

The effect of inorganic acids on reducing iron impurities during iron-rich laterite ore leaching

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ABSTRACT

The recovery of nickel from lateritic ores as the main oxide resources has been always debated. Since it consists of 1.74% Ni, 0.14% Co and 40.8% Fe, co-dissolution of iron occurred by using common lixiviation like sulfuric acid. Therefore, some leaching agents should be sought due to promoting a high dissolution of nickel/cobalt and negligible iron recovery. This research investigates the effect of using organic acids such as gluconic, lactic, and citric acid along with sulfuric acid on recoveries of Ni/Co from iron-rich laterite ore. The results showed that adding sulfuric acid to the optimal combined ratio of the organic acids (gluconic: lactic: citric= 1: 2: 3) to obtain the combined ratio of 6 : 1: 2: 3 (sulfuric: gluconic: lactic: citric acid), simultaneously increasing the temperature from 60 to 90 °C, and increasing the final combined concentration of the acids from 3.5 M to 5 M, significantly increased nickel and cobalt recoveries by 80.4 and 68.7%, respectively, and slightly increased iron extraction by 5.05% all when compared to using the optimal combined ratio of organic acids. The use of 5 M sulfuric acid alone as a leaching agent, at 90 °C, resulted in an 81.11% increase in iron dissolution than the 6: 1: 2: 3 combination. The obtained results indicated that the reaction rate was controlled by the chemical reaction, and the activation energies of 42.71 kJ/mol for nickel and 84.57 kJ/mol for cobalt were consistent with this conclusion, respectively.

Keywords: Laterite, Nickel, Cobalt, Organic acids, Atmospheric leaching

1. Introduction

With industrialization and population growth, the demand for metals has increased. As high-grade nickel sulfide ores are declining, attention has been drawn to laterite ores as critical sources of nickel and cobalt [1, 2]. Limonitic nickel laterites contain 1.0-1.7% nickel and 0.1 -0.2% cobalt [3]. The methods of nickel extraction from laterite ores are divided into two categories: pyrometallurgical and hydrometallurgical methods. Limonite ores are not suitable for pyrometallurgical processing because of their high iron content. Significant amounts of heat must be provided due to the high water content of the laterites. Atmospheric acid leaching is a hydrometallurgical technology that involves bulk, stirred leaching of laterites with dilute sulfuric acid, purification of the leach solution by chemical precipitation, and nickel recovery from purified leaching solution by chemical precipitation or solvent extraction or electrolytic extraction [4].

Among the hydrometallurgical methods, using organic acids as a leaching agent has advantages [3]. For the leaching of nickel laterites, among the various types of organic acids, citric acid results in the highest nickel recovery and good selectivity of nickel versus magnesium [1, 3]. Citric acid is the most effective organic acid for nickel extraction from serpentine-type laterite ores. However, due to its low reactivity with goethite, it is not useful for dissolving nickel from limonite-type laterite ores [5].

Alibhai et al. have studied the samples of laterite ore from Greece. Here, acetic, formic, lactic, oxalic, citric, and sulfuric acid separately with an initial concentration of 0.5 M was the organic and inorganic acids used in this study. Sulfuric and citric acid, respectively, extracted more

than 60% and 40% of the nickel content from the high-grade nickel laterites of Kastoria, Greece (silica-rich). Oxalic acid precipitated nickel oxalate, and the main parameter affecting dissolution was the concentration of hydrogen ions; however, complexation with organic anions was also beneficial [6]. Tang and Valix subsequently investigated the nickel and cobalt dissolution from weathered limonite and saprolites. In this study, chemical dissolution was performed using 1 to 3 M citric, lactic and malic acids, separately. Acid strength from high to low followed the order citric, malic, and lactic acids, respectively. The higher dissolution of cobalt than a nickel in limonite is because cobalt is associated with other minerals such as serpentines, whereas nickel is predominantly associated with goethite [7]. Citric acid is the most effective dissolution agent, and oxalic acid has the least effect. Depending on the ore type, the difference in nickel recovery using citric acid alone or oxalic acid alone is more than 72%. One explanation for this ranking could be that oxalic acid precipitates nickel as nickel oxalate, which has a very low solubility [8]. Astuti et al. (2016), by changing the type of organic and inorganic acids (citric, lactic, oxalic, sulfuric, hydrochloric, nitric acids, as well as the combination of citric acid and sulfuric acids as 3:1, 1:3, and 1:1), compared the citric acid efficiency to other acids for the leaching of saprolitic ores. The results showed that sulfuric acid was more appropriate than citric acid for the leaching of laterites containing goethite (citric acid was not useful for nickel recovery from goethite, but it was practical for nickel recovery from serpentine minerals) [9]. Biswas et al. investigated the effects of citric, oxalic, and gluconic acid concentration (50–150 mmol/L) on nickel and cobalt recoveries from lateritic chromite overburden by changing temperature and time. Extractions of 63.6% for nickel and 44.3% for cobalt were obtained using 150 mmol/L oxalic acid at 80 °C in

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3 hours [10].

In 2018, Javanshir et al. applied leaching operations under atmospheric pressure on low-grade nickel ore from Sarbisheh (The studied sample in forthcoming research was also brought from the same area). Pre-concentration of ore was performed by magnetic separation, but no increase in nickel grade was obtained. Nickel extraction by sulfuric acid for leaching obtained higher values than hydrochloric acid. Optimal laboratory conditions for nickel recovery were $S/L=0.25$, $H_2SO_4=5$ M at $90^\circ C$ for 2 hours. In this study, at the optimal conditions, 95% nickel was recovered, but the authors offered no way to reduce iron dissolution [11].

Based on the research on the chemical dissolution of nickel laterites, it can be concluded that using hybrid ratios of organic acids with the most commonly used inorganic acid (sulfuric acid) as the dissolution agent of laterites can be useful in comparison to the use of a single organic acid [5, 9].

Nickel and cobalt are incorporated into the network structure of precipitated-hydrated iron oxides through either absorption or substitution with iron [12]. Hosseini Nasab et al. investigated the dissolution of nickel and cobalt from the iron-rich laterite sample using different organic acids or sulfuric acid by the design of experiments (Design Expert) and kinetic studies [13, 14]. Hosseini Nasab et al. did not study the iron dissolution of iron-rich laterite samples under optimal conditions using sulphuric acid or the combined organic acids as leaching agents.

This study was performed to complete the previous works of Hosseini Nasab et al. [13, 14] to investigate the iron dissolution in iron-rich laterites. According to the previous study using sulfuric acid, optimal conditions of nickel and cobalt dissolutions were obtained at sulfuric acid concentration=5M, $S/L=0.1$, stirring speed=370 rpm, temperature= $90^\circ C$, and test time=120 min [13]. The highest recoveries of nickel and cobalt were 95.3% and 85.7%, respectively. Other research of the same authors investigated the ability of five organic acids, including gluconic ($C_6H_{12}O_7$), lactic ($C_3H_6O_3$), citric ($C_6H_8O_7$), malic ($C_4H_6O_5$), and oxalic ($C_2H_2O_4$) acids as dissolution agents under the intermediate conditions for the considered parameters, as $S/L=0.2$, organic acid concentration=3.5M, stirring speed=450 rpm, temperature= $60^\circ C$ and test time=2 hours, to leach nickel and cobalt. Then, different ratios of three selected organic acids (gluconic, lactic, citric acid) due to the more solubility of nickel and cobalt of the laterite sample were considered for the next experiments that the optimal combination obtained as gluconic: lactic: citric acids at a ratio of 1: 2: 3. In the following of this research, utilizing the experimental design and kinetic studies, the optimal leaching conditions obtained as final concentration of three organic acids with optimal combination= 3.5 M, $S/L=0.1$, stirring speed=390 rpm, temperature= $75^\circ C$ and leaching time= 2 hours. The highest nickel and cobalt recoveries were 25.5% and 37.6%, respectively [14]. High iron dissolution in iron-rich laterites causes problems at the next processing stages [15-17]. It seems that leaching of the laterite sample using sulfuric acid results in high dissolution of nickel, cobalt, and iron (Sulfuric acid is a corrosive acid with a high ability to dissolve minerals), but using organic acids may cause low iron dissolution with low recoveries of nickel and cobalt (Organic acids alone are weak to dissolve iron-rich laterites).

The authors were trying to find a method to leach more nickel and cobalt by combining organic acids with inorganic acids while decreasing iron dissolution. Sulfuric acid is a corrosive acid, so its use as a leaching agent in limonite laterites also leads to high iron dissolution. In this study, the effect of combining organic acids (citric, lactic, and gluconic acids) with sulfuric acid on the nickel and cobalt recoveries and iron dissolution for iron-rich laterite was investigated.

2. Materials and Methods

2.1. Sample and characterization studies

A laterite sample from eastern Sarbisheh in South Khorasan province (Iran) with a proven reserve of 3,700,000 tones was used in this study. The laterite sample was rich in nickel and cobalt and had high iron

content. Atomic absorption analysis of the laterite sample showed that the average grades of nickel, cobalt, and iron were 1.74, 0.14, and 40.8%, respectively.

The results of the particle size analysis, using Particle Size Analyzer (Micro-Tec Plus), showed that the laterite particles used in this study were fine and in the range of 0.1 to 100 microns. The values of d_{25} , d_{50} , and d_{80} for the initial sample were 2.5, 8.6, and 25.2 μm , respectively, and for the calcined sample at $500^\circ C$ for 2 hours were 5.6, 15.1, and 30.1 μm , respectively (Figure 1).

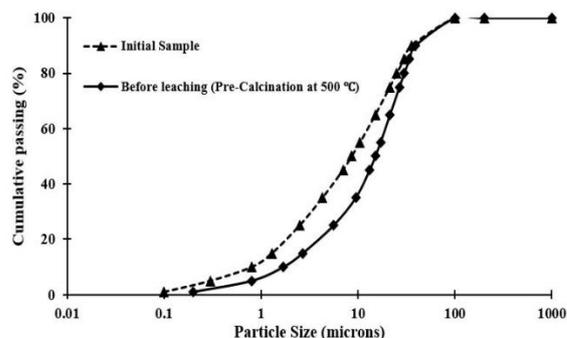


Figure 1. The results of particle size analysis for the initial laterite sample and after calcination.

The results of XRF analysis (MAGIX-PRO) after calcination indicated that the studied sample had high iron, as the Fe_2O_3 content was 61.4%. There was 3% NiO and 0.2% Co_3O_4 as well as 9.2% SiO_2 , 5% Al_2O_3 , 4% CaO, and 0.4% MgO in the chemical composition of this sample. XRD analysis (MPD 3000) for this sample showed that goethite, calcite, hematite, and quartz before calcination, and hematite, quartz, and dolomite after calcination, were the main crystalline phases (Figure 2). Counting time: 0.5 sec, Step size: 0.02, Anode: Cu, Voltage: 40 kV, Current: 30 mA and $2\theta: 4-90^\circ$. Astuti (2015) stated that goethite is the most important component of limonite-type laterite ores [18]. The calcination of laterites changes the mineralogical composition, increases porosity and specific surface area, and makes it more suitable for leaching [19].

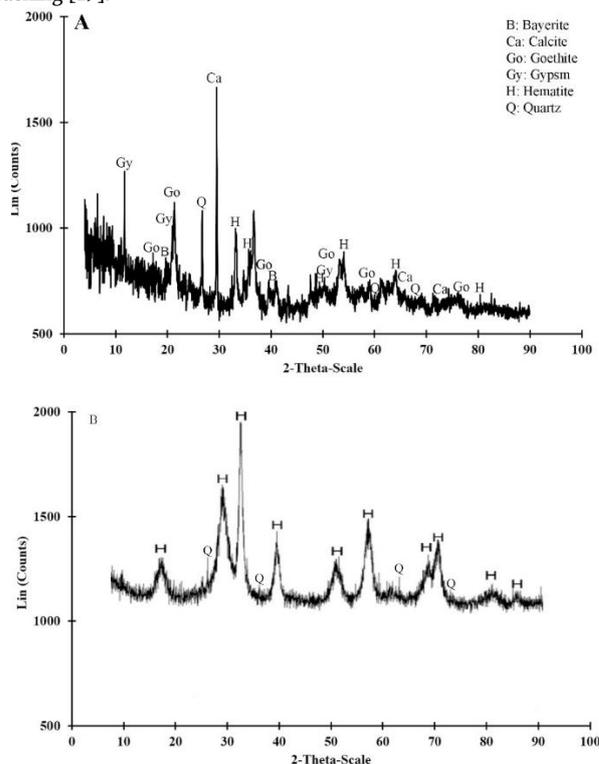


Figure 2. Results of XRD analysis of the laterite sample: A) before calcination and B) after calcination.

The Thermo-gravimetric analysis/Differential thermal analysis (TG/DTA; model: TG 209F3 NETZSCH) curve of studied laterite sample and leaching experiments before and after calcination showed that a calcination temperature of 500 °C yields the highest nickel and cobalt recoveries. Figure 3 shows the two major peaks of the endothermic reaction of structural changes at temperatures around 300 to 700 °C. The selection of 500 °C as the calcination temperature before leaching was due to achieving higher recoveries of nickel and cobalt than the calcination temperatures of 200, 350, and 650 °C, and the TG/DTA curve [13, 14]. The Brunauer–Emmett–Teller (BET) analysis results confirmed that the specific surface area, total volume, and average diameter of the pores before the calcination of the laterite sample were 40.72 m²/g, 0.073 cm³/g, and 7.17 nm, respectively. After calcination at the optimal temperature (500 °C), these values were 183.84 m²/g, 0.25 cm³/g, and 5.40 nm, respectively. In other words, the surface area after calcination increased by 4.5 times, the total volume of the cavities produced after the release of the exhaust of gases increased by 3.4 times, and the average diameter of the holes decreased by 1.3 times as a result of shrinkage at high temperatures. Therefore, for the sample used in this study, calcination was performed at the temperature of 500°C for 2 hours in the furnace (Nabertherm®). Nickel, cobalt, and iron grades of product formed using a calcination temperature of 500 °C were 2.3, 0.17, and 32.7%, respectively, which were considered the feed grades in all leaching tests [13].

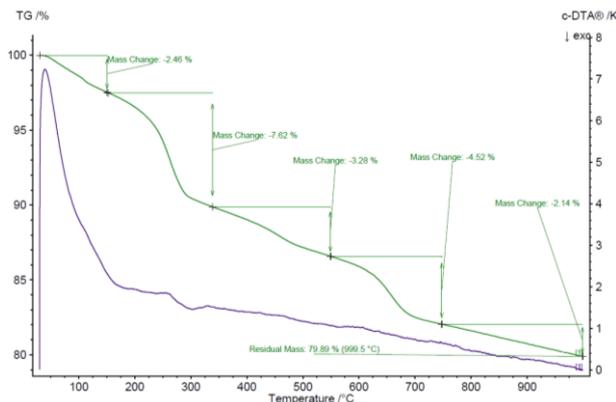


Figure 3. Result of TG/DTA analysis [13].

2.2. Leaching apparatus

Leaching experiments at atmospheric pressure were carried out in a 1-liter glass reactor. The photo of this reactor is shown in Figure 4. Silicon oil bath that was electrically heated, Heidolph mechanical stirrer (Model HPS-55, Germany), Magnetic stirrer (Multi stirrer DM-8 Scinics, Japan), Pyrex glass door which was removed at the time of feed entry, thermometer, periodic sampling from an input, reflux condenser to prevent solution evaporation at high temperatures, and the thermostat were different components of this reactor [13].

2.3. Chemical leaching experiments

Leaching experiments were performed using the combined ratios of organic acids with sulfuric acid. Combined different ratios of organic acids with sulfuric acid were being investigated under experimental conditions as S/L= 0.1, stirring speed= 390 rpm, leaching time= 2 hours, leaching temperatures= 60 and 90 °C, and final acid concentration= 3.5 and 5 M. These parameters were considered at optimal values obtained from Hosseini Nasab et al.'s researches [13, 14]. According to the experimental design results, stirring speed had little effect on nickel and cobalt recoveries. So, it was considered as 390 rpm.

At the end of each leaching experiment, the contents inside the reactor vessel were filtered through a vacuum filter. 5 mL of the filtered solution was slowly removed using a graduated pipette and was diluted using in 50 mL standard balloons, by mixing with distilled water and 98% concentrated sulfuric acid (the ratio can be 100 mL of distilled

water and 20 mL of concentrated acid). The use of concentrated acid in the dilution step was performed to prevent sedimentation of the elements and to reach its pH to about zero. The diluted solutions after each test were analyzed by the atomic absorption spectroscopy method (Varian Spectr AA. 20, America) to determine nickel, cobalt, and iron concentrations. All experiments were repeated at least twice and on occasions three times, and the results of the analysis were averaged. The error of the atomic absorption spectroscopy (AAS) to measure nickel, cobalt, and iron concentrations was 0.5 %.



Figure 4. The photo of the used reactor for leaching experiments [13].

Besides, surface morphology (SEM, FEI QUANTA 450) and elemental analysis (BRUKER XFLASH 6/10) were performed to investigate changes in the laterite surface after leaching.

The kinetic tests, with the optimal values of the acid(s), were performed by changing the temperature and time. The studied temperatures were 30, 45, 60, 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, after solid settling partially, 5 mL of the sample related to the liquid section from above the liquid surface in the reactor were slowly removed using a graduated pipette, and this 5 mL was replaced by a combination of acids with an optimal concentration. 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

In the present study, to confirm high iron dissolution in the optimal conditions reported using sulfuric acid as a leaching agent examined the iron dissolution for a similar sample of more than 96%. On the other hand, adding 50 g/L of citric acid to sulfuric acid and using optimal conditions except at a temperature of 30 °C resulted in recoveries of 15.6% nickel, 26.2% cobalt, and 6.85% iron. These values were 16.8, 19.6, and 9.42%, respectively, when just sulfuric acid was used. In addition, to prove low iron dissolution in the optimal conditions reported using the optimal combination of organic acids as a leaching agent, examined the rate of iron dissolution for the similar sample, which was a low rate of 10.73%.

The experiment paves the way for using combination ratios of organic acids with sulfuric acid.

In the current study, the optimized parameters were then used to run the combined tests of organic acids with sulfuric acid. The only

difference was that instead of considering 75 and 90 °C for leaching time, 60 and 90 °C were used to clarify the differences.

3.1. Effect of combining organic acids with sulfuric acid on Ni, Co, and Fe recoveries

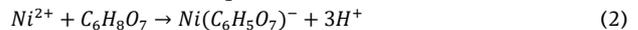
Increasing temperature to 90 °C and using sulfuric acid, significantly increase the nickel and cobalt recoveries and iron dissolution. On this basis, a lower temperature of 60 °C was considered to understand better the impacts of sulfuric acid addition upon the effectiveness of the organic acids. Experiments were then performed to investigate the combined ratios of organic acids with sulfuric acid using the optimal combined concentration of acids= 3.5 M, S/L= 0.1, stirring speed= 390 rpm, temperature= 60 °C, and reaction time= 120 min. The results are presented in Table 1. For these tests, it was noted that after 2 hours of leaching, the dissolution rate of nickel and cobalt is negligible, and the extraction remained essentially constant after that. The reason is that during the time, the remaining nickel and cobalt in solution were associated with the resistant minerals, and the dissolution rate was slow. By organic acids alone as a dissolution agent, cobalt recovery is more susceptible to temperature than nickel recovery. However, using just sulfuric acid as the dissolution agent, nickel recovery is more sensitive to temperature than cobalt recovery [20]. Cobalt is more difficult to leach with just sulfuric acid because manganese oxides are often a major host for cobalt in limonitic laterites. The facilitation of cobalt over nickel extraction by organic acids can be related to the reductive leaching of manganese oxides [21]. The use of 5M acid in this study is due to the significant amount of iron in the laterite sample [22].

Table 1. Combined ratios of organic acids with sulfuric acid (S/L= 0.1, stirring speed= 390 rpm, leaching time= 2 hours).

Temperature (°C)	Final acid concentration (M)	Combined ratio of sulfuric acid: gluconic acid: lactic acid: citric acid, respectively	Ni Recovery (%)	Co Recovery (%)	Fe Dissolution (%)	
60	3.5	1:0:0:0	41.98*	36.54*	43.66*	
		0:1:0:0	10.70	25.91	1.86	
		0:0:1:0	12.51	25.30	3.15	
		0:0:0:1	12.22	25.63	4.02	
		1:1:0:0	37.62	44.01	39.22	
		1:0:1:0	42.89	41.95	48.53	
		1:0:0:1	40.10	43.23	42.44	
		0:1:2:3	19.61	31.18	9.94	
		1:1:2:3	35.79*	35.33*	7.79*	
		1:1:1:1	39.70	33.57	18.98	
		6:1:2:3	44.33*	41.06*	12.71*	
		5	1:0:0:0	65.54	61.9	70.3
			6:1:2:3	67.89*	64.42*	28.01*
		90	5	1:0:0:0	95.33	85.7
6:1:2:3	100*			99.93*	14.99*	

It can be concluded from Table 1 that organic acids have been decreased the extraction of iron. According to Table 1, all combined organic acid ratios as dissolution agents had lower iron dissolution than using just sulfuric acid. Citric acid is the most effective acid for nickel dissolution in saprolitic laterite ores due to its high dissociation constant, and it can form nickel- citrate complexes during metal dissolution [8]. However, this acid does neither recover nickel from goethite [5] nor, in the current study, the calcined feed. The most effective acid to dissolve nickel from goethite is sulfuric acid [18]. According to Table 1, the combined ratio of 0:0:0:1 that uses only citric acid as the dissolution agent enabled only 12.22% of nickel and 25.63% of cobalt to be recovered, whereas sulfuric acid alone in similar condition recovered 41.98% nickel and 36.54% cobalt. Taking citric acid as an example, this can dissolve heavy metals through two mechanisms: the first mechanism, the direct displacement of metal ions from the ore matrix or mineral using hydrogen ions (acidolysis) (equation (1)), and the other mechanism, the formation of complexes and soluble chelates of metal (complexolysis) (equation (2)) [21]. Citric acid forms chelate complexes with both iron and nickel at low pH. Ligands or chelating agents assist the dissolution of minerals by adsorption on the mineral surfaces and highly soluble complexes with metal ions [23]. The

appearance of ligand-metal complexes at the mineral surface shifts the electron density towards the metal ion, thereby destabilizing the M-O network bonds and facilitating the separation of metal ions into solution [23]. Ligands also promote the dissolution of minerals by forming complexes with leached ions in solution, while ligands reduce the apparent dissolution of the mineral [24]. However, sulfuric acid uses only an acidolysis mechanism to attack metals in the mineral, but hydrogen ions of acid can completely dissolve metal ions [25]. Organic acids, which form the nickel complexes, liberate and increase the H⁺ ions in the solution. Therefore, the acidic media help to the dissolution of metals in the laterite [24].



In limonitic ores, the cobalt is the accompaniment with serpentine and the nickel with goethite [7]. As Table 1, the combination of acids rather than using them individually, obtain better results for nickel and cobalt recovery. The reason is that both of the mechanisms (acidolysis and complexolysis) participate and help to the complete dissolution of nickel and cobalt. The iron dissolution by the combination of acids decreases due to the complexolysis mechanism in the presence of organic acids can be formed quickly and the dissolved iron can sediment faster in the leach residue (detachment of the Fe-organic acid complex requires breakage of fewer bonds) [26].

Results of the SEM micrograph, together with the results of elemental EDS of Si, Ni, Co, Fe, Al, and O for the calcined feed, are reported in Figure 5A. The corresponding data for the leached solid product under optimum conditions by sulfuric acid alone (the ratio of 1:0:0:0 in Table 1), the optimal combined ratio of organic acids (0:1:2:3 in Table 1) as well as by adding optimal sulfuric acid to the optimal combined ratio of organic acids (the ratio of 6:1:2:3 in Table 1) are shown in Figures 5B-5D. As the SEM results show, most particles were round and spherical. Under the optimal conditions, the particle surfaces for leaching feed and leached solid products were not significantly different.

The results of elemental EDS for Si, Co, Ni, Fe, Al, Mg, and O reported in Figure 5 reveals that the amounts of Ni and Co in the remaining solid after the indirect bioleaching process were declined except for the ratio of 0:1:2:3. However, the amount of Si before and after leaching treatment remained almost unchanged. These findings indicate that leaching using sulfuric acid with organic acids (6:1:2:3) could solve most of the Ni and Co elements without solving the Si and with no gel production. Besides, a large amount of iron also remains as sediment in the leached solid product.

The presence of citric acid in dissolution with sulfuric acid indicates a beneficial interaction between free hydrogen ions and citrate. In Table 1, the comparison of the ratio 1:0:0:1 (equal use of citric acid (50 %) and sulfuric acid (50%)) with the combined ratio of 1:0:0:0 (100% sulfuric acid as dissolution agent) shows that the nickel recovery and iron dissolution for both ratios are almost identical. In other words, even with a 50% reduction in using sulfuric acid, cobalt recovery, in the 1:0:0:1 combined ratio compared to the combined ratio of 1:0:0:0, increased. All nickel in lizardite can be extracted using citric acid [18]. Sulfuric acid can be used to recover most nickel in goethite or hematite (Figure 5B). Sulfuric acid can dissolve nickel in goethite, hematite, and lizardite [18]. The amount of lizardite in the laterite sample used in this study is low, so even 1 M citric acid is sufficient to dissolve nickel from lizardite. Figure 5C shows that Mg (the main constituent of lizardite) is not a known element in the leached solid product.

In Table 1, by comparing the 1:1:2:3 hybrid ratio with the 1:1:1:1 hybrid ratio, it is apparent that in the 1:1:2:3 hybrid ratio, the amount of sulfuric acid and gluconic acid were halved. Lactic acid is approximately the same value in both ratios, and the amount of citric acid is about double in value. Interestingly, the recovery rates of nickel and cobalt of these two ratios are almost identical. Nickel recovery at a ratio of 1:1:2:3 is slightly lower than the ratio of 1:1:1:1, but cobalt recovery at a ratio of 1:1:2:3 is even more than 1:1:1:1 ratio. Interestingly, the iron dissolution using the 1:1:2:3 ratio decreased by 11.19% compared to the 1:1:1:1 combination ratio. This means that adding sulfuric acid to the optimal combined ratio of organic acids (0:1:

2: 3) and converting it to a 1: 1: 2: 3 ratio can achieve a significant increase in nickel recovery by 16.18%; a slight rise in cobalt recovery by 4.15% and a decrease in iron dissolution by 2.15%.

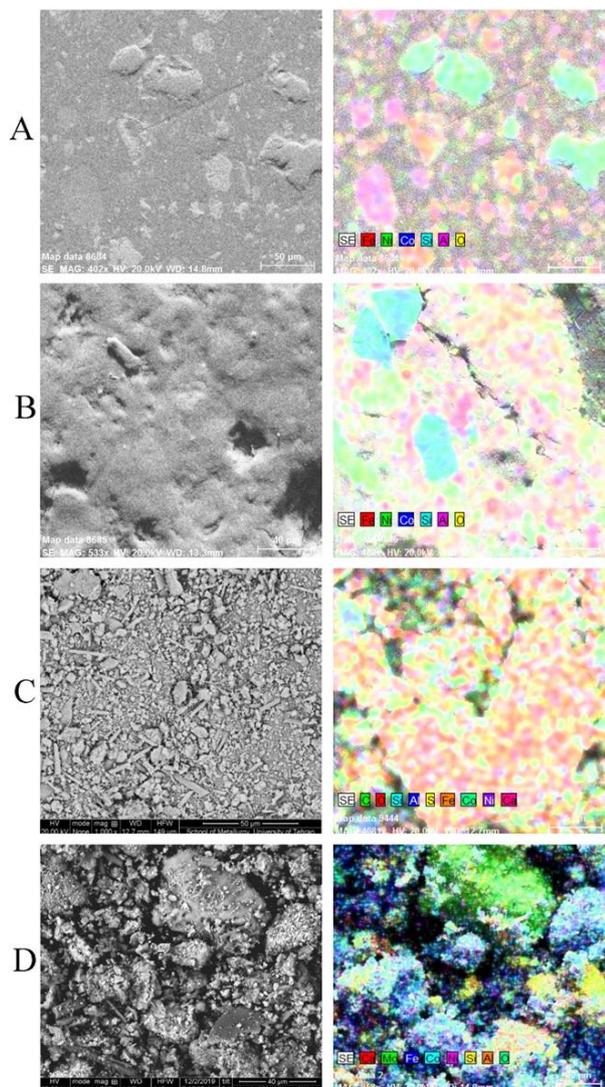


Figure 5. Results of elemental EDS and SEM analysis for A): calcined feed sample at 500 °C; B): leaching by sulfuric acid alone under optimal conditions [13]; C): leaching by the optimal combined ratio of organic acids under optimal conditions [14]; D): leaching by sulfuric acid with the optimal combined ratio of organic acids under optimal conditions.

Gluconic acid is more expensive than the other two organic acids. Thus, although in the 1: 1: 2: 3 combination ratio in comparison with 1: 1: 1: 1, the gluconic acid content is reduced by half, but the final result of nickel and cobalt recoveries are improved, and an iron dissolution decreases. When at 60 °C and an optimal concentration of 3.5 M, 100% of sulfuric acid is used, and gluconic, lactic, and citric acids are not used (1: 0: 0: 0 ratio in Table 1), nickel and cobalt recoveries were 41.98 and 36.54%, respectively, and iron dissolution was 43.66%, which is a significant value. In Table 1, a comparison of the 1: 1: 2: 3 hybrid ratio with the 1: 0: 0: 0 ratio (using only sulfuric acid as solubilizing agent) shows that the nickel and cobalt recoveries of these two ratios are not significantly different. However, the iron dissolution is reduced by 35.87% when the 1: 1: 2: 3 combination ratio is compared to the 1: 0: 0: 0 ratio. Meanwhile, using sulfuric acid as a highly corrosive and non-recyclable acid can be reduced from 100% in the ratio of 1: 0: 0: 0 to 14.3% in the combination ratio of 1: 1: 2: 3. According to the results in Table 1, by comparing the dissolution data of nickel and cobalt at the 1: 0: 0: 0 combination ratio at 90 and 60 °C under identical conditions, as

expected, the recovery rates of nickel and cobalt increase with increasing temperature. On the other hand, iron dissolution as a troublesome element also increases in the solution. If the 6: 1: 2: 3 combination ratio (50% of sulfuric acid, 8.3% of gluconic acid, 16.7% of lactic acid, and 25% of citric acid) is used at 60 °C and a final concentration of 3.5 M, the nickel and cobalt recoveries were 44.33%, 41.06%, respectively, and iron dissolution was 12.71%. Therefore, even nickel and cobalt recoveries increased under similar conditions compared to use merely sulfuric acid. It is interesting that in these conditions, iron dissolution also decreased by about 31%. Using 6: 1: 2: 3 combination ratio at 60 °C and a final concentration of 3.5 M compared to 0: 1: 2: 3 combination ratio under identical conditions, resulted in an increase of 24.72% for nickel recovery, 9.88% for cobalt recovery, and of course 2.77% for iron dissolution. EDS analysis using 0: 1: 2: 3 combination ratio of optimal organic acids under the same conditions (Figure 5C) shows that most of the iron, nickel, and cobalt in the sample were undissolved and remained in the residue. Applying the 6: 1: 2: 3 combination ratio at 60 °C and the final concentration of 5 M compared to use merely sulfuric acid, under similar conditions, resulted in an increase in nickel and cobalt recoveries and a significant decrease in iron dissolution by 42.29%.

The last row in Table 1 shows that increasing the temperature to 90 °C using the 6: 1: 2: 3 combination ratio, results in 100% recovery for nickel and 99.9% for cobalt. Interestingly, iron dissolution by using this combination ratio was reduced to 15.0%. The reason is that increasing the temperature help the complexolysis mechanism can be formed quickly and the dissolved iron can sediment faster in the leach residue (detachment of the Fe-organic acid complex requires breakage of fewer bonds) [26]. Figure 5D also confirms the result obtained from Table 1. Large amounts of iron remained undissolved in the leached solid product (waste). This means that adding sulfuric acid to the optimal combined ratio of organic acids (0: 1: 2: 3), increasing the temperature from 60 to 90 °C, as well as increasing the final concentration of the combined acids from 3.5 M to 5 M and converting this ratio to the 6: 1: 2: 3 combination ratio, a significant increase can be achieved for nickel recovery by 80.4% and cobalt by 68.7% and a slight increase in iron dissolution by 5.05%. Increasing the acid concentration due to the rise of H^+ ions can better contribute to the breakdown of OH^- groups of goethite and lead to the easier dissolution of nickel and cobalt in solution [27]. H^+ ions in sulfuric acid lead to the dissolution of nickel, cobalt, and iron [13]. The presence of organic acids forms a soluble complex of nickel and cobalt and releases these elements, mainly nickel, from iron ores [28]. The high amount of iron released in the solution compared to other elements leads to the deposition of iron in the waste. Therefore, using the optimal combination of organic acids with sulfuric acid it is more comfortable to liberate nickel and cobalt from iron-bearing minerals and to precipitate iron at higher temperatures for the ratio of 6:1:2:3.

The efficiency and cost (regardless of the cost of the temperature) of using sulfuric acid alone (1:0:0:0), the optimal combined ratio of organic acids (0:1:2:3), or the combination of organic acids with sulfuric acid (6:1:2:3) as leaching agent, are compared in Table 2. Costs were calculated in USD.

The cost of leaching agents using the combination of organic acids with sulfuric acid (the ratio of 6:1:2:3) is more than sulfuric acid alone (the ratio of 1:0:0:0). Still, this combination causes high recoveries of nickel and cobalt and the low dissolution of iron. On the other hand, due to diversity and abundant carbon sources in different places like our country, if organic acids are produced in Iran, the use of organic acids with sulfuric acid as leaching agent will require lower capital and operational costs and easier processing of nickel and cobalt in downstream streams due to low iron dissolution while being a safer process (the use of sulfuric acid alone causes high corrosion of equipment). These benefits, along with the fact that using only organic acids are not sufficient for the acceptable dissolution of nickel and cobalt from iron-rich laterites, combining organic acids with sulfuric acid as a leaching agent of iron-rich laterites may become more prominent in the future.

Table 2. Comparison of recovery and cost of using important leaching agents presented in the present study (S/L= 0.1, stirring speed= 390 rpm, temperature= 90 °C, final concentration of acid(s) = 5 M, leaching time= 2 hours).

Leaching agent	Cost of leaching agent compared to the price of sulfuric acid as a unit	Efficiency in removing iron from solution	Recoveries of the nickel and cobalt
Sulfuric acid (1:0:0)	1	Weak (96.1% iron dissolution)	Very good (95.33% Ni and 85.7% Co)
Optimal combined ratio of organic acids (0:1:2:3)	3.63	Very good (12.8% iron dissolution)	Weak (26.37% Ni and 39.13% Co)
Combination of organic acids with sulfuric acid (6:1:2:3)	2.31	Very good (14.99% iron dissolution)	Excellent (100% Ni and 99.93% Co)

3.2. Effects of temperature and time on recoveries

The kinetic study was carried out with S/L= 0.1, stirring speed= 390 rpm, the final concentration of the combination of organic acids with sulfuric acid (6:1:2:3) = 5M, with changing temperature and time. According to Figure 6, by increasing the leaching time and temperature, 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 with sulfuric acid were 90 °C and 2 h, respectively, which yielded the highest recoveries of nickel and cobalt as 100% and 99.9%, respectively. The rate of iron dissolution under these conditions was 15%. After 2 h, the recoveries of nickel and cobalt remained fairly constant.

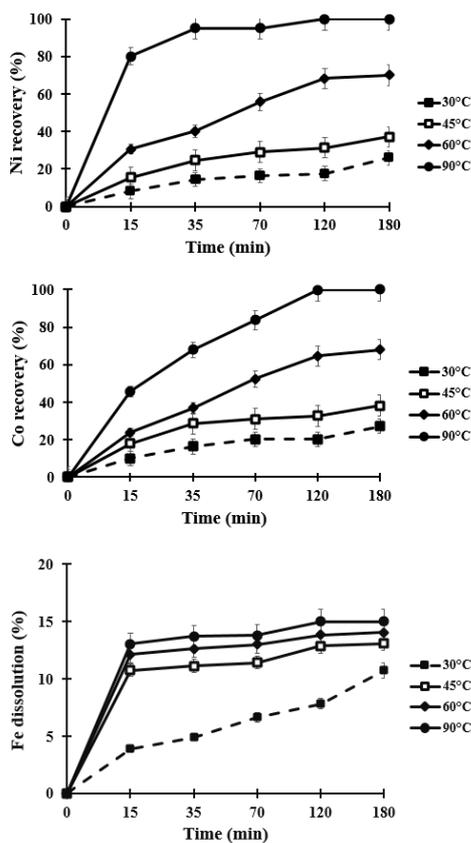


Figure 6. Nickel and cobalt recoveries and iron dissolution at different temperatures and times (combined concentration of organic acids with sulfuric acid =5 M, S/L= 0.1, agitation speed= 390 rpm).

3.3. Kinetic studies

The leaching of minerals can be demonstrated using various models. In Table 2, 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.

Table 3. Equations and mechanisms for dissolutions [13, 14].

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 the product layer
4	$K_t = -\ln(1 - X)$	Mixed control model (surface reaction control; diffusion through sulfur layer)
5	$K_t = 1 - \frac{2}{3}X - (1 - X)^{\frac{1}{3}}$	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	$K_t = 1 - (1 - 0.45X)^{\frac{1}{3}}$	The surface chemical reaction by shrinking the core model

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 2). 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 the release from a solid product layer or through the rate of chemical reaction at the core surface of non-reactive particles [29, 30]. The slowest stage determines the velocity of the leaching reaction [29].

Among the different models presented in Table 2, the two diffusion control and chemical control models (Equations 3 and 4) have the best fitting on the nickel and cobalt data.

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

$$k_t = 1 - (1 - X)^{\frac{1}{3}} \tag{4}$$

The application of the kinetic models of diffusion and chemical controls at different temperatures for the optimal composition of sulfuric acid with organic acids is presented in Figures 7A to 7D.

The values of reaction velocity constants and correlation coefficients for nickel and cobalt at different temperatures are given in Table 3. According to the results and the correlation coefficients obtained from this table, the chemical control model has a better fit compared with the diffusion control.

The Arrhenius relationship was employed to obtain the activation energy values. Using the Arrhenius equation, $k = A \exp(-E_a/RT)$, and plotting $-\ln k$ versus $1000/T$ yields 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 ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), 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 8.

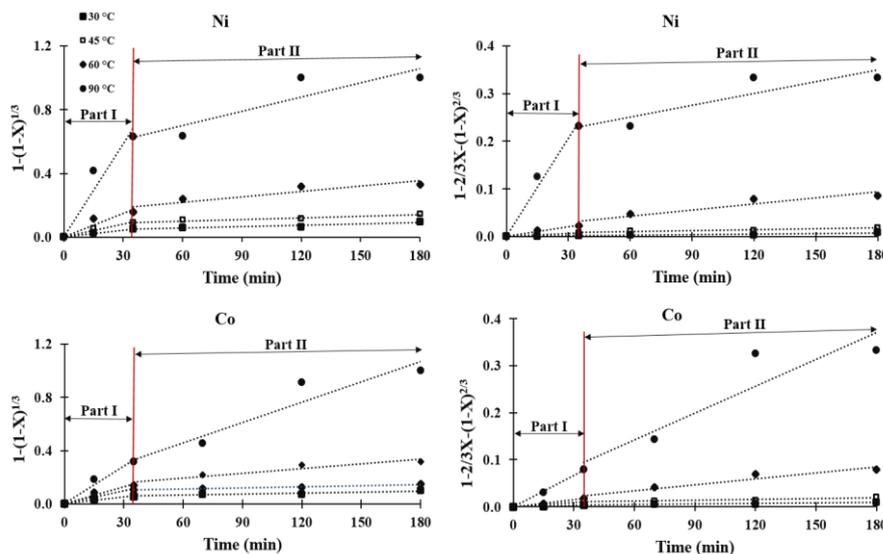


Figure 7. Kinetic modeling of laterite sample dissolution for the nickel and cobalt at 30 °C to 90 °C using the optimal composition of sulfuric acid with organic acids. Left side: Chemical control. Right side: Diffusion control.

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

Temperature (°C)	Ni				Co			
	Diffusion control model		Chemical control model		Diffusion control model		Chemical control model	
	R ²	k (min ⁻¹)	R ²	k (min ⁻¹)	R ²	k (min ⁻¹)	R ²	k (min ⁻¹)
30 (Part 1)	0.9765	0.00007	0.975	0.0015	0.995	0.00009	0.9473	0.0018
30 (Part 2)	0.8518	0.00004	0.884	0.0003	0.8786	0.00004	0.8952	0.0003
45 (Part 1)	0.9953	0.0002	0.9482	0.0027	0.9943	0.0003	0.9516	0.0032
45 (Part 2)	0.9509	0.00007	0.9484	0.0003	0.9477	0.00006	0.9613	0.0003
60 (Part 1)	0.9762	0.0007	0.858	0.005	0.998	0.0005	0.942	0.0043
60 (Part 2)	0.8792	0.0004	0.8486	0.0011	0.9313	0.0004	0.9025	0.0012
90 (Part 1)	0.9781	0.0069	0.9129	0.0196	0.9963	0.0022	0.9586	0.0095
90 (Part 2)	0.8348	0.0008	0.8339	0.003	0.864	0.0019	0.9122	0.0051

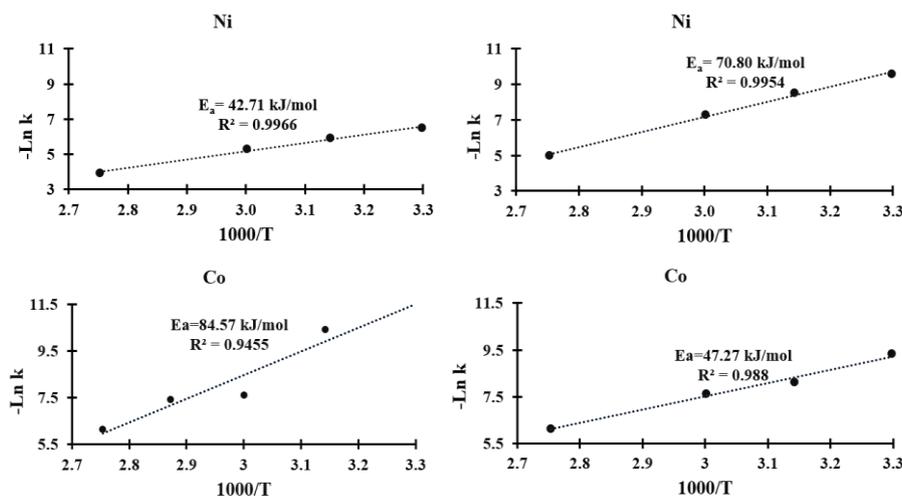


Figure 8. Graph of $-\ln k$ versus $1000/T$ to calculate the activation energies for nickel and cobalt; Left side: Chemical control model. Right side: Diffusion control model.

Figure 8 shows that in the chemical controls for nickel and cobalt, the correlation coefficients are acceptable and $R^2 = 0.9966$ and $R^2 = 0.9455$, respectively. The use of the Arrhenius relationship defines the activation energies of nickel and cobalt for the chemical control models, as follows:

$$E_a = 42.71 \text{ kJ/mol}$$

$$E_a = 84.57 \text{ kJ/mol}$$

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

$$E_a = 70.80 \text{ kJ/mol}$$

$$E_a = 47.27 \text{ kJ/mol}$$

According to Table 3 and the values of activation energies, the chemical control model has a more convenient fitting, and the obtained E_a values are within the limits of chemical 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 [31, 32]. The process of diffusion control is slightly dependent on the temperature but a process with chemical control highly depends on the temperature [33]. Since the equation of chemical control was well-fitted on the dissolution data

of laterite at different temperatures and the activation energy lied within the limits of chemical control, it could accordingly be stated that the chemical control was more effective on laterite dissolution than the diffusion control.

4. Conclusion

The nickel and cobalt dissolution in limonite laterites are associated with iron dissolution. The vital purpose of the present study was to introduce a dissolution agent to increase nickel and cobalt recoveries while decreasing iron dissolution from an iron-rich laterite sample. This goal was obtained using a combination of organic acids with sulfuric acid. Adding sulfuric acid to the optimal combined ratio of the organic acids to give the combined ratio of 6: 1: 2: 3 (sulfuric: gluconic: lactic: citric acids) with the 5 M final combination concentration of these acids, S/L= 0.1, stirring speed= 390 rpm at the temperature of 90 °C and leaching time= 2 hours, increased nickel and cobalt recoveries by 4.67 and 14.23%, respectively, and significantly decreased iron dissolution by 81.11%, all when compared to using sulfuric acid alone under the same conditions. This result is a significant outcome of this work. Considering the abundant carbon sources (in Iran), using organic acids along with sulfuric acid as a solubilizing agent for iron-rich laterites may be beneficial when, compared to the use of sulfuric acid alone, as this also significantly reduces the iron dissolution. Activation energies (E_a) for the chemical control model were 42.71 kJ/mol for nickel and 84.57 kJ/mol for cobalt, which showed that chemical control had more effect on the dissolution rate of iron-rich laterite using an optimal combination of organic acids along with sulfuric acid than diffusion control. Further research is needed to clarify the possible contribution of organic acids' products on decreasing dissolutions of iron.

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