

REDUCTIVE LEACHING OF LIMONITIC LATERITES USING FERROUS SULPHATE

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Abstract

This study was carried out on a limonitic laterite from New Caledonia. The main objective was to evaluate the atmospheric leaching of the ore in ammonium sulphate media using ferrous sulphate as reductant. Different parameters were examined, such as total ammonia concentration, temperature and ferrous sulphate concentration. At 80°C, 130 g/l of total ammonia, 2.73 g FeSO₄/g ore and pH 8.2, nickel extraction was 64 % while 20 % of cobalt remained in solution after 8 hours.

Introduction

Hydrometallurgical treatment for laterites has increased due to the importance these deposits have gained as sources of nickel and cobalt [1, 2]. In recent years many researchers have studied different ways to extract nickel and cobalt by ammoniacal or acidic solution leaching.

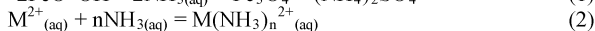
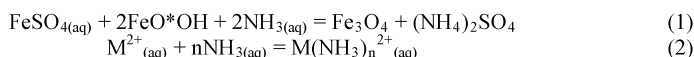
There are a large amount of studies involving acid leaching of laterites. These studies include high pressure and atmospheric leaching to release nickel and cobalt from laterites. In general, acid leaching presents good nickel and cobalt recoveries but the acid consumption, especially under atmospheric conditions, is high and leach liquors require neutralization prior to further treatment [1, 2].

One alternative to acid leaching, the Caron process, includes a reductive roasting stage followed by oxidative ammoniacal leaching. However, this process presents some limitations such as high operational cost, mainly from the drying and reductive roasting stages [3]. Also, low final cobalt recoveries (around 50%), which probably occur due to absorption of cobalt onto ferrihydrite and/or passivation of the Fe-Ni-Co alloys formed during roasting, are a significant economic downside [4,5,6].

In ammonia media, many reducing agents such as ferrous sulphate, glucose, thiosulfate, etc. have been tested to recover nickel and cobalt especially from deep sea manganese nodule ores [7]. The best results have been reported when ferrous sulphate was used with extractions of over 90% achieved for nickel and cobalt [8]. Also, there are some studies where synthetic goethite is directly reduced by ferrous sulphate in ammonia to produce magnetite, where the total transformation is achieved around 130°C [9]. Recent studies used metallic iron as a reducing agent to leach limonites, the results show a partial leach of the ore and the ferrous ion seems to play an important role on leaching kinetics [10].

The present work reports experimental results obtained during the leaching of a limonitic laterite in ammoniacal solutions using ferrous sulphate as a reducing agent under atmospheric

conditions. This study includes the effect of temperature, ammonia concentration and ferrous sulphate concentration. Equation (1) shows the proposed overall chemical reaction for goethite. Based on the Pourbaix diagrams for the Ni-NH₃-H₂O and Co-NH₃-H₂O systems, mono- to hexa-ammines of nickel and cobalt (i.e. 1 ≤ n ≤ 6) can form depending on pH and total ammonia concentration [11-16]. Equation (2) summarizes the reactions for nickel and cobalt complexed in ammoniacal media.



Experimental Procedures

The samples were prepared as follows: 14 kg of limonitic laterite containing approximately 40 wt % water were dried. The P₈₀ of the ore was 40 microns. The sample was dried and homogenized by using a coning and quartering procedure. One representative sample of approximately 3 kg was obtained. Further splitting by coning and quartering was performed to produce smaller laterite samples which were used in the leaching tests. The ore samples were characterized by chemical analysis (ICP), SEM and quantitative X-ray diffraction (QXRD). Selected elements present in the laterite are given in Table 2.1. Table 2.2 shows the crystalline phases found in the laterite as obtained through QXRD.

Table 2.1: Elemental content in the ore

Element	%
Fe	49
Ni	1.4
Co	0.36
Mn	1.4

Table 2.2: XRD quantitative phase analysis (wt.%)

Mineral	% laterite
Goethite	57
Maghemite	13.5
Hematite	5.7
Kaolinite	2.9
Gibbsite	1.3

Experiments were done batch-wise in a 1 L jacketed and baffled glass cell under atmospheric pressure. The chemical reagents were of analytical grade and were used as-received while deionized water was used to make the solutions. Temperature was controlled by circulation of hot water (thermostatically controlled water bath) through the reactor's water jacket. Leach solutions were prepared using ammonium hydroxide and ammonium sulphate. The pH was set above the buffer point of ammonia (which changed with temperature), to ensure the stability of aqueous ammonia and the nickel, cobalt and iron amines. The solutions were sparged with nitrogen gas for 10 minutes prior to heating the solution, to decrease the presence of oxygen and favor the formation of iron amines rather than hydroxides. The experiments were performed at 600 RPM stirring speed with an overhead mixer and a pitch-blade impeller at 10% solids. Samples were taken throughout the course of each experiment (approximately 10 ml of pulp). The samples were separated quickly using a centrifuge. The clear solution was then acidified with 2 M hydrochloric acid and analyzed by AAS for Ni, Fe, Co and Mn. The leach residues

were dried at room temperature and then homogenized to obtain representative samples. The samples were analyzed by ICP and XQRD.

Results and Discussion

The best extraction result for nickel was 64% at 80°C using 2.73 g of FeSO_4 / g of ore and 130 g/l total ammonia over 8 hours. For both cobalt and manganese extractions, the best result obtained was 44% at 45°C using 0.37g FeSO_4 /g of ore and 130 g/l of total ammonia.

Effect of temperature

Leaching experiments were carried out at 20, 45, 65 and 80 °C, keeping the other variables constant. Reducing agent concentration was 0.73g of FeSO_4 / g of ore. Figures 1 and 2 show nickel, cobalt, manganese and iron dissolution. Nickel extraction is very slow at low temperatures but it increases over 65°C. Ferrous is consumed during the reaction and its consumption is faster at higher temperatures. Thus, from Figure 1, it is possible to see that after 8 hours there is no ferrous available to further reduce goethite.

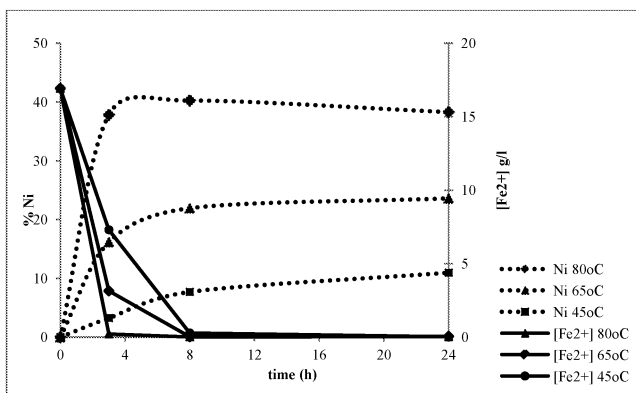


Figure 1: Effect of temperature on nickel extraction and iron behavior in ammonia solutions using ferrous sulphate as reducing agent at 600 RPM during 24 hours.

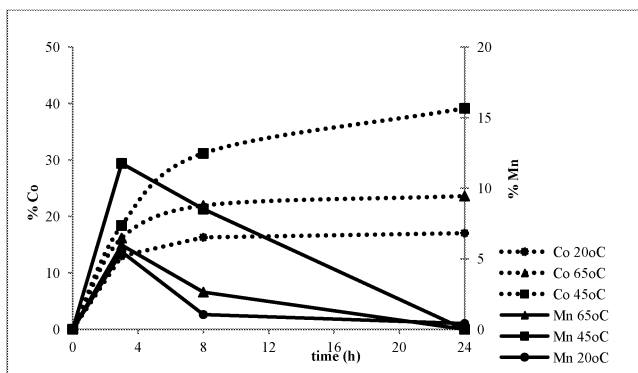


Figure 2: Effect of temperature on cobalt and manganese extraction in ammonia solutions using ferrous sulphate as reducing agent at 600 RPM during 24 hours.

Cobalt and manganese deportment is different than that of nickel. The best result was obtained at 45°C and increasing temperature is detrimental for cobalt and manganese recovery. These metals behave differently due to the fact that they are mainly associated with different mineral phases; cobalt and manganese to asbolane and nickel to goethite [17]. Thus it is not unexpected that these elements can present different kinetics under the same leaching conditions.

The solid phase analyses by QXRD show that the main phase in the residues is magnetite. Also, magnetite concentration increases with temperature. Thermodynamically, oxide formation is favored by temperature [14]. Magnetite formation could explain the low recoveries and losses of cobalt and manganese. There are numerous studies showing that cobalt can co-precipitate with iron and/or manganese oxides because it can replace these cations in the spinel, and that this phenomenon is favored by increased temperatures [7, 18].

Also, the cobalt and manganese may be adsorbed onto oxides and/or hydroxides during leaching. Research has shown that cobalt can be adsorbed onto manganese and iron oxy-hydroxides [19-23]. The capacity for adsorption of manganese oxy-hydroxides is reportedly greater than that of similar iron species [24].

Effect of ferrous sulphate concentration

Figures 3 and 4 show the effect of ferrous sulphate concentration, which included: 0.37, 0.73, 1.5 and 2.73 g of FeSO_4 / g of ore. Nickel extraction increased with ferrous sulphate concentration. At 1.5 g of FeSO_4 / g of ore, 64% Ni extraction was achieved after 24 hours of leaching. Very similar results are obtained using 2.73 g FeSO_4 / g of ore. These results suggest that, beyond 1.5 g of FeSO_4 / g of ore, added reducing agent does not improve extraction. This is probably due to the fact that magnetite precipitates around the goethite particles, thus the reaction between ferrous and goethite is very slow when the magnetite precipitate layer is thick. Figure 5 shows a particle leached partially during the process. Here, it was possible to see how the magnetite precipitates around of goethite particles.

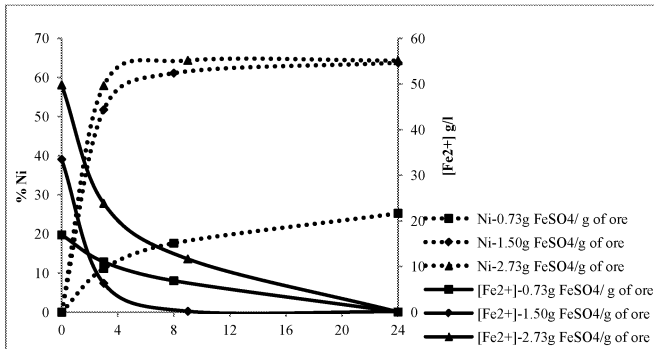


Figure 3: Effect of ferrous sulphate concentration on nickel extraction and iron behavior in ammonia solutions at 80°C, 600 RPM for 24 hours.

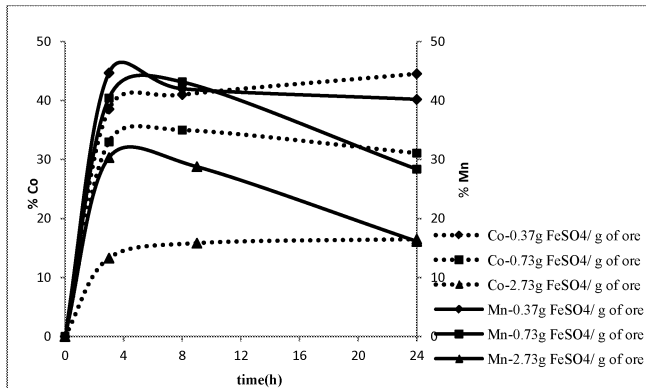


Figure 4: Effect of ferrous sulphate concentration on cobalt and manganese extraction in ammonia solutions at 80°C, 600 RPM for 24 hours.

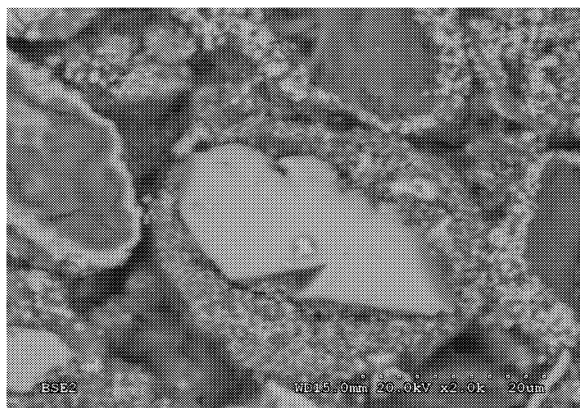


Figure 5: SEM picture of the leached residue after 8 hours at 80°C.

The best results for cobalt and manganese extraction were obtained when the ferrous sulphate concentration was lowest. The maximum cobalt extraction of 44% was obtained after 24 hours of leaching whereas maximum manganese extraction of 44% occurred after 3 hours. High ferrous concentrations were detrimental for cobalt and manganese extraction, likely because they improve goethite reduction resulting in increased magnetite precipitation. Residue analyses show that the magnetite content increased with reductant concentration. These results are in agreement with the observed effect of temperature where precipitation during leaching was detrimental for cobalt and manganese extraction.

Effect of initial ammonia concentration

Figures 6 and 7 show the effect for initial total ammonia concentration. The experiments were conducted above the ammonium/ammonia buffer point to benefit nickel, cobalt and manganese ammine stability. The total ammonia concentration was varied between 65 and 130 g/l.

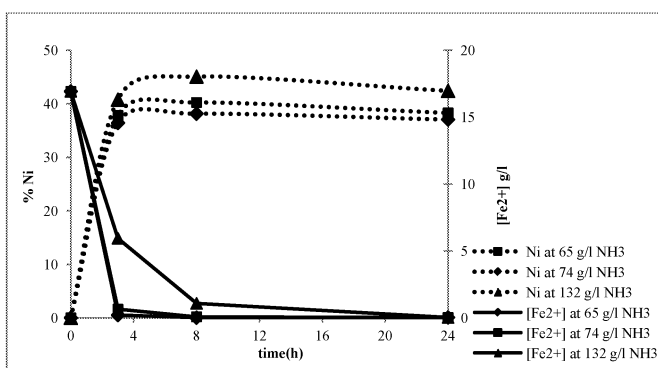


Figure 6: Effect of total ammonia concentration on nickel extraction and iron behavior in ammonia solutions at 80°C, 600 RPM for 24 hours.

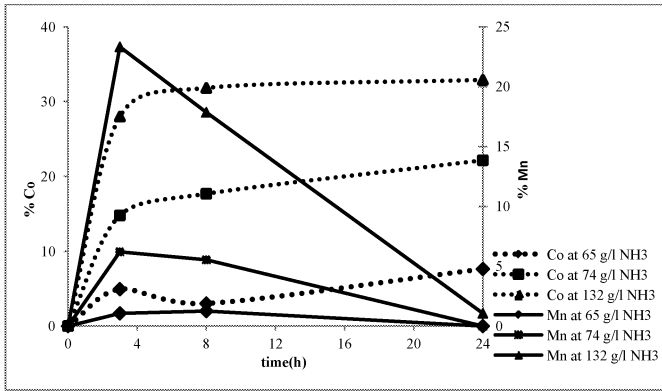


Figure 7: Effect of total ammonia concentration on nickel extraction and iron behavior in ammonia solutions at 80°C, 600RPM for 24 hours.

Increasing ammonia has a strong effect on cobalt and manganese extraction. For nickel, added ammonia concentration improves nickel extraction but the effect is not as significant as for cobalt and manganese. This positive effect is expected because ammonia is a ligand to keep the cations in solution. At higher ammonia concentrations, the thermodynamic stability zones for the amines become larger. When the ammonia concentration is increased, ferrous is consumed more slowly, but the nickel extraction is higher (Figure 6). These results suggest that ferrous' capability to reduce goethite and asbolane concentration is higher when ammonia concentration is increased. The oxidation of some ferrous with oxygen during the leaching is expected, however increasing ammonia concentration seems to help decrease reductant losses.

Concluding Remarks

Results obtained from the present research suggest the limonitic laterite can be partially reduced by ferrous sulphate. Maximum nickel extraction was 64% at 80°C, 2.73 g FeSO₄/g of ore, 130 g/l total ammonia in 10 hours. At the same conditions the cobalt and manganese extractions were only 16% and 43%, respectively. The different leaching behavior between nickel, cobalt and manganese is due to the fact that they are associated with different mineralogical phases.

Nickel extraction is improved by increased temperature, ammonia concentration and ferrous sulphate concentration; cobalt extraction requires low temperature and ferrous sulphate concentration as well as high ammonia concentration. High ferrous sulphates to ore ratios do not improve nickel extraction, likely due to magnetite precipitation around goethite particles, thus preventing contact between particle and reductant.

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