ELECTROCHEMICAL OXIDATION OF CYANIDE AND SIMULTANEOUS REMOVAL OF HEAVY METALS FROM GOLD CYANIDATION WASTEWATER

by

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ABSTRACT

Cyanide is widely used in the gold mining industry to extract gold from different gold-bearing ores and as a result gold cyanidation process wastewater can contain high amounts of cyanide as well as other heavy metals that can pose risks if released to the environment. Electrochemical methods such as electrooxidation have been shown to effectively treat cyanide contaminated wastewater. However, past studies have largely focused on cyanide oxidation and metal recovery using synthetic solutions which may not accurately represent conditions of mining process waters. In the present study, the electrochemical destruction of cyanide and simultaneous removal of heavy metals using a graphite anode and copper cathode under alkaline conditions was investigated. Batch experiments were conducted on synthetic and real gold process wastewaters. First, the kinetics of cyanide electrooxidation were studied by examining the effects of applied voltage, electrolyte composition, and copper concentration. The effects of electrolyte composition were of particular interest as several gold cyanidation facilities have shifted towards using partially desalinized and even raw seawater for their processes. Results indicated that cyanide follows a first order reaction with respect to CN^- ions for most wastewater samples examined. In addition, increased voltage and NaCl concentrations lead to an increase in the rate of cyanide oxidation.

The effect of applied voltage, NaCl concentration and initial cyanide concentration on heavy metal removal was then evaluated for synthetic wastewater samples. Results showed that lower applied voltages and lower NaCl concentrations led to an increased removal of copper. For real process wastewater samples, only the effects of applied voltage and conductivity on metal removal were studied. Results indicated that a higher applied voltage and higher conductivity lead to increased removal of copper and zinc. The variation in results between real and synthetic wastewaters can be attributed to the higher amount and stability of metal-cyanide complexes measured in real process wastewaters. Although optimal conditions for an electrochemical system can vary depending on the water's composition, results indicate that an applied voltage of 5V and addition of NaCl can help increase the rate of cyanide oxidation as well as metal removal. Overall, this study shows that electrochemical treatment of gold cyanidation process water can be an effective method for cyanide oxidation and simultaneous metal recovery.

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LIST OF ABBREVIATIONS

Environmental Protection Agency	EPA
Inductively Coupled Plasma-Atomic Emission Spectroscopy . . . .…	ICP-AES
Ion Chromatography	IC
Weak Acid Dissociable.	WAD
Strong Acid Dissociable.	SAD

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CHAPTER 1 INTRODUCTION

Cyanide is commonly used in the mining industry to extract gold from gold-bearing ores, particularly low-grade ores where gold cannot be extracted through processes such as crushing and gravity separation [1]. As the mineral processing industry has shifted towards low-grade gold ores, sodium cyanide has become the leaching agent of choice as the use of mercury is declining [2]. Gold is extracted through the processes of heap leaching or tank leaching where the cyanide ion (CN^-) forms complexes with gold in ore, allowing it to be solubilized and recovered in downstream processes [3]. The cyanidation process can be carried out in various systems; however, a common method is that of tank leaching where the ore is finely ground and added to a cyanide solution in large tanks. At pH greater than 10, the cyanide ion (CN^-) in solution (Figure 1.1) will dissolve in water and under mildly oxidizing conditions will dissolve the gold contained in the ground ore by forming water soluble gold-cyanide complexes such as $NaAu(CN)_2$ in what is termed a pregnant solution, or a solution containing gold [1] [4]. Activated carbon or zinc metal are then added to the pregnant solution to sorb the gold-cyanide complexes which are later processed as high purity gold. The residual solution is known as barren solution and can be recirculated to extract more gold. However, if the barren solution contains too high of impurities and cannot be recirculated, it will be sent to a treatment system or to disposal [1]. Around 80% of global gold extraction is achieved through heap or tank leaching and around a million tons of ore per year are treated with cyanide [5].

Although cyanide leaching is an effective method for gold extraction, cyanide is toxic and when released to the environment it can result in disruption of aquatic ecosystems and negative public health risks [6] [7]. Cyanide can be deadly to animals as it can inhibit tissue from using oxygen by interfering with a cellular respiratory enzyme known as cytochrome oxidase [8]. Another important consideration when implementing cyanide leaching is the volatilization of hydrogen cyanide (HCN) which forms when the cyanide anion combines with hydrogen ions in the process water [1]. As shown in Figure 1.1, the fraction of hydrogen cyanide gas varies as a function of pH. Above a pH of 11.5, cyanide remains dissolved in the water as CN^-; however, below a pH of 7 all of the cyanide is converted to HCN gas which poses a risk to workers if they are exposed to high concentrations of HCN gas in a confined space [1]. Some programs such as the Cyanide Code have been created to improve management of cyanide in the gold and silver mining industries throughout its use cycle from production to disposal of the chemical. The goal of the Cyanide Code is to protect human health and reduce environmental impacts from unintended cyanide releases [9]. However, even with programs such as the Cyanide Code, there can still be potential risks. As cyanide is an EPA designated priority pollutant that is considered hazardous and toxic, in the U.S., cyanide-containing wastewater must be treated or managed properly to mitigate potential impacts [10].

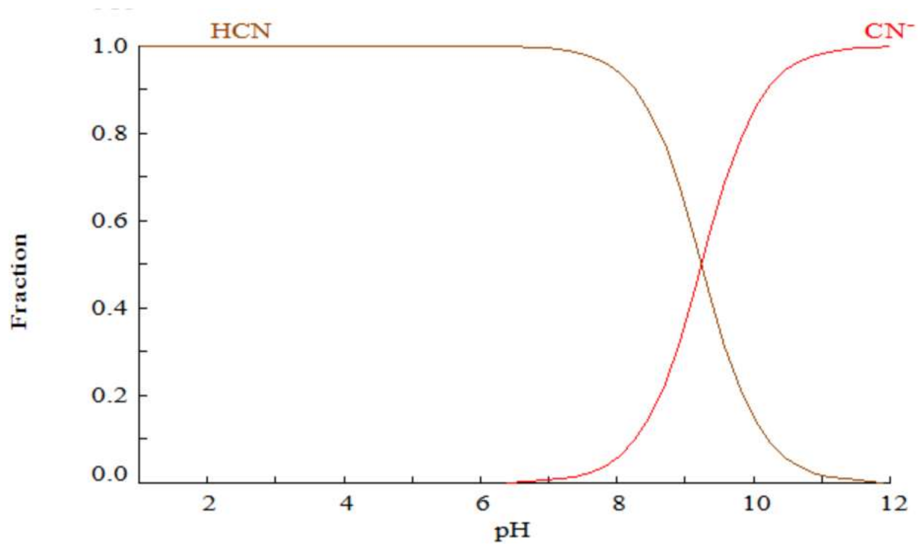


Figure 1.1 Formation of HCN gas as a function of pH.

Various methods for the treatment of wastewaters containing free cyanide and its complexes have been proposed including biological treatment, Caro's acid, hydrogen peroxide, the Inco SO_2/air process and direct alkaline chlorination. Of these, the most commonly applied methods are alkaline chlorination and the Inco SO_2/air process [11] [12]. Through the alkaline chlorination method, cyanide is oxidized to CNO^-, CO_2, N_2, and NH_4^+ [13]. For wastewater that is also high in copper concentrations, the chlorination of cyanide can be followed by removal of cuprous and cupric ions as hydroxide precipitates. The resulting sludge, however, can be difficult to handle [13]. Although the reactants used in the chlorination process can be unsafe to handle, this method is cost effective and widely used as it has proven to be effective in meeting final discharge limits [14]. The SO_2/air process consists of oxidizing free and weak acid dissociable (WAD) cyanide using SO_3^{2-} and precipitating iron or copper cyanide as insoluble solids. However, this process requires building a processing plant and copper must be present at an appropriate concentration for the method to work properly [1] [12]. Moreover, for the process to work well, there must be continuous addition of chemicals and careful process control [12]. Electrochemical treatment methods, which only require electricity inputs, are being studied as a more sustainable and cost-effective alternative since the treatment does not use chemical reagents that are expensive and can be harmful to the environment.

There are a variety of electrochemical methods that have been applied to industrial and water treatment processes including electrodeposition, electrocoagulation, electroflotation, and electrooxidation. For the recovery of metals, electrochemical methods have been used in the metal surface finishing industry, in the printed circuit board manufacturing industry, and in the mining industry through metal electrowinning [15]. In terms of water treatment, electrochemical technologies such as electrooxidation have been previously used in wastewater treatment for the recovery of metals as they can be an energy efficient, cleaner and more versatile technology [16]. Electrooxidation consists of using an electrolytic cell where electrodes are submerged into an electrolyte solution and an electric current is applied to the system. This allows for metal ions to be reduced or recovered to their metal form at the cathode surface and for other species to be oxidized at the anode surface, in some instances to form less toxic compounds [16]. Although studies have shown that electrochemical technologies can be a feasible way to treat and recover heavy metals from wastewater, the technology is still limited, especially for large-scale applications [16].

Numerous previous studies have investigated the use of electrochemical processes for removal of cyanide from mining wastewater. A major reported finding is that cyanide treatment efficiency is dependent on the electrode material used in the electrochemical treatment. Electrode materials reportedly examined in the literature include dimensionally stable anodes (DSA) [14] [17], Ti [18], PbO_2 [19], graphite [7] [20] [21] [18], copper [17], and stainless steel [22] [11] [12] [23]. For alkaline media, some combinations such as $Ti/O_2/RuO_2$ have also been used to increase the electrode's service life [14]. Canizares *et al* tested the effectiveness of anodes based on diamond layers such as boron doped diamond (BDD) which have good chemical resistance and can be very efficient [10]. Results showed that BDD anodes achieved higher total cyanide oxidation rates when compared to other anode materials such as DSA. Tissot and Fragniere reported the use of an electrode of reticulated vitreous carbon coated with PbO_2 for cyanide oxidation. It was determined that this electrode has good stability and works well with water containing cyanide at low concentrations [19]. Carbon-based electrode materials have been of particular interest in recent studies as they can be cheaper and more conducive to CN^- removal [8] [24] [21]. Overall, selection of an effective electrode material depends on multiple factors including availability, cost and treatment effectiveness. For this reason, materials such as graphite, copper and stainless steel exhibit good characteristics for electrochemical treatment systems.

Studies have also investigated the effect of water quality, particularly the concentrations of salts such as NaCl in the supporting electrolyte, on the electrooxidation of cyanide [20]. In a study conducted by Felix-Navarro *et al*, the oxidation of cyanide in the presence of NaCl concentrations up to 0.3M was tested. It was determined that increasing concentrations of chloride in the solution significantly increased the rate of cyanide oxidation [20]. Szpyrkowicz *et al*. also evaluated the addition of NaCl to the electrolyte solution and found that adding NaCl increased cyanide oxidation rates since oxidation of cyanides can be indirectly carried out by the generation of hypochlorite in the solution [23]. Other key aspects that have been investigated by various researchers include the effects of current density and applied cell voltage on the system. Experiments determined that increasing values of applied current density or voltage in turn increased cyanide decay rates [14] [7] [17] [21] [20]. Some studies have also concluded that increasing the applied cell voltage above 6 or 7V does not improve the rate of cyanide oxidation and that in certain cases can decrease cyanide and metals removal efficiency [21] [20] [25].

Another important consideration during electrochemical treatment is the formation of metal-cyanide complexes and their subsequent impact on cyanide removal from gold process wastewater. A large amount of the gold processed using cyanide, is extracted from low-grade ores which contain metals that cyanide will react with such as copper, iron, zinc and nickel [1] [26]. High levels of copper in certain gold-bearing ores, particularly Cu_2S and CuS results in the production of wastewater containing high levels of copper and sulfur compounds in addition to cyanide [12]. When cyanide is complexed with metals such as iron, copper or zinc, the high stability of these compounds can reduce the efficiency of cyanide oxidation [20]. As a result, electrochemical methods have been developed to oxidize cyanide to less toxic compounds at the anode and recover copper and other metals at the cathode [12]. Various papers describe the mechanisms of electrochemical treatment of wastewaters containing copper-cyanide complexes [11] [26] [25][21] [16] [27] [12] [23] and according to B. Malinovic *et al*., in strong alkaline conditions, copper cyanide complexes are oxidized directly to cyanate and copper oxide. According to this mechanism, copper oxides can be formed at the anode which some studies have shown, can increase the oxidation rate of cyanide [28] [17] .

In an electrochemical system with copper and excess cyanide, it has been proposed that copper (II) is reduced to form tricyanocuprate (I) complex as shown in reactions (1.1)-(1.2) [25].

$$Cu^{2+} + e^- \rightarrow Cu^+ \tag{1.1}$$

$$Cu^+ + 3CN^- \leftrightarrow Cu(CN)_3^{2-} \tag{1.2}$$

The main reactions occurring in the cathode are highly dependent on $[CN^-]/[Cu^+]$ ratios and pH of the solution. As seen in Figure 1.2, for very alkaline solutions, only $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ species dominate which is important because these are moderately strong metal-cyanide complexes that will affect cyanide oxidation rates and removal of copper. Dutra *et al*. also postulated that the main cathodic reactions in a copper-cyanide solution can be represented by reactions (1.3)-(1.5) where the reactions depend on the relative cyanide ion and copper ion concentrations in the solution. For higher [CN-]/[Cu+] ratios (above 4), reactions (1.3) and (1.4) predominate [11]. Additionally, the hydrogen evolution reaction (reaction 1.5) occurs at the cathode and can lower current efficiency [11].

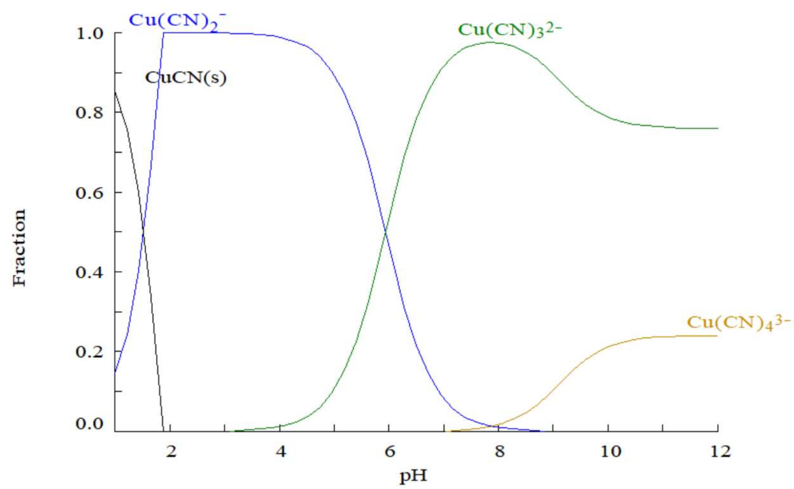


Figure 1.2 Species distribution diagram as a function of pH for a copper-cyanide solution. Diagram conditions: 0.01M CN^-, $1x10^{-5}$M Cu^+.

$$Cu(CN)_3^{2-} + e^- \rightarrow Cu + 3CN^- \quad (E^O = -1.205\,V) \tag{1.3}$$

$$Cu(CN)_4^{3-} + e^- \rightarrow Cu + 4CN^- \quad (E^O = -1.292\,V) \tag{1.4}$$

$$2H_2O + 2e^- \rightarrow H_2 + OH^- \quad (E^O = -0.83\,V) \tag{1.5}$$

On the anode, the main reactions that occur are oxygen evolution and the direct oxidation of cyanide to cyanate and cyanate to CO_2 and N_2 (reactions 1.6-1.8) [11] [20] [25]. Additionally, cyanide-copper complexes can be broken at the anode to produce copper and cyanate ions as shown in reaction 1.9 where E^0 is the standard reduction potential vs. standard hydrogen electrode (SHE) at 25˚C [25].

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad (E^O = 0.40\,V) \tag{1.6}$$

$$CN^- + 2OH^- \rightarrow CNO^- + H_2O + 2e^- \quad (E^O = -0.97\,V) \tag{1.7}$$

$$2CNO^- + OH^- \rightarrow N_2 + 2CO_2 + H_2O + 6e^- \quad (E^O = 0.76\,V) \tag{1.8}$$

$$Cu(CN)_3^{2-} + 6OH^- \rightarrow Cu^+ + 3CNO^- + 3H_2O + 6e^- \quad (E^O = -0.69\,V) \tag{1.9}$$

The work described in the next chapter concerns the study of the electrochemical oxidation of cyanide and simultaneous removal of metals in gold processing wastewater, more specifically wastewater that is high in salinity. Previous studies have only looked at NaCl concentrations of up to 0.3M [20], however, as traditional water resources become depleted, many mines and processing facilities near coastal regions are starting to use partially desalinized and even raw seawater for their gold cyanidation processes [29]. As a result, this water can contain NaCl concentrations much higher than the 0.3M which can affect the oxidation rate of cyanide and overall removal of metals from the water using an electrochemical system [29]. The goal of this study was to determine how gold-processing wastewater with high salinity affects the electrochemical process and how to best optimize these processes to degrade cyanide while simultaneously removing copper and other metals from the water. Additionally, most previous studies have focused on synthetic water solutions for experiments with few studies evaluating real process wastewater whose composition may influence cyanide oxidation and metal removal [30] [7] [11] [12] [18]. Therefore, in this study, experiments were conducted using both synthetic and real process wastewater from three different processing sites. The electrode materials consisted of a graphite anode and copper cathode. The parameters of interest were the applied cell voltage, NaCl concentration, conductivity, initial cyanide concentration and initial copper concentration in the wastewater.

CHAPTER 2 MATERIALS AND METHODS

2.1 Solution Preparation and Real Wastewater collection

Synthetic wastewater was prepared using sodium cyanide (NaCN), sodium hydroxide (NaOH), sodium chloride (NaCl), and for copper recovery experiments, copper (I) cyanide (CuCN). Cyanide concentrations varied from 200-1000 ppm and copper concentrations from 100-600 ppm. To increase the conductivity of the solutions, NaCl was used as the electrolyte. The electrooxidation of cyanide using NaCl was studied at different concentrations varying from 0.3M to 1M. All synthetic solutions were prepared with deionized water. Real process wastewater samples came as barren solutions from three different small gold processing facilities in the Arequipa region of Peru. These waters were transported to the lab facility in Arequipa for electrochemical oxidation experiments. The initial pH of synthetic and real wastewater solutions was adjusted and throughout the experiments maintained at approximately 11.5 by addition of 1M NaOH to avoid release of HCN gas.

2.2 Apparatus

Figure 2.1 presents a diagram of the experimental apparatus used in this study. All experiments were carried out in a 1L beaker which worked as the electrolytic cell. The pH and temperature of the water were measured using a pH meter equipped with a temperature probe (Thermo Scientific Orion model 520A and 420A+) which was suspended by a swing arm electrode holder. Electrical power was supplied using a DC Power Supply made by EXTECH (model 382202, 0 to 18V, 0 to 3A). The beaker was placed on a magnetic stirring plate to keep the solution well mixed throughout the experiment. For the study of cyanide oxidation rates, the anode and cathode materials were composed of pure graphite plate sheets. For the study of copper plating while simultaneously degrading cyanide, the anode was composed of pure graphite plate sheets while the cathode was composed of pure copper sheets (see Figure 2.2). All experiments were carried out at a temperature of 25 ± 1°C. The electrode cross sectional area was approximately 15x3 cm with a 3mm width for graphite sheets and 1mm width for copper sheets. The electrodes were held at a distance of about 3cm from each other. The submerged area of the electrodes in the solution was 19.5 cm^2.

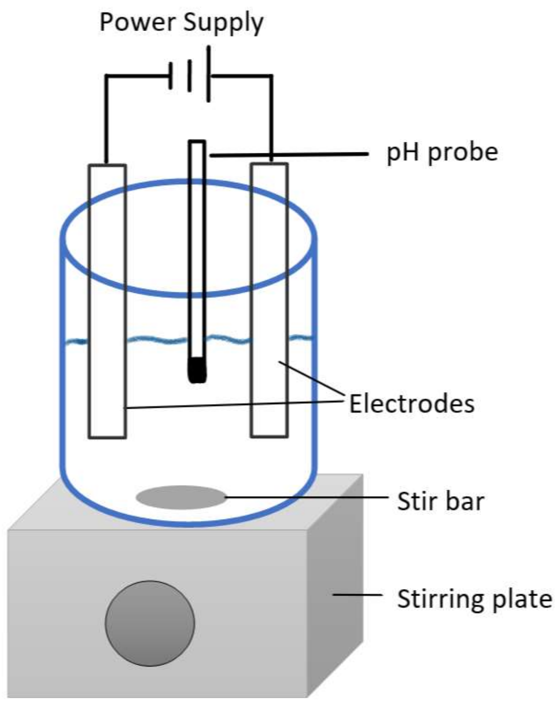
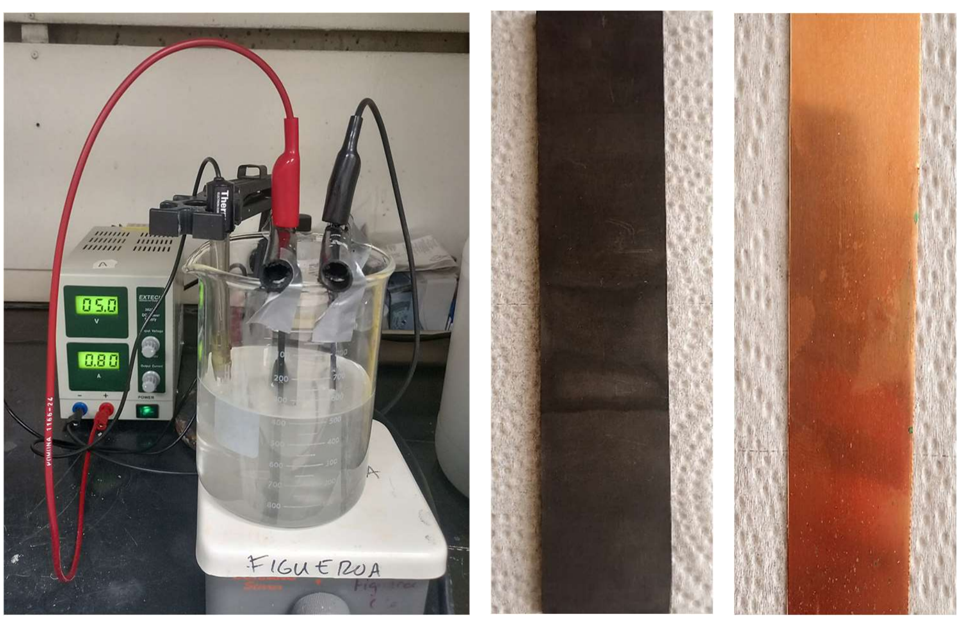


Figure 2.1 Diagram of electrochemical system.



(a) (b) (c)

Figure 2.2 (a) Experimental setup in the lab, (b) graphite plate sheet, (c) copper plate sheet.

2.3 Experimental Procedure

For each experiment, 500mL of solution with the defined experimental parameters was placed into the electrochemical cell (see Table 2.1). The initial pH of the solution was checked using a pH meter and adjusted to 11.5 by adding approximately 1.5mL of 1M NaOH. The pH of the solution was maintained at 11.5 by addition of 1M NaOH throughout the experiment. The voltage was adjusted to the desired value by applying the corresponding current using the power supply current and voltage regulators. A stirring plate and magnet were used to maintain the solution well mixed throughout the experiment. Stirring was important as agitation of the solution can also help increase the rate of the reaction. Samples of 1 to 2mL were withdrawn for chemical analysis using a pipette at varying time intervals which were based on the parameters of each experiment.

Table 2.1 Conditions for synthetic wastewater experiments

Experimental Run	Voltage	NaCl conc. (M)	Copper conc. (ppm)	CN^- conc. (ppm)
1	3	0.3	0	200
2	5	0.3	0	200
3	5	0.5	0	200
4	5	1	0	200
5	5	1	100	200
6	5	1	300	200
7	5	1	600	200
8	3	0.3	300	204
9	3	0.3	300	420
10	4	0.3	300	224
11	4	0.3	300	404
12	3	1	300	221
13	3	1	300	267
14	4	1	300	410
15	4	1	300	482
16	4	1	300	622
17	4	1	300	1067
18	5	1	300	206

2.4 Chemical Analysis

Cyanide concentrations for all samples were measured manually using a HACH Test ‘N Tube (TNT) 862 kit which consists of the pyridine barbituric acid method. Through this method, cyanides react with the chlorinating agent dichloroisocyanuric acid to form cyanogen chloride. This in turn reacts with a pyridine compound in the presence of barbituric acid, condensing to form a violet color which can then be used to determine the concentration of cyanide using a spectrophotometer. In this analysis, a HACH DR5000 UV-Vis spectrophotometer was used. This method is capable of measuring cyanide as CN^- in the range of 0.01 to 0.6 mg/L and samples were diluted accordingly [31]. Analysis of samples for copper concentrations were performed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). ICP-AES is a method of emission spectroscopy that excites atoms and ions with a plasma causing them to emit electromagnetic radiation at wavelengths that are characteristic of a particular element. An argon-based plasma is used which can reach temperatures of 5500-6500 K resulting in a high degree of excitation. The light emitted by the atoms on their return from a high to low energetic state is resolved into a line spectrum. The wavelength is specific for an atom and the intensity gives its concentration [32]. For the determination of inorganic anions, ion chromatography (IC) was used. IC is a type of chromatography where ions and polar molecules are separated based on their affinity to the ion exchange column. The time it takes for each ion to move through the column varies depending on each ion species. The concentration of ions moving through the column is represented by the height of the peak in a chromatogram and can be correlated to the concentration of a particular ion [33]. Analysis of WAD and total cyanide concentrations for real process wastewater samples was performed by Newmont Corporation using the flow injection amperometric method. This method consists of introducing samples into a flow injection analysis (FIA) system where it is acidified to form hydrogen cyanide gas (HCN). HCN diffuses through a hydrophobic gas diffusion membrane from an acidic to an alkaline stream. The cyanide captured in the alkaline stream is sent to an amperometric flow cell detector which uses a silver-working electrode. The silver in the electrode is oxidized at the applied potential and the measured anodic current is proportional to the concentration of cyanide [34]. For total cyanide measurements, the samples are first distilled with a strong acid in the presence of a magnesium chloride catalyst and captured in a sodium hydroxide solution [35]. For WAD cyanide measurements, there may be the addition of a ligand displacement agent when the cyanides are bound to mercury or nickel [34].

2.5 Calculations

2.5.1 Energy Consumption and Current Efficiency Calculations

Energy consumption for each experiment was calculated as kilowatt hour (kWh) per kg of cyanide or metal removed. To calculate kWh the following equation was used:

$$kWh = \frac{V * I * t}{1000} \tag{2.1}$$

where V is the applied voltage, I is the current in amps, and t is the time the experiment was run for in hours. This is then divided by 1000 to convert from Watt hour to Kilowatt hour.

The current efficiency describes the efficiency in which electrons are transferred in an electrochemical system to facilitate a reaction. To calculate current efficiency (E_C), the number of Coulombs used by the reaction of interest is divided by the total number of Coulombs available in the electrochemical system (equation 2.2).

$$E_C = \frac{Coulombs\ used\ by\ reaction\ of\ interest}{Available\ Coulombs} \times 100 \tag{2.2}$$

To calculate the total number of coulombs available in a system equation 2.3 is used where I is the applied current in amps and t is the time the system is operated for in seconds.

$$Available\ Coulombs = I * t \tag{2.3}$$

To calculate the number of coulombs used by a specific reaction, equation 2.4 is used where F is Faraday's constant (96486 Coulombs per mole of electrons), n is the number of displaceable electrons per mole of an atom or compound, m is the molar mass of the displaced compound, ΔC_{exp} is the change in concentration of the compound of interest after an experiment in mg/L, and V is the operating volume of wastewater in L.

$$Coulombs\ used\ by\ reaction = \frac{F * n * \ (\Delta C_{exp}/1000) * V}{m} \tag{2.4}$$

In this study, the reactions of interest are the oxidation of cyanide to cyanate at the anode (reaction 1.7), and the plating of metals such as copper at the cathode (reactions 1.3-1.4).

2.5.2 Metal Removal

To calculate the amount of metal removed from the solution after an experiment, water quality data from ICP-AES analysis was used. Metal concentrations before and after an experiment were measured to determine the change in concentration of that metal. Metal removal in this study is presented as mg of metal removed per area of electrode submerged to compare between experiments. This was calculated using the following equation:

$$metal\ removed = \frac{Ci - Cf}{a_s} * V \tag{2.5}$$

where C_i is the initial metal concentration (in mg/L), C_f the final metal concentration (in mg/L), a_s the area of electrode submerged in the solution (in cm^2), and V the operating volume of wastewater in each experiment (in L).

2.5.3 Weak and Strong Metal-Cyanide Complex Calculations

To calculate the concentrations of weak and strong metal-cyanide complexes as mg/L CN^-, WAD and strong acid dissociable (SAD) cyanide, also known as total cyanide, measurements are used. WAD cyanide is measured as mg/L of CN^- and includes the concentration of weak to moderately strong metal-cyanide complexes as well as free cyanide (Figure 2.3). Weak to moderately strong metal-cyanide complexes include complexes of silver, cadmium, mercury, nickel, copper, and zinc [36]. To determine concentrations of weak metal-cyanide complexes in each solution, free cyanide was subtracted from WAD cyanide concentrations. Total cyanide concentrations are also measured as mg/L CN^- and include WAD cyanide plus strong metal-cyanide complex concentrations (see Figure 2.3). Strong metal-cyanide complexes include complexes of iron, cobalt, and gold [36]. Strong metal-cyanide complex concentrations were calculated by subtracting WAD cyanide from total cyanide concentrations.

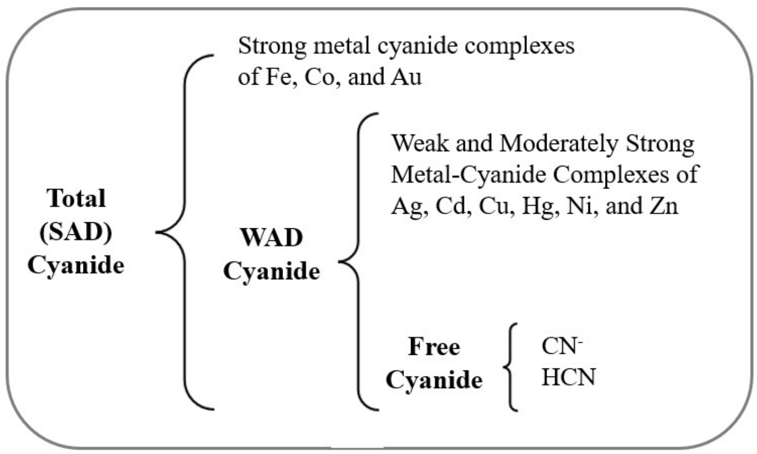


Figure 2.3 WAD and Total Cyanide Definitions

CHAPTER 3 RESULTS AND DISCUSSION

This chapter summarizes research conducted to determine the effects of various parameters on the electrochemical oxidation of cyanide and simultaneous removal of heavy metals from synthetic and real gold process wastewater. The chapter is divided into three sections that consist of real gold process and synthetic wastewater composition (Section 3.1), results and discussion of cyanide oxidation rates (Section 3.2), and results and discussion of heavy metal removal (Section 3.3).

3.1 Synthetic and Real Gold Process Wastewater Composition

Composition of the three gold processing sites sampled in the Arequipa region of Peru are summarized in Table 3.1 while synthetic water composition ranges for conducted experiments are shown in Table 3.2.

Table 3.1 Gold cyanidation process water composition

	Concentration (mg/L)		
Component	**Site 1**	**Site 2**	**Site 3**
pH[1]	10.8	11.3	9.7
WAD Cyanide	1184	2393	2285
Total Cyanide	1435	2670	2783
Free Cyanide (CN^-)	794	1525	1505
Cl^-	821	676	20464
NO_3^-	128	59	542
NO_2^-	217	104	121
SO_4^{2-}	5995	4503	13761
PO_4^{3-}	92	194	0
Ca	1029	1607	1919
S	3796	2681	4447
Na	4953	3189	15192
Sr	6	9	120
K	168	292	359
Si	211	225	221
Zn	130	616	158
Mg	244	243	474
Fe	9	19	2
Cu	226	180	577
As	12	1	4

[1] pH was adjusted upon collection – all waters were pH adjusted to 11.5 prior to electrochemical experiments.

Table 3.2 Synthetic wastewater composition.

Component	Concentration (mg/L)	Added as
pH	11.5	NaOH
CN^-	200-1000	NaCN, CuCN
Cl^-	10500-35500	NaCl
Na	30077-46884	NaCl, NaCN, NaOH
Cu	0-600	CuCN

Real processing wastewaters varied in initial cyanide and heavy metal concentrations. Sites 2 and 3 had similar initial cyanide concentrations which were above 1000 mg/L CN^- while that of site 1 was below 1000 mg/L CN^-. On the other hand, sites 1 and 2 had copper concentrations close to 200 mg/L while that of site 3 had a copper concentration closer to 600 mg/L. Additionally, sites 1 and 3 had similar zinc concentrations while that of site 2 had a higher zinc concentration. Another key difference between all three sites was the Na and Cl^- concentrations. Site 3 had much higher Na and Cl^- concentrations which are expected to have a large effect on the oxidation rate of cyanide and removal of metals such as zinc and copper. All sites had low iron concentrations which means removal of iron should not be of large concern when treating these waters.

Copper and cyanide concentration ranges for synthetic wastewater were chosen to reflect those seen in real process wastewaters. Copper concentrations seen in the real process wastewaters sampled (see Table 3.1) varied between each site with the lowest concentration being 180 mg/L at site 2 and the highest 577 mg/L at site 3. These concentrations of copper are also commonly seen in many barren solutions [1] [37]. The range of copper concentrations tested in synthetic wastewater experiments were chosen to reflect this (Table 3.2). In addition, cyanide concentrations can be near or above 1000 mg/L in real process wastewaters (Table 3.1) and therefore, synthetic solutions were tested at concentrations up to 1000 mg/L CN^-. Cyanide concentrations in barren solutions can also be as low as 50 mg/L [1]. For this study the lowest concentration of cyanide tested was 200 mg/L CN^-.

3.2 Oxidation of Cyanide

This section focuses on the effects of applied cell voltage, NaCl concentration, and initial copper concentration on the kinetics of cyanide electrooxidation. For this analysis, synthetic and real process wastewater was used. The first order rate constant, k, was used to compare the oxidation of cyanide between the three different parameters evaluated. The value for k was determined by fitting the first order degradation model to the experimental data.

3.2.1 Cyanide Oxidation in Synthetic Wastewater

By examining experimental cyanide oxidation data, a first order reaction model was assumed, and the rate constant of cyanide oxidation calculated using the following equation:

$$[CN^-] = [CN^-]_0 e^{-kt} \quad (3.1)$$

where k is the first order rate constant, t is time and $[CN^-]_0$ the initial cyanide concentration in the solution. Although a first order reaction model is not an exact fit for all experiments conducted, particularly at low cyanide concentrations, calculation of k was used to compare the effects of different parameters on cyanide treatment. Experiments for all three tested parameters were fit to a first order reaction model with an R^2 value of 0.98-0.99 which demonstrated that cyanide oxidation generally follows a first order reaction with respect to CN^- ion concentration. Examples of first order kinetic models fit to experimentally determined cyanide oxidation are presented in Figure 3.1.

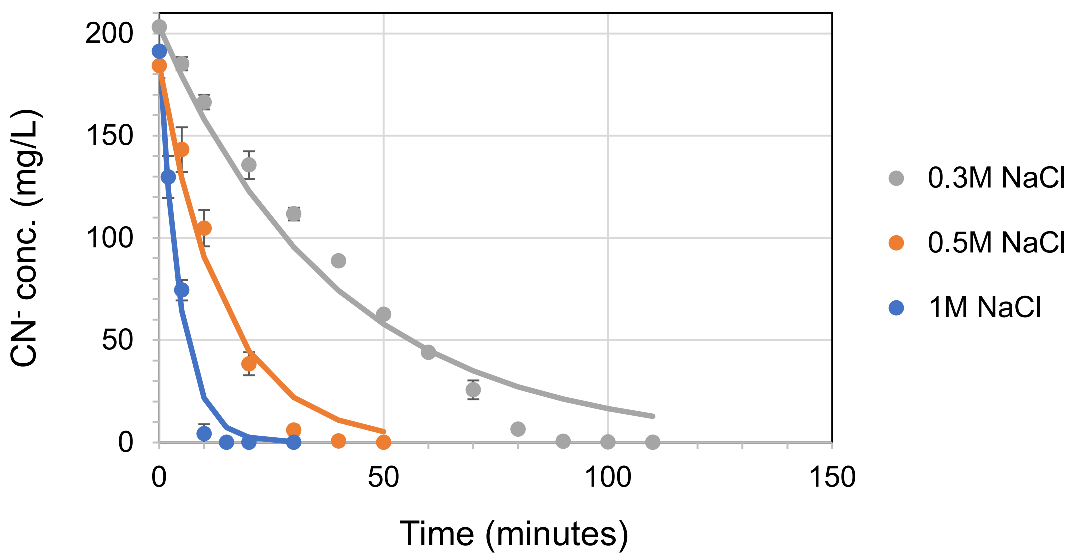
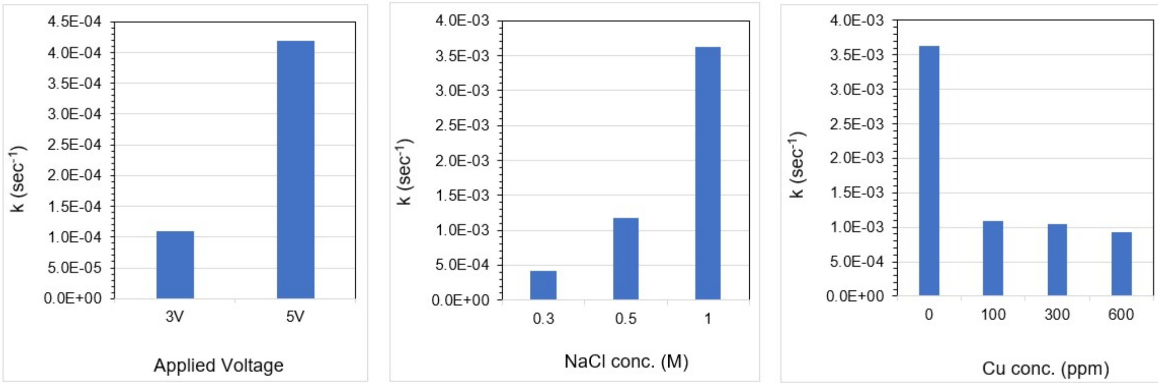


Figure 3.1 Effects of NaCl concentration on the oxidation rate of cyanide. Experiments were conducted at an initial CN^- concentration of 200 mg/L and applied voltage of 5V at three different NaCl concentrations.

The calculated first order rate constants (k values) for different voltage, NaCl and copper concentrations evaluated are presented in Figure 3.2. The collected experimental data along with first order reaction models for each parameter tested are summarized in Appendix A.



(a) (b) (c)

Figure 3.2 Influence of applied voltage, NaCl and copper on first order rate constant, k. (a) Influence of applied voltage at 0.3M NaCl and 200 mg/L total cyanide. (b) Influence of NaCl concentration at an applied voltage of 5V and 200 mg/L total cyanide. (c) Influence of copper concentration at 1M NaCl, 200 mg/L total cyanide and applied voltage of 5V.

Experimental results indicate that the applied cell potential across the anode and cathode has a large effect on the oxidation rate of cyanide. As shown in Figure 3.2, the oxidation of cyanide proceeds at a four times higher rate when 5V is applied compared to 3V. This finding is consistent with the kinetic theory of electrochemical reactions which explains that when the applied voltage is increased, the anodic potential also increases which promotes the reactions occurring at the anode. In this case, the reactions being promoted are those of cyanide oxidation to cyanate and cyanate to CO_2 and N_2 (see reactions 1.7-1.8) [7]. Voltages above 5 were not tested as previous studies have shown that increasing the voltage above 6 can actually slow the rate of cyanide oxidation [25] [20] [21].

Furthermore, results presented in Figure 3.2 indicate that increasing NaCl concentration improves the cyanide oxidation rate. In this study, NaCl concentrations up to 1M were tested to determine the effect of water with high salinity. Over the range of NaCl evaluated, the first order rate constant, k, increased as the concentration of NaCl in the electrolyte was increased (Figures 3.1 and 3.2). This is in part due to an increase in conductivity at higher NaCl concentrations. Previous studies have also postulated that the influence of NaCl on cyanide degradation is due to Cl^- ions being oxidized to free chlorine at the anode (reaction 3.2) which then reacts to form ClO^- ion, also known as hypochlorite (reaction 3.3). The hypochlorite ion is a strong oxidizing agent which can then react with cyanide in alkaline solution to produce nitrogen gas, water, chloride and carbonate ions (reaction 3.4) [20] [10].

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad E^o = +1.36\,V \tag{3.2}$$

$$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O \tag{3.3}$$

$$2CN^- + 5ClO^- + 2OH^- \rightarrow 5Cl^- + N_2 + 2CO_3^{2-} + H_2O \tag{3.4}$$

As previously mentioned, gold processing wastewater can also contain high concentrations of metals, particularly copper, that can form stable complexes with the cyanide ion (CN^-). To evaluate the impact of metal cyanide complexes on cyanide oxidation, copper was added as CuCN to the synthetic wastewater solution used in electrochemical treatment experiments. Results demonstrated that the rate of cyanide oxidation decreased by a factor of three with copper in solution. However, the rate of cyanide oxidation was similar between experiments conducted at lower (100ppm) and higher (600ppm) copper concentrations (Figure 3.2). The decrease in cyanide oxidation rates can likely be attributed to competing reactions occurring at the anode. As represented in reaction 1.9, copper cyanide complexes are also broken at the anode which can reduce efficiency and increase the time needed to oxidize cyanide in the solution [25]. Previous studies have also found that formation of copper oxides at the anode can act as a catalyst for cyanide oxidation [17] [28]. However, in these experiments, copper in the solution did not appear to act as catalyst for cyanide oxidation. This may be due to the oxygen evolution reaction that occurs at the anode (reaction 1.6) which Cheng *et al.* concluded can inhibit the formation of copper oxides at the anode in some cases [21].

When examining the energy consumed during the cyanide oxidation experiments under different conditions (Table 3.3), it can be concluded that a higher applied voltage and NaCl concentration leads to an increased energy consumption per kg of cyanide oxidized. An increased voltage leads to an increased current in the system. Both current and voltage have a direct effect on energy consumption calculations as shown in equation 1.10 therefore increasing both of these also increases energy consumption. The addition of copper to the solution, however, appears to result in a reduction of energy consumption. Additionally, the current efficiency for cyanide oxidation in the system was in the ranges of 20-31% for all conducted experiments (Table 3.3). These current efficiencies are higher than those seen in experiments conducted by Cañizares *et al*. where the reported current efficiencies for cyanide oxidation were in the ranges of 3-8% [10]. Experiments conducted by Sierra-Alvarado *et al.*, on the other hand, reported current efficiencies ranging from 20% to over 90%, however, their synthetic wastewater solutions did not contain any NaCl [7]. There also appears to be some reduction in current efficiency as applied voltage increases. Experiments conducted by Sierra-Alvarado *et al* also indicated a reduction in current efficiency as the applied current density was increased. They concluded that at higher applied current densities, a large amount of the current is used by parasitic reactions such as the oxygen evolution reaction which results in a decrease in the current efficiency for cyanide oxidation [7].

Table 3.3 Current efficiency and energy consumption for cyanide oxidation in synthetic wastewater.

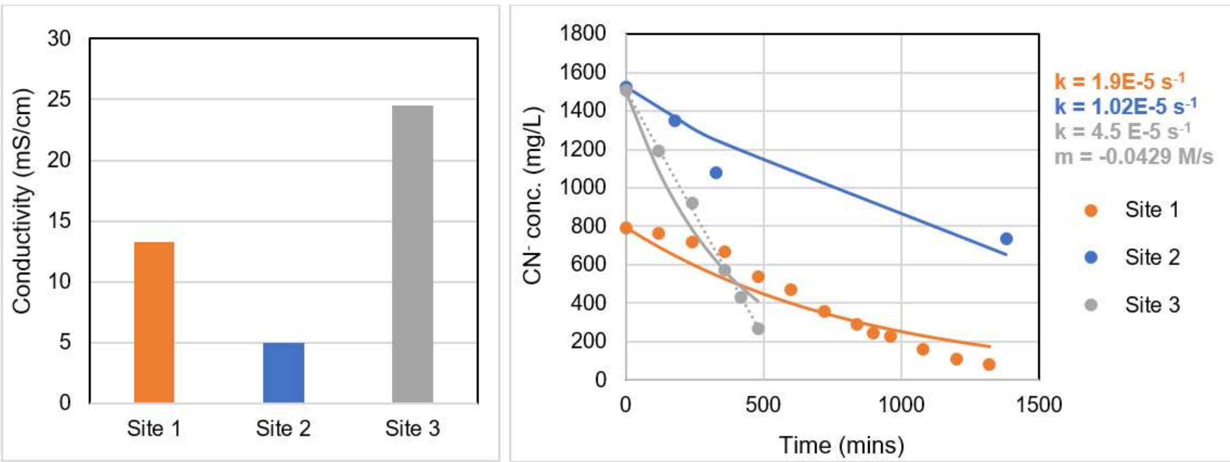
Parameter tested	Condition	Current efficiency (%)	Energy consumption (kWh/kg-CN^-)
Voltage (0.3M NaCl)	3V	31.2	20.4
	5V	23.7	43.4
NaCl conc. (5V)	0.3M	23.7	43.4
	0.5M	25.3	40.5
	1M	20.5	50.3
Copper conc. (5V, 1M NaCl)	0 ppm	20.5	50.3
	100 ppm	29.7	34.6
	300 ppm	22.6	45.6
	600 ppm	24.6	41.9

3.2.2 Cyanide Oxidation in Real Gold Cyanidation Wastewater

Wastewater samples collected from the three processing sites displayed varying measured electrical conductivities, which was used in this study as a surrogate for total dissolved solids (Figure 3.3). Unlike synthetic water solutions, which were composed of NaCl as the electrolyte, real processing water was composed of a mixture of various ions (Table 3.1) although the dominant ions included Na, Cl^- and SO_4^{2-} (Table 3.1). For example, site 3, which had the highest conductivity, also had the highest concentration of Na, Cl^-, and SO_4^{2-} ions when compared to the other two sites. Based on experiments conducted by Felix-Navarro *et al*, however, SO_4^{2-} has a minimal impact on cyanide oxidation rates, with concentrations of Na and Cl^- ions reportedly more important [20]. In the present study, similar effects of electrolyte composition on cyanide oxidation rates were observed between real process wastewater experiments and the synthetic water experiments. For example, results from these experiments show that water with a higher conductivity leads to a much faster rate of cyanide oxidation (Figure 3.3). Water from sites 1 and 2, which had lower conductivity, took close to 23 hours to degrade 89% and 51% of the cyanide respectively, while it took around 8 hours to degrade 82% of the cyanide from site 3 which had a much higher conductivity (see Figure 3.3). Since conductivity is related to the concentration of ions such as Na and Cl^- in the solution, it can be inferred that solutions with a higher concentration of these ions have an increased rate of cyanide oxidation as seen with synthetic water experiments. Compared to synthetic water experiments, however, real process wastewater had an overall slower rate of cyanide oxidation which is likely due to the presence of metal-cyanide complexes that interfere with oxidation reactions. In addition, unlike synthetic water experiments, cyanide oxidation in real wastewater samples did not always appear to follow first order kinetics. Cyanide oxidation from water in sites 1 and 2 fit closer to a first order rate model with R^2 values between 0.93-0.95. Water from site 3, on the other hand, displayed a linear (zero order) rate of cyanide oxidation with an R^2 value of 0.99. Although a first order rate model for site 3 had an R^2 value of 0.96, the zero order rate model had a much closer fit. The zero order rate constant was calculated using the following equation:

$$[CN^-] = mt + [CN^-]_0 \tag{3.5}$$

where m is the zero order rate constant, t is time and $[CN^-]_0$ is the initial cyanide concentration in the solution.



(a) (b)

Figure 3.3 (a) Conductivity in water from 3 gold processing sites. (b) Effect of conductivity on the oxidation rate of cyanide at an applied voltage of 5V.

Further analysis was conducted on wastewater from sites 1 and 2 to determine the effects of applied cell voltage on cyanide oxidation rates. Wastewater from sites 1 and 2 was tested at an applied voltage of 2V and 5V and results fit to a first order reaction model with R^2 values between 0.93-0.98. The experimental data and first order reaction models are presented in Appendix B. First order cyanide oxidation rate constants (k values) for these experiments are shown in Figure 3.4. Similar to synthetic water experiments, results demonstrated that a higher applied voltage led to a faster rate of cyanide oxidation. For site 1, the rate of cyanide oxidation proceeded almost twice as fast while that of site 2 proceeded almost four times as fast when 5V were applied compared to 2V.

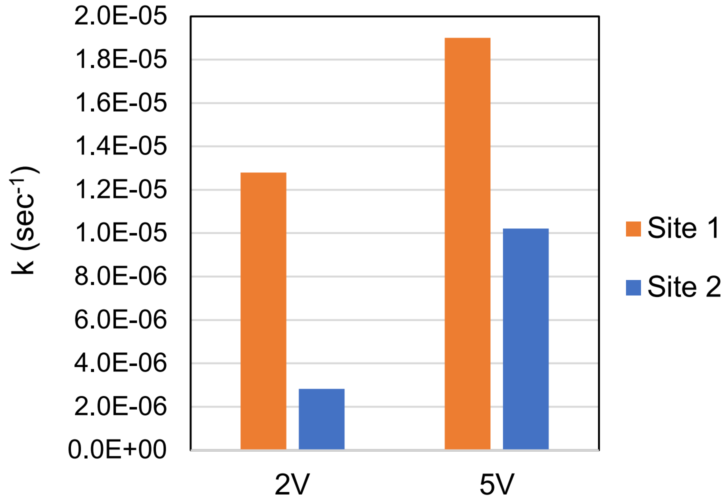


Figure 3.4 Influence of voltage on first order rate constant, k, for sites 1 and 2.

Energy consumption values for cyanide oxidation in real wastewater samples for the different conditions tested are presented in Table 3.4. In general, higher applied voltage resulted in higher energy consumption, however, a higher conductivity resulted in a decrease in energy consumption per kg of cyanide oxidized (Table 3.4). This can likely be attributed to the varying concentrations of Na and Cl^- ions in each wastewater sample. Abdel Aziz *et al.* postulated that increasing NaCl concentration can reduce the cell resistance which should result in a decrease in energy consumption [24]. Although this observation differs from the observed impact of NaCl on cyanide oxidation in synthetic water, energy consumption also depends on the time a system is operated to oxidize cyanide to a predetermined concentration. For instance, water from site 1, which had a lower conductivity, also had a lower amount of cyanide than sites 2 and 3 which reduced the time needed for operation of the electrochemical system and consequently reduced the energy consumption (equation 1.10). Furthermore, in terms of current efficiency, results show that an increased voltage leads to reduced current efficiency which was also seen with synthetic water experiments. An increase in conductivity, on the other hand, led to an increased current efficiency. At the highest conductivity tested, close to 87% current efficiency was calculated. At a higher conductivity, there is an increase of Cl^- in the solution which results demonstrated increases the oxidation rate of cyanide. This may lead to more of the available Coulombs in the system being used for the oxidation of cyanide (reaction 1.7), therefore, an increase in current efficiency for cyanide removal is seen as the conductivity increases.

Table 3.4 Current efficiency and energy consumption for cyanide removal in real wastewater.

Parameter tested	Condition	Current efficiency (%)	Energy consumption (kWh/kg-CN^-)
Voltage (5 mS/cm)	2V	64.4	5.8
	5V	12.4	75.8
Conductivity (5V)	5 mS/cm	29.5	75.8
	13.3 mS/cm	12.4	31.7
	24.5 mS/cm	86.6	10.6

3.3 Heavy Metal Removal/Recovery

This section focuses on the removal/recovery of heavy metals from gold processing wastewater while simultaneously degrading cyanide using electrochemical methods.

3.3.1 Copper Removal/Recovery in Synthetic Wastewater

For synthetic wastewater experiments, copper was added as CuCN to the solution and experiments run until a significant among of cyanide could be removed, in most cases close to or equal to 99%. Experiments were performed to determine the influence of initial cyanide concentration, NaCl concentration, and applied cell voltage on copper removal (Figure 3.5).

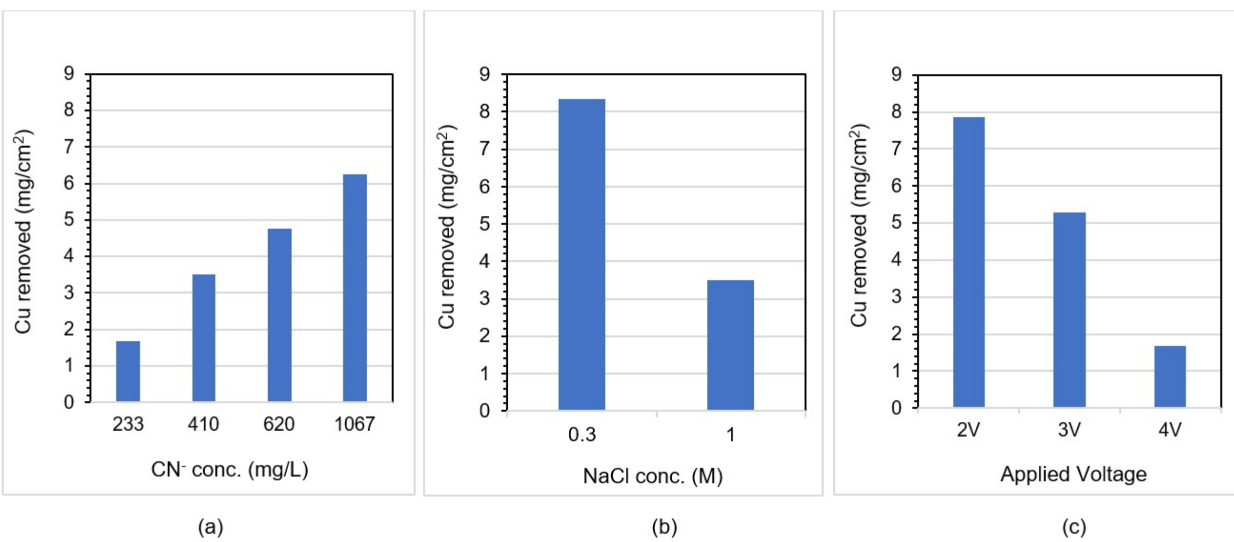


Figure 3.5 Influence of experimental parameters on copper removal/plating from the solution. All experiments were conducted at a copper concentration of 300 mg/L. (a) Influence of initial cyanide concentration at 1M NaCl and 4V. (b) Influence of NaCl concentration at 400 mg/L total cyanide and applied voltage of 4V. (c) Influence of applied voltage at 1M NaCl and 200 mg/L total cyanide.

Results presented in Figure 3.5 (a) indicate that at a fixed copper concentration, increasing the concentration of cyanide in the solution increased the amount of copper plated out of solution onto the cathode. This suggests that higher $[CN^-]/[Cu^+]$ ratios could be beneficial for plating and recovering copper out of solution. However, these experiments were run until over 90% of cyanide had been oxidized. As a result, experiments containing high cyanide concentrations were performed for a longer period of time which may have led to an increase in the amount of copper plated onto the cathode. Figures showing copper removal as mg/cm^2/time are presented in Appendix A and showed a similar pattern of copper removal up to a concentration of 620 mg/L CN- after which the amount of copper removed decreased.

Results also indicate that in synthetic solutions, lower NaCl concentrations can allow more copper to be plated out of the solution (Figure 3.5 (b)). This may be due to the efficiency in which electrons are being transferred to facilitate the reduction of copper reactions (reactions 1.3-1.4). Results for cyanide oxidation in real gold cyanidation wastewaters indicated that at higher NaCl concentrations, the current efficiency of cyanide oxidation increases (Table 3.4). As more electrons are being transferred to facilitate the cyanide oxidation reaction, there are less electrons being transferred for the reduction of copper reactions. This is reflected by the decrease in current efficiency of copper recovery seen higher NaCl concentrations which may explain why less recovery of copper is seen at higher NaCl concentrations (Table 3.5).

Results presented in Figure 3.5 (c) also indicate that better copper removal was achieved at a lower applied voltage. Felix-Navarro *et al*. concluded that reduction of copper is faster at lower applied voltages and in their study, increasing the voltage above 3V slowed the removal of copper ions. They concluded that this is likely due to the evolution of hydrogen gas at the cathode (reaction 1.5) which can interfere with the diffusion of copper ions from the solution onto the cathode surface [25].

Results for percent removal of copper for the experiments conducted in this section are presented in Figure 3.6. The highest percent removal of copper achieved was approximately 52% at an applied voltage of 4V, 0.3M NaCl concentration, and initial cyanide concentration of 400ppm. More removal of copper may be achieved for all experiments if they are run for longer periods of time. In this case, all experiments were stopped once close to 98% of cyanide removal had been achieved.

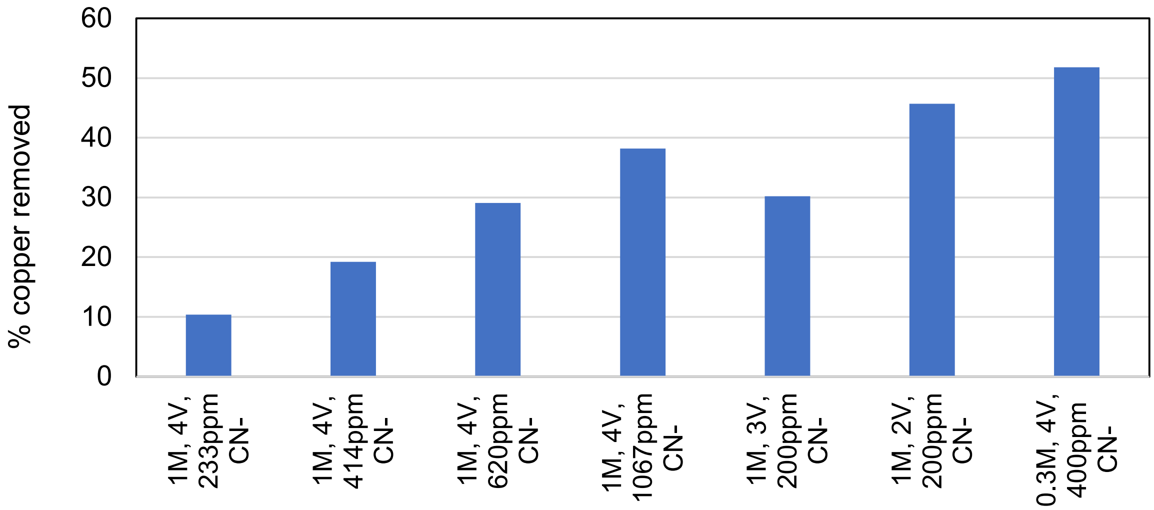


Figure 3.6 Percent of copper removed in synthetic wastewater experiments.

Current efficiency and energy consumption for copper removal were also calculated (see Table 3.5) with energy consumption calculated as kWh per kg of copper removed from solution. Results indicated that current efficiency decreased as NaCl concentrations and applied voltage increased. However, increasing the concentration of cyanide in the solution did not have a large impact on current efficiency. Energy consumption was found to increase as voltage and NaCl concentrations increased.

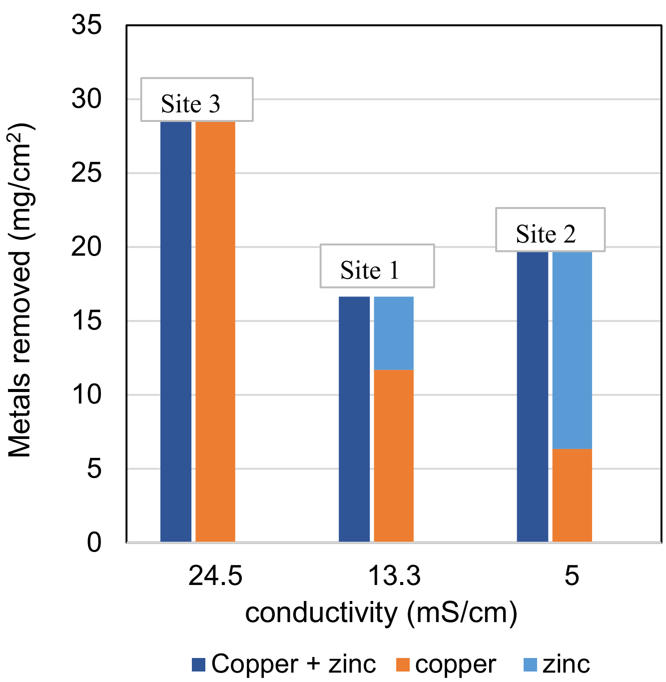
Table 3.5 Current efficiency and energy consumption for copper removal in synthetic wastewater.

Parameter tested	Condition	Current efficiency (%)	Energy consumption (kWh/kg-Cu)
Initial CN- conc. (4V, 1M NaCl, 300ppm Cu)	233 ppm	1.48	114.3
	414 ppm	1.72	98.2
	620 ppm	2.08	81.5
	1067 ppm	1.47	115.4
NaCl conc. (400 ppm CN^-, 5V)	0.3M	4.52	38.3
	1M	1.72	98.2
Applied Voltage (1M NaCl, 200 ppm CN^-)	2V	30.9	2.7
	3V	6.75	18.9
	4V	1.48	114.3

3.3.2 Heavy Metal Removal in Real Gold Cyanidation Wastewater

Experiments were conducted with real process wastewater to determine the effects of conductivity and applied voltage on metal removal. Through ICP-AES analysis of the water, it was determined that there was only significant removal of zinc and copper. As such, only the effects of the selected parameters on removal of zinc and copper were studied.

The effect of conductivity on the removal of copper and zinc from real mining wastewater is presented in Figure 3.7. It was determined that wastewater at site 3, which had the highest conductivity, had better removal of metals from the solution (see Figure 3.7). As previously mentioned, solutions with a higher conductivity also had higher concentration of Na and Cl^- ions (Table 3.1). Unlike results seen with synthetic solutions, real process wastewater experiments show that an increase in the concentration of these ions lead to better removal of metals from the solution. However, although the conductivity was 2.5 times higher at site 1 compared to site 2, there was a similar amount of metal removal seen at these sites. This may be due to site 2 having a higher concentration of zinc in solution (Table 3.1) which led to more zinc being plated out of the solution when compared to site 1. Experiments conducted by Felix-Navarro *et al* using synthetic wastewater demonstrated that higher NaCl concentrations lead to an increase in the copper removal rate which correlates with some of the results seen with real wastewater experiments [25]. However, more experiments with real gold cyanidation wastewaters need to be conducted to conclude the effects of conductivity on removal of metals.



(a)

(b)

Figure 3.7 (a) Influence of conductivity on removal of copper and zinc from real gold process wastewaters. (b) Electrodes after experiment using water from site 3.

Unlike synthetic water experiments, increasing the applied voltage in electrochemical experiments with real wastewater led to higher removal of copper and zinc (Figure 3.8). Water from sites 1 and 2 was tested at 5V and 2V and removal of copper and zinc was higher for both sites at an applied voltage of 5V compared to 2V. Analysis of initial and final weak and strong metal-cyanide complex concentrations in each experiment provides insight for why increasing the applied voltage increases the removal of copper and zinc from wastewaters.

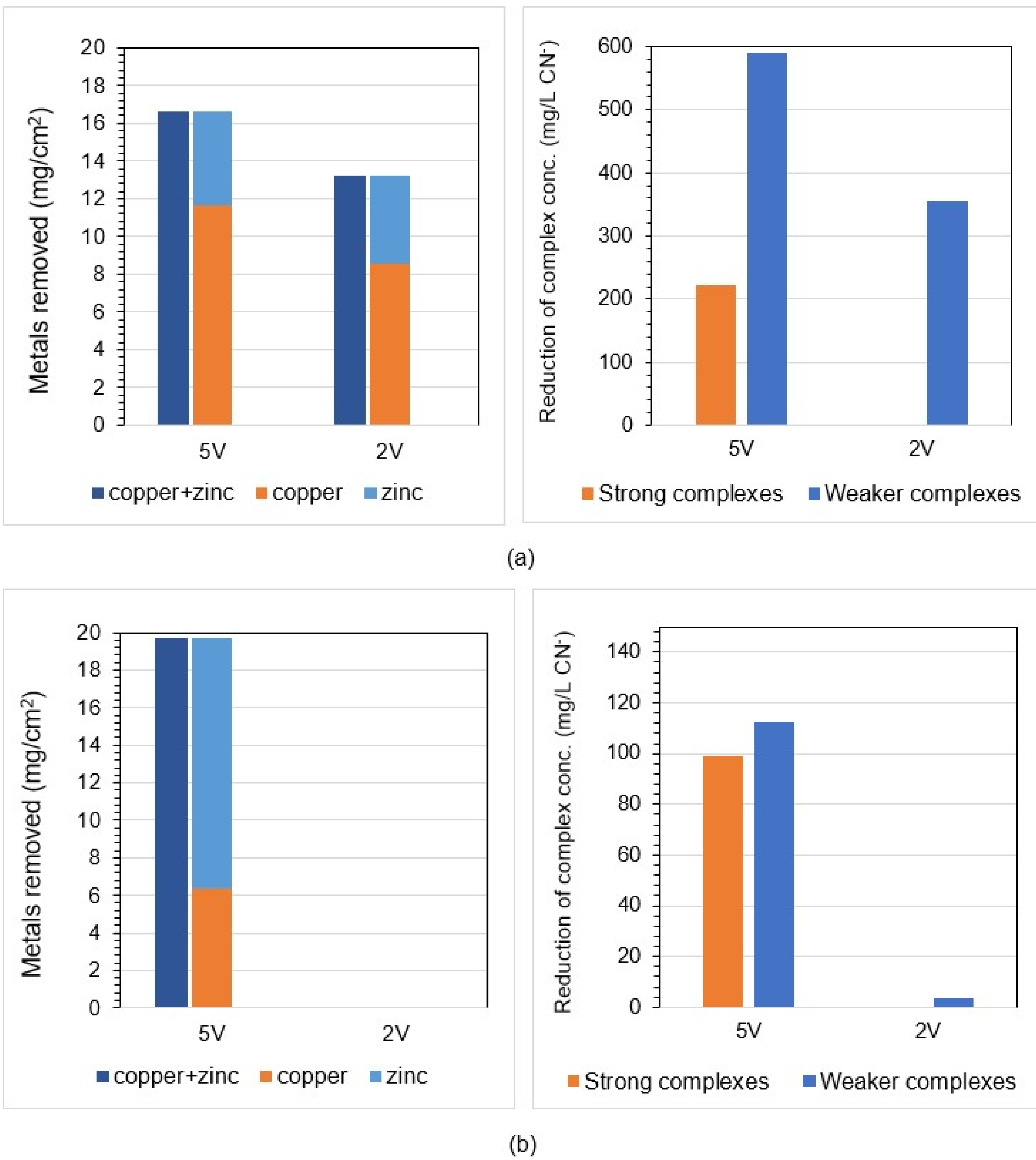


Figure 3.8 Influence of applied voltage on removal of copper and zinc and reduction of strong and weak metal-cyanide complexes in real gold process wastewater at (a) site 1, (b) site 2.

Results show that experiments conducted at 2V led to a small decrease in the concentration of weak complexes and no decrease in concentrations of strong complexes. Experiments conducted at 5V, on the other hand, led to a more significant decrease in the concentration of weak and strong metal-cyanide complexes (Figure 3.8). These results indicate that increasing the applied voltage will lead to more metal-cyanide complexes being broken, particularly weak complexes such as those of copper and zinc. This in turn increases the amount of metal ions in the solution that can be plated onto the cathode surface which is consistent with the results seen at 5V. The mechanism for copper recovery at the cathode is shown in reactions 1.3 and 1.4. For zinc recovery at the cathode, a similar mechanism to copper has been proposed in some studies. Zinc-cyanide complexes at an alkaline pH are mainly composed of $Zn(CN)_4^{2-}$ and $Zn(CN)_3^-$ (Figure 3.9). Wei *et al*. postulated that once these metal-cyanide complexes are decomposed into metal ions of Zn^{2+} (reactions 3.6-3.7), these ions can be deposited onto the cathode surface as their elementary substance (reaction 3.8) [21] [36]. A small portion of metal ions near the anode can also be oxidized and plated onto the anode as CuO and ZnO [21].

$$Zn(CN)_4^{2-} \rightarrow Zn^{2+} + 4CN^- \tag{3.6}$$

$$Zn(CN)_3^{-} \rightarrow Zn^{2+} + 3CN^- \tag{3.7}$$

$$Zn^{2+} + 2e^- \rightarrow Zn \tag{3.8}$$

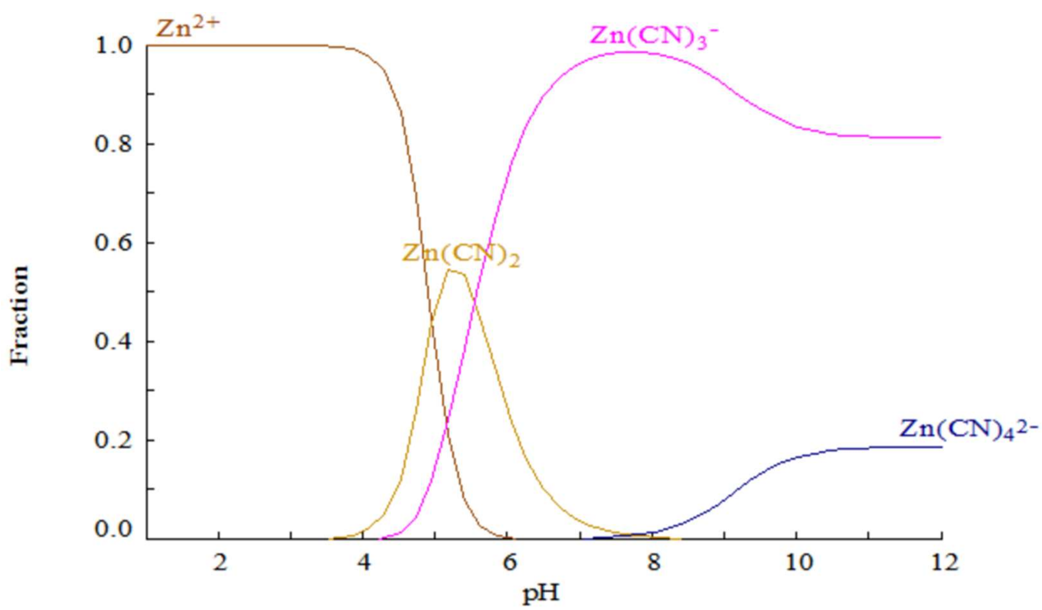


Figure 3.9 Species distribution diagram as a function of pH for a zinc-cyanide solution. Diagram conditions: 0.058M CN^-, 0.0025M Zn^{2+}. These conditions are for site 3, however, the diagram shows the same species distribution for sites 1 and 2.

Results for percent removal of copper, zinc and cyanide in the experiments conducted in this section are presented in Figure 3.10. Overall, results indicate that higher applied voltages increase the percent removal of cyanide and either copper or zinc, especially at sites with higher conductivities such as sites 1 and 3. Above 90% of copper removal and above 80% of cyanide removal was achieved at sites 1 and 3 when 5V were applied. The highest removal of zinc (70%) was achieved at site 1 when 5V were applied. To achieve higher percent removals of copper, zinc, and cyanide, experiments would need to be run for longer periods of time.

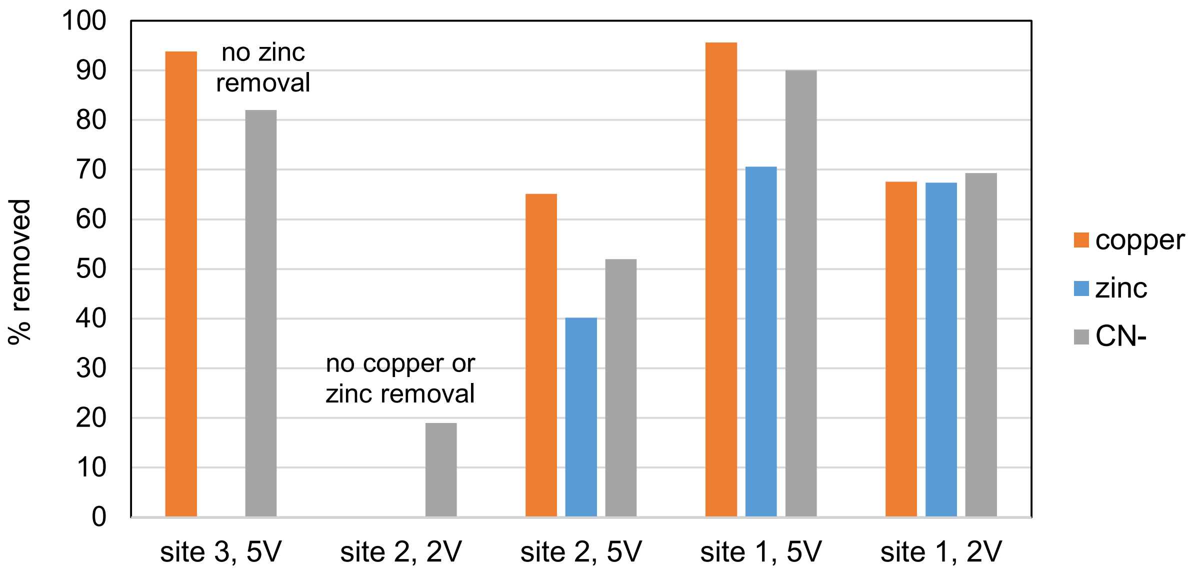


Figure 3.10 Percent removal of copper, zinc, and cyanide in real wastewater experiments.

Current efficiency and energy consumption for metal removal were also analyzed using data generated from these experiments. Energy consumption was calculated as kWh per kg of copper and zinc removed. As seen in Table 3.6, increasing the conductivity in the solution can lead to an increase in current efficiency and reduction of energy consumption. Applying a lower voltage also leads to an increase in current efficiency and reduced energy consumption which is consistent with results seen for synthetic wastewater experiments.

Table 3.6 Current efficiency and energy consumption for metal removal in real wastewater.

Parameter tested	Condition	Current efficiency (%)	Energy consumption (kWh/kg-Zn+Cu)
Conductivity (5V)	24.5 mS/cm	15.8	24.2
	13.3 mS/cm	1.8	269.6
	5 mS/cm	5.9	573.6
Voltage (5 mS/cm)	2V	14.9	40.5
	5V	1.8	573.6

CHAPTER 4 CONCLUSIONS

This study evaluated the effects of different parameters such as applied voltage, initial cyanide and copper concentrations and composition of the electrolyte on the oxidation rates of cyanide and removal of metals from synthetic and real gold cyanidation wastewater. Oxidation rates of cyanide were first studied based on applied voltage, NaCl concentration, conductivity, and copper concentration for synthetic and real mining wastewaters. Results indicate that rates of cyanide oxidation have a closer fit to a first order reaction for all waters tested except for real process wastewater at site 3 which showed a linear (zero order) rate of cyanide oxidation. The oxidation rate also increased with increased conductivity, NaCl concentrations and higher applied voltages.

Copper recovery or removal was then studied based on applied voltage, NaCl concentration and initial cyanide concentration for synthetic wastewaters. Results indicated that for synthetic solutions, which only contained copper, lower voltages, lower NaCl concentrations, and higher initial cyanide concentrations led to increased copper removal. Removal of metals in real process wastewater samples was only studied based on applied voltage and conductivity and results differed from those of synthetic solutions. Results indicated that increasing applied voltage leads to more metal removal as more metal-cyanide complexes are broken at a higher applied voltage. Additionally, increased conductivity, which correlates with an increase in the concentration of Na and Cl^- ions in the solution, appears to lead to more removal of metals, however, more experiments need to be conducted to determine this. ICP-AES analysis showed that there was only a significant decrease in the concentrations of zinc and copper in all conducted experiments. Future work includes conducting more experiments with real gold cyanidation process wastewater to determine optimal conditions based on water composition. In addition, more analysis of products of cyanide oxidation is needed to enhance understanding of reactions occurring in the electrochemical system.

Overall, this study shows that electrochemical methods can effectively be used to degrade cyanide and simultaneously remove metals such as copper and zinc from gold cyanidation wastewaters. Optimal conditions for an electrochemical system can vary depending on the composition of the water being treated, however, for both synthetic and real gold cyanidation process wastewaters, results indicate that addition of NaCl and an applied voltage of 5V can be beneficial as higher NaCl concentrations in the electrolyte and higher applied voltages help increase the oxidation rate of cyanide and removal of metals. For instance, the experiment with real wastewater from site 3 which had the highest measured conductivity and was run at 5V, resulted in over 90% of copper removal and over 80% cyanide removal in a shorter amount of time. Results with real gold cyanidation wastewaters also indicated that an increase in conductivity which correlates with an increase in NaCl concentrations can help decrease energy consumption and increase current efficiency of the system.

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APPENDIX A RESULTS FOR SYNTHETIC WASTEWATER EXPERIMENTS

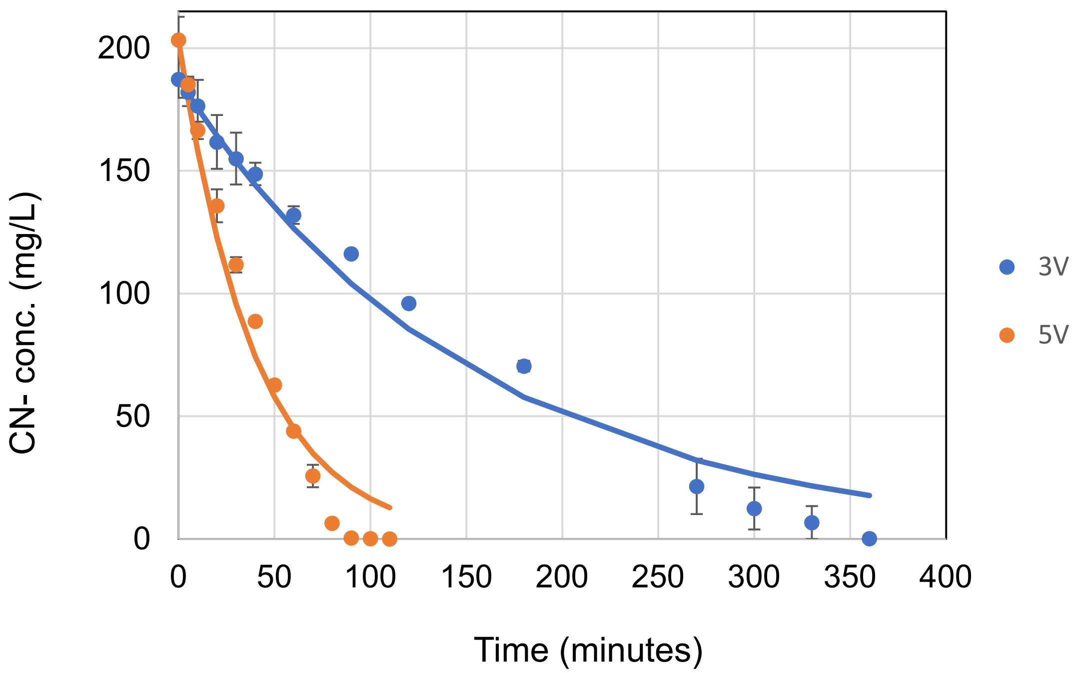


Figure A.1 Effects of applied cell voltage on cyanide oxidation rates. These experiments were run at an initial cyanide concentration of 200 ppm and 0.3M NaCl concentration.

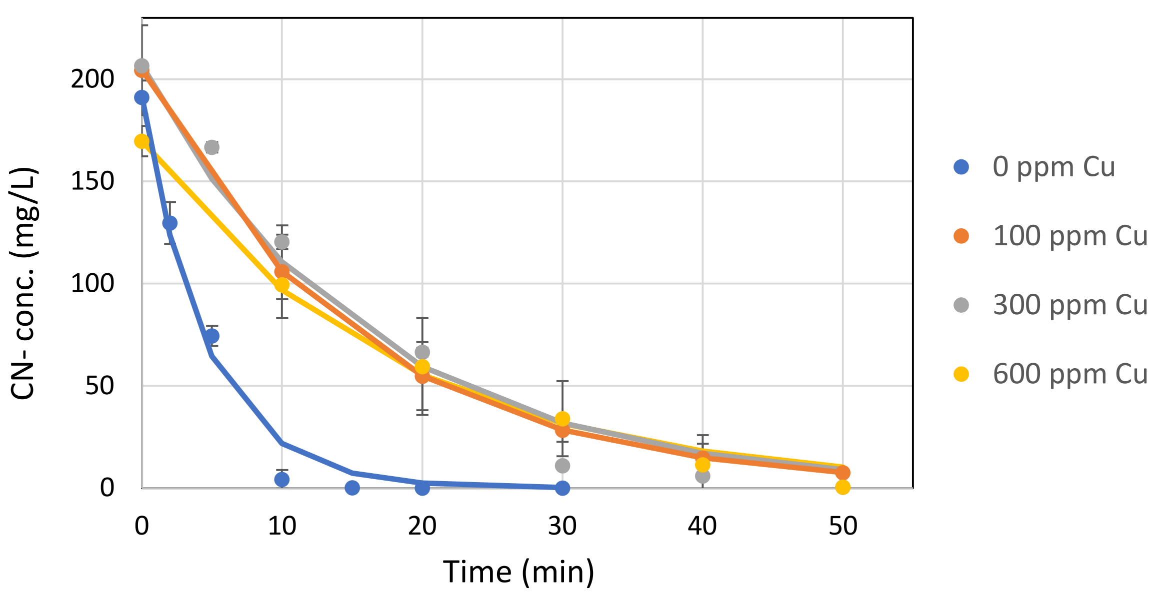
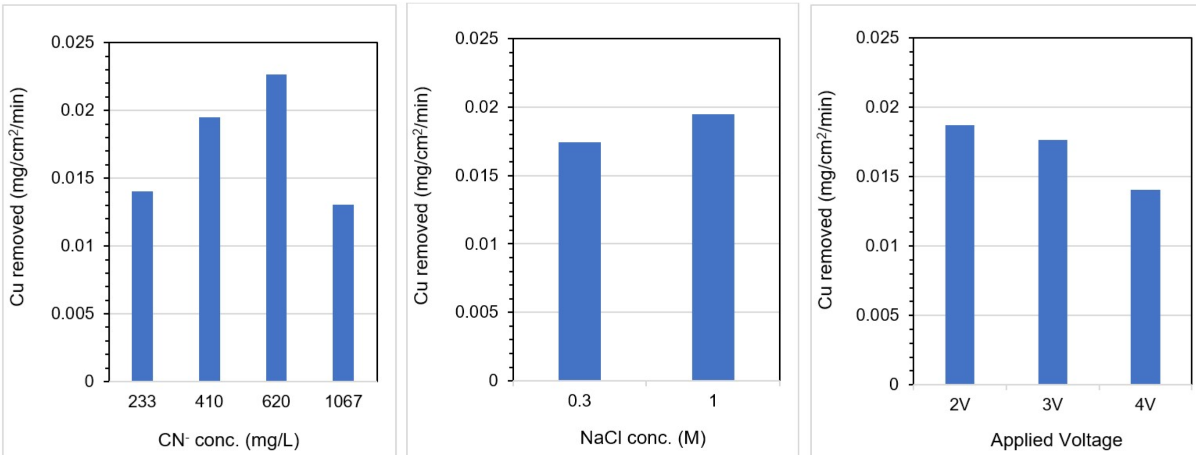


Figure A.2 Effect of copper concentration on cyanide oxidation rates. Synthetic water solution was prepared using NaCN, NaCl and CuCN with a free cyanide concentration of approximately 200 mg/L and 1M NaCl concentration.



(a) (b) (c)

Figure A.3 Influence of experimental parameters on removal of copper as mg per area of electrode submerged per time. All experiments were conducted at a copper concentration of 300 mg/L.(a) Influence of initial CN- concentration at 1M NaCl and 4V. (b) Influence of NaCl concentration at 400 mg/L total cyanide and 4V. (c) Influence of applied voltage at 1M NaCl and 200 mg/L total cyanide.

APPENDIX B RESULTS FOR REAL GOLD CYANIDATION WASTEWATER EXPERIMENTS

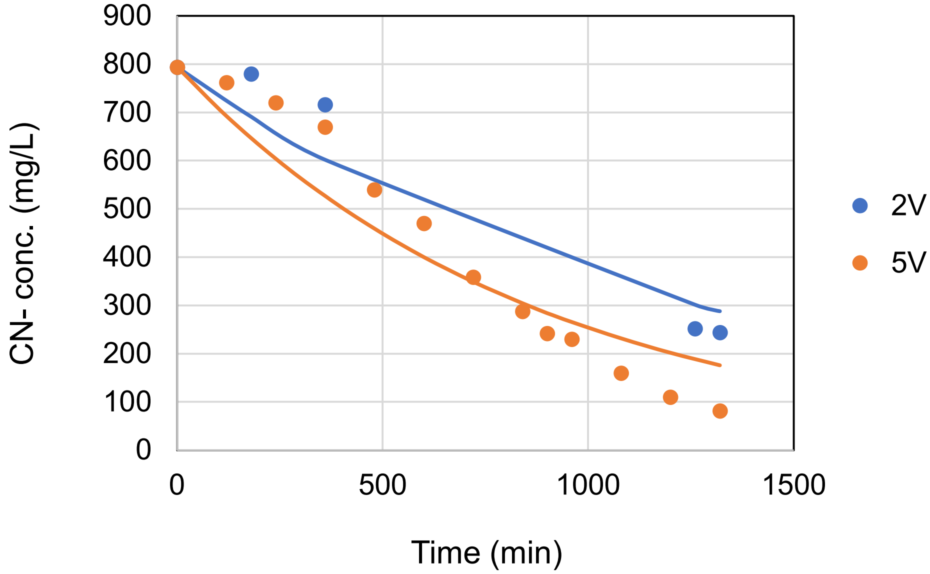


Figure B.1 Effect of voltage on real gold process wastewater (site 1).

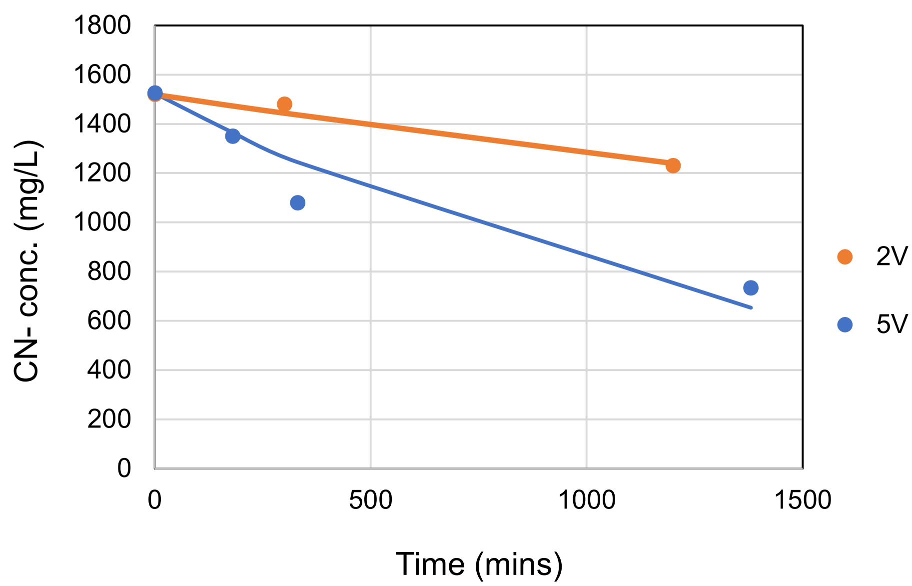


Figure B.2 Effect of voltage on real gold process wastewater (site 2).