# CHARACTERIZATION OF GOLD AND COPPER COMPLEXES IN CYANIDE-GLYCINE SYSTEM BY UV-VIS SPECTROSCOPY

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## ABSTRACT

*In the process of gold ores leaching by glycine and cyanide, the interactions between glycine and cyanide with metals are not well understood and there is little research in this area. The characterization of gold and copper complexes in the cyanide-glycine system by UV-Vis spectroscopy method is studied. Job's method of continuous variation was applied to ascertain the stoichiometry composition of the complexes. The results showed that in the glycine-gold-copper system, although the stability constant of the gold-glycine complex is higher, the dominant species formed is the copper-glycine complex. In the cyanide-gold-copper system, gold forms complexes with cyanide and to a lesser extent glycine, which agrees with their stability constants. If the cyanide and glycine ligands are added to a gold solution, the dominant species in the system is the gold-cyanide complex. In the cyanide-glycine-copper system, the dominant species in the system is the copper-glycine complex. When cyanide and glycine ligands are added to a gold-copper solution, the dominant species in the system are the copper-glycine and the gold-cyanide complexes.*

*Keywords: gold ore leaching, cyanide, glycine, gold complexes, copper complexes, UV-vis spectroscopy.*

## INTRODUCTION

Since the early twentieth century, cyanidation has been the most important method of gold leaching. In this method, gold is dissolved from ore by cyanide solution, and then dissolved gold is recovered using activated carbon, solvent extraction, or electrowinning. Excessive consumption of cyanide in gold mines has devastating environmental effects on water, animals, and plants. Another disadvantage of cyanidation is the presence of elements such as copper, iron, arsenic, zinc, and silver in the gold ores, which are dissolved by the cyanide and increase cyanide consumption[1 - 3]. Many studies have been done to find a suitable lixiviant to replace cyanide. Among them, thiosulfate, thiourea, thiocyanate, and halides have been more attended as alternatives to cyanide, but most of these have been less used on an industrial scale due to technical and economic problems [4 - 9].

Recently several research works conducted on the use of amino acids, especially glycine, as an alternative to cyanide or as cyanide-assisted to reduce its consumption [10 - 15]. The selective leaching of copper from a gold-copper concentrate using glycine and peroxide at room temperature showed that 98 % of total copper dissolved [10]. Another study showed that the glycine–hydrogen peroxide solution could dissolve gold and silver in neutral and alkaline conditions [16]. The results of research on the leaching of gold and copper from gold-copper ores indicated that the gold dissolution rate in the glycine-cyanide system was almost three times higher than that in conventional cyanidation [17]. The leaching of polymetallic gold ore was investigated using cyanide-glycine solutions. The results showed that 75 % of gold was dissolved at 1500 ppm cyanide concentration (without glycine) while 80 % of gold was dissolved at 200 ppm cyanide concentration by adding

0.5 m L$^{-1}$ of glycine, indicating more than 80 % reduction in cyanide consumption [15].

Glycine exists in solutions in 3 different forms; $^+H_3NCH_2COOH$ (cation), $^+H_3NCH_2COO^-$ (zwitterion), and $H_2NCH_2COO^-$ (anion). The cation form predominates at pH values below 2.35, while the anion form predominates at pH values above 9.78 and the zwitterion form predominates at intermediate pH values (2.35 - 9.78) [9, 12, 18].

Glycine can form a strong complex with gold (I) as $Au(NH_2CH_2COO)_2^-$ [9]. The chemistry of gold dissolution in alkaline glycine solutions is described in Eqs. (4 - 7).

Glycine can form soluble complexes with cupric and cuprous ions. The principal copper(II) glycinate complexes are $Cu(H_3NCH_2COO)^{2+}$, $Cu(H_2NCH_2COO)^+$, and $Cu(H_2NCH_2COO)_2$, while the principal Cu(I) species is $Cu(NH_2CH_2COO)_2^-$. Copper metal is oxidized and forms copper (II) glycinate species over a wide range of pH while the copper (I) glycinate complex only appears when total glycine activity is much higher than total copper activity. Glycine appears in the cation form at much lower pH values when complexing copper than it does in the free form. The anionic form of glycine forms more stable copper complexes than the zwitterionic form [18].

The stability constants for copper and gold complexes with cyanide and glycine have been reported by different authors as shown in Table 1.

Many aspects of gold ores leaching by glycine and cyanide lixiviants such as lixiviants molar ratio, presence of other minerals, and complexation of different metals with glycine and cyanide are still not well understood [13, 20, 21]. Knowledge of the interactions between glycine and cyanide with metals is needed to understand better the various aspects of the gold leaching process

and subsequent developments such as gold recovery from the leaching solution by adsorption on active carbon or resins and solvent extraction. And also the gold elution process for gold-loaded carbons and the electrowinning process. However, there is little research in this area [19, 22, 23].

In this research, characterization of gold and copper complexes in cyanide-glycine system by ultraviolet-visible molecular absorption spectroscopy method was studied. The use of glycine for gold leaching is still a new idea. The results of this research can help to improve the selectivity of gold leaching, stability of complexes, and further reduction in cyanide consumption, and finally contribute to the technological development of this idea.

## EXPERIMENTAL

### Materials

Gold and copper standard solution 1000 ppm (Sigma-Aldrich), NaCN, NaOH, glycine, and distilled water were used in this study. All chemicals used were analytical-grade reagents. Gold, copper, glycine, and cyanide solutions with a concentration of 1 ppm were prepared separately by dilution with distilled water.

### Spectrophotometric method

As a result of mixing the ligand and the metal in a solution, complexes are formed according to the Eq. (1):

$$nM + xL \rightarrow M_nL_x \qquad (1)$$

In many cases, it is not possible to separate these complexes and examine them. But some methods can be used to identify and characterize the formed complexes without separating them from the solution. Ultraviolet-visible molecular absorption spectroscopy is a widespread method for the quantitative determination of a large variety of species. This method is used to

Table 1. Stability constant of gold and copper with cyanide and glycine[19].

| Ligand | Gold | | Copper | |
|---|---|---|---|---|
| | Complex | Log β | Complex | Log β |
| Cyanide | $Au(CN)_2^-$ | 38.3 | $Cu(CN)_2^-$ | 16.3 |
| | | | $Cu(CN)_3^{2-}$ | 21.7 |
| | $Au(CN)_4^-$ | 85.0 | $Cu(CN)_4^{3-}$ | 23.1 |
| Glycin | $Au(gly)_2^-$ | 18.0 | $Cu(gly)^+$ | 8.6 |
| | | | $Cu(gly)_2$ | 15.6 |
| | | | $Cu(gly)_2^-$ | 10.1 |

determine the ligand to the metal ratio in the $M_nL_x$ complex, which is possible by the molar ratio method or by the continuous variation method known as the job plot method.

In this research job plot method was used to determine gold and copper complexes. The job method is used in analytical chemistry to determine the stoichiometry of a binding event. In this method, a series of solutions are prepared with different ratios of ligand to metal in which the volume and the sum of the molar concentration of metal and ligand is held constant.

The absorption of each of these solutions is measured by UV-Vis spectroscopy at a specific wavelength and the observed adsorptions are plotted against the mole fractions of these two components. Fig. 1 shows a simple job plot. $X_L$ and $X_M$ are ligand mole fraction and metal mole fraction, respectively, and A is the UV-measured absorption. The ligand number (n) can be determined from Eq. (2):

$$n = \frac{X_{L\,(max)}}{1 - X_{L\,(max)}} \qquad (2)$$

where $X_{L(max)}$ is the molar ligand fraction at which maximum absorption occurred and n is ligand number.

The absorptions of the solutions were measured using a UV-1650 spectrophotometer (Shimadzu, Japan) in a wavelength range of 250 - 800 nm at room temperature.

**Experimental design**

Nine different conditions were taken into account by mixing copper or/and gold with cyanide or/and glycine (Table 2). The complexes formed in each condition were determined by spectrophotometry.

In conditions 1 to 4 (see Table 2), in which the solution contains only one metal and one ligand, the job plot method was used to determine metal complexes. For this purpose, 100 mL solution containing 1 ppm metal, and 100 mL solution containing 1 ppm of ligand were prepared then according to Table 3, ten solutions (total volume of each solution 10 mL) with different volume ratios of metal and ligand solutions were made

by magnetic agitation for 15 min in a beaker. The pH of the solutions was adjusted to 10.5 by adding NaOH. Each solution was placed in a 15 mL glass tube and then scanned by spectrophotometer in a wavelength range of 200 - 800 nm and their absorption was measured.

In conditions 5 to 9 (see Table 2), in which the solution contains two metals or two ligands, just the solution with the metals to the ligands ratio of 7 to 3 was prepared because the results of conditions 1 to 4 showed that the maximum adsorption occurred at this ratio. Then the complexes formed in the solutions were determined by spectrophotometry.
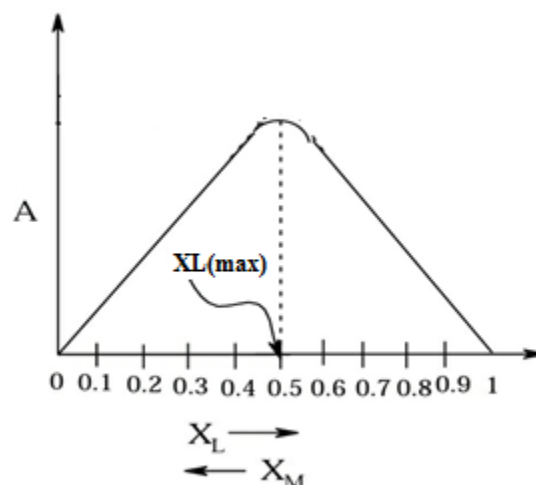


Fig. 1. A simple Job Plot.

Table 2. Different solution conditions.

| Condition | Metal | Ligand |
|-----------|-------|--------|
| 1 | gold | glycine |
| 2 | gold | cyanide |
| 3 | copper | cyanide |
| 4 | copper | glycine |
| 5 | gold + copper | cyanide |
| 6 | gold + copper | glycine |
| 7 | copper | glycine + cyanide |
| 8 | gold | glycine + cyanide |
| 9 | gold + copper | glycine + cyanide |

Table 3. Ratio of metal to ligand in solutions

| ligand solution (mL) | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----------------------|----|----|----|----|----|----|----|----|----|----|
| metal solution (mL) | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 |

## RESULTS AND DISCUSSION

### One metal and one ligand

When the metal is gold and the ligand is glycine, maximum adsorption was obtained at a wavelength of 530.5 nm and the molar ligand fraction of 0.7 ($X_m = 0.7$) (Fig. 2). Therefore according to Eq. (2):

$$n = \frac{X_{L\ (max)}}{1 - X_{L\ (max)}} = \frac{0.7}{1 - 0.7} = 2.33 \cong 2 \qquad (3)$$

It means that the number of ligands is two and the structure of the formed complex is $Au(Gly)_2^-$. In a similar manner, the complexes formed in the presence of one metal and one ligand was determined; the results are summarized and reported in Table 4.

### Two metals or two ligands

Table 5 shows the results of the identification of complexes in the presence of two metals or two ligands. Competition between copper and gold to form complexes with cyanide and glycine can be evaluated from the data presented in Table 5.

The results showed that if the glycine ligand is added to a gold-copper solution, although the stability constant of the gold-glycine complex is higher (see Table 1); the dominant species in the system is the copper-glycine complex.

If the cyanide ligand is added to a gold-copper solution, the dominant species in the system is the gold-cyanide complex which is in agreement with their stability constants (see Table 1).

If the cyanide and glycine ligands are added to a gold solution, the dominant species in the system is the gold-cyanide complex which is in agreement with their stability constants. Gold is a more stable complex with cyanide than glycine:
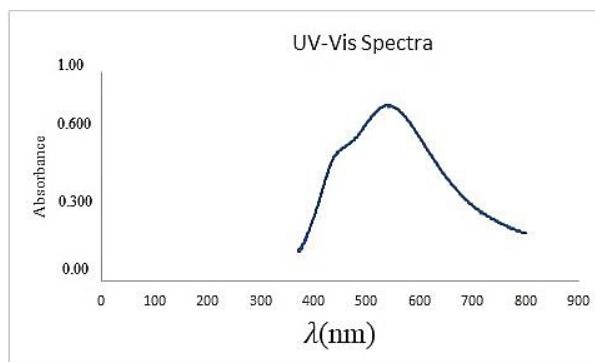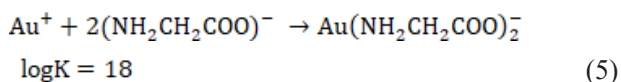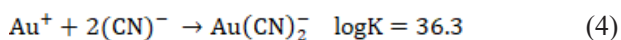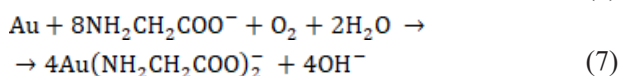


Fig. 2. UV - Vis spectra of gold-glycine complex (the metals to the ligands ratio of 7 to 3).

$$Au^+ + 2(CN)^- \rightarrow Au(CN)_2^- \quad logK = 36.3 \qquad (4)$$

$$Au^+ + 2(NH_2CH_2COO)^- \rightarrow Au(NH_2CH_2COO)_2^-$$
$$logK = 18 \qquad (5)$$

The exact leaching mechanism has not been determined but it is likely gold is complexed by cyanide and to a lesser extent glycine[24]:

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^- \qquad (6)$$

$$Au + 8NH_2CH_2COO^- + O_2 + 2H_2O \rightarrow$$
$$\rightarrow 4Au(NH_2CH_2COO)_2^- + 4OH^- \qquad (7)$$
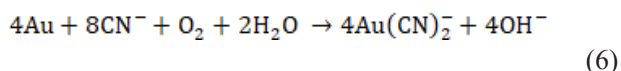
It is also possible under the low or no free cyanide environment gold cyanide is less stable so reverts to the more stable glycinate complex[24]:

$$Au(CN)_2^- + 2(NH_2CH_2COO)^- \rightarrow Au(NH_2CH_2COO)_2^- + 2CN^- \qquad (8)$$
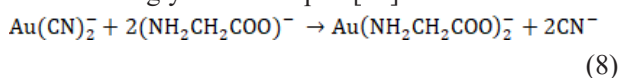
Due to the nature of glycine it is also possible to form a mixed complexation [24]:

$$2Au + 2CN^- + (NH_2CH_2COO)^- + 0.5O_2 + H_2O \rightarrow$$
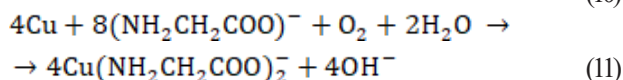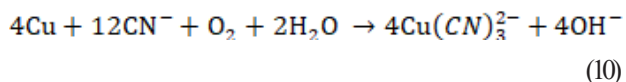$$\rightarrow Au(CN)Au(NH_2CH_2COO) + 2OH^- \qquad (9)$$
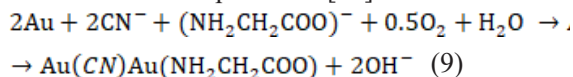
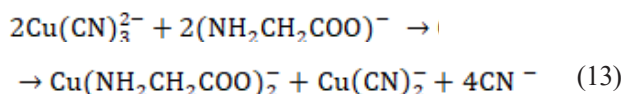If the cyanide and glycine ligands are added to a

Table 4. Identified complexes in the presence of one metal and on ligand.

| condition | Dominant metal complex | Central metal | ligand | Number of ligand branches | Predicted hybridization | Wavelength of maximum absorption |
|---|---|---|---|---|---|---|
| gold+glycine | $[Au(gly)_2]^-$ | $Au^+$ | $gly^-$ | 2 | $SP^3$ | 530.5 nm |
| gold+cyanide | $[Au(CN)_2]^-$ | $Au^+$ | $CN^-$ | 1 | SP | 274 nm |
| copper+glycine | $[Cu(gly)_2]^-$ | $Cu^+$ | $gly^-$ | 2 | $SP^3$ | 328 nm |
| copper+ cyanide | $[Cu(CN)_2]^-$ | $Cu^+$ | $CN^-$ | 1 | SP | 353 nm |

copper solution, the dominant species in the system is the copper-glycine complex which is inconsistent with their stability constants. Copper will form complexes with cyanide or glycine [24]:

$$4Cu + 12CN^- + O_2 + 2H_2O \rightarrow 4Cu(CN)_3^{2-} + 4OH^-$$
(10)

$$4Cu + 8(NH_2CH_2COO)^- + O_2 + 2H_2O \rightarrow$$
$$\rightarrow 4Cu(NH_2CH_2COO)_2^- + 4OH^-$$
(11)

The exact leaching mechanism has not been determined but it is likely copper cyanide will convert back to copper glycinate releasing cyanide for gold leaching[24]:

$$Cu(CN)_2^- + 2(NH_2CH_2COO)^- \rightarrow$$
$$\rightarrow Cu(NH_2CH_2COO)_2^- + 2CN^-$$
(12)

$$2Cu(CN)_3^{2-} + 2(NH_2CH_2COO)^- \rightarrow$$
$$\rightarrow Cu(NH_2CH_2COO)_2^- + Cu(CN)_2^- + 4CN^-$$
(13)

So adding back copper cyanide and recycling is not a bad thing as still leaches gold[24]:

$$4Au + 8Cu(CN)_3^{2-} + O_2 + 2H_2O \rightarrow$$
$$\rightarrow 4Au(CN)_2^- + 8Cu(CN)_2^- + 4OH^-$$
(14)

If the cyanide and glycine ligands are added to a gold-copper solution, the dominant species in the system are the copper-glycine and the gold-cyanide complexes. It does not mean that gold-glycine and copper-cyanide complexes are not formed, but rather that these complexes are less formed.

**CONCLUSIONS**

The study describes the characterization of gold and copper complexes in the cyanide-glycine system by ultraviolet-visible molecular absorption spectroscopy method. The results showed that both copper and gold can form complexes with cyanide and glycine. In the glycine-gold-copper system, in the competition between copper and gold, although the stability constant of the gold-glycine complex is higher, the dominant species formed is the copper-glycine complex. In the cyanide-gold-copper system, gold forms complexes with cyanide and to a lesser extent glycine which is in agreement with their stability constants. It is also possible to form a mixed com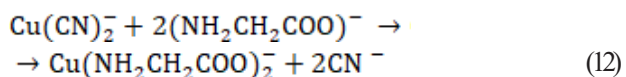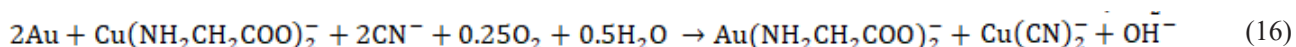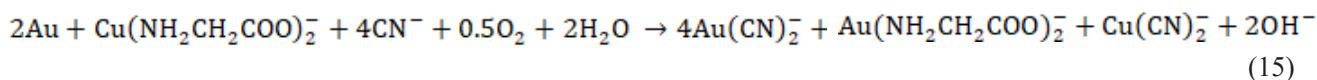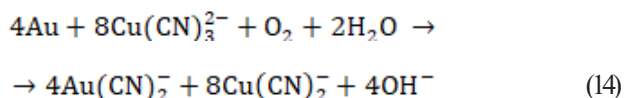plexation. If the cyanide and glycine ligands are added to a gold solution, the dominant species in the system is the gold-cyanide complex. In the cyanide-glycine-copper system, the dominant species in the system is the copper-glycine complex. It is also possible

$$2Au + Cu(NH_2CH_2COO)_2^- + 4CN^- + 0.5O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + Au(NH_2CH_2COO)_2^- + Cu(CN)_2^- + 2OH^-$$
(15)

$$2Au + Cu(NH_2CH_2COO)_2^- + 2CN^- + 0.25O_2 + 0.5H_2O \rightarrow Au(NH_2CH_2COO)_2^- + Cu(CN)_2^- + OH^-$$
(16)

Table 5. Identified complexes in the presence of two metals or two ligands.

| condition | Absorption at wave length 530.5 nm | Absorption at wave length 274 nm | Absorption at wave length 328 nm | Absorption at wave length 353 nm | Dominant metal complex |
|---|---|---|---|---|---|
| gold and copper+glycine | 0.003528 | | 0.005554 | | [Cu(gly)$_2$]$^-$ |
| gold and copper+cyanide | | 0.007965 | | 0.004303 | [Au(CN)$_2$]$^-$ |
| gold+glycine and cyanide | 0.004867 | 0.007813 | | | [Au(CN)$_2$]$^-$ |
| copper+glycine and cyanide | | | 0.00671 | 0.0032 | [Cu(gly)$_2$]$^-$ |
| copper and gold+glycine and cyanid | 0.004545 | 0.02681 | 0.018204 | 0.015869 | [Au(CN)$_2$]$^-$ [Cu(gly)$_2$]$^-$ |

that copper cyanide converts back to copper glycinate and releases cyanide. When cyanide and glycine ligands are added to a gold-copper solution, the dominant species in the system are the copper-glycine and the gold-cyanide complexes. It does not mean that gold-glycine and copper-cyanide complexes are not formed, but rather that these complexes are less formed.

These results were obtained in laboratory conditions, in the actual leaching of gold ore many chemical and physical factors such as concentration of reagents, pH, temperature, ionic strength, dissolved oxygen, and background salts affect the kinetics of gold leaching so more investigation is needed. However, these results can be helpful to a better understanding of gold ore leaching in the presence of cyanide and glycine lixiviants.

## REFERENCES

1. G. Hilson, A.J. Monhemius, Alternatives to cyanide in the gold mining industry: what prospects for the future? Journal of Cleaner production, 14, 12–13, 2006, 1158-1167.

2. D.M. Muir, A review of the selective leaching of gold from oxidised copper--gold ores with ammonia--cyanide and new insights for plant control and operation, Minerals Engineering, 24, 6, 2011, 576-582.

3. F. Habashi, One hundred years of cyanidation, Can. Min. Metall. Bull., 80, 905, 1987, 108-114.

4. M.G. Hasab, F. Rashchi, S. Raygan, Chloride--hypochlorite leaching and hydrochloric acid washing in multi-stages for extraction of gold from a refractory concentrate, Hydrometallurgy, 142, 2014, 56-59.

5. S. Örgül, Ü. Atalay, Reaction chemistry of gold leaching in thiourea solution for a Turkish gold ore, Hydrometallurgy, 67, 1-3, 2002, 71-77.

6. X. Dai and M. I. Jeffrey, The effect of sulfide minerals on the leaching of gold in aerated cyanide solutions, Hydrometallurgy, 82, 3-4, 2006, 118-125.

7. C. Xia, Associated sulfide minerals in thiosulfate leaching of gold: problems and solutions. Queen's University, 2008.

8. S. Zheng, Y. Wang, L. Chai, Research status and prospect of gold leaching in alkaline thiourea solution, Minerals engineering, 19, 13, 2006, 1301-1306.

9. M.G. Aylmore, Alternative lixiviants to cyanide for leaching gold ores, in Advances in gold ore processing, Amsterdam, Netherlands: Elsevier, 2005, pp. 501-539.

10. E.A. Oraby, J.J. Eksteen, The selective leaching of copper from a gold - copper concentrate in glycine solutions, Hydrometallurgy, 150, 2014, 14-19.

11. J.J. Eksteen, E. Oraby, A process for precious metals recovery, PCT/AU2014/ 000877, 2014.

12. J.J. Eksteen, The leaching of gold, silver and their alloys in alkaline glycine-peroxide solutions and their adsorption on carbon, Hydrometallurgy, 152, 2014, 199-203.

13. J.J. Eksteen, E.A. Oraby, The leaching and adsorption of gold using low concentration amino acids and hydrogen peroxide : Effect of catalytic ions , sulphide minerals and amino acid type, Minerais Engineering, 70, 2015, 36-42.

14. M.R. Azadi, A. Karrech, M. Elchalakani, M. Attar, Microfluidic study of sustainable gold leaching using glycine solution, Hydrometallurgy, 185, 2019, 186-193.

15. K. Barani, M. Dehghani, M.R. Azadi, A. Karrech, Leaching of a polymetal gold ore and reducing cyanide consumption using cyanide-glycine solutions, Minerals Engineering, 163, 2021, 106802.

16. E.A. Oraby, J.J. Eksteen, The leaching of gold, silver and their alloys in alkaline glycine--peroxide solutions and their adsorption on carbon, Hydrometallurgy, 152, 2015, 199-203.

17. E.A. Oraby, J.J. Eksteen, B.C. Tanda, Gold and copper leaching from gold-copper ores and concentrates using a synergistic lixiviant mixture of glycine and cyanide, 169, 2017, 339-345.

18. S. Aksu, F.M. Doyle, Electrochemistry of copper in aqueous glycine solutions, Journal of the Electrochemical Society, 148, 1, 2001, B51-B57.

19. E.A. Oraby, J.J. Eksteen, Gold leaching in cyanide-starved copper solutions in the presence of glycine, Hydrometallurgy, 156, 2015, 81-88.

20. A. Azizi, C.F. Petre, F. Larachi, Leveraging strategies to increase gold cyanidation in the presence of sulfide minerals - Packed-bed electrochemical reactor approach, Hydrometallurgy, 111, 2012, 73-81.

21. Z. Deng, E.A. Oraby, J.J. Eksteen, The sulfide precipitation behaviour of Cu and Au from their

aqueous alkaline glycinate and cyanide complexes, Separation and Purification Technology, 218, 2019, 181-190.

22. C.P. Broeksma, Evaluating the applicability of an alkaline amino acid leaching process for base and precious metal leaching from printed circuit board waste, Master Engineering Thesis, Stellenbosch University, 2018.

23. P.J. Tauetsile, E.A. Oraby, J.J. Eksteen, Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper . Part 1 : Isotherms, Separation and Purification Technology, 211, 2019, 594-601.

24. F. Trask, E. Oraby, None and Reduced cyanide gold extraction systems, in ALTA 2020 Online Conference, 2020.