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## Role of Glycine in Cyanidation of Copper Bearing Gold Ores: an Experimental and Molecular Modeling Study

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### Abstract

The presence of copper bearing minerals in cyanidation of gold ores may lead to several challenges in the CIP/CIL circuits. Many solutions have been proposed to address these problems, one being the use of glycine in the cyanidation process. Here, the experimental as well as molecular modelling studies using Density Functional Theory (DFT) have been conducted to investigate the glycine role in cyanidation of copper bearing gold ores. The results show that in the presence of glycine in the solution containing copper-cyanide species and in very low or zero free cyanide content, the dissolution rate of gold is significantly improved (3.02 vs. 0.23 ppm), while no improvement is observed in copper free or cyanide enriched solutions. Molecular modeling has been performed to interpret the laboratory results as well as to identify the mechanisms. The modeling results demonstrate that in cyanide deficient solutions, cyanide complex of copper complexes ( $E = -319 \text{ kCal.mol}^{-1}$ ) is replaced by glycine, and the free cyanide produced results in higher gold cyanidation as well as lower copper cyanide formation.

## 1. Introduction

With the introduction of the gold cyanidation process in 1890, its immediate success in the gold mining industry was achieved all around the world [1]. Since then, this method has been widely used as the main technique for gold ores processing for more than 125 years [2]. The reason for this widespread application can be attributed to the very high efficiency and relatively low cost of cyanidation process [3].

Despite the many benefits of using cyanide in gold extraction, there are challenges associated with this process [4]. One of the major limitations of cyanide application is the presence of cyanide-soluble minerals and compounds in the ores. These materials increase operating costs by consuming cyanide and other chemical reagents and impact

subsequent processes of gold recovery from the leaching solutions [5]. One of the major challenging mineral groups in gold ores is copper bearing minerals [6]. Table 1 lists the major copper minerals and their solubility in alkaline cyanide solutions (particle size of 100%-150 micron and 0.1% sodium cyanide concentration in the solution in equilibrium condition) [7]. Despite the negative effect of sulfide species [2], this table demonstrates that the main challenging copper minerals are oxides. It is interesting that the dominant copper sulfide mineral, chalcopyrite only dissolves up to 6% in cyanide solution and is not challenging in terms of cyanide consumption by dissolved copper as much as other common copper minerals.

**Table 1. Dissolution rate of different copper bearing minerals.**

Mineral	Chemical composition	Copper content %	Dissolution rate % (23 °C)
Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$	55.3	94.5
Malachite	$\text{Cu}_2\text{CO}_3(\text{OH})_2$	57.5	90.2
Chalcocite	$\text{Cu}_2\text{S}$	79.9	90.2
Copper	$\text{Cu}$	100.0	90.0
Cuprite	$\text{Cu}_2\text{O}$	88.8	85.5
Bornite	$\text{Cu}_5\text{FeS}_4$	63.3	70.0
Chrysocolla	$\text{CuSiO}_3$	45.5	11.8
Chalcopyrite	$\text{CuFeS}_2$	34.6	5.6

Copper forms three types of complexes with cyanide including  $\text{Cu}(\text{CN})_2^-$ ,  $\text{Cu}(\text{CN})_3^{-2}$  and  $\text{Cu}(\text{CN})_4^{-3}$ . The speciation of copper cyanide complexes are strongly dictated by pH and  $\text{CN}^-$  to Cu molar ratio [8]. The high order copper cyanide  $\text{Cu}(\text{CN})_4^{-3}$  is abundant at higher pH ( $> 12$ ) and higher  $\text{CN}^-$  to Cu ratios ( $> 6.5$ ), while lower order copper cyanide  $\text{Cu}(\text{CN})_2^-$  is dominant at lower pH (7-9) and lower  $\text{CN}^-$  to Cu ratios ( $< 2.5$ ).  $\text{Cu}(\text{CN})_3^{-2}$  is the predominant specie in a wide range of pH and cyanide concentrations [8]. The  $\text{Cu}(\text{CN})_3^{-2}$  and  $\text{Cu}(\text{CN})_4^{-3}$  species lead to a higher cyanide consumption which can be prevented by controlling the amount of free cyanide (forming lower order copper complexes). However, the competitive effect of these species adsorption on the surface of activated carbon with gold cyanide complex is much lower than that of  $\text{Cu}(\text{CN})_2^-$  [9]. The following effects can be listed as the role of copper bearing minerals in cyanidation of gold ores as have been researched by many researcher works in the last few decades:

1. Gold dissolution by copper cyanide complexes in cyanide deficient solutions [9, 10]
2. Gold pre-robbing by copper sulfide minerals [11]
- 3- Competition with  $\text{Au}(\text{CN})_2^-$  to be adsorbed on the activated carbon surface [7, 12]
4. Cyanide consumption, especially by  $\text{Cu}(\text{CN})_3^{-2}$  and  $\text{Cu}(\text{CN})_4^{-3}$  species [7, 12]
5. Weak acid dissociable (WAD) formation in the tailing [4]

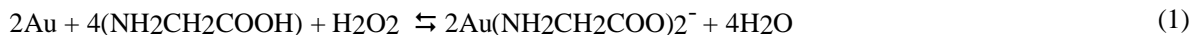
However, the mechanism of interaction between

copper cyanide species in the cyanidation process has not received much attention. It has been clearly demonstrated that only highly soluble copper minerals interfere with gold cyanidation by increasing cyanide consumption [13]. This effect has been attributed to the lack of cyanide for gold dissolution, however staged leaching and reduction of dissolved copper cyanide complexes improve the gold dissolution [13, 14]. A computational modeling study explains this effect by surface passivation of gold via formation of  $\text{AuCN} - \text{CuCN}$  passive layer [6].

Various methods have been developed to overcome this problem over the last few decades and some have been applied on an industrial scale. Five general approaches can be summarized as follows:

1. Copper leaching before cyanidation [15, 16]
2. Flotation of sulfides, roasting the flotation concentrate, and then leaching the roasted concentrate [8, 10]
3. Leaching using cyanide alternatives such as thiourea, thiosulfate or cyanide-ammonia [9, 11]
4. Optimizing the cyanidation operating condition (careful control of free cyanide, adding lead nitrate, staged leaching ...) [12, 17, 18]
5. Recovery of cyanide from gold leaching wastewater (SART, AVR ...) [19]

In the recent years, studies have been conducted on the use of amino acids, especially glycine as an alternative leaching media or in conjunction with cyanide in the gold recovery process [20-24]. Glycine is able to leach gold in the presence of peroxide and form a strong complex with monovalent gold  $\text{Au}(\text{H}_2\text{NCH}_2\text{COO})_2^-$ . Dissolution of gold in glycine alkaline solution is described by the following reaction (Equation 1) [22]:

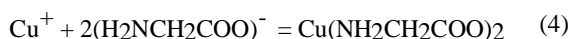
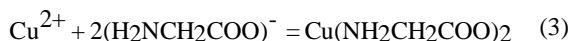
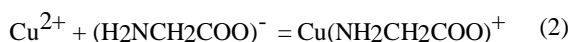


The dissolution rate and stability of gold glycine is dependent on the pH and Eh of the leaching media as well as the presence of peroxide in the alkaline solution. The presence of hydrogen peroxide prominently intensifies the dissolution of both gold and copper [22].

In addition, glycine has demonstrated synergistic effects with cyanide, and can significantly improve gold extraction from copper bearing ores. This process has several advantages including but not limited to less cyanide consumption, higher extraction rate for gold, formation of non-toxic copper glycinate in the wastewater with almost no environmental impacts in comparison with copper cyanide WADs and finally reduction of cyanide deposition to the environment by replacing with a safe and environmentally friendly reagent [24].

Despite the effective role of glycine in gold cyanidation, the synergism mechanism between glycine and cyanide is almost unknown. Three main mechanisms have been proposed to explain the progressive role of glycine in the glycine-gold-copper cyanide system [23].

1. Formation of complexes with copper(I) and copper(II) according to Equation 2, Equation 3, and Equation 4. Thus copper cyanide complexes which consume cyanide required for the gold dissolution is not formed:



2. Dissolution of  $\text{Cu}(\text{OH})_2$  inhibitor layer, which is formed on the gold surface in cyanidation process.
3. Complexing with gold according to the Equation 1 in the presence of an oxidizer, thereby increasing the dissolution rate of gold.

A number of studies have been accomplished on the use of glycine to reduce the negative effect of copper bearing minerals so far. Most of the studies have focused on introducing this alternative leaching media and demonstrating the process improvement in the presence of glycine [25-29]. There is no understanding of how glycine plays the role in copper cyanide bearing solutions. The purpose of this study is to investigate the role of

glycine in the gold cyanidation of copper cyanide bearing solutions using a combination of experimental and molecular modeling methods. For this purpose, glycine has been added to the copper bearing cyanide solution and gold dissolution rate has been examined in different operating conditions. To understand the experimental results, the soluble species are modeled using quantum molecular modeling methods (density functional theory) and molecular-scale interactions between the species were examined. The results of this study can be effectively used in understanding the synergism effect of glycine in gold cyanidation which can be ultimately utilized in optimizing and industrializing of this process.

## 2. Materials and Methods

This study was conducted with two experimental and molecular modelling methodologies; for each, specific materials and methods has been used in accordance with the requirements of the technique.

In the experimental studies, Cu cyanide solutions have been prepared by dissolution of CuCN salt in sodium cyanide solution with the specified concentration of 0.055 mM Cu and CN-/Cu molar ratios of 2:1, 3:1, 4:1, 5:1, 7:1, and 11:1. The leaching rate of pure 24 carat (99.99%) gold foil with precise 4 mg weight was evaluated in these solutions. The required amount of glycine was added to the solutions based on the experimental condition. The variation in the gold leaching rate was investigated by measuring gold content in the solution by atomic absorption spectrometry (Agilent 220AA). All of the raw materials are from Merck products and tests were carried out at ambient temperature and pressure. All of the cyanidation tests were conducted in 200 mL leaching solution over a magnetic stirrer with consistent rpm and pH of 11.5.

DFT calculations have been carried out using the Dmol<sup>3</sup> module implemented in Accelrys Materials Studio version 2017. The copper and gold complexes as well as glycine were modelled using the generalized gradient functional BYLP (exchange functional Becke combined with the Lee–Yang–Parr nonlocal correlation functional), using an Octa-core desktop PC. A double numerical basis set was applied including two atomic orbitals for each occupied orbital for all atoms plus a p-function polarization on hydrogen

atoms (DNP<sup>1</sup>) to represent hydrogen bonding [30]. The convergence criteria for geometry

optimizations are summarized in Table 2.

**Table 2. The convergence tolerances for geometry optimization Calculation Convergence tolerance**

parameters	Tolerances
Maximum displacement	$5 \times 10^{-4}$ Å
Maximum force	$2 \times 10^{-4}$ Hartrees/Å
Energy	$1 \times 10^{-6}$ Hartrees
SCF	$10^{-7}$ Hartrees
	$10^{-6}$ Hartrees only for pentagon fullerene -like model
Smearing	No
Orbital Cut off	5.0 Å

No pseudo-potentials or effective core potentials were utilized in this study, and all the results are based on “all electron relativistic” calculations. To represent the local environment, calculations are performed using continuum solvation model, namely COSMO (COnductor like Screening MOdel) [31]. The dielectric constant of water (78.54) was used to outline the solutions in COSMO, presuming a very dilute media with minor dielectric constant deviation from pure water. Multipolar expansion was used for calculation of the solvation energy for all of the models.

To investigate the feasibility of the reactions, the interaction energy of the reactions was calculated by molecular modeling. For this purpose, the energy difference of each reaction product was calculated from the energy of the reactants. Although research indicates that there is a systematic discrepancy between the free energy computed in molecular modeling by this method and the free energy obtained from thermodynamic measurements [32, 33], it can still serve as a valid basis for comparing the feasibility of different reactions to be used:

$$E_{\text{interaction}} = E_{\text{product1}} + E_{\text{product2}} + E_{\text{products3}} + \dots - (E_{\text{Reactant1}} + E_{\text{Reactant2}} + E_{\text{Reactant3}} + \dots) \quad (5)$$

where  $E_{\text{products}}$  is the total energies of the product clusters and  $E_{\text{reactants}}$  is the total energy of the reactants. The higher negative amounts of interaction energy indicate favorable and stronger reaction compared to positive or lower negative values [34]. Finally, the results of molecular modeling were used to validate and explain the trends observed in laboratory studies.

### 3. Results and Discussion

#### 3.1. Experimental results: Copper free glycine and cyanide media

Cyanide and glycine are both capable of dissolving gold. Figure 1 compares the dissolution rate of pure gold in glycine and cyanide. As shown in Figure 1, the dissolution of gold in 1 M glycine solution (75 g/L) was 0.71 mg/L, in comparison with 0.63 mg/L gold dissolution in 3.8 mM sodium cyanide solution (0.1 g/L). The cyanide concentration was chosen at the lowest amount, about 15 times smaller than the amount of sodium cyanide used in the industry and 260 times lower than glycine concentration to achieve comparable gold dissolution rate.

<sup>1</sup> Double Numerical Polarization

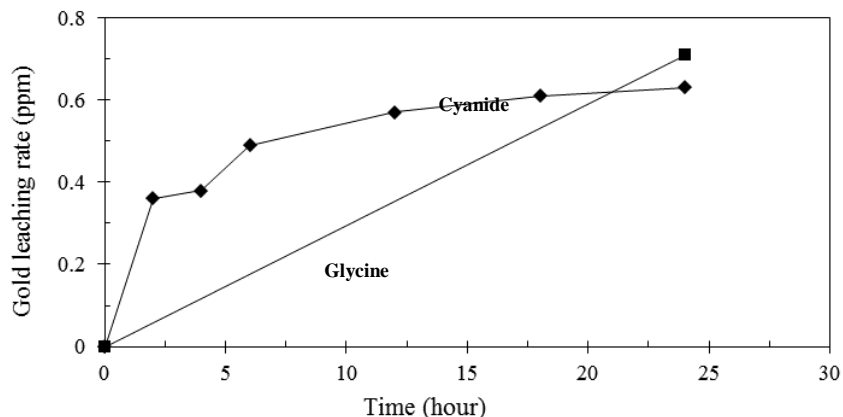


Figure 1. Leaching rate of gold in cyanide and glycine.

### 3.2. Experimental results: Copper bearing glycine and cyanide media

Given that the amount of gold dissolved by glycine is very low and slow, it is not economically feasible to use this process. Figure 2 compares the dissolution rate of gold in the cyanide-glycine-

copper and cyanide-copper systems under the same conditions, which as it can be observed, the gold dissolution in the cyanide-glycine-copper system is significantly improved. In the other words, it is depicted that glycine is only effective in copper bearing solutions.

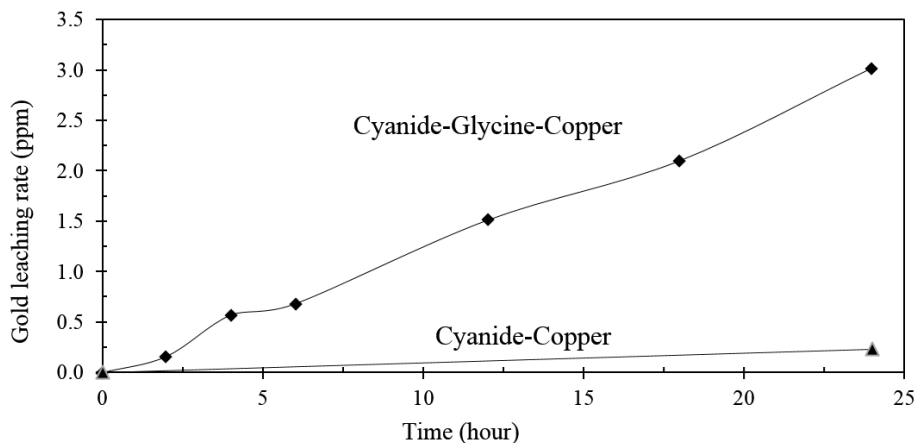


Figure 2. Dissolution rate of gold in cyanide-glycine-copper and cyanide-copper systems under identical conditions of 11 mM cyanide, 5.5 mM copper, and pH 11.5.

### 3.3. Experimental results: Effect of $CN^-/Cu$ ratio

Figure 3 shows the results of leaching experiments at fixed concentrations of glycine of 13 mM and 5.5 mM Cu and different  $CN^-/Cu$  molar ratios (2:1, 3:1, 4:1, 5:1, 7:1, and 11:1). It is

observed that the gold dissolution intensifies with increasing  $CN^-/Cu$  molar ratio to 4:1, while by increasing the  $CN^-/Cu$  ratio higher than 4:1, the amount of gold dissolution declines and then as the amount of cyanide increases, the amount of gold dissolution rises again slowly.

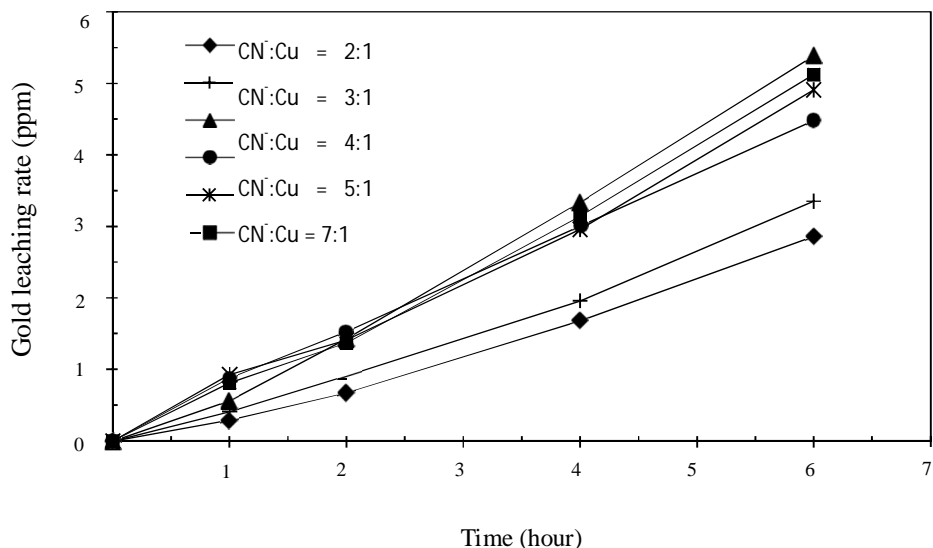


Figure 3. Gold dissolution under different cyanide content, 5.5 mM copper, 13 mM glycine and pH 11.5.

In order to investigate the role of glycine in gold dissolution in the presence of high amount of cyanide ( $\text{CN}^-/\text{Cu} = 11:1$ ), two experiments were performed, one with glycine and another without it in similar conditions (Figure 4). As shown in Figure 4, the solubility of gold in the solution containing

60.5 mM cyanide, 5.5 mM copper, and 13 mM glycine is 4.71 mM, while the solubility of gold in the similar condition without glycine is 5.12 mM.

In other words, when  $\text{CN}^-/\text{Cu}$  is high enough, the significant synergism effect of cyanide and glycine disappears almost completely.

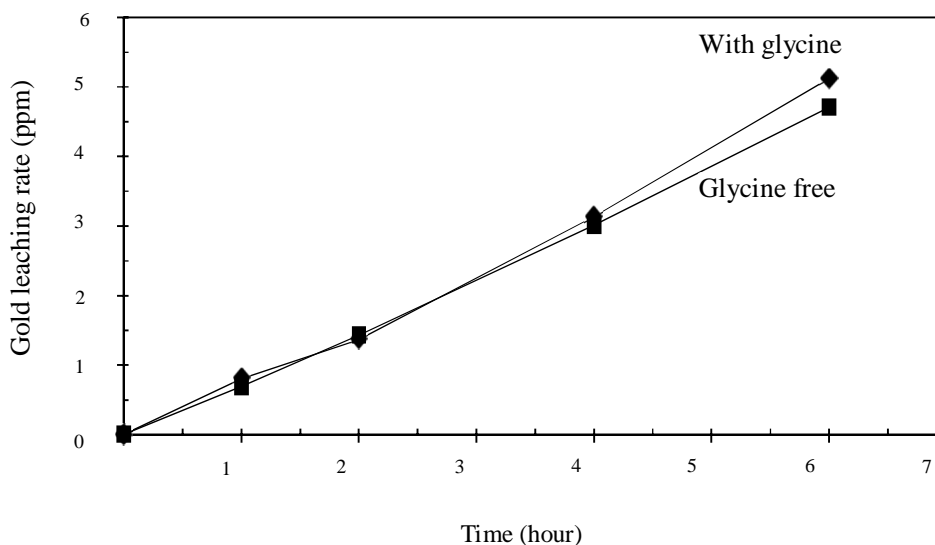


Figure 4. Evaluation of the role of glycine in gold dissolution in a solution containing 60.5 mM cyanide, 5.5 mM copper, and pH 11.5.

### 3.4. Molecular modelling results

In this section, according to the Eh-pH diagram shown in Figure 5, different species that can be formed in this system have been identified and the cluster structures including  $\text{Cu}(\text{Gly})_2^-$ ,  $\text{Cu}(\text{Gly})_2$ ,

$\text{Au}(\text{CN})_2^-$ ,  $\text{Au}(\text{Gly})_2^-$ ,  $\text{CuCN}$ , and  $\text{Cu}(\text{CN})_2^-$  were modeled and shown in Figure 6. The hydration and bonding energy of each of the complexes are also shown in the Table 3 reported. Then the free energy of each of the possible reactions was measured and reported in Table 4.

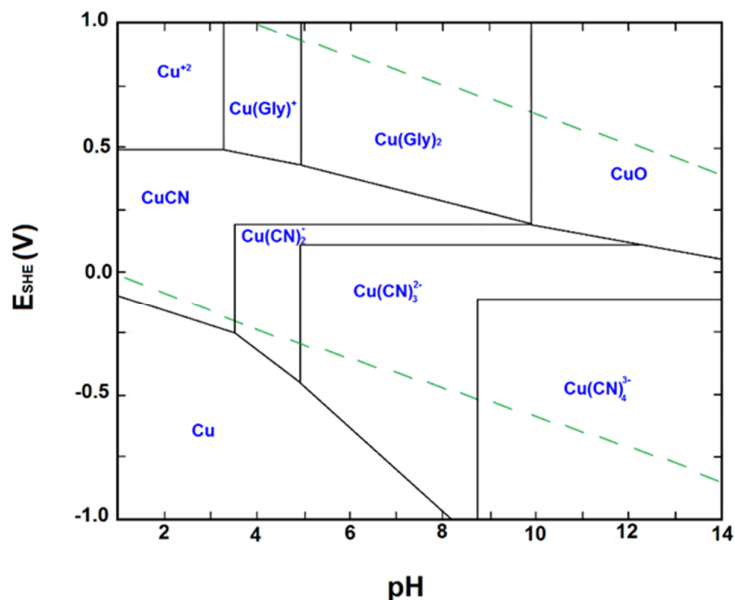


Figure 5. Eh-pH diagram at 11 mM cyanide, 5.5 mM copper, and 1 g/L glycine.

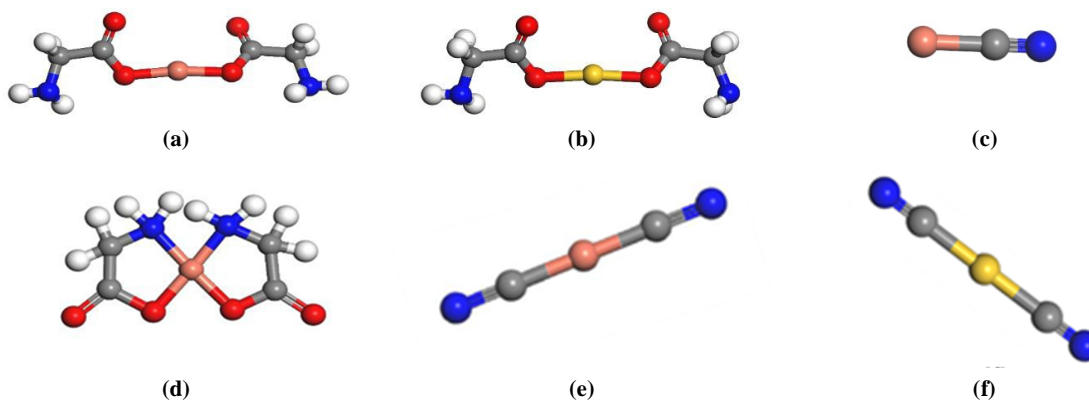


Figure 6. Optimized geometry of (a)  $\text{Cu}(\text{Gly})_2^-$ , (b)  $\text{Au}(\text{Gly})_2^-$ , (c)  $\text{Cu}(\text{Gly})_2$ , (d)  $\text{Cu}(\text{CN})_2^-$ , (e)  $\text{CuCN}$ , and (f)  $\text{Au}(\text{CN})_2^-$  (Yellow: Gold, Red: Copper, Gray: Carbon, Blue: Nitrogen, Red: Oxygen, and White: Hydrogen).

Table 3. Hydration and binding energies of the optimized geometries.

Complex	Hydration energy (Kcal)	Binding energy (Kcal)
$\text{Au}(\text{CN})_2^-$	-50.866	-713.40
$\text{CuCN}$	-17.913	-301.35
$\text{Au}(\text{Gly})_2^-$	-66.602	-1997.30
$\text{Cu}(\text{Gly})_2^-$	-69.663	-2013.70
$\text{Cu}(\text{CN})_2^-$	-53.076	-701.74
$\text{Cu}(\text{Gly})_2$	-59.624	-1933.12

**Table 4. Calculated energy of reactions from DFT results.**

Equation 6	$\text{Au}^+ + 2\text{CN}^- = \text{Au}(\text{CN})_2$	-173
Equation 7	$\text{Cu}^+ + \text{CN}^- = \text{CuCN}$	-80
Equation 8	$\text{Cu}^+ + 2\text{CN}^- = \text{Cu}(\text{CN})_2$	-129
Equation 9	$\text{Cu}^+ + 2\text{Gly}^- = \text{Cu}(\text{Gly})_2$	-91
Equation 10	$\text{Au}^+ + 2\text{Gly}^- = \text{Au}(\text{Gly})_2$	-112
Equation 11	$\text{Cu}^{2+} + 2\text{Gly}^- = \text{Cu}(\text{Gly})_2$	-268
Equation 12	$2 \text{Cu}(\text{CN})_2 + 2\text{Gly}^- = \text{Cu}(\text{Gly})_2 + 3\text{CN}^- + \text{CuCN}$	86
Equation 13	$8 \text{Cu}(\text{CN})_2 + 8\text{Gly}^- + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{Cu}(\text{Gly})_2 + 12\text{CN}^- + 4\text{CuCN} + 4\text{OH}^-$	373
Equation 14	$\text{Au}(\text{Gly})_2 + \text{Cu}(\text{CN})_2 = \text{Au}(\text{CN})_2 + \text{Cu}(\text{Gly})_2$	-23
Equation 15	$\text{Au}(\text{Gly})_2 + \text{Cu}(\text{CN})_2 + \text{O}_2 + 2\text{H}_2\text{O} = \text{Au}(\text{CN})_2 + \text{Cu}(\text{Gly})_2 + 4\text{OH}^-$	-319
Equation 6	$\text{Au}^+ + 2\text{CN}^- = \text{Au}(\text{CN})_2$	-173

According to Table 4, the formation of both gold and copper glycinate are less favorable than cyanide complexes (-112 vs. -173 and -91 vs. -129 kCal/mol). This may explain very well, the lower leaching rate of both copper and gold in glycine systems comparing to cyanide [22-24]. However, the difference between the free energy of reaction with cyanide and glycine is much higher in gold in comparison with copper (-61 vs. -38 kCal/mol). In other words, copper has a lower selectivity for complexation with glycine or cyanide [23]. It is very interesting that although the reaction of glycine with copper is less favorable, ligand exchange between gold glycinate and copper cyanide (Equation 15) results in very high free energy of -319 kCal/mol. This effect is reported here for the first time as one of the synergism effects of glycine with cyanide in copper bearing solutions.

To explain the experimental results and trends reported in different CN<sup>-</sup>/Cu ratios, the free energy of reactions can be effectively used [2, 6, 7]. The leaching rate of gold in glycine is much lower than cyanide due to the much lower free energy. When copper is introduced, in cyanide deficient systems, copper and gold both compete to form complexes with both cyanide and glycine. As copper is more dominant and form more stable complexes with cyanide (-91 vs. -129 kCal/mol), so it overtakes gold and gold forms glycinate complex in lack of cyanide ligands. In the next step a strong reaction between copper cyanide and gold glycinate results in release of cyanide and formation of strong gold complexes.

In higher CN<sup>-</sup>/Cu ratios, the synergism effect of Equation 15 disappears as there is no deficiency for cyanide complexes. This has been confirmed before in experimental studies [23]. However, copper ions form cyanide complexes and consume

significant amount of cyanide so the gold dissolution rate decreases. By increasing the CN<sup>-</sup>/Cu further, there will be enough cyanide ligands for both copper and gold which results in increasing the gold dissolution again and synergism effect disappears.

#### 4. Conclusions

This study attempted to shed light on the synergism effect of glycine in copper bearing gold cyanidation solutions. The experimental and theoretical studies have been used in conjunction to understand the synergism effect. The outcome of this study can be concluded as follows:

- The gold dissolution rate is much lower in glycine solutions in comparison with cyanide and comparable results are achieved in 260 times higher glycine concentrations (1 M glycine and 3.8 mM sodium cyanide).
- The synergism effect of glycine only appears in copper bearing solutions in glycine-cyanide systems. In lack of copper no improvement was observed by comparable gold leaching rate in presence and lack of glycine.
- The CN<sup>-</sup>/Cu molar ratio plays a critical role in effectivity of glycine synergism. In CN<sup>-</sup>/Cu molar ratio lower than 4:1, the gold dissolution is significantly improving in glycine bearing solution, while in higher than 4:1, the effect is less pronounced and increases again upto 11:1.
- The molecular modelling studies explain, almost all the trend observed in the experimental test works based on the free energy of reactions between clusters in COSMO media.
- A strong reaction between copper cyanide and gold glycinate in cyanide deficient solutions seems to be responsible for synergism effect



observed in the copper bearing solutions. The synergism effect disappears in non-deficient solutions.

Although the synergism effect of glycine with cyanide in copper solutions can be explained very well by very high reaction energy of complex replacement between gold and copper, further works needs to be done to explore the effects on anodic oxidation of solid state gold and copper.

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## نقش گلیسین در سیانوراسیون کانسنگ‌های طلا مس-دار: مطالعه تجربی و مدل‌سازی مولکولی

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## چکیده:

وجود کانی‌های حاوی مس در سیانوراسیون کانسنگ‌های طلا می‌تواند به چالش‌های متعددی در مدارهای CIL/CIP منجر شود. راهکارهای مختلفی برای رفع این مشکلات ارائه شده است که استفاده از گلیسین در فرایند سیانوراسیون یکی از آنها است. در این مقاله، مطالعات آزمایشگاهی و مدل‌سازی مولکولی با استفاده از تئوری تابع چگالی (DFT) برای بررسی نقش گلیسین در سیانوراسیون کانسنگ‌های مس‌دار انجام شده است. نتایج نشان می‌دهند حضور گلیسین در محلول‌های حاوی گونه‌های سیانیدی مس و در غلظت‌های بسیار پایین یا صفر سیانور آزاد، نرخ انحلال طلا را به‌طور قابل‌توجهی (3/02 در مقابل 0/23 گرم در تن) بهبود می‌دهد، در حالی‌که در محلول‌های فاقد مس یا غنی از سیانور بهبودی مشاهده نمی‌شود. مدل‌سازی مولکولی برای تجزیه و تحلیل نتایج آزمایشگاهی و همچنین شناسایی مکانیزم‌ها انجام شده است. نتایج مدل‌سازی در محلول‌های فقیر از سیانور نشان می‌دهد که کمپلکس‌های سیانوری مس با گلیسین (انرژی واکنش 319- کیلوکالری بر مول) توسط گلیسین جایگزین شده و سیانور آزاد تولید شده منجر به بهبود بازیابی طلا و از سوی دیگر عدم تشکیل سیانیدهای مس می‌شود.

کلمات کلیدی: گلیسین، سیانید طلا، سیانیدهای مس، DFT.