Extraction of Cobalt (II) From Sulphate Medium and Possible Separation from Nickel (II)

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Received: 19/10/2014 Accepted: 25/11/2014

ABSTRACT

A study has been made on the extraction of Co (II) from sulphate solution using Cyanex 272, [bis (2, 4, 4-trimethyl pentyl) phosphinic acid] dissolved in kerosene. The results demonstrated that the addition of TBP as a modifier to the organic phase avoids the problem of phases disengagement and consequently enhances the extraction process. Accordingly, it has been found that, about 85% of Co(II) of initial concentration of 100 ppm, is extracted from a sulphate solution of pH 5.5 using 0.1 M Cyanex 272 modified with 5% by volume of TBP in kerosene. The extraction percentage has been found to increase to more than 95% by increasing the Cyanex 272 concentration to 0.6 M. Possible separation of Co (II) from Ni (II) was also investigated. Maximum separation between the two elements has been achieved from sulphate solution of pH 5.0 using 0.1M Cyanex 272 modified with 5% by volume TBP diluted with kerosene.

Key words: Cyanex 272, Co (II), Ni (II), Solvent extraction, TBP as a modifier.

1. INTRODUCTION

Cobalt and nickel are generally of important uses especially for metallurgists. Their adjacent position in the first-row transition series results in very similar chemical behavior, which causes problems in their separation. A lot of work on extraction and separation of Co (II) and Ni (II) from aqueous solutions has been reported. Among those reported, solvent extraction studies for Co (II) extraction and separation from other elements especially Ni (II) were generally carried out using different organophosphorous acid reagents (1-9). The extraction selectivity was found to follow the trend: phosphoric acid < phosphonic acid < phosphinic acid under comparable conditions (1,2). Solvent extraction study of Co(II) and Ni(II) was carried out from a super alloy scrap chloride leach solution bearing a high Co and Ni ratio using the sodium salt of PC-88A in kerosene. The extraction rate was found to increase with increase in aqueous phase pH, extractant concentration and temperature (5). Acidic and neutral forms of Cyanex 272 in kerosene were also studied for separation of Co from Ni from ammonium sulphate solution. The separation factor was the highest with 0.1M extractant and equilibrium pH of 5.46 (6). It is also reported that Co and Ni were extracted from sulphate medium using 1.0M Cyanex 272 at pH from 5.1 to 5.3 for Co and at pH from 6.3 to 6.5 for Ni(6). Co and Ni were separated from other elements (rare earth, Fe, Zn and Mn) using PC-88A in kerosene (8). Extraction of Co (II) is also reported to be separated using emulsion liquid membrane technique (10, 11).

In the present work, extraction of Co (II) from sulphate medium was investigated using cyanex 272 in kerosene as extractant. Further, TBP was added to the extractant as a phase modifier. Possible separation of Co (II) from Ni (II) was also studied.
2. EXPERIMENTAL

2.1. Reagents:
In this study, the commercial extractant, Cyanex 272 was used as such without any purification and was obtained from Cytec Inc. Kerosene used as the diluent was obtained from Misr Petroleum Company, Egypt and TBP which acts as a phase modifier was obtained from American Cyanamid, U.S.A. The aqueous solution containing 100 µg/ml cobalt and/or nickel were prepared in ammonium sulphate solution.

2.2. Apparatus:
For the equilibration during batch experiments a good mixing for the two phases was achieved using a thermostatted mechanical shaker of the type Julabo SW – 20C, Germany, controlled within ± 1°C. A centrifuge (Hettich Universal) was used for separating the two phases. The pH of the aqueous solutions was measured using a digital pH-meter (CG 820 Germany) within accuracy of ± 0.01, Uv-Visible Spectrophotometer (SHIMADZU Model UV-160A, Japan) was used for the determination of metals concentration in the aqueous solutions.

2.3. General Procedure:
The diluted H₂SO₄ or NaOH solutions were used to adjust the pH of aqueous solution to the desired value. Equal volumes of the aqueous solution containing the metal ions and the extractant were mixed by shaking for adjusted time and temperature. After equilibrium and phase separation, suitable volume of the aqueous phase was withdrawn for measuring the metal concentration spectrophotometrically using PAR as a coloring reagent (12). The concentration of the metal in the organic phase was calculated from the difference between its concentration in the aqueous phase before and after extraction. The extraction percent, % E was calculated using the equation:

\[
\% E = \left( C_0 - C \right) / C_0 \times 100
\]

Where: \( C_0 \) and C are the concentrations of the metal in the aqueous phase before and after equilibrium, respectively.

3. RESULTS AND DISCUSSION

The different parameters affecting the extraction of Co (II) from sulphate medium using Cyanex 272 as extractant in kerosene were investigated. These parameters include the effect of; pH of the aqueous phase and concentration of the extractant in the organic phase together with the effect of time of mixing and time of centrifugation for phase separation. Unless otherwise stated, the main following conditions were used for studying the effect of each parameter while keeping the others constant; aqueous phase of sulphate solution of pH 5.5 containing 100 ppm of either Co (II) or Ni (II), organic phase of 0.1 M Cyanex 272 diluted with kerosene, aqueous to organic phase ratio 1:1, shaking time for mixing of 5.0 min. and centrifugation time for phase disengagement of 5.0 min.

3.1. Effect of Time of Mixing and Time of Centrifugation:
Initial experiments showed that a shaking time of 2 min for mixing the two phases is sufficient to reach equilibrium. When a centrifugation time of 5.0 min was used for the two phases separation, the results obtained showed that about 30 % of Co (II) is extracted together with 5% of Ni (II). By increasing the time of centrifugation to 60 min, the extraction of Co (II) increases to ~85% and that of Ni (II) increases to 17%. This means that a third phase may be formed which retarded the phase disengagement. Accordingly, it is of interest to study the effect of the centrifugation time on the disengagement of the different phases after extraction. The data obtained are given in Fig (1). To avoid the consumption of time in phases disengagement and to ensure good phases separation, it was decided to add a phase modifier to the solvent. This decision is built on previous work concluding that addition of a modifier improves the time of phases disengagement and avoids a third phase formation if it is expected to occur (1, 6, 13). Addition of a phase modifier causes an increase in the overall
polarity of the solvent medium and thus makes it more compatible for the metal solvates (13). It is also reported that addition of a phase modifier causes a synergic interaction which facilitates stripping with comparatively dilute acids (1, 6).

Fig. (1): Effect of the time of phase separation on the extraction of Co (II) by using Cyanex 272.

3.2. Effect of Hydrogen Ion Concentration in the Aqueous Phase:

The effect of H⁺ concentration (pH) in the aqueous sulphate solution on the extraction % of 100 ppm of Co (II) was studied using 0.1M Cyanex 272 modified with 5% by volume TBP in kerosene, (Fig.2). To achieve the possible separation of Co (II) from Ni (II), the same conditions were applied to the extraction of 100 ppm Ni (II). The data obtained are also given in Fig (2).

It is clear from this figure that the extraction of both elements is negligible in the pH range 2.0 to near 4.0. Beyond pH 4, the extraction of Co (II) starts to increase gradually and reaches about 85% at a pH value of ~ 5.5, after which it gives nearly a plateau till pH 7.0. On the other hand, the extraction of Ni (II) starts to increase from the pH value of about 5.0 and reaches a maximum value, around 20%, at pH of ~ 7.0. This means that possible separation of Co (II) from Ni (II) can be achieved at pH value near 5.0. It is to be mentioned that, when 5% TBP in kerosene was used alone for the extraction of Co ions, an extraction percentage of 9% was achieved. In addition, by increasing the TBP concentration by 3, 5, and 10 % by volume, the extraction of cobalt was found to be 78, 85 and 85%. This means that addition of TBP to the extractant Cyanex 272 enhances the Co extraction process and improves the time of disengagement of the two phases.

Fig. (2): Effect of pH on the extraction of Co (II) and Ni (II) by using Cyanex 272.
3.3. Effect of The Extractant Concentration in the Organic Phase:

The extraction of 100 ppm Co (II) from aqueous sulphate solution of pH 5.5 was studied using different concentrations of Cyanex 272 ranging from 0.01 to 1.0 M in the presence of 5% by volume TBP in kerosene. The data obtained are shown in Fig (3) as a relation between the extraction % and Cyanex 272 concentration. It is clear that the extraction of Co (II) increases sharply with the increase of extractant concentration from 0.01 M till near 0.2 M, after which it increases slightly till 1.0 M.

3.4. Stripping of Cobalt from Loaded Organic Phase:

Selective stripping of the extracted cobalt species contaminated with a minor concentration of nickel from the organic phase was first investigated using 1M of each of the different acid solutions, HCl, HNO₃, and H₂SO₄. The data obtained showed that 51, 93, 99% were stripped, respectively. Accordingly, different concentrations from H₂SO₄ solutions were tested for the stripping of cobalt and nickel. The data obtained are given in Table 1.

![Figur](image.png)

**Fig. (3):** Effect of Cyanex 272 concentration on the extraction of Co (II).

<table>
<thead>
<tr>
<th>H₂SO₄,M</th>
<th>% Stripping of Co(II)</th>
<th>% Stripping of Ni (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>93.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.10</td>
<td>95.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.5</td>
<td>98.0</td>
<td>&lt; 3.0</td>
</tr>
<tr>
<td>1.0</td>
<td>99.0</td>
<td>7.0</td>
</tr>
<tr>
<td>3.0</td>
<td>~ 100.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>

It is clear from this table that, 98 % of cobalt can be stripped contaminated with less than 3 % of the extracted nickel using 0.5 M H₂SO₄.

**CONCLUSION**

It can be concluded from the present investigation that the extraction of Co (II) from sulphate solution using 0.1 M Cyanex 272 modified with 5% by volume TBP diluted with kerosene, increases with increase of pH and reaches maximum ~ 85% , near pH value of 5.5. This value increases to near 95% by increasing the Cyanex concentration to 0.6 M. Addition of 5% of TBP enhances the extraction
process and avoids time consumption of centrifugation for phase separation. Selective separation of Co (II) from Ni (II) can be achieved from a sulphate solution of pH value of 5 using 0.1 M Cyanex 272 modified with 5% TBP in kerosene. Stripping of 98% of Co ions can be obtained using 0.5 M H$_2$SO$_4$ solution together with less than 3% Ni ions. Selective extraction and separation of Co free from Ni can be achieved using more than one step of extraction and stripping.

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