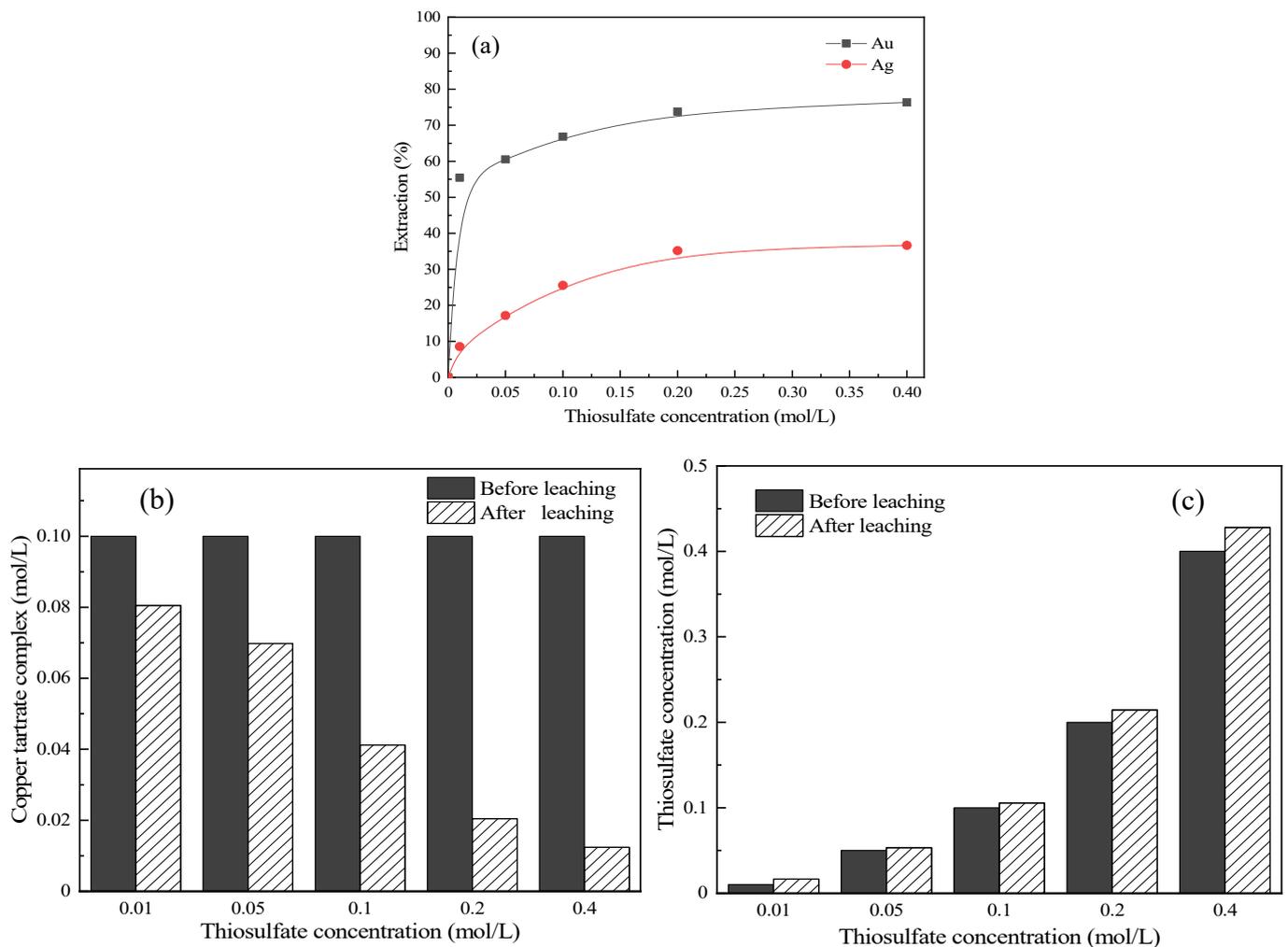


Figure 7. Effect of thiosulfate concentration on (a) gold/silver extraction, (b) copper tartrate complex and (c) thiosulfate concentration (0.1 mol/L CuSO_4 , 0.4 mol/L $\text{Na}_2\text{S}_2\text{O}_3$, 75 °C, initial pulp pH 11.0, and 8 h).

3.2.5. Effect of Temperature

Figure 8a summarizes the effect of temperature on gold and silver extraction in copper-tartrate-thiosulfate solutions. The gold extraction dramatically increases from 18.34% to 74.50% as the temperature increases from 30 °C to 90 °C. The silver leaching rate gently increases from 24.84% to 35.18% when the temperature increases from 30 °C to 75 °C and then decreases to 30.20% as the temperature reaches 90 °C. Clearly, the capability of gold leaching from the sulfide concentrate in copper-tartrate-thiosulfate solutions is more temperature-sensitive than that of silver. This implies that the gold dissolution process in the copper-tartrate-thiosulfate solution may be controlled by chemical reactions, while the leaching process of silver sulfide is mainly controlled by product layer diffusion. As shown in Figure 8b,c, the concentration of the copper tartrate complex decreases with increasing leaching temperature, while the content of thiosulfate in the leaching solutions slightly increases at different temperatures. Thus, a moderate temperature of 75 °C was determined to conduct the following leaching tests.

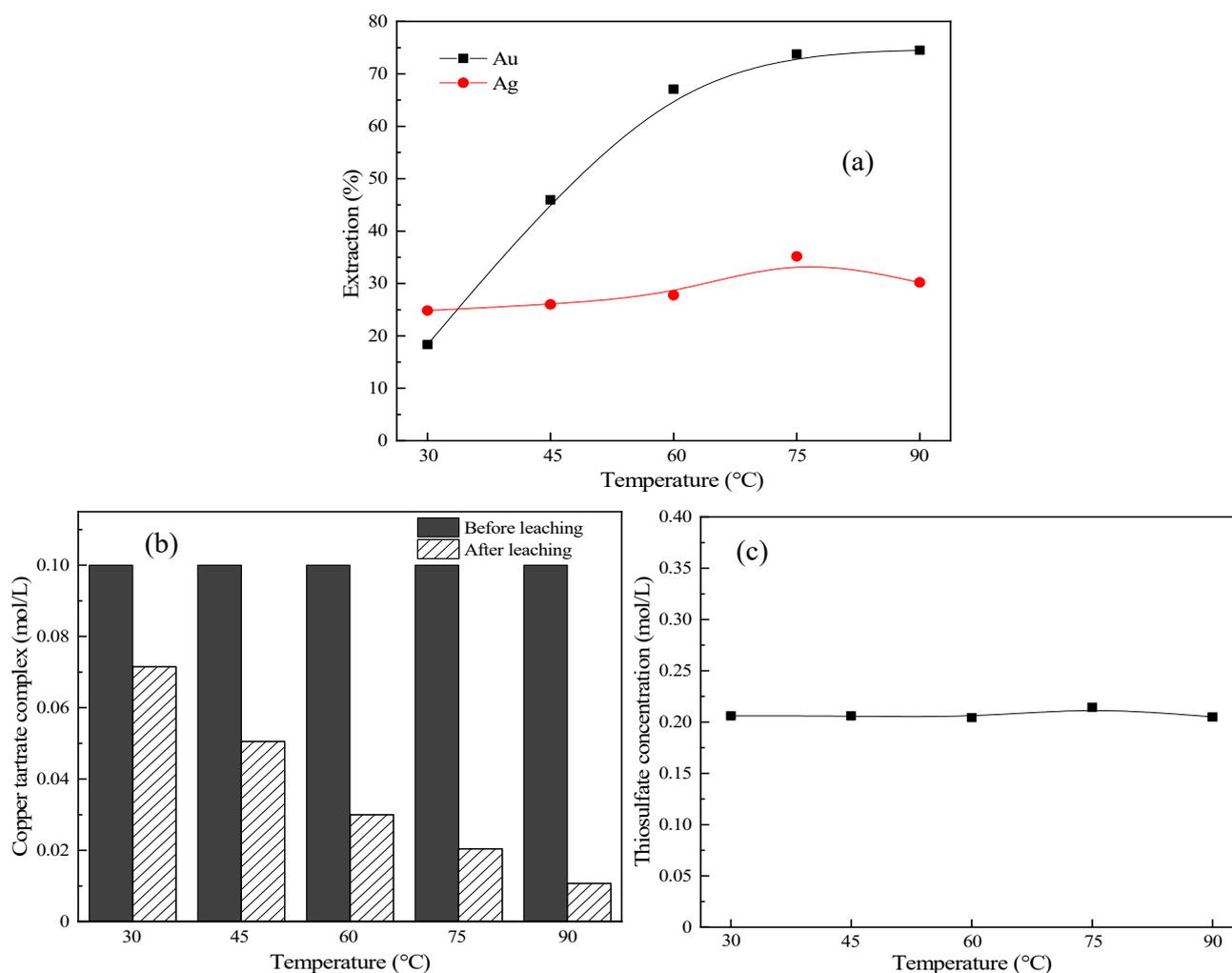


Figure 8. Effect of temperature on (a) gold/silver extraction, (b) copper tartrate complex and (c) thiosulfate concentration (0.1 mol/L CuSO_4 , 0.4 mol/L $\text{Na}_2\text{S}_2\text{O}_3$, 0.2 mol/L thiosulfate, initial pulp pH 11.0, and 8 h).

3.2.6. Effect of Initial Pulp pH

The effect of the initial pulp pH on the extraction of gold/silver was examined, and the results are shown in Figure 9a. The gold extraction increases with a moderate increase in the initial pulp pH in the range of 7.0 to 11.0 and then slightly decreases when the pulp pH reaches 12.0. However, when the initial pulp pH is less than 10.0, the leaching efficiency of gold and silver from the complex sulfide concentrate is extremely low. The thiosulfate consumption dramatically increases as the pulp pH decreases. A maximum silver extraction of 36.33% was obtained when the initial pulp pH was maintained at 10.0; subsequently, the silver leaching rate decreased as the pulp pH increased or decreased. The thiosulfate content slightly increases following 8 h of leaching when the pulp pH is beyond 10.0.

Figure 9b shows the variation in the copper tartrate complex content at different initial pulp pH values. The copper tartrate complex content in the leaching solutions is extremely low following 8 h of leaching. This means that the leaching behavior of the sulfide concentrate with copper-tartrate-thiosulfate solutions is very complicated. Figure 10 shows the variation in the pulp pH before and after leaching with copper-tartrate-thiosulfate solutions. The pH values of the solutions after leaching dramatically decreased when the initial pulp pH was less than 10.0, and the final pH values of the mixed solutions were kept at approximately 5.0. Apparently, suitable alkaline conditions must be maintained to

obtain an acceptable gold and silver leaching rate from the complex sulfide concentrate in copper-tartrate-thiosulfate solutions. Therefore, an initial pulp pH of 11.0 was confirmed to be the optimal choice to conduct the following leaching tests.

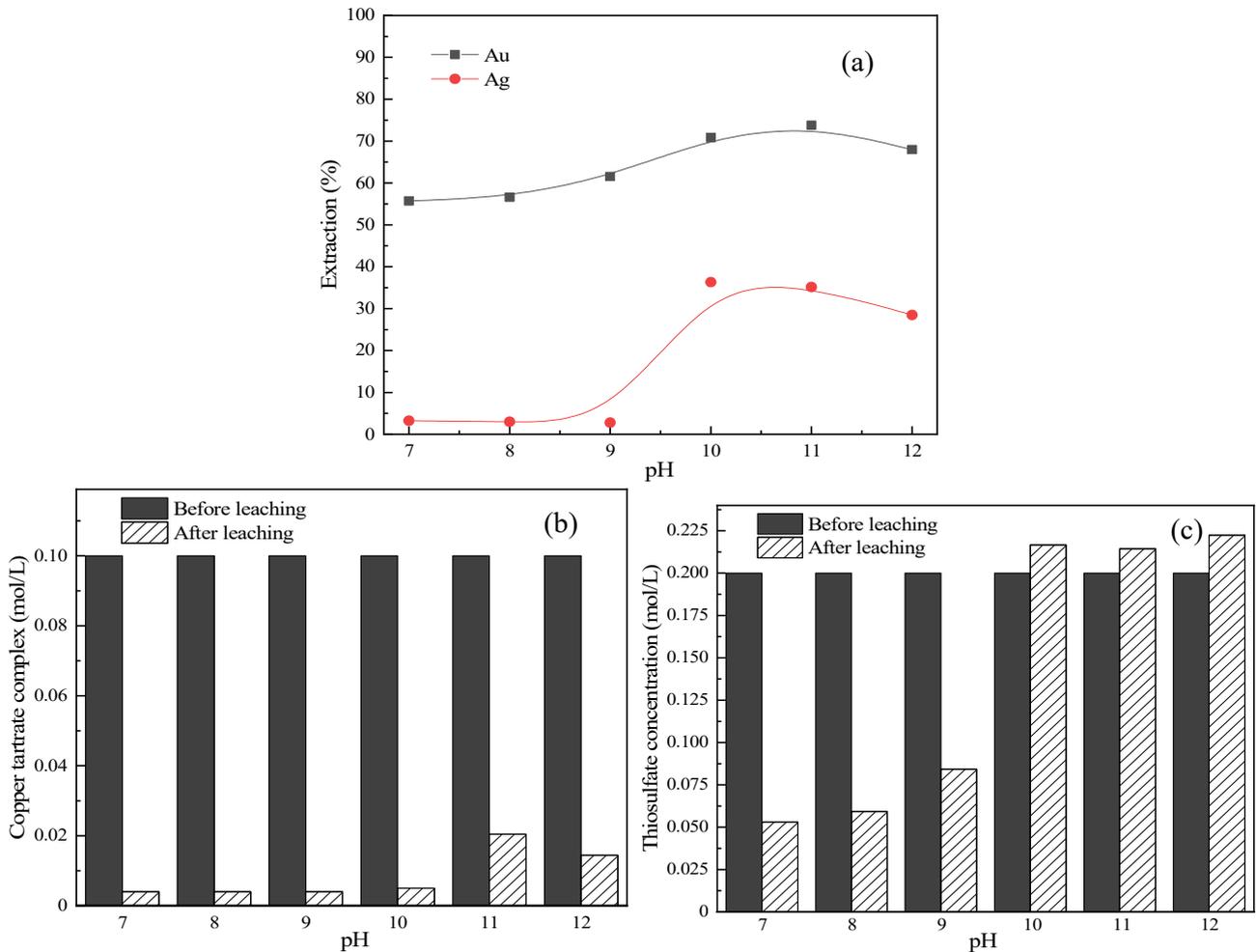


Figure 9. Effect of initial pulp pH on (a) gold/silver extraction, (b) copper tartrate complex, and (c) thiosulfate concentration (0.1 mol/L CuSO_4 , 0.4 mol/L Na_2L , 0.2 mol/L thiosulfate, 75 °C, and 8 h).

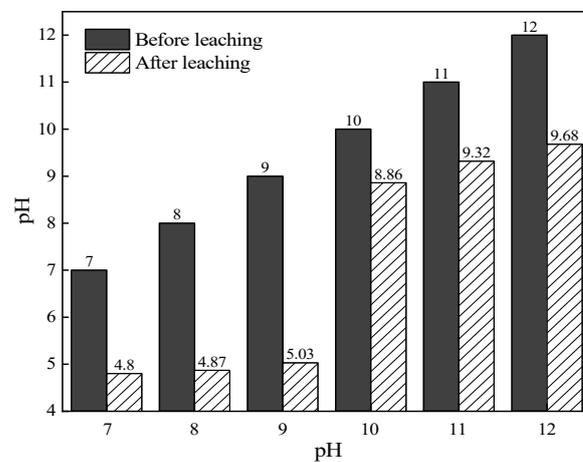


Figure 10. Variation in the pulp pH in copper-tartrate-thiosulfate solutions (0.1 mol/L CuSO_4 , 0.4 mol/L Na_2L , 0.2 mol/L thiosulfate, 75 °C, and 8 h).

3.3. Roasting-Leaching Tests

The gold and silver extraction from direct leaching with copper-tartrate-thiosulfate solutions is much lower than that obtained from cyanidation. Pretreatment of the concentrate with oxidative roasting at different temperatures was conducted to enhance the leaching rate of gold and silver. The results are shown in Figure 11a. Compared to the untreated concentrate, the leaching rate of gold and silver from the calcine with copper-tartrate-thiosulfate solutions can be effectively promoted. Apparently, the effect of roasting temperature on the subsequent gold and silver leaching process is extremely crucial. The gold extraction from the calcine increases from 74.07% to 80.90% as the roasting temperature increases from 300 °C to 400 °C and then decreases to 77.72% as the temperature reaches 700 °C. The silver extraction increases from 56.39% to 70.38% when the temperature increases from 300 °C to 400 °C and then decreases to 53.26% as the temperature attains 700 °C.

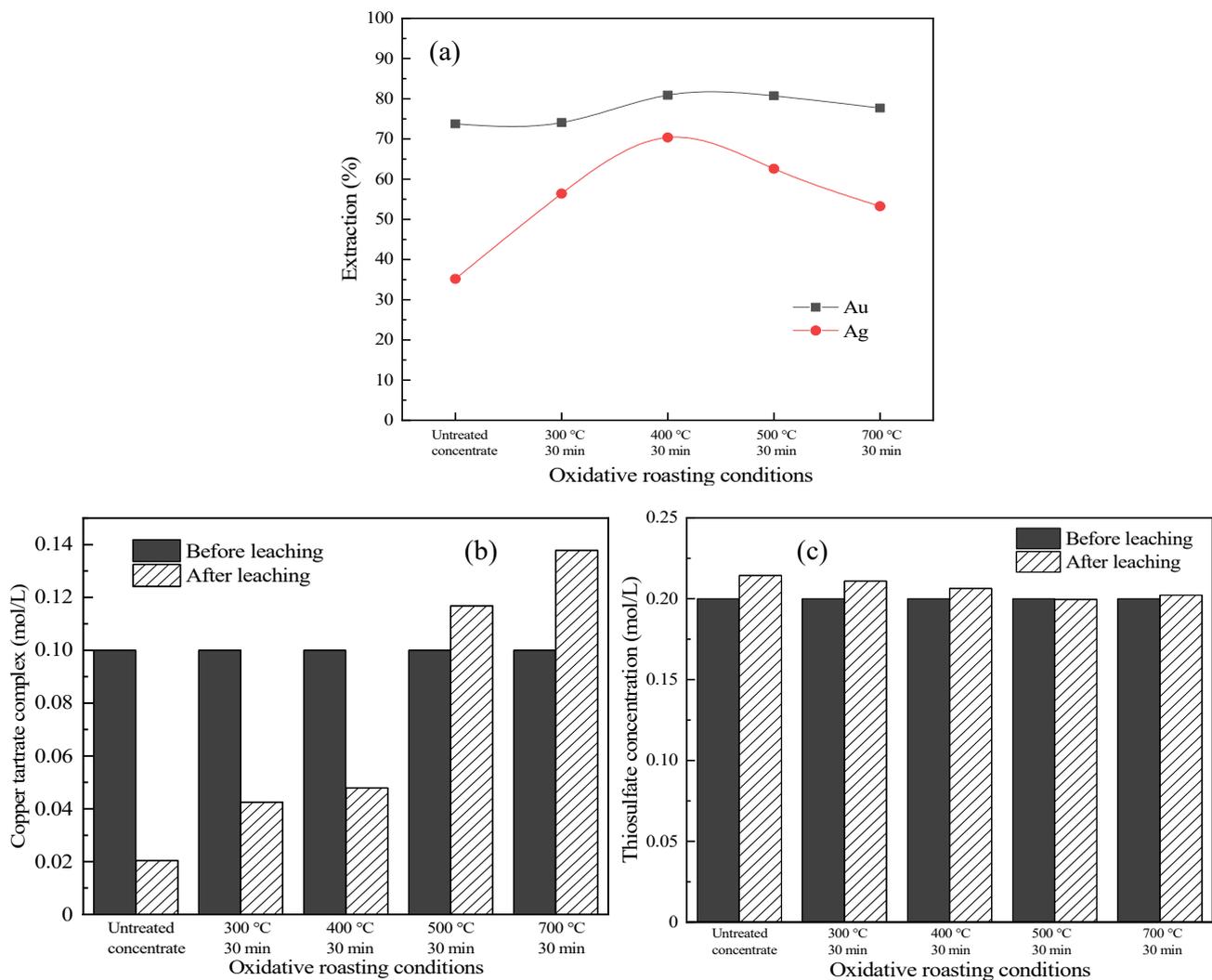


Figure 11. Effect of roasting temperatures on (a) gold/silver extraction, (b) copper tartrate complex and (c) thiosulfate concentration (0.1 mol/L CuSO_4 , 0.4 mol/L Na_2S , 0.2 mol/L thiosulfate, initial pulp pH 11.0, 75 °C, and 8 h).

The oxidative roasting process can effectively eliminate sulfur-bearing species and liberate part of the encapsulated gold and silver, as expressed in Equations (21)–(25). A moderate increase in roasting temperature is beneficial for gold and silver leaching, but a higher temperature seems unattractive in enhancing the leaching rate of gold and silver.

The secondary encapsulation phenomenon by the newly generated hematite (Fe_2O_3) or magnetite (Fe_3O_4) at high temperatures may depress gold and silver leaching, as shown in Figure 12, thereby resulting in a lower extraction of gold and silver.

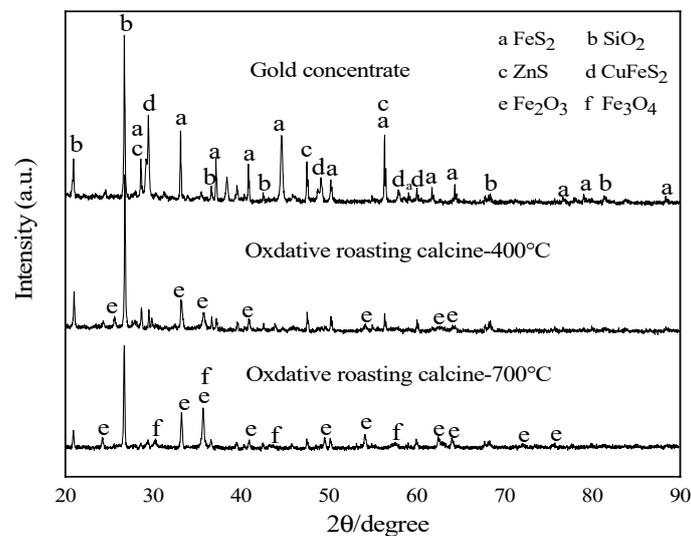
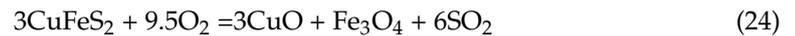
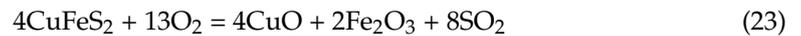
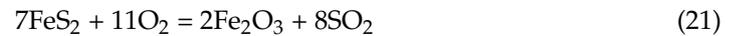


Figure 12. The XRD analysis results of the concentrate and the calcine.

Moreover, the kinetics of Ag dissolution are expected to be much more pronounced than those of Ag_2S when the ore is subjected to oxidative roasting because the reactivity and solubility of Ag_2S are extremely low. Table 4 summarizes the mass loss of the gold concentrate during the oxidative roasting process and the homologous content of sulfur. This shows that the mass loss of the sulfide concentrates increases with increasing temperature because the sulfur-bearing species are released in the form of SO_2 , which can be collected as the raw material of sulfuric acid (H_2SO_4). Meanwhile, due to the regeneration of the copper tartrate complex and partial dissolution of CuO in solutions, the copper ion concentration slightly increases in the leaching solutions, as shown in Figure 11b. The in-situ generation of thiosulfate slightly decreases as the roasting temperature increases because the contents of free sulfur and disulfide ions gradually decrease, as depicted in Figure 11c. However, the consumption of thiosulfate can be negligible during the above leaching tests. Thus, a suitable roasting temperature was determined to be $500\text{ }^\circ\text{C}$ for the following recycling tests.

Table 4. Mass loss of the gold concentrate after oxidative roasting and the homologous content of sulfur.

Sample	Roasting Conditions	Mass Loss (g)	S (ω , %)
Gold concentrate	—	0	26.3
Gold calcine	$300\text{ }^\circ\text{C}$, 30 min	0.74	24.9
Gold calcine	$400\text{ }^\circ\text{C}$, 30 min	1.69	14.2
Gold calcine	$500\text{ }^\circ\text{C}$, 30 min	2.38	12.1
Gold calcine	$700\text{ }^\circ\text{C}$, 30 min	4.69	6.56

3.4. Recycling of the Lixiviant

It is noted that there was a considerable content of copper ions and thiosulfate in the leaching solutions after the oxidative roasting-leaching tests. Therefore, it is expected to recycle the leaching solutions to verify the possibility of reuse of the lixiviants in the copper-tartrate-thiosulfate leaching system. The concentrate is first roasted at 500 °C for 60 min, and then the leaching solution is recycled for countercurrent to leach the fresh gold calcine, and the results are shown in Figure 13.

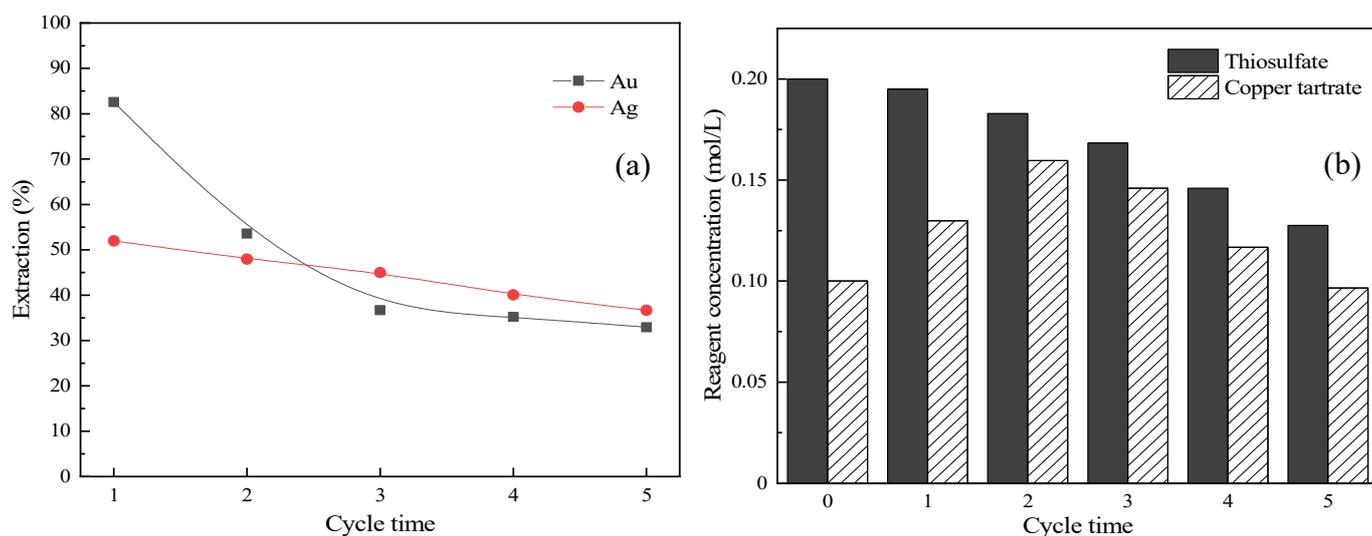


Figure 13. Effect of recycling the lixiviant on (a) gold/silver extraction, (b) reagent concentration (0.1 mol/L CuSO_4 , 0.4 mol/L Na_2L , 0.2 mol/L thiosulfate, initial pulp pH 11.0, 75 °C, and 8 h).

Figure 13a shows that the gold extraction dramatically decreases from 82.60% to 32.94% as the recycling times increase, and the silver leaching rate gently decreases from 51.99% to 36.67%. This means that the capability of gold leaching with copper-tartrate-thiosulfate solutions is more sensitive to the variation in reagent concentrations than that of silver leaching. Figure 13b illustrates the variation in the content of the copper tartrate complex and thiosulfate in the leaching solutions. This shows that the content of the copper tartrate complex increases in the initial period of leaching and then decreases as the recycling times increase. Such an observation may be attributed to the dissolution of CuO and the regeneration of copper tartrate in the fresh leachate. Therefore, the copper ion concentration can be slightly increased. However, the stability of the copper tartrate complex may be severely affected with extended leaching time because the free tartrate is gradually consumed. Figure 13b indicates that the thiosulfate content slightly decreases as the recycling times increase due to the catalytic effect of metal ions (Cu^{2+} , Fe^{3+}) and associated minerals. Clearly, a suitable free tartrate content is of great significance in maintaining the stability of the copper-tartrate-thiosulfate leaching system.

Table 5 shows the content of the copper tartrate complex in the leaching solutions open to the air. The copper ion concentration gradually increases with extended time. This means that the cuprous thiosulfate complex can spontaneously transform into the copper tartrate complex under the catalytic effect of oxygen. Equation (16) depicts the equilibrium reaction between Cu(II)/Cu(I) in copper-tartrate-thiosulfate solutions. This also indicates that there was a considerable content of cuprous thiosulfate complex in the leaching solutions. Thus, it can be concluded that the leaching rate of gold and silver is virtually dependent on the relative concentration ratio of cuprous ions and cuprous ions. Dissolved oxygen may also play a key role in the leaching process.

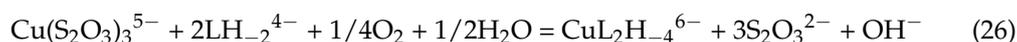


Table 5. Variation in the copper tartrate complex concentration in the leaching solutions (mol/L).

t/Cycle	1	2	3	4	5
0 h	0.1299	0.1596	0.1460	0.1167	0.0966
8 h	0.1561	0.1820	0.1645	0.1341	0.1051
16 h	0.1800	0.1969	0.1790	0.1472	0.1114
24 h	0.1981	0.2092	0.1873	0.1535	0.1117

4. Conclusions

The leaching behaviors of gold and silver from a complex sulfide concentrate were investigated in this work. The following conclusions can be obtained:

- (1) The copper-tartrate-thiosulfate leaching system exhibits promising performance in dealing with the complex sulfide concentrate. An extraction of 74.50% Au and 36.33% Ag can be obtained with the direct leaching of the concentrate. Under the experimental conditions, increasing the temperature and concentrations of copper, tartrate, and thiosulfate can promote gold leaching. Low tartrate content and a moderate increase in temperature and copper and thiosulfate concentrations can accelerate silver leaching, but a higher temperature or copper content may depress silver extraction. A suitable pulp pH is crucial to gold and silver leaching with copper-tartrate-thiosulfate solutions.
- (2) Roasting is an effective pretreatment method to deal with this concentrate. The gold and silver extraction can be significantly increased up to 82.60% and 70.38% when leaching the calcine following the oxidative roasting pretreatment. The secondary encapsulation phenomenon by newly generated hematite and magnetite at high temperatures may depress gold and silver leaching. The recycling of leaching solutions demonstrates that a suitable free tartrate content is of great significance in maintaining the stability of the novel leaching system.
- (3) The presence of tartrate in the copper-thiosulfate solutions can effectively promote the stability of thiosulfate and facilitate the leaching process. As an alternative to the traditional cyanide or copper-ammonia-thiosulfate leaching processes, the copper-tartrate-thiosulfate leaching system provides an environmentally friendly, nontoxic, and relatively low-cost method for gold and silver leaching from ores or concentrates.

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