Optimal Conditions for Ammonia Leaching of Copper/Chalcocite-Rimmed Pyrite: Part 2

Martin Y. Woode [1]
[1]Department of Chemical Engineering
Kwame Nkrumah University of Science & Technology
(KNUST)
Kumasi, Ghana

Mike A. Acheampong [2*]
[2]Department of Chemical Engineering
Kumasi Polytechnic
Kumasi, Ghana

David Azanu [2]
[2]Department of Chemical Engineering
Kumasi Polytechnic
Kumasi, Ghana

Abstract—**The optimal conditions for the leaching of copper/chalcocite-rimmed pyrite was studied in order to understand the effect of varying the Cu:NH$_3$ molar ratio. In the part one of this research, the oxidative ammoniacal leaching of copper/chalcocite-rimmed pyrite was studied under ambient condition for a Redox Quotient (RQ) of up to eight. The optimal leaching was found to occur at RQ = 2. In this second part, the range of RQ has been extended to fifteen and elucidates the heat effect and solubility issues of the leaching process. It was observed that by extending the oxidation intensity to fifteen (RQ = 15), a new maximum leaching of copper occurred at RQ = 10 for all copper to ammonia ratios, which was better than the situation that occurred at RQ = 2 observed in part one. At Cu:NH$_3$ = 1:4 (which corresponds to the stoichiometric ratio) and at RQ = 10, the ammonia leaching was found to be optimal, at least within the range of RQ studied. Due to the high exothermicity of the oxidative ammonia leaching process, it has been suggested that the process be conducted consecutively by first conducting the oxidation process, allowing the solution to cool down, before introducing the ammonia for the actual leaching. This avoids the loss of ammonia through volatilization It was also observed that at copper to ammonia molar ratios higher than stoichiometric (1:6 and 1:8) significant ammonium sulphates were formed.**

Keywords—*Ammonia leaching; Radox quotient; Copper; Chalcocite-rimed pyrite; Optimal conditions*

I. INTRODUCTION

The extractive metallurgy of copper is largely based on the conventional pyrometallurgical treatment process which involves smelting, converting and electrorefining [1]. Chalcopyrite (CuFeS2) 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 [1,3].

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 [4,5]. 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 [6,7]. Elemental sulphur formation contributes to the passivation layer in chalcopyrite leaching [8,9].

Solvent extraction proved to be a cost-effective way to purify and concentrate copper from leach liquors [10]. 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 [11,12]. Copper/ chalcocite-rimmed pyrite usually escapes depression in flotation baths to adulterate the flotation concentrate [13]. 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 [14], 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 for acidic solutions [13,15]. The reason for this is the very high stability constant of ammonia complexes for silver, gold, cobalt, copper, nickel and zinc [11]. 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 [16]. The ammonia leaching process is more environment friendly than conventional acid heap leaching, which uses sulphuric acid to dissolve copper and cobalt [11]. The reported difficulty encountered with the ammonia leaching approach, however, is the formation of ammonium sulphate as a side reaction [13] which leads to loss of ammonia that could otherwise be recycled to improve the economy of the process.
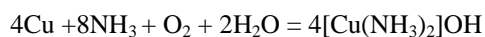
In this work, we searched for leaching conditions that would preclude or minimize the formation of ammonium sulfate and optimize the yield of copper from the rimmed pyrite.
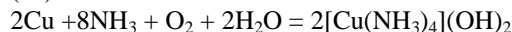
II.   MATERIALS AND METHODS

A. 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:
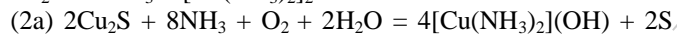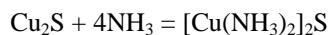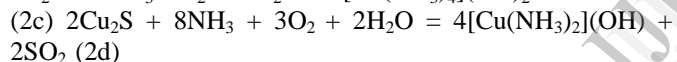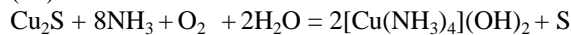
$4Cu + 8NH_3 + O_2 + 2H_2O = 4[Cu(NH_3)_2]OH$
(1a)
$2Cu + 8NH_3 + O_2 + 2H_2O = 2[Cu(NH_3)_4](OH)_2$
(1b)

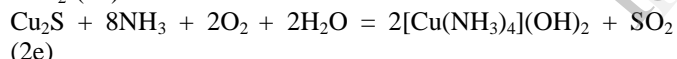For the chalcocite, some of the most probable outcomes are:

$Cu_2S + 4NH_3 = [Cu(NH_3)_2]_2S$
(2a) $2Cu_2S + 8NH_3 + O_2 + 2H_2O = 4[Cu(NH_3)_2](OH) + 2S$
(2b)
$Cu_2S + 8NH_3 + O_2 + 2H_2O = 2[Cu(NH_3)_4](OH)_2 + S$
(2c) $2Cu_2S + 8NH_3 + 3O_2 + 2H_2O = 4[Cu(NH_3)_2](OH) + 2SO_2$ (2d)
$Cu_2S + 8NH_3 + 2O_2 + 2H_2O = 2[Cu(NH_3)_4](OH)_2 + SO_2$
(2e)
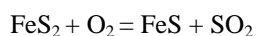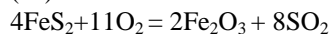$2Cu_2S + 16NH_3 + 5O_2 + 2H_2O = 2[Cu(NH_3)_4](OH)_2 + 2[Cu(NH_3)_4]SO_4$
(2f)

Oxidation of the pyrite may also have the following outcomes:
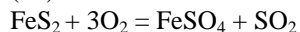
$FeS_2 + O_2 = FeS + SO_2$
(3a)
$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$
(3b)
$FeS_2 + 3O_2 = FeSO_4 + SO_2$
(3c)
$2FeS_2 + 7O_2 = Fe_2(SO_4)_3 + SO_2$
(3d)

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

$4NH_3 + 2SO_2 + O_2 + 2H_2O = 2(NH_4)_2SO_4$ (4)

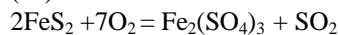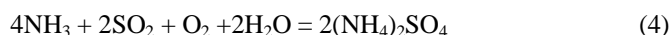The question now is whether it is possible to avert the oxidation of the pyrite during the oxidative leaching process and under which conditions? To answer this question

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).

$$RQ = \frac{\text{Chem. Equivalent of Oxidant used}}{\text{Chem. Equivalent of Cu in Sample}}$$

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.

B. Experimentation

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 16.0. 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 each 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.

In the first part of this work [17], designed to optimize the conditions for ammonia leaching of copper from chalcocite-rimmed pyrite, a copper-to ammonia ratio of 1:4 was used. Here the pH of the leached solution, the products distribution profile, the composition and selectivity were all studied as a function of the oxidation intensity of the leaching environment. For this purpose the ratio of oxidant employed to copper(II) in the leaching sample was defined as Redox Quotient (RQ) and varied. It was observed at that time that RQ = 2, the leached products have the highest composition of copper (35 %) and corresponded to the highest pH of the

solution. The copper-to-sulfur selectivity was however highest when no external oxidant was applied (RQ = 0) and corresponded to the leaching of only chalcocite (Cu/S = 2). Significantly no ammonium sulfate, whose formation has been the bane of many trial efforts, was formed under these conditions. The study was, however, done up to RQ = 8.

This second part of the study affords the opportunity to extend the study over different copper-to-ammonia molar ratios and over a wider range of RQ as well to elucidate some of the heat - effect and solubility issues of the leaching process.

III.   RESULTS AND DISCUSSION

The elemental analysis of the floatation concentrate used and the variation of pH of leached solution with RQ (H_2O_2/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 flotation 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 [4,10]. 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 FLOTATION CONCENTRATE USED.

Element	Mass (%)	Atomic Ratio/Cu	Atomic Ratio/Fe	Atomic 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

The minimum points on the pH profile (Fig. 1) were also found to correspond to moments of maximum sulfate production (Fig. 2).
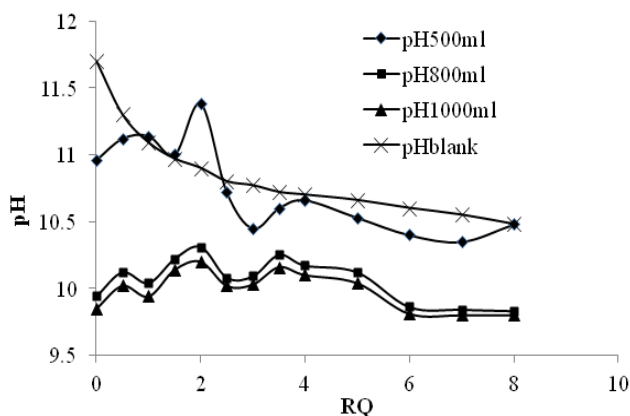

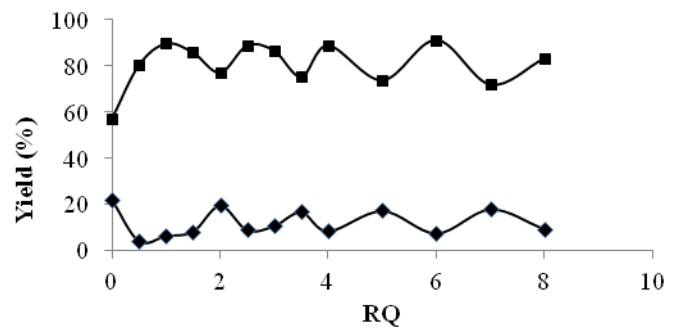**Fig. 1** Variation of pH in the leached solutions

Fig. 2 Yields of Cu(OH)$_2$ (■)and CuSO$_4$.5H$_2$O (♦) with RQ

In part 1 of this research (Woode and Acheampong, 2014), it was found that 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. According to Woode and Acheampong (2014), the atomic ratio Cu/S is exactly 2 for RQ = 0. This means that in the absence of added oxidant during leaching, only chalcocite (Cu_2S) is leached into solution (Eq. 2a). The leached $[Cu(NH_3)_2]S$ is 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 Cu/S > 2, and any combination of series 2 equations with any of the series 3 equations will result in Cu/S < 2. The fact that the Cu/S ratio falls below 2 when oxidants are added shows that more sulfur are 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 is 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 (Woode and Acheampong, 2014). 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 our experiment, though the oxidation intensity reached RQ = 8 [17].

Woode and Acheampong [17] 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. They 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).

By extending the oxidation intensity to RQ = 15, it was observed that for all copper-to-ammonia molar ratios studied, the maximum leaching of copper occurred at RQ = 10 (Fig. 3) which was better than the situation at RQ = 2 earlier observed.
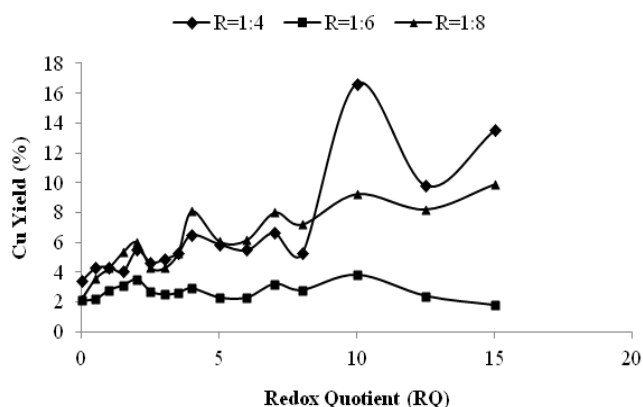

Fig. 3 Yield leached copper (%) as function of RQ for various Cu:NH$_3$ ratios (R)

At Cu:NH$_3$=1:4 (which corresponds to the stoichiometric ratio) and at a RQ = 10, the ammonia leaching was found to be optimal, at least within the range of RQ studied (Fig. 3).

By virtue of the high exothermicity of the reactions involved (e. g Eqs. 5, 6, 7 and 8), the solutions heat up quickly, volatilizing away a greater part of the ammonia used. To demonstrate this fact, the amount of water evaporated away when hydrogen peroxide was reacted with the flotation concentrates alone is shown in Fig. 4.
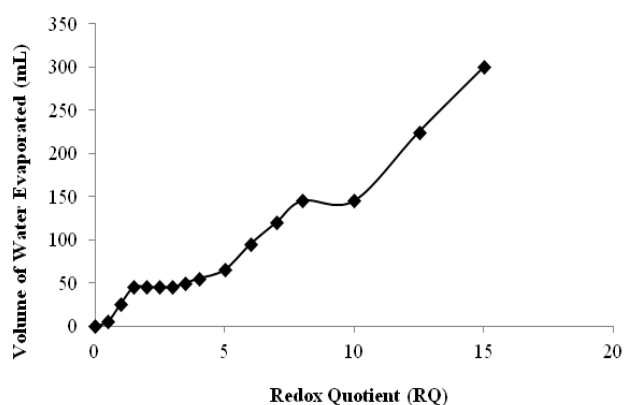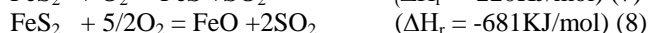
$$Cu_2S + 1/2O_2 = Cu_2O \qquad (\Delta H_r = -94KJ/mol) \quad (5)$$
$$CuS + 1/2O_2 = CuO \qquad (\Delta H_r = -109KJ/mol) \quad (6)$$
$$FeS_2 + O_2 = FeS + SO_2 \qquad (\Delta H_r = -220KJ/mol) \quad (7)$$
$$FeS_2 + 5/2O_2 = FeO + 2SO_2 \qquad (\Delta H_r = -681KJ/mol) \quad (8)$$

Fig. 4 Water evaporated from a total of 600 mL versus RQ

Considering the fact that specific heat of evaporation of water is 2260KJ/Kg and that of ammonia is 1369KJ/Kg, more ammonia would have been lost in this case. To avoid this loss of ammonia, the reactions may better be conducted consecutively by first conducting the oxidation process, allowing the solution to cool down (cooling coils may be used), before introducing the ammonia for the proper leaching process. It was observed that the oxides of copper dissolved better in the ammonia than the sulfides. Additionally, the solubility of ammonia itself in water was very sensitive to temperature as shown in Table 2.

TABLE 2   SOLUBILITY OF AMMONIA IN WATER [18]

Temperature ^{o}C	0	10	20	30	40	50	60	70	80	90	100
Solubility(NH$_3$/ 100g of H$_2$O)	89.7	68.3	52.9	40.9	31.6	23.5	16.8	11.1	6.5	3.0	0

IV.   CONCLUSIONS

By extending the oxidation intensity to RQ = 15, the maximum leaching of copper occurred at RQ = 10 which was better than the situation at RQ = 2 earlier observed (Woode and Acheampong, 2014). At Cu:NH$_3$ = 1:4 and at a RQ = 10, the ammonia leaching was found to be optimal. Given the high exothermicity of the oxidative leaching process and the high volatility of the ammonia involved, the reactions are best conducted at the lowest possible temperatures.

ACKNOWLEDGMENT

REFERENCES

[1]   Velásquez Yévenes, L. (2009). The kinetics of the dissolution of chalcopyrite in chloride media, PhD Thesis, Murdoch University, Australia.

[2]   Ahmadi, A. Schaffie, M. Petersen, J. Schippers, A. and M. Ranjbar, (2011). Conventional and electrochemical bioleaching of chalcopyrite concentrates by moderately thermophilic bacteria at high pulp density. Hydrometallurgy, 106: 84-92.

[3]   Cheng, C.Y., Lawson, F. (1991). The Kinetics of Leaching Chalcocite in Acidic Oxygenated Sulphate-Chloride Solutions. Hydrometallurgy 27: 1991, 249-268.

[4]   Gulfen, M. and Aydin, A.O. (2010). Dissolution of copper from a primary chalcopyrite ore with and without Fe$_2$O$_3$ in sulphuric acid solution. Indian Journal of Chemical Technology, 17: 145-149.

[5]   Bevilaqua, D., Lahti, H., Suegama, P.H., Garcia Jr. O., Benedetti, A.V., Puhakk J.A., Tuovinen, O.H. (2013). Effect of Na-chloride on the bioleaching of a chalcopyrite concentrate in shake flasks and stirred tank bioreactors. Hydrometallurgy, 138: 1-13.

[6]   Al-Harahsheh, M., Kingman, S., Al-Harahsheh, A. (2008). Ferric chloride leaching of chalcopyrite: synergetic effect of CuCl$_2$. Hydrometallurgy, 91: 89-97.

[7]   Carneiro, M.F.C., Leão, V.A. (2007). The role of sodium chloride on surface properties of chalcopyrite leached with ferric sulfate. Hydrometallurgy, 87: 73-82.

[8]   Klauber, C. (2008). A critical review of the surface chemistry of acidic ferric sulphate dissolution of chalcopyrite with regards to hindered dissolution. Int. J. Miner. Process, 86 (1-4): 1-17.

[9]   Watling, H.R. (2006). The bioleaching of sulphide minerals with emphasis on copper sulphides - a review. Hydrometallurgy, 84: 81-108.

[10]   Kordosky, G.A. (2002). Copper recovery using leach/solvent extraction/electrowinning technology: Forty years of innovation, 2.2 million tonnes of copper annually. The Journal of the South African Institute of Mining and Metallurgy, 445-450.

[11]   Tshilombo, K.G. and Mulaba-Bafubiandi, A.F. (2013). Ammonia/nitric Acid Leaching of Copper-Cobalt Oxidized Ore. In proceedings of International Conference on Mining, Mineral

Processing and Metallurgical Engineering (ICMMME'2013), April 15-16, 2013, Johannesburg, South Africa, pp. 120-122.

[12] Bodsworth C. (1994). The extraction and refining of metals (Materials science and Technology). 1st Edition, vol. 2, ch 1. CRC Press, ISBN-13: 978-0849344336.

[13] Chin-Jung, C. and Liu, J.C. (1998). Feasibility of copper leaching from an industrial sludge using ammonia solutions. Journal of Hazardous Material, 58 (1-3): 121-132.

[14] Ntuli, F. Muzenda E., Ramatsa, I. Belaid, M. Kabuba, J. (2011). The Effect of Leaching Time and Ammonia Concentration on the Atmospheric Leaching of Copper, *2nd International Conference on Chemistry and Chemical Engineering,* IPCBEE vol.14, Singapore.

[15] Ochromowicz, K., Jeziorek, M. and Wejman, K. (2014). Copper (Ii) Extraction From Ammonium Leach Solution. Physicochemical Problems of Mineral Processing, 50(1): 327-335.

[16] Park, K-H., Mohapatra, D Nam, C-W. and Kim, H-I. (2006). A comparative study of different leaching processes for the extraction of Cu, Ni and Co from a complex matte. Minerals and Materials Processing Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Korea, pp.305-350.

[17] Woode, M. Y. and Acheampong, M. A. Optimal conditions for ammonia leaching of copper/chalcocite-rimed pyrite: Part1, International Journal of Advance Research, in press.

[18] Pavdelia A. A. and Ponomarevoy, M. A. short handbook of physico-chemical values, Leningrad chemistry, Moscow, Russia, 1983.