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<https://doi.org/10.31643/2019/6445.24>**KILIBAYEVA S. K., AGAPOVA L.YA.*, KVYATKOVSKAYA M.N., AMANZHOLOVA L.U., KUSHCH Y.P.***Satbayev University, Institute of Metallurgy and Ore Beneficiation, Almaty, Kazakhstan, * e-mail: rm.303.imo@mail.ru***PHYSICAL AND CHEMICAL RESEARCHES OF NICKEL-COBALT CONCENTRATES MADE FROM WASTES OF HEAT-RESISTANT NICKEL ALLOYS***Received: 12 June 2019 / Peer reviewed: 1 July 2019 / Accepted: 19 July 2019*

Abstract. The wastes of rhenium-containing heat-resistant nickel alloys (HRNA) contain 50-75% of Ni, 3-15% of Co. While electrochemical processing of the wastes of the HRNA up to 80-90% of Re, Ni and Co passes into the solutions, and a small part of them remains in the anode slurry. The remaining part of the metals from the slurry is chemically dissolved into the solution. After electrochemical treatment of wastes and chemical dissolution of slurry the solutions are combined and Re is extracted from them. The Ni – Co concentrate was precipitated (until a pH of 8–9 was established, at a temperature of 40 °C, by intensive stirring for 1 h) from the raffinate (g/dm³: 14.26 Ni; 2.48 Co) after the extraction of Re by NaOH (500 g/dm³) solution. Physical and chemical studies of the concentrate using X-ray fluorescent, X-ray phase, thermogravimetric and X-ray methods showed that it contains the following phases, wt. %: 62.6 Na₂SO₄; 37.4 Ni₂(NO₃)₂(OH)₂ · 2H₂O and Co(OH)₂. Washing the concentrate from sodium by water at L:S = 10: 1 ratio allowed reducing its mass (~ 2.4 times), reducing the content of sodium, increasing the content of Ni (from 15.68 to 37.55 %) and Co (from 1.89 to 4.48%). When the concentrate is annealed in the temperature range of 300-400 °C, the processes of dehydration of the hydroxides of Ni and Co and their transition to the oxide forms occur. The resulting concentrate can be sent for further processing in order to extract non-ferrous metals from it or used to produce some ferroalloys.

Keywords: wastes of HRNA, raffinate, Ni-Co concentrate, precipitation, washing, annealing.

КИЛИБАЕВА С.К., АГАПОВА Л.Я.*, КВЯТКОВСКАЯ М.Н., АМАНЖОЛОВА Л.У., КУЩ Е.П.*Satbayev University, Металлургия және кен байыту институты, Алматы, Қазақстан, * e-mail: rm.303.imo@mail.ru***ЫСТЫҚҚА ТӨЗІМДІ НИКЕЛЬДІ ҚОРЫТПАЛАРЫНЫҢ ҚАЛДЫҚТАРЫНАН АЛЫНҒАН НИКЕЛЬ-КОБАЛЬТТЫ КОНЦЕНТРАТТАРЫН ФИЗИКАЛЫҚ-ХИМИЯЛЫҚ ЗЕРТТЕУ**

Түйіндеме. Құрамында ренийі бар ыстыққа төзімді никельді қорытпалар (ЫТНҚ) құрамында 50-75 % Ni, 3-15 % Co. ЫТНҚ қалдықтарын электрохимиялық қайта өңдеу барысында 80-90 % дейін Re, Ni және Co ерітіндіге өтеді, ал олардың аз бөлігі анодтық шламда қалады. Шламдан металлардың қалған бөлігін химиялық ерітумен ертіндіге өткізеді. Қалдықтарды электрохимиялық қайта өңдеуден кейінгі және шламдарды химиялық ерітуден кейінгі ертінділерді біріктіріп, экстракция әдісімен олардан Re-ді шығарады. Re-ді экстракциялаудан кейін рафинаттан (г/дм³: 14,26 Ni; 2,48 Co) NaOH (500 г/дм³) ерітіндісімен (рН-тын мәндері 8-9 шейін орналғанша, 40 °C температурада, 1 сағат бойы араласумен) Ni-Co концентраттын тұндыруы өткізілді. Рентгенфлуоресценттік, рентгенфазалық, термогравиметрлік және ИКС әдістері концентраттын физикалық-химиялық зерттеуі оның құрамында келесі фазалар, мас. %: 62,6 Na₂SO₄; 37,4 Ni₂(NO₃)₂(OH)₂·2H₂O и Co(OH)₂ бар екенін көрсетті. С:Қ = 10:1 қатынасында концентратты натрийден сумен шаюда оның массасын азаяды (~ 2,4 есе), натрий құрамы төмендейді, Ni (15,68-ден 37,55 % дейін) мен Co (1,89-ден 4,48 %дейін) құрамы жоғарлайды. Температура 300 – 400 °C интервалында концентратты қыздыруда Ni және Co гидрооксидтерінің дегидратациялау үрдісі болады және олардың оксидтік формаларына көшеді. Алынған концентрат одан әрі қайта өңдеуге жіберілуі мүмкін олардан түсті металдар немесе кейбір ферроқорытпаларын алу мақсатында.

Түйінді сөздер: ЫТНҚ қалдықтары, рафинат, Ni-Co концентраты, тұндыру, шаю, қыздыру

КИЛИБАЕВА С.К., АГАПОВА Л.Я.*, КВЯТКОВСКАЯ М.Н., АМАНЖОЛОВА Л.У., КУЩ Е.П.*Satbayev University, Институт металлургии и обогащения, Алматы, Казахстан, *e-mail: rm.303.imo@mail.ru***ФИЗИКО-ХИМИЧЕСКИЕ ИССЛЕДОВАНИЯ НИКЕЛЬ-КОБАЛЬТОВЫХ КОНЦЕНТРАТОВ, ПОЛУЧЕННЫХ ИЗ ОТХОДОВ ЖАРОПРОЧНЫХ НИКЕЛЕВЫХ СПЛАВОВ**

Аннотация. Отходы ренийсодержащих жаропрочных никелевых сплавов (ЖНС) содержат 50-75 % Ni, 3-15 % Co. При электрохимической переработке отходов ЖНС в растворы переходит до 80-90 % Re, Ni и Co, а незначительная их часть остается в анодном шламе. Из шлама оставшуюся часть металлов химическим растворением переводят в

раствор. Растворы после электрохимической переработки отходов и химического растворения шламов объединяют и методом экстракции извлекают из них Re. Из рафината (г/дм³: 14,26 Ni; 2,48 Co) после экстракции Re раствором NaOH (500 г/дм³) провели осаждение Ni-Co концентрата (до установления значения pH 8-9, при температуре 40 °С, интенсивном перемешивании в течение 1 ч). Физико-химические исследования концентрата рентгенофлуоресцентным, рентгенофазовым, термогравиметрическим и ИКС методами показали, что в нем содержатся следующие фазы, мас. %: 62,6 Na₂SO₄; 37,4 Ni₂(NO₃)₂(OH)₂·2H₂O и Co(OH)₂. Промывка концентрата от натрия водой при Ж:Т = 10:1 позволила уменьшить его массу (~ в 2,4 раза), снизить содержание натрия, повысить содержание Ni (от 15,68 до 37,55 %) и Co (от 1,89 до 4,48 %). При отжиге концентрата в интервале температур 300 – 400 °С происходят процессы дегидратации гидроксидов Ni и Co и перехода их в оксидные формы. Полученный концентрат может быть направлен на дальнейшую переработку с целью извлечения из него цветных металлов или использован для получения некоторых ферросплавов.

Ключевые слова: отходы ЖНС, рафинат, Ni-Co концентрат, осаждение, промывка, отжиг

Introduction. Nowadays, the general metal production faces an obstacle in the efficient and integrated use of secondary raw materials that is becoming increasingly important both world wide and in the Republic of Kazakhstan.

Heat-resistant alloys have been widely used as a special type of structural materials in recent years, connected with the development of various areas of technology. Heat-resistant nickel-based alloys are of particular importance, which include rare and trace elements: rhenium, tungsten, molybdenum, tantalum, niobium, hafnium. Such alloys are widely used in the aerospace industry, nuclear and thermal power, mechanical engineering and petrochemistry [1].

Now the world has accumulated a large amount of the wastes of heat-resistant nickel alloys (HRNA) in the form of scrap parts, with expired service life. The high cost of heat-resistant nickel alloys containing expensive metals (rhenium, tantalum, cobalt, etc.), required to solve the problem of efficient and complex processing of these materials.

Current technologies for the processing of wastes of HRNA can be divided into 4 groups:

- direct pyrometallurgical wastes processing [2];
- oxidative-thermal technologies [3, 4];
- hydrochemical technologies [5, 6];
- electrochemical technologies [7, 8].

Electrochemical methods are often suggested to use for the lump scraps based on the anodic dissolution of the material under the direct or alternating currents transferring either rhenium or a nickel alloy base into solution with the rhenium concentration in the anode slurry [9-10].

Analysing scientific, technical and patent literature has resulted in the present increasing interest of researches in the field of integrated processing of HRNA wastes due to the growing amount of such wastes, which is a valuable secondary raw material.

HRNA generally contain from 50 to 75 wt. % of nickel, from 3 to 15 wt. % of metals such as cobalt, chromium and, aluminum if required, as well as from 1 to 10 wt. % of one or several elements of tantalum, niobium, tungsten, molybdenum, rhenium, platinum, and hafnium series [11].

Therefore, it is also of interest to extract other valuable non-ferrous and rare metals in terms of integrated processing of HRNA wastes along with the expensive rhenium. This is especially true of the metals are quite large contained in the alloy. Here such metals are nickel and cobalt. An integrated processing of HRNA will allow to obtain compounds of these valuable non-ferrous metals. Due to the nature of the HRNA, which determines their resistance to the effects of various kinds, the extraction of valuable metals from the wastes of these alloys presents considerable difficulties.

There is no processing of such secondary raw materials in Kazakhstan. However, a well-known company for the rhenium and its compounds production from sulfur wash-acid of the copper production of RSE Zhezkazganredmet is currently seeking additional raw material sources of rhenium. In this regard, the company has shown interest in wastes of rhenium-containing HRNA.

The Institute of Metallurgy and Ore Benefication JSC of the Republic of Kazakhstan has developed a method for the electrochemical processing of large-volume of rhenium-containing HRNA wastes in the sulfuric acid solutions [12-16]. At this, up to 80-90% of rhenium, nickel and cobalt go into solutions, and a small part of them remain in the anode slurry. To extract the remaining rhenium, nickel and cobalt in the slurry, the anode slurry is sent for chemical dissolution [15]. The resulting solutions after electrochemical processing of wastes and chemical dissolution of anodic slurry are combined and the rhenium is extracted from them [12-13, 16]. Nickel and cobalt remain almost completely in the raffinate sulphate solution after extraction of rhenium, their content may be

depending on the composition of the raw material and the conditions of its processing, on average, g / dm³: 16,85-25,74 Ni; 2.48-3.74 Co.

A wide range of methods of nickel and cobalt deposition from the solutions into a common nickel-cobalt concentrate, for example, sulfides [17–18], but most often they are precipitated from acidic solutions by alkali [12, 16].

This paper presents the results of physical and chemical studies of nickel-cobalt concentrates obtained from the products of electrochemical break-down of HRNA wastes.

Testing. From the sulphate raffinates are left after extraction of rhenium and containing significant amounts of nickel and cobalt, these metals were precipitated into a concentrate using alkali.

The deposition processes were carried out in a thermostated cell (Figure 1) with stirring using a mechanical stirrer using an adjustable speed.



Figure 1 - Laboratory setup for Ni-Co concentrate deposition

The chemical and phase composition of raffinates and processing products (filtrate, service water, Ni-Co concentrate before and after washing) was determined using X-ray fluorescence (spectrometer with wave dispersion Axios PANalytica), X-ray phase diffractometer (D8 Advance diffractometer (BRUKER), radiation Cu. K α); chemical (atomic emission spectroscope Optima 2000 DV, USA, Perkin Elmer), infrared spectroscopic (FTIR spectrometer Thermo Nicolet Avatar 370 FTIR Spectrometer), thermal (STA 449 F3 Jupiter, the results were processed using the NETZSCH Proteus software) methods of analysis.

Testing procedure for the Ni-Co raffinate concentrate deposition. A saturated blue raffinate (Figure 2a) containing g/dm³: Ni — 14.260; Co - 2,481; Re - 0.102; Mo - 0.121; W — 0.012; Al = 1.810; Cr - 2.212 (95.06 g/dm³ of acidity). A predetermined raffinate volume (1 dm³) was poured

into a thermostated cell (Figure 1), the process temperature was maintained at 40 °C, and with continuous stirring at a speed of 700 rpm, a precipitator — NaOH solution (500 g / dm³) was fed until pH 8-9. Then stirring was proceeded for 1 hour. When a precipitant was added to the raffinate, a dark green solution with the precipitate was produced. As the NaOH solution was added, the amount of increased precipitate was formed and the color intensity of the solution increased. The precipitate of Ni-Co concentrate was filtered using a vacuum pump through the two layers of blue tape filter. The mass of the obtained wet Ni-Co concentrate (75.67% of humidity) was 534.23 g.

Then the precipitate was washed with water, filtered and dried in a drying cabinet at a temperature of 105 °C to a constant weight. Dry sediments were ground in a porcelain mortar.

Results and discussion. According to the X-ray analysis data, absorption bands of valence ν (OH) - 3413 cm⁻¹, deformation δ HOH-1647 cm⁻¹ and librational ν_L H₂O - 674 cm⁻¹ of molecular water fluctuations are recorded in the raffinate spectrum (concentrate solution for precipitation) [19]. The group [HSO₄]⁻ - 1196, 1053, 890, 598 cm⁻¹ [20]. The group [SO₄]²⁻ - 1117, 627 cm⁻¹ [18, 20]. The group [NO₃]⁻ - 1386, 1348 cm⁻¹ [19, 22].

The optical density measurements were made at the peak point of the absorption bands describing the fluctuations of ν OH, δ HOH, ν_L H₂O, ν_3 of nitrate-ions, ν_3 (F₂) of sulfate ion, ν_4 (F₂) of sulfate ion, ν_2 (SO₃) of hydrosulfate ion; ν_4 (SO₃) of hydrosulfate ion; ν_1 (S - OH) of hydrosulfate ion; ν_3, ν_5 (OSO) of hydrosulfate ion.

The ultimate composition of the produced concentrate without washing was determined by X-ray fluorescence analysis, wt. %: Ni - 14.786; Co — 1.844; O - 43.912; Na — 21.917; Al = 0.936; Si - 0.075; S - 12,350; Ti = 0.055; Cr - 1,688; Fe - 0.339; As — 0.014; Mo - 0.096; Re - 0.031; Pb - 0.007.

According to the x-ray phase analysis of a dry concentrate without washing, the following phases are in it: a base - 62.6 wt. % of Na₂SO₄; 37.4 wt. % of Ni₂(NO₃)₂(OH)₂·2H₂O and <2.5 wt. % of Co(OH)₂.

The X-ray analysis has shown the following in the Ni-Co concentrate: Thenardite Na₂SO₄ - 1131, 638, 617 cm⁻¹ [20, 22-25]. The group of [SO₄]²⁻ - 1131, 996, 977, 638, 617 cm⁻¹ [19–21]. The group [NO₃]⁻ - 1384, 1040, 833 cm⁻¹ [19, 21]. The band at 996 cm⁻¹ can be attributed to the ν_1 (A₁) fluctuation of iron, cobalt, and nickel sulfates [20, 23]. ALUMINITE Al₂(SO₄)(OH)₄·7H₂O - 977cm⁻¹ [22] may be present. The band at a 406 cm⁻¹ wave

number corresponds to the stretching fluctuations of Co–O, Ni–O [24]. CoO is probably present - 406 cm^{-1} [20, 24]. The spectrum recorded absorption bands of ν (OH) - 3442 cm^{-1} valence and deformation δ HOH- 1635 cm^{-1} oscillations of water molecules [20]. The infrared spectrum of Ni-Co concentrate is in Figure 2.

The filtrate (solution after Ni-Co concentrate precipitating) is a volume of 680 ml. The filtrate is colorless, bright. According to the chemical analysis, the filtrate contains, g / dm³: Ni - 0.460; Co - 0.100; Re - 0.078; Mo — 0.005; W — 0.0001; Al - N/A; Cr - N/A.

Chemical analysis of the filtrates showed that the metals present in the raffinate, when alkali added are almost completely precipitate.

The infrared spectrum of the filtrate recorded absorption bands of valence ν (OH) - 3422 cm^{-1} , deformation δ HOH- 1648 cm^{-1} , and librational ν_L H₂O - 678 cm^{-1} vibrations of molecular water [19]. The group [SO₄]²⁻ is 1108, 624 cm^{-1} [19, 21]. The group [NO₃]⁻ is 1397, 1376 cm^{-1} [19, 21]. In the filtrate, the content of nitrate ion is lower than in the initial solution (raffinate). At the maximum of the absorption band characterizing the vibration of ν_3 (F₂) sulfate ion at a wavenumber of 1108 cm^{-1} , the optical density was 0.515. At the maximum of the absorption band characterizing the vibration of ν_4 (F₂) sulfate ion, at a wavenumber of 629 cm^{-1} ,

the optical density was 0.479. At the maximum of the absorption band, which characterizes the vibration of ν_1 (A₁) sulfate ion, at a wavenumber of 974 cm^{-1} , the optical density was 0.023.

When comparing the spectra of solutions - of the initial raffinate with the filtrate (Figure 3), a decrease in the intensity of the ν OH band in the filtrate is observed after deposition (2) compared with the initial raffinate (1), which indicates a decrease in the salt content in the filtrate.

The study of obtained Ni-Co concentrates without washing using thermogravimetry. Thermogravimetric analysis allows establishing the presence of chemical interaction of substances or phasing transformations by the accompanying thermal effects. The application of the method is based on the tendency of solid materials to chemical and physical transformations, accompanied by thermal effects. All processes occurring during the formation are recorded with a thermogravigram (Figure 4).

Intense endothermic effects on the DTA Ni-Co concentrate curve are manifested with maximum development at $179.7\text{ }^\circ\text{C}$, $281.2\text{ }^\circ\text{C}$, $366.6\text{ }^\circ\text{C}$. They are developed against the background of weight reduction. The additional endothermic effects can be noted on the dDTA curve, with extremes at, $^\circ\text{C}$: 125.2, 144.4, 155.8, 340.8.

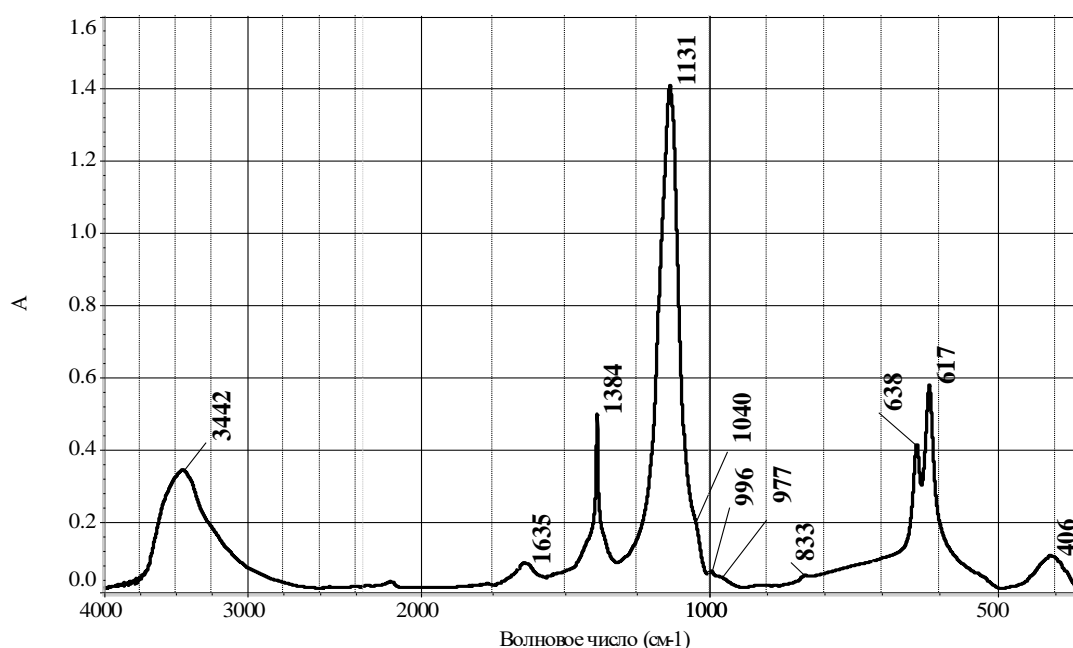


Figure 2 - Infrared spectrum of Ni-Co concentrate without washing

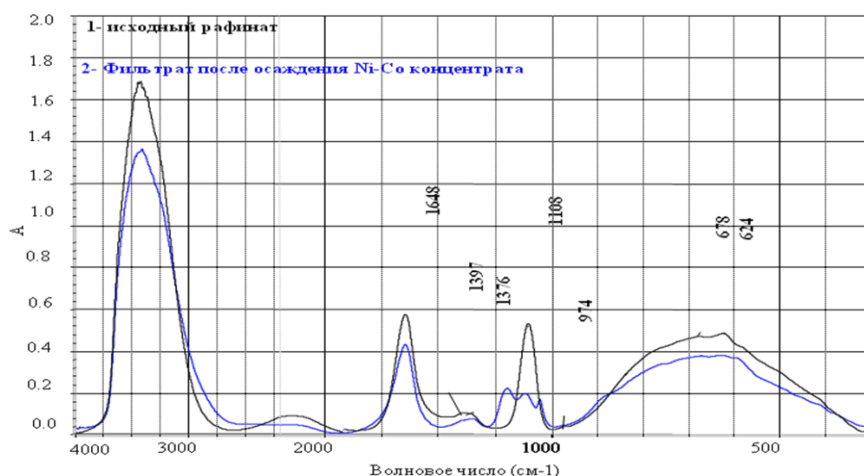


Figure 3 - Comparison of the infrared spectra of the filtrate with the raffinate

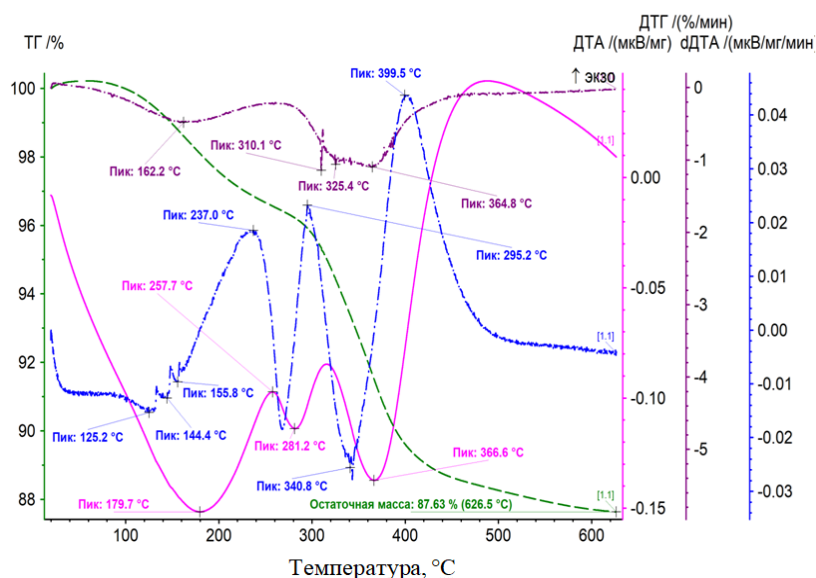


Figure 4 - Thermogravigram of Ni-Co concentrate without washing

There are also exothermic effects with peaks at 237 °C, 295.2 °C, 399.5 °C. In this sample, a high content of sodium, therefore, apparently, the effect of polymorphic transformation of sodium sulfate (281.2 °C) is well manifested even in the DTA curve. Also in this sample, elemental sulfur (125.2 °C), ReO_4 (144.4 °C), ReO_3 impurity (155.8 °C) is present. At 366.6 °C, nickel hydroxide is dehydrated and nickel oxide is formed. This effect can also be a manifestation of the de-concentration of co-oxyoids. Effects with extremes at 179.7 °C (DTA) and 399.5 °C (dDTA) can be associated with the manifestation of chromium hydroxide.

The lows at the DTG curve in the temperature range 300–400 °C reflect the dehydration of Fe, Al, Ni, Cr, Co hydroxides. The presence of amorphous and fine hydroxides is also not excluded. Their dehydration probably reflects a

stretched low at 162.2 °C on the DTG curve, and the products crystallization reflects exothermic effects with peaks at 237 °C, 295.2 °C, 399.5 °C. The total weight loss was 12.37%.

Based on the results, it should be concluded that Ni-Co concentrate is necessary to wash with water from sodium, after precipitating it from the raffinate with a NaOH solution.

Washing of Ni-Co concentrate out of sodium.
We washed the Ni-Co concentrate with distilled water at room temperature 25-27 °C, ratio L:S = 10:1. The concentrate was wet, weight - 100g. The moisture content of the concentrate is 76.35%. Dry concentrate weight is 23.65 g.

The concentrate was pre-dispersed in the water (50 ml), then the pulp was moved to a filter and washed with water to pH7 (by test paper). The results of testing of the Ni-Co concentrate washing process are in Table 1.

The chemical composition of the rinse after washing of the Ni-Co concentrate is, g / dm³: Ni - 0.00025; Co - 0.00005; Re 0.0059; Mo - 0.00032; W

= 0.00023; Al = 0.00022; Cr - 0.00003. The influence of the washing process on the content of elements in the dry concentrates is provided in Table 2.

Table 1 - Washing of nickel-cobalt concentrate with water

Test No	L:S	Service water		Concentrate after washing			Filtration time, min	Drying concentrates, hour
		pH	Volume, ml	Wet weight, g	Humidity, %	Dry weigh, g		
19	10:1	7	975	52,52	81,17	9,89	49	5

Table 2 - Effect of the washing process on the elements content in the dry concentrates before and after washing with water

Element	Content, wt. %		Element	Content, wt. %	
	before washing	after washing		before washing	after washing
Ni	15,68	37,55	Hf	0,05	0,13
Co	1,89	4,48	Si	0,31	0,21
Cr	1,77	4,24	S	11,77	3,65
Al	0,88	2,41	O	43,89	43,33
Mo	0,10	0,22	Na	23,19	2,11
Re	0,04	-	Fe	0,33	0,87
W	0,02	0,02	Ti	0,08	0,52

Note - the dry weight of the concentrate without washing - 23.65 g, after washing - 9.89 g.

As provided by Table 1 and 2 the mass of Ni-Co concentrates decreases (~ 2.4 times), the sodium content in the concentrate decreases, the content of nickel and cobalt increases after washing.

According to X-ray phase analysis (Figure 5), the dry Ni-Co concentrate have the following phases after washing: 33 wt. % Na₂SO₄; the rest is Ni₂(NO₃)₂(OH)₂·2H₂O; Ni(OH)₂ and Co(OH)₂; NiSO₄(H₂O)₇; NiSO₄·6H₂O; CoSO₃·3H₂O.

A decrease in the intensity of the Thenardite Na₂SO₄ – 1129, 638, 617 cm⁻¹ band is observed in the spectra from 4 to 0.85 when comparing the IR spectra of Ni-Co concentrates without washing and after washing with water, which also indicates a decrease in the Na₂SO₄ content in the washed concentrate.

The thermogravigram of a Ni-Co concentrate after washing with water is provided in Figure 6. The DTA curve demonstrates intense endothermic effects with maximum development at 194 °C, 381.8 °C. They are developed against the background of a sample weight reduction.

Additional endothermic effects can be marked with extreme values at 117 °C, 136.9 °C, 148 °C, 180.9 °C, 268.8 °C, 287 °C along the dDTA curve. Exothermic effects are present with peaks at 244.5 °C, 303.5 °C, 415.2 °C as well.

The exothermic effect combination with a peak at 244.5 °C on the dDTA curve and an endothermic effect with an extreme value at 381.8 °C can be interpreted as nickel hydroxide occurrence. The effect at 381.8 °C reflects the dehydration process of this phase and the formation of nickel oxide. The endothermic effect with an extreme value at 268.8 °C on the dDTA curve can be an occurrence of the polymorphic transformation of sodium sulfate. The combination of the endothermic effect with the maximum development at 194 °C and the exothermic effect with a peak at 415.2 °C can be interpreted as a chromium hydroxide occurrence. The exothermic effect reflects the conversion of Cr⁺³ into Cr⁺⁴ with the formation of the α-phase of a variable composition. Since the sample under study may have hydroxides of iron, aluminum, cobalt, so this peak may be an occurrence of the solid solutions formation of spinels.

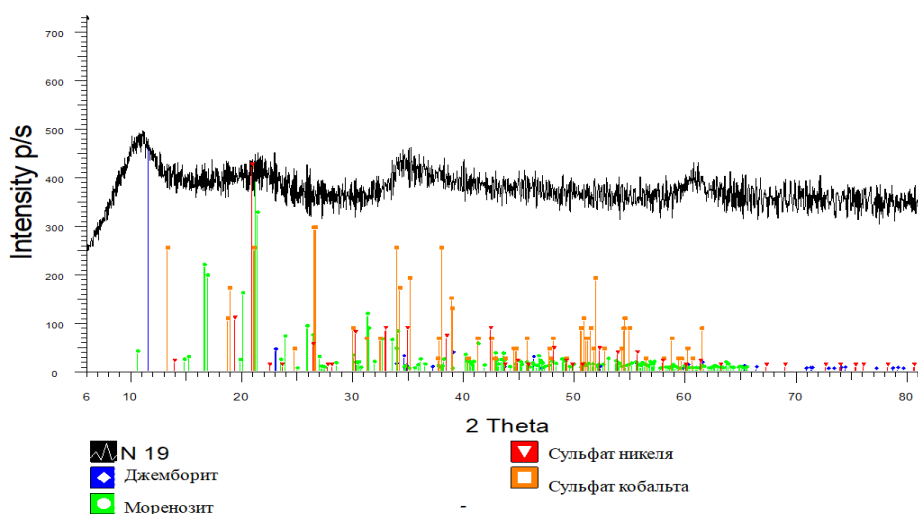


Figure 5 - Diffractogram of Ni-Co concentrate after washing

A number of least values are emphasized on the DTG curve, in the temperature range 300-400 °C, which reflect the hydroxides dehydration Cr, Fe, Al, Ni, Co. In addition, amorphous or finely dispersed Fe, Al, Co. hydroxides may be present in the sample. As well known the cobalt hydroxides include unstable blue and stable pink hydroxide $\text{Co}(\text{OH})_2$, CoOOH oxyhydroxide, hydrated oxides [26]. Blue hydroxide is finely dispersed, it begins to lose water already at 170°C. Pink is resistant to 300°C. Dehydration of the aged rhombohedral CoOOH is at ~ 335 °C. That is to say the effect with

an extreme value at 381.8 °C may also be an occurrence of CoOOH dehydration.

The stretched least value at 192.5 °C on the DTG curve may be an occurrence of the dehydration of amorphous, finely dispersed phases, and the exothermic effects with peaks at 244.5 °C, 303.5 °C, 415.2 °C on the dDTA curve reflecting the crystallization of dehydration products. The total weight loss was 14.96%. The higher mass loss compared to the concentrate without washing (12.37%) is probably due to a higher nickel content in the form of hydroxide.

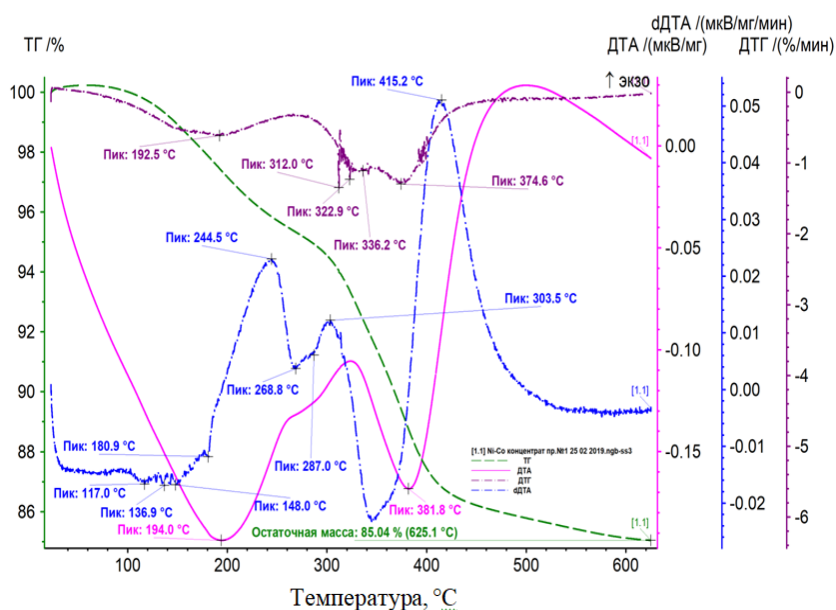


Figure 6 - Thermogravimogram of Ni-Co concentrate after washing with water

To confirm the presence of sodium sulfate, the sample weighing 0.314 g was heated to ~ 860 °C. The endothermic effect with an extreme value at 824.2 °C, which reflects the melting of sodium sulfate was better manifested on this DTA curve.

Thermogravimetric analysis of the concentrates, both without rinsing and after rinsing with water, resulted in that in the temperature range of 300-400 °C occur dehydration of nickel, cobalt, chromium, aluminum, iron hydroxides and their transition into oxide forms.

Annealing of nickel-cobalt concentrates obtained out of the products after the electrochemical break down of the HRNA wastes at a temperature of up to 400 °C will allow to transfer all non-ferrous metal hydroxides to oxides, to reduce the mass of concentrates by 15-20%. Annealed nickel-cobalt concentrates can be used in the smelting of some ferroalloys.

Conclusion. The studies have shown that nickel and cobalt can be isolated from the waste of rhenium-containing heat-resistant nickel alloys in the form of a concentrate. Start with, the large pieces of waste alloys anode dissolved in sulfuric acid solutions to obtain a rhenium-containing solution and anode slurry. Rhenium, nickel and cobalt are extracted into a solution out of the anodic slurry by chemical dissolution. Solutions from the anodic break down of the wastes and chemical dissolution of the slurries are combined and sent for the extraction of rhenium from them. After extraction of rhenium from the raffinate, nickel and cobalt are precipitated with a solution of NaOH (500 g / dm³) until the pH value is 8-9 at a temperature of 40 °C, with intensive stirring of the pulp for 1 hour.

Physical and chemical studies of the obtained concentrate showed that it contains the following phases, wt. %: 62,6 Na₂SO₄; 37,4 Ni₂(NO₃)₂(OH)₂·2H₂O и Co(OH)₂.

Washing the resulting concentrate from sodium with water is proposed at a L:S ratio = 10:1. After the Ni-Co concentrate washing, its mass decreases (~ 2.4 times), the sodium content in the concentrate decreases, the nickel content (from 15.68 to 37.55 wt.%) and cobalt (from 1.89 to 4,48 wt.%).

During the annealing of the concentrate in the temperature range of 300-400 °C, the processes of dehydration of nickel and cobalt hydroxides and their transition into oxide forms occur. In this case, the weight of the concentrate is reduced by 15-20%. The resulting concentrate can be sent for further processing in order to extract non-ferrous metals

from it. Also, nickel-cobalt concentrate can be used to produce some ferroalloys.

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