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Sulfuric acid autoclave dissolution of Ni-Co sulfide deposit

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With increasing use of Cu, Ni and Co metals for different applications and fast depletion of natural land based resources, worldwide efforts are being made to look for alternative resources for the recovery of these metals. One such alternative resource could be the vast oceans, containing these metals in the form of manganese nodules at a depth of about 4–5 km. Many research groups in different countries have been working for more than three decades on the development of copper, nickel, cobalt and manganese recovery processes from manganese nodules by pyro-/or hydrometallurgical routes.

During processing deep ocean manganese nodules from the Clairon-Clipperton fraction zone of the Pacific Ocean by combined pyro-hydrometallurgical route the non-ferrous metals were concentrated in two sulfide deposits – copper and mixed nickel-cobalt. In the present work the experimental results on sulfuric acid autoclave dissolution of the Ni-Co sulfide deposit, containing in mass. %: 30.37 Ni, 3.13 Co, 8.36 Fe, 0.08 Cu, 0.16 Mn, 36.8 S are presented. The effect of the main technological parameters on nickel and cobalt extraction and iron hydrolytic precipitation from the solution were studied. The degree of nickel and cobalt extraction at T= 363K, P_{O_2} = 0.35MPa, mol H_2SO_4/g-ion(Ni+Co) = 0.19, pulp density = 10 % and dissolution time = 180 min were respectively 97.71% and 96.25%, while the degree of iron hydrolytic precipitation was 99.68%.

***Keywords**: manganese nodules, Ni-Co sulfide deposit, sulfuric acid, autoclave dissolution*

INTRODUCTION

With increasing consumption of copper, nickel, cobalt and the fast depletion of natural land ores, worldwide efforts are being made to look for alternative resources for the recovery of these metals. One such alternative resource could be the vast oceans, containing these metals in the form of polymetallic nodules (PN) at a depth of about 2–5 km. The largest congregations are registered in Pacific Ocean between Hawaii and California and around Polynesia. According to Metal Bulletin Research (2005) the reserves of metals (Mn, Ni, Co, Cu, Zn etc.) in them are comparable to those of continental ores. The thorough analysis in this region, were made by R.Kotlinski [1], Andreew et all. [2], B.Agraval at all. [3] and others [4-7].

Many research groups in different countries have been working for more than three decades on the extraction of copper, nickel, cobalt from manganese nodules by pyro-/or hydrometallurgical routes.

Currently, the combined pyro-hydro-metallurgical methods are considered as the most promising methods of PN processing [8-11]. In the pyrometallurgical route of these schemes the non-ferrous metals are concentrated in an intermediate product, a polymetallic alloy (FeCuNiCoMn). 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 %. Further, for extraction of non-ferrous metals and manganese the alloy is treated with sulfuric or hydrochloric acid. The alloy can be also sulfidized with elemental sulfur to matte before the hydrometallurgical treatment [10].

In our previously investigation aqueous SO_2-H_2SO_4-H_2O medium has been used for dissolution of the polymetallic alloy with composition in mass %: 65.90 Fe, 12.07 Cu, 12.81 Ni, 1.33 Co, 5.33 Mn and 2.56 others. [11]. The alloy was obtained by pyrometallurgical processing of PN with composition in mass. %: 24.0 Mn, 5.75 Fe, 1.11 Ni, 1.04 Cu and 0.12Co from Clairon Clipperton Zone of the Pacific Ocean after drying at a temperature of 723K and reduction smelting at 1723-1773K in the present of coke. It has been established that the presence of SO_2 in the solution led to selective dissolution of the alloy: copper was concentrated into insoluble residue with composition in mass %: 54.9 Cu, 4.8 Fe, 3.3 Ni, 0.3 Co, 0.4 Mn and 30.9 S, while Fe, Ni, Co and Mn were extracted in the leach solution. The chemical composition of the solution, in g.L^{-1} was: 32.44 Fe, 0.05 Cu, 6.02 Ni, 0.62 Co, 2.62 Mn.

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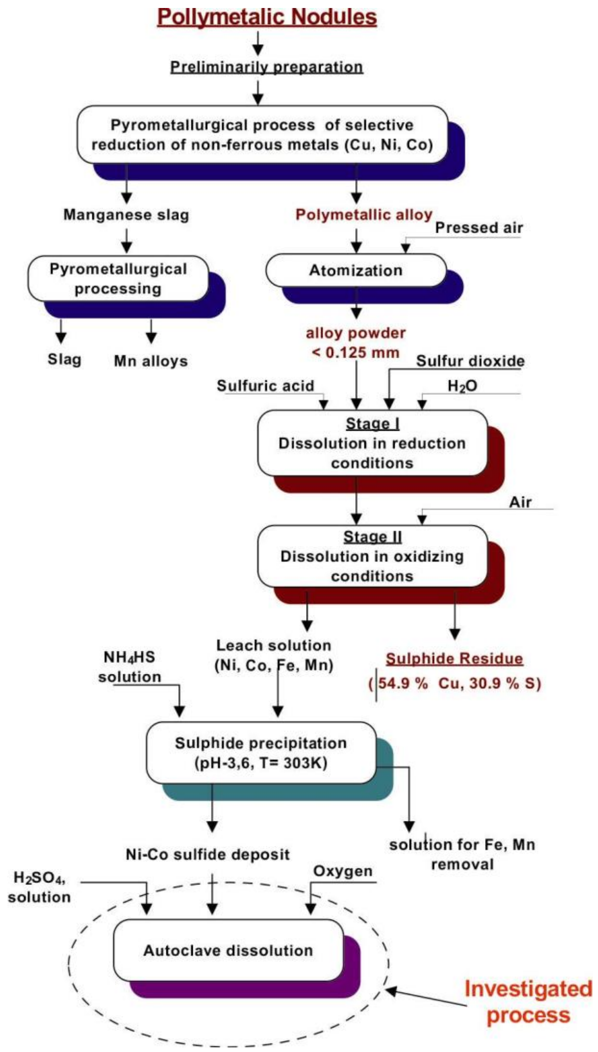

Fig.1. Combined pyro-hydrometallurgical scheme for obtaining of mixed Ni-Co concentrate from polymetallic manganese nodules.

Further Ni and Co were separated from the solution by sulfide precipitation with NH_4HS. In Figure 1 a schematic flow sheet for hydrometallurgical treatment of polymetallic alloy with recovery of copper and mixed Ni-Co concentrate is shown.

The concentrates can be directly processed into copper or nickel plant working on pyrometallurgical scheme. Conventional smelting techniques for processing nickel sulphide concentrates suffer from high capital and energy costs and from the emission of sulphur dioxide into the atmosphere. It is for this reason the hydrometallurgical processes gradually gain an advantage over the pyrometallurgical for production of nickel from sulphide ores. Many of the processes studied to date involve the leaching of an aqueous slurry of the sulphides concentrate in an air or enriched oxygen atmosphere in a pressure vessel (autoclave) at temperatures ranging from 120 to 230 ^{0}C.

In the present work the experimental results on acid autoclave dissolution of the Ni-Co sulfide deposit was presented. The effect of the main technological parameters on nickel and cobalt extraction and iron hydrolytic precipitation from the solution were studied.

EXPERIMENTAL

The process of Ni-Co sulfide deposit precipitation from leach solution was conducted at following conditions: equilibrium pH = 3.6, excess of NH_4HS - 150% more than the required stoichiometric and temperature =30 ^oC. Neutralization of the solution to pH 1.5 was made with lime. The time for precipitation was 30 minute. The experimental conditions and chemical composition of Ni-Co concentrate is given in Table 1.

XRD analysis of the residue was carry out with apparatus TUR M62 with $CuK_{\alpha+\beta}$ radiation. It showed that the main phases present in deposit were nickel and cobalt sulphides (Ni_3S_2 and $CoNi_2S_4$). Identified were also lines of double salts: $NiSO_4.(NH_4)_2SO_4.6H_2O$and $(NH_4)_2.Fe(SO_4)_2.6H_2O$. Based on chemical and XRD analyzes the resulting sulphide residue can be classified as mixed nickel-cobalt concentrate.

Table 1. Chemical composition of the solution and sulfide concentrate obtained after sulfide precipitation of nickel and cobalt.

PRODUCT	CHEMICAL COMPOSITION					
	Fe	Ni	Co	Cu	Mn	S
Initial solution, $g.L^{-l}$	32.44	6.02	0.62	0.05	2.62	-
Ni-Co concentrate, %	8.36	30.37	3.13	0.08	0.16	36.8
Residual solution, $g.L^{-l}$	25.9	0.07	0.01	0.01	1.80	

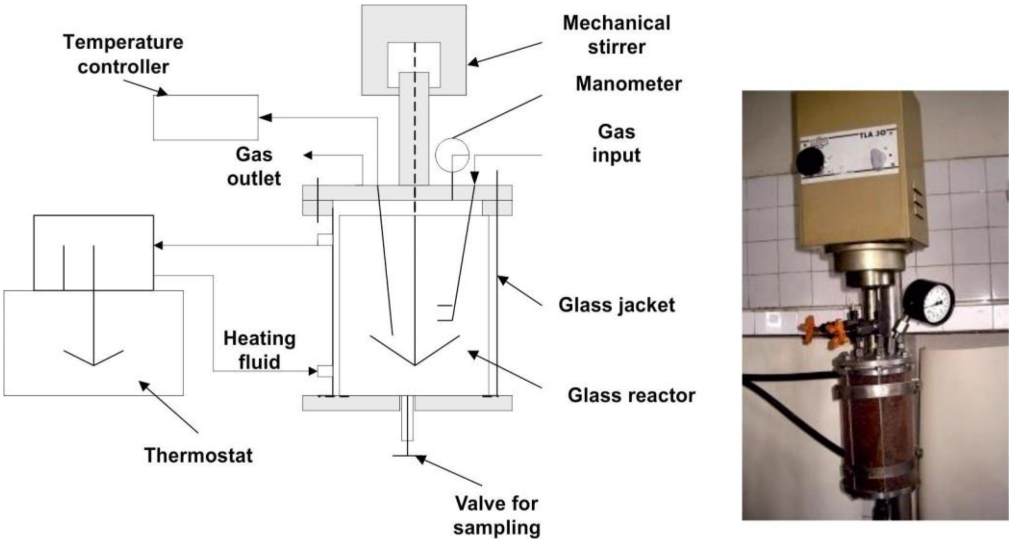

Fig.2. Scheme of laboratory apparatus with an autoclave TLA 30.

RESULTS AND DISCUSSION

The experimental conditions of the conducted experiments and chemical composition of the dissolution products of mixed Ni-Co concentrate are given in Table 2.

Effect of sulfuric acid consumption

For the assessment of this parameter a series of experiments (№ 1, 3 and 5) with duration of 180 min has been carried out. The degree of extraction of nickel and cobalt in solution during the experiment are shown in Fig.3a and b.

Analysis of the results shows that the increase in the sulfuric acid consumption from 0.19 to 1.0 mol H_2SO_4 /g-ion (Ni+Co) ions leads to a slight increase in the degree of extraction of nickel in solution. The degree of cobalt extraction in the solution decreases with decreasing initial concentration of H_2SO_4, which indicates a more difficult dissolution of the cobalt sulphide (Fig 3b)

Effect of temperature and oxygen partial pressure

The oxygen partial pressure and temperature are parameters that influencing on the rate of chemical dissolution of the sulfides and on degree of iron oxidation and its hydrolysis. They were estimated with series of experiments (№1, 2, and 4) carried out at P_{O2}=0.2 и 0.35 MPa, T=363K and 393K and initial ratio of mol H_2SO_4/g-ion (Ni+Co) = 0.19. In Figure 4 are shown respectively the degree of extraction of Ni and Co into solution.

The analysis of the obtained results showed that at T=363K and P_{O2} = 0.35 MPa the extraction of nickel (α_{Ni} = 97.71%) and cobalt (α_{Co} = 96.25%) are carried out with simultaneous purification of the solution from iron (α_{Fe} = 99.68%). With the decrease of P_{O2} up to 0.2 MPa the extraction degree of Ni and Co is increased about 2%, but the conditions of hydrolyses purification of solution from iron significantly are deteriorated (α_{Fe} ~11-13%).

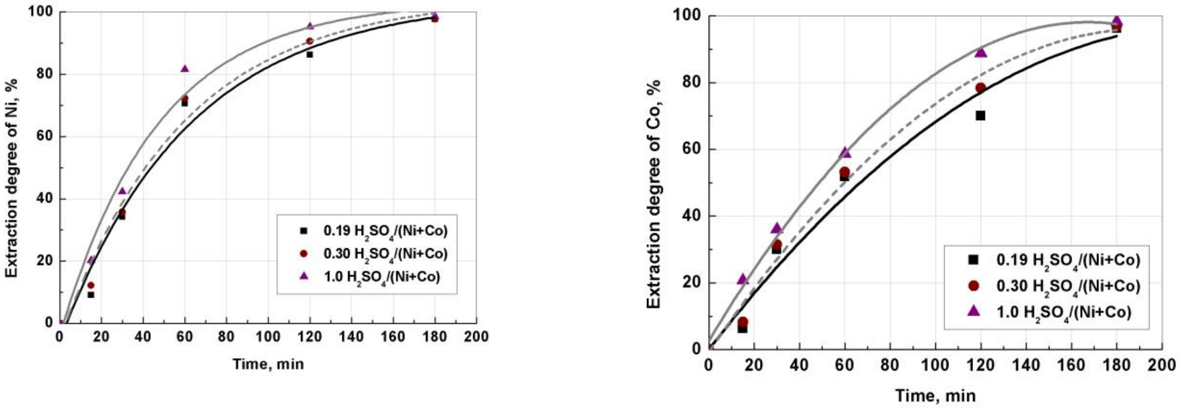

Fig.3. Effect of sulfuric acid concentration on (a) nickel and (b) cobalt extraction degree at T=363 K, P_{O2}=0.35 MPa, 500 rpm and pulp density 10%.

Table 2. The test conditions and experimental results obtained after autoclave dissolution of mixed Ni and Co concentrate.

Test conditions				Product	Chemical composition			
$H_2SO_4/(Ni+Co)$ mol/g-ion	T, K	P_{O2}, MPa	S:L (rpm)		Ni	Co	Fe	S
0.19	363	.35	1:10 (500)	Solution, g/L	29.67	3.01	0.02	-
				Residue, % (m= 2.41g)	2.87	0.48	34.50 (99.68)*	21.05
0.19	393	0.35	1:10 (500)	Solution, g/L	29.91	2.99	0.14	-
				Residue, % (m=2.367g)	1.92	0.60	34.64 (98.09)*	18.95
0.3	363	0.35	1:10 (500)	Solution, g/L	29.68	3.02	0.24	-
				Residue, % (m=2.050g)	3.36	0.50	27.31 (67.03)*	17.34
0.19	363	0.20	1:10 (500)	Solution, g/L	29.66	3.01	6.42	-
				Residue, % (m= 1.03g)	6.87	1.11	18.77 (23.12)*	9.36
1.0	363	0.35	1:10 (500)	Solution, g/L	30.27	3.07	6.52	-
				Residue, % (m= 0.907g)	1.10	0.57	10.5 (11.40)*	82.56
0.19	363	0.35	1:5 (500)	Solution, g/L	57.87	5.78	0.10	-
				Residue, % (m=5.14g)	5.58	0.93	32.10 (98.69)*	18.30
0.19	363	0.35	1:20 (300)	Solution, g/L	12.03	0.86	0.01	-
				Residue, % (m=2.23g)	14.14	3.14	18.70 (99.73)*	6.22
0.19	363	0.35	1:20 (500)	Solution, g/L	14.96	1.52	0.06	
				Residue, % (m=1.19g)	1.88	0.38	34.50 (98.12)*	20.05
0.19	363	0.35	1:20 (700)	Solution, g/L	13.06	0.89	1.34	
				Residue, % (m= 1.469g)	14.42	4.60	19.32 (67.94)*	22.08

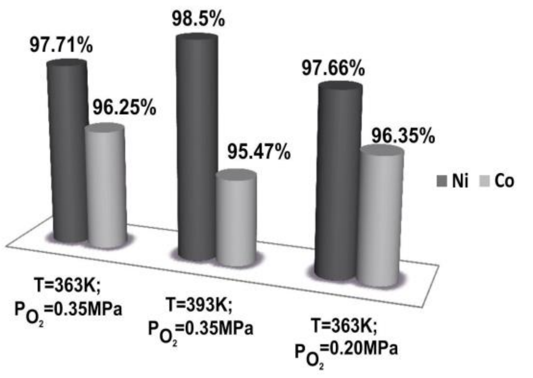

Fig. 4. Effect of temperature and P_{O2} on extraction degree of (a) nickel and (b) cobalt at mol H_2SO_4/g-ions (Ni+Co) = 0.19 and pulp density 10 %.

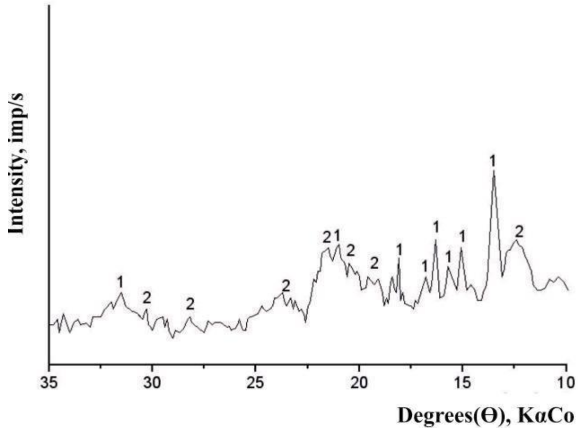

Fig.5. XRD of the residue obtained after dissolution of Ni-Co sulphide deposit at T=363K and P_{O2}=0.2 MPa, Phases: 1 – S°; 2 – FeO.OH.

At the XRD of the insoluble residue obtained at P_{O2} = 0.2 MPa elemental sulfur and iron oxide phase - goethite (FeO.OH) were identified (Fig.5). The absence of distinct peaks of goethite on the XRD shows that he is in amorphous form. Therefore, the decrease in the oxygen partial pressure leads to decrease in the rate of oxidation of Fe^{2+} to Fe^{3+} and deterioration of the conditions for hydrolysis purification of the solution from iron.

Effect of pulp density

To assess the influence of this parameter are carried out experiments (№ 6, 1 and 7) at 5, 10 and 20 % pulp density at constant others parameter. The resulting degree of extraction of nickel and cobalt in the solution are shown in Figure 6.

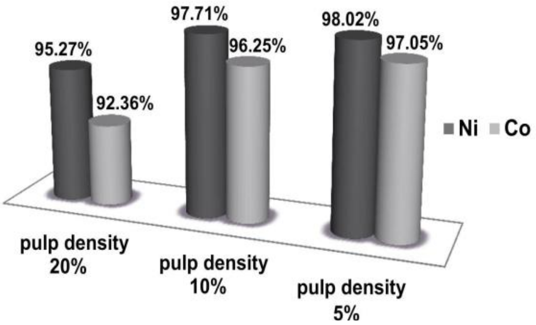

Fig. 6. Effect of pulp density on Ni and Co degree of extraction at T=363 K, P_{O2}=0.35 MPa, mol H_2SO_4/g-ions (Ni+Co) = 0.19 and 500 rpm.

Obviously, the increase of volume of the liquid phase leads to a significant decrease of the concentration of Ni and Co in solution. At all experiments in the insoluble residue about 98% of iron and ~19% elementary sulfur were passed.

Effect of intensity agitation

At diffusion-controllable processes the intensity of stirring has significantly effect on the rate of dissolution. It should be noted that the results give only a qualitative assessment, as the intensity of mixing is determined not only by the speed of the stirrer, but also from the geometric shape of the reactor and stirrer.

The influence of this parameter was evaluated with a series of experiments (№ 7, 8 and 9) at T = 363K, P_{O2} = 0.35MPa, pulp density 5%, initial sulfuric acid expense mol H_2SO_4/g-ion(Ni + Co) = 0.19 and extraction duration = 180 minutes. The dynamics of the Ni and Co dissolution from the concentrate is shown in Figure 7. The chemical compositions of the resulting dissolution products are shown in Table 3.

The analysis of the obtained results showed that maximum degree of metals extraction is reached at 500 rpm. At agitation 300 and 700 rpm a significant decrease in the rate of recovery of nickel and cobalt in the solution was observed. This effect is related to the deterioration of wrapping the solid sulphide particles and dispersion of gas phase in the solution. The last factor influences especially strong on the degree of oxidation of the iron ions and its hydrolysis.

CONCLUSIONS

On the basis of experimental results the optimal technological parameters on sulphuric acid autoclave dissolution of Ni-Co sulphide concentrate obtained during processing of polymetallic nodules have been established: mol ratio of H_2SO_4/gram-ion

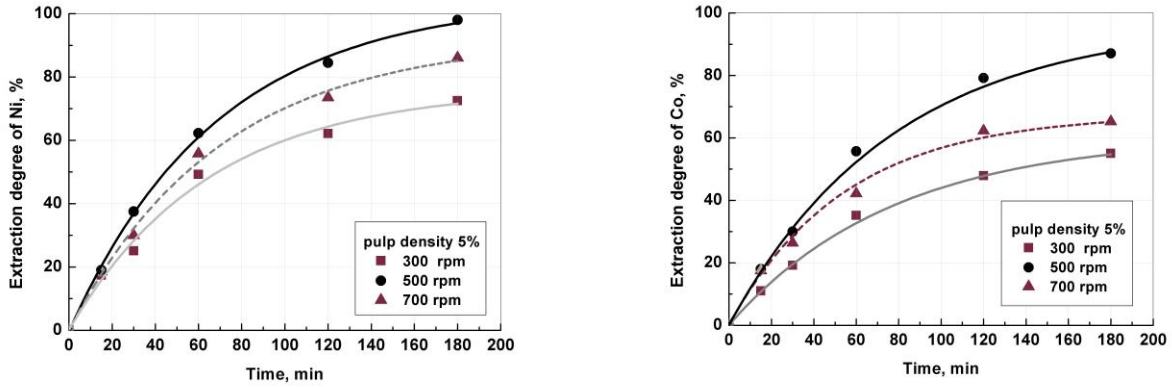

Fig.7. Effect of intensity agitation on (a) nickel and (b) cobalt extraction degree at T=363 K, P_{O2}=0.35 MPa, and mol H_2SO_4/g-ions(Ni+Co) = 0.19.

Table 3. The chemical composition of the products of autoclave dissolution of Ni-Co sulfide concentrate

Products	Ni	Co	Fe	S^o	α_{Ni}, %	α_{Co}, %	α_{Fe}, %	α_S, %
Leach liquor, g.L^{-1}	29.67	3.01	0.02	-	97.71	96.25	-	-
Residue, mass %	2.87	0.48	34.50	21.05	-	-	99.68	13.78

(Ni and Co) = 0.19; Oxygen partial pressure = 0.35 MPa; Temperature = 363K; Intensity of agitation – 500 rpm; Pulp density = 10% w/v; Dissolution time = 3h.

Under these conditions the dissolution of concentrate was carried out with simultaneous purification of the solution from iron in the form of goethite. The composition of leach liquor and insoluble residue are given in Table 3.

Under optimum leaching conditions a leaching efficiency of 97.71 % Ni and 96.25 % Co were achieved. Further the leach liquor can be used to recover Ni and Co, for example by solvent extraction and electrowinning.

The quantity of goethite residue was 0.241 g/g sulphide concentrate. Degree extraction of the iron and sulphur were respectively 99.68 % and 13.78 %. Extraction of sulfur from the residue can be performed by well-known in the metallurgical practice methods.

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СЯРНО-КИСЕЛО АВТОКЛАВНО РАЗТВАРЯНЕ НА Ni-Co СУЛФИДНА УТАЙКА

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(Резюме)

Поради нарастващото потребление на Cu, Ni и Co за различни цели и бързото изчерпване на континенталните им находища, в световен мащаб се полагат усилия за намиране на алтернативни суровини за техния добив. Такъв алтернативен източник могат да бъдат световните океани съдържащи тези метали под формата на манганови конкреции на дълбочина около 4-5 км. Много изследователски групи в различни страни работят вече в продължение на повече от три десетилетия по разработването на технологии за извличане на мед, никел, кобалт и манган от манганови конкреции по хидрометалургичен или пиро-хидрометалургичен път.

При преработване на дълбоководни манганови конкреции от областта Клайрон – Клипертон на Тихия океан по комбинирана пиро-хидрометалургична схема, цветните метали са концентрирани в две сулфидни утайки – медна и смесена никелово-кобалтова. В настоящата статия са представени експериментални резултати по сярнокисело автоклавно разтваряне на получената Ni-Co сулфидна утайка, съдържаща в мас. %: 30.37 Ni, 3.13 Co, 8.36 Fe, 0.08 Cu, 0.16 Mn, 36.8 S. Изследвано е влиянието на основните технологични параметри влияещи върху степента на извличане на никела и кобалта, и хидролизното утаяване на желязото от разтворите. Достигнатите степени на извличане на никела и кобалта при Т= 363К, Po_2 = 0.35МПа, молH_2SO_4/молNi+Co = 0.19, плътност на пулпа = 10% и продължителност на разтварянето = 240 мин са съответно 97.71 % и 96.25%, докато степента на хидролизно утаяване на желязото е 99.68%.