

Article

Enhanced Percolation Leaching of Limonitic Nickel Laterite Ore Using a Combined Sulfuric–Citric Acid System

Sandugash Tanirbergenova ¹, Kaster Kamunur ^{1,2}, Lyazzat Mussapyrova ^{1,2}, Aisulu Batkal ^{1,2},
Anar Esimova ³ and Rashid Nadirov ^{1,2,*}

¹ Institute of Combustion Problems, Almaty 050012, Kazakhstan; lyazzat.mussapyrova@gmail.com (L.M.)

² Faculty of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty 050040, Kazakhstan

³ Department of Biotechnology, M. Auezov South Kazakhstan University, Tauke Khan Avenue 5, Shymkent 160012, Kazakhstan

* Correspondence: nadirov.rashid@gmail.com

Abstract

Percolation leaching of limonite Ni laterite ore (1.42% Ni, 0.07% Co, 27.16% Fe) with sulfuric acid, citric acid, and their mixture was studied at atmospheric pressure and a temperature of 25 °C. Experiments were carried out in columns (diameter 50 mm, height 500 mm, ore weight 1.5 kg) as a laboratory model of heap leaching. The combined H₂SO₄ + C₆H₈O₇ system (10 + 10 g/L) showed a considerable enhancement in Ni extraction. After 21 days, Ni extraction reached 73%, compared with 52% for H₂SO₄ and 42% for citric acid at the same total reagent concentration. In an extended experiment (42 days), the maximum extraction of Ni reached ~83%, while that of Co was ~60%. Differences in the behavior of Ni and Co were revealed. Sulfuric acid is more effective for Ni, while citric acid is more effective for Co, due to differences in these metal species in the ore. Among the tested acid ratios, 10 + 10 g/L provided the best balance for the simultaneous extraction of Ni and Co.

Keywords: nickel laterites; percolation leaching; sulfuric acid; citric acid; combined acid leaching; cobalt

1. Introduction

Nickel laterite ores contain about 70%–72% of the world's aboveground nickel deposits, but in the early 2000s they accounted for only 40%–42% of global nickel production [1,2]. This discrepancy is due to the complex mineral composition of the laterites, the relatively low metal content and the high cost of separating nickel-containing phases. The main use of nickel is still stainless steel production, which accounts for about 70% of the world's nickel consumption [3]. In addition, the demand of the battery industry is growing rapidly. Lee et al. [4] estimated the global nickel consumption in 2023 at about 3.4 million tons and stated that up to 20% of this amount will be used for the production of cathode materials for lithium-ion batteries. This increases the need for additional sources of nickel and promotes the development of methods for processing low-quality laterite ores.

One of the most important industrial processes for processing limonite laterites is high-pressure autoclave leaching (HPAL) [5–7]. This process allows a high nickel and cobalt yield, but requires complex high-pressure equipment, the use of corrosion-resistant materials and significant investments. McDonald and Whittington [8] investigated the atmospheric sulfuric acid leaching of nickel laterites, including reactor, hybrid HPAL-AL and heap leaching methods. They found that the elimination of expensive autoclaves can reduce the



Academic Editor: Sehliselo Ndlovu

Received: 13 August 2026

Revised: 14 September 2026

Accepted: 21 September 2026

Published: 22 September 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and

conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

investment costs, but the advantages of atmospheric leaching depend on the nickel yield, sulfuric acid consumption and the complexity of cleaning the iron-containing solutions.

Citric acid is being studied as a reagent capable of increasing the selectivity of nickel extraction from individual mineral phases of laterite ores. Astuti et al. [9] studied the recovery of nickel from Indonesian saprolite ore at atmospheric pressure. At a citric acid concentration of 1 M, at a temperature of 40 °C and for 15 days, the extraction of nickel reached 95.6%. These results confirmed the effectiveness of the reagent under mild conditions; however, the long duration of the process limits its practical application. Astuti et al. [10] compared citric acid with sulfuric, hydrochloric, nitric, lactic and oxalic acids during the leaching of two Indonesian saprolite ores. In another study, Astuti et al. [11] found that the effectiveness of citric acid leaching strongly depended on the mineral composition of the ore. Ciftci et al. [12] investigated the biocatalytic and chemical leaching of low-grade laterite ore from the Çaldağ deposit using citric, oxalic, acetic and gluconic acids. Kursunoglu et al. [13] found that the addition of citric acid to a sulfuric acid solution increases the dissolution of nickel and especially cobalt, although ascorbic acid turned out to be a more effective additive. These results indicate that the effect of citric acid depends on the mineral composition of the ore, the acidity of the environment and its interaction with the main leaching reagent.

An additional advantage of citric acid is the possibility of its industrial production by microbial fermentation, mainly using *Aspergillus niger*. As a natural organic reagent, it is biodegradable and characterized by relatively low toxicity, which reduces the environmental burden compared to the use of strong mineral acids [14–16]. Mubarok et al. [17] studied the leaching of nickel from Indonesian laterite ore with citric, lactic, acetic, and oxalic acids, considering these reagents as chemical analogues of organic acids produced by fungal cultures. Chaerun et al. [18] studied the bioleaching of limonite and saprolite ores with organic acids produced by *Aspergillus niger*. At 95 °C and 400 rpm, nickel recovery from saprolite reached 88.9% in 4 h, and from limonite 84.9% in 24 h. These results confirmed the possibility of biogenic production of leaching reagents, although the duration of bioleaching and the dependence of the culture liquid composition on the cultivation conditions remain significant limitations. Wanta et al. [19] investigated the kinetics of citric acid leaching of limonite laterite ore at atmospheric pressure. At a citric acid concentration of 0.1 M, a duration of 2 h, and temperatures of 30–85 °C, nickel recovery increased with increasing temperature; the process was described by the collapsing core and lumped parameter models. In a subsequent study by Wanta et al. [20] showed that the kinetics of leaching also depends on the particle size, and the dissolution of nickel is controlled by a reversible chemical reaction and diffusion of products through the forming surface layer.

Despite the selectivity of citric acid, leaching of laterite ores with this reagent is usually characterized by slower kinetics than sulfuric acid leaching, especially at low temperatures [21,22]. This increases the duration of the process and limits the effectiveness of the reagent for limonite laterites. One approach to intensifying organoacid leaching is to combine the proton action of a mineral acid with the complexing capacity of citrate ion. Dissolution of ferrous phases promotes the release of associated Ni, while the formation of soluble nickel-citrate complexes stabilizes nickel in the solution [23]. Yunita and Mubarok [24] studied agitation leaching of limonite and saprolite laterite ores with a mixture of sulfuric and citric acids. For limonite ore, the maximum nickel recovery was 73% using 2 M H₂SO₄ and 0.5 M citric acid, a temperature of 95 °C, a duration of 8 h, and a stirring speed of 200 rpm. The mixture increased nickel recovery compared to individual acids, but no synergistic effect was observed, and selectivity for iron and magnesium decreased.

The most known studies on mixed sulfuric and organic acid systems for Ni laterites have been performed under stirred leaching conditions, where intensive mixing provides continuous renewal of the solid–liquid interface and relatively high mass transfer rates. Column percolation leaching differs fundamentally in that the solution moves through a stationary packed ore bed, and metal extraction is additionally influenced by solution distribution, liquid retention, local flow paths, and progressive changes in the accessibility of reactive mineral surfaces. Therefore, the performance of a reagent system established under stirred conditions cannot be directly extrapolated to percolation or heap leaching. Evaluation of the sulfuric and citric acid combination under prolonged percolation conditions is thus required to evaluate its behavior in a system that more closely represents heap leaching.

The aim of this study was to investigate the percolation leaching of nickel laterite ore with sulfuric, citric, and a mixture of both acids. Ni and Co recovery was compared, the effect of acid ratio was determined, and solid phase changes were assessed using XRD and SEM-EDX analysis. The scientific novelty of this study lies in the comparison of individual and combined acid systems in percolation mode and the establishment of a relationship between the recovery of target metals and changes in the silicate and iron-bearing phases of the ore.

2. Materials and Methods

2.1. Materials

The research object was nickel laterite ore, a loose material that does not require crushing prior to leaching. The ore was used as received, without any preliminary preparation other than averaging using the quartering method.

Sulfuric acid (H_2SO_4 , 98%, analytical grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, $\geq 99.5\%$, analytical grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used to prepare the leaching solutions. The required acid concentrations were obtained by dilution or dissolution in distilled water.

2.2. Percolation Leaching Methodology

The experimental setup for percolation leaching is shown in Figure 1. Leaching experiments were conducted on percolation columns made of transparent plexiglass. The column had an internal diameter of 50 mm and a height of 500 mm. A perforated plate with 1 mm diameter holes was installed at the bottom of the column, over which a filter layer of glass wool ~10 mm thick was placed to prevent the removal of small ore particles. A similar filter layer was placed on top of the loaded ore to ensure uniform distribution of the feed solution.

The loaded ore weighed 1.5 kg. The ore was added in layers of ~300 g, with each layer lightly compacted to ensure uniformity. The ore layer height after loading was ~350 mm. The leach solution was fed from the top down using a peristaltic pump. The irrigation rate was $10 \text{ L}/(\text{m}^2 \text{ h}^{-1})$, corresponding to a volumetric flow rate of ~20 mL/h for a column of this diameter. The productive solution (PLS) was collected in a receiving tank at the bottom of the column.

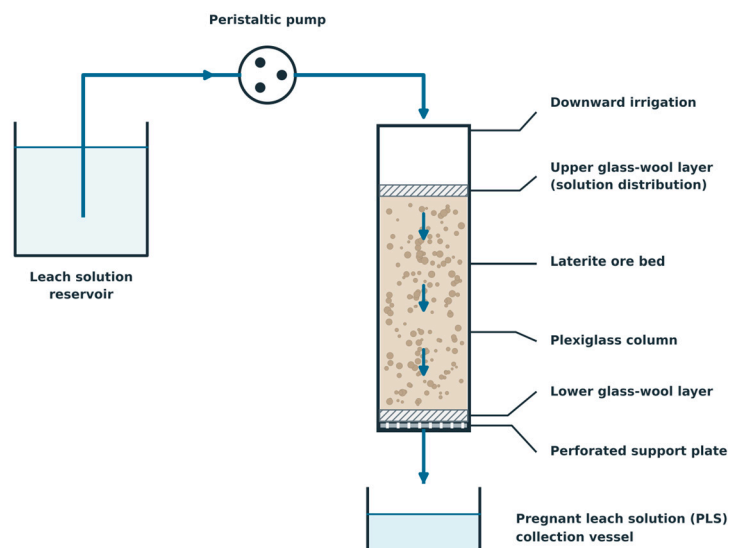


Figure 1. Schematic illustration of the experimental setup for column percolation leaching.

During the experiments, no pronounced deterioration of percolation was observed. The leach solution continued to pass through the ore bed without visible flooding or severe flow restriction. The collected PLS volumes remained consistent with the imposed feed rate.

All experiments were conducted at a temperature of 25 ± 2 °C.

The selected column dimensions, ore loading, and ambient temperature conditions were chosen to provide a laboratory scale representation of heap leaching while maintaining stable downward percolation through the ore bed. This irrigation rate was selected to maintain continuous wetting of the ore bed while avoiding flooding and excessive solution accumulation within the column.

PLS samples were collected daily; the volume and concentrations of Ni, Co, Fe, and Mg were determined in each sample.

The metal recovery rate was calculated cumulatively using the formula:

$$\varepsilon = \frac{\sum C_i \cdot V_i}{m \cdot a} \times 100\% \quad (1)$$

where C_i is the concentration of metal in the i -th sample (g/L), V_i is the volume of the i -th sample (l), m is the mass of the ore (kg), and a is the metal content in the original ore (wt.%).

For comparison of the leaching kinetics, the apparent extraction rate was calculated over selected time intervals from the slope of the cumulative recovery curve as $\Delta R / \Delta t$, where R is the cumulative metal recovery (%) and t is the leaching time (days). The calculated rates are expressed as % day^{−1}.

At the end of each series, the solid residue was removed from the column, washed with distilled water, dried at 60 °C and sent for SEM-EDAX (Mahwah, NJ, USA) analysis (if necessary).

2.3. Characterization of Solid and Liquid Samples

The phase composition of the ore was determined using a DW-27 mini Drawell X-ray diffractometer (Chongqing Drawell Instrument Co., Ltd., Chongqing, China) with Cu K α radiation.

The chemical composition of the ore was determined by ICP-OES using an iCAP Pro XP DUO ICP-OES spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Sample

preparation included complete acid digestion of a 0.5 g sample in a mixture of concentrated HCl, HNO₃, and HF with heating, followed by dissolution of the residue in HCl. The contents of Si, Fe, Ni, Co, Mg, Ca, and Al were determined.

Particle size distribution was determined by sieve analysis. A 500 g sample of ore was sieved through a set of standard sieves with mesh sizes of 5.0; 2.0; 1.0; 0.5; 0.25; 0.1; and 0.044 mm (Retsch GmbH, Haan, Germany). Each fraction was weighed, and the yield of the grade and total yield were calculated. SEM-EDAX mapping of silicon and iron was performed using a scanning electron microscope Phenom XL (Thermo Fisher Scientific, Waltham, MA, USA) (conditions: 20 kV, BSD, vacuum 0.10 Pa).

3. Results and Discussion

3.1. Ore Characterization

The chemical composition of the original ore is presented in Table 1.

Table 1. Selected elemental composition and loss on ignition of the initial ore.

Element	Si	Fe	Ni	Co	Mg	Ca	Al	Cr	LOI
wt %	21.93	27.16	1.42	0.07	2.76	0.59	2.15	1.32	4.3

The chemical composition of the ore is consistent with the results of the X-ray diffraction (XRD) analysis. The iron content is 27.16% by weight, which corresponds to goethite as the main mineral phase. Silicon (21.93%) is mainly associated with quartz and nontronite, identified by diffraction. The low contents of magnesium (2.76%) and aluminum (2.15%) confirm the low proportion of serpentine in the ore. The nickel content is 1.42%, which corresponds to an industrial level for hydrometallurgical treatment.

The particle size distribution of the ore is shown in Figure 2.

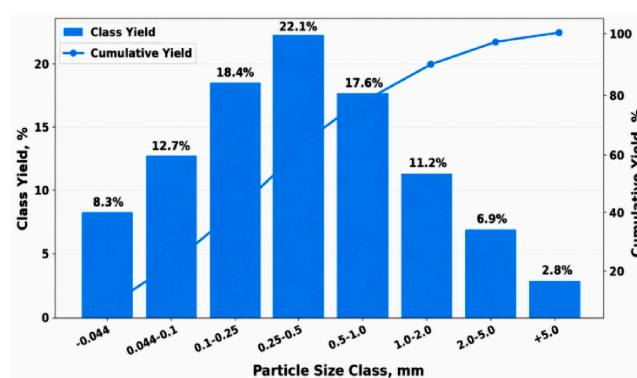


Figure 2. Particle size distribution of the nickel laterite ore.

The grain size of the ore has a wide range of particle sizes. It is almost unimodal, with a maximum in the range 0.25–0.5 mm (22.1%). The adjacent fractions 0.1–0.25 mm (18.4%) and 0.5–1.0 mm (17.6%) also account for a significant share, which explains the regular total yield curve. The content of coarse particles (+5.0 mm) is minimal (2.8%). The total yield of particles smaller than 1 mm is 79.1%, which indicates the loose and poorly cemented nature of the ore.

3.2. Justification for the Choice of Method and Leaching System

The main industrial method of processing limonitic laterite ores is high-pressure assisted leaching (HPAL), but it requires significant investments in high-pressure equipment. Heap leaching, characterized by simple instrumentation and low operating costs, is a more economical alternative.

The low Mg/Ni ratio of 1.9 indicates a relatively low abundance of Mg-bearing silicate phases. Therefore, the leaching system should promote Ni release from both Fe-bearing and silicate phases while maintaining Ni in the productive solution.

A combination of sulfuric and citric acids meets both requirements. Sulfuric acid promotes dissolution of Ni-bearing mineral components, while citric acid can stabilize released Ni^{2+} ions through complex formation. Based on the above, a combined system of $\text{H}_2\text{SO}_4 + \text{C}_6\text{H}_8\text{O}_7$ was chosen for the percolation experiments.

3.3. Nickel and Cobalt Extraction Kinetics

Figure 3 shows the kinetic dependences of nickel concentration in the pregnant solution (a) and total extraction (b) for three leaching systems.

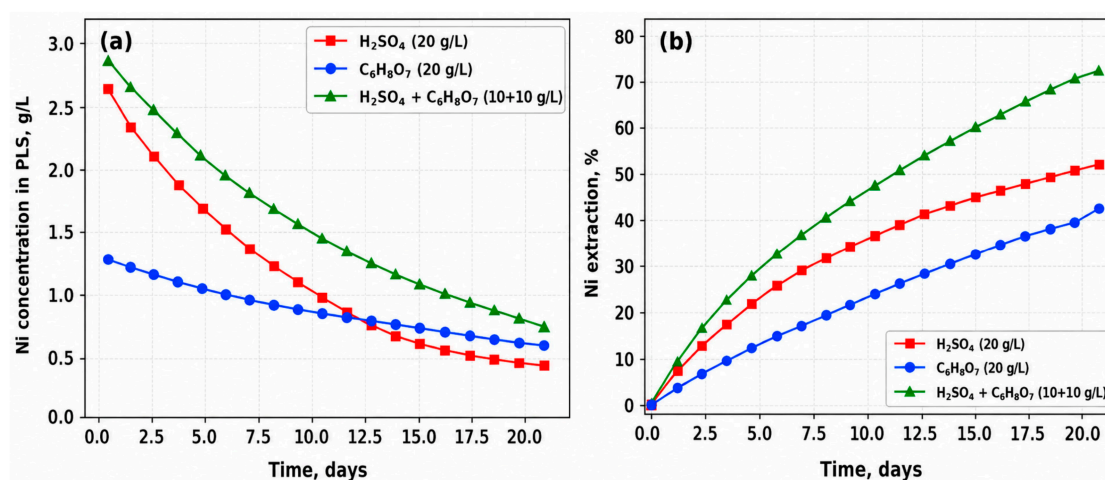


Figure 3. Ni concentration in PLS (a) and cumulative Ni extraction (b) as a function of leaching time for three leaching systems.

The $\text{H}_2\text{SO}_4 + \text{C}_6\text{H}_8\text{O}_7$ mixture at 10 + 10 g/L showed the best results in terms of Ni concentration in PLS (Figure 3a). The concentration was ~2.9 g/L at the beginning and then decreased to ~0.4 g/L by day 21. Overall Ni recovery reached 73% (Figure 3b). It should be noted that Xu et al. [25] also observed the effect of mineralogy on laterite leaching behaviour. Goethite ore in their study showed slower Ni extraction compared to silicate-goethite and saprolite ores.

In the case of sulfuric acid leaching, the initial Ni concentration was also high (~2.7 g/L), but it decreased more rapidly. After 21 days the recovery of Ni was 52%. MacCarthy et al. [26] showed that clay minerals and Mg silicates dissolve before other components, and once these are consumed, the leaching process slows down.

Citric acid shows the lowest initial concentration (about 1.3 g/L), which reflects its weaker action on the mineral matrix. However, the concentration curve shows the most gradual decline. For example, after 12 days, the Ni concentration with citric acid is higher than that with sulfuric acid.

The sulfuric acid extraction curve (Figure 3b) shows a clear slowdown after 14–15 days and a plateau, with the limiting value around 52%. This indicates the practical exhaustion of Ni forms accessible to sulfuric acid. The citric acid curve, by contrast, keeps a steady increase up to day 21 with no signs of reaching a plateau. The combined system also does not reach a plateau by day 21; the curve continues to rise, though the rate slows somewhat. This suggests that the final Ni extraction in a longer experiment could exceed the achieved 73%.

The kinetic dependences of the cobalt concentration in the productive solution (a) and the total extraction (b) for three leaching systems are shown in Figure 4.

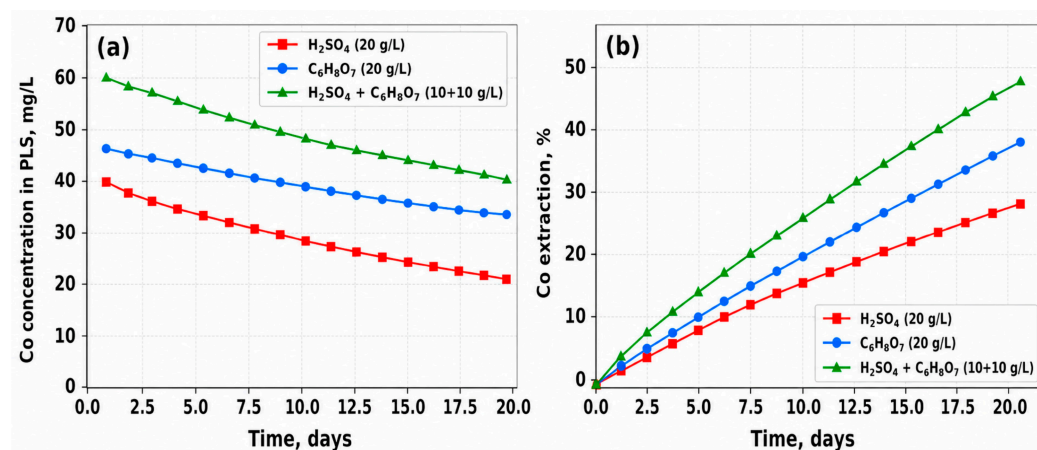


Figure 4. Co concentration in PLS (a) and cumulative Co extraction (b) as a function of leaching time for three leaching systems.

The leaching behavior of Co differs from that of Ni. The Co concentrations in the PLS analysis (Figure 4a) are one to two orders of magnitude lower than those of Ni (mg/L versus g/L), which is due both to the low Co content in the ore (0.07%) and to the different forms of these metals. Unlike Ni, Co does not have a pronounced initial peak of concentration, and the curves fall off monotonically.

A characteristic feature is the changed efficiency of the reagents in comparison with Ni. Citric acid provides a higher Co concentration (initially about 46 mg/L) than sulfuric acid (about 40 mg/L) and retains this advantage. The final Co yield with citric acid (38%) is higher than with sulfuric acid (28%), while the opposite was observed with Ni. This indicates differences in the extraction mechanisms of Ni and Co.

The combined system achieved the best result; within 21 days, 48% was achieved.

The behavior of Fe and Mg, which represent major impurity elements in the leach solution, was also evaluated (Tables S4 and S5). For all three systems, the concentrations of both elements decreased progressively with leaching time. After 21 days, cumulative iron extraction reached 14.2% with H_2SO_4 , 5.9% with citric acid, and 10.0% with the combined H_2SO_4 –citric acid system (Table S4). Thus, despite the high initial Fe content of the ore (27.16 wt.%), Fe dissolution remained considerably lower than Ni extraction, particularly for the combined system, where 73% Ni extraction was achieved together with only 10.0% Fe extraction. This indicates preferential extraction of Ni relative to the dominant Fe-bearing matrix. Mg showed substantially higher mobility than Fe. After 21 days, Mg extraction reached 62.1% with H_2SO_4 , 34.7% with citric acid, and 54.9% with the combined system (Table S5). The comparatively high Mg extraction is consistent with the greater susceptibility of Mg-bearing components to acid attack. The combined acid system therefore provides a favorable differentiation between Ni and Fe, although substantial Mg dissolution remains an important factor for subsequent solution purification.

To quantitatively evaluate the changes in leaching kinetics during the first 21 days, the apparent extraction rates were estimated from the slopes of the cumulative recovery curves ($\Delta R/\Delta t$) over consecutive time intervals; the calculated values are summarized in Tables S1 and S2. For Ni, the combined H_2SO_4 –citric acid system showed the highest apparent extraction rate throughout the 21-day experiment, with approximate values of 5.3, 2.9, and 2.2% day^{-1} for 0–7, 7–14, and 14–21 days, respectively. The corresponding values for H_2SO_4 were approximately 4.1, 2.1, and 1.2% day^{-1} , while citric acid gave approximately 2.5, 1.9,

and $1.7\% \text{ day}^{-1}$. Thus, sulfuric acid provided a relatively high initial Ni extraction rate but showed a pronounced decrease with time, whereas citric acid exhibited a lower initial rate but a more gradual decline. The combined system maintained the highest apparent Ni extraction rate over all three intervals (Table S1).

For Co, the apparent extraction rates for the combined H_2SO_4 –citric acid system were approximately 2.9 , 2.1 , and $1.9\% \text{ day}^{-1}$ for 0–7, 7–14, and 14–21 days, respectively. The corresponding values for citric acid were approximately 2.1 , 1.7 , and $1.6\% \text{ day}^{-1}$, whereas sulfuric acid gave approximately 1.7 , 1.2 , and $1.1\% \text{ day}^{-1}$. Thus, the combined system also maintained the highest apparent Co extraction rate, while citric acid consistently outperformed sulfuric acid (Table S2).

The differences in the extraction rates can be interpreted in terms of the different functions of the two leaching agents. In the H_2SO_4 solution, proton attack on acid-soluble mineral components promotes relatively rapid Ni release during the initial stage of leaching. However, the progressive decrease in the apparent Ni extraction rate suggests that readily accessible Ni-bearing sites become depleted and/or increasingly difficult to access as leaching proceeds. Citric acid provides weaker direct acid attack, which is consistent with its lower initial Ni extraction rate, but citrate ions can form soluble complexes with released metal ions and thereby favor their retention in the aqueous phase. This may account for the more gradual decline in Ni extraction rate and for the comparatively better performance of citric acid toward Co. In the combined H_2SO_4 –citric acid system, these effects act complementarily. Sulfuric acid facilitates the release of metals from the mineral matrix through proton attack, while citrate complexation stabilizes dissolved Ni and Co species in the leach solution. The combined system therefore maintains higher apparent extraction rates than either reagent alone.

Since neither Ni nor Co extraction had reached a clear plateau after 21 days, the experiment with the combined H_2SO_4 – $\text{C}_6\text{H}_8\text{O}_7$ system ($10 + 10 \text{ g/L}$) was extended to 42 days, with PLS samples collected every three days during the extended period (Figure 5).

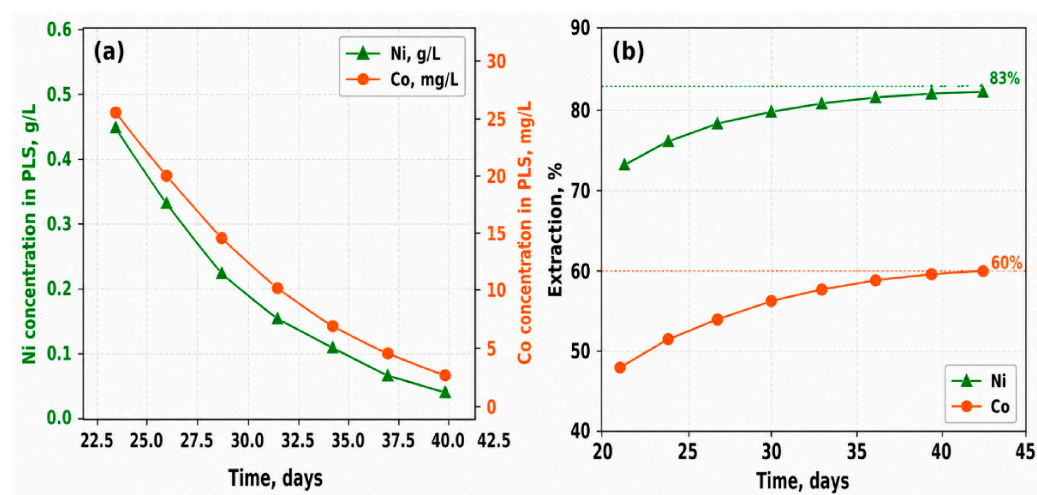


Figure 5. Ni concentration in PLS (a) and cumulative extraction of Ni and Co (b) during the extended percolation experiment (21–42 days) with $\text{H}_2\text{SO}_4 + \text{C}_6\text{H}_8\text{O}_7$ ($10 + 10 \text{ g/L}$).

Ni recovery increased from 73% after 21 days to approximately 83% after 42 days, while Co recovery increased from 48% to approximately 60%. The progressively decreasing slopes of the cumulative recovery curves indicate that extraction approached a plateau during the later stage of the experiment.

The progressive decrease in the extraction rate during the extended experiment was quantified from the slopes of the cumulative recovery curves (Table S3). For Ni, the

apparent extraction rate decreased from approximately $0.87\% \text{ day}^{-1}$ during days 21–27 to $0.42\% \text{ day}^{-1}$ during days 27–33, $0.20\% \text{ day}^{-1}$ during days 33–39, and approximately $0.10\% \text{ day}^{-1}$ during days 39–42. A similar decrease was observed for Co, for which the corresponding apparent extraction rates were approximately 0.96, 0.63, 0.33, and $0.13\% \text{ day}^{-1}$. The slopes of both recovery curves progressively decreased during prolonged leaching, confirming that the extraction of both Ni and Co was approaching a plateau toward the end of the 42-day experiment.

At the final stage of the experiment, Ni concentration in PLS by this point decreases to 0.04–0.12 g/L, making further leaching economically unfeasible. Co recovery reached 60%, reaching a plateau after 36 days. The lower ultimate recovery of cobalt confirms its stronger bond with the Fe-rich and silicate-bearing mineral components of the laterite ore. A gradual increase in recovery is typical of column leaching of laterites. Nosrati et al. [27] obtained up to 90% Ni and 70% Co in 100 days and showed that the duration of the process significantly depends on the mineralogical and particle size distribution of the ore.

To screen the effect of the H_2SO_4 /citric acid ratio, additional experiments were performed at a constant total reagent concentration of 20 g/L using three mass-based compositions: 15 + 5, 10 + 10, and 5 + 15 g/L. The constant total mass concentration was selected to compare the systems at the same overall reagent dosage. Because sulfuric and citric acids differ in molar mass, dissociation behavior, and number of ionizable protons, these compositions are not proton-equivalent (Figure 6).

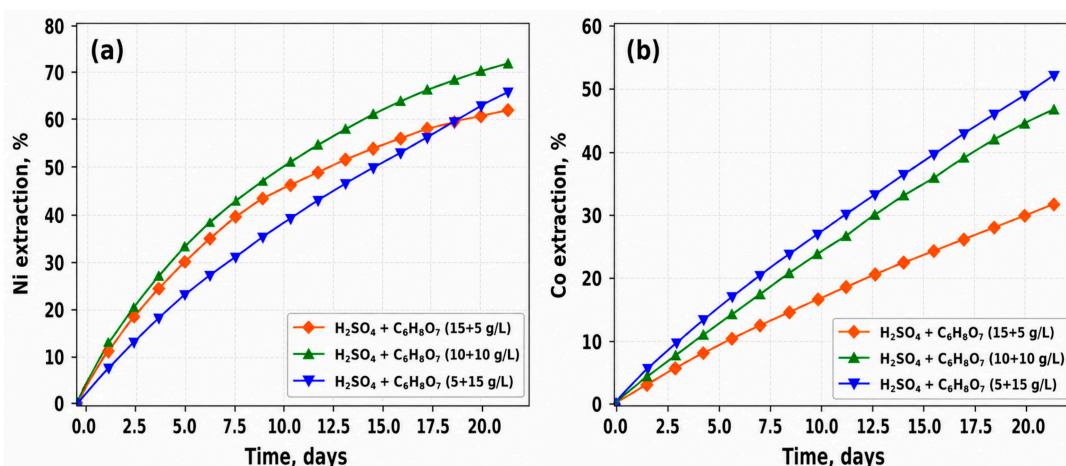


Figure 6. Effect of $\text{H}_2\text{SO}_4/\text{C}_6\text{H}_8\text{O}_7$ ratio on Ni extraction (a) and Co extraction (b) at a total acid concentration of 20 g/L.

For nickel, the maximum yield is achieved with a mixing ratio of 10 + 10 (73%). A predominance of sulfuric acid (15 + 5) leads to a high initial rate, but to an early plateau (62%). A predominance of citric acid (5 + 15) causes a steady growth, but an uncertain matrix degradation rate (65%). For cobalt, on the other hand, the best result is achieved with the 5 + 15 (52%) option, which expands the stronger role of complexation. Among the three tested mass-based acid ratios, 10 + 10 g/L provided the best balance for the simultaneous extraction of Ni and Co within the investigated range. The effect of acid ratio was different for Ni and Co. Increasing the citric acid fraction had a stronger positive effect on Co extraction, while Ni extraction was highest when the two acids were used in equal amounts. This suggests that citrate complexation contributes more strongly to Co extraction, whereas Ni recovery depends on the combined action of sulfuric and citric acids.

3.4. Elemental Mapping of Ore Particles During Leaching Stages

In the initial ore (Figure 7a), silicon is evenly distributed over the entire particle surface, which coincides with a silicate matrix (serpentine, nontronite). After 7 days (Figure 7b), the distribution becomes uneven: regions without a silicon signal occur, which alternate with regions in which silicon is present. This indicates a frontal dissolution process: the solution penetrates along the surface and cracks. In arrears after 21 days (Figure 7c), the silicon signal becomes very weak, indicating substantial dissolution of silicate phases.

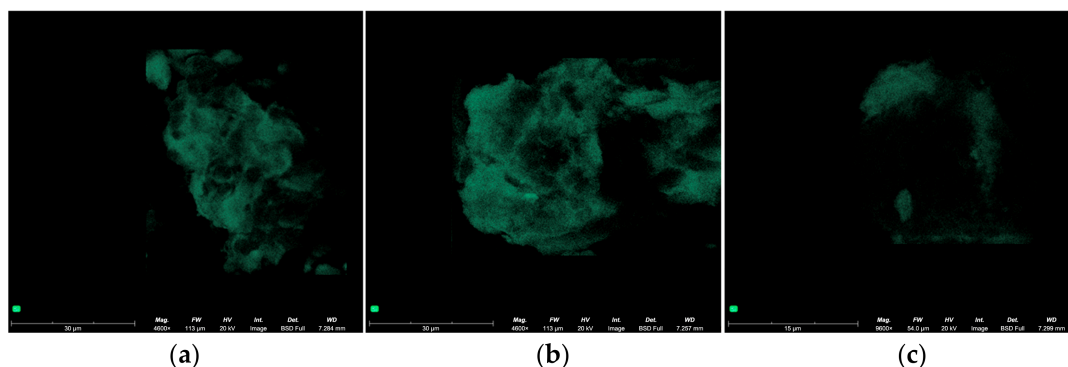


Figure 7. EDAX elemental maps of Si distribution in ore particles: (a) initial ore, (b) after 7 days of leaching, (c) residue after 21 days.

In the initial ore (Figure 8a), Fe is distributed unevenly: pronounced clusters correspond to goethite inclusions, while a scattered signal indicates the presence of Fe in silicates. At the intermediate stage (Figure 8b), the Fe distribution becomes more uniform: as the silicates dissolve, goethite grains are exposed and form a continuous framework. In the residue (Figure 8c), Fe is found throughout the entire particle—it consists almost entirely of goethite.

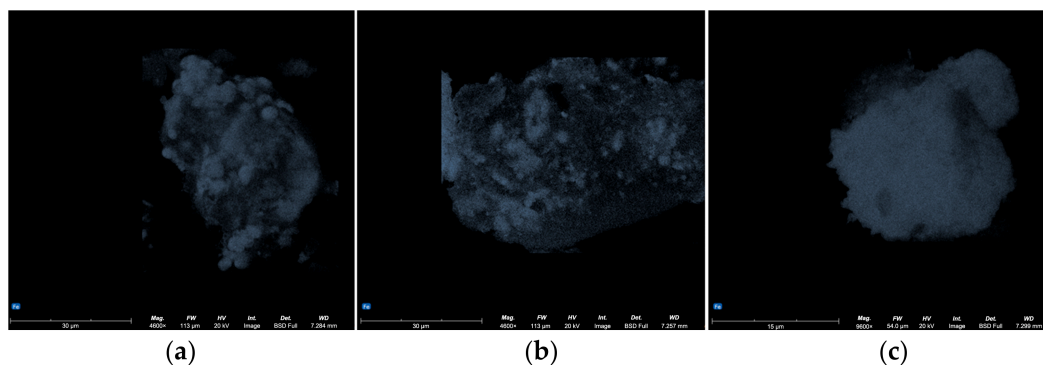


Figure 8. EDAX elemental maps of Fe distribution in ore particles: (a) initial ore, (b) after 7 days of leaching, (c) residue after 21 days.

The obtained mapping data are consistent with the results of chemical analysis of the productive solutions. The strong decrease in the Si signal after 21 days indicates substantial dissolution of silicate phases. This process coincides with significant Ni extraction, suggesting that dissolution of Ni-bearing silicate components contributes to Ni release. The preservation of the Fe-rich framework indicates limited dissolution of the dominant goethite phase. Thus, the microstructural data indicate preferential dissolution of silicate components relative to the goethite-rich matrix during leaching with the combined acid system.

The SEM-EDX observations, jointly with the mineralogical composition of the initial ore, provide a basis for interpreting the probable occurrence of Ni and Co. In limonitic

laterite ores, Ni is commonly distributed between Fe oxyhydroxides and subordinate silicate/clay phases, whereas Co is more strongly associated with Fe- and Mn-bearing components. In the present ore, goethite is the dominant Fe-bearing phase, while serpentine and a minor smectite-type phase are also present. Therefore, Ni is expected to occur both in the Fe-rich matrix and in silicate components, whereas Co is likely more strongly associated with the Fe-rich part of the ore.

3.5. XRD Analysis of Leaching Residues

Figure 9 compares the diffraction patterns of the original ore and the residues after 21 days of percolation leaching with three systems.

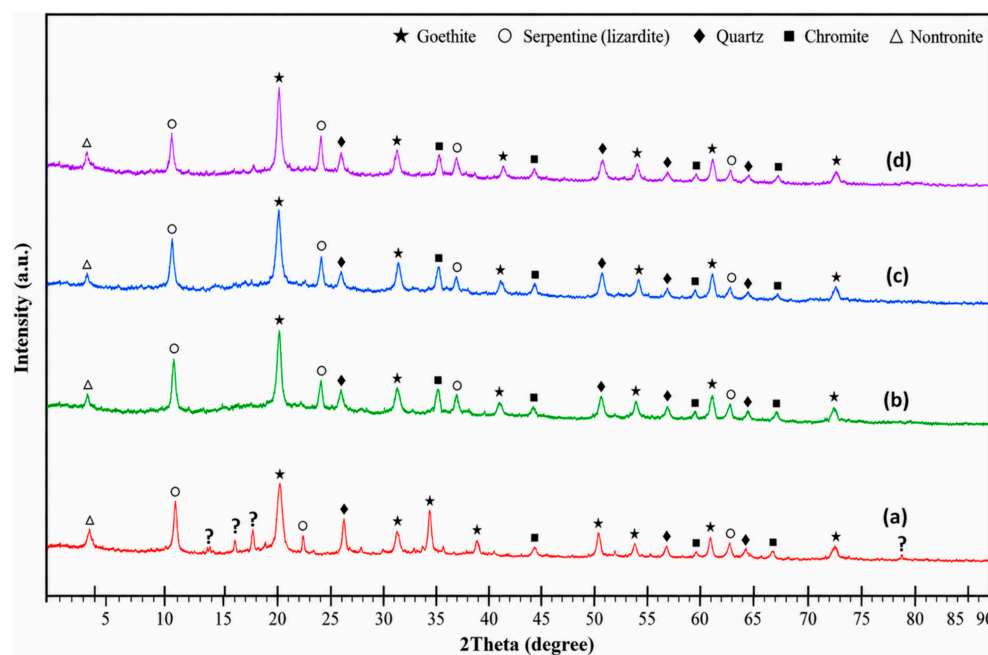


Figure 9. XRD patterns of (a) the initial nickel laterite ore and residues after 21 days of percolation leaching with (b) H_2SO_4 , (c) $\text{C}_6\text{H}_8\text{O}_7$, and (d) $\text{H}_2\text{SO}_4 + \text{C}_6\text{H}_8\text{O}_7$.

The initial material is characterized by goethite ($\alpha\text{-FeOOH}$) as the dominant crystalline Fe-bearing phase. Reflections corresponding to serpentine, represented mainly by lizardite ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), quartz (SiO_2), and chromite (FeCr_2O_4), and a minor nontronite phase are also present. A weak reflection at $2\theta \approx 5^\circ$ is tentatively assigned to nontronite ($(\text{Na,Ca})_{0.3}(\text{Fe}^{3+},\text{Al,Mg})_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$). The strong goethite reflections are consistent with the high Fe content of the ore, while the presence of serpentine and nontronite indicates the contribution of silicate and clay components to the mineral matrix. After the leaching, the crystalline nature is largely preserved in all three residues. Goethite reflections remain clearly detectable, indicating that a substantial part of the Fe-bearing crystalline matrix persists under the applied leaching conditions. Reflections assigned to serpentine are also retained after treatment with each leaching system, and no pronounced decrease in their intensity can be reliably established from the XRD patterns. Quartz and chromite reflections remain detectable in all residues. No distinct new crystalline phases are evident after leaching. The XRD data indicate that the differences in Ni and Co extraction between the leaching systems occur without a major transformation of the bulk crystalline phase assemblage detectable by XRD.

4. Conclusions

This study demonstrates the applicability of a combined sulfuric and citric acid system for percolation leaching of limonitic nickel laterite ore under ambient conditions.

The combined acid system provided a pronounced enhancement in Ni extraction, reaching 73% after 21 days compared with 52% for sulfuric acid and 42% for citric acid at the same total acid concentration. EDAX mapping and XRD analysis of the leaching residues demonstrate significant dissolution of silicate phases, while the goethite-rich structure is mostly preserved.

The combined system determines the difference in the leaching behavior of Ni and Co. Ni extraction is characterized by a high initial rate followed by a slowdown, while Co extraction proceeds more uniformly and without a pronounced initial peak. Citric acid is more effective for Co than sulfuric acid, but for Ni the opposite is true. The ratio 10 + 10 g/L provided the best balance for the simultaneous extraction of Ni and Co.

A prolonged experiment showed that the maximum recovery of Ni was ~83%, and Co ~60%, with a plateau observed after 33–36 days. Further research could focus on optimizing the temperature regime and scaling up the process to assess the applicability of the combined acid system in industrial heap leaching technology.

The main limitations of the proposed approach are the relatively long leaching duration and the acid consumption required to achieve high metal recovery. Further work should therefore focus on reducing the leaching time and reagent consumption while maintaining high Ni and Co recovery.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min16100971/s1>, Table S1. Apparent Ni extraction rates (% day^{−1}) calculated from the slopes of the cumulative recovery curves during the first 21 days of leaching. Table S2. Apparent Co extraction rates (% day^{−1}) calculated from the slopes of the cumulative recovery curves during the first 21 days of leaching. Table S3. Apparent Ni and Co extraction rates (% day^{−1}) during the extended percolation leaching experiment with H₂SO₄ + citric acid (10 + 10 g/L). Table S4. Fe concentration and cumulative Fe extraction during the first 21 days of percolation leaching with H₂SO₄, citric acid, and the combined acid system. Table S5. Mg concentration and cumulative Mg extraction during the first 21 days of percolation leaching with H₂SO₄, citric acid, and the combined acid system.

Author Contributions: Conceptualization, S.T.; methodology, R.N., A.E. and L.M.; validation, K.K., and A.B.; formal analysis, L.M. and K.K.; investigation, A.E., S.T., K.K., L.M. and A.B.; resources, S.T. and R.N.; data curation, K.K., A.E. and L.M.; writing—original draft preparation, R.N., K.K. and S.T.; writing—review and editing, R.N. and S.T.; visualization, K.K., A.B. and L.M.; funding acquisition, R.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant no. BR28713557).

Data Availability Statement: The data supporting the results can be made available from the corresponding author upon request.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Sudol, S. The thunder from down under—everything you wanted to know about nickel laterites but were afraid to ask. *Can. Min. J.* **2005**, *126*, 8–12.
2. Butt, C.R.; Cluzel, D. Nickel laterite ore deposits: Weathered serpentinites. *Elements* **2013**, *9*, 123–128. [[CrossRef](#)]
3. Satritama, B.; Cooper, C.; Fellicia, D.; Pownceby, M.I.; Palanisamy, S.; Ang, A.; Mukhlis, R.Z.; Pye, J.; Rahbari, A.; Brooks, G.A.; et al. Hydrogen plasma for low-carbon extractive metallurgy: Oxides reduction, metals refining, and wastes processing. *J. Sustain. Metall.* **2024**, *10*, 1845–1894. [[CrossRef](#)]

4. Kalungi, P.; Yao, Z.; Huang, H. Aspects of nickel, cobalt and lithium, the three key elements for Li-ion batteries: An overview on resources, demands, and production. *Materials* **2024**, *17*, 4389. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Xiong, X.; Ma, B.; Li, X.; Yu, J.; Shi, L.; Wang, C.; Chen, Y. Hydrometallurgical process and recovery of valuable elements for limonitic laterite: A review. *Chin. J. Chem. Eng.* **2024**, *73*, 189–201. [\[CrossRef\]](#)
6. Fan, Q.; Yuan, S.; Wen, J.; He, J. Review on comprehensive utilization of nickel laterite ore. *Miner. Eng.* **2024**, *218*, 109044. [\[CrossRef\]](#)
7. Msumange, D.A.; Jampaiah, D.; Tardio, J.; Nilsson, M.; Arandiyan, H.; Bhargava, S.K. A review of nickel and cobalt from laterite ores: Toward sustainable extraction pathways for the battery industry. *J. Sustain. Metall.* **2026**, *12*, 1038–1069. [\[CrossRef\]](#)
8. McDonald, R.G.; Whittington, B.I. Atmospheric acid leaching of nickel laterites review: Part I. Sulphuric acid technologies. *Hydrometallurgy* **2008**, *91*, 35–55. [\[CrossRef\]](#)
9. Astuti, W.; Hirajima, T.; Sasaki, K.; Okibe, N. Kinetics of nickel extraction from Indonesian saprolitic ore by citric acid leaching under atmospheric pressure. *Min. Metall. Explor.* **2015**, *32*, 176–185. [\[CrossRef\]](#)
10. Astuti, W.; Hirajima, T.; Sasaki, K.; Okibe, N. Comparison of effectiveness of citric acid and other acids in leaching of low-grade Indonesian saprolitic ores. *Miner. Eng.* **2016**, *85*, 1–16. [\[CrossRef\]](#)
11. Astuti, W.; Hirajima, T.; Sasaki, K.; Okibe, N. Comparison of atmospheric citric acid leaching kinetics of nickel from different Indonesian saprolitic ores. *Hydrometallurgy* **2016**, *161*, 138–151. [\[CrossRef\]](#)
12. Ciftci, H.; Atik, S.; Gurbuz, F. Biocatalytic and chemical leaching of a low-grade nickel laterite ore. *Metall. Res. Technol.* **2018**, *115*, 305. [\[CrossRef\]](#)
13. Kursunoglu, S.; Ichlas, Z.T. Dissolution of lateritic nickel ore using ascorbic acid as synergistic reagent in sulphuric acid solution. *Trans. Nonferrous Met. Soc. China* **2018**, *28*, 1652–1659. [\[CrossRef\]](#)
14. West, T.P. Citric acid production by *Aspergillus niger* using solid-state fermentation of agricultural processing coproducts. *Appl. Biosci.* **2023**, *2*, 1–13. [\[CrossRef\]](#)
15. Pathak, A.; Vinoba, M.; Kothari, R. Emerging role of organic acids in leaching of valuable metals from refinery-spent hydroprocessing catalysts, and potential techno-economic challenges: A review. *Crit. Rev. Environ. Sci. Technol.* **2021**, *51*, 1–43. [\[CrossRef\]](#)
16. Punt, T.; Van Wyk, A.P.; Bradshaw, S.M.; Akdogan, G. Citric acid leaching performance at high solid-to-liquid ratios for lithium-ion battery recycling. *Min. Metall. Explor.* **2024**, *41*, 3463–3474. [\[CrossRef\]](#)
17. Mubarak, M.Z.; Astuti, W.; Chaerun, S.K. Leaching behaviour of nickel from Indonesian laterite ore in some organic acids. In Proceedings of the XIII International Mineral Processing Symposium (IMPS 2012), Bodrum, Turkey, 10–12 October 2012; pp. 523–531.
18. Chaerun, S.K.; Sulisty, R.S.; Minwal, W.P.; Mubarak, M.Z. Indirect bioleaching of low-grade nickel limonite and saprolite ores using fungal metabolic organic acids generated by *Aspergillus niger*. *Hydrometallurgy* **2017**, *174*, 29–37. [\[CrossRef\]](#)
19. Wanta, K.C.; Astuti, W.; Perdana, I.; Petrus, H.T.B.M. Kinetic study in atmospheric pressure organic acid leaching: Shrinking core model versus lump model. *Minerals* **2020**, *10*, 613. [\[CrossRef\]](#)
20. Wanta, K.C.; Astuti, W.; Petrus, H.T.B.M.; Perdana, I. Product diffusion-controlled leaching of nickel laterite using low concentration citric acid leachant at atmospheric condition. *Int. J. Technol.* **2022**, *13*, 410–421. [\[CrossRef\]](#)
21. Tzeferis, P.G.; Agatzini-Leonardou, S. Leaching of nickel and iron from Greek non-sulphide nickeliferous ores by organic acids. *Hydrometallurgy* **1994**, *36*, 345–360. [\[CrossRef\]](#)
22. Carpen, H.L.; Giese, E.C. Enhancement of nickel laterite ore bioleaching by *Burkholderia* sp. using a factorial design. *Appl. Water Sci.* **2022**, *12*, 181. [\[CrossRef\]](#)
23. Borda, J.; Torres, R. Effect of pretreatments to improve nickel leaching from laterites in carboxylic media: Mechanism and kinetic model. *S. Afr. J. Chem. Eng.* **2023**, *46*, 12–21. [\[CrossRef\]](#)
24. Yunita, F.E.; Mubarak, M.Z. Nickel leaching from laterite ores by combination of organic and sulfuric acid. *AIP Conf. Proc.* **2021**, *2382*, 050003. [\[CrossRef\]](#)
25. Xu, D.; Liu, L.X.; Quast, K.; Addai-Mensah, J.; Robinson, D.J. Effect of nickel laterite agglomerate properties on their leaching performance. *Adv. Powder Technol.* **2013**, *24*, 750–756. [\[CrossRef\]](#)
26. MacCarthy, J.; Addai-Mensah, J.; Nosrati, A. Atmospheric acid leaching of siliceous goethitic Ni laterite ore: Effect of solid loading and temperature. *Miner. Eng.* **2014**, *69*, 154–164. [\[CrossRef\]](#)
27. Nosrati, A.; Quast, K.; Xu, D.; Skinner, W.; Robinson, D.J.; Addai-Mensah, J. Agglomeration and column leaching behaviour of nickel laterite ores: Effect of ore mineralogy and particle size distribution. *Hydrometallurgy* **2014**, *146*, 29–39. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.