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Dissolution of Nickel and Cobalt from Iron-Rich Laterite Ores Using Different Organic Acids

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Keywords	Abstract
	Due to the decreasing production of nickel and cobalt from sulfide sources, the Ni and Co
Iron-rich laterites	extraction from the oxide ores (laterites) have become more prevalent. In this research work, the effects of calcination prior to leaching, acid concentration, percent solid, pH,
Ni	and stirring speed on the nickel and cobalt recoveries from an iron-rich laterite ore sample were investigated using different organic acids. Then the response surface methodology
Со	was implemented in order to optimize the various parameters. By the design of experiments, the compound optimal concentrations of the three different organic acids
Leaching	(gluconic acid: lactic acid: citric acid with a ratio of 1:2:3) were 3.18 M, and $S/L = 0.1$, pH = 0.5, and the stirring speed = 386 rpm. With the aid of kinetic studies, a temperature
RSM	of 75 °C, and a test time of 120 minutes, the highest nickel and cobalt recoveries were 25.5% and 37.6%, respectively. In the optimal conditions, the contribution of the percent solids to the nickel recovery was the most and negative, after which the contribution of pH was negative, and finally, the acid concentration had a positive effect. In the optimal conditions, the acid concentration, pH, and solid content were, respectively, important in the cobalt recovery. The SEM results showed that the surface of feed and residue particles in the optimal conditions was not significantly different, and the laboratory data was fitted to a shrinking core model. The results obtained indicated that the reaction rate was controlled by the diffusion reaction at the particle surface, and the activation energies of 11.09 kJ/mol for nickel and 28.04 kJ/mol for cobalt were consistent with this conclusion.

1. Introduction

The main application of nickel is to be added to the alloys of other metals [1]. The recent advances have reduced the dependence on nickel sulfide ores and have opened a new vista for use of laterites as a new source of nickel ore [2-7]. On the other hand, a vast majority of cobalt sources have appeared in the laterite ores [8-10]. The use of cobalt as an important strategic metal in the rechargeable batteries, super-alloys, chemical industry, and a wide range of catalytic processes has increased the demands for cobalt. Nowadays, with increasing demand for

cobalt worldwide, the extraction of laterite ores will normally be more important [8, 11].

In many parts of the world, the nickel deposits are formed after weathering. Nickel limonite laterites, the sample of which is also part of this group of latrites, have 1-1.7% of nickel and 0.1-0.2% of cobalt [12]. The extraction of nickel from laterites is based on both the pyrometallurgic and hydrometallurgical methods, shown schematically in Figure 1 [1].



Figure 1. Operations on laterites [1].

The pyrometallurgical method is more suitable for the magnesium-rich saprolitic deposits, which have lower iron and cobalt contents compared to the limonitic deposits [13]. About 61% of nickel production from laterite resources is related to various hydrometallurgical processes [3]. According to Figure 1, the primary hydrometallurgical processes include the caron process, HPAL (high pressure acid leaching), and acidic leaching processes under the atmospheric pressure [1, 14]. Acid leaching takes place at the atmospheric pressure at temperatures below 100 °C and maximum for 12 h. Laterite leaching at the atmospheric pressure is employed for low-grade nickel bearing laterites with low investment costs, and it is used for leaching of limonitic and saprolitic laterites [1, 11, 13, 15].

Among the different types of organic acids used in nickel laterite leaching, citric acid has the highest nickel recovery and a good selectivity of magnesium [3, 12]. Citric acid has been shown to be the most effective organic acid for nickel extraction from the serpentine type laterite ores but due to the low reactivity of citric acid with goethite, this acid is not efficient for the dissolution of nickel from the limonite type laterite ores [8].

Alibhai et al. (1993) have studied the samples of laterite ore. Acetic, formic, lactic, oxalic, citric, and sulfuric acids with the initial concentrations of 0.5 M were applied as the organic and inorganic acids in this work. Sulfuric acid and citric acid removed more than 60% and 40% of the nickel content in highgrade nickel laterites (silica-rich). Oxalic acid percipitated nickel oxalate, and the main parameter of dissulption was the concentration of hydrogen ion. However, complexation with organic anions was also helpful [16]. Tang and Valix (2004) have examined the dissolutions of nickel and cobalt from limonitic and weathered saprolites. In this research work, chemical dissolutions were performed using 1 to 3 M of citric, lactic, and malic acids. The solution acidity, from high to low, contained citric, malic, and lactic acids, respectively. More dissolution of cobalt than nickel in the limonite was due to the fact that in limonite, cobalt was associated with serpentinic minerals and nickel with goethite [17]. According to the other research works, citric acid was the most effective solubilizing agent and oxalic acid had the minimum effect. To explain, this ranking could be as oxalic acid precipitated nickel as nickel oxalate, which had a very low dissolution capacity [18]. Astuti et al. (2015) have stated that the particle size, pulp density, temperature, and leaching solution acidity are the most important factors affecting the dissolution rate and kinetics of laterites [3]. In addition, Astuti et al. (2016) have changed the type of organic and inorganic acids (citric, lactic, oxalic, sulfuric, hydrochloric, and nitric acids, and the composition of citric acid and sulfuric acid (0.75+ 0.25, 0.5 + 0.5, 0.25 + 0.75 and 1 + 1) to leach saprolitic ores. The nickel recovery was 72% when citric acid or sulfuric acid was individually used and it was 43-45% for the combination of nitric acid and hydrochloric acid with a ratio of 1+1, and was 80% when a combination of citric acid and sulfuric acid with a ratio of 0.75:0.25 was applied. It was also found that using sulfuric acid for leaching laterites containing goethite was more appropriate rather than citric acid [19].

Quast *et al.* (2015) have stated that the removal of coarse fraction particles from the feed (with a lower Ni content than that of the finer particles) by dense media separation, gravity separation, magnetic separation, electrostatic separation or flotation compromise no significant upgrading in Ni values because of the complex mineralogy of laterites [20]. Petrus *et al.* (2018) have examined the effect of pulp density and particle size on the leaching of nickel bearing laterite. The experiments were carried out at the ambient temperature with a stirring speed of 200 rpm. The results obtained showed that the nickel recovery increased with decrease in the pulp percent solids. The solid-liquid ratio of 5% would have the highest nickel recovery [12].

The pyrometallurgical methods such as reduction roasting or smelting process of limonitic laterite require a high temperature and consumption of a high energy [21-24]. Electrowinning practice only remained as a suggested flowsheet for nickeliferous laterites [25]. Approaches such as the atmospheric or pressure acid leaching by sulfuric acid or nitric acid as the leaching agent, reductive acid leaching, high concentration chloride leaching, multi-step leaching by nontronite for neutralization of pregnant leach solution of limonite to reduce residual acid concentration or pug-roast-leach process were utilized to process the laterites. These methods use corrosive acids as the dissolution agent that lead to significant waste disposal issues and environmental damages [1, 26-33]. Dissolution kinetics was investigated only for the nickel element, in laterite ores, and mostly using metabolic acids [34]. Although the grade of nickel is normally low in the laterite deposits, a large volume of nickel reserves in the world are of laterite types. In this research work, the grades of nickel and cobalt were high in comparison with most laterite samples in similar research works. On the other hand, the studied sample had a high iron content. Few studies have focused on a combination of the design expert method (to obtain the optimized parameters such as the acid concentration, pH, percent solids, stirring speed) and the classical method (to determine the optimized time and temperature parameters). So far, the kinetic studies and calcination effect prior to leaching on dissolution for cobalt have not been well done or discussed. An examination of the dissolutions of the three elements nickel, cobalt, and iron simultaneously with a large volume of analysis (use of five organic acids, different combined ratios of these acids, and role of organic acids in pH changes) is another important aspect of this research work. Despite the fact that pure organic acids are weak and the nickel and cobalt recoveries will be accordingly low, in the laterite bioleaching, the heterotrophic microorganisms mainly produce citric, gluconic, lactic, and oxalic acids. Comparison of the Ni and Co recoveries of pure organic acids with the recoveries of organic acids from metabolites was the main necessity to do this research work as well.

2. Materials and methods 2.1. Sample

In this research work, a representative laterite sample from east of Sarbisheh, a city in the southern Khorasan province (Iran), was supplied. The proved reserve of this deposit was about 3,700,000 tons. The laterite sample was rich in nickel and cobalt and it had a high iron content. At first, 300 kg of the representative sample was prepared, and it was then reduced by the mixing, quatering, and riffle dividing methods. In the next step, the final sample was pulverized for the XRD, XRF, and chemical analyses.

2.2. Characterization studies

Elemental analysis of the sample showed that the average grades of nickel, cobalt, and iron were 1.74%, 0.14% and 40.83%, respectively. The results of the particle size analyzer (Micro Tec Plus) by the wet sieving method indicated that the laterite particles were fine and in the range of 0.1-100

microns. The d_{25} , d_{50} , and d_{80} of the sample were 2.5, 8.6, and 25.2 microns, respectively (Figure 2). It should be noted that research works have also presented that in small dimensions, the mineral specific surface and the depth of the acid penetration on the mineral surface increase [17]. During the leaching tests, the initial particle size distribution was constant and did not change.



Figure 2. The curves of particle size analysis: i) untreated sample, ii) after calcination (before leaching), and iii) final residue after leaching.

The result of XRF analysis (MAGIX-PRO) showed that 61.4% of Fe₂O₃ was found in the sample, which indicated a high iron content. About 3% NiO and 0.2% Co₃O₄ in the sample was noticeable to compare the sample used with similar laterite samples from other places. There were also 9.2% of silicon dioxide and 5% of aluminum oxide in this sample. XRD analysis (MPD 3000) of this sample showed that quartz (SiO₂), goethite (FeOOH)), gypsum (CaSO₄.2H₂O), hematite (Fe₂O₃), bayerite (Al (OH) $_3$), and calcite (CaCO₃) were the most abundant crystalline phases, and the ore was a nickel-ferrous laterite of goethite type (Figure 3). To do this analysis, counting time: 0.5 s, step size: 0.02, anode: Cu, voltage: 40 Kv, current: 30 mA, and 20: 4-90°. The results of the mineralogical studies confirmed the involvement of goethite crystals in the margins and the non-metallic mineral center with a magnification of 100 in PPL (Figure 4).



Figure 3. Result of XRD analysis.



Figure 4. Scattering of goethite crystals (Go) on the margins and non-metallic mineral (NM) center.

2.3. Thermal pre-treatment

Thermogravimetric Analysis (TGA, TG 209F3 NETZSCH) and Differential Thermal Analysis (DTA) were employed to study the thermal behavior of the laterite sample at the air atmosphere. The result of this analysis is presented in Figure 5. As the laterite sample was heated, goethite as the main phase of sample mineralogy became hematite, through the following reaction (1):

$$2\alpha(FeOOH) \to \alpha Fe_2O_3 \tag{1}$$

As shown in Figure 5, the TG/DTA curve represents the two main endothermic peaks related to the structural changes at temperatures around 300 °C and 700 °C. The first major peak is at about 300 °C, related to goethite dihydroxylation to hematite. The pure goethite dihydroxylation temperature varies between 274 °C and 305 °C depending on the particle size, crystalization, and type and amount of metal substitution within the goethite structure [35]. The second endothermic peak at about 700 °C is related to the removal of the hydroxyl group and the partial decomposition of silicates such as lizardite (reaction 2). This temperature varies between 500 °C and 800 °C for different ores [35].

$$Mg_{3}Si_{2}(OH)_{4}O_{5} \rightarrow Mg_{2}SiO_{4} + MgSiO_{3} + 2H_{2}O \uparrow \qquad (2)$$



Figure 5. Result of TG/DTA analysis.

Figure 5 shows that the highest recoveries of nickel and cobalt occured for samples that were calcinated at a temperature about $300 \degree C$ to $700 \degree C$ prior to the leaching tests. The furnace model used for calcination before leaching of laterite was Nabertherm®.

2.4. Design of experiments (statistical analysis)

The Design Expert 7 (DX7) software was selected to reduce the number of experiments, optimize them, and study the interactions between the parameters [36, 37]. In this research work, the design of the experiments was implemented using the Response Surface Methodology (RSM) method and with the help of the Design Expert 7 (DX7) software. The RSM method is a laboratory technique used to find an optimal response within the specified range for the parameters [10]. Four effective parameters were selected at three different levels to examine the effectiveness of the parameters. These parameters included the concentration of the organic acid with three levels of 2, 3.5, and 5 M, solid to liquid ratio with three levels of 300, 450, and 600 rpm, and initial pH value with three levels of 0.5, 1, and 1.5. These parameters and their levels were chosen based

on the literature reviews [3, 16, 19, 38]. The recoveries of nickel, cobalt, and iron were considered as responses. The reason for the high acid consumption in this work was the high amount of iron found in the laterite sample. It should be noted that in these experiments, the average particle size was constant. In addition, the temperature was 60 $^{\circ}$ C and the leaching time was 2 h.

2.5. Leaching apparatus and experimental method

Direct leaching tests at the atmospheric pressure were carried out in a one-litre glassy reactor (No. 1 in Figure 6). This reactor was immersed in the electrically heated silicone oil bath (No. 2, Figure 6) equipped with a Heidolph mechanical stirrer (HPS-55 model, Germany) that had a digital controller and a teflon impeller (No. 3, Figure 6). A magnetic stirrer (Multi-stirrer DM-8 Scinics, Japan) was used as the base of the set-up (No. 4, Figure 6). The reactor was equipped with a Pyrex glassy lid with standard taper ports for feed entrance through a glass funnel (No. 5, Figure 6), termperature measurment by thermometer (No. 6 in Figure 6), and periodic sampling (No. 7 in Figure 6). A reflux condenser (No. 8 in Figure 6) was placed in one port to prevent evaporation of the solution and reduce losses, especially at high temperatures. The reactor temperature was then controlled with an accuracy of ± 0.1 °C using a thermostat (No. 9 in Figure 6). The schematic design and the experimental set-up are presented in Figure 6.



Figure 6. Schematic design and actual photo of the leaching reactor.

To figure out the effect of calcination, prior to leaching, the initial sample was kept in furnace for 2 h, at different temperatures, and the leaching tests were then done on the calcinated sample. The leaching process would be 2 h to verify its effective parameters as well as the Ni and Co recoveries. The kinetics studies were performed in about 3 h. At the end of the reaction time, the content of the reactor vessel was filtered with a vacuum filter, and the solution was then analyzed by atomic absorption spectroscopy (Varian Spectr AA.220) to determine the concentrations of nickel, cobalt, and iron. The experiments were performed in duplicates, some were randomly repeated for the third time, and the results were averaged.

2.6. SEM/EDS analysis

The surface analysis studies were carried out to investigate the changes in the surface of laterite during chemical leaching. The results of the SEM (FEI QUANTA 450) micrograph with the results of the EDS (BRUKER XFLASH 6/10) elemental mapping of Si, Ni, Co, and Fe for the feed are given in Figure 7A, and for the leaching residue in optimal condition are presented in Figure 7B. As the SEM results show, most particles are round and spherical. The surface of feed particles and leaching residue in optimal conditions are not very different, and are slightly different in terms of polishing.



Figure 7. Left Column: Results of SEM analysis, and Right Column: Results of EDS mapping (A: Feed sample, B: Leaching residue in optimal conditions).

According to the EDS elemental mapping of Si, Ni, Co, and Fe in the right column of Figure 7, the Ni and Co contents in the residue have greatly decreased after the leaching process. However, the amount of Si before and after leaching has not been significantly changed. This can imply that leaching with organic acids is able to dissolve most of the Ni and Co without dissolving Si and producing the gel.

2.7. Kinetic studies

The kinetic tests, with the optimal values of the four mentioned parameters (percent solids, acid concentration, pH, and agitation speed) were performed by changing the temperature and time. The studied temperatures were 30, 45, 60, 75 and 90 °C, and the duration of the tests was 3 h. The required samples were taken at each temperature after 15, 35, 70, 120 and 180 minutes from the beginning of leaching. In the sampling campaign, the mechanical stirrer was turned off for 3 minutes, and after solid settling partially, 5 mL of the sample related to the liquid section from above the liquid surface in reactor were slowly removed using a graduated pipette, and this 5 mL was replaced by a combination of three organic acids with an optimal concentration, which was 3.18 M. On the other hand, 5 mL of the removed sample at each stage in 50 mL balloons increased in volume by mixing of distilled water and 98% concentrated sulfuric acid (mixing ratio can be 100 mL of distilled water and 20 mL of concentrated acid). In other words, at this stage, dilution was made with 10 times of 5 mL. The use of concentrated acid in the volumetric step was to prevent sedimentation of the elements and reaching its pH to about zero. Finally, the atomic absorption analysis determined the grades of nickel, cobalt, and iron at each temperature and at different times.

3. Results and discussion

3.1. Effect of calcination before leaching on nickel and cobalt extraction

According to the literature reviews, pre-heating of laterites changes the mineralogical composition, increases porosity and specific surface area, and makes it more suitable for leaching [39]. In order to investigate the effect of calcination before leaching on the recoveries of nickel and cobalt, using organic acids, at first, the laterite sample without calcination was subjected to leaching. The conditions of these experiments were as follow: percent solids= 20, concentration of each organic acid= 3.5 M, stirring speed= 450 rpm, initial pH= 1.5, leaching time= 2 hours, and the leaching temperature was 60 °C. Then the laterite sample was then subjected to leaching

similar to the sample without calcination. The selection of 500 °C as the calcination temperature prior to leaching was due to achieving higher recoveries of nickel and cobalt compared to the calcination temperatures of 200, 350 and 650 °C, and the explanations were provided about the TG/DTA curve. In addition, the higher temperature of about 700 °C means the burning of the sample. The results of nickel, cobalt, and iron recoveries without calcination and with calcination at 500 °C prior to leaching were tabulated in Table 1.

Table 1. Dissolution of nickel, cobalt, and iron for five different organic acids with and without calcination of laterite samples at 500 °C prior to leaching (S/L= 0.2, concentration of each organic acid 3.5 M, agitation speed= 450 rpm, initial pH value= 1.5, leaching time= 2 h, and leaching temperature= 60 °C).

	Type of organic acid	Ni recovery (%)	Co recovery (%)	Fe dissulotion (%)
	Gluconic	9.27	22.41	0.79
Without calcination of laterite samples	Lactic	8.87	22.12	2.62
	Citric	9.58	22.74	2.31
	Malic	8.11	21.38	1.90
	Oxalic	6.45	3.56	17.62
	Gluconic	9.66	24.85	0.76
With calcination of	Lactic	11.49	24.22	2.02
laterite samples at 500 °C	Citric	11.17	24.54	1.98
prior to leaching	Malic	9.41	23.30	1.64
- 0	Oxalic	7.51	3.88	26.47

A comparison between the recoveries presented in Table 1 shows that the calcinated samples prior to leaching at 500 °C make higher nickel and cobalt recoveries and a lower iron dissolution. Therefore, calcination before leaching at the optimal temperature of 500 °C is necessary for the higher nickel and cobalt extractions; henceforth, grades of the calcined sample prior to leaching at 500 °C. which were 2.3%, 0.17%, and 32.66% for nickel, cobalt, and iron, respectively, were considered as the feed grades in all the leaching tests. On the other hand, the results of the BET analysis showed that the specific surface area, total volume, and average pore diameter before the calcination of the laterite sample were 40.72±0.18 m²/g, 0.073 cm³/g, and 7.17 nm, respectively, and after calcination at the optimal temperature (500 °C) were 183.84±0.44 m²/g, 0.25 cm³/g, and 5.40 nm, respectively. In other words, the specific surface area after calcination increased by 4.5 times, the total volume of pores (due to the exhaust gases) increased 3.4 times, and the average diameter of the pores decreased by 1.3 times due to shrinkage at high temperatures. It should be noted that the BET (TriStar II Plus Micromeritics) analysis is based on the measurement of the volume of the absorbed and desorbed nitrogen gas by the material surface at a constant liquid nitrogen temperature (77 K).

3.2. Effects of pH, acid type, and their combined ratios

In order to evaluate the effect of the type of organic acid on leaching of the laterite sample, five organic acids including gluconic acid, lactic acid, citric acid, malic acid, and oxalic acid were employed. The recoveries of nickel, cobalt, and iron for these five types of organic acids under non-calcination conditions prior to leaching, and in the condition of calcination at 500 °C prior to leaching are given in Table 1. In these experiments, the pH changes before and after the experiments were measured using a pHmeter (Mettler Toledo MP220, Germany). At the beginning of each test, the pH of the acidic solution was adjusted to 1.5 using sulfuric acid. The S/L ratio was 0.2, organic acid concentration= 3.5 M, agitation speed= 450 rpm, temperature= 60, °C and the experiment time was 2 h.

Using oxalic acid, the pH of the pulp decreased from 1.5 to 0.83 after 2 h, which was due to the formation of the nickel oxalate and cobalt oxalate sedimentations. The sediment forms because of the settlement of the low soluble salts. The solubility of oxalic acid in water was also low. The formation of the nickel oxalate sediment liberated and increased the H^+ ions in the solution. Therefore, the pH will accordingly be lower, and the environment more acidic. As noted earlier, the feed was calcinated at the optimal temperature of 500 °C before leaching. Thus according to Table 1, lactic acid, citric acid,

and gluconic acid were chosen as the optimal organic acids due to the higher solubilities of nickel and cobalt, and their combined ratios were in accordance with Table 2 in the subsequent tests. As shown in Table 1 and mentioned in the introduction, a proof of a higher dissolution of cobalt than nickel in the limonite laterites is the fact of cobalt in limonite is associated with serpentinic minerals, and nickel is involved in goethite [17].

Table 2. Effect of combined ratios of organic acids in dissolution of nickel and cobalt from the laterite sample (temperature= 60 °C, time= 2 h, agitation speed= 450 rpm, acid concentration= 3.5 M, percent solids= 20% W/V, and initial pH= 1 5)

and initial $pH=1.5$).							
Test No.	Acid type	Ratio	Co recovery (%)	Ni recovery (%)	Fe recovery (%)	pH_{Final} - $pH_{Initial}$	
1	Gloconic (G)	-	24.85	9.66	0.76	0.71	
2	Lactic (L)	-	24.22	11.49	2.02	1.09	
3	Citric (C)	-	24.54	11.17	1.98	0.68	
4	G:L:C	1:1:1	29.76	11.98	1.96	0.50	
5	G:L:C	1:1:2	29.88	11.96	2.11	0.94	
6	G:L:C	1:2:1	29.84	12.42	2.13	0.52	
7	G:L:C	2:1:1	28.96	11.78	1.82	0.82	
8	G:L:C	1:2:2	29.82	12.17	2.06	0.50	
9	G:L:C	2:2:1	29.37	11.39	1.80	0.69	
10	G:L:C	1:1:0	27.51	10.54	1.34	0.91	
11	G:L:C	1:0:1	31.72	12.40	1.95	0.66	
12	G:L:C	0:1:1	30.51	12.67	2.19	0.56	
13	G:L:C	2:1:0	28.04	10.53	1.20	1.19	
14	G:L:C	0:1:2	31.69	12.02	1.87	0.66	
15	G:L:C	2:0:1	29.87	12.26	2.20	0.70	
16	G:L:C	0:2:1	29.55	11.67	1.95	0.63	
17	G:L:C	0:1:3	30.53	12.08	2.10	0.82	
18	G:L:C	1:0:3	30.93	12.12	2.12	0.38	
19	G:L:C	3:0:1	31.52	13.36	2.81	1.74	
20	G:L:C	3:1:0	27.44	10.24	1.11	1.31	
21	G:L:C	0:3:1	29.42	12.22	2.07	1.00	
22	G:L:C	2:1:2	31.17	13.89	2.55	0.55	
23	G:L:C	1:1:3	30.20	12.12	2.11	0.94	
24	G:L:C	1:3:1	30.31	12.60	2.15	0.52	
25	G:L:C	3:1:1	29.22	12.96	2.55	0.83	
26	G:L:C	3:2:1	28.86	11.71	1.87	0.87	
27	G:L:C	1:2:3	31.72	13.25	1.93	0.42	
28	G:L:C	2:1:3	29.97	12.44	1.94	0.72	
29	G:L:C	2:3:1	29.17	12.02	1.85	1.07	
30	G:L:C	1:3:2	30.14	13.23	2.32	0.53	
31	G:L:C	2:3:2	30.44	12.61	2.13	0.89	
32	G:L:C	2:2:3	28.84	11.96	1.95	0.68	
33	G:L:C	3:2:2	29.80	12.80	2.37	0.76	
34	G:L:C	3:1:2	30.69	12.88	2.35	0.66	

In the last column of Table 2, the effect of pH changes on leaching was tabulated. The pH was measured at the beginning and end of each test. Of course, before running each test, for the sake of uniformity, the pH was adjusted to 1.5 using sulfuric acid. Therefore, the initial pH of each test was 1.5, and the changes of pH obtained after determining the final pH (Table 2). It could be concluded that the only acid whose concentration increased and could cause an increase in the recovery was citric acid. The pH changes in test No. 3 confirm that citric acid is more convienient to reduce the pH value during the test.

Based on the results obtained, the optimal combinated ratios of organic acids among the three ratios with gluconic acid, lactic acid, and citric acid

are in the tests No. 19, 22, and 27. Between these three tests, the test No. 27 was selected as the optimal test. The reason was the presence of all three acids, higher recovery of cobalt, and lower iron dissolution than those of the tests No.19 and 22. On the other hand, in the test No. 27, the ratio of citric acid was more than the tests No.19 and 22, and as mentioned above, citric acid was the only acid among the three acids whose concentration increase could increase the recoveries of nickel and cobalt. Therefore, the selection of the test with the highest proportion of citric acid can lead to higher recoveries of nickel and cobalt simultaneously. The recoveries of nickel, cobalt, and iron were 13.25, 31.72, and 1.93%, respectively. Generally speaking, by increasing the ratio of citric acid and gluconic acid, the final pH was lower and higher, respectively. Increasing the lactic acid ratio, compared to citric acid and gluconic acid, causes the least change in the final pH.

3.3. Design of experiment and optimization

The experimental design approach was employed to determine the optimized values of the optimal concentration of organic acids (gluconic acid, lactic acid, and citric acid at a ratio of 1: 2: 3), pH, optimal solid content, and optimal stirring speed. In general, according to the results of the experimental design approach, it can be concluded that for two tests with identical conditions but different pH values, although the increase in pH value reduces iron dissolution in the solution, which is in favor of the process, the recoveries of nickel and cobalt decrease in the solution.

3.3.1. Optimization of nickel dissolution

Analysis of variance (ANOVA) for nickel dissolution in the leaching process by organic acids presented that the three parameters acid concentration, percent solids, and pH had significant effects on the nickel recovery.

The F-value of the model was 172.48. Only 0.01% was likely to produce an F-value with this magnitude, which was due to noise. The p-value of the model was less than 0.05, and therefore, the model was meaningful. The p-value of 0.0001 for acid concentration, S/L, and pH indicated that in the model, the effects of acid concentration, solid content, and pH on the Ni recovery were very important. The R-Squared value of 0.9906 indicated that there was a good correlation between the laboratory and predicted values for the Ni recovery. The Adeq. Precision for Ni was 68.11, meaning that the ratio of the effective parameters considered to be the noise and parameters that were effective but not considered were 68 times. Formula (3) gives the nickel recovery in terms of the four effective parameters and their interaction.

Recovery Ni
=
$$+29.53 + 4.84$$
 Acid concentration
- 167.37 S/L + $8.33E$
- 003 Agitation speed - $10.77pH$
+ 0.064 S/L × Agitation speed
+ 7.97 S/L × pH - $5.53E - 003$
× Agitation speed × pH
- 0.77 (Acid concentration)²

$$-005$$
 (Agitation speed)² + 4.43 (pH)²

It can be seen that the contribution of the percentage of solids is more than others but with a negative effect (the more solids, the recovery is less). Afterwards, the pH parameter is negatively affected, and finally, the acid concentration has a positive effect, and the agitation speed parameter is almost ineffective in nickel recovery. The positive coefficients in this formula show a positive effect and the negative coefficients indicate a negative effect on the nickel recovery. By increasing the solid content, the solvent contribution to the free surface decreased, resulting in a dissolution reduction, and consequently, recovery reduction as well. According to the research work done by Petrus et al. (2018), by increasing the solid content, the amount of leaching agent (liquid) will be insufficient to dissolve the metals present in the laterite [12]. Kursunoglu and Kaya (2016), by combining the results from the Littlejohn's work in 2007 and the MacCarthy's work in 2014, described the following reasons for recovery reduction by increasing the solid-to-liquid ratio in laterite leaching [13]:

1) Increasing the amount of silica in the sample creates a diffusion layer on the surface of particle,

2) Access to the unreacted surfaces is limited; H⁺ penetration is limited due to the formation of solid porous layer of the product on the particle surface,

3) Slower leaching of resistant minerals such as hematite and goethite.

Figure 8 shows the 3D models obtained by Formula (3). This model presents the direct interaction between the acid concentration and nickel recovery, and the indirect interaction between the solid content and the nickel recovery. By increasing the acid concentration, minerals such as asbolane and goethite/hematite, which contain more amounts of nickel and cobalt, are more reactive.

In other words, in accordance with Figure 8a, in order to achieve the maximum recovery of nickel, the acid concentration should be high, and the solid content should be low as well. According to Figure 8b, the pH and solid content should be low to achieve the maximum recovery of nickel. Reducing pH increases the reactivity of minerals containing high amounts of nickel and cobalt such as asbolane and goethite/hematite. In accordance with Figure 8c, the low percentage of solid and optimal agitation speed obtain the maximum recovery of nickel.



Figure 8. 3D model of recovery changes versus percent solids and acid concentration for nickel (A) and cobalt (D). Recovery changes versus percent solids and pH for nickel (B) and cobalt (E). Recovery changes versus percent solids and agitation speed for nickel (C) and cobalt (F).

3.3.2. Optimization of cobalt dissolution

Analysis of variance (ANOVA) for cobalt dissolution in the leaching process by organic acids showed that the three parameters acid concentration, percent solids, and pH had significant effects on the cobalt recovery. The F-value of the model was 44.28, and therefore, the model was meaningful. Only 0.01% was likely that this magnitude of F-value could be produced because of the noise. The p-value of the model was less than 0.05, and therefore, the model was meaningful. The R-Squared value of 0.9764 indicated that there was a good correlation between the laboratory and predicted values in the cobalt recovery. Adeq Precision of cobalt was 25.79, meaning that the ratio of the effective parameters considered was 15 times to noise and the parameters that were effective but not considered. The cobalt recovery in terms of the four effective parameters and their interaction is presented in Formula (4):

Recovery Co = +13.57 + 12.42 Acid concentration - 8.97 S/L + 0.029 Agitation speed - 12.21 pH - 15.29 Acid concentration × S/L + 5.66E - 003 Acid concentration × Agitation speed + 2.03 Acid concentration × pH - 0.037 S/L × Agitation speed + 26.84 S/L × pH - 0.026 Agitation speed × pH - 2.00 (Acid concentration)² + 34.65 (S/L)² - 1.86E - 005 (Agitation speed)² + 3.16 (pH)²

Based on the results obtained, the contribution of acid concentration is the highest and positive (the more the acid concentration, the recovery is more), after which the contribution of the pH parameter and afterwards the percentage of solid are negative, and the agitation speed is least effective on the cobalt recovery.

According to Figure 8D, in order to achieve the maximum recovery of cobalt, the acid concentration should be high and the percent solids should be low. As the acid concentration increases, the cobalt recovery increases due to increase in the H⁺ ions in solution and more cobalt dissolution. The plot slope of solid percentage in the pulp versus cobalt recovery is higher than the plot of agitation speed slope versus cobalt recovery, indicating a greater effect of solid percentage on the pulp than the agitation speed on the cobalt recovery. When the percent solids is 10%, the increase in acid concentration is more effective on the cobalt recovery compared with 30% solids in the pulp. As shown in Figure 8E, in order to achieve the highest recovery of cobalt, the pH and solid content should be low. In other words, as the acidity of the pulp increases, the H⁺ ion in the solution increases and more amount of cobalt can be dissolved. As the solid-liquid ratio increases, the pH of the pulp increases; the proof is that in less liquid-to-solid ratios, protons are consumed more quickly. Figure 8F presents that in order to achieve the highest recovery of cobalt, the percentage of pulp solids should be the lowest and the agitation speed should be optimum.

According to the software calculations, the optimal amounts of the parameters that have the highest recoveries of nickel and cobalt simultaneously in the leaching, with the optimal combination of the three organic acids, include the concentration of the optimal combination of organic acids=3.18 M, S/L=0.1, pH=0.5 and the agitation speed= 386 rpm. The highest recoveries of nickel and cobalt according to software calculations were 20.88% and 35.69%, respectively. The recoveries of nickel and cobalt in the validation test under the optimal condition were 21.48% and 35.78%, respectively. The recovery for Ni is, therefore, comparable to 20% determined by Valix et al. (2001) in the citric acid leaching tests [40]. In addition, the highest recovery of Ni in the leaching process of Pomalaa nickel laterite by Wanta et al. (2017) using citric acid as the leachant was 12% at the atmospheric condition and a particle size finer than 75 microns, temperature= 85 °C, citric acid concentration= 0.1 M, pulp density= 20% (w/v), and the leaching time=120 minutes [41].

3.4. Effects of temperature and time on recoveries The kinetic study was carried out with the optimal values of the four parameters acid concentration, percent solids, stirring speed, and pH (as mentioned above), with changing temperature and time. Approximately 1.1 mL of concentrated sulfuric acid was used to adjust pH to 0.5. According to Figures 9A and 9B, by increasing the leaching time, the recoveries of nickel and cobalt increase. The most suitable temperature and test time for leaching the laterite sample using the optimal combination of organic acids were 75 °C and 2 h, respectively. After 2 h, the recoveries of nickel and cobalt remained fairly constant. Therefore, the optimal combined concentration of the three organic acids was 3.18 M. S/L= 0.1, pH= 0.5, agitation speed= 386 rpm, temperature 75 °C, and test time = 120 minutes yielded the highest recoveries of nickel and cobalt, which were 25.5% and 37.6%, respectively. Increasing the temperature up to 75 °C had a positive effect on the recoveries of nickel and cobalt. At the studied temperatures, nickel and cobalt were extracted more efficiently than iron. This was due to the higher contents of nickel and cobalt in goethite than in hematite. It should be noted that at a temperature about 300 °C, goethite was converted to hematite [35].

According to Figure 9, the extraction rate was fast at the beginning of leaching. During the first 15 minutes, the maximum extractions were 31.2% for cobalt and 13.83% for nickel; the cobalt and nickel extractions after 120 minutes reached a maximum of 37.6% and 25.5%, respectively. After 2 h of leaching, the dissolution rates of nickel and cobalt were negligible and remained fairly constant. The reason was that during the time, the remaining nickel and cobalt in solution were associated with the resistant minerals and the dissolution rate was slow. Another consequence of Figure 9 is that if organic acids are used as the dissolution agents, the cobalt recovery is more sensitive to temperature than the nickel recovery. However, if sulfuric acid was used as the dissolution agent, the nickel recovery was more sensitive to temperature than the cobalt recovery [42]. It should be noted that the organic acids are environmentally friendly than the mineral acids. The high acid consumption in this work was

due to the considerable amount of iron [43]. As shown in Figure 9, the recovery rate was expected to increase as temperature rised but this process continued to the temperature of 75 $^{\circ}$ C and then decreased at 90 $^{\circ}$ C. The reason is the structure of lactic acid, which changed at high temperatures [44]. This change in the structure leads to a reduction in the acidity of lactic acid, which reduces the acidity of the optimal composition of organic acids, and it, therefore, leads to the reduction in the nickel and cobalt recoveries.



Figure 9. Nickel and cobalt recoveries at different temperatures and times (combined concentration of organic acids=3.18 M, pH= 0.5, S/L= 0.1, agitation speed= 386 rpm).

In order to evaluate the effect of sulfuric acid used for pH adjustment, two separate leaching tests were carried out under the optimal conditions and a temperature of 75 °C for 2 h. One of these experiments included the dissolutions of nickel, cobalt, and iron by a combination of organic acids without adding sulfuric acid to adjust pH, and another experiment was the dissolutions of nickel, cobalt, and iron by sulfuric acid alone and without adding organic acids. In the experiment, using merely sulfuric acid, an identical amount of sulfuric acid (1 mL) to adjust pH and a temperature of 75 $^{\circ}C$ was used, and the volume was reached to 100 mL with distilled water, and then a dissolution test was performed. In the experiment with sulfuric acid, the recoveries of nickel, cobalt, and iron were 5.04%, 9.82% and 1.09%, respectively. In the experiment, with a combination of organic acids without pH adjustment, the recoveries of nickel, cobalt, and iron were 16.94, 23.87, and 4.05%, respectively. It can be concluded that the droplets of sulfuric acid used to adjust the pH have little effect on the recoveries of nickel, cobalt, and iron, and the optimal combination of organic acids plays a major role to increase the recoveries of nickel and cobalt. The pH adjustment by sulfuric acid to 0.5 resulted in an increase of about 9% in the nickel recovery and about 14% in the cobalt recovery.

3.5. Kinetic studies

Leaching of minerals can be demonstrated using various models. One of the models developed to play an important role in the kinetic expression of the dissolution process in non-catalytic solid-liquid environments is the shrinking core model [45, 46]. The choice of the heterogeneous reaction model depends on the fact that the particle size does not change with leaching and calcination treatments [47]. In order to investigate whether the kinetics of the dissolution process of the laterite sample follows the shrinking core model, the size distribution of the feed sample (calcinated sample prior to leaching in a furnace at a temperature of 500 °C for 2 h) and the size distribution of the solid residue of leaching by organic acids under optimal conditions were determined. The results obtained show that the

calcinated feed particles prior to leaching and solid residue of leaching under optimal condition, as the initial sample without calcination in Figure 2, were fine grain and in the range of 0.1-100 microns. The particle size distribution of calcined feed prior to leaching is not significantly different from the particle size distribution of solid residue of leaching in optimal conditions. In other words, the size distribution before and after leaching has not changed. According to Figure 2, the d₂₅, d₅₀, and d₈₀ for the calcined feed sample at 500 °C for 2 h were 5.6, 15.1, and 30.1 microns, respectively, and the d₂₅, d_{50} , and d_{80} for the solid residue obtained from leaching under optimal condition were 5.1, 16.9, and 33.8 microns, respectively. By checking the graphs, it can be concluded that calcination of the feed sample before leaching would result in partially coarser grains of feed particles but calcined feed before leaching is still fine-grained. In Table 3, a set of dissolution mechanisms is presented with their equations, in which x: the reacted fraction, k: the kinetic constant (reaction rate constant), and t: the reaction time [48].

	Table 3. Equations and mechanisms for dissolutions [48].							
Eq. No.	Model	Mechanism						
1	$K_t = 1 - (1 - X)^{\frac{1}{3}}$	Chemical reaction control						
2	$K_t = 1 - (1 - X)^{\frac{2}{3}}$	Mixed control model by shrinking core model (diffusion control; chemical reaction control)						
3	$K_t = [1 - (1 - X)^{\frac{1}{3}}]^2$	Diffusion through product layer						
4	$K_t = -\ln(1-X)$	Mixed control model (surface reaction control; diffusion through sulfur layer)						
5	$K_t = 1 - \frac{2}{3}X - (1 - X)^{\frac{1}{3}}$ $K_t = 1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}$	Diffusion through a porous product layer by shrinking core model						
6	$K_t = 1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}$	Diffusion control						
7	$K_t = \frac{1}{3} \ln(1 - X) + [(1 - X)^{\frac{-1}{3}} - 1]$	Interfacial transfer and diffusion across the product layer						
8	$K_t = 1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X)$	Diffusion of hydrogen ions through a product layer by shrinking core model						
9	$K_t = 1 - (1 - 0.45X)^{\frac{1}{3}}$	Surface chemical reaction by shrinking core model						

Table 3. Equations and mechanisms for dissolutions [48].

In order to determine the control mechanism of the acidic leaching of the laterite sample, the laboratory data of leaching was fitted with a shrinking core model (equations in Table 3). This model assumes that the solid particle volume retains, while its non-reactive core constantly shrinks with the reaction time, and leads to the formation of a porous layer [49]. In heterogeneous solid-liquid reactions, the soluble reactants penetrate through common surfaces and/or within the solid porous layer, and then the chemical reactions occur. The reaction velocity is controlled by the reactant penetration through a soluble boundary layer or through the release from a solid product layer or through the rate of chemical reaction at the core surface of non-

reactive particles [35, 50]. The slowest stage determines the velocity of the leaching reaction [35]. Among the different models presented in Table 3, the two diffusion control and chemical control models (Equations 5 and 6) have the best fitting on the nickel and cobalt data.

$$k_t = 1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}$$
(5)

$$k_t = 1 - (1 - X)^{\frac{1}{3}} \tag{6}$$

The application of the kinetic models of diffusion and chemical controls at different temperatures for the optimal composition of organic acids is presented in Figures 10A to 10D.



Figure 10. Kinetic modeling of laterite sample dissolution for the nickel and cobalt at 30 °C to 90 °C. Left side: Diffusion control. Right side: Chemical control.

The values of reaction velocity constants and correlation coefficients for nickel and cobalt at different temperatures are given in Table 4. According to the results and the correlation coefficients obtained from this table, the diffusion control model has a better fit compared with the chemical control, especially for nickel.

temperatures.								
	Ni				Со			
	Diffusion	control model	Chemical control model		emical control model Diffusion control model		Chemical control model	
Temperature (°C)	\mathbb{R}^2	$k (\min^{-1})$	\mathbb{R}^2	$k (\min^{-1})$	\mathbb{R}^2	$k (\min^{-1})$	\mathbb{R}^2	$k (\min^{-1})$
30 (Part 1)	0.9887	4.00E-05	0.9718	0.0011	0.9941	6.00E-05	0.9629	0.0013
30 (Part 2)	0.8632	1.00E-05	0.8526	0.0001	0.9178	2.00E-05	0.8974	0.0002
45 (Part 1)	0.9995	6.00E-05	0.9445	0.0012	0.9660	0.0002	0.9922	0.0023
45 (Part 2)	0.8485	2.00E-05	0.8420	0.0002	0.8718	1.00E-05	0.8607	8.00E-05
60 (Part 1)	0.9991	6.00E-05	0.9254	0.0013	0.9575	0.0003	0.9962	0.003
60 (Part 2)	0.8867	2.00E-05	0.8801	0.0002	0.8811	1.00E-05	0.8765	7.00E-05
75 (Part 1)	0.8873	9.00E-05	0.7961	0.0016	0.7956	0.0004	0.7410	0.0035
75 (Part 2)	0.8623	4.00E-05	0.8622	0.0003	0.8258	3.00E-05	0.8187	0.0001
90 (Part 1)	0.9401	8.00E-05	0.8372	0.0015	0.8273	0.0004	0.7596	0.0033
90 (Part 2)	0.8690	3.00E-05	0.8637	0.0002	0.6919	2.00E-05	0.6834	1.00E-04

 Table 4. Values of reaction rate constant and correlation coefficients for nickel and cobalt at different temperatures.

The Arrhenius relationship was employed to obtain the activation energy values. Using the Arrhenius equation, k= A exp (-E_a /RT), and plotting -ln kversus 1000/T yeilds a line with the E_a/R slope. In this equation, k: reaction rate constant, E_a: activation energy (kJ/mol), R: ideal gas constant (8.314 J[°]K⁻¹ mol⁻¹), T: absolute temperature (K), and A: exponential function coefficient. The plot was drawn for two control models, and the activation energy values were then calculated. The plot of these charts and the values of the correlation coefficients are shown in Figure 11.



Figure 11. Graph of -ln k versus 1000/T to calculate the activation energies for nickel and cobalt; Left side: Diffusion control model. Right side: Chemical control model.

Figures 11A and 11B show that in the diffusion controls for nickel and cobalt, the correlation coefficients are acceptable, and are $R^2 = 0.8366$ and $R^2 = 0.843$, respectively. The use of Arrhenius relationship defines the activation energies of nickel and cobalt for the diffusion control models, as follows:

 $E_a = 11.09 \text{ kJ/mol}$

 $E_a = 28.04 \text{ kJ/mol}$

The activation energies of nickel and cobalt for the chemical control equation were obtained as follow:

 $E_a = 5.58 \ kJ/mol$

 $E_a = 14.29 \text{ kJ/mol}$

According to Table 4 and the values of activation energies, the diffusion control model has a more convienient fitting, and the obtained E_a values are within the limits of diffusion control reactions. Generally, the activation energy for the diffusion control is less than 20 kJ/mol, and for the chemical control greater than 40 kJ/mol [51, 52]. The process of diffusion control is slightly dependent on the temperature but a process with the chemical control highly depends on the temperature [45]. Since the equation of diffusion control was well-fitted on the dissolution data of laterite at different temperatures and the activation energy lied within the limits of diffusion control, it could accordingly be stated that the diffusion control was more effective on laterite dissolution than the chemical control. Wanta *et al.* (2017) have concluded the internal diffusion controlled shrinking core model for the leaching process of Pomalaa nickel laterite using citric acid as the leachant [41].

4. Conclusions

In this research work, the dissolution behavior of nickel and cobalt from the iron-rich laterite sample using different organic acids was examined. The main results of this work can be summarized as follow:

- Lactic acid, citric acid, and gluconic acid with a combination ratio of 1: 2: 3 were chosen as the optimal combination of organic acids due to the higher solubility of nickel and cobalt.
- The contribution of percent solids to nickel and cobalt recoveries was the highest and negative, followed by the contribution of the pH parameter as negative, and eventually, the acid concentration as positive. The parameter of agitation speed in the recoveries of nickel and cobalt was almost effectless.
- The optimal concentration of the combination of three organic acids= 3.18 M, and S/L= 0.1, pH= 0.5, agitation speed= 386 rpm, temperature= 75 °C, and time= 120 minutes yeilded the highest recoveries of

nickel and cobalt, which were 25.5% and 37.6%, respectively.

- The laboratory data was fitted to the shrinking core model. The results obtained showed that the reaction rate was controlled by the diffusion reaction, and the activation energies of 11.09 kJ/mol for nickel and 28.04 kJ/mol for cobalt were also consistent with this conclusion.
- According to elemental mapping of EDS, the leaching by organic acids has allowed Ni and Co to be dissolved without dissolving Si and produce the gel.

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Conflict of interest

The authors claim that they have no conflict of interest.

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انحلال نیکل و کبالت از سنگ معدنهای لاتریتی پر آهن با استفاده از اسیدهای آلی مختلف

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چکیدہ:

بدلیل کاهش تولید نیکل و کبالت از منابع سولفیدی، استخراج نیکل و کبالت از سنگ معدنهای اکسیدی (لاتریتها) رواج پیدا کرده است. در این تحقیق، تأثیر کلسیناسیون قبل از لیچینگ، غلظت اسید، درصد جامد، pq و دور همزن بر بازیابیهای نیکل و کبالت از نمونه لاتریتی پرآهن با استفاده از اسیدهای آلی مختلف مورد بررسی قرار گرفت. سپس روش سطح پاسخ برای بهینه سازی پارامترهای مختلف بکار رفت. با استفاده از طراحی آزمایش، غلظت بهینه ترکیب سه اسید آلی مختلف مورد بررسی قرار گرفت. سپس روش سطح پاسخ برای بهینه سازی پارامترهای مختلف بکار رفت. با استفاده از طراحی آزمایش، غلظت بهینه ترکیب سه اسید آلی مختلف (اسید گلوکونیک: اسید لاکتیک: اسید سیتریک با نسبت 12:2) برابر با M S/L=0/1 آما بهینه برابر با 5/0 و دور بهینه همزنی 386 دور بر دقیقه مختلف (اسید گلوکونیک: اسید لاکتیک، در مدهای 75 درجه سانتیگراد و مدت زمان 120 دقیقه از انجام آزمایش، بالاترین بازیابیهای نیکل و کبالت بدست آمد که بود. به کمک مطالعات سینتیکی، در دمای 75 درجه سانتیگراد و مدت زمان 120 دقیقه از انجام آزمایش، بالاترین بازیابیهای نیکل و کبالت بدست آمد که منفی 2016 در صد بود. در شرایط بهینه، سهم پارامتر در صد جامد بر بازیابی نیکل از همه بیشتر و با تأثیر منفی، پس از آن سهم پارامتر H PH با تأثیر بنیکی و در نهایت نیزیابی منهای بیکل و کبالت بدست آمد که منفی و در نهایت غلظت اسید با تأثیر مثبت بود. در شرایط بهینه، بترتیب غلظت اسید، بالاترین بازیابی کبالت دارای اهمیت بودند. نتایج EM منفی و در نهایت غلظت اسید با تأثیر مثبت بود. در شرایط بهینه، بترتیب غلظت اسید، HP و درصد جامد در بازیابی نیکل از همه بیشتر و با تأثیر منفی، پس از آن سهم پارامتر HP با تأثیر منفی و در نهایت غلظت اسید با تأثیر مثبت، سهم پارامتر در صد جامد بر بازیابی نیکل از همه بیشتر و با تأثیر منفی، پس از آن سهم پارامتر در مد جامد بر بازیابی نیکل از همه بیشتر و دادهای آن مان تی بود. تأثیر منفی و در نهایت غلظت اسید با تأثیر مثبت بود. در شرایط بهینه، بترتیب نیکل از همه بیشتر و باز بازش منفی در بازش داد که سرعت واکنش با و اکنش نوده در سرایم باین بازگار بود. نیکل و اماله در ازش داده مدر نمان داد که سرعت واکنش با واکنش نفوذی در سطح ذرات کنترل می شود و انرژی هارای از ال

کلمات کلیدی: لاتریتهای پرآهن، نیکل، کبالت، لیچینگ، RSM.