

RECUPERAÇÃO DE NÍQUEL E COBALTO DE MINÉRIOS LATERÍTICOS EMPREGANDO ACIDO CÍTRICO E SULFÚRICO COMO AGENTES LIXIVIANTES *

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Resumo

O níquel tem sido largamente empregado na produção de aço inoxidável, outras ligas metálicas, e na produção de carros elétricos, cujo incremento vem despertando o desenvolvimento de novas rotas tecnológicas para processamento de minérios lateríticos, que representam cerca de 70% dos depósitos mundiais de níquel. O cobalto é um subproduto da fabricação de níquel e, devido às suas inúmeras aplicações em produtos de alta tecnologia e por sua produção estar concentrada em um único país, é considerado uma matéria-prima crítica para a União Europeia.

O presente estudo teve como objetivo comparar o desempenho do ácido sulfúrico e do ácido cítrico, na recuperação de níquel e cobalto de um minério limonítico de níquel empregando a lixiviação atmosférica. Os resultados obtidos indicaram que dentro dos limites fixados para os ensaios realizados, o ácido cítrico apresentou melhor desempenho, com recuperações estimadas de Ni e de Co de 60% e 100%, nesta ordem. Enquanto as recuperações utilizando ácido sulfúrico para Ni e Co foram de aproximadamente 35% e 50%, respectivamente.

Palavras-chave: Níquel; Cobalto; Minério laterítico; Lixiviação atmosférica.

RECOVERY OF NICKEL AND COBALT FROM LATERITIC ORES USING CITRIC AND SULFURIC ACID AS LEACHING AGENTS

Abstract

Nickel has been widely used in the production of stainless steel, other metal alloys, and in the production of electric cars, the increase of which has been impacting the development of new technological routes for processing lateritic ores, that represent around 70% of the world's nickel deposits. Cobalt is a by-product of nickel production and, due to its numerous applications in high technology products and because its production is concentrated in a single country, it is considered a critical raw material for the European Union. The present study aimed to compare the performance of sulfuric acid and citric acid in the recovery of nickel and cobalt from a nickel limonite ore using atmospheric leaching. The results obtained indicated that within the limits established for the tests carried out, citric acid presented the best performance, with estimated recoveries of Ni and Co of 60% and 100%, in that order. While recoveries using sulfuric acid for Ni and Co were approximately 35% and 50%, respectively

Keywords: Nickel; Cobalt; Lateritic ore; Atmospheric leaching.

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1 INTRODUCTION

The deposits of Brazilian lateritic ores of nickel and cobalt, located in the Brazilian states of Goiás, Pará, Piauí and Minas Gerais, have encouraged the development of several projects aimed at developing new technological routes for the production of these metals, since the only Brazilian unit nickel and cobalt producer suspended its activities in 2016 (1).

As a result, due to the high costs of implantation and maintenance of high pressure acid leaching in the processing of lateritic nickel and cobalt ores, atmospheric leaching using inorganic and organic acids has aroused the interest of researchers in the recovery of these metals, with attention being given to selective precipitation processes, using hydroxides, sulphides or hybrid methods for purifying the leached solutions (2).

Atmospheric sulfuric leaching has the disadvantage of not being selective, dissolving Fe, Mg, Mn which are usually contained in lateritic ores. The control of the main process parameters, such as acid concentration, solid-liquid ratio, temperature, leaching time and agitation can minimize the solubilization of these impurities (3).

Among the organic acids, citric acid is the one with the highest nickel recovery, mainly for lateritic serpentine ores, due to its low reactivity with goethite, citric acid has low performance against limonite ores. Furthermore, citric acid shows greater selectivity in nickel leaching over iron and magnesium (4).

Currently, sulfuric acid is the only commercially employed leaching agent. However, due to the low selectivity of this acid, the selective precipitation step of impurities is an arduous task due to the high concentrations of iron, magnesium and aluminum in the leachate solution, which makes its direct use in the solvent extraction of cobalt and nickel impossible. Thus, citric acid is a promising option for leaching lateritic ores. (5).

2 DEVELOPMENT

2.1 Materials and methods

First, the lateritic ore sample was introduced into a y-type homogenizer and then subjected to the formation of conical and longitudinal rectangular piles and quartering using a Jones riffle splitter.

The leaching solutions were prepared from sulfuric (H_2SO_4) and citric ($C_6H_8O_7$) acids, both with a high degree of purity, diluted in distilled water.

Atmospheric leaching tests were carried out in a glass reactor with a capacity of 1.0 liters, with the suspension being heated using a heating mantle coupled to a thermocouple for temperature control.

For the tests using citric acid as a leaching agent, a 2^4 full factorial experiment design with two center points was prepared, with temperature, citric acid concentration, leaching time and liquid/solid ratio as independent variables. While for the tests using sulfuric acid, a 2^3 full factorial experiment design was elaborated, setting the H_2SO_4 concentration at 2.0 M and having temperature, liquid/solid ratio and leaching time as independent variables.

The concentrations of Ni, Co, Fe and Mg in the leaching liquors and washing waters obtained in the leaching tests were determined by atomic absorption spectrophotometry.

2.2 Results

Table 1 shows the X-ray diffraction analyzes performed on the different granulometric fractions of the lateritic ore. The results indicated that the finer fractions are formed by limonite ore, while the coarser fractions are composed by garnieritic ore. In this way, the average sample presents contents similar to an ore from a serpentine zone. This sample heterogeneity must have contributed to the low nickel and cobalt recovery values obtained in the atmospheric leaching tests.

It should also be noted that cobalt was only detected in the ore fractions between 0.038 and 1.00 mm, indicating that leaching separately from the ore fraction smaller than 0.02 mm, which represents 43.2% of the sample, can be a viable alternative.

Table 1. Chemical analysis of the ore by granulometric range using X-ray diffraction and particle size distribution.

Granulometric range (mm)	NiO (%)	Co ₃ O ₄ (%)	Fe ₂ O ₃ (%)	MgO (%)	SiO ₂ (%)	Size Distribution (%)
(<0.02)	1.80	0.00	49.50	6.50	20.90	43.2
(0,038 x 0,02)	1.81	0.12	48.99	7.58	21.75	13.4
(0,045 x 0,038)	1.85	0.18	48.17	9.66	22.81	4.1
(0,063 x 0,045)	1.88	0.23	44.59	10.74	25.05	5.0
(0,090 x 0,063)	1.81	0.20	37.37	13.01	29.09	5.0
(0,125 x 0,090)	1.89	0.28	31.40	14.53	32.15	3.9
(0,180 x 0,125)	1.44	0.32	20.98	16.50	39.75	3.3
(0,250 x 0,180)	1.40	0.18	15.10	18.00	45.6	2.4
(0,350 x 0,250)	1.50	0.25	12.00	20.5	48.5	1.7
(0,500 x 0,350)	1.60	0.25	9.90	22.2	49.7	1.0
(0,710 x 0,500)	1.50	0.21	9.00	23.8	49.8	1.3
(1,00 x 0,710)	1.60	0.16	8.60	24.7	49.2	1.5
(1,40 x 1,00)	1.50	0.11	8.20	25.6	48.8	1.2
(2,00 x 1,40)	1.50	<0,1	8.50	26.4	47.5	1.9
(2,80 x 2,00)	1.40	0.00	8.30	26.40	48.40	1.5
(4,00 x 2,80)	1.40	0.00	8.50	28.40	47.30	2.1
(5,66 x 4,00)	1.40	0.00	8.40	28.50	48.20	1.6
(7,93 x 5,66)	1.30	0.00	7.50	30.50	45.70	2.3
(9,52 x 7,93)	1.40	0.00	7.70	30.70	46.10	1.2
(12,7 x 9,52)	1.10	0.00	7.90	33.00	43.10	1.3
(>12.7)	2.80	0.00	7.60	35.70	37.50	1.1
Calc. Head	1.73	0.08	38.00	12.35	28.50	-

Table 2 presents the operating conditions of the 18 leaching tests carried out with citric acid, the concentrations of Ni, Co, Fe and Mg and their respective recoveries using citric acid.

Despite using an ore with grades similar to Astuti et al (5), the nickel recovery efficiency was lower and the iron and magnesium solubilities were higher. These facts can be attributed to the heterogeneity of the material used and the mineralogical differences between the ores of both studies.

Table 2. Operating conditions, metal concentrations and recoveries of factorial experiment design performed with citric acid.

Test	Temp. (°C)	Liq/Sol (mL/g)	Time (h)	Citric Acid (M)	Concentration (g/L)				Recovery (%)			
					Ni	Co	Fe	Mg	Ni	Co	Fe	Mg
1	30	1.0	2.0	2.0	0.59	0.07	1.27	1.73	8.07	14.79	0.89	4.34
2	80	1.0	2.0	2.0	2.57	0.37	8.32	16.00	42.43	93.49	7.03	48.22
3	30	3.0	2.0	2.0	0.14	0.00	0.34	0.50	0.49	1.44	0.16	1.20
4	80	3.0	2.0	2.0	1.63	0.20	5.89	10.60	0.40	2,2	0.11	0.50
5	30	1.0	6.0	2.0	1.08	0.17	2.31	3.53	10.42	25,30	1.14	6.21
6	80	1.0	6.0	2.0	2.01	0.27	6.76	13.50	28.91	59.93	4.97	35.45
7	30	3.0	6.0	2.0	0.29	0.02	6.54	0.94	6.62	2.79	0.10	8.12
8	80	3.0	6.0	2.0	2.14	0.26	10.10	13.90	3.58	1.21	0.00	3.44
9	30	1.0	2.0	5.0	0.42	0.24	0.97	1.26	4,03	3.51	0.48	2.22
10	80	1.0	2.0	5.0	3.21	0.40	14.50	19.60	46.18	87.67	10.67	51.47
11	30	3.0	2.0	5.0	0.20	0.01	0.49	0.67	0.88	1.25	10.08	24.05
12	80	3.0	2.0	5.0	1.76	0.22	6.45	11.20	22.60	52.74	8.43	50,88
13	30	1.0	6.0	5.0	0.72	0.09	1.62	2.49	8.39	2.51	2.04	32.47
14	80	1.0	6.0	5.0	3.13	0.39	13.30	19.90	56.28	100	12.23	65.32
15	30	3.0	6.0	5.0	0.30	0.02	0.71	1.01	7.50	2.24	1.82	29,05
16	80	3.0	6.0	5.0	1.62	0.19	6.95	10.40	8.39	2.51	2.04	32.47
17	55	2.0	4.0	3.5	2.06	0.26	5.14	10.20	48.49	93.71	4.33	43.83
18	55	2.0	4.0	3.5	1.49	0.17	3.88	7.86	60.50	100	5.64	58.25

The Pareto diagrams constructed by the Statistica 12.0 software shown in Figure 1 indicated that the temperature rise was the only significant parameter in the nickel recovery. While increases in temperature and citric acid concentration favored cobalt recovery.

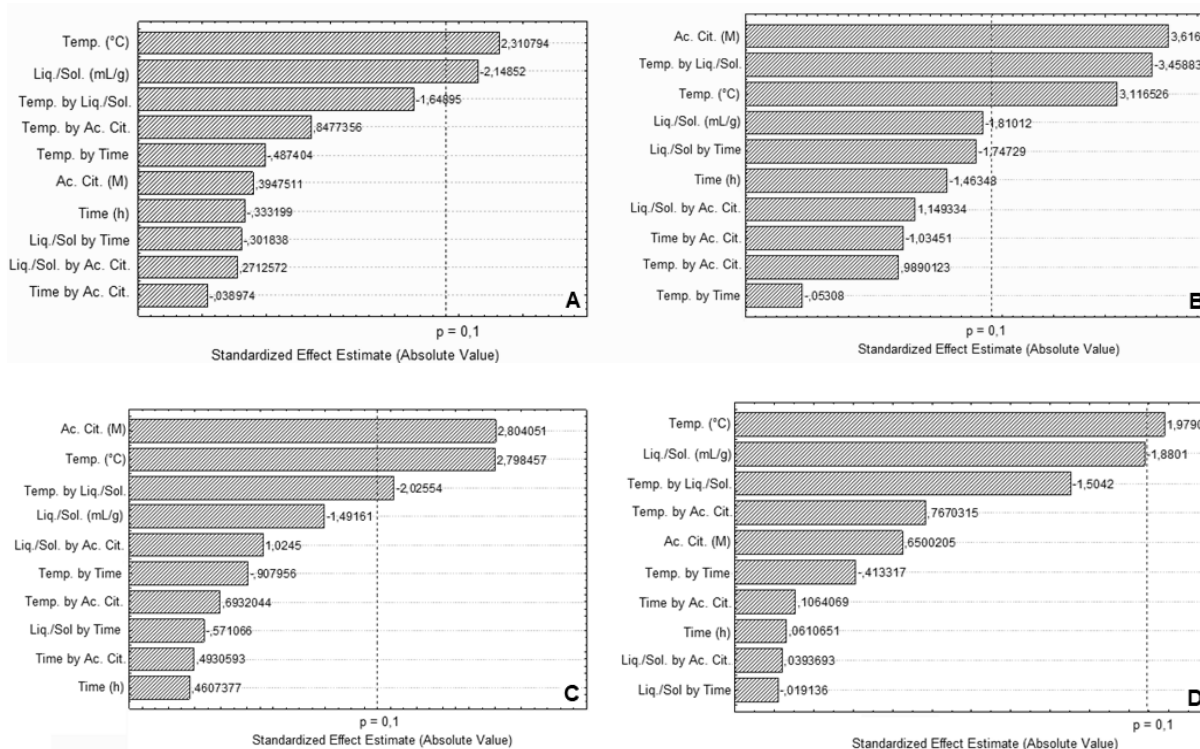


Figure 1. Pareto diagrams for Ni (A), Co (B), Fe (C) and Mg (D) for leaching tests using citric acid.

Increasing temperature reduced the leaching selectivity, favoring both iron and magnesium extraction. While the increase in citric acid consumption only favored the extraction of iron, as can be seen in Figure 1.

The surface graph shown in Figure 2 suggests that if the temperature is kept close to 90°C and liquid-solid ratio of 0.8 (mL/g) nickel recoveries would be close to 60% and 100%, respectively.

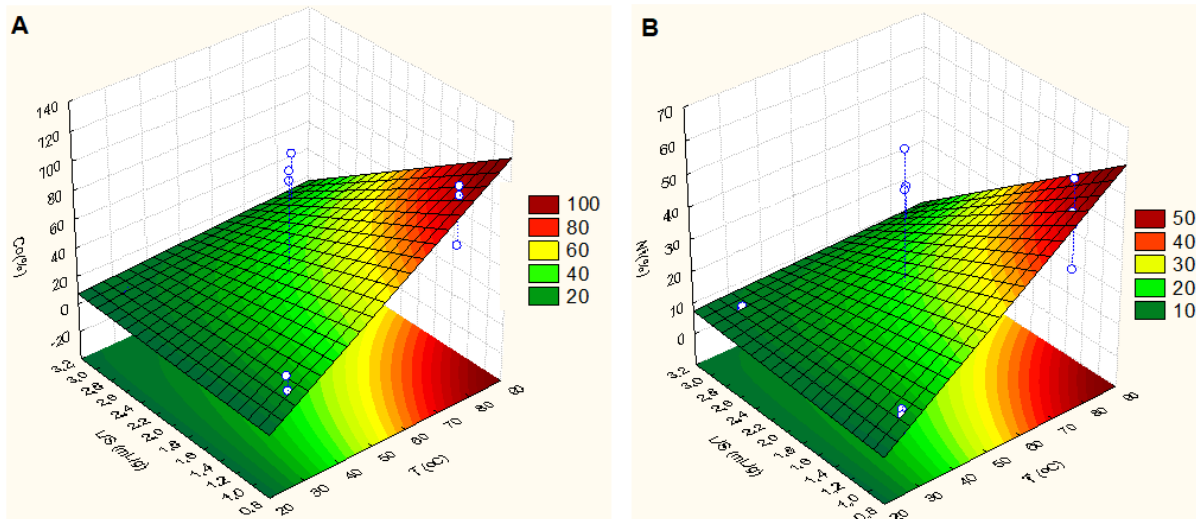


Figure 2. Surface graphs - Influence of temperature and solid-liquid ratio on Co (A) and Ni (B) recoveries for leaching tests using citric acid.

Table 3 presents the operating conditions of the leaching tests using sulfuric acid, as well as the concentrations of Ni, Co, Fe and Mg in the leached solutions and the recovery efficiencies of these respective metals. The results obtained indicated that sulfuric acid had a lower performance than citric acid, as well as a lower selectivity, since the concentrations of iron and magnesium in the solutions were higher.

Table 3. Operating conditions, metal concentrations and recoveries of factorial experiment design performed with sulfuric acid.

Test	Temp. (°C)	L/S (mL/g)	Time (h)	Concentration (g/L)				Recovery (%)			
				Ni	Co	Fe	Mg	Ni	Co	Fe	Mg
1	30	1.0	2.0	0.26	0.01	0.960	1.49	12.72	8.43	2.41	13.31
2	80	1.0	2.0	0.79	0.03	12.71	3.63	38.50	38.36	31.87	32.49
3	30	3.0	2.0	0.76	0.02	3.02	4.77	12.46	8.82	2.52	14.24
4	80	3.0	2.0	1.81	0.07	16.13	14.24	29.54	25.84	13.49	42.50
5	30	1.0	6.0	0.30	0.01	1.25	2.01	14.89	10.74	3.13	18.00
6	80	1.0	6.0	1.06	0.04	4.82	7.45	52.02	42.90	12.09	66.66
7	30	3.0	6.0	1.14	0.09	17.81	4.63	18.66	34.69	14.89	13.83
8	80	3.0	6.0	1.99	0.06	16.09	14.17	32.49	60.40	13.45	42.29

Evaluating the data shown in Figure 3, it can be stated that within the limits set for carrying out the tests with sulfuric acid, only the temperature influenced the nickel recovery. While increases in temperature, solid/liquid ratio and leaching time allowed for greater cobalt recovery. Even being less selective than citric acid, none of the

variables significantly influenced the extraction of iron and magnesium from the lateritic ore.

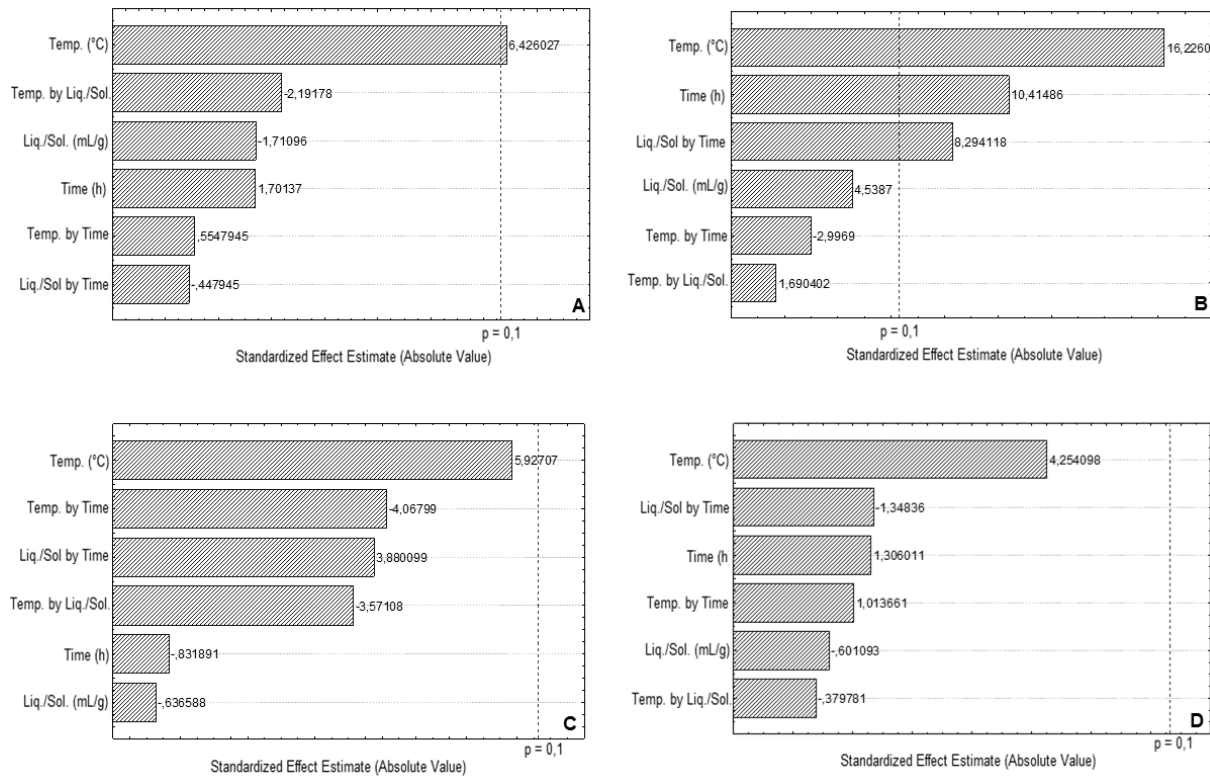


Figure 3. Pareto diagrams for Ni (A), Co (B), Fe (C) and Mg (D) for leaching tests using sulfuric acid.

The surface graphs shown in Figure 4 estimate a nickel extraction close to 35% when the leaching temperature is maintained at 80°C, and a cobalt recovery around 50%, for the same temperature value and 6 hours of leaching.

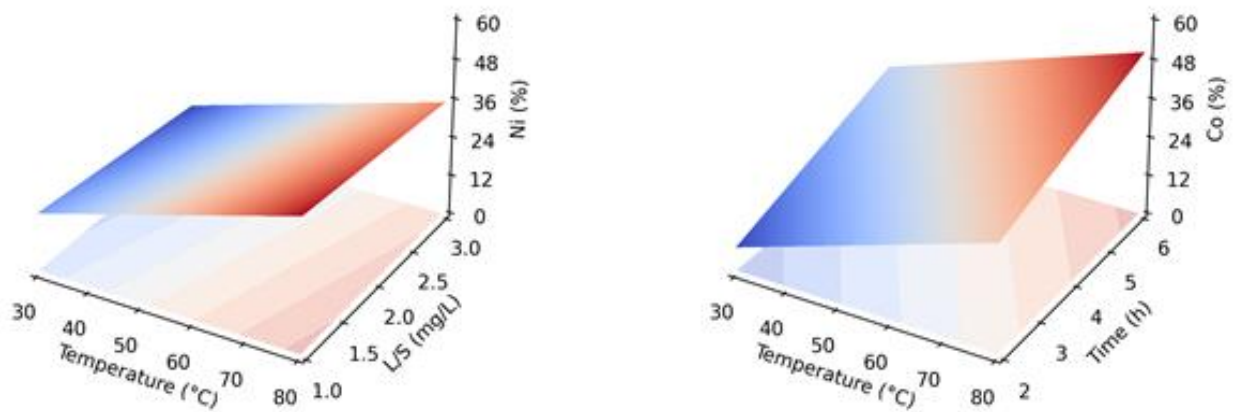


Figure 4. Surface graphs - Influence of temperature and solid-liquid ratio on Co (A) and Ni (B) recoveries for leaching tests using sulfuric acid

3 CONCLUSIONS

Analysis of the ore composition by granulometric range indicated that 43.2% of the sample had limonite characteristics, which certainly must have influenced the cobalt and nickel recoveries.

Citric acid showed better performance and better selectivity when compared to sulfuric acid, estimating a recovery close to 100% of cobalt for leaching temperatures of 80°C and liquid/solid ratio of 0.8 g/L. Under these same conditions, nickel recovery was estimated at 60%.

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