

# Copper-Activated *In Situ* Chemical Oxidation of Cyanide in Water Using Persulfate

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## Abstract

Cyanide is found commonly in effluents coming from metallurgical processes. Cyanide toxicity poses a serious environmental threat. In this study, the stoichiometry, kinetics, and mechanism of the *in situ* chemical oxidation of cyanide in the presence of copper-activated persulfate were investigated. Ion selective electrode (ISE) was used to monitor the concentration of cyanide. Chemical and spectroscopic analyses were employed to characterize the products formed upon oxidation. An accelerated reaction using  $S_2O_8^{2-}$  to destroy cyanide can be achieved via chemical activation with copper (II) ions to generate reactive sulfate radicals ( $SO_4^{\cdot-}$ ).  $Cu^{2+}$  improved the percent removal of cyanide at room temperature. Under the optimum copper to persulfate ratios (1:1 and 1.5:1), 98% of the initial cyanide concentration was degraded at  $t = 90$  minutes. They also obey pseudo-second order kinetics and their forward reactions are relatively favorable based on reaction coefficient values. The  $[Cu]:[S_2O_8^{2-}]$  ratio of 1.5:1 resulted in rapid degradation of cyanide in the first half of the reaction but was accompanied by a decrease afterwards. In contrast, the  $[Cu]:[S_2O_8^{2-}]$  ratio of 1:1 has a longer lasting degradation effect. Unlike other activation methods,  $Cu^{2+}$  does not exert 100% oxidative capacity on cyanide, only around 75%. IR spectroscopic analysis and qualitative test also suggest the formation of thiocyanate and copper (I) cyanide complex, respectively. Thus, persulfate activation by  $Cu^{2+}$  ions improved the cyanide oxidation process.

**Keywords:** kinetics, mechanism, degradation, environment

## Introduction

Several industrial operations such as mining and burning coal or natural gas pose negative impact on the environment. Soil and groundwater pollution, caused by toxic chemicals, heavy metals through industrial refuse, mine tailings, agricultural processes, improper sanitation, spillage of petrochemicals, and ineffective soil and water management, is one of the world's prevalent environmental problems. According to the Mines and Geosciences Bureau – Mining Environment and Safety Division (2006), in the Philippines, extremely high levels of heavy metals in soil are in various proportions in different mining areas plus their transported sediments in the lowland. These chemicals may be foreign to the area or they may be naturally occurring materials that pollute the water by being present in high amounts. Several treatments have been developed for its remedy, such as thermal, biological, physical, and chemical treatments. *In situ* chemical oxidation, abbreviated as ISCO, has received much attention in recent years as a chemical

remediation technique for sites contaminated with organic compounds. It is simply the introduction of oxidants in the subsurface to degrade contaminants, either by decreasing its mass, mobility, and/or toxicity. The common oxidants used are permanganate ( $MnO_4^-$ ), hydrogen peroxide ( $H_2O_2$ ) and iron (Fe) (Fenton-driven or  $H_2O_2$ -derived oxidation), persulfate ( $S_2O_8^{2-}$ ), and ozone ( $O_3$ ) (Huling & Pivetz, 2006). A large number of pollutants can be destroyed using ISCO. Which pollutant to destroy depends on the oxidant. Some of these persistent pollutants are chlorinated carbon compounds, phenols, polycyclic aromatic hydrocarbons (PAHs), and cyanides.

Cyanide, a singly-charged anion of carbon and nitrogen held by triple bond ( $CN^-$ ), is a toxic species. It is generated mostly by metallurgical operations. Cyanide is lethal in a way that it prevents the cells from using oxygen to make energy molecules (Helmenstine, 2018). Cyanide can be destroyed by several methods namely physical, adsorption, complexation, and oxidation methods (Young & Jordan, n.d.). However,

cyanide remediation by *in situ* chemical oxidation has not yet been fully developed. A study of FMC Corporation, a chemical company in Philadelphia supplying industrial and consumer markets, confers that hydrogen peroxide is a powerful oxidant for cyanide destruction (Hydrogen Peroxide and Caro's Acid, n.d.). Conversely, ammonium, sodium, and potassium persulfates will also break down cyanide but will react much slower than that of peroxide. One way to solve this problem is to employ activation in the process – increasing the rate of a reaction by a certain material, in this case, copper (II) ion (Huling & Pivetz, 2006).

The laboratory-scale study of chemical remediation plays a vital role in the design of remediation technologies. Thus, the main goal of this study is to investigate the mechanism of laboratory-scale *in situ* chemical oxidation of cyanide in water with sodium persulfate using copper as an activator. Specifically, it sought to: (i) quantify free cyanide before and after oxidant flush; (ii) evaluate role of copper as an activator in terms of percent cyanide degradation; and (iii) assess the equilibrium and kinetics of the copper-activated oxidation of cyanide using persulfate.

Soil and groundwater remediation are instruments for the protection of natural resources, enhancement of food and water security, and preservation of the environment. Developed chemical oxidation methods have been found to work well through the years. Thus, the study's goals were devised to improve the understanding of the underlying chemistry in *in situ* chemical oxidation.

## Materials and Methods

### Preparation of Reagents and Materials

Reagent grade sodium persulfate was purchased from Chemline Philippines. Cyanide solution was procured from the Department of Environment and Natural Resources – Environmental Management Bureau V (DENR – EMB V). DENR Administrative Order No. 39, Series of 1997, Section 6 and DENR Administrative Order No. 29, Series of 1992, Chapter VI, Section 22 state that cyanide to be produced or used in small quantities solely for experimental or research and development purposes is exempted from the issuance of chemical control order (CCO). Copper sulfate, in its solid form, potassium permanganate, sodium hydroxide and ammonium hydroxide were obtained from Bicol University College of Science Laboratory Instrumentation Office (BUCSLIO).

### Preparation of Cyanide Water Samples

0.3 mL of 100 ppm cyanide standard solution was diluted to 100 mL with cyanide diluent (1.66 g NaOH dissolved in 1 L distilled water) to prepare 0.3 ppm cyanide water sample (American Public Health Association et al., 1999). The same procedure was done for each treatment. Ion Selective Electrode (ISE) was used to quantify  $CN^-$  concentration of samples. The ISE can only detect concentrations ranging from 0.03 to 3.0 ppm.

### Introduction of Copper and Persulfate to Cyanide Samples

For each treatment, the prepared 100 mL cyanide sample was placed in a plastic vial wrapped with aluminum foil. The initial cyanide concentration of each treatment was found to be 0.3 ppm.

Ten vials were grouped into five treatments, two replicates for each. Table 1 shows the concentrations of the five copper sulfate and persulfate combinations. USP Technologies (2018) recommends 1.2 mole ratio of sodium persulfate to cyanide. This corresponds to 0.014 mmol persulfate or 2.66 mg persulfate per vial. To achieve this, 266 mg persulfate was dissolved in 1L distilled water. Ten (10) mL aliquot was added to each vial. According to Liu et al. (2012), the rate of degradation with persulfate can be increased by adding copper and the best copper to persulfate mole ratio is 1:1. Thus, considering the  $\pm 50\%$  threshold, the lower and upper limits of this copper to persulfate ratio were set to 0.5:1 and 1.5:1, respectively. Converting to milligrams, 1.33, 2.66, and 3.99 were obtained. The treatment with 0 mg copper served as the negative control. On the other hand, Burce et al. (2010) used 3.05 g potassium permanganate to 1.00 g cyanide ratio and 50 ppm copper for 500 mL sample solution for the most effective cyanide degradation. Following the ratios from the study of Burce et al. (2010), 0.92 mg of permanganate was used as an oxidant for 0.3 ppm cyanide solution and 5 ppm copper was incorporated for the 100 mL sample of this solution. This served as the positive control. Copper sulfate was mixed with the oxidant first and upon complete dissolution, it was added to the water samples.

**Table 1** Amount of Copper Sulfate and Oxidant for Every Treatment

Treatments	Concentration	
	CuSO <sub>4</sub> (mg)	Oxidant (mg)
1	0.00	
2	1.33	2.66 persulfate
3	2.66	
4	3.99	
5	0.50	0.92 permanganate

### Cyanide Concentration Reading

Aside from keeping the treatments at room temperature, a pH above 9 was maintained by adding 1mL ISA solution (40 g NaOH in 100 mL distilled water) before reading to achieve better reaction conditions (Cyanide Treatment, 2018). The ion selective electrode (ISE) equipment was used to measure the cyanide concentration of the two replicates of each treatment every fifteen minutes (Burce et al., 2010). This is because oxidation by persulfate requires hours to weeks to complete (Huling & Pivetz, 2006).

Percent cyanide degradation ( $X_a$ ) of each treatment at a certain time was calculated using the formula

$$X_a = \frac{A_o - A}{A_o} \times 100\% \quad \text{eq. 1}$$

where  $A_o$  is the initial cyanide concentration and  $A$  is the concentration of cyanide at a specific time. It was calculated to assess and determine the optimum removal of cyanide among the treatments. Oxidation kinetics can be obtained from the percent degradation values.

### Copper Concentration Reading

The copper ion in every treatment was converted to  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex ion by adding 1 mL of 7.5 N ammonia solution and was subjected to spectrophotometric analysis using Genesys 10S UV-Vis Spectrophotometer set at 610 nm for concentration reading (Silava, 2010). Two replicates per treatment were analyzed for copper concentration.

### Stoichiometry and Kinetics

The stoichiometry of the reaction was calculated in terms of the reaction coefficient,  $R_{C,Chem}$  with the formula

$$R_{C,Chem} = \frac{a}{b} = \frac{\Delta \text{CN}^- (\text{in ppm})}{\Delta \text{Cu}^{2+} (\text{in ppm})} \quad \text{eq. 2}$$

where  $a$  and  $b$  are stoichiometric coefficients of the reactants (Nielsen et al., 2003). The reaction coefficient was found as the slope of the cyanide concentration versus copper ion concentration graph. It is a rough estimate for the equilibrium of the reaction.

The kinetics of the oxidation reaction was assessed using the graph of cyanide concentration with respect to time. Linear regression was used to determine the order of the reaction for each treatment. Each graph was compared to zero, pseudo-first, and pseudo-

second order kinetic model plots. The best fit line for each treatment is the one for which the total prediction error is as small as possible. In other words, the treatment with the highest correlation coefficient ( $R^2$ ) to the predicted graph was determined to be the best fit. The slope of the line of each treatment represents the rate constant of that reaction system. Listed below are equations which give the rate constant for each type of reaction.

### Zero Order Reaction

$$k = -R_A = -\frac{dA}{dt} \quad \text{eq. 3}$$

$$k = \frac{A_o X_a}{t} \quad \text{eq. 4}$$

### Pseudo-First Order Reaction

$$k' A = -R_A = -\frac{dA}{dt} = kEA$$

$$k' = \frac{-\ln \frac{A}{A_o}}{t} = \frac{-\ln \ln (1 - X_a)}{t} \quad \text{eq. 6}$$

### Pseudo-Second Order Reaction

$$-R_A = -\frac{dA}{dt} = k'' A^2 = k'' A_o^2 (1 - X_a)^2 \quad \text{eq. 7}$$

$$k'' = \frac{1}{A_o} \frac{X_a}{1 - X_a} \frac{1}{t} \quad \text{eq. 8}$$

where  $k$ ,  $k'$ , and  $k''$  are rate constants for zero order reaction, pseudo-first order reaction, and pseudo-second order reaction, respectively,  $A_o$  is the initial cyanide concentration,  $X_a$  is the percent cyanide degradation,  $t$  is the time elapsed, and  $A$  is the cyanide concentration at a given time.

### Analysis of Variance

One-way ANOVA (Analysis of Variance) was used as the statistical tool to determine the significant difference between means of groups. The results in applying ANOVA provided an F-value, the ratio of the "between" variance over the "within" variance. The statistical significance of the F-value depends on the variability among the data sets and the variability within each data set.

### Post Hoc Test

For an F-value that was significant, that is when the null hypothesis was rejected, a post-hoc test was run to find out where the differences were. Tukey's HSD (Honest Significant Difference) Test was employed because it statistically treats data of equal

sample sizes per group. When the mean difference for any two groups of data was greater than the HSD value, then the groups were said to be significantly different (Beck, 2019).

#### Variability and Reproducibility

Variability in stoichiometry and kinetics were evaluated by conducting three treatments: Treatment 2, Treatment 3, and Treatment 4 which varies on the amount of copper added. To validate the reproducibility or repeatability of the results, the experiment was done in duplicates. Mean and standard deviation were calculated.

## Results and Discussion

### Cyanide Concentration Reading

**Table 2** Mean Cyanide ISE Readings (in ppm) of Treatments

Time (in min)	Treatment 1		Treatment 2		Treatment 3		Treatment 4		Treatment 5	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
0	0.1715	0.0021	0.1455	0.0601	0.1345	0.0417	0.0795	0.0870	0	0
15	0.1640	0.0170	0.1340	0.0510	0.0968	0.0343	0.0164	0.0087	0	0
30	0.1545	0.0219	0.1160	0.0410	0.0233	0.0184	0.0095	0.0052	0	0
45	0.1490	0.0184	0.0659	0.0709	0.0093	0.0029	0.0074	0.0024	0	0
60	0.1290	0.0339	0.0584	0.0631	0.0078	0.0011	0.0072	0.0023	0	0
75	0.1260	0.0071	0.0547	0.0641	0.0046	0.0040	0.0054	0.0045	0	0
90	0.1355	0.0148	0.0178	0.0125	0.0046	0.0052	0.0047	0.0047	0	0

Table 2 shows the ISE readings every 15 minutes for the treatments (Treatment 1 to Treatment 5). During the course of the reaction, Treatment 1, being the negative control with no copper sulfate, exhibited minimal decrease in cyanide concentration from 0.1715 ppm to 0.1355 ppm. Treatment 5, the positive control containing potassium permanganate and copper sulfate, degraded cyanide to the full extent. Among the experimental treatments, the test solution with the least amount of reactant copper (II) ions, Treatment 2, showed marginal cyanide degradation. This can be explained by looking at the reaction on the molecular level. A higher concentration of a reactant leads to more collisions with the other reactant/s in a specific time period (Ball & Key, 2014). Moreover, the concentrations of Treatments 3 and 4 at t = 90 minutes are not significantly different ( $p > 0.05$ ). This can mean that copper concentration to persulfate concentration ratios of one or more can give rise to the same cyanide concentration in the long run.

### FT-IR Spectroscopic Analysis of the Test Solution

Less toxic forms of cyanide may occur either as thiocyanate ( $\text{SCN}^-$ ) or cyanate ( $\text{CNO}^-$ ). To differentiate between these two closely related compounds, infrared spectroscopic analysis was done. IR spectral measurement was carried out on a Perkin-Elmer Spectrum Two FT-IR Instrument. The IR spectrum obtained was then interpreted.

### Hydrogen Peroxide Test on Unknown Precipitate

Excess amount of hydrogen peroxide was added drop by drop to the precipitate formed. This served as a qualitative test for the presence of copper (I) cyanide complex (Bonan et al., 1993).

On the other hand, there is no significant difference between the cyanide concentrations every 15 minutes ( $p > 0.05$ ), except for Treatment 3 ( $p < 0.05$ ), meaning the cyanide concentrations for Treatment 1, Treatment 2, and Treatment 4 decreased gradually. From  $t = 0$  to  $t = 15$  minutes, the concentrations for Treatment 3 are not significantly different. At  $t = 30$  minutes, the amount of cyanide in Treatment 3 was greatly reduced by 0.0735 ppm or 75.9%. Afterwards, the degradation became nearly steady reaching the minimum concentration 0.0046 ppm at  $t = 90$  minutes.

Another factor to consider is the percent degradation or removal of cyanide (Table 3). Maximum removal for Treatment 1 was observed at  $t = 75$  minutes. Persulfate alone was a relatively weak oxidant for cyanide oxidation which accounts for the decrease in percent degradation at the end. Treatment 5 reacted instantaneously and no regeneration of the free cyanide was detected, proving that the reaction went forward favorably. Treatment 2, Treatment 3,

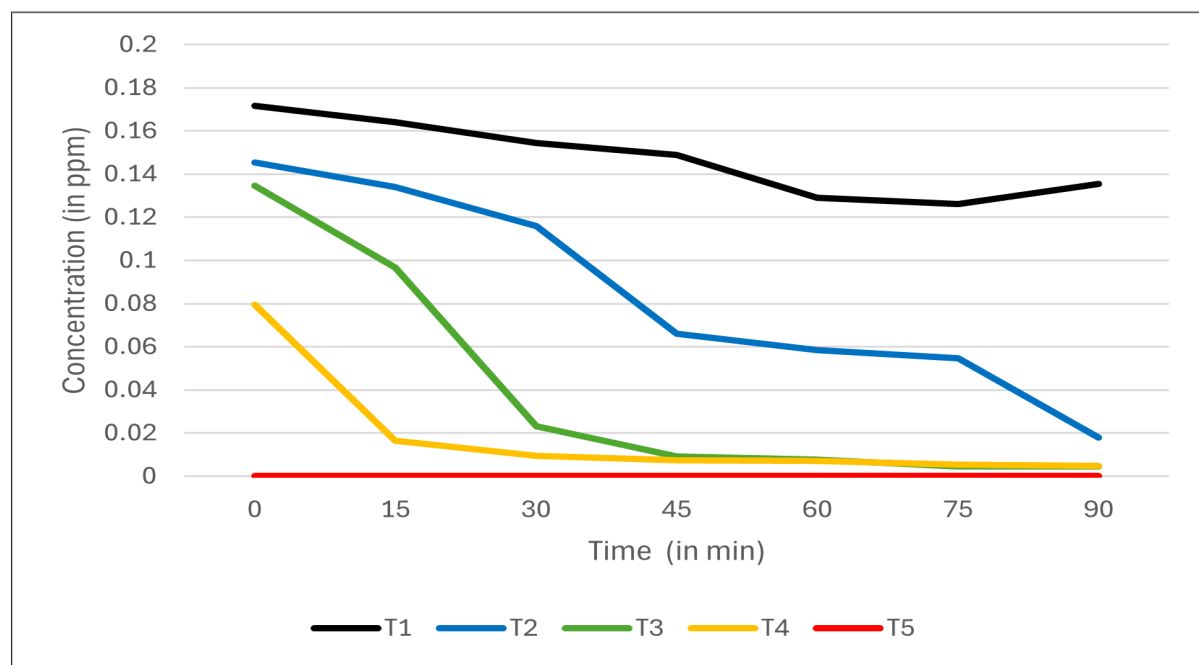
and Treatment 4 showed greatest oxidative capacity of copper (II) ions at t = 90 minutes. Treatment 3 (98.48%) and Treatment 4 (98.43%) did not vary significantly at this point (p > 0.05).

**Table 3** Percent Cyanide Degradation Every 15 Minutes

Time (in min)	Percent Degradation, $X_a$ (in %)				
	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Treatment 5
0	42.83	51.50	55.17	73.50	100.00
15	45.33	55.35	67.75	94.55	100.00
30	48.50	61.33	92.23	96.85	100.00
45	50.33	78.03	96.92	97.53	100.00
60	57.00	80.53	97.40	97.60	100.00
75	58.00	81.78	98.47	98.22	100.00
90	54.83	94.08	98.48	98.43	100.00

Note: Highlighted values are the greatest percent degradation for each treatment.

To distinguish Treatment 3 and Treatment 4 in terms of the manner the reaction proceeded, the average concentration per treatment is plotted in Figure 1. Treatment 3 has a downward slope of 0.001 while Treatment 4 is much steeper and has a downward slope of 0.006. This means that Treatment 4 resulted in rapid degradation only during the first quarter of the oxidation process. Treatment 3, however, was gradual.



**Figure 1** Average Cyanide Concentration (in ppm) with Respect to Time

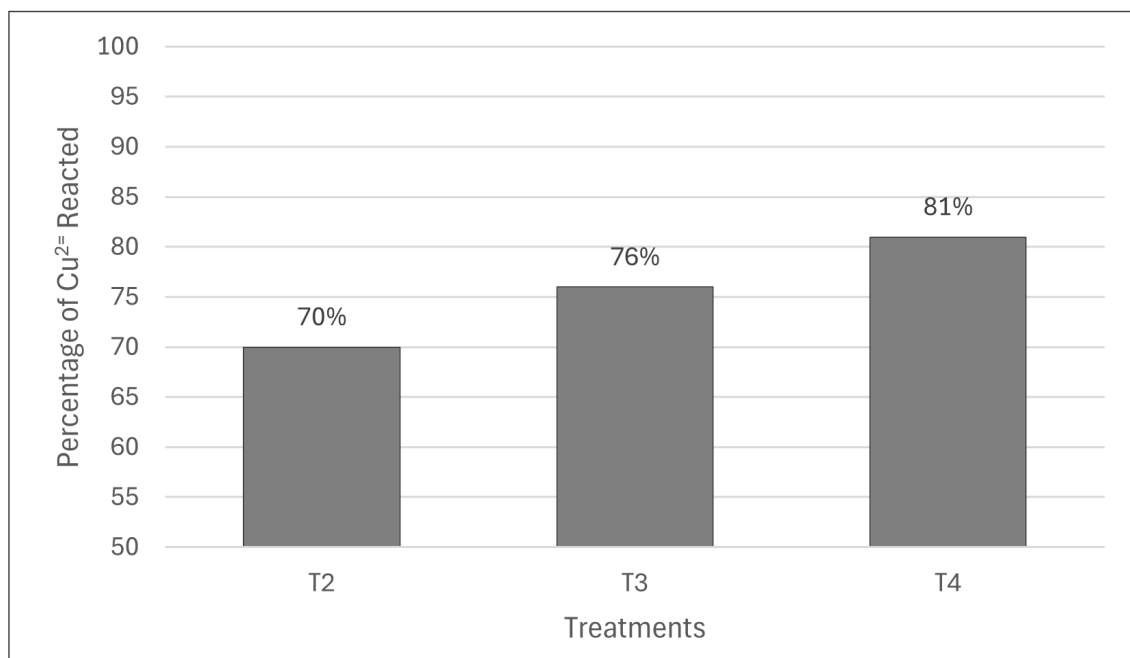
*Copper (II) Ion Concentration Reading*

The concentration of the copper ions left in each treatment was determined using UV-Vis Spectrophotometer. The copper-containing solutions were treated with 7.5 N ammonium hydroxide

solution (eq. 9) to form tetraammine copper (II) complex  $[Cu(NH_3)_4]^{2+}$  (Copper-Ammonia Complex, 2012). Figure 2 shows the amount of reacted cupric ions for each treatment.







**Figure 2** Reacted Cupric Ions in Each Treatment

Based on this figure, copper sulfate acted more of a reactant than a catalyst, consistent with the study of Liu et al. (2012). Treatment 4 has the highest initial copper (II) concentration which was detected at 39.9 ppm. At the end of the reaction, only 7.5 ppm remained. Thus, it has the greatest amount of reacted cupric ions (81%). Treatment 2, on the other hand, has the least starting copper (II) concentration of 13.3 ppm. Only 4.0 ppm was left afterwards. It has then the least amount of reacted cupric ions (70%). Hence, the amount of reacted cupric ions is directly proportional to the initial cupric ion concentration. It was then found out that there is no significant difference ( $p > 0.05$ ) between the amount of reacted cupric ions among the treatments. Thus, an average of 75% Cu<sup>2+</sup> ions (SD = 4.50) introduced were being used up in the cyanide oxidation process. Around 25% remains unreacted.

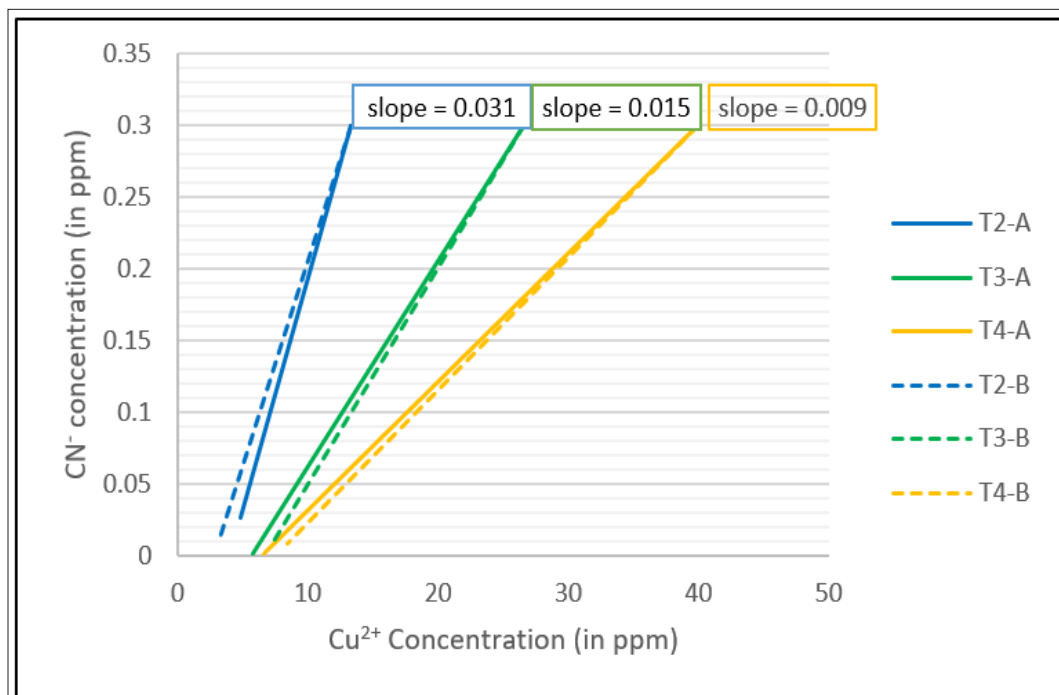
#### *Analysis of Variance (ANOVA) and Post-hoc Test*

One-way analysis of variance shows that there is a statistically significant difference in cyanide degradation between the negative control and the experimental treatments ( $p < 0.05$ ) and no significant difference between the positive control and the experimental treatments ( $p > 0.05$ ). This means that oxidation

by copper-activated persulfate is a feasible cyanide remediation technique. However, this does not necessarily imply that only the copper concentration has a direct causative relationship to the oxidation process. The manner on how the reaction proceeded should be taken into account.

#### *Stoichiometry of the Copper-activated Cyanide Oxidation*

The  $R_{C,chem}$  was determined for each experimental treatment using eq. 2. The slope of each line in Figure 3 depicts the reaction coefficient. The reaction coefficients for Treatment 2, Treatment 3, and Treatment 4, are 0.031, 0.015, and 0.009, respectively. The reactions for Treatment 3 and Treatment 4 have relatively higher tendencies to move forward. Previously, it was observed that the amount of unreacted copper for each treatment is approximately the same. Thus, the differences between these coefficients are brought about by the time dependent cyanide concentrations. Note that the  $R_{C,chem}$  for Treatment 1 is  $\infty$  and  $R_{C,chem}$  for Treatment 5 is zero.



**Figure 3** Free Cyanide vs. Cupric Ion Concentration

*Kinetics of the Reaction*

Kinetic study allows deeper understanding of reactions. Such study leads to the collision model which explains behavior of reacting chemical species (Temperature and Rate, 2019). Using linear regression analysis, the order of the reaction of each treatment with respect to cyanide has been determined. Table 4 shows the reaction rate kinetic models and their correlation coefficients or R square ( $R^2$ ) and from which, the model with the highest  $R^2$  value was chosen.

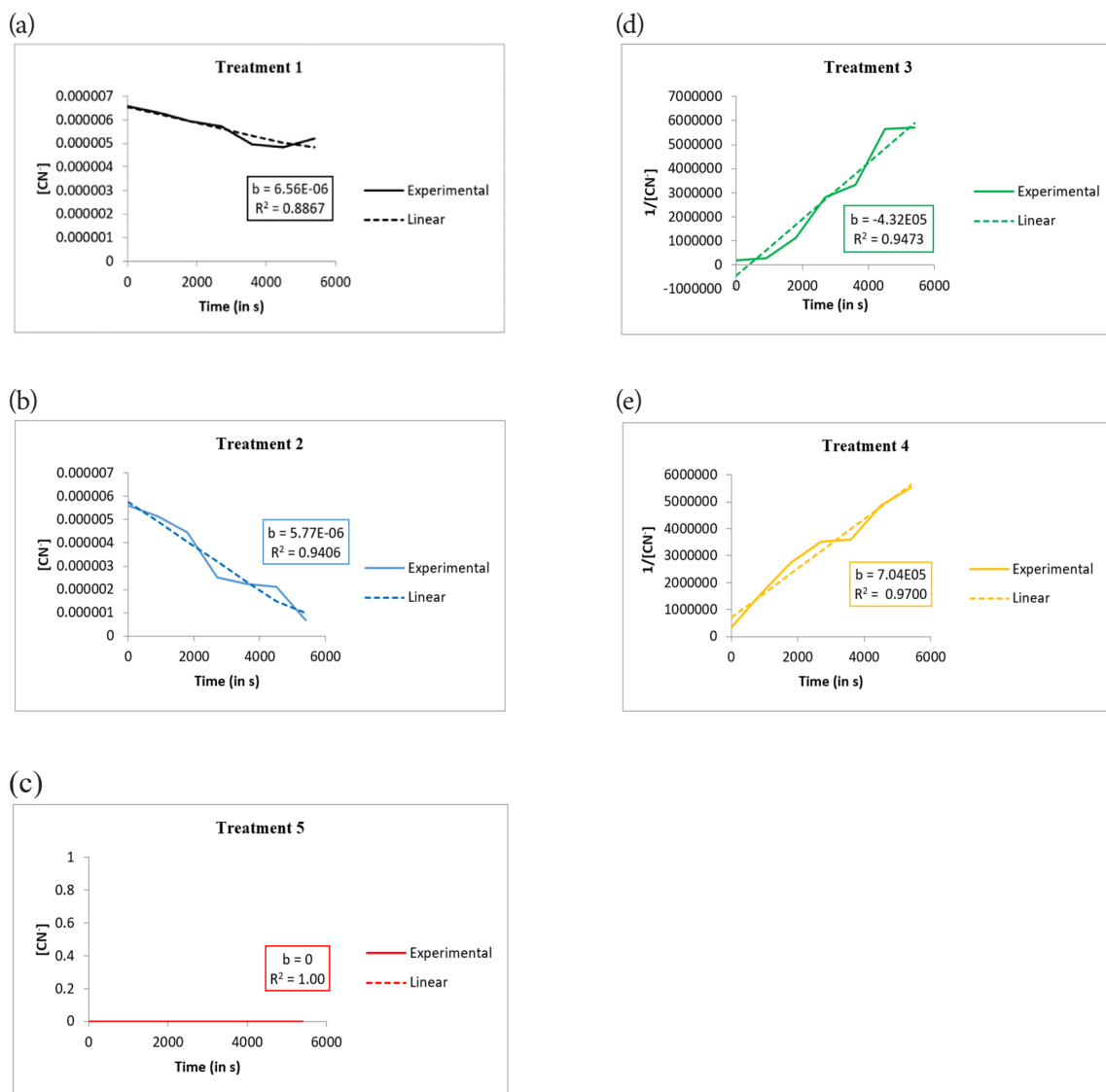
**Table 4** Rate Equations and their Correlation Coefficients

Rate Equation	Correlation Coefficient, $R^2$				
	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Treatment 5
Zero Order	0.8867	0.9406	0.7631	0.5214	1.0000
Pseudo-first Order	0.8729	0.8218	0.9308	0.7809	
Pseudo-second Order	0.8560	0.5703	0.9487	0.9700	

*Note:* Highlighted values are the greatest correlation coefficient for each treatment. Values for pseudo-first order and pseudo-second order  $R^2$  of Treatment 5 were indeterminate.

Treatments 1 and 2, containing zero copper and minimum amount of copper, respectively, obeyed zero order kinetics with respect to cyanide as shown in Figure 4. Treatment 5, being instantaneous, was also zero order. It means that the initial rates of their reactions were independent of the cyanide concentration.

Treatments 3 and 4, however, followed pseudo-second order kinetics (Figure 4), denoting that doubling the cyanide concentration will quadruple the initial rate of the reaction. Since the kinetics for this reaction was computed with respect to cyanide, doubling the copper concentration does not necessarily mean that it will also increase the rate by a factor of four.



**Figure 4** Plots for Zero Order Kinetics (a) Treatment 1, (b) Treatment 2, and (c) Treatment 5; Plots for Pseudo-second Order Kinetics (d) Treatment 3 and (e) Treatment 4

$$y = mx + b \quad \text{eq. 10}$$

Using the y-intercept value (or b value) presented on each graph, a rough estimate of the rate constant with respect to cyanide, represented by k, for each treatment was calculated from the slope (eq. 10). Together with the cyanide concentration, measured in molar (M), it makes up the rate equation for a specific reaction (eq. 11). Table 5 displays the calculated rate constants and proposed rate equations.

where m = slope/rate constant;  
 x = time (in s);  
 y = [CN] for zero order; ln[CN]  
 for pseudo-first order; 1/[CN] for pseudo-  
 second order; and  
 b = y-intercept.

$$\text{rate} = k[\text{CN}]^n \quad \text{eq. 11}$$

where rate = rate of the reaction;  
 k = rate constant;  
 [CN] = cyanide concentration (in M); and  
 n = order of reaction with respect to cyanide.



**Table 5** Rate Constants and Equations of the Different Treatments

	Rate Constant, k	Rate Equation
Treatment 1	$-3.20 \times 10^{-10} \text{ M s}^{-1}$	rate = $k[\text{CN}^-]^0$ rate = k
Treatment 2	$-9.14 \times 10^{-10} \text{ M s}^{-1}$	rate = $k[\text{CN}^-]^0$ rate = k
Treatment 3	$1173 \text{ M}^{-1} \text{ s}^{-1}$	rate = $k[\text{CN}^-]^2$
Treatment 4	$914 \text{ M}^{-1} \text{ s}^{-1}$	rate = $k[\text{CN}^-]^2$
Treatment 5	0	rate = $k[\text{CN}^-]^0$ rate = k

*Variability and Reproducibility*

In Table 6, the  $R_{C,chem}$  values in the three independent treatments (among samples) and in a duplicate experiment (within sample) shows extremely small differences. Among the treatments, the mean value of the reaction coefficient was 0.018 with a standard deviation of . Within the treatments, the mean and standard deviation values are 0.018 and , respectively. The deviations were of the same order of magnitude ( $10^{-3}$ ) which explains the precision in the stoichiometric results. Considering the kinetic aspect of the reaction, the mean values for k were found to be equal among and within samples. The rate constants also showed relatively higher variability (SD=718) than the method's precision (SD=717).

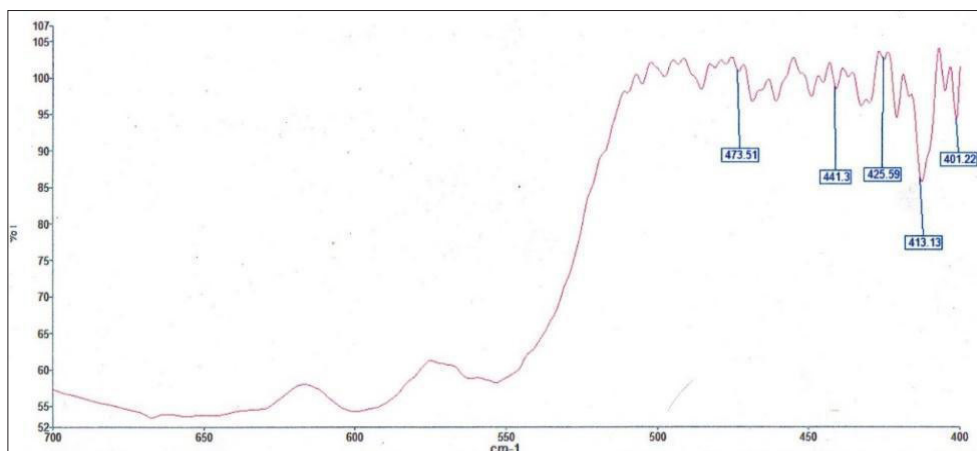
**Table 6** Stoichiometric and Kinetic Parameters

	among samples		within samples	
	mean	standard deviation (SD)	mean	standard deviation (SD)
$R_{C,chem}$	0.018	$9 \times 10^{-3}$	0.018	$1 \times 10^{-3}$
k	922	718	922	717

*FT-IR Spectroscopic Analysis of the Test Solution*

The test solution was subjected to FT-IR Spectroscopy. Since water was used to dissolve cyanide, the absorption bands of this solvent masked out the functional groups of the trace substance being sought for. Sample was then scanned in the IR range of 400 to 700  $\text{cm}^{-1}$ , also known as the “fingerprint region”, and resolution of 0.5  $\text{cm}^{-1}$  to investigate thoroughly the presence of cyanate or any other forms of cyanide.

IR spectrum (Figure 5) revealed characteristic peaks for thiocyanate ( $\text{SCN}^-$ ) instead of cyanate. In conformity to the study of Hirschmann (1963), the weak band at 441.3  $\text{cm}^{-1}$  shows out-of-plane bending vibration of the ion ( $\delta_{\parallel} \approx 450\text{-}460 \text{ cm}^{-1}$ ) while the 401.22  $\text{cm}^{-1}$  signal shows in-plane bending vibration ( $\delta_{\parallel} \approx 405\text{-}409 \text{ cm}^{-1}$ ). Furthermore, the moderate peak at 413.13  $\text{cm}^{-1}$  agrees with the bending vibration of thiocyanate ion in  $\text{CuSCN}$  ( $\delta = 412 \text{ cm}^{-1}$ ) found by Toeniskoetter and Solomon (1967). Similar bending vibration for  $\text{CuSCN}$  was also located by Bowmaker and Hanna (2009) at 427  $\text{cm}^{-1}$  which is in agreement to the 425  $\text{cm}^{-1}$  peak observed in the spectrum below.



**Figure 5** Infrared Spectrum of Test Solution

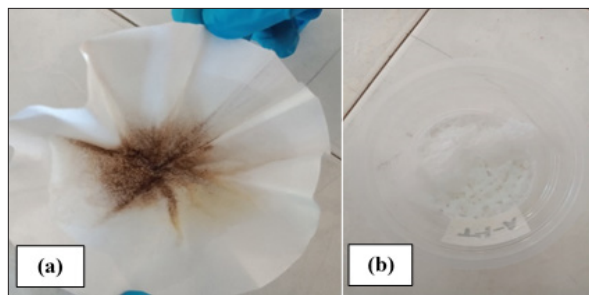
*Hydrogen Peroxide Test on Unknown Precipitate*

Copper combines with cyanide to form a variety of complexes (Michaud, 2017). These compounds can be characterized using spectroscopic techniques. However, in this study, trace amounts of an unknown compound were formed. Thus, only preliminary

chemical tests could be done. According to Bonan, Teixeira, and Kohler (1993), if the cyanide is acting as a ligand of metal cations, oxidation via hydrogen peroxide of the ligand can occur.

Grayish to black precipitate was unexpectedly observed in the test solutions (Figure 6(a)). Their average

masses, after separation by filtration, were 0.029 g, 0.038 g, and 0.035 g for Treatment 2, Treatment 3, and Treatment 4, respectively. Treatment 3, being the sample with the most efficient copper to cyanide ratio, produced the highest amount of residue. After addition of excess hydrogen peroxide, it is shown in Figure 6(b) that the precipitate has been oxidized. This suggests the presence of copper (I) cyanide complex (Bonan et al., 1993). However, additional qualitative tests should be done to further support this data.

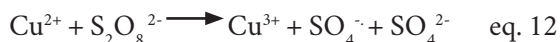


**Figure 6** Unknown Precipitate (a) Before and (b) After Adding Hydrogen Peroxide

#### Proposed Mechanism

Based from these findings, the *in situ* degradation of cyanide using copper-activated persulfate can be described by the following mechanism:

1. The cyanide water sample was prepared by diluting 0.3 mL of 100 ppm stock solution of cyanide into 100 mL water.
2. Copper sulfate was mixed with the prepared sodium persulfate solution to activate the oxidant. The chemical reaction for this is shown below.



$\text{Cu}^{2+}$  activates persulfate to form sulfate radicals and sulfate ions (Liu et al., 2012). It is also stated that  $\text{Cu}^{3+}$  can be formed, however, a higher energy barrier should be jumped over. Thus, formation occurs in a slow process.

3. The activated persulfate was added to the cyanide-containing water samples. From the ions produced in the activation of the oxidant, mechanism of the degradation can be written as follows:



The sulfate radicals formed in the activation process oxidized the  $\text{CN}^-$  ions in the water sample to form thiocyanate, a 100-fold less toxic compound than cyanide. This was observed in the IR spectroscopic analysis. A grayish precipitate was formed. It was treated with hydrogen peroxide and tested positive for

the presence of copper (I) cyanide. Supplementary tests are needed to support these claims.

#### Conclusion

Determination of stoichiometry and kinetics of *in situ* chemical oxidation of cyanide in water using copper-activated sodium persulfate was demonstrated. Five treatments with varying copper to persulfate ratios were prepared and introduced to cyanide samples.

Treatment 4, containing 1.5:1  $\text{Cu}^{2+}$  to  $\text{S}_2\text{O}_8^{2-}$  ratio, underwent an initially fast cyanide degradation, but then slowed down. This can be attributed to the depletion of one or more reactants. Treatment 3, holding a 1:1 ratio of  $\text{Cu}^{2+}$  to  $\text{S}_2\text{O}_8^{2-}$ , was proven to cause a more steady and efficient removal of cyanide. The optimal cyanide degradation for each treatment was observed at  $t = 90$  minutes - 94.08% for Treatment 2, 98.48% for Treatment 3, and 98.43% for Treatment 4.

Cupric ions activated persulfate by forming highly reactive sulfate radicals ( $\text{SO}_4^{\cdot -}$ ). The amount of  $\text{Cu}^{2+}$  being used up is proportional to the initial concentration. Unlike other activation methods, copper does not exert its 100% oxidative capacity on cyanide. Around 25% of its initial concentration remains unreacted.

Reaction coefficients of copper-activated cyanide oxidation are brought about mostly by the time-dependent cyanide concentrations. The reactions for Treatment 3 and Treatment 4 were found to have relatively higher tendencies to move forward. Using linear fit graphs and correlation coefficients, Treatment 2 was found to obey zero order kinetics with  $k = \text{M s}^{-1}$ . Treatments 3 and 4, on the other hand, follow pseudo-second order kinetics with  $k = 1173 \text{ M}^{-1} \text{ s}^{-1}$  and  $914 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

Qualitative analyses of test solution and precipitate after the oxidation process implied the presence of thiocyanate ion ( $\text{SCN}^-$ ), rather than cyanate ion ( $\text{CNO}^-$ ), and copper (I) cyanide complex, respectively. Additional tests should be done to support these findings. Thus, the proposed mechanism for the copper-activated oxidation of cyanide using persulfate is



Cyanide degradation using 1:1 copper to persulfate ratio appears feasible and practical. From an engineering point of view, the proposed mechanism can be used to design equipment for wastewater treatment, specific to cyanide.

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## References

- American Public Health Association, American Water Works Association, Water Environment Federation. (1999). Standard Methods for the Examination of Water and Wastewater.
- Ball, D. W., & Key, J. A. (2014, September 16). Introductory Chemistry – 1st Canadian Edition. Retrieved from <https://opentextbc.ca/introductorychemistry/chapter/factors-that-affect-the-rate-of-reactions-2/>
- Beck, K. (2019, March 02). What Is the Tukey HSD Test? Retrieved from <https://sciencing.com/what-is-the-tukey-hsd-test-12751748.html>
- Bonan, A., Teixeira, L., & Kohler, H. (1993). Kinetics of 'the Oxidation of Free and Copper Cyanides in Aqueous Solutions with Hydrogen Peroxide. Retrieved from <https://www.911metallurgist.com/blog/wp-content/uploads/2016/07/Peroxide-Cyanide.pdf>.
- Bowmaker, G. A. & Hanna, J. V. (2009). IR Spectroscopy of Two Polymorphs of Copper(I) Thiocyanate and of Complexes of Copper(I) Thiocyanate with Thiourea and Ethylenethiourea. *Zeitschrift Für Naturforschung B*, 64(11-12), 1478-1486. doi:10.1515/znb-2009-11-1231
- Burce, A., Realoza, A., Armero, L., & Janaban, P. (2010). Cyanide Detoxification: A Chemical Reaction Analysis and Proposed Equipment Design (Unpublished undergraduate thesis). Bicol University, Legazpi City, Albay.
- Chemical Control Order For Cyanide And Cyanide Compounds. DENR Administrative Order No. 39 (1997). Retrieved from <https://emb.gov.ph/wp-content/uploads/2016/03/DAO-1997-39.pdf>
- Copper-Ammonia Complex. (2012). Chemdemos. Retrieved from <https://chemdemos.uoregon.edu/demos/Copper-Ammonia-Complex>
- Cyanide Treatment with H<sub>2</sub>O<sub>2</sub>. (2018). USP Technologies. Retrieved from <http://www.h2o2.com/industrial/applications.aspx?pid=106&name=Cyanide-Treatment>
- Helmenstine, A.M. (2018). How Does Cyanide Kill? ThoughtCo. Retrieved from <https://www.thoughtco.com/overview-of-cyanide-poison-609287>
- Hirschmann, R. P. (1963). The vibrational spectra of alkyl isocyanates, isothiocyanates and thiocyanates. doi:10.31274/rtd-180814-821
- Huling, S. G., & Pivetz, B.E. (2006). In Situ Chemical Oxidation. US EPA Engineering Issue. Retrieved from <https://clu-in.org/download/contaminantfocus/pcb/ISCO-600R06072.pdf>
- Hydrogen Peroxide and Caro's Acid: Powerful Oxidants for Cyanide Destruction. (n.d.). Retrieved from [https://www.google.com.ph/search?q=hydrogen%2Bperoxide%2Band%2Bcaro%27s%2Bid%2Bpowerful%2Boxidants%2Bfor%2Bcyanide%2Bdestruction&dcr=0&source=Inms&sa=X&ved=0ahUKEwjD-aTreatment\\_57tHYAhVGG5QKHVxcD6sQAUICSgA&biw=1366&bih=566&dpr=1](https://www.google.com.ph/search?q=hydrogen%2Bperoxide%2Band%2Bcaro%27s%2Bid%2Bpowerful%2Boxidants%2Bfor%2Bcyanide%2Bdestruction&dcr=0&source=Inms&sa=X&ved=0ahUKEwjD-aTreatment_57tHYAhVGG5QKHVxcD6sQAUICSgA&biw=1366&bih=566&dpr=1)
- Implementing Rules and Regulations of Republic Act 6969. DENR Administrative Order No. 29 (1992). Retrieved from [https://www.env.gov.jp/en/recycle/asian\\_net/Country\\_Information/Law\\_N\\_Regulation/Philippines/DAO%201992-29.pdf](https://www.env.gov.jp/en/recycle/asian_net/Country_Information/Law_N_Regulation/Philippines/DAO%201992-29.pdf)
- Liu, C., Shih, K., & Sun, C. (2012). Oxidative degradation of propachlor by ferrous and copper ion activated persulfate. *Science of the Total Environment*, 507-512. Retrieved from <https://www.ncbi.nlm.nih.gov/pubmed/22226398>.
- Michaud, L. (2017, March 17). How Copper Affects Cyanidation & Leaching. Retrieved from <https://www.911metallurgist.com/blog/how-copper-affects-cyanidation-leaching>
- Mines and Geosciences Bureau – Mining Environment and Safety Division (MGB – MESD). (2006). Environmental assessment of abandoned Bagacay mine relative to the proposed interim remediation measures of the World Bank supported project. DENR, Quezon City, Philippines.
- Nielsen, Asbjørn H.; Vollertsen, Jes; Hvitved-Jacobsen, Thorkild (2003). Determination of Kinetics and Stoichiometry of Chemical Sulfide Oxidation in Wastewater of Sewer Networks. *Environmental Science & Technology*, 37(17), 3853–3858. doi:10.1021/es0340351
- Silava, N.D. (2010, September 22). Determination of Copper Concentration Using UV-Vis Spectrophotometry. Retrieved from <https://www.scribd.com/doc/42191846/Determination-of-Copper-Concentration-Using-UV-Vis-Spectrophotometry>
- Temperature and Rate. (2019, February 23). ChemLibretexts. Retrieved from [https://chem.libretexts.org/Courses/University\\_of\\_Missouri/MU:\\_1330H\\_\(Keller\)/14:\\_Chemical\\_Kinetics/14.5:\\_Temperature\\_and\\_Rate](https://chem.libretexts.org/Courses/University_of_Missouri/MU:_1330H_(Keller)/14:_Chemical_Kinetics/14.5:_Temperature_and_Rate)
- Toeniskoetter, R. H., & Solomon, S. (1968). Infrared spectra of copper thiocyanate complexes. *Inorganic Chemistry*, 7(3), 617-620. doi:10.1021/ic50061a051
- Young, C.A., & Jordan, T.S. (n.d.). CYANIDE REMEDIATION: CURRENT AND PAST TECHNOLOGIES. Retrieved from <https://pdfs.semanticscholar.org/4bc4/02e3cf80311e0f4b655d1d6f58b5b2591b8e.pdf>

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