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Optimization of Electrometal-Elektrowinning Cobalt Process from the Slag of Nickel Pig Iron (NPI)

Hermida L[1], Sudibyo S[2]*, Supriyatna YI[2], Herlina U[2], Handoko AS[2], Prasetyo E[2], Almutaqii M[2] and Reswari PA[1]

[1]Department of Chemical Engineering, Engineering Faculty, Lampung University, Indonesia
[2]Research Unit for Mineral Technology, Indonesian Institute of Sciences (LIPI), Indonesia

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***Corresponding author:** Sudibyo Sudibyo, Research Unit for Mineral Technology, Indonesian Institute of Sciences (LIPI), Ir. Sutami street Km. 15, Tanjung Bintang, South Lampung district, Lampung Province, Indonesia, Tel: +6285881020870; Email: sudibyo@lipi.go.id

Abstract

Slag from the manufacturing of nickel pig iron (NPI) from laterite soil is still containing 823.7 ppm of cobalt. In this research, the separation process is carried out from slag NPI by using the Response Surface Method (RSM). This method is to determine the optimum conditional process of Electrometal Electrowinning (EMEW) and get an equation model to see the correlation between a variable and know the most significant interfactor interaction. This research was conducted using three parameters, consists of duration of operation, potential voltage, and variable of boric acid. The first step in electro-metal electrowinning is leach the slag using acetic acid, and then extracted in two steps by versatic acid 10 and then with cyanex 272. The organic phase from this extraction then stripped using 6 M sulphuric acid so obtained aqueous phase at pH 5.5 with the highest cobalt content. The best condition of electro-metal electrowinning is obtained at 4.5 V, 2 hours, and 0.5 M of boric acid with 45.8273% of cobalt recovery. Based on statistic analysis using software, time is an individual factor which gives the most significant influence to the percent of generating electrowinning, while the most significant interfactor interaction based on the sequential model sum of squares, lack of fit test, model statistic, and analysis of variance (ANOVA) analysis is a quadratic model with R2 of 0.9544.

Keywords: Cobalt electrowinning; Cobalt extraction; Slag of nickel pig iron; Response surface methods; Cyanex 22

Abbreviations: NPI: Nickel Pig Iron; RSM: Response Surface Method; EMEW: Electrometal Electrowinning; XRF: X-Ray Fluorescence; ANOVA: Analysis of Variance

Introduction

Cobalt is usually found as a mixture in nature as in laterite nickel ore and the result itself is often found as the side product. Laterite with a high level is usually processed with pyrometallurgy to produce nickel pig iron (NPI). the method usually used the pyrometallurgy method, this method remains slag or solid waste. This slag still containing cobalt due to furnace temperature has below the melting point of cobalt [1], and it has cobalt as much as 823.7 ppm inside the NPI slag. Metal recovery from solution with electrolysis process or electrowinning is one of the popular techniques and is often used in the industry by putting the electrodes that are electrified into electrolyte solute, and finally the metal stick into the surface or surround to the cathode [2-4].

In this work, the slag of NPI was leach using acetic acid to dissolve the cobalt [5]. The solvent extraction methods using cyanex were used to separated cobalt from its impurities [6-9]. The cylindrical cathode was used in this research to increase the performance of electrowinning which the electrolyte solution which contains cobalt has flowed from the bottom of the electrowinning cell, this method is known as electro-metal–electrowinning (EMEW) [10]. Batch recycle methods also apply in this EMEW process to ensure all cobalt was completely deposited from the electrolyte solution to the cathode.

In this work, the parameters affected EMEW processes such as DC voltage (volt), duration of the electrochemical process, and the concentration of boric acid (additive electrolyte). The Response Surface Methodology (RSM) was used to obtain the optimum condition and to study the interaction of each factor, parameter on the cobalt metal electrowinning process and mathematical model to predict the mass of cobalt result [11-14].

Research Methodology

This research was conducted using the slag of NPI which is processed in several stages before the electro-metal electrowinning process. First, slag was leached using 2M of CH_3COOH and stir it for 3 days. Then the leaching yield was extracted with 2 extraction processes. First extraction using versatic acid 10 and the second extraction using cyanex 22. The extraction process will produce an organic phase and aqueous, organic phase in the first extraction in stripping using 5M of H_2SO_4 and an organic phase in the second extraction in stripping using 6M of H_2SO_4 for 120 minutes. Stripping yield is obtained aqueous phase and organic, aqueous phase on second stripping yield with pH 5.5 and cobalt content of 0.8524 which will become to cobalt electro-metal electrowinning process. Cobalt electro-metal electrowinning using aluminum as cathode and graphite as an anode. The design experiment process based on central composite design can be seen in Figure 1. The cathode (negative poles (-)) and the cathode (positive poles (+)) were connected to the rectifier and the amperemeter using a cable. This research using a statistic design experiment with the Response Surface method, Central composite design to Electrometal Electrowinning process. This research was done with three parameters such as variations in the electrowinning processing time, variations in potential voltage, and also borid acid (additive electrolyte) concentration. Variations in operating factors and the design of the experiment process based on central composite design can be seen in Tables 1 & 2, respectively.

Factor	Variable that is varied
Time	4 ; 4.5 ; 5
Voltage	1 ; 2 ; 3
Boric Acid	0 ; 0.5 ; 1

Table 1: Variation of Factor Operation.

Run	Time (hr)	Voltage (V)	Boric Acid (M)
1	4	1	0
2	4.5	3.68179	0.5
3	5	1	0
4	4.5	2	0.5
5	4	1	1
6	5	3	0
7	5.3409	2	0.5
8	4.5	2	1.3409
9	4.5	2	0.5
10	5	1	1
11	4.5	2	0.5
12	3.6591	2	0.5
13	5	3	1
14	4.5	2	0.5
15	4	3	0
16	4.5	2	0.5
17	4.5	0.318207	0.5
18	4	3	1
19	4.5	2	0.5
20	4.5	2	-0.3409

Table 2: Design experiment based on Central Composite Design.

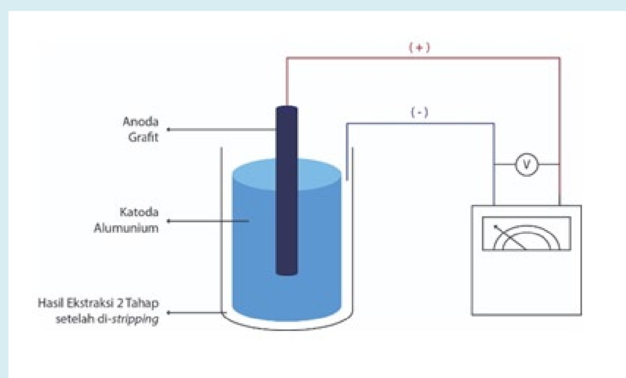

Figure 1: Design of Electrometal electrowinning tank.

Result and Discussion

Using Response Surface Methodology (RSM) with Central Composite Design and analysed using X-Ray Fluorescence (XRF). The experimental data in the electrowinning process can be seen in Table 3. The table shows the analysis result using Software Design Expert 10.0.1. This analysis was conducted to determine the optimum operating conditions, the equation model, and also the suitability model of the electrowinning process.

Run	Factor			Respond Cobalt (% Recovery)	
	Voltage (V)	Time (hr)	Boric Acid (M)	Prediction	Actual
1	4	1	0	8.6426	10.0804
2	4,5	3.68179	0.5	13.9892	10.0019
3	5	1	0	2.5876	1.6927
4	4.5	2	0.5	45.7073	45.8273
5	4	1	1	0.2583	4.209
6	5	3	0	2.9074	1.9238
7	5.3409	2	0	11.2228	13.8938
8	4.5	2	1	27.2642	24.1727
9	4	2	0.5	45.7073	45.8273
10	5	1	1	31.4588	29.7218
11	4	2	0.5	45.7073	45.8273
12	3.6591	2	0.5	9.6043	2.7374
13	5	3	1	17.5273	19.0565
14	4	2	0.5	45.7073	45.8273
15	4	3	0	32.832	36.8872
16	4	2	0.5	45.7073	45.8273
17	4.5	0.318207	0.5	5.909	5.7004
18	4	3	1	9.5474	13.4094
19	4.5	2	0.5	45.7073	45.8273
20	4.5	2	-0.3409	22.0208	20.9163

Table 3: Electrowinning process yield.

Fitting Model and Statistic Analysis

Suitability of the model can be determined by using an experiment which aims to confirm response prediction (cobalt) based on RSM analysis. This analysis using square root transformation. This transformation is used if the data obtained does not get homogeneity of variety or the square root function is to create a variety of data into homogenous.

Based on the analysis of Sum of Squares, the type of model suggested is the quadratic model. Prob > F value less than 0.0001 shows the model is significant to the process carried out. Whereas for Lack of Fit analysis recommended is a type of model with Prob > F less than 0.05 and based on analysis result from software, lack of fit analysis nor produce value prob>F. Hence, the analysis of the suitability of the lack of fit model cannot be done. Based on the model summary statistic obtained a quadratic model with the R^2 value of 0.9544, Std. Dev of 0.6 and PRESS of 26.93. This means that the quadratic model can be used to illustrate the correlation between response and interaction variables.

ANOVA analysis is a technic analysis used to identify the importance of the model obtained and also the parameter itself. Table 4 shows the ANOVA (Analysis of Variance) for the quadratic model that was obtained in the Electrometal Electrowinning cobalt process. A model with F-Value 23.24 and p-value < 0.0001 which shows the suggested and significant model.

ANOVA for Response Surface Quadratic model					
Analysis of variance table [Partial sum of squares - Type III]					
Source	**Sum of Squares**	**Df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	74.15	9	8.24	23.24	< 0.0001
A-Voltage	0.078	1	0.078	0.22	0.6496
B-Time	1.7	1	1.7	4.78	0.0536
C-Boric Acid	1.27	1	1.27	3.59	0.0873
AB	3.79	1	3.79	10.7	0.0084
AC	14.22	1	14.22	40.09	< 0.0001
BC	0.76	1	0.76	2.13	0.1747
A2	27.95	1	27.95	78.82	< 0.0001
B2	26.77	1	26.77	75.5	< 0.0001
C2	6.4	1	6.4	18.05	< 0.0017
Residual	3.55	10	0.35		
Lack of Fit	3.55	5	0.71		
Pure Error	0	5	0		
Cor Total	77.69	19			

Tabel 4: Analysis of Variance (ANOVA).

Based on the analysis, the quadratic equation model has obtained with states the correlation between the percent of cobalt and these tree factor are variated.

Factor Code:

$$Cobalt = 6.76 + 0.075A + 0.35B + 0.31C - 0.69AB + 1.33AC - 0.31BC - 1.39A2 - 1.36B2 - 0.67C^2$$

Actual Factor:

$$Cobalt = -114.85729 + 50.37196(Voltage) + 12.30958(time) - 19.48715(\text{boric acid}) - 1.37731(\text{voltage})(\text{time})$$
$$+5.33204(\text{voltage})(\text{boric acid}) - 0.61515(\text{time})(\text{boric acid}) - 5.57027(voltage)^2 - 1.36294(time)^2$$
$$-2.66586(boric\ acid)^2$$

The Effect of Time, Voltage, and Boric Acid

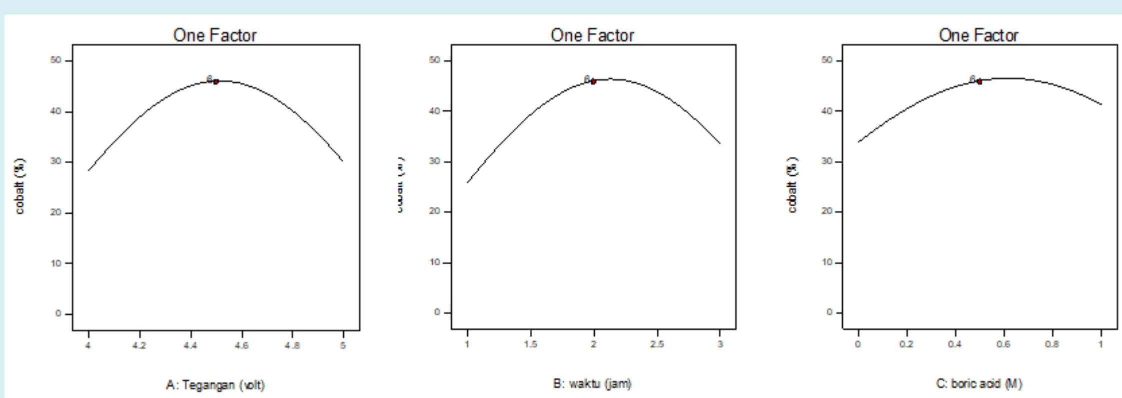

Figure 2: Graphic of the effect of time, voltage, and boric acid.

In this work, the time of operation was varied from 1 to 3 hours), the voltage was varied from 4 to 5 volts, and also borid acid concentration from 0 to1 M as shown in Figure 2. The figure shows that the highest point or optimum condition at 2 hours of time operation, 4.5 Volt of DC voltage, and also 0.5 M of boric acid concentration. From this graphic, we could be seen the variation in addition to a certain content could give a better effect in this research. However, the higher the voltage and boric acid concentration and time of operation will cause the decrease of cobalt content which is caused by a pollutant or another compound that is attached to the surface of the cathode.

Interaction of Interfactor

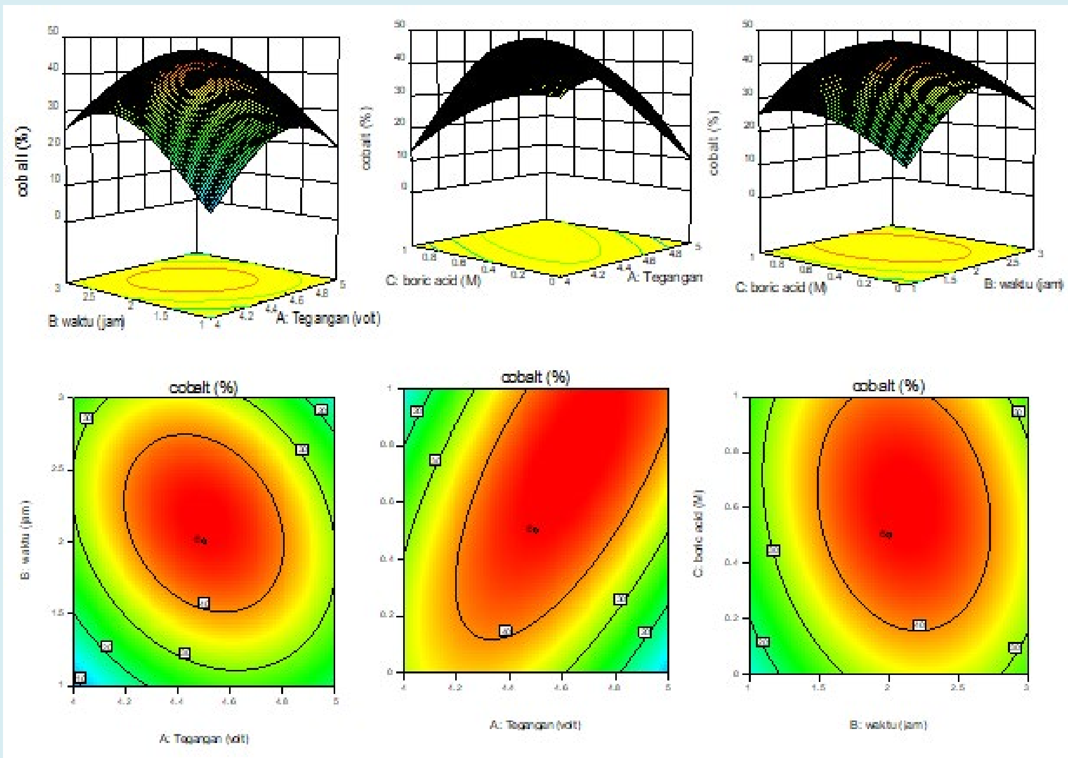

Figure 3: Contour plot graphic and response surface interfactor.

Figure 3 shows the contour plot graphic and response surface interfactor. The figure shows the correlation between the percentage of cobalt and three factors that affect it. The results of the influence of interfactor were listed in Table 5.

Factor	Respond
Time vs Voltage	Significant
Voltage vs Boric Acid	Very significant
Time vs Boric Acid	Less significant

Table 5: The influence of interfactor towards the percentage of cobalt.

Optimum Condition and Model Verification

Table 6 shows that the prediction and experiment result in optimum operating condition. The table shows that the percentage of cobalt value from real experiment than the predicted value by the software is closed with an error value of less than 10%. The error value in the range of 10-15% is still acceptable in the process of optimizing a process. The cobalt percent value which is based on the experiment is smaller than the value of cobalt percent which is predicted by software.

Sample	Voltage (V)	Time (Hour)	Boric Acid (M)	%DE Prediction	Actual
1	4.649	1.985	0.647	45.374	41.1806

Table 6: Prediction and experiment result in Optimum Operation Condition.

Conclusion

The best condition in the Electrometal-Electrowinning (EMEW) process which obtained in 4.5 V, 2 hours, and 0.5 M of boric acid with the cobalt of 45.8273%. RSM statistic analysis result show that time is an individual factor that could give the most significant value to the percentage of generated. While the most significant interfactor interaction is the interaction between voltages and boric acid. The suggested model based on the sequential model sum of squares, lack of fit test, model statistic, and analysis of variance (ANOVA) is a quadratic model with R2 of 0.9544.

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