Nickel-Cobalt Extraction Process from Low-Grade Laterite Ores Using Cyanex 272 and Versatic Acid 10

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Abstrak. *Nickel is a metal that does not exist purely in nature but is mixed in lateritic nickel ore. In this research, the separation process of Nickel from laterite ore using hydrometallurgical process (leaching and solvent extraction). The purpose of this research is to know the optimum condition of nickel extraction process and to know the effect of the variables observed in this research, they are the Citric Acid concentration (2, 3 and 4 M), leaching time (1, 2 and 3 days), percent volume Cyanex 272 (15, 20 and 25% v/v), and percent volume Versatic Acid 10 (0, 5 and 10% v/v). In this research, the leaching process is carried out by heating a mixture of Citric Acid and laterite at 100°C while stirring with 500 rpm stirring speed. The leached filtrate was then dissolved in a mixture of organic solvents in the form of Cyanex 272 and Versatic Acid 10. The results of this study obtained the optimum condition of nickel extraction process at 4M Citric Acid concentration, 2 days leaching time, using Cyanex 272 15% v/v and Versatic Acid 10% v/v, which in that condition obtained the percentage of extraction (% E) for nickel amounted to 96.73%.*
Keywords: Solvent Extraction; Laterite; Leaching; Nickel Cobalt Separation, Hydrometallurgy.

INTRODUCTION

The problems encountered in processing mineral ore into high purity chemicals include the many other components in the mineral ore making it difficult for separation and purification processes, such as nickel which is not present in nature but mixed in laterite nickel ore. Low-grade laterite contains nickel around 0.4% as listed in Table 1. This laterite is very difficult to process but this low-grade laterite is very large in Indonesia. One of the methods which able to overcome this problem is hydrometallurgy (Astuti, Hirajima, Sasaki, & Okibe, 2016). In hydrometallurgy, laterite was processed using solvent extraction to obtain minerals with high purity continue to grow (Guimarães, Da Silva, & Mansur, 2014; Iliev, Stefanova, Lucheva, & Tzonevski, 2012; Kursunoglu, Ichlas, & Kaya, 2017; Ndlovu & Mahlangu, 2008; Park & Mohapatra, 2006; Parmentier, Paradis, Metz, Wiedmer, & Kroon, 2016; Preez & Preston, 2004). Proper use of organic chemicals that can be reused (recycle) is very important in this process.

In this study, the use of Citric Acid was selected in the leaching process, since the use of Citric Acid not only provides high selectivity and nickel gain but also Citric Acid is more environmentally friendly and safer to use than sulfuric acid (Astuti et al., 2016). While the type of organic solution to be used in this extraction process is a mixture of Cyanex 272 with Versatic 10. Cyanex 272 with a concentration of 20% v/v can separate Nickel from zinc, cobalt, and copper but cannot separate nickel from calcium and magnesium. Then to purify the Nickel of the alkaline earth metal is used a mixture of Cyanex 272 and Versatic Acid 10 (Guimarães et al., 2014; Kursunoglu et al., 2017; Ndlovu & Mahlangu, 2008; Preez & Preston, 2004).

In this work, the parameters which affected the nickel extraction were studied and optimized using the design of experiment of Taguchi. This method able to numbers of experiments which this less than another design experiment (Rosa, Robin, Silva, Baldan, & Peres, 2009; Sudibyo, Nurjaman, & Aziz, 2016; Zainal, Shukor, & Razak, 2015). The purpose of this work is to get a higher value of the percentage of the increase of nickel concentration in aqueous solution (% Ni) by studied and optimized the parameters such as an operating duration, flow rate, volume of organic/aqueous, and pH.

MATERIALS AND METHODS

Materials

The raw material used in this research is the laterite of limonite originating from South East Sulawesi, Indonesia. The composition of laterite was tabulated in Table 1. The solvent used in the leaching process is a Citric Acid solution ($C_6H_8O_7$) obtained from Brataco chemical co. ltd. and followed by solvent extraction process using Cyanex 277 (bis (2,4,4-trimethylpentyl) phosphinic acid) and Versatic Acid 10 (Neodecanoic Acid) which had previously been diluted using Toluene.

Methods

In this work, laterite was milled and sieved to get a size of 200 mesh. The laterite was leached in 200 ml of (2, 3 and 4 M) Citric Acid for (1, 2 and 3 days) in magnetic stirrer at a temperature 100°C while stirring with 500 rpm stirring speed. For liquid phase extraction a process, an organic solution of the Cyanex 272 and Versatic acid in Toluene were used. The solvent extraction was carried out in glass separating funnels with capacity 250 ml as shown in Figure 1. The solvent extraction process contains the aqueous and organic phase, which is the aqueous phase contains an amount of nickel. The aqueous phase separated from the organic phase is then analyzed using an Atomic Absorption Spectrophotometric (AAS) analysis to determine the levels of metals present in the aqueous phase.

The composition of laterite was analysed using XRF (Olympus XRF portable), meanwhile the composition of aqueous solution was analyzed using AAS (AA-7000 Shimadzu). The design of experiments of Taguchi was used in this work as listed in Table 2. These experiments have four parameters namely Citric Acid concentration, leaching time, percent volume Cyanex 272, and percent volume Versatic Acid. The Taguchi analysis methods which used to analyze results of the experiment was a signal-to-noise (S/N) ratio of "larger the better" which using equation as follow:

$$S/N = -10*\log(\Sigma(1/Y^2)/n) \qquad (1)$$

where Y = responses for the given factor level combination and n = number of responses in the factor level combination (Rosa et al., 2009).

Table 1. Laterite composition using XRF

Element	wt (%)	Element	wt (%)
LE	79.2882	MnO	0.216
Fe	10.998	Co	0.046
Si	3.88	S	0.046
K	2.079	Sb	0.02
Al	0.701	Cd	0.013
Ni	0.488	Sn	0.014
Ca	0.65	Ti	0.022
Cl	1.253	Zn	0.0076
Cr		0.284	

Table 2. The experimental design using Taguchi method

	Design of Experiment				Experiment Result
Run	Citric Acid Concentration (M)	Leaching Time (days)	Percent Volume Cyanex (% v/v)	Percent Volume Versatic (% v/v)	Percentage of nickel extraction (%E)
1	2	1	15	0	46.20
2	2	2	10	5	47.27
3	2	3	25	10	46.55
4	3	1	10	10	49.33
5	3	2	25	0	59.34
6	3	3	15	5	55.72
7	4	1	25	5	63.27
8	4	2	15	10	96.73
9	4	3	10	0	65.85

Figure 1. The solvent extraction solution in the glass separating funnels

RESULTS AND DISCUSSION

The results of this work were analyzed using a signal to noise (SN) ratio of larger the better of Taguchi were listed in Table 3. The table shows that highest value of delta is the parameter of Citric Acid concentration; hence this parameter is the first rank of the parameter which affects the amount of percentage of nickel extraction (% E). The second, third and fourth rank is the leaching time, percent volume Cyanex and percent volume Versatic respectively.

The results of nickel extraction in percentage extraction (% E) of nickel were listed in Table 2. The percentages of extraction (% E) for nickel is obtained by comparing the mass of nickel extracted with the initial nickel mass in the laterite ore. Based on the result of percentage of extraction (% E) for nickel obtained in table 3, it is found that the

optimum condition of nickel extraction process from laterite occurred in the eighth experiment with the percentage of nickel extraction (% E) at 96,73%.

Table 3. Response Table for Signal to Noise Ratios Larger is Better

Level	Citric Acid Concentration (M)	Leaching Time (days)	Percent Volume Cyanex (% v/v)	Percent Volume Versatic (% v/v)
1	46.67	52.93	66.22	57.13
2	54.8	67.78	54.15	55.42
3	75.28	56.04	56.39	64.2
Delta	28.61	14.85	12.07	8.78
Rank	1	2	3	4

The Effect of Citric Acid Concentrations on the Percentage of Extraction (%E) for Nickel

The effect of Citric acid concentration on the percentage of extraction (% E) for nickel is showed in the graph in Figure 2, the graph shows that the highest percentage of extraction (% E) for nickel obtained during the leaching process using Citric Acid with a concentration of 4 M, it was concluded that the higher concentration of Citric Acid will give percentage of extraction (% E) for nickel also higher.

The mechanism of the solids dissolution process becomes a process controlled by a chemical reaction by increasing the concentration of the reactants in the solution phase [3]. This is supported by the fact that at low concentrations of reactants the dissolution reaction will have a low activation energy, while at high concentrations the dissolution process will have a high activation energy as well. In addition to the low concentrations of the reactants, the dissolution rate is highly dependent on the speed of rotation of stirring (Astuti et al., 2016).

Nickel is an element that is insoluble in water, but it is soluble in acidic solutions. The acid dissolution reaction is as follows:
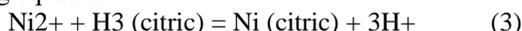
A. The leaching process.
The reactions that occur follow the following equation:
$$NiO + 2H^+ = Ni^{2+} + H_2O \qquad (2)$$

B. Formation of complex (complex) metal with organic acid
The reaction follows the following equation:
$$Ni^{2+} + H_3(citric) = Ni(citric) + 3H^+ \qquad (3)$$

According to the Le Chatelier principle, a reaction will shift against the formation of the product in the event of addition. In the dissolution reaction of Nickel by Citric Acid, the amount of dissolved nickel in acid solution will increase if a number of reactants are NiO and Citric Acid is added. \

In this experiment, a number of reactants in the form of NiO in the laterite ore is made constant at 20% w/v, meaning that in each experiment the amount of NiO mass is unchanged. The addition of reactants can be done by increasing the concentration of Citric Acid used. The higher the concentration of $C_6H_8O_7$ means more H^+ ions that can react with the NiO element causing the amount of dissolved nickel to be more numerous.
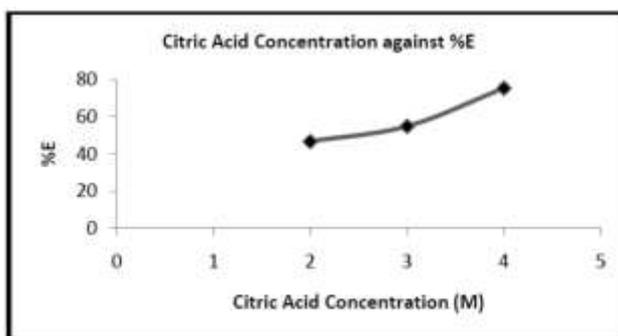
Figure 2. Mean effect plot for citric acid concentration against the percentage of nickel extraction

The Effect of Leaching Time on the Percentage of Extraction (%E) for Nickel

The length of leaching time will facilitate the penetration of the solvent into the raw material, the solubility of Nickel runs slowly in proportion to the increase in time, but after reaching the optimum time the decreased nickel has decreased.

The effect of leaching time on the percentage of extraction (% E) for nickel is shown in the graph in Figure 3, which graph shows that percentage of extraction (% E) for nickel reaches the highest value in two days' time. This is because the nickel present in the laterite is limited and the solvent used has the limit of ability to dissolve the material.

When the leaching time is extended beyond the optimum dissolution time, the amount of dissolved Nickel will be less than the dissolution of other components in the laterite. So the addition of time will cause the decomposition of metal elements other than Nickel including the impurities that cause the percentage concentration of nickel in the leaching solution becomes smaller.
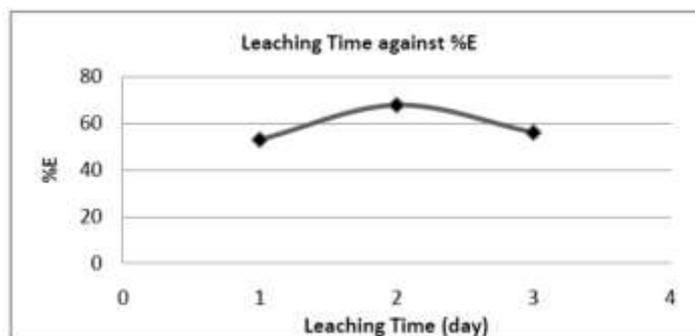

Figure 3. Mean effect plot for leaching time against the percentage of nickel extraction

The Effect of Percentage Cyanex 272 Volume on the Percentage of Extraction for Nickel

The purpose of adding Cyanex 272 to an organic solution is to separate certain metals such as cobalt, copper, and lead from an aqueous solution by using the anion or cationic properties of hydrophobic (water disliking) materials.

The organic solution of Cyanex 272 has a negatively charged hydrophobic property suitable for attracting metals such as cobalt, copper, lead and other metals which have hydrophobic and positively charged properties. For metals such as nickel, iron, vanadium, and other hydrophilic metals are not extracted into organic solutions.

A graph of the relationship between the percentages of the volume of Cyanex 272 used for the extraction process against the percentage of extraction (% E) of obtained nickel is shown in Figure 4. In that Figure, the percentage of extraction (% E) for nickel reaches the highest value when using Cyanex 272 with concentration 20% v/v. This is because at that concentration is the optimum condition where a hydrophobic and positively charged metal such as cobalt will be extracted into an organic solvent. So that is left in aqueous solution is nickel metal and metallic with hydrophilic and hydrophilic resemblance like iron and vanadium, this is what causes the concentration of nickel in aqueous solution to reach the optimum point (Guimarães et al., 2014; Kursunoglu et al., 2017).
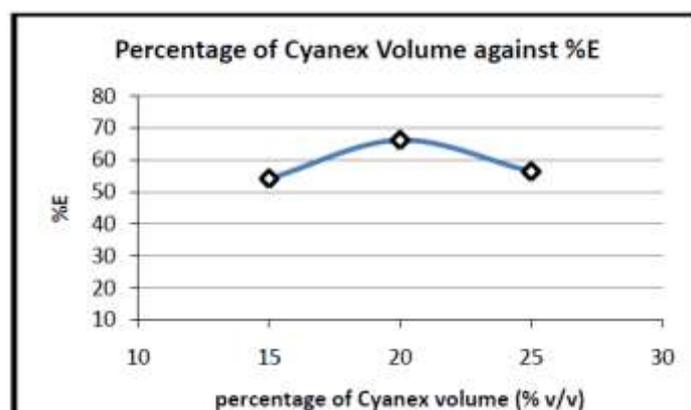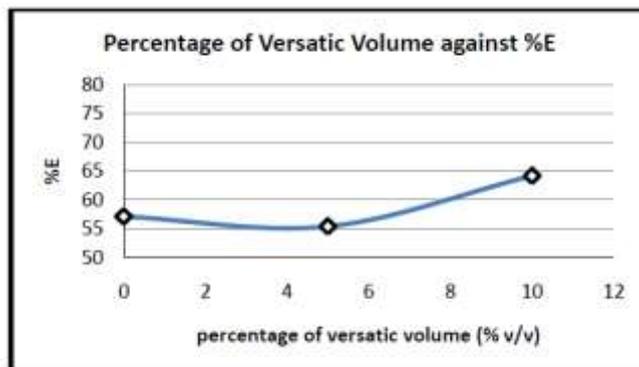

Figure 4. Mean effect plot for the percentage of the cyanex volume against the percentage of nickel extraction

The Effect of Percentage of Versatic 10 Volume on the Percentage of Extraction for Nickel

Versatic Acid 10 has the same function as Cyanex 272 that is to separate certain metals such as cobalt, copper, lead, and other hydrophobic metals from aqueous solutions by using the anion or cation properties of hydrophobic materials. The addition of Versatic acid 10 solutions is used to enhance the ability of the organic phase to extract cobalt by blocking impurities into the organic solvent such as Calcium, Magnesium, and Silicon (Kursunoglu et al., 2017; Ndlovu & Mahlangu, 2008; Preez & Preston, 2004). Meanwhile, Cyanex 272 has a great ability to extract Cobalt but is less selective on Calcium, Magnesium, and Silicon (Guimarães et al., 2014).

A graph of the relationship between the percentage of volume of Versatic Acid 10 used for the extraction process against percentage of extraction (% E) of obtained nickel is shown in Figure 5, that Figure showing that the percentage of extraction (% E) for nickel reaches the highest value when using Versatic Acid 10 with concentration 20% v/v. Percentage of extraction (% E) for nickel reaches the highest value when using Cyanex 272 with concentration 10% v/v.

Figure 5. Mean effect plot for the percentage of versatic volume against the percentage of nickel extraction

CONCLUSIONS

Taguchi methods has successfully optimize the operation condition of the nickel extracting process from laterite ore. The most influential parameter of the increase in nickel concentration is the concentration of Citric Acid. The optimum condition of the nickel extraction process from laterite occurred in the 8th experiment at the time of the concentration of 4 M of Citric Acid acid, 2 day of leaching time and the extracting process using 15% v / v of Cyanex 272 and 10% v / v of Versatic Acid 10.

ACKNOWLEDGEMENTS

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