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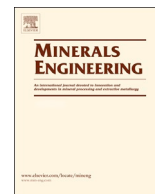
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Leaching and recovery of gold from ore in cyanide-free glycine media

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ABSTRACT

Glycine has recently gained plenty of attention in gold processing as an alternative lixiviant to cyanide due to its non-toxicity, efficiency in metal dissolution as well as selectivity for valuable metals. This paper presents an investigation on the combination of agitated reactor leaching and recovery of gold from mildly refractory ore in cyanide-free alkaline glycine media. Optimal leaching parameters for gold extraction were evaluated using response surface methodology. The investigated parameter range was 0.5–2 M for glycine concentration, pH of 10–12 and temperatures of 23–60 °C, with constant leaching time (24 h) and solid/liquid ratio (100 g/L). Based on the experimental series, a mathematical tool was built to predict gold extraction. It was found that, in the investigated parameter range, glycine concentration did not have a statistically significant effect on gold dissolution. Conversely, both temperature and pH had a substantial role in leaching kinetics. The statistical model suggested that the optimal conditions for gold dissolution were 1.25 M of glycine, pH = 12, and T = 60 °C, corresponding to a predicted 87% gold extraction. The experimental verification showed good reliability of the model with 90% extraction of gold achieved under the predicted optimum conditions. The addition of 15 g/L of activated carbon to the pregnant leach solution (PLS) could provide 100% recovery of gold from solution onto activated carbon, i.e. holistic recovery of 90%. Presence of carbon in leach (CIL) resulted in slightly lower (95%) gold uptake from solution and significantly decreased the holistic gold recovery down to 77%. Additionally, the applicability of direct electrochemical carbon-free recovery method, namely electrodeposition–redox replacement (EDRR), was investigated. In the synthetic solution, a gold recovery as high as 88% was achieved (1247 cycles). However, in the real PLS, only 35% of gold was recovered, which is attributed to different speciation of metals and presence of the other dissolved elements.

1. Introduction

Currently, cyanide is the predominant lixiviant used to extract gold due to its strong complexation with gold and the technical simplicity of the leaching process (Avraamides, 1982; Habashi, 1987; Marsden and House, 2006). However, the use of cyanide can bring challenges in terms of environmental, health and safety aspects (Aylmore, 2005; Laitos, 2012). Also, slow leaching kinetics and high cyanide consumption can be observed in the presence of refractory minerals, carbonaceous matter and copper-bearing gold ores, increasing the costs of processing (Adams, 2016; Hiskey and Atluri, 1988; Hilson and Monhemius, 2006). Nevertheless, alternative methods such as the use of thiosulfate, halides, thiourea, thiocyanate, and bisulfide have to be less toxic, inexpensive, and with high process efficiency in order to challenge

cyanide in industrial gold production (Marsden and House, 2006; Muir and Aylmore, 2004; Nicol et al., 1987; Senanayake, 2004).

At the moment, thiosulfate leaching is the one of the most developed and the only implemented in industry alternative method to cyanidation due to the low toxicity and high efficiency in treatment of preg-robbing gold ore (Breuer and Jeffrey, 2000; Marsden and House, 2006; Muir and Aylmore, 2005). Nevertheless, it still has drawbacks such as complexity of the process, high reagent consumption, sensitivity to the pH and redox conditions, difficult process control, and restricted recyclability (Gos et al., 2001; Hilson and Monhemius, 2006; Muir and Aylmore, 2004). Glycine leaching might offer advantages over thiosulfate, with process simplicity, stability over wide Eh-pH range, easy recyclability and reusability, and non-toxicity (Eksteen and Oraby, 2015; Oraby and Eksteen, 2015a; Tanda et al., 2017).

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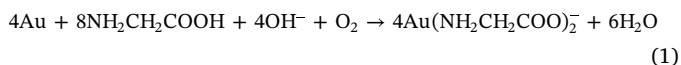
Table 1
Stability constants for gold complexes at 25 °C (Aylmore, 2016).

Ligand	Formula	log β_2	pH range
Cyanide	Au(CN) ₂ ⁻	38.3	> 9
Glycine	Au(H ₂ NCH ₂ COO) ₂ ⁻	18.0	> 9
Thiocyanate	Au(SCN) ₂ ⁻	17.1	< 3
Sulfite	Au(SO ₃) ₂ ³⁻	15.4	> 4
Bromide	AuBr ₂ ⁻	12.0	5–8
Chloride	AuCl ₂ ⁻	9.1	< 3

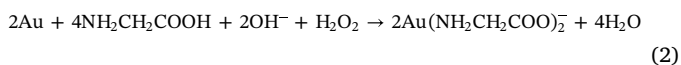
In aqueous solutions, glycine has three different forms with pK_a values at 2.35 and 9.78: the cationic glycinium ion ⁺H₃NCH₂COOH in acidic solutions, the neutral zwitterion ⁺H₃NCH₂COO⁻ in neutral solutions, and the anionic glycinate H₂NCH₂COO⁻ which predominates at pH values above 9.78 (Aksu and Doyle, 2001). Glycine can strongly attract metal ions like Au, Ag, Cu, Zn, Pb, Pd, Cd, Ni, and Co (Eksteen and Oraby, 2015; Oraby et al., 2017; Oraby and Eksteen, 2015a; Perea and Restrepo, 2018). On the other hand, the dissolution of Fe, Mn, Cr, Mg, Al, and Si is negligible in alkaline glycine solution (Eksteen et al., 2016; Eksteen and Oraby, 2015) that provides an advantage for the selective dissolution vs impurities, especially iron, which is the most typical impurity in competing acidic cyanide-free hydrometallurgical processes.

Table 1 presents the stability constants for various gold complexes that are of importance for leaching processes. Apart from Au(CN)₂⁻, Au(H₂NCH₂COO)₂⁻ has the highest stability constant compared to Au(SO₃)₂³⁻, Au(SCN)₂⁻, AuBr₂⁻, and AuCl₂⁻ complexes.

Aylmore (2005) demonstrated the reaction between glycine and gold in the presence of oxygen in an alkaline medium, where the anionic glycinate makes a complex with Au(I) through nitrogen atom in the amino group (–NH₂) as Au(H₂NCH₂COO)₂⁻ (Eq. (1)).



The use of hydrogen peroxide (H₂O₂) as an oxidant instead of oxygen in alkaline glycine solutions for gold dissolution (Eq. (2)) was first presented by Oraby and Eksteen (2015a, 2015b) and Eksteen and Oraby (2015):



They found that the increase in either glycine concentration, temperature, pH or peroxide concentration improves gold dissolution. Furthermore, the presence of cupric ions showed catalytic effect to significantly enhance dissolution of gold in the glycine solution with the use of hydrogen peroxide (Eksteen and Oraby, 2015). Aksu et al. (2003) presented that the copper dissolution can be inhibited by the addition of excess hydrogen peroxide, due to the growth of an oxide-protective film on the copper surface, also applicable to gold. The effect of glycine addition on the extraction of gold in cyanide solution in the presence of copper was investigated by Oraby and Eksteen (2015b) and Oraby et al. (2017) for consideration of treatment of copper-gold ores. The results showed that the addition of glycine improved gold dissolution rate in copper (I)-cyanide solutions, which contain almost no free cyanide in the solution. Eksteen et al. (2017) stated that glycine leaching of gold in agitated reactor seems not feasible in the absence of catalysts (e.g. Cu²⁺, CN⁻ ions). On the other hand, Oraby et al. (2019) have recently reported that aerated alkaline glycine leaching (bottle roll with hole for air access, 15 g/L glycine, pH = 12.5, T = 23–65°C) of paleochannel ores resulted in 85% gold recovery after 336 h. Since the leaching rate was slow, they concluded that glycine is suitable for only heap and in-situ leaching of oxide ores.

The next step after leaching in the hydrometallurgical gold processing is the recovery of gold from the solution. In the gold mining industry, activated carbon is the most widely used extractant to recover

gold from pregnant cyanide leach solution, known as carbon-in-leach (CIL), carbon-in-pulp (CIP), and carbon-in-columns (CIC) processes (Marsden and House, 2006). A number of studies have also been carried out on gold recovery via adsorption onto activated carbon from alkaline glycine alone (Oraby and Eksteen, 2015a; Tauetsile et al., 2018a, 2018b) and in the presence of cyanide (Tauetsile et al., 2019a, 2019b). Oraby and Eksteen (2015a) obtained in four hours a loading of 13.2 g/kg of gold glycinate onto activated carbon. The effect of pH, concentration of glycine, calcium chloride, initial gold, copper and activated carbon on adsorption kinetics of gold and copper onto activated carbon was investigated by Tauetsile et al. (2018b). They found that gold uptake by activated carbon was not affected by the presence of copper in any concentrations and > 98% of gold was recovered onto activated carbon in < 6 h.

An alternative to conventional recovery processes for gold (i.e. carbon adsorption, ion exchange, and solvent extraction) has been developed recently, namely the electrodeposition-redox replacement (EDRR) method for selective gold recovery from cupric chloride leaching solutions (Lundström and Yliniemi, 2017; Korolev et al., 2019, 2018; Yliniemi et al., 2018b) without the addition of any chemical. Gold is recovered by the EDRR method as follows: some of the copper, which is present in large amount in the solution is deposited on the cathode under direct current or potential. Then, the external current or potential is turned off and the redox replacement reaction occurs between dissolved gold and copper, which leads to reduction of gold on the cathode. By running same procedure for a number of cycles, significant amount of gold is recovered (Korolev et al., 2019). Recently, a more detailed gold recovery mechanism was suggested in aqueous chloride as well as in deep eutectic mixture of choline chloride with ethylene glycol in 1:2 M ratio (1:2 ChCl: EG) media: divalent copper oxidizes the elemental copper deposit, which results in enrichment of dissolved cuprous species in the vicinity of electrode, and consequently these cuprous species reduce the dissolved gold species into elemental form (Korolev et al., 2020). Besides the studies on gold recovery in chloride media, EDRR method was also used in recovery of silver from zinc sulfate bath (Halli et al., 2017; Wang et al., 2019) and copper sulfate bath (Hannula et al., 2019), platinum from nickel sulfate solutions (Halli et al., 2018; Yliniemi et al., 2018a) and tellurium from chloride leachates (Halli et al., 2020).

In this study, we investigate the alkaline glycine leaching of gold ore in agitated reactor within typical industrial scale cyanide leaching residence time for evaluation of the process as an alternative to cyanidation. With this aim, a response surface methodology was adopted to investigate the main and interactive effects of glycine concentration, temperature, and pH on gold extraction that can provide support when building hydrometallurgical glycine leaching strategies for the gold ore treatment. Besides the investigation on leaching process, two alternative gold recovery methods were studied: (I) conventional adsorption onto activated carbon, (II) the EDRR approach. The purpose is to demonstrate the potential applicability of the EDRR for recovery of gold from glycine solution as an alternative method to conventional carbon adsorption. If successful, the EDRR could offer a carbon-free method for gold recovery, enabling gold recovery directly into the elemental form.

2. Material and methods

2.1. Sample

A gold ore sample originated from an epithermal deposit with a composition shown in Table 2 was used as a feed material in the leaching experiments. X-ray fluorescence and inductively coupled plasma optical emission spectrometry (ICP-OES; Thermo Scientific iCAP 6000, USA) were used to determine the chemical composition of the sample after total dissolution, whereas gold and silver were analyzed with the lead collection fire assay technique. The main phases were identified by X-ray diffraction and a polished section was studied with

Table 2
Chemical and mineral composition of the gold ore.

Element	Content (%)	Mineral	Content (%)
Au	5.4 (ppm)	Pyrite	0.48
Ag	2 (ppm)	Pyrrhotite	0.14
Fe	0.8	Chalcopyrite	0.06
Cu	0.02	Galena	0.006
Al	8.4	Sphalerite	0.004
Te	0.007	Quartz	58.98
Bi	0.006	Al silicates	20.25
Sb	< 0.002	Biotite	10.11
Pb	< 0.002	Microcline	2.12
As	< 0.002	Others	7.85
S	0.3		
C	< 0.05		

an optical microscope (Zeiss Axioplan 2, Germany) and a scanning electron microscope (SEM; JEOL 700F Japan). Gold particles were identified using the automated rare particle search program of the JEOL 7000F field emission scanning electron microscope. The mineral composition of the sample was estimated based on its chemical composition using HSC Chemistry 10 software.

Mineralogically the ore sample was mainly composed of quartz (ca. 60%) and Al-silicates, micas and feldspars comprise the rest of the sample. The main ore minerals included base metal sulfides and tellurides. Pyrite is the most common sulfide mineral, followed by pyrrhotite and chalcopyrite. The main telluride minerals were tellurobismuthite, altaite, hessite, and frobergite. Gold occurred mostly as fine-grained particles containing an average of 5% Ag and in tellurides, mainly as calaverite (AuTe₂), sylvanite (AuAgTe₄), and kostovite (CuAuTe₄). Native gold was associated commonly with pyrite and calaverite with other tellurides, such as melanite (NiTe₂) and tellurobismuthite (Bi₂Te₃). The native gold grains were usually small size, < 20 μm, both as inclusions and veinlets in pyrite. This composition of the material is very typical for this kind of ore deposits (White and Hedenquist, 1995). In addition, the average particle size (d₉₀) of the sample was 86 μm, which was determined by laser diffraction (Malvern Mastersizer 3000, UK).

2.2. Glycine leaching

All leaching experiments in glycine (C₂H₅NO₂, Sigma-Aldrich, analytical grade) media were carried out in a 1 L glass reactor under atmospheric conditions with a leaching time of 24 h. A GLS-type of titanium impeller was used to agitate the solution at a constant speed of 900 rpm with a solid/liquid ratio of 100 g/L and an oxygen flow rate of 1 L/min. First, initial glycine leaching experiments (E1–E7) were run to observe the effects of glycine concentration (0.5–2 M), pH (10–12), and temperature (22–60 °C) on the amount of gold dissolved into solution (mg/L). Table 3 summarizes the parameters used in the experiments E1–E7.

At the beginning and during the experiments, the pH of the leach solution was adjusted with 12 M sodium hydroxide (NaOH, Sigma-

Table 3
Parameters of initial leaching experiments.

Experiment	Glycine concentration	Temperature	pH
	(M)	(°C)	
E1	0.5	60	12
E2	1.25	60	12
E3	2	60	12
E4	2	20	12
E5	2	40	12
E6	2	60	10
E7	2	60	11

Aldrich, analytical grade) and the redox potential of the solution was measured with a Pt electrode vs. Ag/AgCl reference electrode. Several samples (10 mL) were taken at fixed leaching periods from the leaching slurry and filtered with a 0.45 μm pore size filter. The solids were fed back to the reactor, while the solution samples were diluted and analyzed using ICP–MS (Thermo Scientific iCAP Q, USA) for Au and Ag and ICP–OES for the remaining metals. At the end of the leaching experiments, the filtered solid residue was dried at 60 °C, homogenized and then Au and Ag content was analyzed by the Fire Assay method. Other metals were analyzed using ICP–OES after total dissolution. The metal concentrations of the final solution were determined using the same analysis routine as for the leach solution samples.

2.3. Cyanide leaching

A reference cyanide leaching experiment was carried out in agitated reactor for 24 h with 0.75 g/L sodium cyanide (NaCN, Alfa Aesar, analytical grade) concentration to benchmark the leaching efficiency of glycine. The rest of the leaching conditions for the experiment as follows: pH = 11, room temperature (22 °C), solid/liquid ratio of 500 g/L, 0.5 L/min of air purging. After the leaching experiments, slurry was filtered and concentration of metals in the solution and solid samples were determined by using same analytical method as in glycine leaching.

2.4. Experimental design

The effects of glycine concentration, temperature, and pH on gold extraction were subjected to statistical data analysis to determine the optimal parameters in the alkaline glycine leaching experiments. The investigated parameters (glycine concentration, pH, and temperature) were chosen according to observations on the initial experiments (E1–E7). In this study, MODDE 12.0 software was used for design of the experimental series and statistical analysis of the results. The face-centered central composite design (CCF) – a type of response surface methodology (RSM) – was used to design the experimental series with three factors and three center points (Table 4).

The significance of the parameters and their interaction was tested with P-values. When the P-value is more than $\alpha = 0.05$, it indicates statistically non-significant coefficients at the selected confidence level (95%) and a non-significant P-value always corresponds to a low effect (Celep et al., 2018; Hoenig and Heisey, 2001; Seltman, 2018). Also, the model coefficients of the multiple determinations (R²), Q² (showing an estimate of the future prediction precision), model validity, reproducibility, and analysis of variance (ANOVA) of the regression model were examined to interpret the sufficiency of the fit.

2.5. Recovery experiments

2.5.1. Adsorption

One carbon-in-pregnant leach solution (PLS) and two carbon-in-leach (CIL-1 and CIL-2) recovery tests were run in the 1 L glass reactor using 15 g/L of activated carbon (RO 3515, Norit, technical grade) to adsorb gold from the loaded glycine solution. Activated carbon was

Table 4
Parameters of the CCF experimental design for glycine leaching experiments (N1–N17).

Parameters	Level used, actual (coded)		
	Low (–1)	Medium (0)	High (+1)
X ₁ = glycine concentration (M)	0.5	1.25	2
X ₂ = temperature (°C)	20	40	60
X ₃ = pH	10	11	12

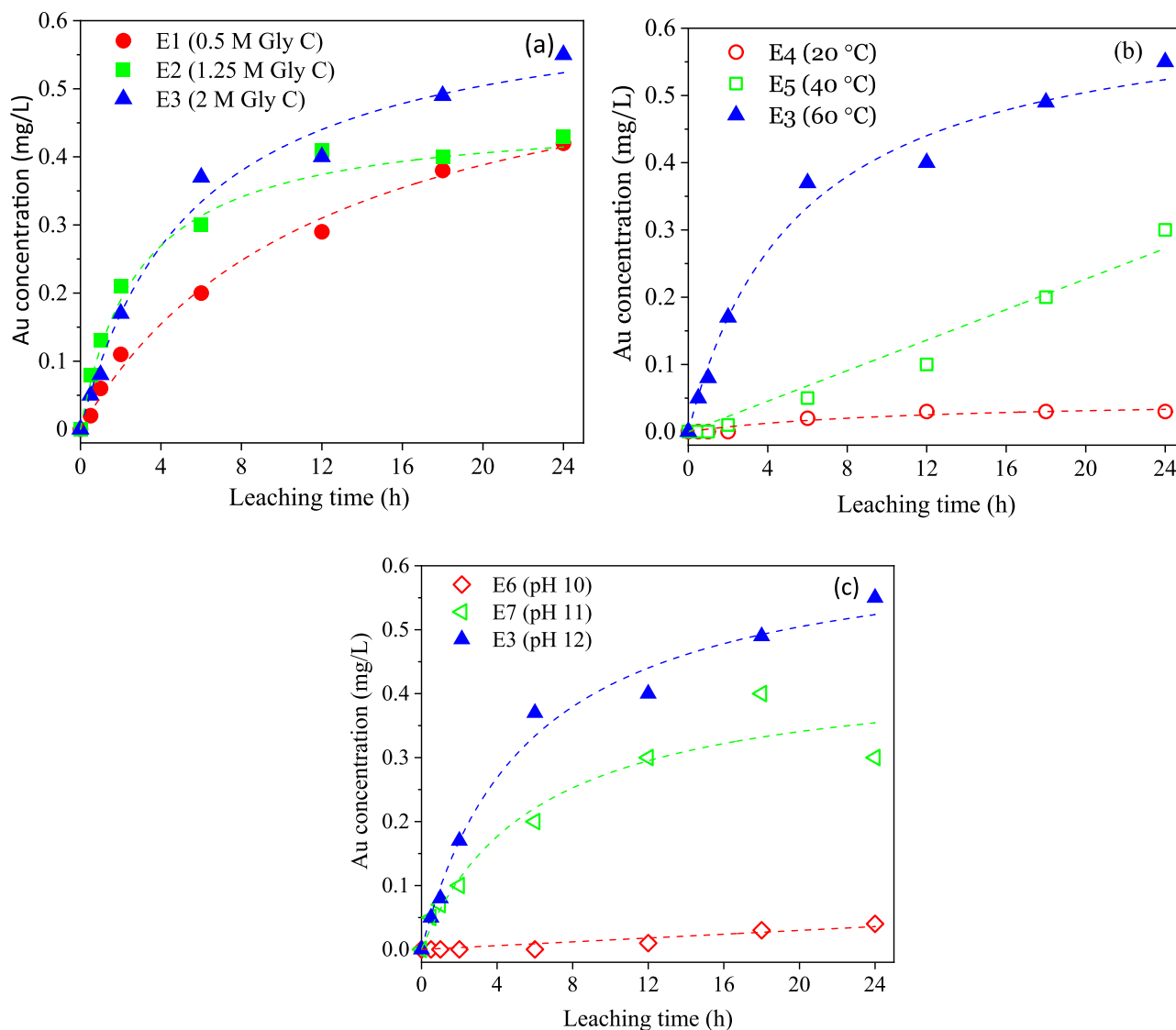


Fig. 1. Effect of (a) glycine concentration, (b) temperature, and (c) pH on gold dissolution (constant parameters were 2 M glycine, $T = 60\text{ }^{\circ}\text{C}$, $\text{pH} = 12$, O_2 feed: 1 L/min).

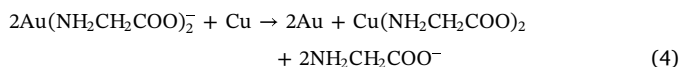
soaked in distilled water for 24 h and screened with a $600\text{ }\mu\text{m}$ sieve prior to recovery tests. Slurry in the adsorption tests was mixed at a lower rotation speed (ca. 500 rpm instead of 900 rpm) to avoid attrition of activated carbon. CIL-1 and CIL-2 tests were run for 24 and 36 h, respectively, with the chosen optimal leach condition where activated carbon was added into the slurries at the beginning of the tests. At the end of both CIL tests, the slurries were filtered, and the cakes were wet-screened using a $300\text{ }\mu\text{m}$ sieve to separate the activated carbon from the final residue. The final residues and activated carbon were dried in the oven at $60\text{ }^{\circ}\text{C}$ and afterwards chemical analyses were applied for both. In the carbon-in-PLS test, activated carbon was added into the filtered pregnant glycine solution at room temperature after the filtration. After the experiment, activated carbon was separated from the solution, dried at $60\text{ }^{\circ}\text{C}$ and analyzed for Au and Ag. During both the carbon-in-PLS and CIL recovery tests, small ($\sim 10\text{ mL}$) solution samples were taken at 0.5, 1, 2, 4, 12, 18, 24, and 36 h for evaluation of gold adsorption onto activated carbon. Au and Ag were analyzed by ICP-MS and the remaining metals by ICP-OES from solution. Glycine concentration in the final solution was not measured. Solid samples were analyzed by the same methods as the samples from the leaching experiments. Determination of the amount of gold (mg/kg) on the activated carbon was carried out by first burning the carbon to ash, then dissolving the

ash in concentrated aqua regia, and lastly analyzing the solution by ICP-MS.

2.5.2. Gold recovery by EDRR method

The EDRR experiments were run in a three-electrode cell (50 cm^3) at room temperature. Glassy carbon (2 cm^2 exposed area, Alfa Aesar, United States) was employed as the working electrode (WE) and a platinum sheet (10 cm^2 , Pt wt.% $\geq 99.5\%$, Kultakeskus Oy, Finland) was utilized as the counter electrode, while the reference electrode was a saturated Hg/Hg₂SO₄ electrode ($+650\text{ mV}$ vs. standard hydrogen electrode). The working electrode was polished with 1200 grade silicon sandpaper to a mirror finish. It was then degreased with ethanol followed by deionized water in an ultrasonic bath and dried in a desiccator. The EDRR measurements were conducted using both synthetic solutions and pregnant leaching solution doped with 500 ppm Cu from copper(II) sulfate pentahydrate (CuSO₄·5H₂O, Sigma-Aldrich, analytical grade) in order to alleviate the influence of the mass transfer process. Synthetic solution was prepared by dissolving in deionized water glycine (C₂H₅NO₂, Sigma-Aldrich, analytical grade), CuSO₄·5H₂O and Gold Atomic Absorption Standard (1000 $\mu\text{g/mL}$ Au, Sigma-Aldrich, analytical grade) in amounts required to obtain concentrations as presented in Table 9. The EDRR method can be generally depicted as follows: in

the electrodeposition stage (ED), copper is potentiostatically electro-deposited on the working electrode at a potential of $-E_1 = -1100$ mV vs. Hg/Hg₂SO₄ for a time of $t_1 = 5$ s (Eq. (3)), after which the redox replacement stage (RR) follows immediately. During the RR stage, the external potential is cut off and the working electrode is kept at open circuit potential (OCP) for a pre-determined time of $t_2 = 55$ s. During this stage, the redox replacement reaction occurs spontaneously between the Cu deposits and Au(NH₂CH₂COO)₂⁻ (Eq. (4)).



Afterwards, another EDRR cycle follows and Au is enriched on the electrode after a number of cycles (n). The morphology and composition of the EDRR products were analyzed by SEM and energy-dispersive X-ray spectroscopy (ThermoFisher Scientific Ultradry EDS Detector, USA). Efficiency of gold recovery was evaluated by comparing the ICP-MS assays of the solution before and after the EDRR measurements.

3. Results and discussion

3.1. Effect of glycine concentration, temperature, and pH on metal dissolution

The initial leaching results showed that the glycine concentration (0.5–2.0 M) has a minor effect on gold dissolution (Fig. 1a). At all studied concentrations, a similar trend was observed at the start of the experiments, where the leaching was nearly linear. Afterward, the rate decreased in the experiments E1 and E3 and a maximum achievable extraction was not reached yet after 24 h. However, in the experiment E3, dissolution rate got to near zero after six hours and maximum achievable extraction was attained. The highest gold concentration (0.55 mg/L) was observed in the highest glycine concentration (2 M) experiment after 24 h, whereas with a glycine concentration of 0.5 M, 0.42 mg/L gold was dissolved into the solution.

In contrast, the effect of temperature was clearly more critical in terms of gold dissolution kinetics. There was only minimal gold dissolution at room temperature, but even at 40 °C gold started to dissolve almost linearly, reaching 0.3 mg/L after 24 h, Fig. 1b, and when the temperature was increased up to 60 °C, gold dissolution reached a highest value of 0.55 mg/L of Au. This can be explained by the fact that the determining step for Au dissolution is reaction rate k – as previously reported in the literature (Eksteen and Oraby, 2015; Oraby et al., 2019; Oraby and Eksteen, 2015b) – and it is strongly related to temperature via the Arrhenius equation (Eq. (5)):

$$k = Ae^{-\frac{E_a}{RT}} \quad (5)$$

where A is an experimental constant, E_a activation energy (in this case for dissolution), R gas constant, and T temperature.

In addition, the effect of pH was also found to be substantial. At pH 10, gold dissolution was very slow and did not improve much during the experiment (0.04 mg/L, 24 h). However, in the experiment E7 at pH 11, the amount of dissolved gold increased up to 0.4 mg/L, and even higher gold dissolution was observed at pH 12. It is clear that high alkaline pH conditions have a positive effect on the dissolution of gold, and this is believed to be due to the stability of gold glycinate and hydroxide ions. Oraby et al. (2019) observed a similar effect of pH on gold extraction using paleochannel ores. According to Eksteen and Oraby (2015), hydroxyl radical ($\cdot\text{OH}$) can be generated from peroxide (Eq. (6)) and it is known to accelerate the dissolution of gold in the presence of oxygen as an oxidant (Nowicka et al., 2010).



Table 5 indicates the concentration of Au, Cu, Fe, and Al (mg/L) in the final pregnant solution from the initial experiments (E1–E7). It can

Table 5
Metal concentrations in pregnant leach solution of initial experiments.

Experiment Name	Au	Cu	Fe	Al
	mg/L	mg/L	mg/L	mg/L
E1	0.42	11	8	29
E2	0.43	6	< 0.01	5
E3	0.55	15	7	34
E4	0.03	5	< 0.01	4
E5	0.30	6	< 0.01	6
E6	0.04	10	15	2
E7	0.30	5	< 0.01	4

be seen that the concentration of Cu in the final solutions was high compared to the other metals due to the selectivity of glycine for copper. It is worth noting that dissolved copper is in fact beneficial for dissolution of gold in glycine media (Eksteen and Oraby 2015) as in alkaline thiosulfate leaching (Molleman and Dreisinger, 2002). In most of the experiments, silver concentration in the PLS was under detection limit (< 0.01 mg/L), even though theoretically it should be soluble in alkaline glycine solution. The reason for this is that silver is present mostly in the form of refractory tellurides, such as sylvanite (AuAgTe₄), which have poor leaching kinetics (Henley et al., 2001). At the same time, in the PLS after the test E3, minor amount of silver (0.01 mg/L) was detected along with a considerable concentration of gold. This is attributed to the fact that soluble native gold grains in the studied material contain ca. 5% of Ag inside, thus increased dissolution of gold also brings up the extraction of silver. Other metals were observed only at very low concentrations and their concentrations were often under the detection limit of the ICP-OES analysis technique.

3.2. Optimization of gold leaching (tests N1–N17)

Based on initial experiments E1–E7, the experimental series was designed using MODDE 12.0 software and performed in a similar manner to the initial experiments. The effect of each factor and their interactions on the gold extraction is presented in Table 6 along with the coefficients of the regression model obtained from CCF experimental design. It was found that the linear, quadratic, and interaction effects of glycine concentration in the 0.5–2 M range were not significant at a 95% confidence level for the gold dissolution, as was the quadratic effect of pH (P-value above 0.05, highlighted in red color). In contrast, the effects of temperature and pH on Au dissolution were found to be significant at a 95% confidence level (i.e. $P < 0.05$). The pH value had a significant effect on gold dissolution as linear and quadratic contributions.

To illustrate the non-significant effect of glycine concentration on Au extraction (%), response surface plots of the model on the dual effect of temperature and pH were constructed, where the glycine concentration as the third variable was kept at a low, medium, and high level. Fig. 2 a–c shows that at all three levels of glycine concentration,

Table 6
Coefficients of the model and effect on Au extraction.

Factor	P	Coefficients	Standard error	Effect
Constant	2.47·10 ⁻⁶	51.112	3.702	
Glycine concentration	0.229	3.6	2.736	7.200
Temperature	0.013	9	2.736	18
pH	0.002	13	2.736	26
Gly*Gly	0.095	-10.197	5.286	-20.394
T*T	0.020	15.803	5.286	31.606
pH*pH	0.072	-11.197	5.286	-22.394
Gly*T	0.585	-1.75	3.059	-3.5
Gly*pH	0.875	0.499	3.059	0.999
T*pH	0.014	10	3.059	20

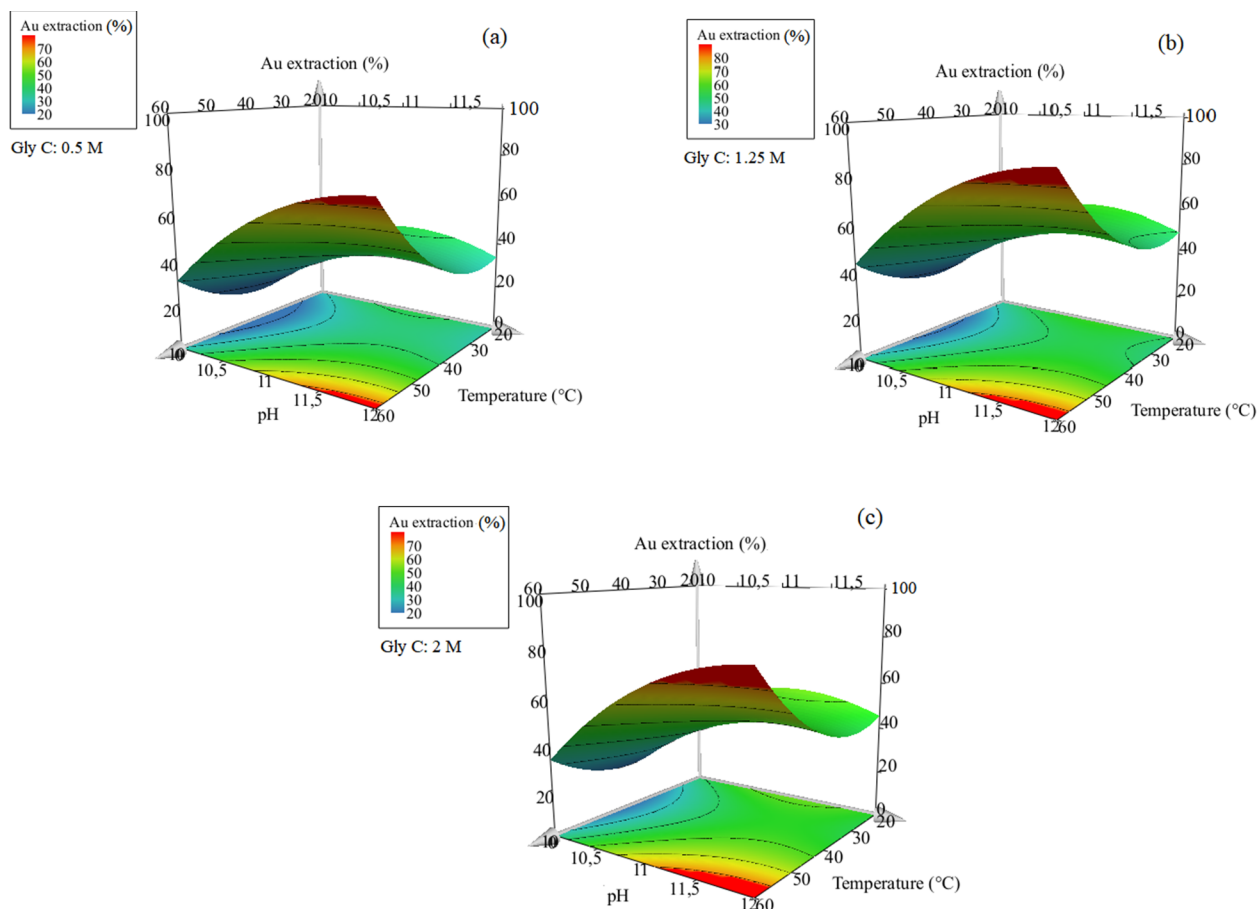


Fig. 2. Response surface plots of double effect of temperature and pH on Au extraction after 24 h leaching at three levels of glycine concentration: (a) low, (b) medium, and (c) high.

maximum extractions of gold were achieved at the highest temperature (60 °C) and with a pH above 11.5, and that the shape of the plots did not change. This confirms that the effect of glycine concentrations of 0.5–2 M on Au extraction is not significant in the studied experimental conditions. Similarly, Broeksma (2018) observed negligible effect of increased glycine concentration on dissolution of copper from PCB waste. They stated that in presence of pure oxygen, rate of dissolution is limited by chemical reaction and when glycine is present in significant excess, rate of dissolution becomes constant since the reaction turns into a zero-order-reaction (Choo et al., 2006). Furthermore, coefficient of the multiple determinations (R^2) of the model was observed at 0.89 with a model validity of 0.39, but Q^2 was found at -0.2 , which should be > 0.1 and 0.5 for a significant and good model, respectively. The reason for the negative Q^2 is that non-significant terms (i.e. glycine concentration) exist in the model.

In order to improve the quality of the model, insignificant factors were omitted, and the model was refitted with two factors: temperature and pH. In the refitted model, the coefficient of the multiple determinations (R^2), Q^2 , model validity, and reproducibility obtained were 0.80, 0.53, 0.38 and 0.97, respectively, which indicated that the model has good predictive ability. Table 7 shows the experimental parameters with actual gold extractions in each experiment conducted (N1–N17) and values predicted by the regression model, where CCF was used for experimental design. The observed Au extraction values were calculated based on the final solid analysis. Predicted extraction values of Au (Y, %) were calculated with two factors (temperature and pH) using the unscaled coefficients of the regression model of the data (Eq. (7)). With the Eq. (7), the predicted Au extraction (%) can be calculated at any given actual value of temperature and pH. As can be seen from Table 7,

the measured and predicted values of gold extraction are in good correlation (i.e., $R^2 = 0.80$).

$$\begin{aligned} Au_{\text{extraction}}(Y, \%) = & -1616.36 - 7, 51792 * T + 315, 528 * pH \\ & + 0, 0308491 * T^2 - 14, 6604 * pH^2 \\ & + 0.5 * T * pH \end{aligned} \quad (7)$$

In the analysis of variance (ANOVA) of the regression model (Table 8), the P value of the model error (0.085) is larger than the significance level ($\alpha = 0.05$), so the null hypothesis (i.e. the variation of the response is described by regression model) could not be rejected (Seltman, 2018). It was concluded that there was not enough evidence at the 95% confidence level to ascertain that there was a lack of fit in the linear regression model. The probability of the regression is significant at a confidence level of 95% (i.e., $P < 0.05$), therefore the model accurately describes the experimental data.

Fig. 3 shows a response 2D contour plot for predicted gold extraction (%) as a function of temperature and pH. It can be interpreted that to be able to achieve high gold extraction, the temperature and pH should be above 55 °C and 11.5, respectively, in the studied range of leaching conditions. Based on the predicted results, the optimal leach conditions for gold extraction chosen were 1.25 M (93.75 g/L) glycine concentration, temperature of 60 °C, and pH = 12.

3.3. Comparison of gold extraction in glycine media with cyanide leaching

One verification experiment (VE) was run for 24 h in leaching conditions of 1 L/min oxygen feed, 100 g/L solid/liquid ratio, and 950 rpm rotational speed to confirm the adequacy of the chosen

Table 7
Designed experimental parameters with observed and predicted Au extraction values.

Experiment ID	Glycine conc. (M)	Temperature (°C)	pH	Au extraction (%)		Relative error (%)
				observed	predicted	
N1	0.5	20	10	22	35	59
N2	2	20	10	39	35	10
N3	0.5	60	10	32	33	3
N4	2	60	10	26	33	27
N5	0.5	20	12	41	41	0
N6	2	20	12	44	41	7
N7	0.5	60	12	75	79	5
N8	2	60	12	87	79	9
N9	0.5	40	11	35	49	40
N10	2	40	11	45	49	9
N11	1.25	20	11	58	52	10
N12	1.25	60	11	74	70	5
N13	1.25	40	10	38	21	45
N14	1.25	40	12	40	47	18
N15	1.25	40	11	55	49	11
N16	1.25	40	11	53	49	8
N17	1.25	40	11	49	49	0

Table 8
The ANOVA table of the regression model.

Source of variation	DF	SS	MS	F	P
Regression	5	4045.79	809.16	9.28	0.001
Residual	11	958.68	87.15		
Lack of fit (model error)	9	940.01	104.45	11.19	0.085
Pure error (replicate error)	2	18.66	9.33		
Total	16	5004.47	312.78		

optimal conditions. The gold extraction in the glycine verification experiment was 90%, which is almost equal to the result (89%) observed in the initial experiment E2. This validates the high replicability of the experiments. To the best of authors knowledge, there is no previous study on glycine leaching that has extracted gold from ores to such value (90%) in absence of any catalysts (Cu^{2+} , CN^-) in aerated solution after 24 h. As demonstrated by Eksteen et al. (2017) and Oraby et al. (2019), using air as oxidant, < 10% gold could be dissolved in comparable time in similar leaching conditions. Therefore, the results imply that intensive agitation together with oxygen purging can significantly enhance the gold extraction rate.

In the cyanide leaching experiment, which was run to compare the gold leaching efficiency of cyanide-free glycine media, only 80% of gold could be extracted in the presence of 0.75 g/L NaCN. The low gold extraction can be attributed to the fact that some of the gold in the ore occurs as gold telluride minerals having slow dissolution characteristic in cyanide solutions, which results in less efficient gold extraction (Zhang et al., 2010). Based on the gold extraction efficiency in the cyanide leaching, the studied gold ore can be classified according to La Brooy et al. (1994) as mildly refractory, i.e. gold extraction in conventional cyanidation is 80–90%.

Fig. 4 illustrates the time-dependent extraction of gold from the ore in glycine and cyanide media. Similar leaching kinetics behavior was observed in glycine and cyanide media at the beginning of both experiments (0–4 h), when the dissolution rate increased almost linearly. Thereafter, dissolution of gold in glycine solution slowed down until maximum achievable extraction was reached in 12 h. In contrast to glycine media, dissolution rate of gold in cyanidation decayed after 6 h of leaching and maximum achievable extraction of gold was not reached after 24 h. This can be attributed to native gold dissolved fast at first, but afterwards gold tellurides begun to dissolve which has slower dissolution in cyanide solution compared to native gold. These results clearly show that for the investigated mildly refractory gold ore,

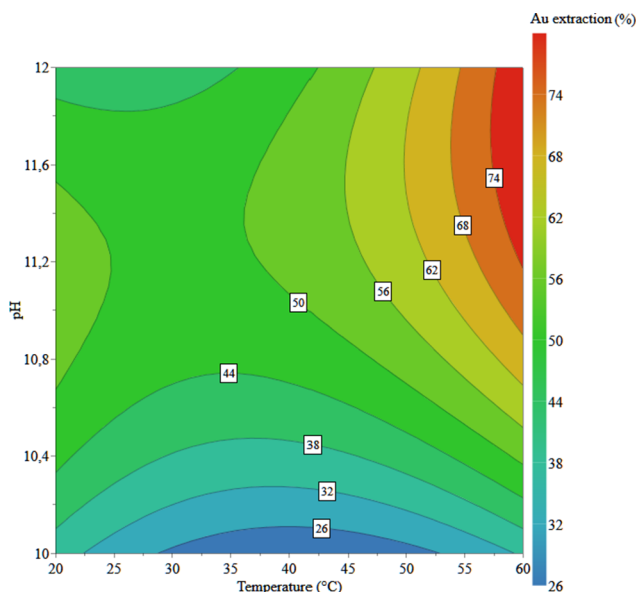


Fig. 3. Predicted effect of temperature and pH on gold extraction (%).

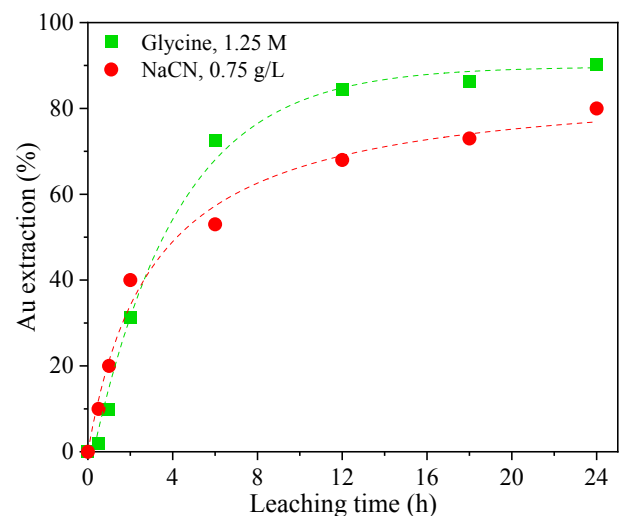


Fig. 4. Extraction of gold as a function of time in glycine leaching (VE) in comparison with conventional cyanidation.

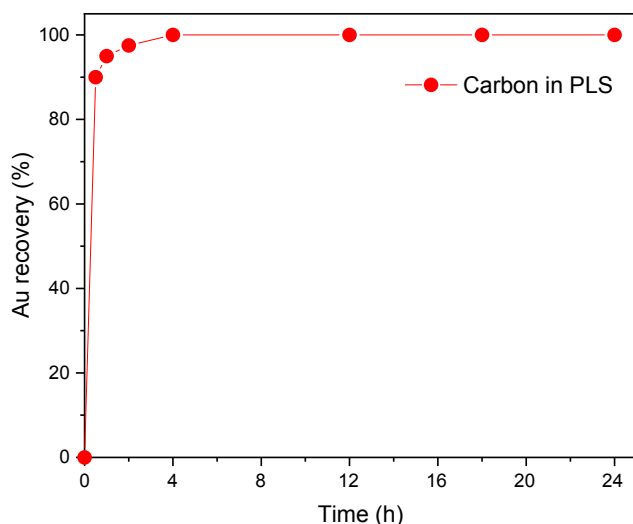


Fig. 5. Recovery of Au from pregnant leach solution by activated carbon (glycine concentration: 1.25 M, Carbon: 15 g/L, T: 23 °C, 24 h of recovery time).

cyanide-free glycine leaching can provide more efficient gold extraction than conventional cyanidation process, without having negative effects of the latter.

3.4. Recovery of gold from solution

3.4.1. Carbon adsorption

Fig. 5 presents the gold recovery from the pregnant leach solution by carbon adsorption as a function of time. The pregnant leach solution with a gold concentration of 0.46 mg/L was taken from the verification leaching experiment after filtration. It can be seen that the gold uptake from the loaded solution reached 100% within four hours, after which the remaining gold concentration in the solution was negligible (< 0.01 mg/L), while 90% of gold was recovered onto activated carbon from the ore used (i.e. holistic recovery). Similarly, [Tautsile et al. \(2018b\)](#) observed efficient gold recovery onto activated carbon using synthetic loaded glycine solution.

In the carbon-in-leach test (CIL-1), the observed gold recovery from solution onto activated carbon was 96%, while holistic recovery of gold remained only at 62%. However, in the longer carbon-in-leach test (36 h, CIL-2) holistic gold recovery of 77% was obtained, whereas the gold uptake from the loaded solution was at the same level (i.e. 95%). The reason for lower holistic gold recovery in CIL method compared to carbon-in-PLS could be attributed to a slower gold extraction from the ore to the solution, which in turn reduces holistic recovery. This assumption was supported by observing 72% extraction of gold from ore into the solution in the CIL-1 test, while longer retention time (36 h) enhanced the dissolution of gold to 83% (CIL-2). [Fleming et al. \(2011\)](#) also demonstrated that in a CIP plant, all the leachable gold is already present in solution before the first carbon adsorption tank providing substantial kinetic driving force for adsorption. In contrast, in CIL plant, when the slurry first meets activated carbon, gold has not yet sufficiently leached, which slows down the rate of gold adsorption onto activated carbon.

Possible explanation for the lower gold leaching efficiencies in the CIL experiment can be the reduced agitation speed (ca. 500 rpm) in comparison with the tests without activated carbon. This would indicate that the leaching kinetics is controlled by diffusion. High mixing rate increases the solution flow past the solid particles and reduces the diffusion layer, which in turn enhance the gold dissolution rate ([Marsden and House, 2006](#)). In order to verify the diffusion limited kinetics and determine an optimal mixing rate in CIL process further studies are needed. Also, [Ahtainen and Lundström \(2019\)](#) found that

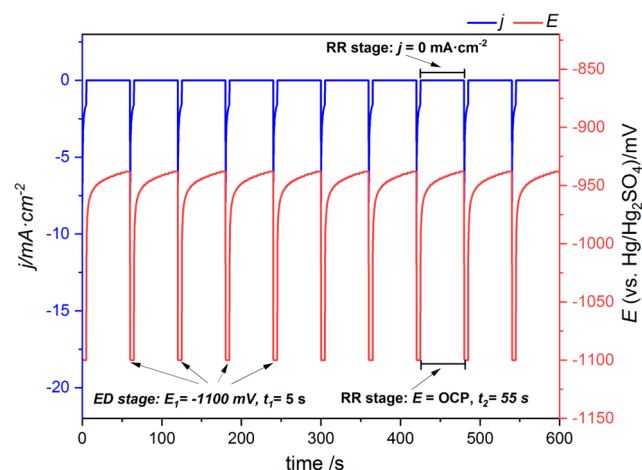


Fig. 6. Time-current-potential profile during EDRR cycles in synthetic solution ([Table 9](#)). Cu is deposited at -1100 mV (vs. Hg/Hg₂SO₄) and then replaced by Au (NH₂CH₂COO)₂⁻ ions at open circuit potential (OCP). The EDRR cycle ends after 55 s of OCP and the next cycle follows.

addition of carbon into leaching reactor decreases the redox potential of the solution by ca. 50–70 mV. This leads to a reduction of an oxidative power of the leaching system and slows down the extraction of gold from ore.

3.4.2. EDRR

The possibility of carbon-free recovery of gold from glycine leaching solution by the EDRR method was demonstrated for the first time in glycine media, using both synthetic solution and PLS obtained in optimum leaching conditions. The copper concentration in the final leach solution was relatively low (15 mg/L), and this can negatively influence the EDRR process due to mass transfer limitations. For this reason, the PLS was further doped with approx. 500 mg/L of Cu to alleviate the influence of mass transfer ([Reyes Cruz et al., 2002](#)). [Fig. 6](#) shows a typical potential-current-time profile of 10 EDRR cycles (Cu electro-deposition for 5 s at -1100 mV vs. Hg/Hg₂SO₄ and redox replacement time of 55 s). [Table 9](#) presents the composition of the solutions utilized for the EDRR experiments.

The substantial difference in Au concentrations in solution before and after EDRR measurements highlights the capability of the EDRR method, as Au recovery from the synthetic solution reached 88% after 1247 EDRR cycles (ca. 20 h); this is an extremely promising result when taking into account the demonstrative nature of the EDRR part of the study, i.e. no full optimization of EDRR parameters were performed prior to recovery. However, only 35% of Au was recovered from the real leaching solution (PLS, [Table 9](#)) during 1440 cycles (24 h), indicating that the presence of other dissolved metal ions as well as their valences have a crucial role in EDRR. Previous study ([Korolev et al., 2020](#)) has demonstrated that the formation Cu(I) species during EDRR in chloride media can reduce gold ions in the vicinity of the electrode and subsequently enhance gold recovery. [O'Connor et al. \(2018\)](#) found that, when glycine is in excess over copper in solution, copper(II) glycinate can reduce to copper(I) glycinate with a standard reduction potential of -167 mV vs. SHE. The redox potential in real

Table 9
Composition of solutions before/after EDRR and Au recovery achieved.

Solution	pH	Cu (mg/L)	Au (mg/L)		Au recovery (%)
			Before EDRR	after EDRR	
Synthetic	11	505	0.5	0.06	88
Real PLS		594	0.46	0.30	35

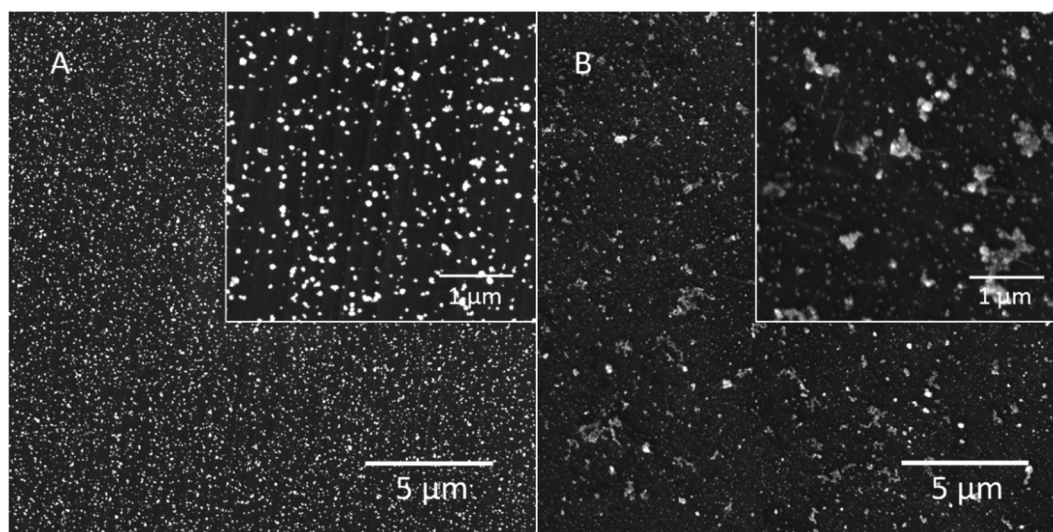


Fig. 7. SEM micrographs of working electrode after EDOR experiments referring to the solution composition in Table 9. (A) synthetic solution, $n = 1247$ cycles; (B) real PLS, $n = 1440$ cycles. (EDOR parameters: $E_1 = -1100$ mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$, $t_1 = 5$ s and $t_2 = 55$ s).

Table 10

EDS quantitative results of particle composition of the working electrode surface after EDOR measurements referring to SEM micrographs in Fig. 7 (average value of 10-point spectra and the background signal carbon (wt%) was excluded).

Sample ID	Au (wt%)	Cu (wt%)
A	58.2	41.8
B	63.3	36.7

PLS was approximately +150 mV vs. SHE, whereas in the synthetic solution it was ca. -250 mV vs. SHE, which is more favorable for copper(I) formation. Consequently, the homogeneous reduction of Au by Cu(I) species may lead a higher recovery of gold from the synthetic solution. Moreover, the presence of other dissolved impurities, such as iron, can also affect the EDOR process. Yliniemi et al. (2018b) demonstrated that Fe^{3+} ions have a competitive reaction during both electrodeposition and redox replacement steps, which could decrease Au recovery. Also, it can decrease the current efficiency of both copper electrodeposition step (Das and Krishna, 1996) and gold deposition step (Brandon et al., 1987). Nevertheless, it is evident that the EDOR phenomenon is applicable in principle in glycine solution as shown with good efficiency rate in synthetic solution, but it requires further investigation as well as optimization of the EDOR process parameters and studying the reaction mechanisms in detail.

SEM micrographs of the working electrode surface after EDOR measurements are shown in Fig. 7a–b. Scattered nanoscale Au/Cu particles were obtained from the synthetic solution, while products from the real solution were found to be in larger clusters. The difference in morphology can be attributed to the impurities in the real leaching solution. EDS results further confirmed the recovery of elemental Au on the electrode (Table 10). It is worth noting that the parameters in this study were not optimized with respect to the product purity but rather to display the capability of Au recovery by EDOR. Nevertheless, our previous work related to EDOR showed that the product quality can be further modified by tailoring the operating parameters (Hannula et al., 2019; Korolev et al., 2018; Wang et al., 2019; Yliniemi et al., 2018b).

4. Conclusions

In this work, the alkaline glycine leaching in agitated reactor was

investigated as a substitute for conventional cyanidation for recovery of gold from ores of epithermal origin. Statistical analysis of the effects of process parameters on dissolution of gold in glycine media revealed that temperature and pH have significant impact on the amount of gold dissolved from the ore, while the influence of glycine concentration is surprisingly negligible in the range studied (0.5–2 M). By using the response surface methodology, the optimum conditions for maximum gold extraction were identified at glycine concentration of 1.25 M, temperature of 60 °C, and pH = 12. Under these conditions the gold extraction of 90% was achieved after 24 h in totally cyanide-free, aerated glycine media. In addition, it was shown that intensive agitation in presence of oxygen is required for high gold extraction within the industrially acceptable timeframe.

With cyanide concentration of 0.75 g/L only 80% gold extraction was achieved, which was attributed to gold telluride minerals in the ore, which lead to categorize the studied gold ore as a mildly refractory. This is actually lower than the gold extraction with cyanide-free glycine leaching (90%). These findings, together with the low price, high recyclability and non-toxicity of glycine, suggest that glycine leaching can be considered as a viable cyanide-free method for recovery of gold from mildly refractory gold ores.

In addition, two methods of gold extraction from the leach solutions, namely carbon adsorption and electrodeposition–redox replacement, were compared. Also, the current study presented for the first time application of carbon-in-leach (CIL) process in glycine media for the recovery of gold, and compared the efficiency with carbon-in-PLS. When activated carbon was added to filtered PLS, it took only 4 h to recover all gold from the solution. Similar level (i.e. 95%) of gold uptake from solution onto the activated carbon was observed with carbon-in-leach approach; however, the holistic recovery of gold in presence of activated carbon was ca. 13% lower than carbon-in-PLS.

Moreover, this study showed for the first time that EDOR can successfully recover dissolved gold from glycine solutions, with a recovery of 88% achieved after 1247 cycles in synthetic solution mimicking the composition of the PLS. Due to the different metal speciation and presence of impurities in the solution, only 35% of gold was recovered after 1440 cycles of EDOR from the real PLS, and in order to achieve higher efficiency systematic optimization of EDOR parameters is needed also for glycine solutions. Overall these results prove the applicability of the EDOR as a carbon-free method for gold recovery from glycine solutions.

CRedit authorship contribution statement

Pelin Altinkaya: Methodology, Investigation, Formal analysis, Visualization, Data curation, Validation, Writing - review & editing. **Zulin Wang:** Methodology, Investigation, Formal analysis, Visualization, Data curation, Validation, Writing - review & editing. **Joseph Hamuyuni:** Writing - review & editing. **Ivan Korolev:** Methodology, Formal analysis. **Joseph Hamuyuni:** . **Mika Haapalainen:** Funding acquisition, Resources, Supervision. **Eero Kolehmainen:** Funding acquisition, Project administration, Resources, Conceptualization, Methodology, Supervision, Validation. **Kirsi Yliniemi:** Funding acquisition, Methodology. **Mari Lundström:** Funding acquisition, Project administration, Resources, Conceptualization, Methodology, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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