The Effect of Leaching Time and Ammonia Concentration on the Atmospheric Leaching of Copper

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Abstract. The effects of ammonia concentration and leaching time were investigated to determine the optimum leaching conditions. The experiments were conducted in a leaching cell submerged in a water bath, with ammonia concentrations of 1.5 M, 2.0 M, 2.5 M and 3.0 M and varying leaching time from 0 to 300 min. Ni-Cu matte containing 23% by mass Cu was used in this experimental study. Increase in the concentration of the lixiviant was found to increase recovery when leaching for 130 minutes, with a recovery of 32.86% Cu using 3 M solution of ammonia. An increase in the leaching time resulted in more copper being leached for all lixiviant concentrations. However, leaching with 2 M ammonia solution gave a higher yield of copper compared to higher concentrations. This anomaly could be a result of cementation; Cu is displaced by Ni as Ni is a more electronegative metal than Cu .It was found that at higher concentrations more nickel was extracted.

Keywords: ammonia, cementation, concentration, leaching, pH.

1. Introduction

The recovery of base metals form matte (a mixture of sulphide and precious metals) has been a critical process in the refining of precious metals. Matte is produced from the smelting of sulphide ores to separate the valuable metals from the gangue. The matte is subsequently leached to recover valuable metals leaving behind a solid residue rich in precious metals. With increasing use of Cu, Ni and Co metals for different application and fast depletion of natural resources, efforts are being made to look for alternative resources for the recovery of these metals.

The combination of hydrometallurgy and pyrometallurgy in the refining of metals from ores has been in use for many years [1]. A considerable amount of investigations have been conducted on ammoniacal leaching of Ni, Cu and Co bearing sulphide and oxide ores. Extensive studies on the recovery of Cu and Ni from the ocean floor manganese nodules by reductive ammoniacal leaching technology have been reported [3]. It has been found by other researchers that the use of oxidant is necessary in order to enhance the dissolution of sulphide mineral. The first step in the hydrometallurgical processing of the Ni-Cu matte is the leaching stage in which the metal values are first dissolved and later recovered in the final stages.

The focus of this work is the leaching of copper from matte produced from the Impala Platinum smelter section in Johannesburg, South Africa. Impala Platinum is one of the world largest producer of platinum group metals (PGM).

2. Structure of Copper and Nickel Sulphides

Djurle [4] studied the phase equilibria in the Cu_2S-CuS region using XRD. The composition of chalcocite is approximately Cu_2S. The orthorhombic low temperature form, α-Cu_2S has a unit cell containing 96 formula units with a=11.881 Å, b=27.323Å, c= 13.491Å, and the sulphur atoms in hexagonal close

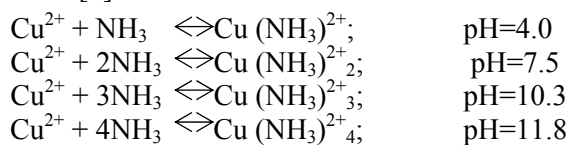---

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packing. The orthohexagonal sub-cell of orthorhombic chalcocite contains four formula units and has á=3.961Å, b=6.830Å and c=6.746Å. The copper deficiency must give $Cu_{1.999}S$ at 25°C, or $Cu_{1.998}S$ at 180°C according to [5]. At 103.5°C ± 1.5°C α-Cu_2S changes to a hexagonal form β-Cu_2S, with unit cell dimensions at 152°C a=3.96Å, c=6.72Å and the sulphur atoms in hexagonal close packing. The copper atoms are distributed statistically between the three kind of interstitial sites-trigonal, diagonal and tetrahedral. Roseboom [5] reported the composition of djurleite to be $Cu_{1.96}S$ and later found djurleite to be stable only below 93°C±2°C. At room temperature the composition range of digenite is $Cu_{1.765}S$ to $Cu_{1.79}S$. The low copper limit is not affected by temperature whereas the copper-rich limit changes to $Cu_{1.83}S$ at 83°C. Digenite of composition $Cu_{1.8}S$ is unstable below about 50°C. The true composition of djurleite is said to be $Cu_{1.96}S$. The composition of covellite is CuS according to [5] and is stable at the temperature of 507°C. The hexagonal unit cell contains six formula units, with a=3,792Å, c=16.344Å. Petterd [7] described the nickel sulphide, Ni_3S_2, and named it heazlewoodite after the locality of its discovery. It was later synthesized by [8].

3. Relevant Previous Studies

Studies by [9] on the dissolution kinetics of malachite in ammonia/ammonium carbonate leaching systems found that interface transfer and diffusion across the product layer controls the leaching process. Bingol et al. [9] found that the optimum conditions were a concentration of ammonia of 5 M and that of ammonium carbonate being 0.3 M for the system, with a leaching time of 120 minutes giving them over 98% of copper recovery. Highest recovery for ammonia alone was 53% with only 5% of copper being recovered when using ammonium carbonate. The increase in recovery of copper from the malachite was also due to the slow drop in the pH of the buffer solution, at +/-0.5, resulting in the formation of stable copper-ammonia complexes [9].

Park et al. [10] found that 2 M ammonium hydroxide plus 2 M of ammonium sulphate recovered 93.8% of copper in their investigation on the oxidative ammonia/ammonium sulphate leaching of a complex synthetic matte (Cu-Ni-Fe-Co). Chang and Liu studies on the feasibility of copper leaching from industrial sludge using ammonia solutions managed to recover 94% of copper after a period of 6 hour [2]. This was done by altering the solid amount by doubling it from 10 g/l to 20 g/l while using 5M of ammonia solution. This recovery was an improvement from the 34% of copper recovered when a solid concentration of 10 g/l was used. The key factor in this study was the maintenance of the pH of the leaching solution at 10 by adding concentrated HNO_3. Chang and Liu [2] also noted the complexing of the Cu^{2+} and ammonia ions. The complexation of the Cu^{2+} ions with ammonia can only happen with NH_3 and not NH_4^+ ions, as the latter is the more dominant species at pH values below 9.3. The complexing reactions are said to take place as follows [2]:

$$Cu^{2+} + NH_3 \Leftrightarrow Cu(NH_3)^{2+}; \quad\quad pH=4.0$$
$$Cu^{2+} + 2NH_3 \Leftrightarrow Cu(NH_3)^{2+}_2; \quad\quad pH=7.5$$
$$Cu^{2+} + 3NH_3 \Leftrightarrow Cu(NH_3)^{2+}_3; \quad\quad pH=10.3$$
$$Cu^{2+} + 4NH_3 \Leftrightarrow Cu(NH_3)^{2+}_4; \quad\quad pH=11.8$$

4. Materials and Methods

4.1. Overview

Different concentrations, 1.5 M, 2.0 M, 2.5 M and 3.0 M of ammonia solution were prepared in 3 L flasks. Leaching tests were conducted in an agitated leaching cell submerged in a water bath for 0 to 300 min.

4.2. Matte preparation

The copper bearing matte was dried to remove the moisture it had acquired in storage. The matte was then milled and screened to give 80% passing -75μm for leaching. The copper matte was analyzed using XRD and SEM, and was found to contain 23% of copper and 37% nickel (Fig 1). The major mineralogical phases in the matte are also shown in Fig 1.
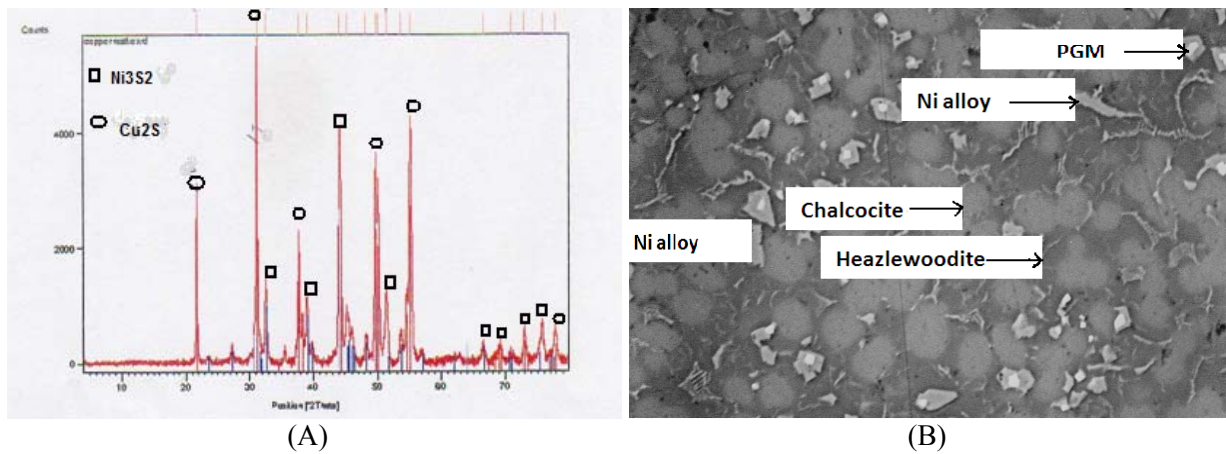
| (A) | (B) |

Fig. 1: (A) XRD results before leaching and (B) SEM results indicating mineralogical phases before leaching.

4.3.   Leaching procedure

The leaching cell was placed in the water bath set at a temperature that would yield a solution temperature of 70°C. 3L of leaching solution at a specific concentration previously prepared was then added into the leaching cell and its temperature and pH monitored. The solution was heated while being continuously agitated at 410 rpm. 66.69 g copper bearing matte was then added into the leaching cell based on the optimum solid loading for the system. The temperature and pH were immediately recorded at the start, and then at 15 min intervals for the first hour when taking samples. Sampling times were then changed to 35 minute intervals for the remainder of the experiments. The samples were pipetted into the sample vials before analysis. The analysis for copper and nickel recovery was performed using the atomic absorption spectroscopy (AAS).

5. Results and Discussion
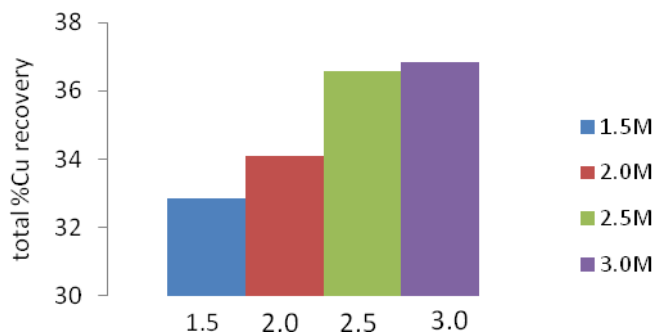
5.1. Effect of Concentration

Fig. 2: The effect of ammonia concentration on the recovery of copper after 130 minutes of leaching

Figure 2 shows the amount of Cu recovered after 130 min for the various concentrations used. An increase in the concentration of the leaching solution resulted in a significant increase in the amount of copper recovered. The amount of copper recovered was generally low for all concentration values. An increase in leaching time resulted in more copper being leached. Figure 3 shows that the amount of copper recovered after a leaching period of 270 min had increased compared to 130 min (Fig 2). The interesting part is that this recovery was obtained when leaching with a concentration of 2.0 M for 270 minutes. This deviation from what was expected could be a result of cementation of the copper from the solution.
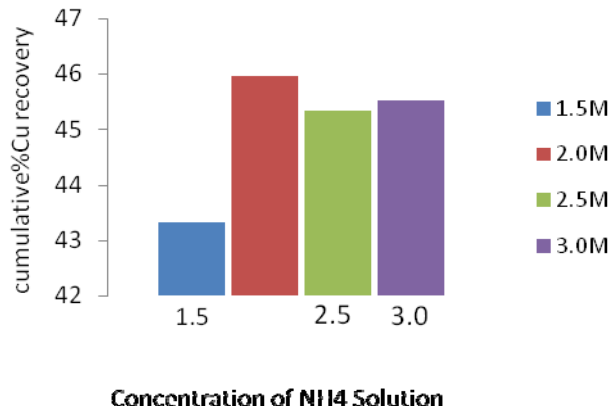
Fig. 3: The effect of ammonia concentration on the recovery of after 270 minutes of leaching
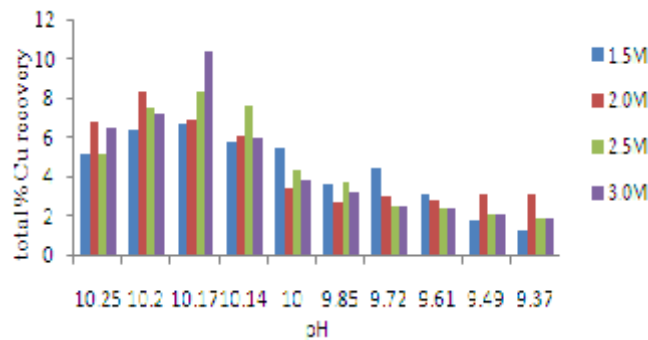

Fig. 4: pH versus the recovery per time interval

Figure 4 shows the effect of pH range on the leaching confirming literature with regard to the stability of ammonia complexes that are formed during the leaching process. Stable copper complexes require a more basic pH, at a range between 8.30 and 10.80, as seen from figure 4. The pH range is within the confines required for formation of stable copper complexes. The low recovery at those low pH values is the result of NH_3 forming NH_4^+ complexes, which do not form complexes with the copper in the solution.

5.1   Effect of Leaching Time

The effect of leaching time was investigated by varying it while maintaining all other leaching parameters constant.
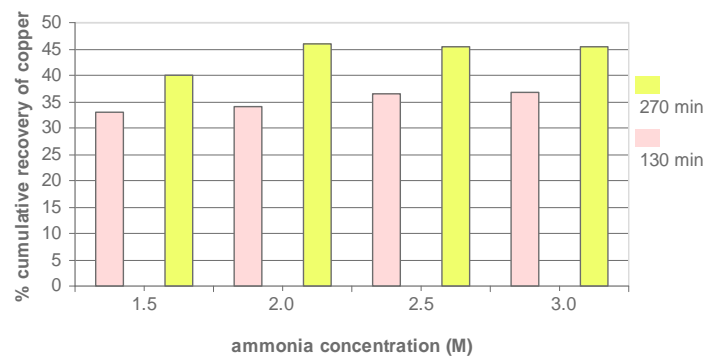

Fig. 5: % copper recovery at 130 minutes and 270 minutes

Figure 5 shows a comparison of the amount of copper recovered when leaching for 130 minutes 270 minutes. From fig 6 it can be observed that rapid leaching of copper occurs in the first 60 minutes of the process, with at least 20 percent being leached. Thereafter the rate of Cu recovery increase steadily. It can be concluded from this study that more copper can still be leached from the matte if the leaching time is increased.
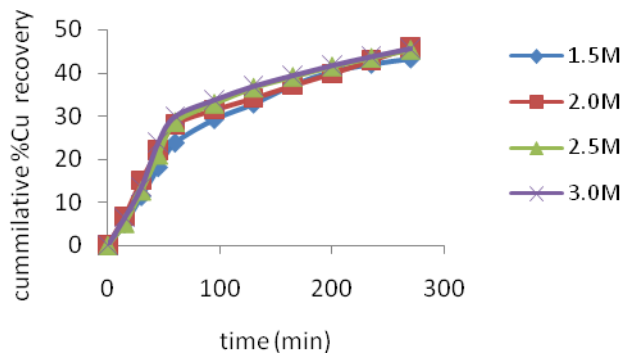
Fig. 6: % cumulative recovery of copper versus time

6. Conclusion

Of the parameters that were investigated in this study, namely leaching time and the concentration of ammonia, it can be deduced that the concentration of the leaching agent increases the extraction of copper. 2M concentration gave the highest recovery after leaching for 270 minutes. Leaching time showed to have great influence on the leaching of copper from the matte, with an average improvement in the recovery of copper at 9.95% after leaching for a period of 270 minutes.

7. Acknowledgements

8. References

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