

Recovery of metals from Cuban nickel tailings by leaching with organic acids followed by precipitation and magnetic separation

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Abstract

The percolation leaching of the Cuban nickel tailings containing 0.34% Ni, 0.08% Co and 44.2% Fe was investigated by using tartaric and oxalic acids at different concentrations. About 70% Ni, 80% Co and 30% Fe were extracted after 5 days of leaching with the mixture of 0.15 mol/L tartaric acid and 0.05 mol/L oxalic acid at ambient temperature and normal pressure. Nickel and cobalt extraction of 80% as well as iron extraction of 50% were achieved from the pregnant solution by means of precipitation at 80 °C for 2 h. The precipitation at ambient temperature led to a similar result after 16 days. Cobalt, nickel and iron oxalates were found in the precipitate by using the X-ray diffraction method. The regeneration of acids during the precipitation step made possible the reuse of the raffinate at the leaching step. Heating of the precipitate at 200 °C increased the metal concentration to 1.22% Ni and 0.33% Co, which can be fed in the existing nickel plant in Moa, Cuba. The magnetic processing of the leaching residues led to a non-magnetic product containing less than 20% Fe and a magnetic product containing more than 50% Fe.

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1. Introduction

Nickel and cobalt are being extracted from the Cuban laterite ores containing more than 1% Ni and 0.15% Co at three hydrometallurgical plants. Two plants are using the Ammoniacal Carbonate Technology (Caron Process) and one plant is using the Acid Pressure Technology. In both technologies only 80–85% Ni and 20–30% Co can be extracted. About 100 million tonnes of the leaching residues containing less than 0.5% Ni and 0.1% Co have been produced in the last 50 years. Due to the serious environmental problem caused by these tailings, several investigations looking for simple operation conditions and low cost technologies are being carried out.

Several authors have investigated the leaching of low-grade nickeliferous laterites using synthetic organic acids or acids obtained during the metabolism of microorganisms [1–6]. Tzeferis [7] extracted 70–72% of nickel by hot leaching at 95 °C of

low grade hematitic laterite from Greece with a solution obtained from the cultivation of fungi at 30 °C. In comparison to several organic acids, Tzeferis and Agatzini [8] found that citric acid was the most effective solvent for nickel. Lactic, formic, acetic and salicylic acids were relatively ineffective. Oxalic acid extracted more iron but no nickel. McKenzie et al. [9] used citric, tartaric and pyruvic acids for the leaching of Indonesian and West Australian laterites at pH 2.3 and at a temperature of 28 °C. Despite having different leachabilities, the authors found chelated nickel complexes in the leaching solution from both samples. Recently, Stamboliadis et al. [10] found that the magnetic processing of the leaching residue of nickeliferous laterites from Greece could lead to an iron concentrate. From the above publication, it is clearly seen that the metal extraction from laterite ores from different origins depends on the mineralogical composition and the geneses of the ore-body. However, the industrial application of bioleaching of such oxidised ores containing low metal amounts can be achieved only by production of organic acids at low cost.

The aim of this study is to focus on the recirculated precipitate amenable to leaching with the existing process. The percolation leaching with tartaric acid as well as a mixture of tartaric and

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oxalic acids was attempted. In addition, extraction of metals from the pregnant solution by precipitation, thermal decomposition of the precipitate and upgrading of iron from the residues of percolation leaching were also carried out.

2. Experimental

2.1. Materials

The sample used in this investigation is from the tailings dam obtained during the ammoniacal carbonate process at the Ernesto Che Guevara nickel plant, Moa (North-East of Cuba). Table 1 shows its chemical composition. Magnetite (Fe_3O_4), quartz (SiO_2), fayalite, forsterite ($\text{Fe,Mg}_2\text{SiO}_4$) were found as the main minerals by means of the RX diffractometer for powder (PHILIPS, Germany). The size analysis, using the "Laser granulometer Model 715" from CILAS (Germany), showed about 54% of the total sample in the fraction to be lower than $20\ \mu\text{m}$. More than 50% of nickel as well as more than 56% of cobalt were found in this fine fraction.

2.2. Percolation leaching

Percolators with a diameter of 8 cm and height of 30 cm were used for all leaching tests. Layers of glass chips were put on the bottom of percolators as inert material. The first layer with a size between 2.5 and 6 mm and the second one between 0.630 and 2.5 mm. Due to the fine size of the feed material, 65 g of glass chips between 100 and $630\ \mu\text{m}$ were added to 65 g of feed material for increasing the porosity and the leaching time. Without adding chips, the maximal leaching time was 1 day, because of low porosity. About 5 L of leaching solution was recirculated at the flow rate of 10 mL/min from a bottle at the top of the percolator using a pump. A mixture of water and analytical tartaric (99.7%) or oxalic acid (>99.0%) was used as the leaching solution for all tests. These acids are from the company Fluka/ Riedel-de Haën, Germany. The solution flow rate of 10 mL/min was constant for all tests. The leach liquor and the residues were analysed for nickel, cobalt and iron by inductive coupled plasma spectroscopy (ICP-OES, axial) or atomic absorption spectroscopy (AAS).

Table 1
Chemical analysis of the nickel tailings from Moa

Element	Amount (%)
Ni	0.34
Co	0.08
Fe	44.2
Mg	3.57
Mn	0.73
Al	5.2
Cr	0.83
Cu	0.01
Zn	0.03
SiO_2	7.8
N	0.01
C	0.84
S	0.08

2.3. Precipitation

The precipitation tests were carried out at $80\ ^\circ\text{C}$ ($\pm 3\ ^\circ\text{C}$) without agitation in an open glass reactor (1 L) with temperature regulation. The heating of leaching solution was carried out using a laboratory electric Hotplate-Stirrer. The regulation of the temperature was carried out using a thermometer connected to the thermostat of Hotplate-Stirrer. A conic and graduated flask (1 L) was used for the precipitation tests at ambient temperature. The process was continued for 16 days without agitation of the solution. Samples of solution were taken every day for analysis of the contents of nickel, cobalt and iron by ICP-OES.

2.4. Thermal decomposition of the precipitate

A muffle furnace was used for the thermal decomposition of the precipitate. For each test, about 3 g of precipitate were maintained at $200\ ^\circ\text{C}$ for 15 min. The roast product was analysed for nickel, cobalt and iron contents by ICP-OES or AAS.

2.5. Magnetic separation of the leaching residues

The upgrading of the secondary tailings from the percolation leaching with organic acids was carried out by using the magnetic Jones-separator (WHIMS). This is a laboratory wet high intensity-magnetic separator used for processing up to 10 L/h of pulp containing 10–30% of solids. A current of 2 A, potential of 150 V and matrix of 2 mm were constant for all tests. Magnetic and non-magnetic products were obtained from each test. All products were analysed for the contents of nickel, cobalt and iron by ICP-OES or AAS.

3. Results and discussion

3.1. Percolation leaching with tartaric acid

The percolation leaching with 0.15 mol/L of tartaric acid concentration was carried out at ambient temperature ($20\text{--}24\ ^\circ\text{C}$) for 5 days. Fig. 1 shows the recovery of nickel, cobalt and iron as a function of leaching time. The extraction kinetics showed that

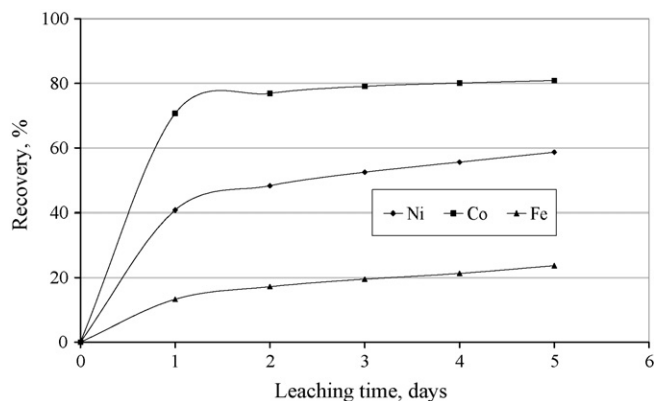


Fig. 1. Metal recovery from leaching of Ni–Co tailings by means of tartaric acid (tartaric acid concentration: 0.15 mol/L, temperature: $20\ ^\circ\text{C}$, flow rate: 10 mL/min).

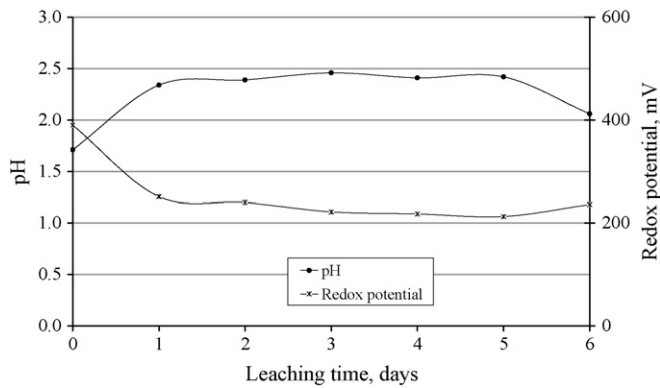


Fig. 2. The pH and redox potential of the solution during the percolation leaching (tartaric acid concentration: 0.15 mol/L, temperature: 20 °C, flow rate: 10 mL/min).

cobalt leaching is faster than Ni and Fe. While the metal recovery in the first 2 days is high, the reaction rate is lower in the last 3 days. The maximum extraction of about 80% Co, 60% Ni and 20% Fe was achieved after 5 days of leaching.

Fig. 2 gives the pH and redox potential of the leaching solution as a function of time. The pH increases simultaneously with the metal recovery during the first day. Thereafter, the pH remains almost constant and decreases after 5 days. Unlike the pH, the redox potential decreases sharply the first leaching day. Thereafter, the redox potential decreased slowly. It is known that the decreasing of pH of the leaching solution is suitable for iron dissolution. The objective of this investigation was to extract selectively cobalt and nickel, and to remain iron in the leaching residues. To avoid the decrease of pH during leaching, another test was conducted with 0.2 mol/L of tartaric acid at the beginning of the leaching and 0.167 mol/L was added after 24 h. While cobalt extraction remained at 80%, the nickel and iron extraction increased up to 70 and 40% respectively after 8 days.

3.2. Percolation leaching with the mixture of tartaric acid and oxalic acid

The percolation leaching with a mixture of 0.15 mol/L tartaric acid and 0.05 mol/L oxalic acid was carried out at ambient temperature (20–24 °C) for a period of 5 days. Fig. 3 shows the nickel, cobalt and iron recovery as a function of leaching time. The nickel recovery of about 60% and the cobalt recovery of about 78% are similar to the values obtained by leaching with only tartaric acid, but the iron recovery after 5 days leaching is higher (35%). Additionally, the metals recovery after the 1 day leaching by tartaric acid is about two times that obtained by using the acid mixture. Fig. 4 shows the change in pH and redox potential during leaching. Here also the pH increases and the redox potential decreases during the first leaching day as observed in the case of tartaric acid leaching, and remained constant thereafter. The increasing of pH could be explain by the increasing of Fe and Ni dissolution. Reactions between Fe–Ni oxides and acids decreases the acid concentration and increases the pH of the solution. This could explain the difference of the

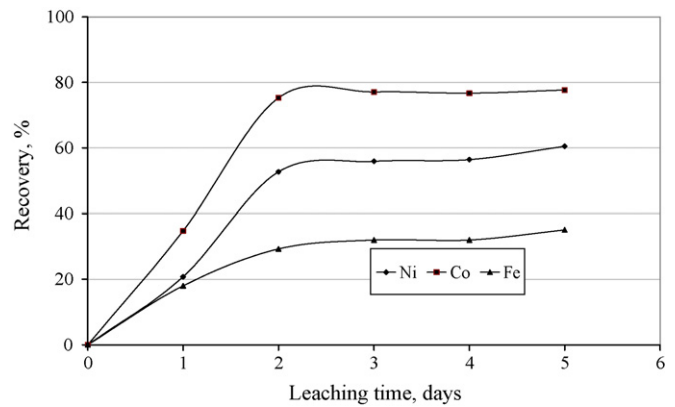


Fig. 3. Metals recovery from the leaching of Ni–Co tailings by means of the mixture of tartaric acid and oxalic acid (acid concentration: 0.15 mol/L tartaric acid and 0.05 mol/L oxalic acid, temperature: 20 °C, flow rate: 10 mL/min).

reaction rates between the first 2 days and the rest of the leaching duration.

3.3. Precipitation and sedimentation of metal salts

The precipitation process at ambient temperature was carried out by maintaining about 1 L of the solution in a conic graduated flask without agitation. Solution obtained after 5 days from the leaching with the mixture of tartaric and oxalic acid was used. The quantity of the precipitate and the pH of the solution were measured every 24 h. Fig. 5 represents the metal content in the solution during the precipitation process and the quantity of precipitate obtained as a function of time. Fig. 6 represents the metal extraction as a function of precipitation duration. About 73% Ni, 73% Co and 48% Fe were extracted from the solution in the first 10 days. After 16 days the precipitation rate increased up to 79% Ni, 78% Co and 52% Fe. By using solutions obtained from the leaching with only tartaric acid only an insignificant quantity of salts was precipitated at ambient temperature after 14 days.

Fig. 6 also shows the pH of the solution during the precipitation process of metal salts at ambient temperature. The decrease of pH could be explained due to the liberation of acid during the

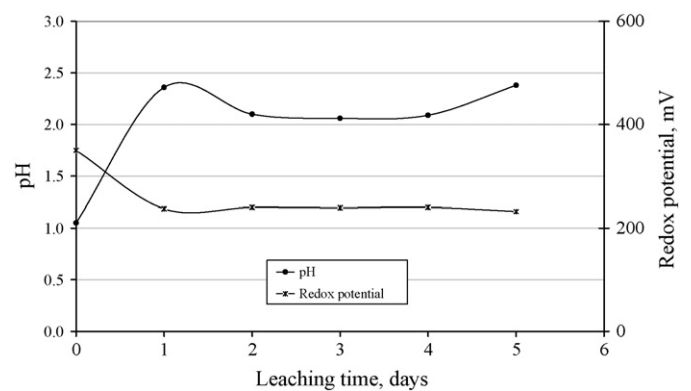


Fig. 4. pH and redox potential of the solution during the percolation leaching (acid concentration: 0.15 mol/L tartaric acid and 0.05 mol/L oxalic acid, temperature: 20 °C, flow rate: 10 mL/min).

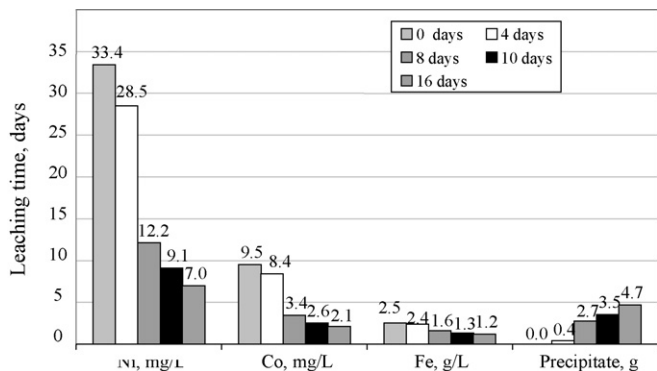


Fig. 5. Metal content in the solution and quantity of precipitate obtained for 1 L as a function of time.

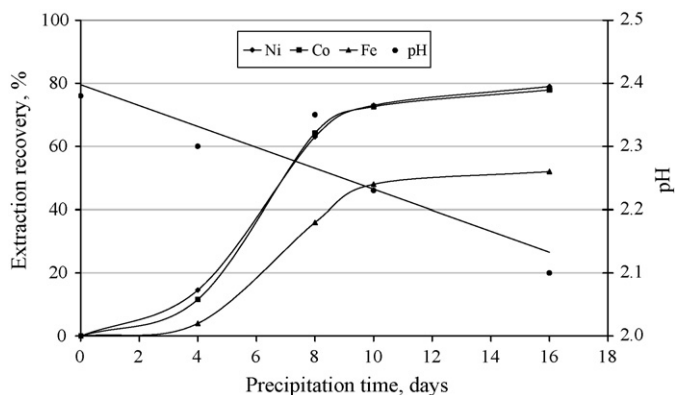


Fig. 6. Metals extraction and pH as a function of precipitation time at ambient temperature.

Table 2
Precipitation recovery at ambient temperature and at 80 °C

	Metal		
	Ni	Co	Fe
Before precipitation (1 L) (%)	100	100	100
Recovery after 4 days at ambient temperature (%)	29.4	48.9	52.2
Recovery after 16 days at ambient temperature (%)	79	78	52
Recovery after heating at 80 °C for 2 h (%)	80	80	52

precipitation process. The X-ray patterns showed that the metal salts in the precipitate are oxalates.

The residual solution from the precipitation at ambient temperature for 16 days containing about 1.2 g/L Fe, 7.0 mg/L Ni and 2.1 mg/L Co was heated at about 80 °C for 2 h. Table 2 shows the metals recovery at ambient temperature and 80 °C. Only an insignificant quantity of salts was precipitated from this

Table 4
Metal contents in the magnetic and non-magnetic products of the secondary tailings from the residues of leaching with mixture of acids (samples from two precipitation tests)

	Magnetic fraction				Non-magnetic fraction			
	Weight (g)	Ni (%)	Co (%)	Fe (%)	Weight (g)	Ni (%)	Co (%)	Fe (%)
Test 1	32.6	0.23	0.03	49.2	3.4	0.20	0.02	20.2
Test 2	35.1	0.20	0.03	50.4	2.9	0.20	0.04	41.0

Table 3
Metal contents in the precipitate before and after thermal treatment as well as the enrichment ratio

	Metal		
	Ni	Co	Fe
Metal contents of the precipitate before heating (%)	0.53	0.14	28.9
Metal contents of the precipitate after heating (%)	1.22	0.33	65.6
Enrichment ratio	2.3	2.4	2.3

final solution. This could mean that the precipitation process was completed at ambient temperature after 16 days.

3.4. Thermal treatment of the precipitate

The objective of thermal treatment of the precipitate was to increase the cobalt and nickel contents by the decomposition of organic salts into inorganic oxides. Table 3 gives the metal contents in the precipitate before and after thermal treatment as well as the enrichment ratio.

An average of 1.3 g of roast product containing 1.2% Ni, 0.3% Co and 65.5% Fe was obtained after heating of about 3 g of precipitate containing 0.5% Ni, 0.14% Co and 28.9% Fe in a muffle furnace at 200 °C for 15 min. This roast product can be fed to the existing nickel plant or used for a Fe–Ni-alloy manufacture. In comparison to the precipitate, an enrichment ratio of about 2.3 was reached for all the metals, nickel, cobalt and iron. Compared to the leaching feed, enrichment ratios of 3:6 for nickel, 4:1 for cobalt and 1:5 for iron were achieved. This corresponds to a global recovery of about 45% Ni, 55% Co and 18% Fe.

3.5. Magnetic separation of the secondary tailings

The objective of the magnetic separation was to increase the iron content in the secondary tailings for use as a raw material in the steel industries. The X-ray patterns show the tailings contain magnetite, fayalite and quartz. It is known that magnetite has a high magnetic susceptibility in comparison to fayalite and quartz. The high intensity magnetic separator was used for that purpose. Table 4 gives the Ni, Co and Fe contents in the magnetic and the non-magnetic products obtained from the feed of around 43% Fe from the residues of leaching with the mixture of acids. The results show the tendency of iron enrichment in the magnetic fraction. Similar results were obtained by Stamboliadis et al. [10] on the magnetic processing of residues from the leaching of laterites with sulphuric acid.

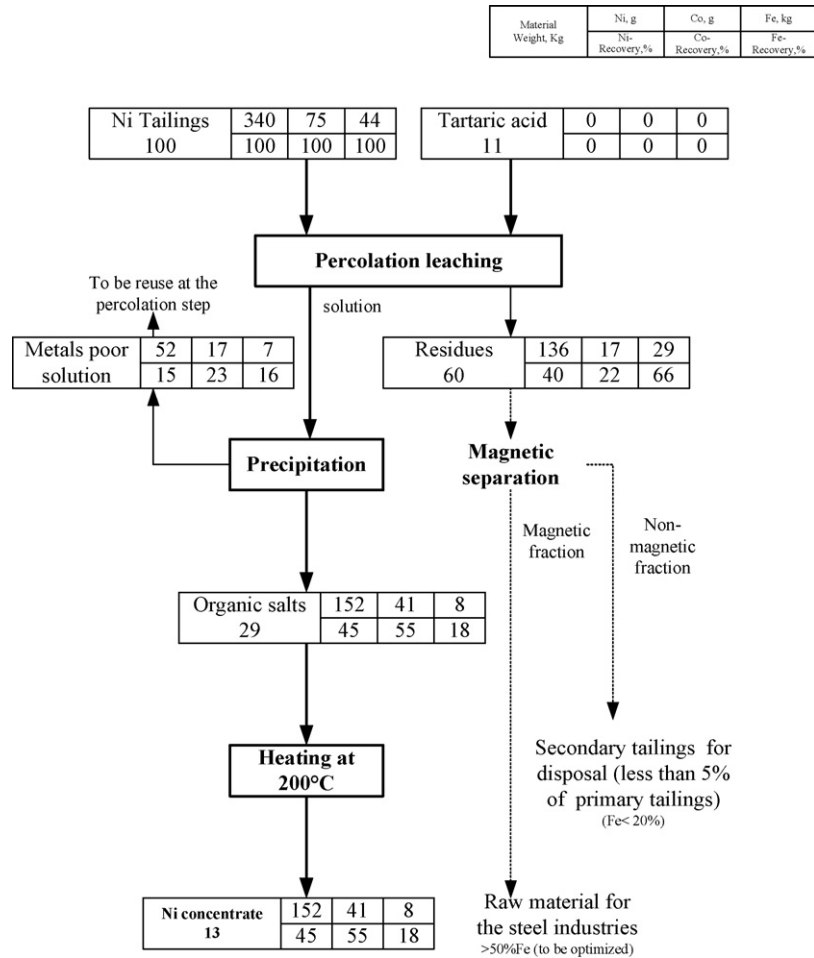


Fig. 7. Proposed flow sheet for the processing of nickel tailings from Moa by means of percolation leaching with organic acids, precipitation and magnetic separation.

3.6. Proposed flow sheet for the processing of nickel tailings from Moa

From the above results the following flow sheet (Fig. 7) has been proposed for the processing of the nickel tailings from Moa. The combination of percolation leaching with tartaric acid, metal salts precipitation from solution, and heating of organic salts at 200 °C can lead to a concentration of nickel and cobalt. In addition, the magnetic separation of leaching residues would lead to a concentrate of iron. This process presents the following advantages: the production of Ni–Co concentrate suitable to be used in the existing nickel–cobalt plant and the reduction of secondary tailings for disposal to about 5% of the primary tailings.

4. Conclusions

The percolation leaching of the Cuban nickel tailings containing 0.34% Ni, 0.08% Co and 44.2% Fe was investigated by using tartaric and oxalic acids.

- About 70% Ni, 80% Co and 30% Fe could be extracted after 5 days leaching with the mixture of 0.15 mol/L tartaric acid and 0.05 mol/L oxalic acid at normal temperature and pressure.

- Extraction of 80% Ni and Co and 50 % Fe from the pregnant solution were achieved by means of precipitation at 80 °C in 2 h. Precipitation at ambient temperature led to similar results after 16 days.
- During the precipitation step, acids are regenerated, which can be reused for leaching.
- Heating the precipitate at 200 °C resulted in a concentrate containing 1.22% Ni and 0.33% Co, which can be fed into the existing nickel plant in Moa, Cuba or used for the Fe–Ni-alloy manufacture. This is corresponding to an enrichment ratio of 3:6 for nickel, 4:1 for cobalt and 1:5 for iron.
- Magnetic processing of leaching residues led to a non-magnetic product containing less than 20% Fe and a magnetic product containing more than 50% Fe, which can be fed to the steel industry.

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