A PRELIMINARY STUDY OF COBALT SOLVENT EXTRACTION FROM NICKEL SULPHATE SOLUTION USING ORGANIC EXTRACTANT-PC-88A

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Abstract

In the present study, a solvent extraction experiment was done to separate cobalt from the nickel sulfate solution using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) as an extractant. The experiment was carried out on a laboratory scale using a separating funnel to extract cobalt from the nickel sulfate solution with PC-88A. The mixed solution was shaken in a separating funnel for a specified time. After the solvent extraction experiment was finished, the organic phase PC-88A was separated from the nickel sulfate solution by decantation. The nickel and cobalt content in the aqueous nickel sulfate solution was then analyzed using AAS (atomic absorption spectrophotometry). In this experiment, the variable for experiments was covering solution pH from 2 to 6, shaking time from 30 minutes to 120 minutes, shaking speed from 20 rpm (revolutions per minute) to 80 rpm, and the volume ratio of aqueous to organic phase (A:O ratio) was from 1:1 to 1:4. The effects that experimental variables to the cobalt extraction were observed in this experiment. The result of the experiment at room temperature, solution pH 5, shaking speed 60 rpm, shaking time 90 minutes, A:O ratio 1:4 and concentration of PC-88A 40% show PC-88A can extract 97.21% of cobalt from nickel sulfate solution. Therefore, it was necessary to conduct two stage extraction process to extract 100% of the cobalt from the nickel sulfate solution.

Keywords: Solvent extraction, nickel, cobalt, nickel sulphate, PC-88A

1. INTRODUCTION

Nickel and cobalt are used extensively in metallurgy and non-metallurgy. There are many uses for nickel, such as stainless steel, high-temperature steel, magnetic materials, electroplating, non-ferrous alloys, ceramic materials, catalysts, batteries, fuel cells, and chemicals [1][2]. There are numerous applications for cobalt in the metallurgical, petroleum, chemical, electronic, pharmaceutical, and medical industries because of its unique chemical and physical properties. Cobalt is commonly used in the metallurgical industry to produce alloy metals for gas turbines, nuclear power plants, engine vanes, automotive engines, engine valves, aviation fuel nozzles, and cutting wear-resistant tools [3][5], magnetic materials such as Alnico and Samarium cobalt [6][8], the catalyst for sulfur removal and oil hydrogenation processes [9][11], drying materials for paint, promoters for the polymerization process [12], pigment materials [13][14], raw materials for rechargeable batteries [15], Fuel Cell Cathode materials [16], and implant materials for heap joints, dentist, cardiovascular stent [17][21]. Cobalt has a broad spectrum application in many industries; therefore cobalt consumption in the world tends to increase [22]. There are predictions that global cobalt consumption will reach 220 000 tons by 2025 and 390 000 tons by 2030 [23].

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Cobalt is generally obtained as a by-product of the nickel, copper, and zinc extraction process [22], [24]-[29] and from used batteries [30]-[31]. Cobalt can also be obtained from the nickel matte [32]-[33] by-product of nickel laterite processing through the caron process or HPAL (high-pressure acid leaching) [1]. In this process, cobalt is obtained through the leaching process of materials containing cobalt, followed by a solvent extraction process to separate the cobalt from other contained elements in the solution and the cobalt deposition process from the solution, including the electrowinning process to precipitate the cobalt from the cobalt chloride solutions [34].

Solvent extraction separate a metal ion from another existing metal ion in a solution (water phase) by adding insoluble organic materials into the water phase to transfer a metal ion from the water phase to the organic phase. The stripping process is carried out to remove the loaded metal from the organic phase. Metals can be separated from complex ions in solutions by solvent extraction because it is an efficient and flexible method [35].

The are many extractants for the cobalt solvent extraction process. The extractants used are Cyanex 272, D2EHPA (acid extractant), Alamine 306, Alamine 304 (base extractant), and Cyanex 923 (solvating extractant). In acidic solutions, Cyanex 272 and D2EHPA have been used to extract cobalt, but when the solution contains ionic manganese, these two extractants are less effective at extracting cobalt, as they can both extract manganese first before extracting cobalt [36]; therefore, alternative extractants are needed for cobalt extraction from nickel sulfate solution.

To separate cobalt from the nickel sulfate solution in this paper, a solvent extraction study has been done by using PC-88A as an organic extractant. This study aims to investigate the effect of solvent extraction parameters, such as shaking speed, shaking time, water phase to organic phase ratio, and solution pH, on cobalt extraction.

2. MATERIALS AND METHODS

2.1 Raw Materials for Experiment

The raw material for this experiment was a nickel sulfate solution containing cobalt ions. To obtain this mixed solution, nickel sulfate hexahydrate (Merck) and cobalt sulfate heptahydrate (Pudak Scientific) were dissolved in H$_2$SO$_4$ (aqueous sulfuric acid) solution and mixed to form a nickel-cobalt sulfate solution with an approximately 10: 0.5 Ni/Co mass ratio. In contrast the organic extractant used in the experiment was 2-ethylhexyl phosphonic acid mono-2-ethylhexyl, known with the trade name PC-88A from Daihachi Chemical. In some experiments, PC-88A was diluted with kerosene to obtain an appropriate PC-88A concentration for the solvent extraction. The detail of the PC-88A Kerosine volume ratio is explained in the section variable for an experiment.

2.2 Variable for Experiment

The variables covered in this solvent extraction experiment were shaking speed 20; 40; 60; 80 rpm, shaking time 30; 45; 60; 90; 120 minutes, a ratio of water to organic phase (A:O ratio) 1:2; 1:3; 1:4, the concentration of PC88A 20, 40, 60, 80, 100%, and pH adjusted with sulfuric acid or sodium hydroxide solutions. Those experimental variables were observed in the cobalt extraction from the nickel sulfate solution by PC-88A.

2.3 Solvent Extraction Experiment

The solvent extraction experiment to extract cobalt from the nickel sulfate-containing ionic cobalt solution (water phase) was carried out by mixing a certain volume of nickel sulfate solution (water phase) with PC-88A (organic phase) in the separating funnel. The mixed solution was shaken for a certain time using a mechanical shaker. After the experiment, the organic phase and the aqueous phase were separated by decantation, and the solution's nickel and cobalt content was then determined using an AAS (atomic absorption spectrophotometry). The percentage of cobalt extraction was calculated using Equation 1.

\[
\% E_{Co} = \frac{[Co]_i - [Co]_A}{[Co]_i} \times 100 \% \quad (1)
\]

Some ionic nickel may be removed from the sulfate solution during the cobalt extraction. As a result, Equation 2 is utilized to determine the percentage of nickel extraction.

\[
\% E_{Ni} = \frac{[Ni]_i - [Ni]_A}{[Ni]_i} \times 100 \% \quad (2)
\]

Where:

\% E$_{Co}$ = Cobalt percent extraction
\% E$_{Ni}$ = Nickel percent extraction

$[Co]_i$ = Cobalt content in the nickel sulfate solution before extraction

$[Co]_A$ = Cobalt content in the nickel sulfate solution after extraction

$[Ni]_i$ = Nickel content in the nickel sulfate solution before extraction
[Ni]_A = Nickel content in the nickel sulfate solution after extraction

3. Result and Discussion

3.1 Effect of Shaking Speed on Cobalt Extraction

The effect of shaking speed on a cobalt extraction from a nickel sulfate solution containing cobalt ions was studied at room temperature, the shaking time was 30 minutes, the water-to-organic phase ratio was 1:1, and the solution pH was 2 and 5, and shaking speeds were 20 rpm, 40 rpm, 60 rpm, and 80 rpm. The result of an experiment in Fig. 1 shows that increasing in shaking speed from 20 rpm to 40 rpm caused a slight increase in the nickel and cobalt extraction, but a further increase in rpm to 80 rpm had not given any significant effect for both cobalt and nickel extractions. This experiment result shows the minimum shaking speed for creating a good contact between organic phase and aqueous phase was at 40 rpm. For shaking speed equal to 40 rpm or longer than 40 rpm, interfacial contact between organic and water phases has been effective for the cobalt transferring process from the water phase to the organic phase. Another research activity show the same tendency during cobalt extraction from nickel chloride solution by using TNOA (tri-normal-octyl-amine) as an organic extractant [37].

3.2 Effect of Shaking Time on Cobalt Extraction

The effect of shaking time on a cobalt and nickel extraction from the nickel sulfate solution containing cobalt ions was investigated at room temperature, with the solution pH ranging between 2 and 5, the volume water to organic phase ratio (A:O ratio) was set to 1:1. The shaking time ranged from 30 minutes to 120 minutes. The results of an experiment are shown in Fig. 2, which demonstrates that increasing the shaking time from 30 minutes to 120 minutes had little effect on the extraction of nickel and cobalt. The experiment's findings indicate that 30 minutes of shaking was the minimum amount of shaking required to transfer cobalt from the water phase to the organic phase. The aqueous and organic phases have been thoroughly mixed for 30 minutes or more of shaking, and the cobalt transfer process is more effective now. The same pattern was seen in a different research project that used TNOA (tri-normal-octyl-amine) as an organic extractant for extracting cobalt from a nickel chloride solution [37].

![Figure 1](image1.png)

Figure 1. Effect of shaking speed on metal extraction, (a) Ni Extraction, and (b) Co extraction

![Figure 2](image2.png)

Figure 2. Shaking time effect on nickel and cobalt extraction, (a) Ni, and (b) Co

3.3 Effect of A:O ratio on Cobalt Extraction

This experiment examined the role of the aqueous to organic phases (A:O) ratio on the extraction of cobalt and nickel from a nickel
sulfate solution containing cobalt ions. The experiment was conducted at room temperature, with the solution's pH range being between 2 and 5, shaking time for 90 minutes, and the A:O ratio varying from 1:1 to 1:4. The experimental results in Fig. 3 show that the percentage of cobalt extraction increases as the A:O ratio increases in all solution pH conditions, due to the increased PC-88A concentration, which encourages cobalt extraction and causes the cobalt extraction from nickel sulfate solution to increase. A higher percentage of cobalt extraction was attained in the solution with an A:O ratio of 1:4 due to the higher PC-88A content, which promotes cobalt extraction.

3.4 Effect of PC 88A Concentration on Cobalt Extraction

The effect of PC-88A concentration on cobalt extraction from the nickel sulfate solution containing cobalt ions was examined at room temperature, with the solution pH ranging between 2 and 5, shaking time was 90 minutes, shaking speed was 60 rpm, A:O ratio was 1:4, and PC 88A concentration varied from 20% to 100%.

![Figure 4](image)

Figure 4. Effect of PC 88A concentration on metal extraction (a) Ni, and (b) Co

The experimental results in Fig. 4 demonstrate that increasing the concentration of PC 88A from 20% to 40% resulted in a slight increase in the extraction of nickel and cobalt, but increasing the concentration of PC 88A from 40% to 100% has had no significant effect on the extraction of nickel and cobalt. As shown by the experiment's findings in Fig. 4, adding PC 88A had less impact on cobalt extraction than raising the solution pH from 2 to 5. Cobalt exists as a cation species in the solution phase, responsible for the increased cobalt extraction at a higher solution pH [39], which is easier to extract by acidic organophosphorus extractant PC-88A [40].

3.5 Effect of Solution pH on Cobalt Extraction

The effect of solution pH on the nickel and cobalt extraction from nickel sulfate solution containing cobalt ions was studied at room
temperature, the PC-88A concentration was 40%, and the solution pH was varied from pH 2 to pH 6. The experimental results in Fig. 5 show that increasing the solution pH from pH 2 to pH 5 causes an increasing in cobalt and nickel extraction. Referring to Equation 3, when the water phase (nickel sulfate solution) is mixed with the organic phase (PC-88A), the ionic cobalt (Co\(^{2+}\)) in the nickel sulfate solution reacts with the organic phase of PC-88A (RH) according to the following reaction:

\[
\text{Co}^{2+} + 2 \text{RH} = \text{R}_2\text{Co} + 2 \text{H}^+ \quad (3)
\]

The equilibrium constant (K) for reaction 3 is expressed by Equation 4 as follows:

\[
K = \frac{[\text{R}_2\text{Co}][\text{H}^+]^2}{[\text{Co}^{2+}][\text{RH}]^2} \quad (4)
\]

And if the cobalt distribution in the organic phase (R\(_2\)Co) and the water phase (Co\(^{2+}\)) is expressed by Equation 5 below:

\[
D = \frac{[\text{R}_2\text{Co}]}{[\text{Co}^{2+}]} \quad (5)
\]

Then Equation 5 is substituted into Equation 4, the equilibrium constant of Equation 3 can be expressed by Equation 6 as follows:

\[
K = \frac{D[\text{H}^+]^2}{[\text{RH}]^2} \quad (6)
\]

And if Equation 6 is expressed in logarithmic form it will create Equation 7 as follows:

\[
\log D = \log K + 2 \log \text{RH} + 2 \text{pH} \quad (7)
\]

Equation 7 shows the increase of pH could increase the cobalt distribution in the organic phase, or the cobalt extraction increases when the solution pH increases. The correlation between pH and with a distribution of cobalt in organic phase (D) in Equation 7 has the same tendencies and with the experimental results in Fig. 5. Another experiment conducted by Julian [38] and Luiz [39] show the same tendencies. Luiz conducted experiment to separate cobalt and nickel from spent nickel–metal–hydride batteries by solvent extraction with D2EHPA (di-2-ethylhexyl phosphoric acid) followed by Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid, and Junlian [38] conducted an experiment to separate cobalt and nickel separation from sulfate solutions by using (2-ethylhexyl) (2,4,4-

3.6 Multistage Extraction using McCabe Thiele Method

The experimental result in Fig. 5 reveals that the maximum value of cobalt extraction with PC 88 A is 97.21% at pH 5. As a result, some cobalt ions remain in the nickel sulfate solution. A multi-stage solvent extraction procedure should be used to obtain more pure nickel sulfate solutions. A cobalt-free nickel sulfate solution is created at this stage.

![Figure 5. Effect of pH on cobalt and nickel extraction](image1)

![Figure 6. McCabe thiele diagram use for the extraction process of Co from nickel sulfate](image2)
This solution composition has been used in previous research to observe the effect of pH, PC 88A concentration, shaking speed, shaking time, and aqueous-to-organic ratio on cobalt extraction. The McCabe Thiele diagram in Fig. 6 shows two stages. The extraction process can separate all the cobalt ions from the nickel sulfate solution using a 40% concentration of PC-88A extractant. In the first extraction stage, it produces a nickel sulfate solution (water phase) containing 0.0114 g/L cobalt ions, and in the second.

4. CONCLUSION

The conclusion of the study on the separation of cobalt from nickel sulfate solution containing cobalt ions using the solvent extraction method is cobalt ion can be separated from nickel sulfate solution containing cobalt ion by solvent extraction method using organic solvent PC-88A. The best condition for cobalt extraction from nickel sulfate solutions is at room temperature, solution pH 5, shaking speed 60 rpm, shaking time 90 minutes, A:O ratio of 1:4 with a PC-88A concentration of 40%. At this condition almost 97.21 % of Cobalt could be extracted from the nickel sulfate solutions. Therefore, the 2-stage extraction process with PC-88A is needed to obtain a more purer nickel sulfate solution.

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