



Article Extraction of Gold and Copper from Flotation Tailings Using Glycine-Ammonia Solutions in the Presence of Permanganate

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Abstract: This study presents the novel idea of a cyanide-free leaching method, i.e., glycine-ammonia leaching in the presence of permanganate, to treat a low-grade and copper-bearing gold tailing. Ammonia played a key role as a pH modifier, lixiviant and potential catalyst (as cupric ammine) in this study. Replacing ammonia with other pH modifiers (i.e., sodium hydroxide or lime) made the extractions infeasibly low (<30%). The increased additions of glycine (23–93 kg/t), ammonia (30–157 kg/t) and permanganate (5–20 kg/t) enhanced gold and copper extractions considerably. Increasing the solids content from 20 to 40% did not make any obvious changes to copper extraction. However, gold leaching kinetics was slightly better at lower solids content. It was indicated that the staged addition of permanganate was unnecessary under the leaching conditions. Recovery of gold by CIL was shown to be feasible, and it improved gold extraction by 15%, but no effect was observed for copper extraction. Percentages of 76.5% gold and 64.5% copper were extracted in 48 h at 20 g/L glycine, 10 kg/t permanganate, 20 g/L carbon, pH 10.5 and 30% solids. Higher extractions could be potentially achieved by further optimization, such as by increasing permanganate addition, extending leaching time and ultra-fine grinding.

Keywords: glycine; ammonia; non-cyanide; gold; copper; low-grade

1. Introduction

Due to its high efficiency and relatively low costs, cyanide has been used for gold extraction for more than one century [1]. It has been reported, however, that the free-milling gold ores that can be easily extracted by cyanide—representing about 18% of the world's gold deposits [2]—are nearly exhausted. The rest of these deposits are often contained in refractory gold ores that are associated with copper minerals [3]. According to the U.S. Geological Survey (USGS), about one-quarter of the undiscovered gold is contained in copper deposits [4]. However, the high copper content and the refractory nature of the ores have made gold extraction problematic and uneconomic. Particularly, high cyanide consumption has been identified due to the inevitable complexation between cyanide and copper (e.g., $Cu(CN)_4^{3-}$). For example, Muir [5] indicated that around 30 kg/t sodium cyanide was required for every 1% reactive copper presence. This has contributed to the abandonment of low-grade copper-bearing tailings and waste generated from gold processing plants. On the other hand, owing to the tremendously high toxicity of cyanide that brings high safety and health risks, the application of cyanide on an industrial scale is even banned in some countries, including Germany, Greece, etc. [6]. Therefore, to develop a suitable method for gold extraction from copper-bearing resources, a "greener" lixiviant is required [7].

Glycine (NH₂CH₂COOH, GlyH), the simplest amino acid, has been actively reported as a new lixiviant since 2013. Figure 1 summarizes the number of publications related to using glycine in the extractive metallurgy of metals. Glycine has been conventionally used as a



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). food additive for humans and animals [8]. It is not toxic nor volatile and can be recycled and mass-produced [8]. When dissolved in water, glycine can exist in three forms: $H_2NCH_2COO^-$ (Gly⁻, glycinate anion), $^+H_3NCH_2COO^-$ (H(Gly), zwitterion) and $^+H_3NCH_2COOH$ ($H_2(Gly)^+$, glycinium cation), as shown in Reaction (1), depending on different pHs [9,10]. In aqueous media, glycine ligand has been shown to have strong affinities with base and precious metals by complexation, especially chalcophile metals [8,10,11]. According to Oraby and Eksteen [11], glycine solution could selectively leach copper over gold as cupric glycinate (Cu(Gly)₂) from gold–copper concentrate at room temperature and with a pH of 10.5–11. However, as summarized in Figure 2, obvious gold dissolution could also be realized using gold-foils at a higher glycine concentration, pH and temperature, or if additional oxidant was added [12–14]. The typical reaction of gold leaching using glycine solution in an alkaline environment with ambient oxygen ingress can be written as the Reaction (2) [8]. Therefore, the ability to dissolve both copper and gold gives glycine the unique potential to treat copper-bearing gold resources.



Figure 1. Number of publications regarding glycine leaching systems used to treat different solid resources since 2013 (data for 2022 is up to March 2022).



Figure 2. Options to increase gold dissolution rate in alkaline glycine solutions (summarized from [12–14]).

$$\begin{array}{c} {}_{pKa=2.4} \\ H_{3}^{+}N \underbrace{O}_{OH} \underbrace{OH^{-}}_{H^{+}} \\ H_{3}^{+}N \underbrace{O}_{O} \underbrace{OH^{-}}_{H^{+}} \\ H_{2}N \underbrace{O}_{O} \\ Glycinium cation \\ Zwitterion \\ Zwitterion \\ Glycinate anion \\ \end{array}$$
(1)

 $2Au (s) + 4NH_2CH_2COO^- + 1/2O_2 (g) + H_2O \rightarrow 2Au(NH_2CH_2COO)_2^- + 2OH^-, \Delta G^{\circ} (25 \ ^{\circ}C) = 195.8 \ \text{KJ/mol}$ (2)

On the basis of Figure 2, recently, Oraby et al. [1] reported a novel system whereby glycine is used as a lixiviant and permanganate as an oxidant to leach gold from gold

ores. The study showed that 85.1% of gold was dissolved into leachate from different ores by leaching with glycine (1.5 kg/t) and potassium permanganate (3 kg/t) for ~ 48 h. The overall reaction during gold dissolution in glycine–permanganate solution is proposed in Reaction (3). This study proved the feasibility of using glycine and other less environmentally harmful oxidants to extract gold from gold ores.

 $3Au + 6NH_2CH_2COO^- + MnO_4^- + 2H_2O \rightarrow MnO_2 (s) + 3Au(NH_2CH_2COO)_2^- + 4OH^-, \Delta G^{\circ}(25 \ ^{\circ}C) = 229.9 \ kJ/mol$ (3)

However, the gold ore samples used in Oraby et al.'s study [1] were quartz-rich (35–100%) and had low sulfur (0.02–2.8%) and copper (0.001–0.01%) contents. Important sulfide-rich and copper-bearing gold resources have not been investigated. The presence of high sulfide and copper could cause significant differences in a gold sample's mineralogy and/or may lead to different leachabilities of metals in glycine solutions.

Therefore, this study, for the first time, investigated the application of a glycine—oxidant leaching system for the leaching of gold and copper from high-sulfide and copper-bearing flotation tailings generated from a gold mine. Potassium permanganate, as a common strong oxidant, was selected as the oxidant for the leaching system. Ammonia, known for its high efficiency in leaching copper [15], was introduced into the system for the first time to promote the extractions and also act as a pH modifier. Various parameters influencing the dissolution of gold and copper were studied. The present study aims to provide a non-cyanide and effective approach for the recovery of gold and the associated copper from low-grade gold sulfide tailings.

2. Materials and Methods

2.1. Materials

The sample used in this study was a sulfide cleaner flotation tailing, obtained from the flotation process of a gold mine. The sample contained 2.10 ppm gold, 1.11% copper and high levels (>7%) of iron, aluminum and sulfur, as shown in Table 1. Figure 3 shows the major compositions of the sample, indicating their high plagioclase, potassium feldspar and pyrite (FeS₂) contents. Although this is not shown in Figure 3 due to a detection limit, it is well known that copper was identified as chalcopyrite (CuFeS₂) and bornite (Cu₅FeS₄) according to the mine information. Figure 4 indicates the particle size distribution of the samples, with P80 being 29.1 μ m, and 96.1% of the particles were \leq 75 μ m.

_	In wt. %								In ppm					
-	Cu	Fe	Mg	Ca	Al	Mn	Со	Pb	S	Si	Au	Zn	Ni	As
Content	1.11	10.10	2.26	3.34	7.44	0.05	0.01	0.015	7.51	21.3	2.10	80	80	50

Table 1. Main elemental content of the flotation tailing samples used in present study.



Figure 3. Composition of the feed samples used in present study.



Figure 4. Particle size distribution of the feed samples used in present study.

2.2. Reagents

The glycine used in the study had \geq 99% purity (HPLC grade). Other chemicals, including potassium permanganate (KMnO₄), sodium hydroxide (NaOH), calcium hydroxide (Ca(OH)₂) and ammonia (25%), had a purity of analytical reagent grade. Activated carbon used in the carbon-in-leach tests was produced from coconut shell, supplied by Jacobi Carbons (PICAGOLD[®] G210AS). Deionized (DI) water was used to prepare solutions for leaching and instrumental analysis samples.

2.3. Experimental Procedures

In all the leaching experiments, 2.5 L plastic Winchester bottles with ~5 mm holes in the lids for air ingress were used as reactors. Unless specified, around 150 g of flotation tailing sample was used for each test with different solid contents, pH levels, and concentrations of glycine and ammonia. After preparing the leaching mixture, different amounts of potassium permanganate (as an oxidant) were added to the leaching bottle. As shown in Table 2, in some tests, permanganate ($KMnO_4$) was introduced in multiple stages, whilst in other tests, it was all added at the beginning. This was done to compare their effects when added to the metal extraction process. The bottle containing the leaching mixture was then transferred to a bottle roller for leaching at 100 rpm and at different temperatures for ~48 h. A 5 mL liquid sample was taken out at 2, 6, 24 and 48 h, respectively. After taking each sample, the measurements of the solution's pH and E_h (mV, vs. Ag/AgCl) values were carried out using a laboratory pH meter (90-FLMV Field Lab Analyser, TPS Pty Ltd., Brendale, Australia). The solution's pH level was controlled at a certain value by adding ammonia. In some tests, in order to investigate the effect of a pH modifier, lime (Ca(OH)₂) or sodium hydroxide was used instead of ammonia. When the leaching was finished, the leaching mixture was separated using a vacuum filter and DI water was used to wash the filter cake, which was then dried at 70 °C overnight.

Table 2. Proportion of permanganate added during the experiments with adding permanganate in multiple stages.

Time, h	0	2	6	24	48
Proportion of permanganate added, %	50	0	25	25	0

2.4. Analysis Method

Gold concentration in liquid samples was analyzed using inductively coupled plasmamass spectrometry (ICP-MS). The copper concentration in liquid samples was analyzed using ICP-optical emission spectrometry (ICP-OES). The analyses of liquid samples were outsourced to an independent institute, Bureau Veritas (Perth, Australia). The extraction of gold (E_{Au} , %) was calculated as presented in Equation (4):

$$E_{Au} = (m_t + m_{s1}) / (m_f + m_{s2} + m_r) \times 100\%$$
(4)

where m_t and m_f are the gold mass contained in leaching solution at time *t* and final time, respectively; m_{s1} and m_{s2} are the gold mass contained in the samples that were sampled out before time *t* and final time, respectively; m_r is the gold mass contained in the residue. The extraction (E_{Cur} %) of copper was calculated using Equation (5):

$$E_{Cu} = (m_t + m_{s1}) / m_{feed} \times 100\%$$
(5)

where m_t and m_{feed} are the copper mass contained in the leaching solution at time *t* and in the feed sample, respectively; m_{s1} is the copper mass contained in the samples that were sampled out before time t.

The content of gold in feed samples was analyzed using a conventional fire assay, followed by ICP-MS. The contents of other metals in feed samples were analyzed using X-ray fluorescence (XRF). The compositions of the feed samples were analyzed using Quantitative X-ray Diffraction (QXRD). The particle size distribution of the feed samples was analyzed with laser diffraction sizing technology using a Malvern Mastersizer 2000 instrument. The content of gold and copper in loaded carbon was determined via ashing and digestion in aqua regia, followed by ICP-MS/OES. All these analyses were conducted by Bureau Veritas. HSC Chemistry 10.0 (Reaction Equations module) was used to calculate the Gibbs free energy (ΔG°) of the reactions in this study.

3. Results and Discussion

3.1. Conventional Cyanidation

In theory, around 17.0-25.5 kg/t cyanide is consumed during its complexing with copper in the feed (as Cu(CN)₃²⁻ or Cu(CN)₂⁻). This implies that a significant amount of cyanide is needed for a satisfactory gold extraction. Exploratory cyanide leaching tests were first conducted to confirm cyanide consumption and served as a benchmark for the novel leaching system proposed in this study. This test was conducted with 52.5 kg/t cyanide, at pH 11, room temperature and with 40% solids, for 48 h. The results show that 88.6% gold and 79.1% copper were extracted into the solution whilst iron concentration was also found to be high at 1.53 g/L. Considering the iron-cyanide coordination number of 5–6 [8], around 10–12 kg/t cyanide would have been consumed. In comparison, another test with a lower cyanide addition of 6.25 kg/t indicates its infeasibility of gold leaching with only 29.8% of the gold extracted. Therefore, using conventional cyanidation to treat such complex gold resources bearing high copper and iron would result in high cyanide consumption which proves the need for a cyanide-free leaching system. In the below sections, the glycine-ammonia leaching system with permanganate used as an oxidant is proposed and investigated.

3.2. Effect of Variables

3.2.1. Effect of Glycine and Ammonia

To study the influence of glycine and ammonia on the leaching of gold and copper, several experiments were carried out with different glycine concentrations (10–40 g/L), 10 kg/t KMnO₄ (added in stages, Table 2), with a pH level of 10.5, with 30% solids and at a temperature of 30 °C each time. To maintain the same pH for each experiment, different amounts of ammonia were added, as shown in Table 3. However, as indicated in Figure 5a,b, the increase in glycine and ammonia concentration did not lead to a significant increase in gold extraction (copper extraction was still affected). It has been intensively reported that both ammonia and glycine can leach copper efficiently by complexation as copper-ammines $(Cu(NH_3)^{2+} \text{ or } Cu(NH_3)_4^{2+})$ and copper glycinate $(Cu(Gly)_2)$, respectively [10,15–18]. For

example, Khezri et al. [18] investigated the leaching of chalcopyrite in glycine solutions, whereby 95.1% of copper was extracted using a mechanically activated sample at 0.4 M glycine, 1 L/min oxygenation and with pH level of 10.5. Based on previous studies on chalcopyrite leaching [17,18], the examples of copper dissolution in this study may be represented as shown in Reactions (6) and (7), which explain the improvement of copper extraction with the rise in glycine and ammonia concentrations. The enhancement of gold extraction at 24 h may be attributed to the catalytic effect of cupric ammine and glycinate. The catalytic effect of Cu(NH₃)₄²⁺ has been well known in thiosulfate leaching of gold [7]. In comparison, Cu(Gly)₂ has been previously demonstrated as having a catalytic effect on gold leaching in glycine solution in the presence of peroxide [12]. In agreement with previous studies [8,19,20], the possible reactions for the catalytic effects were proposed, as shown in Reactions (8)–(10). As shown, Cu(NH₃)₄²⁺ and Cu(Gly)₂ may have played the roles of catalytic oxidants for gold leaching, which would lead to producing Cu(NH₃)²⁺ to be further oxidized back by the strong oxidant permanganate.

Table 3. Ammonia additions at different glycine concentrations (10 kg/t KMnO₄ (stg. addit.), with a pH level of 10.5, with 30% solids and at 30 $^{\circ}$ C).

Glycine Concentration, g/L	10	20	40
Glycine addition, kg/ (t feed)	23.3	46.7	93.3
Ammonia addition, kg NH ₃ / (t feed)	30.3	96.4	156.7





Figure 5. Cont.



Figure 5. Effect of (**a**,**b**) glycine concentration, (**c**,**d**) pH modifier, (**e**,**f**) pH, (**g**,**h**) solid content, (**i**,**j**) method of permanganate addition and (**k**,**l**) permanganate addition on the extraction of gold and copper.

Considering both metals' extraction and the addition of reagents, a glycine concentration of 20 g/L was used for the following tests, at which 96.4 kg/t ammonia was added to maintain the leaching pH of 10.5.

 $2CuFeS_2 + 8NH_3 + (34/3)MnO_4^- + (11/3)H_2O \rightarrow 2Cu(NH_3)_4^{2+} + Fe_2O_3 + 4SO_4^{2-} + (34/3)MnO_2 + (22/3)OH^-, \\ \Delta G^{\circ} (25 \ ^{\circ}C) = -3907.5 \ \text{KJ/mol} \tag{6}$

 $2CuFeS_2 + 4Gly^- + (34/3)MnO_4^- + (11/3)H_2O \rightarrow 2Cu(Gly)_2 + (34/3)MnO_2 + Fe_2O_3 + 4SO_4^{2-} + (22/3)OH^-, \Delta G^{\circ}(25^{\circ}C) = -3946.3 \text{ KJ/mol}$ (7)

$$Cu(NH_3)_4^{2+} + e^- \rightarrow Cu(NH_3)_2^+ + 2NH_3$$
 (8)

$$Cu(Gly)_2 + 2NH_4OH + e^- \rightarrow Cu(NH_3)_2^+ + 2Gly^- + 2H_2O$$
 (9)

 $6Cu(NH_3)_2^{+} + 2MnO_4^{-} + 4H_2O + 6Gly^{-} \rightarrow 3Cu(NH_3)_4^{2+} + 3Cu(Gly)_2 + 2MnO_2 + 8OH^{-}, \Delta G^{\circ} (25 \ ^{\circ}C) = -373.3 \ \text{KJ/mol}$ (10)

3.2.2. Effect of pH Modifier

According to previous studies [10,12], glycine leaching of copper and gold was preferably conducted at pH >10, at which glycinate anion is the predominate species. Therefore, a pH modifier was required for the leaching system. Ammonia added into the system was not only a lixiviant, but also worked as a pH modifier. To compare the effects of different pH modifiers, experiments were performed at 20 g/L glycine, 10 kg/t KMnO₄ (added in stages), with a pH level of 10.5, with 30% solids and at 30 °C. As shown in Figure 5c,d, ammonia allowed for significantly higher extractions of both gold (3–5 times higher) and copper (2-3 times higher) than the extractions from the tests using sodium hydroxide or lime. Figure 6 presents the E_h-pH diagrams of the glycine–(ammonia)–copper–water system. As shown, the addition of ammonia enlarged the solubility area of copper. The presence of copper as chalcopyrite (CuFeS₂) and bornite (Cu₅FeS₄) could lead the way for copper as what is preferable to complex with ammonia as $Cu(NH_3)_2^+$ at the experimental pH of 10.5 (Figure 6). With the increase in E_h from the addition of permanganate, Cu⁺ could be oxidized to Cu^{2+} in order to form cupric glycinate. The increased extraction of copper may have contributed to the higher gold extraction as a result of (1) the catalytic effect of cupric ammine and glycinate (Reaction (8)–(10)), and (2) the release of gold from being possibly locked in copper-bearing minerals (e.g., chalcopyrite).



Figure 6. Eh-pH diagrams of (**a**) glycine-ammonia–copper–water system and (**b**) glycine–copper– water system (with 270 mM glycine, 50 mM copper and at 25 °C (for **a**,**b**) and with 2.43 M ammonia (for **a**), made by Medusa-Hydra software (available at https://www.kth.se/che/medusa/ accessed on 6 February 2022).

3.2.3. Effect of pH

Like glycine concentration, the solution's pH level directly relates to the addition of ammonia and also affects the domination of glycine species in the solution (Reaction (1)), which will, accordingly, affect metals extraction. According to Reaction (1), glycinate anion, that is, to complex with metal cations, becomes predominant in the solution at a pH level of 9.8. A pH level of 9.5–10.5 was indicated as optimum in Oraby et al.'s study [1], which used glycine and permanganate to treat gold ores. Another study [10] showed the highest copper extraction from e-waste at a pH level of 10–10.5 in glycine solutions but the extraction dropped significantly once the pH level reached more than 10.5, possibly due to the formation of copper oxides (also shown in Figure 6). Therefore, in this study, two pH levels of 9.5 and 10.5 were investigated at 20 g/L glycine, 10 kg/t KMnO4 (stg. addit.), with 30% solids and at 30 °C. As revealed in Figure 5e,f, leaching at a pH level of 10.5 resulted in faster kinetics and higher extractions of both gold and copper. This is different from the case of using glycine solution to leach gold ores in the presence of permanganate, as previously reported by Oraby et al. [1]. In the study, pH 9.5 and 10.5 allowed for similar extraction levels of gold at room temperature without ammonia presence. As recorded in this present study, leaching at pH 9.5 had significantly lower ammonia (NH₃) addition compared to pH 10.5 (16.9 vs. 96.4 kg/t). It is, therefore, reasonable to suggest that higher ammonia concentration contributes to higher extractions of gold and copper. A pH level higher than 10.5 was not recommended, due to the relatively high ammonia requirement. For example, a trial test indicated an ammonia addition as high as 493.8 kg/t was necessary to maintain a pH level of 11.25 at 20 g/L glycine and with 30% solids. It should be noted that one can also increase the leaching pH by topping up with sodium hydroxide or lime, but this was excluded from the scope of the present study.

3.2.4. Effect of Solid Content

Solids contents ranging from 20% to 40% were selected to investigate their effect on metals extraction. Due to the change in the sample amount, glycine was added at a fixed amount of 46.7 kg/t (instead of fixed concentration), equivalent to that of 20 g/L glycine and with 30% solids in Table 3. Other conditions were kept at 10 kg/t KMnO_4 (stg. addit.), a pH level of 10.5 and at 30 °C. As shown in Figure 5g, lower solids of 20% had considerably faster kinetics of gold leaching in the initial 24 h, but the leaching remained almost unchanged afterwards. Not surprisingly, leaching at higher solids of 30-40% proceeded at a slower rate, as the solid content affects the diffusion of reactants and products [21]. It is noticeable that gold precipitated back to solution after 24 h at 40% solids. The higher copper concentration in leaching solution (resulted by higher solids content) may have contributed to the gold precipitation. Table 4 shows the copper concentration and extraction at different solids and sampling times. The final copper concentration reached about 4.7 g/L at 40% solids. As gold glycinate (log K_{ML2} = 18.0) is far less stable than gold cyanide ((log $K_{ML2} = 38.3)$ [8], the high copper concentration could have decomposed the gold–glycine complex and resulted in gold precipitation. The solids content in the investigated range (20–40%), however, did not considerably affect copper extraction (Figure 5h and Table 4).

Table 4. Copper concentration in leaching solutions and its extraction with different solid contents and at different sampling times.

Time	20% S	olids	30% S	olids	40% Solids		
Time	Conc., g/L	Extr., %	Conc., g/L	Extr., %	Conc., g/L	Extr., %	
2 h	0.54	19.4	0.91	19.1	1.22	16.8	
6 h	0.81	29.2	1.23	25.8	1.99	27.2	
24 h	1.66	59.2	2.55	52.7	4.09	55.0	
48 h	1.80	64.1	3.26	67.0	4.69	62.9	

3.2.5. Effect of the Method of Permanganate Addition

According to Oraby et al. [1], permanganate could quickly react with glycine to decompose the latter. Therefore, it was necessary to investigate the method of permanganate addition, i.e., it all being added at the start or throughout different stages. In both cases of addition, total permanganate amount was at 10 kg/t KMnO₄. Other conditions were kept at 20 g/L glycine, with 30% solids, with a pH level of 10.5 and at 30 °C. The results (Figure 5i,j) show that permanganate all introduced at one stage had faster kinetics of leaching for both gold and copper and with no obvious detrimental effects observed. To reach similar extraction levels of gold and copper (about 65% for both metals), permanganate all added at the start shortened the leaching time by 24 h, which is a significant increase in production efficiency. It is also noticeable that gold extraction remained unchanged at 2 h and 6 h for the staged addition test. As shown in Table 2, no permanganate was added within the first 6 h after the first addition. The permanganate added may have been starved in 2 h, leading to no further gold dissolution until the next addition. Therefore, the results indicate that it was not necessary to add permanganate in different stages.

3.2.6. Effect of Permanganate Addition

Permanganate addition was a major factor as it was a key oxidant in the system. It cannot be recycled for reuse, as it would reduce to manganese dioxide precipitates [1]. Hence, a low addition should be maintained for economic reasons. Several experiments were performed at 20 g/L glycine, with 30% solids, with a pH level of 10.5 and at 30 °C, with different permanganate amounts added (stg. addit., Table 2). As plotted in Figure 5k,l and as expected, the higher permanganate addition led to faster leaching kinetics and higher extractions of gold and copper. However, permanganate increasing from 10 to 20 kg/t did not increase the final copper extraction at 48 h. Given the economic value of gold, permanganate addition of 20 kg/t is recommended, at which gold and copper extractions reached 76.0% and 68.2%, respectively.

The reaction product of manganese dioxide remains in its residue. Theoretically, if 100% permanganate was reacted at the recommended addition, the manganese dioxide in its residue would be at about 1.1 wt. %. This is considered environmentally benign, with oral (rat) LD50 of manganese dioxide being >3478 mg/kg (versus 3000 mg/kg for sodium chloride).

3.2.7. Effect of Carbon-in-Leach (CIL)

The adsorption of gold by activated carbon is a conventional method of gold recovery in industries. Carbon-in-leach (CIL) refers to the addition of carbon during the leaching process. Various studies have shown the feasibility of this, as well as the investigation into the details of the adsorption of gold and copper glycinates onto carbon [1,22,23]. In the present study, experiments with and without 20 g/L CIL were compared to investigate the extraction and adsorption of metals. Other conditions were fixed at 20 g/L glycine, 10 kg/t KMnO₄ (stg. addit.), with a pH level of 10.5, with 30% solids and at 30 $^{\circ}$ C. As shown in Table 5, by adding 20 g/L carbon at 24 h, gold and copper adsorption of 98% and 35% was achieved, respectively. Importantly, gold extraction overall was elevated by about 15% with the addition of carbon, whilst the CIL did not show obvious effects on the copper extraction. It is possible that the CIL could allow gold to be adsorbed onto carbon in time (before it precipitates) and this removal of product could favor the leaching reactions (Reactions (2) and (3)). The rest of the copper can be recovered by ion exchange resin or sulfide precipitation, which has been previously reported in similar media [2,16,24,25]. The gold-barren solution can be used for the next cycle of leaching, utilizing the remaining glycine. The tests showed that it is feasible to recover gold via carbon adsorption and that the overall gold extraction increased in the presence of carbon.

CIL	Au Conc. in	Cu Conc. in	Extraction of Au	Extraction of Cu
	Solution, μg/L	Solution, mg/L	^{<i>a</i>} , %	^{<i>a</i>} , %
No	620	3260	66.6	67.0
Yes	11	2110	76.5	64.5

Table 5. Effect of carbon addition on metals extraction at 48 h (20 g/L glycine, 10 kg/t KMnO₄ (stg. addit.), with a pH level of 10.5, with 30% solids, at 30 °C; 20 g/L carbon added at 24 h for the CIL test).

^{*a*} The extracted metal refers to the metal extracted into solution for non-CIL test, and into both solution and carbon for CIL test.

4. Conclusions

The present study investigated the extraction of gold and copper from gold sulfide flotation tailings using a cyanide-free leaching method, i.e., glycine-ammonia solution in the presence of permanganate. The characterization indicated that the tailings sample contained 1.11% copper, 10.10% iron and 2.1 ppm gold. In the benchmark cyanidation tests, high contents of copper led to significantly high cyanide consumption, with 52.5 kg/t cyanide consumed for 88.6% gold and 79.1% for copper extractions.

During the non-cyanide leaching with glycine solution, it was found that using ammonia as a pH modifier, instead of sodium hydroxide or lime, enhanced gold (3–5 times higher) and copper (2–3 times higher) extractions significantly. Ammonia added into the system also acted as a lixiviant for copper and, potentially, as a catalyst for gold extraction. The glycine concentration (10–40 g/L), ammonia addition (30–157 kg/t) and pH levels (9.5–10.5) were directly affected by one another and the increase in both glycine and ammonia enhanced gold and copper extractions, as well as leaching kinetics. The staged addition of permanganate turned out to be unnecessary under the experimental conditions. Permanganate addition (5–20 kg/t) played a significant role in metals extraction, and higher addition made for faster and higher extractions. The highest extraction of gold was recorded at 76.0%, with the co-extraction of 68.2% for copper at 20 g/L glycine, 20 kg/t permanganate (staged addition), with a pH level of 10.5, with 30% solids and at 30 °C. Higher extractions could be achieved by ultra-fine grinding or extending leaching time. The recovery of gold via CIL enhanced gold extraction by 15%, but had no obvious effect on copper extraction.

This study provides an alternative and promising cyanide-free leaching process to traditional cyanidation for complex gold–copper ores, concentrates and tailings.

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