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

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Abstract

Slag from the manufacturing of nickel pig iron (NPI) from laterite soil was still containing 823.70 ppm of cobalt. In this research, the separation process was carried out from slag NPI by using the Response Surface Method (RSM). This method was to determine the optimum conditional process of Electrometal Electrowinning (EMEW) and get an equation model to obtain the correlation between a variable and understand the most significant interfactor interaction. This research was conducted using three parameters, consisting of duration of operation, potential voltage, and variable of boric acid. The first step in electro-metal electrowinning was leach the slag using acetic acid and extracted it with versatic acid 10 and cyanex 272 respectively. The organic phase from this extraction was stripped by 6 M sulphuric acid and obtained aqueous phase at pH 5.50 with the highest cobalt content. The best condition of electro-metal electrowinning was obtained at 4.50 V, 2 h, and 0.50 M of boric acid with 45.82 % of cobalt recovery. Based on the statistic analysis using software, time was 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 was quadratic model with R^2 of 0.95.

Keywords: Cobalt Electrowinning; Cobalt Extraction; Slag of Nickel Pig Iron; Response Surface Methods; Cyanex 22

Introduction

Cobalt is usually found as a mixture in nature such as in laterite nickel ore. Laterite with a high level was usually processed with pyrometallurgy to produce a nickel pig iron (NPI). This method remains slag or solid waste which still containing cobalt due to furnace temperature has below the melting point of cobalt [1], and it has cobalt as much as 823.70 ppm inside the NPI slag. The solvent extraction process was a common method to remove impurities [2 – 7]. After the solvent extraction process, metal recovery from solution with the electrolysis process or electrowinning was one of the popular techniques. These methods using the electrodes that are electrified into the electrolyte solution, and hence the metal stick into the surface or surround to the negative electrode (cathode) [8 – 11].

In this work, the slag of NPI was leach using acetic acid to dissolve the cobalt [12]. The solvent extraction methods using cyanex were used to separated cobalt from its impurities [3, 5], [13, 14]. The cylindrical cathode was used in this research to increase the performance of electrowinning, meanwhile, the electrolyte solution which contains cobalt has flowed from the bottom of the electrowinning cell, continuously. This method was known as electro-metal – electrowinning (EMEW) [15]. Batch recycle methods was also applied in this EMEW process, and hence all cobalt from electrolyte solution was completely deposited in the cathode surface.

In this work, the parameters affected EMEW processes such as DC voltage (volt), duration of the electrochemical process, and the concentration of additive electrolyte (boric acid) were investigated. The Response Surface Methodology (RSM) was used in this work to obtain the optimum condition and to study the interaction of each parameter on the cobalt metal electrowinning process. RSM methods also provide a mathematical model to predict the mass of cobalt results [16 – 19].

Materials and Methods

This research was conducted using the slag of NPI which was processed in several stages before the electro-metal electrowinning process such as leaching and solvent extraction process. First, slag was leached using a stirred reactor with 2 M of CH_3COOH for 3 days. Then the leaching yield was filtrated and extracted with 2 extraction processes. First extraction stage using versatic acid 10 and the second extraction stage using cyanex 22. The extraction process will produce an organic phase and aqueous, organic phase in the first extraction in stripping using 5 M of H_2SO_4 and an organic phase in the second extraction in stripping using 6 M of H_2SO_4 for 120 minutes. Stripping yield is obtained aqueous phase and organic, aqueous phase on second stripping yield with pH 5.50 and cobalt content of 0.85 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 was shown in Fig. 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 has been done with three parameters such as variations in the electrowinning processing time, variations in potential voltage, and borid acid (additive electrolyte) concentration. The variations in operating factors and the design of the experiment process based on central composite design are shown in Tables 1 and 2, respectively.

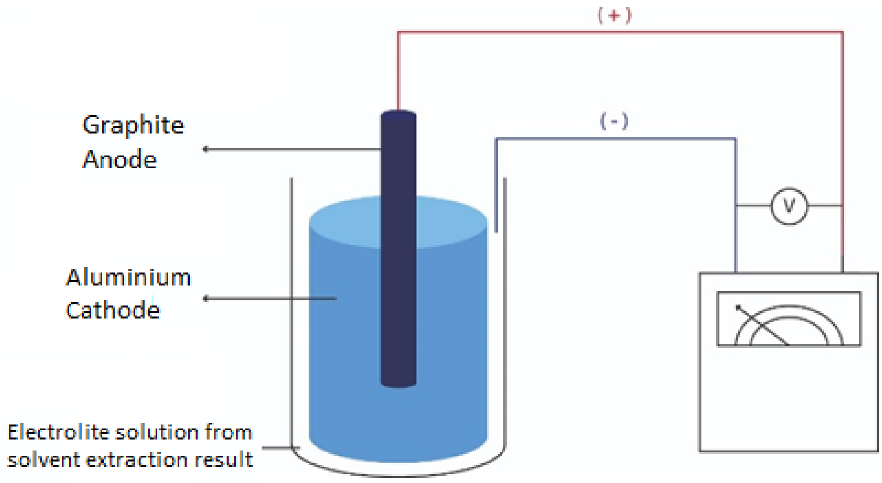

Fig. 1 Experimental design of the electro-metal-electrowinning tank.

Table 1 Variation of Factor Operation.

Factor	variable that is varied
Time	4 ; 4.50 ; 5
Voltage	1 ; 2 ; 3
Boric Acid	0 ; 0.50 ; 1

Table 2 Design experiment based on Central Composite Design.

Run	Time (hr)	Voltage (V)	Boric Acid (M)
1	4	1	0
2	4.50	3.68	0.50
3	5	1	0
4	4.50	2	0.50
5	4	1	1
6	5	3	0
7	5.34	2	0.50
8	4.50	2	1.34
9	4.50	2	0.50
10	5	1	1
11	4.50	2	0.50
12	3.66	2	0.50
13	5	3	1
14	4.50	2	0.50
15	4	3	0
16	4.50	2	0.50
17	4.50	0.32	0.50
18	4	3	1
19	4.50	2	0.50
20	4.50	2	-0.34

Results and Discussion

This work using the Response Surface Methodology (RSM) of design experiments with Central Composite Design (CCD). The electrodeposit result was analysed using X-Ray Fluorescence (XRF) to find out the cobalt content. The experimental data in the electrowinning process are shown in Table 3. The table shows the analysis results 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.

Table 3 Electrowinning process yield.

Run	Factor			Respond Cobalt (% *recovery*)	
	Voltage (V)	Time (hr)	Boric Acid (M)	Prediction	Actual
1	4	1	0	8.64	10.08
2	4.50	3.68	0.50	13.99	10
3	5	1	0	2.59	1.69
4	4.50	2	0.50	45.71	45.83
5	4	1	1	0.26	4.21
6	5	3	0	2.91	1.92
7	5.34	2	0	11.22	13.89
8	4.50	2	1	27.26	24.17
9	4	2	0.50	45.71	45.83
10	5	1	1	31.46	29.72
11	4	2	0.50	45.71	45.83
12	3.66	2	0.50	9.60	2.74
13	5	3	1	17.53	19.06
14	4	2	0.50	45.71	45.83
15	4	3	0	32.83	36.89
16	4	2	0.50	45.71	45.83
17	4.50	0.32	0.50	5.91	5.70
18	4	3	1	9.55	13.41
19	4.50	2	0.50	45.71	45.83
20	4.50	2	-0.34	22.02	20.92

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 uses square root transformation. This transformation was used if the data obtained does not have homogeneity of variety or the square root function was to create a variety of data into homogenous.

Based on the analysis of Sum of Squares, the type of model suggested using the quadratic model. The Prob > F value less than 1×10^{-4} shows that the model was significant to the process carried out. Whereas for Lack of Fit analysis recommended was a type of model with Prob > F less than 0.05 and based on analysis result from software, the 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 0.95, Std. Dev of 0.60 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 was 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 $< 1 \times 10^{-4}$ which shows the suggested and significant model.

Table 4 Analysis of Variance (ANOVA)

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	$< 1 \times 10^{-4}$	Significant
A-Voltage	0.078	1	0.078	0.22	$0.6.5 \times 10^{-1}$	
B-Time	1.70	1	1.70	4.78	5.36×10^{-2}	
C-Boric Acid	1.27	1	1.27	3.59	8.73×10^{-2}	
AB	3.79	1	3.79	10.70	8.40×10^{-3}	
AC	14.22	1	14.22	40.09	$< 1 \times 10^{-4}$	
BC	0.76	1	0.76	2.13	1.75×10^{-1}	
A^2	27.95	1	27.95	78.82	$< 1 \times 10^{-4}$	
B^2	26.77	1	26.77	75.50	$< 1 \times 10^{-4}$	
C^2	6.40	1	6.40	18.05	$< 1.70 \times 10^{-3}$	
Residual	3.55	10	0.35	-	-	
Lack of Fit	3.55	5	0.71	-	-	
Pure Error	0	5	0	-	-	
Cor Total	77.69	19	-	-	-	

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

Factor Code:

$$\text{Cobalt} = 6.76 + 0.075A + 0.35B + 0.31C - 0.69AB + 1.33AC - 0.31B - 1.39A^2 - 1.36B^2 - 0.67C^2 \quad (1)$$

Actual Factor:

$$\text{Cobalt} = -114.85 + 50.37\,(\text{voltage}) + 12.31\,(\text{time}) - 19.48\,(\text{boric acid}) - 1.37\,(\text{voltage})(\text{time}) + 5.33\,(\text{voltage})(\text{boric acid}) - 0.61\,(\text{time})(\text{boric acid}) - 5.58\,(\text{voltage})^2 - 1.36\,(\text{time})^2 - 2.66\,(\text{boric acid})^2 \quad (2)$$

The Effect of Time, Voltage, and Boric Acid

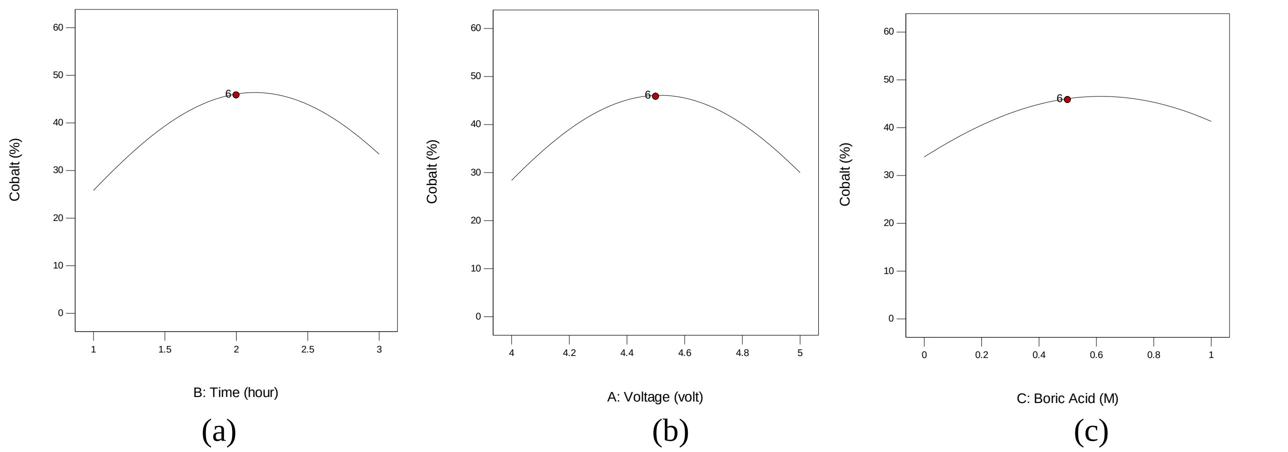

Fig. 2 (a) Graphic of the effect cobalt vs time, (b) Graphic of the effect cobalt vs voltage, and (c) Graphic of the effect cobalt vs boric acid.

Interaction of Interfactor

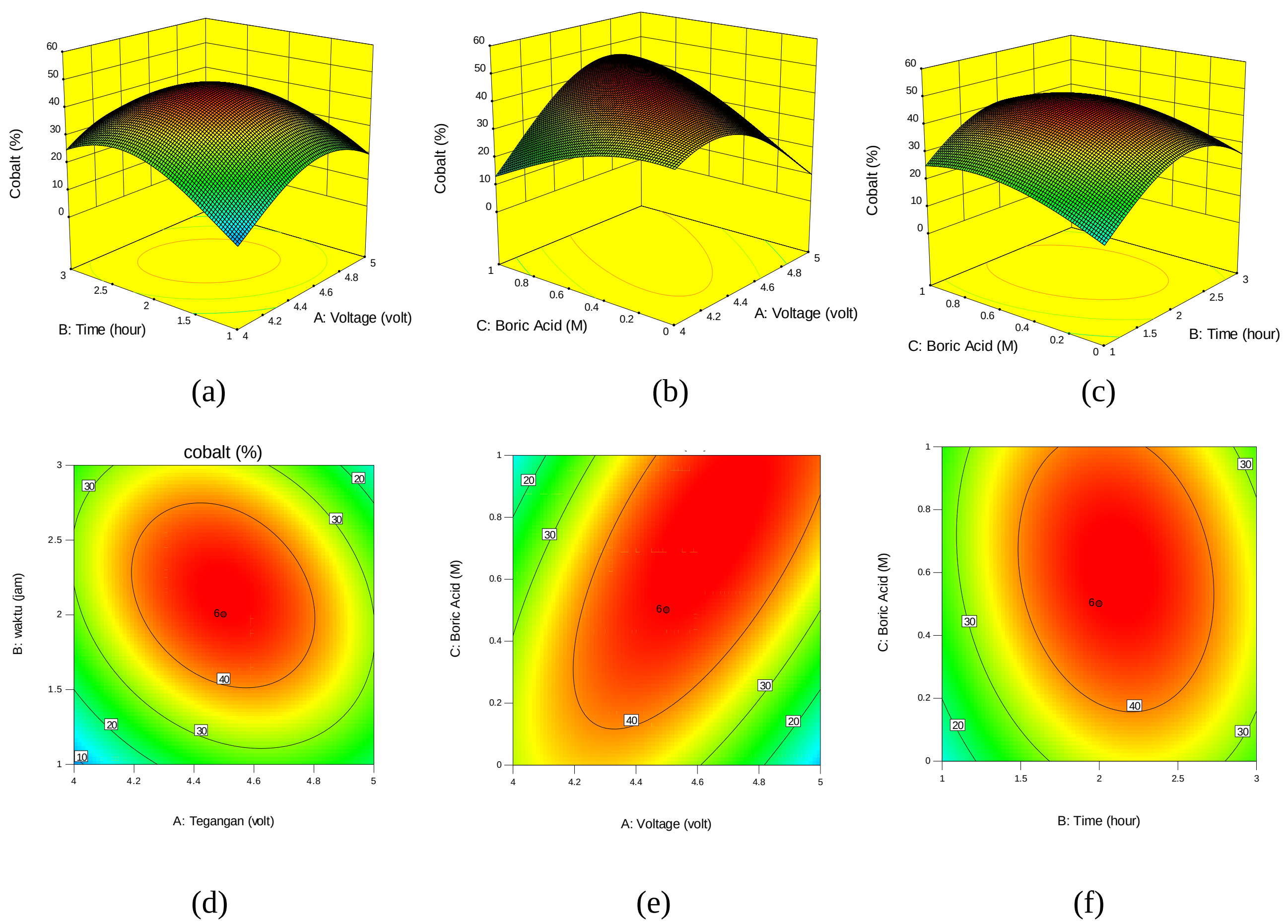

Fig. 3 Response surface interfactor (a) time vs voltage, (b) boric acid vs voltage, (c) boric acid vs time, and Contour plot graphic (d) time vs voltage, (e) boric acid vs voltage, (f) boric acid vs time.

In this work, the time of operation was varied from 1 – 3 h, the voltage was varied from 4 – 5 volts, and also boric acid concentration from 0 – 1 M as shown in Fig. 2. The Fig. 2 shows that the highest point or optimum condition at 2 h of time operation, 4.50 V of DC voltage, and also 0.50 M of boric acid concentration. From this graphic, we can see the variation in addition to a certain content that 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 was caused by a pollutant or another compound that was attached to the surface of the cathode.

Figure 3 shows the contour plot graphic and response surface interfactor. The Fig. 3 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.

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 is less than the predicted value by the software was closed with an error value of less than 10%. The error value in the range of 10 – 15% was still acceptable in the process of optimizing a process. The cobalt percent value which was based on the experiment was smaller than the value of cobalt percent which was predicted by software.

Table 6 Prediction and experiment result in Optimum Operation Condition.

Sample	Voltage (V)	Time (h)	Boric Acid (M)	%DE	
				Prediction	Actual
1	4.65	1.98	0.65	45.37	41.18

Conclusion

The best condition in the Electrometal-Electrowinning (EMEW) process which obtained in this research were 4.50 V, 2 h, and 0.50 M of boric acid with the cobalt of 45.82 %. The RSM statistical analysis result shows that time was an individual factor that could give the most significant value to the percentage generated. While the most significant interfactor interaction was 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) was a quadratic model with R^2 of 0.95.

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