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Two-Stage Hypochlorite Leaching of a Refractory Gold-Molybdenum Concentrate

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Abstract – *The rapid depletion of easily extractive gold ores raised difficulties in using conventional cyanidation for gold extraction. Refractory gold containing gold particles locked in sulfides require pretreatment before gold leaching to achieve favorable gold recoveries. Chlorination using hypochlorite (OCl^-) solution has been explored in processing refractory gold because it can oxidize the sulfides as pretreatment and dissolve gold. In this study, hypochlorite solution is used for two-stage leaching of a refractory gold-molybdenum concentrate involving sulfide oxidation in the first stage and gold dissolution in the second stage. Gold and molybdenum dissolution were determined using sulfide oxidation of 6 hours, liquid to solid volume ratio of 13, and 1.89 M hypochlorite concentration. Reaction mechanism was inferred using the solution Eh and pH. The two-stage hypochlorite leaching yielded gold dissolution of 93.51% and molybdenum dissolution of 88.54%. Based on shrinking-core model, sulfide oxidation is diffusion control with an amorphous oxide forming as the product layer. The use of hypochlorite solution in the two-stage leaching can be a potential simplified alternative for gold extraction of refractory gold-molybdenum concentrates.*

Keywords: *Refractory gold-molybdenum concentrate, sulfide oxidation and gold dissolution, hypochlorite*

I. INTRODUCTION

The depletion of free milling ores, ores that attain gold recovery of 90% or more by cyanidation, raises challenges and difficulties in using conventional cyanidation for gold extraction. Readily-available ores nowadays are refractory gold ores that do not yield acceptable gold recoveries using conventional methods because gold is physically locked as very fine particles in sulfides such as pyrite, arsenopyrite, and chalcopyrite [1,2].

Processing refractory gold ores requires pretreatment prior to leaching to increase gold recovery. Pretreatment decomposes the sulfide matrix and exposes the gold to the lixiviant. Pretreatment can be done through physical treatment such as fine grinding which reduces particle size to liberate fine gold, or through oxidative pretreatment such as roasting which produces sulfur dioxide gas by employing oxidative atmosphere and temperature, pressure oxidation which involves high pressure and temperature conditions, biological oxidation which uses bacteria in sulfide decomposition, and chlorine oxidation [3, 4].

Chlorine oxidation uses chlorine species to oxidize and decompose sulfides. The oxidizing species in an aqueous chlorine solution depends on the solution pH. Aqueous chlorine (Cl_2), hypochlorous acid ($HOCl$), and hypochlorite (OCl^-) are stable at $pH < 3.5$, pH of 3.5-7.5, and $pH > 7.5$, respectively. Hypochlorous acid (E_o $HClO/Cl^- = 1.495V$) is the most effective oxidizer among other species which are aqueous chlorine (E_o Cl_2/Cl^-= 1.359V) and hypochlorite (E_o OCl^-/Cl^-= 0.890V) [3, 5, 6].

Hypochlorite is a strong oxidizing agent that dissolves sulfides such as pyrite, FeS_2, even at room temperature following Equation 1 [7]. The pH of hypochlorite solution can be adjusted to pH 3.5-7.5 to form hypochlorous acid following Equation 2. Hypochlorous acid has high oxidizing power enough to dissolve gold. Thus, a process involving pretreatment followed by gold dissolution using hypochlorite solution at differing pH can be employed. In this way, gold encapsulated by sulfide matrix is exposed first through sulfide oxidation ensuring that gold is already accessible to the lixiviant for gold dissolution following Equation 3.

$$2FeS_2 + 7H_2O + 15OCl^- \leftrightarrow 2Fe(OH)_3 + 4SO_4^{2-} + 8H^+ + 15Cl^- \quad E_0 = 510\ mV \qquad (1)$$
$$OCl^- + H^+ \leftrightarrow HOCl \qquad (2)$$
$$2Au + 3HOCl + 3H^+ + 5Cl^- \leftrightarrow 2[AuCl_4]^- + 3H_2O \quad E_0 = 496\ mV \qquad (3)$$

The use of hypochlorite solution has been widely explored in processing refractory gold ores and concentrates involving pyrite matrix [3, 8]. Oxidation of pyrite has been the major focus of studies in sulfide oxidation and gold dissolution of refractory gold since pyrite is the dominant sulfide encapsulating gold. It is also the most stable sulfide among the common sulfide phases associated with gold [9, 10, 11]. Thus, other sulfides are also oxidized when pyrite is oxidized.

Recovery of other valuable metals from sulfides such as molybdenum from molybdenite using hypochlorite solution has also been explored at alkaline condition following Equation 4 [6, 12, 13].

$$MoS_2 + 9OCl^{-1} + 6OH^- \leftrightarrow MoO_4^{2-} + 9Cl^- + 2SO_4^{2-} + 3H_2O \qquad (4)$$

Although hypochlorite has been investigated for recovery of gold from refractory gold and molybdenum from molybdenite, extraction of gold from refractory gold-molybdenum concentrates using hypochlorite has not yet been explored. Current processing of gold from refractory gold-molybdenum concentrate is through biological oxidation as pretreatment followed by gold cyanide leaching. However, this process has limitations due to sensitivity of bacteria to molybdenum, and this process still involves cyanide for gold leaching [14].

This study aims to investigate the two-stage hypochlorite leaching of a refractory gold-molybdenum concentrate using hypochlorite solution. The developed process can be a potential eco-friendly and simplified alternative for gold extraction of refractory gold-molybdenum concentrates. In addition, this process can treat refractory gold concentrates containing high amounts of molybdenum that cannot be efficiently processed through biological oxidation due to the sensitivity of the bacteria to the molybdenum content.

II. METHODOLOGY

Figure 1 shows the schematic diagram of the experimental procedure. The process involved 2 stages. The first stage involved mixing the concentrate with hypochlorite solution at basic pH to oxidize the sulfides, followed the second stage which involved addition of hypochlorite and adjustment of pH to 6 to dissolve gold. The final solution was filtered, and the residue and leachate were characterized.

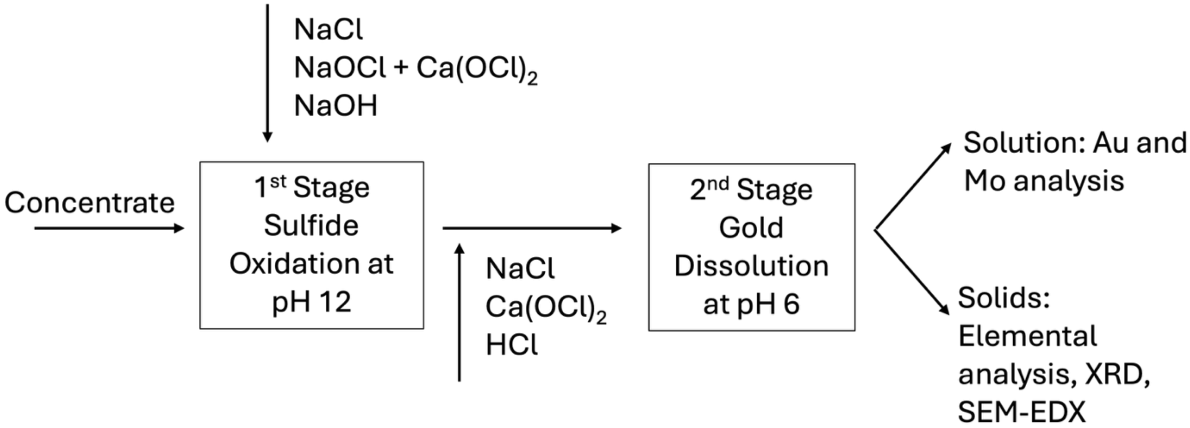


Figure 1. Schematic Diagram of the Experimental Procedure

2.1. Materials and Reagents

Flotation concentrate from a gold processing plant in Quezon, Nueva Vizcaya was used in the experiment. It contains 12.988 ppm gold, 4542 ppm molybdenum, and 18.8 wt% sulfur as determined using fire assay, ICP-MS analysis, and sulfur gravimetry, respectively. X-ray diffraction (XRD) pattern of the concentrate using Cu-Kα (1.541874 A) as shown in Figure 2 reveals major phases of quartz, orthoclase, and pyrite indicating that the flotation concentrate is sulfidic.

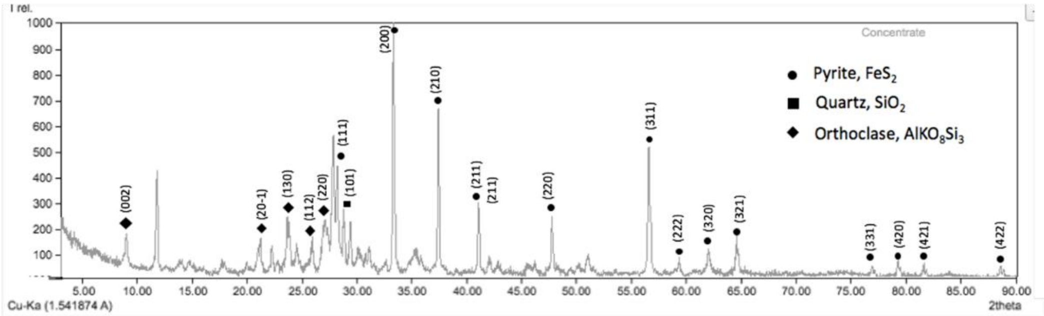


Figure 2. XRD Pattern of Concentrate

Based on the gold occurrence test which involved a series of selective leaching with increasing oxidative strength, it was determined that the concentrate contains 9.75% free gold confirmed using amalgamation, and 44.18% gold that is exposed and associated recovered using cyanidation at 48 hours. However, 40.03% of gold is present as locked in sulfides verified through the gold content of the acid-digested cyanide leach residue. This confirms presence of refractory gold which may not be efficiently recoverable through conventional cyanidation. The balance of 6.69% gold suggests gold locked in silicates.

Reagents for leaching were prepared from 7.81% w/v liquid sodium hypochlorite (NaOCl), 70% calcium hypochlorite ($Ca(OCl)_2$) powder, 99.5% sodium chloride (NaCl) powder, 98% sodium hydroxide (NaOH) pellets, and 37% hydrochloric acid (HCl). Deionized water was added to mix and dilute the solution. Since only 7.81% NaOCl is commercially available, $Ca(OCl)_2$ was used to prepare hypochlorite solution containing higher OCl^- concentration.

2.2. Two-stage hypochlorite leaching

Leaching was done using a 1-L beaker with magnetic stirrer for agitation shown in Figure 3 and using parameters in Table 1 based on the optimum parameters found by Hasab et.al [3] and Regidor et. Al [8]. The solution Eh and pH were monitored using oxidation-reduction potential (ORP) meter and pH meter, respectively. Solution ORP was measured to determine the solution's ability to oxidize or reduce. Positive ORP indicates that the solution is oxidizing and negative ORP indicates that the solution is reducing. For sulfide oxidation and gold dissolution to take place, the solution ORP should be equal or greater than the reaction potentials of these reactions. Reagents to produce a 500-mL lixiviant solution were mixed then concentrate was added. Solution Eh and pH were recorded every 10 minutes for the 1st hour and 20 minutes for the following hours. Ten (10) mL aliquots were taken at a given time interval for gold analysis and kinetics study. After leaching, the solution was filtered. Samples of the filtered solution and leaching residue were obtained for gold and sulfur analysis. Leaching residue was subjected to XRD and SEM-EDX for characterization. Solids were attached to an aluminum stub and subjected to Hitachi-SU3800 SEM Machine and Oxford Ultim Max 40 EDX Machine.

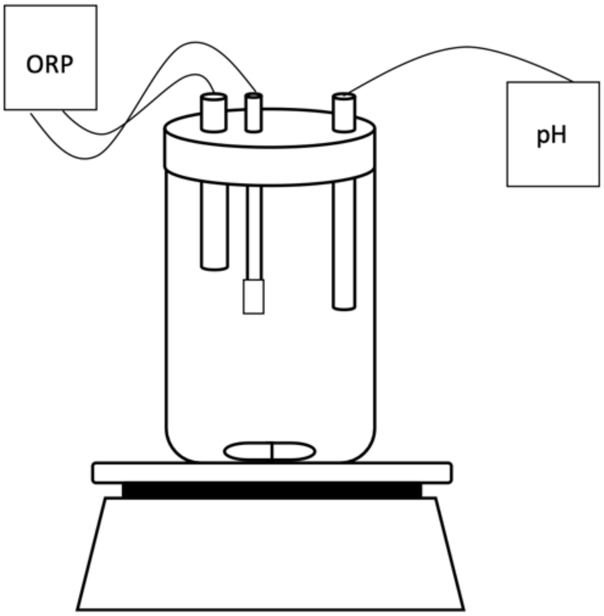


Figure 3. Hypochlorite leaching setup

Table 1. Parameters for Two-stage Hypochlorite Leaching

Stage	**Time, hrs**	**Temp**	**L:S ratio**	**Agitation, rpm**	**NaCl, g/L**	**Ca(OCl,$_2$, g/L**	**OCl^-, M**	**NaOH,% wt / pH**
1st Stage		Ambient	13	500	30	-	1.89	10 wt%
2nd Stage		Ambient	-	500	200	200	-	6

The % gold dissolution was calculated using Equation 5.

$$\% \, Au \, dissolution = \frac{C_{Au}V}{HA \, x \, W_s} \text{ x } 100 \,\% \tag{5}$$

where

C_{Au} = gold concentration of pregnant solution, mg/L
V = volume of pregnant solution, L
HA = gold assay of concentrate, mg/kg
W_s = weight of concentrate, kg

2.3. Sulfide Oxidation Kinetic Study

For the kinetic study of sulfide oxidation for 6 hours, the aliquots that were taken at a given time interval were filtered. Residue was dried and obtained for sulfur analysis. The mass fraction was based on the decrease in sulfur of the residue and calculated using Equation 6. The calculated mass fraction was used to determine the kinetic model with the most linear relationship using the standard equations (7, 8, and 9) for diffusion, chemical reaction, and mixed control, respectively. The equations are based on the shrinking-core model with assumptions that the particles are spherical with a constant particle size, thus no volume changes for the reaction, the particles shrink uniformly while forming a layer with thickness that reaches to a constant during the leaching process, temperature remains constant, and reaction is steady-state [15].

$$Mass \, fraction, X = \frac{(W_C C_C) - (W_R C_R)}{W_C C_C} \tag{6}$$

where

W_C = weight of concentrate, g
C_C = sulfur analysis of concentrate, %
W_R = weight of residue, g
C_R = sulfur analysis of residue, %

$$1 - 3(1-X)^{2/3} + 2(1-X) = k_d t \tag{7}$$

$$1 - (1-X)^{1/3} = k_r t \tag{8}$$

$$(1-2/3X) - (1-X)^{2/3} + B\,(1-(1-X)^{1/3}) = k_m t \tag{9}$$

where

X = fraction reacted
k_d = rate constant for diffusion
k_r = rate constant for chemical reaction
k_m = rate control for mixed control
B = ratio of k_r/k_d, equal to 1
t = reaction time

III. RESULTS AND DISCUSSION

3.1. Two-stage hypochlorite leaching Mechanism

The two-stage hypochlorite leaching yielded a gold dissolution of 93.51%. At the first stage, around 55% Au dissolution was attained as shown in Figure 4. Gold dissolved during this stage could have come from gold particles that are free and exposed, which account for approximately 54% based on the gold occurrence test. Solution pH is at 13 as shown in Figure 5, indicating hypochlorite ions as the dominant oxidizing species. Increase in Eh upon addition of concentrate to lixiviant is observed which indicates start of oxidation. Slight decrease of pH is due to generation of H^+ during oxidation.

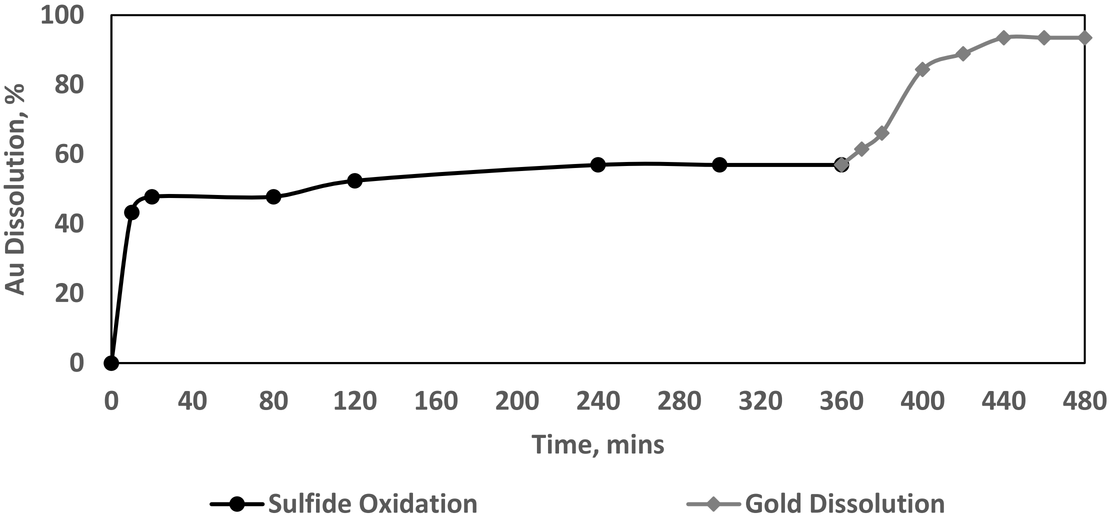


Figure 4. Gold Dissolution of Two-stage Hypochlorite Leaching (Sulfide Oxidation in the 1st stage and Gold Dissolution in the 2nd stage)

Eh was stable at 600 mV (higher than pyrite oxidation by hypochlorite, E_o = 510 mV), indicating oxidation of pyrite by hypochlorite. Since pyrite is more stable than molybdenite based on their rest potential (0.66 V for pyrite, and 0.11V for molybdenite) [11], molybdenite oxidation by hypochlorite occurs first. Pyrite oxidation potential can then be used as basis for oxidation of other sulfides such as molybdenite. Since the solution potential is higher than the pyrite oxidation potential as shown in Figure 5, it can be inferred then that molybdenite oxidation also occurs in this stage. Based on molybdenum concentration of the oxidation residue, molybdenum dissolution of 88.54% was attained after the first stage (oxidation stage) indicating that hypochlorite solution can also be used to dissolve molybdenum from the concentrate. $Fe(OH)_3$, SO_4^{2-}, and MoO_4^{2-} which are products of the sulfide oxidation reactions are stable in this condition.

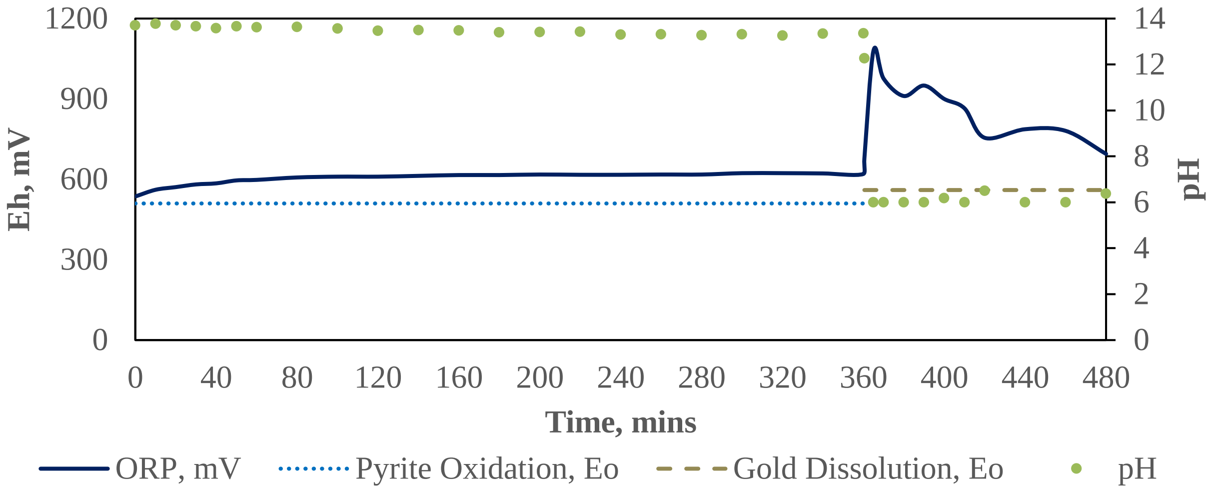


Figure 5. Solution Eh and pH of Two-stage Hypochlorite Leaching

Gold dissolution in Figure 4 rapidly increased during the 2nd stage or the gold dissolution stage together with Eh upon adjustment of pH to 6 as shown in Figure 5 indicating the start of dissolution of refractory gold that has been exposed during the oxidation stage. The increase in Eh at the start of the 2nd stage upon addition of HCl indicates formation of hypochlorous acid, which has the highest oxidation power among chlorine species and able to dissolve gold. As gold dissolution continued to increase in the 2nd stage, Eh decreased indicating consumption of hypochlorous acid to dissolve gold. Eh continues to decrease until it becomes stable at 700 mV with Au dissolution of 93.51%. Gold dissolved during this stage are refractory (those that were unlocked during sulfide oxidation). Remaining 7% of Au that is not dissolved could have been gold locked in silicates (6.69% of Au based on gold occurrence) that are not dissolved by hypochlorite.

3.2. Sulfide Oxidation Kinetic Study

Using the decrease of sulfur in the oxidation residue vs. time, it can be observed that the sulfide oxidation proceeds relatively faster at first 40 minutes of oxidation and slows down until end of oxidation as shown in Figure 6. During leaching of the sulfide concentrate in hypochlorite, pyrite being the major phase is oxidized to iron hydroxide following Equation 1. The iron hydroxide forms as an outer layer with thickness progressively increasing as the reaction proceeds. The iron hydroxide product layer must be penetrated first by the oxidant, which is the hypochlorite ions, for the oxidation to proceed. Thus, slowing down the reaction. In this mechanism, the sulfide oxidation becomes diffusion-controlled by a product layer.

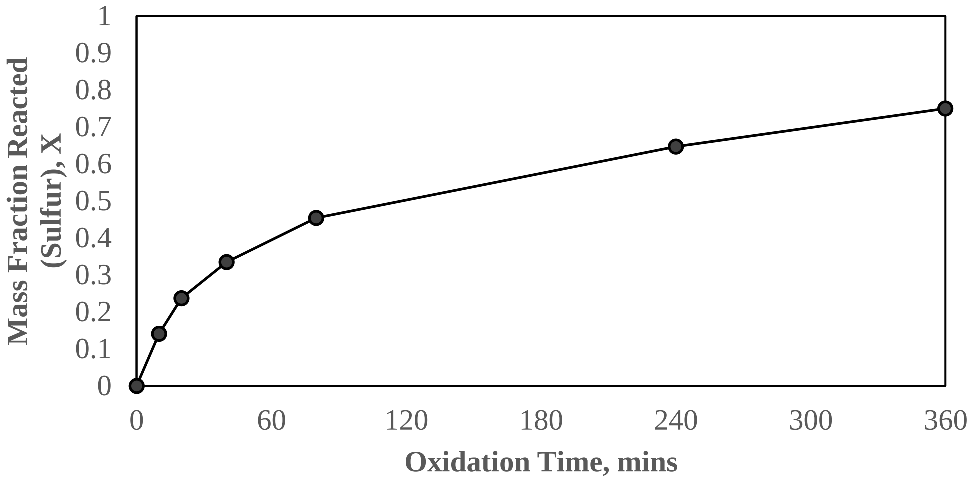
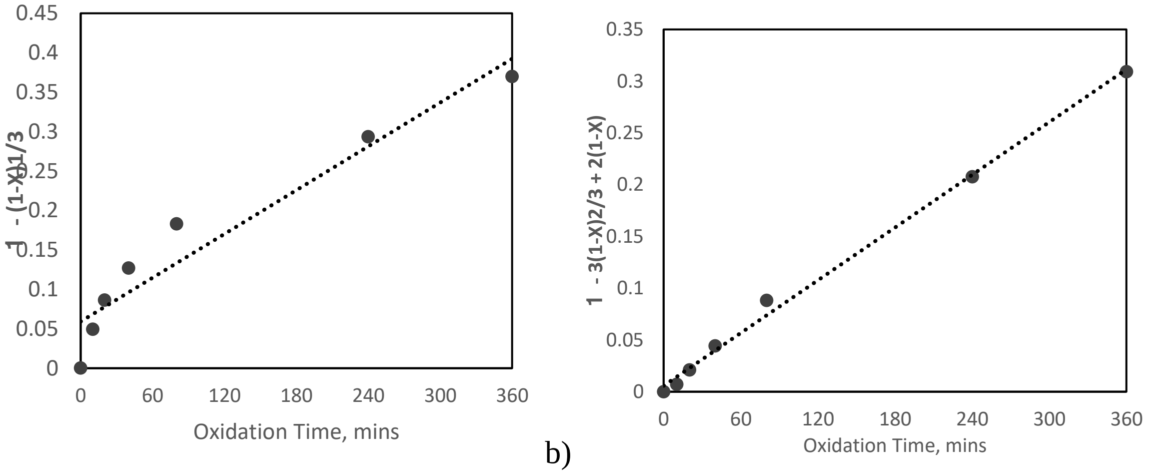


Figure 6. Mass Fraction Reacted (X) during oxidation

Shrinking-core model confirms that sulfide oxidation has a diffusion-control mechanism based on best fit of line as shown in Figure 7. This means that during sulfide oxidation, a product layer is formed during reaction that needs to be penetrated by the hypochlorite ions. The product layer is an oxide layer based on the SEM-EDX analysis as shown in Figure 8 and Table 2. The XRD pattern of the residue (Figure 9) also shows presence of hydroxides, sulfates, and chlorides indicating that sulfide oxidation happened and produced these products following Equation 1, 3, and 4. This agrees with the observed iron hydroxide product layer surrounding the unreacted pyrite core indicating that the sulfide oxidation happened and is product-diffusion controlled [8]. Valenzuela et al. [1] also observed deposits of sulfates and hydroxide on the particles of the refractory gold oxidized by hypochlorite.



a) b)

c)

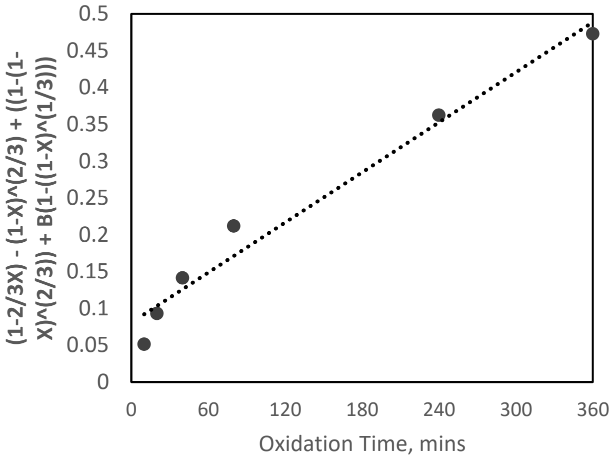
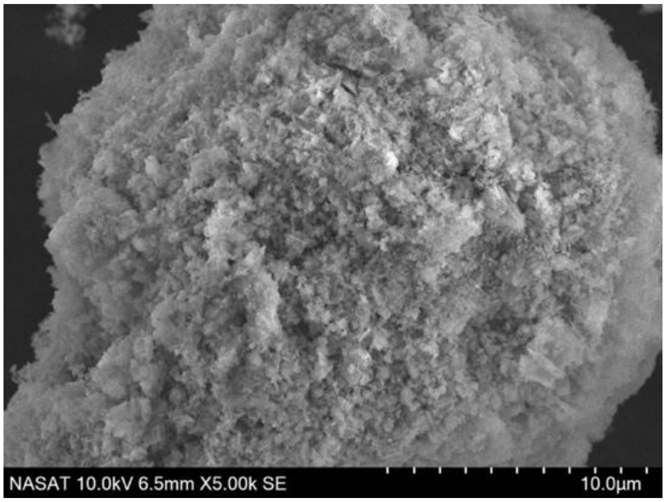
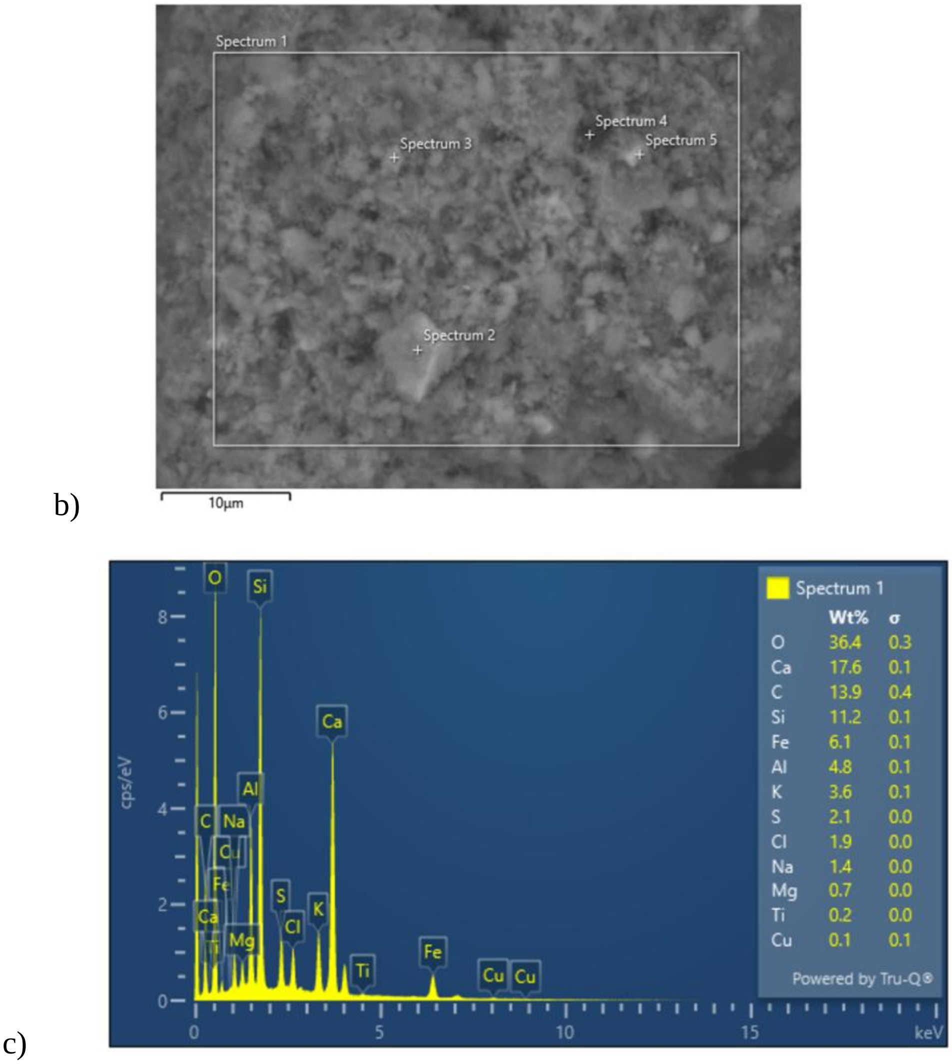


Figure 7. Plots of
a) Chemical Reaction Control Model y = 0.0009x + 0.0592, R^2 = 0.92516
b) Diffusion Control Model y = 0.0008x + 0.0058, R^2 = 0.99614
c) Mixed Control y = 0.0011x + 0.0806, R^2 = 0.97042

However, results from study by Hasab et al. [3] show that first hour of gold leaching of a refractory concentrate by hypochlorite solution has mechanism of chemical reaction control followed by diffusion control at 2nd hour. The chemical control mechanism observed by Hasab et al. [3] at the start in contrast with observations by Regidor et al. [8], Valenzuela et al. [1], and this study is possibly because of the small particle size of the concentrate used in the experiment of Hasab et al. [3] at which 90% of the particles are finer than 37.4 microns. This suggests that the rate of sulfide oxidation and dissolution of the refractory gold-molybdenum concentrate used in this study can be increased by reducing the particle size. Decreasing the particle size may shift the rate-determining step to chemical reaction rate in the 1st hour. It also increases the gold dissolution and reduces the leaching time.

a)





Spectrum 1

	Wt%	σ
O	36.4	0.3
Ca	17.6	0.1
C	13.9	0.4
Si	11.2	0.1
Fe	6.1	0.1
Al	4.8	0.1
K	3.6	0.1
S	2.1	0.0
Cl	1.9	0.0
Na	1.4	0.0
Mg	0.7	0.0
Ti	0.2	0.0
Cu	0.1	0.1

Figure 8. SEM-EDX Results of Sulfide Oxidation Residue a) micrograph of sulfide oxidation residue at X5.00k SE b) Electron Image Map c) EDX Analysis at Spectrum 1

Table 2. Elemental Analysis of Concentrate and Oxidation Residue

Sample	Oxygen, wt%	Sulfur, wt%	Iron, wt%
Concentrate	16.7	19.7	41.3
Oxidation Residue	36.4	2.1	6.2

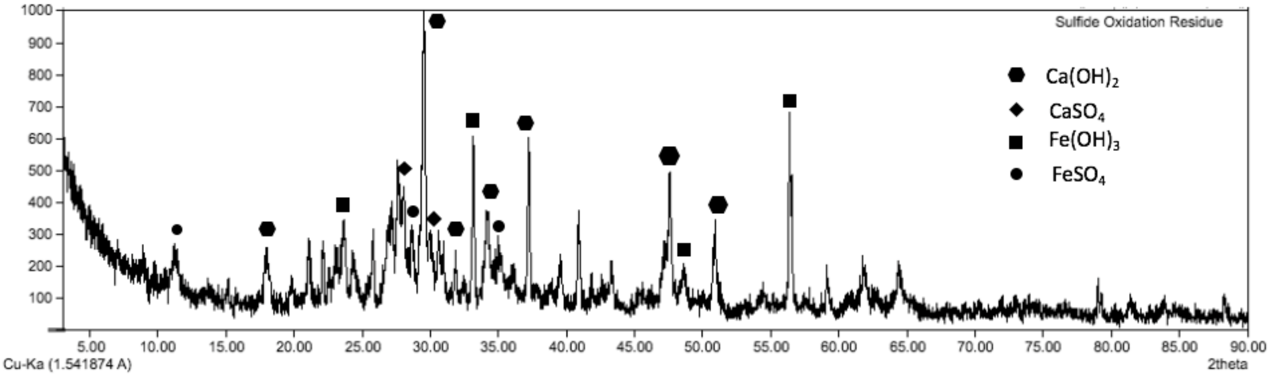


Figure 9. XRD Pattern of Sulfide Oxidation Residue

Based on the results, hypochlorite was able to oxidize sulfides producing hydroxides and sulfates as products and was able to dissolve refractory gold. This shows that the use of hypochlorite solution can be a potential alternative for gold extraction of refractory gold-molybdenum concentrates.

IV. CONCLUSION

This study investigated the two-stage hypochlorite leaching a refractory gold-molybdenum. The two-stage hypochlorite leaching involves sulfide oxidation by hypochlorite ions in the first stage and gold dissolution by hypochlorous acid in the second stage as indicated by the solution Eh and pH. After the 1st stage, gold dissolution of 55% is attained possibly from gold that is amenable to cyanide dissolution. Molybdenum dissolution of 88.54% is also achieved during the oxidation stage indicating that molybdenite oxidation by hypochlorite also occurs and hypochlorite solution can be used to dissolve molybdenum from the concentrate. Gold dissolution of 93.51% is achieved at the end of leaching. Remaining gold that is not dissolved could have been gold locked in silicates that are not dissolved by hypochlorite. Based on the shrinking-core model, rate determining step for sulfide oxidation is diffusion control with an amorphous oxide formed as outer layer. The use of hypochlorite solution can be a potential alternative for gold extraction of refractory gold-molybdenum concentrates

V. ACKNOWLEDGEMENT

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