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3^3 Factorial optimization of cobalt eletrowinning parameters from sulphate media using anode bag

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ABSTRACT

The study focused on the application of factorial optimization technique on the cobalt electrowinning with anode bag and its advantages over conventional electrowinning cell practice. Under fixed electrolyte conditions three parameters viz. pH, Cobalt concentration and current density have been varied at three different level and regression equations have been developed for current efficiency & power consumption and optimized conditions derived. The optimum conditions obtained; Cobalt sulfate concentration 47-50 g/L in Electrolyte, pH 3-4 and 250-280 Ampere / meter square current density when cathode and anode are separated by 40 mm. The average current efficiency increased to 90% against 65% in conventional cell, Power consumption reduced to 30% and the regression equation for power consumption and current efficiency is derived and validity of the equation is tested with F-test. It opens the possibility of operating electrowinning cell even at higher current densities with same efficiency by adjusting the other parameters to increase the productivity.

KEYWORDS

Factorial optimization;
Current efficiency;
Electrowinning;
Anode bag.

INTRODUCTION

Cobalt is strategic and critical silver gray hard metal having applications in diversified industrial, commercial, medicinal, metallurgical fields[1]. Cobalt is most used in the metallurgical field in super alloys, wear resistant coatings, corrosion resistant alloys, high speed alloys and magnetic alloys. In chemical field compounds of cobalt are used in catalyst, adhesives and pigments.

Cobalt is prepared by Electrowinning CoSO4 solution, which consists of the following reactions.

At the cathode :

$$Co^{2+} + 2e^- \rightarrow Co \quad (1)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

ii) At the anode :

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (3)$$

$$Co^{2+} \rightarrow Co^{3+} + e^- \quad (4)$$

The reduction of H+ ions at the cathode results in a rise in pH while the generation of H^+ ion at the anode results in a decrease of pH.

If the anolyte and catholyte are allowed to mix in the conventional Electrowinning, pH as well as Cobalt ion concentration of the electrolyte decreases due to the reaction (3) and (1). The acid mist is formed above the cell due to reaction (2) given above which is environmentally unhealthy to work. This also leads to the loss of electrolyte as well as poor current efficiency of about 65% [2].

The probability of small amount of Co^{3+} formed at the anode[3] as per the equation (4) given above, reaching the Cathode by diffusion is also unavoidable. Moreover the presence of multivalent ion affects the current efficiency as well as the nature of the deposit in morphology.

The other contaminants, which are getting oxidized at the anode and forms insoluble oxides are also getting occluded along with the deposit at the cathode.

Thus there is a need to maintain the pH in order to avoid hydrogen evolution at the cathode as per the equation (2), acid mist generation to keep healthy working atmosphere, need to block the Diffusion of the ions from the anode to the cathode which affects current efficiency and occlusion of the insoluble metal oxide contaminants along with the cobalt deposit to increase the purity. Eventhough the use of anode bag[2,3] solves the above problems by resisting the flow of metal oxides particles and free acid proven commercially, till date there is no study reported regarding the optimization of parameters of cobalt electrowinning with anode bag.

Beyond this, in Cobalt metal production by electrowinning of its salt; the parameters are very critical to operate[4-8]. The influence of parameters on the efficiency also decides the cost of process. Factorial optimization[9] is the effective technique to identify the optimum condition when more number of factors influence the response compare to one factor at a time. The advantages of factorial optimization compared to conventional one factor at a time are, individual effect as well as the interaction effect including multi level interaction, extent of interaction of parameters, equation corresponds to the influence of parameter on the response and reliability as well as reproducibility with error level of the experiments can be identified at the least no of experiments. The intermediate data can also be generated using the equation.

The factorial optimization is the suitable technique for optimizing Electrowinning parameters to get maximum current efficiency. Generally p^k full factorial design can be utilized to optimize the experimental parameters when the no of factors are limited where p- is the no of levels and k – is the no of factors. When large no of the factors influence the response then fraction factorial design is utilized to reduce the no of experiments for optimization.

Thus we have utilized 3^3 full factorial design to optimize the condition for electrowinning of cobalt with the use of anode bag. The choices of factors are pH of pregnant electrolyte, current density and the cobalt concentration in the pregnant electrolyte. The three levels of the factors are as in TABLE 1.

EXPERIMENTAL

All the Electrowinning experiments were performed in an acrylic cell with the capacity of 1.4 lit using the cobalt pregnant electrolyte prepared from AR grade crystal of cobalt sulphate (Merck) with pH around 3 with further pH adjustment using cobalt hydroxide. Through out the experiment Flow rate of pregnant electrolyte is kept at 5 ml /min constantly using peristaltic pump and the distance between the anode and cathode is kept as 40mm. Anolyte and catholyte were separated by a bag made polypropylene hold by polypropylene frame. Acid produced at the anode compartment was sucked out using the peristaltic pump at a constant rate and collected separately

Thus the experimental cell consist of two anodes made of lead – antimony alloy (5×12×80cm) kept inside the poly propylene frame holding anode bag, separated by 40mm from single stainless steel cathode (60×65×2mm) from the centre. It consists of total 29 experiments according to factorial design and the data are as given in TABLE 2.

TABLE 1 : Factors and levels for parameter optimization in cobalt electrowinning

Factors	Levels
pH	3, 4, 5
Current density	200, 300, 400 A/m^2
Co concentration	30, 40, 50 g/L

TABLE 2 : 3^3 Factorial experimental design

Std Order	Run Order	Co grams per liter	pH	Current density A/m^2	Current efficiency in %	power consumption in kWh/Kg
1	1	30	3	200	85.4	3.9
2	2	30	3	300	82	4.18
3	3	30	3	400	75.4	6.1
4	4	30	4	200	91.1	3.82
5	5	30	4	300	78.4	5.69
6	6	30	4	400	77.3	5.87
7	7	30	5	200	89.2	3.76
8	8	30	5	300	89.7	4.56
9	9	30	5	400	80.3	5.84
10	10	40	3	200	83.5	4.38
11	11	40	3	300	90.9	4
12	12	40	3	400	94.9	4.22
13	13	40	4	200	89	3.81
14	14	40	4	300	91	4.1
15	15	40	4	400	92	4.5
16	16	40	5	200	91	3.72
17	17	40	5	300	83	4.43
18	18	40	5	400	76.8	5.32
19	19	50	3	200	94.7	3.84
20	20	50	3	300	91	4.24
21	21	50	3	400	95	4.3
22	22	50	4	200	86.1	4
23	23	50	4	300	88.5	4.01
24	24	50	4	400	90	4.6
25	25	50	5	200	83.4	4.18
26	26	50	5	300	82.1	5.2
27	27	50	5	400	75.4	5.66
12(R1)	28	40	3	400	95.9	4.2
12(R2)	29	40	3	400	95.2	4.26

RESULTS AND DISCUSSION

The experimental results obtained under above designed operational parameter are used to obtain the regression equation, Main effect and interaction effect.

The main effect of the individual parameters has been presented in Figure 1. From main effect plots, it is evident that increase in concentration of Cobalt did not influence beyond 40 gpl on efficiency.

The graphical representation of 3-level interaction effect Figure 2 indicates that at around 40g/L, 4-pH and 200 amp/m2 gives maximum efficiency.

Thus increase in concentration of cobalt beyond 40gpl did not influence on efficiency. Similarly when the pH rises above 4 it did not influence the efficiency. But the exact optimum condition is obtained by taking power consumption also into the consideration.

The mathematical representations of the influence of the parameters on efficiency (Based on least square method and property of orthogonality of matrix) are as given below;

Current efficiency = 70.8056 - 0.05139 Co +10.506pH - 0.195 CD×0.116Co pH

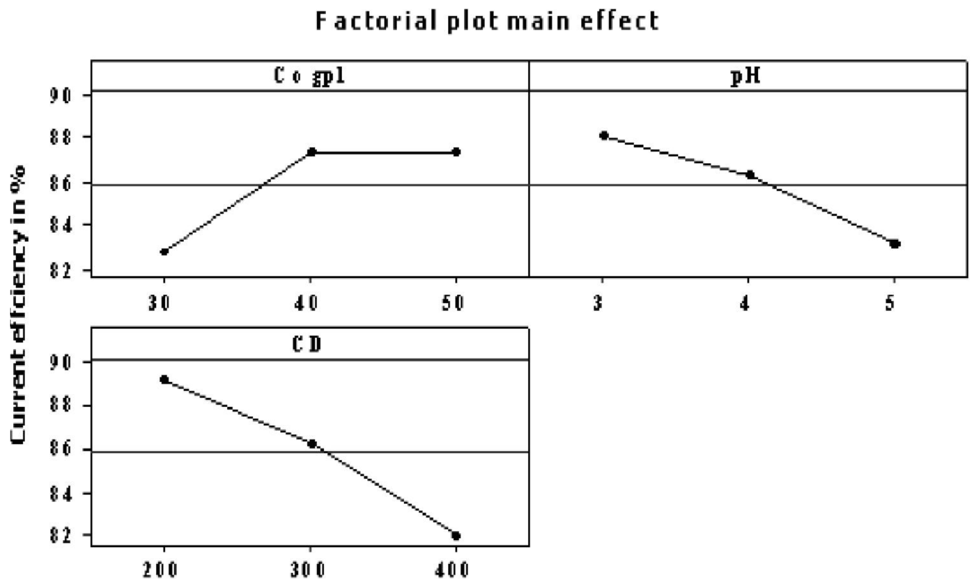

Figure 1 : Main effect of Co gpl, current density and pH

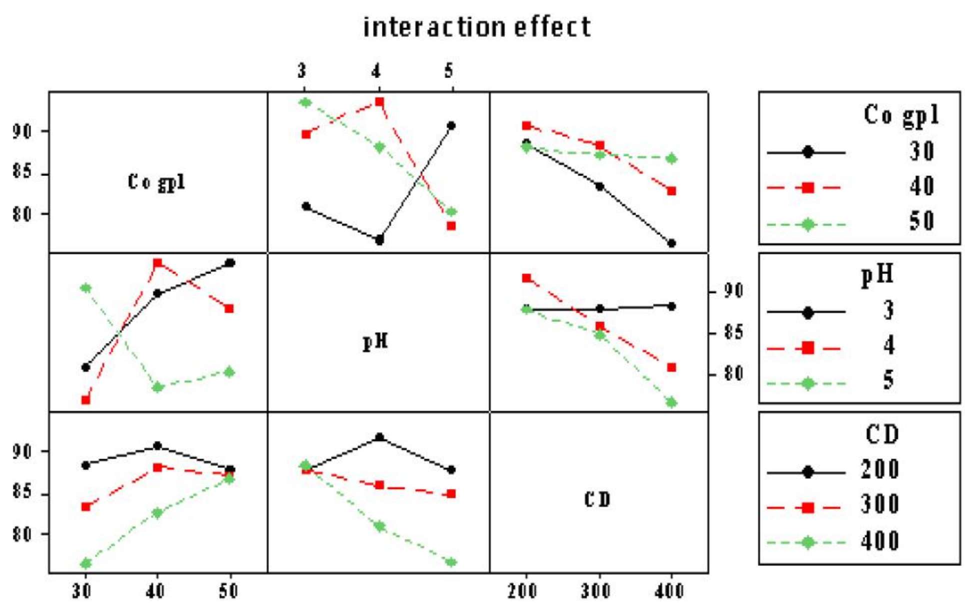

Figure 2 : Interaction effect of pH, Co gpl, current density

+0.007Co CD + 0.019 pHCD - 0.0012 pH CDCo (5)

Power consumption = 0.156 Co + 0.347 pH + 0.033 CD - 0.0204 CopH –0.0009 CoCD - 0.0035 pHCD + 0.00014CopH CD – 1.663 (6)

The above equation is useful when we cannot alter any one of the parameters then we can alter the other parameter in such a way to get the same efficiency. The equation can be used to predict the efficiency by substituting the values of the parameters. The equation can also be used to generate the data for the specific condition.

Figure 3 represents the combined effect of cobalt gpl and pH on current efficiency which indicates that in the region around 40 gpl which joints little less than 4 pH zones has the maximum efficiency and this should be the operational zone for better result.

From the Figure 4 it is clear that the maximum efficiency achieved when current density is around 200 Amp/m^2 and pH is around 4. When the feed pH increased beyond this decreased the efficiency. Similarly when the current density increased beyond 200 also decreased the efficiency.

From the Figure 5 it is observed that the combination of cobalt concentration and current density gives the maximum efficiency when concentration is around 50 gpl and current density is around 200 Amp/m^2.

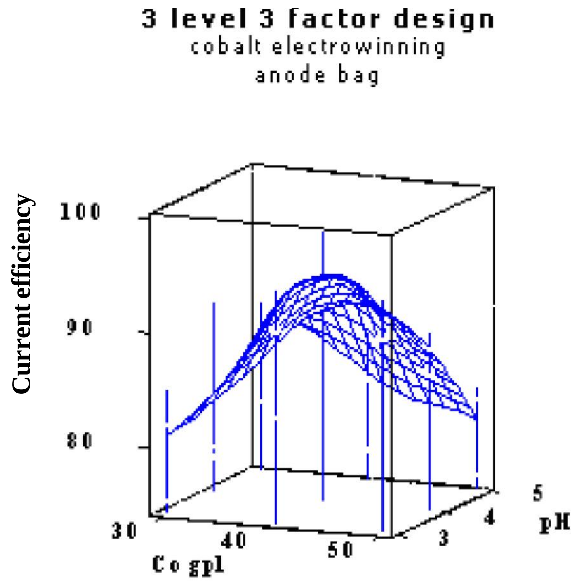

Figure 3 : Combined effect of Co gpl and pH

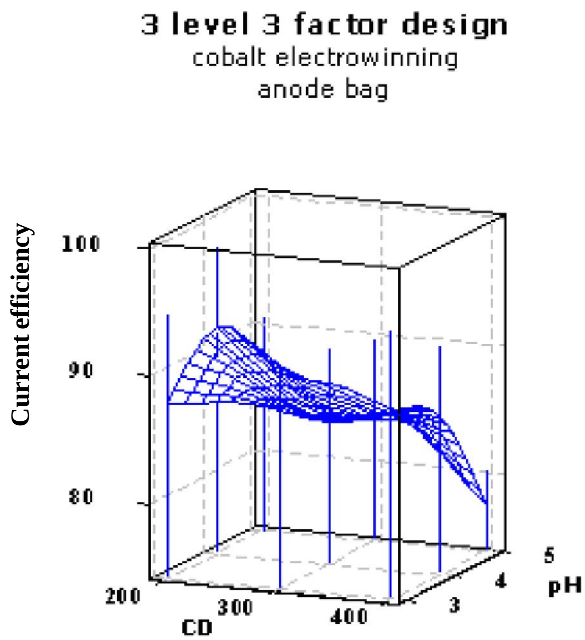

Figure 4 : Combined effect of current density and pH

Fisher's test

The regression equation generated is tested with actual experimental value TABLE 1 using Fisher's test[5], which is defined as below;

F (Fisher distribution) < $F_{(1-\alpha)}$ (γ1, γ2). $F_{(1-\alpha)}$ (γ1, γ2) = tabulated value for Fisher's distribution at 100(1-α) % level of confidence under γ1, γ2 degrees of freedom.

γ1 = Degrees of freedom for the regression values = N-l = 27-8=19

γ2 = Degrees of freedom for replicate values = N-l = 3-1 = 2

The response for 3 replicate experiments (Ref. TABLE 1, 12, 12(R1) & 12(R2)) have been 94.9, 95.9 & 95.2. The variance (Se^2) is calculated using formula and is as below;

$$\mathbf{Se^2 = [\Sigma_1^3 (y- y^{avg})^2]/N\text{-}1 = 0.5266/2 = 0.2633.}$$

Similarly, variance ($S_{res}^{\ 2}$) for response from regression equation

$$\mathbf{S_{res}^{\ 2} = [\Sigma_1^{27} (y- y\hat{})^2]/N\text{-}l = 298/19 = 15.69}$$

So, Fisher's distribution ratio (F) = $S_{res}^{\ 2}/S_e^{\ 2}$ = 15.69/0.2633 = 59.57

The tabulated Value at 99% confidence level i.e. at significance value (α) of 0.01 under γ1 & γ2 of 19 & 2 is 99.5, i.e. $F_{(1-0.01)}$ (19, 2) = 99.5

Thus, F (Fisher distribution) < $F_{(1-0.01)}$ (19, 2) and hence the regression equation fits adequately with the experimental data.

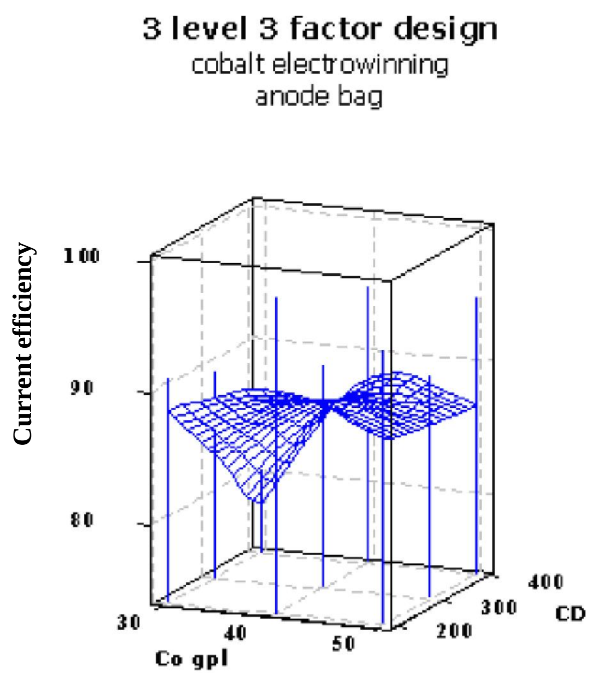

Figure 5 : Combined effect of Co gpl and current density

CONCLUSION

Thus the concept of factorial optimization was utilized to identify the optimum conditions for the production of cobalt metal using anode bag, which was found to be as follows.

1. Optimum Concentration of Cobalt is 47 to 50 gpl
2. Optimum pH is 3 to 4
3. Optimum Current density is 250 to 280 Amp/m^2

Under the above condition the power consumption would be 3.9 Kwhr/kg of cobalt and current efficiency would be 90 %. The regression equation that relates the current efficiency to the parameters was derived which could be utilized to predict the efficiency at the operating condition and also enable us to identify and alter the parameters to get maximum possible practical efficiency. The validity of the equation was tested by F-test.

It opens the possibility of operating electrowinning cell even at higher current densities with same efficiency by adjusting the other parameters to increase the productivity.

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