Effect of pulp density and particle size on indirect bioleaching of Pomalaa nickel laterite using metabolic citric acid

H B T M Petrus¹, K C Wanta², H Setiawan¹, I Perdana¹ and W Astuti³

¹Advanced Material and Sustainable Mineral Processing Research Group, Chemical Engineering Department, University of Gadjah Mada, Yogyakarta, Indonesia
²Chemical Engineering Department, Parahyangan Catholic University, Bandung, Indonesia
³Research Unit for Mineral Technology, Indonesian Institute of Sciences, Lampung Selatan, Indonesia

Email: bayupetrus@ugm.ac.id

Abstract. Nickel laterite ore contains oxide of iron, aluminum or both with nickel, cobalt and chromium which can be leached out using hydrometallurgical process. For the purpose of meeting the world’s increasing demand of nickel, there is a need to invent environmentally friendly process to efficiently leach nickel. This experiment used nickel laterite ore obtained from Pomalaa, South Sulawesi. The leaching agent is metabolic citric acid produced by Aspergillus niger under optimum condition. Leaching process was done in three-necked flask in atmospheric temperature and constant stirring speed of 200 rpm. The variable examined in the experiment was pulp density and particle size of nickel laterite ore. Samples were taken at 3, 7, 10, 14, and 17 minutes and then filtered and diluted to be analyzed using ICP-AES. The result of the experiment showed the maximum recovery of metals increase with the decrease of the pulp density. The maximum recovery for varying pulp density were at 5% solid/liquid ratio and the recovery were Ni at 1.63%, Al at 0.47%, Fe at 0.23% and Mg at 1.09%. The effect of particle size on leaching process showed that the leaching process follows the shrinking core model. The maximum recovery of metals at particle size were at 100-120 mesh with Ni at 1.37%, Fe at 0.10%, Al at 0.72% and Mg at 0.62%.

1. Introduction
Nickel as one of the vital industrial metal has been mined since the nineteenth century. Today, the world’s demand mostly relies on the sulfide ores as the main source of nickel. Laterite ores which contain about 72% of the world’s nickel deposit have not been sufficiently exploited as it only account for only 40% of the world’s nickel production. With increasing nickel demand over the years, there is a need to increase the production of nickel based on laterite ore [1]. Indonesia has in its land one of the largest nickel laterite reserves in the world which were spread mainly on Sulawesi and Papua islands. The processing of those ore though has not been efficient. Only high grade saprolite is being processed for nickel production while the low-grade saprolite and limonite are removed to become waste in the mining areas [2].

While used as a resource for nickel, laterite itself contain mainly the oxide of iron, aluminum or both with nickel, cobalt and chromium as minor compound [3]. Leaching method of laterite ore is very dependent of its content. For ore with high iron content, the reduction method is used ore if the nickel content is high enough, it is better for hydrometallurgical method using organic acid [4], [5].

Within a wide range of organic acids that can be used in the leaching of nickel laterite, citric acid gives the highest percentage of nickel recovery and in addition shows good selectivity of magnesium. Citric acid which can form soluble ligand complex using chelating mechanism can be obtained by...
fermentation of sucrose using Aspergillus niger fungi [6]. The citric acid produced by the excretion process of Aspergillus niger fungi is called metabolic citric acid (MCA).

The leaching behavior and kinetics of nickel laterite is affected by parameters such as particle size, pulp density, temperature and the acidity of leaching solution as observed by previous work [2]. Citric acid is a carboxylic acid with three steps of disassociation based on that premise, the possible reaction on the leaching of nickel laterite can be hypothesized as follows [7], [8]:

1. Acid disassociation
   \[ C_6H_8O_7 \rightarrow (C_6H_4O_7)^{3-} + 3H^+ \]  

2. Proton attack
   \[ NiO + 2H^+ \rightarrow Ni^{2+} + H_2O \]  
   \[ MCO_3 + 2H^+ \rightarrow M^{2+} + H_2O + CO_2 \]  
   With, M = Metals

3. Complexation/chelation
   \[ 2(C_6H_4O_7)^{3-} + 3Ni^{2+} \rightarrow Ni_3(C_6H_4O_7)_2 \]

The kinetic itself can be characterized as shrinking core model (SCM) which reaction rate is affected by (1) diffusion through film on the particle surface, (2) diffusion through ash layer in the particle and (3) surface reaction on unreacted core of particle [9]. Previous work have assessed that for the leaching process of nickel laterite, diffusion is the rate-controlling step in the process [2], [5]. This work is focused on the effect of pulp density and particle size of laterite ore on the leaching process of Pomalaa nickel laterite.

2. Materials and Method

2.1 Materials
In this experiment, nickel laterite of limonite type was mined from Pomalaa in South Sulawesi Province of Indonesia in the form of powder and was crushed to obtain the desired distribution of particle size.

2.2 Citric Acid Production
Citric acid was produced using Aspergillus niger fungi. The culture medium of fungi was made from 3.9 gram of potato dextrose agar (PDA) that was solved in 100 mL aquadest and sterilized using autoclave. Fungi spore was then added to the media and cultured for 7 days.

Substrate was made of 0.25\% (NH_4)_2CO_3, 0.025\% MgSO_4.7H_2O, 0.25\% K_2HPO_4, 0.06 mg/L ZnCl_2 and 1.3 mg/L Fe_2(SO_4)_3 which were solved in aquadest with pH of initial medium of 3.0 to 4.0. and was sterilized using autoclave.

The fermentation process was conducted by adding cultured Aspergillus Niger fungi spore to substrate solution with 50 g/L corn starch as carbon source and 3\% (V/V) methanol as catalyst. The solution was then incubated for 5 days with temperature of 30-35° C in rotary shaker.

The resulting yield was 230 g / 1 kg corn starch with concentration of citric acid produced in medium 0.05 M. Citric acid produced was then separated using centrifugation to obtain metabolic citric acid (MCA) solution.

2.3 Nickel Laterite Leaching
300 mL of metabolic citric acid and 60 gram of Pomalaa nickel laterite with particle size of 100-120 mesh (pulp density 20\%w/v) was combined in a three-necked flask and stirred at 200 rpm on
atmospheric temperature (30-35°C). Samples were taken after 3, 7, 10, 14, and 17 minutes. The experiment was then repeated for pulp density of 5% and 10% and particle size of 60-70 mesh and >200 mesh.

Samples taken were first separated from its solid content using centrifugation at 1,000 rpm for 10 minutes. Liquid samples obtained were then filtrated using syringe filter and then diluted to be analyzed for its metal content using ICP-AES (Optima 8300, Perkin Elmer, USA).

3. Results and Discussion

3.1 Characterization

The nickel laterite was of limonite type [(Fe,Ni)O(OH).nH₂O] mined from Pomalaa, South Sulawesi. For initial measurement, the ore was characterized using X-ray Fluorescence (XRF) for its initial metal content. The result of analysis is on Table 1.

| Metal  | Content, %wt |
|--------|--------------|
| Fe     | 26.04        |
| Si     | 15.46        |
| Mg     | 9.78         |
| Ni     | 2.73         |
| Al     | 2.54         |
| Cr     | 1.01         |
| Mn     | 0.51         |
| Co     | 0.07         |

From the analysis result in Table 1 it is shown that this nickel laterite ore is dominated by Fe (26.04%) while Ni only comprised 2.73% of the ore. This makes the leaching process can be approached in 2 ways, by reducing unneeded metals such as Fe and Mn to obtain Ni [10] or leaching all of metal contained and purifying it in later stage. This research was focused in the latter method to examine the viability of this method using organic acid.

3.2 Leaching process with various pulp density

Figure 1 shows the recovery of Fe, Ni, Al and Mn over time with varying pulp density. It is shown in Figure 1 for all metals; the maximum recovery is decreasing with increasing pulp density. This is due to the amount of liquid reactant, in this case metabolic citric acid is insufficient to leach metals in nickel laterite ore [11]. The recovered amount of pulp density that was 5% for Ni (1.63%), Al (0.47%), Fe (0.23%) and Mg (1.09%) still falls short than synthetic citric acid that could leach about 90% of Ni [6]. The result shows that the leaching process using metabolic citric acid need to be modified, whether by using H₂O₂to reduce metals such as Fe or Mn or refining the metabolic citric acid production process to produce acid with higher concentration.
Figure 1. Effect of pulp density on the recovery of (a) Ni, (b) Fe, (c) Al and (d) Mn in leaching process using metabolic citric acid.

3.3 Leaching process with various particle size

Figure 2. Effect of particle size on the recovery of (a) Ni, (b) Fe, (c) Al and (d) Mn in leaching process using metabolic citric acid
The experiment result in Figure 2 shows the result of recovery of all metals in the leaching process with varying nickel laterite ore size. From the result, it is shown that the maximum recovery of all metals was achieved on ore size of 100-120 mesh with the maximum recovery of Ni at 1.37%, Fe at 0.10%, Al at 0.72% and Mg at 0.62%. The kinetic of leaching process of nickel laterite ore itself followed shrinking core model (SCM) with reactant diffusion through the ash layer as the rate-controlling step [2, 5].

For larger particle size (>200 mesh) it is shown that the recovery rate was slower than from 100-120 mesh of particle size, this was due to wider radius of ash layer formed for larger particle size which hinder the absorption of the reactant to the reaction zone and the desorption of product to the liquid body. For smaller particle size, which means it had larger surface area that supposedly increase the reaction rate. But with increased reaction rate and the complex metal molecules formed on the reaction zone surface caused steric hindrance to the desorption of product. For Mg, particle size did not play role in the recovery rate because of the small size of its molecule which clearly could bypass the hindrance caused by larger product molecules.

4. Conclusion
Experiment results shows that for varying pulp density, the maximum recovery of metals increased with the decrease of the pulp density which was caused by the lack of metabolic citric acid in the solution which also cause the low recovery on this leaching experiment. The maximum recovery of metal at 5% pulp density were at 1.63% for Ni, 0.47% for Al, 0.23% for Fe and 1.09% for Mg.

For the effect of particle size on leaching process, the result shows that the kinetic leaching process followed the SCM with diffusion through the ash layer as the rate-controlling step. The smaller particle size caused lower maximum recovery and recovery rate which was caused by steric hindrance between product molecules, while larger molecule size would also cause the same effect on recovery because the larger ash layer. Mg was exempt from this trend because of its smaller molecule size that will cause it to be able to pass through ash layer and other molecule with less difficulty. The maximum recovery of metals at particle size of 100-120 mesh were Ni at 1.37%, Fe at 0.10%, Al at 0.72% and Mg at 0.62%.

Acknowledgement
The authors acknowledge the support provided by Department of Chemical Engineering, University of Gadjah Mada for the equipment for this experiment. Acknowledgment is also made for materials support provided by Indonesian Institute of Sciences (LIPI).

References
[1] Dalvi A D, Bacon W G, Osborne R C 2004 The Past and the Future of Nickel Laterites PDAC Int. Conv. pp 1-27
[2] Astuti W, Hirajima T, Sasaki K, Okibe N 2015 Miner. Metall. Process. 32 176-85
[3] Olanipekun E O 2000 Int. J. Miner. Process. 60 9-14
[4] Petrus H T B M, Rhamdani A R, Putera A D P, Warmada I W, Yuliansyad A T, Perdana I 2016 IOP Conf. Ser. Mater. Sci. Eng. 162 pp 12019
[5] Wanta K C, Perdana I, Petrus H T B M 2016 IOP Conf. Ser. Mater. Sci. Eng. 162 pp 12018
[6] Mubarok M, Astuti W, Chaerun S 2012 The XIIIth International Mineral Processing Symposium
[7] Simate G S, Ndlovu S, Walubita L F 2010 Hydrometal. 103 150-157
[8] Behera S K, Panda P P, Singh S, Pradhan N, Sukla L B, Mishra B K 2011 Int. Biodeterior. Biodegrad. 65 1035-1042
[9] Levenspiel O 1999 Ind. Eng. Chem. Res. 38 4140-4143.
[10] Senanayake G, Childs J, Akerstrom B D, Pugaev D 2011 Hydrometal. 110 13-32
[11] Coto O, Galizia F, Hernández I, Marrero J, Donati E 2008 Hydrometal. 94 18-22