

A study on the oxidative ammonia/ammonium sulphate leaching of a complex (Cu–Ni–Co–Fe) matte

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Abstract

The oxidative ammonia/ammonium sulphate leaching of an artificial matte was carried out to investigate the extraction behavior of copper, nickel, and cobalt. The composition of the synthetically prepared Cu–Ni–Co–Fe matte was: 24.9% Cu, 35.1% Ni, 4.05% Co, 11.5% Fe, and 24.5% S. The major mineral phases associated with the matte were: CuFeS₂, CuS₂, (FeNi)₉S₈, (FeNi)S₂, Ni₉S₈, Ni₃S₂, (CoFeNi)₉S₈ and Co metal. To optimize the leaching conditions, parameters like oxygen partial pressure, temperature, concentration of leaching reagents and time were studied. Under optimum leaching conditions (2 M NH₄OH + 2 M (NH₄)₂SO₄, 213 psi pressure, 200 °C and 1 h), 93.8% Cu, 85.3% Ni and 76.5% Co were effectively recovered. From the X-ray diffraction analysis, the partially undissolved Cu, Ni and Co phases were assumed to be CuFeS₂, (FeNi)₉S₈ and (CoFeNi)₉S₈, respectively. The iron present in the CuFeS₂ phase was mostly converted to goethite [α-FeO(OH)], as the CuFeS₂ phase dissociated and subsequently remained in the residue.

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1. Introduction

Copper, nickel, and cobalt are generally produced from high grade sulphide/oxide ores or concentrates by the pyrometallurgical smelting reduction and refining process or pyro-hydrometallurgical route. As the reserves of high-grade sulphides diminish, low grade ores need to be processed. For many years these ores were not utilized due to nonavailability of cost effective processes. The development of acid leaching (LX)-solvent extraction (SX)-electrowining (EX) process

during 1970's led to the successful treatment of low grade ores, concentrates/wastes etc., commercially. Presently, about 30% of the total Cu is produced from low grade ores using copper selective oxime based reagents by the hydrometallurgical LX–SX–EX process (Cox, 2004). With increasing use of Cu, Ni and Co metals for different applications and fast depletion of natural land based resources, worldwide efforts are being made to look for alternative resources for the recovery of these metals. One such alternative resource could be the vast oceans, containing these metals in the form of manganese nodules at a depth of about 4–5 km (Rona, 2003). Many research groups in different countries have been working for more than three decades on the development of 3 or 4 metals recovery processes from

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manganese nodules by pyro-/or hydrometallurgical routes (Fuerstenau and Han, 1977; Jung, 1993).

The research group at KIGAM has selected the pyrometallurgical reduction roasting and smelting–sulphidation route to produce Cu, Ni, Co, and Fe rich matte (mixture of molten metallic sulphides) from Pacific Ocean nodules (Nam et al., 2003). This route produces low volumes of matte with high metal content suitable to produce leach liquor containing high concentrations of Cu, Ni, and Co by hydrometallurgical leaching route (Nam et al., 2004).

Ammonia as an effective lixiviant has been widely used in a number of hydrometallurgical processes for many years due to its inherent advantages over alternative reagents. The main advantage is that the basic leach solution alleviates several corrosion problems encountered in the acidic systems. Ammoniacal leaching medium minimizes the possibility of major wasteful components like iron, by their removal during the leaching step as insoluble oxy/hydroxyl compounds. This allows selective extraction of the valuable metals (e.g., copper, cobalt, nickel) as soluble ammine complexes through reactive nitrogen-containing group, leading to higher solubility in most cases (Forward and Peters, 1985). Ammonia is also advantageous in that ammonia and ammonium ion constitute a pH buffer solution. However, it has the disadvantage of operating at relatively high temperature and pressure.

Literature search reveals that a considerable amount of research has been conducted on the ammoniacal leaching of Cu, Ni and Co bearing oxide and sulphide ores, industrial scraps and wastes, over the past few decades. Numerous review articles on such applications can be found in the literature (Kerfoot and Weir, 1988; Arbiter and Fletcher, 1993; Han and Meng, 1993). The thermodynamics and kinetics of reaction systems involving ammonia–copper, ammonia–nickel and ammonia–cobalt have been investigated in detail (Williams and Light, 1978; Boateng and Philips, 1978; Vu and Han, 1977). Extensive studies on the recovery of Cu, Ni and Co from ocean floor manganese nodules by reductive ammoniacal leaching technology have been reported (Han et al., 1974; Das et al., 1986; Acharya and Das, 1987; Mukherjee et al., 2005). It is well known that, the addition of an oxidant is necessary in order to enhance the sulphide dissolution. A number of oxidants have been successfully tested in the ammoniacal leaching of copper sulfides, including bromates, chlorates, oxygen, peroxide, and persulphates (Bell et al., 1995). Oxygen, being the least expensive, is the most widely studied of the oxidants. Several ammoniacal pressure leaching processes have been commercialised successfully around the world. As

far back as 1947, a direct ammonia leaching of Cu, Ni and Co sulphide ores employing high pressure and temperature in an autoclave with oxygen as an oxidant was developed by Sherritt–Gordon at its plant in Fort Saskatchewan, Canada (Forward, 1953). The Arbiter Process (Kuhn et al., 1974) developed in 1970's is another example of ammoniacal pressure leaching. The process used ammonia as a lixiviant at 34.5 kPa with oxygen in a reaction vessel to extract Cu from copper concentrates.

It has been found, that each specific complex sulphide ore is different in nature and must be studied in order to optimize a proper extraction technology. In comparison to copper sulphides and Pb/Zn sulphides, literature on ammoniacal oxygen pressure leaching of multimetal matte (mixture of molten metallic sulphides) containing Cu, Ni, Co and Fe is inadequate.

Our recent study on atmospheric ferric chloride leaching of matte resulted in more than 90% leaching efficiency of Cu, Ni and about 85% of Co using 1.5 M FeCl₃, 0.3 M HCl, 90 °C and 7 h (Park et al., 2006). In the present work, the extraction behavior of Cu, Ni and Co from a synthetically prepared matte has been studied in ammoniacal ammonium sulphate medium. Optimization of process parameters, such as partial pressure of oxygen, temperature, concentration of leaching reagents and time has been carried out.

2. Experimental

2.1. Matte preparation

Synthetic Cu–Ni–Co–Fe matte having similar composition as is expected to be obtained by reduction smelting of the Pacific Ocean nodules followed by sulphidisation of the alloy was prepared by melting the pure metals in required proportions in an induction furnace. A graphite crucible was used for this purpose. Appropriate amount of metals placed in the crucible was heated to about 1500 °C. When the alloy was completely melted and homogenized, sulphur addition was made. To avoid loss due to evaporation, pure sulphur powder was compacted into small cylinders in a mechanical press and manually held into the melt and stirred with a graphite rod. At the end of the run, the crucible was removed from the furnace and cooled to room temperature. The matte was crushed in a jaw crusher, ground in a ball mill and sieved under 100 µm for further study.

2.2. Leaching experiments

The leaching experiments were carried out in a 450 mL capacity autoclave (Model 4562, PAR, USA) with 100 mL

Table 1

The average particle size distribution of the matte

Particle size (μm)	Distribution (wt.%)
–100+63	25.9
–63+25	66.9
–25	7.2

of leach solution and the desired amount of matte. Temperature was controlled through a PID controller with digital read-out for temperature, pressure and agitation speed. The contents were heated to the desired temperature. On attainment of temperature, the contents were stirred at 600 rpm and oxygen was introduced into the system continuously to maintain a constant pressure for the duration of the experiment. Reaction time was counted after the introduction of oxygen into the reactor. Each leaching experiment was performed at 5% (w/v) pulp density (PD) of matte. The contents were cooled, discharged, filtered and analyzed by atomic absorption spectrophotometer (AAS, Varian, Spectr-400) after suitable dilution. The residues were washed, dried in an air oven at 110 °C for 24 h. Known amount of residues were acid digested and analysed for Cu, Ni, Co and Fe. In each case a satisfactory ($\pm 3\%$) material balance was obtained. Particle size measurements were done by a Malvern particle size analyzer (Hydro 2000 M/MU). The mineralogical composition of the matte before and after leaching was carried out by X-ray diffraction analysis (XRD, Rigaku, Model-RH 200, Japan) at a scanning speed of $2^\circ/\text{min}$ with a Cu-K α radiation source. The identification of mineral phases was based on d -values and integrated intensities. The surface area of the matte

was determined by BET method using five-point surface N_2 (Micromeritics, Model-TriStar, V 5.02, USA). Sulphur analysis was done by a LECO SC-432 analyser. A scanning electron microscope (SEM, JEOL, JSM-6380LA) was used for particle observation in the matte before and after leaching.

3. Results and discussion

3.1. Characterization of the matte

The chemical analysis of the synthetically prepared Cu–Ni–Co–Fe matte shows that it contains 24.9% Cu, 35.1% Ni, 4.05% Co, 11.5% Fe, and 24.5% S. It is established that, hydrometallurgical processes, particularly pressure leaching processes, are sensitive to particle size. So in the present study we have reduced the particle size below 100 μm prior to processing by pressure leaching. Table 1 presents the particle size distribution of the bulk sample used in the study. About 67% of the sample was in the range –63+25 m. Specific surface area of the matte was found to be 0.694 m^2/g . The X-ray diffraction pattern of the matte is shown in Fig. 1(a). The major mineral phases identified were: CuFeS_2 , CuS_2 , $(\text{FeNi})_9\text{S}_8$, $(\text{FeNi})\text{S}_2$, Ni_9S_8 , Ni_3S_2 , $(\text{CoFeNi})_9\text{S}_8$ and Co metal. No sulphur was found in free form.

3.2. Leaching study

The combination of ammonia and ammonium salts is known to be a powerful lixiviant used in hydrometallurgical processes. Many metals including Cu, Ni, and Co

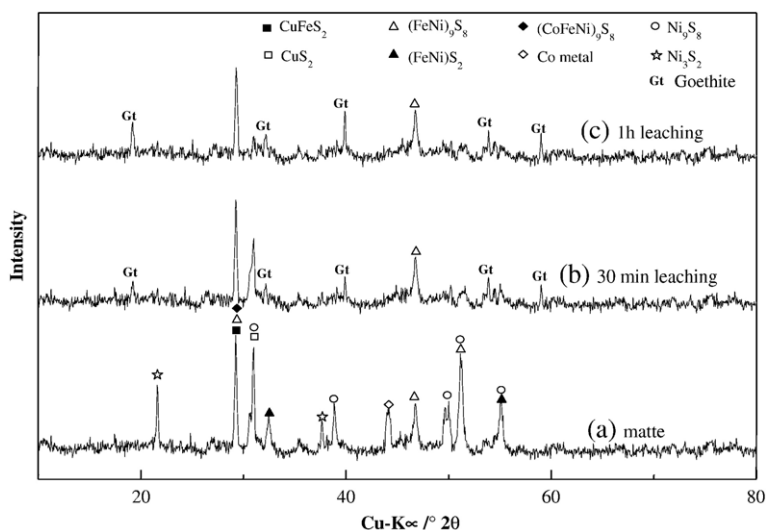


Fig. 1. X-ray diffraction pattern for matte, (a) before leaching, (b and c) after leaching at different times (2 M NH_4OH + 2 M $(\text{NH}_4)_2\text{SO}_4$, 213 psi and 200 °C).

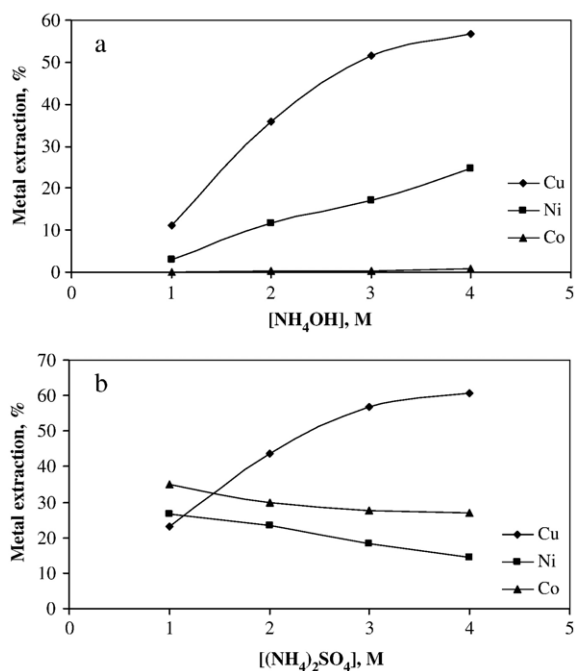


Fig. 2. Effect of, (a) NH₄OH, (b) (NH₄)₂SO₄ concentration on Cu, Ni and Co extraction (Other conditions: 213 psi, 150 °C, 1 h).

can be extracted using the mixture of ammonia and ammonium salts. The detailed chemistry of the oxidative ammonia leach is quite complex and multistep, but the basic principles are reasonably established (Deng, 1993). Briefly, the sulphide component is oxidized to a soluble species, predominantly sulphate (SO₄²⁻) together with some lower oxidation state species such as thiosulphate (S₂O₃²⁻), tri-thionate (S₃O₆²⁻) and sulphamate (NH₄ SO₃ NH₂). The Fe component is oxidized to the +3 state and precipitated as hydrated ferric oxide (Fe₂O₃·H₂O). The Cu and Ni are released in the +2 oxidation state and stabilized in solution by the formation of ammine complexes with NH₃ ligands. On the other hand, cobaltic ammine complexes are more stable compared to cobaltous ammine in the pH range 9.0–11.0.

The mechanism by which pressure leaching processes affect the release of metals from sulphide mineral matrices, is largely dependent on many factors such as temperature, oxygen partial pressure, concentration of leaching reagents, time and process chemistry. Prior to the experiments investigating the effects of NH₄OH together with (NH₄)₂SO₄ at different concentrations, the effects of NH₄OH and (NH₄)₂SO₄ on the extraction behavior of Cu, Ni and Co were investigated separately and presented in Fig. 2(a) and (b), respectively. The conditions maintained during the leaching experiments were: 213 psi oxygen partial pressure, 1 h leaching time and 150 °C temperature. The results showed that, by

increasing NH₄OH concentration from 1 M to 4 M, the Cu extraction increased from 11.2% to 56.8%. The increase was high up to 3 M NH₄OH, and then the extraction slowed down. At the same time, Ni extraction increased steadily from 3.0% to 24.7%. In contrast, Co extraction was negligible (<1%) although NH₄OH concentration was increased from 1 M to 4 M. As shown in Fig. 2(b), by increasing (NH₄)₂SO₄ concentration from 1 M to 4 M, Cu extraction also increased (23.0% to 60.6%), similar to NH₄OH variation results. On the other hand, Ni and Co extraction showed negative trend with increasing (NH₄)₂SO₄ concentration. The Ni extraction decreased from 26.6% to 14.6% and Co extraction decreased from 34.8% to 26.9%, when (NH₄)₂SO₄ concentration increased from 1 M to 4 M. As expected, the pH of the leaching solution increased with increase in NH₄OH concentration, and decreased with increasing (NH₄)₂SO₄ concentration. The pH increased from 10.3 to 11.1, depending on the increase of NH₄OH concentration from 1 M to 4 M. On the other hand, by increasing (NH₄)₂SO₄ concentration from 1 M to 4 M, the pH decreased from 6.8 to 6.2. So, ammonia and ammonium salt concentrations should be optimized to obtain suitable selectivity and also at the same time maximum leaching efficiency.

3.2.1. Effect of time

The effect of leaching time from 15 to 120 min on the extraction of Cu, Ni and Co was studied using 2 M NH₄OH + 1 M (NH₄)₂SO₄, 213 psi pressure and 150 °C temperature. According to experimental results presented in Fig. 3, all three metals showed similar type of extraction behavior. At the beginning of the leaching, extraction rate of all three metals was very fast. Within 15 min, 65.2% Cu, 73.5% Ni and 22.1% Co recovery was achieved. This increased to 91.0%, 86.3% and 45.1% for Cu, Ni and Co, respectively after 60 min leaching time. Beyond 60 min, there was no marked

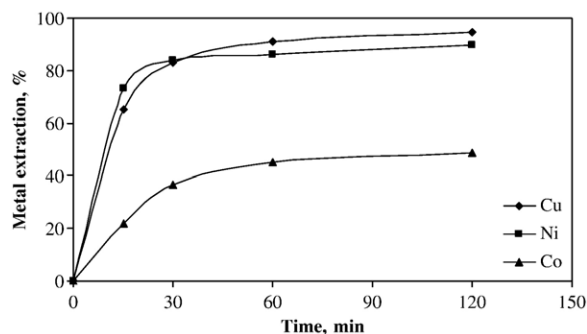


Fig. 3. Effect of time on Cu, Ni and Co extraction (2 M NH₄OH + 1 M (NH₄)₂SO₄, 213 psi and 150 °C).

increase in extraction for the studied metals. So, all further experiments were carried out at 1 h contact time.

3.2.2. Effect of reagents concentration

The variation of NH_4OH concentration at a fixed $(\text{NH}_4)_2\text{SO}_4$ concentration was studied at 213 psi pressure, 150 °C temperature and 1 h contact time. As shown in Fig. 4(a), with increasing NH_4OH concentration from 0.5 to 4 M and keeping $(\text{NH}_4)_2\text{SO}_4$ constant at 1 M, the extraction of Cu, Ni and Co increased from 66.7% to 92.0%, 29.3% to 87.5% and 11.2% to 66.5%, respectively with pH between 8.5 and 9.9. The increase was high up to 2 M NH_4OH for Cu and Ni, and up to 3 M NH_4OH for Co. On the other hand, as shown in Fig. 4(b), varying $(\text{NH}_4)_2\text{SO}_4$ concentration from 1 M to 4 M and keeping 2 M NH_4OH concentration constant, Cu extraction increased marginally from 91.0 to 93.7% and Co extraction increased substantially from 45.1 to 72.3%, whereas Ni extraction showed a negative trend. The Ni extraction decreased from 86.3 to 76.4% when $(\text{NH}_4)_2\text{SO}_4$ concentration was increased from 1 M to 4 M. At the same time, pH also decreased from 9.3 to 8.1. This can be explained by the fact that, at high concentrations of oxygen, a nickel oxide forms at the pH range 6.0–8.0. This oxide remains as a stable phase at

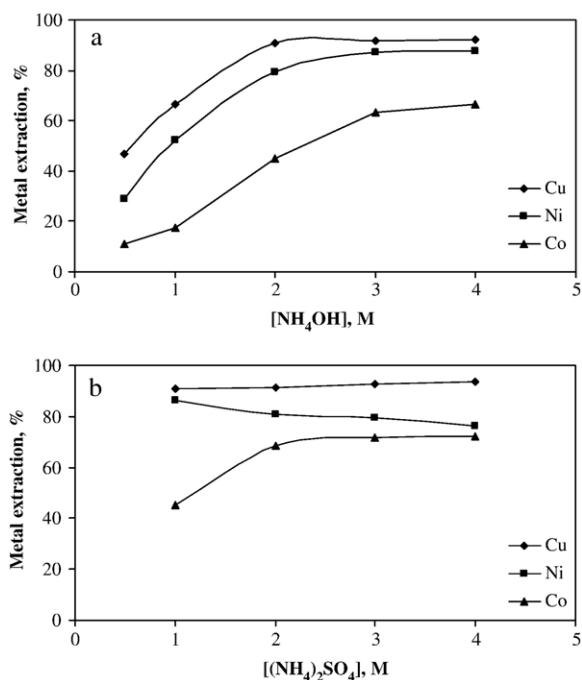


Fig. 4. (a) Effect of NH_4OH concentration on metal extraction at a fixed concentration of $(\text{NH}_4)_2\text{SO}_4$ (b) Effect of $(\text{NH}_4)_2\text{SO}_4$ concentration on metal extraction at a fixed concentration of NH_4OH (Other conditions: 213 psi, 150 °C, 1 h).

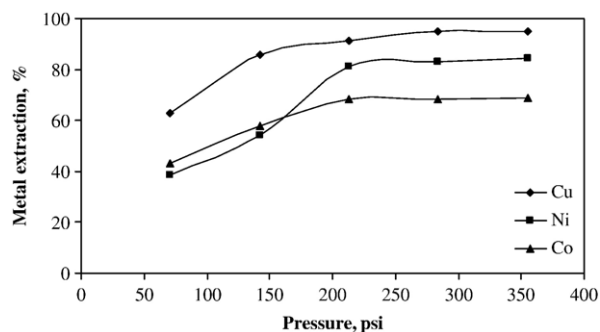


Fig. 5. Effect of oxygen partial pressure on Cu, Ni and Co extraction (2 M NH_4OH + 2 M $(\text{NH}_4)_2\text{SO}_4$, 1 h and 150 °C).

this pH range. However, at higher pH nickel ammine is the most stable species, and any nickel oxide formed initially is soon dissolved with increasing pH, thereby increasing the extraction rate (Meng and Han, 1996). The results imply that the ratio of $\text{NH}_3/\text{NH}_4^+$ is significant to attain higher metal extraction rate.

3.2.3. Effect of oxygen partial pressure

For enhancement of the sulphide dissolution, oxygen has been widely used as an oxidant, because of its low cost and noncorrosive nature. The next set of experiments were carried out to determine the effect of oxygen partial pressure on the metal extraction rate as the concentration of dissolved oxygen in solution is directly related to the partial pressure of oxygen over the solution. The oxygen partial pressure was varied from 71 to 355 psi, keeping all other parameters such as 2 M NH_4OH , 2 M $(\text{NH}_4)_2\text{SO}_4$, temperature at 150 °C and time at 1 h constant. Effect of partial pressure on extraction of Cu, Ni and Co is shown in Fig. 5. Extraction of Cu varied from 63.1 to 95.0%, Ni varied from 38.5 to 84.6% and Co from 43.2 to 69.4% as oxygen pressure was increased from 71 to 355 psi. For all three metals, extraction increase was high up to 213 psi oxygen partial pressure. With further increase in partial pressure up to 355 psi the metal extraction was not significantly increased. In our present experimental conditions, 213 psi oxygen partial pressure was found to be sufficient to oxidize the maximum possible sulphide minerals present in the matte.

3.2.4. Effect of temperature

Low temperature pressure leaching processes below 100 °C have not been popularly accepted because of its characteristic slow extraction efficiencies, and longer residence time for Cu and other metals. Also, high temperature pressure leaching processes have disadvantages like higher oxygen consumption and higher acid production as by-product. The greater heat production in

the reactor vessel also a characteristic problem deals with high temperature pressure leaching processes, which requires longer cooling time and higher energy consumption. Medium temperature pressure leaching processes, operating at temperatures from 120 °C to 190 °C have been the focus for much research and development activity in recent years (Marsden et al., 2004). So in our present study, a temperature range from 100 °C to 200 °C was selected and its effect on metal extraction was studied. Other conditions maintained were 2 M NH_4OH +2 M $(\text{NH}_4)_2\text{SO}_4$, oxygen pressure 213 psi and 1 h. The results are presented in Fig. 6. As shown in the figure, the effect of temperature was found to be more in case of Co and Ni extraction compared to Cu extraction. Cu extraction increased from 75.0 to 91.5% when temperature was increased from 100 to 150 °C; further increase in temperature up to 200 °C had negligible effect. On the other hand, the extraction of Ni and Co increased with increase in temperature. The Ni extraction increased from 62.6 to 85.3% and Co extraction from 45.1 to 76.5%, when temperature was increased from 100 to 200 °C. There was no significant change in pH, which almost remained constant at 8.9 in the whole range of temperature studied. Based on the results, it was observed that 2 M NH_4OH +2 M $(\text{NH}_4)_2\text{SO}_4$, 213 psi pressure, 200 °C temperature and 1 h reaction time appeared to be optimum conditions for extraction of 93.8% Cu, 85.3% Ni and 76.5% Co.

3.3. Morphological and XRD observations

The combined application of XRD and SEM studies can provide useful information on the characterization and leaching of bulk samples. The samples before and after leaching were subjected to XRD analysis to see the phases that disappear and/or the products that form during leaching. Fig. 1(b)–(c) showed the XRD analysis

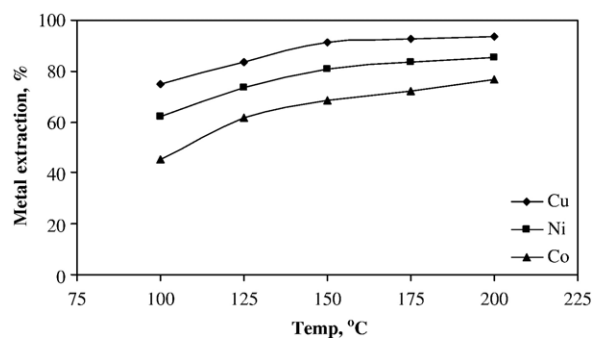


Fig. 6. Effect of temperature on Cu, Ni and Co extraction (2 M NH_4OH +2 M $(\text{NH}_4)_2\text{SO}_4$, 213 psi and 1 h).

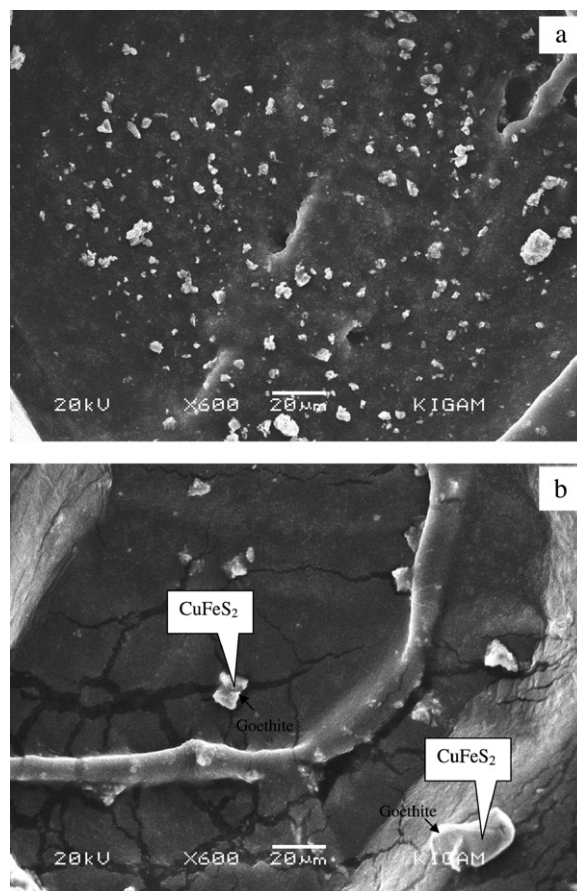


Fig. 7. SEM-micrographs of matte, (a) before leaching, (b) after leaching (2 M NH_4OH +2 M $(\text{NH}_4)_2\text{SO}_4$, pressure: 213 psi, temperature: 200 °C, 1 h).

of matte leached for different times using 2 M NH_4OH +2 M $(\text{NH}_4)_2\text{SO}_4$, 213 psi pressure and 200 °C. It was observed that, some of the mineral phases like Ni_3S_2 , $(\text{FeNi})\text{S}_2$ and Co metal completely dissolved within 30 min of leaching. The dissolution rates of Ni_9S_8 and CuS_2 phases were slow and dissolved completely within 1 h. The intensity of CuFeS_2 lines decreased with progressive leaching. However, the dissolution of CuFeS_2 was incomplete even after 1 h of leaching time. This was supposed to be the contributing factor for the undissolved copper. The CuFeS_2 phase is reported to be the most difficult to leach of all the copper minerals owing to the formation of a tenacious goethite reaction product under certain conditions (Rao and Ray, 1998). As shown in the XRD, goethite peaks start developing as the CuFeS_2 phase dissociated, which increased with leaching time. This indicated that, the iron present in CuFeS_2 was mostly precipitated to goethite and remained in the residue. Similar types of results are also reported by Rao et al., 1993 during ammoniacal

leaching of chalcopyrite. The conclusion was further supported by the SEM study shown in Fig. 7. The photograph in Fig. 7(a) of the matte sample revealed particle aggregates of different initial size without goethite on its surface. After 1 h leaching, goethite was found on the leached surface of the residue, which was subsequently coated around the mineral particles (Fig. 7(b)). These observations indicated that the goethite formed from the iron was released during dissolution of CuFeS_2 . On the other hand, whether Ni and Co associated with Fe phases, behaves in a similar way or not is beyond the scope of our present investigation. As shown in the XRD analysis, the undissolved Ni and Co phases were $(\text{FeNi})_9\text{S}_8$ and $(\text{CoFeNi})_9\text{S}_8$, respectively. Overall, the parameters like leaching temperature, oxygen pressure, pH, and the nature of leaching medium were important factors that influenced the oxidation reaction sequence followed by dissolution of minerals in the present experimental conditions. Further research is being carried out to improve the leaching efficiency of metals, particularly Co, using different oxidants. Another aspect the authors are looking into, is to develop methods for minimizing the goethite product layer formation.

4. Conclusions

In the present paper, the oxidative ammonia/ammonium sulphate leaching of a synthetic matte has been studied to investigate the extraction behavior of Cu, Ni, and Co. It was found that, leaching temperature, oxygen pressure and pH, were important factors that influenced the dissolution of metal sulphide phases present in the matte. The nature of leaching medium, particularly the ratio of $\text{NH}_3/\text{NH}_4^+$ was significant to attain higher metal extraction rate. Under optimum leaching conditions (2 M $\text{NH}_4\text{OH} + 2$ M $(\text{NH}_4)_2\text{SO}_4$, pressure: 213 psi, and temperature: 200 °C and 1 h) a maximum leaching efficiency of 93.8% Cu, 85.3% Ni and 76.5% Co was achieved. Analysis of leach residue by XRD and SEM was found useful in understanding the dissolution behavior of different minerals present in the matte. The partially undissolved Cu, Ni and Co phases identified were CuFeS_2 , $(\text{FeNi})_9\text{S}_8$ and $(\text{CoFeNi})_9\text{S}_8$, respectively. The product layer enveloping the CuFeS_2 particle was identified as goethite which was subsequently coated around the mineral particles thereby hindering the dissolution rate.

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