

SELECTIVE EXTRACTION OF COBALT FROM NICKEL SULPHATE SOLUTIONS BY CYANEX 272

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*University of Chemical Technology and Metallurgy, Sofia, 8KI Ohridski, Bulgaria www.uctm.edu.***Abstract**

The process of recovery and separation of cobalt from acid sulphate solutions containing high concentration of nickel by solvent extraction (SX) was investigated. The commercial product Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) in kerosene was used. The leach liquor used for the present study contained in g/L: 3.01 Co and 30.16 Ni. Before cobalt extraction, impurities, such copper, iron and manganese were removed from the initial solution by the precipitation methods. The solution was obtained after autoclave dissolution of Ni-Co sulphide concentrate, intermediate product of pyro-hydrometallurgical processing of Pacific manganese Nodules.

Cobalt extraction efficiency of > 97 % was achieved with 6 mass % of Cyanex 272 in three counter-current stages at an aqueous (Aq.):organic (Org.) phase ratio of 1:1, temperature 298 K and pH = 6.5. The scrubbing of nickel from the loaded organic phase was carried out with solution containing 3 g/L Co. For the stripping of cobalt from organic phase, synthetic spent cobalt electrolyte containing in g/L: 36 Co, 70 Na₂SO₄ and 6 H₂SO₄ was used. The optimal cobalt stripping efficiency > 99.3% was achieved in two stages at Aq:Org. phase ratio of 1:1.5. A complete flow sheet for the separation and recovery of cobalt was presented.

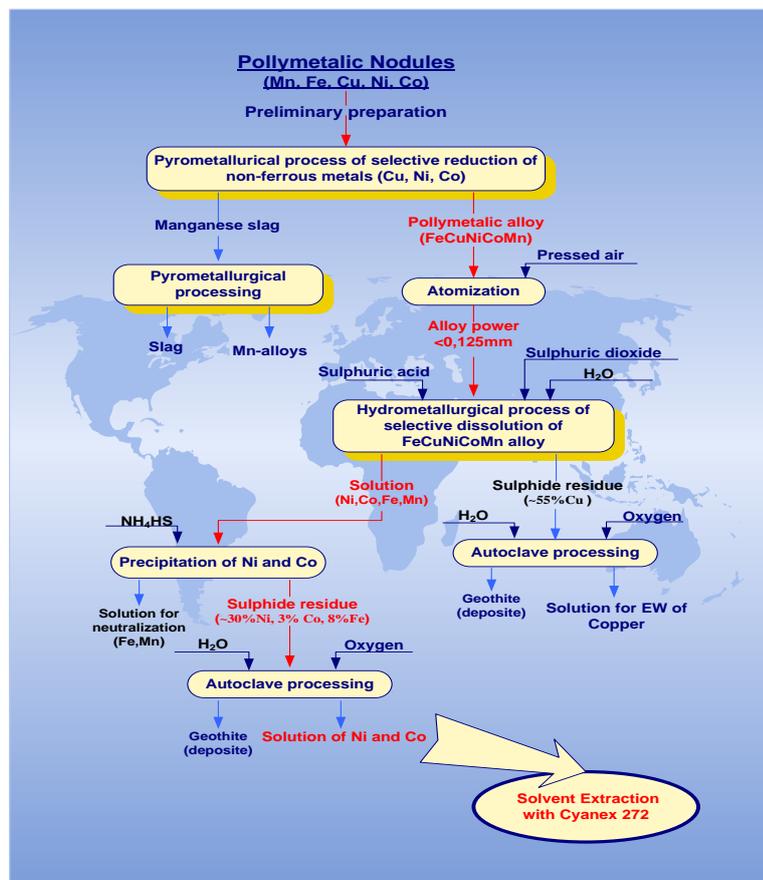
Keywords: cobalt, nickel, solvent extraction, Cyanex 272, manganese nodule

1. INTRODUCTION

It is well known that the concentration of non-ferrous metals (Cu, Ni and Co) in deep-ocean manganese nodules (PN) from the Clairon Clipperton region of the Pacific Ocean is comparable to that of continental ores, therefore they are an alternative mineral source of their production [1]. Currently, the combined pyro-hydrometallurgical methods are considered as the most promising methods of PN processing. In the pyrometallurgical part of these schemes the non-ferrous metals are concentrated in an intermediate product, a polymetal alloy (FeCuNiCoMn) [2]. One specific feature of that alloy is the high Fe content (>65 %) compared to that of Cu and Ni (~12-13 %), and especially that of Co (~1.5 %). The Mn content in the alloy is 5-6 %. Copper, nickel and cobalt are extracted from the alloy by a chemical or electrochemical process [3].

In the process of our previous research, a two-stage technology was developed for dissolution of the alloy in H₂SO₄ solution in the presence of a reductor - SO₂, where more than 97-98 % of Ni, Co, Fe, Mn pass into the solution, while copper is precipitated in the form of copper sulphides. The chemical composition of the solutions obtained, in g/l is: 32-34 Fe, 6-6.8 Ni, 0.6-0.8 Co, 2.6-3 Mn and 0.03-0.05 Cu.

The direct extraction of nickel and cobalt from these solutions is from economic point of view is not lucrative due to their low concentration and high iron concentration in them. For this reason, initially Ni and Co were precipitated, using NH₄HS, as a mixed sulphide sludge (containing > 30 % Ni and Co), further subjected to acid sulphate oxidative autoclave dissolution. Fe present in the sulphide sludge is precipitated in the form of goethite, while Co, Ni pass into the solution. A schematic pyro-hydrometallurgical diagram of nickel and cobalt extraction in concentrated PN solutions is presented in Fig.1.



For the last ten years, liquid-phase extraction (SX) is used for recovery and separation of Co from Ni in acid sulphate solutions. A major advantage of the method is the possibility to combine it with the process of electroextraction, which permits the recovery of high-purity metals. Currently, various reagents for cobalt and nickel SX based on phosphoric, phosphonic and phosphinous acid are available: D2EXPA, PC88A, Cyanex 272, Cyanex 301 [4]. Of these, the extraction agents with highest selectivity with respect to Co are those under the trade name “Cyanex” [5,6].

Fig.1. Pyro-hydrometallurgical diagram of concentration of Co and Ni from manganese nodules from the Clairron Cliperton area of the Pacific Ocean to a solution suitable for SX-EW.

This paper presents experimental results of liquid-phase cobalt extraction from solutions containing

nickel by means of Cyanex 272 for the purpose of obtaining cobalt electrolyte of a purity suitable for the process of electrowinning.

2. EXPERIMENTS

2.1 Methods

For investigation of the liquid-phase extraction process a solution of the following composition (in g/L) was used: 3.01 Co, 30.16 Ni, 0.03 Cu, 0.01 Fe and 0.016 Mn, obtained after autoclave dissolution of mixed Ni-Co sulphide sludge. The solvent extraction of cobalt from the solution was effected using Cyanex 272, a commercial product of the firm Cytec Inc., which is a derivative of di-2,4,4 3-methylphenyl phosphine acid. Kerosene was used as organic solvent.

The solvent extraction was carried out in glass separating funnels with capacity 100 ml. The interchange between the aqueous and organic phases took place by the reversal principle. A rotating machine was used for the purpose, with sockets in which the separating funnels were fitted by means of special braces. The rotation speed was the same in all the experiments – 35 min^{-1} . After the extraction equilibrium was achieved, the separating funnels were left to rest for stratification of the two phases. The equilibrium concentrations of Co and Ni in aqueous and organic phases were determined by analysis of the aqueous phase using an atomic-absorption spectrophotometer Perkin – Elmer 5000. The influence of the main process parameters

on the distribution ratio $D = \left[\frac{c_{Co}^{Org.}}{c_{Co}^{Aq.}} \right]$ and the degree of extraction $E_{Co} = \left\{ \frac{D \frac{V_{Org.}}{V_{Aq.}}}{1 + D \frac{V_{Org.}}{V_{Aq.}}} \cdot 100, \% \right\}$ was studied.

V_{org} and V_{aq} were respectively volumes of the organic and aqueous phases.

3. RESULTS AND DISCUSSION

3.1. Solvent extraction with Cyanex 272

The initial values of the parameters of the cobalt extraction process were determined on the basis of the literature study. These were: solution acidity - pH = 6.5 and extraction temperature - 293K. Due to the high concentration of sulphuric acid in the solution studied (pH = 1) in order to achieve the work pH, the solution was neutralized in advance by lime wash. The effect of the following main parameters was investigated:

- Time of contact between the aqueous and organic phases;
- Extraction agent concentration;
- Solution acidity;
- Extraction capacity of the extraction agent;
- Volume ratio between the aqueous and organic phase.

The obtained results are represented in graphic form in Figs 2-5.

Analysis of the experimental results shows that the time required to achieve equilibrium in the studied system is 120 s. The maximum degree of extraction (62.79 %) was achieved at 9 v/v % Cyanex 272 in the organic phase. The experience of works using the SX process shows that at initial cobalt concentration in the solution 2–3 g/L, it is advisable to work with a lower concentration of Cyanex 272, 6 v/v % for example, and to apply multi-stage extraction. The process takes place within a very narrow interval of pH. At high initial acidity there is practically no extraction process, and at pH > 7, hydrolysis of nickel and cobalt is observed. The results demonstrate that after using of the extracting agent three times, its capacity significantly decreases (< 43.11 %). Upon increase of the organic phase volume to $V_{Org}:V_{Aq} = 1:5$, no significant increase of D_{Co} is observed. Upon single contact between the phases and $V_{Aq}:V_{Org} = 1$, the extraction degree of cobalt increases to 65.78 %.

3.2 Determination of the theoretical number of extraction stages

The theoretical number of extraction stages in a continuous type of counter-current extraction is determined by means of the McCabe–Thiele diagram. The extraction isotherm was built at variation of the aqueous phase/organic phase ratio of $V_{Org}:V_{Aq} = 1:5$ до $V_{Org}:V_{Aq} = 5:1$ and constant other parameters: concentration of the extracting agent - 6 v/v % Cyanex 272, temperature = 293 K, $pH_{init} = 6.5$ and contact time – 180 s.

The diagram shows that in the case of using Cyanex 272 without pretreatment (saponification), irrespective of the aqueous phase/organic phase ratio, more than 1.0 g/L Co will remain in the raffinate which is due to decrease of the solution pH. In practice this means that after each stage of extraction the solution pH has to be adjusted. It was found that, after three-stage counter-current extraction of cobalt with 6 v/v % Cyanex 272 at a ratio of $V_{Aq}/V_{Org}=1$ with adjustment of the aqueous phase pH after each stage of extraction the cobalt concentration in the raffinate is 0.01g/L.

3.3 Scrubbing of a loaded organic phase

After three-stage extraction of cobalt, 0.38 g/L Ni passes into the organic phase. For removal of the nickel it is scrubbed with a solution containing 3.0 g/L Co at pH = 4.5 and ratio of $V_{Aq}/V_{Org}=1:10$. After a single scrubbing the concentration of nickel in the organic phase decreases to 0.028 g/L.

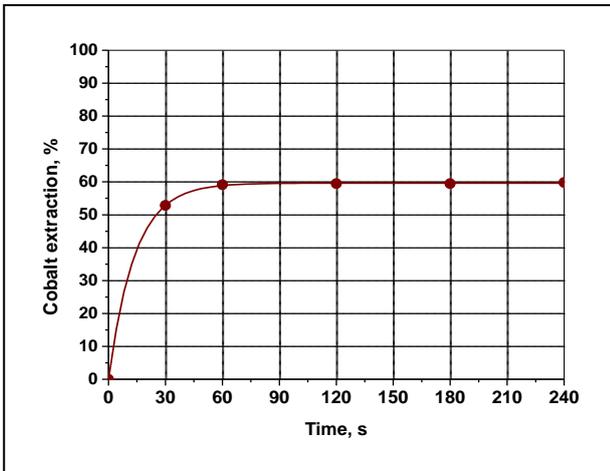


Fig.1. Effect of the contact time between aqua and organic phases on the cobalt extraction

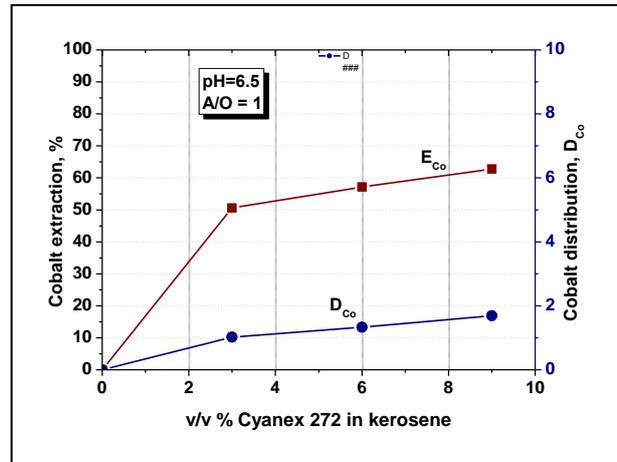


Fig.2. Effect of the Cyanex 272 concentration in kerosene on D_{Co} and cobalt extraction

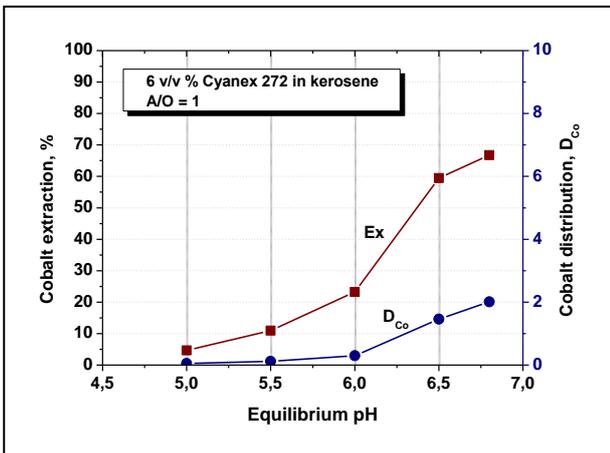


Fig.3. Effect of the equilibrium pH on the D_{Co} and cobalt extraction

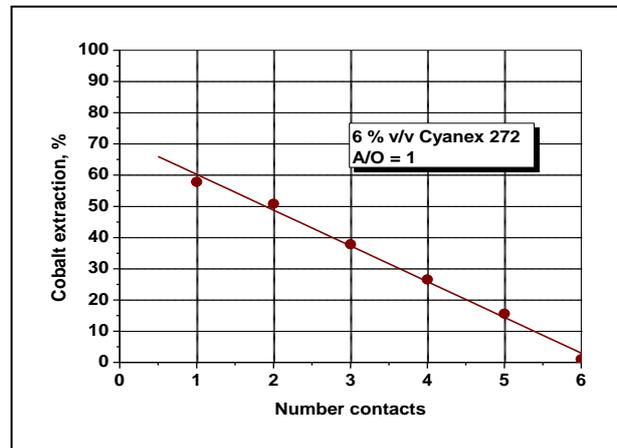


Fig.4. A dependence between the number of contacts and the extraction capacity of Cyanex 272

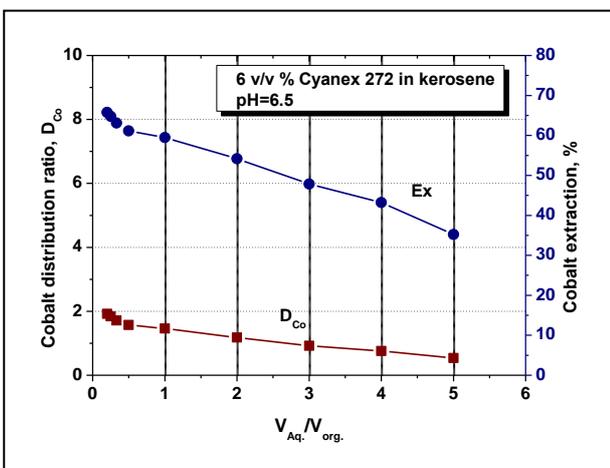


Fig.5. Effect of aqua and organic phase ratio on the D_{Co} and cobalt extraction

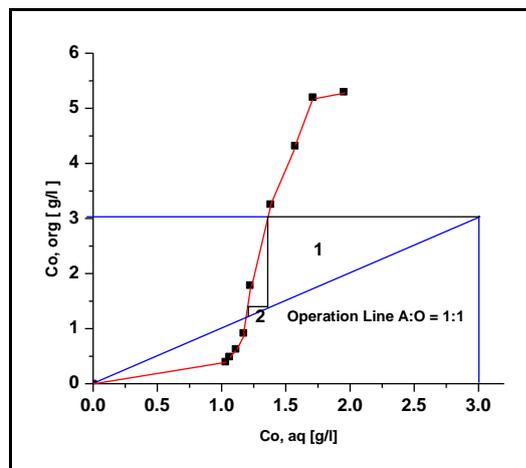


Fig.6. McCabe-Thiele diagram for number of stages for cobalt extraction (pH=6.5, 6 v/v % Cyanex 272 in kerosene)

3.4 Stripping of Cobalt from the organic phase

The next technological operation was the process of stripping of cobalt from the loaded organic phase. The following main parameters were studied:

- concentration of sulphuric acid in the extracting phase;
- volume ratio of the organic and aqueous phases.

The obtained results are presented in Fig. 7 and 8.

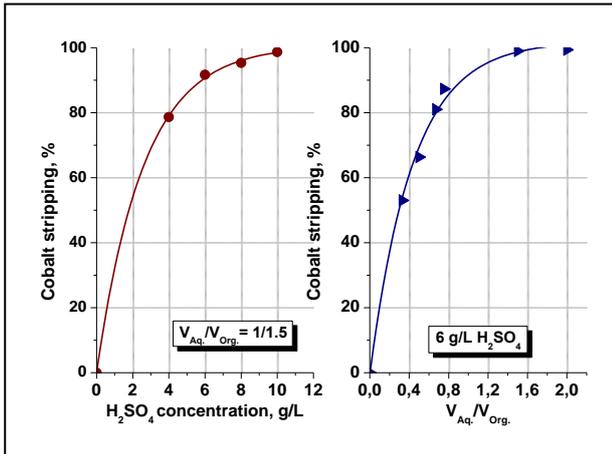


Fig.7. Effect of H₂SO₄ concentration and V_{Aq}/V_{Org} ratio on Co stripping from the organic loaded phase

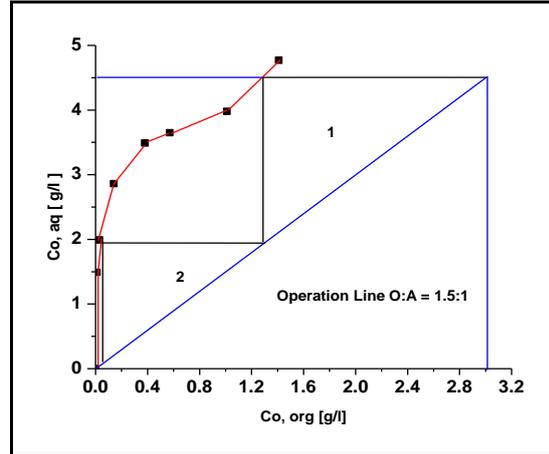


Fig.8. McCabe-Thiele diagram of Co stripping from the organic loaded phase with 6 g/L H₂SO₄ acid

It can be seen that at aqueous/organic ratio $V_{Aq}/V_{Org}=1$ the increase of H₂SO₄ concentration from 4 to 10 g/L leads to increase of the reextraction degree (RE_{Co}) which grew from 78.67 to 98.67%. The maximum degree of RE_{Co} (99.33%), at a single contact of phases was achieved at $V_{Aq}/V_{Org}=2$, in this case the concentration of cobalt in the obtained reextract was the lowest (1.49 g/L). It is obvious that, for complete extraction of cobalt from the loaded organic phase the process of reextraction has to be repeated several times.

3.5 Determination of the theoretical number of stripping stages

For determination of the theoretical number of cobalt stripping stages, the diagram of McCabe-Thiele was built for ratio $V_{Aq}/V_{Org} = 1:1.5$ (Fig.8), using H₂SO₄ solution with concentration 6 g/L as an extraction phase. It was found that after two-stage reextraction, < 0.07 g/L Co is left in the organic phase.

The experience of works operating by the scheme: SX-EW shows that for stripping of cobalt from the loaded organic phase, spent electrolyte with composition: 30÷40 g/L Co, 1÷20 g/L H₂SO₄ and 60-80 g/L Na₂SO₄ is used most commonly. In the two-stage stripping carried out by us we used electrolyte with the following composition: 36 g/L Co, 6 g/L H₂SO₄, and 70 g/L Na₂SO₄. The experiment was performed at $V_{Aq}/V_{Org} = 1:1.5$. It was found that after two-fold contacting of the phases RE_{Co} reaches 99.33 %. 0,01 g/L Co remains in the organic phase. The obtained electrolyte has a concentration of 40.47 g/L Co, pH = 2.4 and can be directly subjected to electrowinning.

4. CONCLUSIONS

On the basis of the experimental research, a schematic process diagram is proposed (Fig.9) of the process of selective counter-current cobalt extraction from an acid sulphate solution containing 30.16 g/l Ni and 3.01g/l Co obtained after oxidative autoclave dissolution of mixed sulphide Co-Ni sludge.

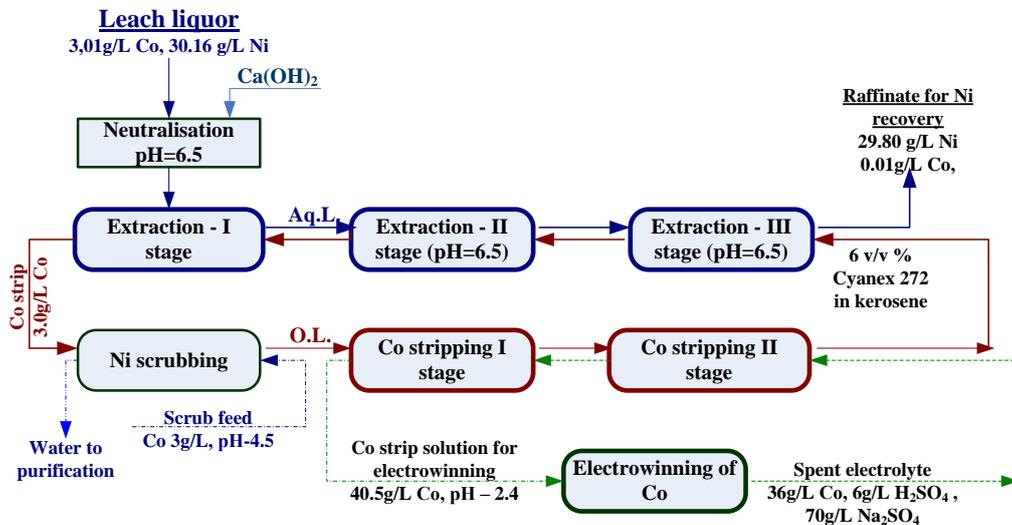


Fig.9 . Flowsheet of the process for the recovery of Co from sulphate leach liquor containing Ni

The developed scheme contains the following main operations:

- ✚ Three-stage, counter-current extraction of cobalt with 6 v/v % Cyanex 272 in kerosene solution at a ratio of $V_{Aq.}/V_{Org.} = 1$, temperature 298 K and pH = 6.5 and adjustment of the aqueous phase pH after each extraction stage. The contact time is 3 min. The degree of cobalt extraction in the organic phase is 99.67 %;

- ✚ Scrubbing of the loaded organic phase with a solution containing 3.0 g/L Co, at pH = 4.5 and ratio of $V_{Aq.}/V_{Org.} = 1:10$, where > 92 % of nickel is removed from the organic phase.

- ✚ Two-stage stripping of cobalt using spent electrolyte containing 6 g/L H_2SO_4 , 36 g/L Co and 70 g/L Na_2SO_4 , at a ratio of $V_{Aq.}/V_{Org.} = 1/1.5$. The obtained cobalt electrolyte can be directly sent for electrowinning. The degree of cobalt extraction from the loaded organic phase in the spent electrolyte is 99.33 %

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