

Article

Characteristics of Gold Minerals in Gold Concentrate with a High Copper Content and Effective Gold Recovery via Flotation and Ammonia Pretreatment–Cyanidation Leaching

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Abstract: The characteristics of ultrafine gold minerals in gold concentrate with a high copper content produced by a large gold mining company in Shandong Province were determined via chemical composition analysis, phase analysis, and mineral liberation analysis. The results showed that the concentrate contained 48.13 g/t gold, which was mainly in the form of native gold and electrum. Regarding the gold mineral particles, 57.65% were completely liberated and 35.75% were associated with chalcopyrite and pyrite. The remainder mainly comprised wrapped intergrowths. The cumulative distributions of native gold and electrum fractions with diameters of less than 75 μm were 82.55% and 90.15%, respectively. Enhanced Cu–S bulk flotation, and then, Cu–S separation from the raw material were proposed to effectively enrich the gold minerals and decrease the treatment throughput during the leaching operation. The optimized conditions yielded a concentrate with a high copper content (3.89% Cu and 545.62 g/t Au contents, and 83.15% Cu and 77.54% Au recoveries) and a concentrate with a high sulfur content (0.059% Cu and 15.03 g/t Au contents, and 83.15% Cu and 21.28% Au recoveries). The capacity of the subsequent leaching process was reduced by 25%. Ammonia pretreatment was introduced to decrease the adverse effect of copper on cyanidation leaching for the copper concentrate. Under the optimized leaching conditions, gold dissolution reached 99.76%, which was approximately 4% higher than that obtained via direct leaching. The NaCN consumption decreased over 10 kg/t. These results could serve as a valuable reference for the economic and green utilization of gold resources from concentrate with a high copper content.

Keywords: gold concentrate with high copper content; enhancing floatation separation; ammonia pretreatment; cyanidation leaching



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1. Introduction

Many gold deposits containing large amounts of copper minerals (>0.3%) and pyrite, in which the gold is mainly randomly distributed in the copper minerals and pyrite, have been found globally [1]. The flotation enrichment of gold-bearing copper minerals and pyrite, and the subsequent gold and silver extraction from the concentrate via roasting and pressure oxidation, are widely used in the gold-mining industry. This process involves conventional roasting treatment and is a mature and stable method for gold and silver extraction, but it is not suitable for small- and medium-scale enterprises because of high investment costs, energy consumption, and environmental damage. Metallurgical treatments have strict requirements for raw material quality; therefore, this method has low applicability for the treatment of complex ores. Pressurized oxidation is widely used globally and many research institutions in China have performed multiple laboratory and expanded tests, and various techniques have been developed. However, these are low-technology methods that

have low economic viability because of high investment and operating costs, and involve complex operations [2–4].

Cyanidation leaching is an important hydrometallurgical method and has been used for extracting precious metals (gold and silver) from original ores and gold-bearing concentrates since the end of the 19th century [5]. This method is still widely used to treat simple quartz-vein-type and pyritic gold ores because it has excellent selectivity and high dissolution for gold and silver in low-grade ores, and enables gold production with high efficiency and at low cost [6,7]. This process has other potential advantages; for example, the final product is high-quality electrolytic gold. Additionally, because this process produces leaching residue with a smaller particle size than that of pyrometallurgy, treatment for the comprehensive recovery of other valuable elements is easier.

Cyanide has high gold dissolution because of its strong complexation with gold, but impurities such as copper and arsenic can also react with cyanide, which adversely affects the cyanidation process [8]. The presence of copper minerals during the cyanidation leaching of copper-bearing gold ores has various disadvantages. Approximately 30 kg/t of NaCN is consumed when the copper mass fraction in the leaching feed is 1% [9]; therefore, it is expensive to isolate gold from gold ores and concentrates with high copper content via direct cyanidation. Additional processes such as acidification, volatilization and reneutralization; sulfidization, acidification, recycling and thickening; adsorption on activated carbon; or ion exchange and extraction are often required for recovering copper and cyanide from the leaching solution. These processes are complex and most involve chemical treatments; therefore, they have high energy consumption and low economic viability. In particular, the recovery of $\text{Fe}(\text{CN})_6^{4-}$ ions formed via the interactions among NaCN, thiocyanate, and iron ions is inefficient [10,11]. Gold leaching is much slower in air-saturated $\text{Cu}(\text{CN})_3^{2-}$ solutions than in free cyanide solutions [2,10]. Therefore, more efficient techniques for treating gold concentrates with high copper contents need to be developed.

Ammonia as a pH modifier, lixiviant and potential catalyst has strong potential for improving gold leaching efficiency at high copper content using cyanidation leaching [12] and non-cyanide leaching [13]. The main result of this is that ammonia can readily eliminate copper interference. Thus, in this study, a novel combined flotation–metallurgical technique was developed, and its feasibility in improving gold and copper recovery from a gold concentrate was evaluated. The concentrate was obtained from a large gold-mining company in Shandong Province, China. The characteristics of the minerals in the gold concentrate were determined via chemical composition analysis, phase analysis, and mineral liberation analysis (MLA). A gold-bearing copper concentrate with high copper and gold grades was enriched via effective Cu–S bulk flotation and subsequent separation from the raw material to decrease the treatment capacity during the leaching operation. Treatment with ammonia before gold leaching was used to decrease the adverse effects of copper in the flotation concentrate. Additionally, the effects of key operating parameters on the flotation–separation and gold-leaching performances were elucidated. The results of this study will facilitate the development of techniques for the effective industrial recovery of gold and copper, which will have economic and environmental benefits for mining companies.

2. Materials and Methods

2.1. Materials

The gold concentrate (raw material) was obtained from a gold-flotation plant in Shandong Province, China. The $-75\ \mu\text{m}$ fraction accounted for 60% of the mass of the raw material.

The chemical composition of the sample (standard deviation less than 0.10%) was determined via acid digestion, followed by inductively coupled plasma optical emission spectrometry and chemical titration. The gold grade was determined using a fire assay, and then, atomic absorption spectroscopy. The raw material contained 48.13 g/t Au,

57.05 g/t Ag, 0.32% Cu, and 38.61% S (Table 1). The copper was mainly present as primary and secondary copper sulfides (Table 2). The copper grades of the primary and secondary copper sulfides in the raw material were 0.29% and 0.03%, respectively. The copper distributions of the primary and secondary copper sulfides relative to total copper were 90.34% and 9.66%, respectively. X-ray diffraction was used to identify the mineralogical phases of the raw material (Figure 1). The results indicated that the main minerals in the sample, in order of abundance, were pyrite (FeS_2), quartz (SiO_2), feldspar (KAlSi_3O_8), muscovite ($\text{KAl}_2[\text{AlSi}_3\text{AlO}_{10}](\text{OH},\text{F})_2$), chalcopyrite (CuFeS_2), and galena (PbS).

Table 1. Chemical composition of the raw material.

Element	Au *	Ag *	Cu	Pb	Zn	S
Content, %	48.13	57.05	0.32	0.04	0.03	38.61
Element	Fe	SiO_2	Al_2O_3	CaO	MgO	K_2O
Content, %	35.40	16.04	4.12	0.57	0.32	1.41

* g/t.

Table 2. Copper-phase analysis of the raw material.

Copper Phase	Primary Copper Sulfides	Secondary Copper Sulfide	Total
Copper grade, %	0.29	0.03	0.32
Copper distributions, %	90.34	9.66	100.00

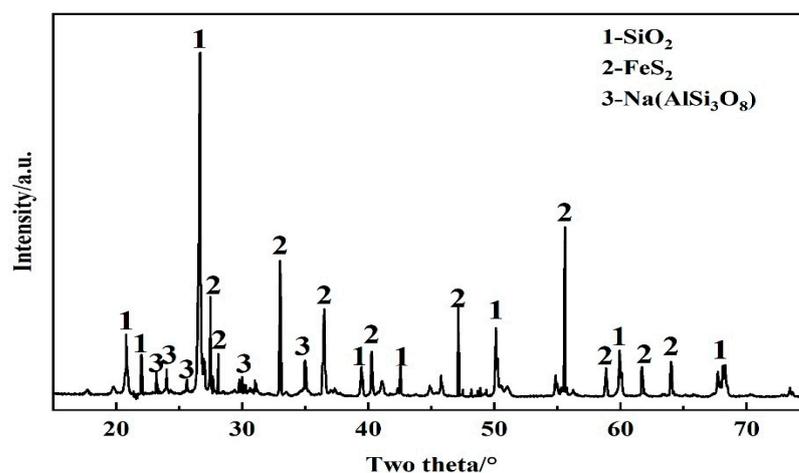


Figure 1. X-ray diffraction pattern of the raw material.

Analytical-grade NaCN was used in all the tests. Analytical-grade lime and sodium hydroxide (Aladdin Chemical Reagent Co., Ltd., Shanghai, China) were used to adjust the pH, and emulsified kerosene and sodium butyl xanthate (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used as collectors. Analytical-grade butyl xanthate and BK204 (main component: carbon alcohol) were used as a collector and frother, respectively. Distilled water was used in all flotation experiments and analytical tests.

2.2. Liberation Analysis of Minerals in Raw Material

Approximately 30,000 particles in the raw material were automatically observed and counted to representatively reflect the liberation characteristics of the target minerals, that is, gold minerals in the raw material, using an MLA instrument (MLA650, FEI Company, Hillsboro, OR, USA). The analytical results were used to identify an appropriate separation technique for the recovery of ultrafine gold and other valuable minerals from the raw material.

2.3. Flotation and Leaching Tests

Prepared samples of the raw material, of 500 g each, were wet-milled using a stirring mill. Flotation tests were performed using a series of different XFG flotation machines. The XFG flotation machines were equipped with flotation cells of different volumes for cleaning (350, 500, and 750 mL) and roughing (1.5 L).

Leaching tests were performed in 80 and 200 mL beakers. A total of 40 or 100 mL tap water was used for the preparation of leaching solutions at the required cyanide strengths (2.5–10.0 g/L). A 50 g sample of gold concentrate with a high sulfur content (HSGC) or a 20 g sample of gold concentrate with a high copper content (HCGC) was added to the beaker (33% pulp density, *w/w*), and then, agitated using an overhead stirrer at a constant stirring speed of 300 rpm. When needed, 25% NH₃ solution was added into the pulp. The tops of the beakers were kept covered during the experiments and the pulp pH was controlled at 11.5–12.5 by adding CaO. After the leaching period (24 or 48 h), the leaching residues were collected via filtration and dried. The residues were then digested in hot aqua regia, and gold, silver, and copper analyses were performed using atomic absorption spectroscopy (Perkin Elmer AAnalyst 400). The amounts of extracted metal were calculated from the amount of metal remaining in the residue. Samples were taken at predetermined intervals and centrifuged to obtain clear supernatants for gold and copper analyses. The concentration of free cyanide was monitored via titration with silver nitrate, with *p*-dimethylaminobenzalrhodanine (0.02% *w/w* in acetone) as the indicator.

3. Results and Discussion

3.1. Occurrence and Characteristics of Key Minerals in Raw Material

3.1.1. Microscopic Parageneses and Liberation Characteristics of Minerals

Figure 2 shows the microscopic parageneses relationship of the gold and other minerals. The gold minerals in the raw material consisted mainly of native gold and electrum. They were distributed in the raw material as individual particles, adjacent intergrowth particles, and wrapped intergrowth particles. Figure 2a,b show that native gold and electrum in the form of individual particles were distributed in the gangue base. Some incompletely liberated native gold and electrum particles were associated with chalcopyrite, pyrite, and quartz (Figure 2c,d). Incompletely liberated native gold and electrum particles were associated with pyrite, for example, as gold finely wrapped in pyrite (Figure 2e,f).

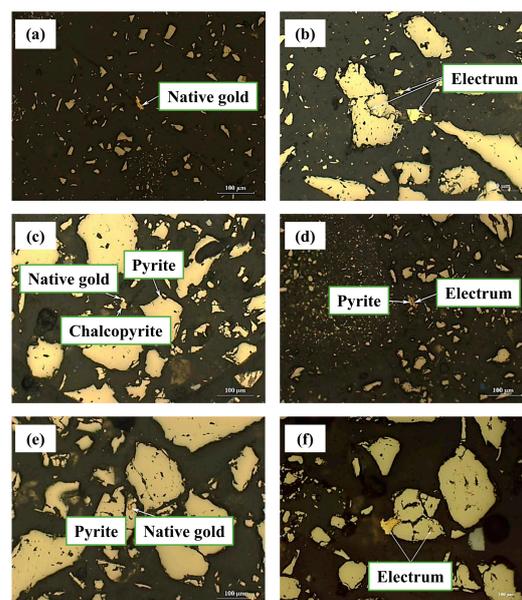


Figure 2. Microscopic parageneses of gold minerals in the raw material. (a) Individual gold minerals; (b–d) gold minerals associated with sulfides; (e,f) gold minerals wrapped in sulfides.

MLA of the raw material was used to determine the liberation characteristics, and the degrees and proportions of liberation of the gold minerals (Table 3). The liberation degree was defined as the relationship between the targeted mineral and others in a particle. The liberation proportion describes the proportion of targeted mineral particles with a certain liberation degree relative to the total observed particles that contain native gold or electrum.

Table 3. Liberation degree analysis of gold minerals in the raw material.

Liberation Degrees	Complete Liberation, %	Adjacent Intergrowth, %		Fine Inclusion, %		Total
		With Sulfides	With Gangue	In Sulfides	In Gangue	
Liberation proportions, %	57.65	35.75	0.69	5.86	0.05	100.00

The data in Table 3 show that the proportion of fully liberated particles in the raw material was 57.65% for gold minerals. The proportions of incompletely liberated gold minerals were 35.75% for adjacent intergrowth with sulfides, 5.86% for fine inclusion in sulfides, and 0.74% for intergrowth of gold and gangue. These results confirm that most of the gold minerals were present as ultrafine individual particles and particles formed via intergrowth with sulfides such as chalcopyrite and pyrite. The latter can be relatively easily collected via sulfide flotation, but the former require enhanced collection via flotation. Therefore, a combination of collectors (butyl xanthate, ammonium dibutyl dithiophosphate, and BK204) was used to facilitate gold mineral collection during flotation. However, attention should focus on wrapped-gold intergrowths because they hinder interactions between cyanide and gold particles, and this reduces the gold dissolution during subsequent leaching with cyanide.

3.1.2. Particle Size Distributions of Gold Minerals

According to the MLA analysis described in Section 3.1.1, the particle size distributions of native gold and electrum in the raw material were investigated (Table 4). The proportions of native gold in the −10, 10–20, 20–40, 40–74, 74–100, and +100 μm fractions were 11.79%, 30.31%, 34.22%, 6.23%, 5.38%, and 12.07%, respectively. The proportions of electrum in the −10, 10–20, 20–40, 40–74, and 74–100 μm fractions were 11.55%, 18.16%, 24.34%, 36.10%, and 9.85%, respectively. The cumulative proportions of native gold and electrum fractions with diameters of less than 75 μm were 82.55% and 90.15%, respectively. These results confirm that native gold and electrum mainly occur as fine and ultrafine particles in the raw material, which is unfavorable for gold recovery during flotation separation. The effective collection of ultrafine native gold is particularly challenging.

Table 4. Particle size distributions of native gold and electrum in the raw material.

Minerals	Distributions in the Size Fraction (%)						Total
	<10 μm	10–20 μm	20–40 μm	40–74 μm	74–100 μm	>100 μm	
Native gold	11.79	30.31	34.22	6.23	5.38	12.07	100.00
Electrum	11.55	18.16	24.34	36.10	9.85	/	100.00

Because of the occurrence and properties of gold minerals in the raw material, an effective Cu–S bulk flotation and Cu–S separation process with enhanced collection by combined collectors was used to achieve effective enrichment of gold minerals and decrease the treatment capacity during the leaching operation. An HCGC and an HSGC were obtained during flotation (Figure 3). The copper content of the HSGC was low and it had little effect on the cyanidation leaching of gold. The copper content of the HCGC was high; therefore, pretreatment before cyanidation was required. Ammonia treatment before gold leaching was therefore used to diminish the adverse effects of copper on cyanidation

leaching of the flotation concentrate. The effects of ammonium addition on the removal of copper before cyanidation leaching and on the cyanidation dissolution were investigated.

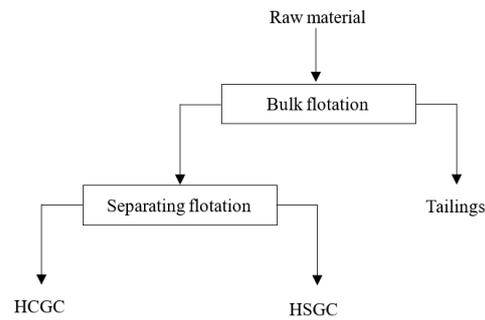


Figure 3. Flowsheet of flotation separation of the raw material (high sulfur content—HSGC, high copper content—HCGC).

3.2. Flotation Tests on the Raw Material

3.2.1. Effect of Grinding Fineness

The size and liberation of minerals in an ore are key factors affecting the separation and recovery performance of the ore. The grinding fineness is defined as the mass fraction (%) of $-38\ \mu\text{m}$ particles. The process shown in Figure 4 was used to investigate the effects of grinding fineness on flotation performance. The results (Figure 5) showed that the grinding fineness greatly affected the separation performance of the HCGC. Copper recovery from the HCGC increased when the grinding fineness was increased from 40% to 50%, whereas the other variables remained constant. When the grinding fineness was further increased, the copper grade and recovery of HCGC decreased. When the grinding fineness exceeded 73.7%, the Cu recovery clearly decreased. A grinding fineness of 73.7% was therefore favorable for both the copper grade and recovery from the concentrate.

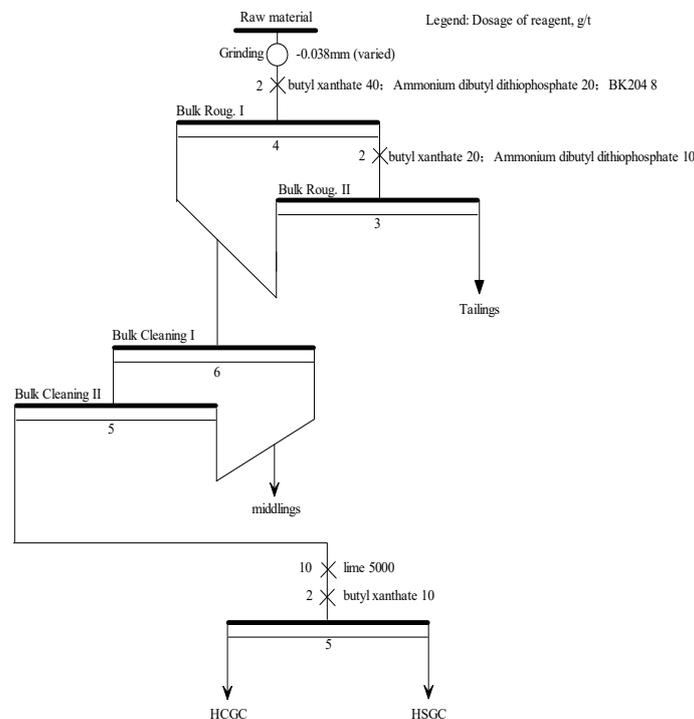


Figure 4. Flowsheet of flotation tests for investigating the effect of grinding fineness.

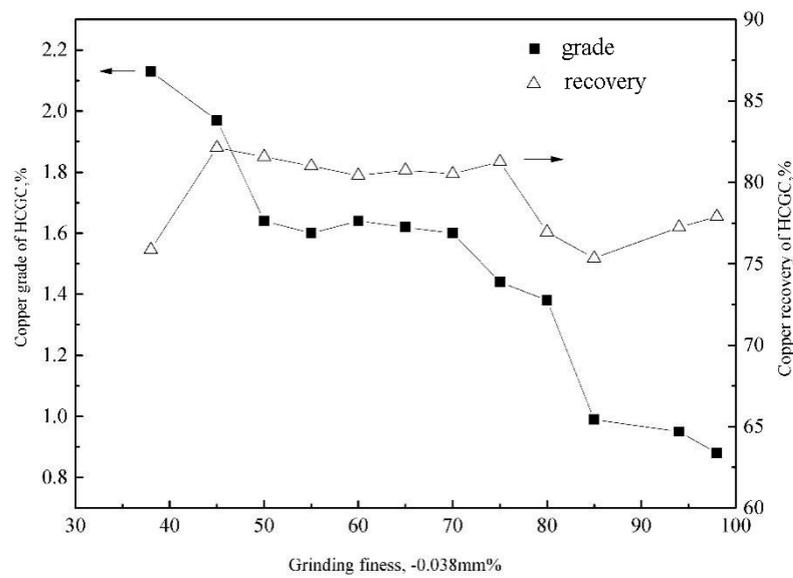


Figure 5. Effect of grinding fineness on flotation separation of the raw material (lime dosage: 4 kg/t).

3.2.2. Effect of Lime Dosage

Figure 6 shows the effect of lime dosage on the separation of copper minerals and pyrite. The copper grade increased and the recovery decreased when the lime dosage was increased from 3 to 5 kg/t. This occurred because the depression of pyrite and chalcopyrite–pyrite intergrowths increased with increasing lime dosage. When the lime dosage was increased to 6 kg/t, the copper grade greatly decreased; however, the copper recovery from HCGC slightly increased. These results indicate that the entrainment of gangue minerals increases at high lime dosages. This was confirmed by the observation that the foam concentrate became sticky at a lime dosage of 6 kg/t, and this decreased the flotation separation index.

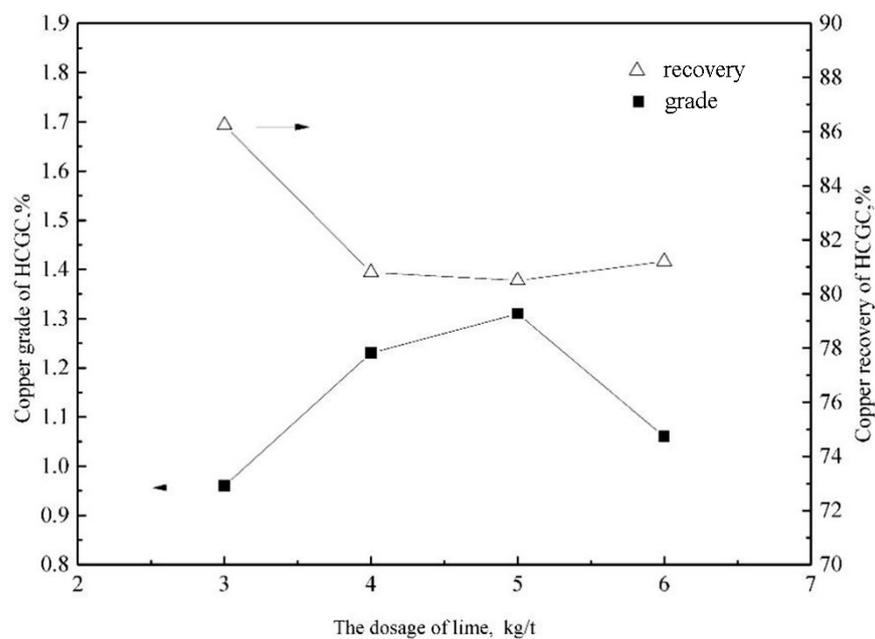


Figure 6. Effect of the lime dosage on flotation separation of the raw material.

Using the optimized operation conditions from the above open-circuit test, a closed-circuit test was carried out as shown in Figure 7. The results are shown in Table 5. Under

the optimum conditions, the flotation separation process produced a high-copper-grade concentrate with a composition of 3.89% Cu and 545.62 g/t Au and recoveries of 83.15% Cu and 77.54% Au, and a high-sulfur-grade concentrate with a composition of 0.059% Cu and 15.03 g/t Au and recoveries of 12.57% Cu and 21.28% Au. The total gold recovery from the copper and sulfur concentrates was 98.82%, and the amount of leaching material was reduced by 25%. In practice, this would decrease the cost of the subsequent leaching process.

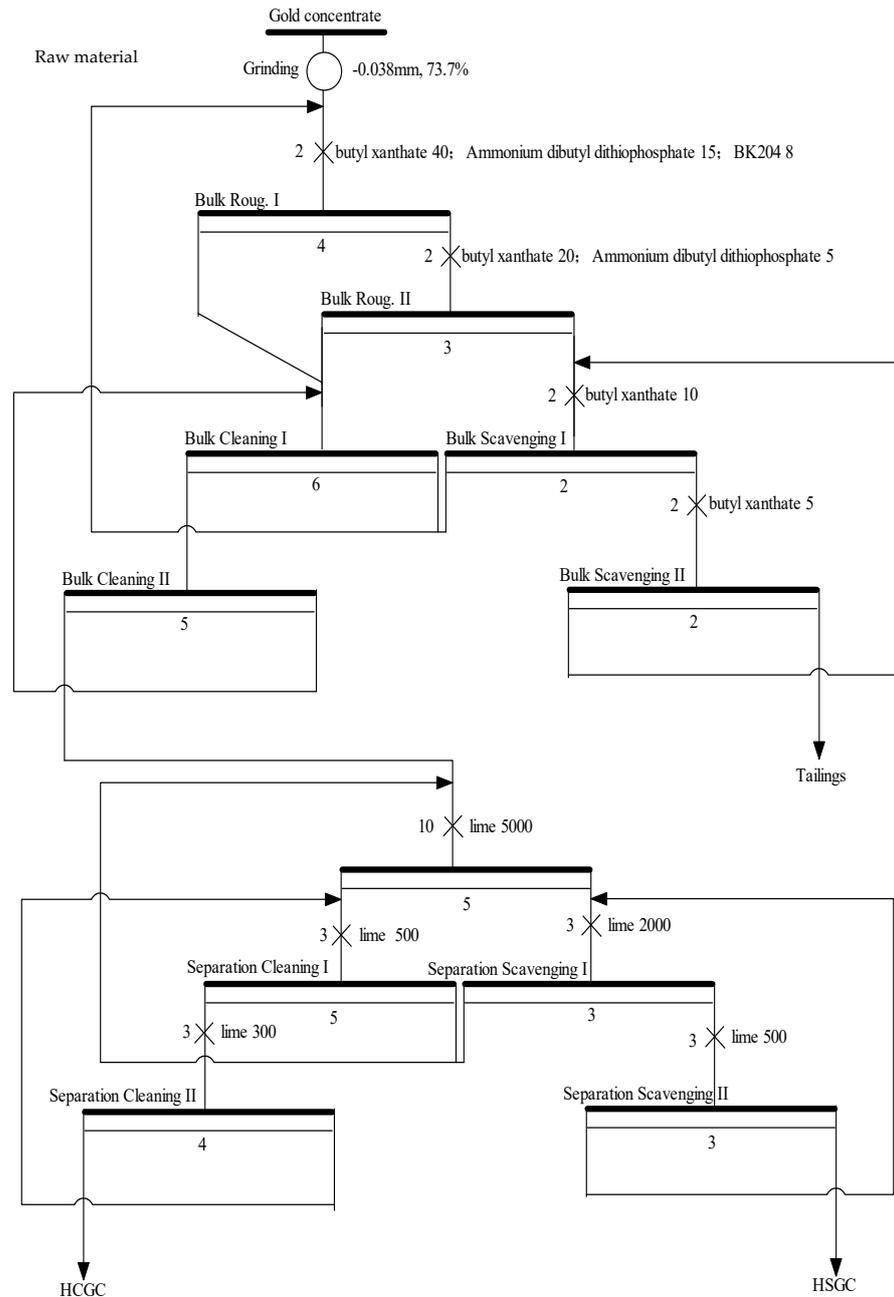


Figure 7. Flowsheet of the closed-cycle flotation test.

Table 5. Results of the closed-cycle flotation test.

Products	Yield, %	Grade			Recovery, %		
		Cu, %	Au, g/t	Ag, g/t	Cu	Au	Ag
HCGC	6.84	3.89	545.62	519.59	83.15	77.54	62.30
HSGC	68.16	0.059	15.03	28.00	12.57	21.28	33.45
Tailings	25.00	0.055	2.26	9.70	4.28	1.18	4.25
Feed	100.00	0.32	48.13	57.05	100.00	100.00	100.00

3.3. HCGC Leaching Tests

3.3.1. Theoretical Analysis of the Leaching Process

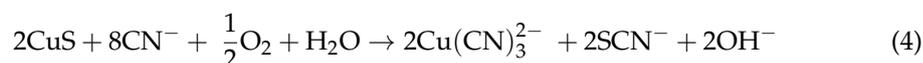
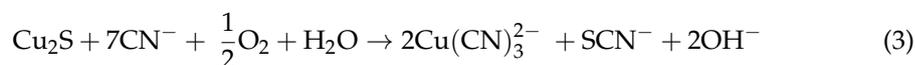
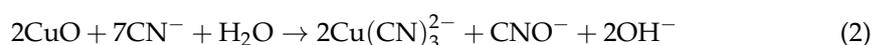
Cyanide can form strong complexes with gold and is the preferred reagent for leaching gold from low-grade ore. Although cyanide is a highly selective leaching reagent for gold, excessive amounts of cyanide are consumed during cyanidation leaching when several metals/minerals are present in the ore (e.g., copper ions and minerals) [14]. The presence of these soluble minerals can interfere with the cyanidation leaching processes and downstream gold production [10,15,16]. The harmful effects of copper are related to its excessive consumption of cyanide.

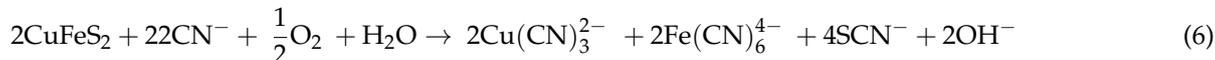
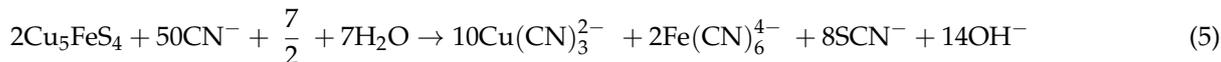
Most copper minerals are highly soluble in cyanide solutions. The copper dissolution and NaCN consumption results are shown in Table 6. Highly stable copper–cyanide species are formed via Equations (1)–(6), and these lead to poor gold extraction when the free cyanide content is insufficient [17,18]. According to Equation (6), the effect of chalcopyrite on the cyanidation of gold is much stronger than its effects on other copper minerals. Approximately 28 kg/t of NaCN is consumed when the proportion of active copper in the ore is 1%. NaCN consumption exceeds 51.5 kg/t for every 1% of copper because of the formation of thiocyanate via Equations (3)–(5) [19].

Table 6. Solubilities of copper minerals in 0.1% NaCN solutions [20].

Minerals	Formula	Copper Dissolution (%) ^a		NaCN Consumption (g)/Cu Dissolution (g)
		23 °C	45 °C	
Azurite	Cu ₃ (CO ₃) ₂ (OH) ₂	94.5	100.0	3.62
Malachite	Cu ₂ (OH) ₂ CO ₃	90.2	100.0	4.48
Chalcocite	Cu ₂ S	90.2	100.0	2.76
Covellite	CuS	-	-	5.15
Native Copper	Cu	90.0	100.0	-
Cuprite	Cu ₂ O	85.5	100.0	4.94
Bornite	Cu ₅ FeS ₄	70.0	100.0	5.13
Enargite	Cu ₃ AsS ₄	65.8	75.1	-
Tetrahedrite	(Cu,Fe,Ag,Zn) ₁₂ Sb ₄ S ₁₃	21.9	43.7	-
Chrysocolla	CuSiO ₃ ·nH ₂ O	11.8	15.7	-
Chalcopyrite	CuFeS ₂	5.6	8.2	2.79

^a Data from Hedley and Tabachnick (1958) [16]. Cyanide consumption is expressed as g of NaCN/g of contained copper. Data were generated via leaching at room temperature for 6 h.





Several alternative processes have been proposed for eliminating copper interference in the cyanidation leaching process to achieve satisfactory gold dissolutions. These methods include flotation; alternative additive leaching processes such as thiosulfate leaching; ammonia–cyanide leaching; pre-aeration; and the addition of lead nitrate [1]. Another proposed method that is used in practice is enhanced cyanidation leaching followed by the recovery of cyanide from wastewater (the sulfidization, acidification, recycling, and thickening process) [21].

3.3.2. Direct Cyanidation Leaching Tests

Direct one-stage cyanidation leaching tests on the copper concentrate were performed with 40% pulp, a lime dosage of 3.8 kg/t, a pH of 12.5, a leaching period of 72 h, mechanical stirring, and various NaCN dosages (20, 40, 60, 80, and 100 kg/t). Figure 8 shows that the gold and silver dissolutions greatly increased when the NaCN dosage was increased from 20 to 60 kg/t. The increases became negligible with further increases in the NaCN dosage. NaCN consumption increased in the investigated NaCN dosage range because of reactions between copper minerals and NaCN.

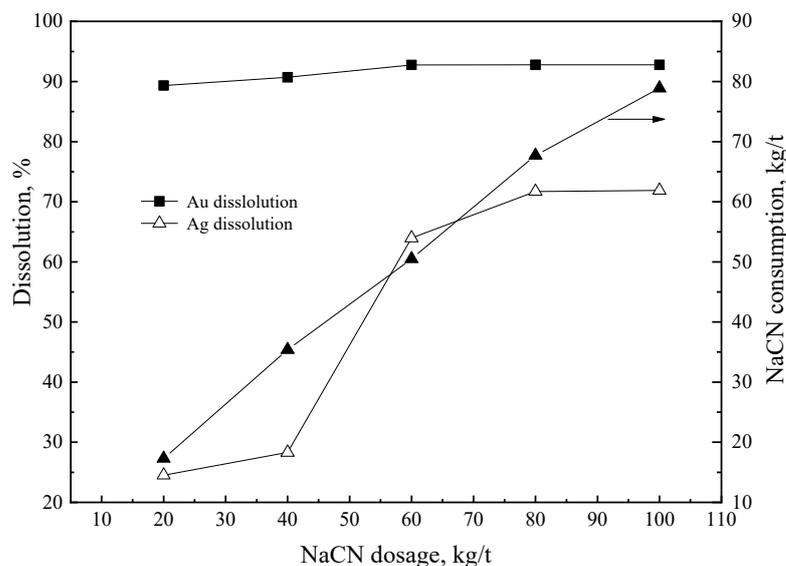


Figure 8. Effects of NaCN dosage on gold and silver dissolutions, and NaCN consumption (direct one-stage leaching process).

Direct two-stage cyanidation leaching tests were performed on a copper concentrate with 40% pulp, a lime dosage of 3.8 kg/t, pH of 12.5, and mechanical stirring. The leaching periods were 48 and 24 h for the first and second stages, respectively. The NaCN dosage was varied in the first stage, but held constant at 20.0 kg/t in the second-stage. Figure 9 shows the effect of the NaCN dosage in the first stage on the gold and silver dissolutions, and NaCN consumption. From Figure 9, the gold dissolution remained at around 91% for all NaCN dosages. By contrast, the silver dissolution increased as the NaCN dosage was increased from 20 to 40 kg/t, and then, remained constant with further increases in the NaCN dosage. Compared with the dissolutions achieved in the direct one-stage

cyanidation, the dissolutions of both gold and silver increased by approximately 4% in the two-stage cyanidation leaching. The NaCN consumption remained high.

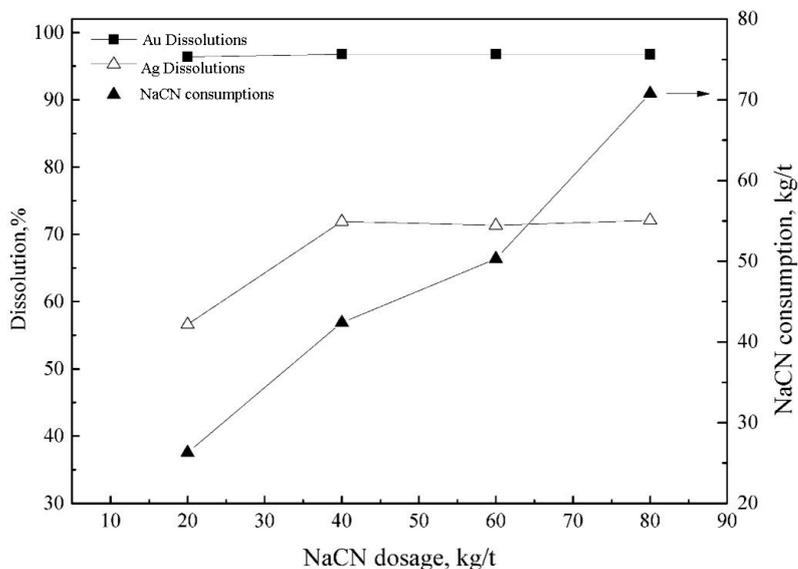


Figure 9. Effect of the NaCN dosage in the first stage on gold and silver dissolutions, and NaCN consumption (direct two-stage leaching process).

Two-stage cyanidation leaching of a copper concentrate was performed with a pulp density of 40%. A lime dosage of 3.8 kg/t was added to the pulp to adjust the pH to 12.5. A two-stage leaching process was used, and the NaCN dosage in the first stage was 40 kg/t. The leaching period in the first stage was 48 h. The filter cake was washed twice after filtration, and the pulp was adjusted again before the second stage of leaching. The dosage of NaCN in the second stage was 10, 20, 30, or 40 kg/t, and the leaching period was 24 h. The results are shown in Figure 10. As shown in Figure 10, the gold dissolution remained at around 96% for all NaCN dosages. By contrast, the silver dissolution increased as the NaCN dosage was increased from 10 to 20 kg/t, and then, remained constant with further increases in the NaCN dosage. These results suggest that satisfactory gold and silver dissolutions are achievable if only the NaCN dosage is not lower than 20 kg/t.

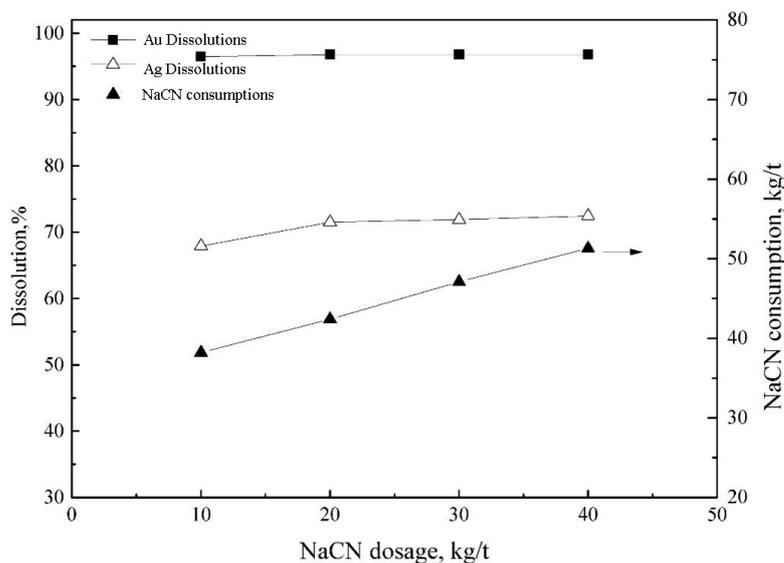


Figure 10. Effect of the NaCN dosage on gold and silver dissolutions, and NaCN consumption in the second stage (direct two-stage leaching process).

3.3.3. Pretreatment–Cyanidation Leaching Tests

A copper concentrate was pretreated by adding ammonium hydroxide solution for 6 h with a pulp density of 40%; lime (3.8 kg/t) was added to the pulp to adjust the pH to 12.5 for subsequent one-stage cyanide leaching, and the leaching periods were 48 h. Figure 11 shows the effect of the ammonium hydroxide dosage on the gold and silver dissolutions. The gold and silver dissolutions, respectively, reached 86.52% and 32.45% in the absence of ammonium hydroxide. It can be seen that both gold and silver increased as the ammonium hydroxide dosage increased from 0 to 40 kg/t. Upon further increasing the ammonium hydroxide dosage, the gold dissolution did not increase, while the Ag dissolution slightly increased. These results indicate that the additional ammonium hydroxide promotes the cyanidation leaching of gold and silver and its dosage of 40 kg/t is favorable for both gold and silver dissolutions.

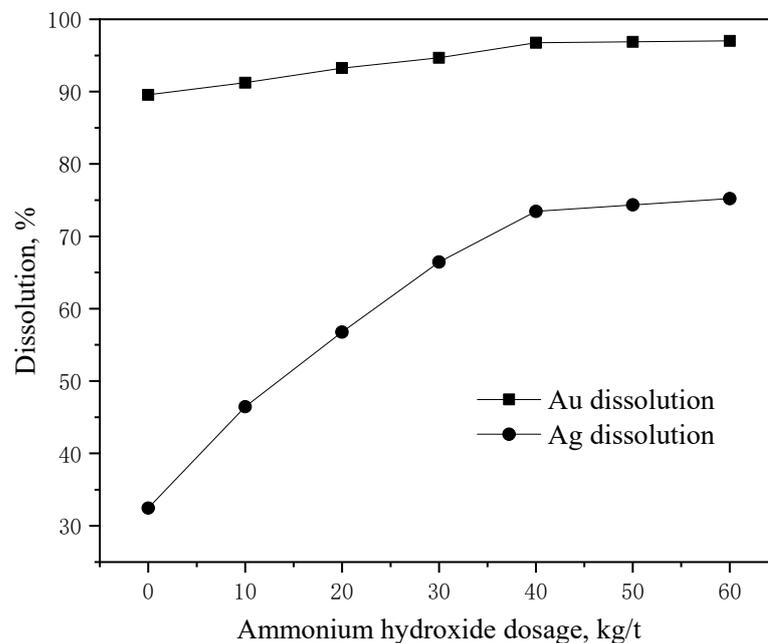


Figure 11. Effect of the NaCN dosage in the first stage on gold and silver dissolutions, and NaCN consumption in the first leaching stage (two-stage leaching process with ammonia pretreatment).

A copper concentrate was pretreated by adding ammonium hydroxide at a dosage of 40 kg/t to the leaching pulp under mechanical stirring. The pretreatment time was 6 h, the pulp density was 40%, and lime (3.8 kg/t) was added to the pulp to adjust the pH to 12.5 for subsequent two-stage cyanide leaching. The leaching periods were 48 and 24 h for the first and second stages, respectively. The added dosage of NaCN in the second-stage leaching remained at 20.0 kg/t. Figure 12 shows the effect of the NaCN dosage in the first stage on the gold and silver dissolutions, and NaCN consumption. As shown in Figure 12, the gold dissolution remained at around 97%–99% for all NaCN dosages. By contrast, the silver dissolution increased as the NaCN dosage was increased from 10 to 20 kg/t, and then, remained constant with further increases in the NaCN dosage. Compared with the dissolutions achieved in the cyanidation leaching without ammonia pretreatment, the gold and silver dissolutions increased by approximately 4% and 3%, respectively, and the NaCN consumption decreased by approximately 10–15 kg/t in the two-stage cyanidation leaching. The reduction in NaCN consumption resulted from the low initial concentration of NaCN. This implies that a much lower initial concentration was required with ammonia pretreatment than without pretreatment, when the gold and silver dissolutions reached maximum values. These results indicate that the ammonia pretreatment improved the gold and silver dissolutions, and effectively reduced NaCN consumption.

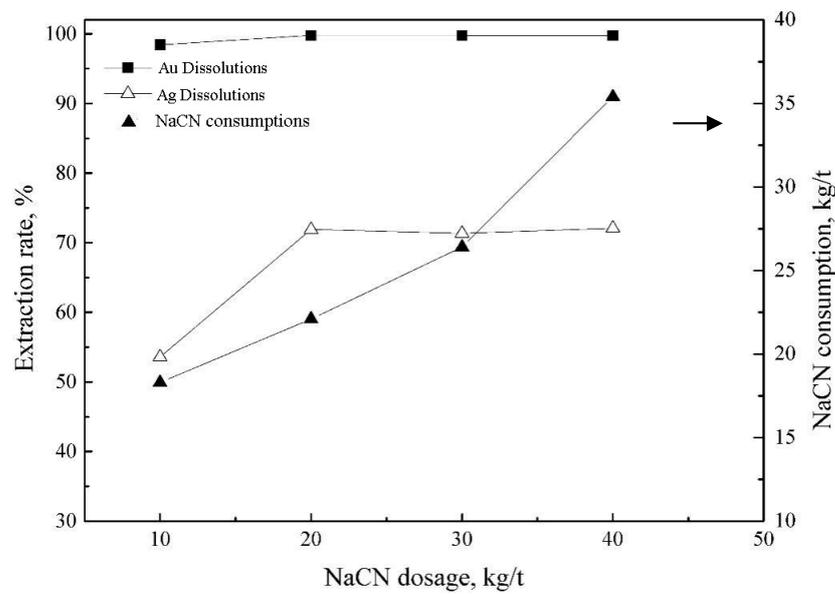


Figure 12. Effect of the NaCN dosage on gold and silver dissolutions, and NaCN consumption in the first leaching stage (two-stage leaching process with ammonia pretreatment).

Ammonium hydroxide (40 kg/t) was added to the pulp for pretreatment under mechanical stirring. The pretreatment period was 6 h and the pulp density was 40%. For leaching, the pulp density was 40% and lime (3.8 kg/t) was added to the pulp to adjust the pH to 12.5. A two-stage leaching process was used. For the first stage, the NaCN dosage was 40 kg/t and the leaching period was 48 h. The filter cake was washed twice after filtration, and the pulp pH was adjusted again before the second stage of leaching. The NaCN dosage for leaching in the second stage was 5, 10, 15, or 20 kg/t, and the leaching period was 24 h. The results are shown in Figure 13. As shown in Figure 13, the gold and silver dissolutions increased as the NaCN dosage was increased from 5 to 15 kg/t, and then, remained constant with further increases in the NaCN dosage. These results suggest that satisfactory gold and silver dissolutions are achievable if only the NaCN dosage is not lower than 15 kg/t.

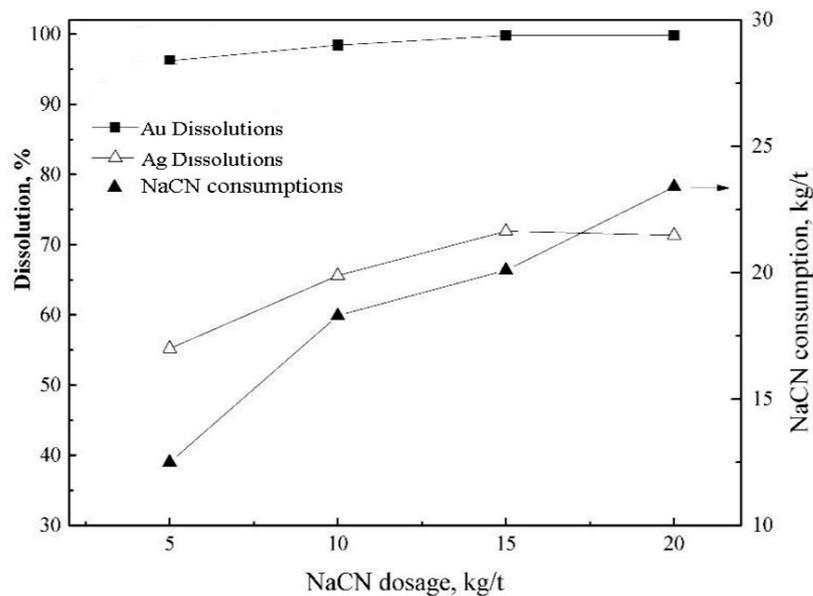


Figure 13. Effect of NaCN dosage on gold and silver dissolutions, and NaCN consumption in the second leaching stage (two-stage leaching process with ammonia pretreatment).

The effect of the two-stage leaching period on the gold and silver dissolutions was investigated with ammonia pretreatment. Ammonia (40 kg/t) was added to the pulp for pretreatment under mechanical stirring. The pretreatment period was 6 h, and the pulp density was 40%. Leaching was performed with a pulp density of 40%, and lime (3.8 kg/t) was added to the pulp to adjust the pH to 12.5. A two-stage leaching process was used, and the NaCN dosage in the first stage was 40 kg/t. The filter cake was washed twice after filtration, and the pulp pH was adjusted again before the second stage of leaching. The NaCN dosage for the second stage was 15 kg/t. The results are shown in Figure 14, where A–G are different combinations of the first- and second-stage leaching periods (24 h + 12 h, 24 h + 24 h, 32 h + 12 h, 32 h + 24 h, 40 h + 12 h, 40 h + 24 h, and 40 h + 36 h). The gold and silver dissolutions increased with increases in the leaching period. The maximum gold dissolution was reached at 56 h and the maximum silver dissolution at 64 h.

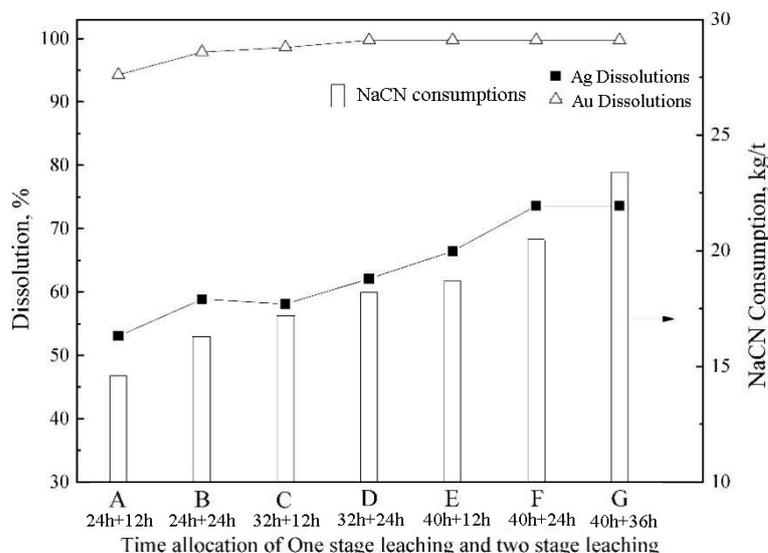


Figure 14. Effect of the leaching period on gold and silver dissolutions, and NaCN consumption.

The pH and free NH_3 concentration are important parameters for controlling the dissolution process. The species $\text{Cu}(\text{NH}_3)_4^{2+}$ is stable at pH 7.9–10.6 (optimum pH: 9.3) under the conditions used in cyanide leaching with ammonia pretreatment. Considering the dependence of sulfide leaching on the free NH_3 concentration, the pH should be controlled at 9.3–10.5 to maintain high concentrations of free NH_3 in solution and to prevent copper precipitation at pH > 10.5.

It has been reported that there is a critical free NH_3 concentration above which the copper in minerals begins to dissolve [10,13,14]. Muir et al. [9] reported that the dissolution of copper sulfides such as bornite and chalcocite in ammonia decreases because of copper oxide formation under highly alkaline conditions (which means that increasing the pH increases the region in which $\text{Cu}(\text{NH}_3)_4^{2+}$ is stable. They suggested adding ammonium salt to control the pH. Speciation calculations suggest that the critical concentration of NH_3 is 0.44 mol/L, which indicates that the dissolution of copper is not limited by the availability of NH_3 in the leaching process. In addition, previous studies have reported consistently low gold dissolution (less than 100 mmol/L) [13,16]. However, in ore leaching, much higher cyanide concentrations are needed because of the consumption of cyanide via its interactions with other metals, sulfide minerals, and formed thiocyanate (Equations (3) and (5)); the reduction of Cu^{2+} (released from Cu^{2+} sulfides); catalytic oxidation of cyanide by air in the presence of Cu^{2+} ; and the volatilization of HCN via aeration/acidification [7,13,19]. Accordingly, the effects of cyanide concentration (2.5–10.0 g/L NaCN) on the extraction of gold and silver were investigated.

The one-stage cyanidation leaching of a copper concentrate was performed with a pulp density of 40%, and we added lime at 3.8 kg/t to adjust the pulp pH to 12.5.

A one-stage leaching process was performed with a NaCN concentration of 2.5, 5.0, or 10.0 g/L. The leaching tests were performed under mechanical stirring. The silver extraction rates and NaCN consumption are shown in Figure 15 (cyanidation leaching process after pretreatment with 35 kg/t NH_3^-) and Figure 16 (direct cyanidation leaching process). The results indicate that the ammonia pretreatment increased the silver dissolution by approximately 4% under optimized conditions.

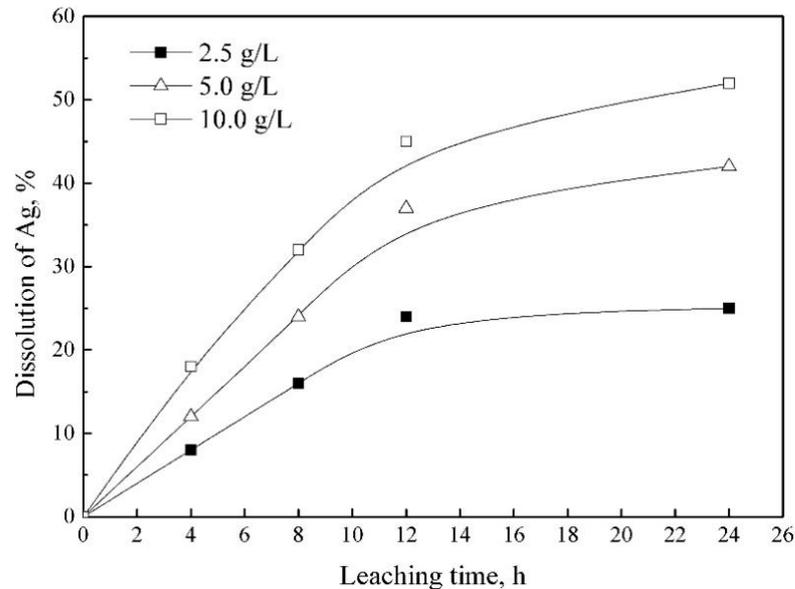


Figure 15. Effect of the NaCN concentration on silver dissolution from high-copper-bearing gold concentrate (cyanidation leaching process after pretreatment with 35 kg/t ammonium hydroxide).

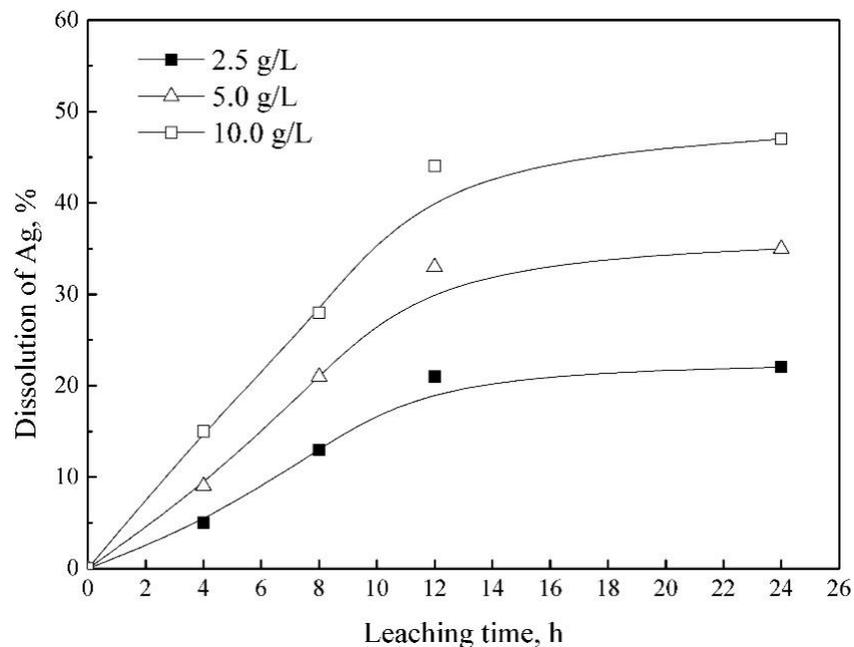


Figure 16. Effect of the NaCN concentration on silver dissolution from high-copper-bearing gold concentrate (direct cyanidation leaching process).

For the copper-containing gold concentrate, we used a flotation–pretreatment–two-stage leaching process. The obtained recoveries for gold and silver are shown in Table 7.

Table 7. Recoveries for flotation–pretreatment–two-stage leaching process.

Products	Yield, %	Flotation Recovery, %		Dissolution for Leaching Feed, %		Total Recovery for Raw Material, %	
		Au	Ag	Au	Ag	Au	Ag
HCGC	6.84	77.54	62.30	99.76	73.58	77.35	45.84
HSGC	68.16	21.28	33.45	96.80	80.92	20.60	27.07
Tailings	25.00	1.18	4.25	95.13	57.73	1.12	2.45
All in leach residue	-	-	-	-	-	0.93	24.64
Feed	100.00	100.00	100.00	-	-	100.00	100.00

4. Conclusions

The raw material contained 48.13 g/t gold, 0.32% copper, and 38.61% sulfur, with the gold mainly in the form of native gold (82.55%) and electrum (90.15%) with diameters less than 75 μm . Regarding the gold, 57.65% was free and 35.75% was associated with chalcopyrite and pyrite. The gangue minerals in the raw material were mainly carbonated quartz and calcite.

With a combination of collectors (butyl xanthate and ammonium dibutyl dithiophosphate) under the optimum conditions, a HCGC with a composition of 3.89% Cu and 545.62 g/t Au and recoveries of 83.15% Cu and 77.54% Au, and a HSGC with a composition of 0.059% Cu and 15.03 g/t Au and recoveries of 83.15% Cu and 21.28% Au, were obtained.

Regarding the HCGC from the floatation process, 99.76% dissolution of gold was achieved via treatment with ammonia before gold leaching. This value is higher than that of direct leaching by approximately 4%. Additionally, the NaCN consumption decreased over 10 kg/t. These results provide a valuable reference for the economic and environmental utilization of gold resources from concentrate with a high copper content.

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