Speciation Modelling of Cyanide in Effluent from Small Scale Gold Mining in Southern Ecuador

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Abstract: Most of the gold mining plants in Ecuador are in the south of the country. Gold extraction processes use large amounts of cyanide and produce industrial wastewater that is discharged into the rivers. These discharges are loaded with cyanide, which is very reactive and easily forms bonds with a wide variety of chemical elements and heavy metals forming different cyanide species. This study aims to simulate the speciation of cyanide in the effluents from small-scale gold mining in Southern Ecuador to analyze these species as potential water pollutants. Visual MINTEQ simulated the speciation models with temperature, pH, and cyanide concentrations, copper, arsenic, iron, and aluminum as input data. Species like CN^-, $HCN_{(aq)}$, and $Cu(CN)^2$ complex are formed in the tailings effluent. This research concludes that the metal-cyanide complexes formed in the study sites are weak complexes that can release free cyanide in acid conditions, becoming dangerous for the environment. The development of future research that incorporates variables such as conductivity, temperature, and redox potential will lead to an accurate assessment of the cyanide impact on the water quality of the rivers, on people who are supplied with this water source, and on the mining workers health.
Keywords: Cyanide, gold- mining, speciation, tailings, complexes.

1. Introduction

Gold extraction activities have increased due to a growing international demand for this metal. The development of new methods for its extraction allows practically finished deposits can be exploited through the cyanide leaching process [1].

This practice has been linked to environmental pollution and health risk due to metals and chemical substances used in the process. Since the '90s, mercury and cyanide were widely used in leaching processes, which significantly improved the recovery of gold. Other chemicals such as lead nitrate are generally added to increase extraction efficiency [2] [3].

The process of extracting gold by mercury amalgam has been set aside. It is an inefficient and dangerous method compared to cyanide since it is heavy and harmful to environmental and public health. Leaching with cyanide allows recovering more than 90% of the gold, compared to 60% using extraction by mercury; however, cyanide is also considered one of the most potent poisons worldwide [4] [5].

Leaching involves contacting the mineral which contains the gold with a previously prepared cyanide solution. Cyanide has a high affinity to metals, tends to bind with gold atoms, and separates it easily from the other minerals present. This chemical process involves the formation of a very stable metal-cyanide complex, and the method is more efficient compared to others used in the past [6].

Cyanide reacts easily with other compounds. Depending on the conditions of the system, it can be combined with a wide variety of other chemical elements such as sulfur, organic carbon compounds, and even with living organisms. Because of cyanide affinity with other metals, it easily forms bonds with gold, copper, zinc, mercury, and iron becoming the known "metal-cyanide complexes" that are usually very soluble in water [7].

In Ecuador, mining represents an ancient activity since 300 BC due to their geological conditions. Gold is the primary extraction product in the country and represents economically significant export items [8].

The context of small-scale mining implies the direct involvement of several communities located near the activated mining companies and in most of these communities, artisanal mining is illegally practiced [9]. Since the growth of illegal, artisanal, and small-scale mining, rivers pollution by toxic substances has increased in this case.

One of the methods used in southern Ecuador for mining is gold extraction through cyanide, which is used in leaching tanks (tailings) as part of the extraction process. This process forms sludge loaded with high levels of heavy metals and toxic cyanide compounds that are discharged into the nearest rivers [10].

Half a ton of mercury is released annually into the rivers and 1.5 to 5 kilograms of sodium cyanide is used for every ton of cyanide tailings, which generate polluted waste with 200 to 300 mg/L of free cyanide. This waste is directly discharged into the rivers or has as destination the debris, causing long-term environmental damage due to the mobilization of heavy metals or the generation of acid drains. In addition, there is a potential short-term risk since the spills can unpredictably percolate into water channels [11] [12].

According to Smith & Terry in 1991, cyanide is present in effluents as free cyanide (CN-), hydrocyanic acid (HCN), and as complexes formed with different chemical elements. These elements usually come from the combination of several chemical agents, including heavy metals, that are used in the extraction of gold. Therefore, it is essential to understand the behavior of cyanide in an aqueous medium, considering the physicochemical characteristics, and its behavior according to the pH variations [13].

Thanks to sophisticated laboratories, it is now possible to determine the concentration of certain cyanide species at low concentrations in water samples [12]. However, since the low amount of existing material and equipment in Ecuador (and usually in most mining countries), it is impossible to determine each specie's concentration and distribution by analytical methods.

1.1. Purpose of this work

The International Standards for Drinking Water of 1958 recommended a maximum permissible concentration of cyanide of 0.01 mg/L, based on its possible harmful effects on health. In 1971, according to the International Standards, the cyanide concentration was reduced to 0.05 mg/L. It was because of hydrogen cyanide residues in some fumigated foods. Additionally, to guarantee the water source is not contaminated by industrial discharges and that the water treatment has been carried out properly [14].

The first edition of the Guidelines for the quality of drinking water published in 1984, established a reference value of 0.1 mg/L as a reasonable limit for the protection of public health. A reference value based on health effects of 0.07 mg/L was established in the 1993 Guidelines, which was considered a protection against short and prolonged exposure [15].

The Ministry of Environment of Ecuador has established a maximum permissible concentration of cyanide of 0.1 mg/L of total cyanide for drinking water [16]. However, since water is used directly from rivers that are located near several mining production plants, the risks are much greater. The combination of cyanide with other harmful agents such as heavy metals should also be considered to determine the behavior and transformation of cyanide when it reaches water bodies like rivers. As mentioned in the introduction, currently, advanced laboratory techniques have been developed. It allows determining the concentration of species in different types of matrixes at trace and ultra-trace levels [17] [18].

The digital models consider different scenarios and the distribution of the chemical compounds to compute reactions such as precipitation, dissolution, complexation, adsorption, ion exchange, solute transport, diffusion, and convection. Each element or molecule's specific speciation or distribution will depend on the total metal concentration, acidity, redox potential, and temperature [19].

Therefore, to establish the species formed in the solution under actual conditions, chemical equilibrium models combined with experimental measurements are proposed in this research work, which has as objective to simulate the speciation of cyanide in the discharge flow of two mining tailings located in the south of Ecuador, to determine the distribution of the cyanide and of species of cyanide formed in the aqueous systems of the study area.

2. Study site

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This study is related to small-scale mining in southern Ecuador, considered the oldest mining area in the country. Nonetheless, mining is practiced at different sites in the country. However, the most significant production of gold mining companies is in the south of the country, and for years has contributed to the contamination of water, soil, and air.

The study area covers the cities of Zaruma and Portovelo in the south of Ecuador, El Oro Province. It is in the southeast of this province, at an altitude of 1200 m.a.s.l. Zaruma is one of the oldest cantons in the El Oro

province, where livestock, agricultural, aquaculture, and mining activities are practiced. 70% of the population is dedicated to mining activity, and it is considered the main source of economic income [20]. Fig 1 details the location of the study sites: points 1 and 2 correspond to water discharged from mining tailings. These two tailings belong to a gold miner located in the upper part of the Puyango river basin. The effluents of these tailings are discharged into La Calera River before its junction with Amarillo River. The junction between La Calera and Amarillo rivers forms the Calera-Amarillo River as seen in Fig 1.
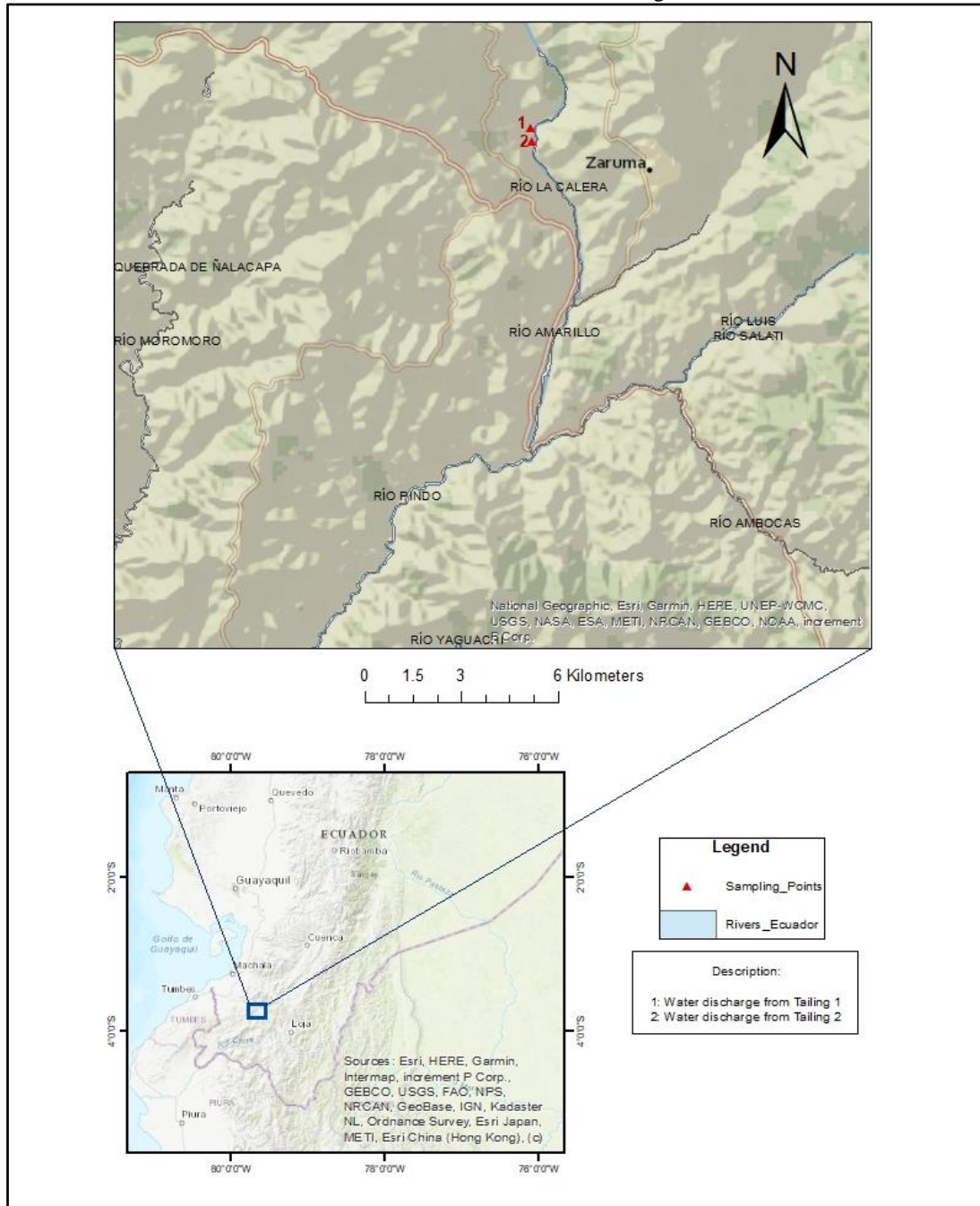

Figure 1. Study site of the research study.

3. Data and Methodology

Cyanide data from secondary sources could be acquired. The data set was obtained from the analysis of water discharges of two tailings tanks, carried out by a mining company. The data is shown in Table 1.

Table 1: Data taken from the first tailings discharge

Parameter	Value	Permissible limit*
pH	7.9	6-9
Temperature (°C)	27.8	
Cyanide	0.84	0.1
Al	0.76	5
As	0.6	0.1
Cu	2.6	1

*Permissible level according to the Ministry of Environment of Ecuador regulation.

Table 2: Data taken from the second tailings discharge.

Parameter	Value	Permissible limit*
pH	7.6	6-9
Temperature (°C)	27.8	
Cyanide (mg/L)	0.012	0.1
Al (mg/L)	3.8	5.0
Fe (mg/L)	8.4	10.0
As (mg/L)	2.1	0.1
Cu (mg/L)	0.104	1.0

*Permissible level according to the Ministry of Environment of Ecuador regulation

The speciation model was developed using Visual MINTEQ software, which is a geochemical model that calculates dominant species based on thermodynamic equilibrium. The data entered consist of cyanide concentrations and various metals reported in secondary data tables such as mercury, copper, arsenic, lead, iron, and others. Also, the pH and temperature of each sample were considered.

Analytical processes performed the physical-chemical characterization of the tailings outflow. Visual MINTEQ complemented this characterization with the simulation of cyanide species and metal-cyanide complexes formed in each system. Many chemical processes were computed simultaneously, such as balancing reactions by calculating equilibrium constants and producing solubility diagrams.

4. Study Results
4.1. Cyanide speciation in water discharges from tailing tank No. 1

Table 1 shows secondary data taken from one of the gold processing plants located near Calera River, in the Puyango River basin. Results of the physical-chemical analyses of water samples came from the discharge of the tailings. In addition, this table shows that the concentrations of cyanide and metals are above the permissible limits, therefore these discharges are potential sources of river pollution.

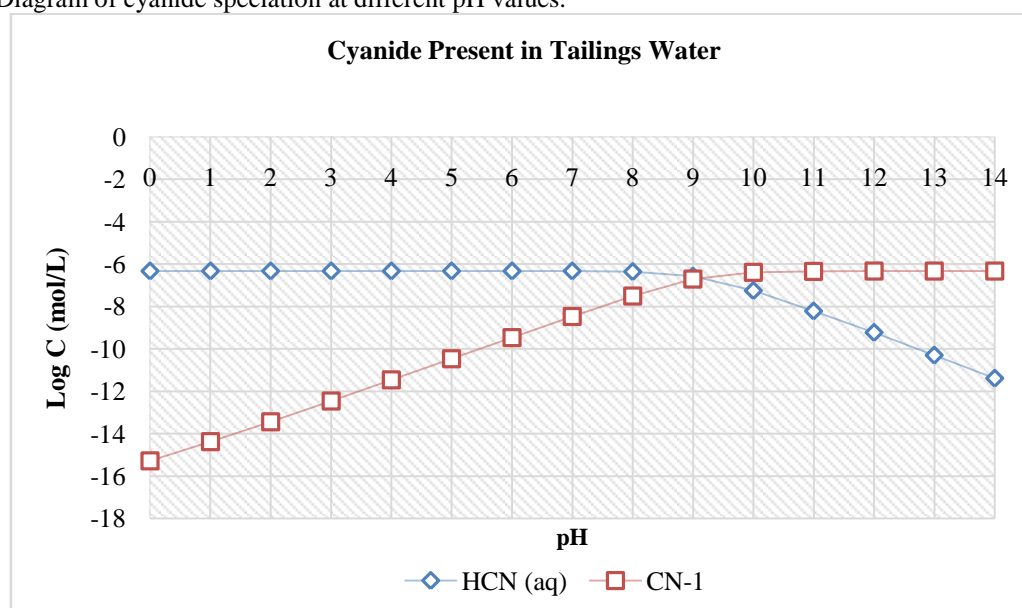4.1.1. Diagram of cyanide speciation at different pH values.

Figure 2: Diagram of cyanide speciation at different pH, cyanide concentration of 0.84 mg/L, and temperature of

27.8 °C (VISUAL MINTEQ). The behavior of free cyanide at different pH values and when the equilibrium between HCN and CN- is reached. Diagrams show the areas of the predominance of aqueous species, and it allows us to predict the species present in aqueous solutions.

As shown in Fig. 2 when cyanide is added to a solution, the concentrations of HCN and CN^- (free cyanide) reach equilibrium at a pH of 9, approximately. According to the literature, the most toxic form of cyanide is hydrogen cyanide (HCN). In the simulation, it can be observed that at 27.8°C and pH 9 the dominant form of cyanide is hydrogen cyanide and above pH 9, the cyanide ion (CN^-) is released. Suppose an effluent with these characteristics is directly discharged to a freshwater body (average pH 6.5 to 8). In that case, the water could become contaminated, and its toxicity should be analyzed according to other conditions such as pH and the chemical compounds discharged. Moreover, the discharges of mining processes are not composed only of cyanide, but of a mixture of chemical elements such as metals and salts. Consequently, the cyanide speciation was simulated in conjunction with other metals at different pH values, considering the formation and distribution of species in equilibrium and the example's actual pH and temperature conditions.
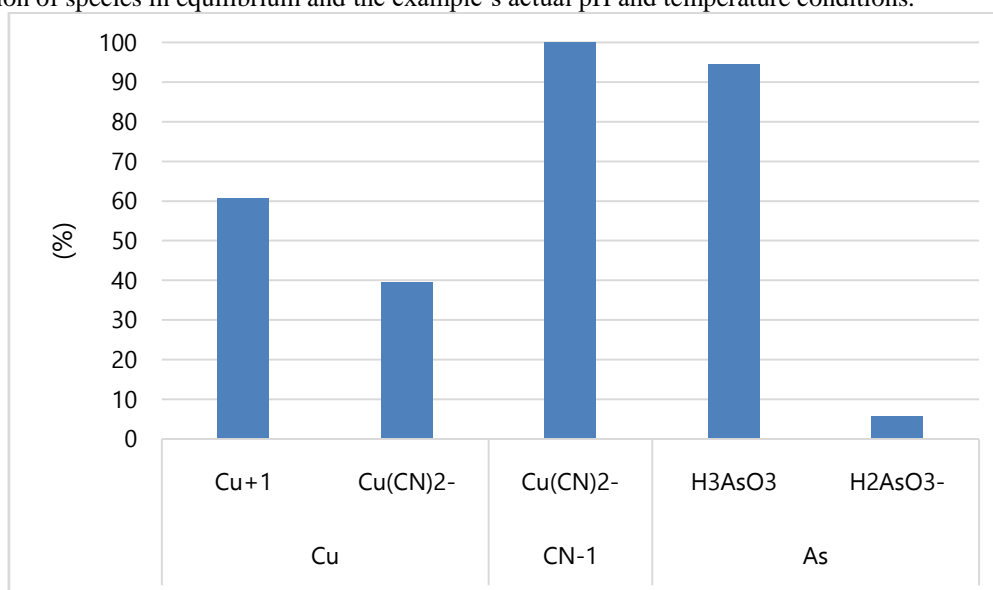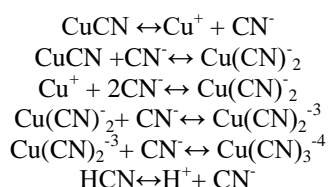

Figure 3: Distribution of the species present in the effluent of first tailing at a pH of 7.9, Cyanide Concentration of 0.84 mg/L, and Temperature of 27.8 °C (Visual MINTEQ).

In the diagram presented in Fig. 3, it can be observed the distribution in percentages of the species formed according to the data provided in Table 1. At the ambient conditions of the samples, arsenic and aluminum do not complex with cyanide. The dominant arsenic species is H_3AsO_3, typical of natural waters with a pH of 5 to 9.

The only metal that interacts with cyanide ions is copper. At a pH of 7.9 and 27.8 °C, 100% cyanide forms the $Cu(CN)_2^-$ complex, this species is also dominant. Metals such as copper, nickel, and silver form moderately strong cyanide complexes, even in very basic solutions, decreasing the amount of free cyanide (CN^-). In the case of aluminum, since this metal does not form complexes with the cyanide ion, the distribution of the species concentration in the solution depends only on the availability of hydroxide ions.

The formation of cupper-cyanide complexes in excess of cyanide forms cyanocuprous ions like $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, $Cu(CN)_4^{3-}$ in aqueous solutions [21]. These species obey the following successive equilibrium steps in reaction with free cyanide:

$$CuCN \leftrightarrow Cu^+ + CN^-$$
$$CuCN + CN^- \leftrightarrow Cu(CN)_2^-$$
$$Cu^+ + 2CN^- \leftrightarrow Cu(CN)_2^-$$
$$Cu(CN)_2^- + CN^- \leftrightarrow Cu(CN)_2^{-3}$$
$$Cu(CN)_2^{-3} + CN^- \leftrightarrow Cu(CN)_3^{-4}$$
$$HCN \leftrightarrow H^+ + CN^-$$

When the molar ratio of cyanide to copper is less than 3, copper cyanide is rapidly oxidized by air, that is, $Cu(CN)_2^-$ is less stable under ambient conditions [21].

Cupric ions react with CN⁻ and form cupric complexes that are unstable and decompose rapidly. It has been reported that when the molar ratio of CN: Cu is not high, cupric ions react with cyanide in an aqueous solution to produce cupric dicyanide, which decomposes into cuprous cyanide and cyanogen. When the molar ratio of cyanide to copper is high, cupric tetracyanide is formed, and rapidly breaks down into cyanogen and a kind of copper [22].
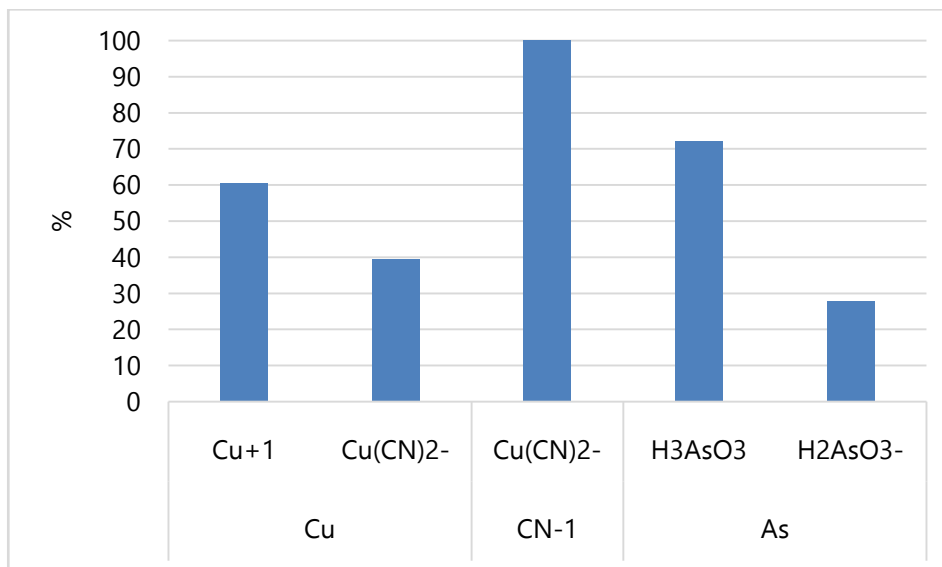

Figure 4: Distribution of Species in equilibrium present in the effluent of Point 1, Cyanide Concentration of 0.84 mg/L, pH 8.71(at equilibrium), Temperature of 27.8 °C (Visual MINTEQ).

A second-round simulation for the data set of point 1 was run to simulate the distribution of the species formed in the solution at equilibrium pH, which is 8.71. In Fig. 5, the percentages of the distribution of the species in equilibrium can be observed. The species concentration is like those discussed in Fig. 4, cyanide is complexing with copper; whereas arsenic, which does not complex with cyanide, is primarily present as H_3AsO_3. The pH at the system reaches the equilibrium in point 1 (Tailing 1) was calculated by Visual Minteq. The chemical equilibrium is defined as the state when the reactants and products are present in concentrations that have no additional tendency to change [23].

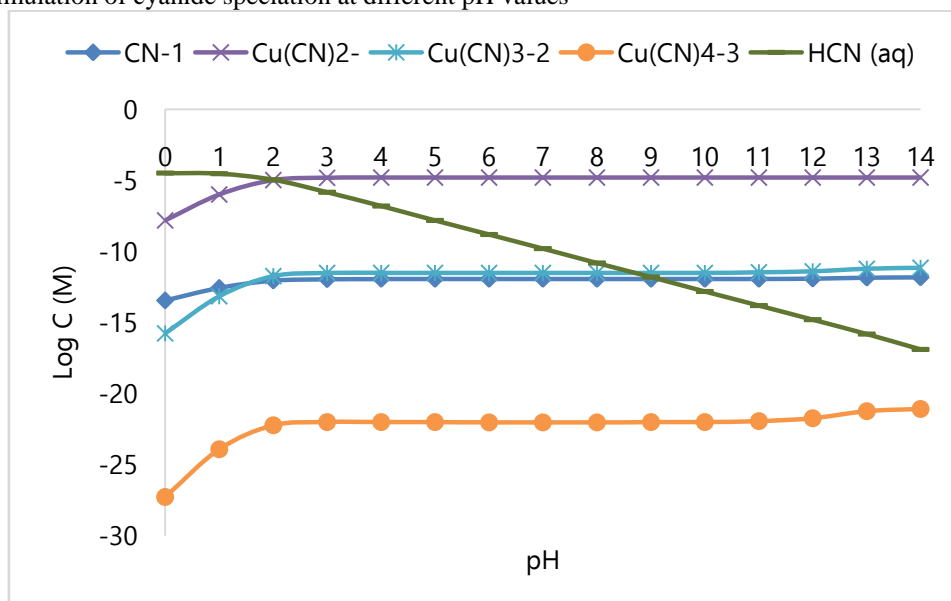4.1.2.   Simulation of cyanide speciation at different pH values

Figure 5: Speciation diagram between cyanide and copper at different pH values, cyanide concentration of 0.84 mg/L and 27.8 °C (VISUAL MINTEQ).

Among the metals present in the characterization of the tailing 1 effluent it is observed that cyanide forms complexes only with copper. In the speciation model shown in Fig. 5, hydrogen cyanide is the dominant species between pH 0 and 2 and at pH 2 its concentration decreases due to the formation of cupric cyanide Cu(CN)2-, which remains as the dominant species from pH 2 to 14.

The species $Cu(CN)_3^{-2}$ and $Cu(CN)_4^{-3}$, are present in quite low concentrations concerning $Cu(CN)_2^-$. However, their behavior for pH is similar; this means that their concentration increases until the solution reaches a pH equal to 2 and remains constant until pH 14.

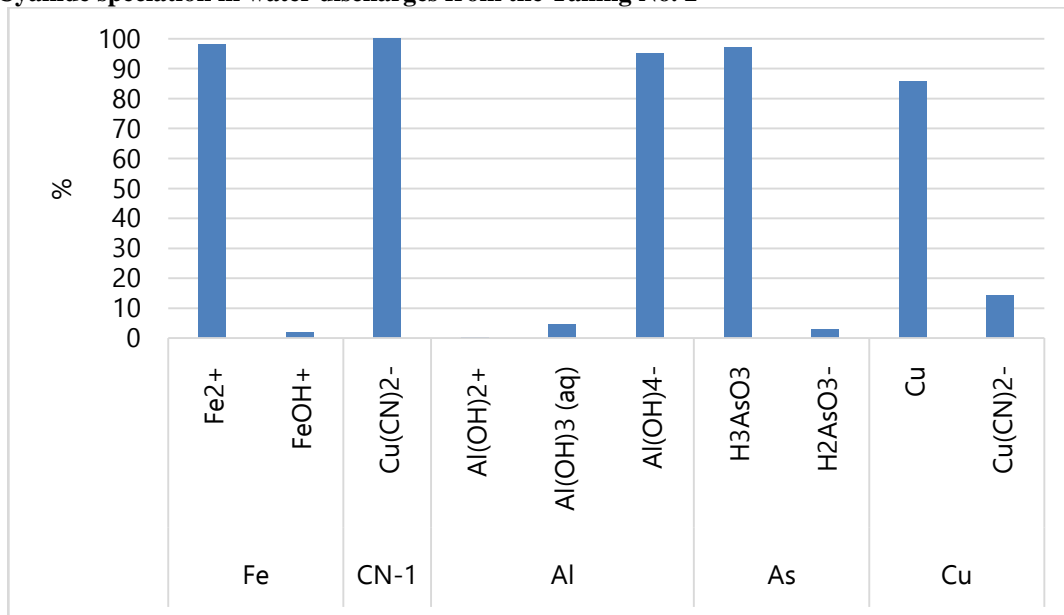### 4.2. Cyanide speciation in water discharges from the Tailing No. 2

Figure 6: Distribution of the species present in the effluent of the Tailing 2 at a sampled pH of 7.6, Cyanide concentration of 0.012 mg/L, and 27.8 °C (Visual MINTEQ).
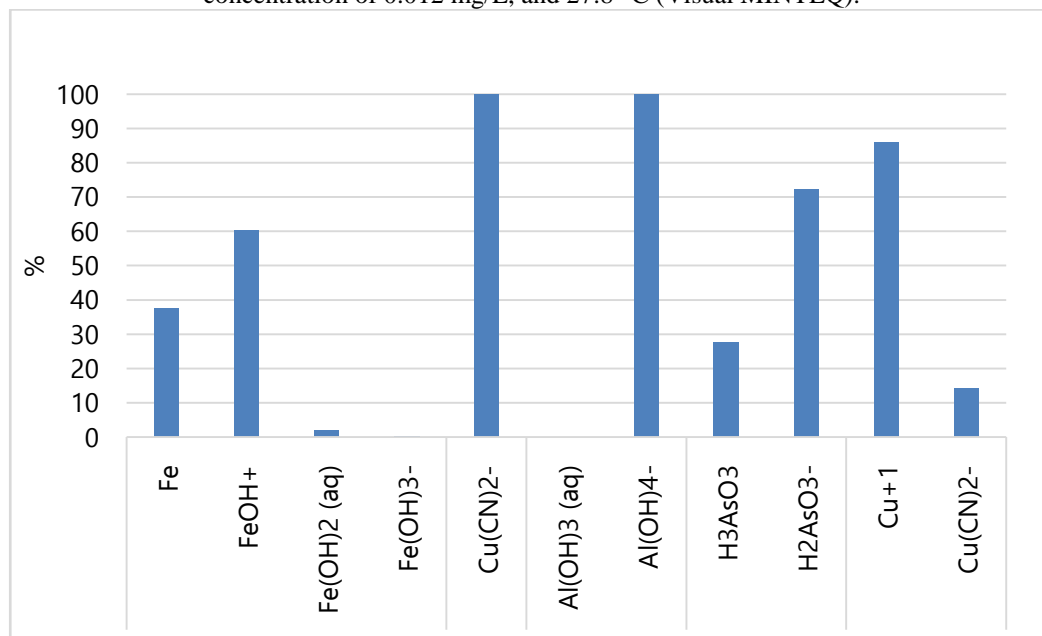

Figure 7: Distribution of species in equilibrium present in the effluent of tailings 2, pH 9.5(At Equilibrium), cyanide concentration of 0.84 mg/L, and temperature of 27.8 C

The physical-chemical characterization of water in this point shows more different metals than in Tailings 1. As shown in the distribution of species in Fig. 6, cyanide does not form complexes other than copper in the presence of other metals such as iron as in the previous study site.

The solution reaches equilibrium at a pH of 9.5. Fig. 7 shows the distribution of the species in percentages and it is observed that 100% of the cyanide ions form the $Cu(CN)_2^-$ complex, while copper is present as $Cu(CN)_2^-$, Although, the complex that dominates the system is the free ion Cu^{+1}.
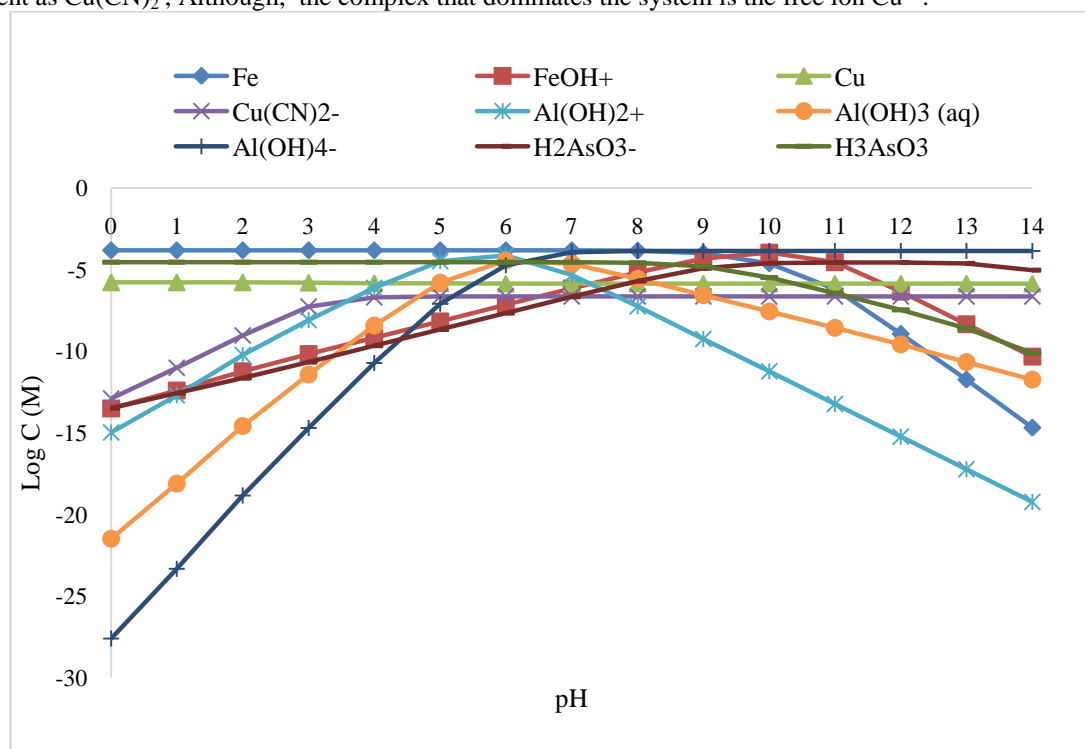

Figure 8: Speciation diagram between cyanide and other metals, at different pH values, Cyanide Concentration of 0.012 mg/L and 27.8°C (Visual MINTEQ).

In the simulation of the speciation between the cyanide ion and other metals present in the water sample, it is observed that copper is the only metal that forms complexes with cyanide in this system (copper-cyanide complex) as is shown in Fig. 8 and described below in Fig. 9.

The $Cu(CN)^{2-}$ complex concentration increases from pH 0 until it reaches its peak at pH 4, where it remains constant. Iron and aluminum combine with the hydroxyl ion (OH^-) forming $FeOH^+$ and aluminum hydroxides and increasing its concentration while releasing the hydroxyl ion until a pH of 10; hydroxyl ion concentration decreases as the iron concentration decreases.

Also, aluminum does not form complexes with cyanide. This result is consistent with the publication of (Benavente & Martínez, 2016), in which the authors mention that this metal does not form complexes with the cyanide ion [12].

As $Al(OH)_3(aq)$, $Al(OH)^{2+}$ and $Al(OH)_4^-$ increase their concentration in a pH range from 0 to 6, since this pH the concentration of the $Al(OH)_3(aq)$ and $Al(OH)_2^+$ decreases. $Al(OH)_4^-$ maintains its concentration up to pH 9, then begins to decrease since the concentration of the species in the solution depends solely on the availability of the hydroxide ions.
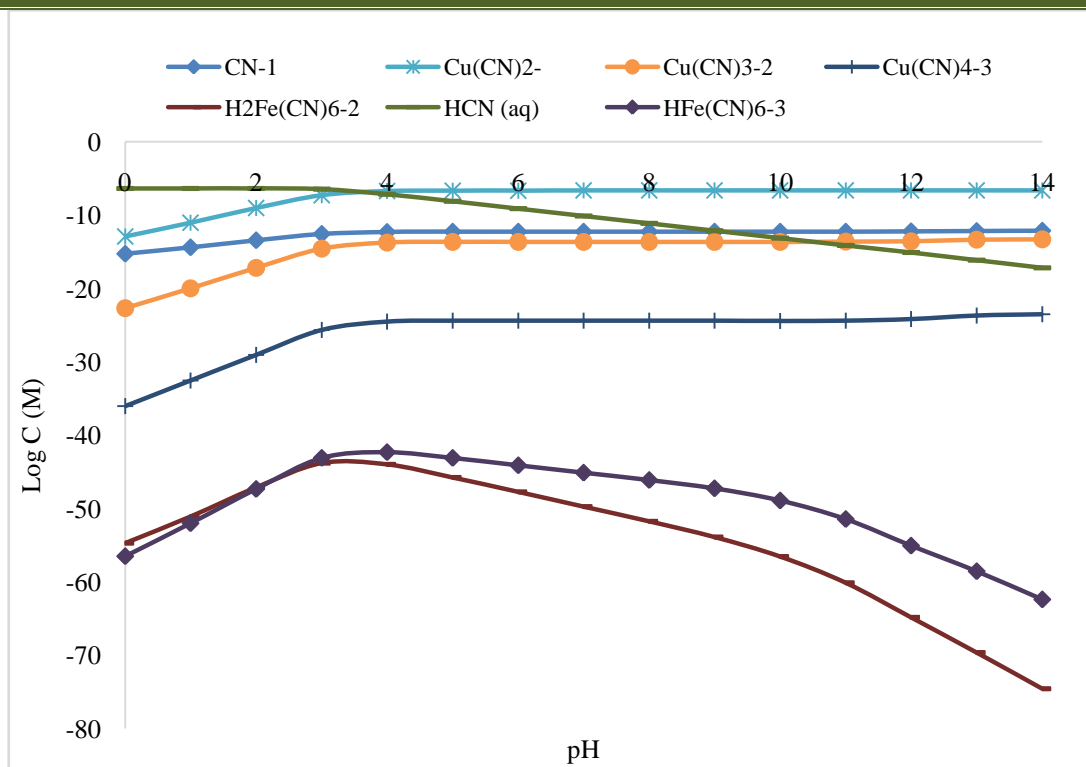
Figure 9: Formation of iron-cyanide and copper-cyanide complexes at different pH values. Cyanide concentration of 0.012 mg/L and 27.8 °C (Visual MINTEQ).

Due to the chemical properties of each element, cyanide tends to react easily with transition metals (copper and iron) however, the iron complexes observed in Fig. 9 do not appear in the distribution of species at pH 7.6 and pH 9.5 (Fig. 6, Fig. 7, and Fig. 9) because their concentrations represent values below 0.0001%. Nevertheless, the iron-cyanide complexes belong to the group of strong complexes, that is, they are a group of stable complexes against dissociation.

The complexes formed between cyanide and copper are the species that predominate the system in the range of pH 4 to pH 14. From pH 4 the $Cu(CN)_2^-$ dominates above the $Cu(CN)_3^{-2}$ and this, in turn, is above the $Cu(CN)_4^{-3}$. The pH at which the system reaches equilibrium is defined by the CN^- and HCN ions concentrations.

Among iron-cyanide complexes, the species $HFe(CN)_6^{-3}$ dominates from pH 2, in the range of pH 0 to pH 2 dominates $H_2Fe(CN)_6^{-2}$. However, they are present in a lower concentration than all other species formed in the system.

In wastewater from industries, cyanide is particularly toxic to fish, even when the cyanide ion concentration is reduced to low concentrations by dilution when it meets water from the receiving body. The cyanide ion can be deactivated or destroyed by iron ions, by forming iron-cyanide complexes. Before developing efficient methods for cyanide removal, the cyanide ion used to be reduced by treatment with ferrous sulfate. This reaction combines Fe2+ with CN- to form iron-cyanide complexes, which are precipitated as Prussian blue, because of the oxidation of Fe2+ to Fe3+ in the presence of potassium ion [24].

5. Conclusions

Calera River, which is the study site is where most of the tailings and effluents from the processing plants of the Puyango basin converge, the pH is alkaline, due to the presence of carbonates and bicarbonates, and calcium oxide. Based on the results obtained, the CN^- and $HCN_{(aq)}$ species are present in each study site, due to the pH range studied being between 7 and 8. This condition is favorable for the release of these species.

The aqueous hydrogen cyanide $HCN_{(aq)}$, is a hydrazide that has a polyatomic ion. The conjugate base of hydrocyanic acid is the cyanide ion (CN^-), therefore HCN dominates at acid pH and CN^- dominates at basic pH. According to the literature review, these two compounds are the most toxic forms of cyanide. Metal-cyanide complexes are less toxic than free cyanide, however, these complexes are broken to produce hydrogen cyanide, which is the usual cause of its toxicity. Some metal cyanide complexes, including copper and mercury cyanides, are toxic to the environment. In the tailings effluent, the simulation shows the formation of $Cu(CN)_2$, since

cyanide has an affinity for transition metals such as copper, mercury, and iron. However, due to its chemical properties cyanide does not complex with lead and arsenic.

Water discharged from tailings 1 and tailings 2 is predominantly contaminated by weak cyanide complexes. These complexes are known as week complexes due to the ease of dissociation; therefore, their stability depends on the degree of acid generation. If these complexes meet acid drainage of the gold mines these species would dissociate, release free cyanide, and become dangerous to the environment. In addition, the water discharges from the tailing at Point 1 have cyanide concentrations above the regulatory concentration limit in Ecuador, 0.01 mg/L for the preservation of flora and fauna in freshwater, and 0.1 mg/L of total cyanide for drinking water. This implies that the water of this site is already contaminated by cyanide.

Speciation of cyanide determines not only the variation of its toxicity but also the formation of complexes that affect its reactivity and its fate in sediments since cyanide can undergo transformation and degradation under appropriate environmental conditions. The predictions models obtained can be used in combination with experimental data taken in situ, to determine the concentration and distribution of species at different pH conditions. Moreover, it can be a valuable tool for a comprehensive assessment of environmental impacts and occupational safety since it facilitates the prediction of species present in the system under various environmental and operating conditions.

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