Investigation of glycine leaching for gold extraction from Witwatersrand gold mine tailings with permanganate pre-treatment

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Abstract

The Southern African region contains abundant gold tailing heaps that are an environmental concern due to dust pollution and chemical contamination of nearby water bodies. Nevertheless, these heaps contain gold with potential to be extracted for financial gain. In this study, the feasibility of extraction of gold from a Witwatersrand gold tailings using glycine was investigated using a two-level full factorial design. Effects of variables such as glycine concentration at levels of 0.5–1.5 M with a solid–liquid ratio of 50–200 g/L were investigated. Although the solid–liquid ratio used in this study was below the industrial norm, it provides a starting point for investigating the applicability of this technology. To enhance the gold extraction, potassium permanganate pretreatment and copper ion addition were adopted. The results revealed that 91.4% gold extraction was achieved after 24 h pre-treatment of the tailings using 2 g/L potassium permanganate followed by subsequent leaching using 1.5 M glycine at pH 12, with 50 g/L solid–liquid ratio and 2 g/L copper ions. Statistically, the solid–liquid ratio and potassium permanganate pre-treatment of the tailings were found to be significant at 95% confidence interval, whilst interactions of copper ions and glycine concentration were significant factors. The work demonstrates that potassium permanganate pre-treatment prior to glycine leaching of low-grade secondary gold resources, such as tailings, can be beneficial. Furthermore, the methodology developed in this work provides an opportunity for further investigation of the recovery of gold hosted in complex mineralogical matrices.

Keywords

tailings, glycine, gold, leaching, potassium permanganate, Cu ions

Introduction

Owing to strong complexation with gold and technical simplicity, cyanidation has been used as the conventional process in the extraction of gold (Fleming, 1992; Nicol et al., 1992). However, the process is reported to impose environmental, health, and safety challenges due to the high toxicity of cyanide (Hilson and Monhemius, 2006). Alternative reagents for gold leaching, such as thiourea, thiosulfate, halide, and thiocyanate that are more environmentally benign have been investigated over the past few decades and have been reported in several reviews (Aylmore, 2016; Gökelma et al., 2016; Hilson and Monhemius, 2006; Prasad et al., 1991). The thiosulfate process is the most developed alternative method for gold leaching, albeit having its technical challenges. These include the high reagent consumption, generation of polythionates, which readily absorb on anion-exchange resins and impair the recovery of gold from solution, complex chemistry, and sensitivity to process conditions like pH and Eh (Aylmore, 2005, 2016).

Glycine was proposed by Eksteen and Oraby (2014) as a potential alternative to the cyanidation process, and has attracted significant attention as a lixiviant in the leaching of metals from ores. It is a cheap, benign, and chemically stable lixiviant for gold dissolution. The process of using glycine is similar to the cyanidation concept, in which oxygen is used to oxidize gold from the metallic state to gold(I), as represented by Reaction 1 (Eksteen and Oraby, 2015; Oraby and Eksteen, 2015b):

$$4\mathrm{Au} + 4\mathrm{NH_2CH_2COOH} + 4\mathrm{NaOH} + \mathrm{O_2} \rightarrow 4\mathrm{Na[Au(NH_2CH_2COO)_2]} + 6\mathrm{H_2O} \quad [1]$$

Oxygen or oxidation is a key process step for the reaction, having significant implications for the kinetics, and therefore the design of the process. It has been noted that, in comparison with cyanide and operated under similar conditions, glycine extraction is significantly slower (Oraby et al., 2019). Slow kinetics prompted the consideration of heap leaching as a feasible process route for gold extraction using this process (Eksteen et al., 2018). To combat limitations that may relate to mass transfer of oxygen in the system, stronger oxidizing agents have been applied, resulting in significant improvements in extraction. Hydrogen peroxide and potassium permanganate are commonly investigated oxidants (Oraby et al., 2020; Perea and Restrepo, 2018). Reactions 2 (Eksteen and Oraby, 2015b) and 3 (Oraby et al., 2020) are proposed for hydrogen peroxide and potassium permanganate, respectively. Up to 85% gold extraction from an oxide ore within 48 h was reported using 2 g/L of potassium permanganate by Oraby et al. (2020). After extraction of the gold glycine complex from the ore, carbon adsorption can effectively recover the gold from the pregnant leach solution, as reported by Eksteen and Oraby (2014) and Tauetsile et al. (2018).

$$2\mathrm{Au} + 4\mathrm{NH_2CH_2COOH} + 2\mathrm{OH^-} + \mathrm{H_2O_2} \rightarrow 2\mathrm{Au(NH_2CH_2COO)_2^-} + 4\mathrm{H_2O} \qquad [2]$$

$$2\mathrm{Au} + 2\mathrm{MnO_4^{2-}} + 4(\mathrm{NH_2CH_2COOH})^- + \mathrm{O_2} \rightarrow 2\mathrm{Au(NH_2CH_2COO)_2}^- + 2\mathrm{MnO_2} + 2\mathrm{C_2O_2^{2-}} + 2\mathrm{NH_3} + 2\mathrm{OH^-} \qquad [3]$$

Given the reported high adsorption recovery, most research efforts have concentrated on exploring alternative approaches to enhance gold leaching within the glycine system. One proposed strategy involves the synergistic use of cyanide, as suggested by Oraby et al. (2017). However, the use of cyanide alongside glycine is an environmental trade-off. Elevated temperatures have been shown to improve extraction of gold, provided the supply of oxygen is sufficient, as shown by Altinkaya (2020) and Broeksma (2018). Various other ways of improving the leaching extent include increasing glycine concentration (Altinkaya et al., 2020) and the inclusion of $\mathrm{Cu^{2+}}$ ions as a catalyst for the leaching process (Eksteen and Oraby, 2015a). The body of work conducted with this method has focused on primary gold sources that have economic grades (Altinkaya et al., 2020; Eksteen et al., 2018; Oraby et al., 2020) compared with the tailings grades in the current study. Therefore, leaching of tailings with alternative lixiviants is certainly a potential area for development.

In this paper, historical tailings samples originating from the processing of Witwatersrand ore body were used as a case study for gold recovery using glycine. To investigate the feasibility of glycine as a lixiviant, parameters such as solid–liquid ratio and glycine concentration were investigated, together with use of permanganate to pre-oxidize gold and copper ions to provide a possible catalyst effect. This paper presents a base-case scenario for further investigation of the potential for the application of glycine leaching for tailings reprocessing.

Experimental

Materials and sample preparation

The sample used for the investigation was collected from the West Rand of the Witwatersrand mining district. Prior to sample characterization, the tailings was prepared to represent the bulk tailings sample. The sample was mixed using a shovel split using the cone-and-quartering technique. Two quarters were taken to a riffle splitter to further obtain a sample for rotary splitting. Four kilograms of samples from this process were taken to a rotary splitter to divide them into ten samples, each of 400 g. These samples were packed into different sample bags for characterization and leaching.

Chemicals and equipment

All experiments were conducted using solutions prepared from analytical-grade reagents and deionized water. The chemicals are listed in Table I with their respective purities. Gold and other elements in solutions were determined by Thermo ICap 6200 inductively coupled plasma optical emission mass spectrometry (ICP-MS) conducted at Stellenbosch University, Central Analysis Facility (CAF).

Sample characterization techniques

Material characterization included the determination of particle size analysis, bulk mineralogy, and qualitative gold imaging. Grain size analysis was carried out to determine the particle size distribution using a Micromeritics Saturn DigiSizer 5200 laser diffraction particle size analyzer. Fire assay was conducted on ten representative samples to determine the gold head grade of the tailings. Bulk mineralogy in the form of quantitative X-ray diffraction (QXRD) using a PANalytical Aeris diffractometer and X-ray fluorescence spectroscopy (XRF) using a PANalytical Axios wavelength-dispersive spectrometer was conducted for chemical analysis. A Zeiss Merlin field-emission gun scanning electron microscope (SEM) was used on a representative sample of the tailings to identify gold grains and their associations. The conditions used for imaging were 20 kV accelerating voltage, a beam current of 16 nA, with a working distance of 9 mm.

Experimental design

Towards understanding the leaching response of the tailings material, cyanidation tests were carried out as a form of diagnostic characterization at 2 kg/t NaCN, initial pH of 11, 50% solids content at ambient conditions. Three tests were conducted and the extent of gold extraction was evaluated. Three additional experimental runs were carried out using the glycine conditions used by Oraby et al. (2020). The tailings material was subsequently leached at 2 g/L glycine concentration (4.6 kg/t glycine), 30% solids content, pH 10.5, 2.0 g/L potassium permanganate, and ambient temperature.

In the main body of the study, a glycine concentration range of 0.5–0.5 M and $\mathrm{Cu^{2+}}$ ion range of 0–2 g/L with a solid–liquid ratio ranging from 50–200 g/L was used to understand their effects on gold leaching. Whilst the solid–liquid ratio is not reflective of an industrial process, which would have higher solid loading of up to 50% (m/v), the study can be used to inform further studies on higher solid–liquid ratios. Glycine concentrations were above stoichiometric requirements for the gold content in the solids to

Table I

Summary of chemicals used in the study

Reagent	Purity, %	Supplier
Glycine	97.0	Sigma Aldrich
Copper(II) sulfate pentahydrate	98.0	Science World
Sodium hydroxide	97.0	Kimix Chemical and Lab Supplies
Potassium permanganate	99.3	Kimix Chemical and Lab Supplies

cater for any free glycine loss by oxidation and with the assumption that free glycine would be recycled in an industrial setting. Cu^{2+} ions were introduced as copper sulfate into the leach system for those experiments investigating its possible catalytic effect. The amount of copper used ensured the glycine-to-gold stoichiometric ratio maintained an excess of glycine. Permanganate was used for pre-treating the tailings to oxidize the material and as an oxidant in leaching step to enhance gold extraction in all experimental runs. Potassium permanganate addition in leaching was used due to its strong oxidizing nature compared with O_2 or H_2O_2. Moreover, there is a claim that it produces manganese dioxide colloids that act as additional oxidants (Oraby et al., 2020; Pratesa et al., 2019).

Experimental procedure

A full factorial design was generated to investigate the effect of glycine concentration, solid–liquid ratio, potassium permanganate pre-treatment, and copper concentration at two levels, according to the high and low values of the ranges stated in the previous section. Table II shows the sixteen experiments conducted in the design of experiments (DOE).

All leaching experiments were conducted in a 2 L reactor open to atmosphere. The agitator was fitted with a two-radial-blade impeller and set at a constant speed of 300 rpm, which was sufficient to keep particles suspended. Although natural aeration was allowed, the use of an oxidant in all experiments was intended to further catalyse oxidation.

Two phases of experimentation were conducted. Phase 1 investigated the effect of potassium permanganate pre-treatment on gold extraction. The pre-treatment procedure summarized in Table III involved oxidizing the tailings (50% solid loading) in 2 g/L potassium permanganate solution for 24 h. The pre-treatment initial conditions were pH 5.10 ± 0.05 and Eh of 110 ± 3 mV, which is in the region for reduction of potassium permanganate (Pourbaix, 1974). In the subsequent leaching stage, alkaline glycine solution was added to the agitated slurry to make up the desired concentration of glycine and solid–liquid ratio required for leaching. Additional potassium permanganate was added to the leach slurry (2 g/L) and a few drops of NaOH were momentarily added to adjust the pH to 12.

Phase 2 involved a study of the effects of glycine concentration and solids loading on the extraction of gold without tailings pre-treatment. The experimental procedure involved the addition of the tailings sample and deionized water to the leaching vessel, followed by the addition of a specific volume of alkaline glycine solution to achieve the required initial glycine concentration. A few drops of 250 g/L permanganate solution was added to obtain an initial 2 g/L permanganate concentration in the leaching solution. This was followed by adjustment of the pH to 12 and commencement of leaching time. For those experimental runs where the effect of copper ions was investigated, a calculated amount of copper sulfate was added to achieve the desired 2 g/L Cu^{2+} initial concentration in the leach solution. The pH was maintained at 12 ± 0.2 during the experiment. Table IV summarizes the leaching conditions applied. Variables are presented within specified ranges, while constant parameters are listed with precise values.

Aliquot samples (10 mL) were collected at different time intervals and filtered using 45 µm filters. At the end of the experiment, the entire pulp was vacuum filtered, followed by washing with deionized water to remove entrained leaching solution. The residue was then left in the oven for 24 h at 50°C to dry. Fire assay was used to determine the gold in the dried residue while ICP-MS was used to analyse the filtrate solutions.

Results and discussion

Tailings characterization results

The particle size distribution of the tailings (Figure 1) showed that

Table III

Summary of pre-treatment conditions

Factor	Value
Pulp loading	50%
Potassium permanganate	2 g/L
pH	Uncontrolled

Table II

Full factorial design table

Test run	S/L ratio (g/L)	Pre-treatment time (h)	Initial glycine concentration (M)	Initial copper ions (g/L)
1	50	24	0.5	2
2	50	0	0.5	2
3	200	0	1.5	0
4	50	24	0.5	0
5	200	24	1.5	0
6	50	0	0.5	0
7	200	24	0.5	2
8	50	24	1.5	0
9	200	0	1.5	2
10	50	0	1.5	0
11	50	24	1.5	2
12	200	0	0.5	2
13	200	24	1.5	2
14	200	0	0.5	0
15	200	24	0.5	0
16	50	0	1.5	2

Table IV

Summary of leaching conditions

Factor	Value	
	1	2
Glycine concentration (mol/L)	0.5–1.5	0.5–1.5
Copper ion concentration (g/L)	0–2	0–2
Potassium permanganate (g/L)	2	2
Solid–liquid ratio (g/L)	50–200	50–200
pH	12	12
Temperature (°C)	Ambient	Ambient
Agitation (rpm)	300	300

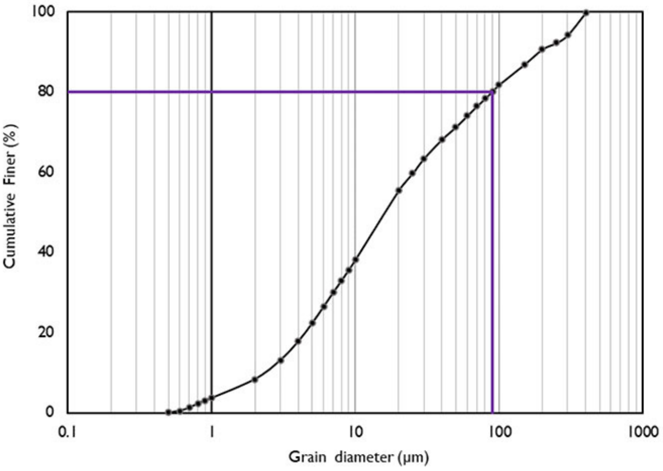


Figure 1—Tailings sample particle size distribution

80% of the sample had a diameter of less than 88 µm, which is close to the conventional value of 80% passing 75 µm used in the leaching of primary sources of gold (Stange, 1999). The gold content of the tailings (bulk head grade) was analysed to be 0.842 ± 0.04 g/t, which is similar to some reported Witwatersrand tailings grades of about 0.5 g/t (Janse van Rensburg, 2016).

XRD and chemical analysis of the tailings samples by XRF are presented in Figure 2 and Table V, respectively. As is typical of the Witwatersrand ores, quartz was the dominant mineral, with a grade of 77.8%. Figure 3 shows an example of SEM imaging conducted on the tailings to identify association and grain size. Discrete particles in the sample were verified to be associated with quartz, with the largest identified grain size being 0.71 µm in diameter.

Cyanidation experiments conducted as described above resulted in 24 h gold extraction of 65.7 ± 2.95%, indicating that the sample can be identified as a moderately refractory material, according to classification by Asamoah et al. (2014). Preliminary tests conducted using glycine leaching conditions applied by Oraby et al. (2020) on this tailings material yielded 15.7 ± 0.82% gold extraction, and therefore a need for alternative measures to increase gold extraction in this material using glycine. Pre-oxidation of the tailings in potassium permanganate prior to leaching was therefore considered in the presence of Cu ions.

Leaching experiments and results

Effect of solid–liquid ratio and reagent dosage

The effect of solid–liquid ratio on gold leaching using alkaline glycine is shown from Figure 4 to Figure 7. Figure 4 shows the effect of solid–liquid ratio on leaching at a concentration of 0.5 M

Table V

X-ray fluorescence analysis of the tailings sample

	%
SiO_2	81.16
TiO_2	0.25
Al_2O_3	9.69
Fe_2O_3	0.36
MnO	0.32
CaO	0.81
Na_2O	0.03
K_2O	1.15
P_2O_5	0.12
Cr_2O_3	0.08
SO_3	1.39
MgO	0.30
Loss on ignition (LOI)	4.24

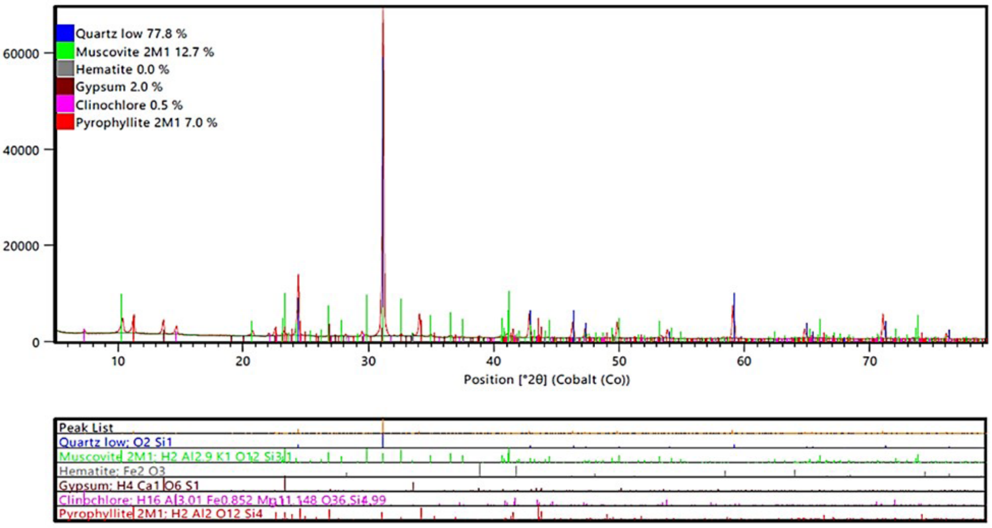
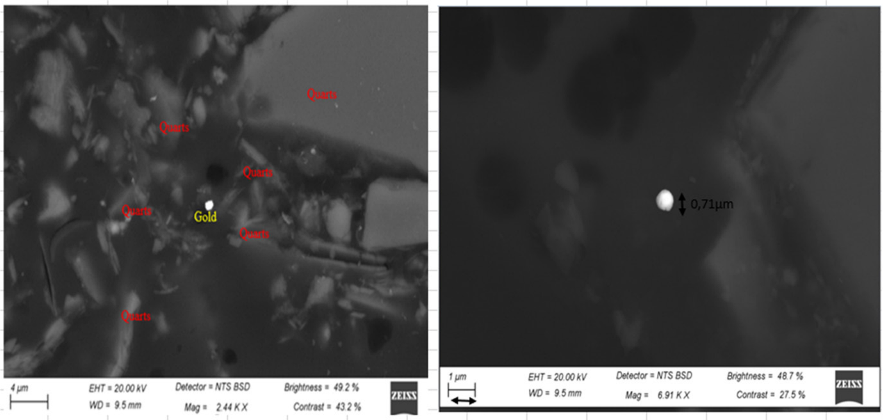
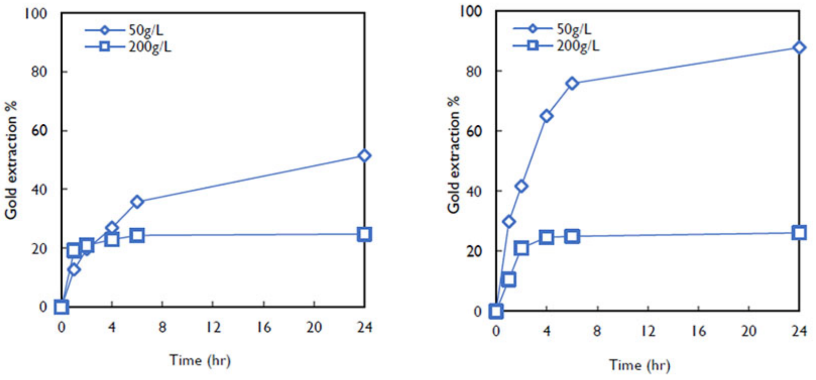


Figure 2—X-ray diffractogram of the tailings sample



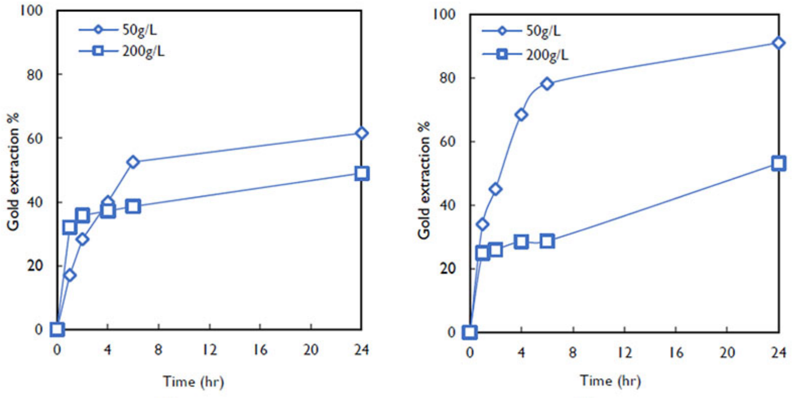
(a) (b)

Figure 3—Images produced by Zeiss Merlin field-emission gun electron microscope to show (a) association and (b) gold grain size in the tailings sample



(a) (b)

Figure 4—Effect of solid–liquid ratio on gold leaching at 0.5 M glycine without tailings pre-treatment at (a) 0 g/L copper ions (b) 2 g/L copper ions



(a) (b)

Figure 5—Effect of solid–liquid ratio on gold leaching at 0.5 M glycine after 24 h tailings pre-treatment in 2 g/L potassium permanganate at (a) 0 g/L copper ions (b) 2 g/L copper ions

glycine for a sample without pre-treatment at (a) 0 g/L copper ions, (b) 2 g/L copper ions. In the absence of copper ions, a maximum extraction of 51.5% was observed for the 50 g/L solid–liquid ratio compared with 24.8% for the 200 g/L solid–liquid ratio, representing an approximate 100% increase in gold extraction. In the presence of copper ions, however, 87.9% gold extraction was observed for 50 g/L compared with 26.2% for 200 g/L solid–liquid ratio in the presence of copper, which is an approximate 335% increase in extraction due to reduction of the solid–liquid ratio. A clear synergism is observed between reduction of solids ratio and presence of copper ions under the conditions of 0.5 M glycine and no pre-treatment. Figure 5 shows the effect of solid–liquid ratio at 0.5 M glycine after 24 h tailings pre-treatment in potassium permanganate at (a) 0 g/L copper ions, (b) 2 g/L copper ions. In the absence of copper, the leached gold amounted to 61.6% for 50 g/L compared with 49.0% for 200 g/L solid–liquid ratio. In the presence of copper ions, extraction of 90.9% was achieved for the 50 g/L solid–liquid ratio and 53.1% for the 200 g/L solid–liquid ratio. It is evidently seen that, in the presence of copper ions, the clear effect of copper ions is noted by improved leaching performance, with extraction being approximately 71% higher at the lower solid–liquid ratio.

At 1.5 M glycine, Figure 6 shows the effect of solid–liquid ratio without tailing pre-treatment for leaching at (a) 0 g/L copper

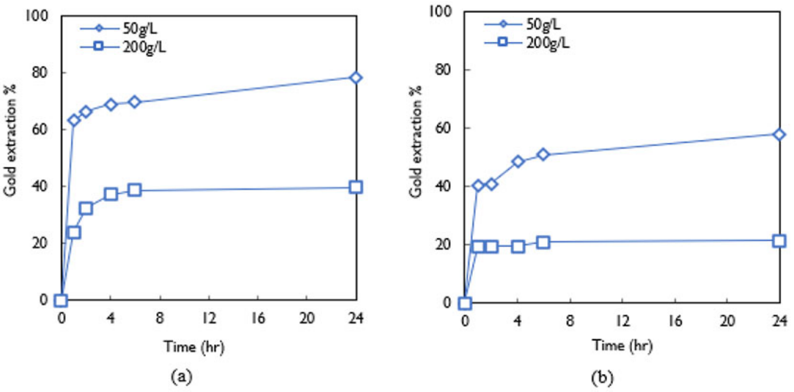


Figure 6—Effect of solid–liquid ratio on gold leaching at 1.5 M glycine without tailings pre-treatment at (a) 0 g/L copper ions (b) 2 g/L copper ions

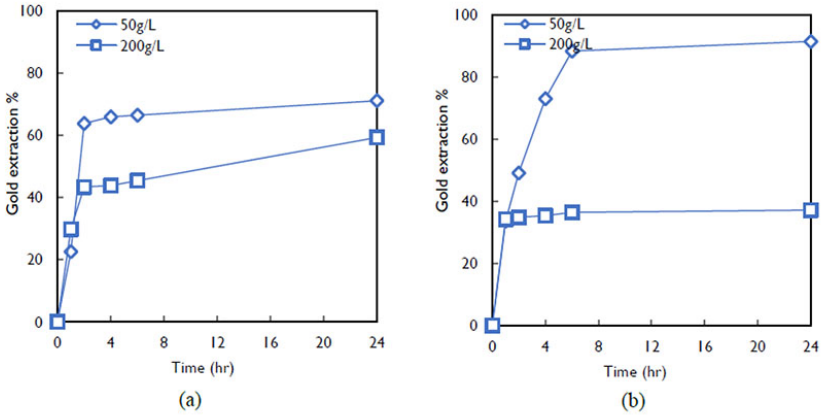


Figure 7—Effect of solid–liquid ratio on gold leaching at 1.5 M glycine after 24 h tailings pre-treatment in 2 g/L potassium permanganate at (a) 0 g/L copper ions (b) 2 g/L copper ions

ions (b) 2 g/L copper ions. In the absence of copper ions, gold extractions were 78.4% and 39.7% for 50 g/L and 200 g/L solids density, respectively. In the presence of copper, extractions were 57.8% and 21.5% for 50 g/L and 200 g/L pulp densities, respectively. Increasing solid–liquid ratio ultimately reduced the extraction of gold by about 100% for each of the solid–liquid ratios investigated.

Extraction results for tailings pre-treatment at 1.5 M glycine are shown in Figure 7, where the effect of solid–liquid ratio at (a) 0 g/L copper ions (b) 2 g/L copper ions is shown. Under these conditions, in the absence of copper ions, gold extractions were 71.0% and 59.2% for 50 g/L and 200 g/L solid–liquid ratios, respectively, which is less than 100% increase in extraction with reduced solid–liquid ratio. In the presence of copper, extractions were 91.4% and 37.1% for 50 g/L and 200 g/L solid–liquid ratios, respectively (248% increase in extraction with reduced solid–liquid ratio).

Previous work on the use of glycine for leaching of gold has shown that a reduction in solid–liquid ratio is directly proportional to an increase in extraction (Oraby et al., 2019). A 20% increase in gold extraction was observed when solid–liquid ratio was changed from 50% to 20% in the leaching of an oxide ore (100% passing 75 μm) using alkaline glycine at 50 g/L concentration. In general, most scholars have shown that decreasing the solid–liquid ratio in a leaching system, regardless of the lixiviant, will support high leaching of gold from the ore (Brittan and Plenge, 2015; Öncel et al., 2005; Tripathi et al., 2012). Notably, under such conditions, reagent dosage (kg/t of ore) increases with a reduction in the amount of solids present and positively affects the diffusion of reactants (glycine) and products (e.g., gold glycinate complex) from the surface. Increased concentration gradients ultimately drive faster mass transfer. For the chemical reaction step, reduced solid–liquid ratio leads to higher excess lixiviant, which ultimately increases the rate of chemical reaction.

The results presented in this study in Figures from 4 to 7 and those from replication of work of Oraby et al. (2020) clearly indicate that a significant increase in reagent dosage ($kg_{glycine}/t_{ore}$) is required to achieve high extraction efficiencies. Figure 8 shows a graph of gold extraction against glycine addition for leaching tests that had no additional treatments, i.e., no pre-treatment or addition of Cu^{2+} ions. In many instances in the literature, it is noted that an increase in glycine concentration results in an increase in gold leaching in the absence of copper ions (Eksteen and Oraby, 2015a; Oraby and Eksteen, 2015b; Oraby et al., 2019, 2020). Figure 8 shows that for

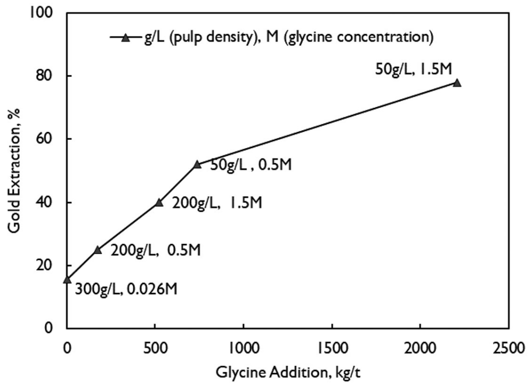


Figure 8—Gold extraction as a function of reagent dosage in the absence of pre-treatment and Cu^{2+} for glycine leaching

this tailings material, an increase in reagent concentration from 4.6 kg/t (300 g/L, 0.026 M) to 174 kg/t (200 g/L, 0.5 M) resulted in a minor increase in extraction (less than 10% points).

It should be noted that the extent of the effect of increasing glycine concentration on extraction is not replicated amongst different leaching materials. For example, Oraby et al. (2019) observed an 18.2% increase in gold dissolution by increasing glycine concentration from 3.75 g/L (0.05 M) to 15 g/L (0.20 M) when leaching an oxide ore in the absence of copper. A similar trend observed by Oraby et al. (2020) was an over 30% increase in extraction when glycine concentration was increased from 0.5 g/L to 2.0 g/L at pH 10.5 and 1 g/L permanganate concentration for an oxide ore.

Within the context of these results, it is also noted that whilst solid–liquid ratio reduction has a notable impact on the recovery, other operating conditions, such as the presence of Cu^{2+} ions and pre-treatment of the material by potassium permanganate prior to alkaline leaching in glycine and permanganate as oxidant, are investigated. The effects of these parameters are expanded further in the following sections.

Effect of permanganate pre-treatment

Figure 9 shows the extraction values for all tests conducted under all conditions tested on the tailings material. All leaching tests were conducted under alkaline conditions, as described in the methods, and included 2 g/L potassium permanganate added to the leach to act as an oxidant. Results indicate high extraction efficiencies under these conditions in comparison with conditions where the pre-treatment was not implemented, except for experiments done at 50 g/L solid–liquid, 1.5 M glycine in the absence of copper. The improved extraction values due to permanganate pretreatment are independent of the presence or absence of Cu^{2+} ions. Highest extraction of gold (91.4%) was observed at 50 g/L solid–liquid ratio and 1.5 M glycine, in the presence of copper ions after pre-oxidation. The second-highest extraction (90.9%) was also noted at 50 g/L solid–liquid ratio but 0.5 M glycine in the presence of copper ions after pre-treatment. These values are within 0.5% points of each other and considered to show negligible difference. What this indicates is that glycine reagent dosage does not control the extraction. Both results are in the presence of Cu^{2+}, however, suggesting that the combination of the presence of Cu species, the action of pre-oxidation, and high reagent dosage has a notable effect on gold extraction.

Investigations conducted to inform the processes occurring during permanganate pre-treatment were carried out using ultraviolet–visible spectroscopy (UV–Vis) of the pre-treatment solution during and after pretreatment to test for any gold species in solution and thereby determine whether any gold species were potentially pre-oxidized. Results in Figure 10(a) show UV-Vis spectra for solutions from 1 h to 24 h of pre-treatment. Figure 10(b) shows UV-Vis spectra for Au(I) and Au(II) chloride in deionized water, which were used as reference spectra to infer the presence of gold species in the pre-treatment solution. Distinct peaks at wavelengths of 280 nm for all solutions collected during

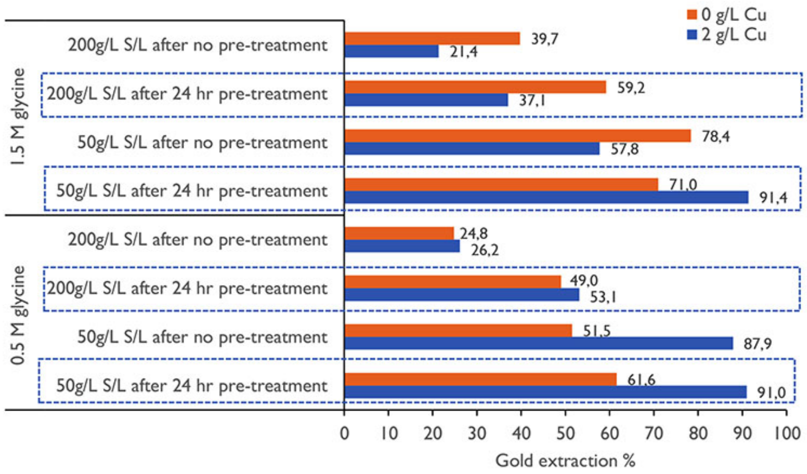
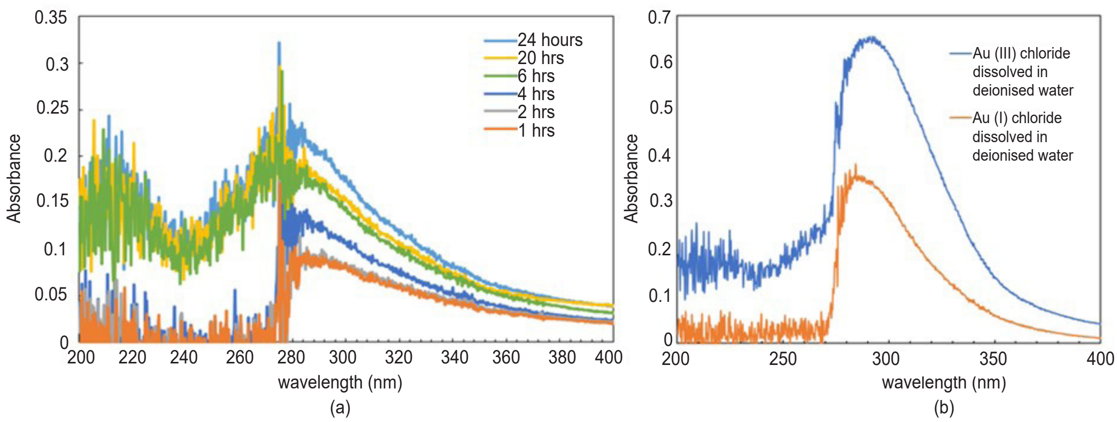


Figure 9—Variation of gold extraction with different conditions employed in this study



(a) (b)

Figure 10—Ultraviolet–visible spectra of (a) solutions from permanganate pre-treatment of tailings under 50% solid–liquid ratio and 2 g/L permanganate ions and (b) gold(I) and gold(III) chloride solutions at 1 g/L concentrations

pre-treatment are shown, with intensity increasing in relation to pre-treatment time, which is an indicator of increased oxidation of gold available to the oxidant. Using Figure 10(b) as a reference, the Au(I) chloride and Au(III) chloride peaks lie closer to the observed 280 nm wavelength, with Au(I) chloride being the closest. It can be inferred that the peak at the 280 nm wavelength may be associated with already-leached gold during pre-treatment in the form of Au(I); however, Au(III) cannot be excluded based on this analysis alone.

Elemental analysis of the pre-treatment solution was also conducted to verify the presence of gold in solution. In addition, other elements found in solution were used as signatures of the dissolution effect of the oxidant on the host minerals in the ore. Figure 11 shows these results, in the form of the degree of extraction of various elements in the tailings during pre-treatment. In Figure 11(a), the results for gold extraction show that up to 5% of gold was leached during this pre-treatment stage. It is possible that the gold may have been readily accessible to the highly oxidising pre-treatment solution, e.g., as the discrete micro-sized particles shown in Figure 3, and therefore readily oxidized into solution by the strong oxidising agent.

It was also hypothesized that pre-treatment may improve gold extraction using glycine by oxidation of grains of gangue minerals, resulting in increased lixiviant exposure to gold. It has been determined that up to 60% of gold is extractable by cyanide under typical cyanidation conditions. Whilst this is not severely refractory, it does indicate some gold to be non-accessible to conventional cyanidation. Pre-treatment/pre-leaching of ore is an ore-conditioning step that has been well documented in the literature for refractory ores using reagents such as sodium hydroxide (Mutimutema et al., 2022; Snyders et al., 2018). It has also been reported that during this step, oxidation of refractory species results in the release of associated gold. In the pre-treatment step applied in this study, the pH was recorded to be pH 5 and Eh of 110 mV, which is a region in which MnO_4^- is reduced to form MnO_2, which is a reduction process that might be responsible for dissolution of minerals during pre-treatment (Pourbaix, 1974). Figure 11(b)–(f) indicate the extraction of elements associated with the gangue mineralogy in the ore, such as Si from quartz and S from gypsum released during pre-oxidation. Elements such as P, Mg, Fe, and S, all contained in the gangue minerals, also increased with time, albeit the levels of extraction were low. Whilst potassium permanganate is a strong oxidising agent, it does not compare with the effect of pre-leaching agents such as caustic.

Effect of glycine and copper concentration

The role of Cu ions in glycine leaching systems is yet to be fully detailed. Previous work, however, has shown that there is a potential for increased extraction due to the presence of Cu ions. Eksteen and Oraby (2015) showed that copper ions accelerated the leaching process in tests that showed more gold extraction compared with leaching without copper at the same experimental conditions. The leaching conditions for that work were 0.1 M glycine, 0.1% H_2O_2, pH 11.9, and 4 mM Cu^{2+} (Eksteen and Oraby, 2015). By contrast, previous work by the same research group showed that increasing glycine concentration in the presence of copper ions led

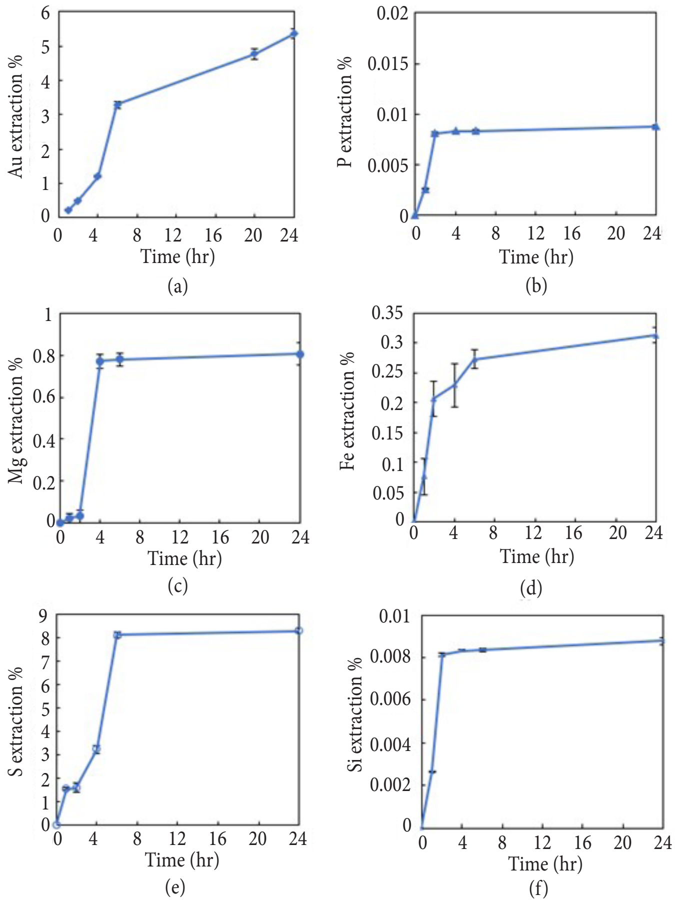


Figure 11—Dissolution of (a) gold, (b) iron, (c) magnesium, (d) silicon, (e) sulfur, and (f) phosphorus during 24 h pre-treatment of the tailings material in 2 g/L potassium permanganate

to reduced extraction of gold (Oraby and Eksteen, 2015a). Linear sweep voltammograms demonstrated that an overvoltage was required for the oxidation of gold in a gold–copper system with excess free glycine molecules compared with no free molecules. This demonstrated that the presence of free glycine has an impact on oxidation. The observation may suggest that the glycine–copper reaction may be strongly dependent on glycine concentration, in addition to yielding reaction products that inhibit gold oxidation.

In Figure 9, the results obtained support the observations of previous studies, despite the subject leached material being different. The presence of Cu ions in the leach is observed to consistently produce greater extraction at glycine concentrations of 0.5 M compared with concentrations of 1.5 M at the same solid–liquid ratio. The only exception is the condition where 50 g/L solid–liquid ratio was leached in 1.5 M glycine after permanganate pre-treatment. Lastly, more work is needed in the glycine context to explain this observed trend and the interaction between copper ions and glycine concentration during gold dissolution.

Repeatability

Figure 12 shows the results for three experiments done at 1.5 M glycine concentration, 50 g/L solid–liquid ratio at 2 g/L copper ions after 24 h pre-treatment of the tailings in 2 g/L potassium permanganate. The experiments were conducted to verify the repeatability of the tests using the conditions that yielded the highest extraction. The 24 h gold extraction was 88.76 ± 2.33%, which represented a coefficient of variation of 0.026, showing that the experiment runs could be repeated without great deviation.

Statistical analysis

Table VI shows the regression analysis used to estimate the relationship (model) between gold extraction and the investigated parameters (effects of pre-treatment, solid–liquid ratio, glycine concentration, and copper concentration) within the investigated ranges. The p-values represent the probability value, which denotes the significance of a factor, which depends on a threshold. The common threshold is 0.05, where $p < 0.05$ represents significance of the factor at 95% confidence interval. The regression coefficient signifies the amount by which a change in the value of the factor must be multiplied to give the corresponding average change in gold extraction for this model. The factor effects and pair interactions were investigated using 24 h leach recoveries as the output response using Design-Expert software.

The results showed that the glycine concentration and copper ion concentrations investigated were insignificant at a 95% confidence interval because the p-values were greater than 0.05. This was experimentally indicated, where the effect of glycine concentration and copper concentration did not have a definite relationship with gold extraction.

Table VI

Statistical summary of p-values and coefficients

Effect	p-value	Coefficient
Glycine concentration (G)	0.79	0.68
Solid–liquid ratio (S/L)	0.00	−17.50
Pre-treatment (PT)	0.02	7.86
Copper concentration (Cu)	0.46	1.90
(G)*S/L	0.96	−0.14
(G) * (PT)	0.96	−0.17
(G) * (Cu)	0.03	−6.99
(S/L) * (PT)	0.27	2.94
(S/L) *(Cu)	0.04	−6.28
(PT)*(Cu)	0.42	2.07

Solid–liquid ratio and pre-treatment were significant as individual variables and so were the glycine–copper and S/L–Cu interactions. The effect of pre-treatment was also found to be significant at a 95% confidence interval. Notably, pre-treatment as a process variable had a positive model coefficient of 7.89, which reflects that gold extraction increased as pre-treatment time increased. In contrast, solid–liquid ratio had a negative coefficient, which is also in agreement with the experimental observation that gold leaching decreased as solid–liquid ratio increased.

As mentioned above, Table VI also demonstrates that there are factor interactions that are significant in this DOE. The two significant interactions are glycine–copper and copper–S/L, as shown in Figure 13 and Figure 14. The glycine–copper interaction chart seen in Figure 13 is in agreement with the qualitative analysis discussed above. Figure 14 exhibits the copper ion–solid–liquid interaction, which statistically shows high gold extraction in the presence of copper at a low solid–liquid ratio, whereas its presence at high solid–liquid ratio results in lower extractions.

Conclusions

A glycine leaching study for a Witwatersrand ore tailings was conducted to investigate the effect of different process variables

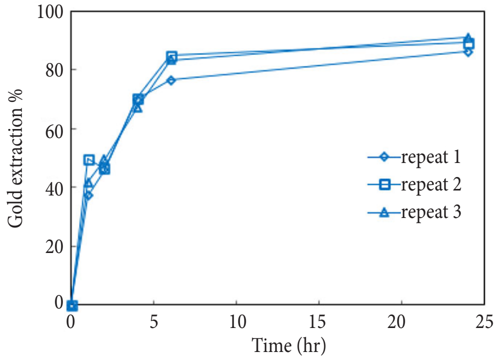


Figure 12—Gold leaching at 1.5 M glycine concentration, 50 g/L solid–liquid ratio at 2 g/L copper ions after 24 h pre-treatment of the tailings sample in 2 g/L potassium permanganate

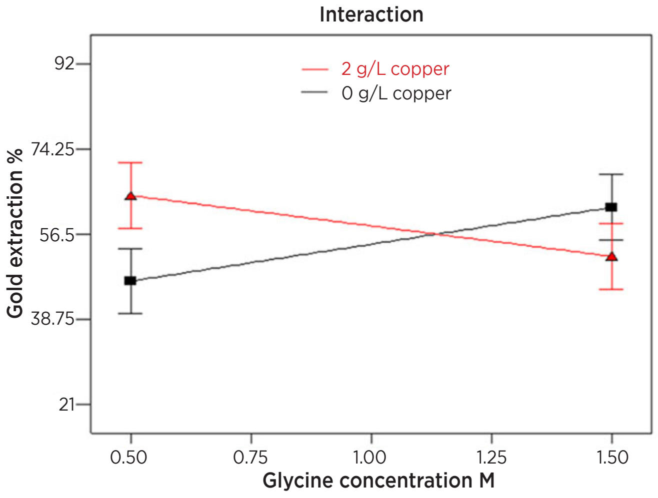


Figure 13—Interaction chart for glycine–copper concentration

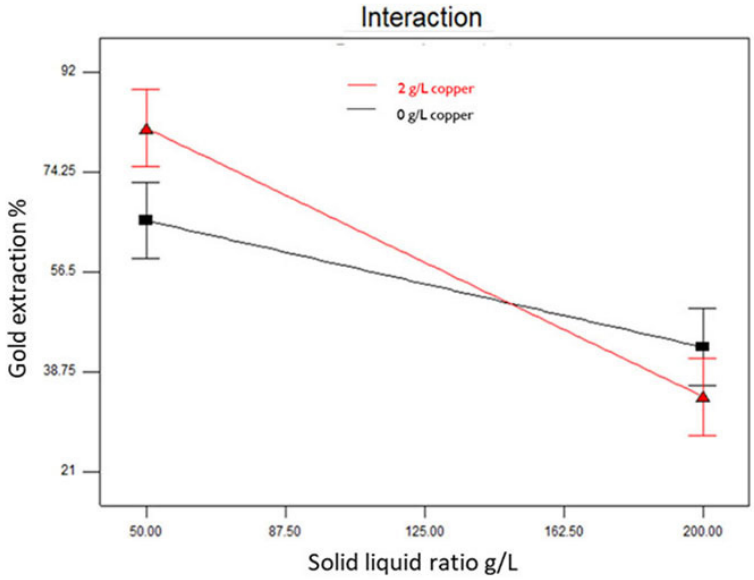


Figure 14—Interaction chart for S/L–copper concentration

on gold extraction. The work showed that high gold extraction was attainable with low solid–liquid ratio and permanganate pre-treatment. The results revealed that 91.4% gold was leached from the pre-oxidized tailings sample within 24 h by using 1.5 M glycine at pH 12 and solid–liquid ratio of 50 g/L with 2 g/L copper concentration. In addition, the absence of pre-treatment under the same conditions yielded 87.9 % gold extraction. Statistical analysis indicated that solid–liquid ratio and pre-treatment were significant variables for the gold leaching. Furthermore, results from the statistical analysis showed that there was significant interaction between glycine concentration and copper ions during the leaching process. High gold extraction was observed to accompany an increase in concentration in the absence of copper; however, the reverse was true and higher extraction accompanied low (0.5 M) glycine concentration and the presence of copper. Although the solid–liquid ratio was below that expected to be economic for a tailings operation, the study has shown that pre-treatment and copper catalysis of the leaching may be opportunities to explore conditions necessary for economic extraction at higher solid–liquid ratio and low glycine dosages. In conclusion, glycine can leach gold from the Witwatersrand gold ore tailings under alkaline conditions with permanganate pre-treatment, but the economic feasibility of such a process requires further study. A potential opportunity for improving extraction of gold from glycine in such a system may be analogous to the carbon-in-pulp (CIP) process applied in cyanidation, in which continuous extraction of the gold complex in-situ may drive the reaction forward.

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