GOLD METAL DISSOLUTION FROM REFRACTORY ORE THROUGH CALCIUM HYPOCHLORITE AND SODIUM CHLORIDE LEACHING PROCESS

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Abstract

Distinguished by its wealth in refractory gold deposits, Davao de Oro in the Philippines has historically relied on cyanidation for gold extraction. This method, while prevalent, employs toxic cyanide, leading to significant environmental and biological risks. The urgency to develop less detrimental and more effective methods of extraction is evident. Hypochlorite has emerged as a viable reagent in the dissolution of refractory gold ores, presenting an environmentally sustainable and safer alternative to traditional cyanide-based processes in terms of production, utilization, and disposal. This study investigates the effects of various pH levels and hypochlorite concentrations on ore dissolution. Notably, in the preliminary oxidation experimental runs, the specific ratios of sodium chloride (NaCl) to calcium hypochlorite ($Ca(OCl)_2$), particularly in the ratio of 15:15 and 20:10, demonstrated efficacy in solution environments maintaining a pH level of 6. With the same pH, the ratio of 60:30 yielded the highest gold dissolution rates, with an average of 86.84% gold recovery, peaking at 97.31% in the final runs. The research aims to contribute substantially to the advancement of gold recovery methods, providing a more environmentally conscious approach compared to the conventional cyanidation process.

Keywords: Gold dissolution, hypochlorite, refractory ore, leaching

1.   INTRODUCTION

Gold ores in the Philippines exhibit a diverse range of characteristics, ranging from varying mineral compositions to differing levels of refractory behavior. While some ores containing iron and copper oxides pose minimal challenges with conventional extraction methods, those found in Davao de Oro, Philippines, like sulfides and carbonaceous ores, resist extraction due to their complex structures, necessitating advanced processing techniques [1]. This refractory behavior is attributed to the presence of minerals, such as pyrite and chalcopyrite, which encapsulate the fine gold particles in the ore, preventing the gold–solvent interaction and subsequent dissolution [2].

Cyanidation, a commonly used method for refractory gold extraction, requires additional steps and higher cyanide amounts to render refractory ores amenable to the process, resulting in low recovery rates below 50 % [3,4]. Recognizing these limitations, efforts have been made to explore alternative methods for enhanced gold recovery [5]. However, challenges arise with alternative solvents like thiourea and thiocyanate, which face issues of cost, instability, and environmental risks [6-8]. Bioleaching, another method, that requires pre-treatments like pressure oxidation and roasting, raises environmental concerns due to the high discharge and pollution threats to the receiving body of water [9,10].

An emerging reagent for gold dissolution, calcium hypochlorite ($Ca(OCl)_2$), presents lower toxicity and cost-effectiveness compared to other reagents [11]. Hydrochlorination aids in processing refractory concentrates by oxidizing carbonaceous contents, thus preventing gold precipitation. Previous studies reveal that the efficiency of hypochlorite leaching depends on a variety of factors like pH level, chloride-hypochlorite ratio, and concentrate particle size, which vary based on the ore type [3,12]. However, research on hypochlorite solutions for gold dissolution in sulfidic refractory ores remains limited, highlighting the need for further investigation.

To bridge this research gap, the study evaluates the effect of varying hypochlorite concentrations and pH levels on refractory gold dissolution, aiming to optimize hypochlorite's potential and promote sustainable mining practices. Understanding the dynamics of hypochlorite interactions with sulfidic concentrates is crucial for advancing metallurgical practices and achieving efficient gold extraction from refractory ores.

2.   MATERIALS AND METHODS

The refractory gold ore sample was obtained from Apex Mining Co., Inc. Mineral liberation analysis (MLA) of the ore conducted showed that approximately 80% of the gold grains are smaller than 12 µm thus particle size of the samples for the experiment was ground to <37.4 µm. The MLA (**Table 1**) also reveals that the ore consists of pyrite (FeS_2), quartz (SiO_2), and chalcopyrite ($CuFeS_2$). The total concentration of the gold present in the concentrate wasanalyzed through atomic absorption spectroscopy (AAS) and found to be at 20.456 g/t.

Table 1 Mineral composition of gold ore using Mineral liberation analyzer

Mineral	Percentage (%)
FeS_2	52.74
SiO_2	28.36
$CuFeS_2$	5.83
$(Zn,Fe)S$	2.31
ClO_2	1.22

The leaching experiments were conducted using beakers on top of a hot plate and a magnetic stirrer to maintain temperature and agitation. The pH and Oxidation-Reduction Potential (ORP) were monitored every 15 minutes during the process.

Preliminary experiments evaluated seven lixiviant solutions (30:1, 25:5, 20:10, 15:15, 10:20, 5:25, and 1:30) with varying concentration ratios of NaCl to $Ca(OCl)_2$, in grams per litre, were prepared. For each concentration ratio, five setups with different pH values (4, 4.5, 5, 5.5, and 6) were prepared. A 10g of concentrate is added to a 150 ml lixiviant solution. The solution is constantly stirred at a rate of 600 revolutions per minute (rpm). The leaching process for each sample was done for 2 hours. Then, the sample of the slurry was withdrawn and filtered. The gold content of the clear solutions was analyzed using an X-ray Fluorescence (XRF).

3.   EXPERIMENTAL RESULTS

3.1.   Ore characterization

Elemental distribution mapping using a Scanning Electron Microscope with Energy Dispersive X-ray (SEM-EDX) was conducted to visualize and characterize the spatial distribution of elements within the ore. The results depicted in **Figure 1**, confirmed that the representative ore contains high amounts of iron and sulfur, likely corresponding to the pyrite quantified from MLA in **Table 1**. Interestingly, small amounts of gold, silver, and tellurium were found to be enclosed within the large mass of iron-sulfur matrix. Trace amounts of copper were also observed attached to the Au-Ag-Te mass. The copper detected is most likely from chalcopyrite.
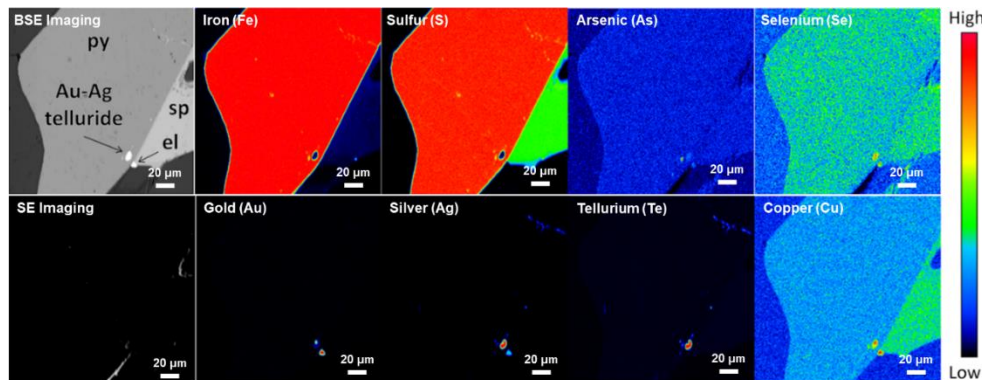
Figure 1 Elemental distribution mapping of representative ore using SEM-EDX. The color indicates the presence of each element (red – high; blue – low)

3.2.   Preliminary oxidation experiments

Based on the ore characterization results, a preliminary pyrite oxidation experiment was designed to determine the optimal pH values and chloride-hypochlorite concentration ratios needed to dissolve the pyrite minerals encasing the gold. Each setup consists of 10 g concentrate and 150 ml lixiviant solutions, stirred at 600 rpm and maintained at 25 °C. The summary of these experiments, shown in **Table 2**, reveals that the ideal pH is 6 and the optimal ratios of lixiviant are 15:15 and 20:10 for NaCl to $Ca(OCl)_2$.

Table 2 Gold detection during preliminary oxidation experiments

Concentration ratio [NaCl:Ca(OCl)$_2$]	pH levels				
	4.0	**4.5**	**5.0**	**5.5**	**6.0**
1:30	ND	ND	ND	ND	ND
5:25	ND	ND	ND	ND	ND
10:20	ND	ND	ND	ND	ND
15:15	ND	ND	ND	ND	0.7 ppm
20:10	ND	ND	ND	ND	0.8 ppm
25:5	ND	ND	ND	ND	ND
30:1	ND	ND	ND	ND	ND

The preliminary analysis likely identified pH 6 because this neutral environment converts hypochlorite ions (OCl^-) to hypochlorous acid (HOCl), a powerful oxidizing agent capable of breaking down the bonds in pyrite, thereby releasing the gold that is trapped within the pyrite structures. Gold was detected only in setups with ratios of 20:10 and 15:15, both providing a balanced amount of Cl^- ions and HOCl to oxidize the pyrite, dissolve the gold, and keep them in solution.

3.3.   Gold dissolution

Gold was detected at a maintained pH level of 6 with two NaCl:$Ca(OCl)_2$ ratios, indicating that the encasing pyrite was effectively oxidized under these conditions. Building on this finding, further leaching experiments were conducted under the same conditions. According to the literature and experimental evidence, pyrite oxidation must precede gold dissolution. Consequently, the study examined varying oxidation times of 2 and 3 hours with reagent ratios of 30:25 and 60:25. The remaining $Ca(OCl)_2$ to achieve 30:30 and 60:30 reagent ratios was added periodically during the subsequent 2-hour leaching period. This incremental addition was necessary due to the high presence of pyrite. The hypochlorite and chloride levels were increased to ensure sufficient availability for effective pyrite oxidation and gold dissolution while maintaining the desired ratio. This adjustment, based on the required stoichiometric amount of HOCl, is further refined by a factor of 1.25 to

accommodate ideal assumption deviations. The results are expressed in terms of percent gold dissolved (%Au), representing the amount of gold present in the pregnant solution derived from a 10 g ore sample.
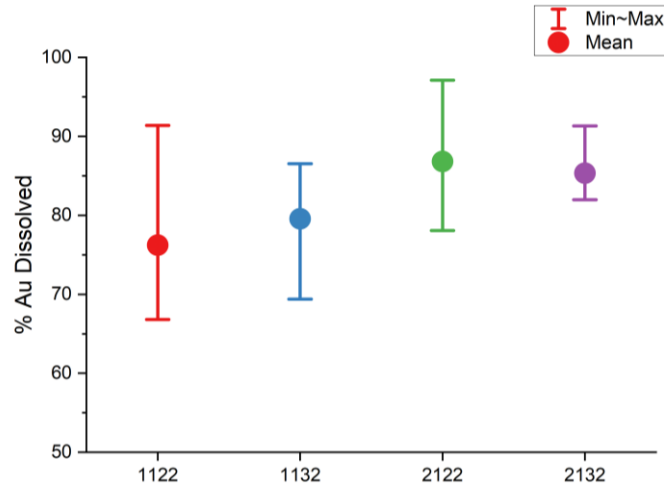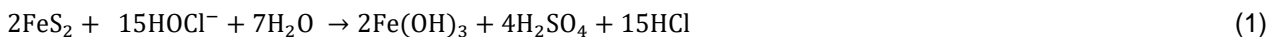

Figure 2 Percent Gold Dissolution. From the left to the right, the x-axis labels refer to NaCl-Ca(OCl)2 ratio, pyrite oxidation time in hours, and leaching time in hours (1122, 1132, 2122, and 2132)

The results of leaching experiments, presented in **Figure 2**, demonstrate the percentage of gold dissolution under four different leaching conditions. The results revealed that setups with 60:30 lixiviant ratio yield more % Au dissolved compared to setups with 30:30 lixiviant ratios. Ata 60:30 ratio, the mean gold dissolution was 86.8% after 2 hours of pyrite oxidation and 2 hours of gold leaching, reaching a maximum gold dissolution 97.3%. Similarly, under a 60:30 ratio, data showed 85.4% after 3 hours of pyrite oxidation and 2 hours of gold leaching. Conversely, setups with a 30:30 lixiviant ratio resulted in lower gold dissolution, with means of 79.6% and 76.2%, under varying oxidation times, respectively, and a minimum of 66.8%. These findings align with existing literature, suggesting that an optimized concentration ratio for hypochlorite leaching involves a higher NaCl amount due to its role in stabilizing gold complexes [13, 14]. Moreover, this mechanism mirrors the leaching process of refractory ore, particularly those rich in pyrite, as NaCl releases chlorine, aiding in the formation of soluble complexes to facilitate hypochlorite oxidation.

As such, we hypothesize that leaching gold from sulfidic refractory ores involves two sequential steps: initial pyrite oxidation followed by the formation of soluble gold-chloride complexes. The study investigated oxidation times of two and three hours. During this period, pyrites (FeS_2) undergo oxidation to produce ferrous hydroxide ($Fe(OH)_3$), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl) as shown in **Equation (1)**. Thereafter, the liberated gold interacts with chlorine ions to generate soluble gold chloride complexes, facilitating gold dissolution as shown in **Equation (2).**
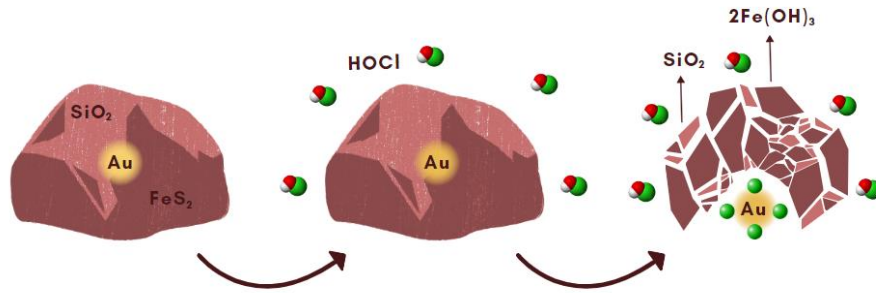
$$2FeS_2 +\ 15HOCl^- + 7H_2O\ \rightarrow 2Fe(OH)_3 + 4H_2SO_4 + 15HCl \tag{1}$$

$$2Au + 3HOCl + 3H^+ + 5Cl^-\ \rightarrow\ 2[AuCl_4]^-\ + 3H_2O \tag{2}$$

Figure 3 Refractory ore leaching mechanism

Figure 3 presents the proposed mechanism of the refractory gold ore dissolution. Under the appropriate pH conditions, the refractory gold undergoes oxidation by the hypochlorous acid that was formed from the dissociation of the hypochlorite ion from calcium hypochlorite. This process leads to the formation of soluble $Fe(OH)_3$, liberating the gold particles for reaction with chlorine. Subsequently, the gold chloride complex isformed, allowing gold oxidation by hypochlorous acid. The quartz (SiO_2) does not readily react with HOCl and is a non-participating compound in this process.

3.4. Effect of pH on gold dissolution

Previous studies emphasized the critical role of pH in the dissolution of gold from sulfidic refractory ores. According to literature, the chloride-hypochlorite system is most effective under slightly acidic to neutral conditions. While hypochlorite has various dissociation products, its most potent oxidizing agent, hypochlorous acid (HOCl), is the most stable within this pH range [12,15]. It is therefore essential to maintain pH throughout the pyrite oxidation and gold leaching experiments. The pH levels were measured every 15 minutes and reported in **Figure 4**.
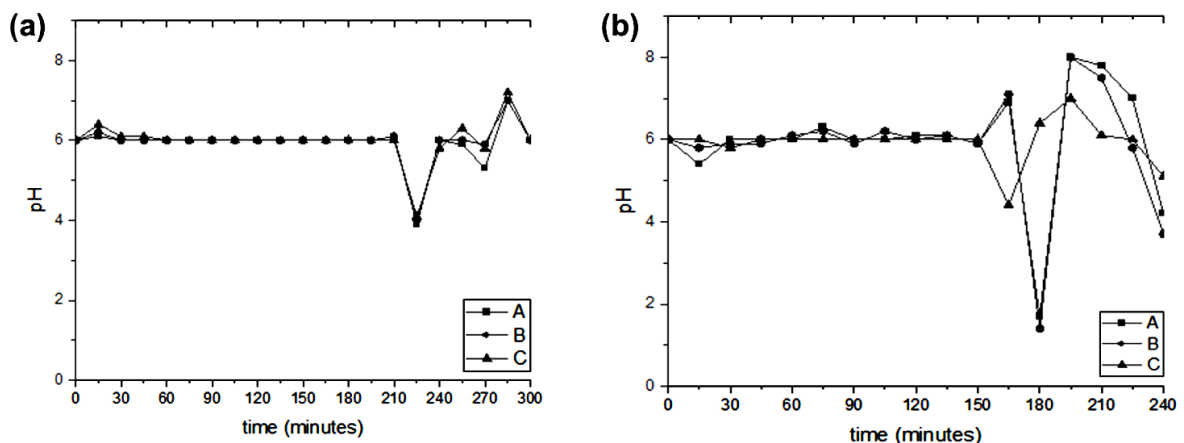

Figure 4 pH monitoring for:(a) 60:30 NaCl:Ca(OCl)$_2$ in 3 hours pyrite oxidation and 2 hours leaching experiment, (b) 30:30 NaCl:Ca(OCl)$_2$ in 2 hours oxidation and 2 hours leaching experiment. A, B, C are the experimental runs

For all cases, the pH levels remained stable throughout the pyrite oxidation stage after the combination of the lixiviant solution and ore concentrates. For the setup with a 60:30 ratio and 3-hour oxidation and 2-hour leaching times (**Figure 4a**), the pH suddenly dropped to pH 4 at the start of the leaching time. A similar observation was made for the setup with a 30:30 ratio and 2-hour oxidation and 2-hour leaching times (**Figure**

4b), where the pH levels became erratic, with one run dropped to a highly acidic region of pH 1.4. This erratic pH behavior can be attributed to the addition of small amounts of $Ca(OCl)_2$ during the leaching period to replenish the lixiviant solution and maintain the ORP of the system at ≥900 mV [15]. This value is maintained to ensure the continuous progression of the oxidation reaction.

Notably, **Figure 4a** shows that the percentages of gold dissolved were 82.7%, 91.3%, and 82.0% for Runs A, B, and C, respectively. In this setup, the pH levels were maintained between 4 and 7.2, which is the ideal range for oxidation via HOCl as an oxidizing agent. This stable pH environment allowed for the effective formation of the gold complex, (AuCl4), which remains in solution yielding higher dissolution rates. Contrary to the previous result, the more erratic the pH levels during the leaching period, the lower the percentage of gold dissolved per setup. As shown in **Figure 4b**, the percentages of gold dissolved were 66.8%, 70.5%, and 91.4% for runs A, B, and C, respectively. In runs A and B, the pH dropped to 1.7 and 1.4, respectively resulting in lower dissolution rates. At this highly acidic pH range, aqueous chlorine is formed instead of HOCl, which easily vaporizes and escapes the system, thus limiting its capacity to dissolve the encasing pyrite [15].

The Spearman correlation between the monitored pH levels across leaching setups and two key variables– parts per million (ppm) of gold and the percentage of gold (% Au) dissolved from the aliquots–was examined. The correlation matrix, presented in **Table 3**, includes the correlation coefficient between these variables. Each cell in the table represents the correlation coefficient between the respective variables, indicating the strength and direction of the relationship between the two variables.

Table 3 Spearman correlation analysis of pH levels, ppm of gold in solution, and %Au dissolved

	Min pH	ppm	%Au
Min pH	1		
ppm	0.74036	1	
%Au	0.78246	0.97902	1

A correlation coefficient of 0.74036 between the minimum pH and the ppm of gold in solution indicates a positive monotonic relationship, suggesting that an increase in pH corresponds to an increase in the amount of gold in solution (ppm). Similarly, a correlation coefficient of 0.78246 between the minimum pH and the %Au dissolved signifies a high positive correlation. This suggests that maintaining the pH within the optimal range, where hypochlorous acid is most stable, enhances the gold dissolution process. Deviations from this pH range compromise the efficiency of gold dissolution. As shown in **Figure 5**, lower pH values correspond to lower gold dissolution rates.
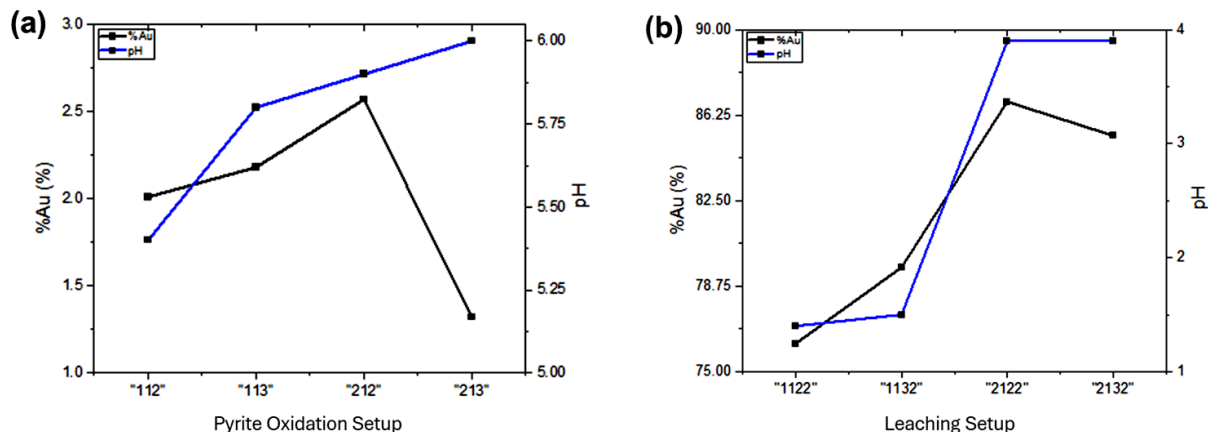

Figure 5 %Au dissolution-pH for:(a) pyrite oxidation in hours,(b) leaching times (hours)

3.5. Effect of varying reagent ratio and pyrite oxidation time

Kruskal-Wallis One-way ANOVA test was used to analyze non-parametric data on the % Au dissolved among different reagent ratios in the experiments. Results of the analysis in **Table 2**, revealed a significant difference in the % Au dissolved across different $NaCl:Ca(OCl)_2$ ratios ($\chi^2(3) = 17.6$, $p < .001$, $\varepsilon^2 = 0.764$). It is shown that there is a significant difference between the observed and expected value since the χ^2 is larger than degrees of freedom (*df*). Furthermore, the p-value < .001 suggests that the data are not coincidental. The ε^2 states the strength of both the independent and dependent variables is 76.4% stating a strong relationship. This indicates that the ratio of NaCl to $Ca(OCl)_2$ significantly influences gold dissolution.

Table 4 Kruskal-Wallis ANOVA test for %Au dissolved vs. reagent ratio w/ pairwise comparisons

		χ^2	*df*	*p*	ε^2
% Au Dissolved		17.6	3	< 0.001	0.764

Dwass-Steel-Critchlow-Fligner pairwise comparisons

Pairwise comparisons - %Au Dissolved

		w	*p*
30:25	30:30	4.076	0.021
30:25	60:25	0.679	0.964
30:25	60:30	4.076	0.021
30:30	60:25	-4.076	0.021
30:30	60:30	1.359	0.772
60:25	60:30	4.076	0.021

Pairwise comparisons using the Dwass-Steel-Critchlow-Fligner method showed that the % Au dissolved for the ratios 30:25 and 30:30 as well as for 60:25 and 60:30 (both with $p = 0.021$), suggests that the addition of the $Ca(OCl)_2$ after pyrite oxidation increases gold dissolution. Comparisons between 30:25 and 60:25, as well as between 30:30 and 60:30, also yielded significant results ($p = 0.021$) highlighting the impact of the increase in NaCl concentration will produce more chloride ion to aid in stabilizing the dissolved gold ions by forming complexes like $[AuCl4]^-$. The results consistently show that increased concentrations of NaCl enhance gold dissolution, although the presence of $Ca(OCl)_2$ in proportions not exceeding those of NaCl, also significantly influences the yield.

Kruskal-Wallis One-way ANOVA test was also used to assess the differences in the percentage of gold (%Au) dissolved across various pyrite oxidation times (2 hours and 3 hours) and to also evaluate the impact of added leaching period after oxidation. The results, detailed in **Table 5**, indicate a significant difference in %Au dissolved among the different conditions (<0.001). Pairwise comparisons using the Dwass-Steel-Critchlow-Fligner method reveal no significant difference between 2 and 3 hours ($p = 1$), or between 2 hours with leaching and 3 hours with leaching ($p = 1$). However, all conditions with only oxidation differ significantly from the added setups with an added leaching period ($p = 0.021$). This implies that leaching substantially increases the dissolution of gold regardless of the pyrite oxidation time. These findings suggest that the leaching process significantly enhances gold dissolution after employing the important stage of pyrite oxidation.

Additionally, the ε^2 values obtained from both tests reported large effect sizes (0.764 and 0.751), suggesting that a substantial portion of the variance in % Au dissolved can be attributed to the differences in the conditions that were tested.

Table 5 Kruskal-Wallis ANOVA test for % Au dissolved vs pyrite oxidation time w/ pairwise comparisons

		χ^2	df	p	ε^2
% Au Dissolved		17.3	3	<0.001	0.751

Dwass-Steel-Critchlow-Fligner pairwise comparisons

Pairwise comparisons - % Au Dissolved

		w	p
2h	3h	0	1
2h	2h w/ L	4.08	0.021
2h	3h w/ L	4.08	0.021
3h	2h w/ L	4.08	0.021
3h	3h w/ L	4.08	0.021
2h w/L	3h w/ L	0	1

4.   CONCLUSION

Based on the experimental findings of this study, it is evident that the most favourable conditions for gold dissolution from sulfidic refractory ores involve a $NaCl:Ca(OCl)_2$ ratio of 60:30, maintained at a pH level of 6. Such conditions yielded the highest gold dissolution rates, with an average of 86.8% gold recovery, peaking at 97.3%. The paper highlights the importance of maintaining slightly acidic to neutral pH conditions to ensure the stability of hypochlorous acid. With its stable presence, elemental analysis confirmed the effective oxidation of pyrite, enabling the liberation of encapsulated gold particles. Deviations from the ideal pH range revealed a significant reduction in the gold dissolution rates.

Furthermore, the study confirmed that the sequential process of pyrite oxidation followed by gold leaching is crucial for maximizing gold recovery. The Kruskal-Wallis ANOVA test underscored the significant impact of the reagent ratio and pyrite oxidation time on the percentage of gold dissolved for processing refractory gold ores. This method not only achieves high gold recovery rates but also advances metallurgical practices by reducing the environmental risks associated with conventional extraction methods. Future research should focus on optimizing these parameters for different ore types and scaling the process for industrial applications, ensuring broader applicability and improved gold recovery efficiencies for a more sustainable gold metal production.

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REFERENCES

[1]   NATARAJAN, K.A. *Experimental and Research Methods in Metals Biotechnology*. Chapter 14. Bangalore: Elsevier, 2018.

[2]   CNLITE Eco-friendly Gold Leaching Reagents. *Leaching Guide of Refractory Gold Ore.* [online]. 2020. [viewed: 2024-04-26]. Available from: https://www.cnlitereagent.com/news/leaching-guide-of-refractory-gold-ore/.

[3]   PLUMLEE, G.S., MORMAN, S., MEEKER, G.P., HOEFEN, T. *The Environmental and Medical Geochemistry of Potentially Hazardous Materials Produced by Disaster.* Denver: Elsevier, 2014.

[4]   QIN, X., GUO, X., TIAN, Q., YU, D., ZHANG, L. *Recovery of gold from sulfide refractory gold ore: Oxidation roasting pretreatment and gold extraction.* Changsa: Elsevier, 2020.

[5]   XU, R., NAN, X., MENG, F., LI, Q., CHEN, X., YANG, Y., XU, B., JIANG, T. Analysis and prediction of the thiourea gold leaching process using grey relational analysis and artificial neural networks. *Minerals.* 2020, vol. 10, issue 9, p. 811.

[6]   RAY, D., BANIASADI, M., GRAVES, J., GREENWOOD, A., FARNAUD, S. Thiourea leaching: An update on a sustainable approach for gold recovery from E-waste. *Journal of Sustainable Metallurgy.* 2022, vol. 8, pp. 597-612. doi: 10.1007/s40831-022-00499-8.

[7]   HUDDY, R., SACHDEVA, R., KADZINGA, F., KANTOR, R., HARRISON, S., BANFIELD, J. Thiocyanate and organic carbon inputs drive convergent selection for specific autotrophic afipia and thiobacillus strains within complex microbiomes. *Frontiers in Microbiology.* 2021, vol. 12. doi: 10.3389/fmicb.2021.643368.

[8]   LI, J., SAFARZADEH, J., MOATS, M.S., MILLER, J.D., LEVIER, K.M., DIETRICH, M., WAN, R.Y. Thiocyanate hydrometallurgy for the recovery of gold. *Hydrometallurgy.* 2011, vol. 113-114, pp. 10-18. https://doi.org/10.1016/j.hydromet.2011.11.007.

[9]   JORGANI, E., SABZKOOHI, H.A. Gold leaching from ores using biogenic lixiviants – A review. *Current Research in Biotechnology.* 2022, vol. 10-20, pp. 10-20. 10.1016/j.crbiot.2021.12.003.

[10]   THOMAS, K.G., PEARSON, M. *Pressure Oxidation Overview.* Canada: Elsevier, 2016.

[11]   BAGHALHA, M. Leaching of an oxide gold ore with chloride/hypochlorite solutions. *Mineral Processing.* 2007, vol. 82, issue 4, pp. 178-186.doi: 10.1016/j.minpro.2006.09.001.

[12]   HASAB, M.G., RASHCHI, F., RAYGAN, S. Chloride–hypochlorite leaching and hydrochloric acid washing in multi-stages for extraction of gold from a refractory concentrate. *Hydrometallurgy.* 2014, vol. 142, pp. 56-59. doi: 10.1016/j.hydromet.2013.11.015.

[13]   ANUAR, W.N.S., ARDANI, R., BAHARUN, N., ISMAIL, S., RAHMAN, S.A. Optimization process of the refractory gold ore extraction by hypochlorite oxidative leaching. *Mining, Metallurgy & Exploration.* 2021, vol. 38, pp. 1191-1201. https://doi.org/10.1007/s42461-020-00376-6.

[14]   NAM, K.S., JUNG, B.H., AN, J.W., HA, T.J., TRAN, T., KIM, M.J. Use of chloride–hypochlorite leachants to recover gold from tailing. *International Journal of Mineral Processing.* 2008, vol. 86, issues 1-4, pp. 131-140. https://doi.org/10.1016/j.minpro.2007.12.003.

[15]   DE CARVALHO, F., RESENDE, A., LEÃO, V. Gold leaching by sodium chloride and calcium hypochlorite solutions. In: *The Minerals, Metals & Extractions.* Minas Gerais: Springer, Charm, 2018, pp. 1787-1796.