



ISSN NO. 2320-5407

Journal homepage: <http://www.journalijar.com>

INTERNATIONAL JOURNAL
OF ADVANCED RESEARCH

RESEARCH ARTICLE

Optimal conditions for ammonia leaching of copper/chalcocite-rimmed pyrite: Part 1

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Manuscript Info

Manuscript History:

Received: 23 March 2014

Final Accepted: 25 April 2014

Published Online: May 2014

Key words:

Ammonia leaching, Redox quotient,

Copper, Chalcocite-rimmed pyrite

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Abstract

Oxidative ammoniacal leaching of copper/chalcocite-rimmed pyrite has been studied with the aim of searching for the optimal conditions for the separation of the pyrite that would preclude the formation of ammonium sulphate, the main drawback of the process. As the Redox Quotient (RQ) was varied, the resulting leached products were analyzed and the pH of the leached solution measured. At ambient temperature and a molar ratio of $\text{Cu}:\text{NH}_3 = 1:4$, it was observed that the amount of oxidant (H_2O_2) supplied during the leaching process determines the maximum or minimum yield of copper. It has been found that the leaching process is most selective with respect to both copper and zinc when no external oxidant is supplied ($\text{RQ} = 0$). The optimum leaching of copper and zinc occurred at $\text{RQ} = 2$. It has been shown that at $\text{RQ} = 8$, no appreciable amounts of ammonium sulphate were formed and that the pH of the leached solutions, the yields of Cu and Zn, and the selectivity of the leaching process with respect to both Cu and Zn, are all periodic functions of the severity of the oxidation environment, as measured by RQ. It has also been demonstrated that even small deviations away from the maxima on the curves can significantly affect the process yield and selectivity negatively. This research showed that the more concentrated the leaching ammonia, the better the copper extraction and that it was more advantageous to do the extraction in multiple cycles in a single operation.

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1. Introduction

The extractive metallurgy of copper is largely based on the conventional pyrometallurgical treatment process which involves smelting, converting and electrorefining (Velásquez Yévenes, 2009; Ahmadi et al., 2011). Chalcopyrite (CuFeS_2) is a primary Cu-sulfide of considerable interest in biohydrometallurgy because it is the most important and abundant copper mineral. It is refractory and has a very low kinetics (Cheng and Lawson, 1991; Velásquez Yévenes, 2009).

Oxidative dissolution of chalcopyrite at ambient temperatures is generally slow and subject to passivation, posing a major challenge for developing bioleaching applications for this recalcitrant mineral (Gulfen and Aydin, 2010; Bevilacqua et al., 2013). Chloride is known to enhance the chemical leaching of chalcopyrite, but much of this effect has been demonstrated at elevated temperatures. Several studies of chalcopyrite leaching with chloride-based solutions have been published over the years (Al-Harashsheh et al., 2008; Carneiro and Leão, 2007; Sato et al., 2000). Elemental sulfur formation contributes to the passivation layer in chalcopyrite leaching (Klauber, 2008; Watling, 2006).

Solvent extraction proved to be a cost-effective way to purify and concentrate copper from leach liquors (Kordosky, 2002). Leaching processes in hydrometallurgy are concerned with the chemical dissolution of the raw materials being treated to form a solution containing the metals to be recovered (Tshilombo and Mulaba-Bafubiandi, 2013;

Bodsworth, 1994). Copper/chalcocite-rimmed pyrite usually escapes depression in flotation baths to adulterate the flotation concentrate (Chin-Jung and Liu, 1998). One of the most promising approaches to deal with this challenge is to leach the copper/chalcocite from the pyrite particles, using ammonia in the presence of air (Ntuli et al., 2011), so that the freed pyrite could be depressed in a subsequent high pH flotation bath.

Ammonia solution as a leaching medium for base metals can be considered as an excellent alternative to acidic solutions (Chin-Jung and Liu, 1998; Ochromowicz et al., 2014). The reason for this is the very high stability constant of ammonia complexes for silver, gold, cobalt, copper, nickel and zinc (Tshilombo and Mulaba-Bafubiandi, 2013). Ammonia leaching is also selective in that it will not dissolve all available nonspecific metals, such as iron and manganese, along with the copper or cobalt, as sulphuric acid does. Ammonia leaching can be used in non-oxidative, oxidative and reductive leaching (Park et al., 2006). The ammonia leaching process is more environment friendly than conventional acid heap leaching, which uses sulphuric acid to dissolve copper and cobalt (Tshilombo and Mulaba-Bafubiandi, 2013). The reported difficulty encountered with the ammonia leaching approach, however, is the formation of ammonium sulphate as a side reaction (Chin-Jung and Liu, 1998) which leads to loss of ammonia that could otherwise be recycled to improve the economy of the process.

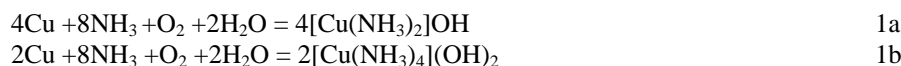
In this work we searched for leaching conditions that would preclude or minimize the formation of ammonium sulfate and optimize the yield of copper from the rimmed pyrite.

Material and Methods

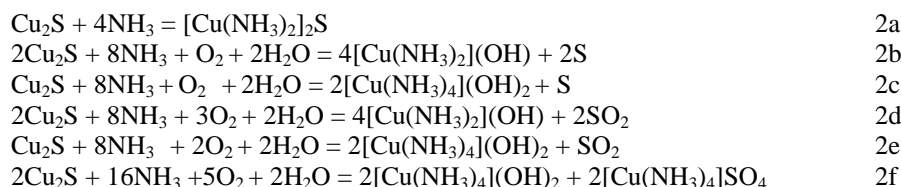
Theory

Microscopy and mineralogical studies have shown that copper concentrates obtained from flotation baths have high intrusion of pyrites. This is made possible because the pyrite particles are usually rimmed with copper or chalcocite. Any attempt to separate the copper or chalcocite from the pyrites through oxidative leaching with ammonia will invariably lead to the oxidation of any or all of the three species involved namely; native copper, chalcocite (Cu_2S) and pyrite (FeS_2).

Depending on the mildness or severity of the oxidation environment, various scenarios may be encountered. For the oxidation of native copper, the thermodynamically most probable outcomes may be:



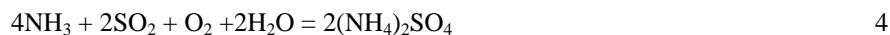
For the chalcocite, some of the most probable outcomes are:



Oxidation of the pyrite may also have the following outcomes:



It is evident from these probable outcomes that it is only when the pyrite is oxidized that sulfur dioxide is produced in excess with the potential for ammonium sulfate formation (Eq. 4).



The question now is whether it is possible to avert the oxidation of the pyrite during the oxidative leaching process and under which conditions? To answer this question, characterization of the mildness or severity of the oxidation

environment by the amount of the chemical equivalent of the oxidant applied to one chemical equivalent of copper in a sample or load being processed was defined as Redox Quotient (RQ).

$$\text{RQ} = \frac{[\text{Chem. Equivalent of Oxidant used}]}{[\text{chem. Equivalent of Cu in sample}]} \\ = \frac{[\text{Eq. of O}_2]}{[\text{Eq. of Cu}]}$$

This parameter will be a measure of intensity of the oxidizing environment which will correspondingly affect the products profile and the pH of the leached solutions.

Besides oxidation intensity, the amount and concentration of the ammonia applied per unit amount of copper in a sample are likely to affect the yield and selectivity of the process and would need to be optimized.

It is also expected that the leaching would be most effectively executed in multiple cycles in which case the need to optimize the number of adequate leaching cycles will arise.

Experimentation

A sample of the flotation concentrate, known to contain rimmed pyrites was analyzed for the elements, especially for Cu, S, Fe and Zn. 100 g portions of the sample were weighed into a number of 1-liter beakers.

In the first series of experiments, the quantities of ammonia taken was such as to fix the molar ratio $\text{Cu:NH}_3 = 1:4$, using the commercial 25 % ammonia solution.

Due to the difficulty involved in measuring the oxygen absorbed from the air during the leaching processes, hydrogen peroxide was used as the oxidant in these experiments.

Hydrogen peroxide (H_2O_2), in simple constant multiples of the chemical equivalent of copper in the 100 g samples, were calculated and measured into the beakers. This made the copper equivalents of H_2O_2 (RQ) in the beakers varies from: 0.0, 0.5, 1.0, 1.5 up to 8.0. Distilled water was added to the content of each beaker to bring its content to 500 mL and turbulently stirred till the pH of the leached solution became invariant with time. A blank experiment was also set up which used the same combination of chemical as in the beakers except the flotation samples were not added. The leached samples were filtered and the sediments dried, weighed and subjected to elemental analysis. The pH of the leached solutions was also measured and analyzed for the elements using AAS. The pH was measured with a SenTix21 pH electrode (WTW model pH323). After this, the contents of the beakers were diluted to 800 mL and later to 1000 mL, taking the pH of the leached solutions at each dilution. The leaching conditions that gave the maximum yield of copper were repeated a number of times on its leached sediment to determine the optimal number of leaching cycles. After the experiments the leached solutions were evaporated to the solid residue at ambient temperature and analyzed for the elements.

Result and Discussion

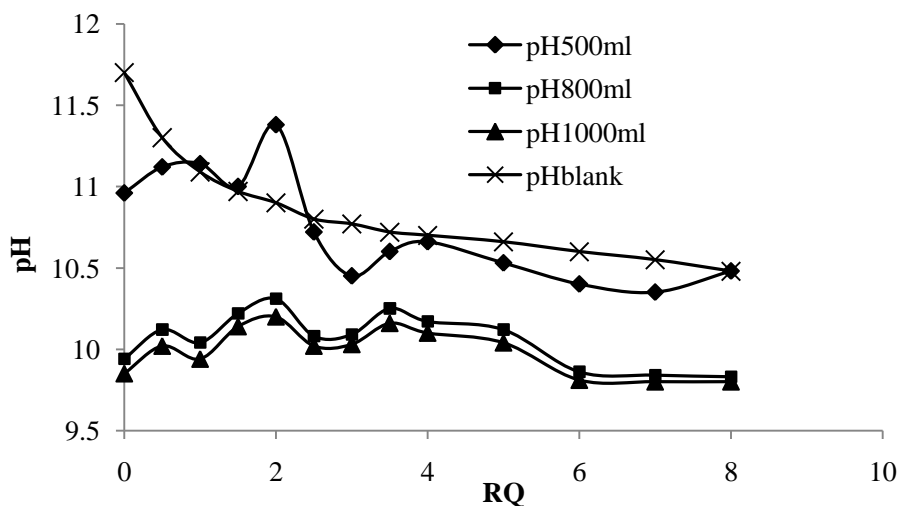
The elemental analysis of the floatation concentrate used and the variation of pH of leached solution with RQ ($\text{H}_2\text{O}_2/\text{Cu}$) are shown in Tables 1 and 2, respectively. Fig.1 shows the graphical representation of the variation of pH in the leached solutions. The elemental analysis of the floatation concentrate sample, which gave an atomic ratio Fe: S~ 1:2, confirms the view already held that pyrite (FeS_2) predominates in the concentrate samples (Kordosky, 2002; Gulfen and Aydin, 2010). It also showed that the three elements; copper, iron and sulfur constitute about 65 % or two-thirds of the samples, the rest being the gangue.

Table 1 Elemental analysis of the floatation concentrate used.

Element	MASS%	At. Ratio/Cu	At. Ratio/Fe	At. Ratio/S
Cu	17.06	1.00	0.66	0.34
Fe	22.77	1.52	1.00	0.51
S	25.50	2.97	1.95	1.00

Table 2 Variation of pH of leached solutions with RQ [$\text{H}_2\text{O}_2/\text{Cu}$].

RQ	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	5.0	6.0	7.0	8.0
pH (500 mL)	10.96	11.12	11.14	11.00	11.38	10.72	10.45	10.60	10.66	10.53	10.40	10.35	10.48
pH (800 mL)	9.94	10.12	10.04	10.22	10.31	10.08	10.09	10.25	10.17	10.12	9.86	9.84	9.83
pH (1000 mL)	9.85	10.02	9.94	10.14	10.20	10.02	10.03	10.16	10.10	10.04	9.81	9.80	9.80
pH (blank)	11.7	11.30	11.09	10.97	10.90	10.80	10.77	10.72	10.70	10.66	10.60	10.55	10.48

**Fig. 1** Variation of pH in the leached solutions

Analysis results of the residues obtained by evaporating the leached solutions to dryness are given in Table 3. From Table 3 the selectivity of Cu and Zn over S, the relative yields of $\text{Cu}(\text{OH})_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as well as the ratio $[(\text{OH})/\text{SO}_4^{2-}]$ with RQ were calculated as shown in Table 4.

Table 3 Analysis of leached materials

RQ	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	5.0	6.0	7.0	8.0
Cu mass%	28.85	23.10	27.02	27.17	32.38	28.42	28.98	30.04	28.12	29.65	28.09	29.97	27.32
Fe mass%	0.14	0.25	0.21	0.08	0.27	0.11	0.15	0.25	0.05	0.11	0.19	0.12	0.13
S mass%	7.28	10.3	11.5	11.0	9.88	11.4	11.4	9.65	11.4	9.45	11.7	9.21	10.7
Zn mass%	0.93	0.57	0.64	0.78	1.04	0.58	0.71	0.82	0.64	0.83	0.54	0.51	0.45
NH_4^+	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace

Table 4 Calculated values of selectivity yield of salts and ion ratios.

RQ	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	5.0	6.0	7.0	8.0
$[\text{Cu}/\text{S}]$	2.00	1.13	1.18	1.24	1.65	1.26	1.31	1.57	1.24	1.60	1.49	1.64	1.28
$[\text{Zn}/\text{S}] \times 100$	6.25	2.71	2.74	3.47	5.14	2.50	3.13	4.16	2.74	4.31	2.25	2.69	2.06
% $\text{Cu}(\text{OH})_2$	22.1	4.1	6.4	8.2	19.5	8.9	10.7	16.7	8.4	17.2	7.5	17.9	9.3
% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	56.8	80.3	85.7	85.8	77.0	88.9	86.6	75.2	88.9	73.7	91.3	71.8	83.4
$[(\text{OH})/\text{SO}_4^{2-}]$	2.00	0.26	0.36	0.46	1.29	0.51	0.63	1.13	0.48	1.19	0.42	0.25	0.57

The yields of copper and zinc in the leaching process are shown in Figures 2 and 3. In Figures 4 and 5, the selectivity of copper and zinc over sulfur are presented. The yields of $\text{Cu}(\text{OH})_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a function of RQ is presented in Figure 6 while the ionic ratio $R = [\text{OH}^-] / \text{SO}_4^{2-}$ versus RQ is shown in Figures 7.

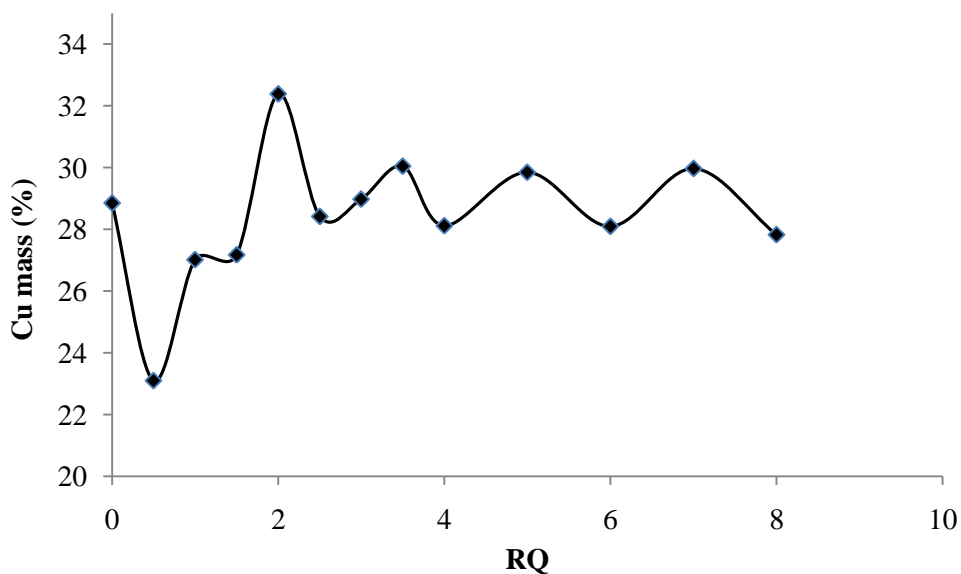


Fig. 2 Yield of Cu with RQ

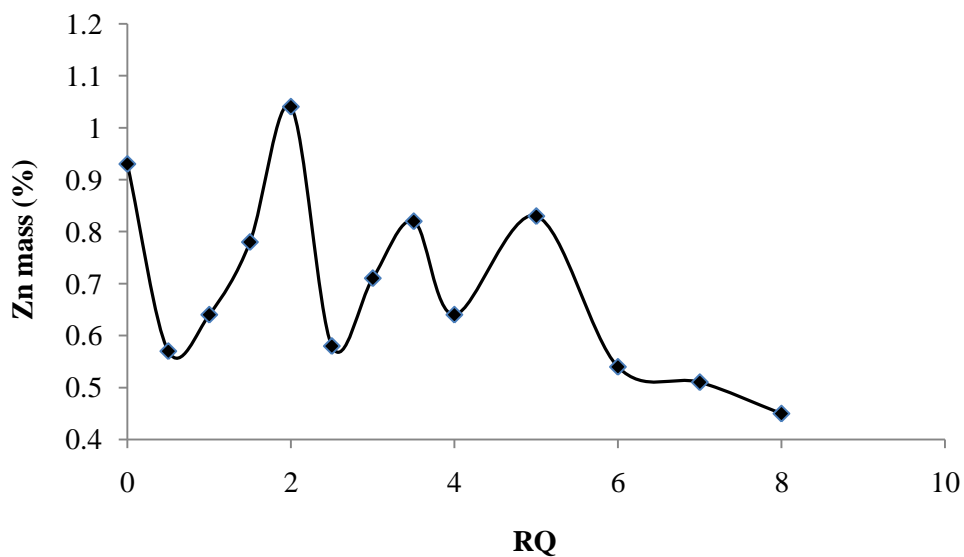


Fig. 3 Yield of Zn with RQ

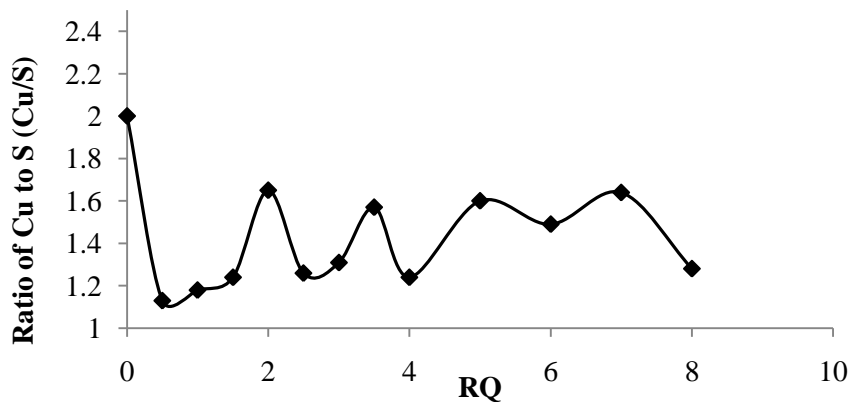


Figure 4 Selectivity of Cu with RQ

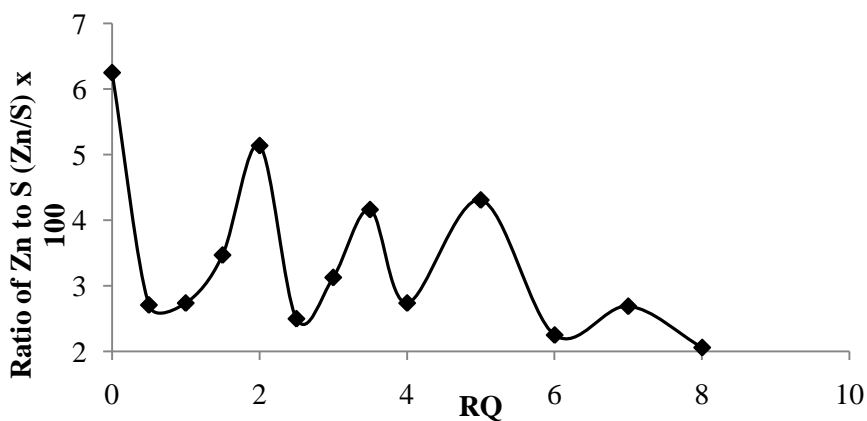


Figure 5 Selectivity of Zn with RQ

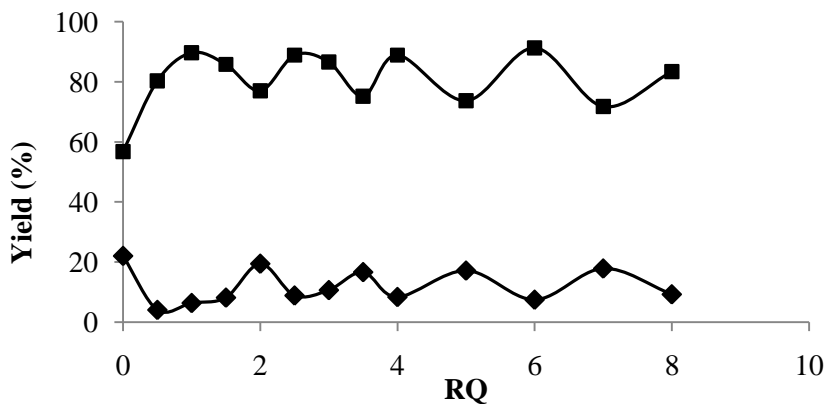


Fig. 6 Yields of Cu(OH)₂ (■) and CuSO₄.5H₂O (◆) with RQ

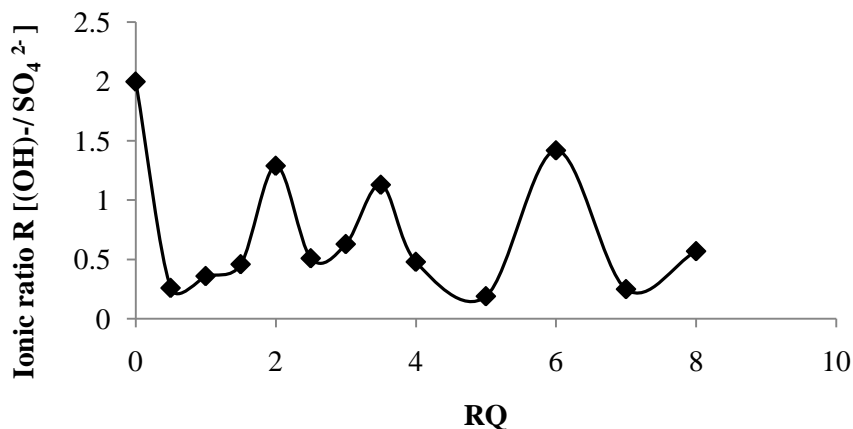


Fig. 7 Variation of the ionic ratio $R = \frac{[(OH)^-]}{SO_4^{2-}}$ with RQ

The filtered sediments from the leached solution were also carefully washed, dried and analyzed for the elements (Table 5). The atomic ratios of Cu to sulfur were calculated and compared to that of the unleached sample (Table 5 and Figure 8).

Table 5 Percent compositions of elements in filtered sediments from leached solutions

RQ	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	5.0	6.0	7.0	8.0
Cu mass%	15.48	15.15	15.35	15.78	15.34	14.99	15.16	15.02	15.16	15.48	15.32	16.14	15.24
Fe mass%	23.45	23.39	23.20	23.45	23.39	23.57	22.28	23.94	23.14	24.67	23.03	21.76	23.53
S mass%	26.7	27.8	28.8	26.7	27.8	27.3	28.8	29.0	30.20	26.8	28.7	28.1	29.3
Zn mass%	1.13	1.17	1.21	1.19	1.18	1.21	1.22	1.17	1.18	1.20	1.20	1.23	1.24
$[Cu/S]_{Leached}$	0.290	0.275	0.268	0.290	0.273	0.276	0.265	0.254	0.252	0.291	0.273	0.288	0.262
$[Cu/S]_{Unleached}$	0.337	0.337	0.337	0.337	0.337	0.337	0.337	0.337	0.337	0.337	0.337	0.337	0.337

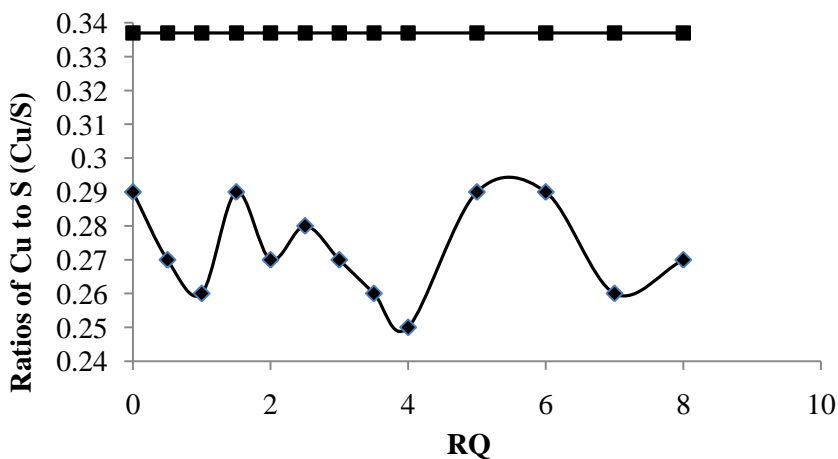


Figure 8 Cu/S profile of the leached sediments (◆) compared to the unleached (■).

The leach process was repeated for a number of times at the most promising value of RQ = 2. The resultant sediments after each leach cycle was dried and analyzed for the elements and the results presented in Table 6. The

atomic ratios of sulfur to copper after each leach cycle was calculated and plotted against the number of cycles (Figure 8).

Table 6 Atomic ratios of sulfur to copper after each leach cycle

No of leach cycles	0	1	2	3	4
[S/Cu]	2.97	3.48	3.70	3.80	3.80

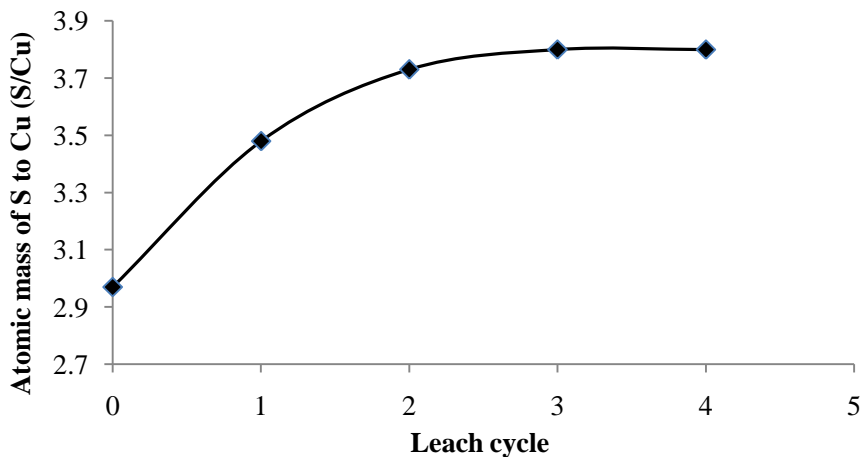


Figure 9 Atomic ratios of sulfur to copper after each leach cycle

The addition of the oxidant (H_2O_2) to the ammonia solution in the absence of the flotation concentrate (blank experiment), monotonically lowered the pH. However, in the presence of the flotation concentrate, the pH profile showed maxima and minima and the leached solutions displayed colors from pale green to deep blue, indicative of solutions of CuSO_4 and the formation of the complex ions $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and/ or $[\text{Cu}(\text{NH}_3)_2]^+$. The most pronounced maximum occurred at $\text{RQ} = 2$ while the most pronounced minimum at $\text{RQ} = 3$. The maximum pH points was found to correspond to points of maximum yield and selectivity of Cu and Zn over sulfur and also corresponded to the maxima for the $(\text{OH})^-/\text{SO}_4^{2-}$ ratio (Figures 2, 3, 4, 5, and 7). The minimum points on the pH profile were also found to correspond to moments of maximum sulfate production (Figure 6).

It is noteworthy that the atomic ratio Cu/S is exactly 2 for $\text{RQ} = 0$. This means that in the absence of added oxidant during leaching, only chalcocite (Cu_2S) is leached into solution, according to equation 2a. The leached $[\text{Cu}(\text{NH}_3)_2]\text{S}$ was further oxidized to the sulfate either by oxygen absorbed during the stirring or previously adsorbed on the flotation samples. It is expected that any combination of series 2 equations (2a, 2b, 2c, 2d, 2e, 2f) with any of the series 1 equation should result in $\text{Cu}/\text{S} > 2$, and any combination of series 2 equations with any of the series 3 equations will result in $\text{Cu}/\text{S} < 2$. The fact that the Cu/S ratio falls below 2 when oxidants were added showed that more sulfur were leached into solution than can be accounted for by Cu_2S alone. The extra sulfur must have found its way into the leached solutions as sulfates by one of the series 3 routes, most probably, via equations 3a since there are no corresponding increases in ferrous/ ferric ions in the solution. The SO_2 produced via these routes has very high solubility, especially in the alkaline environment, and it could easily form sulfites and, consequently, sulfates leading to the decrease in pH. Evidently, while reactions by route 1a, 1b, 2a, 2b and 2c tend to predominantly increase the pH of the leached solutions by generating the complex hydroxides of copper, those by routes 2d, 2e, 2f, 3a, 3b, 3c, and 3d tend to decrease the pH by generating sulfites and sulfates. Clearly the pH of the leached solutions was the resultant of the interplay of these competitive reactions.

It was significant that no measurable amounts of the ammonium ions were detected, which implied that ammonium sulfate was not formed. Iron leached into solution was also insignificant which indicates that reaction by equations

3b, 3c, 3d and 4 did not play any major roles under the conditions of this study, though the oxidation intensity reached $RQ = 8$.

A comparison of Cu/S values for the leached and unleached sediments shows (Figure 7) that the leached sediments become poorer in Cu than the unleached ones. The experiment to determine the number of adequate leaching cycles also clearly indicated that under the conditions of the extractions, no more than three leaching cycles is enough since after the third cycle there could not be any further improvement in copper leaching with respect to sulfur content of the sediments (Figure 9).

Conclusions

This work has showed that at ambient conditions and at a fixed $Cu:NH_3=1:4$ the amount of oxidant supplied during the ammonia leaching process is of critical importance and it can lead to operating the process at a minimum or maximum leaching of Cu.

It has been found that the process is most selective when no oxidant is externally supplied. However, for maximum yield of the process it is better to supply the oxidant at a rate equal to twice the chemical equivalent of Cu in the load ($RQ = 2$).

It has been shown that, indeed up to $RQ = 8$, the pH of the leached solutions, the yields of copper and zinc and their selectivity are all periodic functions of oxidation intensity as measured by the Redox Quotient used (RQ). The plots have almost sinusoidal profiles (Figures 3, 4, 5, 6, and 7) with a period of 1.5 or 2.0 Redox Quotient.

It has also been demonstrated that small deviations from the RQ values corresponding to the maxima on the curves can significantly affect the process negatively, and that the optimal leaching conditions correspond to the point when the pH of the leached solutions reaches their very maximum value.

It was found that the more concentrated the ammonia solution used, the better the Cu extraction and that it was more advantageous to do the extraction in multiple cycles than in a single operation.

A method to determine the number of optimal leaching cycles has been worked out and successfully demonstrated.

Finally, this work showed that within the limits of our experimental conditions ($RQ \leq 8$), no measureable amount of ammonium sulfate was formed and no appreciable amount of iron was leached into solution.

Recommendations

1. This work forms only the first part of the investigations designed to fully ascertain the optimal conditions for ammonia leach of chalcocite rimmed pyrite. Conclusions made here therefore are valid only for the ambient conditions and for the fixed molar ratio of $Cu: NH_3=1:4$. It is recommended that for a wider generalization of these findings, the processes should be studied at different fixed molar ratios of $Cu: NH_3$ and, at conditions different from ambient.
2. The steam stripping stage to retrieve the ammonia for recycle should also be studied and characterized.
3. For the purposes of engineering design of the process, it will be necessary to study the heat effects and the kinetics of the reactions involved.
4. It was observed that the flotation concentrates must have adsorbed substantial amounts of oxygen even before being used. It would be helpful if this quantity of residual oxygen could be measured and factored.

Acknowledgement

The authors gratefully acknowledge the use of laboratory facilities at Robinson Nevada Mining Company at Ruth, USA in this research.

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