PHILIPPINE ENGINEERING JOURNAL
PEJ 2022; Vol. 43, No. 2: 57-70

Received: 06 June 2022
Accepted: 22 December 2022

Oxidation and Dissolution of Refractory Gold Concentrate in Alkaline Hypochlorite Solutions

Hanna Czarise E. Regidor, Herman D. Mendoza and Manolo G. Mena
Department of Mining Metallurgical and Materials Engineering,
College of Engineering, University of the Philippines Diliman, Quezon City, Philippines

Abstract – *With the decreasing availability of free milling gold ores today, the development of processes that can treat refractory ores are important. A promising option from these is chlorination. It is capable of both dissolving the gold and oxidizing the ore, which removes the "refractory" nature of the ore. A staged leaching process can then be used where the first part would focus on the pretreatment oxidation of the refractory ore, followed by the second part where the dissolution of the gold exposed will be the focus. In this study, a Box-Behnken test of the pretreatment process has been conducted. The chlorination process consists of oxidation using hypochlorite-bearing reagents at alkaline conditions. Screening tests were done to determine the significant factors, and it was found that the factors hypochlorite concentration, percent solids, and oxidation time had a significant effect on the oxidation and dissolution of gold. Three levels were set for each of these factors in the optimization tests, and results show that a gold recovery of 83% can be obtained at 4.3 hours of oxidation, 0.6 moles of hypochlorite and 28% percent solids from a sulfide concentrate grading 102.5 g Au, leaving 17.4 g/t Au in the tails. Powder XRD patterns and SEM-EDS results validated that oxidation took place.*

Keywords: Electrochemical Oxidation, Hypochlorite, Chlorination, Response Surface Methodology

I. INTRODUCTION

Different ores would have different responses when subjected to extraction processes. In order to determine the suitable processing method that the ore needs, information about its mineralogy is important.

Gold ores are commonly classified into two categories: (1) free-milling (non-refractory); and (2) refractory gold ores. Free-milling gold ores are gold ores where over 90% of the gold can be recovered through conventional cyanidation or cyanidation combined with gravity concentration processes. Refractory gold ores are gold ores that do not yield high gold recoveries when subjected to the cyanidation process. There are two possible reasons for this: first, the gold ore has components or materials (i.e. carbonaceous materials) that promote "preg robbing" of gold; or second, majority of the gold are physically locked in sulphide minerals or oxides, and therefore require an additional pre-treatment process to expose the gold and render it amenable for leaching or dissolution [1, 2].

For a refractory gold ore where gold is locked inside the pyrite grain, pretreatment is necessary to recover the gold. The pretreatment usually involves decomposition of the sulphide structure to allow the lixiviant access to the gold. In the oxidation process using hypochlorite, the oxidizing species would depend on the pH of the process. The chlorine species existing in aqueous solutions depends on the pH of the solution, namely aqueous chlorine (Cl_{2aq}), hypochlorous (HOCl), and hypochlorite (OCl^-). The stability region of the aqueous chlorine is from pH 3.5 and below, pH values between 3.5 and 7.5 for the hypochlorous species, and pH values above 7.5 for the hypochlorite species, as shown in Figure 1 [3].

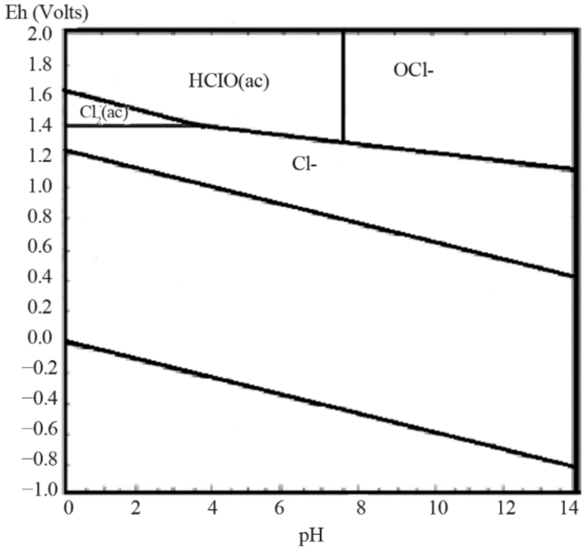

Figure 1. Pourbaix Diagram of Chlorine in Water [4]

Pretreatment by hypochlorite is advantageous in that the pretreatment process can proceed directly to the leaching process without filtering out the solids. If hypochlorite-bearing reagents are used and the pH of the pretreatment process is lowered to 7-8, hypochlorous ions can form. These readily react with the exposed gold brought about by the pretreatment process without the need to filter out the solids. [8] This can lead to a modification of the chlorination process where a staged-leaching process consisting of two general stages. The first part will focus on the pretreatment process of exposing locked gold in alkaline conditions, while the second part will focus on the dissolution of the gold. It is important to optimize the pretreatment process to make sure that most of the gold is exposed and recovered in the leaching process. In this study, the Box-Behnken response surface methodology was used to obtain the optimum settings for the pretreatment process.

I. METHODOLOGY

2.1 Materials

Sulfidic flotation concentrates obtained from a pilot plant in Itogon, Benguet were used in the experiments. They contained 102.5 g/t Au and 45.44% sulfur. The pyrite content was 65.9% with the balance mostly composed of silica. The following technical grade reagents were mixed to form the solutions used in the experiment: sodium hypochlorite (NaOCl), calcium hypochlorite ($Ca(OCl)_2$), sodium chloride (NaCl) and sodium hydroxide (NaOH). Deionized water was used to ensure that no interfering ions were present in the tests.

A representative sample of the flotation concentrate was sent to third party testing for gold and sulfur content analysis using fire assay and gravimetric methods. The gold content of the aliquot samples was analyzed using a Perkin-Elmer PinAAcle 900 Flame Atomic Absorption Spectrometer (FAAS). Scanning electron microscopy energy-dispersive spectroscopy (SEM-EDS) analysis was done using Hitachi SU8230 Fe-SEM equipment, and mineral characterization were conducted using powder x-ray diffraction analysis through an Olympus TERRA Field Portable XRD equipment.

EDS results were analyzed by calculating the atomic percent of each element in the result. The following equation is used.

$$\text{Atomic Percent} = \frac{Weight\ Percent}{Molecular\ Weight}\, x \left(1/\sum \frac{Weight\ Percent}{Molecular\ Weight}\right) x\ 100\% \qquad (1)$$

Mineral identification of the powder x-ray diffraction graphs was done using a Match! Software. X-ray fluorescence analysis results were used to determine the elemental percentage composition of the flotation concentrate (Appendix 1-a), which in turn were used as the basis for the minerals used in the semi-quantitative analysis in XRD (Appendix 2).

Semi-quantitative analysis for a sample containing two phases can be done using Klug's equation [6].

$$x_i = \frac{\left(\frac{I_1^{mix}}{I_1^{pure}}\right)A_2}{A_1 - \left(\frac{I_1^{mix}}{I_1^{pure}}\right)(A_1 - A_2)}\, x100\% \qquad (2)$$

Where x_i – percent weight fraction
I_1^{mix} – integrated intensity of phase 1 in the mixture
I_1^{pure} – intensity of the phase 1 in a pure sample
A_1 – mass absorption coefficient of the phase 1
A_2 – mass absorption coefficient of the phase 2

The ratio of I_1^{mix}/I_1^{pure} can be obtained in the phase selection using the Match! software. For a mineral phase, the mass absorption coefficient can be determined using the following equation [12]:

$$A_{mineral} = \sum_{i=1}^{n} w_i A_i \qquad (3)$$

Where w_i – atomic weight fraction
A_i – mass absorption coefficient of the element

The atomic weight fraction can be determined using the following equation:

$$w_i = \frac{\eta_i AW_i}{\sum_j \eta_j AW_j} \tag{4}$$

Where w_i – atomic weight fraction
η_i – number of formula units of the element
AW_i – atomic weight of the element i.

2.2 Optimization Tests

Response surface methodology was employed to obtain the optimum settings of the significant factors that affect the oxidation process of leaching [5]. Screening tests that involve 2k factorial designs are first employed to determine the significant factors, followed by the response surface methodology. All tests were done in one-liter glass beakers, equipped with an over-head stirrer that had an rpm of 300. The reagents were first mixed until a homogenized solution was produced. Flotation concentrate samples weighing 100 grams each were then added, and the solution's pH was monitored at regular time intervals throughout the test period.

2.2.1 Screening Tests

Screening tests were done to determine the factors that were significant enough to be included in the surface response methodology. Two 2^k full factorial designs were used to determine the significant factors. The first factorial design consists of the factors hypochlorite concentration and oxidation time, while the second factorial design included the factors percent solids and lixiviant composition (Appendix 3). The method used here was a two-stage chlorination test wherein after the oxidation pretreatment process, the dissolution process started by lowering the solution pH from 12 to 11.5 and fixed amounts of $Ca(OCl)_2$ and NaCl were added to replenish the lixiviant. The solution pH was monitored and upon reaching the value of 7, was maintained in that value using sodium hydroxide. The leaching process parameters remained constant for all setups.

Table 1. Design of Experiment of the Screening Tests

Setup	**First Factorial Design**		**Second Factorial Design**	
	Hypochlorite Concentration	Oxidation Time	% Solids	Lixiviant Mix
A	0.11 moles	2 hours	5%	Mixed NaOCl + $Ca(OCl)_2$
B	0.22 moles	2 hours	5%	$Ca(OCl)_2$ only
C	0.11 moles	6 hours	18%	Mixed NaOCl + $Ca(OCl)_2$
D	0.22 moles	6 hours	18%	$Ca(OCl)_2$ only

2.2.2 Optimization Test

From the screening tests, the significant factors obtained were oxidation time, and percent solids. Hypochlorite concentration was also added in the optimization tests. A three-level experiment design using the significant factors in the screening tests was done using the Box-

Behnken method to determine the optimum settings for this flotation concentrate (Appendix 4).

Table 2. Design of Experiments for the Optimization Test

Setup	Oxidation Time	Hypochlorite Concentration	% Solids
1	3 hours	0.47 moles	30%
2	3 hours	0.24 moles	40%
3	3 hours	0.47 moles	30%
4	3 hours	0.71 moles	40%
5	3 hours	0.24 moles	20%
6	1 hour	0.47 moles	40%
7	5 hours	0.47 moles	40%
8	1 hour	0.47 moles	20%
9	5 hours	0.24 moles	30%
10	1 hour	0.24 moles	30%
11	3 hours	0.47 moles	30%
12	3 hours	0.71 moles	20%
13	5 hours	0.47 moles	20%
14	5 hours	0.71 moles	30%
15	1 hour	0.71 moles	30%

The optimization tests were done in a one-liter glass beaker, equipped with an over-head stirrer that had an rpm of 300, equivalent to a tip speed of 0.94 m/s. Like in the screening tests, the lixiviant reagents were first homogenized prior to the addition of the flotation concentrate. The solution's pH was monitored at regular time intervals, and aliquots were obtained throughout the oxidation process.

III. RESULTS AND DISCUSSION

3.1 Optimization Test

3.1.1 Screening Tests

The following recovery values were obtained in the first screening test, with the coded values of the factors. The recoveries obtained show that as you increase the hypochlorite concentration from 0.11 moles to 0.22 moles and the oxidation time from 2 hours to 6 hours, the gold recovered increases as well. This is expected because increasing the hypochlorite concentration would mean that more hypochlorous acid is available to dissolve the gold. A longer oxidation time would mean a longer contact time with the lixiviant.

Table 3. First Screening Test Recoveries

Setup	Hypochlorite Concentration	Oxidation Time	% Recovery
A	0.11 moles	2 hours	54.9 %
B	0.22 moles	2 hours	68.5 %
C	0.11 moles	6 hours	79.0 %
D	0.22 moles	6 hours	90.3 %

For the second screening test, the recoveries obtained show that for the same lixiviant composition, increasing the percent solids from 5% to 18% decreases the recovered gold. This is expected since decreasing the percent solids increases the surface area exposed to the lixiviant at any time. For the same percent solids, changing the lixiviant composition to that of a mixed composition of NaOCl and $Ca(OCl)_2$ increases the recovery. These results were expected because using sodium hypochlorite results in faster kinetics [8]. While calcium hypochlorite can yield two moles of hypochlorite, it has slower kinetics, and it needs to be dissolved into solution first because of its commercially available form [3].

Table 4. Second Screening Test Recoveries

Setup	% Solids	Lixiviant Composition	% Recovery
E	5%	Mixed NaOCl + $Ca(OCl)_2$	92.4%
F	5%	$Ca(OCl)_2$ only	75.8%
G	18%	Mixed NaOCl + $Ca(OCl)_2$	81.8%
H	18%	$Ca(OCl)_2$ only	20.5%

It can be inferred from the analysis of variance results that the significant factors are solution percent solid, oxidation time and the lixiviant composition, with the computed values for the F-test higher than the critical F-value. The F-test results (with α value of 0.01) and p values of the tests are shown in Table 5.

Table 5. F-Test Results and P Values

Factors	F-computed	F-critical	P
Hypochlorite Concentration	8.26	8.45	0.0453
Oxidation Time	28.05		0.0061
% Solids	9.04		0.0397
Lixiviant Composition	10.08		0.0303

Despite the hypochlorite concentration not being significant in the analysis of variance, it was still included in the optimization test due to the limitations on the commercially available form of hypochlorite. Screening test results showed a higher recovery value in the setups with mixed lixiviants as compared to those that only contains calcium hypochlorite. The two commercially available hypochlorite-bearing reagents are sodium hypochlorite and calcium hypochlorite. Sodium hypochlorite has faster kinetics than calcium hypochlorite, but commercially available sodium hypochlorite has only up to 7% concentration. Calcium hypochlorite, on the other hand, is commercially available as a solid reagent and can produce two moles of hypochlorite for each mole of calcium hypochlorite in solution. Mixing the two reagents can compensate for each reagent's disadvantages. The lixiviant composition was then made constant to a mixture of hypochlorite-bearing reagents in the optimization tests.

Samples of the flotation concentrate and solid residue after the oxidation process were tested using powder x-ray diffraction analysis, the results of which are shown in Figure 2 and Figure 3.

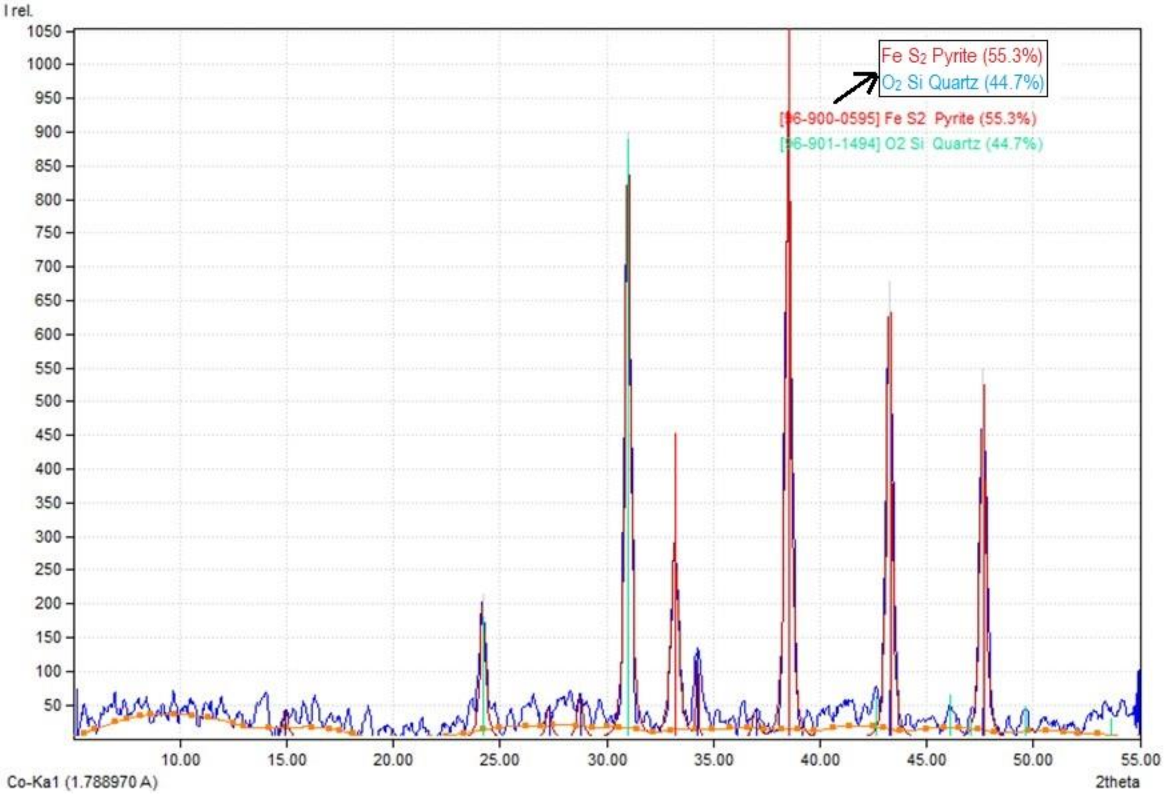

Figure 2. X-ray diffraction plot of the flotation concentrate

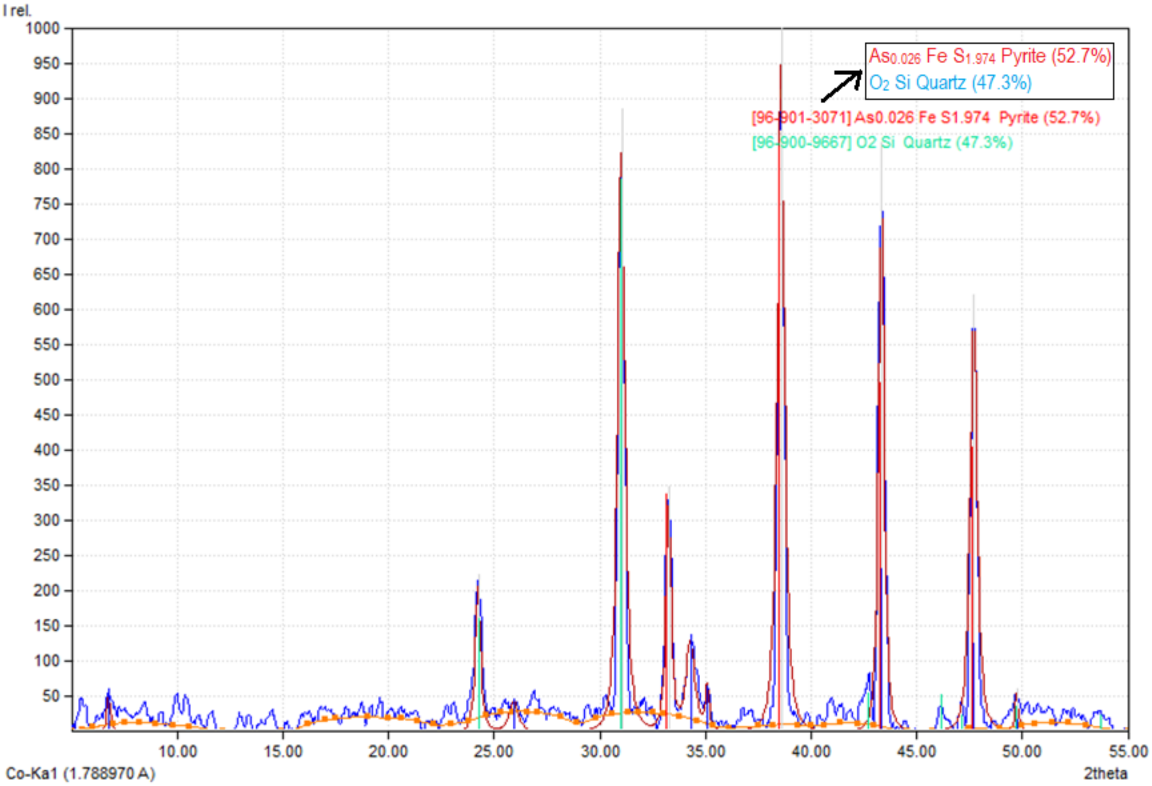

Figure 3. X-ray diffraction plot of the oxidation residue

X-ray fluorescence analysis was also conducted, and results show that the elements that were predominant in the samples were iron, sulfur and silicon, indicating that semi-quantitative analysis using Klug's equation for a sample containing two phases can be conducted [6,7].

Semi-quantitative analysis results of the flotation concentrate and oxidation residue can be seen in Table 6. Results show that the fraction of pyrite reduced from 65.9% to 57.1% after the oxidation process, which indicates that the oxidation was not sufficient in oxidizing the pyrite but can be attributed to the oxidation that took place in the setup. Further oxidation of the remaining pyrite in the residue can lead to the liberation of locked unrecovered gold, making it amenable for further leaching and recovery.

Table 6. Relative Amounts of Pyrite in the Oxidation Test using Klug's Equation

Sample	Percent Weight Fraction	Percent Decrease
Flotation Concentrate	65.9%	13.4%
Oxidation Residue	57.1%	

3.1.2 Optimization Tests

The optimization runs were conducted for the flotation concentrate sample grading 102.5 g/t Au, and the following tailings and corresponding gold recoveries were obtained.

Table 7. Optimization Test Recoveries

Setup	Oxidation Time	OCl^- Concentration	% Solids	Residue Grade, g/T	% Recovery
1	3 hours	0.47 moles	30%	100.96	1.5
2	3 hours	0.24 moles	40%	28.39	72.3
3	3 hours	0.47 moles	30%	98.71	3.7
4	3 hours	0.71 moles	40%	100.86	1.6
5	3 hours	0.24 moles	20%	96.45	5.9
6	1 hour	0.47 moles	40%	81.9	20.1
7	5 hours	0.47 moles	40%	99.12	3.3
8	1 hour	0.47 moles	20%	60.48	41.0
9	5 hours	0.24 moles	30%	100.55	1.9
10	1 hour	0.24 moles	30%	32.19	68.6
11	3 hours	0.47 moles	30%	54.02	47.3
12	3 hours	0.71 moles	20%	24.09	76.5
13	5 hours	0.47 moles	20%	70.52	31.2
14	5 hours	0.71 moles	30%	15.17	85.2
15	1 hour	0.71 moles	30%	86.72	15.4

Using the results in Table 7, optimization analysis using the Box-Behnken method was conducted, and the data fit the quadratic model the most.

Analysis of variance (Appendix 6, Table 8) results show that the quadratic model is significant, with the F-value of 9.52. The p-values of A, B, A^2, B^2 and C^2 show that these terms are significant. This means that these factors have a significant effect on the response, the recovery of gold, and that the system is in the optimal region. A regression analysis was conducted removing the insignificant interaction effects (Appendix 6, Table 9) and a better fit was obtained.

The equation that shows the relationship of the response with the factors is shown below. This equation can be used in identifying the relative impact of the factors by comparing their coefficients. It shows that percent solids have the highest impact, followed by the hypochlorite concentration and then oxidation time.

$$\%Gold\ Recovery= \\ 73.46+18.88A+13.21B-6.53C-17.99A^2-19.59B^2-40.32C^2 \tag{5}$$

Where A = oxidation time, minutes
B = hypochlorite concentration, moles
C = percent solids, percent

Evaluation of three-dimensional surface plots of the factors and their effect on the response gives vital information on the behavior of the experimental design [8].

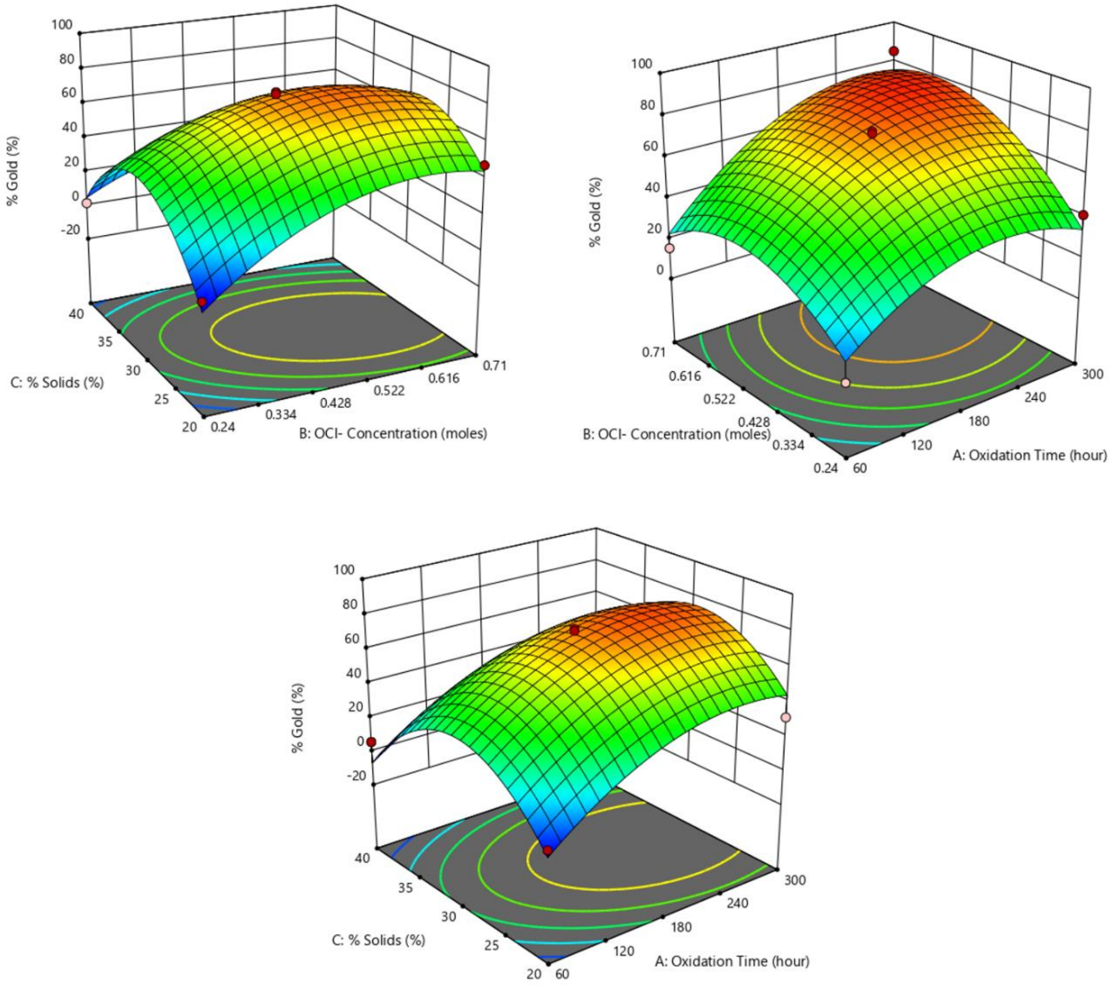

Figure 4. 3-D surface plots of the combination effect of the three factors: A- Oxidation Time, B- Hypochlorite Concentration, and C- % Solids

The graphs in Figure 4 show that increasing both the hypochlorite concentration from 0.24 moles to 0.71 moles and oxidation time from 1 hour to 5 hours increases the percentage of gold recovered. Increasing either of the two with percent solids shows that gold recovered increases until it reaches approximately 28% percent solid value after which the recovery decreases. This shows that an optimum percent solid value exists where the gold recovery is highest. It means that increasing either the oxidation time or hypochlorite concentration when it is in combination with the percent solids value at the peak increases the gold recovery.

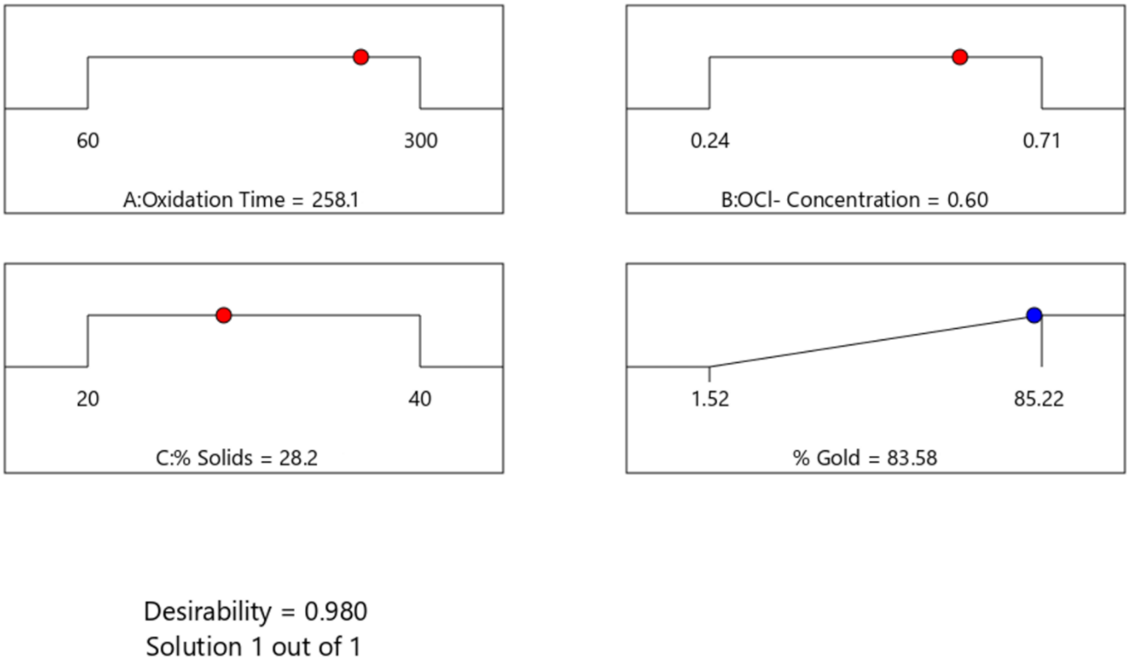

Figure 5. Solution to the optimization test

The solution to the optimization test in Figure 5 shows that up to approximately 83% gold recovery can be achieved with the following conditions: oxidation time of 4.3 hours, hypochlorite concentration of 0.6 moles, and 28% solids. These oxidation conditions shows promising results since this would mean that a high gold recovery can be achieved in less than 5 hours at the end of the oxidation stage. Extending the oxidation time beyond 5 hours could also lead to a further increase in the recovery of gold, as shown in the optimization run results in Table 7.

A scanning electron microscopy image of the solid residue in Figure 6 below showed a layer surrounding a grain. Energy dispersive spectroscopy analysis of the area showed that the region in the mineral grain had a higher sulphur and iron element weight percent than the spectra obtained in the layer. The atomic percent of each element in the grain showed that the amount of sulphur was approximately twice the amount of iron, as shown in Table 8 below. It shows that in the EDS results no other metallic elements other than iron was present, which means that the iron may be associated with the sulphur. It may be inferred in the atomic percent results that the grain is composed of pyrite. It also further confirms the sulphidic nature of the flotation concentrate sample. The atomic percent of each element in the EDS results in the layer showed that the amount of iron was higher than half the amount of the sulphur. This means that some of the iron detected may not be associated with the sulphur. Hydrogen cannot be detected using EDS, and considering the reactions involved in the leaching process, it may be inferred that the excess iron that cannot be associated to the sulphur may be associated with the oxygen in the EDS results. The high amount of oxygen in the EDS results of the outer layer suggests that it is an oxide layer.

Table 8. Normalized EDS Results of the Outer Layer and Grain

Element	Atomic Percent	
	Layer	Grain
O	87.98	12.91
S	6.78	57.53
Fe	5.23	29.56

The conformity of the layer to the shape of the grain suggests that the mechanism of oxidation was a product layer diffusion process. The findings of one study of pyrite oxidation, however, showed that the reaction was chemical reaction controlled [10]. But another study that observed the oxidation of chalcopyrite showed that the oxidation process was product layer diffusion controlled [11]. Yet another study showed that the leaching of gold in refractory gold ores was both product layer diffusion and chemical reaction controlled, with the contribution of the product layer diffusion greater than that of the chemical reaction control [3].

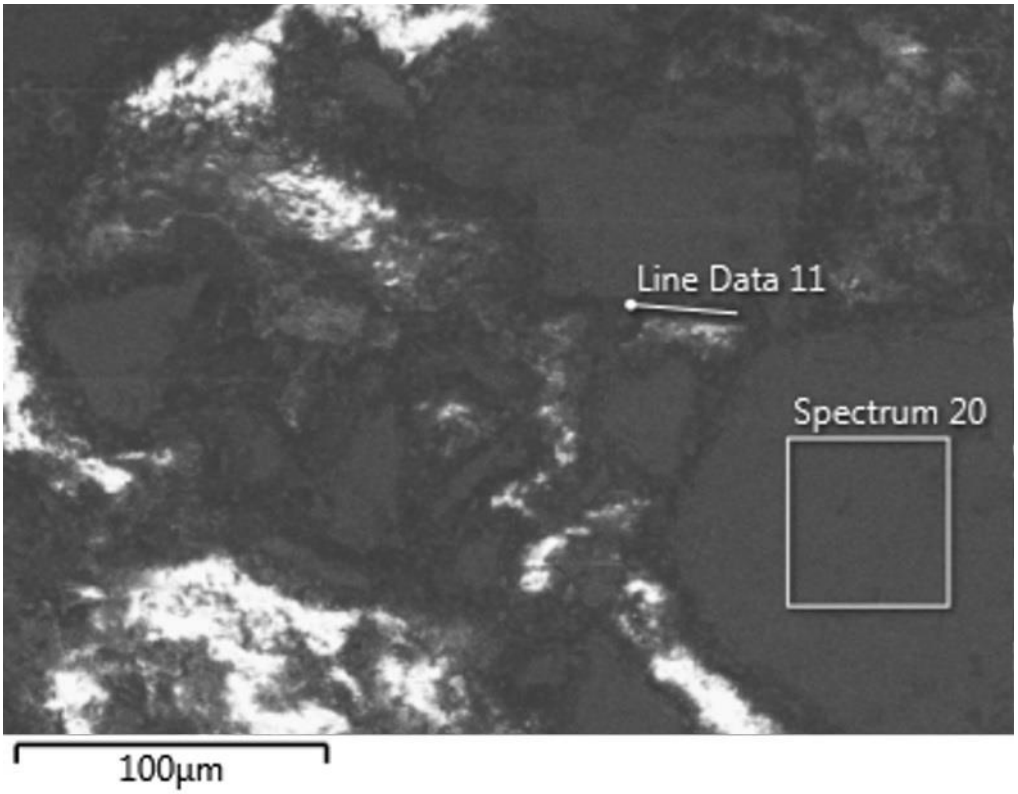

Figure 6. SEM-EDS image of the oxidation residue

IV. CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

Optimum settings for the simultaneous oxidation and dissolution of refractory flotation gold concentrate were obtained using the Box-Behnken experiment design. The solution obtained in the optimization test showed that a maximum of approximately 83% gold recovery can be achieved in sulfidic concentrates containing 102.5 g/T gold when the oxidation time is 4.3 hours, hypochlorite concentration is 0.6 moles, and the solution has 28% solids.

From the experiments conducted, the following conclusions and observations can be inferred:

1) From the screening tests, the factors hypochlorite concentration, oxidation time, and percent solids were found to have a significant effect on the recovery of gold. Increasing the hypochlorite concentration and oxidation time increases the gold recovery, while decreasing the percent solids increases it. These effects of the factors with the response were observed in the screening tests and can be inferred in the equation obtained in the optimization test where the hypochlorite concentration and oxidation time were found to have a proportional relationship with gold recovery.

2) Scanning electron microscopy image coupled with energy dispersive spectrometry suggests that the mechanism of the oxidation process by hypochlorite was product layer diffusion controlled. Powder x-ray diffraction results shows a 13.4% decrease in the semi-quantitative analysis of the pyrite phase after the oxidation process, validating that oxidation took place.

4.2 Recommendations

The use of hypochlorite-bearing reagents in chlorination was proven to be promising as an alternative to the conventional cyanidation process. The resulting recovery of 83% could still be further improved to achieve higher recoveries. Further studies that can be conducted would be confirmatory test of the optimum settings, possible optimization of the second stage of the process, studies on the effect of the hypochlorite oxidation individually with the possible sulfide minerals present in the flotation concentrate (as in complex sulphide flotation concentrates), and effect of other parameters that were not considered in the study on the chlorination process. The parameters used in the optimization tests could also be expanded to obtain a wider range of results and to obtain the exact values where the peak of the 3-D surface plots decreases. Comparative studies from other existing pre-treatment processes in treating refractory gold ores could also be considered. Recovery of the dissolved gold, comparative dissolution tests with other lixiviants and treatment of the effluent and barren ore could also be considered for future studies.

REFERENCES

[1] SGS Minerals Technical Bulletin. 2004-03. Retrieved from http://www.sgs.com/-/media/global/documents/technical-documents/sgs-technical-papers/sgs-min-tp2004-03-process-mineralogy-of-gold-ores.pdf on 17 Dec 2017.

[2] Albion Process Russia. 2012. Retrieved from http://www.albionprocess.com/en/downloads/TechnicalPapers/Options-to-Treat-Refractory-Ores.pdf on 17 Dec 2017.

[3] Hasab MG, Rashchi F, Raygan S. 2013. Chloride-hypochlorite oxidation and leaching of refractory sulfide gold concentrate. Physicochem. Probl. Miner. Process. 49:61–70.

[4] Valenzuela A, Valenzuela JL, Parga JR. 2013. Effect of pretreatment of sulfide refractory concentrate with sodium hypochlorite, followed by extraction of gold by pressure cyanidation, on gold removal. Adv. In Chem. Engg. and Science. 3:171–177.

[5] Stat-Ease Inc. 2011. Retrieved from http://www.statease.com/productattachments/index/download?id-242 on 22 Jan 2018.

[6] James RC. 2012. Introduction quantitative x-ray diffraction methods. The University of New Mexico.

[7] Han I, Kolayli H, Sahin M. 2011. Determination of mass attenuation coefficients for natural minerals from different places of Turkey. International Journal of the Physical Sciences. 6:4798–4801.

[8] Marsden JO, House CI. 2006. The chemistry of gold extraction. 2nd ed. Littleton, Colorado.

[9] Guyo U, Makawa T, Moyo M, Nharingo T, NYamunda BC, Mugadza T. 2015. Application of response surface methodology for Cd(II) adsorption on maize tassel-magnetite nanohybrid adsorbent. Journal of Environmental Chemical Engineering. 3:2472–2483.

[10] Sun H, Chen M, Zou L, Shu R, Ruan R. 2013. Study of the kinetics of pyrite oxidation under controlled redox potential. Hydrometallurgy. 55:13–19.

[11] Backstead LW, Munoz PB, Sepulveda JL, Herbst JA, Miller JD, Olson FA, Wadsworth ME. 1976. Acid feric sulfate leaching of attritor-ground chalcopyrite concentrates. Extractive Metallurgy of Copper. p 615–631.