

Optimization of The Electro Metal Electrowinning Process for Nickel Metal from The Solvent Extraction of Low-grade Laterite using Versatic 10 and Cyanex 272

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Abstract

Low-grade nickel Laterite ores from Southeast Sulawesi (Indonesia) which has 0.50% nickel content was used in this study still contain a lot of impurities. One method which able to separate nickel and cobalt from low-grade nickel laterite is hydro-electrometallurgy. In the previous research phase of solvent extraction, Versatic Acid 10 was chosen as an extractant to separate calcium and magnesium from the ore. This process produced a mix of nickel with cobalt. To separate nickel from cobalt, the selection of extractant Cyanex 272 was used, therefore nickel remains in its aqueous phase while cobalt is in the organic phase. Nickel in the aqueous phase is then purified by another recovery technique such as electrowinning Electro Metal Winning (EMEW) technology. This process is still not established for processing nickel from laterite ores. The observed process parameters in this research are time; voltage; flow rate; and boric acid concentration to get the optimum results in this EMEW process. The result shows that the optimum addition of boric acid is 1 M with 1.39 mg nickel, the optimum voltage in this EMEW process is 4 volts with 1.55 mg nickel, the optimum time is two hours with the amount of nickel metal is 1.67 mg, and the optimum flow rate is 1 L min⁻¹ with 1.82 mg nickel.

KEYWORDS: Laterite, Electro Metal Electrowinning, Solvent Extraction, Cylindrical Electrode

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Introduction

Indonesia is the seventh-largest nickel reserves in the world [1]. The potential of nickel in Indonesia itself is on Sulawesi Island, southeast Kalimantan, Maluku, and Papua. Indonesia has the potential to be a producer of mineral-based chemicals, one of which is laterite nickel ore. Indonesia, for example, has reserves of nickel oxide ore of around 16% of the world's reserves of nickel oxide [2], but this abundant natural wealth has not been used too much to produce. Issuance of Indonesian Minister of Energy and Mineral Resources Regulation No. 5/2017 which explains the permissibility of the export of low-grade nickel ore (Ni below 1.70%) with the condition that the company's technology development process it in the next five years, adds to the importance of research for processing laterite nickel ore in Indonesia. If mineral ore in Indonesia can be processed and utilized, it will greatly help save

the costs incurred for purchasing chemicals from abroad.

In general, nickel laterite is divided into two types, namely limonite and saprolite [3]. Both are indifferent depths and have different levels of nickel content, with saprolite ore having a higher nickel content (1.50 – 3.00%) [4]. The limonite is ore with a low nickel content (below 1.5%), which causes the nickel refining process with the technique of pyrometallurgy (melting with high temperatures) to be very expensive to do. In limonite the silica content contained in the ore tends to be absent, therefore processing techniques with hydrometallurgical lines are an economical choice. The technique of processing laterite with gradual extraction to obtain high purity minerals continues to grow. The proper use of organic chemicals and can be reused (recycle) becomes very important in this process.

Electrometal Mining Limited, Australia, has been developing a unique metal electrowinning technique since 1994 which was later referred to as the EMEW cell. The pumped solution enters the tube at high speed and flows in a manner such that contact between metal ions and the surface in the cathode is continuously updated and the balance between supply and demand (the amount of current given the electrode) is more direct and effective [5]. Thus, the use of EMEW cells for metal extraction becomes more productive than those obtained by conventional methods. The advantages of this EMEW process include:

- Easy to install
- Environmentally friendly
- It can be operated on a large scale process,
- Electrolyte solutions can be recycled,
- Can produce high purity metals
- It can be operated in metal solutions with low concentrations [6 – 8].

The additive electrolyte has been used in electrowinning to increase the quality of the product. The study of additive electrolyte in cobalt electrowinning conducted by Daniel Assumpção (2012) regarding nickel separation using the electrowinning system concluded that with a variety of conditions carried out and with the addition of boric acid can separate nickel as much as 91 wt% of NiMH from battery [9], but for nickel from laterite, it has not yet been developed. So in addition to the influence of boric acid, various process variations are examined, namely flow rate, voltage, and time, considering that these 3 parameters are important parameters of the success of the process but still not stable for processing the separation of nickel from laterite ore with the EMEW system.

Materials and Methods

In this study, laterite ores mined from Southeast Sulawesi was tested using X-Ray Fluorescence (XRF). Based on the XRF data in Table 1 which shows that the nickel content in

the ore is 0.51%, it can be seen that laterite ore used is limonite laterite, namely laterite ore with nickel content below 1.5%. Laterite ores are divided into two types, namely limonite and saprolite. Saprolite laterite ore has a higher nickel content than limonite types which is above 1.50%, while limonite laterite ore levels are below 1.50% [4].

The raw material used is 10 Kg of laterite ore which is dissolved in 50 L of a mixture of Water and Acetic Acid. A total of 25 L of pregnant leach solutions that were submerged for 6 months (vat-leaching) were then recovered using the solvent extraction process. At this stage, Versatic Acid 10 is chosen as a reactant to separate calcium and magnesium elements from the ore. The results of this stage are the separation of metals such as calcium and magnesium in the aqueous phase, while nickel and cobalt are still mixed in the organic phase. The extraction process parameters using Versatic Acid 10 are based on the results of previous research which is a Taguchi optimization with a processing time of 2 hours and a volume ratio of O: A is 1 : 2 [10], data in Table 2.

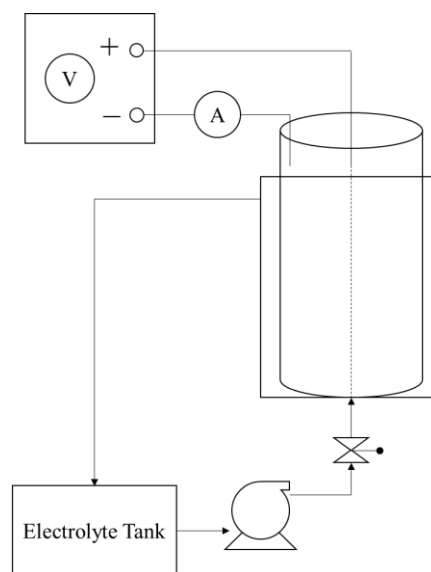


Fig 1. Design of EMEW Experiment Equipment

Table 1 XRF Results of Raw Laterite Ore

Element	Wt (%)	Element	Wt (%)	Element	Wt (%)
LE	78.25	Al	0.56	Ca	0.70
Fe	10.97	Ni	0.51	S	0.02
Si	5.43	Cr	0.32	Sb	0.02
K	1.53	Mn	0.18	Sn	0.02
Cl	1.41	Co	0.04	Cd	0.02
				Zn	0.01

Then the Cyanex 272 extractant was selected in the next solvent extraction process, so nickel remains in the aqueous phase while cobalt in its organic (org) phase. Nickel in the aqueous (aq) phase is then purified by another recovery technique such as electrowinning EMEW technology (Fig. 1). The resume of the leaching process until the process of solvent extraction is shown in Fig. 2.

Results and Discussion

This experiment uses a 1.5-liter EMEW cell which aims to deposit nickel metal from the raw material of limonite ore. The experimental design and experimental results can be seen in Table 3.

broader. The factors that influence the characteristics of an experimental quality can be known by calculating the Average and S/N ratio, so that the influential factors can be given special attention. The disadvantage of this method is that if this experiment is carried out with many factors and interactions, there will be a mixture of several interactions by the main factors. As a result, the accuracy of the experimental results will be reduced, if the neglected interaction does affect the observed characteristics. The Taguchi method is very well used for analysis that uses 3 to 50 variables and has several conditions in each variable [11].

Using a signal to noise (SN) ratio based on larger is better mode from Taguchi Analysis, Table 4 shows that the highest delta value from this electrowinning experiment is the flow rate

Table 2. Taguchi Optimization of Solvent Extraction Experiment Using Versatic Acid 10 [10]

pH	Flowrate (L min ⁻¹)	Organic/Aqueous	Time (h)	Calcium Increase Factor	SNRA1	MEAN1
2.00	1.00	0.25	1	0.57	-4.82	0.57
2.00	1.75	0.50	2	1.46	3.31	1.46
2.00	2.50	0.75	3	1.04	0.32	1.04
2.50	1.00	0.50	3	0.26	-11.51	0.26
2.50	1.75	0.75	1	0.34	-9.32	0.35
2.50	2.50	0.25	2	0.36	-8.88	0.36
3.00	1.00	0.75	2	0.25	-12.19	0.25
3.00	1.75	0.25	3	0.23	-12.78	0.23
3.00	2.50	0.50	1	0.35	-9.12	0.35

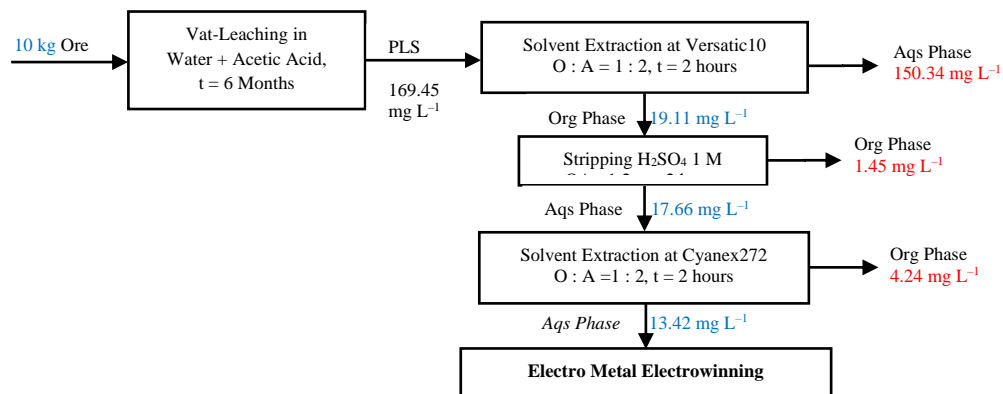


Fig 2. Schematic Diagram of the Process Before Electrowinning

The advantage of using the Taguchi method is that it can reduce the number of experiments if compared to using a full factorial trial, which saves time and money (especially in prototype scale experiments like this). Then can save on average and variations in quality characteristics at once, so that the scope of problem-solving is

parameter. In practice, the flow rate plays an important role in the electrowinning process of EMEW technology, which has a different form compared to conventional electrowinning cells. By setting the right flow rate, contact between ions can be continuously updated. The voltage, duration of the process, and concentration of

addition of boric acid are in the 2nd, 3rd and 4th positions which influence the deposit of nickel-metal at the cathode.

that with a flow rate of 1 liter/minute or about almost 70% of the total capacity, the electrowinning process runs more effectively.

Table 3. Taguchi Experiment Design and Experiment Results of EMEW

Run	Taguchi Experiment Design				Results		
	Time (h)	Flow Rate (L min ⁻¹)	Volt (V)	Boric Acid Concentration (M)	Nickel Content (%)	Nickel deposit (mg)	Nickel Yield
1	1	0.30	2	0.50	0.23	0.61	4550719
2	1	0.70	3	1.00	0.33	0.80	5950577
3	1	1.00	4	1.50	0.73	1.95	1454968
4	2	0.30	3	1.50	0.33	0.85	6313486
5	2	0.70	4	0.50	0.67	1.75	1304856
6	2	1.00	2	1.00	0.93	2.42	1801387
7	3	0.30	4	1.00	0.37	0.94	7010409
8	3	0.70	2	1.50	0.40	1.09	8159332
9	3	1.00	3	0.50	0.41	1.10	8190351

Table 4. Response Table for Signal to Noise Ratios Larger is better

Level	Time(h)	Flow Rate (L min ⁻¹)	Volt (V)	Boric Acid (M)
1	0.14	- 2.08	1.39	0.47
2	3.70	1.23	- 0.86	1.73
3	0.36	4.77	3.38	1.72
Delta	3.84	6.85	4.24	1.26
Rank	3.00	1.00	2.00	4.00

Effect of EMEW Processing Flow Rate on Deposited Nickel Metal Mass

In the process of Electro Metal Electrowinning, the flow rate plays an important role. With effective speed (not too fast but not too slow) it can produce optimum precious metal deposits. In this study, the flow rate was varied from 0.30, 0.70 and 1 L min⁻¹. The effect of the flow rate on the average deposit of nickel metal is shown in Fig 3. Based on this graph, we can find out that the maximum flow rate of 1 L min⁻¹ produces more deposited nickel metal. By increasing the speed of the flow rate to 1 L min⁻¹, the pumped solution will flow circularly in a tube more effectively, so that the contact between nickel ions and the inner surface of the cathode is continuously updated with supply balance (distribution and number of metal ions in solution) with demand (the amount of current given to the electrode) is more direct and more effective [5]. In the experiment, Electro Metal Electrowinning in this study used the capacity of 1.50 L (prototype scale experiment). This means

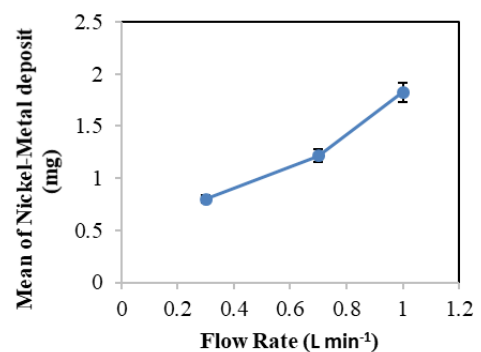


Fig 3. Effect of flow rate on deposited nickel-metal mass

Effect of EMEW Processing Voltage on Deposited Nickel Metal Mass

With the variation of voltage used in this study is 2; 3; and 4 V, the difference in the yield of nickel-metal deposited at the cathode is obtained each run. The greater the potential

difference or voltage is given from the source, the greater the nickel-metal deposit that should have been generated. However, at certain voltages, in this case, 3 V, the effect of hydrogen evolution can disrupt the nickel deposition process during the electrowinning process. This causes the nickel metal to be obtained to be less at the cathode.

The deposition mechanism is initiated by surrounding metal ions by polarizing solvent molecules. Near the cathode surface, an Electrical Double Layer (EDL) area is formed which acts as a dielectric layer. With the thrust force of the electric potential and aided by chemical reactions, metal ions move toward the cathode surface and capturing electrons from the cathode while depositing themselves at the cathode surface. The greater the voltage applied, the greater the nickel-metal is taken and deposited at the cathode. In Fig 4, it appears that the largest voltage, 4 V, produces more deposits, this is because the electric field is large, the ions or electrons will move faster so that the EMEW process generally generates more nickel-metal deposits.

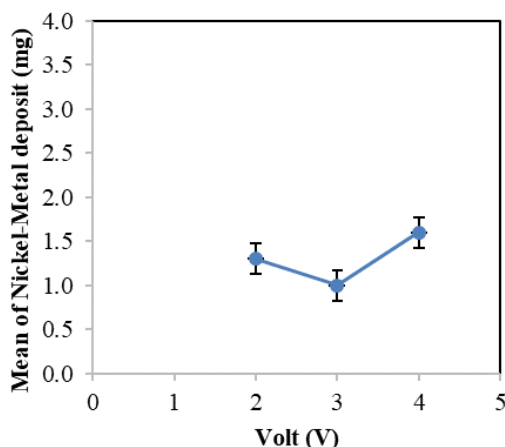


Fig 4. Effect of voltage on deposited nickel-metal mass

Effect of EMEW Processing Time on Deposited Nickel Metal Mass

In this work, the EMEW processing time is varied at 1, 2 and 3 h. The longer the duration of the EMEW process, the greater the mass of nickel deposited, in this experiment is indicated when the operating time is set for 1 and 2 h. Two hours is the optimum time in this experiment. At that time the number of nickel deposits at the cathode increased significantly. But the opposite happens when the electrowinning process is added to 3 h. In this condition, more impurity metals such as Zircon (Zr) and Light Element (LE) are deposited

in the cathode (Fig. 5), so that the nickel at the cathode is reduced. Elements known as light elements in the context of X-ray fluorescence include magnesium (Mg), silicon (Si), phosphorus (P), sulfur (S), and chlorine (Cl). On the graph it appears that in the span of 2 h, the acquisition of nickel in the electrowinning process increases effectively, this is also indicated by the low content of impurity metals. The next phenomenon when the processing time is extended to 3 h, nickel-metal has decreased due to the level of impurity metal derived from electrolyte solutions, more and more also deposited at the cathode.

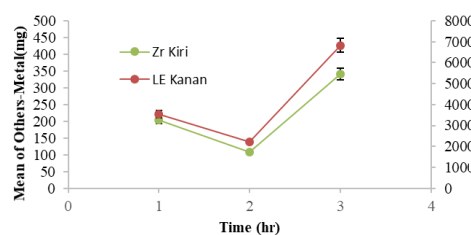


Fig 5. Effect of time on deposits of impurity metals mass II

With the increasing length of time, the more metal deposition can be formed at the cathode. The effect of the time variations in this experiment is shown in Fig 6. Based on the graph, it is clear that 2 h is the most optimum time, while the decline occurs when the operating time is 3 h.

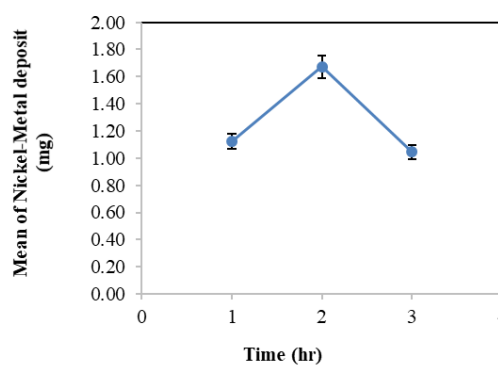


Fig 6. Effect of time on deposited nickel-metal mass II

Effect of Boric Acid Concentration on Deposited Nickel Metal Mass

The effect of the concentration of boric acid on Electro Metal Electrowinning (EMEW) processing was investigated with variations in the

addition of each of 0.50; 1; and 1.50 M. Seen from Table 6 the results of the Taguchi experimental design analysis, found the optimum results at the 6th run with the concentration of addition of boric acid 1 M. Plot graph Fig. 7 results of this experiment show that the addition of boric acid concentration will increase metal deposits nickel, but if more than its optimum concentration, the value of nickel-metal deposits stagnates.

Based on the data, the addition of boric acid 1.5 M will produce nickel metal deposits which are almost as large as 1 M, 1.23 mg, and 1.39 mg respectively. This phenomenon indicates that boric acid used more than 1 M will be detrimental to the use of materials. The addition of boric acid additives can increase cathode polarization in the electrowinning. In electrodeposition, boric acid is absorbed by the cathode surface which increases the potential deposition of Ni^{2+} . Boric and Ni^{2+} can form nickel borate which can increase the overpotential hydrogen and reduce H_2 evolution [12].

According to Nickel Institute, the parameters of the addition of boric acid ranged from 30 – 45 gr L^{-1} , or equivalent to 0.5 to ± 1 M. In an experiment with a concentration of 1.5 M borate added, it decreased the amount of electrodepositing nickel [13]. This is because the increase in boric acid concentration will increase the viscosity of the electrolyte solution (according to observations in the field) so that it will reduce the transfer of nickel-metal mass to the electrode.

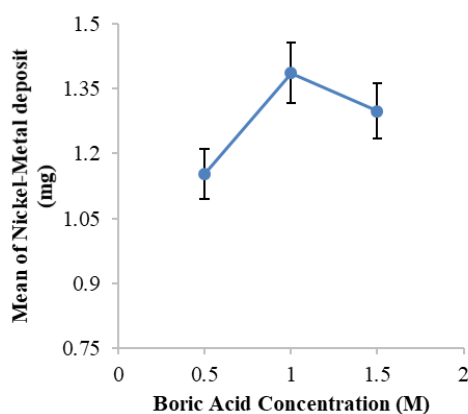


Fig 7. Effect of boric acid concentration on deposited nickel-metal mass II

Conclusion

The optimum conditions of the EMEW based on Taguchi analysis are at 2 hours of

operation duration, 4 V of DC voltage, 1 L min^{-1} of flowrate, and 1 M of boric acid additive (H_3BO_3) concentration. The nickel yield is very low due to the low nickel content in electrolyte solution in EMEW process. The low nickel content in EMEW process since of the solvent extraction and stripping only treat small amount of leaching solution in single batch process. The organic solution of solvent extraction and aqueous solution of stripping able to treat more than three times of batch process of leaching process.

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