



Removing Trace Co from NiSO₄ Solutions Using Cyanex 272

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To cite this article:

Yongfa Song, Guangxin Wang, Bin Yang, Yaqiong Li. Removing Trace Co from NiSO₄ Solutions Using Cyanex 272. *International Journal of Biomedical Science and Engineering*. Vol. 6, No. 2, 2018, pp. 52-58. doi: 10.11648/j.ijbse.20180602.15

Received: August 12, 2018; **Accepted:** August 22, 2018; **Published:** September 17, 2018

Abstract: Although there are many articles about the effective separation of cobalt and nickel, the investigation on separation of trace cobalt and high concentration nickel are still poorly reported. In this paper, the process of extraction and separation of trace cobalt from sulfate solution containing high concentration of nickel was systematically investigated. The commercial product Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid) in kerosence was used. The initial solution used for the present study contained in [Co] 25.45 mg/L and [Ni] 96.00 g/L. A cobalt extraction rate of more than 99% has been achieved under the condition of 10 vol. % Cyanex 272, O/A 1:1, pH 5.5, and 60°C, with cobalt concentration being reduced from 25.45 to below 0.5 mg/L. NiSO₄ solution with such a low Co level is required for producing ultra-high 5N-6N purity nickel. In addition, high pH value, high Cyanex 272 concentration in organic phase, high O/A ratio, and adding TBP to the organic phase can lead to increased Ni loss.

Keywords: Trace Cobalt, Nickel Sulfate Solution, Cyanex272, Extraction

1. Introduction

Nickel and cobalt are two elements that have very similar aqueous chemical properties due to their adjacent position in transition metal series in the periodic table [1]. When these elements are both present in aqueous solution, they cannot be easily separated by a simple separation method such as chemical precipitation by pH adjustment. The methods to Separate and recover cobalt and nickel in aqueous solution is usually used by oxidative precipitation, ion exchange resin and solvent extraction [2]. Several phosphorus extractants have been proposed in literature for separation of cobalt and nickel [3-12]. Since the role of phosphorus acid is known, separation of Ni and Co in sulfuric acid solution by solvent extraction is significantly developed. An extensive literature search reveals that most of the studies about Cyanex 272 reported so far dealt with rather high cobalt contents in nickel sulfate solutions. Previous studies focused on cobalt solution with higher concentration to separate cobalt and nickel using Cyanex 272. M. Z. Mubarak et al. [13]. reported Cyanex 272 can be effectively used to separate cobalt and nickel in a solution with low nitrate concentration, but the initial

concentration of the solution is 1.13 g/L Ni and 0.14 g/L Co. Peter Iliev et al. [14] investigated the process of separation of cobalt from acid sulphate solutions containing 3.01 g/L Co and 30.16 g/L Ni using Cyanex 272 by solvent extraction, in which cobalt extraction efficiency of >97% was achieved in three counter-current stages. A large number of studies focused on g/L- grade cobalt solution, such as Zhaowu Zhu [15] (100 g/L Ni, 1.4 g/L Co), Kyung-Ho Park [16] (Co= 1.78 g/L and Ni = 16.78 g/L), P. K. Parhi [17] (2.012 g/L Co, 23.747 g/L Ni).

In order to recover cobalt and nickel with high purity from these solutions, separation of cobalt and nickel from solution is necessary. It is difficult to obtain pure cobalt and nickel compounds because of the difficulties in separating cobalt from nickel.

In this review, a systematic study of the extraction behavior and removal of trace cobalt from high concentration of nickel sulfate solution using Cyanex 272 is investigated. For this purpose, the present paper focuses on extraction parameters such as temperature, pH value, extractant concentration, and organic to aqueous phase ratio (O/A) with the aim to thoroughly remove cobalt from nickel sulfate solution. The

results are presented of extraction of cobalt and nickel. It can provide reference for the separation of trace cobalt and nickel and the production of high purity nickel sulphate and high purity nickel.

2. Experimental

2.1. Reagents

Nickel sulfate was purchased from Jinchuan Group Co., Jinchang China. Commercial extractant bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272, >85% purity) was purchased from Cytec Canada Inc. Tributyl Phosphate (TBP) was used as phase modifier throughout all experiments. Sulfonated kerosene, used as a diluent, was obtained from Xiangyang Fusen Petrochemical Co., Maoming China. Analytical grade sodium hydroxide (NaOH) and hydrochloric acid (HCl) were also used in this study. The organic solution was prepared by diluting a mixture of Cyanex 272 and TBP with sulfonated kerosene. And it was used for extraction process.

Aqueous nickel sulfate (NiSO₄) solutions contained [Co] 25.45 mg/L and [Ni] 96.00 g/L was prepared by dissolving analytical grade reagents NiSO₄·6H₂O in distilled water. Adjustment of pH value of aqueous solutions was done by adding NaOH and/or HCl.

3. Results and Discussion

3.1. Effect of pH on Cobalt and Nickel Separation

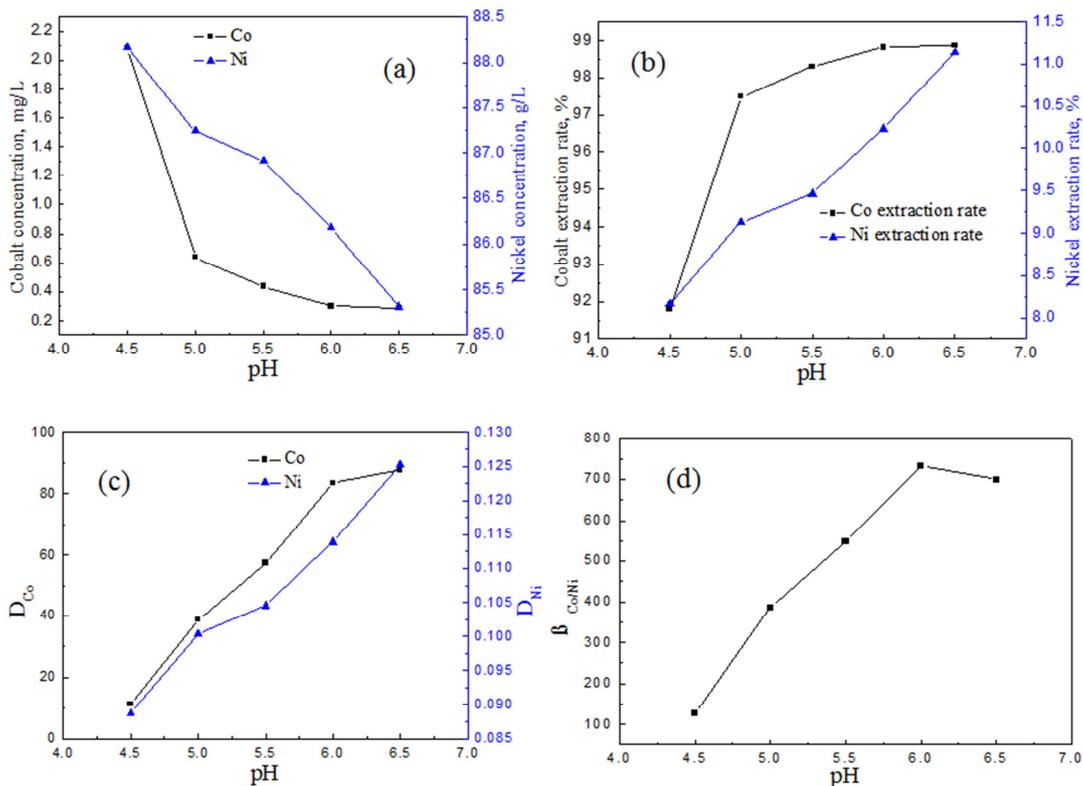


Figure 1. Effect of pH value of aqueous solution: (a) Co and Ni concentrations in the raffinate, (b) Co and Ni extraction rates (E%), (c) Co and Ni distribution ratios (D), (d) Co/Ni separation factor (β_{Co/Ni}).

2.2. Solvent Extraction Procedure

Suitable volumes of aqueous feed and organic phase were contacted for 30 min in a beaker at a certain stirring speed to assure equilibrium conditions. Then, the mixture of aqueous and organic phases was transferred to a separating funnel and retained there for 5 minutes to allow a complete separation of the two phases. Finally, metal concentrations in different samples were analyzed by ICP-OES 8000 (PekinElmer, USA).

Based on results of ICP-OES, distribution ratio (D), extraction rate (E%) and separation factor (β_{Co/Ni}) were calculated using following equations.

$$D_{Me} = \frac{\overline{[M_e]}}{[M_e]} \quad (1)$$

$$E\% = \frac{[M_t] - [M_e]}{[M_t]} \times 100 \quad (2)$$

$$\beta_{Co/Ni} = \frac{D_{Co}}{D_{Ni}} = \frac{\frac{[\overline{Co}]}{[Co]}}{\frac{[\overline{Ni}]}{[Ni]}} \quad (3)$$

Here, $\overline{[M_e]}$ and $[M_e]$ are concentrations of metal ions in organic and aqueous phases, respectively. $[M_t]$ and $[M_e]$ represent the initial and final concentration of a metal ion in aqueous phase, respectively.

Figure 1 shows the effect of pH value of aqueous solution on Co extraction. For these tests, the organic solution containing 10 vol.% Cyanex 272 and 10 vol.% TBP was used. Other parameters were O/A = 1:1 and 60°C. It can be seen from Figure 1a that both Co and Ni concentrations in aqueous solution decrease with increasing pH value. This means that the higher the pH value, the better is the Co extraction. However, Ni loss increases with increasing pH value, too (Figure 1b). For example, Co and Ni concentrations were measured to be about 2.10 mg/L and 88.17 g/L at pH4.5, which correspond to a Co extraction rate of 91.8% and a Ni loss of 8.2%, respectively. When pH increased to 6.5, Co and Ni concentrations were measured to be about 0.29 mg/L and 85.31 g/L, corresponding to a Co extraction rate of 98.87% and a Ni loss of 11.14%, respectively. It is visible from Figure 1c that the distribution ratio of cobalt D_{Co} quickly increases from about 10 at pH 4.5 to about 90 at pH 6.5, whereas the distribution ratio of nickel D_{Ni} slightly increases from 0.089 to 0.125. Figure 1d shows how Co/Ni separation factor $\beta_{Co/Ni}$ changes with increasing pH value.

It has been reported that the acidic form of Cyanex 272

exists as a dimer, while its saponified form exists as a monomer [8, 10, 17]. With a 60% saponification in this study, Cyanex 272 exists in both dimer and monomer forms. Therefore, following reactions take place during extraction:



All these reactions are reversible. With increasing pH value, the hydrogen ion concentration $H^+_{(aq)}$ decreases. Thus, a higher pH value is conducive to extraction of cobalt according to reactions (6) and (7). At the same time, an increased Ni loss is observed for increasing pH value due to reactions (4) and (5). Taking into account the loss rate of nickel and ensuring low concentration of cobalt in solution, pH 5.5 is beneficial to cobalt removal.

3.2. Effect of Concentration of Cyanex272 on Cobalt and Nickel Separation

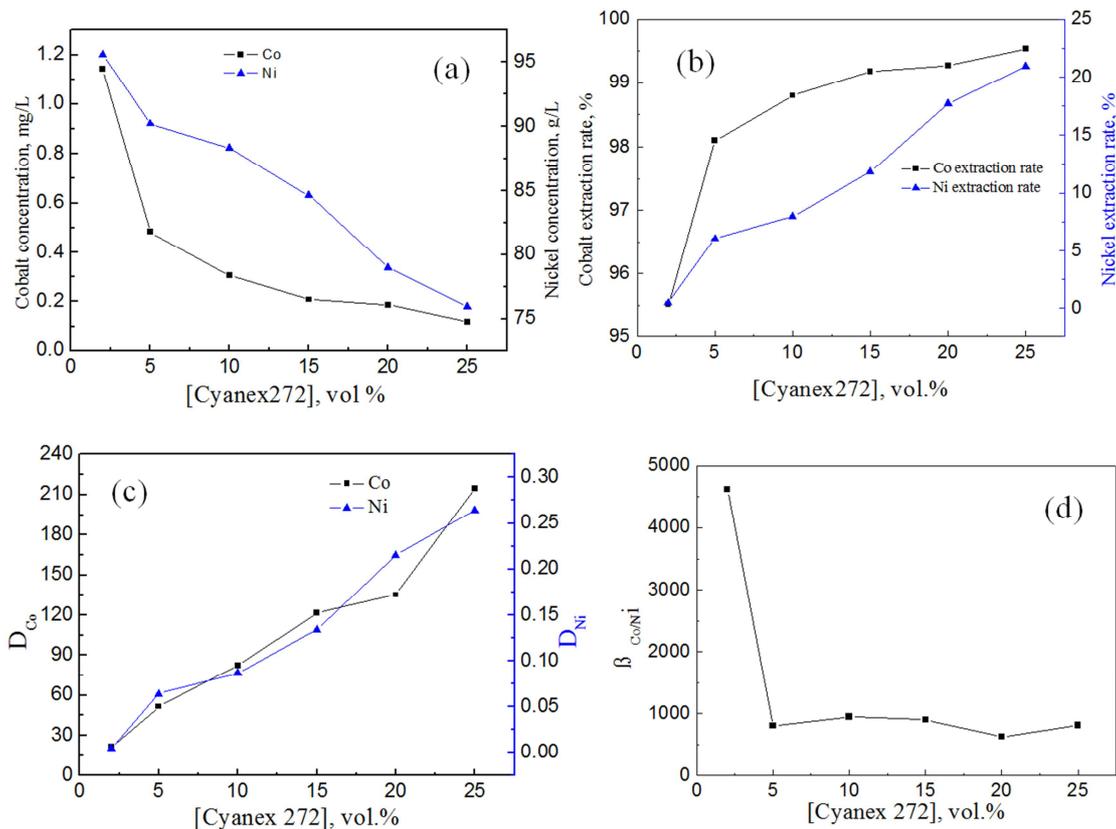


Figure 2. Effect of concentration of Cyanex272: (a) Co and Ni concentrations in the raffinate, (b) Co and Ni extraction rates ($E\%$), (c) Co and Ni distribution ratios (D), (d) Co/Ni separation factor ($\beta_{Co/Ni}$).

Figure 2 shows the effect of Cyanex 272 concentration on Co extraction. For these tests, pH 5.5, 10 vol.% TBP, O/A = 1:1, and 60°C were kept constant. With increasing Cyanex 272 concentration, changes of Co and Ni concentrations, their

extraction rates, and distribution ratios show similar trends as observed for increasing pH value (comparing Figure 1a-1c with Figure 2a-2c). This can be easily understood when taking a look at the above-mentioned reactions (4)-(7). With

increasing Cyanex 272 concentration, more and more A⁻_(org) and (HA)_(org) are available for reactions with Co and Ni ions. Based on the principle of chemical equilibrium, it has the same effect as decreasing H⁺

concentration. Considering the high cost of Cyanex 272 and the high Ni loss, So Cyanex 272 concentration should not exceed 10 vol.%.

3.3. Effect of Phase Ratio on Cobalt and Nickel Separation

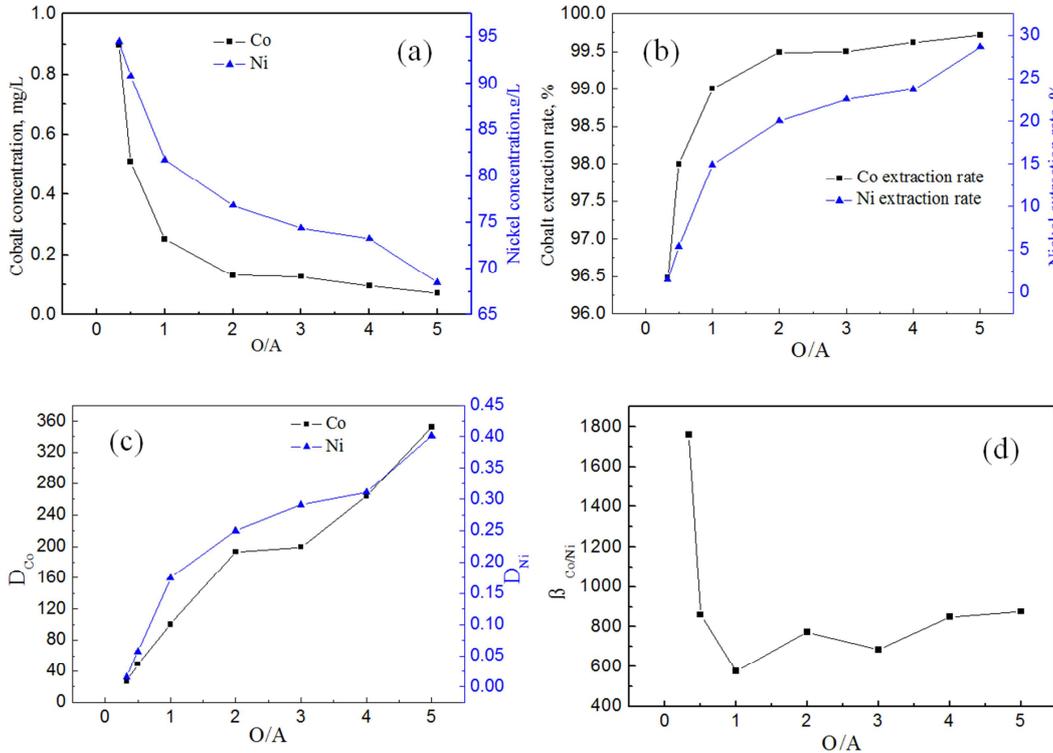


Figure 3. Effect of phase ratio: (a) Co and Ni concentrations in the raffinate, (b) Co and Ni extraction rates (E%), (c) Co and Ni distribution ratios (D), (d) Co/Ni separation factor (β_{Co/Ni}).

Figure 3 shows the effect of phase ratio (O/A) on Co extraction. For these tests, the organic solution contained 10 vol.% Cyanex 272 and 10 vol.% TBP, the aqueous solution had a pH 5.5 and the test temperature was 60°C. With increasing phase ratio, changes of Co and Ni concentrations, their extraction rates, and distribution ratios show again similar trends as observed for increasing pH value (comparing Figure 1a-1c with Figure 3a-3c). This again can be easily understood when bearing the above-mentioned reactions (4) - (7) in mind. With increasing

phase ratio, increased amounts of A⁻_(org) and (HA)_(org) are available for reactions with Co and Ni ions. This is beneficial for these reactions toward the positive direction, thus showing the same effect as decreasing H⁺ concentration. However, an increase of phase ratio will increase Cyanex 272 usage and Ni loss. At O/A = 1:1, Co concentration is about 0.2 mg/L, low enough for nickel sulfate solution. Therefore, an O/A ratio of 1:1 is reasonable.

3.4. Effect of TBP Addition on Cobalt and Nickel Separation

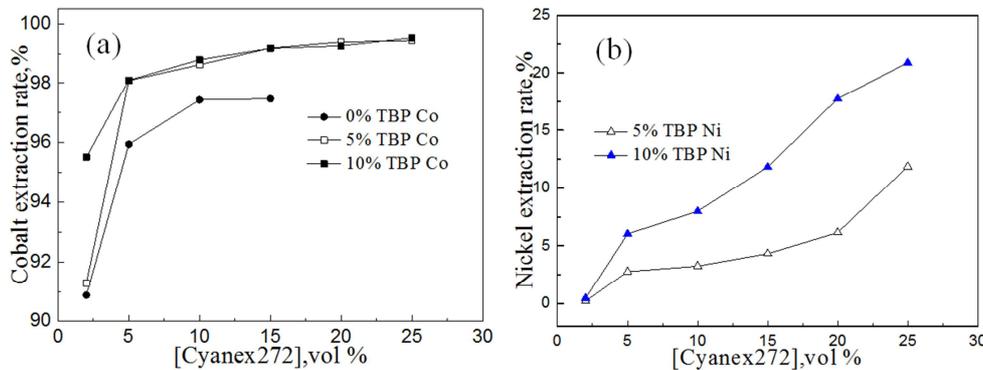
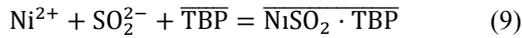
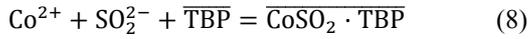


Figure 4. Effect of TBP addition on Co extraction from nickel sulfate solution (a) cobalt extraction rate, (b) nickel extraction rate.

TBP was reported to have synergistic effects together with Cyanex 272 on extraction of cobalt and nickel. It can react with cobalt and nickel as follows:



In addition, TBP is cheaper than Cyanex 272. Thus it may make sense from an economic viewpoint to explore the possibility to partially replace Cyanex 272 with TBP. In order to study the effect of TBP addition on extraction, 5 vol.% and 10 vol.% TBP were added to organic solutions, while keeping O/A = 1:1, pH 5.5 and 60°C constant. Figure 4 shows the test results. It can be observed from Figure 4 that Ni extraction rates

are higher with 10 vol.% TBP than with 5 vol.% TBP. But for Co extraction rate, TBP has only a small effect at low Cyanex 272 concentration. For 5 vol.% Cyanex 272 and above, almost same Co extraction rates were obtained for both 5 vol.% and 10 vol.% TBP. In this study, the aqueous solution contains very low Co. Its extraction requires a small amount of Cyanex 272. Hence, an increase of Cyanex 272 as well as TBP has little influence on cobalt extraction rate. Due to the much larger quantity of Ni ions in aqueous solution, both Cyanex 272 and TBP can react with Ni ions, leading to an increased nickel loss at higher Cyanex 272 and TBP concentrations. Therefore, the addition of 5% TBP is beneficial to cobalt removal.

3.5. Effect of Temperature on Cobalt and Nickel Separation

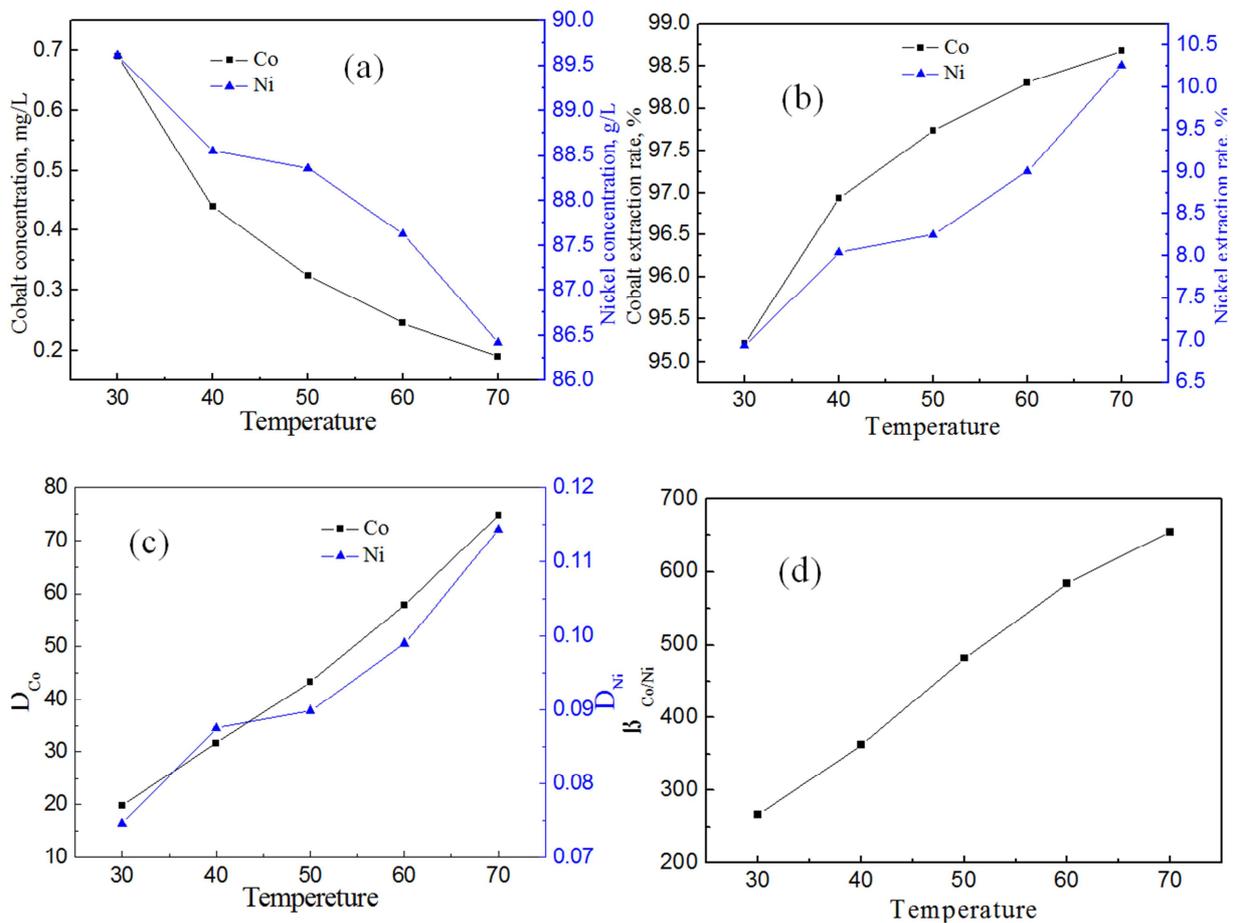


Figure 5. Effect of temperature: (a) Co and Ni concentrations in the raffinate, (b) Co and Ni extraction rates ($E\%$), (c) Co and Ni distribution ratios (D), (d) Co/Ni separation factor ($\beta_{\text{Co/Ni}}$).

Figure 5 shows the effect of temperature on Co extraction with an organic solution containing 10 vol.% Cyanex 272 and 10 vol.% TBP, an aqueous solution of pH 5.5, and an phase ratio O/A = 1:1. Here, one can see that temperature has a great influence on the extraction process. When temperature increased from 30°C to 70°C, Co concentration was reduced from about 0.69 mg/L to about 0.19 mg/L, and Ni

concentration decreased from 89.61 g/L to 86.42 g/L (Figure 5a). The corresponding changes of extraction rates were from 95.21% to 98.68% for Co, and from 6.94% to 10.26% for Ni (Figure 5b). The Co distribution ratio D_{Co} clearly increases with increasing temperature, whereas the Ni distribution ratio D_{Ni} changes little from 0.075 to 0.114 (Figure 5c).

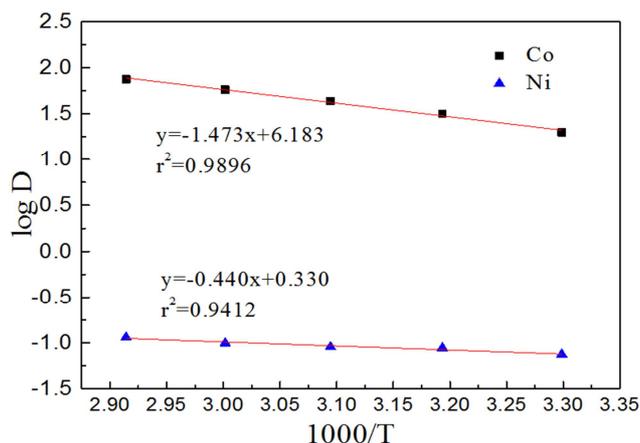


Figure 6. Plots of $\log D$ vs. $1000/T$ for Co and Ni extraction using 10 vol.% Cyanex 272.

Figure 6 shows plots of $\log D$ versus $1000/T$ (K^{-1}) based on the prominent Van't Hoff equation:

$$\log D = -\frac{\Delta H}{2.303RT} + K^* \quad (10)$$

In this equation, D is distribution ratio, R is gas constant (8.314 J/(mol·K)), T is absolute temperature (K), ΔH is reaction enthalpy (J/mol), K^* is a constant. From the slopes of two straight lines in Figure 6, reaction enthalpy (ΔH) was calculated to be 28.21 KJ/mol and 8.43 KJ/mol for Co and Ni, respectively. The positive reaction enthalpies ($\Delta H > 0$) indicate that the extraction process is endothermically driven [5, 8]. The larger enthalpy value (28.21 KJ/mol) for Co suggests that the temperature effect on Co extraction is larger than that on Ni extraction [1]. Thus, an increase of temperature is beneficial for Co extraction. But on the other hand, a volatilization of organic phase can be a problem at high temperature. In this study, some volatilization of organic phase was observed at 70°C.

3.6. About the Co/Ni Separation Factor $\beta_{Co/Ni}$

As shown in Figure 1d, Figure 2d, Figure 3d and Figure 5d, quite different Co/Ni separation factors were determined in this study. Most of them are below 1000, smaller than 3936 as reported in [6-8]. This is understandable because this study deals with very low initial Co concentrations. At such low Co concentrations, it is difficult to achieve a very high Co distribution ratio D_{Co} and a very low Ni distribution ratio D_{Ni} at the same time. Thus, it is difficult to obtain a high Co/Ni separation factor ($\beta_{Co/Ni} = D_{Co} / D_{Ni}$). There is only one large Co/Ni separation factor of 4700 in this study (Figure 2d), which was obtained for a test with a very low Cyanex 272 concentration of 2.5 vol.%. In this case, D_{Ni} is extremely low because not much extractant is available to extract Ni ions.

4. Conclusions

Trace Co extraction from nickel sulfate solution using

Cyanex 272 has been investigated in this study. Based on results obtained, following conclusions can be drawn.

- 1) Co concentration can be reduced via an extraction process with 10 vol.% Cyanex 272 at O/A 1:1, pH 5.5, 60°C in one stage from about 25.45 mg/L to below 0.5 mg/L.
- 2) Co extraction using Cyanex 272 is an endothermic process. An increase of temperature is beneficial to Co extraction. But at 70°C, a volatilization of organic phase can be a problem.
- 3) When dealing with very low initial Co concentrations such as in this study, high pH value of aqueous solution, high Cyanex 272 concentration in organic phase, high O/A ratio, and adding TBP to the organic phase can lead to increased Ni loss.

Acknowledgements

This work was financially supported by the Chinese 02 Special Fund (2017ZX02408003) as well as the Chinese 1000 Plan for High Level Foreign Experts (WQ20154100278).

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