

UDC 669.53

EXTRACTION OF COPPER, COBALT AND NICKEL IONS FROM AQUEOUS SOLUTIONS BY EXTRACTANT CYANEX 272

Lidiya A. VOROPANOVA, Viktoriya P. PUKHOVA

North Caucasus Mining and Metallurgical Institute (State Technological University), Vladikavkaz, Russia

The extractant CYANEX 272, which active component is di(2,4,4-trimethylpentyl)-phosphinic acid (C_8H_{17})₂POOH, is effective for extraction of copper (II), cobalt (II) and nickel (II) ions. The extraction of metal ions using di(2,4,4-trimethylpentyl)-phosphinic acid as an extractant is carried out due to the formation of an organophosphorus complex with wide pH range: copper at pH > 2, cobalt at pH > 3, and nickel at pH > 5. They are extracted with an organic phase: copper at pH = 3-7, cobalt at pH = 4-7, and nickel at pH = 6-9, and precipitate in the organophosphorus compound: copper at pH > 7, cobalt at pH ≥ 8, and nickel at pH ≥ 10. The possibility of separation of copper (II) and cobalt (II) is insignificant, the stripping of copper (II) and nickel (II) happens at pH = 4-6, and the stripping of cobalt (II) and any of nickel (II) – at pH = 5-6.

The obtained results of ion extraction of the investigated metals can be used not only for processing of technological solutions, but also for purification of effluents from industrial enterprises and mine waters, heap and underground leaching solutions, etc. from the ions of studied metal ions.

Key words: aqueous solution; extraction; extractant; copper; cobalt; nickel

How to cite this article: Voropanova L.A., Pukhova V.P. Extraction of Copper, Cobalt and Nickel Ions from Aqueous Solutions by Extractant Cyanex 272. Journal of Mining Institute. 2018. Vol. 233, p. 498-505. DOI: 10.31897/PMI.2018.5.498

Introduction. The extraction of cobalt from nickel solutions by alkyl phosphinic acids is largely covered in literature. It is known that to extract cobalt ions from aqueous solutions of sulphates and nickel chlorides it is efficient to perform it with CYANEX 272 extractant, the active component of which is di (2,4,4-trimethylpentyl)-phosphinic acid (C_8H_{17})₂POOH [1-13]. Metals are extracted by means of a cation exchange mechanism. The CYANEX 272 extractant can be totally mixed with aromatic and aliphatic solvents and is very resistant to heating and hydrolysis, it shows a high selective ability to separate cobalt from nickel, both in sulfate and chloride media, has low ability to extract calcium ions, which excludes gypsum contamination that may appear in the liquid extraction cycle.

It is known that cobalt is extracted selectively from nickel salt solutions within a narrow range: pH ≈ 5. However, the extraction of copper, cobalt and especially nickel in their joint presence in solution, and the extraction of copper and cobalt impurities from solutions of macro quantities of nickel salts has been little studied. The processes of interaction of the extractant with solutions of salts at pH > 7 have not been studied.

Materials and methods of research. The objectives of this study are to find the optimal conditions for the selective and combined extraction of copper, cobalt and nickel by extracting the CYANEX 272 extractant and reextraction from solutions having complex composition, as well as to study the conditions for extracting copper and cobalt impurities from solutions with macro quantities of nickel salts, including usage of kerosene as diluent extractant, and study of the processes of interaction of the extractant with solutions of salts at pH > 7.

Crystalline hydrates of salts $CuSO_4 \cdot 5H_2O$, $CoSO_4 \cdot 7H_2O$ and $NiCl_2 \cdot 6H_2O$ were used to prepare solutions. The extraction was carried out with stirring and constant pH adjustment, NaOH and H_2SO_4 solutions were used as neutralizers. The experiments were carried out at room temperature.

Figure 1 shows the scheme of units for extraction and reextraction.

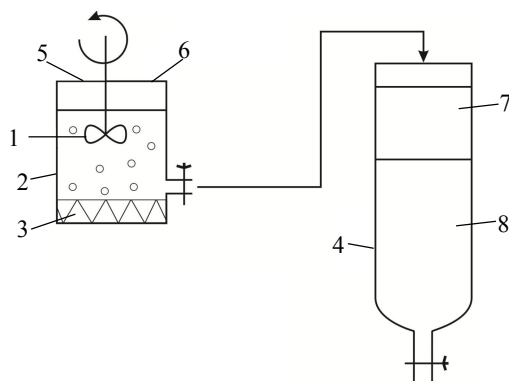


Fig. 1. The scheme of extraction units
1 – mixer; 2 – beaker; 3 – thermal element;
4 – separatory funnel; 5 – initial solution;
6 – extractant; 7 – extract; 8 – raffinate

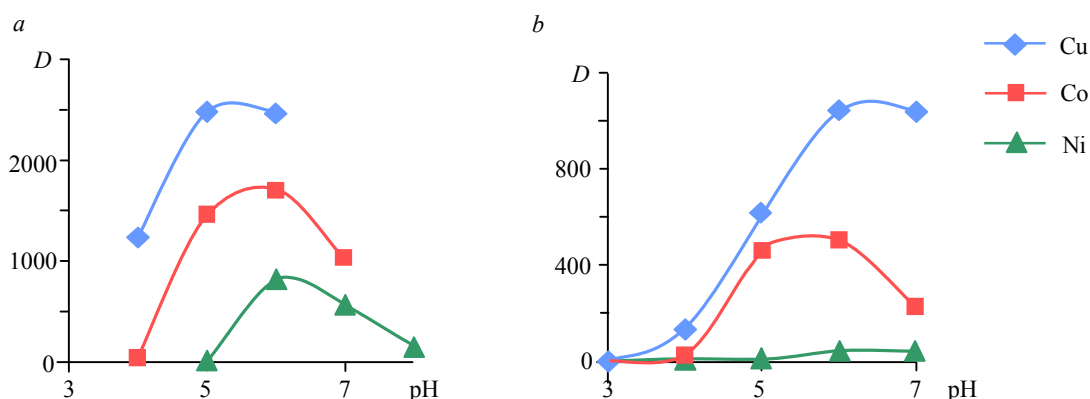


Fig.2. Dependency of distribution coefficient D from solution pH of salts CuSO_4 , CoSO_4 and NiSO_4 :
 a – individual solutions; b – mixed solutions

A beaker with the initial solution containing extractable ions and the extractant was placed on a thermal element to heat the mixture to a predetermined temperature. For better mass transfer, the contents of the beaker were stirred with a mixer for a preset amount of time. The mixture was then transferred to a separatory funnel, where it was settled and separated into extract and raffinate. After settling they were poured into separate containers through the lower outlet of the separatory funnel and analyzed.

The extraction results were evaluated by the residual concentration of C (in grams per cubic decimeter) of metal ions in the raffinate, the distribution coefficient $D = C_{\text{org}}/C_{\text{aq}}$, the extraction of metals in the organic phase (in percent by weight of the initial phase), and the separation coefficient $\beta = D_{\text{Me}_1} / D_{\text{Me}_2}$.

Results and discussion. Figure 2 shows the dependency of the distribution coefficient D on the pH of the aqueous solution of salts CuSO_4 , CoSO_4 and NiSO_4 .

The concentration of initial solutions by the sum of metals was, mg/dm^3 : 400-550 for individual solutions and 660-770 for mixed solutions of metal salts. The set pH was maintained for 0.1-1.5 hours, afterwards it changed insignificantly. The initial aqueous-oil emulsion contained 5 % by weight of the extractant (ratio of aqueous and organic phases A:O = 19:1). The volumes of the organic and aqueous phases changed insignificantly in comparison to initial ones: the volume of the organic phase remained unchanged and the water content was 0.8-1.0.

In Table 1, according to Fig.2, the best extraction results from individual solutions of salts and from mixed solutions of CuSO_4 , CoSO_4 and NiSO_4 salts obtained in 0.5 h.

Table 1

The best extraction results from individual and mixed solutions of CuSO_4 , CoSO_4 and NiSO_4 salts with CYANEX extractant 272

Metal	Concentration of initial solution, mg/dm^3	Extraction results			
		pH	Residual concentration, mg/dm^3	Distribution coefficient D	Extraction, % by weight from initial solution
<i>Extraction of individual solutions</i>					
Cu	395	4	6	1232	98.5
Cu	395	5	3	2483	99.2
Cu	395	6	3	2483	99.2
Co	546	5	7	1463	98.7
Co	546	6	6	1710	98.9
Co	546	7	10	1018	98.2
Ni	533	6	12	825	97.7
Ni	533	7	17	577	96.8
Ni	533	8	58	156	89.1

End of Table 1

Metal	Concentration of initial solution, mg/dm ³	Extraction results			
		pH	Residual concentration, mg/dm ³	Distribution coefficient <i>D</i>	Extraction, % by weight from initial solution
<i>Extraction of mixed solutions of salts</i>					
Cu	168	4	21	133	87.5
Cu	168	5	5	619	97.0
Cu	168	6	3	1045	98.2
Cu	168	7	3	1045	98.2
Co	276	5	11	458	96.0
Co	276	6	10	505	96.4
Co	276	7	22	219	92.0
Ni	241	6	73	44	69.8
Ni	241	7	78	40	67.8
Ni	241	8	83	36	65.5

In alkaline medium at pH > 7 from individual solutions metals precipitate in the organophosphorus compound in the gel-like form. The solution was separated from the precipitate through a medium density filter. The filtration was done fast. The filtrate was analyzed for the metal content.

At pH = 8-11, the blue precipitate was formed in the solution of copper sulfate. At pH = 12, a gel-like precipitate of brown color is formed. The best precipitation results were obtained at pH = 12: the minimum residual concentration $C = 5 \text{ mg/dm}^3$ Cu (II), extraction 98.7 % by weight.

At pH = 8-9 the solution of cobaltous sulphate has noticeable blue precipitate. The best precipitation results were obtained at pH = 8: the minimum residual concentration $C = 74 \text{ mg/dm}^3$ Co (II), extraction 86.4 % by weight.

During extraction of nickel at pH = 7-9, the organic phase had the form of a lump with higher density and viscosity. The solution was filtered to remove light turbidity.

At pH = 10-12, the green gel-like precipitate is formed. When settling for more than 24 hours, the ratio between the volumes of clarified aqueous phase and precipitate was 2:1. The best precipitation results were obtained at pH = 12: the minimum residual concentration was $C = 1 \text{ mg/dm}^3$ Ni (II), extraction 99.8 % by weight.

The separation factors β of copper, cobalt and nickel ions, calculated from the data in Fig.2 and Table 1, are given in Table 2 and in Fig. 3.

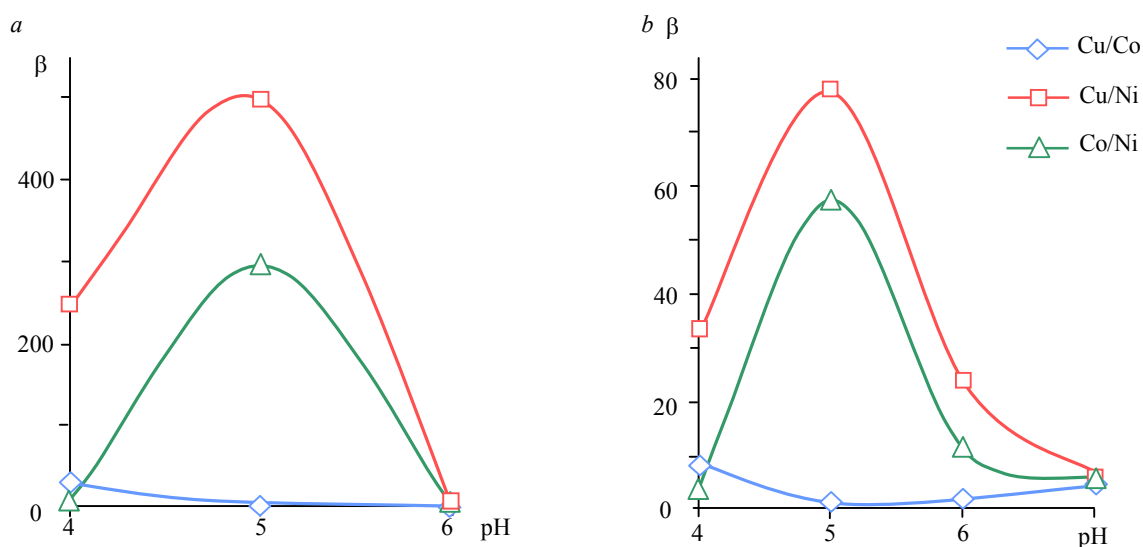


Fig.3. Separation factors β of copper, cobalt and nickel ions during extraction from sulfate solutions of their salts (extractant – CYANEX 272): *a* – from individual solutions; *b* – from mixed solutions of salts



Table 2

Separation factors β of copper, cobalt and nickel ions during extraction from sulfate solutions of their salts (extractant – CYANEX 272)

Extraction pH	β					
	From individual solutions			From mixed solutions		
	Cu/Co	Cu/Ni	Co/Ni	Cu/Co	Cu/Ni	Co/Ni
4	30.0	246.4	8.2	8.3	33.3	4.0
5	1.7	496.6	292.6	1.4	77.4	57.3
6	1.5	3.0	2.1	2.1	23.8	11.5
7	–	–	1.8	4.8	6.1	5.5

According to the data in Tables 1 and 2 and Figures 2 and 3 the following conclusions can be drawn:

1. The extraction of metal ions using di(2,4,4-trimethylpentyl)-phosphinic acid as reagent is carried out due to the formation of an organophosphorus complex with wide pH range:

- copper is formed at pH > 3, cobalt – at pH > 4, nickel – at pH > 5.

They are extracted at organic phase:

- copper – at pH = 3-7, cobalt – at pH = 4-7, nickel – at pH = 5-9.

They are precipitated as a part of organophosphorus compound:

- copper – at pH > 7, cobalt – at pH \geq 7, nickel – at pH \geq 10.

2. Selective extraction of studied ions from aqueous solutions of sulfates during extraction is possible with the following sequence in terms of pH values:

- from individual solutions

Ion	Cu	Co	Ni
pH	4-5	5-6	6-8

- from mixed aqueous solutions of salts

Ion	Cu	Co	Ni
pH	4	5	6

3. The possibility of separation of copper (II) and cobalt (II) is insignificant, and stripping of copper (II) and cobalt (II) from nickel (II) occurs at pH = 5.

4. The extraction of copper (II), cobalt (II) and nickel (II) ions when they are combined in sulfate solutions is much lower than during extraction from individual sulfate solutions.

Table 3 shows the results of reextraction of copper, cobalt and nickel ions from the extracts obtained in the experiments presented in Table 1.

Table 3

Results of extraction of copper, cobalt and nickel ions form extract

Extraction pH	Reextraction pH _{limit}	Reextraction pH _{end}	Metal concentration, mg/dm ³						Coefficient of distribution <i>D</i> between organic and aqueous phases			β			Extraction in reextract, % by weight from initial solution		
			In the initial extract, <i>V</i> = 10 cm ³			In reextract, <i>V</i> = 50 cm ³											
			Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni	Cu/Co	Cu/Ni	Co/Ni	Cu	Co	Ni
4	1	0.84	2793	–	–	525.6	558.6	0	0.3	–	–	–	–	–	–	–	–
5	1	0.87	3097	5035	–	581.4	1003.2	155.8	0.3	0.02	–	15	–	–	93.8	–	–
6	1	0.87	3135	5054	3192	562.4	1005.4	572.4	0.6	0.03	0.6	20	1	0.05	89.6	99.6	89.6
7	0	1.10	4788	4826	3097	463.6	955.6	562.4	0.6	0.05	0.5	12	1.2	0.1	48.5	99.0	90.7

From the data in Table 3 it follows that reextraction is effective at pH < 1, when extraction was carried out at pH 4-6, and at pH < 0, when extraction was carried out at pH 7-8.

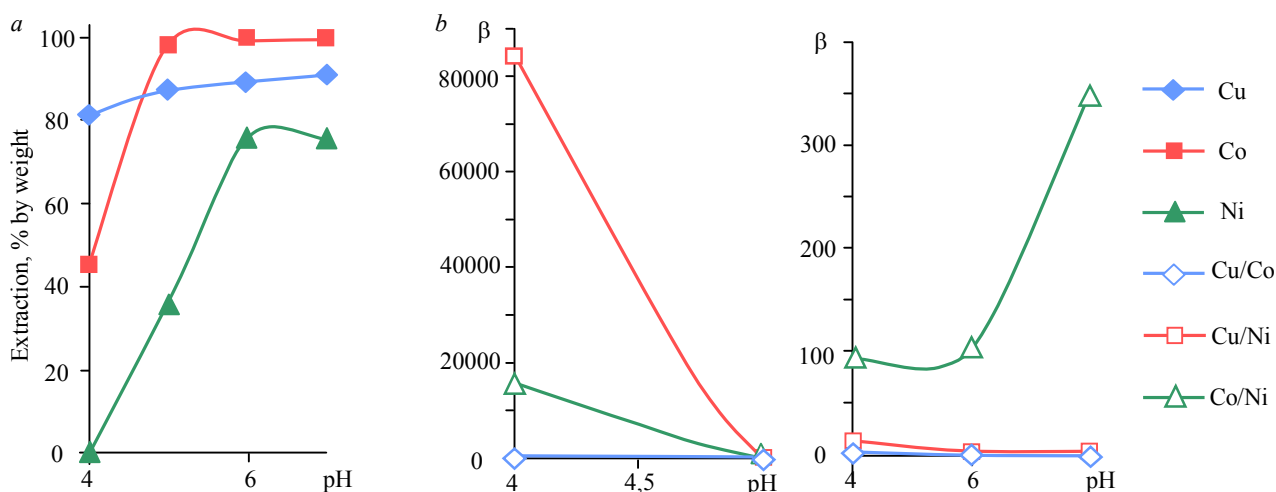


Fig.4. Results of batch extraction of metal ions from mixed sulfate solutions of salts in relation to solution pH:
a – extraction, b – separation coefficient

Table 4 and Figure 4 show the extraction results, which were carried out at a ratio of organic and aqueous phases of O:A = 1:19, a stepwise increase in the pH of the solution during the extraction according to the 4 → 5 → 6 scheme and subsequent reextraction of each step at pH = 1 and the ratio O:A = 1: 5. The extraction time was 30 minutes and reextraction – 24 hours.

Table 4

Results of batch extraction of metal ions from aqueous sulfate mixed solutions of salts

Extraction pH	Reextraction pH _{end}	Concentration, mg/dm ³								
		Initial solution, V = 190 cm ³			Reextractant, V = 50 cm ³			Raffinate		
		Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni
4	0.17	168	323	176	520.6	558.6	0	30.9	176.0	176.0
5	1.30	168	323	176	38.0	646.0	239.4	21.0	6.1	113.0
6	1.34	168	323	176	11.4	19.0	266.0	18.0	1.0	42.9
7	1.36	168	323	176	11.4	3.8	0	15.0	0.3	42.9

Extraction pH	D			β			Total extraction in reextractant, % by weight from initial solution		
	Cu	Co	Ni	Cu/Co	Cu/ Ni	Co/Ni	Cu	Co	Ni
4	84.3	15.9	0.001	5.3	84300	15900	81.6	45.5	0.01
5	133.0	987.1	10.6	0.1	12.5	93.1	87.5	98.1	35.8
6	158.3	6118	58.9	0.03	2.7	103.9	89.3	99.7	75.6
7	193.8	20437.7	58.9	0.01	3.3	347.0	91.1	99.9	75.6

It follows from the data in Table 4 and in Figure 4 that, when the content in the initial solution (mg/dm³) is 168 Cu, 323 Co, 176 Ni, at pH = 4 of copper 82 %, at pH = 5 of cobalt 98 % and at pH = 6 of nickel 76 %.

Selective extraction of non-ferrous metals can be accomplished by fractional extraction with a gradual change in the solution pH and maintaining the changed pH value at each batch extraction; extraction of predominantly copper ions is carried out by extraction at pH = 4, cobalt at pH = 5, and nickel at pH = 6-7.

Table 5 and Figure 5 show the results of batch extraction of copper (II) and cobalt (II) ions against the background of the nickel (II) macro component. The extraction was carried out at a ratio of the organic and aqueous phases of O: A = 1:19 and a stepwise increase in the pH of the solution during the extraction process according to the scheme 4→5→6 at the extraction time for each step no more than 2 hours, the subsequent reextraction of each step at pH = -0.5, the ratio of O: A = 1: 5 and 2 days reextraction.

The composition of raffinate (extractant CYANEX 272, extraction time at each stage was not more than 2 hours) is the following: concentration, mg/dm³: Cu-35, Co-148, Ni-55300; composition, % by weight: Cu – 0.06, Co – 0.27, Ni – 99.67.

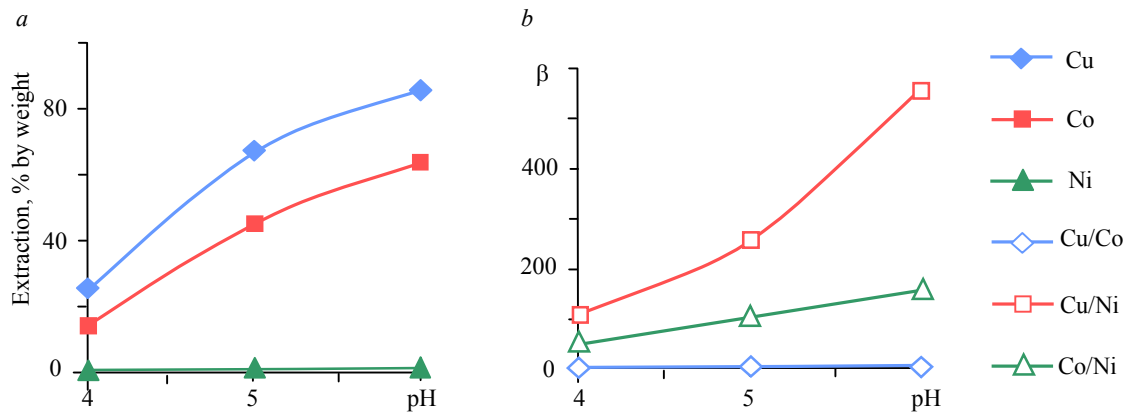


Fig.5. Results of batch extraction of metal ions from aqueous mixed sulfate solutions of salts against the nickel (II) micro component in relation to solution pH: *a* – extraction, *b* – separation coefficient

Table 5

Results of batch extraction of metal ions from aqueous sulfate mixed solutions of salts against the nickel (II) macro component, extractant CYANEX 272

Extraction pH	Reextraction pH _{end}	Concentration, mg/dm ³								
		Initial solution, V = 190 cm ³			Reextractant, V = 50 cm ³			Raffinate		
		Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni
4	-0.37	286	416	55950	270	228	613	215.1	356.1	55782.2
5	-0.07	286	416	55950	460	485	982	94.1	228.4	55502.4
6	-0.06	286	416	55950	205	293	751	40.0	151.4	55334.6

Extraction pH	D			β			Total extraction in reextractant, % by weight from initial solution		
	Cu	Co	Ni	Cu/Co	Cu/Ni	Co/Ni	Cu	Co	Ni
4	6.3	3.2	0.06	2.0	105	53.3	24.8	14.4	0.3
5	38.7	15.6	0.15	2.5	258	104	67.1	45.1	0.8
6	116.9	33.2	0.21	3.5	556.7	158.1	86.0	63.6	1.1

From data in Table 5 and Figure 5 it follows that when the initial solution has (mg/dm³) 286 Cu, 416 Co, 55950 Ni, at pH = 4 we extract 25 % of copper, at pH = 5 of cobalt 45 % and at pH = 6 of nickel 1 %, the ratio of metals in raffinate after extraction allows to have nickel with purity of 99.7 %.

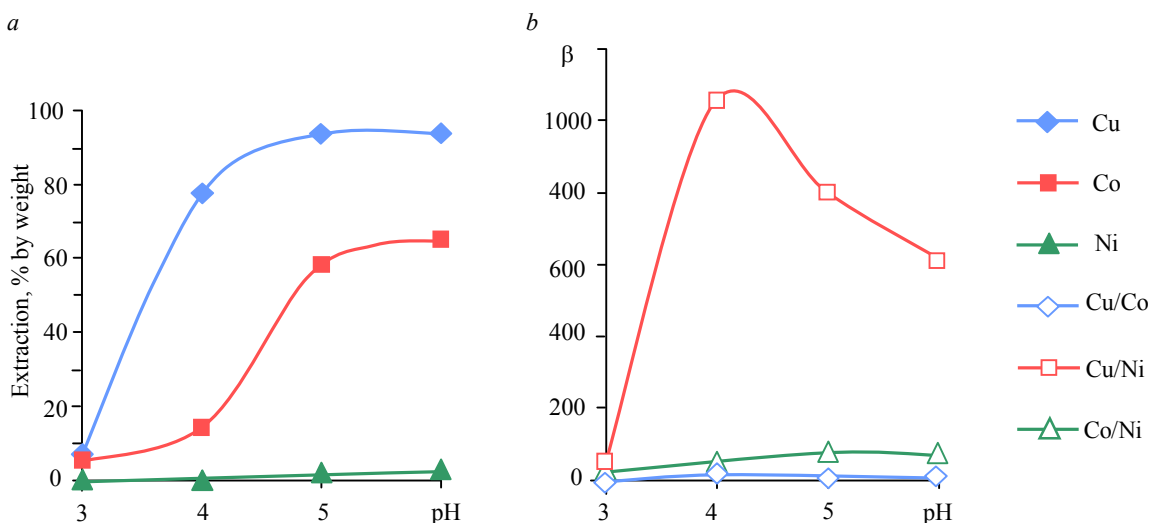


Fig.6. Results of batch extraction of metal ions from aqueous mixed sulfate solutions of salts against the nickel (II) macro component in relation to solution pH: *a* – extraction, *b* – separation coefficient. Extractant 30 % solution of CYANEX 272 in kerosene



From the data in Tables 4-5 and Fig. 4-5 it follows that a significant increase (by more than 2 orders of magnitude) in the concentration of nickel ions in the solution reduces the recovery of copper and cobalt.

Table 6 and Figure 6 show the extraction of copper (II) and cobalt (II) ions against the background of the nickel (II) macro component, extraction was carried out at a ratio of the organic and aqueous phases of O: A = 1: 6 (the extractant used 30 % solution of CYANEX 272 in kerosene) and a stepwise increase in the pH of the solution during the extraction according to the scheme of 3→4→5→6 at the extraction time for each step no more than 2 hours, and subsequent reextraction of each step at pH = -0.5, the ratio O: A = 1: 5 and the time of reextraction – 3 days.

The composition of raffinate (extractant – 30 % solution of CYANEX 272 in kerosene) is the following: concentration, mg/dm³: Cu – 0; Co – 100; Ni – 59900; composition, % by weight: Cu – 0; Co – 0.17; Ni – 99.83.

Table 6

Results of batch extraction of metal ions from aqueous sulfate mixed solutions of salts, extractant – 30 % solution of CYANEX 272 in kerosene, extraction time at each step is not more than 2 hours

Extraction pH	Reextraction pH _{end}	Concentration, mg/dm ³								
		Initial solution, V = 190 cm ³			Reextractant, V = 50 cm ³			Raffinate		
		Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni
3	-0.60	278	266	61600	72	52	420	259.9	252.4	61476.8
4	-0.70	278	266	61600	75	96	500	61.7	227.4	61353.6
5	-0.95	278	266	61600	16	440	3360	17.8	111.2	60491.2
6	-1.00	278	266	61600	40	74	1800	16.1	91.8	59998.4

Extraction pH	D			β			Total extraction in reextractant, % by weight from initial solution		
	Cu	Co	Ni	Cu/Co	Cu/Ni	Co/Ni	Cu	Co	Ni
3	0.4	0.3	0.01	1.3	40	30	6.8	5.1	0.2
4	21.0	1.0	0.02	21.0	1050	50	77.8	44.6	0.4
5	87.7	8.4	0.11	10.4	797.3	76.4	93.6	63.2	1.4
6	97.6	11.4	0.16	8.6	610	71.3	94.2	65.5	1.8

From data in Table 6 and Figure 6 it follows that when the initial solution has (mg/dm³) 278 Cu, 266 Co, 61600 Ni, at pH = 4 we extract 78 % of copper, at pH = 5 of cobalt 58 % and at pH = 6 of nickel 2.6 %, the ratio of metals in raffinate after extraction allows to have nickel with purity of 99.8 %.

From the data in Tables 5-6 and Figs. 5-6 it follows that the use of kerosene as a diluent increases the extraction of copper and cobalt.

Conclusions

1. Extractant CYANEX 272 is effective for the extraction of copper (II), cobalt (II) and nickel (II) ions.
2. The possibility of copper (II) and cobalt (II) separation is insignificant, and the stripping of copper (II) and cobalt (II) from nickel (II) occurs at pH = 5.
3. The obtained results of ion extraction of the investigated metals can be used not only for processing of technological solutions, but also for purification of effluents from industrial enterprises and mine waters, heap and underground leaching solutions, etc from the ions of studied metal ions.

Acknowledgment. The research was carried out with the financial support of the RFBR and the Ministry of Education and Science of the Republic of North Ossetia-Alania within the framework of the scientific project N 17-48-150696/17.



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Authors: **Lidiya A. Voropanova**, Doctor of Engineering Sciences, Professor, lidiya_metall@mail.ru (North Caucasus Mining and Metallurgical Institute (State Technological University), Vladikavkaz, Russia), **Viktoriya P. Pukhova**, Candidate of Engineering Sciences, Engineer, puhova-vikochka@mail.ru (North Caucasus Mining and Metallurgical Institute (State Technological University), Vladikavkaz, Russia).

The paper was received on 11 September, 2017.

The paper was accepted for publication on 8 May, 2018.