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Atmospheric hydrochloric and nitric acid leaching of a limonite ore from the Wolo mine area, Southeast Sulawesi, Indonesia

Sufriadin[1,*], Malyanus YEPTA[1], Irzal NUR[1], Purwanto[1], Rizky AMALIA[1], Ulva Ria IRFAN[2], Djabal Nur BASIR[3], Tsubasa OTAKE[4]

[1] *Department of Mining Engineering, Hasanuddin University, Kampus Teknik UNHAS, Jl. Poros Malino KM.6, Bontomarannu, Gowa 92171, Sulawesi Selatan, Indonesia*
[2] *Department of Geological Engineering, Hasanuddin University, Kampus Teknik UNHAS, Jl. Poros Malino KM.6, Bontomarannu, Gowa 92171, Sulawesi Selatan, Indonesia*
[3] *Department of Chemistry, Hasanuddin University, Jl. Perintis Kemerdekaan KM.10, Tamalanrea, Makassar 90245, Sulawesi Selatan, Indonesia*
[4] *Division of Sustainable Resources Engineering, Hokkaido University, Kita 13 Nishi 8, Sapporo 060-8638, Japan*

***Corresponding author e-mail**: sufri.as@unhas.ac.id

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Abstract

The atmospheric acid leaching studies of a limonite ore sample from the Wolo mine area, Southeast Sulawesi, Indonesia, have been performed using hydrochloric acid (HCl) and nitric acid (HNO_3). The objectives of these studies were to compare the leaching degree of metals (Ni, Co, Fe, and Al) and to analyze the dissolution behavior of minerals under different acid concentrations. Mineralogical characterization of the ore sample was conducted using optical microscopy, scanning electron microscopy (SEM), and X-ray diffraction, whereas chemical composition was determined by X-ray fluorescence (XRF) spectrometry and atomic absorption spectroscopy (AAS), respectively. An atmospheric leaching test was done with the variables of acid concentration, leaching duration of 90 min, and leaching temperature of 100°C. Limonite ore samples contain goethite, gibbsite, talc, quartz, and lizardite. It was revealed that as much as 92.22% of Ni and 90.14% of Fe could be leached using 3 M HCl, whereas only 63.14% of Ni and 38.74% of Fe could be extracted from limonite ore using 3 M HNO_3. The higher leaching degree of Fe in HCl indicates low selectivity with Ni, which might contaminate pregnant leach solution (PLS), leading to further complications in the purification process. Results of the leaching experiment show that goethite was more easily dissolved in HCl than in HNO_3.

1. Introduction

The increased demand for nickel, mainly in the manufacturing of electric vehicle batteries, has led to increased research into the extraction of this metal from various sources. Approximately 69% of world nickel production is used in stainless steel, 11% in battery production, 7% in non-ferrous alloys, and the rest is utilized in plating, alloys, and foundries [1]. Nickel can be recovered from two primary sources: nickel sulfide, and nickel laterite ores. About 70% of world Ni resources are supplied by nickel laterite, and only around 30% are derived from Ni sulfide [2]. However, the majority of the Ni mine production still comes from Ni sulfide ore due to relatively lower operating costs for the processing of this ore. Steady decreases in global Ni sulfide ore reserves make the recovery of Ni and other valuable metals from laterite ores attractive. Indonesia has the largest nickel production, with an amount of up to 1.6 million tons, or 48.5% of the world's mine production [3].

Nickel laterite ore is formed by the chemical weathering of ultramafic rocks containing Ni-bearing minerals such as olivine and serpentine, which commonly takes place in tropical regions [4]. Typical laterite ores are generally divided into the saprolite zone, which is located on the lower part of the profile, and the limonite zone, which is situated on the upper part of the profile. The saprolite zone is characterized by a higher Ni grade (1.6% to 2.3%) and higher Mg and Si. In contrast, the limonite zone generally contains a low grade of Ni (1.2% to 1.7%), higher in Fe but lower in Mg and Si [5].

Processing of nickel laterite ores can be performed either by pyrometallurgical or hydrometallurgical methods. Pyrometallurgy is a suitable method for the processing of saprolite ore economically. However, this process is disadvantageous due to its considerable energy consumption. Hydrometallurgy is a viable option for the processing of limonite ore due to the lower energy requirement and the fact that some valuable metals can be recovered simultaneously [6,7].

At present, commercially hydrometallurgical processing of limonite ores includes high-pressure acid leaching (HPAL) using sulfuric acid as a lixiviant [8]. Higher capital and operational costs with more acid neutralization are the main drawbacks of the HPAL process. It is therefore, the atmospheric pressure leaching (AL) method has drawn increasing attention in recent years [9]. The disadvantages of sulfuric

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acid atmospheric leaching are longer leaching times, lower metal recoveries, and higher acid consumption [10]. Nevertheless, the AL method has some advantages and future prospects, such as lower investment costs, a lower energy requirement, and simpler process equipment [11]. Beside H_2SO_4, HCl and HNO_3 have also been extensively employed in the extraction of metals from laterite ores. Some advantages of using HCl as a lixiviant are easier recovery of free acid from its waste solution, easier separation of metal chloride, and chloride liquor containing Ni, Fe, and Mg could be separated via spray roasting [12]. Similarly, the merits of using HNO_3 as a solvent are that is easily dissolves of valuable metals, divalent iron can be readily precipitated as hematite, and it is easily regenerated [13]. Acid leaching of limonite is a complex process where its performances are influenced either by the physicochemical properties of the ore or leaching parameters. The aims of this paper were to discuss the comparison of the effect of HCl and HNO_3 concentration as lixiviants in the leaching of target metals (Ni, Co, Fe, and Al) and the dissolution behavior of minerals in a limonite ore.

2. Experimental

2.1 Material

The limonite ore sample used in this study was collected from a nickel laterite mine area located in the Wolo district of Kolaka Regency, Southeast Sulawesi, Indonesia. Approximately 10 kg of the limonite ore sample was taken from an active mine site. The sample was ground and then sieved into 100-mesh-size fractions.

2.2 Leaching procedure

A batch atmospheric leaching experiment of a limonite ore sample was performed using a 500 mL two-necked, flat-bottom flask (Figure 1). It was placed in the heating mantle on a digital hot plate equipped with a magnetic stirrer (Corning PC-420D model, USA). A thermometer was enclosed in the flask and submerged partially in the slurry to monitor the temperature during leaching. A reflux condenser was also attached to the glass reactor to inhibit evaporation losses. Hydrochloride (HCl) and nitric (HNO_3) acids with various concentrations (2, 3, 4, and 6 M) were used as leaching agents.

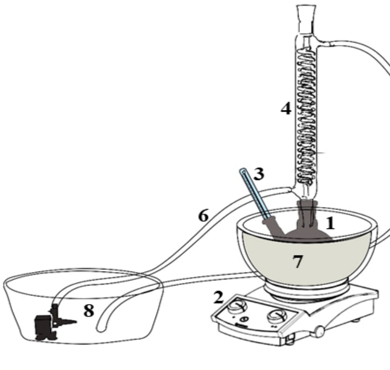

Figure 1. Schematic of leaching experimental setup (1-two neck flat bottom flask, 2-hot plate magnetic stirrer, 3-thermometer, 4-condenser, 5-tap water outlet, 6-tap water inlet, 7-water bath, 8-water circulation)

The experimental conditions were set as follows: particle size of 200 mesh, leaching temperature of 100°C, solid-to-liquid ratio of 1:10, leaching time of 90 min, and stirring speed of 450 rpm. After the leaching experiment was accomplished, the pregnant leach solutions (PLS) and leach residues were separated using filter paper (Whatman No. 42) in a Buchner funnel. The PLS were further analyzed by AAS to determine Ni, Co, Fe, and Al content, whereas leach residues were washed with deionized water three times to remove their acid content. Solid residues were then dried in an oven at 100°C for 2 h and examined by using XRD and SEM to find out the phase and textural change, respectively. This activity was done at the Mineral Processing Laboratory, Hasanuddin University Makassar.

2.3 Analytical methods

The mineralogical characterization of the limonite ore sample was carried out using an optical polarized microscope (Nikon Eclipse LV100N POL) under the reflection light mode polished section, XRD (Shimadzu Maxima X-7000 diffractometer), and SEM-EDX (Quanta FEI-450). For the XRD analysis, the sample was scanned at room temperature using Cu-Kα radiation with a voltage of 40 kV and a current of 30 mA. The scan range (2θ angle) was 5° to 70° with a step size of 0.02°. All these analyses were carried out at the Department of Geological Engineering, Hasanuddin University. The chemical composition of limonite ore samples was determined using XRF method (Bruker S8 Tiger WDXRF spectrometer), whereas the concentrations of Ni, Co, Fe, and Al in the leached solution were measured using an atomic absorption spectrometer (AAS). The leaching efficiency of metals was calculated using the following Equation (1) [14]:

$$\chi = \frac{c.v}{m.k} \times 100 \tag{1}$$

where χ is leaching efficiency of metal (%), c is metal concentration in pregnant solution ($mg \cdot L^{-1}$), v is volume of solution (L), m is mass of the ore (g), and k is metal grade of the ore ($mg \cdot kg^{-1}$).

3. Results and discussion

3.1 Material characterization

The results of ore characterization using optical microscopic and SEM methods are demonstrated in Figure 2. It is shown that the ore was mainly composed of goethite [$FeO(OH)$], followed by gibbsite [$AlO(OH)$]. Goethite is characterized by acicular and subhedral to unhedral textures. Talc [$Mg_3Si_4O_{10}(OH)_2$], quartz [SiO_2], and lizardite [$Mg_3Si_2O_5(OH)_4$] were also detected within the sample in small quantities. Most minerals are likely subrounded to subangular shapes with a wide range of grain sizes. Hematite was also identified, and it could be formed through the partial alteration of goethite during advanced chemical weathering.

The X-ray powder diffraction pattern of the limonite ore sample is depicted in Figure 3. The presence of goethite [$FeO(OH)$] is indicated by the high reflection intensities at the 2θ angles of 22.3°, 26.9°, and 53.3°, corresponding to the basal spacing of 4.17 Å, 2.43 Å, and 1.71 Å, respectively. The occurrence of a peak at 18.3° 2θ (d_{002} ~4.83 Å) is a diagnostic peak of gibbsite [AlO(OH)]. Other peaks with d-values of 2.69 Å and 2.23 Å also belong to gibbsite. The peaks occurring at 9.5° and 28.6° 2θ with respective d-values of 9.30 Å and 3.12 Å are characteristic peaks of talc [$Mg_3Si_4O_{10}(OH)_2$]. Reflection intensity with d-values of 7.15 Å and 3.55 Å are typical peaks of lizardite [$Mg_3Si_2O_5(OH)_2$], a serpentine group mineral. Quartz [SiO_2] appearance is characterized by the presence of peaks with d-values of 4.25 Å and 3.34 Å.

In general, the XRD pattern of the analyzed sample shows broad peaks mainly of goethite, indicating poor crystallinities. The main carriers of Ni and Co are most likely attached to goethite and possibly to lizardite. Nickel and cobalt can substitute for Fe in the goethite structure or can be adsorbed on the surface of goethite [15].

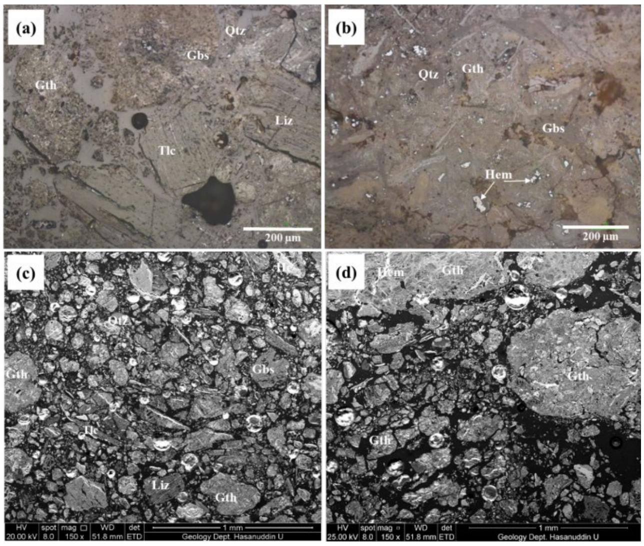

Figure 2. Optical photomicrographs (a; b) and SEM-BSE images (c; d) of limonite sample showing the textural features that are mainly composed of goethite (Gth) with subordinate of gibbsite (Gbs), talc (Tlc), lizardite (Liz), quartz (Qtz) and hematite (Hem).

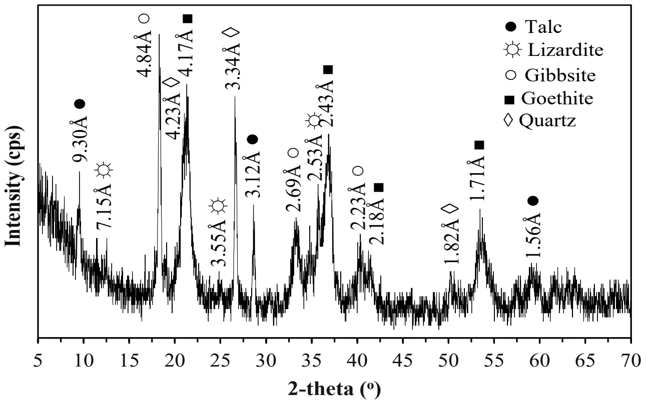

Figure 3. X ray diffraction pattern of a limonite ore sample

The chemical composition of the ore sample analyzed by XRF is provided in Table 1. Iron and aluminum concentrations show higher values. These are consistent with the domination of goethite followed by gibbsite in the ore, which is typical of limonite. The concentration of MgO is low and it could be related to the presence talc and lizardite. Meanwhile, significant content of SiO_2 in the ore might be assigned to the presence of quartz. Chromium and Ni have relatively lower values.

3.2 Effect of HCl and HNO_3 concentration on the leaching of target metals

A series of experiments were performed to find out the effect of acid concentrations on the leaching efficiency of Ni, Co, Al, and Fe. The results of HCl leaching are presented in Figure 4(a). It is exhibited that leaching with 2 M HCl resulted in the extraction of 69.76% Ni, 68.15% Fe, and 15.09% Co. In contrast, only 1.44% of Al could be leached from the ore at the same acid concentration. Leaching of Ni, Fe, and Co increases rapidly at 3 M HCl, reaching 92.22%, 90.14%, and 42.37%, respectively. As the HCl concentration rises to 4 M, the extractions of Ni, Fe, and Co show slight enhancement with values of 92.65% Ni, 92.0% Fe, and 51.13% Co. Further increases in HCl concentrations at 6 M reveal only a slow increase in Ni, Fe, and Co, with values of 93.23%, 94.60%, and 58.63%, respectively. In the case of Al leaching, it shows very low efficiency, with a value of 3.92% at 6 M HCl.

The graph illustrating the effect of HNO_3 concentration on the leaching efficiency of Ni, Fe, Co, and Al is presented in Figure 4(b). It is shown that the leaching of limonite with 2 M HNO_3 results in the extraction of 43.29% Ni, 29.25% Fe, 42.27% Co, and 12,87% Al. The increase in HNO_3 concentration at 3 M has led to a rapid elevation in the extraction of Ni, with a value of 63.14%. The extraction of Fe and Al shows slightly elevated rates of 38.72% and 16.49%, respectively. On the contrary, the leaching of Co decreased to 28.86%. A further increase in HNO_3 concentration at 4 M has induced a sharp increase in Ni extraction with a rate of 85.93% Ni. Other metals extracted, such as Fe, Co, and Al, slowly rise. The maximum leaching degree of Ni was achieved using 6 M HNO_3 with a value of 99.57%, while the Fe extraction was significantly decreased to 22.56%.

The comparison between HCl and HNO_3 for the atmospheric leaching of limonite ore exhibits different characteristics. For HCl leaching, it was shown that Ni and Fe have similar behavior, indicating that both of these metals are located in the same minerals, mainly goethite [FeO(OH)]. Some Ni may substitute for Fe in the goethite structure, so it is required to break down the FeNi-O bond to release Ni into solution. A better leaching degree of Ni could be obtained using 3 M of HCl. However, the high leaching degree of Fe at this experimental condition indicates low selectivity. In practice, it is undesirable due to the difficulty of further metal separation and purification [16].

Table 1. Chemical composition of limonite ore determined by XRF method.

Oxides/Elements (%)									SiO_2/MgO
Fe_2O_3	MgO	SiO_2	Al_2O_3	MnO	TiO_2	Cr	Ni	Co	
56.28	1.34	14.02	11.35	0.55	0.25	1.55	1.37	0.07	10.46

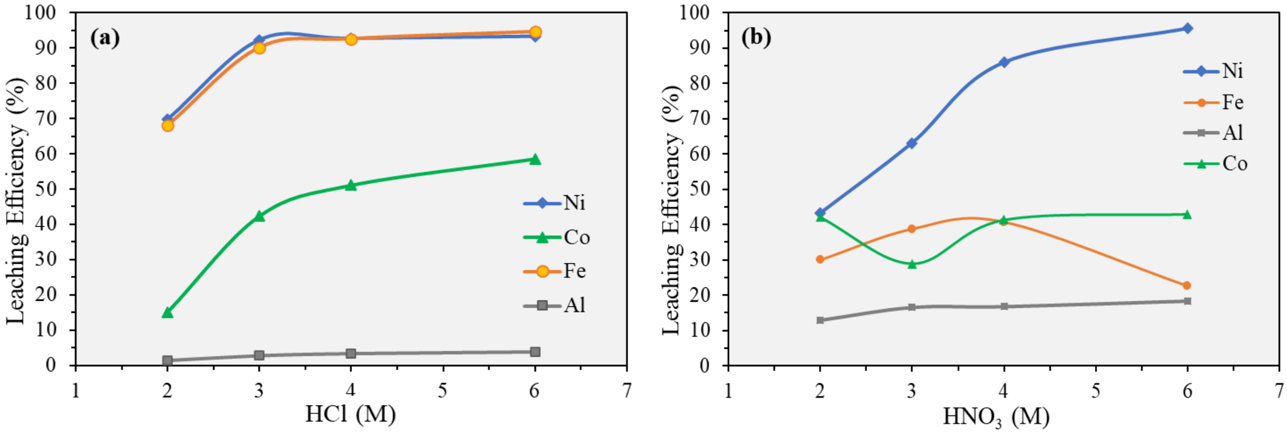

Figure 4. The effect of acid concentrations to the leaching rates of Ni, Fe, Co, and Al in limonite, HCl (a) and HNO_3 (b).

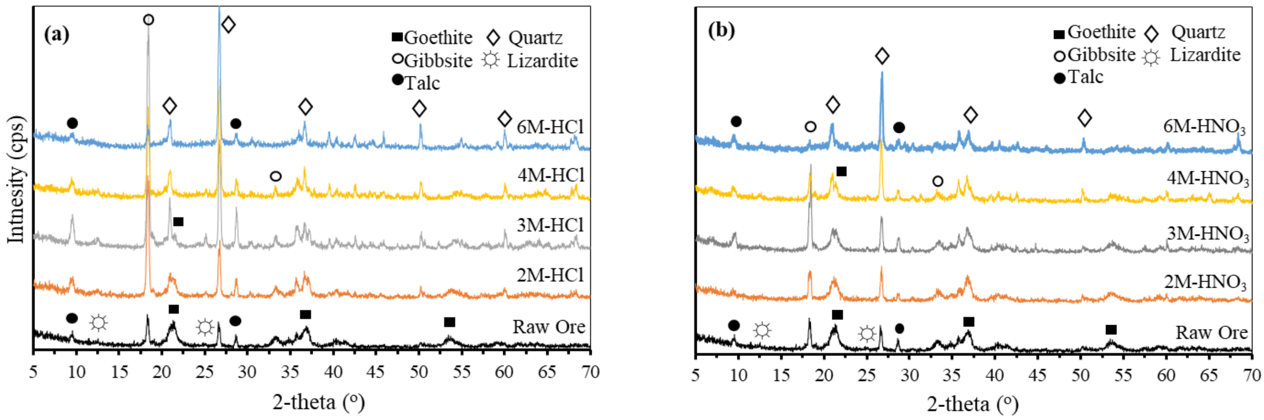

Figure 5. Diffraction patterns of leached residues after acid leaching with various concentrations. (a) chloride acid and (b) nitric acid.

With respect to HNO_3 leaching, it is shown that Ni and Co extraction rates were 1.5 times less than HCl leaching with a 3 M concentration. This implies that HCl leaching in this experiment was more effective than HNO_3. However, the leaching of Ni with HNO_3 was more selective toward Fe, implying a beneficial effect during further metal separation. Leaching efficiencies of other metals (Al and Co) were quite low, even with the increase in HNO_3 concentration.

3.3 Dissolution behavior of minerals in limonite ore

The dissolution of limonite in acids includes heterogenic reactions because it involves various minerals with different crystal structures and crystal sizes. The dissolution mechanism of minerals, particularly Ni-containing phases, in the acidic solutions can be analyzed by comparing the XRD patterns of raw ore and solid residues at different acid concentrations to observe any change in peak characteristics during the leaching process. Figure 5 represents the comparison of XRD patterns between original ore and solid residues resulting from HCl leaching (Figure 5(a)) and HNO_3 leaching (Figure 5(b)). Assuming goethite as the main Ni-bearing mineral in the ore, the difference of XRD patterns between raw ore and leached residues indicates that goethite with peak intensity of 2θ angle at 21.3° (d_{hkl}~4.17 Å) has gradually diminished when leached with 2 M and 3 M HCl. However, it totally disappeared when leached with 4 M HCl. In contrast, this goethite peak intensity still appears until leaching with 4 M HNO_3, and it has only completely disappeared when leached with 6 M HNO_3. This implies that goethite has dissolved more readily in HCl than in HNO_3. The dissolution of goethite in HCl and HNO_3 may follow a chemical reaction as expressed in Equation (2) and Equation (3) respectively.

$$FeOOH + 3HCl \rightarrow FeCl_3 + 2H_2O \quad (2)$$

$$FeOOH + HNO_3 \rightarrow FeNO_3 + H_2O \quad (3)$$

The presence of protons (H^+) both in HCl and HNO_3 is needed for goethite dissolution, leading to the leaching out of nickel from the goethite structure. The existence of Cl^- may assist in accelerating the dissolution of Fe and Ni in goethite through the formation of a Fe-Cl complex on the mineral surface [17,18]. Conversely, NO_3^- in HNO_3 do not form similar surface complex with Fe, so protonation of surface is only triggered by H^+ [19]. Therefore, the lower dissolution of goethite in HNO_3 solution as compared to HCl might partly be due to the lower reactivities of NO_3^-.

Gibbsite with an interplanar spacing of 8.30 Å shows the most intense reflection mainly when leached with 3 M acids, but it strongly decreases in peak intensity when leached with 6 M of both acids, suggesting that gibbsite has undergone partially dissolution. Reflection of talc at 9.5° 2θ (d_{001}~9.30 Å) and quartz at 26.6° 2θ (d_{011}~3.34 Å) remains strong either in the original ore sample or in solid residues, indicating that talc and quartz were not dissolved in both acids.

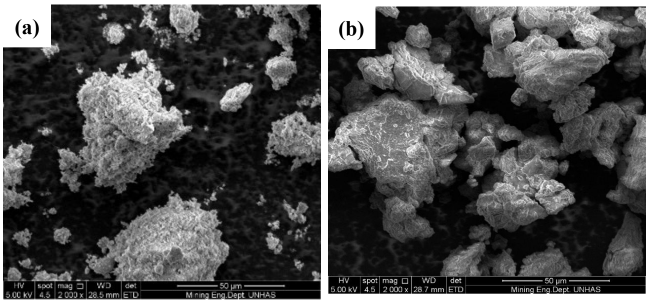

Figure 6. Secondary electron images of original limonite ore (a) and solid residue after leaching with 6 M HCl (b).

By contrasting the original texture and morphology of the limonite ore sample with leached residues, it is possible to decipher the evidence of mineral dissolution after acid leaching. The SEM images showing morphological characteristics between the original ore and solid residues after leaching with 6 M HCl are presented in Figure 6. As shown in Figure 6(a), the morphologies of raw ore exhibit aggregate-like particles and porous, rough, and bumpy surfaces. On the other hand, the morphologies of solid residues, as depicted in Figure 6(b), show relatively smooth surface materials with exfoliation lamella and shrinkage grains.

The leaching mechanism of minerals in limonite ore can be explained by using the shrinking-core model [20]. Initially, the reaction takes place between outer skin of ore particles and acids, leading to dissolution of the surface solid. Further reactions move into the core, making the successive inner layer dissolve. However, the shrinking-core model assumes that particles are dense. Eventually the ore particles are porous, as shown in Figure 6(a), so reactions are also controlled by the diffusion process at the late stage [21]. It is generally postulated that dissolution of minerals either in HCl or HNO_3 with decreasing order would be: goethite > lizardite > gibbsite > talc > quartz

4. Conclusion

This study concentrated on the metal leaching and dissolution of minerals in limonite ore from the Wolo mine area of southeast Sulawesi, Indonesia. The limonite ore is mainly composed of goethite with subordinate gibbsite, talc, quartz, and trace lizardite. The experimental results demonstrated that the leaching efficiency of Ni at 3 M HCl is 1.5 times higher than that of HCl. This might be due to the protonation of a Cl–Fe complex on the mineral surface, which aids in enhancing the dissolution of Fe and Ni-bearing minerals. However, the higher leaching efficiency of Fe in HCl has led to contamination of PLS. This is unfavorable because it will interfere with the further separation of Ni from PLS during the purification process. On the other hand, leaching with a higher concentration of HNO_3 shows a significant increase in Ni but a strong decrease in Fe in PLS, indicating higher selectivity. On the basis of XRD and SEM data, it is revealed that goethite, the principle Ni-bearing phase, is more readily dissolved in HCl as compared to HNO_3.

References

[1] Nickel Institute, "About Nickel". https://nickelinstitute.org/about-nickel/. Accessed on 17 August 2023.

[2] C. R. M. Butt, and D. Cluzel, "Nickel laterite ore deposits: weathered serpentinites," *Elements*, vol. 9, pp. 123-128, 2013.

[3] U.S. Geological Survey, "Mineral commodity summaries": U.S. Geological Survey, 210 p, 2023. https://doi.org/10.3133/mcs2023US, Accessed on 15 October 2023.

[4] A. Ito, T. Otake, A. Maulana, K. Sanematsu, Sufriadin, and T. Sato, "Geochemical constraints on the mobilization on the mobilization of Ni and critical metals in laterite deposits, Sulawesi, Indonesia: A mass-balance approach", *Resources Geology*, vol.71, pp. 255-282, 2021.

[5] V. I. Lakshmanan, R. Sridhar, J. Chen, and M. A. Halim, "Development of mixed-chloride hydrometallurgical processes for the recovery of value metals from various resources", *Transaction of Indian Institute of Metallurgy,* vol. 69, pp. 39-50, 2016.

[6] Sufriadin, S. Widodo, I. Nur, A. Ilyas, and M. Y. Ashari, "Extraction of nickel and cobalt from sulawesi limonite ore in nitric acid solution at atmospheric pressure", *IOP Conference Series.: Material Science and. Engineering,* vol. 875, p. 012053, 2020.

[7] K. Liu, Q. Y. Chen, H. P. Hu, and Y. Yin, "Characterization and leaching behavior of lizardite in Yunjiang laterite ore", *Applied Clay Science*, vol. 47, pp. 311-316, 2010.

[8] Z. Zhou, B. Ma, C. Wang, Y. Chen, W. Zhang, and K. Huang, "Enrichment of scandium and aluminum from limonitic laterite during the nitric acid pressure leaching process", *Hydrometallurgy*, vol. 208, 2022.

[9] J. Li, Y. Yang, Y. Wen, W. Liu, Y. Chu, R. Wang, and Z. Xu, "Leaching kinetics and mechanism of laterite with NH_4C–HCl solution", *Minerals*, vol.10, 2020.

[10] S. Stanković, S. Stopić, M. Sokić, B. Marković, and B. Friedrich, "Review of the past, present, and future of the hydrometallurgical production of nickel and cobalt from lateritic ores". *Metallurgical and Material Engineering*, vol.26, no. 2, pp. 199-208, 2020.

[11] M. A. R. Onal, and Y. A.Topkaya, "Pressure acid leaching of Çaldağ lateritic nickel ore: An alternative to heap leaching", *Hydrometallurgy,* vol.142, pp. 98-107, 2014.

[12] J. Li, D. Xiong, H. Chen, R. Wang, and Y. Liang, "Physicochemical factors affecting leaching of laterite ore in hydrochloric acid", *Hydrometallurgy,* vol.129-130, pp.14-18, 2012.

[13] B. Ma, W. Yang, B. Yang, C. Wang, Y. Chen, and Y. Zhang, "Pilot-scale plant study on the innovative nitric acid pressure leaching technology for laterite ores", *Hydrometallurgy*, vol. 155, pp. 88-94, 2015.

[14] M. Rao, J. Chen, T. Zhang, M. Hu, J. You, and J. Luo, "Atmospheric acid leaching of powdery Ni-Co-Fe alloy derived from reductive roasting of limonitic laterite ore and recovery of battery grade iron phosphate", *Hydrometallurgy*, vol. 218, pp. 1-10, 2023.

[15] I. M. Ugwu, and D. M. Sherman, "The solubility of goethite with structurally incorporated nickel and cobalt: Implication for laterites", *Chemical Geology*, vol. 518, pp. 1-8, 2019.

[16] Y. Changa, K. Zhao, and B. Pešić, "Selective leaching of nickel from pre-reduced limonitic laterite under moderate HPAL conditions- Part I: Dissolution", *Journal of Mining and Metallurgy, Section B. Metallurgy*, vol.52, pp. 127-134, 2016.

[17] A. Garces-Granda, G.T. Lapidus, and O.J. Restrepo-Baena, "Effect of a thermal pretreatment on dissolution kinetics of a

limonitic laterite ore in chloride media", *Hydrometalurgy*, vol. 196, p. 105428, 2020.

[18] R.G. McDonald, and B.I. Whittington, "Atmospheric acid leaching of nickel laterites review. Part II. Chloride and bio-technologies", *Hydrometallurgy*, vol. 91, pp. 56-69, 2008.

[19] F. He, B. Ma, C. Wang, and Y. Chen, "Mineral evolution and porous kinetics of limonitic laterite during nitric acid pressure leaching", *Mineral Engineering*, vol.181, p. 107544, 2022.

[20] O. Levenspiel, "Chemical reaction engineering" 3rd ed. John Wiley & Sons, Inc. New York, 668 p. 1999.

[21] F. He, B. Ma, C. Wang, Y. Zuo, and Y. Chen, "Dissolution behavior and porous kinetics of limonitic laterite during nitric acid atmospheric leaching", *Mineral Engineering,* vol.185, p. 107671, 2022.